

The Synthesis and Characterisation of Fused Aromatic Hydrocarbons and Their Material and Ligand Applications

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**A thesis submitted to the University of Dublin for the degree of
Doctor of Philosophy**

**School of Chemistry
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2019

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Summary

Chapter One: This chapter provides a general introduction to the field of polycyclic aromatic hydrocarbon (PAH) chemistry, with the aim of providing context for the work described in subsequent chapters. After a short account of the properties of PAHs, a brief summary of the synthetic methods employed towards their preparation is given, with a focus on the oxidative cyclodehydrogenation of polyphenylene precursors, and heteroatom substitution. This chapter also describes materials applications for these compounds. An introduction to the photophysical terminology employed in later chapters is also provided.

Chapter Two: This chapter begins with a general introduction to graphene and its smaller derivatives, and the competing methods for their preparation. A literature review on the emerging field of on-surface chemistry is given, with particular attention paid to heteroatom-containing systems. The concepts of on-surface synthesis and GNRs (graphene nanoribbons) are discussed in detail. A detailed account is also given of synthetic work towards PAH-based precursors for on-surface chemistry, prepared with the aim of achieving extended GNRs. The on-surface behaviour of these compounds on a metal substrate is then described, with STM and AFM techniques being employed.

Chapter Three: This chapter provides a brief account of the synthetic routes towards, and photophysical properties of Pt(II) acetylides. Initial synthetic efforts towards Pt(II) acetylides with terpyridine-type coordinating ligands and HBC (hexa-*peri*-hexabenzocoronene)-based chromophoric cores are described. A more successful synthetic route was found to be with cyclometalating ligands, and the synthetic routes to mono- and di-substituted Pt(II) HBC acetylides are described. The photophysical and electrochemical properties of these complexes and their precursor ligands are also described.

Chapter Four: This chapter describes the synthesis and photophysical properties of a family of bis-pyrenyl Pt(II) acetylides, bearing N[^]N coordinated ligands with varying conjugation and substitution. A systematic study of the effect of varying the LUMO energy on the emissive properties of these compounds was undertaken. The photophysical and

electrochemical behaviour of the complexes are described and compared. Initial evaluation of the behaviour of one of the Pt(II) acetylides as a triplet photosensitiser was also undertaken.

Chapter Five: This chapter describes the synthesis of a family of Ir(III) complexes, each bearing a highly conjugated, partially-fused N[^]N ligand, previously developed in the Draper group. A detailed analysis of the NMR spectra of the complexes is given, followed by a summary and comparison of their photophysical and electrochemical behaviour.

Chapter Six: This chapter provides a short summary of the work undertaken, and the conclusions that may be derived from it.

Chapter Seven: This chapter describes the various experimental methods carried out to synthesise and characterise the compounds described in this thesis.

Acknowledgements

Firstly I must thank my supervisor Prof. Sylvia Draper for providing me with the opportunity to join her research group, and for her support and advice over the course of this research project. I must also thank all the members of the Draper group for their help, advice, and encouragement over the past four years. To those who were in the group during the early days of my studies – Niamh, Lankani, Gearóid, Colm, Bryan, Nitheen, Yue, and Jungsi – thank you for the warm welcome. To the current group members – Rob, Justo, Colin, Claire, Martha, Nidhi, Lukas, Raj, Nicolas, and Xiaoneng – thank you all for your encouragement and help (and for putting up with me as I tried to write up my thesis!). I owe an enormous debt of gratitude to three people in particular; to Colm, who gave so much advice and taught me so much during my first few months; to Prof. Sarath Perera, whose tireless enthusiasm, synthetic expertise, and guidance was always appreciated; and finally to Rob, who always had the time to offer ideas and advice, and whose proof-reading efforts (and many, many visits to the Fluorolog to offer advice on emission spectra) were invaluable.

I must also thank all the technical staff in Trinity College for their help over the past few years, in particular Dr. John O'Brien, who always went above and beyond to help with NMR spectra. I also have to thank Dr. Martin Feeney and Dr. Gary Hessman for their help with mass spectrometry, and Dr. Manuel Reuther for technical help. Thanks to Dr. Brendan Twamley for his crystallographic expertise. Thanks also to Adam, my undergraduate student, for all his hard work. I must sincerely thank collaborators in Universität Bern in Switzerland, particularly Dr. Shi-Xia Liu, and all those in the research group of Dr. Harald Fuchs at the University of Münster.

Finally, I must thank my family, for all their encouragement and support over the past four years.

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Abbreviations

1D	one-dimensional
2D	two-dimensional
Å	Angstrom
AFM	atomic force microscopy
Alq ₃	(tris(8-quinolino)aluminium)
Ar	aryl
bpy	2,2'-bipyridine
br	broad
Bu	butyl
°C	degrees Celsius
<i>ca.</i>	<i>circa</i>
cat.	catalytic
CBP	4,4'-N,N'-dicarbazole-biphenyl
CHP	cyclohexa- <i>m</i> -phenylene or cyclohexa- <i>o-p-o-p-o-p</i> -phenylene
CNT	carbon nanotube
COSY	correlation spectroscopy
Cp*	pentamethylcyclopentadiene
CT	charge transfer
CV	cyclic voltammetry
CVD	chemical vapour deposition
d	doublet
dd	doublet of doublets
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEPT	distortionless enhancement by polarisation transfer
DFT	density functional theory
DBTF	dibromoterfluorene
DIPA	diisopropylamine

DLC	discotic liquid crystal
DMF	dimethylformamide
DMPD	1,4-dimethylpiperazine-2,3-dione
DMSO	dimethylsulfoxide
DPA	9,10-diphenylanthracene
DPBF	1,3-diphenylisobenzofuran
dppz	dipyrido[3,2- <i>a</i> :2',3'- <i>c</i>]phenazine
e ⁻	electron
EBL	electron beam lithography
EDG	electron-donating group
EI-MS	electron-impact mass spectrometry
em	emission
ESI-MS	electrospray ionisation mass spectrometry
EtOH	ethanol
EWG	electron-withdrawing group
exc	excitation
Fc/Fc ⁺	ferrocene/ferrocenium
FET	field-effect transistor
FTIR	Fourier transform infrared spectroscopy
g	gram
GIC	graphite intercalation compound
GNR	graphene nanoribbon
GO	graphene oxide
h	hour
HBC	hexa- <i>peri</i> -hexabenzocoronene
HMBC	heteronuclear multiple-bond correlation
HOMO	highest occupied molecular orbital
HOPG	highly ordered pyrolytic graphene

HPB	hexaphenylbenzene
HPHAC	hexapyrollohexaazacoronene
HREELS	high resolution electron energy loss spectroscopy
HRMS	high resolution mass spectrometry
HSB	heterosuperbenzene
HSQ	hydrogen silsesquioxane
HSQC	heteronuclear single quantum coherence
hr	hour
Hz	Hertz
IL	intraligand
IR	infrared
<i>J</i>	coupling constant
K	Kelvin
L	ligand
LC	ligand centred
LCD	liquid-crystal display
LLCT	ligand-to-ligand charge transfer
LMCT	ligand-to-metal charge transfer
LUMO	lowest unoccupied molecular orbital
m	multiplet
M	molarity
mol	mole
m.p.	melting point
m/z	mass to charge ratio
MALDI-TOF MS	matrix-assisted laser desorption/ionisation – time of flight mass spectrometry
MC	metal-centred
Me	methyl

MeOH	methanol
MeNO ₂	nitromethane
mg	milligram
MHz	megahertz
mL	millilitre
MLCT	metal-to-ligand charge transfer
ML'LCT	(metal-ligand)-to-ligand charge transfer
MMLCT	metal-metal-ligand charge transfer
mmol	millimole
MS	mass spectrometry
MWCNT	multi-walled carbon nanotube
mV	millivolt
nc-AFM	non-contact atomic force microscopy
N-GNR	nitrogen-containing graphene nanoribbon
N-½HSB	half-cyclised nitrogen heterosuperbenzene
N-⅔HSB	two-thirds cyclised nitrogen heterosuperbenzene
N-HSB	nitrogen heterosuperbenzene
NIR	near-infrared
nm	nanometre
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
ns	nanosecond
OFET	organic field effect transistor
OLED	organic light-emitting diode
ORR	oxygen reduction reaction
ORTEP	Oak Ridge thermal ellipsoid plot
ox	oxidation

p-GNR	pristine graphene nanoribbon
PAH	polycyclic aromatic hydrocarbon
PAO	platinum acetylide oligomer
PCE	power conversion efficiency
Ph	phenyl
phen	1,10-phenanthroline
PhOLED	phosphorescent organic light-emitting diode
PIFA	(bis(trifluoroacetoxy)iodo)benzene
ppm	parts per million
ppy	2-phenylpyridine
Pr	propyl
PR-TRMC	pulse-radiolysis time-resolved microwave conductivity
Q/quat	quaternary carbon
RIE	reactive ion etch
ROESY	rotating frame Overhauser effect spectroscopy
RT	room temperature
s	singlet
SCE	saturated calomel electrode
SEM	scanning electron microscopy
sh	shoulder
SOC	spin-orbit coupling
STM	scanning tunneling microscopy
STS	scanning tunneling spectroscopy
SWCNT	single-walled carbon nanotube
T	triplet
t	tertiary
T _o	extrapolated onset temperature
TAC	time to amplitude converter

TBC	tribenzocoronene
TCSPC	time-correlated single photon counting
terpy	2,2':6',2''-terpyridine
<i>tert</i>	tertiary
THF	tetrahydrofuran
TLC	thin-layer chromatography
TM	transition metal
TMS	trimethylsilyl
TOCSY	total correlation spectroscopy
TPP	tetraphenylporphyrin
TTA	triplet-triplet annihilation
UHV	ultra-high vacuum
UV-Vis	ultraviolet-visible
XPS	X-ray photoelectron spectroscopy
V	Volts
vs.	<i>versus</i>
°	degrees
δ	chemical shift
Δ	heat
ΔE_p	peak potential separation
ϵ	molar extinction coefficient
λ	wavelength
μs	microsecond
τ	lifetime
Φ	quantum yield
ν	stretching frequency
%	percentage

Chapter One

The Synthesis and Characterisation of Fused Aromatic Hydrocarbons and Their Material and Ligand Applications – Introduction

1.1 Introduction

The aim of this chapter is to give a very brief overview of the field of materials chemistry, giving context to the work carried out in the following chapters of this thesis, and the application of π -conjugated materials based around polycyclic aromatic hydrocarbons (PAHs) within it. Subsequent chapters will introduce different materials and ligand applications of conjugated systems, with each chapter providing a more in-depth discussion of the relevant field. This thesis will describe the synthesis of conjugated materials *via* traditional wet chemistry techniques, and also by the newly emerging on-surface synthesis method. Transition metal complexes bearing conjugated, PAH-based ligands, centred on those of platinum and iridium, will also be discussed.

1.2 Materials Chemistry

The field of materials chemistry is rapidly expanding, and the last few decades have witnessed the area of organic electronics move from mostly academic curiosity to materials that have begun to push the boundaries of device fabrication. As silicon-based electronic devices have begun to near the limits of their development,¹ devices based upon organic electronics have started to emerge as alternative candidates, due to their potential for facile processing, lightweight devices, and large-area fabrication.^{2, 3} Organic electronics refers to the use of conjugated molecules as the active components in a device.⁴ Since it was first demonstrated that organic semiconductors could emit light, the research interest in this field has grown rapidly. One of the major initial breakthroughs was reported in 1987, by Tang and Van Slyke, working at the Eastman Kodak company, who reported the first thin-film organic light emitting diode (OLED).⁵ This demonstration of light emission from a thin film paved the way for the highly efficient OLED technologies now appearing on the market *e.g.* in television screens, and displays in mobile devices. A key driving force in the development of emissive organic materials for OLED applications is the potential for considerable energy savings from these materials, *versus* traditional display technologies that require back-lighting, such as liquid-crystalline displays (LCDs). It is envisaged that very thin, flexible displays will be possible from solely organic materials.⁶ Organic electronics are of significant interest for photovoltaic devices, as the organic materials envisaged could be deposited over large areas, with low-cost processing techniques, which would lead to substantial cost savings over current inorganic semiconductor production techniques.⁶

Various different types of π -conjugated systems have been investigated as the materials for electronic devices. Their key requirements are stability and charge-carrier mobility.⁷ A class of π -conjugated organic materials that have emerged as promising candidates for applications in organic electronics are polycyclic aromatic hydrocarbons (PAHs). These materials, which may be viewed as synthetically accessible fragments of graphene, have witnessed a resurgence in research interest.⁸

Graphene, an extended sheet of a single layer of sp^2 -hybridised carbon atoms, has been the subject of intense research activity since its successful isolation by Novoselov and Geim in 2004.⁹ It has attracted particular interest for its very high charge-carrier mobilities, leading to substantial investigations into its potential for future electronics.⁸ The Achilles heel of pristine graphene is that it does not possess a band-gap, *i.e.* a gap between the energy of the valence and conduction bands, meaning that its conduction cannot be switched on and off, therefore restricting its use as a semiconductor. Further to this, there are difficulties in preparing the material with a high degree of accuracy and in scalable quantities. It has been found that smaller, confined segments of graphene, graphene nanoribbons and nanographenes, do exhibit a band-gap, which is dependent on their size and edge-configuration.⁸ Two distinct strategies have emerged towards the production of graphene and its smaller derivatives, top-down methods, which include techniques such as lithographic cutting, and unzipping of carbon nanotubes, and bottom-up methods, which involve the chemical synthesis of nanographenes. These strategies are discussed in detail in Chapter Two. The top-down methods suffer from a lack of control over edge structure and size-distribution, whereas the bottom-up methods offer a much greater degree of precision. Larger PAHs are often also referred to as nanographenes,¹⁰ and generally possess an average diameter below 10 nm.⁷ The size relationship between the parent material graphene and its smaller derivatives is displayed in Figure 1.1.

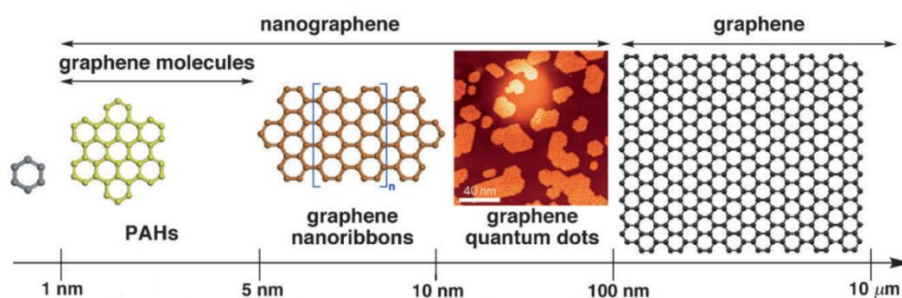


Figure 1.1: The size relationship between the parent material graphene and its derivatives. Adapted from Chen *et al.*¹¹

1.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) were first isolated from coal tar in the nineteenth century.¹² They are widely found in oil and coal deposits, and are also formed during the combustion of fossil fuels. Despite their widespread environmental presence, synthetic chemical methods are required to obtain pure samples of PAHs with the desired morphology and functionality.¹³ The term ‘aromatic’ refers to systems which obey Hückel’s rule, which states that planar, conjugated, monocyclic systems possessing $(4n+2)\pi$ electrons display an enhanced stability, *e.g.* benzene.¹⁴ The conjugated π bonds permit delocalisation of the π electrons across the system, giving rise to a lower energy, closed shell (*i.e.* all bonding molecular orbitals fully occupied) structure. Systems with $4n\pi$ electrons are more reactive, and are termed ‘anti-aromatic’.¹⁴ Early chemical syntheses of PAH-type compounds were reported by Clar *et al.* in the 1950s using rather harsh conditions.^{12, 15} Since then, a number of milder approaches have been developed, allowing access to a wide range of variously sized and functionalised PAH derivatives. A number of representative examples of PAHs are displayed in Fig. 1.2 (where ‘LC’ designates a literature compound).

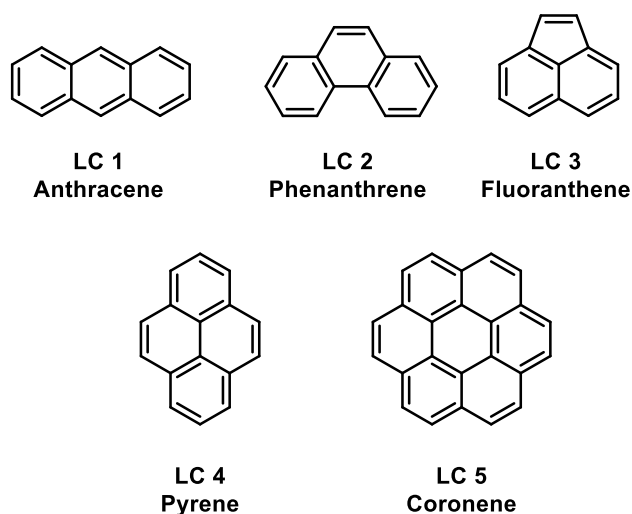


Figure 1.2: Examples of polycyclic aromatic hydrocarbons (PAHs).

PAHs often possess very different optical and chemical properties, depending on their size and geometry. The manner in which the six-membered rings are arranged can lead to two different arrangements of the periphery of PAHs, known as ‘armchair’ or ‘zig-zag’ edges (Fig. 1.3 (a)). These different edge structures lead to very different reactivities, with a higher stabilisation being observed for armchair-type structures. A lower resonance stabilisation is achieved with zig-zag edges, and consequently, larger PAHs with zig-zag

edges can only be handled under inert atmospheres.¹⁰ The stability, and reactivity of a PAH can also be estimated by a rule developed by Clar. The sextet rule states that if the π electrons of each ring can be grouped into sextets, which have a strong aromatic stabilisation, the structure exhibits a higher degree of stability.¹⁰ A PAH which possesses many sextet groups is therefore more stable, and less likely to undergo chemical reactions. A common example of the difference in stability between PAHs which possess different numbers of sextets is that of triphenylene and tetracene (Fig. 1.3 (b)). Triphenylene exhibits a very high degree of stability due to all 18 π electrons being possible to be grouped as sextets. Its isomer, tetracene, does not exhibit this stability because only one sextet may be assigned to one of the rings at a time.¹⁰ A structure such as triphenylene, where all the π electrons can be grouped as sextets and there are no remaining isolated double bonds, is known as ‘fully-benzenoid’.

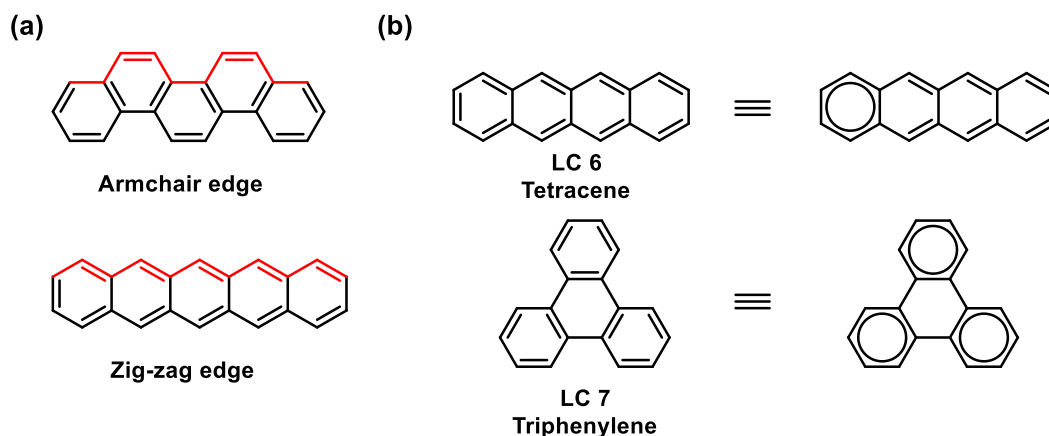


Figure 1.3: (a) The different peripheral arrangements of PAHs. (b) The different electronic structures of triphenylene and tetracene lead to different stabilities. The electron sextets are denoted by rings. Adapted from Rieger et al.¹⁰

A number of very large PAH-type molecules have been synthesised, one of the largest being a disk-shaped PAH consisting of 222 carbon atoms.¹⁶ However, the solubility of these larger compounds is usually very low. Substitution of the periphery of PAHs, such as with *tert*-butyl groups or alkyl chains, leads to improved solubility and much more facile solution processing. PAH-type molecules, generally those which are fully-benzenoid, with appropriately substituted peripheries can exhibit liquid crystalline properties.⁷ This property makes them attractive for applications in organic electronics.^{17, 18} Termed ‘discotic liquid crystals’ or DLCs, these disk-like PAH compounds can self-assemble into columnar mesophases, with a stacked arrangement (Fig. 1.4 (a)). The periphery of these PAHs are

generally substituted with long alkyl chains. The π -stacking interactions between the aromatic cores of each PAH lead to the columnar stacking interactions, with the stacking leading to enhanced charge carrier mobilities.¹⁹ The central aromatic core provides the means for one-dimensional charge-carrier transport, which can be measured with pulse-radiolysis time resolved microwave conductivity (PR-TRMC) experiments.²⁰ Triphenylene (**LC 7**) exhibits columnar mesophases with high charge carrier mobility, as determined by PR-TRMC. One of the most intensely investigated all-benzenoid PAHs is known as hexa-*peri*-hexabenzocoronene (HBC, **LC 8**, Fig. 1.4 (b)), which consists of 13 fused rings.¹⁰ This PAH may be accessed by a variety of synthetic routes, and its derivatives been incorporated successfully into a number of devices.^{13, 21} One of the highest charge-carrier mobilities for a liquid crystal has been reported for a HBC derivative, $1.1 \text{ cm}^2/\text{Vs}$.¹⁷ The larger aromatic core of HBC leads to enhanced stability and improved charge-carrier mobility.¹⁸ Unsubstituted HBC is highly insoluble, and the periphery is usually substituted with appropriate solubilising groups.²²

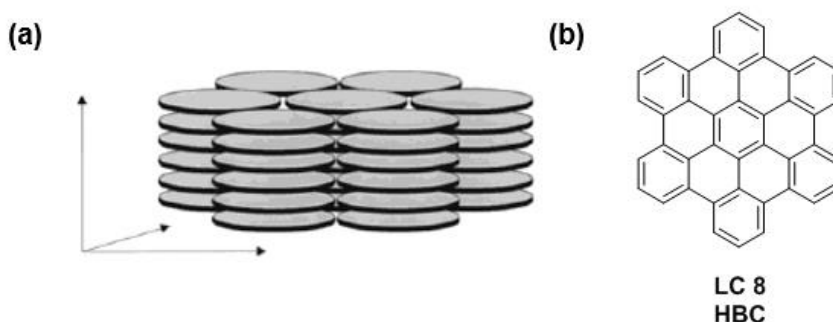
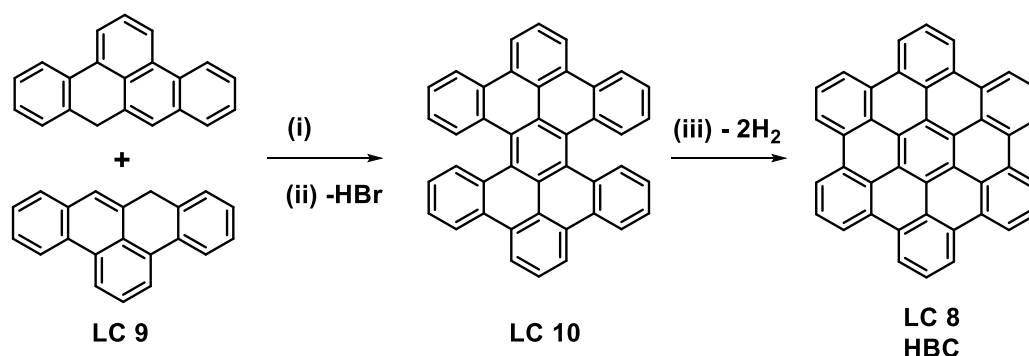


Figure 1.4: (a) A depiction of the stacking arrangement exhibited by discotic liquid crystals. From Watson *et al.*²³ (b) The structure of unsubstituted hexa-*peri*-hexabenzocoronene (HBC).

1.4 Synthetic Routes Towards PAHs

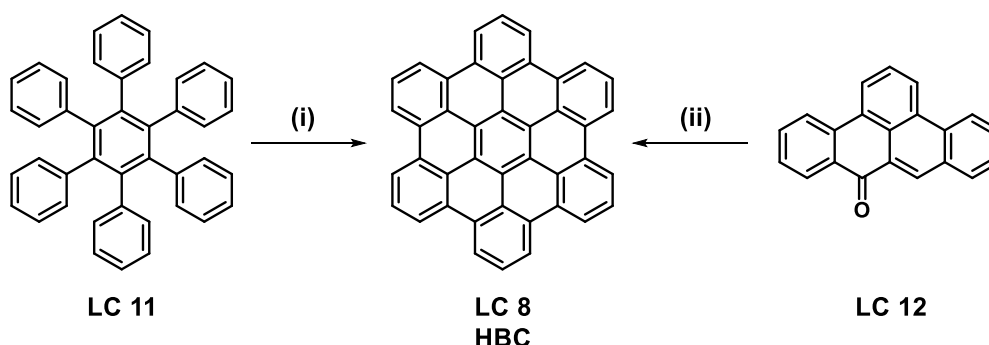
Early synthetic methods towards PAHs employed harsh conditions, such as high temperatures and strongly oxidising reaction melts.²⁴ These initial methods were pioneered by Scholl and Clar in the early to mid-twentieth century.^{15, 25} Subsequently, a number of milder routes were developed, during the 1990s, by the Müllen group.²⁶⁻²⁸ These methods predominantly involve the intramolecular cyclodehydrogenation of a polyphenylene precursor to generate a planarised, fused PAH. As the most intensely investigated PAH, and

since this thesis focuses upon systems based on it, the following section will focus mostly on the synthetic methods towards HBC and its derivatives. However, the general modern route towards most PAH-type systems is based upon similar principles, *i.e.* the preparation of a suitable polyphenylene and its subsequent cyclodehydrogenation. The first synthesis of HBC was reported *via* a different route by Clar *et al.* in 1958 (Scheme 1.1).^{29, 30} They reported that the bromination of 2:3-7:8-dibenzo-*peri*-naphthene gave a dark brown perbromide, which upon heating to 153 °C gave tetrabenzoperopyrene (**LC 10**). Further heating of the tetrabenzoperopyrene to 481 °C gave HBC.



Scheme 1.1: Synthetic route towards HBC, as devised by Clar *et al.*²⁹ (i) Br_2 , C_6H_6 . (ii) 153 °C. (iii) 481 °C.

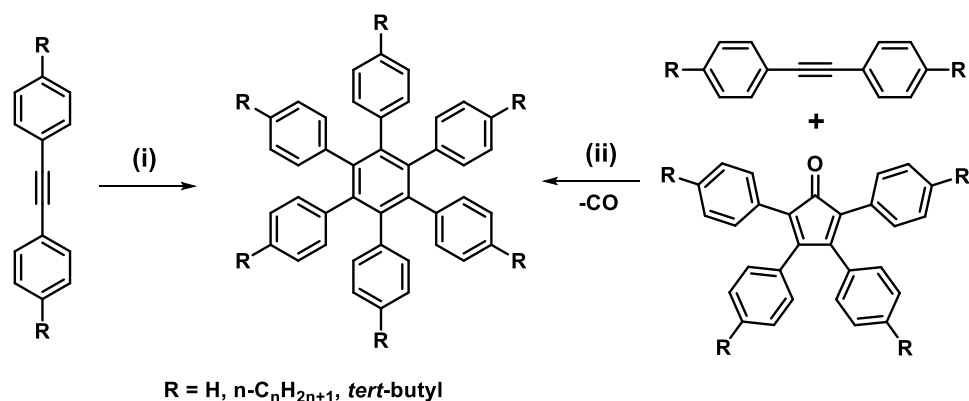
Halleux *et al.* reported two different methods towards HBC later in 1958.³¹ Their first route involved the treatment of hexaphenylbenzene (**LC 11**) with molten $\text{AlCl}_3/\text{NaCl}$, which produced HBC in 3 % yield. They also reported the reaction of dibenzo-1,9;2,3-anthrone (**LC 12**) with Zn/ZnCl_2 also gave HBC, in 8 % yield (Scheme 1.2).



Scheme 1.2: The synthetic routes to HBC reported by Halleux *et al.*³¹ (i) $\text{AlCl}_3/\text{NaCl}$. (ii) Zn/ZnCl_2 .

1.4.1 Modern Routes to PAH Precursors

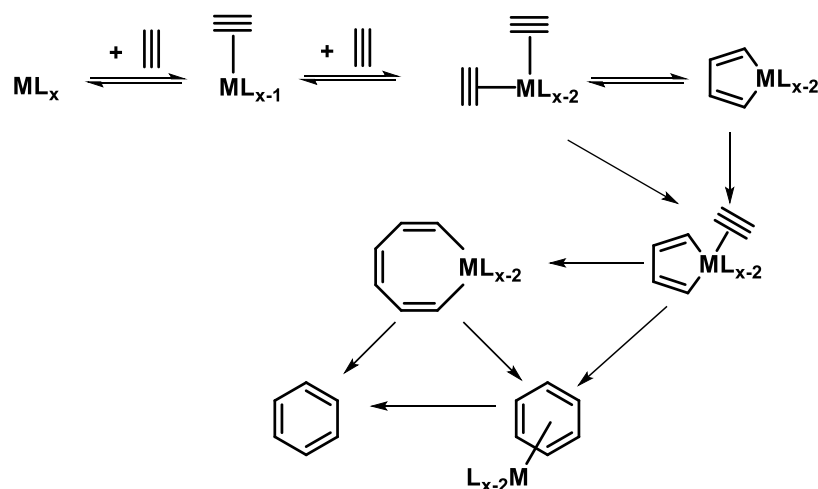
The Müllen group have been instrumental in developing much improved synthetic methods towards HBC-type compounds which give higher yields and more facile work-up.²¹ Two strategies have emerged for the reliable and scalable preparation of HBCs; both methods hinge upon the synthesis of a hexaphenylbenzene (polyphenylene) precursor which is subsequently cyclodehydrogenated to give the HBC derivative. The two routes to the hexaphenylbenzene are *via* the cobalt carbonyl-catalysed [2 + 2 + 2] cyclotrimerisation of an appropriately substituted alkyne, or *via* the Diels-Alder [4+2] cycloaddition between appropriately substituted cyclopentadienone and an alkyne. The two approaches are depicted in Scheme 1.3.



Scheme 1.3: The two different approaches to polyphenylene precursors for functionalised HBCs. (i) $Co_2(CO)_8$, 1,4-dioxane, reflux. (ii) Diphenylether or benzophenone, reflux.

The cyclotrimerisation route involves conditions that are tolerant of halogen and alkyl substituents, providing a means of introducing functionalisation and/or solubilising groups into the periphery of the highly insoluble HBC core.²⁴ The [2 + 2 + 2] cyclotrimerisation of an alkyne was first reported by Berthelot in 1866, who observed the formation of benzene from three molecules of acetylene, at high temperature (*ca.* 400 °C).³² The first metal-catalysed cyclotrimerisation was reported by Reppe in 1948, who described the Ni(II) catalysed cyclotrimerisation of acetylene to benzene, cyclooctatetraene and styrene.³⁴⁻³⁶ The cobalt carbonyl catalyst has proven highly useful for the preparation of hexaphenylbenzenes with six-fold symmetry. For example, the hexaphenylbenzene **LC 11** (Scheme 1.2) may be produced in almost quantitative yield from the cobalt carbonyl-catalysed cyclotrimerisation of commercially available diphenylacetylene.²³ Vollhardt has proposed a general mechanism for the metal-catalysed cyclotrimerisation process,³⁷ which

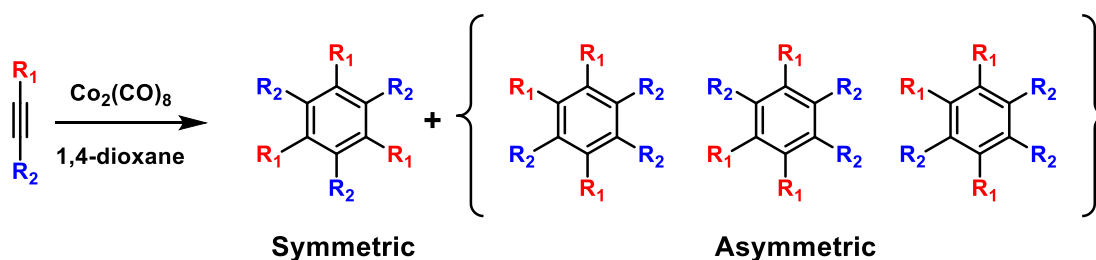
is depicted in Scheme 1.4. It is thought that initially one, and then a further alkyne displace the ligands on the metal, to form alkyne complexes. Vollhardt proposes two possible subsequent routes; oxidative coupling to give a metallocyclopentadiene, which may then coordinate a third alkyne, or direct conversion to the alkyne-coordinated metallocyclopentadiene, without the intermediate step.³⁷ There are then two possible routes after this step. The metallocycloheptatriene may be formed by alkyne insertion, or the benzene complex may be formed by Diels-Alder [4+2] cycloaddition. Decoordination of the metal then yields the cycloadduct.



Scheme 1.4: The mechanism proposed for metal-catalysed [2 + 2 + 2] cyclotrimerisation. From Vollhardt.³⁷

While the cyclotrimerisation of alkynes presents a useful method of generating polyphenylenes with six-fold symmetry, there are some drawbacks to this approach. The first is that the chosen functional groups must be compatible with the catalyst. For example, attempts to cyclotrimerise 1,2-di(pyrimidin-5-yl)ethyne have failed, as the acetylene in this case forms a complex with the catalyst.²¹ Also, the R groups that are introduced at the periphery, such as *tert*-butyls, are restricted to one type, unless an asymmetric alkyne is chosen.²⁰ The cyclotrimerisation of an asymmetric alkyne, although presenting a route towards greater functionalisation, presents a drawback in that it results in two products which must be separated, the symmetric isomer and the asymmetric isomer. This is due to the asymmetric nature of the alkyne, which may be combined in several different ways. Therefore the cyclotrimerisation of an asymmetric alkyne leads to regioisomeric 1,2,4- and 1,3,5-trisubstituted benzenes.³³ Although challenging, it is often possible to separate these isomers by chromatography. The formation of these isomers is depicted in Scheme 1.5,

where it is noted that statistically the asymmetric regioisomer is formed in a 3:1 ratio to the symmetric regioisomer.



Scheme 1.5: The formation of symmetric and asymmetric regioisomers from an asymmetric alkyne.³⁸

The Diels-Alder [4+2] cycloaddition presents a versatile route towards polyphenylenes with a lower degree of symmetry. This route (depicted as route (ii) in Scheme 1.3) involves subjecting an alkyne to a [4+2] cycloaddition with a tetraphenylcyclopentadienone.²⁴ A Diels-Alder adduct is formed which spontaneously extrudes carbon monoxide (CO) to give the desired product.²⁴ Different substituents may be incorporated into the alkyne and the cyclopentadienone precursors, leading to a hexaphenylbenzene with a broad range of functionalisation possibilities.

The Diels-Alder reaction is a cycloaddition reaction named after its two discoverers, Otto Diels and Kurt Alder, who first reported it in 1928.^{39, 40} The reaction is termed a pericyclic process, as it occurs in a single step, with no intermediate stages involved.⁴¹ The reactants add together *via* a cyclic transition state, with both of the carbon-carbon bonds forming at the same time. It has proven immensely useful, particularly in the total synthesis of natural products. The reaction takes place between two components termed the diene and dienophile (Fig. 1.5 (a)). It occurs by head-on overlap of the two p orbitals of the dienophile (which has 2π electrons) with two p orbitals of the conjugated diene (which has 4π electrons).⁴¹ The *s-cis* conformation of the diene is required for the reaction to proceed. Cyclic dienes, such as the cyclopentadienones discussed here, are permanently in the *s-cis* conformation, and therefore well-suited to Diels-Alder reactions.¹⁴ It is stereospecific, as the stereochemistry of the dienophile is maintained in the product.⁴¹ The reaction depicted in Fig. 1.5 (a), a common literature example, actually gives a poor yield, due to the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels of the diene and dienophile being far apart in energy.¹⁴ The majority of Diels-Alder reactions involve electron-deficient dienophiles and electron-rich dienes, referred to as

normal electron demand reactions. In this situation, the energy of the HOMO level of the electron-rich diene is high, and the energy of the LUMO is low in the electron-poor dienophile. This leads to a smaller energy gap, and improved overlap in the transition state (Fig. 1.5 (b)).¹⁴ This is achieved by conjugating the diene with electron-donating groups (EDG) and the dienophile with electron-withdrawing groups (EWG). A greater cycloaddition reactivity is obtained with a smaller HOMO-LUMO gap.⁴² The electron-withdrawing group lowers the LUMO energy by making the dienophile less nucleophilic (*i.e.* the addition of an electron is more facile). The opposite case, which is rarer, is where the dienophile is electron-rich and the diene is electron poor, and is termed the reverse electron demand Diels-Alder.¹⁴

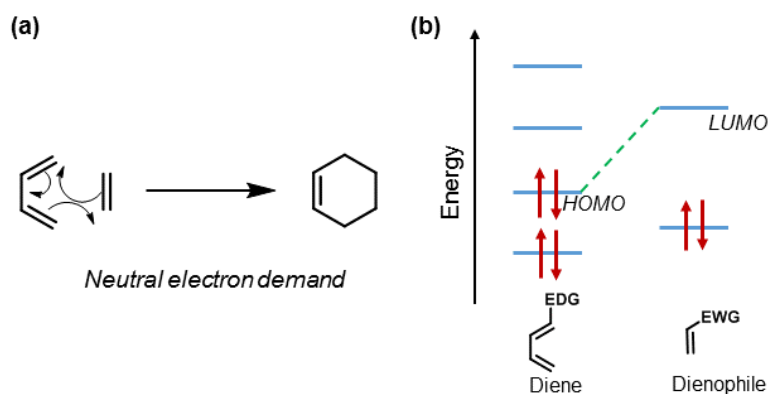
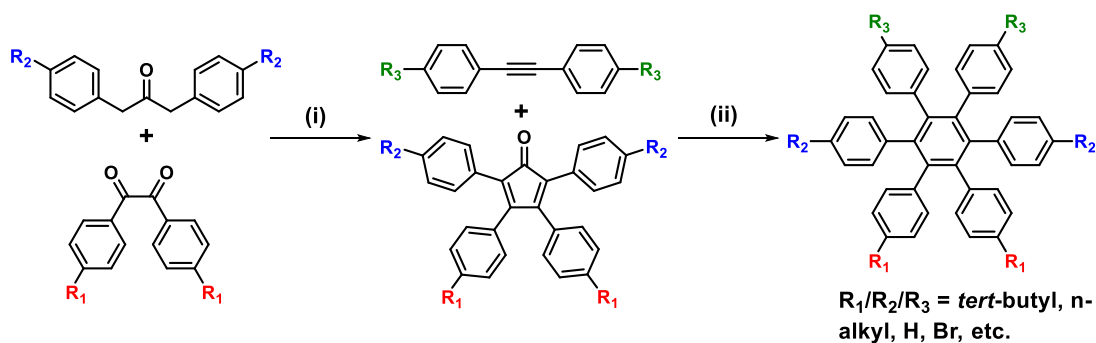


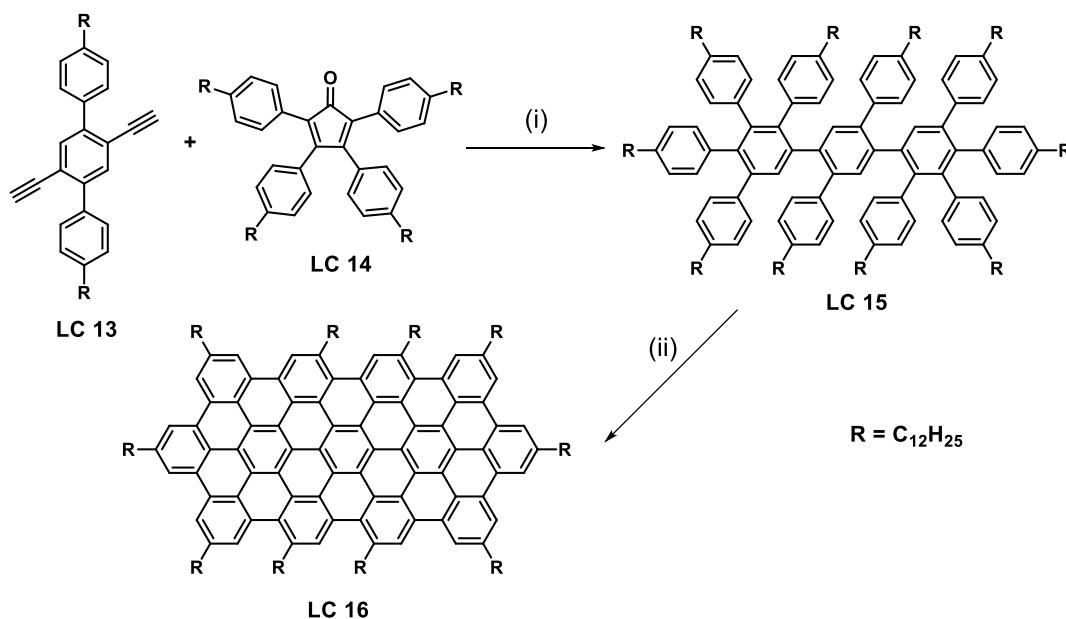
Figure 1.5: (a) Depiction of the concerted Diels-Alder reaction between a dienophile and a diene. (b) An energy diagram depicting the HOMO-LUMO separation in the normal electron demand case.

As a route towards the synthesis of structurally defined PAHs, the Diels-Alder cycloaddition has proved enormously useful, particularly for the synthesis of HBC derivatives. Through the appropriate substitution of both the alkyne and the cyclopentadienone, it is therefore possible to produce a PAH with a very high degree of functionalisation. The cyclopentadienone precursor is generally prepared through the base-catalysed double Knoevenagel condensation of a 1,2-diketone and a 1,3-diarylaceton.⁴³ The 1,2-diketones are prepared by the synthesis described by Mueller-Westerhoff *et al.*,⁴⁴ which is further described in Chapter Three. The 1,3-diarylaceton are usually prepared according to a procedure developed by Des Abbayes *et al.*⁴⁵ The manner in which the Diels-Alder methodology allows facile and extensive asymmetric functionalisation in hexaphenylbenzene precursors to HBC-type systems is displayed in Scheme 1.5.



Scheme 1.5: The synthetic route towards HBC precursors with controlled asymmetric functionalisation, introduced via different components. (i) Double Knoevenagel condensation. (ii) Diels-Alder reaction.

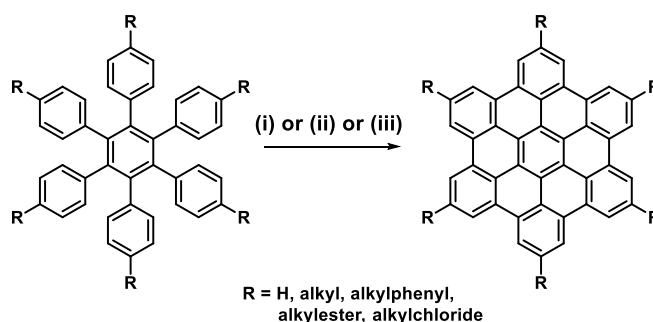
The [4+2] Diels-Alder reaction has been employed to generate polyphenylenes much larger than hexaphenylbenzenes, and provides an elegant route to these larger structures. An example of a larger polyphenylene (78 carbons) synthesised by Böhme *et al.* through Diels-Alder methodology is shown in Scheme 1.6.⁴⁶ Their careful design of a terphenyl derivative (**LC 13**) provided access to polyphenylene **LC 15**. In this example, the fully-planarised PAH derivative of **LC 15** is achieved through intramolecular cyclodehydrogenation with FeCl_3 as oxidant. Whether the polyphenylene precursor has been prepared *via* cyclotrimerisation or *via* the Diels-Alder approach, the key remaining step is therefore intramolecular cyclodehydrogenation, which may be achieved by a number of methods.



Scheme 1.6: The synthetic route to a 78-carbon PAH, as devised by Böhme *et al.*⁴⁶ (i) Ph_2O , 200 °C, 90 %. (ii) FeCl_3 , CH_3NO_2 , CH_2Cl_2 , 83 %.

1.4.2 Oxidative Cyclodehydrogenation

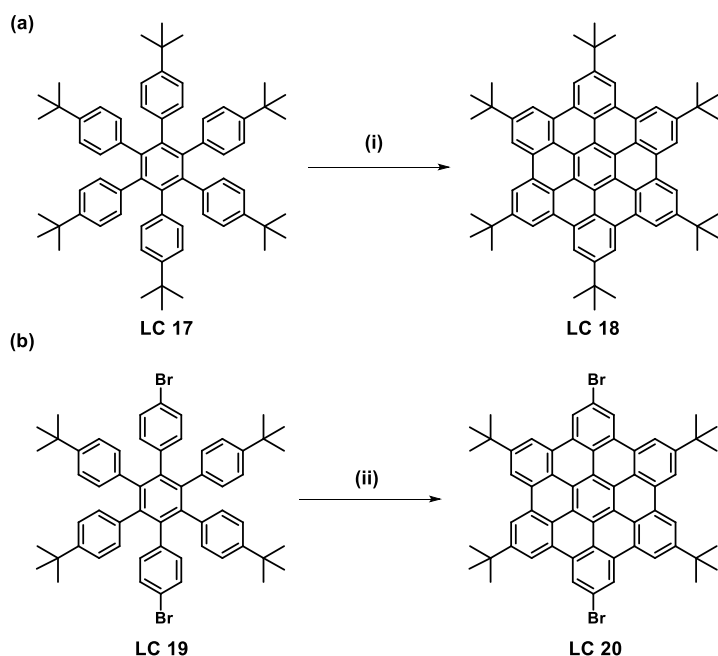
The conversion of polyphenylenes to PAH derivatives is typically undertaken by generating C-C bond closures, *via* a process termed oxidative cyclodehydrogenation, also known as the Scholl oxidation. It was Scholl and Seer who first reported this process in 1910, after they employed AlCl_3 melts to fuse biaryls, with atmospheric oxygen as the oxidant.^{24, 25} Milder conditions were developed by Kovacic *et al.* in the 1960s, who reported that the combination of CuCl_2 as oxidant, with AlCl_3 as a Lewis acid, resulted in the polymerisation of benzene to poly(*p*-phenylene) at temperatures as low as 35-37 °C.⁴⁷⁻⁴⁹ They also reported the use of FeCl_3 to promote C-C bond formation, which does not require an additional oxidant, as it possesses an oxidation potential high enough for bond formation.¹² From the 1990s onwards, the Müllen group have led the way towards efficient methods for the generation of PAHs by oxidative cyclodehydrogenation of polyphenylenes, particularly in the case of HBC.²¹ Early work by the Müllen group described the oxidative cyclodehydrogenation of alkyl-substituted hexaphenylbenzenes with $\text{AlCl}_3/\text{Cu}(\text{OTf})_2$ or $\text{CuCl}_2/\text{AlCl}_3$ in carbon disulfide.^{12, 27} A more versatile route has proven to be an FeCl_3 /nitromethane mixture in dichloromethane, which is more tolerant of different functional groups.²⁰ This milder method also decreased the amount of unwanted side-reactions, such as dealkylation and chlorination.¹³ Continuous bubbling of the reaction mixture with N_2 gas, driving off hydrochloric acid formed during the reaction, also further reduces the formation of any chlorinated by-products. The general process of cyclodehydrogenation of HBC is summarised in Scheme 1.7.



Scheme 1.7: Various routes to fully-fused HBC derivatives.¹² (i) $\text{CuCl}_2/\text{AlCl}_3$, (ii) $\text{Cu}(\text{OTf})_2/\text{AlCl}_3$, (iii) $\text{FeCl}_3/\text{CH}_3\text{NO}_2$.

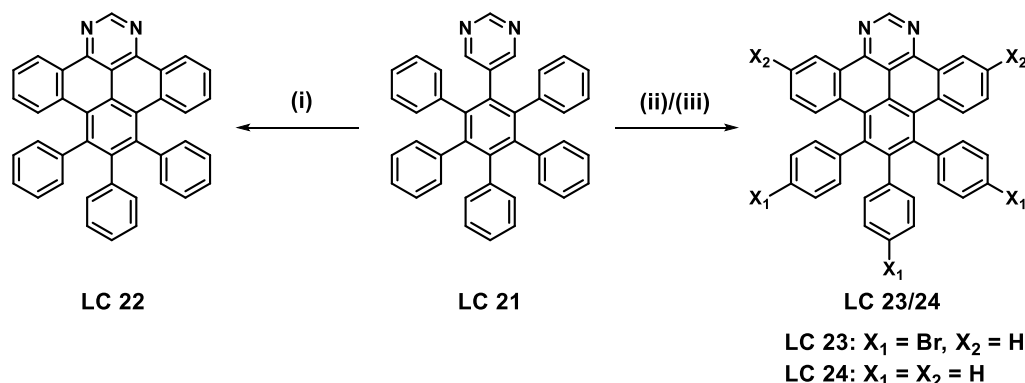
It is important to note that where the precursor polyphenylenes are, in general, relatively soluble, unsubstituted PAHs are generally quite insoluble in organic solvents, due to π - π stacking interactions, and it is common to introduce various solubilising groups to the

periphery *e.g.* *tert*-butyl. Non-covalent electrostatic interactions between the π clouds of adjacent aromatic rings, often referred to as π - π stacking interactions, most often manifest as being offset-stacked or T-shaped in arrangement, and face-centred stacking is rare.⁵⁰ A recent development has been the use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as oxidant in the presence of an acid.^{51, 52} In 2009, Zhai *et al.* reported that the DDQ/H⁺ combination was an efficient route for the intramolecular cyclodehydrogenation of a variety of polyphenylenes to PAHs, including the *tert*-butyl substituted hexaphenylbenzene to its corresponding HBC derivative **LC 18** (Scheme 1.8 (a)). This route presented the advantage of avoiding chlorinated by-products commonly obtained *via* the other routes. Unlike the large excess of FeCl₃ required to perform the Scholl reaction, the DDQ-mediated process requires only one equivalent of DDQ per bond to be closed. In 2012, Jones *et al.* extended this methodology to electron-poor bromo-hexaphenylbenzenes (Scheme 1.8 (b)), and reported the ability to produce the HBC derivatives in high yields and scalable quantities.⁵¹ They employed the stronger acid CF₃SO₃H to effect the full cyclodehydrogenation of **LC 19**. This HBC derivative, **LC 20**, was previously unreported, highlighting how the substitution of the aromatic core can have a significant effect on the success and extent of cyclodehydrogenation. Electron-withdrawing or donor groups can hinder full cyclodehydrogenation, and lead to partially-fused products.¹³



Scheme 1.8: (a) The DDQ/H⁺ combination employed by Rathore *et al.* to generate a fully-fused, soluble HBC derivative.⁵² (i) DDQ, CH₂Cl₂, Me₃SO₃H, 99 %. (b) The bromo-HBC derivative synthesised by Jones *et al.*⁵¹ (ii) DDQ, CH₂Cl₂, CF₃SO₃H, 91 %.

Recent work by Delaney *et al.* has introduced a further means of achieving the cyclodehydrogenation of PAHs.⁵³ This work introduced a novel means of creating partially-fused PAHs, depending on their substitution. The treatment of diazapolyphenylenes with elemental bromine induced C-C bond formation at the pyrimidine rings. The authors also demonstrated that controlled bromination of unsubstituted phenyl rings could also be achieved, thereby introducing further functionality. The presence of pyrimidyl rings appears to be a requirement for the process, as with all-carbon systems, only bromination, with no C-C bond formation was observed. Heating of the polyphenylene **LC 21** in toluene with molecular bromine yielded the partially-fused PAH **LC 22** in quantitative yield (Scheme 1.9). In neat molecular bromine, a variety of products, depending on the reaction time, were observed. These were separable by chromatography. Improved yields of **LC 24** were observed by refluxing in CHCl_3 . This high-yielding method to partially-fused PAHs has opened up a new pathway to precursors for on-surface chemistry, which is discussed in Chapter Two, and also to intriguing ligands for transition metal complexes.

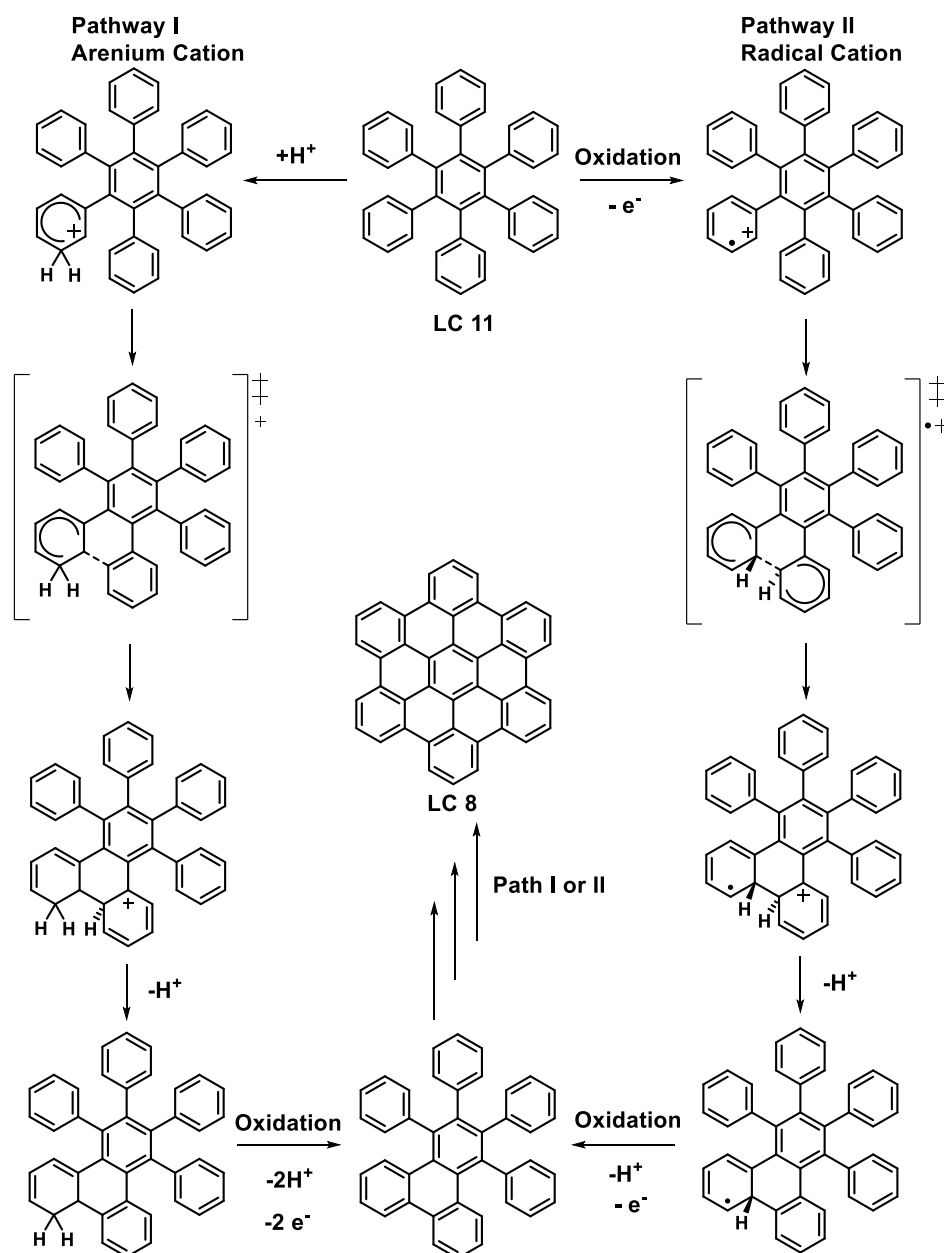


Scheme 1.9: The route to partially-fused PAHs, devised by Delaney *et al.* (i) Br_2 , toluene, 90 °C, 2 h, 85 %. (ii) **LC 23/LC 24:** Br_2 , RT. (iii) **LC 24:** Br_2 , CHCl_3 , reflux 3h, 50 %.

1.4.3 The Mechanism of Oxidative Cyclodehydrogenation

The mechanism by which the oxidative cyclodehydrogenation process occurs has been the subject of much debate within the scientific community. Since partially-fused compounds are often observed, the process has been suggested as occurring in a stepwise process.^{13, 54} Two possible routes have been suggested, (i) the arenium cation mechanism, involving proton transfer, and (ii) the radical cation mechanism, involving electron

transfer.⁵⁵ The two pathways are contrasted in Scheme 1.10, where they are applied to the example of the oxidative cyclodehydrogenation of **LC 11** to **LC 8** (HBC).



Scheme 1.10: The mechanisms proposed for oxidative cyclodehydrogenation, applied to the example of the cyclodehydrogenation of **LC 11** to HBC (**LC 8**). Adapted from Seyler *et al.*¹³

For both proposed mechanisms, the process proceeds stepwise and contiguously, and has been termed a ‘slippery slope’ as the formation of the first bond occurs slowest, with subsequent C-C bond formations being increasingly exergonic.⁵⁵ Computational studies by Rempala *et al.* have suggested that the arenium cation mechanism involves lower energy transition states.⁵⁶ The arenium cation pathway is proposed to begin *via* initial protonation,

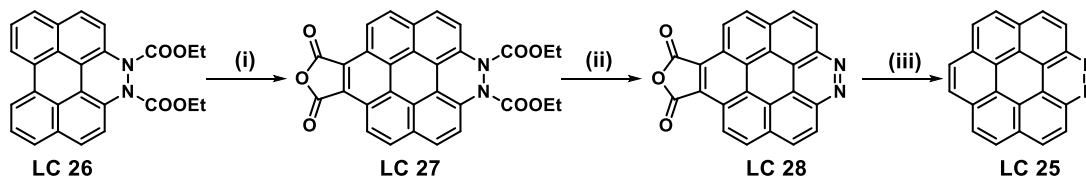
followed by the σ complex forming a C-C bond with an adjacent aryl ring. Deprotonation and dehydrogenation provides the fused compound. Rempala *et al.* suggest that Brønsted acids are catalysts in this process.⁵⁶ However, their calculations fail to account for the presence of partially-fused products, such as those that have been observed by the Müllen group.⁵⁴ Recent experimental observations of Zhai *et al.* have indicated the opposite, that the radical cation mechanism is most likely.⁵⁷ The mechanism for this process involves an initial removal of an electron by the oxidant (Scheme 1.10). An electrophilic C-C bond forming reaction then occurs with an adjacent aryl group, followed by deprotonation and then the formal loss of a hydrogen atom.

1.5 Introducing Heteroatoms to PAHs

The discovery of graphene and its potential application in electronics has spurred research into methods by which to influence the electronic properties of the material, and its smaller PAH derivatives.⁵⁸ The introduction of heteroatoms (*e.g.* N, S, O, B) to PAHs has emerged as a valuable tool for the modification of the electronic and optical properties. Introducing heteroatoms to extended graphene sheets is problematic, as precise placement of the heteroatoms is very challenging.⁸ This is further discussed in Chapter Two. In contrast, smaller PAH-type compounds which are synthetically accessible through organic chemical methods, present a means of introducing heteroatoms with atomic precision, with control over the placement, doping concentration and the periphery.⁸ Heteroatom substitution of PAHs, sometimes referred to as ‘doping’ (in analogy to the doping of semiconductors or graphene), usually involves the replacement of an sp^2 carbon with a heteroatom.⁵⁹ Nitrogen has predominated as the heteroatom most commonly employed in the synthesis of heteroatom PAHs, due to a greater abundance of synthetic methods available, and the often improved stability of these systems, compared with other heteroatom-substituted systems. The all-carbon PAH counterparts greatly outnumber the heteroatom substituted PAHs due to the often challenging syntheses required.

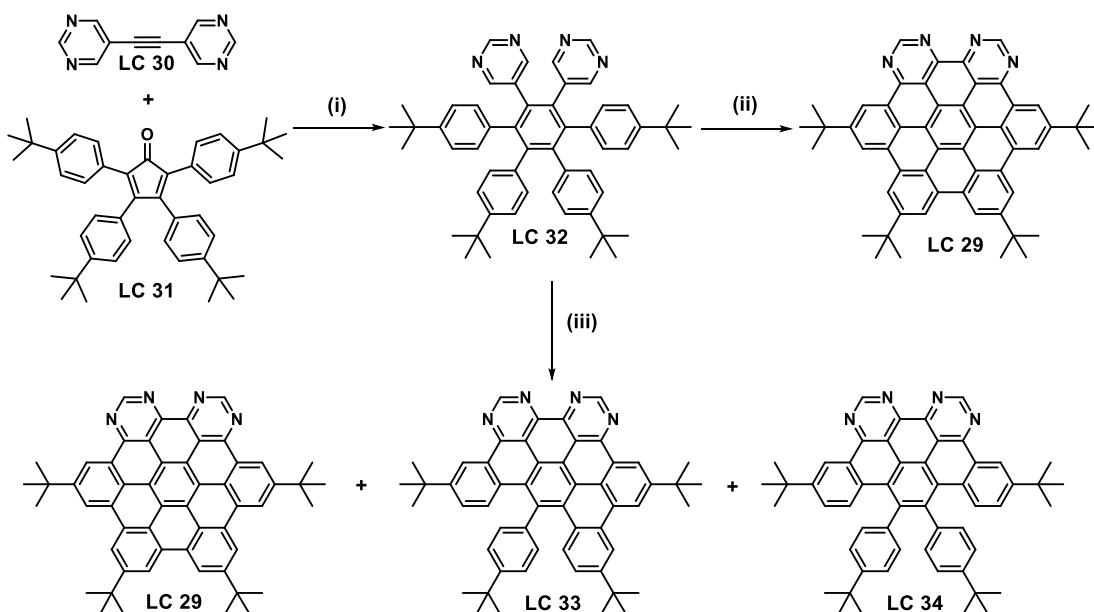
An example of an early report of an N-substituted PAH is that of 1,2-diazacoronene (**LC 25**), synthesised by Tokita *et al.* in 1982.⁶⁰ Treatment of 1,2-diazabenz[ghi]perylene (**LC 26**) with maleic anhydride, in the presence of chloranil, yielded **LC 27** (Scheme 1.11). Hydrolysis and acidification then yielded the anhydride **LC 28**. The desired **LC 25** was obtained by the action of soda-lime on **LC 28**. The product **LC 25**, a yellow solid, was quite

insoluble in organic solvents. The authors stated that the UV-Vis absorption spectrum remained quite similar to that of coronene (**LC 5**).



Scheme 1.11: The synthesis of 1,2-diazacoronene by Tokita *et al.*⁶⁰ (i) Chloranil, maleic anhydride, reflux, 20 min., 61 %. (ii) NaOH, benzyl alcohol, 100 °C, 30 min., 70 %. (iii) Soda lime, 320 °C (1 h), followed by 350 °C (2 h), 26 %.

The 2002 report by the Draper group of a hexa-*peri*-hexabenzocoronene with peripheral N-substitution brought forward revived interest in N-substituted PAHs.⁶¹ This compound, termed N-HSB (nitrogen hetero-superbenzene, **LC 29**), was synthesised through a [4+2] Diels-Alder cycloaddition with 1,2-di(pyrimidin-5-yl)ethyne (**LC 30**) and 2,3,4,5-tetrakis(4-(tert-butyl)phenyl)cyclopenta-2,4-dien-1-one (**LC 31**), yielding the N-substituted polyphenylene precursor **LC 32** (Scheme 1.12). Oxidative cyclodehydrogenation with $\text{AlCl}_3/\text{CuCl}_2$ in CS_2 yielded the fully-fused product **LC 29**. Changing the oxidative cyclodehydrogenation conditions, and employing the milder FeCl_3 -mediated route, led to the formation of the fully fused product, a two-thirds fused analogue, termed $\frac{2}{3}$ -N-HSB (**LC 33**), and the half-cyclised analogue, termed $\frac{1}{2}$ -N-HSB (**LC 34**) (Scheme 1.12, route (iii)).⁶² ⁶³ The partially-fused compounds appear to be thermodynamically stable, as attempts to cyclodehydrogenate them further, *via* the AlCl_3 method, were not successful.

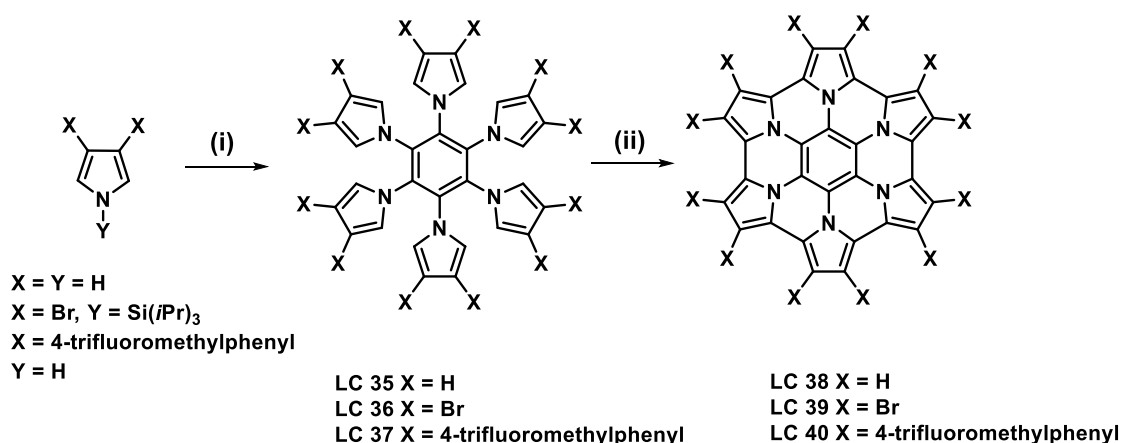


Scheme 1.12: Synthesis of N-HSB (**LC 29**) and partially-fused derivatives, as reported by Draper *et al.*⁶¹⁻⁶³ (i) Ph_2CO , reflux, 1 h, 81 %. (ii) AlCl_3 , CuCl_2 , CS_2 , RT, 72 h, 49 %. (iii) FeCl_3 , MeNO_2 , CH_2Cl_2 , RT. Yields: 45 % (**LC 29**), 23 % (**LC 33**), 20 % (**LC 34**).

The incorporation of the N atoms in the periphery of these compounds led to electron-deficient derivatives of HBC, with low-lying π^* acceptor orbitals. These compounds displayed good solubility, and also N^N ligand functionality. Both Pd(II) and Ru(II) complexes have been reported of **LC 29**. Complexation of Pd(II) led to a quenching of the emission, whilst coordination to Ru(II) led to absorption throughout the visible region (referred to as a ‘black’ metal-to-ligand charge transfer (MLCT) absorber), and emission in the near-infrared (NIR) region. A Ru(II) complex of **LC 34** also displayed NIR emission, slightly more blue-shifted than that of the more conjugated **LC 29**. These complexes, and Ir(III) complexes of a 6N-substituted analogue of N-HSB are further discussed in Chapter Five. As observed from the results discussed above, the oxidative cyclodehydrogenation of N-substituted hexaphenylbenzenes is challenging and often results in mixtures of fused and partially-fused products. All-carbon systems tend to oxidise rapidly, in comparison with N-substituted systems.⁶⁴ The extent of cyclodehydrogenation of these systems seems dependent on both the nature of their substitution and the cyclodehydrogenation conditions employed. The method of using molecular bromine as oxidant to effect the cyclodehydrogenation of N-containing systems, as discussed earlier, has provided a more predictable route to the partially-fused N-substituted PAHs. This method only gives bond closure between pyrimidyl rings and the phenyl rings adjacent, allowing selective access to

partially-fused products. The Draper group have also reported the use of electron-donating methoxy groups in HBC-type systems to promote the cyclodehydrogenation process, and reduce the abundance of partially-fused products.⁶⁴ Incorporation of methoxy groups can result in full bond closure in systems which exhibit partial fusion without these groups. The use of the DDQ/H⁺ process to effect the cyclodehydrogenation of N-substituted hexaphenylbenzenes has also been recently reported, and is a further complementary method to the preparation of N-substituted PAHs.⁶⁵ This technique, and its application to 6N systems, is also further discussed in Chapter Five. The mechanism of oxidative cyclodehydrogenation of PAHs with peripheral N-substitution has been suggested by Rempala *et al.* as being *via* the arenium cation mechanism.⁵⁶ Initial protonation most likely occurs at the pyrimidyl rings, which then act as electrophiles, explaining the initial formation of bonds between the pyrimidyl and adjacent phenyl rings.

Takase *et al.* have reported a series of electron-rich fully-fused N-substituted PAHs, obtained from the oxidative cyclodehydrogenation of hexapyrrollobenzenes (Scheme 1.13), which they named hexapyrrollohexaazacoronenes (HPHACs, **LC 38-40**).^{66, 67} These compounds exhibited four reversible one-electron reduction waves in cyclic voltammetry experiments, showing that higher oxidation states of these compounds are stabilised by the interior nitrogen atoms. This redox behaviour suggested the π -system of these compounds exhibited potential as a charge-carrier material in organic electronics.⁶⁶ Subsequent work showed that stepwise replacement of the pyrrole rings with dialkoxybenzene rings significantly affected the optical properties of these compounds. The emission colour changed from red to green as the number of pyrrole rings was reduced. The family of compounds also exhibited small S₁-T₁ energy gaps (< 0.36 eV), suggesting application as emissive materials that exhibit thermally activated delayed fluorescence (*i.e.* efficient T₁→S₁ intersystem crossing).⁶⁷



Scheme 1.13: Synthesis of HPHACs, devised by Takase *et al.*⁶⁶ (i) NaH or NaOMe, DMF, hexafluorobenzene. (ii) FeCl₃, MeNO₂, CH₂Cl₂, hydrazine.

Building upon initial work by Bouit *et al.*, who reported the successful incorporation of phosphorus into PAH-type compounds,⁶⁸ Riobé *et al.* have recently investigated the coordination ability of the same compounds.⁶⁹ They prepared Pd(II), Cu(I), Re(I), and Au(I) complexes, and reported that the different metals (and their different coordination numbers) had a pronounced impact on the solid state behaviour, and a wide variety of solid-state structures were observed. The emissive behaviour of the complexes remained dominated by the ligand.

1.6 Applications of PAHs

As mentioned previously, HBCs substituted with solubilising alkyl chains demonstrate discotic liquid crystalline behaviour, exhibiting intense π - π interactions of the aromatic cores and behaving as ‘molecular wires’, and consequently have been incorporated into electronic devices such as OFETs (organic field-effect transistors).⁷⁰ Research interest in OFETs stems from their potential for large-area coverage, structural flexibility and low-cost processing.⁷¹ The structure of a typical OFET is displayed in Fig. 1.6 (a). Organic semiconducting materials are classified as being n-type or p-type, depending on whether they transport electrons or holes, respectively, as the majority charge-carriers.⁷² Unsubstituted HBC is a hole transporting (p-type) material.¹³ However, with substitution, HBC derivatives can exhibit n-type (electron transporting) behaviour. A hexafluoro-substituted HBC has been shown to exhibit n-type behaviour.⁷³ In a typical p-type OFET the conduction of charge between the source and drain electrodes is controlled by the gate

voltage. When the gate is positive with respect to the source, the semiconducting material is depleted of carriers. When the gate is negative with respect to the source, charge carriers accumulate in the channel between the source and the drain. The resulting drain current is then proportional to the mobility of the charge carriers in the material.⁷¹ Excellent charge carrier mobility has been observed by Pisula *et al.*, who employed zone-casting techniques to deposit highly-ordered columnar structures of the HBC derivative **LC 41** in Fig. 1.6 (b), forming OFET devices.⁷⁴ In relation to the schematic of an OFET in Fig. 1.6 (a), the HBC derivatives were employed as the semiconductor layer. Zone-casting refers to the deposition of an organic material onto a moving support, shown schematically in Fig. 1.6 (c).²¹ They reported mobilities as high as $1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The theoretical maximum value for charge-carrier mobility for discotic materials is $15.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, but it has been put forward that a value of $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ would be sufficient for high-speed digital circuits.^{75, 76} Therefore much research interest involves the optimisation of these materials, and refinement of deposition techniques that minimise the intracolumnar defects that cause lower carrier mobilities.

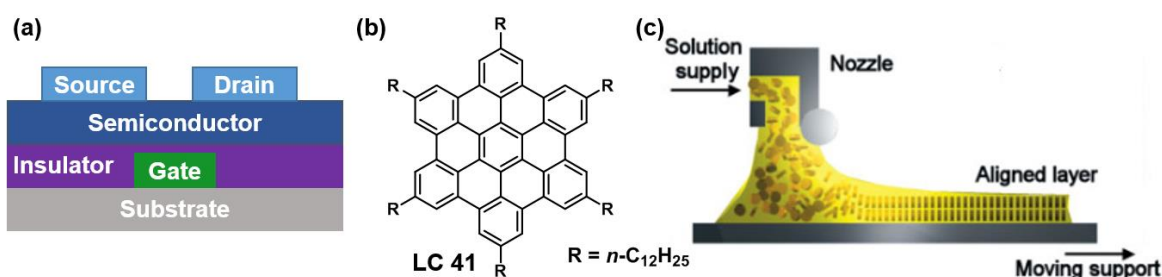


Figure 1.6: (a) Simplified schematic of a typical p-type OFET.⁷¹ (b) Structure of HBC derivative **LC 41** employed by Pisula *et al.* for deposition by zone-casting, a process depicted in (c).⁷⁴

PAHs have also attracted interest as conductive materials in solar cells. Wong *et al.* have reported a series of 9,9-dioctylfluorenyl hexa-peri-hexabenzocoronene (FHBC) compounds, which were employed as the donor component in photovoltaic cells, and which gave promising results.⁷⁷ The power conversion efficiency (PCE) of these cells was 1.5 %, later improved to 2.5 % by the incorporation of thiophene dendrons.⁷⁸ These values are lower than current silicon-based systems (which are typically in the region of 10-25 % PCE), but further optimisation could lead to very promising characteristics.

A very recent application of PAHs, and their precursor polyphenylenes, has been the use of these compounds as molecular precursors for on-surface chemistry, such as in the

formation of graphene nanoribbons (GNRs). The ability to control the structure, and placement of heteroatoms, in small PAHs has led to significant research efforts in this field. Halogenated precursor molecules can be deposited onto reactive metal substrates, and subsequently C-C bonds can be formed, leading to atomically precise narrow ribbons of graphene, which behave as semiconductors due to quantum confinement.⁷⁹ That this process is carried out on a substrate, rather than in solution, circumvents the difficulties associated with the progressive insolubility of these larger systems. This topic is further described in detail in Chapter Two.

A substantial portion of the work reported here describes the use of PAH-type compounds as ligands in transition metal complexes, specifically those of platinum and iridium. The large, extended π -systems of PAH-type ligands mediate the optical and electronic properties of the metal centre *e.g.* Ru(II) complexes of N-HSB and its analogues. Various coordination modes may be employed when using conjugated systems as ligands, such as π -coordination, σ -bond coordination or N[^]N coordination. This thesis will describe metal complexes of fused and partially-fused PAHs (of which there are relatively few reports), and evaluate their photophysical properties.

Photoactive transition metal (TM) complexes (particularly those of Ir(III) and Pt(II)) have attracted much research interest, predominantly for applications as efficient emissive materials in electronic devices such as OLEDs (which convert electrical energy into photoluminescence).⁸⁰ These metal complexes have been extensively studied for application in phosphorescent OLEDs (PhOLEDs). A graphical depiction of an OLED is displayed in Fig. 1.7, where the emissive layer (in this case an organic material) is sandwiched between two metal electrodes. If a potential is applied across the electrodes, the organic emissive layer at the cathode is reduced, and at the anode, it is oxidised, producing electron and hole carriers respectively.⁸¹ These move across the organic material, and can combine with carriers of the opposite sign, to produce a molecule in the ground state, and an exciton.⁸¹ Emission then occurs *via* relaxation of the exciton to the ground state. The initial OLED devices utilised singlet (fluorescent) emitters, which harvested only singlet excitons (with any triplet states generated being deactivated through non-radiative means).⁸² Singlet and triplet excitons refer to the two types of excited molecular states formed upon electron-hole recombination, and are formed in a ratio of 1:3 respectively.⁸³ OLEDs featuring singlet emitters are therefore theoretically only 25 % efficient.⁸² PhOLEDs can harvest both singlet and triplet excitons through emission from phosphorescence, and can therefore in theory be

100 % efficient.⁸¹ The efficient intersystem crossing introduced by the metal centre enables all the generated excitons to be harvested.⁸⁴ The phosphorescent component is generally added as a dopant into the emissive layer, the remainder of which is comprised of a host material such as Alq₃ (tris(8-quinolinato)aluminium) or CBP (4,4'-N,N'-dicarbazole-biphenyl).⁸¹ The doping concentration is usually maintained at a low level to avoid triplet-triplet annihilation (TTA) or concentration quenching effects (*e.g.* excimers).⁸² The often long excited-state lifetimes of transition metal complexes have also prompted their use as triplet photosensitisers, particularly for TTA-upconversion.^{85, 86} This is a strategy for improving the efficiency of the light-harvesting ability of solar cells, and is further discussed in Chapter Four.

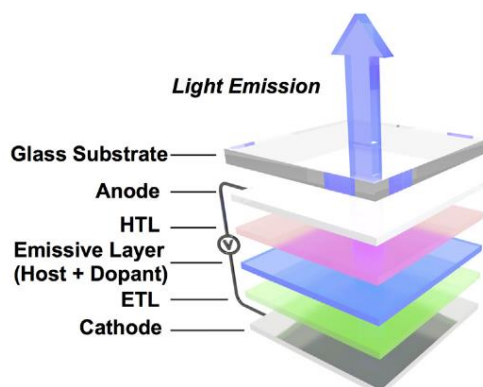


Figure 1.7: Schematic depiction of an OLED (HTL, hole transport layer; ETL, electron transport layer). Adapted from Kirlikovali et al.⁸⁷

1.7 Photophysical Terminology

The relevant chapters which follow will introduce the respective fields, and properties, of the compounds and/or metal complexes, which are discussed in more detail. A general description of the terms used when describing the photophysics of these complexes, and their PAH precursors, is given in Fig. 1.8. The possible transitions for an organic compound are displayed in Fig. 1.8 (a), along with the relative ordering of the relevant orbitals. Although there are six possible transitions ($\sigma\text{-}\sigma^*$, $\sigma\text{-}\pi^*$, $\pi\text{-}\pi^*$, $\pi\text{-}\sigma^*$, $n\text{-}\pi^*$, and $n\text{-}\sigma^*$), only the $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ are generally measurable, as the low-intensity $\sigma\text{-}\pi^*$ and $\pi\text{-}\sigma^*$ are obscured by the stronger $\pi\text{-}\pi^*$ transitions, and the $\sigma\text{-}\sigma^*$ transitions are in the far-UV region, which is inaccessible.⁸⁸ In Fig. 1.8 (b), a generalised MO (molecular orbital) diagram for an octahedral metal complex is displayed. The MOs can be classified according to the

degree of contribution from atomic orbitals (*e.g.* the π_L orbital is predominantly ligand-based and bonding in nature, while the σ_{M^*} is predominantly metal-based and is antibonding).⁸⁹ Excited states, formed by the promotion of an electron from an occupied MO to a vacant MO, can result in a variety of configurations, including metal-centred (MC or d-d), metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), and ligand-centred/intraligand (LC/IL). The relative ordering of the energies of these orbitals depends on both the nature of the metal and the ligands. MLCT transitions are observed when the metal is easily oxidised and a ligand is easy to reduce, and *vice-versa* for LMCT transitions. LC transitions are often observed where ligands are aromatic and possess extended π and π^* orbitals.⁸⁹

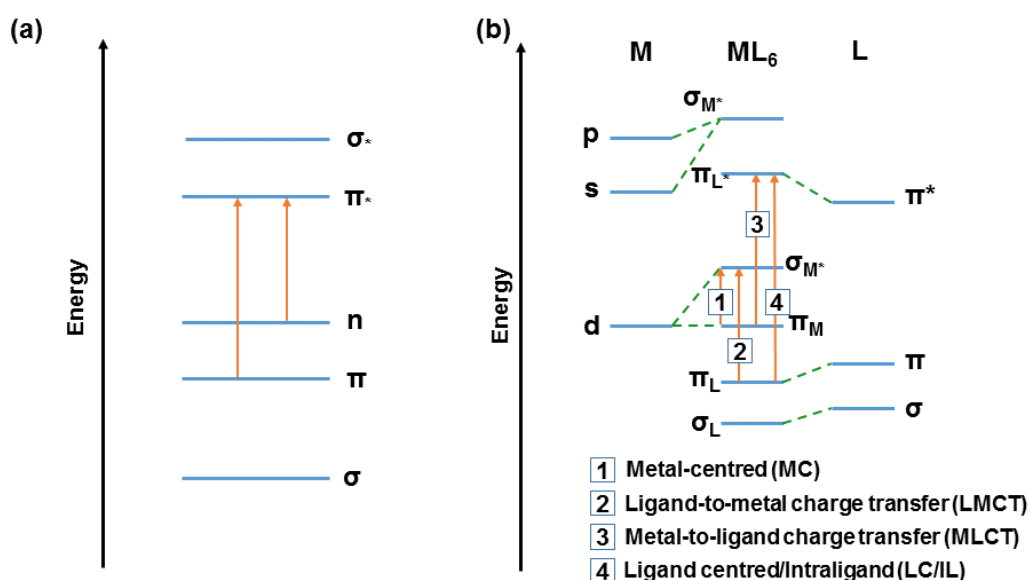


Figure 1.8: (a) MO diagram displaying relative orbital energy levels in an organic molecule, with π - π^* and n - π^* transitions highlighted. Adapted from Wardle.⁸⁸ (b) Generalised MO diagram for an octahedral metal complex of a transition metal (ML_6), with possible transitions highlighted. Adapted from Balzani.⁸⁹

1.8 Aims of this Thesis

This thesis presents work across several different fields, which are linked together by the common theme of fused or partially-fused PAHs. It goes some way towards investigating the effect of the incorporation of extended, and highly conjugated systems, in a variety of applications. Although much work on PAH-based systems including those of HBC has already been undertaken, as highlighted in this chapter and in the following

sections, the scarcity of N-containing systems is noted. These N-containing systems offer the ability for ligand coordination, paving the way toward potentially useful metal complexes with rich photophysical properties. Introducing N atoms also offers a method of altering the electronic and optical properties of PAHs, which is becoming of increasing importance as they become promising candidates for future electronic applications.

Chapter Two aims to introduce the field of on-surface chemistry, and describe the synthesis of potential precursors for the formation of graphene nanoribbons and nanographenes. The synthetic methods to prepare suitably functionalised derivatives will be described, including the [4+2] Diels-Alder cycloaddition and various methods of intramolecular cyclodehydrogenation. Through deposition of these precursors on a reactive metal substrate, and their subsequent polymerisation, it is hoped to give a further contribution to the relatively sparse field of N-containing polyaromatics suitable for on-surface chemistry.

Chapter Three will describe synthetic attempts towards a series of Pt(II) acetylides with HBC cores. This chapter builds upon earlier work reported in the Draper group on Pt(II) acetylides,⁹⁰ but aims to incorporate di-substitution of the HBC core with Pt(II) centres, and an N[^]N[^]C ligand, the photophysical properties of which had not been previously examined. It is aimed to characterise the complexes by NMR, followed by a thorough investigation of their photophysical and electrochemical properties. The motivation behind this work is the potential for the incorporation of a metal centre to enhance the phosphorescence quantum yields of the HBC chromophore through intersystem crossing, and to contribute to the few reports of organometallic derivatives of HBC.

Chapter Four will describe the synthesis of a family of Pt(II) acetylides, with partially-fused N[^]N coordinating ligands, based around the structural motif of 1,10-phenanthroline. The majority of previous reports of these Pt(II) acetylides employ less-conjugated systems, which has warranted a systematic investigation of the effect of employing more conjugated PAH-based ligands. It is hoped to characterise these complexes by a number of means, including NMR spectroscopy, HRMS, and cyclic voltammetry (CV). Initial evaluation of the suitability of the most promising of these complexes as a triplet photosensitiser will also be undertaken.

Chapter Five aims to describe the synthetic attempts towards a family of bis-cyclometalated Ir(III) complexes, which feature a highly-conjugated, partially-fused N[^]N

ligand obtained through [2 + 2 + 2] cyclotrimerisation. The literature reports of cyclometallated Ir(III) complexes featuring strong emission suitable for incorporation into electronic devices prompted the investigation as to whether the incorporation of a highly conjugated system could result in attractive photophysical properties in such complexes. The chapter describes the synthesis of three complexes, one of which incorporates strongly absorbing coumarin 6 cyclometalating ligands. This ligand was chosen for its very strong absorption in the visible region, and as the previous reports of Ir(III) complexes with both coumarin 6 and conjugated N[^]N ligands had attractive photophysical properties.⁹¹ It is aimed to investigate whether the incorporation of a highly conjugated ligand, in conjunction with suitable ancillary ligands, can yield Ir(III) complexes with promising emissive properties.

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Chapter Two

Examining the On-Surface Behaviour of N-Functionalised Aromatic Frameworks

2.1 Introduction

The isolation of single-layer graphite, known as ‘graphene’, in 2004 by Novoselov and Geim, heralded a new era in materials chemistry, bringing the reality of organic electronic devices a step closer.¹ Graphene is a one-atom-thick two-dimensional sheet of sp^2 hybridised carbon arranged in a hexagonal network. Its long range π -conjugation lends it unprecedented mechanical, thermal and optical properties.² The unique and fascinating properties of this material have propelled it to the vanguard of materials research, although to date it remains a mostly theoretical proposition, as it has yet to be used in any large scale capacity. A variety of reasons for this will be discussed herein. The excitement surrounding this material is due to its potential to revolutionise the field of electronics, as it exhibits very high charge-carrier mobility (measured as high as $15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) under ambient conditions.³ Charge-carrier mobility is a measure of the speed of the carriers (electrons/holes) in a material when an electric field is applied, and is indicative of the charge transport efficiency of a material.⁴ Prospective applications in electronics include transparent conductive coatings, such as used in OLEDs and touch screen displays, where its mechanical flexibility and durability would be highly desirable. Other possible applications include transistors, photodetectors, composite materials and sensors.⁵ However, ideal graphene, as an extended honeycomb network of carbon atoms, exhibits no band-gap, which severely hampers its potential for device implementation, particularly in field-effect transistors (FETs). Another significant drawback is the difficulty of preparing the pristine material, with well-defined edges, in a scalable and reproducible manner.

It has been demonstrated that confinement of graphene in one dimension leads to the creation of a band-gap in the material.⁶ As mentioned in Chapter One, narrow ribbons of graphene are referred to as graphene nanoribbons (GNRs). Due to the quantum confinement effect, graphene nanoribbons display a finite band-gap when their width is below 10 nm.^{6, 7} This creation of a band-gap results in semiconducting properties, which makes GNRs more suitable candidates for electronic devices than pristine graphene. As a result, one of the most significant challenges in materials chemistry has become the production of GNRs with controlled width and edge structures with atomic precision (*i.e.* with no defects). Creating narrow ribbons of graphene is not quite as straightforward as it sounds; even the slightest of edge defects are predicted to adversely affect the electrical properties.⁸ The obtainment of GNRs with atomically precise edges is therefore of much interest. The controlled introduction of heteroatoms into GNRs, in the same way as dopants are introduced into

silicon-based semiconductors, is expected to facilitate the modulation of their electronic properties. Proof-of-concept devices have already been reported, including FETs.⁹ A number of different approaches towards GNRs have been developed, which will be discussed in this chapter.

2.1.1 Methods of Graphene and Graphene Nanoribbon Production

For many years, graphene was thought too unstable to exist. Although widespread research into its synthesis began in earnest after 2004, single-layer graphite (the term graphene was only coined in 1986)¹⁰ had been reported in earlier work. In 1948, Ruess and Vogt reported a TEM (transmission electron micrograph) image of single-layer graphite, which was followed by further reports from Boehm *et al.* in 1962.¹¹⁻¹³ However, most of the work that followed these early reports was theoretical. In the short space of time since Novoselov and Geim's breakthrough in 2004, the methods by which graphene and its derivatives may be produced have developed considerably. Two competing strategies exist for the production of graphene, namely the top-down method, where a bulk material is processed and divided to yield the desired product, and the bottom-up method, where smaller precursors are employed to generate larger frameworks (Fig. 2.1). It has been proposed that top-down methods are analogous to the chopping down of a tree, the trunk of which is then chiselled into the desired shape (or like carving a building into rock). Conversely, the bottom-up method has been suggested to be analogous to planting a seed which then grows to provide a tree of the desired size and shape (or like constructing a building from the ground up with blocks).¹⁴ The top-down method encompasses a variety of techniques, most notably mechanical exfoliation, lithographic cutting and chemical oxidation/exfoliation of graphite followed by reduction of graphene oxide (GO).¹⁵ Bottom-up methods include chemical vapour deposition (CVD), thermal decomposition of SiC, and lastly, forming the basis of the discussion of this chapter, organic synthetic methods involving small precursor molecules. This chapter will give a brief, general overview of graphene production and its development, but will focus specifically on the synthesis of graphene nanoribbons (GNRs), and the challenges associated with it. The bottom-up synthetic approach, and results from selected precursors, will then be discussed. Both the top-down and bottom-up methodologies have advantages and also drawbacks; however at the present moment, it appears that bottom-up techniques present the most promising way forward.

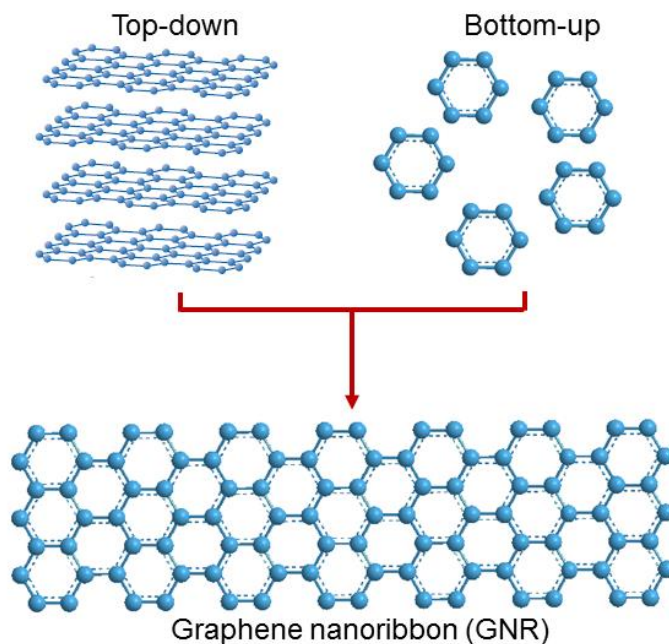


Figure 2.1: A general comparison of the two competing routes towards GNRs. Image of graphite adapted from Geim et al.³

2.1.2 Top-Down Methods Towards Graphene and GNRs

Since the first experimental isolation of graphene, top-down methods have predominated as the technique of choice for its production, mostly due to issues of cost and scalability. Mechanical exfoliation, as pioneered by Novoselov and Geim, can produce samples of high quality, although the method cannot produce graphene in either high yields or in high throughput.¹⁻³ It generally involves the cleavage of layers of graphene from a bulk highly ordered pyrolytic graphite (HOPG) surface. Scotch tape is applied to the surface, and with repeat applications of the tape, the graphitic layer eventually becomes thinner and finally, single-layer. The longitudinal or transverse force applied to the layered graphite structure overcomes the van der Waals forces between the layers and permits their separation. The interlayer distance has been determined as 3.34 Å and the interlayer bond energy as 2 eV/nm².¹⁶ The exfoliation may be carried out not only with Scotch tape, but also with ultrasonication or electric fields.^{17, 18} In a research setting, where graphene is required on a small scale, it continues to play an important role in generating high quality graphene flakes relatively quickly, and was key to the generation of the samples investigated in the early studies on single-layer graphene.¹⁹ However this technique is labour- and time-

intensive and difficult, if not impossible to scale to a commercial level. For larger scale production, the top-down approaches of solution-based exfoliation and also the chemical oxidation/exfoliation of graphite, followed by reduction of graphite oxide (GO) have become more widespread. These solution-based methods are of particular interest due to the ability to deposit graphene from solution onto a surface or substrate.

A popular solution-based route is through the reduction of graphite oxide (GO) to graphene. In this approach, GO is produced by oxidising graphite with strong acids, followed by intercalation and exfoliation in water. Ruoff *et al.* were the first to propose a solution-based method to produce single-layer graphene in 2006.²⁰ Oxidation of graphite by Hummer's method (the treatment of graphite with NaNO_3 and KMnO_4 in concentrated H_2SO_4) yields graphite oxide (GO), which exists as a layered stack of puckered sheets exhibiting AB stacking. During oxidation, epoxide and hydroxyl functionalities are introduced into the basal planes. The hydrophilicity induced by these functional groups leads to water becoming intercalated between the sheets, which can be dispersed individually.² The GO thus obtained is non-conducting, and reduction using various chemical agents, such as hydrazine hydrate, is required to restore the electrical properties.²¹ There are several drawbacks to this methodology, notably that the subsequent reduction of the hydrophilic oxygen-containing groups acts to reduce solubility and causes aggregation of the sheets, but also that the reduction of GO to pristine graphene does not go to completion.²² Significant structural defects are introduced through the oxidation of graphite, resulting in inferior electronic properties of the reduced graphene oxide sheets, and as a consequence, much research work is ongoing towards removing these.²³ This method does, however, benefit from its ability to be scaled up to very large quantities, as graphite is low-cost and widely available.

The controlled formation of ribbons of graphene, known as graphene nanoribbons (GNRs) has been the subject of intense research activity in the past decade. As discussed previously, these narrow ribbons display a band gap inversely proportional to their width, due to quantum confinement effects.^{6, 24} Top-down GNR production methods involve taking large-area graphene, generally produced *via* the methods discussed above, and cutting it into ribbons.

The longitudinal unzipping of carbon nanotubes (CNTs), which may be thought of as rolled graphene sheets, has emerged as a useful means of generating GNRs of defined

width. In 2009, Kosynkin *et al.* proposed a method of producing graphene nanoribbons through the lengthwise cutting (unzipping) of CNTs (Fig. 2.2).²⁵ This method is a solution-mediated process in which the CNT is suspended in concentrated sulfuric acid and subsequently treated with 500 wt% KMnO_4 , a similar process to that used to produce GO from graphite. The ribbon structures produced by Kosynkin *et al.* were observed to be highly soluble in polar organic solvents and water, with the unzipping process appearing to occur along a straight line. The unzipping of single-walled CNTs (SWCNTs) produced single layer graphene nanoribbons, whilst unzipping multi-walled CNTs (MWCNTs) produced multi-layered graphene. Although this method produced large amounts of ribbon-shaped graphene fragments, the authors noted that the electronic properties were inferior to that of mechanically produced graphene, due to their residual oxidised defect sites. Some of the electronic properties could be restored, however, through treatment with N_2H_4 or annealing in H_2 . Dimiev *et al.* have proposed that three consecutive steps occur in the unzipping of MWCNTs; intercalation-unzipping, oxidation and exfoliation.²⁶ The mechanism appears to be an intercalation-driven process, rather than an oxidative chemical bond cleavage-driven process.

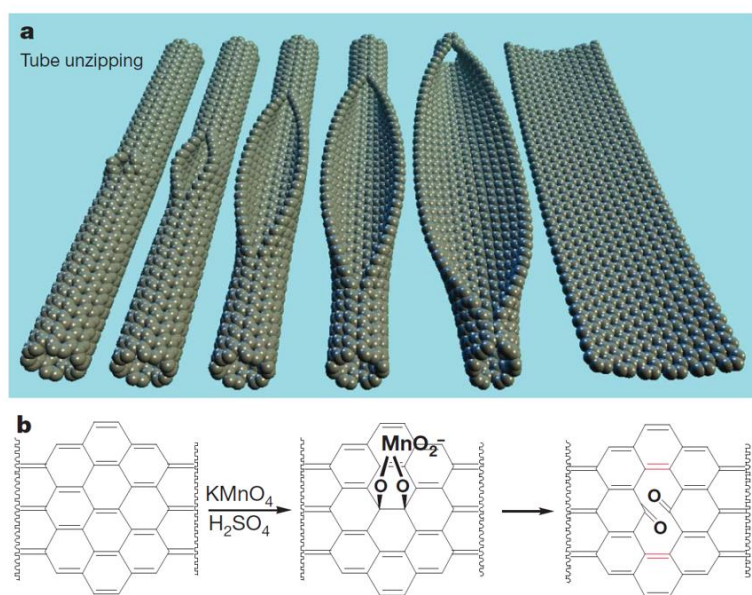


Figure 2.2: (a) A representation of the CNT unzipping process, generating GNRs. (b) A mechanism proposed for this unzipping process. Adapted from Kosynkin *et al.*²⁵

A further refined approach, introducing a lower number of defects, was reported in 2011, employing hot potassium vapour to generate pristine graphene nanoribbons, again by Kosynkin *et al.*²⁷ The lack of an oxidation step introduced fewer defects, with electronic

properties similar to those of mechanically exfoliated graphene. The treatment with potassium vapour resulted in stacked GNRs with edges terminated with potassium atoms, which were subsequently removed by treatment with ethanol. Exfoliation of the stacked, exfoliated ribbons was achieved through treatment with chlorosulfonic acid. AFM (atomic force microscopy) and SEM (scanning electron microscopy) were employed to visualise the GNRs formed (Fig. 2.3). This approach to generate GNRs from CNTs exploits the ability of alkali metals to intercalate graphite and induce lattice expansion, in turn inducing stress on the concentric CNT walls and causing their subsequent unzipping. Overall, the process of producing GNRs through the unzipping of CNTs does present some potential for scalability, however, the method introduces defect sites at the edges requiring further processing and does not provide the synthesis of GNRs with complete atomic precision.

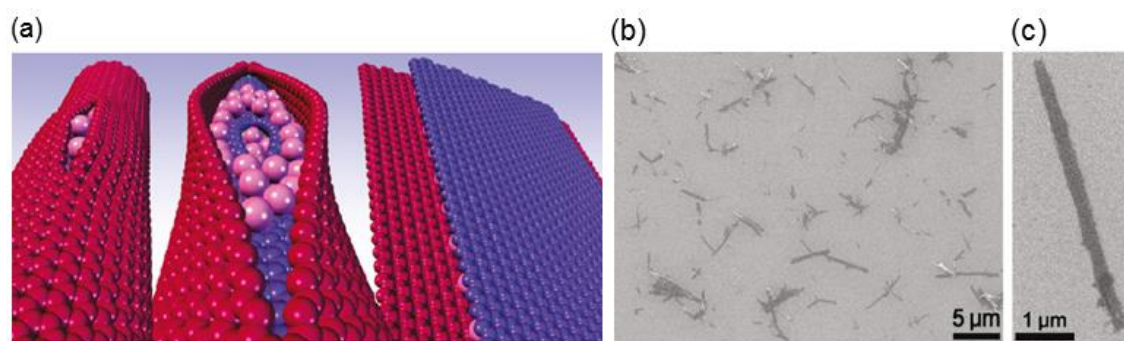


Figure 2.3: Molecular representation of unzipping process through potassium metal intercalation of CNTs. Note that the potassium metal atoms bonded to the edges of the GNRs are omitted for clarity. (b) SEM image of GNRs on Si/SiO₂. (c) An isolated GNR stack, displaying relatively parallel edges. Images from Kosynkin *et al.*²⁷

Lithographic patterning is another top-down method whereby graphene flakes, usually first produced by mechanical exfoliation, are deposited onto a substrate, such as SiO₂, and a protective mask exhibiting a pattern is placed on top. Exposure of the materials to an electron beam results in the generation of a patterned graphene structure. This method was demonstrated by Han *et al.* in 2007, who used an oxygen plasma to etch away areas of graphene not covered by the protective mask.²⁸ The mask defined GNRs with widths of 10-100 nm, and lengths of 1-2 μm. This EBL (electron-beam lithography) methodology presents a route from the large, irregular graphene flakes produced *via* other top-down methods towards GNRs more suitable for incorporation into devices. The method of EBL has the ability to produce GNRs which are positioned precisely on a substrate, but it has several notable drawbacks. The main drawback is a resolution limitation of approximately 10 nm

and below, which hinders device applications at RT. Also, the damage induced by the etching of the electron beam means that the edges of the ribbons produced are not atomically precise and thus result in GNRs with dangling bonds and varying functional groups at the edges, which serve to diminish their electronic properties. Finally, the complete removal of the protective mask can be challenging as some residue is often left behind.²⁹

2.1.3 The Introduction of Heteroatoms to GNRs via the Top-Down Approach

The introduction of nitrogen atoms into GNRs has been achieved through the modification of the aforementioned top-down methods, albeit in a slightly crude manner. Bottom-up methods provide a more precise route toward heteroatom placement and substitution levels, which will be discussed later. Top-down methods towards N-substituted GNRs are primarily based upon the treatment of previously prepared pristine graphene or GNRs or by the unzipping of nitrogen-containing CNTs. In 2013, Cruz-Silva *et al.* reported N-substituted GNRs (N-GNRs) obtained through the unzipping of nitrogen-doped multiwalled CNTs (CN_x-MWCNTs).³⁰ The nitrogen-doped CNT precursors were obtained by CVD (chemical vapour deposition) with a 6 wt.% solution of ferrocene as catalyst and benzylamine as a carbon-nitrogen source. The unzipping of the CNTs was carried out in H₂SO₄ and H₃PO₄ in the presence of KMnO₄. The N-content of the GNRs was observed to decrease depending on oxidation time, by as much as from 1.56 to 0.31 atom percent. The year after, Liu *et al.* also reported N-GNRs obtained from unzipping pristine CNTs which were then thermally treated with aniline to form N-GNRs (Fig. 2.4 (a)). Aniline was polymerised on the surface of the GNRs, following which, pyrolysis at 900 °C yielded N-GNRs. XPS experiments revealed that most of the N atoms introduced into the GNRs were either quaternary or pyridinic. Variation of the aniline amounts led to N-content between 4.1 to 8.3 atom percent.³¹ The various types of N-substitution possible are displayed in Fig. 2.4 (b).

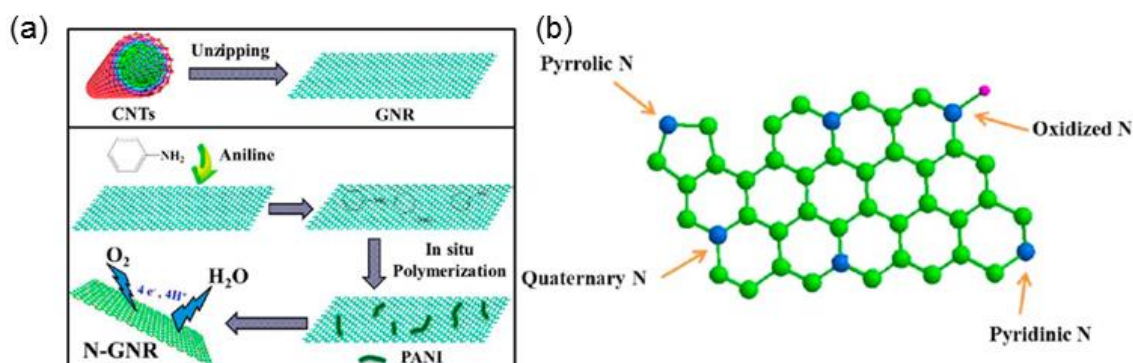


Figure 2.4: (a) The synthetic scheme towards N-GNRs through thermal treatment with aniline. (b) The various bonding configurations possible in N-GNRs. Both (a) and (b) adapted from Liu *et al.*³¹

Some improvement has been reported by Kundu and co-workers quite recently, who reported high levels of N-doping (8.24%) in GNRs produced *via* the unzipping of MWCNTs which were subsequently treated with hydrazine hydrate.³² Their widths were however in the region of ~30-55 nm. Top down methods such as these do not provide any control over the exact placement of N atoms, and furthermore the oxidation step required to unzip the CNT precursor produces defect sites along the edges of the GNRs, rendering them less attractive for electronics applications. These top-down synthesised N-GNRs do however show some promise as catalysts for the oxygen reduction reaction (ORR). This is one of the key processes taking place in a fuel cell, and requires a highly efficient catalyst as the reduction of oxygen is quite sluggish. Typically, a fuel cell operates through the electrochemical reduction of oxygen and the oxidation of a fuel, usually H₂, producing only water as a by-product. At the moment, platinum catalysts are typically employed, but their expense and limited availability hampers the widespread uptake of this technology.³³ Thus low-cost catalytic materials capable of performing the ORR efficiently are highly sought after. In terms of N-GNRs, it has been observed that quaternary and pyridinic N substitution display the highest level of catalytic activity in the ORR, although there remains some ambiguity over which of the two is most important.^{31, 34} The N-GNRs produced by Kundu *et al.* have shown very promising catalytic activity when compared to the standard Pt/C benchmark. This catalytic activity has also been noted for larger-area N-doped graphene, not only N-GNRs, and the development of such materials for the ORR is becoming a highly active research area.³³

The top-down methods towards GNRs discussed above are intended as a general, brief overview of the field of top-down graphene synthesis; the field itself is enormously active and ever-expanding, with further refinements to each method in continuous development. However, to date, the preparation of nanographenes and GNRs through the aforementioned methods still have major obstacles to overcome, i.e. the attainment of edge structures with absolute atomic precision, the precise placement of heteroatoms (dopants) and the ability to prepare GNRs less than 10 nm wide in a scalable manner. Since even the slightest amount of edge defects can lead to less desirable electronic properties (*e.g.* areas of electron localisation),^{35, 36} bottom-up methods present an increasingly viable alternative.

2.1.4 Bottom-Up Methods Towards Graphene and GNRs

Bottom-up methods present a number of contrasting advantages and disadvantages in comparison to the aforementioned top-down methods. This contrasting method of taking molecular building blocks and tailoring them to produce GNRs and nanographenes of desired size and shape, has major advantages in that through sensible design of the precursor blocks, it is possible to prepare extended structures with a very high degree of precision in terms of heteroatom placement, and a very high degree of control over the edge structure. The principal methods of bottom-up synthesis comprise epitaxial growth on SiC, chemical vapour deposition (CVD) and organic synthetic methods.

Epitaxial growth (the growth of a single crystal film on a crystalline substrate) on silicon carbide (SiC) has emerged as a promising route towards GNRs, as pioneered by Sprinkle *et al.*³⁷ This method involves the growth of graphene on a SiC substrate *via* the thermal decomposition of SiC, usually at a temperature of approximately 1100 °C (i.e. the surface of the SiC decomposes to produce graphene layers which sit on top of remaining SiC). The main advantage of this technique is that no further transfer onto a different substrate for device processing is required, as the graphene or GNR is produced directly on the semiconducting SiC substrate. Usually the decomposition process is performed in a furnace, with a high pressure of argon present. Unlike CVD, a precursor gas is not required; the thermal decomposition of the substrate acts as a carbon source. The mechanism by which the thermal decomposition of SiC leads to graphene growth is through the sublimation of Si at high temperature, at a rate much faster than C, due to its higher vapour pressure.³⁸ The carbon remaining on the substrate then reconstructs to form a graphene layer. The facets of

the underlying SiC substrate control the morphology of the graphene produced epitaxially. SiC exhibits a regular terrace pattern under the conditions required for graphene growth. This terrace, or step, pattern has been regarded as problematic, but Sprinkle *et al.* noted that growth of graphene nanostructures on these areas was continuous, and exploited this phenomenon to create a methodology for the production of GNRs.³⁷ In order to introduce facets with controlled placement, nickel lines were produced on the SiC by photolithographic definition, and then transferred into it by a fluorine-based reactive ion etch (RIE). After the nickel mask had been removed, heating of the substrate to 1200-1300 °C led to step flow, where the abrupt, sharp step relaxed to form a more gradual sloped structure (a (110) facet) (Fig. 2.5).

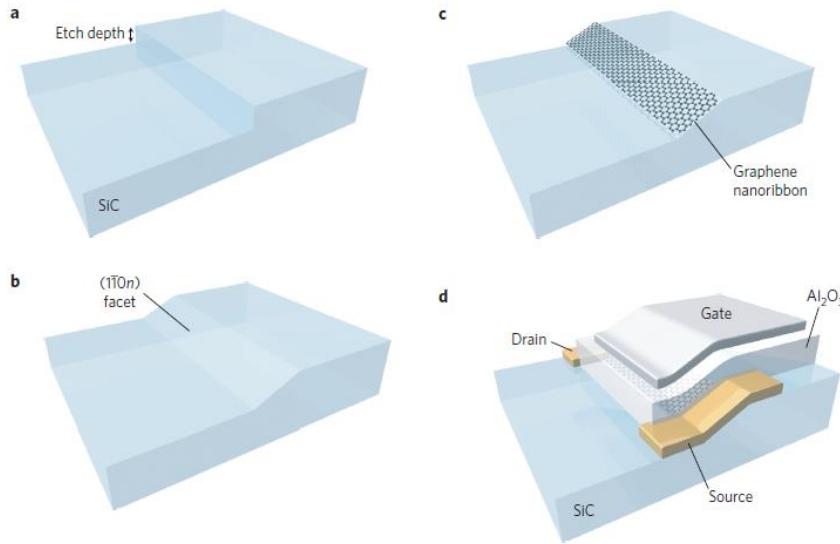
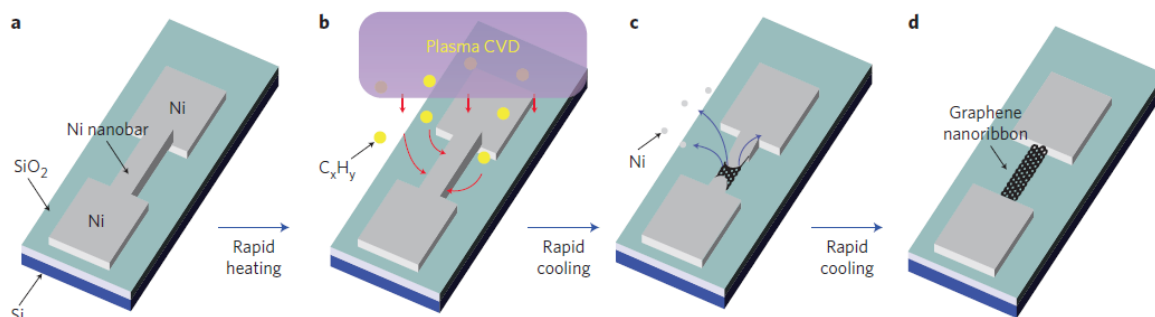


Figure 2.5: A depiction of GNR fabrication, in a process designed by Sprinkle *et al.*³⁷ (a) The etching process of the SiC crystal. (b) Step flow of the crystal after heating to 1200-1300 °C. (c) Further heating to 1450 °C yields a GNR on the stepped facet. (d) A schematic of a top-gated field-effect transistor fabricated from SiC-grown GNR. Image from Sprinkle *et al.*³⁷

Careful timing and heating to 1450 °C then caused formation of GNRs on the facets only, as demonstrated by Raman spectroscopy. The authors claim the etching process is relatively straightforward and provides nanometre precision. The depth of the etching into the substrate controls the width of the GNR (shown in Fig. 2.5 (a)); in this case, an etch depth of 20 nm resulted in a GNR 40 nm wide. Further refinement of this method is required for lower GNR widths. Hwang *et al.* have used standard lithographic cutting techniques on

large-area epitaxially grown graphene to generate 10 nm wide GNRs with semiconducting behaviour. This suggests a combination of techniques may be required.⁹ Although epitaxial growth on SiC presents a promising route towards the scalable production of graphene and GNRs, the very high cost of the SiC substrate remains a substantial barrier.

Chemical vapour deposition (CVD) as a means of producing GNRs has gained a steady interest. As discussed earlier, it has been extensively used for the production of CNTs, but since the surge in research in GNRs, it has played an important role in also producing GNRs directly. Molecular precursors in gaseous form, such as methane or ethylene, are deposited onto a metallic template at high temperatures (typically 700-1000 °C), whereupon graphene nanoribbons are formed once the C-H bonds have been broken. The size of the resulting GNRs depends on the template. Nickel nanobars were used by Kato *et al.* as templates for nanoribbon growth.³⁹ Using electron-beam lithography, they formed the nanobars from nickel electrodes on an SiO₂ substrate. Heating the substrate to ~900 °C and subsequent CVD of a mixture of methane and hydrogen gases resulted in the formation of GNRs. The nickel nanobars were either partially or completely converted to GNRs, and it was noted that the GNR width did not exceed that of the nanobar (Fig. 2.6).



Scheme 2.1: The fabrication of GNRs via CVD, as reported by Kato *et al.*³⁹ (a) A nickel nanobar, formed by lithography. (b) Depiction of CVD process. (c) Formation of GNRs with volatilisation of Ni. (d). GNR formed between two nickel electrodes.

The nanobars are sacrificial, and become volatilised in the thinner regions due to the high temperatures employed, leaving the GNRs behind, in between the nickel electrodes. In order to produce GNRs with widths below 30 nm, a nanobar with a width of less than 50 nm is required. The limit of resolution in patterning the Ni template limited the GNR width to ~23 nm. The authors discovered that the process requires a high amount of precursor hydrocarbon gas and relatively thin nickel nanobars. TEM (transmission electron microscopy) revealed the GNRs were multi-layered with 0.34 nm spacing in between the

electrodes. An advantage of this technique is that no lithography is required to further process the GNRs, so the edge structure remains intact. The CVD process itself is quite scalable, but the requirement for lithographic patterning of the template remains expensive and time-consuming.²⁹

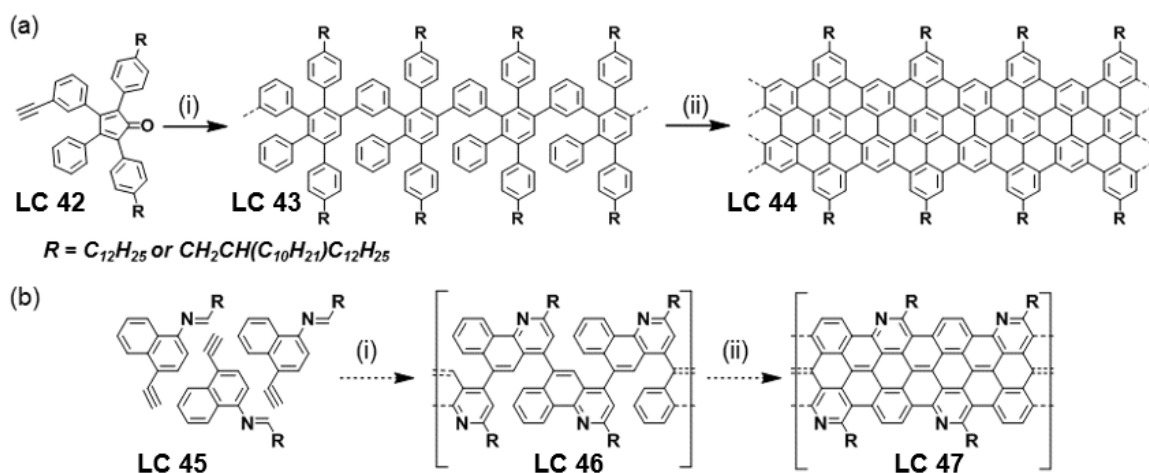
2.1.5 Bottom-Up Organic Synthetic Methods

Fine-tuning of the electronic band-gap of GNRs can be achieved through the precise introduction of heteroatoms, in a similar manner to that by which dopants are added to silicon-based semiconductors.⁴⁰ The precise, controlled introduction of heteroatoms and the attainment of regular, defect-free edge structures remain significant challenges with the methods previously described. Two complimentary bottom-up techniques based on organic chemical methods have emerged for the production of GNRs: the solution-based synthesis of GNRs from smaller monomeric precursors, and the on-surface coupling of small monomeric precursors on reactive metal substrates. These methods rely on the organic synthesis of precursors, which permits the introduction of heteroatoms with an enormous degree of accuracy and avoids the need for lithographic techniques, giving excellent control over the edge structures. Typically, small polyphenylene molecules with halogen functionalities are employed, and subsequent coupling and intramolecular cyclodehydrogenation steps yield GNRs. A wide variety of GNR shapes is therefore possible, depending on the monomer design, making it possible to optimise the structure depending upon the application. There have been limited reports of N-substituted GNRs produced by solution-based methods in the literature until quite recently.

2.1.6 Solution-Based Methods

Stille *et al.* reported the synthesis of fully conjugated ladder-type polymers in 1970, although due to their high insolubility as a result of π - π interactions, their characterisation remained inconclusive until 1994, when subsequent work by Schlüter *et al.* introduced solubilising groups.⁴¹⁻⁴³ Although these were not referred to as GNRs at the time, they can be viewed as such.⁴³ Further early work reported by the Müllen group in 2000 and 2003, referred to them as ‘graphite ribbons’, which were generated *via* repetitive Diels-Alder reactions.^{44, 45} The Diels-Alder approach towards GNRs has since been further refined,

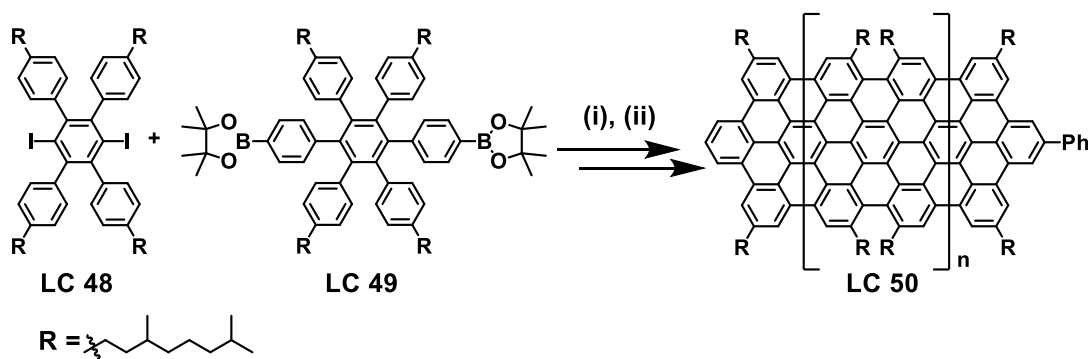
notably in the elegant synthesis of Narita *et al.*⁴⁶ This approach, using a single, carefully designed precursor (**LC 42**), avoids the need for any catalyst or other reagents, and the Diels-Alder cycloaddition takes place in a simple refluxing diphenyl ether solution or a melt at 260-270 °C (Scheme 2.2 (a)). The cyclodehydrogenation step to yield the fully cyclised GNR **LC 44** was conducted in CH₂Cl₂ with FeCl₃ as the oxidant. The GNRs produced were determined to be over 200 nm in length and exhibited a novel cove-type structure. The high degree of insolubility displayed by the GNRs produced precluded their full characterisation, yet much data in agreement with theoretical models was obtained from solid state ¹H NMR, MALDI-MS and Raman spectroscopy. Dibble *et al.* have proposed extending the Diels-Alder method towards N-GNRs.⁴⁷ An aza-Diels-Alder (also known as Povarov) reaction has been used by the authors to form a polybenzoquinoline-type GNR precursor (**LC 45**) from alkyne and aldimine functionalised monomers (Scheme 2.2 (b)). However, neither the polyphenylene precursor (**LC 46**) nor the planarised GNR (**LC 47**) have yet been synthesised, as the authors envisage its cyclodehydrogenation occurring *via* on-surface methods.



Scheme 2.2: (a) The synthetic route towards GNRs via the Diels-Alder reaction, as devised by Narita *et al.*⁴⁶ (i) Diels-Alder reaction (ii) Intramolecular cyclodehydrogenation (b) Precursor monomers (**LC 45**) reported by Dibble *et al.*,⁴⁷ with proposed GNR formation.

The Suzuki reaction has been studied extensively for GNR formation since the report by Yang *et al.* in 2008.⁴⁸ The Suzuki-Miyaura polymerisation of a boronic-ester functionalised hexaphenylbenzene (**LC 49**) led to the extended polyphenylenes in 75% yield (Scheme 2.3). Subsequent intramolecular cyclodehydrogenation generated the planarised derivative (**LC 50**), which was soluble in common organic solvents due to the alkyl

substituents on the periphery, reducing the tendency towards aggregation. The length of these GNRs was however, only at most 12 nm, thought to be due to steric hindrance between the bulky monomers and the rigid backbone of the polymer.



Scheme 2.3: Synthesis of GNRs via the Suzuki polymerisation, as reported by Yang et al.⁴⁸

(i) Suzuki coupling (ii) Intramolecular cyclodehydrogenation.

N-GNRs have also been synthesised through the Suzuki polymerisation, by Kim *et al* (Fig. 2.6).⁴⁹ The use of different combinations of the dibromobenzene (**LC 51**) and dibromopyrazine (**LC 52**) starting materials, in conjunction with the diboronated naphthalene (**LC 53**) led to GNRs with differing levels of N-substitution. It was noted that the higher the degree of N-substitution, the higher the electron mobility was, indicating that the charge transport characteristics could be modulated *via* controlled levels of heteroatom substitution. The GNR produced solely with the dibromopyrazine derivative (**LC 55**) yielded the highest electron mobility ($1.02 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

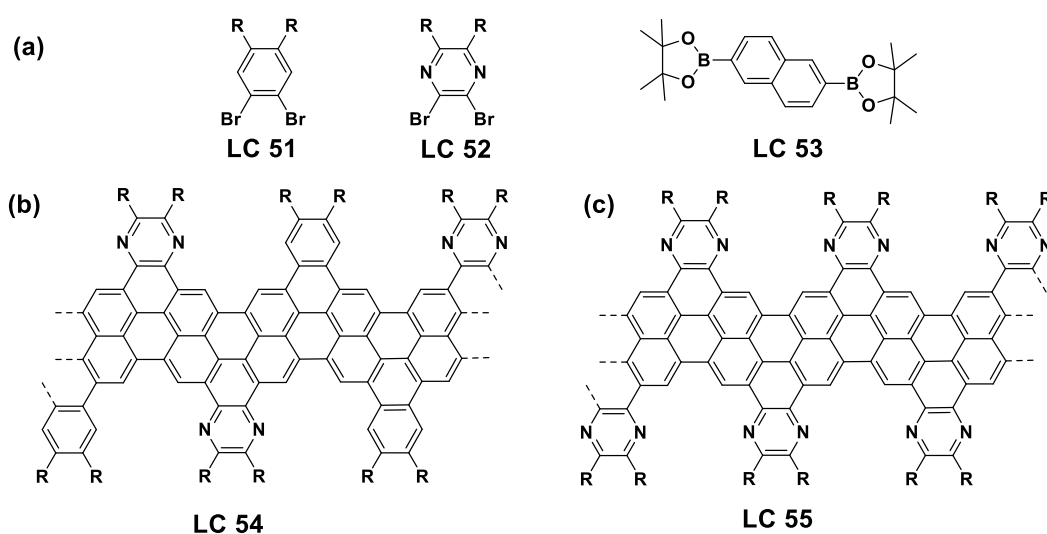


Figure 2.6: *N*-GNRs with varying degrees of *N*-substitution, synthesised through Suzuki-type polymerisation reactions. $R = OC_{12}H_{25}$.⁴⁹

The Yamamoto coupling has also been intensively investigated for its potential to generate GNRs in solution. This approach avoids the need for two different monomers, as one dihalogenated monomer can be utilised to create extended structures. Vo *et al.* have led the way in this field, first with their report of the gram-scale preparation of an all-carbon chevron GNR in 2014.⁵⁰ Their process began with the synthesis of 6,11-dibromo-1,2,3,4-tetraphenyltriphenylene (**LC 56**, Fig. 2.7) and its subsequent polymerisation in a Ni^0 -catalysed Yamamoto process. The polymerised species was then treated with Scholl conditions and FeCl_3 to yield a chevron-type GNR which was ~ 1 nm wide. Various techniques were used to characterise the GNRs, including STM, which confirmed the success of the cyclodehydrogenation step. The authors extended this synthetic strategy towards N-GNRs soon after, by modifying the triphenylene precursor.⁵¹ Introduction of N functionality was achieved through a suitably functionalised alkyne which, after Diels-Alder cycloaddition with the 5,10-dibromo-1,3-diphenyl-2H-cyclopenta[1]phenanthren-2-one precursor yielded a monomer suitable for Yamamoto coupling, and cyclodehydrogenation of the resulting polymer with FeCl_3 produced a 4N-GNR (4N referring to 4 nitrogen atoms per unit cell, (**LC 57**, Fig. 2.7 (b)). XPS (X-ray photoelectron spectroscopy) and EDX (energy dispersive X-ray spectroscopy) were used to confirm the presence of N atoms in the GNR structures. Vo and co-workers then reported the 8N variant of the GNR, through the same in-solution techniques, in 2015 (**LC 59**, Fig. 2.7).⁵² The precursor **LC 58** was modified through similar means to the previous variant, and the GNR was again formed in solution through the same methodology.

Mixing of the N-containing and all-carbon variants of the monomer could allow further control over the N-content in the GNR, but this has not yet been carried out in solution. The optical properties of the 4N and 8N GNRs, whose bandgaps were determined to be 1.6 and 1.9 eV respectively, were similar to the pristine (all-carbon) variant, whose optical bandgap was 1.6 eV. The authors noted that the N-substituted systems, after deposition on Au(111), displayed hydrogen-bonding interactions that permitted individual GNRs to coordinate in planar sheets (Fig. 2.8 (a) and (b)). In solution, they exhibited further hierarchical assembly behaviour due to Van der Waals and π -stacking interactions to form 3D stacks, which suggests that careful modification of GNRs *via* N-substitution could promote self-assembly behaviour of these structures (Fig. 2.8 (c)). This behaviour was observed by STM imaging of drop-cast solutions of the N-GNRs, where no individual ribbons were observed, only aggregated structures.

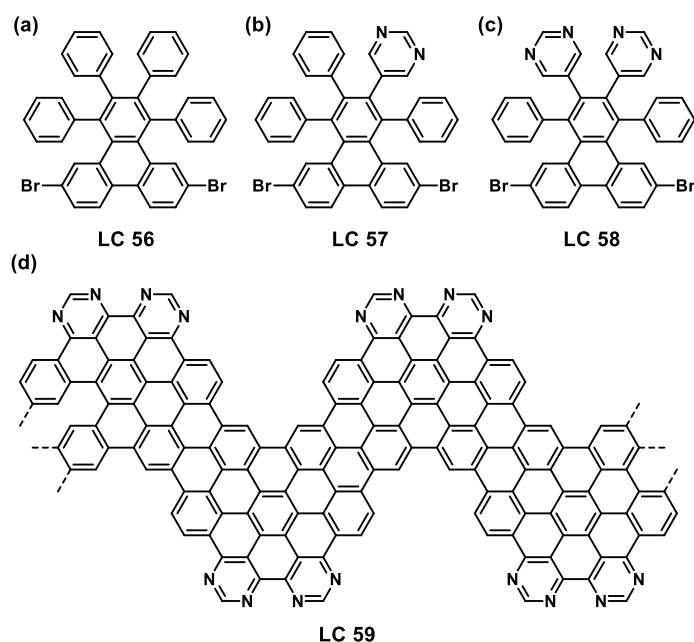


Figure 2.7: (a) All-carbon triphenylene-based precursor towards chevron GNRs. (b) and (c) display varying levels of N-substitution. (d) The GNR formed from precursor LC 58.

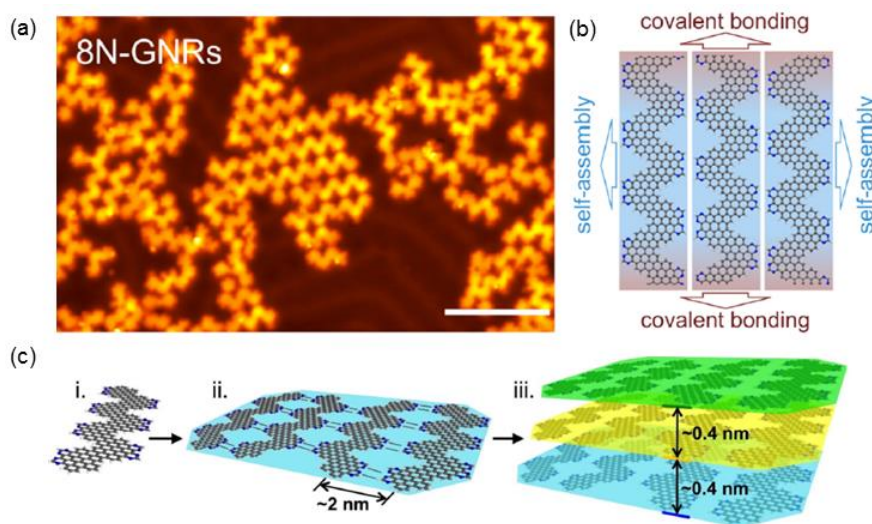


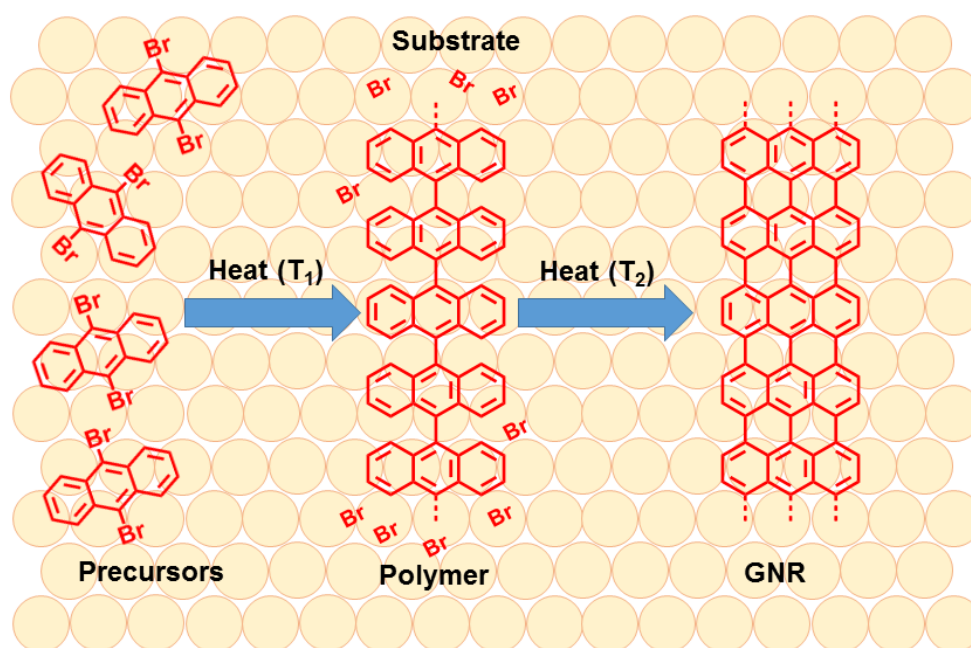
Figure 2.8: (a) STM image of 8N-GNRs on Au(111) as prepared by Vo et al.⁵² Scale bar = 10 nm. (b) Proposed schematic of interactions between N-GNRs. (c) Proposed scheme of aggregation in solution, forming 3D stacks. Adapted from Vo et al.⁵²

2.1.7 On-Surface Synthesis

Significant progress has been achieved through current in-solution methods, however the challenge of processing highly insoluble large organic polymers remains a stumbling

block. The characterisation of GNRs produced in solution is quite difficult, particularly in terms of microscopic analysis, (*e.g.* by STM) due to their tendency to aggregate and also the problem of transferring them to a substrate without contamination.⁴³ The strong π - π stacking of GNRs in solution raises the sublimation temperature above the point at which thermal decomposition occurs, hampering any effort to deposit them onto a substrate by thermal evaporation.⁵³ These difficulties have led to the emergence of a rapidly developing new field known as on-surface synthesis.

To give an outline of the procedure of on-surface synthesis, the process begins with the selection of a suitable small molecular precursor, which can be envisaged as a building block. Generally, one or more halogen atoms are incorporated into the precursor in order to provide a coupling functionality. This is the same principle as required for in-solution synthesis, indeed many of the precursors suitable for in-solution synthetic techniques as described earlier are also suitable for on-surface techniques. The process begins with the evaporation of the precursor molecule, usually under ultrahigh vacuum (UHV, $<10^{-9}$ mbar), onto a reactive metal substrate such as Au(111) or Ag(111). Heating of the substrate induces carbon-halogen bond cleavage, generating surface-stabilised radical species (although on particularly reactive substrates this dehalogenation process may occur spontaneously at RT). Further heating of the substrate then induces radical polymerisation whereby the radical species diffuse across the surface and form C-C bonds through Ullman-type coupling reactions. This yields polymeric structures linked by single C-C bonds, in a similar manner to the polymers formed by the Yamamoto or Suzuki couplings described earlier. After the formation of the polymeric chains, heating to higher temperatures has been found to induce intramolecular cyclodehydrogenation, yielding extended GNRs with a very high degree of atomic precision. The process is summarised in Scheme 2.4.



Scheme 2.4: A general scheme for the formation of GNRs via the bottom-up method from molecular precursors on reactive metal substrates.

2.1.8 On-Surface Polymerisation

The Ullmann reaction is an important class of carbon-carbon bond forming reactions, first reported in 1901.⁵⁴ It generally involves two aryl halides being reacted with one equivalent of copper powder at high temperatures (over 200 °C), producing a biaryl species.⁵⁵ During the traditional in-solution Ullmann reaction, radical species are formed following the cleavage of carbon-halogen bonds which then form intermediate complexes with copper. Although these are not stable in solution, on metal surfaces they are metastable at room temperature but following annealing (heating) at higher temperatures, the copper atoms are released and covalent C-C bonds are formed. The ability to form extended carbon frameworks through the on-surface formation of covalent C-C bonds *via* dehalogenation was not reported until 2007, when Grill *et al.* described the formation of extended molecular networks through porphyrin-based building blocks deposited on a gold surface.⁵⁶ The authors deposited tetra(4-bromophenyl)porphyrin (Br₄TPP, **LC 60**) on Au(111) at RT and monitored the behaviour of the compound on the surface at different temperatures *via* STM (Fig. 2.9).

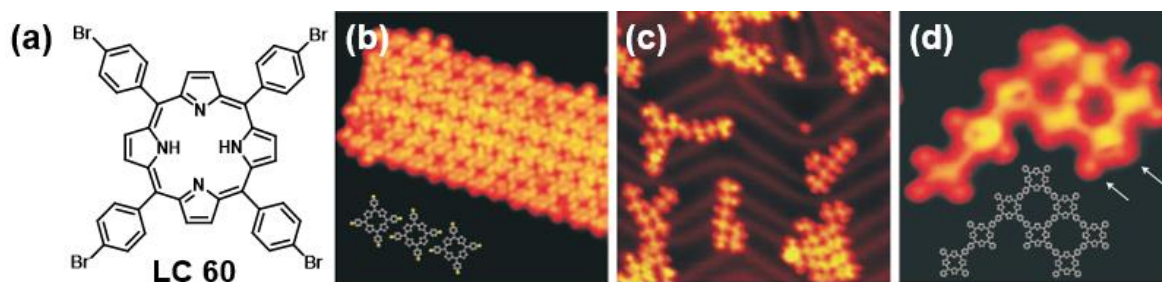


Figure 2.9: (a) The tetra(4-bromophenyl)porphyrin (Br_4TPP) precursor as prepared by Grill *et al.*⁵⁶ (b) STM image of intact Br_4TPP molecules prior to polymerisation with corresponding structures inset. (c) STM image after activation of molecules, causing polymerisation. (d) Enhanced ($8.5 \times 8.5 \text{ nm}^2$) STM of covalently-bonded network. Left and right arrows indicate legs with and without bromine atoms, respectively. Adapted from Grill *et al.*⁵⁶

Different nanostructures were realised upon the surface depending on the thermal treatment, for example if the evaporation of the precursor was carried out at 550 K or less, then the molecules remained intact and formed highly ordered islands on the substrate (Fig. 2.9 (b)). Further thermal activation (*i.e.* heating of the substrate) was then required to induce dehalogenation and intermolecular coupling. However if the evaporation temperature was increased to at least 590 K, then dehalogenation occurred within the evaporator and not on the substrate, and covalently-linked nanostructures were formed, rather than ordered islands. They observed the formation of extended, covalently bound networks on the surface, the shape of which could be influenced through modification of the precursor *e.g.* incorporation of only two Br substituents instead of four (*trans*- Br_2TPP) led to the formation of linear chains of covalently linked porphyrins. These observations laid the foundations for on-surface chemistry.

Further on-surface synthetic work was carried out by Gutzler *et al.* in 2009, who reported 2D covalent organic frameworks (COFs) grown from 1,3,5-tris(4-bromophenyl)benzene (TBB, **LC 61**, Fig. 2.10 (a)) on Cu(111), Ag(110), and graphite(001).⁵⁷ In the case of the inert graphite(001) surface, it was observed that it did not catalyse the surface-mediated homolysis of the C-Br bond, whereas deposition on Cu(111) and Ag(110) resulted in bond cleavage. Therefore the metal substrate acts not only as a support, but also plays a critical catalytic role. It was observed that the radicals formed by dehalogenation coordinate to metal atoms supplied from the surface in an intermediate step, rather than immediately forming C-C bonds. Follow-up work in 2010 from the same group

examined the differences in reactivity of the same molecule on different substrates.⁵⁸ At RT, the substrates Cu(111) and Ag(110) were sufficiently reactive to catalyse the cleavage of the C-Br bonds, but Ag(111) did not, the TBB thus remaining intact post-deposition. The authors also discovered that dehalogenation did not occur on any substrate at low temperatures (~ 80 K), evidence that thermal activation is required (Fig. 2.10 (b)). A two-step process was put forward as the mechanism for dehalogenation, where first, charge transfer between the adsorbed molecule and the surface leads to partial filling of a π^* orbital. The level of filling increases with surface interaction strength (*i.e.* largest on copper), and it is then proposed that in a second step, thermally activated charge transfer from the π^* orbitals into σ^* orbitals (antibonding with respect to the C-Br bonds) causes these bonds to become destabilised, resulting in dehalogenation.

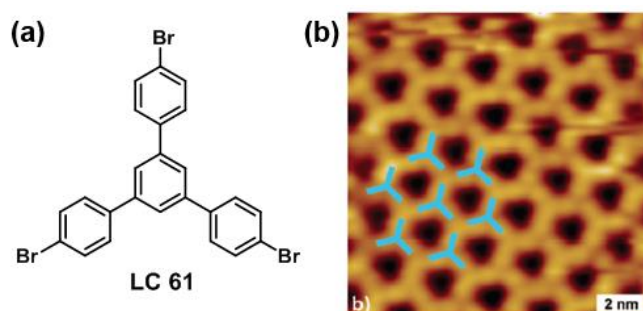


Figure 2.10: (a) Structure of TBB (LC 61). (b) STM of TBB deposited on Cu(111) at 80 K, with intact molecules (overlaid in blue) showing non-covalent interactions.

The behaviour of iodine and bromine functionalities on Au(111), Ag(111) and Cu(111) have been compared computationally by Björk *et al.*, who reported that DFT (density functional theory) showed that the largest barrier for dehalogenation was exhibited by Au(111) and the lowest by Cu(111), which indicates Cu(111) is most reactive.⁵⁹ They also determined that dehalogenation barriers are generally lower for iodine than for bromine, which has been proven experimentally.⁶⁰ Gutzler *et al.* found that the C-Br bond is fully cleaved on Cu(111) at RT.⁵⁷ However it has been found that it remains intact on the Au(111) surface.⁶¹ In the case of Ag(111), the cleavage of the C-Br bond coincides with RT, so the Ag is considered to be of intermediate reactivity.⁶² The cleaved halogen atoms remain on the surface, even at elevated temperatures. Gutzler *et al.* reported the onset of desorption of Br atoms as occurring at 400 °C. Therefore the polymerisation and cyclodehydrogenation steps most likely occur in the presence of chemisorbed halogen atoms.

Taking advantage of the different reactivities of bromine and iodine, Lafferentz and Grill returned in 2012 with a report of a tetraphenylporphyrin bearing both bromo and iodo functionalities (trans-Br₂I₂TPP, **LC 62**, Fig. 2.11).⁶³ Due to the different activation temperatures, the porphyrins could be coupled selectively depending on the temperature. At 120 °C on Au(111), efficient polymerisation through the cleavage of the iodine bonds was observed, with the bromine atoms remaining attached (Fig. 2.11 (c)). Annealing to 250 °C, supplying more thermal energy, results in the formation of 2D networks from the linear chains due to dissociation of bromine (Fig. 2.11 (d)).

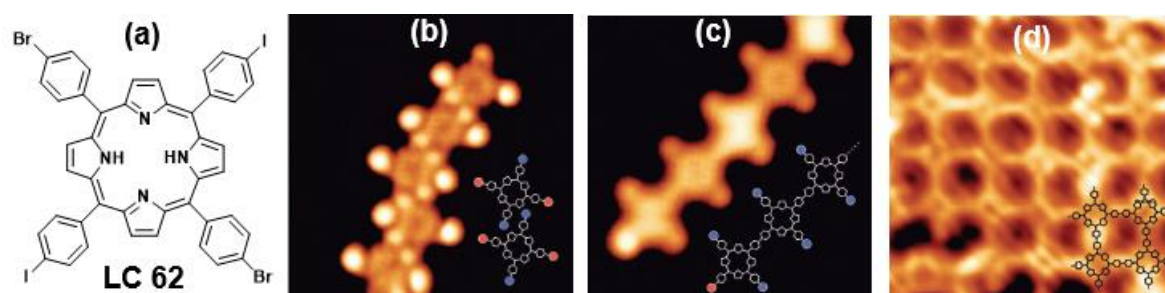
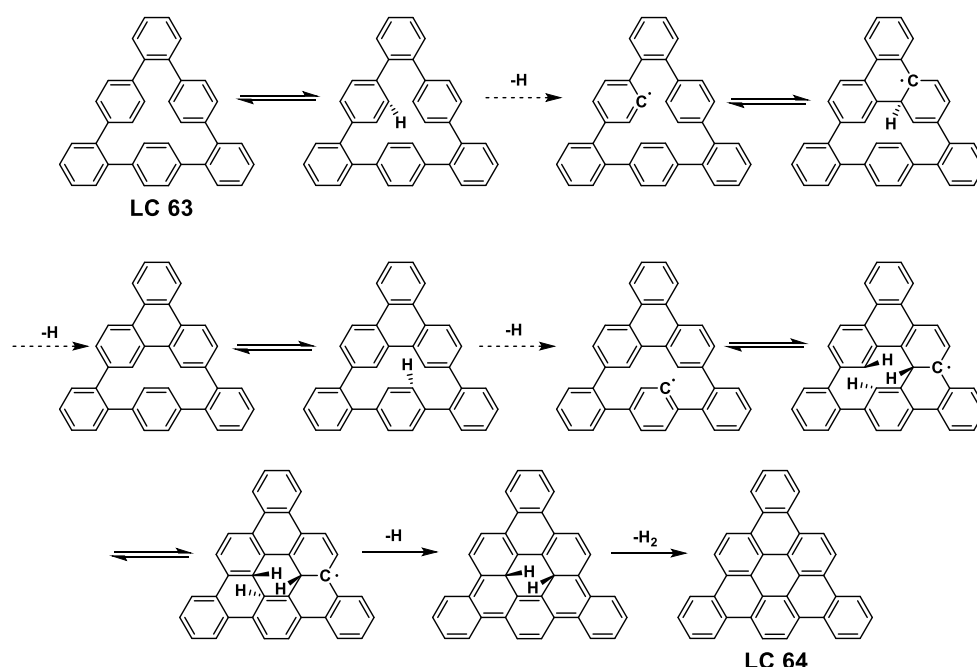


Figure 2.11: (a) Trans-Br₂I₂TPP (**LC 62**). (b) STM image of trans-Br₂I₂TPP on Au(111) after deposition at 80 K (-193 °C). (c) STM image of polymer created after annealing to 120 °C. (d) STM image of 2D network created upon annealing to 250 °C. Adapted from Grill *et al.*⁶³

2.1.9 On-Surface Cyclodehydrogenation

Following cleavage of the halogen atoms and formation of the surface-stabilised radical species, the Ullmann-type polymerisation step can be achieved, followed by cyclodehydrogenation. Reports of on-surface cyclodehydrogenation for the preparation of nanographenes were published as early as 1999, several years before the isolation of monolayer graphene. That year, Weiss and co-workers reported the thermally induced cyclodehydrogenation of a HBC precursor on Cu(111),⁶⁴ and in 2001, Beernink *et al.* extended this to Cu(110) and found that planar PAHs could be produced from hexaphenylbenzene or diphenylacetylene after thermal treatment on the surface.⁶⁵ There was little investigation of the mechanistic processes undertaken, and direct visualisation of the surface by STM was not reported. In 2011 Treier *et al.* published an important paper on the mechanism of intramolecular cyclodehydrogenation on a reactive metal substrate.⁵³ They chose to examine the behaviour of a prototypical PAH, cyclohexa-*o-p-o-p-o-p*-phenylene

(CHP, **LC 63**) on Cu(111). After deposition of **LC 63** on the substrate at RT, two different phases were observed; a close-packed phase and also wire-like supramolecular structures. They noted that **LC 63** arranged itself as dimers on the substrate, with bright protrusions evident. These protrusions were attributed to the *p*-phenylene units tilted with respect to the substrate (*i.e.* not lying flat upon it). Following annealing to approximately 500 K, the fully cyclodehydrogenated and planarised tribenzocoronene (TBC, **LC 64**) product was observed by STM. Further analysis with DFT calculations provided evidence for a mechanism involving catalytic activation by the substrate which is enhanced by adsorbate-substrate interactions. Five reaction intermediates were proposed from the DFT results, two of which were experimentally observed by STM. The final TBC product was much more stable than the intermediates, with the total energy gain of the cyclodehydrogenation process calculated as being 1.08 eV. They proposed that initially, the copper-promoted removal of a hydrogen atom from one of the para-phenylene rings, forming a radical, begins the process. Following which, rotation of this ring towards its nearest neighbour forms a C-C bond through radical aromatic addition, with copper-promoted removal of the corresponding hydrogen atom. Finally, recombinative H₂ removal completes the process. The entire sequence to cyclodehydrogenate **LC 63** to TBC (**LC 64**) involves 5 reaction intermediates and six steps (Scheme 2.5).



Scheme 2.5: The detailed mechanism for the on-surface cyclodehydrogenation of CHP to TBC, as proposed by Treier et al.⁵³

Treier *et al.* report that the mechanism they have proposed is not only specific to the CHP case and should apply to many surface-assisted cyclodehydrogenation processes. They further propose that there are two main driving forces for intramolecular cyclodehydrogenation on metal surfaces. The first is the catalytic solvation of hydrogen atoms by the substrate, and second the Van der Waals forces between the adsorbed molecules and the substrate, which cause molecular strain and in turn weaken the C-H bonds. It is also expected that the stabilisation of radical species by the substrate plays an important role.⁶⁶ The growth of GNR chains is affected by hydrogen atoms on the surface – this can cause the chains to become passivated, forming C-H bonds at either end, instead of continuing to couple to form longer polymers.⁶⁷ If the cyclodehydrogenation step begins to occur in the temperature range of polymerisation, this becomes an issue – hence the importance of selecting a substrate or experimental conditions that allow a lower polymerisation temperature.

The application of these fundamental studies on on-surface reactivity to GNR preparation only began in earnest after the publication of the 2010 work of Cai *et al.*, who demonstrated an elegant method for the preparation of GNRs on Au(111) (Figure 2.12).⁶⁸ The authors selected 10,10'-dibromo-9,9'-bianthryl (DBBA, **LC 65**) as the precursor monomer, the width of which dictated the final width of the GNR. Sublimation of DBBA onto the Au(111) substrate led to carbon-halogen bond cleavage and the dehalogenated derivative then existing as a surface-stabilised biradical species. The first thermal activation step, carried out at 200 °C, led to linear polymer chains, due to the diffusion and coupling of the radical species on the surface. Intramolecular cyclodehydrogenation was then subsequently induced by further annealing to 400 °C, and produced armchair-type GNRs (**LC 67**) which were seven carbon atoms wide (denoted as $N = 7$). Experimental and simulated STM results gave good agreement, and indicated atomically precise GNRs with fully hydrogen-terminated edges. STS (scanning tunnelling spectroscopy) determined the band-gap of this $N = 7$ GNR as being 2.3 eV on Au(111).⁶⁹ The authors also described the formation of chevron-type GNRs on Au(111) *via* the same on-surface method (Fig. 2.12 (d)), achieved through the precursor monomer (**LC 56**), as later employed by Vo *et al.* in solution.⁵⁰ Cyclodehydrogenation of the polymer was achieved at 440 °C, and it was noted through STM measurements that the planarisation of the GNR caused a reduction in the height of the polymer on the substrate from 0.25 nm to 0.18 nm.

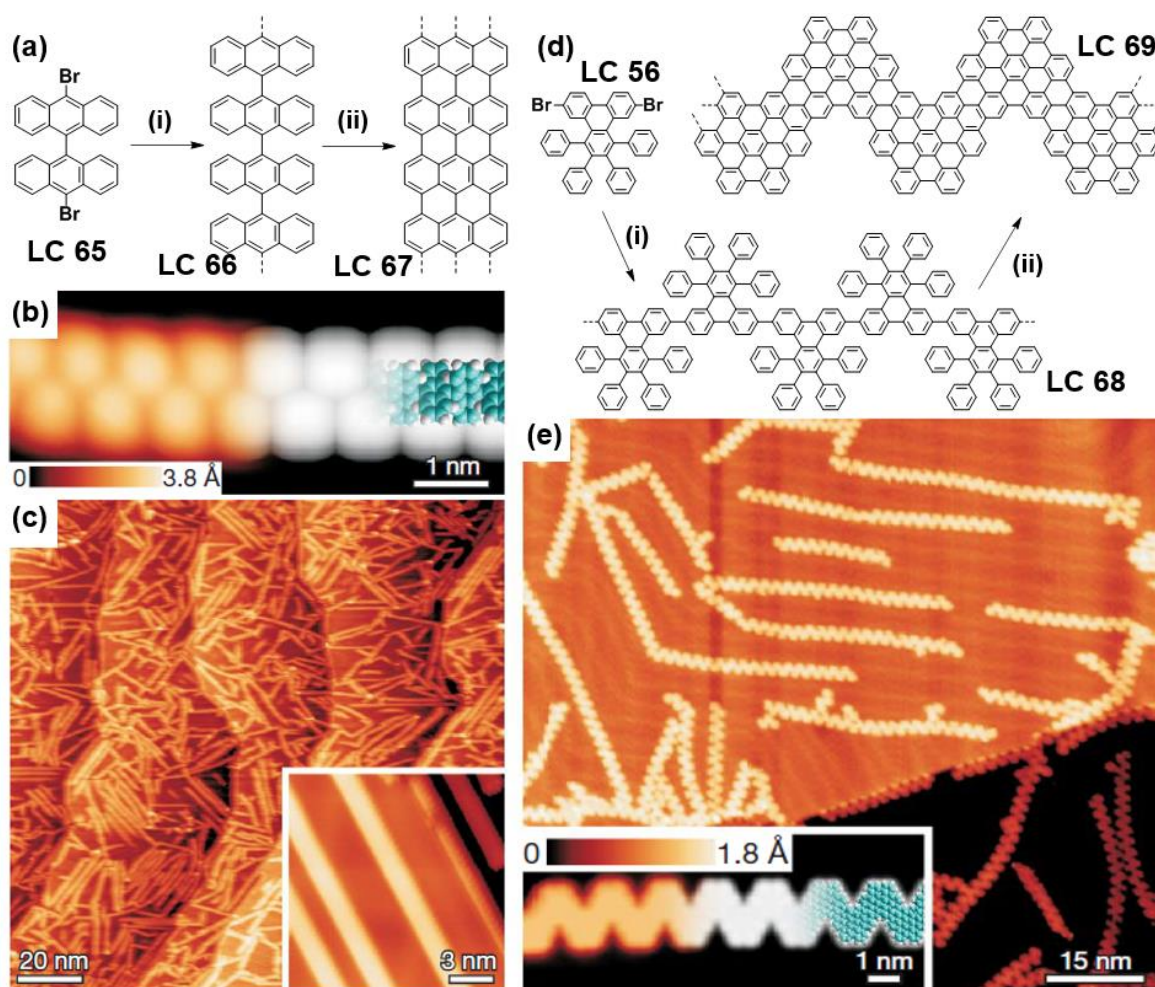


Figure 2.12: (a) GNRs yielded from DBBA on Au(111). (i) 200 °C, (ii) 400 °C. (b) STM image of the polyanthrylene chain prior to cyclodehydrogenation (left) and DFT simulation of the STM image (right) with overlaid molecular model. (c) STM overview of linear GNRs from DBBA after cyclodehydrogenation, and inset, a higher resolution STM. (d) Scheme displaying chevron GNRs from triphenylene precursor. (i) 250 °C, (ii) 440 °C. (e) STM overview of cyclodehydrogenated chevron GNRs on Au(111), and inset, an STM image of a chevron GNR, with DFT simulated image (right, greyscale) and overlaid molecular model. Adapted from Cai *et al.*⁶⁸

The GNR fabrication strategy originally employed by Cai *et al.* has since been applied to a wide variety of suitable precursors, and significant progress has been made in the field on-surface synthesis. The synthesis of GNRs of varying widths and edge structures have since been reported, in efforts to modulate measured band-gaps.⁴³ For example, the DBBA precursor **LC 65** can be extended to produce wider GNRs, such as the 13-carbon atom wide GNRs reported by Chen *et al.*, which had a band gap of 1.4 eV.⁷⁰ The on-surface behaviour of HBC (hexa-*peri*-hexabenzocoronene) based precursors has also been

investigated. In 2013, Gille *et al.* published an account of precursor monomers suitable for the generation of GNRs and extended networks.⁷¹ Their proposals included the all-carbon dibromo-HBC, which being substituted in the *para* position, was proposed as being suitable for the generation of GNRs (**LC 70**, Fig. 2.13 (a)). They also put forward a HBC precursor thought suitable for the creation of an extended network through varying iodo- and bromo-substitution (**LC 71**, Fig. 2.13 (b)). With two iodo functionalities *para* to each other, and the remaining four positions occupied by bromo substituents, it was thought that this structure presented a means of generating first a GNR, through cleavage of only the C-I bonds at a lower temperature, then generation of an extended network through cleavage of the C-Br bonds at elevated temperatures. In 2014, the behaviour of **LC 70** on Au(111) and Cu(111) was investigated.⁷² It was observed that linear chains of HBC molecules were formed on Au(111), through covalent C-C bond formation after annealing to 520 K (Fig. 2.13 (c)), but on Cu(111), the HBC molecules are dehalogenated at RT, and form coordination bonds with the Cu adatoms. Annealing on Cu(111) led to desorption from the surface before covalent bond formation.

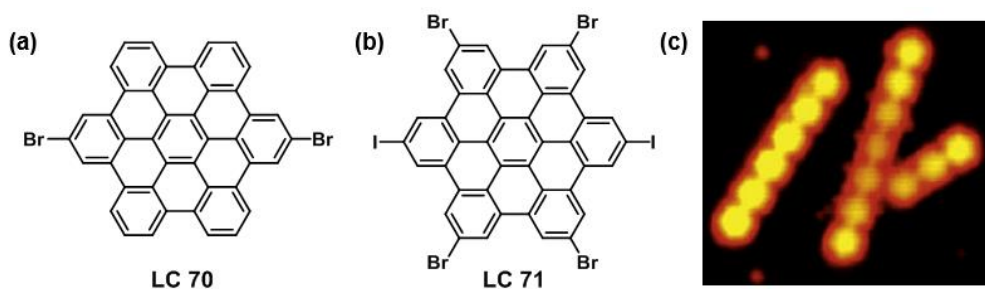


Figure 2.13: (a) Dibromo-HBC **LC 70**. (b) HBC with Br and I functionality (**LC 71**). (c) STM image of **LC 70** on Au(111) after annealing to 520 K. From Koch *et al.*⁷²

2.1.10 On-Surface Synthesis and Heteroatom Substitution

The introduction of heteroatoms as a means of controlling the band-gap remains an area of GNR research with many new avenues as yet unexplored. The introduction of heteroatoms (often referred to as “doping” in the literature) through the bottom-up method allows them to be sited with atomic precision. In 2013 Bronner *et al.* reported on-surface synthesised chevron-type GNRs which exhibited controlled N substitution.⁷³ By modifying the monomer (**LC 56**), with either one or two N atoms (**LC 72/ LC 73**), through Diels-Alder reactions with appropriate alkynes, they were able to produce GNRs with varying degrees

of N-substitution (Fig. 2.14 (a)). Electronic high-resolution electron energy loss spectroscopy (HREELS) was employed to investigate the effect of N substitution on the band gap by exciting valence band to conduction band transitions. UPS (ultraviolet photoelectron spectroscopy) was also used to determine the band-gap of the GNR relative to the underlying substrate (Au(111)). The HREELS results showed that the bandgap had been reduced only slightly, compared with the pristine (unsubstituted, all-carbon) variant of the GNR. For example, the band-gap of the doubly N-substituted GNR (from **LC 73**) was lowered by 3%. However, the UPS measurements revealed that the overall band energies were lowered depending on the level of N-substitution, with a lowering of 0.1 eV per N atom (Fig. 2.14 (b)). The authors concluded that although the magnitude of the band-gap itself remains largely unchanged with increasing N-substitution, the energy of the band-gap is shifted linearly, which opens up a method of tuning the energy levels of a GNR to that of the Fermi level of an underlying substrate. STM images of these GNRs were not reported.

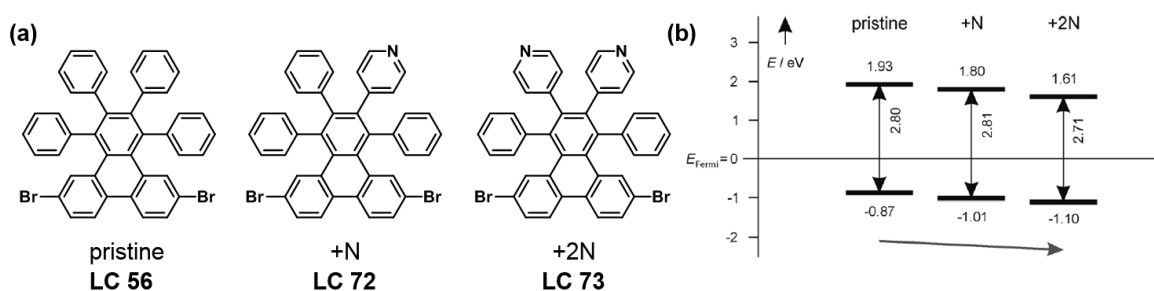


Figure 2.14: (a) The three precursors with varying degrees of N-substitution as investigated by Bronner *et al.* and (b) a graphical description of the band-gap size relative to the Fermi level of the gold substrate, reproduced from Bronner *et al.*⁷³

This work was further investigated by Zhang *et al.* who used STM and STS (scanning tunnelling spectroscopy) to further probe the behaviour of the GNR obtained from **LC 73**. Their use of DFT in combination with STM confirmed its synthesis, and STS revealed a band-gap of 1.02 eV.⁷⁴ Interestingly, the authors also investigated the effect of the degree of coverage of the precursor on the substrate upon the length and quality of the GNRs obtained. In the case of monolayer coverage of the surface, it was observed that the GNRs were quite short, and in certain areas only dimers and trimers were produced, rather than polymers. This was explained by considering that in order to polymerise and form extended GNRs, the monomers require a certain amount of space in which to diffuse and attain the correct orientation. At higher surface coverages, this ability to move is hindered, resulting in shorter nanostructures. The implication is that for optimal GNR growth, sub-monolayer conditions

are required. This work revealed that the controlled introduction of N atoms into GNRs does not greatly affect the band-gap, but that they result in a shift of the band energies, the extent of which can be precisely tuned through the level of substitution.

Cai *et al.* returned to the forefront of GNR synthesis with their prominent 2014 publication detailing the controlled heteroatom substitution of GNRs through the synthesis of an N-containing precursor monomer.⁷⁵ In this instance, they employed a mixture of substituted and unsubstituted monomers, and observed that the resulting formations consisted of alternating segments of pristine (unsubstituted) nanoribbons (p-GNRs) and nitrogen-substituted nanoribbons (N-GNRs), which were observed to behave as p-n junctions. The same monomer, **LC 56**, as used to prepare the earlier pristine chevron-type GNR was modified *via* the incorporation of dipyrimidyl units to give (5,5'-(6,11-dibromo-1,4-diphenyltriphenylene-2,3-diyl, **LC 58**, Fig. 2.15 (a)). After deposition of solely this monomer on Au(111), the resulting N-GNRs were formed in the same manner as previous, polymerisation at 200 °C and subsequent cyclodehydrogenation at 400 °C (Fig. 2.15 (a)). As mentioned earlier, Vo *et al.* have also reported this GNR, but obtained through solution-based methods.⁵² It should be noted that the STM images of the GNRs do not clearly distinguish N and C atoms, thus the N-GNRs appear identical to the pristine-type. The authors noticed that the N-GNRs exhibited a different type of packing arrangement to the p-GNRs, which were attributed to attractive N-H interactions between peripheral bipyrimidine units of the neighbouring N-GNRs, providing a means of distinguishing them. STM imaging revealed they had arranged themselves in a slightly shifted antiparallel arrangement and became aggregated, unlike p-GNRs which repel each other. They then investigated the ability to form a structure consisting of alternating segments of p- and N-GNRs. The same on-surface methodology was employed and yielded GNRs with varying substitution levels. STM cannot distinguish the two sections, but the attractive interactions between certain sections provides evidence for the location of the N-GNR sections (Fig. 2.15 (c) and (d)). Differential conductance measurements (dI/dV) provided further confirmation of the assignment of various sections. Investigation of the electronic properties by DFT and further conductance measurements revealed a shift of the band structure, by 0.55 eV and 0.45 eV of the valence and conduction bands respectively, at the points where the p- and N-GNRs met, termed a “heterojunction”. This behaviour is characteristic of p-n junctions and its realisation in a single GNR suggests that p-N-GNR heterostructures display a great deal of potential as versatile, tuneable components in electronics. The authors claim that the introduction of

nitrogen atoms into precursor monomers results in a GNR with a band-gap shifted down in energy by about 0.13 eV per nitrogen atom, which highlights how the on-surface method provides a significant degree of control and precision over the preparation of GNRs and facilitates the tuning of their electronic properties.

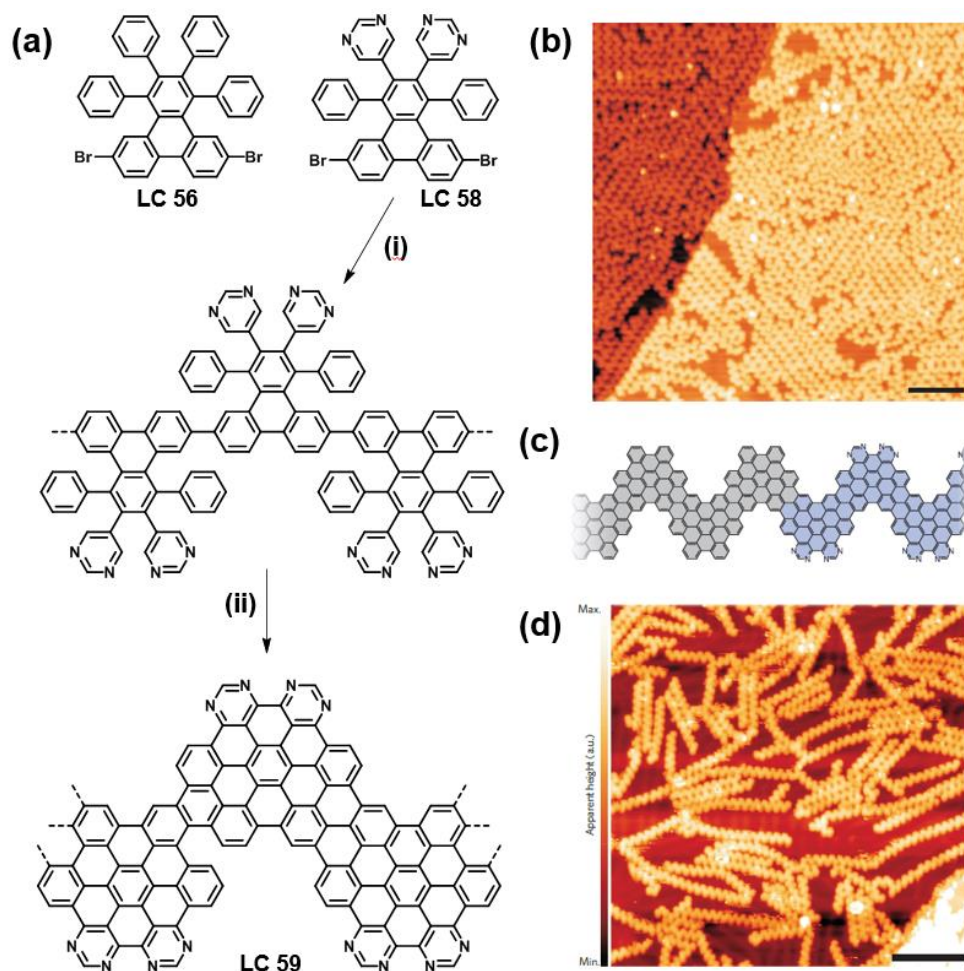


Figure 2.15: (a) Two GNR precursors as synthesised by Cai *et al.*, of which the 4N-substituted was used to build a GNR on Au(111) (i) 200 °C, (ii) 400 °C. (b) An STM overview of the fully cyclodehydrogenated GNR depicted in (a) with scale bar as 10 nm. (c) A graphical description of the GNR heterojunctions prepared from all-carbon monomers (grey) and N-substituted monomers (blue) and (d) an STM overview of the GNR heterojunctions on Au(111) with scale bar as 15 nm.⁷⁵

Apart from these reports of N-GNRs, other literature examples prepared by either the on-surface method, or by other bottom-up methods, are relatively scarce. Intriguing on-surface work has recently been carried out by Marangoni *et al.*, who have reported GNR heterojunctions formed from only one molecular precursor, rather than two different

precursors (**LC 74**, Fig. 2.16 (a)).⁷⁶ The use of two different precursors, such as in the work of Cai *et al.*, provides no control over the sequence of the monomers in the polymeric chain, and leads to random arrangements. Marangoni *et al.* have exploited the previously reported on-surface behaviour of the 9-methyl-9*H*-carbazole moiety to create GNRs that can undergo functionalisation through rearrangement in the later stages of synthesis. After deposition of the monomer **LC 74** on the surface, a thermally induced ring expansion/dehydrogenation results in the methyl-substituted carbazole moiety either rearranging to form an electron-poor phenanthridine unit or losing the methyl functionality to generate an electron rich unsubstituted carbazole. After the usual annealing process to cleave the C-Br bonds (200 °C) and cyclodehydrogenation (complete by 400 °C) on Au(111), chevron-type GNRs were observed by STM, of an average length of 12 nm (**LC 75**). In order to ascertain the structures at the edges of the GNRs, the authors used nc-AFM (non-contact atomic force microscopy), which revealed two different structural motifs. The presence of both the six-membered phenanthridine and five-membered carbazole were confirmed (Fig. 2.16 (c) and (d)), but it was noted that they randomly coexist along the lengths of the GNRs.

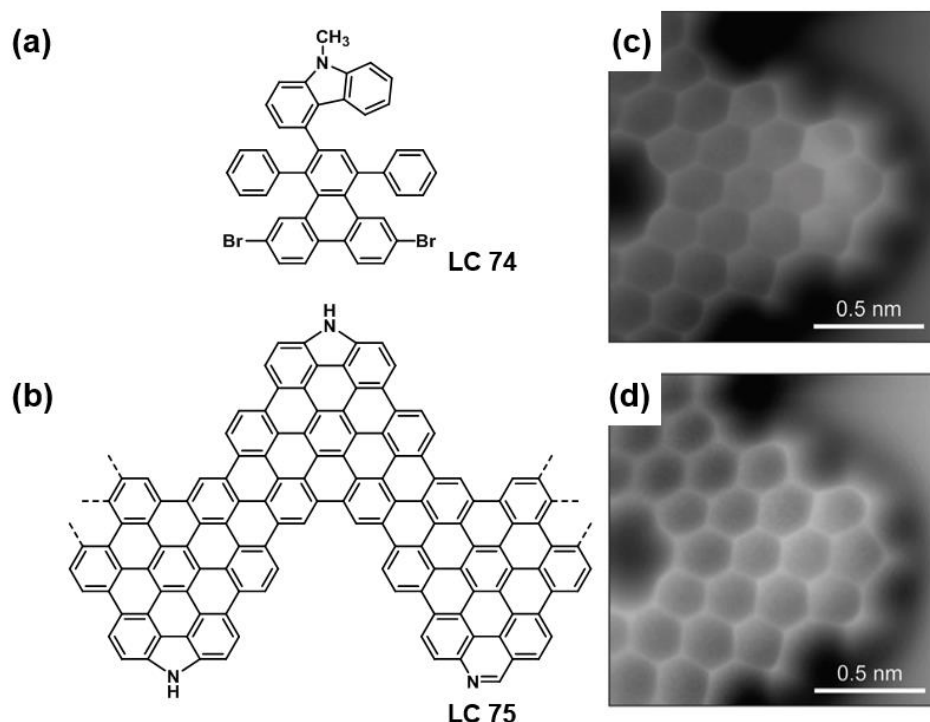
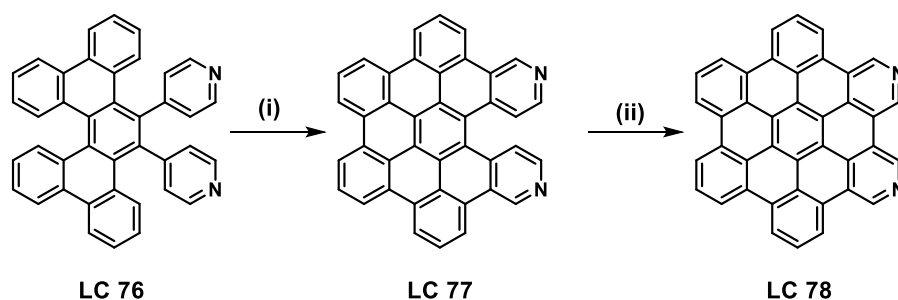


Figure 2.16: (a) A carbazole-substituted molecular precursor, (b) the GNR derived from it, exhibiting edge reconstruction from thermal rearrangement, (c) nc-AFM (non-contact AFM) image of phenanthridine-fused moiety and (d) nc-AFM image of carbazole-fused moiety. From Marangoni *et al.*⁷⁶

The formation of the unsubstituted carbazole was proposed to be caused by homolytic cleavage of the N-CH₃ bond, forming radical species which then reacted with hydrogen atoms on the surface that had been lost in the cyclodehydrogenation step. The phenanthridine unit could be formed by one of two proposed mechanisms; beginning with either homolytic cleavage of one of the two N-C_{aryl} bonds, or the homolysis of a metal C-H bond. Although the sequence of electron-rich carbazole and electron-poor phenanthridine units is not uniform, this work does demonstrate the possibility of forming GNR heterojunctions from a single precursor and can be viewed as a step forwards from the 2014 work of Cai and co-workers.

Although not strictly speaking N-GNRs but rather N-containing nanographenes, Pinardi *et al.* have investigated the cyclodehydrogenation behaviour of a pyridyl-disubstituted dibenzo[5]helicene (**LC 76**, Scheme 2.6), which was shown to sequentially form different nanostructures on a Pt(111) surface, with thermal treatment.⁷⁷ Depending on the substrate temperature, varying degrees of bond closure were achieved, with claimed efficiencies of up to 100%. At 440 K, partial cyclodehydrogenation was observed (**LC 77**), and further annealing to 650 K yielded fully fused N-substituted nanographenes (**LC 78**, Scheme 2.6). Higher temperatures (770 K) led to the loss of hydrogen atoms from the edges of the molecules, resulting in the nanographenes becoming bound to the surface.



Scheme 2.6: On-surface cyclodehydrogenation of dibenzo[5]helicene as reported by Pinardi *et al.* (i) Thermal annealing to 440 K (167 °C), followed by (ii) annealing to 650 K (377 °C) on a Pt(111) surface.⁷⁷

The incorporation of boron atoms into GNRs has lately emerged as a method of modifying the band gap, although the electronic effects of boron dopants are as yet not completely understood.⁷⁸ Edge-substitution, such as described in the examples of N-GNRs above, does not greatly affect the band-gap itself but it is a means of effectively and precisely controlling the energies of the band structures. The lone pairs of the nitrogen atoms are not

in conjugation with the π system in GNRs with edge structure substitution. However, incorporation of heteroatoms directly into the GNR backbone allows heteroatom p_z orbitals to interact with the π system. In 2015, Kawai *et al.* published an $N = 7$ boron-containing armchair GNR, from a precursor somewhat analogous to DBBA (**LC 79**, Fig. 2.17 (a)).⁷⁹ Further computational work by Cloke *et al.* indicated that the band-gap for the same GNR is reduced substantially by the presence of boron, which induces the formation of a new acceptor band 0.8 eV above the valence band.⁸⁰ Kawai and co-workers followed this up in 2018 with a report of an $N = 7$ GNR grown on Au(111) containing both N and B atoms.⁸¹ The precursor resembled that previously reported by Kawai, with three anthracene units, of which the middle possessed a central C_4BN ring (**LC 80**, Fig. 2.17 (b)). Unlike the C-Br substituted analogue, however, this precursor possessed C-Cl and C-I halogen substituents, which due to its asymmetric nature led to two different possible products (i.e. formation of C-C bonds from dissociation of two C-I bonds, or from dissociation of C-Cl and C-I). AFM with a CO tip was able to resolve the different heteroatoms *via* their Van der Waals radius. It was not possible to precisely measure the level of the valence band, but it was noted that the bands appeared to be shifted upward with minimal change in the band energies.

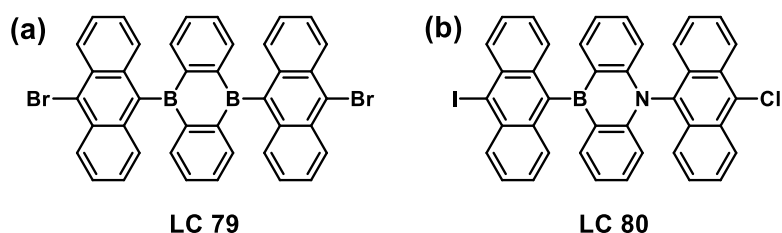


Figure 2.17: (a) Precursor synthesised by Kawai *et al.* towards the preparation of boron-substituted GNRs and (b) a further modified precursor providing access to BN-substituted GNRs.^{79, 81}

2.1.11 Challenges to be Addressed

There are a number of challenges that must be overcome for GNRs to become viable for incorporation into devices. Firstly, there is the problem of transferring GNRs grown on reactive metal surfaces onto insulating substrates such as SiO_2 which are suitable for device application, and secondly, to produce GNRs in a scalable manner. Bennett *et al.* have designed a reproducible and scalable route to transfer GNRs grown on a metallic substrate to an insulating substrate (Figure 2.18 (a)).⁸² In this process, the GNRs are grown on an Au

substrate which is in turn on top of a mica layer. In order to remove the GNRs from the Au, poly-methylmethacrylate (PMMA) is spun-cast onto the GNRs and heated to 180 °C for 10 minutes. The layered system is then floated on concentrated hydrofluoric acid (HF) and agitated. This step causes the mica substrate to delaminate from the stack. The PMMA/GNR/Au system left behind is rinsed with water and drawn onto the desired substrate surface (in this case SiO₂). After the film is adhered to the substrate it is then heated to remove any remaining water. The PMMA layer can be easily washed away with acetone, thus leaving GNRs on the insulating substrate. To prove their concept, the authors fabricated FET transistors from GNRs obtained in this way, using lithographically defined Pd, which forms the source and drain contacts (Figure 2.18 (b)). Their studies revealed the GNRs to be quite sensitive to their environment and that they displayed a high Schottky barrier, which they suggest might be overcome with wider GNRs that have lower band-gaps. Llinas and co-workers gave this research area a boost in 2017 when they successfully produced FETs based on 9 and 13 atom wide GNRs that displayed excellent switching behaviour.⁸³ These developments suggest that GNR-based devices may very well play an important role in future electronic applications.

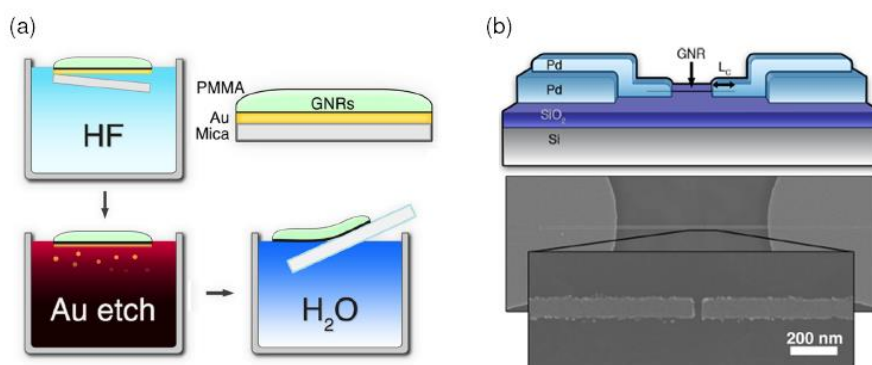


Figure 2.18: (a) Graphical depiction of a process designed to extract GNRs on to a useful substrate for device fabrication. (b) Schematic of a GNR-FET. Adapted from Bennett *et al.*⁸²

The issue of scalability has been addressed by Chen *et al.*⁸⁴ In order to circumnavigate the drawbacks of bottom-up solution-based methods (solubility, aggregation etc.) and the often costly and sometimes low yielding on-surface methods, an ambient pressure CVD-based methodology has been devised. With a range of precursors, some including N and S substitution, the authors found that it was possible to grow GNRs on an Au/mica substrate under ambient conditions. The mild conditions permitted the use of MALDI mass spectrometry to analyse the polyphenylene precursors, and determine their

precise chemical composition, although the fully cyclodehydrogenated GNRs did not yield useful mass spectra, perhaps due to their strong interaction with the Au substrate preventing their desorption. Prior to this report, it had not been possible to say with absolute certainty the chemical composition of heteroatom-containing GNRs, since STM cannot distinguish N and C atoms clearly due to their very similar topographic morphology. STM, HREELS and XPS analyses did prove that the quality of these GNRs were similar to those grown under UHV.

Fairbrother and co-workers have recently investigated whether the expensive ultrahigh vacuum conditions (UHV) commonly employed in research settings could be avoided, thus making large-scale manufacturing processes more facile.⁸⁵ The authors fabricated GNRs under high vacuum conditions (which are typically in the region of 10^{-6} mbar), which are commonly used in the semiconductor industry. $N = 7$ armchair GNRs were successfully grown from DBBA under these conditions, and those grown on Au substrates were noted as being stable for several months, under ambient conditions. It was noted however, that if the pressure was increased above 10^{-7} mbar, the growth characteristics of the GNRs were adversely affected by the presence of water and oxygen contaminants. Careful decontamination of the substrates before deposition of the precursors was discovered to get around this and allow synthesis of high-quality GNRs at 10^{-6} mbar. The stability of the GNRs grown this way was confirmed by the fabrication of FETs, which displayed semiconducting behaviour.

2.1.12 Chapter Aims

A significant amount of research work has been carried out by the Draper group on N-substituted materials, most notably N-substituted hexa-peri-hexabenzocoronenes (referred to as Nitrogen-heterosuperbenzene or N-HSB). As there is a paucity of work relating to HBC-type molecules or their precursors, hexaphenylbenzenes (HPBs), and on-surface synthesis, it was decided to investigate how these systems could be exploited to generate on-surface architectures in the same manner as those described earlier in this chapter. The degree to which these HBC-type platforms can be functionalised is quite high. Therefore the aim of this work is to generate HBC-type precursor monomers suitable for on-surface coupling and investigate how they behave. The potential to generate novel types of N-GNRs is a key factor driving this investigation.

The success obtained with triphenylene-based precursors, such as those described by Vo *et al.*⁵² leads to questions about the possibility of generating similar GNR systems from functionalised hexaphenylbenzenes. It would be envisaged that halogen substitution at one side of a HBC-type molecule and N-substitution at the other would lead to a GNR potentially displaying N-substituted moieties at the periphery and small voids, or pores, in the inner areas. Further to this, recent work in the Draper group has revealed methods by which partially fused (cyclodehydrogenated) molecules may be prepared. It is also therefore of some interest to investigate how these partially fused systems behave compared with their unfused counterparts. The elucidation of the cyclodehydrogenation-related behaviour of these systems on reactive metal substrates would provide a useful comparison to their cyclodehydrogenation behaviour in solution. It is hoped that the findings of these preliminary investigations into the reactivity of these compounds will provide either novel frameworks suitable for further studies towards their practicality for application, or at the very least provide some fundamental observations on the behaviour of such systems, which may be used to inform future routes in this rapidly developing field. The synthetic route towards three precursor monomers will be described, one of which is a previously unreported compound. Their previously undocumented on-surface behaviour will then be investigated and described. The three precursors, **5**, **6**, and **9** are displayed in Figure 2.19 (a), below. It would be of interest to see whether GNRs derived from these precursors are able to undergo edge-fusion, where GNRs laterally fuse to their nearest neighbours, creating extended frameworks that are multiple GNRs wide.

The band-gap of a GNR may be influenced by heteroatom doping and width modification, as previously discussed. These precursors are therefore of interest, since they display high levels of N-doping (substitution). It has also been suggested that opening pores in GNRs can influence the band-gap, although literature reports of this are scarce. Zheng *et al.* reported porous GNRs obtained via the unzipping of CNTs, but the pores were highly irregular in size and distribution.⁸⁶ Therefore the potential for these precursors to generate GNRs displaying regular pores is intriguing. The N-GNR that these precursors could produce is depicted in Fig. 2.19 (b) where the pore type voids are evident.

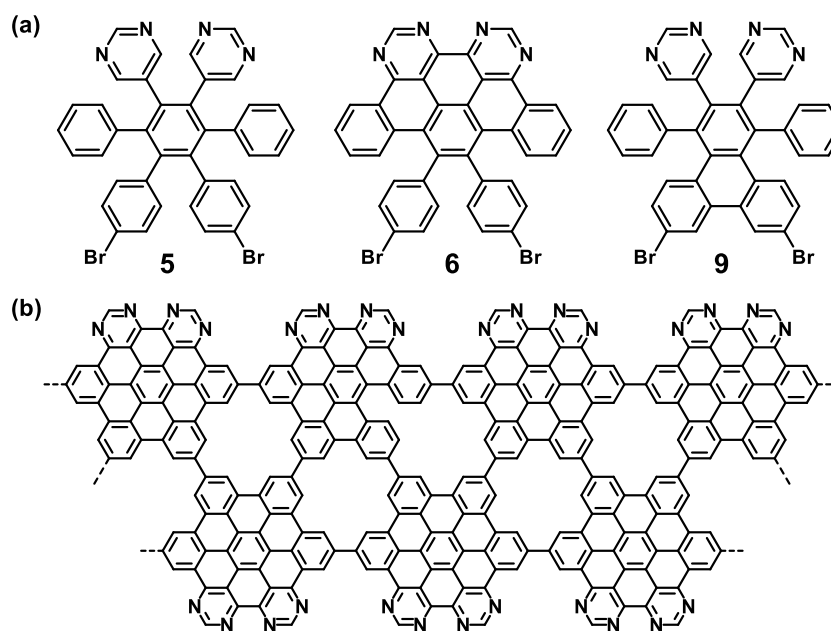


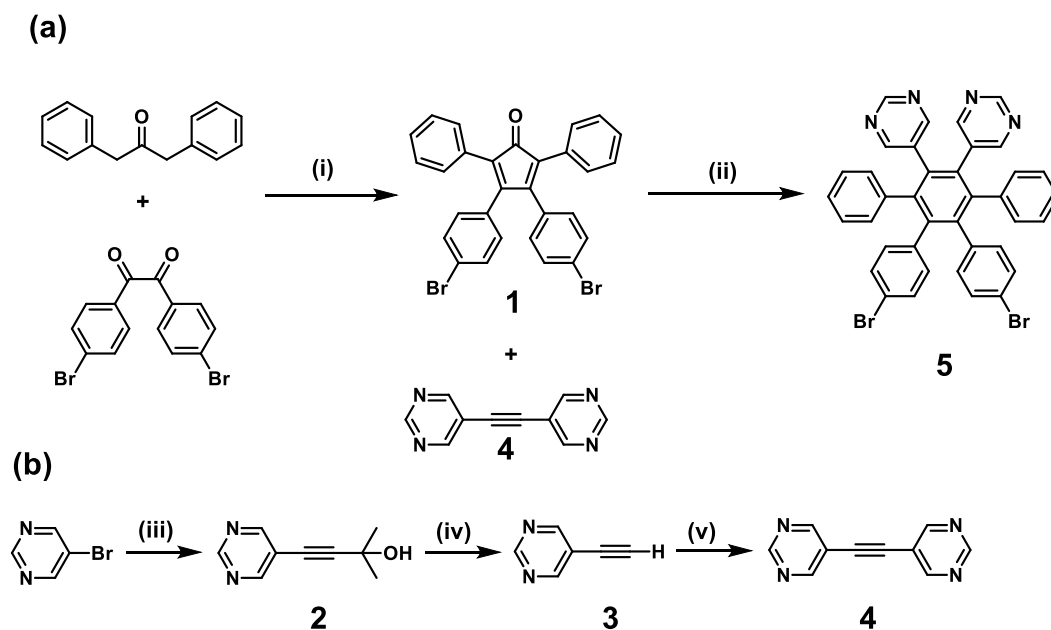
Figure 2.19: (a) The three precursors which will be synthesised and investigated for their ability to form N-GNRs. (b) The type of GNR possible from these precursors.

2.2 Synthesis and Characterisation of Precursor Monomers

The synthesis of the required precursor monomers began according to the general procedures outlined in Chapter 1 relating to the preparation of substituted hexaphenylbenzene and hexa-*peri*-hexabenzocoronene-based compounds. Generally, the procedure towards these types of compounds begins with a Knoevenagel condensation between a diketone and a monoketone, yielding a cyclopentadienone-based compound. A Diels-Alder cycloaddition between the cyclopentadienone and a suitable alkyne affords the hexaphenylbenzene, which, if desired, may be fully or partially cyclodehydrogenated, to yield the hexa-*peri*-hexabenzocoronene (HBC) derivative.

2.2.1 Synthesis of Precursors 5 and 6

The synthesis of the first precursor commenced with a double Knoevenagel condensation reaction between the commercially available 4,4'-dibromobenzil and 1,3-diphenylpropan-2-one (Scheme 2.7).



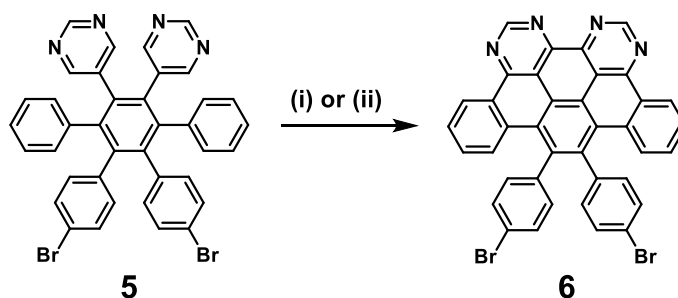
Scheme 2.7: Synthetic route towards precursor 5. (i) EtOH, KOH, reflux, 1 h, 78 %. (ii) Ph₂CO, 280 °C, 60 %. (iii) Diethylamine, Pd(PPh₃)₂Cl₂, CuI, 2-methyl-3-butyn-2-ol, 3 h, 76%. (iv) NaOH, toluene, reflux, 4 h, 78 %. (v) 5-bromopyrimidine, Pd(PPh₃)₂Cl₂, CuI, Et₃N, toluene, 41 %.

Reflux of the starting materials in ethanol, followed by the slow addition of KOH and further heating for one hour yielded the desired 3,4-bis(4-bromophenyl)-2,5-diphenylcyclopenta-2,4-dien-1-one **1** in 78 % yield. The introduction of the pendant pyrimidyl groups was achieved through a Diels-Alder cycloaddition between this and the ligand 1,2-di(pyrimidin-5-yl)ethyne **4**. The ligand **4** was prepared according to slightly modified literature procedures, beginning with the introduction of an alkyne functionality with a butynol protecting group to 5-bromopyrimidine *via* a Sonogashira cross-coupling reaction, followed by deprotection of the product **2** with NaOH in refluxing toluene to give 5-ethynylpyrimidine **3**. Removal of the toluene solvent and purification was achieved *via* chromatography on SiO₂ (CH₂Cl₂, followed by CH₂Cl₂/MeOH 20:1 v/v to elute the product). A further Sonogashira cross-coupling of **3**, again with 5-bromopyrimidine, yielded the desired dipyrimidyl ligand **4** in 41 % yield. The Diels-Alder reaction between the dipyrimidyl ligand and the cyclopentadienone was carried out in a benzophenone melt heated to 280 °C by a sand microburner. Column chromatography (SiO₂, CH₂Cl₂/MeOH 95:5 v/v) and subsequent precipitation from CH₂Cl₂/MeOH yielded the compound **5** as an off-white solid in 60 % yield.

Following the synthetic methodology previously developed within the Draper group to partially fuse N-containing polyaromatic systems,⁸⁷ **5** was added to a pressure tube with toluene (10 mL), and an excess of bromine (2 mL) was then added carefully. The Teflon screw top lid was closed and the tube was heated to 90 °C for 2 hours. Following the cooling of the reaction mixture, a reddish-yellow precipitate was observed. Decanting the supernatant solution and subsequent washing of the precipitate with cold MeOH yielded **6**, a yellow powder, in 40 % yield, with no side product formation observed (Scheme 2.10). It is noted that the unsubstituted phenyl rings do not become brominated during this process. Although similar all-carbon systems have been fully-fused with the same conditions,⁸⁸ in this case the phenyl rings bearing the electron-withdrawing bromine atoms appear deactivated toward the cyclodehydrogenation process.

Subsequent work by the author has revealed that this partial cyclodehydrogenation of **5** may also be achieved with the combination of DDQ (dichlorodicyanoquinone) and trifluoromethanesulfonic acid, again resulting in only one product (*i.e.* no other partially-fused or fully-fused compounds are present). The yields are comparable (Scheme 2.8), but the advantage in this case is the ability to avoid the use of molecular bromine, which is rather difficult to handle. A simple neutralisation of the acid with K₂CO₃ and precipitation of the

product from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ yields the product. This finding builds upon earlier reports of the cyclodehydrogenation of halogenated HBCs by Jones *et al.*, and also previous preliminary investigations in the Draper group.^{88, 89}



Scheme 2.8: Route towards partially-fused precursor **6** via molecular bromine. (i) Br_2 , toluene, 90 °C, 2 h, 40 %. (ii) DDQ, $\text{CF}_3\text{SO}_3\text{H}$, CH_2Cl_2 , RT, 2 h, 54 %.

2.2.2 Characterisation of Precursors **5** and **6**

The compounds **5** and **6** were characterised by NMR spectroscopy, HRMS and FTIR, which were in good agreement with a previous report.⁹⁰ Examination of the ^1H NMR spectrum of **5** presents the expected pattern from the equivalent pyrimidyl groups (Fig. 2.20), with H_1 the most downfield, due to the deshielding effect of the adjacent nitrogen atoms, followed by H_2 , in both cases being observed as singlets. The protons belonging to the middle phenyl rings (H_3 , H_4 and H_5) are equivalent on both sides of the molecule due to its symmetry. The *ortho*- and *para*-substituted protons ($\text{H}_{3/5}$) overlap and are observed as a multiplet at δ 7.0 ppm, as is common for this type of substituted ring system, whilst the meta protons H_4 are evident at δ 6.8 ppm. The protons of the bromo-substituted rings are evident at δ 7.1 ppm and δ 6.7 ppm (H_6 and H_7 respectively), with the characteristic ‘roofing’ effect between them making their identification and relation more facile. The ^1H - ^{13}C HSQC experiment is displayed in Fig. 2.21.

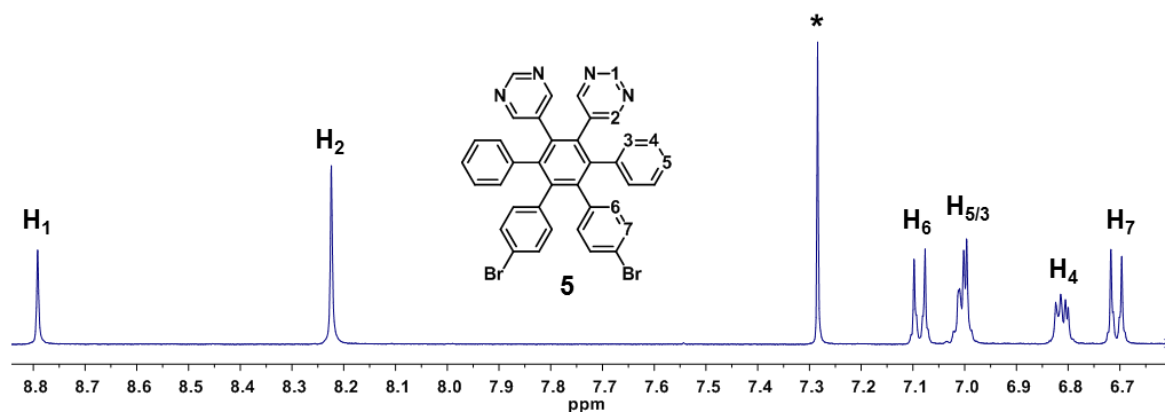


Figure 2.20: The ^1H NMR spectrum of **5** (400 MHz, CDCl_3 , RT). * denotes residual solvent peak.

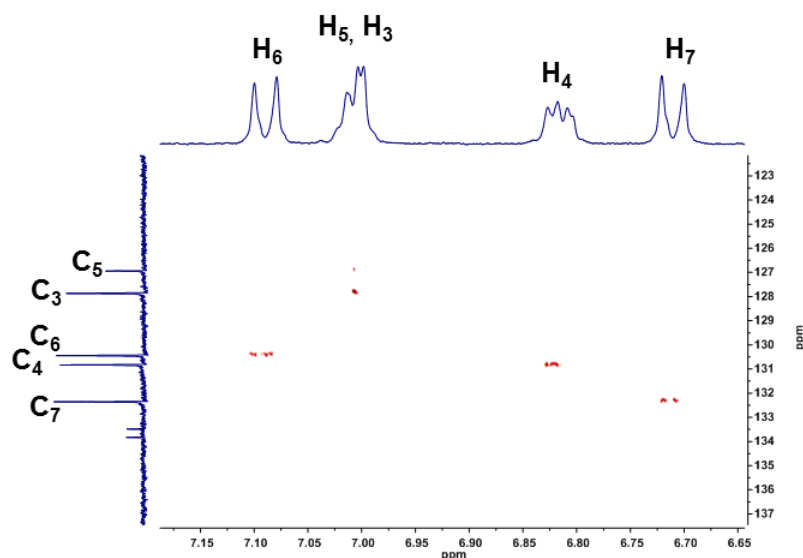


Figure 2.21: (a) HSQC experiment used to aid the assignment of **5** (600 MHz, CDCl_3 , RT).

HRMS analysis (MALDI-TOF) identified the compound **5** at $m/z = 695.0475$, which corresponds to the protonated molecule $[\text{M}+\text{H}]^+$, for which the corresponding calculated mass is 695.0446 (for $[\text{C}_{38}\text{H}_{25}\text{N}_4\text{Br}_2]^+$).

The ^1H NMR spectrum of **6** (Fig. 2.22) corresponds closely to that of **5**, with the exception of the protons previously labelled H_2 and H_3 in Fig. 2.20, which are longer present due to the bond closure at these sites. All signals are shifted downfield in comparison to the spectrum of **5**. H_1 has been shifted from δ 8.8 ppm to δ 10.1 ppm. A combination of HSQC and HMBC experiments aided the full elucidation of the spectrum (Fig. 2.23), from which it was found that H_4 is responsible for the doublet at 9.4 ppm with a coupling constant of $J = 8$ Hz, possibly coupling to H_5 . The spectra of **5** and **6** are compared in Fig. 2.24, where the

magnitude of the deshielding effects resulting from the cyclodehydrogenation can be observed.

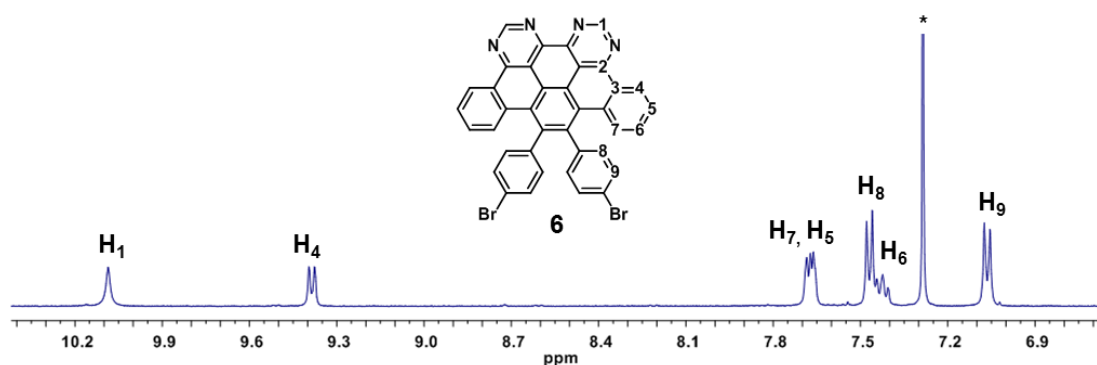


Figure 2.22: The ^1H NMR spectrum of **6**, with the ^1H - ^{13}C HSQC experiment inset (CDCl_3 , RT, 400 MHz). * denotes residual CHCl_3 solvent peak.

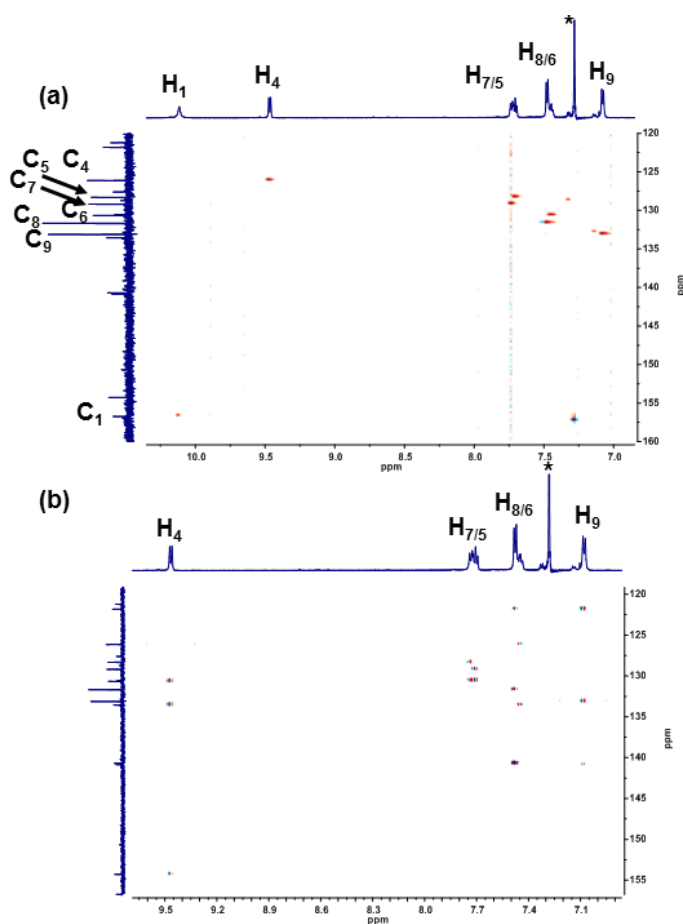


Figure 2.23: (a) HSQC and (b) HMBC experiments employed to elucidate the NMR of **5** (600 MHz, CDCl_3 RT). * denotes residual CHCl_3 solvent peak.

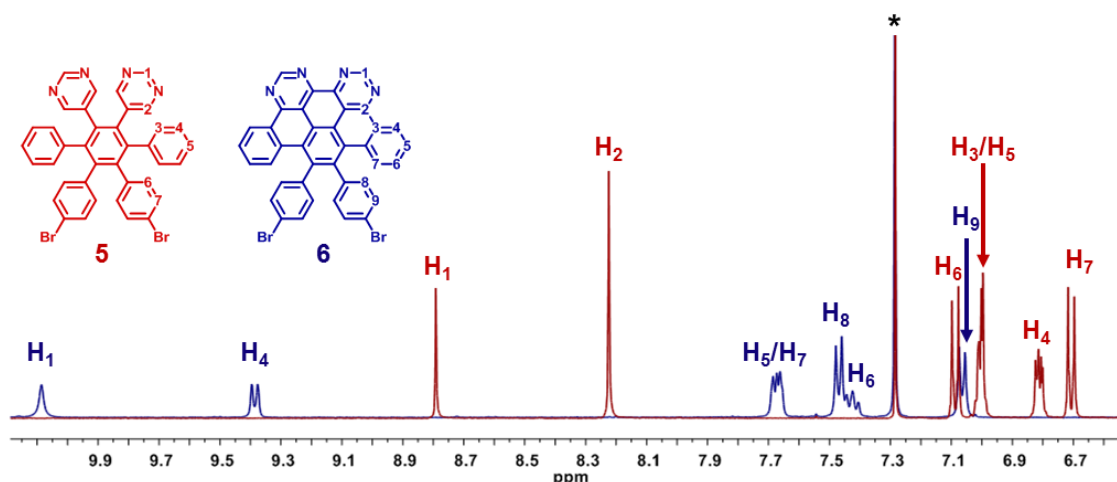
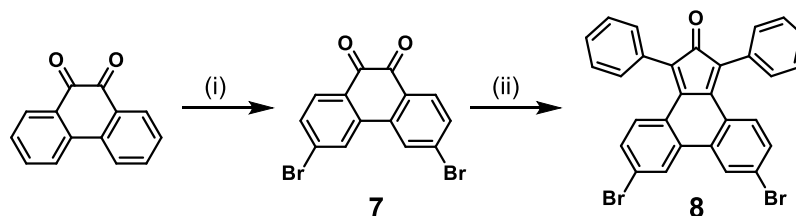


Figure 2.24: The overlaid spectra of **5** (red) and **6** (blue), displaying the magnitude of the deshielding observed. * denotes CHCl_3 residual peak.

2.2.3 Synthesis and Characterisation of **9**

The synthesis of novel compound **9** began by introducing the required halogen functionality into the phenanthrene core. Following a literature procedure,⁹¹ this was achieved by taking the commercially available 9,10-phenanthrenequinone and treating it with molecular bromine in refluxing nitrobenzene (Scheme 2.9), yielding the required 3,6-dibromophenanthrene-9,10-dione **7**. Recrystallisation from acetic acid gave the pure product in 63 % yield. A subsequent double-Knoevenagel condensation with 1,3-diphenylpropan-2-one yielded the desired product, 6,9-dibromo-1,3-diphenyl-2H-cyclopenta[*l*]phenanthren-2-one (**8**), in a 49 % yield (Scheme 2.9).

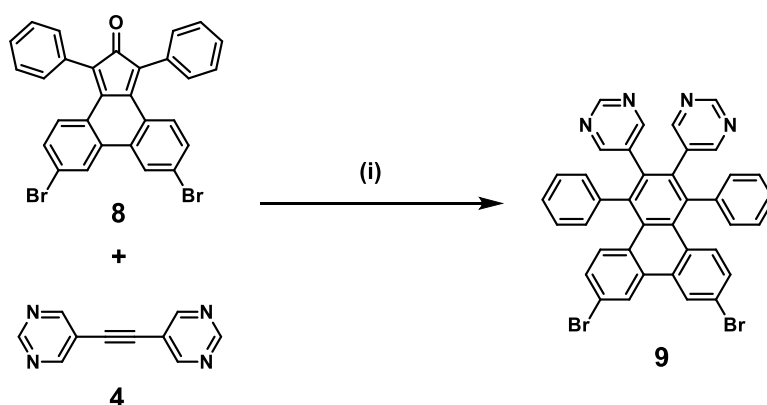


Scheme 2.9: Synthetic route towards 6,9-dibromo-1,3-diphenyl-2H-cyclopenta[*l*]phenanthren-2-one (**8**) (i) Br_2 , $\text{C}_6\text{H}_5\text{NO}_2$, reflux, 63 %. (ii) 1,3-diphenyl-2-propanone, KOH , EtOH , 70°C , 49%.

This product proved to be quite insoluble, and was readily filtered off directly from the reaction mixture. However, a subsequent ^1H NMR displayed evidence of impurities,

necessitating its purification. This proved quite challenging as its insolubility precluded column chromatography and thin-layer chromatography. It was found that carefully filtering and then slowly washing the compound with small amounts of cold CH_2Cl_2 yielded a satisfactorily clean product, as observed by ^1H NMR in CD_2Cl_2 solvent. The identity of the product was further confirmed by HRMS.

Introduction of the pyrimidyl rings was again through the same methodology as for **5**, a Diels-Alder cycloaddition between dipyrimidyl **4** and **8** in a benzophenone melt, with heating provided by a sand microburner (Scheme 2.10). Initially, the reaction mixture was heated to approximately $280\text{ }^\circ\text{C}$ and held there for two hours. TLC analysis (SiO_2 , CH_2Cl_2 :MeOH 20:1, v/v) indicated that a significant amount of starting material remained. The temperature was slowly increased to approximately $325\text{ }^\circ\text{C}$ and after a further two hours the reaction was judged complete, as indicated by further TLC analysis. The compound **9** was purified by column chromatography (precipitation directly from the reaction mixture failed to provide adequate purification) on silica (CH_2Cl_2 :MeOH 20:1, v/v), and then precipitated from CH_2Cl_2 /MeOH, yielding a pale yellow powder in 16 % yield. The low yield obtained in this case may be due to some decomposition of the starting material at the high temperature required, as evidenced by the formation of black insoluble material in the reaction flask. Should this synthesis be repeated in future, it may be necessary to shorten the reaction time considerably.



Scheme 2.10: Diels-Alder cycloaddition generating **9**. (i) Ph_2CO , $325\text{ }^\circ\text{C}$, 16%.

Several techniques were employed to characterise **9**, including ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The ^1H NMR spectrum of **9** is displayed in Fig. 2.25. In a similar fashion to the previous pyrimidyl-substituted compounds, the proton between the two N atoms of the pyrimidyl ring (H_1) appears furthest downfield. The ‘inner’ proton of the phenanthrene core

(H₁₀) appears next, deshielded due to its proximity to the electron-withdrawing Br atom. The remaining pyrimidyl proton H₂ integrates for the expected 4 H atoms. The ¹³C{¹H} NMR spectrum of **9** is displayed in Fig. 2.26. Further elucidation of the ¹H spectrum was achieved through the use of TOCSY and ¹H-¹³C HSQC experiments (Fig. 2.27), identifying the protons of the phenanthrene unit and those of the unsubstituted phenyl rings, many of which overlapped, resulting in the multiplet signals observed.

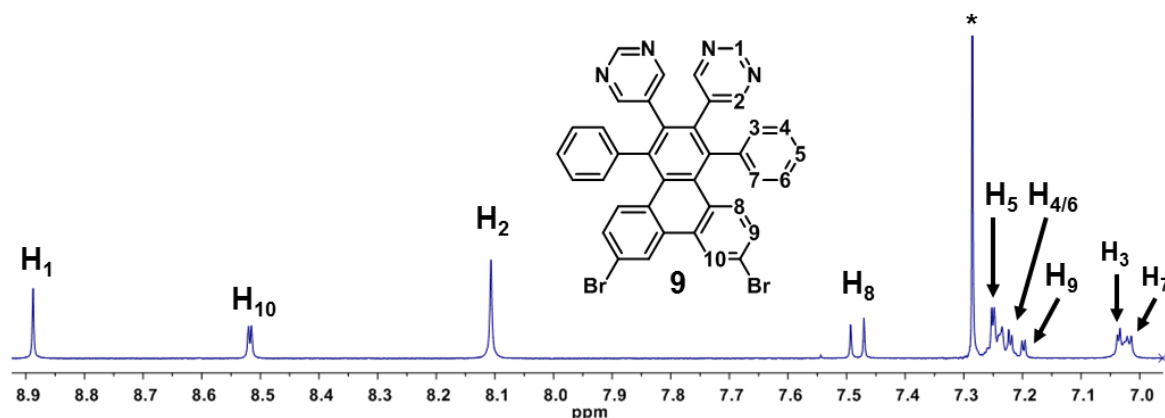


Figure 2.25: The ¹H NMR spectrum of **9** and (inset) the numbering scheme employed (400 MHz, CDCl₃, RT). * denotes CHCl₃ residual solvent peak.

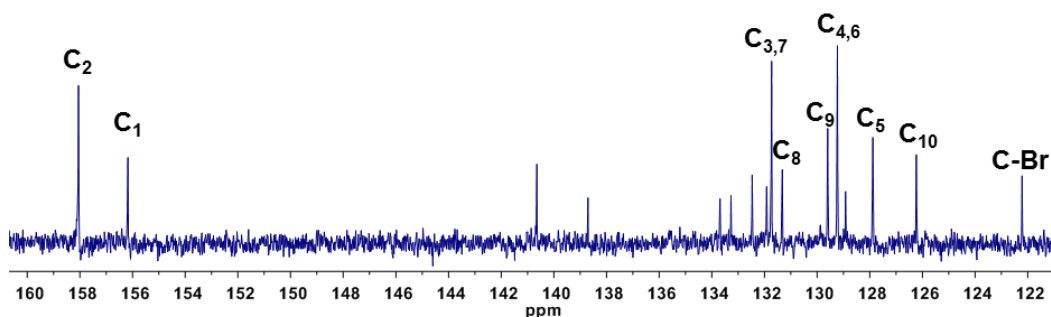


Figure 2.26: The ¹³C NMR of **9** (proton-decoupled), with peaks assigned to their corresponding proton number. Unlabelled peaks indicate quaternary carbons (101 MHz, CDCl₃, RT).

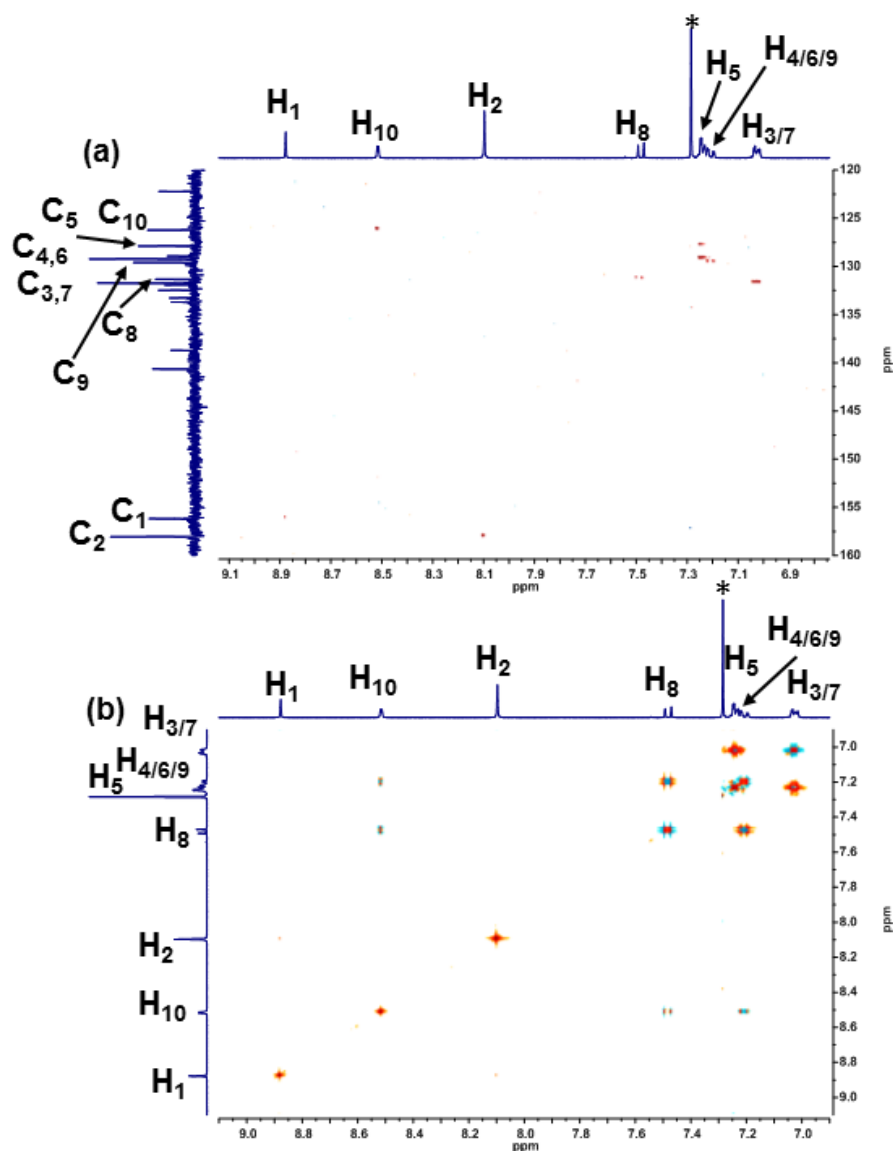


Figure 2.27: (a) HSQC and (b) TOCSY experiments used to further elucidate the NMR behaviour of **9** (400 MHz, CDCl_3 , RT). * denotes residual CHCl_3 solvent.

Further confirmation of the identity of this compound was obtained by HRMS, which displayed a peak at $m/z = 693.0301$, with a calculated value of $m/z = 693.0284$, corresponding to the protonated molecule $[\text{C}_{38}\text{H}_{23}\text{Br}_2\text{N}_4]^+$. The HRMS results for **5**, **6**, and **9** are summarised in Table 2.1.

Table 2.1: HRMS results for compounds **5**, **6** (MALDI-TOF), and **9** (ESI-MS).

Compound	Formula	Calculated m/z	Found m/z	Molecular Ion
5	$[\text{C}_{38}\text{H}_{25}\text{N}_4\text{Br}_2]^+$	695.0446	695.0475	$[\text{M}+\text{H}]^+$
6	$[\text{C}_{38}\text{H}_{19}\text{N}_4\text{Br}_2]^+$	688.9976	688.9987	$[\text{M}+\text{H}]^+$
9	$[\text{C}_{38}\text{H}_{23}\text{Br}_2\text{N}_4]^+$	693.0284	693.0301	$[\text{M}+\text{H}]^+$

Although it was possible to grow crystals of **9**, they did not diffract very well and did not generate high quality data. It was, however, possible to obtain the unit cell (Fig. 2.28) which was solved by Dr. Brendan Twamley, and which contains three molecules of **9**, along with several coordinated solvent molecules (four MeOH molecules and two H₂O molecules). Crystallographic data is provided in the Annex.

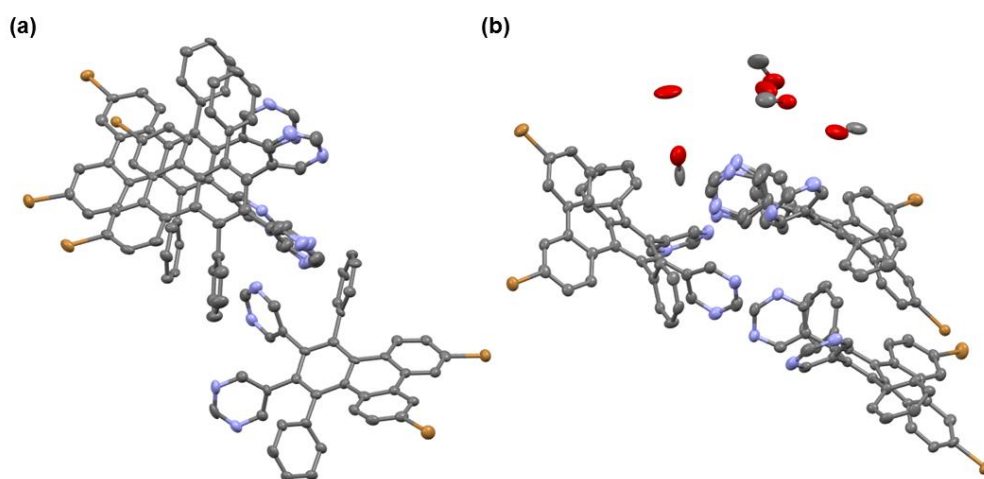


Figure 2.28: (a) Asymmetric unit of **9**, with thermal ellipsoids shown at 50 % probability. Residual solvent atoms omitted for clarity. (b) The fully occupied asymmetric unit with residual MeOH and H₂O atoms. In both (a) and (b) hydrogen atoms are omitted for clarity, and thermal ellipsoids are displayed at 50 % probability. N atoms are displayed in purple and bromine in brown.

2.3 Preliminary Investigations into Thermal Stability

In order to establish whether the precursors were suitable for on-surface studies, it was necessary to confirm their thermal stability. This was carried out by thermal gravimetric analysis (TGA). As has been discussed previously, polymerisation processes on reactive

metal substrates (*e.g.* Au(111)) often take place in the region of 200 °C, and subsequent cyclodehydrogenation steps are often observed in the region of 400 °C. These temperatures often vary depending on substrate reactivity. Therefore **5** and **6** were analysed to determine their thermal stability at these temperatures. The thermal stability was recorded under nitrogen, to prevent oxidation processes at higher temperatures, with a heating rate of 10 °C per minute, after an initial isothermal step of heating to 120 °C for 1 hour (in order to remove any residual solvents). At first glance, there is a dramatic difference between the polyphenylene **5** and the partially-fused **6** (Figs. 2.29 and 2.30, respectively). This is not unexpected, as the thermal stability of such systems is often increased with increasing degrees of planarisation. The extrapolated onset temperature (T_o) of degradation of **5** is approximately 345 °C, which may be compared with the onset temperature of approximately 434 °C for its partially cyclised analogue **6**. It is noted that compound **6** undergoes a slow onset of decomposition before this sudden change. These findings suggest that **6** is a more suitable candidate for on-surface processes. The onset of degradation of compound **5** is below 400 °C, the usual temperature required for cyclodehydrogenation. This may become an issue if cyclodehydrogenation cannot be achieved at lower temperatures.

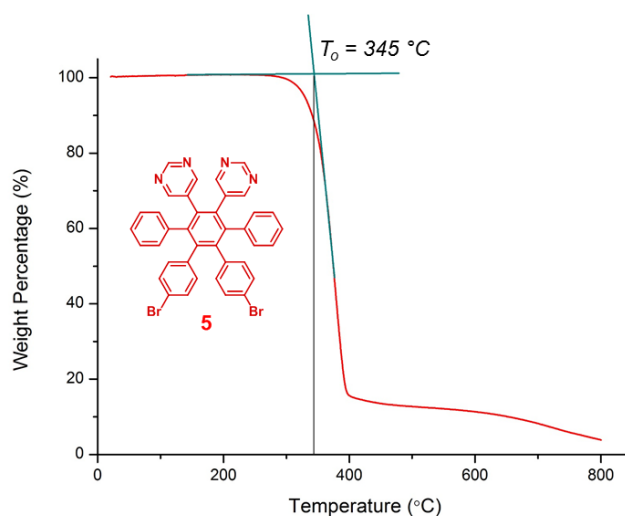


Figure 2.29: Thermal gravimetric analysis of **5**. Recorded whilst heating at 10 °C per minute under N_2 .

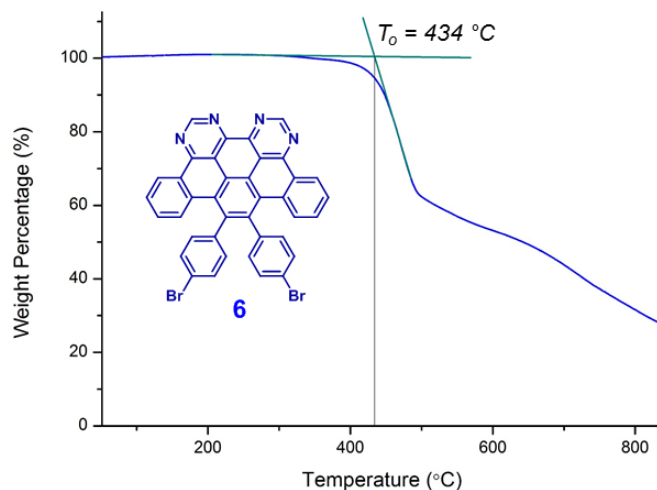


Figure 2.30: Thermal gravimetric analysis of **6**. Recorded whilst heating at 10 °C per minute under N_2 .

It is noted in Fig. 2.30 that the TGA curve of **6** does not fall sharply after the initial onset of thermal degradation, suggesting that there are partially oxidised products of decomposition which display high thermal stability. The thermal stability of **9** was characterised in the same manner as for **5** and **6** (Fig. 2.31). Since **9** displays a partially-fused moiety, it would be expected that it would display a higher degree of thermal stability than the entirely unfused polyphenylene **5**.

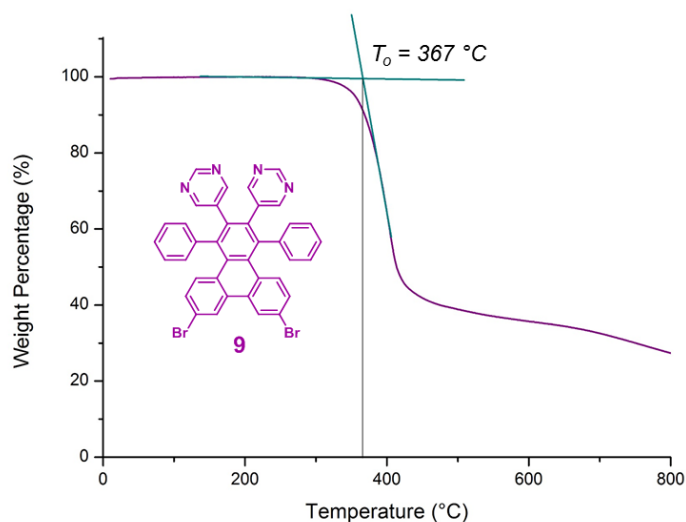


Fig. 2.31: TGA plot of **9**. Recorded under N_2 , with heating at a rate of 10 °C per minute.

Thermal gravimetric analysis of **9** reveals that it is indeed more stable than **5**, but falls short of the thermal stability of the more planar **6**, which is not unexpected. From the TGA curve, the onset temperature (T_o) of degradation can be extrapolated as 367 °C. As the temperature

required for cyclodehydrogenation on metal substrates is usually 400 °C, the stability of **9** at high substrate temperatures may be an issue. However, given that this compound displays a high similarity in terms of its structure to triphenylene molecules already reported to successfully form GNRs at temperatures of approx. 400 °C, it is anticipated that **9** may also be suitably stable once deposited on the substrate under UHV. Following these initial studies on thermal stability, the on-surface reactivities of **5**, **6**, and **9** were investigated.

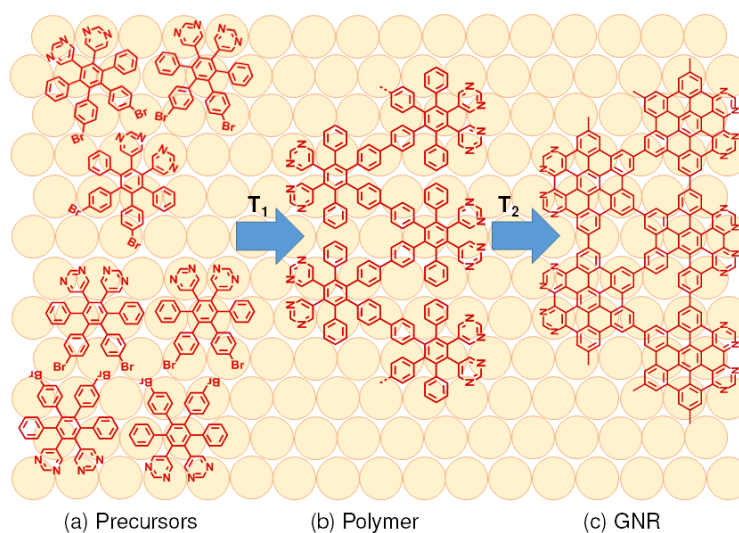
2.4 On-Surface Behaviour of Precursors **5**, **6** and **9**

2.4.1 Investigation of the On-Surface Behaviour of **5**

As previously discussed, the on-surface behaviour of phenanthrene based systems have been extensively investigated on reactive metal surfaces, particularly Au(111). Halogen functionalised hexaphenylbenzene-type or hexabenzocoronene-type systems, such as **5** and **6** have received less attention in the literature, and in particular there is a scarcity of these systems which are N-substituted. It is the intention of this work to investigate their reactivity and potential for generating extended aromatic systems such as GNRs. Given the ease with which a hexaphenylbenzene-type system may be functionalised (*e.g.* with halogen functionalities, or with heteroatom introduction) they present intriguing candidates for on-surface studies and their potential to generate extended on-surface frameworks. The design of these precursors would, if polymerisation on the surface was successful, generate N-GNRs with a regular porous structure.

The on-surface measurements described here were carried out with the kind collaboration of Prof. Silvio DeCurtins and Dr. Shi-Xia Liu at the University of Bern in Switzerland. Au(111) was selected as the most suitable substrate. As noted by Basagni *et al.* it is regarded as the best compromise between mobility of the precursor, catalytic activity and weak absorption of halogen atoms.^{92, 93} The other common substrates Cu(111) and Ag(111), due to their higher catalytic activity, often give access to polymerisation and cyclodehydrogenation at lower temperatures. However, they often also generate organometallic networks, hindering molecular diffusion and therefore hindering GNR growth (as noted by Han *et al.* and mentioned in the introduction).⁹⁴ Given the literature work carried out on similar phenanthrene-based systems, it is instructive to attempt to predict the potential outcome of the series of reactions to be carried out on the surface. A general scheme depicting the proposed behaviour of **5** on Au(111) is shown in Scheme 2.11. Firstly,

the monomers are expected to either form a close-packed arrangement or a random arrangement on the surface. With heating to approximately 200 °C, it is hoped that dehalogenation will be induced, resulting in covalent C-C bond formation. A further increase in temperature (to ~400 °C) is expected to result in cyclodehydrogenation of any polymeric structures formed. There have been several reports of lateral GNR fusion in the literature, *i.e.* where GNRs formed through on-surface processes may form C-C bonds to the GNRs either side, thus forming much wider structures.^{95, 96} In this way, annealing the substrate to higher temperatures could lead to extended N-containing frameworks, which could be viewed as highly N-substituted graphene. A depiction of how this might occur is shown in Fig. 2.32.



Scheme 2.11: A general schematic for the expected behaviour of 5 post-deposition. (a) The monomers may adopt a random arrangement or a close-packed arrangement. (b) Annealing resulting in dehalogenation and C-C bond formation. (c) Cyclodehydrogenation.

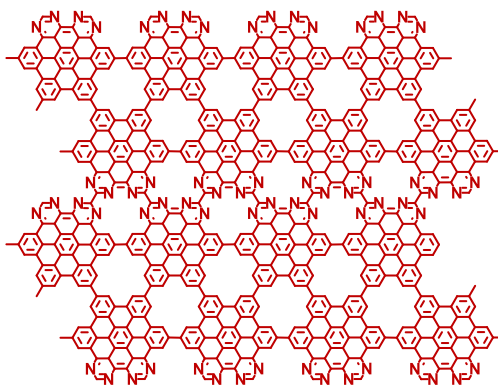


Figure 2.32: Annealing the substrate to higher temperatures may result in dehydrogenative edge fusion, leading to porous, N-containing graphene.

Compound **5** was deposited on Au(111) by thermal evaporation from a quartz crucible under UHV. The substrate was held at RT during the deposition process. The substrate was then scanned by STM to image the resulting on-surface behaviour. The monomer is observed to have formed a close-packed, self-assembly type structure on the surface, in a zigzag pattern along the herringbone reconstruction of the Au(111) surface (Fig. 2.33). The closeness of the packing makes it quite difficult to distinguish individual molecules. In order to initiate dehalogenation and subsequent polymerisation, the substrate was then heated to 200 °C for 20 minutes. Observation of the STM images obtained after the annealing process reveal that polymerisation appears not to have taken place, and that the close-packed molecular islands visible at RT still appear present (Fig. 2.34). There are some small white dots which have appeared, which may be detached bromine atoms, although this is unconfirmed.

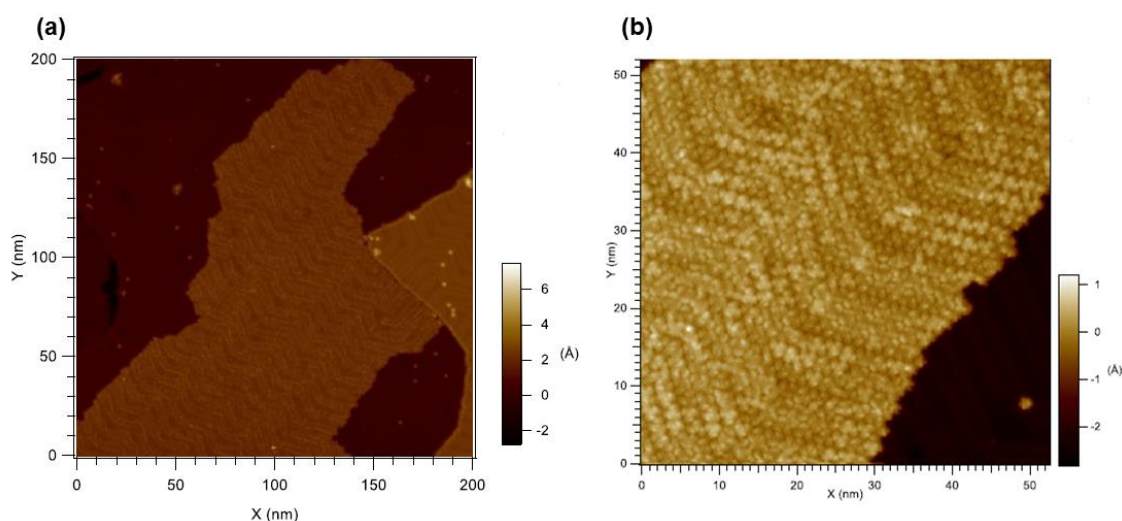


Figure 2.33: (a) STM image of **5** deposited on an Au(111) substrate held at RT. (b) Magnified view of close-packed structure formed by **5**. Scale bar indicates distance from STM tip to surface of substrate in Angstroms (Å).

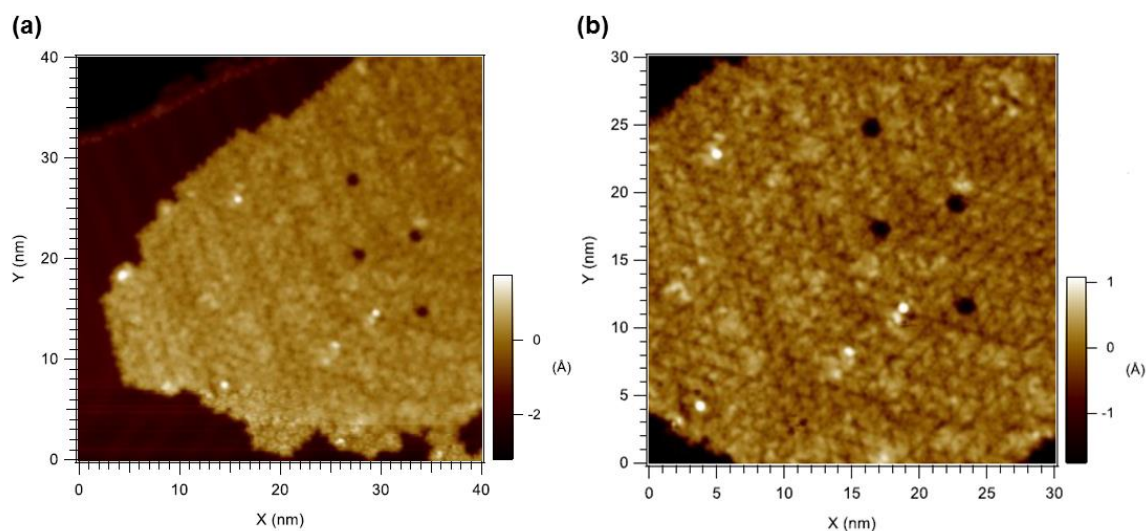


Figure 2.34: (a) STM image of **5** on Au(111) substrate post-annealing to 200 °C and (b) a closer view of the self-assembly structures observed. Scale bar indicates distance from STM tip to surface of substrate in Angstroms (Å).

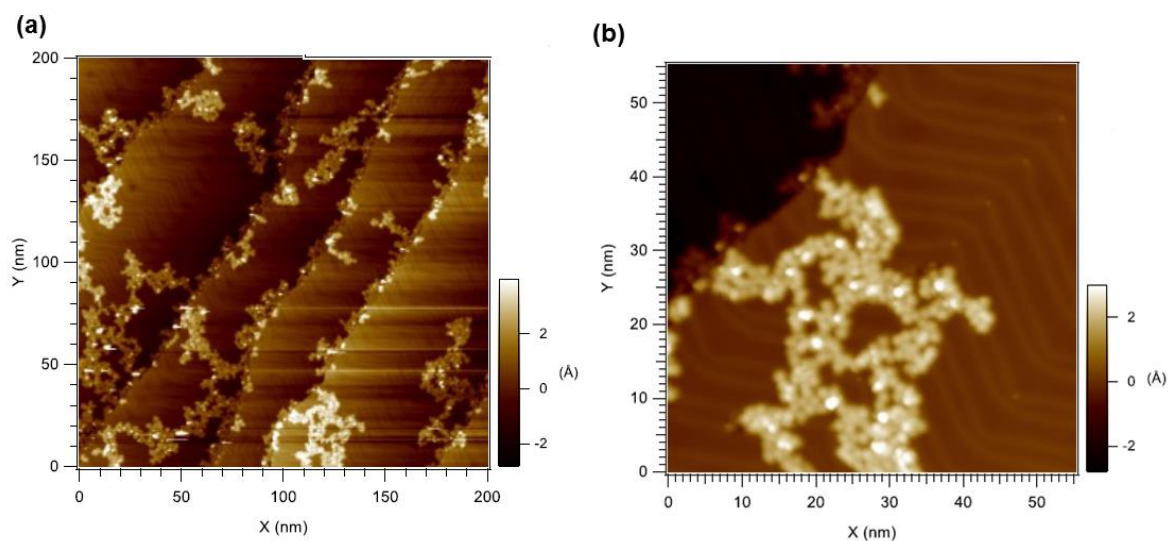


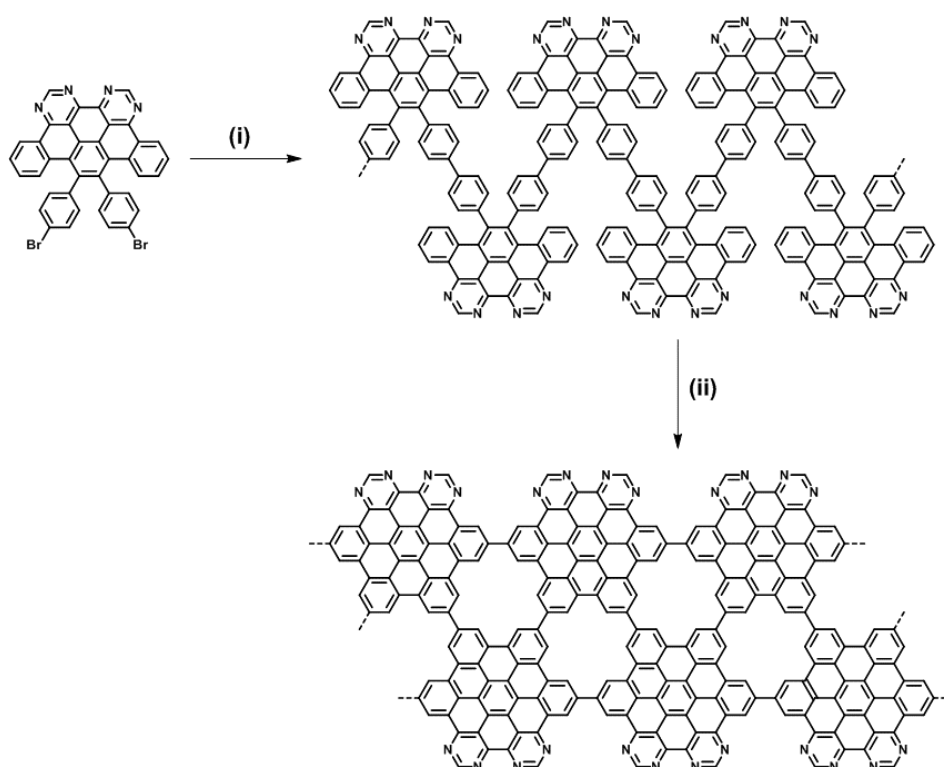
Figure 2.35: (a) and (b) STM images of on-surface frameworks observed after annealing **5** on Au(111) to 350 °C. Scale bar indicates distance from STM tip to surface of substrate in Angstroms (Å).

Further annealing to 350 °C provided STM images of molecular clusters. The densely close-packed arrangement is no longer in evidence, and has been replaced with highly disordered ribbon-like structures which appear to consist of small clusters (Fig. 2.35). Therefore **5** appears unable to form linear polymeric chains, and there does not appear to even be any evidence of smaller polymeric structures *i.e.* dimers or trimers. It may be the

case that the close-packing interaction of **5** was too strong to allow efficient diffusion across the substrate, thus preventing any chance of covalent bond formation. It was therefore of interest to see whether the more planar **6** would be able to diffuse more easily across the surface and form polymeric structures.

2.4.2 Investigation of the On-Surface Behaviour of **6**

The partially-fused **6** was chosen as a candidate for on-surface studies, in order to study whether further cyclodehydrogenation would occur on the surface, and its propensity to form linear, regular networks or extended systems on a surface. Given that the system exhibited a pre-fused moiety prior to on-surface cyclodehydrogenation, it was posited that this system presented a possible means of controlling the degree of aromatisation of the species resulting from on-surface polymerisation; *i.e.* that it may be possible to generate systems displaying partial fusion, if the on-surface cyclodehydrogenation step is omitted, and also completely fused systems (Scheme 2.12).



Scheme 2.12: The desired outcome of the on-surface polymerisation and intramolecular cyclodehydrogenation of **6** on Au(111) after (i) annealing to the temperature required for polymerisation and (ii) further annealing to induce cyclodehydrogenation.

Compound **6** was deposited on Au(111) and its behaviour was investigated by STM. The first step was to deposit the precursor, **6** at room temperature onto the substrate. This was achieved by thermal evaporation of the precursor, under UHV, to the Au(111) substrate, which is initially held at room temperature. The initial self-assembly structures may then be examined by STM. With heating of the substrate, usually to between 150-200 °C, in order to induce the required dehalogenation, the resulting structures may again be scanned with the STM. Further heating of the substrate, usually in the region of 350-400 °C, is expected to induce intramolecular cyclodehydrogenation. In the case of **6**, the deposition at RT is expected to result in closely packed self-assembly structures, similar to those observed in the case of **5**. With heating of the substrate, it is expected that the C-Br bonds will be cleaved, and covalent bond formation will occur, resulting in the formation of extended linear structures, which are partially fused. Heating to the higher temperatures required for cyclodehydrogenation is then hoped to result in complete closure of the remaining unfused phenyl rings of **6**. The desired outcome of the two processes to (i) to polymerise and (ii) to induce intramolecular cyclodehydrogenation are summarised in Scheme 2.11, therefore potentially generating the same GNR as was hoped for precursor **5**.

Upon deposition of **6** on to the Au(111) surface at RT, it was observed by STM that close packed islands were observed on the surface, with the majority of molecules arranging themselves into dimers. These STM scans are displayed in Fig. 2.36 below, with a representative dimer highlighted in red.

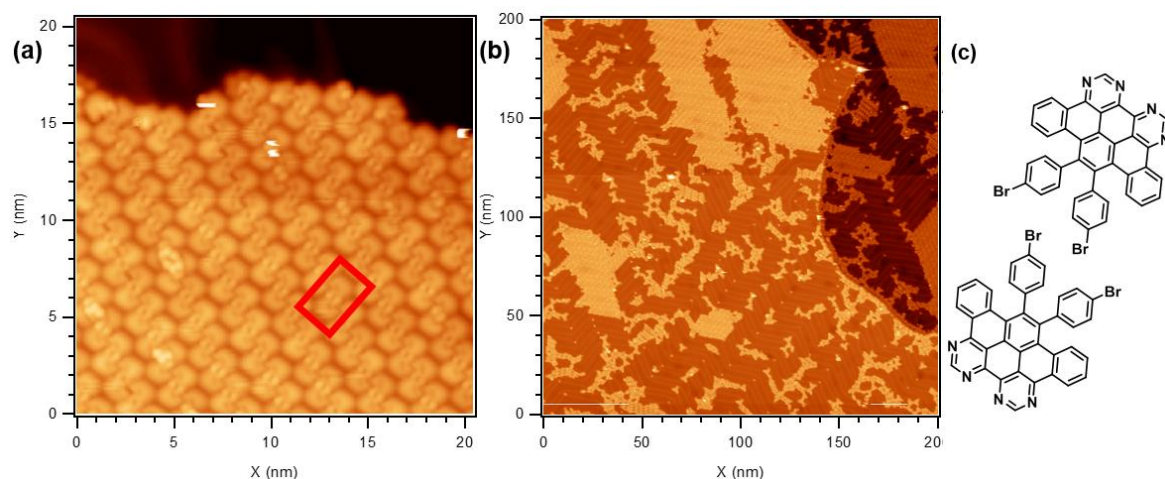


Figure 2.36: (a) An STM image of the RT formation of dimers on the Au(111) surface, with a dimer highlighted in red, (b) an STM overview displaying the close-packed islands and (c) a graphical illustration of the orientation of the dimers observed.

With subsequent heating of the Au(111) substrate to 200 °C, with a view to dehalogenation and consequent polymerisation, it was observed that covalent bonds appear to have been formed, as was anticipated. However, it appears that in place of linear polymeric species required for the formation of GNRs, dimeric and trimeric species have been linked by covalent bonds, as evidenced by the close-packed molecular islands which were obtained. The STM images of these are displayed in Fig. 2.37, where (a) gives an overview of the substrate, demonstrating the molecular islands formed and where (b) and (c) illustrate the dimers and trimers. It is intriguing to note that there appears to be no evidence of any linear polymeric species – only the dimeric and trimeric species.

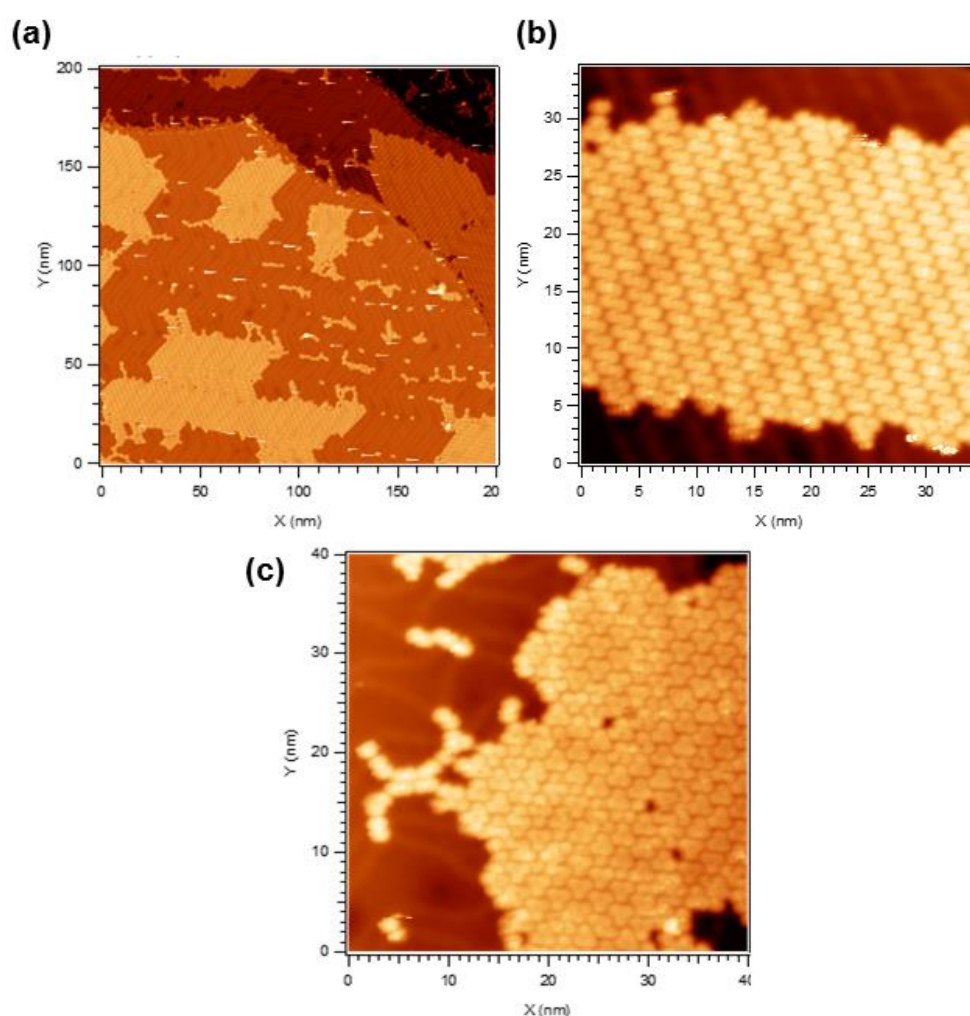


Figure 2.37: STM images of **6** after annealing to 200 °C. (a) An overview of the substrate, (b) close-packed covalently linked dimers and (c) close-packed covalently linked trimers.

It has been proposed by Zhang *et al.* that at high surface concentrations of the precursor, the formation of dimers and trimers is favoured, rather than the formation of linear species.⁷⁴ This is thought to be a result of the limited space available for the monomers at

high (monolayer) concentrations, which inhibits their ability to arrange in the correct orientations for polymerisation. It can be therefore concluded that for the efficient formation of larger GNR-type structures, it is crucial that sub-monolayer coverage is maintained on the surface. Whilst the formation of GNRs or elongated structures was not observed for **6**, the formation of these dimers and trimers remains intriguing, as these highly N-substituted systems remain largely absent from the literature, and their solution synthesis would be expected to be highly challenging.

In order to investigate the on-surface intramolecular cyclodehydrogenation behaviour of **6**, the substrate was then heated further, to 300 °C, which was observed to be sufficient to induce the process. The resulting structures on the Au(111) surface are displayed in Fig. 2.38.

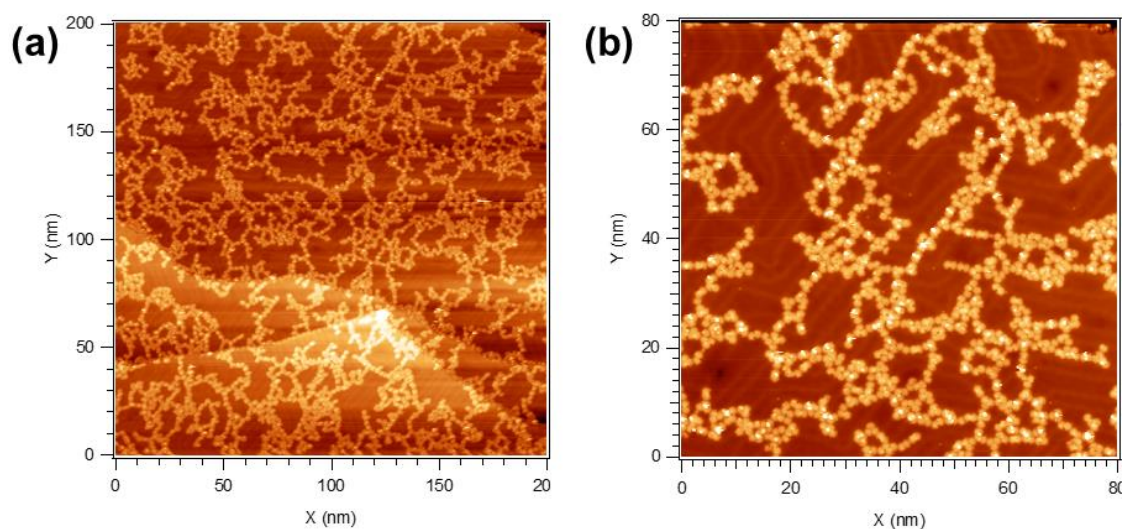


Figure 2.38: (a) An overview of the Au(111) surface after annealing to 300 °C and (b) a further magnified view of the surface.

The close packed islands of dimers and trimers are no longer observed after the annealing process, being replaced by ribbon-like structures arranged in a more spaced and irregular manner. Again, GNR-type structures are not evident, with the ribbon-like arrangements being composed of cyclodehydrogenated dimers and trimers. In order to ascertain the extent of the cyclodehydrogenation process and help confirm further the identity of the different species on the surface, atomic force microscopy (AFM) was employed to image the topography of the surface, due to its higher resolution. The AFM images reveal three distinct nanostructures: (i) dimers that are linked *via* a single C-C bond (Fig. 2.39 (a)), (ii) dimers which are linked by three C-C bonds (i.e. they are fully

cyclodehydrogenated) (Fig. 2.39 (b)) and (iii) trimeric species, where each monomer is linked to another by one C-C bond each (Fig. 2.40).

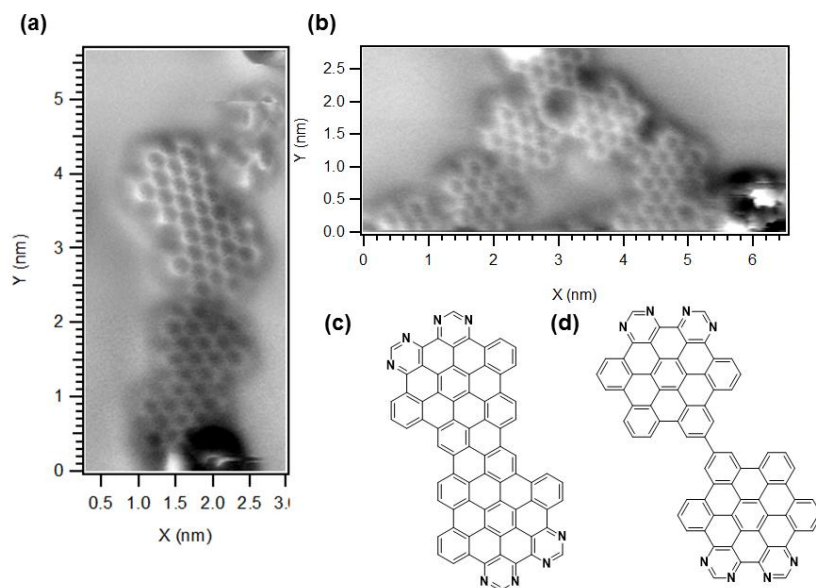


Figure 2.39: (a) AFM image of a fully cyclodehydrogenated dimer and (b) AFM image of a partially cyclodehydrogenated dimer. (c) and (d) depict proposed structures of (a) and (b) respectively.

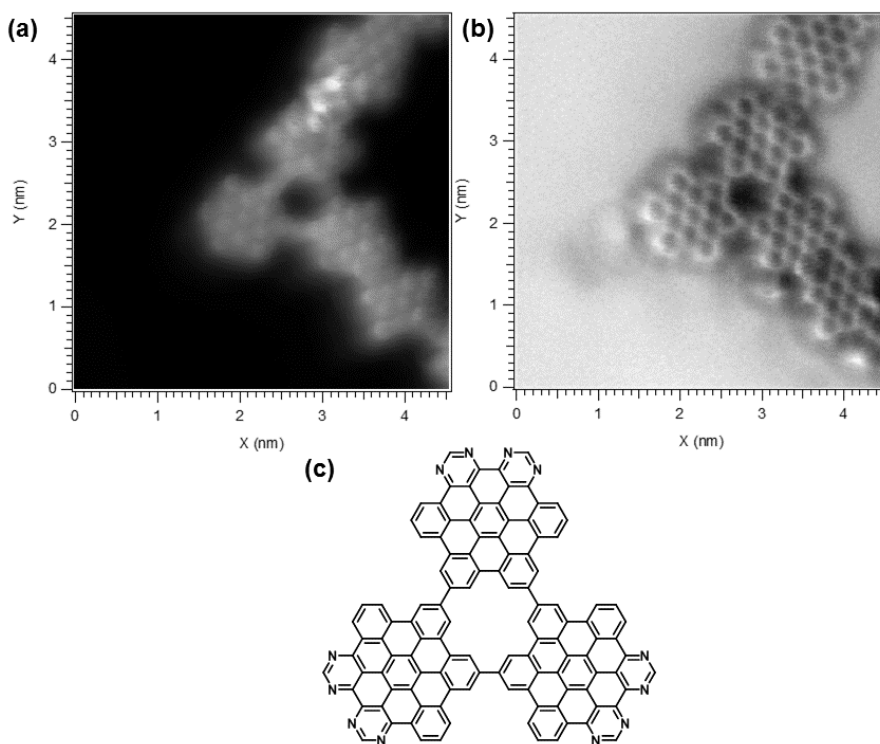


Figure 2.40: (a) and (b) depict a trimeric arrangement formed by C-C bonds, which is fully cyclodehydrogenated. (c) The proposed molecular structure of this trimeric arrangement.

Whilst the formation of extended linear structures has not been observed with **6**, intriguing dimeric and trimeric species have been formed. As the solution synthesis of these would be highly challenging, they are interesting molecules in themselves, particularly since they display a high degree of N-substitution. If a substrate were to be densely functionalised with these systems, they potentially would be of interest for catalytic applications, such as in the ORR, as discussed earlier. The formation of dimers, trimers may be due to excessively high levels of monomers on the substrate, thus hindering their diffusion and ability to create linear structures.⁷⁴ This may have been a contributing factor to the lack of success observed in this regard. Attention was then turned to precursor **9**, which bearing most resemblance to previously successful literature compounds, was hoped to form GNR-type structures.

2.4.3 Investigating the On-Surface Behaviour of **9**

The precursor **9** was deposited on Au(111) in the same manner as those previously investigated, and the same procedures were carried out, namely annealing to the temperature required for C-C bond formation and then further annealing to induce intramolecular cyclodehydrogenation, with each step being investigated by STM. The room temperature self-assembly arrangement is displayed in Fig. 2.41, where (a) provides an overview of the molecular islands and clusters formed post deposition, and (b) displays these from a more magnified perspective. It may be assumed at this point the C-Br bonds remain intact, as has been observed for the two previous systems described and in numerous literature examples.

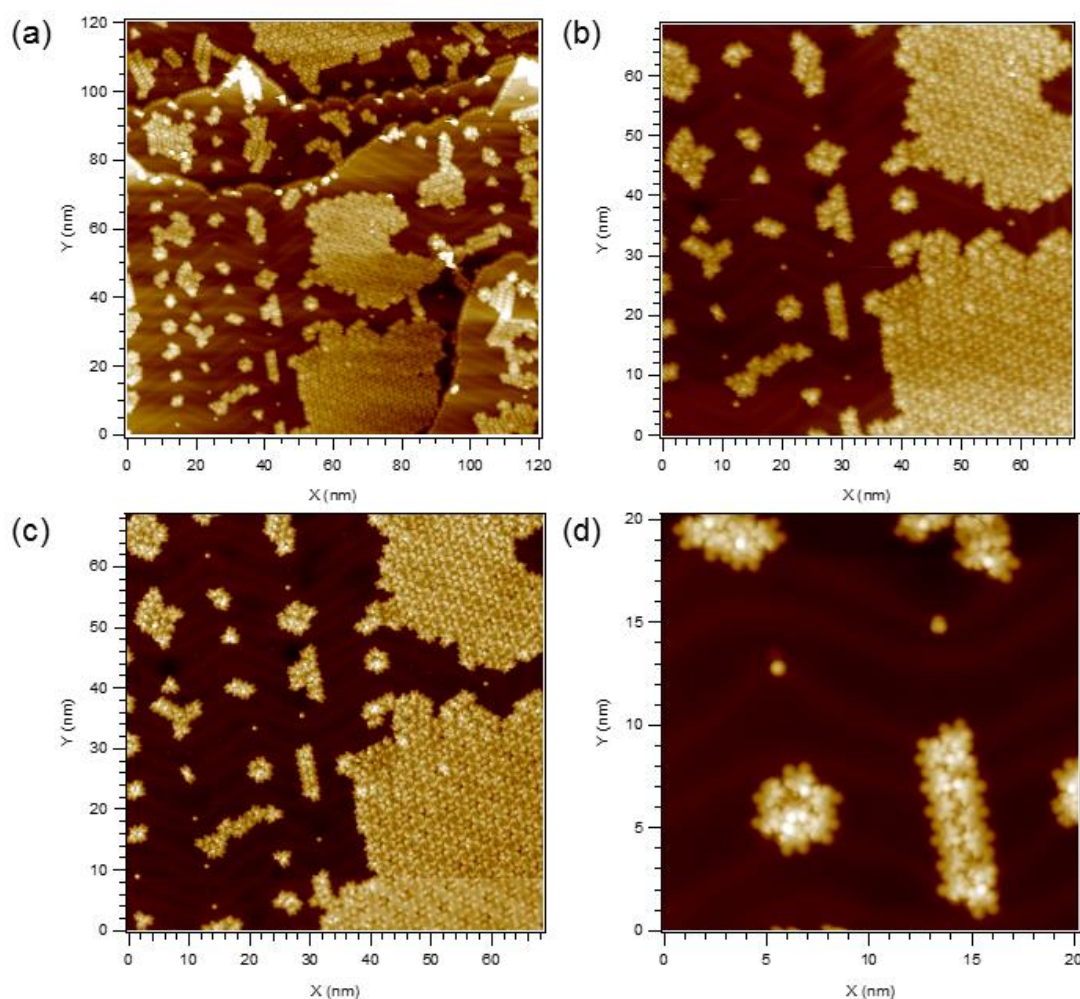


Figure 2.41: (a) an overview of the molecular islands and clusters formed at RT by precursor **9** and (b) a magnified view, (c) and (d) provide further magnified views, with (d) clearly showing the molecular clusters obtained.

Thermal annealing of the substrate to 200 °C for 15 minutes led to the structures displayed in Fig. 2.42. It may be observed that the majority of the structures on the surface remain as mostly irregular islands, but closer inspection reveals that there are a number of polymeric GNR-type structures of the type which were proposed as being possible to form. It is interesting to note the packing arrangement the polymers appear to have adopted, where they line up in a slightly staggered arrangement along the edge of each adjacent GNR. This is reminiscent of the earlier discussed N-H interaction between adjacent GNRs as proposed by Vo *et al.* which led to the linear arrangement of their chevron-type GNRs (see Fig. 2.8).⁵² The level of resolution obtained in these images makes it difficult to ascertain whether any degree of cyclodehydrogenation has yet occurred.

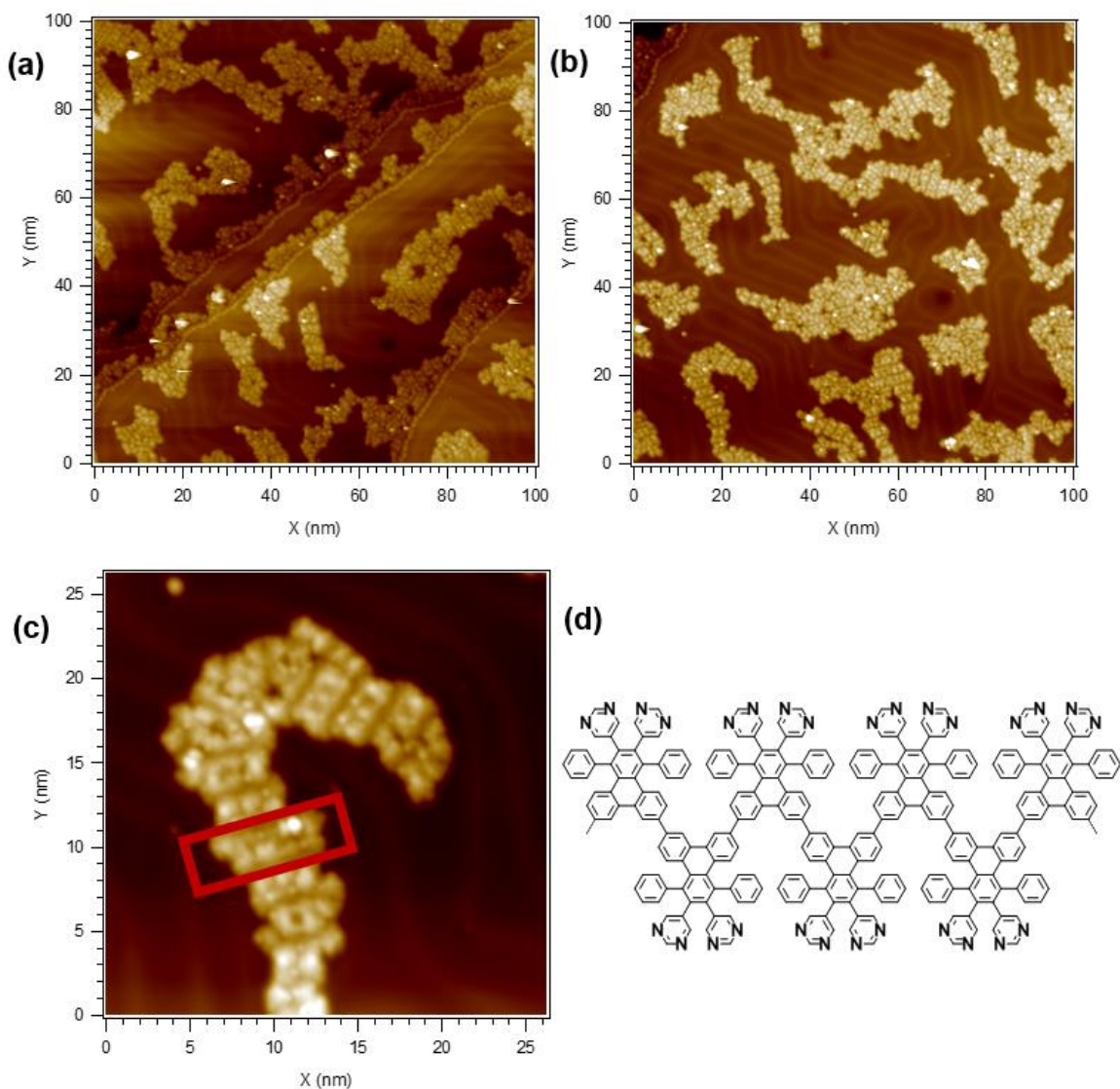


Figure 2.42: (a) and (b) display overviews of the Au(111) substrate following annealing to 200 °C. (c) A magnified view of several polymeric structures, with one unit highlighted in red and (d) the proposed type of structure corresponding to the area highlighted in red.

Further thermal annealing to 350 °C for 15 minutes led to another change in the observed structures on the surface, due to the onset of intramolecular cyclodehydrogenation. As previously witnessed, the majority of the structures on the surface are clusters which are covalently bonded and arranged in very irregular fashions. However, the polymeric structures observed in Figure 2.42 appear to have now become cyclodehydrogenated (Fig. 2.43), resulting in the formation of short GNR-type structures, confirming that the on-surface synthesis of these architectures is possible, although unpredictable and perhaps a little low-yielding under this specific set of conditions. Again, it is interesting to note the apparent N-

H interaction between adjacent GNRs, resulting in the stacked arrangement most evident in Fig. 2.43 (c).

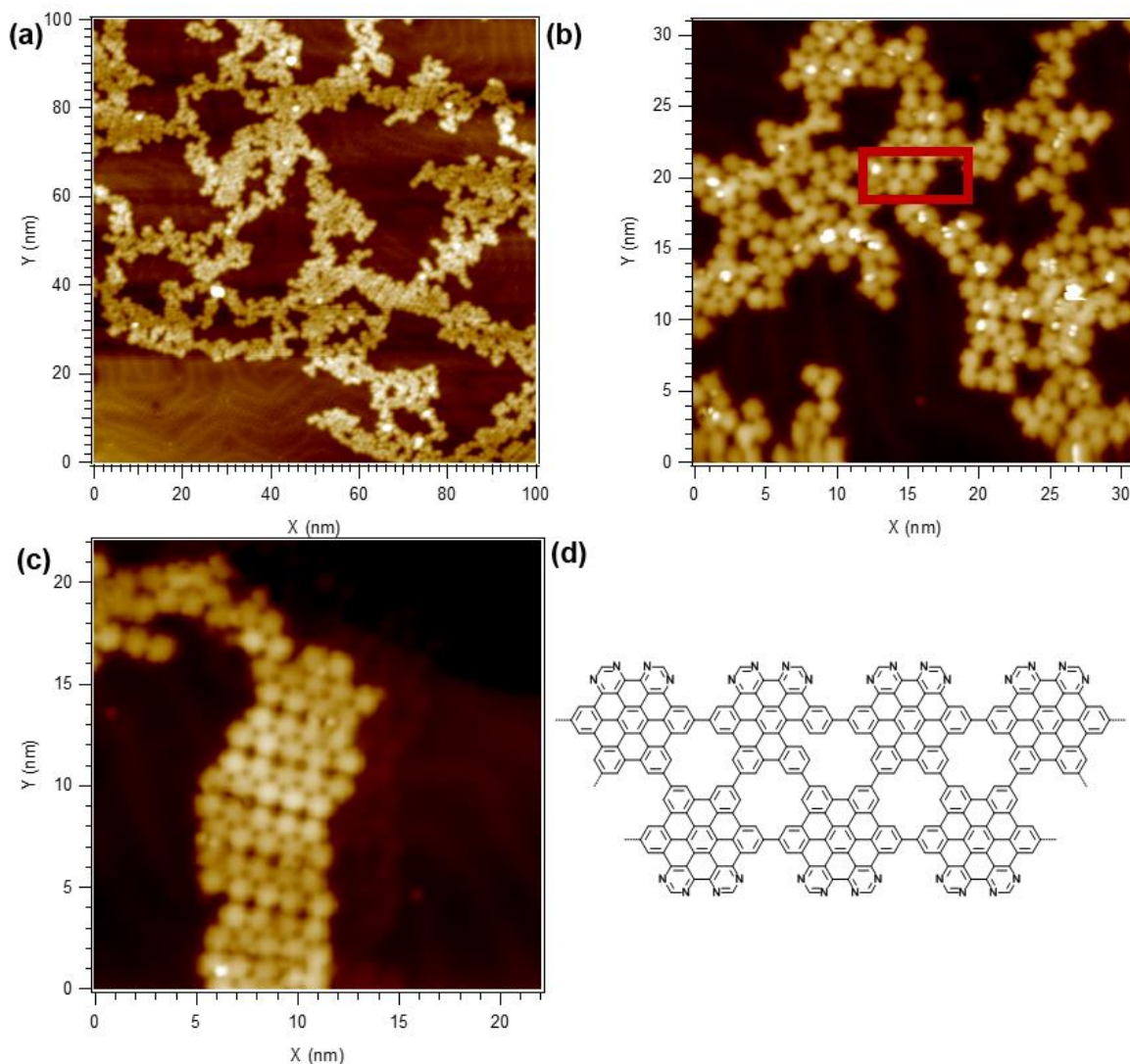


Figure 2.43: (a) **9** on the Au(111) surface after annealing to 350 °C and (b) the short polymeric chains observed in some areas (highlighted in red) with (c) providing a representation of the proposed structure highlighted in (b).

Since this precursor formed GNRs, unlike **5** and **6**, it was decided to carry on to the next step – to investigate whether it was possible for the GNRs to link *via* edge fusion. The substrate was annealed at 450 °C for 15 minutes, and the resulting STM scans of the substrate after this process are displayed in Fig. 2.44. Unfortunately it appears that no inter-ribbon coupling has occurred – the GNRs and other structures do not appear to have changed in their appearance, and spaces are still evident between each GNR length. Therefore although this precursor is able to produce short GNRs, it does not appear a viable route towards porous

N-containing graphene. Whether the choice of substrate is a factor here is as yet unclear. As previously discussed, it would be anticipated that if the more reactive copper substrate Cu(111) had been employed, dehalogenation would have occurred more readily, but the various polymerisation and cyclodehydrogenation processes may have overlapped, thus hindering GNR formation. If Ag(111) had been employed, surface diffusion of the radical species may have been limited, as this substrate often results in organometallic intermediates.

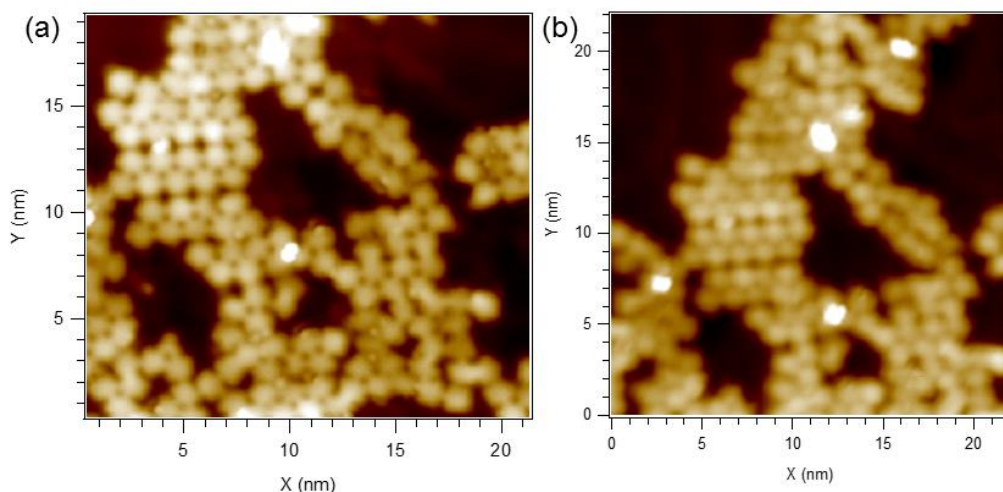


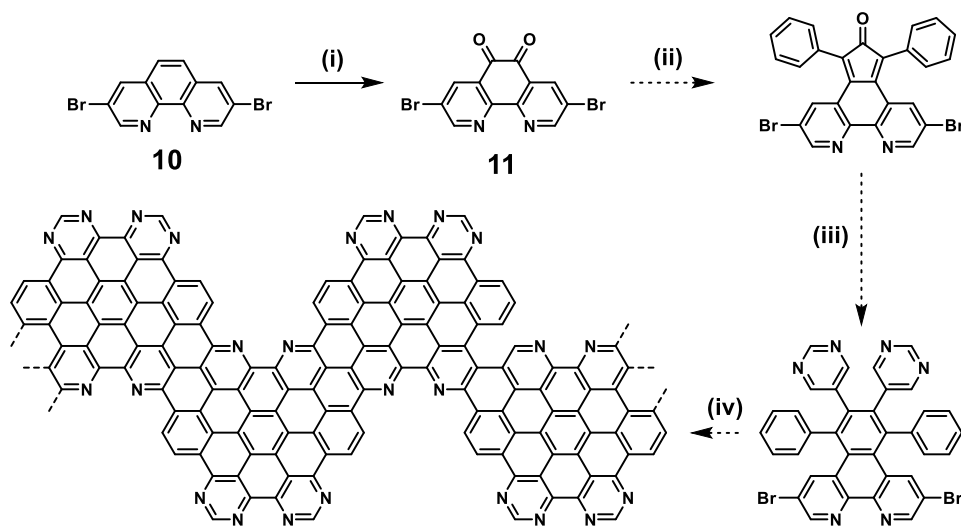
Figure 2.44: (a) and (b) STM images of GNRs on Au(111) of **9** post-annealing to 450 °C. No inter-ribbon coupling is observed.

2.5 Ongoing Synthesis and Future Work

The intriguing dimers and trimers exhibited by **6** are currently the focus of intensive research in the Draper group, directed towards their generation by the coupling of **6** through solution-based methods. This work is at the early stages, and although such extended PAH-based systems are expected to be highly insoluble, it would provide a useful form of comparison to the surface-based approach, and enable their properties to be further characterised (*e.g.* by NMR, HRMS, thermal stability *etc.*). If such polymeric compounds could be produced more reliably in solution and then subsequently deposited onto substrates, this would provide an alternative route towards these systems.

Extension of this work towards more highly N-substituted GNRs is ongoing, and preliminary work towards this end has been undertaken by the author. If a phenanthroline unit could be incorporated in place of the phenanthrene unit of **9**, it may then be possible to

produce a GNR with unprecedented levels of N-substitution. This system would bear close resemblance to the phenanthrene-based precursors employed by Cai *et al.* and also Vo *et al.*,^{52, 75} but would also include two nitrogen atoms in the bay area of the phenanthroline unit. Synthesis would begin in a similar manner as for compounds **5**, **6** and **9**, *i.e.* a Knoevenagel condensation with a monoketone and a brominated phenanthrene-dione, followed by a Diels-Alder cycloaddition with the same dipyrimidyl ligand as used previously to generate a precursor with pyrimidine and phen-type substitution. (Scheme 2.13).



Scheme 2.13: The intended synthetic route towards novel N-GNRs. (i) H_2SO_4 , HNO_3 , KBr , reflux, 22 %. (ii) Knoevenagel condensation. (iii) Diels-Alder cycloaddition with dipyrimidyl acetylene. (iv) Deposition and growth under UHV on a metal substrate.

Synthetic efforts towards this precursor have so far not been successful. Although the 3,8-dibromo-1,10-phenanthroline-5,6-dione product **11** could be easily derived from 1,10-phenanthroline, the subsequent step to generate the cyclopentadienone has not yet yielded any success. The issue here may be solubility, as is common with many phenanthroline-based systems. If the conditions for the Knoevenagel could be optimised, this would be an enormous step forward for N-GNRs.

Efforts to prepare and characterise other precursors are ongoing, whose on-surface reactivities has not yet been investigated. These compounds would display intriguing properties, not for GNR formation, but for extended graphene-like frameworks with very high levels of N-substitution. In a similar manner to the porous N-substituted graphene it was thought possible to generate from **5** via edge fusion of GNRs, these compounds could generate similar porous frameworks. The dicobalt octacarbonyl-catalysed cyclotrimerisation

of functionalised alkynes permits the creation of hexaphenylbenzenes with a degree of functionalisation difficult to achieve with other methods. As precursors for cyclotrimerisation, compounds **12** and **13** were prepared with Sonogashira reactions according to a slightly modified literature procedure (Fig. 2.45).⁹⁷

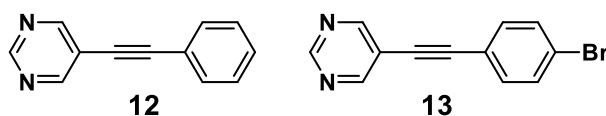
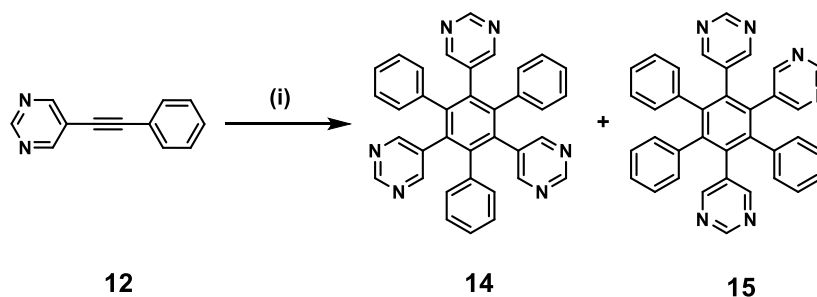


Figure 2.45: Two functionalised alkynes intended for cyclotrimerisation.

The trimerisation of **12** yielded two pyrimidyl-substituted isomers, **14** and **15** (Scheme 2.14). The synthesis of these compounds had been undertaken previously within the group as a means of investigating the pyrimidyl to phenyl ring closure observed with elemental bromine.⁹⁰ Compound **14** is of most interest due to its symmetrical nature, and therefore more predictable on-surface behaviour. The separation of these isomers is quite challenging as, being isomers, they exhibit very similar R_f values, which necessitated the use of very long SiO_2 chromatography columns. A combination of column chromatography and preparative thin layer chromatography yielded **14** and **15**, eluting with CH_2Cl_2 :MeOH (96:4 (v/v)), providing both compounds in yields of 4% (**14**) and 10% (**15**) respectively.



Scheme 2.14: The trimerisation of **12** gave rise to a symmetric (**14**) and an asymmetric isomer (**15**). (i) Reflux in 1,4-dioxane with Co_2CO_8 , 48 h. Yields: 4 % (**14**), 10 % (**15**).

The symmetric isomer **14**, which was the target compound, has been successfully isolated and characterised by ^1H and ^{13}C NMR (Fig. 2.46) and HRMS, at m/z 541.2141 for $\text{C}_{36}\text{H}_{25}\text{N}_6$ $[\text{M}+\text{H}]^+$ (calc. 541.2141). Compounds **14** and **15** are both of interest for their cyclodehydrogenation behaviour on a reactive surface, as much more highly N-containing nanographenes than that investigated by Pinardi *et al* (Scheme 2.6).⁷⁷ The in-solution cyclodehydrogenation behaviour of a similar 6N polyphenylene (identical to **15** except

incorporating *tert*-butyls) was recently reported by the Draper group. It was found that only 5 out of the 6 bonds would close, even with harsh reaction conditions⁸⁹ – therefore it would be enlightening to study whether full cyclodehydrogenation could occur on a surface.

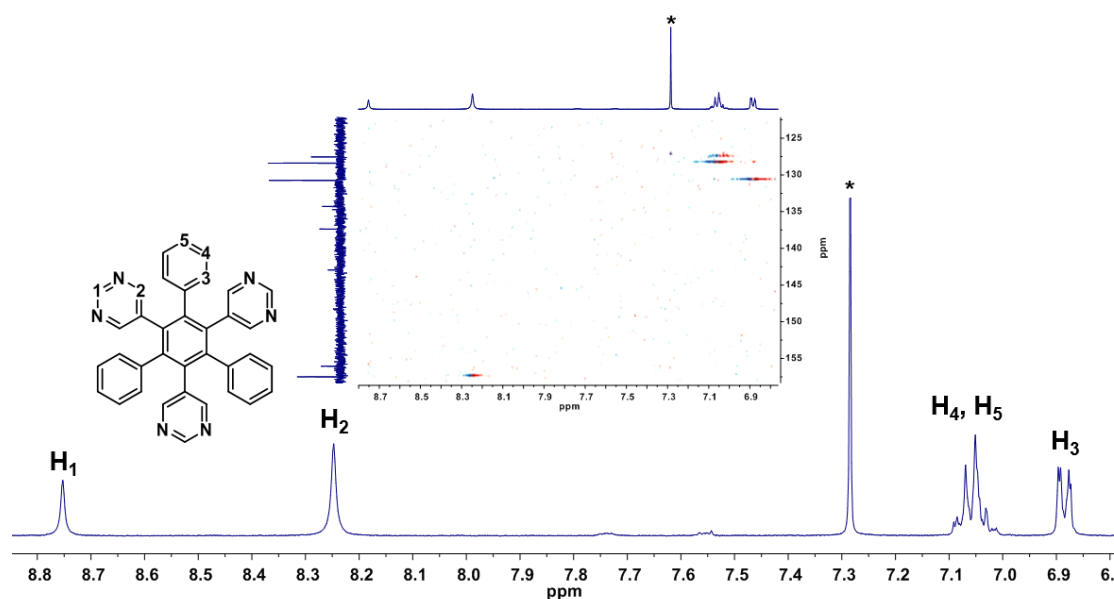
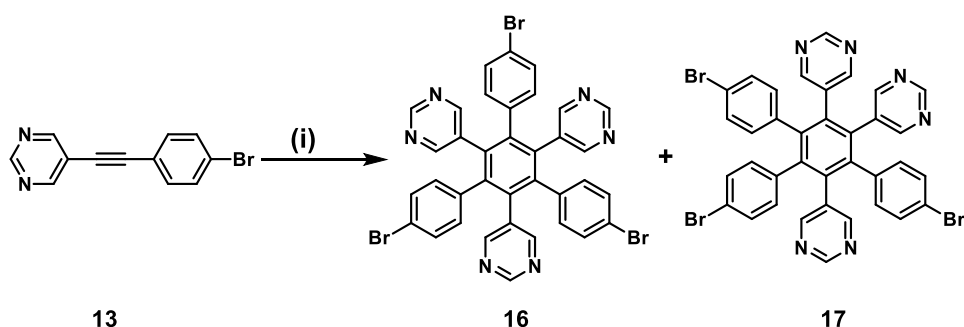


Figure 2.46: ^1H NMR of **14** (CDCl_3 , RT, 400 MHz. * denotes residual solvent peak). Inset is the HSQC experiment.

The incorporation of halogen moieties into the periphery of **14** would yield a precursor with a very high degree of N-substitution that also exhibited an ability to form C-C bonds to form extended covalent structures. The halogen functionality was introduced by modifying the alkyne precursor, which then under the same methodology, was cyclotrimerised to give the symmetric (**16**) and asymmetric (**17**) hexaphenylbenzenes depicted in Scheme 2.15.



Scheme 2.15: The formation of symmetric and asymmetric isomers from **13**. (i) Co_2CO_8 , 1,4-dioxane, reflux, 5 % yield (symmetric isomer).

Purification by preparative TLC (thin-layer chromatography) (CH_2Cl_2 :MeOH, 5%, v/v) yielded the symmetric isomer. ^1H , ^{13}C and C-H HSQC spectra were employed to characterise **16** (Fig. 2.47). Significant problems were encountered attempting to isolate **17**, which exhibited a very similar R_f to **16**. This isomer has not yet been successfully purified, fortunately however, it is the symmetric isomer which is of most interest for its on-surface behaviour.

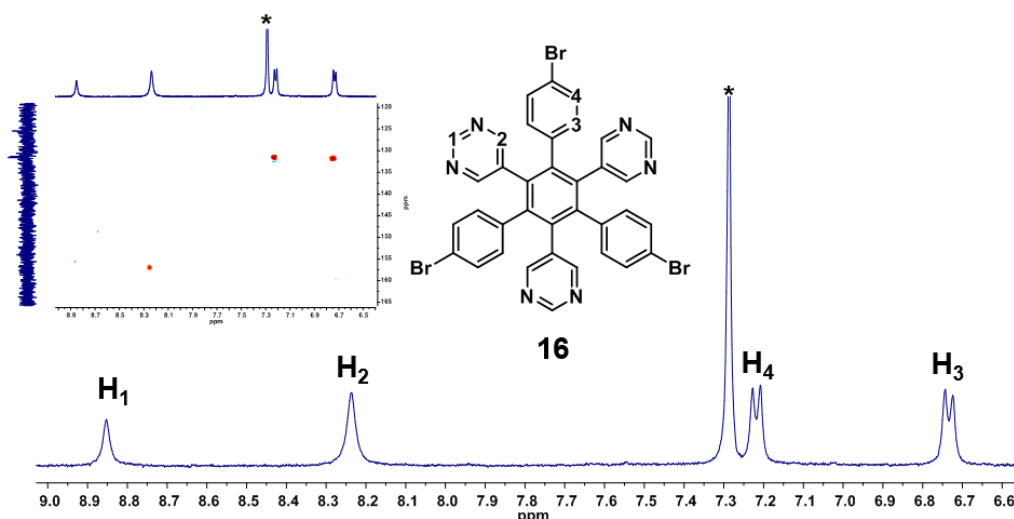


Figure 2.47: The ^1H NMR spectrum of **16** (400 MHz, CDCl_3 solvent, RT). * denotes residual solvent peak.

The formation of extended networks from a compound such as **16** is not without precedence. Bieri *et al.* have demonstrated the possibility of creating similar frameworks from hexaiodo-cyclohexa-m-phenylene (I-CHP, **LC 81**) on various surfaces (Fig. 2.48).⁹⁸ If such frameworks could be created on a surface from **16**, the degree of N-functionalisation would be enormously high and precisely controlled (Fig. 2.48 (c)). This would be of enormous research interest for its catalytic properties, for processes such as the ORR. Also of interest would be the potential for these systems to act as surface templates, since they would exhibit regular pores.

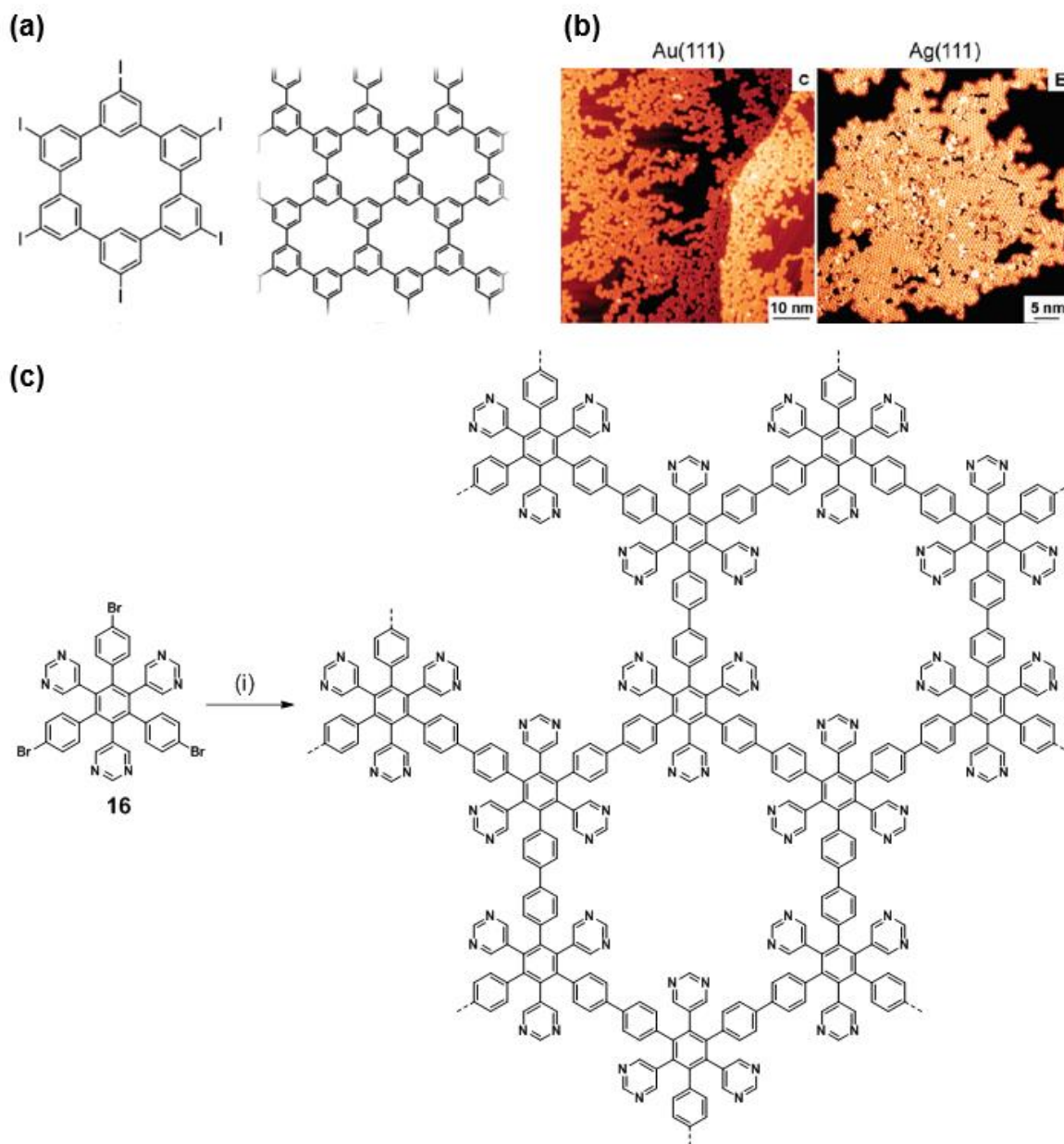


Figure 2.48: (a) The hexaiodo-functionalised **LC 81** molecule and (b) the polyphenylene networks formed upon annealing the substrate.⁹⁸ (c) A depiction of the possible polyphenylene framework formed by **16** if it was deposited on a reactive metal substrate such as Au(111). Further annealing would be expected to form the cyclodehydrogenated analogue.

2.6 Summary and Conclusions

This chapter has aimed to give a general overview of the field of GNR synthesis, and by extension, graphene synthesis. Three precursors were synthesised, characterised and their

ability to generate N-GNRs on a metal substrate was investigated. In the case of precursor **5**, which was deposited on Au(111), promising results were not obtained, perhaps due to a lack of surface mobility. Precursor **6**, the partially-fused analogue of **5**, was also investigated. This precursor yielded covalently-bonded products, but no linear GNR-type structures. Instead, the products appeared to be exclusively dimers and trimers. The modification of the precursor to a hitherto-unreported nitrogen-containing triphenylene-based system, **9**, yielded much more exciting results. Although short, N-GNRs were formed by **9** on Au(111), which appeared fully cyclodehydrogenated. AFM work is required to fully characterise the on-surface morphology of these systems. These types of N-GNR are as yet unreported and display an intriguing porous structure. Reports of similar ‘porous’ GNRs are quite rare in the literature. The optimisation of the process by which longer GNRs could be formed with this precursor remains an area to be explored. This may involve the use of different substrates, such as Cu(111).

The work presented in this chapter has provided some interesting insights into the reactivity of N-containing systems on metal surfaces. From the rather unpromising results obtained from the unfused precursor **5**, much more encouraging results were later observed with the partially-fused **6** and **9**. From the STM images formed by the triphenylene-based **9**, it appears that the GNRs are on average composed of five monomer units on each side of the GNR. This may be due to a lack of mobility on the surface. It is intriguing to note the effect the extent of planarisation had on the on-surface behaviour. The entirely unfused **5** displayed only close-packed arrangements, whereas the half-cyclised **6** formed only dimers and trimers. The phenanthrene-based **9**, differing from **5** only in the closure of a single bond, displayed the only GNR formation. In terms of achieving longer GNRs, there are some factors that could be addressed. Surface coverage may be an issue, in that too many monomers may have been present, but the STM images show optimal coverage. The use of a different, more reactive substrate such as Ag(111) may be worth investigating, but literature work suggests Au(111) is generally the ideal substrate for such systems.

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Chapter Three

Platinum(II) Acetylide Complexes with HBC Ligands

3.1 Introduction

Platinum(II) acetylides are a class of metal complexes that have recently attracted a great deal of research attention. This is a result of their interesting photophysical properties, which lend them to a diverse range of potential applications such as emissive materials for OLEDs, and as DNA intercalators. This chapter aims to describe the synthetic challenges towards new Pt(II) acetylide complexes which incorporate ligands based upon hexa-*peri*-hexabenzocoronene (HBC). The Draper group has built up a wealth of expertise relating to HBC and its derivatives, and have consequently prepared several organometallic complexes incorporating functionalised HBCs. This chapter extends this work, concentrating on the preparation of dinuclear Pt(II) complexes of HBC, of which, at the time of writing, there appears to have been only one previous report.¹

3.1.1 Transition Metals and Metal-Alkynyl Complexes

The photophysics of transition metal complexes have long been the subject of intense scientific research. Since the first report of luminescence from tris-2,2'-bipyridine-ruthenium(II) (**LC 82**, Fig. 3.1) by Paris and Brandt in 1959, such complexes have been widely investigated.² In the case of tris-2,2'-bipyridine-ruthenium(II), the observed emission was initially believed to be fluorescence, but was later shown to be a charge-transfer based process by G. Crosby in the mid-1970s.³ Transition metal complexes with metal-to-ligand charge transfer (MLCT) excited states have attractive properties, such as long luminescence lifetimes, photoluminescence and strong absorption of light in the visible region.⁴ Transition metal complexes, such as those of Ruthenium, Iridium and Platinum, often display efficient phosphorescence at room temperature. This is attributed to spin-orbit coupling, which facilitates intersystem crossing, and results in longer-lived triplet excited states and, therefore, potentially more efficient radiative decay from the triplet state. When compared with solely organic lumophores, transition metal complexes incorporating π -conjugated ligands often display much richer photophysical properties. Mixing of the metal and ligand orbitals can result not only in the aforementioned MLCT, but also ligand-to-metal charge transfer (LMCT), ligand-ligand charge transfer (LLCT) and metal-centred (MC) transitions. Careful modification of the ligands can modulate the energy levels of these states, thereby providing a method of tuning their emissive properties.⁵ Extensive progress has been

achieved towards the implementation of such emissive complexes towards materials applications. Examples of these include as emissive materials for phosphorescent OLEDs (Fig. 3.1 (b)),⁶ biological probes,⁷ bioimaging agents,⁸ photocatalysis,⁹ and as photosensitisers for use in triplet-triplet annihilation upconversion (TTA-UC) and photodynamic therapy (PDT).^{10, 11} TTA-UC is a method by which solar energy may be harnessed more efficiently, and will be discussed in detail in Chapter Four.

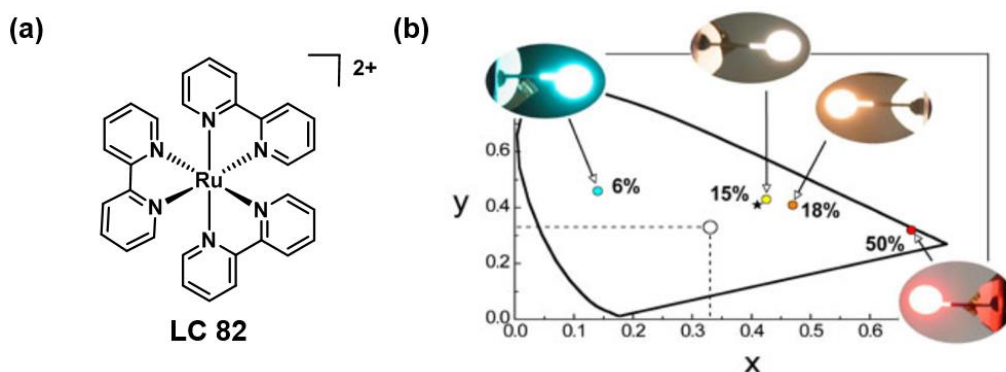


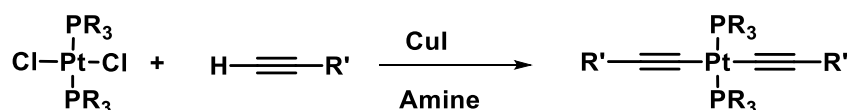
Figure 3.1: Structure of $[Ru(bpy)_3]^{2+}$. (b) CIE (Commission Internationale de l'Eclairage) chromaticity diagram, and inset, emission colour, from phosphorescent OLEDs fabricated from an $N^{\wedge}C^{\wedge}N$ -coordinated Pt(II) complex dopant. The colour is tuned by variation of dopant amount. Adapted from Cocchi et al.¹²

Metal acetylides have been known since 1960,¹³ and feature attractive properties for materials applications.¹⁴ The acetylide ligand, due to its linear geometry, acts as a linker unit and may be thought of as a ‘molecular wire’ that permits communication between the substituents either side of the $C\equiv C$ bond. Much work has centred upon polymeric species containing acetylide units, which are electrically conductive, can display non-linear optical responses and can form liquid-crystal phases.¹⁵ The bonding in acetylide-containing systems has been studied in great detail, and it has been revealed that acetylides are strong field ligands, similar to $-CN$ in their position in the spectrochemical series. The acetylide ligands in transition metal alkynyl complexes can be regarded as $HC\equiv C^-$, and they possess similar electronic properties to CN^- , CO and N_2 .¹⁶ Acetylides possess empty π^* orbitals suitable for π -backbonding, although it seems that $M\rightarrow C$ π -backbonding does not play a major part in the bonding behaviour of acetylide complexes. The energy gap between the HOMO of the metal d orbitals and the LUMO of the acetylide π^* orbitals has been suggested to be too large (c. 15 eV) for efficient π -accepting interactions.¹⁵ The interaction between a metal and acetylide ligand is therefore mostly σ -donating from the acetylide into empty metal-centred

orbitals. As acetylides are strong field ligands, they have the effect of raising the energy of the d-d states in their complexes, making them less accessible. This in turn increases the luminescence, as low-lying d-d states can deactivate the radiative decay of emissive states (*e.g.* MLCT). Thus acetylide complexes are often highly emissive at RT.

3.1.2 Introducing Pt(II) Acetylides

Oligomeric square-planar platinum(II) acetylides were reported as early as 1975 by Sonogashira and Hagihara,¹⁷ who then reported more refined syntheses in 1977 and 1978, including those of the general formula *cis*- and *trans*-(PR₃)₂Pt(C≡CR')₂.¹⁸⁻²⁰ Their general method was the copper(I) iodide catalysed dehydrohalogenative coupling of a platinum chloride precursor and a terminal alkyne under basic conditions (Scheme 3.1). Without the presence of CuI, it is possible to produce only the mono-substituted acetylide. In these types of complexes, the R group of the phosphine is generally aliphatic and contributes to the materials properties, *e.g.* solubility and crystallinity. The R' group is generally a chromophoric π -conjugated aromatic group that dominates the photophysical characteristics of the system.²¹ Most early work focused on oligomeric systems. This made spectroscopic work difficult, and it was not until the late 1980s and early 1990s that in-depth photophysical studies began to be undertaken on monomeric Pt(II) acetylide systems.



Scheme 3.1: General scheme for the formation of Pt(II) acetylides, as devised by Sonogashira and co-workers.^{18, 20}

The sustained research interest in Pt(II) acetylides has been due to their unusual photophysical properties. The coupling of a π -conjugated aryl acetylide to a heavy metal facilitates spin-orbit coupling. They generally absorb over a wide range of the visible spectrum, have good photochemical stability and exhibit relatively long-lived excited states.²² Early work on the photophysics of Pt(II) acetylides was carried out by Sacksteder *et al.* in 1991, who reported that Pt(II) acetylides of the formula *trans*-Pt(C≡CR)₂(PEt₃)₂ (where R = H or Ph, **LC 83**/**LC 84**, Fig. 3.2 (a)) gave intense 77 K emission spectra and had site-selective differences (where quite different emission spectra were obtained with variation in the excitation wavelength) in their luminescence spectra. Widespread research

into such compounds began after Chan *et al.* reported a platinum(II) acetylide complex with an aromatic diimine ligand in 1994, which gave intense emission in solution at RT (**LC 85**, Fig. 3.2 (b)).²³ The authors attributed this behaviour as being due to a triplet metal-to-ligand charge transfer (MLCT) $[\text{Pt} \rightarrow \pi^*_{\text{phen}}]$ excited state. Since then, the research area has blossomed.

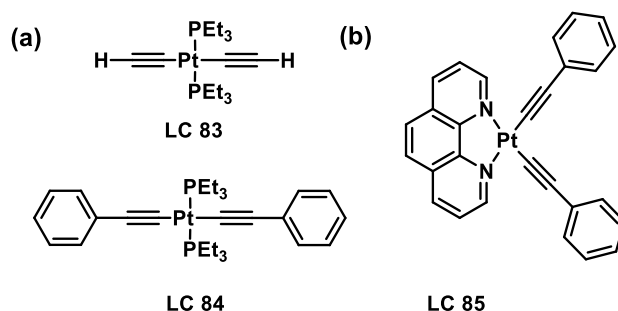


Figure 3.2: Examples of platinum acetylides. (a) Pt(II) acetylides whose spectroscopic properties were investigated by Sacksteder *et al.*²⁴ (b) The Pt(II) acetylide reported by Chan *et al.*²³

The square planar nature of these complexes may be explained by considering their electronic properties. Pt(II) has the electronic configuration d^8 , and in the presence of strong field ligands exhibits a preference to form square planar complexes (Fig. 3.3 (a)). This square planar arrangement permits three of the occupied orbitals to be stabilised whilst an unoccupied orbital is pushed upwards in energy (Fig. 3.3 (b)).²⁵ For Pt(II), the ligand field is generally so large that its complexes are usually always square planar. This arrangement of orbitals means that the dx^2-y^2 is strongly antibonding in nature, and if it becomes populated by excitation of light, the molecule becomes distorted. This has the side-effect of displacing the d-d excited state, so that its potential energy surface is displaced in comparison to the ground state. This makes the possibility of deactivation of the excited state by non-radiative means through internal conversion (IC) or intersystem crossing (ISC) more likely, as there is a thermally accessible isoenergetic crossing point. In the case of Pt(II) complexes the MLCT and LC states (which often lie at lower energy levels than the d-d state), these states may actually become deactivated by the d-d state which can be thermally accessed at RT and serve as a drain on luminescent excited states (Fig. 3.3 (c)).²⁵ As mentioned earlier, this can be countered, either with strong field ligands that raise the d-d state to an inaccessible level, or by the presence of emissive states that are low in energy.

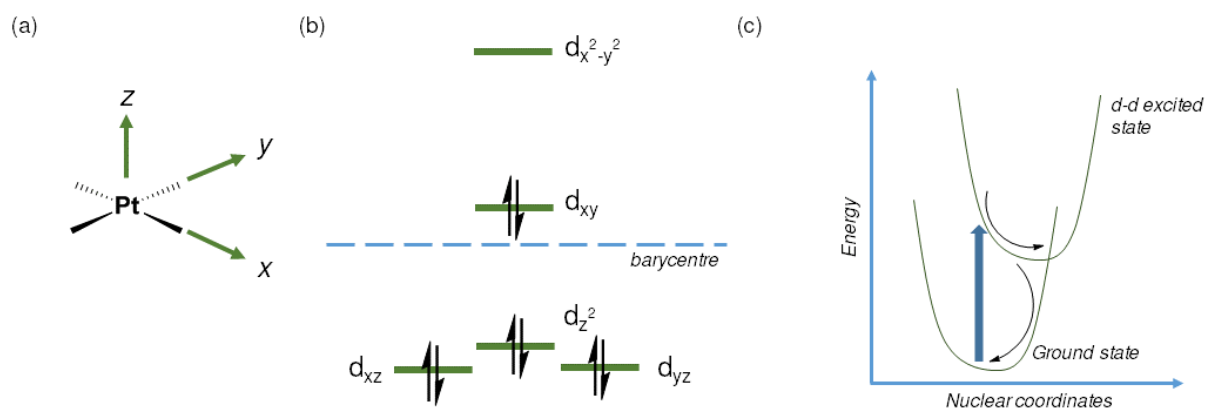


Figure 3.3: (a) Pt centre in a square planar configuration. (b) Ligand field splitting diagram of Pt(II) in a square planar arrangement. (c) A depiction of how the potential energy surface of the d-d state is displaced in an excited square planar d^8 complex. Adapted from Williams.²⁵

3.1.3 Types of Pt(II) Acetylides

Platinum acetylides may be broadly classed into two categories; those that are charged and those that are neutral. Those that are charged can then be subdivided into cationic and anionic platinum complexes. Neutral platinum acetylides consist of four sub-types with the general formulae $\text{Pt}(\text{N}^{\wedge}\text{N})(\text{C}\equiv\text{CR})_2$, $\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}\equiv\text{CR})$, *cis*- $\text{Pt}(\text{P}^{\wedge}\text{P})(\text{C}\equiv\text{CR})_2$ and *trans*- $\text{Pt}(\text{PR}_3)_2(\text{C}\equiv\text{CR})_2$. Cationic acetylide complexes usually have the general formula $[\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})(\text{C}\equiv\text{CR})]^+\text{X}^-$. Anionic complexes generally follow the formula $\text{M}_2[\text{Pt}(\text{C}\equiv\text{CR})_4]$, where M represents the counter cations of K^+ or NBu_4^+ .¹⁴ The anionic complexes are outside the scope of this work and will not be discussed here. In the interest of brevity and clarity, this introduction will consider different Pt(II) acetylides in terms of their ligand coordination type *e.g.* phosphine ligands, or tridentate *etc.* These will be briefly discussed in terms of their synthesis and photophysical behaviour. Since the first reported Pt(II) acetylides by Sonogashira and Hagihara were based upon phosphine ligands, the discussion will begin with those. Acetylides of the type $\text{Pt}(\text{N}^{\wedge}\text{N})(\text{C}\equiv\text{CR})_2$ will be discussed in Chapter Four, which describes the synthesis of such complexes. This chapter will focus on acetylide complexes of the type $\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}\equiv\text{CR})$ and $[\text{Pt}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})(\text{C}\equiv\text{CR})]^+\text{X}^-$.

3.1.4 Pt(II) Complexes with Phosphine-Based Ligands

After the initial synthetic reports of these neutral complexes in the 1970s, Sacksteder and co-workers began photophysical research in this field in 1991, reporting on a series of mononuclear Pt(II) complexes, *trans*-Pt(H)Cl(PEt₃)₂, *trans*-Pt(C≡CH)₂(PEt₃)₂ and *trans*-Pt(C≡CPh)₂(PEt₃)₂ (**LC 86-88**, respectively).²⁴ They noted the parent complexes *cis*- and *trans*-PtCl₂(PEt₃)₂ (**LC 89-90**) were non-emissive, but that when one –Cl ligand was replaced by a hydride (**LC 86**), a sharp emission was observed at 77 K. This was assigned as being due to the higher crystal field strength of the hydride, making deactivation of emissive states through metal-localised d-d states less facile. It was further suggested that the excited state in the dichloride complexes (**LC 89-90**) is tetrahedral, owing to distortion caused by population of the d-d state, which is corroborated by their facile *cis-trans* photoisomerisation.²⁶ In comparison, the acetylide complexes (**LC 87-88**) exhibit different photophysical behaviour. These were quite emissive at 77 K, attributed to phosphorescence, and the emission was assigned as being MLCT in character. Interesting work on linear Pt(II) acetylides was later reported in 2002 by Liu, Schanze and co-workers, who synthesised Pt-acetylide oligomers (PAOs) that contained up to seven Pt(II) centres.²⁷ By synthesising a series of oligomers, it was observed that the singlet excited state was considerably delocalised across several repeat units. As the oligomer length was increased, a red-shift was observed in the ground-state fluorescence and absorption spectra. Conversely, phosphorescence measurements were barely affected by oligomer length, suggesting the triplet excited state is delocalised over one or at most two repeat units.

3.1.5 Extending Pt(II) Acetylides to HBC

The interaction of platinum acetylides of this type with large polycyclic aromatic hydrocarbons (PAHs) has also been investigated. The interaction of a metal with a large conjugated aromatic framework such as that of HBC would be expected to affect its electronic properties. The presence of the metal would be expected to lead to enhanced spin-orbit coupling and to permit more facile access to the triplet state. An ethynyl linker would assist communication between the metal centre and a HBC molecule, as it preserves conjugation. Reports of Pt(II)-HBC complexes are limited in the literature, and the earliest of these, both published in 2006, will now be described.

Kim and co-workers have reported a HBC molecule functionalised with Pt(II) acetylides of the formula *trans*-(Ar-C≡C-)₂Pt(PBu₃)₂.²⁸ They reported two complexes, one where the Pt(II) is linked to the HBC unit with a single ethynyl linker (**LC 91**, Fig. 3.4) and another where there is separation by a 1,4-phenylene ethynylene spacer (**LC 92**, Fig. 3.4). Their experiments showed that the aggregation of the Pt-HBCs suppressed the triplet lifetime and yield. The electronic structure of the triplet state was not much affected by aggregation however, which suggested that the triplet state remained localised on each HBC chromophore, and was relatively unperturbed by intermolecular π - π interactions. The synthesis of these compounds was achieved by coupling the intermediate iodo-HBC, either directly with a Pt(II) acetylide, or by functionalisation with an alkyne group which was then coupled to the requisite acetylide. Luminescence experiments at RT showed that the Pt-HBC with a single ethynyl spacer, **LC 91**, showed very little fluorescence but significant phosphorescence, suggesting $S_1 \rightarrow T_1$ is quite efficient. For the other Pt-HBC complex, **LC 92**, with the presence of an additional spacer, the fluorescence emission is much more significant. This was attributed to phosphorescence due to the long lifetime (over 20 μ s for both complexes). The presence of this emission can be explained by the presence of the heavy Pt atom increasing the efficiency of ISC from S_1 to T_1 . The similar band shapes suggest that the lowest excited triplet states for both are located on the HBC unit, which was also suggested by DFT. Studies on the effects of different solvents on the luminescence spectra revealed that the Pt-HBC complexes tend to aggregate, which caused quenching of the triplet state only (as evidenced by a decrease in triplet lifetime and phosphorescence intensity), but there was no evidence to support the idea of the formation of triplet excimers. In THF, the complexes were well solvated, but the extent of solvation was observed to decrease in CH₂Cl₂ and become quite poor in hexane. The authors suggested that these observations were due to π - π stacking. This study demonstrated how the optical properties of the HBC unit could be affected by coupling it to a metal centre.

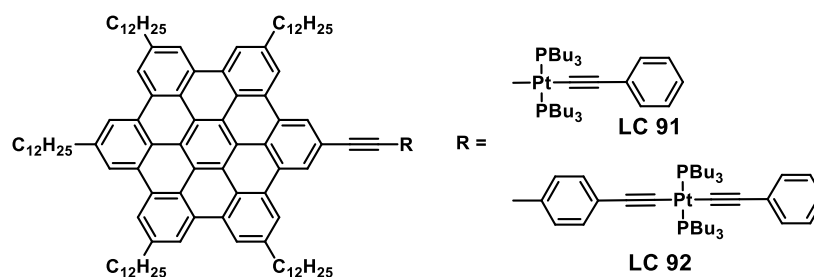


Figure 3.4: HBC molecule functionalised with different Pt(II) acetylides, as prepared by Kim et al.²⁸

Further work on Pt-HBC complexes was reported by the Müllen group in the same year. El Hamaoui *et al.* detailed their synthesis of a HBC-Pt₂ complex (*e.g.* disubstituted in the *para* positions, **LC 94**, Fig. 3.5), and an unsubstituted analogue (**LC 93**, Fig. 3.5).¹ In this case, the Pt atoms were bonded directly to the HBC core, without an ethynyl linker. The synthetic procedure required a dibromo-HBC starting material which underwent oxidative addition to Pt(PEt)₃, followed by the CuI-catalysed coupling of the Pt complex to phenylacetylene. The all-carbon analogue **LC 93** was substituted entirely with the alkyl chains in order to provide a comparator. The UV-Vis spectrum of the HBC-Pt₂ **LC 94** exhibited a slight red-shift, indicating that conjugation is spread across the phenylacetylene units through the Pt centres. The presence of the Pt atoms was found to decrease the lifetime of phosphorescence by three orders of magnitude, although the quantum yield of phosphorescence was found to be rather low ($\Phi \approx 1\%$). No residual fluorescence was observed for the HBC-Pt₂ complex **LC 94**, whereas for **LC 93**, delayed fluorescence was observed at RT, which demonstrates the effect of the spin-orbit coupling in the metal complex.

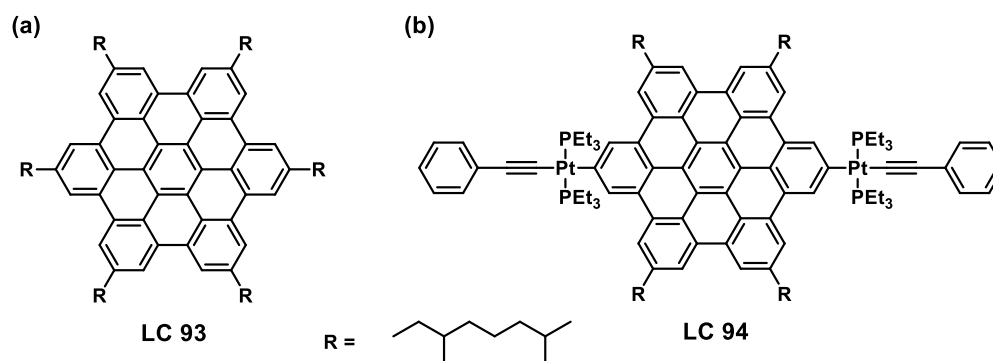
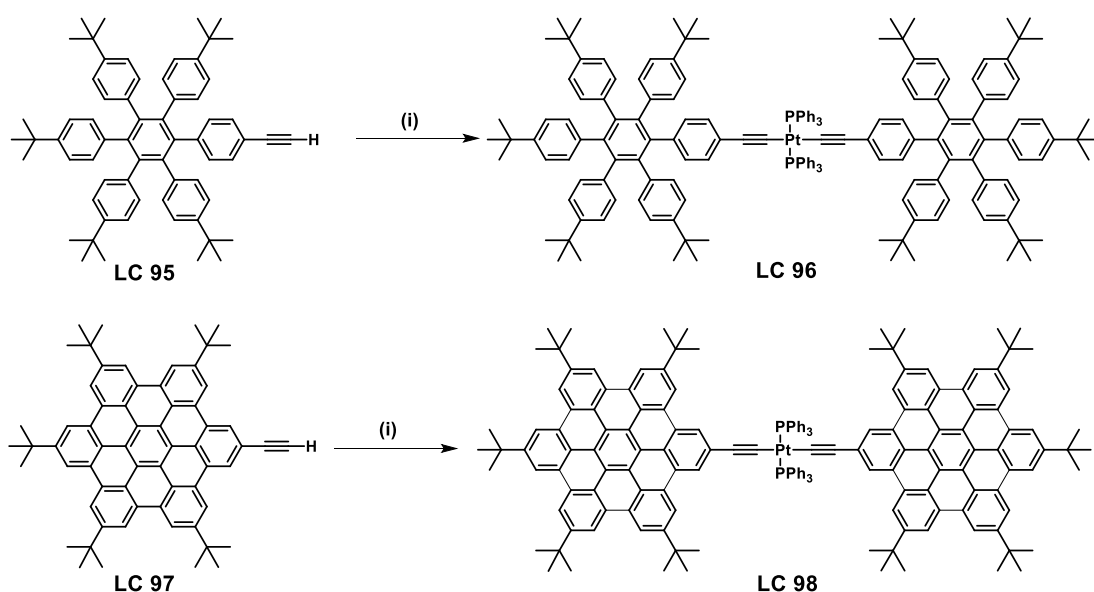


Figure 3.5: (a) Unsubstituted, all-carbon HBC with solubilising alkyl chains on the periphery and (b) the same HBC core functionalised with Pt(II) acetylides.¹

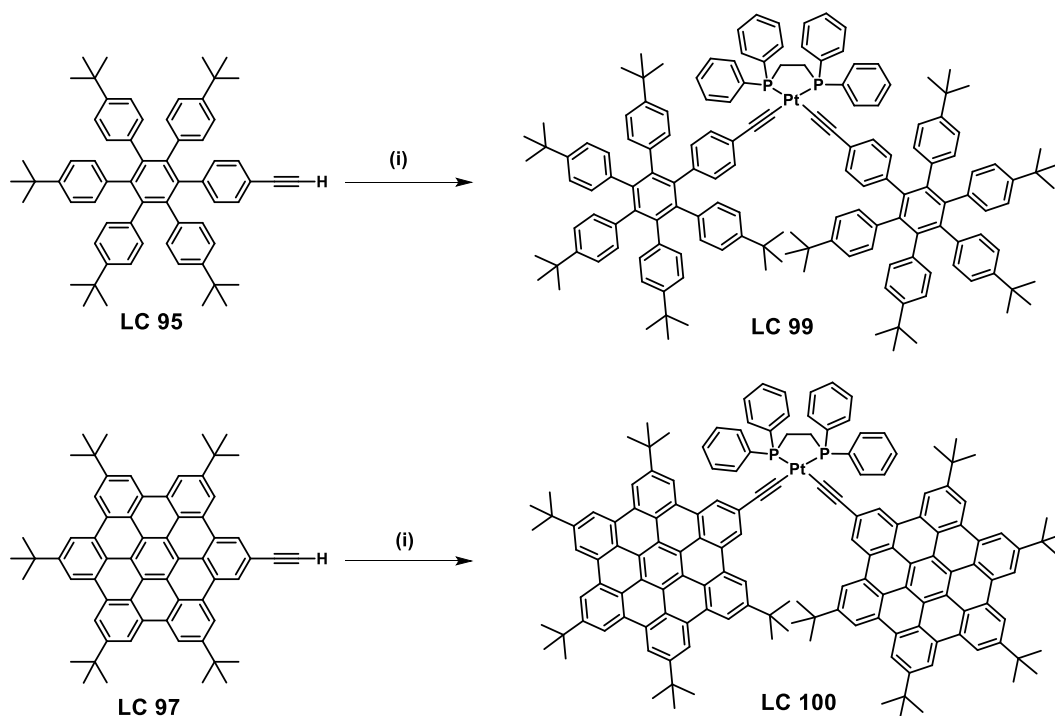
Within the Draper group, there has been significant work published on similar Pt(II) acetylides featuring HBC moieties. Nolan and co-workers published an account of four novel *cis*- and *trans*-Pt(II) acetylides in 2011.²⁹ Each *cis*- and *trans*- derivative incorporated either the fully-fused, planar HBC ligand or its uncyclised hexaphenylbenzene precursor. In this manner, it was possible to compare the effects of both cyclisation and geometry. The *trans*-derivatives were prepared in a similar way as the previous HBC-Pt complexes. The mono-substitution of a hexaphenylbenzene with an alkyne (**LC 95**) permitted dehydrohalogenative coupling with *cis*-[Pt(PPh₃)₂Cl₂] yielding the *trans*-acetylide **LC 96**. Cyclodehydrogenation

of the hexaphenylbenzene precursor (**LC 95**) gave access to the fused derivative, **LC 98** (Scheme 3.2).

The relative scarcity of *cis*- acetylides in the literature until recently is due to their thermodynamic instability when compared with the *trans*- isomer.^{20, 30} This can be overcome by the use of either chelating phosphine ligands or diimine complexes. In this case, access to the *cis*- isomers was made possible through the use of a chelating phosphine, *cis*-[Pt(dppe)Cl₂] (where dppe = 1,2-bis(diphenylphosphanyl)ethane), in an otherwise analogous synthetic route to that used for the *trans*- acetylides (Scheme 3.3). This provided an uncyclised acetylide derivative **LC 99** and a cyclised derivative **LC 100**.



Scheme 3.2: The synthetic route towards *trans* Pt(II) complexes **LC 96** and **LC 98**. (i) *cis*-[Pt(PPh₃)₂Cl₂] (0.5 equiv.), CuI (cat.), CH₂Cl₂, *i*-Pr₂NH.²⁹



Scheme 3.3: The synthetic route towards *trans* Pt(II) complexes **LC 99** and **LC 100**. (i) *cis*-[Pt(dppe)Cl₂] (0.5 equiv.), CuI (cat.), CH₂Cl₂, *i*-Pr₂NH.²⁹

The absorption spectra of **LC 96** and **LC 99** displayed ligand-based absorption bands and MLCT bands (Fig. 3.6 (a)). The MLCT band of **LC 96** is red-shifted compared to **LC 99**, which the authors suggested was the result of more effective conjugation through the Pt(II) centre in the *trans* arrangement. The absorption spectra of cyclised **LC 98** and **LC 100** show distinctive absorption bands from the HBC (Fig. 3.6 (b)) but again, the *trans* is slightly red-shifted. In terms of emission spectra, it was discovered that for both the cyclised and uncyclised complexes, the emission was dependent on excitation wavelength. A higher energy ligand-based fluorescence was exhibited by all four compounds, with lower energy bands ($\lambda \approx 578$ nm) also observed (Fig. 3.6 (c) and (d)), which had significant phosphorescent character. Long lifetimes were obtained for both **LC 98** and **LC 100** with respect to the phosphorescent band (18.3 and 30.9 μ s respectively). The authors concluded that optimal π conjugation was achieved with the *trans* configuration, as this arrangement yielded improved fluorescence lifetimes, longer phosphorescence lifetimes and redshifted absorption.

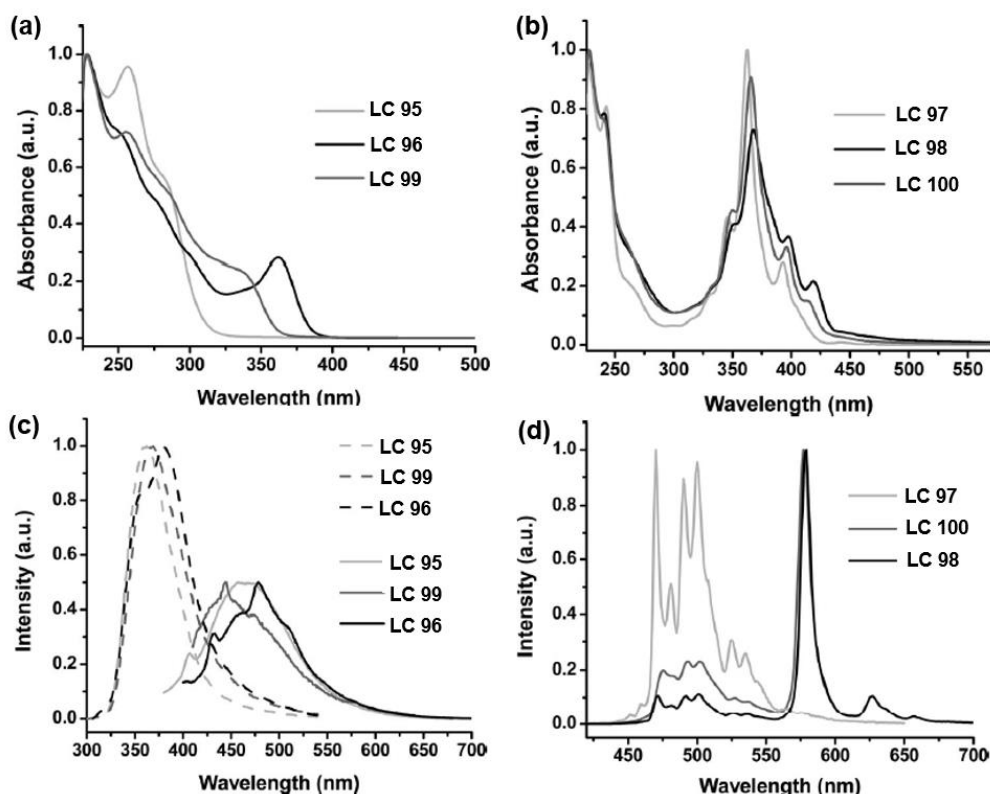


Figure 3.6: (a) UV-Vis absorption spectra of **LC 95**, **96**, and **99** (CH₂Cl₂, ca. 10⁻⁵ M). (b) UV-Vis absorption spectra of **LC 97**, **98** and **100** (CH₂Cl₂, ca. 10⁻⁵ M). (c) RT emission spectra of **LC 95**, **96** and **99** in Ar-degassed CH₂Cl₂, showing the two emission bands for each compound (dependent on excitation wavelength, ca. 10⁻⁵ M). (d) RT emission spectra of **LC 97**, **LC 98**, and **LC 100** in Ar-degassed CH₂Cl₂, ca. 10⁻⁵ M. Adapted from Nolan et. al.²⁹

This chapter will describe what can be considered as a follow-up to this work, but will consider HBC units connected to Pt(II) acetylides bearing N[^]N[^]N (terpyridine) and cyclometallating N[^]N[^]C ligands, which appear not to have been explored in the literature at the time of writing.

3.1.6 Pt(II) acetylide complexes with N[^]N[^]N ligands

This chapter will detail attempts towards N[^]N[^]N, and later, N[^]N[^]C Pt(II) acetylides incorporating HBC. Therefore this section will give a short account of some of the important reported advances in N[^]N[^]N Pt(II) acetylide complexes. Unlike the compounds described previously, complexes with tridentate N[^]N[^]N (terpyridine or terpy) ligands are charged. Interest in these types of complex is due to the higher rigidity enforced by the tridentate ligand, which reduces the likelihood of non-radiative decay through molecular distortion.

Morgan and Burstall gave an early account of Pt(II) complexes with tridentate ligands in 1934,³¹ and many complexes with the general formula $[\text{Pt}(\text{tpy})\text{X}]^+$ have been reported since, where X is generally a halide or CN^- ligand.³² Strong field ligands are necessary to raise the d-d states in these complexes, which makes acetylides ideal.

Yam and co-workers reported the first series of Pt(II) acetylide complexes with terpy ligands in 2001.³³ The series, based on the general formula $[\text{Pt}(\text{trpy})(\text{C}\equiv\text{CR})]\text{PF}_6$, with different R groups of varying electron-donating ability, gave long-lived excited states. They found that a more electron withdrawing R group on the acetylide yielded a higher emission energy. As the electron-donating ability of the R group increased, emission was shifted to longer wavelengths. They assigned the emission as being primarily $^3\text{MLCT}$ in nature, with some $^3\text{LLCT}$ character (acetylide-to-terpyridine ligand-ligand charge transfer). Yang *et al.* later reported a series of Pt(II) 4'-p-tolyl-terpyridyl acetylide complexes, in an effort to improve the low quantum yields of those examples previously reported (which were not greater than 1×10^{-2}).³⁴ Through variation of the terminal group on the acetylide and also variation of the terpyridyl group, they reported complexes with long-lived emission from the $^3\text{MLCT}$ state and with lifetimes greater than 10 μs and quantum yields of over $\Phi = 0.25$. As the electron-donating ability of the ligand on the acetylide was increased, it was reported that the emission was shifted to lower energies.

Rachford *et al.* have investigated the effect of incorporating larger polyaromatic systems on the acetylide unit.³⁵ They synthesised $[\text{Pt}(\text{}^t\text{Bu}_3\text{tpy})(\text{C}\equiv\text{C-perylen})]\text{BF}_4$ (**LC 101**, Fig. 3.7 (a)) and $\text{Pt}(\text{dbbpy})(\text{C}\equiv\text{C-perylen})_2$ (**LC 102**, Fig. 3.7 (b)), where ${}^t\text{Bu}_3\text{tpy}$ is 4,4',4''-tri(*tert*-butyl)-2,2':6'2''-terpyridine and dbbpy is 4,4'-di(*tert*-butyl)-2,2'-bipyridine. Upon excitation, these compounds did not photoluminesce. However, the authors provided evidence for the formation of a triplet state, since they were able to sensitise singlet oxygen. Further transient absorption (TA) experiments confirmed that the lowest excited state was ^3IL . An unusual property of these complexes were the long-lived excited states that were produced (3.0 and 5.7 μs , for **LC 101** and **LC 102**, respectively), which did not yield any photoluminescence.

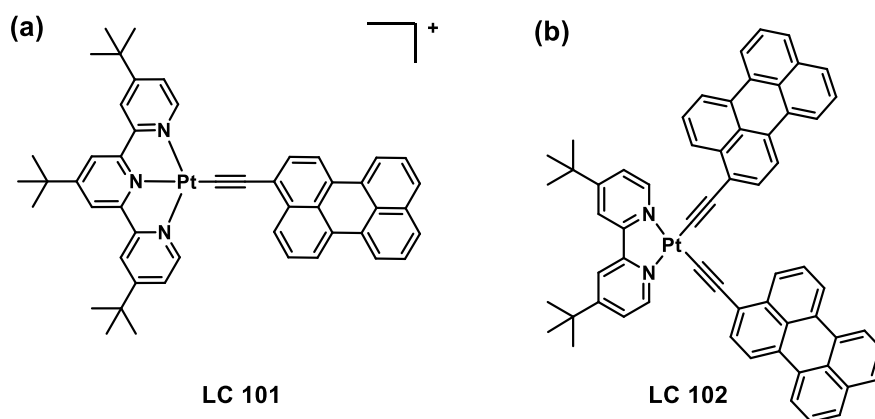


Figure 3.7: Pt(II) acetylides with appended perylene units.³⁵

Interesting work was reported by Camerel and Ziessel in 2007, who described the properties of Pt(II) terpyridine complexes that were able to form gels and liquid crystals.³⁶ They designed systems that could form liquid crystals by selecting polyimine-based ligands, which exhibit π - π stacking, and incorporating Pt, thus introducing a heavy-atom effect and the possibility of metal-metal interactions, since Pt favours a square planar configuration. They produced Pt(II) acetylides by coupling [Pt(terpy)Cl]BF₄ with terminal ethynyl derivatives possessing methyl (**LC 103**), dodecyl (C₁₂H₂₅, **LC 104**), or phytol-based (C₂₀H₄₁, **LC 105**) substituents. The complexes displayed strong solvatochromism. The dodecyl-substituted complex (**LC 104**) displayed a strong phosphorescence emission at 830 nm in non-polar dodecane, but upon addition of MeOH, this is gradually quenched and a new band at 635 nm emerges. The band at 835 nm, in pure dodecane, was assigned to a ³MMLCT (metal-metal-ligand charge transfer) state, and in a mixture of CH₂Cl₂ and MeOH, the strong emission at 644 nm was assigned to a mixed ³MLCT/³LLCT state. The authors proposed that the non-polar dodecane may be encouraging aggregation of the complexes and encouraging Pt-Pt, Pt- π and π - π^* stacking interactions. The dodecyl-substituted compound formed gels in dodecane, with a minimum gelation concentration of 7.5 mmol L⁻¹. This gelation process was thermally controlled: heating above 60 °C produced a deep red liquid, but cooling to RT produced dark green gels. Hydrogen bonding was observed in the gel state by IR spectroscopy. TEM (transmission electron microscopy) imaging revealed that the dodecyl-substituted complex was arranged in a network of interlocked fibres several hundred nanometres long, suggesting that strong intermolecular interactions such as hydrogen bonding and Pt-Pt interactions drive the self-assembly process responsible for the gel forming behaviour.

3.1.7 Pt(II) acetylide complexes with N[^]N[^]C ligands

Exploration of tridentate ligands has been extended to cyclometallating analogues. These types of complex are attractive for the same reasons as their N[^]N[^]N analogues, in that they inhibit the D_{2d} distortion that diimine complexes can undergo, thereby reducing non-radiative means of deactivation, and it would be expected that a cyclometallating N[^]N[^]C would provide better luminescence quantum yields than the corresponding bidentate N[^]C ligand.³⁷ Pt(II) acetylide complexes bearing N[^]N[^]C ligands have attractive properties for efficient luminescence behaviour, since they exhibit high rigidity due to the N[^]N[^]C ligand, and also contain two strong-field ligands *i.e.* the cyclometallating carbon and the acetylide co-ligand. The d-d states in N[^]N[^]C complexes are usually higher than those in their N[^]N[^]N counterparts. The anionic acetylide ligand confers neutrality upon the complex, simplifying synthetic procedures.

Much of the literature work on Pt(II) complexes bearing N[^]N[^]C ligands has been published by Che *et al.*, who provided the first report of luminescence from a diimine Pt(II) complex (**LC 85**), as described earlier. In 2004, they carried out a systematic investigation of 33 variants of a cyclometallated Pt(II) acetylide.³⁸ The choice of cyclometallating and σ -alkynyl ligands had a marked influence on the emissive properties of these complexes. It was possible to tune the emission colour of the complexes from green-yellow to saturated red. All of these compounds were highly luminescent in solution and gave quantum yields in the region of $\Phi = 0.05$ -0.10. These compounds displayed good characteristics for light-emitting materials and some of them were successfully incorporated into OLEDs, a process described in the same publication. Latouche *et al.* later presented cyclometallated Pt(II) acetylides incorporating pyridyl substituted acetylide ligands, an example of which, **LC 106**, is presented in Fig. 3.8 (a).³⁹ The pyridyl ring appended to the end of the acetylide ligand acted as a site for protonation or methylation and also as a host receptor for binding metal cations. Examination of the photophysical properties of these complexes revealed that the emission from the neutral complexes was due to a mixture of ³LLCT and ³MLCT. Qiu and co-workers successfully synthesised a series of Pt(II) acetylides in which they appended an arylamino substituent at the 4- position of the C[^]N[^]N ligands (Fig. 3.8 displays the unsubstituted variant **LC 107** (b) and the arylamino substituted derivative **LC 108** (c)).⁴⁰ This was intended to act as an electron donor in order to enhance the charge transfer process between the Pt(II) centre and the ligands and to tune the photophysical properties by varying the electron-donating abilities. The authors reported that the arylamino groups strengthened

the donor-acceptor interactions and yielded absorption spectra with intense bands in the 300–500 nm region. Luminescence lifetimes and quantum yields were higher for the arylamino-substituted systems than for those without (*e.g.* increasing from 0.9 to 4.5 μ s).

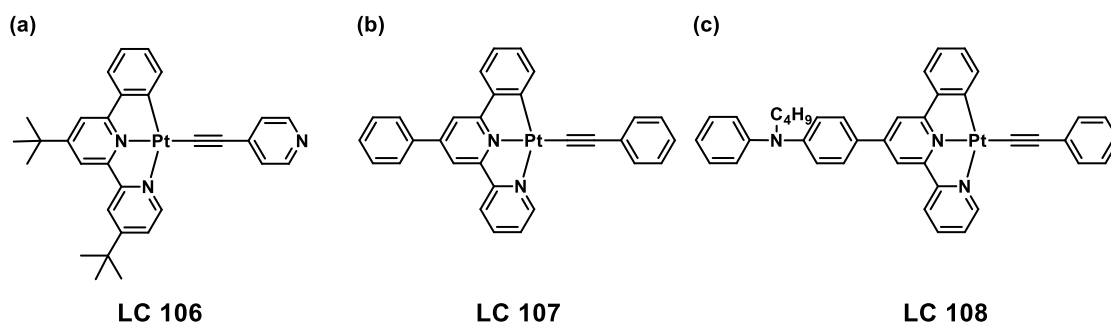


Figure 3.8: (a) Cyclometallated acetylide **LC 106** reported by Latouche *et al.*³⁹ (b) and (c) Cyclometallated acetylides with $N^{\wedge}N^{\wedge}C$ ligands as produced by Qiu *et al.*⁴⁰

3.1.8 Chapter Aims

It is the intention of this chapter to describe synthetic attempts towards Pt(II) acetylides bearing both HBC cores and either terpyridine (terpy) or cyclometallated ($N^{\wedge}N^{\wedge}C$) ligands. The photophysical characterisation of the Pt(II) acetylides with $N^{\wedge}N^{\wedge}C$ ligands will also be described. The encouraging properties of the Pt(II) acetylide complexes of HBC, reported both within the Draper group and in the wider literature, such as long triplet lifetimes and RT phosphorescence, are the motivation behind the investigation of these systems. Historically, there have been few other reports of organometallic complexes of HBC. Of those not described in the introduction, most are complexes of nitrogen-containing HBC, known as N-HSB, although reports of these are also relatively scarce. This chapter aims to extend the range of metal complexes of HBC and to probe its properties as a highly conjugated polyaromatic ligand. The incorporation of the Pt centre *via* a σ -alkynyl unit is expected to facilitate efficient ISC. Furthermore, the incorporation of terpyridine ($N^{\wedge}N^{\wedge}N$) or $N^{\wedge}N^{\wedge}C$ -type ligands has been reported to yield improved photophysical properties due to increased rigidity. The incorporation of such ligands has not yet been explored, and might be expected to lead to intriguing photophysical behaviour. The initial part of this chapter will describe attempts towards dinuclear HBC-based Pt(II) acetylides incorporating $N^{\wedge}N^{\wedge}N$ ligands (Fig. 3.9 (a)). The syntheses of these proved highly challenging, particularly in terms of solubility, which led to further attempts towards HBC-

based Pt(II) acetylides with $N^{\wedge}N^{\wedge}C$ ligands, which were hoped to exhibit improved properties. The majority of this chapter will describe attempts towards these $N^{\wedge}N^{\wedge}C$ complexes (Fig. 3.9 (b)).

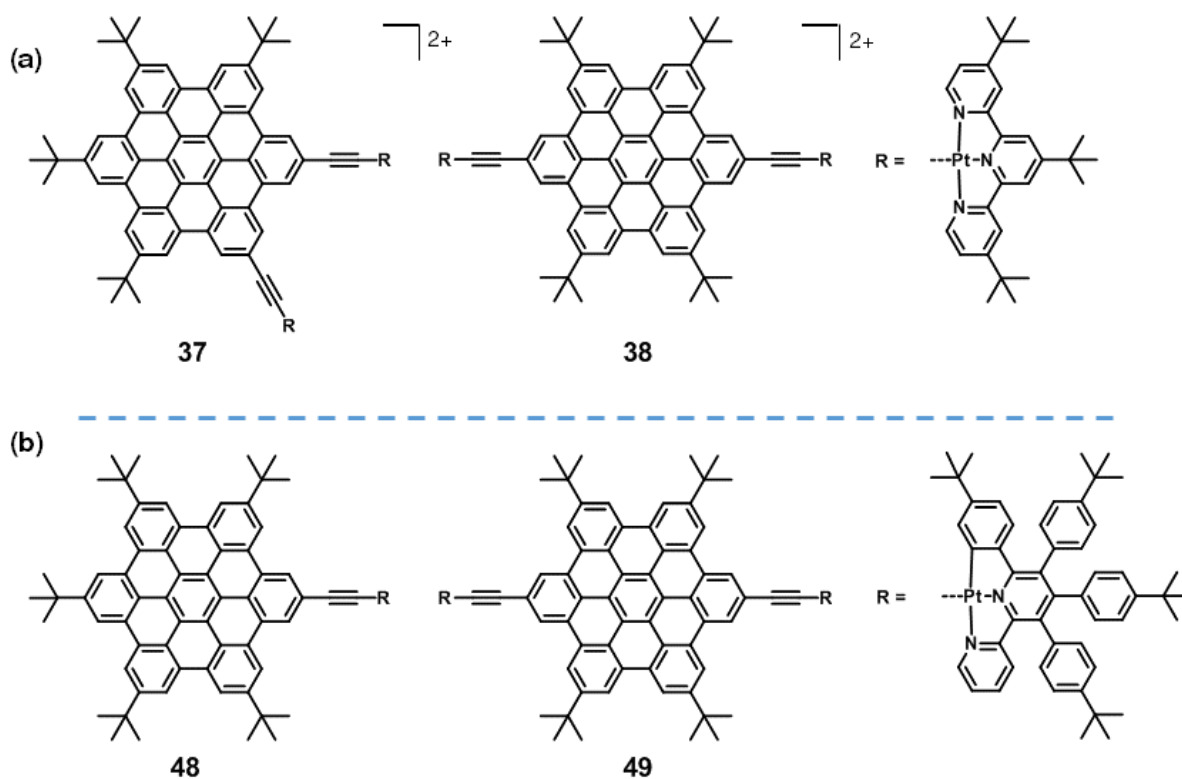
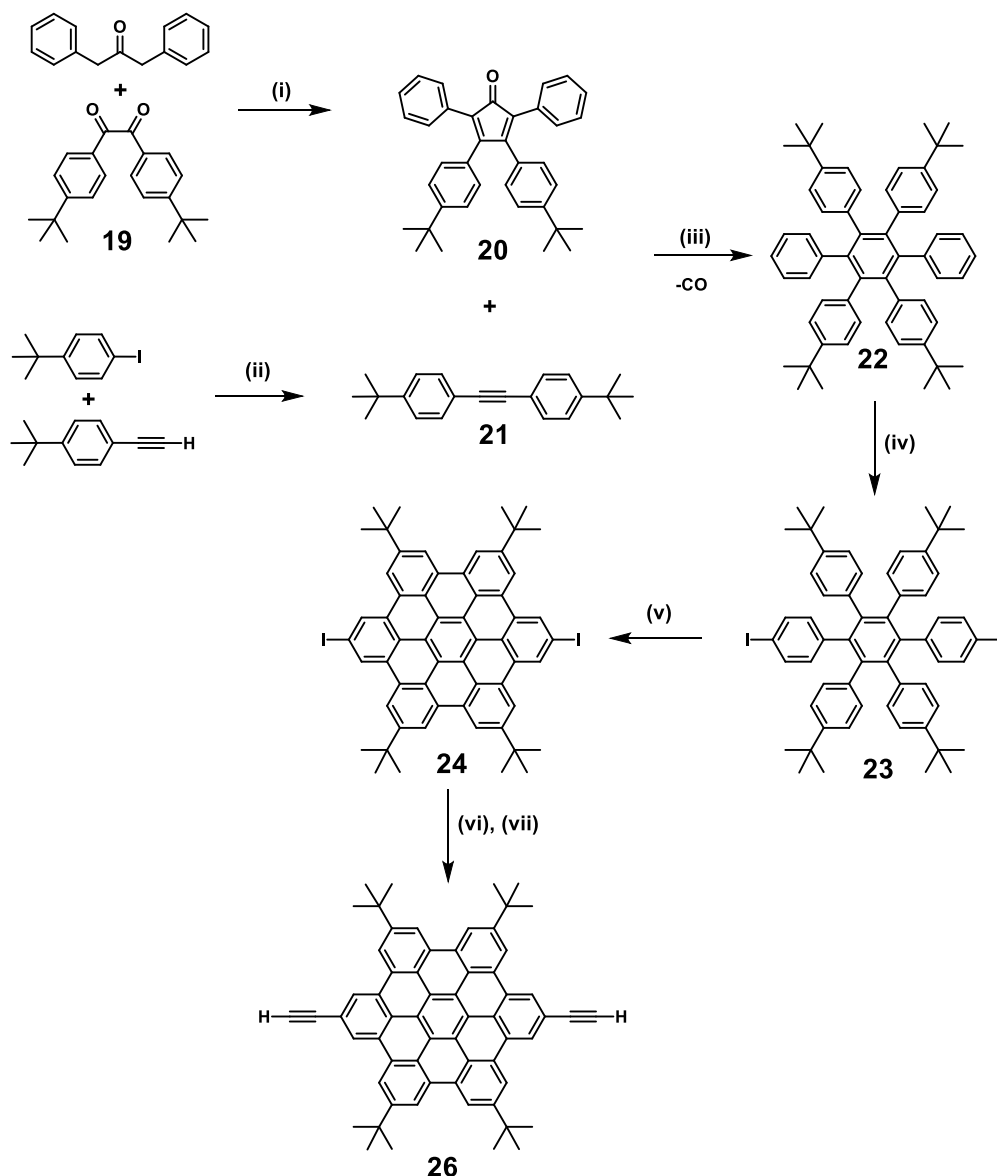


Figure 3.9: Target Pt(II) acetylide complexes, (a) with $N^{\wedge}N^{\wedge}N$ -coordinated ligands and (b) $N^{\wedge}N^{\wedge}C$ -coordinated ligands.

3.2 Synthesis of Pt-Substituted HBCs with N[^]N[^]N-Based Ligands

3.2.1 Preparation of Ethynyl-HBC Precursors

According to the synthetic strategy developed by Sonogashira *et al.* towards platinum acetylides, two distinct units are required, a platinum chloride precursor and a suitably functionalised terminal alkyne. The target molecules, Pt(II) acetylides with HBC cores, can thus be broken down into these two precursors *e.g.* a platinum chloride derivative featuring a terpyridyl ligand, and a HBC unit featuring the desired terminal alkyne units, in the required *ortho* or *para* arrangements. If the synthetic procedure were to be attempted the other way, it would require selective deprotection of the acetylide unit *i.e.* initial deprotection on one side for coupling with the chloride complex, and subsequently deprotection of the remaining side for coupling to the HBC unit. As this was envisaged to be synthetically quite challenging, the method of first functionalising the HBC with terminal alkyne units, and then coupling with the chloride precursor was thought to be the most favourable route to proceed with, and has already been proven to be effective in the literature. The preparation of these complexes began with the functionalisation of the HBC core with ethynyl substituents in both the *ortho* and *trans* positions. It was anticipated that these disubstituted HBCs could then undergo the copper(I) catalysed dehydrohalogenation reaction with suitable Pt precursors, as reported by Sonogashira *et al.* The synthetic procedure to generate the required HBC precursors began with the *para* derivative, in accordance with the general scheme below (Scheme 3.4).



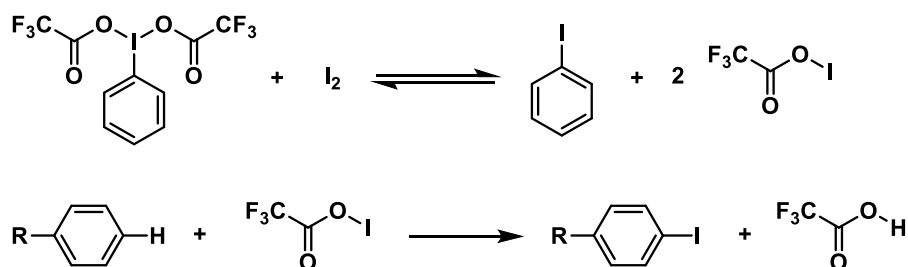
Scheme 3.4: Synthetic procedure towards **26**. (i) KOH, EtOH, reflux, 2 h, 65 %. (ii) $\text{Pd(PPh}_3)_2\text{Cl}_2$, CuI, piperidine, 18 h, 87 %. (iii) Ph_2CO , 350 °C, 4 h, 59 %. (iv) PIFA, I_2 , CH_2Cl_2 , CHCl_3 , 48 h, 66 %. (v) DDQ, $\text{CF}_3\text{SO}_3\text{H}$, CH_2Cl_2 , RT, 2h, 76%. (vi) (triisopropylsilyl)acetylene, $\text{Pd(PPh}_3)_4$, CuI, piperidine, 55 °C, 18 h, 45 %. (vii) TBAF, THF, RT, 2h, 89 %.

The synthesis began with the preparation of 1,2-bis-(4-*tert*-butylphenyl)ethane-1,2-dione (diketone **19**) by the method of Mueller-Westerhoff *et al.*⁴¹ This reaction involved the lithiation of 4-*tert*-butyl-bromobenzene with *n*-BuLi at -78 °C in THF, and subsequent reaction with DMPD (1,4-dimethylpiperazine-2,3-dione), with quenching of the reaction by HCl. The DMPD (**18**) was itself prepared from a procedure established in the same paper, from the reaction of equal amounts of diethyl oxalate and N,N'-dimethylethylene-diamine in

diethyl ether. The cyclopentadienone precursor **20** was then prepared *via* a double Knoevenagel condensation between the diketone and the commercially available 1,3-diphenylpropan-2-one in refluxing EtOH, in the presence of KOH (Scheme 3.4). This was easily obtained from the reaction mixture upon cooling and filtering, with no further purification required. A subsequent Diels-Alder cycloaddition with 1,2-bis(4-(tert-butyl)phenyl)ethyne **21** generated the desired hexaphenylbenzene derivative, which was isolated in 59 % yield by precipitation with a mixture of CH₂Cl₂ and MeOH. The 1,2-bis(4-(tert-butyl)phenyl)ethyne (**21**) was prepared according to the method of Herwig *et al.* and involved the Sonogashira coupling of the commercially available 1-(tert-butyl)-4-iodobenzene and 1-(tert-butyl)-4-ethynylbenzene in piperidine, with CuI and Pd(PPh₃)₄ as catalysts.⁴²

With the hexaphenylbenzene derivative **22** prepared, it was then possible to introduce the required iodine functionality. Whilst it is synthetically much more facile to incorporate bromo-substituents into such a system, it has been noted in the literature, and in previous work by the author, that bromo substituents on hexaphenylbenzene or HBC scaffolds appear quite deactivated in comparison with other aryl systems.⁴³ It has been suggested that this is either because the lability of the bromine atoms is decreased once attached to such an electron-rich system, or that these compounds act as efficient Pd(II) ligands.⁴³ Since iodo-functionalities are more reactive in Sonogashira coupling reactions, it was decided that this was the most promising route to avoid low yields in coupling reactions. The route followed here is the most synthetically facile. Following a procedure developed by Merkushev *et al.* for the iodination of aromatic compounds (Scheme 3.5),⁴⁴ and which was initially extended to HBC systems by F. Murphy of the Draper group,⁴⁵ it was possible to introduce iodine substituents to the unsubstituted phenyl rings of the hexaphenylbenzene **22**. This was achieved by reaction of **22** with I₂ (in slight excess) in the presence of (bis(trifluoroacetoxy)iodobenzene) (PIFA, approximately 2 equivalents) in a mixture of CH₂Cl₂ and CHCl₃. The reaction proceeds through PIFA reacting with iodine to produce iodobenzene and trifluoroacetylhypoiodide. The trifluoroacetylhypoiodide is relatively unstable and reacts with a phenyl group by electrophilic aromatic substitution to form the desired iodinated product, and also trifluoroacetic acid as a side product (Scheme 3.4). In the case of **23**, iodination only occurred at the unsubstituted *para* positions, and workup was achieved by washing with Na₂S₂O₄ solution to remove residual iodine, yielding the product in 66 % yield. The yield of this same compound has been previously reported as 92 %, ⁴⁶ but

this was not achieved in this instance. It was noted that further small amounts of iodine were required to be added over the course of the reaction in order to drive the process, with progress being monitored by TLC.



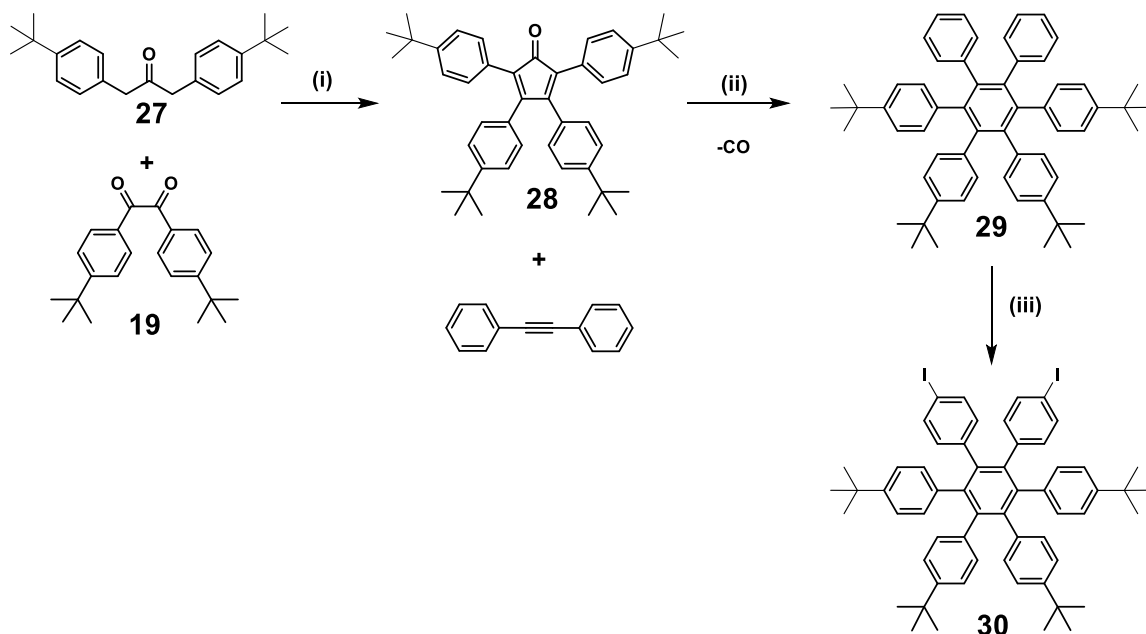
Scheme 3.5: General scheme for the formation of aryl iodides via the method of Merkushev et al.⁴⁴

The synthetic procedure then continued with intramolecular cyclodehydrogenation, in order to generate the desired fully-fused HBC system. Previous work in the Draper group towards **24** (Scheme 3.4) has employed FeCl_3 as oxidant in a mixture of nitromethane and CH_2Cl_2 . This gave the cyclodehydrogenated compound **24** in 81 % yield.⁴⁵ Following the recent reports of DDQ being successfully employed as an oxidant in the cyclodehydrogenation process,⁴⁷ it was decided to investigate its efficacy in this particular system. Compound **23** was dissolved in dry CH_2Cl_2 under N_2 , and six equivalents of DDQ were added. After stirring at RT for 15 minutes, trifluoromethanesulfonic acid was added (6 equivalents). Immediately a dark red colour was observed and the solution was stirred for 2 hours. The mixture was neutralised by K_2CO_3 and a yellow solid was precipitated with CH_2Cl_2 and MeOH in 76 % yield. The yield for this process is therefore slightly lower than with the FeCl_3 , although very similar. The greater ease with which the DDQ-mediated process may be undertaken still makes it an attractive method for the generation of these compounds. The FeCl_3 method requires both freshly distilled nitromethane and CH_2Cl_2 and requires a more complex experimental setup, including being bubbled continuously with a stream of N_2 (least 12 hours), whereas the DDQ process is generally complete in 2 hours and requires only dry CH_2Cl_2 as solvent.

The cyclised *para*-iodo HBC, **24**, was then functionalised with (triisopropylsilyl)acetylene through standard Sonogashira cross-coupling methodology, with CuI and $\text{Pd}(\text{PPh}_3)_4$ as catalysts, and piperidine as solvent and also as the required base (Scheme 3.4). The *para*-iodo HBC **24** was insoluble in piperidine, yet as the reaction proceeded, it gradually dissolved due to the solubilising effects of the bulky TIPS

(triisopropylsilyl) groups. It was found that the reaction did not proceed in THF/triethylamine, most likely due to solubility issues. The *para*-TIPS ethynyl-HBC was isolated through purification on SiO₂ using a mixture of hexanes and CH₂Cl₂ (9:1 v/v), giving **25** in 45 % yield. This compound displayed low solubility in CH₂Cl₂, which was then further decreased once the TIPS protecting groups were removed. This was possibly due to an increase in aggregation/ π - π stacking of the more planar deprotected *para*-ethynyl-HBC, which the TIPS groups had previously disrupted. The deprotection of **25** was achieved by the use of TBAF (tetrabutylammonium fluoride) in THF, stirring for 2 hours at RT, and yielding the *para*-substituted diethynyl-HBC **26** in 89 % yield.

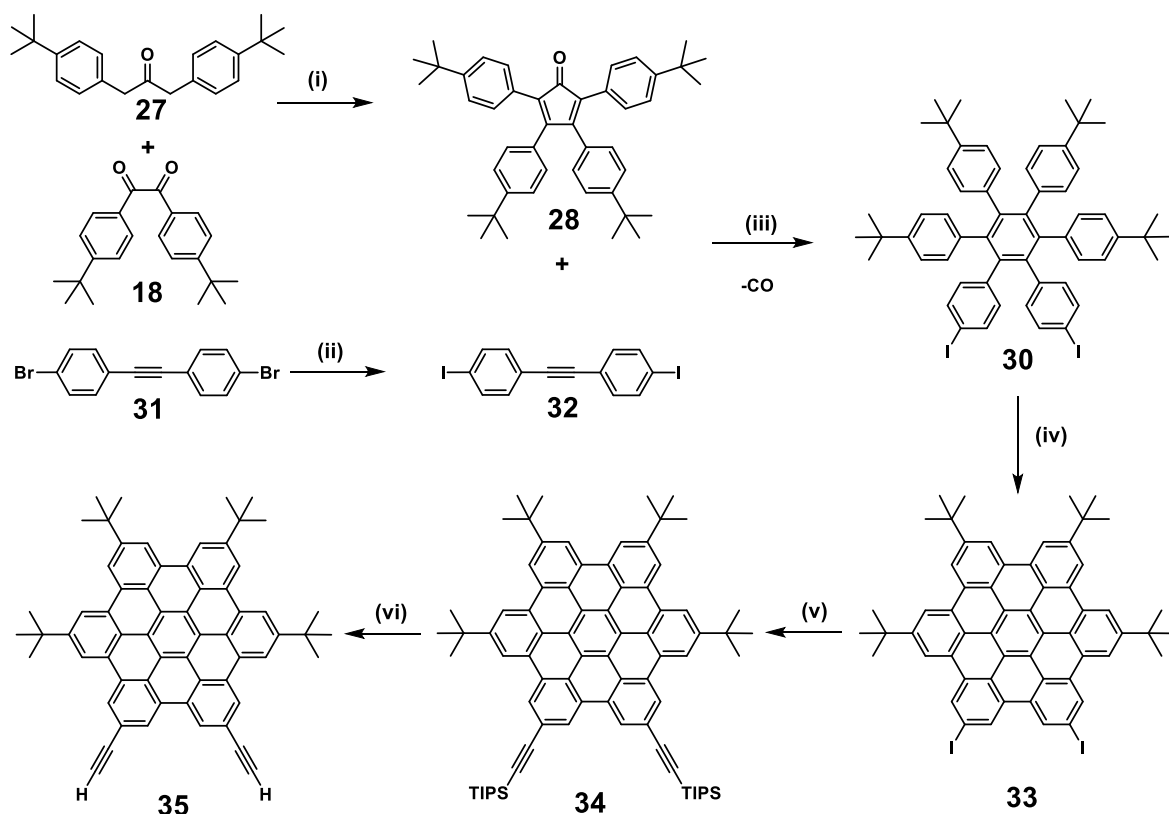
The *ortho* analogue was prepared with very similar methodology as for the *para*-ethynyl-HBC. First, the required cyclopentadienone **28** was prepared from the *tert*-butyl substituted monoketone **27** and diketone **19**. The *tert*-butyl substituted monoketone was prepared according to the method of Des Abbayes *et al.*⁴⁸ The cyclopentadienone **28** was then used to generate the required hexaphenylbenzene, through a Diels-Alder cycloaddition with the commercially available diphenylacetylene. This resulted in a hexaphenylbenzene, **29**, which was unsubstituted in the *ortho* positions. Subsequently, the same methodology was used to introduce iodo functionalities into these positions (*i.e.* treatment with PIFA and I₂ in CH₂Cl₂ and CHCl₃) (Scheme 3.6).



Scheme 3.6: Initial synthetic pathway towards *ortho*-substituted ethynyl-HBC **30**. (i) KOH, EtOH, reflux, 2.5 h, 47 %. (ii) Ph₂CO, 350 °C, 4 h, 89 %. (iii) PIFA, I₂, CH₂Cl₂, CHCl₃, 48 h, 50 %.

This step proved problematic, as mixtures of mono-iodinated and di-iodinated products were obtained in a very sluggish process, even after several subsequent additions of I₂ and PIFA. The iodination process appeared less efficient for the *ortho* compound compared to the *para* compound. Although yields of up to 73 % have been reported for this same reaction,⁴⁶ after repeating this experiment and again receiving mixed products in low yields, it was therefore decided that better yields might be obtained through introduction of the iodo-functionalities through the acetylene precursor. The most facile route towards 1,2-bis(4-iodophenyl)ethyne was judged to be *via* the generation of the bromo-substituted analogue, 1,2-bis(4-bromophenyl)ethyne and then to exchange the bromo substituents for iodo, by lithiation, according to the procedure reported by Bertrand *et al.*⁴⁹ To this end, the 1,2-bis(4-bromophenyl)ethyne **31** was prepared by Sonogashira cross-coupling (Scheme 3.8), and then was treated with *n*-BuLi at -78 °C in THF. A solution of I₂ in THF was added slowly by cannula, and the mixture was stirred for 4 hours. The product, 1,2-bis(4-iodophenyl)ethyne **32**, was precipitated from CH₂Cl₂ and MeOH in 38 % yield. This low yield may have been due to quenching of the *n*-BuLi from residual water in the solvent or reagents, but enough product was obtained to facilitate the next steps (Scheme 3.7).

A Diels-Alder cycloaddition between the cyclopentadienone **28** and 1,2-bis(4-iodophenyl)ethyne **32** was carried out in benzophenone at 250 °C for 1 hour (Scheme 3.7), followed by 350 °C for 3 hours. Purification by column chromatography (SiO₂, hexane:CH₂Cl₂ 8:2 v/v) yielded **30**. The intramolecular cyclodehydrogenation and subsequent coupling of (triisopropylsilyl)acetylene were then carried out in the same manner as for the *para*-substituted ethynyl-HBC. This yielded the *ortho*-substituted (triisopropylsilyl)ethynyl-HBC **34** which was then deprotected with TBAF in THF to yield the desired *ortho*-ethynyl-HBC **35**, which was observed to be relatively insoluble in common organic solvents.



Scheme 3.7: Modified synthetic pathway to *ortho*-substituted ethynyl-HBC **35**. (i) KOH, EtOH, reflux, 2.5 h, 47 %. (ii) *n*-BuLi, I₂, THF, -78 °C 4h, 38 %. (iii) Ph₂CO, 350 °C, 4 h, 44 %. (iv) DDQ, CF₃SO₃H, CH₂Cl₂, 2 h, 81 %. (v) (triisopropylsilyl)acetylene, Pd(PPh₃)₄, CuI, piperidine, 55 °C, 18 h, 42 %. (vi) TBAF, THF, RT, 2h, 80 %.

3.2.2 Characterisation of Ethynyl-HBC Precursors

The ethynyl-HBC precursors were characterised by ¹H NMR spectroscopy, HRMS, and FTIR. The ¹H and ¹³C{¹H} NMR spectra of both the hexaphenylbenzene compounds, **23** and **30** (i.e. uncyclised) agreed with a previous report.⁴⁵ The cyclodehydrogenated *ortho* and *para*-substituted diiodo-HBC **24** and **33**, previously prepared by FeCl₃ mediated cyclodehydrogenation rather than DDQ/H⁺, were also in agreement with previous reports, and the NMR data is summarised in the experimental chapter.^{45, 50} The poor solubility of these precursors precluded well-resolved ¹³C{¹H} NMR data from being obtained. The coupling of the *para*- and *ortho*-substituted diiodo-HBCs with TIPS-acetylene and subsequent deprotection with TBAF (tetrabutylammonium fluoride) in THF led to the precursor *para*- and *ortho*-ethynyl-HBC precursors **26** and **35** required for the synthesis of acetylide complexes. These quite insoluble precursors were then characterised by NMR

spectroscopy and their ^1H NMR spectra are displayed in Figure 3.10. Their synthesis was further confirmed by HRMS, with the results summarised in Table 3.1.

Table 3.1: Mass Spectral Analysis (HR MALDI-TOF) for compounds **26** and **35** (m/z in $m.u.$)

Compound	Formula	Calculated m/z	Found m/z	Molecular Ion
26	$\text{C}_{62}\text{H}_{50}$	794.3913	794.3914	$[\text{M}^+]$
35	$\text{C}_{62}\text{H}_{50}$	794.3913	794.3942	$[\text{M}^+]$

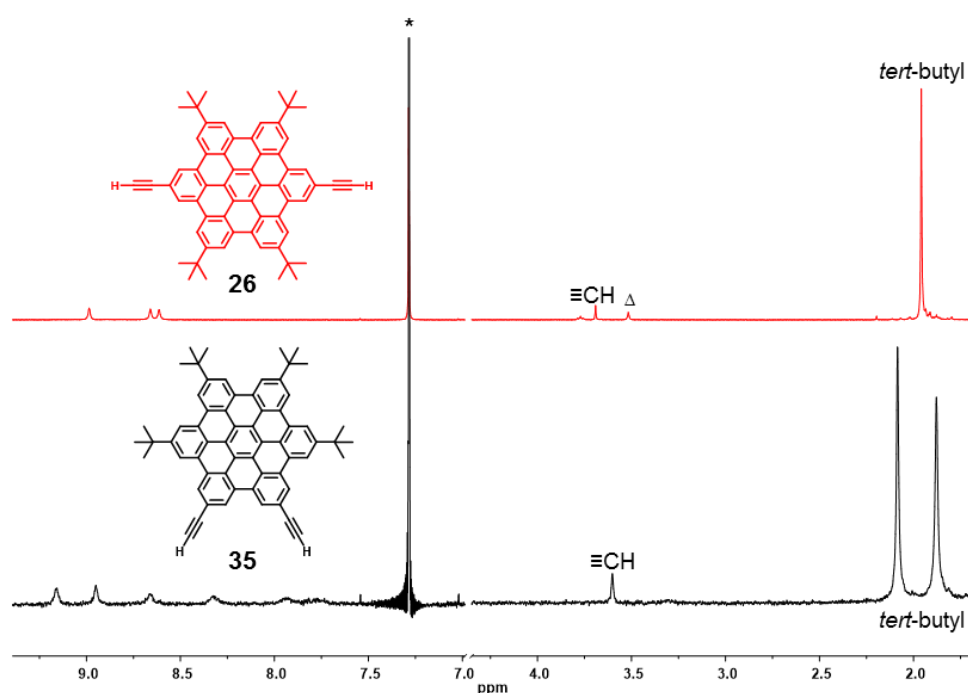


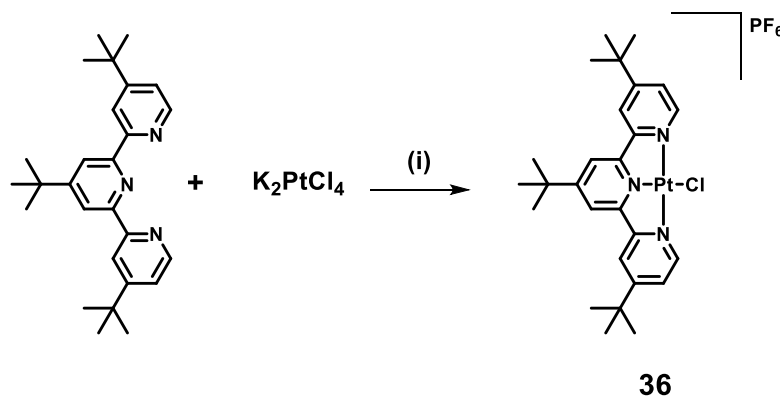
Figure 3.10: ^1H NMR spectra of **26** and **35** (400 MHz, CDCl_3 , RT. * denotes residual chloroform solvent peak, and Δ denotes residual MeOH. For clarity the spectrum is edited between 4.5 and 7.0 ppm).

In the same manner as for the iodo-HBC compounds, the extent of the π - π stacking of these compounds led to a very high degree of insolubility which precluded full NMR analysis. However, the ^1H spectra conform to the expected pattern, and are similar to those the cyclodehydrogenated iodo-precursors. For **26**, there are three singlets observed at δ 8.98, 8.66 and 8.61 ppm, corresponding to the expected three equivalent types of proton signals. The *tert*-butyl peak is clearly observed as a singlet at δ 1.96 ppm, since all the *tert*-butyl protons are chemically equivalent. The proton signal corresponding to the terminal alkyne units is assigned to the peak visible at δ 3.68 ppm, which is in the expected region. The

integration values agree with these assignments. The ^1H NMR spectrum of **35** also displays the expected number of peaks, although poorly resolved. There are six equivalent types of aromatic proton in this system, and correspondingly, there are six peaks observed in the aromatic region, three of which are very broad. In contrast to the spectrum of **26**, there are two distinct tert-butyl peaks corresponding to the two different environments. The terminal acetylene protons are assigned to the peak visible at δ 3.60 ppm.

3.2.3 Synthesis of N[^]N[^]N Pt(II) Complexes

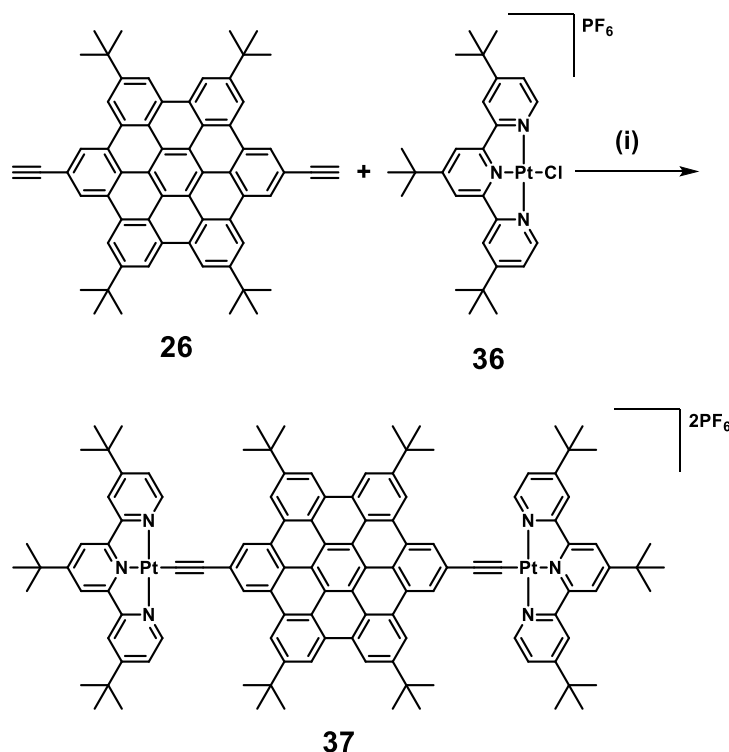
Following on from the successful preparation of the *ortho* and *para* ethynyl-HBC units, the synthesis of the target Pt(II) acetylides continued with the preparation of the required Pt(II) terpyridine precursor (Scheme 3.8). This followed a literature procedure,⁵¹ whereby K_2PtCl_4 was combined with the commercially available ligand 4,4',4''-tri-tert-butyl-2,2':6',2''-terpyridine ($^t\text{Bu}_3\text{tpy}$) in a mixture of water and CH_3CN and heated to reflux for 24 hours. The resulting yellow solution was filtered hot into an aqueous solution of KPF_6 to give a yellow solid, the complex $[\text{Pt}(^t\text{Bu}_3\text{tpy})\text{Cl}]\text{PF}_6$ (**36**), which was then subsequently filtered. This compound was characterised by ^1H NMR spectroscopy, $^{13}\text{C}\{^1\text{H}\}$ NMR, and HRMS.



Scheme 3.8: The preparation of platinum precursor complex **36**. (i) $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, reflux, 24 h, KPF_6 (aq.), 37 %.

The preparation of **36** led to the final stages of synthesis of the target compounds. This was achieved according to the same method as employed by Sonogashira *et al.*, a copper iodide-catalysed dehydrohalogenative coupling between the terminal alkyne-functionalised HBCs **26** and **35** and the $[\text{Pt}(^t\text{Bu}_3\text{tpy})\text{Cl}]\text{PF}_6$ complex **36**. In the case of the *para*-substituted **37**, this was achieved by stirring **26** and the $[\text{Pt}(^t\text{Bu}_3\text{tpy})\text{Cl}]\text{PF}_6$ precursor under N_2 in freshly

distilled and degassed CH_2Cl_2 and diisopropylamine (DIPA), in the presence of CuI (Scheme 3.9).



Scheme 3.9: Synthetic scheme towards **37**. (i) CuI, CH_2Cl_2 , DIPA, RT.

The result was a highly insoluble red precipitate, which was isolated by filtration. HRMS indicated that the desired product (**37**) had indeed been produced, but also displayed some impurities, which TLC analysis also confirmed. Close analysis of the MALDI-TOF mass spectrum of **37** (Fig. 3.11) reveals that although the desired product is observed, the mono-platinated analogue is also present (*i.e.* where only one of the two ethynyl units has coupled to the $[\text{Pt}(\text{tBu}_3\text{tpy})\text{Cl}]\text{PF}_6$), which is found at $m/z = 1389.6340$ (calc. $m/z = 1389.6313$). It is possible the mono-substituted product is apparent in the mass spectrum due to fragmentation, but the multiple products observed by TLC suggest that the reaction has not gone to completion. Several other unknown impurities are also present in the mass spectrum, including a peak at $m/z = 2380.9878$, which may correspond to three of the ethynyl-HBC units homo-coupled together (calc. $m/z = 2379.1425$), a possible example of Glaser coupling. NMR analysis of the crude material did not produce satisfactory spectra, so purification by column chromatography and thin-layer TLC plate chromatography was attempted. This was severely hampered by both the tremendous insolubility and quite low

yield of the reaction. Mass-spectral analysis after purification by TLC plate still indicated a mixture of the fully-platinated and mono-platinated species.

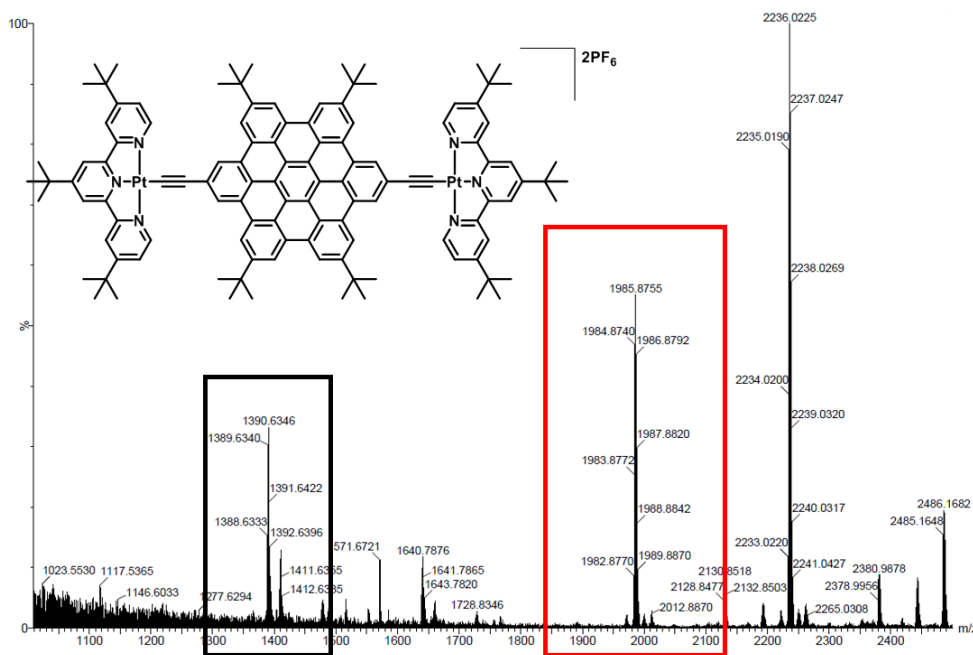
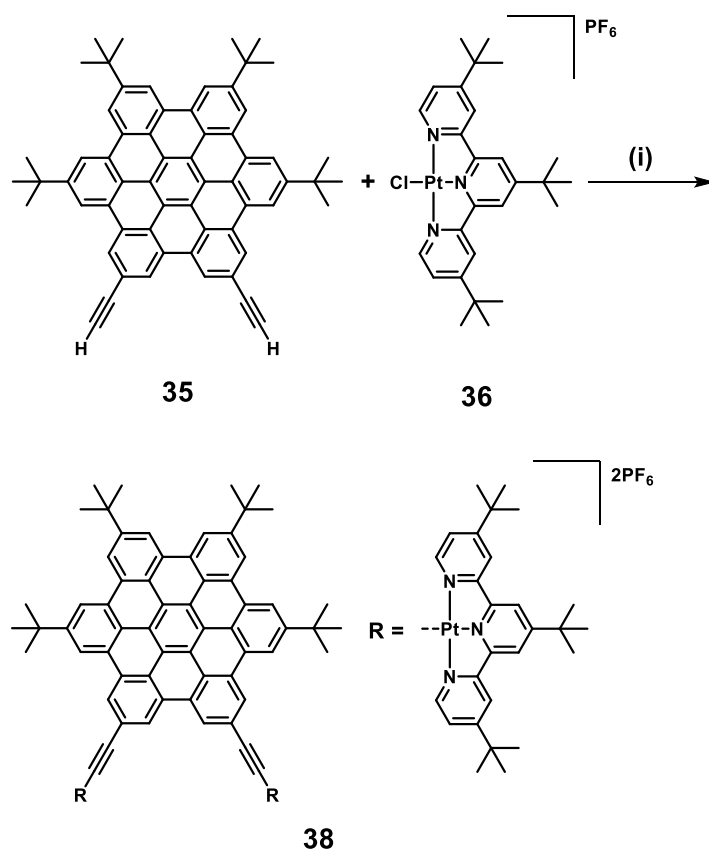


Figure 3.11: MALDI-TOF mass spectrum of **37** (in CH₂Cl₂), displaying the peak assigned to the desired product (highlighted in red) and the peak associated with the mono-platinated derivative (highlighted in black).

Bearing these difficulties in mind, attention was then turned to the *ortho*-substituted analogue, **38**, in the hope that it may display improved solubility. The synthetic procedure was followed in the same way as that for **37** (Scheme 3.10). Again, the resulting red solid was observed to be highly insoluble. MALDI-TOF mass spectral analysis (Fig. 3.12) once again showed that despite long reaction times (up to 72 hours), the mono-platinated derivative was once again present, this time in what appeared to be significantly higher concentration than for the *para* analogue. This suggests steric factors may be playing a role in this case. Attempts to purify the compound led to much difficulty and ever-dwindling yields, with MS analysis indicating that the compound remained impure. Therefore it was thought necessary to adopt a different synthetic strategy that would still incorporate the HBC cores, but would lead to compounds with improved properties for solution processing.



Scheme 3.10: Synthetic scheme towards **38**. (i) CuI, CH₂Cl₂, DIPA, RT.

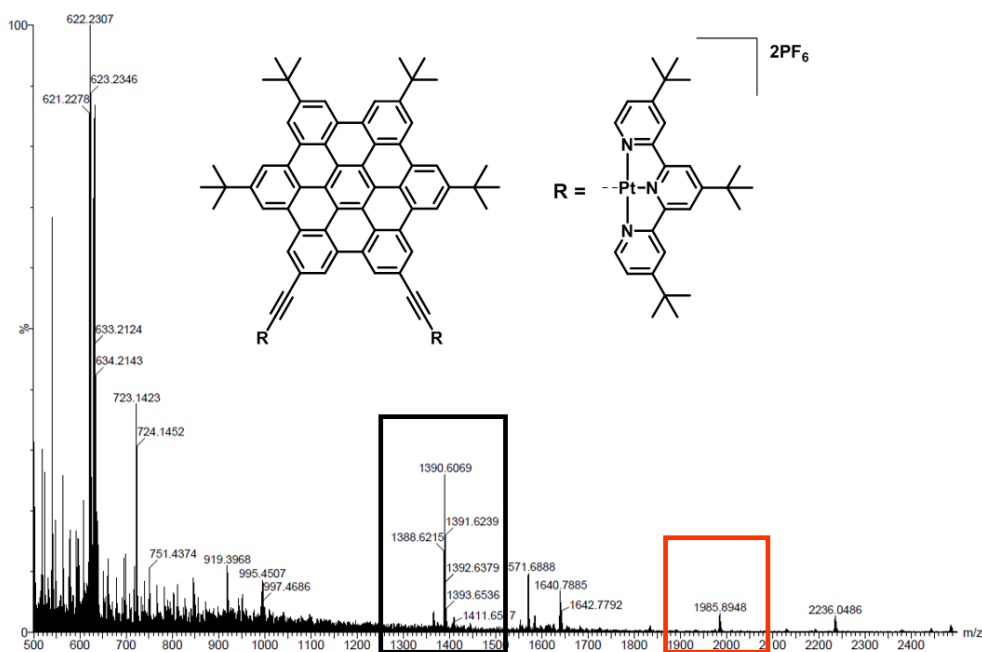


Figure 3.12: MALDI-TOF mass spectrum of **38** (in CH₂Cl₂), displaying the peak assigned to the desired product (highlighted in red) and the peak associated with the mono-platinated derivative (highlighted in black).

Table 3.2: Mass Spectral Analysis (HR MALDI-TOF) for compounds **37** and **38** (m/z in *m.u.*)

Compound	Formula	Calculated m/z	Found m/z	Molecular Ion
37	C ₁₁₆ H ₁₁₈ N ₆ Pt ₂	1984.8713	1984.8714	[M-2(PF ₆)] ⁺
38	C ₁₁₆ H ₁₁₈ N ₆ Pt ₂	1984.8713	1984.8748	[M-2(PF ₆)] ⁺

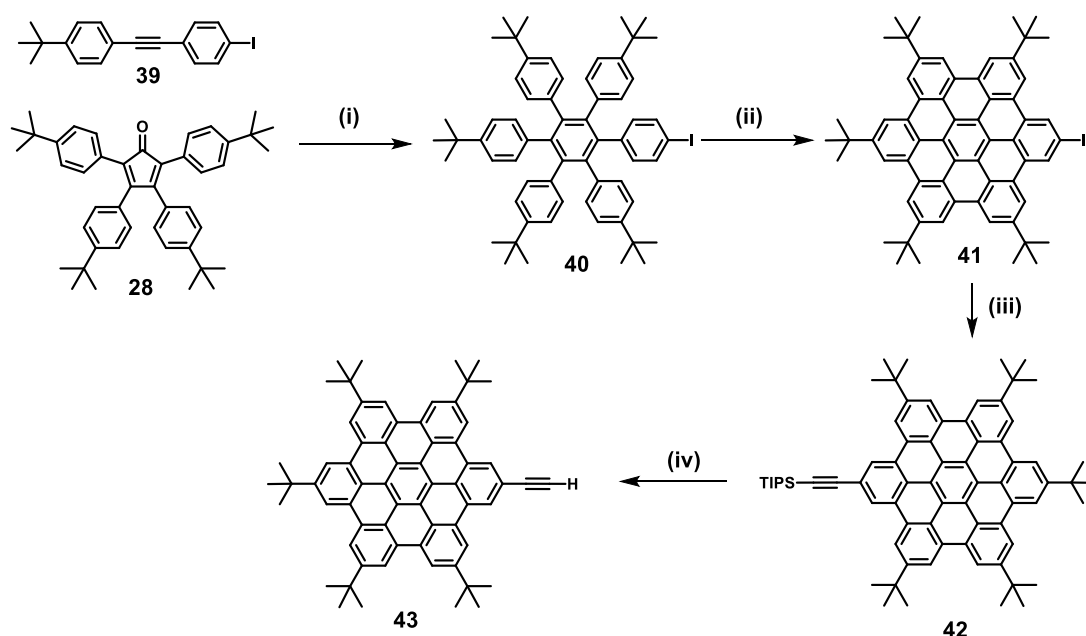
3.3 Synthesis of N[^]N[^]C Pt(II) Acetylides

3.3.1 Preparation of Ethynyl-HBC Cores

Given the insolubility problems encountered with N[^]N[^]N-type acetylides, it was decided to change from working with charged complexes to working with neutral complexes. Since cyclometallating N[^]N[^]C-type ligands have been investigated in the literature and found to have interesting photophysical properties, with a rigidity similar to that of N[^]N[^]N- type complexes, it was thought worthwhile to investigate their suitability towards making Pt(II) acetylide complexes of HBC which exhibited improved solubility. Rather than simply making an *ortho* and *para* derivative, it was thought more instructive to create a series of compounds which would act more effectively as comparators of the effects of inclusion of Pt(II) centres to the HBC core. Therefore, the aim then focused on generating a mono-substituted HBC (*i.e.* with one Pt(II) acetylide unit) and also to generate a *para*-substituted HBC. In this way, the effect on the photophysical properties of mono- and di-substituted HBC cores with Pt(II) acetylides could be investigated. It was also expected that a mono-substituted analogue would be more readily soluble.

The process towards making these began with the synthesis of the *para*-substituted di-ethynyl-HBC, in the same manner as described previously (Scheme 3.4). In order to also produce a mono-substituted analogue, it was therefore also necessary to produce the corresponding mono-substituted ethynyl-HBC **43**. This was prepared with similar methodology as previously described (Scheme 3.11). Beginning from the cyclopentadienone **28**, it was possible to introduce a single iodo functionality through a Diels-Alder cycloaddition with the alkyne 4-iodo-4'-*tert*-butylphenylacetylene (**39**). This alkyne was produced according to a literature method in reasonable yield (53 %), through the Sonogashira coupling of 1,4-diiodobenzene and 4-*tert*-butylphenylacetylene.⁵² A Diels-Alder cycloaddition in benzophenone solvent at approx. 310 °C between this acetylene and the relevant cyclopentadienone (**28**) yielded the iodo-hexaphenylbenzene **40** in 81 % yield.

Subsequently, this was then cyclodehydrogenated with a combination of DDQ and $\text{CF}_3\text{SO}_3\text{H}$ in CH_2Cl_2 to yield ‘iodo-HBC’ **41** as a red solid in 86 % yield, with no side-product formation (*e.g.* partially-fused derivatives). The introduction of the ethynyl functionality was again carried out in the same manner as before, with the exception that for the coupling reaction between iodo-HBC and TIPS-acetylene, it was possible to use a combination of THF and triethylamine rather than piperidine, due to the much higher solubility of the mono-substituted iodo-HBC, in comparison with the di-substituted forms discussed earlier. Purification of this compound, **42**, was by column chromatography on SiO_2 (petroleum ether: CH_2Cl_2 3:1 v/v), with the product eluting as an orange solid in 83 % yield. Preparation of the ethynyl-HBC, **43**, was then achieved through deprotection of **42** with TBAF in THF in 94 % yield, and which gave characterisation data in agreement with previous reports.⁴⁶



Scheme 3.11: Synthetic scheme towards **43**. (i) Ph_2CO , 310 °C, 4 h, 81 % yield. (ii) DDQ, $\text{CF}_3\text{SO}_3\text{H}$, CH_2Cl_2 , RT, 2 h, 86 %. (iii) Triisopropylsilylacetylene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , THF, Et_3N , RT, 18 h, 83 %. (iv) TBAF, THF, RT, 3 h, 94 %.

3.3.2 Characterisation of Ethynyl-HBC **43**

The mono-substituted ethynyl HBC **LC 97** (hereafter referred to as **43**) was characterised by NMR spectroscopy and HRMS, in good agreement with previous literature reports.^{45, 46} The ^1H NMR spectrum (Fig. 3.13) is presented here as a comparison with the di-ethynyl derivative, and also as a comparison with the corresponding Pt(II) acetylide derivative.

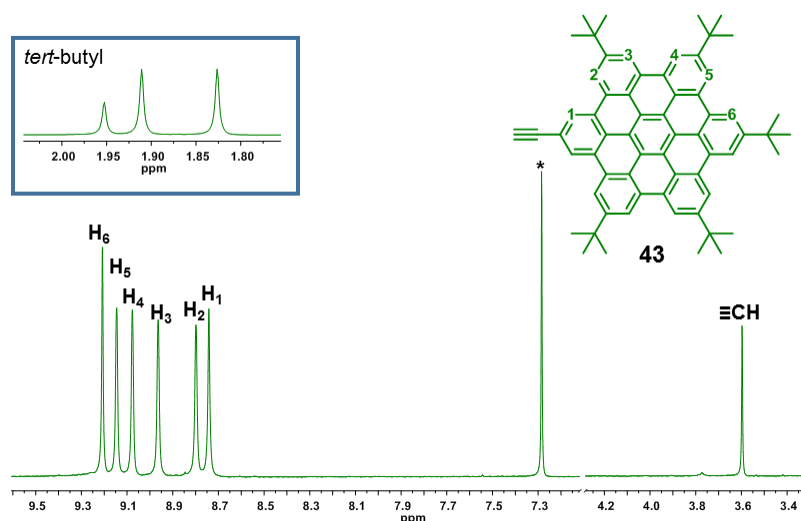


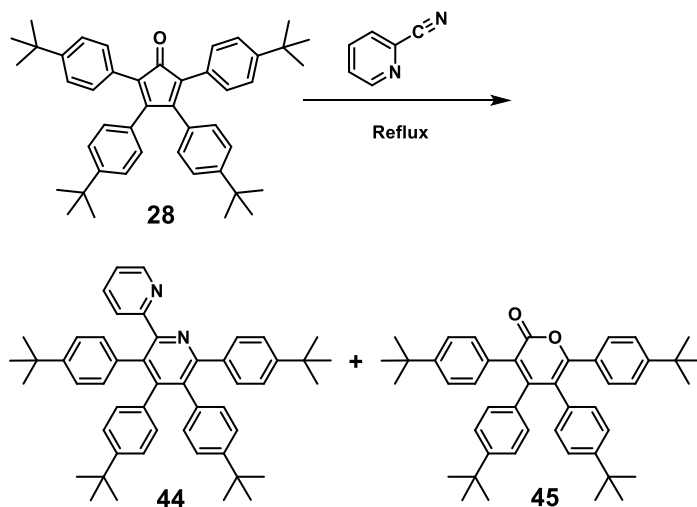
Figure 3.13: ^1H NMR spectrum of **43** (CDCl_3 , 400 MHz, RT). * denotes CHCl_3 residual solvent peak.

The ^1H NMR spectrum exhibits six distinct singlets in the aromatic region, along with the expected *tert*-butyl groups and also a singlet at 3.60 ppm, which is assigned to the terminal alkyne proton. Due to the symmetric nature of the molecule, there are two equivalent pairs of *tert*-butyls (*i.e.* they are in the same chemical environment), and another, in a different chemical environment, opposite the ethynyl unit. The *tert*-butyl group opposite the ethynyl unit is assigned to the most deshielded *tert*-butyl peak, which integrates for 9 protons. The spectrum is in agreement with a previous report.⁴⁶

3.3.3 Synthesis of N[^]N[^]C Precursors

Given the insolubility problems encountered earlier, it was decided to include *tert*-butyl solubilising groups in the new N[^]N[^]C ligand. The chosen ligand, 4-*tert*-butyl-substituted **44** (Scheme 3.12), was reported in the PhD thesis of C. Ollagnier, who interestingly noted that if the Diels-Alder cycloaddition was carried out in air, a lactone side-product was formed (**45**, Scheme 3.12).⁵³ The side product reduced the yield of the desired product to just 5.5 %, but under argon, the yield increased to 92 %. This side-product formation, the insertion of an oxygen atom into the five-membered ring, is an example of Baeyer-Villiger oxidation from atmospheric oxygen. First reported in 1899, the Baeyer-Villiger reaction generally involves the formation of lactones or esters from ketones, with

peroxides or peroxyacids as oxidants, proceeding *via* nucleophilic attack of the oxidant on the carbonyl group.⁵⁴ The use of atmospheric oxygen as an oxidant has been also reported.⁵⁵



Scheme 3.12: Synthetic route towards **44**, with lactone side-product formation (**45**).⁵³

The synthesis of **44** was achieved by Diels-Alder cycloaddition of **28** with 2-cyanopyridine for 30 hours at *ca.* 250 °C, giving the product in 44 % yield. The reaction was carried out in an inert atmosphere, yet the lactone side-product **45** was also observed in 16 % yield. Although the reaction mixture was degassed by vacuum/N₂ cycles, it is likely that some residual O₂ remained. Fortunately, it was possible to obtain crystals of the lactone side-product, which were suitable for x-ray crystallographic analysis, which was carried out by Dr. Brendan Twamley. The ORTEP plot in Fig. 3.14 (a) reveals the disorder in the lactone unit of 50 % across a two-fold axis and is modelled with ISOR restraints. The packing behaviour is displayed in Fig. 3.14 (b).

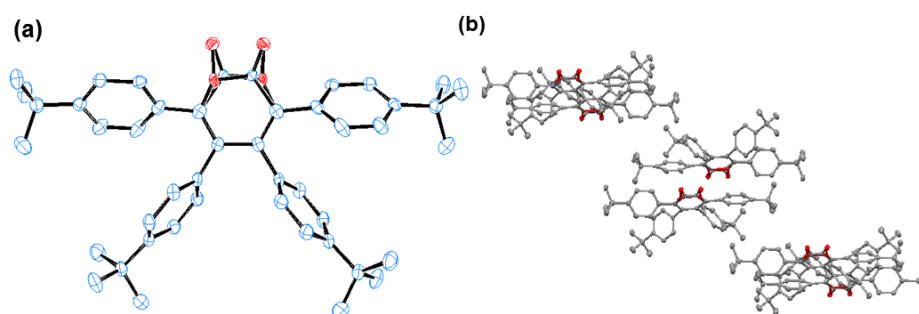
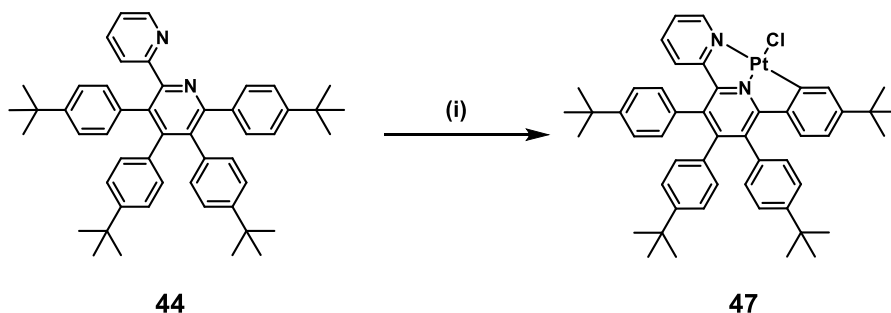


Fig. 3.14 (a) ORTEP plot of asymmetric unit of **45**, showing the disorder of 50 % over a two-fold axis. (b) Packing arrangement of **45**. Thermal ellipsoids shown at 50 %. Hydrogen atoms omitted for clarity.

With the N[^]N[^]C ligand **44** prepared, it was then possible to synthesise the platinum chloride derivative. The platinum source chosen this time was [PtCl₂(DMSO)₂], in the place of K₂PtCl₄. This was chosen due to the low yields encountered with the preparation of **36**, and it has been noted in the literature that the complex [PtCl₂(DMSO)₂], bearing labile DMSO ligands, is a useful and convenient source of Pt, and can lead to improved yields and cleaner reactions.⁵⁶ Reflux of **44** with [PtCl₂(DMSO)₂] (**46**) in chloroform and triethylamine for 24 hours gave **47** as an orange solid in good yield (Scheme 3.13, 83 %).



Scheme 3.13: The preparation of **47** from **44**. (i) PtCl₂(DMSO)₂, Et₃N, CHCl₃, 60 °C, 24 h, 83 %.

After precipitation from MeOH and drying, it was possible to characterise **47** by NMR spectroscopy (Fig. 3.16). Attempts to grow crystals large enough for single-molecule x-ray analysis were not successful from CH₂Cl₂ and MeOH, but slow evaporation from benzene yielded suitable crystals (crystallographic data is presented in the annex). Examination of the packing structure (Fig. 3.15) reveals a Pt-Pt distance of 4.465 Å, with a high degree of disorder observed in one of the pendant *tert*-butyl groups and three coordinated benzene molecules per unit cell. The crystal structure of **47** was solved by Dr. Brendan Twamley. The bond lengths around the Pt centre are presented in Table 3.3, according to the numbering scheme in Figure 3.15 (a), with the Pt-Cl bond exhibiting the greatest length.

Table 3.3: Bond length data around Pt centre of **47**. Values in brackets give estimated standard deviation.

Bond	Bond Length (Å)
Pt-Cl ₁	2.3024 (14)
Pt-N ₁	2.081 (5)
Pt-N ₈	1.963 (5)
Pt-C ₁₄	1.988 (6)

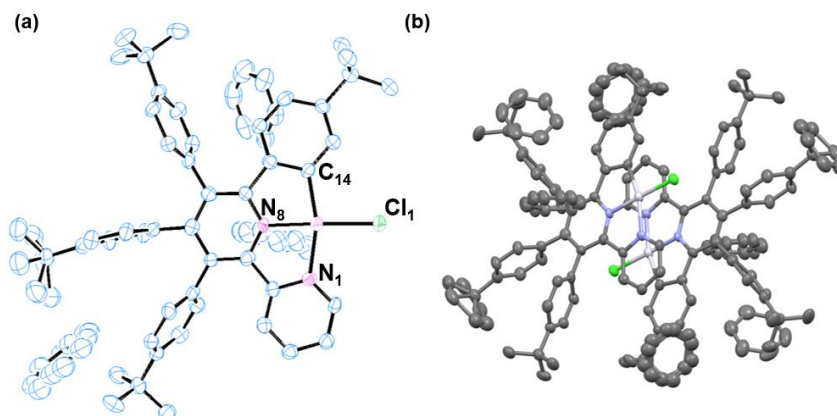


Figure 3.15: (a) Asymmetric unit of **47**, with three coordinated benzene molecules also present. (b) Packing structure of **47**. Thermal ellipsoids shown at 50 % probability and hydrogen atoms omitted for clarity.

3.3.4 Characterisation of N[^]N[^]C Precursors

A range of methods were employed to characterise the N[^]N[^]C precursor compounds **44**, **45** and **47**. The ¹H NMR spectrum of **44** is displayed in Fig. 3.16. This compound has been previously reported in the PhD thesis of C. Ollagnier (2005),⁵³ however it is useful to include it here as reference for later discussion of the NMR spectra of the final Pt(II) acetylide products.⁵⁷

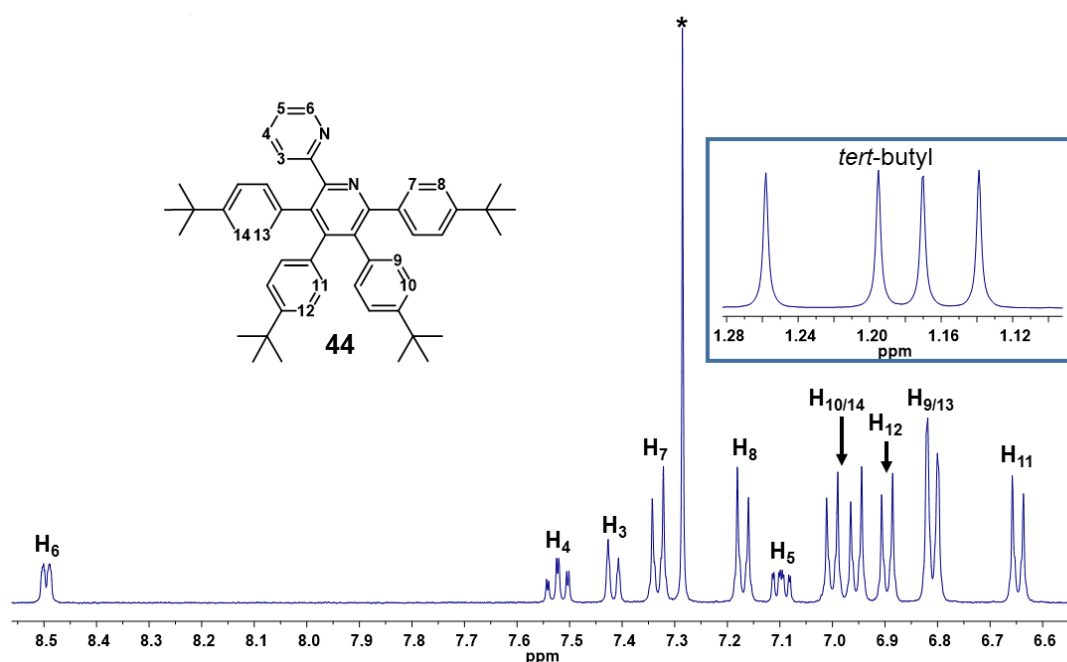


Figure 3.16: ¹H NMR spectrum of **44**, CDCl₃, 400 MHz, RT. * denotes residual solvent peak.

The proton NMR spectrum of **44** was assigned with the aid of ^1H - ^{13}C HSQC, 2D TOCSY (Fig. 3.17) and NOE (nuclear Overhauser spectroscopy) experiments. The most downfield signal is assigned to H_6 , the proton nearest the electron-withdrawing pyridine N. There are three other characteristic peaks integrating to one proton each, at δ 7.52, 7.42 and 7.10 ppm, which are also originating from the same pyridine ring. H_3 may be assigned based on its multiplicity as a doublet, as both H_4 and H_5 are expected to occur as triplets. These were differentiated through examination of a HMBC spectrum, as the proton signal assigned to H_3 gives an interaction with the carbon atom assigned to H_5 , three bonds away. This assignment agrees with the expected behaviour due to the inductive effects of the N atom (whereby H_4 and H_6 are the most deshielded). The four AB patterns from the four pendant phenyl rings are evident as doublets. These were assigned with the aid of TOCSY experiments, which showed the four spin systems. The most deshielded of the AB patterns may be assigned to H_7 and H_8 which are nearest the central pyridine N. Nuclear Overhauser experiments showed through-space correlations between H_7 and the overlapping doublets at δ 6.81 ppm, indicating that H_9 may be assigned here, and also between H_3 and the same doublet at δ 6.81 ppm, indicating that H_{13} may also be assigned here. Therefore the least deshielded set of doublets may be assigned to H_{11} and H_{12} , with H_{12} being most deshielded as is expected.

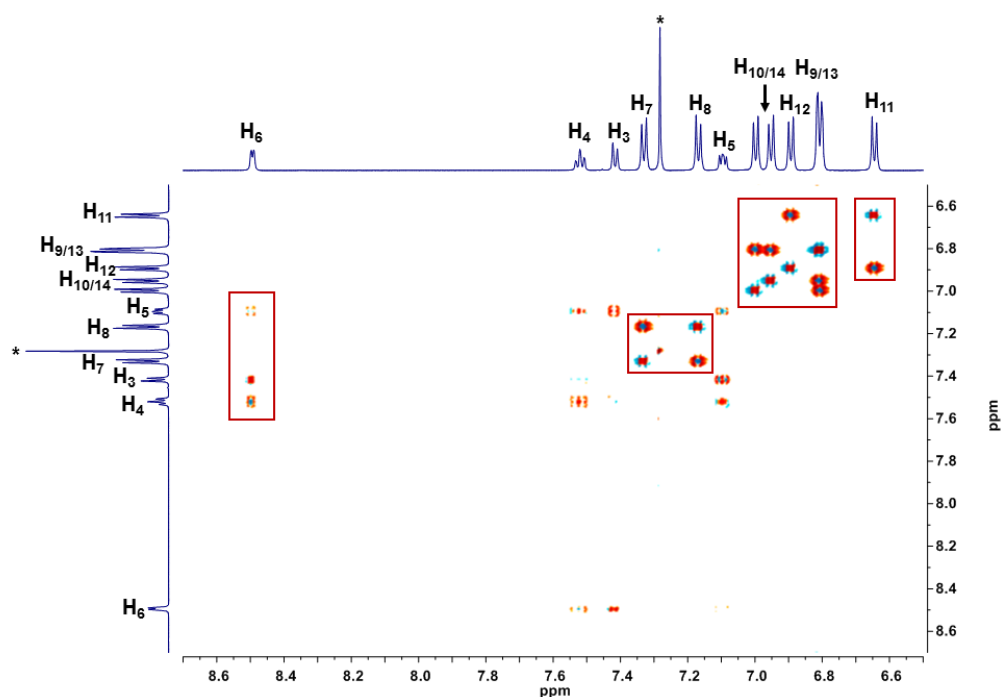


Figure 3.17: The ^1H - ^1H TOCSY experiment used to aid the assignment of **44**, with the spin systems highlighted in red (CDCl_3 , 400 MHz, RT).

The lactone side-product **45** was also characterised by ^1H NMR spectroscopy and the spectrum is displayed in Figure 3.18. Although this compound had been previously reported, the NMR spectra remained unassigned. A combination of TOCSY, HMBC, NOESY (nuclear Overhauser spectroscopy) and ROESY (Rotating-frame Overhauser spectroscopy) was used to fully elucidate the ^1H and ^{13}C of **45**. The ^1H NMR spectrum exhibits seven signals in the aromatic region, all appearing as doublets, and also four singlet peaks between δ 1.14 and δ 1.28 ppm, which account for the *tert*-butyl protons. In the aromatic region, there are four pairs of AB systems, with an overlapping pair at δ 7.06 ppm. A 2D-TOCSY experiment permitted the four different spin systems, corresponding to the four phenyl rings, to be visualised. Each of these rings experiences a different chemical environment due to the unsymmetrical nature of the molecule. The TOCSY showed that the most deshielded signal at δ 7.33 ppm exhibits a correlation with the signal at δ 7.21 ppm. The peak at δ 7.33 ppm is assigned to the proton which is closest to the electron-withdrawing oxygen within the central lactone ring, H₆. Based upon its spin-spin correlation with the signal at δ 7.21 ppm, this signal may be assigned as H₇. An NOE experiment showed that the *tert*-butyl protons at 1.28 ppm have a through-space interaction with the H₇ protons, confirming the position of the protons H₇ on the ring. Subsequent examination of the HMBC experiment (Fig. 3.19, inset) revealed that the *tert*-butyl protons labelled H₁₀ display a correlation with the ^{13}C signal at δ 152.5 ppm, which in turn also correlates with H₇ at δ 7.33 ppm. The protons labelled H₆ also display a three-bond correlation with C₄, the ^{13}C signal at δ 155.8 ppm, which is deshielded due to its proximity to the central oxygen atom. Investigation of the three-bond interactions (*via* the HMBC experiment) of H₇ concluded that they display interactions with the ^{13}C signals at δ 130.0 (C₅) and δ 34.7 (C₉) ppm. The very upfield signal at δ 34.7 is therefore the quaternary carbon attached to the *tert*-butyl groups, leaving the signal at δ 130.0 ppm as the quaternary carbon *para* to the *tert*-butyl group. The use of the TOCSY and HMBC experiments permitted the assignment of the rest of the ^1H and ^{13}C resonances of the phenyl rings in the same manner, with the 2D NOE confirming which *tert*-butyl signal was associated with each phenyl ring.

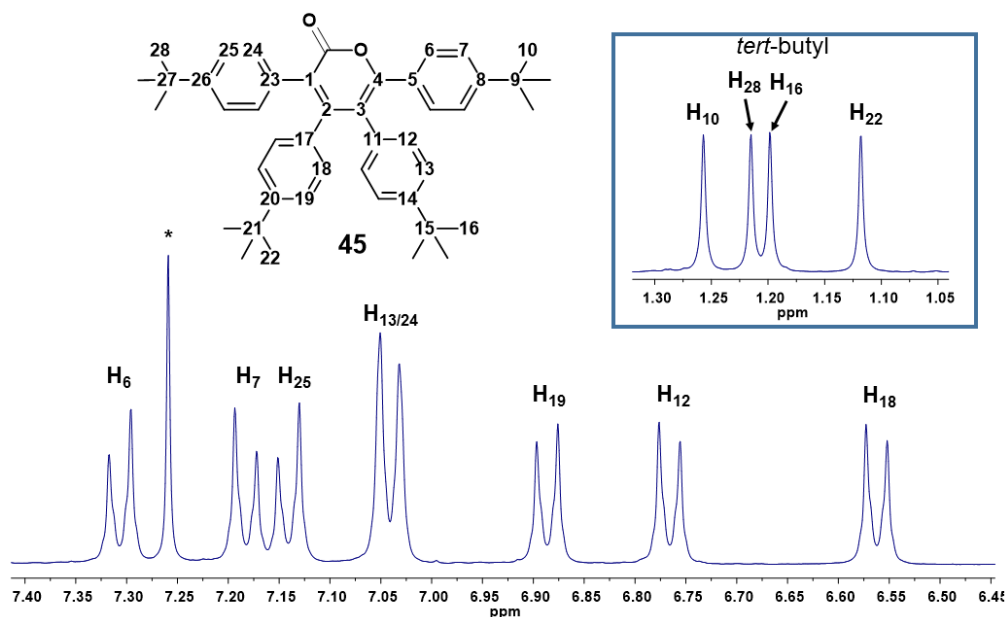


Figure 3.18: ^1H NMR spectrum of **45** (CDCl_3 , 400 MHz, RT). * denotes residual solvent peak.

The definitive assignment of the location of each phenyl ring relative to the central lactone moiety required further NMR experiments. Although the NOE, HMBC and TOCSY experiments provided sufficient information to conclude the assignment of the four independent phenyl rings and their related substituents, their positions around the central lactone moiety remained unclear. The positions of these rings were confirmed through selective NOE spectra. This allowed a through-space interaction to be observed between the ^1H signals at δ 6.79 ppm and δ 7.21 and δ 7.33 ppm, *i.e.* demonstrating that H_{12} neighbours the ring which H_6 and H_7 are on. H_6 and H_7 show no other through-space interactions so are therefore have only one adjacent phenyl ring. H_{12} also showed a through space interaction with H_{18} and H_{19} , confirming that the phenyl ring bearing protons H_{12} and H_{13} lies between the rings bearing H_6 and H_{18} . This leaves the phenyl ring bearing H_{24} and H_{25} as the remaining phenyl ring with one neighbour. The fully assigned $^{13}\text{C}\{^1\text{H}\}$ spectrum is displayed in Fig. 3.19.

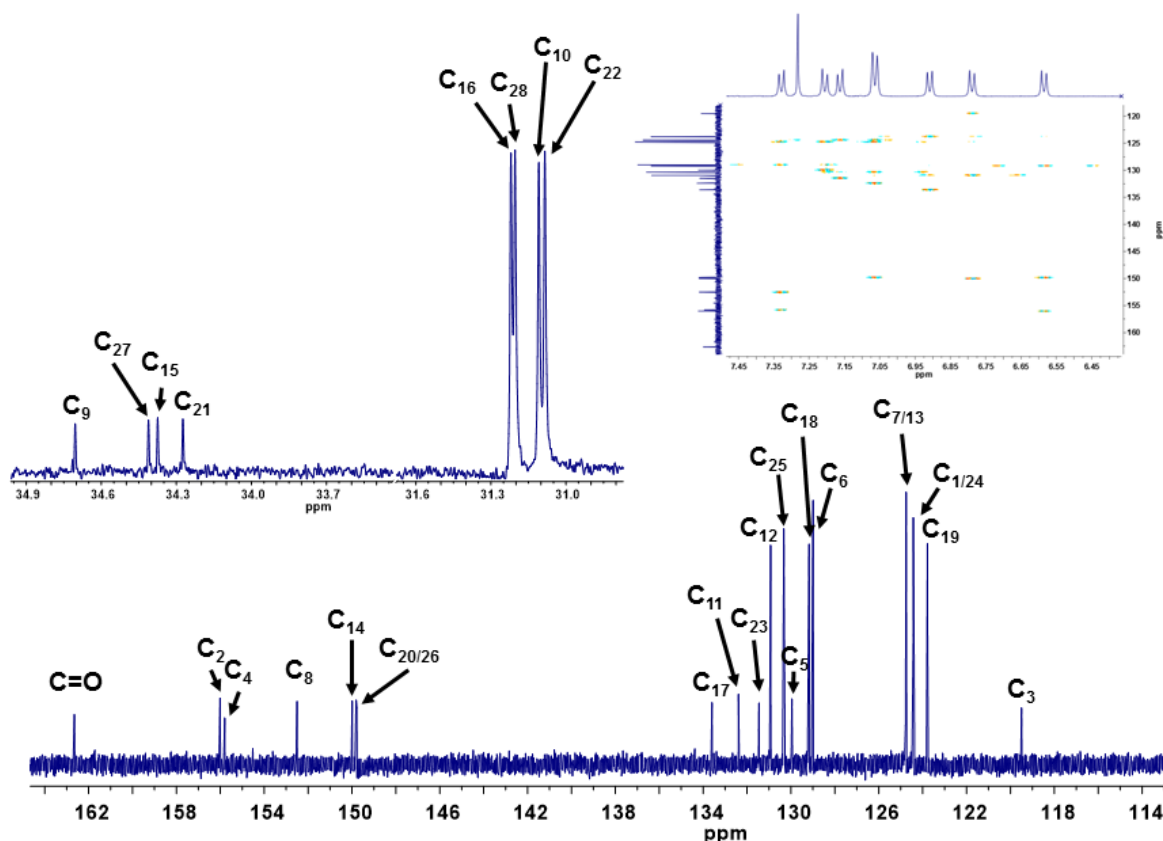


Figure 3.19: The ^{13}C (proton decoupled) NMR spectrum of **45** (CDCl_3 , 600 MHz, RT). Inset top left is the tert-butyl region between 35.0 and 30.0 ppm and inset top right is the HMBC experiment.

The cyclometallated compound **47** displays a similar proton NMR spectrum to the free ligand **44** (Fig. 3.20). The proton nearest the pyridine N, H_6 , is once again observed most downfield as a doublet at δ 9.34 ppm. A new signal has appeared at δ 7.93 ppm, which is not observed in the spectrum of **44**. This is from H_8 , and it displays ^1H - ^{195}Pt satellite peaks ($J_{\text{Pt-H}} = 43.0$ Hz), since it is closest to the Pt atom. It is noted that H_7 is no longer observed due to cyclometallation. A 2D TOCSY experiment revealed that H_3 appears at δ 6.73 ppm and H_4 and H_5 overlap as a multiplet at δ 7.47 ppm. The TOCSY also identified H_{10} and H_{11} , the assignment of which was confirmed by HMBC. The remaining peaks in the spectrum account for the aromatic protons of the pendant phenyl rings. Further confirmation of the synthesis of this compound was provided by HRMS (Table 3.4).

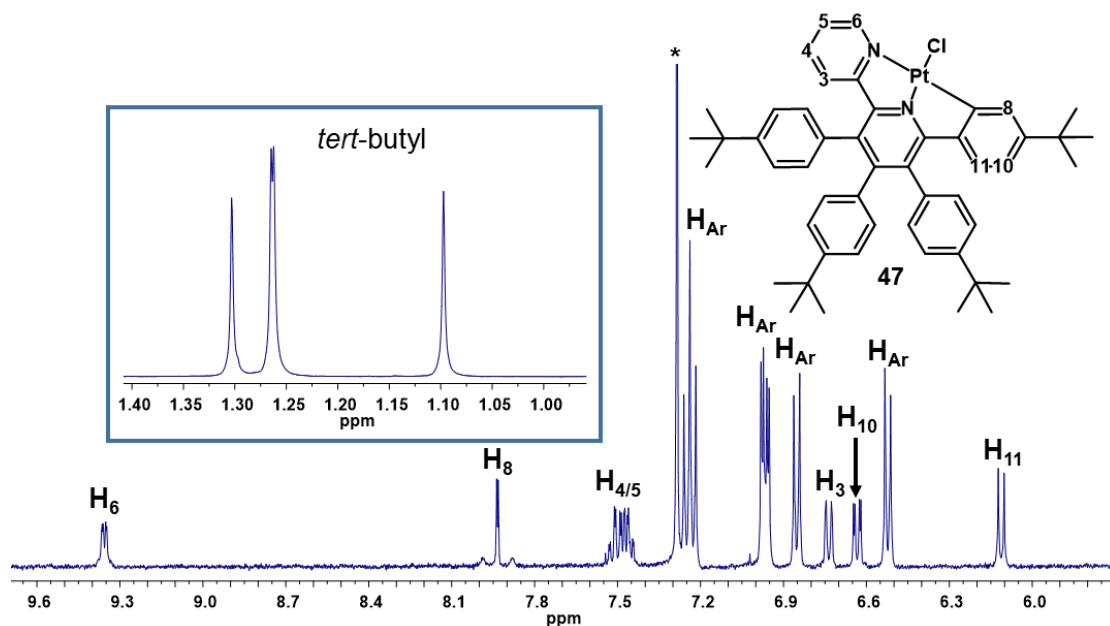


Figure 3.20: ^1H NMR spectrum of cyclometallated platinum chloride precursor, **47** (400 MHz, CDCl_3 , RT). Asterisk denotes residual solvent peak.

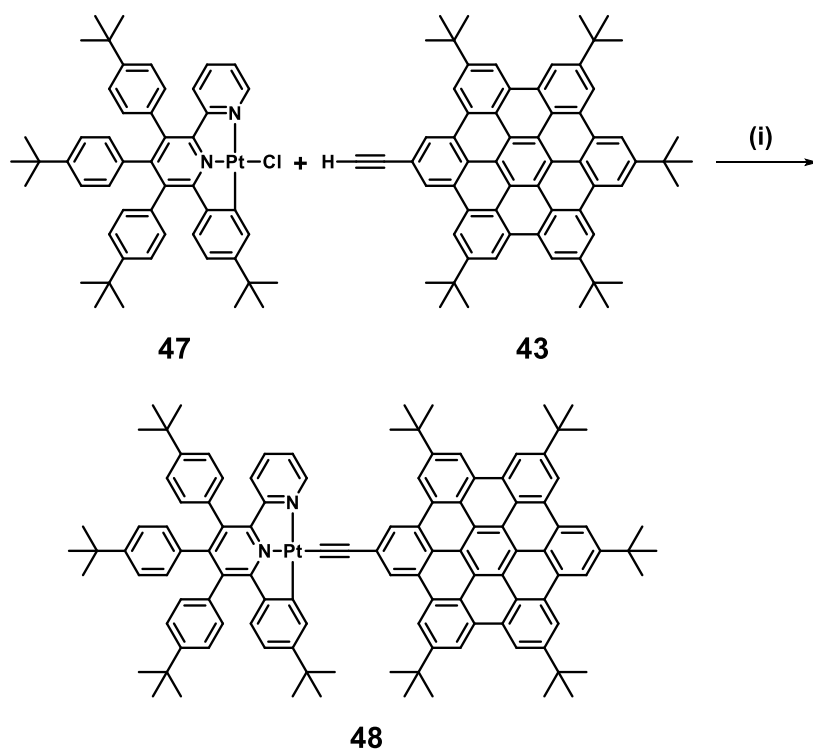
Table 3.4: Mass Spectral Analysis (HR MALDI-TOF) for compounds **44**, **45** and **47** (m/z in $m.u.$)

Compound	Formula	Calculated m/z	Found m/z	Molecular Ion
44	$\text{C}_{50}\text{H}_{56}\text{N}_2$	684.4400	684.4462	$[\text{M}^+]$
45	$\text{C}_{45}\text{H}_{53}\text{O}_2$	625.4046	625.4072	$[\text{M}+\text{H}]^+$
47	$\text{C}_{50}\text{H}_{55}\text{N}_2\text{Pt}$	877.3935	877.3958	$[\text{M}-\text{Cl}]$

3.3.5 Synthesis of $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ -type Pt(II) Acetylides **48** and **49**

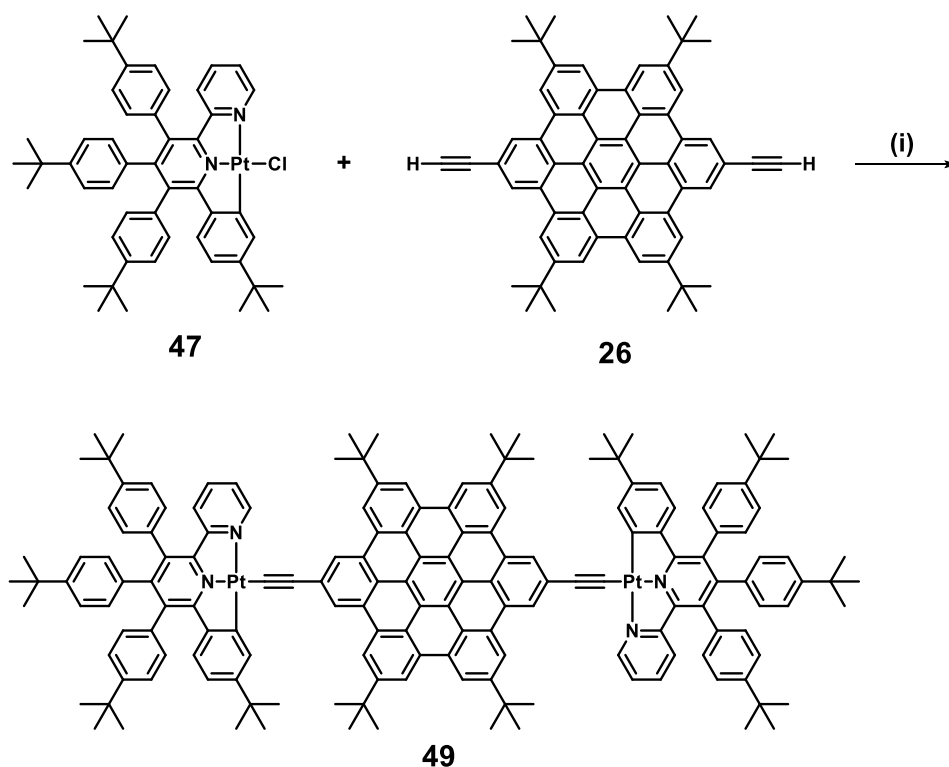
The successful preparation of the ethynyl-HBC cores and **47**, the cyclometallated Pt complex, led to the final stages of synthesis of the Pt(II) acetylides. As before, this was achieved through the conditions developed by Sonogashira *i.e.* a CuI-mediated dehydrohalogenative coupling in the presence of a base (Scheme 3.14). Platinum chloride precursor **47** (in slight excess) and the mono-substituted ethynyl-HBC **43** were combined in a mixture of dry dichloromethane and diisopropylamine in the presence of a catalytic amount of CuI (15 %) and stirred under N_2 for 40 hours. Concentration of the reaction mixture *in vacuo* and addition of a small amount of MeOH provided an orange precipitate. This was

carefully filtered and washed with further amounts of cold MeOH. NMR analysis indicated the successful synthesis of **48**, which was further confirmed by HRMS.



Scheme 3.14: The synthetic procedure toward the preparation of **48**. (i) CuI, DIPA, CH₂Cl₂, RT, 40 h, 86 %.

The same methodology was applied to the synthesis of the diplatinum analogue **49** (Scheme 3.15). Under the same reaction conditions, *para*-ethynyl-HBC **26** was combined with **47** in CH₂Cl₂ and diisopropylamine under N₂, with CuI as catalyst. The reaction was allowed stir for 72 hours in this case, as TLC analysis after 24 hours indicated some remaining starting material. The work-up was performed in the same way, *via* concentration, addition of MeOH, and then filtration. NMR and HRMS analysis of the orange precipitate indicated that the desired product **49** had been successfully formed.



Scheme 3.15: Synthesis of **49**. (i) CuI , DIPA , CH_2Cl_2 , RT, 72 h, 73 %.

3.3.6 Characterisation of Pt(II) Acetylides **48** and **49**

While the mono-substituted **48** displayed reasonable solubility in common solvents such as CH_2Cl_2 and THF, di-substituted HBC **49** displayed low/poor solubility in CHCl_3 . Although this presented some difficulties, particularly when preparing solutions for photophysical measurements, it was possible to acquire a satisfactory ^1H NMR spectrum of **49** in CDCl_3 . Both compounds were therefore characterised by NMR spectroscopy, HRMS and IR. The generation of single crystals of these complexes is an ongoing challenge, due to their tendency to precipitate out of solution rather quickly. The ^1H NMR spectrum of **48** is displayed in Fig. 3.21. The most characteristic signal in the ^1H NMR spectrum of **48** is the most downfield H_6 , occurring as a doublet due to its position in the pyridine ring. The protons of the periphery of the HBC unit are observed at δ 9.54, 9.39 and 9.33 ppm, the latter of which is a peak resulting from overlapping signals. Integration of these signals yields twelve protons as expected, since there are six pairs of equivalent protons on this part of the molecule due to the axis of symmetry through the ethynyl unit. The signal at δ 9.54 and δ 9.39 ppm account for two protons each and the signal at δ 9.33 ppm accounts for eight. A HMBC experiment yielded correlations between these HBC protons and the relevant *tert*-

butyl signals substituted on the outer HBC rings (which account for the signals at δ 1.85 and δ 1.83 ppm). Selective TOCSY experiments, which investigated the pyridine ring, found interactions between the signals at δ 9.68 (H₆), 6.81 and 7.56 ppm. The 2D TOCSY gave further insight into the interactions between the spin system of the pyridine ring. The most downfield signal, H₆, gave interactions with the signals at δ 7.56, 7.47 and 6.86 ppm. These therefore account for protons H₃, H₄ and H₅. Since H₃ is expected to occur as a doublet and be least deshielded by the pyridine N, it is assigned to the signal at 6.86 ppm. The signals at δ 7.56 and 7.47 ppm therefore account for protons H₄ and H₅, occurring as multiplets. These can be further elucidated by consultation of the ¹H-¹³C HSQC (Fig. 3.22) and HMBC experiments. The signal assigned to H₃ corresponds to the ¹³C signal at δ 126.96 ppm. This ¹³C signal displays a correlation with the proton signal at δ 7.48 ppm. Therefore, since the HMBC experiment gives three-bond correlations, it may be proposed that the signal at δ 7.48 ppm accounts for proton H₅, since it is three bonds away from the ¹³C signal assigned to H₃. This is confirmed by checking whether the ¹³C signal corresponding to H₅ has a correlation in the HMBC experiment with H₃, which is indeed the case. This leaves, by elimination, H₄, which may be assigned to the resonance at 7.56 ppm. Checking the HMBC experiment, H₄ gives a correlation with the ¹³C signal assigned to H₆ at δ 151.8 ppm, which provides further confirmation.

Assignment of the cyclometallated ring was achieved in much the same manner. From consultation of the ¹H NMR spectrum of Pt-Cl precursor **47**, it is noted that H₈ is relatively deshielded and occurs as a doublet at δ 7.94 ppm, with satellite peaks resulting from ¹H-¹⁹⁵Pt splitting. A very similar signal is observed in the ¹H spectrum of **48**, but which is further deshielded, occurring at δ 8.46 ppm. The ¹H-¹⁹⁵Pt splitting is less evident, but remains faintly visible. The assignment of this signal is supported by the TOCSY and HMBC experiments. The TOCSY experiment shows that H₈ is in the same spin system as only two other proton signals, which are those at δ 6.67 and 6.27 ppm. From the HSQC, H₈ corresponds to a carbon signal, C₈, at δ 135.4 ppm. The HMBC experiment shows that H₈ correlates to two ¹³C signals, δ 145.7 and 120.3 ppm respectively. As the ¹H signal at δ 6.27 ppm corresponds to δ 120.3 ppm (via the HSQC experiment) it may therefore be assigned to H₁₀, which is three bonds away from the C₈. The other ¹³C signal which H₈ correlates with in the HMBC experiment may be attributed to the quaternary carbon three bonds away, *para* to the *tert*-butyl group. This leaves the signal at δ 6.67 ppm to be attributed to H₁₁. As expected, this is a doublet, since it couples only to H₁₀. From the HSQC experiment C₁₁ is

the signal at δ 129.0 ppm. Examination of the HMBC experiment shows that H_{11} correlates to two ^{13}C signals, at δ 153.7 and δ 144.6 ppm. These are both quaternary carbons, as expected and therefore account for the cyclometallated carbon, and also the carbon attached to the *tert*-butyl group, C_9 . The HMBC shows that the ^{13}C signal at δ 153.7 ppm displays a correlation with the *tert*-butyl peak at δ 1.32 ppm, which allows δ 153.7 ppm to be assigned as C_9 . By the process of elimination, the signal at δ 144.6 ppm may be assigned to the cyclometallated carbon. The remaining signals in the ^1H NMR spectrum account for the remaining aromatic protons of the cyclometallating ligand, which are in very similar chemical environments and give integration values as expected (all integration values are listed in the experimental section). These are denoted H_{Ar} (Ar = Aryl) in Fig. 3.21.

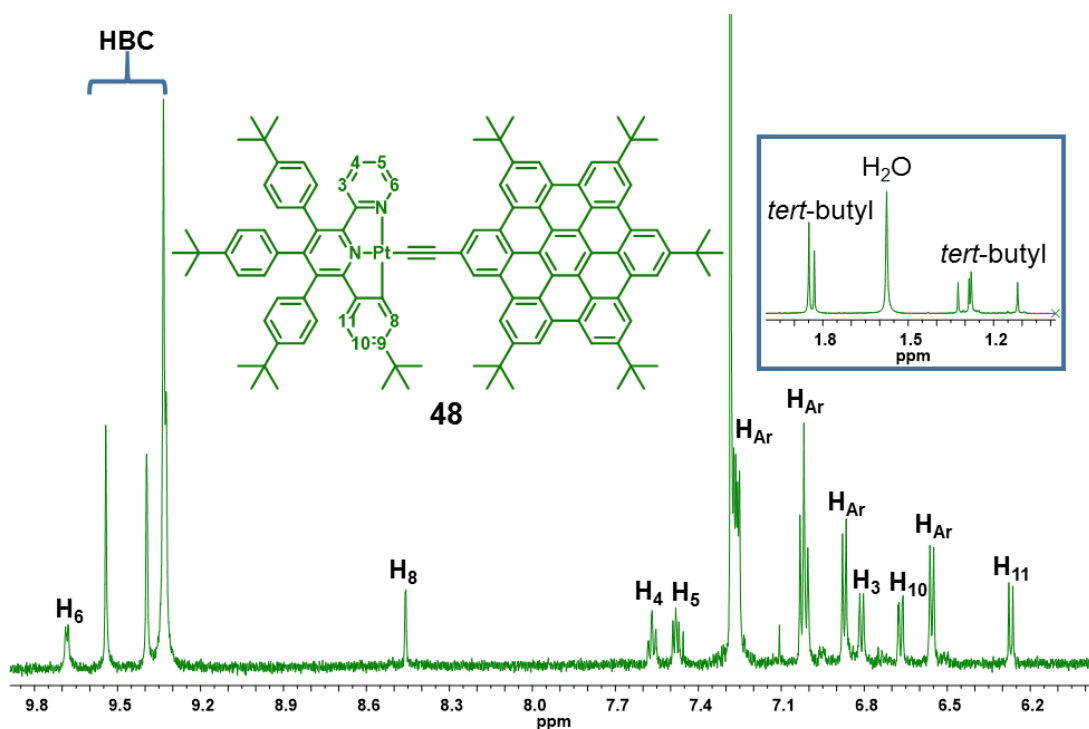


Figure 3.21: ^1H NMR spectrum of **48** (600 MHz, CDCl_3 , RT). Inset displays *tert*-butyl peaks.

* denotes residual CHCl_3 solvent.

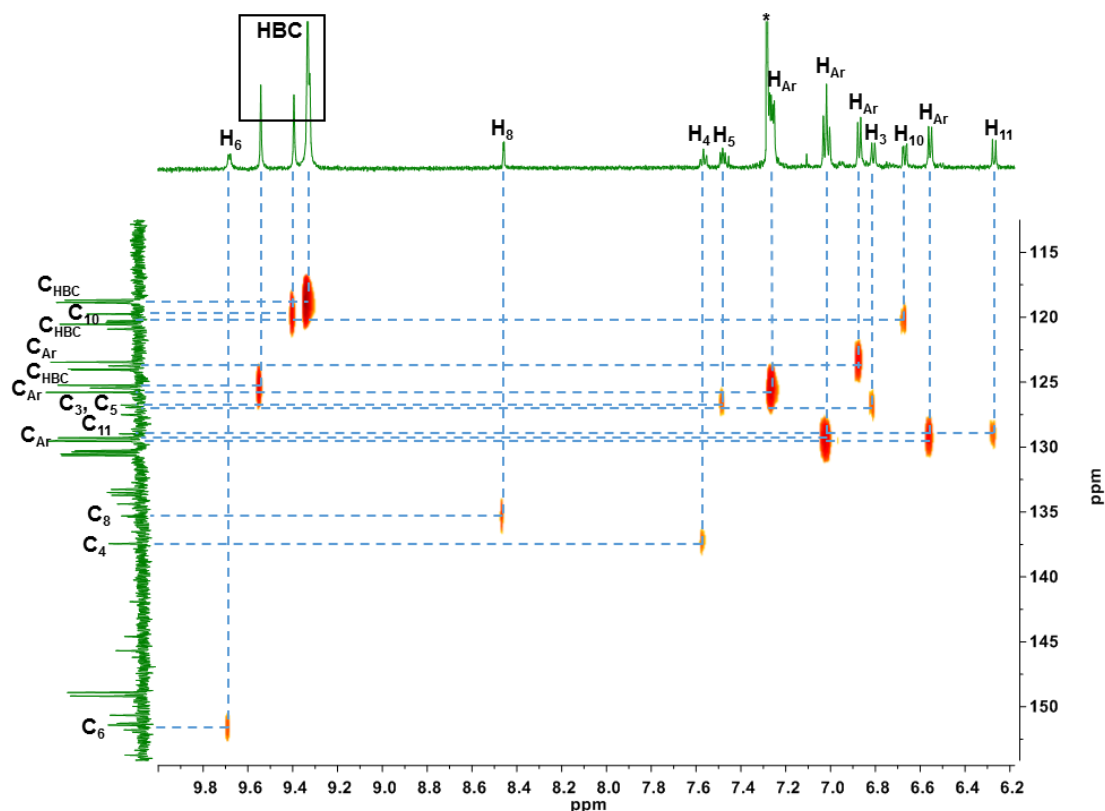


Figure 3.22: HSQC experiment used to aid the assignment of **48** (600 MHz, CDCl_3 , RT). * denotes residual CHCl_3 peak.

The ^1H NMR spectrum of **49** (Fig. 3.23) is quite similar to that of **48**. However, due to the very high degree of insolubility, it was not possible to record a satisfactory $^{13}\text{C}\{^1\text{H}\}$ spectrum, even after long data collection times. The assignment of the ^1H NMR spectrum was aided by a HSQC experiment. The most downfield signal may be assigned to H_6 , in common with the pattern observed with the mono-substituted **48**. The primary difference between **48** and **49** is the increased symmetry of the HBC core, since both sides are now substituted. There are therefore only three types of inequivalent aromatic proton on the periphery of the HBC core, with twelve in total. These are observed as singlets at δ 9.54, 9.38, and 9.32 ppm respectively. The proton next to the cyclometallated carbon, H_8 , is once again observed in a similar position as for the same type of proton in **48**. Although not as well resolved as the same signals in **48**, the signals attributed to H_4 and H_5 are once more observed in similar positions. Although a HMBC experiment was run, it was not possible to collect enough data to obtain correlations between the protons of the pyridine ring. It is however quite likely that H_4 and H_5 occur in the same pattern as for **48**, as their chemical environment remains almost identical. It is anticipated that H_{10} and H_{11} also occur in the same manner as in **48**, *i.e.* H_{11} is least deshielded. It is also noted that the remaining aromatic

protons of the cyclometallating ligand give a set of signals in the same pattern as previously, with some degree of overlap with the CDCl_3 solvent signal. The HMBC experiment indicates that the *tert*-butyl peaks possessed by the central HBC core are observed overlapping at δ 1.80 ppm. The identity of **49** was further confirmed by HRMS, with the result displayed in Table 3.5.

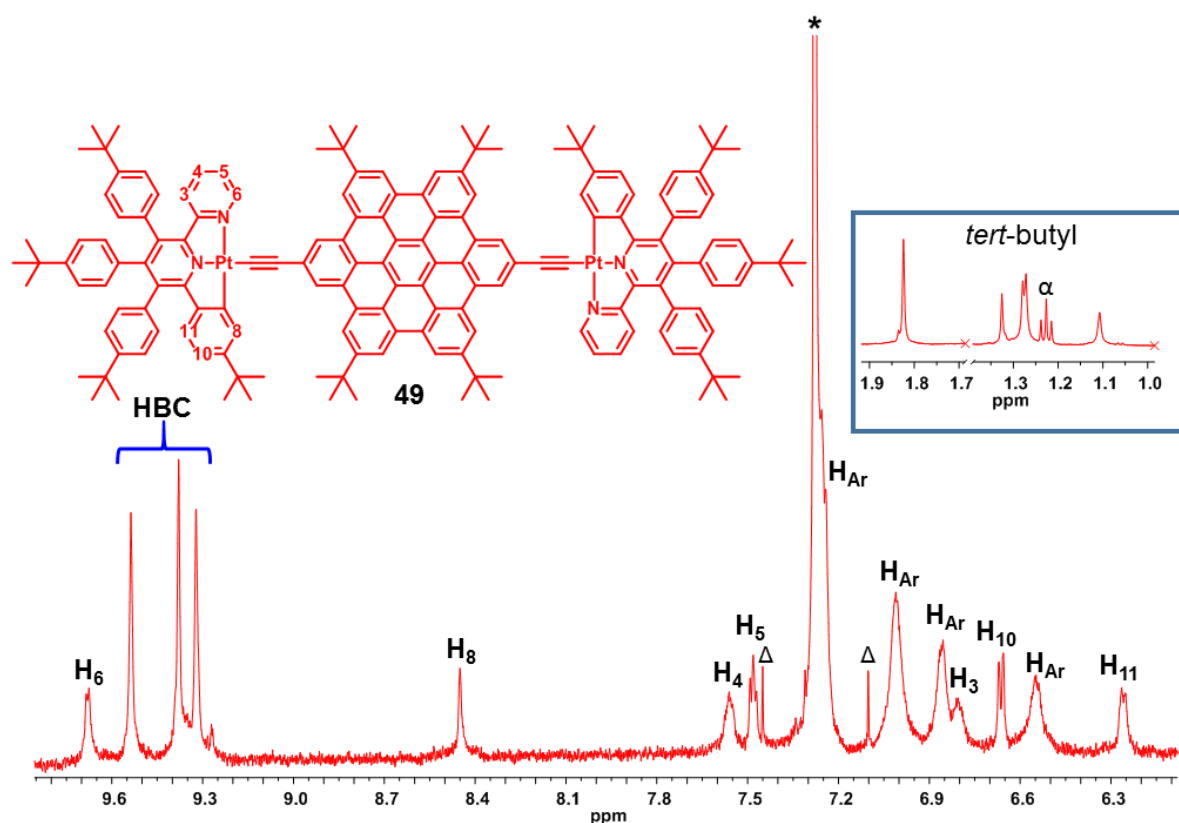


Figure 3.23: ^1H NMR spectrum of **49**, with inset, the *tert*-butyl peaks (600 MHz, CDCl_3 , RT). * denotes residual CHCl_3 solvent peak, Δ denotes CDCl_3 satellite peaks, and α denotes residual diethyl ether.

Table 3.5: Mass Spectral Analysis (HR MALDI-TOF) for compounds **48** and **49** (m/z in $m.u.$).

Compound	Formula	Calculated m/z	Found m/z	Molecular Ion
48	$\text{C}_{114}\text{H}_{113}\text{N}_4\text{Pt}_2$	1704.8552	1704.8494	$[\text{M}+\text{H}]^+$
49	$\text{C}_{162}\text{H}_{158}\text{N}_4\text{Pt}_2$	2549.1782	2549.1794	$[\text{M}^+]$

3.4 Preliminary Photophysical Analysis of Pt(II) Acetylides and their Precursors

3.4.1. UV-Visible Absorption Studies of Ligands and Pt(II) Acetylides

Based upon the literature reports of the interesting photophysical behaviour of Pt(II) acetylides, particularly those with appended HBC cores, it was undertaken to investigate the optical behaviour of the Pt(II) acetylides **48** and **49**. The very low degree of solubility of **49** necessitated the use of CHCl_3 as solvent for these measurements. Although literature reports have mentioned HBC-type compounds are often well solvated in THF,^{28, 45} this was not the case for **49** and indeed it was only sparingly soluble in CHCl_3 and relatively insoluble in CH_2Cl_2 . All UV-Vis data are summarised in Table 3.6.

Initial studies focused on the UV-Visible spectra of these complexes and their precursors. The absorption spectra of precursor compounds **26**, **43**, **44**, **47**, and final Pt(II) acetylide complexes **48** and **49** are displayed in Fig. 3.24. The absorption spectra (normalised for clarity, non-normalised absorption spectra are displayed in Section 3.4.2) of the precursor compounds are displayed in Fig. 3.24 (a), and for comparison, the absorption spectra of the final complexes **48** and **49** are again presented in Fig. 3.24 (b), along with the precursor diethynyl-HBC **26**, for the purpose of comparison.

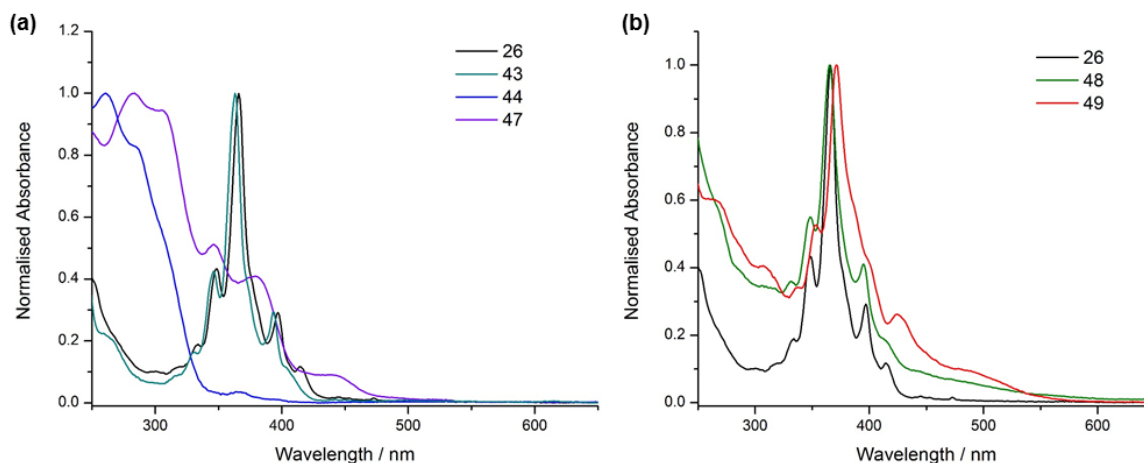


Figure 3.24: (a) Normalised UV-Visible absorption spectra of **26**, **43**, **44** and **47** (CHCl_3 , **44**, **49** at 1×10^{-5} M, **26**, **43** at 1×10^{-6} M). (b) UV-Visible absorption spectrum of **26**, **48** and **49** (1×10^{-6} M, CHCl_3).

The UV-Visible absorption spectrum of $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ ligand **44** (Fig. 3.24) displays a broad absorption characteristic of a polyphenylene-type compound, due to the freely rotating phenyl rings,⁵⁸ between $\lambda = 250$ and 350 nm. The high number of vibrational levels in such a system tends to broaden the absorptions observed, which are further broadened by

interaction with solvent molecules. In contrast, rigid systems often display absorptions with fine structure.⁵⁹ Compound **44** displays an absorption maximum at $\lambda = 261$ nm, with a shoulder at $\lambda = 285$ nm. An N-substituted system such as **44** is expected to display both $\pi-\pi^*$ and $n-\pi^*$ bands, but the nature of the absorption bands of **44** is unclear. However, generally $\pi-\pi^*$ transitions are observed at higher energies and with greater intensity than for $n-\pi^*$,⁵⁹ which suggests that the absorption maximum at $\lambda = 260$ nm may have significant $\pi-\pi^*$ character. Upon coordination with Pt, forming the Pt(II) chloride derivative **47**, a lower energy absorption band is observed at $\lambda = 283$ nm, with a shoulder at $\lambda = 307$ nm, similar to the free ligand **44**, but slightly red-shifted (Fig. 3.24). A number of new bands appear due to complexation, at $\lambda = 346$, 380, and 440 nm. The band at $\lambda = 440$ nm is characteristic of an MLCT transition, and is similar to those reported for other Pt(II) diimine complexes with halide ligands.^{60, 61} Miskowski *et al.* have conducted systematic investigations of Pt(II) diimine complexes with halide ligands, and have reported that the extended ‘tail’ of the MLCT band in such complexes, appearing with very low intensity, is due to d-d excited states, also referred to as metal-centred (MC) transitions.⁶⁰ A similar feature is observed in the UV-Vis spectrum of **47**, and as the lowest excited state in such Pt(II) complexes are often d-d states, this is not unexpected.

Table 3.6: UV-Visible absorption data for **44**, **47**, **26**, **43**, **48** and **49** (**44**, **47** at 1×10^{-5} M, all others at 1×10^{-6} M, all recorded in CHCl_3).

Compound	λ_{max} [nm] ($\epsilon \times 10^{-4}$ [$\text{M}^{-1} \text{cm}^{-1}$])
44	261 (2.66), 285 (2.19), 310 _{sh} (1.26)
47	283 (2.88), 307 (2.71), 346 (1.46), 380 (1.17), 440 (0.25), 488 (0.04)
43	317 (1.5), 330 (2.8), 346 (7.5), 363 (17.9), 375 (6.5), 394 (5.2), 404 _{sh} (2.0), 442 (0.24), 450 (0.12)
26	317 (2.7), 333 (4.4), 348 (10.4), 367 (23.9), 377 _{sh} (9.3), 396 (6.9), 415 (2.7), 445 (0.4), 473 (0.2)
48	265 _{sh} (11.9), 316 (7.0), 330 (7.3), 349 (11.2), 365 (20.5), 395 (8.4), 414 (3.8), 443 (1.9), 485 (1.2)
49	265 (10.8), 308 (7.1), 337 (6.0), 353 (9.3), 371 (18.1), 388 _{sh} (10.1), 400 _{sh} (7.5), 423 (4.5), 485 (1.6) 495 (1.4).

Early photophysical investigations into HBC-type compounds were carried out by Clar *et al.*, who identified three main absorption bands, the α , β and p bands.⁶² The absorption spectrum of diethynyl-HBC **26** (Fig. 3.24) is very similar to that of the previously reported mono-ethynyl analogue, **43**.²⁹ For **26**, the spectrum is dominated by an absorption at $\lambda_{\text{max}} = 367$ nm (known as the β band according to Clar's notation) with two lower intensity peaks at $\lambda = 348$ and 396 nm (the latter known as the ' p ' band) either side. These bands are characteristic of the HBC moiety,^{52, 63} and the high degree of planarity of **26** has resulted in an absorption spectrum with a high degree of fine structure. In the case of mono-ethynyl HBC **43**, the absorption spectrum is very slightly blue-shifted with respect to that of diethynyl equivalent **26**, with the $\lambda_{\text{max}} = 363$ nm, and the absorbance at *ca.* $\lambda = 414$ nm exhibited by **26** is not observed. Kim *et al.*, who have reported Pt(II) acetylides incorporating HBC (See Fig. 3.4), obtained an almost identical absorption spectrum of the TIPS-substituted analogue of **43**.²⁸ They attributed the low-energy absorptions at *ca.* $\lambda = 410$ and 393 nm to symmetry-disallowed transitions, and the higher-energy β band transition at *ca.* $\lambda = 363$ nm to a symmetry-allowed transition. In the case of **26**, a very low-energy transition may be observed at $\lambda = 473$ nm, denoted by Clar as the α band. Previous literature investigations into the behaviour of HBC-type compounds indicates that this is most likely the 0-0 transition,⁶⁴ which in this case corresponds to a HOMO-LUMO transition of 2.62 eV. This is not easily observed in the spectrum of **43**, perhaps due to it possessing a single ethynyl unit and therefore a higher degree of symmetry, making the transition less allowed. The parent unsubstituted and therefore highly symmetric hexa-*peri*-hexabenzocoronene exhibits only a very weakly observed α band.⁶⁴

The absorption spectra of the Pt(II) acetylides **48** and **49** are presented in Fig. 3.24 (b), along with the absorption spectrum of **26** for comparison. It is evident that the absorption spectra of the acetylide compounds **48** and **49** remain dominated by the HBC chromophore, and are remarkably similar to the absorption profiles of the ethynyl-HBC precursors. There appears to be little contribution from the ligands **44** and **47**, however both complexes display extended bands in the region where MLCT absorptions are usually observed. Both **48** and **49** display slightly broadened absorption profiles in comparison to those of precursor ligands **26** and **43**, and are both also slightly-red-shifted in comparison with their respective precursor HBC ligands. The mono-substituted Pt(II) acetylide **48** exhibits a λ_{max} at 366 nm (the β band), in comparison with its HBC precursor which exhibits a λ_{max} at 363 nm. The di-substituted Pt(II) acetylide **49** exhibits a λ_{max} at 371 nm, while precursor **26** exhibits a λ_{max} at

366 nm. It may be noted that the profile of **49** is quite broadened in comparison with that of **48**, perhaps as a result of the larger molecule possessing slightly lower solubility. The *p* band of **48** is clearly visible at $\lambda = 396$ nm, but is not well resolved in the spectrum of **49**, appearing as a shoulder at $\lambda = 400$ nm. Both **48** and **49** exhibit bands at $\lambda = 416$ and 426 nm respectively (and also a shoulder extending beyond 500 nm), which are not present in the UV-Vis spectra of precursor ligands **26** and **43**, suggesting that these may be due to MLCT transitions.

3.4.2 UV-Visible Solvatochromism Studies

In order to further probe the nature of the absorption bands of these compounds, it was decided to undertake solvatochromism studies. Solvatochromism is most apparent in absorption bands with charge transfer (CT) character.^{65, 66} Often, due to the formation of an excited state, a change in the dipole moment of the molecule occurs. The shell of solvating molecules surrounding the excited molecule do not have enough time to rearrange around the excited molecule and are therefore not appropriately orientated. This results in a higher energy for the transition, which increases in more polar solvents.⁶⁵ In the case of π - π^* transitions, the dipole moment increases upon excitation, and the excited state will experience a greater degree of stabilisation in a polarisable solvent. This results in a shift in the absorption to longer wavelengths (*i.e.* a red-shift).⁶⁷ If a molecule experiences a decrease in its dipole moment in the excited state, its absorption will be shifted to higher energies (a blue-shift) in more polar solvents, which is often the case for n - π^* transitions. This is because upon excitation of an n - π^* state, the magnitude of the dipole moment decreases, but the surrounding shell of solvent molecules do not have time to rearrange themselves to suit this, due to the Franck-Condon factor. This effect results in an increase in the transition energy, a blue-shift, to shorter wavelengths.⁶⁵

The UV-Visible spectra of **44** in solvents of varying polarity are overlaid in Fig. 3.25. The bands are remarkably similar, even between very non-polar solvents such as hexane and polar solvents such as methanol. Therefore the ground state of this molecule is relatively unaffected by solvent polarity.

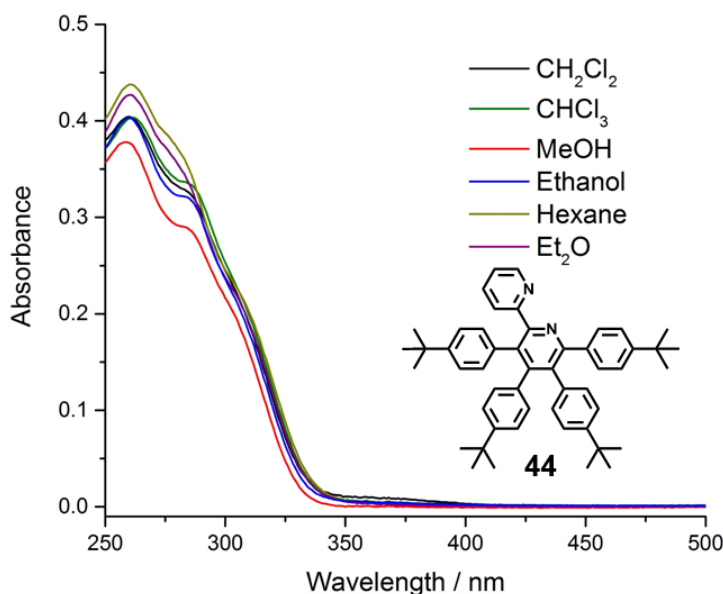


Figure 3.25: UV-Visible absorption spectra of **44** in solvents of varying polarity (1×10^{-5} M).

There is a very slight shift of the band at $\lambda = 261$ nm (in CH_2Cl_2), which may be seen to decrease in intensity and undergo a very minor blue-shift towards shorter wavelengths in more polar solvents, suggesting that the band exhibits some $n\text{-}\pi^*$ character. It is likely that these bands are actually comprised of a mixture of $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ states, as $\pi\text{-}\pi^*$ states often do not show a high degree of solvatochromism.⁶⁵ The shoulder at $\lambda = 284$ nm in CH_2Cl_2 exhibits a slight hypsochromic shift in the less polar solvents hexane and Et_2O , and is assigned as being primarily $\pi\text{-}\pi^*$ in character. Overall, **44** does not display any significant solvatochromic behaviour.

The platinum chloride compound **47** was also subjected to the same solvatochromic studies (Fig. 3.26). The high-energy absorptions, ca. $\lambda = 290$ nm, show little change in different polarities, suggesting these bands have more $\pi\text{-}\pi^*$ character. They are observed to decrease in intensity in the more polar solvents EtOH and MeOH. A more apparent sensitivity toward solvent polarity is exhibited by the lower energy bands, indicating that they are comprised of a high degree of charge-transfer (CT) character. This is shown in the inset section of Fig. 3.26.

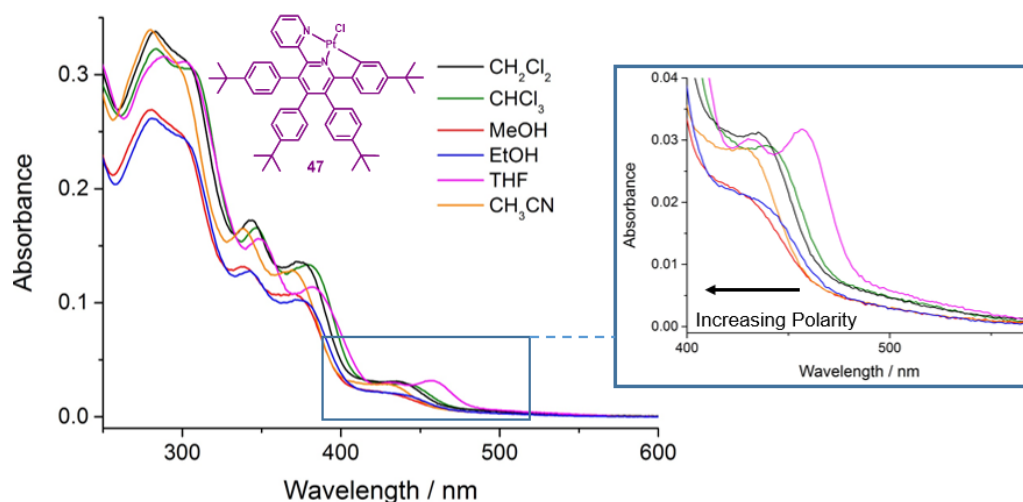


Figure 3.26: The UV-Visible absorption spectra of **47** in solvents of varying polarity, and inset, an expanded view of the region between 400 and 540 nm (1×10^{-5} M).

The bands at $\lambda = 345$ and 380 nm in CHCl_3 both display a high degree of solvatochromism and are blue-shifted in more polar solvents, known as negative solvatochromism. This blue-shift, or hypsochromic shift, is characteristic of a CT transition.^{60, 68} Since these absorptions are not observed in the UV-Vis of the parent ligand **44**, it is likely that they are MLCT-type transitions ($^1\text{MLCT}$ or $^3\text{MLCT}$), which is supported by their sensitivity to solvent polarity. This implies that the ground state involved in these transitions is better stabilised in more polar solvents, and therefore possesses a higher dipole moment in the ground state than the excited state.^{69, 70} The band at $\lambda = 440$ nm in CHCl_3 also experiences a very high degree of solvatochromism, also displaying a blue-shift, which is highlighted in the inset section of Fig. 3.26. This is also indicative of CT character. These bands are most likely $[\text{d}(\text{Pt}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N}^{\wedge}\text{C})]$ in origin. Cheung *et al.* have tentatively assigned similar bands in the UV-Vis absorption spectrum of $[\text{Pt}(\text{phbpy})\text{Cl}]$ (where phbpy is 6-phenyl-2,2'-bipyridine) as being $^3\text{MLCT}$ in nature.⁷¹ The d-d transition, suggested to be perhaps responsible for the extended, low-intensity absorption at lowest energy in the absorption spectrum, does not display any solvatochromism, as is usual for these transitions.⁷⁰

Investigation of the solvatochromism of the absorption bands of final complexes **48** and **49** were hampered by poor solubility in solvents other than CHCl_3 , but it was possible to obtain spectra in dilute solutions of toluene, diethyl ether, MeOH and THF (Fig. 3.27 (a) and (b)). Although **48** displayed reasonable to very good solubility in most of these solvents, **49** remained reluctant to solubilise in anything other than CHCl_3 , and as a result, the

absorption band intensities of **49** are not definite. They do however provide an indication of its behaviour in more polar solvents. In the case of **48**, the β band of the HBC chromophore, $\lambda = 365$ nm in CHCl_3 , is hardly affected by changing polarity. This is assigned as predominantly $\pi\text{-}\pi^*$ in origin. The absorption profiles in both CHCl_3 and toluene are quite similar and the best resolved of the series, suggesting that toluene is also a good solvent for this complex. The p band, $\lambda = 395$ nm in CHCl_3 , appears very slightly blue-shifted in diethyl ether ($\lambda = 392$ nm), but this may be due to poor solubility, and a clear trend is not evident. An expanded view is provided in the inset portion of Fig. 3.27 (a). The extended band, beyond $\lambda \approx 420$ nm, exhibiting what appears to be slight solvatochromism, is tentatively assigned as $^3\text{MLCT}$ in nature, but may also be a mixture of LLCT transitions (π acetylide $\rightarrow \pi^* \text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ ligand) and potentially also metal-ligand to ligand charge transfer (ML'LCT).

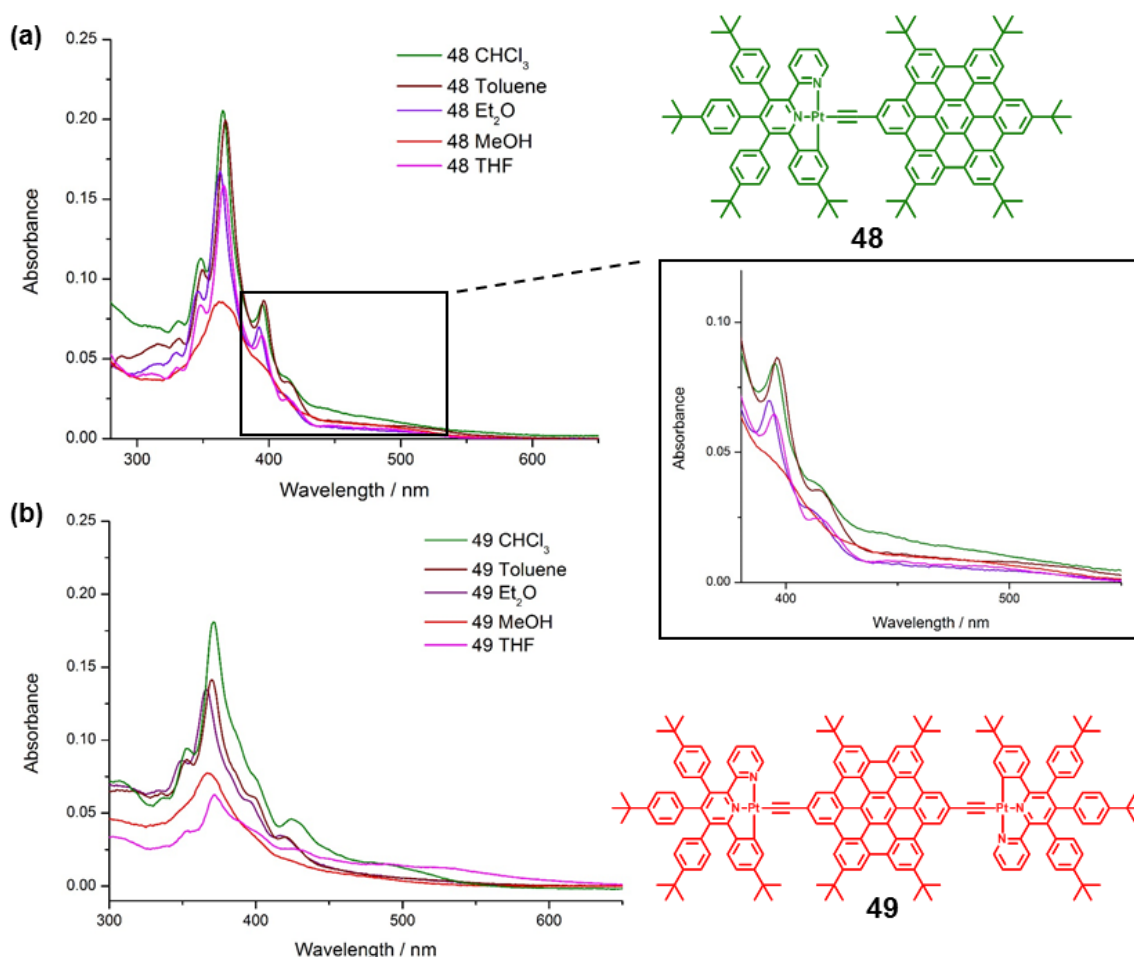


Figure 3.27: (a) Solvatochromic investigation of **48** (1×10^{-6} M), with inset, an expanded view of the region between 380 and 600 nm. (b) Solvatochromic investigation of **49** ($\sim 1 \times 10^{-6}$ M).

For **49**, solvatochromic studies are not particularly conclusive due to the solubility issue. Although reasonably well-solvated in toluene and diethyl ether, THF and MeOH yield very broad and low-intensity spectra with little definition. The less polar THF appears to extend the lowest energy transition, which is most likely a band possessing MLCT character, beyond its absorption in CHCl_3 . The same band is slightly blue-shifted in MeOH, which is supportive of its possession of CT character. However, due to the poor resolution, this is a hesitant assignment, since the same bands in **48** do not exhibit a general trend.

3.4.3 Effects of Protonation on UV-Visible Spectrum of **44**

The protonation of a molecule can aid the identification of its absorption bands. In a UV-Vis absorption spectrum, bands that display $n\text{-}\pi^*$ character will decrease in intensity upon addition of acid. This is because when protonated, the n (non-bonding) orbital becomes a lower energy bonding σ orbital. The process is summarised in Figure 3.28 (a). As the molecule becomes more positive, the electrons become held more tightly, so the MO (molecular orbital) energy levels are lowered. The spectral behaviour of **44** upon protonation was monitored by addition of aliquots of 1×10^{-3} M TFA, and the results displayed in Fig. 3.28 (b). Upon addition of the aliquots of TFA, the UV-Vis profile gradually changes from a broad, relatively undefined profile to having two well defined absorptions at $\lambda = 297$ and 364 nm. The absorption band of the unprotonated species, at $\lambda = 259$ nm, gradually decreases in intensity with acid addition, indicating that it possesses $n\text{-}\pi^*$ character. A new absorption band at $\lambda = 364$ nm is observed, and the shoulder at $\lambda = 284$ nm gradually becomes red-shifted and more defined. These new absorbance bands are quite red-shifted from the unprotonated species. Since $n\text{-}\pi^*$ transitions are known to decrease in intensity upon protonation, it is likely these new bands have strong $\pi\text{-}\pi$ character. Beyond the addition of one molar equivalent of TFA, the absorption bands are observed to change in intensity more slowly, up to 3.3 equivalents. Beyond the addition of 3.3 equivalents of TFA, the isosbestic point at $\lambda = 287$ nm is no longer clearly observed, suggesting that further processes may be occurring at higher concentrations of TFA (i.e. other than the initial protonation at the $\text{N}^{\wedge}\text{N}$ site). After the addition of twenty equivalents, there is little further change. It is clear that the protonation of **44** results in significant changes to its optical properties. Although the identity of the protonated species is unclear, studies by Armaroli *et al.* have shown that

phenanthroline based compounds, which possess N[^]N coordination sites, share one proton between the two nitrogen atoms after protonation.⁷²

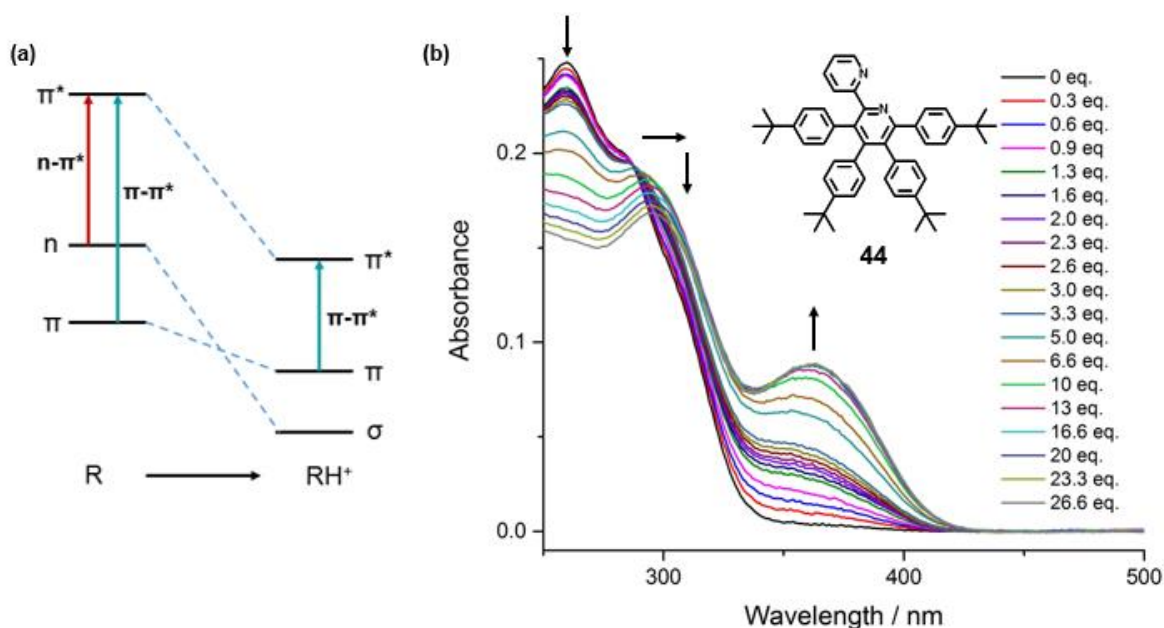


Figure 3.28: (a) MO diagram representing the consequence of protonation of a lone pair. (b) UV-Vis spectral changes of **44** (1×10^{-5} M) upon addition of aliquots of TFA (1×10^{-3} M).

3.4.4 Emission Spectra of Precursor Ligands

The emission spectra of precursor ligands **44** and **26** were obtained, and are described in this section. The emission spectrum of mono-ethynyl HBC **43** has been previously reported by Nolan *et al.*,²⁹ and is presented in Fig. 3.6 (d). All emission data is presented in Table 3.7. In Fig. 3.29, the overlaid emission spectra of **44** in CHCl₃ and CH₂Cl₂ are presented. Although a wide range of solvents was trialled, it was found that satisfactory emission spectra were only obtainable in CHCl₃ and CH₂Cl₂, most likely for reasons of solubility.

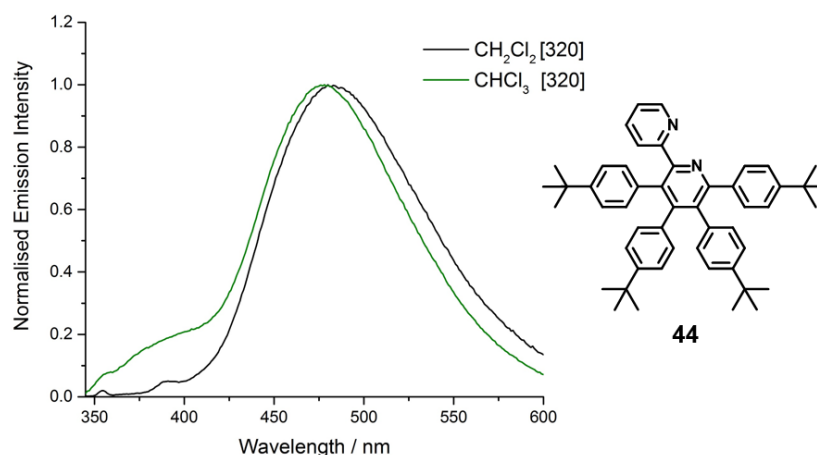


Fig. 3.29: Emission spectra of **44** in CH_2Cl_2 and CHCl_3 ($1 \times 10^{-5} \text{ M}$, $\lambda_{\text{exc}} = 320 \text{ nm}$).

44 displays a broad emission profile in both CH_2Cl_2 and CHCl_3 , (at $\lambda = 482$ and 479 respectively) which is very slightly red-shifted in CH_2Cl_2 . In both cases the excitation wavelength was $\lambda_{\text{exc}} = 320 \text{ nm}$, however no appreciable change was observed with variation of the excitation wavelength. The broad shape of the emission of **44** was shown to be independent of concentration (Fig. 3.30 (a)). In order to further probe the nature of the emission of **44**, the effect of protonation on the emission spectrum was investigated. The effect of the addition of aliquots of TFA ($1 \times 10^{-3} \text{ M}$) to **44** is displayed in Fig. 3.30 (b).

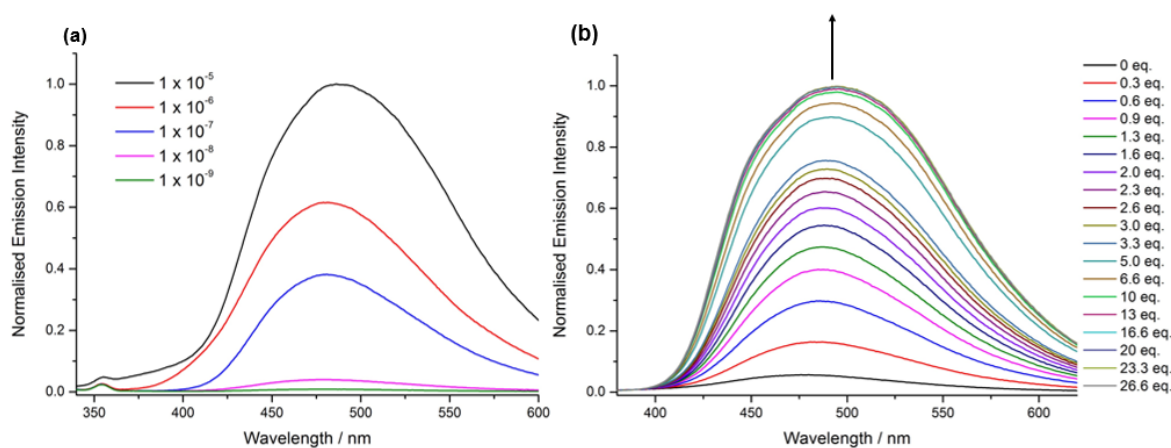


Figure 3.30: (a) The effect of concentration on the emission profile of **44** (solvent CH_2Cl_2). $\lambda_{\text{exc}} = 320 \text{ nm}$ in all cases. (b) The effect of protonation (with TFA, $1 \times 10^{-3} \text{ M}$) on the emission spectrum of **44** ($\lambda_{\text{exc}} = 320 \text{ nm}$, $1 \times 10^{-5} \text{ M}$, CH_2Cl_2).

The addition of TFA ($1 \times 10^{-3} \text{ M}$) does not induce a change in the emission profile of **44**, which remains remarkably broad and unstructured, but the luminescence intensity is greatly increased. A possible explanation for this is that, upon protonation, the weakly emissive $\text{n}-\pi^*$ no longer dominates the emission spectrum, and the more emissive $\pi-\pi^*$ becomes the

lowest excited state, therefore resulting in the increase in luminescence intensity. Since $n-\pi^*$ states are often not emissive, as transitions between $^1(n-\pi^*)$ to the ground state (S_0) are somewhat forbidden,⁷³ this accounts for the relatively low luminescence of the free ligand compared to the protonated species. Beyond the addition of one equivalent of TFA, the rate of increase in emission intensity slows. After the addition of ten equivalents of TFA, the emission displays little change. The quantum yield of luminescence was determined by the relative method, using quinine sulfate in 0.5 M H_2SO_4 as a reference, and was determined as $\Phi_{em} = 0.06$.

The emission spectrum of **47**, the platinum chloride derivative of **44**, is displayed in Fig 3.31 (a), along with the excitation spectrum. The emission maximum of **47** was observed at $\lambda_{em} = 612$ nm, and the emission profile observed is quite broad, suggesting ^3MLCT (metal-to-ligand charge transfer) character.^{25, 74} The low-temperature emission spectrum of **47**, recorded in a 4:1 EtOH:MeOH glass, is displayed in Fig. 3.31 (b), and is overlaid with the RT emission spectrum in $CHCl_3$. Three distinct bands are observed, the most intense at $\lambda_{em} = 550$ nm, and two less intense bands at $\lambda_{em} = 596$ and 643 nm. A significant blue-shift is observed at 77 K, indicating that the emission is strongly CT in nature. This is because in the rigid glass, the dipoles of the solvent are unable to relax around the dipole of the excited state.^{75, 76} In order to further probe whether the emission was from a triplet state, the emission from the degassed solution was compared to an aerated solution (under identical conditions/spectrometer settings), and the comparison is displayed in Fig. 3.31 (c). Since triplet states are susceptible to quenching by oxygen, the decrease in emission intensity indicates some triplet character. The emission of **47** is significantly red-shifted compared to the free ligand **44** ($\lambda_{em} = 479$ nm). Solvatochromism studies were also carried out in order to further probe the emissive nature of the complex, and the results are displayed in Fig. 3.31 (d).

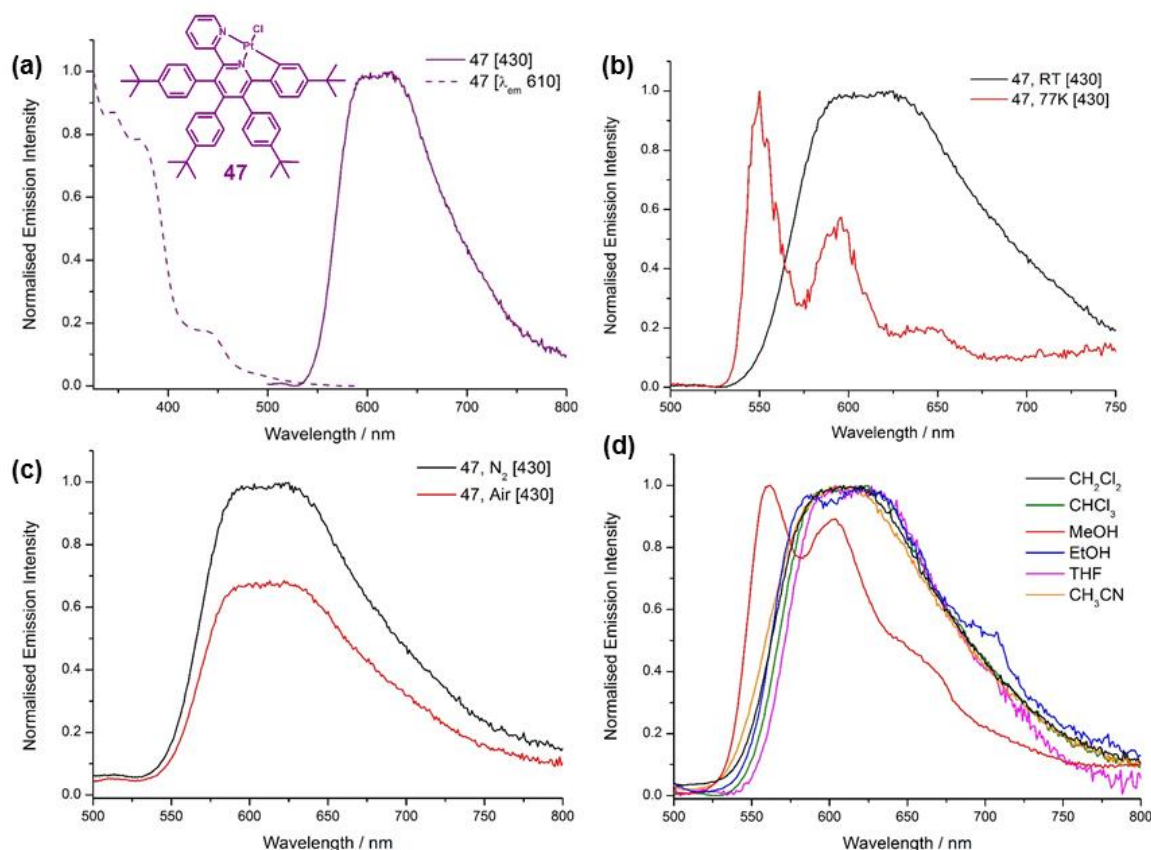


Figure 3.31: (a) Emission (solid line, [$\lambda_{exc} = 430$ nm]) and excitation (dashed line, [$\lambda_{em} = 610$ nm]) of **47** (1×10^{-5} M, CHCl_3). (b) Comparison of RT (298 K) and LT (77 K) emission spectra of **47** (1×10^{-5} M, CHCl_3 (RT), 4:1 EtOH:MeOH (77 K)). (c) Comparison of emission spectra of degassed and aerated solutions of **47** (1×10^{-5} M, CHCl_3). (d) Emission spectra of **47** in different solvents (1×10^{-5} M).

It was observed that the emission maximum changed little between the majority of the solvents chosen. However in MeOH, a significant blue-shift is observed, with two components clearly visible. In the other solvents, these two components appear as poorly-defined shoulders. This shift in energy is indicative of a CT (charge transfer) state, and suggests that the excited state of **47** is less polar than the ground state. The lifetime of the emission of **47** was determined with bi-exponential fitting as being 198 ns (80 %) and 330 ns (20 %), and the quantum yield as $\Phi_{em} = 0.014$ (vs. $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$). Complexes similar to **47** have been reported as emitting from a $^3\text{MLCT}$ state.⁷⁷ As mentioned earlier, simple Pt(II) complexes such as $[\text{Pt}(\text{bpy})_2\text{Cl}_2]$ are non-luminescent at RT due to deactivating low-lying d-d states.⁷⁷ $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ coordinating ligands are strong-field, and raise the energy of the d-d states, and also inhibit molecular distortion. An $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ Pt(II) complex analogous to **47**, $[\text{Pt}(\text{phbpy})\text{Cl}]$, exhibits a $^3\text{MLCT}$ excited state, with $\lambda_{em} = 563$ nm, $\tau = 280$ ns and a quantum

yield of $\Phi_{\text{em}} = 0.012$ (in CHCl_3).^{25, 71} In comparison with this complex, **47**, with a more conjugated N[^]N[^]C ligand, exhibits a shorter lifetime and a similar quantum yield. The freely-rotating phenyl rings of **47** may be providing a non-radiative pathway for deactivation of the excited state.

The emission spectrum of **26** (Fig. 3.32) was recorded in CHCl_3 and yielded a highly structured emission profile that is almost identical to that of the previously reported mono-substituted **43** (Fig. 3.6).^{29, 52} For **43**, the reported $\lambda_{\text{max}} = 471$ nm, and **26** exhibits the same band at $\lambda_{\text{max}} = 472$ nm, and both exhibit the same fine structure between 480 and 570 nm. The excitation spectrum of **26** is in good agreement with the absorption spectrum. The emission band has been previously assigned as $^1(\pi-\pi^*)$ emission from the HBC core.⁴⁶ This suggests that the ethynyl moieties have little impact on the fluorescence, since the emission spectrum is very similar to HBC molecules with alkyl substituents in all six positions.^{28, 63} Kim *et al.* suggest that since there is a very weak onset of fluorescence in a mono-substituted ethynyl-HBC (Fig. 3.4, differing only from **43** in possessing long carbon chains at the periphery, rather than *tert*-butyl groups), which is also observed in the cases of **26** ($\lambda \approx 450$ nm) and **43**, that the emission from the lowest singlet excited state is forbidden. They also suggest that the complex fine structure in the emission spectrum is due to several singlet excited states in close proximity.²⁸ The quantum yield of **26** was measured relative to quinine sulfate by the relative method,⁷⁸ and was recorded as $\Phi_{\text{em}} = 0.05$, which is similar with that previously reported for **43** ($\Phi_{\text{em}} = 0.08$).⁴⁶

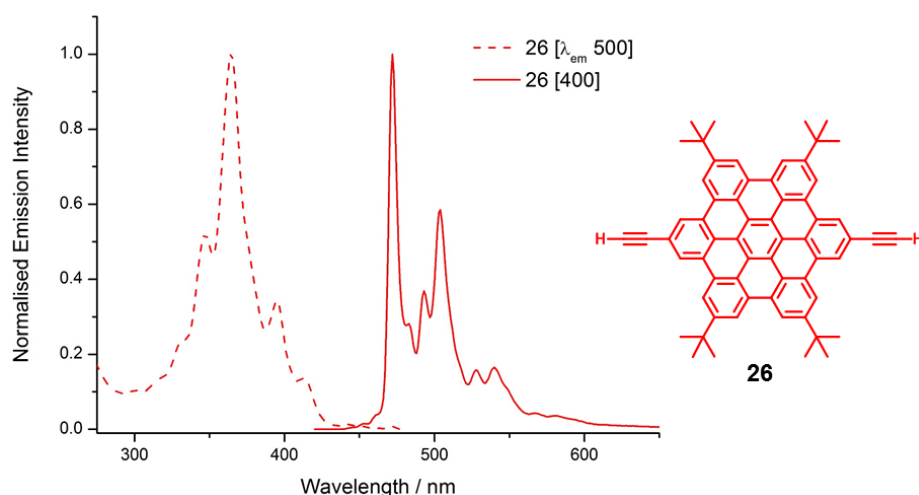


Figure 3.32: Overlaid normalised RT emission (solid line, $\lambda_{\text{exc}} = 400$ nm) and excitation spectra (dashed line, $\lambda_{\text{em}} = 500$ nm) of **26** (1×10^{-6} M, CHCl_3).

3.4.5 Emission Spectra of Pt(II) Acetylides **48** and **49**

The emission and excitation spectra of **48** and **49** are overlaid in Fig. 3.33 (a), and the associated data is presented in Table 3.7. Rather than exhibiting the fine structure displayed by HBC ligands **26** and **43**, a very broad emission is observed for both complexes **48** and **49**, which is almost identical in profile. This profile is independent of concentration for both complexes (10^{-6} - 10^{-8} M). Compared to **48**, a very slight red-shift is observed for **49**, whose emission maximum is observed at $\lambda_{\text{max}} = 597$ nm. Compound **48** displays an emission maximum at $\lambda_{\text{max}} = 595$ nm. There appears to be a shoulder at lower energies in both complexes ($\lambda = 634$ nm for **48** and $\lambda = 636$ nm for **49**). The emission spectra in Fig. 3.33 (a) were obtained by excitation into the lowest energy bands in the UV-Visible spectrum (ca. 500 and 520 nm for **48** and **49** respectively). Excitation at $\lambda = 420$ nm gives the emission spectra in Fig. 3.33 (b), where a low-energy emission may be observed, which is most intense at $\lambda = 481$ nm. The excitation spectra of **48** and **49** are also displayed in Fig. 3.33 (a) and are in good agreement with the UV-Vis absorption spectra.

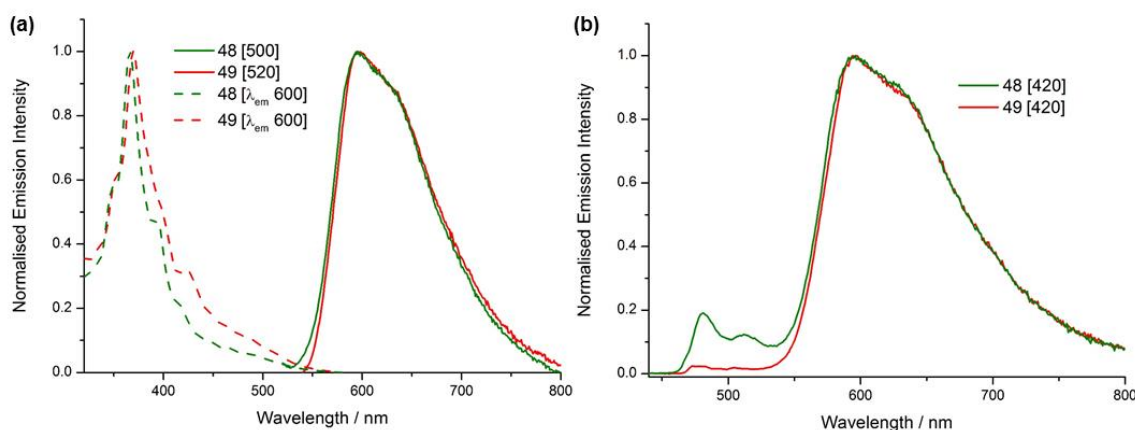


Figure 3.33: (a) Normalised emission (solid line, λ_{exc} [nm]) and excitation spectra (dashed line, $\lambda_{\text{em}} = 600$ nm in both cases) of **48** and **49** (1×10^{-6} , CHCl_3 , RT, N_2 degassed). (b) Normalised emission spectra of **48** and **49** upon excitation at 420 nm (1×10^{-6} , CHCl_3 , RT, N_2 degassed).

In comparison with the previous literature reports of Pt(II) acetylides with HBC cores, these spectra are in some ways quite different. Those reported by Nolan *et al.* show a remarkable degree of fine structure at RT with the emission spectra dominated by narrow-bandwidth phosphorescence attributed to the HBC chromophore at $\lambda \approx 578$ nm (see Fig. 3.6 (d)).²⁹ This narrow-bandwidth phosphorescence has also been observed by Kim *et al.* and El Hamaoui *et al.*^{1, 28} In the case of Nolan *et al.* and Kim *et al.*, after excitation at $\lambda \approx 420$ nm,

it was also observed that the onset of emission began at $\lambda \approx 470$ nm, which was attributed to fluorescence from the HBC chromophore, and which was identical to the uncomplexed HBC ligand. A similar situation seems to be occurring with **48** and **49**, in that upon excitation at higher energy ($\lambda_{\text{exc}} = 420$ nm), the early onset of emission is observed. For **48** and **49**, this onset has an emission maximum at $\lambda_{\text{max}} \approx 480$ nm, which is slightly red-shifted from the previous reports. The intensity of this fluorescence emission is markedly decreased in the case of **49**. This may be due to the increased influence of two Pt centres, in comparison to the single Pt centre possessed by **48**, which displays a much higher intensity fluorescence. The two Pt centres of **49** would be expected to enhance the rate of intersystem crossing (ISC) to the triplet state, thereby decreasing radiative decay *via* fluorescence. Excitation of **48** at longer wavelengths than $\lambda = 420$ nm, *e.g.* 480 nm still yields this fluorescence emission, suggesting that emission from the HBC chromophore persists beyond the absorption of the free HBC ligand. The Pt centre in **48** is quite a distance from the furthest side of the HBC, which may be a factor in the observation of this more intense fluorescence emission. Of the Pt(II) acetylides reported bearing N[^]N[^]C coordinating ligands, Latouche *et al.* report that at RT, a degassed solution of the complex in Fig. 3.8 (a) yields a very broad emission profile with unresolved bands.³⁹ At low temperature (77 K), this is changed markedly, and the emission profile exhibits a much higher degree of fine structure. Lu *et al.* have also reported a series of Pt(II) acetylides with N[^]N[^]C cyclometallating ligands that yield broad emission spectra at RT.³⁸

In order to further probe the nature of the emissive states of **48** and **49**, low temperature spectra were recorded at 77 K in a 4:1 EtOH:MeOH glass (Fig. 3.34 (a) and (b)). Both emission profiles are quite different at low temperature. For **48** (Fig. 3.34 (a)), the previously broad emission profile is now quite well defined, and a narrow band is observed at $\lambda_{\text{max}} = 581$ nm after excitation at either 420 or 500 nm, which previous reports attribute to the HBC chromophore.^{28, 29} Kim *et al.* derive the triplet energy of the HBC chromophore from this band as 2.14 eV.²⁸ From the $\lambda_{\text{max}} = 581$ nm of **48**, this gives a triplet energy of 2.13 eV. The emergence of fine structure at 77 K may be due to the hindered rotation of the phenyl rings of the N[^]N[^]C ligand, which in solution are free to rotate. For **48**, a blue-shift has occurred between the emission maximum observed at RT and that at 77 K (RT: $\lambda_{\text{max}} = 595$ nm. 77 K: $\lambda_{\text{max}} = 581$ nm). This blue shift is expected behaviour for a ³MLCT excited state.^{4, 74, 79} The low-energy fluorescence observed from **48** at $\lambda \approx 480$ nm, upon excitation at 420 nm at RT, appears to become negligible at 77 K.

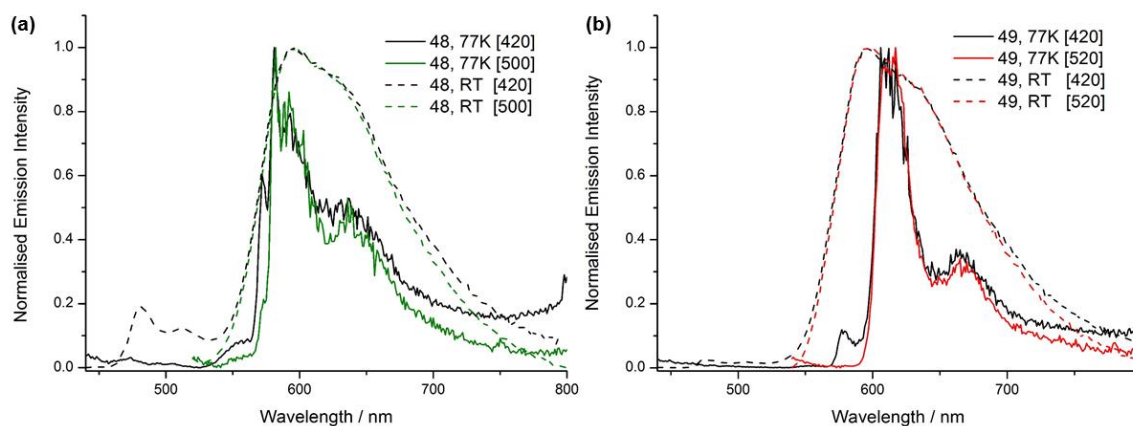


Figure 3.34: (a) Low-temperature (77 K) emission spectra of **48**, (solid line, $\sim 1 \times 10^{-6}$ M, recorded in a glass of 4:1 EtOH:MeOH), with the RT emission spectra overlaid for comparison (dashed line, 1×10^{-6} M, CHCl_3). (b) Low-temperature (77 K) emission spectra of **49**, (solid line, $\sim 1 \times 10^{-6}$ M, recorded in a glass of 4:1 EtOH:MeOH), with the RT emission spectra overlaid for comparison (dashed line, 1×10^{-6} M, CHCl_3).

The emission spectrum of **49** at 77 K does not exhibit a blue-shift of the same magnitude as for **48**. The very small shift is not as indicative of a $^3\text{MLCT}$ excited state. If excited at 420 nm, rather than 520 nm, a small shoulder is apparent at $\lambda = 578$ nm. The nature of the excited state of **49** is therefore complex. Recent studies have shown that the lowest excited states in Pt(II) acetylide complexes may also possess contributions from LLCT (ligand-to-ligand charge transfer) transitions (in this case, π acetylide to π^* $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$).^{80, 81} The electronic coupling of acetylide π orbitals and d orbitals of the Pt centre in similar Pt(II) acetylides has led to the suggestion of excited states with (metal-ligand)-to-ligand charge transfer (ML'LCT) character (in this case, the transition $[\text{Pt}(\text{d})/\pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N}^{\wedge}\text{C})]$).⁸² The broad RT emission profile of **49** at RT is more suggestive of MLCT with possibly some LLCT or ML'LCT character, rather than $^3\text{LC}/^3\text{IL}$, as these emissive states often show a degree of fine structure.⁸³ There may also be a similar LLCT/ML'LCT contribution to the emissive state of **48**. DFT computational studies are desirable to shed more light on the nature of the excited states of these complexes.

3.4.6 Solvatochromism and Degassing Studies of **48** and **49**

Solvatochromism studies were also carried out on both **48** and **49** (Fig. 3.35). Negative solvatochromism was observed for **48**, which is further indication of a MLCT

emissive state (Fig. 3.35 (a) and (c)).⁷⁴ In solvents of higher polarity, the emission is shifted to higher energies. In MeOH, a higher degree of fine structure is observed, possibly due to poor solvation. The behaviour of **49** is slightly more complex. In CHCl₃, THF and toluene, the emission profiles remain broadly similar, upon excitation at both 420 and 500 nm (Fig. 3.35 (b) and (d)). A relatively small shift in the emission maximum is observed in all cases, but in the more polar EtOH and MeOH, a very broad emission is observed at $\lambda \approx 688$ nm, red-shifted from the emission in CHCl₃. As **49** is only very poorly solvated in MeOH and EtOH, this red-shift may be due to aggregation-induced emission.⁸⁴ The small magnitude of the shift of the emission maximum of **49** suggests that the emissive state of **49** may not possess significant CT character (*e.g.* a significant change in dipole moment in the excited state), which is further supported by the small shift at 77 K.

The emissive behaviour in non-degassed solutions was also investigated. As phosphorescence is often quenched in aerated solutions by collisions with molecular oxygen, a decrease in luminescence intensity would be predicted for a compound which possesses phosphorescent character. Emission spectra from aerated and degassed solutions of **48** and **49** were recorded, which exhibited a significant decrease in luminescence intensity in the aerated samples (Fig. 3.36 (a) and (b)), evidence that their emissive states possess significant phosphorescent character. These studies revealed that both compounds are quite significantly more emissive upon excitation at higher energies (420 nm), rather than upon excitation at lower energies (500-520 nm). The emission is most likely to possess a very significant contribution from the HBC chromophore, since excitation at 420 nm is in the region where the HBC is likely to still be absorbing.

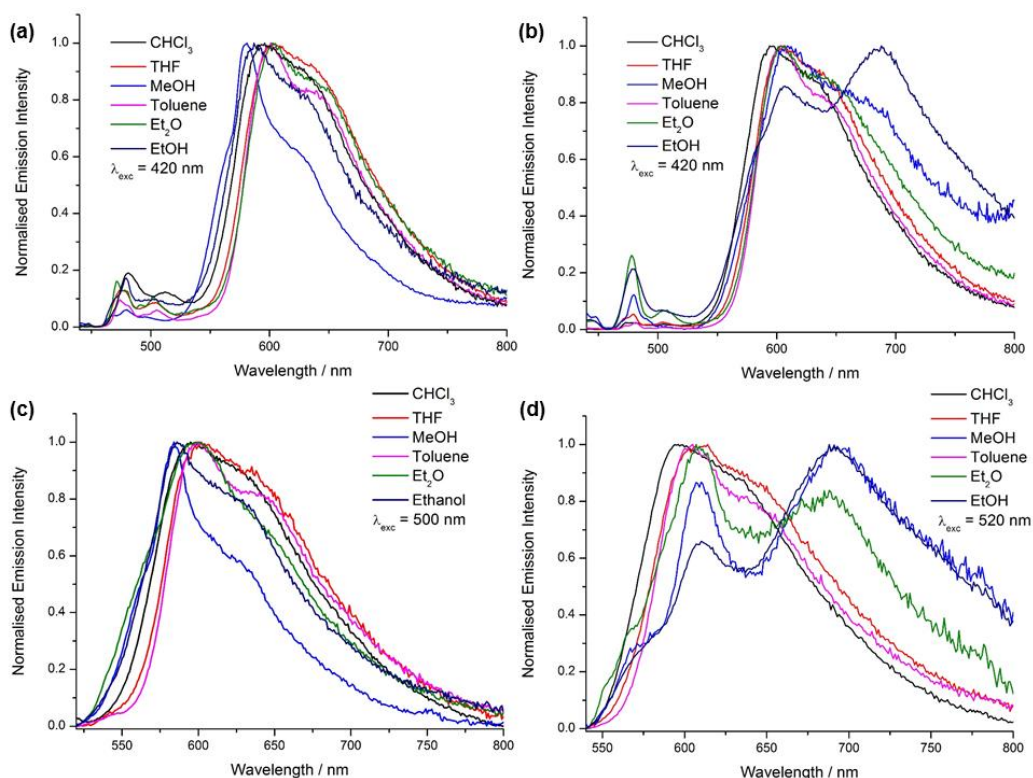


Figure 3.35: (a) and (b) Overlaid normalised emission spectra of **48** and **49** respectively in solvents of varying polarity (1×10^{-6} M, $\lambda_{exc} = 420$ nm in all cases). (c) and (d) Overlaid normalised emission spectra of **48** and **49** respectively in solvents of varying polarity ($\sim 1 \times 10^{-6}$ M, $\lambda_{exc} = 500$ nm (**48**) or $\lambda_{exc} = 520$ nm (**49**)).

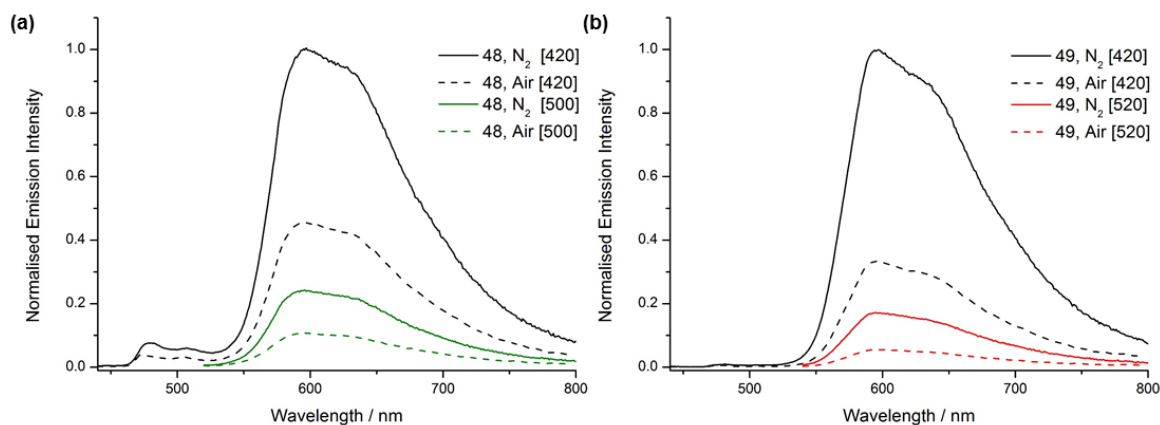


Figure 3.36: (a) Emission spectra of **48** recorded in N_2 -degassed solution and aerated solution. (b) Emission spectra of **49** recorded in N_2 -degassed solution and aerated solution. $\lambda_{exc} = [\text{nm}]$.

In order to determine the efficiency of this emissive process, the quantum yields of emission were measured in N_2 -degassed solutions for both **48** and **49** via the relative method,

using Ru(bpy)₃ as a standard. The quantum yields are similar; for **48**, $\Phi_{\text{em}} = 0.04$ and for **49** $\Phi_{\text{em}} = 0.03$, indicating that the process is most likely competing with other modes of deactivation. The quantum yields of **48** and **49** are slightly reduced compared to their ethynyl-HBC precursors. The lifetimes of emission of **48** and **49** were recorded in degassed solutions, and the results are summarised in Table 3.7. Both compounds displayed similar lifetimes, *ca.* 350 ns, with the decay curves for both requiring bi-exponential fitting. Since the emission profiles of both **48** and **49** appear to both show two shoulders (*e.g.* for **48**, $\lambda_{\text{em}} = 595$ and $\lambda_{\text{em}} = 634$) it is not unexpected that a bi-exponential function is required. Measuring the lifetimes at each of these shoulders gave similar values (Table 3.7). The lifetimes obtained are typical of MLCT-based emission, rather than LC/IL-based emission, which are generally longer.⁸⁵

Table 3.7: Emission data for Pt(II) acetylides **48** and **49** and precursor ligands.

Compound	Medium (Temp. [K])	$\lambda_{em}[nm]$ ($\lambda_{exc}[nm]$)	Lifetime τ [ns] ($\lambda_{exc}/\lambda_{em}$ nm)	Φ_{em} ($\lambda_{exc}[nm]$)
26^a	CHCl ₃ (298 K)	460 _{wk} , 472 _{max} , 484 _{sh} , 493, 503, 528, 540, 567 _{wk} (400)	10 (370/470)	0.05 (400)
43^{*a}	CH ₂ Cl ₂ (298 K)	460 _{wk} , 471 _{max} , 481, 490, 500, 524, 535, 545 _{sh} , 563 _{wk} (390)	12 (3 %), 24 (97 %) (370/470)	0.08 (390)
44^a	CHCl ₃ (298 K)	479 _{max} (320)	--†	0.06 (320)
47^b	CHCl ₃	612 _{max} (430)	198 (80 %), 330 (20 %) (370/430)	0.014 (430)
	EtOH:MeOH (77 K)	550 _{max} , 596, 643 (430)		
48^b	CHCl ₃ (298 K)	595 _{max} , 634 _{sh} , (500) 481, 512, 595 _{max} , 634 _{sh} (420)	350 (61 %), 490 (39 %) (370/600) 390 (97 %), 990 (3%) (370/640)	0.06 (420) 0.04 (500)
	EtOH:MeOH (77 K)	581 _{max} , 593, 637 (500/420)		
49^b	CHCl ₃ (298 K)	597 _{max} , 636 _{sh} (520) 480, 511, 597 _{max} , 636 _{sh} (420)	350 (76 %), 650 (24 %) (370/600) 350 (74 %), 640 (26 %) (370/640)	0.03 (420), 0.03 (520)
	EtOH:MeOH (77 K)	608, 617 _{max} , 665 (520) 578, 606 _{max} , 611, 627 _{sh} , 665 (420)		

**As previously reported by Nolan et al.²⁹ ^a Recorded in non-degassed solutions. ^b Recorded in degassed solutions. † Lifetime too short for accurate measurement due to machine limitations (> 1 ns).*

3.5 Electrochemistry - Cyclic Voltammetry

3.5.1 Electrochemical Properties of Precursor Compounds

The electrochemical properties of the compounds were investigated by cyclic voltammetry (CV). Solutions of the compounds (CH_2Cl_2 , 1×10^{-4} M) were degassed by bubbling with N_2 , and then analysed under an atmosphere of N_2 . The cyclic voltammograms of the oxidation processes of **26**, **44**, and **47** are depicted in Fig. 3.37, and the relevant data is summarised in Table 3.8. The potentials given in this section are quoted *versus* Fc/Fc^+ (set as 0.0 V). Although the photophysical studies were carried out in CHCl_3 , for reasons of solubility, it was found that clear voltammograms could not be obtained in this solvent, and CH_2Cl_2 was chosen. The di-substituted ethynyl-HBC **26** displays two quasi-reversible oxidations ($E_{1/2} = 0.61$ V and 0.92 V). These are slightly more positive than the oxidation processes reported for the mono-substituted ethynyl-HBC **43**, as reported by Dr. D. Nolan.⁴⁶ **43** is reported as displaying one reversible oxidation process, and one quasi-reversible oxidation process, at 0.57 V and 0.83 V, (vs. Fc/Fc^+) respectively, suggesting that the di-substituted ethynyl-HBC **26** is slightly more difficult to oxidise (*i.e.* the HOMO level is slightly lower in energy). The first oxidation of $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ ligand **44** is observed to be irreversible, occurring at 0.97 V. The Pt(II) chloride complex, **47**, displays two irreversible oxidations, at 0.66 V, and a less clearly observed oxidation at 0.96 V. The first oxidation, at 0.66 V, is assigned to a $\text{Pt(II)} \rightarrow \text{Pt(III)}$ process, which are generally irreversible.⁸⁶ The oxidation at 0.96 V is in essentially the same position as that of the free ligand, and is therefore assigned as being ligand-based. The lower resolution of this oxidation peak may be due to the presence of another metal-based oxidation peak underlying it.

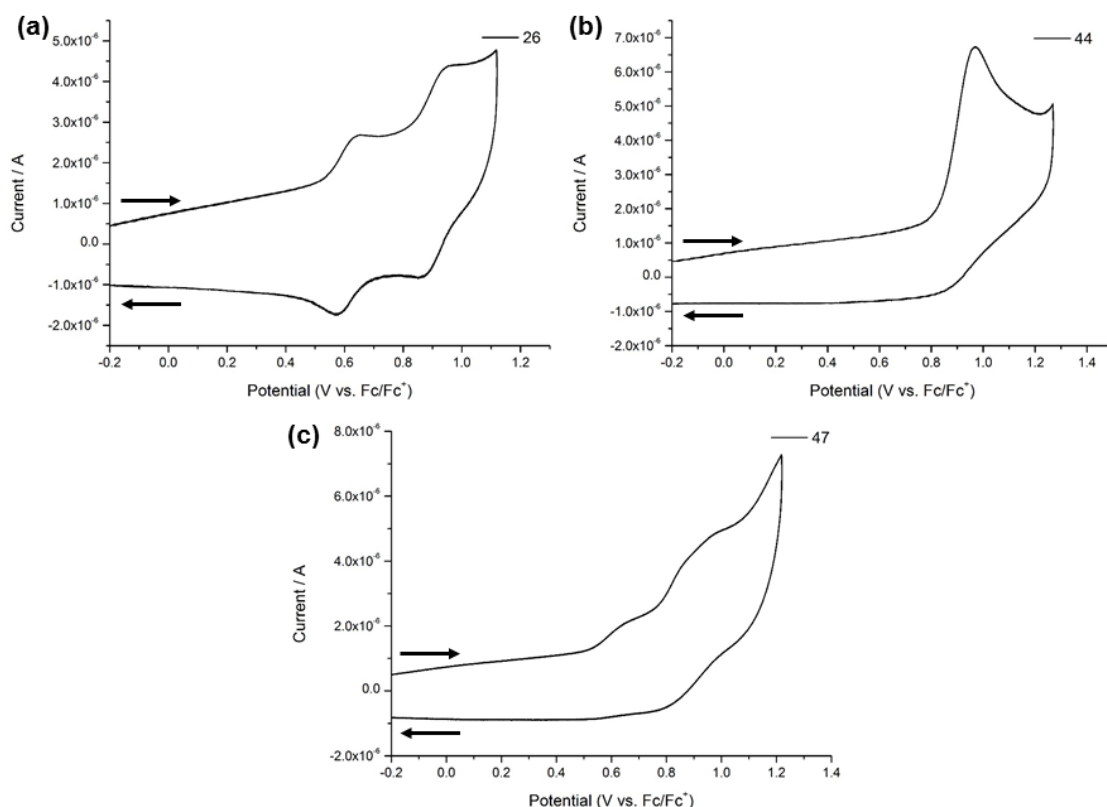


Figure 3.37: Cyclic voltammograms of **26**, **44**, and **47**, showing the oxidation processes (1×10^{-4} M, CH_2Cl_2 , vs. Fc/Fc^+ , with 0.1 M TBAPF_6 as supporting electrolyte) with a scan rate of 0.1 V s^{-1} . Arrows indicate direction of scan.

The corresponding reduction scans of the same compounds are displayed in Fig. 3.38. The reduction of HBC **26** is observed at $E_p = -1.45 \text{ V}$ (vs. Fc/Fc^+). A return peak associated with this process is observed at $E_p = -1.20 \text{ V}$, and since the ΔE_p value is quite high (250 mV) it is assigned as being an irreversible process. The $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ ligand **44** displays a single irreversible reduction at $E_p = -2.10 \text{ V}$, with no return peak observed for the process. The Pt(II) chloride complex, **47**, yields a reversible reduction at $E_{1/2} = -1.86 \text{ V}$. This is assigned to a ligand-based process, since the reduction of Pt(II) to Pt(I) would be expected to be an irreversible process, as Pt(I) species are unstable.⁸⁶ This further indicates that the emissive state of **47** is MLCT in nature, since the electrochemical oxidation appears to be metal-based, and the reduction appears to be ligand-based.

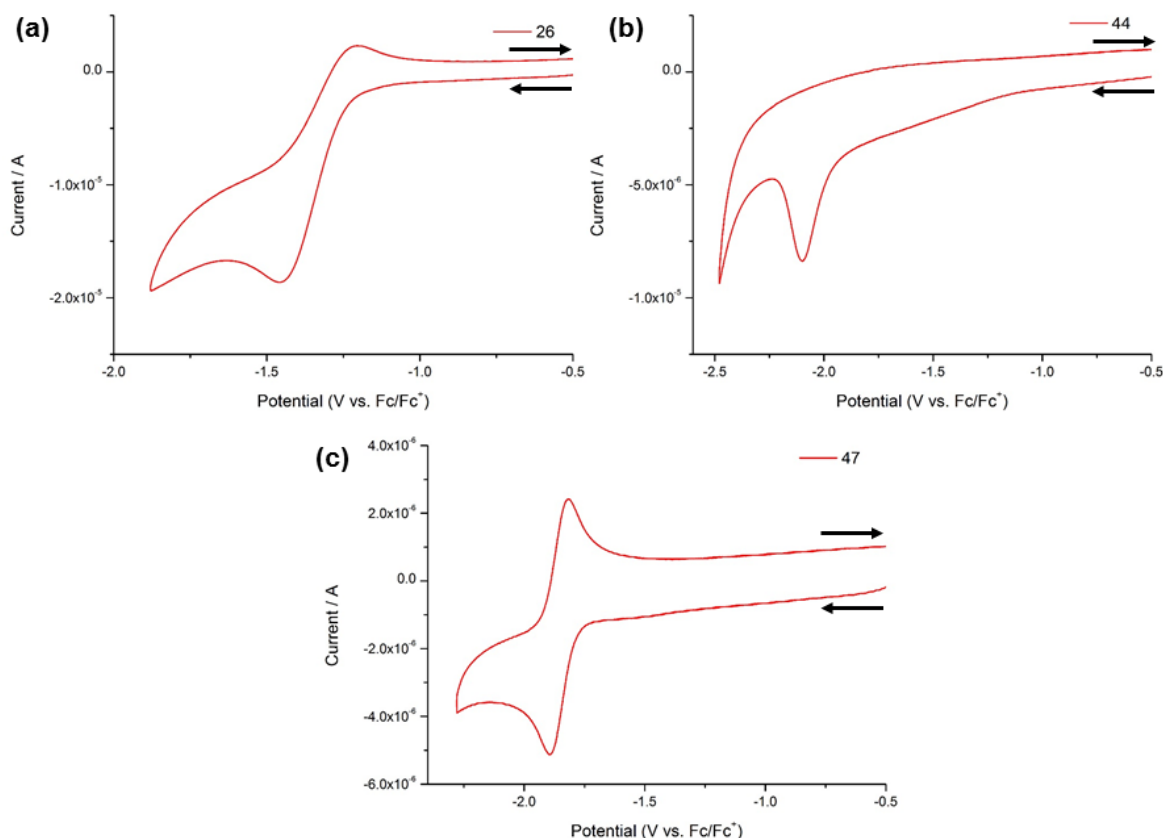


Figure 3.38: Cyclic voltammograms of **26**, **44**, and **47**, showing the reduction processes (1×10^{-4} M, CH_2Cl_2 , vs. Fc/Fc^+ , with 0.1 M TBAPF_6 as supporting electrolyte) with a scan rate of 0.1 V s^{-1} . Arrows indicate direction of scan.

3.5.2 Electrochemical Properties of Pt(II) Acetylides **48** and **49**

Cyclic voltammograms of Pt(II) acetylide complexes **48** and **49** are displayed in Fig. 3.39. The mono-Pt(II) complex, **48**, displays an irreversible oxidation at $E_p = 0.50 \text{ V}$, which is assigned to the oxidation of $\text{Pt(II)} \rightarrow \text{Pt(III)}$ (Fig. 3.39 (a)). The oxidation of **49** appeared to be beyond the solvent window, as no oxidation process was clearly observed. However, the lack of an oxidation peak may in fact be due to the poor solubility of this compound. The reduction of **48** is observed as a quasi-reversible couple at $E_{1/2} = -1.86 \text{ V}$. This is assigned as occurring on the $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ -Pt moiety, due to its similarity to the reductive behaviour of **47**. This assignment therefore leads to the indication that the HOMO of **48** is based upon the Pt(II) centre, and the LUMO is localised on the $\text{N}^{\wedge}\text{N}^{\wedge}\text{C}$ -Pt(II) moiety. The reduction process of **49** is shown in Fig. 3.39 (c) and is quite similar to that of **48**. It is observed as a quasi-reversible couple at $E_{1/2} = -1.87 \text{ V}$, and based upon its similarity to **48**, is assigned as being

primarily N[^]N[^]C-Pt based. It is observed at only a very slightly more negative potential than that of **48**, suggesting that the inclusion of the second Pt(II) centre has had little effect on the LUMO energy. The similarity of the emission energy for **48** and **49** is further indication that this is the case.

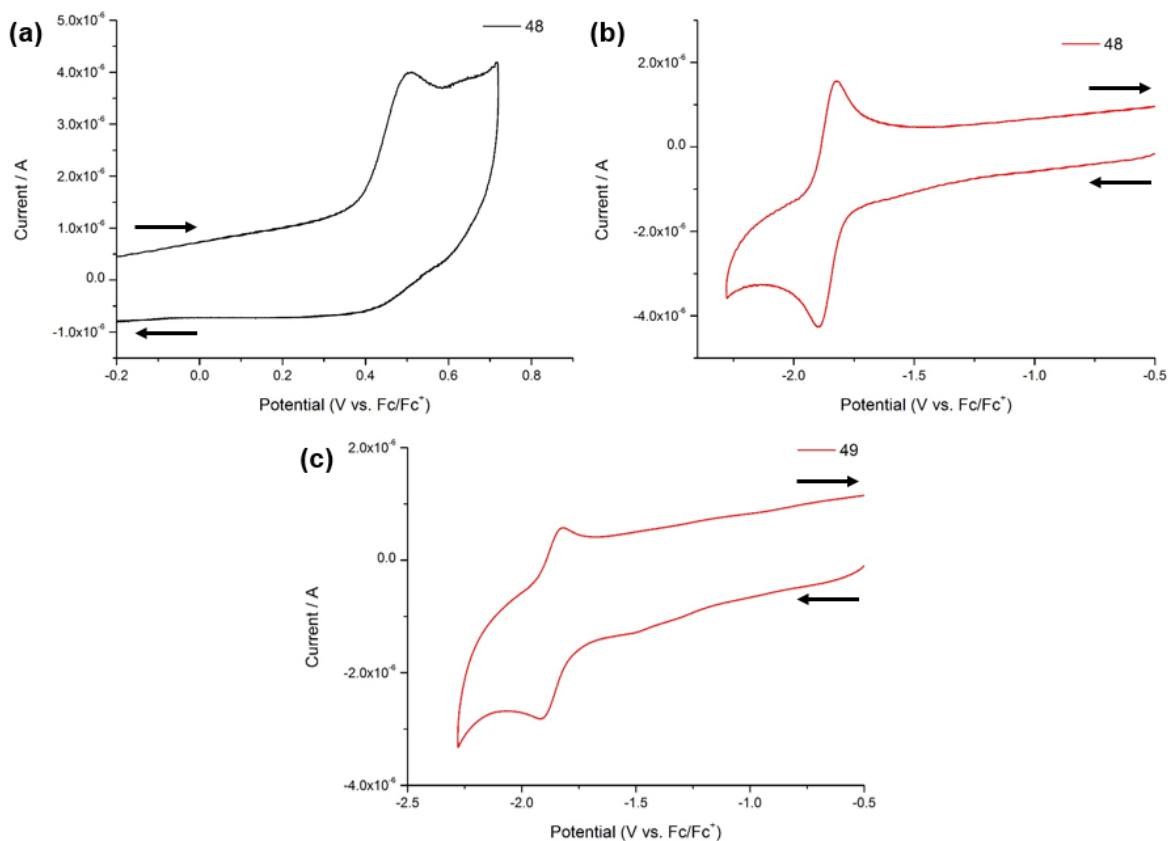


Figure 3.39: (a) and (b) Cyclic voltammograms of the oxidation and reduction processes, respectively, of **48**, and (c) the reduction process of **49** (1×10^{-4} M, CH_2Cl_2 , vs. Fc/Fc^+ , with 0.1 M TBAPF_6 as supporting electrolyte with a scan rate of 0.1 V s^{-1}). Arrows indicate direction of scan.

The Pt(II) HBC-acetylides reported by Kim *et al.* gave no well-resolved cyclic voltammograms, although they report a broad quasi-reversible oxidation wave at 0.4 V vs. Fc/Fc^+ (reported in the paper as 0.8 V vs. SCE, converted to Fc/Fc^+ by subtraction of 0.4 V) for a Pt(II) acetylide connected to a HBC core with a single ethynyl linking unit (Fig. 3.4).²⁸ They do not assign the nature of the oxidation, but explain the poor resolution of the voltammograms as being due to aggregation of the compounds, and/or coating of the electrode surface by oxidised products. The oxidation of **48** is therefore in a similar region. Of the Pt(II) HBC-acetylides reported by Nolan *et al.* (Fig. 3.6), the *trans*-Pt(II) acetylide **LC 98** was too insoluble for electrochemical measurement, but the *cis*-Pt(II) acetylide, **LC**

100, exhibited an irreversible oxidation at 0.49 V and a reversible oxidation at 0.87 V (vs. Fc/Fc⁺). The oxidation at 0.49 V was assigned to the Pt(II)→Pt(III) oxidation process, and the reversible oxidation at 0.87 V was assigned to the HBC ligand. Lu *et al.* have reported that the first reduction for a series of Pt(II) acetylides with cyclometallating ligands is observed in the region of -1.60 to -1.80 V (vs. Fc/Fc⁺).³⁸ They assign this process as being based upon the C[^]N[^]N ligand. In their case, the C[^]N[^]N ligands are less conjugated than **44**, which suggests that the extra conjugation of **44** has resulted in a decrease in the LUMO energy, and as a consequence, is easier to reduce. They report that the oxidation potentials for these acetylides are quite low (0.01-0.47 V vs. Fc/Fc⁺), and seem to vary with C[^]N[^]N ligand functionality.

Table 3.8: Electrochemical data. * denotes irreversible process (with E_p value quoted). Values versus the Fc/Fc⁺ couple (0.0 V).

Compound	Oxidation	Reduction
	$E_{1/2}V$, [$\Delta E_p/mV$]	$E_{1/2}V$, [$\Delta E_p/mV$]
26	0.61 [80], 0.92 [90]	-1.45*
44	0.97*	-2.10*
47	0.66*, 0.96*	-1.86 [70]
48	0.50*	-1.86 [80]
49	--	-1.87 [90]

3.6 Conclusions and Future Work

This chapter has described the synthesis and characterisation of two novel Pt(II) acetylides, **48** and **49**, bearing both N[^]N[^]C-type coordinating ligands and highly conjugated HBC-based chromophoric centres. A derivative bearing one Pt(II) acetylide moiety attached to a HBC core (**48**) and a derivative bearing two Pt(II) acetylide units (**49**) were prepared. Initial attempts focused on preparing N[^]N[^]N-type coordinated analogues of these were not successful due to very low solubility and poor yields. The selection of a suitable N[^]N[^]C-type ligand enhanced the solubility of the compounds considerably and permitted their isolation, purification and characterisation. Literature reports of Pt(II) acetylides bearing such conjugated cores are rare, and only one report has been published to date of a HBC core disubstituted with Pt(II) acetylides.¹ The formation of a disubstituted derivative was

achieved through the synthesis of the previously unreported diethynyl-HBC **26**, whose photophysical characterisation revealed it to behave in an almost identical fashion to that of the previously reported ethynyl-HBC **43**. The cyclometallating ligand **44** was characterised photophysically for the first time, and revealed unusual behaviour in both UV-Vis absorption and fluorescence emission spectroscopy. Subsequent protonation studies suggest that the unprotonated ligand may possess an $n\text{-}\pi^*$ lowest excited state, which upon protonation yields to a more emissive $\pi\text{-}\pi^*$ state.

Although **48** and **49** exhibited improved solubility to their $N\wedge N\wedge N$ -ligand containing counterparts, their solubility remained relatively low, and their characterisation posed some challenges. Photophysical analysis of **48** and **49** revealed UV-Visible spectra dominated by the HBC unit, with an extended band at $\lambda \approx 450$ nm. Very broad emission spectra at RT were observed, which displayed much more definition at 77 K. In the case of **48**, an emission profile very similar to those previously reported for Pt(II) acetylides was observed at 77 K, and the extent of the blue-shift of the emission is suggestive of a $^3\text{MLCT}/^3\text{LLCT}$ (or $\text{ML}'\text{LCT}$) emissive state. Although **49** gave some fine structure in its emission spectrum at 77 K, it is unclear whether the emission is primarily CT-based, and whether the triplet state is located on the HBC unit, although its tremendous insolubility may be contributing to its more unusual behaviour. Solvatochromism studies on the emission spectra of **48** provided further indication that its emissive state is most likely primarily CT in character. Future work may involve computational studies to further probe the nature of the emissive states of these compounds.

The limited range of organometallic compounds incorporating the intriguing HBC chromophore has been extended by this work. The extension of the novel $[\text{Pt}(N\wedge N\wedge C)\text{Cl}]$ complex **47**, with its extended polyphenylene cyclometallating ligand, towards the synthesis of Pt(II) acetylides with other PAH-based systems would be of interest. It would be useful to vary the substituent PAH moieties (*e.g.* with 1-ethynylpyrene, phenylacetylene *etc.*) in order to further probe the emissive behaviour of this novel ligand (Fig. 3.40). It has been reported that organometallic compounds in which $S_1\text{-}T_1$ intersystem crossing and the rate of radiative decay from $T_1 \rightarrow S_0$ is enhanced, exhibit potential for optoelectronic applications.^{28, 87} Phosphorescent materials such as these, which emit efficiently from triplet excited states, have been shown to increase the efficiency of organic light-emitting devices,⁸⁸ and as such, compounds such as **48** and **49** represent contributions towards initial studies for materials suitable for these applications. Pt (II) complexes with strong-field acetylide co-ligands often

display long-lived room temperature phosphorescence, making them ideal candidates for future electronic applications. Furthermore, the development of the cyclometallating ligand **44** towards Pt(II) acetylides presents a further means of influencing the luminescence of such complexes, due to the higher field strength and the extra rigidity imparted by cyclometallating ligands over diimine and terpyridine ligands. Fig. 3.40 displays two novel compounds incorporating **44**, which would be expected to display improved solubility due to the smaller arylacetylide ligands. It would also be intriguing to study whether the planarisation (*i.e.* intramolecular cyclodehydrogenation) of ligand **44** may lead to improved photophysical properties, due to further enhanced rigidity.

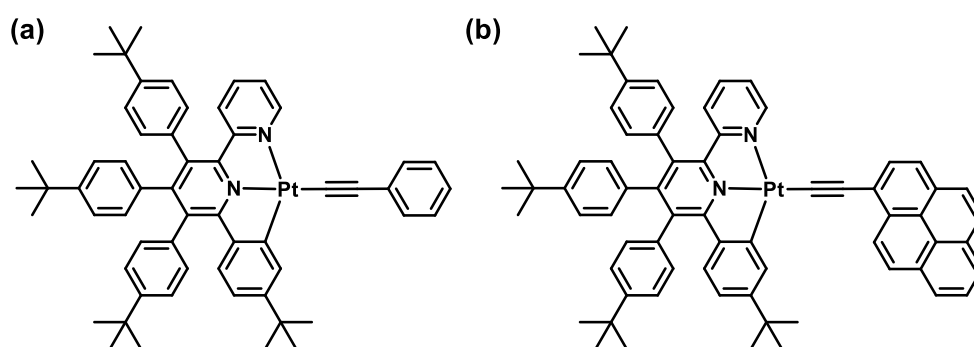


Figure 3.40: (a) and (b) Examples of future novel Pt(II) acetylides with N^NC ligands.

Functionalisation of the HBC core of the acetylides described in this chapter would provide another route to novel Pt(II) acetylides, which would be expected to exhibit different photophysical properties. In Fig. 3.41 (a), a proposed compound analogous to **49** is displayed. The N-substitution, achievable through a Diels-Alder cycloaddition generating an N-HSB-type aromatic core, as discussed in Chapter One, may lead to improved solubility, and offer further coordination possibility. Further improved solubility could be generated through the structure shown in Fig. 3.41 (b), where a partially-fused core is employed. This could be generated by oxidative cyclodehydrogenation of the precursor N-containing polyphenylene with Br₂.

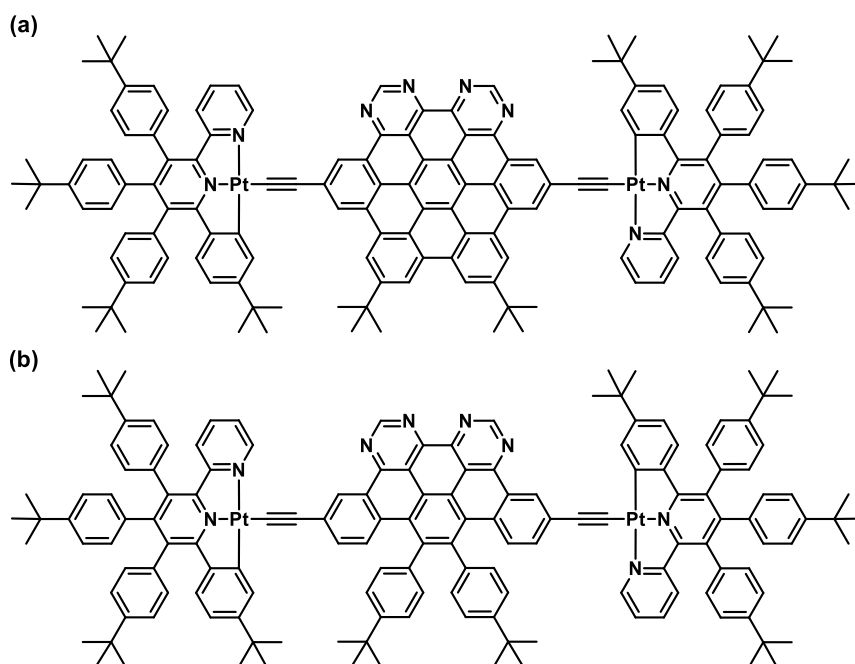


Figure 3.41: Future work. (a) A Pt(II) acetylide with aromatic core based on *N*-HSB. (b) A Pt(II) acetylide with partially-fused core, obtainable through Br_2 mediated oxidative cyclodehydrogenation.

The solubility of a dinuclear system such as **49** could be improved by incorporating a smaller aromatic core, which is less likely to undergo such extensive aggregation in solution. An example of such a compound is displayed in Fig. 3.42. This compound would be accessible through coupling of the commercially available 1,6-dibromopyrene with ethynyl units, permitting coupling to the Pt centre of a ligand such as **47**. Synthetic access to a mononuclear analogue should also be relatively facile.

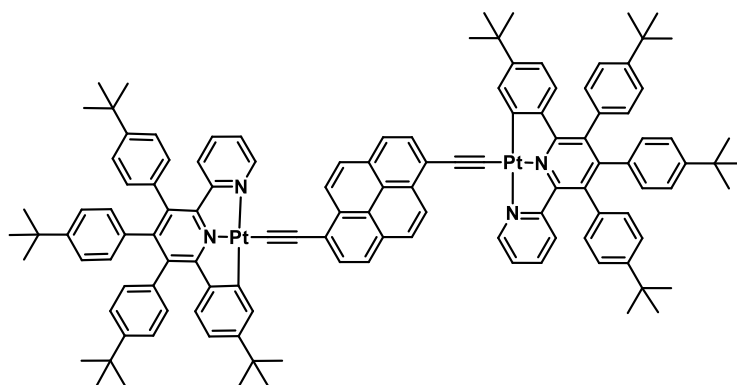


Figure 3.42: A Pt(II) acetylide with a smaller chromophoric core, based upon 1,6-diethynylpyrene.

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Chapter Four

The Synthesis and Characterisation of Phosphorescent Pt(II) Acetylides with Polyaromatic Diimine (N[^]N) Ligands

4.1 Introduction

This chapter intends to describe the synthesis and characterisation of a range of novel Pt(II) acetylides featuring diimine ($N^{\wedge}N$ coordinating) ligands which display varying degrees of conjugation and substitution. As discussed in Chapter Three, Pt(II) acetylides bearing diimine-based ligands, such as those based upon 1,10-phenanthroline or 2,2'-bipyridine, have been widely investigated for their useful properties, such as room-temperature luminescence. However, most research to date has focused upon modification of the acetylide substituents, and little work has been carried out to investigate the effect of modification of the diimine ligands. It has been reported that the HOMO energy level of these complexes resides mostly on the metal centre, and the LUMO resides mostly upon the diimine ligand.^{1, 2} Therefore it is of interest to note whether modification of the diimine constituent, and extending its conjugation, provides a useful means of control over the optical properties of these types of compounds.

4.1.1 Pt(II) Acetylides with Diimine ($N^{\wedge}N$) Ligands

Since the first report of a Pt(II) diimine complex with acetylides as the anionic ligands in 1994 by Chan *et al.*,³ which displayed room-temperature luminescence, such complexes have been widely investigated. This initial report gave very brief details of the synthesis of the complex $Pt(phen)(C\equiv CPh)_2$, where phen represents 1,10-phenanthroline (**LC 85**, Fig. 4.1 (a)). The emission was explained as being due to a $Pt(d)-\pi^*(phen)$ ^3MLCT excited state. Hissler *et al.* note that the energy of the emission from these acetylide complexes (^3MLCT) is therefore in between those of the di(cyanide) and dithiolate complexes, which give, respectively, emission from $^3(\pi-\pi^*)$ states or from CT from an orbital of mixed metal/dithiolate character to a diimine orbital.¹ Subsequent work by James *et al.* in 1997 gave a more detailed account of the synthesis and initial photophysics of a group of similar compounds (**LC 109-111**, Fig. 4.1 (b)) with the general formula, $Pt(Me_2bpy)(C\equiv CPh)_2$ (where Me_2bpy is 4,4'-dimethyl-2,2'-dipyridine).⁴ The synthesis of these complexes was achieved by the reaction of $[Pt(Me_2bpy)Cl_2]$ with an excess of the relevant terminal alkyne ($H\equiv C-Ar$) in $CH_2Cl_2/iPrNH_2$ with a catalytic amount of CuI , in a dehydrohalogenative coupling reaction, a synthetic route initially devised by Sonogashira and co-workers in the 1970s.⁵ The $Pt(diimine)Cl_2$ precursor is generally prepared by two routes; either with K_2PtCl_4 in acidic, aqueous media, or with $Pt(DMSO)_2Cl_2$ in an organic

solvent, where the diimine ligand displaces the more labile ligands.⁶ The report by James *et al.* led to renewed interest in these complexes, and subsequently the Schanze and Eisenberg groups began conducting systematic investigations of such Pt(II) acetylide complexes and their luminescence properties.

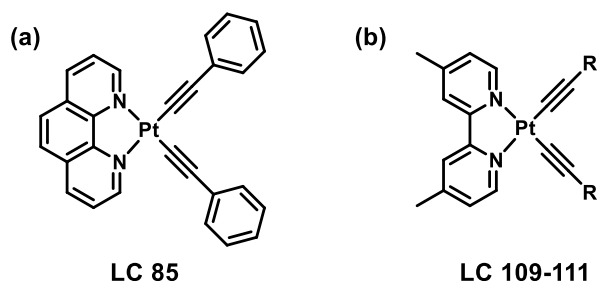


Figure 4.1: (a) The first reported diimine Pt(II) acetylide,³ and (b) the diimine Pt(II) acetylides as reported by James *et al.*, where $R = C_6H_4-4-CH_3$, C_6H_5 , $C_6H_4-4-NO_2$.⁴

Hissler *et al.*, of the Eisenberg group, conducted a study on how varying the diimine or varying the acetylide ligand affected the excited state of Pt(II) acetylides of the formula $Pt(\text{diimine})(C\equiv CPh)_2$.¹ To achieve this, they synthesised two groups of Pt(II) acetylides, one in which the diimine ligand was varied, holding the acetylide ligand constant, and another in which the diimine was held constant and the acetylide was varied. They observed that shifts to lower energies in the emission spectra were obtained as the electron-withdrawing ability of the diimine ligand increased and as the electron donating ability of the acetylide ligand increased, which are indicative of a mainly metal-based HOMO and a LUMO based on a diimine π^* orbital. Their investigation concluded that the HOMO-LUMO gap was more affected by modification of the diimine ligand than the acetylide ligands, which was suggested to be due to the acetylide ligands being some distance away from the metal centre. The emitting state (observed to be long-lived, with lifetimes of up to 5600 ns) was consistent with a ^3MLCT assignment, where modification of the diimine affects the LUMO energy and modification of the acetylide ligands affords a small effect on the Pt-based HOMO.

The Schanze group reported a similar study in 2001, and came to similar conclusions, *i.e.* that the emissive state in such complexes is generally the low-lying $Pt \rightarrow \text{diimine } ^3MLCT$ state.⁷ However in some cases, they noticed that emission was characteristic of IL (intraligand) $^3\pi-\pi^*$ states, originating mostly from the acetylide ligands. This was observed where the diimine ligand was held constant, but the electron-demand of the acetylide was varied. The evidence for IL emission, rather than MLCT, was provided by recording an emission spectrum at low temperature (80 K) that did not vary with that recorded at RT. If

the energy of emission is observed to change with temperature, it is characteristic of a charge-transfer excited state.⁸ This phenomenon is known as ‘luminescence rigidochromism’.⁹ Generally MLCT emission occurs from a higher energy in rigid media (*e.g.* a frozen glass) than in solution. This is due to the dipole orientation of the solvent being frozen in rigid media, and therefore unable to be rearranged, or relax, around the dipole of the excited state of the solute.¹⁰

The Castellano group have carried out significant work on Pt(II) acetylide complexes with diimine ligands, and in 2003, demonstrated how the incorporation of Pt(II) acetylides could be used to produce long-lived phosphorescence from the arylacetylide.¹¹ They incorporated pyrene chromophores into the acetylide units, generating the complex [Pt(dbbpy)(C≡C-pyrene)₂] (**LC 112**) where dbbpy represents 4,4’-di(*tert*-butyl)-2,2’-bipyridine (Fig. 4.2 (a)).

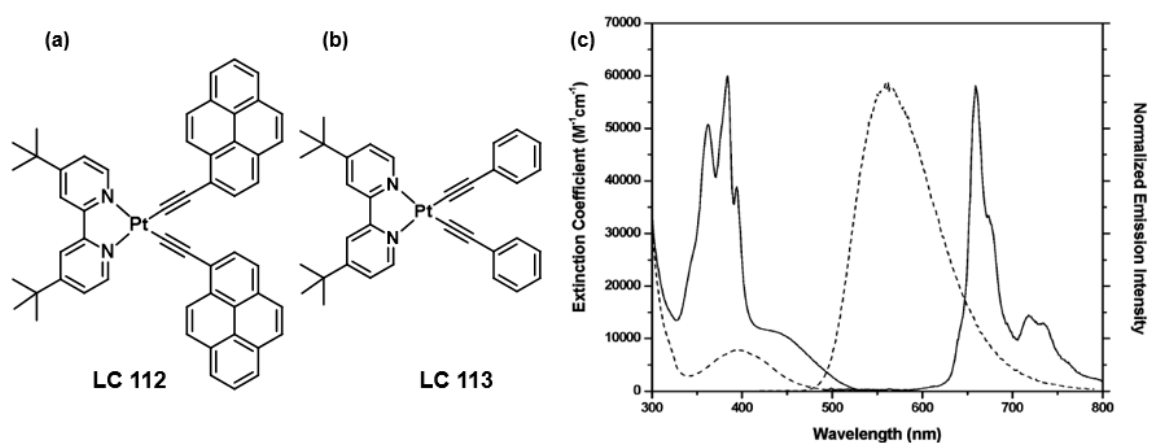


Figure 4.2: Pt(II) acetylides investigated by Pomestchenko *et al.*¹¹ (a) Pt(dbbpy)(C≡C-pyrene)₂. (b) Pt(dbbpy)(C≡CPh)₂. (c) UV-Visible absorption and emission spectra of Pt(dbbpy)(C≡C-pyrene)₂ (solid lines) and of Pt(dbbpy)(C≡CPh)₂ (dashed lines). (c) is taken from Pomestchenko *et al.*¹¹

They reported that upon excitation into the low energy MLCT bands (at $\lambda = 480$ nm, see UV-Vis spectrum in Fig 4.2 (c)), they could generate long-lived phosphorescence at room temperature. This was attributed to ³IL phosphorescence from the pyrenyl moieties, which were internally sensitised by the ³MLCT state, aided by the heavy atom effect of the platinum. The ³IL nature of the luminescence was confirmed by transient absorption (TA) measurements and measurement of the emission spectra at RT and 77 K. The very small Stokes shift in the RT and 77 K emission spectra were characteristic of ³IL emission. In comparison, the complex Pt(dbbpy)(C≡CPh)₂ (*i.e.* incorporating phenyl groups in place of

the pyrene moieties, **LC 113**, Fig. 4.2 (b)) yielded a $^3\text{MLCT}$ emission 2800 cm^{-1} higher in energy (Fig. 4.2 (c)).

In 2004, they followed this work up by reporting a similar complex with 1-ethynyl-naphthalene ligands in place of the 1-ethynylpyrene (**LC 114**), demonstrating that the lowest-energy excited state could be switched between either ^3CT or ^3IL , depending on the solvent polarity. In low-polarity solvents, the lowest excited state is mostly $^3\text{MLCT}$ in character and mostly ^3IL in higher polarity solvents. However, some mixing of these states was observed under all conditions and it was not possible to assign a state solely as ^3IL or $^3\text{MLCT}$.¹² As previously discussed, acetylides are strong σ donors. However, arylacetylides are stronger σ donors than alkylacetylides. A study of how the emissive properties could be tuned by incorporating weaker σ donors, in this case, acetylides bearing trimethylsilyl (TMS) groups, reported Pt(II) diimine complexes that exhibited green luminescence from an MLCT excited state.¹³

Most of the literature reports on diimine Pt(II) acetylide complexes have concentrated on modification of the acetylide co-ligands (*e.g.* substituting pyrene for phenyl groups), yet much research still awaits on modification of the diimine ligand, which for most of the reported complexes is dbbpy. Therefore, this chapter will describe attempts towards larger, conjugated systems that are employed as the diimine ligands, whilst keeping the acetylide co-ligands the same. Through this approach, it is hoped to influence the level of the LUMO of the complex towards more attractive photophysical properties.

4.1.2 Applications of Diimine (N[^]N) Pt(II) Acetylides

Pt(II) acetylide complexes are promising candidates for many applications, such as the emissive components in organic light-emitting diodes (OLEDs),^{14, 15} sensitisation of singlet oxygen,¹⁶ photocatalytic hydrogen production,¹⁷ and as chemosensors for biological processes.¹⁸ The relative ease with which the acetylide ligands may be modified allows quite precise modification of the photophysical behaviour of these complexes. As discussed in Chapter Three, Pt(II) acetylides have attracted considerable interest for applications in phosphorescent OLEDs.¹⁵ This is because the incorporation of organometallic complexes such as Pt(II) acetylides can promote, through the heavy atom effect, emission from triplet states that would be otherwise wasted. The generally long-lived triplet states of Pt(II) acetylides have also made them intriguing candidates for triplet-triplet annihilation

upconversion (TTA-UC), and some very promising results have been obtained for such systems, which are discussed in the following section.

4.1.3 TTA-Upconversion

TTA-UC, first reported by Parker and Hatchard in 1962,¹⁹ is a process in which low-energy photons are absorbed and high-energy photons are emitted. The process may also be summarised as the population of an excited state at higher energy, after excitation at lower energy. The primary application of TTA-UC, for which it is currently receiving substantial research efforts, is in the harvesting of solar energy in a more efficient manner than currently possible, which is a pressing matter as energy generation begins to move away from environmentally damaging fossil fuels. Currently, many dye-sensitised solar cells (DSSCs) are unable to utilise the low-energy light from the sun in the near-IR region, and therefore are not harvesting the energy in the solar spectrum efficiently. The incorporation of upconverting materials into solar cells would allow low energy photons to be converted to high energy photons, thus improving the efficiency significantly.²⁰ Upconversion may be achieved by a number of methods including with two-photon absorption (TPA) dyes, with inorganic crystals and rare-earth materials (*e.g.* lanthanide complexes). These methods are problematic, in that they require light of a high power density (*e.g.* from a laser) and suffer from weak absorption of visible light. However, triplet-triplet annihilation has recently emerged as a very promising new route toward efficient upconversion, since this approach can make use of low-power non-coherent radiation (such as solar light) and can exhibit strong absorption of visible light.²⁰

The process of TTA-UC hinges upon the interaction between a sensitiser and an acceptor molecule. The sensitised component absorbs lower energy light, resulting in a transition from its ground state (S_0) to its excited state (S_1). The sensitiser is generally a molecule that exhibits efficient intersystem crossing so that the T_1 excited state may be populated with minimal energy loss. The triplet energy is then transferred *via* triplet-triplet energy transfer (TTET) to the acceptor molecule. A requirement for this process is an acceptor possessing a long-lived triplet state which is of lower energy than the sensitiser. This energy transfer between the donor and acceptor usually requires wavefunction overlap, and is considered a Dexter process.²¹ The collision of two triplet acceptors results in triplet-triplet annihilation (TTA), producing a singlet encounter complex, which then undergoes

internal conversion to form an acceptor in the S_1 state, which yields the upconverted fluorescence, and an acceptor in the ground state. This process is in accordance with the spin-statistic law, which states that upon the encounter of two triplet acceptor molecules, one of nine spin states is produced with equal probability. These nine states consist of five quintets, three triplets and one singlet. As the singlet state is produced in one-ninth probability, the efficiency of the process would be expected to be limited to 11.1 %. However, there have been several compounds reported that have given quantum yields above 11.1 %, ^{22, 23} which suggests that the triplets, and possibly quintets, are also yielding upconverted fluorescence.^{24, 25} The processes of TTA-UC, TTET and TTA are depicted in a schematic manner in Fig. 4.3.

Radiative decay from the excited acceptor produces upconverted fluorescence. Typical acceptor molecules are conjugated aromatics such as 9,10-diphenylanthracene (DPA), boron-dipyrromethene (BODIPY) and perylene. A general requirement for the acceptor molecule is that the T_1 state is higher than half of the energy of the S_1 state (thus allowing for an efficient TTA process). The acceptor must also have a long-lived triplet state. The quantum yield of upconversion gives the overall efficiency of a sensitizer in the TTA-UC process, and can be summarised by Equation 4.1, where Φ_q is the energy transfer efficiency of the TTET process, Φ_{TTA} is the efficiency of the production of the singlet state by the TTA process, and Φ_F is the fluorescence quantum yield of the acceptor.²⁰ The efficiency of the TTET process may be measured with quenching experiments, using the triplet acceptor as the quencher. Experimentally, the quantum yield of upconversion is measured by using Equation 4.2, which uses relative actinometry to calculate the efficiency of the process. In this equation, Φ , A , I and η refer to the quantum yield, absorbance, integrated photoluminescence intensity and refractive index, respectively, and the subscripts 'sam' and 'std' refer to the sample under investigation and the reference standard respectively. The equation is multiplied by two, because the process involves the absorption of two photons to provide one upconverted photon.²⁵ The corresponding terms labelled with the subscript 'std' refer to the reference sample employed.

$$\Phi_{UC} = \Phi_q \times \Phi_{TTA} \times \Phi_F$$

Equation 4.1: The quantum yield of upconversion.

$$\Phi_{UC} = 2\Phi_{std} \times \left(\frac{A_{std}}{A_{sam}}\right) \times \left(\frac{I_{sam}}{I_{std}}\right) \times \left(\frac{\eta_{sam}}{\eta_{std}}\right)^2$$

Equation 4.2: Experimental determination of the quantum yield of upconversion.

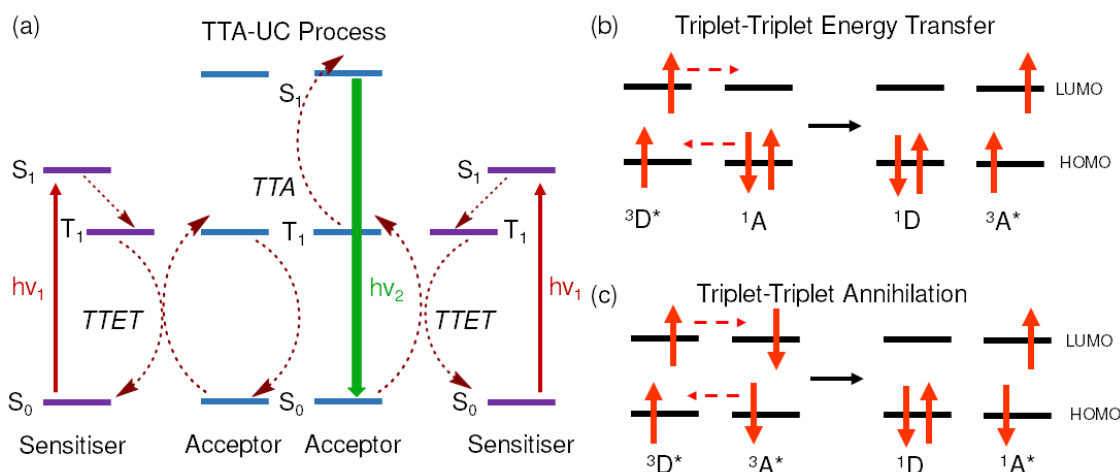


Figure 4.3: (a) A depiction of the TTA-upconversion process. Upon excitation of a sensitiser with low-energy light ($h\nu_1$), it becomes excited and its T_1 state becomes populated by ISC. TTET then results in an acceptor molecule in the T_1 state and the sensitiser returns to S_0 . TTA subsequently occurs, with emission ($h\nu_2$) from the S_1 state of the acceptor. (b) and (c) depict the TTET and TTA processes respectively. (a) is reproduced from Cheng et al.²⁶

Triplet photosensitisers which are suitable for the TTA process are usually organometallic complexes, where the presence of heavy atoms is beneficial for ISC. Examples of these include Ru(II) polypyridine complexes, Pt(II) and Pd(II) porphyrin complexes.²⁷ Recent work in the Draper group has concentrated upon Ir(III) and Ru(II)-based photosensitisers suitable for TTA-UC.^{28, 29} Since Pt(II) acetylides are known to exhibit long triplet lifetimes, and their photophysical properties are readily modified, they are ideal candidates as triplet photosensitisers, particularly for an application such as TTA-UC. The first report of a Pt(II) acetylide being used to promote photon upconversion was reported by the Eisenberg group in 2010.³⁰ In this example, the authors employed a Pt(II) acetylide terpyridine complex to sensitise the excited state of the acceptor 9,10-diphenylanthracene (DPA). Since the Pt(II) acetylide complex can be excited *via* the MLCT band in the visible region, where DPA does not absorb, it was possible to selectively excite the acetylide, which in turn sensitised DPA. In the presence of DPA, the emission from the acetylide was quantitatively quenched, and an upconverted blue fluorescence emission was obtained.

In 2012, Ji *et al.* published an account describing the efficacy of various Pt(II) acetylides with diimine ligands as triplet sensitisers in the TTA process.²⁷ Those possessing larger aromatic acetylide ligands, such as 1-ethynylpyrene, yielded strong upconversion, but the variant possessing only a simple phenylacetylide ligand did not yield upconverted fluorescence. This was proposed as being due to the complexes that gave strong upconversion possessing long-lived ^3IL states, whereas the simpler complex with phenylacetylide ligands possessed a short-lived $^3\text{MLCT}$ state. The upconversion quantum yields obtained for the diimine complexes bearing 1-ethynylpyrene and 1,8-naphthalimide ligands were $\Phi_{\text{UC}} = 14.2$ and 18.1 % respectively, which were much higher than the 1.1 % yield reported by the Eisenberg group with the terpyridine complex. The higher upconversion quantum yields were proposed as being due to the complexes exhibiting very long triplet lifetimes (therefore providing higher probability of interaction with acceptor molecules) and also high T_1 state energy levels, which acts to drive the TTET process.

A further report of high quantum yields of upconversion from Pt(II) diimine acetylides was made by Zhong *et al.* in 2017.³¹ Noting the promising characteristics of the previously investigated acetylides for TTA-UC, they examined whether creating complexes possessing two different chromophores, would result in a complex with enhanced light-harvesting ability. They introduced both 1-ethynylpyrene (Py) and 1,8-naphthalimide ligands (NI) onto the Pt(dbby) diimine scaffold (**LC 115**), through a coupling reaction catalysed by CuI with a mixture of the two ligands (Fig. 4.4 (a)). The mixed complex gave absorbance further into the visible region than the all-pyrene analogue (**LC 112**). No fluorescence emission was observed for the mixed complex **LC 115**, which gave phosphorescence at RT, suggesting very efficient ISC. The emission profile of the complex was identical to that of the analogue possessing only 1-ethynylpyrene ligands (**LC 112**, Fig. 4.4 (b)), suggesting that the emission from the NI moiety is quenched by intramolecular energy transfer. Transient absorption and DFT experiments revealed that the emissive state was ^3IL , localised on the Py moiety. The complex therefore exhibited extended absorbance into the visible range due to the NI ligand, but with the excited state remaining localised on the Py. The complex **LC 115** also gave very promising results as a triplet photosensitiser, with a high upconversion quantum yield of $\Phi_{\text{UC}} = 34$ %. With their ease of derivatisation leading to modifiable photophysical properties, platinum acetylides therefore continue to be promising candidates for TTA-UC.

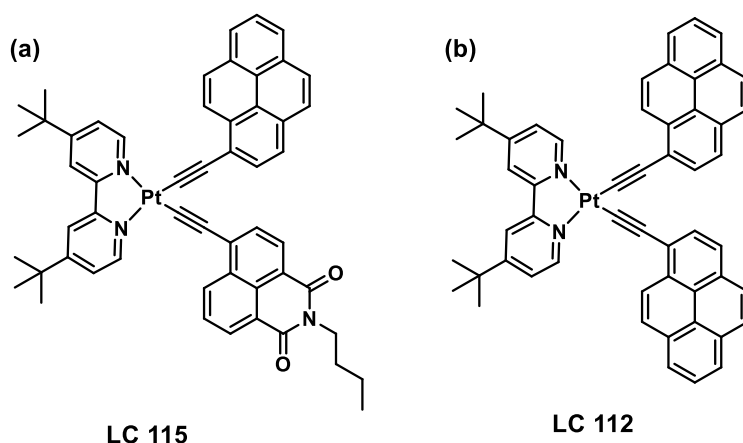


Figure 4.4: (a) The complex prepared by Zhong et al with mixed arylacetylide ligands. (b) and (c) The analogues with only pyrene (Py) and naphthalimide (NI) ligands.³¹

4.1.4 Chapter Aims

The aim of this chapter is to describe the synthetic efforts towards, and photophysical characterisation of, a family of Pt(II) acetylides bearing diimine ligands with extended polyaromatic structures. There have been several systematic investigations of the consequences of modifying the acetylide ligands, but relatively few focusing on the impact of modifying the diimine ligand moiety. As the LUMO of most Pt(II) acetylide complexes is localised on the diimine ligand,³² it is of interest to probe the manner in which extended conjugation affects the electronic properties. The majority of Pt(II) acetylides reported feature the versatile and easily available dbbpy (4,4'-di(tert-butyl)-2,2'-bipyridine) ligand. The Draper group has extensive experience with large polyaromatic systems, and has recently developed methods towards novel ligands based upon 1,10-phenanthroline.^{33, 34} Such novel N[^]N coordinating ligands are ideal candidates for a study based upon investigating the effects of increasing conjugation. Introducing diimine ligands with a higher degree of conjugation, and therefore lower-lying LUMO orbitals, may have an impact on the emissive properties. A decrease in the HOMO-LUMO gap might therefore be expected to shift the emission from the visible region closer to the near-infrared.³⁵ This chapter will therefore discuss the synthesis of several polyaromatic ligands based upon the 1,10-phenanthroline building block, the preparation of Pt(II) acetylides from them, and then describe their initial photophysical characterisation. The target compounds are displayed in Fig. 4.5, and have been designed so that they feature both varying degrees of conjugation, and in one case, the inclusion of N atoms. The N-substituted system was chosen in order to

determine the impact of the inclusion of the electron-withdrawing N-atoms would have an appreciable effect on the energy levels of the diimine ligand, and render it more electron-accepting. The acetylide ligand is held constant, and 1-ethynylpyrene has been chosen for its promising properties, as discussed above. The complexes are expected to display properties (*e.g.* long luminescence lifetime) which may be desirable for applications as triplet photosensitisers in the TTA-UC process, and their suitability for such applications will be discussed.

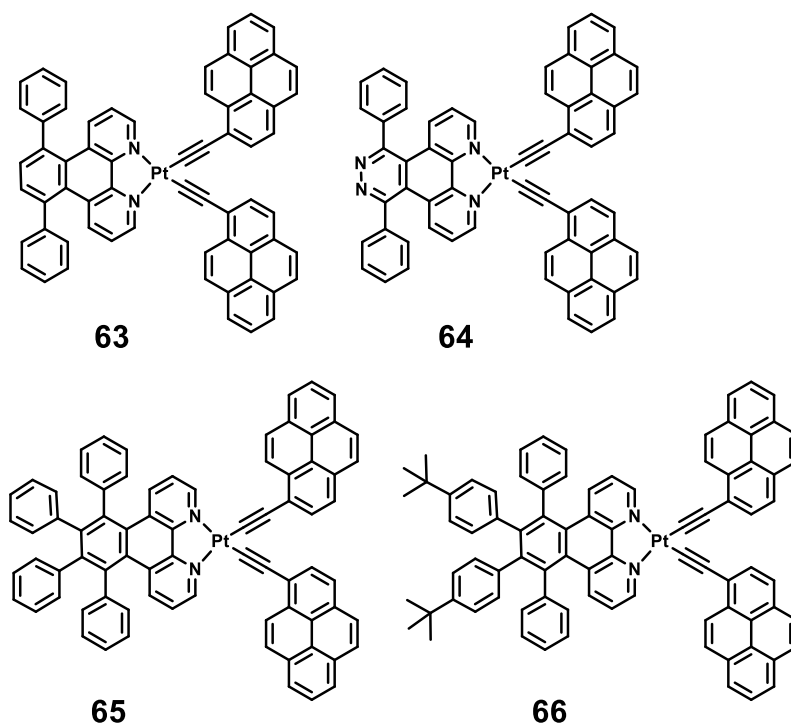
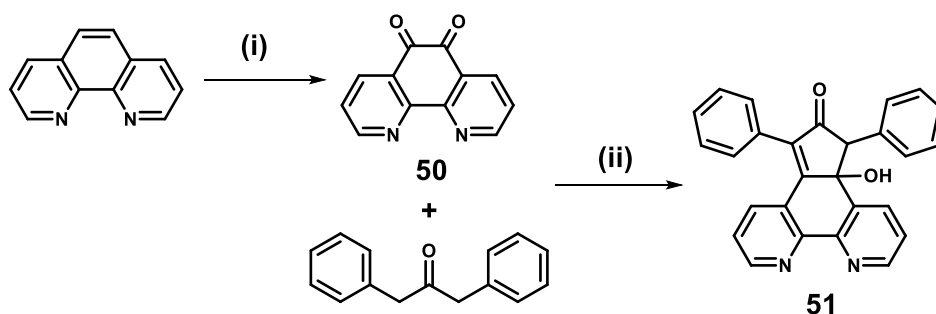


Figure 4.5: The range of Pt(II) acetylides with extended polyaromatic ligands based upon 1,10-phenanthroline, with varying degrees of conjugation and substitution, that are proposed.

4.2 Synthesis of Pt(II) Acetylides with Diimine-based Ligands

4.2.1 Synthesis of Precursor Polyaromatic Diimine (N[^]N) Ligands

The 1,10-phenanthroline moiety presents a very useful building block for the preparation of extended polyaromatic systems with an N[^]N coordination ability. This section will describe the synthesis of four ligands based upon 1,10-phenanthroline, two of which have been previously prepared by Dr. R. Conway-Kenny,³⁴ and a further two based on procedures developed in the Draper group.³³ In all cases, the synthesis began with the preparation of 1,10-phenanthroline-5,6-dione (**50**). This was carried out according to the procedure reported by Yamada *et al.*,³⁶ and involved the mixing of 1,10-phenanthroline and KBr in a mixture of refluxing H₂SO₄ and HNO₃. After the mixture was neutralised with NH₄OH (aq.), extracted into CH₂Cl₂, and recrystallized from hot EtOH, the dione was obtained in 53 % yield (Scheme 4.1). Access to all four required ligands was then made possible from a cyclopentadienone precursor, which was itself prepared *via* a two-fold Knoevenagel condensation between the commercially available 1,3-diphenylpropan-2-one and **50**. The product, the cyclopenta-product 4b-hydroxy-5,7-diphenyl-4b,5-dihydro-6H-cyclopenta[f][1,10]phenanthrolin-6-one **51**, had been previously prepared by Dr. B. Lankage according to a conventional method (*i.e.* a Knoevenagel condensation catalysed by KOH in EtOH solvent).³⁴ It has been subsequently discovered that this cyclopenta-product can be prepared in more consistent, higher yields by substituting the KOH with piperidine as base, and the EtOH solvent with MeOH.³³



Scheme 4.1: The preparation of a 1,10-phenanthroline-derived cyclopentadienone. (i) KBr, H₂SO₄, HNO₃, 130 °C, 3h, 53 %. (ii) Piperidine, MeOH, 18h, RT, N₂, 72 %.

It is noted that whether KOH or piperidine is employed as the base, both routes generate the single-hydroxy cyclopenta-product **51**, rather than the expected cyclopentadienone. In the subsequent steps to prepare the extended polyaromatic systems,

i.e. through a Diels-Alder reaction, the single-hydroxy product is converted *in-situ* to the fully dehydrated analogue at high temperature (Scheme 4.2). The progress of the loss of the hydroxy moiety is easily observed by the formation of a dark blue colour, which is characteristic of **52**. The preparation of **51** led to a platform upon which a family of phenanthroline-based polyaromatic ligands could be prepared, either *via* the more traditional high-temperature Diels-Alder method, or *via* novel low temperature methods recently developed in the Draper group. The ^1H NMR spectrum of **51** and the relevant assignments are displayed in Figure 4.6.

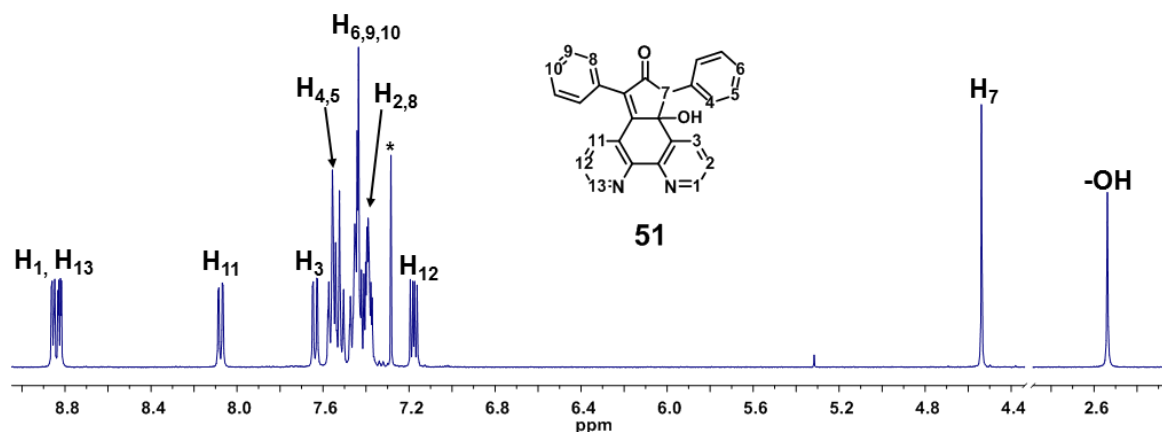
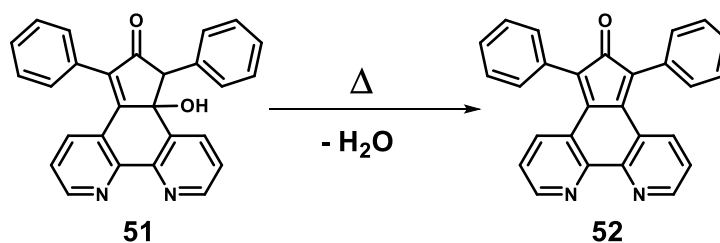


Figure 4.6: ^1H NMR spectrum of **51** (400 MHz, CDCl_3 , RT). * denotes residual solvent peak.



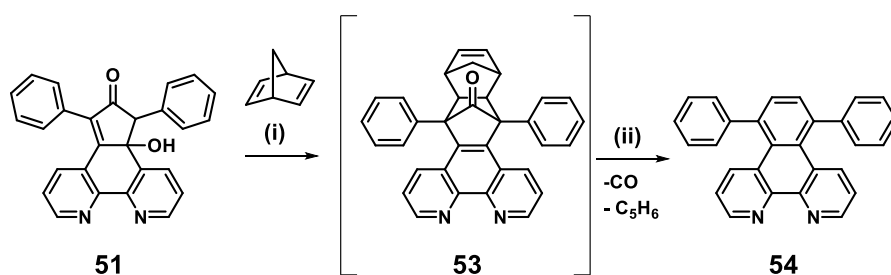
Scheme 4.2: General scheme for the *in-situ* preparation of **52** from the single-hydroxy analogue, **51**.

4.2.2 Synthesis of 5,8-diphenylbenzo[f][1,10]phenanthroline (**54**)

The compound 5,8-diphenylbenzo[f][1,10]phenanthroline **54** was prepared according to a procedure previously developed in the Draper group by Dr. R. Conway-Kenny.³³ It has been discovered that **52** can be prepared *in-situ* at lower temperatures than those commonly required for Diels-Alder reactions, which are generally in the region of 250–300 °C. In the search for conditions that would accommodate a wider range of functional

groups to be introduced into the as yet relatively new phenanthroline-based polyaromatic systems, it was observed that **51** can be dehydrated with neutral alumina in refluxing chlorobenzene. The issue with the generation of **52** at higher temperatures, such as those of a Diels-Alder reaction, is that a degree of decomposition is often observed for these systems. Therefore this method was developed in order to not only improve the yields of the preparation of these compounds but also to introduce a means of functionalising polyaromatic phenanthroline-based compounds with functional groups which are not stable at higher temperatures.

The preparation of **54** was achieved in a two-step procedure (Scheme 4.3). The single-hydroxy **51** was added to neutral alumina in chlorobenzene and heated to reflux for 3 hours. The colour of the solution slowly changed from pale yellow to the expected dark blue colour of **52** on achieving the reflux temperature. Norbornadiene was then added and the mixture was left to reflux overnight. The norbornadiene reacted with the cyclopentadienone in a Diels-Alder cycloaddition, generating first the proposed intermediate compound **53**, which then subsequently underwent a retro Diels-Alder step to form **54** and side-product cyclopenta-1,3-dione, along with the expulsion of CO. The desired compound **54** was isolated by column chromatography (CH₂Cl₂:MeOH, 20:1, v/v). Other alkene-type sources caused the formation of other phenanthroline intermediates, which then failed to generate **54** successfully.³³



Scheme 4.3: (i) Al₂O₃, chlorobenzene, 130 °C. (ii) 1,2-dichlorobenzene, 150 °C, 20 %.

Previous attempts toward **54** revealed that reflux at 130 °C in chlorobenzene produced a mixture of the desired compound and also the intermediate CO bridged compound **53** (Scheme 4.3).³³ The same study then found that heating to 150 °C in the higher boiling point solvent 1,2-dichlorobenzene, afforded **54** only, due to the higher temperature required for the retro Diels-Alder reaction to take place. As there is no trace of a retro Diels-Alder product still containing the CO moiety, it is assumed that these processes (loss of CO and the retro

Diels-Alder step) occur simultaneously. However, attempts to confirm this have not yet been undertaken.

Examination of the ^1H NMR spectrum of **54** (Fig 4.7) reveals there are three peaks characteristic of a phenanthroline moiety, at δ 8.96, 8.00, and 7.12 ppm, which each integrate to two protons. The most downfield, at δ 8.96 ppm, may be assigned to H_1 , due to its proximity to the nitrogen atom. The peak at δ 8.00 ppm may then be assigned to H_3 , which although further from the nitrogen atom than H_2 , experiences a greater degree of deshielding due to resonance effects. The signal at δ 7.12 ppm may then be assigned to H_2 . The two equivalent protons of the central benzene ring occur as a singlet, integrating to two protons, at δ 7.62 ppm. The protons labelled H_4 , H_5 and H_6 are assigned to the most intense signal at δ 7.47 ppm, which at first glance is observed to resemble a singlet, but the HSQC experiment reveals it is composed of overlapping signals (Figure 4.7, inset). Further confirmation of the identity of **54** was provided by HRMS (see Table 4.1).

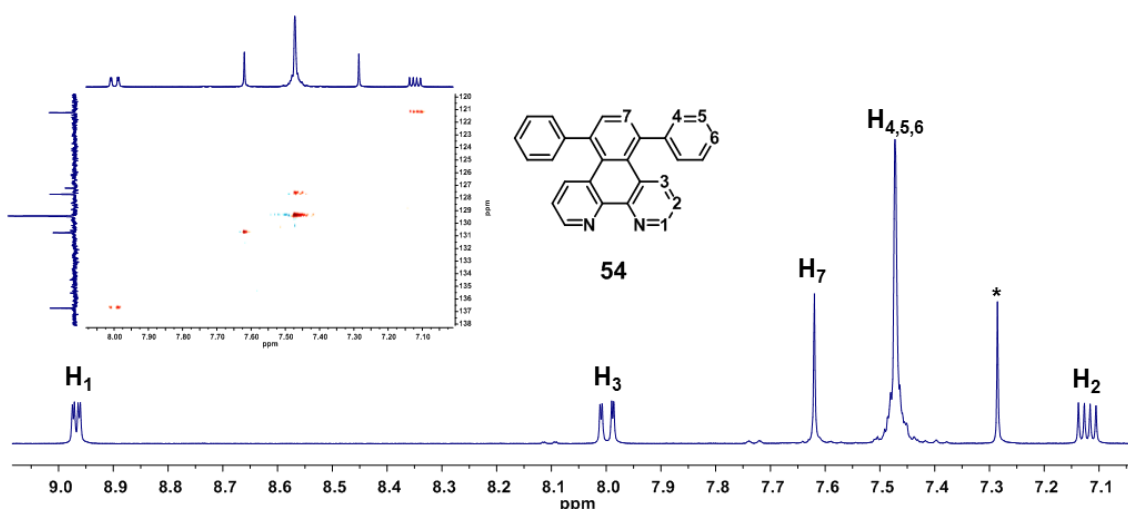
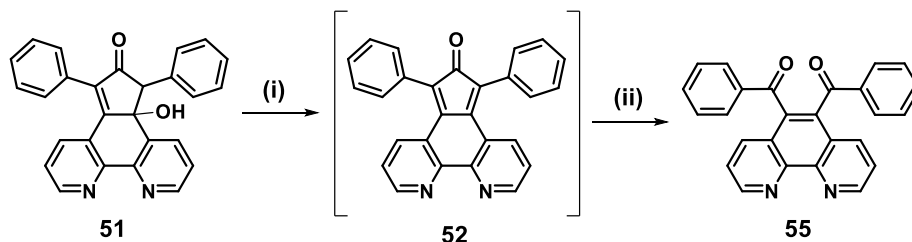


Figure 4.7: ^1H NMR spectrum of **54**, and inset, the HSQC experiment (400 MHz, CDCl_3 , RT. * denotes residual solvent peak.)

4.2.3 Synthesis of 5,8-diphenylpyridazino[4,5-f][1,10]phenanthroline (**56**)

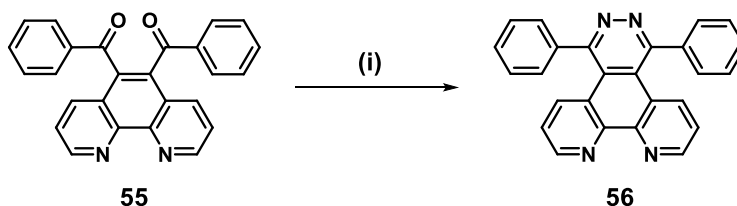
The preparation of the pyridazine-substituted analogue of **54** was undertaken according to a method also developed by Dr. R. Conway-Kenny.³³ This unusual ligand was prepared from precursor **51** via a two-step process (Scheme 4.4). The first step involved generating the ring-opened derivative of **51**, after which it was possible to generate the pyridazine ring in a subsequent step. The conditions for the ring-opening reaction are based

upon observations originally made by Marchand *et al.* in 2002, who noted that in the presence of atmospheric O_2 , phencyclone, the phenanthrene-based analogue of **51**, underwent thermal autoxidation in refluxing xylene or chlorobenzene.³⁷ They proposed that the mechanism for the ring-opening reaction is the stepwise 1,4-addition of $^3O_2$ to the diene system of the cyclopentenone, which forms an endoperoxide. The extrusion of CO is proposed to then lead to the ring-opened product. The ring-opening of **51** was undertaken with similar conditions to those of Marchand *et al.*³⁷ A mixture of **51** and neutral alumina was refluxed in chlorobenzene for 18 hours in air. The alumina was added to generate the required diene **52** from the single-hydroxy derivative **51**. The progress of the reaction could be monitored visually; the characteristic deep blue colour of **52** appeared after 3-4 hours, which gradually then faded to a brown colour as the ring-opened diketone **55** was formed. After removal of the solvent, **55** was obtained by precipitation from diethyl ether, with no further purification necessary. Confirmation of its structure were provided by NMR and HRMS.



Scheme 4.4: Synthesis of **55**. (i) Al_2O_3 , chlorobenzene, $130\text{ }^\circ\text{C}$, 4 h. (ii) Chlorobenzene, O_2 , $130\text{ }^\circ\text{C}$, 14 h, 35 %.

The second step, the synthesis of 5,8-diphenylpyridazino[4,5-f][1,10]phenanthroline (**56**) was achieved through the double Schiff-type condensation of hydrazine hydrate (60 %) and **55**, with two water molecules being lost in the process (Scheme 4.5). This was carried out in EtOH solvent, with KOH as catalyst, and after removal of solvent and precipitation from diethyl ether, **56** was obtained in 44 % yield. This was characterised by NMR, HRMS (data summarised in Table 4.1) and IR, which are in good agreement with the previous report.³³



Scheme 4.5: Synthesis of **56**. (i) $N_2H_4.H_2O$, KOH, EtOH, $80\text{ }^\circ\text{C}$, N_2 , 16 h, 44 %.

The ^1H NMR spectrum of **56** (Fig. 4.8) exhibits a similar appearance to that of **54**, with three signals characteristic of a phenanthroline moiety at δ 9.20, 8.21, and 7.35 ppm. A selective TOCSY experiment confirmed that these three signals were in the same spin system. The most downfield may be assigned to H_1 and that at δ 8.21 ppm may be assigned to H_3 , leaving H_2 as most upfield, an assignment aided by their respective splitting patterns. A HSQC experiment allowed the $^{13}\text{C}\{^1\text{H}\}$ signals to be assigned and a HMBC experiment confirmed these assignments.

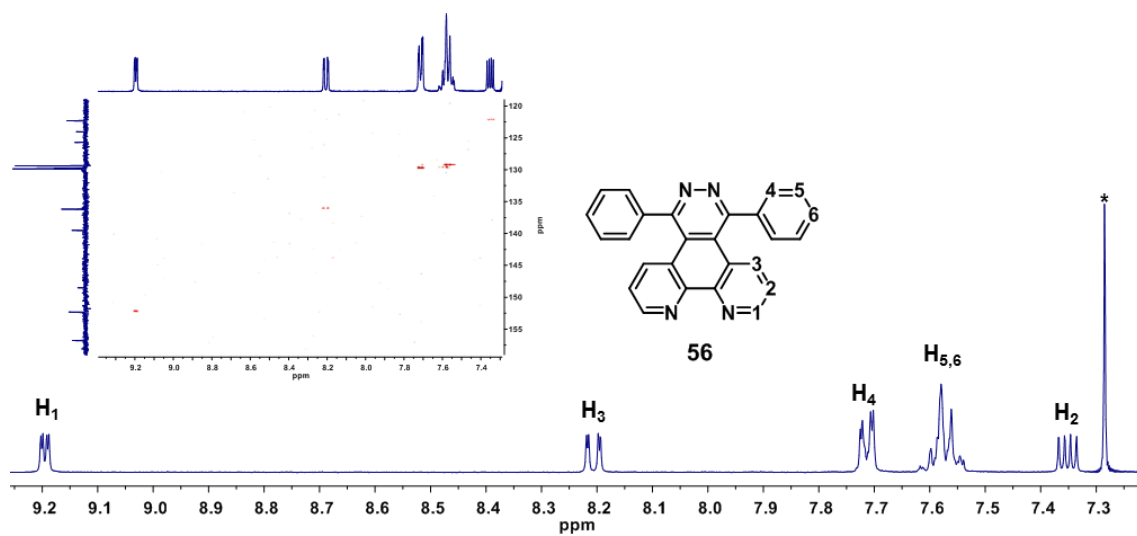
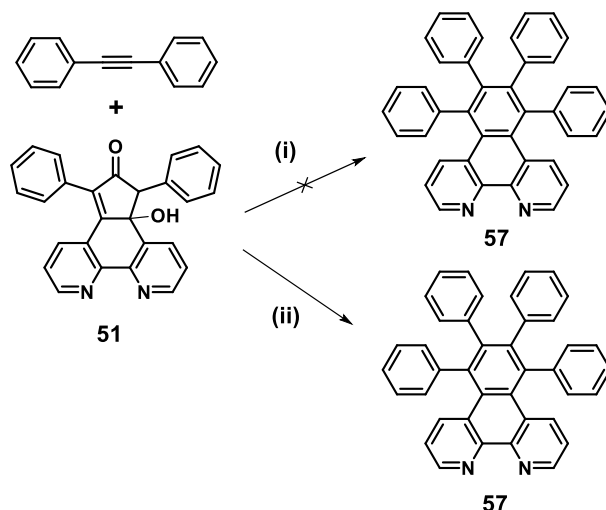


Figure 4.8: ^1H NMR spectrum of **56** with inset, the HSQC experiment (400 MHz, CDCl_3 , RT. * denotes residual solvent peak).

4.2.4 Synthesis of 5,6,7,8-tetraphenylbenzo[f][1,10]phenanthroline (**57**)

The synthesis of the more extended analogue of **54** was achieved through the Diels-Alder method. Although the synthesis of **54** was carried out with a Diels-Alder cycloaddition with norbornadiene at a relatively low temperature (150 $^\circ\text{C}$), it has been reported that the Diels-Alder reaction between **51** and phenylacetylene will not take place under such conditions (Scheme 4.6 (i)).³³ It was therefore thought necessary to use the more traditional route at higher temperatures (~ 300 $^\circ\text{C}$). The reaction between **51** and the commercially available reagent phenylacetylene was carried out in a benzophenone melt at 300 $^\circ\text{C}$ (Scheme 4.6 (ii)). The colour of the reaction mixture was observed to quickly change from light brown to a dark colour, indicative of the *in-situ* formation of **52** via loss of the hydroxyl group. It was noted that some decomposition seemed to have occurred, as some unidentified black material was obtained along with the product, after the reaction had been judged

complete by TLC. After removal of this decomposition product by column chromatography (SiO_2 , CH_2Cl_2 :MeOH 100:2, v/v), the product **57** was obtained in 15 % yield. Therefore the high temperature required for this reaction to proceed also leads to some decomposition, and in future it may be necessary to carry out the reaction while slowly and incrementally increasing the temperature of the benzophenone melt, until an optimal temperature is reached (whilst monitoring the progress of the reaction by TLC). The compound **56** was characterised by NMR spectroscopy (Fig. 4.9), HRMS and IR.



Scheme 4.6: Routes toward **57**. (i) Chlorobenzene, 130 °C, 16 h. Reported as unsuccessful.³³
(ii) Ph_2CO , 300 °C, N_2 , 3 h, 15 %.

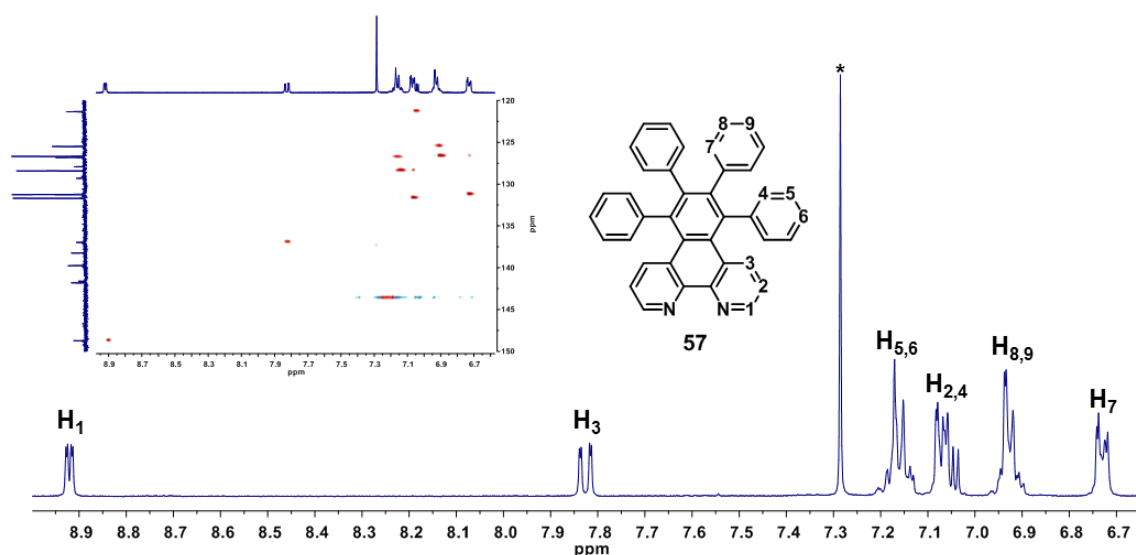
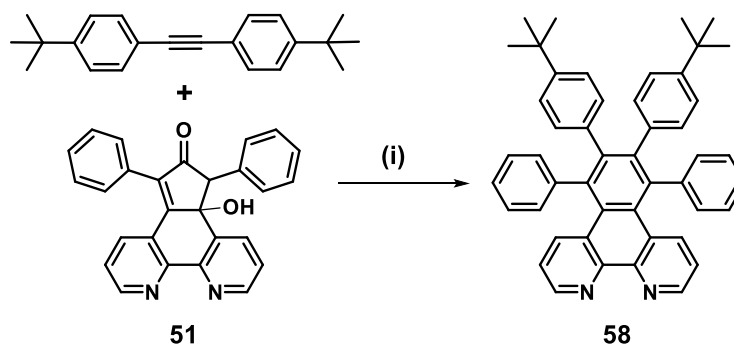


Figure 4.9: ^1H NMR of **57** with inset, the HSQC experiment (400 MHz, CDCl_3 , RT. * denotes residual solvent peak).

The ^1H NMR spectrum of **57** displays the same pattern for the phenanthroline protons as for **54** and **56**. A selective TOCSY confirmed that the proton signals at δ 8.89, 7.81 and 7.04 ppm belonged to the same spin system and may be assigned to phenanthroline protons H_1 , H_3 and H_2 respectively. A further selective TOCSY indicated that the signals at δ 6.90 and 6.72 ppm belonged to their own spin system. They may therefore be assigned to the protons H_7 , H_8 and H_9 . Protons H_8 and H_9 overlap, and H_7 is least deshielded, as is common for this type of substituted ring system. ^1H - ^{13}C HSQC and HMBC experiments aided these assignments. The remaining signals may be assigned to the middle phenyl rings bearing H_4 , H_5 and H_6 , which exhibit the same type of behaviour *i.e.* the *para* proton overlaps with the *meta*, and the *ortho* is least deshielded.

4.2.5 Synthesis of 6,7-bis(4-(*tert*-butyl)phenyl)-5,8-diphenylbenzo[f][1,10]phenanthroline (**58**)

Following the preparation of ligands **54**, **56** and **57**, it was decided to also prepare a derivative bearing solubilising *tert*-butyl groups, as Pt(II) acetylides such as those proposed could be reasonably expected to give some solubility issues, owing to the presence of both a bulky and partially planar aromatic ligand, such as **57**, and also the planar pyrene moieties. Therefore a derivative of **57** incorporating *tert*-butyl groups, the synthesis of which was reported once previously,³⁴ was prepared by the same methodology, a Diels-Alder [4+2] cycloaddition in a benzophenone melt (Scheme 4.7). The required alkyne, functionalised with *tert*-butyl groups, was prepared according to a literature procedure.³⁸ The desired product, **58**, was isolated from the reaction mixture and purified by column chromatography (SiO_2 , CH_2Cl_2 :MeOH, 100:2 v/v).



Scheme 4.7: Preparation of **58**. (i) Ph_2CO , 300 °C, N_2 , 3 h, 16 %.

The moderate yield (16 %) and the presence of an unidentified black side-product, in the same manner as in the preparation of **57**, suggests some decomposition is occurring at the elevated temperature required for the reaction to proceed. The ^1H NMR spectrum of **58** (Fig. 4.10) is very similar to that of its counterpart **57**. Again, the most characteristic peaks are those of the phenanthroline moiety, at δ 8.95, 7.85 and 7.07 ppm, which are assigned to H_1 , H_3 and H_2 respectively. The signal from H_2 is overlapping in a multiplet with H_4 . This was elucidated with a ^1H - ^{13}C HSQC experiment (Fig. 4.11) and a selective TOCSY, which indicated the signals corresponding to the spin system of the phenanthroline moiety. Another selective TOCSY correlated the signals at δ 6.88 and 6.58 ppm, which appear as a pair of doublets. These two signals may therefore be assigned to the phenyl ring bearing the *tert*-butyl groups. As with **57**, these may be assigned to H_7 and H_8 , with H_7 being the least deshielded. This was confirmed with a HMBC experiment, as the quaternary carbon that the *tert*-butyl protons show a three-bond correlation to also gives a three-bond correlation to the signal assigned to H_7 . The remaining signals at δ 7.17, 7.14 and 7.07 are assigned to H_6 , H_5 and H_4 respectively, with confirmation of their respective assignments from their integration values and the HMBC experiment. The *tert*-butyl protons are observed as a singlet at δ 1.17 ppm. Further identification of **58** was provided by IR and HRMS (see Table 4.1).

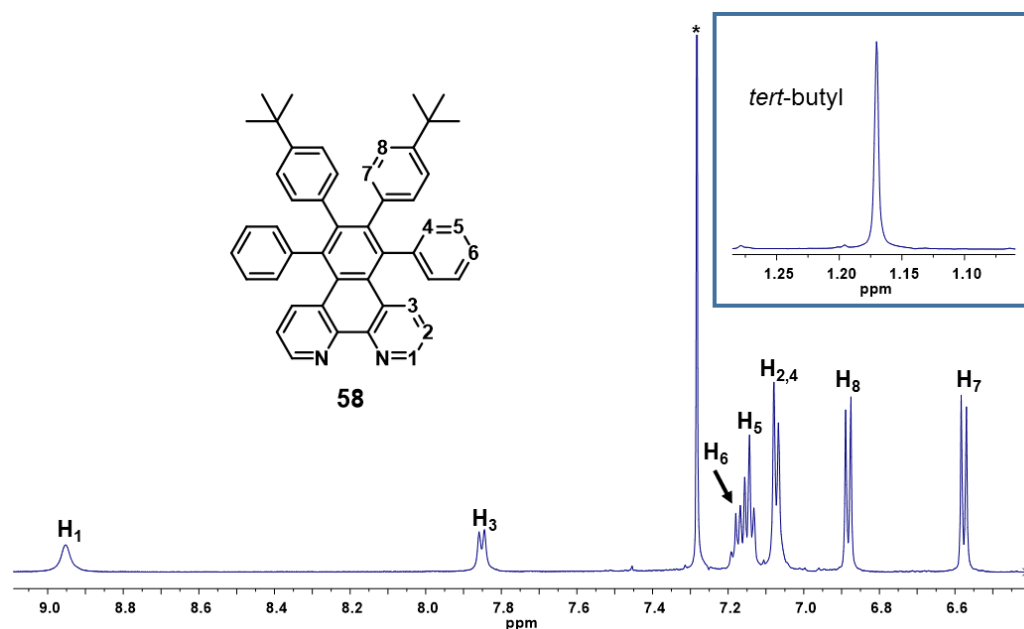


Figure 4.10: ^1H NMR spectrum of **58** with inset, *tert*-butyl signal (600 MHz, CDCl_3 , RT. * denotes residual solvent peak.).

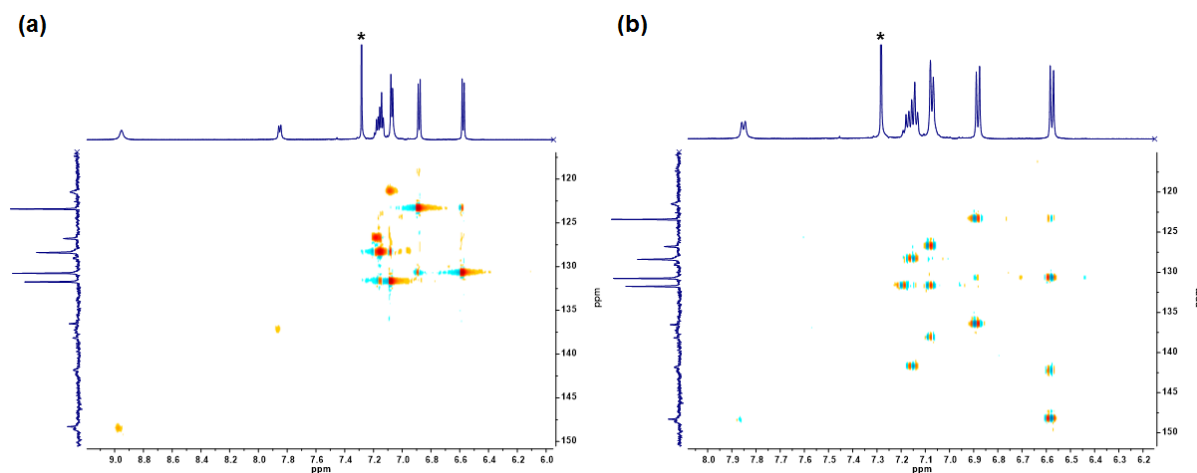


Figure 4.11: 2D NMR experiments to aid assignment of **58**. (a) ^1H - ^{13}C HSQC (aromatic region) and (b) HMBC (aromatic region), (600 MHz, CDCl_3 , RT. * denotes residual solvent peak.).

Further confirmation of the identity of **58** was provided by the crystal structure obtained. Crystals were grown by slow evaporation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ and yielded a partially twinned structure with a high degree of disorder, which was solved by Dr. B. Twamley. The unit cell is occupied by one molecule of **58** and disordered MeOH solvent molecules (Fig. 4.12 (a)). The phenyl rings are observed to be twisted out of the plane of the phenanthroline moiety due to steric requirements. The phenanthroline moiety itself is also slightly non-planar, with respect to the central ring.

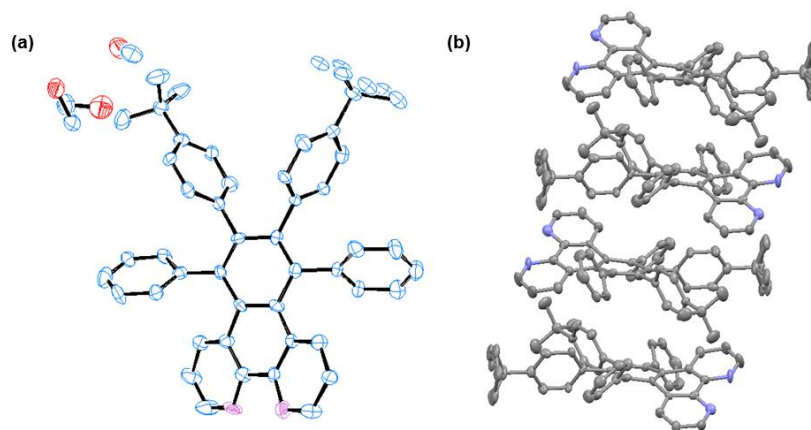


Figure 4.12: (a) Asymmetric unit of **58**, with disordered tert-butyl groups and disordered MeOH solvent. Atomic displacement shown at 50 % probability and hydrogen atoms omitted for clarity. (b) Packing diagram of **58**, viewed along the 'b' axis, with disordered solvent molecules and hydrogen atoms removed for clarity. Atomic displacement shown at 50 % probability.

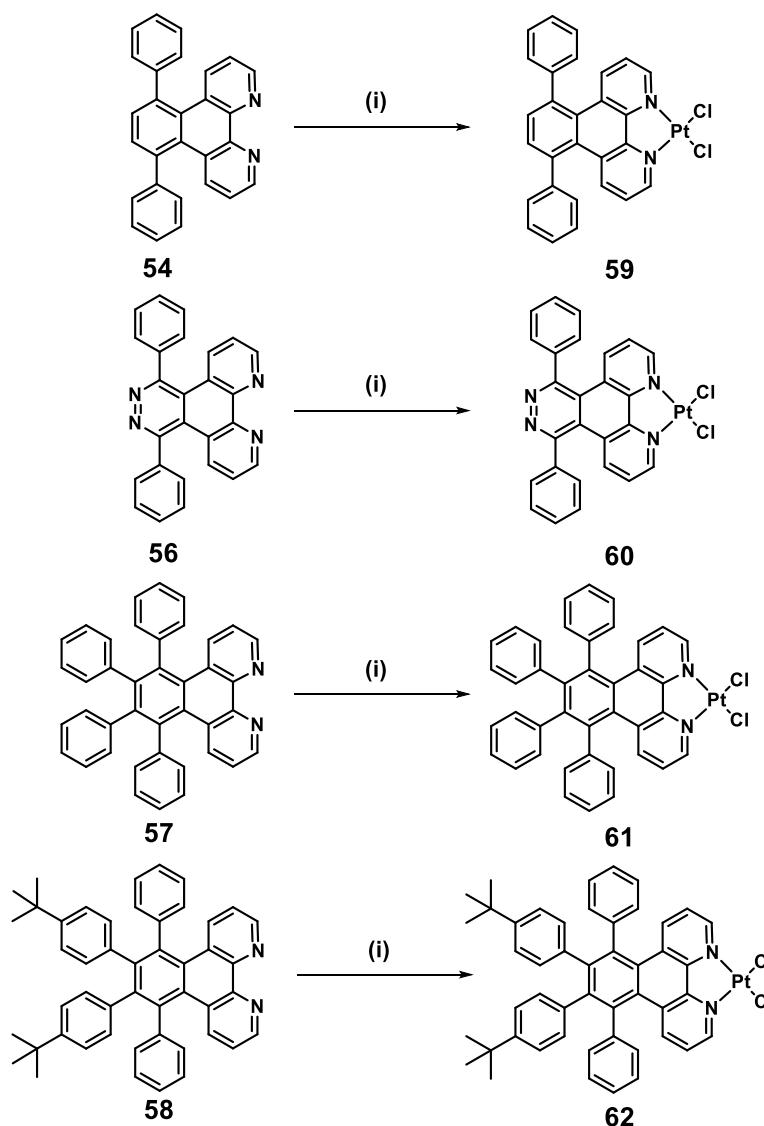
Table 4.1: Mass spectrometry data for ligands **51-58**.

Compound	Formula	Calc. m/z	Found m/z	Molecular Ion
51	C ₂₇ H ₁₉ N ₂ O ₂	403.1441	403.1449	[M+H] ⁺
54	C ₂₈ H ₁₉ N ₂	383.1543	383.1538	[M+H] ⁺
55	C ₂₆ H ₁₆ N ₂ NaO ₂	411.1104	411.1109	[M+Na] ⁺
56	C ₂₆ H ₁₆ N ₄ Na	407.1267	407.1276	[M+Na] ⁺
57	C ₄₀ H ₂₇ N ₂	535.2169	535.2157	[M+H] ⁺
58	C ₄₈ H ₄₃ N ₂	647.3426	647.3429	[M+H] ⁺

4.3 Synthesis and Characterisation of Pt(L)Cl₂ Precursors (L = Diimine N^N Ligand)

4.3.1 Synthetic Method for Preparation of Pt(L)Cl₂ Precursors

In order to prepare platinum acetylides from N^N ligands **54**, **56**, **57** and **58**, it was first necessary to first prepare the platinum chloride derivatives (of general formula Pt(L)Cl₂, where L = polyaromatic ligand). This was achieved through the use of the platinum source Pt(DMSO)₂Cl₂ (**46**), where the diimine ligand can displace the more labile DMSO ligands. The appropriate ligand and Pt(DMSO)₂Cl₂ were added to CHCl₃ solvent and heated to reflux for 1 hour. After this time, concentration of the solvent and addition of a small amount of MeOH was sufficient to precipitate the desired platinum chloride compound (Scheme 4.8).



Scheme 4.8: Synthesis of $\text{Pt}(\text{L})\text{Cl}_2$ complexes from the diimine ligands. (i) CHCl_3 , 60°C , 1 hr. Yields: 91 (**59**), 89 (**60**), 94 (**61**), 63 (**62**) %.

4.3.2 Characterisation of $\text{Pt}(\text{L})\text{Cl}_2$ Precursors

The characterisation of the four $\text{Pt}(\text{L})\text{Cl}_2$ compounds was achieved by NMR spectroscopy, HRMS and IR spectroscopy. The ^1H NMR spectra of **59-62** are displayed in Fig. 4.13. The most notable difference between the ^1H NMR spectra of these compounds and their uncomplexed precursor ligands is that in the case of the platinum chlorides, the phenanthroline protons are deshielded. This is due to the square planar nature of the complex leading to the proximity of the electron-withdrawing Cl^- ligands to the phenanthroline ligand, which imparts a deshielding effect on the nearby protons.³⁹ For example, in the case of **59**,

H₁ is deshielded by δ 0.83 ppm (from δ 8.97 ppm in **54** to δ 9.80 ppm in **59**). The chemical shifts of the phenanthroline protons before and after complexation are summarised in Table 4.2. The remaining aromatic protons (*i.e.* those not in the phenanthroline moiety and therefore furthest from the Pt centre) are largely unaffected by the complexation. For compounds **60** and **61**, their high degree of insolubility precluded the obtainment of a full $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. Further confirmation of the identity of these compounds was provided by HRMS, and the results are summarised in Table 4.3. Although **62** could not be identified by HRMS, its identity was confirmed by X-ray crystallography (Fig. 4.17).

Table 4.2: ^1H NMR chemical shifts of protons of phenanthroline moiety after complexation.

L/ Pt(L)Cl₂	Proton Signal	H₁ (ppm)	H₂ (ppm)	H₃ (ppm)
54/59		8.97/9.80	7.12/7.34	8.00/8.22
56/60		9.19/9.69	7.35/7.50	8.21/8.41
57/61		8.90/9.74	7.04/7.23	7.82/7.99
58/62		8.95/9.77	7.07/7.26	7.85/7.99

Table 4.3: Mass spectrometry data for ligands **59-62**.

Compound	Formula	Calc. m/z	Found m/z	Molecular Ion
59	C ₂₈ H ₁₈ Cl ₂ N ₂ NaPt	670.0390	670.0381	[M+Na] ⁺
60	C ₂₆ H ₁₆ Cl ₂ N ₄ NaPt	672.0294	672.0289	[M+Na] ⁺
61	C ₄₀ H ₂₆ Cl ₂ N ₂ NaPt	822.1016	822.1009	[M+Na] ⁺
62	C ₄₈ H ₄₂ ClN ₂ Pt	876.2684	--	--

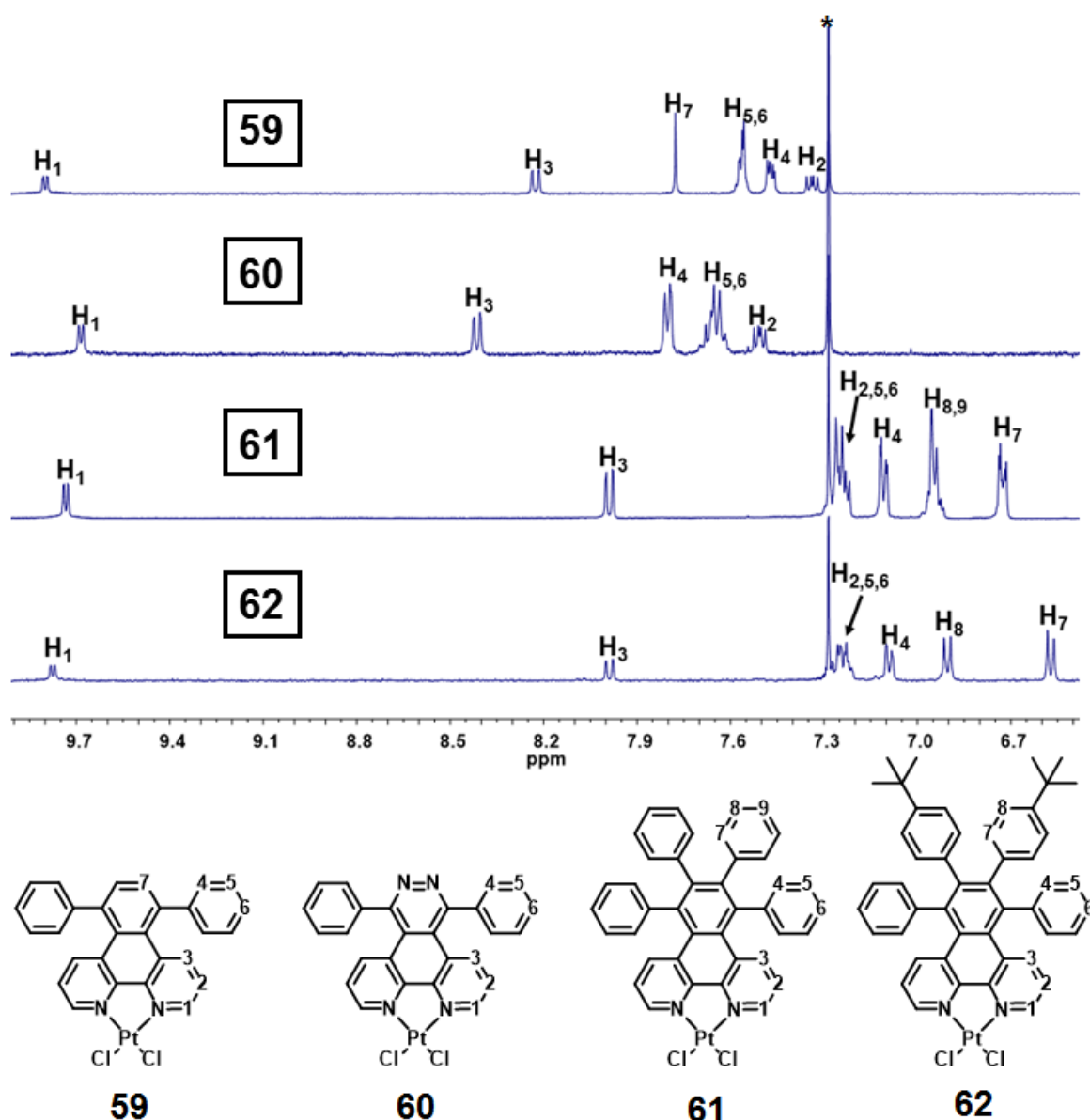


Figure 4.13: ^1H NMR spectra of $\text{Pt}(\text{L})\text{Cl}_2$ complexes **59-62** (400-600 MHz, CDCl_3 , RT. * denotes residual solvent peak).

In the cases of **59** and **62**, it was possible to obtain crystal samples suitable for X-ray analysis. Crystals of **59**, in the form of orange needles, were obtained by slow evaporation of $\text{CH}_2\text{Cl}_2/\text{MeOH}$. The crystal structure was solved by Dr. Brendan Twamley, and the crystal was found to be of the triclinic system, and of space group $\text{P}\bar{1}$. The unit cell features two independent molecules and a guest CH_2Cl_2 molecule (Fig. 4.14). The refinement data for **59** is provided in the Annex.

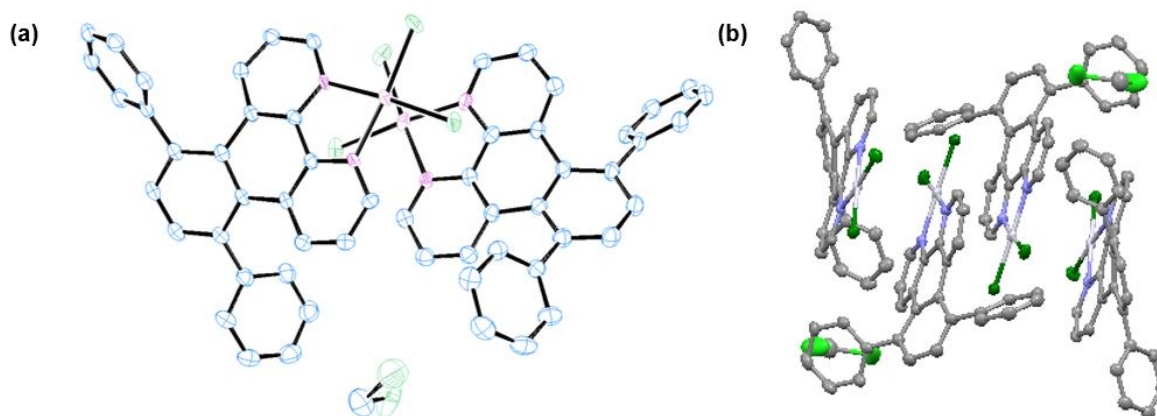


Figure 4.14: (a) Asymmetric unit of **59**. (b) Packing diagram of **59**, showing staggered arrangement. Viewed normal to the 'a' axis. H atoms omitted for clarity and atomic displacement at 50 % probability.

Examination of the bond angles around the Pt centres reveal a distorted square-planar geometry imposed by the diimine ligands. Both the independent molecules in the unit cell exhibit slightly different bond angles, which are summarised in Table 4.4, and the numbering scheme employed is illustrated in Fig. 4.15.

Table 4.4: Bond angles around platinum centres in X-ray crystal structure of **59**. Values in brackets give estimated standard deviation.

Bond Angle	Angle (°)
Cl ₁ Pt ₁ N ₁	94.29 (12)
N ₁ Pt ₁ N ₂	80.62 (16)
N ₂ Pt ₁ Cl ₂	94.98 (12)
Cl ₂ Pt ₁ Cl ₁	90.11 (5)
Cl ₃ Pt ₂ N ₃	95.03 (13)
N ₃ Pt ₂ N ₄	81.29 (17)
Cl ₄ Pt ₂ Cl ₃	93.76 (13)
Cl ₄ Pt ₂ Cl ₃	89.92 (6)

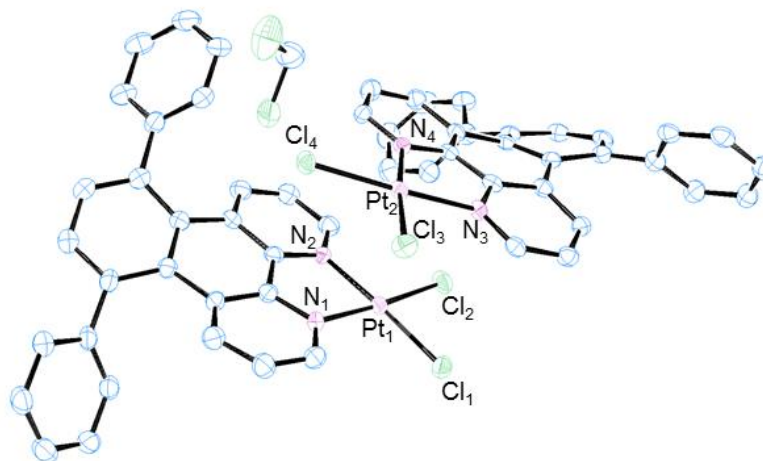


Figure 4.15: Numbering scheme for measurement of bond angles of **59** (see Table 4.4).

The distance between the Pt atoms in the asymmetric unit is 3.4815 Å (estimated standard deviation: 11), which is suggestive of a Pt-Pt interaction. A similar value, 3.45 Å, has been reported for the compound [Pt(bpy)Cl₂] (in its red form), which has been suggested as leading to a linear Pt-Pt chain.^{40, 41} The zig-zag pattern of the Pt-Pt chain is often observed in such Pt-Pt interactions.⁴² The presence of Pt-Pt interactions is due to the overlap of the 5d_{z²} and 6p_z orbitals of adjacent platinum atoms (made possible by the square planar geometry of the ligands). Upon interaction, the fully occupied 5d_{z²} orbitals are split to give a lower bonding orbital (the dσ) and a higher antibonding orbital (the dσ*) (Fig. 4.16).

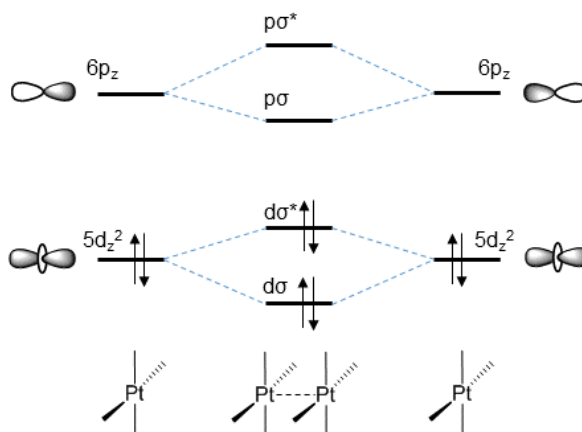


Figure 4.16: MO diagram explaining the interaction of Pt centres leading to Pt-Pt bonding. Figure reproduced from Connick *et al.*⁴²

The empty 6p_z orbitals also form two new orbitals, the pσ and pσ*. Both the 5d_{z²} orbitals are filled prior to interaction, so no formal bonding takes place, but the interaction of the empty pσ and pσ* orbitals has a stabilising effect on the dσ and dσ*, known as a

configuration interaction.⁴² The non-degenerate MOs of the interacting complex, which have the same symmetry, repel each other, with the lower MO moving to lower energy and the higher MO moving to higher energy. The same process occurs with the MOs derived from the 6pz orbitals. This leads to an overall decrease in energy and a bonding interaction.⁴³

The packing of the crystal structure suggests the Pt-Pt interaction is most significant in determining the arrangement, and π - π interactions do not seem to be playing a prominent part. A similar scenario is observed for **62** (Fig. 4.17). However in this case the crystals obtained were of a lower quality, and only partial data could be obtained (therefore no refinement data for this compound was available). The unit cell (as solved by Dr. B. Twamley) displays three independent molecules and one guest molecule of CH₂Cl₂. Again, the square planar nature of the complexes is evident and some degree of Pt-Pt interaction is suggested by the packing diagram, which shows the same zig-zag staggered arrangement of the Pt centres (Fig. 4.17 (b)).

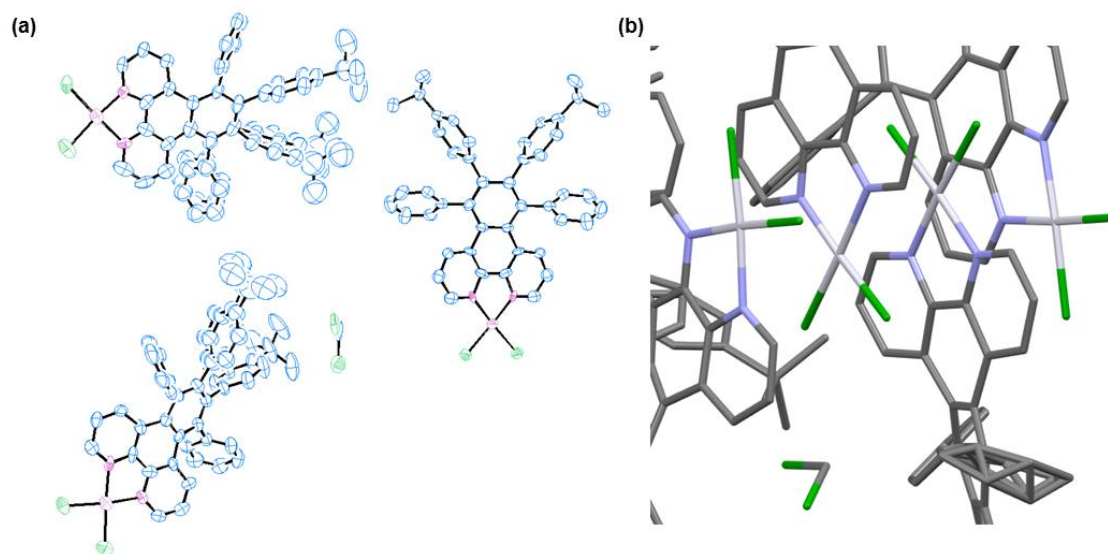


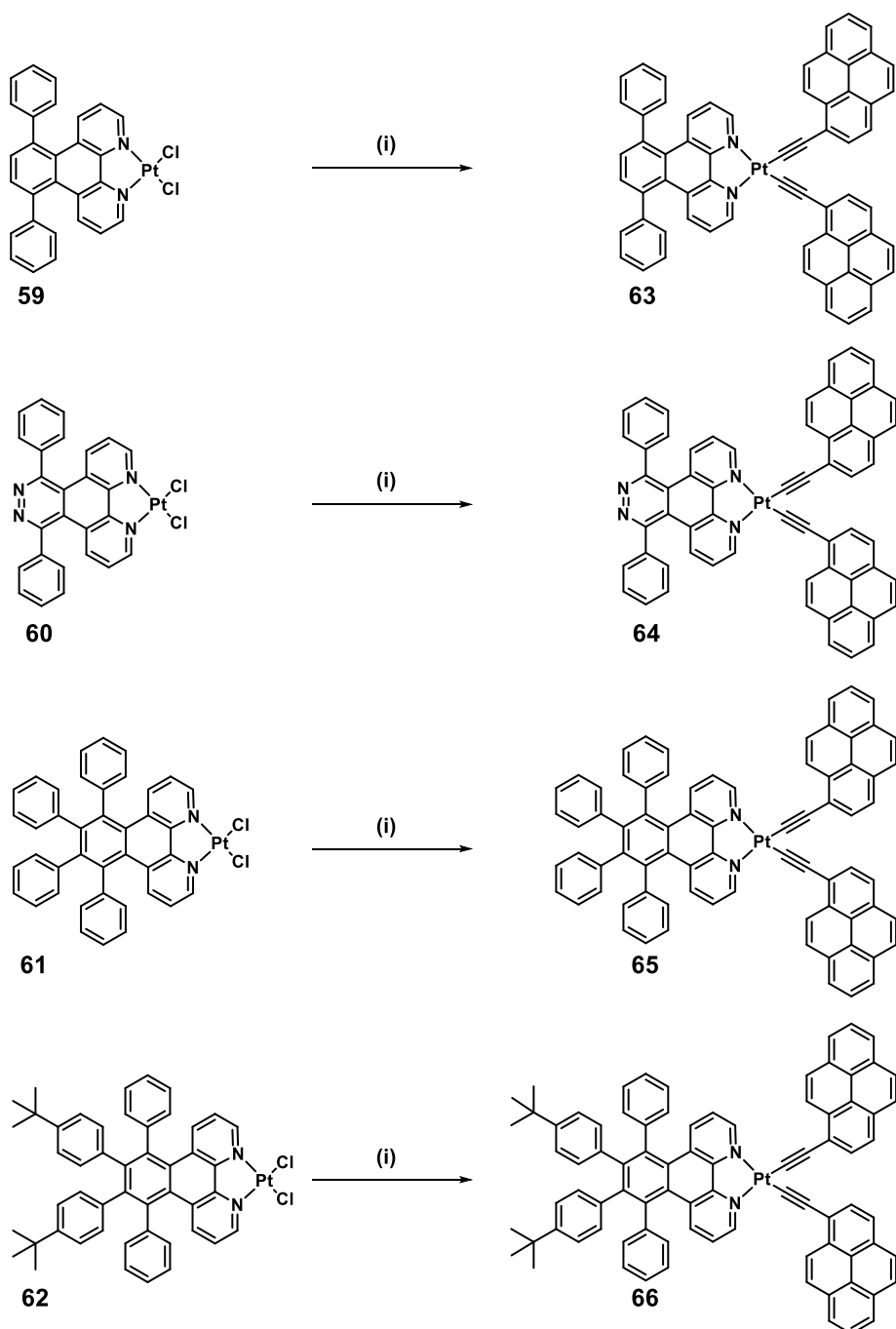
Figure 4.17: Asymmetric unit of **62**, displaying three independent molecules in the unit cell, with CH₂Cl₂ atom. (b) Partial view of packing diagram, suggestive of Pt-Pt interaction. Hydrogen atoms omitted for clarity, and in (a) atomic displacement at 50 % probability.

For the purpose of clarity, a partial view of the packing diagram is shown, with bonds displayed as ‘sticks’. A high degree of disorder is observed in the *tert*-butyl groups and the phenyl rings outside the phenanthroline moiety, which may be due to their less hindered ability to rotate. Obtaining high quality crystal samples of such complexes is often challenging, owing to their low solubility, and their propensity toward quick crystal growth along the Pt-Pt chain which leads to long thin needles that are often twinned.⁴²

4.4 Synthesis of Pt(II) Acetylides with Diimine (N[^]N) Ligands (63-66)

The syntheses of the final Pt(II) acetylide complexes, **63-66**, were achieved by the same general method as for the acetylides described in Chapter Three, *i.e.* a CuI catalysed metathesis reaction between a platinum chloride complex and a terminal alkyne,^{5, 6} In this case, the platinum chloride complexes are the [Pt(L)Cl₂] complexes prepared in Section 4.3, and a terminal alkyne, which in this instance is the commercially available 1-ethynylpyrene. All Pt(II) acetylide complexes were prepared under the same reaction conditions, in a mixture of CH₂Cl₂ and diisopropylamine (DIPA), with CuI catalyst, and were stirred at RT under N₂ for 48 hours (Scheme 4.9). The 1-ethynylpyrene was added in excess (3 equivalents) to aid complete conversion of the platinum chloride complexes, and the CuI catalyst was present at 10 mol %. In all cases, the progress of the reaction could be monitored visually, as the product gradually precipitated from the reaction mixture as a reddish-orange solid. Purification of the complexes was achieved by column chromatography (SiO₂, CH₂Cl₂:MeOH 10:1 v/v), with the removal of excess 1-ethynylpyrene proving quite challenging. For **66**, further purification on a preparative TLC plate was required to remove trace impurities, with the several purification steps impacting upon the yield of the compound (15 %).

Although **66**, with its *tert*-butyl solubilising groups displayed moderate solubility, the purification of compounds **63**, **64**, and **65** posed significant challenges, as all three displayed relatively low solubility, with **63** being only poorly soluble, and **64** and **65** being almost completely insoluble in common solvents. The moderately low yields obtained for these compounds is most likely due to losses from precipitation whilst they were being purified by chromatography (literature yield from synthesis of **LC 112** ([Pt(dbbpy)(C≡C-pyrene)₂): 45 %).¹¹



Scheme 4.9: Synthesis of Pt(II) acetylides with diimine ligands. (i) 1-ethynylpyrene, CuI, CH₂Cl₂, DIPA, RT, N₂, 48 h. Yields: 25 % (**63**), 26 % (**64**), 23 % (**65**), 15 % (**66**).

4.5 Characterisation of Pt(II) Acetylides with Diimine (N[^]N) Ligands (**63-66**)

Characterisation of compounds **63-66** proved to be a challenge, due to the low yields and high degrees of insolubility. It was however, possible to obtain ¹H NMR spectra of all four compounds and in some cases ¹³C{¹H} NMR spectra. Mass spectral analysis confirmed

the successful synthesis of all four compounds, and the respective data are summarised in Table 4.5.

Table 4.5: HRMS data for compounds 63-66.

Compound	Formula	Calc. m/z	Found m/z	Molecular Ion
63	C ₆₄ H ₃₆ N ₂ NaPt	1050.2424	1050.2408	[M+Na] ⁺
64	C ₆₂ H ₃₄ N ₄ Pt	1029.2431	1029.2482	[M] ⁺
65	C ₇₆ H ₄₄ N ₂ Pt	1179.3152	1179.3191	[M] ⁺
66	C ₈₄ H ₆₀ N ₂ Pt	1291.4404	1291.4464	[M] ⁺

4.5.1 NMR Analysis of 63 [(Pt(L)(C≡C-pyrene)₂] (L = 59)

The ¹H NMR spectrum of **63** (Fig. 4.18) was assigned with the aid of a 2D TOCSY experiment, and also ¹H-¹³C HSQC and HMBC experiments (Figs. 4.19 and 4.20), although the very high extent of insolubility prevented the obtainment of a full ¹³C{¹H} spectrum.

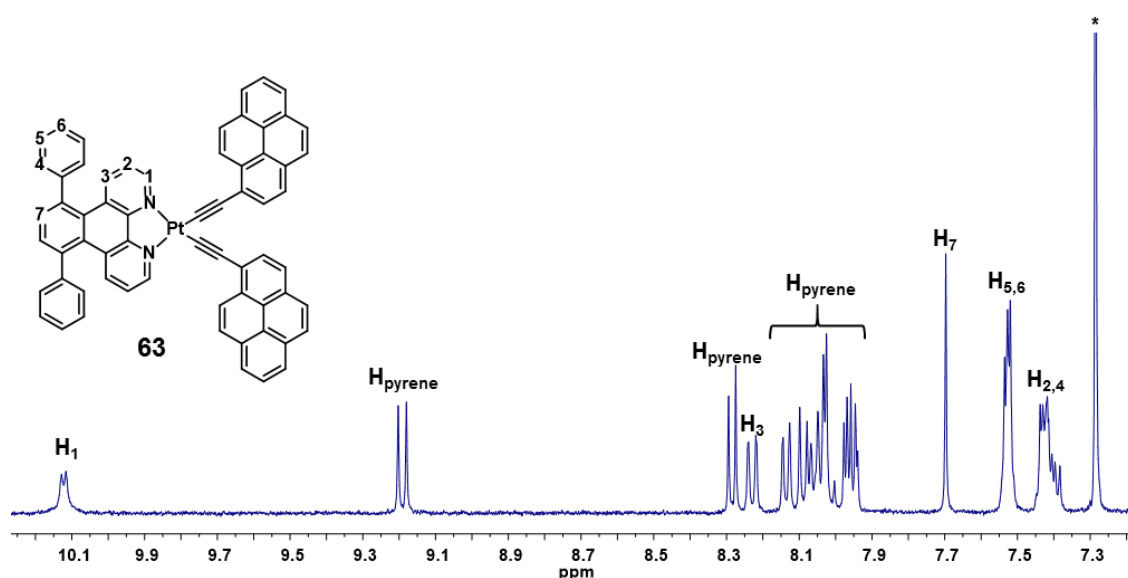


Figure 4.18: The ¹H NMR spectrum of **63** (400 MHz, CDCl₃ RT. * denotes residual CHCl₃ peak.).

The most downfield proton is as expected H₁, of the phenanthroline moiety, which shows spin-spin correlations with the signals at δ 8.23 and 7.39 ppm, which may be assigned to protons H₃ and H₂ respectively. The proton H₁ has undergone a slight downfield shift from the [Pt(N[^]N)Cl₂] precursor (from δ 9.80 to δ 10.12 ppm), after the exchange of the chloride

ligands for acetylides. The relatively downfield doublet at δ 9.19 ppm corresponds to protons of the appended pyrene ligands, and integrates to two protons. Another doublet originating from the pyrene moieties and integrating to two protons is observed at δ 8.28 ppm. The complex multiplet between δ 8.16 and 7.93 ppm corresponds to further signals from the pyrene protons. The singlet at δ 7.70 ppm, which does not exhibit any spin-spin interactions in the TOCSY experiment is assigned to the protons labelled H₇. The overlapping aromatic proton signals at δ 7.53 ppm are assigned to the protons labelled H₅ and H₆ and integrate to 6. The multiplet at δ 7.42 ppm is therefore assigned to the protons labelled H₄, which overlap with the signal from the H₂ protons (as revealed by the TOCSY experiment). The signals obtained correspond well with the spectrum obtained by Pomestchenko *et al.* for the analogous **LC 112** complex (Fig. 4.2).¹¹

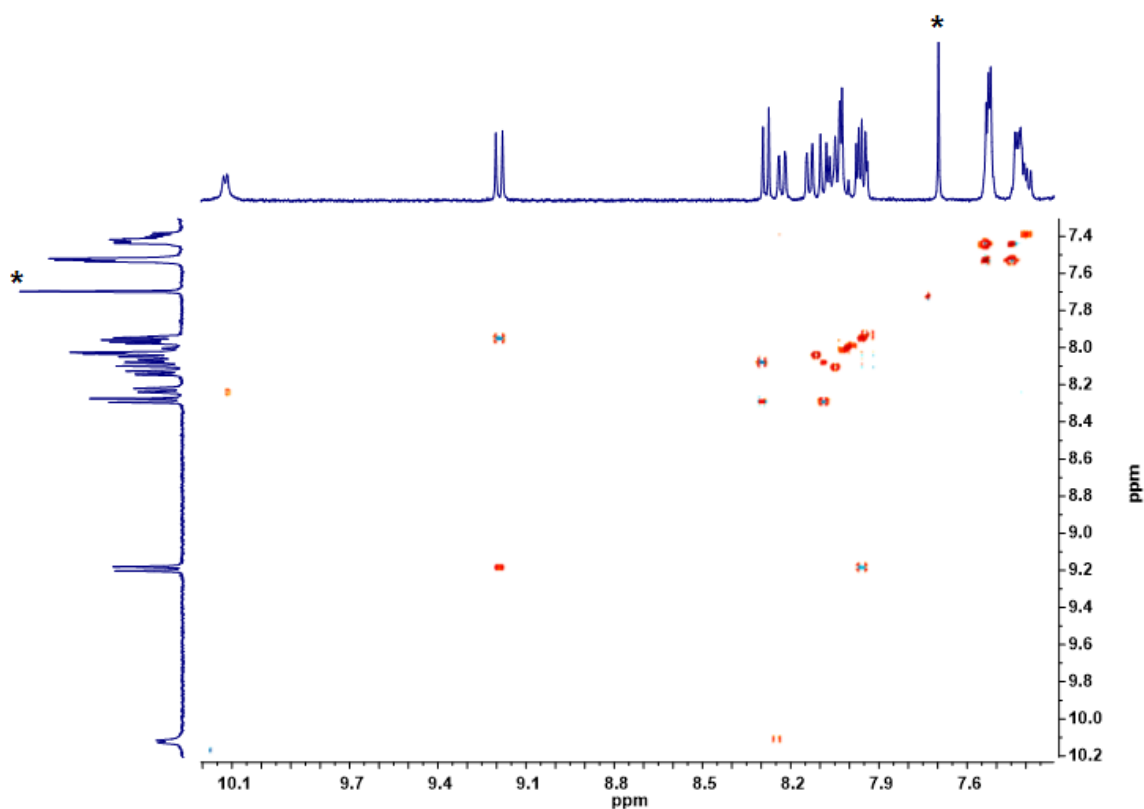


Figure 4.19: ^1H - ^1H TOCSY of **63** (400 MHz, CDCl_3 , RT). * denotes residual CHCl_3 solvent.

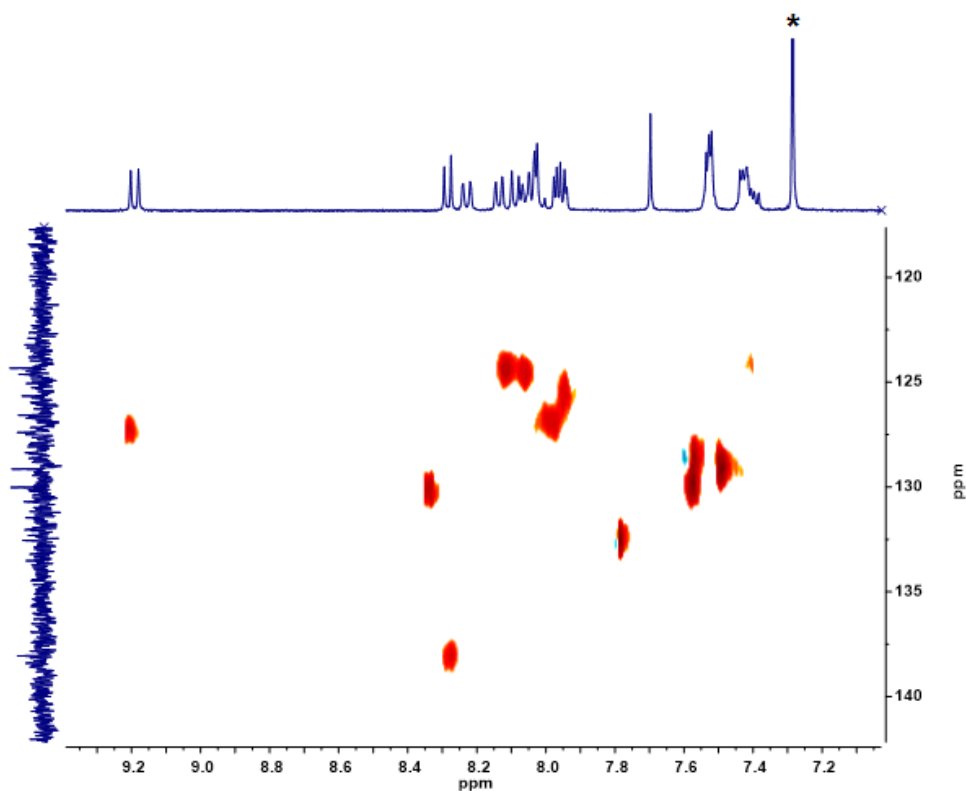


Figure 4.20: ^1H - ^{13}C HSQC spectrum of **63** (400 MHz, CDCl_3 , RT). * denotes residual CHCl_3 solvent.

4.5.2 NMR Analysis of **64** $[(\text{Pt}(\text{L})(\text{C}\equiv\text{C-pyrene})_2]$ (**L** = **60**)

The ^1H NMR spectrum of **64** is presented in Fig. 4.21. The very high degree of insolubility of this complex prevented a satisfactory spectrum being obtained in CDCl_3 , and after testing a range of solvents, it was found that DMSO-d_6 gave the best results. However, even DMSO-d_6 yielded a spectrum which still exhibits a high degree of noise, and it did not prove possible to obtain a $^{13}\text{C}\{^1\text{H}\}$ spectrum. It is however possible to observe the relevant ^1H signals, and based upon integration values and the previously assigned spectrum of **63**, to tentatively assign the signals observed. Once again, the most downfield signal, at δ 10.07 ppm, is characteristic of the phenanthroline moiety and may be assigned to H_1 . In common with the acetylide complex **63**, H_1 is observed to undergo a downfield shift after addition of the acetylide ligands. The doublet at δ 8.98 ppm is assigned to the pyrene moiety, and the complex multiplet between δ 8.38 and δ 7.95 is assigned to the pyrene moiety and also H_3 . The remaining aromatic signals are assigned H_4 (7.73 ppm) and H_2 , H_5 and H_6 (overlapping

between δ 7.58 and 7.69 ppm). The identity of this compound was further confirmed by HRMS (Table 4.5).

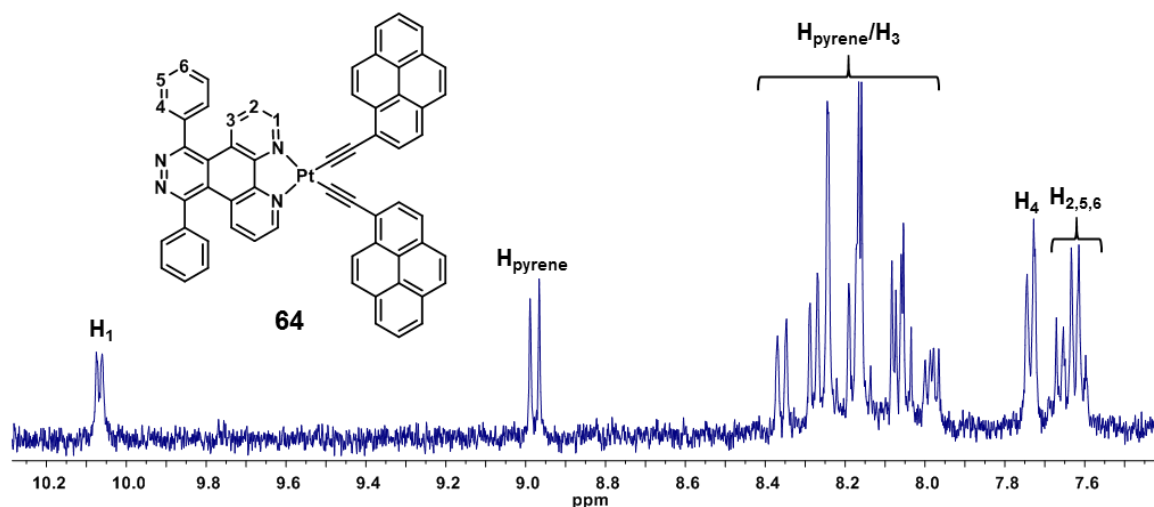


Figure 4.21: The ^1H NMR spectrum of **64** (400 MHz, DMSO-d_6 , RT).

4.5.3 NMR Analysis of **65** [(Pt(L)(C $\equiv$ C-pyrene) $_2$] (L = **61**)

It was found that **65** was only very sparingly soluble in most common solvents. Attempts were made to record the ^1H NMR spectrum of this compound in CDCl_3 , CD_3CN , and CD_2Cl_2 , however in these solvents the compound was almost insoluble. The only solvent which gave a useful spectrum was DMSO-d_6 . However, recording the spectrum in DMSO-d_6 required variable-temperature NMR in order to aid the solubility. The effect can be observed in Fig. 4.22, where in (a) the ^1H NMR spectrum of **65** is very broad and quite poorly defined. However upon heating to 60 $^\circ\text{C}$, the spectrum is quite improved and easier to interpret (Fig. 4.22 (b)). It is however, in comparison with the spectrum of **63**, still very poorly resolved. In any case it was not possible to obtain further spectra (*e.g.* $^{13}\text{C}\{^1\text{H}\}$, ^1H - ^{13}C HSQC *etc.*) due to the tremendous insolubility.

The low resolution of the ^1H NMR spectrum of **65** prevents its conclusive assignment. It is possible to compare it with the ^1H NMR spectrum of the similar complex **63**, and the precursor chloride complex **61**. The ^1H NMR spectrum of **65** bears a very strong resemblance to those of the other Pt(II) acetylides **63** and **64**. Therefore it is most likely that the most downfield peak at 9.90 ppm is H_1 of the phenanthroline moiety, and that the doublet at δ 9.02 ppm is attributable to the pyrene ligands. The multiplet between δ 8.00 and 8.28

ppm is most likely to be also attributable to the pyrene moiety and H₃. The identity of the peak at δ 7.68 ppm is a little more ambiguous, but is most likely a resonance from the pyrene protons. The signals at δ 7.28, 7.22, 6.93 and 6.81 ppm are indicative of the protons of the phenyl rings of the diimine ligand, and are assigned based on the ¹H NMR spectra of the precursor ligand and its corresponding [Pt(N[^]N)Cl₂] complex. Although these assignments are only tentative, the identity of the compound being that suggested is supported by the HRMS result (Table 4.5) and its similarity to the previously characterised compounds.

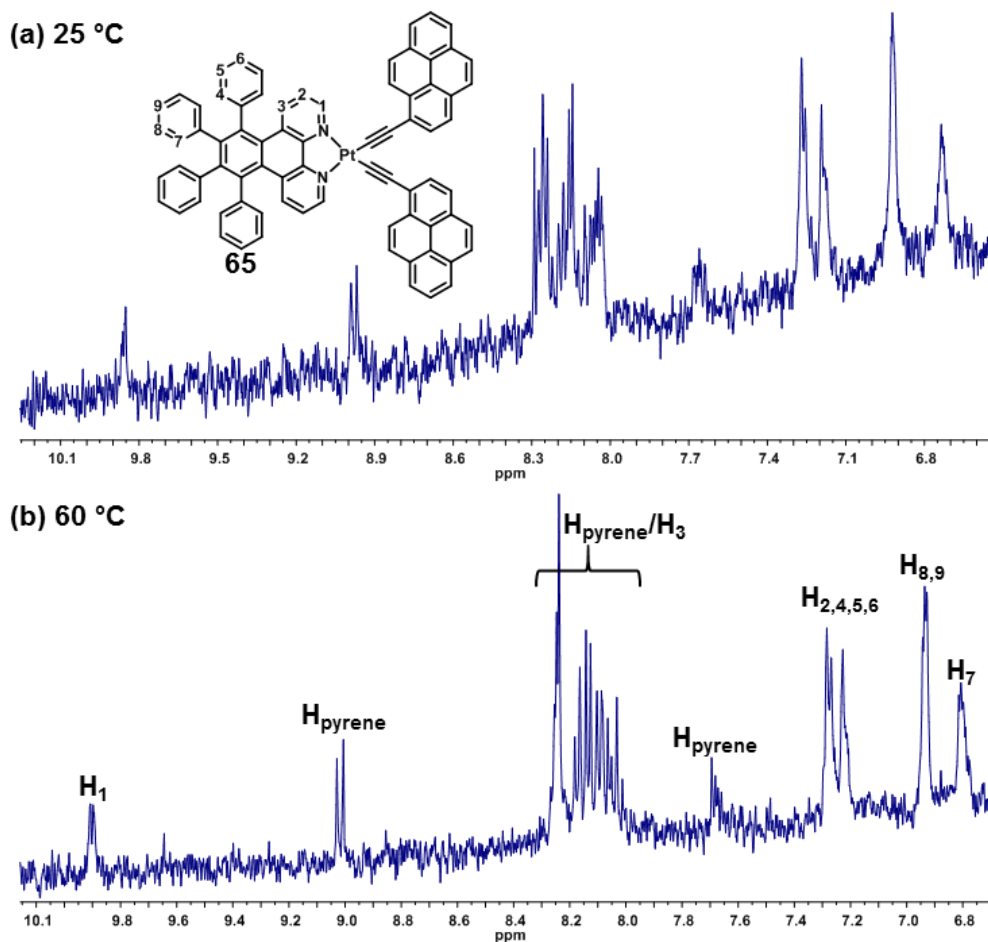


Figure 4.22: Variable-temperature NMR experiments. (a) ¹H NMR spectrum of **65** (400 MHz, DMSO-*d*₆, 25 °C). (b) ¹H NMR spectrum of **65** (400 MHz, DMSO-*d*₆, 60 °C).

4.5.4 NMR Analysis of **66** [(Pt(L)(C≡C-pyrene)₂] (L = **62**)

The NMR analysis of **66** was made much more facile than that of the previously described Pt(II) acetylides, as the introduction of the *tert*-butyl groups led to a much increased level of solubility, and even made it possible to obtain a satisfactory ¹³C{¹H} NMR

spectrum. The NMR spectra of **66** were recorded in CDCl₃ and it was not necessary to use variable temperature methods. The ¹H NMR spectrum of **66** is presented in Fig. 4.23, and it follows the same general pattern as those previously described. A ¹H-¹³C HSQC experiment and a HMBC experiment were used to aid the assignment (Figs. 4.24 and 4.25). The most downfield signal is attributed to H₁ of the phenanthroline moiety. In common with compounds **64-66**, H₃ and H₂ are further upfield and may be identified through their correlations with each other in the HMBC experiment. The protons of the phenyl ring bearing the *tert*-butyl groups, H₇ and H₈ are assigned to the signals at δ 6.50 and 6.87 ppm respectively, which each integrate to four protons. This assignment is further confirmed by the HMBC experiment, which shows that both the *tert*-butyl protons, and the protons assigned as H₇, show a three-bond correlation to the same quaternary carbon *i.e.* the carbon of the phenyl ring bearing the *tert*-butyl group. A selective TOCSY confirmed that both H₇ and H₈ were in the same spin system. This confirms the position of H₇. The protons labelled as H₄ are assigned to the signal at δ 7.08 ppm, based upon their integration value of four, by comparison with the [Pt(N[^]N)Cl₂] precursor, and the HMBC experiment, which shows a three-bond correlation between the H₄ protons and the ¹³C signal associated with the H₆ protons. The H₂, H₅, and H₆ protons are observed as an overlapping multiplet (also partially overlapping with the CDCl₃ solvent signal). The satellite peaks from the CDCl₃ solvent are observed at δ 7.54 and 7.02 ppm.

In common with the compounds **64-66**, the signal at δ 9.20 ppm is assigned to protons of the pyrene ligands, and the series of overlapping signals between δ 7.92 and 8.16 ppm are also assigned to the pyrene ligands. The HMBC experiment permitted the assignment of H₉ to the doublet at δ 8.30 ppm, of the pyrene ligands, since the ¹³C{¹H} signal corresponding to the alkyne carbon closest to the pyrene ligand (101.2 ppm) shows a three-bond correlation with the ¹H signal at δ 8.30 ppm. The *tert*-butyl protons are observed as a singlet at δ 1.17 ppm, and integrate to 18 protons, as expected. The ¹³C NMR spectrum (proton decoupled) of **66** is displayed in Figure 4.26. Further confirmation of the identity of **66** was provided by HRMS (Table 4.5).

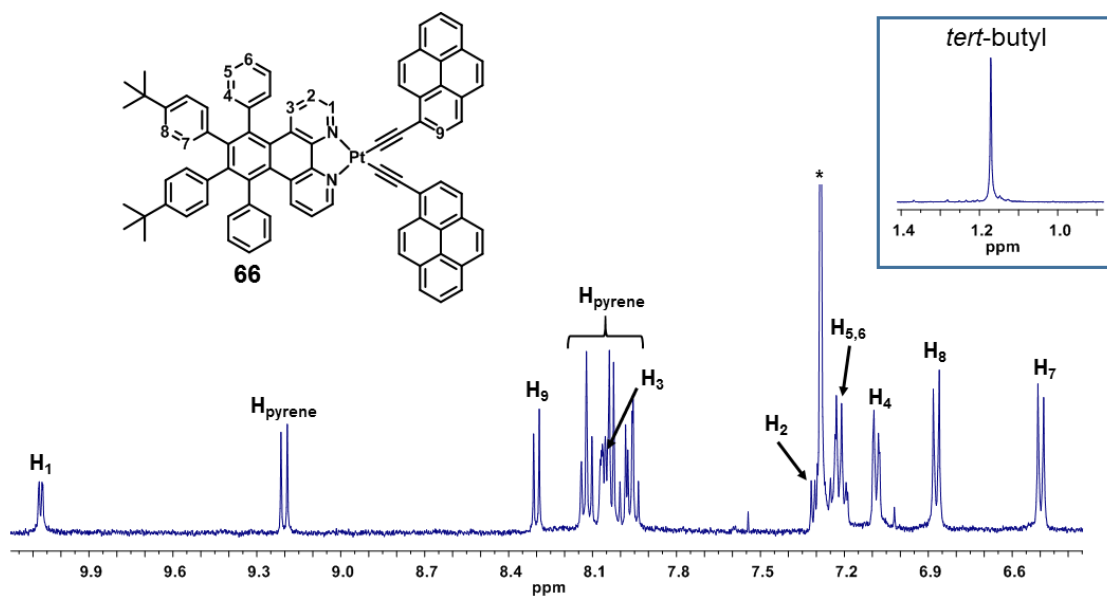


Figure 4.23: ^1H NMR spectrum of **66** (400 MHz, CDCl_3 , RT). * denotes residual CHCl_3 peak.

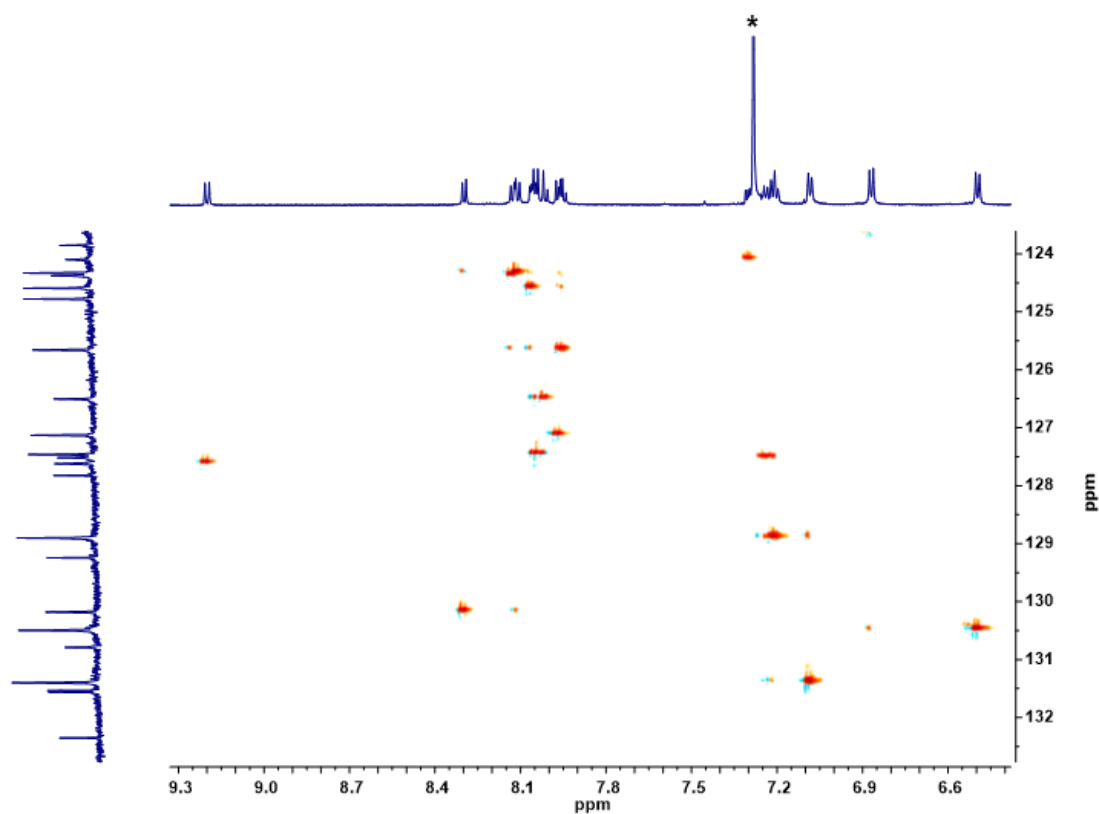


Figure 4.24: (a) ^1H - ^{13}C HSQC spectrum of **66** (600 MHz, CDCl_3 , RT). * denotes residual solvent peak.

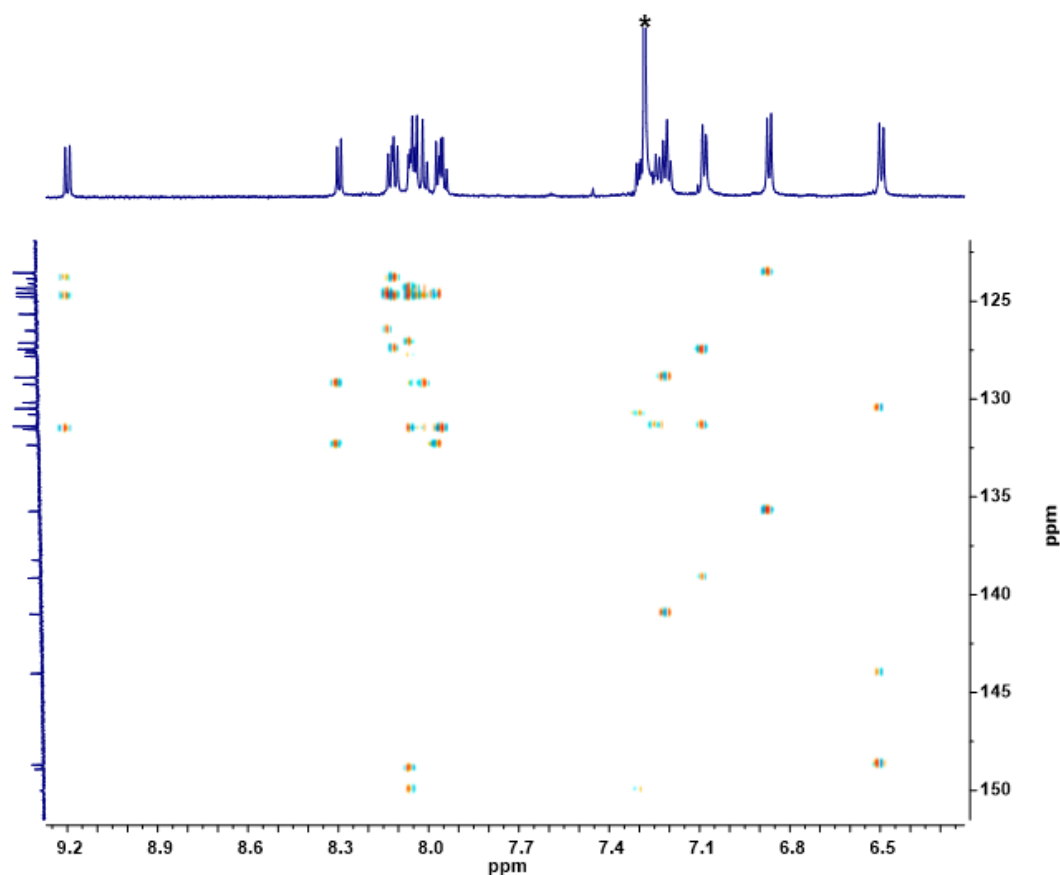


Figure 4.25: HMBC spectrum of **66** (600 MHz, CDCl_3 , RT). * denotes residual solvent peak.

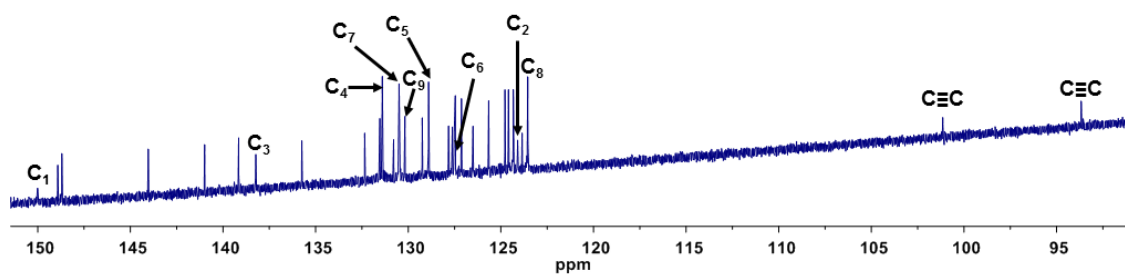


Figure 4.26: Aromatic region of ^{13}C spectrum (proton decoupled) of **66**, with selected resonances labelled. Unlabelled resonances correspond to either pyrene C-H or quaternary carbons. (600 MHz, CDCl_3 , RT).

4.6 Photophysical Studies

4.6.1 Photophysical Investigation of Diimine Ligands

The UV-Vis absorption and emission behaviour of ligands **54**, **56**, **57** and **58** were examined. The UV-Vis spectra are displayed in Fig. 4.27 (a), and the excitation and emission spectra are displayed in Fig. 4.27 (b). The UV-Visible absorption spectra of all four compounds are quite similar and are dominated by intense π - π^* absorptions. The more conjugated variants, **57** and **58**, which possess two extra phenyl rings, are observed to show a more red-shifted absorption ($\lambda_{\text{max}} = 285$ and 290 nm, respectively). This red-shift with conjugation is characteristic of π - π^* transitions.⁴⁴ The less conjugated **54** and **56** are slightly blue-shifted in comparison ($\lambda_{\text{max}} = 273$ and 275 nm, respectively). The absorption spectrum of compound **56**, which possesses a pyridazine ring in place of the phenyl ring of **54**, exhibits low intensity shoulders at $\lambda = 336$ and 354 nm. As these are not observed for **54**, they are most likely arising due to transitions of the pyridazine ring. The absorption data corresponding to the ligands is summarised in Table 4.6.

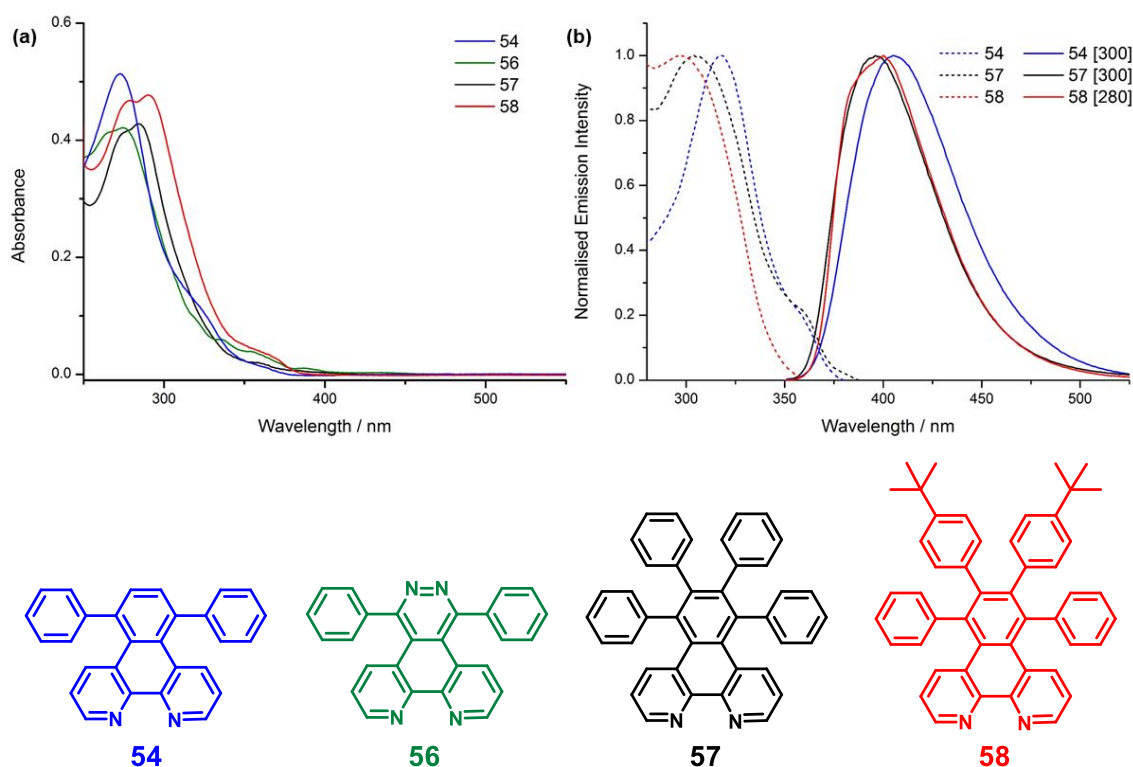


Figure 4.27: (a) UV-Visible absorption spectra of ligands **54**, **56**, **57** and **58** (1×10^{-5} M, CH_2Cl_2 , RT). (b) Normalised emission (solid line, $\lambda_{\text{exc}} = [\text{nm}]$) and excitation spectra (dashed line, $\lambda_{\text{em}} = 405$ (**54**), 400 (**56**), 400 (**57**)) of ligands **54**, **56**, **57** and **58** (1×10^{-5} M, CH_2Cl_2 , RT).

Table 4.6: UV-Visible absorption data for compounds **54**, **56**, **57**, and **58**.

Compound	λ_{max} [nm] ($\epsilon \times 10^{-4}$ [M ⁻¹ cm ⁻¹])
54	273 _{max} (5.12), 323 _{sh} (1.14)
56	266 (4.14), 275 _{max} (4.21), 336 _{sh} (0.59), 355 _{sh} (0.39)
57	274 (4.14), 284 _{max} (4.28), 359 _{sh} (0.19)
58	278 (4.65), 290 _{max} (4.77), 357 _{sh} (0.42)

The excitation spectra of the ligands (Fig. 4.27 (b)) are observed to correspond well with the absorption profiles of the ligands. However, it did not prove possible to obtain an emission or excitation spectrum from the very poorly emissive **56**. The emission profiles of **54**, **57** and **58** are quite similar. The emission profile of **54** ($\lambda_{\text{em}} = 405$ nm) is observed to be slightly red-shifted in comparison with the profiles of the other two ligands ($\lambda_{\text{em}} = 396$ -400 nm). The emission data for ligands **54**, **56**, **57** and **58** is summarised in Table 4.7. The quantum yields of fluorescence were measured by the relative method, as outlined by Brouwer,⁴⁵ using quinine sulfate in H₂SO₄ as a reference standard.

Table 4.7: Emission data for ligands **54**, **56**, **57**, and **58**. * Compound was non-emissive.

Compound	Medium (Temp.)	λ_{em} [nm] (λ_{exc} [nm])	Lifetime τ [ns] ($\lambda_{\text{exc}}/\lambda_{\text{em}}$ nm)	Φ_{em}
54	CH ₂ Cl ₂ (RT)	405 (300)	2 (370/405)	0.04
56	CH ₂ Cl ₂ (RT)	--*	--*	--*
57	CH ₂ Cl ₂ (RT)	398 (300)	3 (370/400)	0.03
58	CH ₂ Cl ₂ (RT)	400 (280)	4 (370/400)	0.03

4.6.2 Photophysical Investigation of [Pt(L)Cl₂] Complexes (L = **54**, **56**, **57**, or **58**)

The UV-Visible absorption spectra of platinum chloride complexes **59-62** are displayed in Fig. 4.28. It can be observed that after complexation of the Pt metal, the complexes exhibit new absorption bands in the region of 350-400 nm. Miskowski *et al.* investigated the absorption behaviour of a range of Pt(II) diimine complexes, including the analogous complex Pt(phen)Cl₂ (where phen is 1,10-phenanthroline).⁴⁶ For Pt(phen)Cl₂, they reported a UV-Vis absorption spectrum that is broadly similar to the four complexes

described here. They also observed a very weakly resolved, extended shoulder at ~ 450 nm as the lowest energy transition, which they attributed to a singlet-triplet $\pi \rightarrow \pi^*$ transition. In the case of the four complexes **59-62**, this feature does not seem to be present, as by 450 nm, there appears to be negligible absorption. The UV-Vis spectra of **59-62** are dominated by the diimine ligand $\pi\text{-}\pi^*$ absorptions and it is possible that other features due to complexation are being obscured by these. However, comparison with the precursor ligands suggests that the absorption band at ~ 400 nm, which is present only in the platinum chloride complexes, is arising from complexation of the platinum centre and may be MLCT or MC in origin. The UV-Vis absorption data for compounds **59-62** is summarised in Table 4.8. These complexes were observed to almost completely non-luminescent, and did not yield emission spectra. This may be a consequence of low-lying d-d states deactivating the emissive state.

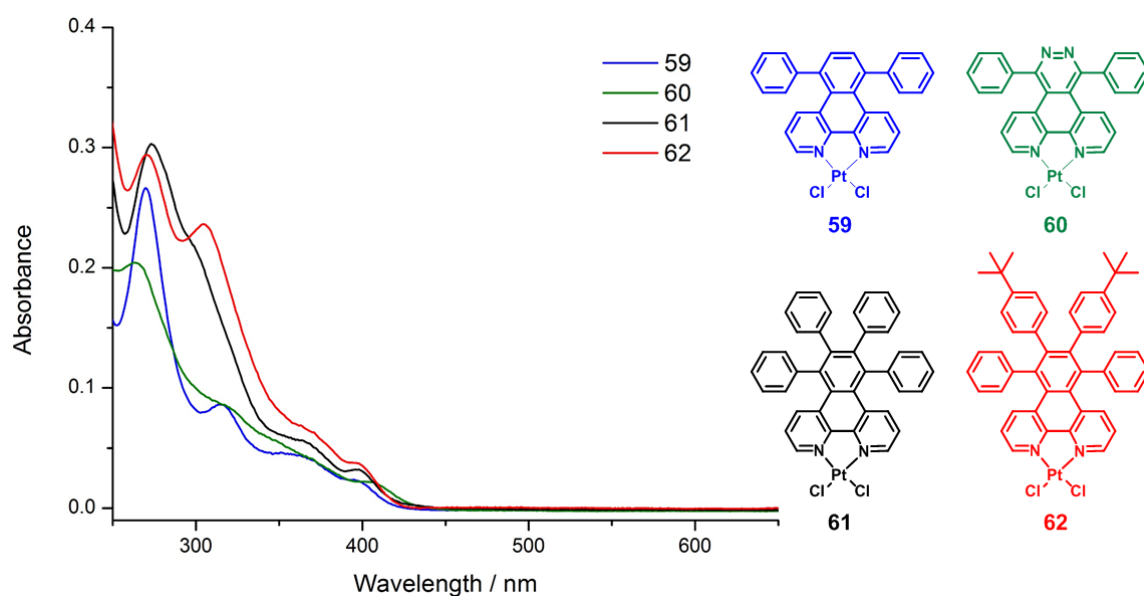


Figure 4.28: UV-Visible absorption spectra of complexes **59-62** (1×10^{-5} M, CH_2Cl_2 , RT).

Table 4.8: UV-Visible absorption data for **59-62**.

Compound	λ_{max} [nm] ($\epsilon \times 10^{-4}$ [$\text{M}^{-1} \text{cm}^{-1}$])
59	270 _{max} (2.66), 316 (0.86), 361 (0.43), 396 (0.23)
60	264 _{max} (2.04), 319 _{sh} (0.85), 348 _{sh} (0.55), 405 (0.23)
61	274 _{max} (3.03), 298 _{sh} (2.20), 364 _{sh} (0.56), 397 (0.32)
62	270 _{max} (2.93), 305 (2.36), 364 _{sh} (0.69), 397 (0.37)

4.6.3 UV-Visible Spectra of [Pt(L)(C≡C-pyrene)₂] Complexes (L = 54, 56, 57, or 58)

The UV-Visible absorption spectra of the Pt(II) acetylide complexes **63–66** are presented in Figure 4.29. The spectra of all four compounds are dominated by intense absorbance bands between *ca.* 350 nm and 400 nm. These are assigned as arising from the pyrene moieties, and are $\pi\text{-}\pi^*$ transitions, based upon their absence in the UV-Vis spectra of the precursor compounds and literature comparison; they are strikingly similar to the UV-Vis absorption spectrum of **LC 112**, as reported by Pomestchenko *et al* (Fig. 4.2 (c)).¹¹ The lowest-energy absorption bands in all four complexes (*ca.* 450 nm) are assigned to MLCT transitions ($d\pi\text{ Pt} \rightarrow \pi^*_{\text{diimine}}$), based upon the same assignment by Pomestchenko. *et al.*, and also the solvatochromic nature of these bands (Fig. 4.30).¹¹ For **64**, a slightly less intense absorbance is observed, but the effect of the introduction of the pyridazine ring has resulted in the MLCT band being pushed significantly further towards the red region of the spectrum (a bathochromic shift).

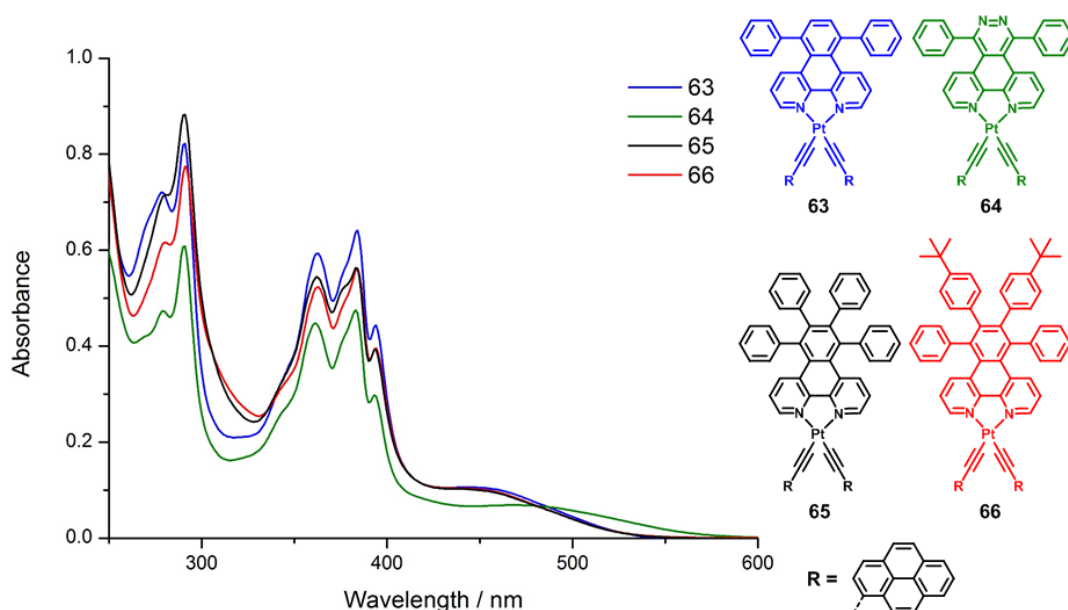


Figure 4.29: (a) UV-Visible absorption spectra of complexes **63–66** (1×10^{-5} M, CH_2Cl_2 , RT).

The effect of solvent polarity on the UV-Visible absorption spectra (Fig. 4.30) reveals not only the CT nature of the bands at $\lambda \approx 450$ nm, but also reveals that the more intense bands between $\lambda \approx 350\text{--}400$ nm, arising from the pyrene ligands, also possess some degree of CT character, or perhaps also overlap the MLCT bands.¹¹ In all cases, the compounds display negative solvatochromism, whereby the more polar solvents result in a shift of the absorption bands at $\lambda \approx 450$ nm to higher energies.⁴⁷ In toluene, the absorptions

of all four complexes are shifted towards the red region of the spectrum. The poor solubility of these complexes prevented clear absorption spectra being obtained in EtOH and MeOH.

Table 4.8: UV-Visible absorption data for 63-66.

Compound	λ_{max} [nm] ($\epsilon \times 10^{-4}$ [$\text{M}^{-1} \text{cm}^{-1}$])
63	279 (7.21), 290 (8.22), 362 (5.92), 384 (6.41), 394 (4.44), 448 (1.06)
64	279 (4.74), 290 (6.08), 343 _{sh} (2.63), 361 (4.49), 383 (4.75), 393 (2.97), 475 (0.68)
65	280 _{sh} (7.12), 290 (8.81), 362 (5.46), 383 (5.64), 394 (3.94), 442 (1.03)
66	280 (6.14), 291 (7.74), 343 _{sh} (3.13), 363 (5.22), 383 (5.59), 394 (3.92), 442 (0.105)

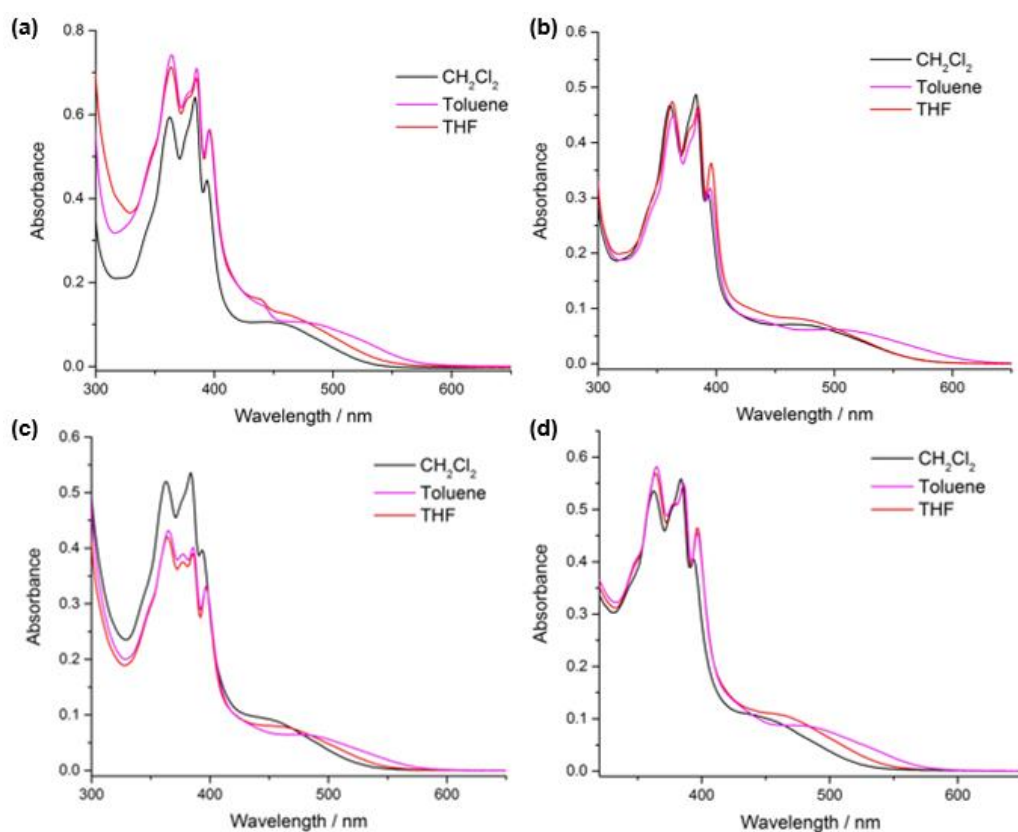


Figure 4.30: Effects of the variation of solvent on the normalised UV-Visible absorption spectra of (a) 63, (b) 64, (c) 65, and (d) 66 ($\sim 1 \times 10^{-5}$ M, RT).

4.6.4 Emission Spectra of [Pt(L)(C≡C-pyrene)₂] Complexes (L = 54, 56, 57, or 58)

Emission spectra of all four complexes were recorded as dilute solutions (1×10^{-5} M) in degassed CH_2Cl_2 . The emission in all cases was almost completely quenched in non-degassed solutions. The emission profile is similar for all four complexes, an emission maximum as a sharp narrow band at $\lambda_{\text{em}} \approx 660$ nm, with a lower intensity band at $\lambda_{\text{em}} \approx 730$ nm (Fig. 4.31). Although pyrene is often known for the formation of excimeric (excited-state dimer) species in solution, resulting in red-shifted and broadened emission spectra,⁴⁴ for these complexes no such evidence for excimer formation is observed, and the emission profile appears independent of concentration ($10^{-5} - 10^{-8}$ M). The emission profiles of **63** and **66** are remarkably similar. The pyridazine substituted **65** displays a slight red-shift in comparison to the other three compounds, and a broader emission profile, which is most likely due to its low solubility. The excitation spectra of the complexes (obtained by monitoring the emission from the emission maximum at $\lambda_{\text{em}} = 660$ nm) are in all cases superimposable with their corresponding UV-Visible absorption spectra. Quantum yields of emission were measured by the relative method, as outlined by Brouwer,⁴⁵ with the use of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ ($\Phi_{\text{em}} = 0.06$) as a reference standard, and the results are summarised in Table 4.9, along with the emission data.

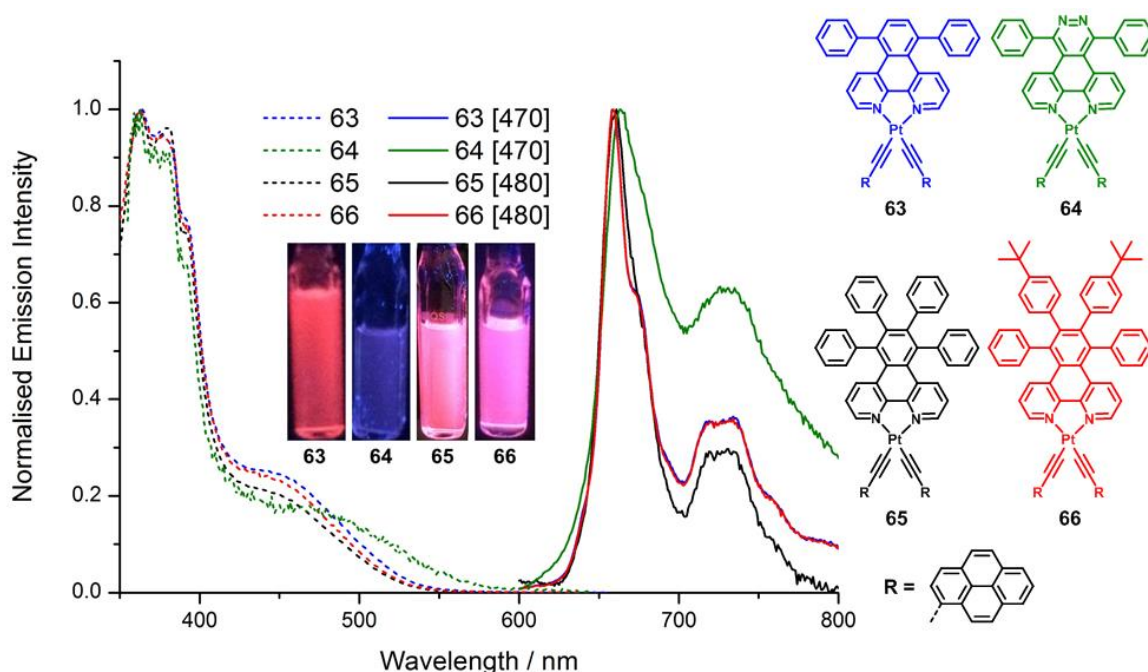


Figure 4.31: Emission (solid line, λ_{exc} [nm]) and excitation (dashed line, $\lambda_{\text{em}} = 660$ nm) spectra of compounds **63-66** (CH_2Cl_2 , RT, N_2 degassed). Inset are photographs of the degassed solutions of **63-66** under excitation at $\lambda = 365$ nm.

The effect of solvent polarity on the excited state of the complexes was also probed (Fig. 4.32). In all cases, the difference in the emission energies, is quite small. For **63**, reasonable solubility was observed in a range of solvents. The less polar solvents (toluene, diethyl ether) produced a very slight red-shift in the emission spectrum, although very little difference in emission energy was observed between CH_2Cl_2 and the more polar EtOH. Much lower solubility was observed for **64**, which only yielded emission spectra in toluene, THF and CH_2Cl_2 . The emission profile in THF was significantly sharpened in comparison to that recorded in CH_2Cl_2 , suggesting that in THF it is better solvated. In toluene, **64** is only poorly solvated, and a very broad, red-shifted emission is observed. Although **65** proved so insoluble that NMR analysis was quite difficult, it did yield satisfactory emission spectra, due to the lower concentrations required, even in highly polar MeOH (in which the other three complexes were insoluble, and non-emissive). A slight red-shift is observed in THF, toluene and diethyl ether in comparison to CH_2Cl_2 , and in EtOH and MeOH, similar very broad and red-shifted emission profiles are observed. The extent of insolubility in these solvents resulted in a high degree of noise in the spectrum. The red-shift which is observed in all solvents is suggestive that some aggregation may be occurring, particularly in EtOH and MeOH. A similar situation is observed for **66**, which displays very minor changes in the emission energy with varying polarity (CH_2Cl_2 , THF, toluene), but displays a broadened red-shifted emission in EtOH and diethyl ether (Et_2O). The very small shift in the emission maxima of these complexes with solvent polarity is not strongly indicative of MLCT emission, which usually involves a change in dipole moment, and generally are broad, with little vibrational structure.⁴⁸ The fine-structure and insensitivity to environment polarity is more indicative of ^3IL emission, where there is no significant change in dipole moment involved.

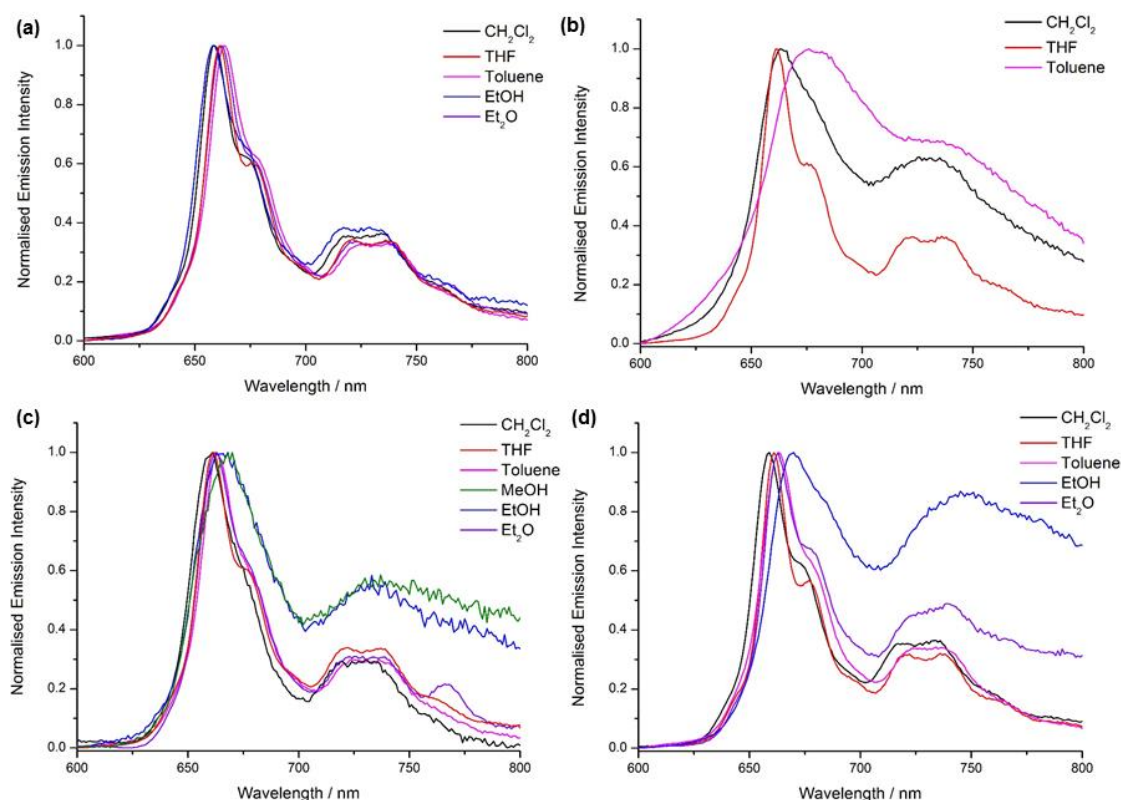


Figure 4.32: Investigations into the effect of solvent polarity on **63** (a), **64** (b), **65** (c) and **66** (d) (1×10^{-5} M, $\lambda_{exc} = 480$ nm).

In order to further investigate the nature of the emissive state of these complexes, low-temperature (77 K) measurements were carried out. An emissive MLCT state generally exhibits a shift to higher emission energies (*i.e.* a blue-shift) in rigid media, due to the solvent molecules being unable to rearrange themselves around the excited-state molecule and its dipole moment.¹⁰ The relevant spectra are displayed in Fig. 4.33, and it is observed that all four complexes show only a very small shift in the emission energy (known as a thermally-induced Stokes shift) at 77 K, in a rigid glass of 4:1 EtOH:MeOH. A shift to higher energy emission is not observed in any case, which is not indicative of an MLCT state, and rather suggests a ^3IL emissive state.

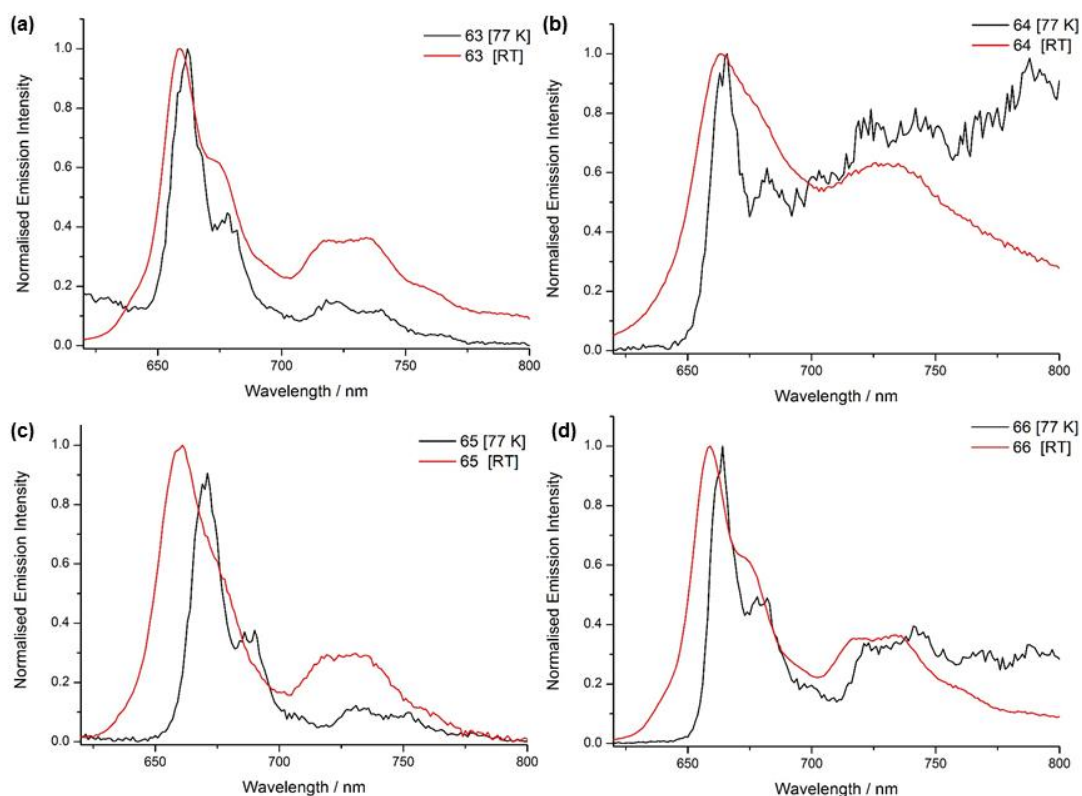


Figure 4.33: Low-temperature (77 K) emission spectra of **63** (a), **64** (b), **65** (c), and **66** (d) ($\sim 1 \times 10^{-5}$ M, 4:1 EtOH:MeOH, black lines), overlaid with their respective RT emission spectra (1×10^{-5} M, CH_2Cl_2 , red lines).

The effect of the presence of molecular oxygen on the complexes was also investigated. In Fig. 4.34, the effect on the emissive behaviour of degassing the samples (via a minimum of three freeze-pump-thaw cycles under argon gas) is compared with the emission of the same aerated samples. For **63**, **65** and **66**, the change in emission intensity is dramatic, with the degassed samples showing a very intense emission, and the aerated samples being largely non-emissive. For **64**, the emission of the aerated solution appears much more intense in comparison to those of the other three complexes. However, **64** was observed to give a much less intense emission, even when degassed, than the other three complexes. The effect of the inclusion of the pyridazine ring appears to have resulted in a significant decrease in luminescence, and the difference in emission intensity between the aerated and degassed samples appears to be simply a result of an overall less emissive complex. The results from these degassing experiments are indicative of phosphorescence emission, as long-lived triplet states are susceptible to deactivation through quenching by molecular oxygen. The energy from the excited triplet state of the complex is transferred to ground-state triplet oxygen ($^3\text{O}_2$), forming excited state singlet oxygen ($^1\text{O}_2$).⁴⁹

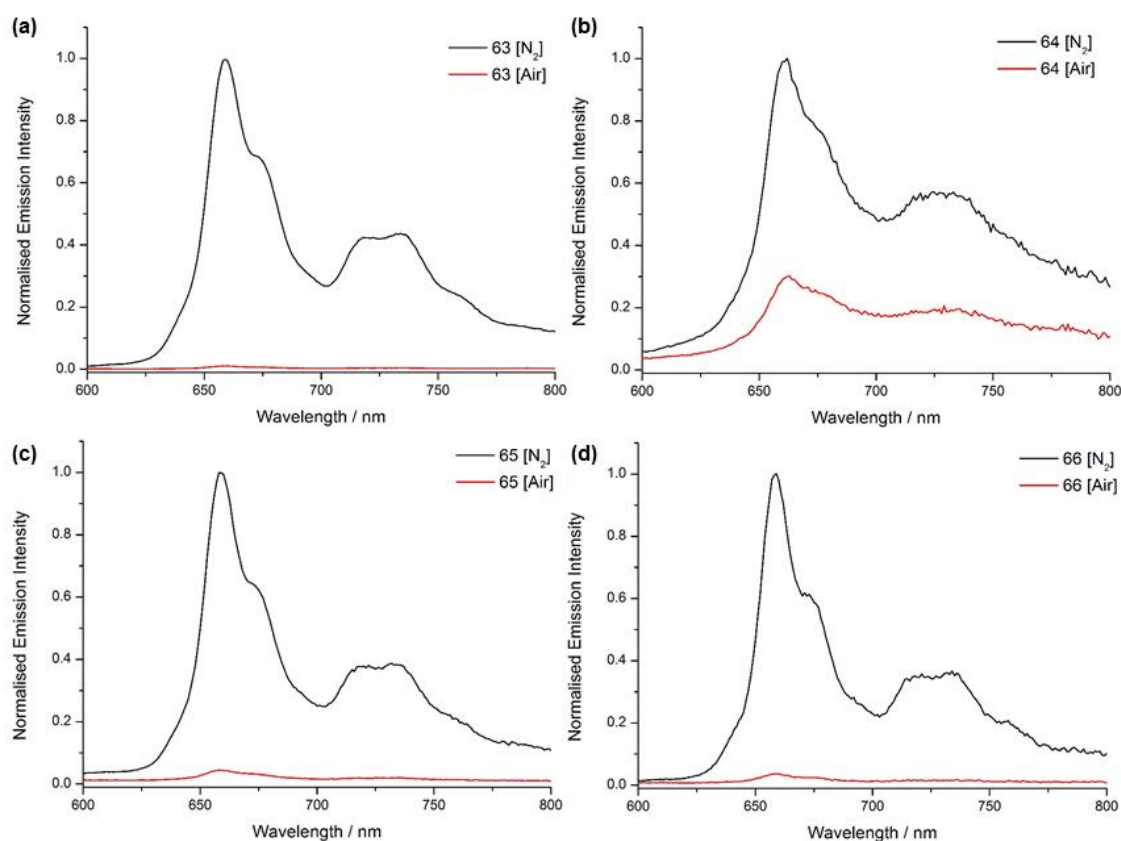


Figure 4.34: Comparison of emission intensity of degassed (black line) and aerated (red line) solutions of **63** (a), **64** (b), **65** (c), and **66** (d) ($\sim 1 \times 10^{-5}$ M, CH_2Cl_2 , RT).

Table 4.9: Emission data for compounds **63-66**.

Compound	Medium (Temp.)	λ_{em} [nm]	Lifetime τ [μs]	Φ_{em}
		(λ_{exc} [nm])	($\lambda_{\text{exc}}/\lambda_{\text{em}}$ nm)	
63	CH_2Cl_2 (RT)	659 (470)	47	0.09
	4:1 EtOH:MeOH (77 K)	662 (480)		
64	CH_2Cl_2 (RT)	663 (470)	25	0.002
	4:1 EtOH:MeOH (77 K)	665 (480)		
65	CH_2Cl_2 (RT)	660 (480)	38	0.02
	4:1 EtOH:MeOH (77 K)	670 (480)		
66	CH_2Cl_2 (RT)	659 (480)	63	0.03
	4:1 EtOH:MeOH (77 K)	664 (480)		

4.6.5 Phosphorescence Emission Lifetimes

The lifetimes of the phosphorescence emission of complexes **63-66** were measured in argon-degassed solutions at RT, and the decay traces are presented in Fig. 4.35. The phosphorescence lifetime of **63** was measured at the Dalian University of Technology by Dr. J. Wang, while those of **64-66** were measured in Trinity College Dublin. For **64**, mono-exponential fitting was possible, while for the remaining complexes, bi-exponential fitting was required. The lifetimes are summarised in Table 4.9. The least emissive complex, **64**, yielded the shortest lifetime (25 μ s), while **66** displayed the longest (63 μ s).

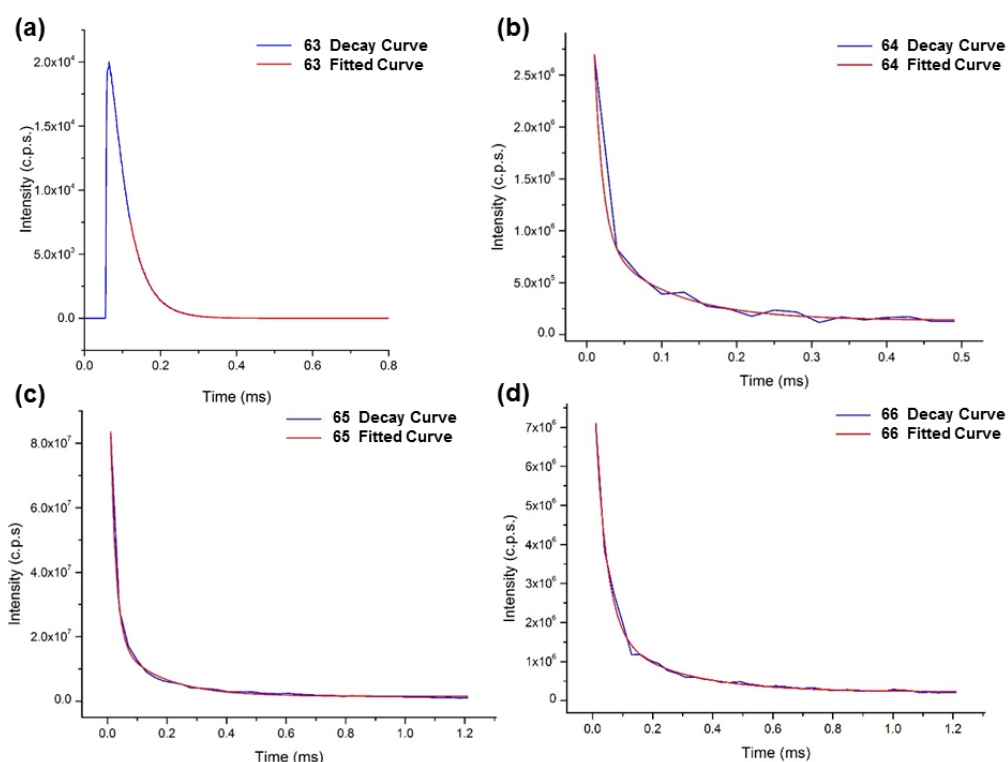


Figure 4.35: Phosphorescence lifetime decay traces of **63** (a), **64** (b), **65** (c) and **66** (d). Recorded in argon-degassed solutions at RT in CH_3CN (**63**) or CH_2Cl_2 (**64-66**).

4.7 Electrochemical Studies

The compounds prepared in this chapter were investigated in terms of their redox behaviour, using cyclic voltammetry (CV), and all potentials quoted are given vs. Ag/AgCl, for literature comparison. Solutions of the compounds (CH_2Cl_2 , 1×10^{-4} M) were first degassed by bubbling with N_2 and then analysed under a steady flow of N_2 . Full details of the procedures employed are given in the experimental section.

4.7.1 Redox Behaviour of Ligands **54**, **56**, **57** and **58**

The electrochemical oxidation processes of ligands **54**, **56**, **57** and **58** were observed to be beyond the CH₂Cl₂ solvent window in all cases. Although acetonitrile has a larger solvent window for cyclic voltammetry measurements (~ 3.5 V), the compounds were not sufficiently soluble in it for measurement. The reduction scans of **54**, **56**, **57**, and **58** are displayed in Fig. 4.36. Compounds **54** and **56** exhibited one reversible reduction process each. Compound **54** gives a reductive potential ($E_{1/2}$) of -1.29 V, yet **56** gives a reductive potential ($E_{1/2}$) of -1.57 V. This is unexpected, as the pyridazine ring of **56** was expected to substantially lower the LUMO energy of the compound, thus resulting in a lower reduction potential. However, measurements were recorded independently three times, with a similar value being obtained in each CV experiment. One suggested explanation may be that CH₂Cl₂ is acidic, and the increased number of nitrogen atoms within the aromatic core be liable to further protonation *versus* those of the phenanthroline ring system common to all the compounds tested. This is postulated to affect the LUMO energy of **56**. However, use of an acid or base to probe this explanation in the CV experiment was ruled out due to assumed distorting effects of the electrochemical behaviour of the chosen acid or base. Compounds **57** and **58** do not exhibit reversible behaviour, as although a return wave is observed in the reduction scan, the ΔE_p value is in both cases much too high to indicate a reversible process (see Table 4.10 for electrochemical data). The inclusion of the *tert*-butyl groups in **58** does not appear to have significantly affected the LUMO energy of the compound. However, the lower reductive potentials of these compounds *versus* **54** shows the effect of the inclusion of further phenyl rings to the periphery of the compound, with a substantial lowering of the LUMO energy in both.

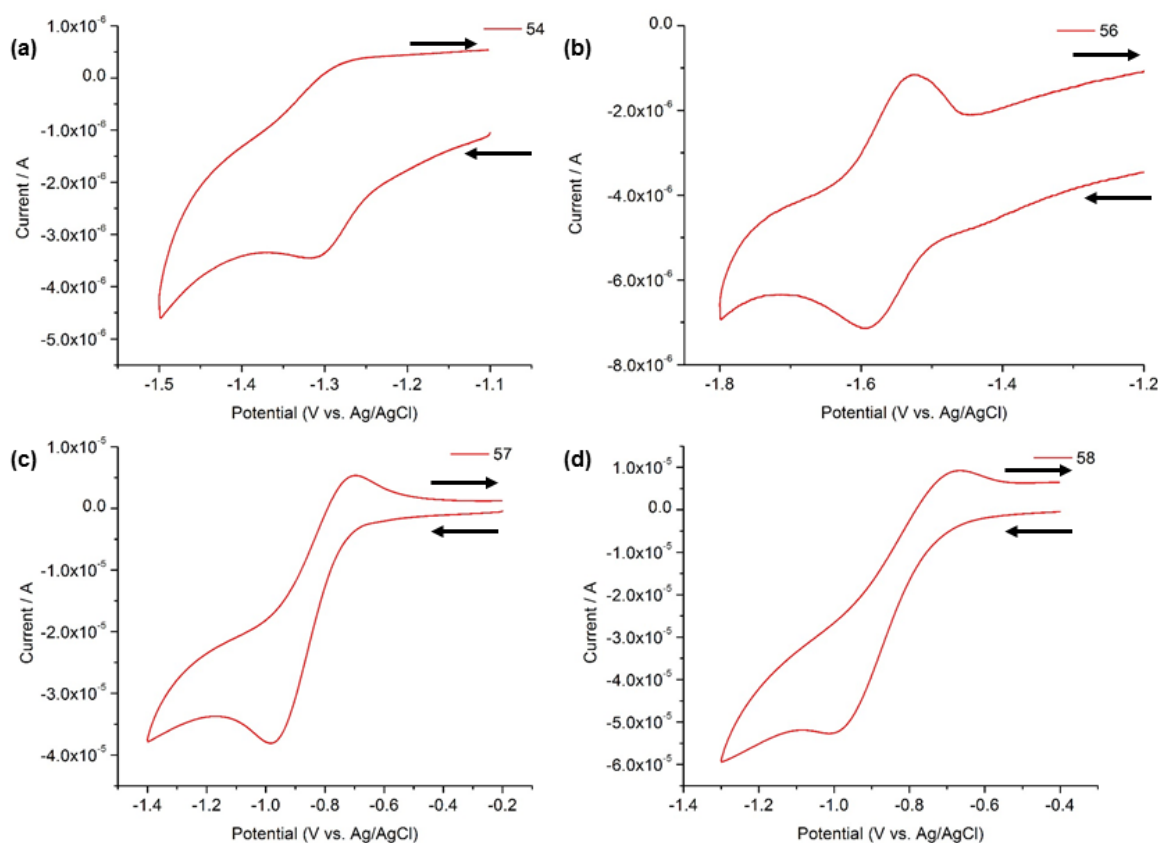


Figure 4.36: Reduction scans of (a) **54**, (b) **56**, (c) **57**, and (d) **58** (CH_2Cl_2 , RT, 1×10^{-4} M, with 0.1 M $\text{Bu}_4\text{N}[\text{PF}_6]$ as supporting electrolyte) with a scan rate of 0.1 V s^{-1} . Arrows indicate direction of scan.

4.7.2 Redox Behaviour of $[\text{Pt}(\text{L})\text{Cl}_2]$ Complexes ($\text{L} = \mathbf{54}, \mathbf{56}, \mathbf{57}, \text{ or } \mathbf{58}$)

The platinum dichloride derivatives of the four ligands were examined in terms of their redox behaviour (Fig. 4.37 and 4.38). An oxidation process (Fig. 4.37) is observed at a poorly resolved irreversible peak at 1.62 V for **59**, 1.74 V for **61**, and 1.63 V for **62**. Reports of similar $\text{Pt}(\text{II})$ compounds indicate irreversible oxidation processes in the region 0.4 - 1.3 V.⁵⁰⁻⁵² The irreversible oxidative processes observed here are assigned to metal-based oxidations ($\text{Pt}(\text{II}) \rightarrow \text{Pt}(\text{III})$), given that the oxidation of the ligands appears to be beyond the solvent window. For **60**, there appears two broad, irreversible oxidations, at 0.66 V and 1.16 V respectively. The faint peak at 0.66 V may be arising from a residual impurity. The oxidised metal species, $\text{Pt}(\text{III})$ is expected to be highly unstable, and, in general, reduction or oxidation processes on $\text{Pt}(\text{II})$ complexes are observed to be irreversible.^{52, 53} Given that the ligand oxidation is beyond the solvent window, these oxidations may be metal-based,

but since similar peaks are not observed in the cyclic voltammograms of the other three complexes, it may be the case that a mixture of ligand-based and metal-based oxidations are being observed, which are obscured by solvent oxidation in the other three cases.

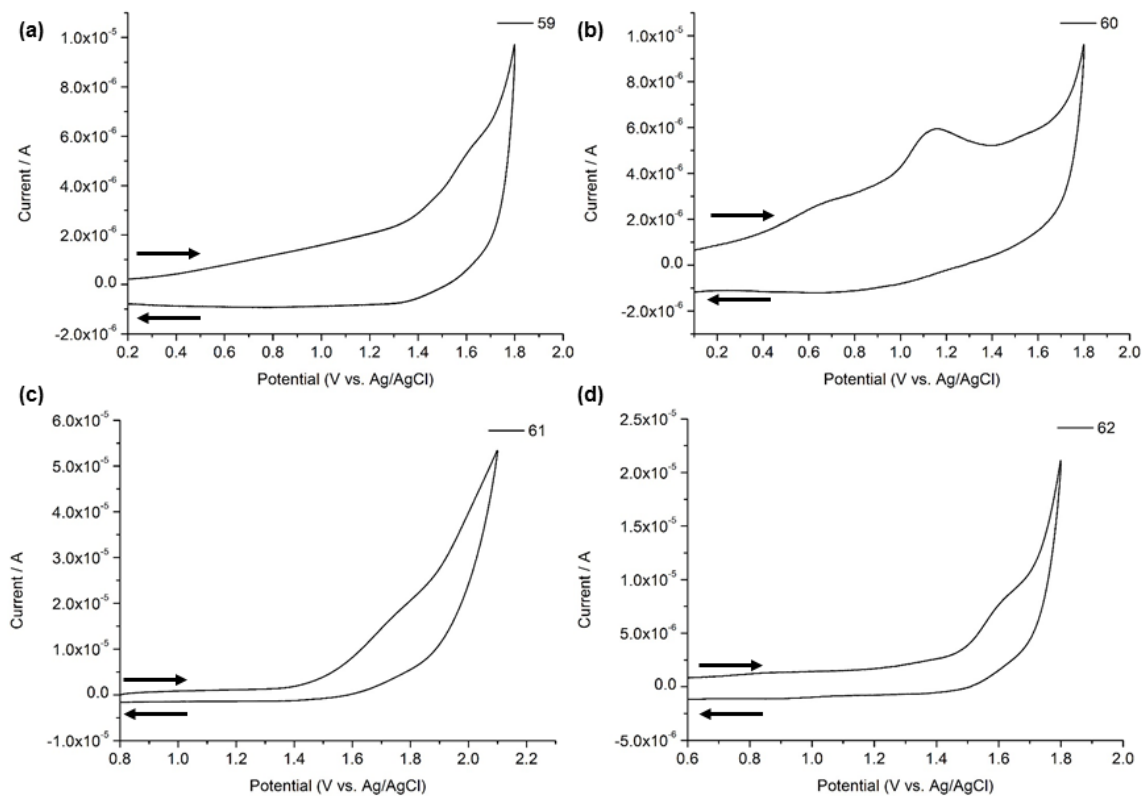


Figure 4.37: Cyclic voltammograms of (a) 59, (b) 60, (c) 61 and (d) 62, showing the oxidation processes (1×10^{-4} M, CH_2Cl_2 , vs. Ag/AgCl, with 0.1 M TBAPF_6 as supporting electrolyte) with a scan rate of 0.1 V s^{-1} . Arrows indicate direction of scan.

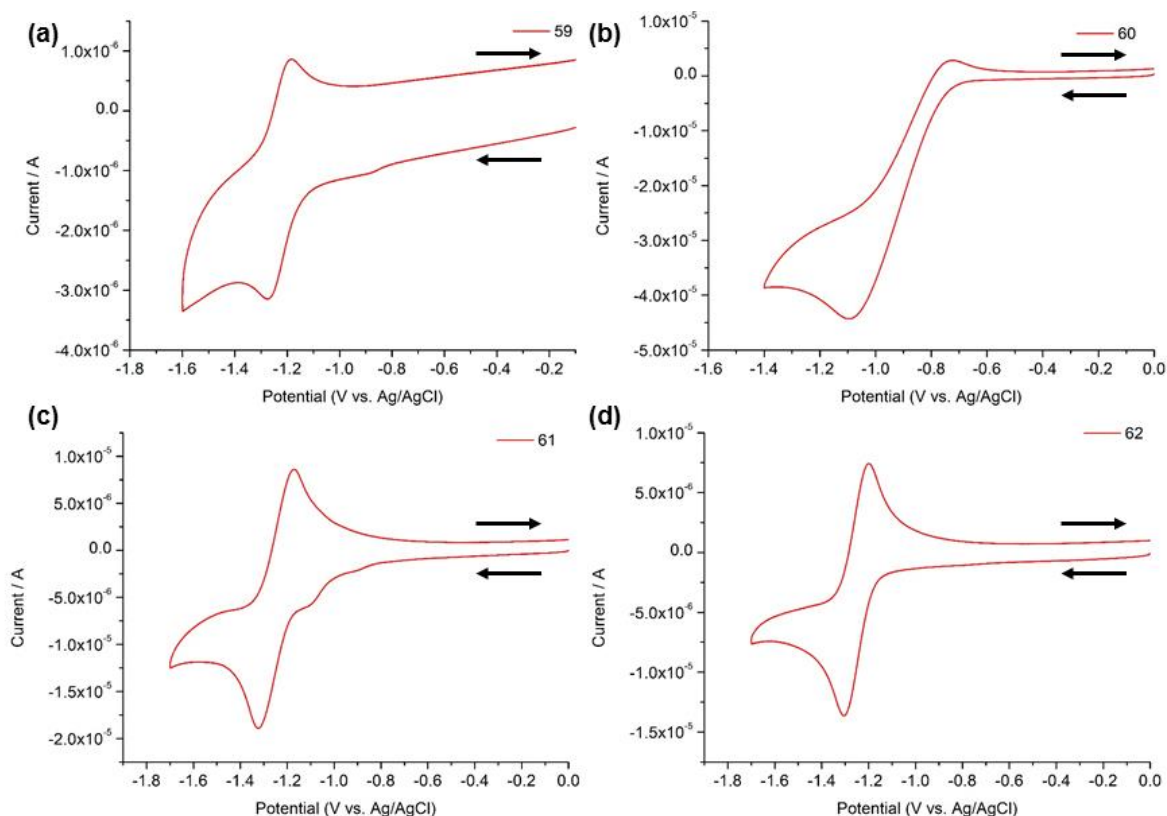


Figure 4.38: Cyclic voltammograms of (a) **59**, (b) **60**, (c) **61** and (d) **62**, showing the reduction processes (1×10^{-4} M, CH_2Cl_2 , vs. Ag/AgCl, with 0.1 M TBAPF₆ as supporting electrolyte) with a scan rate of 0.1 V s^{-1} . Arrows indicate direction of scan.

The reduction processes of **59-62** are given in Fig. 4.38. For **59**, a reversible reduction ($\Delta E_p = 80$) is observed. This reduction is assigned to a phenanthroline ligand-based reduction process. Similar reduction behaviour is observed for both **61** and **62**, which both exhibit a reduction peak in the same region. The difference between the reduction peaks associated return peaks in the reduction scans of **61** and **62** suggests a degree of quasi-reversibility or irreversibility. The artefact observed at -1.10 V in the reduction scan of **61** is assigned as arising from a residual impurity. The compound **60**, with a pyridazine ring, displays an irreversible reduction process, as the separation between the reduction and return waves is far beyond the ideal value. This reduction process is observed at a less negative potential than for the other compounds, which suggests that the LUMO is at a lower energy relative to complexes **59**, **61**, and **62**.

4.7.3 Redox Behaviour of Pt(II) Acetylide Complexes 63-66

The redox behaviour of the target Pt(II) acetylide complexes was also examined. Pomestchenko *et al.* have reported that the similar [Pt(dbbpy)(C≡C-pyrene)₂] complex (**LC 112**) exhibits a reductive process at -1.35 V (vs. Ag/AgCl) and a metal-based oxidative processes at 0.95 V and 1.11 V.¹¹ They also reported that the free ligand, 1-ethynylpyrene, undergoes a reductive process at -1.73 V, which indicated that the lowest electron-accepting orbital of the acetylide complex was located upon the diimine (dbbpy) ligand.¹¹

In the cases of Pt(II) acetylide complexes **63-66**, the oxidative processes are in general, quite similar (Fig. 4.39). The hard solubility of these complexes led to voltammograms that were less resolved than those obtained for their precursors. Compounds **63**, **65** and **66** display weakly observed irreversible oxidations at *ca.* 0.86 V (*E_p*), which are slightly lower than that of **LC 112** (0.95 V). This oxidation is assigned to the Pt(II)→Pt(III) process, since it is irreversible. The lower oxidation potential suggests a higher degree of electron density at the metal centre, making it easier to oxidise. All complexes display another weakly observed oxidation at *ca.* 1.25 V, which is assigned to a metal-based process, based upon the assignment made by Zhong *et al.*, also on **LC 112**.³¹ Further oxidative processes are not clearly observed for **63**, but for **64**, **65** and **66**, a further oxidation process is weakly observed at 1.69, 1.68, and 1.66 V respectively, which may correspond to a diimine-based reduction. The first oxidation process assigned as Pt(II)→Pt(III), observed for complexes **63**, **65** and **66**, is not clearly observed for **64**, which exhibits a slightly different oxidation profile, with less resolution. For **64**, irreversible oxidations are observed at 1.26 and 1.68 V, which are assigned as metal-based (Pt(II)→Pt(III)) and diimine ligand-based, respectively. Hissler *et al.* have reported that for a series of Pt(II) acetylide complexes, oxidations are not clearly observed up to 1.6 V vs. an NHE (normal hydrogen electrode) electrode, after which point, if observed, they are irreversible.¹

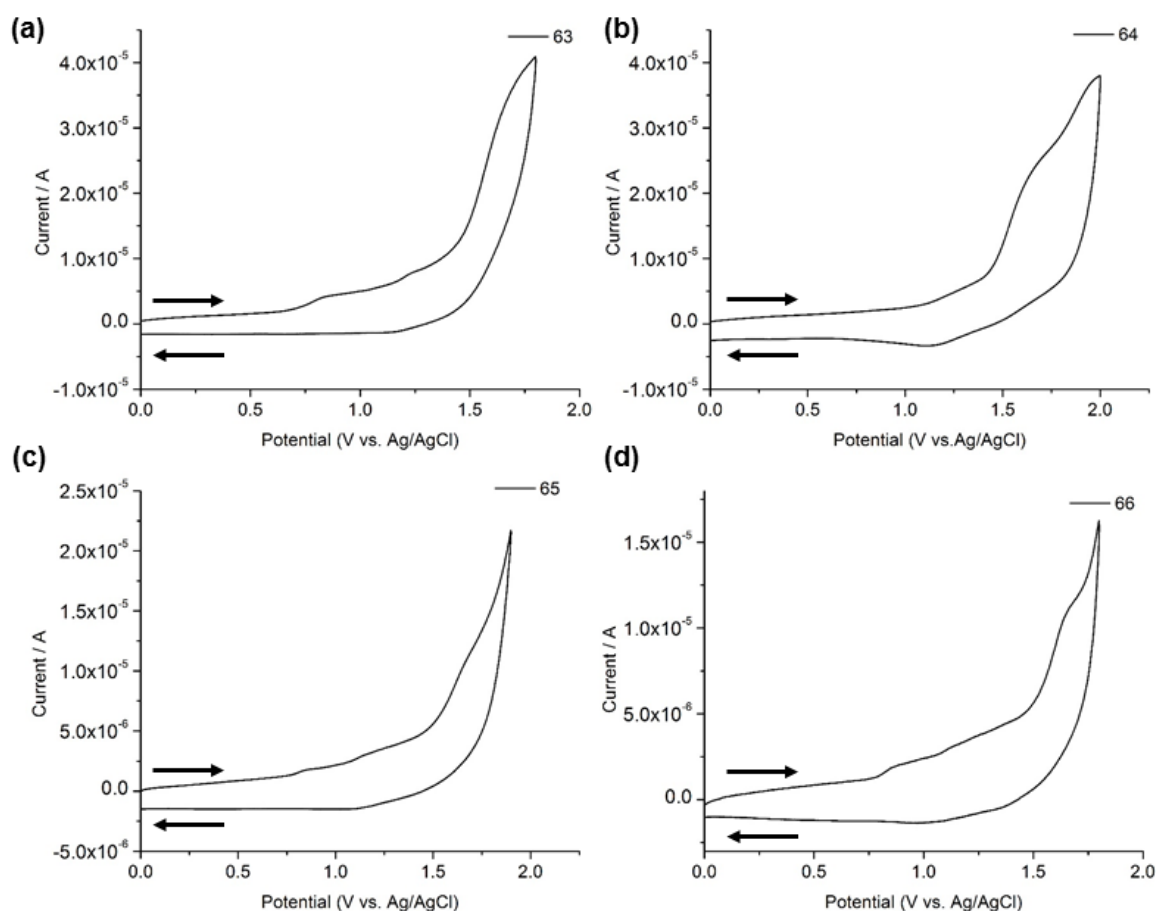


Figure 4.39: Cyclic voltammograms showing the oxidative processes of (a) **63**, (b) **64**, (c) **65**, and (d) **66** (1×10^{-4} M, CH_2Cl_2 , vs. Ag/AgCl, with 0.1 M TBAPF₆ as supporting electrolyte) with a scan rate of 0.1 V s^{-1} . Arrows indicate direction of scan.

The reductive cyclic voltammetry studies on the complexes are shown in Fig. 4.40. Again, all four complexes give similar behaviour. Complexes **63**, **65**, and **66** display reversible reductions with $E_{1/2}$ values of -1.27, -1.31, and -1.32 V respectively. This is assigned to a reduction of the diimine (N[^]N) ligands, and is less negative than that reported by Pomestchenko *et al.* for the reduction of the dbby diimine ligand in the complex **LC 112** (-1.35 V vs. Ag/AgCl).¹¹ The less negative potentials required to reduce **63**, **65**, and **66** indicate that the LUMO of these complexes is slightly lower in energy than that of [Pt(dbppy)(C $\equiv$ C-pyrene)₂], which has a less conjugated diimine ligand. In the case of **65**, no further reduction process is clearly observed. Hissler *et al.* demonstrated that modification of the diimine ligand had a pronounced effect on the reduction potential of Pt(II) acetylides, and also showed that modification of the arylacetylide units appears to have little effect on

the reduction potentials (and also therefore the LUMO energy).¹ For **63** and **66**, another irreversible reduction is observed at -1.63 V, which may correspond to a second reduction of the diimine ligand or the ethynylpyrene moieties. For **63**, another irreversible reduction is observed at -1.73 V, which is assigned to the ethynylpyrene ligands.¹¹ This reduction is also weakly observed for **64**, which displays a slightly different reductive behaviour. Compound **64** exhibits a reversible reduction at $E_{1/2} = -1.02$ V, which is at a significantly less negative potential than required for the other complexes, suggesting that the lowest orbital capable of accepting an electron in this complex is lying at a lower energy than that of the other three, due to the effect of inclusion of the pyridazine ring. Two further reductive processes are observed for **64**, the aforementioned irreversible reduction at -1.76 V, corresponding to the pyrene moiety, and also at -1.61 V, most likely a further reduction of the diimine ligand.

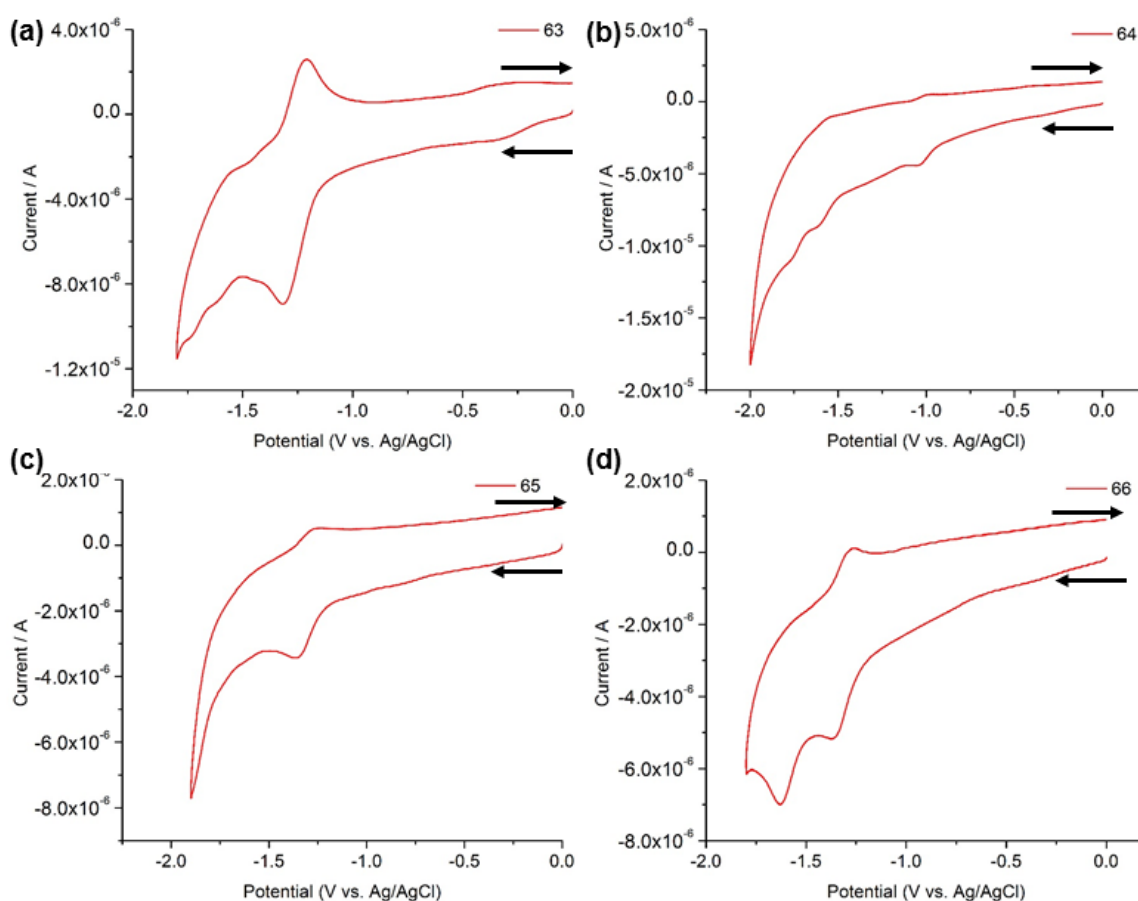


Figure 4.40: Cyclic voltammograms showing the reductive processes of (a) **63**, (b) **64**, (c) **65**, and (d) **66** (1×10^{-4} M, CH_2Cl_2 , vs. Ag/AgCl, with 0.1 M TBAPF₆ as supporting electrolyte) with a scan rate of 0.1 V s^{-1} . Arrows indicate direction of scan.

Table 4.10: Electrochemical data. * denotes irreversible process (with E_p value), and as all oxidations were irreversible, only the E_p value is quoted for these.

Compound	Oxidation E_{pa}/V	Reduction $E_{1/2}V, [\Delta E_p/mV]$
54	--	-1.29 [40]
56	--	-1.57 [70]
57	--	-0.98*
58	--	-1.01*
59	1.62	-1.23 [80]
60	0.66, 1.16	-1.09*
61	1.74	-1.32*
62	1.63	-1.31*
63	0.86, 1.24	-1.27 [90], -1.61*, -1.73*
64	1.26, 1.68	-1.02 [30], -1.61*, -1.76*
65	0.86, 1.22, 1.68	-1.31 [80], -1.73*
66	0.87, 1.26, 1.66	-1.32 [90], -1.63*

4.8 Initial Evaluation of **64** as a Triplet Photosensitiser

Since Pt(II) acetylides with appended arylacetylide ligands have been shown to be effective triplet photosensitisers, particularly for applications in TTA-upconversion,²⁷ it was undertaken to evaluate the properties of **63**, which displayed a combination of good solubility and long phosphorescence lifetime. A number of studies were carried out on **63**, in collaboration with Dr. Junsu Wang, at the Dalian University of Technology. Transient absorption (TA) measurements on **63** (Fig. 4.41 (a)) confirmed the emission is originating from the pyrene moieties, which is further indication that excitation into the MLCT bands ($\lambda \approx 480$ nm) produces sensitised ^3IL phosphorescence from the pyrene moieties. Significant ground-state bleaching was observed between $\lambda = 327$ to 409 nm, which is in agreement with the absorption bands assigned to the ethynylpyrene ligands in the UV-Vis absorption spectrum. The absorption between $\lambda = 409$ -710 nm is assigned to triplet-triplet absorptions of the ethynylpyrene moieties, and the negative absorption above $\lambda = 710$ nm is attributed to the phosphorescence emission. Very similar TA results were reported for the complex **LC**

112 by Pomestchenko *et al.*¹¹ The lifetime of the triplet excited state of **63** at RT was measured as being 56.4 μs (the decay trace is presented in Fig. 4.41 (b)). For reference, Zhong *et al.* have reported the triplet lifetime of **LC 112** as being 32 μs .³¹ This relatively long triplet excited state is suggestive that **63** could provide an efficient TTET process *e.g.* for TTA-upconversion.

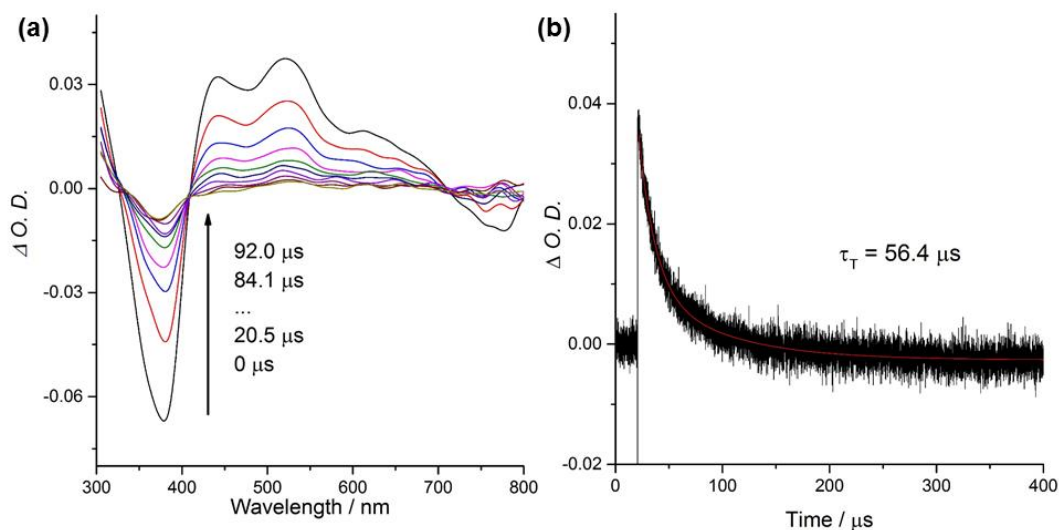


Figure 4.41: (a) Nanosecond time-scaled transient difference absorption spectra of **64** ($\lambda_{exc} = 450\text{ nm}$) (b) The decay trace at $\lambda = 465\text{ nm}$. ($1 \times 10^{-5}\text{ M}$, deaerated CH_3CN , RT).

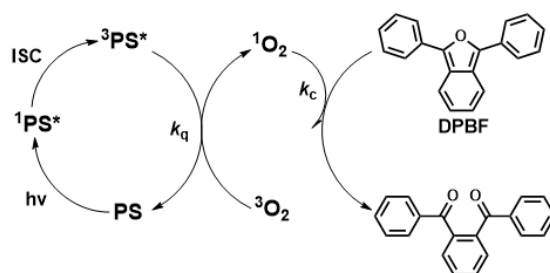
In order to probe the ability of **63** to transfer its triplet excited state, *i.e.* to act as a triplet photosensitiser, the singlet oxygen quantum yield was measured. This measurement gives an indication of the efficiency of the photosensitiser in transferring its triplet state, in this case to ground state $^3\text{O}_2$, and thereby forming $^1\text{O}_2$. The formation of $^1\text{O}_2$ is measured by its reaction with a $^1\text{O}_2$ scavenger, a commonly used example being 1,3-diphenylisobenzofuran (DPBF). Upon excitation of the sensitiser (in this case **63**), it is initially excited to the singlet state, and then through ISC, the excited triplet state is populated. The sensitiser can then transfer its energy from the triplet excited state to ground state $^3\text{O}_2$. This results in the formation of oxygen in its excited state, $^1\text{O}_2$. The highly reactive $^1\text{O}_2$ then reacts with the scavenger and causes it to be oxidised. This oxidation results in a change in the UV-Vis absorption spectrum, which can be easily monitored. The efficiency of the process is calculated by comparison with that of a known reference, which in this case was $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, which gives a $^1\text{O}_2$ quantum yield of $\Phi_{\Delta} = 0.57$ in CH_3CN . The quantum yield is calculated by Equation 4.3, where the subscripts ‘sam’ and ‘ref’ refer to

the sample under investigation and the reference compound respectively. The ‘k’ value is the slope of the plot of absorbance of the scavenger molecule against irradiation time, F refers to the rates of light absorption at the irradiation wavelength, and is calculated from $F = 1 - 10^{-OD}$ (where OD represents optical density) and η represents the refractive indices of the solutions of the sample and reference.⁵⁴

$$\Phi_{\Delta sam} = \Phi_{\Delta ref} \times \frac{k_{sam}}{k_{ref}} \times \frac{F_{ref}}{F_{sam}} \times \left(\frac{\eta_{sam}}{\eta_{ref}} \right)^2$$

Equation 4.3: Calculation of the singlet oxygen quantum yield.

The $^1O_2$ quantum yield of **63** was measured using $[Ru(bpy)_3](PF_6)_2$ as a reference standard, and DPBF as the $^1O_2$ scavenger. As DPBF gives a characteristic absorbance at $\lambda = 410$ nm, its oxidation by $^1O_2$ can be monitored by measuring the decrease in absorbance of this peak. Upon oxidation by $^1O_2$, DPBF forms *o*-dibenzoylbenzene, which has no absorption in the visible range.⁵⁵ A mechanism for the overall process is given in Scheme 4.10. The cross-point of absorbance of **63** and the reference standard was measured ($\lambda = 434$ nm), which determined the wavelength of irradiation. A solution of the scavenger, DPBF, was adjusted to an absorbance of approximately 1.0 in CH_3CN , and was added to a cuvette. A solution of **63** was then added to the DPBF (the absorbance of the photosensitiser was adjusted to approximately 0.2). The absorbance of this solution was then measured after irradiation at $\lambda = 434$ nm at 10 second intervals, for a total of 140 seconds. A graph could then be constructed of the absorbance maxima of DPBF at $\lambda = 410$ nm versus the irradiation time. The slope of this plot, ‘k’ in Equation 4.3, which along with the slope obtained for the reference standard, could be used to calculate the $^1O_2$ quantum yield of **63**, which was determined to be $\Phi_{\Delta} = 0.59$, and suggests a relatively efficient triplet energy transfer process. The decrease in absorbance of the DPBF after irradiation in the presence of **63** is shown in Fig. 4.42. By means of comparison, Zhong *et al.* have determined the $^1O_2$ quantum yield of $[Pt(dbbpy)(C\equiv C\text{-pyrene})_2]$ (**LC 112**) as being $\Phi_{\Delta} = 0.75$, and that of **LC 115** (structures given in Fig. 4.4) being $\Phi_{\Delta} = 0.74$ and 0.76 respectively.³¹ The combination of the long triplet lifetime and good $^1O_2$ quantum yield presents **63** as being a promising candidate for the future investigation of its upconversion quantum yield, and therefore its viability as a photosensitiser for TTA-upconversion applications. Ji *et al.* and Zhong *et al.* have shown similar Pt(II) acetylide complexes have given promising results as photosensitisers for TTA-UC.^{27, 31}



Scheme 4.10: A generalised mechanism for the oxidation of DPBF through the formation of $^1\text{O}_2$ by a photosensitiser, where PS, k_q and k_c represent the photosensitiser, quenching constant of the excited triplet state of the photosensitiser and the rate constant of formation of the oxidised product respectively.

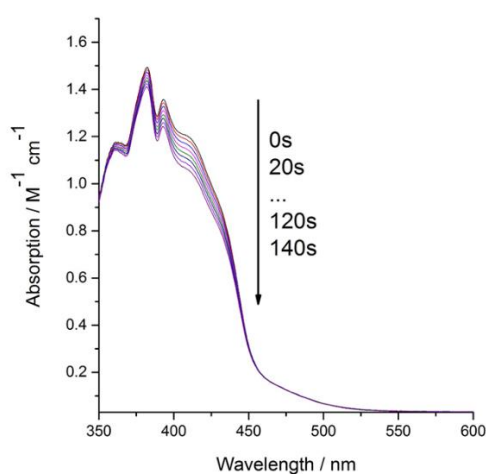


Figure 4.42: The decrease in absorbance of DPBF after irradiation at 434 nm at 10 second intervals up to 140 seconds, in the presence of **63** (CH_3CN , RT).

4.9 Conclusions and Future Work

This chapter has described the synthesis and characterisation of a family of Pt(II) acetylides, bearing diimine ligands which were designed around a highly-conjugated platform based upon 1,10-phenanthroline. The aim of this chapter was to investigate whether modification of the LUMO of the often quite emissive Pt(II) acetylides, through variation of the degree of conjugation of the diimine ligand, would have an appreciable and desirable impact on their photophysical properties. Building upon work reported by Pomestchenko *et al.* on the complex **LC 112** $[\text{Pt}(\text{dbbpy})(\text{C}\equiv\text{C-pyrene})_2]$,¹¹ this chapter describes how the variation of the conjugation of the diimine ligand in complexes of general formula $[\text{Pt}(\text{diimine})(\text{C}\equiv\text{C-pyrene})_2]$ in general provided complexes with very similar photophysical

properties. Excitation into the lowest energy absorption of these complexes, assigned as MLCT ($d\pi \text{ Pt} \rightarrow \pi^*$ diimine), led to sensitised ^3IL emission from the appended pyrene moieties on the opposite side of the molecule (Fig. 4.43). The phosphorescent character of the emission was indicated by its strong quenching in air, and its large Stokes shift.

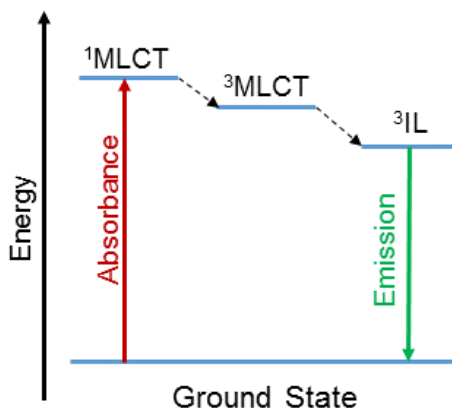


Figure 4.43: Schematic MO diagram showing the proposed nature of the emissive states of Pt(II) acetylides **63-66**.

The emission profiles of the Pt(II) acetylides synthesised herein are remarkably similar to that of the parent $[\text{Pt}(\text{dbbpy})(\text{C}\equiv\text{C-pyrene})_2]$ complex (**LC 112**) and are not appreciably red-shifted, indicating that variation of the diimine ligand has only a very minor impact on the photophysical properties. Incorporation of a pyridazine ring into the diimine ligand, as for **64**, led to a red-shifted and extended MLCT absorption band, although the emission profile remained identical to those of the other complexes. The pyridazine ring, however, led to less favourable properties, such as quite poor solubility and a much decreased emissivity. The luminescence lifetimes of the Pt(II) acetylides described in this chapter are again quite similar to that of $[\text{Pt}(\text{dbbpy})(\text{C}\equiv\text{C-pyrene})_2]$ (**LC 112**) which has been reported as $48.5 \mu\text{s}$,¹¹ *e.g.* $47 \mu\text{s}$ for **63**, and $63 \mu\text{s}$ for **66**. Cyclic voltammetric studies indicated that the LUMO of these complexes was indeed lowered slightly to that of the dbbpy complex. The studies carried out within this chapter indicate that lowering of the energy of the LUMO appears to have little impact on the emissive properties, which appear dominated by ^3IL emission. Considering the Pt(II) acetylides reported by Hissler *et al.*, who investigated the effect of varying the diimine ligand, and holding the arylacetylide ligands constant as simple phenylacetylides,¹ it is likely that the differing levels of conjugation of the ligands investigated here would have more of an impact on the photophysical properties of the complexes if the emitting state was $^3\text{MLCT}$, rather than ^3IL . However the short luminescence

lifetimes of complexes emitting from $^3\text{MLCT}$ states are of less interest for applications such as upconversion *etc.*

The relatively long lifetime of these complexes lends themselves towards applications as triplet photosensitisers. Preliminary studies on the suitability of **63** as a photosensitiser for the TTA process indicated a long-lived triplet state (56.4 μs) and good $^1\text{O}_2$ quantum yield ($\Phi_{\Delta} = 0.57$). Although **63** has desirable properties as a photosensitiser, Pt(II) acetylide complexes with improved properties as sensitisers have been recently reported.³¹ The compounds reported in this chapter may, in themselves, not exhibit photophysical properties warranting their deployment in TTA-upconversion devices *e.g.* solar cells. However, these compounds do confirm the enormous potential of the Pt(II) acetylide complex as a starting point for highly emissive complexes yielding room-temperature luminescence. The importance of the introduction of solubilising groups to such complexes has been highlighted by this work. The work reported here indicates that efficient modification of the photophysical properties may not be through modification of the diimine ligand through conjugation. In future, more efficient modification may be found through careful selection of the appended arylacetylide ligands.

Given the excellent results recently reported by Zhong *et al.* on Pt(II) acetylides with mixed ethynylpyrene and ethynyl naphthalimide ligands while keeping the diimine ligand as dbbpy (Fig. 4.4),³¹ it would be of interest to probe whether the replacement of the dbbpy ligand with one of the more conjugated ligands described here would produce an appreciable difference. Since ligands **56** and **57** yielded Pt(II) acetylides with high insolubility, the more soluble ligands **54** and **58** are better candidates for any future studies (Fig. 4.44 (a)). Considering the relative ease with which the arylacetylide ligands of Pt(II) acetylides may be introduced, it would also be of interest to synthesise the equivalents of the complexes here with phenylacetylide ligands, and probe the effects of the more conjugated ligands on an emissive state more likely to be $^3\text{MLCT}$ in origin (Fig. 4.44 (b)). The introduction of an arylacetylide ligand with greater conjugation than that of pyrene, such as HBC, should also be synthetically accessible and would represent a further step in the understanding of the nature of the emissive state of such complexes (Fig. 4.44 (c)).

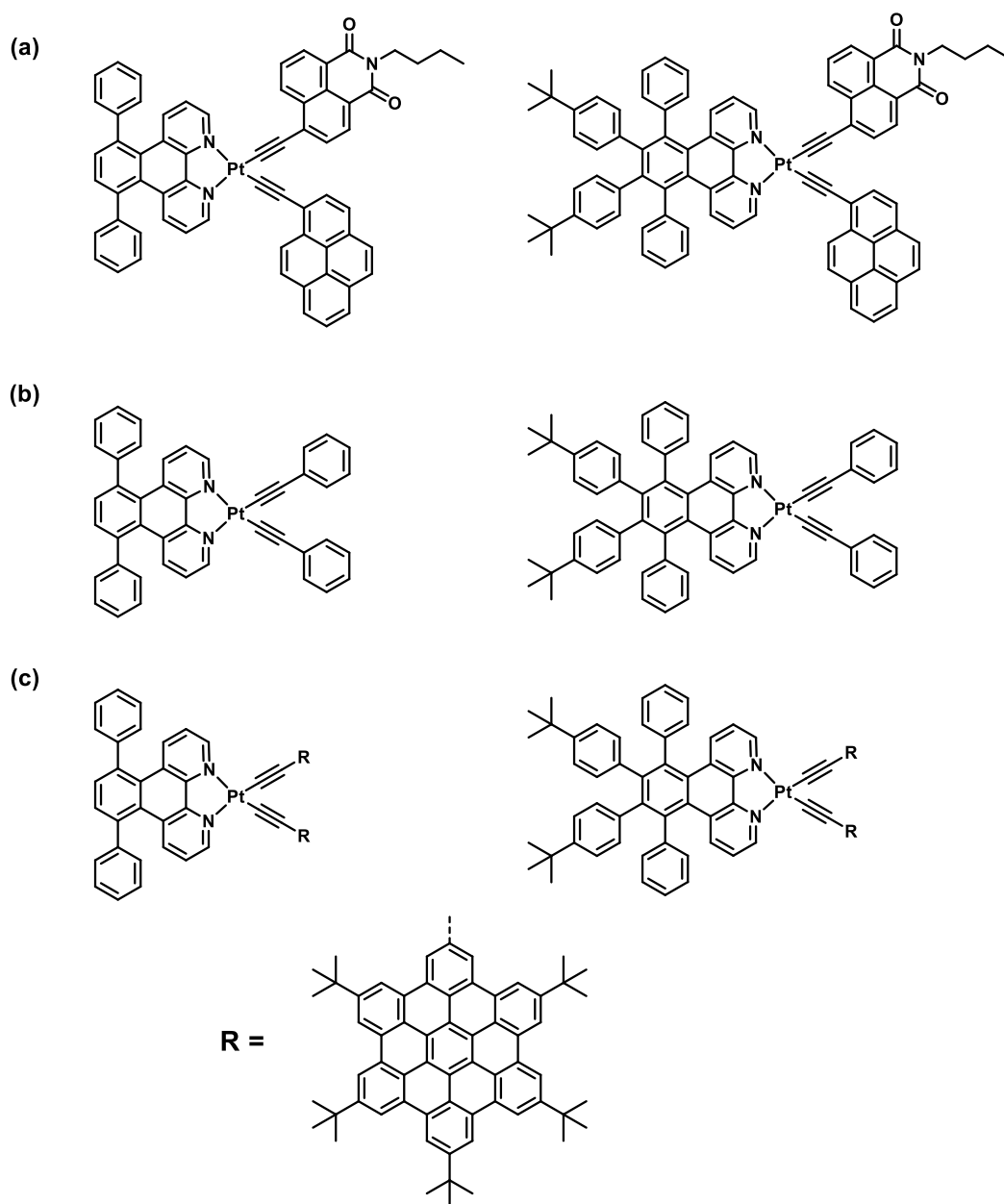


Figure 4.44: Proposed future compounds. (a) Pt(II) acetylides based upon ligands **54** and **58**. (b) Pt(II) acetylides with phenylacetylide ligands. (c) Pt(II) acetylides with a large HBC chromophore.

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Chapter Five

Iridium(III) Complexes of a Partially-Fused N-Containing Polyaromatic Ligand

5.1 Introduction

Iridium complexes have garnered a significant deal of research attention in the past two decades, most notably for their often impressive emissive behaviour. They generally exhibit high chemical and thermal stability, long-lived excited states, high quantum yields, and tuneable photophysical and electrochemical properties.^{1, 2} As a consequence of these desirable properties, they have attracted particular attention for their application in OLEDs.³ This chapter will, after a brief description of the general properties of iridium complexes, describe synthetic attempts towards novel Ir(III) complexes which feature an unusual, partially-fused PAH-type ligand, and will also describe their photophysical properties. It is aimed to explore how the extended conjugation of a large polyaromatic ligand affects the photophysical properties, and furthermore, whether the incorporation of strongly-absorbing cyclometallating ligands leads to desirable properties that might indicate potential for emissive applications or as a triplet photosensitiser.

5.1.1 An Introduction to Iridium(III) Complexes

Phosphorescent Ir(III) complexes are currently generating widespread research interest due to their attractive properties mentioned above, such as high quantum yields, colour tunability and good thermal stability.^{4, 5} Early research work on luminescent transition-metal complexes focused on those of ruthenium, such as the archetypal $[\text{Ru}(\text{bpy})_3]^{2+}$. However, these complexes have fallen out of favour due to their limited colour-tuning abilities, as a result of their low-lying and therefore deactivating metal-centred states.⁶ The attractive properties of iridium complexes originate from the strong spin-orbit coupling that they exhibit, as a result of the presence of the 5d metal centre. This strong spin-orbit coupling facilitates efficient intersystem crossing (ISC) from singlet to triplet states, and the mixing of these states allows for a relaxation of the forbidden nature of the radiative decay of the triplet state.⁵ Unlike Ru(II) complexes, Ir(III) complexes have an increased ligand-field stabilisation energy (LFSE), which makes the metal-centred (d-d) states less accessible. Cyclometallating ligands are predominantly used with Ir(III) centres, and as these are considered to be strong-field ligands, the LFSE is further improved.⁷ As result of this large ligand-field splitting, cyclometalated Ir(III) complexes can yield deep-blue emission, whereas Ru(II) diimine complexes are limited to emission at longer wavelengths (in the red-orange region).⁸

5.1.2 Synthesis of Cyclometalated Iridium(III) Complexes

The preparation of cyclometalated Ir(III) complexes usually begins with the preparation of the μ -dichloro-bridged Ir(III) dimer $[\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{-}\mu\text{-Cl}]_2$ from the reaction between the required $\text{C}^{\wedge}\text{N}$ ligand and $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$. The mononuclear Ir(III) complex may then be prepared by treatment of the dimer with either a cyclometallating ($\text{C}^{\wedge}\text{N}$) or diimine ($\text{N}^{\wedge}\text{N}$) ligand.⁹ King *et al.* reported the first triply cyclometalated Ir(III) complex in 1985, *fac*-Ir(ppy)₃ (**LC 116-f**, Fig. 5.1 (a)), which was formed as a minor by-product (10 % yield) during the preparation of $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ from ppy and $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ ('ppy' refers to 2-phenylpyridine).¹⁰ Improved syntheses of this complex have since been reported by Dedeian *et al.*, who employed $\text{Ir}(\text{acac})_3$ as starting material (where acac represents acetoacetate), rather than IrCl_3 ,¹¹ and also by Colombo *et al.*, who noted that good yields could be obtained by reaction of the μ -dichloro-bridged Ir(III) dimer $[\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{-}\mu\text{-Cl}]_2$ with the free cyclometallating ligand ($\text{HC}^{\wedge}\text{N}$).¹² The meridional (abbreviated as *mer*) isomers of $\text{Ir}(\text{C}^{\wedge}\text{N})_3$ complexes such as *mer*-Ir(ppy)₃ (**LC 116-m**, Fig. 5.1 (b)) may be obtained at lower reaction temperatures, indicating that they are the kinetically favoured product, whilst the *fac* isomers are suggested to be thermodynamically favoured as they are formed at higher temperatures.⁵ This has been suggested as being a result of the strong *trans*-effect of the aryl groups, which are opposite to each other in the *mer* isomers, but in the *fac* isomers are opposite neutral donating groups (*e.g.* pyridyl).¹³

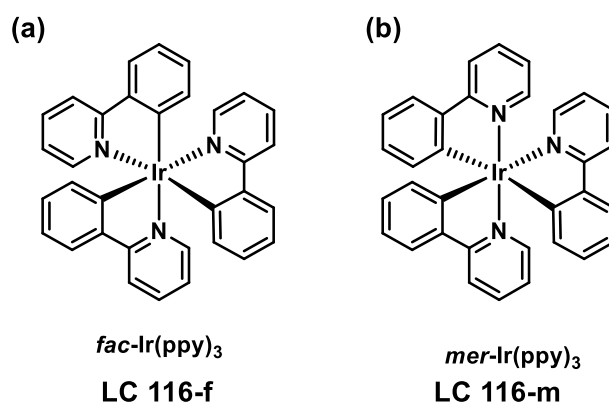


Figure 5.1: Structures of tris-cyclometalated Ir(III) complexes, (a) *fac*-Ir(ppy)₃ (**LC 116-f**) and (b) *mer*-Ir(ppy)₃ (**LC 116-m**).

Bis-cyclometalated Ir(III) complexes are generally derived from the appropriate dichloro-bridged dimer complexes. The diiridium dimer may then be cleaved with an ancillary ligand, such as 2,2'-bipyridine (bpy) to give a mononuclear Ir(III) complex. The

net charge on the complex is therefore determined by the nature of the ancillary ligand.⁶ The modification and variation of the respective cyclometallating and ancillary ligands therefore provide a means of control over the photophysical properties which are required. Commonly employed ligands for these complexes are 2,2'-bipyridine (bpy), acetoacetate (acac), and picolinate (pic) and their derivatives. The corresponding complexes derived from these, **LC 117-119** respectively, are displayed in Fig. 5.2. To prepare the acetoacetate and picolinate-derived complexes, the general method involves rather harsh conditions; a mixture of the required diiridium dimer, the required ligand, a base such as Na₂CO₃ and a high boiling-point alcohol, although milder conditions have been developed.¹³ The bis-cyclometalated complexes usually exhibit *trans*-N,N' geometry, which is due to the precursor chloro-bridged complexes also featuring this geometry and therefore imposing it on the subsequently formed mononuclear complex.⁸ Preparation of Ir(III) bis-cyclometalated complexes with diimine (N^N) ligands such as bpy are usually *via* milder approaches, through reaction of the chloro-bridged diiridium dimer with the required diimine, with no base required. Neve *et al.* reported a successful general, and quite mild, procedure for the preparation of such complexes in 1999, which involves the reflux of the dichloro-bridge diiridium dimer with the required ligand, in a mixture of dichloromethane and methanol.¹⁴ These Ir(C^N)₂(N^N) complexes are cationic, whereas those with cyclometalated ligands are neutral. The cationic Ir(III) complexes are attractive for their photophysical properties and also for their good solubility in polar solvents and aqueous media.¹⁵

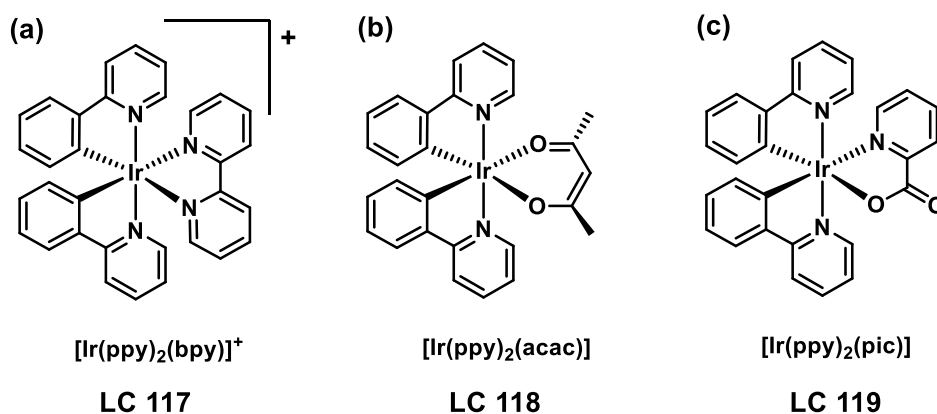


Figure 5.2: Structures of common bis-cyclometalated Ir(III) complexes, (a) $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, (b) $[\text{Ir}(\text{ppy})_2(\text{acac})]$, and (c) $[\text{Ir}(\text{ppy})_2(\text{pic})]$.⁸

5.1.3 Photophysics of Iridium Complexes

Cyclometalated Ir(III) complexes exhibit lowest excited states that are thought to consist of a mixture of MLCT (metal-to-ligand charge transfer) states, where an electron is promoted from a d orbital of the metal to an empty π^* orbital located on a ligand, and LC (ligand-centred) states, where an electron is promoted from a ligand π orbital to a ligand π^* orbital.⁶ The Ir metal centre imparts strong spin-orbit coupling, and this permits excited singlet states to undergo highly efficient intersystem crossing to the triplet state, resulting in high phosphorescence quantum yields.³ The very strong spin-orbit coupling of Ir causes some interaction between the lowest excited triplet state and excited singlet states, providing the lowest triplet excited state (T_1) with some singlet character. The mixing of states allows excited singlet excited states to enter the triplet manifold rapidly *via* intersystem crossing, and absorption of a photon that populates a singlet excited state can therefore result in emission from the lowest triplet excited state.⁸ The mixing of MLCT and LC states is depicted schematically in Fig. 5.3.

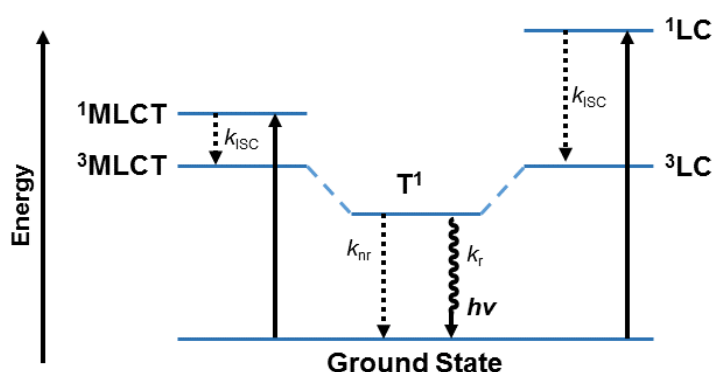


Figure 5.3: A schematic depiction of how the energetic proximity of the $^3\text{MLCT}$ and ^3LC states of cyclometalated Ir(III) complexes often leads to a lowest excited state (T_1) with mixed $^3\text{MLCT}$ - ^3LC character. The radiative pathways to the ground state are denoted by k_r and the non-radiative pathways by k_{nr} . The rate of ISC is denoted by k_{ISC} . Figure adapted from Lowry et al.⁶

The $^3\text{MLCT}$ or ^3LC states are lowest in energy in cyclometalated Ir(III) compounds due to the large ligand-field splitting values (Δ_o) between the filled t_2 and empty e orbitals. The strong ligand field imposed by the σ -donating cyclometallating ligands pushes the e orbitals above the ligand π^* orbital, therefore reducing the possibility of non-radiative decay from a ^3MC (metal-centred) state.⁸

The absorption, emission, and excitation spectra of *fac*-Ir(ppy)₃ (hereafter referred to as Ir(ppy)₃, **LC 116**), as recorded by Hofbeck *et al.*, are displayed in Fig. 5.4.¹⁶ The lowest energy absorption of this complex is generally assigned as being ¹MLCT in nature, and the emitting state is assigned as being predominantly ³MLCT in nature.¹⁷ However, the situation is slightly more complex than this, and a more accurate description refers to the lowest singlet absorptions as being mixed ¹MLCT/¹LC, due to the proximal energy levels of these states, and the molecular HOMO is usually made up of contributions from metal dπ and C^N ligand π* orbitals. Low-energy absorptions, between 425 and 500 nm, are observed in the absorption spectrum of Ir(ppy)₃, which are usually assigned as being ³MLCT, although the accurate differentiation of ¹MLCT and ³MLCT absorptions is challenging.¹⁶ The strong spin-orbit coupling facilitates this phenomenon, which is thought to give a lowest excited state with ³MLCT and ³LC character, and also some ¹MLCT contribution.⁸ At 77 K, an excitation spectrum of Ir(ppy)₃ provided a clearly defined lowest energy triplet absorption band (³MLCT), a process which usually exhibits low extinction coefficients due to its forbidden nature.

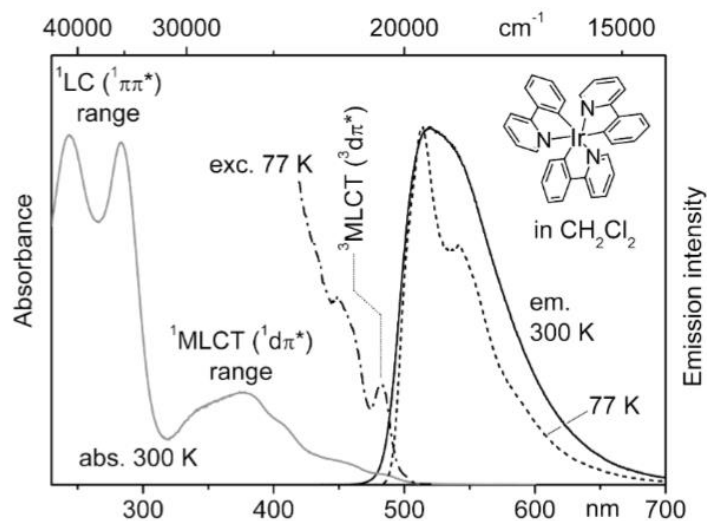


Figure 5.4: The UV-Vis absorption, emission and excitation spectra of Ir(ppy)₃ ($\sim 2 \times 10^{-5}$ M, CH₂Cl₂, 300 K/77 K). Image obtained from Hofbeck *et al.*¹⁶

The photophysical properties of neutral bis-cyclometalated Ir(III) complexes are often dominated by LC states of the cyclometallating ligand and MLCT states, as the lowest triplet energy levels of the ancillary ligands, such as acetoacetate, are usually higher in energy.^{5, 18} Liu *et al.* have shown that if the ancillary ligands are designed to have triplet excited states lower than the ³MLCT or (C^N) ³LC states, then the emissive state is dominated by the ancillary ligand.¹⁹ For cationic Ir(III) complexes, those of general formula

$[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$, the photophysics are also characterised by emitting triplet states of mixed $^3\text{MLCT}$ and ^3LC character. If the triplet state of the diimine ligand is lower than that of the cyclometallating ligands, it then acts as the chromophoric moiety, although in the case of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, the dominant emissive state switches to ^3LC in the crystalline state.⁸ Colombo *et al.* have shown that the photophysical behaviour of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (**LC 120**) is rather complex.²⁰ At ambient temperature, in solution, the emission is from a $^3\text{MLCT}$ state ($d\pi \text{ Ir} \rightarrow \text{bpy}$). However, in a crystalline host, the emissive state appears to be ^3LC (centred on the $\text{C}^{\wedge}\text{N}$ ligands), where the close proximity of the slightly higher energy $^3\text{MLCT}$ leads to some mixing of CT and LC characteristics. Therefore for this complex, the $^3\text{MLCT}$ emissive state is stabilised in fluid solution compared to the ^3LC , while in the crystalline state it is the opposite. Recent reports have suggested that the emission from similar cationic complexes is from a mixture of $^3\text{MLCT}$ and $^3\text{LLCT}$ states.^{21,22} This is because computational studies have indicated that the HOMO of these complexes is primarily Ir $d\pi$ and $\text{C}^{\wedge}\text{N}$ ligand π orbital-based, whereas the LUMO is typically comprised of the diimine π^* orbital.²¹

5.1.4 Tuning the Optical Properties of Ir(III) Complexes

The energy of the lowest excited states of cyclometalated Ir(III) complexes may be controlled *via* the adjustment of metal and ligand orbitals, which in turn may be achieved either by substituent effects, or altering the parent ligand structure.⁶ $\text{Ir}(\text{ppy})_3$ is considered an efficient green emitter, but access to blue or red emission requires ligand modification.²³ Beeby *et al.* have shown that modifying just one of the ppy ligands of $\text{Ir}(\text{ppy})_3$ allowed access to an Ir(III) complex which yielded orange emission ($\lambda_{\text{max}} \approx 600 \text{ nm}$).²³ They added a formyl group to one of the ppy ligands, creating the complex *fac*-bis(2-phenylpyridyl)-2-(4'-formylphenyl)-pyridyliridium(III), or $\text{Ir}(\text{ppy})_2\text{fppy}$ (**LC 121**). The complex exhibited similar absorption behaviour to $\text{Ir}(\text{ppy})_3$, and its emission spectra exhibited solvatochromic behaviour, suggesting a $^3\text{MLCT}$ excited state. The lowest-energy excited state was proposed as being localised on the formyl-substituted ligand, as the carbonyl group lowered its energy relative to the other two ppy ligands. The simple modification of a single ligand therefore resulted in emission at a different wavelength ($\lambda_{\text{max}} \approx 600 \text{ nm}$).

Tsuboyama *et al.* have reported a series of homoleptic *fac*- $\text{Ir}(\text{C}^{\wedge}\text{N})_3$ complexes.²⁴ Based around $\text{Ir}(\text{thpy})_3$ (thpy = 2-(2-thienyl)pyridine), which affords yellow phosphorescence, they synthesised Ir(III) complexes with extra conjugation and varying

substituents such as methyl and trifluoromethyl. They found that the yellow emission of Ir(thpy)₃ (**LC 122**), from a ³π-π* excited state, was shifted to red (*i.e.* a bathochromic shift) with the introduction of these substituents. The enhanced donor-acceptor (DA) character of the ligands, upon introduction of the substituents such as trifluoromethyls, and the increased conjugation of the ligands, were concluded to have resulted in the red-shift of the emission spectra. It was noted that as the emission was pushed further to the red, the quantum yields of phosphorescence of the thiophene-based complexes decreased. The authors also reported a series of homoleptic complexes with isoquinoline-derived (piq) ligands. These complexes exhibited large bathochromic shifts compared to Ir(ppy)₃ and Ir(thpy)₃, and based upon their broad emission profiles and rigidochromic effects, they were proposed to exhibit ³MLCT emission. These complexes gave higher quantum yields than the thpy-derived complexes, and gave red emission beyond λ = 620 nm.

In order to modulate the emissive properties of cationic Ir(III) complexes, the two types of ligands, the C[^]N cyclometallating ligands and the N[^]N bipyridine-like ligands, may be varied independently in order to bring about the required behaviour.²⁵ De Angelis *et al.* have systematically varied both the C[^]N and N[^]N ligands in order to further understand the effects of ligand functionalisation. They compared three cationic Ir(III) complexes, with the first, [Ir(ppy)₂(dbbpy)](PF₆) (**LC 123**, dbbpy = 4,4'-di(*tert*-butyl)-2,2'-bipyridine) acting as a reference, and a second analogous compound (**LC 124** Fig. 5.5), [Ir(ppy)₂(4,4'-dimethylamino-2,2'-bipyridine)](PF₆), providing an insight into the effect of electron-releasing substituents on the N[^]N ligand. A third complex, [Ir(Fppy)₂(4,4'-dimethylamino-2,2'-bipyridine)](PF₆) (where Fppy = 2-(2,4-difluorophenyl)pyridine) was synthesised to investigate the combined effect of electron-withdrawing substituents on the N[^]C ligands and electron-releasing substituents on the N[^]N ligand (**LC 125**, Fig. 5.5). DFT and TD-DFT calculations showed that the LUMO remained centred on the N[^]N ligand across the series, and the HOMO-LUMO gap increased on going from **LC 123** to **LC 125**. This agreed with the blue-shift observed in the emission spectra of the complexes. The electron-releasing amino groups destabilised the diimine-based LUMO (as shown by electrochemical measurements), and therefore increased the HOMO-LUMO gap, yielding emission at higher energies. The electron-withdrawing substituents on the C[^]N ligands of **LC 125** resulted in the HOMO being stabilised, and thereby increasing the HOMO-LUMO gap in this complex, compared with **LC 124**.

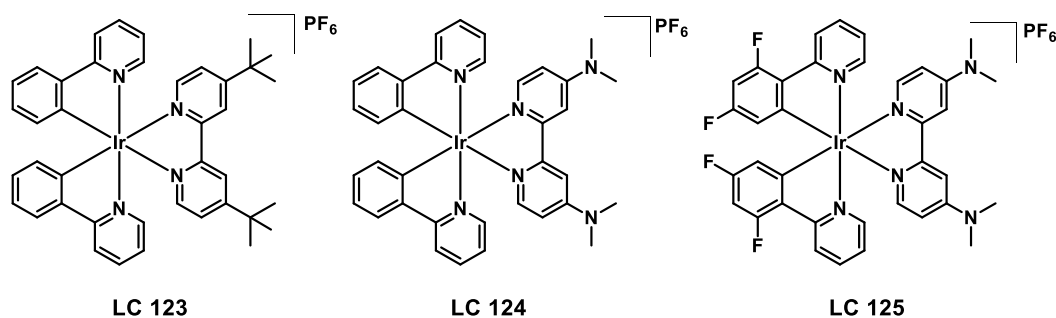


Figure 5.5: Cyclometalated Ir(III) complexes, as reported by De Angelis et al.²⁵

Tuning the emissive properties of bis-cyclometalated Ir(III) complexes may also be achieved through introducing differing degrees of conjugation of the C[^]N or ancillary (such as N[^]N) ligands.⁶ This was demonstrated by Zhao and co-workers.¹⁵ They reported a series of complexes where the C[^]N cyclometallating ligand was held constant as 1-phenylisoquinoline (piq), and the N[^]N ligand was systematically varied in terms of its conjugation. The authors chose bipyridine (bpy), phenanthroline (phen), 2-pyridylquinoline (pyqu), 2,2'-biquinoline (bqu), 1,1'-biisoquinoline (biqu), and 2-(2-quinolinyl)quinoxaline (quqo) as the N[^]N ligands (giving complexes **LC 126-131** respectively). Cyclic voltammetry and DFT indicated that the LUMO was localised on the N[^]N ligands, leading to the suggestion that the excited state of these complexes contained both MLCT [$(d\pi(\text{Ir}) \rightarrow \pi^*_{\text{N}^{\wedge}\text{N}})$] and LLCT [$\pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi^*_{\text{N}^{\wedge}\text{N}}$] transitions. The emission spectra of the complexes were red-shifted with increasing conjugation of the N[^]N ligands (from 586 to 732 nm). The complexes with bpy and phen ligands did not display a rigidochromic effect at 77 K, and also displayed only a small dependence on solvent polarity, suggesting that they emitted from a state which was mixed in character, with contribution not only from the aforementioned CT states, but also from ³LC ($\pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi^*_{\text{C}^{\wedge}\text{N}}$) states. This was attributed to the close proximity of the ³LC and ³MLCT states. The remaining complexes, with more conjugated ligands, exhibited emissive behaviour more associated with CT states (*e.g.* broadened emission profiles *etc.*), with little ³LC character in evidence. The increase in conjugation of the N[^]N ligand led to a decrease in the LUMO across the series of complexes, while the HOMO remained very similar. This led to different ³MLCT energies for each complex. Therefore those with the least-conjugated ligands (bpy and phen) had the highest ³MLCT energies, and this resulted in an increased ³LC character, whereas those with lower ³MLCT energies displayed only small contributions from the ³LC state.

The Draper group have reported a series of Ir(III) complexes designed as photosensitisers with a particular focus on their application for TTA-upconversion.²⁶ A series of bis-cyclometalated Ir(III) complexes with 3-(2-benzothiazolyl)-7-(diethylamino)coumarin (hereafter referred to as ‘coumarin 6’) as the C[^]N ligands and 1,10-phenanthroline-derived N[^]N ancillary ligands were reported (Fig. 5.6).

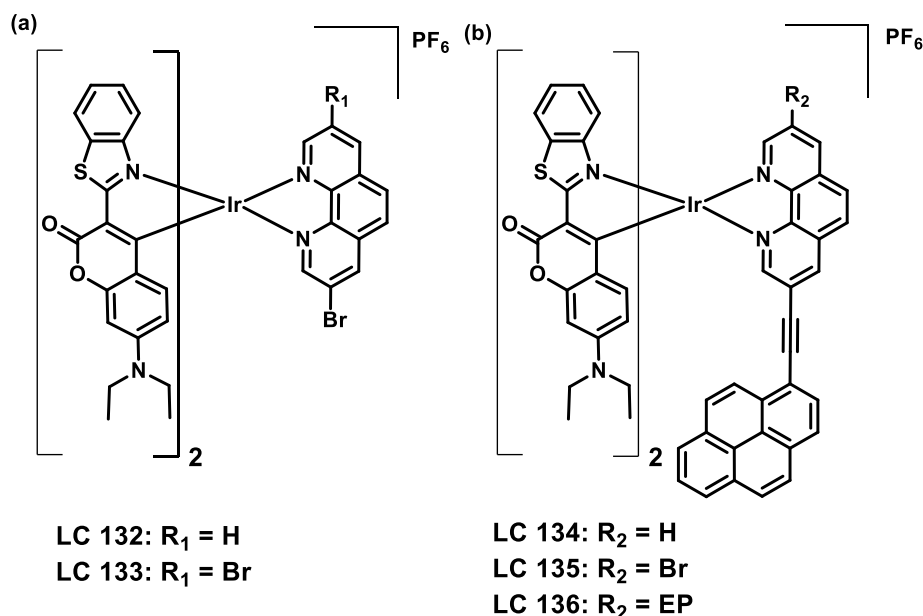


Figure 5.6: Ir(III) complexes reported by Lu et al., with coumarin 6 cyclometallating ligands and substituted N[^]N ligands derived from 1,10-phenanthroline with (a) depicting bromine-substituted variants and (b) displaying ethynylpyrene (EP) substituted variants.²⁶

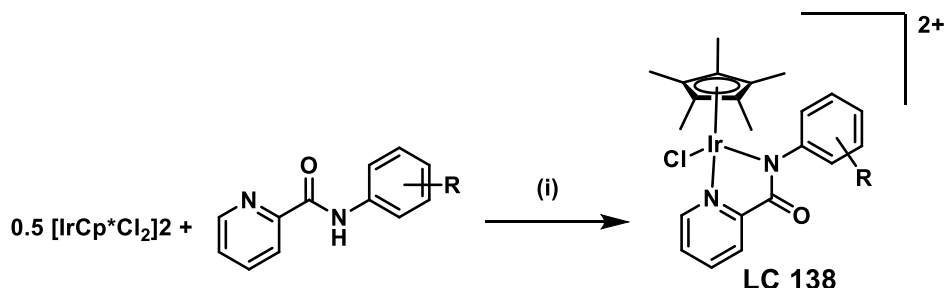
The coumarin 6 cyclometallating ligands were chosen due to their strong absorption in the visible region, and were chosen strategically in order to further improve the light-harvesting properties of a family of complexes which previously possessed simpler 2-phenylpyridine C[^]N ligands (*c.f.* Chapter Four, Fig. 4.6). The compounds displayed intense absorbance in the UV-Vis (up to $\epsilon = 1.34 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), attributed to the coumarin 6, and exhibited different emission spectra depending on the presence and position of ethynylpyrene (abbreviated as EP) ligands. For example, the Ir(III) complex **LC 133**, displayed a broad absorption with short lifetime, which was attributed to a ³LC state localised on the coumarin 6 ligands. In comparison, the addition of ethynylpyrene moieties to the phenanthroline ancillary ligand led to a red-shift in emission, and a much more structured emission profile. The emission maximum was observed to red-shift with increasing π conjugation. The mono-substituted pyrene complex **LC 134** exhibited an emission maximum at $\lambda = 685 \text{ nm}$, whilst the disubstituted pyrene complex **LC 136** displayed an

emission maximum at $\lambda = 690$ nm. The long phosphorescence lifetimes for these complexes (e.g. 77.5 μ s for the dipyrrene complex) and the structured emission profiles led to the excited states of these complexes being assigned as ^3IL in nature. This was further supported by computational studies, which showed that the excited state for the pyrene-substituted complexes was localised on the ethynylpyrene and phen portions of the complex. In contrast, the excited states of the unsubstituted complexes were mainly localised on the coumarin 6 ligands, with a small contribution from the Ir(III) centre and the phen ligand. The long triplet lifetimes of the ethynylpyrene-appended complexes were evident from their very high singlet oxygen quantum yields (all in the region of $\Phi_{\Delta} = 80$ %). The less conjugated complexes without ethynylpyrene ligands gave lower singlet oxygen quantum yields, due to their shorter triplet lifetimes. The pyrene-substituted complexes were investigated as triplet photosensitisers, and exhibited impressive quantum yields of upconversion. The complex with ethynylpyrene substituted on the 3-position of the phen moiety (**LC 134**) gave a high upconversion quantum yield of $\Phi_{\text{UC}} = 27.5$ %. In comparison, the complex $[\text{Ir}(\text{ppy})_2(3\text{-EP-phen})]^+$ (i.e. without the strongly absorbing coumarin 6 ligands), **LC 137**, gave an upconversion quantum yield of 30.2 %. However, the absorption of this complex is quite low at the excitation wavelength, leading to fewer molecules in the triplet excited state available for participation in the TTET process. Zhao *et al.* have proposed an improved method of determining the upconversion capability of a complex (η), where the molar absorption coefficient (ϵ) is taken into account, calculated as $\eta = \epsilon \times \Phi_{\text{UC}}$.²⁷ This new measure of upconversion capability leads to **LC 134** possessing a much higher upconversion capability ($3.60 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$) than the ppy-containing analogue **LC 137** ($8.90 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$). Interestingly, the complex with an extra appended ethynylpyrene moiety (**LC 136**) did not display any photophysical advantage over the singly-substituted derivative.

5.1.5 Other Modes of Coordination to Ir(III) Centres

Another class of Ir(III) complexes that have attracted research attention are known as half-sandwich complexes. These have found applications in catalysis, such as C-H activation, and quite recently have become intriguing candidates as anticancer therapeutic agents.²⁸⁻³⁰ Such complexes, usually containing pentamethylcyclopentadienyl (Cp^*) ligands, are readily accessed *via* the commercially available Ir(III) dichloride dimer $[\text{Cp}^*\text{IrCl}_2]_2$. Access to the mononuclear $[\text{Cp}^*\text{Ir}(\text{N}^{\wedge}\text{N})\text{Cl}]^+$ or $[\text{Cp}^*\text{Ir}(\text{C}^{\wedge}\text{N})]^+$ derivatives is achieved in a

similar manner as for the cyclometalated complexes discussed earlier. For example, Lucas *et al.* report the synthesis of an Ir(III) Cp* halide picolinamide complex (**LC 138**) via the reflux of the [Cp*IrCl₂]₂ dimer with the picolinamide dimer in EtOH, with NH₄PF₆ (Scheme 5.1).³¹ They also report access to derivatives with N^O and O^O coordination.



Scheme 5.1: Synthetic route towards a mononuclear Ir(III) Cp* complex, as reported by Lucas *et al.*³¹ (i) NH₄PF₆, EtOH, reflux.

Ir(III) half-sandwich complexes are receiving interest as anticancer agents, due to their relative stability and inertness – as therapeutic drugs they are likely to reach a biological target site without suffering any modification.²⁸ Ir(III) complexes with electron-rich Cp* ligands are highly stable and are therefore most suitable as drug candidates.²⁸ Extension of the π -coordinated Cp* ring leads to increased cellular activity, perhaps due to increased hydrophobicity which leads to increased cellular accumulation. Different chelating ligands, such as N^N and N^O, can lead to different selectivity for DNA base-pair sites.³² Blakemore *et al.* have reported the catalytic activity of a range of Ir(III) Cp* complexes with N^N and N^C ligands (such as bpy, ppy, and phen) for the homogenous oxidation of water to oxygen.³³ These Ir(III) catalysts gave rapid O₂ evolution for several hours, with turnover frequencies in the range of ten per minute. Such Ir(III) complexes have also been found to be good catalysts for the photochemical water-gas shift reaction (WGSR).^{34, 35}

5.1.6 Introducing a Highly-Conjugated N^N Ligand

The research into nanographenes undertaken by the Draper group has yielded a number of highly-conjugated N-containing compounds, such as N-HSB.³⁶ These highly conjugated aromatic cores possess peripheral nitrogen atoms, providing ligand functionality. Their interest as ligands for metal complexes stems from their exceptionally low-lying LUMO levels.³⁷ There is a scarcity of such large, conjugated polyimine systems in the literature,³⁸ which is notable in the context of the modulation of photophysical properties of

coordination complexes, such as the Ir(III) complexes discussed above. Their fused or partially-fused nature, lends a further method by which their optical behaviour may be influenced. The most common route towards extended polyimine systems has been traditionally *via* 1,10-phenanthroline-derived ligands, such as dipyrido[3,2-a:2',3'-c]phenazine (dppz) (**LC 139**, Fig. 5.7).³⁸ These ligands developed by the Draper group therefore present an alternative route. Several metal complexes of N-HSB and its derivatives have been reported, including Ru(II) complexes of N-HSB, and its half-cyclised analogue, $\frac{1}{2}$ -N-HSB (**LC 140** and **LC 141**, Fig 5.7 (b) and (c) respectively).^{37, 39} As an example of conjugation levels being exploited for different optical properties, the $[\text{Ru}(\text{bpy})_2(\text{N-HSB})]^{2+}$ (**LC 140**) complex, with its fully-fused aromatic core, exhibits extended absorption to $\lambda \approx 615$ nm, as a consequence of the very low-lying π^* acceptor orbitals. The emission from this complex, after excitation at $\lambda_{\text{exc}} = 615$ nm, was observed to occur in the near-infrared (NIR) range, with $\lambda_{\text{max}} = 880$ nm. The half-cyclised analogue, **LC 141**, exhibited a lowest energy UV-Vis absorption at $\lambda = 591$ nm and an emission maximum at $\lambda_{\text{max}} = 868$ nm, both slightly reduced from the fully-cyclised counterpart due to the decrease in conjugation. The excited state lifetime of the **LC 140** complex was 39 ns, compared with 23 ns for the **LC 141** complex, a result of the decreased conjugation and rigidity and therefore leading to further modes of non-radiative deactivation.

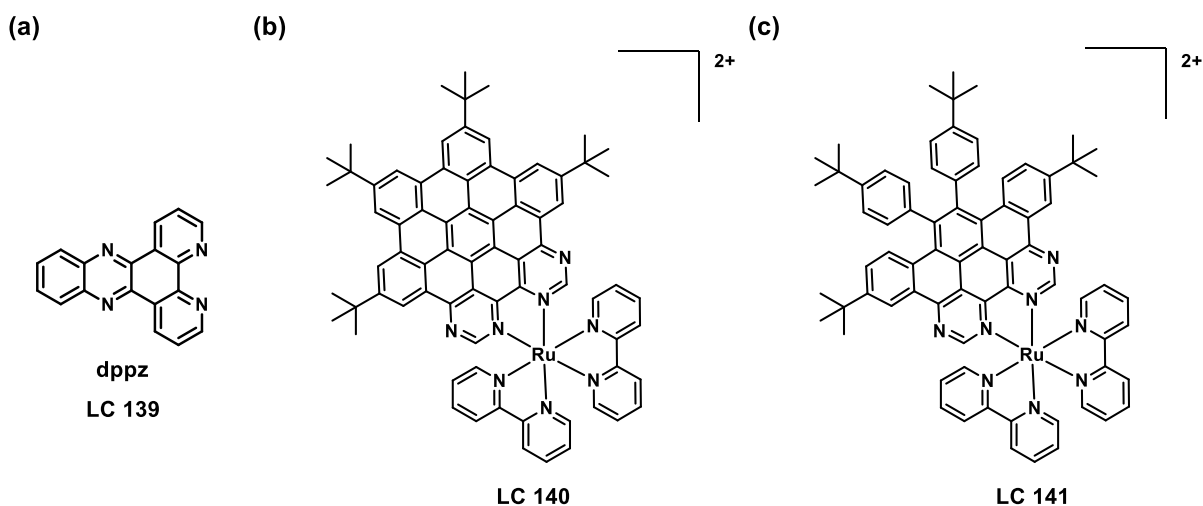
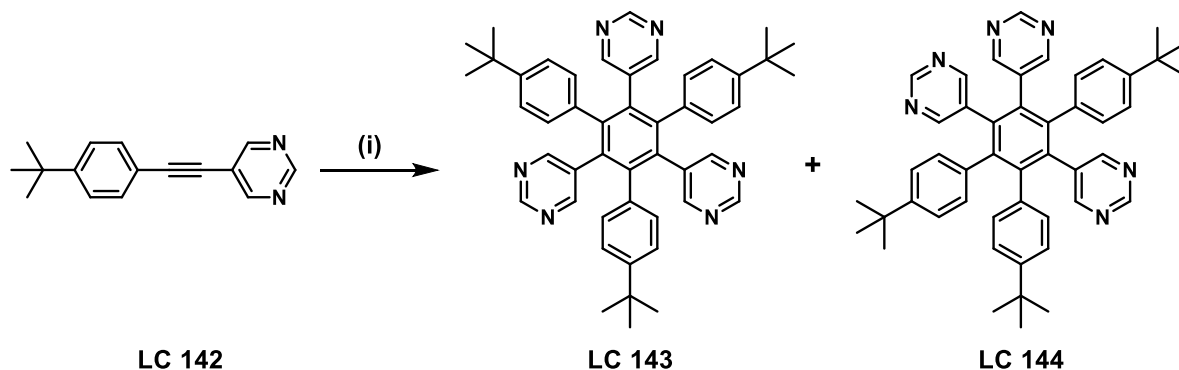


Figure 5.7: (a) Structure of dipyrido[3,2-a:2',3'-c]phenazine (dppz). (b) Structure of $[\text{Ru}(\text{bpy})_2(\text{N-HSB})]^{2+}$.³⁹ (c) Structure of $[\text{Ru}(\text{bpy})_2(\frac{1}{2}\text{-N-HSB})]^{2+}$.³⁷

Recently, it has been demonstrated that nanographenes with a very high degree of functionalisation (six nitrogen atoms or '6N') can be prepared through the cobalt-catalysed cyclotrimerisation of alkynes and their subsequent cyclodehydrogenation. Wijesinghe *et al.*

have reported a series of nanographenes obtained in a two-step process, where firstly a hexaphenylbenzene precursor is synthesised *via* the dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) catalysed cyclotrimerisation of an appropriately substituted alkyne.⁴⁰ The hexaphenylbenzene may then undergo oxidative cyclodehydrogenation, various methods of which can be employed, to generate a nanographene. The application of such N-containing compounds, obtained through cyclotrimerisation as ligands for coordination complexes does not yet appear to have been reported in the literature at the time of writing. This chapter will therefore discuss the synthesis of an N^N ligand, first reported by Dr. L. Wijesinghe,⁴¹ and its behaviour as a ligand in a family of Ir(III) complexes. The cyclotrimerisation of the alkyne 5-((4-(tert-butyl)phenyl)ethynyl)pyrimidine (**LC 142**) gives produces two products, due to the asymmetric nature of the alkyne precursor (Scheme 5.2). The asymmetric product (**LC 144**) is obtained in higher yield than the symmetric product (**LC 143**), as statistically the production of an asymmetric combination of the alkynes to produce an asymmetric product is three times more likely than the generation of a symmetric product.

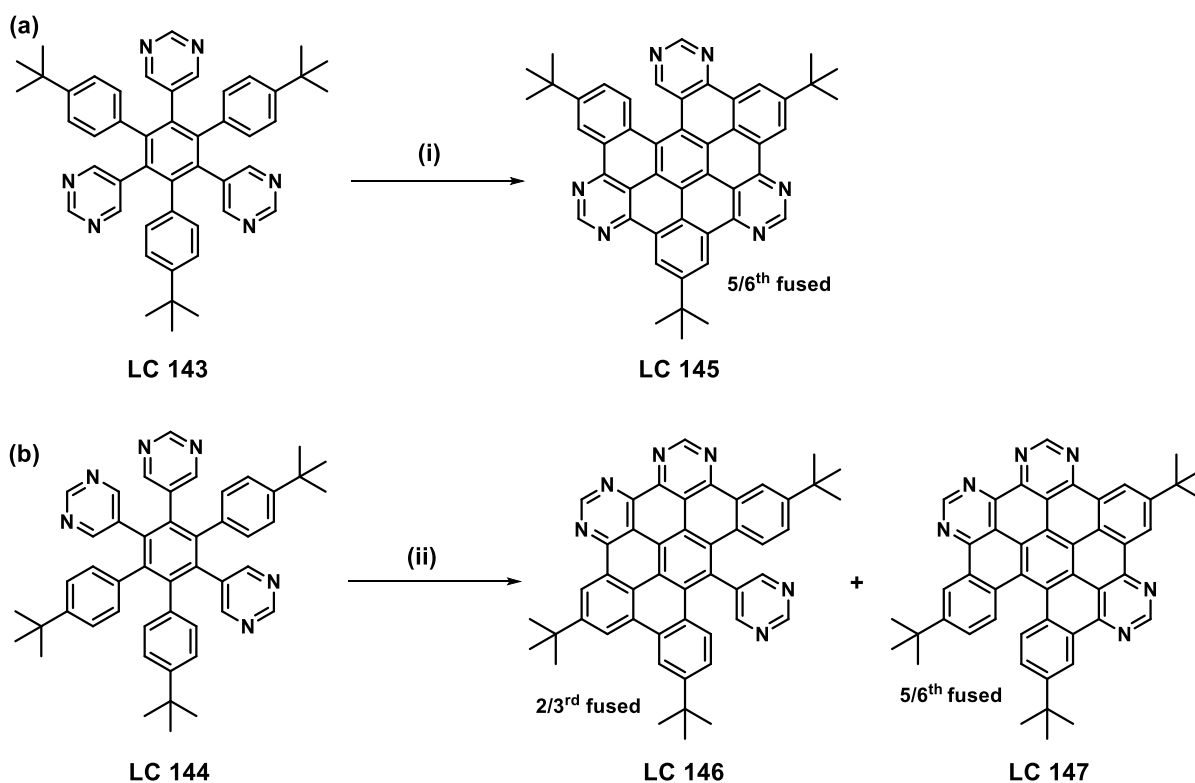


Scheme 5.2: The synthetic route towards 6N-hexaphenylbenzenes, as devised by Dr. L. Wijesinghe.⁴¹ (i) $\text{Co}_2(\text{CO})_8$, 1,4-dioxane, reflux, 24 h. Reported yields: 27 % (symmetric product) and 68 % (asymmetric product).

In order to generate nanographene-type compounds from these products, a variety of oxidative cyclodehydrogenation techniques have been attempted.⁴¹ Treatment of the symmetric isomer **LC 143** with $\text{AlCl}_3/\text{CuCl}_2$ yielded many partially-fused products, which were not possible to separate. Under the FeCl_3 cyclodehydrogenation route, a similar mixture of products was obtained including the $\frac{1}{2}$ fused (*i.e.* three out of six bonds closed), $\frac{2}{3}$ rd fused and $\frac{5}{6}$ th fused products. A trace of the fully-fused product was observed by HRMS. The $\frac{5}{6}$ th fused product was possible to isolate by preparative thin layer chromatography (**LC 145**, Scheme 5.3 (a)). Attempts to cyclodehydrogenate the symmetric hexaphenylbenzene with a

combination of DDQ and methanesulfonic acid (MeSO_3H) did not form any fused products.⁴¹

Oxidative cyclodehydrogenation of the asymmetric hexaphenylbenzene **LC 144** was also attempted with the same three routes. With the $\text{AlCl}_3/\text{CuCl}_2$ method, mass spectrometry showed many partially-fused products, with only the 5th fused being possible to isolate, in low yield (5 %). The FeCl_3 route provided both the 2^{3rd} fused and 5th fused products (**LC 146** and **LC 147**, Scheme 5.3 (b)), with no fully-fused product (*i.e.* with all six bonds being closed) observed. The DDQ/ MeSO_3H route provided the 5th fused product as the major product in 60 % yield. Attempts to generate the fully-fused product, under harsher conditions, with $\text{CF}_3\text{SO}_3\text{H}$ (trifluoromethanesulfonic acid) in place of MeSO_3H , were not successful, with bond closure only proceeding as far as the 5th fused product.⁴⁰



Scheme 5.3: Partially fused products isolated after the oxidative cyclodehydrogenation of the 6N (a) symmetric and (b) asymmetric compounds.⁴¹ (i) FeCl_3 , MeNO_2 , CH_2Cl_2 , 23 %. (ii) FeCl_3 , MeNO_2 , CH_2Cl_2 , yield 5th fused: 20 %, yield 2^{3rd} fused: 10 %.

The synthesis of compounds such as these is challenging, particularly in terms of separation of the symmetric and asymmetric isomers and the subsequent separation of

partially-fused products, as their structural similarities lead to very similar R_f values. Nevertheless, the asymmetric 5%th fused product may be generated in yields sufficient for further investigation of its properties as a coordinating ligand. The asymmetric nature of this compound leads to two pyrimidine rings in close proximity to one another, providing N[^]N coordination ability to an intriguing, highly N-substituted aromatic framework with extensive π delocalisation.

5.1.7 Chapter Aims

Reports of organometallic complexes of compounds HBC-type compounds are scarce. The coordination properties of the unusual 6N-nanographene systems synthesised by Dr. L. Wijesinghe have yet to be investigated. This chapter aims to describe the synthetic attempts towards Ir(III) complexes of the 5%th-fused compound **LC 147**, and their initial photophysical characterisation. As this is a highly-conjugated system, it would be anticipated that this would facilitate some degree of tuning of the optical properties through the lowering of the LUMO energy level, relative to an Ir(III) complex such as $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$. This chapter aims to give an overview of the syntheses and photophysical properties of Ir(III) complexes of this highly unusual ligand. Three different ligand cyclometallating ligand systems have been chosen; the widely employed ppy ligands, the strongly absorbing visible-region coumarin 6 ligands, and the Cp* ligand as an alternative coordination mode (Fig. 5.8). The previous report by Lu *et al.* of bis-cyclometalated Ir(III) complexes bearing coumarin 6 cyclometalating ligands, which exhibited excellent characteristics for applications as triplet photosensitisers, has prompted the incorporation of the coumarin 6 ligands in one of the complexes investigated.²⁶

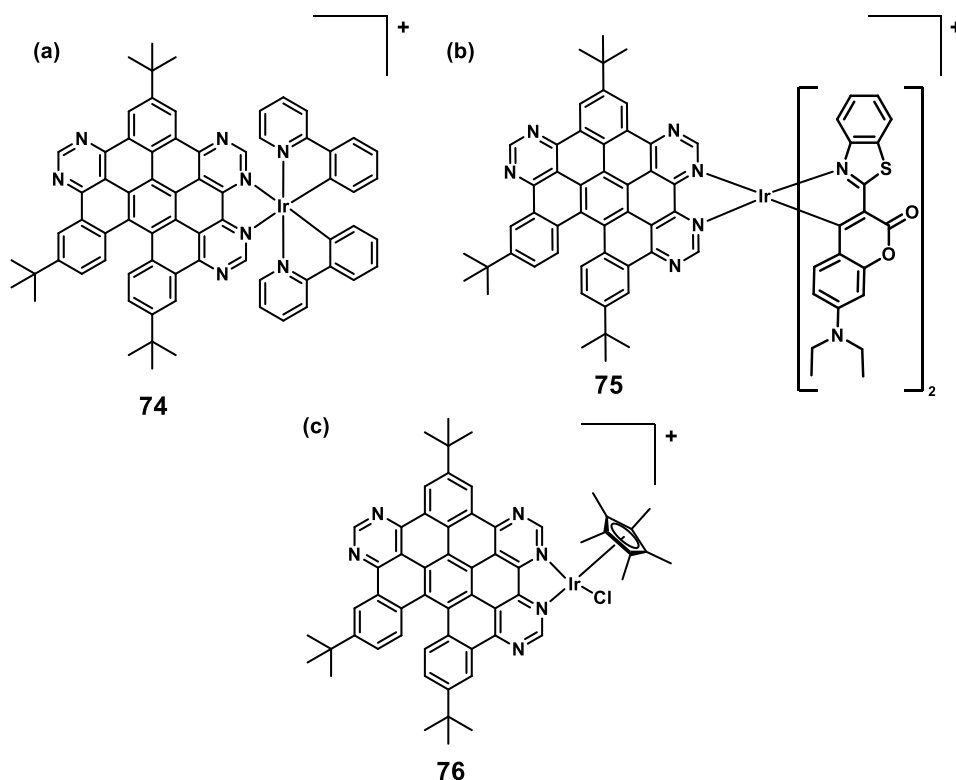


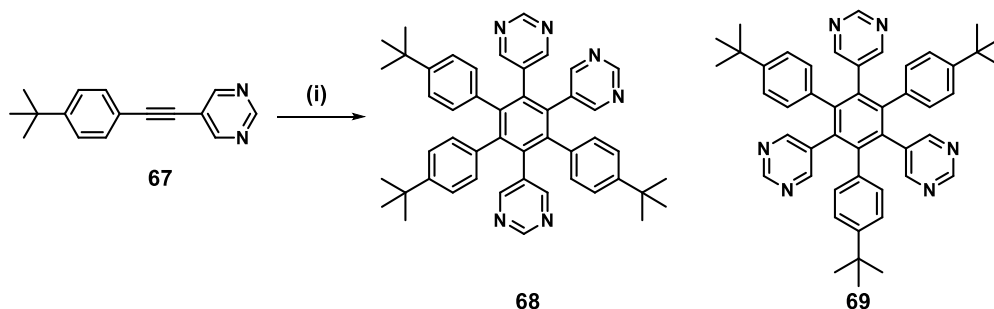
Figure 5.8: Proposed structures of Ir(III) complexes, featuring a 5/6th fused 6N nanographene as N^N ligand, with (a) 2-phenylpyridine, (b) coumarin 6, and (c) Cp* ligands.

5.2 Results and Discussion

5.2.1 Synthesis of 5/6th Fused Precursor Ligand and Ir(III) Complexes

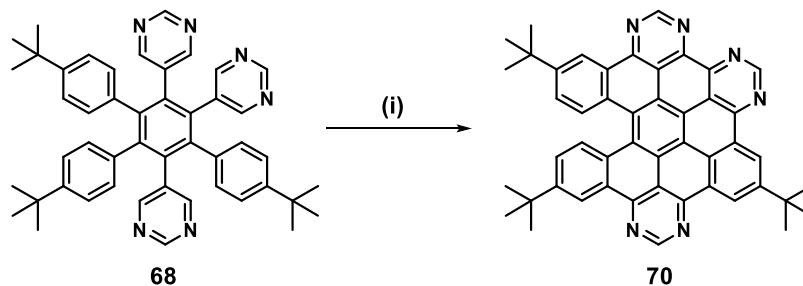
The synthetic route towards Ir(III) complexes with the 5/6th fused N^N ligand began with the preparation of the required hexaphenylbenzene precursor. This was achieved firstly by preparation of the alkyne 5-((4-(tert-butyl)phenyl)ethynyl)pyrimidine (**LC 142**, hereafter numbered **67**). This was carried out according to a reported procedure, with a Cu(I)-catalysed Sonogashira coupling reaction between the commercially available 5-bromopyrimidine and 4-tert-butylphenylacetylene. After column chromatography (SiO₂, CH₂Cl₂:CH₃OH, 50:1, v/v), **67** was obtained as a yellow solid in 41 % yield. The generation of the required hexaphenylbenzene precursor (**LC 144**, hereafter numbered **68**, was then achieved by the dicobalt octacarbonyl-catalysed cyclotrimerisation of **67** (Scheme 5.4). This reaction led to two products, as expected, the desired asymmetric isomer **68**, and also the symmetric isomer (**LC 145**, hereafter numbered **69**). Separation of these isomers was achieved through careful column chromatography (SiO₂, CH₂Cl₂:MeOH, 25:1, v/v). Both isomers were obtained as

white solids, with the asymmetric being obtained in 47 % yield and the symmetric in 3 % yield. The low yield of the symmetric isomer resulted from difficulty in separation of the isomers. The compounds were characterised by NMR spectroscopy, which was in agreement with the previous reports.^{40, 41} The mass spectral data for **68** and **69** are presented in Table 5.1.



Scheme 5.4: Preparation of asymmetric (**68**) and symmetric (**69**) isomers. (i) $\text{Co}_2(\text{CO})_8$, 1,4-dioxane, 115 °C, 48 h. Yield **68**: 47 %. Yield **69**: 3 %

The 5/6th fused asymmetric ligand (**LC 147**, hereafter referred to as **70**) was subsequently prepared from **68** via its oxidative cyclodehydrogenation, a process which employed a combination of DDQ and $\text{CF}_3\text{SO}_3\text{H}$ (Scheme 5.5).



Scheme 5.5: Synthesis of 5/6th fused asymmetric N^{N} ligand **70**. (i) DDQ, $\text{CF}_3\text{SO}_3\text{H}$, CH_2Cl_2 , RT, N_2 , 3 h, 30 %.

Under nitrogen, the precursor, **68**, was dissolved in dry, degassed CH_2Cl_2 , and six equivalents of DDQ were added. After stirring until all solids had dissolved, $\text{CF}_3\text{SO}_3\text{H}$ (six equivalents) was added carefully, and an immediate colour change to dark red was observed. The mixture was then stirred at RT for three hours. After neutralisation with K_2CO_3 and subsequent work-up, the 5/6th fused product was obtained after purification by preparative plate chromatography, which removed a trace impurity that HRMS indicated was the 2/3-fused product. Although six equivalents of DDQ and acid were added (*i.e.* one equivalent per possible bond closure) it is noted that no trace of the fully fused product was observed.

The ^1H NMR spectrum of **70** is displayed in Fig. 5.9. It is in agreement with the previous report,⁴¹ and integrates to the expected eleven protons. It is displayed here for the purpose of comparison with its Ir(III) complexes. The pyrimidyl protons H_1 and H_2 are observed most downfield, as singlets. The remaining pyrimidyl proton, H_5 , is observed slightly more upfield at 10.09 ppm. The overlapping singlets at 10.11 ppm are assigned to H_3 and H_4 . The presence of the upfield aromatic signals at 7.74 ppm is confirmation that full bond closure was not achieved. H_9 and H_8 are observed as overlapping doublets at 7.74 ppm. H_{10} and H_7 are assigned to the doublets at 8.84 and 8.82 ppm respectively.

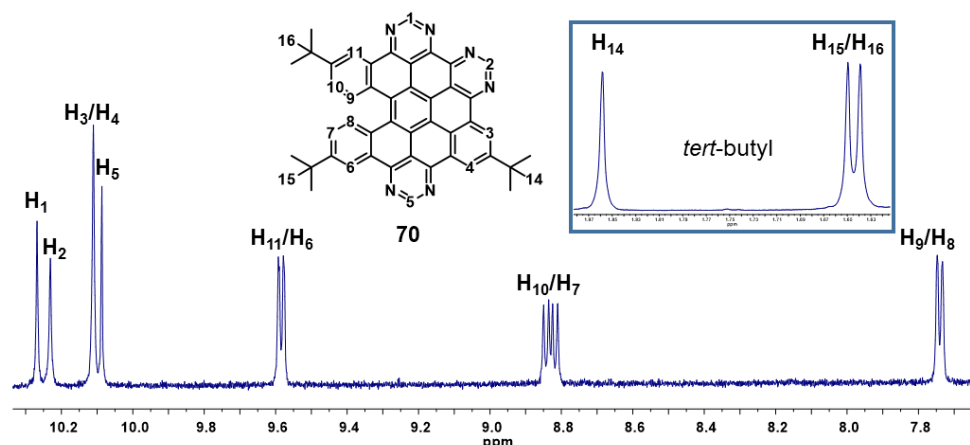


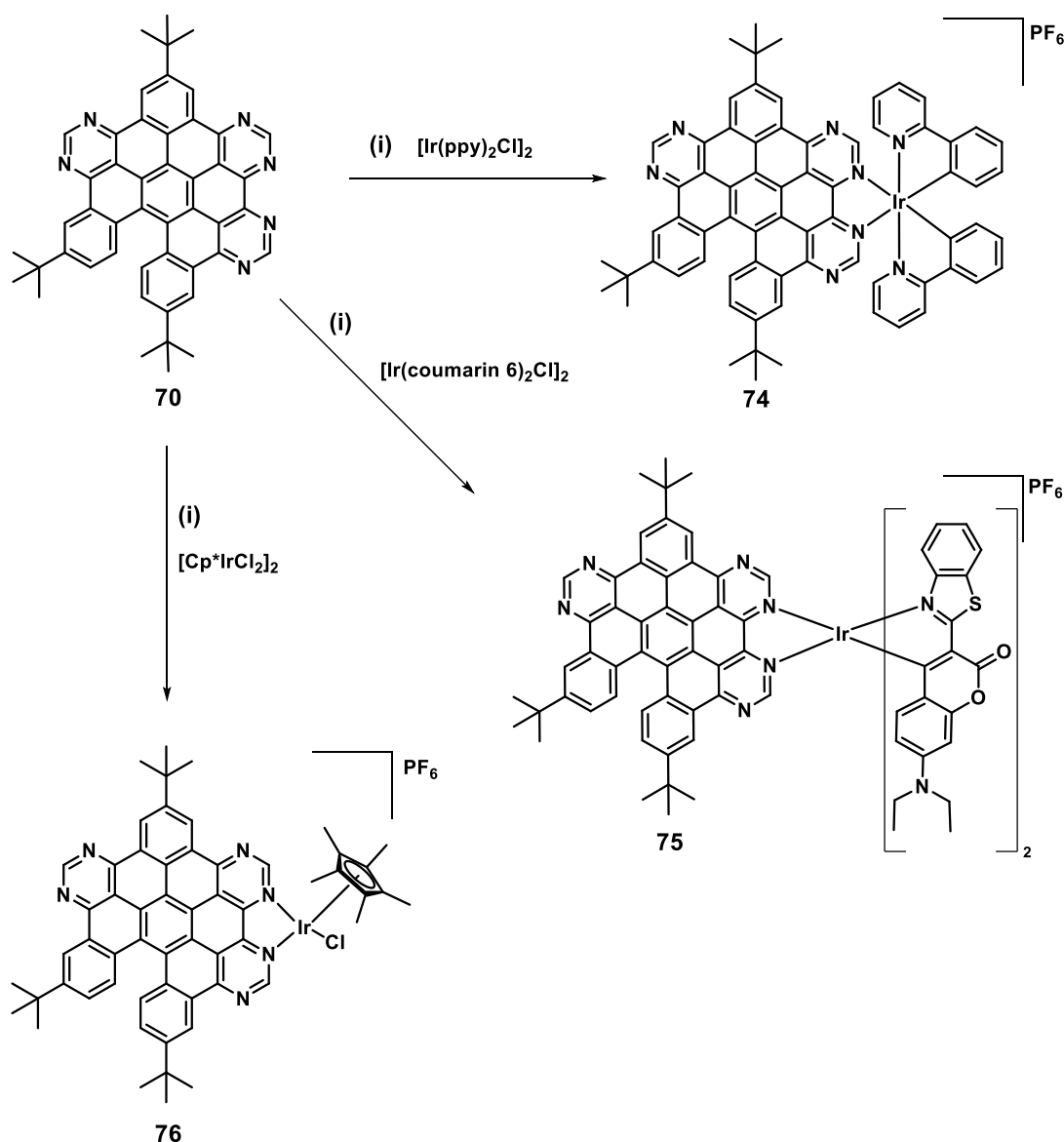
Figure 5.9: ^1H NMR spectrum of **70**, with *tert*-butyl region displayed as inset region (600 MHz, CDCl_3 , RT).

A ^1H - ^1H COSY indicated the coupling patterns between these protons and aided their identification. H_{11} and H_6 are observed as a pseudo-doublet at 9.58 ppm. A 2D-NOE experiment yielded the through-space interactions with the relevant *tert*-butyl groups H_{14} , H_{15} and H_{16} . Further confirmation of the structural identity of **70** was given by mass spectrometry (data presented in Table 5.1).

Table 5.1: HRMS data for precursor complexes **68**, **69** and **70**.

Compound	Formula	Calc. m/z	Found m/z	Molecular Ion
68	$\text{C}_{48}\text{H}_{49}\text{N}_6$	709.4013	709.3998	$[\text{M}+\text{H}]^+$
69	$\text{C}_{48}\text{H}_{49}\text{N}_6$	709.4013	709.4023	$[\text{M}+\text{H}]^+$
70	$\text{C}_{48}\text{H}_{39}\text{N}_6$	699.3231	699.3215	$[\text{M}+\text{H}]^+$

The synthetic route to the Ir(III) complexes followed the same general procedure as that reported by Neve *et al.*¹⁴ The required μ -dichloro-bridged Ir(III) dimers, [Ir(ppy)₂Cl]₂ (**71**), [Ir(coumarin 6)₂Cl]₂ (**72**) and [Cp*IrCl₂]₂ (**73**) were produced according to slightly modified literature procedures.^{42, 43} The synthesis of the three Ir(III) complexes, **74**, **75** and **76**, was achieved by combining the N[^]N ligand **70** with the appropriate μ -dichloro-bridged Ir(III) dimer in a mixture of refluxing CHCl₃ and MeOH, with NH₄PF₆ as the source of the required counterion (Scheme 5.6). Isolation and purification of the complexes was achieved by concentration of the solvent and addition of a small volume of MeOH to precipitate the product. Residual impurities were then removed by preparative plate chromatography (SiO₂, CH₂Cl₂:CH₃OH, 100:3 v/v).



Scheme 5.6: Synthetic pathway to Ir(III) complexes **74-76**. (i) NH₄PF₆, CHCl₃, MeOH, reflux, 2 h, N₂. Yields of **74**, **75** and **76** were 73 %, 37 %, and 60 % respectively.

5.2.2 Characterisation of Ir(III) Complexes

The Ir(III) complexes **74**, **75**, and **76** were characterised by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and mass spectrometry (HRMS data is presented in Table 5.2). The interpretation of the NMR spectra of these complexes proved quite challenging, as each signal appears to be split into two, *e.g.* where one may expect a singlet, what appears to be a doublet is observed. This is proposed to be due to the asymmetric nature of the N[^]N ligand **70**, which is also expected to be partially twisted due to its partially fused nature. The complexes are therefore proposed to exist as isomers, depending on the orientation of the N[^]N ligand. As each signal in the NMR spectra appears in the same relative abundance as its counterpart, it seems that the isomers exist in a relatively equal (*i.e.* 50:50) presence. The difference imposed by the asymmetric N[^]N ligand is displayed schematically in Fig. 5.10, where the difference is highlighted in red and blue. The effect of the twist of the ligand is proposed to result in two systems after coordination of the metal centre, one in which the partially-fused moiety is pointing upwards in relation to the plane of the molecule, and another where it is pointing downwards (Fig. 5.10 (c)). There are therefore two environments which are observed upon coordination to the metal centre. As the R_f values for these different forms are identical, they were not separable. As bidentate ligands lead to stereoisomerism, it is expected that each of the different structural isomers observed in the NMR experiments would also each exist as two enantiomeric forms (Δ and Λ).

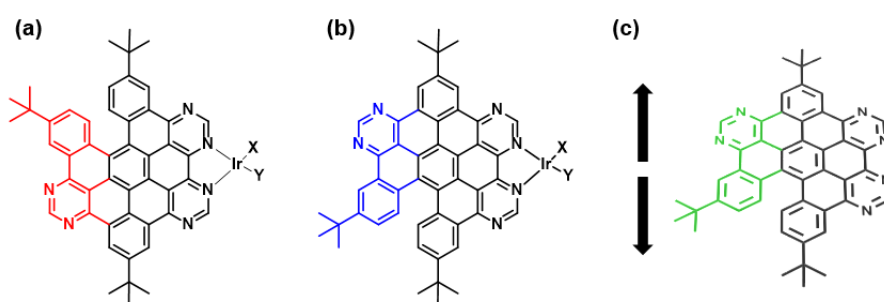


Figure 5.10: Depictions of the different chemical environments imposed on the Ir(III) complexes of **70**, depending on the orientation of the ligand as (a) or (b). X and Y depict generic coordinating ligands. (c) A graphical depiction of the proposed 'twist' of the ligand.

The ^1H NMR spectrum of **74** is displayed in Fig. 5.12, with the numbering system displayed in Fig. 5.11. Due to the complex and highly similar nature of the signals, the designation of x or x' (where x represents the proton number) is assigned arbitrarily to each isomeric form. The NMR spectra proved quite complex, as a result of the presence of the two isomers. However, the most downfield (deshielded) peaks are highly characteristic of

the pyrimidyl and H_{3/3'} and H_{4/4'} protons, and appear in a similar manner as in the ¹H NMR spectrum of the free ligand **70**. Unlike in the free ligand, where they appear as singlets, in the complex **74**, they each appear as pairs of overlapping singlets due to the presence of two isomers. A TOCSY experiment (Fig. 5.14) reveals that only two of these pairs of signals (δ 10.04 and 10.19 ppm) display a spin-spin interaction, and therefore may be assigned to H_{3/3'} and H_{4/4'}. This is also supported by the ¹H-¹³C HSQC spectrum, which shows that the ¹³C signals associated with these are relatively upfield, and therefore are not pyrimidyl protons (Fig. 5.13, selected resonances are labelled). Further investigation of the HSQC spectrum shows that only one other set of pyrimidyl protons are observed at δ 10.11 ppm, which are assigned to H_{5/5'}. In order to distinguish H_{3/3'} from H_{4/4'}, a HMBC spectrum provided evidence for a three-bond couplings between the set of protons H_{5/5'} and the pair of protons H_{4/4'} to the same quaternary carbon. Therefore H_{4/4'} are most downfield at δ 10.19 ppm, and H_{3/3'} are slightly more upfield at δ 10.04 ppm. The pyrimidyl protons H_{1/1'} and H_{2/2'} are shifted upfield upon complexation. The proton signals corresponding to H₁ and H₂ overlap closely, with H₁ slightly more upfield, and H₂ slightly more downfield. These were differentiated by the correlation of H_{2/2'} with the same quaternary carbon that H_{3/3'} display a correlation with. A high degree of splitting is observed between H₂ and H_{2'}, and H₁ and H_{1'}. Their identity is further supported by the TOCSY experiment, which does not show any spin-correlation between these proton signals. The signals assigned to H₁₁ and H_{11'} appear as doublets in a similar range as in the free ligand. The signal assigned to H₁₁ is slightly more upfield than H_{11'}. These were assigned with reference to the HMBC spectrum, which provided evidence for the three-bond correlation of the H₁₁ and H_{11'} signals with the same quaternary carbon (of the pyrimidine ring) that H₁ and H_{1'}, respectively, are also in correlation with. The identity of H₁₁ and H_{11'} allowed the identities of H₁₀, H_{10'}, H₉ and H_{9'} to be also revealed, due to their spin-interactions in the TOCSY experiment (highlighted in red in Fig. 5.14). The remaining signals at δ 9.59 ppm and 9.57 ppm were assigned to H₆ and H_{6'}, although the complex and overlapping nature of these signals did not allow their differentiation. Consulting the TOCSY experiment identified the signals associated with the H₇, H_{7'}, H₈ and H_{8'} protons. A further selective TOCSY experiment confirmed that the signals at δ 9.60 (H₆/H_{6'}), 8.91 (H₇/H_{7'}) and 7.76 (H₈/H_{8'}) were in the same spin system.

The proton signals from the 2-phenylpyridine ligands are observed more upfield than those of the N^N ligand, and the different isomers have led to the presence of many overlapping signals. The TOCSY experiment identified the various spin systems, and

allowed some relation between the signals to be made. The pyridine ring is denoted 'B' and the phenyl ring is denoted 'A'. The majority of the proton signals assigned to the phenyl ring 'A' appear more upfield than those of the pyridine ring, as expected. The HSQC experiment gives further confirmation of the assignments, as the ^{13}C signals associated with the pyridine ring appear further downfield than those associated with phenyl ring 'A'. The *tert*-butyl signals, which appear each as pairs of closely-spaced singlets (with a larger degree of difference between H_{12} and $\text{H}_{12'}$) were assigned based on the C-H correlations identified through the HMBC experiment and the relevant protons of the ligand. The $\text{H}_{14}/\text{H}_{14'}$ *tert*-butyl signals are observed as being most deshielded, due to their central location in the fused portion of the ligand (therefore experiencing a higher degree of ring current).

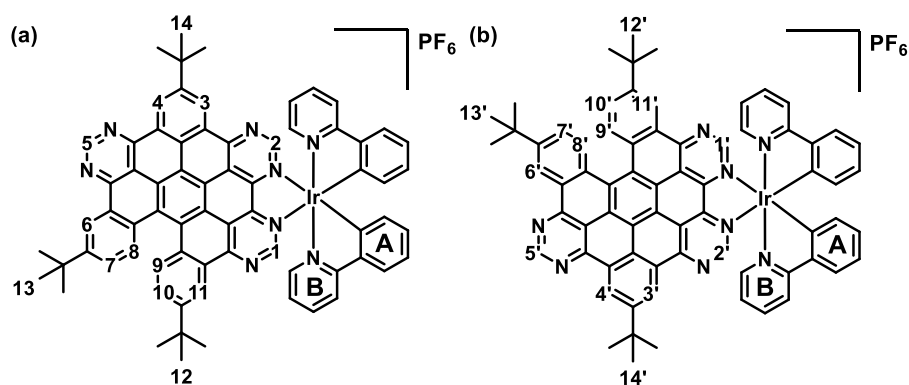


Figure 5.11: Proposed numbering scheme for two isomers of **74**.

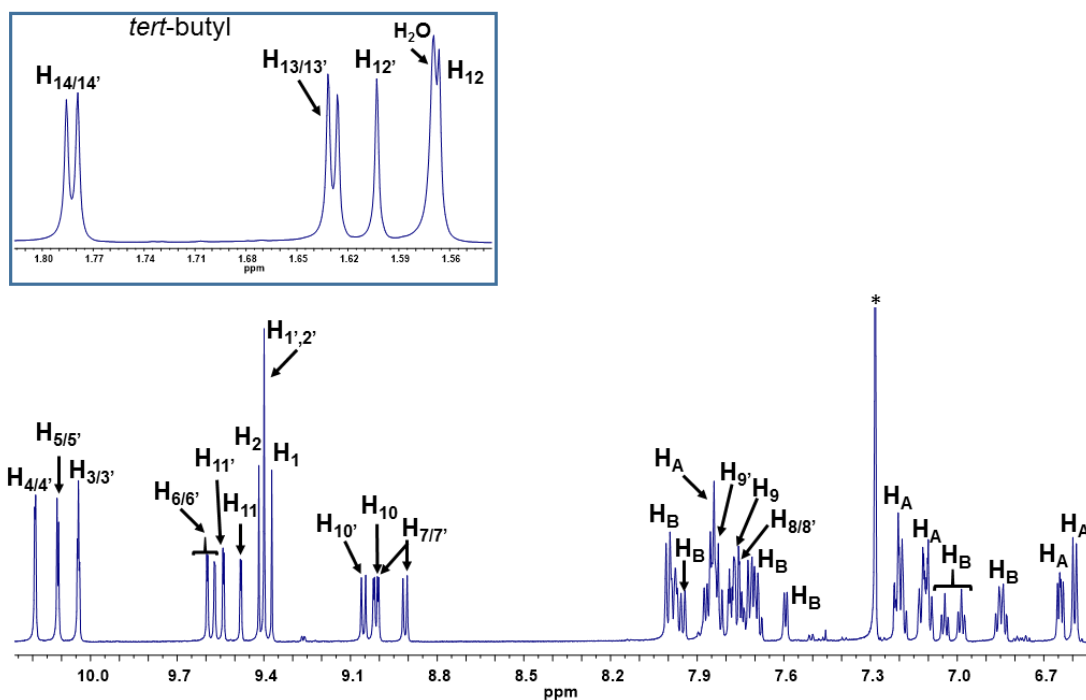


Figure 5.12: ^1H NMR spectrum of **74**, with *tert*-butyl region as inset (CDCl_3 , 600 MHz, RT). * denotes residual solvent peak.

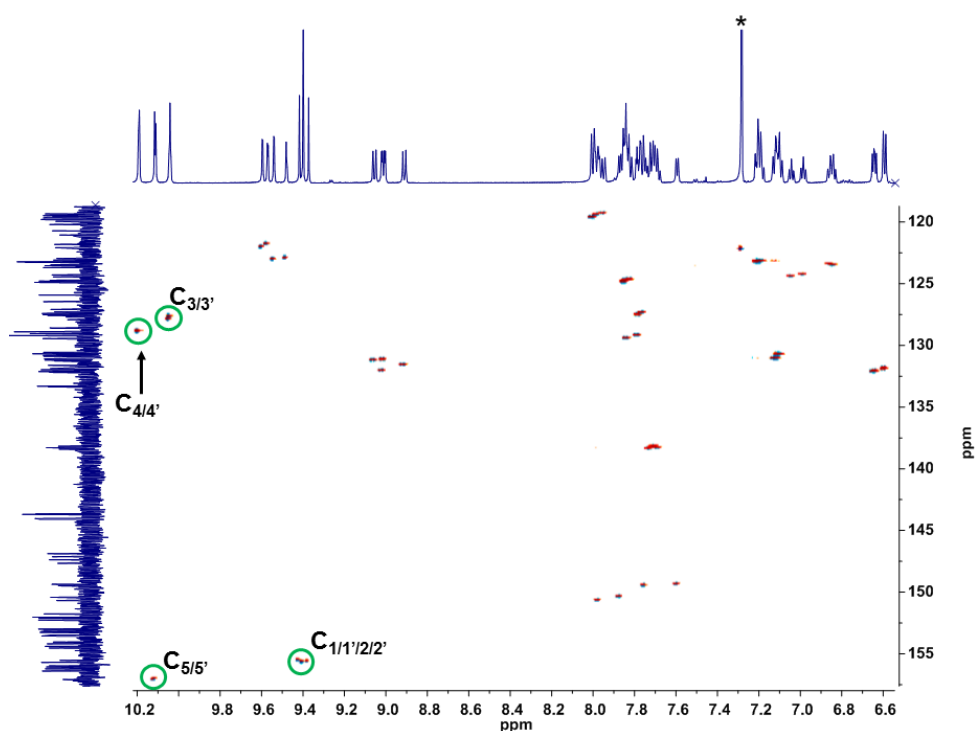


Figure 5.13: ^1H - ^{13}C HSQC spectrum of **74** (CDCl_3 , 600/150 MHz, RT). * denotes residual solvent peak. Selected correlations are labelled.

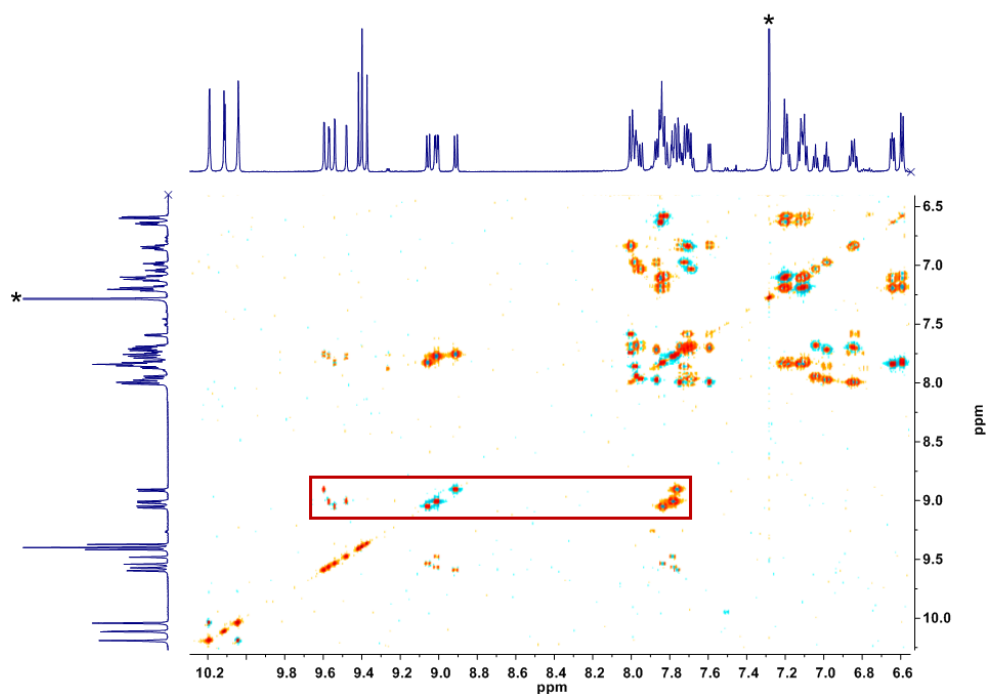


Figure 5.14: ^1H - ^1H TOCSY spectrum of **74** (CDCl_3 , 600 MHz, RT). * denotes residual solvent peak. Selected spin-system highlighted in red.

The ^1H NMR spectrum of **75** follows a similar pattern to that of **74**, due to the presence of two isomers. Again, the most downfield peaks are attributed to the pyrimidyl protons, H_1 , H_2 , and H_5 , and also the aromatic protons of the most fused portion of the molecule, H_3 and H_4 . The numbering scheme employed for the two isomers is shown in Fig. 5.15. The ^1H NMR spectrum is displayed in Fig. 5.16.

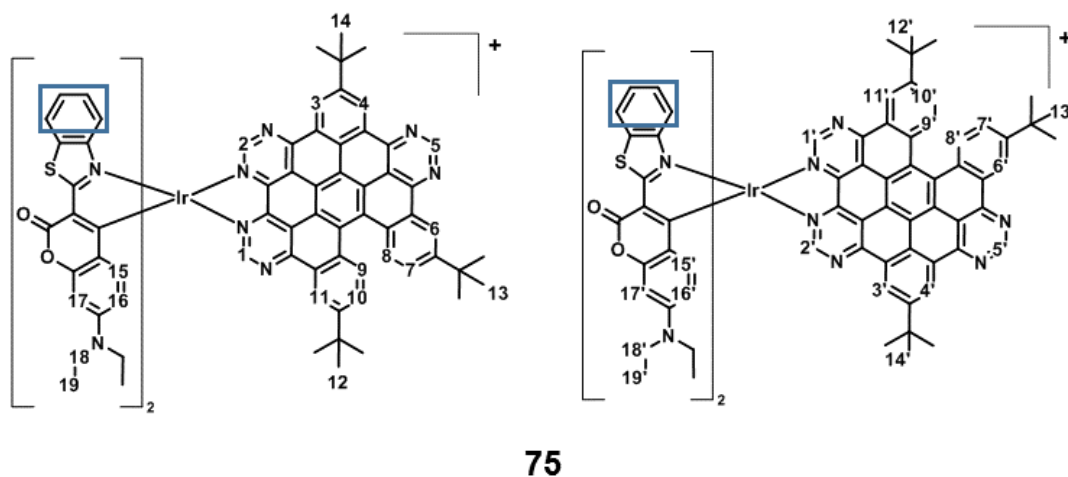


Figure 5.15: The NMR numbering scheme for both isomeric forms of **75**. The phenyl protons of the coumarin 6 ligands are highlighted in blue.

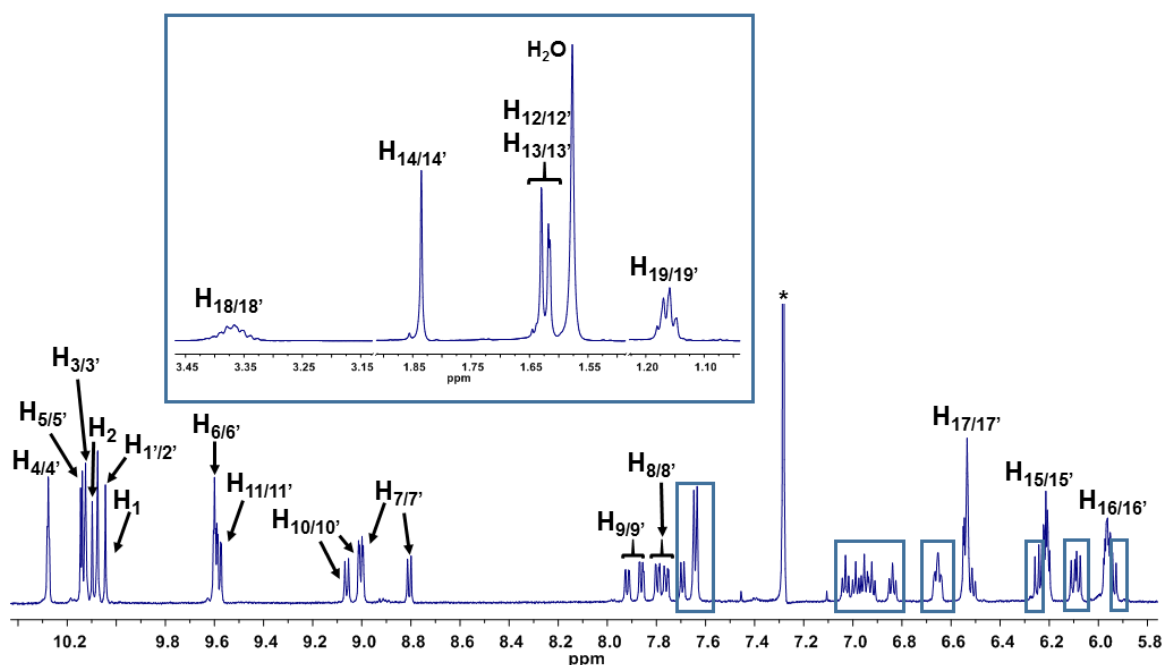


Figure 5.16: The ^1H NMR spectrum of **75** (CDCl_3 , 600 MHz, RT). * denotes residual solvent peak. Inset displays upfield region (1.10-3.45 ppm). Phenyl protons of coumarin 6 ligands highlighted in blue.

This spectrum was assigned in much the same way as that of **74**, beginning with the most downfield peaks, from δ 10.03 to 10.29 ppm, which are derived from the 5%th fused ligand. A ^1H - ^{13}C HSQC experiment (Fig. 5.17) indicated that $\text{H}_{3/3'}$ and $\text{H}_{4/4'}$ were attributable to the signals at δ 10.28 and 10.13 ppm, based upon their less deshielded corresponding ^{13}C values (as the ^{13}C resonances of the pyrimidyl ^1H signals are expected to be more deshielded). This assignment was further supported by a 2D TOCSY experiment (Fig. 5.18), which showed that only the peaks at δ 10.28 and 10.13 ppm gave a spin-interaction. A 2D ROESY experiment also gave evidence of a through-space interaction between these protons. A combination of the HMBC, TOCSY and NOESY experiments led to the assignment of the remaining signals from the N[^]N ligand, in the same manner as for **74**. The proton signals of the coumarin 6 cyclometalated ligands were assigned beginning with the $-\text{CH}_2$ and $-\text{CH}_3$ moieties of the carbon chain. These signals show a NOESY (through-space) interaction, and a spin-spin interaction. The $-\text{CH}_2$ ($\text{H}_{18/18'}$) protons were assigned to the multiplet at δ 3.37 ppm, and the $-\text{CH}_3$ ($\text{H}_{19/19'}$) protons to the more upfield signal at δ 1.16 ppm. The $\text{H}_{18/18'}$ protons show a three-bond HMBC correlation to a quaternary carbon (bonded to the N of the aniline ring) in the lactone ring of the coumarin 6. This quaternary carbon gives a further three-bond correlation with the proton signal at δ 6.21 ppm (observed as a multiplet due to overlap). Based on the three-bond correlation, the signal at δ 6.21 is assigned to $\text{H}_{15/15'}$. Investigation of the spin-spin interactions that $\text{H}_{15/15'}$ exhibit, identifies $\text{H}_{16/16'}$ and $\text{H}_{17/17'}$, which are assigned to the signals at δ 5.97 and 6.54 respectively. The $\text{H}_{17/17'}$ protons are assigned as being more deshielded than the $\text{H}_{16/16'}$ protons based upon their proximity to the electron-withdrawing oxygen atom. The 2D NOE experiment confirms these assignments, showing that a through space interaction is observed between the $-\text{CH}_2$ ($\text{H}_{18/18'}$) protons, and the $\text{H}_{16/16'}$ and $\text{H}_{17/17'}$ protons. The proton signals arising from the four-spin phenyl rings of the coumarin 6 ligands (marked in blue in Fig. 5.15 and Fig. 5.16) are observed as a series of signals, many of which are overlapping with others, between δ 5.91 and 7.72 ppm.

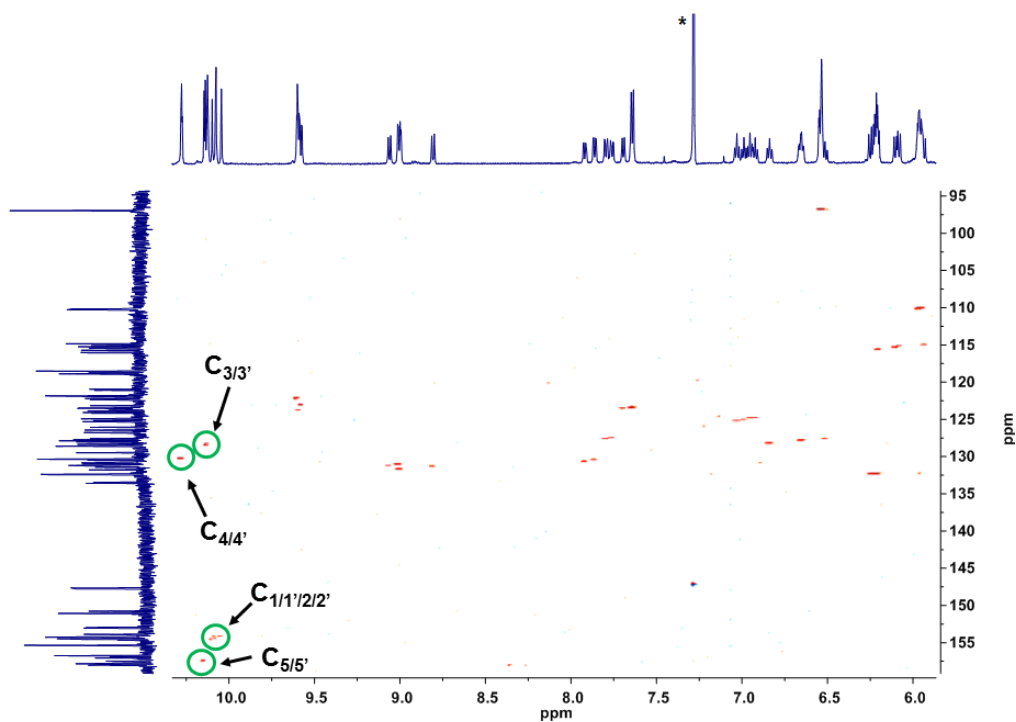


Figure 5.17: ^1H - ^{13}C HSQC spectrum of **75** (aromatic region), with selected correlations labelled (CDCl_3 , 600/150 MHz, RT). * denotes residual solvent peak.

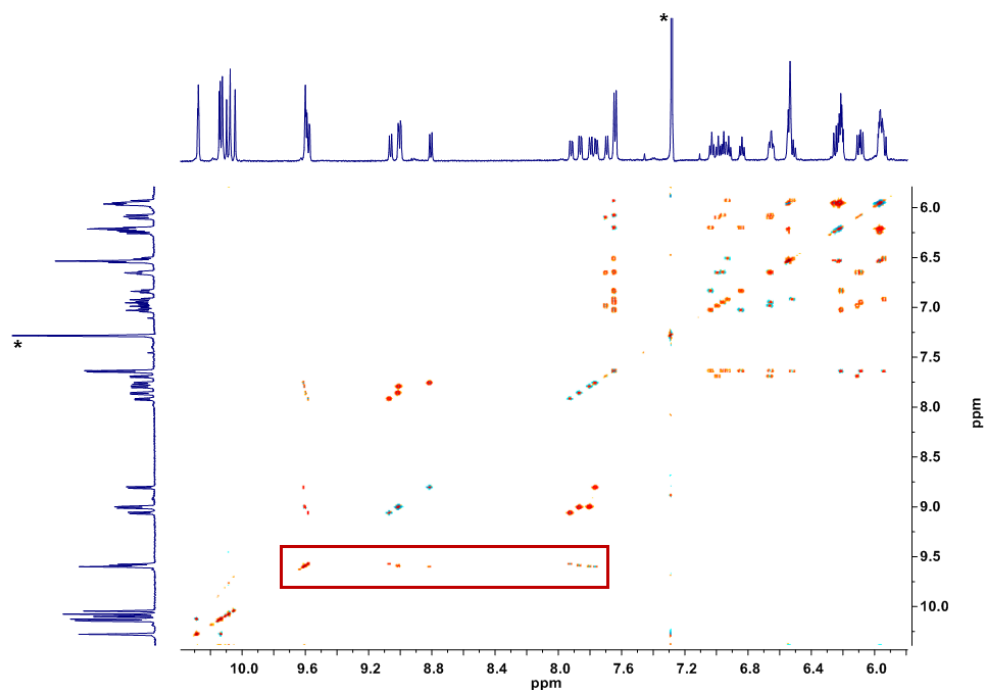


Figure 5.18: ^1H - ^1H TOCSY spectrum of **75** (600 MHz, CDCl_3 , RT). * denotes residual solvent peak. Selected spin system highlighted in red.

The ^1H NMR spectrum of **76** was elucidated in a similar manner as for **74** and **75**, a process made more facile due to its simpler ligand system. The ^1H spectrum is displayed in Fig. 5.20 (with the corresponding numbering scheme in Fig. 5.19) and shows a very similar pattern as was observed for the previous two complexes, with the pyrimidyl protons $\text{H}_{5/5'}$ and the protons of the fully fused portion, $\text{H}_{3/3'}$ and $\text{H}_{4/4'}$, being furthest downfield. $\text{H}_{1/1'}$ and $\text{H}_{2/2'}$ are again observed slightly more upfield.

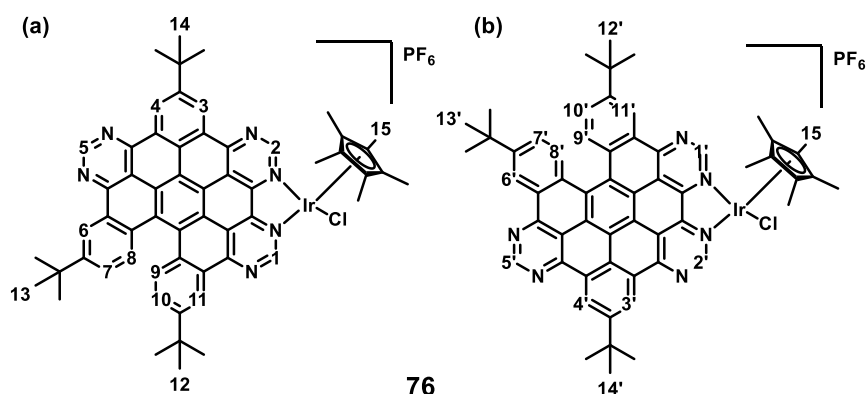


Figure 5.19: The proposed numbering scheme for the two isomeric forms of **76**.

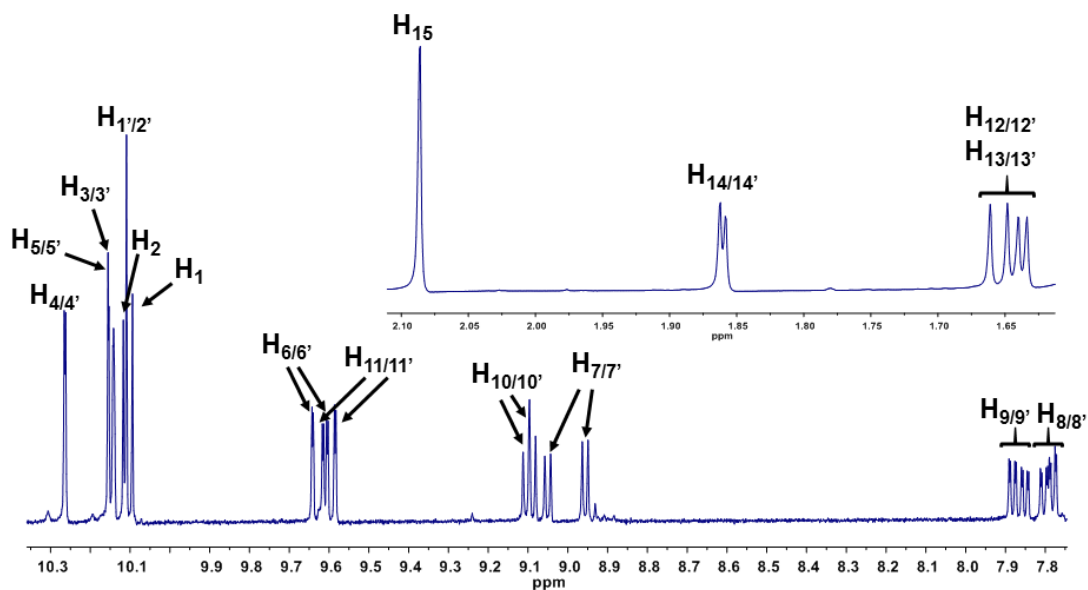


Figure 5.20: ^1H NMR spectrum of **76**, with inset, the upfield region (CDCl_3 , 600 MHz, RT).

A ROESY experiment confirmed the through-space correlation with these protons and those assigned $\text{H}_{14/14'}$ (Fig. 5.21). The combination of ^1H - ^{13}C HSQC (Fig. 5.22), ^1H - ^1H TOCSY (Fig. 5.23) and HMBC experiments aided the assignment, with the assignments being made in the same way as previously. The Cp^* protons are observed quite upfield at δ 2.09 ppm as a singlet. The signals arising from the $\text{N}^{\wedge}\text{N}$ ligand are observed to be present in two

equivalent pairs, once again indicating the presence of isomeric forms. The TOCSY spectrum shows how the spin-interactions enabled the identification of the various ^1H signals, and the HSQC spectrum is annotated with selected correlations. A ROESY experiment also showed a through-space interaction between the Cp^* protons and the $\text{H}_{3/3'}$ protons, indicating that there is interaction between the ligands.

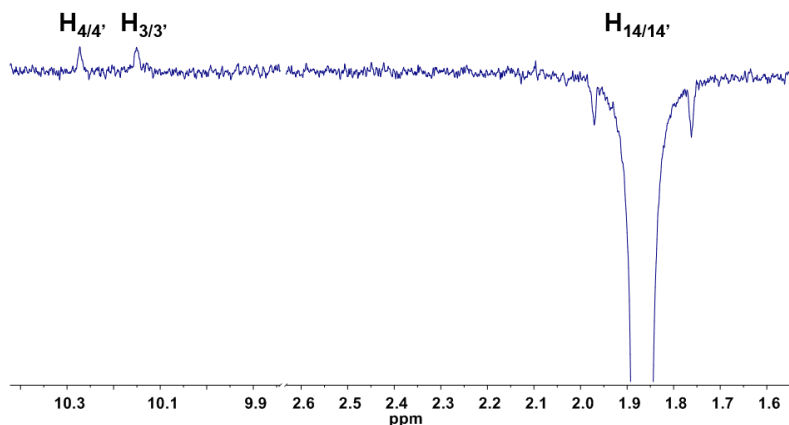


Figure 5.21: Selective ROESY, showing correlation between tert-butyl protons $\text{H}_{14/14'}$ and $\text{H}_{4/4'}$ and $\text{H}_{3/3'}$ (CDCl_3 , 600 MHz, RT).

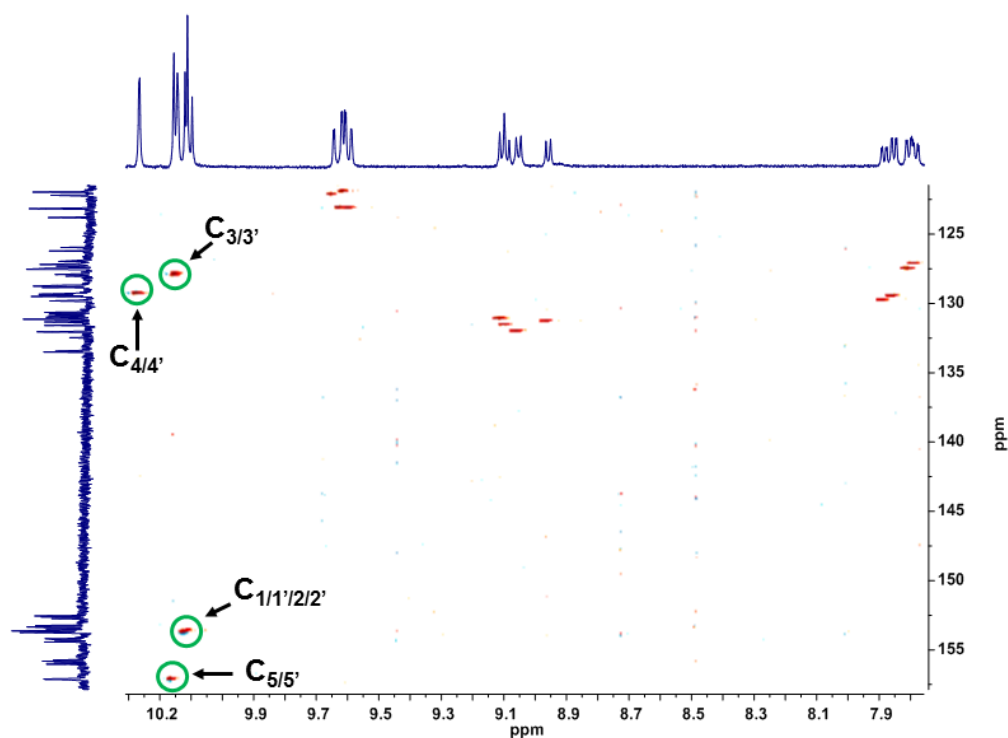


Figure 5.22: Aromatic region of ^1H - ^{13}C HSQC spectrum of **76** (CDCl_3 , 150/600 MHz, RT). Selected correlations are labelled.

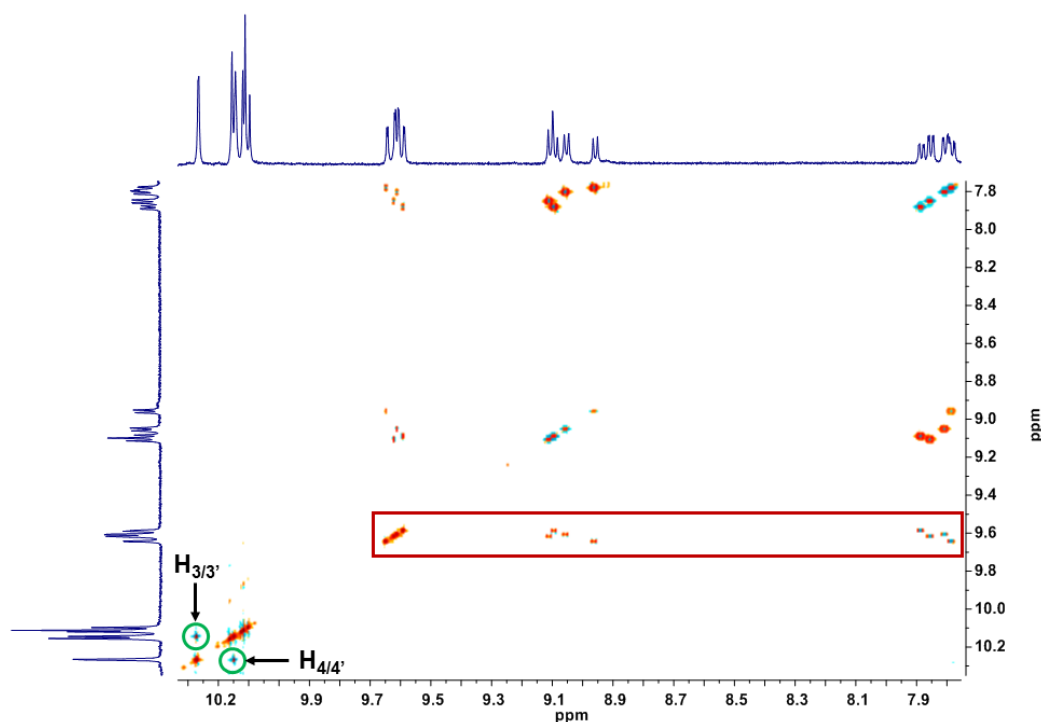


Figure 5.23: Aromatic region of ^1H - ^1H TOCSY spectrum of **76** (CDCl_3 , 600 MHz, RT). Selected spin-spin interactions are labelled.

Table 5.2: HRMS data for Ir(III) complexes **74**, **75**, and **76**.

Compound	Formula	Calc. m/z	Found m/z	Molecular Ion
74	$\text{C}_{70}\text{H}_{54}\text{N}_8\text{Ir}$	1199.4101	1199.4076	$[\text{M-PF}_6]^+$
75	$\text{C}_{88}\text{H}_{72}\text{N}_{10}\text{O}_4\text{S}_2\text{Ir}$	1589.4809	1589.4827	$[\text{M-PF}_6]^+$
76	$\text{C}_{58}\text{H}_{53}\text{N}_6\text{ClIr}$	1061.3650	1061.3629	$[\text{M-PF}_6]^+$

5.3 Photophysical Investigation of Ir(III) Complexes

5.3.1 UV-Vis Absorption Spectra

The UV-Visible spectra of **74**, **75**, and **76** were measured as 1×10^{-5} M solutions in CH_2Cl_2 . The UV-Visible spectrum of precursor ligand **70** is shown in Fig. 5.24 as a comparison. It displays a quite structured absorption profile, with $\lambda_{\text{max}} = 257$ nm. It has been previously reported that the band at $\lambda = 386$ nm possesses $n\text{-}\pi^*$ character, based upon its decrease in absorbance after titration with trifluoroacetic acid (TFA).⁴¹ The lowest energy absorption band appears at $\lambda = 473$ nm.

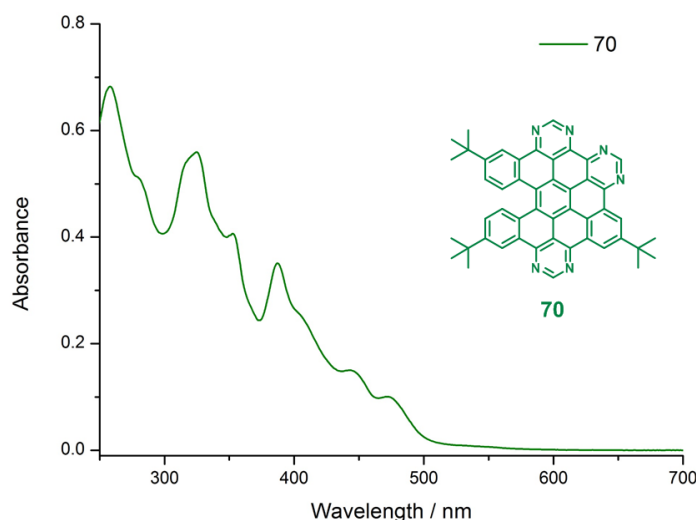


Figure 5.24: UV-Vis absorption spectrum of **70** (CH_2Cl_2 , 1×10^{-5} M, RT).

The UV-Vis absorption spectra of the Ir(III) complexes are markedly different to that of the free N[^]N ligand **70**. It is observed that **74** and **76** exhibit broadly similar absorption profiles (Fig. 5.25). The UV-Vis data for the complexes are summarised in Table 5.3.

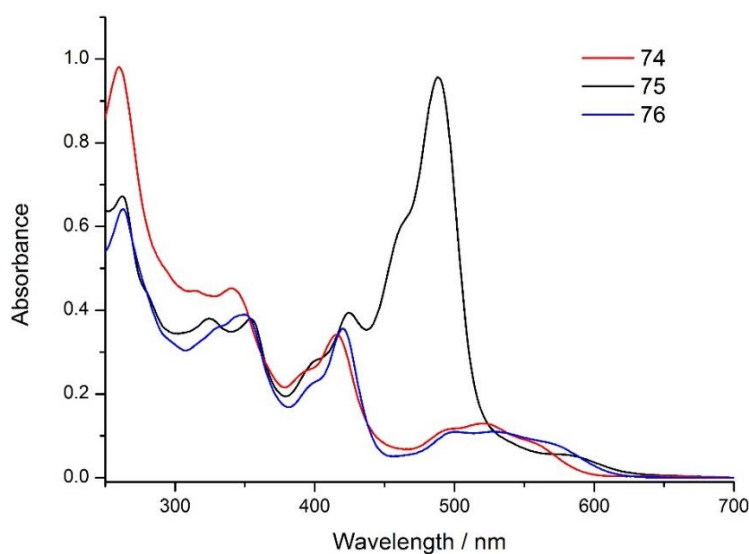


Figure 5.25: UV-Vis absorption spectra of Ir(III) complexes **74**, **75**, and **76** (CH_2Cl_2 , 1×10^{-5} M, RT).

The absorption spectrum of **75** is however dominated by an absorption band at $\lambda_{\text{max}} = 488$ nm. This intense absorbance is attributed to the coumarin 6 ligands, which are absent in the other two complexes. This is most likely an ILCT transition within the coumarin 6 ligand.⁴⁴ Similar intense absorbance bands, attributed to the coumarin 6 ligands in structurally related Ir(III) complexes, have been reported by Lu *et al.* and Takizawa *et al.*²⁶,⁴⁴ The choice of coumarin 6 ligands has therefore resulted in a significant increase in the

molar extinction coefficient, in comparison with the ppy-complex. The shoulder at $\lambda = 463$ nm is also attributed to the coumarin 6 ligands. Comparing the absorption spectra of the Ir(III) complexes with that of **70**, the lower-energy absorption bands of the ligand are obscured upon coordination. The highest energy band at $\lambda \approx 260$ nm in all Ir(III) complexes is almost identical in position to the same band in the free ligand, and is therefore assigned as N[^]N ligand-based. It is most likely π - π^* in origin due to its intensity and position (π - π^* transitions are often observed at higher energies than n- π^* transitions). This band is much higher in intensity for **74**, suggesting that π - π^* transitions within the ppy ligands are also contributing to this band. Similarly, the bands at $\lambda = 323$ nm and $\lambda = 353$ nm in the free ligand are observed in the absorption spectra of the Ir(III) complexes, but appear sensitive to complexation. In the ppy-containing complex **74**, these bands are both shifted hypsochromically. In the coumarin 6 complex (**75**), they are largely unchanged (appearing at $\lambda = 324$ nm and $\lambda = 355$ nm respectively). The higher energy band is shifted bathochromically in the Cp^{*}Cl-containing **76**. The band at $\lambda \approx 420$ nm, observed in all three complexes is not observed in the free ligand, and is most likely a CT transition. The absorption of the Ir(III) complexes is observed to continue much further into the red region, compared with the free ligand. For **74**, three significant bands are observed, at $\lambda = 496$, 520, and 555 nm. In the case of **75**, the intense absorption of the coumarin 6 ligands appears to obscure any underlying transitions below $\lambda \approx 550$ nm. A single band at $\lambda = 578$ nm is observed, significantly red-shifted compared to the ppy-containing complex. The Cp^{*} substituted compound **76** exhibits three bands in this region, similar to **74**, at $\lambda = 498$, 531, and 567 nm. The quite significant extent of the shift of these bands into the red region is most likely a consequence of the highly conjugated N[^]N ligand **70** lowering the LUMO energy level. The bands at $\lambda = 496$, and $\lambda = 498$ nm in complexes **74** and **76** respectively, are likely derived from the N[^]N ligand, which exhibits a lowest energy absorption band at $\lambda = 473$ nm, and is likely π - π^* in character.

The lower energy bands in all three complexes, beyond 500 nm, are proposed as being attributable to ¹MLCT or ³MLCT transitions. Takizawa *et al.* have reported an Ir(III) complex with coumarin 6 cyclometallating ligands, and a conjugated N[^]N 2,2'-biquinoline ligand, which yielded an absorption spectrum with a similar extended absorption beyond the coumarin bands.⁴⁴ They attributed this to MLLCT or LLCT transitions related to the 2,2'-biquinoline ligand. They also reported an analogous complex with 2,2'-bipyridine (less conjugated than 2,2'-biquinoline) as the N[^]N ligand. This complex did not exhibit such

extended bands. The Ir(III) complexes reported by Lu *et al.* (Fig. 5.6) yielded similar strong absorption bands (*ca.* 488 nm) related to the coumarin 6 ligands, but do not appear to exhibit extended absorption bands such as observed for **74**, **75**, and **76**.²⁶ ³MLCT transitions, which are formally spin-forbidden, are observed in Ir(III) complexes due to spin-orbit coupling with singlet states that are spin-allowed.¹² It is therefore proposed that for the complexes **74**, **75**, and **76**, the absorption band at $\lambda \approx 420$ nm is likely to possess ¹MLCT character, possibly with LLCT and MLLCT contribution. For **74** and **76**, which exhibit bands at $\lambda = 520$ nm and 531 nm respectively, this is attributable to a ¹MLCT/MLLCT transition. It has been stated that such bands in complexes of the type $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]$ are often mixed ¹MLCT/¹LLCT.⁸ The further lower intensity band beyond $\lambda = 550$ nm observed in all three complexes is most likely ³MLCT in origin, as it is expected to be slightly lower in intensity than a ¹MLCT absorption due to its forbidden nature. As the photophysical behaviour of Ir(III) complexes are often complex, these assignments are tentative, and in future, DFT studies would be a useful means of confirmation. It is noted that the absorption bands beyond 600 nm do not return to zero immediately, and that weak absorption is observed until *ca.* 650 nm, which may be due to the lowest-energy triplet absorptions. Such transitions are often not clearly observed, and usually possess very low extinction coefficients.⁸

Table 5.3: UV-Vis absorption data for complexes **70**, **74**, **75**, and **76**.

Compound	λ_{max} [nm] ($\epsilon \times 10^{-4}$ [$\text{M}^{-1} \text{cm}^{-1}$])
70	258 (6.83), 280 _{sh} (5.11), 325 (5.59), 353 (4.11), 387 (3.50), 443 (1.51), 473 (1.00)
74	260 (9.83), 314 (4.48), 341 (4.54), 393 _{sh} (2.55), 416 (3.43), 496 (1.17), 520 (1.31), 555, (0.86), 650 (0.03)
75	262 (6.73), 324 (3.82), 355 (3.79), 398 _{sh} (2.78), 425 (3.94), 463 (6.08), 488 (9.57), 578 (0.57)
76	263 (6.39), 330 (3.56), 350 (3.90), 400 _{sh} (2.29), 420 (3.58), 500 (1.09), 529 (1.11), 563 (0.87)

5.3.2 UV-Vis Solvatochromism Studies

In an effort to further probe the nature of the absorbance bands exhibited by **74**, **75**, and **76**, solvatochromism studies were carried out. The effect of solvent polarity on the absorption spectrum of **74** is displayed in Fig. 5.26.

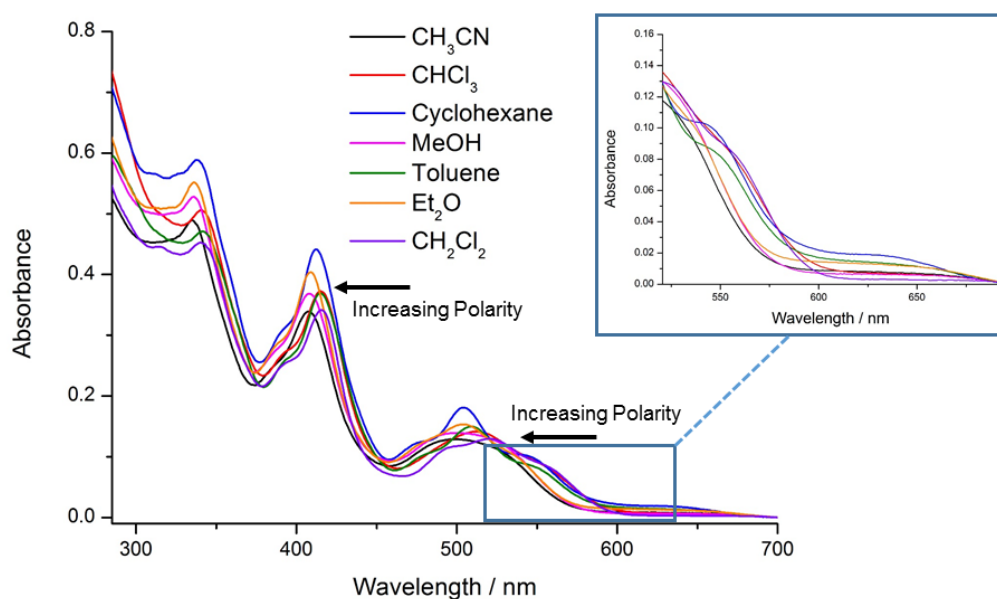


Figure 5.26: The effect of solvent polarity on the UV-Vis absorption spectrum of **74** (1×10^{-5} M, RT).

The variation of solvent polarity has brought with it changes in the positions of most of the absorbance bands. The band at $\lambda = 316$ nm is only clearly visible in CH_2Cl_2 , and is obscured in the remaining solvents. The band at $\lambda = 340$ nm in CH_2Cl_2 is observed to shift slightly with polarity, indicating it possesses some CT character. The band observed at $\lambda = 415$ nm in CH_2Cl_2 is observed to exhibit solvatochromic behaviour, supporting its earlier assignment as CT-based. This band shifts hypsochromically (*i.e.* a blue-shift to higher energy) with increasing polarity (e.g. in MeOH (polar), $\lambda = 408$ nm, in cyclohexane (non-polar) $\lambda = 412$ nm). This negative solvatochromism indicates that what is most likely an MLCT transition ($d \rightarrow \pi^*$) results in a decrease in the dipole moment of the excited state, which leads to the relevant absorption band being more stabilised in the ground state, in polar media, than the excited state.⁴⁵ A similar situation is evident for the bands beyond 500 nm. Overall, the solvatochromic trend is not as clear for the bands at $\lambda = 497$ and $\lambda = 520$ nm in CH_2Cl_2 . The band at $\lambda = 520$ nm in CH_2Cl_2 exhibits a significant shift in non-polar cyclohexane to 503 nm, and an increase in intensity. The lowest-energy well defined absorption band, attributed to a $^3\text{MLCT}$ transition at 555 nm in CH_2Cl_2 shows a clearer trend towards negative solvatochromism, and the sensitivity of this band towards polar/non-polar solvent is supportive of its CT-based assignment.

The effect of solvent polarity on the absorption spectrum of **75** is presented in Fig. 5.27. The band at $\lambda = 324$ nm in CH_2Cl_2 exhibits only minor solvatochromic differences.

The remaining major bands in the UV-Vis spectrum exhibit what appears to be negative solvatochromism. The intense absorbance at $\lambda = 488$ nm in CH_2Cl_2 gives minor shifts with varying polarity (e.g. in MeOH $\lambda_{\text{max}} = 482$ nm, in toluene $\lambda_{\text{max}} = 485$ nm). The absorption bands beyond 500 nm also appear sensitive to solvent polarity, with negative solvatochromism being observed (e.g. in CH_2Cl_2 , $\lambda_{\text{max}} = 578$ nm, in MeOH $\lambda_{\text{max}} = 562$ nm). This is again indicative of CT character within these bands. Although **74** and **76** gave satisfactory absorption spectra in cyclohexane, **75** did not yield a satisfactory absorption spectrum in this solvent due to poor solvation.

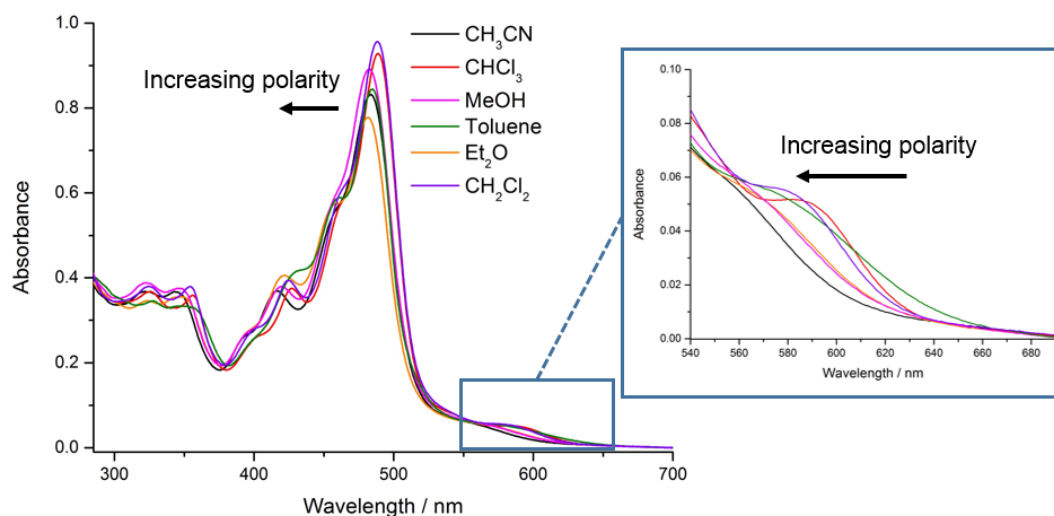


Figure 5.27: The effect of solvent polarity on the UV-Vis absorption spectrum of **75** (1×10^{-5} M, RT), with inset, the region between 540-680 nm.

The remaining complex, **76**, also displays solvatochromic behaviour (Fig. 5.28). The trend for the absorbance band at $\lambda = 349$ in CH_2Cl_2 appears to be a minor shift toward negative solvatochromism, giving a blue-shift with increasing solvent polarity. This indicates that this band possesses some degree of CT character. The majority of the significant bands exhibit an increase in intensity in Et_2O , along with the largest blue-shift, which is surprising since although Et_2O is slightly polar, it is much less than MeOH, which would be expected to induce the largest shift. This suggests that differing solubility or solvent interactions may also be influencing the band positions and intensities.

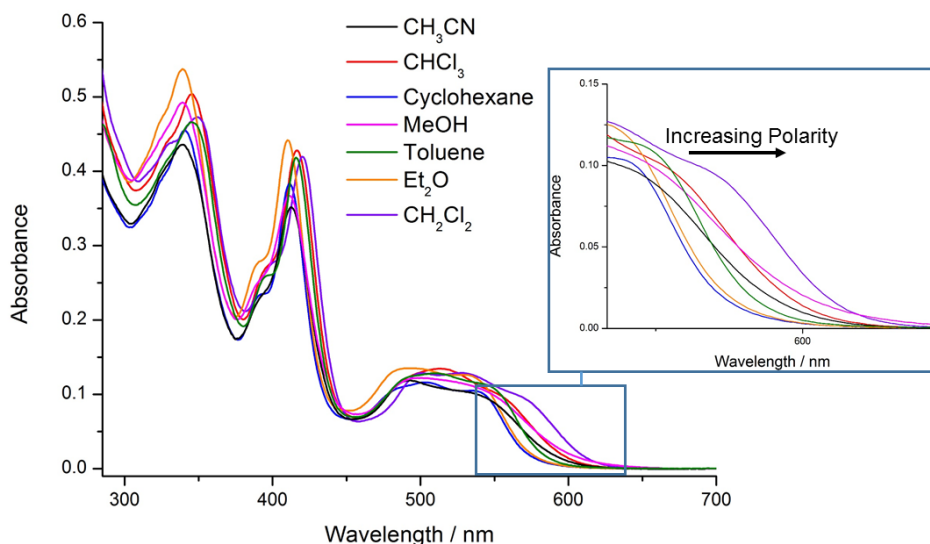


Figure 5.28: The effect of varying solvent polarity on the UV-Vis absorption spectrum of **76** (1×10^{-5} M, RT), with inset, the region between 540 nm and 640 nm.

The band at $\lambda = 420$ nm in CH_2Cl_2 also appears sensitive to its environment, but the trend here is unclear. This band shifts to $\lambda = 411$ nm in both cyclohexane and MeOH, suggesting that there may be two different components contributing to this band. A clearer trend is observed for the lowest-energy transition, at 567 nm in CH_2Cl_2 . This band appears to exhibit positive solvatochromism, where the introduction of a more polar solvent leads to a bathochromic shift (towards lower energies). The most red-shifted band is observed in CH_2Cl_2 , which may be due to enhanced solubility. The remaining solvents lead to a clear trend towards positive solvatochromism (e.g. cyclohexane: $\lambda = 538$ nm, CHCl_3 : $\lambda = 550$ nm). The subtle sensitivity of this band to solvent polarity is perhaps indicative of an MLCT assignment, and the positive solvatochromic behaviour suggests an excited state with a different electronic structure to the other Ir(III) complexes **74** and **75**, which is not unexpected, due to the very different coordinating ligands of **76**. This assignment is made tentatively, since the greatest red-shift is observed in CH_2Cl_2 – this may be indicating that poorer solvation in the other solvents is playing a role. The excited state of **76** is therefore more likely to possess a greater dipole moment than its ground state.

5.3.3 UV-Vis Acid Titration Spectra

In order to further probe the nature of the bands observed in the UV-Vis spectra of **74**, **75**, and **76**, acid titration spectra were carried out. This procedure involved the addition

of aliquots of trifluoroacetic acid (TFA) at 0.1 M concentration to a cuvette with a 1×10^{-5} M solution of the relevant compound. The absorbance was measured after each addition. The spectrum obtained after addition of TFA (up to 800 μL) to **74** is displayed in Fig. 5.29, with an inset displaying a magnified view of the region between 400-600 nm.

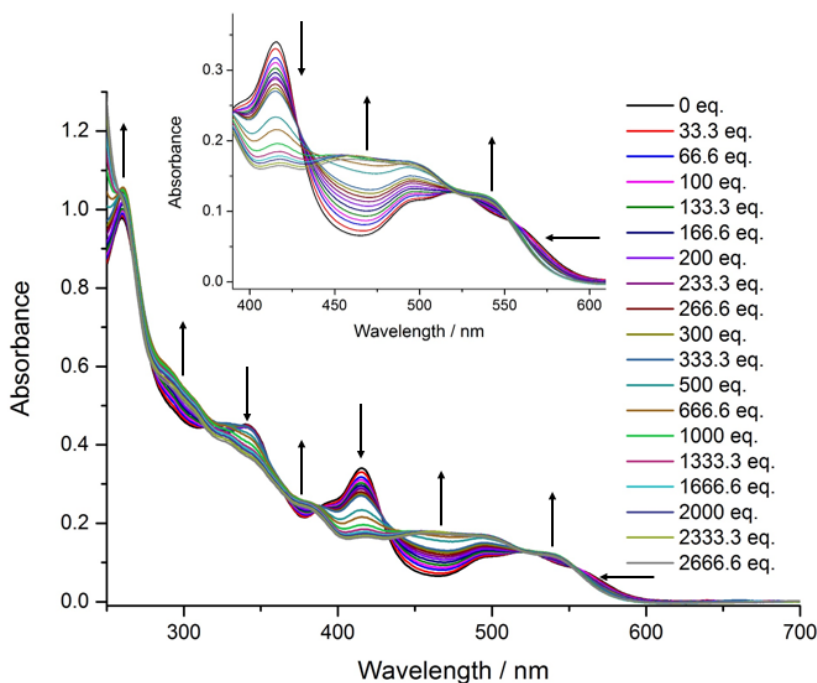


Figure 5.29: The effect of addition of aliquots of TFA (0.1 M in CH_2Cl_2) to the UV-Vis absorption spectrum of **74** (1×10^{-5} M, CH_2Cl_2 , RT). Arrows indicate direction of increase/decrease in band absorbance/wavelength.

In some instances, increases in absorbance are observed, and in others, decreases in absorbance. Below *ca.* 350 nm, the changes are not as pronounced. The band at $\lambda = 261$ nm increases slightly with acid addition, which is more indicative of $\pi\text{-}\pi^*$ nature rather than $\text{n-}\pi^*$, and a shoulder begins to emerge at *ca.* 290 nm due to the newly-protonated species. A significant decrease in absorbance is exhibited by the band at $\lambda = 341$ nm, indicating that it possesses some $\text{n-}\pi^*$ character. The protonation of a lone-pair results in the formation of a σ -bonding orbital from the previous n orbital, leading to the gradual decrease in intensity of absorption bands derived from $\text{n-}\pi^*$ transitions.⁴⁶ A further significant decrease is exhibited by the band at $\lambda = 416$ nm, also suggesting that this band possesses strong $\text{n-}\pi^*$ character. A new band appears at 465 nm, arising from the protonated species. The intensity of the band at $\lambda = 496$ nm increases slightly with acid addition. Isosbestic points are visible at $\lambda = 524$ nm and 555 nm, where the protonated and neutral species are in equilibrium.⁴⁷ A decrease in intensity, and a slight hypsochromic shift, is displayed by the band at 555 nm. At higher

concentrations, beyond 500 equivalents of TFA, the isosbestic points become less clearly observed. This is most likely a result of the high acid concentrations affecting the intrinsic properties of the solvent (such as ionic strength and refractive index).⁴⁸ The acid titration spectrum of **75** is displayed in Fig. 5.30. The most noticeable feature is the significant decrease in intensity of the absorbance band attributed to the coumarin 6 ligands ($\lambda = 488$ nm), indicating that this possesses a very strong degree of $n\text{-}\pi^*$ character. In a previous report, this band was attributed to $\pi\text{-}\pi^*$ transitions,²⁶ but the results obtained here are much more strongly suggestive that this band is predominantly $n\text{-}\pi^*$ in character.

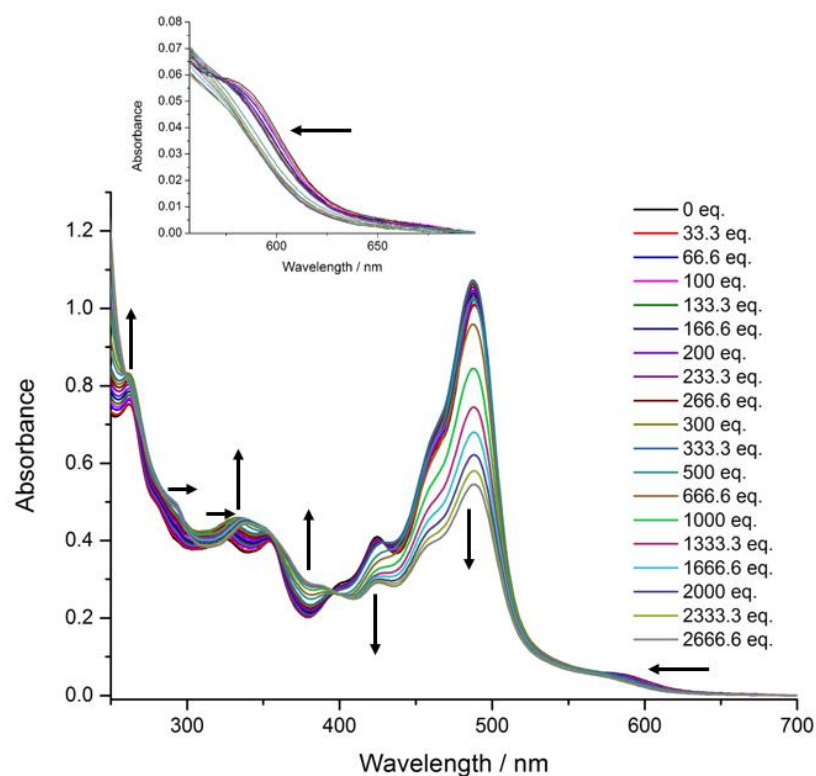


Figure 5.30: The effect of addition of aliquots of TFA (0.1 M, CH_2Cl_2) to the UV-Vis absorption spectrum of **75** (1×10^{-5} M, CH_2Cl_2 , RT), with inset, the region between 550-700 nm.

The band at $\lambda = 425$ nm is also observed to decrease upon acid addition. An isosbestic point is evident at $\lambda = 395$ nm. The low-energy band at $\lambda = 578$ nm (Fig. 5.30, inset) is observed to shift hypsochromically upon acid addition, in common with the behaviour of **74**. An increase in absorbance occurs at 379 nm. The band at $\lambda = 355$ appears largely unaffected by protonation, however the band at $\lambda = 324$ nm displays a significant bathochromic shift. The titration of **75** therefore shows that the most intense absorption band at $\lambda = 488$ nm is strongly

$n\text{-}\pi^*$ in character, whereas the other bands are less sensitive, and more suggestive of $\pi\text{-}\pi^*$ character.

The effect of protonation on the UV-Vis absorption spectrum of **76** (Fig. 5.31) is in general less pronounced than that exhibited by **75**. The region beyond *ca.* 480 nm shows minor changes upon protonation, with the same hypsochromic shift being observed for the low-energy band at $\lambda = 567$ nm, as was observed for the previous two complexes (Fig. 5.31, inset). The band at $\lambda = 420$ nm undergoes a gradual decrease in intensity after protonation, indicating $n\text{-}\pi^*$ character. The same trend is observed for the bands at $\lambda = 329$ and 347 nm. The intense band at 262 nm is shown to decrease very gradually with acid addition. As before, the isosbestic points become less clear at higher acid concentrations (beyond 500 equivalents). The small magnitude of the decrease in this band's intensity supports its assignment as $\pi\text{-}\pi^*$ based. Overall, this complex displays only very minor sensitivity to protonation, particularly the $\lambda = 500\text{-}600$ nm region (MLCT). In general, the absorption spectra of the three complexes appear to exhibit very low sensitivity to protonation, particularly considering the high concentration of acid required to induce spectral changes. Only **75** yielded a significant change, the decrease in absorbance of the band attributed to the coumarin-6 moiety.

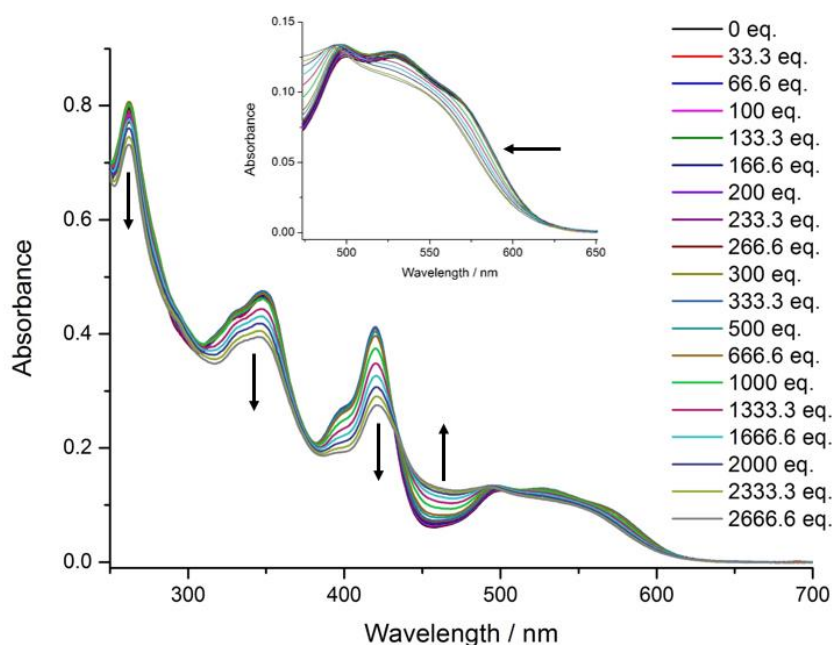


Figure 5.31: The effect of addition of aliquots of TFA (0.1 M, CH_2Cl_2) to the UV-Vis absorption spectrum of **76**, with inset, the region between 450-650 nm (1×10^{-5} M, CH_2Cl_2 , RT).

5.3.4 Emission Spectra of Ir(III) Complexes

The emissive behaviour of the three Ir(III) complexes was investigated. The emission and excitation spectra of the precursor ligand **70** are displayed in Fig. 5.32, for comparison with the final Ir(III) complexes. The emissive behaviour of this ligand has been previously reported, and the spectra obtained here are in agreement.⁴¹ Excitation of **70** at 390 nm provides the emission spectrum in Fig. 5.32, and an excitation spectrum monitoring the emission maximum at $\lambda_{\text{max}} = 520$ nm provides an excitation spectrum which is a good match for the UV-Vis spectrum. There is no fine-structure evident in the emission spectrum, even though the molecule is expected to have a degree of rigidity.

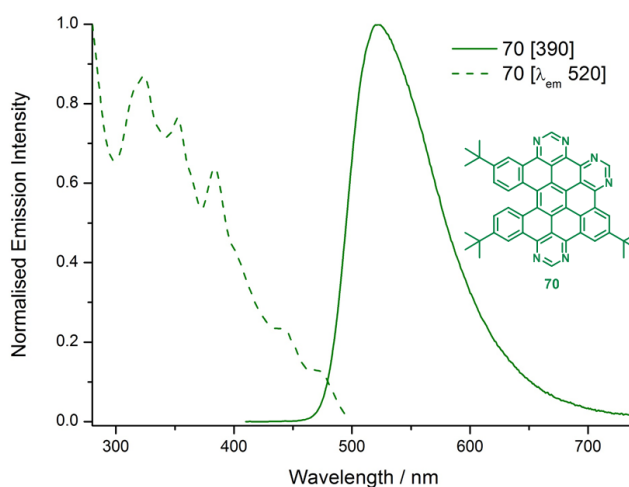


Figure 5.32: The emission (solid line, $\lambda_{\text{exc}} = 390$ nm) and excitation (dashed line, $\lambda_{\text{em}} = 520$ nm) of precursor ligand **70**.

Since **74** exhibited good solubility in CH_2Cl_2 , the emissive behaviour of this complex was initially investigated in this solvent. It was subsequently noted that a much improved emission spectrum was obtained in CH_3CN . The emission and excitation spectrum of **74** in argon-degassed CH_3CN is displayed in Fig. 5.33.

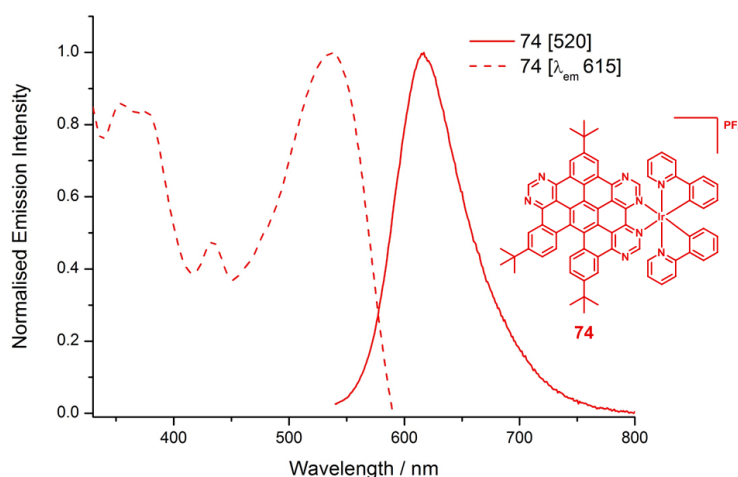


Figure 5.33: The emission (solid line, $\lambda_{\text{exc}} = 520$ nm) and excitation (dashed line, $\lambda_{\text{em}} = 615$ nm) of Ir(III) complex **74**.

The complex is only very weakly luminescent, suggesting that decay of the excited state by non-radiative means is quite efficient. The emission exhibits a maximum at $\lambda_{\text{em}} = 616$ nm. The broad emission profile of **74** suggests MLCT-based emission rather than ligand-centred/intraligand (LC/IL) which often exhibits fine structure. The excitation spectrum indicates emission is most intense from the region of the UV-Vis spectrum assigned to the MLCT region ($\lambda = 520$ nm). The very low luminescence from **74** led to a quantum yield below $\Phi = 0.001$ %, with comparison to $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$. The lifetime of emission, recorded in degassed CH_3CN , was calculated with a bi-exponential decay function, giving the lifetime as being composed of two contributions: $\tau = 490$ ns (93 %) and 61 ns (7 %). As ligand-centred/intra-ligand states generally give very long lifetimes, the lifetime obtained for **74** is more indicative of MLCT-based emission. The lifetime of the similar complex $[\text{Ir}(\text{ppy})_2(\text{bpy})](\text{PF}_6)$ is slightly shorter than that of **74**, at $\tau = 390$ ns.⁴⁹

The emission spectrum of **75** is presented in Fig. 5.34. The excitation spectrum (detected at $\lambda = 570$ nm, is also presented, and indicates emission from the MLCT/coumarin 6 region. The excitation spectrum detected at the emission maximum, $\lambda_{\text{em}} = 530$ nm, is in agreement with that detected from the shoulder at $\lambda = 570$ nm (Fig. 5.35) but the spectral window is limited at this detection wavelength due to instrumental limitations. This complex was relatively non-emissive, in common with **74**, and the quantum yield of emission, measured against $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ was also below $\Phi = 0.001$ %. The emission from **75** ($\lambda_{\text{em}} = 530$ nm) occurs in the same region as the free N^{^N} ligand ($\lambda_{\text{em}} = 520$ nm), but in the case of **75**, additional shoulders are observed at $\lambda_{\text{em}} = 570$ and 625 nm.

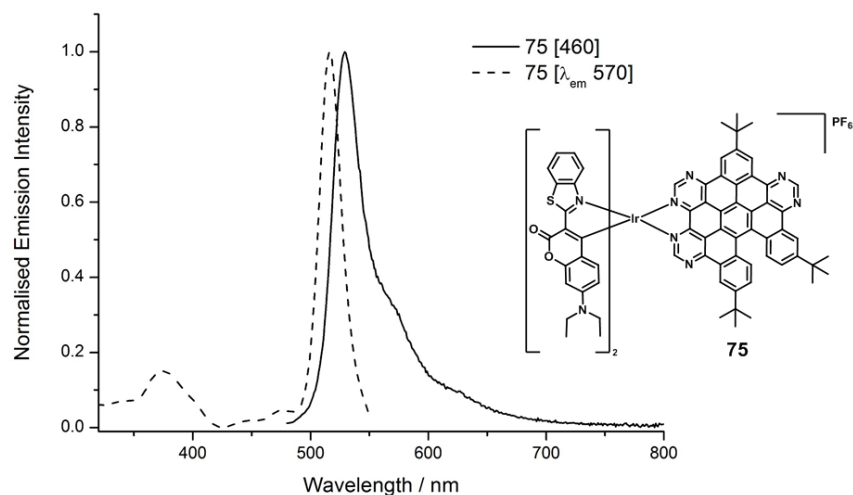


Figure 5.34: The emission (solid line, $\lambda_{exc} = 460$ nm) and excitation (dashed line, $\lambda_{em} = 570$ nm) of Ir(III) complex **75**.

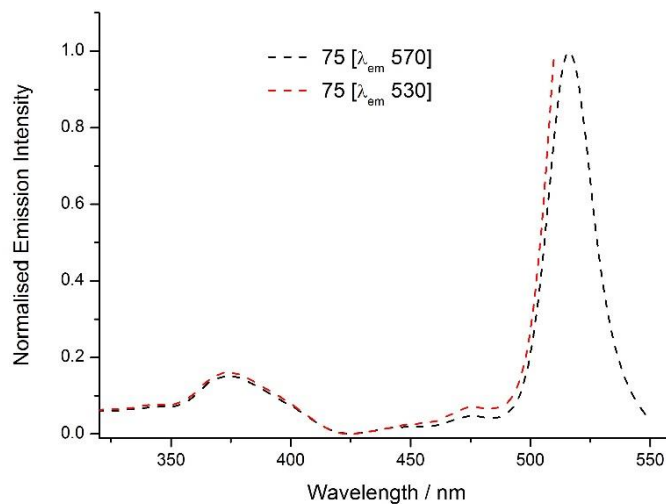


Figure 5.35: Comparison of excitation spectra of **75**, detected at 570 nm (black line) and 530 nm (red line).

The lifetime of the emission of **75** was observed to be extremely short. Bi-exponential fitting of the lifetime decay curve gave a lifetime of $\tau = 1.9$ ns (89 %) and 9.4 ns (11 %). The very low intensity of the emission of **75** made recording the lifetime challenging. The 1.9 ns component of its lifetime may have been influenced or introduced by the laser light source. The emissive properties of **75** suggests that decay of the excited state by non-radiative means is competing very strongly with the emissive processes. The complex **76** gave a much more red-shifted emission than that observed for **74** and **75**, but remained relatively non-emissive. The emission and excitation spectra of **76** are displayed in Fig. 5.36.

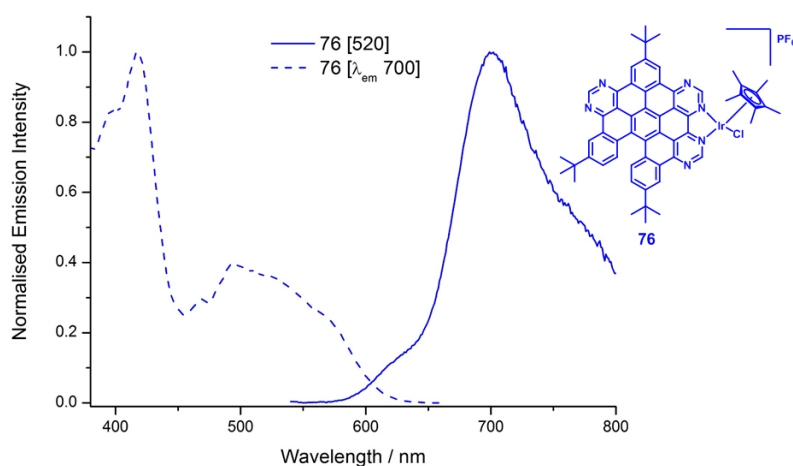


Figure 5.36: The emission (solid line, $\lambda_{exc} = 520$ nm) and excitation (dashed line, $\lambda_{em} = 700$ nm) of Ir(III) complex **76**.

The emission spectrum of **76** is relatively broad and centred at an emission maximum of $\lambda_{em} = 700$ nm. The excitation spectrum indicates emission is derived from the area in the absorption spectrum assigned as being MLCT in origin. The quantum yield of this complex was again very low. The relatively broad nature of the emission profile of **76** and its very short lifetime (1.7 ns (3 %), 7.8 ns (97 %)) are suggestive that the emissive state of this complex is CT-based, rather than LC/IL. Ir(III) complexes often possess T_1 (lowest excited states) of mixed character. It appears that the T_1 states of these complexes are predominantly MLCT-based, however given the complex structural nature of **74**, **75**, and **76**, this remains a tentative assignment.

5.3.5 Emission Solvatochromism of Ir(III) Complexes 74-76

In order to further study the nature of the emissive states of these Ir(III) complexes, the effect of solvent polarity on the energies of their excited states was probed. The resulting emission spectra are displayed in Fig. 5.37. It is immediately evident that all three complexes exhibit quite different behaviours.

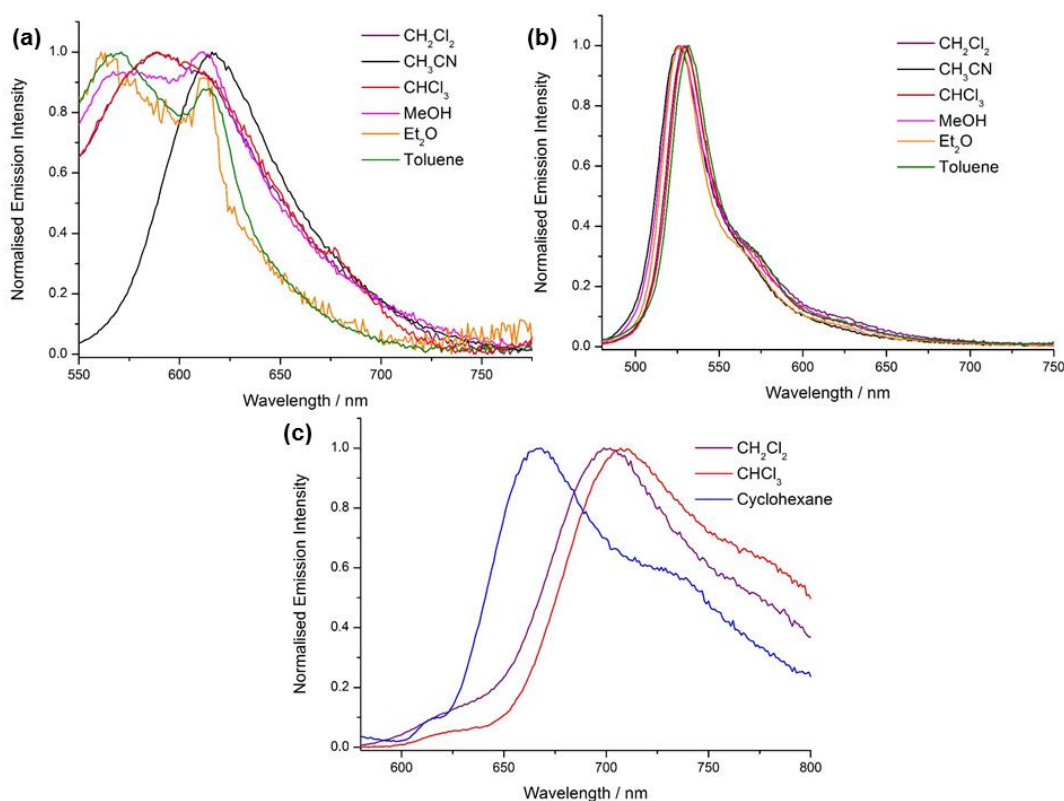


Figure 5.37: The effect of solvent polarity on the emission spectra of (a) **74** ($\lambda_{exc} = 520$ nm), (b) **75**, ($\lambda_{exc} = 460$ nm), and (c) **76** ($\lambda_{exc} = 520$ nm). In all cases, concentration was 1×10^{-5} M.

In the case of **74**, the only well-defined emission is observed in CH_3CN , with all other solvents giving quite different emission behaviour (Fig. 5.37 (a)). This is attributed to what appears to be much lower solubility and/or also much lower emissivity in the other solvents, as evidenced by the high degree of noise in the spectra, in comparison with that recorded in CH_3CN . The peak observed at $\lambda_{em} = 616$ nm in CH_3CN , is also observed in the other chosen solvents, and the sensitivity of this band towards solvent polarity appears rather minor (*e.g.* in CH_3CN , $\lambda_{em} = 616$ nm, whilst in MeOH $\lambda_{em} = 612$ nm, and in CH_2Cl_2 , $\lambda_{em} = 614$ nm). A new band is apparent at $\lambda \approx 570$ nm, which is not observed in CH_3CN . It appears relatively insensitive to solvent polarity, and is not clearly resolved in CH_2Cl_2 or CHCl_3 . This may be attributable to $\pi\text{-}\pi^*$ emission from the appended $\text{N}^{\wedge}\text{N}$ ligand, based upon its position. Different behaviour is observed for **75** which maintains its spectral profile in the range of solvents studied (Fig. 5.37 (b)). The emission maximum at $\lambda_{em} = 530$ nm appears relatively insensitive to varying solvent polarity, but exhibits a trend pointing towards negative solvatochromism, as a shift to higher energies is observed in more polar solvents (*e.g.* in MeOH , $\lambda_{em} = 526$ nm, whilst in the less polar toluene, $\lambda_{em} = 532$ nm). The enhanced solubility

of **75** is likely due to the coumarin 6 cyclometallating ligands, and their carbon chains. An opposite trend is observed for the poorly-emissive **76**, which only yielded emission spectra in a small range of solvents (Fig. 5.37 (c)). However, a large solvatochromic shift was observed for **76**, which gave emission maxima of $\lambda_{\text{em}} = 700$ nm in CH_2Cl_2 , and $\lambda_{\text{em}} = 667$ nm in cyclohexane. In the slightly more polar CHCl_3 , a bathochromic shift was observed to $\lambda_{\text{em}} = 709$ nm, indicating that the excited state is stabilised in more polar media, and that the dipole moment associated with the excited state is therefore higher than that of the ground state.

5.3.6 Further Photophysical Investigation of **74**, **75**, and **76**

The effect of the presence of oxygen on the emissive properties of the complexes was also investigated. A significant decrease in the emission intensity from an aerated sample vs. a degassed sample is indicative of long-lived triplet states that are quenched by collisions with molecular oxygen. The emission spectra arising from aerated and degassed samples of **74**, **75**, and **76** are presented in Fig. 5.38. Both **74** and **75** display almost no sensitivity towards the presence of oxygen, suggesting that the excited states may possess some ligand-centred character, as well as CT. Their almost non-emissive nature does however make the definitive assignment more difficult. The extended tail of the emission spectrum of **75** appears to show a degree of sensitivity towards oxygen. The Cp^* complex **76** displays a slightly higher sensitivity towards the presence of oxygen, but still does not display a significant degree of quenching. Attempts to record low-temperature emission spectra of **74** and **75** were not successful, as at 77 K, the complexes appeared to be non-luminescent. It may be the case that the complexes are so weakly luminescent that it was not possible to observe a signal above the background noise level in the 77 K spectrum. It was, however, possible to obtain an emission spectrum of **76** at 77 K, which is displayed in Fig. 5.39. The emission maximum is observed to have shifted from $\lambda_{\text{em}} = 700$ nm in solution, to $\lambda_{\text{em}} = 659$ nm in the glass. The hypsochromic shift observed in the glass, compared to the solution emission spectrum, indicates a charge-transfer transition, where the dipole moment associated with the excited state no longer experiences a solvent relaxation effect, due to the inability of the surrounding solvent molecules to reorient their dipoles in the rigid medium.⁵⁰

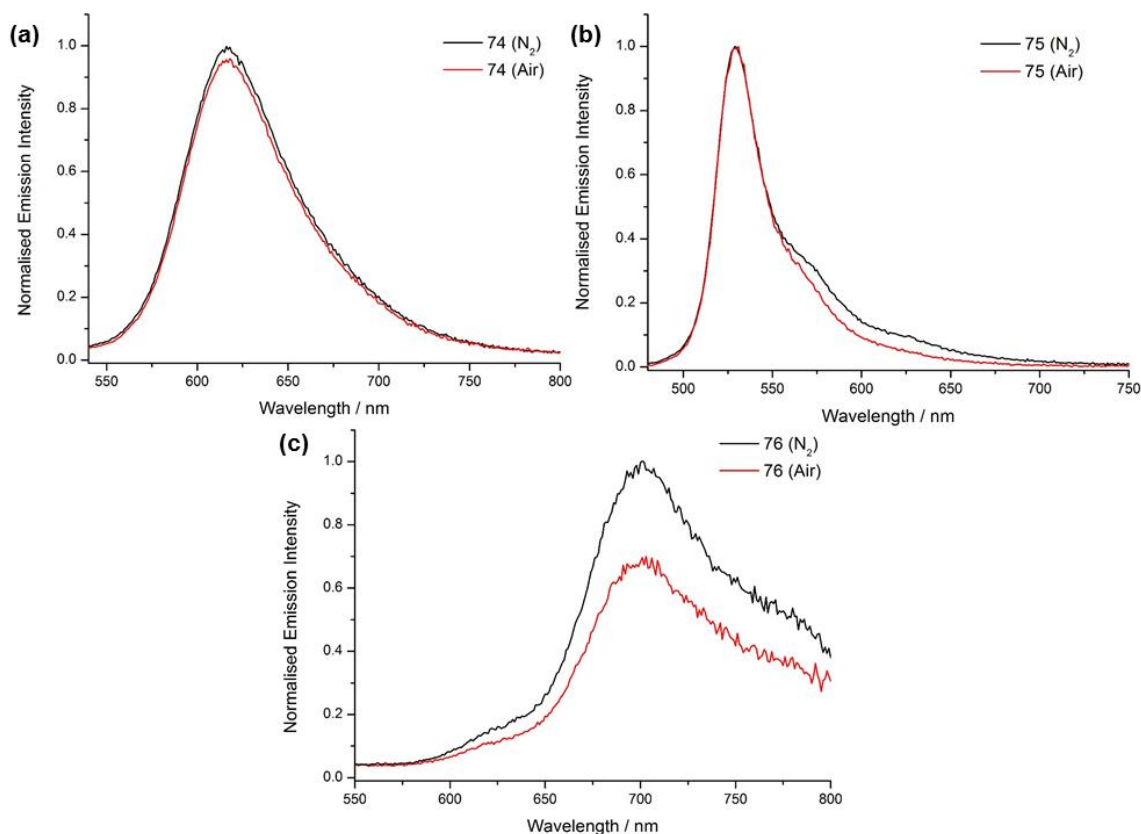


Figure 5.38: RT emission spectra of (a) **74** ($\lambda_{exc} = 460$ nm), (b) **75** ($\lambda_{exc} = 520$ nm), and (c) **76** ($\lambda_{exc} = 520$ nm), recorded in N_2 -degassed solutions (black lines) and aerated solutions (red lines). The concentration of the solutions was 1×10^{-5} M in all cases.

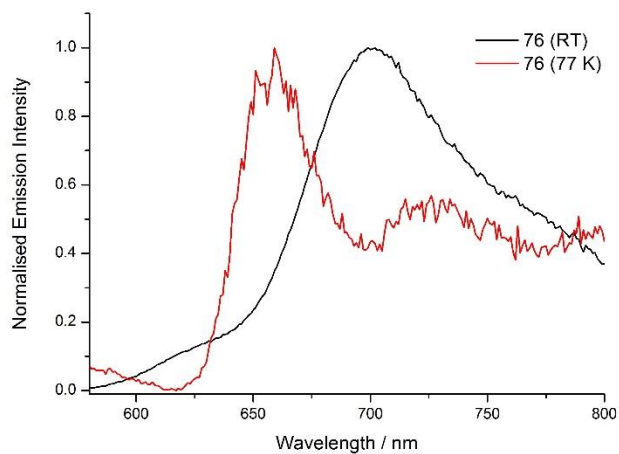


Figure 5.39: The RT (298 K, black line, 1×10^{-5} M, CH_2Cl_2) and LT (77 K, red line, 1×10^{-5} M, recorded in a 4:1 EtOH/MeOH glass) emission spectra of **76**.

Table 5.4: Emission, lifetime and quantum yield data for compounds **70**, **74**, **75**, and **76**.

Compound	Medium (Temp.)	λ_{em} [nm] (λ_{exc} [nm])	Lifetime τ [ns] ($\lambda_{\text{exc}}/\lambda_{\text{em}}$ nm)	Φ_{em}
70	CH ₂ Cl ₂ (RT)	520 (390)	7.2 (370/520)	0.37
74	CH ₂ Cl ₂ (RT)	616 (460)	490 (93 %), 61 (7 %) (370/615)	0.0002
75	CH ₂ Cl ₂ (RT)	530, 570 _{sh} , 625 _{sh} (460)	1.92 (89 %), 9.4 (11 %) (370/530)	0.0004
76	CH ₂ Cl ₂ (RT) 4:1 EtOH/MeOH (77 K)	700 (520) 659 (520)	1.7 (3 %), 7.8 (97 %) (370/700)	0.008

5.4 Electrochemical Properties of Ir(III) Complexes **74**, **75**, and **76**

The complexes were further characterised by cyclic voltammetry (CV), in 1×10^{-4} M solutions, under N₂. A detailed description of the experimental setup is given in Chapter Seven. The potentials quoted here are vs. the Fc/Fc⁺ oxidation (0.0 V). The solvent chosen for the measurements was CH₂Cl₂, as initial attempts to record measurements in CH₃CN gave much poorer resolution. The electrochemical behaviour of **70** has been previously investigated, and is presented here as a reference to the behaviour of the Ir(III) complexes.⁴¹ The oxidation scans of the ligand **70**, and Ir complexes **74**, **75**, and **76** are presented in Fig. 5.40. Electrochemical data for these complexes is presented in Table 5.5.

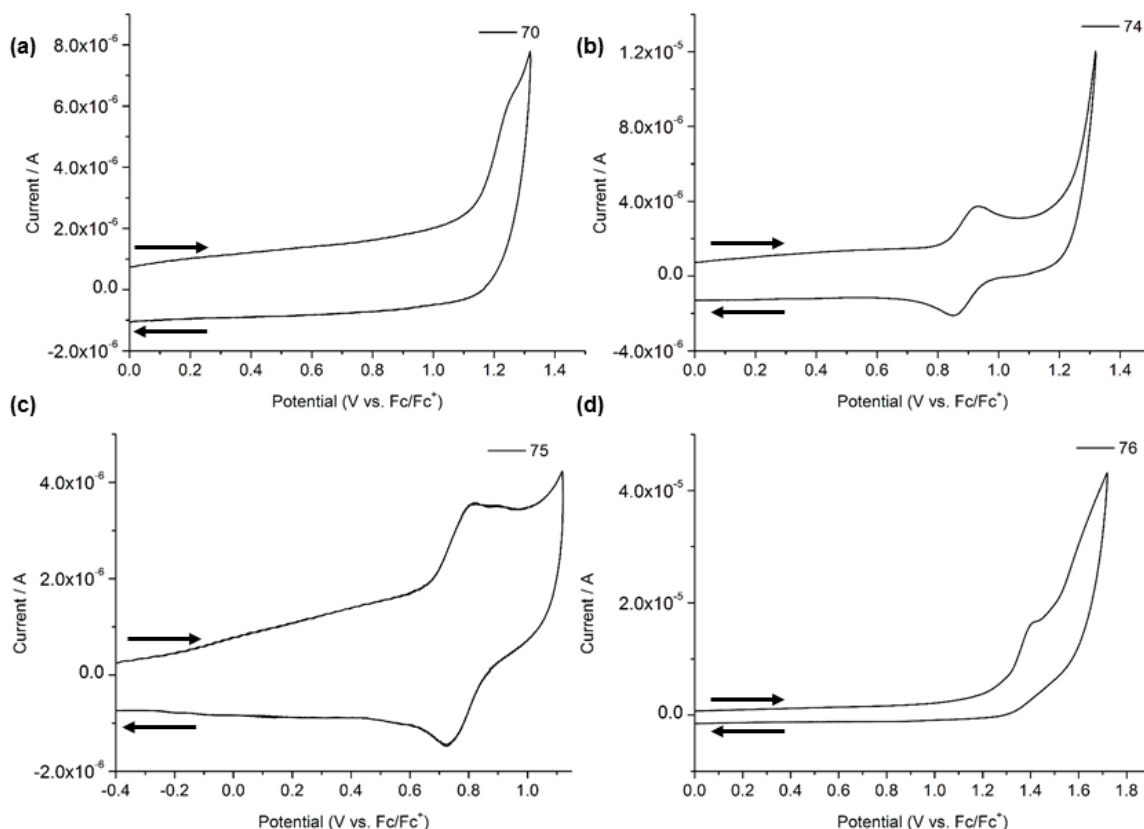


Figure 5.40: Cyclic voltammograms showing the oxidation processes observed for (a) **70**, (b) **74**, (c) **75**, and (d) **76** (recorded as 1×10^{-4} M solutions in 0.1 M TBAPF₆, scan rate 0.1 V/s, vs Fc/Fc⁺).

The free ligand **70** displays a single irreversible oxidation at 1.26 V (Fig. 5.40 (a)), which is in agreement with the previous report.⁴¹ The ppy-containing **74** displays a first reversible oxidation at 0.89 V (Fig. 5.40 (b)). Based upon the previous report of the analogous complex [Ir(ppy)₂(bpy)](PF₆) exhibiting a reversible oxidation wave at 0.86 vs. Fc/Fc⁺,⁵² the value obtained for **74** is therefore very similar. The $E_{1/2}$ value (calculated from the difference between the cathodic and anodic peaks, $E_{pa}-E_{pc}$) is close to the theoretical value for a fully-reversible couple of 59 mV, indicating that this is a reversible oxidation process.⁵³ This process has been previously assigned as being principally the Ir(III)→Ir(IV) oxidation.²¹ In complexes such as these, there is thought to be a strong contribution to the HOMO from the cyclometallating ligands, which if substantial, leads to a progressively more irreversible oxidation process.⁵⁴ This irreversibility arises from the removal of an electron from the Ir($d\pi$)- σC^- orbital, leading to weakening and subsequent breaking of the Ir-C⁻ bond, meaning that σ -bond orbital oxidation is generally irreversible.⁵⁵ An oxidation process which is only metal-based is generally fully reversible.²¹ The primarily metal-based Ir(III)→Ir(IV)

oxidation observed for **74** is therefore also likely to contain a minor degree of contribution from the ppy ligands. A similar oxidation couple is observed for **75**, at 0.77 V. This is less positive than the oxidation of **74**, indicating that the conjugated coumarin 6 ligands provide more stabilisation of the HOMO level than the ppy ligands.

An irreversible oxidation is observed for **76** (Fig. 5.40 (d)) at 1.40 V. Given that the emission of **76** is characteristic of a CT state, it is likely that the T_1 state of this complex is mixed in character, and the HOMO is not entirely centred upon the Ir(III) centre. If the HOMO was predominantly sited on the Ir(III) centre, a reversible process would be expected. The cyclometalating Cp^* may be contributing to the HOMO, and has resulted in an irreversible oxidation process, possibly due to removal of an electron from a $Ir(d\pi)-\sigma C^-$ orbital, as discussed above. Caix *et al.* have reported that the complexes $[Cp^*Ir(bpy)Cl]^+$ and $[Cp^*(phen)Cl]^+$ display irreversible oxidations at $E_p = 0.92$ V and 0.88 V respectively (reported as 1.40 V and 1.36 V, respectively, vs. Ag/AgCl, converted to approximate Fc/Fc^+ scale by subtraction of 0.48 V).³⁴ They assigned this process to the oxidation of the metal-bound Cp^* ring. It is therefore likely that the irreversible oxidation observed for **76** ($E_p = 1.40$ V) is derived from a Cp^* -based oxidation process. This occurs at much more positive potentials than for the complexes investigated by Caix *et al.*, suggesting that the HOMO of **76** is much less stabilised.

The corresponding reduction scans associated with compounds **70**, **74**, **75**, and **76** are presented in Fig. 5.41. The free $N^{\wedge}N$ ligand **70** displays three major reduction processes, at $E_{1/2} = -1.89$, and -2.08 V, which are quasi-reversible (Fig. 5.41 (a)). A further reduction is observed at $E_p = -1.56$ V, which is assigned as being irreversible due to the high degree of separation of the reduction and return waves. These reductions are attributed to stepwise reductions, most likely of the pyrimidyl moieties. A very similar pattern is observed for the reduction scan of **74**, however the reduction waves are significantly more positive than for the free ligand (Fig. 5.41 (b)). This indicates that the LUMO of **74** is localised on the $N^{\wedge}N$ ligand, and is substantially stabilised (*i.e.* easier to reduce) in comparison with the free ligand. The first reduction of the analogous complex $[Ir(ppy)_2(bpy)]^+$ has been reported as occurring at -1.77 V (vs. Fc/Fc^+), and has been assigned as a one-electron reduction of the bpy ($N^{\wedge}N$) moiety.⁵² Ohsawa *et al.* report a further three more negative reduction processes at -2.42 , -2.77 , and -3.00 V, which are assigned to further one-electron reductions of the previously reduced bpy, and also the two ppy ligands.⁵² The three reduction processes observed for **74** are therefore highly likely to be derived from the $N^{\wedge}N$ ligand, as reduction

of the ppy moieties would be expected to be observed beyond the solvent window. The reduction behaviour of **75** (Fig. 5.41 (c)) is again very similar to that of **74**, indicating that the LUMO of this compound is primarily based upon the N[^]N ligand. Comparing the $E_{1/2}$ potentials observed for **74** and **75**, they are slightly shifted. The first reduction of **74** is observed at -0.92 V, whereas for **75** the first reduction is observed at -0.77 V. This indicates that **74** is therefore more difficult to reduce, and that the energy of the LUMO of **75** appears to have been substantially lowered. Takizawa *et al.* have reported the bpy-substituted analogue of **75**, the complex $[\text{Ir}(\text{coumarin } 6)_2(\text{bpy})](\text{PF}_6)$.⁴⁴ They report an oxidation wave for this complex at $E_{1/2} = 0.68$ V, and a reduction wave at $E_{1/2} = -1.62$ V (vs. Fc/Fc^+). They also report a similar complex, with a more conjugated ligand, 2,2'-biquinoline (bqu), of formula $[\text{Ir}(\text{coumarin } 6)_2(\text{bqu})](\text{PF}_6)$. This complex exhibited an oxidation wave at $E_{1/2} = 0.73$ V, and a reduction wave at $E_{1/2} = -1.18$ V. The more conjugated complex therefore appears to be reduced at less negative potentials. It is therefore likely that the enhanced conjugation introduced by N[^]N ligand **70** has resulted in a significant decrease in the LUMO energy of **75** relative to these literature examples.

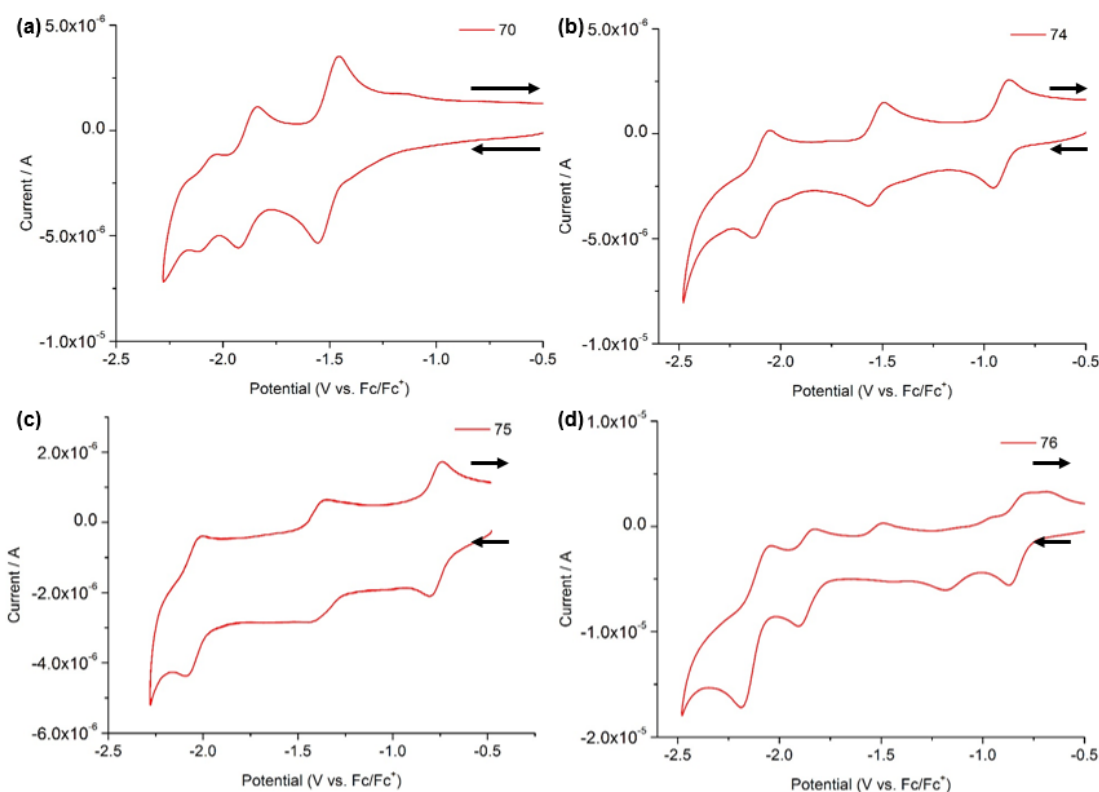


Figure 5.41: Cyclic voltammograms showing the reduction processes observed for (a) **70**, (b) **74**, (c) **75**, and (d) **76** (recorded as 1×10^{-4} M solutions in 0.1 M TBAPF₆, scan rate 0.1 V/s, vs Fc/Fc^+).

The three well-defined reduction waves that are attributed to the N[^]N ligand in **74** and **75** are not as clearly defined in the reduction scan of **76** (Fig. 5.41 (d)). Several reduction processes are observed, the first of which appears as a poorly defined couple at $E_{1/2} = -0.83$ V. Second and third reduction processes are observed at $E_{1/2} = -1.06$ V and $E_p = -1.49$ V respectively. The LUMO of this complex appears to be similar in energy to those of **74** and **75**. Kaim *et al.* suggest that reduction of the similar complex $[\text{Cp}^*\text{Ir}(\text{bpy})\text{Cl}]^+$ by cyclic voltammetry leads to dissociation of the chloride ligand.⁵⁶ They report reductions for this complex at $E_p = -1.08$ V and $E_p = -1.43$ V (vs. Fc/Fc^+), and a further reduction at $E_{1/2} = -2.82$ V, the latter being assigned to a bpy-based reduction. They assign the initial reduction as being a two-electron reduction of the metal centre ($\text{Ir(III)} \rightarrow \text{Ir(I)}$). Caix *et al.* also report that the reduction of the same complex, $[\text{Cp}^*\text{Ir}(\text{bpy})\text{Cl}]^+$, is due to the same two-electron reduction of the metal centre. They observed a slow reduction process at *ca.* -1.65 V vs. Fc/Fc^+ (reported as -1.17 V vs. Ag/AgCl) with a return peak exhibiting a large separation to the initial reduction peak ($\Delta E_p = 390$ mV). This process is believed to be coupled to the loss of the chloride ligand, resulting in a tri-coordinated complex. In relation to **76**, the first reduction process appears complex with two anodic peaks in close proximity. The couple at -0.83 V is assigned to the N[^]N ligand, based upon its electrochemical reversibility. The other nearby anodic peak may be a return peak associated with the reduction of the Ir centre. The very sluggish reduction observed at $E_p = -1.19$ V is attributable to the metal-based reduction process ($\text{Ir(III)} \rightarrow \text{Ir(I)}$). The return wave for this process is poorly defined. At more negative potentials, a poorly defined anodic peak is observed at $E_p = -1.49$ V, which has no clearly defined corresponding cathodic peak. The nature of this peak is unclear, and is therefore tentatively assigned as a metal-based process, since the reduction of the N[^]N ligand would be expected to be reversible (by comparison to the behaviour of **70**). The remaining reduction processes (respectively, $E_{1/2} = -1.87$, $E_p = -2.19$ V) are assigned to the N[^]N ligand.

Table 5.5: Electrochemical data for **70**, **74**, **75**, and **76** (all values quoted vs. Fc/Fc^+). * denotes irreversible process, and E_p value is quoted.

Compound	Oxidation	Reduction
	E_{pa}/V	$E_{1/2}\text{V}$, $[\Delta E_p/\text{mV}]$
70	1.26*	-1.56*, -1.89 [90], -2.08 [80]
74	0.89 [80]	-0.92 [70], -1.54 [70], -2.1 [80]
75	0.77 [90]	-0.77 [60], -1.40 [70], -2.05 [80]
76	1.40*	-0.83 [90], -1.19*, -1.49*, -1.87 [70], -2.19*

5.5 Conclusions and Future Work

This chapter has described the synthesis and characterisation of three novel Ir(III) complexes, all of which feature a bidentate ligand with a very high level of conjugation. The preparation of the N[^]N ligand **70** is challenging, particularly in amounts high enough for further investigation as a coordinating ligand. The application of such highly conjugated systems as coordinating ligands has little precedence in the literature. The Ru(II) complexes of N-HSB, and its half-cyclised analogue, exhibited interesting photophysical properties as NIR emitters. Initial work centred on determining whether **74** and **75** are NIR emitters has thus far proved inconclusive due to instrumental limitations, and this warrants future investigation. The relatively non-emissive nature of the complexes suggests a very efficient non-radiative decay pathway. This non-emissive behaviour has also resulted in the assignment of their emissive states being quite challenging. The lack of significant CT contribution is indicated by the lack of significant solvatochromism of the emission bands of these complexes. In the case of **76**, there does appear to be a more significant CT contribution, with reference to the slightly higher sensitivity towards oxygen, and the solvatochromic behaviour observed. The small Stokes shifts observed for **74** and particularly **75** are more indicative of fluorescence. Ladouceur *et al.* have reported that for a series of bis-cyclometalated Ir(III) complexes, those with ppy cyclometallating ligands and bpy

ligands functionalised with dimethylamino groups gave much reduced emission intensity from a $^3\text{ILCT}$ state.²¹ They observed a very-low intensity emission, assigned to a fluorescence mechanism, for a diethylamino-substituted complex, which they explained as being due to thermally-induced repopulation of the singlet state, from the triplet state. The Ir(III) complexes reported by Takizawa *et al.* displayed intriguing emissive properties.⁴⁴ The complexes $[\text{Ir}(\text{coumarin } 6)_2(\text{bpy})](\text{PF}_6)$ and $[\text{Ir}(\text{coumarin } 6)_2(\text{phen})](\text{PF}_6)$ (where phen is 1,10-phenanthroline) displayed emission maxima at $\lambda = 589$ nm, and gave lifetimes of 6.21 and 7.06 μs respectively. The nature of the emissive states of these complexes was assigned as ^3LC in nature, due to the fine structure observed. They also reported a similar complex, with a more conjugated ligand, which was non-emissive at RT, $[\text{Ir}(\text{coumarin } 6)_2(\text{bqu})](\text{PF}_6)$, (where bqu = 2,2'-biquinoline), but yielded an emission at $\lambda = 644$ nm at 77 K. They attributed the non-luminescent behaviour at RT to a fast non-radiative decay pathway. Since **74** and **75** appeared non-emissive at 77 K in the visible region (up to $\lambda = 850$ nm), it is intended to investigate whether any low-temperature emission is observed in the NIR region. The UV-Vis absorption profiles of **74**, **75**, and **76** are significantly shifted into the visible region (such compounds are known as 'black MLCT absorbers'),⁵⁷ due to the low-lying π -orbitals of the N^N ligand. The introduction of the coumarin 6 cyclometallating ligands into **75** resulted in a sizeable increase in the molar extinction coefficient, compared with the ppy-substituted analogue **74**. These properties might have been anticipated to lead towards promising applications as triplet photosensitisers. However, the very short emission lifetimes recorded for the complexes **74**, **75**, and **76** indicate that these Ir(III) complexes are not suitable candidates for applications where long-lived triplet states are required. The introduction of the coumarin 6 cyclometallating ligands appears to have led to a sizeable decrease in the lifetime of emission (**74**: 490 ns; **75**: 1.9 ns). This study has shed light on the intriguing behaviour of a highly conjugated asymmetric N^N ligand. The synthesis of **76**, with its different coordination sphere, led to a useful comparison of the emissive properties, as it exhibits more ^3CT character. The Pt(II) acetylides synthesised in Chapter Four featured conjugated ligands based upon 1,10-phenanthroline – a possible alternative to these ligands would be a compound such as **70** (Fig. 5.42 (a)).

Future work is aimed towards examining whether any emission is derived from **74**, **75** and **76** in the NIR region, at RT or 77 K. It would also be instructive to prepare the Ru(II) analogue of **74** (Fig. 5.42 (b)), to compare not only the different photophysical behaviour of these complexes, but also to compare to the behaviour of the Ru(II) complexes of N-HSB.

The ligand behaviour of the $\frac{2}{3}$ -fused analogue of **70** would also be of interest, although the preparation of this compound in amounts significant enough for further work would be expected to be challenging (Fig. 5.42 (c)). Given that Ir(III) half-sandwich complexes have been reported as exhibiting potential as catalysts and anticancer therapeutic agents, the investigation, with the aid of a suitable collaboration, of the biological or catalytic properties of **76** would also be relevant.

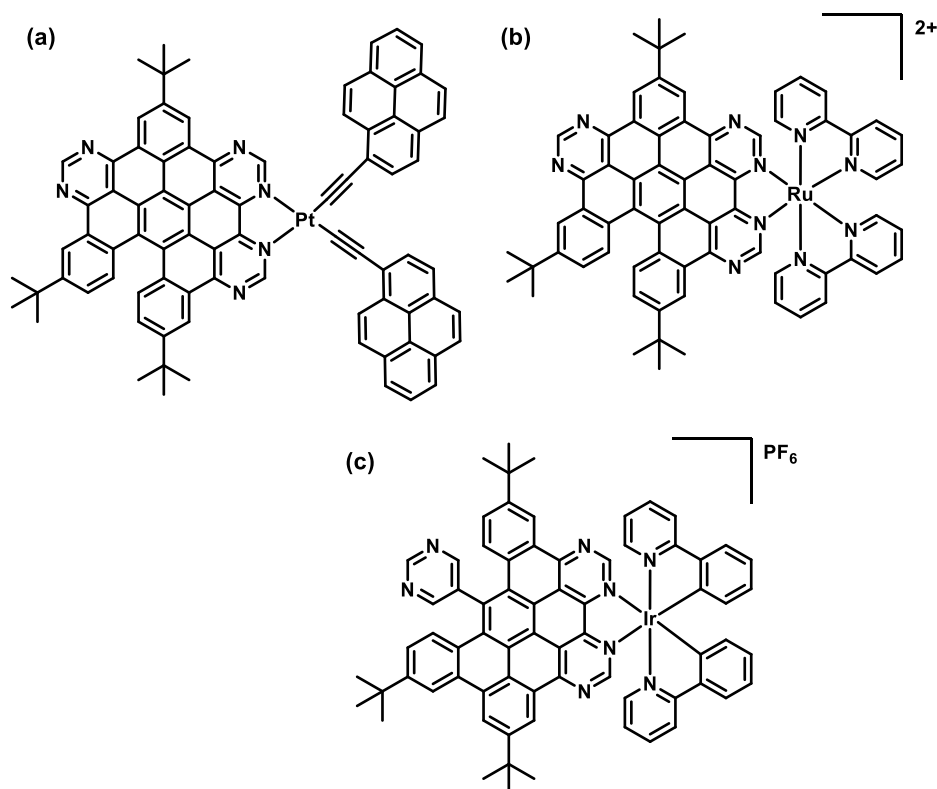


Figure 5.42: Possible metal complexes based upon N^N ligand **70**.

Potential routes to novel PAH-based compounds with two coordination sites are shown in Fig. 5.43. In Fig. 5.43 (a), a derivative of N-HSB is shown, with pyrimidinyl rings incorporated at either side. The synthesis of this compound would necessitate the preparation of a cyclopentadienone precursor with pyrimidinyl rings, which has not yet been reported, and which would be expected to be challenging to synthesise. The ligand in Fig. 5.43 (b) builds upon the work described in Chapter Four, incorporating a phen-based PAH, therefore exhibiting two different coordination sites. A potential synthetic route to a larger, extended system is displayed in Fig. 5.44, where a Diels-Alder cycloaddition between an ethynyl-functionalised biaryl and a phen-based precursor and subsequent cyclodehydrogenation would lead to a PAH with a very high degree of conjugation and two coordination sites. The dinuclear complexes that these ligands could generate would be of interest to probe metal-

metal interactions. Dinuclear metal complexes have been investigated for their photoactive properties, photoinduced charge separation and long-range electron transfer.^{58, 59} Energy transfer along predetermined pathways, of interest for electronic devices, can be achieved with careful ligand design.⁵⁹

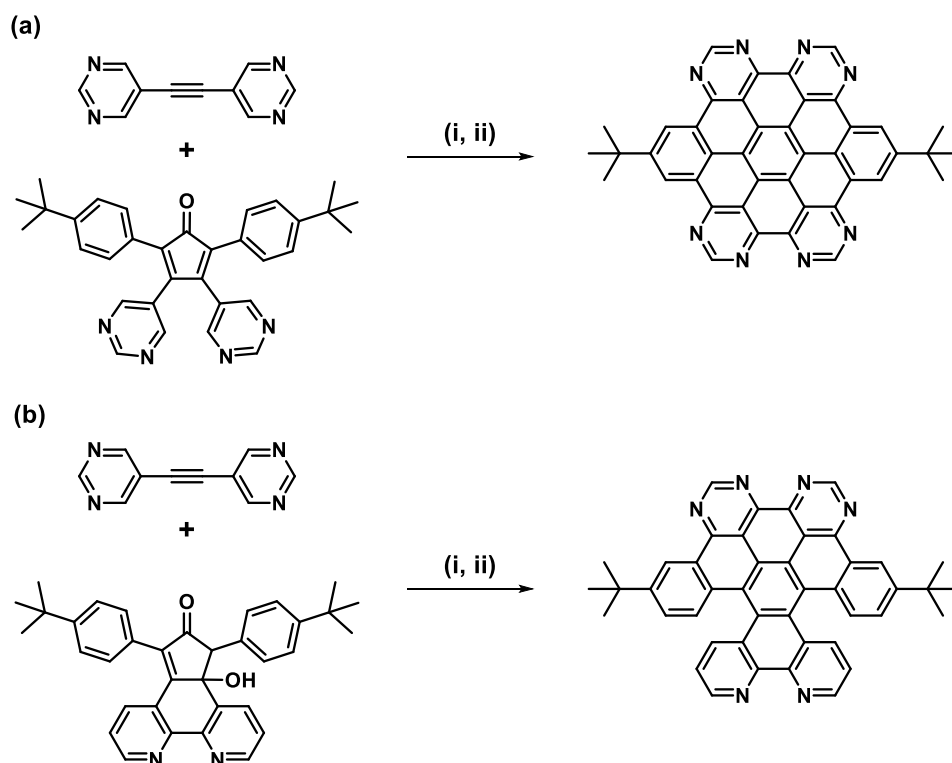


Figure 5.43: Future routes to PAH-based N^N coordinating ligands. (a) An N-HSB analogue. (b) A phen-based ligand with two N^N coordination sites. (i) Diels-Alder cycloaddition. (ii) Oxidative cyclodehydrogenation.

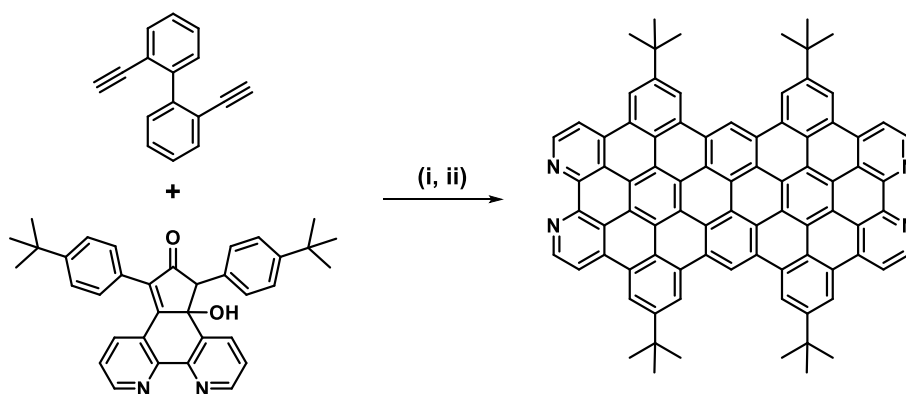


Fig. 5.44: Possible route to an extended PAH with two N^N coordination sites. (i) Diels-Alder cycloaddition. (ii) Oxidative cyclodehydrogenation.

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Chapter Five

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Chapter Six

Conclusions

6.1 General Conclusions

This section aims to give a brief summary of the work undertaken in this thesis and provide some concluding remarks. The four experimental chapters have each described various applications of PAH-based systems. The aim of this thesis was to extend the range of applications for a broad range of PAH-based systems, with a particular focus on those with N-substitution, since there is a relative scarcity of these in the literature due to the often challenging synthetic procedures required. A further aspect of this work involved the use of fully-fused, and also partially-fused systems, generated predominantly *via* oxidative cyclodehydrogenation with DDQ/H⁺, a method which has proven to be a useful and convenient means of generating PAH derivatives. The employment of extended, aromatic compounds, particularly those with N-substitution, as ligands in coordination complexes remains a topic which has many avenues left unexplored. The work described in this thesis, which details the behaviour of a number of transition metal complexes bearing PAH-based ligands in a variety of coordination modes is a small step towards a wider understanding of the behaviour of such extended ligand architectures.

Chapter Two gave an account of a rapidly developing field, on-surface chemistry. This technique represents a breakthrough as a means of preparing suitable organic frameworks on substrates for a variety of applications such as electronic devices and catalysis. The development of new materials suitable for this field has inspired a host of new PAH-based and polyphenylene-based precursors in the literature, and the rapid progress being made in the improvement of on-surface techniques has given access to frameworks that are inaccessible by traditional means. This chapter described the synthesis of a novel N-substituted PAH (**9**) designed for on-surface studies, with the aim of producing highly N-substituted graphene nanoribbons, with the possibility of creating extended porous frameworks. Two further N-substituted compounds, previously developed within the Draper group, were also subjected to the same on-surface studies. These compounds displayed intriguing dimer and trimer formation and on-surface cyclodehydrogenation, but did not form extended networks. The new phenanthrene-based **9** did, however, lead to the formation of short graphene nanoribbon-type structures. Although short, the ribbons formed by **9** provide a useful insight into the behaviour of larger PAH-based systems on reactive metal substrates. Work is ongoing to investigate whether lower surface coverage of the precursor material could lead to more optimal on-surface growth, and therefore lead to longer ribbons in greater abundance. This chapter also discussed the initial synthetic steps towards

intriguing hexaphenylbenzene-type precursors with a very high degree of N-substitution. The future investigation of the on-surface behaviour of these systems would represent another step towards understanding the utility of such materials, and their behaviour, for on-surface growth.

Chapter Three gave an account of a very different area of PAH-based chemistry. Pt(II) acetylides have garnered much research interest over the past few decades due to their intriguing photophysical properties, such as room-temperature phosphorescence. Building upon previous work on Pt(II) acetylides in the Draper group, this chapter described initial synthetic attempts towards such complexes with N[^]N[^]N coordinated Pt centres and HBC chromophoric cores. Access to *ortho* and *para* substituted ethynyl-HBC derivatives was made possible through oxidative cyclodehydrogenation of the iodo-substituted precursors via a DDQ/H⁺ mediated process, followed by a subsequent coupling of the required alkyne moiety. The synthetic challenges and solubility issues encountered during the preparation of the corresponding Pt(II) derivatives of these led to a modified synthetic pathway incorporating N[^]N[^]C cyclometallating ligands. The improved solubility of these compounds led to their characterisation and photophysical investigation. The broad emission profiles at RT observed for these compounds were suggestive of CT excited states, supported by their emission lifetimes being in the typical CT range. The sensitivity of these complexes to molecular oxygen suggested strong phosphorescent character. The preparation of these complexes represents a new family of organometallic HBC derivatives, of which there are relatively few in the literature. This chapter also presents a number of complexes based upon the structural motifs investigated, which are proposed for future study.

Chapter Four presented the synthesis and characterisation of a family of Pt(II) acetylides with N[^]N coordinating ligands based upon extended derivatives of 1,10-phenanthroline (phen). Utilising synthetic pathways previously developed in the Draper group to obtain two phen-based precursors, and extending the Diels-Alder methodology to yield two further phen-based precursors, these partially-fused PAH derivatives were then utilised as the N[^]N coordinating ligands for complexes of general formula [Pt(phen)(C≡C-pyrene)₂]. The aim of this work was to probe whether the extended conjugation, and therefore low-lying π* acceptor levels of these phen-based ligands could be an effective method for modulating the photophysical properties of their respective Pt(II) complexes. Significant synthetic challenges were encountered due to the poor solubility of these systems, but the judicious introduction of *tert*-butyl groups led to a variant with much

improved solubility. The photophysical investigation carried out on this family of complexes revealed room-temperature phosphorescence which was almost quantitatively quenched by molecular oxygen, and long lifetimes of emission. The emissive state of these complexes was proposed as being pyrene-based ^3IL . The emission from all complexes was remarkably similar, although a pyridazine-containing derivative proved almost non-luminescent. The emission profiles were observed to remain almost identical with increased conjugation, and corresponded remarkably closely to the literature results obtained for a much simpler 2,2'-bipyridine-based $\text{N}^{\wedge}\text{N}$ ligand. Initial studies revealed one of the complexes to behave as a relatively efficient triplet photosensitiser, due to its long triplet lifetime. This chapter therefore provided an insight into the ligand applications of a family of PAH derivatives, and revealed that the increased conjugation offered by these systems is not an efficient means of modulating the photophysical properties of $\text{N}^{\wedge}\text{N}$ bis-pyrenyl acetylides. Future work proposed the incorporation of varied acetylide substituents in order to probe whether more desirable properties may be obtained with different chromophoric units, and whether complexes which displayed MLCT emission, rather than IL, could have a greater degree of photophysical control exerted by more conjugated $\text{N}^{\wedge}\text{N}$ ligands.

Chapter Five described the application of a partially-fused, highly-conjugated $\text{N}^{\wedge}\text{N}$ ligand towards the preparation of a family of Ir(III) complexes. Cyclometalated Ir(III) complexes have received widespread research attention over the past two decades due to their often strong emission, attractive for electronic devices such as OLEDs. It was aimed to investigate whether the very low-lying π^* acceptor orbitals of this ligand would have an appreciable impact on the photophysical properties of bis-cyclometalated Ir(III) complexes. Three different complexes were chosen, including a derivative with 2-phenylpyridine cyclometalating ligands, to serve as a simple literature comparator, and a derivative with strongly absorbing coumarin 6 cyclometalating ligands. The coumarin 6 ligands were selected due to previous work within the Draper group reporting Ir(III) complexes with both coumarin 6 ligands and extended $\text{N}^{\wedge}\text{N}$ ligands, based upon phen derivatives, that yielded very strong-light harvesting ability and excellent characteristics for applications as triplet photosensitisers. This chapter also described an Ir(III) complex featuring a coordinated Cp^* ring, as a further probe of the behaviour of the selected $\text{N}^{\wedge}\text{N}$ ligand. It was found that the NMR spectra of the complexes prepared were rather complex, which was proposed as being due to the existence of two isomers, due to the asymmetric nature of the $\text{N}^{\wedge}\text{N}$ ligand. The photophysical investigation of the complexes revealed them to be almost non-luminescent

in the visible region, which made the precise assignment of their excited states challenging. Protonation of the complexes led to only minor changes in their UV-Vis absorption spectra, with the exception of the coumarin 6 substituted complex. It was found that the main absorption band of this complex exhibited significant quenching upon protonation, leading to its assignment as being primarily $n\text{-}\pi^*$ in character. Only the Cp^* complex proved emissive at 77 K, and yielded a blue-shifted emission indicative of CT character. Work is ongoing to investigate whether any emission from these complexes is observed in the near-infrared region (NIR). A number of synthetically accessible future $\text{N}^{\wedge}\text{N}$ frameworks are also proposed in this chapter. Although the compounds proved non-luminescent in the visible region, their NMR behaviour is intriguing, and these complexes represent a further step towards understanding the behaviour of Ir(III) complexes with conjugated $\text{N}^{\wedge}\text{N}$ ligands.

Overall, this thesis has described the synthesis and characterisation of a variety of PAH-based systems. Each chapter has aimed to provide a thorough examination of the behaviour of such systems, and although they are only very small steps in a vast and diverse field of research, it is hoped that they contribute in some way to a further understanding of their behaviour.

Chapter Seven

Experimental Methods

7.1 General Methods

All synthetic procedures described here, unless otherwise stated, were performed under an inert atmosphere of argon or nitrogen gas, using standard Schlenk and vacuum line conditions. Solvents used in the synthetic methods described here were dried using the appropriate drying agents, and distilled under an inert atmosphere. Flash chromatography was performed using silica gel 60 (particle size 0.04-0.063 mm) obtained from Sigma-Aldrich Corporation or VWR. NMR spectra were recorded on (i) a Bruker Avance DPX-400 MHz spectrometer (operating at 400.13 MHz for ^1H , 100.6 MHz for ^{13}C); (ii) a Bruker AV(III) 400 MHz spectrometer (operating at 400.23 MHz for ^1H , 100.6 MHz for ^{13}C); (iii) a Bruker AV-600 MHz spectrometer (operating at 600.13 MHz for ^1H , 150.9 MHz for ^{13}C). ^1H and ^{13}C signals were referenced according to the solvent chosen. ^{13}C NMR spectra were proton decoupled. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hertz. IR spectra were recorded as neat samples on a Perkin-Elmer 100 FT-IR spectrometer, which was fitted with a Universal-ATR sampling accessory. IR data is reported in cm^{-1} . Melting points are given uncorrected and were measured in capillary tubes with a Griffin MFB-590 melting point apparatus. Elemental analyses (CHN) were obtained from the Microanalytical Laboratory, University College Dublin. Microwave reactions were performed with a CEM Discover S-Class Single Mode microwave reactor. The reactions were performed in the appropriate glass vials, with 'snap-cap' lids.

MALDI-TOF mass spectra were acquired using a Waters Maldi Q-ToF Premier spectrometer, using DCTB (trans-2-[3-4-tert-butylphenyl]-2-methyl-2-propenylidene]malononitrile) as a Maldi matrix. Accurate MALDI-TOF mass spectra were referenced against [Glu]-Fibrinopeptide B ($1570.6 \text{ g mol}^{-1}$). EI (electron impact) mass spectra were recorded with a GCT Premier Micromass time-of-flight mass spectrometer (TOF), with Heptacosyl (+) was used as an internal lock mass. Electrospray mass spectra (ESI-MS) were obtained with a Micromass time-of-flight mass spectrometer (TOF), interfaced to a Waters 2690 HPLC, and were referenced to leucine enkephalin (555.6 g mol^{-1}). APCI (atmospheric-pressure chemical ionisation) mass spectra were obtained with a Bruker micrOTOF-Q III spectrometer interfaced to a Dionex UltiMate 3000 LC or direct insertion probe.

Cyclic voltammetry was performed with a CH Instruments Electrochemical Analyser Model 600B. Solutions of the compounds ($1 \times 10^{-4} \text{ M}$) were degassed by bubbling with N_2 , and then subsequently analysed under an atmosphere of N_2 . A standard three-electrode cell,

using an Ag/AgCl reference electrode, a Pt wire counter electrode, and a glassy carbon working electrode (of area 0.0707 cm^2) was used. The electrodes were first rinsed with deionised water and then again in the appropriate solvent used for the measurements. In the case of the glassy carbon electrode, it was carefully polished with alumina powder and inspected before each use. The supporting electrolyte used in all cases was tetra-*n*-butylammonium hexafluorophosphate ($\text{Bu}_4\text{N}[\text{PF}_6]$) (0.1 M). The ferrocene/ferrocenium couple (Fc/Fc^+) was used as an internal standard, and the potentials quoted are referenced to it (0.0 V) where appropriate.

All photophysical measurements were carried out with HPLC grade solvents, and were obtained with $1 \times 1\text{ cm}^2$ quartz cuvettes. Where appropriate, deaerated solutions were obtained using specialised freeze-pump-thaw degassing cuvettes, and the solutions were subjected to at least three freeze-pump-thaw cycles. UV-Visible absorption spectra were obtained with a Shimadzu UV-2450 recording spectrophotometer. Emission and excitation spectra were obtained with (i) a Horiba Jobin-Yvon Fluorolog FL-3-11 spectrofluorometer with double grating emission and excitation monochromators or (ii) a Horiba Fluoromax 4-P spectrofluorometer. Emission lifetime measurements were obtained with a Jobin Yvon FluoroHub single photon counting controller fitted with a Jobin-Yvon NanoLED of the appropriate excitation wavelength. The TAC ranges were set to approximately twenty times the average decay time, and the start-stop ratio (α) was maintained below 2 %, to prevent pile-up. Data was fit with mono-exponential decays where possible, with χ^2 values as close to 1 as possible, and Durbin-Watson parameters of approximately 2. Bi-exponential fitting was used where mono-exponential fitting was not sufficient. Short lifetimes (in the nanosecond range) were corrected with an instrument response factor (IRF), which was a non-scattering solution of silica particles (Ludox, Sigma-Aldrich). Low temperature (77 K) emission measurements were obtained with a thin tube in a quartz Dewar filled with liquid nitrogen. Emission quantum yields were measured using the single-point method, as outlined by Brouwer *et al.*¹ Quinine sulfate ($\Phi_{\text{em}} = 0.546$ in 0.5 M H_2SO_4) and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ ($\Phi_{\text{em}} = 0.06$ in CH_3CN) were used as reference standards where appropriate. Transient absorption (TA) spectra and singlet oxygen quantum yields were recorded by Dr. Junsu Wang at the Dalian University of Technology.

Crystal and structural data is presented in the Annex. All single-crystal analyses were performed by Dr. Brendan Twamley in the University of Dublin, Trinity College, using a Bruker SMART APEX CCD diffractometer or a Bruker APEX2 Duo diffractometer. The

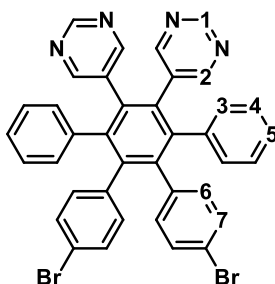
APEX CCD diffractometer utilised graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å), whereas the APEX2 Duo utilised two radiation sources, a Mo-K α source, and a high-intensity Cu-K α source ($\lambda = 1.5418$ Å) generated from a microfocus anode. Data reduction was performed using SAINT. Intensities were corrected for Lorentz and polarisation effects and for absorption by SADABS. The structures were solved by direct methods using SHELXS and refined on F^2 using all data by full-matrix least-squares procedures with SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalents of their carrier carbons. For chiral space groups, absolute structure determination was based on the Flack parameter. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [\max((F_o^2) + 2(F_c^2))/3]$. Final Fourier syntheses did not show significant residual electron density in chemically sensible positions. The SQUEEZE/PLATON program was used in structural refinement in cases where there were a large number of disordered solvent molecules in the structure. STM images were obtained with a commercial low-temperature STM (Scienta Omicron) was used for sample preparation and characterization *in situ* under ultra-high vacuum (UHV) conditions with a base pressure below 1×10^{-10} mbar. The Au(111) single crystal was cleaned by standard argon sputtering and annealing cycles. The molecules were thermally evaporated from quartz crucibles at Au(111) held at room temperature. The sample was annealed to 200 °C and 350 °C to activate dehalogenation and cyclodehydrogenation reactions. All the STM images were taken at constant current mode.

The compounds **1**, **2** and **3** were synthesised according to published procedures.²⁻⁴ 1,2-di(pyrimidin-5-yl)ethyne (**4**) was prepared according to the method of Vo *et al.*⁵ The compounds **7** and **8** were prepared according to the methods described by Wettach *et al.*⁶ 3,8-dibromo-1,10-phenanthroline (**10**) and 3,8-dibromo-1,10-phenanthroline-5,6-dione (**11**) were prepared according to the methods of Saitoh *et al.* and Yamada *et al.* respectively.^{7, 8} **12** and **13** were prepared according to a slightly modified procedure reported by Nagarajan *et al.*^{9, 10} The cyclotrimerised compounds **14**, **15**, and **16** were prepared according to the method outlined in the thesis of Dr. C. Delaney, with their characterisation data also presented here.¹¹ **18** (DMPD) and **19** were prepared according to the method of Mueller-Westerhoff *et al.*¹² **21** was prepared according to the method of Herwig *et al.*¹³ **28** was prepared according to a literature method.² **20**, **22**, **24**, **29**, and **40** were prepared according to methods developed in the Draper group.¹⁴⁻¹⁷ **27** was synthesised according to the method

of Des Abbayes *et al.*¹⁸ **36** was synthesised according to the method of Lai *et al.*¹⁹ **32** was prepared according to the method reported by Bertrand *et al.*²⁰ **46**, **50**, **68** and **69** and **70** were prepared according to literature procedures.^{8, 21, 22, 23} Compounds **71**, **72**, and **73** were also prepared according to literature procedures.^{24, 25}

7.2 Synthetic Procedures

5,5'-(5',6'-bis(4-bromophenyl)-[1,1':4',1''-terphenyl]-2',3'-diyl)dipyrimidine (**5**)



1,2-di(pyrimidin-5-yl)ethyne (74 mg, 0.40 mmol) and 3,4-bis(4-bromophenyl)-2,5-diphenylcyclopenta-2,4-dien-1-one (200 mg, 0.37 mmol) were added to benzophenone (600 mg) and heated to 280 °C under N₂ with a sand microburner. After 3 hours, the reaction mixture was cooled and purified by column chromatography (SiO₂, CH₂Cl₂:MeOH 4:1 v/v) to yield a white solid.

Yield: 155 mg, 60 %.

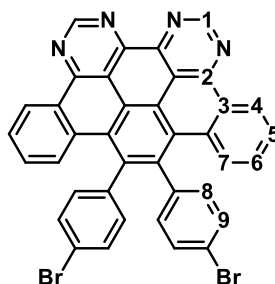
¹H NMR: (400 MHz, CDCl₃) δ 8.79 (s, 2H, H₁), 8.23 (s, 4H, H₂), 7.09 (d, 4H, ³J(HH) = 8.4 Hz, H₆), 7.00 (m, 6H, H_{3/5}), 6.82 (m, 4H, H₄), 6.71 (d, 4H, ³J(HH) = 8.4 Hz, H₇) ppm.

¹³C NMR: (150 MHz, CDCl₃): δ 157.8 (4C, C₂), 156.3 (2C, C₁), 141.8 (2C, C_Q), 141.3 (2C, C_Q), 138.0 (2C, C_Q), 137.9 (2C, C_Q), 133.8 (2C, C_Q), 133.5 (2C, C_Q), 132.4 (4C, C₇), 130.8 (C₄), 130.4 (H₆), 127.9 (4C, C₃), 126.9 (2C, C₅), 120.6 (C-Br) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂): found: 695.0478; calcd. 695.0446 for C₃₈H₂₅N₄Br₂, [M+H]⁺.

IR: (ATR, ν_{max}/cm⁻¹) 3032 (C-H_{Ar}), 2363, 2332, 1548, 1488, 1398, 1072, 1014, 830, 751, 724, 702 (C-Br), 631.

CHN: Found: C, 65.19; H, 3.18; N 7.85, calcd. C, 65.54; H, 3.47; N, 8.04, for C₃₈H₂₄N₄Br₂.

15,16-bis(4-bromophenyl)-5,7,8,10-tetraazatribenzo[fg,ij,rst]pentaphene (6)**Method A:**¹¹

5,5'-(5',6'-bis(4-bromophenyl)-[1,1':4',1''-terphenyl]-2',3'-diyl)dipyrimidine (100 mg, 0.144 mmol) was added to a pressure tube. Toluene (10 mL) was added, and the solution was stirred. Bromine (2 mL, 39 mmol) was carefully added, and the pressure tube was closed. The mixture was heated to 90 °C for 2 hours. After the mixture had cooled, it was filtered, and washed with MeOH. The product was then recrystallized from CH₂Cl₂ and MeOH, to give a red solid.

Yield: 40 mg, 40 %.

Method B:

5,5'-(5',6'-bis(4-bromophenyl)-[1,1':4',1''-terphenyl]-2',3'-diyl)dipyrimidine (30 mg, 0.043 mmol) and DDQ (59 mg, 0.258 mmol) were combined and dissolved in dry CH₂Cl₂ under N₂. Trifluoromethanesulfonic acid (0.23 mL, 0.258 mmol) was added carefully, and an immediate colour change to dark red/scarlet was observed. The mixture was stirred for 2 h, after which it was neutralised with K₂CO₃ (aq.), washed with brine, and extracted into CH₂Cl₂. Concentration of the solvent to a low volume and precipitation with MeOH gave the product as a yellow solid.

Yield: 16 mg, 54 %.

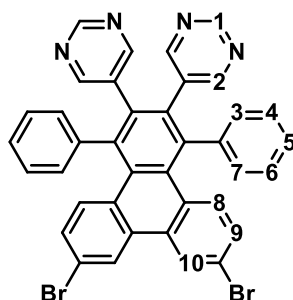
¹H NMR: (600 MHz, CDCl₃) δ 10.12 (s, 2H, H₁), 9.47 (d, 2H, ³J(HH) = 8.0 Hz, H₄), 7.73 (d, 2H, ³J(HH) = 8.0 Hz, H₇), 7.71 (t, 2H, ³J(HH) = 7.5 Hz, H₅), 7.48 (d, 4H, ³J(HH) = 7.8 Hz, H₈), 7.45 (2H, m, H₆), 7.08 (d, 4H, ³J(HH) = 7.8 Hz, H₉).

¹³C NMR: (150 MHz, CDCl₃) δ 156.8 (2C, C₁), 154.3 (2C, C₂), 140.7 (2C, C_Q), 140.8 (2C, C_Q), 133.6 (2C, C_Q), 133.1 (4C, C₉), 131.7 (4C, C₈), 130.7 (2C, C₆), 130.6 (2C, C_Q), 129.2 (2C, C₇), 128.8 (2C, C_Q), 128.3 (2C, C₅), 127.6 (2C, C_Q), 126.1 (2C, C₄), 121.8 (2C, C_Q), 121.2 (2C, C_Q), 117.8 (2C, C_Q) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂): found: 688.9987; calcd. 688.9976 for C₃₈H₁₉N₄Br₂, [M+H]⁺.

IR: (ATR, $\nu_{\max}$ /cm⁻¹): 1567, 1531, 1487, 1366, 1070, 1011, 845, 830, 767, 741, 675 (C-Br), 583, 556.

5-(7,10-dibromo-3-(4,5-dihydropyrimidin-5-yl)-1,4-diphenyltriphenylen-2-yl)pyrimidine (9)



¹H NMR: (400 MHz, CDCl₃) δ 8.88 (s, 2H, H₁), 8.51 (d, 2H, ³J = 2 Hz, H₁₀), 8.10 (s, 4H, H₂), 7.48 (d, 2H, ³J = 8.6 Hz, H₈), 7.25 (m, 2H, H₅), 7.24 (m, 4H, H_{4,6}), 7.21 (m, 2H, H₉), 7.03 (m, 4H, H_{3,7}).

¹³C NMR: (100 MHz, CDCl₃) δ 158.1, (4C, C-H_{Ar}, C₂), 156.2 (2C, C-H_{Ar}, C₁), 140.7 (2C, C_{Quat}), 138.7 (2C, C_{Quat}), 133.7 (2C, C_{Quat}), 133.3 (2C, C_{Quat}), 132.5 (2C, C_{Quat}), 131.9 (2C, C_{Quat}), 131.8 (4C, C-H_{Ar}, C_{3,7}), 131.4 (2C, C-H_{Ar}, H₈), 129.6 (2C, C-H_{Ar}, C₉), 129.3 (4C, C-H_{Ar}, C_{4,6}), 129.0 (2C, C_{Quat}), 127.9 (2C, C-H_{Ar}, C₅), 126.2 (2C, C-H_{Ar}, C₁₀), 122.2 (2C, C-Br).

HRMS: (m/z) calculated for [C₃₈H₂₃Br₂N₄], [M+H]⁺: 693.0284, found 693.0301

IR (ATR, $\nu_{\max}$ /cm⁻¹) 1661, 1591, 1549, 1488, 1422, 1375, 1187, 1120, 1023, 867, 837, 816, 704, 630 (C-Br), 538.

m.p. >300 °C

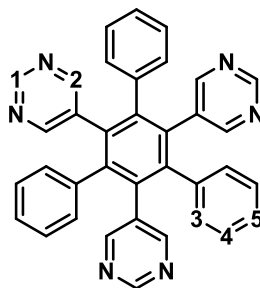
CHN: Found: C, 65.54; H, 2.81; N 8.29, calcd. C, 65.73; H, 3.19; N, 8.07, for C₃₈H₂₂Br₂N₄.

Preparation of 5,5',5''-(5'-phenyl-[1,1':3',1''-terphenyl]-2',4',6'-triyl)tripyrimidine (14) and 5,5',5''-(5'-phenyl-[1,1':2',1''-terphenyl]-3',4',6'-triyl)tripyrimidine (15)¹¹

5-(phenylethynyl)pyrimidine (114 mg, 0.630 mmol) and dicobaltoctacarbonyl (43 mg, 0.126 mmol) were combined and degassed by vacuum/Ar cycles. 1,4-dioxane (10 mL) was added *via* a syringe. The solution was heated at reflux (115 °C) for 48 h. The solvent was removed under vacuum and the solid obtained was dissolved in CH₂Cl₂ and filtered through a short

plug of celite. Column chromatography (SiO₂, CH₂Cl₂:MeOH, 95:5 (v/v)) failed to provide adequate separation of the two isomers. A preparative plate (SiO₂, CH₂Cl₂:MeOH, 96:4 (v/v)) provided separation of both the asymmetric and symmetric isomers, providing the symmetric isomer (**14**) in 4% yield and the asymmetric (**15**) in 10% yield.

Characterisation of 5,5',5''-(5'-phenyl-[1,1':3',1''-terphenyl]-2',4',6'-triyl)tripyrimidine (14**)**

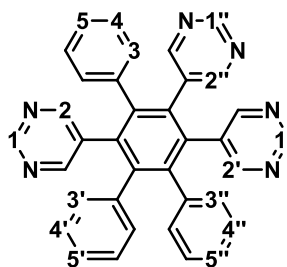


¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 3H, H₁), 8.25 (s, 6H, H₂), 7.01-7.10 (m, 9H, H_{4,5}), 6.88 (d, 6H, ³J(HH) = 8 Hz, H₃) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 157.5 (6C, C₂), 156.0 (3C, C₁), 143.0 (3C, C_{Quat}), 137.4 (3C, C_{Quat}), 134.7 (3C, C_{Quat}), 134.3 (3C, C_{Quat}), 130.7 (6C, C₃), 128.4 (6C, C₄), 127.6 (3C, C₅) ppm.

HRMS: (m/z, ESI, acetonitrile) found: 541.2141; calcd. 541.2141 for C₃₆H₂₅N₆ ([M+H]⁺).

Characterisation of 5,5',5''-(5'-phenyl-[1,1':2',1''-terphenyl]-3',4',6'-triyl)tripyrimidine (15**)**



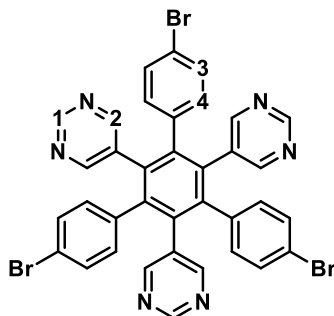
¹H NMR (600 MHz, CDCl₃) δ 8.81 (s, 1H, H_{1'}), 8.80 (s, 1H, H_{1''}), 8.75 (s, 1H, H₁), 8.27 (s, 2H, H_{2'}), 8.26 (s, 2H, H_{2''}), 8.24 (s, 2H, H₂), 7.09-7.02 (m, 3H, H_{5'}, H_{5''}, H₅), 7.01-6.96 (m, 6H, H_{3'}, H_{3''}, H₃), 6.90-6.83 (m, 6H, H_{4'}, H_{4''}, H₄) ppm.

¹³C NMR (150 MHz, CDCl₃) δ 157.78 (2C, C_{2'}, C_{2''}), 157.45 (1C, C₂), 156.49 (1C, C_{1'}), 156.41 (1C, C_{1''}), 155.93 (1C, C₁), 143.18 (1C, C_{Quat}), 142.32 (1C, C_{Quat}), 142.07 (1C, C_{Quat}), 137.85 (1C, C_{Quat}), 137.71 (1C, C_{Quat}), 137.22 (1C, C_{Quat}), 135.32 (1C, C_{Quat}), 134.90 (1C, C_{Quat}), 134.26 (1C, C_{Quat}),

133.84 (1C, C_{Quat}), 133.74 (1C, C_{Quat}), 133.28 (1C, C_{Quat}), 133.11 (1C, C_{Quat}), 130.77 (2C, C_{4'}), 130.73 (2C, C_{4''}), 130.68 (2C, C₄), 128.43 (2C, C_{5'}, C_{5''}), 127.82 (2C, C_{3'}), 127.78 (2C, C_{3''}), 127.58 (1C, C₅), 126.99 (1C, C₃) ppm.

HRMS: (m/z, ESI, acetonitrile) found: 541.2141; calcd. 541.2141 for C₃₆H₂₅N₆ ([M+H]⁺).

5-((4-bromophenyl)ethynyl)pyrimidine (**16**)



5-((4-bromophenyl)ethynyl)pyrimidine (328 mg, 1.27 mmol) and dicobalt octacarbonyl (86.6 mg, 0.25 mmol) were combined and degassed by vacuum/argon cycles. 1,4-dioxane (10 mL) was added *via* syringe. The solution was heated at reflux for 5 days, while the reaction progress was monitored *via* TLC. The solvent was removed under vacuum, and the solid then obtained was dissolved in CH₂Cl₂ and filtered through celite. Column chromatography (SiO₂, CH₂Cl₂:MeOH, 96:4 (v/v)) separated remaining starting material but failed to provide adequate separation of the two product isomers (the symmetric **16** and asymmetric **17**). A preparative plate (SiO₂, CH₂Cl₂:MeOH, 95:5 (v/v)) provided separation of the symmetric isomer, **16**, in 5% (15 mg) yield.

Yield: 15 mg, 5 %.

¹H NMR: (400 MHz, CDCl₃) δ = 8.87 (s, 3H, H₁), 8.24 (s, 6H, H₂), 7.20 (m, 6H, H₄), 6.72 (m, 6H, H₃).

¹³C NMR: (100 MHz, CDCl₃) δ = 157.0 (6C, C₂), 155.78 (3C, C₁), 141.5 (3C, C_{Quat}), 134.2 (3C, C_{Quat}), 135.4 (3C, C_{Quat}), 132.1 (6C, C₃), 131.6 (3C, C_{Quat}), 131.8 (6C, C₄), 122.0 (3C, C-Br).

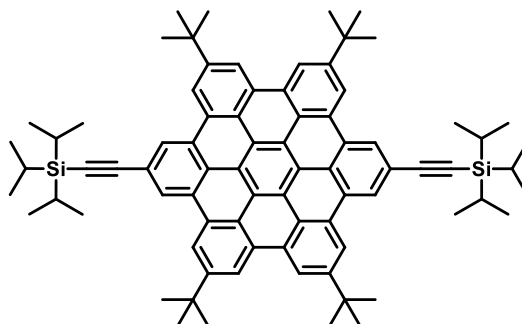
HRMS: (m/z, ESI, acetonitrile) found: 774.9478; calcd. 774.9546 for C₃₆H₂₂Br₃N₆ ([M+H]⁺).

¹H NMR: (400 MHz, CDCl₃) δ 7.28-7.23 (m, 10H, H_{Ar}), 7.17 (d, 4H, ³J(HH) = 8.6 Hz, H_{Ar}), 6.84 (d, 4H, ³J(HH) = 8.6 Hz, H_{Ar}), 1.29 (s, 18H, -CH₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 496.2779; calcd. 496.2766 for C₃₇H₃₆O [M]⁺.

IR: (neat, $\nu_{\text{bar}}/\text{cm}^{-1}$) 3052 (C-H, H_{Ar}), 2961 (C-H, CH_3), 1710 (C=O), 1605, 1490, 1358, 1302, 1111, 1014, 920, 846, 762, 714, 694, 586.

Triisopropyl((5,8,14,17-tetra-tert-butyl-11-((triisopropylsilyl)ethynyl)hexabenzob[bc,ef,hi,kl,no,qr]coronen-2-yl)ethynyl)silane
(25)



2,5,11,14-tetra-tert-butyl-8,17-diiodohexabenzob[bc,ef,hi,kl,no,qr]coronene (70 mg, 0.069 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 0.007 mmol) and CuI (4 mg, 0.020 mmol) were combined and degassed by vacuum/ N_2 cycles. To the solids, piperidine (10 mL) was added *via* syringe, and the mixture was stirred. Triisopropylsilylacetylene (0.02 mL, 0.153 mmol) was then added and the solution was heated to 55 °C for 24 h. After ~1 hr, it was noted that all previously insoluble starting materials had dissolved entirely. The solvent was removed and the solids were dissolved in CH_2Cl_2 (50 mL) and washed with H_2O (3 x 50 mL). Purification by column chromatography (SiO_2 , hexanes: CH_2Cl_2 9:1) gave a bright yellow solid.

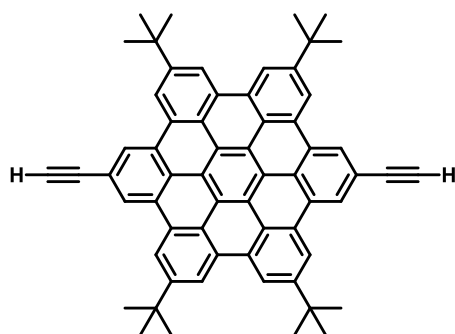
Yield: 35 mg, 45 %.

^1H NMR: (400 MHz, CDCl_3) δ 8.93 (s, 4H, H_{Ar}), 8.60 (s, 8H, H_{Ar}), 1.99 (s, 36H, $-\text{CH}_3$), 1.51 (m, 42H, $-\text{CH}_3$) ppm.

^{13}C NMR: (100 MHz, CDCl_3): δ 147.6 (C_Q), 129.6 (C_Q), 129.0 (C_Q), 128.5 (C_Q), 124.6 (4C, C_{HAr}), 123.9 (C_Q), 122.2 (C_Q), 120.0 (C_Q), 119.3 (4C, C_{HAr}), 119.3 (C_Q), 119.0 (C_Q), 118.4 (4C, C_{HAr}), 109.0 (C_Q), 118.4 (C_Q), 109.0 (C_Q), 91.1 (C_Q), 90.2 (C_Q), 81.6 (C_Q), 32.5 ($-\text{CH}_3$), 19.2 ($-\text{CH}_3$), 11.8 (CH) ppm.

HRMS: (m/z, MALDI, CH_2Cl_2) found: 1106.6588; calcd. 1106.6581 for $\text{C}_{80}\text{H}_{90}\text{Si}_2$ [M^+].

IR: (neat, $\nu_{\text{bar}}/\text{cm}^{-1}$) 2953, 2864, 1462, 1370, 1262, 1222, 1073, 1016, 996, 979, 882, 866, 1606, 1578, 781, 745, 685, 662, 580, 500, 474.

2,5,11,14-tetra-tert-butyl-8,17-diethynylhexabenzob[bc,ef,hi,kl,no,qr]coronene (26)

Triisopropyl((5,8,14,17-tetra-tert-butyl-11-((triisopropylsilyl)ethynyl)hexabenzob[bc,ef,hi,kl,no,qr]coronen-2-yl)ethynyl)silane (30 mg, 0.027 mol) was dissolved in THF (5 mL) and then TBAF(tetra-n-butylammonium fluoride) (0.5 mL, 0.5 mmol) was added. The solution was stirred at RT for 2 hours, after which time the THF was removed by rotary evaporation and the solid was dissolved in the minimum amount of CH₂Cl₂. A few drops of cold MeOH were added to precipitate the compound as a yellow solid.

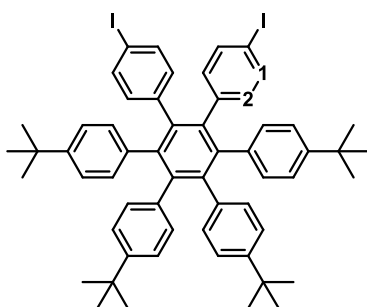
Yield: 19 mg, 89 %.

¹H NMR: (400 MHz, CDCl₃) δ 8.99 (s, 4H, H_{Ar}), 8.66 (s, 4H, H_{Ar}), 8.61 (s, 4H, H_{Ar}), 3.69 (2H, s, C≡C-H), 1.96 (s, 36H, -CH₃)

The very high degree of insolubility precluded the obtainment of a ¹³C NMR spectrum.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 794.3914; calcd. 794.3913 for C₆₂H₅₀ [M⁺].

IR: (neat, ν bar/cm⁻¹) 3287 (C≡C-H), 2952, 1605, 1574, 1462, 1368, 1261, 940, 867, 736, 638, 605.

4,4''-di-tert-butyl-3',4'-bis(4-(tert-butyl)phenyl)-5',6'-bis(4-iodophenyl)-1,1':2',1''-terphenyl¹⁴ (30)

Method A:

4,4''-di-tert-butyl-3',4'-bis(4-(tert-butyl)phenyl)-5',6'-diphenyl-1,1':2',1''-terphenyl (99 mg, 0.130 mmol) and PIFA (170 mg, 0.291 mmol) were dissolved in CHCl_3 (14 mL) and CH_2Cl_2 (14 mL). The mixture was degassed by three freeze-pump-thaw cycles. Iodine (50.2 mg, 0.198 mmol) was added, which was then stirred under N_2 , in darkness, for 48 hours. TLC analysis after this time indicated remaining starting material, so further PIFA (31 mg, 0.072 mmol) and iodine (13 mg, 0.051 mmol) were added, and the mixture was stirred for a further 16 hours. CH_2Cl_2 (100 mL) was added to the mixture, which was then washed with an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_4$ (1 x 50 mL) and deionised water (2 x 50 mL). The organic layer was separated and dried with MgSO_4 , and the solvents removed *in vacuo*. The solid obtained was then dissolved in Et_2O (*ca.* 5 mL) and the product was then precipitated upon the addition of cold MeOH (*ca.* 20 mL). The product was filtered and washed with further amounts of cold MeOH.

Yield: 66 mg, 50 %.

Method B:

2,3,4,5-tetrakis(4-(tert-butyl)phenyl)cyclopenta-2,4-dien-1-one (200 mg, 0.328 mmol) and 1,2-bis(4-iodophenyl)ethyne (141 mg, 0.327 mmol) were combined and added to benzophenone (700 mg) in an RBF. The mixture was degassed by vacuum/argon cycles, and then heated to 250 °C for 2 hours, under N_2 . After this time, TLC analysis indicated remaining starting material, so the temperature was increased to 350 °C, and the mixture was heated for a further 3 hours. The reaction mixture was dissolved in CH_2Cl_2 (~ 5 mL) and subjected to column chromatography (SiO_2 , Hexanes: CH_2Cl_2 (4:1) (v/v)). The product was obtained as an off-white solid.

Yield: 145 mg, 44 %.

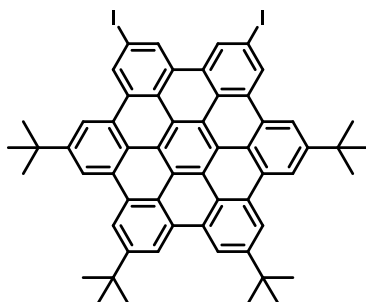
^1H NMR: (400 MHz, CDCl_3) δ 7.22 (d, 4H, $^3J(\text{HH}) = 8.4$ Hz, H_1), 6.87 (d, 4H, $^3J(\text{HH}) = 8.4$ Hz, H_{Ar}), 6.82 (d, 4H, $^3J(\text{HH}) = 8.4$ Hz, H_{Ar}), 6.63-6.68 (m, 8H, H_{Ar}), 6.58 (d, 4H, $^3J(\text{HH}) = 8.3$ Hz, H_2), 1.15 (s, 18H, $-\text{CH}_3$), 1.11 (s, 18H, $-\text{CH}_3$) ppm.

^{13}C NMR: (100 MHz, CDCl_3): δ 148.0 (C_Q), 147.6 (C_Q), 141.3 (C_Q), 140.4 (C_Q), 140.4 (C_Q), 138.4 (C_Q), 137.5 (C_Q), 137.3 (C_Q), 137.2 (C_Q), 135.8 (4C, C_1), 133.4 (4C, C_1), 130.9 (4C, C_{HAr}), 130.9 (4C, C_{HAr}), 123.4 (4C, C_{HAr}), 123.1 (4C, C_{HAr}), 91.1 (2C, C-I), 34.1 (2C, C_Q , C- CH_3), 34.1 (2C, C_Q , C- CH_3), 31.2 (6C, C- CH_3), 31.2 (6C, C- CH_3) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 1010.2785; calcd. 1010.2785 for C₅₈H₆₀I₂ [M⁺].

IR: (neat, ν_{bar} /cm⁻¹) 2961, 2902, 2870, 1510, 1486, 1391, 1362, 1269, 1201, 1146, 1104, 1061, 1006, 859, 824, 773, 723, 612, 558, 570, 511.

2,5,8,11-tetra-tert-butyl-14,17-diiodohexabenzob[bc,ef,hi,kl,no,qr]coronene (33)



4,4''-di-tert-butyl-3',4'-bis(4-(tert-butyl)phenyl)-5',6'-bis(4-iodophenyl)-1,1':2',1''-terphenyl (120 mg, 0.118 mmol) and DDQ (162 mg, 0.713 mmol) were added to dry CH₂Cl₂ (20 mL), and placed under an atmosphere of N₂. The mixture was stirred for 15 minutes, until all solids had dissolved. CF₃SO₃H (0.06 mL, 0.713 mmol) was added by syringe, and an immediate colour change to dark red was observed. The mixture was stirred for 2 hours at RT. The solution was neutralised with K₂CO₃ and then diluted and extracted with CH₂Cl₂ (~ 60 mL). The organic layer was washed with brine, separated, and dried with MgSO₄. Concentration of the solvent *in vacuo*, and subsequent addition of cold MeOH, gave the product as a yellow solid.

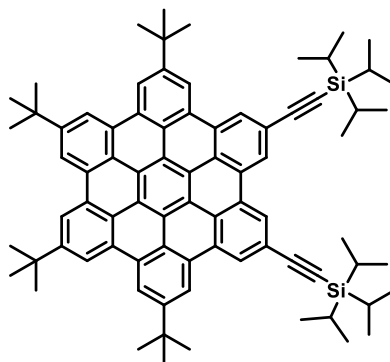
Yield: 95 mg, 81 %.

¹H NMR: (400 MHz, CDCl₃) δ 9.09 (s, 2H), 8.83 (s, 2H), 8.51 (s, 2H), 7.99 (s, 2H), 7.73 (s, 2H), 7.47 (s, 2H), 2.10 (s, 18H, -CH₃), 1.88 (s, 18H, -CH₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 998.1875; calcd. 998.1846 for C₅₈H₄₈I₂ [M⁺].

IR: (neat, ν_{bar} /cm⁻¹) 2953, 2867, 1608, 1568, 1480, 1462, 1393, 1367, 1262, 1204, 1008, 865, 840, 743, 686, 636.

((8,11,14,17-tetra-tert-butylhexabenzo[bc,ef,hi,kl,no,qr]coronene-2,5-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (34)



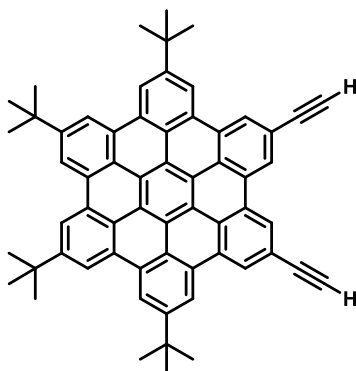
2,5,8,11-tetra-tert-butyl-14,17-diiodohexabenzo[bc,ef,hi,kl,no,qr]coronene (65 mg, 0.065 mmol), Pd(PPh₃)₄ (7.4 mg, 0.006 mmol) and CuI (3.7 mg, 0.019 mmol) were added to a 25 mL 2-neck flask and degassed by vacuum/argon cycles. Piperidine (10 mL) was degassed by freeze-pump-thaw (3 cycles) and added to the solids by cannula. (Triisopropylsilyl)acetylene (0.03 mL, 0.142 mmol) was added by syringe. The mixture was heated to 55 °C for 18 hours. The solvent was removed by rotary evaporation, and the residue was dissolved in CH₂Cl₂. The solution was washed with H₂O (2 x 50 mL) and dried over MgSO₄. The solvent was concentrated, and the product was obtained after column chromatography (SiO₂, CH₂Cl₂:Hexane, 1:4 (v/v)).

Yield: 30 mg, 42 %.

¹H NMR: (400 MHz, CDCl₃) δ 9.07 (s, 2H, H_{Ar}), 8.93 (s, 2H, H_{Ar}), 8.79 (s, 2H, H_{Ar}), 8.55 (s, 2H, H_{Ar}), 8.41 (m, 4H, H_{Ar}), 2.09 (s, 18H), 1.93 (s, 18H), 1.48 (s, 42H).

HRMS: (m/z, MALDI, CH₂Cl₂) found: 1106.6619; calcd. 1106.6581 for C₈₀H₉₀I₂ [M⁺].

IR: (neat, ν_{bar} /cm⁻¹) 2951, 2865, 2140, 1608, 1577, 1462, 1422, 1369, 1263, 1072, 997, 882, 865, 793, 744, 680, 616, 566.

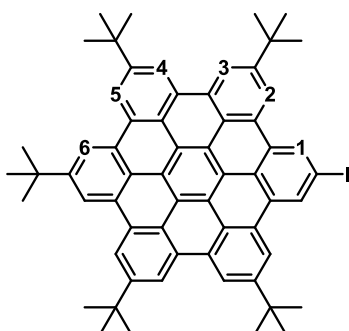
2,5,8,11-tetra-tert-butyl-14,17-diethynylhexabenzob[bc,ef,hi,kl,no,qr]coronene (35)

((8,11,14,17-tetra-tert-butylhexabenzob[bc,ef,hi,kl,no,qr]coronene-2,5-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (30 mg, 0.027 mmol) was dissolved in THF (5 mL) under N₂, and TBAF (0.5 mL, 0.5 mmol) was then added by syringe. The solution was stirred for 2 hours at RT. The THF was removed by rotary evaporation, and the residue was dissolved in the minimum amount of CH₂Cl₂. The addition of MeOH precipitated the product as a bright yellow solid.

Yield: 17 mg, 80 %.

¹H NMR: (400 MHz, CDCl₃) δ 9.16 (s, 2H, H_{Ar}), 8.95 (s, 2H, H_{Ar}), 8.66 (s, 2H, H_{Ar}), 8.33 (s, 2H, H_{Ar}), 7.93 (s, 2H, H_{Ar}), 7.77 (s, 2H, H_{Ar}), 3.60 (s, 2H, C≡CH), 2.08 (s, 18H, -CH₃), 1.88 (s, 18H, -CH₃).

HRMS: (m/z, MALDI, CH₂Cl₂) found: 794.3942; calcd. 794.3913 for C₆₂H₅₀ [M⁺].

2,5,8,11,14-penta-tert-butyl-17-iodohexabenzob[bc,ef,hi,kl,no,qr]coronene (41)

4,4''-di-tert-butyl-3',4',5'-tris(4-(tert-butyl)phenyl)-6'-(4-iodophenyl)-1,1':2',1''-terphenyl (100 mg, 0.106 mmol) was dissolved in dry CH₂Cl₂. DDQ (147 mg, 0.646 mmol) was carefully added under an atmosphere of N₂, resulting in a yellow solution. CF₃SO₃H (0.05 mL, 0.646 mmol) was added *via* syringe, resulting in an immediate colour change to dark

red. The mixture was stirred for 2 hours, after which it was neutralised with a saturated solution of K_2CO_3 (aq.) and diluted with CH_2Cl_2 (ca. 50 mL). The aqueous layer was separated, and the organic layer washed with deionised water (2 x 50 ml). After drying with MgSO_4 , the solvent was removed *in vacuo* to yield a dark red solid.

Yield: 85 mg, 86%.

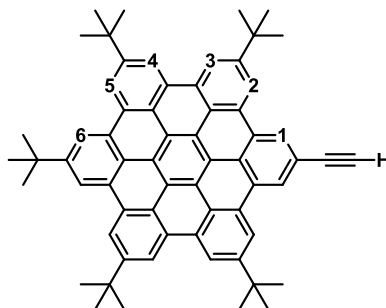
^1H NMR: (400 MHz, CDCl_3) δ 9.22 (s, 2H, H_6), 9.17 (s, 2H, H_5), 9.10 (s, 2H, H_4), 9.02 (s, 2H, H_3), 8.96 (s, 2H, H_1), 8.77 (s, 2H, H_2), 1.94 (s, 9H, $-\text{CH}_3$), 1.90 (s, 18H, $-\text{CH}_3$), 1.83 (s, 18H, $-\text{CH}_3$) ppm.

^{13}C NMR: (101 MHz, CDCl_3) δ 148.7, 148.54, 148.52, 132.1, 130.3, 130.1, 130.0, 129.83, 128.78, 128.4, 124.2, 123.4, 123.3, 120.4, 120.0, 119.9, 119.1, 119.0, 118.8, 118.7, 118.6, 35.8, 35.74, 35.68, 32.17, 32.14, 32.09 ppm.

HRMS: (m/z, MALDI, CH_2Cl_2) found: 928.3517, calcd. 928.3505 for $\text{C}_{62}\text{H}_{57}\text{I}$ $[\text{M}]^+$.

IR: (neat, $\nu_{\text{bar}}/\text{cm}^{-1}$) 2953, 2866, 1610, 1571, 1478, 1459, 1393, 1368, 1263, 1225, 1202, 1024, 942, 852, 867, 746, 629, 597, 553.

2,5,8,11,14-penta-tert-butyl-17-ethynylhexabenzob[bc,ef,hi,kl,no,qr]coronene (43)



Step I: Preparation of triisopropyl((5,8,11,14,17-penta-tert-butylhexabenzob[bc,ef,hi,kl,no,qr]coronen-2-yl)ethynyl)silane (42):

To a solution of distilled triethylamine (5 ml) and dry THF (10 ml) was added I-HBC (80 mg, 0.086 mmol), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (3.62 mg, 0.005 mmol), and CuI (1.97 mg, 0.005 mmol), after which the solution was degassed. Triisopropylsilylacetylene (0.058 ml, 0.258 mmol) was added *via* syringe and the solution was stirred overnight under N_2 . The solvents were removed under vacuum and the compound purified *via* column chromatography on SiO_2 (Petroleum ether: CH_2Cl_2 3:1 v/v), yielding **42** as an orange solid in 83 % yield.

Step II: Preparation of 2,5,8,11,14-penta-tert-butyl-17-ethynylhexabenzob[bc,ef,hi,kl,no,q_r]coronene (43)

Triisopropyl((5,8,11,14,17-penta-tert-butylhexabenzob[bc,ef,hi,kl,no,q_r]coronen-2-yl)ethynyl)silane (61 mg,) was dissolved in dry THF, under N₂. TBAF (0.2 mL,) was added *via* syringe, and the mixture was stirred at RT for 3 hours. The solvent was removed in vacuo and the desired compound was obtained by crystallisation from CH₂Cl₂/MeOH.

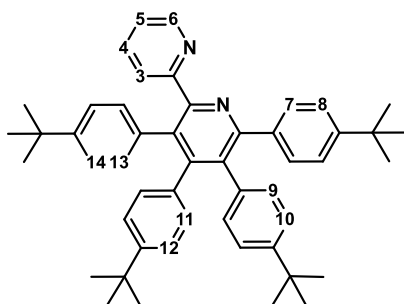
Yield: 48 mg, 94 %.

¹H NMR: (400 MHz, CDCl₃) δ 9.21 (s, 2H, H₆), 9.15 (s, 2H, H₅), 9.08 (s, 2H, H₄), 8.96 (s, 2H, H₃), 8.80 (s, 2H, H₂), 8.74 (s, 2H, H₁), 3.60 (s, 1H, C≡H), 1.95 (s, 9H, -CH₃), 1.91 (s, 18H, -CH₃), 1.83 (s, 18H, -CH₃) ppm.

¹³C NMR: (101 MHz, CDCl₃) δ 148.5 (C_Q), 148.3 (C_Q), 148.25 (C_Q), 130.3 (C_Q), 130.0 (C_Q), 129.94 (C_Q), 129.94 (C_Q), 129.7 (C_Q), 128.9 (C_Q), 124.6 (2C, C₁), 123.2 (C_Q), 123.1 (C_Q), 120.3 (C_Q), 120.1 (C_Q), 119.8 (C_Q), 119.1 (2C, C₂), 118.8 (C_Q), 118.63 (C_Q), 118.59 (2C, C₄), 118.57 (2C, C₆), 118.5 (4C, C₃,C₅), 85.8 (1C, C≡C), 77.8 (1C, C≡C), 35.8 (1C, C_Q, -C-CH₃), 35.7 (2C, C_Q, -C-CH₃), 35.6 (2C, C_Q, -C-CH₃), 32.19 (3C, -C-(CH₃)₃), 32.15 (6C, -C-(CH₃)₃), 32.10 (6C, -C-(CH₃)₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 826.4548; calcd. 826.4539 for C₆₄H₅₈ [M]⁺.

3,4,5,6-tetra(4-tert-butylphenyl)-2,2'-bipyridine (44)



2,3,4,5-tetrakis(4-(tert-butyl)phenyl)cyclopenta-2,4-dien-1-one **31** (275 mg, 0.443 mmol) and 2-cyanopyridine (920 mg) were combined in an RBF fitted with a condenser and heated to reflux with a sand microburner (external temperature 250 °C). The mixture was stirred under N₂ for 30 h and subsequently allowed to cool, yielding a brown solid. Separation from the lactone by-product was achieved by column chromatography (SiO₂, hexanes:diethyl ether 2:1 v/v), which gave a white solid.

Yield: 120 mg, 44%.

¹H NMR: (400 MHz, CDCl₃) δ 8.49 (d, 1H, ³J(HH) = 4.9 Hz, H₆), 7.52 (dt, 1H, ³J(HH) = 7.7 Hz, ⁴J(HH) = 1.8 Hz, H₄), 7.42 (d, 1H, ³J(HH) = 8.1 Hz, H₃), 7.33 (d, 2H, ³J(HH) = 8.6 Hz, H₇), 7.17 (d, 2H, ³J(HH) = 8.5 Hz, H₈), 7.10 (m, 1H, ³J(HH) = 4.5 Hz, ⁴J(HH) = 1.3 Hz, H₅), 7.00 (d, 2H, ³J(HH) = 8.5 Hz, H_{10/14}), 6.95 (d, 2H, ³J(HH) = 8.2 Hz, H_{10/14}), 6.90 (d, 2H, ³J(HH) = 8.5 Hz, H₁₂), 6.81 (d, 4H, ³J(HH) = 8.1 Hz, H₉/H₁₃), 6.65 (d, 2H, ³J(HH) = 8.5 Hz, H₁₁), 1.26 (s, 9H, -CH₃), 1.19 (s, 9H, -CH₃), 1.17 (s, 9H, -CH₃), 1.14 (s, 9H, -CH₃) ppm.

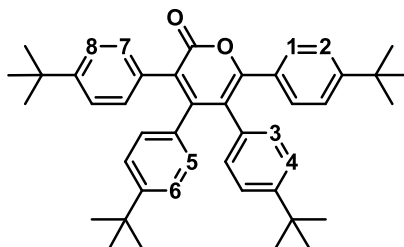
¹³C NMR: (101 MHz, CDCl₃) δ 159.3, 156.5, 155.3, 150.8, 149.9, 148.9, 148.7 (1C, C₆), 148.7, 148.6, 138.0, 135.5 (C₄), 135.1, 134.9, 134.3, 130.9 (2C, C_{9/13}), 130.7 (2C, C_{9/13}), 130.0 (2C, C₁₁), 129.9 (2C, C₇), 125.1 (1C, C₃), 124.3 (2C, C₈), 124.0 (2C, C_{10/14}), 123.9 (2C, C_{10/14}), 123.5 (2C, C₁₂), 122.0 (1C, C₅), 34.4 (C-CH₃), 34.3 (C-CH₃), 34.2 (C-CH₃), 34.2 (C-CH₃), 31.3 (C-CH₃), 31.2 (C-CH₃), 31.2 (C-CH₃), 31.1 (C-CH₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 684.4462; calcd. 684.443 for C₅₀H₅₆N₂ [M⁺].

CHN: Found: C, 86.25; H, 7.96; N 3.84, calcd. C, 86.52; H, 8.34; N 4.00, for C₅₀H₅₆N₂·0.5MeOH.

IR (ATR, ν_{max}/cm⁻¹) 2961, 2867, 1585, 1472, 1389, 1362, 1269, 1141, 1018, 834, 745.

3,4,5,6-tetrakis(4-(tert-butyl)phenyl)-2H-pyran-2-one (45)



Isolated as a by-product during the synthesis of **47**. The compound was isolated by column chromatography (SiO₂, hexanes:diethyl ether 2:1 v/v) as white solid.

¹H NMR: (600 MHz, CDCl₃) δ 7.33 (d, 2H, ³J(HH) = 8.6 Hz, H₁), 7.21 (d, 2H, ³J(HH) = 8.7 Hz, H₂), 7.16 (d, 2H, ³J(HH) = 8.7 Hz, H₈), 7.06 (d, 4H, ³J(HH) = 7.5 Hz, H₇/H₄), 6.91 (d, 2H, ³J(HH) = 8.4 Hz, H₆), 6.79 (d, 2H, ³J(HH) = 8.4 Hz, H₃), 6.58 (d, 2H, ³J(HH) = 8.4 Hz, H₅), 1.26 (s, 9H, -CH₃), 1.22 (s, 9H, -CH₃), 1.20 (s, 9H, -CH₃), 1.12 (s, 9H, -CH₃) ppm.

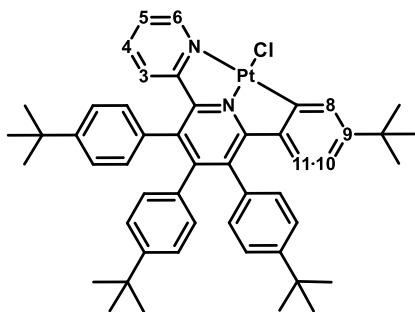
¹³C NMR: (150 MHz, CDCl₃) δ 162.7 (C=O), 156.0 (C_Q), 155.8 (C_Q), 152.5 (C_Q), 150.0 (C_Q), 149.8 (C_Q), 149.8 (C_Q), 133.6 (C_Q), 132.4 (C_Q), 131.5 (C_Q), 130.9 (C₃), 130.3 (C₈), 129.2 (C₅), 129.0 (C₁), 124.8 (C₄), 124.8 (C₂), 124.4 (C₇), 123.8 (C₆), 119.5 (C_Q), 34.7 (C-CH₃), 34.4 (C-CH₃), 34.4 (C-CH₃), 34.3 (C-CH₃), 31.2 (C-CH₃), 31.2 (C-CH₃), 31.1 (C-CH₃), 31.1 (C-CH₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 625.4072, calc. 625.4046 for C₄₅H₅₃O₂ [M+H]⁺.

IR: (ATR, ν_{max} /cm⁻¹) 2951, 1715 (C=O), 1612, 1459, 1364, 1269, 1102, 1015, 922, 837, 821, 791, 654, 618.

CHN: Found: C, 85.84; H, 8.52, calcd. (%) for C₄₅H₅₂O₂: C, 86.49; H, 8.39.

[PtCl(L)] (L = 3,4,5,6-tetra(4-*tert*-butylphenyl)-2,2'-bipyridine (47))



To a flask containing the ligand 3,4,5,6-tetra(4-*tert*-butylphenyl)-2,2'-bipyridine (30 mg, 0.043 mmol) and [PtCl₂(DMSO)₂] (18 mg, 0.043 mmol) was added triethylamine (2 mL) and CHCl₃ (3 mL). The resulting mixture was refluxed for 24 h, after which time the solvents were concentrated *in vacuo* and to which a few drops of MeOH were added to yield a yellow precipitate. The precipitate was subsequently filtered, washed with cold MeOH and dried, to give the desired complex.

Yield: 33 mg, 83%.

¹H NMR (400 MHz, CDCl₃) δ 9.36 (d, 1H, ³J(HH) = 5.5 Hz, H₆), 7.94 (d, 1H, ³J(PtH) = 43.0 Hz, ⁴J(HH) = 2.1 Hz, H₈), 7.54-7.44 (m, 2H, H₄/H₅), 7.24 (t, 4H, ³J(HH) = 8.5 Hz, H_{Ar}), 6.97 (d, 2H, ³J(HH) = 8.4, H_{Ar}), 6.97 (dd, 2H, ³J(HH) = 8.1 Hz, ⁴J(HH) = 3.7 Hz, H_{Ar}), 6.85 (d, 2H, ³J(HH) = 8.4 Hz, H_{Ar}), 6.74 (d, 1H, ³J(HH) = 8.1 Hz, H₃), 6.65 (dd, 1H, ³J(HH) = 8.5, ⁴J(HH) = 2.3, H₁₀), 6.52 (d, 2H, ³J(HH) = 8.4 Hz, H_{Ar}), 6.11 (d, 1H, ³J(HH) = 8.5 Hz, H₁₁), 1.30 (s, 9H, -CH₃), 1.26 (s, 18H, -CH₃), 1.10 (s, 9H, -CH₃) ppm.

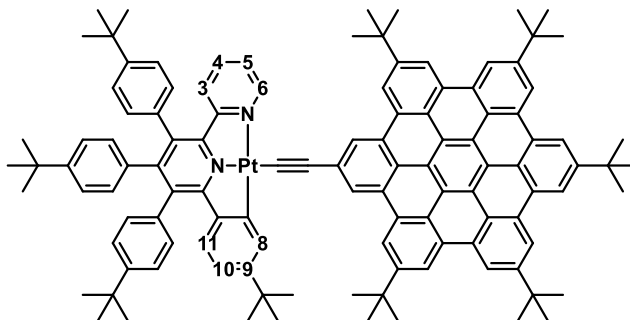
¹³C NMR: (150 MHz, CDCl₃) δ 164.1 (C_Q), 158.5 (C_Q), 154.5 (C_Q), 153.5 (C_Q), 151.5 (C_Q), 151.3 (C_Q), 150.8 (C_Q), 150.2 (C_Q), 149.2 (C_Q), 148.7 (1C, C₆), 144.7 (C_Q), 137.8 (1C, C_{4/5}), 135.3 (C_Q), 134.4 (C_Q), 133.6 (C_Q), 133.1 (C_Q), 133.0 (C_Q), 131.6 (1C, C₈), 129.5 (C_{Ar}), 129.4 (C_Q), 129.1 (C_{Ar}), 128.9 (1C, C₁₁), 126.7 (1C, C₃), 126.3 (1C, C_{4/5}), 125.8 (C_{Ar}), 125.3 (C_{Ar}), 123.5 (C_{Ar}), 120.5 (1C, C₁₀), 35.0 (C-CH₃), 34.6 (C-CH₃), 34.5 (C-CH₃), 34.2 (C-CH₃), 31.2 (C-CH₃), 31.2 (C-CH₃), 31.2 (C-CH₃), 31.0 (C-CH₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 877.3958; calcd. 877.3935 for C₅₀H₅₅N₂Pt [M-Cl].

CHN: Found: C, 65.10; H, 5.80; N 2.98, calcd. (%) for $C_{50}H_{55}N_2ClPt$: C, 65.67; H, 6.06; N 3.06.

IR: (ATR, $\nu_{\max}/\text{cm}^{-1}$) 2961, 1585, 1472, 1414, 1393, 1363, 1270, 1186, 1072, 1113, 1023, 830, 775, 680, 666.

[Pt(C $\equiv$ C-HBC)L] (L = 3,4,5,6-tetra(4-*tert*-butylphenyl)-2,2'-bipyridine (48))



[PtCl(L)] (Compound **49**, where L = 3,4,5,6-tetra(4-*tert*-butylphenyl)-2,2'-bipyridine) (20 mg, 0.0218 mmol) and 2,5,8,11,14-penta-*tert*-butyl-17-ethynylhexabenzo[bc,ef,hi,kl,no,qr]coronene (18 mg, 0.0217 mmol) were combined with CuI (1.0 mg, 0.005 mmol) and degassed by vacuum/ N_2 cycles. Freshly distilled, degassed and dried diisopropylamine (2 mL) and CH_2Cl_2 (8 mL) were added by cannula. The mixture was stirred for 40 h at room temperature under N_2 , by which time an orange precipitate was obtained. The solvents were concentrated to a low volume and a few drops of MeOH were added to yield the precipitate. This was then filtered and washed with cold MeOH.

Yield: 32 mg, 86 %

^1H NMR: (600 MHz, $CDCl_3$) δ 9.67 (d, 1H, $^3J(HH) = 5.3$ Hz, H_6), 9.54 (s, 2H, H_{HBC}), 9.39 (s, 2H, H_{HBC}), 9.33 (m, 8H, H_{HBC}), 8.46 (d, 1H, $^3J(PtH) = 42.9$ Hz, $^4J(HH) = 2.0$ Hz, H_8), 7.57 (m, 1H, H_4), 7.48 (m, 1H, H_5), 7.26 (m, 4H, $^3J(HH) = 8.5$ Hz, H_{Ar}), 7.02 (m, 4H, H_{Ar}), 6.87 (d, 2H, $^3J(HH) = 8.4$ Hz, H_{Ar}), 6.81 (d, 1H, $^3J(HH) = 8.4$ Hz, H_3), 6.67 (dd, 1H, $^3J(HH) = 8.9$, $^4J(HH) = 2.2$, H_{10}), 6.55 (d, 2H, $^3J(HH) = 8.4$ Hz, H_{Ar}), 6.27 (d, 1H, $^3J(HH) = 8.4$ Hz, H_{11}), 1.85 (s, 27H, $-CH_3$), 1.83 (s, 18H, $-CH_3$), 1.29 (s, 9H, $-CH_3$), 1.28 (s, 18H, $-CH_3$), 1.12 (s, 9H, $-CH_3$) ppm.

^{13}C NMR: (151 MHz, $CDCl_3$): δ 163.0 (C_Q), 159.3 (1C, C_2), 155.00 (C_Q), 153.7 (C_9), 151.8 (C_6), 151.4 (C_Q), 151.3 (C_Q), 150.7 (C_Q), 149.2 (C_Q), 149.1 (C_Q), 148.9 (C_Q), 146.2, 145.7 (C_Q), 144.6 (C-Pt), 141.9 (C_Q), 137.5 (1C, C_4), 135.4 (C_8), 135.3, 134.4, 133.7, 133.5, 133.3, 130.7, 130.6, 130.5, 130.5, 130.4, 130.3, 129.6 (C_{Ar}), 129.5 (C_{Ar}), 129.3 (C_{Ar}), 129.0 (1C, C_{11}), 127.5, 126.9 (1C, C_3), 126.8 (1C, C_5), 125.8 (C_{Ar}), 125.5 (C_{HBC}), 125.2 (C_{Ar}), 124.1, 124.1, 124.0, 123.8, 123.5 (C_{Ar}), 120.9, 120.6, 120.5, 120.4 (C_{HBC}), 120.3 (C_{10}), 119.8, 118.9 (C_{HBC}), 118.9 (C_{HBC}), 118.8, 118.7, 108.9 ($C\equiv C$), 107.7 ($C\equiv C$), 53.4, 35.8 ($C-CH_3$), 35.7 ($C-CH_3$), 34.8 ($C-CH_3$), 34.6 ($C-CH_3$), 34.5 ($C-CH_3$),

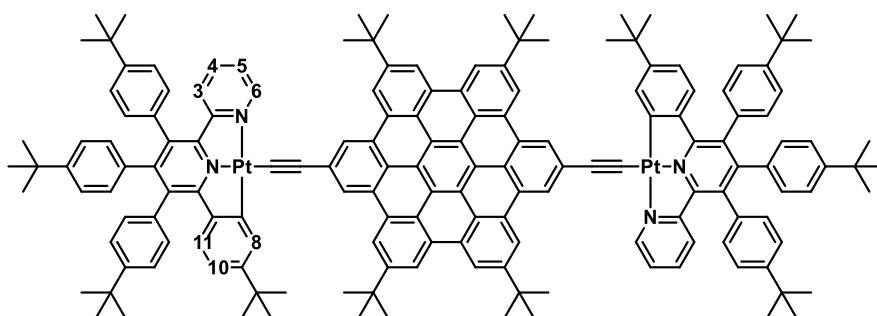
34.2 (C-CH₃), 32.1 (C-CH₃), 32.0 (C-CH₃), 31.3 (C-CH₃), 31.2 (C-CH₃), 31.0 (C-CH₃), 29.7 (C-CH₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂): found: 1704.8494; calcd. 1704.8552 for C₁₁₄H₁₁₃N₂Pt, [M+H]⁺.

IR: (ATR, ν_{max}/cm⁻¹) 2954, 2105, 1603, 1580, 1463, 1393, 1363, 1261, 1202, 1107, 1023, 942, 870, 847, 833, 778, 744, 684.

CHN: Found: C, 80.36; H, 6.16; N, 1.40; calcd. (%) for C₁₁₄H₁₁₂N₂Pt: C, 80.30; H, 6.62; N, 1.64.

[Pt((C≡C)₂HBC)L₂] (L = 3,4,5,6-Tetra(4-*tert*-butylphenyl)-2,2'-bipyridine (49)



Following the same general procedure as for **50**, the [PtCl(L)] precursor **49** (33 mg, 0.036 mmol) was combined with 2,5,11,14-tetra-*tert*-butyl-8,17-diethynylhexabenzocorone (26) (14 mg, 0.0176 mmol) and CuI (1.0 mg, 0.005 mmol). After degassing the solids by several vacuum/N₂ cycles, a mixture of dry and degassed diisopropylamine (3 mL) and CH₂Cl₂ (12 mL) was added by cannula. The resulting mixture was stirred under N₂ for 72 hours at RT, after which time an orange precipitate was evident. The solvents were concentrated *in vacuo* and a few drops of MeOH were added to precipitate the product. The precipitate was then filtered and washed with cold MeOH and Et₂O.

Yield: 33 mg, 73 %.

¹H NMR: (600 MHz, CDCl₃) δ 9.68 (d, 2H, ³J(HH) = 5.3 Hz, H₆), 9.54 (s, 4H, H_{HBC}), 9.38 (s, 4H, H_{HBC}), 9.32 (s, 4H, H_{HBC}), 8.45 (s, 2H, H₈), 7.56 (m, 2H, H₄), 7.48 (m, 2H, H₅), 7.29-7.23 (m, 8H, H_{Ar}), 7.01 (m, 8H, H_{Ar}), 6.86 (br m, 4H, H_{Ar}), 6.81 (s, 2H, H₃), 6.67 (d, 2H, ³J(HH) = 8.6 Hz, H₁₀), 6.56 (br m, 4H, H_{Ar}), 6.26 (d, 2H, ³J(HH) = 8.6 Hz, H₁₁), 1.82 (s, 36H, -CH₃), 1.33 (s, 18H, -CH₃), 1.28 (s, 18H, -CH₃), 1.27 (s, 18H, -CH₃), 1.11 (s, 18H, -CH₃) ppm.

¹³C NMR: (151 MHz, CDCl₃): δ 151.8 (2C, C₆), 137.6 (2C, C₄), 135.4 (2C, C₈), 129.6 (8C, C_{Ar}), 129.4 (4C, C_{Ar}), 129.0 (2C, C₁₁), 127.0 (2C, C₃), 126.7 (2C, C₅), 125.6 (8C, C_{Ar}), 125.4 (4C, C_{HBC}), 123.5 (4C, C_{Ar}), 120.3 (2C, C₁₀), 119.7 (4C, C_{HBC}), 118.7 (4C, C_{HBC}), 32.1 (C-CH₃), 31.2 (C-CH₃), 31.2 (C-CH₃), 31.2 (C-CH₃), 31.0 (C-CH₃) ppm.

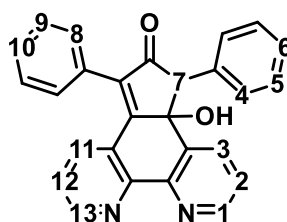
The very high degree of insolubility of this compound precluded the obtainment of a full ^{13}C NMR spectrum.

IR: (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$) 2953, 2101, 1600, 1581, 1462, 1394, 1362, 1262, 1202, 1118, 1024, 942, 870, 847, 832, 779, 745, 681.

HRMS: (m/z, MALDI, CH_2Cl_2): found: 2549.1794; calcd. 2549.1782 for $\text{C}_{162}\text{H}_{158}\text{N}_4\text{Pt}_2$, $[\text{M}]^+$.

CHN: Found: C, 71.70; H, 5.78; N, 1.96; calcd. (%) for $\text{C}_{162}\text{H}_{158}\text{N}_4\text{Pt}_2$: C, 76.27; H, 6.24; N, 2.20.

4b-hydroxy-5,7-diphenyl-4b,5-dihydro-6H-cyclopenta[f][1,10]phenanthroline-6-one²⁶
(51)



1,10-phenanthroline-5,6-dione (0.99 g, 4.7 mmol) and 1,3-diphenylpropan-2-one (1.33 g, 6.33 mmol) were combined in MeOH (10 mL), under an atmosphere of N_2 . Piperidine (0.5 mL, 5.06 mmol) was added by syringe, and the mixture was stirred for 16 hours. After this time, an off-white precipitate was observed, which was filtered from the reaction mixture and washed with cold MeOH. The product, **51**, was obtained as a white solid.

Yield: 1.76 g, 90 %.

^1H NMR: (400 MHz, CDCl_3) δ 8.86 (dd, 1H, $^3J(\text{HH}) = 4.6$ Hz, $^4J(\text{HH}) = 1.6$ Hz, H_1), 8.82 (dd, 1H, $^3J(\text{HH}) = 4.6$ Hz, $^4J(\text{HH}) = 1.7$ Hz, H_{13}), 8.08 (dd, 1H, $^3J(\text{HH}) = 7.6$ Hz, $^4J(\text{HH}) = 1.6$ Hz, H_{11}), 7.64 (dd, 1H, $^3J(\text{HH}) = 7.9$ Hz, $^4J(\text{HH}) = 1.8$ Hz, H_3), 7.59-7.49 (m, 4H, H_4 , H_5), 7.48-7.36 (m, 7H, $\text{H}_2, \text{H}_8, \text{H}_9$, H_{10}), 7.18 (dd, 1H, $^3J(\text{HH}) = 7.9$ Hz, $^4J(\text{HH}) = 4.7$ Hz, H_{12}), 4.54 (s, 1H, H_7), 2.54 (s, 1H, -OH) ppm.

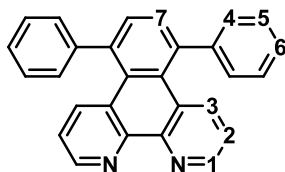
^{13}C NMR: (101 MHz CDCl_3) δ 202.8 (1C, C=O), 158.8 (C_Q), 152.6 (1C, C_1), 150.9 (1C, C_{13}), 150.3 (C_Q), 150.2 (C_Q), 140.3 (C_Q), 136.6 (1C, C_3), 136.5 (C_Q), 134.9 (C_Q), 133.9 (1C, C_{11}), 131.9 (1C, C_8), 129.9 (C_Q), 129.2 (1C, C_6), 129.1 (2C, C_4), 129.0 (4C, C_5, C_9), 128.3 (1C, C_{10}), 125.2 (C_Q), 124.6 (1C, C_{12}), 123.7 (1C, C_2), 74.8 (1C, C-OH), 61.0 (1C, C_7) ppm.

HRMS: (m/z, APCI, CH_2Cl_2) found: 403.1449; calcd. 403.1447 for $\text{C}_{27}\text{H}_{19}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$.

IR: (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$) 3667, 3220 (-OH), 1706 (C=O), 1556, 1415 (C=C), 1340, 1199, 1149, 1088 (C-O), 971, 815, 763, 741, 697.

CHN: Found: C, 77.79; H, 4.25; N, 6.79; calcd. (%) for $C_{27}H_{18}N_2O_2$: C, 80.58; H, 4.51; N, 6.96.

5,8-diphenylbenzo[f][1,10]phenanthroline²⁶ (54)



4b-hydroxy-5,7-diphenyl-4b,5-dihydro-6H-cyclopenta[f][1,10]phenanthroline-6-one (0.50 g, 1.24 mmol) and Al_2O_3 (2.50 g, 25 mmol) were added to dry, degassed chlorobenzene (55 mL) in an RBF. The mixture was heated to reflux (130 °C) for 3 hours under N_2 . 2,5-norbornadiene (1 mL, 9.83 mmol) was then added by syringe and refluxed for a further hour. The reaction mixture was allowed to cool and the solvent was removed in vacuo. The residue was dissolved in 1,2-dichlorobenzene (60 mL) and heated to 150 °C for 16 hours under N_2 . The solvent was removed in vacuo and purified by column chromatography (SiO_2 , CH_2Cl_2 :MeOH, 95:5 (v/v)) to give the product as an off-white solid.

Yield: 99 mg, 20 %.

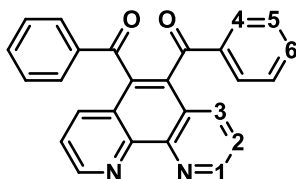
^1H NMR: (400 MHz, $CDCl_3$) δ 8.97 (dd, 2H, $^3J(HH) = 4.3$ Hz, $^4J(HH) = 1.5$ Hz, H_1), 8.00 (dd, 2H, $^3J(HH) = 8.5$ Hz, $^4J(HH) = 1.5$ Hz, H_3), 7.62 (s, 2H, H_7), 7.47 (m, 10H, H_4 , H_5 , H_6), 7.12 (dd, 2H, $^3J(HH) = 8.5$ Hz, $^4J(HH) = 4.3$ Hz, H_2) ppm.

^{13}C NMR: (101 MHz, $CDCl_3$) δ 149.5 (2C, C_1), 147.1 (2C, C_Q), 143.6 (2C, C_Q), 139.9 (2C, C_Q), 136.7 (2C, C_3), 130.8 (2C, C_7), 129.4 (10C, C_4 , C_5 , C_Q), 127.7 (2C, C_6), 127.2 (2C, C_Q), 121.2 (2C, C_2) ppm.

HRMS: (m/z, ESI, CH_2Cl_2) found: 383.1538; calcd. 383.1543 for $C_{28}H_{19}N_2$ $[M+H]^+$.

IR: (neat, ν_{bar}/cm^{-1}) 2970 (C-H_(Ar)), 1661, 1537 (C=C), 1425, 1470, 1425 (C=C), 1395, 1158, 1104, 951, 771, 739, 702.

(1,10-phenanthroline-5,6-diyl)bis(phenylmethanone)²⁶ (55)



4b-hydroxy-5,7-diphenyl-4b,5-dihydro-6H-cyclopenta[f][1,10]phenanthroline-6-one (0.50 g, 1.24 mmol) and Al_2O_3 (2.50 g, 25 mmol) were combined in an RBF. Chlorobenzene (50

mL) was added and the mixture was heated to reflux for 14 hours. After the solvent was removed *in vacuo*, the desired product was precipitated using Et₂O, and subsequently filtered and washed with cold MeOH, to give a white powder.

Yield: 164 mg, 35 %.

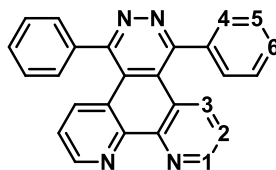
¹H NMR: (400 MHz, CDCl₃) δ 9.31 (dd, 2H, ³J(HH) = 4.2 Hz, ⁴J(HH) = 1.5 Hz, H₁), 8.10 (dd, 2H, ³J(HH) = 8.4 Hz, ⁴J(HH) = 1.6 Hz, H₃), 7.73 (d, 4H, ³J(HH) = 7.5 Hz, H₄), 7.65-7.56 (m, 4H, H₂/H₆), 7.40 (t, 4H, H₅) ppm.

¹³C NMR: (101 MHz, CDCl₃) δ 196.1 (2C, C=O), 151.7 (2C, C₁), 146.1 (2C, C_Q), 137.2 (2C, C_Q), 135.3 (2C, C₃), 134.7 (2C, C₆), 134.4 (2C, C_Q), 130.2 (4C, C₄), 128.8 (4C, C₅), 125.7 (2C, C_Q), 123.2 (2C, C_Q) ppm.

HRMS: (m/z, ESI, CH₂Cl₂) found: 411.1109; calcd. 411.1104 for C₂₆H₁₆N₂NaO₂ [M+Na]⁺.

IR: (neat, ν_{bar} /cm⁻¹) 3056 (C-H_(Ar)), 3036 (C-H_(Ar)), 1649 (C=O), 1594, 1501, 1452 (C=C), 1423, 1291, 1239, 1179, 874, 795, 735, 698, 667.

5,8-diphenylpyridazino[4,5-f][1,10]phenanthroline²⁶ (56)



(1,10-phenanthroline-5,6-diyl)bis(phenylmethanone) (130 mg, 0.33 mmol) and KOH (90 mg, 1.61 mmol) were combined in an RBF, and stirred in EtOH (10 mL). N₂H₄·H₂O (0.150 g, 50-60 %, 1.5 mmol) was added slowly, *via* a syringe. The mixture was then heated to reflux for 16 hours, under N₂. The solvent was removed *in vacuo*, and the product was precipitated using Et₂O, to give an off-white powder.

Yield: 55 mg, 44 %.

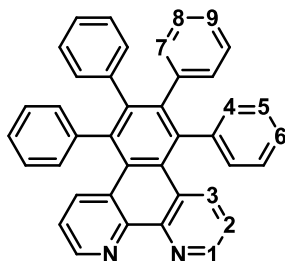
¹H NMR: (400 MHz, CDCl₃) δ 9.19 (dd, 2H, ³J(HH) = 4.5 Hz, ⁴J(HH) = 1.6 Hz, H₁), 8.21 (dd, 2H, ³J(HH) = 8.6 Hz, ⁴J(HH) = 1.7 Hz, H₃), 7.71 (dd, 2H, ³J(HH) = 7.9 Hz, ⁴J(HH) = 2.0 Hz, H₄), 7.54-7.60 (m, H₅/H₆), 7.35 (dd, 2H, ³J(HH) = 8.5 Hz, ⁴J(HH) = 4.3 Hz, H₂) ppm.

¹³C NMR: (101 MHz, CDCl₃) δ 156.8 (2C, C_Q), 152.3 (2C, C₁), 148.5 (2C, C_Q), 139.5 (2C, C_Q), 136.2 (2C, C₃), 129.9 (4C, C₄), 129.8 (2C, C₆), 129.4 (4C, C₅), 125.7 (2C, C_Q), 124.1 (2C, C_Q), 122.3 (2C, C₂).

HRMS: (m/z, ESI, CH₂Cl₂) found: 407.1276; calcd. 407.1267 for C₂₆H₁₆N₄Na [M+Na]⁺.

IR: (neat, $\nu_{\text{bar}}/\text{cm}^{-1}$) 3053 ($\text{C-H}_{(\text{Ar})}$), 2974 ($\text{C-H}_{(\text{Ar})}$), 1491, 1443 ($\text{C}=\text{C}$), 1369, 1112, 1015, 874, 823, 775, 745, 701, 620.

5,6,7,8-tetraphenylbenzo[f][1,10]phenanthroline (57)



4b-hydroxy-5,7-diphenyl-4b,5-dihydro-6H-cyclopenta[f][1,10]phenanthroline-6-one (500 mg, 1.2 mmol) and diphenylacetylene (270 mg, 1.5 mmol) were combined and added to benzophenone (1.00 g) in an RBF. The mixture was degassed by vacuum/argon cycles and then heated to 300 °C for 3 hours, with the reaction mixture changing colour from off-white to dark brown. The reaction mixture was then allowed to cool and dissolved in CH_2Cl_2 (ca. 5 mL). The product was purified by column chromatography (SiO_2 , CH_2Cl_2 :MeOH, 100:2 (v/v)) and obtained as an off-white powder.

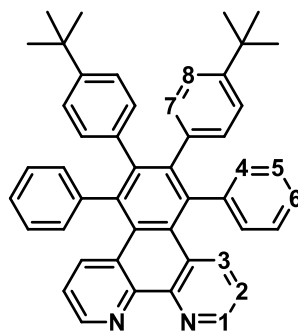
Yield: 94 mg, 15 %.

^1H NMR: (400 MHz, CDCl_3) δ 8.92 (dd, 2H, $^3J(\text{HH}) = 4.4$ Hz, $^4J(\text{HH}) = 1.7$ Hz, H_1), 7.83 (dd, 2H, $^3J(\text{HH}) = 8.6$ Hz, $^4J(\text{HH}) = 1.5$ Hz, H_3), 7.13-7.19 (m, 6H, H_5, H_6), 7.03-7.09 (m, 6H, H_2, H_4), 6.89-6.96 (m, 6H, H_8, H_9), 6.71-6.75 (m, 4H, H_7) ppm.

^{13}C NMR: (101 MHz, CDCl_3) δ 149.0 (2C, C_1), 147.3 (2C, C_Q), 141.2 (2C, C_Q), 141.5 (2C, C_Q), 139.7 (2C, C_Q), 138.2 (2C, C_Q), 136.8 (2C, C_3), 131.8 (4C, C_4), 131.3 (4C, C_7), 129.5 (2C, C_Q), 128.4 (4C, C_5), 127.8 (2C, C_Q), 126.8 (6C, C_6, C_8), 125.6 (2C, C_9), 121.3 (2C, C_2) ppm.

HRMS: (m/z, ESI, CH_2Cl_2) found: 535.2157; calcd. 535.2169 for $\text{C}_{40}\text{H}_{27}\text{N}_2$ $[\text{M}+\text{H}]^+$.

IR: (neat, $\nu_{\text{bar}}/\text{cm}^{-1}$) 2980 ($\text{C-H}_{(\text{Ar})}$), 1601, 1564, 1496, 1444 ($\text{C}=\text{C}$), 1425 ($\text{C}=\text{C}$), 1375, 1160, 1072, 1027, 953, 807, 741, 699.

6,7-bis(4-(tert-butyl)phenyl)-5,8-diphenylbenzo[f][1,10]phenanthroline (58)

4b-hydroxy-5,7-diphenyl-4b,5-dihydro-6H-cyclopenta[f][1,10]phenanthroline-6-one (200 mg, 0.50 mmol) and 1,2-bis(4-(tert-butyl)phenyl)ethyne (173 mg, 0.60 mmol) were combined and added to benzophenone (800 mg). The mixture was degassed by vacuum/argon cycles and then heated to 300 °C for 3 hours, under N₂. The reaction mixture was then cooled and taken into CH₂Cl₂ (ca. 5 mL). The product was then obtained *via* purification by column chromatography (SiO₂, CH₂Cl₂:MeOH, 100:2 (v/v)) to give an off-white solid.

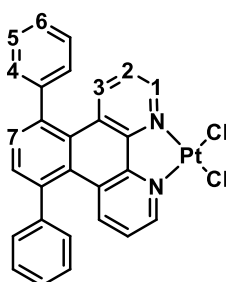
Yield: 50 mg, 16 %.

¹H NMR: (400 MHz, CDCl₃) δ 8.91 (dd, 2H, ³J(HH) = 4.4 Hz, ⁴J(HH) = 1.7 Hz, H₁), 7.83 (dd, 2H, ³J(HH) = 8.6 Hz, ⁴J(HH) = 1.6 Hz, H₃), 7.11-7.20 (m, 6H, H₅, H₆), 7.02-7.09 (m, 6H, H₂, H₄), 6.88 (d, 4H, ³J(HH) = 8.6 Hz, H₈), 6.58 (d, 4H, ³J(HH) = 8.6 Hz, H₇), 1.17 (s, 18H, -CH₃) ppm.

¹³C NMR: (101 MHz, CDCl₃) δ 149.0 (2C, C₁), 148.2 (C_Q), 147.3 (C_Q), 142.0 (2C, C_Q), 138.0 (C_Q), 136.8 (2C, C₃), 136.7 (C_Q), 131.8 (4C, C₄), 130.8 (4C, C₇), 129.3 (C_Q), 128.3 (4C, C₅), 127.9 (C_Q), 126.7 (2C, C₆), 123.4 (4C, C₈), 121.2 (2C, C₂), 34.2 (2C, -C-CH₃), 31.2 (6C, -CH₃) ppm.

HRMS: (m/z, APCI, CH₂Cl₂) found: 647.3429; calcd. 647.3426 for C₄₈H₄₃N₂ [M+H]⁺.

IR: (neat, ν̄/cm⁻¹) 2958 (C-H stretch), 1564, 1464 (C=C), 1423 (C=C), 1364 (CH₃ bending), 1266, 1113, 1022, 845, 802, 750, 707.

[Pt(L)Cl₂] (L = 54) (Compound 59)

5,8-diphenylbenzo[f][1,10]phenanthroline (20 mg, 0.05 mmol) and $\text{Pt}(\text{DMSO})_2\text{Cl}_2$ (21 mg, 0.05 mmol) were combined and then dissolved in CHCl_3 (3 mL). The mixture was then heated to reflux for 1 hour. Once cooled, the solution was filtered and then concentrated *in vacuo*. The product was subsequently precipitated with MeOH and filtered, generating a yellow solid.

Yield: 31 mg, 91 %.

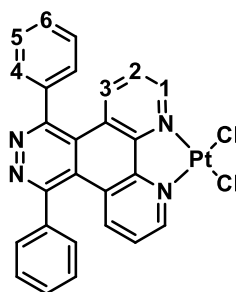
^1H NMR: (600 MHz, CDCl_3) δ 9.80 (dd, 2H, $^3J(\text{HH}) = 5.5$ Hz, $^4J(\text{HH}) = 1.0$ Hz, H_1), 8.23 (dd, 2H, $^3J(\text{HH}) = 8.8$ Hz, $^4J(\text{HH}) = 1.1$ Hz, H_3), 7.78 (s, 2H, H_7), 7.54-7.59 (m, 6H, H_5, H_6), 7.45-7.49 (m, 4H, H_4), 7.34 (dd, 2H, $^3J(\text{HH}) = 8.5$ Hz, $^4J(\text{HH}) = 5.3$ Hz, H_2) ppm.

^{13}C NMR: (150 MHz, CDCl_3) δ 149.3 (C_Q), 148.5 (2C, C_1), 142.2 (C_Q), 141.3 (C_Q), 138.3 (2C, C_3), 132.8 (2C, C_7), 130.5 (C_Q), 130.1 (4C, C_5), 129.2 (4C, C_4), 128.8 (2C, C_6), 127.6 (C_Q), 123.7 (2C, C_2) ppm.

HRMS: (m/z, ESI, CH_2Cl_2) found: 670.0381; calcd. 670.0390 for $\text{C}_{28}\text{H}_{18}\text{Cl}_2\text{N}_2\text{NaPt} [\text{M}+\text{Na}]^+$.

IR: (neat, $\nu_{\text{bar}}/\text{cm}^{-1}$) 2980 (C-H), 1598, 1495, 1441 (C=C), 1402, 1377, 1264, 1157, 1074, 870, 803, 767, 716, 699.

[Pt(L)Cl₂] (L = 56) (Compound 60)



5,8-diphenylpyridazino[4,5-f][1,10]phenanthroline (20 mg, 0.05 mmol) and $\text{Pt}(\text{DMSO})_2\text{Cl}_2$ (21 mg, 0.05 mmol) were combined and added to CHCl_3 (3 mL) in an RBF. The mixture was heated to reflux for 1 hour. After the mixture had cooled, it was filtered, concentrated *in vacuo*, and a small amount of MeOH was added to precipitate the product. The yellow solid obtained was filtered and washed with cold MeOH.

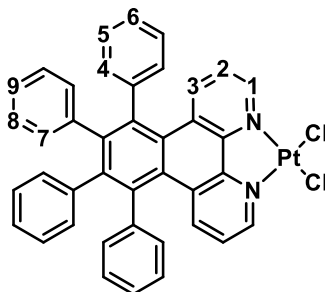
Yield: 30 mg, 89 %.

^1H NMR: (400 MHz, CDCl_3) δ 9.69 (d, 2H, $^3J(\text{HH}) = 5.5$ Hz, H_1), 8.41 (d, 2H, $^3J(\text{HH}) = 8.7$ Hz, H_3), 7.80 (d, 4H, $^3J(\text{HH}) = 7.1$ Hz, H_4), 7.60-7.70 (m, 6H, H_5, H_6), 7.51 (dd, 2H, $^3J(\text{HH}) = 8.6$ Hz, $^3J(\text{HH}) = 5.4$ Hz, H_2) ppm.

HRMS: (m/z, ESI, CH₂Cl₂) found: 672.0289; calcd. 672.0294 for C₂₆H₁₆Cl₂N₄NaPt [M+Na]⁺.

IR: (neat, ν bar/cm⁻¹) 2980 (C-H), 1574, 1443 (C=C), 1377, 1253, 1154, 1073, 1022, 954, 763, 700.

[Pt(L)Cl₂] (L = 57) (Compound 61)



5,6,7,8-tetraphenylbenzo[f][1,10]phenanthroline (20 mg, 0.037 mmol) and Pt(DMSO)₂Cl₂ (15.3 mg, 0.036 mmol) were combined in CHCl₃ (2 mL) and heated to reflux for 1 hour. The solution was then cooled and concentrated in vacuo. The addition of MeOH caused the product to precipitate, which was then collected by filtration and washed with cold MeOH.

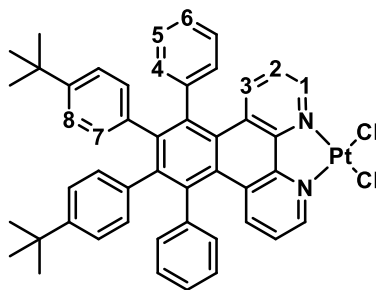
Yield: 27 mg, 94 %.

¹H NMR: (400 MHz, CDCl₃) δ 9.73 (dd, 2H, ³J(HH) = 5.4 Hz, ⁴J(HH) = 1.1 Hz, H₁), 7.99 (dd, 2H, ³J(HH) = 8.8 Hz, ⁴J(HH) = 1.1 Hz, H₃), 7.21-7.28 (m, 8H, H₂, H₅, H₆), 7.11 (dd, 4H, ³J(HH) = 6.4 Hz, ⁴J(HH) = 1.8 Hz, H₄), 6.91-6.97 (m, 6H, H₈, H₉), 6.70-6.75 (m, 4H, H₇) ppm.

HRMS: (m/z, ESI, CH₂Cl₂) found: 822.1009; calcd. 822.1016 for C₄₀H₂₆Cl₂N₂NaPt [M+Na]⁺.

IR: (neat, ν bar/cm⁻¹) 3656 (C-H), 2980 (C-H), 1600, 1494, 1439 (C=C), 1378, 1332, 1255, 1154, 1073, 1022, 953, 802, 736, 717, 698.

[Pt(L)Cl₂] (L = 58) (Compound 62)



6,7-bis(4-(tert-butyl)phenyl)-5,8-diphenylbenzo[f][1,10]phenanthroline (35 mg, 0.054 mmol) and Pt(DMSO)₂Cl₂ (23 mg, 0.054 mmol) were added to CHCl₃, and the mixture was then heated to reflux for 1 hour. The solution was allowed to cool and then concentrated *in*

vacuo to a low volume. The product was precipitated with a few drops of MeOH and isolated by filtration. The yellow solid obtained was washed with cold MeOH.

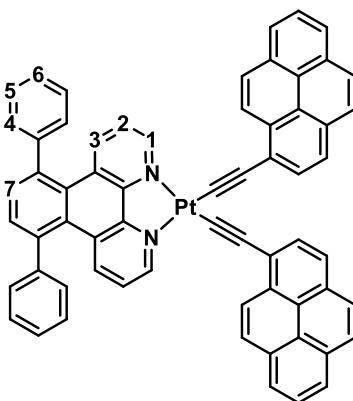
Yield: 31 mg, 63 %.

^1H NMR: (400 MHz, CDCl_3) δ 9.78 (d, 2H, $^3J(\text{HH}) = 5.3$ Hz, H_1), 7.99 (d, 2H, $^3J(\text{HH}) = 8.9$ Hz, H_3), 7.20-7.28 (m, 8H, $\text{H}_2, \text{H}_5, \text{H}_6$), 7.09 (d, 4H, $^3J(\text{HH}) = 6.8$ Hz, H_4), 6.90 (d, 4H, $^3J(\text{HH}) = 8.2$ Hz, H_8), 6.57 (d, 4H, $^3J(\text{HH}) = 8.2$ Hz, H_7), 1.16 (s, 18H, $-\text{CH}_3$) ppm.

^{13}C NMR: (150 MHz, CDCl_3) δ 149.3 (C_Q), 148.9 (C_Q), 148.0 (2C, C_1), 144.5 (C_Q), 140.7 (C_Q), 139.4 (C_Q), 138.5 (2C, C_3), 135.6 (C_Q), 131.3 (4C, C_4), 131.0 (C_Q), 130.4 (4C, C_7), 129.1 (4C, C_5), 127.7 (2C, C_6), 127.4 (C_Q), 123.7 (4C, C_8), 123.5 (2C, C_2), 34.2 (2C, $\text{C}-\text{CH}_3$), 31.2 (6C, $-\text{CH}_3$) ppm.

IR: (neat, $\text{vbar}/\text{cm}^{-1}$) 2955 (C-H), 2161, 1976, 1510, 1441 (C=C), 1382, 1361, 1268, 1199, 1111, 1074, 1023, 919, 844, 796, 746, 703.

[Pt(L)(C $\equiv$ C-pyrene) $_2$] (L = **54) (Compound **63**)**



Compound **59** ([Pt(L)Cl $_2$], where L = **54**) (20 mg, 0.031 mmol) and CuI (0.5 mg, 0.003 mmol) were added to a Schlenk flask and degassed by several vacuum/argon cycles. A mixture of CH_2Cl_2 and DIPA (20 mL, 3:1 (v/v)) was degassed and added to the solids by cannula. 1-ethynylpyrene (21 mg, 0.093 mmol) was quickly added, and the mixture was stirred at RT for 48 hours. The solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 . The product was obtained after purification by column chromatography (SiO_2 , initially eluting with CH_2Cl_2 only, followed by CH_2Cl_2 :MeOH, 10:1 (v/v)).

Yield: 8 mg, 25 %.

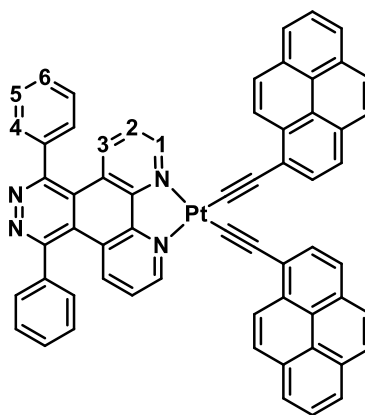
^1H NMR: (400 MHz, CDCl_3) δ 10.12 (d, 2H, $^3J(\text{HH}) = 4.6$ Hz, H_1), 9.19 (d, 2H, $^3J(\text{HH}) = 9.1$ Hz, H_{Pyrene}), 8.28 (d, 2H, $^3J(\text{HH}) = 7.9$ Hz, H_{Pyrene}), 8.23 (dd, 2H, $^3J(\text{HH}) = 8.7$ Hz, $^4J(\text{HH}) = 1.1$ Hz, H_3), 8.14 (d, 2H, $^3J(\text{HH}) = 7.2$ Hz, H_{Pyrene}), 7.93-8.11 (m, 12H, H_{Pyrene}), 7.70 (s, 2H, H_7), 7.51-7.55 (m, 6H, H_5, H_6), 7.38-7.45 (m, 6H, H_2, H_4) ppm.

HRMS: (m/z, ESI, CH₂Cl₂) found: 1050.2408; calcd. 1050.2424 for C₆₄H₃₆N₂NaPt [M+Na]⁺.

IR: (neat, ν bar/cm⁻¹) 2980 (C-H), 2096 (C≡C), 1599, 1494, 1439 (C=C), 1379, 1332, 1255, 1153, 1072, 1021, 953, 838, 803, 766, 699.

CHN: Found: C, 70.09; H, 3.13; N, 2.27; calcd. (%) for C₆₄H₃₆N₂Pt: C, 74.77; H, 3.53; N, 2.72.

[Pt(L)(C≡C-pyrene)₂] (L = 56) (Compound 64)



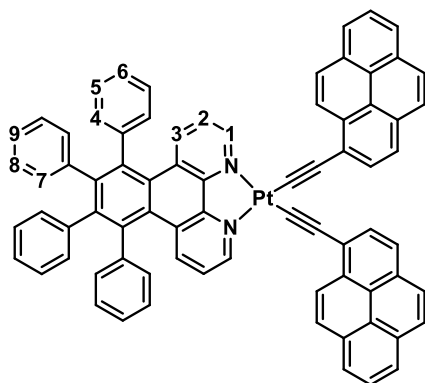
Compound **60** ([Pt(L)Cl₂], where L = **56**) (20 mg, 0.031 mmol) and CuI (0.5 mg, 0.003 mmol) were placed in a Schlenk flask and degassed by vacuum/argon cycles. CH₂Cl₂ and DIPA (3:1 (v/v), 40 mL) were combined, degassed (by freeze-pump-thaw), and added to the solids by cannula. 1-ethynylpyrene (21 mg, 0.093 mmol) was quickly added to the reaction mixture, which was then stirred for 48 hours at RT, under N₂. The solvents were then removed *in vacuo*, and the residue was dissolved in CH₂Cl₂. The product was obtained as a reddish-orange solid after column chromatography (eluting firstly with CH₂Cl₂, then with CH₂Cl₂:MeOH 10:1 (v/v) to elute the product).

Yield: 8.2 mg, 26 %.

¹H NMR: (400 MHz, DMSO-d₆) δ 10.07 (d, 2H, ³J(HH) = 5.9 Hz, H₁), 8.98 (d, 2H, ³J(HH) = 9.2 Hz, H_{pyrene}), 7.96-8.36 (m, 18H, H_{pyrene}, H₃), 7.74 (d, 4H, ³J(HH) = 7.8 Hz, H₄), 7.59-7.68 (m, 8H, H₂, H₅, H₆) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 1029.2482; calcd. 1029.2431 for C₆₂H₃₄N₄Pt [M]⁺.

IR: (neat, ν bar/cm⁻¹) 2980 (C-H), 2888, 2094 (C≡C), 1598, 1576, 1440 (C=C), 1379, 1253, 1154, 1073, 953, 844, 803, 763, 719, 700.

[Pt(L)(C≡C-pyrene)₂] (L = 57) (Compound 65)

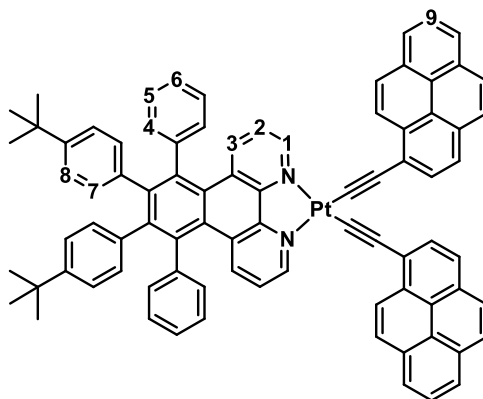
Compound **61** ([Pt(L)Cl₂], where L = **57**) (20 mg, 0.025 mmol) and CuI (0.5 mg, 0.003 mmol) were combined in a Schlenk flask and degassed by vacuum/argon cycles. CH₂Cl₂ and DIPA (3:1 (v/v), 40 mL) were combined and degassed (by freeze-pump-thaw) and then added to the solids by cannula. 1-ethynylpyrene (17 mg, 0.075 mmol) was added to the flask, which was then maintained under an atmosphere of N₂. The mixture was stirred for 48 hours at RT. The solvents were subsequently removed by rotary evaporation, and the residue was dissolved in CH₂Cl₂. The compound was then purified by column chromatography on SiO₂, eluting firstly with CH₂Cl₂ only, and then eluting the product with CH₂Cl₂:MeOH 10:1 (v/v). The product was obtained as a quite insoluble reddish-orange powder.

Yield: 6.7 mg, 23 %.

¹H NMR: (400 MHz, DMSO-d₆, 60 °C) δ 9.91 (d, 2H, ³J(HH) = 5.6 Hz, H₁), 9.02 (d, 2H, ³J(HH) = 9.5 Hz, H_{Pyrene}), 8.01-8.28 (m, 16H, H_{Pyrene}), 7.69 (m, 2H, H_{Pyrene}), 7.24 (m, 12H, H₂,H₄,H₅,H₆), 6.93 (m, 6H, H₈,H₉), 6.81 (m, 4H, H₇) ppm (*due to the insolubility of this compound, these assignments are tentative*).

HRMS: (m/z, MALDI, CH₂Cl₂) found: 1179.3191; calcd. 1179.3152 for C₇₆H₄₄N₂Pt [M]⁺.

IR: (neat, ν_{bar} /cm⁻¹) 2980 (C-H), 2888 (C-H), 2098 (C≡C), 1976, 1599, 1440, 1380, 1252, 1153, 1073, 1020, 954, 804, 764, 699.

[Pt(L)(C≡C-pyrene)₂] (L = 58) (Compound 66)

Compound **62** ([Pt(L)Cl₂], where L = **58**) (20 mg, 0.022 mmol) and CuI (0.4 mg, 0.002 mmol) were added to a Schlenk flask and degassed by several vacuum/argon cycles. CH₂Cl₂ and DIPA (3:1, (v/v) 40 mL) were combined, degassed and added to the solids by cannula. 1-ethynylpyrene (17 mg, 0.075 mmol) was added, and the mixture was stirred at RT, under N₂, for 48 hours. The solvents were removed *in vacuo*, and the residue was then dissolved in CH₂Cl₂ and subjected to column chromatography on SiO₂, eluting firstly with CH₂Cl₂ only, and then with CH₂Cl₂:MeOH 10:1 (v/v) to give the product as a reddish-brown powder. Further purification with a preparative TLC plate was required to remove residual 1-ethynylpyrene (SiO₂, CH₂Cl₂:MeOH, 20:1 (v/v)).

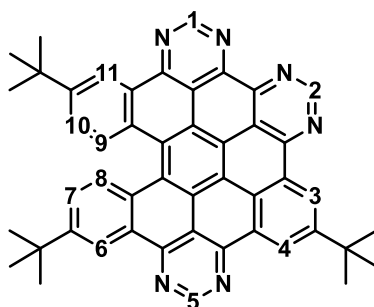
Yield: 4.2 mg, 15 %.

¹H NMR: (600 MHz, CDCl₃) δ 10.07 (d, 2H, ³J(HH) = 4.9 Hz, H₁), 9.20 (d, 2H, ³J(HH) = 9.0 Hz, H_{Pyrene}), 8.30 (d, 2H, ³J(HH) = 8.0 Hz, H₉), 8.10-8.14 (m, 4H, H_{Pyrene}), 8.00-8.07 (m, 8H, H₃, H_{Pyrene}), 7.94-7.98 (m, 4H, H_{Pyrene}), 7.19-7.31 (m, 8H, H₂, H₅, H₆), 7.1 (d, 4H, ³J(HH) = 7.1 Hz, H₄), 6.87 (d, 4H, ³J(HH) = 8.1 Hz, H₈), 6.50 (d, 4H, ³J(HH) = 8.1 Hz, H₇), 1.17 (s, 18H, -CH₃) ppm.

¹³C NMR: (150 MHz, CDCl₃) δ 150.0 (2C, C₁), 148.9 (C_Q), 148.7 (C_Q), 144.0 (C_Q), 141.0 (C_Q), 139.2 (C_Q), 138.2 (2C, C₃), 135.8 (C_Q), 132.4 (C_Q), 131.6 (C_Q), 131.5 (C_Q), 131.4 (4C, C₄), 130.8 (C_Q), 130.5 (4C, C₇), 130.2 (2C, C₉), 129.2 (C_Q), 128.9 (4C, C₅), 127.8 (C_Q), 127.6 (2C, C_{Pyrene}), 127.5 (2C, C₆), 127.5 (C_{Pyrene}), 127.1 (C_{Pyrene}), 126.5 (C_Q), 125.7 (C_{Pyrene}), 124.8 (C_Q), 124.6 (C_{Pyrene}), 124.4 (C_{Pyrene}), 124.3 (C_{Pyrene}), 124.1 (2C, C₂), 123.9 (C_Q), 123.6 (4C, C₈), 101.2 (2C, C≡C), 93.7 (2C, C≡C), 34.2 (2C, C-CH₃), 31.2 (6C, C-CH₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 1291.4464; calcd. 1291.4404 for C₈₄H₆₀N₂Pt [M]⁺.

IR: (neat, $\bar{\nu}$ /cm⁻¹) 2959 (C-H), 2094 (C≡C), 1596, 1500, 1485 (C=C), 1436 (C=C), 1378, 1361, 1266, 1230, 1181, 1022, 843, 802, 721.

5th-Asym-HASB²² (70)

5,5',5''-(4,4''-di-tert-butyl-5'-(4-(tert-butyl)phenyl)-[1,1':2',1''-terphenyl]-3',4',6'-triyl)tripyrimidine (**68**, 70 mg, 0.099 mmol) and DDQ (134 mg, 0.592 mmol) were added to dry CH₂Cl₂, under N₂. The mixture was stirred for 15 minutes, until all solids were dissolved. CF₃SO₃H (0.05 mL, 0.592 mmol) was added slowly by syringe. An immediate colour change to dark red was observed. The mixture was stirred at RT for 3 hours. The solution was neutralised with K₂CO₃ and diluted with CH₂Cl₂. The organic layer was washed with H₂O (30 mL) and brine (30 mL) and then dried over MgSO₄. Concentration of the solvent in vacuo and subsequent purification by preparative plate chromatography (SiO₂, CH₂Cl₂:MeOH, 25:1, v/v) gave the desired product as an orange solid.

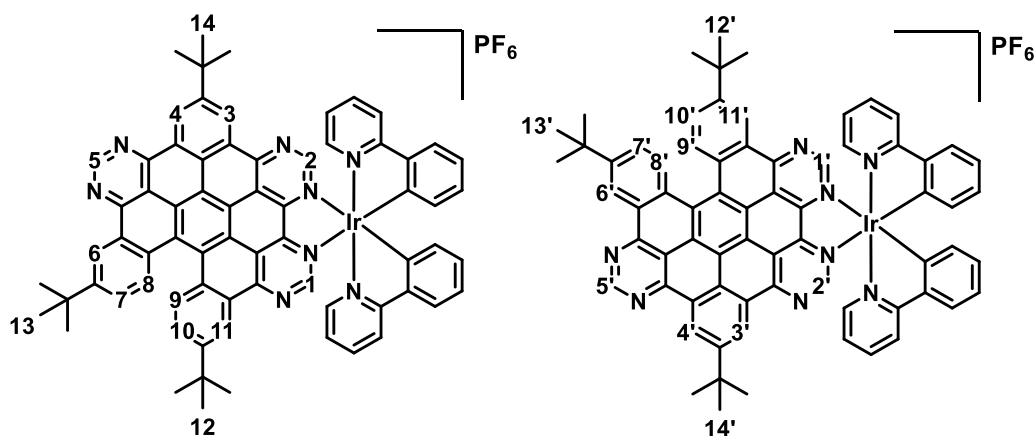
Yield: 21 mg, 30 %.

¹H NMR: (600 MHz, CDCl₃) δ 10.27 (s, 1H, H₁), 10.23 (s, 1H, H₂), 10.11 (s, 2H, H₃/H₄), 10.09 (s, 1H, H₅), 9.58 (m, 2H, H₁₁/H₆), 8.84 (d, 1H, ³J(HH) = 8.5 Hz, H₁₀), 8.82 (d, 1H, ³J(HH) = 8.5 Hz, H₇), 7.74 (d, 2H, ³J(HH) = 8.7 Hz, H₉/H₈), 1.86 (s, 9H, -CH₃), 1.65 (s, 9H, -CH₃), 1.64 (9H, s, -CH₃) ppm.

¹³C NMR: (150 MHz, CDCl₃) δ 157.2 (1C, C₂), 157.1 (1C, C₁), 156.7 (1C, C₅), 154.7 (C_Q), 154.6 (C_Q), 153.93 (C_Q), 153.85 (C_Q), 152.6 (C_Q), 152.5 (C_Q), 151.6 (C_Q), 151.4 (C_Q), 131.6 (C_Q), 131.1 (1C, C₁₀), 131.0 (1C, C₇), 130.0 (C_Q), 129.8 (C_Q), 128.5 (C_Q), 127.6 (1C, C₈), 127.4 (1C, C₉), 127.0 (C_Q), 126.8 (1C, C₃), 126.5 (1C, C₄), 124.7 (C_Q), 124.5 (C_Q), 122.1 (1C, C₁₁), 121.9 (C_Q), 121.8 (1C, C₆), 120.0 (C_Q), 119.6 (C_Q), 118.6 (C_Q), 118.5 (C_Q), 117.5 (C_Q), 115.2 (C_Q), 36.3 (1C, -C-(CH₃)₃), 35.54 (1C, -C-(CH₃)₃), 35.52 (1C, -C-(CH₃)₃), 31.9 (3C, -C-(CH₃)₃), 31.5 (3C, -C-(CH₃)₃), 31.4 (3C, -C-(CH₃)₃) ppm.

HRMS: (m/z, APCI, CH₂Cl₂) found: 699.3215, calcd. 699.3231 for C₄₈H₃₉N₆ [M+H]⁺.

IR: (neat, $\bar{\nu}$ /cm⁻¹) 2957, 1604, 1545, 1530, 1464, 1396, 1368, 1325, 1298, 1253, 1022, 911, 891, 844, 821, 795, 692, 678.

[Ir(ppy)₂(⁵/₆th-Asym-HASB)]PF₆ (74)

⁵/₆th-Asym-HASB (7.8 mg, 0.012 mmol), [Ir(ppy)₂Cl₂] (6 mg, 0.006 mmol) and NH₄PF₆ (5 mg, 0.031 mmol) were added to 1 mL of CHCl₃ and 0.5 mL MeOH. The mixture was refluxed for 2 hours, yielding a dark brown solution. This was concentrated under vacuum and a few drops of MeOH were added to precipitate the compound as a purple solid.

Yield: 11 mg, 73 %.

¹H NMR: (600 MHz, CDCl₃) δ 10.19 (m, 2H, H_{4/4'}), 10.12 (m, 2H, H_{5/5'}), 10.04 (m, 2H, H_{3/3'}), 9.59 (d, 1H, *J*(HH) = 2.3 Hz, H_{6/6'}), 9.57 (d, 1H, *J*(HH) = 2.3 Hz, H_{6/6'}), 9.54 (d, 1H, *J*(HH) = 2.1 Hz, H_{11/11'}), 9.48 (d, 1H, *J*(HH) = 2.1 Hz, H_{11/11'}), 9.42 (s, 1H, H₂), 9.40 (m, 2H, H_{1/1'}, H_{2/2'}), 9.37 (s, 1H, H₁), 9.06 (m, 1H, H_{10/10'}), 9.02 (m, 2H, H₁₀, H_{7/7'}), 8.92 (m, 1H, H_{7/7'}), 7.93-8.02 (m, 5H, H_B), 7.67-7.89 (m, 14 H, H_B, H_{8'}, H₉, H_{9'}, H_B), 7.60 (d, 1H, H_B), 7.17-7.22 (m, 4H, H_A), 7.08-7.14 (m, 4H, H_A), 7.04 (m, 1H, H_B), 6.99 (m, 1H, H_B), 6.83-6.87 (m, 2H, H_B), 6.63-6.65 (m, 2H, H_A), 6.60 (d, 2H, H_A), 1.79 (s, 9H, -CH₃), 1.78 (s, 9H, -CH₃), 1.63 (s, 9H, -CH₃), 1.63 (s, 9H, -CH₃), 1.60 (s, 9H, -CH₃), 1.57 (s, 9H, -CH₃) ppm.

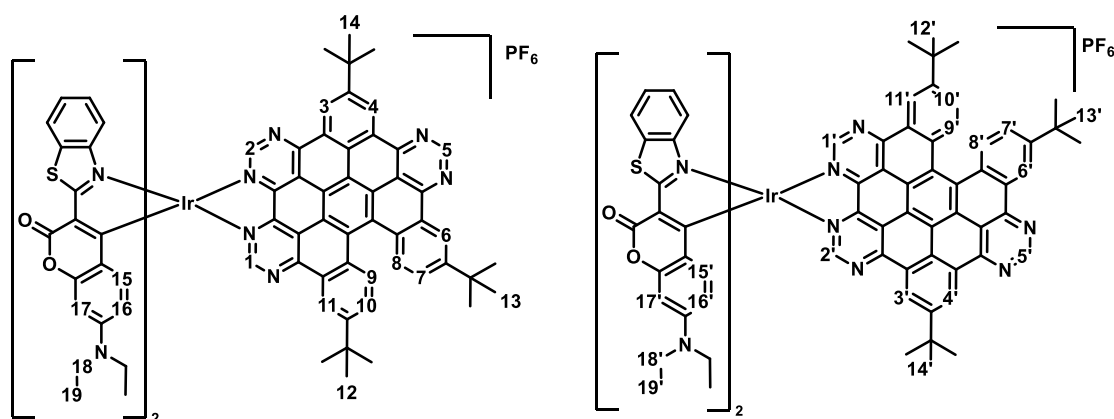
¹³C NMR: (150 MHz, CDCl₃) δ 168.1 (C_B), 168.0 (C_B), 167.4 (C_B), 167.2 (C_B), 157.08 (C_{5/5'}), 157.05 (C_{5/5'}), 156.4 (C_Q), 156.2 (C_Q), 156.1 (C_Q), 156.0 (C_Q), 155.69 (C_{1'/2'}), 155.63 (C₁), 155.53 (C₂), 154.5 (C_Q), 154.4 (C_Q), 154.05 (C_Q), 153.55 (C_Q), 153.48 (C_Q), 153.25 (C_Q), 153.20 (C_Q), 153.1 (C_Q), 153.0 (C_Q), 152.3 (C_Q), 152.1 (C_Q), 152.0 (C_Q), 151.8 (C_Q), 150.68 (C_B), 150.41 (C_B), 149.5 (C_B), 149.4 (C_B), 147.7 (C_Q), 147.4 (C_Q), 147.1 (C_Q), 146.9 (C_Q), 144.1 (C_Q), 144.0 (C_Q), 143.7 (C_Q), 143.65 (C_Q), 138.4 (C_B), 138.33 (C_B), 138.32 (C_B), 138.29 (C_B), 138.2 (C_B), 133.4 (C_Q), 133.3 (C_Q), 132.2 (C_A), 132.12 (C_A), 132.09 (C_{10/7/7'}), 132.0 (C_Q), 131.9 (C_A), 131.6 (C_{7/7'}), 131.3 (C_{10'}), 131.2 (C_{10/7/7'}), 131.11 (C_A), 131.10 (C_A), 131.0 (C_Q), 130.9 (C_Q), 130.8 (C_A), 130.75 (C_A), 130.7 (C_Q), 130.6 (C_Q), 129.5 (C_{9'}), 129.23 (C_{9/8/8'}), 129.20 (C_{9/8/8'}), 129.05 (C_Q), 128.9 (C_{4/4'}), 128.61 (C_Q), 128.58 (C_Q), 127.9 (C_{3/3'}), 127.7 (C_{3/3'}), 127.6 (C_{8/8'}), 127.5 (C_Q), 127.41 (C_Q),

127.38 (C₈/C_{8'}), 127.3 (C_Q), 127.1 (C_Q), 126.45 (C_Q), 125.92 (C_Q), 124.89 (C_A), 124.88 (C_A), 124.79 (C_A), 124.72 (C_B), 124.4 (C_B), 124.3 (C_B), 123.7 (C_B), 123.54 (C_B), 123.51 (C_B), 123.5 (C_B), 123.3 (C_A), 123.28 (C_A), 123.1 (C_{11'}), 123.0 (C₁₁), 122.1 (C₆/C_{6'}), 121.8 (C₆/C_{6'}), 121.1 (C_Q), 120.7 (C_Q), 120.2 (C_Q), 119.9 (C_Q), 119.82 (C_Q), 119.79 (C_Q), 119.68 (C_B), 119.67 (C_B), 119.62 (C_Q), 119.6 (C_Q), 119.5 (C_B), 119.3 (C_B), 117.4 (C_Q), 117.1 (C_Q), 115.31 (C_Q), 115.28 (C_Q), 36.3 (-C-(CH₃)₃), 35.61 (-C-(CH₃)₃), 35.59 (-C-(CH₃)₃), 35.56 (-C-(CH₃)₃), 35.5 (-C-(CH₃)₃), 31.75 (C₁₄/C_{14'}, -CH₃), 31.74 (C₁₄/C_{14'}, -CH₃), 31.45 (C₁₃/C_{13'}, -CH₃), 31.44 (C₁₃/C_{13'}, -CH₃), 31.30 (C₁₂/C_{12'}, -CH₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 1199.4076, calc. 1199.4101 for [C₇₀H₅₄N₈Ir]⁺, [M-PF₆]⁺.

IR: (neat, ν bar/cm⁻¹) 2960, 1608, 1538, 1479, 1408, 1373, 1254, 1163, 838, 756, 734, 678, 630, 557.

[Ir(coumarin 6)₂(5th-Asym-HASB)]PF₆ (75)



5th-Asym-HASB (8 mg, 0.011 mmol) [Ir(coumarin 6)₂Cl₂]₂ (11.12 mg, 0.006 mmol) and NH₄PF₆ (4.6 mg, 0.028 mmol) were added to CHCl₃ (1 mL) and MeOH (0.5 mL). The suspension was refluxed for 3.5 hours and subsequently concentrated under vacuum. A few drops of MeOH were then added to precipitate the product. Further purification of the crude material was achieved by preparative plate chromatography (CH₂Cl₂:MeOH, 100:3, v/v) to yield a dark reddish-brown solid.

Yield: 7 mg, 37 %.

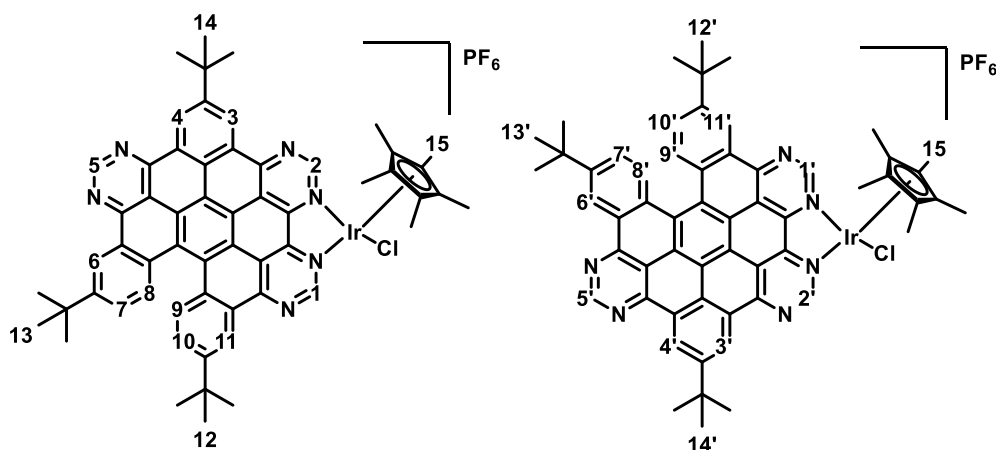
¹H NMR: (600 MHz, CDCl₃) δ 10.28 (m, 2H, H₄,H_{4'}), 10.15 (s, 1H, H_{5/5'}), 10.14 (s, 1H, H_{5/5'}), 10.13 (m, 2H, H₃,H_{3'}), 10.10 (s, 1H, H₂), 10.08 (m, 2H, H₁, H_{2'}), 10.04 (s, 1H, H₁), 9.57-9.60 (m, 4H, H₆,H_{6'},H₁₁,H_{11'}), 9.06 (d, 1H, ³J(HH) = 8.5 Hz, H₁₀/H_{10'}), 9.01 (d, 1H, ³J(HH) = 8.5 Hz, H₁₀/H_{10'}), 9.00 (d, 1H, ³J(HH) = 8.5 Hz, H₇/H_{7'}), 8.80 (d, 1H, ³J(HH) = 8.5 Hz, H₇/H_{7'}), 7.92 (dd, 1H, ³J(HH) = 8.6 Hz, ⁴J(HH) = 2.0 Hz, H_{9/9'}), 7.86 (dd, 1H, ³J(HH) = 8.6 Hz, ⁴J(HH) = 2.0 Hz, H_{9/9'}), 7.80 (dd, 1H, ³J(HH) = 8.6 Hz, ⁴J(HH) = 2.0 Hz, H_{8/8'}), 7.76 (dd, 1H, ³J(HH) = 8.6 Hz, ⁴J(HH) = 2.0 Hz, H_{8/8'}), 7.70 (d, 1H, ³J(HH) = 7.8 Hz, H_{Ar}), 7.64 (d, 3H, ³J(HH) = 7.8 Hz, H_{Ar}), 7.03 (t, 1H, ³J(HH) = 7.5 Hz, H_{Ar}), 6.99 (t, 1H, ³J(HH) = 7.5 Hz, H_{Ar}), 6.95 (t, 1H, ³J(HH) = 7.5 Hz, H_{Ar}), 6.92 (t, 1H, ³J(HH) =

7.5 Hz, H_{Ar}), 6.84 (t, 1H, ³J(HH) = 8.0 Hz, H_{Ar}), 6.63-6.68 (m, 2H, H_{Ar}), 6.49-6.56 (m, 5H, H₁₇, H_{17'}, H_{Ar}), 6.19-6.26 (m, 5H, H₁₅, H_{15'}, H_{Ar}), 6.06-6.12 (m, 2H, H_{Ar}), 5.92-5.98 (m, 5H, H₁₆, H_{16'}, H_{Ar}), 3.37 (m, 16H, H₁₈/H_{18'}), 1.84 (s, 18H, -CH₃), 1.63 (s, 18H, -CH₃), 1.62 (s, 18H, -CH₃), 1.16 (m, 24H, H₁₉, H_{19'}) ppm.

¹³C NMR: (150 MHz, CDCl₃) δ 177.6 (coumarin 6, C_Q), 177.53 (coumarin 6, C_Q), 177.51 (coumarin 6, C_Q), 177.42 (coumarin 6, C_Q), 177.36 (coumarin 6, C_Q), 177.2 (coumarin 6, C_Q), 158.0, 157.9, 157.8, 157.6 (C₅/C_{5'}), 157.5 (C₅/C_{5'}), 157.1 (C_Q), 157.0 (C_Q), 156.8 (C_Q), 155.38 (C_Q), 155.35 (C_Q), 154.68 (C_Q), 154.65 (C₂), 154.6 (C_Q), 154.50 (C_Q), 154.47 (C₁/C_{2'}), 154.4 (C_Q), 154.3 (C_Q), 154.26 (C₁), 154.24 (C₁/C_{2'}), 154.2 (C_Q), 153.91 (C_Q), 153.88 (C_Q), 153.1 (C_Q), 153.01 (C_Q), 152.97 (C_Q), 152.9 (C_Q), 151.2 (C_Q), 151.1 (C_Q), 150.8 (C_Q), 147.8 (C_Q), 147.7 (C_Q), 147.66 (C_Q), 147.65 (C_Q), 133.6 (C_Q), 133.5 (C_Q), 132.4 (C₁₅/C_{15'}), 132.37 (C₁₅/C_{15'}), 131.8 (C₁₀/C_{10'}/C₇/C_{7'}), 131.4 (C₇/C_{7'}), 131.3 (C₁₀/C_{10'}), 131.24 (C_Q), 131.21 (C_Q), 131.19 (C_Q), 131.13 (C₁₀/C_{10'}/C₇/C_{7'}), 130.99 (C_Q), 130.89 (C_Q), 130.84 (C_Q), 130.76 (C₉/C_{9'}), 130.5 (C₉/C_{9'}), 130.4 (C₄/C_{4'}), 130.3 (C₄/C_{4'}), 129.48 (C_Q), 129.46 (C_Q), 128.61 (C₃/C_{3'}), 128.58 (C_Q), 128.55 (C_Q), 128.38 (C_Q), 128.35 (C₃/C_{3'}), 128.3 (C_{Ar}, coumarin 6), 128.02 (C_Q), 128.0 (C_{Ar}, coumarin 6), 127.9 (C_{Ar}, coumarin 6), 127.73 (C₈/C_{8'}), 127.70 (C_{Ar}, coumarin 6), 127.60 (C₈/C_{8'}), 126.83 (C_Q), 126.77 (C_Q), 126.4 (C_Q), 126.1 (C_Q), 125.3 (C_{Ar}, coumarin 6), 125.2 (C_{Ar}, coumarin 6), 124.94 (C_{Ar}, coumarin 6), 124.91 (C_{Ar}, coumarin 6), 124.2 (C_Q), 124.1 (C_Q), 123.9 (C₁₁/C_{11'}), 123.64 (C_Q), 123.60 (C_{Ar}, coumarin 6), 123.53 (C_{Ar}, coumarin 6), 123.47 (C_{Ar}, coumarin 6), 123.2 (C₁₁/C_{11'}), 122.4 (C₆/C_{6'}), 122.2 (C₆/C_{6'}), 122.0 (C_Q), 121.9 (C_Q), 121.8 (C_Q), 121.1 (C_Q), 121.0 (C_Q), 118.93 (C_Q), 118.88 (C_Q), 118.85 (C_Q), 118.80 (C_Q), 118.6 (C_Q), 118.5 (C_Q), 116.1 (C_Q), 116.0 (C_Q), 115.7 (C_{Ar}, coumarin 6), 115.4 (C_{Ar}, coumarin 6), 115.2 (C_{Ar}, coumarin 6), 115.1 (C_{Ar}, coumarin 6), 114.9 (C_Q), 110.3 (C₁₆/C_{16'}), 110.24 (C₁₆/C_{16'}), 110.20 (C₁₆/C_{16'}), 110.16 (C₁₆/C_{16'}), 96.98 (C₁₇/C_{17'}), 96.96 (C₁₇/C_{17'}), 96.94 (C₁₇/C_{17'}), 45.0 (C₁₈/C_{18'}, -CH₂-CH₃), 36.5 (C_Q, -C-(CH₃)₃), 35.7 (C_Q, -C-(CH₃)₃), 31.7 (C₁₄/C_{14'}, -CH₃), 31.38 (C₁₂/C_{12'}/C₁₃/C_{13'}, -CH₃), 31.24 (C₁₂/C_{12'}/C₁₃/C_{13'}, -CH₃), 12.5 (C₁₉/C_{19'}, -CH₂-CH₃) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 1589.4827, calcd. 1589.4809 for [C₈₈H₇₂N₁₀O₄S₂Ir], [M-PF₆]⁺.

IR: (neat, ν_{bar}/cm⁻¹) 2960, 2920, 2853, 1692, 1607, 1534, 1442, 1407, 1355, 1281, 1255, 1134, 1077, 1028, 962, 840, 731, 701, 558.

[IrCl(Cp*)(5th-Asym-HASB)]PF₆ (76)

5th-Asym-HASB (7.7 mg, 0.011 mmol) [IrCp*Cl₂]₂ (4.4 mg, 0.006 mmol) and NH₄PF₆ (4.8 mg, 0.029 mmol) were added to CHCl₃ (1 mL) and MeOH (0.5 mL). The suspension was refluxed for 2.5 hours and subsequently concentrated under vacuum. A few drops of MeOH were then added to precipitate the product. Further purification of the crude material was achieved by preparative plate chromatography (CH₂Cl₂:MeOH, 100:3, v/v) to yield a dark red solid.

Yield: 8 mg, 60 %.

¹H NMR: (600 MHz, CDCl₃) δ 10.27 (m, 2H, H₄,H_{4'}), 10.16 (m, 2H, H₅,H_{5'}), 10.14 (m, 2H, H₃,H_{3'}), 10.12 (s, 1H, H₂), 10.11 (m, 2H, H_{1'},H_{2'}), 10.09 (s, 1H, H₁), 9.64 (d, 1H, ³J(HH) = 2.1 Hz, H_{6/6'}), 9.61 (d, 1H, ³J(HH) = 2.1 Hz, H_{11/11'}), 9.60 (d, 1H, ³J(HH) = 2.1 Hz, H_{6/6'}), 9.59 (d, 1H, ³J(HH) = 2.1 Hz, H_{11/11'}), 9.10 (m, 2H, H₁₀,H_{10'}), 9.05 (d, 1H, ³J(HH) = 8.6 Hz, H_{7/7'}), 8.96 (d, 1H, ³J(HH) = 8.6 Hz, H_{7/7'}), 7.88 (dd, 1H, ³J(HH) = 8.6 Hz, ⁴J(HH) = 2.1 Hz, H_{9/9'}), 7.85 (dd, 1H, ³J(HH) = 8.6 Hz, ⁴J(HH) = 2.1 Hz, H_{9/9'}), 7.80 (dd, 1H, 8.6 Hz, ³J(HH) = 8.6 Hz, ⁴J(HH) = 2.0 Hz, H_{8/8'}), 7.78 (dd, 1H, ³J(HH) = 8.6 Hz, ³J(HH) = 2.1 Hz, H_{8/8'}), 2.09 (s, 30H, Cp*-H), 1.86 (s, 9H, -CH₃), 1.86 (s, 9H, -CH₃), 1.66 (s, 9H, -CH₃), 1.65 (s, 9H, -CH₃), 1.64 (s, 9H, -CH₃), 1.63 (s, 9H, -CH₃) ppm.

¹³C NMR: (150 MHz, CDCl₃) δ 157.18 (C_Q), 157.13 (C₅/C_{5'}), 157.10 (C₅/C_{5'}), 156.03 (C_Q), 155.95 (C_Q), 155.8 (C_Q), 155.7 (C_Q), 154.4 (C_Q), 154.30 (C_Q), 154.25 (C_Q), 154.2 (C_Q), 153.74 (C_{1'}/C₂/C_{2'}), 153.63 (C_{1'}/C_{2'}), 153.60 (C₁), 153.5 (C_Q), 153.4 (C_Q), 153.37 (C_Q), 153.24 (C_Q), 152.8 (C_Q), 152.7 (C_Q), 152.6 (C_Q), 152.5 (C_Q), 133.5 (C_Q), 133.4 (C_Q), 132.5 (C_Q), 132.1 (C₇/C_{7'}), 131.6 (C₁₀/C_{10'}), 131.3 (C₇/C_{7'}), 131.14 (C₁₀/C_{10'}), 130.98 (C_Q), 130.7 (C_Q), 130.6 (C_Q), 129.8 (C₉/C_{9'}), 129.5 (C₉/C_{9'}), 129.41 (C_Q), 129.3 (C₄/C_{4'}), 128.75 (C_Q), 128.7 (C_Q), 128.0 (C₃/C_{3'}), 127.9 (C₃/C_{3'}), 127.53 (C₈/C_{8'}), 127.46 (C_Q), 127.3 (C_Q), 127.2 (C_Q), 127.16 (C₈/C_{8'}), 127.0 (C_Q), 126.2 (C_Q), 126.0 (C_Q), 123.81 (C_Q), 123.78 (C_Q), 123.18 (C_Q), 123.16 (C_Q), 122.19 (C₆/C_{6'}), 121.97 (C₆/C_{6'}), 121.0 (C_Q), 119.78 (C_Q), 119.72 (C_Q), 119.62 (C_Q), 119.55 (C_Q), 119.4 (C_Q), 117.3 (C_Q), 117.1 (C_Q), 115.34 (C_Q), 115.28

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(C_Q), 90.2 (C_Q, Cp*), 90.1 (C_Q, Cp*), 36.4 (C_Q, -C-(CH₃)₃), 35.6 (C_Q, -C-(CH₃)₃), 31.8 (C₁₄, C_{14'}, -CH₃), 31.4 (C₁₂/C_{12'}/C₁₃/C_{13'}, -CH₃), 31.3 (C₁₂/C_{12'}/C₁₃/C_{13'}, -CH₃), 9.4 (C₁₅, Cp*) ppm.

HRMS: (m/z, MALDI, CH₂Cl₂) found: 1061.3629, calc. 1061.3650 for [C₅₈H₅₃N₆ClIr]⁺, [M-PF₆]⁺.

IR: (neat, ν bar/cm⁻¹) 2957, 2923, 2854, 1731, 1627, 1612, 1569, 1538, 1463, 1444, 1375, 1298, 1259, 1207, 1075, 1028, 835, 692, 615, 556.

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Annex

I. Crystallographic Tables

Table 1. Crystal data and structure refinement for **9**.

Empirical formula	$\text{C}_{115.75}\text{H}_{73.50}\text{Br}_6\text{N}_{12}\text{O}_{2.50}$	
Formula weight	2151.82	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 12.4222(4)$ Å	$\alpha = 74.732(2)^\circ$.
	$b = 18.8524(7)$ Å	$\beta = 89.794(2)^\circ$.
	$c = 22.9249(9)$ Å	$\gamma = 71.192(2)^\circ$.
Volume	$4883.2(3)$ Å ³	
Z	2	
Density (calculated)	1.463 Mg/m ³	
Absorption coefficient	3.444 mm ⁻¹	
F(000)	2164	
Crystal size	0.24 x 0.06 x 0.03 mm ³	
Theta range for data collection	2.006 to 59.497°.	
Index ranges	$-13 \leq h \leq 13$, $-21 \leq k \leq 20$, $-25 \leq l \leq 25$	
Reflections collected	34529	
Independent reflections	13799 [R(int) = 0.0581]	
Completeness to theta = 59.497°	96.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2709 and 0.1402	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13799 / 171 / 1329	
Goodness-of-fit on F ²	1.029	
Final R indices [I > 2σ(I)]	R1 = 0.0792, wR2 = 0.2139	
R indices (all data)	R1 = 0.1001, wR2 = 0.2323	
Largest diff. peak and hole	2.841 and -0.561 e.Å ⁻³	

Table 2. Crystal data and structure refinement for **45**.

Empirical formula	C ₄₅ H ₅₂ O ₂	
Formula weight	624.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 29.292(3) Å	$\alpha = 90^\circ$.
	b = 11.2001(12) Å	$\beta = 99.179(6)^\circ$.
	c = 11.2390(11) Å	$\gamma = 90^\circ$.
Volume	3639.9(7) Å ³	
Z	4	
Density (calculated)	1.140 Mg/m ³	
Absorption coefficient	0.068 mm ⁻¹	
F(000)	1352	
Crystal size	0.39 x 0.07 x 0.07 mm ³	
Theta range for data collection	2.600 to 26.588°.	
Index ranges	-36 ≤ h ≤ 36, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	
Reflections collected	30944	
Independent reflections	3779 [R(int) = 0.1141]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6672	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3779 / 18 / 232	
Goodness-of-fit on F ²	1.052	
Final R indices [I > 2σ(I)]	R1 = 0.0538, wR2 = 0.1245	
R indices (all data)	R1 = 0.0916, wR2 = 0.1443	
Largest diff. peak and hole	0.260 and -0.200 e.Å ⁻³	

Table 3. Crystal data and structure refinement for **47**.

Empirical formula	$C_{68}H_{73}ClN_2Pt$	
Formula weight	1148.82	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 10.4366(4)$ Å	$\alpha = 69.666(2)^\circ$.
	$b = 16.2577(6)$ Å	$\beta = 84.919(2)^\circ$.
	$c = 17.8914(7)$ Å	$\gamma = 85.125(2)^\circ$.
Volume	$2830.58(19)$ Å ³	
Z	2	
Density (calculated)	1.348 Mg/m ³	
Absorption coefficient	5.380 mm ⁻¹	
F(000)	1180	
Crystal size	$0.13 \times 0.09 \times 0.03$ mm ³	
Theta range for data collection	2.639 to 69.934° .	
Index ranges	$-12 \leq h \leq 12$, $-17 \leq k \leq 19$, $-21 \leq l \leq 21$	
Reflections collected	36741	
Independent reflections	10572 [$R(\text{int}) = 0.0672$]	
Completeness to $\theta = 67.679^\circ$	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5586	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10572 / 402 / 775	
Goodness-of-fit on F^2	1.078	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0565$, $wR2 = 0.1482$	
R indices (all data)	$R1 = 0.0663$, $wR2 = 0.1549$	
Largest diff. peak and hole	1.227 and -1.386 e.Å ⁻³	

Table 4. Crystal data and structure refinement for **58**.

Empirical formula	$C_{24.88}H_{24.50}NO_{0.88}$	
Formula weight	351.45	
Temperature	105.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 10.873(4)$ Å	$\alpha = 74.021(10)^\circ$.
	$b = 13.216(5)$ Å	$\beta = 77.980(10)^\circ$.
	$c = 15.650(6)$ Å	$\gamma = 71.801(11)^\circ$.
Volume	$2035.2(13)$ Å ³	
Z	4	
Density (calculated)	1.147 Mg/m ³	
Absorption coefficient	0.069 mm ⁻¹	
F(000)	751	
Crystal size	$0.27 \times 0.16 \times 0.04$ mm ³	
Theta range for data collection	2.860 to 25.517° .	
Index ranges	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$	
Reflections collected	13411	
Independent reflections	13411 [$R(\text{int}) = 0.1679$]	
Completeness to $\theta = 25.242^\circ$	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745211 and 0.656857	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13411 / 140 / 547	
Goodness-of-fit on F^2	1.004	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1052$, $wR2 = 0.2239$	
R indices (all data)	$R1 = 0.2954$, $wR2 = 0.3187$	
Largest diff. peak and hole	0.699 and -0.348 e.Å ⁻³	

Table 5. Crystal data and structure refinement for **59**.

Empirical formula	$C_{28.50}H_{19}Cl_3N_2Pt$	
Formula weight	690.90	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 12.847(4)$ Å	$\alpha = 71.575(11)^\circ$.
	$b = 13.991(5)$ Å	$\beta = 78.362(12)^\circ$.
	$c = 14.293(4)$ Å	$\gamma = 85.443(10)^\circ$.
Volume	$2387.1(13)$ Å ³	
Z	4	
Density (calculated)	1.922 Mg/m ³	
Absorption coefficient	14.250 mm ⁻¹	
F(000)	1332	
Crystal size	$0.35 \times 0.05 \times 0.05$ mm ³	
Theta range for data collection	3.317 to 69.696° .	
Index ranges	$-15 \leq h \leq 15$, $-17 \leq k \leq 15$, $-17 \leq l \leq 17$	
Reflections collected	32117	
Independent reflections	8863 [$R(\text{int}) = 0.0417$]	
Completeness to $\theta = 67.679^\circ$	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.3562	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8863 / 0 / 622	
Goodness-of-fit on F^2	1.069	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0387$, $wR2 = 0.1047$	
R indices (all data)	$R1 = 0.0404$, $wR2 = 0.1063$	
Largest diff. peak and hole	2.082 and -1.776 e.Å ⁻³	

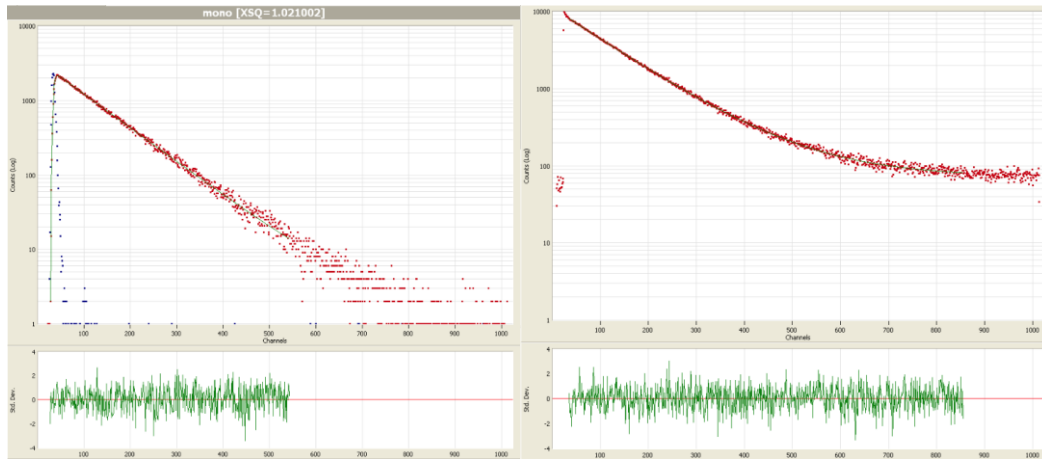
II. Emission Lifetime Data

Red plot: decay

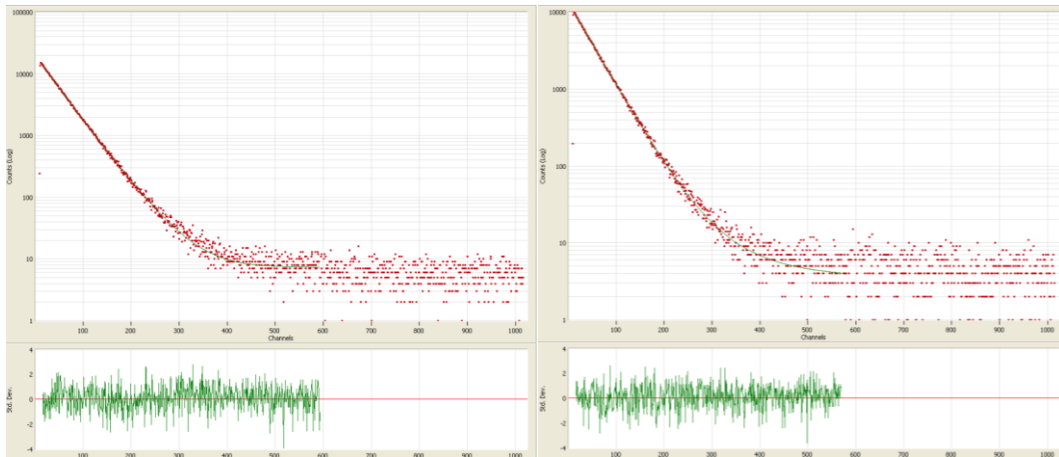
Blue plot: IRF (instrument response factor)

Green plot: Fit and residuals

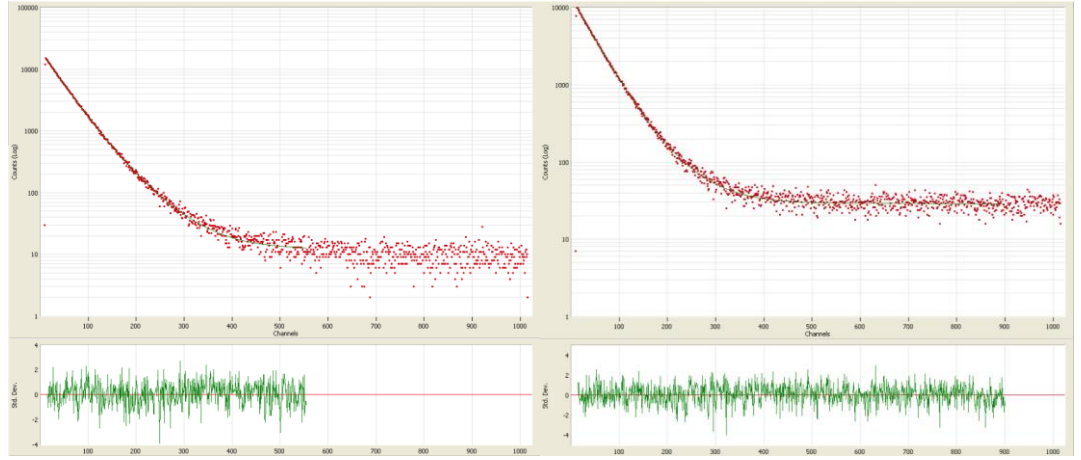
1. Lifetime decay plot of **26** (left, $\chi^2 = 1.02$), lifetime decay plot of **47**: (right, $\chi^2 = 0.97$):



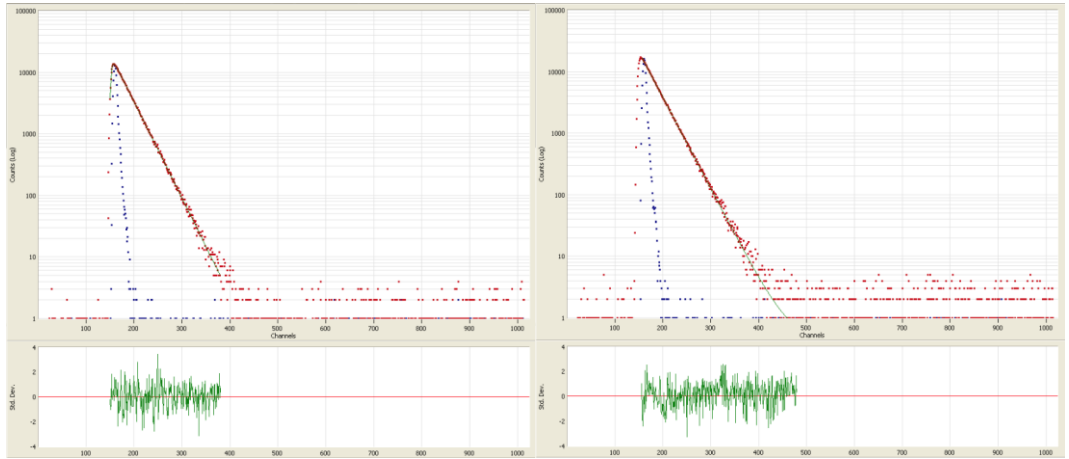
2. Lifetime decay plot of **48** (left, $\lambda_{em} = 600$ nm, $\chi^2 = 1.07$), lifetime decay plot of **48** (right, $\lambda_{em} = 640$ nm, $\chi^2 = 1.02$)



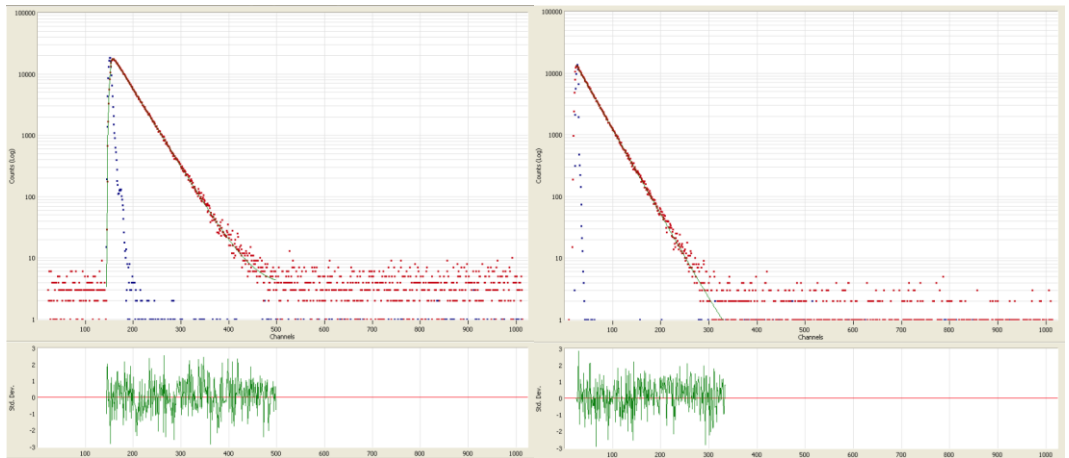
3. Lifetime decay plot of **49**: (left, $\lambda_{\text{em}} = 600 \text{ nm}$, $\chi^2 = 0.99$), lifetime decay plot of **49**: (right, $\lambda_{\text{em}} = 640 \text{ nm}$, $\chi^2 = 1.06$)



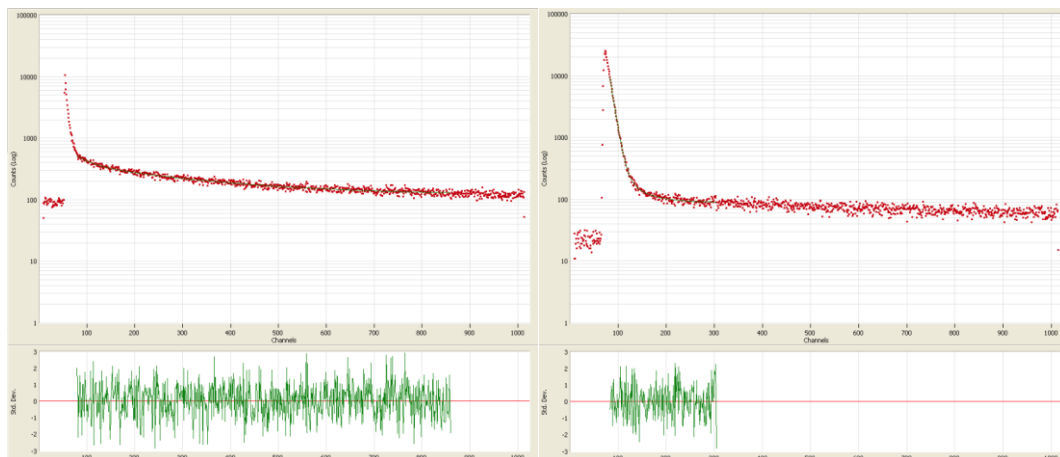
4. Lifetime decay plot of **54**: (left, $\lambda_{\text{em}} = 405 \text{ nm}$, $\chi^2 = 1.12$), lifetime decay plot of **57**: (right, $\lambda_{\text{em}} = 400 \text{ nm}$, $\chi^2 = 1.16$)



5. Lifetime decay plots of **58** (left, $\lambda_{\text{em}} = 400 \text{ nm}$, $\chi^2 = 1.01$), and **70**: (right, $\lambda_{\text{em}} = 520 \text{ nm}$, $\chi^2 = 0.98$)



6. Lifetime decay plot of **74**: (left, $\lambda_{\text{em}} = 615 \text{ nm}$, $\chi^2 = 1.02$), and **75**: (right, $\lambda_{\text{em}} = 530 \text{ nm}$, $\chi^2 = 1.00$)



7. Lifetime decay plot of **76**: ($\lambda_{\text{em}} = 700 \text{ nm}$, $\chi^2 = 1.12$)

