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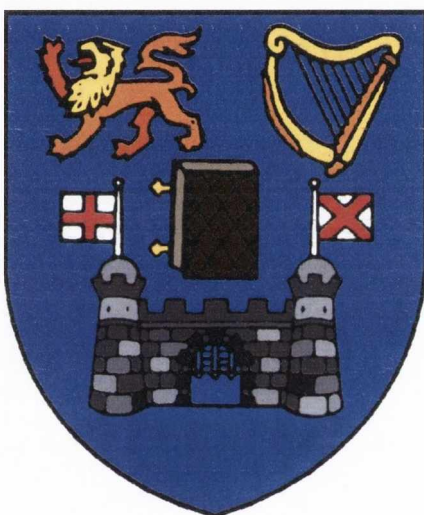
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The Synthesis, Characterisation and Photophysical Properties of Novel Tri- Substituted-8-Azafluoranthene Compounds and Their Cu(I) Complexes

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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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Summary

Chapter 1: This chapter details the synthesis and characterisation of a family of novel tri-substituted-8-azafluoranthene compounds that have N^N bidentate ligand capabilities. The compounds are synthesised *via* a Diels-Alder cycloaddition and two methods of synthesis are employed; a conventional method using a sand bath to heat the reaction and a microwave assisted method. The methods are compared for efficiency. The resulting six compounds; 7,10-diphenyl-9-(2-pyridyl)-8-azafluoranthene (**6**), 7,10-diphenyl-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**7**), 7,10-diphenyl-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**8**), 7,10-di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (**9**), 7,10-di[(4-trifluoromethyl)phenyl]-9-(2-pyridyl)-8-azafluoranthene (**10**) and 7,10-di(4-*tert*-butylphenyl)-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**13**) are fully characterised by NMR and mass spectrometry.

Chapter 2: This chapter details the photophysical investigation of each of the six ligands described in Chapter one. The absorption spectra of each ligand were obtained and the effect of acid on the absorption bands was investigated. The emission spectra were measured at two concentrations and at two temperatures, as well as in the solid state. The ligands exhibit interesting photophysical properties and are found to have exceptionally long lived excited state lifetimes in solid state and at low temperatures.

Chapter 3: This chapter details the synthesis and characterisation of nine Cu(I) complexes. Two families of complexes were prepared, three homoleptic complexes and six heteroleptic complexes with phosphine based auxiliary ligands. The photophysical and electrochemical properties of these complexes were investigated and the effect ligand substituents had on each is discussed. The heteroleptic Cu(I) xantphos ligands exhibit emission from MLCT states at low temperatures and these bands have excited state lifetimes in the microsecond range.

Chapter 4: This chapter details the attempted synthesis of pyrazine-bridged azafluoranthene compounds and the difficulties encountered, resulting in a change in the design of the target molecule to yield the novel terpyridine-bridged fluoranthene compound 6,6''-di(7,10-diphenylfluoranthene)-2,2':6'2''-terpyridine

Chapter 5: This chapter provides a full account of the experimental details of this work

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Abbreviation

μL	micro-litre
μs	micro-second
1D	One-dimensional
2D	Two-dimensional
A	Area
$\text{\AA}$	Angstrom
a.u.	Atomic units
Abs.	Absorption
AcOH	Acetic acid
Anal.	Elemental analysis
Ar	aryl
br	Broad
Calcd.	Calculated
cat.	Catalytic
cm^{-1}	wavenumber
COSY	Correlation Spectroscopy
CT	Charge transfer
CV	Cyclic voltammograms
d	Doublet
dd	Doublet of doublets
DEPT	Distortionless Enhancement by Polarisation Transfer
DMPD	1,4-dimethylpiperazine-2,3-dione

DMSO	Dimethyl sulfoxide
E	Redox Potential
e.s.	excited state
em.	Emission
eq.	equivalents
ES-MS	Electrospray mass spectrometry
EtOH	Ethanol
Exc.	Excitation
Fc/Fc ⁺	Ferrocene/ferrocenium
fl.	Flourescence
g.s.	ground state
HBC	Hexa- <i>peri</i> -hexabenzocoronene
HMBC	Heteronuclear Multi-Bond Connectivity
HOMO	Highest Occupied Molecular Orbital
HPB	Hexaphenylbenzene
hr.	Hour
HSQC	Heteronuclear Single Quantum Coherence
Hz	Hertz
IC	Internal conversion
IL	Intra-ligand
IR	Infrared
ISC	Inter-system crossing
<i>J</i>	Coupling constant

L'LCT	Ligand-to-ligand charge transfer
LC	Ligand-centred
LMCT	Ligand-to-metal charge transfer
LUMO	Lowest Unoccupied Molecular Orbital
M	metal
M	mol L ⁻¹
m	Multiplet
m.u.	Mass units
m/z	Mass to charge ratio
MALDI-TOF MS	Matrix-assisted laser desorption/ionisation-time of flight mass spectrometry
max	maximum
MC	Metal-centred
Me	Methyl
MeOH	Methanol
mg	Milligram
MHz	Megahertz
MLCT	Metal-to-ligand charge transfer
mmol	millimole
MS	Mass spectrometry
N- _{1/2} HSB	Half cyclised nitrogen heterosuperbenzene
N-HSB	Nitrogen Heterosuperbenzene
nm	nanometre

NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser effect
ns	nano-second
OLED	Organic Light Emitting Device
PAH	Polycyclic Aromatic Hydrocarbon
pd	<i>Pseudo</i> -doublet
Ph	Phenyl
phen	1,10-phenanthroline
ppm	Parts per million
Pr	propyl
pt	<i>Pseudo</i> -triplet
q	Quartet
Q/quat	Quaternary carbon
R.T.	Room temperature
ROESY	Rotating Frame Overhauser Effect Spectroscopy
s	Singlet
s	Strong
sat.	Saturated
sh	shoulder
t	triplet (NMR)
tBU	<i>Tert</i> -butyl
Terpy	2,2':6',2''-terpyridine
THF	Tetrahydrofuran

TLC	Thin-layer chromatography
TMS	Trimethylsilyl
TOCSY	Total Correlation Spectroscopy
UV-Vis	Ultraviolet-visible
V	Volts
vs.	versus
Wk <i>or</i> w	Weak
xs.	Excess
δ	Chemical shift
ΔE_p	Peak potential separation
ΔE_s	Stokes shift
ϵ	Molar extinction coefficient
η	Refractive index
λ	Wavelength
τ	Excited state Lifetime
ν	Stretching frequency
Φ	Quantum yield

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Chapter 1:

**Synthesis and Characterisation of Tri-
substituted-8-azafluoranthenes**

1.1 Introduction

1.1.1 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are two dimensional graphitic segments composed of sp^2 -hybridised carbons. PAHs are widely found in pollutant residues resulting from the combustion of coal and other organic materials.¹ PAH chemistry has become a substantial research area mainly due to the fact that the molecules represent synthetically accessible graphene derivatives. Like graphene, PAHs are highly conjugated systems and have wide ranging applications in organic electronic devices and solar cells.² The variety of potential uses are aided by their high symmetry and charge carrier mobility as well as their excellent stability and facile self-assembly.³ The pioneering work by Scholl and Clar which began in the 1950s described the synthesis of many PAH compounds using very harsh conditions, including high temperatures and strong oxidising agents.⁴⁻⁷ Despite their complexity many have been fully characterised thanks to advances made in analytical techniques. They can be subdivided into two classes – alternant and nonalternant PAHs. Nonalternant PAHs contain aromatic rings of varying size whereas alternant PAHs comprise only six-membered rings. More recently, many selective synthetic routes to PAHs using mild reaction conditions have emerged.¹ The PAH family consists of a very large number of compounds and some examples are shown in Figure 1.1-1.

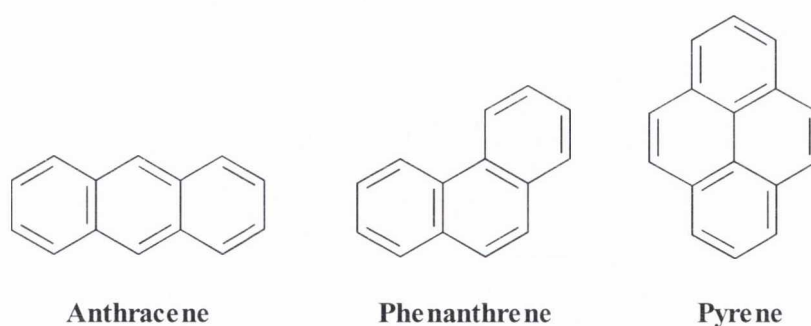


Figure 1.1-1: Examples of polycyclic aromatic hydrocarbons (PAHs).

1.1.2 Hexa-*peri*-hexabenzocoronene

Possibly the best known example of an alternant PAH is hexa-*peri*-hexabenzocoronene (HBC), an aromatic molecule consisting of 13 fused six-membered rings. HBC is highly symmetric and stable. The extensive electron delocalisation over its large π -conjugated network is analogous to the delocalisation of electrons within a benzene

ring. It was this similarity to benzene that prompted researchers to call HBC “superbenzene”.⁸

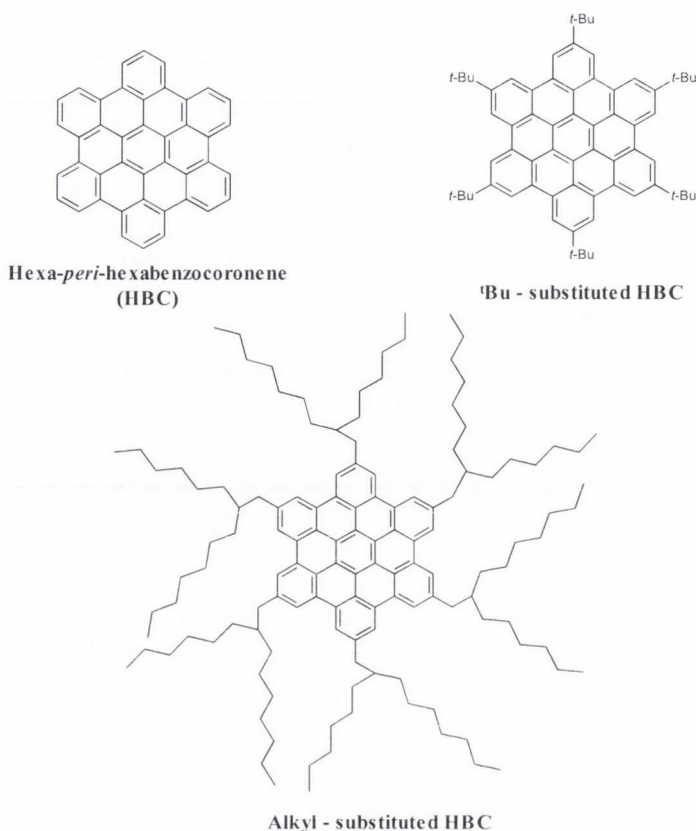
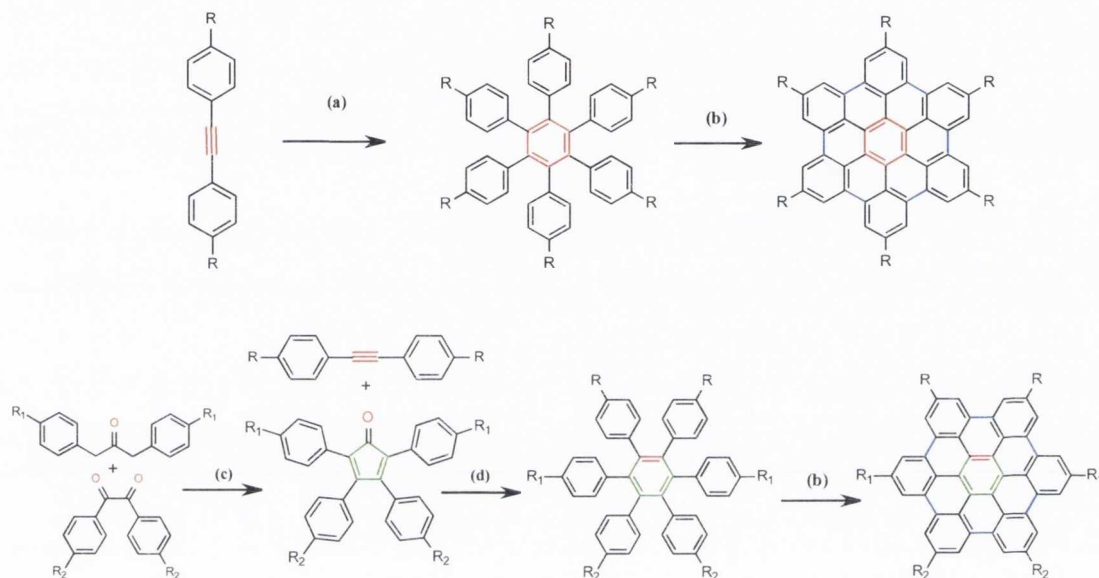


Figure 1.1-2: Hexa-*peri*-hexabenzocoronene (HBC) and some of its substituted derivatives.

Much work has been carried out to develop the synthesis, functionalisation and characterisation of HBC and its derivatives (Figure 1.1-2). Planar HBC has been shown to stack in a columnar fashion through π - π interactions. Significant aggregation is undesirable from a synthetic point of view as it can hamper the characterisation of the molecules. It has been found that by varying the substituents on the periphery of the HBC scaffold, the extent and nature of the aggregation can be controlled. Müllen *et al* have shown that incorporating alkyl chains of varying length around the aromatic core gives rise to columnar stacks of HBC molecules with high charge carrier mobility along the columnar axis. Discotic liquid crystal behaviour in such compounds has resulted in them being studied as possible active components in electronic devices.⁹ In contrast, the inclusion of tertiary-butyl groups has been shown to increase the solubility of the HBC compounds as their steric bulk is sufficient to hinder such uniform stacking.¹⁰

1.1.2.1 Synthesis of HBC

Historically the synthesis of PAHs proved difficult, requiring harsh reaction conditions and affording low yields. Clar *et al* synthesised the first HBC in the 1950s, but in poor yield.¹¹ Many attempts to improve on Clar's work resulted in similarly low yield synthetic routes until the work of Müllen *et al* in the 1990s gave rise to the efficient synthesis of HBC and many of its derivatives used today.^{12,13}



Scheme 1.1-1: Synthesis of HBC derivatives via cyclotrimerisation (top) and via a stepwise route to a selectively functionalised product (bottom). (a) $\text{Co}_2(\text{CO})_8$, dioxane, 105°C . (b) Oxidative cyclodehydrogenation, FeCl_3 , CH_2Cl_2 , CH_3NO_2 (c) two-fold Knoevenagel condensation reaction, MeOH , NaOH . (d) Diels-Alder cycloaddition reaction.

Scheme 1.1-1 shows the two most common synthetic routes to functionalised HBCs. Both procedures require the synthesis of hexaphenylbenzene precursors which then undergo oxidative cyclodehydrogenation to yield the cyclised HBC. The synthesis of a symmetrical HBC derivative can be achieved by preparing a substituted diarylacetylene suitable for transition-metal catalysed cyclotrimerisation.¹⁴ The advantage of this synthetic route is that a variety of functionalised acetylenes survive the milder conditions necessary for this reaction. The multi-step synthesis of asymmetrical HBC derivatives is somewhat more difficult. Starting with a two-fold Knoevenagel condensation reaction between a functionalised 1,3-diarlypropanone and a 1,2-diketone to form a substituted tetraarylcyclopentadienone. This tetraarylcyclopentadienone then

undergoes a [2+4] Diels-Alder cycloaddition with a substituted diarylacetylene to afford a range of asymmetrically substituted hexaphenylbenzenes for oxidative cyclodehydrogenation.

1.1.2.2 Oxidative cyclodehydrogenation

Complete cyclodehydrogenation of hexaphenylbenzene results in the formation of six new carbon-carbon bonds and the aromatisation of the precursor to planar, fully fused HBC. Oxidative cyclodehydrogenation, based on the Scholl reaction, is the acid-catalyzed oxidative condensation of aryl groups.¹⁵ The intramolecular variation of this reaction has proven very useful in the synthesis of large PAHs consisting of over 100 new carbon-carbon bonds.¹⁶ The most popular conditions are those described by Kovacic and involve the use of transition metal chloride salts of copper(II) or iron(III).¹⁷ In the case of CuCl_2 , AlCl_3 is required to act as Lewis acid catalyst in a solution of carbon disulfide whereas FeCl_3 serves a dual purpose as it acts as both a Lewis acid and oxidant in a solution of nitromethane and dichloromethane. The exact mechanism of this reaction has sparked much discussion in recent years and it is not fully understood. There are two main schools of thought, one that it involves an arenium cation mechanism and proton transfer and the other that it involves a radical cation mechanism and electron transfer.^{15,18} Regardless of the exact mechanism, it has been established that for both cases, the formation of the new carbon-carbon bonds occurs in a stepwise fashion, with the first bond the slowest and subsequent bond formations expedited consecutively until complete cyclisation is achieved. This cascade process gives rise to the term 'slippery slope'.¹⁵

1.1.3 Nitrogen hetero-superbenzene (N-HSB)

It has been shown that the incorporation of nitrogen-heteroatoms into graphitic molecules modifies their electronic properties, increasing their overall electron-accepting character and reducing the energy of the first excited state. The implication is that the inclusion of nitrogen atoms reduces the need for extensive aromatic platforms and simultaneously offers them new potential as ligands in the formation of metal-based fluorescent materials. Draper *et al* have synthesised a family of nitrogen containing polyaromatic hydrocarbons dubbed Nitrogen Hetero-Superbenzenes (N-HSBs) due to their resemblance to HBC. The N-HSBs are prepared in much the same way as the asymmetric HBC outlined in Scheme 1.1-1, with the nitrogen atoms

incorporated into the diarylacetylene. The final step is still an oxidative cyclodehydrogenation to form the planar fully-cyclised compound, however, depending on the conditions employed, it can generate a number of products.¹⁹ The use of AlCl_3 and CuCl_2 in carbon disulfide affords only the desired fully-cyclised N-HSB²⁰ whereas the use of FeCl_3 in nitromethane:dichloromethane yields a mixture of products including the ‘half-cyclised’ derivative abbreviated to N- $\frac{1}{2}$ HSB. More recently, work within the group has resulted in the isolation of a further two derivatives from the FeCl_3 reaction mixture; a $\frac{2}{3}$ rd–cyclised N-HSB (**b**) and a $\frac{5}{6}$ th–cyclised N-HSB (**c**). It is obvious from these results that the presence of the nitrogen atoms significantly alters the efficacy of the Scholl reaction. Work by King *et al* has suggested an arenium cation mechanism to explain the formation of partially fused N-HSB derivatives¹⁸ suggesting that the pyrimidine rings are the first to be protonated and this is followed by the formation of a new carbon-carbon bond between the pyrimidine units. For the subsequent ring closures protonation of an adjacent phenyl ring is necessary however this is made more unlikely by the fact that the molecule now holds a positive charge on the already protonated nitrogen atoms. This explanation is further supported by the fact that partially cyclised derivatives are rarely isolated in all-carbon polyphenylene systems.¹⁸

It is evident that the inclusion of nitrogen atoms into graphene like molecules has many advantages, but also makes their preparation at the final oxidative cyclodehydrogenation step more problematic. One way to overcome this problem is to design a family of nitrogen-containing ligands based on a smaller pre-fused PAH. The reduction in size of the target molecules improves solubility, making characterisation easier, and the incorporation of a pre-fused moiety potentially renders cyclodehydrogenation unnecessary. To this end, fluoranthene was chosen in this work as the central motif on which to build nitrogen containing PAHs.

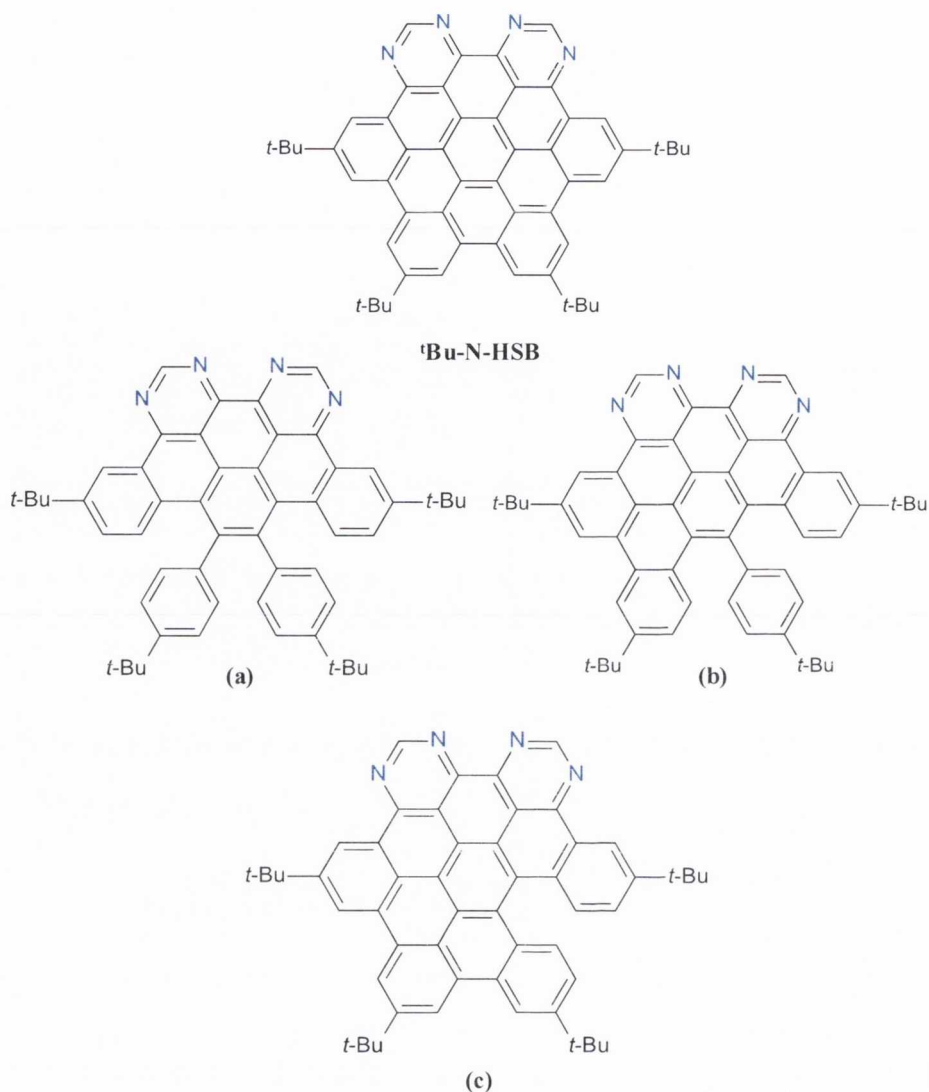


Figure 1.1-3 Fully-cyclised ^tBu-N-HSB and its partially cyclised derivatives; ^tBu-N-¹/₂HSB (a), ^tBu-N-²/₃HSB (b) and ^tBu-N-⁵/₆HSB (c).

1.1.4 Fluoranthene

Fluoranthene is a nonalternant polycyclic aromatic hydrocarbon (PAH) consisting of a naphthalene moiety joined to benzene by a five membered ring. The structure and numbering system for fluoranthene, which is shown in Figure 1.1-4 was originally proposed by Braun and Anton and was subsequently adopted by *Chemical Abstracts*.²¹ Fluoranthene was first discovered by Dumas and Laurent in the 1830s whilst extracting mercury ores to give a hydrocarbon fraction they named idrialene. It was not until 1880

that the compound now known as fluoranthene was fully isolated as part of concurrent work undertaken by Goldschmiedt²² and Fittig and Gebhard.²³

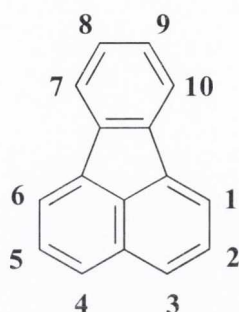


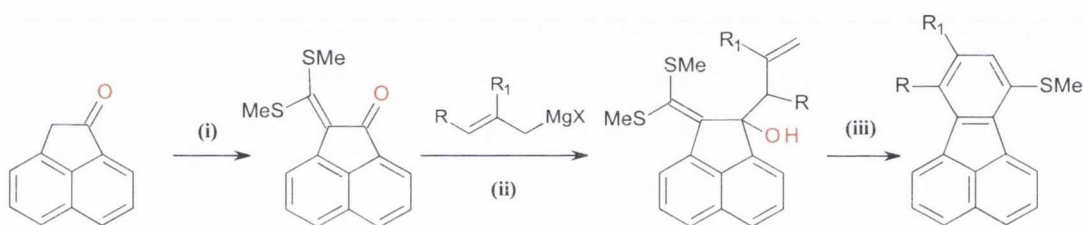
Figure 1.1-4: Structure and numbering system adopted for fluoranthene.

Once the structure of fluoranthene was elucidated, there was much interest in the characteristics of fluoranthenes and studies of their photophysical properties followed^{24,25}, however this initial interest faded fast. This trend was soon to change. In the last two decades there has been a resurgence of interest in fluoranthene based molecules, particularly as the active light emitting layer of optical electronic devices. The majority of the work that was done focused on the use of fluoranthenes as precursors to perylenes, which are important chromophores in dyes and more recently in photovoltaic cell applications on inter- and intra-molecular cyclodehydrogenation.²⁶ There are also examples of fluoranthenes being used in novel synthetic routes towards fullerenes.²⁷

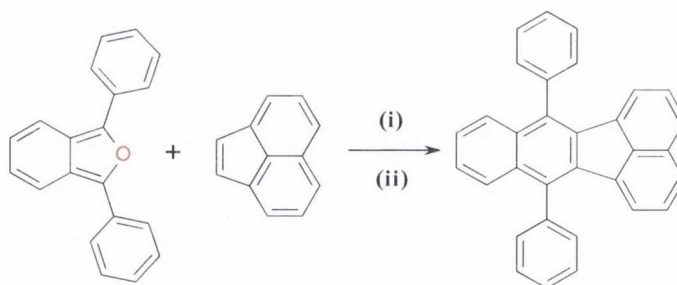
1.1.4.1 Synthesis of fluoranthene based molecules

In 1998 González and co-workers reported a new type of intramolecular thermal cycloaddition that they used for the annulation of an aryl ring onto naphthalene derivatives to afford fluoranthene compounds.²⁸ In 2000, Scott *et al* discovered the formation of unusual side products from the gas phase pyrolysis of 2-bromobenzoyl PAHs and proceeded to examine the flash vacuum pyrolysis of benzo[b]biphenylene in order to gain some mechanistic understanding of the reaction. The main products from this reaction were indeno[2,1- α]indene and fluoranthene.²⁹ Panda *et al* have described an efficient route to both all-carbon and heterocyclic fluoranthene analogues. The all-carbon analogues are synthesised by treating acenaphthenone with sodium hydride and carbon disulfide in a DMF/Benzene solution, this is followed by an alkylation with dimethyl sulfate to afford an α -oxoketene dithioacetal which then underwent further

treatment with allylmagnesium chloride to form the corresponding carbinol acetal in good yield. The final step is the cyclotrimerization of the carbinol in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at reflux in benzene to give the desired 7-(methylthio)fluoranthene (Scheme 1.1-2).³⁰ The heterocyclic analogues will be discussed in section 1.1.4.4. Despite the good yields reported for this synthesis it requires many steps and reagents compared to the more synthetically accessible fluoranthene compounds (7,12-diphenyl)benzo[k]fluoranthene. This is synthesised *via* a Diels-Alder cycloaddition between diphenylisobenzofuran and acenaphthylene and proceeds in good yield (Scheme 1.1-3).^{31,32} This basic structure has been frequently modified resulting in a wide range of fluoranthene based compounds, some of which are discussed in more detail in 1.1.4.2.



Scheme 1.1-2: Synthesis of a 7-(methylthio)fluoranthene. $R = \text{H}$ or Me , $R_1 = \text{H}$ or Me .
(i) (a) $\text{NaH}/\text{CS}_2/\text{C}_6\text{H}_6/\text{DMF}/0^\circ\text{C}$ (b) Me_2SO_4 (2.5 equivalents) (ii) Et_2O (iii) $\text{BF}_3 \cdot \text{Et}_2\text{O}/\text{C}_6\text{H}_6/\Delta$.



Scheme 1.1-3: Synthesis of (7,12-diphenyl)benzo[k]fluoranthene. (i) Reflux, *p*-xylene, 18hr (ii) Anhydrous trifluoroacetic acid, CH_2Cl_2 , reflux, 18hr

1.1.4.2 Applications of fluoranthene based molecules

Fluorescent molecules have a wide range of applications in chemical sensors, as components in solar cells, and in various light emitting devices.^{33,34} To be a successful candidate for incorporation into an Organic Light Emitting Diode (OLED) a fluorescent

molecule should exhibit high solid-state luminescence and charge carrier-mobility, good thermal and oxidative stability, excellent film formation and morphology and colour purity.³⁵ In the literature many fused extended aromatic graphite-like compounds, show promise in this regard.³⁶

Due to their excellent light-emitting properties, fluoranthene based molecules have been employed in electroluminescent device fabrication, most notably as the emissive layer of OLEDs. Depending on the functionalisation of the fluoranthene core, the luminescence of the molecules can be finely tuned to cover a wide range of wavelengths. This fact is best illustrated by the work of Pei and co-workers who have synthesised a series of fluoranthene-fused imide derivatives and have successfully tuned both the photophysical and electrochemical properties by careful functional substitution.³⁷

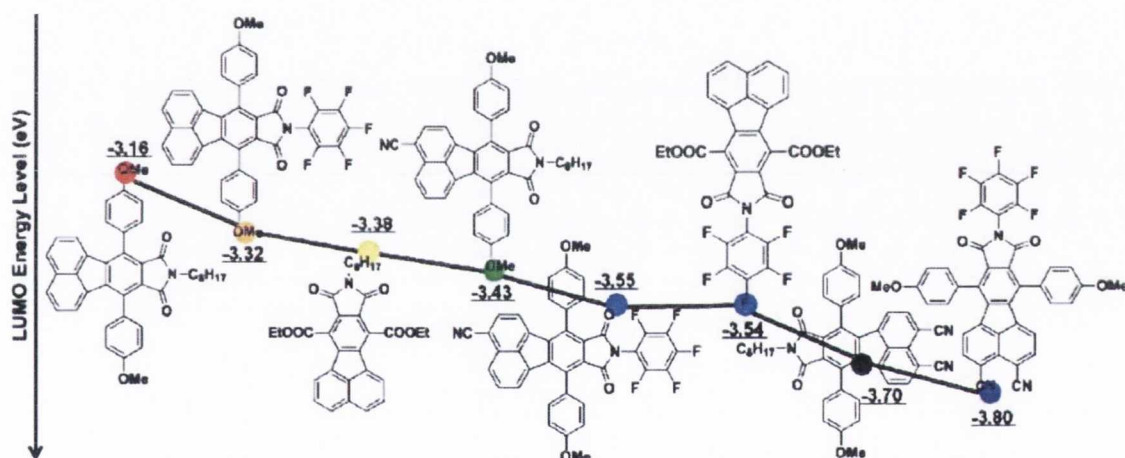


Figure 1.1-5: A series of fluoranthene-fused polycyclic imide derivatives synthesised by Pei *et al* illustrating the successful tuning of the optical properties of the molecules.³⁷

Recent work in 2008 by Tong *et al* has shown a highly efficient non-doped green organic light-emitting device based on the fluoranthene-based compound 3,6-di[8-(7,10-diphenylfluoranthenyl)]phenyl-9-[8-(7,10-diphenylfluoranthenyl)]phenylcarbazole (TDPFPC). The structure of this compound and the architecture of the nondoped optoelectric device is shown in Figure 1.1-6.³⁸ Other examples of green emitting fluoranthene based compounds are benzo[k]fluoranthene derivatives that were synthesised by Chen *et al* in 2010. Careful substitution of the fluoranthene moiety renders these derivatives asymmetric. This reduces the close packing of the molecules in the solid state and disfavours crystallisation so that amorphous films suitable for

incorporation into devices can be prepared.³⁹ The benzo[k]fluoranthene derivatives underwent palladium catalyzed coupling with diarylamine moieties as shown in Scheme 1.1-4. Each of these compounds exhibits many of the necessary properties for inclusion in electroluminescent devices such as low oxidation potential as well as high thermal stability. The compounds act as both the emitting layer and hole-transporting layer in nondoped devices and can achieve efficient green emission under low driving voltages.³⁹

Examples of stable yellow-fluorescent fluoranthene compounds have also been described in the literature. These compounds combine an amine donor and a nitrile acceptor on a fluoranthene core.⁴⁰ These are rare however as the majority of fluoranthene based compounds are blue-emitters. Since the development of OLED technology there has been a need for small, robust, blue-emitting molecules. Many red and green emitting compounds have been successfully synthesised and used in OLEDs with high efficiencies of 10cd/A and lifetimes of up to 100,000 hours, but due to the large band gap needed (≥ 3.0 eV) for blue light emission, few blue emitters that meet all the criteria necessary for device incorporation have been found.^{41,42} Recently, a number of blue emitting fluoranthene compounds have been synthesised and have shown promise in device testing, in particular a range of compounds based on 7,8,10-triphenylfluoranthene (TPF).⁴³⁻⁴⁶

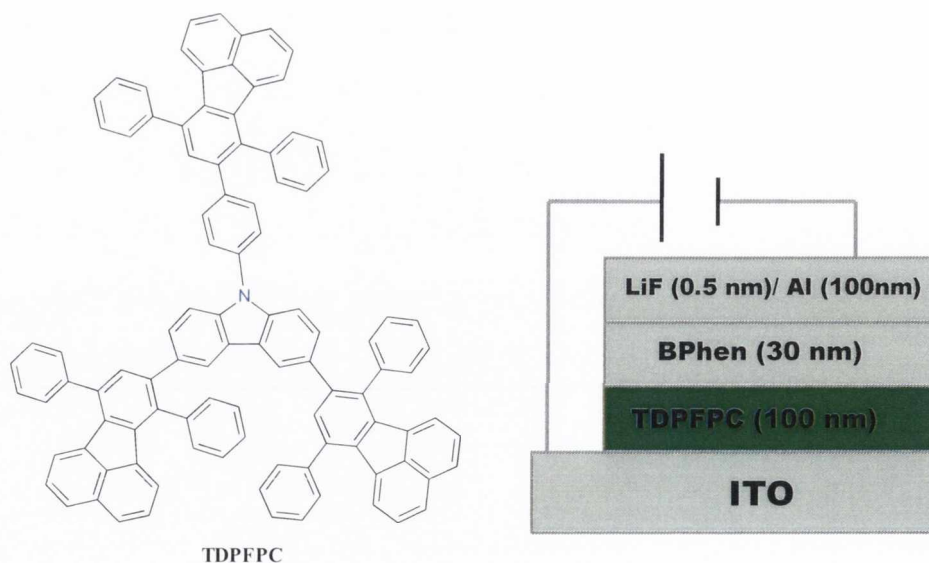
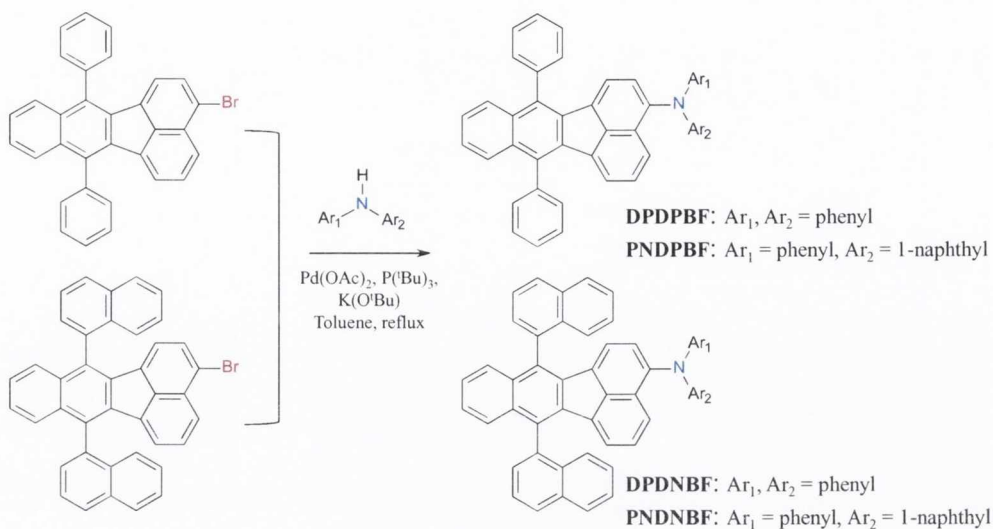


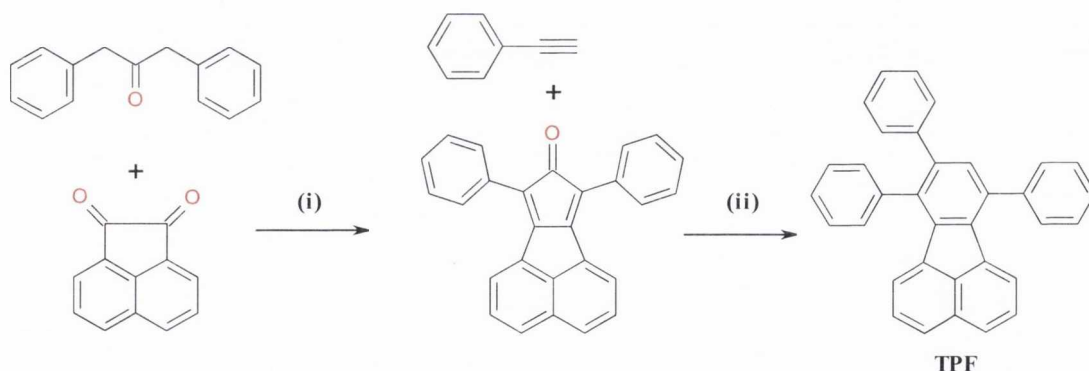
Figure 1.1-6: The structure of TDPFPC and the composition of the OLED architecture by Tong and co-workers. (Bphen = 4,7-diphenyl-1,10-phenanthroline)



Scheme 1.1-4: Synthetic route to diarylamine-substituted benzo[k]fluoranthene derivatives by Chen *et al.*³⁹

1.1.4.3 Triphenylfluoranthene

Among the most studied of the fluoranthene based compounds is 7,8,10-triphenylfluoranthene (TPF). This tri-substituted fluoranthene compound was first synthesised by Chiechi *et al* in 2006. It has attracted much interest as a robust blue-emitting fluorophore that exhibits solid state fluorescence. It is synthesised in two steps from commercially available starting materials as shown in Scheme 1.1-5. The first step is a double Knoevenagel condensation between propan-2-one and acenaphthenequinone followed by a Diels-Alder addition of phenylacetylene to afford 7,8,10-triphenylfluoranthene in good yield.



Scheme 1.1-5: Synthesis of 7,8,10-triphenylfluoranthene in two steps from commercially available starting materials. (i) MeOH, NaOH, R.T. (ii) xylene, Δ .

Unlike the unsubstituted fluoranthene which can form stable anions that have a sufficient lifetime to dimerize,⁴⁷ TPF does not form dimers as this is prevented by the three phenyl substituents. It was also found that the inclusion of three phenyl rings did not significantly change the HOMO/LUMO gap from that of fluoranthene, hence its blue emission, however, the introduction of other functional groups such as esters, carboxylic acids and halides, gave rise to green/yellow emission and in some cases caused problems with solubility. The photophysical properties of TPF will be discussed in more detail in Chapter 2. On testing the compound in the light emitting layer of a device it was found that the maximum efficiency was comparable to other fluorescent blue light emitting hydrocarbons such as anthracene derivatives, however bright blue emission was achieved using a single emissive layer thus simplifying the device fabrication process. This efficiency was increased by adding a small amount of TPF (6%) to a dipyrenylfluorene derivative (DPF), the structure of which is shown in Figure 1.1-7.⁴⁴ Marchioni *et al* have investigated the use of TPF in blended films and observed a two-fold enhancement of the photoluminescence quantum yield for the polymer MEH-PPV on blending it with TPF during film casting (Figure 1.1-7).⁴⁸ Following from the work done on TPF, many derivatives of this simple compound were synthesised. One such derivative is 4-(7,10-diphenylfluoranthene-8-yl)-N,N-diphenylbenzenamine (TPADPF). On device testing this compound proved to be highly efficient without the need for doping, showing that careful modification of the basic TPF structure could improve its properties and increase its quantum efficiency.⁴⁶ 7,10-diphenyl-8-(1-naphthyl)fluoranthene (DPNF) and 7,10-diphenyl-8-(9-phenanthrenyl)fluoranthene (dppf) were synthesised by Kim *et al* who investigated their thermal and optoelectronic properties in non-doped devices. It was found that both compounds exhibited good electroluminescence efficiency in the blue region, with the values of DPNF being very similar to TPF, however dppf, with its phenanthrene group in the 8 position, showed better power efficiency than TPF and DPNF.⁴²

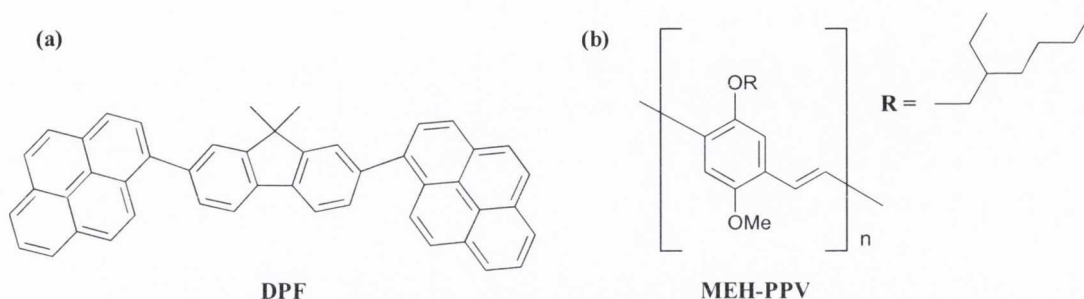


Figure 1.1-7: (a) Molecular structure of the dipyrenylfluorene derivative (DPF), the compound doped with with 6% TPF that has been incorporated into a device. (b) Structural formula of poly(2-methoxy 5-[2'-ethylhexyloxy]-p-phenylenevinylene) or MEH-PPV

Another example of a non-doped blue OLED device is one based on a diphenylfluoranthene-substituted fluorene derivative 2,7-di-[8-(7,10-diphenylfluoranthenyl)]-9,9-dimethylfluorene (DFDF). This device shows stable colour purity over a wide range of driving voltages as well as high current and power efficiencies.⁴⁵ More recently, Thomas and co-workers have designed a family of tetraphenylfluoranthene based triaryl amines as hole-transporting and emitting materials.⁴⁹ Following this they reported a series of solution processable indoloquinoline derivatives that contain bulky PAHs, including fluoranthene, and exhibit blue emission with moderate quantum efficiency. The compounds were successfully applied as both the electron-transporting and emitting layer in multilayered OLEDs.⁵⁰ The molecular structures of each of the compounds discussed are shown in Figure 1.1-8.

In the five years following the facile synthetic route to TPF reported by Chiechi *et al*, much work has been done on improving its optoelectronic properties. Simple substitution of the phenyl ring in the 8 position has led to enhanced efficiency in devices that no longer require doping. More complex functional group substitutions have been employed to further tune the photophysical properties with devices existing today that use the fluoranthene based compound as both the hole transporting and light emitting layers. As yet however, there is only one example of a trisubstituted fluoranthene compound that has ligand capability, 7,10-diphenyl-8-(2-pyridyl)-fluoranthene. This compound was synthesised as part of a family of compounds, and

their corresponding iridium complexes, by Chou *et al* in 2007.⁵¹ the structure of this ligand is shown in Figure 1.1-9.

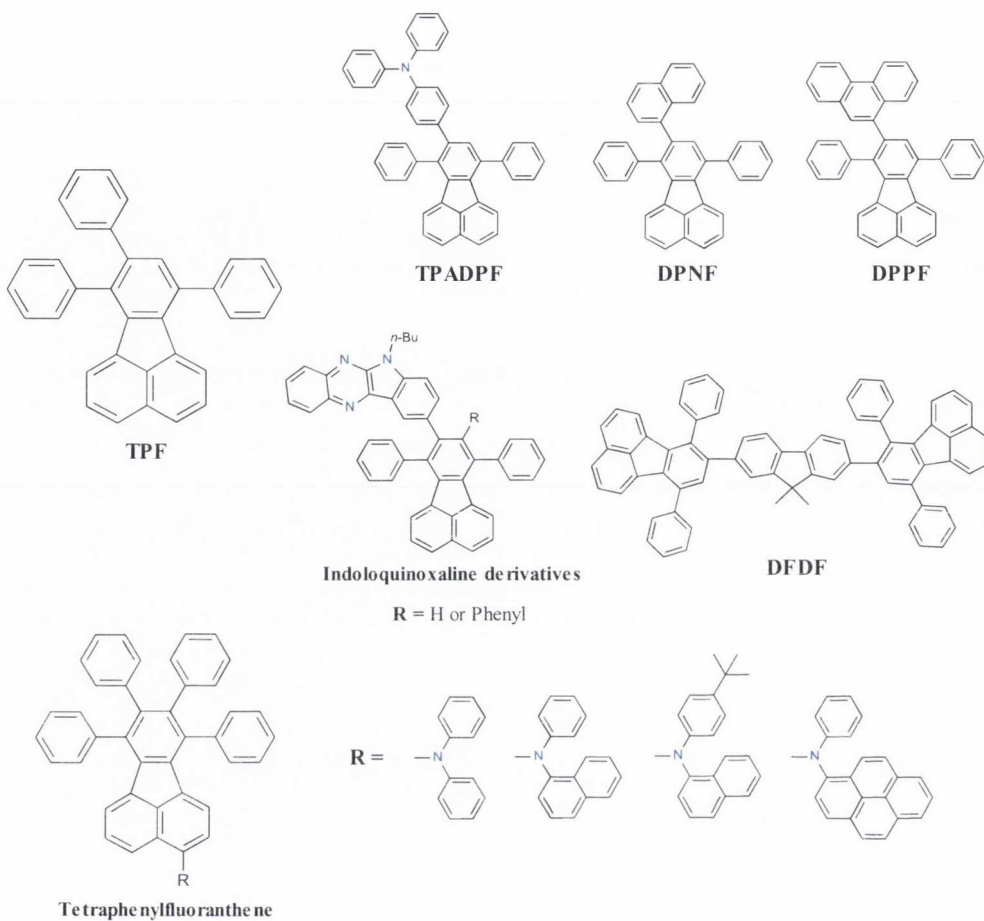


Figure 1.1-8: Molecular structures of the substituted TPF compounds (top) and of the tetraphenylfluoranthene-based triarylamine compounds (bottom).



Figure 1.1-9: Molecular structure of 7,10-diphenyl-8-(2-pyridyl)-fluoranthene and its $\text{Ir}(7,10\text{-diphenyl-8-(2-pyridyl)-fluoranthene})_2(\text{acac})$ complex.⁵¹

1.1.4.4 Azafluoranthene

Azafluoranthenes are fluoranthenes that have a nitrogen atom incorporated directly into the fused ring system. The azafluoranthenes are derivatives of indeno[1,2,3-*ij*]isoquinoline shown in Figure 1.1-10.

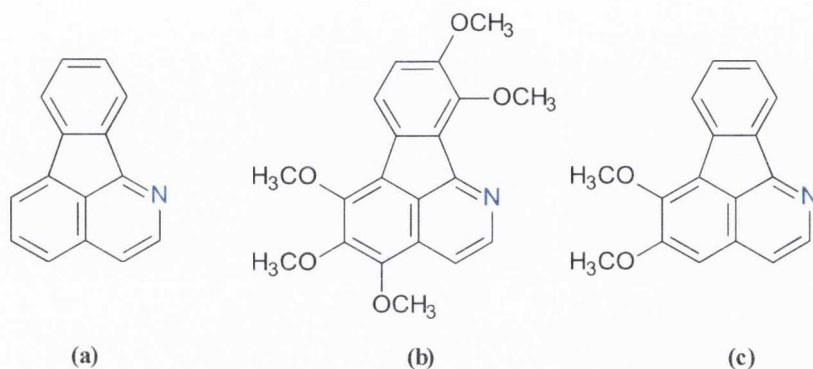
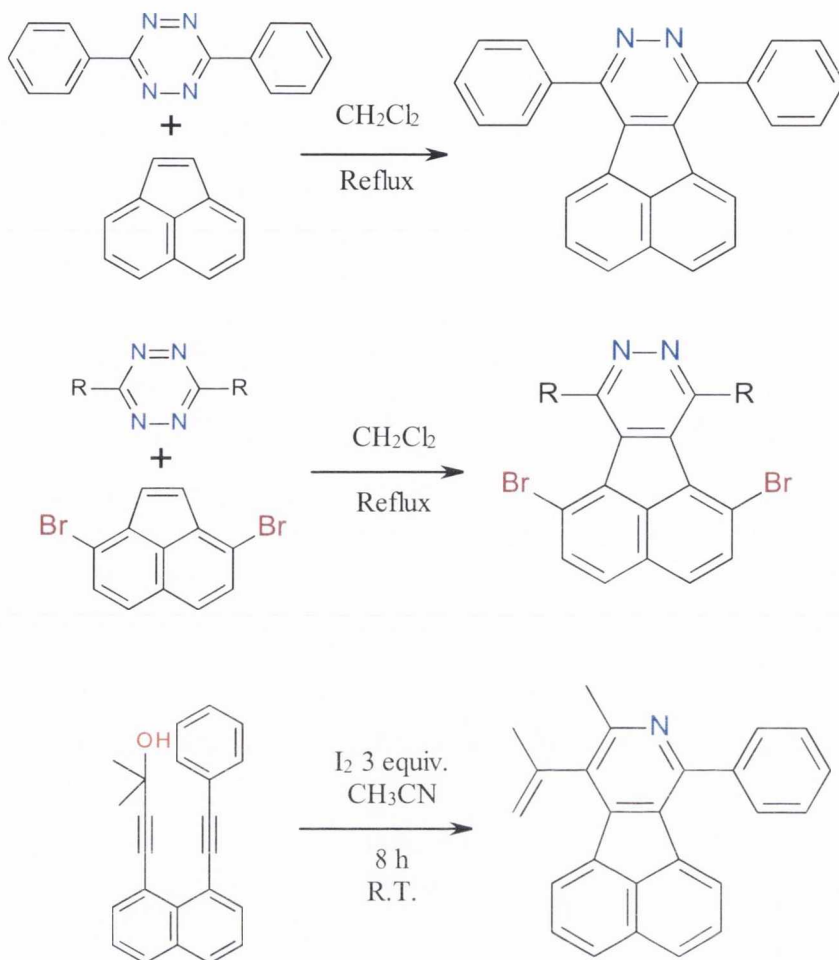


Figure 1.1-10: (a) indeno[1,2,3-*ij*]isoquinoline or 1-azafluoranthene, (b) imelutiene and (c) triclisine.

Like fluoranthene, the parent azafluoranthene is a component of coal tar and cigarette smoke and is a known air pollutant as well as being found as a component of several naturally occurring chemical compounds known as alkaloids.⁵² These include imelutiene and triclisine, compounds that have been extracted from natural sources. The location of the nitrogen atom can vary and examples of these compounds with the heteroatom incorporated into the benzene unit can be found in the literature. Sasaki *et al* reported the synthesis of a diazafluoranthene derivative 7,10-diphenyl-8,9-diazafluoranthene in 1974 *via* a cycloaddition reaction between acenaphthylene and 3,6-disubstituted *s*-tetrazines.⁵³ This synthesis was modified by Rahanyan *et al* in 2009 to yield a range of 3,4,7,10-tetrasubstituted-diazafluoranthenes.⁵⁴ More recently, Chen *et al* have reported the synthesis of a series of trisubstituted azafluoranthene compounds from an iodine-mediated electrophilic cyclisation of rigid parallel triple bonds mapped from 1,8-dialkyl-naphthalenes in acetonitrile.⁵⁵ However, to date there are no examples of 7,9,10-triphenyl-8-azafluoranthenes in the literature.



Scheme 1.1-6: Synthesis of 7,10-diphenyl-8,9-diazafluoranthene (top), synthetic route to 3,4,7,10-tetrasubstituted-diazafluoranthenes (middle) and synthesis of trisubstituted-8-azafluoranthene (bottom).

1.1.5 Microwave Chemistry

Microwave technology was developed in the 1940s as an essential part of RADAR transmitters. The next thirty years saw its widespread use as a domestic appliance for heating water laden food stuffs and for industrial processes such as the drying of nylon fibres. It was not until 1986, that Gedye⁵⁶ and Majetich⁵⁷ proved that a variety of organic reactions could be accelerated under microwave conditions. Since then the use of microwave dielectric heating in organic, inorganic and organometallic chemistry has flourished, with over 2000 papers describing the application and benefits of this relatively new technique for the synthesis of new compounds.⁵⁸ The earliest reports of microwave enhanced synthesis describe the use of modified domestic microwave ovens however, as the technique grew in popularity specially designed microwave reactors

became more widely available making microwave chemistry more accessible and much safer.⁵⁹⁻⁶³

1.1.5.1 Microwave dielectric heating

Microwaves are a type of electromagnetic energy found at the lower frequency end (300 to 300,000 MHz) of the electromagnetic spectrum. They comprise both an electric and magnetic field, however, only the former transfers heat to a substance. Only molecular rotations are affected as the energy in microwave photons is low insufficient to break molecular bonds (0.15 kJ/mole compared to 335 - 502 kJ/mole) i.e. the effect of microwave absorption is purely kinetic. 2450 MHz is the preferred frequency of microwave devices as it provides a suitable penetration depth to interact with laboratory samples and there are many available power sources to generate microwaves at this frequency.

Before the advent of microwave reactors, chemical syntheses were exclusively accomplished by conductive heating using an external heat. The heat must first pass through the walls of the reaction vessel in order to reach the solvent and reactants. This is an inefficient method of transferring energy and depending on the thermal conductivity of the various materials can be time consuming. It can mean that the temperature of the reaction vessel is higher than that of the reaction mixture (until thermal equilibrium is reached). In comparison, microwave heating is a more efficient process. It is dependent on a number of different factors, one of which is the dielectric constant (ϵ') of the solvent or substrates. The dielectric constant is a measure of the ability of the reactant molecules to be polarized by the electric field⁵⁸ and in simple terms indicates how efficiently the electromagnetic radiation is converted into heat.⁶⁴ The term dielectric loss (ϵ'') refers to the amount of microwave energy that has been lost to the reaction by being dissipated as heat. The heating pattern of a sample exposed to microwave irradiation depends upon the dissipation or loss factor ($\tan \delta$), the ratio of the dielectric loss to its dielectric constant;

$$\tan \delta = \epsilon'' / \epsilon'$$

A reaction mixture with a high $\tan \delta$ value is required for efficient microwave absorption and, therefore, rapid heating.⁵⁸ Typically, microwave energy is transferred to the reaction mixture by two mechanisms - dipole rotation or ionic conduction.⁶⁵⁻⁶⁸

Unlike conductive heating, the microwaves couple directly to the molecules present in the reaction mixture (*vide infra*) meaning that the process is not dependent on the thermal conductivity of the reaction vessel, resulting in an instantaneous rise in temperature due to localised superheating of any molecules that react with either of the two fundamental mechanisms for energy transfer mentioned above. The main differences between conductive heating and microwave heating are illustrated in Figure 1.1-11.

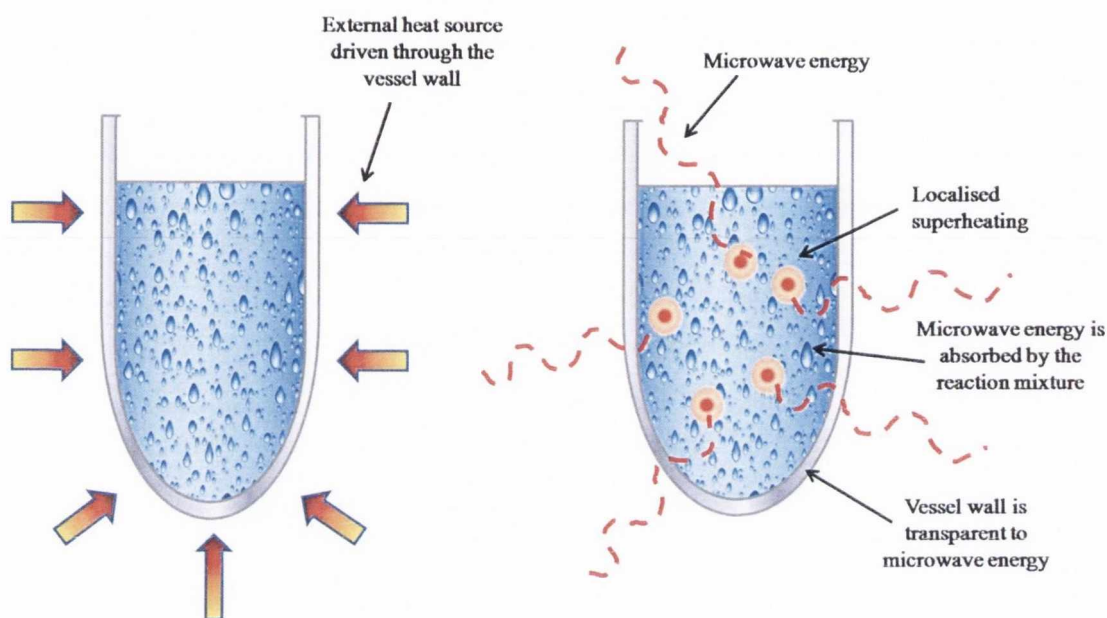


Figure 1.1-11: Schematic diagram showing the different mechanisms of conductive heating (left) and how microwave energy permeates a reaction vessel to cause dielectric heating (right).

1.1.5.2 Dipole rotation and ionic conduction

Dipole rotation is a process by which polar molecules try to orient themselves with the rapidly changing electric field of the microwave. It is the rotational motion of the molecule as it tries to align itself with the electric field that results in the transfer of energy in the form of heat. Any polar species i.e. solvent, substrate or reactant will undergo this process of energy transfer but to varying degrees. The efficacy of heating by dipole rotation is dependent upon the reaction mixture's characteristic dielectric relaxation time, which is itself dependent on both the temperature and the viscosity of the reaction mixture.

Ionic conduction only occurs if there are free ions or ionic species present in the substance being heated. Similar to dipole rotation, ionic motion is generated as the molecules align themselves with the rapidly changing electric field causing instantaneous superheating as outlined above. As the temperature increases the transfer of energy becomes more efficient.^{65,67}

1.1.5.3 Solvent choice for microwave reactions

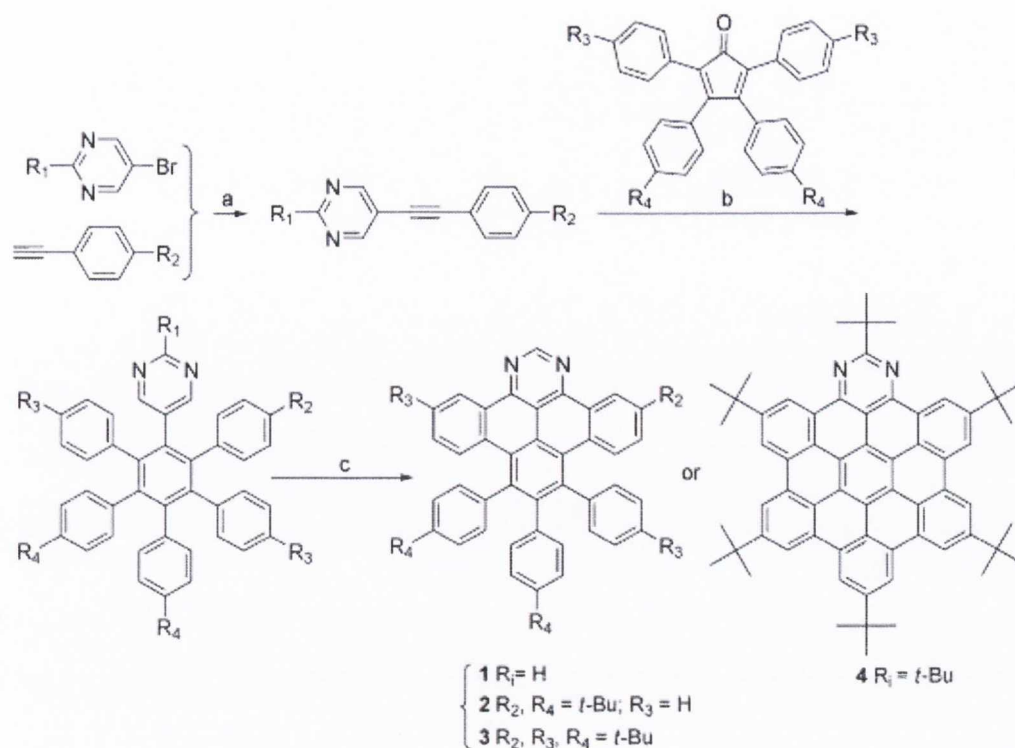
Solvents play a very important role in microwave chemistry.^{65,69,70} One of the most important characteristics of a suitable solvent for microwave synthesis is its polarity as the greater the polarity of the reaction mixture, the greater its ability to couple with the microwave energy. There are many factors that influence the efficacy of microwave heating, but the main three factors are dissipation factor, dielectric constant and dielectric loss. Molecules with large dipole moments also have large dielectric constants as polarization largely depends on dipole rotation. The dielectric relaxation time (which is the time it takes a molecule to achieve 63% of its return to randomised disorder once the electric field has been removed) has a large effect on the three main parameters.^{67,68} The dielectric relaxation time can be influenced by the volume of the reaction mixture, the frequency of the microwave energy, the temperature of the reaction and the functional groups present. As most commercial microwave reactors are set to a frequency of 2450 MHz only temperature can externally change the three main parameters i.e. as the temperature increases, the relaxation time and dielectric parameters will decrease resulting in less efficient coupling to the electric field.^{63,65-68} Hence, when choosing a solvent for microwave syntheses the most important consideration is not the boiling point (as microwave energy will reach and bypass the boiling point of most solvents in seconds) but a high dielectric loss value. The dielectric constant, dissipation factor and dielectric loss for three common solvents are summarised in Table 1.1-1. These three solvents represent three groups of common solvents – high (DMSO), medium (H₂O) and low (CH₂Cl₂) absorbing solvents.⁶⁵

Table 1.1-1: Dielectric constant, dissipation factor and dielectric loss for three common solvents measured at R.T. and 2450 MHz.

Solvent	Dielectric Constant (ϵ')	Dissipation factor ($\tan \delta$)	Dielectric Loss (ϵ'')
DMSO	45.0	0.825	37.125
H ₂ O	80.4	0.123	9.889
CH ₂ Cl ₂	9.1	0.042	0.382

1.1.5.4 Microwave assisted organic synthesis

In the literature examples of microwave assisted organic synthesis for almost every type of organic reaction can be found. Some inorganic reactions have also been improved using microwaves including a range of metal catalysed coupling reactions such as Stille couplings⁷¹, Suzuki couplings⁷², Negishi couplings⁷³, Heck couplings⁷⁴, cyanation reactions⁷⁵ and Sonogashira cross couplings^{76,77}. There are also many examples of time consuming Diels-Alder reactions being improved under microwave conditions with reaction times being decreased dramatically.⁷⁷⁻⁷⁹ Gourdon *et al* have recently reported the synthesis of N-HSB-like compounds from the cyclodehydrogenation of hetero-oligophenylenes which were synthesised using microwave heating (Scheme 1.1-7). They found that by using microwave heating that the Sonogashira cross-coupling reactions were completed in less than thirty minutes in good yields, the acetylene 5-(phenylethynyl)pyrimidine was produced in 93% yield which is significantly higher than the same reaction carried out under conventional heating methods.⁸⁰⁻⁸² The Diels-Alder reactions were performed in diphenylether at 260 °C for 45 min, again a shorter reaction time than similar cycloaddition reactions reported in the literature.⁸³



Scheme 1.1-7: General route towards pyrimidyl-penta-phenylbenzenes and their cyclodehydrogenated products. (a) Sonogashira coupling, μw , (b) [2+4] Diels-Alder cycloaddition, Ph_2O , μw , (c) cyclodehydrogenation, FeCl_3 , CH_2Cl_2 , CH_3NO_2 .⁷⁷

1.1.6 Design of ligands

This work details the preparation of a family of novel ligands based on the fluoranthene functional group. The series of ligands form the first known family of 8-azafluoranthene compounds. Treating this 8-azafluoranthene core as a molecular scaffold it was possible to add substituents in the 7, 9 and 10 positions. The inclusion of a pyridine ring in the 9 position of the azafluoranthene core imparts N^N bidentate ligand capability to the compounds, resulting in endless potential coordination with a variety of transition metals. The incorporation of phenyl rings in the 7 and 10 positions of the azafluoranthene core add a further dimension to the coordination possibilities by creating a potential orthometallation site. Both electron-donating and electron-withdrawing substituents could be incorporated to tune the optical properties of both the molecules and their coordination complexes.

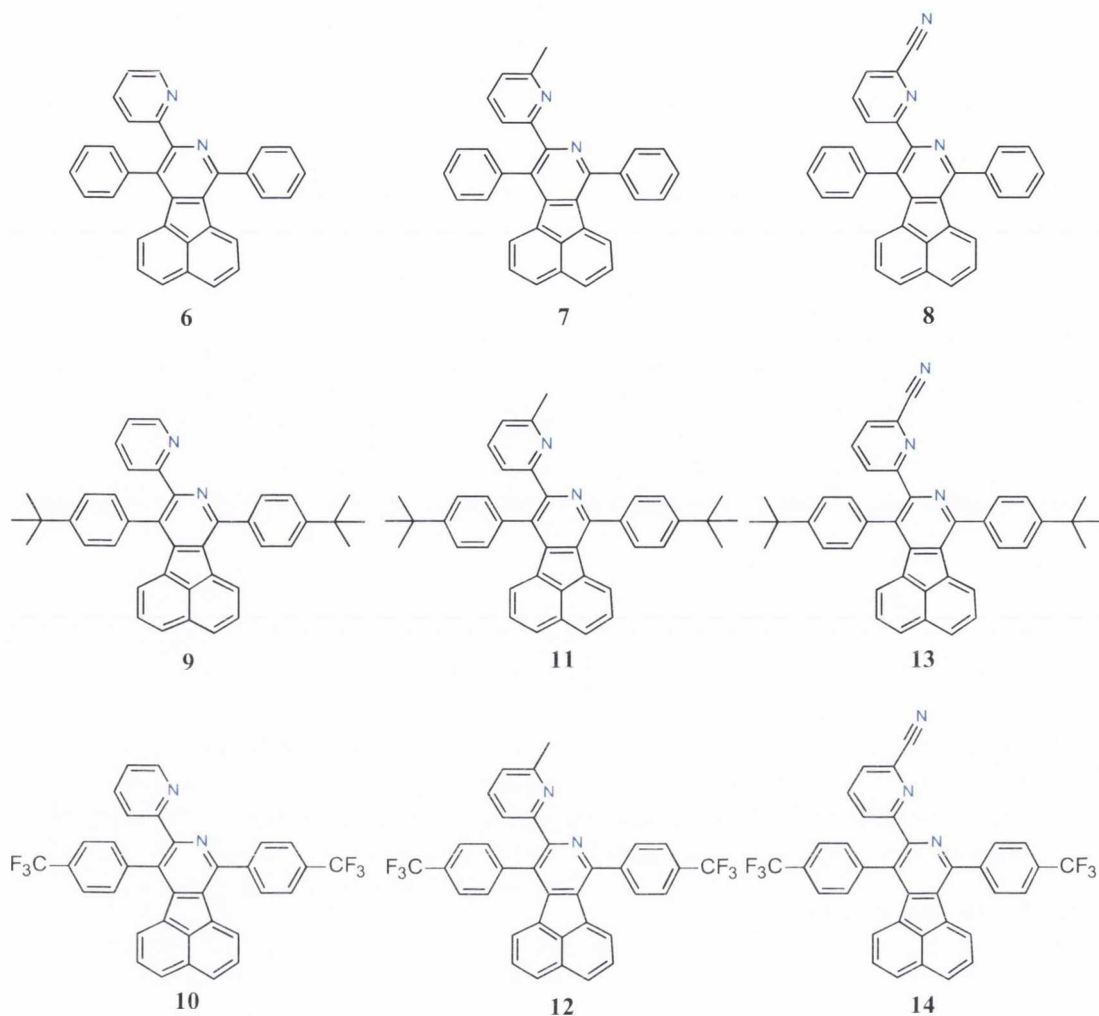
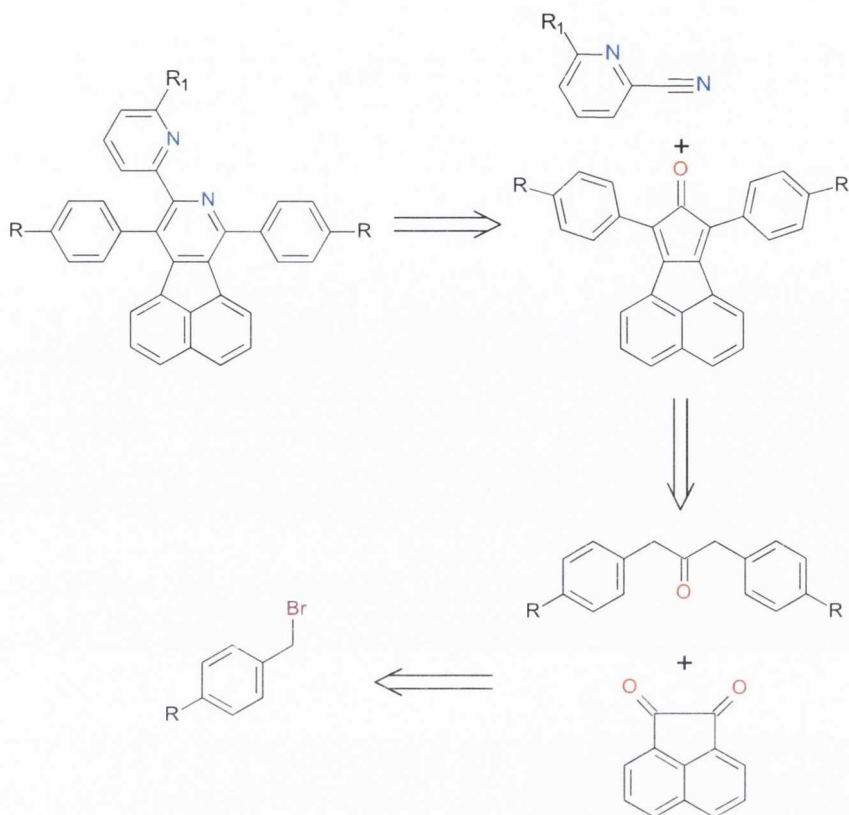


Figure 1.1-12: Target 8-azafluoranthene ligands.

1.2 Results and Discussion

1.2.1 Synthetic pathway towards trisubstituted 8-azafluoranthenes

The target compounds were synthesised by a [2+4] Diels-Alder cycloaddition between commercially available substituted 2-pyridinecarbonitrile and a substituted cyclopentaacenaphthylenone as shown in Scheme 1.2-1. All Diels-Alder cycloadditions were performed under both microwave and conventional heating methods to ascertain the best method.



Scheme 1.2-1: Retrosynthetic pathway to the desired substituted azafluoranthene.

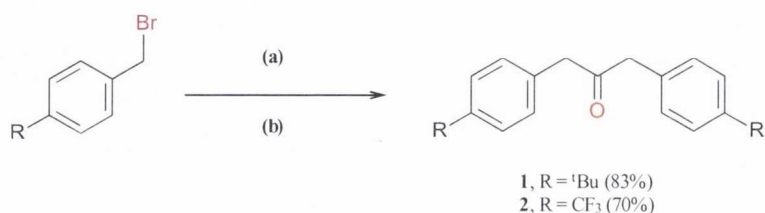
1.2.2 Synthesis of cyclopentaacenaphthylenone derivatives

The cyclopentaacenaphthylenone derivatives were synthesized *via* a two-fold Knoevenagel condensation reaction between the commercially available acenaphthenequinone and a series of 1, 3-diarylpropan-2-ones.

1.2.2.1 Synthesis of 1, 3-diarylpropan-2-ones 1 and 2

Two 1,3-diaryl-2-propanones were prepared according to literature procedures. 1,3-Bis(4-*tert*-butylphenyl)propan-2-one (1) was prepared *via* a biphasic phase transfer carbonylation, with $t\text{Bu}_4\text{N}^+(\text{HSO}_4)^-$ acting as the phase transfer catalyst and the $\text{Fe}(\text{CO})_5$ as the source of CO.⁸⁴ The reagents were left stirring at room temperature overnight as outlined in Scheme 1.2-2. The reaction mixture was subsequently stirred in air for 2 hr to oxidise, after which 10% HCl was added to afford the ketone product. On extraction and work-up, the product appeared as a crystalline white solid in 83% yield. 1,3-Di[4-(trifluoromethyl)phenyl]propan-2-one (2) was prepared from the reaction of commercially available 4-(bromomethyl)-(trifluoromethyl)benzene with diiron nonacarbonyl in dry *n*-octane.⁸⁵ The reagents were left to reflux under nitrogen for 18

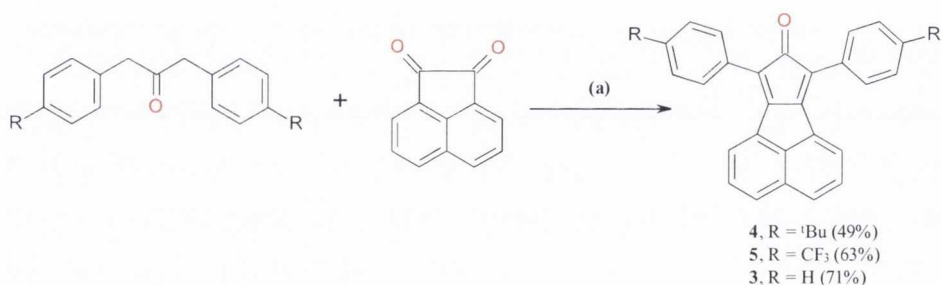
hr. The resultant precipitate was filtered and extracted five times with boiling toluene. The filtrate and the five extracts were combined and the solvents were removed by distillation. The resulting solid residue was purified by column chromatography using neutral alumina as the stationary phase and diethyl ether: petroleum ether (2:5) as eluent to give the product as a crystalline white solid in 70% yield.



Scheme 1.2-2: Synthesis of starting materials 15 and 16. (a) 4-tertbutylbenzyl bromide, ^tBu₄N⁺(HSO₄)⁻, Fe(CO)₅, Ca(OH)₂ in CH₂Cl₂:H₂O (1:1 v/v), RT, 24 hr. (b) 4-(bromomethyl)-(trifluoromethyl)benzene, Fe₂(CO)₉, n-octane, 130°C, 18hr.

1.2.2.2 Two-fold Knoevenagel condensation reaction

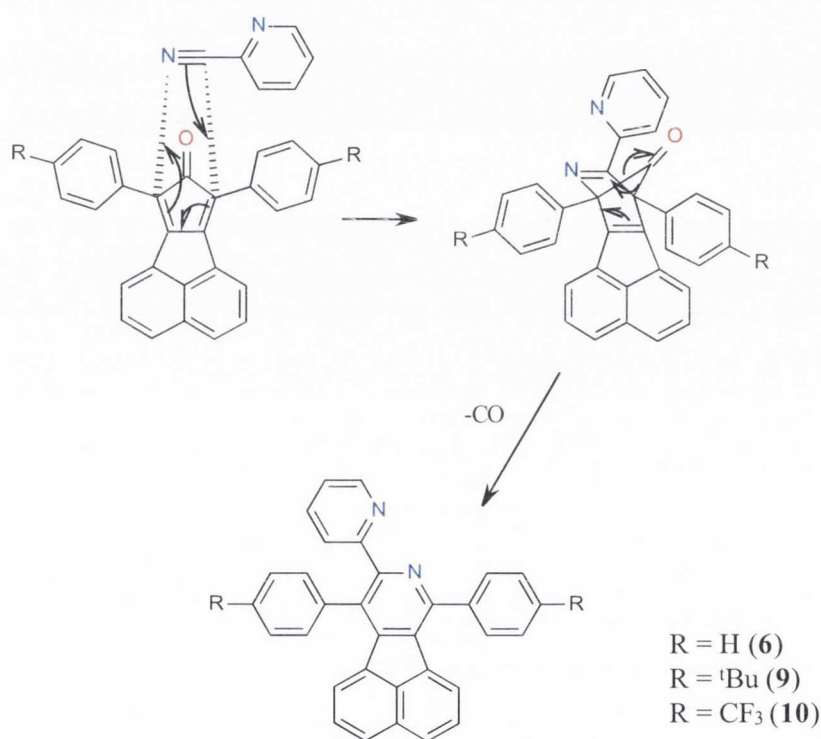
The cyclopentaacenaphthylenones were synthesized *via* a two-fold Knoevenagel condensation reaction between the commercially available acenaphthenequinone and each of the three 1,3-diarylpropan-2-ones – **1**, **2** and the commercially available 1,3-diphenyl-propan-2-one. The reagents were stirred at room temperature in methanol overnight in the presence of sodium hydroxide to yield the desired 7,9-diphenyl-cyclopenta[*a*]acenaphthylen-8-one (**3**), 7,9-bis(4-*tert*-butylphenyl)-8*H*-cyclopenta[*l*]acenaphthylen-8-one (**4**) and 7,9-bis[4-(trifluoromethyl)phenyl]-8*H*-cyclopenta[*l*]acenaphthylen-8-one (**5**). These required no further purification (Scheme 1.2-3).



Scheme 1.2-3: Synthesis of starting materials 3, 4 and 5. (a) NaOH, MeOH, stirring, RT, 24hr.

1.3 [2+4] Diels-Alder cycloaddition reaction

[2+4] Diels-Alder cycloaddition reactions usually occur between a conjugated diene (cyclopentaacenaphthylenone) and a dienophile (usually a substituted alkene), to form a substituted cyclohexene system. In synthesising the target azafluoranthene compounds however, a substituted heterocyclic carbonitrile was used as dienophile, resulting in a double bond in place of the more usual single bond formed by the cycloaddition of an alkene. The use of a carbonitrile, in place of the more usual substituted alkene, is important for two reasons; the triple bond renders the cycloaddition adduct aromatic, and the nitrogen atom generates an azafluoranthene core (Scheme 1.3-1).



Scheme 1.3-1: Reaction mechanism of the [2+4] Diels-Alder cycloaddition between a cyclopentaacenaphthylenone and 2-pyridinecarbonitrile. The loss of CO gives rise to the aromatic core of the azafluoranthene.

By varying the combinations of cyclopentaacenaphthylenones and 2-pyridinecarbonitrile compounds undergoing reaction, it should be possible to create a library of compounds. The use of a carbonitrile as the dienophile however poses some problems as both the diene and dienophile are electron rich. Harsh reaction conditions are required, (temperatures of up to 300 °C) and the reactions proceed very slowly,

(taking up to 48 hrs).⁸⁶ In view of these facts, two approaches to the synthesis of the target compounds were undertaken; heating by conventional methods and microwave dielectric heating.

1.4 Synthesis of ligands; Conventional heating vs. Microwave dielectric heating

Each Diels-Alder reaction was attempted by conventional heating and by microwave dielectric heating in order to ascertain the best method. For conventional heating the reactants were placed in a 10 mL round bottomed flask and heated to 300°C under an inert atmosphere *via* a sand bath for 2 – 8 days. For the microwave heating the reactants were placed in a 10 mL glass vessel with a snap cap and heated in a CEM S-class Discovery Microwave reactor to 280°C at 150W for 4 or 5 hr.

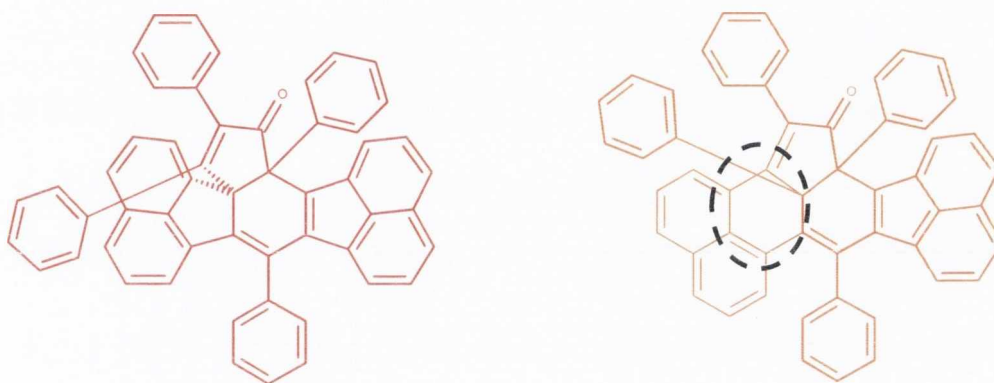
1.4.1 Synthesis of ligands 6, 7 and 8.

The first group of ligands to be synthesised are the 7,10-diphenyl-9-(2-pyridyl)-8-azafluoranthenes, where the 6 position of the pyridyl ring is systematically substituted. The ligands are formed by the reaction of 7,9-diphenyl-cyclopenta[*a*]acenaphthylen-8-one (**3**) with 2-pyridinecarbonitrile, 6-methyl-2-pyridinecarbonitrile and 2,6-pyridinedicarbonitrile respectively.

1.4.1.1 Synthesis of 7,10-Diphenyl-9-(2-pyridyl)-8-azafluoranthene (**6**)

7,10-Diphenyl-9-(2-pyridyl)-8-azafluoranthene (**6**) was synthesised from the Diels-Alder reaction of **3** with commercially available 2-pyridinecarbonitrile. The low melting point 2-pyridinecarbonitrile was present in a ten-fold excess and as a result no solvent was required for the reaction. The reaction was performed under both conventional methods and by microwave heating. It was found, on careful monitoring of the reaction mixture by TLC that the reaction took 48 hr to go to completion using the conventional heating methods. This was in stark contrast to the 4 hr required for the microwave heating method. The optimum conditions for the reaction in the microwave reactor were obtained by a trial and error approach, again with careful monitoring of the reaction mixture by TLC. The purification of the desired ligand was arduous due to the presence of unwanted side products that had the double effect of reducing the yield of the target compound by consuming the starting materials, and adding to the already considerable difficulty of successfully purifying the ligand. The side products are the result of a dimerisation reaction between molecules of **3** which then undergo a

rearrangement to form two distinct and highly coloured compounds. Work within the group has led to the elucidation of both compounds by NMR analysis and X-ray crystallography, the chemical structures of the compounds are shown in Figure 1.4-1. The most notable difference between the two compounds is a carbon rearrangement around the cyclopentanone. In one case it forms part of a fused aromatic core containing an additional six membered ring (circled in Figure 1.4-1). This rearrangement has not been observed previously.⁸⁷



*Figure 1.4-1: Graphical representation of the two distinct dimerisation products obtained as side products in the reaction of **3** with 2-pyridinecarbonitrile.*

Column chromatography on silica using a hexane:dichloromethane (7:3 v/v) solution mixture as the eluent removed the unwanted side products. Stepping up the polarity of the eluent (100% dichloromethane) removed the excess 2-pyridinecarbonitrile. Finally a mixture of dichloromethane:methanol (95:5 v/v) as eluent yielded ligand **6** as a yellow solid in moderate yields (24% for the conventional method and 32% yield for the microwave method). The higher yield for the microwave reaction can be attributed to the fact that less side products were formed under microwave heating and as a result more of the cyclopentaacenaphthylenone was available to react.

Ligand **6** was fully characterised using ^1H and ^{13}C {H} NMR spectroscopy. The molecular structure was determined by single crystal X-ray diffraction. The electrospray mass spectrum of **6** contains a peak at $m/z = 433.1711$ m.u. for $[\text{M}+\text{H}]^+$ which is in excellent agreement with the calculated value of $m/z = 433.1705$ m.u. for $[\text{C}_{32}\text{H}_{21}\text{N}_2]^+$.

1.4.1.2 Crystal structure of 7,10-diphenyl-9-(2-pyridyl)-8-azafluoranthene (6)

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane: methanol solution of **6**. Compound **6** crystallises in the triclinic space group P-1. The unit cell consists of two molecules of **6**. The molecules form dimers that arrange in a head to head fashion with the pyridyl rings of both molecules in the same plane and orientated toward one and other resulting in strong hydrogen bonding existing between the nitrogen atom of the pyridyl ring of one molecule and the hydrogen atom of the other molecule's pyridyl ring ($N \cdots C$ 3.48 Å). The naphthyl moiety of the azafluoranthene is planar however the nitrogen containing ring is twisted out of this plane by $\sim 7^\circ$. The phenyl and pyridyl rings adjacent to the nitrogen atom of the azafluoranthene core are twisted out of the average plane of the central pyridyl ring by 47° and 46° respectively, whereas the remaining pendant phenyl ring is twisted by $\sim 57^\circ$ (Figure 1.4-2 (b)).

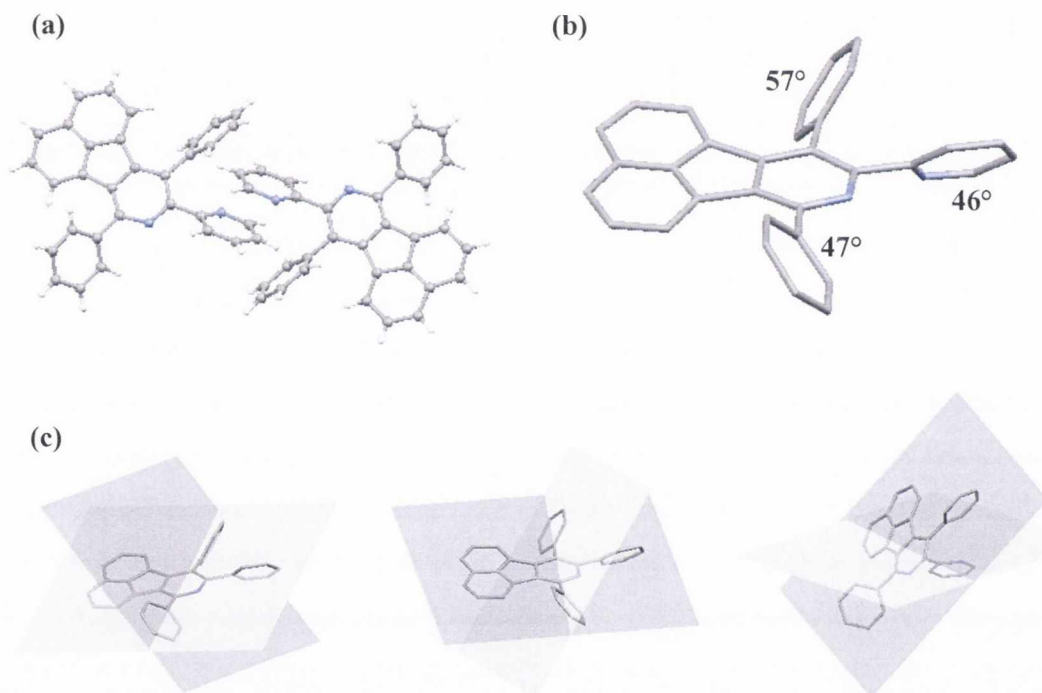


Figure 1.4-2: (a) Ball and stick representation of packing of two molecules of the asymmetric unit in the crystal structure of **6** (carbon atoms in grey, nitrogen atoms in blue and hydrogen atoms in white). (b) Stick-frame representation of one molecule of **6** (hydrogen atoms omitted for clarity) showing the angles of twist from the central aromatic ring plane of the pyridyl and phenyl rings. (c) Graphical representation of the central pyridine ring plane and each of the pendant phenyl/pyridyl ring planes.

Figure 1.4-3 shows the distances between the phenyl rings of two molecules as 7.47 Å. This is an important interaction as it causes the dimers to form a staggered packing arrangement (Figure 1.4-3 (b)).

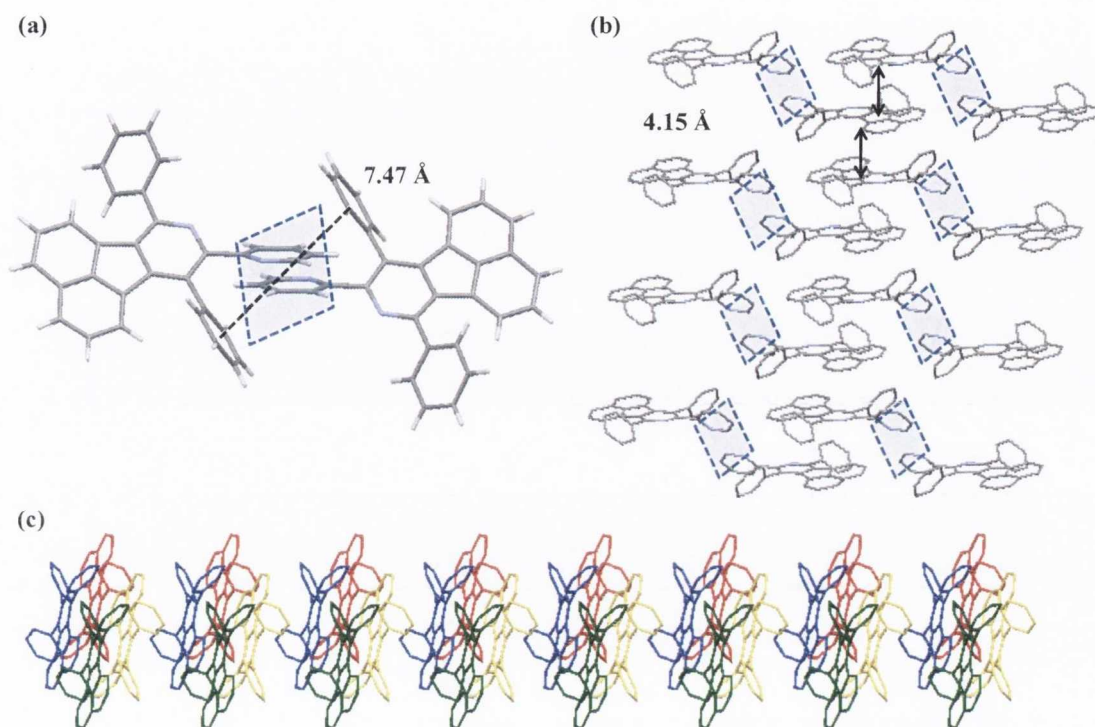


Figure 1.4-3: (a) Graphical representation of the unit cell of **6** showing that the pyridyl rings occupy the same plane (blue box) and the distance between the phenyl rings of the molecules. (b) Crystal packing structure as viewed along the b-axis showing the staggered stacking of the dimers with a distance of 4.15 Å between the planar aromatic core of the molecules (c) Packing arrangement of two pairs of dimers (red + blue and green + yellow) along the c-axis.

1.4.1.3 Synthesis of 7,10-diphenyl-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**7**)

7,10-Diphenyl-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**7**) was synthesised from the Diels-Alder reaction of **3** with commercially available 6-methyl-2-pyridinecarbonitrile. As the melting point for this reagent was much higher than that of 2-pyridinecarbonitrile, a high boiling solvent was required. Benzophenone was the solvent of choice. The reaction was performed under both conventional methods and by microwave heating. It was found, by TLC that the reaction took 72 hr to go to completion using conventional heating methods and 5 hr on microwave heating. Purification was again difficult due to the generation of unwanted side products⁸⁷ as in

the preparation of **6**, however column chromatography on silica using hexane:dichloromethane (13:8 v/v) as eluent successfully removed these side products. Benzophenone was removed using the more polar 100% dichloromethane as eluent and a mixture of dichloromethane:methanol (92:8 v/v) as eluent finally yielded **7** as an impure dark brown solid. A short silica column using hexane:ethyl acetate (1:1 v/v) as eluent afforded the product as a pale yellow solid in low yield, 19% for the conventional method and 26% for the microwave method. The lower yield of **7** compared to **6** may be due to the presence of the slightly electron donating methyl group on the six-position of the carbonitrile, increasing the electron density of the already electron rich carbonitrile.

Ligand **7** was fully characterised using ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopy. The electrospray mass spectrum of **7** shows the product with a peak at $m/z = 447.1858$ m.u. for $[\text{M}+\text{H}]^+$ which is in excellent agreement with the calculated value of $m/z = 447.1861$ m.u. for $[\text{C}_{33}\text{H}_{23}\text{N}_2]^+$.

1.4.1.4 Synthesis of 7,10-diphenyl-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**8**)

7,10-Diphenyl-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**8**) was synthesised from the Diels-Alder reaction of **3** with commercially available 6-cyano-2-pyridinecarbonitrile using benzophenone as the solvent. The reaction took 50 hr to go to completion *via* conventional heating and 5 hr *via* the microwave heating method. The optimal conditions for the reaction in the microwave reactor were obtained by trial and error and the reaction was less plagued by unwanted side products because of the electron withdrawing effects of the cyano group in the six position of the carbonitrile which should favour the cycloaddition. Column chromatography on silica using hexane:dichloromethane (8:3 v/v) as eluent removed the unwanted side products and benzophenone was removed using 100% dichloromethane as eluent. A mixture of dichloromethane: methanol (97:3 v/v) as eluent yielded **8** as a deep yellow solid without need for further purification. With a yield of 38% for the conventional method and a 49% for the microwave method, this reaction as expected gave better yields compared to **6** and **7**.

Ligand **8** was fully characterised using ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopy. The electrospray mass spectrum of **8** shows the product at $m/z = 458.1667$ m.u. for $[\text{M}+\text{H}]^+$

which is in excellent agreement with the calculated value of $m/z = 458.1657$ m.u. for $[\text{C}_{33}\text{H}_{20}\text{N}_3]^+$.

1.4.2 NMR numbering system

The same labelling system was used for NMR characterisation of each ligand. Due to the asymmetry of the compounds it is necessary to distinguish between each side of the compounds. For the purposes of labelling the naphthyl unit is divided into two parts, with the signals on the side of the molecule containing the nitrogen in the azafluoranthene core being represented by 1', 2' and 3' and those on the all carbon side of the azafluoranthene core labelled 1, 2 and 3 as shown in Figure 1.4-4. The same system is used for the pendant phenyl rings, the phenyl ring adjacent to the nitrogen atom of the central pyridyl ring of the azafluoranthene core is assigned 4', 5' and 6', whilst the ring on the all carbon side is assigned 4, 5 and 6. Finally the pendant pyridyl ring is numbered 7, 8, 9 and 10. This numbering system is used throughout this work.

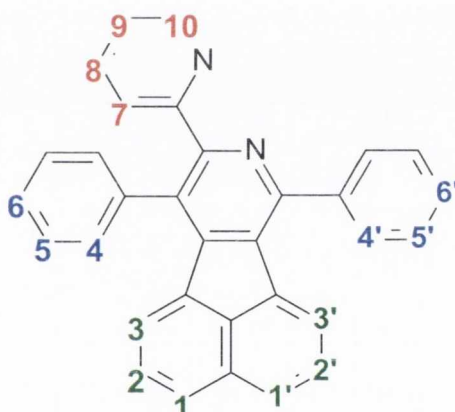


Figure 1.4-4: Labelling system used for NMR characterisation of each ligand.

1.4.3 Spectroscopic characterisation of 6,7, and 8

Each ligand was fully characterised using ^1H and ^{13}C {H} NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **6** are discussed in detail and aided the assignment of those of **7** and **8**.

1.4.3.1 ^1H NMR spectrum of **6**

The atom labelling scheme and fully assigned ^1H NMR spectrum of **6** are shown in Figure 1.4-5. The protons belonging to the same spin system were identified by ^1H – ^1H COSY 2D correlation experiments.

There are two distinct naphthyl 3-spin systems due to the asymmetric nature of the azafluoranthene – H1, H2, H3 and H1', H2', H3', where H' represent the naphthyl protons on the same side of the molecule as the nitrogen atom of the azafluoranthene. There are also two phenyl 3-spin systems and one 4-spin system attributed to the pyridyl ring protons. The signals integrate to a total of 20 protons as expected. The most deshielded signal appears at δ 8.48 ppm and belongs to H10 due to its proximity to the nitrogen atom of the pyridine ring. It is split by the adjacent H9 into a doublet with a small coupling constant of $^3J_{\text{HH}} = 5.0$ Hz. The next most downfield signal is that of H4' which appears as a doublet that integrates for two protons at δ 7.93 ppm with a coupling constant of $^3J_{\text{HH}} = 7.5$ Hz. This downfield shift is due to its position adjacent to the nitrogen atom of the azafluoranthene.

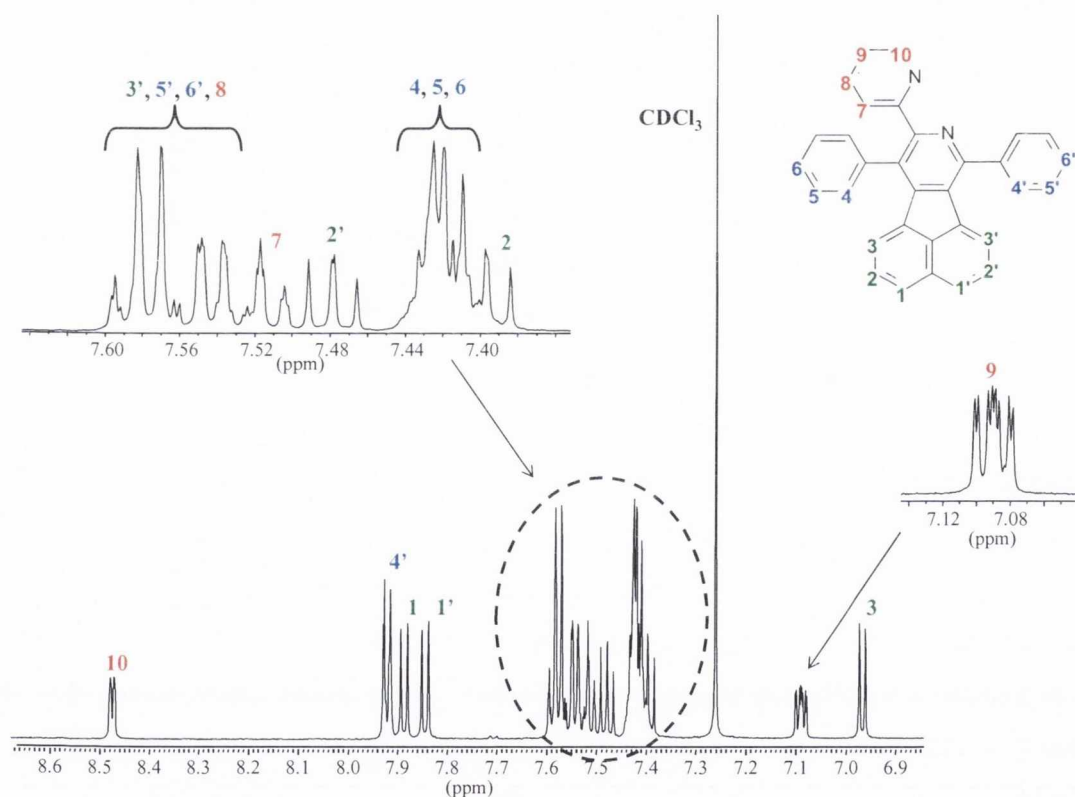


Figure 1.4-5: ^1H NMR spectrum of **6** in CDCl_3 (600.1 MHz, R.T.). Atom labelling is as per inset.

There are two doublets that integrate for one proton each at δ 7.89 and 7.85 ppm. These signals are attributed to H1 and H1' respectively of the naphthyl moiety of the

fluoranthene unit and each have a coupling constant of $^3J_{\text{HH}} = 8.0$ Hz. This larger coupling constant is typical of all-carbon aromatic rings.

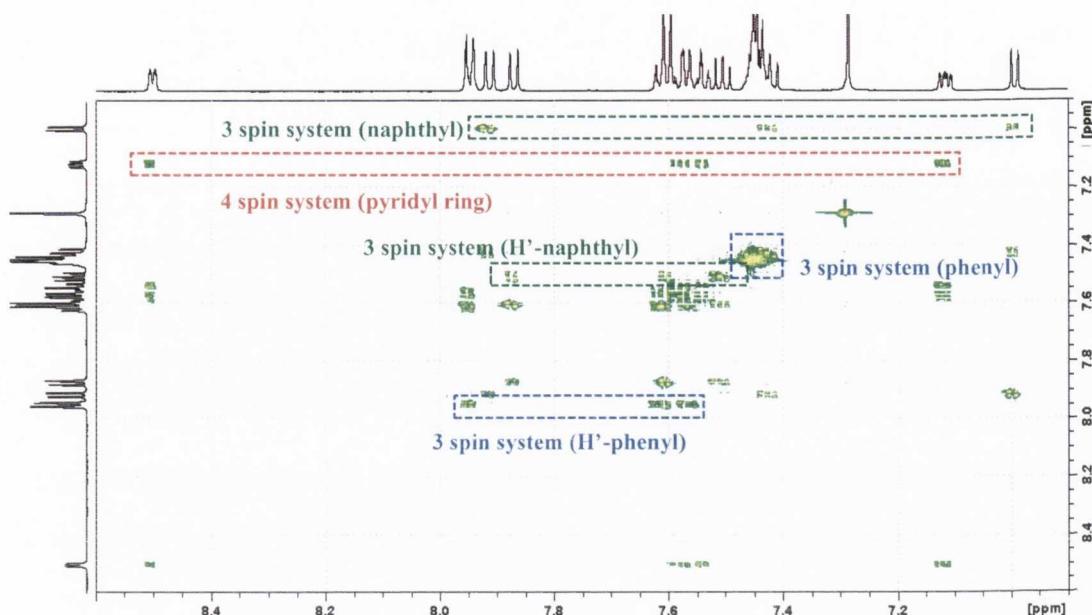


Figure 1.4-6: ^1H - ^1H COSY experiment of **6** showing four distinct spin systems.

Despite the overlapped nature of the signals, assignment was possible using 2D correlation experiments (Figure 1.4-6 and enlarged portion of Figure 1.4-7). The multiplet spanning δ 7.60 to 7.52 ppm integrates for five protons. The ^1H - ^1H COSY spectrum clearly shows that the overlapped region consists of four distinct signals from three separate spin systems; two phenyl ring signals, one naphthyl signal and one pyridyl ring signal. These signals have been assigned to H5', the first of the two phenyl signals that accounts for two of the five protons, closely overlapped by H3', the naphthyl signal. The pyridyl ring proton H8 is overlapped with the remaining phenyl signal H6'. The signals that appear as a multiplet at δ 7.51 – 7.46 ppm integrate for two protons; H7 of the pyridyl ring and H2', the final signal of the H'-naphthyl ring. The remaining phenyl ring protons appear as a multiplet at δ 7.44 – 7.38 ppm that integrates for six protons, five of which are ascribed to H4, H5 and H6. The remaining proton is the naphthyl proton H2. The signal at δ 7.09 ppm appears as a doublet of doublets of doublets and integrates for one proton with coupling constants of $^3J_{\text{HH}} = 1.2, 5.0$ and 7.5 Hz. It is assigned to H9. The upfield doublet at δ 6.97 ppm is due to the last remaining proton of the naphthyl moiety H3.

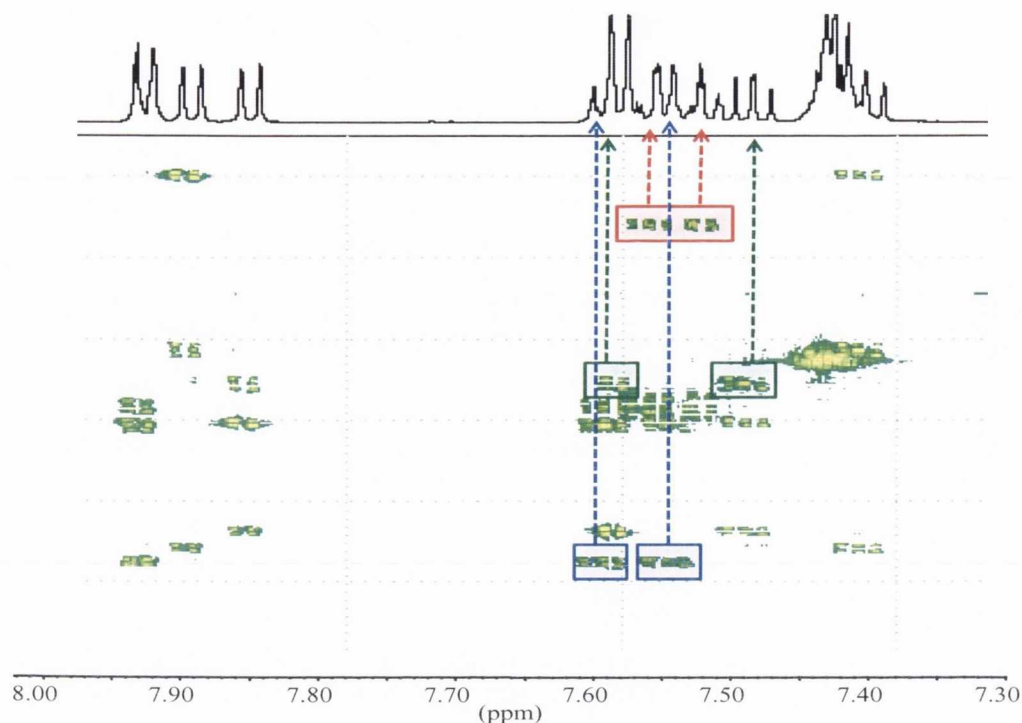


Figure 1.4-7: Enlarged region of ^1H - ^1H COSY experiment of **6** showing the assignment of the multiplets spanning δ 7.60 – 7.46 ppm to the three distinct spin systems; phenyl (blue), naphthyl (green) and pyridyl (red)

1.4.3.2 ^{13}C NMR spectrum of **6**

The ^{13}C $\{^1\text{H}\}$ NMR spectrum of **6** is shown in Figure 1.4-8. The spectrum was assigned using a HSQC (Heteronuclear Single Quantum Coherence), a ^1H - ^{13}C COSY experiment, which facilitates the assignment of the ^{13}C signal to which each proton is directly attached.

There are a total of twenty-eight signals in the ^{13}C spectrum, with twelve quaternary carbons and sixteen C – H signals. The quaternary carbons are labelled as in Figure 1.4-8. As expected the most downfield of the C – H signals are C10 and C8 which are *ortho* and *para* to the nitrogen of the pyridine ring (δ 148.4 ppm δ 135.2 ppm respectively). The ^{13}C signals for C4 and C4' occur at δ 129.6 and 128.8 ppm with another ten methine signals found very close together over a range of approx 2 ppm. Their complete assignment is shown in the enlarged region of the spectrum inset in Figure 1.4-8. The signals due to the remaining C3 and C3' of the naphthyl moiety and

C7 and C9 of the pyridyl ring are found at δ 124.9, δ 123.9, δ 124.6 and δ 121.6 ppm respectively.

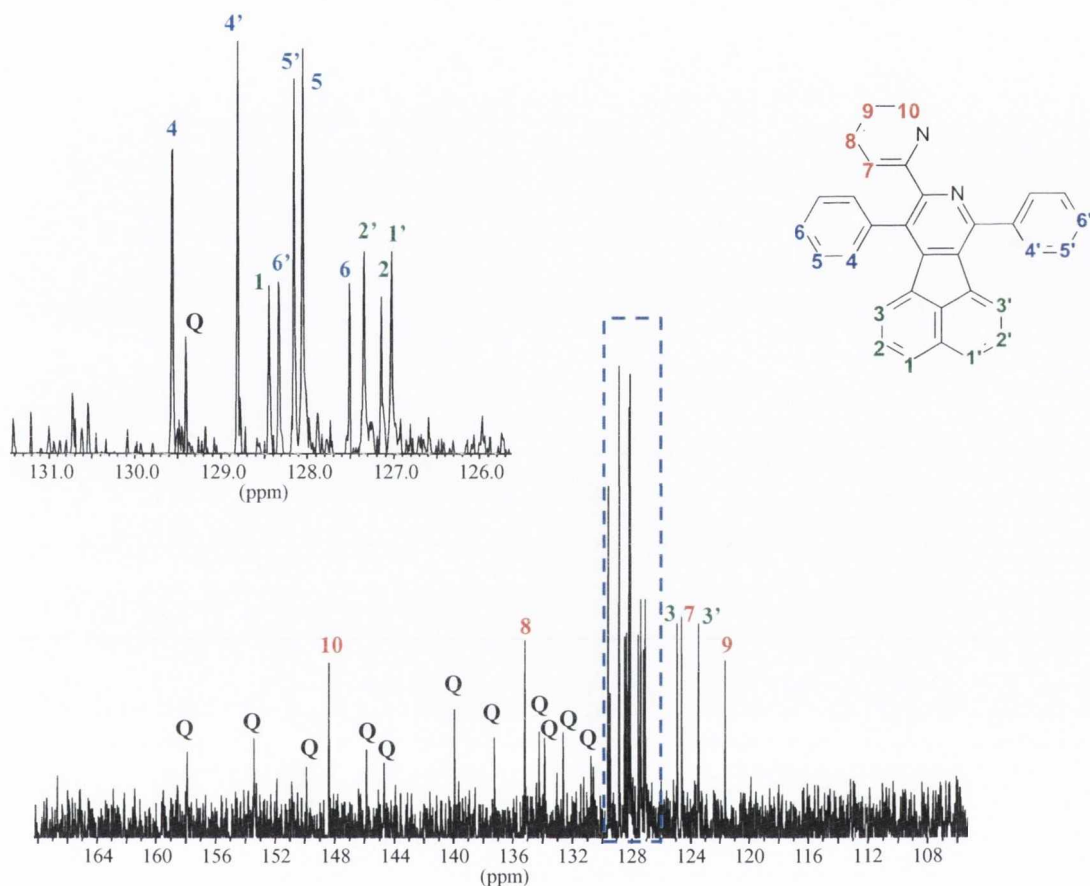


Figure 1.4-8: $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of **6** in CDCl_3 (100.6 MHz, R.T.). Atom labelling as per inset picture, Q denotes quaternary carbons.

1.4.3.3 ^1H NMR spectra of **7** and **8**

The fully assigned ^1H NMR spectrum of **7** is shown in Figure 1.4-9. The protons belonging to the same spin system were identified by $^1\text{H} - ^1\text{H}$ COSY 2D correlation experiments. The aromatic region displays two distinct naphthyl 3-spin systems due to the asymmetry of the compound, two phenyl 3-spin systems and a final 3-spin system attributed to the pyridyl protons. The signals integrate to a total of 22 protons as expected.

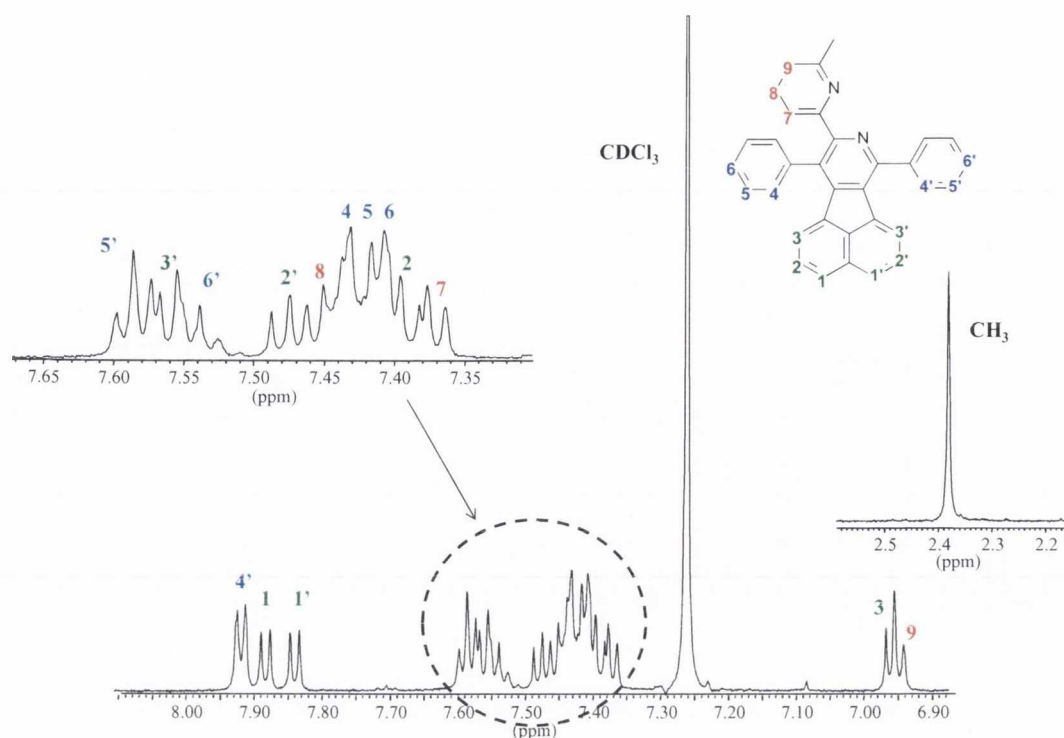


Figure 1.4-9: ^1H NMR spectrum of **7** in CDCl_3 (600.1 MHz, R.T.). Atom labelling as per inset picture.

The most notable difference in the ^1H NMR spectra of **7** compared to **6** is the absence of the signal at δ 8.48 ppm (H10) which is replaced by a methyl group in **7**. The result is that the most deshielded proton in the spectrum of **7** is H4', which appears as a doublet at δ 7.92 ppm and integrates for two protons. The inclusion of the methyl group causes other, more subtle changes throughout the spectrum, particularly to the other protons of the pyridine ring, H7, H8 and H9 (*vide infra*). The next most downfield signals are two doublets that appear at δ 7.89 and 7.84 ppm respectively, as in **6** these doublets integrate for one proton each and are assigned to H1 and H1'. Similar to **6**, there is a large region of overlapping signals. This comprises several multiplets integrating for a total of thirteen protons. This region is enlarged in the inset of Figure 1.4-9. The first substantial multiplet (δ 7.60 – 7.54 ppm) integrates for four protons and using 2D correlation experiments this was found to be due to H5', H3' and H6' respectively. The next signal is a discernible doublet of doublets with $^3J_{\text{HH}}$ 7.8, 7.1 Hz and is due to H2'. The subsequent signals appear as another large multiplet from δ 7.45 – 7.40 ppm with an integration of six protons which include H8 from the pyridyl ring which has shifted quite substantially upfield compared to its corresponding signal

in the spectrum of **6**, and the remaining phenyl protons H4-H6. H2 appears as a multiplet at δ 7.39 ppm. The doublet at δ 7.37 ppm is ascribed to H7 and has also undergone an upfield shift compared to its counterpart in **6**. The two upfield and overlapping doublets δ 6.96 ppm integrate for two protons. They are attributed to H3 and the last remaining pyridyl proton H9. H9 has also been shifted upfield due to the presence of the methyl group. The remaining signal in the spectrum is due to the methyl and is a singlet at δ 2.39 ppm integrating for three protons.

The fully assigned ^1H NMR spectrum of **8** is shown in Figure 1.4-10. Again, protons belonging to the same spin system were identified by $^1\text{H} - ^1\text{H}$ COSY 2D correlation experiments. As is common to **6** and **7** the $^1\text{H} - ^1\text{H}$ COSY displays two distinct naphthyl 3-spin systems due to the asymmetry of the compound, two phenyl 3-spin systems and a final 3-spin system again attributed to the pyridyl protons. The signals integrate to a total of 19 protons as expected.

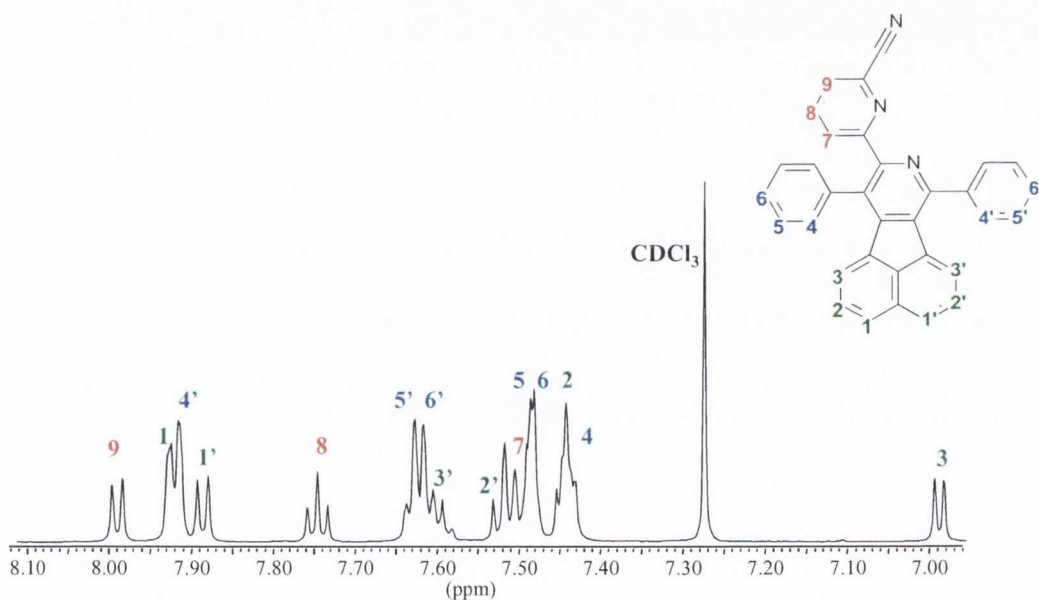


Figure 1.4-10: ^1H NMR spectrum of **8** in CDCl_3 (600.1 MHz, R.T.). Atom labelling as per inset.

Comparable to the ^1H NMR spectrum of **6**, the proton signal at δ 8.48 ppm is absent as it has been replaced by a cyano group. The presence of the strongly electron withdrawing cyano group has a marked effect on the spectrum of **8**, the most obvious

difference being the large chemical shift of H9 which has become the most deshielded signal appearing at δ 8.01 ppm. This is in contrast to its counterpart in **7** that was shifted upfield due to the presence of the slightly electron donating methyl group. The remaining pyridyl ring protons, H7 and H8, are also affected by the electron withdrawing effect of the cyano group but to a lesser extent with both appearing more downfield than their corresponding signals in the spectra of **6** and **7**. H8 appears as a distinct doublet of doublets with $^3J_{\text{HH}} = 8.3$ and 7.3 Hz at δ 7.76 ppm and H7 is found at δ 7.52 as part of a large multiplet that spans from δ 7.53 – 7.48 ppm. These differences are best observed by overlaying the three spectra (Figure 1.4-11). The chemical shifts of the pyridyl ring protons of each of the ligands **6**, **7** and **8** are summarised in Table 1.4-1.

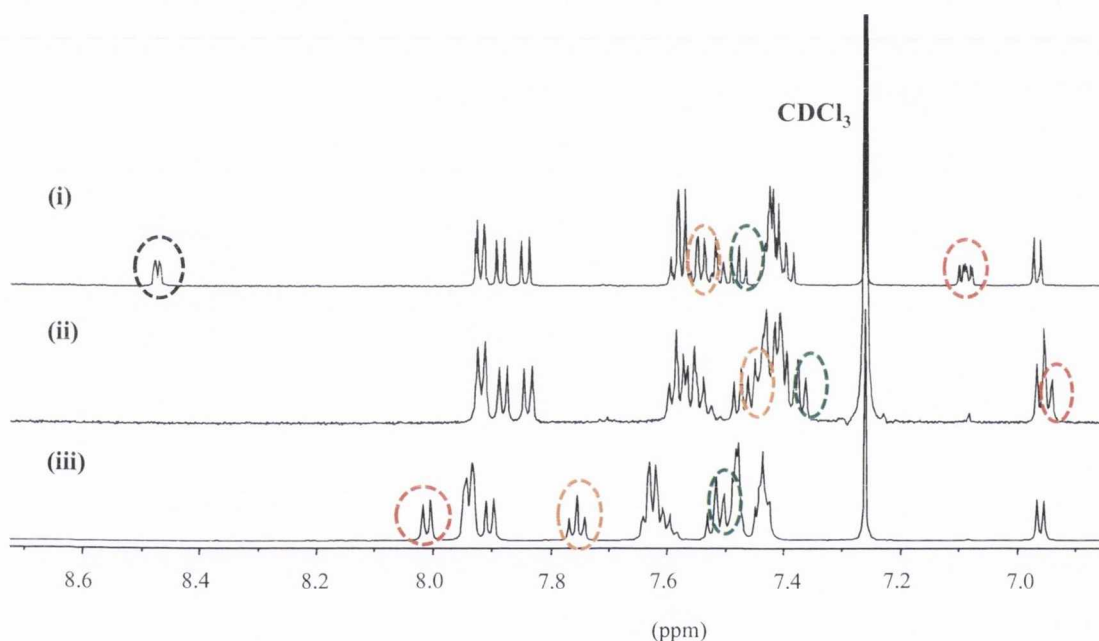


Figure 1.4-11: ^1H NMR spectra of (i) **6**, (ii) **7** and (iii) **8** showing the chemical shifts of the pyridyl ring protons H10 (black), H9 (red), H8 (orange) and H7 (green).

Table 1.4-1: ^1H NMR chemical shifts of the pyridyl ring protons of **6**, **7** and **8**.

Ligand	H10	H9	H8	H7
6	δ 8.48 ppm	δ 7.09 ppm	$\sim \delta$ 7.5 ppm	$\sim \delta$ 7.4 ppm
7	-	δ 6.96 ppm	$\sim \delta$ 7.4 ppm	δ 7.37 ppm
8	-	δ 8.01 ppm	δ 7.76 ppm	$\sim \delta$ 7.5 ppm

The multiplet appearing at δ 7.94 ppm integrates for two protons and is attributed to the overlapping doublets of H4' and H1, followed by the doublet of H1' at δ 7.91 ppm. The overlap of H4' and H1 is due to the presence of the cyano group, both signals are shifted downfield compared to the same protons in **6** and **7**. Using a 2D 1H-1H COSY experiment the multiplet that spans δ 7.64- 7.58 ppm and integrates for four protons, was assigned to the three remaining H'-phenyl ring protons, H5' and H6', and one naphthyl proton, H3'.

The inclusion of electron donating (ED) and electron withdrawing (EW) groups on compounds **7** and **8** has had the expected effect on their corresponding ^1H NMR spectra. The slightly donating methyl group of **7** causes upfield shifts of the pyridyl ring protons due to the shielding effect of the added electron density. The strongly withdrawing cyano group draws the electron density away from the remaining pyridyl ring protons which become deshielded and shifted downfield. This trend is most pronounced for the proton *ortho* to the ED or EW group, H9 in both cases (see Table 1.4-1). The naphthyl and phenyl ring chemical shifts of **7** and **8** compared to **6** are summarised in Table 1.4-2.

Table 1.4-2: ^1H NMR chemical shifts of the naphthyl and phenyl rings of **6**, **7** and **8**.

Ligand	^1H NMR chemical shifts (δ)					
	(ppm)					
	H1	H2	H3	H4	H5 & H6	
		H1'	H2'	H3'	H4'	H5' & H6'
6	7.89	~7.39	6.97	~7.45	7.46-7.41	
		7.85	~7.48	~7.58	7.93	7.60-7.54
7	7.89	7.39	6.96	~7.43	7.43-7.40	
		7.84	7.47	7.56	7.92	7.59, 7.54
8	7.94	7.45	6.98	7.43	7.50-7.48	
		7.91	7.53	7.60	7.94	7.64-7.61

1.4.3.4 ^{13}C NMR spectra of **7** and **8**

The ^{13}C $\{^1\text{H}\}$ NMR spectrum of **7** is shown in Figure 1.4-12. The spectrum was assigned using a HSQC experiment to ascertain the ^{13}C signal to which each proton is directly attached. The spectrum consists of a total of twenty-seven signals, with

thirteen quaternary carbons and fifteen C – H signals, one less than **6** as C10 now supports a methyl group. The quaternary carbons are assigned in full in Figure 1.4-12. The most downfield methine signal is due to C8 at δ 135.7 ppm. The spectrum then follows a similar pattern to the ^{13}C NMR spectrum of **6**, with ten methine signals occurring close together over a range of approx 3 ppm, the complete assignment of these signals is shown in Figure 1.4-12 section (a). The remaining four signals of the aromatic region are attributed to C3 and C3' (δ 125.2 and 123.6 ppm), the remaining naphthyl carbons, and the final pyridyl carbons C7 and C9 respectively (δ 121.6 and 121.4 ppm). The signal at δ 24.0 ppm is the methyl ^{13}C signal.

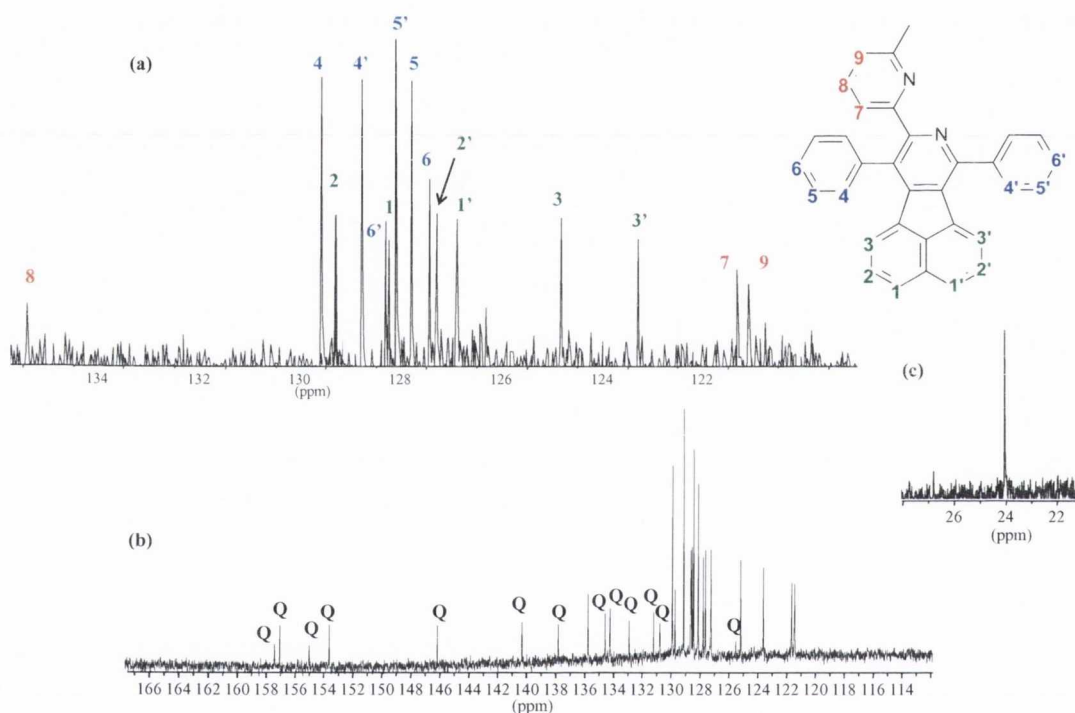


Figure 1.4-12: (a) DEPT 135 experiment, showing only CH carbons. (b) ^{13}C { ^1H } NMR spectrum of **7** in CDCl_3 (100.6 MHz, R.T.) Atom labelling as per inset, Q denotes quaternary carbons. (c) Methyl signal.

The ^{13}C { ^1H } NMR spectrum of **8** is shown in Figure 1.4-13. The spectrum consists of a total of twenty-nine signals, with fourteen quaternary carbons, one of which is the cyano group ($\text{C}\equiv\text{N}$) and fifteen C – H signals. The quaternary carbons are assigned in full in Figure 1.4-13. The most downfield methine signal is C8 at δ 136.9 ppm. The spectrum then follows a similar pattern to the ^{13}C NMR spectra of **6** and **7**, with less than 2 ppm separating eleven methine signals, some of which overlap. The complete assignment of these signals is shown in Figure 1.4-13 and was achieved using HSQC

and HMBC experiments. The remaining three signals have been assigned to H9, H1 and H1' at δ 127.2, δ 126.2 and δ 124.6 ppm respectively. The signal at δ 117.1 ppm is characteristic of the cyano group.

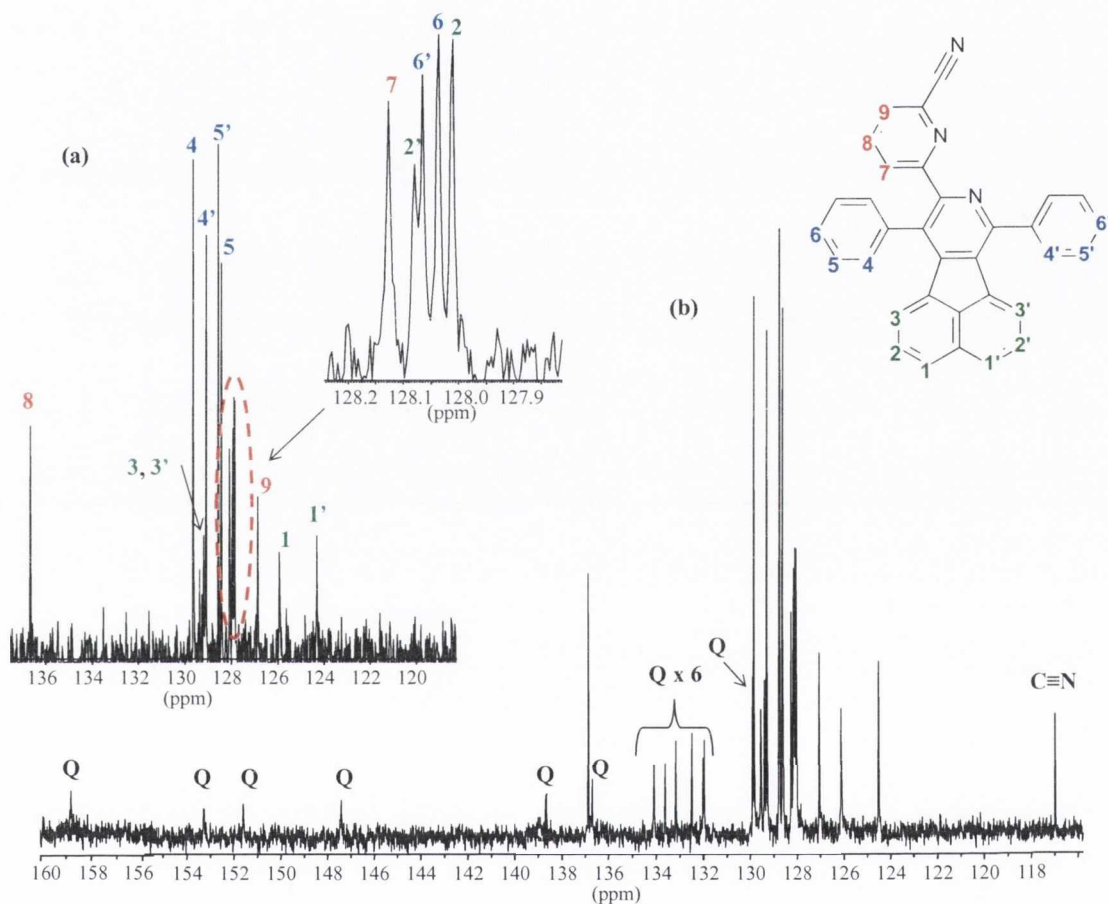


Figure 1.4-13: (a) Enlarged section of the ^{13}C $\{^1\text{H}\}$ NMR spectrum of **8** with full assignment. (b) ^{13}C $\{^1\text{H}\}$ NMR spectrum of **8** in CDCl_3 (100.6 MHz, R.T.) Atom labelling as per inset. Q denotes quaternary carbons.

The comparative ^{13}C NMR chemical shifts of **6**, **7** and **8** are summarised in Table 1.4-3 and Table 1.4-4.

Table 1.4-3: ^{13}C NMR chemical shifts of the pyridyl ring carbons of **6**, **7** and **8**.

Ligand	C10	C9	C8	C7
6	δ 148.4 ppm	δ 121.6 ppm	δ 135.2 ppm	δ 124.6 ppm
7	-	δ 121.4 ppm	δ 135.7 ppm	δ 121.6 ppm
8	-	δ 127.2 ppm	δ 136.9 ppm	δ 128.4 ppm

The effect of the electron donating and electron withdrawing groups is less pronounced in the ^{13}C NMR spectra of **7** and **8**, but some differences are observed, particularly with respect to the pyridyl ring carbons. The most notable of these changes is the downfield chemical shift by almost 6 ppm of the carbon (C9) *ortho* to the strongly electron withdrawing cyano group, and by 4 ppm of the carbon (C7) *para* to it. In contrast, the electron donating methyl group of **7** has little effect on the chemical shift of its neighbouring carbon but does cause an upfield shift of 3 ppm to the carbon (C7) *para* to it. The carbon in the *meta* position (C8) of both **7** and **8** is only marginally effected, as expected. The shifts of the naphthyl and phenyl ring carbons of **7** and **8** are unremarkable and follow a general pattern as is seen in Table 1.4-4.

Table 1.4-4: ^{13}C NMR chemical shifts of carbons of the naphthyl and phenyl rings of **6**, **7** and **8**.

Ligand	^{13}C NMR chemical shifts (δ) for the naphthyl and phenyl carbons.							
	(ppm)							
	C1	C2	C3	C4	C5	C6		
		C1'	C2'	C3'	C4'	C5'	C6'	
6	128.5	127.2	124.9	129.6	128.1	127.5		
		127.0	127.3	123.4	128.8	128.2	128.3	
7	128.5	129.7	125.2	129.9	128.1	127.7		
		127.2	127.6	123.6	129.1	128.4	128.1	
8	126.2	128.1	129.7	129.9	128.8	128.2		
		124.6	128.2	129.5	129.4	128.9	128.2	

1.4.4 Synthesis of ligands **9** and **10**

The second group of ligands to be synthesised consists of two compounds that are analogues of **6**, with the pendant phenyl rings substituted with electron withdrawing or electron donating groups respectively. The ligands are formed by the reaction of 7,9-

bis(4-*tert*-butylphenyl)-8*H*-cyclopenta[*I*]acenaphthylene (4) or 7,9-bis[4-(trifluoromethyl)phenyl]-8*H*-cyclopenta[*I*]acenaphthylene (5) with 2-pyridinecarbonitrile.

1.4.4.1 Synthesis of 7,10-Di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (9)

7,10-Di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (9) was synthesised from the Diels-Alder reaction of 4 with 2-pyridinecarbonitrile. No solvent was required for the reaction as the 2-pyridinecarbonitrile was present in a large excess. The reaction was performed under both conventional methods and by microwave heating. It was found, on careful monitoring of the reaction mixture by TLC that the reaction took 48 hr to go to completion when using the conventional heating methods compared to the 4 hr required for the microwave heating method. Using TLC to monitor the reaction carefully the optimum conditions for the reaction in the microwave reactor were obtained by a trial and error approach and were in line with those found for the synthesis of 6. The purification of 9 was made difficult by the presence of unwanted side products comparable to those observed in the synthesis of 6. Column chromatography on silica using hexane: dichloromethane (8:3 v/v) as eluent removed the unwanted side products, this was followed by a mixture of dichloromethane:methanol (97:3 v/v) as eluent which afforded 9 as a deep yellow solid without need for further purification. With a yield of 36% for the conventional method and 42% for the microwave method, this reaction was more successful than that of 6.

Ligand 9 was fully characterised using ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopy. The electrospray mass spectrum of 9 contains a peak at $m/z = 545.2966$ m.u. for $[\text{M}+\text{H}]^+$ which is in excellent agreement with the calculated parent value of $m/z = 545.2957$ m.u. for $[\text{C}_{33}\text{H}_{20}\text{N}_3]^+$.

1.4.4.2 Synthesis of 7,10-Di[(4-trifluoromethyl)phenyl]-9-(2-pyridyl)-8-azafluoranthene (10)

7,10-di[(4-trifluoromethyl)phenyl]-9-(2-pyridyl)-8-azafluoranthene (10) was synthesised from the Diels-Alder reaction of 5 with 2-pyridinecarbonitrile, which again acted as the solvent as it was present in excess. The reaction was performed using both conventional methods and by microwave heating. It was found, by careful monitoring

of the reaction mixture by TLC that the reaction took 36 hr to go to completion when using conventional heating and only 4 hr on microwave heating. The purification of **10** was easier than that of the previous ligands as there was significantly less side products. Column chromatography on silica using ethyl acetate (100%) as eluent yielded **10** as a brown solid which needed further purification. This was dissolved in dichloromethane and stirred with activated charcoal for 24 hr. On filtering and drying the desired product appeared as a pale yellow solid in a yield of 45% for the conventional method and a better yield of 55% for the microwave method.

Ligand **10** was fully characterised using ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopy. The electrospray mass spectrum of **10** contains a peak at $m/z = 569.1459$ m.u. for $[\text{M}+\text{H}]^+$ which is in excellent agreement with the calculated value of $m/z = 569.1452$ m.u. for $\text{C}_{34}\text{H}_{18}\text{F}_6\text{N}_2$.

1.4.5 Spectroscopic characterisation of **9** and **10**

Both **9** and **10** were fully characterised using ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopy, the spectra were compared to that of **6** in order to ascertain the effect of the electron withdrawing and donating groups on the ligands.

1.4.5.1 ^1H NMR spectra of **9** and **10**

The fully assigned ^1H NMR spectrum of **9** is shown in Figure 1.4-14. The protons belonging to the same spin system were identified by $^1\text{H} - ^1\text{H}$ COSY 2D correlation experiments. The spectrum integrates for 18 aromatic signals and 18 methine signals. Due to the presence of the tertiary butyl groups in the H6/H6' position of the compound there are less signals in the aromatic region resulting in less overlap compared to **6**. As in **6** the most deshielded signal is the proton *ortho* to the nitrogen of the pyridyl ring, H10 as a broad singlet at δ 8.56 ppm. This is followed by another broad signal at δ 7.92 ppm that integrates for two protons and is ascribed to H4'. The doublets appearing at δ 7.90 and δ 7.86 ppm that integrate for one proton each are due to H1 and H1' respectively. Unlike **6** the signal for H3', which appears at δ 7.73 ppm, is a distinct doublet and has shifted downfield. The signal for H5' also appears as a doublet integrating for two protons at δ 7.60 ppm which is in almost identical agreement to the position of the corresponding signal in **6**. The multiplet spanning δ 7.57 – 7.50 ppm integrates for two protons and has been assigned to H2' and H8, this is in contrast to the spectrum of **6** where the signal for H2' appears more shielded than that of H8. The

second multiplet, spanning δ 7.45 – 7.42 ppm integrates for three protons, two of these are due to H5 and the remaining one to H2. The signals for these protons are similar to their counterparts in **6**. The doublet at δ 7.41 ppm is ascribed to one of the pyridyl protons, H7 which appears more upfield than its **6** analogue. H4 is more shielded than in **6** appearing as a doublet at δ 7.35 ppm. The final pyridyl proton, H9, is seen as a broad singlet at δ 7.14 ppm followed by a doublet at δ 6.99 ppm which is attributed to H3, the final naphthyl proton. The two tertiary butyl groups appear at δ 1.43 and δ 1.39 ppm and integrate for nine protons each.

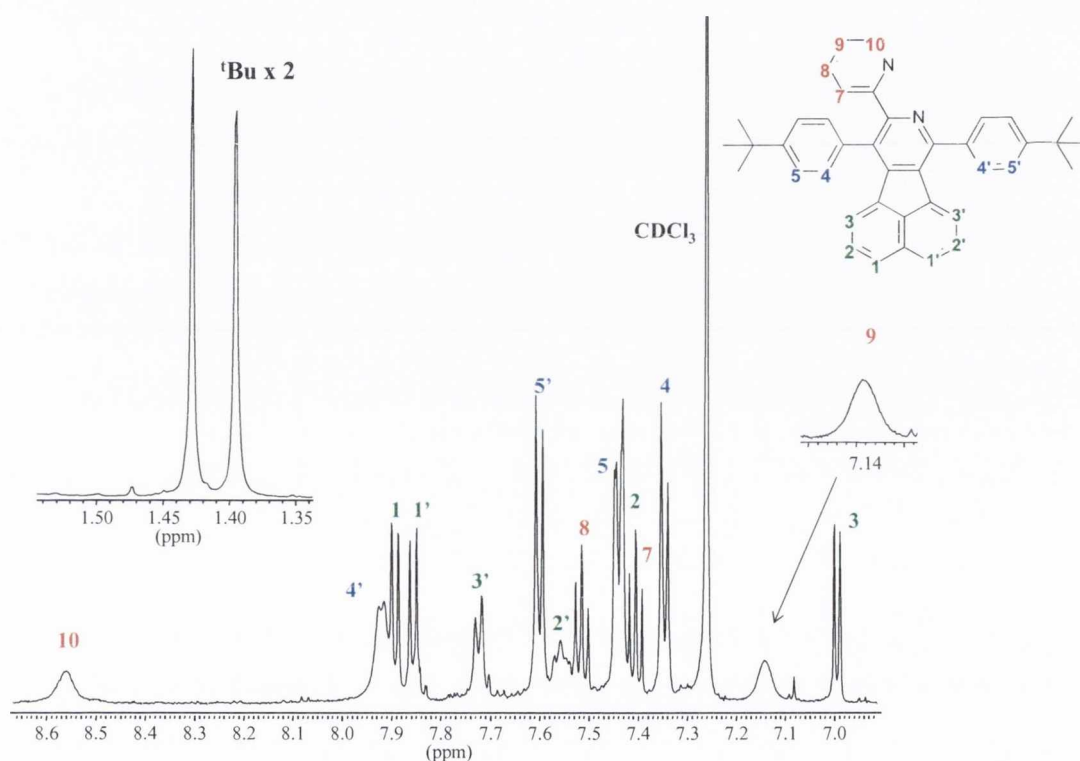


Figure 1.4-14: ^1H NMR spectrum of **9** in CDCl_3 (600.1 MHz, R.T.). Atom labelling is as per inset.

The fully assigned ^1H NMR spectrum of **10** is shown in Figure 1.4-15. Protons belonging to the same spin system were identified by ^1H – ^1H COSY 2D correlation experiments. The spectrum integrates for 18 aromatic signals. As expected, the most downfield signal belongs to H10 at δ 8.39 ppm and this is followed by H4' at δ 8.08 ppm which has shifted downfield due to the strongly electron withdrawing

trifluoromethyl group in the H6 position. A similar effect is observed for the other phenyl ring protons (*vide infra*). Characteristically, the next two signals are doublets that integrate for one proton each and are assigned to H1 and H1' at δ 7.95 and δ 7.91 ppm, respectively. In contrast to both **6** and **9** the next signal, a doublet integrating for two protons, is due to H5'. This signal is significantly shifted downfield compared to its counterparts in **6** and **9**, again due to the strongly electron withdrawing nature of the trifluoromethyl group directly adjacent to it.

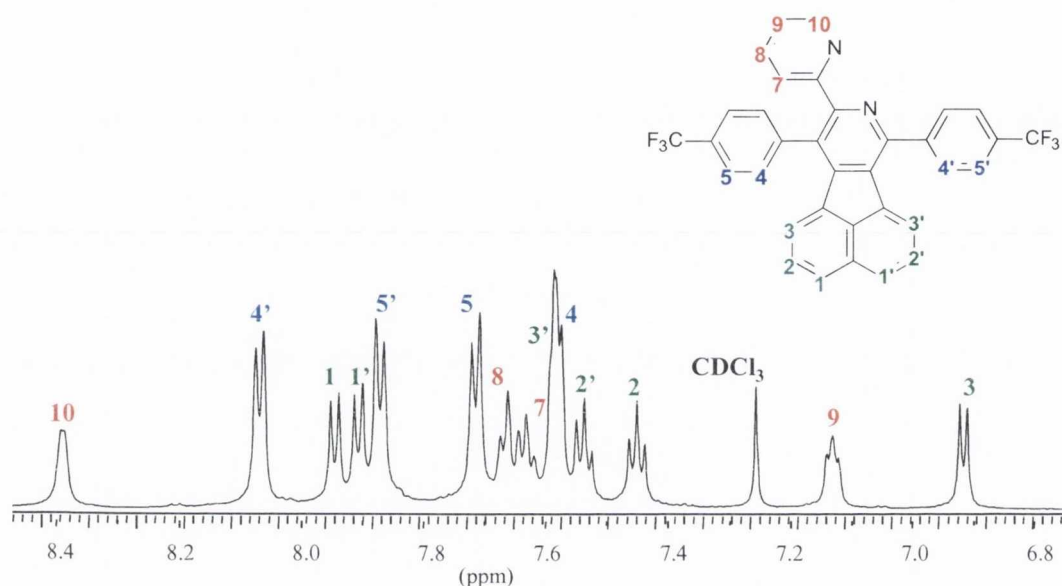


Figure 1.4-15: ^1H NMR spectrum of **10** in CDCl_3 (600.1 MHz, R.T.). Atom labelling is as per inset.

This is followed by H5 at δ 7.72 ppm which has also been affected by the trifluoromethyl group and undergone a downfield shift. The signals at δ 7.66 and δ 7.63 ppm are assigned to two pyridyl ring protons, H8 and H7 respectively, followed by two overlapping signals to give a multiplet that spans δ 7.59 – 7.56 ppm and integrates for three protons. This is ascribed to H3' and the final phenyl ring protons H4. H2' and H2 appear as two distinct doublet of doublets at δ 7.54 and δ 7.45 respectively followed by the final pyridyl ring proton H9 at δ 7.13 ppm. The doublet at δ 6.92 ppm is assigned to H3 and is the final proton in the spectrum.

Table 1.4-5: ^1H NMR chemical shifts of the naphthyl and phenyl rings of **9** and **10** in comparison to **6**

Ligand	^1H NMR chemical shifts (δ)					
	(ppm)					
	H1	H2	H3	H4	H5	
		H1'	H2'	H3'	H4'	H5'
6	7.89	~7.39	6.97	~7.45	~7.48	
		7.85	~7.48	~7.58	7.93	~7.57
9	7.90	7.42	6.99	7.35	7.45	
		7.86	7.57	7.73	7.92	7.60
10	7.95	7.45	6.92	7.56	7.72	
		7.91	7.54	7.59	8.08	7.88

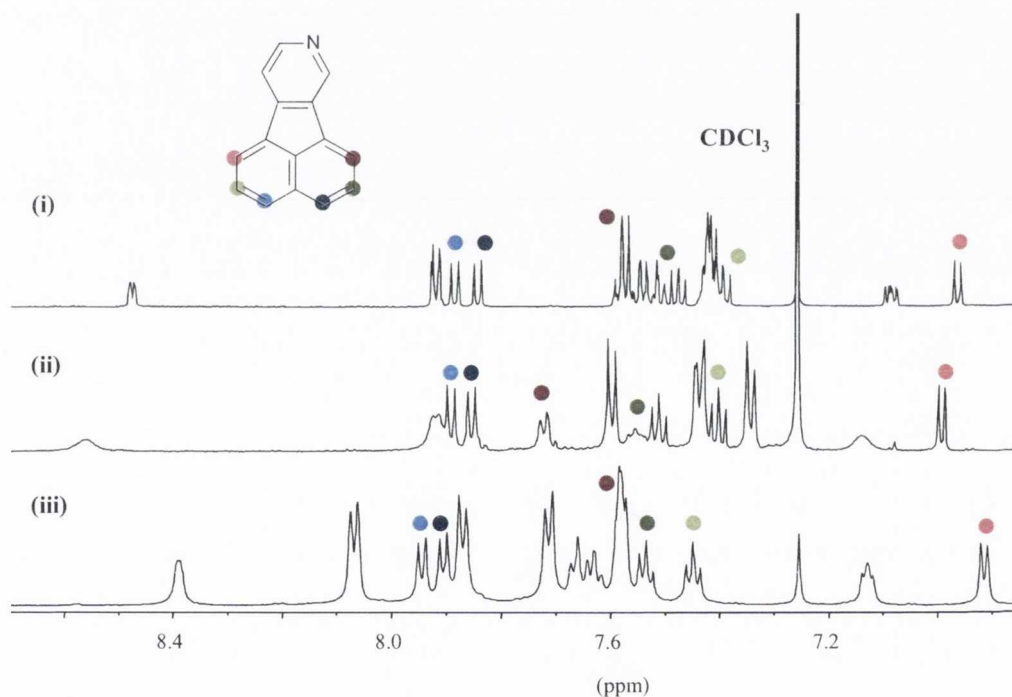


Figure 1.4-16: ^1H NMR spectra of (i) **6**, (ii) **9** and (iii) **10** in CDCl_3 (600.1 MHz, R.T.) highlighting the chemical shifts of the naphthyl proton signals.

The chemical shifts of the naphthyl and phenyl protons are summarised in Table 1.4-5. From these chemical shifts it can be seen that the electron withdrawing trifluoromethyl group exerts a stronger influence on the chemical shifts of the ligands than the electron donating tertiary butyl group. Unsurprisingly the protons that are most affected by the substitution of the H6/H6' position of the phenyl rings are the remaining phenyl ring

protons H5/H5' and H4/H4'. The pattern of the naphthyl protons is illustrated in Figure 1.4-16. By overlaying the spectra it is clear that there is little change observed.

1.4.5.2 ^{13}C NMR spectra of **9** and **10**

The fully assigned ^{13}C $\{^1\text{H}\}$ NMR spectrum of **9** is shown in Figure 1.4-17. The spectrum was assigned using HSQC and HMBC experiments. There are a total of thirty-one signals in the ^{13}C spectrum; sixteen quaternary carbons including the two tertiary butyl carbons, fourteen C – H signals and one methyl group signal. The quaternary carbons are assigned as in Figure 1.4-17.

The most downfield of the C – H signals are C10 and C8 at δ 148.7 ppm and δ 135.3 ppm respectively, this is due to the fact that these carbons are *ortho* and *para* to the nitrogen of the pyridyl ring. The spectrum follows a similar pattern to that of **6** with the next signals being attributed to C4 (δ 129.6 ppm) and C4' (δ 128.8 ppm).

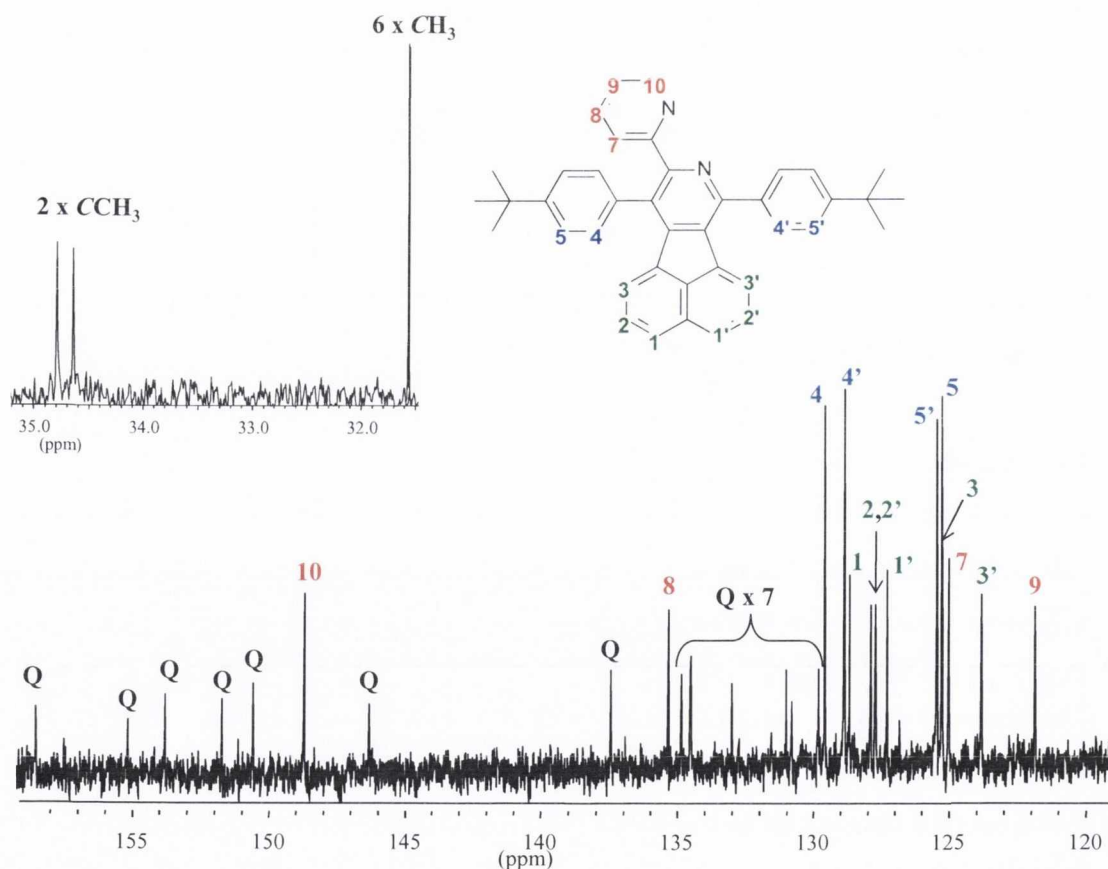


Figure 1.4-17: ^{13}C $\{^1\text{H}\}$ NMR spectrum of **9** in CDCl_3 (100.6 MHz, R.T.). Atom labelling as per picture inset, Q denotes quaternary carbons.

Due to the substitution of the compound in the C6/C6' positions there are two less C – H signals compared to the same region in the spectrum of **6**. The absence of these signals also has an effect on the order of the remaining phenyl ring carbon signals, with C5' and C5 experiencing an upfield shift to δ 125.4 and δ 125.3 ppm respectively. The signals for C1, C2, C2' and C1' undergo no significant change compared to **6**, nor do the remaining four aromatic signals C3, C7, C3' and C9 which appear at δ 125.2, δ 125.0, δ 124.8 and δ 121.9 ppm. Finally, there are three signals in the aliphatic region of the spectrum. The signals at δ 34.8 and δ 34.6 ppm are ascribed to the quaternary carbons of the tertiary butyl groups with the remaining signal at δ 31.4 ppm representing the six CH₃ carbons of the tertiary butyl groups.

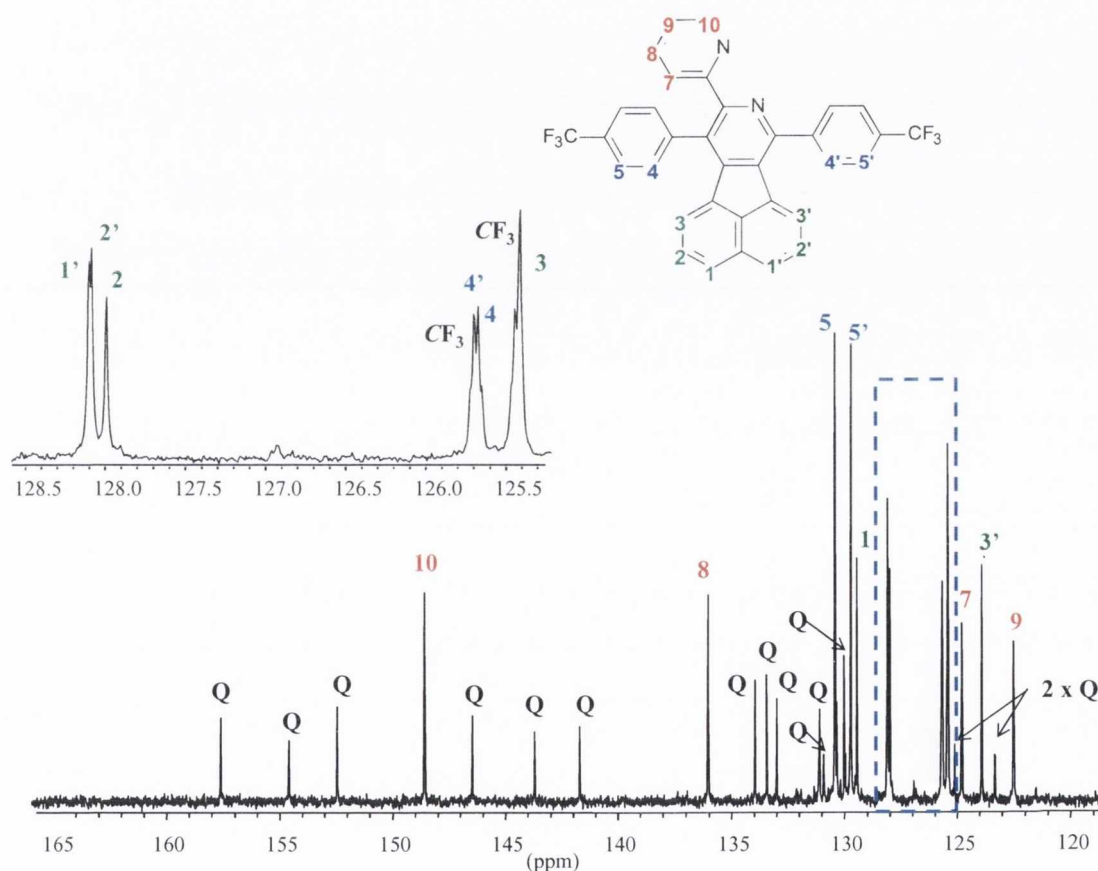


Figure 1.4-18: $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of **10** in CDCl_3 (100.6 MHz, R.T.). Atom labelling as per picture inset.

The $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of **10** is shown in Figure 1.4-18. The spectrum consists of a total of thirty signals; fourteen quaternary carbons, fourteen C – H signals and two CF₃ signals. The quaternary carbons are assigned in full in Figure 1.4-18. Similar to **6** and **9**, the most downfield of the C – H signals is that of C10 at δ 148.6 ppm. This is

again followed by C8 at δ 136.1 ppm. Due to the influence of the strongly electron-withdrawing trifluoromethyl group on the pendant phenyl rings there is a notable difference in the order of the carbon signals in the spectrum of **10** when compared to the spectra of **6** and **9**. C5 appears at δ 130.4 ppm followed by C5' and C1 (δ 129.7 ppm and δ 129.5 ppm respectively). Following this there are two sets of overlapping signals which are shown more clearly in the inset of Figure 1.4-18. The first overlapping signals are attributed to C1', C2' and C2 (δ 128.1, δ 128.1 and δ 128.0 ppm). The second set of overlapping signals is more complex as it contains both CF₃ carbons at δ 125.7 and δ 125.5 ppm. The signals of C4 and C4' also fall within this range of signals at δ 125.7 ppm. The remaining four signals follow the same pattern as those of **6** and **9** with C3 at δ 125.4 ppm followed by C7 at δ 124.8 ppm, C3' at δ 123.9 ppm and finally C9 at δ 122.5 ppm.

The comparative ¹³C NMR chemical shifts of **6**, **9** and **10** are summarised in Table 1.4-6 and Table 1.4-7.

*Table 1.4-6: ¹³C NMR chemical shifts of the pyridyl ring carbons of **6**, **9** and **10***

Ligand	C10	C9	C8	C7
6	δ 148.4 ppm	δ 121.6 ppm	δ 135.2 ppm	δ 124.6 ppm
9	δ 148.7 ppm	δ 121.9 ppm	δ 135.3 ppm	δ 125.0 ppm
10	δ 148.6 ppm	δ 122.5 ppm	δ 136.1 ppm	δ 124.8 ppm

The electron-withdrawing and electron donating groups in the C6/C6' position of **9** and **10** have a negligible effect on the pyridyl ring carbons, which is unsurprising given the distance between the C6/C6' positions and the pyridyl ring protons.

Table 1.4-7: ¹³C NMR chemical shifts of the naphthyl and phenyl ring carbons of **6**, **9** and **10**

Ligand	¹³ C NMR chemical shifts (δ) for the naphthyl and phenyl carbons.						
	(ppm)						
	C1	C2	C3	C4	C5	C6	
	C1'	C2'	C3'	C4'		C5'	C6'
6	128.5	127.2	124.9	129.6	128.1	127.5	
	127.0	127.3	123.4	128.8		128.2	128.3
9	128.7	127.7	125.2	129.6	125.3	-	
	127.3	127.9	123.8	128.8		125.4	-
10	129.5	128.0	125.4	125.7	130.4	-	
	128.1	128.1	123.9	125.7		129.7	-

As expected, the effect of the electron withdrawing and donating groups is more pronounced in the chemical shifts of the phenyl ring carbon signals. The carbon adjacent to the electron donating group of **9** is shifted upfield compared to the unsubstituted **6** as there is greater electron density centred on the phenyl ring causing the carbon to become more shielded. In contrast, the electron withdrawing group of **10** has the opposite effect, drawing electron density away from the phenyl ring causing the signal for the adjacent carbon to appear more downfield compared to **6**.

1.4.5.3 ¹⁹F NMR spectrum of **10**

The corresponding ¹⁹F NMR spectrum of **10** is shown in Figure 1.4-19. The spectrum shows two signals at δ -63.3 and δ -63.1 ppm. Both signals appear as singlets as the fluorine atoms in each of the trifluoromethyl groups are in chemically equivalent environments.

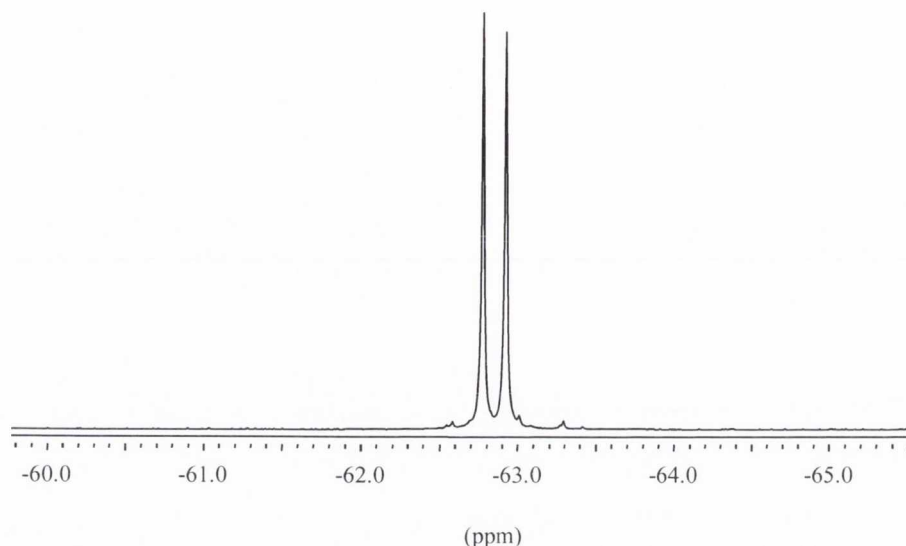


Figure 1.4-19: ^{19}F NMR of **10**, (CDCl_3 , 400.1 MHz, R.T.)

1.4.6 Synthesis of ligands **11** and **12**

The third group of ligands to be synthesised consists of two compounds that are derivatives of **7**, with the pendant phenyl rings substituted with electron withdrawing or electron donating groups respectively. The ligands are formed by the reaction of 7,9-bis(4-*tert*-butylphenyl)-8*H*-cyclopenta[*I*]acenaphthylene (**4**) or 7,9-bis[4-(trifluoromethyl)phenyl]-8*H*-cyclopenta[*I*]acenaphthylene (**5**) with 6-methyl-2-pyridinecarbonitrile.

1.4.6.1 Synthesis of 7,10-di(4-*tert*-butylphenyl)-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**11**)

7,10-Di(4-*tert*-butylphenyl)-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**11**) was synthesised from the Diels-Alder reaction of **4** with commercially available 6-methyl-2-pyridinecarbonitrile in a benzophenone melt. The reaction was performed under both conventional methods and by microwave heating. By constant monitoring of the reaction mixture by TLC it was found that the reaction took 5 days to go to completion when using the conventional heating methods compared to 5 hr required for microwave heating. As with the previous ligands, purification of **11** was made very difficult due to the presence of unwanted side products. Column chromatography on silica using hexane: dichloromethane (8:3 v/v) as eluent removed the unwanted side products, this was followed by dichloromethane (100%) to remove the benzophenone. Finally, a mixture of dichloromethane: methanol (97:3 v/v) as eluent afforded **11** as a dark brown solid that needed further purification. Column chromatography on silica using ethyl

acetate (100%) eventually afforded the crude product as a pale brown solid in quite a poor yield of < 5% for the conventional method and a similarly disappointing yield of ~ 5% for the microwave method. With such low yields this reaction was the least successful and produced more side-products than any of the desired compound. This can be attributed to the fact that both reactants are substituted with electron donating groups and as a result of this there is an even higher electron density on the already electron rich starting materials. This is undesirable for Diels-Alder cycloadditions as, generally, one of the components (usually the dienophile) of the reaction must be electron-deficient for the reaction to proceed in good yield.⁸⁸

Owing to the poor yield and the difficulties eradicating the side products **11** could not be fully characterised using ^1H and ^{13}C { ^1H } NMR spectroscopy. However, the electrospray mass spectrum of **11** contains a peak at $m/z = 559.3107$ m.u. for $[\text{M}+\text{H}]^+$ which is in excellent agreement with the calculated value of $m/z = 559.3113$ m.u. for $[\text{C}_{33}\text{H}_{20}\text{N}_3]^+$.

1.4.6.2 Synthesis of 7,10-di[(4-trifluoromethyl)phenyl]-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**12**)

7,10-Di[(4-trifluoromethyl)phenyl]-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**12**) was synthesised from the Diels-Alder reaction of **5** with 6-methyl-2-pyridinecarbonitrile, again with benzophenone as the solvent. The reaction was performed under both conventional methods and by microwave heating, with the reaction using conventional heating methods taking 4 days to go to completion compared to the 5 hr under microwave conditions. The purification of **12** proved very difficult. Column chromatography on silica using ethyl acetate (100%) as eluent yielded **12** as a brown solid which needed further purification. Further column chromatography using dichloromethane:methanol solution as eluent again afforded **12** as an impure brown solid. This was dissolved in dichloromethane and precipitated with cold methanol but still did not yield the desired pure product. This was surprising as the starting materials contained electron withdrawing (on the diene) and donating groups (on the dienophile). This suggests that the positioning of the electron withdrawing/donating groups plays an important role in the efficiency and success of the reaction.

Ligand **12** could not be characterised using ^1H and ^{13}C { ^1H } NMR spectroscopy. The electrospray mass spectrum of **12** however contains a peak at $m/z = 583.1697$ m.u. for

$[M+H]^+$ which is in excellent agreement with the calculated value of $m/z = 583.1657$ m.u. for $[C_{35}H_{20}F_6N_2]^+$.

1.4.7 Synthesis of ligands 13 and 14

The final group of ligands to be synthesised consists of two compounds that are derivatives of **8**, with the pendant phenyl rings substituted with electron withdrawing or electron donating groups respectively. The ligands are formed by the reaction of 7,9-bis(4-*tert*-butylphenyl)-8*H*-cyclopenta[*l*]acenaphthylene (**4**) or 7,9-bis[4-(trifluoromethyl)phenyl]-8*H*-cyclopenta[*l*]acenaphthylene (**5**) with 2,6-pyridinedicarbonitrile.

1.4.7.1 Synthesis of 7,10-di(4-*tert*-butylphenyl)-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**13**)

7,10-Di(4-*tert*-butylphenyl)-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**13**) was synthesised from the Diels-Alder reaction of **4** with commercially available 2,6-pyridinedicarbonitrile in a benzophenone melt by both conventional methods and microwave heating. By constant monitoring of the reaction mixture by TLC it was found that the reaction took 48 hr to go to completion when using the conventional heating methods compared to 4 hr required for microwave heating. As with the previous ligands, purification of **13** was made more difficult due to the presence of unwanted side products. Column chromatography on silica using hexane: dichloromethane (8:3 v/v) as eluent removed the unwanted side products; this was followed by dichloromethane (100%) to remove the benzophenone. Finally, a mixture of dichloromethane: methanol (97:3 v/v) as eluent afforded **13** as a dark brown solid that needed further purification. It was dissolved in dichloromethane and stirred with activated charcoal for 24 hr. On filtering and drying the desired product appeared as a pale brown solid in a yield of 28% for the conventional method and a better yield of 36% for the microwave method.

Ligand **13** was fully characterised using 1H and ^{13}C { H } NMR spectroscopy. The electrospray mass spectrum of **13** contains a peak at $m/z = 570.2921$ m.u. for $[M+H]^+$ which is in excellent agreement with the calculated value of $m/z = 570.2909$ m.u. for $[C_{33}H_{20}N_3]^+$.

1.4.7.2 Synthesis of 7,10-di[(4-trifluoromethyl)phenyl]-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**14**)

7,10-Di[(4-trifluoromethyl)phenyl]-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**14**) was synthesised from the Diels-Alder reaction of **5** with commercially available 2,6-pyridinedicarbonitrile in a benzophenone melt. Both conventional methods and microwave heating were employed with the reaction taking 5 days to go to completion using conventional heating methods but only 5 hr under microwave conditions. Purification of **14** was achieved by column chromatography on silica using hexane: dichloromethane (8:3 v/v) as eluent to remove the unwanted side products, this was followed by dichloromethane (100%) to remove the benzophenone. Finally, a mixture of dichloromethane: methanol (97:3 v/v) as eluent afforded **14** as a dark brown solid that needed further purification. It was loaded on to dry silica using ethyl acetate (100%) as eluent to afford the product as a pale brown solid. This was dissolved in dichloromethane and precipitated with cold methanol. On filtering and drying the desired product appeared as a pale yellow solid in a yield of 18% for the conventional method and a better yield of 34% for the microwave method. On further investigation however, it was discovered that a large portion of the yellow powder was in fact the 2,6-pyridinedicarbonitrile (1.4.8.1). The actual yield of the desired compound was estimated to be less than 2% for both methods, making this reaction as unsuccessful as **11**.

Ligand **14** was not fully characterised using ^1H and ^{13}C {H} NMR spectroscopy. The electrospray mass spectrum of **14**, however, did contain the desired product peak at $m/z = 594.1399$ m.u. for $[\text{M}+\text{H}]^+$ which is in excellent agreement with the calculated value of $m/z = 594.1405$ m.u. for $[\text{C}_{33}\text{H}_{20}\text{N}_3]^+$.

1.4.8 Spectroscopic characterisation of **13** and **14**

13 was fully characterised using ^1H and ^{13}C {H} NMR spectroscopy, with **14** only characterised by ^1H NMR as part of a mixture. The spectra are then compared to that of **8** in order to ascertain the effect of the electron withdrawing and donating groups on the ligands.

1.4.8.1 ^1H NMR spectra of **13** and **14**

The fully assigned ^1H NMR spectrum of **13** is shown in Figure 1.4-20. The protons belonging to the same spin system were identified by $^1\text{H} - ^1\text{H}$ COSY 2D correlation experiments. The spectrum integrates to a total of 17 aromatic signals and 18 methine signals. Due to the presence of the tertiary butyl groups in the H6/H6' position of the compound there are less signals in the aromatic region resulting in less overlap compared to **8**. The most downfield signal at δ 8.00 ppm appears as a doublet with a coupling constant of $^3J_{\text{HH}} = 8.0$ Hz and is assigned to the naphthyl proton H1'. This is followed by another doublet at δ 7.95 ppm, again with a coupling constant of $^3J_{\text{HH}} = 8.0$ Hz, attributed to H1. This is followed by two overlapping doublets that appear as a multiplet spanning δ 7.91 – 7.89 ppm and integrate for three protons, H9 and H4' respectively. A second set of overlapping signals appears at δ 7.78 – 7.72 ppm; integrating for two protons these signals are ascribed to H8 and H2'. A doublet with $^3J_{\text{HH}} = 8.0$ Hz at 7.66 ppm integrates for two protons, H5'. The signal at δ 7.55 ppm integrates for one proton and is the second of the pyridyl protons, H7, appearing as a doublet of doublets. Following this is a multiplet (δ 7.52 – 7.49 ppm) integrating for three protons, H5 and H3'. This is immediately followed by another doublet of doublets integrating for one proton at δ 7.45 ppm and can be attributed to H2. The remaining aromatic signals are both doublets, the doublet at δ 7.36 ppm integrates for two protons and is the final phenyl ring signal H4, whereas the doublet at δ 7.05 ppm integrates for one proton and is the final naphthyl signal H3. There are two singlets at δ 1.47 and δ 1.45 ppm that both integrate for nine protons each and are due to the two tertiary butyl groups in the H6/H6' positions.

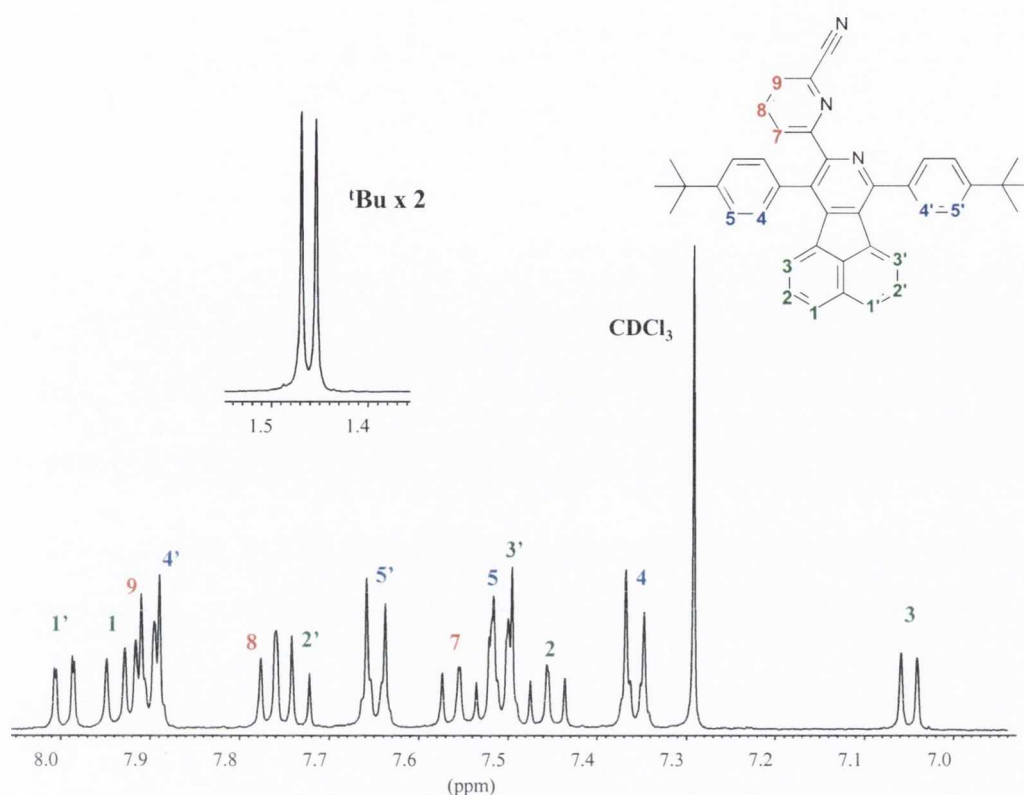


Figure 1.4-20 : ^1H NMR spectrum of **13** in CDCl_3 (600.1 MHz, R.T.). Atom labelling is as per inset.

The ^1H NMR spectrum of **14** is shown in Figure 1.4-21. It is clear from the spectra that a large amount of starting material remains in the sample. Despite this, the peaks corresponding to the desired product are still visible. As it was not possible to perform 2D correlation experiments on the sample the spectra could not be fully characterised. However, as there are similar patterns followed by the family of fluoranthene ligands, it can be assumed that this compound is no different; using this and the integration values of the peaks, it was possible to estimate which signals correspond to which protons, as shown in Figure 1.4-21.

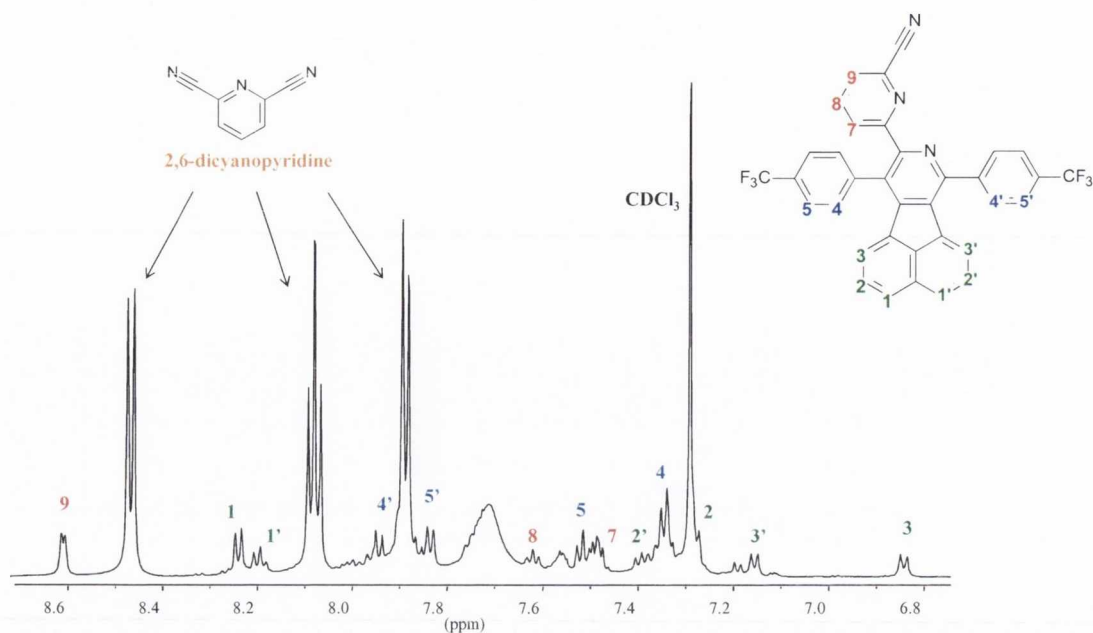


Figure 1.4-21: ^1H NMR spectra of the mixture of **14** and starting material 2,6-pyridinedicarbonitrile

1.4.8.2 ^{13}C NMR spectra of **13**

The fully assigned ^{13}C { ^1H } NMR spectrum of **13** is shown in Figure 1.4-22. The spectrum was assigned using HSQC and HMBC experiments. The quaternary carbons are assigned as in Figure 1.4-22

The most downfield of the C – H signals is C8 at δ 136.6 ppm. The spectrum then follows a similar pattern to the ^{13}C NMR spectra of **8**, with less than 2 ppm (δ 129.5 – 127.5 ppm) separating seven methine signals, some of which overlap. The complete assignment of these signals is shown in Figure 1.4-22 and was achieved using HSQC and HMBC experiments. C3' appears at δ 126.7 ppm followed by C3 at δ 125.7 ppm. C5' and C5 appear close together at δ 125.6 and δ 125.4 ppm respectively and are followed by the remaining methine signal C2 at δ 124.2 ppm. The signal at δ 116.9 ppm is characteristic of the cyano group. Two signals at δ 34.8 and δ 34.7 ppm are attributed to the quaternary carbons of the tertiary butyl groups. The final two signals are the CH_3 carbons of the tertiary butyl groups at δ 31.5 and δ 31.0 ppm respectively.

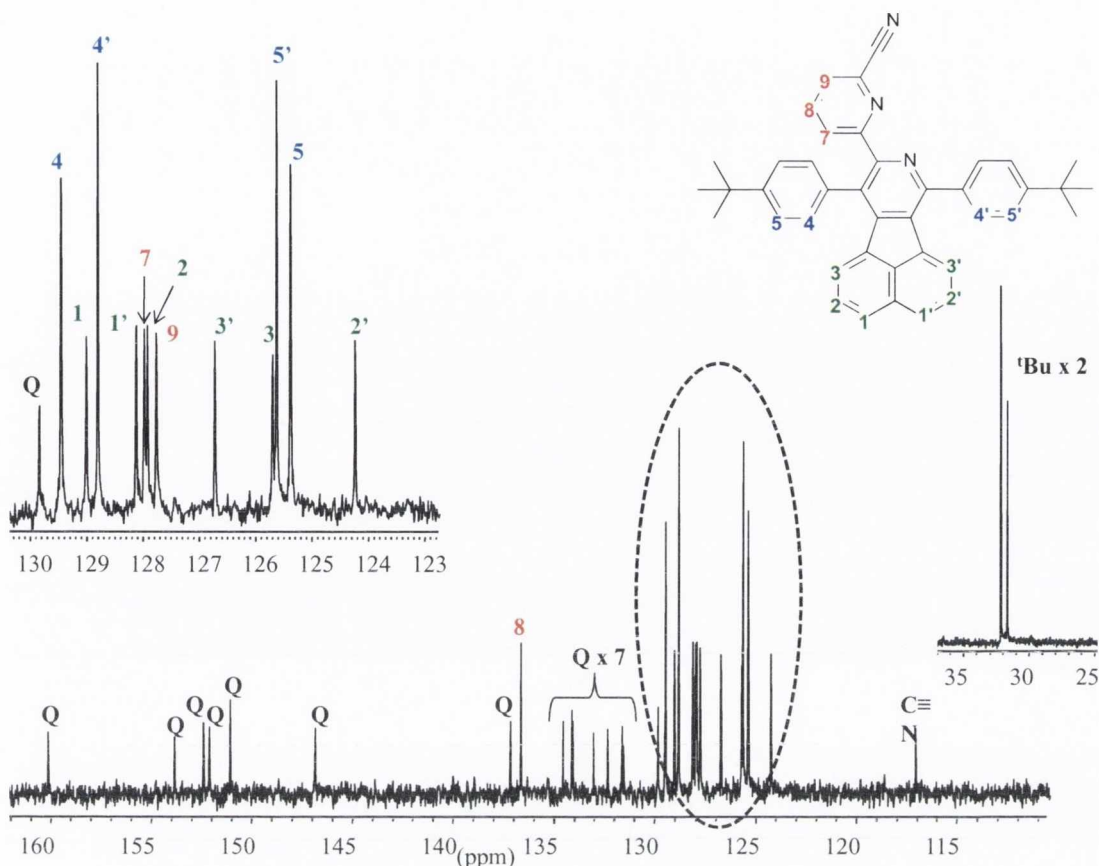


Figure 1.4-22: ^{13}C { ^1H } NMR spectrum of **13** in CDCl_3 (600.1 MHz, R.T.). Atom labelling as per inset picture.

1.5 Conclusions and Outlook

The aim of this work was to synthesise a family of novel ligands based on the fluoranthene functional group using the [2+4] Diels-Alder cycloaddition reaction. The incorporation of a nitrogen atom directly into the fluoranthene core would potentially impart ligand capabilities on the molecules therefore opening up a whole new facet of hitherto unexplored coordination chemistry. Further functionalisation, using both electron-donating and electron-withdrawing substituents, was undertaken in order to attempt to tune the optical properties of both the molecules and their potential coordination complexes.

Of the nine target ligands six were synthesised and purified in good yield, namely **6**, **7**, **8**, **9**, **10** and **13**. The remaining three, **11**, **12** and **14**, were successfully formed during reaction but could not be satisfactorily separated from the reaction mixture to facilitate full characterisation. Unsurprisingly, the least successful reactions were those between starting materials that possessed similar functional groups, i.e. both containing electron

donating groups (**11**) or electron withdrawing groups (**14**). Unexpectedly however, the reaction to form **12** was unsuccessful as only trace amounts of the desired product were found. This suggests that the placement of the electron withdrawing and electron donating groups plays a crucial part in the outcome of the reaction.

The purification of the compounds proved challenging and very time consuming, often requiring a number of purification attempts. The yields were marginally improved on using microwave chemistry instead of the conventional heating methods. The improvement in yield, however, was not the main advantage of using microwave irradiation; reaction times were significantly reduced in the microwave reactor, taking on average 4 – 5 hr for the reaction to go to completion compared to the 48 hr – 10 day reaction times required for the conventional heating method reactions.

Chapter 2:

**Investigations of the Photophysical and
Electrochemical Properties of 8-Azafluoranthene
Compounds**

2.1 Introduction

Once the structure of fluoranthene was elucidated there followed many studies of its photophysical properties. This initial interest slowed somewhat until more recently when the search for efficient, cheap and robust blue light emitters reignited the interest in fluoranthene and fluoranthene based molecules.^{43,44,46}

2.1.1 Photophysical characteristics of fluoranthene

The absorption spectrum of fluoranthene was published by Orchin *et al* in 1947.⁸⁹ It consists of three main, highly structured bands centred at 240, 285 and 300 – 370 nm respectively.

In 1968 Berlman *et al* reported the anomalous fluorescence characteristics of fluoranthene and three of its derivatives.⁹⁰ They found that for fluoranthene in particular, there were four irregular fluorescence characteristics: unusual fluorescence lifetime values, a surprisingly large Stokes shift, a relative immunity to oxygen quenching and also to concentration quenching. The first of these abnormal characteristics concerned the value of the measured fluorescence lifetime of $\tau = 53$ ns. This was many times greater than the calculated value of $\tau_{0c} = 16.4$ ns, a phenomenon also observed in biphenyl⁹¹ (which has a calculated value of $\tau_{0c} = 2.8$ ns and a measured value of $\tau = 16$ ns). This similarity to biphenyl is unsurprising considering both compounds are structurally related (Figure 2.1-1). The explanation for this is the occurrence of a partially hidden transition from the weak absorption band at 390 nm which represents a transition from a lower energy level than that represented by the much more intense and higher energy bands at 360 nm and 324 nm.^{92,93} This is further confirmed by the large Stokes shift of almost 4000 cm^{-1} (56 nm) which is also observed for biphenyl (3300 cm^{-1}).

The relative immunity to concentration quenching and excimer formation is most likely due to steric hindrance in both the excited and ground states. Fluoranthenes reduced sensitivity to oxygen quenching compared to similar polycyclic aromatic hydrocarbons is not yet fully understood.⁹⁰ This work was furthered by Güsten *et al* who detailed the absorption and emission spectra of fluoranthene and four of its benzo analogues, as well as their fluorescence lifetimes and quantum yields.⁹⁴

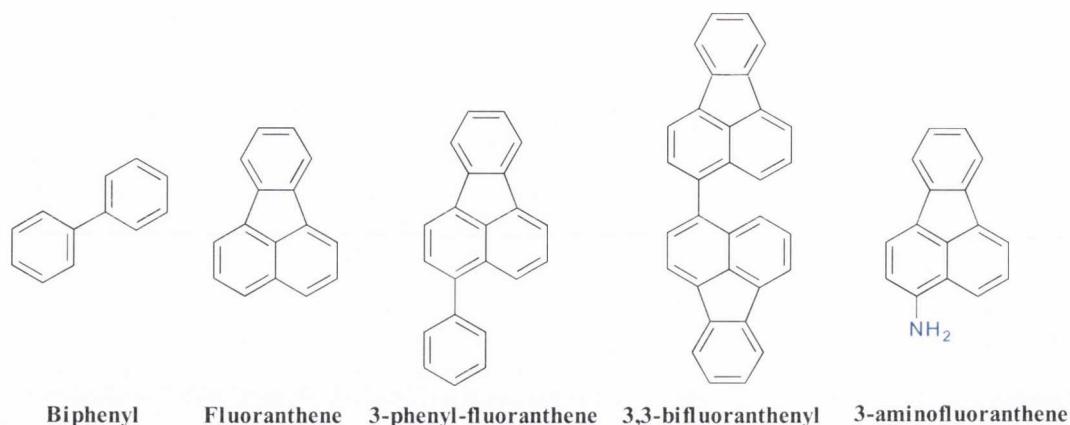


Figure 2.1-1: Biphenyl, fluoranthene and the three fluoranthene derivatives examined by Berlman *et al.*⁹⁰

They explained how the discordance between the experimental value of the fluorescence decay lifetime and the calculated value computed using the Strickler-Berg formula, can be taken as evidence that fluorescence takes place from a partially forbidden transition.⁹⁰⁻⁹⁴ Theoretical calculations have shown that the intense bands ranging from 300 – 400 nm in the absorption spectrum of fluoranthene represent a composite of at least three transitions, not a single transition as was previously thought.^{95,96}

In 1985, Amin *et al* published the excitation and emission spectra of fluoranthene and a range of fluoranthene derivatives illustrating the effect that various substituents have on the emission properties.²⁴ The parent fluoranthene compound exhibits blue emission with λ_{em} at 447 nm and 456 nm. This blue emission is a very desirable characteristic of many fluoranthene compounds and has resulted in many fluoranthene based molecules being incorporated into organic light emitting devices (OLEDs).

2.1.2 Triphenylfluoranthene

The photophysical properties of triphenylfluoranthene (TPF) have sparked much interest as the molecule is a robust blue-emitter. TPF, as well as compounds based on the TPF motif, have been incorporated successfully into electroluminescent devices.^{42-44,48}

One of the characteristics that singled out TPF as a promising candidate for device incorporation is its apparent resistance to solid-state quenching/excimer formation as well as a high thermal stability. The quantum yield of TPF is not the highest of the

fluoranthene family, benzo[k]fluoranthene having a quantum yield of 100%, however; unlike TPF and fluoranthene itself, benzo[k]fluoranthene emission is completely quenched in the solid state. The relative quantum yield of TPF is reported by Chiechi *et al* as being solvent dependent with $\Phi = 0.38$ in CH_2Cl_2 and $\Phi = 0.52$ in cyclohexene. Solid state quantum yield measurements of TPF in PMMA (poly(methyl)methyl acrylate) were recorded and reached $\Phi = 0.86$. This high value has been attributed to the effect of the rigid PMMA matrix which further hinders the rotation of the pendant phenyl rings and distortions of the planar fluoranthene core.⁴³

2.1.2.1 Absorption and emission spectra of TPF

The absorption spectrum and normalised emission spectra of TPF reported by Chiechi *et al*⁴³ are shown in Figure 2.1-2.

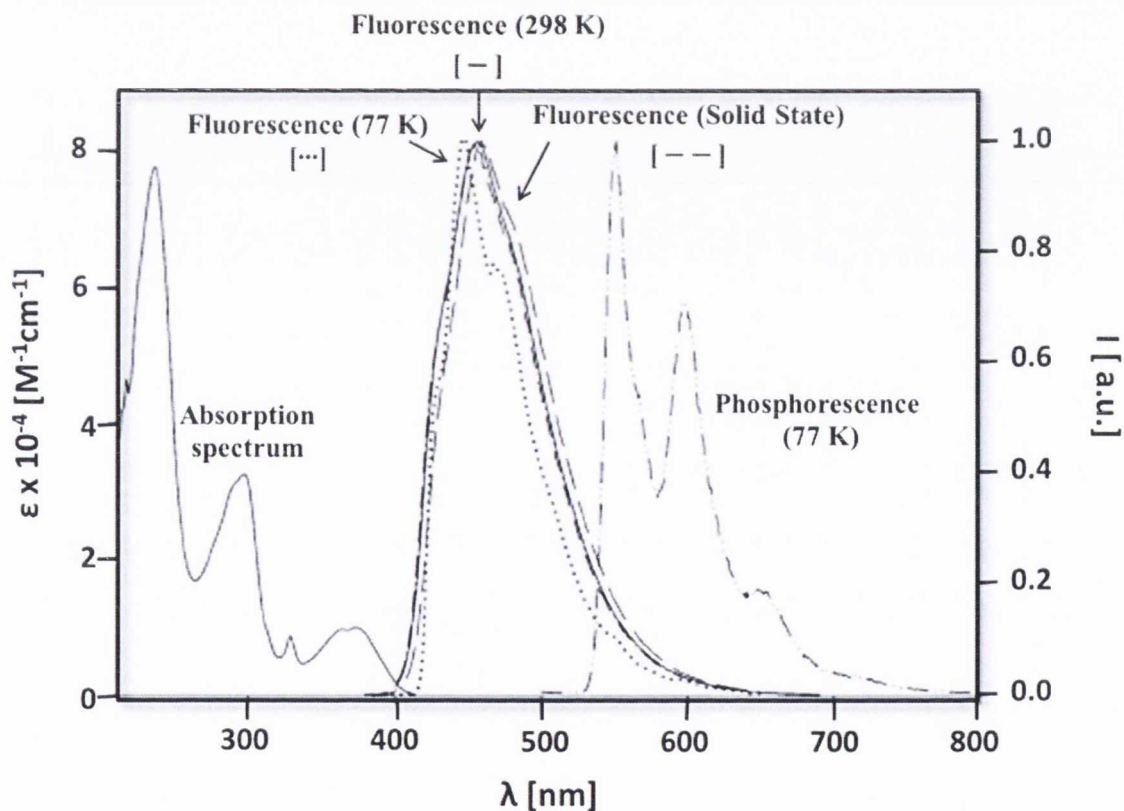


Figure 2.1-2: Absorption/normalised emission spectrum of TPF from Chiechi *et al*.⁴³

The absorption spectrum resembles the absorption spectrum of fluoranthene with a strong band at 350 – 400 nm. The bands at 240 and 290 nm have become more intense than those in fluoranthene due to the three phenyl substituents. These phenyl rings enjoy free rotation about the planar fluoranthene core and as a result the absorption

spectrum has lost some of the structure observed for fluoranthene. The emission spectrum of TPF in CH_2Cl_2 at 77 K exhibits three peaks each at different wavelengths: λ_{423} , 448_{max} and 478 nm. On moving to solution measurements at 298 K, the λ_{max} is red shifted to 458 nm. There is a further red shift to 468 nm in the solid state.

2.1.3 Photophysical properties of fluoranthene-fused imide derivatives

Ding *et al* have reported the synthesis and photophysical characterisation of a family of fluoranthene-fused imide compounds.³⁷ The photophysical properties were investigated in dilute CH_2Cl_2 solutions or in thin films. The structures of the compounds, labelled 9 – 16, are shown in Figure 2.1-3 with the emission spectra of the compounds inset.

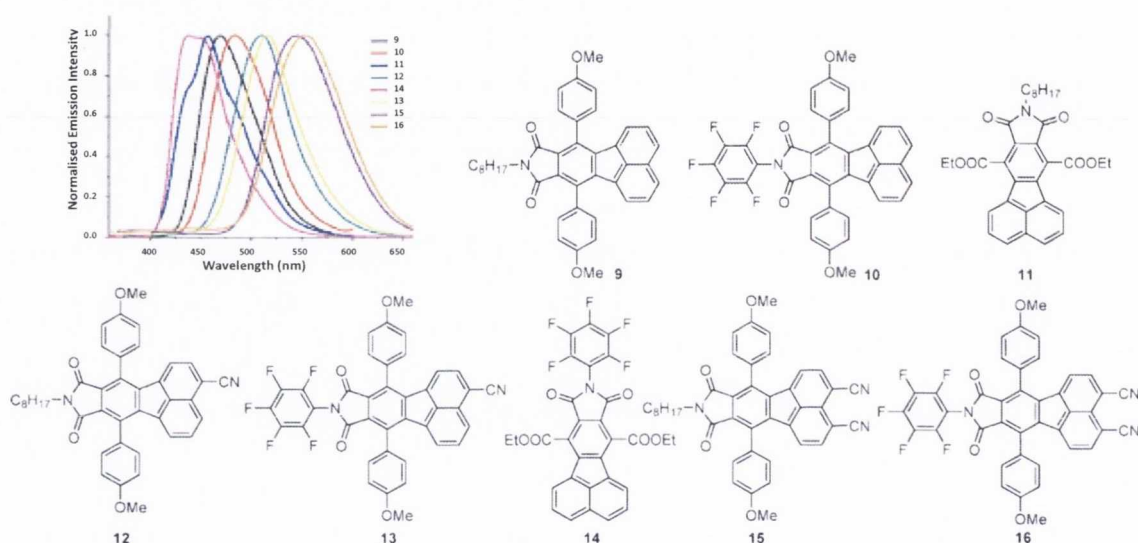


Figure 2.1-3: The molecular structures of the eight fluoranthene-fused imide derivatives and the emission spectra of each in CH_2Cl_2 (inset).

The emission profiles of these compounds are similar to TPF though the λ_{max} of the emission is red shifted compared to that of TPF in solution at room temperature. The λ_{max} emission of 9 is 469 nm and on altering the substituents of both the fluoranthene core and the imide moiety the emission maximum becomes more and more red shifted with 16 having a λ_{max} of 553 nm. The emission has been successfully tuned by varying the peripheral substituents.

The absorption spectra of these imide functionalised fluoranthenes are also red shifted relative to TPF, with the λ_{max} values for each of the compounds 9 – 16 falling within the 393 – 413 nm range. The incorporation of the ethoxycarbonyl group in 11 causes a blue shift compared to 9 whereas those of 12 and 15 exhibit a red shift which is in agreement

with the increase of the electron-withdrawing ability which affects an increase of the conjugation length. The position of the pentafluorophenyl group of 10 causes only a 10 nm red-shift compared to 9 due to the positioning; as it is located at the node of the molecule it has little effect on the photophysical properties. Compared to the solution state, the absorption wavelengths of all of the compounds in thin films are slightly red shifted due to the aggregation of the compounds in the solid state.

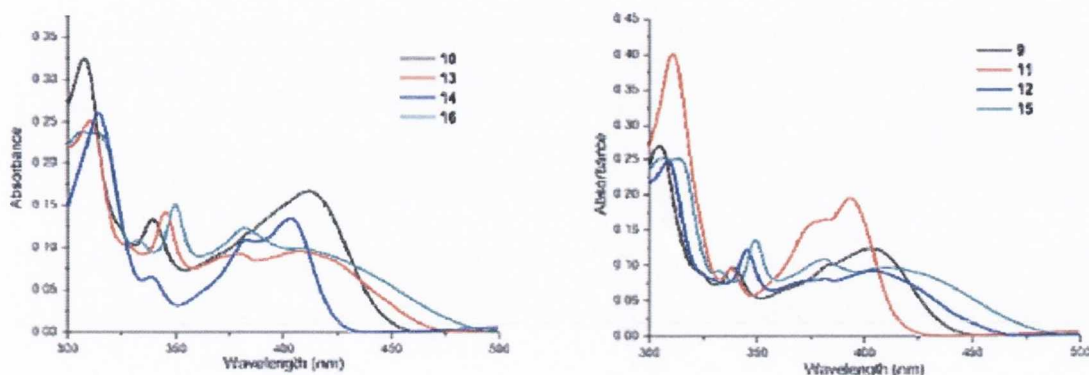


Figure 2.1-4: Absorption spectra of the fluoranthene-fused imide compounds in CH_2Cl_2 solutions and thin films reported by Ding et al.³⁷

2.1.4 Electrochemical properties of Fluoranthene, TPF and fluoranthene-fused imide compounds

Unsubstituted fluoranthene forms stable radical anions that have a sufficiently long lifetime to form dimers. This dimerisation is prevented in the other fluoranthene based compounds by the substituents in the 7, 8 and 10 positions; three phenyl substituents in the case of TPF. TPF exhibits a stable reversible reduction but the same stability is not observed for the oxidation. Despite the introduction of the three phenyl substituents there is no significant change in the redox potentials (or HOMO/LUMO gap) from that of fluoranthene. The anodic peak potential of fluoranthene is $E_p^a = 1.617$ V and the cathodic half potential $E_{1/2}^c = -1.81$ V compared to $E_p^a = 1.61$ V and $E_{1/2}^c = -1.72$ V for TPF.⁴³

The fluoranthene-fused imide compounds each exhibit two reduction bands in their cyclic voltammograms, the first of which is attributed to the monoanion and the second band to the dianion formation. The reduction band shifted gradually on introducing electron-withdrawing substituents.³⁷ It was found that the LUMO energy levels of the fluoranthene core are affected by the introduction of electron withdrawing groups and as such are tuned to become potential candidates for air-stable *n*-type semiconductors.

2.2 Photophysics of azafluoranthene compounds **6** - **10** and **13**

The photophysical properties of the ligands **6** - **10** and **13** were investigated and are discussed in detail below.

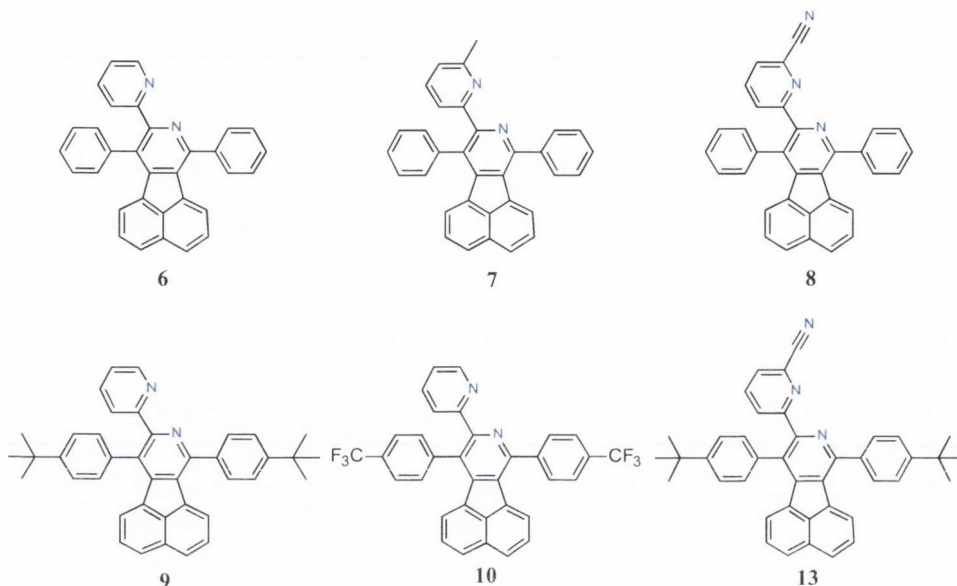


Figure 2.2-1: Structure of the azafluoranthene ligands **6** - **10** and **13** discussed in this chapter.

2.3 UV – Visible Absorption Spectra

The normalised absorption spectra of each of the ligands 7,10-diphenyl-9-(2-pyridyl)-8-azafluoranthene (**6**), 7,10-diphenyl-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**7**), 7,10-diphenyl-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**8**), 7,10-di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (**9**), 7,10-di[(4-trifluoromethyl)phenyl]-9-(2-pyridyl)-8-azafluoranthene (**10**) and 7,10-di(4-*tert*-butylphenyl)-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**13**) is shown in Figure 2.3-1 with relevant data summarised in Table 2.3-1.

As **6** is the only unsubstituted ligand it is taken as the archetypal compound to which each of the other ligands are compared. The absorption spectrum of **6** is similar to that of triphenylfluoranthene (TPF) with a broad band at 350 – 400 nm attributed to the fluoranthene moiety, as well as the other strong bands at ~240 nm and ~295 nm. The intense bands at ~240 for each of the ligands have been assigned as π - π^* in origin involving the pyridyl and phenyl rings of the compounds, with extinction coefficients indicative of the spin allowed nature of the transition (ϵ in the range 29,000 – 130,000 $\text{M}^{-1} \text{cm}^{-1}$).⁹⁷ The weaker band at ~325 nm is also present in both the spectra of TPF and

6. The incorporation of the nitrogen atom into the fluoranthene core, and the replacement of the phenyl ring with a pyridine ring, has an effect on the absorption spectra of **6** compared to TPF. A new band appears at ~ 270 nm that is not present in the spectrum of TPF and as such can be attributed to the $n\text{-}\pi^*$ transitions of the lone-pair electrons of the nitrogen atoms with contributions from the $\pi\text{-}\pi^*$ transitions.

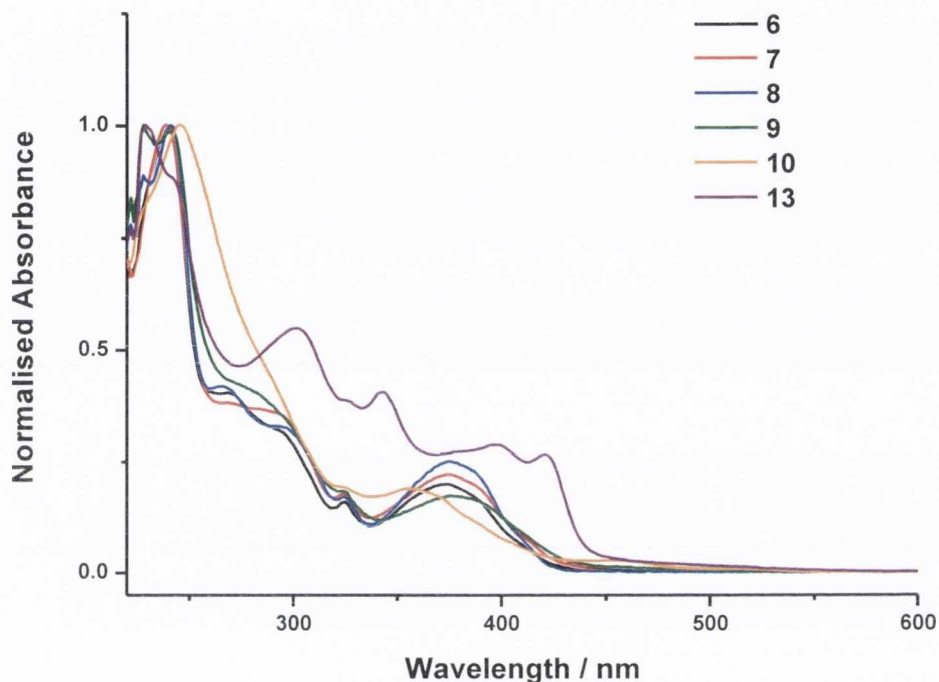


Figure 2.3-1: UV-visible absorption spectra of ligands **6**, **7**, **8**, **9**, **10** and **13** in dichloromethane. ($1 \times 10^{-3} M$)

The incorporation of a methyl group onto the pyridine ring of **7** has little effect on the absorption spectrum as it is almost identical to that of **6** with only a small difference in the 270 – 295 nm region. The same is true of **8**; the cyano group of the pyridine ring has almost no effect on the absorption spectrum. The incorporation of electron donating tertiary butyl groups in the pendant phenyl rings of **9** does have an effect on the absorption spectrum with the bands at 272 and 297 nm being replaced by one broad band at 284 nm. The addition of electron withdrawing trifluoromethyl groups in the pendant phenyl rings of **10** have a significant effect of the absorption spectrum which becomes less structured with only three distinct bands. The lowest energy bands of **9** and **10** are shifted compared to that of **6** (373 nm), with that of **9** undergoing a bathochromic shift to 380 nm and **10** a hypsochromic shift to 358 nm. The shift in **9** corresponds to an increase in electron density on its highest energy filled π -orbital, the

HOMO, resulting in the destabilisation of the orbital and an overall smaller HOMO-LUMO gap than in **6**. The opposite is true for **10** where the electron withdrawing trifluoromethyl groups stabilises, i.e. lowers, the energy of the HOMO to give a hypsochromic shift when compared to **6**. The most dramatic effect comes from the incorporation of both electron donating groups, *via* the pendant phenyl rings, and an electron withdrawing group, *via* the pyridine ring, in ligand **13**. The lowest energy absorption band of the spectrum becomes red shifted relative to that of **6**. This can again be attributed to an increase in electron density on the HOMO, resulting in the destabilisation of the orbital and an overall smaller HOMO-LUMO gap as is the case with **9**. The spectrum also becomes more structured. One explanation of this is that the rotation of the pendant phenyl rings is restricted resulting in the more structured absorption spectra. Interactions between the nitrogen atom of the cyano group of the pyridine ring in the 9 position and the hydrogen atoms of the tertiary butyl group on the phenyl ring in the 10 position are the most likely cause of this restricted rotation.

*Table 2.3-1: Room temperature UV-Visible spectral data for ligands **6** - **10** and **13** in CH_2Cl_2 ($\sim 10^{-5} \text{ M}$)*

Compound	λ_{max} [nm] (ϵ [$\text{M}^{-1} \text{ cm}^{-1}$])
6	240 (49,270), 272 (19,780), 297 (16,050), 325 (8,035), 373 (10,385)
7	239 (52,220), 292 (18,600), 325 (9,330), 374 (3,740)
8	242 (29,280), 267 (11,940), 296 (9,410), 324 (4,770), 375 (7,210)
9	242 (29,190), 284 (11,880), 323 (5,390), 380 (5,070)
10	245 (130,430), 324 (24,300), 358 (25,280), 455 (4,230)
13	229 (56,740), 245 (49,120), 302 (31,380), 327 _{sh} (22,110), 344 (23,760), 398 (17,150), 422 (15,500)

2.3.1 Effect of acid on the absorption spectra of **6** - **10** and **13**

Acid titrations were performed on each of the ligands in order to determine which bands contain $n\text{-}\pi^*$ character as according to Kasha's criteria these bands would be most affected on protonation.⁹⁸

In each of the six spectra there are absorption bands centred $\sim 240 \text{ nm}$. This band is also present in the absorption spectrum of TPF and therefore should be assigned as $\pi\text{-}\pi^*$ in

character. However, these bands decrease on addition of acid in each of the six acid titration spectra which has resulted in these bands being assigned as having some $n\text{-}\pi^*$ character.

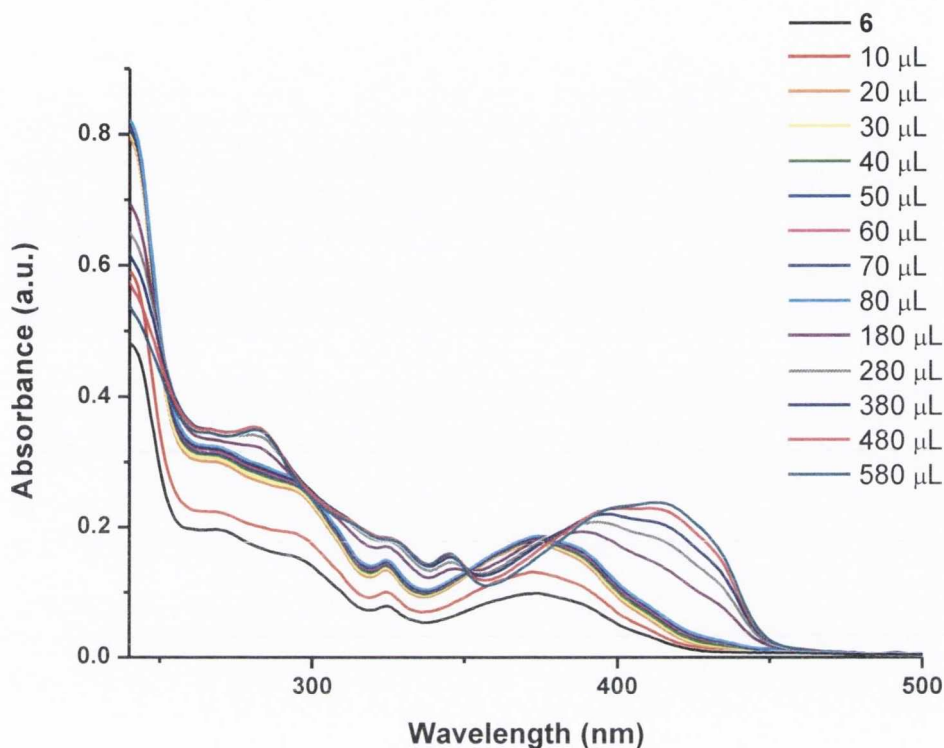


Figure 2.3-2: UV-Visible absorption spectrum of **6** in CH_2Cl_2 on treatment with 0.1 M CF_3COOH .

The absorption spectrum of **6** is shown in Figure 2.3-2. 10 μL aliquots of 0.1 M CF_3COOH were added to a 10^{-5} M solution of **6** in CH_2Cl_2 . On addition of the first 10 μL of acid there is a noticeable increase in absorbance but no bathochromic or hypsochromic shifts of any of the bands. Subsequent 10 μL aliquot additions up to a total of 80 μL of the acid still had little effect on the absorption spectrum, with still none of the bands becoming shifted but with an increase in absorbance. On addition of 100 μL aliquots of acid however, there is a significant change in the absorption spectrum; a new band appears at 282 nm whereas the band at 297 nm disappears. As a result of this the band at 297 nm can be described as having $n\text{-}\pi^*$ character. The small band at 325 nm also begins to disappear and is replaced by a band at 344 nm. The strong band at 340 – 400 nm undergoes a bathochromic shift on protonation, with the

λ_{max} shifting from 373 nm to 413 nm, confirming its π - π^* nature as once protonated the orbitals become lower in energy. The presence of an isosbestic point at 351 nm confirms the presence of two species in solution; the ligand **6** and its protonated form.

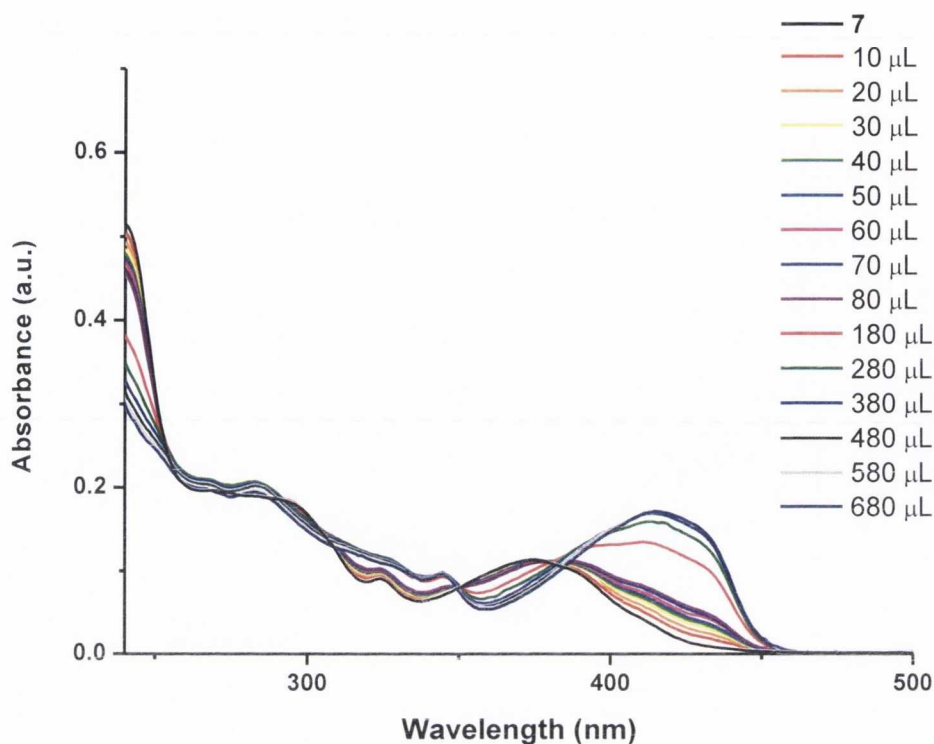


Figure 2.3-3: UV-Visible absorption spectrum of **7** in CH_2Cl_2 on treatment with 0.1 M CF_3COOH .

The absorption spectrum of **7** is shown in Figure 2.3-3. 10 μL aliquots of 0.1 M CF_3COOH were added to a 10^{-5} M solution of **7** in CH_2Cl_2 . Again, subsequent 10 μL aliquot additions up to a total of 80 μL of the acid had only a small effect on the absorption spectrum, with the bands at 325 and 374 nm becoming slightly red shifted coupled with a negligible increase in absorbance. On addition of 100 μL aliquots of acid however, there is a more noticeable change in the absorption spectrum; new bands appears at 268 and 284 nm, replacing a broad absorption band at 292 nm. As a result of this the band at 292 nm can be described as having n - π^* character. As with **6**, the small band at 325 nm also begins to disappear and is replaced by a band at 346 nm. The strong band at 350 – 410 nm undergoes a red shift on protonation, with the λ_{max} shifting from 374 nm to 416 nm with a shoulder at 435 nm. The presence of isosbestic points at

349 and 385 nm confirms the presence of two species in solution; the ligand **7** and its protonated form.

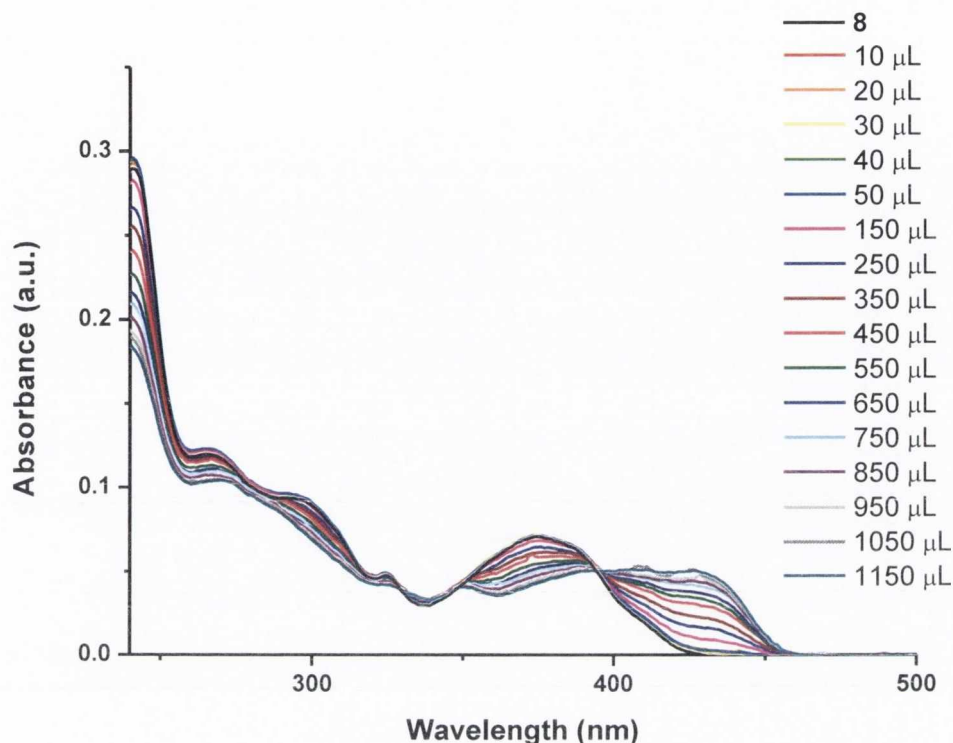


Figure 2.3-4: UV-Visible absorption spectrum of **8** in CH_2Cl_2 on treatment with 0.1 M CF_3COOH .

The absorption spectrum of **8** is shown in Figure 2.3-4. 10 μL aliquots of 0.1 M CF_3COOH were added to a 10^{-5} M solution of **8** in CH_2Cl_2 . The addition of 50 μL of acid had no effect on the absorption spectrum. The difficulty in protonating **8** compared to the previous two compounds is most likely the presence of the electron withdrawing cyano group. On addition of 100 μL aliquots of acid however, there is a more noticeable change in the absorption spectrum; the band at 296 nm disappears resulting in this band being describe as having $n\text{-}\pi^*$ character. As with **6** and **7**, the small band at 324 nm also begins to disappear and is replaced by a band at 350 nm. The strong band at 350 – 410 nm undergoes a red shift on protonation, with the λ_{max} shifting from 375 nm to 431 nm and can also be assigned as having $\pi\text{-}\pi^*$ character. The presence of a

very obvious isosbestic point at 394 nm confirms the presence of two species in solution; the ligand **9** and its protonated form.

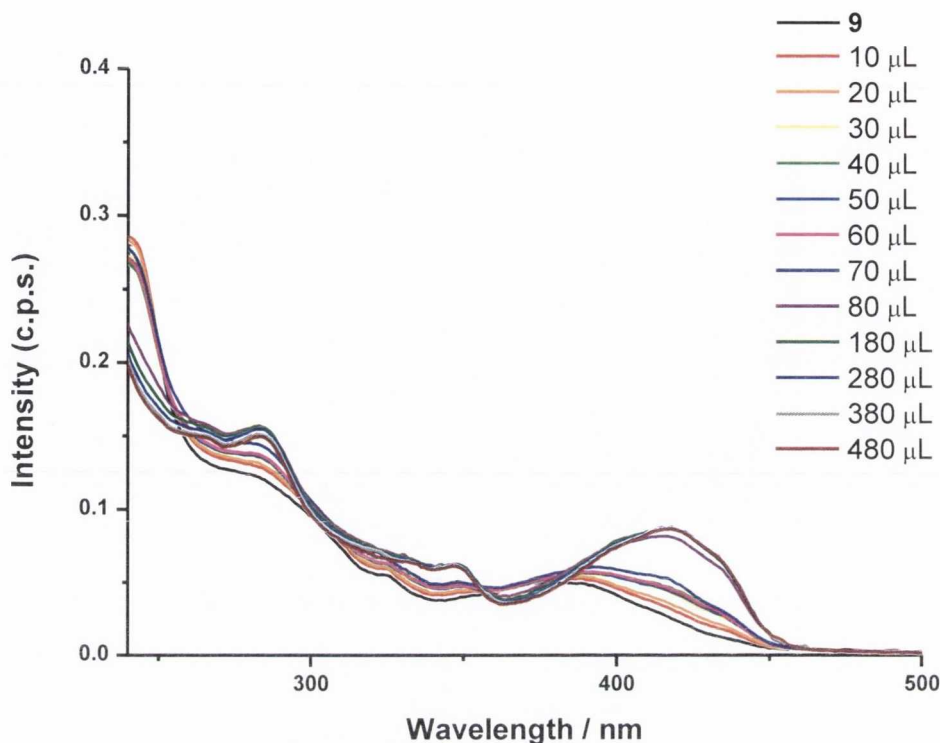


Figure 2.3-5: UV-Visible absorption spectrum of **9** in CH_2Cl_2 on treatment with $0.1 \text{ M CF}_3\text{COOH}$.

The absorption spectrum of **9** is shown in Figure 2.3-5. 10 μL aliquots of $0.1 \text{ M CF}_3\text{COOH}$ were added to a 10^{-5} M solution of **9** in CH_2Cl_2 .

The addition of 80 μL of acid had very little effect on the absorption spectrum with only a slight red shift observed for the strong band at 350 – 420 nm. On addition of 100 μL aliquots of acid however, there is a more significant change in the absorption spectrum; the broad band at 284 nm is replaced by two sharper bands at 265 and 285 nm. As with all previous compounds, the small band at 324 nm also begins to disappear and is replaced by a band at 349 nm. The strong band at 350 – 410 nm undergoes a red shift on protonation, with the λ_{max} shifting from 380 nm to 418 nm and can also be assigned as having $\pi\text{-}\pi^*$ character. The presence of isosbestic points at 356 and 383 nm confirms the presence of two species in solution; the ligand **9** and its protonated form.

Unlike **6**, there is no sudden increase in absorption on adding acid. This may be due to the stabilising effects of the electron donating tertiary butyl groups of the pendant phenyl rings of **9** compared to the unsubstituted phenyl rings of **6**.

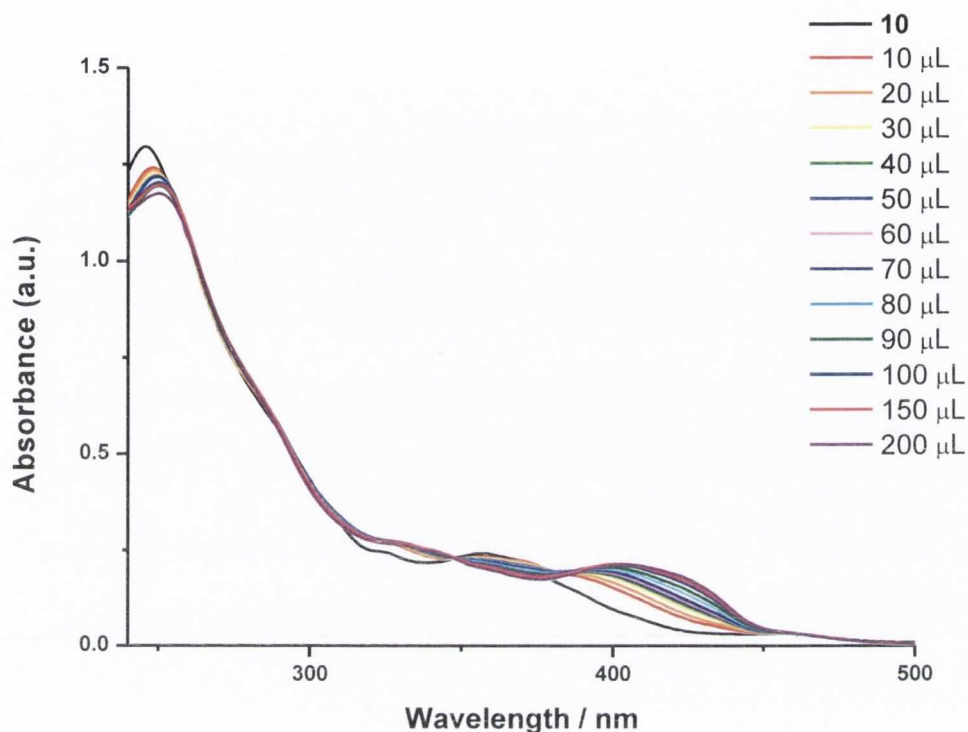


Figure 2.3-6: : UV-Visible absorption spectrum of **10** in CH_2Cl_2 on treatment with 0.1 M CF_3COOH .

The absorption spectrum of **10** is shown in Figure 2.3-6. 10 μL aliquots of 0.1 M CF_3COOH were added to a 10^{-5} M solution of **10** in CH_2Cl_2 . The addition of 90 μL of acid had an appreciable effect on the absorption spectrum. The strong band at 350 – 410 nm undergoes a red shift on protonation, with the λ_{max} shifting from 358 nm to 402 nm and can be assigned as having $\pi\text{-}\pi^*$ character. The band at 324 nm is also red shifted. On addition of 100 μL aliquots of acid however, there is no significant change in the absorption spectrum. The presence of isosbestic points at 347 and 386 nm confirms the presence of two species in solution; the ligand **10** and its protonated form. As with **9**, there is no sudden increase in absorption on adding acid as is seen for **6**. However, unlike **9**, the shifts in the spectra are very gradual on acid addition and increasing the amount of acid added has no great effect; addition of 100 μL aliquots of acid to **9** had a significant effect on the spectrum. Again, this may be due to the effects

of the electron withdrawing trifluoromethyl groups of the pendant phenyl rings of **10** compared to the electron donation tertiary butyl groups of **9** or the unsubstituted phenyl rings of **6**.

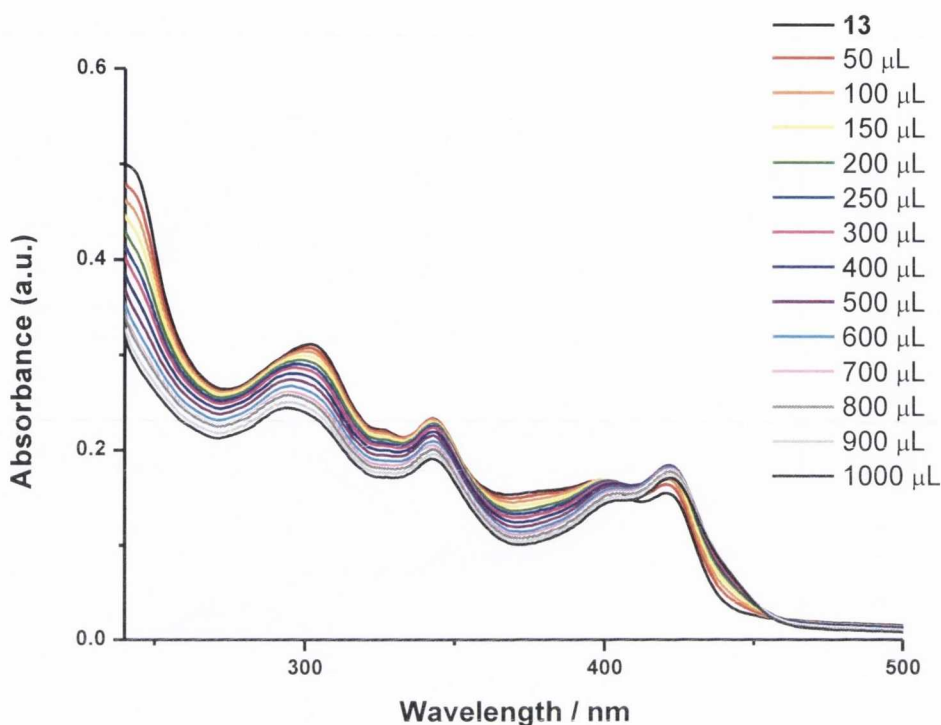


Figure 2.3-7: UV-Visible absorption spectrum of **13** in CH_2Cl_2 on treatment with 0.1 M CF_3COOH .

The absorption spectrum of **13** is shown in Figure 2.3-7. 50 μL aliquots of 0.1 M CF_3COOH were added to a 10^{-5} M solution of **13** in CH_2Cl_2 as the addition of smaller aliquots had a negligible effect. Unlike the previous compounds, the addition of acid has little or no effect on the absorption spectrum of **13**. The band at 398 nm eventually begins to lower in intensity and experience a slight bathochromic shift to 402 nm and the band at 422 nm grows in intensity on addition of acid and also experiences a slight red shift to 424 nm, however, this appears to be predominantly a dilution effect caused by the large amount of acid added. This may be due to the incorporation of both electron donating substituents, in the form of the tertiary butyl groups, as was seen for **9**, coupled with the inclusion of an electron withdrawing group, the cyano group, as was seen for **8** thus rendering **13** very difficult to protonate.

2.4 Electrochemical properties of ligands 6 - 10 and 13

Cyclic voltammetric (CV) studies were carried out on 1 mM solutions of **6**, **7**, **8**, **9**, **10** and **13** in CH_2Cl_2 (0.1 M $n\text{Bu}_4\text{NPF}_6$). Cyclic voltammograms were carried out using a Ag/AgCl reference electrode, a Pt wire counter electrode and a glassy carbon working electrode.

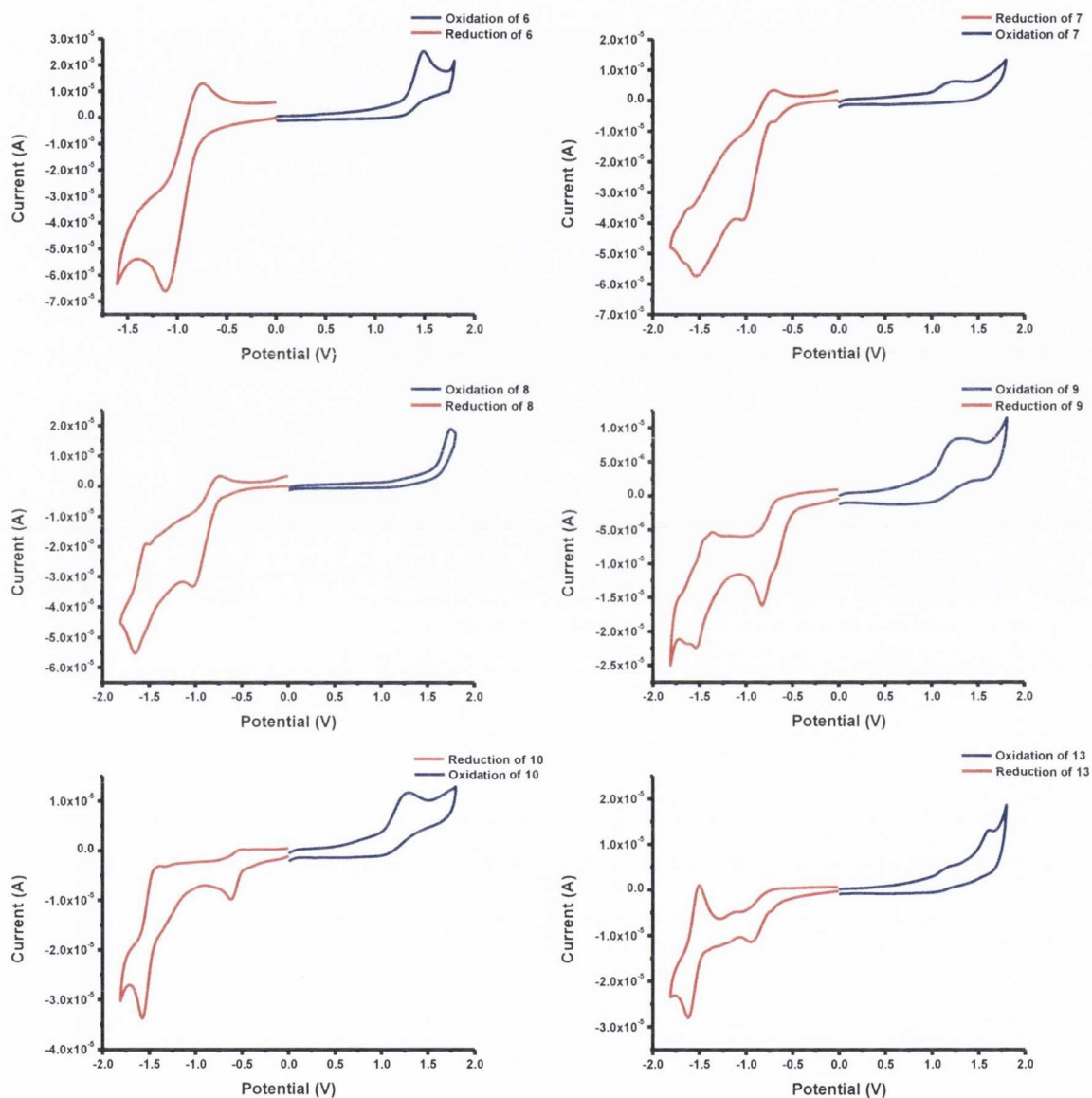


Figure 2.4-1: Cyclic Voltammograms of **6**, **7**, **8**, **9**, **10** and **13** in CH_2Cl_2 and 0.1 M TBAPF_6 . Scan rate = 0.1V/s for both oxidation and reduction versus Ag/AgCl.

The oxidation wave for each ligand exhibits one irreversible oxidation process between +1.19 and +1.74 V. The oxidation of the unsubstituted ligand **6** occurs at +1.49 V, a value less positive than that of its all carbon analogue TPF ($E_{\text{pa}} = +1.61$ V). The less

positive value for the nitrogen containing **6** suggests that the incorporation of the nitrogen atoms makes it easier to remove an electron from the HOMO of the molecule. As expected, the oxidation of the methyl-substituted **7** (+1.19 V) and tertiary butyl substituted **9** (+1.26) are much less positive than that of **6** due to the inclusion of the electron-releasing methyl or tertiary butyl substituents. The incorporation of the strongly electron-withdrawing cyano group of **8** also has a significant effect on the oxidation potential resulting in the most positive potential of all six ligands, +1.74 V. The electron-withdrawing trifluoromethyl substituents of **10**, however, have a much less significant effect on the oxidation potential with a value of +1.28 V, suggesting that the location of the substituents may be an important factor. The oxidation potential of **13** is the second highest at +1.62 V. Similar to **8**, **13** contains a strongly electron-withdrawing cyano group. Unlike **8** however, **13** also has electron-donating tertiary butyl groups which result in the lower oxidation potential than that of **8**.

The majority of the reduction waves for each ligand exhibit at least one quasi reversible reduction between -0.58 and -1.55 V. As the only unsubstituted compound, **6** is one of the more easily reduced of the six ligands, with a reduction potential of -0.59 V. The methyl substituted **7** has two quasi reversible reduction processes, the first occurring at -0.86 V and the second at a much more negative value of -1.34 V, as is an observable trend among the compounds. The cyano substituted **8** again has two quasi reversible reduction processes, the first occurring at -0.89 V and the second at a more negative value of -1.09 V. The second reduction process occurs at a less negative potential than that of **7**, possibly due to the electron withdrawing cyano group thus making the compound more easily reduced. The reduction wave of **10** also displays two quasi reversible reductions, the first at -0.58 V, a value very close to that of the unsubstituted **6**. Unlike **6** however, there is a second reduction process at -0.99 V, suggesting that the electron withdrawing trifluoromethyl groups of the pendant phenyl rings help to facilitate a second reduction. Only **9** and **13**, the compounds that contain peripheral phenyl rings substituted with electron donating tertiary butyl groups, experience irreversible reductions at $E_p = -0.82$ and $E_p = -0.92$ respectively. Both compounds also exhibit a second, quasi reversible reduction process at -0.94 V for **9** and a much more negative value of -1.55 V for **13**. This may be explained by the presence of the electron withdrawing cyano group present in **13** which may result in the larger reduction

potential due to the increased electron density centred on that fragment of the compound.

Table 2.4-1: Electrochemical data for ligands 6 - 10 and 13.

Compound	Oxidation E_{pa}/V	Reduction E_p/V	Reduction $E_{1/2}/V$ [$\Delta E_p/mV$]
6	+1.49	-	-0.59 [351]
7	+1.19	-	-0.86 [330], -1.34 [400]
8	+1.74	-	-0.89 [277], -1.09 [112]
9	+1.26	-0.82	-0.94 [166]
10	+1.28	-	-0.58 [61], -0.99 [156]
13	+1.62	-0.92	-1.55 [114]

2.5 Emission properties of ligands 6 - 10 and 13

The photoluminescence properties of each of the ligands 7,10-diphenyl-9-(2-pyridyl)-8-azafluoranthene (**6**), 7,10-diphenyl-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**7**), 7,10-diphenyl-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**8**), 7,10-di(4-tert-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (**9**), 7,10-di[(4-trifluoromethyl)phenyl]-9-(2-pyridyl)-8-azafluoranthene (**10**) and 7,10-di(4-tert-butylphenyl)-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**13**) are discussed. The results are summarised in Table 2.5-1.

Table 2.5-1: Emission data for ligands **6** - **10** and **13** in solid state and in solution (CH_2Cl_2) at 298K and 77K.

	Medium (T[K])	$\lambda_{\text{em}}[\text{nm}]$ ($\lambda_{\text{exc}}[\text{nm}]$)	τ [ns] ($\lambda_{\text{exc}}[\text{nm}]$ $\lambda_{\text{em}}[\text{nm}]$) ^a
6	Solid (298)	456, 492 _{max} , 533 _{sh} (360)	0.35 μs (28%), 1.9 μs (72%) (370/456)
			2.3 μs (17%), 19.4 μs (83%) (370/492)
			0.48 μs (27%), 2.7 μs (73%) (370/533)
	$\sim 10^{-3}\text{M}$ CH_2Cl_2 (298)	458 _w , 485 _{max} (360)	2.0 (100%) (370/458)
			2.9 (63%), 24.6 (37%) (370/485)
	CH_2Cl_2 (77)	506 _w , 528 _{max} , 580 _{sh} (360)	0.34 μs (24%), 1.8 μs (76%) (370/506)
$\sim 10^{-5}\text{M}$	CH_2Cl_2 (298)	432 _w , 456 _{max} , 486 _{sh} (360)	20.5 μs (82%), 2.1 μs (18%) (370/528)
			7.9 (20%), 1.6 (80%) (370/433)
			2.6 (60%), 9.0 (40%) (370/455)
	CH_2Cl_2 (77)	430, 488 _{max} , 520 _{sh} (360)	11.2 (51%), 3.4 (49%) (370/480)
			10.4 μs (76%), 1.1 μs (24%) (370/488)
			23.7 μs (81%), 2.3 μs (19%) (370/520)
7	Solid (298)	526 _{max} , 550 _{sh} (360)	2.0 μs (16%), 16.9 μs (84%) (370/530)
			2.5 μs (15%), 19.4 μs (85%) (370/550)
	$\sim 10^{-3}\text{M}$ CH_2Cl_2 (298)	461, 485 _{max} , 516 _{sh} (360) 565 _{max} , 630, 660 _{sh} (505)	10.2 (28%), 2.2 (72%) (370/461)
			19.9 (28%), 2.8 (72%) (370/485)

	CH ₂ Cl ₂ (77)	506 _{max} , 575 _{sh} (360)	14.0 μs (89%), 1.4 μs (11%) (370/506) 1.8 μs (15%), 15.9 μs (85%) (370/520) 544, 572 _{max} , 616 _{sh} (515)
~10 ⁻⁵ M	CH ₂ Cl ₂ (298)	458 _{max} , 478 _{sh} (345)	2.4 (61%), 12.4 (39%) (370/458) 3.0 (36%), 12.6 (64%) (370/478)
	CH ₂ Cl ₂ (77)	433, 453 _{max} , 481 _{sh} (360)	6.6 (67%), 68.6 (33%) (370/433) 14.7 μs (89%), 1.2 μs (11%) (370/453)
8	Solid (298)	461, 488 _{max} , 518 _{sh} (315)	3.0 μs (16%), 21.4 μs (84%) (370/488)
~10 ⁻³ M	CH ₂ Cl ₂ (298)	459 _{max} , 483 _{sh} (360)	17.5 (10%), 2.8 (90%) (370/459) 2.8 (79%), 8.0 (21%) (370/483)
	CH ₂ Cl ₂ (77)	458 _{sh} , 481 _{max} , (320)	13.4 μs (89%), 1.1 μs (11%) (370/481)
~10 ⁻⁵ M	CH ₂ Cl ₂ (298)	431 _{sh} , 454 _{max} , 485 _{sh} (325)	11.4 (11%), 2.4 (89%) (370/431) 13.3 (13%), 2.5 (87%) (370/454)
	CH ₂ Cl ₂ (77)	425 _{sh} , 450 _{max} , 487 _{sh} (315)	12.6 μs (92%), 1.0 μs (8%) (370/450)
9	Solid (298)	493, 518 _{max} , 560 _w (360)	2.4 μs (15%), 18.0 μs (85%) (370/493) 2.6 μs (14%), 19.0 μs (86%) (370/518) 2.6 μs (13%), 18.6 μs (87%) (370/560)
	CH ₂ Cl ₂	458 _{sh} , 489 _{max} , 515 _w (360)	4 (85%), 0.8 (15%) (370/458)

$\sim 10^{-3}\text{M}$	(298)		54.1 (15%), 6.0 (85%) (370/490)
	CH_2Cl_2 (77)	509, 535 _{max} , 576 _{sh} (360)	10.8 μs (100%) (370/509) 24.3 μs (79%), 3.5 μs (21%) (370/535)
$\sim 10^{-5}\text{M}$	CH_2Cl_2 (298)	459 _{max} , 477 _{sh} (360)	2.6 (56%), 8.4 (44%) (370/457) 3.3 (49%), 9.1 (51%) (370/477)
	CH_2Cl_2 (77)	428, 452, 494 _{max} , 522 _{sh} (360)	18.0 μs (84%), 2.2 μs (16%) (370/522)
10	Solid (298)	415, 439, 474 _{max} , 497 _{sh} (360)	12.4 μs (71%), 0.5 μs (29%) (370/439) 6.9 μs (83%), 0.4 μs (17%) (370/497)
$\sim 10^{-3}\text{M}$	CH_2Cl_2 (298)	435, 489 _{max} (360)	13.5 (13%), 2.8 (87%) (370/489)
	CH_2Cl_2 (77)	439, 498 _{max} , 585 _{sh} (360)	2.1 μs (85%), 2.9 (15%) (370/439) 11.8 μs (89%), 0.8 μs (11%) (370/481)
$\sim 10^{-5}\text{M}$	CH_2Cl_2 (298)	432 _w , 455 _{max} , 489 _{sh} (320)	2.6 (77%), 10.9 (23%) (370/432) 13.5 (13%), 2.8 (87%) (370/489)
	CH_2Cl_2 (77)	434, 458 _{max} , 484 (360)	11.2 μs (100%) (370/484)
13	Solid (298)	443, 481 _{max} , 513, 552 (360)	14.6 μs (88%), 1.4 (12%) (370/481) 2.9 μs (16%), 20.1 μs (84%) (370/513) 2.2 μs (16%), 17.0 μs (84%) (370/552)
	CH_2Cl_2	530, 569 _{max} , 610 _{sh} (360)	49.5 (47%), 8.1 (53%) (370/569)

$\sim 10^{-3}\text{M}$	(298)		62.7 (47%), 9.8 (53%) (370/610)
	CH_2Cl_2 (77)	496 _w , 520 _{max} , 565 _{sh} (360)	1.7 μs (11%), 16.6 (89%) (370/496) 18.6 μs (88%), 1.4 μs (12%) (370/520) 19.4 μs (84%), 2.3 μs (16%) (370/565)
$\sim 10^{-5}\text{M}$	(298)		
	CH_2Cl_2	439 _w , 461 _{max} , 487 _{sh} (360)	16.1 (61%), 6.1 (39%) (370/439) 27.7 (33%), 6.1 (67%) (370/458) 9.9 (63%), 42.2 (37%) (370/487)
	CH_2Cl_2 (77)	444, 473 _{max} , 505 _{sh} (360)	1.1 μs (69%), 0.1 (31%) (370/444) 17.8 (83%), 1.8 μs (17%) (370/473) 15.7 μs (88%), 1.2 μs (12%) (370/505)

^a Estimated uncertainty on $\tau \pm 10\%$

2.5.1 Room temperature 10^{-5} and 10^{-3} M solutions in CH_2Cl_2

The emission spectra of ligands **6**, **7**, **8** and **9** as 10^{-5} M solutions in CH_2Cl_2 at room temperature are shown in Figure 2.5-2. The excitation spectra of ligands **6** to **9** follow a similar pattern with three or four distinct bands observed for each.

The emission spectrum of **6** exhibits an emission at 432 nm followed by the λ_{max} at 456 nm. A shoulder at 486 nm is also present. The emission profile of **7** is somewhat red shifted in comparison to **6** with a λ_{max} of 458 nm and exhibits a slightly more pronounced emission band at 478 nm. The opposite is observed in the emission spectrum of **8**, there is a very slight blue shift (~ 2 nm) compared to **6**, (λ_{max} 454 nm). **9** has an emission maximum at 459 nm and a shoulder at 477 nm. The observed Stokes shifts between the lowest energy band of the excitation spectra, and the onset of fluorescence are quite large (40 nm, 34 nm, 41 nm and 44 nm for **6**, **7**, **8** and **9** respectively), suggesting a significant change in the geometry of the excited state (S_1) and the ground state (S_0). This large Stokes shift could also be attributed to charge transfer in the excited state.

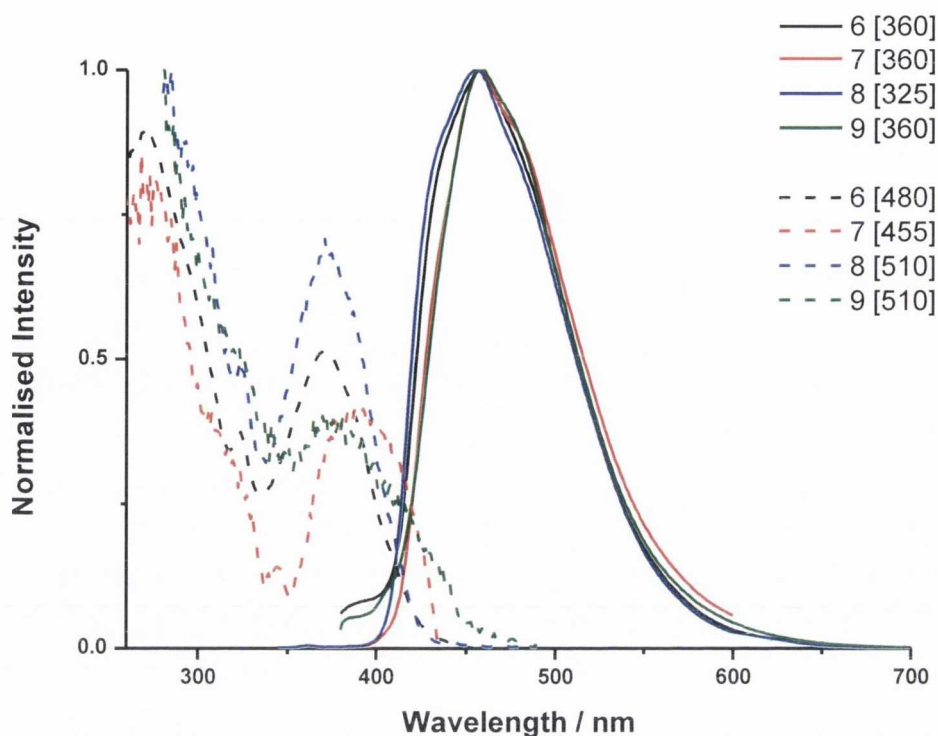


Figure 2.5-1: Normalised emission (solid line, $[\lambda_{\text{exc}}/\text{nm}]$) and excitation (dashed line, $[\lambda_{\text{em}}/\text{nm}]$) spectra of ligands **6**, **7**, **8** and **9** in CH_2Cl_2 (10^{-5} M) at 298 K.

The emission spectra of ligands **10** and **13** at 10^{-5} M solutions in CH_2Cl_2 at room temperature are shown in Figure 2.5-2. The emission spectrum of **10** exhibits a λ_{max} at 455 nm, which is a slight blue shift when compared to **6**. A weak shoulder at 432 nm is also observed, and a distinct shoulder at 480 nm. The emission profile of **13** is broad with λ_{max} at 461 nm and a weak band at 439 nm.

The effect of the electron-donating/electron withdrawing groups on the π -orbital (HOMO) of each compound can explain the slight variations in emission maxima. Due to the inclusion of the electron rich substituents in **7**, **9** and **13**, the HOMO is destabilised relative to **6** resulting in a smaller HOMO-LUMO gap and a red shifted emission. The opposite is true for that of **8** and **10**, the π -orbital is stabilised by the electron withdrawing cyano or trifluoromethyl groups and therefore lowering the energy of the π -orbital HOMO, resulting in a larger HOMO-LUMO gap and a blue shift on emission.

A mirror symmetry is observed between the excitation and emission spectra of both **10** and **13**. The observed Stokes shift between the maxima of the excitation and emission

spectra of **10** and **13** are quite large (63 nm, 3,290 cm^{-1} and 80 nm, 4160 cm^{-1} respectively). A large Stokes shift indicates that significant geometric changes occur between the ground state (S_0) and the singlet excited state (S_1).⁹⁸ This large Stokes shift is also a characteristic of unsubstituted fluoranthene.⁹⁰

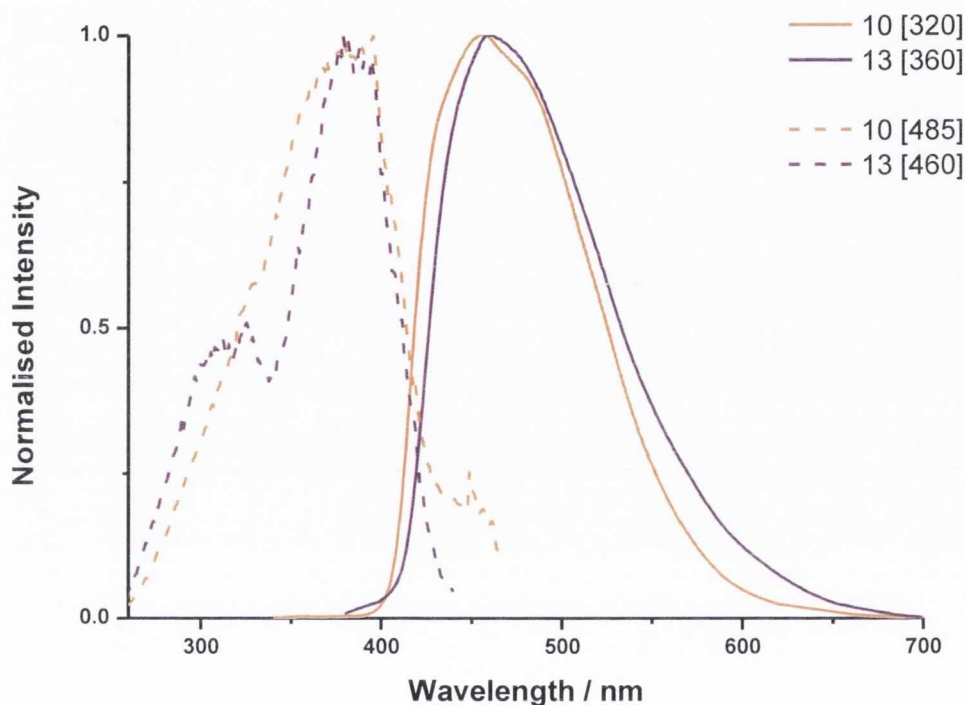


Figure 2.5-2: Normalised emission (solid line, $[\lambda_{exc}/nm]$) and excitation (dashed line, $[\lambda_{em}/nm]$) spectra of ligands **10** and **13** in CH_2Cl_2 (10^{-5} M) at 298 K.

On increasing the concentration of the solutions to 10^{-3} M there is a significant change in the emission spectra of each of the ligands as seen in Figure 2.5-3. This variation in emission maxima can be explained by possible stacking interactions or aggregation effects due to the increased concentration.^{99,100} A general red shift is observed for the emission maxima of each of the ligands, which suggests some aggregation, but to varying degrees. The λ_{max} of **6** has red shifted by 29 nm, possibly as a result of increased π - π stacking interaction of the planar fluoranthene core or aggregation both of which could be caused by the increase in concentration. **7**, **9** and **10** follow the same

pattern with red shifts of 27, 30 and 34 nm respectively. This slightly longer red shift may be explained by the additions of the methyl group (**7**), the tertiary butyl groups (**9**) and the trifluoromethyl groups (**10**) which, despite their ability to hinder uniform stacking interactions in large polycyclic hydrocarbons¹⁰, don't seem to have the same affect in the smaller fluoranthene based compounds described here. This may be due to an increase in the size of the compounds, increase in conjugation or that the conformation of the stacking is consistent with the conformational preferences of opposing tertiary butyl groups, as is seen by Fronczek *et al* for ferrocene complexes bearing tertiary butyl groups.¹⁰¹ **7** also exhibits a lower energy broad emission shoulder at ~560 nm that is not present at the lower concentration. Again, this may be explained by aggregation in solution due to the increased concentration. The most significant shift is observed for **13** which is red shifted by 108 nm. This suggests that at the higher concentration there are strong interactions between the molecules in solution. These interactions could arise in a number of ways; π - π stacking interactions between the fluoranthene moieties of the molecules despite the presence of tertiary butyl groups, hydrogen bonding between the hydrogen atoms and the nitrogen of the cyano group on adjacent molecules, or a combination of all of the above. Interestingly, only **8** seems to be unaffected by the change in concentration, with a red shift of only 5 nm. As **8** and **13** only differ by the incorporation of tertiary butyl substituents, it is obvious that these tertiary butyl groups play an important role in the emission properties of the compounds at this concentration, whether through increased stacking interactions between molecules or through hydrogen bonding interactions.

The emission spectrum of **7** at this concentration is not independent of excitation wavelength. On excitation at lower energy (505 nm), a lower energy emission profile is observed with a λ_{max} of 565 nm. This is not observed for any of the other ligands and as such may be attributed to the inclusion of the methyl group on **7**, and is, most likely, not a fluoranthene based emission.

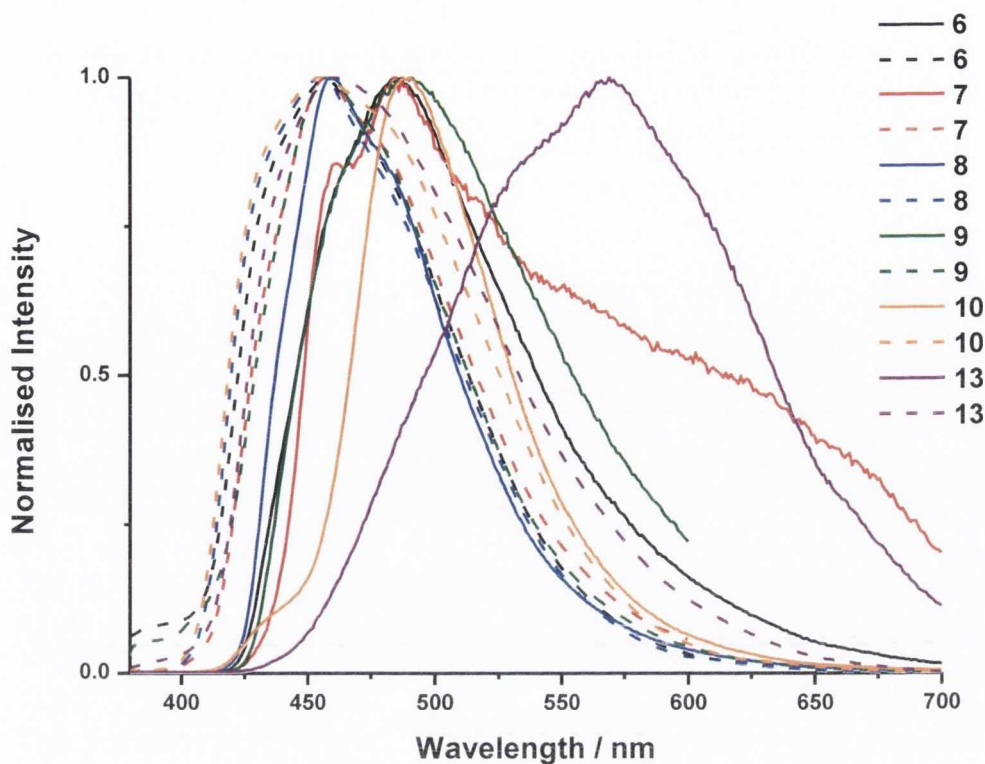


Figure 2.5-3: Normalised emission spectra of **6**, **7**, **8**, **9**, **10** and **13** at 10^{-5} M (dashed line, λ_{exc} as for Figure 1.5-1) and 10^{-3} M (solid line, λ_{exc} 360) concentration in CH_2Cl_2 at room temperature (λ_{exc} 360).

The measured excited state lifetimes for these compounds at room temperature, at both concentrations, are in the nanosecond region and are summarised in Table 2.5-1. For all but one measurement the excited state lifetimes are fit to biexponential decays. In all but one case the monoexponential decays yielded a poor fit ($\chi^2 < 0.8$; Durbin Watson parameter > 2.2).

2.5.2 Low temperature 10^{-5} and 10^{-3} M solutions in CH_2Cl_2

The emission spectra of ligands **6** - **10** and **13** at 10^{-5} M concentration at 77 K are shown in Figure 2.5-4. In general, a red shift is observed for the emission maxima of each of the ligands **6**, **9**, **10** and **13**, whereas a small blue shift is observed for **7** and **8**. The blue shift observed for **7** and **8** may be attributed to the rigidochromic effect, an effect whereby the frozen (or solid) matrix restricts any distortions of the excited state of the molecule to relieve strain, resulting in the emission appearing at higher energy.¹⁰² The red shifts of the remaining ligands can be explained by aggregation effects as red shifts in the emission spectra of many π -conjugated systems have frequently been

observed upon increasing the concentration and in the solid state, such as on thin-film formation.^{99,100} Also, possible contributions from coplanarisation and twisting of the aryl groups, as has been suggested by Bunz *et al* for simpler polymeric systems, may be a factor.¹⁰³

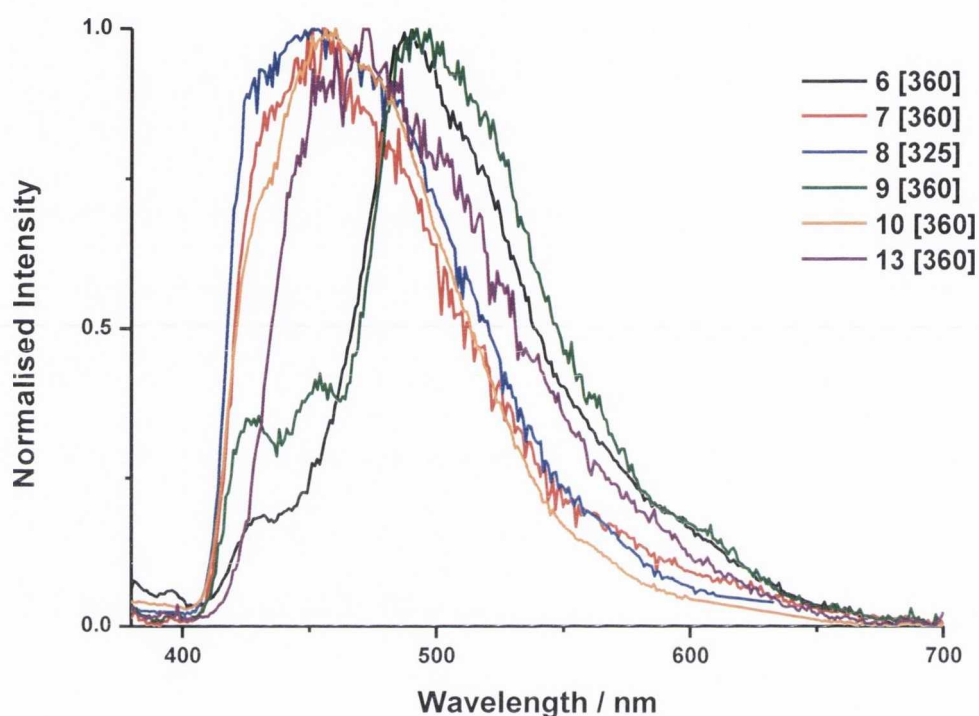


Figure 2.5-4: Normalised emission spectra of **6**, **7**, **8**, **9**, **10** and **13** at 10^{-5} M concentration in CH_2Cl_2 at 77K. (λ_{exc} 360 nm.)

The emission maximum of **6** exhibits an emission maximum at λ 488 nm with a red shift of 32 nm compared to that of the room temperature spectrum, and a weak higher energy emission band at 430 nm that is not present in the room temperature spectrum. Similar weak higher energy emission bands are observed for the low temperature spectrum of **9** at 428 and 452 nm respectively, followed by λ_{max} at 494 nm. The low temperature spectrum of **10** only experiences a small red shift of 3 nm (λ_{max} at 458 nm) and does not exhibit any weak higher energy bands but a distinct shoulder is present at 434 nm. **13** also does not exhibit any weak higher energy bands, only a broad emission centred at λ_{max} 473 nm, a value red shifted by 12 nm compared to the room temperature

spectrum. **7** and **8** both experience slight blue shifts compared to their room temperature emission spectra. The emission spectrum of **7** is broad with a λ_{max} at 453 nm, a blue shift of 5 nm. **8** has a similar emission profile, with a λ_{max} at 450 nm, a blue shift of 4 nm. The low temperature lifetimes of the ligands are dramatically increased compared to the room temperature measurements (Table 2.5-1). In contrast to room temperature measurements, which were in the nanosecond region, excited state lifetimes of microsecond duration were recorded at low temperature. A similar phenomenon has been observed for other π -conjugated systems on going to low temperatures, though not to such an extent.¹⁰⁴ As the radiative lifetimes of hydrocarbons can vary greatly, with ~ 1 nanosecond values, for compounds with allowed $S_0 - S_1$ transitions, up to many microseconds for compounds that have a forbidden $S_0 - S_1$ transition¹⁰⁵ in their absorption spectra, one explanation could be that in room temperature solution, the compounds have an allowed $S_0 - S_1$ transition but on going to low temperatures this transition may become forbidden due to restrictions of rotations or distortions in the frozen matrix. The short room temperature excited state lifetime measurements can be assigned to $^1\pi-\pi^*$ states whereas the longer lifetimes exhibited at low temperatures are more likely to be a mixture of possible $^3\pi-\pi^*$ and $^3n-\pi^*$ states with possible interligand charge transfer. The large Stokes shifts of the ligands is also an indicator of charge transfer processes.

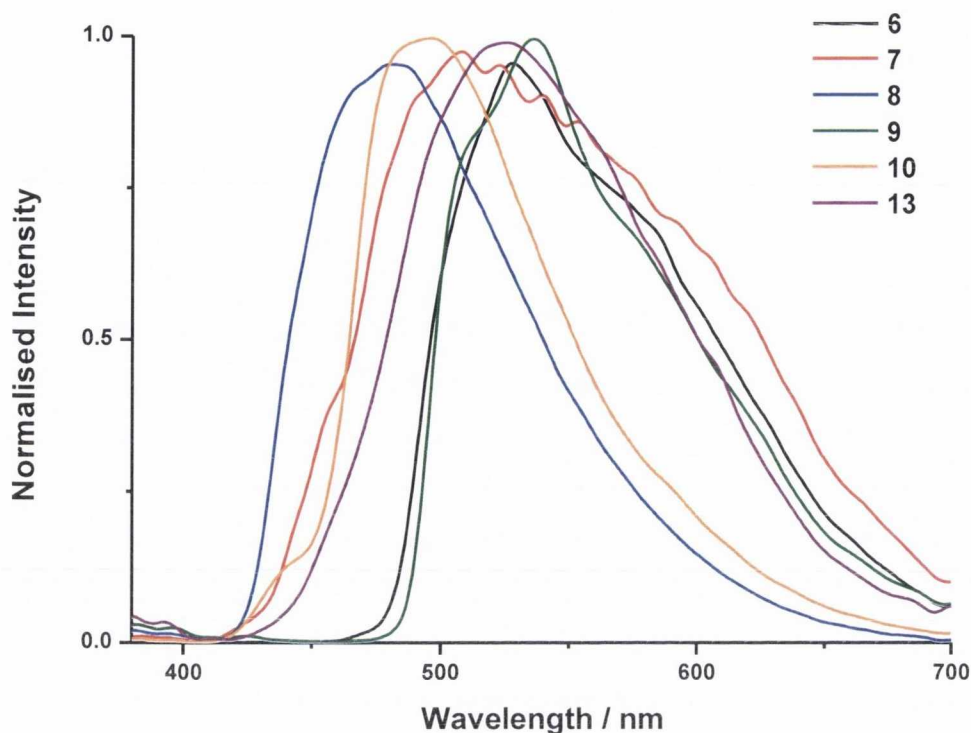


Figure 2.5-5: Normalised emission spectra of **6**, **7**, **8**, **9**, **10** and **13** at 10^{-3} M concentration in CH_2Cl_2 at 77K, λ_{exc} 360.

On increasing the concentration to 10^{-3} M only one blue shift is observed, for **13**. The emission maximum is blue shifted by 49 nm to 520 nm. This can only be attributed to the rigidochromic effect discussed previously. The remaining five ligands exhibit red shifted emission compared to their room temperature counterparts. **6** experiences a large red shift of 43 nm resulting in a λ_{max} of 528 nm, there is also a shoulder present at 580 nm. **7** and **8** follow a similar pattern but have smaller red shifts of 21 (**7**) and 22 (**8**) nm respectively. The λ_{max} of **7** appears at 506 nm that of **8** appears at 481 nm. The emission spectrum of **9** exhibits the largest red shift, 46 nm, of all five ligands. The λ_{max} appears at 535 nm. The smallest red shift is observed for **10**, with a λ_{max} of 498 nm compared to the λ_{max} of 489 nm for the room temperature spectrum. Once again the low temperature lifetimes of the ligands are dramatically increased compared to the room temperature measurements (Table 2.5-1).

2.5.3 Solid state emission spectra of 6 - 10 and 13

The solid state emission spectra of the ligands **6** - **10** and **13** are shown in Figure 2.5-6. The emission spectra, in general, are much more structured. The spectrum of **6** exhibits three distinct emission bands, a weak band at 456 nm followed by the emission maximum at 492 nm and an emission shoulder at 533 nm. **7** is not structured and appears as a broad emission centred at 526 nm. The spectrum of **8** contains two distinct emission bands, a band at 461 nm followed by the λ_{max} at 488 nm. **9** is somewhat less structured with a shoulder at 493 nm and a λ_{max} of 518 nm. There is also a weak emission observed $\sim$ 560 nm. The spectrum of **10** is highly structured with emission bands at 415, 439 and λ_{max} at 474 nm. This high structure is also present in **13** with a λ_{max} of 481 nm. This is followed by two lower energy emission bands at 513 and 552 nm. There is also a very weak higher energy band at 443 nm.

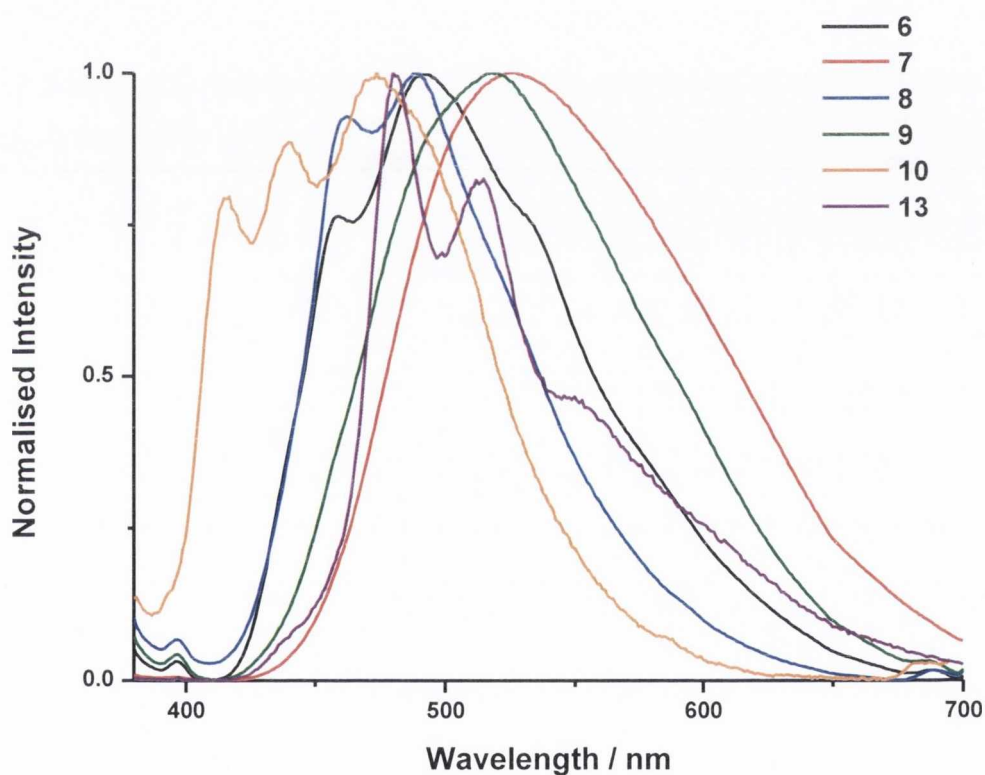


Figure 2.5-6: Normalised solid state emission spectra of **6**, **7**, **8**, **9**, **10** and **13**, λ_{exc} 360 nm.

The solid state emission maxima of the ligands are all red shifted compared to their room temperature (298 K) and low temperature (77 K) 10^{-5} M concentration

counterparts. For **6** and **9**, the emission maxima of the low temperature solution spectra at 10^{-3} M concentration experience a larger red shift than the solid state emission, whereas for **7** and **8** the largest red shifts are observed for the solid state emission. **10** and **13** exhibit larger red shifts for the emission spectra of both room and low temperature solutions at 10^{-3} M concentration than for solid state emission, suggesting that solvent effects play a part in the aggregation processes of both **10** and **13**. The emission maxima are summarised in Table 2.5-2. Again, as for the low temperature excited state lifetime measurements, the excited state lifetimes are in the microsecond range. This corroborates the explanation that in room temperature solution, the compounds have an allowed $S_0 - S_1$ transition but on going to low temperatures, or in this case solid state, this transition may become forbidden due to restrictions of rotations or distortions in the frozen or solid matrix.

Table 2.5-2: Emission maxima for ligands 6, 7, 8, 9, 10 and 13 in solid state and solution at various concentrations and temperatures.

Compound	Solid $\lambda_{\max}$	10^{-5} $\lambda_{\max}$	10^{-3} $\lambda_{\max}$	10^{-5} $\lambda_{\max}$	10^{-3} $\lambda_{\max}$
	298 K (nm)	298 K (nm)	298 K (nm)	77 K (nm)	77 K (nm)
6	492	456	485	488	528
7	526	458	485	453	506
8	488	454	459	450	481
9	518	459	489	494	535
10	474	455	489	458	498
13	481	461	569	473	520

2.5.4 Effect of acid on the emission spectra of 6 - 10 and 13

Acid titrations were performed on each of the ligands in order to determine the effect protonation has on the emission spectra. 10 μ L aliquots of 0.1 M CF_3COOH were added to 10^{-5} M solution of the ligands in CH_2Cl_2 . The emission spectra are shown in Figure 2.5-7.

The addition of trifluoroacetic acid would be expected to quench the fluorescence of the compounds¹⁰⁶, however, all but one of the compounds exhibit increased fluorescence on addition of the acid. This phenomenon has been seen in polypyridyl compounds,¹⁰⁷ and pyridine and its derivatives which are known to be nonfluorescent, fluoresce on protonation.^{108,109} This increase in fluorescence can be possibly explained

in part by the protonation of the peripheral pyridyl ring of the compounds by the acid, resulting in the turning on of the pyridyl fluorescence.

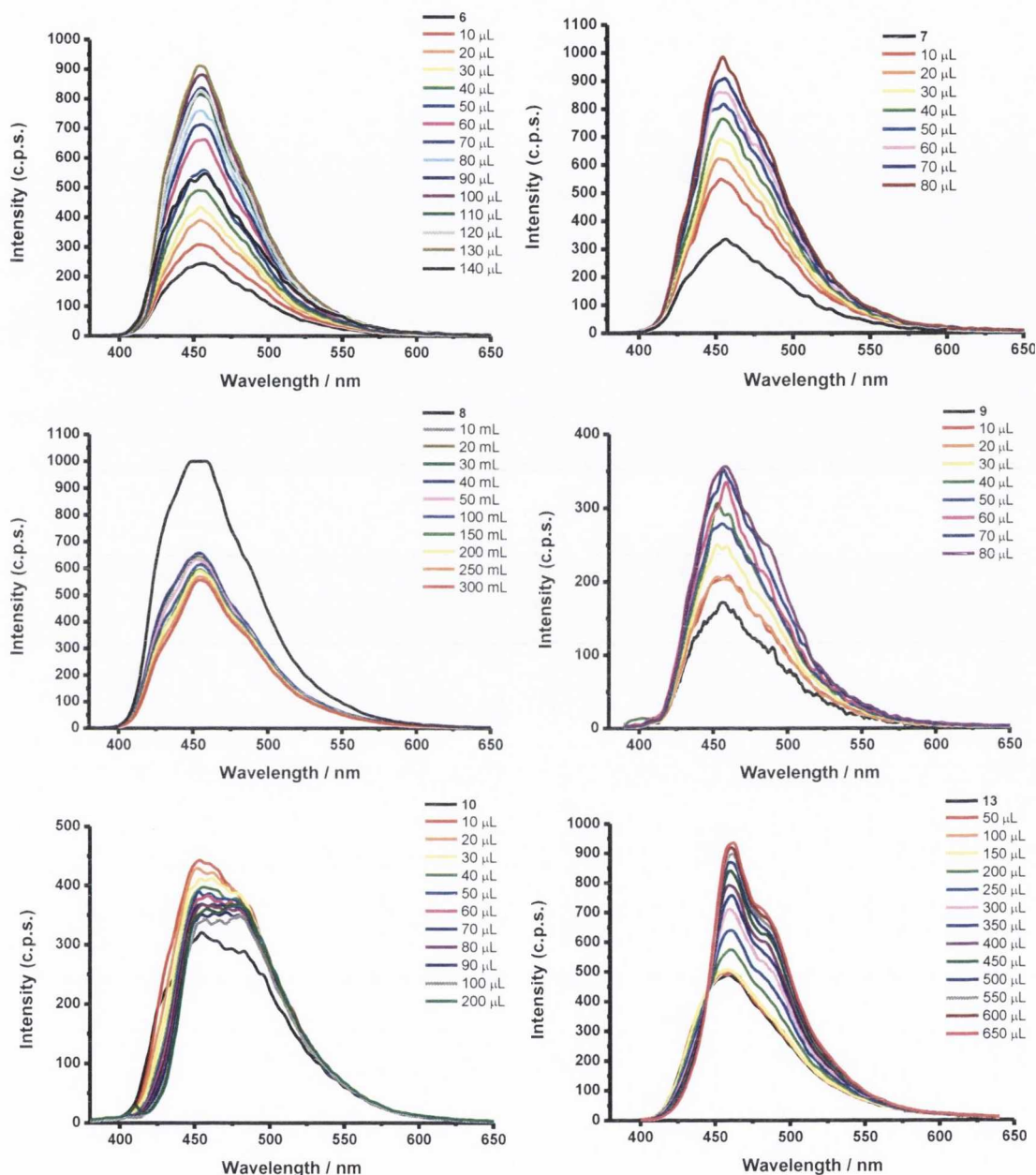


Figure 2.5-7: Emission spectra of each of the ligands **6**, **7**, **8**, **9**, **10** and **13** in CH_2Cl_2 on treatment with 0.1 M CF_3COOH .

The emission spectrum of **6** does not change on addition of acid but continues to increase in intensity with each addition. The same is true for **7** however the increase in intensity happens less gradually than for **6**, with a sharp rise in intensity observed after only one addition of 10 μL of acid. Of all six ligands, only the fluorescence of **8** is

quenched on acid addition. This could be due to the incorporation of the cyano group, as protonation of the nitrogen alpha to the cyano group of **8** would be very difficult, resulting in protonation occurring at the nitrogen of the central azafluoranthene ring thus quenching the fluoranthene emission. The emission spectra of **9** show a general increase on addition of acid, but to a lesser extent than **6** and **7**. **10** shows an initial increase in intensity that gradually decreases on acid addition, with the emission maximum also becoming gradually replaced by a more red shifted band. The emission intensity of **13** again increases on addition of acid, however larger volumes of acid were required for protonation. As acid is added a new, red shifted, emission band begins to appear which may be attributed to the protonated species. A similar trend is also observed for a series of phenanthroline based compounds described by Armaroli *et al*, whereby on addition of acid the fluorescence signal increases and measured quantum yields reach very high values compared to the unprotonated compounds.¹¹⁰

2.5.5 Quantum yield measurements

Photoluminescent quantum yields of emission (Φ) were measured for each of the ligands **6** - **10** and **13** using optically dilute solutions of each in CH₂Cl₂ in an integrating sphere and taken as an average of three experiments.¹¹¹ The photoluminescent quantum yield value is a ratio of "number of photons emitted" to "number of photons absorbed". The number of absorbed photons is calculated by monitoring the scattered excitation peak – firstly with an empty sphere, and secondly with the sample in the sphere. The difference in peak intensity between these two measurements is caused by sample absorption, and thus the number of absorbed photons can be calculated. The number of emitted photons is calculated directly from the acquired emission spectrum. There are four measurements, all of which are made "in beam", with the cuvette/sample in the same position. The blank is a cell filled with clean solvent only.

The quantum yield value is then calculated using the following equation:

$$\Phi = \frac{E_C - E_A}{L_A - L_C}$$

Where L_A = scatter of blank in sphere (using a suitable ND filter); E_A = fluorescence of blank in sphere; L_C = scatter of sample in sphere (using a suitable ND filter); E_C = fluorescence of sample in sphere

The quantum yield measurements are summarised in Table 2.5-3. The quantum yield measured for **6** was, at 8.8%, the lowest of all six compounds. This is a much lower value than that reported for the all-carbon analogue triphenylfluoranthene (TPF) (38%), suggesting that the incorporation of the nitrogen atoms has a negative effect of the fluorescence efficiency by enhancing the non-radiative decay pathways compared to those for TPF. The addition of an electron donating methyl group on the peripheral pyridyl ring for **7** marginally increases the quantum yield to 12.4%, but the inclusion of electron donating tertiary butyl groups on the peripheral phenyl rings for **9** has a much more significant effect, increasing the quantum yield to 22.9%. This suggests that the location of the donating substituents is very important. An electron withdrawing cyano group on the peripheral pyridyl ring of **8** also has a significant effect, increasing the quantum yield to 31%, whereas the strongly electron withdrawing trifluoromethyl groups of **10** have very little effect, only marginally increasing the quantum yield to 9.7%. Interestingly, by incorporating both an electron withdrawing cyano group in the peripheral pyridyl ring and electron donating tertiary butyl groups on the peripheral phenyl rings the quantum yield is dramatically increased to 38.8%.

Table 2.5-3: Quantum yield measurements of optically dilute solutions of **6-10** and **13** in CH_2Cl_2

Compound	Quantum Yield (Φ) ^a
6	8.8 %
7	12.4 %
8	31.0 %
9	22.9 %
10	9.7 %
13	38.8 %

^a Associated error on $\Phi = \pm 10\%$

2.6 Conclusions

The photophysical and electrochemical properties of each of the ligands 7,10-diphenyl-9-(2-pyridyl)-8-azafluoranthene (**6**), 7,10-diphenyl-9-(6-methyl-2-pyridyl)-8-azafluoranthene (**7**), 7,10-diphenyl-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**8**), 7,10-di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (**9**), 7,10-di[(4-trifluoromethyl)phenyl]-9-(2-pyridyl)-8-azafluoranthene (**10**) and 7,10-di(4-*tert*-butylphenyl)-9-(6-cyano-2-pyridyl)-8-azafluoranthene (**13**) were investigated.

The absorption spectra of the ligands follow a general pattern with fluoranthene centred bands appearing in the 350 – 400 nm range, as is seen for the all carbon analogue TPF. Other strong bands at 240 and 295 nm are present in all spectra and have been assigned as π - π^* in origin. A new band at ~270 nm appears in the spectra of all six compounds that is not present in that of TPF and as such was assigned as having n - π^* character. It was found that substitution of the pyridyl ring with electron donating/withdrawing groups, or substitution of the peripheral phenyl rings with electron-donating tertiary butyl groups, had only a marginal effect on the absorption spectra. The substitution of the peripheral phenyl rings with electron withdrawing groups, however, had a significant effect, as did the combination of electron withdrawing group (on the pyridyl ring) and electron donating groups (tertiary butyl on the peripheral phenyl rings).

UV-Visible absorption acid titration experiments of each of the six ligands with 0.1 M trifluoroacetic acid were conducted to determine which of the absorption bands contained n - π^* character. It was found that the strong bands at ~240 nm contained n - π^* character as they diminished on addition of acid, as did the smaller bands centred ~295 – 300 nm. The strong fluoranthene centred absorptions at 350 – 400 nm experienced a red shift on addition of acid and the presence of isosbestic points confirmed the presence of two species in the solutions – the original ligand and its protonated form.

All oxidation processes were irreversible. The oxidation process of the unsubstituted ligand **6** occurs at a less positive potential than its all carbon analogue TPF (1.49 V vs 1.61 V) suggesting that the incorporation of the nitrogen atoms renders the compound more easily oxidised. It was found that the inclusion of electron donating groups in **7** and **9** further facilitated the oxidation process as both occur at much less positive values than **6**, (1.19 V and 1.26 V respectively). Similarly, the incorporation of the electron withdrawing cyano group in **8**, results in a more positive oxidation potential of 1.74 V. The same is not true of the trifluoromethyl groups of **10**, with an oxidation potential of 1.28 V they have the opposite effect as they facilitate the oxidation when compared to the unsubstituted **6**. The combined electron donating and electron withdrawing groups of **13** result in the second largest oxidation potential, 1.62 V. This is further evidence that the cyano group of the pyridyl ring has the biggest effect on the oxidation potential as the incorporation of the tertiary butyl groups in **13** only caused a small reduction in potential when compared to **8**. The majority of the reduction waves for each ligand exhibit at least one quasi reversible reduction between -0.58 and -1.55 V. **6** is one of the

more easily reduced of the six ligands, with a reduction potential of -0.59 V. As with the oxidations, substitution patterns play a role in determining the reduction potentials. The electron withdrawing and donating groups facilitate a second reduction, resulting in two quasi reversible reduction processes for **7**, **8** and **10**. Only **9** and **13** experience irreversible reductions, most likely due to the tertiary butyl substituents that are common to both, as well as a second, quasi reversible reduction process. The more negative value for **13** is due to the inclusion of the electron withdrawing cyano group which may result in increased electron density centred on that fragment of the compound.

The emission properties of each of the six ligands were investigated at two concentrations (10^{-5} M and 10^{-3} M, CH_2Cl_2), at two temperatures (room temperature [298 K] and low temperature [77 K]) and in the solid state. It was found that at room temperature, the 10^{-5} M concentration solutions behaved in a similar way with $\lambda_{\text{max}} \sim 460$ nm. The emission spectra are all independent of excitation wavelength. The excitation spectra of **6**, **7**, **8** and **9** follow a similar pattern with three distinct bands while those of **10** and **13** exhibit a mirror symmetry with the emission spectra. On increasing the concentration there was a significant shift in the emission spectra caused by aggregation effects, as has been reported for many π -conjugated systems. A similar phenomenon is observed for the low temperature measurements at both concentrations, with a general red shift, due to aggregation and possible coplanarisation effects, evident for the majority of the spectra at 10^{-5} M concentrations, with only **7** and **8** experiencing a slight blue shift caused by the rigidochromic effect. At 10^{-3} M concentrations, only **13** exhibits a blue shift, again due to the rigidochromic effect. The solid state emission spectra all experience a red shift compared to their room temperature counterparts, as would be expected due to aggregation effects.

The excited state lifetimes of each ligand were also recorded at two concentrations (10^{-5} M and 10^{-3} M, CH_2Cl_2), at two temperatures (room temperature [298 K] and low temperature [77 K]) and in the solid state. There is a dramatic increase in excited state lifetime on going from room temperature solution to both low temperature solution and to solid state. The room temperature solution lifetimes are in the nanosecond (10^{-9} s) range whereas the low temperature and solid state lifetimes are in the microsecond (10^{-6} s). A similar phenomenon has been observed for other π -conjugated systems whereby the lifetime is increased significantly at low temperatures, however not to this extent.

Another explanation is the presence of a forbidden $S_0 - S_1$ transition in the absorption spectrum that is allowed in solution but due to restrictions of the frozen matrix/solid matrix becomes forbidden as systems with forbidden $S_0 - S_1$ transition are known to have excited state lifetimes in the microsecond region.

Acid titration experiments of each of the six ligands with 0.1 M trifluoroacetic acid were conducted and their emission spectra recorded. In general, the addition of acid increased the fluorescence intensity. Only **8** and **10** did not follow this trend, with the fluorescence of **8** being quenched on addition of acid and the initial increase in fluorescence intensity for **10** which subsequently decreased on further additions of acid. It is suggested that the increase in fluorescence observed for **6**, **7**, **9** and **13** may be due to the protonation of the pyridyl ring as, when protonated, pyridine becomes fluorescent. The quenching of fluorescence of **8** may be due to the presence of the cyano group. 2-Cyanopyridine has a negative pKa value (-0.26) it is itself very acid and therefore difficult to protonate. As the pyridyl ring of **8** is structurally related to 2-cyanopyridine it can be assumed that the pKa of this pyridyl ring is quite low resulting in the preferential protonation of the azafluoranthene nitrogen atom and the subsequent quenching of fluorescence.

The quantum yields of each of the six ligands were measured and it was found that the position of the electron withdrawing and electron donating substituents plays a vital role in their enhancement, with a combination of electron donating/withdrawing groups giving the highest value of 38.8 % for **13**.

2.7 Future work

Now that the photophysical and electrochemical properties of the six novel compounds have been investigated, the next step would be to test their suitability for device incorporation. Many fluoranthene based compounds have been employed as the light emitting layer of optoelectronic devices, whether as a single emissive layer or as blended films.^{43,48}

Chapter 3:

**Synthesis, Characterisation and Optical
Properties of Cu(I) Complexes of the 8-
Azafluoranthene Compounds**

3.1 Introduction

Copper is a transition metal element that, unlike many of its d-block counterparts, has a very high natural abundance. This natural abundance, coupled with many desirable qualities such as high ductility, malleability, thermal and electrical conductivity and resistance to corrosion have made copper a major industrial metal, second only to iron and aluminium in terms of quantities consumed annually.

3.1.1 Ground and excited state configurations of Cu(I) complexes

Copper has two active oxidation states, Cu(I) and Cu(II), the later has a d^9 electronic configuration and compounds with this configuration are usually highly coloured due to metal-centred absorptions. These absorptions usually deactivate *via* non-radiative pathways rendering Cu(II) complexes non luminescent. Cu(I) complexes, on the other hand, due to their closed shell d^{10} configuration, have much more interesting optical properties. There are many reports in the literature regarding Cu(I) – diimine ((N^N)₂) complexes and a wide range of sophisticated supramolecular architectures using [Cu(N^N)₂]⁺ templates have been prepared including catenanes, rotaxanes, knots, helicates and macrocycles among others.¹¹²⁻¹¹⁹ Heteroleptic systems of the type [Cu(N^N)(P^P)] have also gained interest, as the incorporation of bidentate phosphine ligands into the coordination sphere has further enhanced the optical properties of Cu(I) complexes.¹²⁰⁻¹²²

Cu(I)-diimine complexes, where the diimine is usually a 1,10-phenanthroline based compound, favour a tetrahedral geometry due to the filled d -orbitals that lead to a symmetric localisation of the electronic charge.^{112,123} However most complexes exhibit a distorted tetrahedral geometry due to various other factors such as π - π stacking interactions,¹²⁴ as well as the size, chemical nature and positions of the substituents of the phenanthroline systems. This distortion is often described as “rocking”, “flattening” and “wagging” and exerts a major influence on the photoluminescent properties of the complex.¹²³ Upon excitation, the MLCT state of the Cu(I) complex is populated followed by a change in formal oxidation state from Cu(I) to Cu(II), this is then followed by structural changes related to the preferred geometries of the states, i.e. the tetrahedral geometry becomes flattened as Cu(II) favours a square planar geometry.¹²⁵ Because of this flattening, an additional axial coordination site is exposed that can undergo nucleophilic attack to generate a “pentacoordinated exciplex” and therefore quench luminescence, as depicted in Figure 3.1-1.^{123,126}

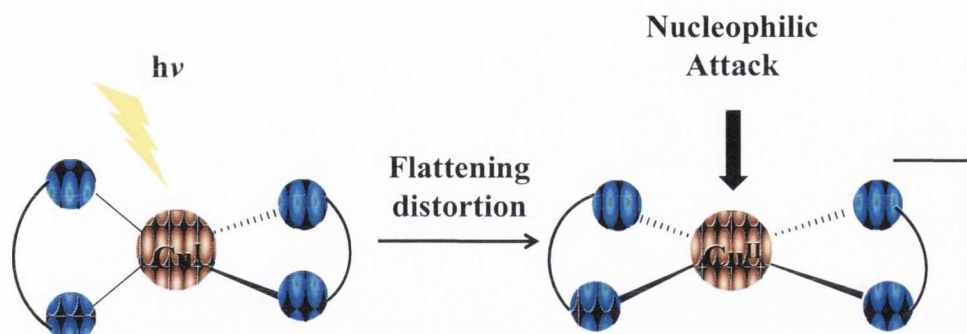


Figure 3.1-1: Excitation of the Cu(I) complex leads to a flattening distortion which then leads to exciplex formation via nucleophilic attack of the additional axial coordination site.¹²³

This phenomenon can be overcome, however, by intelligent ligand design that can work to limit the formation of exciplexes and also enhance the luminescence properties.

3.1.2 Bis-phenanthroline based Cu(I) complexes

The most extensively studied of all Cu(I) complexes are those containing phenanthroline based ligands. The coordination environment of Cu(I)-phenanthrolines is somewhat less demanding than other coordination systems and as a result allows extended structural distortions in the ground and excited states and therefore enables a fine tuning of the photophysical and electrochemical properties.¹²⁷ Although these systems tend to exhibit weak emission and short excited state lifetimes, these have been improved on incorporating bulky substituents that prevent exciplex formation and as a result enhance the photoluminescent properties of the systems.^{128,129} Miller *et al* have reported that there are at least two major structural distortions occurring in the MLCT excited states of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]$ type complexes (where $\text{N}^{\wedge}\text{N}$ = phenanthroline based ligands) that impact on their photophysical properties. The first of these is the “flattening” distortion due to the geometrical preferences of the Cu(II) ion outlined previously and can be overcome by incorporation of bulky substituents. However, substituents that are too large preclude formation of the bis(phenanthroline) complex suggesting there is an optimum substituent size. The second major distortion involves the delocalisation of the excited electron over the π^* -system of one ligand as the radical anion. This distortion can be limited by including substituents that increase the π -delocalisation into ligand design (Figure 3.1-2).^{130,131}

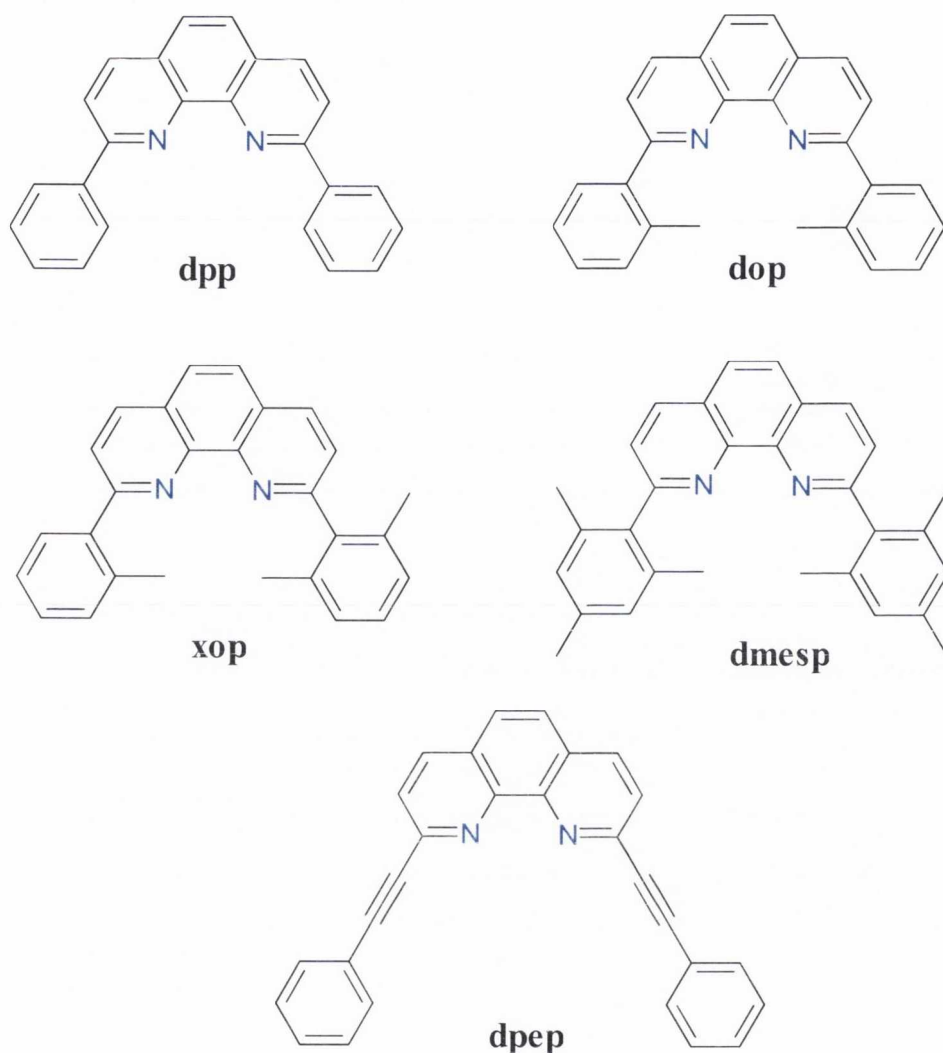


Figure 3.1-2: Five 1,10-phenanthroline based N^N bidentate ligands designed by Miller et al. **dpp** = 2,9-diphenyl-1,10-phenanthroline, **dop** = 2,9-di-(2-methylphenyl)-1,10-phenanthroline, **xop** = 2-(2-methylphenyl)-9-(2,6-dimethylphenyl)-1,10-phenanthroline, **dpep** = 2,9-diphenylethynyl-1,10-phenanthroline, **dmesp** = 2,9-dimesityl-1,10-phenanthroline.¹³⁰

3.1.2.1 Absorption and emission spectra of [Cu(N^N)₂]⁺ complexes

The absorption spectra of bis(phenanthroline) based complexes are dominated by ligand-centred (LC) bands typical of the π - π^* transitions associated with these ligands in the UV range while much less intense bands, attributed to metal to ligand charge transfer (MLCT) electronic transitions, are seen in the visible range of the spectrum.¹³² It was found that the positioning of aryl substituents on the phenanthroline based ligand has a significant effect on the absorption spectrum, with less intense absorptions for

aryl substituents in the 2 and 9 positions when compared to alkyl substituents. In contrast, incorporating aryl substituents into the 4 and 7 positions strongly enhances absorption and red shifts the absorption maximum.¹²⁷ These aryl substituents can also induce π -stacking interactions which in turn affect the absorption spectra as they can distort the geometry of the coordination sphere and previously forbidden transitions are made allowed.¹²⁴

McMillin and co-workers have shown that the emission from Cu(I)-phenanthroline based complexes arises from two MLCT excited states, a singlet ($^1\text{MLCT}$) and triplet ($^3\text{MLCT}$) state, in thermal equilibrium. At room temperature the lower lying $^3\text{MLCT}$ level is more densely populated than the $^1\text{MLCT}$ level however, it is the excited molecules of the singlet state that are responsible for most of the observed room temperature luminescence.¹³³ In general, spectral position, quantum yields and excited state lifetimes of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ complexes are highly changeable depending on the degree of distortion from the ideal tetrahedral geometry experienced by the excited state molecule, as discussed previously.

3.1.3 Heteroleptic Cu(I) complexes of the $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]$ type

Another, more successful, approach to overcoming the shortfalls of the $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ complexes was devised by McMillin *et al* who incorporated phosphine ligands into these systems resulting in greatly enhanced photophysical properties.^{120,121} The bulky bidentate phosphines inhibit exciplex formation and the resulting $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ type complexes are able to absorb throughout the visible region. As with the $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ complexes, the bands in the UV range of the spectrum are ligand-centred bands typical of the π - π^* transitions of both the N-donor and phosphine ligands.¹³⁴ Despite not being directly involved in the MLCT transitions, the phosphine based ligands can result in shifting the MLCT to higher energy, compared to the homoleptic analogues, due to their electron withdrawing ability.¹³⁵⁻¹³⁷ Both steric and electronic properties of the phosphine ligands can impact those of the complex. The incorporation of the electron-withdrawing, and bulky, POP ligand into a Cu(I) phenanthroline based complex results in a significant enhancement of the luminescence properties such as higher quantum yields and longer excited state lifetimes.¹³⁸ Zhang *et al* have reported that $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ complexes undergo phosphorescence enhancement triggered by π -stacking in the solid state if the diimine ligand can supply a π surface.¹³⁹

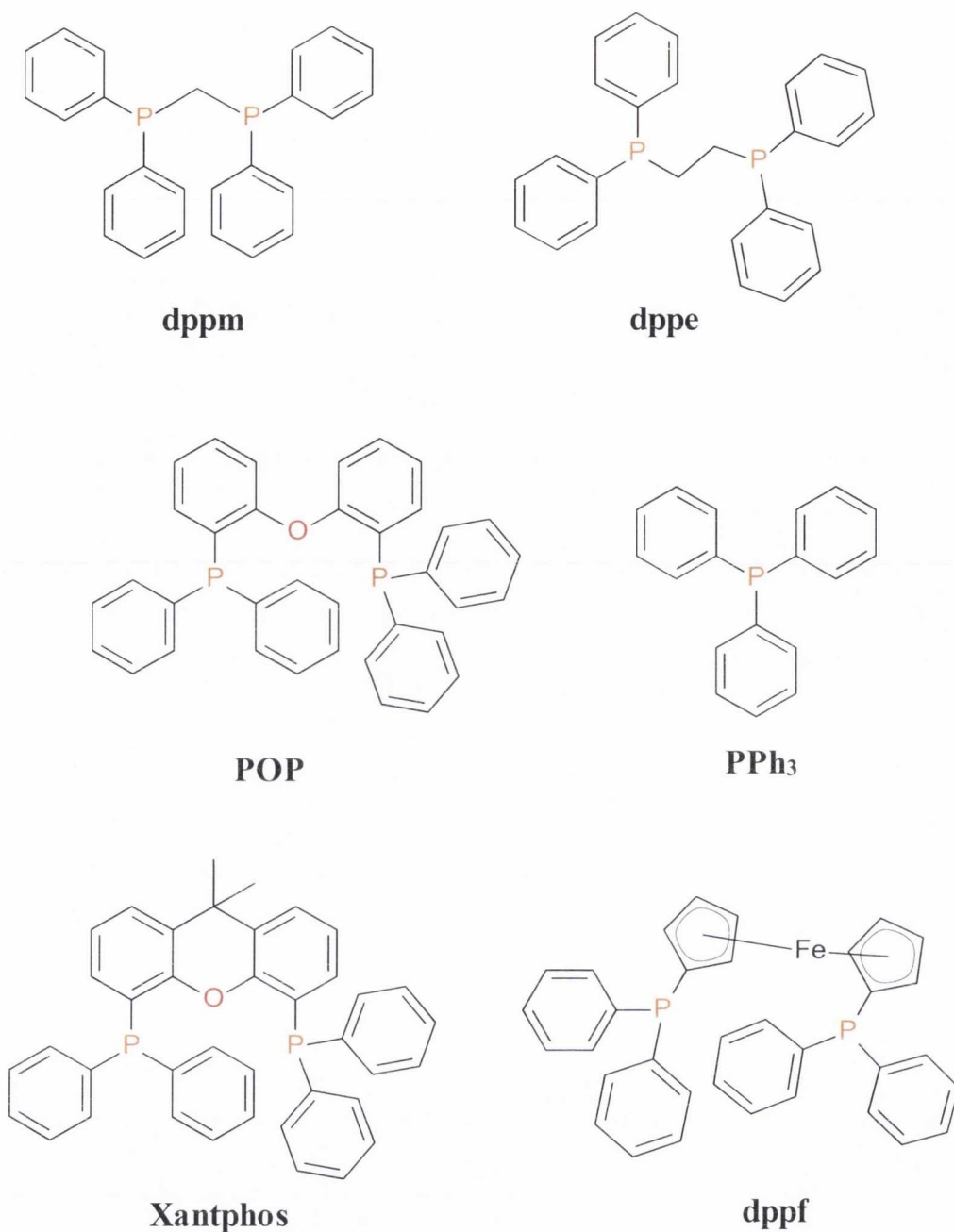


Figure 3.1-3: Some ligands typically used as P-P units in $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ complexes. **dppm** = bis(diphenylphosphino)methane, **dppe** = bis(diphenylphosphino)ethane, **POP** = bis[2-(diphenylphosphino)phenyl]ether, **PPh₃** = triphenylphosphine, **Xantphos** = 4,5-bis(diphenylphosphino)9,9-dimethylxanthene, **dppf** = 1,1'-bis(diphenylphosphino)ferrocene.

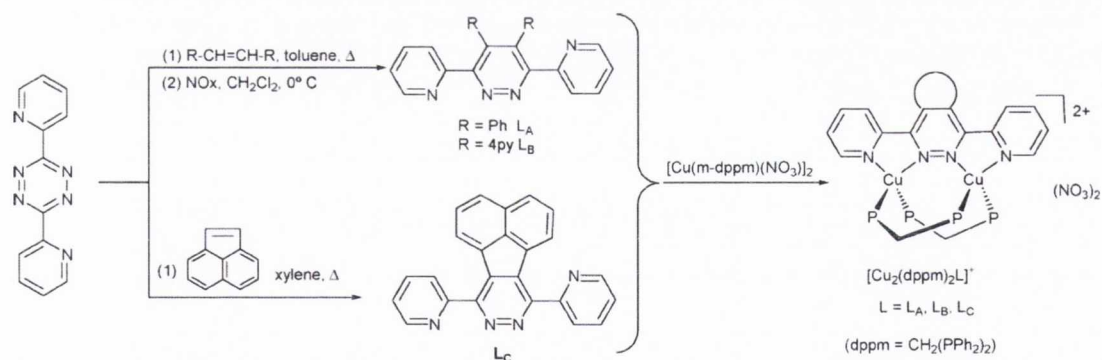
The luminescence efficiency of the MLCT excited states of these types of complexes can also undergo exciplex formation and subsequent quenching, similar to that

observed for the Cu(I) bis(phenanthroline) complexes. It is for this reason that careful selection of the substituents on both the diimine and phosphine ligands is vital to ensure protection against exciplex formation.

3.1.4 Azafluoranthene based complexes

As seen from the preceding discussion, the electronic nature, bulk and rigidity of the diimine ligand all play an important role in determining the photophysical properties of the resultant Cu(I) complexes. Departure from the traditional phenanthroline based systems has been slow but there are some examples in the literature of other diimine based ligands proving that there is scope to rethink and redesign ligand systems.^{140,141}

Recent work by Gil *et al* has shown the use of extended polyaromatic pyridazines and diazafluoranthenes as new N-donor motifs in the formation of dimeric Cu(I) bisphosphine systems. In these systems the N-donor ligands act as bridging supports to a rigid eight membered ring comprising two copper metal centres and the dppm phosphine ligands. This provides a structured framework to secure the distorted tetrahedral geometry of the copper centres and therefore prevents exciplex formation. The new dinuclear diazafluoranthene system exhibits a very long excited state lifetime of 22.8 μ s, the longest reported for this type of complex.¹⁴¹



Scheme 3.1-1: Synthetic route towards $[Cu_2(\mu-dppm)_2(\mu-L)](NO_3)_2$ from Gil *et al*.¹⁴¹

With this in mind, a series of homoleptic and heteroleptic copper complexes based on the N^N bidentate azafluoranthene ligands described in chapters 1 and 2 was designed. It was hoped that the peripheral phenyl ring adjacent to the nitrogen atom of the azafluoranthene core, and any substituents on the peripheral pyridyl ring, would hinder the formation of the exciplex in the homoleptic complexes.

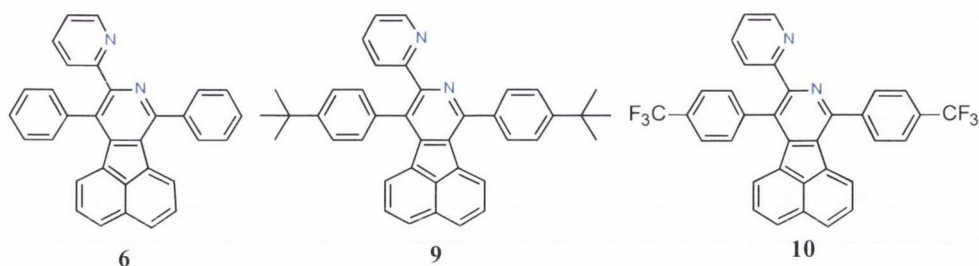


Figure 3.1-4: *N,N* bidentate azafluoranthene ligands

Two phosphine based compounds, 4,5-bis(diphenylphosphino)9,9-dimethylxanthene (xantphos) and 1,1-bis(diphenylphosphino)ferrocene (dppf), were also chosen as auxiliary ligands for the heteroleptic complexes, as they would serve to further enhance the photoluminescent properties of the systems. It was found that only the ligands **6**, **9** and **10** would form the heteroleptic complexes as ligands **7**, **8** and **13** could not be forced to coordinate to the phosphine ligands, instead only forming the homoleptic complexes. This may have been due to the bulky substituents *ortho* to the nitrogen atom of the peripheral pyridyl ring that were hoped would hinder exciplex formation, but instead hindered complex formation. As a result, the series of comparable complexes consists of only homoleptic and heteroleptic complexes of ligands **6**, **9** and **10** (Figure 3.1-4).

3.2 Synthesis of complexes

3.2.1 Synthesis of homoleptic Cu(I) complexes of **6**, **9** and **10**.

A general method was employed for the synthesis of homoleptic Cu(I) complexes of ligands **6**, **9** and **10**. Each ligand was dissolved in 10mL of dichloromethane, to this was added [Cu(MeCN)₄]PF₆ and the solution was stirred at room temperature for 2 hr. On completion of the reaction the solution was filtered through celite to remove any solid impurities or undissolved salt. The volume of the reaction mixture was reduced under vacuum and the desired complex was precipitated out on addition of hexane. Each of the three homoleptic complexes [Cu**6**₂]PF₆ (**15**), [Cu**9**₂]PF₆ (**16**) and [Cu**10**₂]PF₆ (**17**) were purple solids.

3.2.2 Spectroscopic characterisation of **15**, **16** and **17**

Each complex was fully characterised using ¹H and, where possible, ¹³C {¹H} NMR spectroscopy. The ¹H and ¹³C NMR spectra of **15** are discussed in detail and were used to assign those of **16** and **17**.

3.2.2.1 ^1H NMR spectrum of **15**

The fully assigned ^1H NMR spectrum of **15** is shown in Figure 3.2-1. The complex has a plane of symmetry, thus making the NMR spectrum more straightforward to assign. The protons belonging to the same spin system were identified by $^1\text{H} - ^1\text{H}$ COSY 2D correlation experiments. As with the free ligand (**6**) there are two distinct naphthyl 3-spin systems, two phenyl 3-spin systems and one 4-spin system that is attributed to the pyridyl ring.

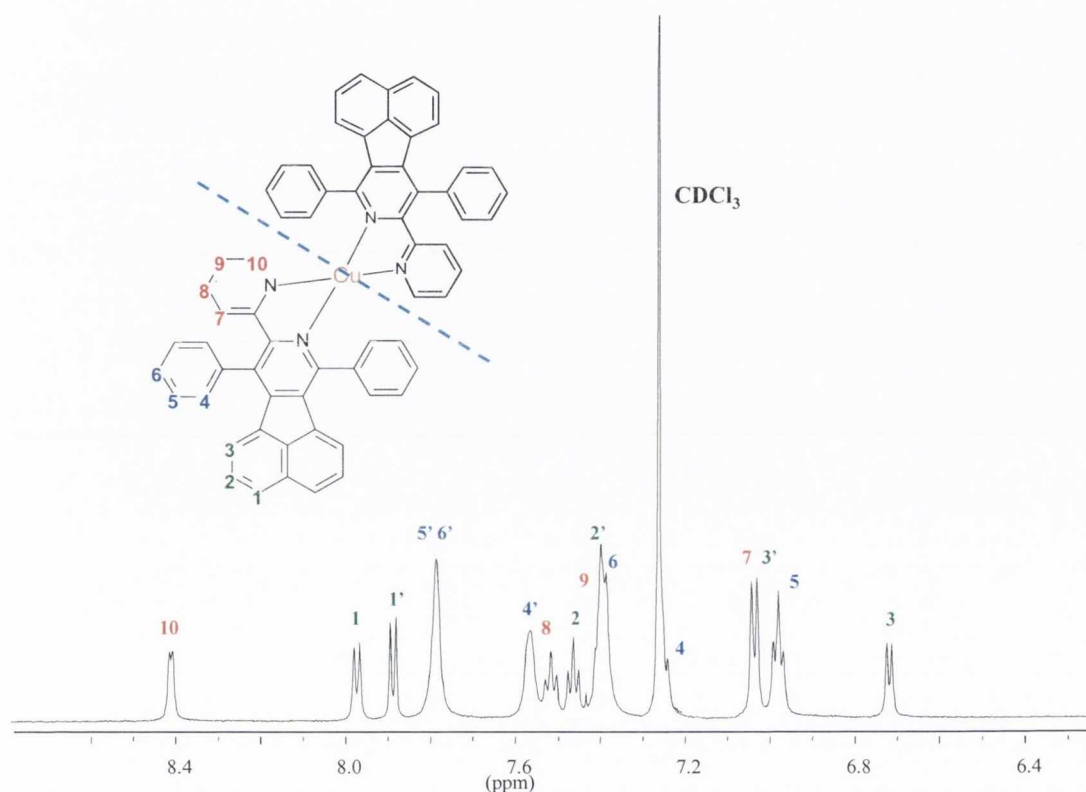


Figure 3.2-1: ^1H NMR spectrum of **15** in CDCl_3 (600.1 MHz, R.T.). Atom labelling as per inset.

The signals integrate to a total of 20 protons (due to the plane of symmetry present in the complex). The most deshielded signal is that of H10 and appears at δ 8.41 ppm as a doublet with a small coupling constant of $^3J_{\text{HH}} = 4\text{ Hz}$ as is characteristic of pyridyl ring protons. This is followed by two signals at δ 7.98 and δ 7.89 ppm respectively integrating for one proton each, which both appear as doublets with identical coupling constants of $^3J_{\text{HH}} 8.0\text{ Hz}$. These correspond to the naphthyl protons H1 and H1'. The broad singlet at δ 7.78 ppm integrates for three protons and from the 2D correlation experiments can be assigned to the phenyl ring protons H5' and H6'. Another broad

singlet appears at δ 7.56 ppm that integrates for two protons, H4'. The broadness of the phenyl ring signals can be explained by their proximity to the copper atom. The signal at δ 7.52 ppm appears a doublet of doublets that integrates for one proton and is assigned as the second of the pyridyl ring protons, H8. This is immediately followed by another doublet of doublets at δ 7.46 ppm, this time caused by the naphthyl proton H2. A multiplet spanning δ 7.43 – 7.39 ppm integrates for three protons and is a combination of three overlapping signals. From the $^1\text{H} - ^1\text{H}$ COSY these signals can be assigned as H9, H2' and H6 (Figure 3.2-2).

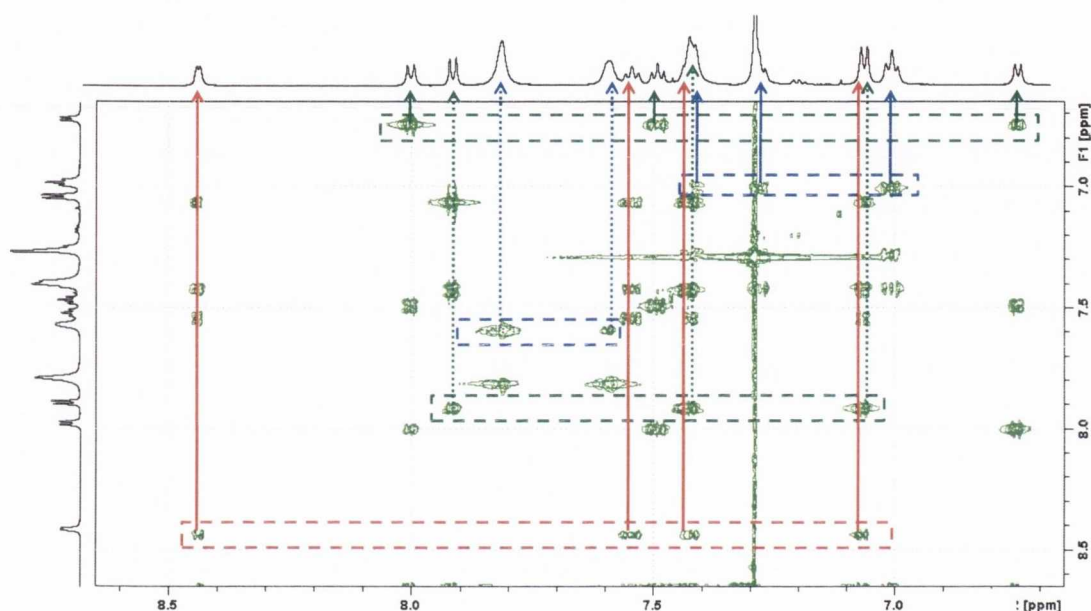


Figure 3.2-2: $^1\text{H} - ^1\text{H}$ COSY experiment of **15** showing the assignment of the various spin systems – pyridyl (red), naphthyl (green) and phenyl (blue).

The signal at δ 7.24 ppm overlaps with the residual chloroform peak and is attributed to H4. Two overlapping doublets appear at δ 7.04 ppm that integrate for two protons, H7 and H3' respectively. A doublet of doublets at δ 6.98 ppm integrates for two protons and is assigned to the final phenyl ring protons, H5. The signal at δ 6.72 ppm belongs to the remaining naphthyl ring proton H3.

3.2.2.2 ^{13}C NMR spectrum of **15**

The ^{13}C $\{^1\text{H}\}$ NMR spectrum of **15** is shown in Figure 3.2-3. The spectrum was assigned using a HSQC (Heteronuclear Single Quantum Coherence); a $^1\text{H} - ^{13}\text{C}$ COSY

experiment, which facilitates the assignment of the ^{13}C signal to which each proton is directly attached.

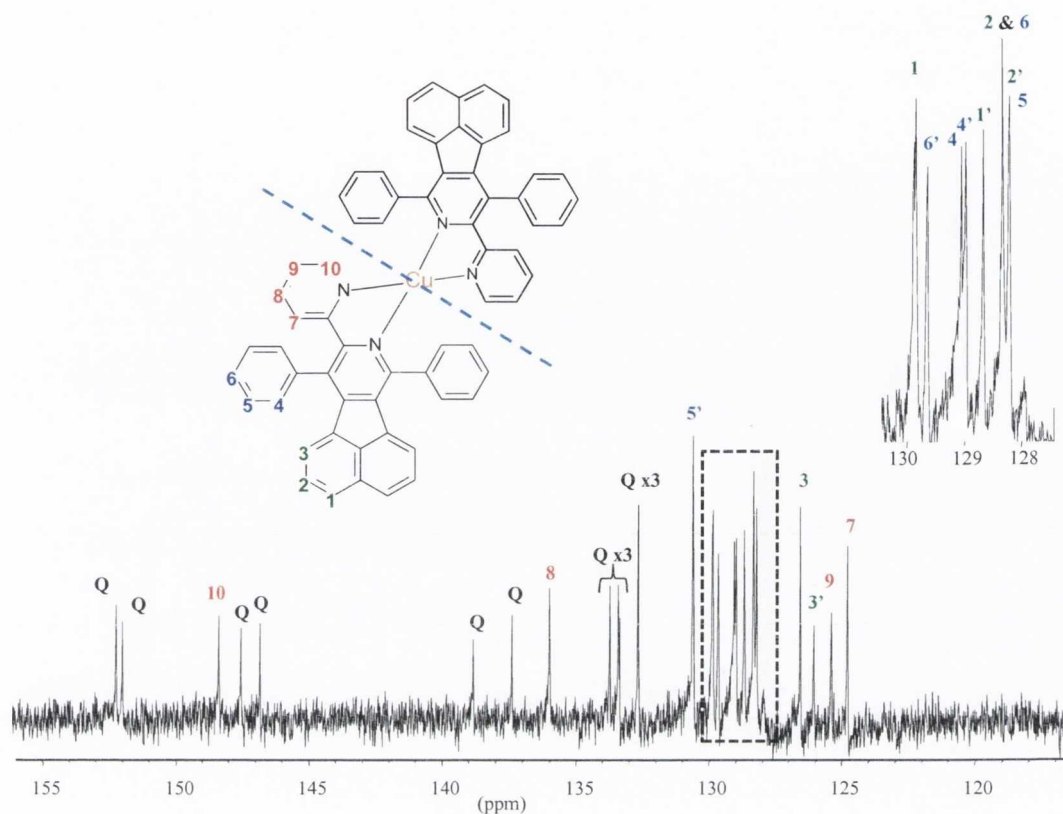


Figure 3.2-3: ^{13}C $\{^1\text{H}\}$ NMR spectrum of **15** in CDCl_3 (100.6 MHz, R.T.). Atom labelling as per inset, Q denotes quaternary carbons.

There are a total of 24 signals in the ^{13}C spectrum which is less than expected. This is due to the fact that some of the signals overlap. The quaternary carbon signal at δ 132.6 ppm is uncharacteristically intense for a single quaternary carbon; it is in fact three overlapping quaternary carbon signals. The remainder of the quaternary signals are assigned in full in Figure 3.2-3. As expected the most downfield of the C – H signals are C10 and C8 at δ 148.4 and δ 135.9 ppm respectively, these are the carbons *ortho* and *para* to the nitrogen of the pyridyl ring. The signal at δ 130.6 ppm is attributed to C5', and is closely followed by seven methine signals found very close together over a range of three ppm. The complete assignment of these signals is shown in the enlarged region of the spectrum inset in Figure 3.2-3. The remaining signals at δ 126.6, δ 126.1, δ 125.4 and δ 124.8 ppm have been assigned to C3, C3', C9 and C7, respectively.

3.2.2.3 ^1H NMR spectrum of **16** and **17**

The fully assigned ^1H NMR spectrum of **16** is shown in Figure 3.2-4. This complex also has a plane of symmetry. The protons belonging to the same spin system were identified by $^1\text{H} - ^1\text{H}$ COSY 2D correlation experiments. As with the free ligand (**9**) there are two distinct naphthyl 3-spin systems, two phenyl 2-spin systems and one 4-spin system that is attributed to the pyridyl ring.

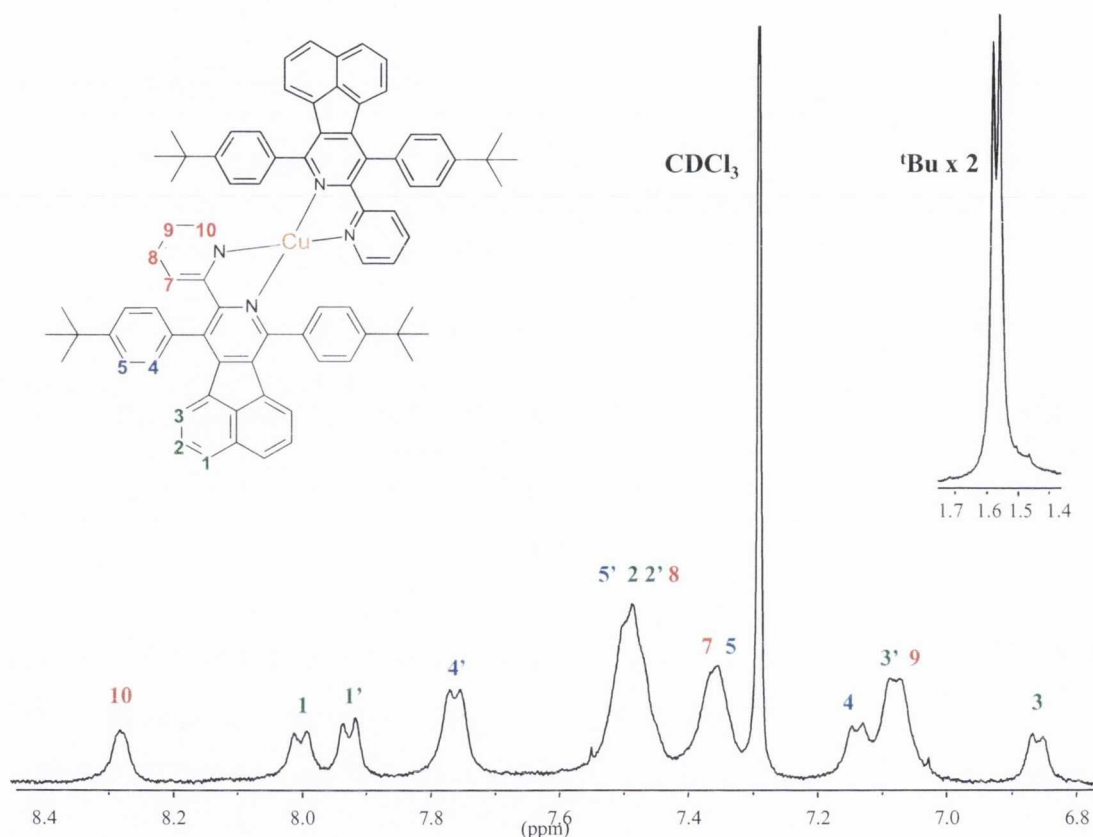


Figure 3.2-4: ^1H NMR spectrum of **16** in CDCl_3 (600.1 MHz, R.T.). Atom labelling as per inset.

In contrast to the spectrum of **15**, the signals in this spectrum appear much broader as a result of possible stacking effects in solution. This coupled with the presence of the copper atom have resulted in much broader peaks than would normally be expected for metal complexes. The most downfield signal appears as a broad singlet at δ 8.28 ppm and is attributed to H10 and is followed by two broad doublets at δ 8.01 and δ 7.99 ppm, respectively, that both integrate for one proton each with coupling constants of $^3J_{\text{HH}} = 7.5$ Hz assigned to H1 and H1'. Moving increasingly upfield the next signal is

also a broad doublet that integrates for two protons and with a coupling constant of $^3J_{\text{HH}} = 6.3$ Hz at δ 7.76 ppm which is attributed to H4'. A multiplet spanning δ 7.55 – 7.43 ppm integrates for five protons and from the $^1\text{H} - ^1\text{H}$ COSY it can be assigned as H5', H2, H2' and H8. A second multiplet at δ 7.40 – 7.32 ppm integrates for three protons and again for the $^1\text{H} - ^1\text{H}$ COSY it can be assigned as H5 and H7. At δ 7.14 ppm appears a doublet that integrates for two protons, H4, this is followed immediately by another broad multiplet at δ 7.08 ppm that also integrates for two protons, H3' and H9. The final aromatic signal appears as a doublet at δ 6.87 ppm and is assigned as H3. Two overlapping singlets at δ 1.58 and 1.56 ppm are attributed to the tertiary butyl protons.

The fully assigned ^1H NMR spectrum of **17** is shown in Figure 3.2-5. The complex also has a plane of symmetry. The protons belonging to the same spin system were identified by $^1\text{H} - ^1\text{H}$ COSY 2D correlation experiments.

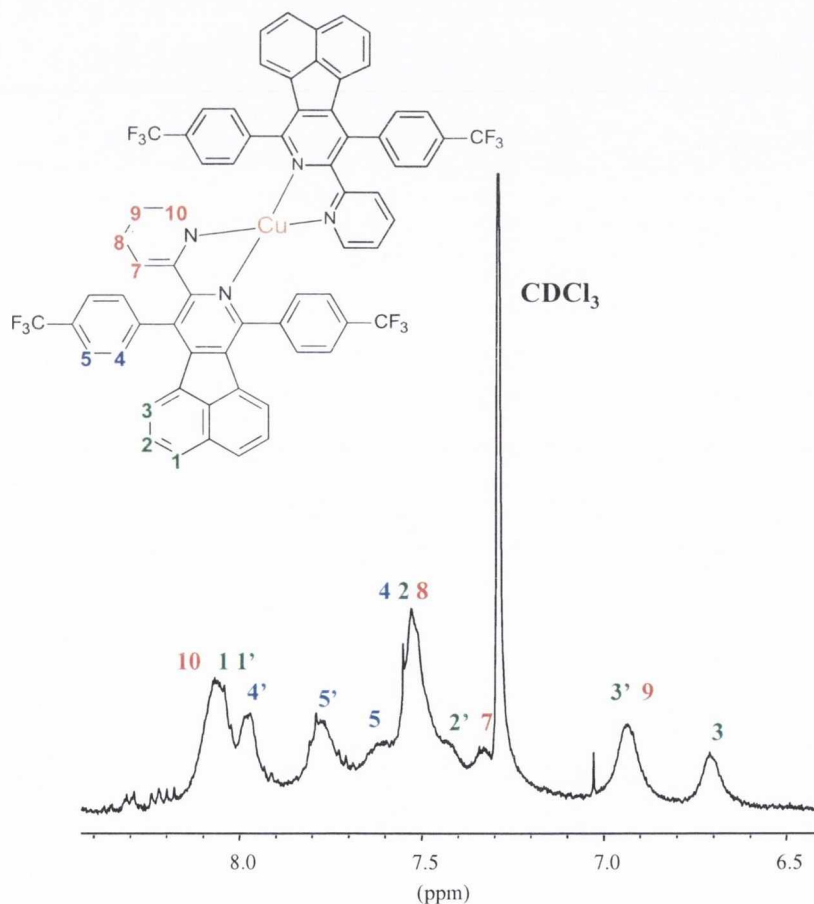


Figure 3.2-5: ^1H NMR spectrum of **17** in CDCl_3 (600.1 MHz, R.T.). Atom labelling as per inset.

As with the free ligand (**10**) there are two distinct naphthyl 3-spin systems, two phenyl 2-spin systems and one 4-spin system that is attributed to the pyridyl ring. The inclusion of CF_3 groups as well as a copper metal centre, have had a marked effect on the quality of NMR obtained. The signals are broad and the resolution quite poor but they could still be assigned appropriately. The first of the signals is a very broad multiplet spanning δ 8.14 – 7.93 ppm that integrates for five protons, from this integration and from the patterns observed in the previous NMR spectra this multiplet has been assigned to H10, H1, H1' and H4'. Following this is another broad signal that integrates for two protons at δ 7.78 ppm and is attributed to H5'. The next section of the spectrum contains many overlapping signals over the range δ 7.65 – 7.39 ppm, this range of signals integrates for seven protons in total, the first two of which are assigned as H5. This is followed by H4, H2 and H8 which appear within a region of overlapping signals which also include H7. The remaining two signals again appear as broad peaks at δ 6.94 and 6.71 ppm and integrate for two and one protons respectively, the first is attributed to H3' and H9 and the last to H3.

Attempts to obtain ^{13}C NMR spectra of complexes **16** and **17** were unsuccessful.

3.2.3 Synthesis of heteroleptic Cu(I) complexes of **6**, **9** and **10** with xantphos

A general method was employed for the synthesis of heteroleptic Cu(I) complexes of ligands **6**, **9** and **10**. Each ligand was dissolved in 10mL of dichloromethane, to this was added a solution of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ and 4,5-bis(diphenylphosphino)9,9-dimethylxanthene (xantphos), and the solution was stirred at room temperature for 2 hr. On completion the reaction mixture was filtered through celite to remove any solid impurities or undissolved salt. The volume of the reaction mixture was reduced under vacuum and the desired complex was precipitated out on addition of hexane. Each of the three homoleptic complexes $[\text{6CuXantphos}]\text{PF}_6$ (**18**), $[\text{9CuXantphos}]\text{PF}_6$ (**19**) and $[\text{10CuXantphos}]\text{PF}_6$ (**20**) were yellow solids.

3.2.4 Spectroscopic characterisation of complexes **18**, **19** and **20**

Each complex was fully characterised using ^1H and, where possible, ^{13}C {H} NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **18** are discussed in detail and were used to support the assignment of the spectra of **19** and **20**.

3.2.4.1 ^1H NMR spectrum of **18**

The fully assigned ^1H NMR spectrum of **18** is shown in Figure 3.2-6. The spectrum integrates for a total of fifty-two protons; twenty azafluoranthene protons and thirty-two xantphos protons. The protons were assigned using 2D-correlation experiments. As with the free ligand (**6**) there are two distinct naphthyl 3-spin systems, two phenyl 3-spin systems and one 4-spin system that is attributed to the pyridyl ring. In addition to this are the xantphos spin systems, which are more difficult to assign due to the overlapping nature of the signals and their poorer resolution.

The most downfield of the signals integrates for one proton and is the naphthyl proton H1', this appears as a doublet at δ 8.10 ppm with a coupling constant $^3J_{\text{HH}} = 8.0$ Hz. Following this is a second doublet at δ 7.98 ppm ($^3J_{\text{HH}} = 8.0$ Hz) that integrates for one proton and is assigned to H1. The next signal is a multiplet spanning δ 7.74 – 7.67 ppm that integrates for five protons. A $^1\text{H} - ^1\text{H}$ COSY experiment allowed this to be assigned to the phenyl ring protons H4', H5' overlapped with the pyridyl proton H10. At δ 7.59 ppm a doublet of doublets that integrates for one proton is seen, it is the second of the naphthyl ring protons H2'. The subsequent signals over the range δ 7.50 – 7.39 overlap to a certain degree as can be seen in Figure 3.2-6. The first of the overlapping signals appears as a broad singlet that integrates for three protons. From the $^1\text{H} - ^1\text{H}$ COSY it is found that this signal is due to two of the xantphos protons and the phenyl ring proton H6'. Immediately following this is a multiplet that integrates for two protons, H8 and H2, one pyridyl and one naphthyl proton respectively. The next of the xantphos protons appears in the region δ 7.33 – 7.25 ppm and is again overlapped with a phenyl ring proton H6 resulting in a multiplet that integrates for two protons at δ 7.31 ppm followed by a multiplet at δ 7.26 ppm that integrates for one xantphos proton. A multiplet at δ 7.22 ppm integrating for one proton is ascribed to H7, a pyridyl ring proton. This is followed by a large multiplet that integrates for a total of fifteen protons over the range δ 7.14 – 7.04 ppm, ten of these protons are due to two of the phenyl rings attached to the phosphorus of the xantphos ligand. The remaining five protons are the phenyl ring protons H4 and H5 and the naphthyl ring proton H3'. A second large, very broad, multiplet spanning δ 7.00 – 6.87 integrates for a total of ten protons and is assigned to the remaining two phenyl rings of the xantphos ligand. The remaining two xantphos protons appear as a broad singlet that overlaps with the remaining pyridyl proton H9 at δ 6.65 ppm. The final aromatic signal is a doublet that integrates for one

proton and is the last unassigned naphthyl proton H3 at δ 6.62 ppm. There is one signal in the aliphatic range of the spectrum, a singlet that integrates for six protons at δ 2.16 ppm and is attributed to the methyl protons of the xantphos ligand.

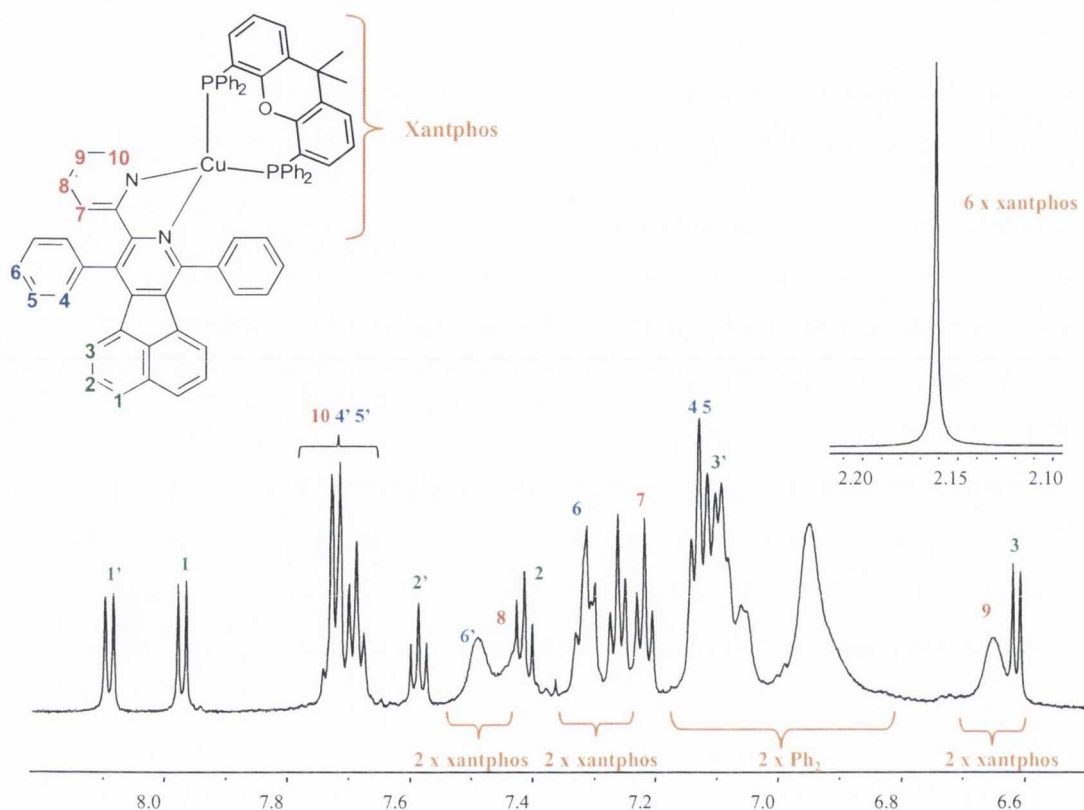


Figure 3.2-6: ^1H NMR spectrum of **18** in CH_2Cl_2 (600.1 MHz, R.T.) Atom labelling as per inset picture.

3.2.4.2 ^{13}C NMR spectrum of **18**

It was not possible to obtain a well resolved ^{13}C NMR spectrum of **18** and therefore the assignment of the xantphos carbon signals was not made. Figure 3.2-7 shows the assignment of the quaternary carbons of the azafluoranthene ligand. A selected region of the $^{13}\text{C} - ^1\text{H}$ COSY NMR spectrum of **18** is shown in Figure 3.2-8. This region of the spectrum facilitated the assignment of the ^{13}C atoms to which each azafluoranthene proton is directly attached.

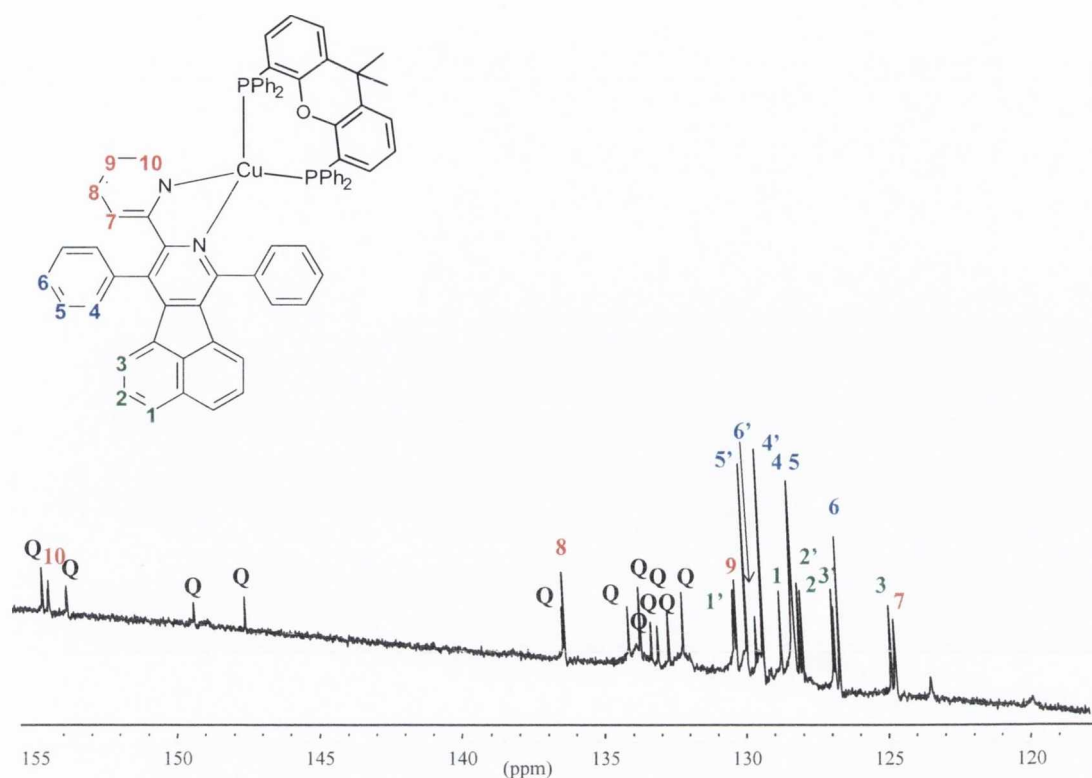


Figure 3.2-7: ^{13}C NMR spectrum of **18** in CH_2Cl_2 (100.1 MHz, R.T.). Atom labelling as per inset picture. *Q* denotes quaternary carbon.

The quaternary carbons are assigned as shown in Figure 3.2-7. The most downfield of the C – H signals is C10 at δ 154.5 ppm, followed by C8 at δ 136.52 ppm. C1' and C9 appear very close together at δ 130.5 and δ 130.4 ppm respectively, followed closely by the signals for the phenyl ring closest to the nitrogen of the azafluoranthene, C5', C6' and C4' (δ 130.1, δ 129.8 and δ 129.5 ppm). The downfield shift of C9 may be attributed to the incorporation of the phosphine ligand as it has shifted significantly when compared to the free ligand **6** (δ 121.6 ppm) and also the homoleptic copper complex **15** (δ 125.4 ppm). The next signal appears at δ 128.9 ppm and is attributed to C1. The remaining naphthyl and phenyl signals follow, with C4 and C5 overlapping at δ 128.5 ppm followed by C2' and C2 at δ 128.3 and δ 128.2 ppm respectively. C3' appears at δ 127.1 ppm closely followed by the remaining phenyl ring carbon C6 at δ 126.9 ppm. The final two aromatic carbon signals are assigned to C3 and C7 at δ 125.1 and δ 124.9 ppm respectively.

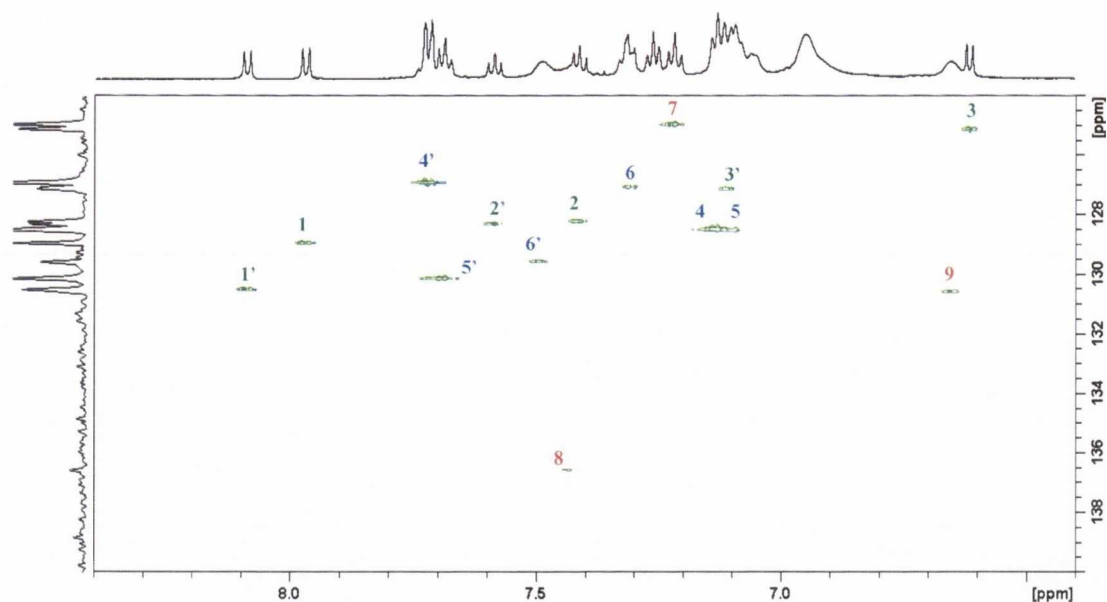


Figure 3.2-8: HSQC experiment of **18** in CH_2Cl_2 (600.1 MHz, R.T.).

3.2.4.3 ^1H NMR spectra of **19** and **20**

The fully assigned ^1H NMR spectrum of **19** is shown in Figure 3.2-9. The spectrum integrates for a total of fifty protons; eighteen azafluoranthene protons and thirty-two xantphos protons. The protons were again assigned using 2D-correlation experiments. As with the free ligand (**9**) there are two distinct naphthyl 3-spin systems, two phenyl 2-spin systems and one 4-spin system that is attributed to the pyridyl ring. There are also spin systems that are due to the xantphos protons, however these signals are much harder to comprehensively assign due to the large degree of overlap and the poorer resolution.

Due to the functionalisation of the azafluoranthene ligand in the H6/H6' positions there are less ligand signals in the spectrum of complex **19**, chemical shifts and assignments are the same or similar to those of **18** for the first few signals i.e. H1', H1, H10 and H4'. There is a distinct doublet of doublets that integrates for one proton and is attributed to H2' at δ 7.51 ppm, but the subsequent portion of the spectrum shows a great deal of overlap and as such was treated as a large multiplet spanning δ 7.45 – 7.02 ppm. This collection of signals integrated for twenty-six protons, sixteen of which can be attributed to the xantphos ligand protons. The remaining ten protons were assigned using the ^1H – ^1H COSY spectrum. The first of the azafluoranthene signals in the multiplet is H5', which is buried in the δ 7.41 – 7.39 region. This is followed by H2 and

H8 which appear in the region of δ 7.37 – 7.32 ppm. The remaining azafluoranthene ligand phenyl ring protons appear at δ 7.24 – 7.20 (H4) and δ 7.15 – 7.14 (H5) ppm respectively. Immediately following this is H7 in the region δ 7.14 – 7.12 ppm and finally H3' is found at δ 7.04 ppm.

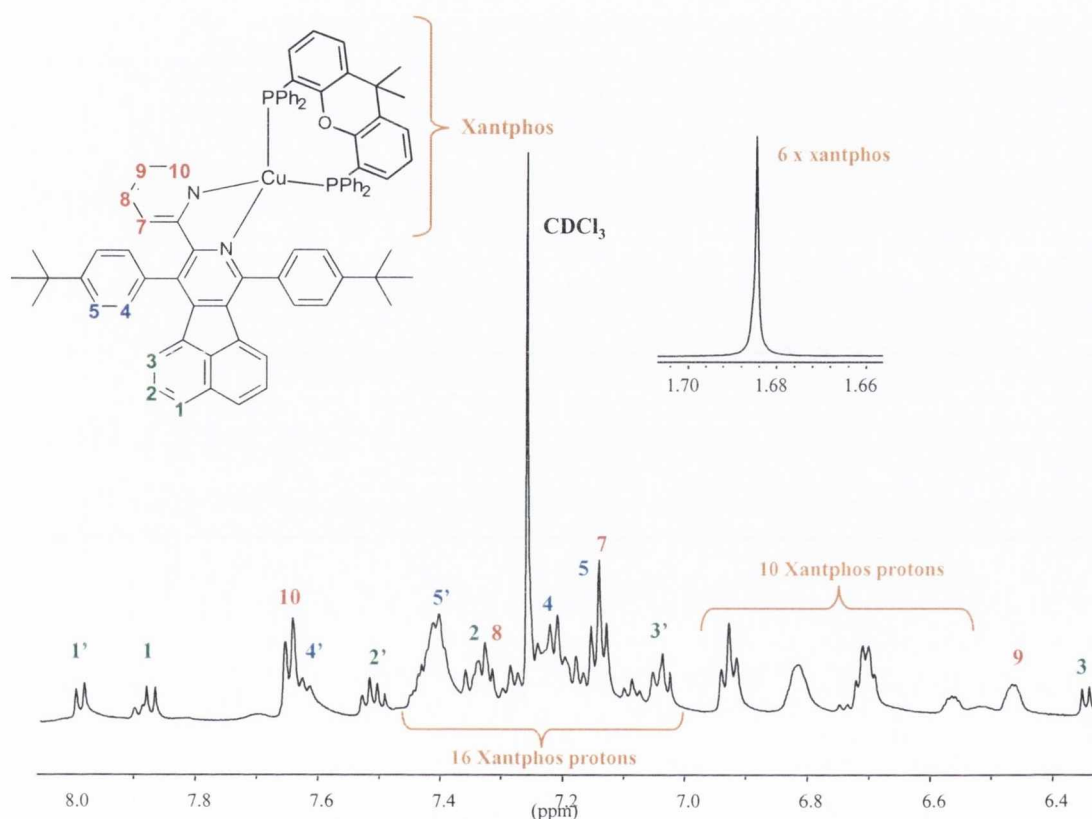


Figure 3.2-9: ^1H NMR spectrum of **19** (CDCl_3 , 600.1 MHz, R.T.). Atom labelling as per picture inset.

There are four xantphos ligand signals at δ 6.93, δ 6.82, δ 6.71 and δ 6.56 ppm that integrate to a total of ten protons. It was not possible to fully assign these fully however the integration shows that all twenty-six aromatic xantphos protons are present. The broad signal at δ 6.46 ppm integrates for one proton and is attributed to H9 whereas the final aromatic signal, a doublet at δ 6.34 ppm, is assigned as H3. There are three aliphatic signals, a singlet at δ 1.69 ppm that integrates to six protons and is assigned to the methyl protons of the xanthene unit of the xantphos ligand, and two overlapping singlets at δ 1.47 and δ 1.45 ppm respectively, that integrate for eighteen protons due to the tertiary butyl protons of the azafluoranthene ligand.

The fully assigned ^1H NMR spectrum of **20** is shown in Figure 3.2-10. The spectrum integrates to a total of fifty protons; eighteen azafluoranthene protons and thirty-two xantphos protons. The protons were again assigned using 2D-correlation experiments. As with the free ligand (**10**) there are two distinct naphthyl 3-spin systems, two phenyl 2-spin systems and one 4-spin system that is attributed to the pyridyl ring. Again there are additional spin systems due to the xantphos protons that cannot be comprehensively assigned due to a large degree of overlap and poorer resolution, in this region of the spectrum.

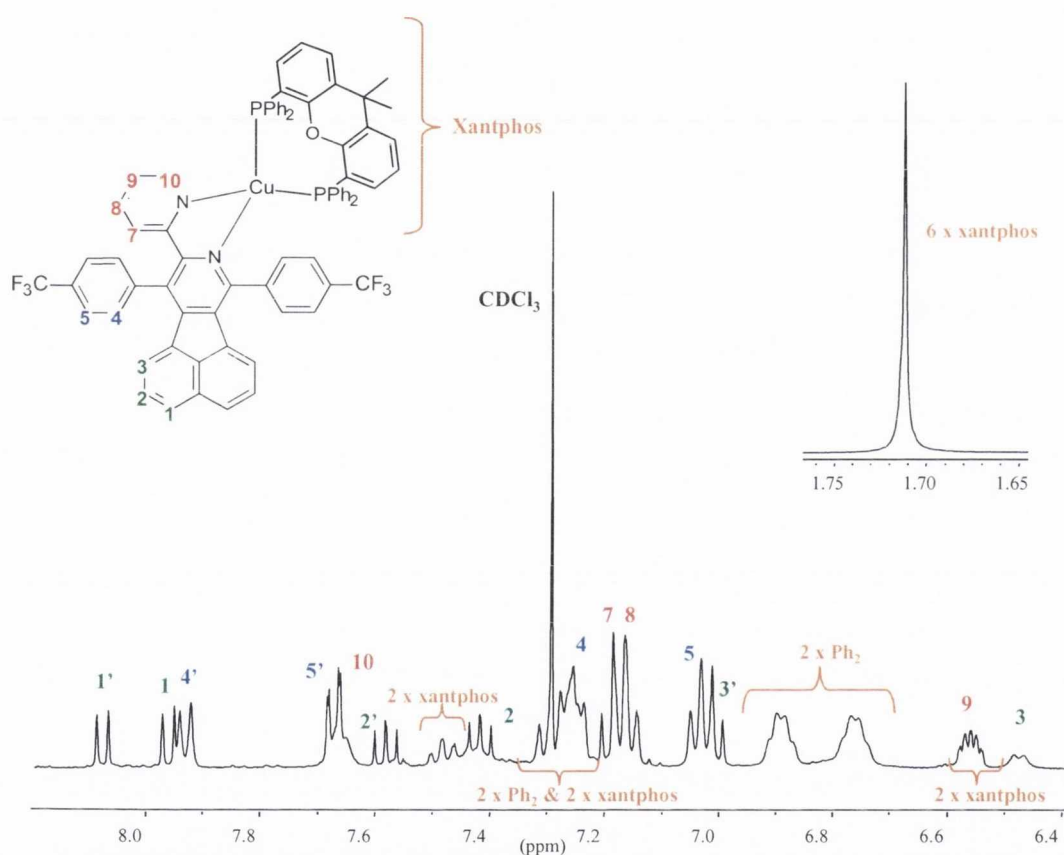


Figure 3.2-10: ^1H NMR spectrum of **20** (CDCl_3 , 600.1 MHz, R.T.). Atom labelling as per inset.

Due to the effect of the strongly electron withdrawing trifluoromethyl group of the azafluoranthene ligand the pattern of ^1H NMR signals is altered compared to **18** and **19**, the most notable difference being the position of the $\text{H}4'$ and $\text{H}5'$ signals.

The most down field of the signals in the spectrum of 20 integrates for one proton and is the naphthyl proton H1', this appears as a doublet at δ 8.08 ppm with a coupling constant $^3J_{HH} = 8.6$ Hz and is followed by two overlapping doublets at δ 7.96 and δ 7.93 ppm respectively. The first doublet integrates for one proton and is attributed to H1; the second doublet integrates for two protons and is assigned as H4'. The next signal is a multiplet spanning δ 7.68 – 7.63 ppm and integrates for three protons, using the $^1H - ^1H$ COSY experiment it was possible to assign this multiplet to the phenyl ring protons H5' and the pyridyl proton H10. The upfield shift of the H5' signal relative to the complexes discussed previously can be attributed to the fact that this proton is situated *ortho* to the electron withdrawing CF_3 . The next signal appears as a doublet of doublets at δ 7.58 ppm that integrates for one proton; the second of the naphthyl ring protons H2'. This is followed by another doublet of doublets at δ 7.48 ppm that integrates for two protons and is the first of the xantphos signals. This signal appears broader than the azafluoranthene proton signals. A third doublet of doublets appears at δ 7.42 ppm and is due to the naphthyl proton H2. A large multiplet spanning the range δ 7.31 – 7.23 ppm integrates to a total of twelve protons. From the $^1H - ^1H$ COSY it was found that only two of these protons belong to the azafluoranthene ligand (the phenyl ring protons H4) ten of the protons buried in this multiplet are due to two of the phenyl rings of the bis-diphenylphosphine portion of xantphos. The next signal is again a multiplet that integrates for four protons over the range δ 7.21 – 7.14 ppm. Using the $^1H - ^1H$ COSY it was possible to assign two of the protons to H7 and H8. The remaining two are attributed to the dimethylxanthene portion of the xantphos ligand. The next signal is a multiplet integrating for three protons over the region δ 7.05 – 6.99 ppm, again using the $^1H - ^1H$ COSY it was found that these signals were attributable to H5 and H3'. Two broad multiplets integrating for five protons each appear at δ 6.91 – 6.86 ppm and δ 6.78 – 6.73 ppm, respectively. These are due to the remaining two phenyl rings of the bis-diphenylphosphine portion of the xantphos ligand. The final xantphos signals overlap with the pyridyl ring signal, H9, to appear as a multiplet that integrates for three protons at δ 6.58 – 6.53 ppm. The final aromatic signal is a doublet at δ 6.47 ppm that integrates for one proton and is the final naphthyl proton H3. There is one signal in the aliphatic range of the spectrum, a singlet that integrates for six protons at δ 1.70 ppm and is attributed to the methyl protons of the xantphos ligand.

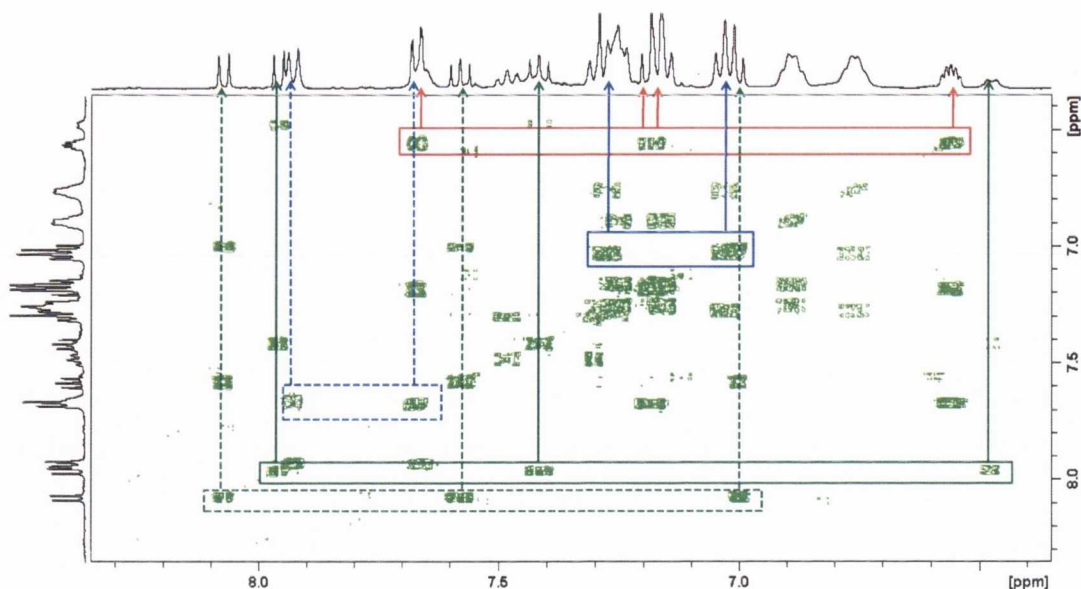


Figure 3.2-11: $^1\text{H}-^1\text{H}$ COSY experiment of **20** showing the assignment of the various spin systems – pyridyl (red), naphthyl (green) and phenyl (blue).

3.2.4.4 ^{13}C NMR spectra of **19**

The ^{13}C NMR spectrum of **19** was assigned using both HMBC and HSQC experiments. A high quality ^{13}C NMR spectrum was obtained showing not only the azafluoranthene carbons but also each xantphos carbon, thus making the assignment quite arduous as the spectrum contained over sixty signals.

The sixteen quaternary carbons of the azafluoranthene ligand have been fully assigned and details can be found in the experimental section of Chapter 5. Figure 3.2-12 shows a DEPT 135 spectrum of **19** where only the C – H and CH_3 carbons are shown. Using this spectrum in conjunction with the HSQC spectrum it was possible to assign the ^{13}C signals of the azafluoranthene ligand.

The most downfield of these signals appears at δ 136.8 ppm and is assigned to C8. This downfield shift is most likely due to the influence of the copper metal drawing the electron density away from the C8 position through the coordinated nitrogen atom *para* to it. The next most downfield signal is assigned to C10 at δ 134.4 ppm. This is then followed by a number of signals that are due to the phenyl rings of the xantphos ligand. The next azafluoranthene signal appears at δ 130.8 ppm and is attributed to C9, as with **18** the shift in C9 compared to the free ligand **9** is significant (δ 121.9 ppm for **9**).

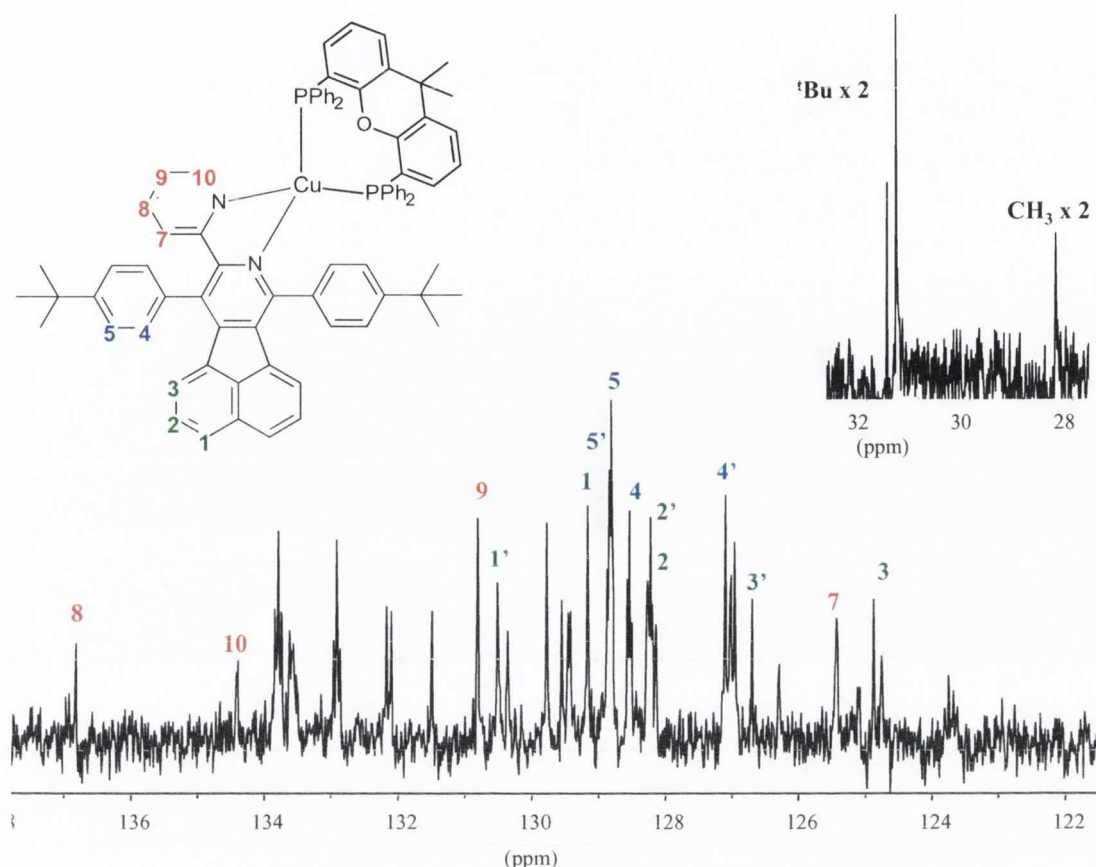


Figure 3.2-12: ^{13}C NMR DEPT experiment showing the C – H carbons of **19**. (CDCl_3 , 600.1 MHz, R.T.). Atom labelling as per inset.

The signal at δ 130.4 ppm is assigned to C1' and is followed by more xantphos signals, in this case the phenyl rings of the bis-diphenylphosphine portion of the ligand. The signals for C1, C5', C5 and C4 follow at δ 129.1, δ 128.8, δ 128.8 and δ 128.5 ppm respectively. The signals for C2' and C2, (δ 128.2 and δ 128.1 ppm), overlap with a xantphos signal from the xanthene portion of the ligand. C4' is assigned to the signal at δ 127.1 ppm and is followed by C3', C7 and C3 at δ 126.3, δ 125.4 and 124.9 ppm respectively. The tertiary butyl groups of the azafluoranthene ligand appear at δ 31.6 and 31.4 ppm and are followed by the methyl carbons of the xantphos ligand at δ 28.3 ppm.

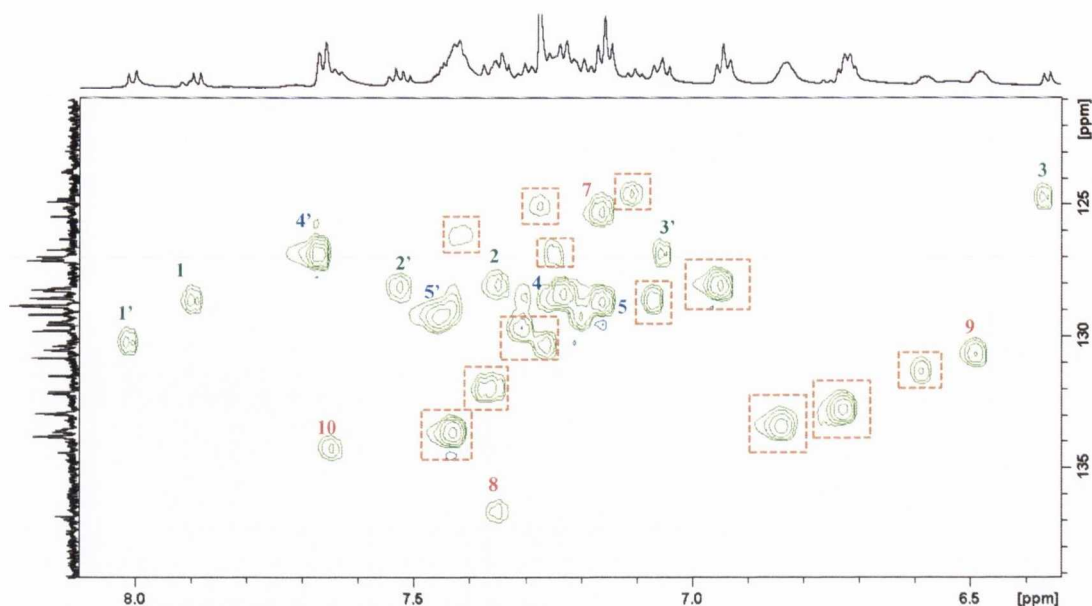


Figure 3.2-13: HSQC experiment of **19** showing the assignment of the azafluoranthene carbon atoms (numbers) and the xantphos carbon atoms (orange boxes).

Attempts to obtain a high resolution ^{13}C NMR spectrum of **20** were unsuccessful.

3.2.4.5 X-Ray crystal structures of **18**

Crystals suitable for x-ray diffraction were obtained from slow evaporation of a solution of dichloromethane and methanol of **18**.

Figure 3.2-14 shows the asymmetric unit of the crystal structure of **18**. The unit cell contains one molecule of **18** and a PF_6 molecule (not shown). **18** crystallises in the monoclinic $\text{P}2_1/\text{n}$ space group. The complex exhibits a distorted tetrahedral geometry about the metal centre and selected bond angles and bond lengths are shown in Table 3.2-1 and are in agreement with similar complexes reported in the literature.^{142,143}

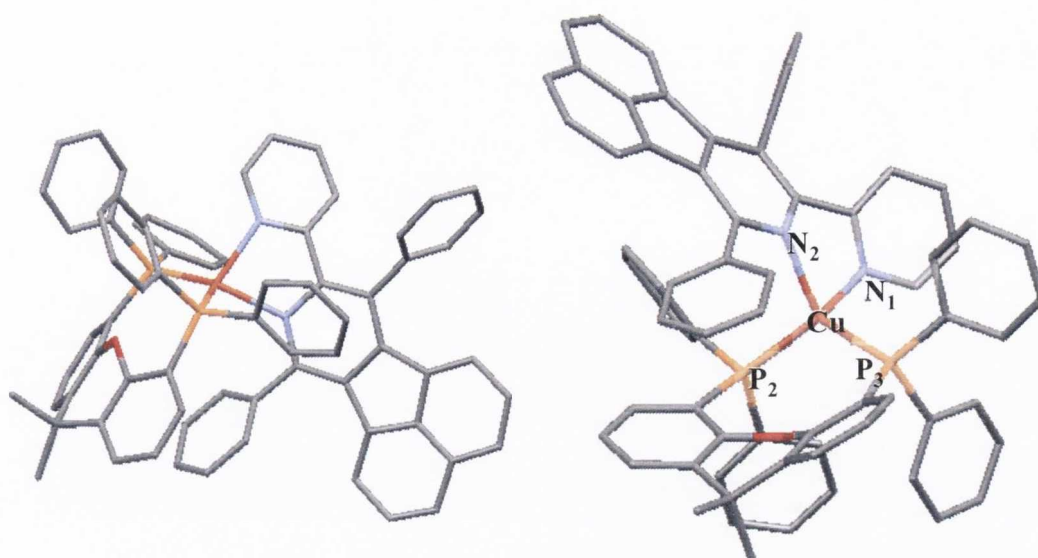


Figure 3.2-14: Asymmetric unit of **18** (left) with nitrogen atoms in blue, carbon atoms in grey, oxygen atoms in red, phosphorus atoms in orange and copper atoms on dark orange. (hydrogen atoms omitted for clarity). Atom labelling of the metal centre and N[^]N and P[^]P atoms (right).

Table 3.2-1: Selected bond angles and bond lengths for **18**

Selected bond angles (°)		Selected bond lengths (Å)	
N(1)-Cu(1)-N(2)	80.50(14)	Cu(1)-N(1)	2.085(4)
N(1)-Cu(1)-P(3)	105.15(10)	Cu(1)-N(2)	2.157(4)
N(2)-Cu(1)-P(3)	124.91(10)	Cu(1)-P(3)	2.2723(12)
N(1)-Cu(1)-P(2)	114.33(10)	Cu(1)-P(2)	2.2759(14)
N(2)-Cu(1)-P(2)	105.54(10)	Cu(1)-N(1)	2.085(4)
P(3)-Cu(1)-P(2)	119.76(4)	Cu(1)-N(2)	2.157(4)
N(1)-Cu(1)-N(2)	80.50(14)	Cu(1)-P(3)	2.2723(12)

There are strong $\pi\pi$ -stacking interactions evident in the crystal packing structure of **18**, with the molecules arranged in a staggered fashion with the planar fluoranthene core oriented toward each other to form the staggered packing structure that results in a zig-zag pattern shown in Figure 3.2-16

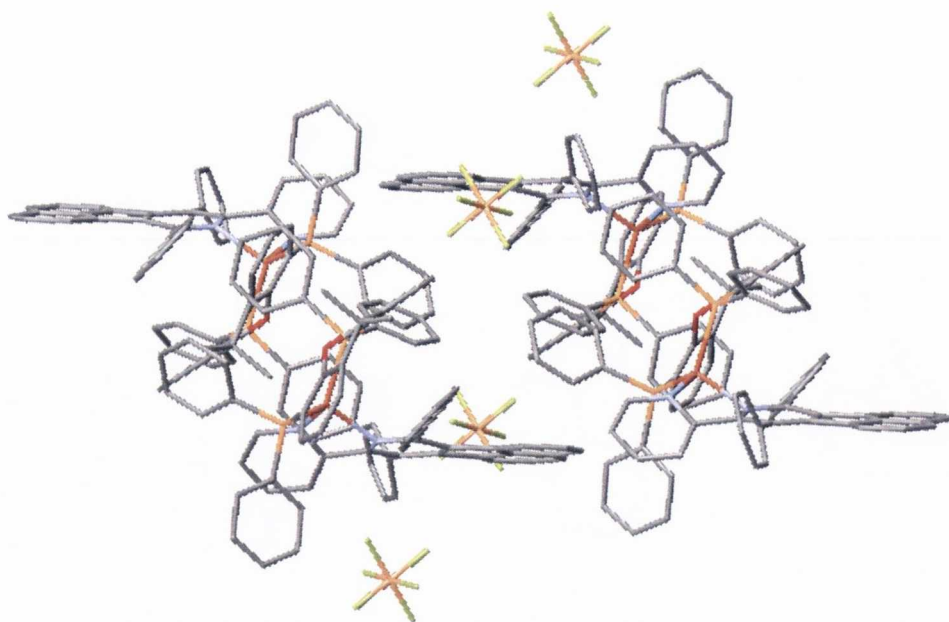


Figure 3.2-15: Graphical representation of the $\pi\pi$ -stacking of two molecules of **18** (distance ~ 8.8 Å) and the contributions of the PF_6 counter ions.

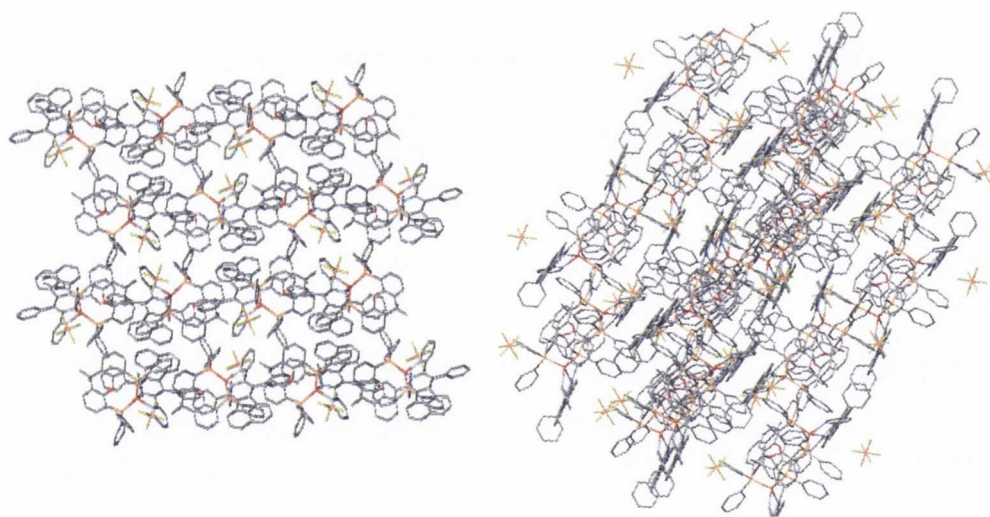


Figure 3.2-16: Staggered packing structures of **18** exhibiting a zig-zag pattern.

3.2.5 Synthesis of heteroleptic Cu(I) complexes of **6**, **9** and **10** with dppf

A general method was employed for the synthesis of heteroleptic Cu(I) complexes of ligands **6**, **9** and **10**. Each ligand was dissolved in 10 mL of dichloromethane, to this was added a solution of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ and 1,1-bis(diphenylphosphino)ferrocene (dppf) and the solution was stirred at room temperature for 2 hr. On completion of the

reaction the solution was filtered through celite to remove any solid impurities or undissolved salt. The volume of the reaction mixture was reduced under vacuum and the desired complex was precipitated out on addition of hexane. Each of the three heteroleptic complexes $[6\text{Cu}(\text{dppf})]\text{PF}_6$ (**21**), $[9\text{Cu}(\text{dppf})]\text{PF}_6$ (**22**) and $[10\text{Cu}(\text{dppf})]\text{PF}_6$ (**23**) were yellow solids.

3.2.6 Spectroscopic characterisation of **21**, **22** and **23**

Each complex was fully characterised using ^1H and, where possible, ^{13}C $\{^1\text{H}\}$ NMR spectroscopy. The ^1H and ^{13}C NMR spectra of **21** are discussed in detail and were used to facilitate the assignment of **22** and **23**.

3.2.6.1 ^1H NMR spectrum of **21**

The fully assigned ^1H NMR spectrum of **21** is shown in Figure 3.2-17. The spectrum integrates to a total of forty-eight protons, twenty-eight dppf protons and twenty azafluoranthene protons. The protons belonging to the same spin system were identified using $^1\text{H} - ^1\text{H}$ COSY 2D correlation experiments (Figure 3.2-18).

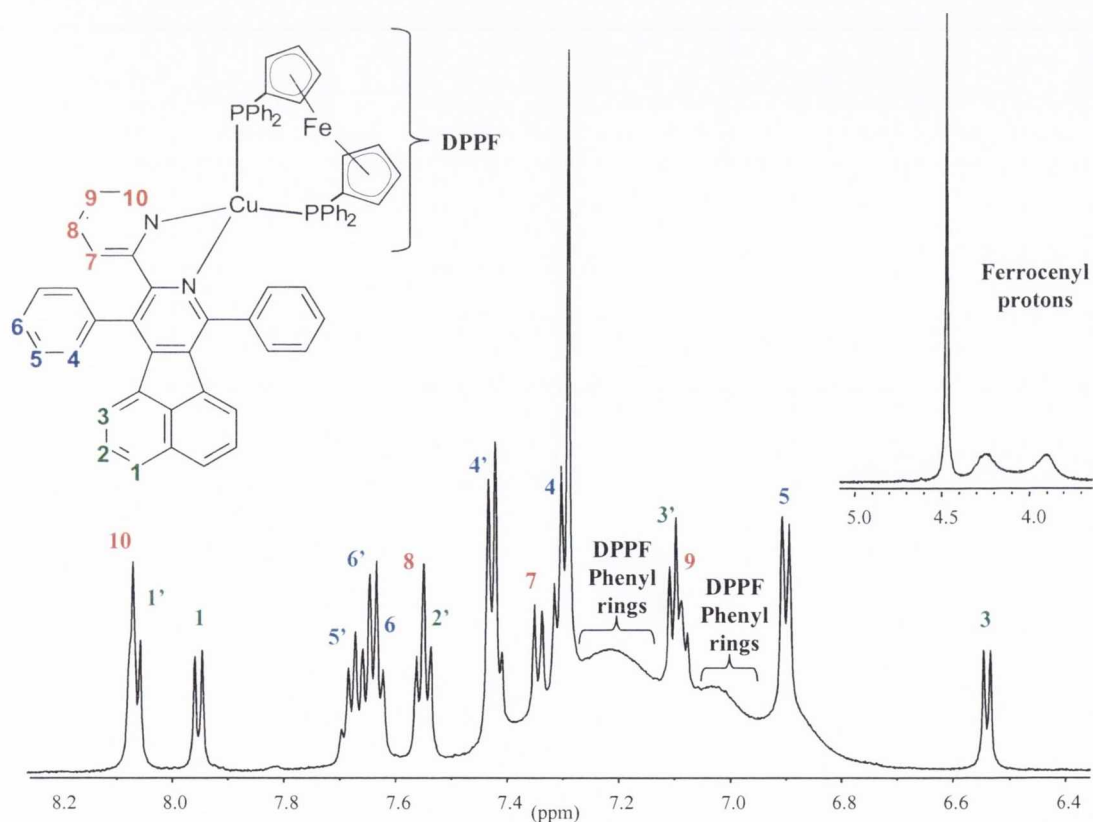


Figure 3.2-17: ^1H NMR spectrum of **21**, (CDCl_3 , 600.1 MHz, R.T.). Atom labelling as per picture inset.

The most downfield of the signals is at δ 8.07 ppm and consists of two overlapping doublets, H10 and H1'. As with all previous complexes H1' is followed closely by H1, a doublet at δ 7.95 ppm. A multiplet spanning the range δ 7.69 – 7.62 ppm integrating for four protons was assigned using the $^1\text{H} - ^1\text{H}$ COSY spectrum as all phenyl ring protons; H5', H6' and H6. A pair of overlapping doublets appears at δ 7.55 ppm and integrates for two protons which can be attributed to H8 and H2'. From Figure 3.2-17 it is clear that there is a large area of overlap in the middle region of the spectrum, this is due to the twenty phenyl ring protons of the dppf ligand that appear as very broad signals. The sharper, more resolved signals can, however, be assigned to azafluoranthene protons using the $^1\text{H} - ^1\text{H}$ COSY spectrum. The first of these signals is a multiplet that has been assigned to H4' and H2 at δ 7.44 – 7.41 ppm. This is followed by another doublet, this time assigned to H7, at δ 7.34 ppm which is immediately followed by a multiplet at δ 7.30 ppm that is attributed to H4. The signals for H3' and H9 appear as a multiplet at δ 7.11 – 7.07 ppm, followed by the signal for H5 at δ 6.90 ppm. The final azafluoranthene signal appears as a doublet at δ 6.54 ppm and is attributed to H3. The ferrocenyl protons appear farther upfield with a singlet that integrates for four protons at δ 4.47 ppm and two broad singlets at δ 4.25 and δ 3.90 ppm that integrate for two protons each.

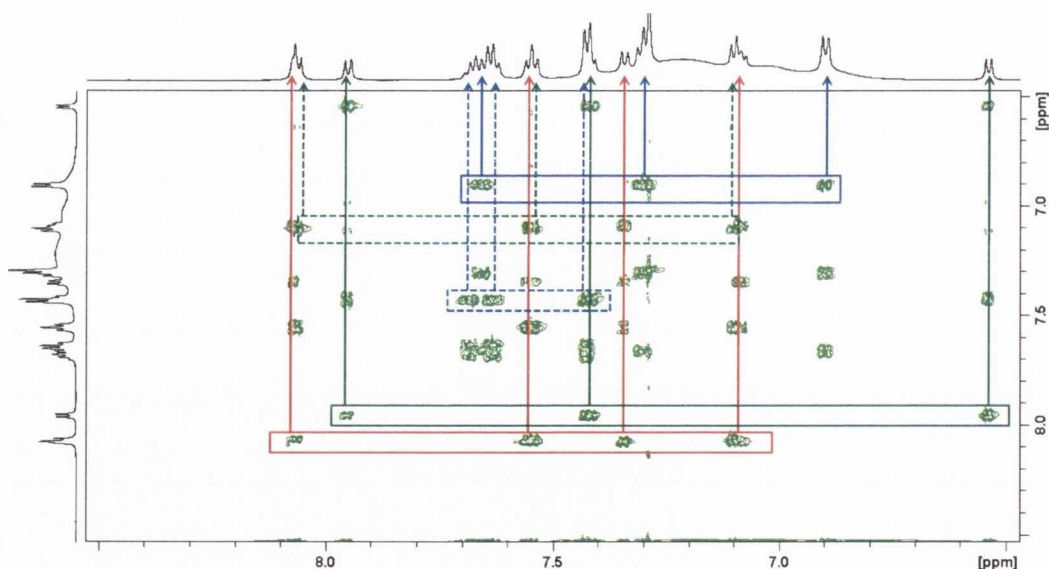


Figure 3.2-18: $^1\text{H} - ^1\text{H}$ COSY experiment of **21** showing the assignment of the various spin systems – pyridyl (red), naphthyl (green) and phenyl (blue).

3.2.6.2 ^{13}C NMR spectrum of **21**

The ^{13}C NMR spectrum of **21** is shown in Figure 3.2-19. The spectrum was assigned using a HSQC experiment. There are a total of twenty-eight azafluoranthene signals in the ^{13}C NMR spectrum and two ferrocenyl carbon signals. The carbons due to the phenyl rings of the dppf ligand are largely absent. Of the twenty-eight azafluoranthene signals, twelve are quaternary carbons and are assigned in full in Figure 3.2-19. Of the remaining C – H signals, the most downfield is C10 at δ 149.1 ppm followed by C8 at δ 136.8 ppm. The signals attributed to C1' (δ 130.5 ppm), C5' (δ 130.1 ppm), C6' (δ 129.9 ppm) and C6 (δ 129.6 ppm) occur in close proximity to each other with only one ppm separating all four signals. The same is true of the signals assigned to C4', C4 and C5 at δ 129.5, δ 129.3 and δ 128.9 ppm respectively. The signal for C1 appears at δ 128.8 ppm, closely followed by those of C2' and C2 at δ 128.2 and δ 128.1. The signal at δ 128.6 ppm does not correspond to an azafluoranthene carbon and therefore can be assumed to be a phenyl ring carbon of the dppf ligand, however no other phenyl ring carbon signals are observed, possibly due to low resolution of the spectrum caused by low solubility of the sample or possible stacking interactions in the solution. C7 and C3' appear at δ 127.3 and δ 126.9 ppm, followed by C3 (δ 125.1 ppm) and C9 (δ 124.4 ppm). The two ferrocenyl carbon signals are observed however, at δ 74.0 and δ 71.7 ppm respectively. The signal at δ 74.0 ppm appears as a triplet as it is split by the phosphorous atoms and can therefore be assigned to the ferrocenyl carbons adjacent to the phosphine fragment of the dppf ligand.

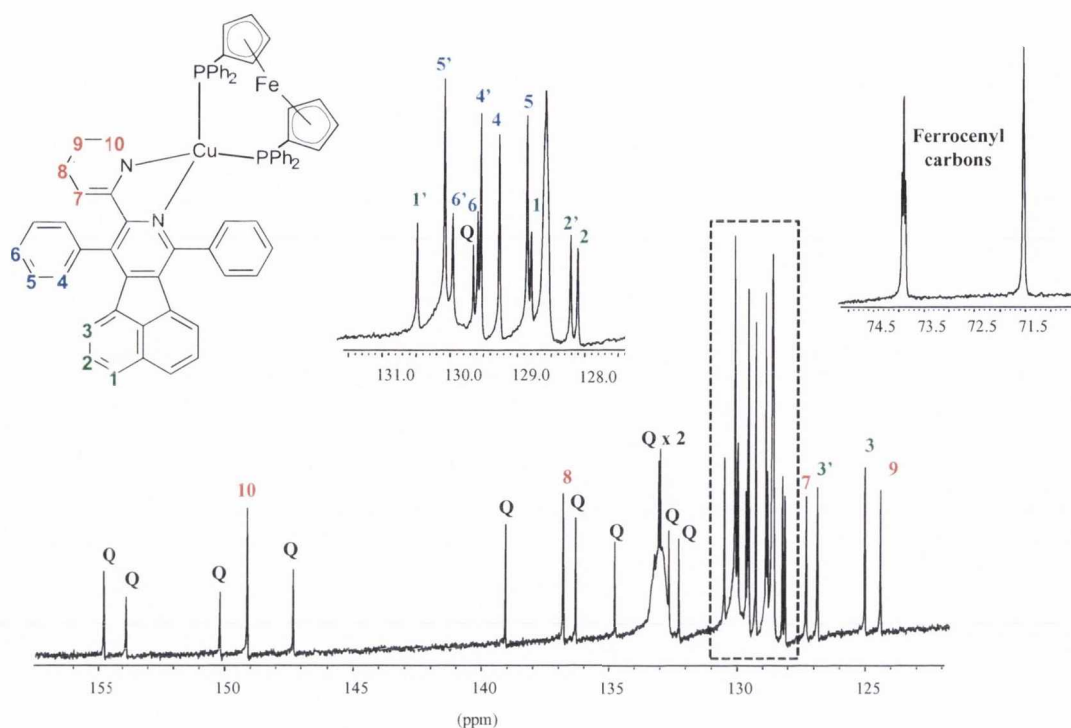


Figure 3.2-19: ^{13}C NMR spectrum of **21**, (CDCl_3 , 600.1 MHz, R.T.). Atom labelling as per picture inset.

3.2.6.3 ^1H NMR spectra of **22** and **23**

The ^1H NMR spectrum of **22** is shown in Figure 3.2-20. The signals are poorly resolved and this could be due to a number of reasons such as the effect of the copper metal centre or the effect of the ferrocene centre on the relaxation time of complex. The addition of the tertiary butyl groups on this compound may also facilitate stacking in solution which could also be a factor in the reduced quality of the NMR data in comparison to **21**. Despite the poor resolution it was still possible to assign the azafluoranthene protons using a $^1\text{H} - ^1\text{H}$ COSY experiment and the patterns observed for the complexes discussed previously.

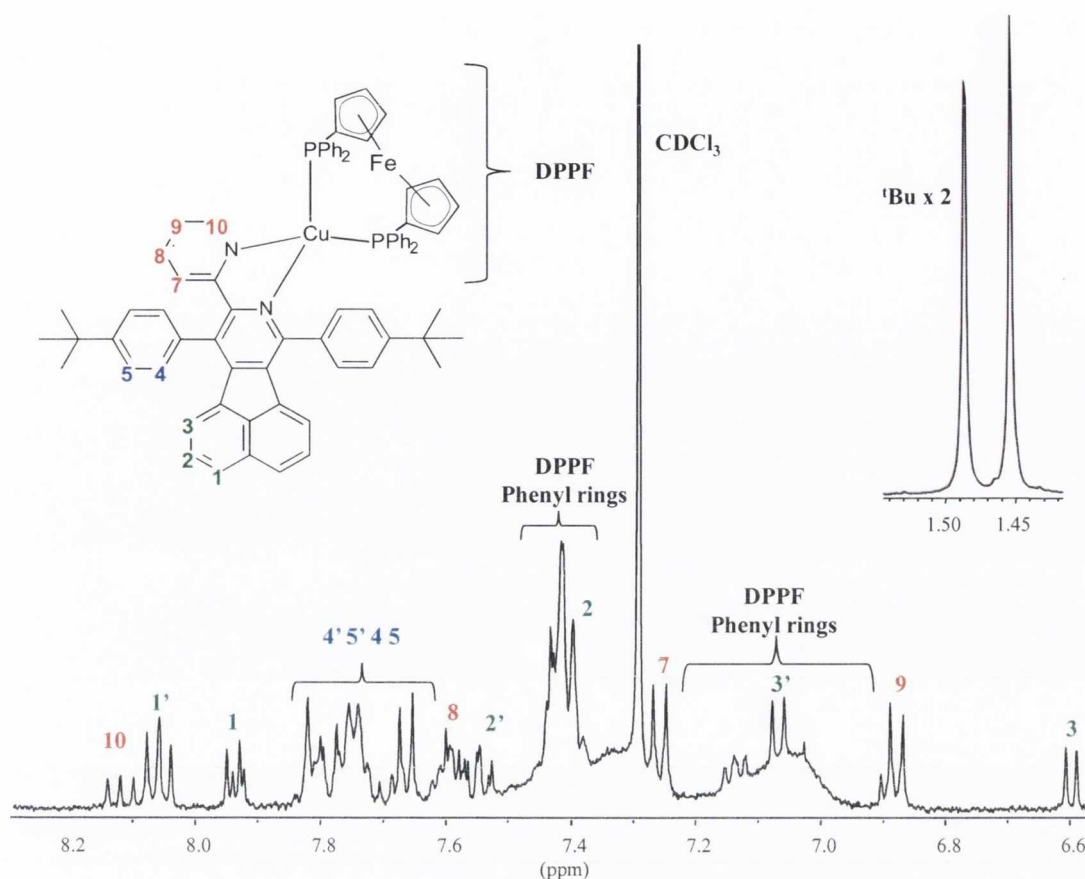


Figure 3.2-20: ^1H NMR spectrum of **22**, (CDCl_3 , 600.1 MHz, R.T.). Atom labelling as per picture inset.

The most downfield signal appears as two overlapping signals over the range δ 8.14 – 8.04 ppm and is assigned to H10 and H1'. H1 also appears as a multiplet at δ 7.95 – 7.92 ppm. This is followed by a large area of overlapping signals to give a large multiplet spanning δ 7.81 – 7.65 ppm that integrates for eight protons, the phenyl ring protons H4', H5', H4 and H5 respectively. Following this is another, smaller, multiplet integrating for two protons at δ 7.62 – 7.52 ppm and is attributed to H8 and H2'. The signal for H2 is buried under the dppf phenyl ring signals which appear as a large multiplet at δ 7.46 – 7.34 ppm. This multiplet integrates for eleven protons, ten of which are due to the protons of the phenyl rings of the dppf ligand. A doublet at δ 7.25 ppm is assigned to H7 and is immediately followed by a second large, broad multiplet spanning the region δ 7.21 – 6.92 ppm that again integrates for eleven protons. This has been assigned to the second pair of dppf phenyl rings and also, from the ^1H – ^1H COSY, to H3'. A doublet at δ 6.88 ppm integrates for one proton and is attributed to H9. The final signal in this region is another doublet at δ 6.59 ppm and is the remaining naphthyl signal H3. The ferrocenyl protons appear as two broad overlapping

signals at δ 4.41, integrating for four protons, and at δ 4.38 ppm, integrating for two protons. This is followed by another broad singlet at δ 4.22 ppm that integrates for two protons. The tertiary butyl protons are found as two singlets at δ 1.49 and 1.45 ppm respectively.

The ^1H NMR spectrum of **23** is shown in Figure 3.2-21. The signals are very poorly resolved due to a number of reasons such as the effect of the copper metal centre or the effect of the ferrocene centre on the relaxation time of complex. Although this was also the case for **21** and **22**, the addition of the trifluoromethyl groups has a significant effect on the resolution of the NMR data and in every case (**17**, **20** and **23**) has made obtaining a good quality ^1H NMR spectrum more difficult. Due to the very poor resolution this complex could only be assigned using the integration values in conjunction with the patterns observed for the complexes discussed previously.

The most downfield signal appears at δ 8.5 ppm and integrates for one proton and is tentatively assigned as H10 as this follows the pattern of **21** and **22**. This is followed by a number of very poorly resolved peaks that are thought to be H4', H1 and H1' as this again follows the patterns set by the previous complexes containing a dppf ligand. A large portion of the spectrum cannot be clearly assigned but contains the remaining phenyl ring signals H5', H4 and H5, as well as the naphthyl signals H2' and H2. The pyridyl signals H8 and H7 are also buried in this region along with the four phenyl rings of the dppf ligand. The doublet at δ 6.8 ppm is assigned as H3', and is followed by a broad multiplet at 6.7 ppm that integrates for one proton; the remaining pyridyl proton H9. The final signal in this region of the spectrum is a doublet at 6.6 ppm and is assigned to H3. The ferrocenyl protons appear at δ 4.5, δ 4.2 and δ 3.9 ppm but are very poorly resolved.

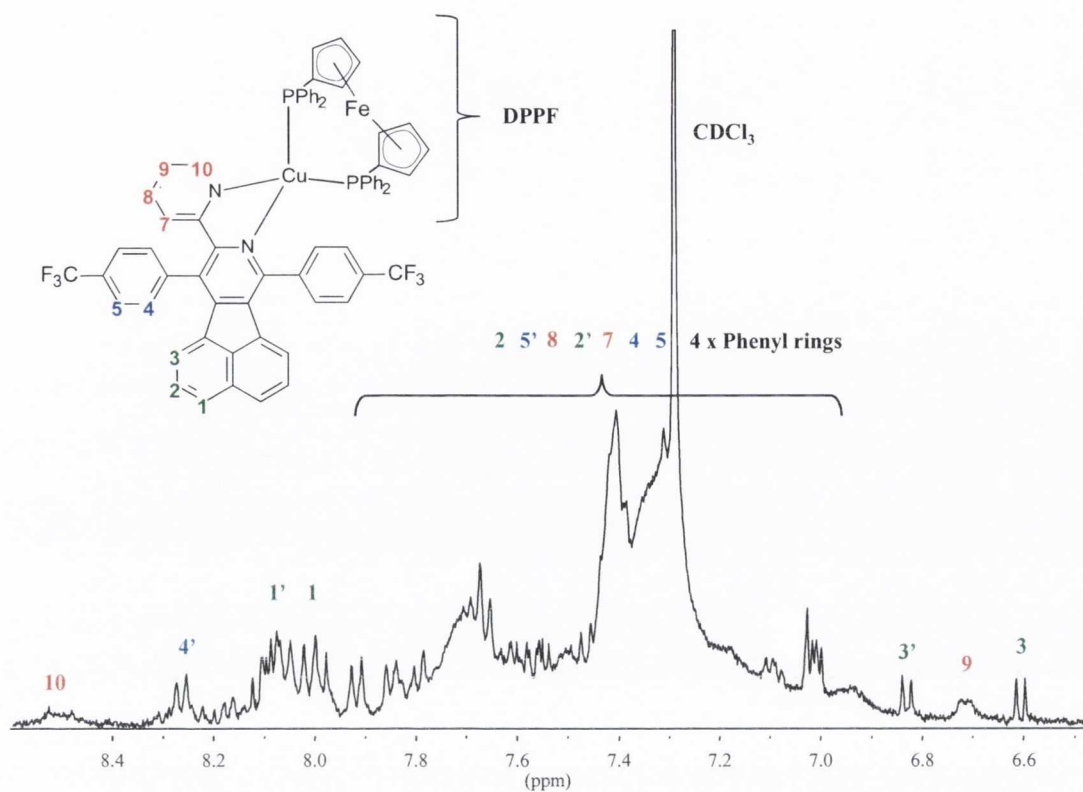


Figure 3.2-21: Poorly resolved ^1H NMR spectrum of **23**, (CDCl_3 , 600.1 MHz, R.T.). Atom labelling as per inset.

Attempts to obtain a high resolution ^{13}C NMR spectrum for **22** and **23** were unsuccessful.

3.2.7 Mass spectrometry

Each complex was characterised by mass spectrometry and the results are summarised in Table 3.2-2.

Table 3.2-2: ESI⁺/MALDI mass spectra results for complexes 15 to 23

Complex	Formula	Calculated Mass	Mass
15	C ₆₄ H ₄₀ CuN ₄	927.2549 m.u.	927.2545 m.u. for [M+H] ⁺ (ESI ⁺)
16	C ₈₀ H ₇₂ CuN ₄	1151.5053 m.u.	1151.5105 m.u. for [M] ⁺ (MALDI)
17	C ₆₈ H ₃₆ CuF ₁₂ N ₄	1199.2144 m.u.	1199.2131 m.u. for [M] ⁺ (MALDI)
18	C ₇₁ H ₅₂ CuN ₂ OP ₂	1073.2851 m.u.	1073.2844 m.u. for [M] ⁺ (ESI ⁺)
19	C ₇₉ H ₇₀ CuN ₂ OP ₂	1185.4103 m.u.	1185.4131 m.u. for [M] ⁺ (MALDI)
20	C ₇₃ H ₅₀ CuF ₆ N ₂ OP ₂	1209.2599 m.u.	1209.2581 m.u. for [M] ⁺ (MALDI)
21	C ₆₆ H ₄₈ CuFeN ₂ P ₂	1049.1938 m.u.	1049.1934 m.u. for [M] ⁺ (ESI ⁺)
22	C ₇₄ H ₆₄ CuFeN ₂ P ₂	1161.3190 m.u.	1161.3192 m.u. for [M] ⁺ (MALDI)
23	C ₆₈ H ₅₆ CuF ₆ FeN ₂ P ₂	1196.2468 m.u.	1196.2451 m.u. for [M] ⁺ (MALDI)

3.3 UV-Visible absorption spectra

The UV-Visible absorption spectra of each of the complexes **15** - **23** were recorded in dichloromethane using 1×10^{-5} M solutions. The spectra are first discussed in groups according to the azafluoranthene ligand they contain and as such the spectra of each compound containing ligand **6** will be discussed, followed by those containing ligand **9** and finally those containing ligand **10**. Subsequently, the spectra will be grouped according to type i.e. the homoleptic complexes are compared and discussed followed by the heteroleptic complexes which are further divided by auxiliary ligand into the xantphos containing ligands and the dppf containing ligands.

As for the Cu(I) phenanthroline based complexes described in the literature, the UV region of each of the spectra are dominated by ligand-centred (LC) bands arising from spin-allowed π - π^* transition. The visible region hosts the metal to ligand charge

transfer bands that have been assigned to $[d(\text{Cu}) \rightarrow (\text{N}^{\wedge}\text{N})]$ transitions and all exhibit typical MLCT extinction coefficients (Table 3.3-1).

Table 3.3-1: Room temperature UV-Visible spectral data for complexes 15 - 23 in CH_2Cl_2 (10^{-5}M)

Compound	λ_{max} [nm] ($\epsilon \text{ M}^{-1}\text{cm}^{-1}$)
15	226 (36,010), 246 (29,920), 297 (18,6400), 328 _{sh} (10,300), 382 (16,930), 536 (2,760)
16	227 (28,640), 252 (23,920), 288 _{sh} (15,210), 307 _{sh} (12,610), 346 (6,600), 399 (11,890), 417 _{sh} (10,020), 521 (950)
17	227 (76,130), 250 (59,650), 282 (41,390), 311 _{sh} (32,870), 329 _{sh} (22,850), 392 (33,160), 533 (3,680)
18	226 (40,980), 252 (28,780), 276 (21,900), 331 _{sh} (7,740), 392 (8,460), 451 _{sh} (2,280)
19	226 (30,620), 249 (22,980), 273 (16,960), 293 _{sh} (13,900), 332 _{sh} (5,905), 395 (6,360), 419 _{sh} (5,190), 449 _{sh} (1,650)
20	226 (61,020), 278 (29,920), 329 _{sh} (9,920), 390 (8,030), 451 (3,060)
21	227 (42,220), 253 _{sh} (27,700), 273 (19,590), 308 (13,230), 331 (8,990), 395 (8,810), 465 _{sh} (1,390)
22	227 (130,110), 252 (96,380), 311 (45,890), 332 _{sh} (33,560), 399 (27,850), 421 _{sh} (24,200), 460 _{sh} (6,100).
23	226 (150,810), 249 (106,020), 281 (67,770), 312 (49,470), 331 (35,980), 386 (33,570), 413 _{sh} (22,390), 457 (7,650)

3.3.1 UV-Visible absorption spectra of 6, 15, 18 and 21

Figure 3.3-1 shows the UV-Visible absorption spectra of the free ligand **6** and its three copper (I) complexes; the homoleptic complex **15** and the two heteroleptic complexes **18** and **21**.

The absorption spectra of the free ligand (**6**) and the three complexes (**15**, **18** and **21**) all feature a strong band centred between 330 – 420 nm. This band is attributed to the fluoranthene core of the ligands and is present throughout each of the spectra. This band becomes broader and red shifted on complexation, shifting from 373 nm for **6** to 384 nm for the homoleptic copper(I) complex **15**. There is a further shift in the heteroleptic copper(I) complexes, with **18** shifting to 395 nm and **21** to 398 nm.

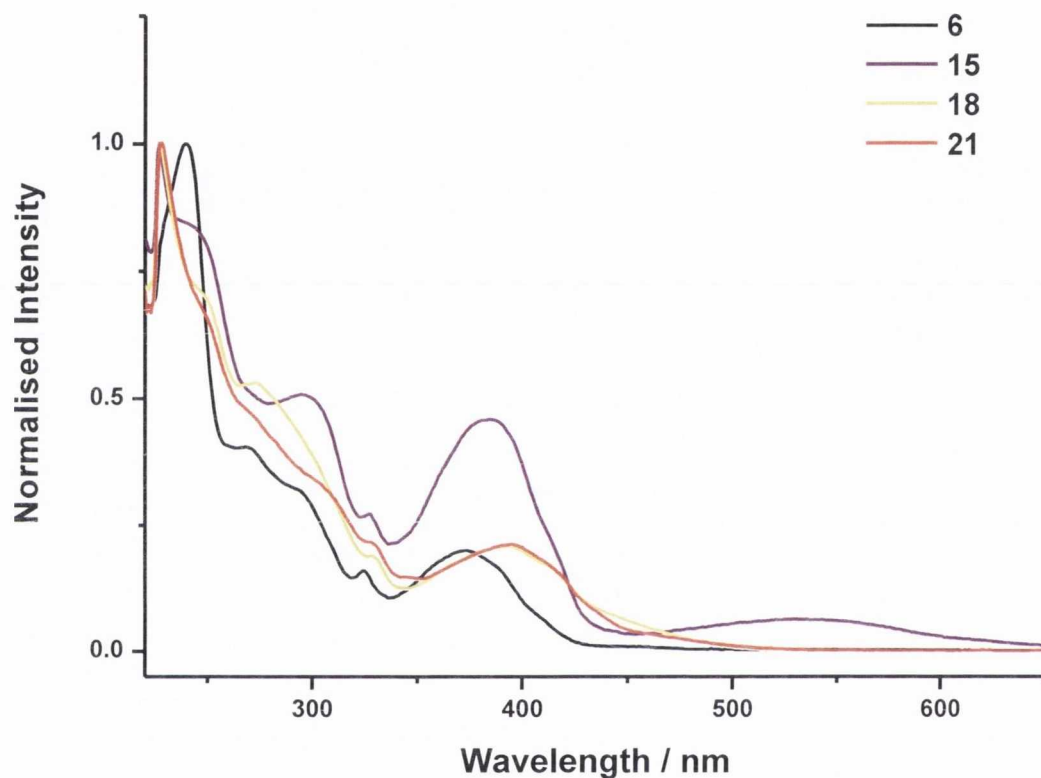


Figure 3.3-1: UV-Visible absorption spectra of complexes **6**, **15**, **18** and **21** in CH_2Cl_2 at $1 \times 10^{-5} \text{ M}$ concentration.

The band at 540 nm for **15** has been assigned to a spin-allowed metal to ligand charge transfer (MLCT) transition and has an extinction coefficient of $\epsilon \sim 2600 \text{ M}^{-1} \text{ cm}^{-1}$ which is typical of metal complexes of this nature. This MLCT band is more pronounced in the homoleptic complex with the MLCT bands for the heteroleptic complexes appearing as shoulders at 451 and 465 nm respectively. This blue shift relative to the homoleptic copper(I) complex is due to the incorporation of the phosphine ligands. Though the phosphine ligands are not directly involved in the MLCT, their electron withdrawing ability results in the shift to higher energies.^{135,136} The MLCT bands are also responsible for the purple (**15**) and yellow (**18** and **21**) colours of the complexes.

3.3.2 UV-Visible absorption spectra of **9**, **16**, **19** and **22**

Figure 3.3-2 shows the UV-Visible absorption spectra of the free ligand **9** and its three copper (I) complexes; the homoleptic complex **16** and the two heteroleptic complexes **19** and **22**. The absorption spectra of the free ligand (**9**) and the three complexes (**16**, **19** and **22**) again feature the strong fluoranthene absorption band centred between 330 – 420 nm. This band becomes broader and red shifted on complexation, shifting from 380 nm for **9** to 399 nm for the homoleptic copper(I) complex **16**, to 395 nm for the heteroleptic copper(I) complex **19** and to 396 nm for the second heteroleptic copper(I) complex **22**.

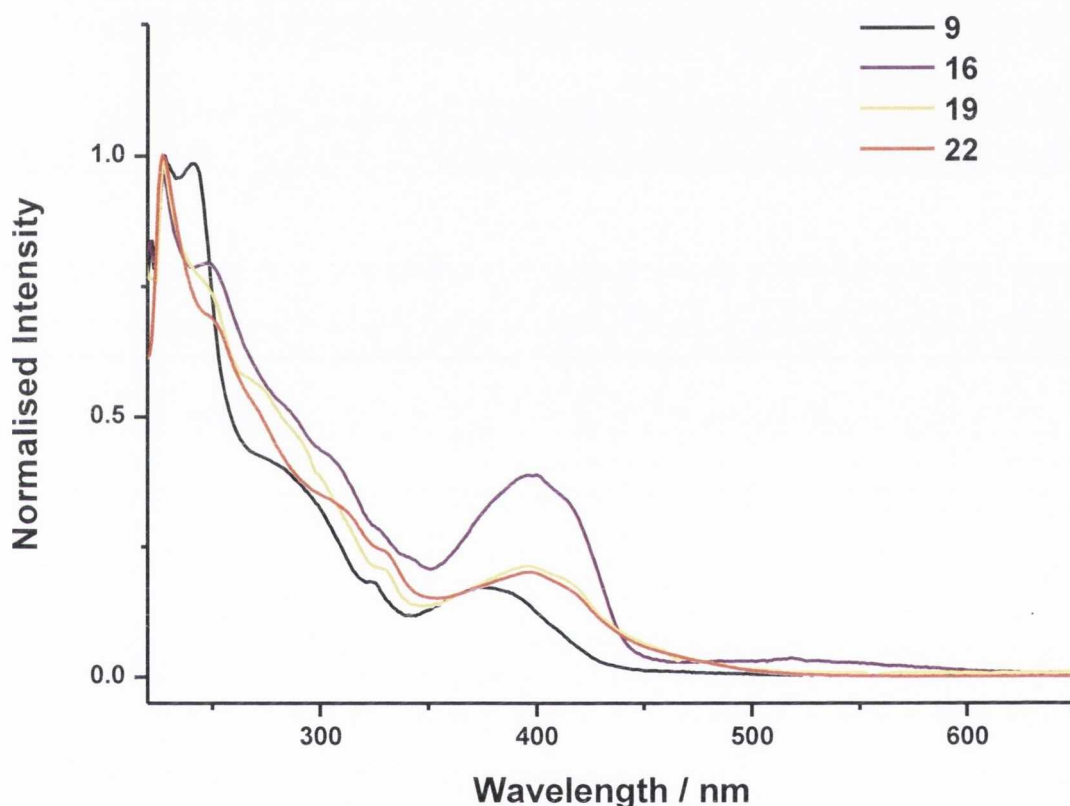


Figure 3.3-2: UV-Visible absorption spectra of complexes **9**, **16**, **19** and **22** in CH_2Cl_2 at $1 \times 10^{-5} \text{ M}$ concentration.

The main MLCT band is more pronounced for the homoleptic copper(I) complex **16** than it is for the heteroleptic complexes. It appears as a band at 521 nm. The MLCT bands of **19** and **22** appear as broad shoulders at 449 and 460 nm respectively, again the blue shift relative to **16** is due to the electron withdrawing ability of the phosphine ligands shifting the absorption to higher energies.¹³⁷

3.3.3 UV-Visible absorption spectra of **10**, **17**, **20** and **23**

Figure 3.3-3 shows the UV-Visible absorption spectra of the free ligand **10** and its three copper (I) complexes; the homoleptic complex **17** and the two heteroleptic complexes **20** and **23**. The strong fluoranthene absorption band centred between 340 – 450 nm is once again a feature of the spectra of the free ligand and each of the complexes. This band becomes broader and red shifted on complexation, shifting from 358 nm for **10** to 392 nm for the homoleptic copper(I) complex **17**, to 390 nm for the heteroleptic copper(I) complex **20** and to 386 nm for the second heteroleptic copper(I) complex **23**.

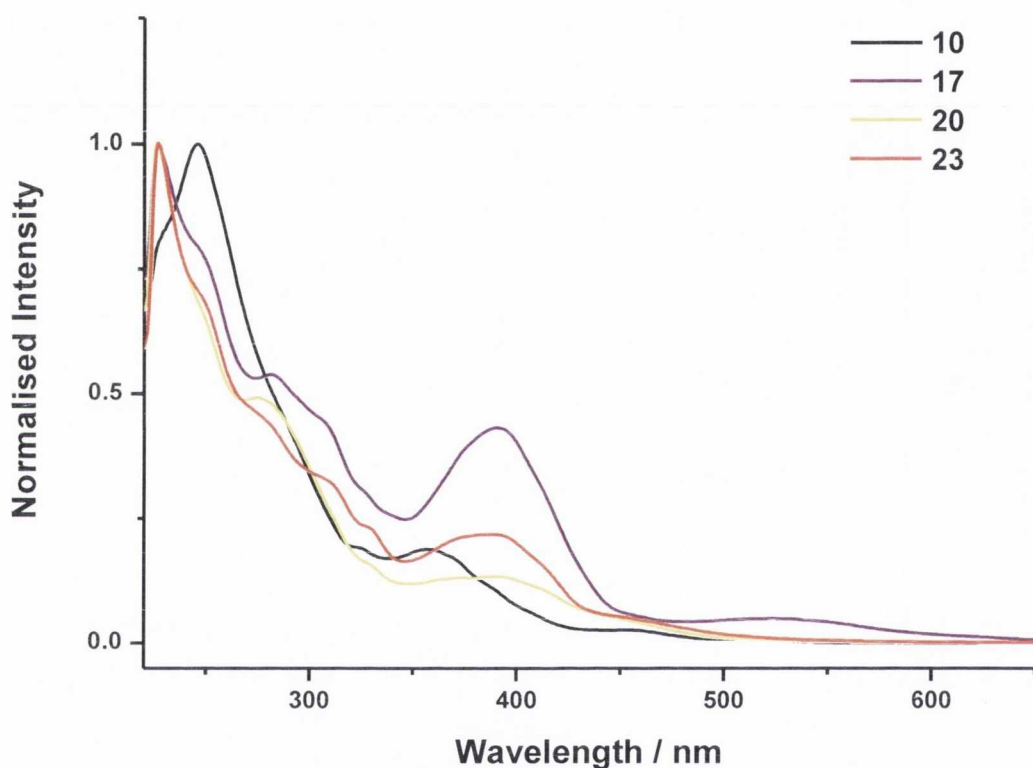


Figure 3.3-3: UV-Visible absorption spectra of complexes **10**, **17**, **20** and **23** in CH_2Cl_2 at $1 \times 10^{-5} \text{ M}$ concentration.

The band at 533 nm for **17** is the spin-allowed metal to ligand charge transfer (MLCT) transition that has been observed for the previous homoleptic complexes and has an extinction coefficient of $\epsilon \sim 3,700 \text{ M}^{-1} \text{ cm}^{-1}$ which is, again, typical of metal complexes of this nature. This MLCT band is more pronounced in the homoleptic complex with these bands appearing as shoulders at 451 (**20**) and 457 (**23**) nm respectively. This blue

shift relative to the homoleptic copper(I) complex is due to the incorporation of the phosphine ligands.^{135,136}

3.3.4 UV-Visible absorption spectra of the homoleptic complexes **15**, **16** and **17**

Figure 3.3-4 shows the UV-Visible spectrum of each of the homoleptic copper(I) complexes of the ligands **6**, **9** and **10**. By directly comparing the absorption spectra of the three homoleptic complexes it is possible to see the effects, if any, that ligand substituents have. The ligand-centred bands in the UV region of the spectrum are affected by the different substituents of the peripheral phenyl rings of the ligands.

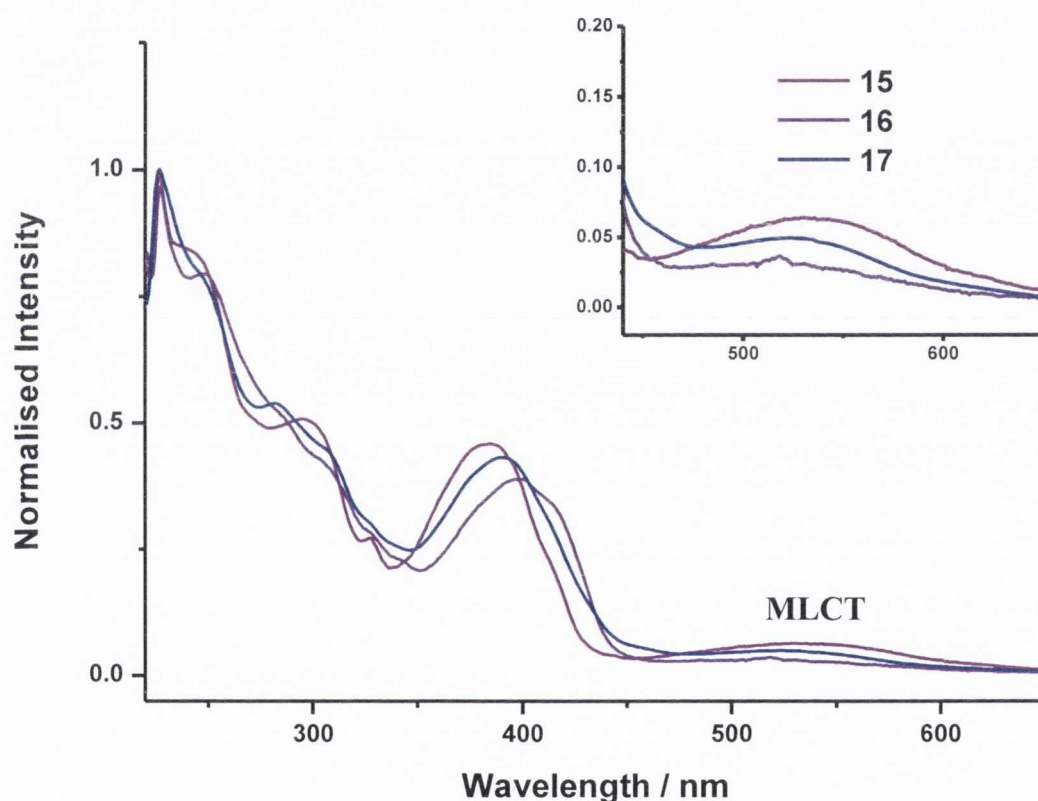


Figure 3.3-4: UV-Visible absorption spectra of complexes **15**, **16** and **17** in CH_2Cl_2 at 10^{-5} M concentration. The enlarged portion of the spectra shows the MLCT band.

15 is taken as the archetypal compound as it bears no phenyl substituents. The strong fluoranthene π - π^* band is centred at 382 nm, whereas those of the tertiary butyl substituted **16** and trifluoromethyl substituted **17** are red shifted to 399 and 392 nm respectively. As expected, the electron donating tertiary butyl groups of **16** induce a red shift due to the increase in electron density on the HOMO which results in a destabilisation of the orbital and a smaller HOMO-LUMO gap than **15**. The red shift

for **17** is more surprising as the incorporation of electron withdrawing groups usually works to lower the energy of the HOMO resulting in a larger HOMO-LUMO gap and a shift to higher energies. This red shift can therefore be attributed to π -stacking interactions of the complex. The MLCT bands are also affected by the ligand substituents, with both **16** (521 nm) and **17** (533 nm) experiencing small blue shifts compared to **15** (536 nm). These shifts are possibly due to the effect of the bulky tertiary butyl, and trifluoromethyl groups on the copper centre.

3.3.5 UV-Visible absorption spectra of the heteroleptic complexes **18**, **19** and **20**

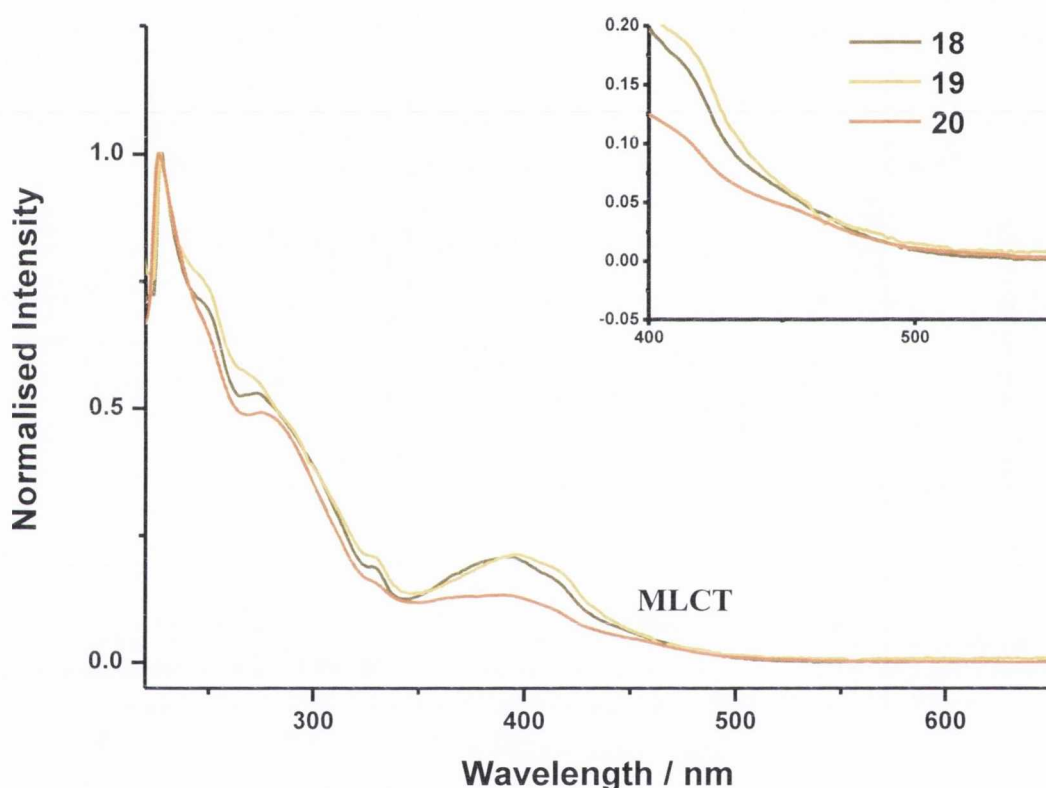


Figure 3.3-5: UV-Visible absorption spectra of complexes **18**, **19** and **20** in CH_2Cl_2 at 10^{-5} M concentration. The enlarged portion of the spectra shows the MLCT band.

Figure 3.3-5 shows the UV-Visible spectrum of each of the heteroleptic copper(I) xantphos complexes of the ligands **6**, **9** and **10**. The ligand-centred bands in the UV region of the spectrum are affected to less of a degree by the different substituents of the peripheral phenyl rings of the ligands than the homoleptic complexes. The fluoranthene centred $\pi-\pi^*$ band for each of the complexes follows the expected trend observed for the free azafluoranthene ligands; **19** is red shifted compared to **18** due to

the inclusion of the electron donating tertiary butyl groups that act to destabilise the HOMO and therefore lower the HOMO-LUMO gap, resulting in a shift to lower energy, while **20** experiences a small blue shift caused by the electron withdrawing trifluoromethyl groups that stabilize the HOMO resulting in a shift to higher energy. The incorporation of the phosphine ligand resulted in a large blue shift of the MLCT band compared to the homoleptic complexes, with the new MLCT bands appearing as shoulders of the more intense fluoranthene centred absorption band.

3.3.6 UV-Visible absorption spectra of the heteroleptic complexes **21**, **22** and **23**

Figure 3.3-6 shows the UV-Visible spectrum of each of the heteroleptic copper(I) dppf complexes of the ligands **6**, **9** and **10**.

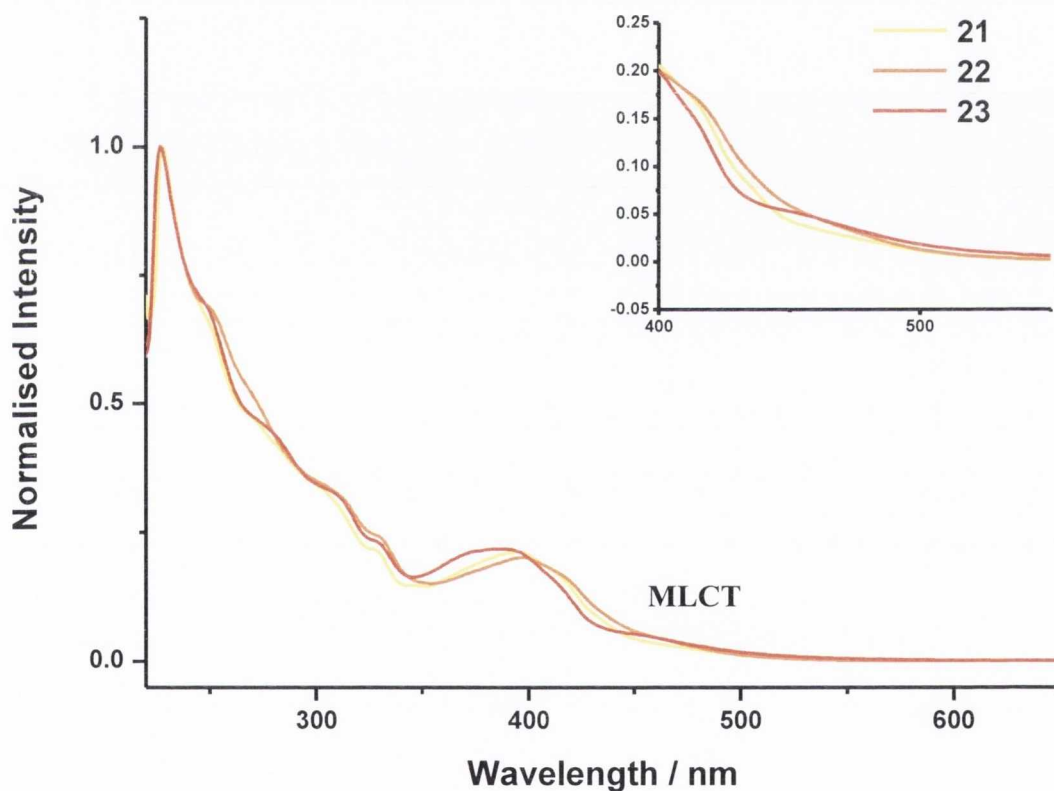


Figure 3.3-6: UV-Visible absorption spectra of complexes **21**, **22** and **23** in CH_2Cl_2 at 10^{-5} M concentration. The enlarged portion of the spectra shows the MLCT band.

The ligand-centred bands in the UV region of the spectrum are largely unaffected by the different substituents of the peripheral phenyl rings of the ligands. As with the heteroleptic Cu(I) xantphos complexes, the fluoranthene centred π - π^* band for each of

the complexes follows the expected trend observed for the free azafluoranthene ligands; **22** is red shifted compared to **21** due to the inclusion of the electron donating tertiary butyl groups that act to destabilise the HOMO and therefore lower the HOMO-LUMO gap, resulting in a shift to lower energy, while **23** experiences a small blue shift caused by the electron withdrawing trifluoromethyl groups that stabilize the HOMO resulting in a shift to higher energy. Again, as with the Cu(I) xantphos complexes, the incorporation of the phosphine ligand resulted in a large blue shift of the MLCT band compared to the homoleptic complexes, with the new MLCT bands appearing as shoulders of the more intense fluoranthene centred absorption band.

3.4 Electrochemical properties of complexes 15-23

Cyclic voltammetric (CV) studies were carried out on 1 mM solutions of the complexes **15** - **23**. The results are summarised in Table 3.4-1. Cyclic voltammograms were carried out using a Ag/AgCl electrode as reference electrode, a Pt wire counter electrode and a glassy carbon working electrode.

Table 3.4-1: Electrochemical data for complexes **15-23** in CH_2Cl_2 at 298 K

Compound	Oxidation $E_{\text{pa}}/\text{V}^{\text{a}}$	Oxidation $E_{1/2}/\text{V}[\Delta E_{\text{p}}/\text{mV}]$	Reduction $E_{\text{p}}/\text{V}^{\text{b}}$	Reduction $E_{1/2}/\text{V}[\Delta E_{\text{p}}/\text{mV}]$
15		+0.48 [105]	-1.38, -1.53	
16		+0.50 [117]	-1.32, -1.54	-1.67 [70]
17		+0.64 [99]	-1.41	-1.23 [74]
18	+0.87	+1.28 [70]	-1.33	
19	+0.85	+1.32 [10]	-0.89	-1.34 [88], -1.62 [64]
20	+0.62, +1.36,	-	-0.79	-1.23 [83]
21	+0.76, +1.56,	-	-1.33	-1.64 [58]
22	+0.49, +0.81, +1.64	-	-1.34	-1.62 [80]
23	+0.54, +1.58	+0.83 [60]	-1.24	-1.55 [84]

^a Irreversible/quasi reversible oxidation process, E_{pa}/V (anodic peak potential) quoted; ^b Irreversible/quasi reversible reduction process, E_{p}/V (cathodic peak potential) quoted; scan rate = 0.1 Vs^{-1} .

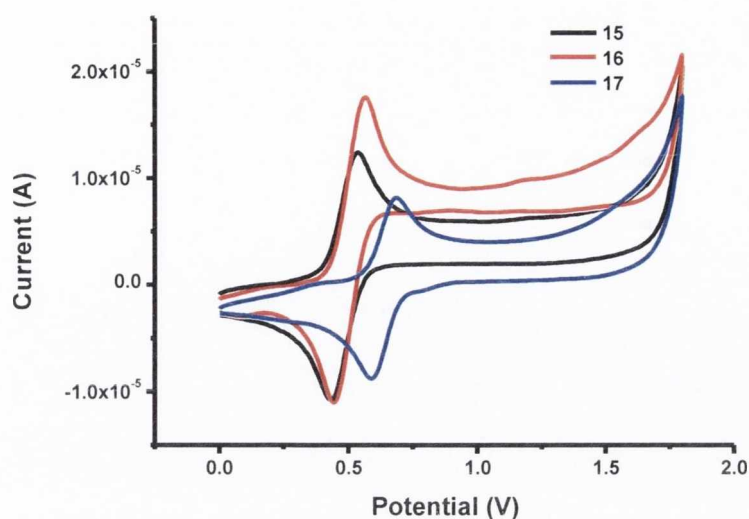


Figure 3.4-1: Cyclic voltammograms of complexes **15**, **16** and **17** showing the oxidation process. (1 mM in CH_2Cl_2 , vs. Fc/Fc^+)

Figure 3.4-1 shows the oxidation process for each of the homoleptic Cu(I) complexes **15**, **16** and **17**. Each of the complexes exhibit a reversible one-electron process assigned to the oxidation of the metal centre as has been reported previously for homoleptic Cu(I) bis(phenanthroline) complexes.¹⁴⁴ The oxidation of Cu(I) to Cu(II) is accompanied by the “flattening” rearrangement from the pseudotetrahedral geometry to a distorted square planar one and as this has been shown to be strongly affected by bulky substituents.¹⁴³ The relatively low potentials at which oxidation occurs in these systems suggests that the bulk of the substituents is not sufficient to prevent exciplex formation, with only marginally higher potentials required for oxidation of **16** and **17**.

Figure 3.4-2 shows the reduction process for each of the homoleptic Cu(I) complexes **15**, **16** and **17**. All three complexes exhibit similar reduction processes with **17** being the most easily reduced with a reversible reduction with a small peak potential of 74 mV that is indicative of a kinetically reversible oxidation process. **16** also displays a reversible oxidation (-1.67 V) with the remainder of the processed being quasi-reversible.

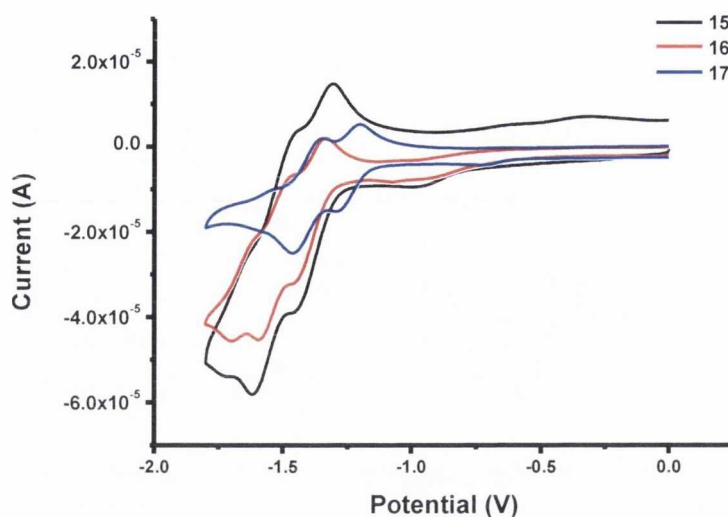


Figure 3.4-2: Cyclic voltammograms of complexes **15**, **16** and **17** showing the reduction process. (1 mM in CH_2Cl_2 , vs. Ag/AgCl)

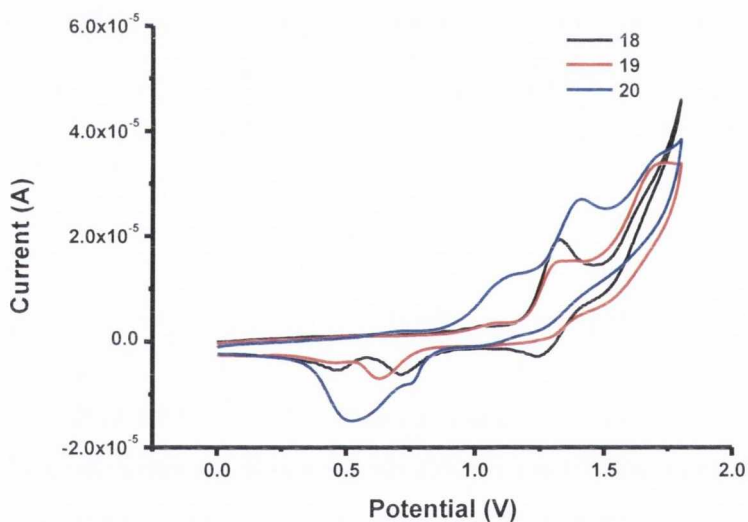


Figure 3.4-3: Cyclic voltammograms of complexes **18**, **19** and **20** showing the oxidation process. (1 mM in CH_2Cl_2 , vs. Ag/AgCl)

Figure 3.4-3 shows the oxidation process for each of the heteroleptic Cu(I) xantphos complexes **18**, **19** and **20**. The first oxidation process occurs at a higher potential for these systems than for their homoleptic counterparts. This is because the electron withdrawing effect of the phosphine unit on the metal centre tends to disfavour the $\text{Cu(I)} \rightarrow \text{N-N}$ electron donation and this is reflected by the higher oxidation potential

(and the blue shift of the MLCT in the absorption spectra) compared to the homoleptic complexes.

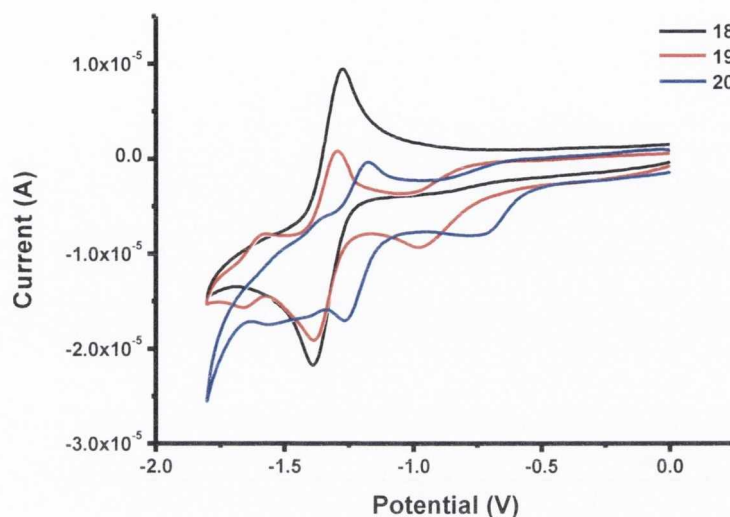


Figure 3.4-4: Cyclic voltammograms of complexes **18**, **19** and **20** showing the reduction process. (1 mM in CH_2Cl_2 , vs. Ag/AgCl)

Figure 3.4-4 shows the reduction process for each of the heteroleptic Cu(I) xantphos complexes **18**, **19** and **20**. The electron donating and electron withdrawing substituents of the azafluoranthene ligand have a significant effect on the reduction processes. **18**, with the unsubstituted azafluoranthene ligand only exhibits one quasi reversible reduction whereas the reduction processes for **19** (tertiary butyl substituted azafluoranthene ligand) and **20** (trifluoromethyl substituted azafluoranthene ligand) are more complex, with one quasi reversible and two reversible processes observed for **19**, and one non reversible followed by one reversible process for **20**.

Figure 3.4-5 shows the oxidation process for each of the heteroleptic Cu(I) xantphos complexes **21**, **22** and **23**. The Fc/Fc^+ oxidation process occurs between 0.76 – 0.83 V for each of the complexes, values similar to those reported for heteroleptic Cu(I) complexes containing phenanthroline-type and dppf ligands and those of the Cu(I)/Cu(II) occurring at significantly more positive potentials of between 1.56 – 1.64 V.¹⁴⁵ The phosphine ligand is again a contributing factor to the higher oxidation potential.

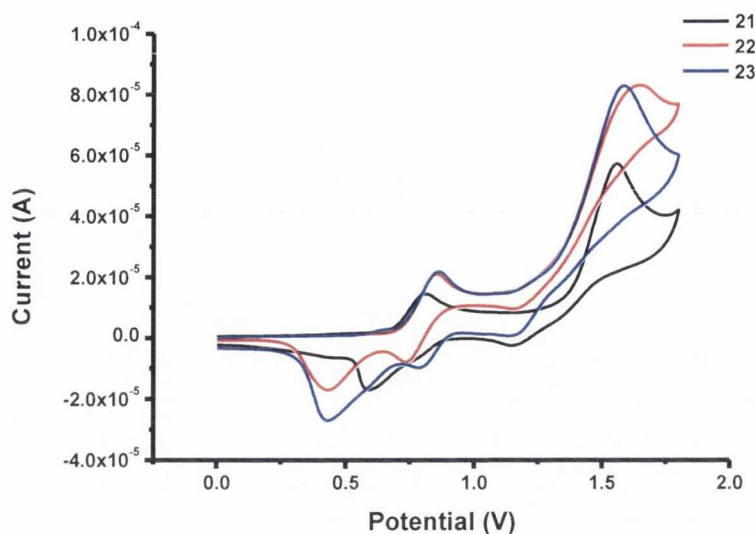


Figure 3.4-5: Cyclic voltammograms of complexes **21**, **22** and **23** showing the oxidation process. (1 mM in CH_2Cl_2 , vs. Fc/Fc^+)

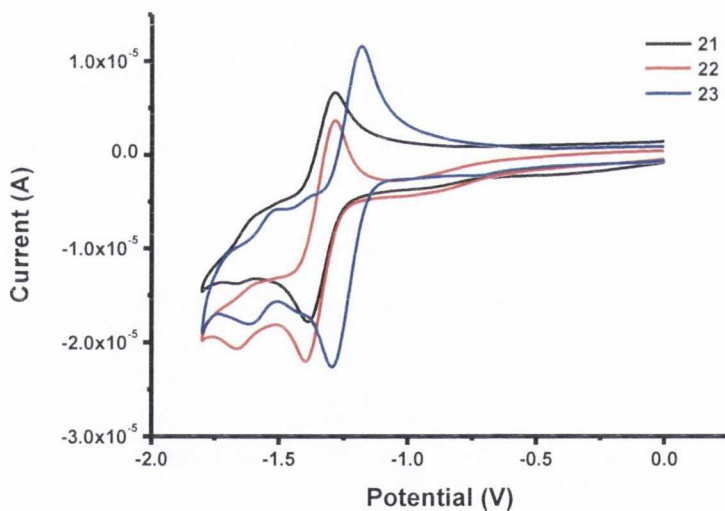


Figure 3.4-6: Cyclic voltammograms of complexes **21**, **22** and **23** showing the reduction process. (1 mM in CH_2Cl_2 , vs. Ag/AgCl)

Figure 3.4-6 shows the reduction process for each of the heteroleptic Cu(I) xantphos complexes **21**, **22** and **23**. Each complex exhibits a quasi reversible reduction followed by a fully reversible reduction and again the electron donicity of the substituents of the azafluoranthene ligands plays a small role, with the reduction potential of the trifluoromethyl azafluoranthene ligand complex being the easiest to reduce.

3.5 Emission properties of the complexes 15-20

The photoluminescent properties of each of the six Cu(I) complexes **15-20** are discussed. The Cu(I) dppf complexes are non-emissive due to the ferrocene metal centre which acts to quench the luminescence, and as a result these complexes will not be discussed further. The results are summarised in Table 3.5-1.

Table 3.5-1: Emission data for complexes **15-20** in air-equilibrated CH_2Cl_2 (10^{-5} M) at 298 and 77K.

Compound	Temp. (K)	λ_{em} [nm] (λ_{exc} [nm])	τ [μs] (λ_{em} [nm] λ_{exc} [nm])
15	298	450 _{max} , 473 (360)	-
	77	406 _w , 457 _{max} , 488, 545 _w (360)	-
16	298	452 _{max} , 476 (360)	-
	77	410 _w , 432 _{max} , 472 _{sh} , 581 (360)	-
17	298	452 _{max} , 472 (360)	-
	77	430, 458 _{max} , 482 (360)	-
18	298	453 _{max} , 474 (360)	-
	77	482 _w , 572 _{max} , 621 (360)	2.1 (19%), 18.5 (81%) (370/572) 2.7 (18%), 29.3 (82%) (370/621)
19	298	450 _{max} , 476 _{sh} , 669 _w (360)	-
	77	432 _w , 571 _{max} , 623, 685 _w (360)	1.1 (12%), 12.9 (88%) (370/570) 1.0 (7%), 9.9 (93%) (370/622)
20	298	403 _w , 451, 484 _{max} (360)	-
	77	459 _{max} , 484, 586 _w , 685 _w (360)	0.64 (28%), 4.9 (72%) (370/484)

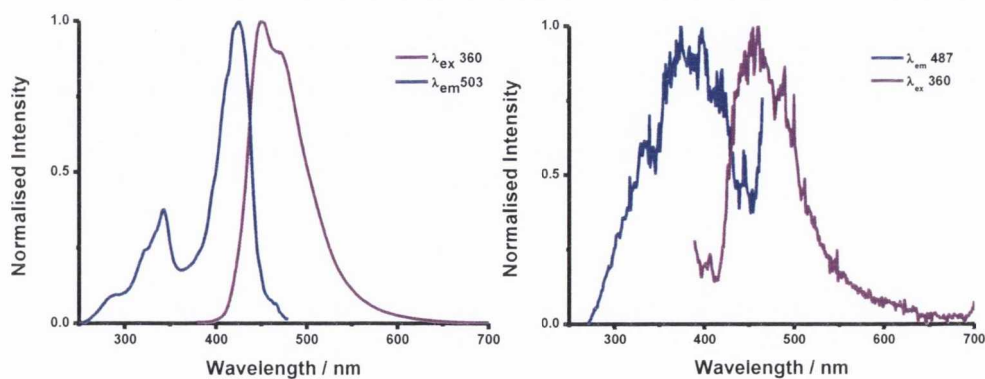


Figure 3.5-1: Normalised excitation and emission spectra of **15** at 10^{-5} M concentration in CH_2Cl_2 at 298 (left) and 77(right) K.

Figure 3.5-1 shows the excitation and emission spectra of **15** at room and low temperatures in air-equilibrated solution. At room temperature the emission maximum is centred at 450 nm which is similar to that of the free ligand **6** suggesting that the metal centre does not exert a strong effect on the emission processes. On going to low temperature a red shift is observed which can be attributed to aggregation effects. The unremarkable emission from this complex is a suggestion that oxygen quenching is a factor or that exciplex formation has occurred.

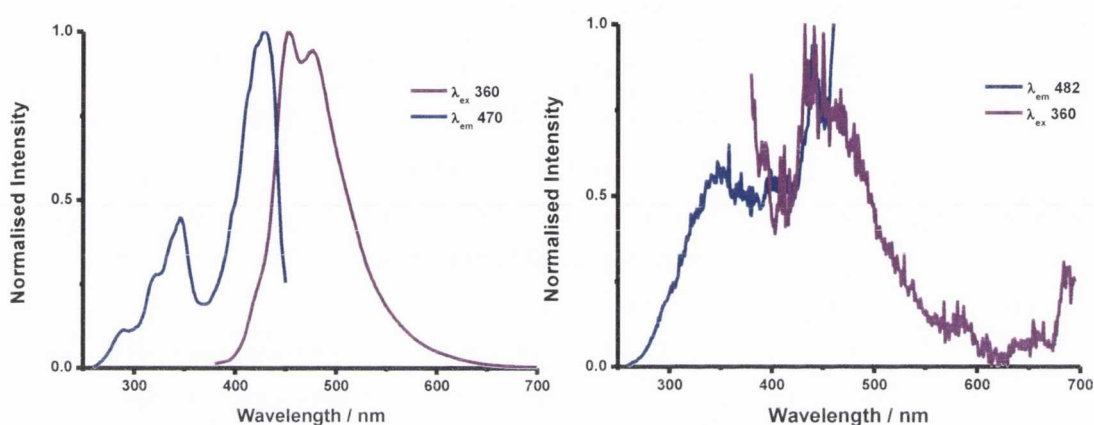


Figure 3.5-2: Normalised excitation and emission spectra of **16** at 10^{-5} M concentration in CH_2Cl_2 at 298 (left) and 77(right) K.

Figure 3.5-2 shows the excitation and emission spectra of **16** at room and low temperatures in air-equilibrated solution. At room temperature the emission maximum is centred at 452 nm which is slightly blue shifted when compared to the free ligand **9** suggesting that the metal centre does not exert a very strong effect on the emission. On going to low temperature a blue shift is observed which can be attributed to the rigidochromic effect. Again, as with **15**, oxygen quenching or exciplex formation may have occurred.

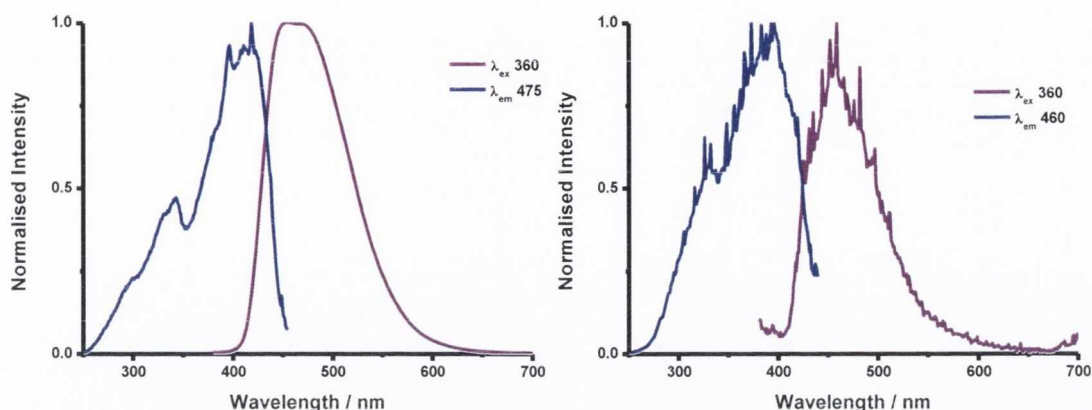


Figure 3.5-3: Normalised excitation and emission spectra of **17** at 10^{-5} M concentration in CH_2Cl_2 at 298 (left) and 77(right) K.

Figure 3.5-3 shows the excitation and emission spectra of **17** at room and low temperatures in air-equilibrated solution. At room temperature the emission maximum is centred at 452 nm which, like **16**, is slightly blue shifted when compared to the free ligand **10** suggesting that the metal centre does not exert a very strong effect on the emission. On going to low temperature a slight red shift is observed which may be due to aggregation effects. Again, as with **15** and **16**, oxygen quenching or exciplex formation may have occurred.

In general, the emission spectra of the homoleptic complexes are unremarkable either due to exciplex formation or, more likely, oxygen quenching. As a result of this excited state lifetimes of the homoleptic complexes were not measured and interest was instead focused on the heteroleptic Cu(I) xantphos systems.

Figure 3.5-4 shows the excitation and emission spectra of **18** at room and low temperatures in air-equilibrated solution. At room temperature the emission is ligand centred at 453 nm, however, on going to low temperature there is a dramatic change in the emission spectrum with the ligand-centred emission red shifting to a weak band at 482 nm and two new emission bands appearing at 572 (λ_{max}) and 621 nm. These bands can be attributed to radiative decay from the MLCT states.^{112,141} On measuring the corresponding excited state lifetimes it was found that the decays are biexponential and exhibit lifetimes in the microsecond range (Table 3.5-1).

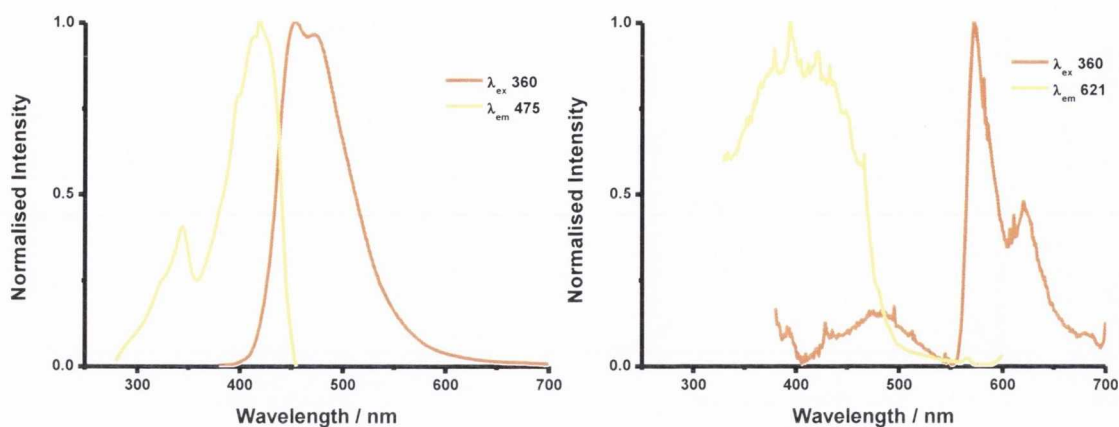


Figure 3.5-4: Normalised excitation and emission spectra of **18** at 10^{-5} M concentration in CH_2Cl_2 at 298 (left) and 77(right) K.

Figure 3.5-5 shows the excitation and emission spectra of **19** at room and low temperatures in air-equilibrated solution. As was the case for **18**, at room temperature the emission is ligand centred at 450 nm, however, on going to low temperature there is a dramatic change in the emission spectrum with the ligand-centred emission blue shifting to a weak band at 432 nm and two new emission bands appearing at 571 (λ_{max}) and 623 nm.

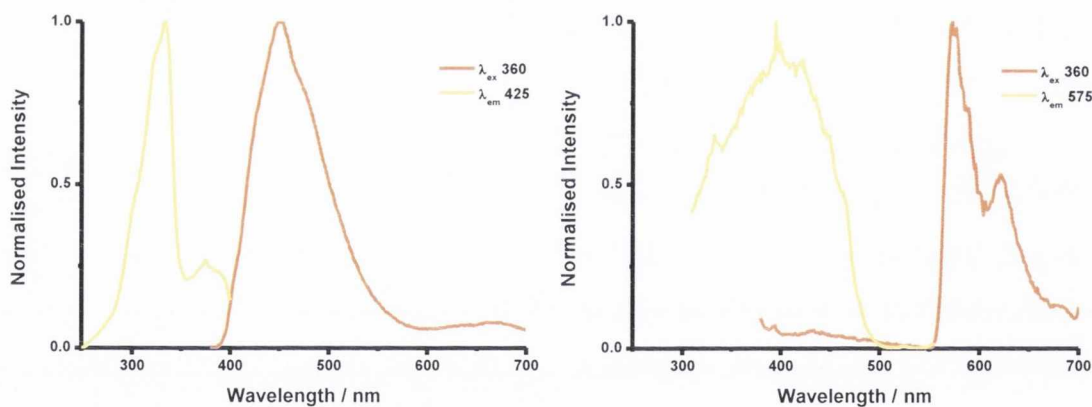


Figure 3.5-5: Normalised excitation and emission spectra of **19** at 10^{-5} M concentration in CH_2Cl_2 at 298 (left) and 77(right) K.

This is almost identical to the corresponding spectrum of **18** and as such these bands can also be ascribed to MLCT states. On measuring the corresponding excited state lifetimes it was found that the decays are biexponential and exhibit lifetimes in the

microsecond range but are considerably shorter than those measured for **18** (Table 3.5-1).

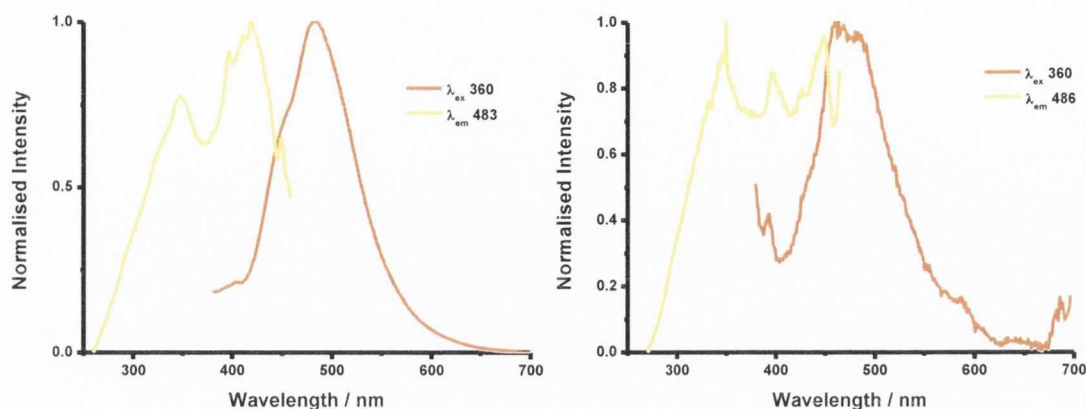


Figure 3.5-6: Normalised excitation and emission spectra of **20** at 10^{-5} M concentration in CH_2Cl_2 at 298 (left) and 77(right) K.

Figure 3.5-6 shows the excitation and emission spectra of **20** at room and low temperatures in air-equilibrated solution. Unlike **18** and **19**, at room temperature the emission is centred at 484 nm and on going to low temperature there is only a small blue shift in the emission spectrum and two very weak emission bands appearing at 586 (λ_{max}) and 685 nm. This suggests that **20** is more susceptible to exciplex formation or oxygen quenching than either **18** or **19**. The measured excited state lifetime for this complex are also much shorter (Table 3.5-1).

3.6 Conclusions and outlook

Three novel homoleptic Cu(I) complexes of the type $[\text{Cu(I)(N}^{\wedge}\text{N)}_2]^+$, where ($\text{N}^{\wedge}\text{N}$) = **6**, **9** and **10**, have been successfully synthesised and characterised by NMR and mass spectroscopy. A further six novel heteroleptic Cu(I) complexes of the type $[\text{Cu(I)(N}^{\wedge}\text{N)(P}^{\wedge}\text{P)}]^+$ have been successfully synthesised and characterised by NMR and mass spectroscopy. Each of the heteroleptic complexes of the azafluoranthene ligands **6**, **9** and **10** varies in the auxiliary phosphine ligand attached.

The electrochemical and photophysical properties of each of the complexes were investigated. The absorption spectra of each of the complexes were discussed first in groups with the same azafluoranthene ligand and then in groups of the same type, i.e. homoleptic and heteroleptic, which was further divided by auxiliary phosphine ligand. The homoleptic complexes exhibit many of the absorption bands that are common to

the Cu(I) bis(phenanthroline) type complexes that are discussed in depth in the literature. The UV region of the spectrum is dominated by ligand-centred bands with the MLCT bands attributed to $[d(\text{Cu}) \rightarrow (\text{N}^{\wedge}\text{N})]$ transitions, appearing at much lower energy in the visible region. It is these absorptions in the visible range of the spectrum that give rise to the purple colour of the homoleptic complexes. A general trend is observed when comparing the absorption spectra of the homoleptic and heteroleptic complexes, the presence of the electron withdrawing phosphine ligands results in a dramatic blue shift of the MLCT, despite the fact that the phosphine ligand is not directly involved in the MLCT transitions. When comparing complexes of the same type the effects of the substituents of the azafluoranthene ligands become more apparent with blue shifts of the MLCT bands observed when the bulky electron donating and electron withdrawing groups of complexes **16** and **17** are present compared to **15**. Both families of heteroleptic complexes follow the expected trend with the electron donating groups of **19** and **22** causing a slightly red shifted absorption whereas the electron withdrawing groups of **20** and **23** experience a blue shifted absorption.

The electrochemical properties of each complex were also investigated and it was found that the homoleptic complexes each undergo a reversible oxidation at relatively low potentials suggesting the bulk of the substituents on **16** and **17** are not sufficient to protect against exciplex formation resulting from the flattening of the tetrahedral Cu(I) geometry on oxidation to Cu(II). The oxidation processes for the heteroleptic Cu(I) xantphos systems were observed to occur at higher oxidation potentials due to the electron withdrawing nature of the phosphine ligand that tends to disfavour Cu(I) $\rightarrow$ N-N electron donation. The second heteroleptic Cu(I) dppf complexes display two oxidation processes, the first due to the ferrocene metal centre and the second due to the Cu(I) metal centre, with potentials similar to phenanthroline Cu(I) dppf systems described by Armaroli *et al.*

The reduction processes are all quite similar, with the electron donicity of the substituents exhibiting some effect on the reduction potential.

The Cu(I) dppf complexes did not exhibit any luminescence and this is thought to be due to the possible quenching effect of the ferrocene moiety. Therefore the photoluminescent properties of six of the complexes were investigated at both room

and low temperature; the homoleptic complexes and the Cu(I) xantphos complexes. The homoleptic complexes were found to exhibit mainly ligand-centred emission at both room and low temperatures and this can be attributed to either oxygen quenching or exciplex formation. The heteroleptic Cu(I) xantphos complexes on the other hand were shown to exhibit emission from MLCT states at low temperature, even in the presence of oxygen. The corresponding excited state lifetimes are in the microsecond range which is unusual for Cu(I) complexes of this type.

Future work will include a more detailed investigation into the luminescence properties of these complexes, in particular, solid state measurements and measurements of degassed samples of each and quantum yield measurements of the MLCT emission.

Chapter 4:

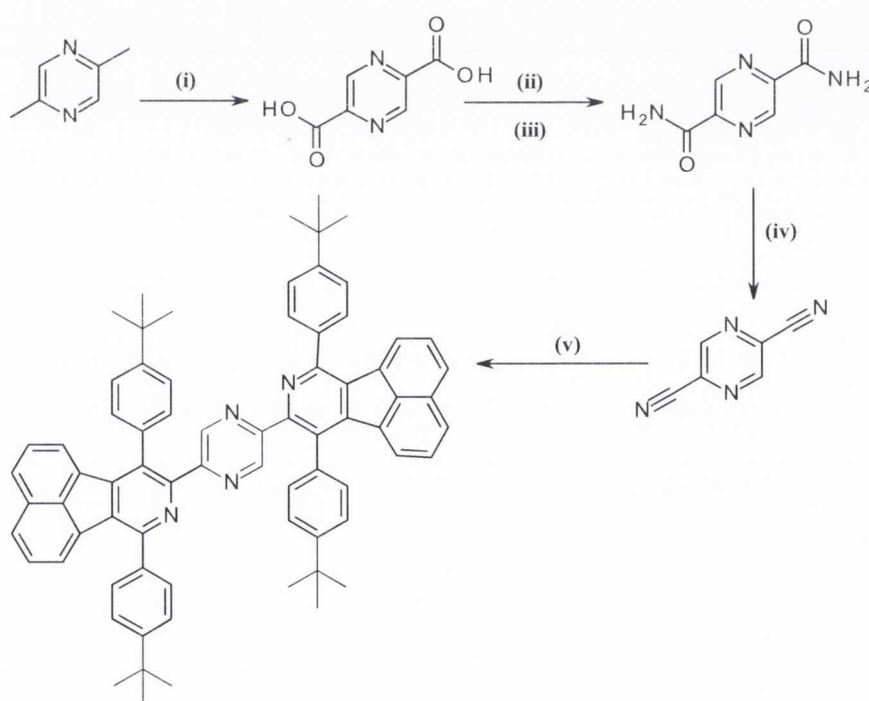
**Attempted Synthesis of Pyrazine-Bridged
Azafluoranthene Compounds**

4.1 Introduction

This chapter describes the attempted synthesis of a new family of fluoranthene-containing pyridine-centred compounds linked *via* a pyrazine molecule. The advantage of a pyrazine bridge between these molecules is that it enables the coordination of two metal centres to one compound as there are two possible coordination sites within the target compound. Furthermore, there are two possible modes of coordination; bidentate N^N coordination or tridentate N^N^C coordination. These compounds are related to those described in Chapter 1 as they also contain a nitrogen atom in the 8 position of the fluoranthene core. The difficulties encountered, in particular with the purification of the products obtained, will be discussed, as well as the strategies adopted to overcome the synthetic difficulties.

4.2 Pyrazine-bridged azafluoranthenes

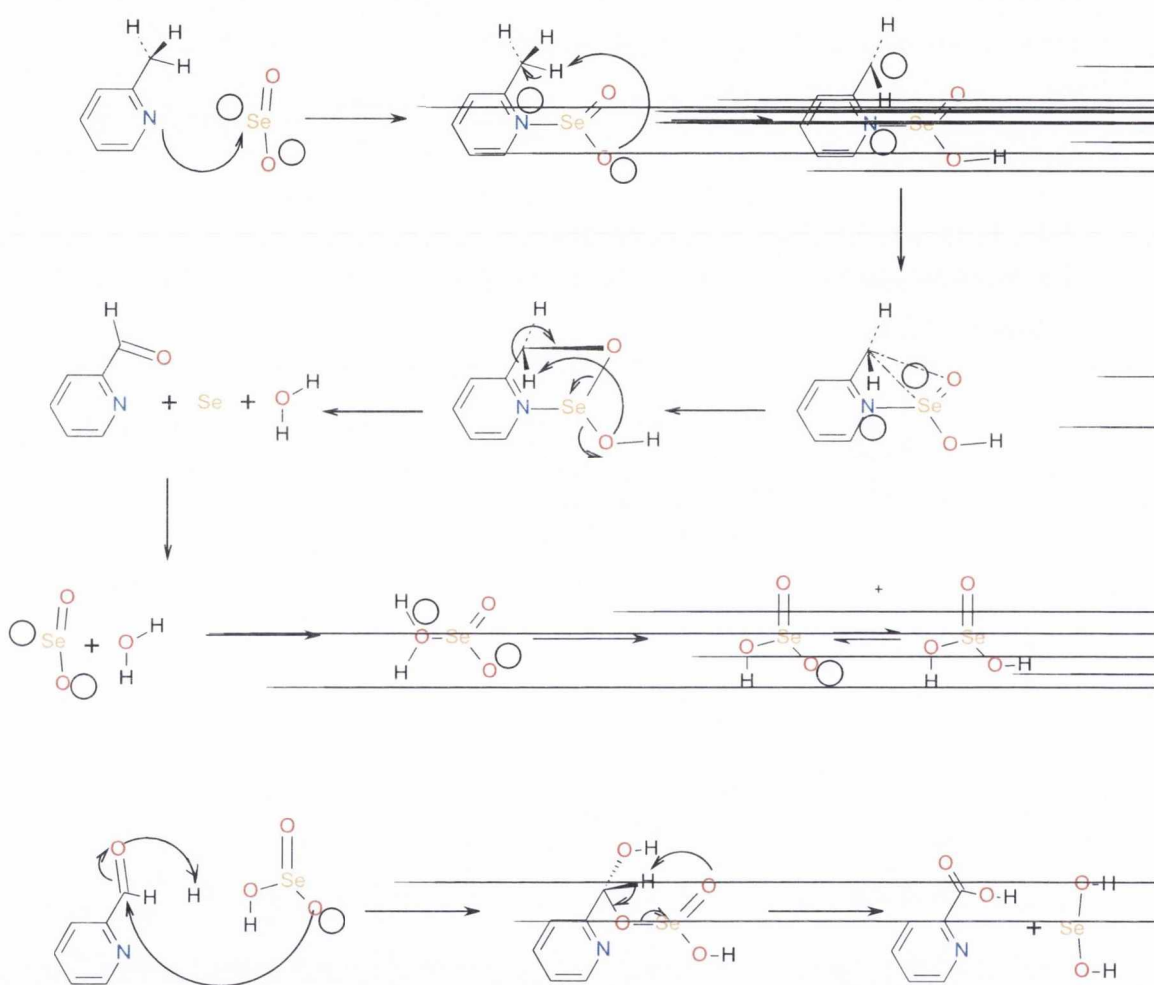
The synthetic route toward a new pyrazine bridged azafluoranthene compound is shown in Scheme 4.2-1.



Scheme 4.2-1: Synthetic route to azafluoranthenes ligand. (i) SeO_2 , $\text{py}:\text{H}_2\text{O}$, 120°C , 16 h, 78% (ii) DMF , SOCl_2 , 100°C , 1h, 90%, (iii) NH_3 , -30°C , (iv) DMF , SOCl_2 , -20°C to room temp., 67%, (v) 4, 300°C , 10 days.

4.2.1 Synthesis of 2,5-dicyanopyrazine

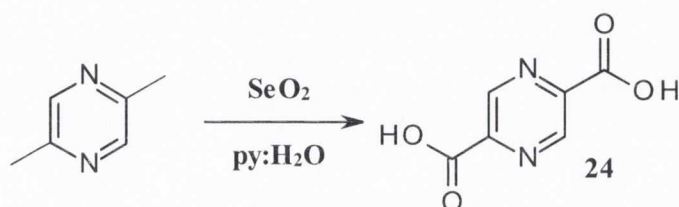
The four step synthesis of 2,5-dicyanopyrazine from commercially available 2,5-dimethylpyrazine proved challenging. The first step involves the oxidation of the methyl groups of 2,5-methylpyrazine to carboxylic acids. As the more conventional oxidising agents had no effect on the 2,5-methylpyrazine, selenium dioxide was used to achieve oxidation. The mechanism by which the selenium dioxide oxidises the methyl group of 2-methylpyridine as an example is shown in Scheme 4.2-2.



Scheme 4.2-2: Mechanism of the oxidation of the methyl group to a carboxylic acid by selenium dioxide.

This was carried out in a solution of pyridine and water and refluxed at 120° C overnight. The boiling solution turned from a clear yellow colour to a deep reddish brown after fifteen minutes of reflux and the selenium gradually formed a greenish-black precipitate. The work-up of the reaction was modified from the work-up

described by Zhang *et al.*¹⁴⁶ On modification, it was possible to significantly expedite the process as several time-consuming steps were combined. The reaction mixture was allowed to cool to room temperature and filtered, with the remaining precipitate stirred in 2N ammonium hydroxide. The combined filtrates were then stirred in 2N ammonium hydroxide with activated charcoal. On filtration the filtrate was then reduced in volume and to this was added concentrated hydrochloric acid, resulting in the desired product precipitating as a white powder that was collected and dried to give a yield of 78%.



Scheme 4.2-3: Oxidation of 2,5-dimethylpyrazine to form 2,5-pyrazinedicarboxylic acid (24)

24 was characterised by ^1H NMR, ^{13}C NMR and FTIR spectroscopy. The ^1H NMR spectrum is shown in Figure 4.2-1.

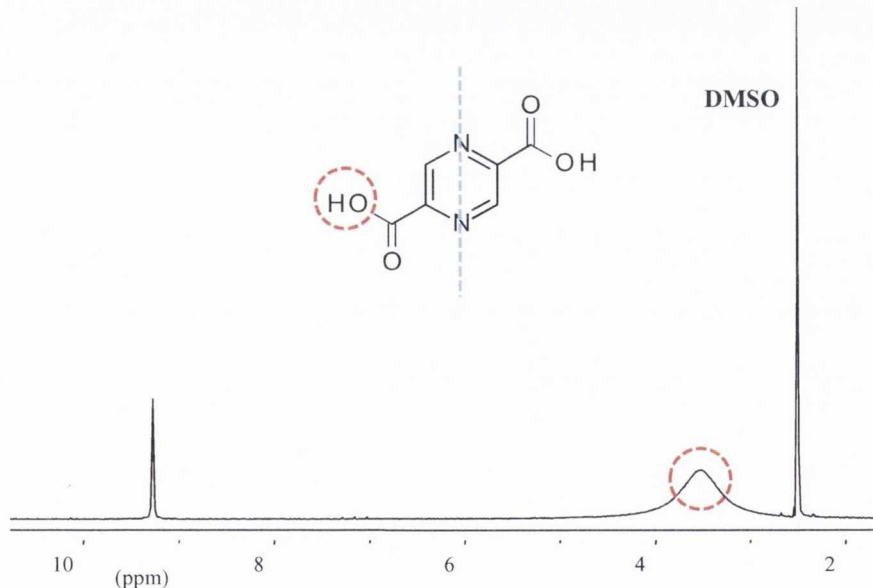


Figure 4.2-1: ^1H NMR spectrum of **24** in $\text{DMSO-}d_6$ (400.1 MHz, R.T.)

Due to the symmetry of the compound, the ^1H NMR spectrum consists of only two signals, a singlet at δ 9.27 ppm which is assigned to the only pyrazine proton and a broad singlet at δ 3.5 ppm that is due to the proton of the OH group of the carboxylic

acid. The ^{13}C NMR spectrum consists of only three signals, the furthest downfield, at δ 164.8 ppm is attributed to the carbon of the carboxylic acid. This is followed by a quaternary carbon signal at δ 146.0 ppm and the pyrazine carbon at δ 145.3 ppm. The structure was also confirmed by the FTIR spectrum which shows characteristic OH and C=O stretches at $3100 - 2400\text{ cm}^{-1}$ and 1712 cm^{-1} respectively.

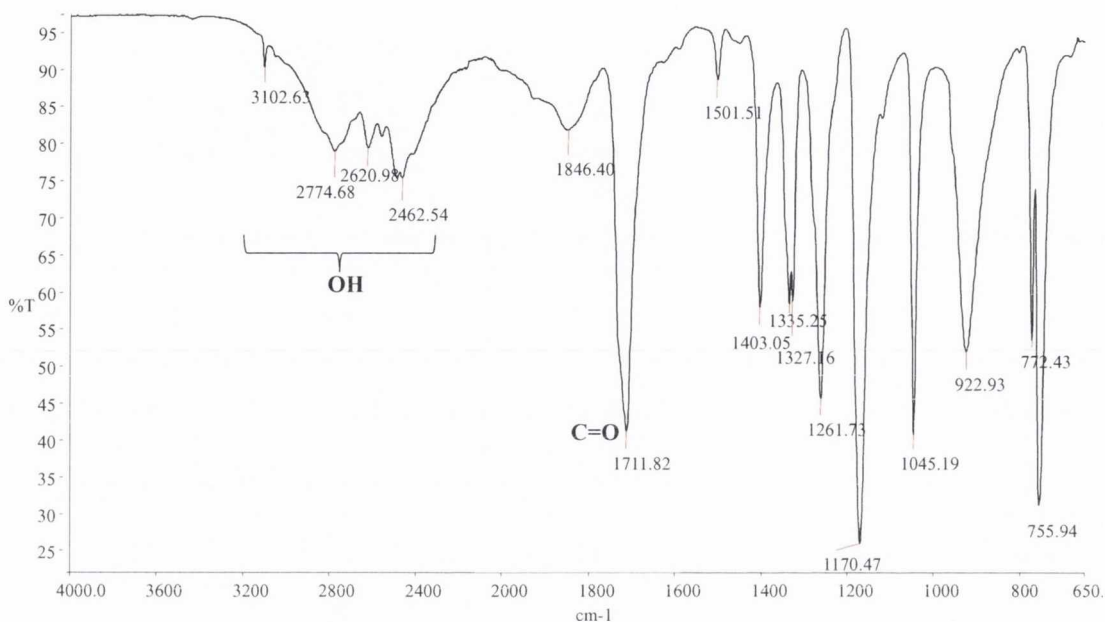
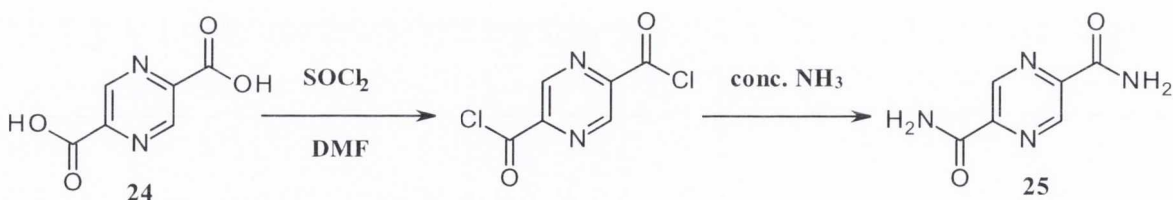


Figure 4.2-2: FTIR(Diamond ATR, Solid) spectrum of **24** showing the OH and C=O stretches of the compound.

Step two involved the preparation of the acylchloride from the 2,5-pyrazinedicarboxylic acid using thionyl chloride in DMF. Step three was the conversion of the acylchloride to the 2,5-pyrazinedicarboxylic acid diamide (**25**) using concentrated ammonia. This reaction proved to be extremely violent, with large volumes of HCl gas evolved on addition of the ammonia, and as a result was carried out at -30°C .



Scheme 4.2-4: Formation of the acylchloride from **24** and subsequent transformation to the 2,5-dicarboxylic acid diamide (**25**)

Again, **25** was characterised by ^1H NMR, ^{13}C NMR and FTIR spectroscopy.

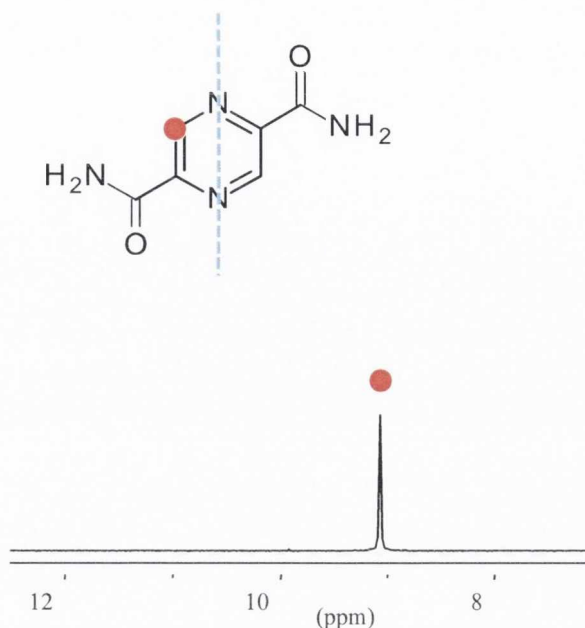
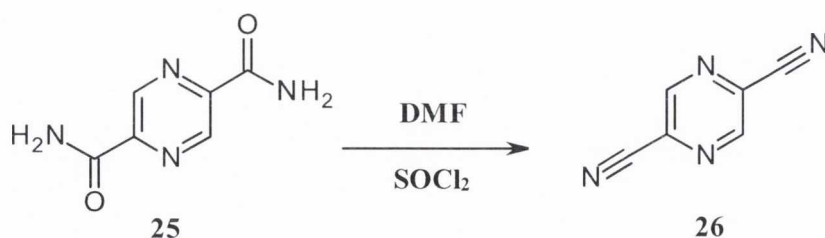


Figure 4.2-3: ^1H NMR spectrum of **25** (DMSO, 400.1 MHz, R.T.)

Due to the symmetry of the compound the ^1H NMR spectrum of **25** is very simple, containing only one signal at δ 9.16 ppm which corresponds to the pyrazine protons. The N-H₂ protons are not seen however the characteristic N-H bond stretches are seen in the FTIR spectrum at 3418 cm^{-1} and the N-H bend at 1588 cm^{-1} as well as the C=O stretch at 1672 cm^{-1} .

The final step was the conversion of the amide groups to cyano groups. This was achieved by the addition of thionyl chloride to a solution of **25** in DMF at -20°C . The thionyl chloride was added gradually over a two hour period and the temperature was monitored carefully and not allowed to exceed 0°C .



Scheme 4.2-5: Conversion of the acid amide groups of **25** to cyano groups to give 2,5-dicyanopyrazine (**26**)

The reaction mixture was then stirred at room temperature for forty-eight hours. This was followed by the work up described by Suenaga *et al.*¹⁴⁷ where, upon completion of the reaction, the contents were poured over ice water and a precipitate formed. This precipitate was filtered and recrystallised from toluene to yield the desired product.

26 was characterised by ^1H NMR, ^{13}C NMR and FTIR spectroscopy. The ^1H and ^{13}C NMRs are shown in

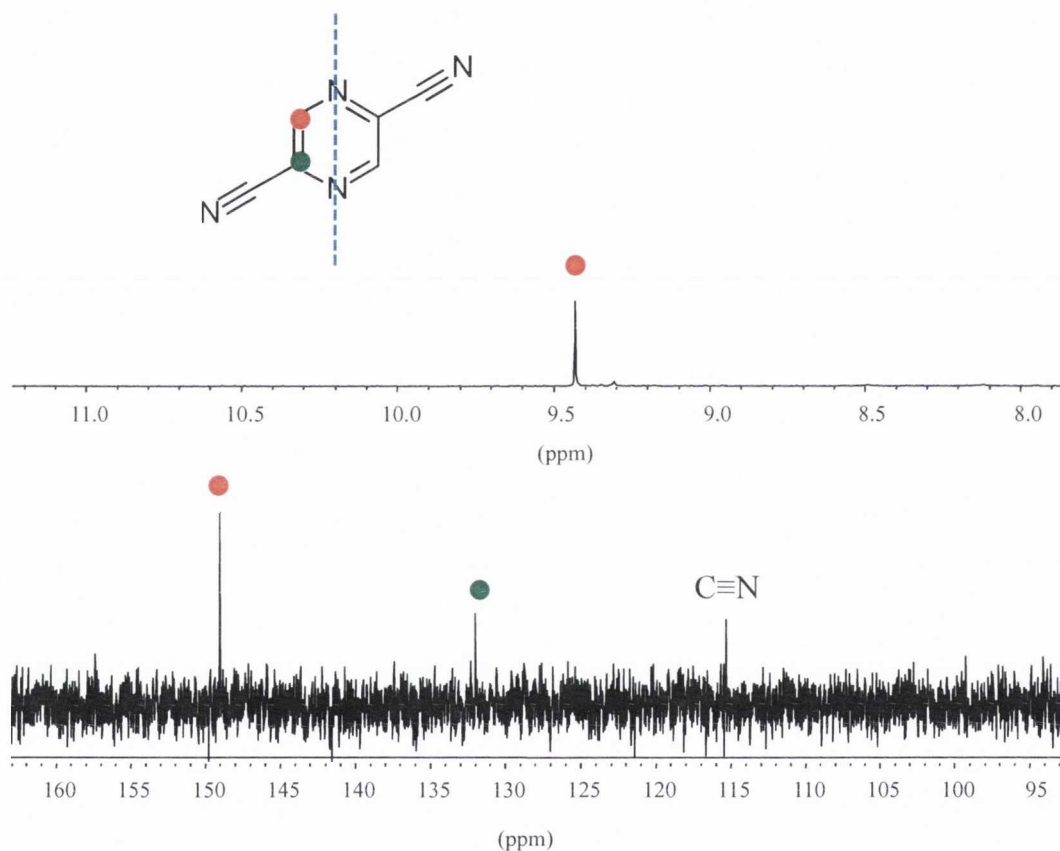
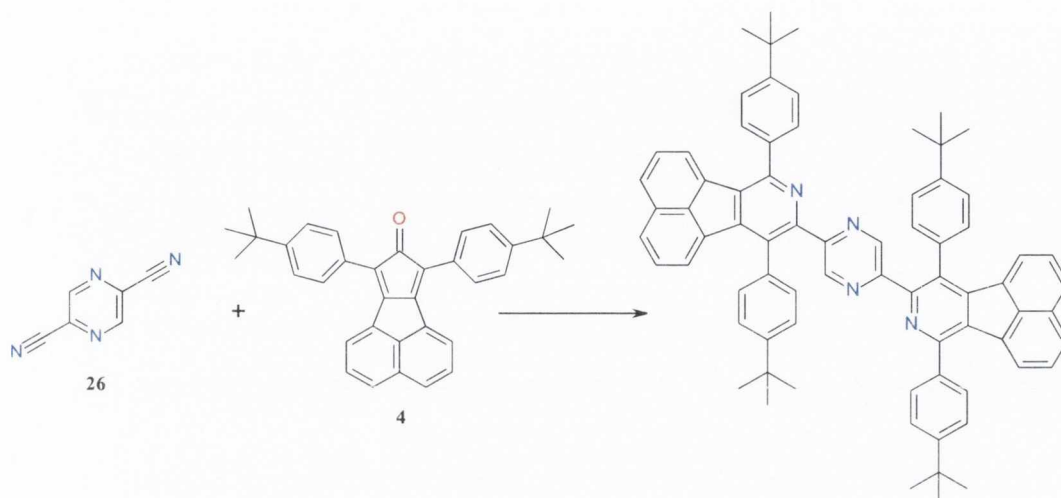


Figure 4.2-4: ^1H NMR (top) and ^{13}C NMR (bottom) spectra of **26** (DMSO, 400.1 MHz, R.T.)

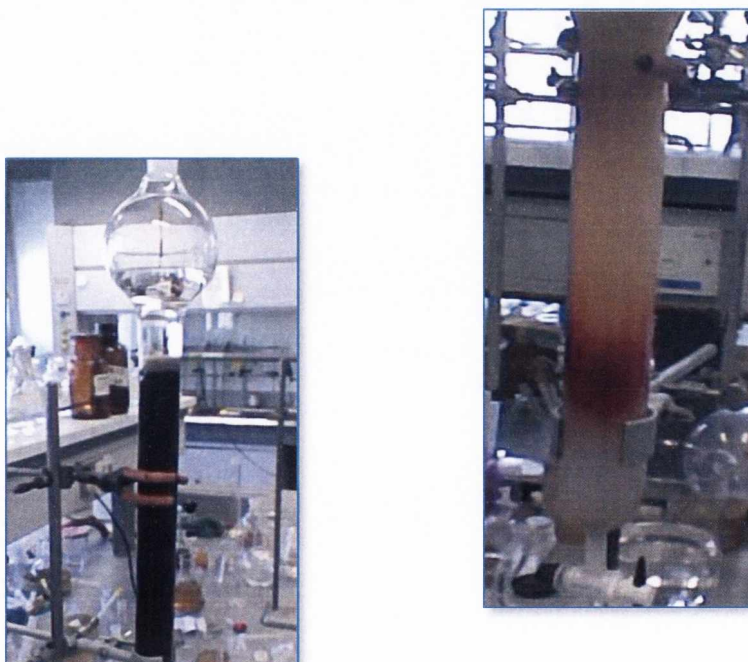
Due to the symmetry of the molecule there is only one signal in the ^1H NMR spectrum and this corresponds to the protons of the pyrazine ring. The ^{13}C NMR spectrum shows three signals, the most downfield of these appearing at δ 149.3 ppm. This signal is attributed to the C-H carbon of the pyrazine ring. Following this is a quaternary carbon signal at δ 132.3 ppm, and finally the cyano group carbon signal at the characteristic δ 115.5 ppm. The FTIR spectrum also shows this cyano group with a stretch at 2248 cm^{-1} .

4.2.2 Attempted synthesis of 2,5-di(7,10-bis-(4-*tert*-butylphenyl)-acenaphtho[1,2-*c*]pyrid-9-yl)-pyrazine

26 was reacted with 2.2 equivalents of **4** in a benzophenone melt in a small round bottom flask. The mixture was heated to 300°C for 72 hr in a sand bath, under an inert atmosphere.



*Scheme 4.2-6: Proposed reaction of **26** with **4** to yield the desired pyrazine-bridged azafluoranthene compound. 300° C, benzophenone, 72 h.*



*Figure 4.2-5: The first attempt at separating the products of the reaction mixture (left) and the eventual isolation of a red product, **27** (right).*

On completion of the reaction the product was purified by column chromatography. This separation proved to be laborious and the mixture did not separate well despite using a number of different solvent systems. Eventually a red product was isolated and crystals suitable for X-ray analysis were grown by slow solvent evaporation. The crystal structure showed the product to be a tetra-substituted thiophene compound. The fluoranthene-containing cyclopentadienone derivative had lost its C=O, however instead of a Diels-Alder cycloaddition, the C=O was replaced with a sulfur atom. The sulfur containing fluoranthene compound, 7,9-bis(4-tert-butylphenyl)-8-thia-cyclopenta[α]acenaphthylene (**27**), has not previously been reported in the literature.

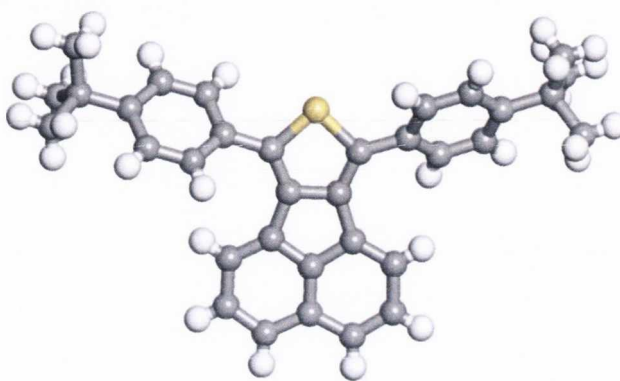


Figure 4.2-6: X-ray structure of a novel sulfur containing fluoranthene compound 27. Sulfur atom in yellow.

Two distinct but crystallographically similar molecules, A and B, are found in the unit cell. The fused thiophene-naphthylene unit is planar, the molecules differ only by the angles of the phenyl rings, that are twisted out of plane.

In the three dimensional structure different interactions are observed between protons of the tertiary butyl groups of A and B, and the aromatic density of the thiophene rings. A-A interactions, B-B interactions and A-B interactions can all be seen. Each thiophene ring is sandwiched between the tertiary butyl groups of another molecule to form the packing arrangement in Figure 14. The distance ($H_A \cdots \text{Centroid}_B$, 2.827Å- 3.153Å) and the angles ($C-H \cdots \text{Centroid}$, 134.58° – 169.11°) observed are similar to those reported in the literature.¹⁴⁸

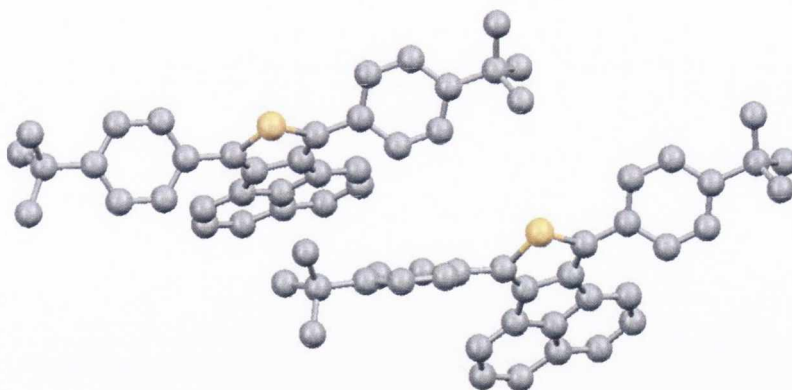


Figure 4.2-7: Unit cell of **27** showing the two distinct crystallographic species (referred to as *A* and *B*) that differ only by the angle of the phenyl rings. Hydrogen atoms omitted for clarity.

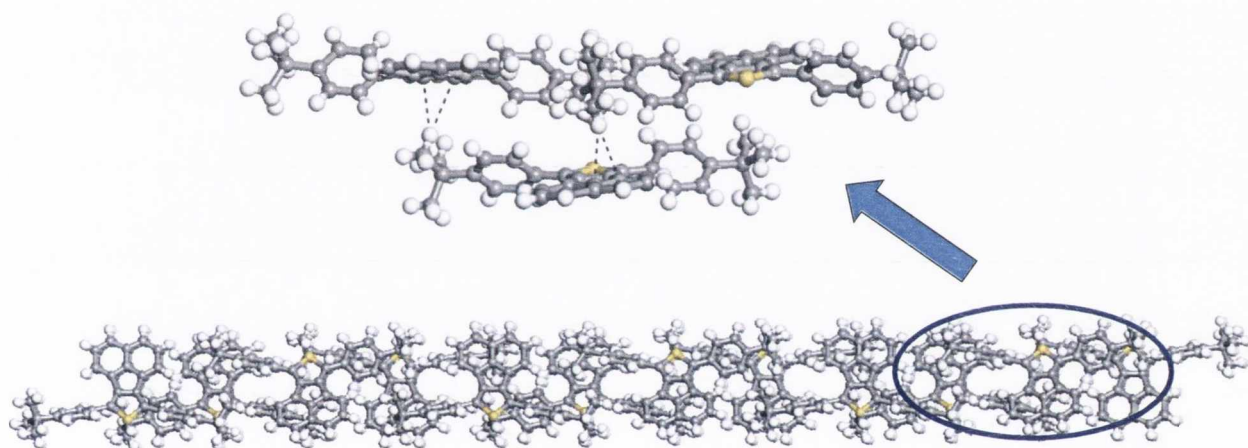


Figure 4.2-8: Perspective view of the packing arrangement of **27** showing the hydrogen bonding between molecules

Further separation of the reaction mixture yielded two more products, the highly coloured dimerisation products formed from the reaction of two equivalents of the cyclopentaacenaphthenone **4** previously described in Chapter 1. No trace of the desired product was found in any of the column fractions.

In an attempt to discover what was causing this unexpected product to form the same reaction was carried out with **26** and commercially available tetraphenylcyclopentadienone (tetracyclone) shown in Figure 4.2-9.

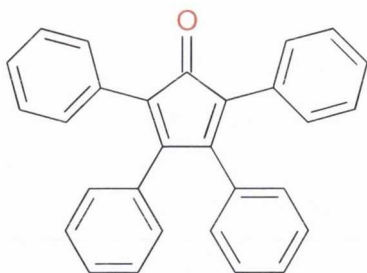


Figure 4.2-9: Structure of tetracyclone (tetracyclone)

26 was reacted with 2.2 equivalents of tetracyclone in a 10 mL round bottom flask. The mixture was heated to 300°C for 24 hr in a sand bath, under an inert atmosphere. On completion of the reaction the product was precipitated out from dichloromethane and acetone as a pale brown powder. NMR analysis showed the product to be another tetra-substituted thiophene compound that has been described previously in the literature.¹⁴⁹

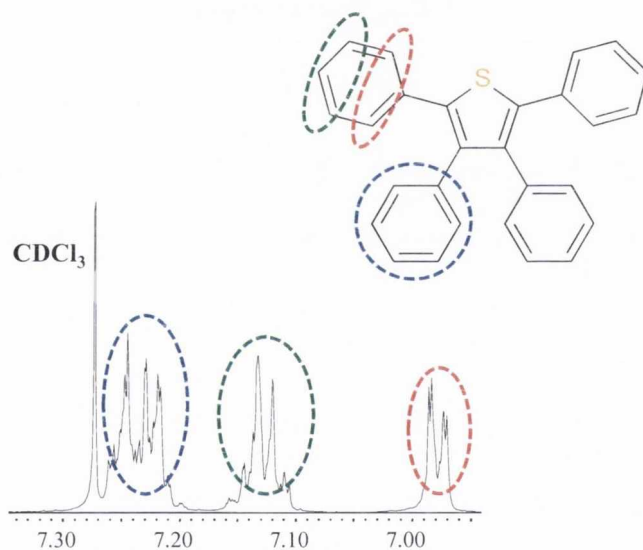


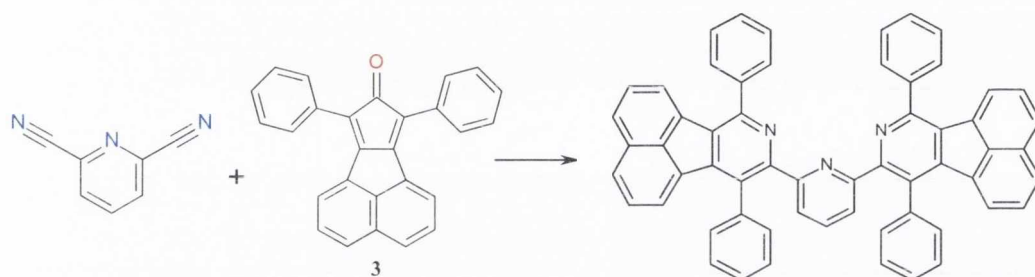
Figure 4.2-10: ^1H NMR spectrum of tetraphenylthiophene (**28**), (400.1 MHz, CDCl_3 , R.T.)

On further investigation, it was found that **26** was not entirely pure and contained some residual sulfur, most likely from the addition of thionyl chloride during its preparation. It is thought that the sulfur reacted with the cyclopentadienone derivatives before the Diels-Alder cycloaddition could take place, as forcing high temperatures, are required for the cycloaddition to proceed. Despite numerous attempts, including substituting the thionyl chloride in the second step of the synthesis with phosphorus(IV)-oxychloride, a

completely pure sample of **26** could not be successfully synthesised, resulting in a necessary change of target molecule.

4.3 Terpyridine-bridged azafluoranthenes

Following on from the work described in Chapter 1 regarding the synthesis of the tri-substituted 8-azafluoranthene compounds containing cyano groups it was decided to repeat this reaction with two equivalents of cyclopentaacenaphthenone in order to synthesise a bridged compound that incorporates a terpyridine moiety. Unlike the original target molecules there is only one coordination site. The advantage of this reaction was the commercial availability of the starting material 2,6-dicyanopyridine, eliminating many steps and the possibility of side reactions from impurities or residues.

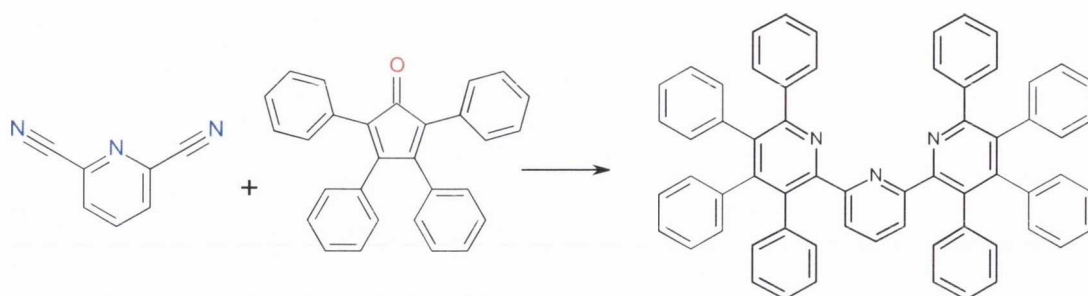


*Scheme 4.3-1: Synthetic route using two equivalents of **3** to yield new target terpyridine-bridged molecule.*

Due to the difficulties encountered with previous attempts to complete a double Diels-Alder cycloaddition it was decided to try a test reaction with two commercially available starting materials in order to optimise conditions before using the more valuable fluoranthene starting materials.

4.3.1 Test reaction between 2,6-dicyanopyridine and tetracyclone

For the first test reaction, 2,6-dicyanopyridine and benzophenone were placed in a 10 mL round bottomed flask, with a 2.2 equivalent excess of tetracyclone and were heated to 300°C in a sand bath.



Scheme 4.3-2: Test reaction using two equivalents of tetracyclone to yield a polyphenyl terpyridine-centred compound

The reaction was monitored by TLC and stopped when all the 2,6-dicyanopyridine had been consumed, which took 6 days. The mixture was then separated by column chromatography. This proved very difficult as it was discovered that despite displaying good separation on a silica TLC plate, the products of the reaction adhere strongly to silica gel, as is a common problem with basic molecules, and in particular with terpyridine systems, resulting in the loss of a large amount of the products. The reaction was repeated numerous times and finally a sample of product was isolated, after separation by column chromatography using basic alumina as the stationary phase with various solvent systems and a final separation on a preparative TLC plate. The sample was analysed by NMR and HRMS and showed a mixture of products (Figure 4.3-1).

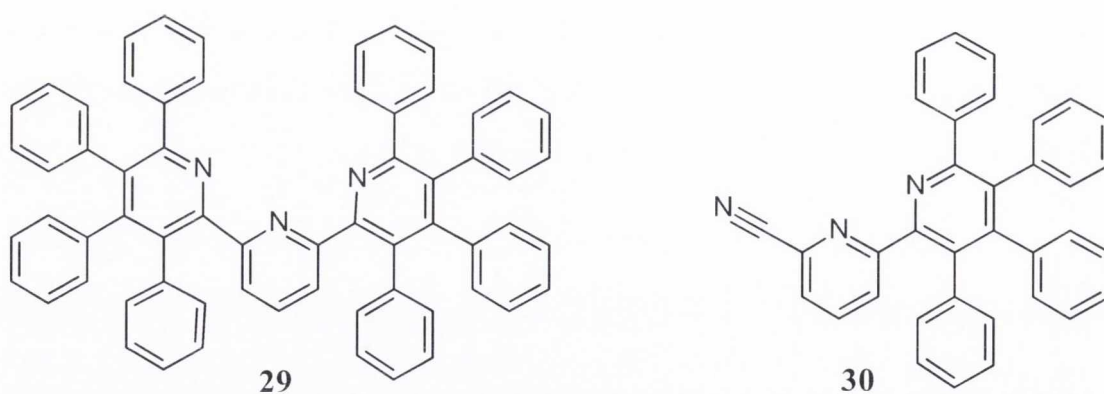


Figure 4.3-1: Mixture of products obtained from the reaction of 2,6-dicyanopyridine and tetracyclone, the double Diels-Alder cycloaddition product (29) and the single Diels-Alder cycloaddition product (30)

A test for the terpyridine moiety, with an iron(II) salt was also carried out on the sample. On addition of the salt to a solution of the product, the solution turned a deep purple colour, which is indicative of the presence of terpyridine in a reaction mixture.¹⁵⁰ Mass spectrometry also confirms the presence of both products, but with the double Diels-Alder product present in higher abundance.

4.3.2 ¹H NMR spectrum of **29** and **30**

Figure 4.3-2 shows the ¹H NMR of **29** and **30**. The major product is the double cycloaddition compound, **29**. The pendant pyridyl ring protons of **30** are the most downfield signals, appearing at δ 8.35, δ 8.01 and δ 7.90 ppm. The central pyridyl ring protons of **29** are shifted upfield appearing as a doublet, triplet and doublet at δ 7.84, δ 7.75 and δ 7.52, respectively. The remaining signals are the overlapping phenyl ring signals.

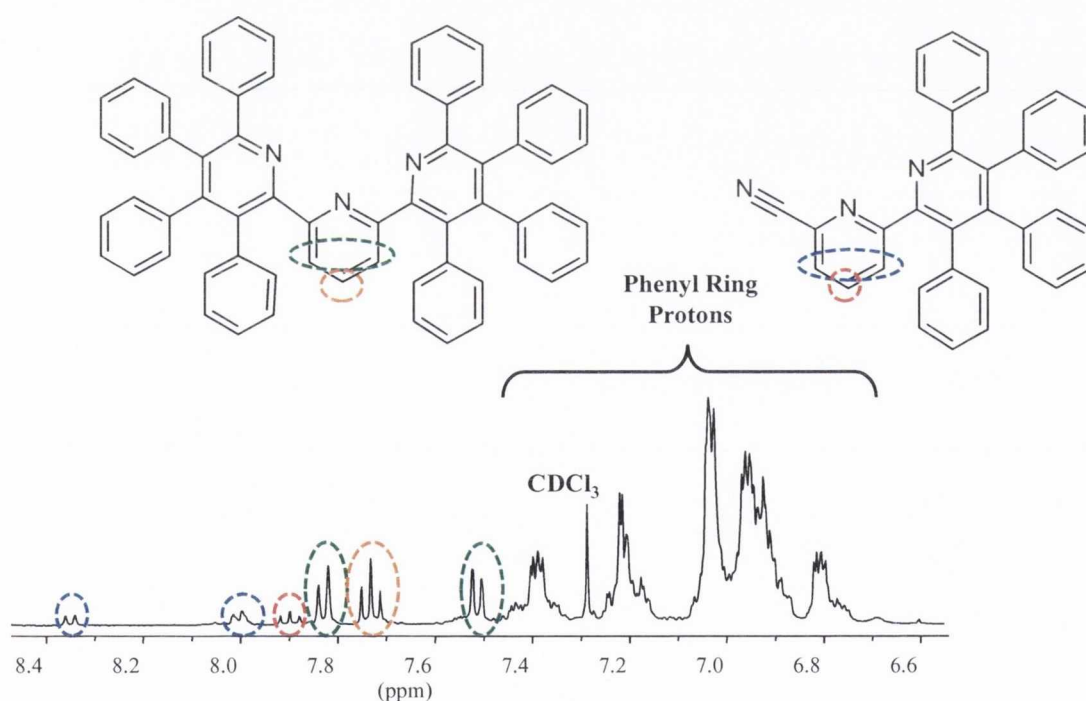


Figure 4.3-2: ¹H NMR spectrum of **29** and **30**, (400.1 MHz, CDCl₃, R.T.)

Despite many attempts to push the reaction to completion, including performing the reaction under higher pressure in the microwave reactor, using a Lewis acid (AlCl₃) to catalyse the reaction and trying the reaction in two steps - a pure sample of **29** was never obtained. The reaction was attempted with the fluoranthene cyclopentadienones **3**

and **4**, however, despite many attempts, the reaction would only proceed half way to form **8** and **13**. Again, more forcing conditions such as higher pressure, or the addition of a Lewis acid, increasing the ratio to as much as 10:1 diene:dienophile had no effect on the outcome. This resulted in the need for a further change to the target molecules.

4.4 Terpyridine bridged fluoranthene compounds

As the double Diels-Alder cycloaddition utilising cyano-groups as the dienophile was not working a new approach was needed to synthesis the desired compounds. The target compounds were altered to become fluoranthene moieties linked *via* a terpyridine bridge, as shown in Figure 4.4-1. The compound no longer contains a nitrogen atom in the central ring of the fluoranthene core, and as such could be synthesised by an all carbon Diels-Alder cycloaddition. These all carbon reactions typically afford higher yields and require less forcing conditions than their nitrogen containing counterparts.

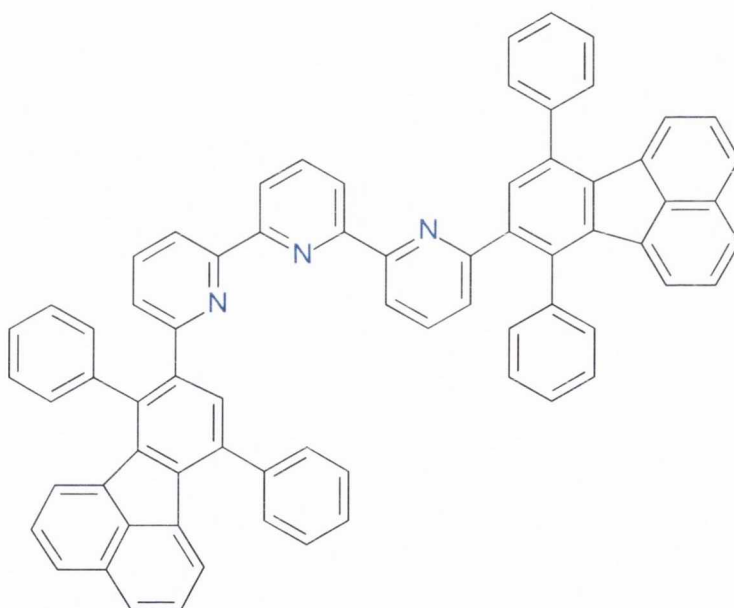
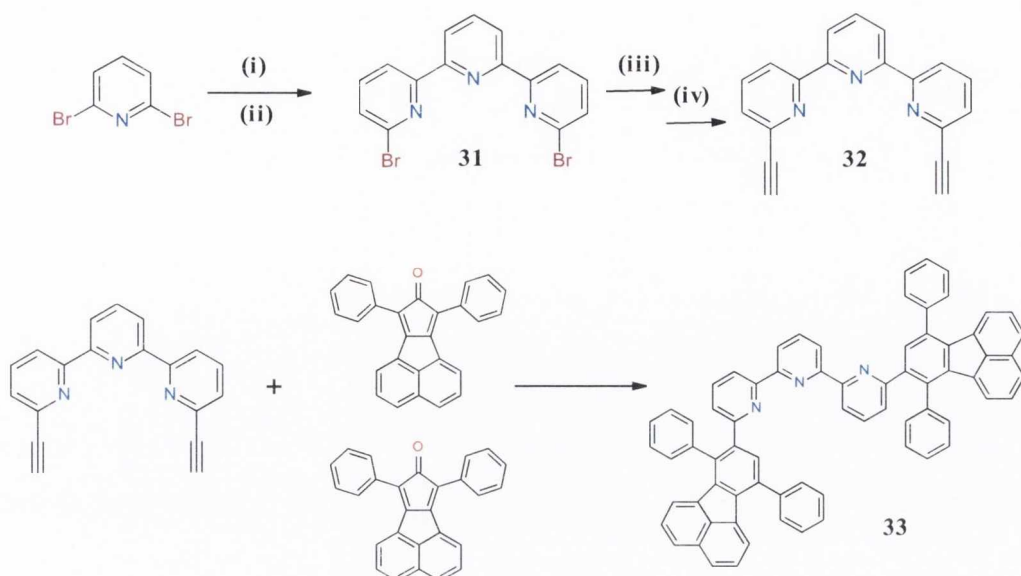


Figure 4.4-1: New target compound, 6,6''-di(7,10-diphenylfluoranthene)-2,2':6'2''-terpyridine (**33**).

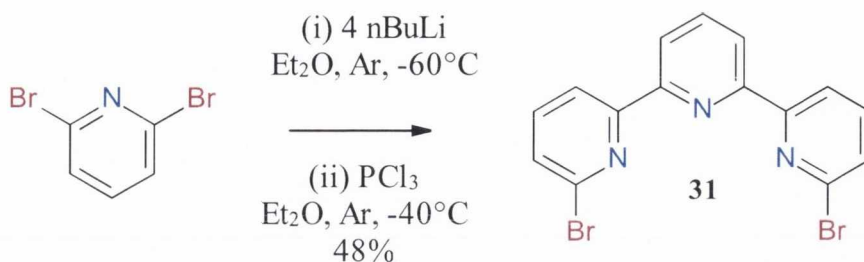
The synthetic pathway towards the new target molecule is shown in Scheme 4.4-1. The overall synthesis requires four steps, three of which are to synthesise the 6,6''-diethynyl-2,2':6'2''-terpyridine from commercially available 2,6-dibromopyridine.



Scheme 4.4-1: Synthetic route toward the terpyridine bridged fluoranthene compound **33**. Top: (i) 4 *n*-BuLi, Et₂O, Ar, -60° C (ii) PCl₃, Et₂O, Ar, -40° C (iii) 2-Methyl-3-butyn-2-ol (2.5 equiv), *n*Pr₂NH₂, [Pd⁰(PPh₃)₄] (6 mol %), 60° C (iv) toluene, NaOH, 100° C. Bottom: Benzophenone melt, 300° C, 72 h.

4.4.1 Synthesis of 6,6''-dibromo-2,2':6'2''-terpyridine (**31**)

The first step is the synthesis of 6,6''-dibromo-2,2':6'2''-terpyridine from commercially available 2,6-dibromopyridine following the method of Uchida *et al.*¹⁵¹ A solution of the starting material in ether was cooled to -60° C under argon. To this was added four equivalents of butyl lithium in hexane. The reaction mixture was stirred for two hours at -40° C. Following this, a solution of PCl₃ in ether was added dropwise over a period of two hours with constant stirring. The mixture was then stirred at -40° C for a further twenty hours. Once the mixture had reached room temperature it was poured into water and the resulting precipitate was collected by filtration. The solid was then dissolved in boiling toluene and any remaining solid impurities were removed by filtration. The hot toluene was then passed through a short silica gel column. The resulting fractions were combined and the solvent was removed to give the product as a white crystalline solid.¹⁵¹

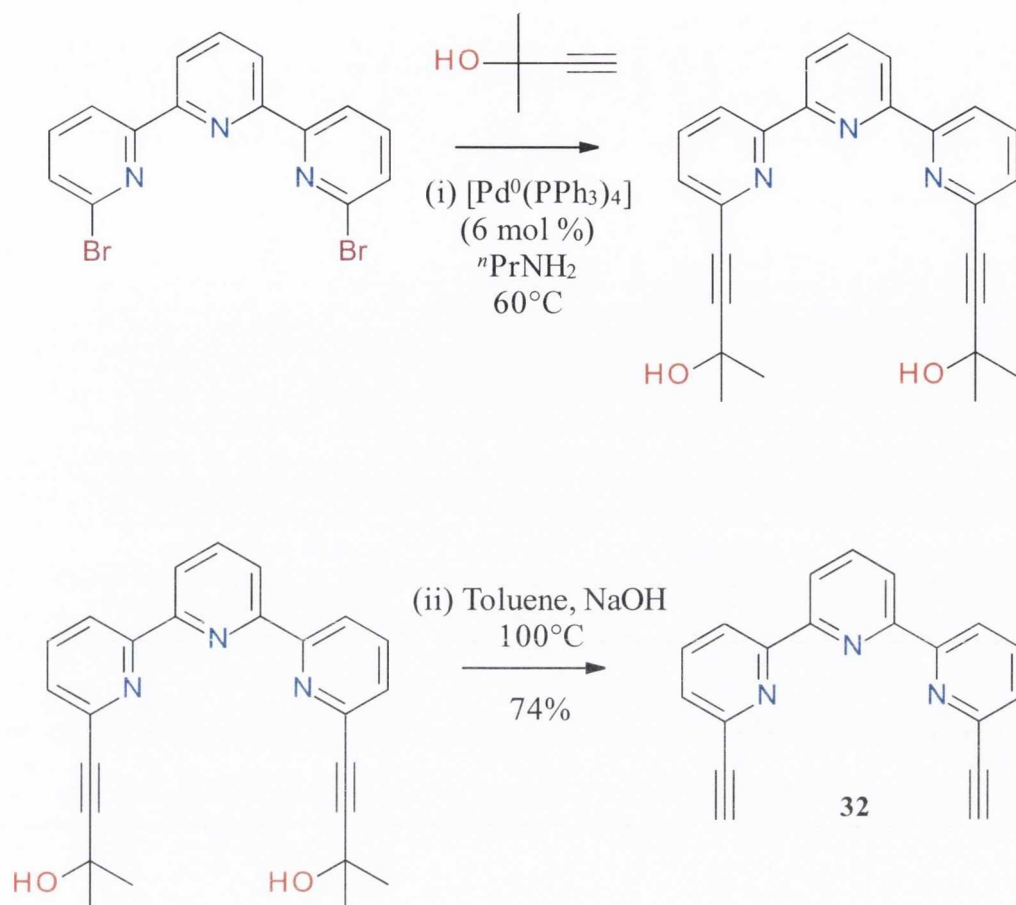


Scheme 4.4-2: Synthesis of 6,6''-dibromo-2,2':6'2''-terpyridine (31) from commercially available 2,6-dibromopyridine

31 was characterised by ESI mass spectrometry which shows the product with a peak at $m/z = 411.9059$ m.u. for $[M+H]^+$ which is in excellent agreement with the calculated value of $m/z = 411.9061$ m.u. for $C_{15}H_9N_3Br_2Na$, $[M + H]$. The melting point of 264 - 265 °C is also in very close agreement with those quoted in the literature (lit. 263 – 264 °C).¹⁵¹

4.4.2 Synthesis of 6,6''-diethynyl-2,2':6'2''-terpyridine (32)

The second part of the synthesis involved a palladium catalysed Sonogashira cross coupling reaction of **31** with 2-methyl-3-butyn-2-ol, a protected acetylene, as outlined by Annunziata¹⁵² *et al* and Khatyr¹⁵³ *et al*. To a solution of 6,6''-dibromo-2,2':6'2''-terpyridine in isopropylamine was added 6 mol% palladium catalyst and 2.5 equivalents of the alcohol. The solution was degassed by argon bubbling and the reaction was carried out under argon for 3 hr at 60° C. The solvent was then removed under vacuum leaving behind a dark brown precipitate. The precipitate was washed with water and extracted into dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulfate and the solvent was removed to give a brown precipitate, the protected 6,6''-diethynyl-2,2':6'2''-terpyridine.



Scheme 4.4-3: Sonogashira cross-coupling reaction of **31** with 2-methyl-3-butyn-2-ol (top) and the deprotection to yield 6,6''-diethynyl-2,2':6'2''-terpyridine (**32**)

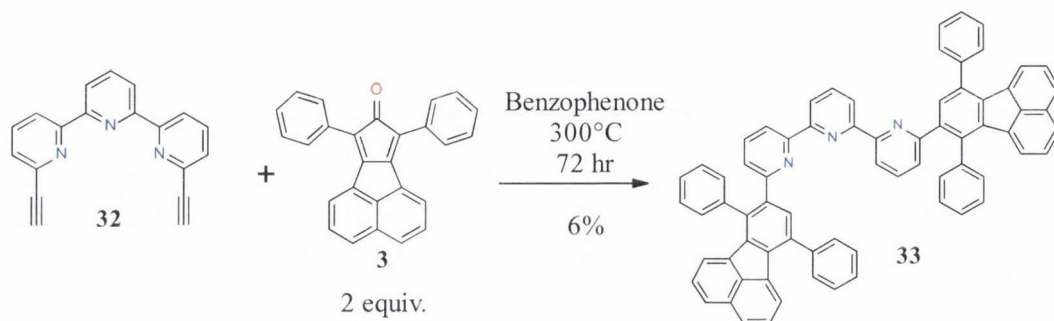
The next step was the deprotection and was carried out on the crude product. The crude product was dissolved in toluene and to this was added an excess of NaOH. The mixture was refluxed overnight and was then filtered to remove remaining solid sodium hydroxide. The product was purified by column chromatography on silica gel, using dichloromethane: methanol (20:1) as the eluent, to give 6,6''-diethynyl-2,2':6'2''-terpyridine as an off white crystalline solid.

32 was characterised by ^1H NMR and FTIR spectroscopy, with the data from both methods in excellent agreement with those in the literature.¹⁵²

4.4.3 Synthesis of 6,6''-di(7,10-diphenylfluoranthene)-2,2':6'2''-terpyridine (**33**)

The final product, 6,6''-di(7,10-diphenylfluoranthene)-2,2':6'2''-terpyridine, was synthesised *via* a double Diels-Alder cycloaddition between two equivalents of **3** and

one equivalent of **32**. The reaction was performed in a benzophenone melt at 300° C over three days.



*Scheme 4.4-4: Diels-Alder cycloaddition between **32** and **3** to yield **33***

Careful monitoring by TLC showed that the reaction had gone to completion. Purification of the product proved difficult and several attempts to separate the product from the reaction mixture, using flash chromatography with silica gel as the stationary phase, were unsuccessful. Finally, a combination of solvent systems was found that resulted in clean separation of the product. The first of the systems was hexane:dichloromethane (7:3) which removed the small amount of the highly coloured red and orange dimerisation products that had formed. This was followed by dichloromethane (100%) to remove the benzophenone. The product was then stripped from the column using a dichloromethane:methanol solution (85:15). The product was then dry loaded onto silica and run through a second column using ethyl acetate as the eluent. The dry loading of the product ensured that the many impurities from the high temperature reaction remained at the baseline as they were not soluble in ethyl acetate. The desired product ran very slowly. It was collected and the solvent was removed to give a viscous liquid, due mainly to residual ethyl acetate. This was removed by running the product through a short silica plug using dichloromethane as eluent. Once the ethyl acetate had been removed the product was stripped from the column using dichloromethane:methanol (90:10). The solvent was removed to give a pale brown solid, this was dissolved in the minimum amount of dichloromethane and precipitated out with cold methanol to afford the desired compound in a low yield of 6%. This low yield is due mainly to the difficulty purifying the compound. Much of the product was lost in the unsuccessful purification attempts.

4.4.3.1 Characterisation of **33**

33 was characterised by ESI mass spectrometry which shows the product with a peak at $m/z = 938.3517$ m.u. for $[M+H]^+$ which is in excellent agreement with the calculated value of $m/z = 938.3535$ m.u. for $C_{71}H_{43}N_3$, $[M H]^+$.

4.5 Summary and Conclusions

The original aim of this work was to synthesise a family of pyrazine-bridged azafluoranthene compounds *via* a Diels-Alder cycloaddition between 2,5-dicyanopyrazine and two equivalents of a cyclopentaacenaphthylenone. During these attempts a novel sulfur containing compound, 9-bis(4-tert-butylphenyl)-8-thia-cyclopenta[α]acenaphthylene (**27**), was synthesised. The source of the sulfur was thought to be residual thionyl chloride from the synthesis of 2,5-dicyanopyrazine. This synthesis proved challenging and a pure sample of the final product could not be obtained despite many attempts. This was compounded by the fact that during a test reaction a second sulfur containing compound, a tetra-phenyl thiophene, was synthesised but this compound has been reported previously in the literature.¹⁴⁹ As a result of the sulfur impurity, it was not possible to synthesise the pyrazine bridged azafluoranthene compound.

A new family of compounds were designed, this time incorporating a terpyridine moiety as a bridge between two azafluoranthene compounds. This was building from the synthesis of ligands **8** and **13** (Chapter 1) from the Diels-Alder reaction of 2,6-pyridinedicarbonitrile and one equivalent of a cyclopentaacenaphthenone. The reactions were first carried out using a commercially available cyclopentadienone to save the more precious fluoranthene starting materials. This reaction did proceed but purification proved difficult as the main product, the double cycloaddition product (**29**) could not be separated from the single cycloaddition product (**30**). The reaction was repeated with the fluoranthene cyclopentadienone however, despite many attempts, the reaction would only proceed half way to form **8** and **13**. More forcing conditions such as higher pressure, or the addition of a Lewis acid, increasing the ratio to as much as 10:1 diene:dienophile had no effect on the outcome.

As a result of these unsuccessful Diels-Alder cycloaddition with the cyano groups acting as dienophile, it was decided to alter the target molecules once again, this time to remove the nitrogen atom from the fluoranthene core thus eliminating the need for the

cyano group. The result would be an all-carbon fluoranthene compound bridged by a terpyridine moiety. The required starting materials for this all-carbon Diels-Alder cycloaddition were successfully synthesised from commercially available 2,6-dibromopyridine in three steps. The first step was the synthesis of the 6,6''-dibromo-2,2':6'2''-terpyridine (**31**), followed by a Sonogashira cross-coupling reaction and subsequent acetylene deprotection to yield 6,6''-diethynyl-2,2':6'2''-terpyridine (**32**) in good yield. The final step was a double Diels-Alder cycloaddition between **32** and **3** to form 6,6''-di(7,10-diphenylfluoranthene)-2,2':6'2''-terpyridine (**33**).

4.6 Future work

Building from the work described in section 4.4, it should be possible to optimise the reaction conditions and synthesise a family of terpyridine bridged fluoranthene ligands. These ligands have multiple possible coordination sites and the ability to facilitate two metal centres. The substitution of the pendant phenyl rings of the fluoranthene moiety will help tune the optical properties of the resulting metal complexes as has been shown in Chapter 3.

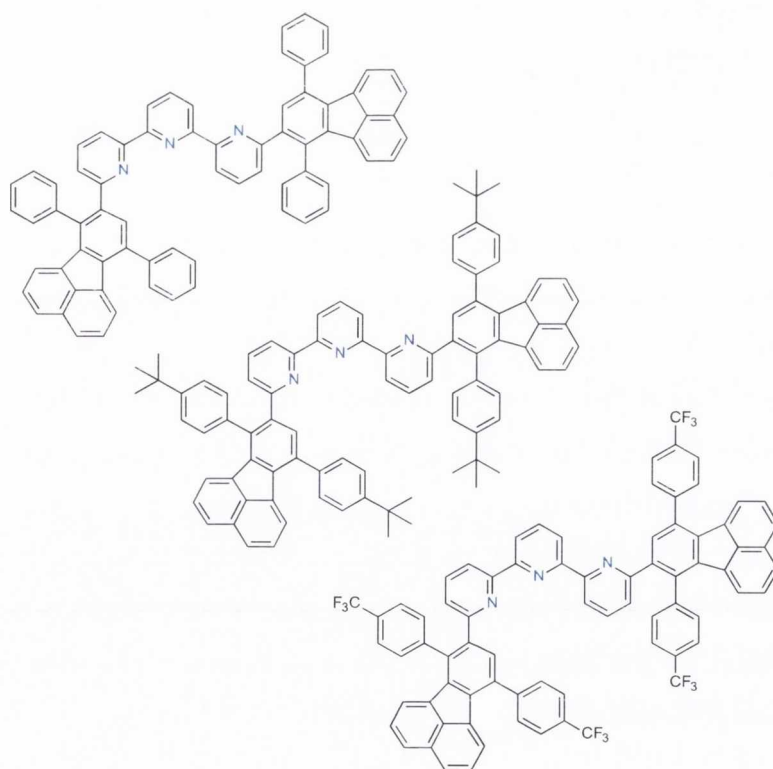


Figure 4.6-1: Possible family of terpyridine-bridged fluoranthene compounds

Chapter 5:

Experimental

5.1 General Methods

Unless otherwise stated, all reactions were carried out under an inert atmosphere of either nitrogen or argon using standard Schlenk techniques. Solvents were distilled under nitrogen and dried with appropriate drying agents under a nitrogen atmosphere; Dichloromethane and isopropylamine distilled over CaH_2 , THF over sodium wire with benzophenone.

Flash chromatography was performed using silica gel 60, particle size 0.04-0.063 mm (Aldrich) or aluminum oxide, Brockmann Activity I basic particle size 0.05-0.15 mm (Fluka) as the stationary phase. All other chemicals were obtained from commercial sources unless otherwise stated.

IR spectra were recorded as neat samples on a Perkin Elmer Spectrum One FTIR Spectrometer with a Universal-ATR sampling accessory.

Electrospray mass spectra were obtained on a Micromass LCT electrospray mass spectrometer. MALDI-TOF mass spectra were recorded on a Waters MALDI-QTOF Premier spectrometer using α -cyano-4-hydroxy cinnamic acid matrix. Accurate mass spectra were referenced against Leucine Enkephalin (555.6 g mol^{-1}) or [Glu¹]-Fibrinopeptide B ($1570.6 \text{ g mol}^{-1}$).

Nuclear magnetic resonance data was recorded on Bruker DPX 400 spectrometer, operating at frequencies: 400.1 MHz for ^1H and 100.6 MHz for ^{13}C , and on Bruker Avance II 600 spectrometer, Cryo Probe, operating at frequencies: 600.1 MHz for ^1H and 150.9 MHz for ^{13}C , both were standardised with respect to TMS. ^{19}F spectra were standardised relative to CFCl_3 . Chemical shifts (δ) are reported in ppm and coupling constants (J) are given in Hz.

Cyclic voltammetry was carried out using a CH Instruments Electrochemical Analyser Model 600B. 1mM solutions of ligands and complexes in dichloromethane using tetra-n-butylammonium hexafluorophosphate (TBAPF_6 , 0.1M), as the supporting electrolyte, were used. A standard three electrode cell was used with a glassy carbon working electrode, a Pt wire counter electrode and a Ag/AgCl (sat. KCl) reference electrode. Potentials are quoted versus Ag/AgCl. Solutions were degassed for several minutes by nitrogen bubbling before performing the experiments and a constant stream of nitrogen gas over the solution was maintained throughout the experiment.

UV-Visible absorption spectra were recorded as optically dilute solutions (10^{-5} – 10^{-6} M) in 1x1 cm² quartz cuvettes on a Shimadzu UV-2450 spectrophotometer. Corrected steady-state solution (10^{-3} – 10^{-5} M) and solid-state emission spectra at 298K and 77K were recorded on a Horiba Jovin Yvon Fluorolog 3-22 spectrometer with double grating emission and excitation monochromators. Lifetimes were measured on a Jobin Yvon Fluorohub single photon counting controller fitted with a 370 nm Jobin Yvon NanoLED. The observed decays were fitted using the DataStation v2.4 programme.

Quantum yields were recorded on a Horiba Jovin Yvon Fluorolog 3-22 spectrometer with an Integrating Sphere accessory.

Single-crystal analyses were performed by Drs. Tom McCabe and Longsheng Wang with a Bruker SMART APEX CCD diffractometer or a Rigaku Saturn-724 CCD diffractometer at the temperatures specified in the crystallographic tables. Data integration and reduction were carried out using Bruker Saint+ Version 6.45 software and corrected for absorption and polarization effects using SADABS Version 2.10 Software. Space group determination, structure solution and refinement were obtained using Shelxtl* ver. 6.14 software. *Software Reference Manual, version 5.625, Bruker Analytical X-Ray Systems Inc., Madison, WI, 2001. Sheldrick, G. M. SHELXTL, An Integrated System for Data Collection, Processing, Structure Solution and Refinement, Bruker Analytical X-Ray Systems Inc., Madison, WI, 2001. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were fixed from the residual electron density using appropriate HFIX commands. Intermolecular interactions were computed using the PLATON programme.

Microwave reaction were carried out in a CEM Discover S-Class Single Mode Microwave reactor, using SPS mode. All reactions were performed in specialised sealed 'snap-cap' vials under pressure.

5.2 Synthesis of Starting Materials

5.2.1 Synthesis of 1,3-bis(4-tert-butylphenyl)propan-2-one¹⁵⁴ (1)

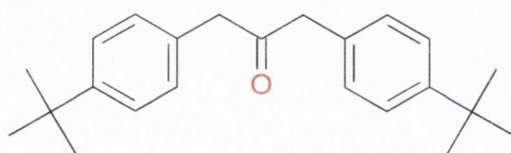
A mixture containing calcium hydroxide (4.25 g, 57.35 mmol) and tetrabutylammonium hydrogen sulfate (2.35 g, 6.93 mmol) in dichloromethane and water (1:1, 200 mL), was degassed by bubbling nitrogen gas through it for 15 min. 4-Tertbutylbenzyl bromide (6.18g, 5.0mL, 27.21 mmol) was then added followed by iron pentacarbonyl (2.5g, 1.73mL, 12.76 mmol). The reaction mixture was stirred at room

temperature for 24 h with a constant stream of nitrogen being circulated over the solution. The reaction mixture was oxidised in air for 1 h and then acidified with a 10% hydrochloric acid solution (90 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 50mL). The combined organic extracts were dried over anhydrous magnesium sulfate and the solvent was removed to give a dark brown solid, which was crystallised from methanol to give the product as a white solid. Yield (1.5 g, 70%).

IR (neat) $\nu_{\text{cm}^{-1}}$: 2954 (CH_3), 1702 ($\text{C}=\text{O}$), 1509, 1192, 1019, 839, 817 ($\text{C}_{\text{aromatic}}$), and 713.

^1H -NMR (400 MHz, CDCl_3 , δ in ppm): 7.37 (d, 4H, $^3\text{J}(\text{HH})$ 8.0 Hz, ArH), 7.12 (d, 4H, $^3\text{J}(\text{HH})$ 8.0 Hz, ArH), 3.71 (s, 4H, CH_2) and 1.33 (s, 18H, CMe_3).

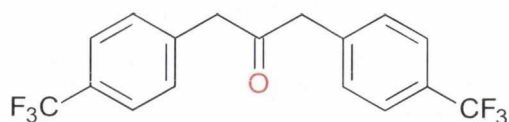
^{13}C -NMR (100 MHz, CDCl_3 , δ in ppm): 205.81 (1C, $\text{C}=\text{O}$), 149.43 (2C, C_{quat}), 130.54 (2C, C_{quat}), 128.71 (4C, C_{aryl}), 125.19 (4C, C_{aryl}), 48.13 (2C, CH_2), 34.02 (2C, CMe_3) and 30.90 (6C, CMe_3).



5.2.2 Synthesis of 1,3-di[4-(trifluoromethyl)phenyl]propan-2-one¹⁵⁵ (2)

A solution of 4-(bromomethyl)-(trifluoromethyl)benzene (4.78 g, 20.0 mmol) and diiron nonacarbonyl (10.92 g, 30.0 mmol) in dry n-octane (100 mL) was refluxed under an inert atmosphere for 18 hr. On cooling to room temperature a precipitate formed and was removed by filtration and extracted five times with boiling toluene. The filtrate and the five extracts were combined and the solvents were removed by distillation. The solid residue was purified by column chromatography with neutral alumina and diethyl-ether:light petroleum (2:5) as the eluent. Yield (2.57g, 75%). Mp

^1H -NMR (400 MHz, CDCl_3 , δ in ppm): 7.62 (d, 4H, $^3\text{J}(\text{HH})$ 8.0 Hz, ArH), 7.31 (d, 4H, $^3\text{J}(\text{HH})$ 8.0 Hz, ArH) and 3.87 (s, 4H, CH_2).



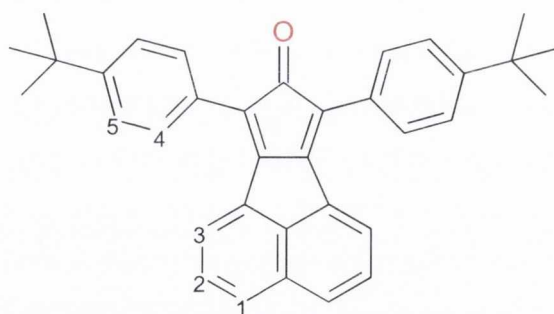
5.2.3 Synthesis of 7,9-bis(4-*tert*-butylphenyl)-8*H*-cyclopenta[*l*]acenaphthylen-8-one (4)

Acenaphthenequinone (400 mg, 2.19 mmol), 1,3-bis(4-*tert*-butylphenyl)propan-2-one (700 mg, 2.2 mmol) and NaOH (100 mg) were stirred at room temperature in methanol (50 mL) for 24 h. The resulting black-brown precipitate was filtered, washed with methanol and dried in vacuum. Yield (494 mg, 49%). An analytical sample was crystallised from dichloromethane/methanol.

IR (neat) cm^{-1} : 2958 (CH_3), 1701 ($\text{C}=\text{O}$), 1507 ($\text{C}_{\text{aromatic}}$), 1360, 1271, 1131, 846, 826 and 773.

^1H -NMR (400 MHz, CDCl_3 , δ in ppm): 8.12 (d, 2H, $^3\text{J}(\text{HH})$, 7.0 Hz, H^1), 7.88 (d, 2H, $^3\text{J}(\text{HH})$, 8.0 Hz, H^3), 7.81 (d, 4H, $^3\text{J}(\text{HH})$, 8.0 Hz, H^4), 7.62 (t, 2H, $^3\text{J}(\text{HH})$, 7.5 Hz, H^2), 7.58 (d, 4H, $^3\text{J}(\text{HH})$, 8.0 Hz, H^5) and 1.42 (s, 18H, CMe_3).

^{13}C -NMR (100 MHz, CDCl_3 , δ in ppm): 153.19 (1C, $\text{C}=\text{O}$), 150.91 (C_{quat}), 144.21 (C_{quat}), 131.67 (C_{quat}), 131.29 (C_{quat}), 128.30 (2C, C_{aryl}), 128.11 (C_{quat}), 127.90 (2C, C_{aryl}), 127.03 (2C, C_{aryl}), 125.13 (2C, C_{aryl}), 125.11 (C_{quat}), 121.07 (C_{quat}), 120.42 (2C, C_{aryl}), 50.45 (2C, C_{aryl}), 34.39 (2C, CMe_3) and 30.52 (6C, CMe_3).



5.2.4 Synthesis of 7,9-Bis[(4-trifluoromethyl)phenyl]-8*H*-cyclopenta[*l*]acenaphthylen-8-one (5)

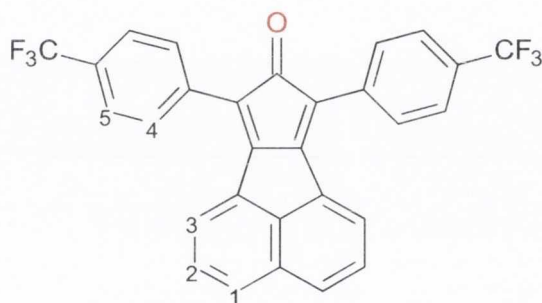
Acenaphthenequinone (400 mg, 2.19 mmol), 1,3-di[4-(trifluoromethyl)phenyl]propan-2-one (700 mg, 2.2 mmol) and KOH (100 mg) were stirred at room temperature in

methanol (50 mL) for 24 h. The resulting black-brown precipitate was filtered, washed with methanol and dried in vacuum. Yield (590 mg, 63%) An analytical sample was crystallised from dichloromethane/methanol.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ in ppm): 8.09 (d, 2H, $^3\text{J}(\text{HH})$, 7.0 Hz, H^1), 7.98 (d, 2H, $^3\text{J}(\text{HH})$, 8.0 Hz, H^3), 7.83 (d, 4H, $^3\text{J}(\text{HH})$, 8.0 Hz, H^4), 7.67 (t, 2H, $^3\text{J}(\text{HH})$, 7.5 Hz, H^2), 7.68 (d, 4H, $^3\text{J}(\text{HH})$, 8.0 Hz, H^5)

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ in ppm): 155.8 (1C, $\text{C}=\text{O}$), 145.0 (C_{quat}), 134.8 (C_{quat}), 132.6 (C_{quat}), 132.2 (C_{quat}), 131.7 (C_{quat}), 130.8 (C_{quat}), 130.1 (C_{quat}), 129.9 (C_{quat}), 129.3 (2C, C_{aryl}), 128.6 (2C, C_{aryl}), 125.6 (2C, C_{aryl}), 125.5 (2C, C_{aryl}), 121.07 (C_{quat}), 121.4 (2C, C_{aryl}), 50.45 (2C, C_{aryl}),

$^{19}\text{F-NMR}$ (376.5 MHz, CDCl_3 , R.T.): δ -62.6 ppm

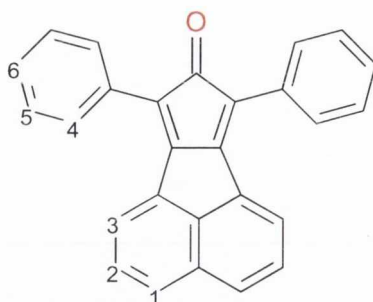


5.2.5 Synthesis of 7,9-Diphenyl-cyclopenta[a]acenaphthylen-8-one¹⁵⁶ (3)

Acenaphthenequinone (0.8g, 4.39mmol), 1,3-diphenylpropan-2-one (0.95g, 4.52 mmol) and NaOH (0.2 g) were stirred at room temperature in methanol (60 mL) for 24 h. The resulting blue-black precipitate was filtered, washed with methanol and dried in vacuum. Yield (1.11g, 71%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ in ppm): 8.11 (d, 2H, $^3\text{J}(\text{HH})$, 7.0 Hz, H^1), 7.91 (d, 2H, $^3\text{J}(\text{HH})$, 8.0 Hz, H^3), 7.87 (d, 4H, $^3\text{J}(\text{HH})$, 8.0 Hz, H^4), 7.64 (t, 2H, $^3\text{J}(\text{HH})$, 7.5 Hz, H^2), 7.57 (t, 4H, $^3\text{J}(\text{HH})$, 7.5 Hz, H^5) and 7.46 (t, 2H, $^3\text{J}(\text{HH})$, 7 Hz, H^6).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ in ppm): 154.25 (1C, $\text{C}=\text{O}$), 144.78 (C_{quat}), 132.15 (C_{quat}), 131.56 (C_{quat}), 131.46 (C_{quat}), 129.09 (2C, C_{aryl}), 128.61 (C_{quat}), 128.45 (2C, C_{aryl}), 128.32 (2C, C_{aryl}), 127.79 (2C, C_{aryl}), 121.67 (C_{quat}), 120.96 (2C, C_{aryl}), and 120.42 (2C, C_{aryl}).



5.3 Synthesis of 8-Azafluoranthene Ligands

5.3.1 Synthesis of 7,10-Diphenyl-9-(2-pyridyl)-8-azafluoranthene (6)

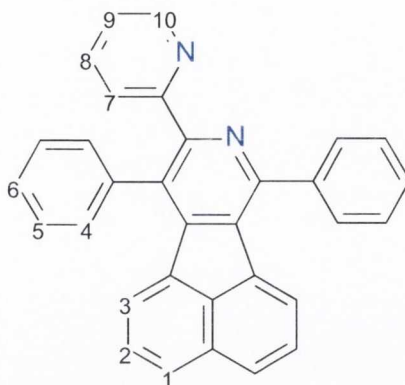
7,9-diphenyl-8*H*-cyclopenta[1]acenaphthylenone (600 mg, 1.7 mmol) and 2-cyanopyridine (1.1 g, 11.6 mmol) were stirred under nitrogen, external temperature 300°C for 48 hr. The resulting brownish red solution was allowed to cool to form a brown solid which was then purified by flash chromatography on silica gel using a dichloromethane:methanol solution as the eluent. This gave the ligand as a pale yellow solid. Yield 176 mg, 24%. Mp > 300°C. Found: C, 80.76; H, 4.24; N, 5.61 calcd. (%) for C₃₂H₂₁N₂·0.5CH₂Cl₂: C, 79.31; H, 4.20; N, 5.69.

IR (neat) ν 3006, 1586, 1475, 1422, 1402, 1276, 1261, 828, 766, 749, 704 cm⁻¹.

ESI-MS (acetonitrile, *m/z*): found: 433.1711, calcd. 433.1705, for C₃₂H₂₁N₂, [M+1]⁺.

¹H NMR (400 MHz, CDCl₃, δ in ppm): δ 8.48 (br, m, 1H, ³J(HH) 5.0 Hz, H¹⁰), 7.93 (d, 2H, ³J(HH) 7.5 Hz, H⁴), 7.89 (d, 1H, ³J(HH) 8.0 Hz, H¹), 7.85 (d, 1H, ³J(HH) 8.0 Hz, H¹), 7.60-7.52 (m, 5H, H³, H⁵, H⁶ and H⁸), 7.51-7.46 (m, 2H, H² and H⁷), 7.44-7.38 (m, 6H, H², H⁴, H⁵ and H⁶), 7.09 (m, 1H, ³J(HH) 5.0, 7.5 Hz, ⁴J(HH) 1.5 Hz, H⁹) and 6.97 (d, 1H, ³J(HH) 7.0 Hz, H³).

¹³C NMR (100 MHz, CDCl₃, δ in ppm): δ 157.9 (C_{quat}), 153.5 (C_{quat}), 149.9 (C_{quat}), 148.4 (1C, C¹⁰), 145.0 (C_{quat}), 144.9 (C_{quat}), 140.0 (C_{quat}), 137.2 (C_{quat}), 135.2 (1C, C⁸), 134.2 (C_{quat}), 133.8 (C_{quat}), 132.6 (C_{quat}), 130.7 (C_{quat}), 129.6 (2C, C⁴), 129.4 (C_{quat}), 128.8 (2C, C⁴), 128.5 (1C, C¹), 128.3 (1C, C⁶), 128.2 (2C, C⁵), 128.1 (1C, C⁵), 127.5 (1C, C⁶), 127.3 (1C, C²), 127.2 (1C, C²), 127.0 (1C, C¹), 124.9 (1C, C³), 124.6 (1C, C⁷), 123.4 (1C, C³), 121.6 (1C, C⁹).



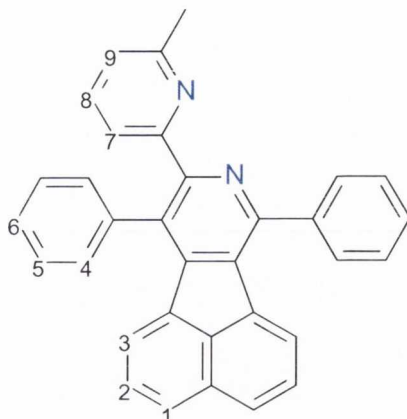
5.3.2 Synthesis of 7,10-Diphenyl-9-(6-methyl-2-pyridyl)-8-azafluoranthene (7)

7,9-diphenyl-8*H*-cyclopenta[*I*]acenaphthylen-8-one (600 mg, 1.7 mmol) and 6-methyl-2-pyridinecarbonitrile (1.1 g, 9.3 mmol) were heated under nitrogen in a benzophenone melt, external temperature 300°C for 7 days. The resulting brownish red solution was allowed to cool to form a brown solid which was then purified by flash chromatography on silica gel using a dichloromethane:methanol solution as the eluent. This gave the ligand as a pale yellow solid. Yield 154 mg, 19%. Mp >300°C

ESI-MS (acetonitrile, *m/z*): found: 447.1858, calcd. 447.1861, for C₃₃H₂₃N₂, [M+1]⁺.

¹H NMR (600 MHz, CDCl₃, δ in ppm): 7.92 (d, 2H, ³J(HH) 7.5 Hz, H^{4'}), 7.89 (d, 1H, ³J(HH) 8.2 Hz, H¹), 7.84 (d, 1H, ³J(HH) 8.2 Hz, H^{1'}), 7.59 (m, 2H, H^{5'}), 7.56 (m, 1H, H^{3'}), 7.54 (m, 1H, H^{6'}), 7.47 (dd, 1H, ³J(HH) 7.8, 7.1 Hz, H^{2'}), 7.45 – 7.40 (m, 6H, H⁸, H⁴, H⁵ & H⁶), 7.39 (m, 1H, H²), 7.37 (d, 1H, ³J(HH) 7.8 Hz, H⁷), 6.96 (dd, 2H, ³J(HH) 7.2, 7.8 Hz, H³ & H⁹) and 2.39 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃, δ in ppm): 157.4 (1C, C_{quat}), 157.1 (1C, C_{quat}), 154.9 (1C, C_{quat}), 153.6 (1C, C_{quat}), 146.2 (1C, C_{quat}), 140.3 (1C, C_{quat}), 137.8 (1C, C_{quat}), 135.7 (1C, C⁸), 134.6 (1C, C_{quat}), 134.2 (1C, C_{quat}), 132.9 (1C, C_{quat}), 131.2 (1C, C_{quat}), 130.8 (1C, C_{quat}), 129.9 (2C, C⁴), 129.7 (1C, C²), 129.1 (2C, C^{4'}), 128.6 (1C, C^{6'}), 128.5 (1C, C¹), 128.4 (2C, C^{5'}), 128.1 (2C, C⁵), 127.7 (1C, C⁶), 127.6 (1C, C^{2'}), 127.2 (1C, C^{1'}), 125.5 (1C, C_{quat}), 125.2 (1C, C³), 123.6 (1C, C^{3'}), 121.6 (1C, C⁷), 121.4 (1C, C⁹) and 24.0 (1C, CH₃).



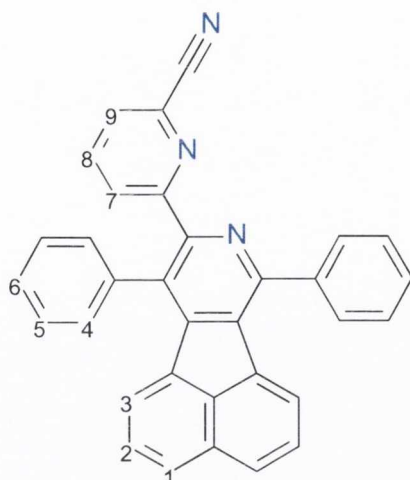
5.3.3 Synthesis of 7,10-Diphenyl-9-(6-cyano-2-pyridyl)-8-azafluoranthene (8)

7,9-diphenyl-8*H*-cyclopenta[1]acenaphthylen-8-one (600 mg, 1.7 mmol) and 2,6-dicyanopyridine (1.1 g, 8.5 mmol) were heated under nitrogen in a benzophenone melt, external temperature 300°C for 7 days. The resulting brownish red solution was allowed to cool to form a brown solid which was then purified by flash chromatography on silica gel using a dichloromethane:methanol solution as the eluent. This gave the ligand as a pale yellow solid. Yield 295 mg, 38%. Mp > 300°C. Found: C, 86.76; H, 4.04; N, 9.26 calcd. (%) for C₃₃H₂₀N₃: C, 86.63; H, 4.19; N, 9.18.

ESI-MS (acetonitrile, *m/z*): found: 458.1667, calcd. 458.1657, for C₃₃H₂₀N₃, [M+1]⁺.

¹H NMR (600 MHz, CDCl₃, δ in ppm): 8.01 (d, 1H, ³J(HH) 8.3 Hz, H⁹), 7.94 (m, 3H, H^{4'} & H¹), 7.91 (d, 1H, ³J(HH) 8.3 Hz, H^{1'}), 7.76 (dd, 1H, ³J(HH) 8.3, 7.3 Hz, H⁸), 7.64-7.58 (m, 4H, H^{3'}, H^{5'} & H^{6'}), 7.53-7.48 (m, 5H, H^{2'}, H⁵, H⁶ & H⁷), 7.45-7.43 (m, 3H, H² & H⁴) and 6.98 (d, 1H, ³J(HH) 8.3 Hz, H³).

¹³C NMR (100 MHz, CDCl₃, δ in ppm): 158.9 (1C, C_{quat}), 153.3 (1C, C_{quat}), 151.6 (1C, C_{quat}), 147.4 (1C, C_{quat}), 138.9 (1C, C_{quat}), 136.9 (1C, C⁸), 136.8 (1C, C_{quat}), 134.2 (1C, C_{quat}), 133.7 (1C, C_{quat}), 133.3 (1C, C_{quat}), 132.6 (1C, C_{quat}), 132.1 (1C, C_{quat}), 132.0 (1C, C_{quat}), 130.0 (1C, C_{quat}), 129.9 (2C, C⁴), 129.7 (1C, C³), 129.5 (1C, C^{3'}), 129.4 (2C, C^{4'}), 128.9 (2C, C^{5'}), 128.8 (2C, C⁵), 128.4 (1C, C⁷), 128.2 (1C, C^{2'}), 128.2 (1C, C^{6'}), 128.2 (1C, C⁶), 128.1 (1C, C²), 127.2 (1C, C⁹), 126.2 (1C, C¹), 124.6 (1C, C^{1'}) and 117.1 (1C, C≡N).



5.3.4 Synthesis of 7,10-Di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (9)

7,9-Bis(4-*tert*-butylphenyl)-8*H*-cyclopenta[*I*]acenaphthylen-8-one (350 mg, 0.7 mmol) and 2-cyanopyridine (1.0 g, 9.6 mmol) were stirred, external temperature 280° C, under nitrogen for 60 h. The resulting brownish red solution was allowed to cool. Chromatography on silica using methanol/dichloromethane gave the ligand as a pale yellow crystalline solid. Yield (138 mg, 36%). Mp > 300°C. Found: C, 83.13; H, 6.34; N, 5.55 calcd. (%) for C₄₀H₃₇N₂:0.5 CH₂Cl₂; C, 83.01; H, 6.29; N, 5.55.

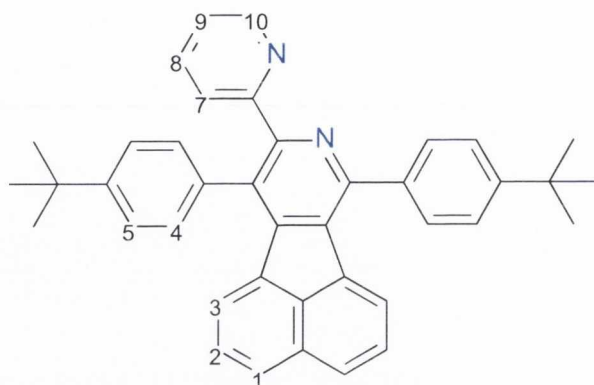
IR (neat) cm⁻¹: 2958, 1701, 1473, 1360, 1271, 1130, 840, 825 and 773.

ESI-MS (acetonitrile, *m/z*): found: 545.2966, calcd. 545.2957, for C₄₀H₃₇N₂, [M+1]⁺.

¹H-NMR (400 MHz, CDCl₃, δ in ppm): 8.56 (br, m, 1H, ³J(HH) 4.0 Hz, H¹⁰), 7.92 (d, 2H, ³J(HH) 8.5 Hz, H^{4'}), 7.90 (d, 1H, ³J(HH) 8.0 Hz, H¹), 7.86 (d, 1H, ³J(HH) 8.0 Hz, H^{1'}), 7.73 (d, 1H, ³J(HH) 7.0 Hz, H^{3'}), 7.60 (d, 2H, ³J(HH) 8.5 Hz, H^{5'}), 7.57-7.50 (m, 2H, H^{2'} and H⁸), 7.45-7.42 (m, 3H, ³J(HH) 8.5 Hz, H⁵ and H²), 7.41 (d, 1H, ³J(HH) 8.0 Hz, H⁷), 7.35 (d, 2H, ³J(HH) 8.5 Hz, H⁴), 7.14 (m, 1H, H⁹), 6.99 (d, 1H, ³J(HH) 7.0 Hz, H³), 1.43 (s, 9H, CMe₃) and 1.39 (s, 9H, CMe₃).

¹³C-NMR (100 MHz, CDCl₃, δ in ppm): 158.5 (C_{quat}), 155.1 (C_{quat}), 153.8 (C_{quat}), 151.7 (C_{quat}), 150.6 (C_{quat}), 148.7 (1C, C¹⁰), 146.3 (C_{quat}), 137.4 (C_{quat}), 135.3 (1C, C⁸), 134.8 (C_{quat}), 134.5 (C_{quat}), 134.4 (C_{quat}), 133.0 (C_{quat}), 131.0 (C_{quat}), 130.8 (C_{quat}), 129.8 (C_{quat}), 129.6 (2C, C⁴), 128.8 (2C, C^{4'}), 128.7 (1C, C¹), 127.9 (1C, C^{2'}), 127.7 (1C, C²), 127.3 (1C, C^{1'}), 125.4 (2C, C^{5'}), 125.3 (2C, C⁵), 125.2 (1C, C³), 125.0 (1C, C⁷),

123.8 (1C, C^{3'}), 121.9 (1C, C⁹), 34.8 (1C, CMe₃), 34.6 (1C, CMe₃) and 31.4 (6C, CMe₃).



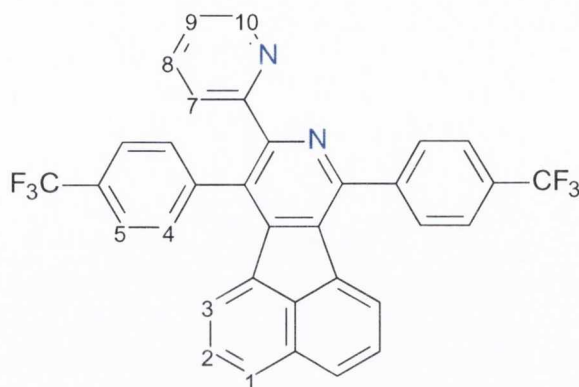
5.3.5 Synthesis of 7,10-Di[(4-trifluoromethyl)phenyl]-9-(2-pyridyl)-8-azafluoranthene (10)

7,9-Bis[(4-trifluoromethyl)phenyl]-8*H*-cyclopenta[*l*]acenaphthylen-8-one (350 mg, 0.8 mmol) and 2-cyanopyridine (1.0 g 9.6 mmol) were stirred, external temperature 280° C, under nitrogen for 60 h. The resulting brownish red solution was allowed to cool. Chromatography on silica using methanol/dichloromethane gave the ligand as a pale yellow crystalline solid. Yield 200 mg 45%. Mp > 300°C. Found: C, 69.54; H, 3.61; N, 4.30 calcd. (%) for C₃₄H₁₈F₆N₂:MeOH; C, 70.00; H, 3.69; N, 4.66

ESI-MS (acetonitrile, *m/z*): found: 569.1459, calcd. 569.1452, for C₃₄H₁₈F₆N₂, [M+1]⁺.

¹H-NMR (400 MHz, CDCl₃, δ in ppm): 8.39 (br, s, 1H, H¹⁰), 8.08 (d, 2H, ³J(HH) 7.8 Hz, H^{4'}), 7.95 (d, 1H, ³J(HH) 8.7 Hz, H¹), 7.91 (d, 1H, ³J(HH) 8.7 Hz, H^{1'}), 7.88 (d, 2H, ³J(HH) 8.7 Hz, H^{5'}), 7.72 (d, 2H, ³J(HH) 7.8 Hz, H⁵), 7.66 (m, 1H, H⁷), 7.63 (dd, 1H, ³J(HH) 7.0, 7.8 Hz, H⁸), 7.59 – 7.56 (m, 3H, H^{3'} & H⁴) 7.54 (dd, 1H, ³J(HH) 7.8 Hz, H^{2'}), 7.45 (dd, 1H, ³J(HH) 6, 7.8 Hz, H²), 7.13 (m, 1H, H⁹), 6.92 (d, 1H, ³J(HH) 7.0 Hz, H³).

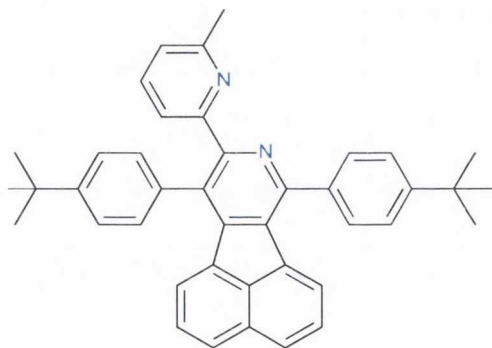
¹³C-NMR (100 MHz, CDCl₃, δ in ppm): 157.6 (C_{quat}), 154.6 (C_{quat}), 152.4 (C_{quat}), 148.6 (1C, C¹⁰), 146.5 (C_{quat}), 143.7 (C_{quat}), 141.7 (C_{quat}), 136.1 (1C, C⁸), 133.9 (C_{quat}), 133.4 (C_{quat}), 132.9 (C_{quat}), 131.3 (C_{quat}), 130.4 (2C, C⁵), 130.3 (C_{quat}), 129.7 (2C, C^{5'}), 129.5 (1C, C¹), 128.1 (1C, C^{1'}), 128.1 (1C, C^{2'}), 128.0 (1C, C²), 125.7 (CF₃), 125.7 (2C, C^{4'}), 125.7 (2C, C⁴), 125.5 (CF₃), 125.4 (1C, C³), 125.1 (C_{quat}), 124.8 (1C, C⁷), 123.9 (1C, C^{3'}), 123.3 (C_{quat}), 122.5 (1C, C⁹).



5.3.6 Synthesis of 7,10-Di(4-*tert*-butylphenyl)-9-(6-methyl-2-pyridyl)-8-azafluoranthene (11)

7,9-Bis(4-*tert*-butylphenyl)-8*H*-cyclopenta[*l*]acenaphthylen-8-one (350 mg, 0.75 mmol) and 6-methyl-2-pyridinecarbonitrile (1.0 g 8.5 mmol) were stirred, external temperature 280° C, under nitrogen for 60 h. The resulting brownish red solution was allowed to cool. Chromatography on silica using methanol/dichloromethane gave the ligand as a crude brown solid. Yield 14mg, 4%

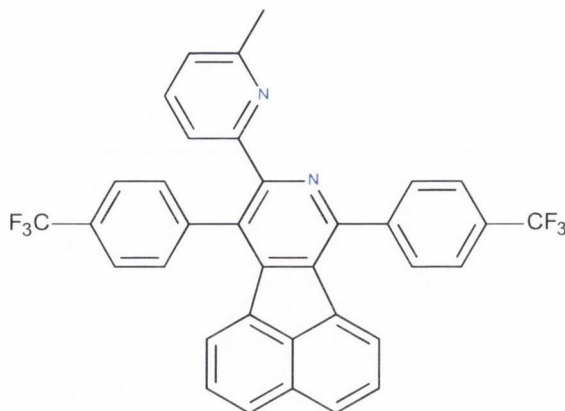
ESI-MS (acetonitrile, *m/z*): found: 559.3043, calcd. 559.3035, for C₄₁H₃₈N₂, [M+1]⁺.



5.3.7 Synthesis of 7,10-Di[(4-trifluoromethyl)phenyl]-9-(6-methyl-2-pyridyl)-8-azafluoranthene (12)

7,9-Bis[(4-trifluoromethyl)phenyl]-8*H*-cyclopenta[*l*]acenaphthylen-8-one (350 mg, 0.7 mmol) and 2-cyanopyridine (1.0 g 9.6 mmol) were stirred, external temperature 280° C, under nitrogen for 60 h. The resulting brownish red solution was allowed to cool. Chromatography on silica using methanol/dichloromethane gave the ligand as a crude brown solid. Crude yield 20 mg, 5%.

ESI-MS (acetonitrile, m/z): found: 583.1697, calcd. 583.1657, for $C_{35}H_{20}F_6N_2$, $[M+1]^+$.



5.3.8 Synthesis of 7,10-Di(4-*tert*-butylphenyl)-9-(6-cyano-2-pyridyl)-8-azafluoranthene (13)

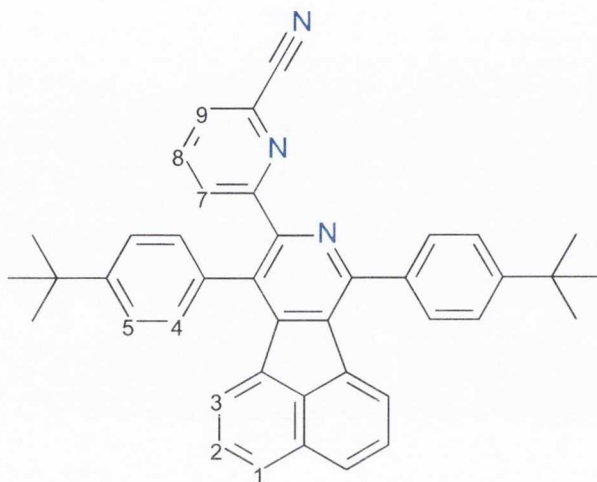
7,9-di(4-*tert*-butylphenyl)-8*H*-cyclopenta[1]acenaphthylen-8-one (300 mg, 0.64 mmol) and 2,6-dicyanopyridine (1.1 g, 11.6 mmol) were heated under nitrogen in a benzophenone melt, external temperature 300°C for 7 days. The resulting brownish red solution was allowed to cool to form a brown solid which was then purified by flash chromatography on silica gel using a dichloromethane:methanol solution as the eluent. This gave the ligand as a pale brown solid. Yield 100 mg, 28%. Mp > 300° C. Found: C, 80.60; H, 5.59; N, 9.08 calcd. (%) for $C_{41}H_{36}N_3 \cdot C_6H_4N_2 \cdot 0.5CH_2Cl_2$; C, 79.81; H, 5.58; N, 9.70.

ESI-MS (acetonitrile, m/z): found: 570.2921, calcd. 570.2909, for $C_{41}H_{36}N_3$, $[M+1]^+$.

1H NMR (600 MHz, $CDCl_3$, δ in ppm): 8.07 (d, 1H, $^3J(HH)$ 7.9 Hz, H^1), 8.02 (d, 1H, $^3J(HH)$ 7.9 Hz, $H^{1'}$), 7.98 (d, 2H, $^3J(HH)$ 6.4 Hz, H^4), 7.79 (dd, 1H, $^3J(HH)$ 7.4, 8.1 Hz, H^9), 7.75 (d, 1H, $^3J(HH)$ 7.4 Hz, $H^{3'}$), 7.71 (d, 2H, $^3J(HH)$ 7.4 Hz, H^5), 7.63 (dd, 1H, $^3J(HH)$ 8.1, 7.4 Hz, $H^{2'}$), 7.59 (d, 2H, $^3J(HH)$ 7.4 Hz, H^7 & H^8), 7.54 – 7.52 (m, 3H, H^2 & H^4), 7.37 (d, 2H, $^3J(HH)$ 7.4 Hz, H^5), 7.12 (d, 1H, $^3J(HH)$ 6.6 Hz, H^3), 1.48 (s, 9H, CMe_3) and 1.45 (s, 9H, CMe_3).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 160.1 (C_{quat}), 153.9 (C_{quat}), 152.5 (C_{quat}), 152.3 (C_{quat}), 151.0 (C_{quat}), 146.9 (C_{quat}), 137.2 (C_{quat}), 136.6 (1C, C^8), 134.8 (C_{quat}), 134.2 (C_{quat}), 134.1 (C_{quat}), 133.1 (C_{quat}), 132.3 (C_{quat}), 131.7 (C_{quat}), 131.6 (C_{quat}), 129.8

(C_{quat}), 129.5 (2C, C⁴), 129.0 (1C, C¹), 128.7 (2C, C^{4'}), 128.2 (1C, C^{1'}), 128.0 (1C, C⁷), 127.9 (1C, C²), 127.7 (1C, C⁹), 126.7 (1C, C^{3'}), 125.7 (1C, C³), 125.6 (2C, C^{5'}), 125.4 (2C, C⁵), 124.2 (1C, C²), 116.9 (C≡N), 34.8 (CMe₃), 34.7 (CMe₃), 31.5 (CMe₃) and 31.0 (CMe₃).



5.3.9 Synthesis of 7,10-di[(4-trifluoromethyl)phenyl]-9-(6-cyano-2-pyridyl)-8-azafluoranthene (14)

7,9-Bis[4-trifluoromethyl]phenyl]-8*H*-cyclopenta[*l*]acenaphthylen-8-one (300 mg, 0.64 mmol) and 2,6-dicyanopyridine (1.1 g, 11.6 mmol) were heated under nitrogen in a benzophenone melt, external temperature 300°C for 7 days. Purification by column chromatography on silica using hexane: dichloromethane (8:3 v/v) as eluent followed by dichloromethane (100%) and a mixture of dichloromethane: methanol (97:3 v/v) as eluent afforded a dark brown solid that was dry loaded onto silica using ethyl acetate (100%) as eluent to afford the product as a pale brown solid. This was dissolved in dichloromethane and precipitated with cold methanol. Product was a mixture that could not be successfully separated.

ESI-MS (acetonitrile, *m/z*): found: 594.1399, calcd. 594.1405, for C₃₃H₂₀N₃, [M+1]⁺.

5.4 Synthesis of Copper(I) Complexes

5.4.1 Synthesis of [Cu(6)₂] (15)

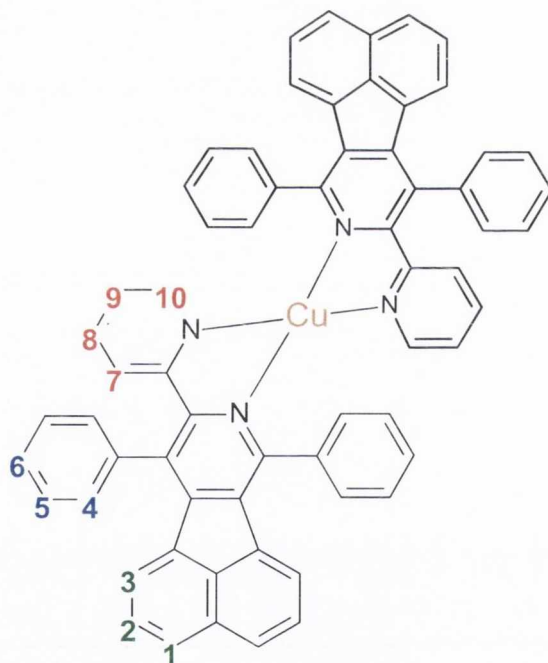
7,10-Diphenyl-9-(2-pyridyl)-8-azafluoranthene (60 mg, 0.139 mmol, 2.1 equiv.) was added to a stirred solution of [Cu(MeCN)₄]PF₆ (25 mg, 0.067 mmol) in dichloromethane (15 mL). On addition of the ligand the solution turned a deep purple colour. The solution was stirred at room temperature for 30 min, washed through celite and the

volume reduced *in vacuo*. The desired product was precipitated out with hexane and collected as a dark green powder. (Yield 54.1 mg, 87 %)

ESI-MS (acetonitrile, m/z): found: 927.2545, calcd. 927.2549, for $C_{64}H_{40}CuN_4$, $[M]^+$

1H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, 1H, $^3J(HH)$ 4 Hz, H^{10}), 7.98 (d, 1H, $^3J(HH)$ 8 Hz, H^1), 7.89 (d, 1H, $^3J(HH)$ 8 Hz, $H^{1'}$), 7.78 (br s, 3H, $H^{5'}$ & H^6), 7.56 (br s, 2H, $H^{4'}$), 7.52 (m, 1H, $^3J(HH)$ 7.7 Hz, H^8), 7.46 (m, 1H, $^3J(HH)$ 7.7 Hz, H^2), 7.43 – 7.39 (m, 3H, H^9 , $H^{2'}$ & H^6), 7.24 (d, 2H, H^4), 7.04 (d, 2H, $^3J(HH)$ 7.7 Hz, H^7 & $H^{3'}$), 6.98 (dd, 2H, $^3J(HH)$ 7.3, 8 Hz, H^5) and 6.72 (d, 1H, $^3J(HH)$ 7 Hz, H^3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2 (C_{quat}), 151.9 (C_{quat}), 148.4 (1C, C^{10}), 147.5 (C_{quat}), 146.8 (C_{quat}), 138.8 (C_{quat}), 137.4 (C_{quat}), 135.9 (1C, C^8), 133.7 (C_{quat}), 133.0 (C_{quat}), 133.3 (C_{quat}), 132.6 (C_{quat}), 130.6 (2C, $C^{5'}$), 129.8 (1C, C^1), 129.6 (1C, C^6), 129.0 (2C, C^4), 128.9 (2C, $C^{4'}$), 128.7 (1C, $C^{1'}$), 128.3 (2C, C^2 & C^6), 128.2 (1C, $C^{2'}$), 128.1 (2C, C^5), 126.6 (1C, C^3), 126.1 (1C, $C^{3'}$), 125.4 (2C, C^9) and 124.8 (1C, C^7).



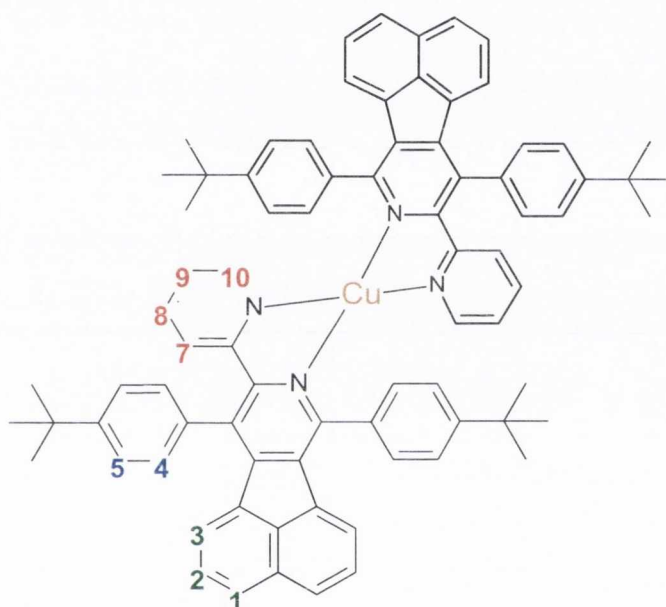
5.4.2 Synthesis of $[Cu(9)_2]$ (16)

7,10-Di[(4-tertbutyl)phenyl]-9-(2-pyridyl)-8-azafluoranthene (70 mg, 0.135 mmol), was added to a stirred solution of $[Cu(MeCN)_4]PF_6$ (25 mg, 0.067 mmol) in dichloromethane (15 mL). On addition of the ligand the solution turned a deep purple

colour. The solution was stirred at room temperature for 30 min, washed through celite and the volume reduced *in vacuo*. The desired product was precipitated out with hexane and collected as a dark green powder. Yield 61 mg, 80 %

ESI-MS (acetonitrile, m/z): found: 1151.5105, calcd. 1152.5053, for $C_{80}H_{72}CuN_4$, $[M]^+$

1H NMR (400 MHz, $CDCl_3$): δ 8.28 (br s, 1H, H^{10}), 8.01 (d, 1H, $^3J(HH)$ 7.5 Hz, H^1), 7.99 (d, 1H, $^3J(HH)$ 7.5 Hz, $H^{1'}$), 7.78 (br d, 2H, $^3J(HH)$ 6.3 Hz, H^4), 7.55 – 7.43 (br m, 5H, $H^{5'}$, H^2 , $H^{2'}$ & H^8), 7.40 – 7.32 (m, 3H, H^5 & H^7), 7.14 (d, 2H, $^3J(HH)$ 6.4 Hz, H^4), 7.08 (m, 2H, $H^{3'}$ & H^9), 6.87 (d, 1H, H^3), 1.58 (s, 9H, CMe_3) and 1.56 (s, 9H, CMe_3).



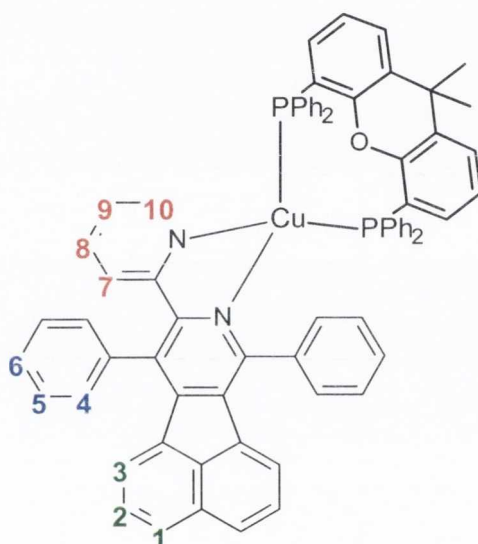
5.4.3 Synthesis of $[Cu(10)_2]$ (17)

7,10-Di[(4-trifluoromethyl)phenyl]-9-(2-pyridyl)-8-azafluoranthene (80 mg, 0.14 mmol, 2.1 equiv.) was added to a stirred solution of $[Cu(MeCN)_4]PF_6$ (25 mg, 0.067 mmol) in dichloromethane (15 mL). On addition of the ligand the solution turned a deep purple colour. The solution was stirred at room temperature for 30 min, washed through celite and the volume reduced *in vacuo*. The desired product was precipitated out with hexane and collected as a dark green powder. Yield 52 mg, 64 %

ESI-MS (acetonitrile, m/z): found: 1199.2061, calcd. 1199.2044, for $C_{68}H_{36}CuF_{12}N_4$, $[M]^+$

H^7), 7.14 – 7.04 (m, 15H, H^4 , H^5 , $H^{3'}$ and $10H^{\text{phenyl}}$), 7.00 – 6.87 (m, 10H, H^{phenyl}), 6.65 (br s, 3H, $2H^{\text{xant}}$ and H^9), 6.62 (d, 1H, H^3) and 2.16 (s, 6H, $2CH_3$).

^{13}C NMR (100 MHz, CDCl_3): δ 155.0 (C_{quat}), 154.5 (1C, C^{10}), 154.0 (C_{quat}), 149.3 (C_{quat}), 147.7 (C_{quat}), 136.8 (C_{quat}), 136.4 (1C, C^8), 134.2 (C_{quat}), 133.9 (C_{quat}), 133.8 (C_{quat}), 133.3 (C_{quat}), 133.0 (C_{quat}), 132.7 (C_{quat}), 132.1 (C_{quat}), 130.5 (1C, $\text{C}^{1'}$), 130.4 (1C, C^9), 130.1 (2C, $\text{C}^{5'}$), 129.8 (1C, $\text{C}^{6'}$), 129.5 (2C, $\text{C}^{4'}$), 128.9 (1C, C^1), 128.5 (4C, C^4 and C^5), 128.3 (1C, $\text{C}^{2'}$), 128.2 (1C, C^2), 127.1 (1C, $\text{C}^{3'}$), 126.9 (1C, C^6), 125.1 (1C, C^3), and 124.9 (1C, C^7).



5.4.5 Synthesis of [9CuXantphos] (19)

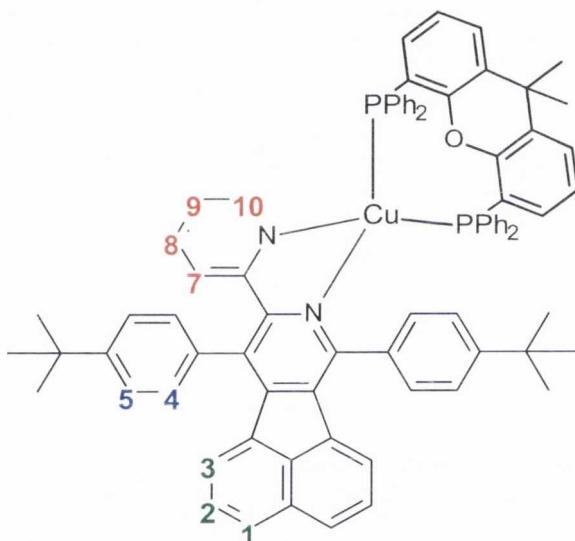
7,10-Di(4-tertbutyl)phenyl-9-(2-pyridyl)-8-azafluoranthene (38 mg, 0.07 mmol, 1.1 equiv.) was added to a stirred solution of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (25 mg, 0.067 mmol) and xantphos (40 mg, .07 mmol) in dichloromethane (15 mL). On addition of the ligand the slolution turned a deep yellow colour. The solution was stirred at room temperature for 30 min, washed through celite and the volume reduced *in vacuo*. The desired product was precipitated out with pet. ether and collected as a deep yellow powder. Yield 57 mg, 69 %

ESI-MS (acetonitrile, m/z): found: 1185.4131, calcd. 1185.4103, for $\text{C}_{79}\text{H}_{70}\text{CuN}_2\text{OP}_2$, $[\text{M}]^+$

^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, 1H, $H^{1'}$), 7.87 (d, 1H, H^1), 7.66 – 7.61 (m, 3H, H^{10} & $H^{4'}$), 7.51 (dd, 1H, $H^{2'}$), 7.45 – 7.02 (m, 16H, H^{xant}), 7.41 – 7.39 (m, 2H, $H^{5'}$),

7.37 – 7.32 (m, 2H, H² and H⁸), 7.24 – 7.14 (m, 4H, H⁴ & H⁵), 7.14 – 7.12 (m, 1H, H⁷), 7.04 (m, 1H, H³), 6.93 (m, 2H, H^{xant}), 6.82 (m, 3H, H^{xant}), 6.71 (m, 3H, H^{xant}), 6.56 (m, 2H, H^{xant}), 6.46 (m, 1H, H⁹), 6.34 (m, 1H, H³), 1.69 (s, 6H, 2CH₃), 1.47 (s, 9H, CMe₃) and 1.45 (s, 9H, CMe₃).

¹³C NMR (100 MHz, CDCl₃): δ 154.7 (C_{quat}), 154.6 (C_{quat}), 154.35 (C_{quat}), 153.9 (C_{quat}), 153.2 (C_{quat}), 152.2 (C_{quat}), 149.6 (C_{quat}), 148.0 (C_{quat}), 147.5 (C_{quat}), 136.8 (1C, C⁸), 136.5 (C_{quat}), 134.6 (C_{quat}), 134.4 (1C, C¹⁰), 133.2 (C_{quat}), 133.1 (C_{quat}), 133.0 (C_{quat}), 130.8 (1C, C⁹), 130.4 (1C, C¹), 129.1 (1C, C¹), 128.8 (2C, C⁵), 128.8 (2C, C⁵), 128.5 (2C, C⁴), 128.2 (1C, C²), 128.1 (1C, C²), 127.1 (2C, C⁴), 126.3 (1C, C³), 125.4 (1C, C⁷), 124.9 (1C, C³), 31.6 (6C, CMe₃), 31.4 (3C, CMe₃), and 28.3 (2C, 2CH₃).



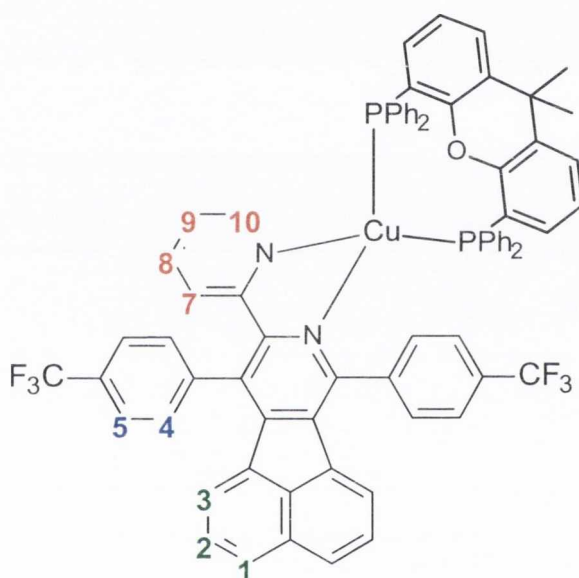
5.4.6 Synthesis of [10CuXantphos] (20)

7,10-Di(4-trifluoromethyl)phenyl-9-(2-pyridyl)-8-azafluoranthene (40 mg, 0.07 mmol, 1.1 equiv.) was added to a stirred solution of [Cu(MeCN)₄]PF₆ (25 mg, 0.067 mmol) and xantphos (40 mg, 0.07 mmol) in dichloromethane (15 mL). On addition of the ligand the solution turned a deep yellow colour. The solution was stirred at room temperature for 30 min, washed through celite and the volume reduced *in vacuo*. The desired product was precipitated out with pet. ether and collected as a deep yellow powder. Yield 37 mg, 44 %

ESI-MS (acetonitrile, m/z): found: 1209.2581, calcd. 1209.2599, for $C_{73}H_{50}CuF_6N_2OP_2$, $[M]^+$

1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, 1H, $^3J(HH)$ 8.6Hz, $H^{1'}$), 7.96 (d, 1H, $H^{1'}$), 7.93 (d, 2H, $H^{4'}$), 7.68 – 7.63 (m, 3H, $H^{5'}$ & H^{10}), 7.58 (dd, 1H, $H^{2'}$), 7.48 (m, 2H, H^{xant}), 7.42 (dd, 1H, $H^{2'}$), 7.31 – 7.23 (m, 12H, $10H^{phenyl}$ & H^4), 7.21 – 7.14 (m, 4H, H^7 , H^8 & $2H^{xant}$), 7.05 – 6.99 (m, 3H, H^5 & $H^{3'}$), 6.91 – 6.86 (m, 5H, H^{phenyl}), 6.78 – 6.73 (m, 5H, H^{phenyl}), 6.58 – 6.53 (m, 3H, H^9 & $2H^{xant}$), 6.47 (d, 1H, $H^{3'}$) and 1.70 (s, 6H, $2CH_3$).

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -73.1, -75.0 ppm.



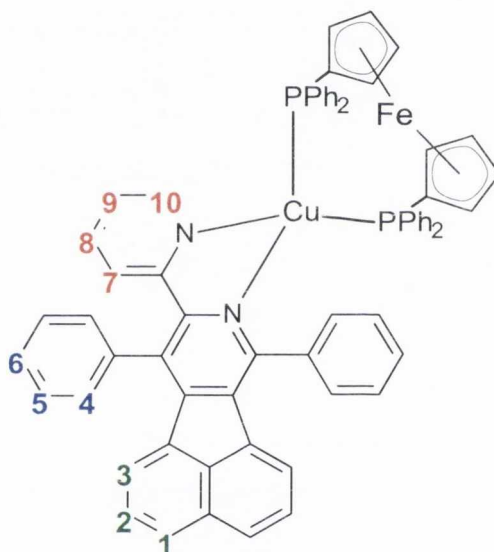
5.4.7 Synthesis of $[6Cu(dppf)]$ (21)

7,10-Diphenyl-9-(2-pyridyl)-8-azafluoranthene (30 mg, 0.07 mmol, 1.1 equiv.) was added to a stirred solution of $[Cu(MeCN)_4]PF_6$ (25 mg, 0.067 mmol) and dppf (39 mg, 0.07 mmol) in dichloromethane (15 mL). On addition of the ligand the solution turned a deep yellow colour. The solution was stirred at room temperature for 30 min, washed through celite and the volume reduced *in vacuo*. The desired product was precipitated out with pet. ether and collected as an orange solid. (Yield 52 mg, 71 %)

ESI-MS (acetonitrile, m/z): found: 1049.1934, calcd. 1049.1938, for $C_{66}H_{48}CuFeN_2P_2$, $[M]^+$

^1H NMR (400 MHz, CDCl_3): δ 8.07 (d, 2H, H^{10} & $\text{H}^{1'}$), 7.95 (d, 1H, H^1), 7.69 – 7.62 (m, 4H, $\text{H}^{5'}$, $\text{H}^{6'}$ & H^6), 7.55 (dd, 2H, H^8 & $\text{H}^{2'}$), 7.44 – 6.80 (m, 20H, H^{phenyl}) 7.44 – 7.41 (m, 3H, $\text{H}^{4'}$ & H^2), 7.34 (d, 1H, H^7), 7.30 (m, 2H, H^4), 7.11 – 7.07 (m, 2H, $\text{H}^{3'}$ & H^9), 6.90 (d, 2H, H^5), 6.54 (d, 1H, H^3), 4.47 (s, 4H, $\text{H}^{\text{Ferrocene}}$), 4.25 (br s, 2H, $\text{H}^{\text{ferrocene}}$) and 3.90 (br s, 2H, $\text{H}^{\text{ferrocene}}$).

^{13}C NMR (100 MHz, CDCl_3): δ 154.8 (C_{quat}), 153.9 (C_{quat}), 150.2 (C_{quat}), 148.4 (1C, C^{10}), 147.3 (C_{quat}), 139.1 (C_{quat}), 136.8 (1C, C^8), 136.3 (C_{quat}), 134.8 (C_{quat}), 133.1 (C_{quat}), 133.0 (C_{quat}), 132.6 (C_{quat}), 132.2 (C_{quat}), 130.5 (1C, $\text{C}^{1'}$), 130.1 (2C, $\text{C}^{5'}$), 129.9 (1C, $\text{C}^{6'}$), 129.6 (1C, C^6), 129.5 (2C, $\text{C}^{4'}$), 129.3 (1C, C^4), 128.9 (2C, C^5), 128.8 (1C, C^1), 128.2 (1C, $\text{C}^{2'}$), 128.1 (1C, C^2), 127.3 (1C, C^7), 126.9 (1C, C^3), 125.1 (1C, C^3), 124.4 (1C, C^9), 74.0 (4C, $\text{C}^{\text{Ferrocene}}$) and 71.1 (4C, $\text{C}^{\text{Ferrocene}}$).

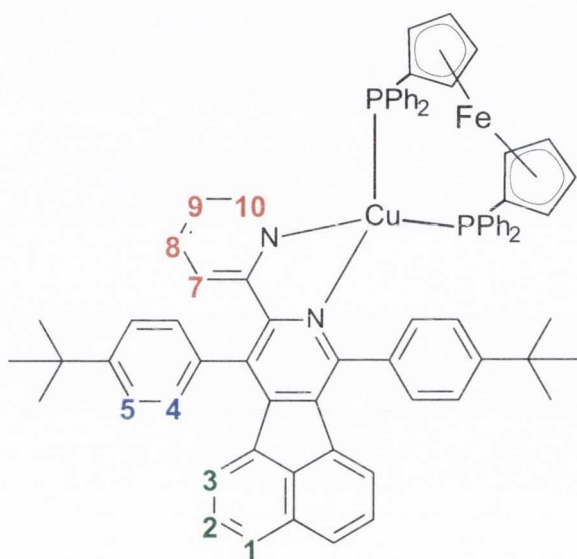


5.4.8 Synthesis of $[\text{Cu}_9(\text{dppf})]$ (22)

7,10-Di(4-tertbutyl)phenyl-9-(2-pyridyl)-8-azafluoranthene (38 mg, 0.07 mmol, 1.1 equiv.) was added to a stirred solution of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (25 mg, 0.067 mmol) and dppf (39 mg, 0.07 mmol) in dichloromethane (15 mL). On addition of the ligand the solution turned a deep yellow colour. The solution was stirred at room temperature for 30 min, washed through celite and the volume reduced *in vacuo*. The desired product was precipitated out with pet. ether and collected as an orange solid. (Yield 61 mg, 76 %)

ESI-MS (acetonitrile, m/z): found: 1161.3192, calcd. 1161.3190, for $C_{74}H_{64}CuFeN_2P_2$, $[M]^+$

1H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.04 (m, 2H, H^{10} & $H^{1'}$), 7.95 – 7.92 (m, 1H, H^1), 7.81 – 7.65 (m, 8H, $H^{4'}$, $H^{5'}$, H^4 & H^5), 7.62 – 7.52 (m, 2H, H^8 & $H^{2'}$), 7.46 – 7.34 (m, 11H, $10H^{phenyl}$ & H^2), 7.25 (d, 1H, H^7), 7.21 – 6.92 (m, 11H, $10H^{phenyl}$ & $H^{3'}$), 6.88 (d, 1H, H^9), 6.59 (d, 1H, H^3), 4.41 (br s, 4H, $H^{Ferrocene}$), 4.38 (br s, 2H, $H^{Ferrocene}$), 4.22 (br s, 2H, $H^{Ferrocene}$), 1.49 (s, 9H, CMe_3) and 1.45 (s, 9H, CMe_3)



5.4.9 Synthesis of $[Cu10(dppf)]$ (23)

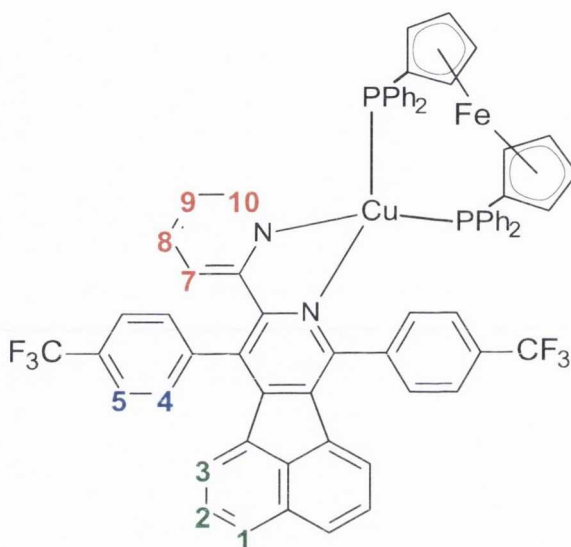
7,10-Di(4-trifluoromethyl)phenyl-9-(2-pyridyl)-8-azafluoranthene (40 mg, 0.07 mmol, 1.1 equiv.) was added to a stirred solution of $[Cu(MeCN)_4]PF_6$ (25 mg, 0.067 mmol) and dppf (39 mg, 0.07 mmol) in dichloromethane (15 mL). On addition of the ligand the solution turned a deep yellow colour. The solution was stirred at room temperature for 30 min, washed through celite and the volume reduced *in vacuo*. The desired product was precipitated out with pet. ether and collected as an orange solid. Yield 33 mg, 40 %

ESI-MS (acetonitrile, m/z): found: 1196.2451 calcd. 1196.2468 for $C_{68}H_{56}CuF_6FeN_2P_2$, $[M]^+$

1H NMR (400 MHz, $CDCl_3$): δ 8.5 (br m, 1H, H^{10}), 8.3 – 7.95 (m, 4H, $H^{4'}$, $H^{1'}$ & H^1), 7.95 – 6.9 (m, 30H, $20H^{phenyl}$, $H^{5'}$, H^4 , H^5 , $H^{2'}$, H^2 , H^8 and H^7), 6.8 (d, 1H, $H^{3'}$), 6.7 (br

d, 1H, H⁹), 6.6 (d, 1H, H³), 4.5 (br s, 4H, H^{Ferrocene}), 4.2 (br s, 2H, H^{Ferrocene}) and 3.9 (br s, 2H, H^{Ferrocene}).

¹⁹F NMR (376.5 MHz, CDCl₃): δ -72.6, -74.5 ppm.



5.5 Synthesis of Terpyridine based ligands

5.5.1 Synthesis of 2,5-pyrazinedicarboxylic acid¹⁴⁶ (24)

To a solution of selenium dioxide (25g, 225.3 mmol) in pyridine and water (10:1, 100mL) was added 2,5-dimethylpyrazine (5ml, 45.8mmol). The mixture was heated to reflux under argon overnight to yield a dark brown precipitate and a clear brown solution. The precipitate was filtered and then stirred overnight in solution 2N ammonia (150mL) and activated charcoal. The mixture was then filtered and to this was added conc. HCl (60mL) forming a white precipitate that was collected and dried to give the product as an off white solid. Yield (6.02g, 78%).

IR (neat) cm⁻¹: 3400-2100(br), 1710, 1502, 1403, 1335, 1261, 1170, 1045, 922, 759.

¹H-NMR (400 MHz, DMSO, δ in ppm): 9.27 (s, 2H, H_{pyrazine}).

¹³C-NMR (100 MHz, DMSO, δ in ppm): 164.83 (1C, C=OOH), 146.04 (C_{quat}), 145.28 (C_{pyrazine}).



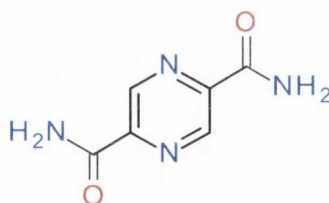
5.5.2 Synthesis of 2,5-pyrazinedicarboxylic acid diamide¹⁴⁶ (25)

A solution of 2,5-pyrazinedicarboxylic acid (2.0g, 11.9mmol), thionyl chloride (20mL, 274.2mmol) and dry DMF (5mL) was heated to reflux for 2h at 80°C. After cooling the solvent was removed to give a yellow-orange solid. To this conc. ammonia (30mL) was added dropwise over 1h at -30°C. The mixture was then warmed to room temperature and stirred overnight. An additional 20mL of conc. ammonia was then added, the resulting precipitate was then filtered and washed with cold conc. ammonia. This was then dried under vacuum at 100°C to yield the product as a pale brown solid. Yield (1.82g, 91%).

IR (neat) cm^{-1} : 3418, 3155, 1672, 1588, 1417, 1302, 1179, 1034, 816, 717.

^1H -NMR (400 MHz, DMSO, δ in ppm): 9.16 (s, 2H, $\text{H}_{\text{pyrazine}}$).

^{13}C -NMR (100 MHz, DMSO, δ in ppm): 164.44 (1C, $\text{C}=\text{ONH}_2$), 146.76 (C_{quat}), 142.01 ($\text{C}_{\text{pyrazine}}$).



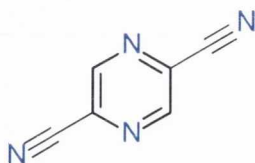
5.5.3 Synthesis of 2,5-dicyanopyrazine¹⁴⁷ (26)

To 2,5-pyrazinedicarboxylic acid diamide (0.6 g, 3.6 mmol) in dry DMF (30mL) at -10°C was added thionyl chloride (1mL) dropwise over 30 min, with the reaction temperature increasing gradually. The mixture was then left to stir at room temperature overnight. The resulting dark brown solution was poured over ice water and extracted with dichloromethane (3 x 50mL) and dried over anhydrous magnesium sulfate to afford the product as a light brown solid. Yield (0.4g, 67%).

IR (neat) cm^{-1} : 3081, 2248, 1893, 1466, 1309, 1186, 1159, 1026, 939.

^1H -NMR (400 MHz, DMSO, δ in ppm): 9.4 (s, 1H, $\text{H}_{\text{pyrazine}}$).

^{13}C -NMR (100 MHz, DMSO, δ in ppm): 149.27 ($\text{C}_{\text{pyrazine}}$), 132.32 (C_{quat}), 115.48 (C_{quat}).

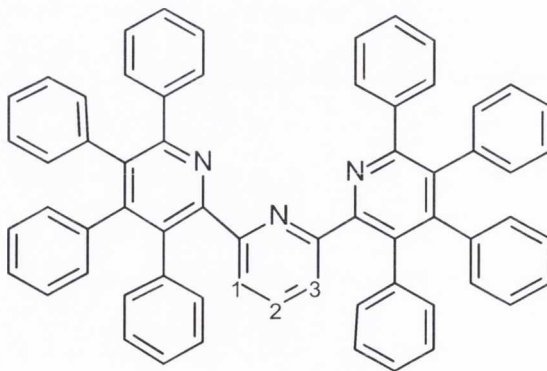


5.5.4 Synthesis of 2,6-bis(2,3,4,5-tetraphenylpyridyl)pyridine (30)

2,6-dicyanopyridine (80 mg, 0.619 mmol), tetraphenylcyclopentadienone (475 mg, 1.36 mmol) and benzophenone (600 mg) were heated at 300°C under nitrogen for 6 days. The mixture was then separated by column chromatography on silica gel using dichloromethane as the eluent to remove the benzophenone and tetraphenylcyclopentadienone. The product was removed with methanol. A second column was run on silica to remove any remaining impurities, however the product adhered to the silica and was removed with triethylamine. A third column was run on alumina using dichloromethane as the eluent to yield a pale yellow product. This product was then further separated on a silica preparative TLC plate to give an off white powder in low yield. (20 mg, 4%)

ESI-MS (DMSO, m/z): found: 864.3346, calcd. 864.3354, for $\text{C}_{68}\text{H}_{56}\text{CuFeN}_2\text{P}_2$, $[\text{MNa}]^+$

^1H -NMR (600 MHz, CDCl_3 , δ in ppm): 7.84 (d, 1H, $^3J(\text{HH})$ 7.5 Hz, H1), 7.75 (t, 1H, $^3J(\text{HH})$ 7.5 Hz, H2), 7.52 (d, 1H, $^3J(\text{HH})$ 7.5 Hz, H3), 7.53-7.34 (m, 4H, H_{aryl}), 7.23-7.19 (m, 6H, H_{aryl}), 7.04-6.92 (m, 26H, H_{aryl}) and 6.82-6.77 (m, 4H, H_{aryl}).



5.5.5 Synthesis of 6,6''-dibromo-2,2':6'2''-terpyridine¹⁵¹ (31)

To a cooled (- 60 °C) solution of 2,6-dibromopyridine (11.85g, 50 mmol) in Et₂O (50 mL) was added a solution of n-BuLi (50 mmol) in hexane. The mixture was stirred at - 40 °C for 2 hr after which a solution of PCl₃ (1.72 g, 12.5 mmol) in Et₂O (50 mL) was added dropwise over a period of 2 hr. the mixture was then stirred at - 40 °C for 20 hr. The mixture was set to warm to room temperature and then poured into H₂O (100 mL). The solid product was collected by filtration and washed with H₂O and dried. The solid was dissolved in hot toluene (400 mL) and was passed through a short silica gel column. The toluene was removed under reduced pressure and the residue washed with Et₂O to give the desired product as a white crystalline solid. (2.35 g, 48%)

Mp 264 - 265 °C (lit. 263 – 264 °C)

ESI-MS (DMSO, m/z): found: 411.9059, calcd. 411.9061, for C₁₅H₉N₃Br₂Na, [M + H]

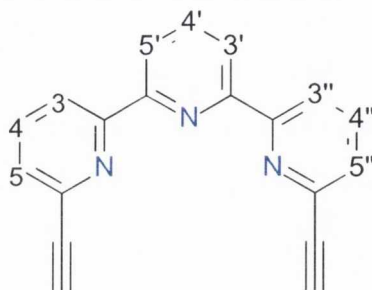


5.5.6 Synthesis of 6,6''-diethynyl-2,2':6'2''-terpyridine^{157,158} (32)

To a solution of 6,6''-dibromo-2,2':6'2''-terpyridine (1g, 2.55 mmol) in *n*Pr₂NH₂ was added [Pd⁰(PPh₃)₄] (6 mol %) and 2-Methyl-3-butyne-2-ol (0.9 mL, 9.0 mmol) in a Schlenk flask and degassed by bubbling Ar through. The reaction mixture was stirred under argon for 3hr at 60° C. The solvent was then removed under vacuum leaving behind a dark brown precipitate. The precipitate was washed with water and extracted into dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulfate and the solvent was removed to give a brown precipitate. This precipitate was dissolved in toluene (100 mL) and to this was added an excess of NaOH (0.15g). The mixture was refluxed overnight and was then filtered to remove remaining solid sodium hydroxide. The product was purified by column chromatography on silica gel, using dichloromethane: methanol (20:1) as the eluent, to give a an off white crystalline solid in good yield. (0.53 g, 74%).

IR (neat) cm⁻¹: 3300 (C≡C-H), 2108 (-C≡C-).

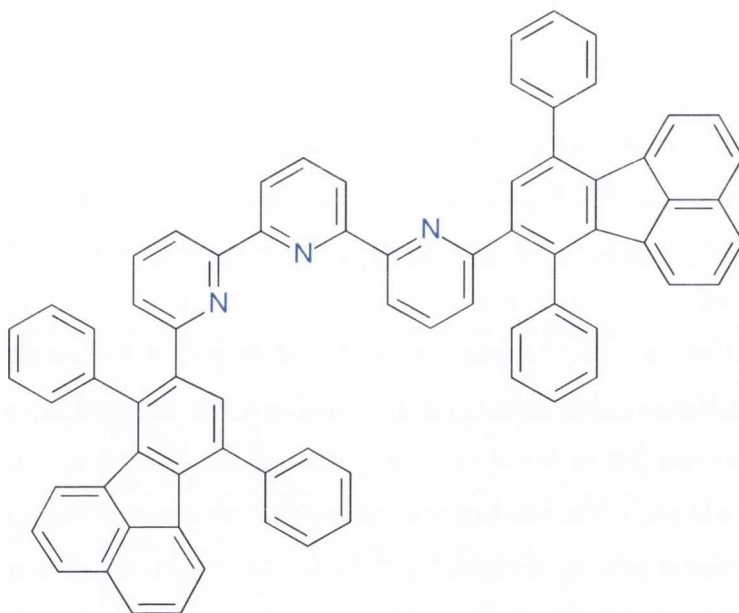
$^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ in ppm): 8.58 (dd, 2H, $^3J(\text{HH})$ 8.0, 1.0 Hz, H3 & H3''), 8.56 (d, 2H, $^3J(\text{HH})$ 8.0 Hz, H3' & H5'), 7.96 (t, 1H, $^3J(\text{HH})$ 7.9, 1.0 Hz, H4'), 7.81 (t, 2H, $^3J(\text{HH})$ 8.0 Hz, H4 & H4''), 7.53 (dd, 2H, $^3J(\text{HH})$ 7.7, 1.0 Hz, H5 & H5''), 3.2 (s, 2H, $\text{C}\equiv\text{C-H}$)



5.5.7 Synthesis of 6,6''-di(7,10-diphenylfluoranthene)-2,2':6'2''-terpyridine (33)

6,6''-diethynyl-2,2':6'2''-terpyridine (0.53g, 1.88 mmol) and 7,9-Diphenyl-cyclopenta[*a*]acenaphthylen-8-one (1.42 g, 4.0 mmol) were heated to 280°C in a benzophenone melt for 72hr. The mixture was cooled to room temperature and the resulting brown solid was purified by flash chromatography using silica gel and dichloromethane:methanol (95:5) as the eluent. (0.1 g, 6%)

ESI-MS (CH_3CN , m/z): found: 938.3517, calcd. 938.3535, for $\text{C}_{71}\text{H}_{43}\text{N}_3$, $[\text{M} + \text{H}]$



Annex:

References and Crystallographic Data

6.1 References

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6.2 Crystallographic Data of 6, 18 and 27

6.2.1 Crystal data and structure refinement for 6

Identification code	Compound 6	
Empirical formula	C ₃₂ H ₂₀ N ₂	
Formula weight	432.50	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4664(17) Å	α = 102.34(3)°.
	b = 10.481(2) Å	β = 99.43(3)°.
	c = 12.509(3) Å	γ = 91.50(3)°.
Volume	1067.5(4) Å ³	
Z	2	
Density (calculated)	1.346 Mg/m ³	
Absorption coefficient	0.079 mm ⁻¹	
F(000)	452	
Crystal size	0.3 x 0.2 x 0.15 mm ³	
Theta range for data collection	1.69 to 24.99°.	
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14	
Reflections collected	11302	
Independent reflections	3717 [R(int) = 0.0266]	
Completeness to theta = 24.99°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9143 and 0.8395	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3717 / 0 / 307	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2σ(I)]	R1 = 0.0349, wR2 = 0.0837	
R indices (all data)	R1 = 0.0459, wR2 = 0.0895	
Largest diff. peak and hole	0.178 and -0.169 e.Å ⁻³	

6.2.2 Crystal data and structure refinement for 18

Identification code	Compound 18	
Empirical formula	C71 H52 Cu F6 N2 O P3	
Formula weight	1219.60	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 14.169(3) Å	$\alpha = 90^\circ$.
	b = 20.050(4) Å	$\beta = 91.86(3)^\circ$.
	c = 19.874(4) Å	$\gamma = 90^\circ$.
Volume	5643.0(19) Å ³	
Z	4	
Density (calculated)	1.436 Mg/m ³	
Absorption coefficient	0.542 mm ⁻¹	
F(000)	2512	
Crystal size	? x ? x ? mm ³	
Theta range for data collection	1.44 to 25.00°.	
Index ranges	-11 ≤ h ≤ 16, -23 ≤ k ≤ 23, -23 ≤ l ≤ 23	
Reflections collected	44412	
Independent reflections	9889 [R(int) = 0.0442]	
Completeness to theta = 25.00°	99.5 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9889 / 0 / 759	
Goodness-of-fit on F ²	1.257	
Final R indices [I > 2σ(I)]	R1 = 0.0635, wR2 = 0.2014	
R indices (all data)	R1 = 0.0794, wR2 = 0.2428	
Largest diff. peak and hole	1.104 and -1.322 e.Å ⁻³	

6.2.3 Crystal data and structure refinement for 27.

Identification code	Compound 27	
Empirical formula	C140 H0 Cl0 N0 S2	
Formula weight	1745.52	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0187(5) Å	$\alpha = 90.0710(10)^\circ$.
	b = 10.3328(5) Å	$\beta = 90.3290(10)^\circ$.
	c = 26.1092(12) Å	$\gamma = 98.0510(10)^\circ$.
Volume	2676.2(2) Å ³	
Z	1	
Density (calculated)	1.083 Mg/m ³	
Absorption coefficient	0.100 mm ⁻¹	
F(000)	872	
Crystal size	0.27 x 0.18 x 0.10 mm ³	
Theta range for data collection	0.78 to 25.07°.	
Index ranges	-11<=h<=11, -12<=k<=12, -31<=l<=31	
Reflections collected	29143	
Independent reflections	9458 [R(int) = 0.1047]	
Completeness to theta = 25.07°	99.6 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9458 / 0 / 632	
Goodness-of-fit on F ²	0.962	
Final R indices [I>2sigma(I)]	R1 = 0.0754, wR2 = 0.1810	
R indices (all data)	R1 = 0.1167, wR2 = 0.2020	
Extinction coefficient	0.0003(4)	
Largest diff. peak and hole	0.399 and -0.546 e.Å ⁻³	