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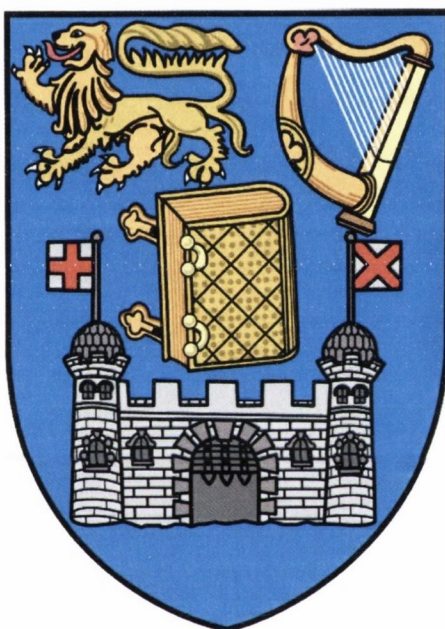
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Functionalising and nitrogen-doping molecular graphenes: The chemical, optical and electronic consequences

Lankani Priyangika Wijesinghe



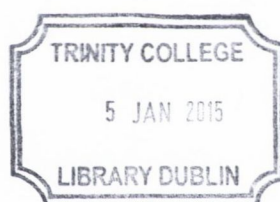
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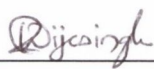
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Lankani Priyangika Wijesinghe

Summary

Chapter 1: This chapter gives a comprehensive literature review to the field of graphitic materials with particular focus on polyaromatic hydrocarbons (PAHs). The latter section will focus on the key oxidative cyclodehydrogenation reaction.

Chapter 2: This chapter details the synthesis and characterisation of a novel family of 2N-doped heterosuperbenzenes [diazasuperbenzenes (DASB)] with varying peripheral functionalisation. The first section focuses on the synthesis and characterisation of 2N-doped hexaarylbenzenes *via* the [2+4] Diels-Alder route, which are the synthetic precursors to DASBs.

The second section discusses regarding the oxidative cyclodehydrogenation of 2N polyphenylenes to obtain planarised DASBs. A family of fully fused DASBs were synthesised along with partially fused products. Comparatively, the methoxy functionalised polyphenylene precursor undergoes an efficient oxidative cyclodehydrogenation showing that electron donating methoxy functionalisation facilitates Scholl mechanism. The analysis of the single crystal structure of methoxy functionalised DASB reveals that the positioning of the methoxy groups has a profound effect on the supramolecular order observed in these crystalline nanographenes. The methoxy groups engaged in weak H-bonding appears to assist the molecules to orient in a head-to-tail arrangement within columnar π - π stacks.

Chapter 3: This chapter outlines the synthesis and characterisation of a novel family of 6N-doped heterosuperbenzenes [hexaazasuperbenzenes (HASB)] which vary in their peripheral functionalisation. The 6N polyphenylene precursors were synthesised *via* $\text{Co}_2(\text{CO})_8$ catalysed [2+2+2] cyclotrimerisation of asymmetric monopyrimidyl acetylene starting material. The cyclotrimerisation route provides a convenient one-step synthetic route to HASB polyphenylene precursors compared to the multistep route employed for the synthesis of DASBs. Overall, the oxidative cyclodehydrogenation of the 6N systems proved to be synthetically far more challenging than their 2N or 4N counterparts, as it resulted in a myriad of partially fused products and for the *tert*-butyl functionalised asymmetric polyphenylene, the $5/6^{\text{th}}$ fused product proved to be the most stable end product.

Chapter 4: provides a full account of the experimental work carried out in this research.

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Table of Contents

Declaration	i
Summary.....	iii
Acknowledgements	v
Table of Contents.....	vii
List of Figures.....	xi
List of Schemes.....	xv
List of Tables.....	xvii
Abbreviations	xix
1. Introduction to graphitic molecules	1
1.1 Introduction	1
1.2 Graphene	1
1.3 Polyaromatic hydrocarbons.....	5
1.3.1 Properties of PAH	8
1.3.2 HBC derivatives and their applications	11
1.4 Heteroatom doped PAHs.....	14
1.4.1 Nitrogen Heterosuperbenzene (N-HSB).....	16
1.5 Polyphenylenes	17
1.5.1 Hexaphenylbenzenes	18
1.5.2 Synthesis of Hexaphenylbenzenes.....	18
1.5.3 Polyphenylenes and their applications.....	20
1.6 Cyclodehydrogenation	23
1.6.1 Surface-assisted cyclodehydrogenation	24
1.6.2 Scholl reaction mechanism	25
1.7 Aims of the project.....	28
2. Diazasuperbenzenes: synthesis and characterization.....	31
2.1 Introduction	33

2.1.1	Diels-Alder reaction	33
2.1.2	Microwave-mediated synthesis	34
2.1.3	Aims of this work	35
2.2	Diaza-polyphenylenes	36
2.2.1	Synthesis and characterisation of asymmetric aryl-acetylenes	36
2.2.2	Synthesis of polyphenylenes	38
2.2.3	NMR studies of polyphenylenes 73-77	41
2.2.4	Molecular structure determination of polyphenylenes 73 and 74	46
2.2.5	Photophysical studies of polyphenylenes 73-77	49
2.3	Oxidative cyclodehydrogenation	55
2.4	Synthesis of DASB derivatives	58
2.4.1	Cyclodehydrogenation of 73	58
2.4.2	Cyclodehydrogenation of 74	60
2.4.3	Cyclodehydrogenation of 76	61
2.4.4	Cyclodehydrogenation of methoxy polyphenylenes 75 and 77	62
2.5	Characterisation of the DASB derivatives.....	64
2.5.1	NMR spectroscopic characterisation of 78, 80 and 82	64
2.5.2	Single crystal X-ray analysis of 82	70
2.5.3	Characterisation of ½- fused 83	74
2.5.4	Characterisation of ⅓ rd fused DASB derivatives	75
2.6	Photophysical analysis.....	80
2.6.1	UV-Vis absorption studies of fully-fused DASBs 78, 80 and 82	80
2.6.2	UV-Vis absorption studies of partially fused DASB derivatives.....	83
2.6.3	Protonation studies of 78	84
2.6.4	Solvent dependency studies of 82	86
2.6.5	Emission studies of fully-fused DASBs 78, 80 and 82	88
2.6.6	Emission studies of partially fused DASB derivatives	93

2.6.7	Electrochemical properties of DASB derivatives	95
2.7	Conclusions	98
3.	Hexaazasuperbenzenes: Synthesis and Characterisation	101
3.1	Introduction	103
3.1.1	[2+2+2] cyclotrimerisation	103
3.1.2	Aims of this work	106
3.2	Synthesis and characterisation of Hexaazasuperbenzenes	107
3.2.1	Synthesis and characterisation of polyphenylenes 87 and 88	107
3.2.2	Oxidative cyclodehydrogenation of 87	111
3.2.3	Oxidative cyclodehydrogenation of 88	118
3.2.4	Characterisation of ⁵ / ₆ -Sym-HASB (91).....	119
3.2.5	Synthesis and characterisation of polyphenylenes 94a and 94b	121
3.2.6	Synthesis and characterisation of polyphenylenes 95 and 96	123
3.2.7	Cyclodehydrogenation of polyphenylene 95 and 96	125
3.3	Photophysical studies of 6N systems	128
3.3.1	Photophysical studies of 6N polyphenylenes 87 , 88 , 95 and 96	128
3.3.2	Photophysical studies of HASB derivatives	132
3.3.3	Solvent dependency studies of 89	135
3.3.4	Emission studies of HASB derivatives	136
3.3.5	Electrochemistry studies of HASBs	138
3.4	Conclusions	140
3.5	Future work	141
4.	Experimental	145
4.1	General methods.....	147
4.2	Synthesis of Diazasuperbenzenes	150
4.2.1	5-(4- <i>tert</i> -Butylphenylethynyl)pyrimidine (70)	150
4.2.2	5-(Phenylethynyl)pyrimidine (71)	151

4.2.3	5-(3,4,5-Trimethoxyphenylethynyl)pyrimidine (72).....	152
4.2.4	2,3,4,5,6-Penta(4- <i>tert</i> -butylphenyl)-1-(5-pyrimidyl) benzene (73)	153
4.2.5	2,3,4,5- Tetrakis(4- <i>tert</i> -butylphenyl)-6-phenyl-1-(5-pyrimidyl)-benzene (74).....	154
4.2.6	2,3,4,5-Tetrakis(4- <i>tert</i> -butylphenyl)-6-(3,4,5-trimethoxyphenyl)-1-(5-pyrimidyl)- benzene (75).....	155
4.2.7	2,3,4,5-Tetrakis(phenyl)-6-(4- <i>tert</i> -butylphenyl)-1-(5-pyrimidyl)-benzene (76)	156
4.2.8	2,3,4,5-Tetrakis(phenyl)-6-(3,4,5-trimethoxyphenyl)-1-(5-pyrimidyl)-benzene (77)	157
4.2.9	Cyclodehydrogenation of 73	158
4.2.10	Cyclodehydrogenation of 74	160
4.2.11	Cyclodehydrogenation of 75	163
4.2.12	Cyclodehydrogenation of 76	166
4.2.13	Cyclodehydrogenation of 77	167
4.3	Synthesis of Hexaazasuperbenzenes	168
4.3.1	Cyclotrimerisation of (4- <i>tert</i> -butylphenyl)(5-pyrimidyl)acetylene.....	168
4.3.2	5-(4- <i>tert</i> -Butylphenylethynyl)(2- <i>tert</i> -butyl)pyrimidine (93).....	170
4.3.3	Cyclotrimerisation of 5-(4- <i>tert</i> -butylphenylethynyl)(2- <i>tert</i> -butyl)pyrimidine	170
4.3.4	Cyclotrimerisation of (3,4,5-trimethoxyphenyl)(5-pyrimidyl)acetylene	171
4.3.5	Cyclodehydrogenation of 87	173
4.3.6	Cyclodehydrogenation of 88	176
4.3.7	Cyclodehydrogenation of 95	177
4.3.8	Cyclodehydrogenation of 96	178
5.	References	179
6.	Annex.....	185

List of Figures

Figure 1.1: Schematic illustration of graphene terminology according to size	2
Figure 1.2: Nanographenes with varied aromatic platforms.....	3
Figure 1.3: Schematic representation of bandgap opening via N-doping.....	4
Figure 1.4: The early synthetic approaches towards parent HBC synthesis.....	6
Figure 1.5: Examples of PAH families	7
Figure 1.6: UV-Vis absorption spectrum of HBC (1) in 1,2,4-trichlorobenzene.	7
Figure 1.7: Correlation of the HOMO-LUMO bandgap versus PAH size	8
Figure 1.8: Various peripheries of PAHs.....	9
Figure 1.9: Absorption and emission spectra of PAHs 1a and 28	10
Figure 1.10: Examples of some nanographenes and graphene nanoribbons.	11
Figure 1.11: Single crystal X-ray structure of permethoxylated HBC (37).....	12
Figure 1.12: Photodiode based on HBC-PhC ₁₂ and PDI materials.....	13
Figure 1.13: Absorption and emission spectra of 40 , 41 and 42 in CH ₂ Cl ₂ at 20 °C.....	14
Figure 1.14: Single crystal X-ray structures of PPAH (43) and BPAH (44).....	15
Figure 1.15: Hexapyrrolohexaazacoronenes (45).....	16
Figure 1.16: Some conjugated polymers.	20
Figure 1.17: Blue emitting dendrimer (60) and polyphenylene triad (61).....	21
Figure 1.18: Fourth generation PPD (62) and ruthenium(II) bipyridyl complex (63)....	22
Figure 1.19: Surface mediated GNR synthesis from bianthryl monomer precursor	25
Figure 1.20: Targeted diaza and hexaazasuperbenzenes.	29
Figure 2.1: Schematic representation of the frontier orbitals of a Diels-Alder reaction in normal and inverse electron demand.	34
Figure 2.2: Target diazasuperbenzene molecules.	35
Figure 2.3: ¹ H NMR spectrum of 72 in CDCl ₃ (600 MHz, RT).....	37
Figure 2.4: ¹³ C NMR spectrum of 72 in CDCl ₃ (151 MHz, R.T).....	38
Figure 2.5: Target 2N polyphenylene systems as molecular precursors to DASBs.	40
Figure 2.6: ¹ H-NMR spectra of polyphenylenes 73 , 74 and 76 in CDCl ₃ (600 MHz) ...	41
Figure 2.7: ¹ H-NMR spectra of polyphenylenes 75 and 77 in CDCl ₃ (600 MHz)	42
Figure 2.8: ¹ H- ¹ H COSY spectrum of 75 in CDCl ₃ , 600 MHz, R.T.	43
Figure 2.9: NOE spectra of 75 in CDCl ₃ , 600 MHz, R.T.....	44
Figure 2.10: HSQC spectrum of 75 in CDCl ₃ at R.T (600 MHz).....	45
Figure 2.11: DEPT 135 and ¹³ C NMR spectra of 75 in CDCl ₃ at R.T (600 MHz)..	46

Figure 2.12: ORTEP representations of the molecular structures of 73 and 74	47
Figure 2.13: Representation of the lattice stabilising interactions in 74	48
Figure 2.14: Representation of the lattice stabilising interactions in 74	48
Figure 2.15: The normalised UV-Vis spectra of polyphenylenes 73-77 in (C ₂ H ₅) ₂ O. ...	49
Figure 2.16: Emission spectra of polyphenylenes 73-77 in (C ₂ H ₅) ₂ O ,R.T.....	51
Figure 2.17: Solvent dependency UV-Vis absorption spectra of 73 and 75	52
Figure 2.18: Solvent dependency emission studies of 73 and 75 (~10 ⁻⁵ M), RT	52
Figure 2.19: UV-Vis absorption spectral changes of 73 upon acid addition.	53
Figure 2.20: Emission spectral changes of 73 upon acid addition	54
Figure 2.21: Cyclodehydrogenation para-dimethoxy substituted hexaphenylbenzene...	57
Figure 2.22: ¹ H-NMR spectra of fully-fused DASB 78 , 80 and 82 in CDCl ₃ at RT (400.1 MHz).....	65
Figure 2.23: ¹ H NMR spectra of 82 in CDCl ₃ at RT (600 MHz).....	65
Figure 2.24: HSQC analysis of 82 in CDCl ₃ at RT (600 MHz)	66
Figure 2.25: Section of the NOESY spectrum of 82 in CDCl ₃ at RT (600 MHz).	67
Figure 2.26: ¹³ C NMR spectrum of 82 in CDCl ₃ at RT (151 MHz).	68
Figure 2.27: Aromatic region of 82 at various temperatures in CDCl ₃ , 400 MHz.....	69
Figure 2.28: Aromatic region of 82 at different concentrations in CDCl ₃ , 600 MHz.....	70
Figure 2.29: Asymmetric unit of the single crystal structures of 82	71
Figure 2.30: Head-to-tail packing arrangement of 82 and	72
Figure 2.31: The ABCABC packing arrangement of N-HSB (47)	72
Figure 2.32: Single crystal structure of paramethoxy-TASB (104)	73
Figure 2.33: Molecular packing arrangement of 82	73
Figure 2.34: ¹ H NMR spectra of 83 in CDCl ₃ at RT (600 MHz)	74
Figure 2.35: ¹ H- ¹ H COSY spectrum of 83 in CDCl ₃ (600 MHz), RT.....	75
Figure 2.36: Aromatic region of the 1/3-fused DASB's 79 , 81 and 84 in CDCl ₃ at RT...	76
Figure 2.37: ¹ H NMR spectra of 81 in CDCl ₃ at RT (600 MHz)	77
Figure 2.38: Aromatic region of the ¹ H- ¹ H COSY spectrum of 81 in CDCl ₃	77
Figure 2.39: Ortep representation of 84 with displacement ellipsoids at 50%.	78
Figure 2.40: The intermolecular interactions of 84	79
Figure 2.41: Packing diagram of 84	79
Figure 2.42: Absorption spectra of 78 and N-HSB (47) in toluene	80
Figure 2.43: The overlaid absorption spectra of 80 and 82 in toluene.....	82
Figure 2.44: The overlaid absorption spectra of partially-fused DASBs in toluene	83

Figure 2.45: UV-Vis absorption spectral changes of 78 upon acid addition	84
Figure 2.46: Emission spectral changes of 78 (CH ₂ Cl ₂) upon acid addition	85
Figure 2.47: Overlaid UV-Vis absorption spectra of 82 in various solvents.....	87
Figure 2.48: The emission spectra of 82 in various solvents.....	88
Figure 2.49: The overlaid emission spectra 78 , 80 , 82 and 47 in toluene, R.T	89
Figure 2.50: The overlaid absorption, excitation and emission spectra 82 in toluene....	90
Figure 2.51: Emission spectra for compounds 78 , 80 and 82 in toluene (R.T) and butyronitrile (77 K)	92
Figure 2.52: Emission spectra partially fused DASBs 79 , 81 , 83 , 84 and 86 in toluene	94
Figure 2.53: Cyclic voltammograms of 78 , 80 and 82	95
Figure 3.1: Target molecules of the HASB family.	106
Figure 3.2: ¹ H NMR spectra of 87 and 88 in CDCl ₃ at RT, 400 MHz	108
Figure 3.3: ¹ H- ¹ H and ¹³ C- ¹ H COSY spectra of 87 in CDCl ₃ at RT, 600 MHz.	109
Figure 3.4: Single crystal structure of 88	110
Figure 3.5: Molecular packing arrangement of 88	111
Figure 3.6: Preparative thin layer chromatography separation of 89	112
Figure 3.7: ¹ H-NMR spectra of 89 in CDCl ₃ at RT (600 MHz).	114
Figure 3.8: ¹ H- ¹ H COSY spectrum of 89 in CDCl ₃ , RT, 600 MHz.	114
Figure 3.9: ¹³ C- ¹ H COSY spectrum of 89 in CDCl ₃ , RT, 600 MHz.	115
Figure 3.10: ¹ H NMR spectra of 90 in CDCl ₃ at RT (600 MHz)	116
Figure 3.11: Aromatic region of the ¹³ C- ¹ H COSY spectrum of 90 in CDCl ₃	117
Figure 3.12: ¹ H-NMR spectra of 91 in CDCl ₃ at RT (600 MHz).....	119
Figure 3.13: ¹ H- ¹ H COSY spectrum of 91 in CDCl ₃ , RT, 600 MHz.	120
Figure 3.14: The ¹ H-NMR spectra of 94a and 94s in CDCl ₃ , RT, 400 MHz.....	122
Figure 3.15: Mass spectral models for ⁵ / ₆ th and ½-fused products.	122
Figure 3.16: ¹ H-NMR spectra of asymmetric 95 and symmetric 96 in CDCl ₃ at R.T..	123
Figure 3.17: The HSQC spectrum of 95 in CDCl ₃ , 600 MHz, RT.	124
Figure 3.18: ¹ H-NMR of fully-fused 97 in CDCl ₃ at RT (600 MHz).....	126
Figure 3.19: Mass spectral analysis of Methoxy HASBs 98 and 99	127
Figure 3.20: UV-Vis spectra of 6N polyphenylenes (87 , 88 , 95 and 96) in CHCl ₃	128
Figure 3.21: Emission spectra of 6N polyphenylenes (87 , 88 , 95 and 96) in CHCl ₃ ...	129
Figure 3.22: UV-Vis absorption spectral changes of 87 upon acid addition	130
Figure 3.23: Emission spectral changes of 87 upon acid addition.....	131
Figure 3.24: UV-Vis absorption spectra of HASB (89 , 90 , 91 and 97) in toluene	132

Figure 3.25: UV-Vis absorption spectral changes of 89 upon acid addition	133
Figure 3.26: Emission spectral changes of 89 (CH ₂ Cl ₂) upon acid addition	134
Figure 3.27: Absorption and emission spectra of 89 in various solvents at RT.....	135
Figure 3.28: Emission spectra HASB systems (89 , 90 , 91 and 97) in toluene at R.T. .	136
Figure 3.29: The overlaid absorption and emission spectra 97 in toluene.	137
Figure 3.30: Cyclic voltammograms of 89 , 90 and 91	139
Figure 3.31: Proposed synthetic route to a larger N-doped aromatic platform.....	142
Figure 3.32: Novel route to symmetric polyphenylenes	142

List of Schemes

Scheme 1.1: The synthesis of N-HSB via oxidative cyclodehydrogenation.	16
Scheme 1.2: Various synthetic routes to hexaphenylbenzenes.....	19
Scheme 1.3: Proposed mechanism of the Scholl reaction.....	25
Scheme 1.4: Cyclodehydrogenation pathways: arenium cation mechanism and radical cation mechanism.	27
Scheme 2.1: Synthesis of asymmetric aryl acetylenes 70 , 71 and 72	36
Scheme 2.2:[2+4]-Diels-Alder route to 2N polyphenylene precursors.	38
Scheme 2.3:Synthesis of 2,3,4,5-tetra-(4-tert-butylphenyl) cyclopentadienone (52a)...	39
Scheme 2.4: Intramolecular Scholl reaction.	55
Scheme 2.5: Cyclodehydrogenation of 73	58
Scheme 2.6: Cyclodehydrogenation of 74	60
Scheme 2.7: Cyclodehydrogenation of 76	61
Scheme 2.8: Cyclodehydrogenation of 75	62
Scheme 2.9: Cyclodehydrogenation of 77	63
Scheme 3.1: Schematic representation of intermolecular [2+2+2]-cycloaddition.	103
Scheme 3.2: The general mechanism of cyclotrimerisation of acetylenes.....	104
Scheme 3.3: Illustration of the trimerisation of an asymmetric alkyne.	105
Scheme 3.4: Synthesis of 6N polyphenylenes 87 and 88	107
Scheme 3.5: Cyclodehydrogenation of asymmetric 87	111
Scheme 3.6: Cyclodehydrogenation of symmetric 88	118
Scheme 3.7: Synthesis of 6N polyphenylenes 94a and 94s	121
Scheme 3.8: Synthetic route to 6N polyphenylenes 95 and 96	123
Scheme 3.9: Cyclodehydrogenation of 95	125
Scheme 3.10: Cyclodehydrogenation of 96	127

List of Tables

Table 2.1: NOE spectra of 75 in CDCl ₃ at RT.....	45
Table 2.2: The tilt angles of the peripheral rings of 4 and 5	47
Table 2.3: UV-Visible spectral data of 73-77 in diethylether.....	50
Table 2.4: Emission spectral data of 73-77 in diethylether at R.T.	51
Table 2.5: UV-Visible spectral data for 78, 80, 82 and 47 in toluene	83
Table 2.6: UV-Visible spectral data of partially fused DASB derivatives in toluene. ...	84
Table 2.7: Emission spectral data of fully-fused DASBs (CHCl ₃)......	91
Table 2.8: Emission spectral data of partially fused DASBs in toluene at R.T.....	94
Table 2.9: Electrochemical data for fully-fused DASBs 78, 80 and 82	96
Table 2.10: Electrochemical data for partially fused DASBs.....	97
Table 3.1: UV-Visible and emission data observed for 6N polyphenylenes 87, 88, 95 and 96 in CHCl ₃	129
Table 3.2: UV-Visible spectral data for HASB's 89, 90, 91, 97 in toluene	133
Table 3.3: Emission spectral data of HASB compounds.....	137
Table 3.4: Electrochemical data for fully-fused HASBs 89, 90 and 91	140

Abbreviations

1D	one-dimensional
2D	two-dimensional
Å	Angstrom
Ar	aryl
a.u.	arbitrary units
Bpy	2,2'-bipyridine
Bu	butyl
°C	degrees Celsius
cm	centimetre
COSY	correlation spectroscopy
Cp	cyclopentadiene
CV	cyclic voltammetry
CVD	chemical vapour deposition
d	doublet
dd	doublet of doublets
DASB	diazasuperbenzene
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEPT	distortionless enhancement by polarisation transfer
DFT	density functional theory
DIPA	diisopropylamine
DMF	dimethylformamide
DMPD	1,4-dimethylpiperazine-2,3-dione
DMSO	dimethylsulfoxide
dppz	dipyrido[3,2-a:2'-3'-c]phenazine
DSC	differential scanning calorimetry
e⁻	electron
EI-MS	electron impact mass spectrometry
em	emission
EPR	electron paramagnetic resonance
ESI-MS	electrospray mass spectrometry

exc	excitation
g	gram
GIR	graphite intercalation compounds
GNR	graphene nanoribbons
GO	graphene oxide
HASB	hexaazasuperbenzene
HBC	hexa-peri-hexabenzocoronene
HMBC	heteronuclear multiple-bond correlation
HMQC	heteronuclear multiple-quantum correlation
HOMO	highest occupied molecular orbital
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectrometry
HSB	heterosuperbenzene
hr	hour
Hz	Hertz
IR	infrared
<i>J</i>	coupling constant
K	Kelvin
kJ	kilojoule
L	ligand
LD-TOF	laser desorption –time-of-flight mass spectrometry
LMCT	ligand-to-metal-charge transfer
LUMO	lowest unoccupied molecular orbital
m	multiplet
M	metal
M	molarity
min	minute
mol	mole
m.p.	melting point
m.u.	mass units
<i>m/z</i>	mass to charge ratio
MALDI-TOF MS	matrix-assisted laser desorption/ionisation – time of flight mass spectrometry
max	maximum
Me	methyl

mg	milligram
MHz	megahertz
mL	millilitre
MLCT	metal to ligand charge transfer
mmol	millimole
mol	mole
MS	mass spectrometry
mmol	millimole
mV	milliVolt
N-½HSB	half-cyclised nitrogen-heterosuperbenzene
N-HSB	nitrogen-heterosuperbenzene
nm	nanometer
NMI-PMI-TDI	naphthalenemonoimide-perylenemonoimides-
NMR	terrylenediimide
	nuclear magnetic resonance
nOe	nuclear Overhauser effect
ns	nanoseconds
OFET	organic field effect transistor
OLED	organic light emitting diode
OPV	organic photovoltaics
ox.	oxidation
PAH	polycyclic aromatic hydrocarbon
Ph	phenyl
phen	1,10-phenanthroline
PIFA	(bis(trifluoroacetoxy)iodo)benzene
ppm	parts per million
ppy	2-phenylpyridine
QCM	quartz crystal microbalance
RT	room temperature
S	singlet
SCE	standard calomel electrode
sec	second
sh	shoulder
solv.	solvent
T	triplet

<i>t</i> or <i>tert</i>	tertiary
TAC	time to amplitude converter
TASB	tetraazasuperbenzene
TCSPC	time-correlated single photon counting
TD DFT	time dependent density functional theory
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	tetramethylsilane
TOCSY	total correlation spectroscopy
TPA	two-photon absorption dyes
tpy	terpyridine
UV/Vis	ultraviolet-visible
vs.	versus
WAXS	wide-angle x-ray spectroscopy
°	degrees
δ	chemical shift
Δ	heat
ε	molar absorption coefficient
Λ	wavelength
μs	microsecond
τ	half life
%	percentage

1. Introduction to graphitic molecules

1.1 Introduction

The development of the organic photovoltaic cell,¹ light emitting diode (LED),² and field-effect transistor (FET)³ in the mid 1980s initiated a widespread interest in organic materials as potential candidates for electronic devices. Since then the quest for novel organic materials with efficient charge carrier transporting properties has been investigated intensively in both academic and industrial settings. Inorganic materials such as gallium arsenide and inorganic silicon are widely used in electronic devices at present. However, the optimisation of inorganic devices is reaching its limits, especially with respect to cost and processability of the material. Organic materials have several advantageous properties such as their light weight, flexibility, ease of tunability and cheap processing cost, making them viable alternatives. The trade-off is lower charge carrier mobility in these organic systems, which limit their performance compared to their inorganic counterparts. These have been shown to have efficient electron mobility a few orders of magnitude higher. For example, organic photovoltaic devices (e.g. dye-sensitized solar cells) with maximum efficiencies of up to 13 %⁴ have been reported while inorganic solar cells can reach efficiencies over 30 % (up to 15–20 % for commercially available materials).

Organic chemists have investigated various π -conjugated systems as active materials for electronic devices. The range extends from 1D organic semiconducting polymers to supramolecular structures such as 3D dendrimers.^{5, 6} In addition to charge-carrier mobility, the microscopic and macroscopic order of the molecules in solid state is also critical for their usage in devices. Further, miniaturisation down to the single-molecule level is also highly desired. In this context, graphene-type molecules, typically large polycyclic aromatic hydrocarbons (PAHs), have gained enormous interest with their unique self-organization behavior and promising electronic properties for applications in organic electronics.⁷

1.2 Graphene

Graphene is a two dimensional atomically thick sheet of sp^2 hybridised carbons arranged in a honeycomb crystal lattice and can be thought of as the basic building block for graphitic materials of all other dimensionalities including 0D fullerenes, 1D nanotubes or 3D graphite. Graphene was first isolated by Geim and Novoselov *et al.* in 2004 through a micromechanical cleavage approach by repeated peeling of highly

ordered pyrolysed graphite (HOPG).⁸ These pioneering experiments to characterise the physical properties of graphene were recognized with 2010 Nobel Prize in Physics. These breakthroughs lead to widespread interest in exploring the properties of graphene in both academia and industry. Graphene is nick-named a ‘miracle material’⁹ due to its extraordinary properties such as mechanical stiffness, strength and elasticity, high electrical and thermal conductivity which make it a promising candidate for practical applications in a variety of fields including electronics,¹⁰ sensing,¹¹ catalysis,¹² energy storage,¹³ and biological labeling.¹⁴

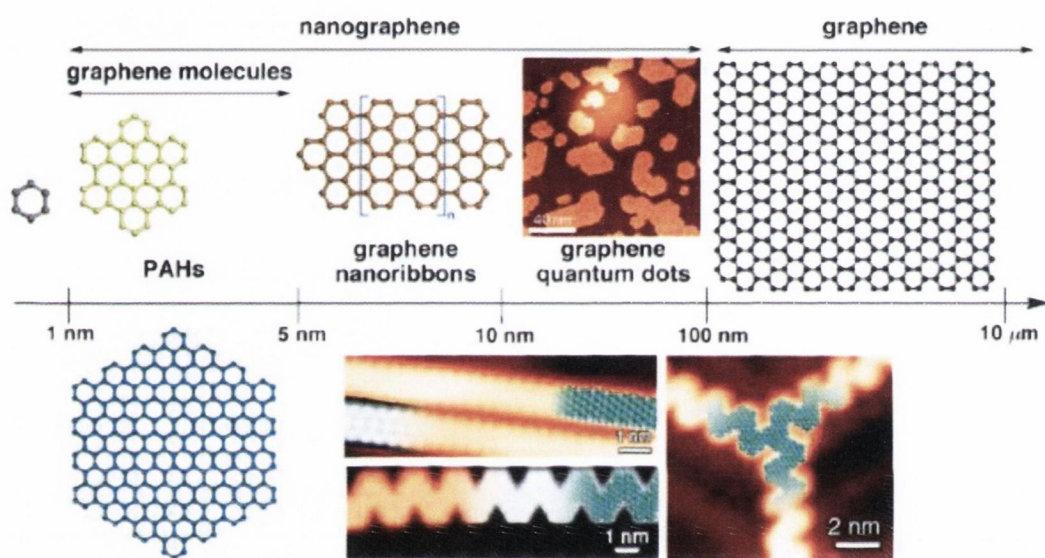


Figure 1.1: Schematic illustration of graphene terminology defined according to their size scale (taken without modification from *Angew. Chem. Int. Ed.* 2012, 51, 7640-7654 by Müllen et. al).¹⁵

Various terminologies have been employed to define graphitic material. In an excellent review Müllen and co-workers have attempted to describe various terminology used in graphenes according to their size scale as illustrated below in Figure 1.1.¹⁵ Graphene molecules are described as large PAHs with sizes of 1-5 nm, whereas graphene nanoribbons (GNRs) are defined as a graphene strip with a width of less than 10 nm and an aspect ratio (length:width) higher than 10. GNRs with widths greater than 10 nm are called quasi-GNRs. Nanographenes are defined as graphene fragments ranging from 1 to 100 nm in size, and other hexagonal sp^2 carbon networks exceeding 100 nm are regarded as graphene.

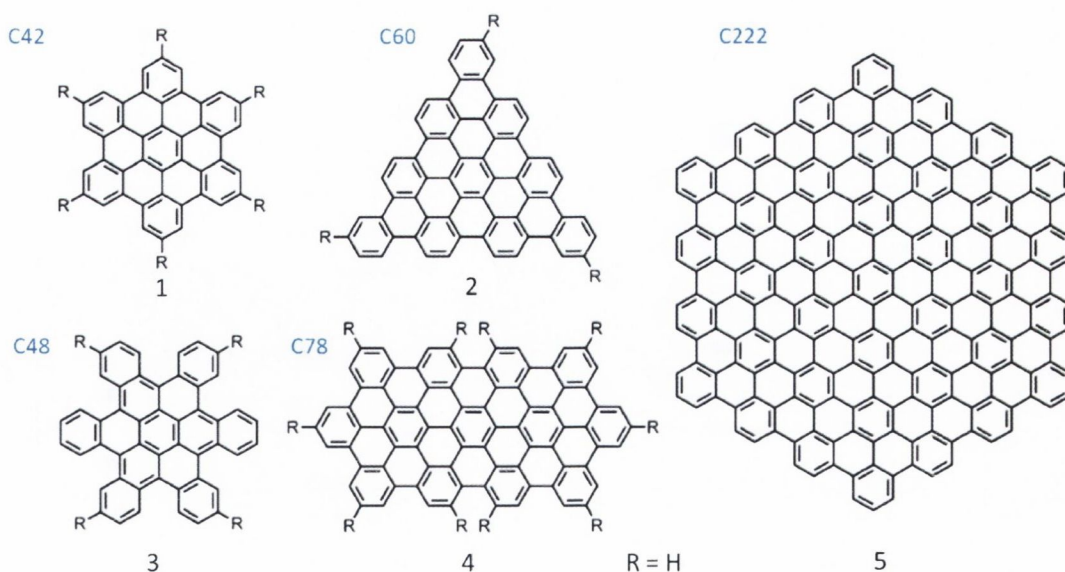


Figure 1.2: Nanographenes with varied aromatic platforms.

Two main strategies have been established for graphene synthesis: exfoliating graphite towards graphene known as “top down” and building up graphene from molecular building blocks, the “bottom up” approach. The top down methods include mechanical exfoliation of highly ordered pyrolytic graphene (HOPG),⁸ solution-based exfoliation of graphite intercalation compounds (GIC),¹⁶ and chemical oxidation/exfoliation of graphite followed by reduction of graphene oxide (GO). The bottom up approach for graphene synthesis include epitaxial growth on metallic substrates by chemical vapour deposition (CVD)¹⁷ and thermal decomposition of SiC.¹⁸ Graphene with well defined size, shape, and edge structure is crucial for opening up the energy band gap of graphene and exploring its properties for potential use in electronic devices.

Despite the various approaches for the synthesis of graphene, the main obstacle at present is the lack of an efficient way to reliably produce graphene in both large quantities and high quality with well defined structure. Synthetic organic chemistry based routes starting with polyphenylene precursor molecules have come to the forefront as a more viable strategy to create structurally defined graphenes. Müllen among others have pioneered the work in this area and have established synthetic protocols for development of well-defined nanographenes and graphene nanoribbons.¹⁹ At present, the largest synthesised monodisperse nanographene molecule consists of 222 carbon atoms (**5**) with a disk diameter of 3.2 nm (Figure 1.2).²⁰ Hexa-*peri*-

hexabenzocoronene (**1**) is one of the smallest and widely investigated nanographenes consisting of 13 fused aromatic rings with a disk diameter of 1.4 nm⁶ (Figure 1.2).

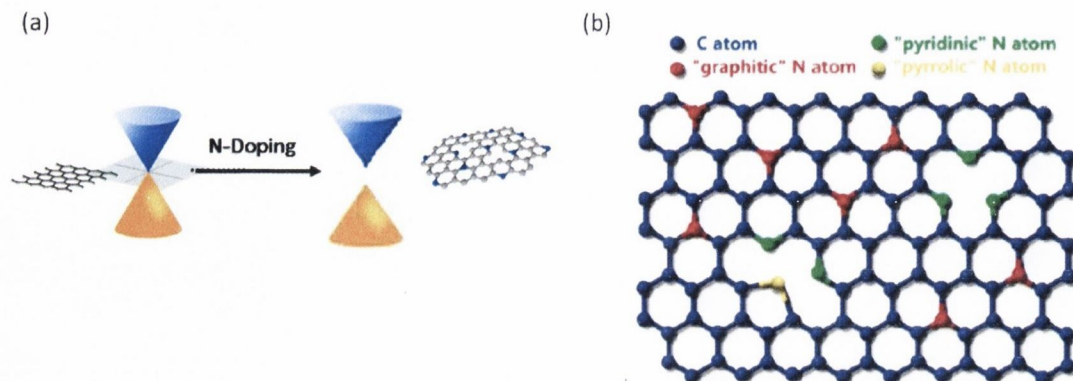


Figure 1.3: (a) Schematic representation of bandgap opening via N-doping; (b) schematic representation of types of nitrogen atoms in N-doped graphene: graphitic, pyridinic and pyrrolic types.²¹

Although graphene holds potential as a candidate in widespread applications, its intrinsic zero band gap character impedes usage [Figure 1.3 (a)]. Therefore, various approaches have been attempted to open and tune the band gap of graphenes which endows semiconducting properties. One approach is the synthesis of graphene nanoribbons (GNR) with defined width and edges, which allows tuning of chemical and electronic properties of graphene. Recent work by Fasel and coworkers have shown the well defined graphene nanoribbons can be successfully synthesised through surface chemistry from polyphenylenes using a bottom up approach.²²

Another alternate strategy is to dope graphenes with heteroatoms such as N, B, P or S atoms. For example, N-doping graphene gives rise to *n*-type semiconducting behavior. The incorporation of nitrogen atoms in the graphene matrix can lead to three types of possible C–N bonding: the graphitic, pyridinic and pyrrolic C–N configurations [Figure 1.3(b)]. Multiple methods have been attempted in the synthesis of N-graphenes, however CVD²¹ and chemical synthesis²³ are the most popular. Wei *et al.* reports the first successful experimental synthesis of N-doped graphene *via* CVD method and they have further gone on to study the electronic of fabricated a field-effect transistors based on N-doped graphene and the results show that it behaves like an *n*-type doped semiconductor with lower conductivity, lower mobility and larger on/off current ratio compared to its pristine graphene counterpart.²¹ The foreign nitrogen atoms may release electrons into graphene and modify the electronic structure of it, leading to *n*-type

doping of graphene and opening the band gap. Furthermore, N-doped graphenes have been used as efficient metal-free electrocatalyst for oxygen reduction in fuel cells.²⁴ Various other graphene related carbon allotropes such as graphyne, graphane, graphdiyne and graphenylene are also been explored as alternant candidates for nano electronic devices.²⁵

1.3 Polyaromatic hydrocarbons

Polyaromatic hydrocarbons (PAHs) are one of the widely investigated classes of compounds in organic synthetic chemistry and materials science.²⁶ They can be regarded as two dimensional graphitic segments composed of sp^2 hybridised carbons. The π electrons are delocalised in a honeycomb network of carbon atoms, with an interlayer spacing of 3.4 Å. These large π -conjugated systems enable efficient absorption of visible and near-infrared light and π - π stacking layers allow significant intermolecular interactions, which are important solid state properties for their use in optoelectronic devices.^{7, 27, 28} PAHs can be found naturally in oil, coal, tar and are produced in combustion of organic material.²⁹

Initial work in to the synthesis and characterisation of PAHs were carried out by Scholl and Clar in the first half of the 20th century.³⁰ They employed harsh conditions such as high temperature and strong oxidising agents for the synthesis and obtained very low product yields. In 1958, the synthesis of HBC (**1**) was first reported by Clar and Ironside, and was later followed up by, Halleux³¹ and Schmidt *et al.*³² who reported alternative methods toward the parent HBC synthesis, depicted in Figure 1.4. In 1990's Müllen and coworkers used milder reaction conditions for the synthesis of HBC³³ by intramolecular oxidative cyclodehydrogenation of hexaphenylbenzene with Cu(II) salts (CuCl₂ catalysed by AlCl₃). This method has later been extended to the synthesis of more complex PAHs with different shapes and sizes.

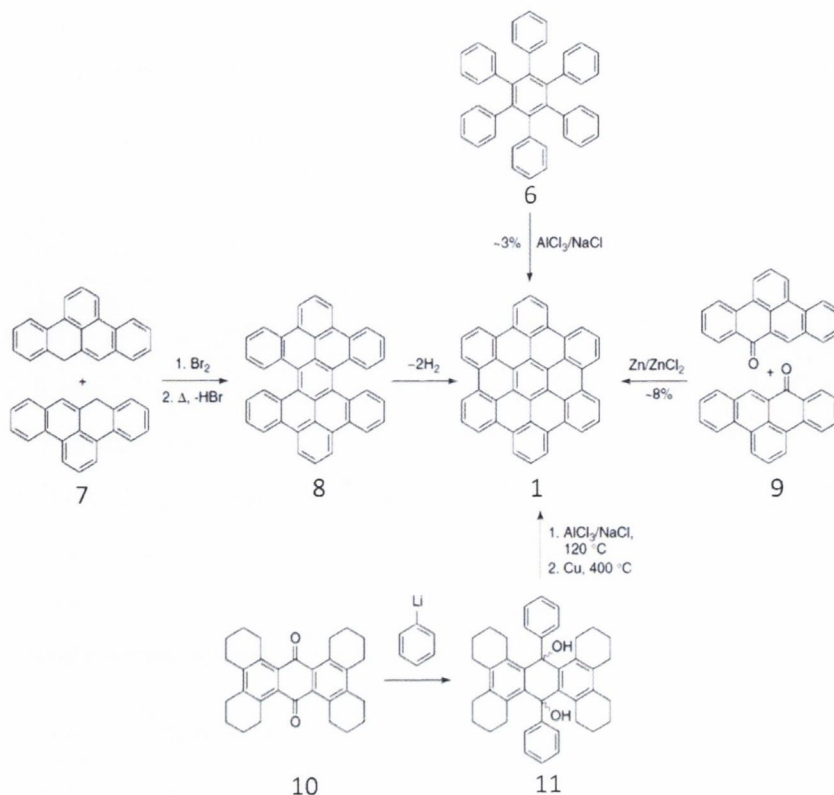


Figure 1.4: The early synthetic approaches towards parent HBC synthesis.

PAHs are classified according to the arrangement of the benzenoid rings. The two most commonly known classes are the “acenes” where the benzenoid rings are fused in a linear arrangement and the “phenes”, where the benzenoid rings are arranged in an angular arrangement.³⁴ Anthracene (**12**) is the smallest member of the “acene” family and includes members such as tetracene, pentacene (**13**), hexacene where increasing the number of six-membered rings decrease both the energy gap and the chemical stability (Figure 1.5). Commonly known “phenes” include phenanthrene (**14**), tetraphene and pentaphenes (**15**). “Circulenes” are obtained when benzenoid rings are arranged in a macrocyclic structure. Coronene (**17**) is an important member with its derivative “Hexa-*peri*-hexabenzocoronene [HBC (**1**)] been the most extensively investigated (Figure 1.5).

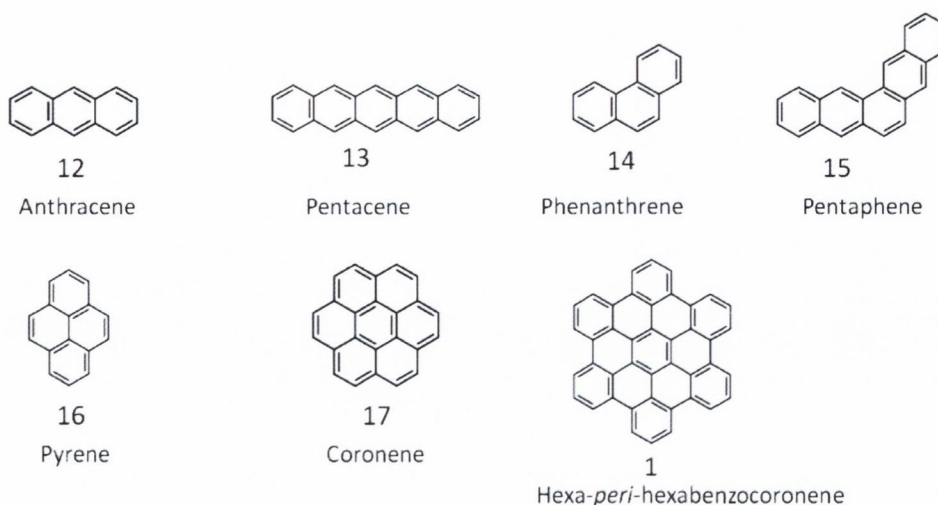


Figure 1.5: Examples of PAH's with belonging to "acenes", "phenes" and "circulenes".

Typically, UV-Visible spectra of PAHs reveal three main bands (α , β and p-bands) according to nomenclature introduced by E. Clar.³⁵ α and β bands depended on the overall size of the aromatic system, whereas the position of the p-band was symmetry-controlled. The β band is due to the electronic interaction between the benzenoid rings and the localization of the π electrons in the excited state gives rise to the p band. The α -band is the lowest energy band, which has usually low intensity due to the forbidden nature of the S_0 - S_1 transition. Figure 1.6 depicts the UV-Vis spectrum of HBC (**1**) in 1,2,4-trichloroethane and it clearly shows that the α -band is strictly forbidden in D_{6h} symmetry molecules.³²

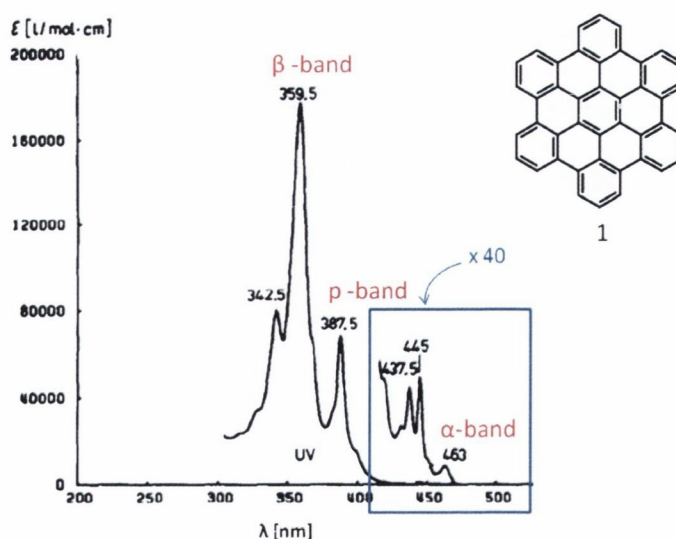


Figure 1.6: UV-Vis absorption spectrum of HBC (**1**) in 1,2,4-trichlorobenzene.³²

1.3.1 Properties of PAH

The variation of the symmetry, size, shape and peripheral substitution has a distinct impact upon the properties of PAHs.⁶ These can fundamentally alter the nature of π interactions, tune the HOMO-LUMO gap, facilitate the film-forming capabilities of the product and even predetermine to an extent its degree of aromaticity. In other words, these structural parameters of the molecules allow a sensitive tuning of the electronic and supramolecular properties, which are key requirements for the successful implementation as semiconducting material in electronic devices.⁷

1.3.1.1 Size

Increasing the size of the aromatic core leads to greater electron delocalisation of π electrons and results in a corresponding decrease in HOMO-LUMO energy gap. Smaller energy gap shifts the emission maxima to lower energies and is readily visible in the colours of the materials as depicted in Figure 1.7, **1a** (C_{42}) to **19** (C_{78}).⁶ Furthermore, Debije *et al.* reported that the size of the aromatic core displays a strong dependence of the intercolumnar packing dimensions as well as the charge transfer mobility values of the PAHs.³⁶ The increased overlap of large π -surfaces improves the overall order of the columnar superstructures and thus enabling efficient charge carrier mobility.

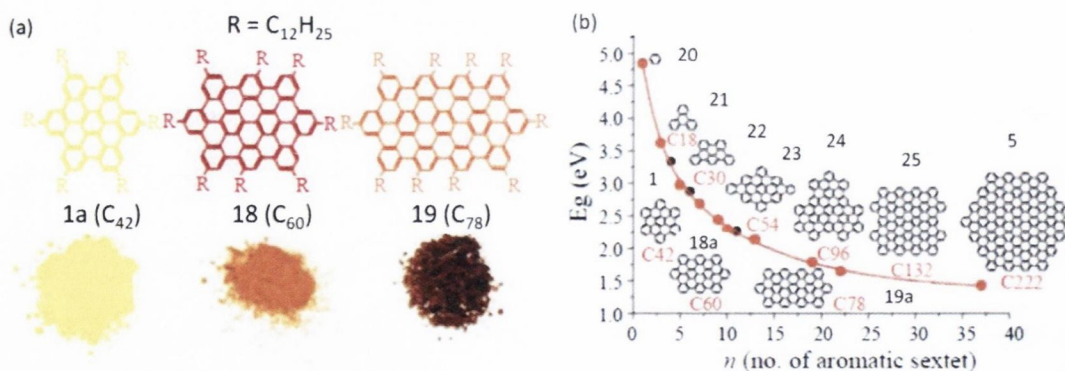


Figure 1.7: (a) PAHs showing the bathochromic shift of absorption with increasing size (b) Correlation of the HOMO-LUMO bandgap versus the number of aromatic sextets (taken without modification from *Angew. Chem. Int. Ed.* 2005, 44, 5592-5629 by Grimsdale *et. al.*).⁶

1.3.1.2 Periphery

In PAHs, the nature of the periphery is also an important factor which contributes to the electronic properties and chemical reactivity.³⁷ “Arm-chair” (in **26**) and “zigzag” (in **13**) are the two most prominent peripheries seen in acenes and phenes type of PAHs respectively (Figure 1.8). Other type of peripheries includes “cove”, “bay” and “fjord” (in **27**). According to Clar’s classification, the graphitic molecules with “arm-chair” and “cove” peripheries are all benzenoid PAHs. The periphery shape has a direct effect on the photophysical properties and the chemical reactivity of these molecules. For the “acene” and “phene” series, the UV-vis absorption and fluorescence spectra shift dramatically when the number of phenyl rings increases and the chemical reactivity also increases. In contrast, the emission shifts for all benzenoid PAHs with either “armchair” or “cove” type edges is smaller and they show higher chemical stability. HBC has an armchair periphery and is therefore highly stable.

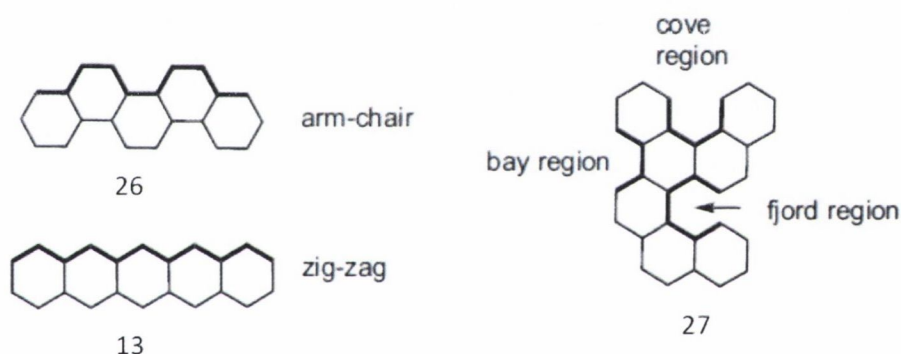


Figure 1.8: Various peripheries of PAHs.

1.3.1.3 Symmetry

Kaster *et al.*, have studied a series of PAHs with varied symmetries in order to establish a connectivity between the electronic spectra and symmetry of PAHs. Both UV-visible absorption and computational studies revealed that highly symmetric PAHs [e.g. D_{6h} (**1a**) or D_{3h}] have fewer transitions showing narrower spectrum when compared to their lower-symmetric counterparts [e.g. C_{2v} (**28**), D_{3h}] (Figure 1.9).³⁷ Symmetry reductions lead to more allowed transitions and therefore to broader spectra. In contrast, the photoluminescence spectra are broader and more structured in high symmetric systems due to symmetry forbidden transitions from S_1 to ground state S_0 . Furthermore, the 0-0 transition (α band) in high symmetric compounds are only weakly allowed and becomes more intense as the symmetry is reduced. In addition, two-dimensional wide angle X-

ray scattering (2D-WAXS) and differential scanning calorimetry (DSC) experiments suggest that an aromatic core with higher symmetry enhances the supramolecular order.

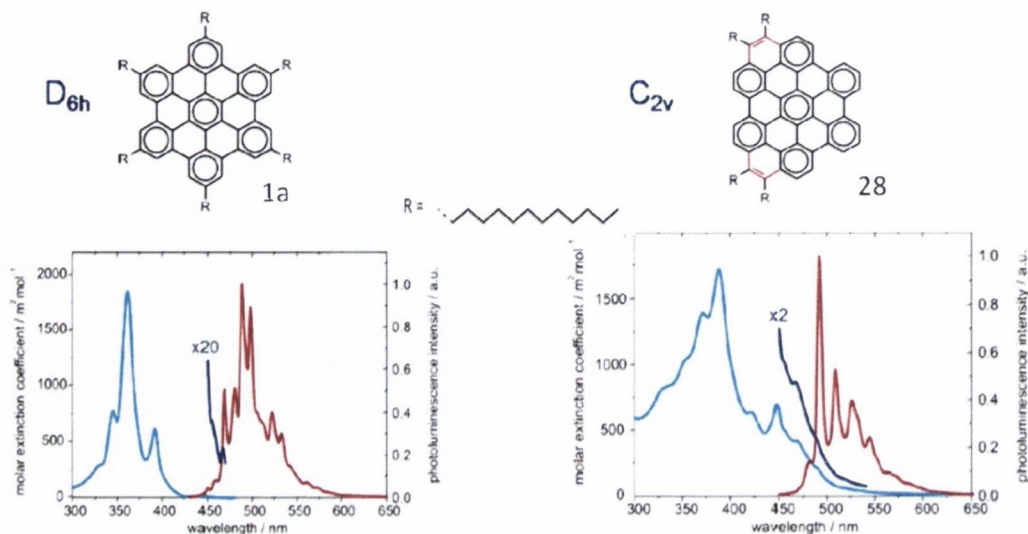


Figure 1.9: UV-vis absorption and photoluminescence emission spectra of PAH with D_{6h} (**1a**) and C_{2v} (**28**) symmetry.³⁷

The synthetic advances made in the oxidative cyclodehydrogenation have led to development of a large array of nanographenes and graphene nanoribbons. To date, conventional solution based oxidative cyclodehydrogenation of polyphenylene precursors has been favoured to generate graphene derivatives [Figure 1.10 (a)-(f)]. Recently, surface mediated cyclodehydrogenation has attracted extensive interest as an alternative route towards generation of graphitic systems [e.g. **35** and **36** (Figure 1.10)]. This method overcomes the solubility problems encountered in the synthesis of larger graphenes using wet chemical synthesis. A more detailed discussion of oxidative cyclodehydrogenation is included in Section 1.6.

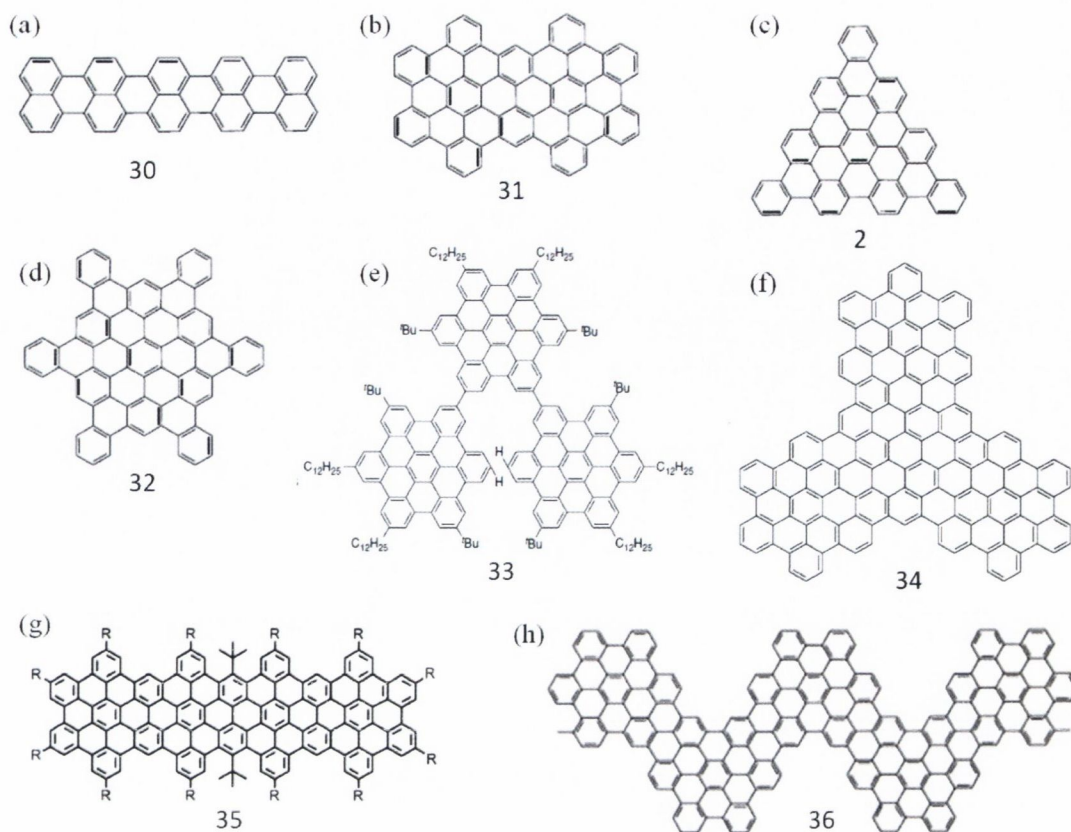


Figure 1.10: Examples of some nanographenes and graphene nanoribbons.

1.3.2 HBC derivatives and their applications

HBC molecules undergo self assembly in both the solid state and in solution by stacking of the disc-like molecules *via* π - π interactions. Extensive aggregation is undesirable and needs to be controlled by careful choice of substituent along the periphery of the HBC unit. Peripheral substitution with flexible aliphatic alkyl chains gives rise to discotic liquid crystal behavior where as functionalisation with saturated alkyl chains gives thermotropic liquid crystalline behavior.³⁸ Furthermore, the peripheral aliphatic substituents form an insulating layer around the aromatic core, promoting intermolecular charge mobility along the columnar stacking axis.

Unsubstituted HBC suffers from poor solubility due to extensive aggregation. Functionalisation with *tert*-butyl substituents along the periphery of the HBC core improves the solubility significantly. The steric hindrance of the bulky *tert*-butyl substituents hinders the π - π stacking to a great extent, thereby improving the solubility in organic solvents. It is further supported by the crystal structure of hexa-*tert*-butyl substituted which shows dimeric packing arrangement in solid state with an interdimer

distance of 3.44 Å.³⁹ An extremely non-planar HBC derivative was synthesised by Müllen and coworkers upon permethoxylation of the periphery.⁴⁰ The X-ray single-crystal analysis revealed that per-methoxylated HBC (**37**) has an extraordinary “double-concave” conformation in which the dramatic deviation from planarity arises due to the steric congestion in the bay region. It exhibits a herringbone-type lattice structure with a large interplanar distance of 13.05 Å. In addition, the double concave surface allows the inclusion of suitable guest molecules on both sides of the molecule, making it an excellent supramolecular host for guest molecules such as perfluorobenzene and fullerene.⁴⁰ Figure 1.11 shows that C₆₀ can be perfectly accommodated by the double concave of permethoxylated HBC and is organised into 1D columnar structure.

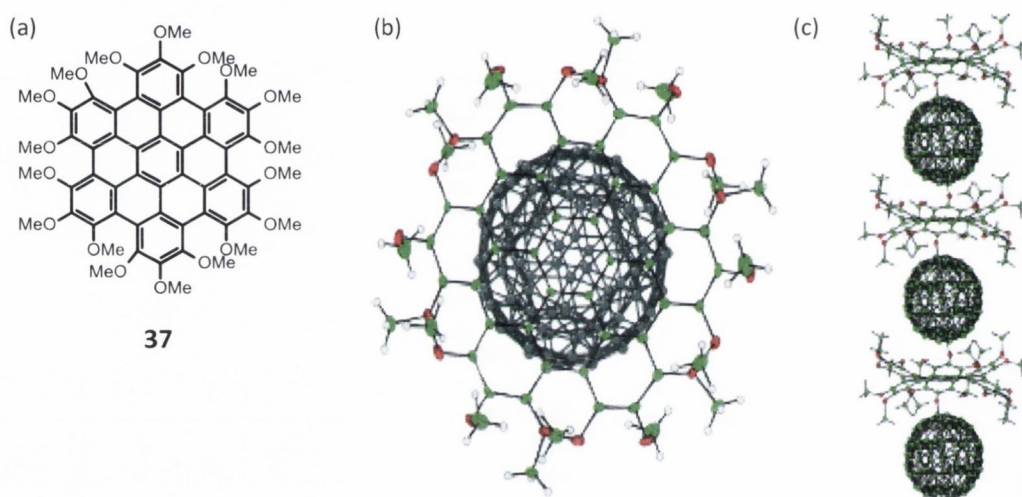


Figure 1.11: (a) Permethoxylated HBC (**37**) (b) top view of the single crystal structure of the complex formed between fullerene and permethoxylated HBC and (c) side view of the columnar packing arrangement (taken without modification from *Angew. Chem. Int. Ed.* 2005, 44, 1247-1250 by Wang et al.).⁴⁰

From a device development perspective, the controlled alignment of the discotic material is the key issue for achieving good performance criteria such as high charge carrier mobility. This can be achieved by both structural modification and the choice of processing technique such as alignment layers, zone-casting or LB (Langmuir–Blodgett) techniques. Also, easy solution processing and self-healing properties of HBC derivatives are advantageous in usage in devices.

PR-TRMC (pulse-radiolysis time-resolved microwave conductivity technique) studies have shown that the π - π stacked columnar structures of HBC can have an intrinsic

charge carrier mobility of upto $1.1 \text{ cm}^2/\text{Vs}$.⁴¹ This has stimulated the incorporation of these distinctive materials in electronic devices including organic solar cells and FETs. Depending on substituents on the HBC core and OFET fabrication methods, charge mobility can range from 10^{-6} to $10^{-2} \text{ cm}^2/\text{Vs}$.²⁸ Unsubstituted HBC acts as a hole transporting material (p-type) with a hole mobility of up to $3.3 \times 10^{-2} \text{ cm}^2/\text{Vs}^{-1}$ whereas, functionalisation with fluorine substituents (hexafluoro-HBC) gives it electron transport properties (n-type) with an electron mobility of $1.6 \times 10^{-2} \text{ cm}^2/\text{Vs}$.⁴² Schmit-Mende *et al.* have studied a combination of electron-donating alkyl substituted HBCs [**39** (HBC-PhC₁₂)] with electron-accepting perylene diimides [**38** (PDI)] as donor and acceptor layers respectively in a photodiode.⁴³ The power conversion efficiency (PCE) of this HBC-PDI blended system was 1.95% at 490 nm under very low intensity light ($0.47 \text{ W}/\text{cm}^2$). Although this value is less than the commercial PV material, further development should generate alternative viable materials for these devices.

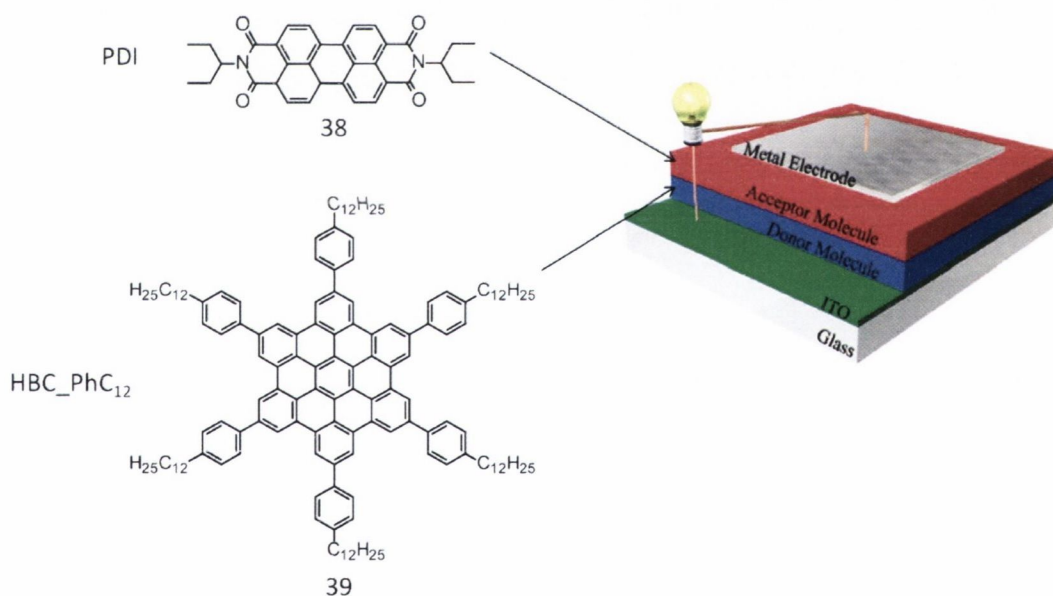


Figure 1.12: Photodiode based on discotic LC (HBC-PhC₁₂) and crystalline (PDI) materials.⁴³

HBC derivatives have also been used in some biological applications including two photon cell imaging,⁴⁴ as sensors of volatile organic materials⁴⁵ and as negative electrodes in Li ion batteries.⁴⁶

1.4 Heteroatom doped PAHs

The incorporation of heteroatoms (e.g. N, S, P, B) into the periphery of polycyclic aromatic hydrocarbon derivatives has a significant influence on their electronic and optical properties.

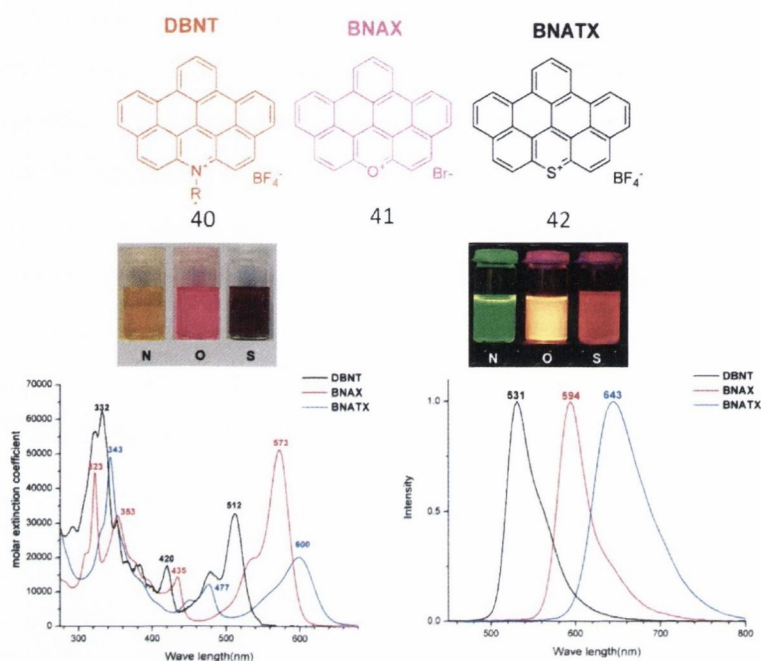


Figure 1.13: UV-Vis absorption and emission spectra of DBNT, BNAX and BNATX in CH_2Cl_2 at 20 °C.⁴⁷

Wu *et al.* have investigated the substitution effect of a series of nitrogen, oxygen and sulfur containing positively charged highly fluorescent PAHs with the same aromatic backbone. DBNT [40 (N-doped)], BNAX [41 (O-doped)] and BNATX [42 (S-doped)] were successfully synthesised *via* a photolytic cyclodehydrogenation process from the corresponding acridinium, xanthylium, and thioxanthylium precursors respectively.⁴⁷ Remarkably, the photophysical properties of these cationic salts varied drastically depending on the type of heteroatom substitution as depicted in Figure 1.13. These results clearly demonstrate the possibility of fine-tuning the optoelectronic properties of PAHs through the incorporation of different heteroatoms without changing the size of aromatic framework.

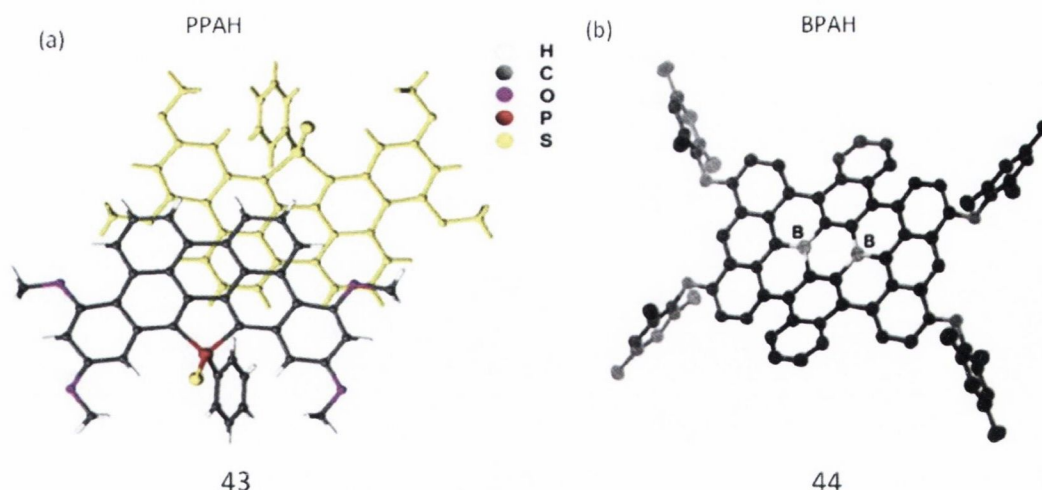


Figure 1.14: Single crystal X-ray structures of (a) PPAH (**43** - taken without modification from *J. Am. Chem. Soc.*, 2012, 134, 6524-6527 by Réau *et al.*) and (b) BPAH (**44** - taken without modification from *Angew. Chem. Int. Ed.*, 2012, **51**, 12206-12210 by Saito *et al.*).

Compared to other heteroatom doped systems, reports of phosphorous doped PAH systems are relatively scarce. Réau and coworkers have reported a successfully synthesised a novel family of P-containing PAHs (**43**).⁴⁸ In this work, a sulfur containing phosphole with an aromatic backbone was used as the polyphenylene precursor and the subsequent oxidative photocyclisation of the polyphenylene followed by desulfurisation gave rise to these P-containing PAH [Figure 1.14(a)]. The presence of a reactive P centre within the sp^2 -C skeleton allows facile functionalisation to extend this novel family of P-doped PAHs and also to use it as a coordinating ligand. Recently, Saito and co-workers have synthesised an interesting B-containing PAH (**44**) by inclusion of a planar boron atom at the centre of a thiophene-doped aromatic platform [Figure 1.14(b)]. It shows reversible multiredox properties and also acts as a black absorber and a near IR emitter, making it a promising candidate for applications.⁴⁹

Takase *et al.* have synthesised a series of pyrrole-fused azacoronenes called hexapyrrolohexaazacoronene (HPHAC) *via* oxidative cyclodehydrogenation of hexapyrrolylbenzene and subsequent neutralization (Figure 1.15).^{50, 51} It is the first example of an extended disk type π -system with multiple interior nitrogen atoms. The reversible redox behaviour of this system makes it potentially interesting as electrochromic and charge-carrier transporting material in organic electronics.

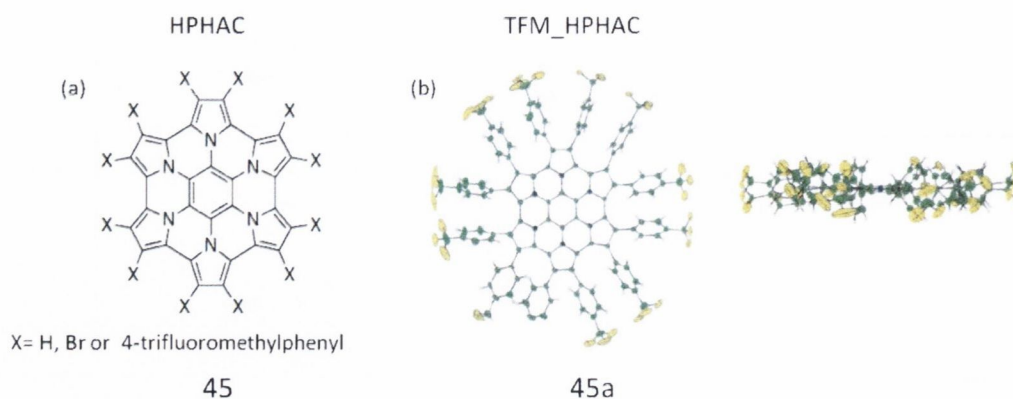
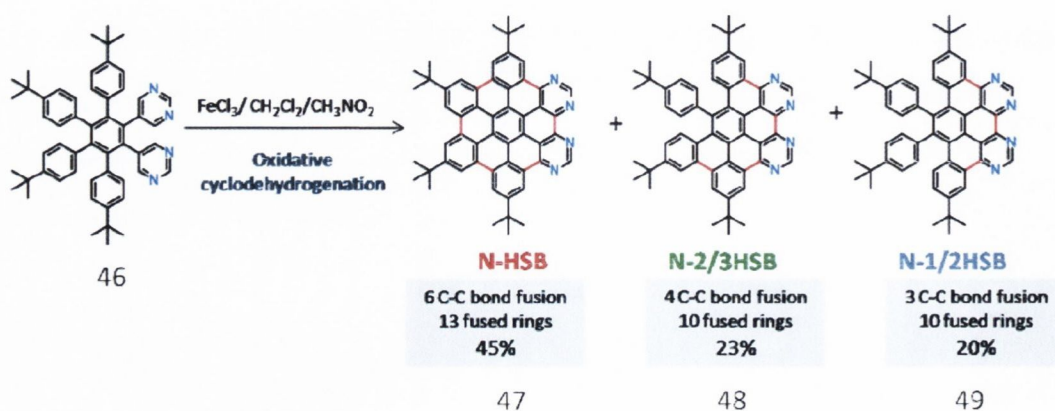


Figure 1.15: (a) Hexapyrrolohexaazacoronenes (45 - HPHAC) and (b) top and side views of X-ray structure of 4-trifluoromethylphenyl HPHAC (45a - TFM_HPHAC) (taken without modification from *Angew. Chem. Int. Ed.*, 2007, 46, 5524-5527 by Takase et al.)⁵⁰

1.4.1 Nitrogen Heterosuperbenzene (N-HSB)

The incorporation of nitrogen atoms into the periphery of hexabenzocoronene core were first established by Draper and co-workers, and has led to the formation of a family of compounds known as the nitrogen heterosuperbenzenes (N-HSBs).³³ The nitrogen atoms were incorporated into the HBC periphery by careful modification of the synthetic precursors. In the polyphenylene precursor, the 4N heteroatoms were introduced *via* dipyrimidyl acetylene which was used as the dienophile in the [2+4] Diels-Alder reactions. The incorporation of imines on the edges of the carbon framework renders it electron accepting in nature and enhances the π -electron mobility of the molecule. Protonation of the peripheral nitrogen atoms results in quenching of the strong green emission, indicating a significant alteration in the π -electron density within the molecule.



Scheme 1.1: The synthesis of N-HSB via oxidative cyclodehydrogenation.

Initially, the oxidative cyclodehydrogenation of N-HSB polyphenylene was carried out using $\text{AlCl}_3/\text{CuCl}_2$ in carbon disulfide and yielded only the fully fused N-HSB molecule in 49 % yield.³³ Under the same conditions, the oxidative cyclodehydrogenation of the all carbon analogue hexa(peri-*tert*-butylphenyl)benzene cyclises with a yield of >80 %.⁵² This indicates that the presence of the nitrogen atoms in the periphery of the hexaphenylbenzene precursor has a significant effect on the efficiency of the Scholl reaction. Alternatively, using FeCl_3 as the catalyst with dichloromethane/nitromethane results in N-HSB (**47**) as the major product (45 %) along with its partially fused daughter molecules N- $\frac{2}{3}$ HSB [(**48**) four C-C bonds fused] and N- $\frac{1}{2}$ HSB [(**49**) three C-C bonds fused] in 23 % and 20 % yields respectively (Scheme 1.1).^{53, 54} Attempts to completely cyclise these partially fused products using AlCl_3 system have been unsuccessful, demonstrating that these products are also thermodynamically stable in their own right. Furthermore, it shows that the oxidative cyclodehydrogenation of these N-doped systems is dependent on the synthetic route employed and proves to be far more challenging than their all carbon analogues.

The positioning of nitrogen atoms in N-HSB framework makes it suitable for coordination to metal centres. Studies have been carried out within the group coordinating these N-HSB derivatives to various metal centres such as Ru(II), Os(II), Ir(III) and Pd(II).^{53, 55} These compounds show interesting photophysical and supramolecular behavior. For example, the Ru(II) coordination complex is a black MLCT absorber and a near IR emitter, and has potential applications in solid-state electroluminescent devices. In addition, sulfur doped compounds (e.g. S-HSB) have also been synthesised in the group, and show fascinating emission and electrochemical properties.⁵⁶

1.5 Polyphenylenes

Polyphenylenes consist of two or more conjugated benzene or aryl rings that are attached to form differently patterned molecules in varying size and shape. Phenylene-based conjugated material can provide versatile platforms for the development of graphene sheets *via* cyclodehydrogenation. They can be categorised into several classes depending on their shape: linear, hexagonal-shaped, star-shaped, ribbon shaped and dendrimers and hyperbranched polymers.⁵⁷

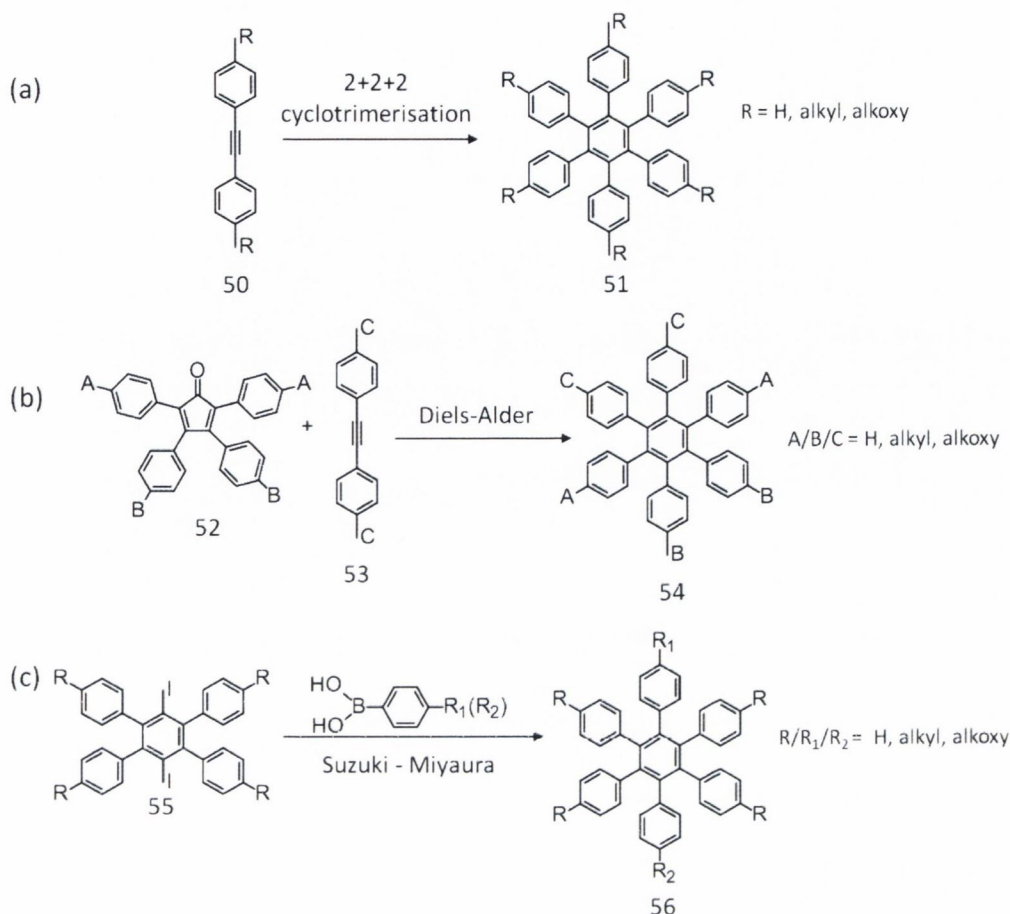
1.5.1 Hexaphenylbenzenes

The key synthetic precursors to HBCs are hexaphenylbenzenes (HPB). The planarisation of HPB under oxidative cyclodehydrogenation conditions results in planar HBCs. Hexaphenylbenzenes have also attracted wide attention in other areas such as dendrimer research and as supramolecular hosts to a variety of guest molecules.^{58, 59} Hexaphenylbenzene can be considered as molecular propellers with its six outer aryl rings twisted with angles ranging from 65-75° (for unsubstituted hexaphenylbenzene) with respect to the central benzene ring. Both steric and electronic factors influence the tilt angle and normally the steric interactions are minimized by a perpendicular arrangement of the peripheral phenyl rings about the central ring. A range of N-doped and S-doped polyphenylenes have been successfully synthesised within the Draper group.^{53, 60} In general, they show a unidirectional twisting of aryl and heteroaryl rings about the central ring, with tilt angles varying from 59-87°.

1.5.2 Synthesis of Hexaphenylbenzenes

Hexaphenylbenzenes can be synthesised *via* three main routes: (a) transition-metal catalysed cyclotrimerisation of substituted diarylacetylene, (b) intramolecular Diels-Alder reaction between appropriately substituted tetraarylcyclopentadienone and diarylacetylene derivatives or (c) Suzuki-Miyaura cross-coupling reaction between halobenzenes and boronic acids (Scheme 1.2).

Synthetically, intermolecular [2+2+2] cycloaddition of diarylacetylenes offers a convenient one step route to polyphenylenes with hexagonal symmetry [Scheme 1.2(a)].⁶¹ The cyclotrimerisation may be catalysed by a large number of transition metal systems (for example $\text{CpCo}(\text{CO})_2$),⁶² however the most popular catalyst is dicobaltoctacarbonyl, widely used by Müllen *et al.* for the synthesis of large number of polyphenylenes with different sizes.⁶¹ Cyclotrimerisation also offers the possibility of introducing solubilising substituents into the larger PAHs by using substituted arylacetylenes. [2+2+2]-cycloaddition of an asymmetric diarylacetylene give rise to both symmetric and asymmetric products in 1:3 ratio. The present work focuses on the synthesis of N-doped polyphenylenes based on dicobaltoctacarbonyl catalysed cyclotrimerisation of asymmetric acetylenes and will be discussed in detail in Chapter 3.



Scheme 1.2: Various synthetic routes to hexaphenylbenzenes.

[2+4] Diels-Alder cycloaddition of tetraaryl cyclopentadienone (diene) with an arylacetylene (dienophile) is a well established method for the controlled synthesis of polyaryl compounds [Scheme 1.2(b)].⁶³ In a [2+4]-cycloaddition, a dienophile stereospecifically adds to the 1 and 4 positions of the conjugated diene component, to generate a six membered ring through two C-C bond formations. Extended oligophenylene derivatives as precursors for large, all-benzenoid hydrocarbons with various topologies can be prepared easily by the intermolecular [2+4] cycloaddition.⁶³ By altering the number of acetylene spacers in the alkyne precursor, the size and dimensions of the poly substituted product can be altered. In N-HSB polyphenylene precursor, the nitrogen atoms were incorporated *via* the dipyrimidyl acetylene precursor. This project focuses on the synthesis of N-doped polyphenylenes *via* [2+4]-Diels Alder reaction and will be discussed broadly in Chapter 2.

The recently developed Suzuki-Miyaura cross coupling route provides a novel route to HPB synthesis using arylboronic acids with 1,4-diiodo-2,3,5,6-tetraarylbenzenes

[Scheme 1.2(c)].⁶⁴ The selectivity of this coupling reaction allows a convenient approach to synthesize both symmetrically and unsymmetrically substituted HPBs.

1.5.3 Polyphenylenes and their applications

As discussed above, polyphenylenes are the key synthetic precursors to PAHs or nanographenes. However, they are a versatile class of molecules in their own right with potential applications in diverse fields.⁵⁷ Architectures of polyphenylenes can vary from 1D conjugated polymers to large 3D polyphenylene dendrimers.

1.5.3.1 Conjugated polymers

Conjugated polymers consist of both linear rod-shaped polymers and π -conjugated macrocycles. These polymers are generally insoluble, however by introducing solubilizing groups (e.g. **57**) onto the main chain the processability of these polymers can be dramatically improved. Furthermore, introduction of electron-rich/ electron-poor groups or heteroatoms (e.g. **58** and **59**) within the backbone allows the bandgap of the molecules to be controlled (Figure 1.16).

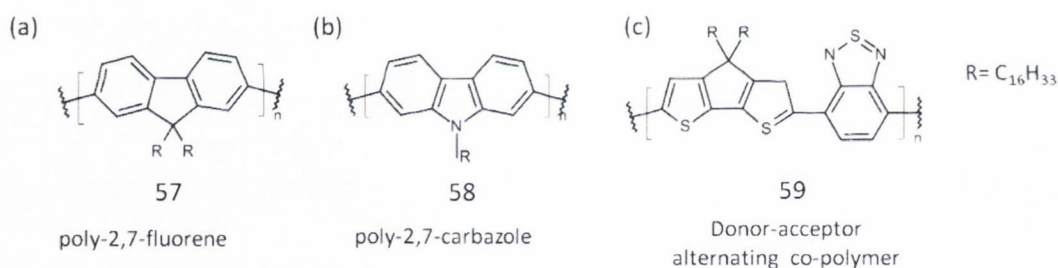


Figure 1.16: Some conjugated polymers.

These conjugated polymers are successfully applied in building of organic field effect transistors (OFETs), as blue-emitting materials in organic light-emitting diodes (OLEDs)^{65, 66} or electron donors in organic photovoltaics (OPVs).⁶⁷

1.5.3.2 Polyphenylene dendrimers

Polyphenylene dendrimers (PPDs) are another class of compounds which have found wide range of applications. They are orderly branched and monodisperse macromolecules constituted of substituted phenyl rings or incorporate different functionalised moieties. These molecules have several key advantageous properties

including high thermal and chemical stability and the inherent rigid and shape persistent structure.

PPD systems allow incorporation of large numbers of functional groups into a single molecule and these combined functionalities can lead to achieve advantageous synergistic effects. Furthermore, these systems benefit from the bulky nature of the PPD scaffold which suppresses chromophore aggregation and enhances photoluminescence intensities.

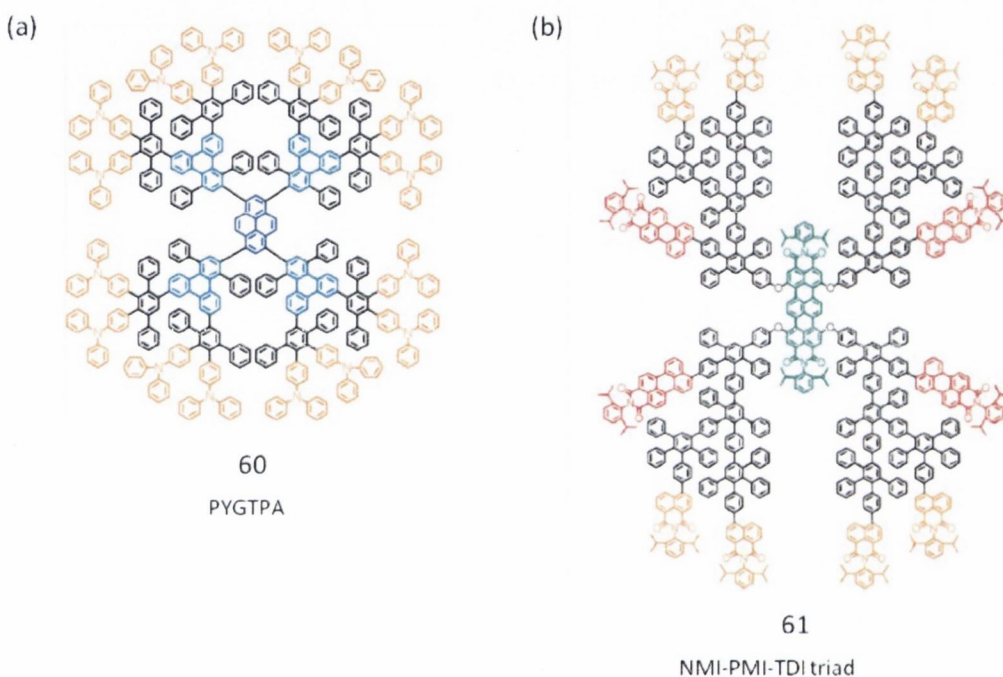


Figure 1.17: (a) Blue emitting dendrimer with a pyrene core (**60**)⁶⁸; (b) polyphenylene triad (**61**).⁶⁹

PYGTPA (**60**) consists of a core-shell-surface multi-functional structure using a blue fluorescent pyrene core with triphenylene dendrons and triphenylamine surface groups [Figure 1.17(a)].⁶⁸ This system is reported as one of the best fluorescence-based blue-emitting organic molecules with a luminance of up to 1400 cd/m². Efficient excitation energy transfer from the triphenylene shell to the pyrene core substantially enhances the quantum yield efficiency while TPA groups facilitate the hole capturing and injection ability in the device applications. Furthermore, Weil *et al.* have reported a dendritic triad (NMI-PMI-TDI triad, **61**) based on the chromophores naphthalenedicarboximide (NMI), perylenedicarboximide (PMI) and terrylene-tetracarboxydiimide (TDI) which contain site specific placement of chromophores [Figure 1.17 (b)].⁶⁹ This system acts as

an efficient light harvesting molecule and absorbs over the whole range of the visible spectrum.

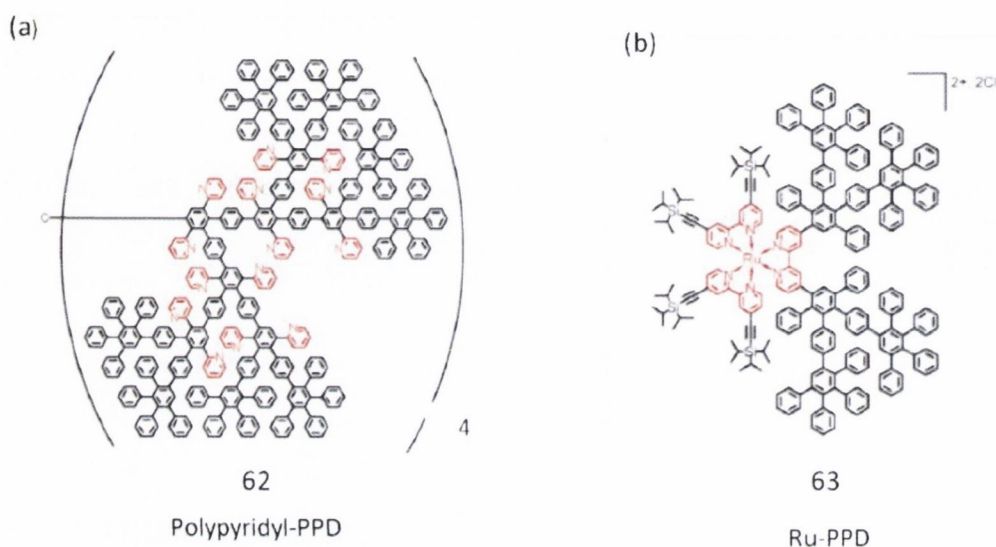


Figure 1.18: (a) Fourth generation PPD (**62**) with internal pyridine moieties which acts as a TATP sensor;⁷⁰ (b) A ruthenium(II) bipyridyl complex (**63**) serving as a desymmetrized core for the build-up of non-symmetric PPDs.⁷¹

Polyphenylene dendrimer materials contain internal voids and channels between dendron branches as a result of the rigid framework. Crystal structures of different PPDs have revealed that solvent molecules are readily trapped within both intra- and intermolecular PPD cavities.⁷² The ability of rigid PPDs to interact with guest molecules through their hydrophobic voids has been explored in the field of host-guest chemistry⁷³ and for the design of highly sensitive and specific chemical sensors.⁵⁸ A well-known application of dendritic host-guest chemistry is the possibility to solubilize guest molecules in unusual environments *via* dendritic encapsulation.⁷⁴ It has been achieved by introduction of suitable functionalities in the dendritic core or in the scaffold to facilitate solubilization. Furthermore, introduction of functionality within dendritic voids can be used to enhance the ability of dendrimers to take up guests. For example, a fourth generation PPD (**62**) bearing 56 pyridyl functions within its interior [Figure 1.18 (a)] shows surprisingly high affinity towards the explosive triacetone triperoxide (TATP).⁷⁰ The high affinity of polypyridyl-PPD (**62**) to TATP was utilised by Lubczyk *et al.* to develop a highly sensitive TATP detector. Upon coating a polypyridyl-PPD (**62**) layer on a quartz crystal microbalance (QCM) detector Lubczyk showed that sensor had a TATP detection sensitivity as low as 0.1 ppm.

Furthermore, polyphenylene derivatives have also been used as ligands in encapsulated transition metal complexes, i.e. Ru(II)⁷¹, Ir(III).⁷⁵ These large molecular architectures gives tremendous scope for tuning a wide range of properties such as color tuning, intermolecular interactions, charge mobility and exciton diffusion which are important parameters for device development. Figure 1.18(b) shows a bipyridyl complex of Ru²⁺ that was utilized as a PPD core (**63**), where the stepwise development of center offered a facile route towards globally desymmetrized PPD structures.⁷¹

1.6 Cyclodehydrogenation

The generation of new C-C bonds *via* oxidative coupling of benzenes and its derivatives has been widely investigated over the years. Intramolecular oxidative cyclodehydrogenations have been extensively used in the synthesis of π -conjugated systems with extended aromatic frameworks such as PAH starting from polyphenylene precursors.

In the early 1920s Scholl and coworkers developed a synthetic route using molten AlCl₃ with atmospheric oxygen as the oxidant to fuse biaryls, such as 1,1'-binaphthyl, to *peri*-condensed aromatic systems. In 1960s, Kovacic and coworkers further investigated aryl-aryl bond formation by applying various Lewis acid/oxidant combinations (e.g. AlCl₃/CuCl₂) and successfully polymerized benzene and its derivatives to form poly(*p*-phenylene)s.⁷⁶⁻⁷⁸ The use of FeCl₃, as both a mild Lewis acid and an oxidizing agent, renders the addition of an auxillary oxidant unnecessary. This Lewis acid catalysed oxidative cyclodehydrogenation is known as the “Scholl reaction”. Müllen and co-workers have demonstrated that the intramolecular Scholl reaction is useful for the synthesis of various polyphenylene precursors ranging from hexaphenylbenzenes to large dendritic arene precursors. Many C-C bonds between unfunctionalized aryl moieties can be formed using the FeCl₃ conditions and Müllen *et al.* reported the successful closure of 126 bonds in a single reaction step.⁷⁹ Other oxidants have also been explored in the Scholl reaction and include Ti(O₂CCF₃)₃ in CF₃COOH or BF₃.Et₂O,⁸⁰ Pb(OAc)₄/ BF₃.Et₂O in MeCN,⁸¹ triethyloxonium hexachloroantimonate (Et₃O⁺SbCl₆⁻),⁸² SbCl₅,⁸³ (CF₃COO)₂I^{III}C₆H₅ (PIFA) with BF₃.Et₂O in CH₂Cl₂,⁸⁴ MoCl₅,⁸⁵ and dichlorodicyano-*p*-benzoquinone (DDQ)/H⁺.⁸⁶

Various other methods have also been studied to achieve C-C bond formation including base-induced cyclodehydrogenation, oxidative photocyclisation (Mallory reaction) and

surface-assisted cyclodehydrogenation. Base induced cyclodehydrogenation has been used mainly in extended aromatic systems containing electron withdrawing functionalities such as perylene diimides or rylene diimides.⁸⁷ Commonly used base combinations include molten KOH, K_2CO_3 in ethanolamine and diazabicyclo[4.3.0]non-5-ene (DBN), sodium tert-butoxide in diglyme. This method have opened up new route for synthesis of perylene dyes which have significant importance in optoelectronic applications, including sensitizers in dye sensitized solar cells and n-type semiconductors in FETs. Oxidative photocyclisation of stilbene-type compounds has been extensively applied to the synthesis of condensed aromatic and heteroaromatic compounds. Nuckoll and coworkers have synthesised contorted hexa-*cata*-hexabenzocoronene and its derivatives *via* irradiation of a bisolefin precursor.⁸⁸

1.6.1 Surface-assisted cyclodehydrogenation

Surface-assisted cyclodehydrogenation has attracted wide interest due to its many advantages over conventional solution based methods. Insolubility of large oligophenylene precursors in common organic solvents have hampered the progress of solution based methods, in the synthesis of graphene derivatives with extended aromatic platforms. They also suffer from intrinsic reactivity and regioselectivity problems leading to incomplete cyclisations,⁸⁹ unexpected alkyl migrations/rearrangements.⁹⁰ On surface covalent synthesis surmounts these obstacles and provides a powerful alternative for bottom-up synthesis of graphene derivatives.

Initially, Müllen and co-workers have developed a thermally induced cyclodehydrogenation route to synthesise HBC starting from hexaphenylbenzene precursor on a Cu(111) surface.⁹¹ Recent work by Fasel and coworkers have shown that this method can be extended to develop atomically precise graphene nanoribbons starting from a dihalogenated 10,10'-dibromo-9,9'-bianthryl monomer (Figure 1.19).²² In this process, the initial coupling of the dehalogenated monomers at 200 °C yields polymeric chains and second annealing of the sample at 400 °C induces an intramolecular cyclodehydrogenation and planarisation of the polymer chain, resulting in the formation of the fully aromatic nanoribbon. This surface approach is advantageous since the topology of the resulting graphene nanoribbons can be directly determined by the precursor monomers. In addition, Pinardi and co-workers have

extended this development to nitrogen doped nanographene systems using the surface mediated cyclodehydrogenation method.²³

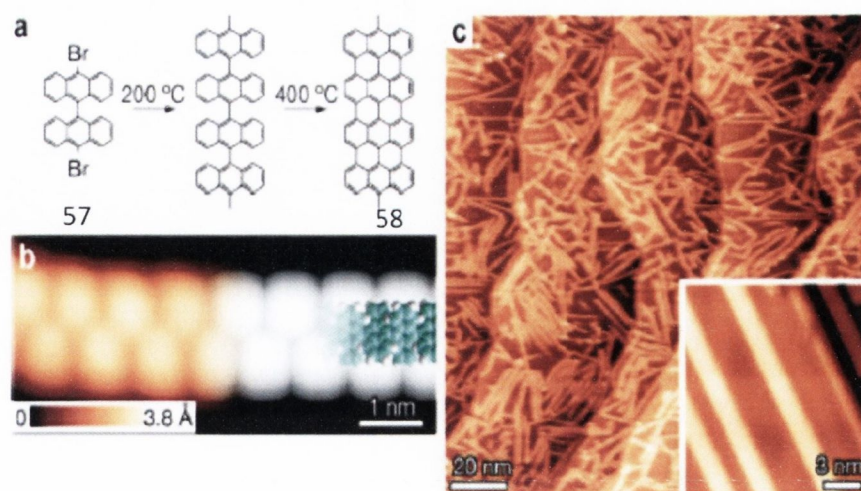
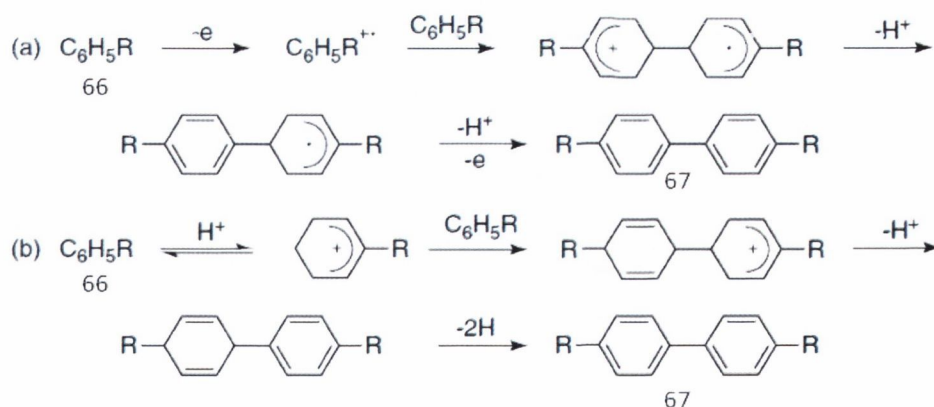


Figure 1.19: (a) Surface mediated GNR synthesis from bianthryl monomer precursor; (b) STM image after surface assisted C-C coupling at 200 °C and DFT based simulation of the STM image (right) partially overlaid; (c) overview STM image after cyclodehydrogenation at 400 °C (taken with modification from Nature, 2010, 466, 470-473 by Fasel et al.)²²

1.6.2 Scholl reaction mechanism

The detailed mechanism of the Scholl reaction has been under extensive debate over the past years and still remains elusive. Two principle reaction pathways have been proposed: (a) radical cation mechanism (electron transfer) and (b) arenium cation mechanism (proton transfer).⁹²



Scheme 1.3: Proposed mechanism of the Scholl reaction (a) radical cation mechanism (b) arenium cation mechanism.

(a) Radical cation mechanism

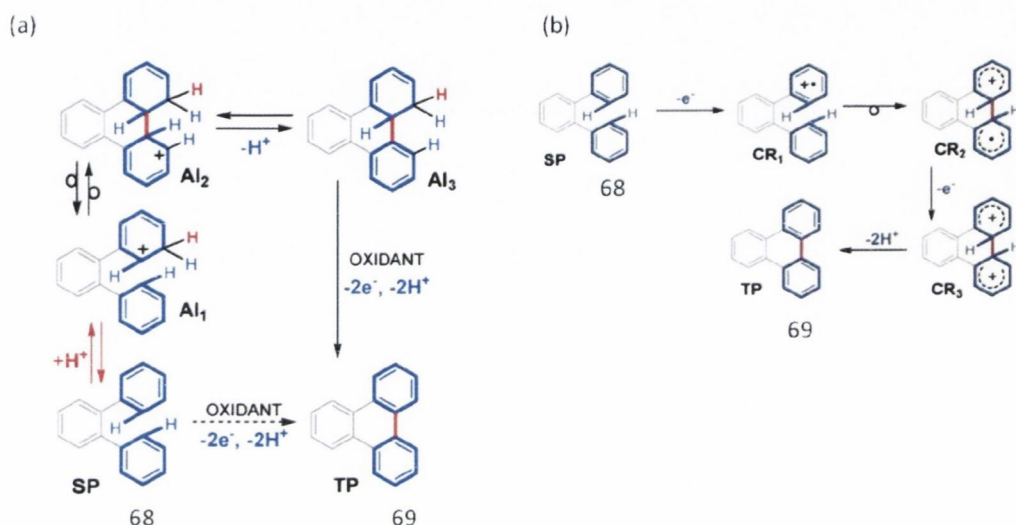
The radical cation mechanism was initially proposed by Rooney and Pink⁹³ and has been studied experimentally by Hammerich and Parker⁹⁴ and computationally by Negri and coworkers.⁹⁵ The mechanistic route can be explained in a simplified manner for the formation of a biphenyl derivative **67** [Scheme 1.3(a)]. Firstly, a radical cation intermediate is formed by removal of an electron by the oxidant (eg. FeCl_3). Then, the second aryl ring undergoes an electrophilic attack by the reactive radical intermediate, to form a new C-C bond. Subsequently one proton is eliminated and one of the six membered ring is aromatised. In order to complete the aromatisation, a second radical cation is formed by extraction of an electron, followed by elimination of the remaining proton to form the biphenyl derivative.

(b) Arenium cation mechanism

King and co-workers have carried out an extensive investigation using both experimental and computational studies to prove that the Scholl reaction occurs *via* a diamagnetic arenium ion intermediate.⁹⁶ According to King *et al.*, the initial protonation occurs due to the adventitious acids in various oxidising systems used in the reaction. After protonation the resulting σ complex reacts with another aryl ring to generate a new C-C bond [Scheme 1.3(b)]. Deprotonation, followed by dehydrogenation restores the aromaticity of the biphenyl compound. They also suggest that these reactions are accelerated as they proceed due to the formation of two equivalents of acid per C-C bond. There is no experimental evidence to prove this statement however. They further state that in the intramolecular Scholl reaction, C-C bonds are likely formed in a stepwise and contiguous manner, with the first being formed the slowest. The reaction is increasingly exergonic and formation of large PAHs arises from the “slippery slope” phenomenon.

A careful mechanistic study reported by Rathore and co-workers using a DDQ/H^+ system and FeCl_3 as oxidants, show strong experimental evidence that the reaction proceeded largely *via* a cation radical mechanism.⁹⁷ They have used a series of Scholl precursors varying from terphenyl to hexaphenylbenzene derivatives. The key point they use to disprove the arenium cation mechanism is the necessity of powerful oxidants such as FeCl_3 or DDQ/H^+ for Scholl reaction. In oxidative cyclodehydrogenation of terphenyl (**68**), if the reaction proceeds *via* an arenium cation mechanism, for the

aromatisation of the dihydroaromatic intermediate AI_3 [Scheme 1.4(a)] a weak oxidant such as I_2 is sufficient. However, in the cation radical pathway, an initial 1-electron oxidation is facilitated by the oxidant, to form a cation radical, which then undergoes an intramolecular C-C bond formation to yield a distonic radical cation (CR_2) [Scheme 1.4(b)]. The distonic nature of this rearranged radical cation facilitates the removal of a second electron at a lower potential and leads to the formation of a dicationic intermediate (CR_3), which loses two protons to yield the aromatic species (**69**).



Scheme 1.4: Cyclodehydrogenation pathways (a) arenium cation mechanism; (b) radical cation mechanism.

Based on this evidence, it is plausible to suggest that the radical cation mechanism is more favoured than the arenium cation mechanism in the oxidative cyclodehydrogenation of polyphenylenes. Further, Rathore *et al.* states that the distinction of the two mechanisms is especially difficult due to the coexistence and ready interchangeability of both reactive intermediates (radical cation vs arenium cation) under Scholl reaction conditions. Therefore, the extent to which one mechanism operates at the expense of the other mechanism depends on the chemical structure of the particular precursor, and the reaction conditions applied.

Work within the Draper group on N-doped polyphenylenes have shown that the initial C-C bond formation occur on phenyl rings directly adjacent to the pyrimidine rings. Therefore, the initial step in the cyclodehydrogenation of N-doped polyphenylenes is most likely the protonation of the basic pyrimidine rings in preference to protonation of the other phenyl rings. King *et al.* proposes that arenium cation mechanism applies for

these N-doped systems.⁹⁸ The protonated or doubly protonated pyrimidine ring could act as an electrophile, explaining bond formation around pyrimidine rings initially. The protonation of the phenyl rings will be difficult as the basic nitrogen-sites will be protonated first and bears a positive charge. King *et al.* further suggest that even if the protonation of the phenyl substituents was possible, the N-protonated PAH core would still be a poor nucleophile and inhibit the electrophilic attack. This inherent problem in N-doped systems provides evidence for the partially fused products. The difficulty of cyclodehydrogenation of N-containing units was further proved in the Draper group by a recent work by Graczyk *et al.* in attempts to attach a terpyridyl unit onto a polyphenylene backbone.⁹⁹ Under FeCl_3 conditions, the all carbon portion was successfully fused, resulting in it being the major product (with no closure of the terpyridyl portion) and only 5 % of terpyridyl fused PAH was obtained. Also, the possibility of coordination of N-sites to Lewis acids such as FeCl_3 or $\text{AlCl}_3/\text{CuCl}_2$ under cyclodehydrogenation conditions further complicates the understanding of the mechanism pathway.

1.7 Aims of the project

The parent N-HSB, combines the properties of its all-carbon analogue, hexa-*peri*-hexabenzocoronene (HBC) with added bidentate ligand functionality, electron-accepting characteristics and increased solubility. This unique class of compounds exhibits interesting optical and electronic properties with potential applications in field-effect transistors and as light emitting layers in OLED or photovoltaic devices. This work details our efforts towards the expansion of the N-HSB family, with varying the degree of nitrogen doping and peripheral substitution, with the main objective of investigating the structure-property relationship of these molecules.

Initial work on N-HSB derivatives were carried out by Dr. Daniel Gregg and Dr. Buddhie Lankage in the Draper group and they mainly focused on 4N containing N-HSB derivatives.^{53, 100} This projects aims to prepare two series of 2N and 6N containing polyphenylenes as precursors to fully fused diaza and hexaaza superbenzenes and study the effect of varying degree of N doping (Figure 1.20).

Generally in polyphenylene synthesis, [2+4]-Diels Alder reaction is widely used for generating asymmetric polyphenylenes, whereas [2+2+2] cyclotrimerisation is used in the synthesis of symmetric polyphenylenes. In the parent N-HSB, four nitrogens were

incorporated *via* the dipyrimidyl acetylene unit in a [2+4]-Diels Alder cycloaddition. [2+2+2] cyclotrimerisation has not previously been investigated in the synthesis of N-doped polyphenylenes and we aim to investigate it as a novel route to synthesise N-doped polyphenylenes.

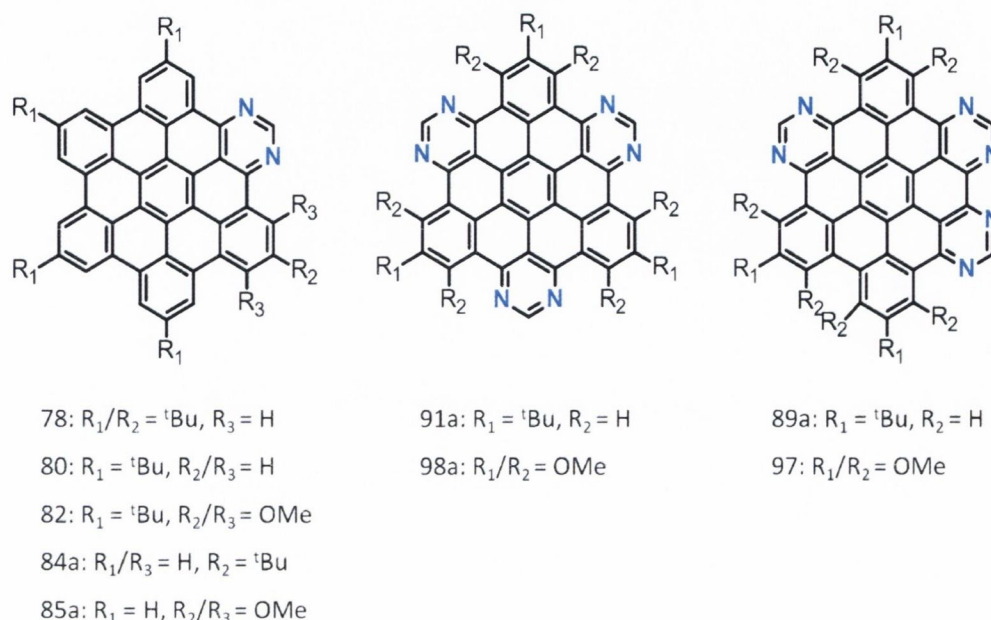


Figure 1.20: Targeted diaza and hexaazasuperbenzenes.

This work also aims to investigate the effect of varying the number of nitrogens and peripheral substitution on the efficiency of the cyclodehydrogenation process. Methoxy substitution has shown to increase the efficiency of the cyclodehydrogenation procedure in all carbon systems.⁹⁰ Therefore, we set about generating a series of 2N and 6N nitrogen doped nanographenes with differing methoxy substitution patterns. We aim to determine the multiple and potentially positive effects of methoxy substitution in promoting cyclodehydrogenation in the nitrogen-doped polyphenylene precursors. Further, we aimed to extensively study the photophysical and supramolecular properties of these novel N-doped systems as a function of their molecular structure.

2. Diazasuperbenzenes: synthesis and characterisation

2.1 Introduction

This chapter describes the synthesis and structural/photophysical characterisation of a series of novel 2N-doped heterosuperbenzenes called diazasuperbenzenes (DASB) with varying functional groups around the periphery. This chapter consists of a brief introduction, followed by two main sections. The latter comprise (i) the synthesis of N-doped hexaarylbenzenes *via* the [2+4]-Diels-Alder route, along with their spectroscopic characterisation, (ii) their oxidative cyclodehydrogenation and consequent structural/photophysical characterisation.

2.1.1 Diels-Alder reaction

The Diels–Alder reaction is widely used in synthetic organic chemistry as a reliable method for forming six-membered ring systems with good control over regio and stereo-chemical properties.¹⁰¹ In a typical [2+4] cycloaddition reaction, a dienophile (2π electrons) regiospecifically adds to a conjugated 1, 4-diene (4π electrons) to generate a six membered ring through the formation of two C-C σ -bonds. The ease of the Diels-Alder reaction is influenced by the substituents. Typically an electron rich diene and an electron poor dienophile is more favourable for the “normal electron demand” pathway. This combination of reactants is associated with a decrease in the energy barrier as the electron donating groups on the diene raises the energy of the HOMO, while the electron accepting groups on the dienophile lowers the energy of LUMO (Figure 2.1). In contrast, in the “inverse electron demand” pathway an electron-rich dienophile and an electron-poor diene is favoured, as it is a diene LUMO-dienophile HOMO controlled reaction.

As discussed in Chapter 1, the [2+4]-Diels-Alder reaction has been used extensively in the synthesis of hexaphenylbenzenes, which are molecular precursors to HBC derivatives. This route can give more choice for functionalisation of the peripheral aryl rings with various substituents when compared to the [2+2+2] cyclotrimerisation route. [2+4]-Diels-Alder reaction route has also been used in the synthesis of extended oligophenylene derivatives with various topologies.^{79, 102} This chapter discusses the synthesis of N-doped hexaphenylbenzenes as molecular precursor to DASBs *via* [2+4] Diels-Alder route using monopyrimidyl substituted aryl acetylenes and tetraarylcyclopentadienones.

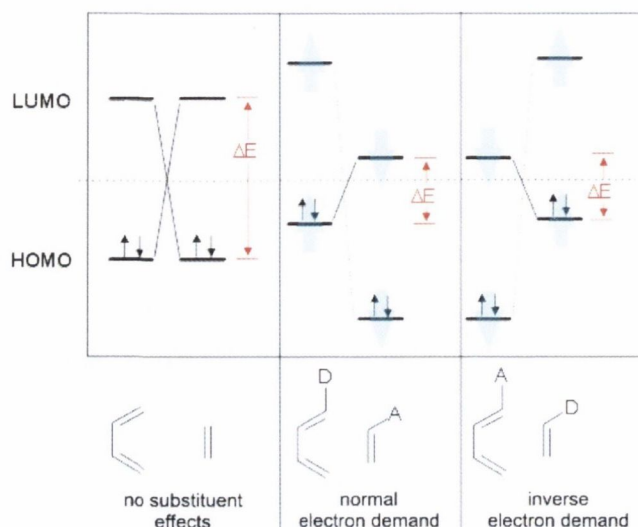


Figure 2.1: Schematic representation of the frontier orbitals of a Diels-Alder reaction in normal and inverse electron demand (A=electron acceptor, D=electron donor).

2.1.2 Microwave-mediated synthesis

Microwave-mediated synthesis have emerged as very efficient routes in organic synthetic reactions delivering high yields in a short period of time.¹⁰³ Recently, many Sonogashira,¹⁰⁴ Heck,¹⁰⁵ Suzuki¹⁰⁶ and Negishi¹⁰⁷ type coupling reactions have been reported using microwave synthesis techniques. These reactions can be carried out in modified domestic microwaves or more efficiently by specially designed commercial equipment. The main drawback of the domestic microwave is the inconsistent heating pattern due to the formation of “hot and cold spots” which decreases the reproducibility of results. In addition, the lack of pressure control leads to high pressure in the vessels and increases the safety risk. In contrast, commercial systems demonstrate ease of temperature control and allow for consistent heating and pressure.

In microwave heating, the microwaves couple directly with molecules that possess a dipole moment (or have ionic character) and makes the molecules orient themselves in line with the electric field. The rotational motion of the molecule during alignment results in the transfer of energy in the form of heat and gives rise to instantaneous localised superheating. This process is called dielectric heating. In addition, microwave heating is independent of the thermal conductivity of the vessel as it heats from the inside outward. Solvents also play a key role in the efficiency of microwave synthesis and generally solvents with a high dielectric constant (such as DMF or CH_2Cl_2) are preferred over high boiling solvents.¹⁰⁸ Furthermore, the effect of microwave heating on

transition metal catalysed coupling reactions are important, in improving the efficiency of these reactions.¹⁰⁹ In our work the synthesis of some aryl acetylenes were carried out using microwave-assisted Sonogashira reactions as will be discussed further in the sections below.

2.1.3 Aims of this work

Varying the degree of nitrogen doping with careful choice of peripheral substitution may unlock new applications for nanographene materials. At the outset, it is important to understand the chemical and then the physical and electronic consequences of these changes. This work aims to develop a novel family of 2N-doped diazasuperbenzenes with varying functional groups on the periphery. The initial target molecules are shown in Figure 2.2. The main objective was to investigate the effect of 2N-doping and peripheral functionalisation with electron donating substituents (methoxy and *tert*-butyl) on the challenging oxidative cyclodehydrogenation step. Furthermore, we aimed to explore the photophysical and supramolecular influences brought about by the reducing the degree of N-doping and nature and position of the substituents compared with the parent N-HSB (**47**) molecule.

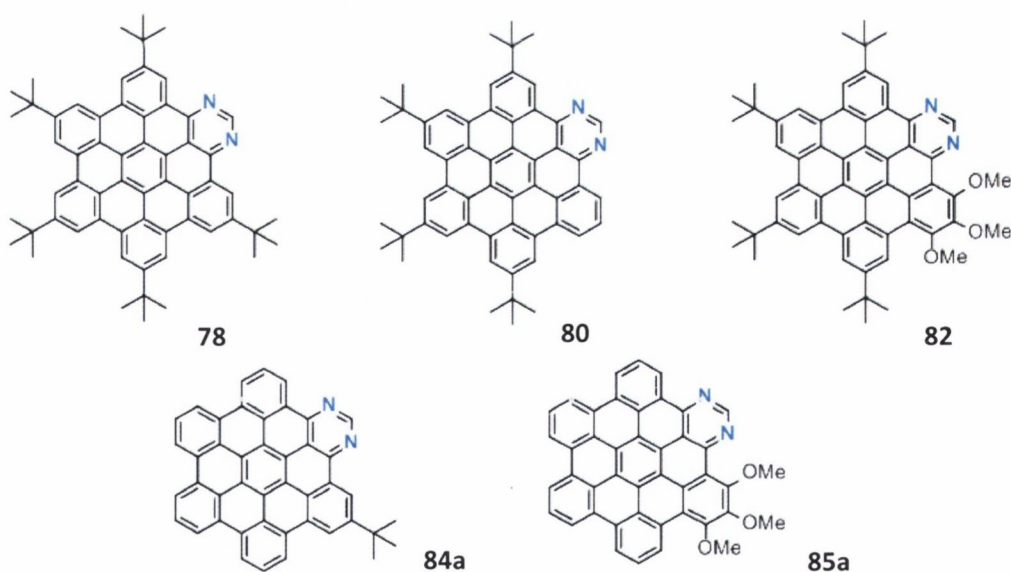


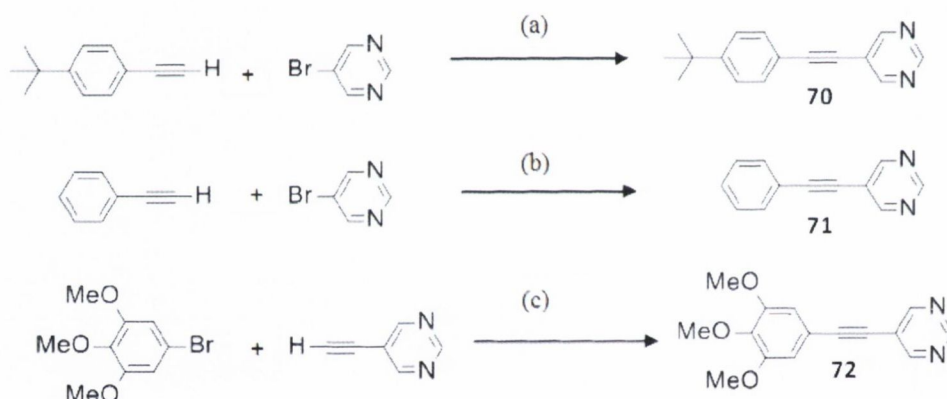
Figure 2.2: Target diazasuperbenzene molecules.

2.2 Diaza-polyphenylenes

Diaza-polyphenylene consists of 2N atoms in the hexaphenylbenzene molecule. Firstly the synthesis of the molecules will be discussed along with their NMR, mass spectrometry and single X-ray characterisation. Secondly, the photophysical characterisation of these 2N polyphenylenes will be discussed in detail.

2.2.1 Synthesis and characterisation of asymmetric aryl-acetylenes

The nitrogen atoms were incorporated onto the polyphenylene precursor *via* the pyrimidine-substituted aryl acetylene precursors. 5-(4-*tert*-butylphenylethynyl)pyrimidine (**70**) was synthesised using a reported procedure,⁵³ which employs a conventional palladium-catalysed Sonogashira reaction between two commercially available reagents, 4-*tert*-butylphenyl acetylene and 5-bromopyrimidine.



Scheme 2.1: Synthesis of asymmetric aryl acetylenes. (a) Pd(PPh₃)₂Cl₂ (5 mol%) , CuI (6 mol%), C₆H₅CH₂N(C₂H₅)₃⁺Cl⁻, toluene: aq. NaOH (1:1 v/v), 65 °C, 1h, 55% (b) Pd(PPh₃)₄ (1.6 mol%), CuI (2 mol%), DMF:DIPA (1:3), μ w 150 W, 115 °C, 25 min, 90% (c) Pd(PPh₃)₂Cl₂ (2 mol%), CuI (2 mol%) , PPh₃, DMF:DIPA (1:3), μ w 150 W, 115°C, 25 min, 45%.

Gourdon *et al.* have reported a convenient method to synthesise pyrimidyl based arylacetylenes using microwave heating.¹¹⁰ They have used temperatures below 120 °C to avoid decomposition of the palladium catalyst. In our work, 5-phenylethynylpyrimidine (**71**) and (3,4,5-trimethoxyphenyl)(5-pyrimidyl)acetylene (**72**) were synthesised using the same microwave conditions reported by Gourdon and co-workers. Compound **71** synthesised according to a modified literature procedure using commercially available starting materials.¹¹⁰ The purification was simplified, as the

product was obtained as a pale yellow crystalline solid upon re-crystallisation with methanol in good yield (90%). The synthesis of 3,4,5-trimethoxyphenyl)(5-pyrimidyl)acetylene (**72**) requires 5-ethynylpyrimidine, which is synthesised using a two step procedure.³³ Firstly, 2-methyl-4-pyrimidin-5-yl-but-3-yn-2-ol was synthesised *via* a palladium catalysed Sonogashira reaction between commercially available 5-bromopyrimidine and 2-methyl-3-butyn-2-ol. Secondly, deprotection of the triple bond with NaOH in toluene yielded 5-ethynylpyrimidine. Commercially available 5-bromo-1,2,3-trimethoxybenzene and 5-ethynylpyrimidine were dissolved in a solution of DMF and diisopropylamine (1:3 v/v) bubbled with nitrogen. To this solution, triphenylphosphine, bis(triphenylphosphine) palladium(II)dichloride (2 mol%) and copper(I) iodide (2 mol%) were added and the mixture was irradiated using microwave radiation at 150 W, 115 °C for 25 min. After cooling, the brown suspension was extracted with Et₂O, followed by washing with saturated NH₄Cl and water. The organic layer was dried over MgSO₄ and concentrated *in vacuo* to obtain **72** as off white crystals (45%). Compound **72** was characterised by NMR and IR spectroscopy, mass spectrometry and elemental analysis.

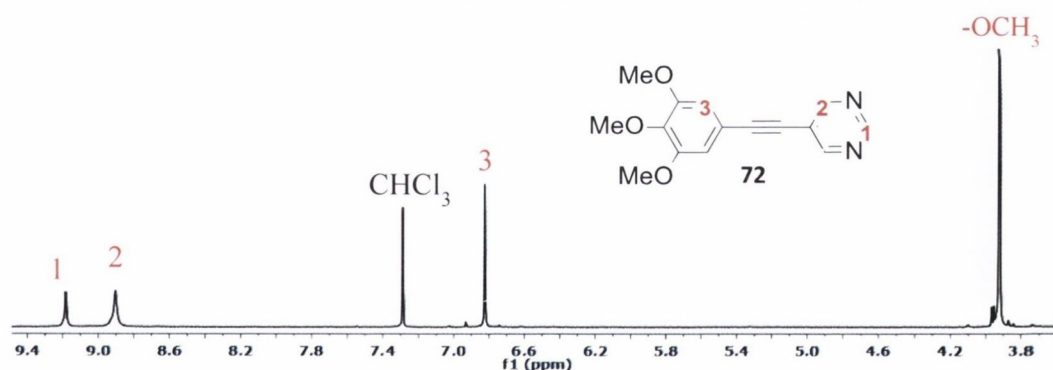


Figure 2.3: ¹H NMR spectrum of **72** in CDCl₃ (600 MHz, RT). Atom labelling as per inset figure.

In the ¹H-NMR spectrum of **72**, the most downfield singlet signals in the region $\delta = 9.18$ ppm and $\delta = 8.90$ ppm are the pyrimidyl protons H1 and H2, and integrate for 1 and 2 protons respectively (Figure 2.3). These appear in the expected region for pyrimidyl containing aryl acetylenes.³³ The next most downfield signal, at $\delta = 6.82$ ppm, is attributed to H3 on the methoxy functionalised aryl ring and integrates for 2 protons. The signals due to the methoxy protons are overlapped and appears as a single signal at $\delta = 3.93$ ppm integrating for a total of 9 protons.

The full assignment of the ^{13}C NMR spectrum of **72** is depicted in Figure 2.4.

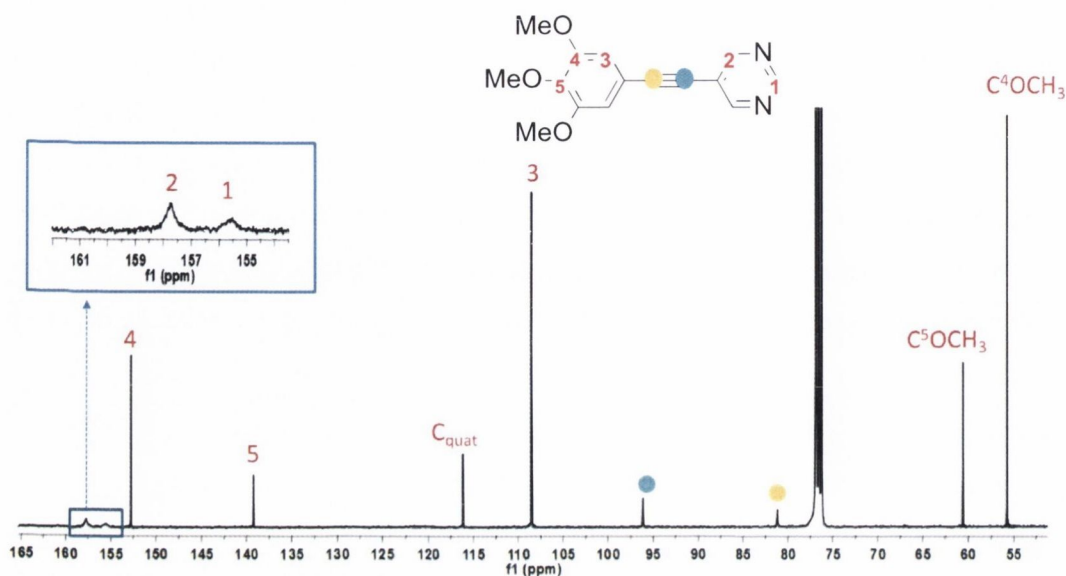


Figure 2.4: ^{13}C NMR spectrum of **72** in CDCl_3 (151 MHz, R.T.). Atom labelling as per inset.

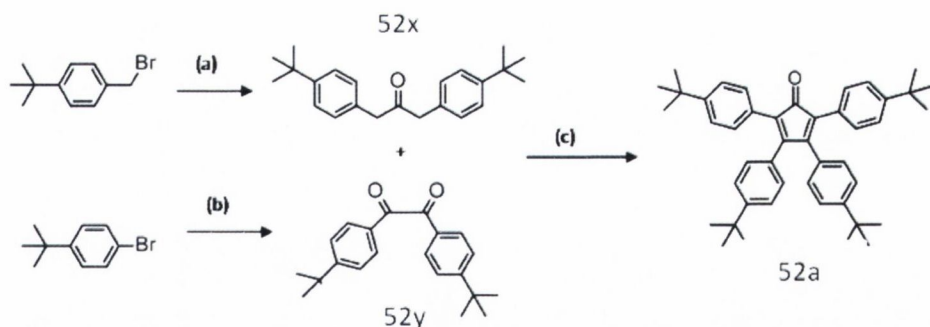
2.2.2 Synthesis of polyphenylenes

The polyphenylene precursors to DASBs were synthesised *via* the [2+4]-Diels-Alder cycloaddition reaction between a suitably functionalised cyclopentadienone and an arylacetylene. The nitrogens atoms were incorporated into the hexaaryl derivatives *via* a monopyrimidyl substituted acetylene unit (Scheme 2.2)



Scheme 2.2: [2+4]-Diels-Alder route to 2N polyphenylene precursors; (a) benzophenone, 280-300 °C, 2hrs, under Ar.

Commercially available tetraphenylcyclopentadienone was used in the synthesis of **76** and **77** (Figure 2.5). *Tert*-butyl functionalised tetraaryl cyclopentadienone (**52a**) was used in the synthesis of **73-75** (Figure 2.5), and required a multi-step synthetic route (Scheme 2.3).



Scheme 2.3: Synthetic route to 2,3,4,5-tetra-(4-tert-butylphenyl) cyclopentadienone (**52a**). (a) $\text{Ca}(\text{OH})_2$, ${}^t\text{Bu}_4\text{N}^+(\text{HSO}_4)^-$, $\text{Fe}(\text{CO})_5$, $\text{CH}_2\text{Cl}_2:\text{H}_2\text{O}$ (1:1 v/v), R.T. (b) (i) $n\text{-BuLi}$, -78°C , THF, (ii) DMPD, (iii) aq. HCl (10 %). (c) KOH, $\text{C}_2\text{H}_5\text{OH}$, 80°C .

The *tert*-butylphenyl substituted monoketone (**52x**), *tert*-butyl substituted diketone (**52y**) and the tetraarylcyclopentadienone (**52a**) have been synthesised previously in the Draper group.³³ The monoketone, 1,3-bis-(4-*tert*-butylphenyl)propan-2-one (**52x**) was prepared *via* a liquid-liquid phase-transfer carbonylation reaction, with $\text{Fe}(\text{CO})_5$ as the source of CO and ${}^t\text{Bu}_4\text{N}^+(\text{HSO}_4)^-$ as phase transfer catalyst. The diketone, 2,5-bis-(4-*tert*-butylphenyl)ethane-1,2-dione (**52y**) was prepared by lithiation of 4-*tert*-butylbromobenzene with $n\text{-BuLi}$ at -78°C in THF, followed by a reaction with DMPD (1,4-dimethylpiperazine-2,3-dione) and subsequent quenching with aq. HCl. The two-fold Knoevenagel condensation between monoketone (**52x**) and diketone (**52y**) in an ethanolic potassium hydroxide solution yielded the 2,3,4,5-tetra-(4-*tert*-butylphenyl) cyclopentadienone (**52a**) as a dark purple crystalline solid, along with the loss of two molecules of water.

Arylacetylenes, (4-*tert*-butylphenyl)(5-pyrimidyl)acetylene (**70**), 5-(2-phenylethynyl)pyrimidine (**71**) and (3,4,5-trimethoxyphenyl)(5-pyrimidyl)acetylene (**72**) were reacted with 2,3,4,5-tetra-(4-*tert*-butylphenyl) cyclopentadienone (**52a**) in Diels-Alder [2+4] cycloadditions to obtain the polyphenylenes, 2,3,4,5,6-penta(4-*tert*-butylphenyl)-1-(5-pyrimidyl) benzene (**73**), 2,3,4,5-tetrakis(4-*tert*-butylphenyl)-6-phenyl-(5-pyrimidyl)-benzene (**74**) and 5-[2,3,4,5-tetrakis(4-*tert*-butylphenyl)-6-(3,4,5-trimethylphenyl)phenyl]pyrimidine (**75**) respectively (Figure 2.5).

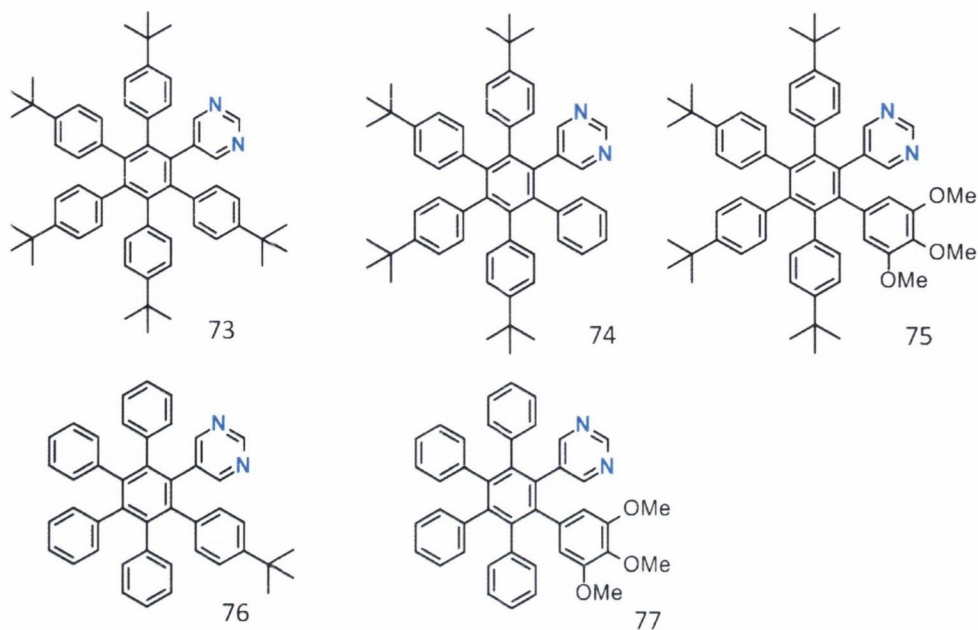


Figure 2.5: The target 2N polyphenylene systems as molecular precursors to DASBs.

Arylacetylenes **70** and **71** were reacted with commercially available tetraphenylcyclopentadienone under Diels-Alder reaction conditions to obtain 2,3,4,5-tetrakis(phenyl)-6-(4-tert-butylphenyl)-1-(5-pyrimidyl)- benzene (**76**) and 2,3,4,5-tetrakis(phenyl)-6-(3,4,5-trimethoxyphenyl)- 1-(5-pyrimidyl)- benzene (**77**) (Figure 2.5). For all of the above reactions a similar synthetic strategy was employed which can be summarised as follows.

The arylacetylene and tetraarylcyclopentadienone was heated to 280-300 °C in a benzophenone melt for approximately 1-2 hrs until the dark purple colouration of the tetraarylcyclopentadienone disappeared completely. The reaction mixture is a dark brown solution at the end of the reaction time. The product was purified using column chromatography on silica, eluting first with CH₂Cl₂ to remove unreacted cyclopentadienone and benzophenone, and then changing to CH₂Cl₂: MeOH to elute the product. The procedure for isolating each of the polyphenylenes is detailed in the experimental section in Chapter 5.

Polyphenylenes **74**, **75**, **76** and **77** were fully characterised using ¹H and ¹³C NMR spectroscopy, infrared spectroscopy and elemental analysis. Polyphenylene **73** had been previously synthesised and NMR spectroscopy and mass spectrometry data were in good agreement with the reported values.¹¹⁰ Compounds **73** and **74** were structurally

characterised by single crystal X-ray diffraction. The photophysical investigation of these polyphenylenes will be discussed in Section 2.2.5.

2.2.3 NMR studies of polyphenylenes 73-77

The ^1H -NMR spectra of the polyphenylenes **73**, **74** and **76** in CDCl_3 , are relatively similar and are shown as overlaid spectra in Figure 2.6.

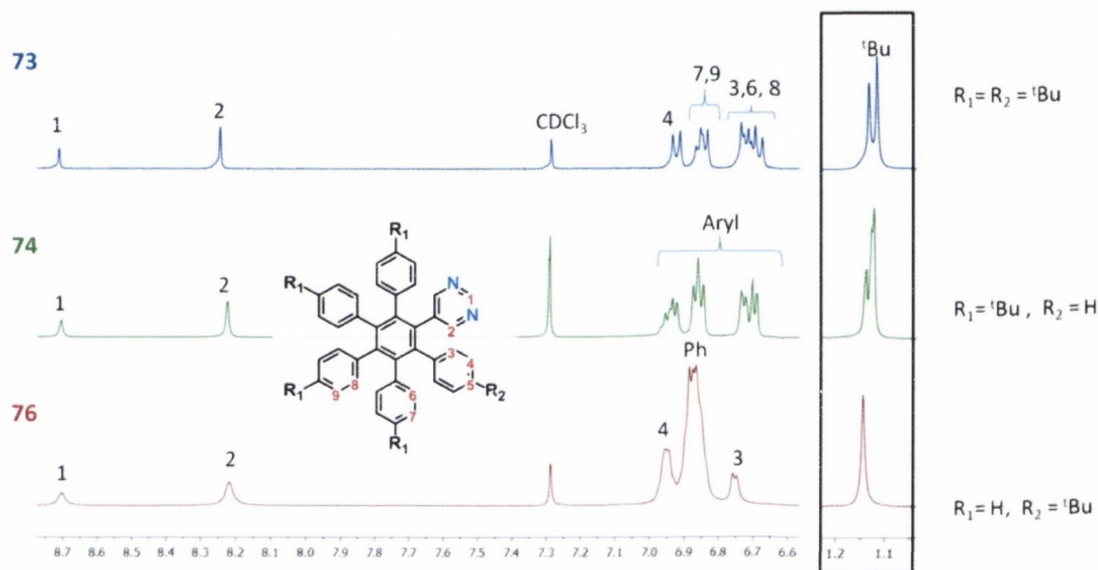


Figure 2.6: ^1H NMR spectra of polyphenylenes **73**, **74** and **76** in CDCl_3 at room temperature (600 MHz) with inset aliphatic region. Atom labelling as per inset figure.

The aromatic region of the spectra consists of two prominent downfield signals which are attributed to the pyrimidyl protons. In all the spectra, a singlet appearing at $\delta = 8.70$ ppm integrates for one proton is assigned to H1, and the singlet at $\delta = 8.20$ ppm integrating for two protons assigned to H2. This trend, followed the pattern observed for the N-doped aryl acetylenes **70-72**, and is comparable with other N-doped polyphenylene precursors.^{33, 60} The pyrimidyl protons are the most deshielded due to the electron withdrawing nature of the nitrogen atoms. The resonances of the phenyl and *tert*-butyl aromatic ring protons appear as a series of overlapping signals in the region between $\delta = 6.97$ -6.65 ppm. Compound **73** has a symmetry axis running through the molecule and this simplified the assignment of the spectrum. The aliphatic region mainly comprises the *tert*-butyl signals, integrating to 45H, 36H and 9H in **73**, **74** and **76** respectively.

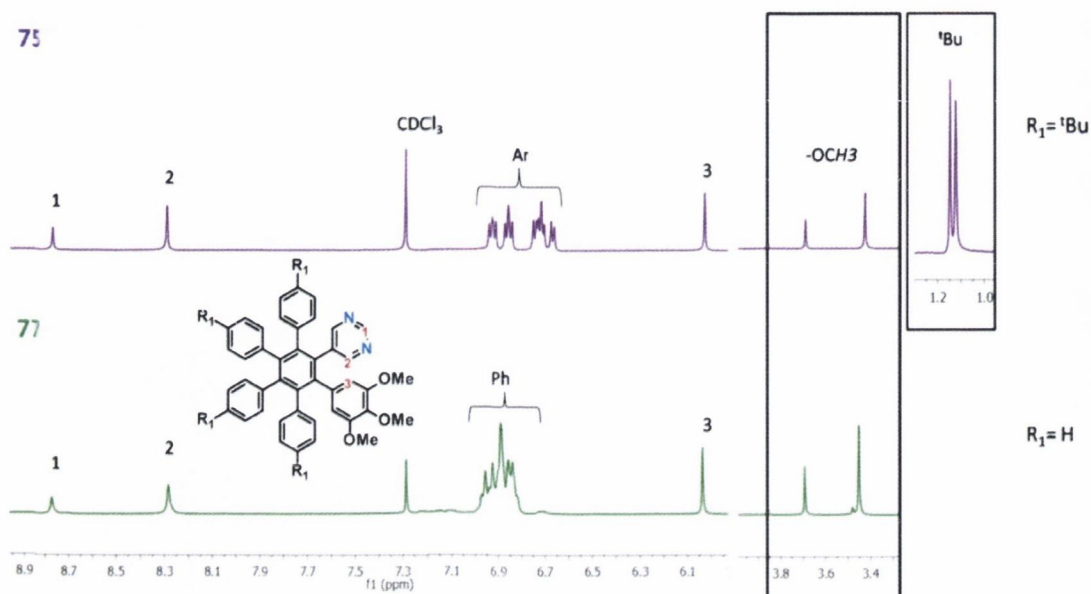


Figure 2.7: ^1H NMR spectra of polyphenylenes **75** and **77** in CDCl_3 at room temperature (600 MHz) with inset aliphatic region. Atom labelling as per inset figure.

A similar pattern was observed in aromatic regions of methoxy functionalised 2N polyphenylenes, **75** and **77** (Figure 2.7), with the most downfield signals attributed to pyrimidyl protons, H1 at $\delta = 8.78$ ppm and H2 at $\delta = 8.37$ ppm. The ^1H -NMR spectra of **77** shows overlapping phenyl proton resonances that appear as a multiplet in the region between $\delta = 7.27$ -7.09 ppm. In comparison, the aromatic region of polyphenylene **75** is considerably more resolved. The assignment of the aromatic signals was problematic in both **75** and **77** due to the overlap of signals and the asymmetry of the compounds. Various 1D and 2D NMR techniques were used to aid the assignment. The prominent singlet at around $\delta = 6$ ppm is attributed to H3 in the methoxy functionalised ring. Since the strategies employed for assignment of all these polyphenylene were similar, in the interest of conciseness, the assignment of ^1H and ^{13}C spectra of compound **75** will be discussed in detail.

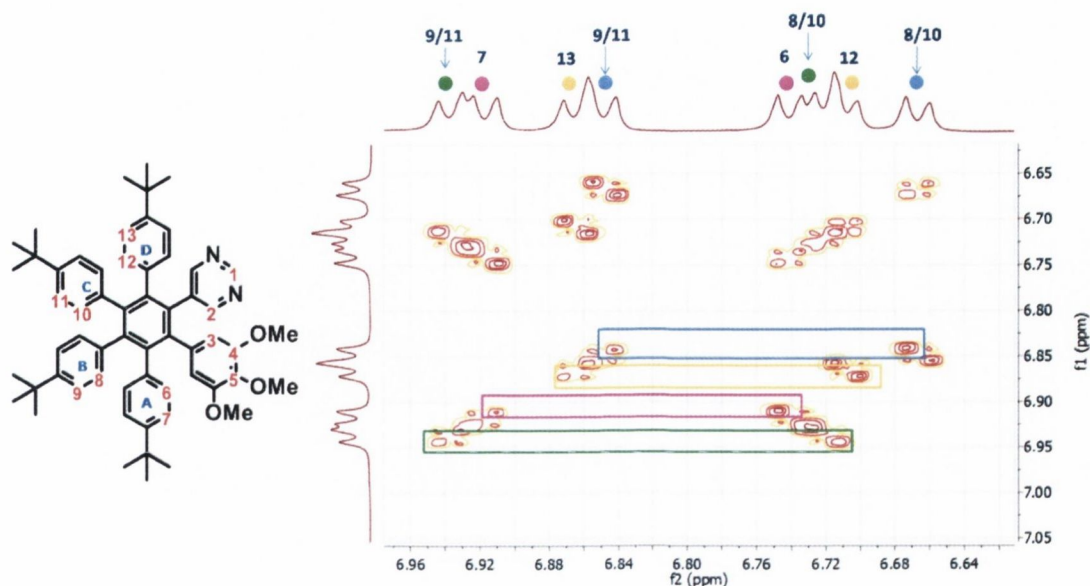


Figure 2.8: Aromatic region of the ^1H - ^1H COSY spectrum of **75** in CDCl_3 , 600 MHz, R.T.

Apart from the pyrimidyl and methoxy functionalised rings, compound **75** consists of four two spin systems, for each *tert*-butyl substituted aromatic ring. The ^1H - ^1H COSY (COrrrelation SpectroscopY) spectrum shows the connection of proton spins through bonds, and was used to identify protons on the same spin system. The aromatic signals in **75** appear as a series of overlapped doublets. Figure 2.8 shows the aromatic region of the ^1H - ^1H COSY spectrum of **75**. Protons within the same spin system were identified during the analysis and are highlighted as coloured rectangles. The NOE (Nuclear Overhauser Effect) spectrum complemented the ^1H - ^1H COSY spectrum in the assignment of these signals (Figure 2.9). NOE is a useful technique in the identification of aromatic signals which are in close proximity to functional groups such as *tert*-butyls. In this method, the selective irradiation of an individual *tert*-butyl resonance gives an NOE enhancement on adjacent spins through space. A series of selective irradiations of resonances at $\delta = 8.78$, 8.29, 6.02 ppm, -OMe and *tert*-butyl signals, were carried out and the responses obtained responses are presented in Table 2.1. Since *tert*-butyl signals at $\delta = 1.15$ and 1.12 ppm are very close to each other, it was difficult to selectively irradiate each signal separately. Each of the *tert*-butyl signals integrate for 18H respectively indicating that two sets of $-\text{C}(\text{CH}_3)_3$ groups are under each peak.

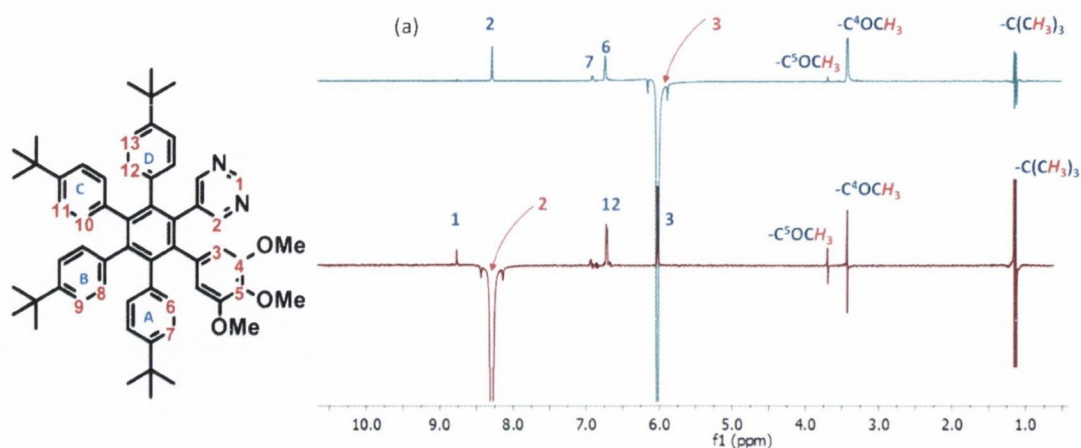
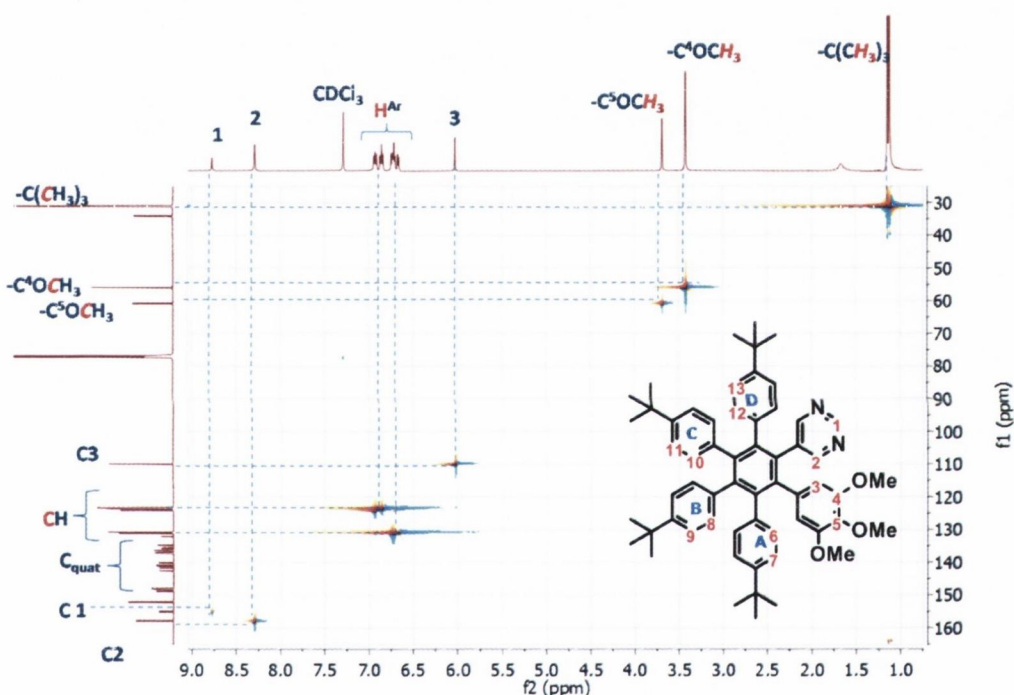


Figure 2.9: NOE spectra of **75** in CDCl_3 on irradiation at (a) $\delta = 6.02$ ppm and (b) $\delta = 8.29$ ppm, 600 MHz, R.T.

Irradiation at $\delta = 8.78$ ppm gave a direct NOE response for the signal at $\delta = 3.42$ ppm and it was identified as C^4OCH_3 group which is the nearest neighbour to H1. When $\delta = 8.22$ ppm was irradiated it correlated to signals at $\delta = 6.02$ ppm (H3) and $\delta = 6.71$ ppm (H12) along with a *tert*-butyl resonance. Since H12 was identified, the ^1H - ^1H COSY spectrum was used to identify its spin-paired partner H13, as the overlapped doublet at $\delta = 6.87$ ppm. Similarly, an NOE response on irradiating at $\delta = 6.02$ ppm along with the ^1H - ^1H COSY spectrum data allowed the assignment of H7 and H6 at $\delta = 6.92$ and $\delta = 6.74$ respectively. Irradiation at $\delta = 3.42$ ppm further confirmed the assignment and allowed the identification of the *tert*-butyl signal of ring A (inset Figure 2.9) at $\delta = 1.15$ ppm. Assignment of rings A and D along with other reported N-doped polyphenylenes^{53, 100} show that in the pendant aryl rings, the inner protons closest to the central phenyl ring are more shielded with respect to the outer protons. Based on these assignments, the protons on rings B and C were tentatively assigned as shown in Figure 2.8. The HSQC (Heteronuclear Single Quantum Coherence) spectrum detects ^{13}C - ^1H correlations, and facilitates the direct assignment of the ^{13}C signals to their attached protons. The HSQC spectrum of **75** is shown in Figure 2.10.

Table 2.1: Selected irradiations and responses of NOE spectra of **75** in CDCl₃ at RT.

Irradiated signal (ppm)	δ (ppm) of response signals
H1 (8.78)	3.42 (C ⁴ OCH ₃), 1.15 and 1.12 (^t Bu)
H2 (8.29)	6.71 (H12), 6.02 (H3), 1.15 and 1.12 (^t Bu)
H3 (6.02)	6.74 (H6), 8.29 (H2), 3.42 (C ⁴ OCH ₃), 6.92 (H7)
C ⁴ OCH ₃ (3.42)	6.02 (H3), 6.74 (H6), 6.92 (H7), 8.29 (H2), 1.15 (Ring A ^t Bu)
C ⁵ OCH ₃ (3.69)	3.42 (C ⁴ OCH ₃), 6.02 (H3)

Figure 2.10: HSQC spectrum of **75** in CDCl₃ at R.T (600 MHz), atom labelling as per inset figure.

DEPT 90 and DEPT 135 spectra complemented the HSQC spectra in the assignment of the ¹³C spectrum of **75**. In a DEPT 90 experiment, only methine (CH) carbons appear as positive signals and quaternary carbons are not observed. In a DEPT 135 spectrum, all methine (CH) and methyl (CH₃) carbons appear in one phase and methylene carbons (CH₂) in the opposite phase. This enables the differentiation of methylene carbons.

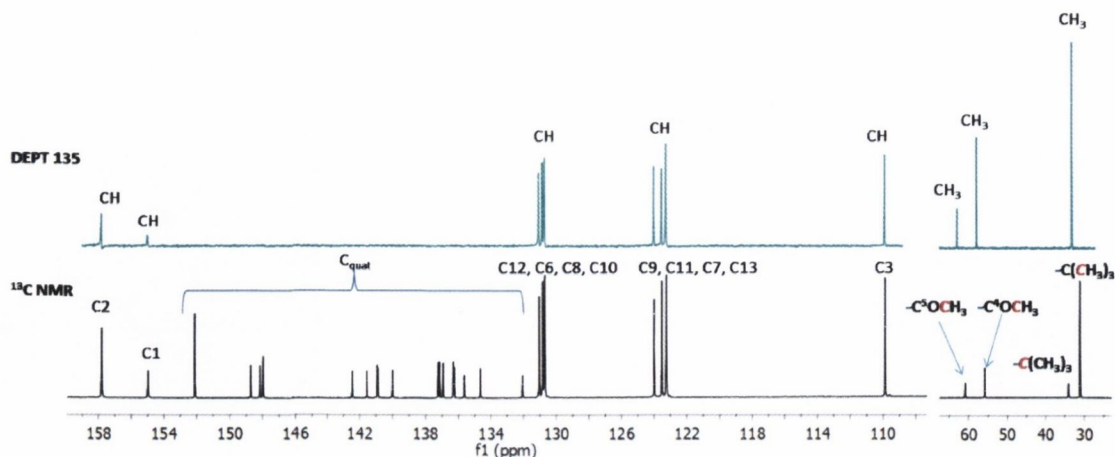


Figure 2.11: DEPT 135 and ^{13}C NMR spectra of **75** in CDCl_3 at room temperature (600 MHz). Atom labelling as per inset in Figure 2.10.

According to DEPT 135 spectrum (Figure 2.11) there are 11 aromatic CH signals and the two most downfield signals at $\delta = 157.8$ and 155.0 ppm are attributable to the pyrimidyl carbons (see HSQC spectrum in Figure 2.10). The four signals in the $\delta = 131.0$ - 130.69 ppm are assigned as the aryl carbons C6, C8, C10 and C12 and the other four signals at $\delta = 124$ - 123.4 ppm are attributed to C7, C9, C11, C13. The remaining CH signal at $\delta = 110$ ppm is assigned to C3. Out of the four signals in the aliphatic region of the ^{13}C NMR spectrum of **75**, the signal at 34.0 ppm is a quaternary carbon and is attributable to $-\text{C}(\text{CH}_3)_3$.

2.2.4 Molecular structure determination of polyphenylenes **73** and **74**

Colourless single crystals of both **73** and **74** suitable for single crystal X ray analysis were obtained by crystallising in a CH_2Cl_2 /methanol solvent system. Compound **73** crystallises in the triclinic, $\overline{\text{P1}}$ space group with four molecules in the unit cell. The asymmetric unit of **73** consist of 2 molecules. Compound **74** crystallises in the monoclinic, $\text{P2}_1/\text{C}$ space group with 4 molecules in the unit cell and a single molecule in the asymmetric unit. Reasonably good quality data were obtained for both **73** and **74** with R values, 9.43 % and 6.28 % respectively.

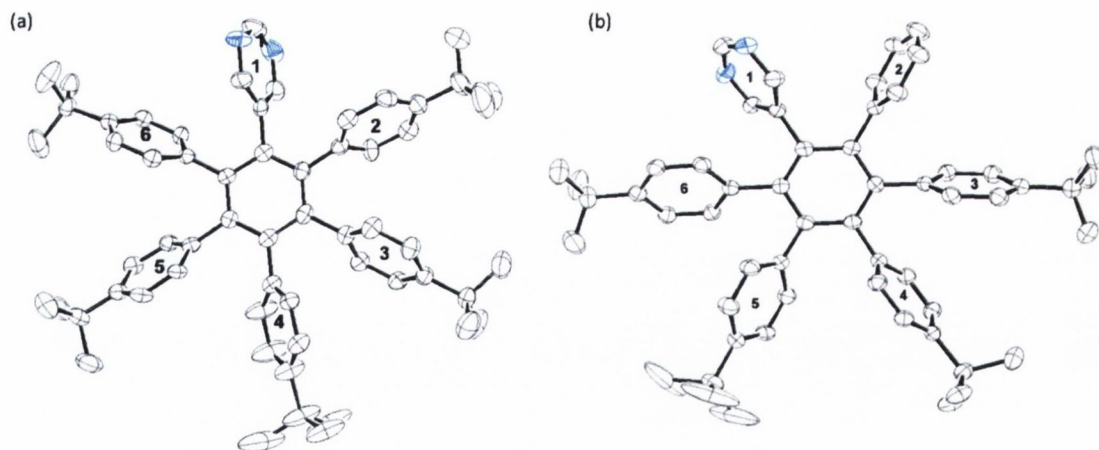


Figure 2.12: ORTEP representations¹¹¹ of the molecular structures of (a) **73** and (b) **74** (hydrogen atoms are omitted for clarity, tert-butyl group diffractions are elongated due to thermal movement).

Both molecules have a propeller-like structure, with the six aryl substituents twisted at angles varying from 60–79° from the plane of the central benzene ring. The outer rings are tilted in order to relieve the steric strain between the aromatic hydrogens. Table 2.2 details the tilt angles between the mean planes of each terminal ring and the central ring. The tilt angles are similar to the values observed for hexaphenylbenzene (approx. 65°)¹¹² and the majority of 4N-doped polyphenylenes synthesised within the Draper group.^{53, 60}

Table 2.2: The tilt angles of the peripheral rings with respect to the central phenyl ring of **73** and **74**. Please refer Figure 2.12 for numbering of rings.

Compound	Ring number and tilt angle w.r.t central ring [°]						Average tilt angle [°]
	1 (py)	2	3	4	5	6	
73	78.94	68.23	60.06	63.10	60.03	66.94	66.21
74	66.58	66.60	64.26	68.11	62.11	56.57	64.04

Interestingly, the pyrimidyl ring in compound **73** is markedly more perpendicular (78.94°) compared to the other aryl rings. This could be due to the fact that both nitrogen atoms on the pyrimidine ring form weak intermolecular hydrogen bonding interactions with the adjacent molecules as depicted in Figure 2.13. This comprises N1···H-C1 (3.361(7) Å) and N2···H-C2 (3.346(8) Å) interactions and is typical of weak aryl hydrogen donor bonds present.¹¹³ A similarly large tilt angle of the pyrimidyl ring (78.3°) was observed in the crystal structure of parent N-HSB polyphenylene (**46**)

where a pyrimidyl ring interdigitates with that of an adjacent molecule giving rise to C-H $\cdots$ π and π - π face-to-face interactions.⁶⁰

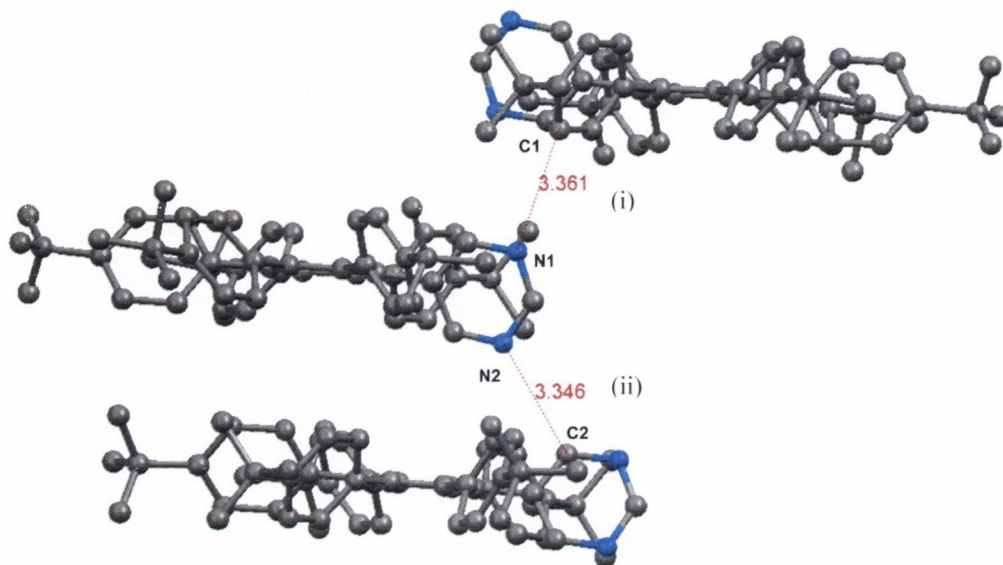


Figure 2.13: Representation of the lattice stabilising interactions in **74** (distances marked in Å) using Mercury program.¹¹⁴ H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (i) $1-x, 2-y, -z$; (ii) $-1+x, y, z$.

Molecules of **74** are mainly connected through N $\cdots$ H-C [3.512(7) Å] intermolecular interactions as illustrated in Figure 2.14. In addition, weak intermolecular C $\cdots$ H interactions contribute to form a self-assembled close packed arrangement. When viewed along the 'c' axis the pyrimidine rings on adjacent molecules tend to be aligned facing one other.

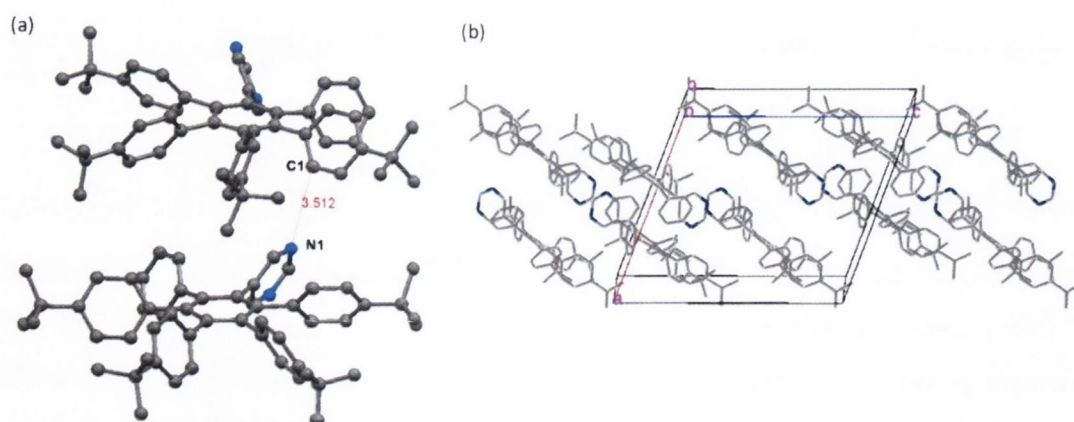


Figure 2.14: (a) Representation of the lattice stabilising interactions in **74**; (b) crystal packing arrangement of **74** along the 'c' axis (distances marked in Å). H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $x, 1.5-y, 1/2+z$.

2.2.5 Photophysical studies of polyphenylenes 73-77

The UV-visible absorption spectra of the 2N polyphenylenes **73-77** are presented in Figure 2.15 with relevant data in Table 2.3. The absorption spectra were recorded in diethylether in order to maximise the UV spectral window.

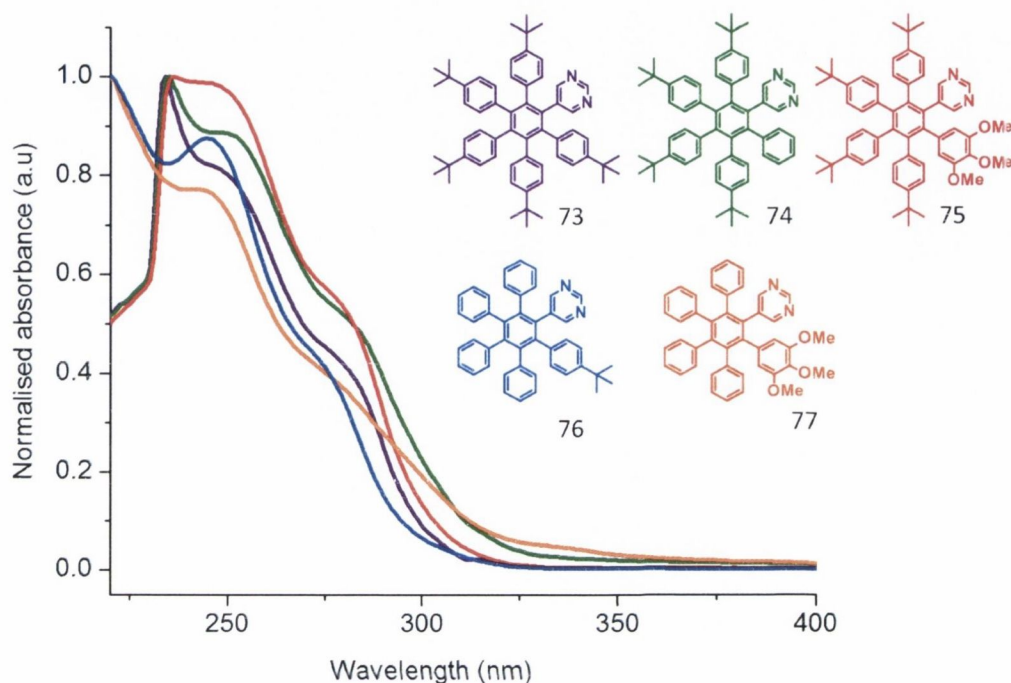


Figure 2.15: The normalised UV-Vis spectra of polyphenylenes **73-77** in diethylether ($\sim 10^{-5} M$).

The absorption spectra of the six 2N doped polyphenylenes **73-77** feature strong bands in the near UV-region of the spectrum. In general, the absorptions are quite broad and unstructured, indicative of the free rotation of the pendent aryl rings. The ground state steric hindrance in these polyphenylenes imposes a non-planar conformation on the chromophore, making the absorption spectra structureless.¹¹⁵ The spectra are similar to those of the 4N polyphenylenes which also show a similar broad structureless absorption in the UV region.^{53, 100}

The absorption spectra of N-doped polyphenylenes (**73-77**) consist of both $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ transitions, however the broad nature of the spectra hinders identification of specific absorption bands. The high molar extinction coefficients of these bands further suggest $\pi\text{-}\pi^*$ nature of the absorption bands which typically display $\epsilon = 10^3 - 10^5 \text{ M}^{-1}\text{cm}^{-1}$. The all-carbon hexaphenylbenzene exhibits an electronic spectrum with an absorption maximum at $\lambda = 246 \text{ nm}$ and a shoulder at $\lambda = 268 \text{ nm}$ while the parent 4N N-HSB

polyphenylene precursor (**46**) has an absorption maximum at $\lambda = 282$ nm in 1,2-dichloroethane.¹⁰⁰ With the incorporation of electron withdrawing nitrogens in to the polyphenylene precursor, a permanent dipole moment is induced along the plane of the molecule. The polar nature of N-doped polyphenylenes results in a red shift in the main absorption bands compared to their all-carbon counterparts. Interestingly, the spectra of 2N polyphenylenes **73-77** combine the features of both hexaphenylbenzenes and 4N polyphenylenes, showing absorption bands around $\lambda = 250$ nm and $\lambda = 280$ nm (Table 2.3). Furthermore, for compounds **76** and **77** a higher energy band around $\lambda = 210$ nm is visible, which coincides with the solvent cut-off.

Table 2.3: The absorption maxima observed in the UV-Vis absorption spectra of **73-77** in diethylether.

Compound	λ_{max} [nm] ($\epsilon \times 10^4$ [$\text{M}^{-1} \text{cm}^{-1}$])
73	233 (8.8), 250 (7.1), 280 (3.7)
74	236 (10.3), 248 (9.0), 280 (4.5)
75	234 (9.1), 250 (8.0), 284 (4.4)
76	245 (8.8), 275 (3.0)
77	245 (8.0), 280 (2.0)

The permanent dipole moment on N-doped polyphenylenes can be varied by changing the substituents on the peripheral aryl rings. Upon substitution, the dipole moment of the ground state and/or first excited state is changed and thus alters the spectroscopic characteristics. The position of electron donating methoxy substituents has significant effect on the dipole moment of the molecules. When methoxy groups are substituted *para* with respect to the pyrimidyl rings the absorption spectra shows a greater bathochromic shift than their *ortho* substituted counterparts.⁵³ As expected, methoxy functionalisation of polyphenylenes **75** and **77** at the *ortho* position did not affect the absorption spectra significantly.

The overlaid luminescence spectra of polyphenylenes **73-77** in diethyl ether are shown in Figure 2.16. The variation in substituents shows a more profound trend in the emission profile in comparison with the absorption profile. The methoxy substituted polyphenylenes **75** and **77** undergo a more significant bathochromic shift in their emission spectra with $\lambda_{\text{max}}^{\text{em}}$ at 395 nm and 408 nm respectively.

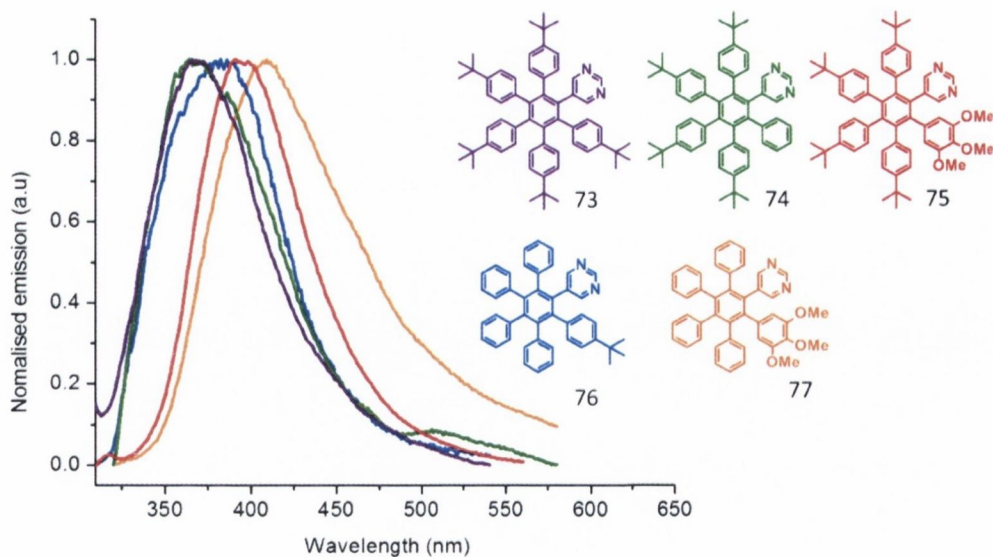


Figure 2.16: The normalised emission spectra of polyphenylenes 73-77 in diethylether ($\sim 10^{-5}M$) at $\lambda_{exc} = 300\text{ nm}$ at R.T.

This trend has also been observed in other 4N methoxy substituted polyphenylenes synthesised within the group.⁵³ Joshi *et al.* reported a 3,8-substituted derivative of 1,10-phenanthroline with electron donating methoxy groups which showed similar red shifted emission. Therefore, the energy gap between the n and π^* orbital transition is decreased and results in red shifted spectra. The emission state of these polyphenylenes could be a combination of both π, π^* and n, π^* states. In order to further investigate the nature of the excited state, solvent dependency and protonation studies were carried out.

Table 2.4: The emission maxima observed in the emission spectra of 73-77 in diethylether ($\sim 10^{-5}M$) at R.T.

Compound	λ_{em} [nm] (λ_{exc} [nm])
73	366 (300)
74	366 (300)
75	395 (300)
76	382 (300)
77	408 (300)

2.2.5.1 Solvent dependency studies of absorption spectra of polyphenylenes

The UV-Vis absorption spectra for all the polyphenylene compounds were recorded in three solvent systems of increasing polarity, however for the sake of brevity, polyphenylenes 73 and 75 will be discussed.

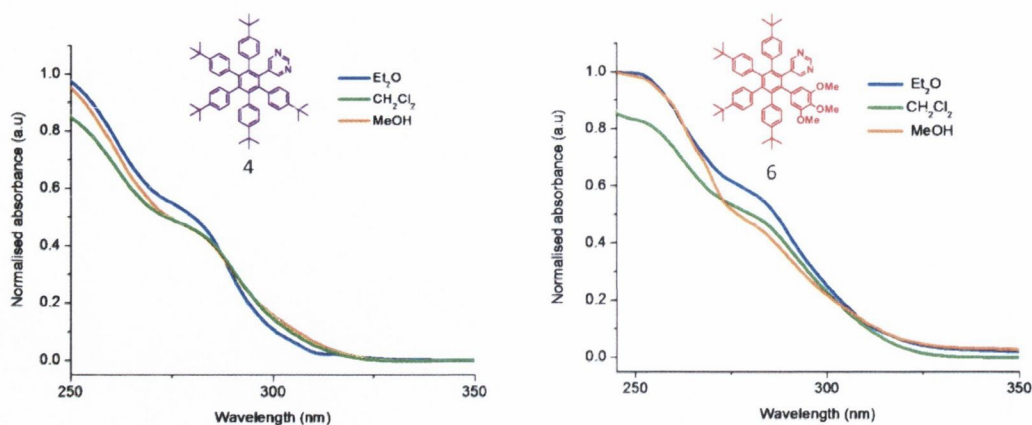


Figure 2.17: Solvent dependency UV-Vis absorption spectra; (a) **73** (b) **75** ($\sim 10^{-5}$ M).

The UV-Vis absorption spectra of **73** and **75** show marginal shifts with changes in solvent polarity (Figure 2.17). It indicates that the ground state molecule is rather insensitive to nature of the solvent. According to the Frank-Condon principle, electronic absorption occurs so fast (less than 10^{-15} s) that there is no time for molecular motion during the absorption process and only the solvent molecules directly adjacent to the absorbing species can affect the absorption spectrum.¹¹⁶

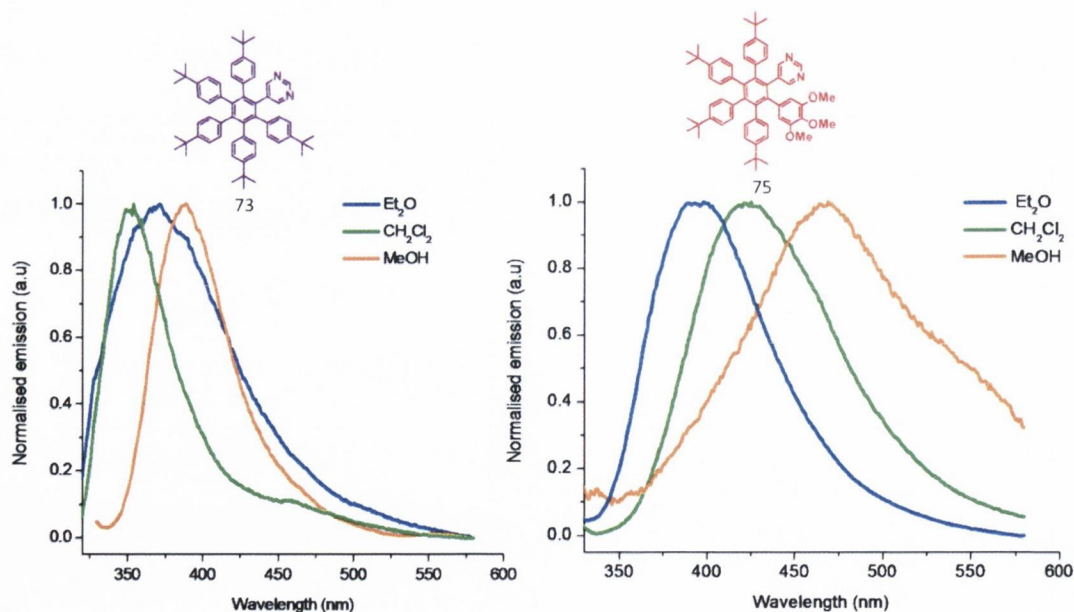


Figure 2.18: Solvent dependency emission studies; (a) **73** (b) **75** ($\sim 10^{-5}$ M), RT, $\lambda_{exc}=300\text{nm}$

In contrast, the emission spectra of both **73** and **75** show a relatively pronounced shift of their $\lambda_{\text{max}}^{\text{em}}$ with changes in solvent polarity, indicating that the excited state is relatively more susceptible to changes in solvent polarity than the ground state (Figure 2.18). The

red-shift observed in high polarity solvents is indicative of the greater stabilisation of the excited state by solvent molecules.¹¹⁷ In comparison with absorption, emission occurs over a longer period of time (fluorescence $\sim 10^{-7} \times 10^{-9}$ s) and provides the opportunity for the excited state molecules to interact with solvent molecules.¹¹⁶ In particular, **75** shows a significant bathochromic shift of $\lambda_{\text{max}}^{\text{em}}$ of approximately 3950 cm^{-1} , in going from diethylether to methanol. This trend occurs in polar molecules that are likely to have enlarged dipoles and charge-transfer character in their excited state.¹¹⁸ Furthermore, the solvent dependency studies suggest that the emissive excited state of both **73** and **75** has π - π^* character as it is red shifted with increasing solvent polarity.

2.2.5.2 Protonation studies of polyphenylene (**73**)

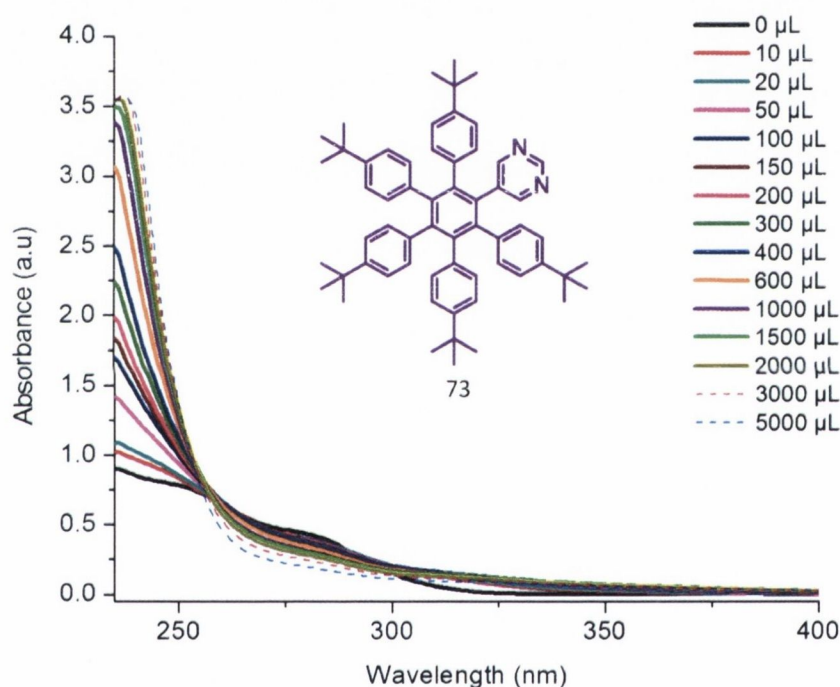


Figure 2.19: UV-Vis absorption spectral changes of **73** ($1 \times 10^{-5} \text{ M}$) upon sequential addition of 0.1 M trifluoroacetic acid in CH_2Cl_2 .

The UV-Vis absorption spectra of **73** upon sequential addition of trifluoroacetic acid in CH_2Cl_2 is shown in Figure 2.19. Compound **73** shows a broad absorption in the UV-Vis region with the main bands at $\lambda = 253 \text{ nm}$ and $\lambda = 283 \text{ nm}$ in CH_2Cl_2 . The band at $\lambda = 283 \text{ nm}$ is promptly quenched upon addition of the acid, with a new band of lower energy forming around $\lambda = 325 \text{ nm}$. This suggest that the absorption band at $\lambda = 283 \text{ nm}$ has a significant n - π^* contribution as it decreases in intensity upon addition of acid. Two isobestic points are evident at $\lambda = 258 \text{ nm}$ and 300 nm , indicating an equilibrium

between the neutral and newly formed protonated species. Furthermore, increasing the additions of acid (eg. 3000-5000 μL shown in dotted line in Figure 2.19 causes these isobestic points to be perturbed, which is attributed to solvent effects caused by a change in solvent polarity on acid addition, or the possible emergence of a doubly protonated species. A similar decrease in absorption bands at $\lambda = 280\text{ nm}$ and $\lambda = 303\text{ nm}$ has been reported for a phenanthroline based polyphenylene synthesised in the group. The latter were attributed to transitions with $n\text{-}\pi^*$ character.⁵³

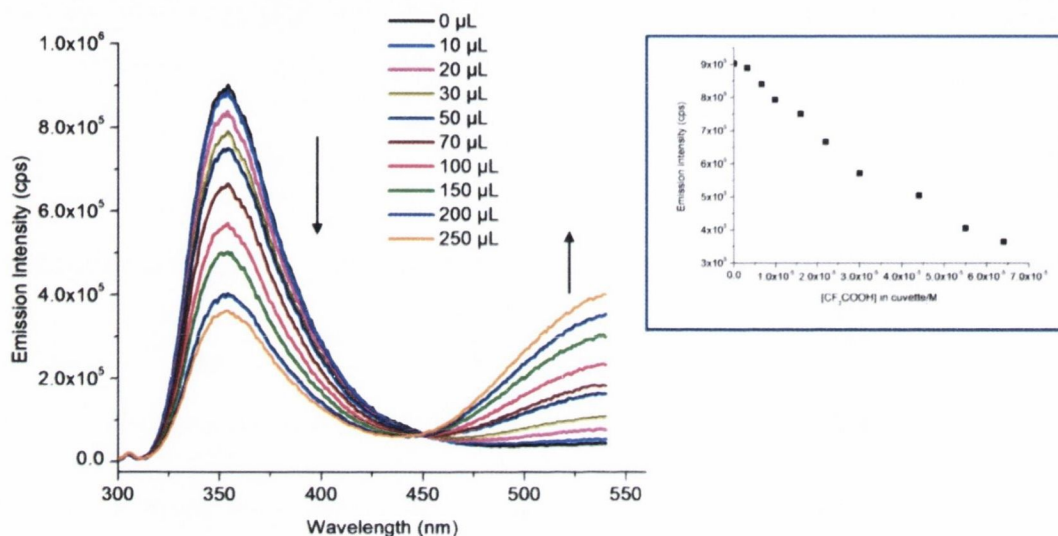
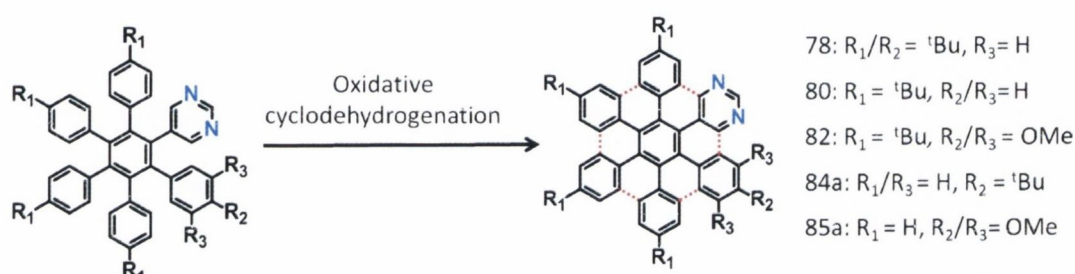


Figure 2.20: Emission spectral changes of **73** ($1 \times 10^{-5}\text{ M}$) upon sequential addition of ($1 \times 10^{-3}\text{ M}$) trifluoroacetic acid in CH_2Cl_2 at room temperature ($\lambda_{\text{exc}} = 280\text{ nm}$). Inset shows the change in intensity observed at $\lambda_{\text{max}} = 354\text{ nm}$ with increasing acid in the cuvette.

The corresponding emission acid addition studies of **73** in CH_2Cl_2 shows gradual quenching of the emission maximum at $\lambda = 354\text{ nm}$ upon sequential addition of trifluoroacetic acid ($1 \times 10^{-3}\text{ M}$) aliquots, and a new band around $\lambda = 540\text{ nm}$ arising from the protonated form. An isoemissive point is formed at $\lambda = 450\text{ nm}$, indicating an equilibrium between neutral and newly formed protonated species. The newly formed band is dramatically red shifted with respect to the emission maxima of the neutral species i.e. 9730.1 cm^{-1} .

2.3 Oxidative cyclodehydrogenation

Intramolecular oxidative cyclodehydrogenation is the key synthetic step in obtaining planarised N-doped molecular graphenes *via* polyphenylene precursors (Scheme 2.4). In comparison with all carbon systems, the Scholl reaction of N-doped systems is far more synthetically challenging as it results a mixture of compounds with varying degrees of aromaticity.^{53, 54} With the objective to prepare a series of 2N-doped heterosuperbenzenes and subsequently investigate their chemical, physical and supramolecular properties, we investigated the intramolecular Scholl reaction of polyphenylene precursors **73-77**.



Scheme 2.4: Intramolecular Scholl reaction.

The mechanistic details regarding the oxidative cyclodehydrogenation of polyphenylenes were discussed broadly in Chapter 1. In this study, two synthetic routes were explored for the oxidative cyclodehydrogenation of 2N polyphenylenes; (i) the FeCl_3 route and (ii) dichlorodi-cyano-p-benzoquinone (DDQ)/ acid route. The FeCl_3 /nitromethane/ CH_2Cl_2 system was first employed by Müllen and co-workers for the successful oxidative cyclodehydrogenation of hexa-*tert*-butyl functionalised hexaphenylbenzenes to obtain hexa-*tert*-butyl HBC.³⁹ This synthetic breakthrough led to the synthesis of HBC under milder conditions in an efficient manner. Using FeCl_3 as both a mild Lewis acid and an oxidising agent renders the addition of an auxiliary oxidant unnecessary. In addition, the milder reaction conditions improve functional group tolerance. This route has been used for the successful synthesis of PAHs of various topologies and sizes.¹⁵

Recently, DDQ/ H^+ oxidation system has been explored as a metal free alternative route for the oxidative cyclodehydrogenation of various aromatic donors.^{86, 119, 120} Rathore and co-worker have pioneered work in this area and have successfully synthesised a number of substituted triphenylenes and hexa-peri-hexabenzocoronenes under these

mild conditions.^{86, 97} These findings show that the DDQ/H⁺ oxidation system can oxidize a variety of aromatic donors (D) with oxidation potential as high as ~1.7 V vs. SCE, to the corresponding cation radicals. In addition, only 1 equivalent of DDQ per C-C bond formation is needed for the completion of Scholl reaction and avoids the use of excess catalyst as in the FeCl₃ route.

Wong and co-workers have successfully used this DDQ approach for the oxidative cyclodehydrogenation of electron-poor arenes with bromo and fluoro substituents which previously were not tolerated by the FeCl₃ route.¹¹⁹ Furthermore, the FeCl₃ route leads to contamination of products by chlorination, and generates undesirable iron residues. For N-doped systems, the bipyrimidine type coordination sites (i.e. N-HSB) leads to the formation of unwanted iron complexes. The DDQ route overcomes many of these problems and the reduced catalyst (DDQ-H₂) can be readily recycled to DDQ by oxidation with nitric acid. To date, the DDQ/acid method has not been tested for N-doped systems and this work aims to investigate this route as an alternant for the cyclodehydrogenation of N-doped polyphenylenes.

The peripheral substituents play a key role in the oxidative cyclodehydrogenation of the polyphenylene precursors. Electron donating substituent groups such as methoxy groups both direct and promote C-C bond formation under Scholl reaction conditions. However, the positioning of the methoxy substituents play a key role in determining the outcome of the final product. Dou *et al.* report the oxidative cyclodehydrogenation of *para*-dimethoxy hexaphenylbenzene under FeCl₃ in CH₂Cl₂ conditions which results *meta*-dimethoxy-substituted HBC (**101**) (20%), accompanied by bis-spirocyclic dienone (**102**) (70%) rather than the expected *p*-dimethoxy-substituted HBC (**103**) [Figure 2.21(a)].⁹⁰ A similar phenomenon has also been reported by Gregg *et al.* for the oxidative cyclodehydrogenation 4N doped polyphenylene precursor with *para* methoxy phenyl rings.⁶⁰

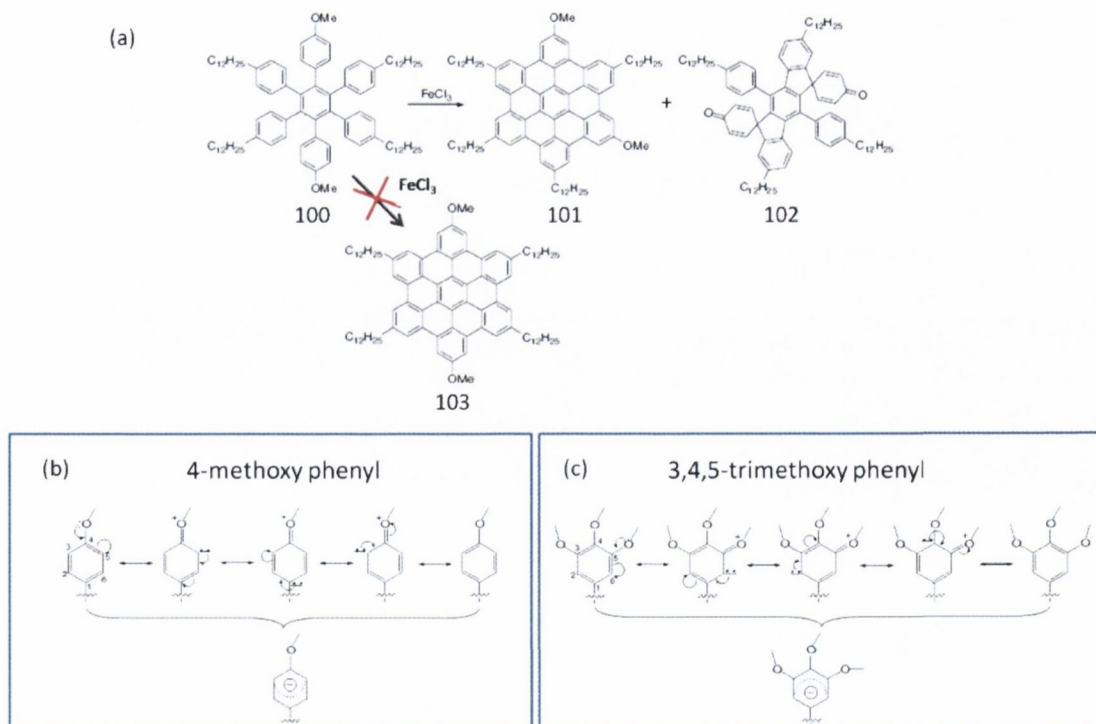


Figure 2.21: (a) Cyclodehydrogenation *para*-dimethoxy substituted hexaphenylbenzene (**100**) to give unexpected *meta*-dimethoxy substituted (**101**) and bis-spirocyclic dienone (**102**).⁹⁰ Inset (b) shows the resonance structure of 4-methoxyphenyl showing activation at 1st, 3rd and 5th positions, (c) shows the resonance structure of 3,4,5-trimethoxyphenyl showing activation mainly at the 2nd and 6th positions.

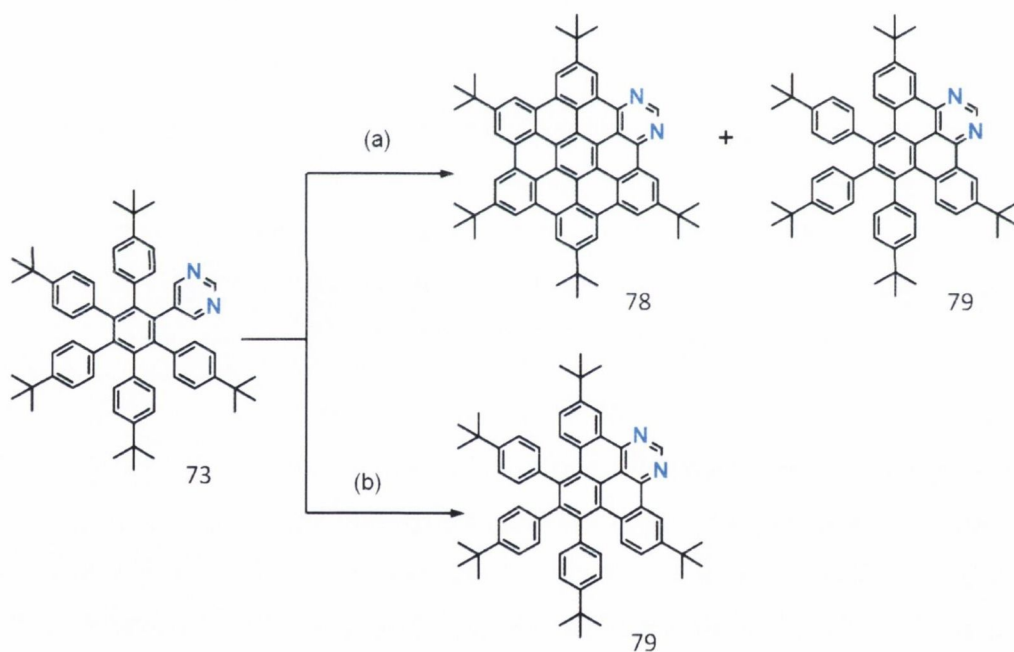
In the presence of Lewis acids the *para*-methoxy polyphenylene precursor appears to have undergone ether cleavage, oxidation to quinonoid structures and subsequent C-C bond formation between phenyl rings. In 4-methoxyphenyl, both *ortho* (3rd and 5th)- or *para* (1st)-positions would be activated through resonance stabilization as shown in inset (b) Figure 2.21. Therefore, even though 4-methoxyphenyl is a good nucleophile, the activation at incorrect sites and subsequent C-C bond formation gives rise to undesired spirocyclic compounds. In this work, in order to avoid formation of the bis-spirocyclic dienone product, 3,4,5-trimethoxyphenyl rings were strategically employed in both 2N polyphenylene precursors **75** and **77**. In 3,4,5-trimethoxyphenyl systems the *meta* (2nd and 6th positions) and the *para* (4th position) positions are activated during the reaction as shown in Figure 2.21 inset (c). The dimethoxy groups at 3rd and 5th positions has a greater influence in activating positions 2 and 6 compared to 4 and facilitates in obtaining the desired product.

2.4 Synthesis of DASB derivatives

Oxidative cyclodehydrogenation of polyphenylene **73-77** were attempted using both $\text{FeCl}_3/\text{CH}_2\text{Cl}_2/\text{CH}_3\text{NO}_2$ and/or DDQ/H^+ route. Firstly the synthesis of DASB derivatives will be discussed followed by characterisation of the compounds in Section 2.5.

2.4.1 Cyclodehydrogenation of **73**

Oxidative cyclodehydrogenation of **73** was attempted *via* both routes discussed above (Scheme 2.5). In the first route, FeCl_3 dissolved CH_3NO_2 was added dropwise into a solution of **73** in CH_2Cl_2 . The reaction mixture was left stirring for 24 hr with a stream of nitrogen bubbling through the solution. After work up, the preliminary mass spectral analysis of the crude material indicated the presence of a mixture of products, showing mainly the presence of the fully-fused product (six C-C bonds formed) **78** and $\frac{1}{3}^{\text{rd}}$ fused ($\frac{1}{3}^{\text{rd}}$ fused (two C-C bonds formed) **79**.



*Scheme 2.5: Cyclodehydrogenation of **73**. (a) FeCl_3 (30 eq.), CH_3NO_2 , CH_2Cl_2 , 298 K, Ar bubbling, 24 h, **78**: 20 %; **79**: 49 % (b) DDQ (2.5 eq.), MeSO_3H , CH_2Cl_2 , 0 °C, **79**: 80 %.*

The products were purified by column chromatography using a CH_2Cl_2 as the eluent to isolate **79**. The polarity of the eluent was increased using $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ (10:0.2) to elute **78**. Removal of solvents from the fractions gave **78** as a yellow precipitate in 20 % yield along with the $\frac{1}{3}^{\text{rd}}$ fused **79** as a white precipitate in 49 % yield. Both mass and

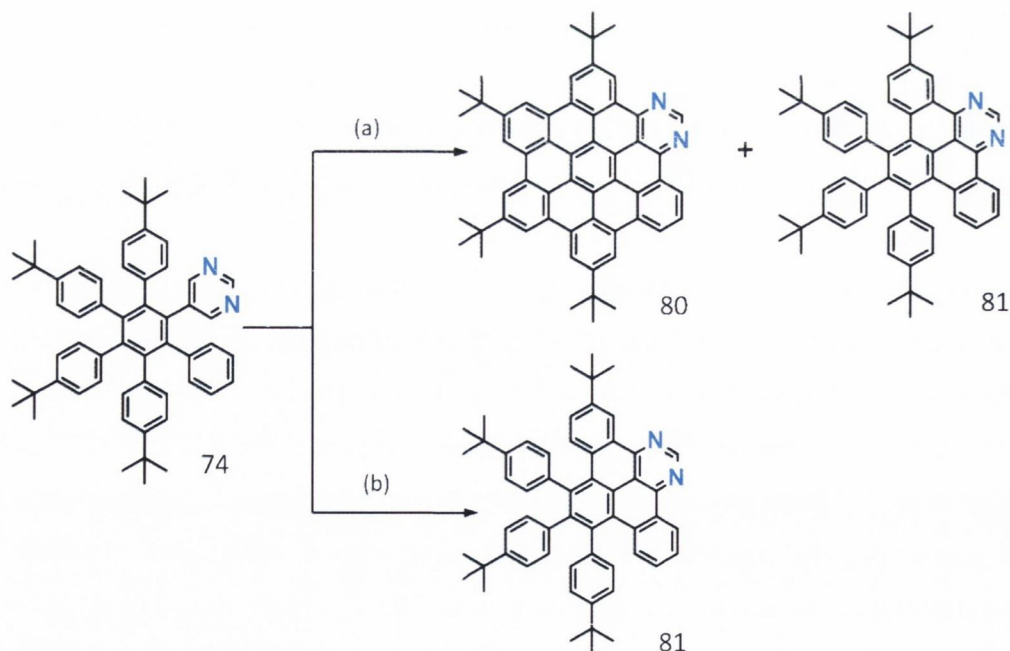
NMR analysis of **79** were in agreement with the reported values¹¹⁰ and the characterisation of novel compound **78** will be discussed in detail in Section 2.5.

The oxidative cyclodehydrogenation of **73** has also been attempted by Gourdon and co-workers using both $\text{AlCl}_3/\text{CuCl}_2/\text{CS}_2$ and $\text{FeCl}_3/\text{CH}_3\text{NO}_2/\text{CH}_2\text{Cl}_2$ conditions.¹¹⁰ The use of $\text{AlCl}_3/\text{CuCl}_2$ system resulted in a range of insoluble products which were identified as a mixture of polychlorinated products by mass spectrometry analysis. Under FeCl_3 conditions, using comparable equivalents of FeCl_3 they have reported only the isolation of the $\frac{1}{3}^{\text{rd}}$ N-HSB (**79**) in 85 % yield with the formation of C-C bonds in the *ortho* position with respect to the pyrimidine nitrogens. No photophysical study of any of the products has been reported by Gourdon and co-workers. The reasons for the differences in results obtained are as yet unknown. Compared to the all-carbon analogues, the oxidative cyclodehydrogenation of N-doped polyphenylenes is far more challenging and is very sensitive to the reaction conditions employed, i.e., strictly inert conditions, anhydrous FeCl_3 and freshly distilled CH_2Cl_2 .

As discussed above, Rathore and co workers report that 1 equivalent of DDQ is sufficient for 1 C-C bond closure.⁸⁶ Polyphenylene **73** was dissolved in CH_2Cl_2 followed by dropwise addition of methanesulfonic acid (Scheme 2.5). The reaction mixture rapidly changed colour to a bright orange upon addition of the acid and was cooled at 0 °C for 15 min. DDQ (2.5 eq) dissolved in CH_2Cl_2 was added to the reaction mixture and the reaction was stirred for further 90 min at 0 °C. The reaction mixture gradually changed colour to a dark purple colour. Subsequent quenching and work up of the reaction evaporation of solvent afforded **79** as a white precipitate in 80 % yield. The NMR analysis (discussed in Section 2.5.4) shows that the two C-C bond closure has taken place at the *ortho* position to the pyrimidine nitrogens in the DDQ/ H^+ route, and is similar to the $\frac{1}{3}^{\text{rd}}$ fused product obtained in the FeCl_3 route. Since the initial test reaction was successful, the reaction was repeated using excess equivalents of DDQ (10 equivalents) with the aim of obtaining fully-fused **78**. The same procedure as discussed above was followed, however the reaction only resulted the $\frac{1}{3}^{\text{rd}}$ fused **79** in 82 % yield. Therefore, these results show that despite the use of excess DDQ, the reaction does not proceed to complete ring closure for 2N doped polyphenylene **73**.

2.4.2 Cyclodehydrogenation of 74

A similar synthetic approach was employed for the oxidative cyclodehydrogenation of **74** (Scheme 2.6). In the first route, FeCl_3 dissolved in CH_3NO_2 was added dropwise into a solution of **74** in CH_2Cl_2 and was stirred for 24 h with nitrogen bubbling. A similar work up as for **73** was followed upon quenching with methanol. Column chromatography was attempted using CH_2Cl_2 as the eluent, however a successful separation of the products was not observed. Therefore, preparative plate chromatography was employed. A toluene:methanol (100:0.5) solvent system resulted in a good separation on the preparative plate, giving two prominent bands, an orange band close to the baseline and a yellow band above it. However, several other bands were also observed in the preparative plate indicating the presence of other partially fused by-products. Careful extraction and subsequent drying of the orange band yielded the fully-fused product (six C-C bonds closed) **80** as a dark yellow solid (15 %) and the yellow band yielded the $\frac{1}{3}^{\text{rd}}$ -fused product (two C-C bonds closed) **81** as a yellow solid (40 %). The detailed characterisation of novel compounds **80** and **81** will be discussed in Section 2.5.

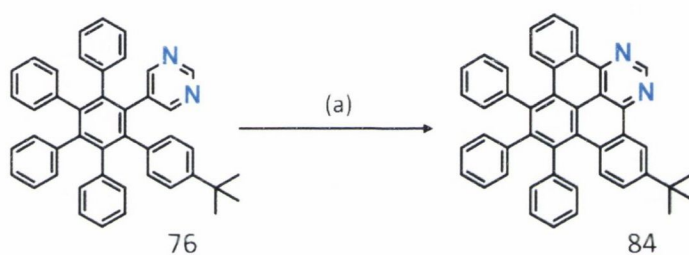


*Scheme 2.6: Cyclodehydrogenation of 74. (a) FeCl_3 (30 eq.), CH_3NO_2 , CH_2Cl_2 , 298 K, Ar bubbling, 24 h, **80**: 15 % ; **81**: 40 % (b) DDQ (10 eq.), MeSO_3H , CH_2Cl_2 , 0 °C, **81**: 62 %.*

The DDQ/H⁺ route was also explored using the same procedure as that adopted for **73** with 10 eq of DDQ. Subsequent workup resulted in only the 1/3rd fused product **81** as an off white solid in 62 % yield. The position of the ring closure was confirmed by NMR analysis (see Section 2.5.4) and shows that the two C-C bond closures has taken place at *ortho*-position with respect to the pyrimidine ring. Interestingly, this is similar to the trend observed for **73**, indicating that 1/3rd fused product is favoured in the DDQ/H⁺ route for 2N systems.

2.4.3 Cyclodehydrogenation of **76**

Polyphenylene **76** was synthesised using commercially available tetraphenylcyclopentadienone with the aim of reducing the multistep synthesis to obtain DASB derivatives. The cyclodehydrogenation of **76** was attempted using FeCl₃ as the oxidant (Scheme 2.7).



Scheme 2.7: Cyclodehydrogenation of **76** (a) FeCl₃ (30 eq.), CH₃NO₂, CH₂Cl₂, 298 K, Ar bubbling, 24 h, **84**: 78 %.

The reaction mixture turned green upon initial addition of FeCl₃ in nitromethane. The reaction was stirred for 24 h and was subsequently quenched by the addition of methanol. The reaction mixture was reduced *in vacuo* and resulted in an off white precipitate. The precipitate was filtered and washed with cold methanol. ESI mass spectral analysis (Section 2.5) showed the presence of 1/3rd fused product with NMR analysis confirmed the isolation of **84** as the only product with two C-C bond closure at *ortho*-position to the pyrimidine ring (Section 2.5.4). In addition, single crystal X-ray structure of **84** was also obtained which further confirmed the structure (Section 2.5.4.2).

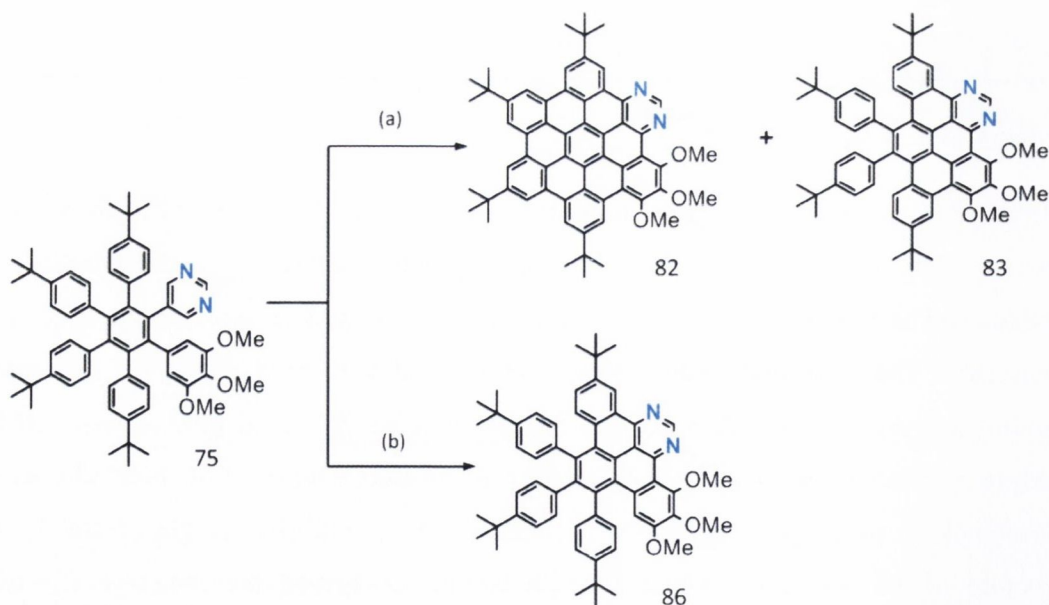
Despite careful analysis of the mass spectra of the crude material, even traces of the fully-fused system could not be detected. It is interesting to note the effect of electron donating *tert*-butyl groups on the ring closure of the N-doped systems. Incorporation of bulky *tert*-butyl groups improves the solubility of the fused products drastically. In

addition, it facilitates the oxidative cyclodehydrogenation by increasing the electron density of substituted rings making the electrophilic attack by the protonated nitrogens more feasible to form C-C bonds. Therefore, in comparison with *tert*-butyl vs unsubstituted phenyl rings the *tert*-butyl functionalised rings are more likely to undergo electrophilic attack leading to C-C bond formation. A similar phenomenon has also been reported by Gourdon *et al.* for 2N systems developed with unsubstituted phenyl rings and the major product isolated was 1/3rd fused system.¹¹⁰ They believe that the presence of unsubstituted phenyl groups in *para*-position to the central benzene could favour oligomerization. Furthermore, they report that the complexation of Lewis acid to the pyrimidyl nitrogen, would also favour the polymerization and the chlorination.

2.4.4 Cyclodehydrogenation of methoxy polyphenylenes 75 and 77

2.4.4.1 Cyclodehydrogenation of 75

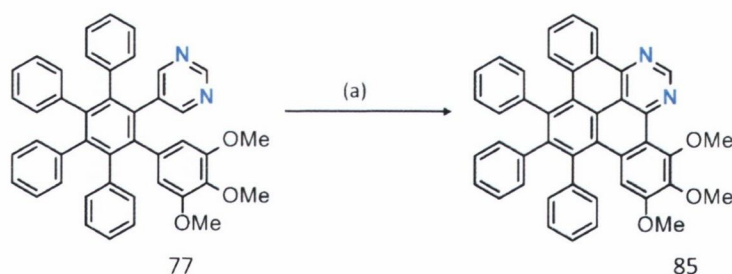
Oxidative cyclodehydrogenation of **75** was attempted using both methods as discussed previously. FeCl₃-mediated oxidative cyclodehydrogenation of **75** resulted in two main products: fully-fused (six C-C bonds closed) **82** and its half-fused daughter (three C-C bonds closed) **83** (Scheme 2.8).



*Scheme 2.8: Cyclodehydrogenation of 75. (a) FeCl₃ (30 eq.), CH₃NO₂, CH₂Cl₂, 298 K, Ar bubbling, 24 h; **82**: 40 % and **83**: 20 % (b) DDQ (10 eq.), MeSO₃H, CH₂Cl₂, 0 °C; **86**: 50 %.*

Both compounds were isolated using preparative plate chromatography, using CH_2Cl_2 as the eluent. After separation the preparative plate showed two prominent bands, a dark orange band close to the baseline and a yellow band above it under UV irradiation. Extraction and subsequent drying of the orange band yielded the fully-fused product **82** as a dark yellow solid (40 %). The yellow band corresponded to the half-fused product **83** a yellow solid (20 %). Separation *via* column chromatography (SiO_2) was also attempted using $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ as the eluent, however, it was not as successful as the preparative plate method.

The ESI mass spectral analysis confirmed the presence of both **82** and **83** with isotopic distribution patterns matching with the theoretical values (Section 2.5). NMR analysis of **83** confirmed the positions of C-C bond closure has taken place at *ortho* position to the pyrimidine ring (see Section 2.5.3). The single crystal X-ray structure of **82** was also obtained and will be discussed in Section 2.5.2. Furthermore, in comparison with non methoxy systems, there is an increase in the yield of the fully-fused product upon incorporation of the methoxy substituents. It is evident that electron donating methoxy groups also facilitates oxidative cyclodehydrogenation in these N-doped systems as in their all carbon analogues.¹²¹



Scheme 2.9: Cyclodehydrogenation of 77. (a) FeCl_3 (30 eq.), CH_3NO_2 , CH_2Cl_2 , 298 K, Ar bubbling, 24 h, 52 %.

Since DDQ/H^+ method for both polyphenylenes **73** and **74**, resulted in the generation of the $\frac{1}{3}^{\text{rd}}$ fused product as the main product, we believed that incorporation of electron-donating methoxy groups would help the ring closure resulting in fully-fused system. The oxidative cyclodehydrogenation of methoxy substituted **77** was attempted using DDQ/H^+ oxidant system. The reaction was carried out several times, modifying the experimental parameters (i.e. such as addition of DDQ dissolved in DCM dropwise to the reaction mixture, addition of DDQ directly as a solid and also keeping for reaction times as long as 48 h). Irrespective of the modifications, the reaction resulted in only the

formation of the $\frac{1}{3}^{\text{rd}}$ fused **86** with two C-C bond closure around the pyrimidyl ring. Therefore, these results show that the incorporation of the methoxy substituents has no direct influence on oxidative cyclodehydrogenation using the DDQ/H⁺ method.

Cyclodehydrogenation of **77** was also attempted using FeCl₃ as the oxidant. The reaction mixture was stirred for 24 h and subsequently quenched with addition of methanol. The solvents were removed *in vacuo* and resulted in a dark brown precipitate. The precipitate was re-crystallised with methanol resulting in the pale brown precipitate. Mass spectral analysis confirmed the presence of the $\frac{1}{3}^{\text{rd}}$ fused product **85** and the NMR techniques confirmed that the ring closure has taken place at *ortho*-position to the pyrimidine ring.

2.5 Characterisation of the DASB derivatives

In this section, the characterisation of the fully-fused DASB derivatives **78**, **80** and **82** will be discussed followed by the characterisation of the partially fused derivatives, half fused **83** and $\frac{1}{3}^{\text{rd}}$ fused **79**, **81**, **84-86**. For the sake of brevity, only some selected NMR assignments will be discussed in detail. In addition, single crystal x-ray structures were obtained for fully-fused product **82** and $\frac{1}{3}^{\text{rd}}$ fused product **84** and will be discussed.

2.5.1 NMR spectroscopic characterisation of **78**, **80** and **82**

The overlaid aromatic region of the fully-fused DASBs **78**, **80** and **82** are shown in Figure 2.22. In these fully-fused systems, the aromatic signals appear as a series of well-resolved singlets. By comparing **82** with **78** and **80**, it is evident that the aromatic signals undergo a considerable downfield shift, situated at $\delta = 10.43 - 9.34$ ppm. Interestingly, this trend has also been observed for methoxy substituted 4N systems with aromatic signals appearing in a similar lower field region.⁵³ In general, the aromatic signals of **78** and **80** are located in the region $\delta = 9.97 - 8.86$ ppm, which has been observed for other non methoxy 4N systems [i.e. N-HSB (**47**)]. An exception is the signal at $\delta = 7.95$ ppm attributed for H3 in **80**. Compound **78** has a C₂ axis of symmetry running through the molecule⁵ and therefore simplifies the spectrum compared to asymmetric **80** and **82**. All three spectra were assigned using various 2D NMR techniques and a similar strategy was employed in the assignment of the signals. Therefore, in the interest of conciseness the assignment of **82** will be discussed in detail.

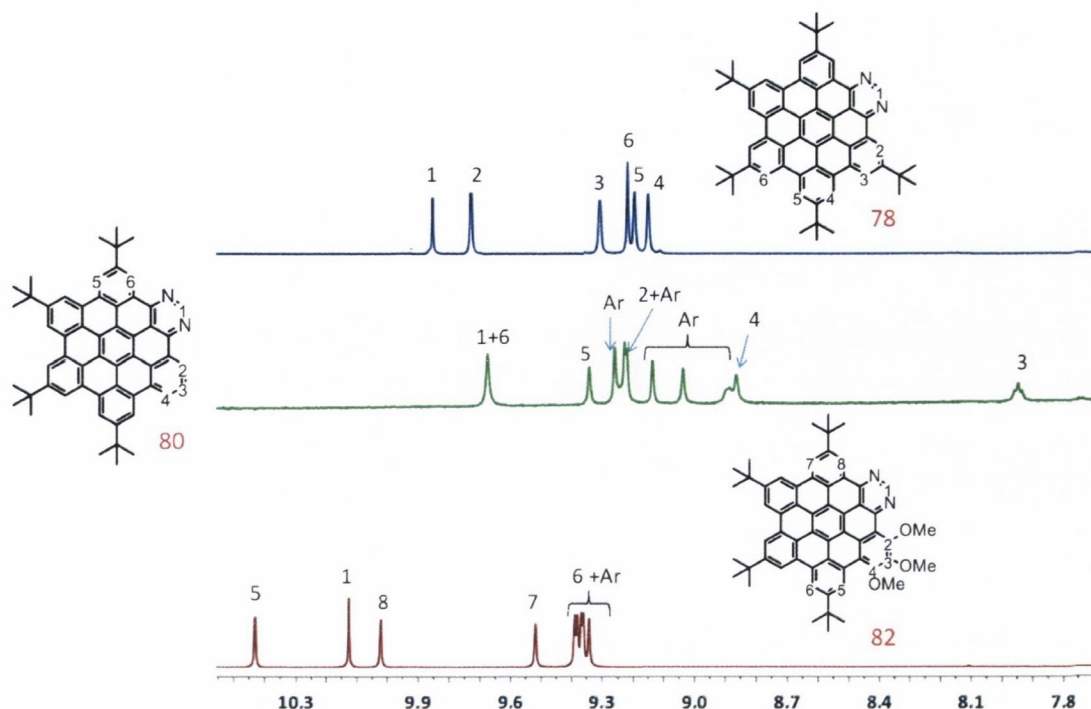


Figure 2.22: The overlaid aromatic region of the ^1H -NMR spectra of fully-fused DASB **78**, **80** and **82** in CDCl_3 at RT (400.1 MHz). Atom labelling as per inset figure.

All three spectra were assigned using various 2D NMR techniques and a similar strategy was employed in the assignment of the signals. Therefore, in the interest of conciseness the assignment of **82** will be discussed in detail.

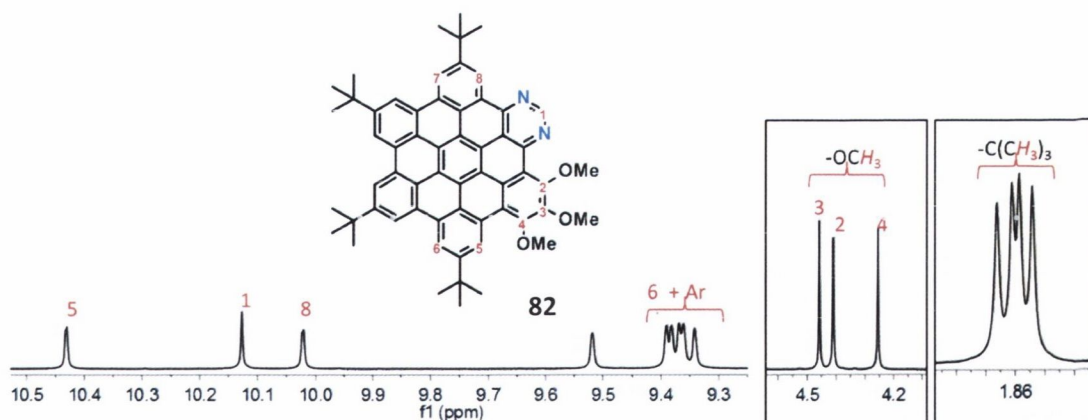


Figure 2.23: ^1H NMR spectra of **82** in CDCl_3 at RT (600 MHz) with inset showing the aliphatic region. Atom labelling as per inset figure.

The aromatic region of the ^1H NMR spectrum of **82** consists of 9 singlets each of which integrate to 1 proton (Figure 2.23). The four most downfield protons in the region $\delta = 10.45$ - 9.51 ppm are well-separated which enabled conclusive assignment using various

2D NMR (HSQC, HMBC and NOESY) techniques. H6 and the remaining aryl singlets appear as set of overlapped signals in the region $\delta = 9.38$ - 9.34 ppm, thereby precluding the full assignment. It is interesting to note that the proton responsible for the most downfield singlets in the spectra of **82** is not located on the carbon between the two nitrogens in the pyrimidyl ring, as observed for the other members of the non-methoxy 2N (Figure 2.22) and 4N systems.³³ The most downfield signal at $\delta = 10.45$ ppm in **82** belongs to H5 which is adjacent to the $-\text{OMe}$ group on C4. This assignment was confirmed with the aid of both HSQC and NOESY spectra and will be discussed in detail below.

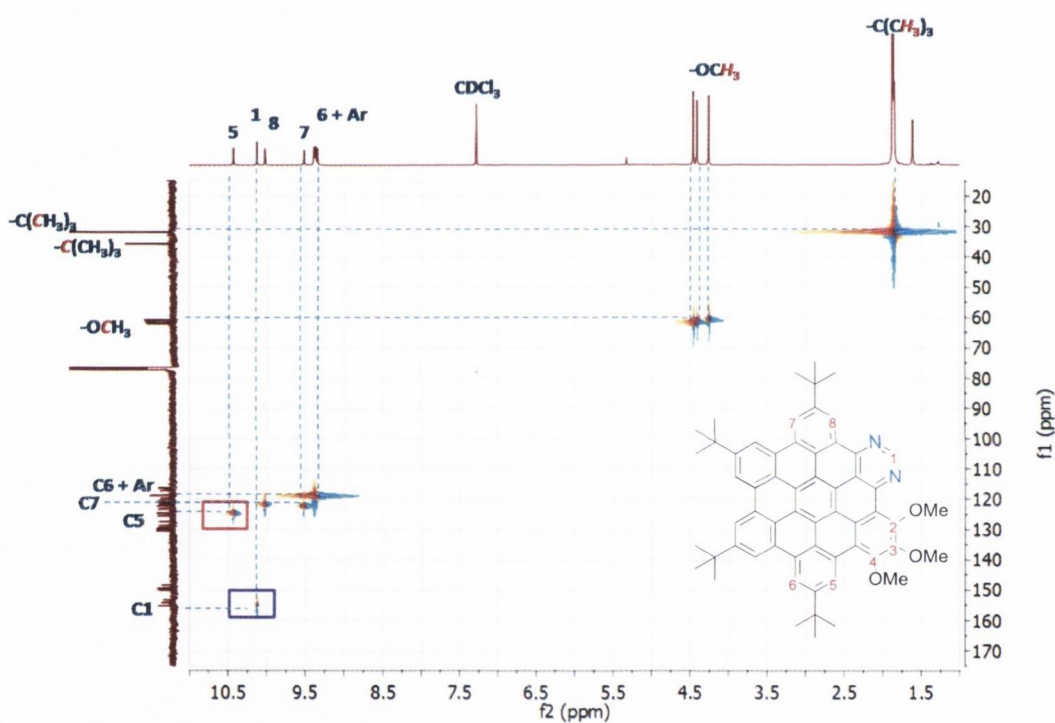


Figure 2.24: HSQC analysis of **82** in CDCl_3 at RT (600 MHz) showing C-H correlations.

Generally, the carbon between the two nitrogens in the pyrimidyl ring appear around $\delta = 154$ - 156 ppm for other known non-methoxy N-HSB compounds.^{53, 100} Examination of the ^{13}C - ^1H HSQC 2D spectrum of **82** reveal that most downfield carbon signal at $\delta = 155.5$ ppm (C1) does not correlate with the most deshielded proton signal at $\delta = 10.45$ ppm as expected, instead correlating with the proton signal at $\delta = 10.12$ ppm (marked in the 'purple box'). Since C1 is a pyrimidyl carbon, the correlation confirms the assignment of the proton signal at $\delta = 10.12$ ppm as the pyrimidyl proton H1. The carbon signal at $\delta = 124.9$ ppm (C5) correlates with the most downfield proton signal at

$\delta = 10.45$ ppm (marked in the 'red box'). This assignment was further supported by NOESY spectrum (Figure 2.25) which shows a 2D representation of ^1H interactions through space.

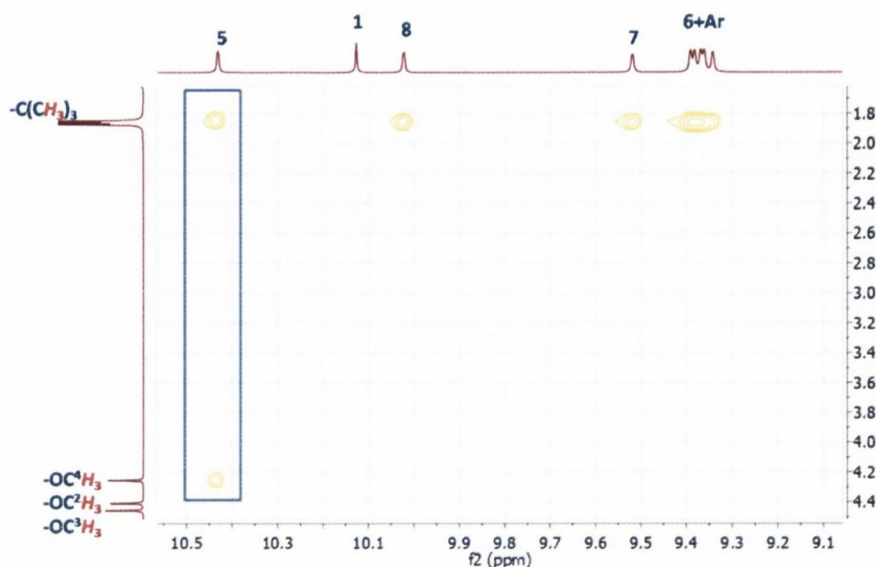


Figure 2.25: Section of the NOESY spectrum of **82** in CDCl_3 at RT (600 MHz).

According to the NOESY spectrum of **82**, all of the aromatic signals except H1 show cross peaks with *tert*-butyl signals ($\delta = 1.87 - 1.84$ ppm), providing further evidence of the assignment of H1 as the pyrimidyl proton. In addition to the *tert*-butyl correlations, the most downfield ^1H signal at $\delta = 10.45$ ppm shows an interaction with the methoxy group on C4. It shows that through space signal at $\delta = 10.45$ ppm is in close proximity to C4OCH_3 and is assigned to H5. The NOESY spectrum was further useful in the assignment of the aromatic signals adjacent to both pyrimidine and methoxy functionalised rings (not shown in Figure 2.26). The ^1H signal at $\delta = 10.45$ ppm (H5) also shows a small correlation with singlet at $\delta = 9.38$ ppm and it was attributed to H6. Similarly the singlet at $\delta = 10.02$ ppm (H8) correlates with $\delta = 9.51$ ppm and is assigned as H7.

Assignment of the ^{13}C NMR spectrum was achieved with the aid of HSQC, HMBC and a series of DEPT 90 and 135 spectra. HMBC (Heteronuclear Multiple Bond Connectivity) experiments incorporate a long range pulse delay into the HSQC pulse sequence to filter out one-bond correlations and is a useful tool in determining connectivity through ^2J and ^3J correlations, even through quaternary carbons. Figure 2.26 shows the fully assigned ^{13}C spectrum of **82**.

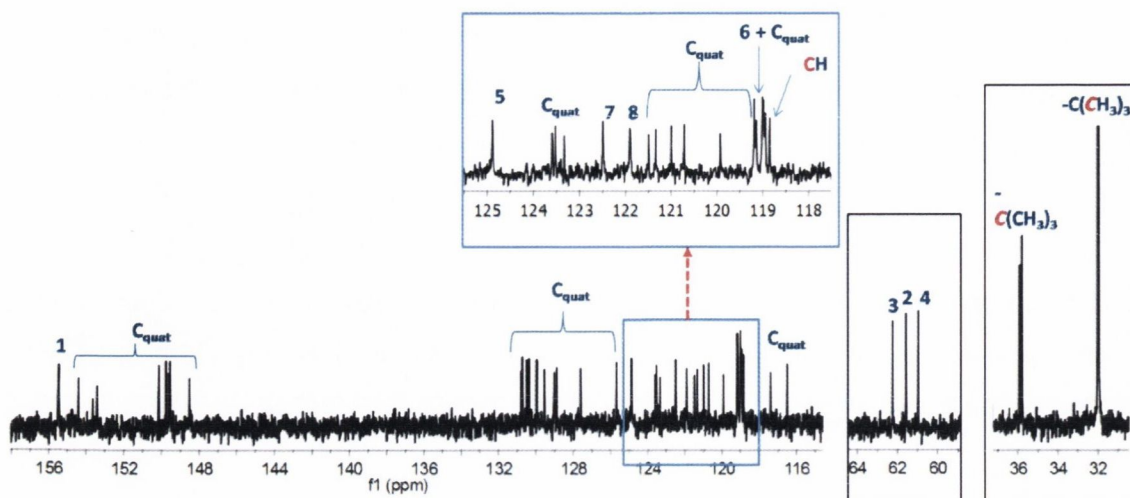


Figure 2.26: ^{13}C NMR spectrum of **82** in CDCl_3 at RT (151 MHz).

2.5.1.1 Aggregation studies

Graphene-type molecules are known to aggregate in solution due to extensive π - π interactions.¹²² NMR spectroscopy has been used as an important tool for investigating the aggregation of compounds. Moore *et al.* have successfully used solid state NMR studies to investigate the π - π interactions that give rise to aggregation in phenyl acetylene macrocycles.¹²³ Also, Fechtenkötter *et al.* have used concentration dependent and variable temperature NMR studies to investigate aggregation properties of long chain HBC derivatives.¹²⁴ In their study, decreasing the concentration from 12.36×10^{-3} to $0.82 \times 10^{-3} \text{ mol L}^{-1}$ have resulted in a shift to lower field by $\Delta\delta = 0.33 \text{ ppm}$ for the signals arising from the core protons and a weaker downfield shift of $\alpha\text{-CH}_2$ protons of the alkyl side chains. N-HSB (**47**) has a permanent dipole moment due to the presence of electron withdrawing nitrogen atoms which gives a large electrostatic contribution to the dimer interactions. This, along with the large aromatic core, ensures extensive π - π overlap of neighbouring molecules in a columnar stacks. π - π Stacking can form face-to-face (H) or edge-to-face (J) aggregates. In N-doped systems it is believed that face-to-face, head-to tail type aggregation is preferred as it allows maximising the overlap of the dipole's opposite charges. Both variable temperature and concentration dependent NMR studies of N-HSB (**47**) in CDCl_3 show extensive aggregation in solution. In this study, ^1H NMR studies were used to qualitatively assess the influence of concentration and temperature on the aggregation of fully-fused aromatic product **82** in solution.

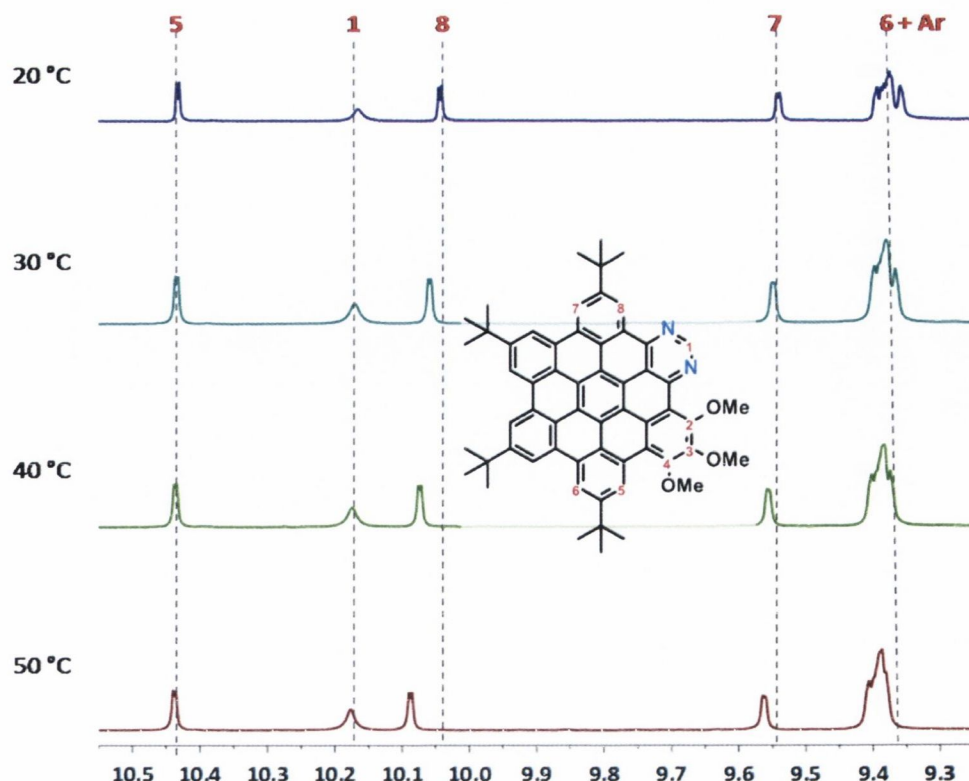


Figure 2.27: Aromatic region of **82** shown at various temperatures in CDCl₃ (concentration = 1.13×10^{-2} M), 400 MHz.

The NMR of **82** in CDCl₃ was monitored at the temperature ranging from 20 °C to 50 °C measuring in 10 °C increments. The changes observed in the aromatic region of the spectra are shown in Figure 2.27. Interestingly, the peaks corresponding to H1 and H5 do not show significant shifts with increasing temperature. The remaining aromatic protons show noticeable shifts to lower field with increasing temperature with H8 showing the most dramatic downfield shift of all ($\Delta\delta = 0.05$ ppm). These shifts are attributed to a decrease in aggregation with increasing temperature over the temperature range studied. In N-HSB (**47**), the pyrimidyl protons are the most deshielded showing shifts of $\Delta\delta = 0.05$ ppm (21 – 40 °C).¹⁰⁰ However, N-HSB shows a two-fold axis of symmetry. It is likely that the position of the methoxy groups is inhibiting further aggregation and interactions between neighbouring pyrimidyl protons.

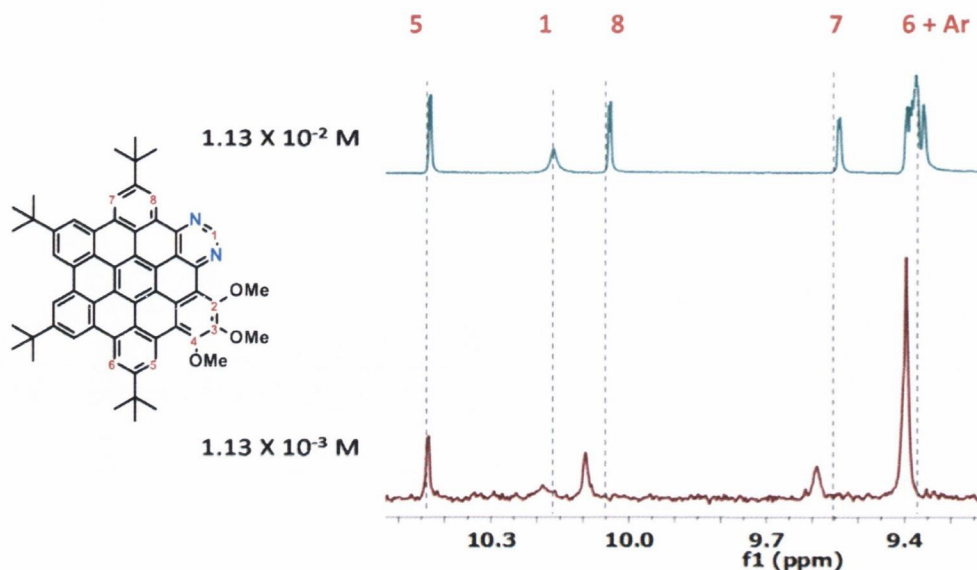


Figure 2.28: Aromatic region of **82** shown at different concentrations in CDCl₃ (concentration = 1.13 × 10⁻² M), 600 MHz.

The corresponding concentration dependent studies were carried out using a series of 10 fold dilutions ranging from 1.13 × 10⁻² M to 1.13 × 10⁻⁵ M. Only the first two dilutions (~10⁻² M and ~10⁻³ M) were sensitive for NMR detection and shown Figure 2.28. By decreasing the concentration from 1.13 × 10⁻² M to 1.13 × 10⁻³ M marginal shifts to the lower field were observed most noticeably for H8 and H7. This is further suggestive of aggregation occurring in solution.

2.5.2 Single crystal X-ray analysis of **82**

Crystals of **82** suitable for single crystal X-ray diffraction analysis were grown from dichloromethane/methanol solution. The single crystal X-ray analysis of **82** provides some insight into the interaction in solid state. **82** crystallises in a monoclinic P2₁/c space group with four molecules per unit cell. The asymmetric unit of **82** is shown in Figure 2.29. The crystal structure of **82** is not strictly planar, with ring X bending above the mean plane and ring Y below the plane of the central benzene ring by 9.29° and 12.36° respectively. This is attributed to the trimethoxy substituents reorienting to avoid steric congestion of neighbouring methoxy substituents (Figure 2.29). The *tert*-butyl group in ring Z is disordered and it was modelled appropriately using partial occupancy refinements.

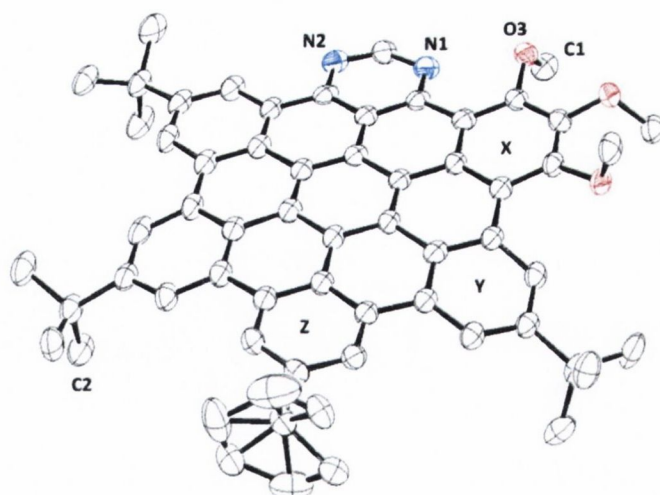


Figure 2.29: Asymmetric unit of the single crystal structures of **82** [one *tert*-butyl group (ring *z*) was disordered in two positions with a refined occupancy of 56:44%. H atoms are omitted for clarity].

In ring ‘X’, the methoxy groups arrange themselves in a ‘one up, two down’ arrangement. This has a profound effect on the packing in the crystal structure, resulting in offset head-to-tail dimers (AB) in a columnar stack [Figure 2.30 (a)]. The $\pi \cdots \pi$ stacking is reflected in the short intra-dimer distance (A-B is 3.34(3) Å), while the inter-dimer distance is longer [AB-AB is 3.64(3) Å, see Figure 2.30 (b)]. The crystal structure of hexa-*tert*-butyl HBC shows a much longer inter dimer distance of 3.44(2) Å.¹²⁵ Furthermore, the AB dimers in **82** are not arranged in typical Bernal packing as in HBC, but are offset by 3.12(3) Å. The crystals of **82** are held together through inter- and intra-molecular hydrogen bonding, in addition to π - π interactions. Intramolecular H-bonding is observed (N1 $\cdots$ H-C1 (3.072(7) Å) with a donor acceptor bond angle of 112.65° (Figure 2.29). Intermolecular hydrogen bonding exists between O3 $\cdots$ H-C2 (3.495(8) Å, 153.62°, symmetry transformation used to generate equivalent atoms *x*, $\frac{1}{2}$ -*y*, $-\frac{1}{2}$ +*z*). Overall, the C-C distances are between 1.38-1.46 Å which is expected for a delocalised aromatic system.

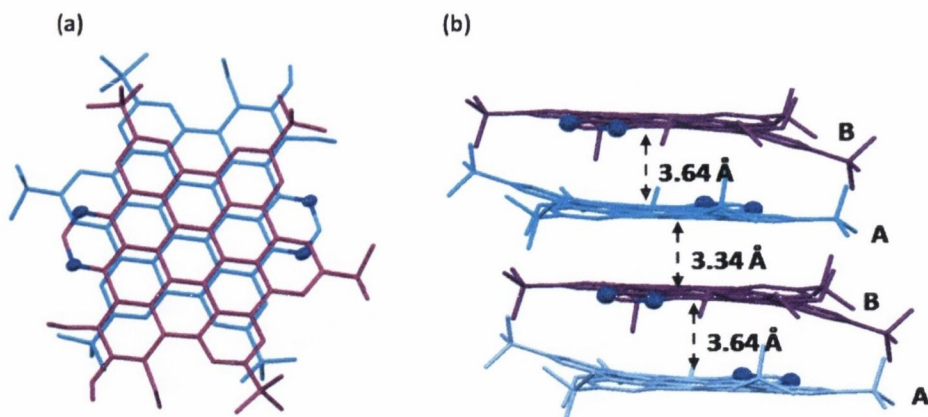


Figure 2.30: (a) Head-to-tail packing arrangement of **82** and (b) off-set columnar packing arrangement view perpendicular to π - π interaction. Symmetry transformations used to generate equivalent atoms, (i) $-x, 1-y, 2-z$, (ii) $-x, -y, 2-z$ and (iii) $x, -1+y, z$.

To further understand effects of methoxy groups on the packing, structure **82** was compared with N-HSB (**47**) crystal structure obtained by Dr. Buddhie Lankage. The N-HSB crystal was grown by slow evaporation of a solution of N-HSB (**47**) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ solvent system and was studied using Synchrotron X rays generated (Figure 2.31).⁵³ N-HSB also exists as dimers stabilised by π - π interactions, with an inter-dimer distances of approximately 3.70(2) Å which is slightly larger than the distances observed for both HBC and **82**. Interestingly, N-HSB (**47**) shows an ABCABC columnar packing with helical rearrangement within stacks in contrast to ABAB packing arrangement observed in **82**. The formation of a head-to-tail dimers in **82** suggests that either the presence of nitrogen atoms or the methoxy units (*via* H-bonding) are directing the orientation of the individual molecules in the columnar stacks.

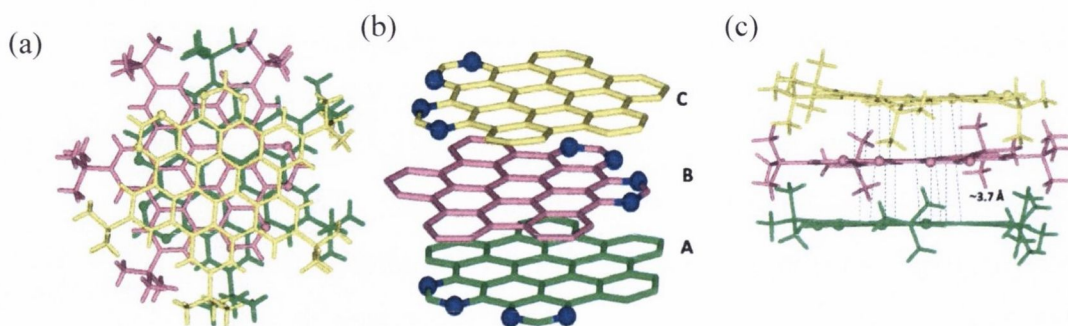


Figure 2.31: The ABCABC packing arrangement of N-HSB (**47**) (a) view along the 'a' axis, (b) helical arrangement of the stacks (c) view perpendicular to the π - π interactions.⁵³

A similar phenomenon has also been observed for 4N-six methoxy substituted system paramethoxy-TASB (**104**) where the trimethoxy substituted rings are positioned *para* to each other (Figure 2.32).⁵³ Similar to **82**, the methoxy groups exist in a ‘two up, one down’ arrangement on each ring resulting in offset head-to-tail dimers (AB) in a columnar stack [(Figure 2.32 (b)]. Paramethoxy-TASB (**104**) adopts a similar packing arrangement to **82**, however the intradimer $\pi \cdots \pi$ distances are longer (3.48 Å) with a smaller offset (1.25 Å) and the distances between the dimers are slightly shorter (3.51 Å). Also in paramethoxy-TASB, the dimers are held together by intermolecular hydrogen bonds between a methoxy-based methyl H and a methoxy O and a pyrimidyl N atom, [O1 $\cdots$ H-C4 (3.53(2)) Å and N1 $\cdots$ H-C3 (3.50(3)) Å]. This further supports the fact that the hydrogen bonding in these methoxy substituted systems are directing the columnar arrangement.

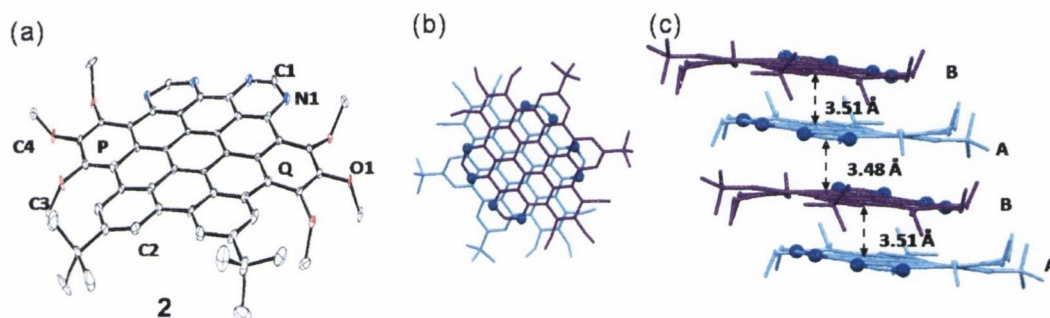


Figure 2.32: (a) Single crystal structure of paramethoxy-TASB (**104**) (b) head-to-tail packing arrangement (c) off-set columnar packing arrangement view perpendicular to $\pi \cdots \pi$ interaction.⁵³ Symmetry transformations used to generate equivalent atoms: (i) $1-x, -y, 2-z$, (ii) $2-x, -y, 2-z$ and (iii) $-1+x, y, z$.

Overall packing arrangement of **82** shows a herringbone type packing arrangement, similar to the packing observed in both HBC (**1**) and N-HSB (**47**).

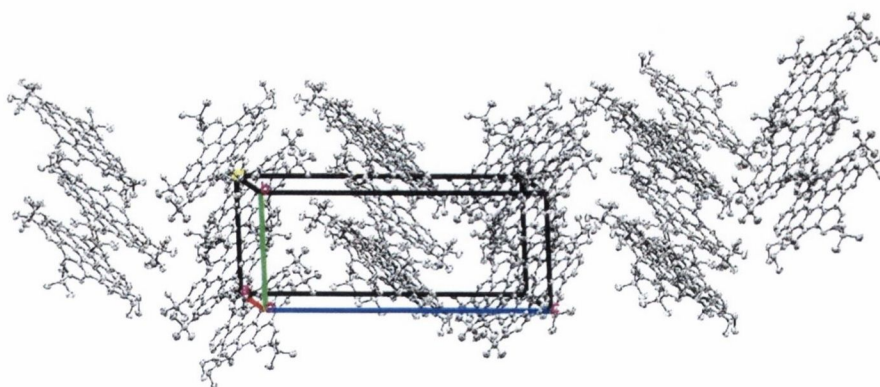


Figure 2.33: Molecular packing arrangement of **82** along ‘a’ axis.

2.5.3 Characterisation of ½- fused **83**

The ESI mass spectral analysis confirmed the presence of half fused product (3 C-C bonds closed) **83** with found m/z $C_{59}H_{61}N_2O_3$ $[M+H]^+$ at 845.4672 that matches with the calculated mass at 845.4682. The positions of the three bond closure were identified using NMR analysis. By comparison of the 1H -NMR spectrum of fully-fused product **82** (Figure 2.23), the corresponding 1H -NMR spectrum of **83** shows additional doublets in the aromatic region indicating the presence of free aryl rings. The downfielded singlets at $\delta = 9.92$, 9.57 and 9.44 ppm were due to the fused portion of the molecule and appears slightly upfield region compared to fully-fused **82**. The assignment of the proton spectrum of **83** was complimented by HSQC and NOE spectral analysis.

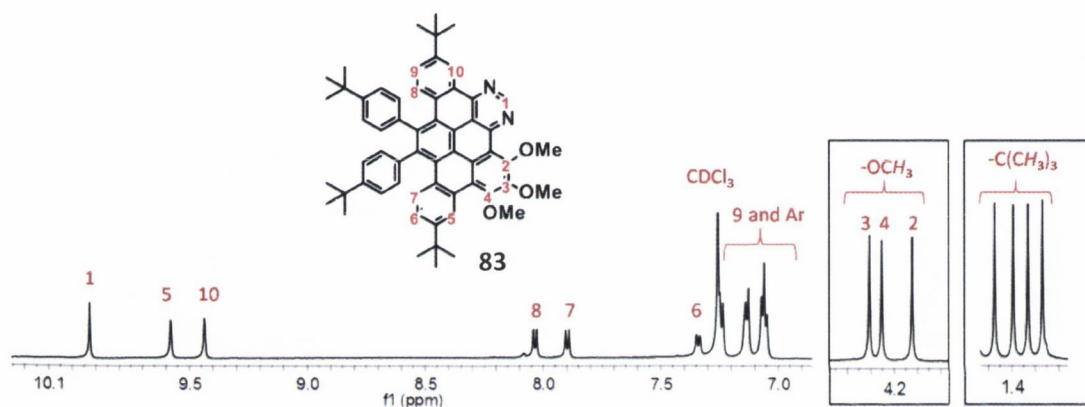


Figure 2.34: 1H NMR spectra of **83** in $CDCl_3$ at RT (600 MHz) with inset showing the aliphatic region. Atom labelling as per inset figure.

The most down field singlet at $\delta = 9.92$ ppm was assigned as H1. This assignment was further supported by the 1H - ^{13}C HSQC spectrum indicating the correlation of H1 to a pyrimidyl carbon at $\delta = 155.1$ ppm. The 1H - 1H COSY spectrum shows the presence of two 2-spin systems (marked as 'pink' and 'blue' rectangles) and two 3-spin systems (marked as 'green' and 'yellow' rectangles) indicating the presence two free aryl rings and two partially fused rings respectively. In N-doped systems the ring closure generally initiates around the pyrimidine rings^{53, 100, 110} therefore the structure presented above (Figure 2.34) was initially suggested. Careful analysis of all 1D and 2D NMR results proved that the suggested structure was accurate.

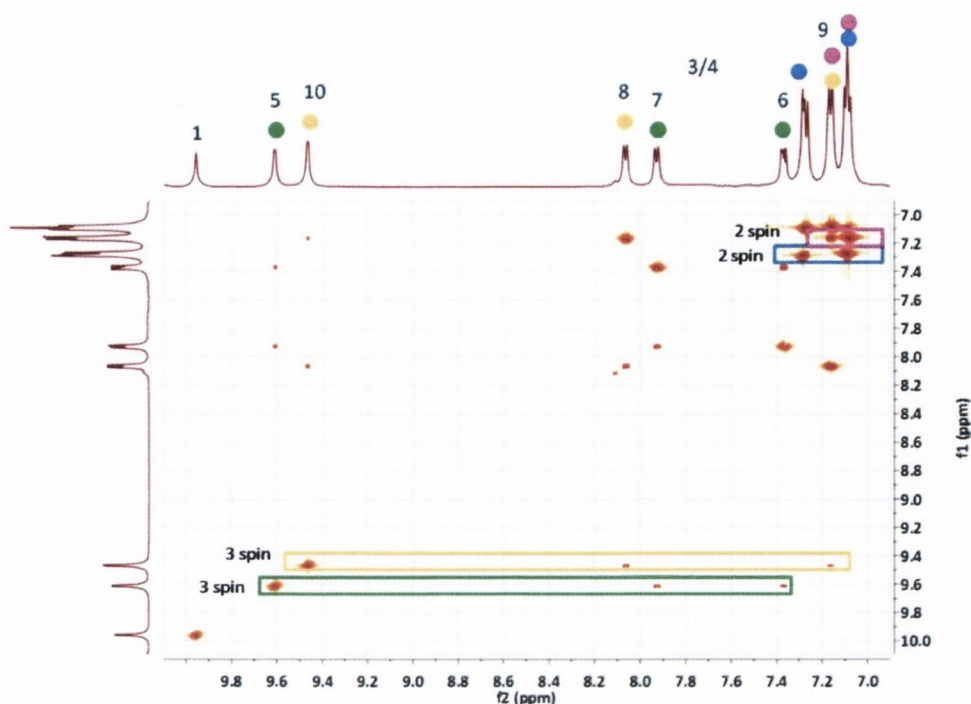


Figure 2.35: Aromatic region of the ^1H - ^1H COSY spectrum of **83** in CDCl_3 (600 MHz), RT.

The singlets at $\delta = 9.58$ ppm and $\delta = 9.43$ ppm were assigned to H5 and H10 respectively. NOE irradiation on H5 and H10 differentiated between the two singlets as H5 shows close through space correlations to the methoxy signals. The ^1H - ^1H COSY spectrum enabled the identification of the signals in the spin system for both H5 and H10 (as shown in Figure 2.35). The J values were in agreeable range for ^3J (~ 9.0 Hz) splitting. The assignment of the free aryl signals was hindered due to the overlap of the signals and the inability to irradiate the *tert*-butyl signals in close proximity at their individual frequencies.

2.5.4 Characterisation of $\frac{1}{3}$ rd fused DASB derivatives

It is interesting to note that the oxidative cyclodehydrogenation of all 2N polyphenylenes investigated (**73-77**) resulted in the $\frac{1}{3}$ rd fused product (two C-C bonds closed) using either FeCl_3 or DDQ/H^+ as the oxidant. Along with the preliminary mass spectrometry results, NMR analysis was used to identify the positioning of bond closure in the $\frac{1}{3}$ rd fused products.

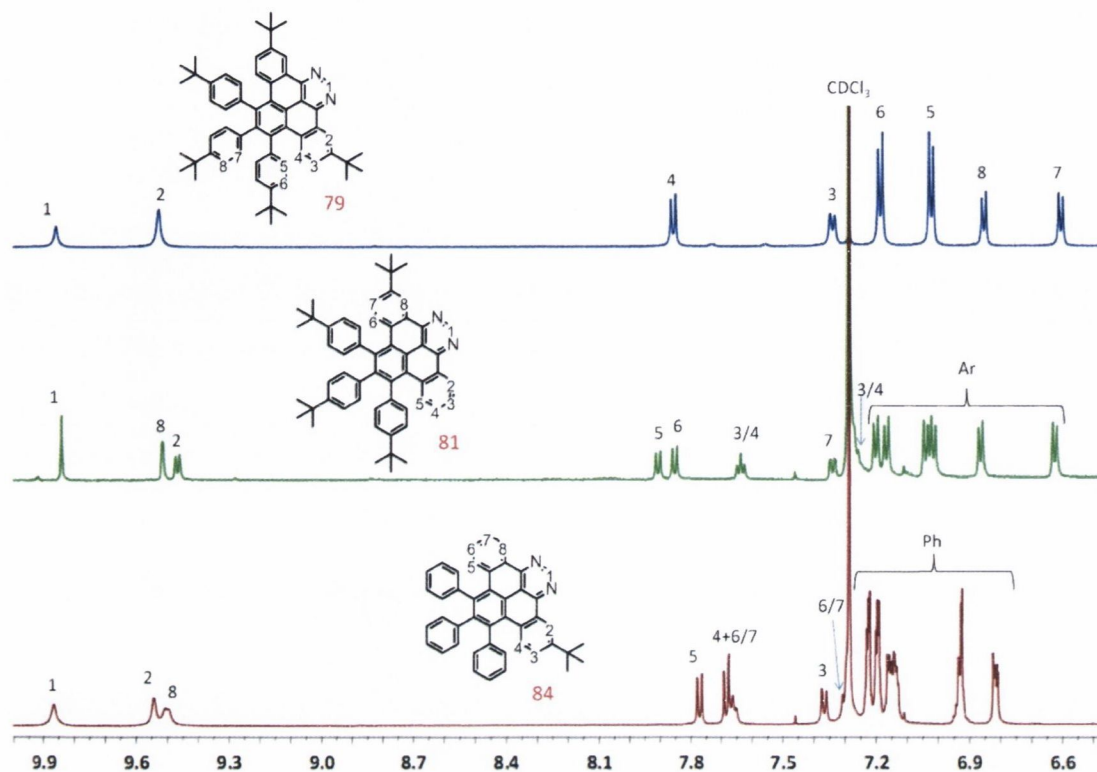
2.5.4.1 ^1H NMR characterisation of $\frac{1}{3}$ rd fused DASB derivatives

Figure 2.36: Overlaid aromatic region of the $\frac{1}{3}$ -fused DASB's **79**, **81** and **84** in CDCl_3 at RT.

In comparison with the polyphenylene precursors (Figure 2.6), the aromatic region of the $\frac{1}{3}$ rd fused products show downfield aromatic signals in the region $\delta = 9.85 - 9.45$ ppm, which belong to the fused portion of the molecule. By comparing **79** with **81** and **84**, it is evident that **79** shows a simplified spectrum due to the presence of the C_2 axis of symmetry through the molecule. Also **79** and **81** shows a series of doublets in the region $\delta = 8.0 - 6.5$ ppm compared to **84** due to the presence of aryl rings showing AB spin patterns. In the interest of conciseness only the assignment of spectra of **81** will be discussed in detail.

All three spectra showed a similar pattern with the most downfield singlet around $\delta \sim 9.85$ ppm attributed to H1 with the second most downfield signal $\delta \sim 9.5$ ppm owing to H2/H8 which are protons directly adjacent to the pyrimidyl ring in the fused platform. The pyrimidyl protons are the most deshielded due to the electron withdrawing ability of the nitrogen atoms. The resonances of the phenyl and *tert*-butyl containing aromatic ring protons appear as a series of overlapping signals in the region between $\delta = 6.97 - 6.65$ ppm. A similar strategy was employed for the assignment of the ^1H NMR signals.

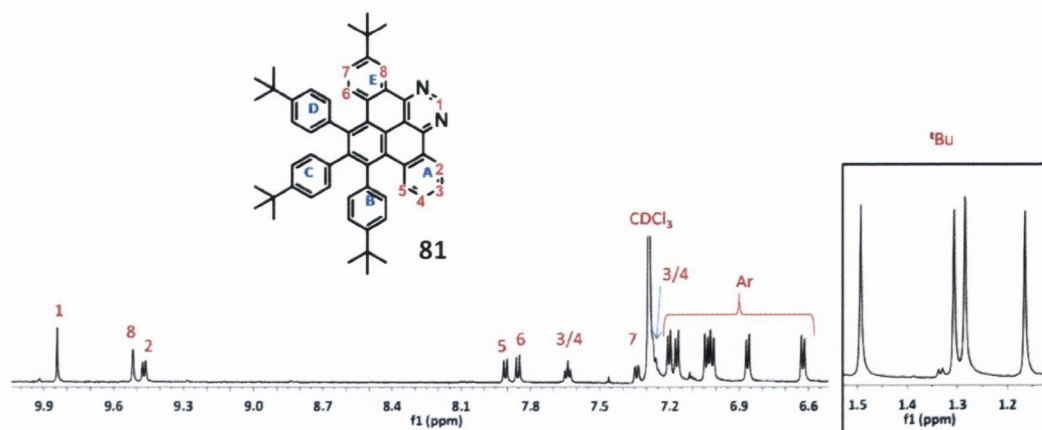


Figure 2.37: ^1H NMR spectra of **81** in CDCl_3 at RT (600 MHz) with inset showing the aliphatic region. Atom labelling as per inset figure.

Figure 2.37 shows the ^1H NMR spectrum of **81** along with the ^1H - ^1H COSY spectrum in Figure 2.38. Analysis of ^1H - ^1H COSY spectrum of **81** shows the presence of several spin systems. It consists of three 2 spin systems, one 3 spin system and one 4 spin system, as highlighted in the coloured boxes in Figure 2.38. The four spin and three spin systems can be attributed to ring A and E respectively with the two spin systems attributing to free aryl rings B, C and D. NOE spectra complemented the ^1H - ^1H COSY spectrum in the assignment of these signals and splitting patterns were also useful to differentiate the signals.

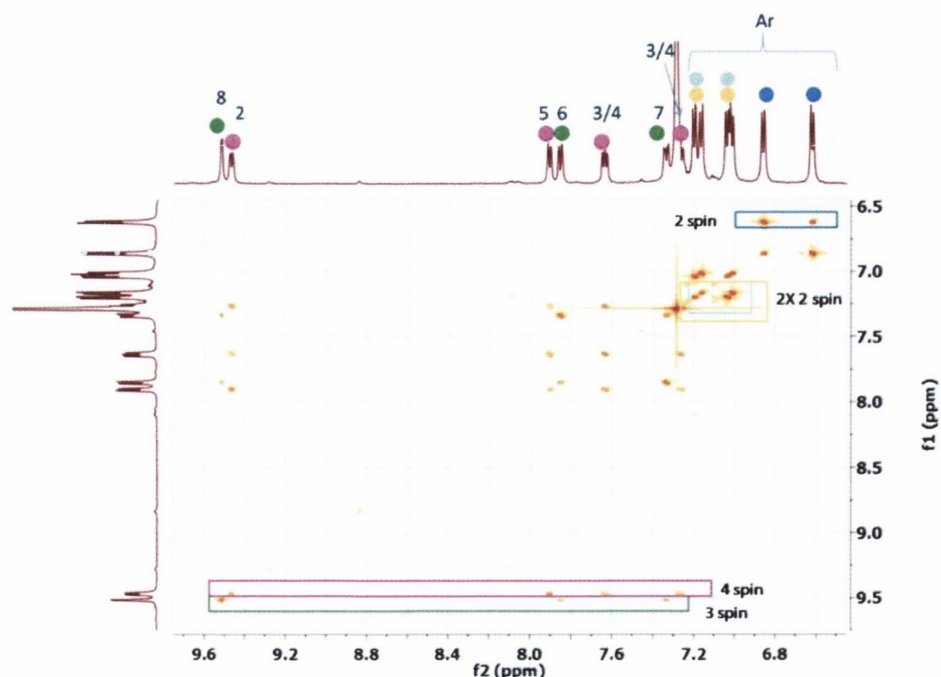


Figure 2.38: Aromatic region of the ^1H - ^1H COSY spectrum of **81** in CDCl_3 .

2.5.4.2 Single crystal X-ray analysis of **84**

The structure of the $\frac{1}{3}$ rd fused species was further confirmed by the analysis of the single crystal X-ray structure of **84**. Colourless single crystals of **84** suitable for X-ray analysis were obtained by crystallising in CH₂Cl₂/ethyl acetate solvent system (Figure 2.39).

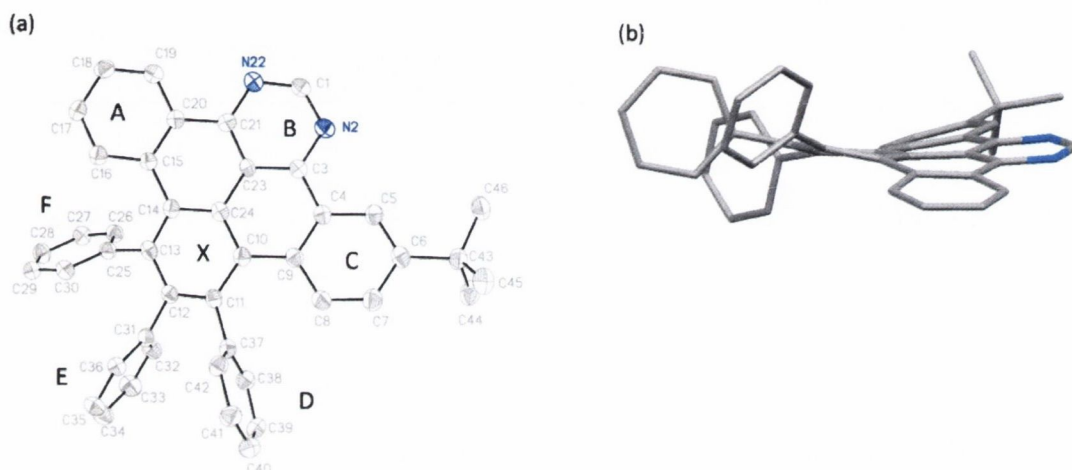


Figure 2.39: (a) Ortep representation¹¹¹ of **84** with displacement ellipsoids at 50%. Hydrogen atoms omitted for clarity; (b) view along the 'b' axis.

Compound **84** crystallises in an orthorhombic Pca-21 space group with four molecules in the unit cell. The asymmetric unit consists of a single molecule. The crystals show reasonably good quality data with R1 value of 5.49 % and a goodness-of-fit of 1.004. The fused portion of **84** shows a twisted nature with respect to the central phenyl ring X, with rings B and C bending above the plane by 15.54° and 20.0° respectively and ring A bending by 18.82° below the plane. This feature is more prominently visible when viewed along the 'b' axis as shown in Figure 2.39. Interestingly, rings D and E are markedly more perpendicular to the central phenyl ring (with tilt angles at 80.37° and 83.22° respectively) in comparison to ring F which shows a smaller twist at 65.06° and is similar in size to the tilt angles observed in polyphenylene precursors (see Table 2.2).

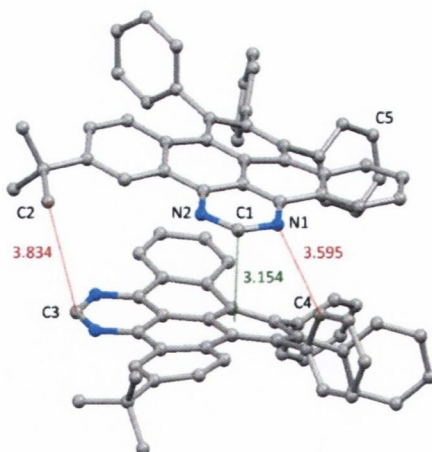


Figure 2.40: The intermolecular interactions of **84** (distances marked in Å). H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: $\frac{1}{2} + x, 2 - y, z$.

The fused portions of the adjacent molecules in **84** shows some overlap of the aromatic regions, in particular the central ring of one ring and the pyrimidyl portion of the other ring. With respect to the central ring centroids in adjacent molecules they are offset by 5.64 Å. Compound **84** shows π - π face-to-face interactions with some portions of the adjacent molecule. The molecules in **84** are held together by various N $\cdots$ H and C $\cdots$ H intermolecular interactions (Figure 2.40). The main interactions include N1 $\cdots$ H-C4 (3.59(1) Å) and N2 $\cdots$ H-C5 (3.31(2) Å) interactions and is typical of weak aryl hydrogen donor bonds present.¹¹³ In addition, intermolecular C $\cdots$ H interactions are observed between C3 $\cdots$ H-C2 (3.83(2)) Å forming a closed packed arrangement. The packing arrangement shows a herringbone type packing arrangement.

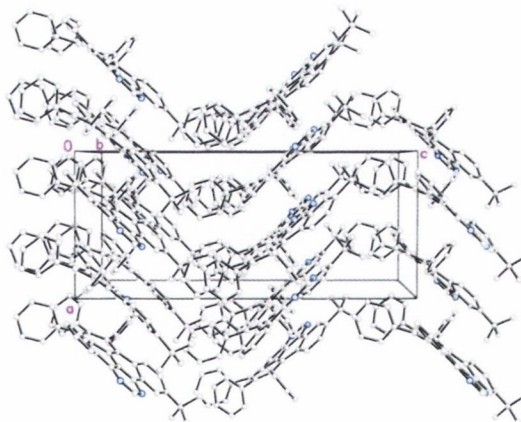


Figure 2.41: Packing diagram of **84** viewed along the b axis. Displacement ellipsoids shown at 50 %. Hydrogen atoms omitted for clarity.

2.6 Photophysical analysis

2.6.1 UV-Vis absorption studies of fully-fused DASBs **78**, **80** and **82**

The UV-Vis absorption spectrum of N-HSB (**47**) along with its 2N-doped analogue **78** is shown in Figure 2.42 (a) and the inset (c) shows the absorption spectrum of the all carbon analogue HBC. In comparison with the polyphenylene precursors (Figure 2.15), the increase in both planarity and rigidity of the platform leads to well resolved absorption spectra with clear vibronic progression.

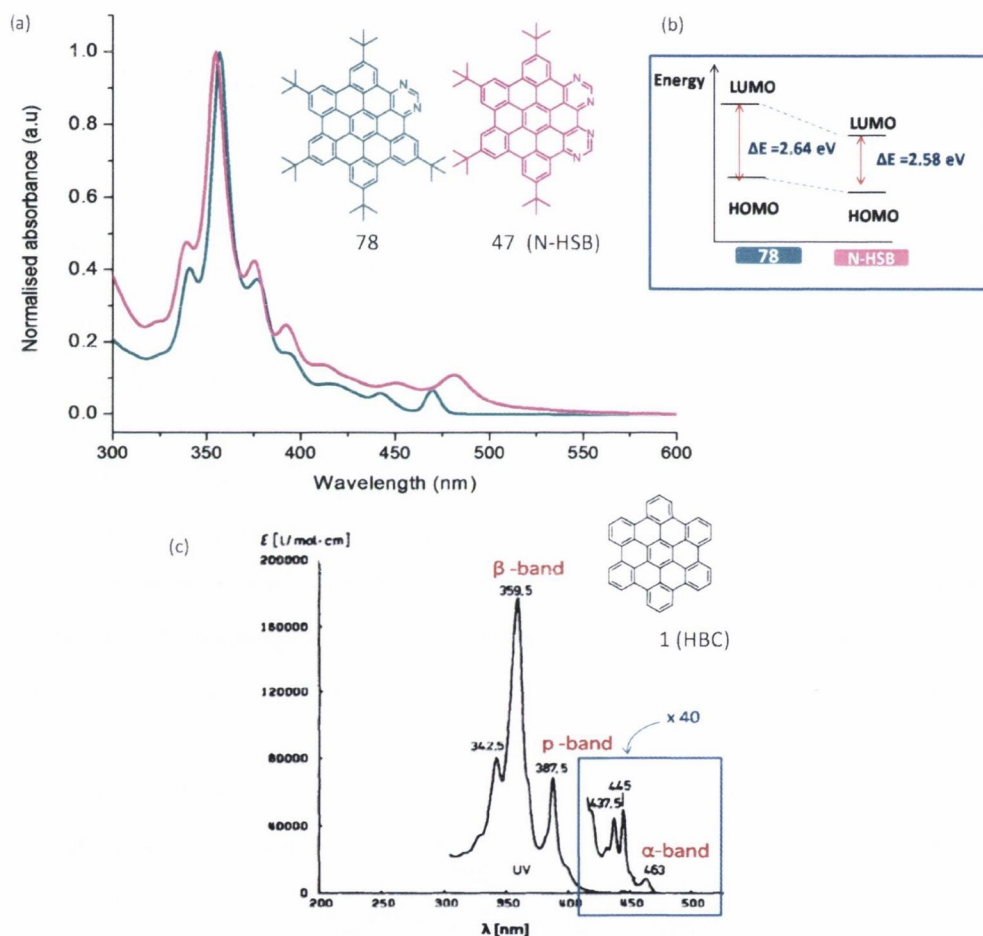


Figure 2.42: Overlaid absorption spectra of **78** and N-HSB (**47**) in toluene ($\sim 10^{-6}$ M). Inset shows the (a) simplified energy level diagram showing the HOMO-LUMO gaps in **78** and N-HSB (**47**) (b) UV-Vis absorption spectrum of HBC (**1**) in 1,2,4-trichlorobenzene.³²

As discussed in Chapter 1, PAHs typically show three types of bands, α , β and p bands according to Clar's nomenclature [see inset Figure 2.42 (c)].¹²⁶ By comparing the UV-Vis absorption spectra of N-HSB (**47**) and its 2N analogue **78** with the all carbon analogue HBC (**1**), we can clearly see that the typical line shape of the absorption spectra is

retained. It indicates that despite the chemical modification, the characteristic of the HBC chromophore is still evident in the N-doped systems. The UV-Vis absorption spectrum of **78** has a $\lambda_{\text{max}} = 357$ nm, and is slightly red-shifted (by 2 nm) compared to N-HSB, which exhibits a $\lambda_{\text{max}}^{\text{abs}} = 355$ nm. In general, this band is relatively insensitive to both substitution and solvent polarity, as is characteristic of the β band described by Clar.¹²⁷

The additional absorption band at $\lambda = 376$ nm, is unique to N-doped systems and is absent in all carbon analogues. p-Bands, thought to be associated with electron delocalisation in the excited state, are also evident in the fully-fused systems and are centred around $\lambda \sim 400$ nm. Compared to the all carbon analogue, a large increase is observed in the molar absorptivity of the bands at longer wavelengths in N-containing systems (Figure 2.42). The weak band at $\lambda = 463$ nm ($\epsilon = 220 \text{ M}^{-1} \text{ cm}^{-1}$) in HBC is assigned as the 0-0 transition, which is symmetry forbidden in D_{6h} symmetry.³² Hendel *et al.* confirmed this assignment by the synthesis and comparison of a methyl substituted HBC derivative of lower symmetry (D_{2h}), which showed a significant enhancement of the 0-0 transition.³² The symmetry is further decreased to C_{2v} in the N-doped systems **78** and N-HSB (**47**), and explains the increase in intensity of the lower energy bands, in particular the α -band. Therefore, the lowest energy bands in both spectra are assigned as the 0-0 $^1(\pi, \pi^*)$ transition, with enhanced molar absorptivity. In comparison to **78**, N-HSB (**47**) shows an increased intensity of the α -band and is red shifted by 486 cm^{-1} . These 0-0 bands represent a pure HOMO-LUMO transition, with energies of 2.64 eV for **78** and 2.58 eV for N-HSB in CHCl_3 [see inset Figure 2.42 (b)]. Increasing the number of electron withdrawing nitrogens in N-HSB (4N) compared to **78** (2N) leads to a greater stabilisation of the LUMO, resulting in a decreased HOMO-LUMO gap and therefore a red shift in the lower energy absorption bands. This is reminiscent of the smaller band gap found in N-containing systems of higher N-doping by Bronner *et al.*¹²⁸

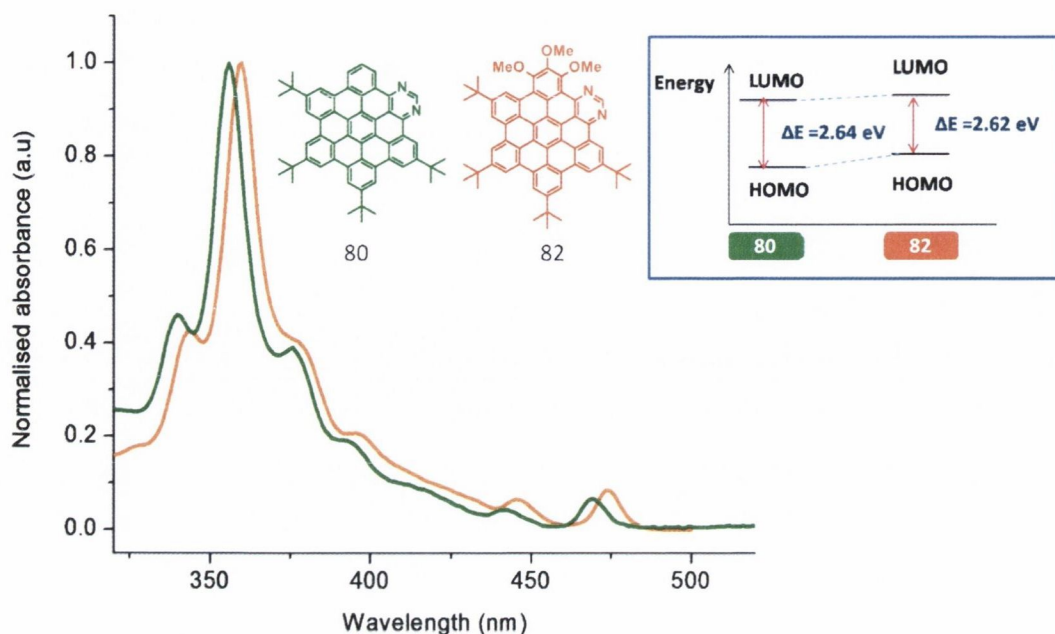


Figure 2.43: The overlaid absorption spectra of **80** and **82** in toluene ($\sim 10^{-6} M$). Inset shows a simplified energy level diagram with HOMO-LUMO energy gaps in **80** and **82**.

To investigate the effect of methoxy substituents on the N-containing chromophore, the absorption spectrum of **80** was compared with that of **82**. The absorption spectra of the methoxy functionalised **82** displays a bathochromic shift of all the main absorption bands and appears to have a higher molar absorptivity compared to **80**. The electron donating methoxy substituents in **82** destabilise the HOMO, thereby decreasing the HOMO-LUMO gap which leads to a red shifted absorption spectrum in **82** (inset Figure 2.43). HOMO-LUMO energy gaps calculated using the α bands in the two compounds also show that the corresponding HOMO-LUMO gap is smaller for **82** (2.62 eV) compared to **80** (2.64 eV). This trend has also been observed for other 4N substituted methoxy systems developed in the group.⁵³ Furthermore, Armaroli and co-workers have reported similar behaviour in methoxy substituted 1,10-phenathroline derivatives which show bathochromic shifts in their absorption spectra upon methoxy substitution.¹²⁹

The molar extinction coefficients for the α -bands ($10000\text{--}17000\text{ M}^{-1}\text{cm}^{-1}$) indicate that the transitions from the ground to the excited singlet state ($S_0 \rightarrow S_1$) are allowed for these N-doped systems (Table 2.5). Yamaguchi *et al.* have carried out a detail photophysical study on the effect of substituents in HBC systems.¹³⁰ Their findings reveal that the α -band is strongly affected by both type and position of substituents. Furthermore, the substituent effect at the *para*-position of HBC is stronger than those at the *ortho*-position, with *meta*-substitution showing negligible influence. In these novel

DASB systems, substituents are varied at *ortho*-position. Methoxy substituted **82** shows both hyperchromic and bathochromic shift of the α -band in comparison to **78**.

Table 2.5: The absorption maxima observed in the UV-Vis absorption spectra of **78**, **80**, **82** and N-HSB (**47**) in toluene ($\sim 10^{-6}$ M).

Compound	λ_{max} [nm] ($\epsilon \times 10^4$ [$\text{M}^{-1} \text{cm}^{-1}$])
78	340 (6.1), 357 (15.2), 377 (5.7), 393 (2.6), 420 (1.3), 443 (0.9), 470 (1.0)
80	340 (7.1), 356 (17.1), 376 (6.7), 394 (3.0), 419 (1.5), 442 (1.1), 469 (1.2)
82	343 (8.6), 360 (20.3), 378 (8.1), 398 (3.9), 445 (1.1), 474 (1.7)
N-HSB (47)	339 (5.7), 355 (13.7), 376 (5.4), 393 (3.2), 413 (1.5), 451 (1.0), 481 (1.4)

2.6.2 UV-Vis absorption studies of partially fused DASB derivatives

The overlaid absorption spectrum of the partially fused 2N systems in toluene are shown in Figure 2.44. The partially fused systems' absorption spectra lack the clear fine structure seen in the rigid fully-fused DASBs. The $\frac{1}{2}$ -fused product (**83**) shows a $\lambda_{\text{max}}^{\text{abs}} = 310$ nm and is hypsochromically shifted compared to its fully-fused counterpart **82** ($\lambda_{\text{max}}^{\text{abs}} = 360$ nm) due to the reduced π -conjugation of **83**. The aromatic platform is further reduced in the $\frac{1}{3}$ rd fused species and they show broad and unstructured spectra due to the rotation of the free aryl rings.

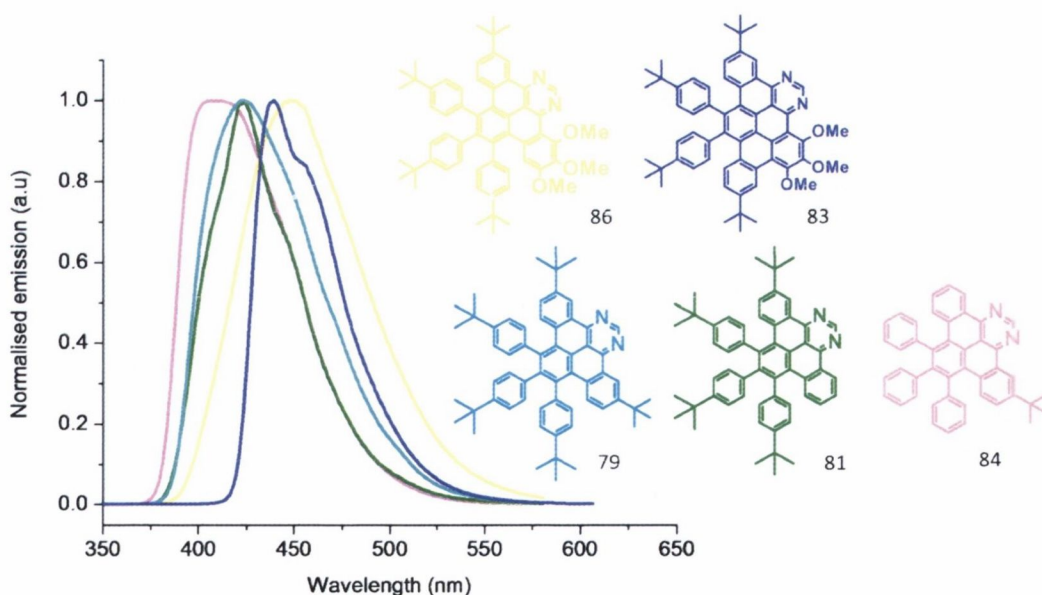


Figure 2.44: The overlaid absorption spectra of partially fused DASBs in toluene ($\sim 10^{-5}$ M).

Methoxy functionalised **86** shows the most red shifted spectra, with increased molar absorbance coefficients. The lowest energy band of **83** (at $\lambda = 424$ nm) is blue shifted in **86** (at $\lambda = 390$ nm) due to the reduction in the degree of conjugation and the depletion of the π -electron density.

Table 2.6: The absorption maxima observed in the UV-Vis absorption spectra of partially fused DASB derivatives in toluene ($\sim 10^{-6}$ M).

Compound	λ_{max} [nm] ($\epsilon \times 10^4$ [$\text{M}^{-1} \text{cm}^{-1}$])
79	308 (4.2), 319 (3.0), 368 (2.8), 386 (2.6)
81	307 (4.1), 319 (3.1), 366 (2.6), 385 (2.5)
83	310 (6.8), 337 _{sh} (3.7), 385 (1.7), 401 (1.7), 424 (1.4)
84	304 (4.4), 317 (3.1), 364 (2.7), 384 (2.2)
86	320 (5.5), 369 (3.5), 390 (3.4)

2.6.3 Protonation studies of **78**

To further understand the behaviour of the chromophoric unit of **78** the effect of protonation of the N atoms was studied. The presence of 2N atoms in the platform confers proton accepting capability on **78**, but no N $\wedge$ N ligand functionality.

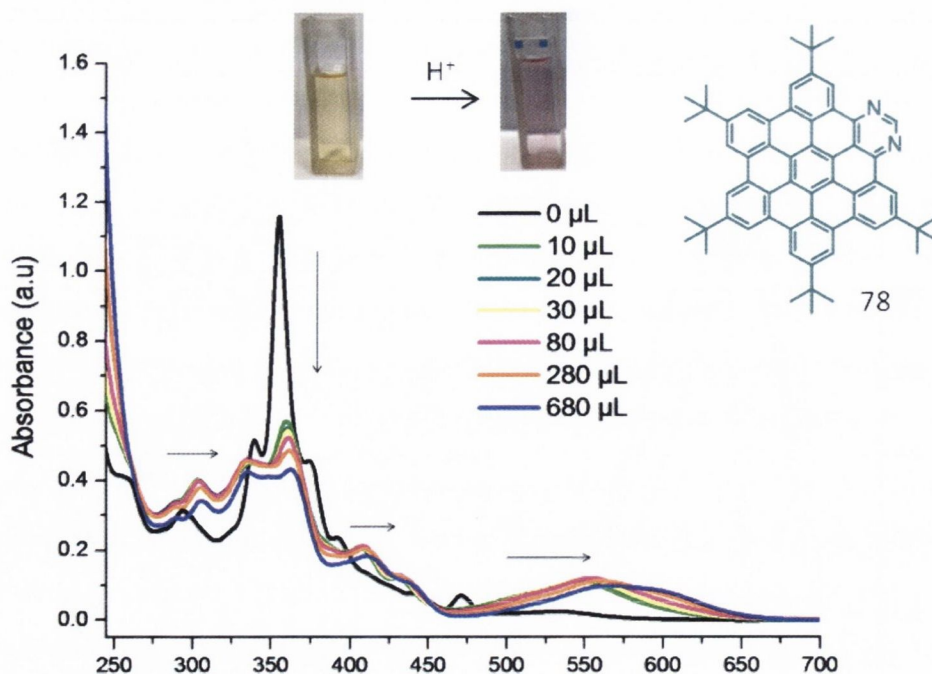


Figure 2.45: UV-Vis absorption spectral changes of **78** (1×10^{-5} M) upon sequential addition of 0.1 M trifluoroacetic acid in CH_2Cl_2 .

The effect of sequential addition of trifluoroacetic acid upon **78** is shown in Figure 2.45. The $\lambda_{\text{max}}^{\text{abs}} = 356 \text{ nm}$ (β band) is reduced in intensity upon addition of the acid suggesting that the main absorption band has a significant $n\text{-}\pi^*$ contribution. β -Bands are generally $\pi\text{-}\pi^*$ in character, however in N-doped systems some underlying $n\text{-}\pi^*$ contribution is observed. β Bands of the parent N-HSB³³ and other 4N systems⁵³ therefore show a hypochromic behaviour upon acid addition. The band at $\lambda = 376 \text{ nm}$, which is unique to N-doped systems, has disappeared upon acid addition thereby suggesting $n\text{-}\pi^*$ origin. According to Kasha's criteria, an $n\text{-}\pi^*$ transition will disappear in acidic media.¹¹⁷ The p-band at $\lambda = 400 \text{ nm}$ has also slightly red shifted upon acid addition. The newly formed protonated species shows a broad red shifted absorption band at $\lambda \sim 560 \text{ nm}$. The isobestic point at $\lambda = 453 \text{ nm}$ indicates an equilibrium between the neutral and newly-formed mono protonated species. The acid addition studies show that nitrogen protonation has a profound electronic effect on the π -electron density throughout the system.

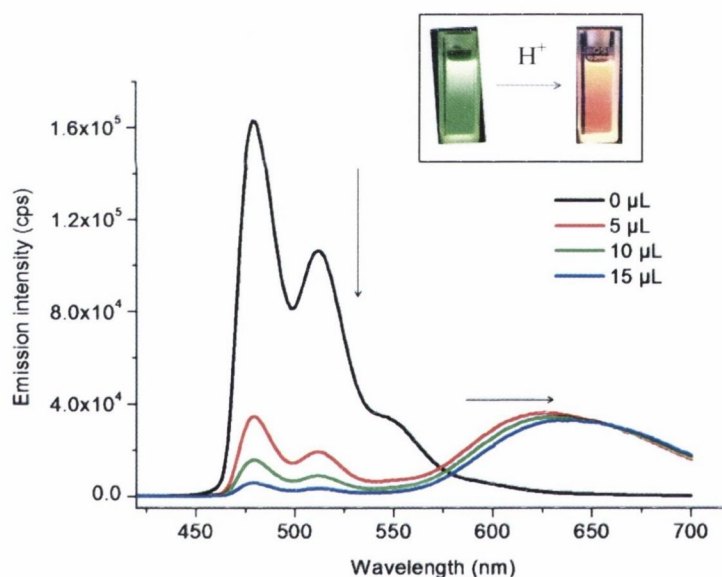


Figure 2.46: Emission spectral changes of **78** (CH_2Cl_2 , $1 \times 10^{-5} \text{ M}$) upon sequential addition of 0.1 M trifluoroacetic acid. Inset is the emission of **78** in CH_2Cl_2 , $\lambda_{\text{exc}} = 355 \text{ nm}$ before (green) and after protonation (orange).

The corresponding emission acid addition studies of **78** in CH_2Cl_2 shows dramatic quenching of the emission bands at $\lambda = 479, 512$ and 551 nm upon sequential addition of trifluoroacetic acid ($1 \times 10^{-3} \text{ M}$) aliquots. A new red shifted band is formed around $\lambda = 635 \text{ nm}$ due to the emission from the newly formed protonated species. The formation

of a new protonated species is evident in the change of colour of **78** in CH_2Cl_2 from green to red upon protonation as shown in Figure 2.46 inset. The dramatic decrease in intensity of the neutral form upon acid addition could be mainly due to two factors. Firstly, the protonation leads to decrease in the concentration of the neutral form and thereby reduce the emission intensity. Secondly, the newly formed protonated species absorbs at $\lambda \sim 560 \text{ nm}$ (Figure 2.46) which overlaps with the emission of the neutral form, resulting in a reduced intensity of the neutral form. Furthermore, the vibronic progressions observed for the three main bands of **78** (i.e. $\sim 1350 \text{ cm}^{-1}$) together with the intense emission suggest that the emissive state of the **78** is predominantly $\pi\text{-}\pi^*$ in nature. For N-HSB in toluene, protonation experiments reveal a similar quenching behaviour of the emission spectra.³³

It is indicative that mono-protonation takes place initially upon acid addition with the loss of isobestic point under high acidic concentrations. Also, the design of the molecule **78** restricts sharing of the proton, unlike phenanthroline based systems where the proton is typically shared between the two nitrogens.¹³¹ Armaroli *et al.* have carried out an extensive study on protonation of phenanthroline based systems and their findings reveal that, for a molecule in the excited state, there is little chance for protonation or deprotonation to occur. This is because the excited state lifetime of the system is much shorter than the rate of protonation.^{132, 133} Although the proton affinity in the singlet excited state is higher than that in the ground state, the protonation and deprotonation processes are too slow to compete with the excited-state decay. Therefore, the intensity changes seen in the luminescence spectra are a reflection of the ground-state acid-base equilibrium. This means that we can relate the trends in absorption and emission in a meaningful way.

2.6.4 Solvent dependency studies of **82**

Solvent dependency studies can be used as a useful tool to distinguish between the $\text{n-}\pi^*$ and $\pi\text{-}\pi^*$ transitions in absorption and emission spectra. In general, polar solvents stabilise n orbitals more than π orbitals, and π^* orbitals more than π orbitals as these states are more polar in character. As a result, in polar solvents a shift to shorter wavelength is observed for $\text{n-}\pi^*$ transitions and a red shift is observed for $\pi\text{-}\pi^*$ transitions. This is due to the $\pi\text{-}\pi^*$ excited state being more polar than ground state, and is better stabilised by polar solvents, reducing the energy difference between the two energy states.¹¹⁷

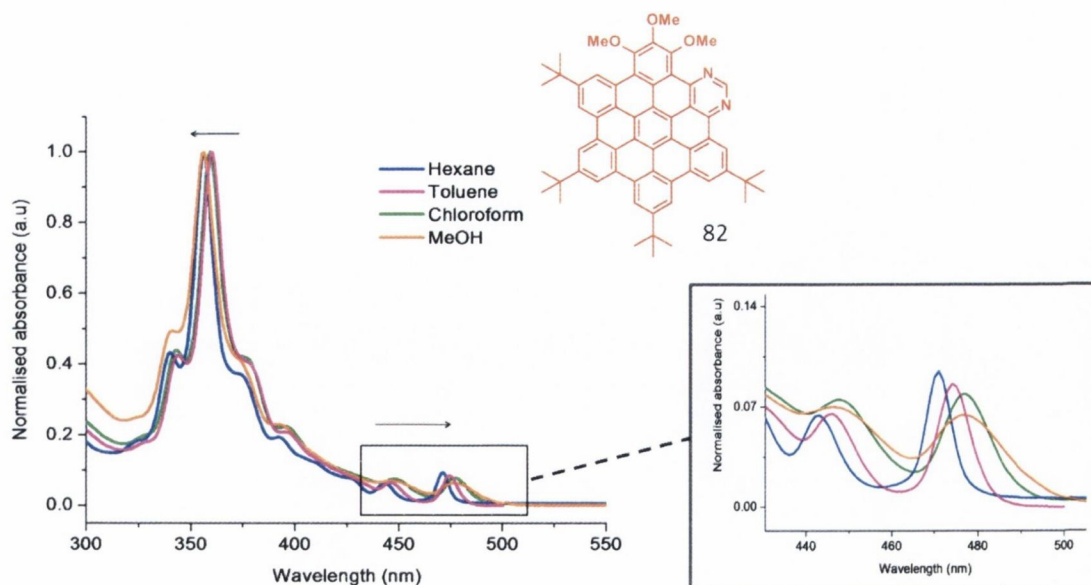


Figure 2.47: Overlaid UV-Vis absorption spectra of **82** in various solvents ($\sim 10^{-5}M$).

The solvent dependency studies of **82** shows a bathochromic shift along with slight broadening of the lower energy bands, and hypsochromic shift of the principal band at $\lambda_{\max} \sim 355$ nm with increasing solvent polarity (Figure 2.47). Therefore, the lower energy absorption bands of **82** has π - π^* character whereas the main band at $\lambda_{\max} \sim 355$ nm has some underlying n - π^* contribution, arising from the presence of lone pairs in the system. These results support the assignments proposed following protonation studies. (Figure 2.45).

The corresponding solvent dependency study of **82**'s emission is presented in Figure 2.48. The compounds are intensely fluorescent (as shown in inset), and display prominent vibrational progressions in non-polar solvents. The vibronic fine structure observed in non-polar solvents is lost upon increasing the solvent polarity (due to H-bonding) and exhibits a significant bathochromic shift of the $\lambda_{\max}^{\text{ems}}$ ($\sim 1630 \text{ cm}^{-1}$) in going from hexane to methanol. This agrees with the assignment of the first excited state S_1 as having π - π^* character. As emission occurs over a timescale it provides the opportunity for the excited state molecules to interact with solvent molecules to a greater extent. The excited state is more polar than the ground state, and as a result non-polar molecules interact less with the excited molecules. Therefore, in non-polar solvents such as hexane the emission occurs mainly from the free excited state molecules rather than the solvated molecules resulting in a structured spectrum. In contrast, in polar solvents such as methanol, the solvent molecules interact more

strongly with the excited state, lowers its energy and shifts the emission to longer wavelengths. The gradual broadening of the emission spectra with increasing solvent polarity is due to the formation of hydrogen bonds.

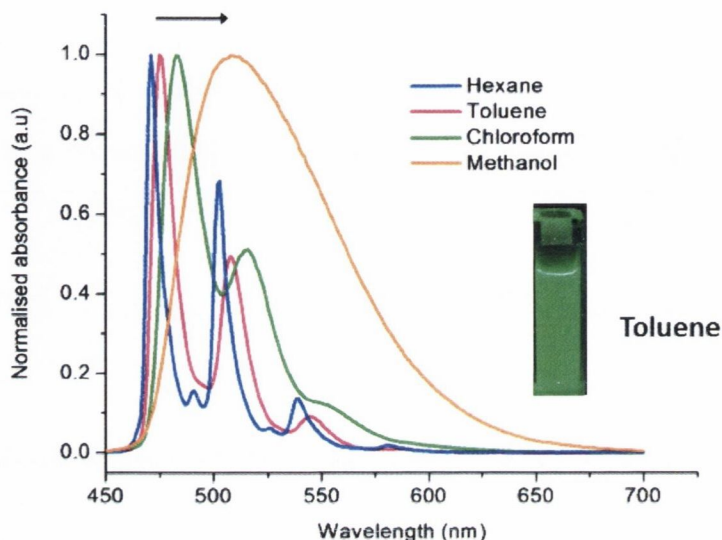


Figure 2.48: The emission spectra of **82** in various solvents ($\sim 10^{-6}$ M).

Considering the donor-acceptor nature of **82**, it can be surmised that the initial locally-excited state can give rise to an intramolecular charge-transfer (i.e., the LUMO now has a high electron density on the nitrogen atoms than the HOMO) state which is highly stabilised by polar solvents. Increasing the solvent dielectric constant enhances the formation of charge-transfer state. This rationalises both the dramatic solvatochromic shifts observed, and the broadness of the emission in methanol. Furthermore, comparison of the solvatochromic behaviour of **82** with paramethoxy-TASB (**104**) structure shown in Figure 2.32) shows that the higher inherent dipole moment arising from the greater number of opposing N-atoms and methoxy substituents in paramethoxy-TASB (**104**) gives a far greater solvatochromic shift (3500 cm^{-1}) in going from hexane to methanol.

2.6.5 Emission studies of fully-fused DASBs **78**, **80** and **82**

The overlaid emission spectra of the fully-fused DASBs **78**, **80**, **82** along with N-HSB (**47**) are shown in Figure 2.49: (a). All three fully-fused DASB derivatives exhibit similar structural features with prominent vibrational spacing ($\sim 1350\text{ cm}^{-1}$) due to the rigid nature of the systems. The methoxy substituted **82** shows bathochromically shifted emission spectrum ($\lambda_{\text{em}} = 475_{\text{max}}, 508$ and 544 nm) compared to the non methoxy

derivatives **78** ($\lambda_{\text{em}} = 475_{\text{max}}, 508$ and 544 nm) and **80** ($\lambda_{\text{em}} = 475_{\text{max}}, 508$ and 544 nm). The electron-donating methoxy substituents in **82** destabilises the HOMO and therefore reduces the HOMO-LUMO gap resulting in a red shifted spectra.

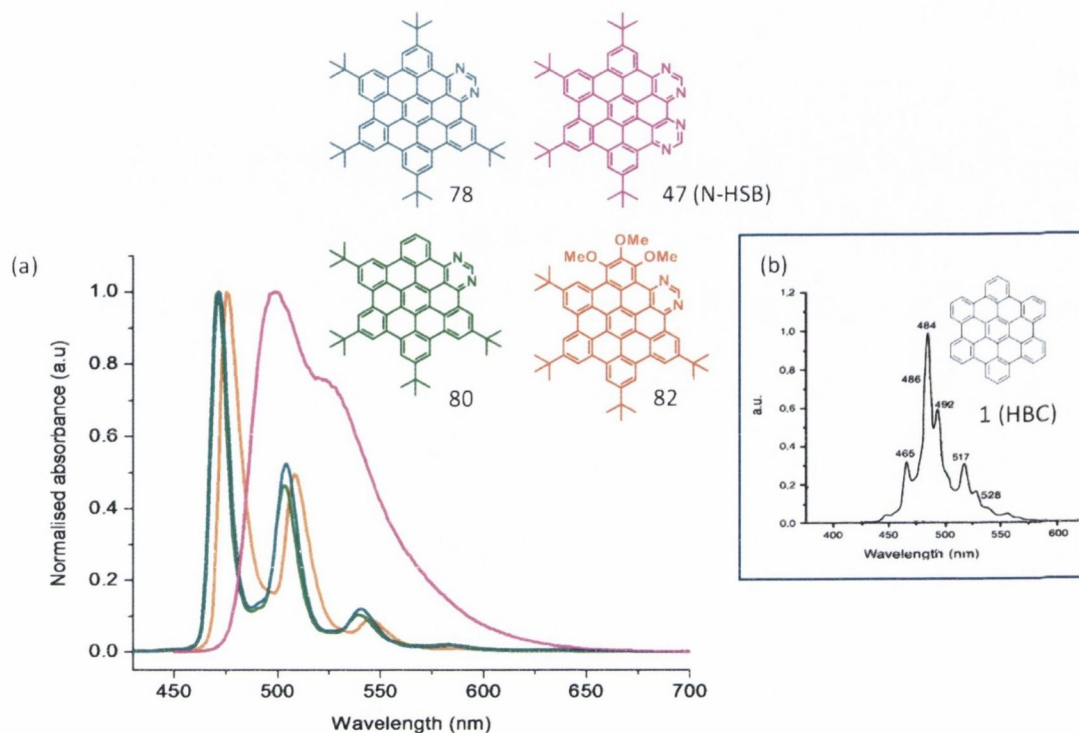


Figure 2.49: (a) Overlaid emission spectra **78**, **80**, **82** and N-HSB (**47**) in toluene with $\lambda_{\text{exc}} = 360$ nm ($\sim 10^{-6}$ M) at R.T. Inset (b) shows fluorescence emission spectrum of HBC in 1,2,4-trichlorobenzene.³²

The inset in Figure 2.49: (b) shows the fluorescence emission spectra of HBC (in 1,2,4-trichlorobenzene) which exhibits a structured spectrum with $\lambda_{\text{em}}^{\text{max}} = 484$ nm. Since the studies were carried out in different solvents it is difficult to compare shifts of the N-doped vs all carbon species. The structural features are similar to those observed for 2N doped systems, however in N-HSB (**47**) the unstructured nature of the band suggests strong interaction between the solvent and the excited state compound. The most important difference between the fluorescence spectra of HBC and N-doped systems is the significant increase in the enhancement of the 0-0 transition. This is expected as the molecular symmetry of the molecule has lowered from D_{6h} for HBC to C_{2v} for **78**. [Figure 2.49: (a) and (b)].

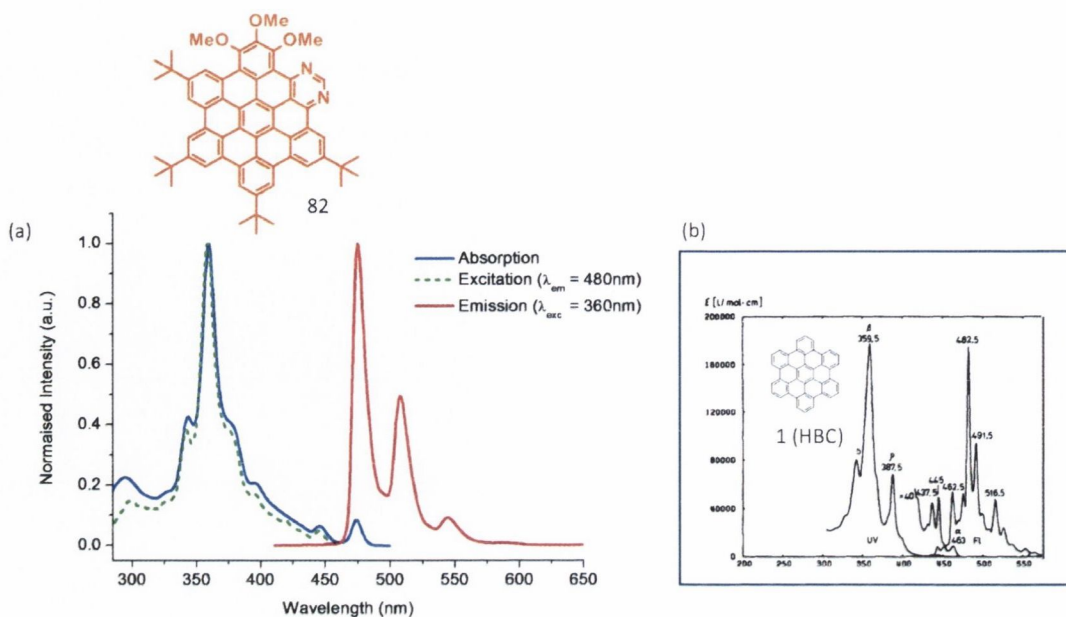


Figure 2.50: (a) The overlaid absorption, excitation and emission spectra **82** in toluene with $\lambda_{exc} = 360\text{ nm}$ ($\sim 10^{-6}\text{ M}$) and (b) absorption and emission spectra of HBC (**1**) in 1,2,4-trichlorobenzene.

82 [Figure 2.50 (a)] shows a clear 0-0 transition at $\lambda = 474\text{ nm}$ in both absorption and emission spectra. The overlap of the 0-0 transitions in the absorption and emission spectra in **82** suggest that there is less solvent stabilisation in the excited state in toluene. Generally, the 0-0 bands lie at slightly different wavelengths in absorption and emission due to the energy loss to the solvent environment. For molecules in solution, the solvent cages surrounding the ground-state and excited-state molecules are different. Since the electronic transitions occur at much faster rates than solvent-cage rearrangement, the energy changes involved in absorption and emission are different. Furthermore, the similarity in the overlaid absorption and excitation spectra for **82** is indicative of a single emitting species at room temperature and also shows that aggregation is not occurring at concentration studied ($\sim 10^{-6}\text{ M}$). The identical behaviour of the two spectra show that there is little configurational change between the ground state (S_0) and the excited state (S_1) due to the structural rigidity of the molecule.

Table 2.7: Emission spectral data of fully-fused DASBs ($a \cdot 10^{-6}$ M; b in CHCl_3).

Compound	Medium (T[K]) ^a	λ_{em} [nm] (λ_{exc} [nm])	τ (ns) (λ_{exc} [nm]/ λ_{em})	Φ_{em} ^b
78	Toluene (298)	471 _{max} , 504, 541 (360)	12 (340/ 470)	0.45
	Butyronitrile (77)	475, 506, 542 _{wk} , 562 _{max} , 604, 617, 656, 675, 687 (360)		
80	Toluene (298)	471 _{max} , 502, 539 (360)	11 (340/ 471)	0.46
	Butyronitrile (77)	485, 519, 568 _{max} , 612, 624, 665, 681 (360)		
82	Toluene (298)	475 _{max} , 508, 544 (360)	8.8 (340/ 475)	0.53
	Butyronitrile (77)	476 _{max} , 510, 545 _{wk} , 558, 615, 686 (360)		
N-HSB (47)	Toluene (298)	494 _{max} , 524 _{sh} (360)	13 (340/ 494)	0.21

Lifetime measurements were carried out on dilute ($\sim 10^{-6}$ M), air-equilibrated toluene solution using the TCSPC method. All lifetimes were best fit using a monoexponential decay regime. All fused DASB derivatives showed similar lifetimes in the ns range (8–12 ns) and is in a similar scale to the lifetime observed for N-HSB (**47**)¹⁰⁰ (Table 2.7). These nanoscale lifetime further confirms that the emission is mainly from the $^1(\pi-\pi^*)$ excited state.¹¹⁷ A series of substituted azacoronene compounds synthesised by Takase *et al.* also show fluorescence lifetime in nanosecond scale.⁵¹

The overlaid room temperature and low temperature emission spectra of **78**, **80** and **82** are presented in Figure 2.51. There are noticeable changes in the emission spectra at 77 K, when compared with their room temperature counterparts. The emission bands of all three spectra have undergone a bathochromic shift with decreasing emission intensities of the main room temperature band at $\lambda \sim 470$ nm. The low temperature bands also have a structured nature which suggests triplet character. The vibrational spacing is in the range of $1600 - 1620 \text{ cm}^{-1}$, indicating C=N stretching frequencies, which suggest emission from $^3(n-\pi^*)$ state. Therefore, it is likely that the broad low temperature emission profile contains two contributions from a $^1(\pi-\pi^*)$ state and a triplet state. According to El-Sayed's rule for intramolecular energy transfer, when S_1 state is $^1(\pi-$

π^*), intersystem crossing to $^3(n-\pi^*)$ state is favoured, while intersystem crossing $^3(\pi-\pi^*)$ state is strongly spin-forbidden.¹¹⁷ The presence of reasonably strong phosphorescence therefore shows that there must be a $^3(n-\pi^*)$ level close in energy to the $^1(\pi-\pi^*)$ and that the molecule either phosphoresces from there or *via* a lower lying $^3(\pi-\pi^*)$. Investigation is ongoing to measure the low temperature lifetimes of these compounds, in order to further understand the nature of this emissive state.

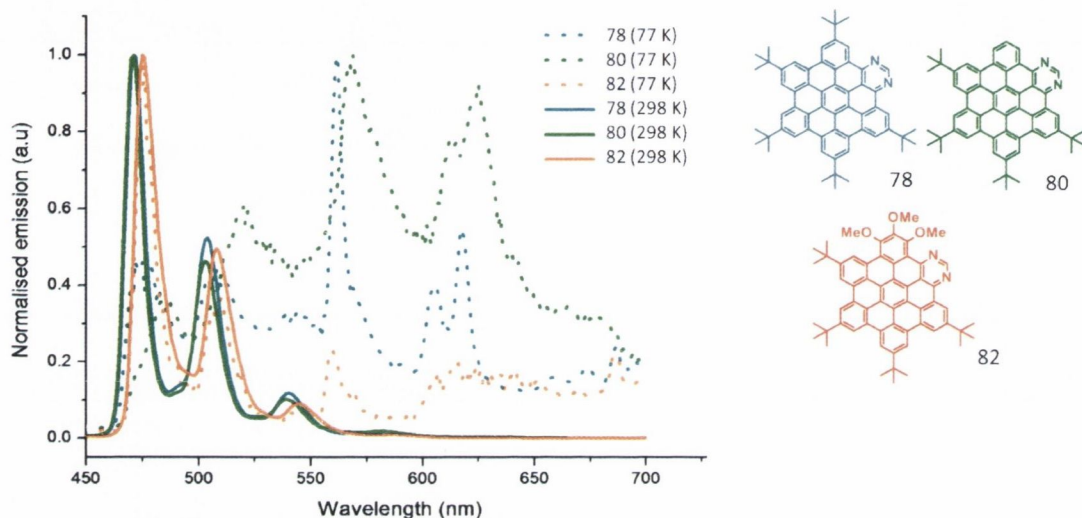


Figure 2.51: Normalised room temperature (–) and low temperature (---) emission spectra recorded for compounds **78**, **80** and **82** in toluene and butyronitrile respectively with $\lambda_{exc} = 360$ nm.

Quantum yields of emissions (ϕ_{em}) for the fully-fused DASB derivatives (**78**, **80** and **82**) were measured using the method of Demas and Crosby, employing a suitable reference compound whose quantum yield is accurately known.¹³⁴ Quinine sulphate in 0.5 M H_2SO_4 solution (λ_{exc} 310 nm, $\phi_{em} = 0.546$) was used as the reference as these references absorb strongly at the chosen excitation wavelength of the sample and emit at a similar region. Corrections were made for the difference in refractive indices of the media used for the standard and the sample. Quantum yields were measured using the equation given below

$$\phi_x = \phi_{ST} \left(\frac{Grad_x}{Grad_{ST}} \right) \left(\frac{\eta_x^2}{\eta_{ST}^2} \right)$$

where *ST* and *x* refer to the standard and the unknown respectively. $Grad_x$ and $Grad_{ST}$ are the gradients of unknown and standard for plots of area under the emission curve vs absorbance and η is the refractive index of the solvents used.

Compound **82** shows the highest emission quantum yield of 0.53, with **78** ($\phi_{\text{em}} = 0.45$) and **80** ($\phi_{\text{em}} = 0.46$) reporting the quantum yields in a similar magnitude. Paramethoxy-TASB (**104**) shows a ϕ_{em} of 0.32 in CHCl_3 . These results show that the peripheral substituents somewhat influence the fluorescence quantum yield of these compounds. Yamaguchi *et al.* has carried out a detailed investigation to study the effect of substituents on HBC periphery and the influence on the fluorescence quantum yields.¹³⁰ Their findings reveal that both electron-donating and electron withdrawing substituents on HBC facilitates in increasing the efficiency of the fluorescence quantum yields in the order of 0.10. Furthermore, the positioning of substituents also play a key role with substituent effect on the HBC core, increasing in the order of *meta*, *ortho* and *para* substituents. Amino-substituted HBC with amino groups at the *para* position showed the highest quantum yield ($\phi_{\text{F}} = 0.33$) with the *para* methoxy substituted HBC displaying a quantum yield of $\phi_{\text{F}} = 0.15$. Both experimental and theoretical calculations carried out by Yamaguchi *et al.* show that the magnitude of the quantum yields are related with the intensity of the α -bands.¹³⁰ Therefore, HBCs with more allowed 0-0 transition have higher fluorescence quantum yields. Taking in to consideration these facts we can surmise that in **82** both the asymmetric nature of the chromophore (therefore, allowed 0-0 transition, Table 2.5) and electron donating trimethoxy groups led to higher quantum yield efficiency ($\phi_{\text{F}} = 0.53$). Also, the additional *tert*-butyl group in **78** has a negligible influence on the chromophore resulting quantum yields in a similar range for both **78** ($\phi_{\text{em}} = 0.45$) and **80** ($\phi_{\text{em}} = 0.46$).

2.6.6 Emission studies of partially fused DASB derivatives

The emission spectra of the partially fused DASB derivatives (Figure 2.52) are all hypsochromically shifted with respect to their fully-fused counterparts (Figure 2.49:). This is due to the reduction in the degree of π -conjugation and rigidity of the systems. Furthermore, the vibronic progressions of the fully-fused systems have been lost, which results in broad structureless emissions in partially fused systems. Methoxy-substituted **83** and **86** show the most red-shifted emission spectra due to the electron donating methoxy substituents increasing the energy of the HOMO and thereby reducing the HOMO-LUMO gap.

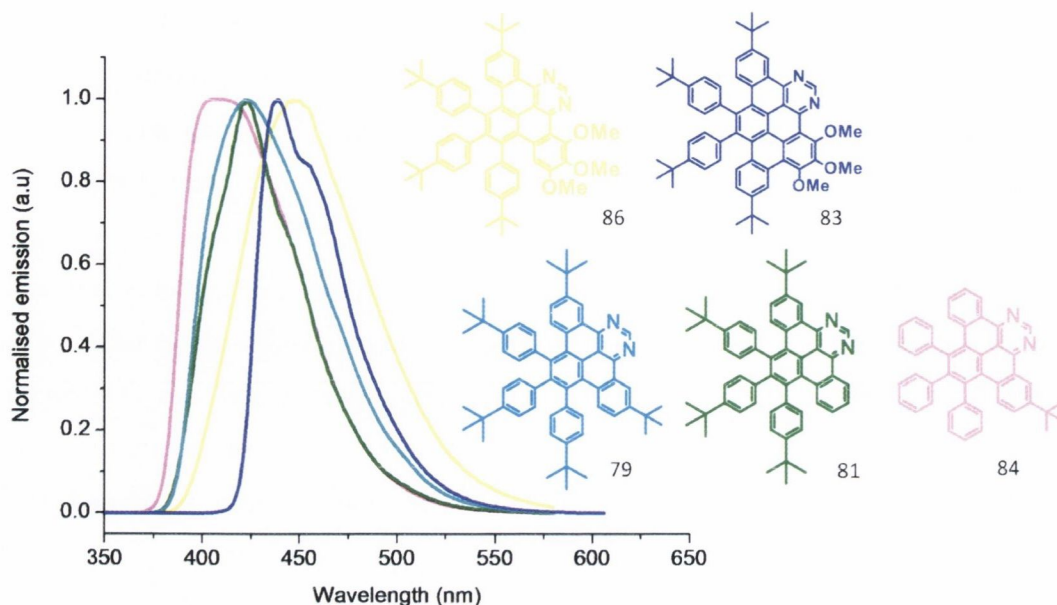


Figure 2.52: Overlaid emission spectra partially fused DASB derivatives in toluene with $\lambda_{exc} = 300$ nm for **79**, **81**, **84** and **86** and $\lambda_{exc} = 313$ nm for **83** ($\sim 10^{-6}$ M) at R.T.

All partially fused DASB derivatives showed similar short lifetimes in the ns range (2–4 ns). Quantum yields of the compounds **79**, **81** and **83** were measured using Demas and Crosby method as discussed for the fully-fused counterparts, using quinine sulphate in 0.5 M H_2SO_4 solution as the reference. $\frac{1}{3}$ -Fused **79** ($\phi_{em} = 0.057$) and **81** ($\phi_{em} = 0.06$) reported very low quantum yields with $\frac{1}{2}$ -fused **83** ($\phi_{em} = 0.21$) reporting a slightly higher value. Radiationless intramolecular IC and ISC processes compete with emission of fluorescence thereby reducing the quantum yield. In these partially fused molecules, the free rotating aryl rings provide a deactivation pathway for the excited state *via* radiationless pathways thus resulting in low quantum yields.

Table 2.8: Emission spectral data of partially fused DASBs in toluene ($\sim 10^{-6}$ M) at R.T.

Compound	λ_{em} [nm] (λ_{exc} [nm])	τ (ns) (λ_{exc} [nm]/ λ_{em})
79 ($\frac{1}{3}$ -fused)	423 (300)	2.0 (340/ 420)
81 ($\frac{1}{3}$ -fused)	423 (300)	2.3 (340/ 420)
83 ($\frac{1}{2}$ -fused)	438, 457 (313)	3.54 (340/44)
84 ($\frac{1}{3}$ -fused)	410 (300)	3.5 (340/ 410)
86 ($\frac{1}{3}$ -fused)	450 (300)	3.3 (340/ 450)

2.6.7 Electrochemical properties of DASB derivatives

To further understand the relative positions of the HOMO and LUMO levels in DASB systems, electrochemical measurements were undertaken. Cyclic voltammetric studies for DASB derivatives **78-84** were carried out in 1 mM solutions of CH_2Cl_2 (0.1 M $n\text{Bu}_4\text{NPF}_6$) using Ag/AgCl electrode or SCE as the reference electrode, a Pt wire as the counter electrode and glassy carbon working electrode. All the potentials are quoted vs the Fc/Fc^+ couple (0.0 V) and referenced to internal to ferrocene added at the end of each experiment.

In order to compare the effect of N-doping on the electrochemical properties, redox values of the tert-butyl functionalised hexabenzocoronene [^tBu -HBC (**1b**)] were compared with the 2N (**78**) and 4N [N-HSB (**47**)] analogues. Herwig et al. has reported oxidation ($E_{1/2} = +0.99$ V, $+1.42$ V in CH_2Cl_2) and reduction ($E_{1/2} = -2.10$ V, -2.40 V) potentials for ^tBu -HBC (**1b**) vs SCE.³⁹ For ease of comparison the potentials were converted to Fc/Fc^+ scale (based on values reported by Geiger *et al.*¹³⁵ for different organic solvents) and tabulated in Table 2.9 along with the fully-fused DASB derivatives. Figure 2.53 shows the electrochemical spectra for **78**, **80** and **82**.

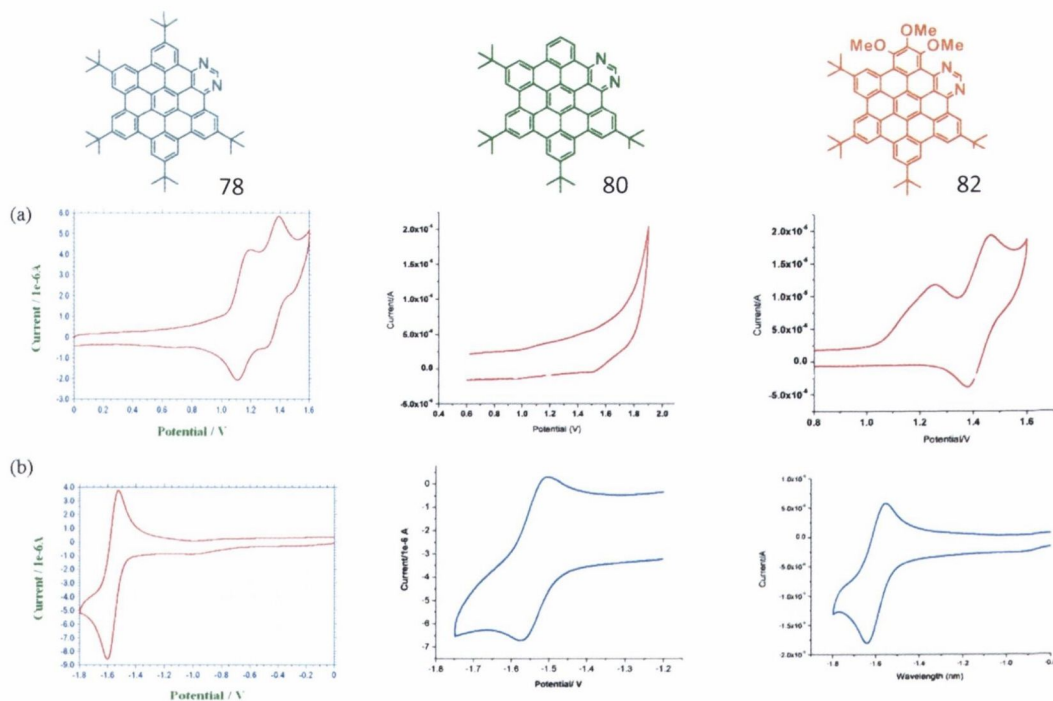


Figure 2.53: Cyclic voltammograms of **78**, **80** and **82** showing (a) oxidation and (b) reduction in 1 mM solutions of CH_2Cl_2 (0.1 M $n\text{Bu}_4\text{NPF}_6$) using Ag/AgCl electrode (in **80**) or SCE (in **78** and **82**) as the reference electrode.

DASB **78** shows a reversible oxidation waves at $E_{1/2}$ +0.70 V, +0.89 V and its trimethoxy substituted counterpart **82** present an irreversible first oxidation wave at anodic potential (E_{pa}) of +0.78 V along with a reversible second oxidation wave at +0.997 V. By comparing the first oxidation waves of **78** and **82** it is evident that **78** is easier to oxidise than **82**. This is further emphasised by the second oxidation potentials. It was anticipated that incorporation of electron donating trimethoxy units would destabilise the HOMO and therefore make the oxidation of **82** relatively easier at a lower oxidation potential compared to **78**. In the case of N-HSB (**47**) vs Paramethoxy-TASB (**104**) there is a significant lowering of first oxidation potential with incorporation of 6 methoxy units increasing the energy of the HOMO thereby makes removing an electron easier from the HOMO. Corresponding reduction waves show no change and appears in a similar region for both compounds at $E_{1/2}$ = -2.02 V. Unusually, **80** did not show any oxidation within the spectral window analysed but shows a reversible reduction at $E_{1/2}$ = -2.03 V. This shows that the changes in functionalisation do not have any significant impact on the LUMO of the DASB compounds under investigation.

Table 2.9: Electrochemical data for fully-fused DASBs **78**, **80** and **82** along with N-HSB (**47**), paramethoxy-TASB (**104**) and hexa-tert-butyl-hexa-peri-hexabenzocoronene [^tBu-HBC (**1b**)].

Compound	Oxidation $E_{1/2}$ /V [ΔE_p mV]	Reduction $E_{1/2}$ /V [ΔE_p (mV)]
78	+0.70 [90], +0.89 [85]	-2.02 [83]
80	-	-2.03 [73]
82	+0.78, +0.997 [79]	-2.02 [89]
47 (N-HSB - 4N) ^[54]	+0.9 ^b	-1.56 [60], -2.00 [102], -2.32
104 [Paramethoxy-TASB (4N)]	+0.65, +0.82, +1.03	-1.62 [79], -1.80 [78], -1.94 [89]
1b [^t Bu-HBC] ^[39]	+0.53, +0.88	-2.66, -2.96*

In deoxygenated dichloromethane (0.1 M, ⁿBu₄NPF₆) at 298K, scan rate = 100 mV s⁻¹, reported vs. Fc/Fc⁺; ^b Irreversible/quasi-reversible oxidation process, E_{pa} /V (anodic peak potential) quoted; ^c ΔE_p = E_{pa} - E_{pc} , peak potential separation.; ^d Reversible oxidation process, $E_{1/2}$ /V [ΔE_p /mV] quoted.* reported in THF.

In comparison of the methoxy substituted systems **82** and Paramethoxy-TASB (**104**), is the most readily oxidised, presenting an irreversible wave at an anodic peak potential (E_{pa}) of 0.65 V vs. Fc/Fc^+ vs **82** (E_{pa} 0.78 V). This behaviour can be rationalised by considering the substitution pattern of the compounds. The six electron donating methoxy groups on the para-trimethoxyphenyl groups of Paramethoxy-TASB (**104**) act to destabilize the HOMO. The lower number of electron donating substituents on **82** raises their oxidation potentials by stabilising the HOMO. Under a reducing potential, it is observed that the compounds containing the most electron-withdrawing N-atoms are the most easily reduced: **82** (2 N atoms) displays a reversible reduction wave at $E_{1/2}$ - 2.02 V, compared with Paramethoxy-TASB (**104**), which is cathodically shifted to $E_{1/2}$ - 1.62 V due to the LUMO-destabilising effects of its six methoxy substituents.

The first oxidation waves of ^tBu-HBC [(**1b**)-all carbon] $E_{1/2} = +0.53$, **78** (2N) $E_{1/2} = +0.70$ and N-HSB [(**47**)-4N] $E_{pa} = +0.90$ show that the ease of oxidation reduces with increasing the degree on N-dopants. This behaviour can be rationalised by the depletion of the electron density of the aromatic platform with increasing the number of N atoms. As a result it further stabilises the HOMO and makes the oxidation most difficult in 4N doped N-HSB. The corresponding reduction potentials show that the compounds containing the most electron withdrawing nitrogen atoms are the most easily reduced. Therefore, N-HSB is the most easily reduced with first reduction potential at $E_{1/2} = -1.56$ V followed by **78** $E_{1/2} = -2.02$ V. All carbon analogue ^tBu-HBC is the most difficult to reduce showing a high first reduction potential at $E_{1/2} = -2.66$ V.

Table 2.10: Electrochemical data for partially fused DASBs.

Compound	Oxidation E_{pa} (mV) ^b	Reduction [ΔE_p (mV)]
79 (1/3-fused)	+1.12	-2.07 [40]
81 (1/3-fused)	+1.15	-2.24 [119]
83 (1/2-fused)	+0.86	-2.10 [95]
84 (1/3-fused)	+1.23	-2.23 [108]
85 (1/3-fused)	+0.91	-2.26 [45]

In deoxygenated dichloromethane (0.1 M, ⁿBu₄NPF₆) at 298K, scan rate = 100 mVs⁻¹, reported vs. Fc/Fc^+ ; ^b Irreversible/quasi-reversible oxidation process, E_{pa}/V (anodic peak potential) quoted; ^c $\Delta E_p = E_{pa} - E_{pc}$, peak potential separation.; ^d Reversible oxidation process, $E_{1/2}/V$ [$\Delta E_p/mV$] quoted.

Table 2.10 shows the electrochemical results for the partially fused DASB derivatives. Examination of the relevant oxidation waves of each derivative shows that the $\frac{1}{2}$ -fused methoxy system **83** has the lowest oxidation potential ($E_{\text{pa}} = +0.86$ V). The lowered aromaticity of the $\frac{1}{3}$ rd derivatives serves to further stabilise its HOMO resulting in higher anodic potential. **85** shows a relatively lowered first oxidation potential and could be as a result of the electron donating methoxy substituents destabilising the HOMO. The corresponding reduction potentials does not show prominent trend with respect to the changes in substitution/degree of aromaticity in the partially fused DASBs. These systems are far more difficult to reduce compared to their fully-fused counterparts, due to its reduced aromaticity and relatively destabilised LUMO.

2.7 Conclusions

This chapter details the synthesis and characterisation of a novel family of 2N-doped heterosuperbenzenes [diazasuperbenzenes (DASB)] with varying peripheral functionalisation. The main objective of this work was to investigate the chemical, physical and electronic consequences brought about by changes in the degree of N-doping and substitution in comparison with the parent N-HSB molecule. The polyphenylene precursors to DASBs (**73** - **77**) were synthesised *via* the [2+4]-Diels-Alder cycloaddition reaction between a suitably functionalised cyclopentadienone and an arylacetylene. The nitrogens were incorporated into the hexaaryl derivatives *via* a monopyrimidyl substituted acetylene unit. Microwave-assisted Sonogashira cross coupling reactions were employed to synthesise the acetylene precursors in good yields with short reaction times.

The oxidative cyclodehydrogenation of the polyphenylene precursors (**73-75**) were attempted *via* two routes: (i) FeCl_3 route and (ii) DDQ/H^+ route. The oxidative cyclodehydrogenation of polyphenylenes **73** and **74** *via* the FeCl_3 route resulted in the successful synthesis of fully-fused DASB **78** and **80** along with the $\frac{1}{3}$ -fused (two C-C bonds fused) **79** and **81**. Methoxy-functionalised **75** resulted in the fully-fused **82** and $\frac{1}{2}$ -fused (three C-C bonds fused) **83**. The fully-fused **82** was isolated in relatively high yield compared to **78** and **80**, showing that incorporation of electron donating methoxy functional groups increases the efficiency of the Scholl reaction. Oxidative cyclodehydrogenation of the tetracyclone-derived polyphenylenes **76** and **77** *via* the FeCl_3 route resulted only resulted in the $\frac{1}{3}$ -fused (two C-C bonds closed) products (**84**

and **85**) and proved the importance of electron donating *tert*-butyl groups on the ring closure of the N-doped systems.

The DDQ/H⁺ route has not been previously investigated as a method for synthesising N-doped polyphenylenes. Oxidative cyclodehydrogenation of polyphenylenes **73-75** was studied *via* the DDQ/H⁺ route, resulting in the 1/3rd-fused (two C-C bond fused) products (**79**, **80** and **86**) in high yields and relatively facile purification. Interestingly, the two C-C bond formations occurred on either side of the pyrimidine ring, as in the FeCl₃ route, suggesting that the pyrimidine rings is the preferred site for initiation of the oxidative cyclodehydrogenation process, irrespective of the route employed.

The single crystal X-ray diffraction studies of polyphenylenes **73**, and **74**, the 1/3rd-fused counterpart (**84**) and the fully-fused DASB product (**82**) provided an useful insight to solid-state properties of these systems. Both polyphenylenes **73** and **74** exhibit a propeller-like structure, with the six aryl substituents twisted at angles varying from 60° to 79° from the plane of the central benzene ring. In the 1/3rd-fused **84**, the fused portion of the molecules shows a twisted nature with respect to the central phenyl ring, with the free phenyl rings being markedly more perpendicular. The analysis of the single crystal structure of fully-fused **82** reveals that the positioning of the methoxy groups has a profound effect on the supramolecular order observed in these crystalline nanographenes. The propensity for methoxy groups to engage in weak H-bonding appears to assist the molecules to orient in a head-to-tail arrangement within columnar π - π stacks. These results are promising, as the interlayer control is of paramount importance in device fabrication for usage in OLEDs.

The photophysical and electrochemical studies were important to identify the structure-property relationships of these N-doped molecular graphenes. The absorption spectra of the 2N polyphenylenes (**73-77**) feature broad, unstructured absorption and emission spectra in the UV region. The fully-fused DASB systems (**78**, **80** and **82**) of the molecules show well-resolved absorption and emission owing to the structural rigidity of the molecules. Both absorption and emission spectra were bathochromically-shifted due to the increased aromaticity of the platform. The electron-donating methoxy substituents in **82** shows the most red-shifted emission spectrum ($\lambda_{\text{max}} = 475_{\text{max}}$) indicating a small HOMO-LUMO gap due to destabilisation of the HOMO. Furthermore, the observed solvatochromic shifts ($\sim 1630 \text{ cm}^{-1}$) in methoxy-functionalised **82** is indicative of the significant inherent dipole moment of the fully-

fused systems. **82** shows the highest emission quantum yield of 53 % and in general, all fused DASBs showed higher quantum yields than their 4N counterparts.

Emission lifetimes of fully-fused DASB's were in the ns scale (~ 8 -12 ns) and suggest π - π^* emissive state at room temperature. The low temperature emission (77 K) spectra of **78**, **80** and **82** show noticeable changes compared with their room temperature emissions. Spectra were bathochromically shifted and displayed decreasing emission intensities of the bands at $\lambda \sim 470$ nm. The new bands appearing at low temperature have a structured nature which suggests triplet character. The preliminary results suggest emission from $^3(n-\pi^*)$.

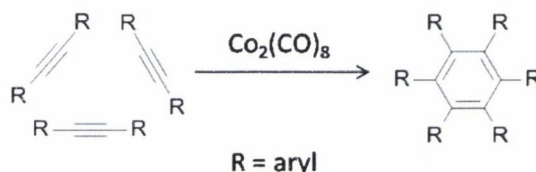
The information ascertained from the photophysical measurements correlates well with their electrochemical properties. An increase in the number of electron-donating methoxy groups destabilises the HOMO, thereby promoting easier oxidation. This effect, along with an increase in the number of electron-accepting nitrogen atoms (which serves to stabilise the LUMO), allowed us to effect a reduction in the HOMO-LUMO gap. These results are promising as they show that we are able to control the electronic properties of these molecular graphene systems through functionalisation, without the need for further extension of the aromatic platforms.

3. Hexaazasuperbenzenes: Synthesis and Characterisation

3.1 Introduction

This chapter describes the synthesis and structural/photophysical characterisation of a series of novel 6N-doped heterosuperbenzenes called hexazasuperbenzenes (HASB) with varying functional groups around the periphery. This chapter consists of a brief introduction, followed by two main sections. It comprises (i) the synthesis of 6N-doped hexaarylbenzenes *via* the [2+2+2] cyclotrimerisation route, along with their oxidative cyclodehydrogenation to develop hexaazasuperbenzene (HASB) followed by (ii) spectroscopical characterisation and consequent structural/photophysical characterisation.

3.1.1 [2+2+2] cyclotrimerisation

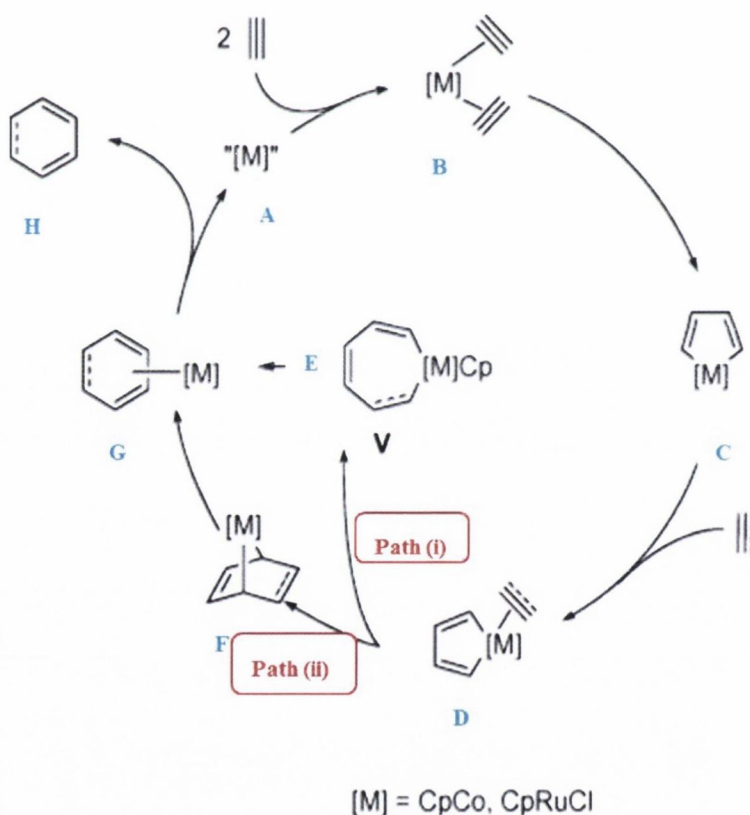


Scheme 3.1: Schematic representation of intermolecular [2+2+2]-cycloaddition.

[2+2+2] cycloadditions involving alkynes have been used to generate annulated benzene derivatives and is known as an elegant method for the construction of polycyclic aromatics (Scheme 3.1). Since Berthelot's discovery of benzene formation *via* thermal cyclization of three acetylene molecules in 1866,¹³⁶ several advances in this area have been made. A major breakthrough was when Reppe *et al.*¹³⁷ developed the first synthesis of transition metal catalysed [2+2+2] cycloaddition in 1948. Since then, organic chemists have used transition metal catalysed [2+2+2] cycloaddition as an atom-efficient and functional group tolerant reaction for aromatic ring formation. A range of carbo- and heterocycles have been synthesised using various unsaturated substrates such as alkynes, nitriles, alkenes, imines, isocyanates and isothiocyanates.^{138, 139} Various transition metals such as Co, Fe, Ni, Pd, Re, Rh and Ru have been explored as potential catalysts.¹⁴⁰⁻¹⁴³ Among these catalysts, non-expensive cobalt complexes have proved to be versatile reagents for achieving good chemo-, regio- and stereoselectivities with high product yields.¹⁴⁴ Vollhardt *et al.*⁶² have pioneered the work in the area of cobalt mediated cyclotrimerisation and have used cobalt-based catalyst in the preparation of various natural products, pharmaceutically significant

molecules and functional materials.^{144 145} $[\text{CpCo}(\text{CO})_2]$ has proved to be the most popular and versatile reagent of the cobalt catalyst family, for $[2+2+2]$ cyclotrimerisation of alkynes. Generally, cyclotrimerisations are carried out under refluxing conditions in organic solvents. Recently various other reaction media have been also reported including aqueous media¹⁴⁶ and ionic liquids.¹⁴⁷

Various experimental and theoretical studies have been carried out to elucidate the reaction pathway of $[2+2+2]$ cyclotrimerisation. The mechanistic rationale of these processes depends on several factors, including the nature of the metal, ligands and substrate partners. Scheme 3.2 depicts a general pathway proposed based and show that the intermolecular trimerisation can proceed *via* two different routes involving either a cycloheptatriene [Path (i)] or a norbornadiene [Path (ii)] intermediate.

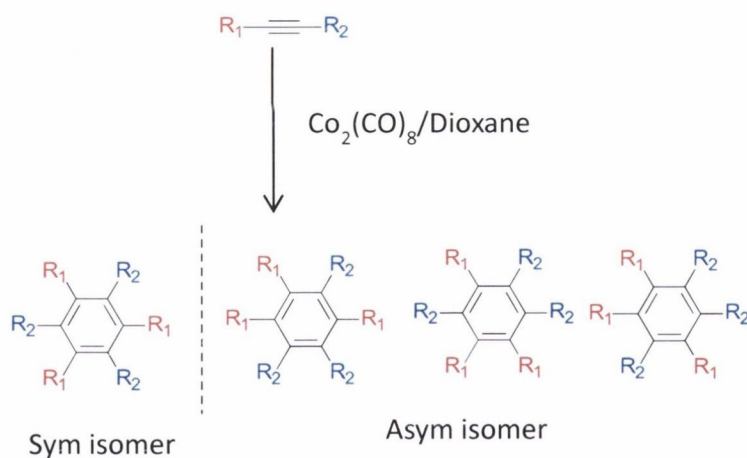


Scheme 3.2: The general mechanism of cyclotrimerisation of alkynes.¹³⁸

Initially, two alkyne partners coordinate to the metal (A) and the resulting complex B forms metallacyclopentadiene C by subsequent oxidative coupling. The third unsaturated partner coordinates to give D, which follows two possible paths: (i) insertion into the M–C bond to give cycloheptametallacycle E, which after reductive elimination gives complex G, or (ii) intramolecular $[4+2]$ cycloaddition to form bicyclic

complex F, which after isomerization affords complex G. Finally, decoordination of the metal produces the cycloadduct H.

Mullen *et al.* have explored [2+2+2] cyclotrimerisation as a convenient route to generate hexaphenylbenzene derivatives in a single step (Scheme 3.1).^{52, 62, 148} Furthermore, this approach has been used to develop larger polyphenylene systems where the hexaphenylbenzene core remains intact. The choice of the appropriate catalyst is key to the success of the synthesis and $[\text{Co}_2(\text{CO})_8]$ has appeared as a good candidate for the cyclotrimerization of alkynes. In this work, we mainly focused on using $[\text{Co}_2(\text{CO})_8]$ as the catalyst for development of 6N polyphenylene precursors using asymmetric acetylenes. [2+2+2] cyclotrimerisation of a symmetric acetylene gives rise to a single isomer, whereas two polyphenylene isomers are generally formed on the trimerisation of disubstituted alkynes: the symmetric (sym) isomer (in which a C_3 rotational axis exists) and the asymmetric isomer (with no rotational axis). On statistical grounds the sym:asym product ratio should be 1:3 based on the arrangement of the substituents (Scheme 3.3).



Scheme 3.3: Illustration of the 1:3 statistical ratio of symmetric: asymmetric products on the trimerisation of an asymmetric alkyne.

Various studies have shown that several factors influence the ratio of the symmetric and antisymmetric isomer formed. These include the temperature, solvent, the ligands attached to the metal precursor, the size of the substituent on the alkyne been trimerised and the presence of any other metal in the reaction mixture.¹⁴⁹ Hilt and coworkers^{150, 151} have shown that when the substituents differ significantly either electronically or sterically, the relative concentration of the asymmetric isomer increases. The trimerisation of acetylenes going *via* the norbornene-type intermediate is the route

expected for aromatically substituted alkynes. As the norbornene-like intermediate is more sterically hindered at the two quaternary positions, the alkynes will trimerise in such away as to minimize the hindrance at these positions. If the substituents at the alkyne are significantly different the smaller of the two will take up the quaternary position and as a result the antisymmetric isomer of the trimerised product is favoured. This phenomenon has been observed by Dr. Colin Martin, in the Draper group upon cyclotrimerisation of both 3-thienylethylene and 2-thienylethylene, resulting only in the asymmetric isomer being formed.¹⁵²

3.1.2 Aims of this work

Based on successful synthesis of both diazasuperbenzene (2N) and tetraazasuperbenzene (4N) families, the aim of this chapter is to investigate the chemical and photophysical properties of a 6N doped hexasuperbenzene (HASB) family. The initial target molecules are shown in Figure 3.1. Generally, the [2+4] Diels-Alder reaction is widely used in the synthesis of polyphenylene precursors and is the only route explored so far for the generation of N-doped polyphenylenes. As discussed in Chapter 2, this route involves a multi step synthesis for the generation of the polyphenylene precursors. To best of our knowledge [2+2+2] cyclotrimerisation has not been explored for the generation of N-doped polyphenylenes. Cyclotrimerisation of dipyrimidyl acetylene has previously been attempted by Mullen *et al.* and was unsuccessful due to the formation of a stable cobalt complex.²⁶



Figure 3.1: Target molecules of the HASB family.

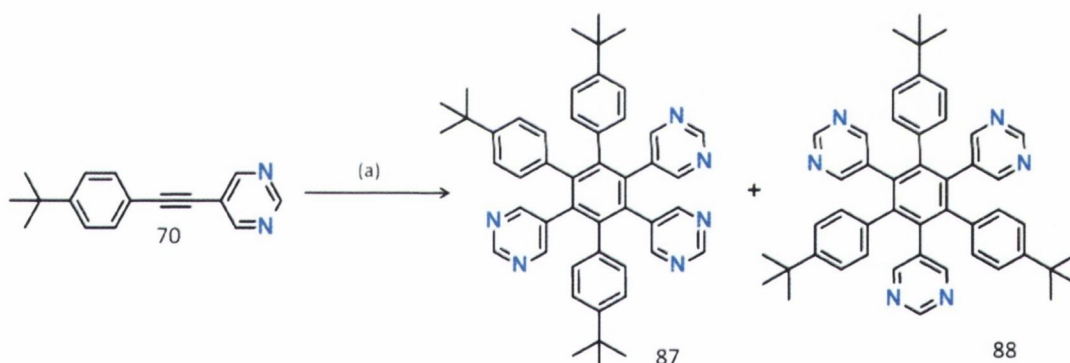
This work aims to explore [2+2+2] cyclotrimerisation as a novel convenient route to 6N-doped polyphenylene precursors using a series of monopyrimidyl acetylenes with $Co_2(CO)_8$ as the catalyst. We further aim to oxidatively cyclodehydrogenate the 6N doped polyphenylenes to develop a hexaazasuperbenzenes (HASB) and explore the

photophysical and supramolecular influences brought about by the increasing the degree of N-doping and nature and position of the substituents compared with the 2N and 4N doped systems.

3.2 Synthesis and characterisation of Hexaazasuperbenzenes

3.2.1 Synthesis and characterisation of polyphenylenes **87** and **88**

Dicobalt octacarbonyl catalysed cyclotrimerisation of **70** gives two products: asymmetric 3,5,6-tri-(4-*tert*-butylphenyl)-1,2,4-tri(5-pyrimidyl)benzene (**87**) and symmetric 2,4,6-tri(4-*tert*-butylphenyl)-1,3,5-tri(5-pyrimidyl)benzene (**88**) [Scheme 3.4]. The two products were successfully isolated by column chromatography eluting with CH₂Cl₂:CH₃OH (1:0.04). In this solvent system **88** showed a R_f of 0.31 and **87** a R_f of 0.57. Both **87** and **88** were isolated as white crystalline solids in 27 % and 68 % yields respectively, showing an approximately ratio of 3:1 for asymmetric (**87**) and symmetric (**88**) products.



Scheme 3.4: Synthetic route to 6N polyphenylenes **87** and **88**; (a) Co₂(CO)₈, dioxane, 115 °C, 24 h, under N₂.

The ¹H-NMR spectra of novel symmetric (**88**) and asymmetric (**87**) polyphenylenes are shown in Figure 3.2. Compound **88** exhibits a simpler spectrum due to the presence of a C₃ symmetry axis. In both spectra, the most deshielded signals in the δ 8.81- 8.22 ppm region are due to the pyrimidine ring protons, with the most downfield singlet at δ = ~ 8.8 ppm attributed to the proton between the two nitrogens (H1). In comparison with the 2N polyphenylenes the pyrimidyl proton signals in 6N polyphenylenes are further deshielded by ~ 0.1 ppm. The aryl ring protons appear in the region (δ = 7.04 - 6.70 ppm) in both spectra.

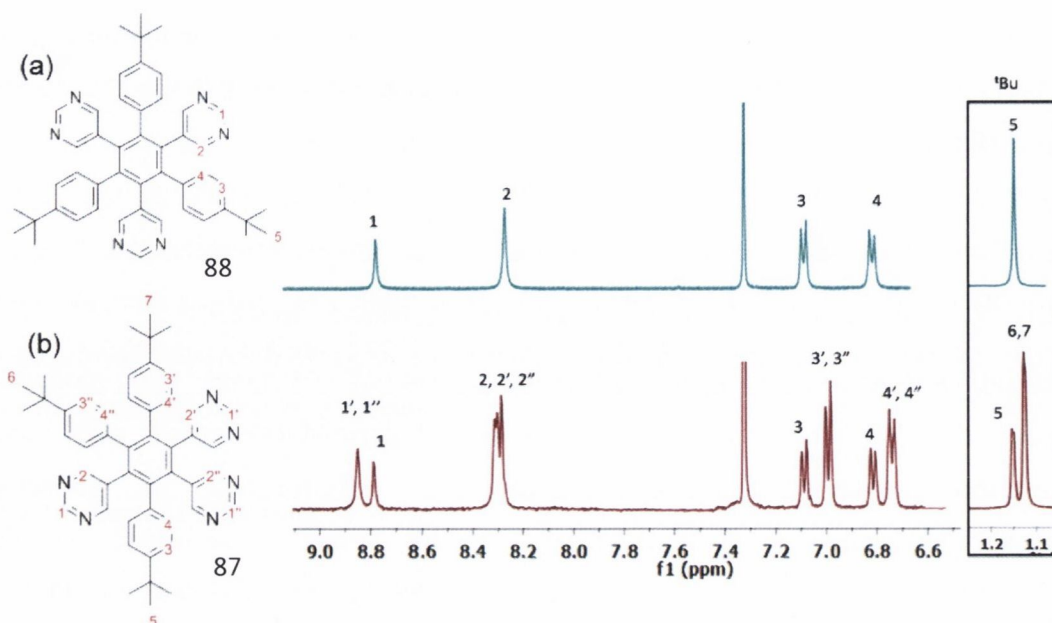


Figure 3.2: ^1H NMR spectra of **87** and **88** in CDCl_3 at RT, 400 MHz (a) aromatic region (b) aliphatic region for *tert*-butyl groups. (a) and (b) are not drawn on the same scale.

Compound **88** shows only two doublets (H3 and H4) with an AB pattern, whereas **87** exhibits more signals as expected due to the asymmetric nature of the compound. All the *tert*-butyl signals in **88** appear as a single signal at $\delta = 1.1$ ppm, integrating for 27 protons. The aliphatic region of **87** shows two singlets at $\delta = 1.15$ ppm and $\delta = 1.12$ ppm for *tert*-butyl protons, integrating for 9 and 18 protons respectively. Two *tert*-butyl signals (labeled '6' and '7') are overlapped at $\delta = 1.12$ ppm. The assignment of the signals in both spectra was aided by various 1D and 2D NMR techniques and the detailed assignment of compound **87** will be discussed next.

In the ^1H - ^1H COSY spectrum of **87** [Figure 3.3 (a)], the most downfield signals at $\delta \sim 8.8$ ppm and $\delta \sim 8.3$ ppm does not show any correlations with any other aromatic signals, confirming the assignment as pyrimidyl protons. This assignment was further supported by the HSQC spectrum, with the correlated carbons appearing in the 155–158 ppm region [Figure 3.3 (b)]. Apart from the pyrimidyl rings, compound **87** consists of three AB spin systems, for each *tert*-butyl substituted aromatic ring. They appear as a series of doublets in the region $\delta \sim 7.1$ – 6.7 ppm, with H3 and H4 appearing as a well separated set of doublets with 3J splitting of 8.0 Hz.

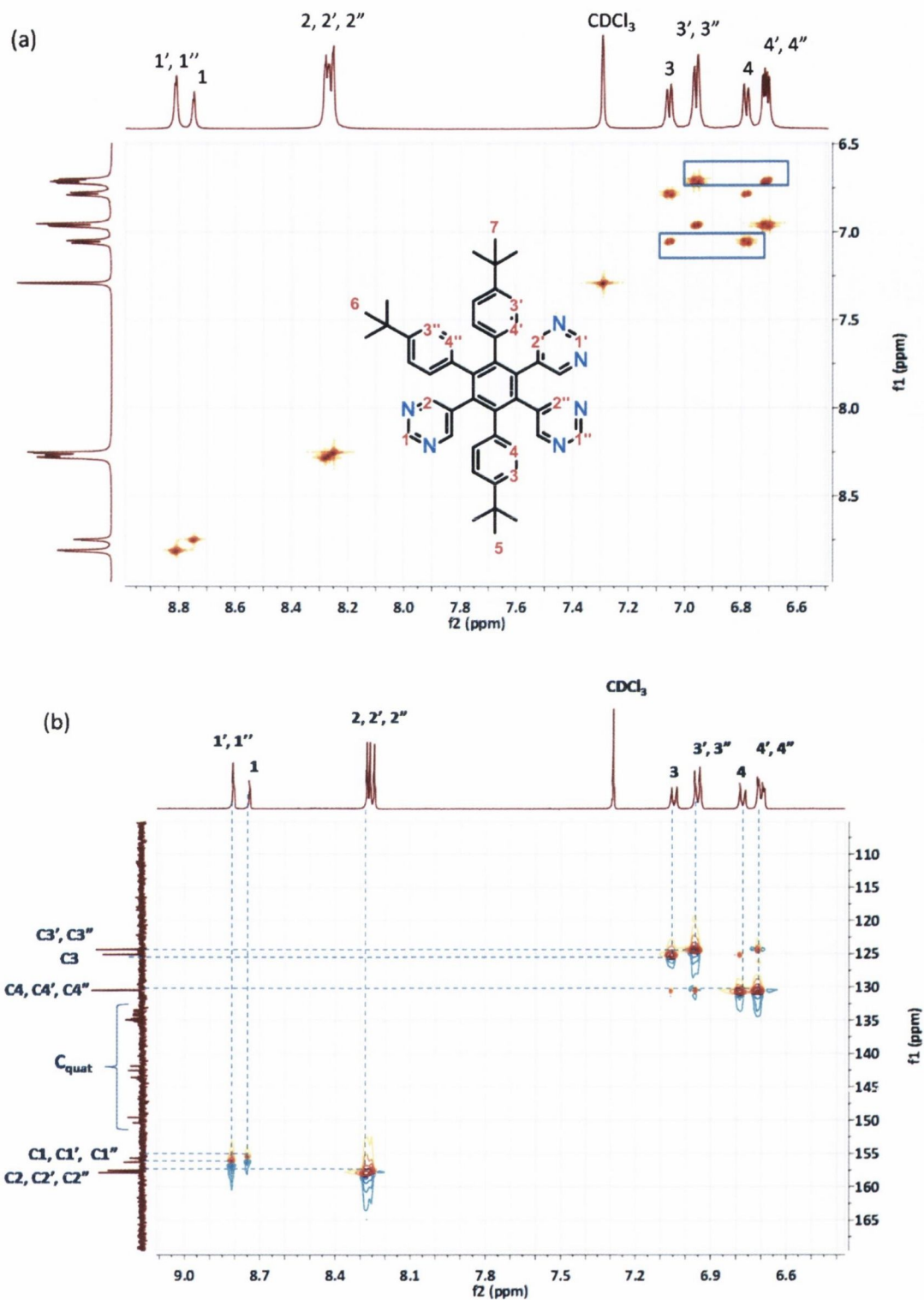


Figure 3.3: Aromatic region of the (a) ^1H - ^1H COSY spectrum (b) ^{13}C - ^1H COSY of **87** in CDCl_3 at RT, 600 MHz.

X-ray structure analysis of **88**

The successful preparation of the two isomers was further confirmed by obtaining a crystal structure of the asymmetric isomers **88**. Colourless single crystals of **88** suitable for single crystal X-ray analysis were obtained by crystallising from a CH_2Cl_2 /ethyl acetate solvent system. **88** crystallises in a triclinic, P-1 space group with the asymmetric unit consisting of two molecules of **88** and a water molecule. The unit cell consists of four molecules of **88** and two water molecules. The crystals show reasonably good quality data with $R1 = 8.07\%$, $wR2 = 14.03\%$.

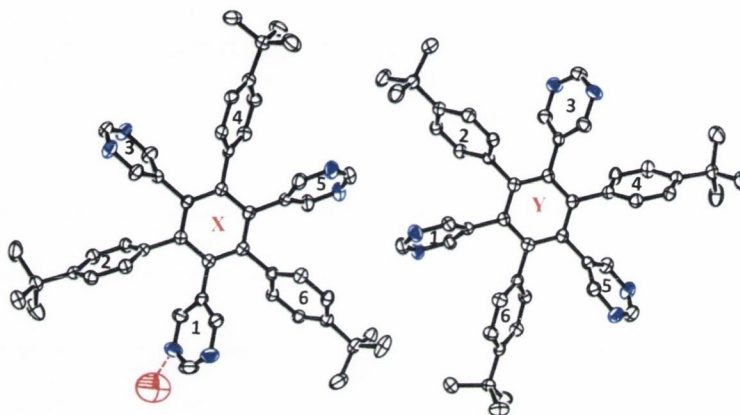


Figure 3.4: The asymmetric unit of **88** (hydrogen atoms are omitted for clarity).

The molecule has a propeller-like structure, with the six aryl substituents twisted at angles varying from 58 – 76° from the plane of the central benzene ring. This arrangement relieves the steric strain between the aromatic hydrogens. The tilt angles are similar to the values observed for 2N- (discussed in Chapter 2) and 4N-doped polyphenylenes synthesised within the Draper group.^{53, 60} In **88**, the asymmetric unit consists of two molecules of **88** and a water molecule (Figure 3.4). There is a hydrogen bonding interactions between a nitrogen atom in of pyrimidine ring 1 and the water molecule ($\text{N}\cdots\text{H}-\text{O} = 2.784(6) \text{ \AA}$) as depicted in Figure 3.4. This interaction is important in the crystal packing arrangement of **88** and helps to hold the molecules together in the lattice (Figure 3.5).

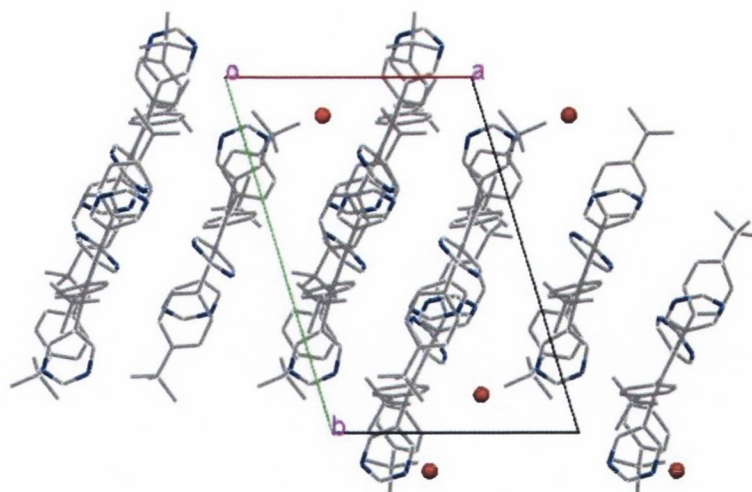
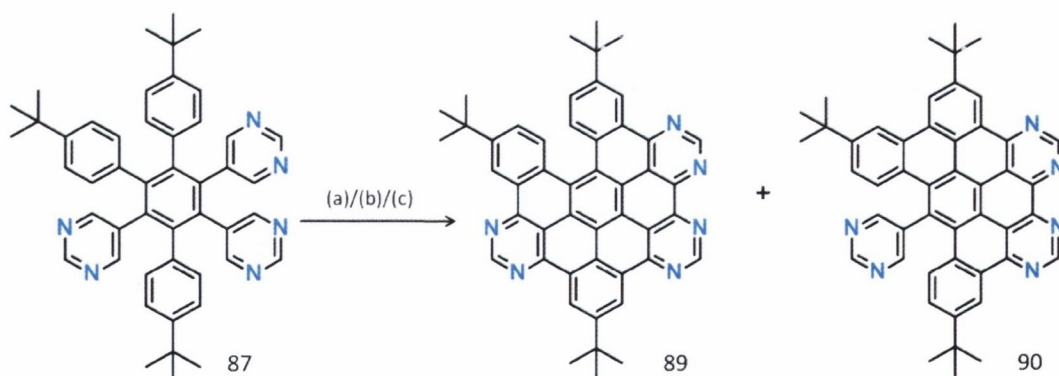


Figure 3.5: Molecular packing arrangement of **88** viewed along the 'c' axis.

3.2.2 Oxidative cyclodehydrogenation of **87**

The oxidative cyclodehydrogenation of **87** was attempted *via* three routes (i) $\text{AlCl}_3/\text{CuCl}_2/\text{CS}_2$ (ii) $\text{FeCl}_3/\text{CH}_3\text{NO}_2/\text{CH}_2\text{Cl}_2$ and (iii) $\text{DDQ}/\text{MeSO}_3\text{H}/\text{CH}_2\text{Cl}_2$ routes (Scheme 3.5). It was anticipated initially that the increased number of electron withdrawing nitrogen atoms in these 6N polyphenylenes systems would make the oxidative cyclodehydrogenation relatively more difficult than the 2N and 4N counterparts. Therefore, a strong aluminium(III) chloride/copper(II) chloride oxidation system was used initially to cyclodehydrogenate **87** using CS_2 as the solvent. The reaction was stirred at room temperature for 3 days and the reaction mixture appeared as a dark green solution. Subsequent extraction and work up to remove copper residues using a 10% ammonia solution, resulted a dark brown precipitate.



Scheme 3.5: Oxidative cyclodehydrogenation of asymmetric **87** (a) $\text{AlCl}_3/\text{CuCl}_2/\text{CS}_2$, 298 K, 72 h, **89**: 5 % (b) FeCl_3 , CH_3NO_2 , CH_2Cl_2 , 298 K, Ar bubbling, 72 h, **89**: 20 %; **90**: 10 % (c) DDQ (10 eq.), MeSO_3H , CH_2Cl_2 , 0 °C, **89**: 60 %.

The TLC analysis of the crude material showed a myriad of products and the preliminary mass spectral analysis confirmed the presence of a series of varied degree of bond closure products including $\frac{1}{3}^{\text{rd}}$ fused (two C-C bonds), $\frac{1}{2}$ fused (three C-C bonds), $\frac{2}{3}^{\text{rd}}$ fused (four C-C bonds) and $\frac{5}{6}^{\text{th}}$ fused (five C-C bonds) products. Despite harsh AlCl_3 conditions employed, the mass spectral analysis did not show even traces of the fully-fused product. Preparative thin layer chromatography (SiO_2 , 10:0.3, toluene: methanol) resulted in a good separation and the $\frac{5}{6}$ -Asym-HASB (**89**) was isolated, however in very low yield of 5%.

Secondly, FeCl_3 conditions were employed to attempt oxidative cyclodehydrogenation of **87**. FeCl_3 dissolved CH_3NO_2 was added dropwise into a solution of **87** in CH_2Cl_2 . The reaction mixture was left stirring for 24 hr with a stream of nitrogen bubbling through the solution to remove the HCl gas produced during the reaction. The reaction was quenched with addition of CH_3OH and subsequent work up resulted in a dark orange crude product. The preliminary mass spectral analysis of the crude product showed $\frac{5}{6}^{\text{th}}$ fused product as the predominant product along with the $\frac{2}{3}^{\text{rd}}$ fused species. Preparative thin layer chromatography (SiO_2 , 25:1, toluene: methanol) was used to isolate the products. These were the first isolated members of the HASB family. $\frac{5}{6}$ -asym-HASB (**89**) (five C-C bonds fused) was isolated as an orange solid in 20 % yield and $\frac{2}{3}$ -asym-HASB (**90**) (four C-C bonds fused) as a dark yellow solid in 10 % yield. The reaction was attempted several times with extended reaction times of up to 72 h using excess iron(III) chloride catalyst, however full cyclisation did not occur. This suggests that both **89** and **90** are thermodynamically stable molecules in their own right, as observed for partially cyclised N-HSB derivatives.^{153, 154}

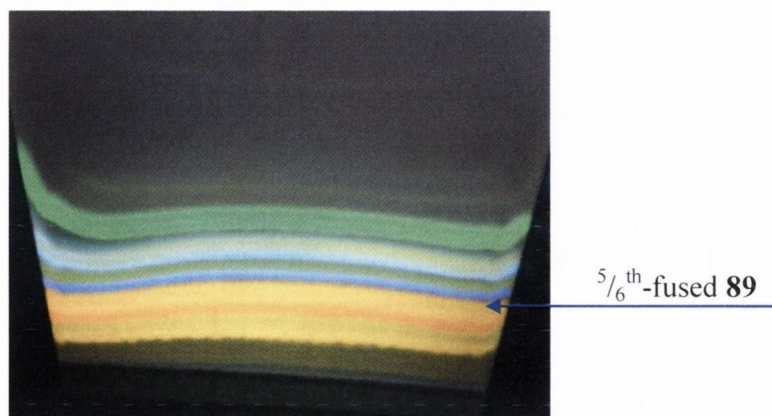


Figure 3.6: Preparative thin layer chromatography (SiO_2 , 25:1, toluene: methanol) separation of the $\frac{5}{6}^{\text{th}}$ fused product **89**.

The reaction was also attempted using DDQ/ MeSO₃H/ CH₂Cl₂ as alternative reagents for the oxidative cyclodehydrogenation of **87**. Previously for the 2N systems discussed in Chapter 2, the DDQ route only resulted in ring closure around the pyrimidine ring which generates the $\frac{1}{3}^{\text{rd}}$ fused species for all the systems studied. Therefore, it was interesting to study the effect of DDQ/H⁺ system on ring closure of the 6N systems. Polyphenylene **87** was dissolved in CH₂Cl₂ followed by dropwise addition of methanesulfonic acid. The reaction mixture rapidly changed colour to a bright orange upon addition of the acid and was cooled at 0 °C for 15 min. DDQ (10 eq.) dissolved in CH₂Cl₂ was added to the reaction mixture and the reaction was stirred for 48 hrs until there was no presence of starting material, observed by TLC. The reaction mixture gradually changed colour to a dark green. Subsequent quenching and work up of the reaction, evaporation of solvent afforded a yellow precipitate. The mass spectral analysis showed the presence of the $\frac{5}{6}^{\text{th}}$ fused species as the major product. Preparative thin layer chromatography was used to isolate the product as shown in Figure 3.6. It illustrates that the major product in the DDQ route is the $\frac{5}{6}^{\text{th}}$ fused species unlike in other routes discussed above. In addition, some of the pure $\frac{5}{6}^{\text{th}}$ product was isolated by precipitating it from the mother liquor with an overall yield of 60%. Interestingly, the five C-C bond closure has taken place at the same positions as the $\frac{5}{6}^{\text{th}}$ compounds obtained *via* the AlCl₃ and FeCl₃ routes. This indicates that the $\frac{5}{6}^{\text{th}}$ fused **89** is the preferred final product in the oxidative cyclodehydrogenation of **87**.

3.2.2.1 Characterisation of $\frac{5}{6}$ -Asym-HASB (**89**)

The ESI mass spectral analysis of **89** in toluene displays an isotropic distribution pattern for the C₄₈H₃₈N₆, [M+Na]⁺ ion at *m/z* 721.3060 that matches the calculated mass *m/z* 721.3056. This indicates the presence of $\frac{5}{6}^{\text{th}}$ fused (five C-C bonds closed) product. NMR analysis was used to identify the position of the C-C bond closure.

The aromatic region of **89** comprises of a series of well-resolved singlets in the region δ = 10.20 - 9.54 ppm, showing a higher degree of ring current in comparison to its unfused precursor **87**. (Figure 3.7). The presence of a series of doublets in the region δ = 8.72 - 7.70 ppm signify the presence of unfused aryl rings. The aromatic signals integrate to a total of 11 protons. The well-resolved coupling information from ¹H-NMR, ¹H-¹H COSY and HSQC NMR spectra and NOE experiments permitted the complete assignment of these aromatic proton signals.

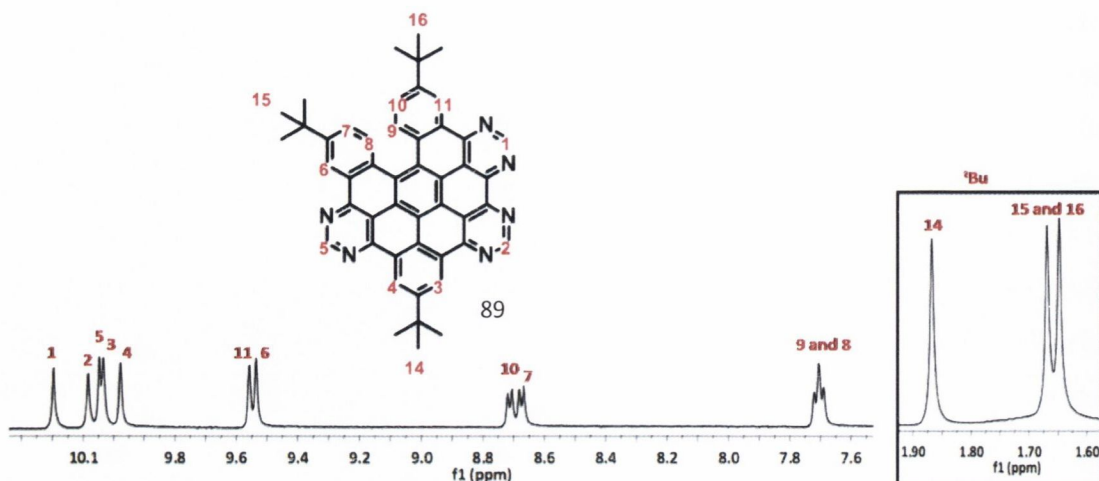


Figure 3.7: ^1H -NMR spectra of **89** in CDCl_3 at RT (600 MHz) with inset showing the aliphatic region. Atom labelling as per inset figure.

The three lowest field singlets at $\delta = 10.20$, 10.09 and 10.05 ppm were attributed to the pyrimidyl protons H1, H2 and H5 respectively. This assignment was further supported by the HSQC spectrum, with the correlated carbons appearing in the 155–158 ppm region (Figure 3.9). The singlets at $\delta = 10.03$ and 9.98 ppm integrate for one proton each and were assigned as H3 and H4 of the fused portion of the molecule. The assignments were further confirmed by the correlations (marked in the 'red' box) observed in the ^1H - ^1H COSY spectrum (Figure 3.8).

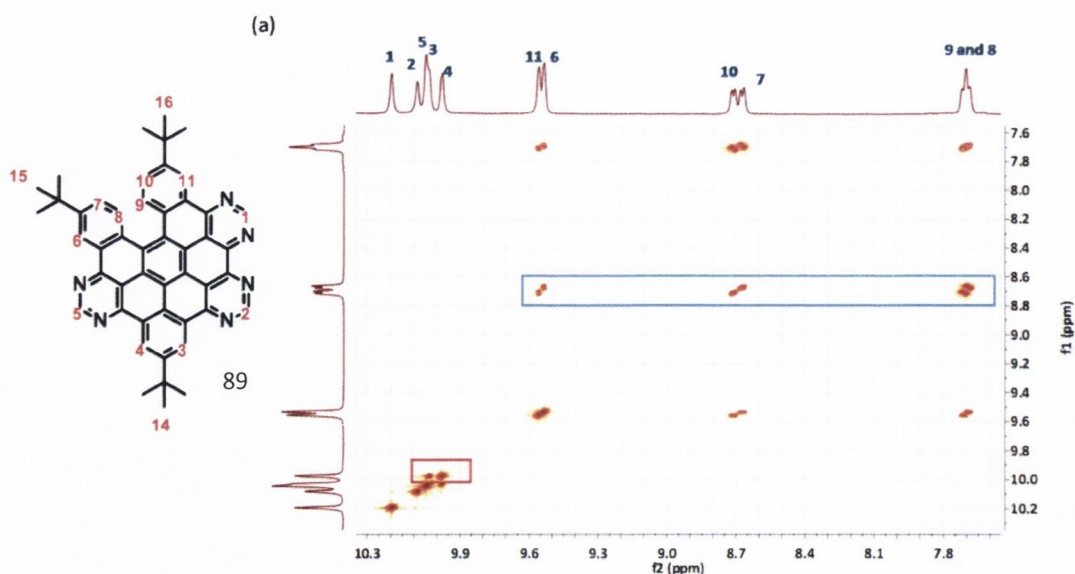


Figure 3.8: Aromatic region of (a) ^1H - ^1H COSY spectrum of **89** in CDCl_3 , RT, 600 MHz.

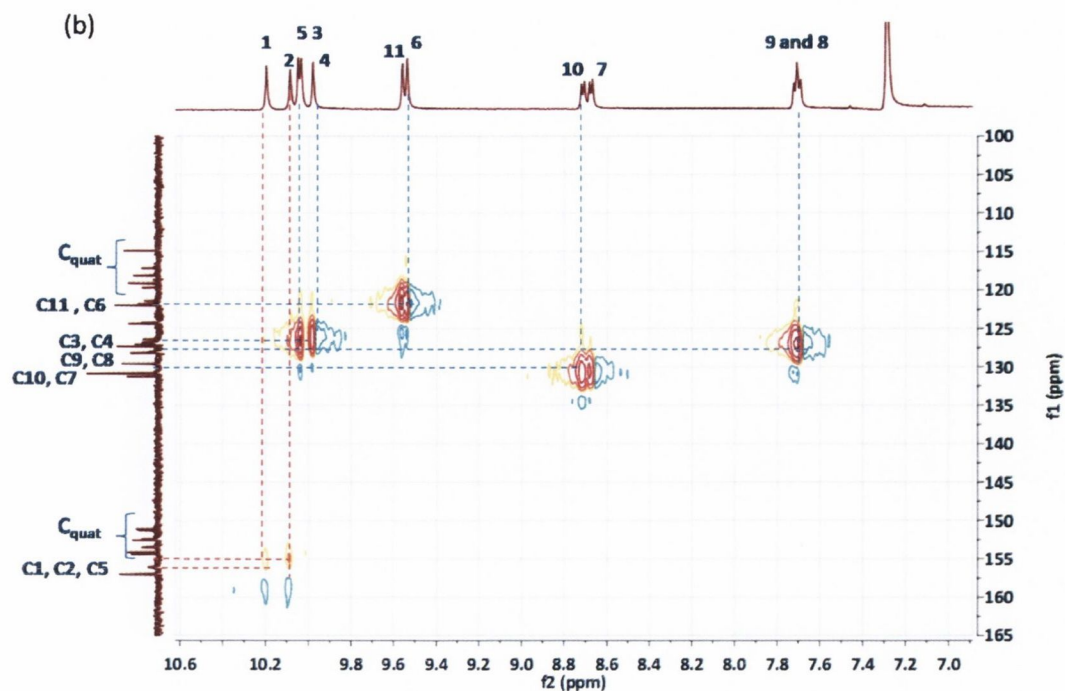


Figure 3.9: Aromatic region of ^{13}C - ^1H COSY spectrum of **89** in CDCl_3 , RT, 600 MHz.

The analysis of the ^1H - ^1H COSY spectrum also shows the presence of two AMX spin systems (marked in the “blue box”) indicating the lack of bond closure between the *tert*-butyl containing aryl rings. Based on these structural information, it was confirmed that there is no C-C bond closure between adjacent *tert*-butyl containing aryl rings, resulting in the structure shown above for **89**. The two singlets at $\delta \sim 9.6$ ppm were attributed to H11 and H6, with their respective partner signals appearing in the region $\delta \sim 8.8$ -7.6 ppm as series of doublets. The ^1H -NMR spectrum also shows three aliphatic signals for the three sets of *tert*-butyl protons. The *tert*-butyl protons, attached to the fully-fused aryl ring, are the most deshielded signals and appear at $\delta = 1.86$ ppm (marked as ‘14’) whereas the *tert*-butyl protons in the partially fused aryl rings appear at $\delta = 1.6$ ppm (marked as ‘15’ and 16’) as two singlets, each integrating for 9 protons.

3.2.2.2 Characterisation of $^{2/3}$ -Asym-HASB (**90**)

The ESI mass spectral analysis of **90** in toluene displays an isotropic distribution pattern for the $\text{C}_{48}\text{H}_{41}\text{N}_6$, $[\text{M}+\text{H}]^+$ ion at m/z 701.3393 that matches that generated from the simulated mass m/z 701.3390. As discussed for **89**, the NMR analysis was employed to identify the positions of the bond fusions in **90**.

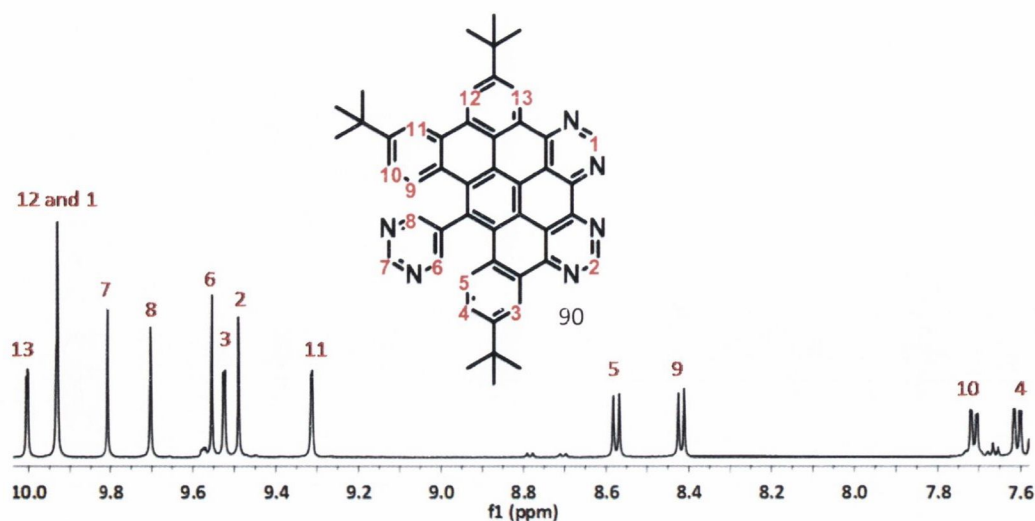


Figure 3.10: ¹H NMR spectra of **90** in CDCl₃ at RT (600 MHz) with inset showing the aliphatic region. Atom labelling as per inset figure.

In comparison with the $5/6^{th}$ fused species **89**, the aromatic region signals are slightly more upfielded in **21** and additional doublets are observed due to the unfused portion of the molecule. Twelve aromatic signals are apparent in the aromatic region, which integrate for 13 protons (Figure 3.10). The well-resolved coupling information from ¹H-NMR, ¹H-¹H and HSQC NMR spectra and NOE experiments permitted the complete assignment of these aromatic proton signals.

The most deshielded singlet in the ¹H-NMR spectrum of **90** is at $\delta = 10.00$ ppm and is assigned to H13. This differs from the trend previously observed. Generally, the most downfield signals in N-HSB ($\delta = 10.16$ – 10.10 ppm region) and in its partially-fused derivatives (N- $1/2$ HSB and N- $2/3$ HSB) belong to the pyrimidyl protons.^{53, 155} However, a similar feature was observed for the methoxy substituted DASB **82** (discussed in Chapter 2) where the most downfielded signal belong to aryl proton adjacent to a methoxy substituent. The signal at $\delta = 9.93$ ppm integrates for two protons with HSQC spectrum (Figure 3.11) showing that the two protons belong to an aryl proton and a pyrimidyl proton.

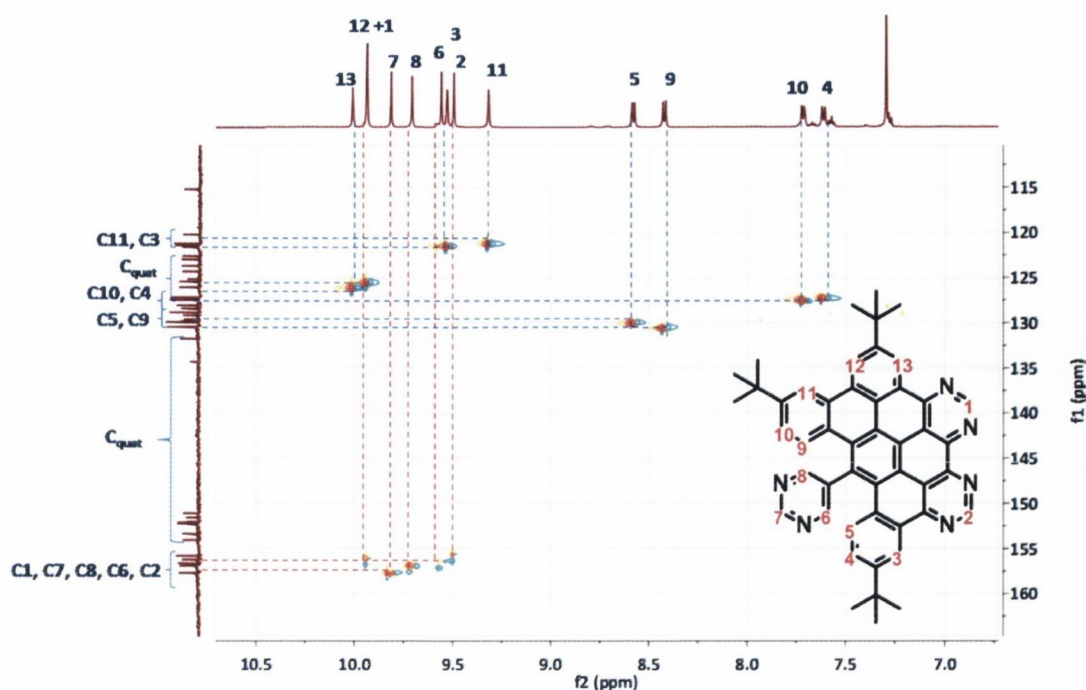
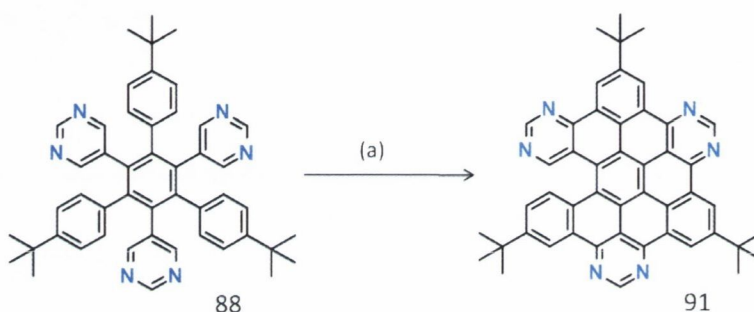


Figure 3.11: Aromatic region of the ^{13}C - ^1H COSY spectrum of **90** in CDCl_3 .

Together with ^1H - ^1H COSY spectrum correlations, the signal at $\delta = 9.93$ ppm was attributed to pyrimidyl H1 and aryl H12. The ^1H - ^1H COSY spectrum shows the presence of two AMX spin systems indicating the presence of two partially fused *tert*-butyl aryl rings. Based on this structural information, the structure of **90** was deduced as shown with no C-C bond closure between the pyrimidyl ring positioned between the *tert*-butyl functionalised aryl rings. Furthermore, the analysis of the HSQC spectra showed the presence of 4 additional pyrimidyl signals. The free pyrimidyl ring shows signals at $\delta = 9.81, 9.70, 9.55$ ppm which were tentatively attributed to H7, H8 and H6 respectively. These assignments are based on correlations shown in the ^1H - ^1H COSY spectrum. The remaining singlets at $\delta = 9.52$ ppm and $\delta = 9.31$ ppm were assigned to partially fused *tert*-butyl ring protons H3 and H11 respectively with the series of doublets in the region $\delta = 8.6$ – 7.6 ppm belonging to these partially fused aryl rings. The ^1H -NMR spectrum also shows three aliphatic signals for the three sets of *tert*-butyl protons. The *tert*-butyl protons attached to the fully-fused aryl ring are the most deshielded at $\delta 1.77$ ppm (marked as '14') whereas the *tert*-butyl protons in the partially fused phenyl rings (marked as '15' and '16') appear in the $\delta 1.5$ – 1.6 ppm region as two singlets, each integrating for 9 protons.

3.2.3 Oxidative cyclodehydrogenation of **88**

The oxidative cyclodehydrogenation of the symmetric isomer **88** was also attempted *via* all three routes mentioned above (Scheme 3.6). The AlCl_3 route resulted in a myriad of partially-fused products, according to the mass spectrometric analysis of the crude material. Despite several attempts, separation using preparative thin layer chromatography did not result in a successful isolation of any of the products. However, careful analysis of the mass spectral data of the crude product indicates that as in **87**, the fully-fused product was not observed *via* the AlCl_3 route.



Scheme 3.6: Oxidative cyclodehydrogenation of symmetric **88** (a) AlCl_3 , CuCl_2 , CS_2 , 298 K, 72 h (b) FeCl_3 , CH_3NO_2 , CH_2Cl_2 , 298 K, Ar bubbling, 72 h, **91**: 23 %.

Then, the oxidative cyclodehydrogenation of **88** was attempted under milder FeCl_3 conditions, resulting in a mixture of products. The preliminary mass spectrometry results show the presence of a series of various bond closure products including $\frac{1}{2}$ -fused (three C-C bonds), $\frac{2}{3}$ rd-fused (four C-C bonds) and $\frac{5}{6}$ th-fused (five C-C bonds) products with traces of the fully-fused product upon 72 h reaction time. After 24 hr reaction time, the mass spectral analysis showed the $\frac{5}{6}$ th-fused product as major product, with trace amounts of multiple partially fused products. Preparative thin layer chromatography (SiO_2 , 10:0.4, toluene: CH_3OH) resulted in a good separation and the $\frac{5}{6}$ -Sym-HASB (**91**) was successfully isolated.

The DDQ/H^+ route was also attempted as an alternate route, although only preliminary investigation was carried out. It did not show the formation of any new product and starting material was recovered after reaction time of 72 h. This is surprising, given the successful application of this route in the cyclodehydrogenation of **87**. Further reaction attempts needs to be carried out varying the reaction conditions.

3.2.4 Characterisation of $^{5/6}$ -Sym-HASB (**91**)

The ESI mass spectral analysis of **91** in dichloromethane displays an isotropic distribution pattern for the $C_{48}H_{39}N_6$, $[M+H]^+$ ion at m/z 699.3236. This agrees with the calculated mass m/z 699.3236, confirming the presence of the $^{5/6}$ th-fused product (see inset in Figure 3.12)

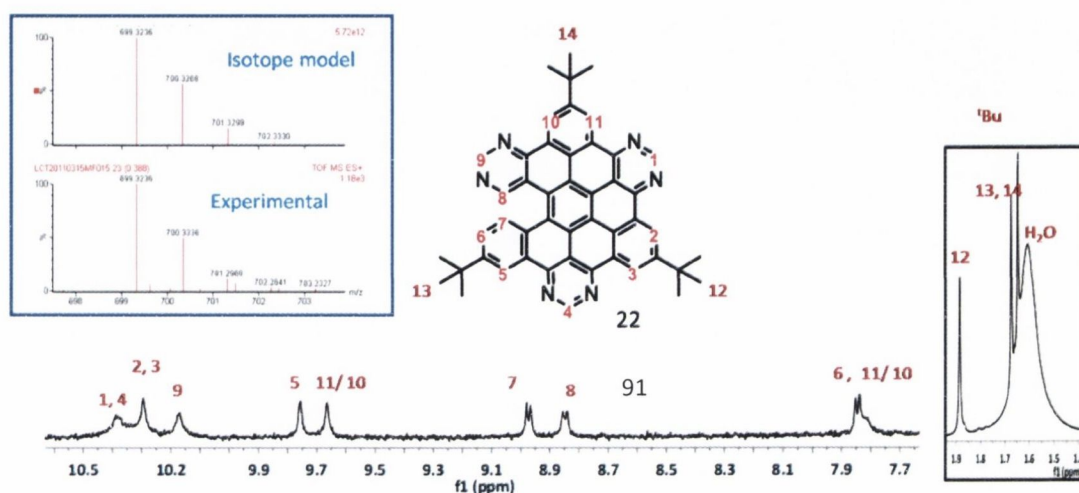


Figure 3.12: 1H -NMR spectra of **91** in $CDCl_3$ at RT (600 MHz) with inset (right) showing the aliphatic region Atom labelling as per figure. Inset at top showing the simulated and experimental mass spectrometry analysis of **91**.

Since the starting polyphenylene precursor (**88**) is highly symmetric, the structure of the $^{5/6}$ th-fused product was elucidated easily. Despite this, the compound showed extensive aggregation in solution (Figure 3.12) making the assignment of **91** more challenging than the other partially fused products. This feature is evident from the broad nature of aromatic peaks, in particular the pyrimidyl protons. Furthermore, the extensive stacking in solution prevented obtaining a ^{13}C -NMR of the compound, which is vital for the accurate assignment of the 1H -NMR spectra. Therefore, the 1H -NMR of **91** was assigned tentatively based on the analysis of 1H - 1H COSY spectra.

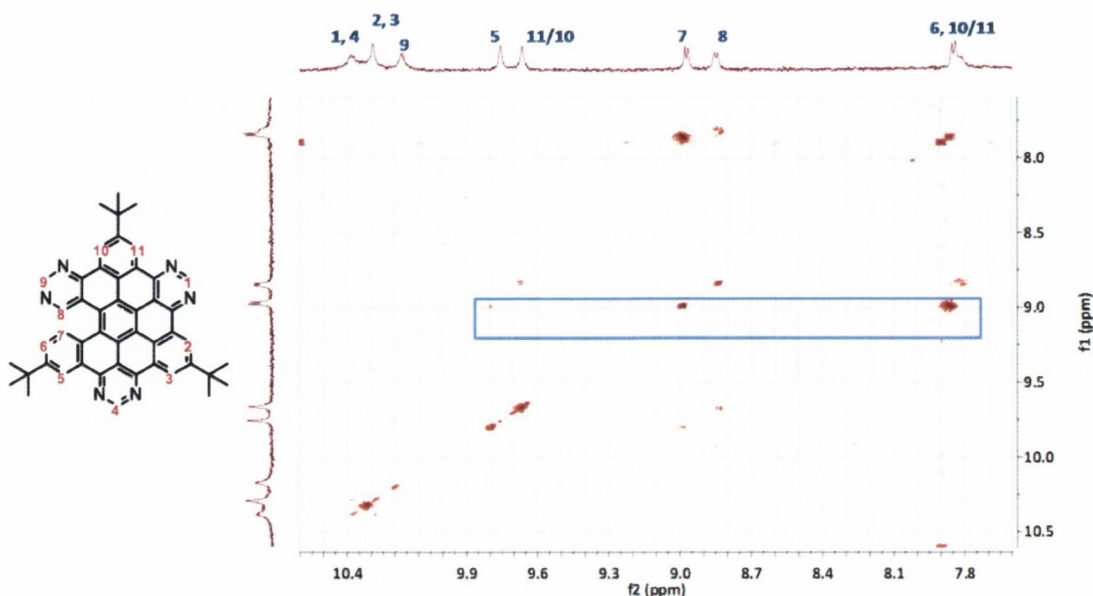
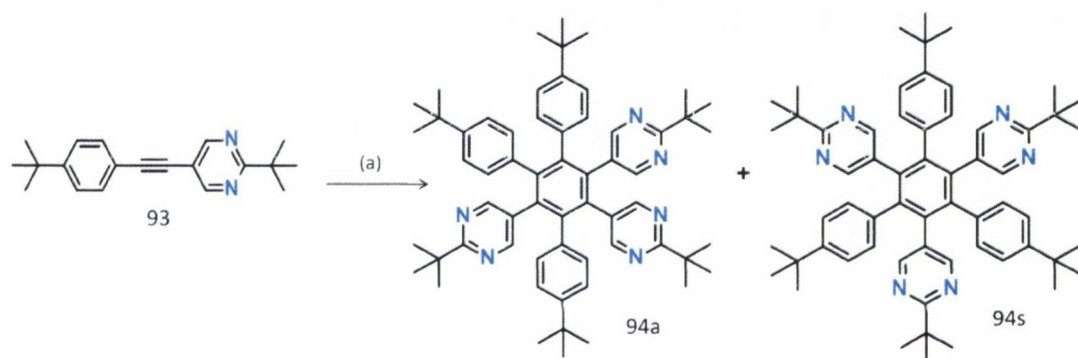


Figure 3.13: Aromatic region of the ^1H - ^1H COSY spectrum of **91** in CDCl_3 , RT, 600 MHz.

Unlike in $5/6^{\text{th}}$ -asym-HASB (**89**), the most downfield signals in the spectra of $5/6^{\text{th}}$ -sym-HASB (**91**) occur at $\delta = 10.37$ ppm. These are assigned as the pyrimidyl protons H1 and H4, following the general trend observed for other N-HSB family compounds. The 1H - 1H COSY spectrum (Figure 3.13) shows an AMX spin system (marked in the 'blue box') which can be attributed to H5, H7 and H6 with ^3J coupling (~ 8.0 Hz) for both H6 and H7 signals. The peaks at $\delta = 10.18$ ppm and $\delta = 8.85$ ppm were attributed to partially fused pyrimidyl ring signals and was further confirmed by HSQC correlations. Due to the extensive aggregation it was difficult to conclusively assign on the basis of the splitting pattern of the signals, as they may be influenced by the effect of adjacent molecules. The remaining signals at $\delta = 9.66$ ppm and $\delta = 7.85$ ppm were tentatively assigned H10/H11. The aliphatic region shows three signals for the three sets of *tert*-butyl protons. The *tert*-butyl protons attached to the fully-fused aryl ring are the most deshielded at $\delta = 1.88$ ppm (marked as '12') whereas the *tert*-butyl protons in the partially fused phenyl rings (marked as '13' and '14') appear in the δ 1.7-1.6 ppm region as two singlets, each integrating for 9 protons.

3.2.5 Synthesis and characterisation of polyphenylenes **94a** and **94b**

Gourdon *et al.* have reported that the substitution of the hydrogen atom in position 2 (proton between the two nitrogens) in the pyrimidine ring by a *tert*-butyl group has a profound effect on the reactivity of these compounds.¹¹⁰ In their work, when the position 2 of the pyrimidine ring was substituted by a *tert*-butyl group, the Scholl reaction was complete and resulted in a fully-fused diaza-hexa-*peri*-benzocoronene compound. Since the ring closure did not go to completion for 6N polyphenylenes **87** and **88**, Gourdon's strategy was applied with the aim of obtaining a fully-fused HASB species. It was believed that the incorporation of the *tert*-butyl unit at the blocking position will prevent complexation at N-sites by steric crowding and also increases the solubility of reagents, intermediates and products.



Scheme 3.7: Synthesis of 6N polyphenylenes **94a** and **94s** (a) $\text{Co}_2(\text{CO})_8$, dioxane, 115 °C, 24 h, under N_2 .

93 was synthesised *via* microwave Sonogashira conditions using commercially available starting materials 4-*tert* butylphenylacetylene and 5-bromo-2-*tert*-butylpyrimidine in 87 % yield. The $\text{Co}_2(\text{CO})_8$ catalysed cyclotrimerisation of **93** resulted both asymmetric and symmetric isomers **94a** and **94s**. Separation of the two isomers was attempted by various methods including column chromatography and preparative plate chromatography using $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ (10:0.2) as the eluent, however the separation was unsuccessful. Crystallisation was then attempted in order to isolate the symmetric isomer. Crystals were obtained using $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ solvent systems by slow evaporation of solvent, however, the single crystal X-ray analysis show the presence of both isomers in the crystal lattice and proved difficult to solve.

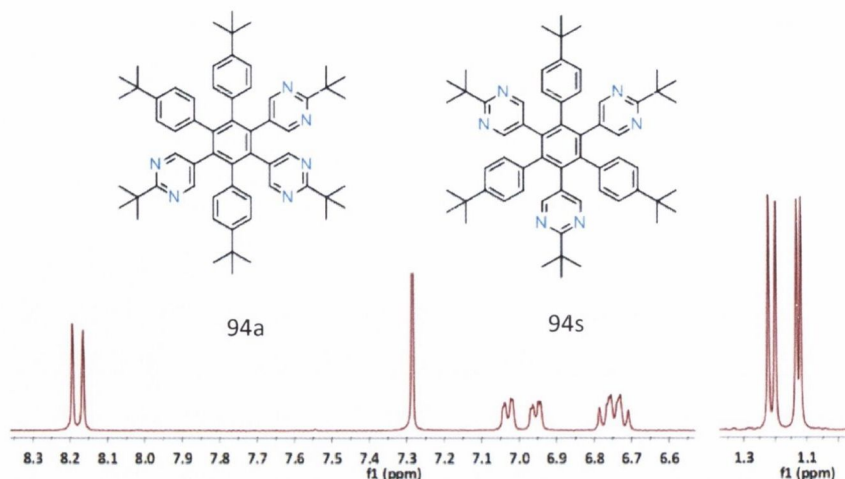


Figure 3.14: The ^1H -NMR spectra of the isomeric mixture of **94a** and **94s** in CDCl_3 , RT, 400 MHz.

The ^1H -NMR spectrum of the product is presented in Figure 3.14. It shows that the product consists of an approximately 50:50 mixture of the two isomers. The positioning of the six *tert*-butyl rings around the periphery further complicated the characterisation of the two isomers using other NMR techniques. Despite the inability to separate the two isomers, oxidative cyclodehydrogenation of the mixture was attempted in order to study the influence of the *tert*-butyl groups on the ring closure. $\text{AlCl}_3/\text{CuCl}_2$ conditions were employed to cyclise the mixture, and the preliminary mass spectral analysis of the crude showed the presence of the mainly $5/6$ -fused and $1/2$ -fused species as shown in Figure 3.15. This further shows that the incorporation of the *tert*-butyl groups between the pyrimidyl nitrogens does not have a significant impact on complete ring closure of the polyphenylenes **94a/94s**.

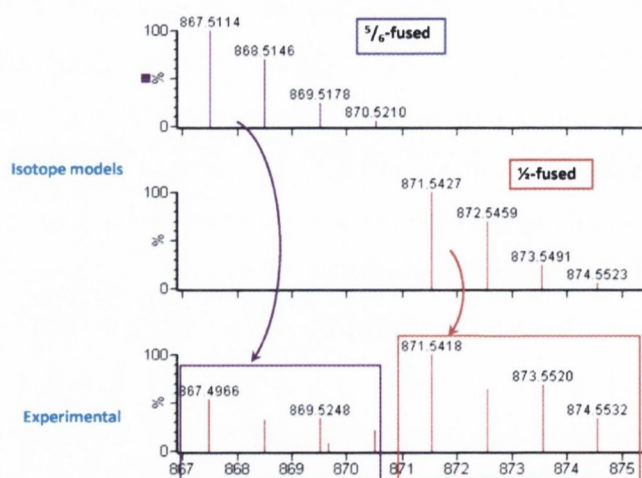


Figure 3.15: Experimental and simulated isotopic mass spectral models for $5/6^{\text{th}}$ and $1/2$ -fused products.

3.2.6 Synthesis and characterisation of polyphenylenes **95** and **96**

Electron-donating methoxy groups are known to increase the efficacy of the oxidative cyclodehydrogenation step.¹²¹ Since the complete oxidation of the *tert*-butyl functionalised 6N polyphenylene precursors was not successful, electron-donating methoxy groups were incorporated into the periphery of 6N polyphenylenes with the aim of obtaining a fully closed HASB system.



Scheme 3.8: Synthetic route to 6N polyphenylenes **95** and **96**; (a) $\text{Co}_2(\text{CO})_8$, dioxane, 115 °C, 24 h, under N_2 .

Trimethoxy functionalised acetylene **72** was synthesised *via* Sonogashira reaction of commercially available starting materials under microwave conditions as discussed in Chapter 2. Dicobalt octacarbonyl catalysed cyclotrimerisation of **72** gives two products: asymmetric 3,5,6-tri-(3,4,5-trimethoxyphenyl)-1,2,4-tri-(5-pyrimidyl)benzene (**95**) and symmetric 2,4,6-tri-(3,4,5-trimethoxyphenyl)-1,3,5-tri-(5-pyrimidyl)benzene (**96**) [Scheme 3.8] The two products were successfully isolated by column chromatography eluting with $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ (10:0.4) solvent system.

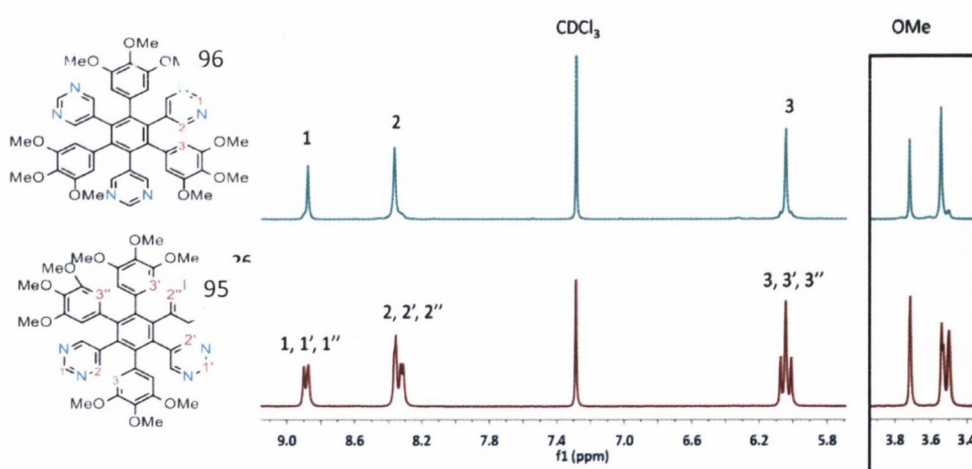


Figure 3.16: ^1H -NMR spectra of asymmetric **95** and symmetric **96** in CDCl_3 at *R.T.*

The ^1H NMR spectra of the symmetric **96** and asymmetric **95** are presented in Figure 3.16. **96** exhibits a simplified spectrum due to the presence of a C_3 symmetry axis. The aromatic region of the spectra comprise of two set of signals, the down fielded pyrimidyl protons ($\delta \sim 8.2$ - 8.9 ppm) and aryl protons of the methoxy functionalised rings at $\delta = \sim 6.0$ ppm. The methoxy signals appear in the $\delta \sim 3.4$ - 3.7 ppm. The assignment of the signals in both spectra was aided by various 1D and 2D NMR techniques and the assignment of compound **96** will be discussed briefly along with the analysis of HSQC spectrum.

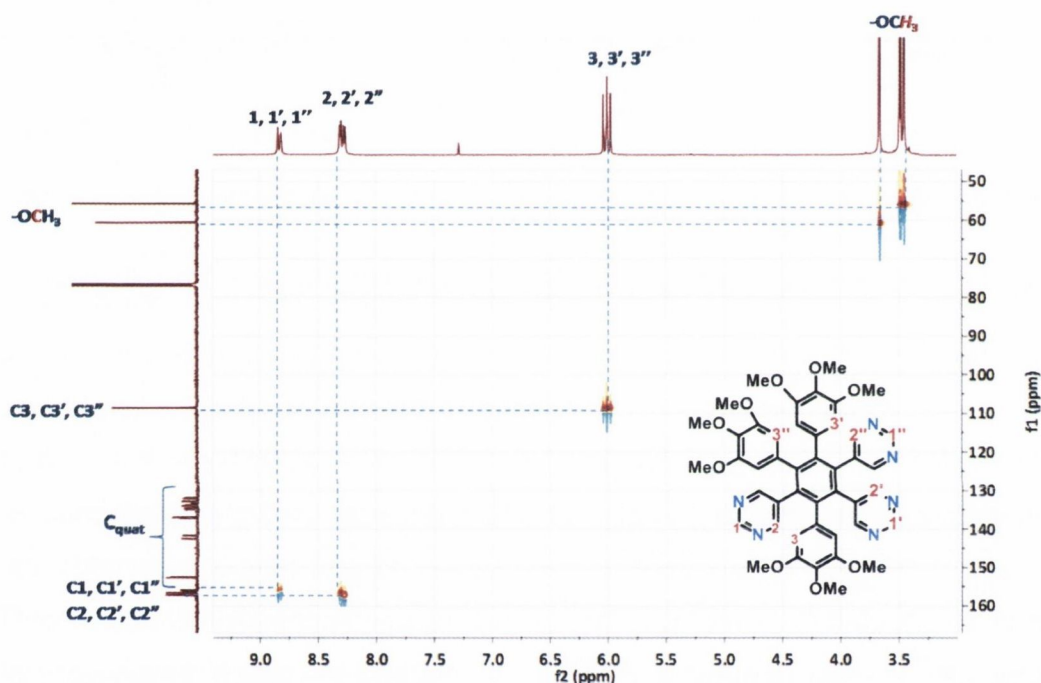
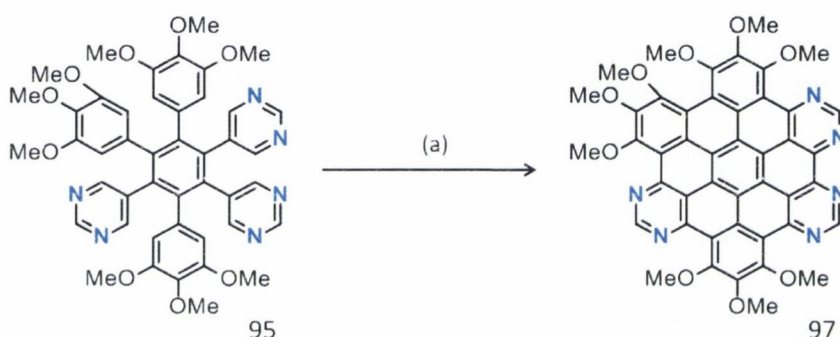


Figure 3.17: The HSQC spectrum of **95** in CDCl_3 , 600 MHz, RT.

The ^{13}C - ^1H COSY spectrum of **95** [Figure 3.17(a)] illustrates that the most downfield signals at $\delta = \sim 8.8$ ppm and $\delta = \sim 8.3$ ppm correlate to carbons appearing in the 155-158 ppm region. These are attributed to the pyrimidyl protons. The three proton signals at $\delta = \sim 6.0$ ppm was assigned to H3, H3' and H3'' on the methoxy substituted ring with the respective carbon signals appearing at $\delta = 110$ ppm. The assignment was further confirmed by NOE experiment on pyrimidyl protons at $\delta = \sim 8.3$ ppm (H2) showing direct correlations through space with the H3 signals.

3.2.7 Cyclodehydrogenation of polyphenylene **95** and **96**

The oxidative cyclodehydrogenation of **95** was attempted in a manner analogous to that of **87**, using 30 equivalents of FeCl_3 (5 equivalents of FeCl_3 per C-C bond). FeCl_3 was dissolved in CH_3NO_2 and added dropwise into a solution of **95** in CH_2Cl_2 . Unlike in **87**, initial addition of FeCl_3 resulted in a colour change to dark green indicating the initiation of the reaction. The reaction mixture was left stirring for 24 hr with a stream of nitrogen bubbling through the solution to remove the HCl gas produced during the reaction. The reaction was quenched with addition of CH_3OH , and solvent volume was reduced *in vacuo*. The product was dissolved in CH_2Cl_2 and washed with water to remove iron residues.



Scheme 3.9: Cyclodehydrogenation of **95**. (a) FeCl_3 (30 eq.), CH_3NO_2 , CH_2Cl_2 , 298 K, Ar bubbling, 24 h, **97**:10 %.

Preliminary mass spectral analysis of the crude material indicated the presence of a mixture of products, showing mainly the presence of the fully-fused product (six C-C bonds closed) **97** as the predominant product (Scheme 3.9), along with a $5/6^{\text{th}}$ fused product (five C-C bonds closed). The separation of the two products was extremely tedious due to only one C-C bond difference between them. This resulted in both compounds appearing at close proximity on the thin layer preparative plate. Several solvent systems were attempted to separate the products and finally $\text{C}_7\text{H}_8:\text{CH}_3\text{OH}$ (20:1) system proved to give the best separation. The yield of the pure isolated fully-fused product **97** was very low due to challenges faced in purification. It is the first fully-fused member of the HASB family of compounds. These results show that the incorporation of electron-donating methoxy substituents facilitate complete ring closure in the 6N polyphenylene systems.

3.2.7.1 Characterisation of methoxy-HASB (97)

The ESI mass spectral analysis of **97** in dichloromethane displays an isotropic distribution pattern for the $C_{45}H_{31}N_6O_9$, $[M+H]^+$ ion at m/z 799.2156 that matches the calculated mass m/z 799.2153, confirming the presence of the fully-fused product **97**. [see inset (b) in Figure 3.18].

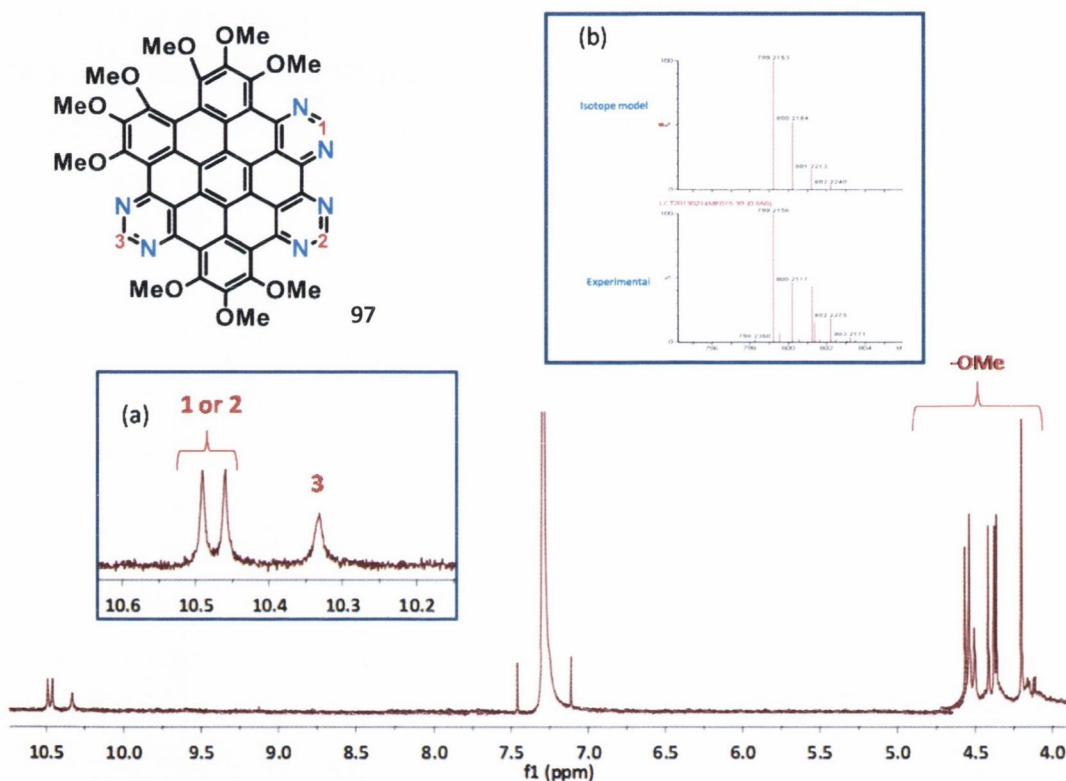
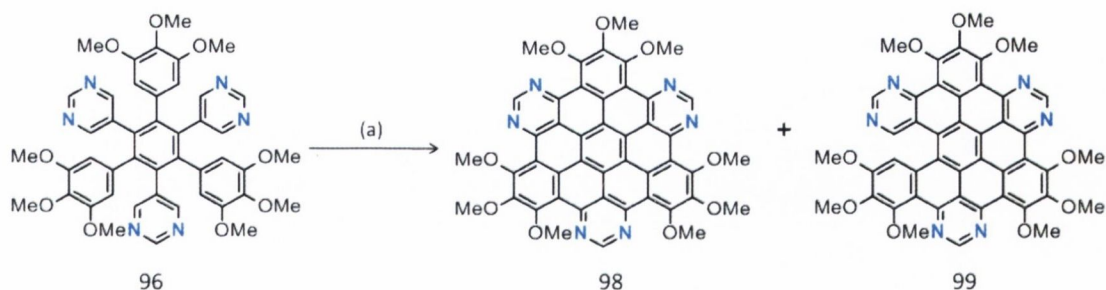


Figure 3.18: 1H -NMR of fully-fused **97** in $CDCl_3$ at RT (600 MHz) with inset (a) showing the a magnified image pyrimidyl region and (b) showing the simulated and experimental mass spectral analysis of **97**. Atom labelling as per figure.

The 1H -NMR spectrum of **97** is simplified due to the presence of only three pyrimidyl proton signals in the aromatic region (Figure 3.18). The two proton signals at $\delta = 10.49$ ppm and $\delta = 10.46$ ppm integrate to one proton, each being attributed to H1 and H2. The proton signal at $\delta = 10.33$ ppm was assigned to H3. The methoxy signals appear as a set of overlapped singlets in the region $\delta = 4.6 - 4.2$ ppm. The low yield prevented a ^{13}C -NMR spectrum of **97** from being obtained.

The oxidative cyclodehydrogenation of symmetric isomer **96** was also attempted under $FeCl_3$ conditions as discussed for **95** (Scheme 3.10). The preliminary mass spectral analysis of the crude product resulted in both the fully-fused **98** and $5/6^{th}$ -fused **99**, as

observed for **95** (Figure 3.19). However, despite several attempts using thin layer preparative plate in various solvent systems we were unable to separate the two products.



Scheme 3.10: Cyclodehydrogenation of **96**. (a) FeCl_3 (35eq.), CH_3NO_2 , CH_2Cl_2 , 298 K, Ar bubbling, 24 h.

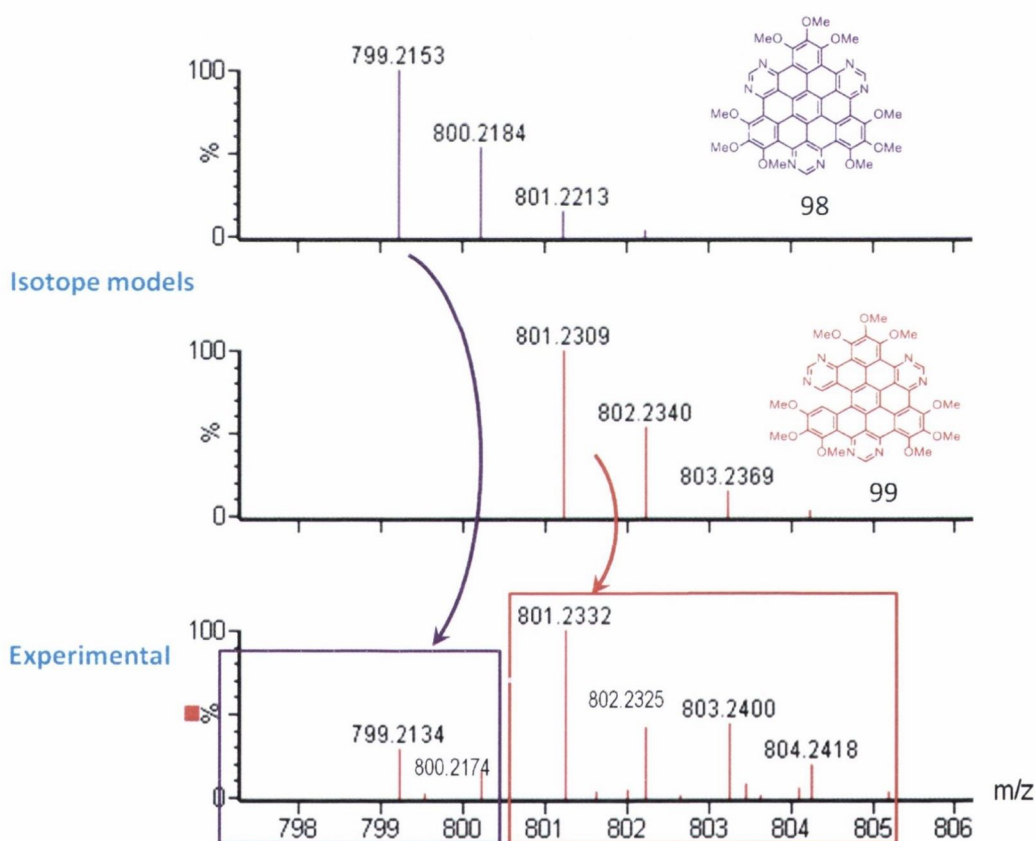


Figure 3.19: Experimental and simulated isotopic mass spectral models for fully-fused methoxy HASB **98** and $^{5/6}$ fused **99**.

3.3 Photophysical studies of 6N systems

3.3.1 Photophysical studies of 6N polyphenylenes **87**, **88**, **95** and **96**

The UV-visible absorption spectra of the 6N polyphenylenes (**87**, **88**, **95** and **96**) are presented in Figure 3.20 with relevant data in Table 3.1.

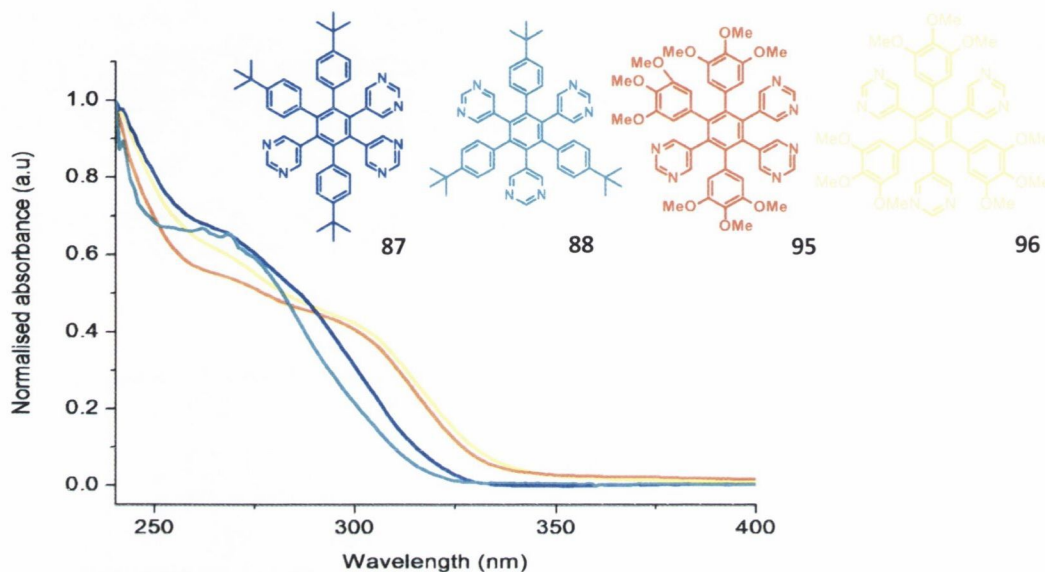


Figure 3.20: The normalised UV-Vis spectra of 6N polyphenylenes (**87**, **88**, **95** and **96**) in chloroform ($\sim 10^{-5} M$).

The absorption spectra of the 6N doped polyphenylenes (**87**, **88**, **95** and **96**) feature broad and unstructured bands in the UV region (Figure 3.20). These spectra consist of both $n-\pi^*$ and $\pi-\pi^*$ transitions, however the broad nature of the spectra hinders identification of specific absorption bands. They follow a similar trend to absorption spectra of both 2N and 4N polyphenylenes.^{53,100} By comparing the *tert*-butyl substituted polyphenylene (**87** and **88**) to the methoxy substituted polyphenylene (**95** and **96**) spectra, it is evident that the methoxy functionalised **95** and **96** shows a more pronounced red shifted absorption ($\lambda = 297$ nm) compared to the *tert*-butyl substituted ($\lambda = 270$ nm). The high molar extinction coefficients of these bands suggest $\pi-\pi^*$ nature of the absorption.

Table 3.1: The absorption and emission data observed for 6N polyphenylenes **87**, **88**, **95** and **96** in chloroform ($\sim 10^{-5} M$).

Compound	$\lambda_{\max}$ [nm] ($\epsilon \times 10^4$ [$M^{-1} \text{cm}^{-1}$])	λ_{em} [nm] (λ_{exc} [nm])
87	270 (2.6)	357 (300)
88	270 (2.4)	369 (300)
95	297 (3.3)	415 (300)
96	297 (3.4)	426 (300)

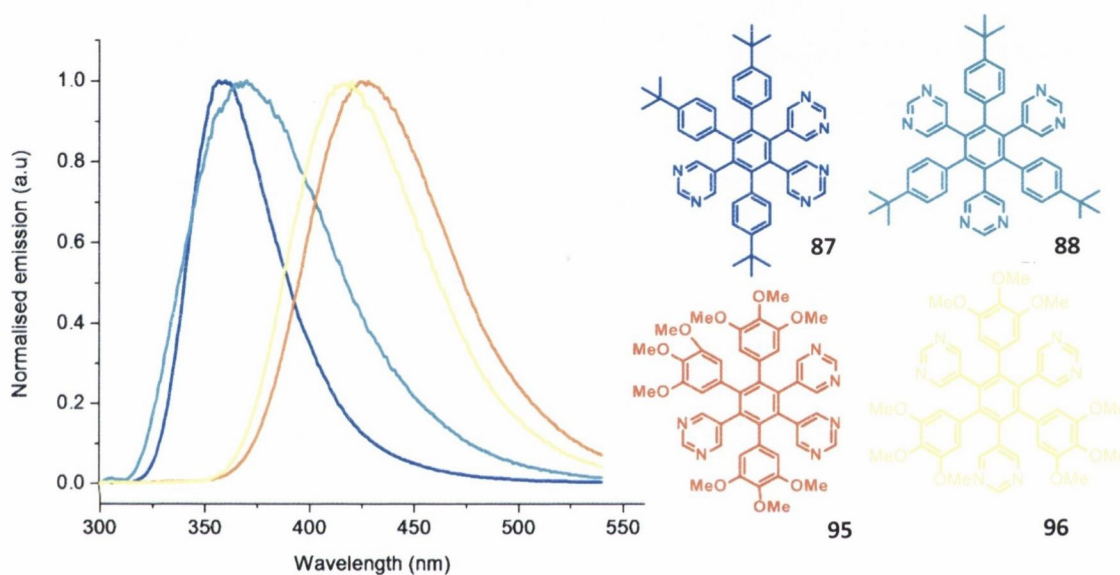


Figure 3.21: The normalised emission spectra of 6N polyphenylenes (**87**, **88**, **95** and **96**) in chloroform ($\sim 10^{-5} M$) at $\lambda_{\text{exc}} = 300$ nm, R.T.

The overlaid luminescence spectra of the 6N polyphenylenes in CHCl_3 are shown in Figure 3.21 along with emission data tabulated in Table 3.1. The methoxy substituted polyphenylenes **95** and **96** undergo a significant bathochromic shift ($\sim 4000 \text{ cm}^{-1}$) in their emission spectra, with $\lambda_{\max}^{\text{em}}$ at 426 nm and 415 nm respectively. The emission maxima of the tert-butyl derivatives **87** and **88** are comparatively blue shifted at 357 nm and 369 nm respectively. This trend was also observed in the 2N polyphenylenes (*tert*-butyl **78** vs. methoxy **82**), however was less pronounced ($\sim 2000 \text{ cm}^{-1}$) compared to the 6N systems, as the increase number of methoxy substituents in the 6N systems leads to a greater bathochromic shift. The electron-donating methoxy substituents destabilises the HOMO, thereby decreasing the HOMO-LUMO gap, which leads to a red shifted emission. The emitting state of these polyphenylenes was further investigated through protonation studies.

3.3.1.1 Protonation studies of 6N polyphenylenes

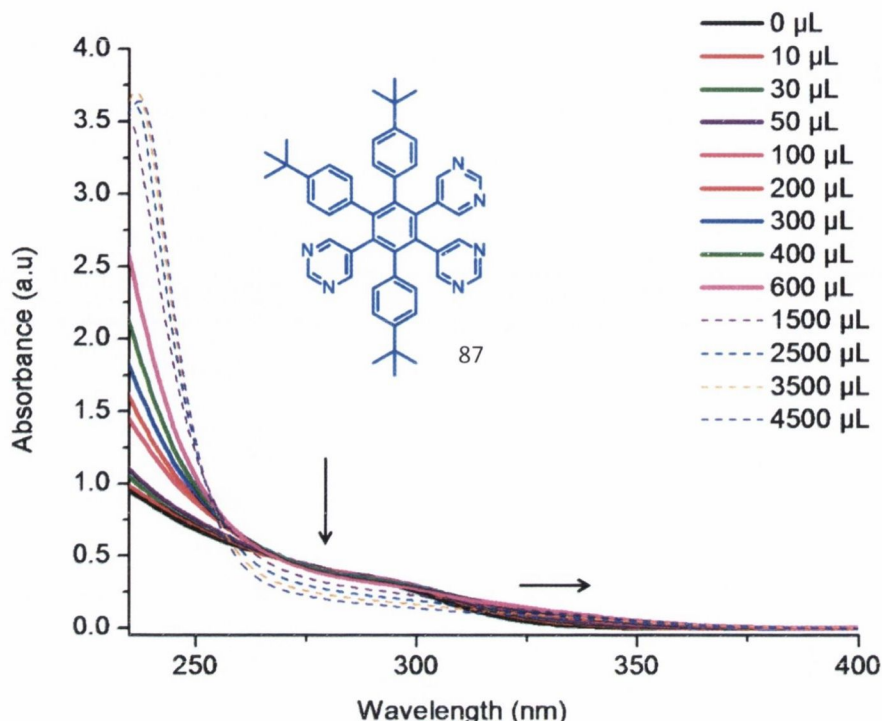


Figure 3.22: UV-Vis absorption spectral changes of **87** (1×10^{-5} M) upon sequential addition of 0.1 M trifluoroacetic acid in CH_2Cl_2 .

The UV-Vis absorption spectra of **87** upon sequential addition of trifluoroacetic acid in CH_2Cl_2 , is shown in Figure 3.22. **87** shows a broad absorption in the UV-Vis region with the main bands appearing at $\lambda = 275$ nm in CH_2Cl_2 . The band at $\lambda = 275$ nm is promptly quenched upon addition of the acid indicating $n\text{-}\pi^*$ character as specified by Kasha's rule. A new band of lower energy forming around $\lambda = 325$ nm arising due to the newly-formed protonated species. Two isobestic points are evident at $\lambda = 260$ nm and 307 nm, indicating an equilibrium between the neutral and newly-formed protonated species. Furthermore, increasing the additions of acid (eg. 3000 - 4500 μL shown in dotted line) causes these isobestic points to be perturbed. This is attributed to solvent affects caused by a change in solvent polarity on acid addition, or the possible emergence of a multiple protonated species. The protonation studies of 6N polyphenylene **87** shows a similar trend to 2N polyphenylene **79** discussed in Chapter 2.

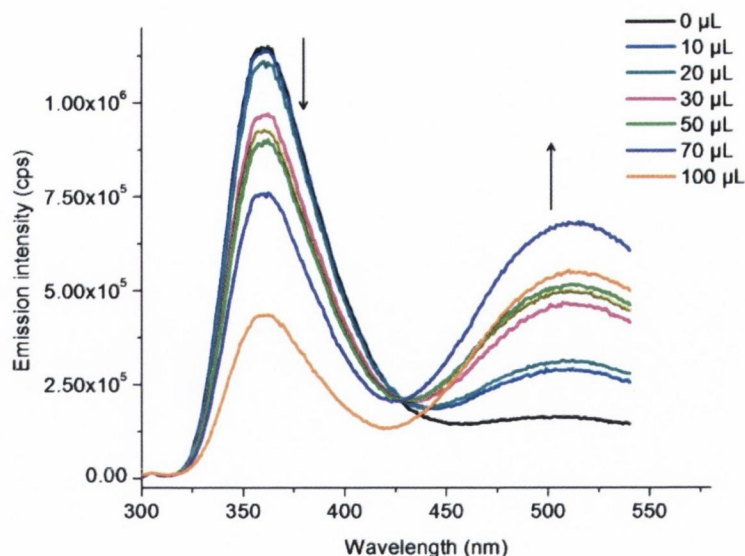


Figure 3.23: Emission spectral changes of **87** ($1 \times 10^{-5} \text{ M}$) upon sequential addition of ($1 \times 10^{-3} \text{ M}$) trifluoroacetic acid in CH_2Cl_2 at room temperature ($\lambda_{\text{exc}} = 280 \text{ nm}$).

The corresponding emission acid addition studies of **87** in CH_2Cl_2 shows gradual quenching of the emission maximum at $\lambda = 360 \text{ nm}$ upon sequential addition of trifluoroacetic acid ($1 \times 10^{-3} \text{ M}$) aliquots, and a new red shifted band is formed around $\lambda = 540 \text{ nm}$ due to the emission of the newly-formed protonated species (Figure 3.23). The newly-formed band is dramatically red shifted with respect to the emission maxima of the neutral species i.e. 8246.5 cm^{-1} . Both the decrease in concentration of the neutral form due to protonation, and the spectral overlap of the absorption of the protonated species, lead to a decrease in intensity of the main band at $\lambda = 360 \text{ nm}$, upon acid addition. An isoemissive point is formed at $\lambda = 425 \text{ nm}$, indicating equilibrium between the neutral and newly-formed protonated species, and upon excess acid addition (i.e. $100 \mu\text{L}$) the isoemissive point is also perturbed. This follows the trend observed in both 2N and 4N polyphenylene systems.⁵³ The decrease of emission intensity upon acid addition is indicative of a $\pi\text{-}\pi^*$ emissive state.

3.3.2 Photophysical studies of HASB derivatives

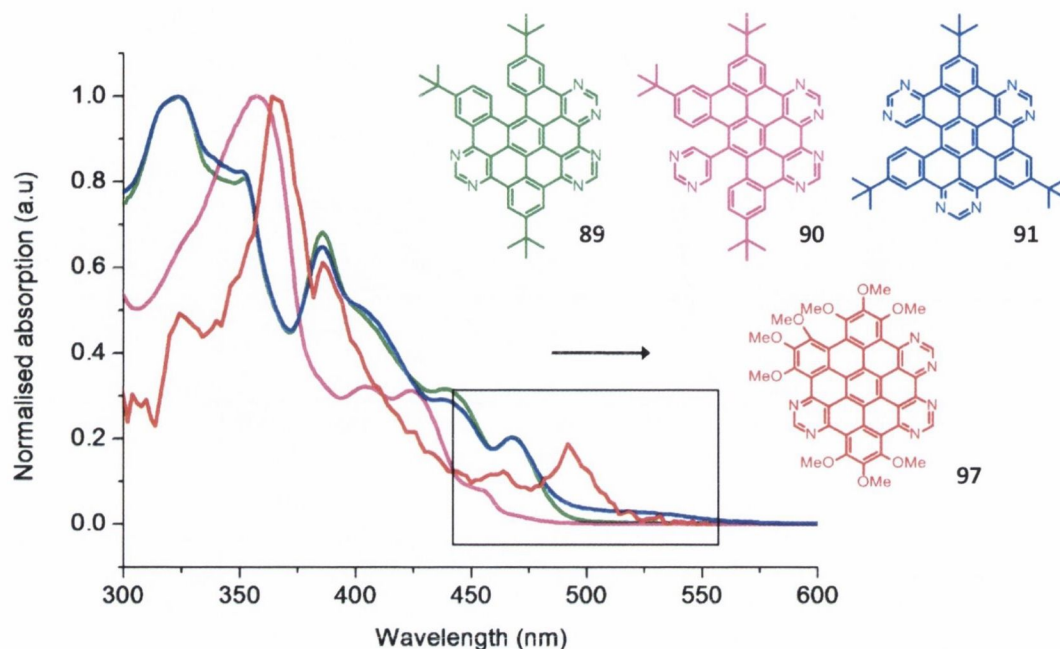


Figure 3.24: The overlaid UV-Vis absorption spectra of HASB (**89**, **90**, **91** and **97**) in toluene ($\sim 10^{-6} M$).

The UV-Vis absorption spectra of the HASB systems are shown in Figure 3.24. Both $5/6^{\text{th}}$ -fused **89** and **91** show comparable structural features in the absorption bands ($\lambda_{\text{max}}^{\text{abs}} = 345 \text{ nm}$). $2/3$ -fused **90** shows a slightly hypsochromically shifted spectrum compared to **89** and **91** (marked in 'grey box'), due to the decrease in the aromatic platform in size. The methoxy HASB **97** shows a typical band structure of a fully-fused system centered around $\lambda_{\text{max}}^{\text{abs}} = 365 \text{ nm}$. The main absorption band has slightly red shifted compared to methoxy DASB **82** ($\lambda_{\text{max}}^{\text{abs}} = 360 \text{ nm}$), with the lowest energy band at $\lambda = 492 \text{ nm}$ now red shifted by $\sim 770 \text{ cm}^{-1}$ compared to **82** (Table 3.2). The additional electron-donating methoxy substituents in **97** destabilise the HOMO to a greater extent than the comparable effect for **82**, thereby decreasing the HOMO-LUMO gap. This leads to a red shifted absorption spectrum in **97**. In addition, the stabilisation of the LUMO in **97** (6N) due to the increase number of N atoms compared to **82** (2N), also contribute to reducing the HOMO-LUMO gap. This gap can directly calculated using the α -band position of the compounds, revealing that the gap is smaller for **97** (2.52 eV) than in **82** (2.61 eV). Armaroli and co-workers have previously shown that the electron-donating substituents affect the absorbance and emission spectra and the extent of red-shift increases with the electron-donating properties of the substituents.¹⁵⁶

Table 3.2: The absorption maxima observed in the UV-Vis absorption spectra of HASB's **89**, **90**, **91**, **97** along with N-HSB (**47**) and methoxy DASB **82** in toluene ($\sim 10^{-6}$ M).

Compound	λ_{max} [nm] ($\epsilon \times 10^4$ [M ⁻¹ cm ⁻¹])
89	323 (11.3), 352 (9.2), 385 (7.8), 440 (3.5), 468 (2.2)
90	295 (1.8), 357 (5.0), 405 (2.1), 423 (2.0), 455 (0.8)
91	323 (11.0), 352 (9.1), 385 (7.6), 440 (3.3), 468 (2.1)
97	325 (6.0), 365 (12.1), 386 (8.1), 462 (2.9), 492 (3.3)
N-HSB (47)	339 (5.7), 355 (13.7), 376 (5.4), 393 (3.2), 413 (1.5), 451 (1.0), 481 (1.4)
82	343 (8.6), 360 (20.3), 378 (8.1), 398 (3.9), 445 (1.1), 474 (1.7)

3.3.2.1 Protonation studies of **89**

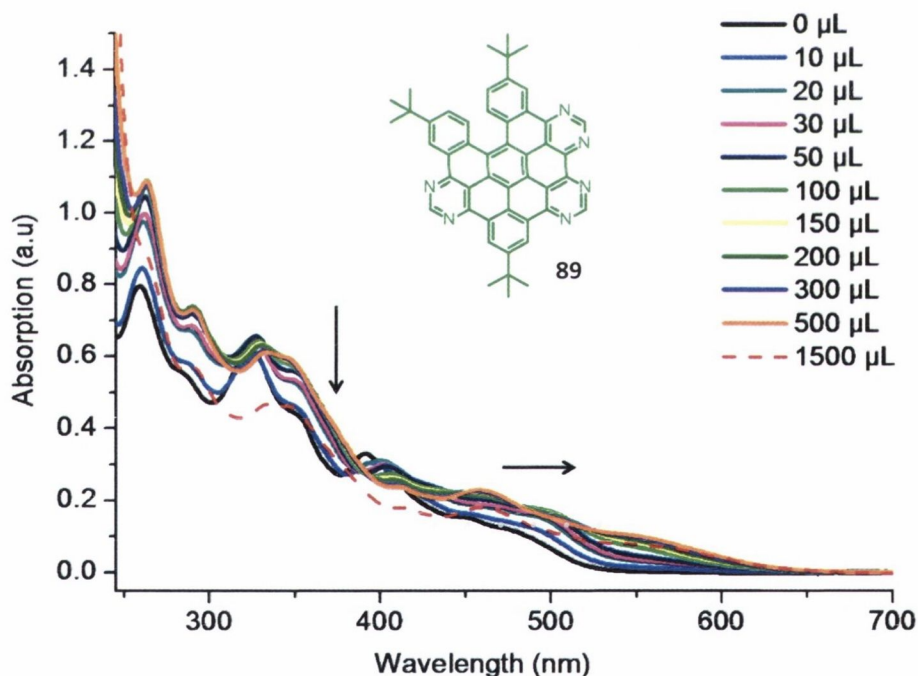


Figure 3.25: UV-Vis absorption spectral changes of **89** (1×10^{-5} M) upon sequential addition of 0.1 M trifluoroacetic acid in CH_2Cl_2 .

Figure 3.25 shows the UV-Vis absorption spectra obtained for **89** upon gradual addition of aliquots of trifluoroacetic acid to a solution of **89** in CH_2Cl_2 (1×10^{-5} M). Unlike in the fully-fused 2N system **78**, the changes observed for $^{5/6}$ -fused **89** are not as pronounced. The main absorption band at $\lambda = 323$ nm is slightly red shifted, with the

band at $\lambda = 385$ nm showing a reduced intensity along with a bathchromic shift. The reduction in intensity of the band at $\lambda = 385$ nm indicate some $n-\pi^*$ character. An isobestic point is apparent at $\lambda \sim 370$ nm and is due to the presence of both neutral and protonated species at equilibrium. The appearance of a new low energy band at $\lambda \sim 540$ nm is due to the absorption form the newly-formed protonated species.

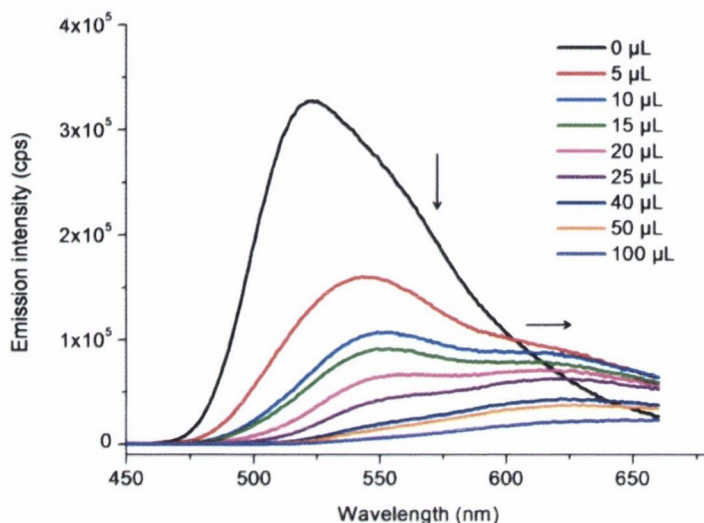


Figure 3.26: Emission spectral changes of **89** (CH_2Cl_2 , 1×10^{-5} M) upon sequential addition of 0.1 M trifluoroacetic acid.

The corresponding emission acid addition studies of **89** in CH_2Cl_2 shows gradual quenching of the emission bands at $\lambda = 520$ nm upon sequential addition of trifluoroacetic acid (1×10^{-3} M) aliquots. The decrease in emission intensity upon acid addition could be due to two main factors.

Firstly, the protonation leads to decrease in the concentration of the neutral form and thereby reduce the emission intensity. Secondly, the newly-formed protonated species absorbs at $\lambda \sim 540$ nm (Figure 3.25) which overlaps with the emission of the neutral form (Figure 3.26), resulting in reduced intensity of the neutral form. There is no indication of the emission due to the protonated species within the spectral window analysed. The $\text{N}^{\wedge}\text{N}$ coordination site in **89** allows sharing of the proton similar to 1,10-phenanthroline based systems where the proton is typically shared between the two nitrogens in weak acids as observed by Amaroli.¹³¹ However, further studies needs to be carried out to identify the nature of the protonated species.

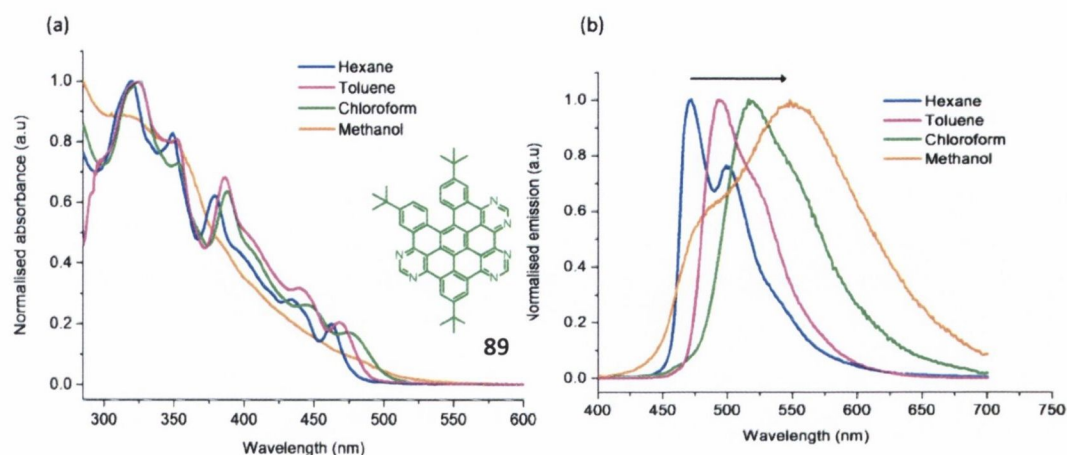
3.3.3 Solvent dependency studies of **89**

Figure 3.27: The (a) absorption and (b) emission spectra of **89** in various solvents ($\sim 10^{-6}$ M) at RT.

Solvent dependency studies are a useful tool to investigate the nature of transitions in absorption and emission spectra. The solvent dependency studies of **89** shows a bathochromic shift along with slight broadening of the lower energy bands. [Figure 3.27 (a)]. This is in agreement to the trend observed in DASB systems discussed in Chapter 2.

The corresponding emission solvent dependency study of **89** is presented in Figure 3.27 (b). The compounds are intensely fluorescent, and exhibit prominent vibrational progressions in non-polar solvent (e.g. hexane). As the solvent polarity is increased, the vibronic progression is lost and a broad emission results particularly in methanol. There is a significant bathochromic shift of the λ_{max} (~ 2900 cm^{-1}) in going from hexane to methanol. This agrees with the assignment of the first excited state S_1 as $^1(\pi-\pi^*)$ character.¹¹⁷ Generally, in polar solvents such as methanol, the solvent molecules interact more strongly with the excited state, lowering its energy and shift the emission to longer wavelengths.

3.3.4 Emission studies of HASB derivatives

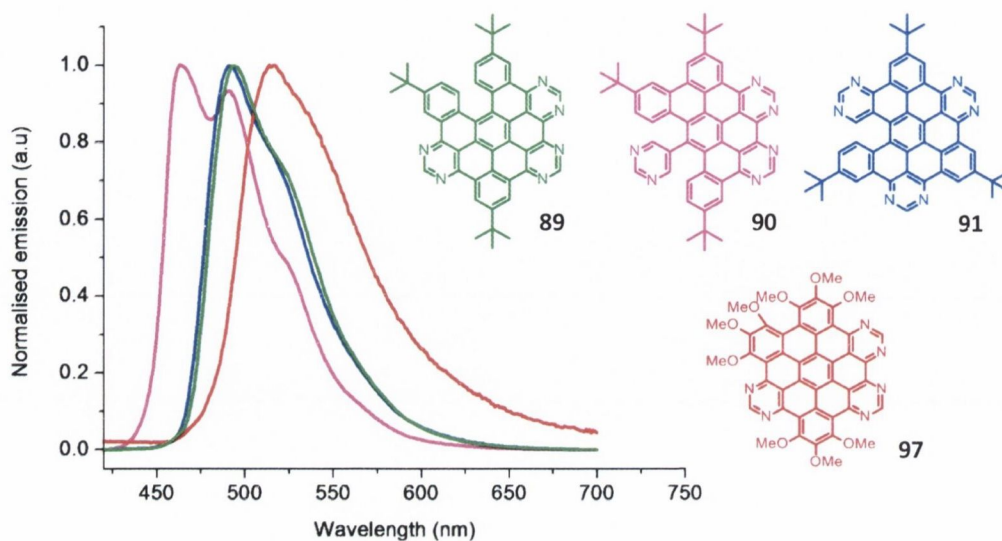


Figure 3.28: Overlaid emission spectra HASB systems (**89**, **90**, **91** and **97**) in toluene with $\lambda_{exc} = 360$ nm ($\sim 10^{-6}$ M) at R.T.

The overlaid emission spectra of the partially fused HASBs **89**, **90**, **91** and **97** are shown in Figure 3.28. These molecules lack the vibronic fine structure in their emission bands that was previously observed for the fully-fused 2N counterparts discussed in Chapter 2. The $5/6^{\text{th}}$ fused **89** and **91** shows a similar spectral shape with $\lambda_{em}^{\text{max}} = 495$ nm. The $2/3$ -fused **90** shows a relatively blue shifted spectrum compared to $5/6^{\text{th}}$ fused **89** and **91** with $\lambda_{\text{max}}^{\text{em}} = 463$ nm and a second band appearing at $\lambda = 495$ nm. This is explained by the partially fused platform and decrease in conjugation which results in hypsochromic shift observed in the $\lambda_{\text{max}}^{\text{em}}$ of the compound **90** relative to **89** and **91**. Attempts to obtain a fully-fused *tert*-butyl 6N system were not successful as the $5/6^{\text{th}}$ fused product proved to be the most stable end product. It prevented investigating an overall comparative photophysical study of 2N, 4N and 6N systems. It is interesting to note that the emission spectra of $5/6^{\text{th}}$ -fused products resemble that of N-HSB with $\lambda_{em}^{\text{max}} = 494$ nm in toluene. Furthermore, the DASBs shows well-resolved structured emission spectra (i.e. **78**, $\lambda_{em} = 475_{\text{max}}$, 508 and 544 nm), similar to its all carbon analogue HBC and upon increasing the number of the N-dopants in the platform, the vibronic structure observed in the emission is lost. This could be mainly due to the presence of more hydrogen bonding sites with increase N atoms.

Table 3.3: Emission results of HASB compounds

Compound	λ_{em} [nm] (λ_{exc} [nm])	τ (ns) (λ_{exc} [nm]/ λ_{em})
89	495 (360)	6.9 (340/ 495)
90	495 (360)	5.3 (340/ 495)
91	463 _{max} , 495 (360)	7.8 (295/ 463)
97	514 (360)	4.6 (340/ 514)

The 6N methoxy substituted **97** shows a broad emission with $\lambda_{max} = 515$ nm and is further red shifted compared to the *tert*-butyl counterparts (**89**, **90** and **91**). Both the inclusion of electron-donating methoxy substituents and the increase in conjugation contribute for the bathochromic shift in emission observed in **97**. Furthermore, **97** also shows significant overlap of the 0-0 transition at $\lambda = 495$ nm in both absorption and emission spectra suggesting that there is less solvent stabilisation by toluene in the excited state (Figure 3.29).

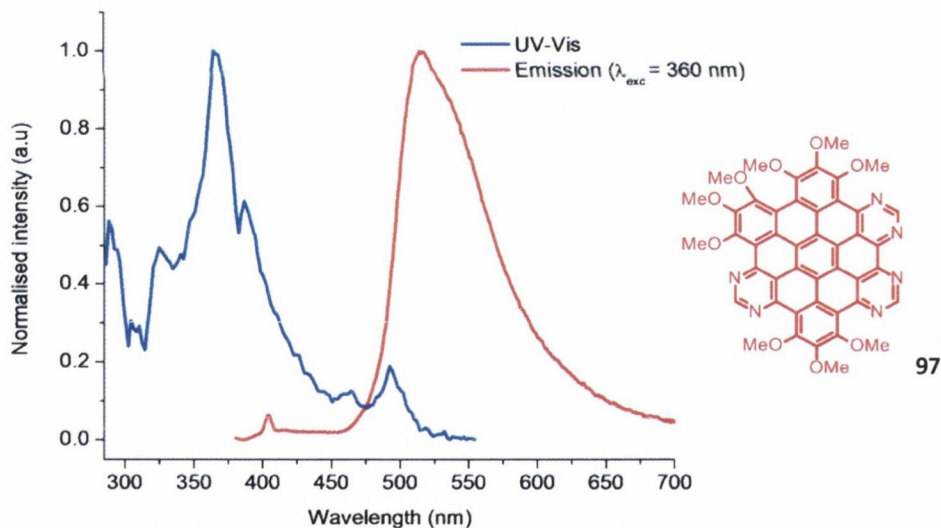


Figure 3.29: The overlaid absorption and emission spectra **97** in toluene with $\lambda_{exc} = 360$ nm ($\sim 10^{-6}$ M).

As DASB derivatives, HASB systems also showed comparable lifetimes in the ns range (4-8 ns)). These nanoscale lifetimes further confirm that the emission is mainly from the $^1(\pi-\pi^*)$ excited state.¹¹⁷ The quantum yields of $^5/6^{th}$ -Asym-HASB **89** was measured using Demas and Crosby method¹³⁴ (discussed in Section 2.3.3.5) using quinine sulphate in 0.5 M H₂SO₄ solution (λ_{exc} 310 nm, $\phi_{em} = 0.546$) as the standard. **89** displays

an emission quantum yield of $\phi_{\text{em}} = 0.32$ in CHCl_3 . The quantum yield is decreased in magnitude relative comparison to DASB **78** ($\phi_{\text{em}} = 0.45$). $^{5/6}$ fused **89** compound's lack of molecular rigidity could lead to deactivation of the excited state *via* non-radiative pathways, resulting a reduced quantum yield.

3.3.5 Electrochemistry studies of HASBs

To further understand the relative positions of the HOMO and LUMO levels in HASB systems, electrochemical measurements were undertaken. Cyclic voltammetric studies for HASB derivatives **89-91** were carried out in 1 mM solutions of CH_2Cl_2 (0.1 M $^n\text{Bu}_4\text{NPF}_6$) using Ag/AgCl electrode or SCE as the reference electrode, a Pt wire as the counter electrode and glassy carbon working electrode. The electrochemical properties of fully-fused **97** could not be investigated due to the poor yields obtained for the reaction. All the potentials are quoted vs the Fc/Fc^+ couple (0.0 V) and referenced to internal ferrocene added at the end of each experiment.

$^{5/6}$ -Asym-HASB **89** shows an irreversible first oxidation wave at $E_{\text{pa}} = +1.25$ V, with $^{5/6}$ -Sym-HASB **91** showing no clear oxidation potential within the spectral window analysed (Figure 3.30). The $^{2/3}$ -fused **90** ($E_{\text{pa}} = +1.3$ V) showed a slightly higher oxidation potential compared to its $^{5/6}$ -fused counterpart **89**. The reduced aromaticity in **90** could lead to a stabilized HOMO making the oxidation in **90** slightly more difficult than **89**. As shown in Table 3.4, comparing the oxidation potentials of all-carbon ^tBu -HBC, **78** (2N), **47** [N-HSB, 4N] together with **89** (6N) show a clear trend. The degree of difficulty of oxidation will increase with number of N-dopants in the aromatic platform. The inclusion of additional N-atoms in to the hexasuperbenzene periphery reduces the electron density of the aromatic platform, leading to stabilisation of the HOMO. As a result it makes the oxidation of the 6N systems far more difficult compared to the all-carbon/ 2N or 4N counterparts, despite the partially fused nature in **89**.

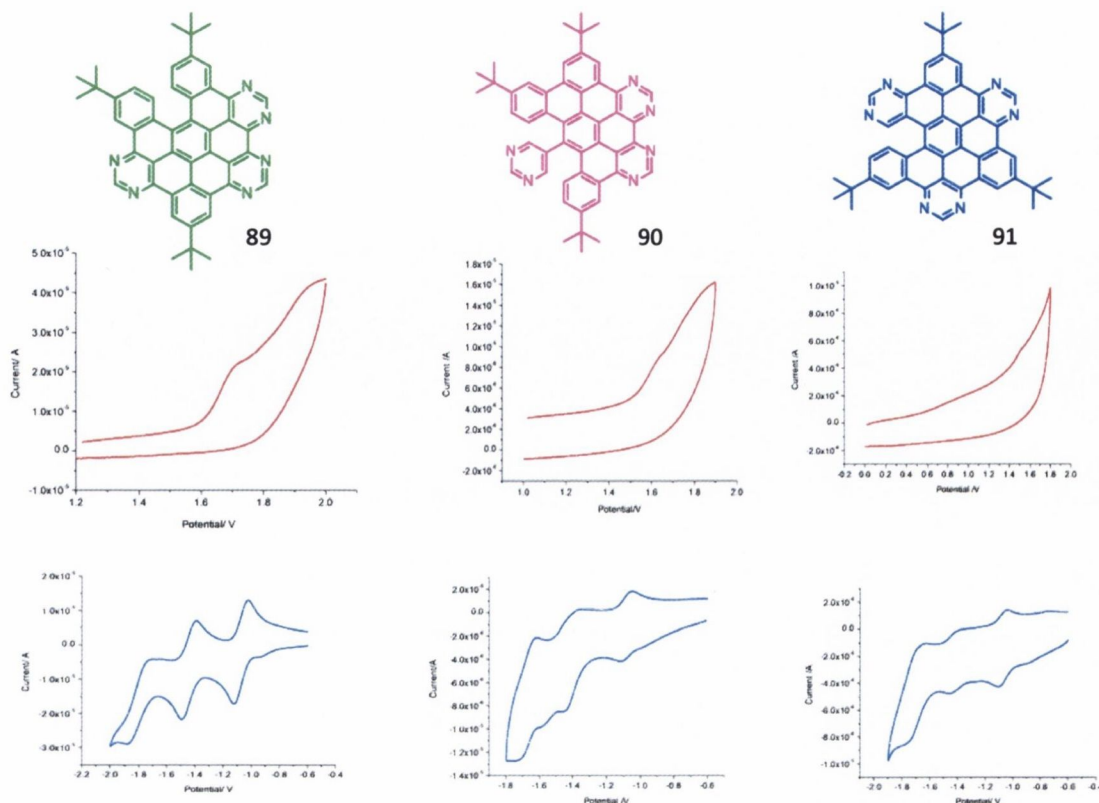


Figure 3.30: Cyclic voltammograms of **89**, **90** and **91** showing (a) oxidation and (b) reduction in 1 mM solutions of CH_2Cl_2 (0.1 M $n\text{Bu}_4\text{NPF}_6$) using Ag/AgCl electrode as the reference electrode.

$^{5/6}$ -Asym-HASB **89** shows three reversible reduction potentials at $E_{1/2} = -1.57$ V, -1.94 V and -2.32 with $^{5/6}$ -Sym-HASB **91** ($E_{1/2} = -1.55$ V, -1.91 V, -2.19 V) showing similar reduction potentials. The reduction spectrum of **91** is broader compared to **89** which shows clear sharper reduction peaks. This supports the observation that the compound undergoes stacking in solution at higher concentrations as observed by the NMR studies (Section 3.2.4). The corresponding reduction potentials of 6N systems showed an opposite trend as expected, with 6N systems been the most easiest to reduce compared to all-carbon/ 2N or 4N systems (Table 3.4). This shows that increasing the number of N-dopants in the aromatic platform confers electron accepting properties on the molecule and stabilization of the LUMO occurs.

Table 3.4: Electrochemical data for fully-fused HASBs **89**, **90** and **91** along with **78**, *N*-HSB and hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene (*^tBu-HBC*).

Compound	Oxidation $E_{1/2}/V[\Delta E_p$ mV]	Reduction $E_{1/2}/V [\Delta E_p$ (mV)]
89	+1.25 ^b	-1.57 [95], -1.94 [99], -2.32 [133]
90	+1.3 ^b	-1.56 [55], -1.88 [59], -2.18 [91]
91	No oxidation	-1.55 [48], -1.91 [43], -2.19 [45]
78	+0.70 [90], +0.89 [85]	-2.02 [83]
47 [<i>N</i> -HSB (4N)] ^[54]	+0.9 ^b	-1.56 [60], -2.00 [102], -2.32
1b (<i>^tBu-HBC</i>) ^[39]	+0.53, +0.88	-2.66, -2.96*

In deoxygenated dichloromethane (0.1 M, *n*Bu₄NPF₆) at 298K, scan rate = 100 mVs⁻¹, reported vs. Fc/Fc⁺; *b* Irreversible/quasi-reversible oxidation process, E_{pa}/V (anodic peak potential) quoted; $c\Delta E_p = E_{pa} - E_{pc}$, peak potential separation.; *d* Reversible oxidation process, $E_{1/2}/V [\Delta E_p/mV]$ quoted.* reported in THF.

3.4 Conclusions

This chapter outlines the synthesis and characterisation of a novel family of 6N-doped heterosuperbenzenes (hexaazasuperbenzenes (HASBs)) which vary in their peripheral functionalisation. The 6N polyphenylene precursors were synthesised *via* Co₂(CO)₈ catalysed [2+2+2] cyclotrimerisation of asymmetric monopyrimidyl acetylene starting material. The cyclotrimerisation route provides a convenient one-step synthetic route to HASB polyphenylene precursors compared to the multistep route employed for the synthesis of DASBs. The cyclotrimerisation of asymmetric acetylenes **70** and **72** resulted in both asymmetric and symmetric polyphenylene products in approximately 3:1 ratio. Cyclotrimerised products of **93** also show the presence of both isomers in the NMR analysis. Despite several attempts the two isomers could not be separated.

The oxidative cyclodehydrogenation of the *tert*-butyl functionalised polyphenylenes (**87** and **88**) were attempted *via* three methods: (i) the AlCl₃/CuCl₂ route (i) the FeCl₃ route and (ii) the DDQ/H⁺ route. In the oxidative cyclodehydrogenation of **87**, the major product is the ⁵/₆th fused product (**89**), irrespective of the route taken. This indicates that

the $5/6^{\text{th}}$ -Asym HASB **89** is the preferred final product in the oxidative cyclodehydrogenation of **87**. The symmetric isomer **88** also resulted in a $5/6^{\text{th}}$ -Sym HASB (**91**) *via* the FeCl_3 route. Surprisingly, the ring closure did not go to completion for the *tert*-butyl functionalised 6N systems. However, with the incorporation of the methoxy functionalised groups (in **95** and **96**), the Scholl reaction was more efficient. This resulted both fully-fused and $5/6^{\text{th}}$ -fused products as the major products. Isolation of the products proved to be tedious and only fully fused **97** was isolated in relatively low yield. Overall, the oxidative cyclodehydrogenation of the 6N systems proved to be synthetically far more challenging than their 2N or 4N counterparts, as it resulted in a myriad of partially fused products.

The photophysical investigation of these compounds shows a similar trend to the TASB (4N) systems, showing structured absorption profiles along with broad emissions profiles ($\lambda_{\text{max}} \sim 500 \text{ nm}$) in the visible region. In contrast, DASB shows well-resolved structured absorption and emission spectra, similar to HBC. The presence of more hydrogen bonding sites with increasing N-doping could result in these changes. The electrochemical measurements of the HASB derivatives show that they are easier to reduce compared to all-carbon/ 2N or 4N analogues. This is due to the N-dopants in the aromatic platform stabilising the LUMO. These results further shows our ability to control both the optical and electronic properties of these nanographenes *via* simple chemical alterations.

3.5 Future work

The Draper group has gained a broad insight in to the chemical, optical and electronic properties of N-doped molecular graphenes through the research carried out over the last few years since the original synthesis of parent N-HSB molecule. Therefore, it would be interesting to explore the properties of larger N-doped graphitic platforms (Figure 3.31) shows a potential synthetic route for the generation of a larger N-doped polyphenylene precursor *via* a combination of [2+4] Diels-Alder and [2+2+2] cyclotrimerisation routes. The successful oxidative cyclodehydrogenation of the polyphenylene precursor would give rise to a larger N-doped aromatic platform.

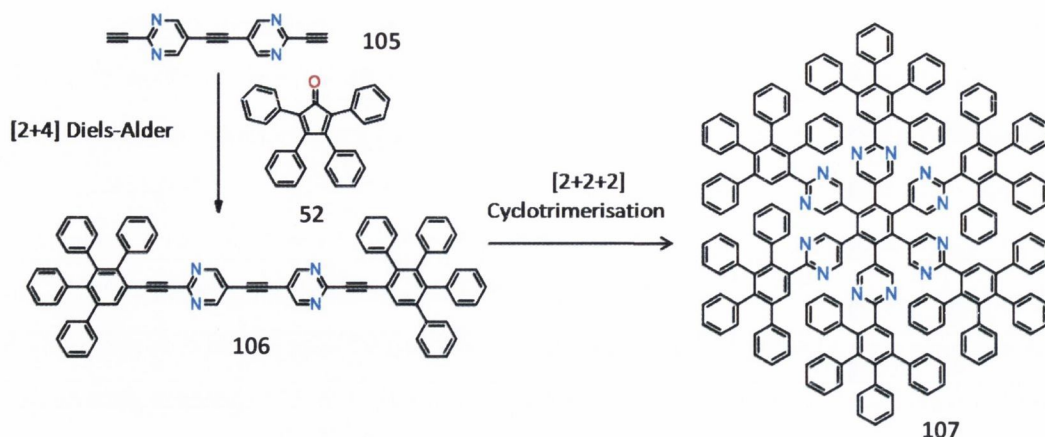


Figure 3.31: Proposed synthetic route to a larger N-doped aromatic platform.

All-carbon, HPB and HBC derivatives with C_3 symmetry are established as an invaluable class of compounds.^{157, 158} The [2+2+2] cyclotrimerisation of unsymmetrical acetylenes offers a new convenient route towards such systems. As discussed above, the issue with this method is the formation of both symmetrical and asymmetrical isomers, which prove very challenging to isolate. This method also tends to form a propensity of the less valuable asymmetric isomer. Kojima *et al.*¹⁵⁹ have recently reported a novel route to create C_3 -symmetrical polyphenylenes *via* a selective late-stage desymmetrization approach, utilising a thermodynamically controlled ArBr/ArLi exchange reaction (Figure 3.32). This approach would also be useful for the investigation N-doped systems to achieve controlled synthesis of C_3 symmetric N-doped polyphenylene precursors.

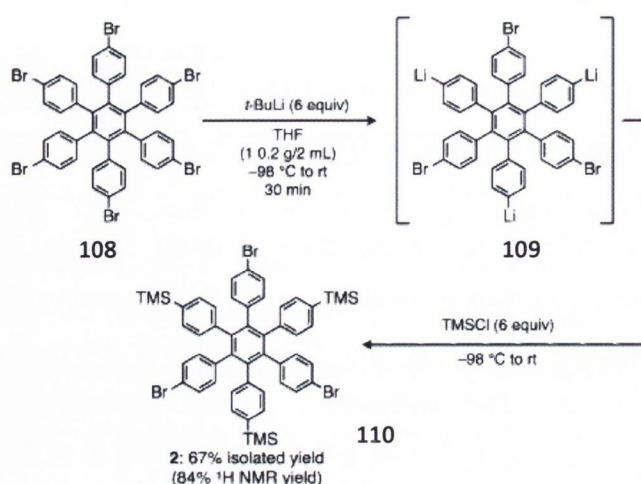


Figure 3.32: Novel route to symmetric polyphenylenes shown by Kojima *et al.*¹⁵⁹

While conventional solution-based oxidative cyclodehydrogenation of polyphenylene precursors has been favoured to generate graphene derivatives, surface mediated cyclodehydrogenation has recently attracted extensive interest as an alternative route towards generating graphitic systems, in particular graphene nanoribbons.²² This method overcomes the solubility problems encountered in the synthesis of larger graphenes using wet chemical synthesis. Nitrogen-doping of graphene systems have also been explored widely due to the interesting potential applications such as oxygen reduction catalysts^{24, 160} and N-type semiconductors for FETs¹⁶¹. Among the various routes employed, surface mediated cyclodehydrogenation of N-doped systems has attracted wide interest.^{162, 163 164} Preliminary studies are ongoing in the group to explore the surface mediated synthesis of N-containing platforms *via* halogenated N-doped precursors.¹⁶⁵ In this route only low temperatures are needed for the on-surface cyclodehydrogenation of polyphenylenes. This makes the approach potentially compatible with standard complementary metal-oxide semiconductor (CMOS) fabrication processes, and opens a new route to the commercialisation of nanographene based electronics.

4. Experimental

4.1 General methods

Unless otherwise stated, all reactions were carried out under an inert atmosphere of either nitrogen or argon using standard Schlenk and vacuum line techniques. Solvents were dried using appropriate drying agents and distilled under a nitrogen atmosphere, CH_2Cl_2 , diisopropylamine, triethylamine distilled over CaH_2 and THF and toluene over sodium/benzophenone. Flash chromatography was performed using silica gel 60 (Sigma Aldrich), particle size 0.04-0.063 mm as the stationary phase. All chemicals were obtained from commercial sources (Sigma-Aldrich Ltd.) and were used without further purification unless otherwise stated.

The known compounds dichlorobis(triphenylphosphine) palladium(II)1,4-dimethylpiperazine-2,3-dione (DMPD),¹⁶⁶ 1,3-bis-(4-*tert*-butylphenyl)propan-2-one,³³ 2-bis-(4-*tert*-butylphenyl)ethane-1,2-dione,³³ 2,3,4,5-tetra-(4-*tert*-butylphenyl)cyclopentadienone,³³ 2-methyl-4-pyrimidin-5-yl-but-3-yn-2-ol,³³ 5-ethynylpyrimidine,³³ di(pyrimidin-3,5-yl)acetylene,³³ 1,2-dipyrimidyl-3,4,5,6-tetra(4-*tert*-butylphenyl)benzene,³³ Tetra-*peri*-(*tert*-butyl-benzo)-di-*peri*-(pyrimidino)-coronene,³³ 1,3-bis(3,4,5-*tri*-methoxyphenyl)propan-2-one,⁵³ 3,4-bis(4-*tert*-butylphenyl)-2,5-bis(3,4,5-*tri*-methoxyphenyl)cyclopenta-2,4-dienone,⁵³ 1,2-dipyrimidyl-3,6-bis(3,4,5-*tri*-methoxyphenyl)-4,5-bis(4-*tert*-butylphenyl)benzene,⁵³ di-*peri*-(*tert*-butylbenzo)-di-*peri*-(*tri*-methoxybenzo)-di-*peri*-(pyrimidino)-coronene⁵³ were synthesised according to literature procedures.

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

IR spectra (reported in cm^{-1}) were recorded as neat samples on a Perkin-Elmer Spectrum 100 FT-IR spectrometer equipped with a Universal-ATR sampling accessory.

Electrospray mass spectra (ESI-MS) were recorded on a Micromass-LCT spectrometer. MALDI-TOF mass spectra were recorded on a Waters MALDI-QTOF Premier spectrometer using an α -cyano-4-hydroxy cinnamic acid matrix. Accurate mass spectra were referenced against Leucine enkephalin (555.6 g mol^{-1}) or [Glu¹]-Fibrinopeptide B ($1570.6 \text{ g mol}^{-1}$) and reported to within 5 ppm. All samples were dissolved in toluene, CHCl_3 or CH_2Cl_2 unless otherwise stated.

Elemental analyses were performed in the Microanalytical Laboratory, University College Dublin. Melting points are given uncorrected and were measured in capillary tubes using a Griffin melting point apparatus.

NMR spectra were recorded in CDCl_3 on (i) Bruker Avance DPX-400 MHz spectrometer (operating at 400.13 for ^1H , 100.6 MHz for ^{13}C); (ii) Bruker AV-400 MHz spectrometer operating at 400.13 MHz for ^1H , 100.6 MHz for ^{13}C or (iii) Bruker AV-600 MHz spectrometer (600 MHz for ^1H , 150.6 MHz for ^{13}C). ^1H and ^{13}C NMR spectra were referenced relative to TMS (δ 0.00 ppm). ^{13}C NMR spectra were proton decoupled. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hertz.

X-ray crystallography: Crystal and structural experimental data are summarised in the annex. The single crystal analyses were performed by Dr. Thomas McCabe, Dr. Longsheng Wang or Dr. Brendan Twamley in Trinity College with a Bruker SMART APEX CCD diffractometer (Compound **73**), a Rigaku Saturn-724 diffractometer (Compound **88**) or a Bruker APEX2 Duo diffractometer (Compounds **74**, **82** and **84**). The Bruker SMART APEX CCD and the Rigaku Saturn-724 diffractometers utilise a graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) source, while the Bruker APEX2 Duo utilises two radiation sources, a Mo- $K\alpha$ source and a high intensity Cu- $K\alpha$ source ($\lambda = 1.5418 \text{ \AA}$) generated from a microfocus anode. This Cu source was especially useful for the analysis of small crystal samples. The omega and phi scans method was used to collect either a full sphere or hemisphere of data for each crystal with a detector to crystal distance of either 5 or 6 cm. Data reduction was performed using SAINT. Intensities were corrected for Lorentz and polarization effects and for absorption using SADABS. Space group were determined from systematic absences and checked for higher symmetry. The structures were solved by direct methods using SHELXS and refined on F^2 using all data by full-matrix least-squares procedures with SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. For chiral space groups, absolute structure determination was based on the Flack parameter. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [\max(F_o^2) + 2(F_c^2)]/3$. In all cases, final Fourier syntheses showed no significant residual electron density in chemically sensible positions. Severely disordered CH_3OH solvent molecules were also present in the structure of **82**. PLATON/SQUEEZE reports a solvent accessible void

of $131 \text{ \AA}^3$, and the estimated number of electrons within the void is 40, which corresponds to roughly two CH_3OH molecules. A t butyl group (C58 and C60) in **82** was disordered. It was modelled in two positions with free variables for the site occupancy with a refined value of 56 and 44% for each moiety. Restraints (DFIX/ EADP constraint) were applied to the C(ipso)-C(terminal) bonds and the model was refined to convergence.

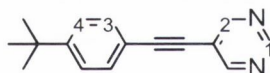
Photophysical measurements: All photophysical measurements were carried out with solutions containing in $1 \times 1 \text{ cm}^2$ quartz cuvettes in HPLC grade solvents. UV-Visible absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Emission and excitation spectra were obtained on a Perkin-Elmer LS55 fluorimeter or on a Horiba-Jobin-Yvon Fluorolog FL-3-11 spectrophotometer with double grating emission and excitation monochromators. Emission lifetime measurements were performed with an IBH Datastation HUB 5000F using NanoLED pulsed diode laser excitation sources of appropriate wavelength. Appropriate excitation repetition rates were chosen in order to ensure that no re-excitation of the sample occurred until the decay has reached the baseline. TAC (time to amplitude convertor) ranges were set at approximately twenty times the expected average decay time, and were less than the reciprocal of the source repetition rate. To prevent pile-up, the start-stop ratio (α) was maintained at less than 2%. If the repetition rates required were $> 100 \text{ kHz}$, the experiments were carried out in reverse mode. Data was fit using monoexponential decays where possible, while attempting to maintain a χ^2 statistic of ~ 1 , a Durbin-Watson statistic of ~ 2 , a random spread of residuals with approximately 60 % of residuals within one standard deviation of the fitted parameter, and over 99 % of the residuals within 3 standard deviations. When these parameters could not be satisfied (particularly where non-random behaviour was observed in the residuals plot), biexponential fits were obtained instead. The same criteria as above were applied to these residuals/fits. For shorter lifetimes (in the nanosecond range), the instrument response factor (IRF) was estimated through running a scattering solution with the detector set to the excitation wavelength. When reconvolution failed, this IRF estimate was used to aid analysis through tail fitting. The solvents and compounds used in this study were of spectroscopic grade. The optical density of the solutions at the excitation wavelength was less 0.15 when recorded in a 1 cm pathlength cuvette. Low temperature measurements were carried out in a thin quartz tube using a dewar filled with liquid nitrogen. Emission quantum yields of the solutions were measured by the Demas and Crosby¹⁶⁷ method and were measured relative to quinine

sulfate in 0.5 M H_2SO_4 ($\Phi_{\text{em}} = 0.546$),¹⁶⁸ for compounds all compounds shown and relative to coumarin 6 in ethanol ($\Phi_{\text{em}} = 0.78$)¹⁶⁹ for paramethoxy-TASB (**104**). Corrections were made for the difference in refractive index of the sample and reference solutions.

Electrochemistry: Cyclic voltammetry was performed by using a CH instruments Electrochemical Analyser Model 600B. Cyclic voltammograms were measured on 1 mM solutions of ligands in CH_2Cl_2 by using tetra-*n*-butylammonium hexafluorophosphate (TBAPF_6 , 0.1 M) as supporting electrolyte. A standard three-electrode cell was employed with a glassy carbon working electrode, a Pt wire counter electrode, and an SCE or Ag/AgCl electrode as the reference electrode. Potentials are quoted vs. the ferrocene/ferrocenium couple (0.0 V), and all potentials were referenced against the ferrocene internal standard which was added at the end of each experiment. Solutions were degassed for several minutes by nitrogen bubbling before the experiments were performed, and a flow of nitrogen over the solution was maintained for the duration of the experiment.

4.2 Synthesis of Diazasuperbenzenes

4.2.1 5-(4-*tert*-Butylphenylethynyl)pyrimidine (**70**)



5-Bromopyrimidine (1.0 g, 6.30 mmol), benzyltriethyl ammonium chloride (50 mg, 0.21 mmol), copper(I) iodide (68 mg, 0.36 mmol) and bis(triphenylphosphine) palladium(II) dichloride (220 mg, 0.32 mmol) were dissolved in toluene (5 mL). Aqueous sodium hydroxide (5.5 M, 4.5 mL) was added, followed by the dropwise addition of 4-*tert*-butylphenyl acetylene (1.0 g, 1.2 mL, 6.60 mmol). The mixture was stirred for 1 h at 65 °C. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (50 mL x 4). The organic extracts were combined, dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (SiO_2 , CH_2Cl_2 : CH_3OH , 50:1) and recrystallised from CH_3OH to give light yellow crystals (810 mg, 3.42 mmol, 55 %).

¹H-NMR (400 MHz, 20 °C, CDCl₃, δ in ppm): 9.16 (s, 1H, H¹), 8.88 (s, 2H, H²), 7.52 (d, 2H, ³J_{HH} = 8.5 Hz, H³), 7.43 (d, 2H, ³J_{HH} = 8.5 Hz, H⁴), 1.36 (s, 9H, C(CH₃)₃).

¹³C-NMR (100 MHz, 20 °C, CDCl₃, δ in ppm): 158.6 (2C, C²), 156.5 (1C, C¹), 152.9 (1C, C_{quat/aryl}), 131.6 (2C, C⁴), 125.6 (2C, C³), 120.2 (1C, C_{quat/Ar}), 118.7 (1C, C_{quat/Ar}), 96.6 (1C, pyrimidyl-C≡C-Ar), 81.3 (1C, pyrimidyl-C≡C-Ar), 34.5 (1C, C(CH₃)₃) and 30.7 (3C, C(CH₃)₃).

HRMS (ESI-MS, CH₂Cl₂): calculated for C₁₆H₁₇N₂, [M+H]⁺ *m/z*, 237.1392; found 237.1389.

M.p. 77 - 79 °C.

IR (neat) $\bar{\nu}$ in cm⁻¹: 2960, 2217 (C≡C), 1542, 1505, 1414, 1362, 1266, 1185, 1165, 1110, 916, 829, 720.

CHN: calculated (%) for C₁₆H₁₆N₂: C, 81.32; H, 6.82, N, 11.85. Found C, 81.26; H, 6.85, N, 11.76.

4.2.2 5-(Phenylethynyl)pyrimidine (**71**)

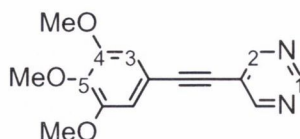


Compound **71** was prepared by modifying a related literature procedure.¹¹⁰ To a degassed solution of DMF (3 mL) and DIPA (6 mL), 5-bromo-pyrimidine (1.0 g, 6.3 mmol) and phenylacetylene (0.68 mL, 6.3 mmol) were added. The mixture was bubbled under a continuous stream of N₂. Tetrakis(triphenylphosphine)palladium(0) (116 mg, 0.1 mmol) and copper(I) iodide (23 mg, 0.12 mmol) were added and irradiated at 150 W, 115 °C for 25 min. After cooling the dark brown suspension was extracted with diethylether (50 mL x 2) and filtered. The solution was washed with saturated NH₄Cl (2 x 25 mL), water (2 x 25 mL) and finally dried over MgSO₄. The filtrate was concentrated *in vacuo* and pale yellow crystals were obtained. Crystals were washed with cold CH₃OH upon filtration (1.02 g, 5.66 mmol, 90.2 %).

¹H-NMR (400 MHz, CDCl₃, δ in ppm): 9.17 (s, 1H, H¹), 8.90 (s, 2H, H²), 7.58 (m, 2H, H^{Ar}), 7.40 (m, 3H, H^{Ar}).

HRMS (ESI-MS, CH₂Cl₂): calculated for C₁₂H₉N₂, [M+H]⁺ *m/z*, 181.0766; found 181.0766.

4.2.3 5-(3,4,5-Trimethoxyphenylethynyl)pyrimidine (72)



5-Bromo-1,2,3-trimethoxybenzene (247 mg, 1 mmol) and 5-ethynylpyrimidine (104 mg, 1 mmol) were added to a solution of DMF (0.5 mL) and DIPA (1.5 mL) bubbled over nitrogen. To this solution, triphenylphosphine (23 mg, 0.087 mmol), bis(triphenylphosphine) palladium(II)dichloride (15 mg, 0.021 mmol) and copper(I) iodide (4 mg, 0.02 mmol) were added and the mixture was irradiated at 150 W, 115 °C for 25 min. The brown suspension was cooled and extracted with Et₂O (2 x 50 mL), filtered and washed with saturated NH₄Cl (2 x 25 mL), water (2 x 25 mL) and then dried over MgSO₄. Off white crystals were obtained when the filtrate was concentrated *in vacuo*. Crystals were filtered and washed with cold CH₃OH, (122 mg, 0.45 mmol, 45 %).

¹H-NMR (400 MHz, 20 °C, CDCl₃, δ in ppm): 9.18 (s, 1H, H¹), 8.90 (s, 2H, H²), 6.82 (s, 2H, H³), 3.93 (s, 9H, OCH₃).

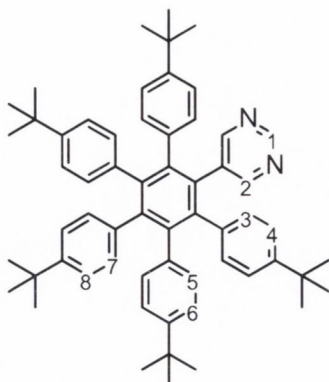
¹³C-NMR (150 MHz, 20 °C, CDCl₃, δ in ppm): 157.8 (2C, C²), 155.6 (1C, C¹), 152.8 (2C, C⁴), 139.2 (1C, C⁵), 116.2 (C_{quat}), 108.5 (2C, C³), 96.2 (pyrimidyl-C≡C-Ar), 81.2 (pyrimidyl-C≡C-Ar), 60.6 (1C, -C⁵OCH₃), 55.8 (2C, -C⁴OCH₃).

HRMS (ESI-MS, CH₂Cl₂): calculated for C₁₅H₁₅N₂O₃, [M+H]⁺ *m/z*, 271.1083; found 271.1077.

M.p. 136 - 140 °C.

IR (neat) $\bar{\nu}$ in cm⁻¹: 3067, 3013, 2928, 2834, 2209 (C≡C), 1578, 1541, 1505, 1469, 1355, 1237, 1120, 822, 765.

CHN: calculated (%) for C₁₅H₁₄N₂O₃: C, 66.66; H, 5.22, N, 10.36. found C, 66.33; H, 4.93; N, 10.04.

4.2.4 2,3,4,5,6-Penta(4-*tert*-butylphenyl)-1-(5-pyrimidyl) benzene (73)

Compound **70** (150 mg, 0.634 mmol), 2,3,4,5-tetra(*tert*-butylphenyl)cyclopentadien-1-one (390 mg, 0.640 mmol) and benzophenone (750 mg, 4.11 mmol) were heated to reflux over a sand bath for 2 hr in a round bottom flask attached to an N₂ air condenser. The colour changed from purple to brown after 1 hr. The product was cooled and purified by column chromatography (SiO₂, CH₂Cl₂ as the eluent). Benzophenone was eluted first followed by product fractions. The product fractions were concentrated *in vacuo* and **73** was obtained as a white solid, (396 mg, 0.49 mmol, 77 %).

¹H-NMR (400 MHz, 20 °C, CDCl₃, δ in ppm): 8.70 (s, 1H, H¹), 8.32 (s, 2H, H²), 6.92 (d, 4H, ³J_{HH} = 8.5 Hz, H⁴), 6.85 (d, 2H, ³J_{HH} = 8.5 Hz, H⁸), 6.84 (d, 4H, ³J_{HH} = 8.5 Hz, H⁶), 6.72 (d, 4H, ³J_{HH} = 8.5 Hz, H³), 6.71 (d, 2H, ³J_{HH} = 8.5 Hz, H⁷), 6.68 (d, 4H, ³J_{HH} = 8.5 Hz, H⁵), 1.13 (s, 18H, -C(CH₃)₃) and 1.11 (s, 27H, -C(CH₃)₃).

¹³C-NMR (150 MHz, 20 °C, CDCl₃, δ in ppm): 157.6 (2C, C²), 154.5 (1C, C¹), 148.1 (C_{quat}), 147.3 (C_{quat}), 140.7 (C_{quat}), 140.2 (C_{quat}), 136.9 (C_{quat}), 136.7 (C_{quat}), 136.0 (C_{quat}), 134.9 (C_{quat}), 131.9 (C_{quat}), 130.6 (4C, C³), 130.4 (2C, C⁷), 130.3 (4C, C⁵), 123.5 (4C, C⁴), 122.8 (6C, C⁶ and C⁸) 33.7 (2C, -C(CH₃)₃), 33.6 (3C, -C(CH₃)₃), 30.7 (9C, -C(CH₃)₃) and 30.7 (6C, -C(CH₃)₃).

HRMS (ESI-MS, CHCl₃): calculated for C₆₀H₆₉N₂, [M+H]⁺ *m/z*, 817.5461; found 817.5463.

M.p. 275-277 °C.

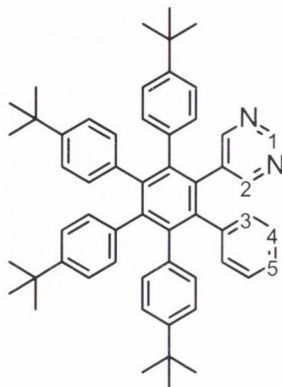
IR (neat) $\bar{\nu}$ in cm⁻¹: 2960, 2902, 2865, 1551, 1512, 1460, 1361, 1270, 853, 831 and 780.

CHN: calculated (%) for C₆₀H₆₈N₂: C, 88.18; H, 8.39; N 3.43. Found: C, 87.90; H, 8.32; N 3.19.

UV-Vis [(C₂H₅)₂O, nm]: 233 ($\lambda_{\text{max}}^{\text{abs}}$), 250, 280.

Fluorescence [(C₂H₅)₂O, nm, λ_{exc} = 300 nm, RT]: 366 nm ($\lambda_{\text{max}}^{\text{em}}$).

4.2.5 2,3,4,5- Tetrakis(4-*tert*-butylphenyl)-6-phenyl-1-(5-pyrimidyl)-benzene (74)



Compound **71** (61 mg, 0.34 mmol), 2,3,4,5-tetra(4-*tert*-butylphenyl)cyclopenta-2,4-dienone (200 mg, 0.328 mmol) and benzophenone (450 mg, 2.47 mmol) were combined to synthesise **74**, according to the procedure adopted for **73** (Section 4.2.4). The product was purified by column chromatography (SiO₂, CH₂Cl₂ followed by CH₂Cl₂:CH₃OH (50:1) once the benzophenone had eluted) and recrystallised from CH₃OH to give **74** as a white solid (200 mg, 0.26 mmol, 80 %).

¹H-NMR (600 MHz, 20 °C, CDCl₃, δ in ppm): 8.70 (s, 1H, H¹), 8.22 (s, 2H, H²), 6.98 - 6.90 (m, 5H, H^{Ar}), 6.89 - 6.82 (m, 6H, H^{Ar}), 6.75-6.71 (m, 6H, H^{Ar}), 6.70 (m, 4H, H^{Ar}), 1.14 (s, 9H, -C(CH₃)₃) and 1.12 (s, 27H, -C(CH₃)₃).

¹³C-NMR (151 MHz, 20 °C, CDCl₃, δ in ppm): 157.9 (2C, C²), 154.7 (1C, C¹), 148.5 (C_{quat}), 147.9 (C_{quat}), 147.8 (C_{quat}), 147.7 (C_{quat}), 142.3 (C_{quat}), 141.2 (C_{quat}), 140.7 (C_{quat}), 140.5 (C_{quat}), 140.1 (C_{quat}), 139.4 (C_{quat}), 137.1 (C_{quat}), 136.9 (C_{quat}), 136.8 (C_{quat}), 136.2 (C_{quat}), 135.3 (C_{quat}), 132.1 (C_{quat}), 131.3 (CH), 130.9 (CH), 130.7 (CH), 130.6 (CH), 127.1 (CH), 125.8 (CH), 123.2 (CH), 123.1 (CH), 123.0 (CH), 34.0 (2C, -C(CH₃)₃), 33.94 (1C, -C(CH₃)₃), 33.92 (1C, -C(CH₃)₃), 30.99 (2C, -C(CH₃)₃), 30.96 (2C, -C(CH₃)₃).

HRMS (ESI-MS, CHCl₃): calculated for C₅₆H₆₁N₂, [M+H]⁺ *m/z*, 761.4835; found 761.4840.

M.p. 274-276 °C.

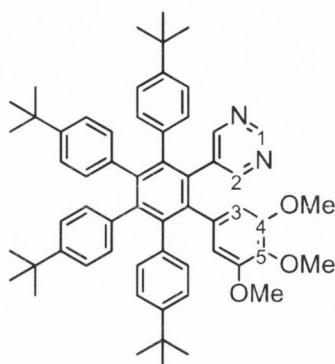
IR (neat) $\bar{\nu}$ in cm⁻¹: 2958, 2865, 1553, 1506, 1461, 1390, 1361, 1270, 1188, 1118, 1021, 852, 830, 780.

CHN: calculated (%) for $C_{56}H_{60}N_2$ C, 88.37; H, 7.95; N 3.68. Found: C, 88.29; H, 7.81; N 3.56.

UV-Vis [$(C_2H_5)_2O$, nm]: 236 (λ_{max}^{abs}), 248, 280.

Fluorescence [$(C_2H_5)_2O$, nm, $\lambda_{exc} = 300$ nm, RT]: 366 nm (λ_{max}^{em}).

4.2.6 2,3,4,5-Tetrakis(4-*tert*-butylphenyl)-6-(3,4,5-trimethoxyphenyl)-1-(5-pyrimidyl)- benzene (75)



Compound **72** (44 mg, 0.164 mmol), 2,3,4,5-tetra(4-*tert*-butylphenyl)cyclopenta-2,4-dienone (100 mg, 0.164 mmol), and benzophenone (450 mg, 2.47 mmol) were combined to synthesise **75**, following the procedure discussed for **73** (Section 4.2.4). The mixture was refluxed for 2 h and after cooling, the product was purified by column chromatography (SiO_2 , CH_2Cl_2 followed by $CH_2Cl_2:CH_3OH$, 50:1 once the benzophenone had eluted) and recrystallized from hexane/ CH_3OH to give off-white crystals of **75** (75 mg, 0.088 mmol, 54 %).

1H -NMR (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 8.77 (s, 1H, H^1), 8.29 (s, 2H, H^2), 6.94 (d, $^3J_{HH} = 8.2$ Hz, 2H, H^{Ar}), 6.92 (d, $^3J_{HH} = 8.3$ Hz, 2H, H^{Ar}), 6.85 (m, 4H, H^{Ar}), 6.74 (d, $^3J_{HH} = 8.3$ Hz, 2H, H^{Ar}), 6.71 (m, 4H, H^{Ar}), 6.66 (d, $^3J_{HH} = 8.0$ Hz, 2H, H^{Ar}), 6.02 (s, 2H, H^3), 3.69 (s, 3H, $-C^5OCH_3$), 3.42 (s, 6H, $-C^4OCH_3$), 1.15 (s, 18H, $-C(CH_3)_3$), 1.12 (s, 18H, $-C(CH_3)_3$).

^{13}C -NMR (150 MHz, 20 °C, $CDCl_3$, δ in ppm): 157.8 (2C, C^2), 155.0 (1C, C^1), 152.1 (C_{quat}), 148.7 (C_{quat}), 148.2 (C_{quat}), 147.98 (C_{quat}), 147.96 (C_{quat}), 142.5 (C_{quat}), 141.6 (C_{quat}), 141.0 (C_{quat}), 140.9 (C_{quat}), 140.0 (C_{quat}), 137.2 (C_{quat}), 137.2 (C_{quat}), 136.9 (C_{quat}), 136.3 (C_{quat}), 136.2 (C_{quat}), 135.6 (C_{quat}), 134.7 (C_{quat}), 132.1 (C_{quat}), 131.0 (2C, CH), 130.83 (2C, CH), 130.72 (2C, CH), 130.69 (2C, CH), 124.0 (2C, CH), 123.5 (2C, CH), 123.26 (2C, CH), 123.25 (2C, CH), 109.9 (2C, C^3), 60.9 (1C, $-C^5OCH_3$), 55.9 (2C, $-C^4OCH_3$).

C^4OCH_3), 34.19 (1C,-C(CH₃)₃), 34.15 (1C,-C(CH₃)₃), 34.08 (1C,-C(CH₃)₃), 34.07 (1C,-C(CH₃)₃), 31.15 (3C, -C(CH₃)₃), 31.13 (6C, -C(CH₃)₃), 31.10 (3C, -C(CH₃)₃).

HRMS (ESI-MS, CHCl₃): calculated for C₅₉H₆₇N₂O₃, [M+H]⁺ *m/z*, 851.5152; found 851.5160.

M.p. 262-264 °C.

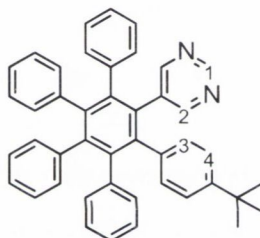
CHN: calculated (%) for C₅₉H₆₆N₂O₃: C, 83.25; H, 7.82; N, 3.29. found C, 82.93; H, 7.64; N, 3.19.

IR (neat) $\bar{\nu}$ in cm⁻¹: 2961, 2905, 2867 (CH₃ stretch), 1583, 1509 (C=C), 1555, 1462 (C=N), 1509, 1404, 1361 (CH₃ bend), 1238, 1188, 1128 (OCH₃) 833 and 779.

UV-Vis [(C₂H₅)₂O, nm]: 234 ($\lambda_{\max}^{\text{abs}}$), 250, 284.

Fluorescence [(C₂H₅)₂O, nm, λ_{exc} = 300 nm, RT]: 395 nm ($\lambda_{\max}^{\text{em}}$).

4.2.7 2,3,4,5-Tetrakis(phenyl)-6-(4-*tert*-butylphenyl)-1-(5-pyrimidyl)-benzene (76)



A mixture of **70** (122 mg, 0.52 mmol), 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (200 mg, 0.52 mmol), and benzophenone (450 mg, 2.47 mmol) was used to synthesise **76** following the procedure adopted for **73** (Section 4.2.4). The product was purified by column chromatography (SiO₂, CH₂Cl₂ as the eluent) and recrystallized from CH₃OH to give off-white crystals of **76** (258 mg, 0.43 mmol, 84 %).

¹H-NMR (600 MHz, 20 °C, CDCl₃, δ in ppm): 8.70 (s, 1H, H¹), 8.22 (s, 2H, H²), 6.94 (d, ³*J*_{HH} = 6.8 Hz, 2H, H⁴), 6.87 (m, 20H, H^{Ph}), 6.74 (d, ³*J*_{HH} = 6.85 Hz, 2H, H³), 1.15 (s, 9H, -C(CH₃)₃).

¹³C-NMR (101 MHz, 20 °C, CDCl₃, δ in ppm): 157.4 (2C, C²), 154.5 (1C, C¹), 152.1 (C_{quat}), 148.4 (C_{quat}), 141.4 (C_{quat}), 140.6 (C_{quat}), 140.4 (C_{quat}), 140.3 (C_{quat}), 139.6 (C_{quat}), 139.4 (C_{quat}), 138.9 (C_{quat}), 135.6 (C_{quat}), 131.2 (C_{quat}), 131.1 (CH), 131.0 (CH), 130.8 (C³), 130.7 (CH), 130.4 (CH), 126.9 (CH), 126.3 (CH), 126.26 (CH), 126.2 (CH), 125.7 (CH), 125.04 (CH), 124.97 (CH), 123.7 (C⁴), 33.8 (1C,-C(CH₃)₃), 30.6 (1C,-C(CH₃)₃).

HRMS (ESI-MS, CHCl_3): calculated for $\text{C}_{44}\text{H}_{37}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z , 593.2951; found 593.2950.

M.p. 298 – 300 °C.

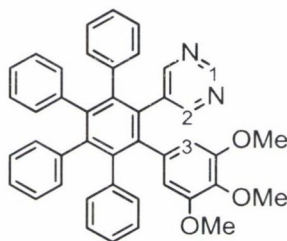
IR (neat) $\bar{\nu}$ in cm^{-1} : 2958, 2865, 1551, 1495, 1440, 1392, 1270, 1180, 1025, 1070, 907, 845 and 786.

CHN: calculated (%) for $\text{C}_{44}\text{H}_{36}\text{N}_2$ C, 89.15; H, 6.12; N 4.73. Found: C, 89.17; H, 6.08; N 4.72.

UV-Vis [$(\text{C}_2\text{H}_5)_2\text{O}$, nm]: 245 ($\lambda_{\text{max}}^{\text{abs}}$), 275.

Fluorescence [$(\text{C}_2\text{H}_5)_2\text{O}$, nm, $\lambda_{\text{exc}} = 300$ nm, RT]: 382 nm ($\lambda_{\text{max}}^{\text{em}}$).

4.2.8 2,3,4,5-Tetrakis(phenyl)-6-(3,4,5-trimethoxyphenyl)-1-(5-pyrimidyl)-benzene (77)



A mixture of **72** (140 mg, 0.52 mmol), 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (200 mg, 0.52 mmol), and benzophenone (450 mg, 2.47 mmol) was used to synthesise **77** following the procedure adopted for **73** (Section 4.2.4). The product was purified by column chromatography [SiO_2 , CH_2Cl_2 followed by $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ (10:0.1) once the benzophenone had eluted] and recrystallized from CH_3OH to give off-white crystals of **77** (197 mg, 0.34 mmol, 66 %).

$^1\text{H-NMR}$ (600 MHz, 20 °C, CDCl_3 , δ in ppm): 8.77 (s, 1H, H^1), 8.28 (s, 2H, H^2), 6.89 (m, 20H, H^{Ph}), 6.04 (s, 2H, H^3), 3.69 (s, 3H, $-\text{OCH}_3$), 3.45 (s, 6H, $-\text{OCH}_3$).

$^{13}\text{C-NMR}$ (101 MHz, 20 °C, CDCl_3 , δ in ppm): 157.2 (2C, C^2), 154.7 (1C, C^1), 151.7 (C_{quat}), 141.7 (C_{quat}), 140.6 (C_{quat}), 140.5 (C_{quat}), 140.4 (C_{quat}), 139.98 (C_{quat}), 139.5 (C_{quat}), 139.4 (C_{quat}), 139.2 (C_{quat}), 138.7 (C_{quat}), 135.9 (C_{quat}), 134.90 (C_{quat}), 133.8 (C_{quat}), 132.1 (C_{quat}), 130.8 (CH), 130.7 (CH), 130.6 (CH), 130.5 (CH), 128.5 (C_{quat}), 127.0 (CH), 126.5 (CH), 126.4 (CH), 126.3 (CH), 125.8 (CH), 125.3 (CH), 125.2 (CH), 109.1 (2C, C^3), 60.4 (1C, $-\text{OCH}_3$), 55.7 ($-\text{OCH}_3$), 55.5 ($-\text{OCH}_3$).

HRMS (ESI-MS, CHCl₃): calculated for C₄₃H₃₅N₂O₃, [M+H]⁺ *m/z*, 627.2648; found 627.2664.

M.p. 248-250 °C.

IR (neat) $\bar{\nu}$ in cm⁻¹: 2900, 2880, 1550, 1508, 1393, 1296, 1235, 1180, 1125, 1024, 1002, 923, 839, 774.

UV-Vis [(C₂H₅)₂O, nm]: 245 ($\lambda_{\max}^{\text{abs}}$), 280.

Fluorescence [(C₂H₅)₂O, nm, λ_{exc} = 300 nm, RT]: 408 nm ($\lambda_{\max}^{\text{em}}$).

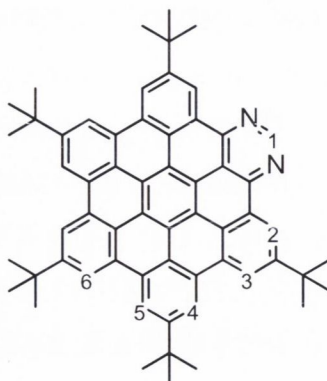
4.2.9 Cyclodehydrogenation of **73**

Oxidative cyclodehydrogenation of **73** was carried out *via* two methods; **Method A** - FeCl₃ route and **Method B** – using the DDQ/H⁺ route.

Method A

A solution of FeCl₃ (700 mg, 4.28 mmol) in nitromethane (4 mL) was added dropwise to a solution containing **73** (150 mg, 0.183 mmol) in CH₂Cl₂ (60 mL). The reaction mixture was left stirring for 24 h with a stream of nitrogen bubbling through the solution. The reaction mixture was then quenched with CH₃OH (10 mL) and concentrated to give a dark precipitate which was filtered and washed with CH₃OH and then with water (152 mg). The products were separated by chromatography on silica using CH₂Cl₂ as the eluent to isolate 1/3rd-cyclised (two C-C bonds fused) compound **79** (73 mg, 0.09 mmol, 49 %), then the polarity of the column was increased using CH₂Cl₂:CH₃OH (50:1) to elute the fully-cyclised (six C-C bonds closed), 1,3-diazasuperbenzene **78** (53 mg, 0.065 mmol, 35 %).

5, 8, 11, 14, 17-Penta-(*tert*-butyl)-1,3-diazasuperbenzene (**78**)



$^1\text{H-NMR}$ (600 MHz, 20 °C, CDCl_3 , δ in ppm): 9.97 (s, 1H, H^1), 9.88 (d, 2H, $^4J_{\text{HH}} = 1.5$ Hz, H^2), 9.44 (d, 2H, $^4J_{\text{HH}} = 1.5$ Hz, H^3), 9.30 (s, 2H, H^6), 9.29 (s, 2H, H^5), 9.23 (s, 2H, H^4), 1.88 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.86 (s, 18H, $-\text{C}(\text{CH}_3)_3$) and 1.85 (s, 18H, $-\text{C}(\text{CH}_3)_3$).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ in ppm): 155.5 (1C, C^1), 122.3 (2C, C^3), 121.8 (2C, C^2), 119.0 (4C, C^5 and C^6), 118.8 (2C, C^4), 32.1 ($-\text{C}(\text{CH}_3)_3$).

HRMS (ESI-MS, CHCl_3): calculated for $\text{C}_{60}\text{H}_{57}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z , 805.4522; found 805.4553.

M.p >360 °C.

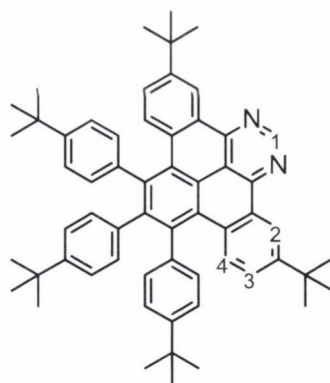
IR (neat) $\bar{\nu}$ in cm^{-1} : 2954, 1607, 1576, 1554, 1465 1363, 1261, 1239 and 867.

CHN: calculated for (%) for $\text{C}_{60}\text{H}_{56}\text{N}_2 \cdot 0.4\text{CH}_2\text{Cl}_2$: C, 86.42; H, 6.82; N, 3.33. Found C, 86.52; H, 6.95; N, 3.09.

UV-Vis (C_7H_8 , nm): 340, 357 ($\lambda_{\text{max}}^{\text{abs}}$), 377, 393, 420, 443, 470.

Fluorescence (C_7H_8 , nm, $\lambda_{\text{exc}} = 360$ nm, RT): 471 ($\lambda_{\text{max}}^{\text{em}}$), 504, 541.

$\frac{1}{3}$ -*Tert*-butyl-DASB (**79**)



$^1\text{H-NMR}$ (600 MHz, 20 °C, CDCl_3 , δ in ppm): 9.86 (s, 1H, H^1), 9.53 (s, 1H, H^2), 7.86 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, H^4), 7.34 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, H^3), 7.19 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, H^{Ar}), 7.02 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, H^{Ar}), 6.86 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, H^{Ar}), 6.60 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, H^{Ar}), 1.49 (s, 18H, $-\text{C}(\text{CH}_3)_3$), 1.31 (s, 18H, $-\text{C}(\text{CH}_3)_3$), 1.16 (s, 9H, $-\text{C}(\text{CH}_3)_3$). The analyses of product **79** were consistent with the literature values.¹¹⁰

UV-Vis (C_7H_8 , nm): 308 ($\lambda_{\text{max}}^{\text{abs}}$), 319, 368, 386.

Fluorescence (C_7H_8 , nm, $\lambda_{\text{exc}} = 300$ nm, RT): 423 ($\lambda_{\text{max}}^{\text{em}}$).

Method B

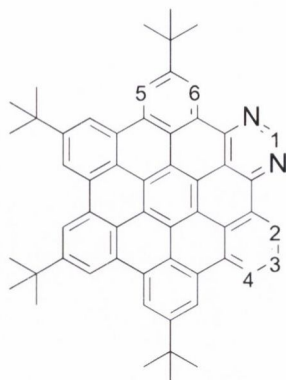
Compound **73** (50 mg, 0.061 mmol) was dissolved in CH₂Cl₂ (9 mL), and methanesulfonic acid (0.5 mL) was added. The reaction mixture rapidly changed colour to a bright orange upon addition of acid and the mixture was cooled at 0 °C for 15 min. DDQ was dissolved in CH₂Cl₂ (1 mL) and was added dropwise to the reaction mixture. The reaction mixture gradually changed to a dark purple colouration and was stirred at 0 °C under argon for 1.5 h. After completion of the reaction, it was quenched on addition of saturated aqueous solution of NaHCO₃ (20 mL). The organic layer was separated and washed with brine solution and water, and dried over Na₂SO₄. The removal of solvent *in vacuo* afforded 1/3rd-fused **79** (two C-C bonds fused) as an off white solid, which was filtered and washed with cold CH₃OH (35 mg, 0.043 mmol, 70 %).

The analyses of product **79** were consistent with the literature values.¹¹⁰

4.2.10 Cyclodehydrogenation of 74

Oxidative cyclodehydrogenation of **74** was carried out *via* two methods; **Method A** - FeCl₃ route and **Method B** - using the DDQ/H⁺ route.

Method A in Section 4.2.9 was followed to synthesise fully-fused **80** (six C-C bonds closed) and 1/2-fused **81** (three C-C bonds closed) using iron(III) chloride (620 mg, 3.82 mmol) in nitromethane (3 mL) and **74** (100 mg, 0.13 mmol) in CH₂Cl₂ (30 mL) for 24 h. The organic layer was washed with water (2 x 25 mL) to remove unwanted iron residue. The solution was neutralised by adding aqueous NaOH dropwise, dried over MgSO₄ and evaporated *in vacuo* to dryness. A yellow precipitate was obtained. The products were separated by thin layer preparative plate chromatography (SiO₂, toluene:CH₃OH, 100:0.5), which showed two prominent bands: an orange band close to the baseline and a yellow band above it. Extraction and subsequent drying of the orange band yielded the fully-fused product **80** as a dark yellow solid (15 mg, 0.02 mmol, 15 %) and the yellow band yielded the 1/3rd-fused (two C-C bonds fused) product **81** as a yellow solid (40 mg, 0.052 mmol, 40 %).

5, 8, 11, 14-Tetra-(*tert*-butyl)-1,3-diazasuperbenzene (80)

$^1\text{H-NMR}$ (600 MHz, 20 °C, CDCl_3 , δ in ppm): 9.68 (s, 2H, H^1 and H^6), 9.34 (s, 1H, H^5), 9.26 (s, 1H, H^{Ar}), 9.23 (m, 3H, H^2 and H^{Ar}), 9.14 (s, 1H, H^{Ar}), 9.04 (s, 1H, H^{Ar}), 8.89 (d, 1H, H^4), 8.86 (s, 1H, H^{Ar}), 7.95 (t, 1H, $^3J_{\text{HH}} = 6.0$ Hz, H^3), 1.95 (s, 9H $-\text{C}(\text{CH}_3)_3$), 1.94 (s, 9H $-\text{C}(\text{CH}_3)_3$), 1.89 (s, 9H $-\text{C}(\text{CH}_3)_3$), 1.82 (s, 9H $-\text{C}(\text{CH}_3)_3$).

$^{13}\text{C-NMR}$ (151 MHz, 20 °C, CDCl_3 , δ in ppm): 155.27 (1C, C^1), 153.16 (C_{quat}), 152.80 (C_{quat}), 149.47 (C_{quat}), 149.24 (C_{quat}), 149.05 (C_{quat}), 148.90 (C_{quat}), 130.46 (C_{quat}), 130.20 (C_{quat}), 130.11 (C_{quat}), 130.03 (C_{quat}), 129.63 (C_{quat}), 129.40 (C_{quat}), 128.34 (C_{quat}), 128.12 (C_{quat}), 126.92 (C_{quat}), 126.34 (1C, C^3), 125.40 (C_{quat}), 124.79 (1C, C^4), 124.21 (1C, C^2), 123.06 (C_{quat}), 122.61 (C_{quat}), 122.31 (1C, C^5), 121.74 (1C, C^6), 120.48 (C_{quat}), 120.38 (C_{quat}), 120.28 (C_{quat}), 119.07 (2C, CH), 119.01 (CH), 118.9 (1C, CH), 118.81 (2C, CH), 118.29 (C_{quat}), 118.09 (C_{quat}), 116.50 (C_{quat}), 115.43 (C_{quat}), 35.89 (1C, $-\text{C}(\text{CH}_3)_3$), 35.86 (1C, $-\text{C}(\text{CH}_3)_3$), 35.81 (1C, $-\text{C}(\text{CH}_3)_3$), 35.70 (1C, $-\text{C}(\text{CH}_3)_3$), 32.13 (1C, $-\text{C}(\text{CH}_3)_3$), 32.11 (1C, $-\text{C}(\text{CH}_3)_3$), 32.04 (1C, $-\text{C}(\text{CH}_3)_3$), 31.92 (1C, $-\text{C}(\text{CH}_3)_3$).

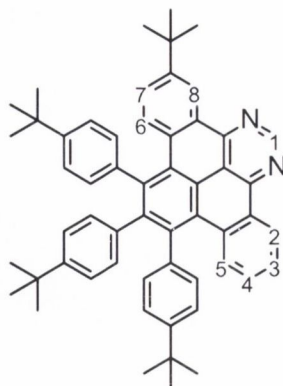
HRMS (ESI-MS, CHCl_3): calculated for $\text{C}_{56}\text{H}_{49}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z , 749.3896; found 749.3884.

M.p > 360 °C.

IR (neat) vbar in cm^{-1} : 2952, 1603, 1574, 1554, 1460 1362, 1259, 1239 and 865.

UV-Vis (C_7H_8 , nm): 340, 356 ($\lambda_{\text{max}}^{\text{abs}}$), 376, 394, 419, 442, 469.

Fluorescence (C_7H_8 , nm, $\lambda_{\text{exc}} = 360$ nm, RT): 471 ($\lambda_{\text{max}}^{\text{em}}$), 502, 539.

$\frac{1}{3}$ rd-Phenyl-DASB (81)

^1H NMR (600 MHz, 20 °C, CDCl_3 , δ in ppm): 9.84 (s, 1H, H^1), 9.52 (d, 1H, $^4J_{\text{HH}} = 2.0$ Hz, H^8), 9.47 (d, 1H, $^3J_{\text{HH}} = 7.3$ Hz, H^2), 7.91 (d, 1H, $^3J_{\text{HH}} = 8.4$ Hz, H^5), 7.85 (d, 1H, $^3J_{\text{HH}} = 9$ Hz, H^6), 7.64 (t, 1H, $^3J_{\text{HH}} = 6.0$ Hz, $\text{H}^{3/4}$), 7.34 (dd, 1H, $^3J_{\text{HH}} = 9.2$ Hz, $^4J_{\text{HH}} = 2.2$ Hz, H^7), 7.27 (triplet overlapping with CHCl_3 , 1H, $\text{H}^{3/4}$), 7.20 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, H^{Ar}), 7.17 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, H^{Ar}), 7.04 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, H^{Ar}), 7.01 (d, 2H, $^3J_{\text{HH}} = 8.3$ Hz, H^{Ar}), 6.86 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, H^{Ar}), 6.62 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, H^{Ar}), 1.56 (s, 9H $-\text{C}(\text{CH}_3)_3$), 1.31 (s, 9H $-\text{C}(\text{CH}_3)_3$), 1.28 (s, 9H $-\text{C}(\text{CH}_3)_3$), 1.16 (s, 9H $-\text{C}(\text{CH}_3)_3$).

^{13}C NMR (151 MHz, 20 °C, CDCl_3 , δ in ppm): 155.2 (1C, C^1), 153.2 (C_{quat}), 152.9 (C_{quat}), 149.8 (C_{quat}), 149.25 (C_{quat}), 149.22 (C_{quat}), 147.6 (C_{quat}), 144.86 (C_{quat}), 139.86 (C_{quat}), 139.79 (C_{quat}), 139.63 (C_{quat}), 139.39 (C_{quat}), 137.15 (C_{quat}), 134.26 (C_{quat}), 131.93 (C_{quat}), 131.01 (CH), 130.54 (CH), 130.43 (CH), 130.24 (CH), 129.93 (C_{quat}), 129.72 (1C, C^5), 129.30 (1C, C^6), 128.70 (1C, $\text{C}^{3/4}$), 127.02 (1C, C^7), 126.78 (1C, $\text{C}^{3/4}$), 126.74 (C_{quat}), 126.61 (C_{quat}), 125.02 (1C, C^2), 124.68 (CH), 124.64 (CH), 123.35 (C_{quat}), 122.64 (CH), 121.10 (1C, C^8), 114.97 (C_{quat}), 34.80 (1C, $-\text{C}(\text{CH}_3)_3$), 34.28 (1C, $-\text{C}(\text{CH}_3)_3$), 34.25 (1C, $-\text{C}(\text{CH}_3)_3$), 33.93 (1C, $-\text{C}(\text{CH}_3)_3$), 31.15 (2C, $-\text{C}(\text{CH}_3)_3$), 31.07 (2C, $-\text{C}(\text{CH}_3)_3$).

HRMS (ESI-MS, CHCl_3): calculated for $\text{C}_{56}\text{H}_{57}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z , 757.4522; found 757.4529.

M.p. 330 - 332 °C.

IR (neat) $\bar{\nu}$ in cm^{-1} : 2961, 2903, 1575, 1543, 1461, 1396, 1362, 1296, 1250, 1119, 1105, 1022, 854, 826, 767.

UV-Vis (C_7H_8 , nm): 307 ($\lambda_{\text{max}}^{\text{abs}}$), 319, 366, 385.

Fluorescence (C_7H_8 , nm, $\lambda_{\text{exc}} = 300$ nm, RT): 423 ($\lambda_{\text{max}}^{\text{em}}$).

Method B in Section 4.2.9 was followed as an alternative method. Compound **74** (50 mg, 0.066 mmol) was dissolved in CH_2Cl_2 (9 mL), and methanesulfonic acid (0.5 mL) was added. DDQ (150 mg, 0.66 mmol) was dissolved in CH_2Cl_2 (1 mL) and was added dropwise to the reaction mixture. After workup, removal of solvent *in vacuo* yielded $\frac{1}{3}$ rd-fused **81** (two C-C bonds fused) as off white solid, which was filtered and washed with cold CH_3OH (31 mg, 0.04 mmol, 62 %).

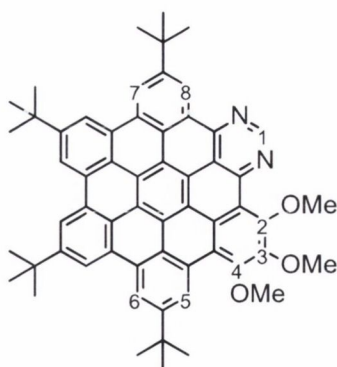
The analyses of product **81** were consistent with those obtained by **Method A**.

4.2.11 Cyclodehydrogenation of **75**

Oxidative cyclodehydrogenation of **6** was carried out *via* two methods; **Method A** - FeCl_3 route and **Method B** - using the DDQ/ H^+ route.

Method A in Section 4.2.9 was followed to synthesise fully-fused **82** and $\frac{1}{2}$ -fused (three C-C bonds closed) **83** using iron(III) chloride (320 mg, 1.97 mmol) in nitromethane (2 mL) and **75** (50 mg, 0.058 mmol) in CH_2Cl_2 (30 mL) for 24 h. The products were isolated by preparative plate chromatography (SiO_2 , CH_2Cl_2). Two main bands were observed: an orange band closer to the baseline and a yellow band above it. Extraction and subsequent drying of the orange band yielded the fully fused product **82** as a dark yellow solid (20 mg, 0.023 mmol, 40 %) and the yellow band yielded the $\frac{1}{2}$ -fused **83** as a yellow solid (10 mg, 0.011 mmol, 20 %).

Tetra-(8,11,14,17-*tert*-butyl)-(4,5,6-trimethoxy)-1,3-diazasuperbenzene (**82**)



¹H-NMR (600 MHz, 20 °C, CDCl_3 , δ in ppm): 10.43 (s, 1H, H^5), 10.13 (s, 1H, H^1), 10.02 (s, 1H, H^8), 9.51 (s, 1H, H^7), 9.39 (s, 1H), 9.38 (s, 1H, H^6), 9.37 (s, 1H), 9.36 (s, 1H), 9.34 (s, 1H), 4.46 (s, 3H, $-\text{C}^3\text{OCH}_3$), 4.41 (s, 3H, $-\text{C}^2\text{OCH}_3$), 4.25 (s, 3H, -

C^4OCH_3), 1.87 (s, 9H, $-C(CH_3)_3$), 1.86 (s, 9H $-C(CH_3)_3$), 1.85 (s, 9H $-C(CH_3)_3$), 1.84 (s, 9H $-C(CH_3)_3$).

^{13}C -NMR (150 MHz, 20 °C, $CDCl_3$, δ in ppm): 155.5 (1C, C^1), 154.4 (C_{quat}), 153.7 (C_{quat}), 153.4 (C_{quat}), 150.1 (C_{quat}), 149.8 (C_{quat}), 149.6 (C_{quat}), 149.56 (C_{quat}), 148.53 (C_{quat}), 130.8 (C_{quat}), 130.7 (C_{quat}), 130.5 (C_{quat}), 130.4 (C_{quat}), 130.0 (C_{quat}), 129.6 (C_{quat}), 129.0 (C_{quat}), 128.9 (C_{quat}), 127.6 (C_{quat}), 125.7 (C_{quat}), 124.9 (1C, C^5), 123.6 (C_{quat}), 123.5 (C_{quat}), 123.3 (C_{quat}), 122.5 (1C, C^7), 121.9 (1C, C^8), 121.5 (C_{quat}), 121.3 (C_{quat}), 121.0 (1C, C_{quat}), 120.7 (1C, C_{quat}), 119.9 (1C, C_{quat}), 119.2 (1C, C_{quat}), 119.18 (1C, C^6), 119.14 (1C, CH), 119.0 (1C, CH), 118.95 (1C, CH), 118.85 (1C, CH), 117.4 (2C, C_{quat}), 116.5 (2C, C_{quat}), 62.2 (1C, $-C^3OCH_3$), 61.6 (2C, $-C^2OCH_3$), 61.0 (2C, $-C^4OCH_3$), 35.9 (2C, $-C(CH_3)_3$), 35.8 (2C, $-C(CH_3)_3$), 32.01 (1C, $-C(CH_3)_3$), 32.0 (2C, $-C(CH_3)_3$), 31.9 (1C, $-C(CH_3)_3$).

HRMS (ESI-MS, CH_2Cl_2): calculated for $C_{59}H_{55}N_2O_3$, $[M+H]^+$ m/z , 839.4213; found 839.4214.

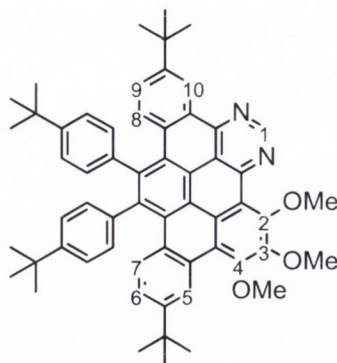
M.p > 300°C.

IR (neat) $\bar{\nu}$ in cm^{-1} : 3179, 2955, 2863, 1603, 1580, 1393, 1364, 1257, 868, 747.

UV-Vis (C_7H_8 , nm): 343, 360 (λ_{max}^{abs}), 378, 398, 445, 474

Fluorescence (C_7H_8 , nm, λ_{exc} = 360 nm, RT): 475 (λ_{max}^{em}), 508, 544.

$\frac{1}{2}$ -Methoxy-DASB (83)



1H -NMR (600 MHz, 20 °C, $CDCl_3$, δ in ppm): 9.92 (s, 1H, H^1), 9.58 (s, 1H, H^5), 9.43 (s, 1H, H^{10}), 8.03 (d, $^3J_{HH}$ = 9.04 Hz, 1H, H^8), 7.85 (d, $^3J_{HH}$ = 9.03 Hz, 1H, H^7), 7.34 (d, $^3J_{HH}$ = 9.03 Hz, 1H, H^6), 7.23 (overlapping with $CHCl_3$, 2H, H^{Ar}), 7.13 (m, 3H, H^9 and H^{Ar}), 7.05 (m, 4H, H^{Ar}), 4.30 (s, 3H, $-OC^3H_3$), 4.25 (s, 3H, $-OC^4H_3$), 4.12 (s, 3H, $-OC^2H_3$),

1.47 (s, 9H, -C(CH₃)₃), 1.39 (s, 9H, -C(CH₃)₃), 1.33 (s, 9H, -C(CH₃)₃), 1.26 (s, 9H, -C(CH₃)₃).

¹³C-NMR (150 MHz, 20 °C, CDCl₃, δ in ppm): 155.1 (1C, C¹), 154.1 (C_{quat}), 153.6 (C_{quat}), 153.2 (C_{quat}), 152.7 (C_{quat}), 150.0 (C_{quat}), 149.7 (C_{quat}), 149.3 (C_{quat}), 148.9 (C_{quat}), 148.1 (C_{quat}), 140.7 (C_{quat}), 140.1 (C_{quat}), 140.09 (C_{quat}), 139.96 (C_{quat}), 131.86 (1C, CH), 131.2 (1C, CH), 130.3 (C_{quat}), 129.69 (1C, C⁸), 129.59 (1C, CH), 128.9 (1C, C⁷), 128.3 (C_{quat}), 128.2 (C_{quat}), 127.2 (1C, C⁶), 126.7 s(C_{quat}), 125.5 (C_{quat}), 124.6 (1C, CH), 124.1 (1C, C⁹), 123.8 (C_{quat}), 123.5 (1C, C¹⁰), 123.4 (1C, CH), 121.2 (1C, C⁵), 120.8 (C_{quat}), 120.3 (C_{quat}), 117.8 (C_{quat}), 115.4 (C_{quat}), 62.1 (1C, -C³OCH₃), 61.68 (1C, -C⁴OCH₃), 61.66 (1C, -C²OCH₃), 35.0 (2C, -C(CH₃)₃), 34.5 (1C, -C(CH₃)₃), 34.4 (1C, -C(CH₃)₃), 31.43 (3C, -C(CH₃)₃), 31.36 (3C, -C(CH₃)₃), 31.33 (6C, -C(CH₃)₃).

HRMS (ESI-MS, CH₂Cl₂): calculated for C₅₉H₆₁N₂O₃ [M+H]⁺ *m/z* 845.4682; found 845.4672.

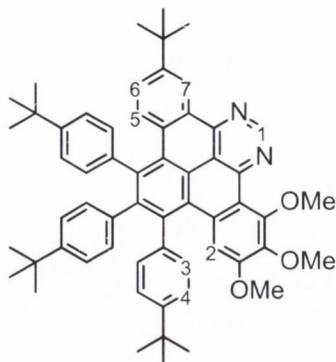
M.p > 360°C.

IR (neat) $\bar{\nu}$ in cm⁻¹: 2954 (C-H), 2868, 1738, 1578, 1450, 1379, 1217, 1146 (C-OR), 1019, 904, 830.

UV-Vis (C₇H₈, nm): 310 ($\lambda_{\max}^{\text{abs}}$), 337_{sh}, 385, 401, 424.

Fluorescence (C₇H₈, nm, λ_{exc} = 313 nm, RT): 438 ($\lambda_{\max}^{\text{em}}$), 457_{sh}.

Method B in Section 4.2.9 was used as an alternative synthetic method. Compound **75** (50 mg, 0.058 mmol) was dissolved in CH₂Cl₂ (9 mL), and methanesulfonic acid (0.5mL) was added. DDQ (133 mg, 0.588 mmol) was dissolved in CH₂Cl₂ (1 mL) and was added dropwise to the reaction mixture. After workup, the removal of solvent *in vacuo* afforded $\frac{1}{3}$ rd fused (two C-C bonds fused) **86** was obtained as a off white solid, which was filtered and washed with cold CH₃OH (25mg, 0.029 mmol, 50%).

$\frac{1}{3}$ -Methoxy-DASB (86)

$^1\text{H-NMR}$ (600 MHz, 20 °C, CDCl_3 , δ in ppm): 9.96 (s, 1H, H^1), 9.56 (s, 1H, H^7), 9.51 (s, 1H, H^2), 7.87 (br s, 1H, H^6), 7.70 (br s, 1H, H^5), 7.46 (s, 1H, H^{Ar}), 7.29 (overlapping with CHCl_3 , 3H, H^{Ar}), 7.23 (d, $^3J_{\text{HH}} = 8.04$ Hz, 1H, H^3), 7.20 (d, $^3J_{\text{HH}} = 6.45$ Hz, 1H, H^{Ar}), 7.04 (m, 4H, H^{Ar}), 6.88 (d, $^3J_{\text{HH}} = 7.70$ Hz, 1H, H^{Ar}), 6.61 (d, $^3J_{\text{HH}} = 8.04$ Hz, 1H, H^4), 4.03 (s, 6H, $-\text{OCH}_3$), 3.23 (s, 3H, $-\text{OCH}_3$), 1.49 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.32 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.29 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.19 (s, 9H, $-\text{C}(\text{CH}_3)_3$).

HRMS (ESI-MS, CH_2Cl_2): calculated for $\text{C}_{59}\text{H}_{63}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ m/z 847.4882; found 847.4890.

M.p 310 -312 °C.

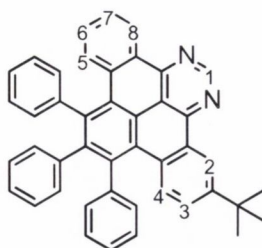
IR (neat) vbar in cm^{-1} : 2958 (C-H), 1561, 1542, 1474, 1397, 1253, 1116 (C-OR), 1022, 856.

UV-Vis (C_7H_8 , nm): 320 ($\lambda_{\text{max}}^{\text{abs}}$), 369, 390.

Fluorescence (C_7H_8 , nm, $\lambda_{\text{exc}} = 300$ nm, RT): 450 ($\lambda_{\text{max}}^{\text{em}}$).

4.2.12 Cyclodehydrogenation of 76

Method A in Section 4.2.9 was followed to synthesise **84**, using iron(III) chloride (817 mg, 5.04 mmol) in nitromethane (3 mL) and **7** (100 mg, 0.17 mmol) in CH_2Cl_2 (40 mL) for 24h. After quenching with CH_3OH , the organic layer was reduced *in vacuo* and $\frac{1}{3}^{\text{rd}}$ fused **84** was obtained as an off-white precipitate. The crystals were washed with cold CH_3OH (77 mg, 0.13 mmol, 78 %).

$\frac{1}{3}$ rd-fused DASB (84)

¹H-NMR (600 MHz, 20 °C, CDCl₃, δ in ppm): 9.87 (s, 1H, H¹), 9.54 (s, 1H, H²), 9.51 (d, ³*J*_{HH} = 6.0 Hz, 1H, H⁸), 7.77 (d, ³*J*_{HH} = 8.6 Hz, 1H, H⁵), 7.68 (d, ³*J*_{HH} = 9.3 Hz, 1H, H⁴), 7.66 (m, 1H, H⁷), 7.37 (d, ³*J*_{HH} = 9.3 Hz, 1H, H³), 7.31 (overlapping with CHCl₃, 1H, H⁶), 7.23 (m, 3H, H^{Ph}), 7.20 (m, 3H, H^{Ph}), 7.15 (m, 4H, H^{Ph}), 6.93 (m, 3H), 6.81 (m, 2H), 1.5 (s, 9H -C(CH₃)₃).

¹³C-NMR (150 MHz, 20 °C, CDCl₃, δ in ppm): 153.2 (1C, C¹), 144.17 (C_{quat}), 142.55 (C_{quat}), 139.94 (C_{quat}), 139.43 (C_{quat}), 139.28 (C_{quat}), 139.23 (C_{quat}), 134.15 (C_{quat}), 131.82 (C_{quat}), 131.49 (CH), 131.07 (CH), 130.95 (CH), 129.68 (1C, C⁵), 129.32 (1C, C⁴), 129.09 (1C, C⁶), 128.09 (CH), 128.05 (CH), 127.40 (1C, C³), 127.13 (1C, C⁷), 127.03 (C_{quat}), 126.91 (C_{quat}), 126.54 (CH), 126.50 (CH), 126.27 (CH), 125.33 (1C, C⁸), 121.46 (1C, C²), 114.78 (C_{quat}), 34.89 (1C, -C(CH₃)₃), 31.16 (1C, -C(CH₃)₃).

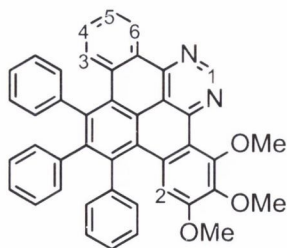
HRMS (ESI-MS, CHCl₃): calculated for C₄₄H₃₃N₂, [M+H]⁺ *m/z*, 589.2644; found 589.2632.

M.p 310 - 312 °C.

IR (neat) $\bar{\nu}$ in cm⁻¹: 3174, 2868, 1601, 1578, 1391, 1374, 1259, 831, 747.

4.2.13 Cyclodehydrogenation of 77

Method A in Section 4.2.9 was used to synthesise **85**. Iron(III) chloride (0.77 g, 4.76 mmol) was dissolved in nitromethane (3 mL) and **77** (0.10 g, 0.16 mmol) in CH₂Cl₂ (30 mL). The reaction mixture was stirred for 24 h and subsequently quenched with addition of CH₃OH. The solvents were removed in *vacuo* and resulted in a dark brown precipitate. The precipitate was re-crystallised with CH₃OH resulting in the pale brown precipitate (52 mg, 0.083 mmol, 52 %).

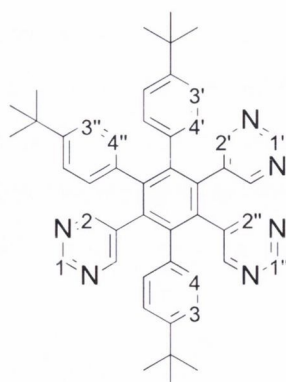
$\frac{1}{3}$ rd-fused DASB (85)

¹H-NMR (600 MHz, 20 °C, CDCl₃, δ in ppm): 9.96 (s, 1H, H¹), 9.52 (s, 1H, H²), 9.42 (d, 1H, H⁶), 8.04 (d, 1H, H³), 7.85 (d), 7.66 (t, 1H, H⁴ or H⁵), 7.44 (t, 1H, H⁴ or H⁵), 7.26, 7.19, 6.91, 6.81, 4.33 (s, 3H, -OCH₃), 4.18 (s, 3H, -OCH₃), 4.08 (s, 3H, -OCH₃).

HRMS (ESI-MS, CHCl₃): calculated for C₄₃H₃₁N₂O₃, [M+H]⁺ *m/z*, 623.2318, found 623.2323.

4.3 Synthesis of Hexaazasuperbenzenes**4.3.1 Cyclotrimerisation of (4-*tert*-butylphenyl)(5-pyrimidyl)acetylene**

Compound **70** (150 mg, 0.63 mmol) and dicobalt octacarbonyl (43.3 mg, 0.13 mmol) were heated at reflux temperature in dioxane (7 mL) for 24 h. The solvent was reduced in *vacuo*, dissolved in CH₂Cl₂ and filtered through celite to remove cobalt particles. The products were purified by column chromatography (SiO₂, CH₂Cl₂:CH₃OH, 25:1). Both asymmetric **87** (*R*_f = 0.31) and symmetric **88** (*R*_f = 0.57) products were isolated as white crystalline solids, **87** (102 mg, 0.144 mmol, 68%) and **88** (40.5 mg, 0.057 mmol, 27%) yields.

3,5,6-Tri-(4-*tert*-butylphenyl)-1,2,4-tri-(5-pyrimidyl)benzene (87)

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ in ppm): 8.81 (s, 2H, $\text{H}^{1'}$ and $\text{H}^{1''}$), 8.74 (s, 1H, H^1), 8.27 (s, 2H, $\text{H}^{2'}$ or $\text{H}^{2''}$), 8.26 (s, 2H, $\text{H}^{2'}$ or $\text{H}^{2''}$), 8.24 (s, 2H, H^2), 7.04 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, H^3), 6.95 (d, 4H, $^3J_{\text{HH}} = 8.0$ Hz, $\text{H}^{3'}$ and $\text{H}^{3''}$), 6.77 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, H^4), 6.70 (m, 4H, $\text{H}^{4'}$ and $\text{H}^{4''}$), 1.15 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.12 (s, 18H, $\text{C}(\text{CH}_3)_3$).

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , δ in ppm): 157.83 (2C, $\text{C}^{2'}$ or $\text{C}^{2''}$), 157.81 (2C, $\text{C}^{2'}$ or $\text{C}^{2''}$), 157.5 (2C, C^2), 156.2 (2C, $\text{C}^{1'}$ and $\text{C}^{1''}$), 155.6 (1C, C^1), 150.3 (C_{quat}), 149.6 (C_{quat}), 149.5 (C_{quat}), 143.5 (C_{quat}), 142.6 (C_{quat}), 141.9 (C_{quat}), 135.2 (C_{quat}), 134.9 (C_{quat}), 134.8 (C_{quat}), 134.6 (C_{quat}), 134.2 (C_{quat}), 134.0 (C_{quat}), 133.7 (C_{quat}), 133.6 (C_{quat}), 133.4 (C_{quat}), 130.6 (2C, C^3), 130.5 (2C, $\text{C}^{3'}$ or $\text{C}^{3''}$), 130.4 (2C, $\text{C}^{3'}$ or $\text{C}^{3''}$), 125.1 (2C, C^4), 124.4 (2C, $\text{C}^{4'}$ or $\text{C}^{4''}$), 124.3 (2C, $\text{C}^{4'}$ or $\text{C}^{4''}$), 34.2 (3C, $-\text{C}(\text{CH}_3)_3$), 31.0 (9C, $-\text{C}(\text{CH}_3)_3$).

HRMS (ESI-MS, CHCl_3): calculated for $\text{C}_{48}\text{H}_{49}\text{N}_6$, $[\text{M}+\text{H}]^+$ m/z , 709.4019; found 709.3990.

M.p > 360 °C.

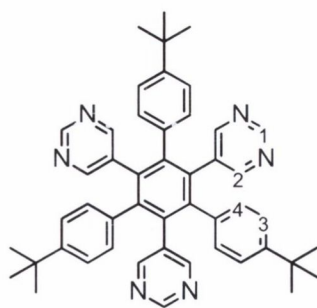
IR (neat) $\bar{\nu}$ in cm^{-1} : 3047 ($\text{CH}_{\text{aromatic}}$), 2868, 1578, 1548 ($\text{C}=\text{N}$), 1418 ($\text{C}=\text{C}$), 1388 (CH_3), 1269, 1174, 1019, 837, 786, 732.

CHN: Calculated (%) for $\text{C}_{48}\text{H}_{49}\text{N}_6$: C, 82.32; H, 6.82, N, 11.85. Found: C, 81.10; H, 6.68, N, 11.94.

UV-Vis (CHCl_3 , nm): 270 ($\lambda_{\text{max}}^{\text{abs}}$).

Fluorescence (CHCl_3 , nm, $\lambda_{\text{exc}} = 300$ nm, RT): 357 ($\lambda_{\text{max}}^{\text{em}}$).

2,4,6-Tri-(4-*tert*-butylphenyl)-1,3,5-tri-(5-pyrimidyl)benzene (88)



$^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ in ppm): 8.73 (s, 3H, H^1), 8.22 (s, 6H, H^2), 7.04 (d, 6H, $^3J_{\text{HH}} = 8.5$ Hz, H^3), 6.77 (d, 6H, $^3J_{\text{HH}} = 8.5$ Hz, H^4), 1.14 (s, 27H, $\text{C}(\text{CH}_3)_3$).

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , δ in ppm): 157.5 (6C, C^2), 155.7 (3C, C^1), 150.3 (C_{quat}), 142.9 (C_{quat}), 134.4 (C_{quat}), 134.3 (C_{quat}), 133.8 (C_{quat}), 130.5 (6C, C^4), 125.1 (6C, C^3), 34.3 (3C, $-\text{C}(\text{CH}_3)_3$) and 31.0 (9C, $-\text{C}(\text{CH}_3)_3$).

HRMS (ESI-MS, CHCl₃): calculated for C₄₈H₄₉N₆, [M+H]⁺ *m/z*, 709.4019; found 709.3983.

M.p > 360 °C.

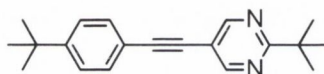
IR (neat) $\bar{\nu}$ in cm⁻¹: 3038 (CH_{aromatic}), 2904, 2868, 1576, 1548 (C=N), 1508, 1464, 1390 (CH₃), 1185, 833, 783.

CHN: Calculated (%) for C₄₈H₄₉N₆: C, 82.32; H, 6.82, N, 11.85. Found: C, 81.09; H, 6.88, N, 12.03.

UV-Vis (CHCl₃, nm): 270 ($\lambda_{\max}^{\text{abs}}$).

Fluorescence (CHCl₃, nm, λ_{exc} = 300 nm, RT): 369 ($\lambda_{\max}^{\text{em}}$).

4.3.2 5-(4-*tert*-Butylphenylethynyl)(2-*tert*-butyl)pyrimidine (**93**)



Compound **93** was prepared by modifying a related literature procedure.¹¹⁰ To a degassed solution of DMF (0.5 mL) and DIPA (1.5 mL), 1-*tert*-butyl-4-ethynylbenzene (158 mg, 1 mmol), 5-bromo-2-*tert*-butylpyrimidine (215 mg, 1 mmol) were added. To the mixture, triphenylphosphine (23 mg, 0.087 mmol), Pd(PPh₃)₃Cl₂ (15 mg, 0.021 mmol) and CuI (4 mg, 0.02 mmol), and the mixture was irradiated at 150 W, 115 °C, 25 min. After cooling the dark brown suspension was extracted with diethylether (50 mL x 2) and filtered. The solution was washed with saturated NH₄Cl (2 x 25 mL), water (2 x 25 mL) and finally dried over MgSO₄. Solvent was removed *in vacuo* and pale yellow crystal of **93** were obtained, which were washed with CH₃OH. (253 mg, 0.35 mmol, 86 %).

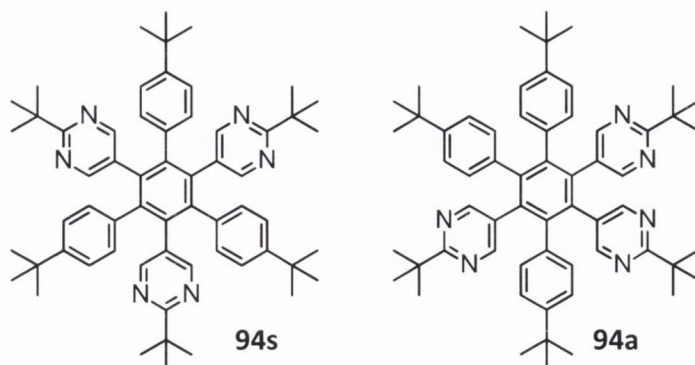
¹H-NMR (600 MHz, 20 °C, CDCl₃, δ in ppm): 8.81 (s, 2H, H¹), 7.51 (d, 2H, ³*J*_{HH} = 8.1 Hz, H²), 7.42 (d, 2H, ³*J*_{HH} = 8.1 Hz, H³), 1.45 (s, 9H, C(CH₃)₃), 1.36 (s, 9H, C(CH₃)₃).

The analyses of product **93** were consistent with the literature values.¹¹⁰

4.3.3 Cyclotrimerisation of 5-(4-*tert*-butylphenylethynyl)(2-*tert*-butyl)pyrimidine

Compound **93** (100 mg, 0.34 mmol) and dicobalt octacarbonyl (23.3 mg, 0.068 mmol) were heated at reflux temperature in dioxane (5 mL) for 24 h. The solvent was reduced *in vacuo*, dissolved in CH₂Cl₂ and filtered through celite to remove cobalt particles. Upon removal of solvent a white precipitate was obtained. Purification of the two isomers (**94a**

and **94s**) were attempted using column chromatography (SiO_2 , CH_2Cl_2 : CH_3OH , 25:1) and thin layer preparative plates, however was not successful, (91.5 mg).

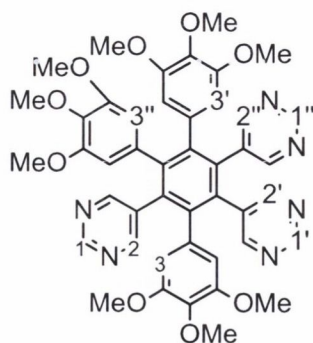


HRMS (ESI-MS, CH_2Cl_2): calculated for $\text{C}_{60}\text{H}_{73}\text{N}_6$, $[\text{M}+\text{H}]^+$ m/z , 877.5819; found 877.5823.

4.3.4 Cyclotrimerisation of (3,4,5-trimethoxyphenyl)(5-pyrimidyl)acetylene

Compound **72** (150 mg, 0.55 mmol) and dicobalt octacarbonyl (43.3 mg, 0.13 mmol) were heated at reflux temperature in dioxane (7 mL) for 24 h. The solvent was reduced in *vacuo*, dissolved in CH_2Cl_2 and filtered through celite to remove cobalt particles. The products were purified by column chromatography (SiO_2 , CH_2Cl_2 : CH_3OH , 25:1). Both asymmetric **95** ($R_f = 0.24$) and symmetric **96** ($R_f = 0.33$) products were isolated as white crystalline solids with **95** (95 mg, 0.12 mmol, 63 %) and **96** (25 mg, 0.03 mmol, 17 %) yields.

3,5,6-Tri-(3,4,5-trimethoxyphenyl)-1,2,4-tri-(5-pyrimidyl)benzene (**95**)



^1H -NMR (600 MHz, 20 °C, CDCl_3 , δ in ppm): 8.84 (s, 1H, H1'/H1''), 8.82 (s, 1H, H1'/H1''), 8.81 (s, 1H, H1), 8.28 (m, 6H, H2, H2' and H2''), 3.66, 3.49, 3.48, 3.46, 3.43 (- OCH_3).

^{13}C -NMR (150 MHz, 20 °C, CDCl_3 , δ in ppm): 157.36 (1C, $\text{C}^{2'}$ or $\text{C}^{2''}$), 157.26 (1C, $\text{C}^{2'}$ or $\text{C}^{2''}$), 156.75 (1C, $\text{C}^{2'}$ or $\text{C}^{2''}$), 156.68 (1C, $\text{C}^{2'}$ or $\text{C}^{2''}$), 156.47 (2C, C^2), 156.41 (1C, C^1), 156.06 (1C, $\text{C}^{1'}$ or $\text{C}^{1''}$), 156.01 (1C, $\text{C}^{1'}$ or $\text{C}^{1''}$), 152.83 (C_{quat}), 152.79 (C_{quat}), 152.58 (C_{quat}), 152.55 (C_{quat}), 142.72 (C_{quat}), 142.63 (C_{quat}), 141.83 (C_{quat}), 137.27 (C_{quat}), 137.24 (C_{quat}), 137.05 (C_{quat}), 135.01 (C_{quat}), 134.67 (C_{quat}), 134.01 (C_{quat}), 133.94 (C_{quat}), 133.79 (C_{quat}), 133.67 (C_{quat}), 133.23 (C_{quat}), 132.98 (C_{quat}), 132.94 (C_{quat}), 132.77 (C_{quat}), 132.09 (C_{quat}), 131.90 (C_{quat}), 108.72 (2C, C^3), 108.64 (2C, C^3), 108.61 (2C, C^3), 60.73 (3C, $-\text{OCH}_3$), 55.95 (6C, $-\text{OCH}_3$).

HRMS (MALDI-TOF, CHCl_3): calculated for $\text{C}_{45}\text{H}_{42}\text{N}_6\text{O}_9$, $[\text{M}+\text{H}]^+$ m/z , 810.3013; found 810.2988.

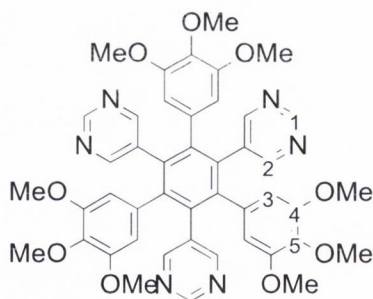
M.p 243 - 245 °C.

IR (neat) $\bar{\nu}$ in cm^{-1} : 2960 (C-H), 1580, 1452, 1411, 1294, 1321, 1238, 1118 (C-OR), 1000, 972, 830, 767.

UV-Vis (CHCl_3 , nm): 270 ($\lambda_{\text{max}}^{\text{abs}}$).

Fluorescence (CHCl_3 , nm, $\lambda_{\text{exc}} = 300$ nm, RT): 357 ($\lambda_{\text{max}}^{\text{em}}$).

2,4,6-tri-(3,4,5-Trimethoxyphenyl)-1,3,5-tri-(5-pyrimidyl)benzene (96)



^1H -NMR (600 MHz, 20 °C, CDCl_3 , δ in ppm): 8.87 (s, 3H, H^1), 8.34 (s, 6H, H^2), 6.04 (s, 6H, H^3), 3.72 (s, 9H, $-\text{C}^5\text{OCH}_3$), 3.54 (s, 18H, $-\text{C}^4\text{OCH}_3$).

^{13}C -NMR (150 MHz, CDCl_3 , δ in ppm): 156.74 (6C, C^2), 156.04 (3C, C^1), 152.86 (C_{quat}), 142.73 (C_{quat}), 137.34 (C_{quat}), 132.04 (C_{quat}), 108.69 (6C, C^3), 60.80 (6C- C^5OCH_3), 56.07 (3C, $-\text{C}^4\text{OCH}_3$).

HRMS (MALDI-TOF, CHCl_3): calculated for $\text{C}_{45}\text{H}_{42}\text{N}_6\text{O}_9$, $[\text{M}+\text{H}]^+$ m/z , 810.3013; found 810.2986.

M.p 240 - 242 °C.

IR (neat) $\bar{\nu}$ in cm^{-1} : 2961 (C-H), 1579, 1452, 1411, 1294, 1321, 1238, 1118 (C-OR), 1000, 972, 830, 767.

UV-Vis (CHCl_3 , nm): 270 ($\lambda_{\text{max}}^{\text{abs}}$).

Fluorescence (CHCl_3 , nm, $\lambda_{\text{exc}} = 300 \text{ nm}$, RT): 357 ($\lambda_{\text{max}}^{\text{em}}$).

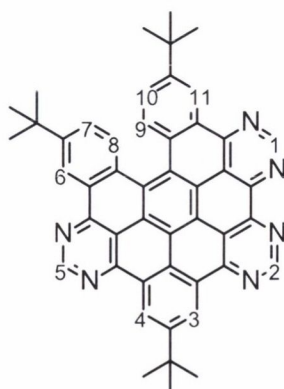
4.3.5 Cyclodehydrogenation of **87**

Oxidative cyclodehydrogenation of **87** was carried out *via* three methods; **Method A** - FeCl_3 route and **Method B** - $\text{AlCl}_3/\text{CuCl}_2$ route and **Method C** - DDQ/ H^+ route.

Method A

A solution of iron(III) trichloride (602 mg, 3.70 mmol), in nitromethane (3 mL) was added dropwise to a stirred solution of **87** (100 mg, 0.14 mmol) in CH_2Cl_2 (40 mL). After stirring for 24 h under argon at room temperature, the reaction was quenched with CH_3OH (20 mL) and was left stirring for another 30 min. The solvent was reduced *in vacuo*, and was redissolved in CHCl_3 . The organic solution was washed with saturated NaHCO_3 (1 x 25 mL), water (2 x 25 mL) and finally dried over MgSO_4 . Preparative thin layer chromatography (SiO_2 , $\text{C}_7\text{H}_8:\text{CH}_3\text{OH}$, 25:1,) was used to isolate the products. Two main bands were observed: an orange band closer to the baseline and a yellow band above it. $^{5/6}$ -Asym-HASB (**89**) (five C-C bonds fused) was isolated as an orange solid in 20 % yield (20 mg, 0.03 mmol) and $^{2/3}$ -asym-HASB (**90**) (four C-C bonds fused) as a dark yellow solid in 10 % yield (10 mg, 0.014 mmol).

$^{5/6}$ -Asym-HASB (**89**)



$^1\text{H-NMR}$ (600 MHz, 20 °C, CDCl_3 , δ in ppm): 10.20 (s, 1H, H^1), 10.09 (s, 1H, H^2), 10.05 (s, 1H, H^5), 10.03 (s, 1H, H^3), 9.98 (s, 1H, H^4), 9.56 (s, 1H, H^{11}), 9.54 (s, 1H,

H⁸), 8.72 (d, $^3J_{\text{HH}} = 8.6$ Hz, 1H, H⁹), 8.68 (d, $^3J_{\text{HH}} = 8.6$ Hz, 1H, H⁸), 7.72 (m, 2H, H⁷ and H¹⁰), 1.87 (s, 9H, -C(CH₃)₃) 1.67 (s, 9H, -C(CH₃)₃), 1.65 (s, 9H, -C(CH₃)₃).

¹³C NMR (150 MHz, 20 °C, CDCl₃, δ in ppm): 157.09 (1C, C¹), 157.01 (1C, C²), 156.04 (1C, C⁵), 154.32 (C_{quat}), 154.14 (C_{quat}), 153.50 (C_{quat}), 153.38 (C_{quat}), 152.50 (C_{quat}), 152.37 (C_{quat}), 151.24 (C_{quat}), 151.03 (C_{quat}), 131.19 (C_{quat}), 130.83 (1C, C¹⁰), 130.76 (1C, C⁷), 129.54 (C_{quat}), 128.16 (C_{quat}), 127.31 (1C, C⁸), 127.05 (1C, C⁹), 126.90 (1C, C³), 126.88 (C_{quat}), 126.71 (C_{quat}), 126.33 (1C, C⁴), 124.34 (C_{quat}), 121.96 (1C, C¹¹), 121.76 (1C, C⁶), 121.35 (C_{quat}), 121.29 (C_{quat}), 119.66 (C_{quat}), 119.11 (C_{quat}), 118.14 (C_{quat}), 118.07 (C_{quat}), 117.16 (C_{quat}), 114.87 (C_{quat}), 36.11 (1C, -C(CH₃)₃), 35.40 (1C, -C(CH₃)₃), 35.35 (1C, -C(CH₃)₃), 31.7 (3C, -C(CH₃)₃), 31.33 (3C, -C(CH₃)₃), 31.27 (3C, -C(CH₃)₃).

HRMS (ESI-MS, C₇H₈): calculated for C₄₈H₃₈N₆, [M+Na]⁺ *m/z*, 721.3056; found 721.3060.

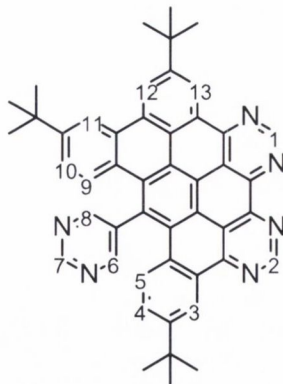
M.p > 360 °C.

IR (neat) $\bar{\nu}$ in cm⁻¹: 2958 (C-H), 1603, 1560, 1528, 1465, 1395, 1367, 1296, 1252, 1121, 910, 887, 845, 792.

UV-Vis (C₇H₈, nm): 323 ($\lambda_{\text{max}}^{\text{abs}}$), 352, 385, 440, 468.

Fluorescence (C₇H₈, nm, $\lambda_{\text{exc}} = 360$ nm, RT): 495 ($\lambda_{\text{max}}^{\text{em}}$).

²/₃-Asym-HASB (90)



¹H-NMR (600 MHz, 20 °C, CDCl₃, δ in ppm): 10.01 (s, 1H, H¹³), 9.93 (s, 2H, H¹² and H¹), 9.81 (s, 1H, H⁷), 9.70 (s, 1H, H⁸), 9.56 (s, 1H, H⁶), 9.53 (s, 1H, H³), 9.49 (s, 1H, H²), 9.31 (s, 1H, H¹¹), 8.58 (d, 1H, $^3J_{\text{HH}} = 8.1$ Hz, H⁵), 8.41 (d, 1H, $^3J_{\text{HH}} = 8.8$ Hz, H⁹), 7.71 (d, 1H, $^3J_{\text{HH}} = 7.4$ Hz, H¹⁰), 7.61 (d, 1H, $^3J_{\text{HH}} = 8.8$ Hz, H⁴), 1.78 (s, 9H, C(CH₃)₃), 1.62 (s, 9H, C(CH₃)₃), 1.60 (s, 9H, C(CH₃)₃).

^{13}C -NMR (150 MHz, 20 °C, CDCl_3 , δ in ppm): 157.67 (1C, C), 156.88 (1C, C), 156.63 (1C, C^1), 156.22 (1C, C^1), 155.79 (1C, C^1), 154.03 (C_{quat}), 153.32 (C_{quat}), 152.22 (C_{quat}), 152.07 (C_{quat}), 151.98 (C_{quat}), 151.55 (C_{quat}), 151.08 (C_{quat}), 134.30 (C_{quat}), 131.77 (C_{quat}), 130.46 (C_{quat}), 130.43 (C_{quat}), 129.94 (C_{quat}), 129.83 (C_{quat}), 129.60 (C_{quat}), 129.19 (C_{quat}), 128.88 (C_{quat}), 128.85 (C_{quat}), 128.40 (C_{quat}), 128.07 (C_{quat}), 128.03, 127.46, 127.23, 127.18, 126.08 (1C, C), 125.46 (1C, C), 125.15 (C_{quat}), 124.29 (C_{quat}), 123.67 (C_{quat}), 122.97 (C_{quat}), 122.60 (C_{quat}), 121.62 (C_{quat}), 121.52 (C_{quat}), 121.39 (1C, C), 121.17 (1C, C), 120.17 (C_{quat}), 115.21 (C_{quat}), 35.89 (1C, $-\text{C}(\text{CH}_3)_3$), 35.28 (1C, $-\text{C}(\text{CH}_3)_3$), 35.24 (1C, $-\text{C}(\text{CH}_3)_3$), 31.62 (3C, $-\text{C}(\text{CH}_3)_3$), 31.29 (3C, $-\text{C}(\text{CH}_3)_3$), 31.21 (3C, $-\text{C}(\text{CH}_3)_3$).

HRMS (ESI-MS, C_7H_8) calculated for $\text{C}_{48}\text{H}_{41}\text{N}_6$, $[\text{M}+\text{H}]^+$ m/z 701.3393; found 701.3390.

UV-Vis (C_7H_8 , nm): 323 ($\lambda_{\text{max}}^{\text{abs}}$), 352, 385, 440, 468.

Fluorescence (C_7H_8 , nm, $\lambda_{\text{exc}} = 360$ nm, RT): 495 ($\lambda_{\text{max}}^{\text{em}}$).

Method B

A solution mixture of **87** (50 mg, 0.07 mmol), AlCl_3 (140 mg, 1.05 mmol), and CuCl_2 (141 mg, 1.05 mmol) in CS_2 (15 mL) was stirred for 72 h at room temperature. The resulting black solid was allowed to settle and CS_2 was removed. The black solid was suspended in an aqueous 10 % ammonia solution (35 mL), extracted into chloroform and washed with water and the organic layer was dried over MgSO_4 . The preliminary mass spectral results shows a mixture of products including $1/3^{\text{rd}}$ fused (two C-C bonds), $1/2$ fused (three C-C bonds), $2/3^{\text{rd}}$ fused (four C-C bonds) and $5/6^{\text{th}}$ fused (five C-C bonds) products. $5/6^{\text{th}}$ -fused (five C-C bonds closed). Purification was carried out using preparative thin-layer chromatography (SiO_2 , C_7H_8 : CH_3OH , 25:1). The preparative plate showed a myriad of bands and only $5/6$ -Asym-HASB (**89**) was successfully isolated as an orange solid in low yield (5 mg, 0.007 mmol, 5%).

The analyses of the products $5/6$ -Asym-HASB (**89**), was consistent with the results obtained by **Method A**.

Method C

Compound **87** (50 mg, 0.071 mmol) was dissolved in CH_2Cl_2 (10 mL), and methanesulfonic acid (1.0 mL) was added. The reaction mixture rapidly changed colour to a yellow upon addition of acid and the mixture was cooled at 0 °C for 15 min. DDQ

was dissolved in CH_2Cl_2 (4 mL) and was added dropwise to the reaction mixture. The reaction mixture gradually changed to a dark green coloration (after 2 hrs), and was stirred at $0\text{ }^\circ\text{C}$ for 5 h and left stirring at room temperature under argon for 48 h. After completion of the reaction, it was quenched with addition of saturated aqueous solution of NaHCO_3 (20 mL). The organic layer was separated and washed with brine solution and water, and dried over Na_2SO_4 . The removal of solvent *in vacuo* afforded a yellow precipitate. Thin layer preparative plate (SiO_2 , C_7H_8 : CH_3OH , 20:1) separation, resulted in the isolation of the $5/6^{\text{th}}$ -Asym-HASB (**89**) as a yellow solid. In addition, the $5/6^{\text{th}}$ product was isolated by precipitating it from the mother liquor, giving an overall yield of 60 %, (30 mg, 0.042 mmol).

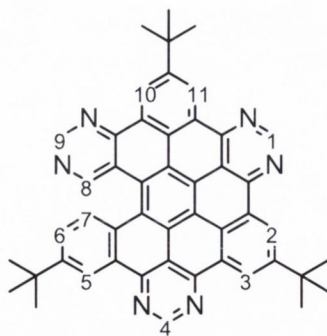
The analyses of the products $5/6$ -Asym-HASB (**89**), was consistent with the results obtained by **Method A**.

4.3.6 Cyclodehydrogenation of **88**

Oxidative cyclodehydrogenation of **88** was carried out *via* three methods; **Method A** - FeCl_3 route and **Method B** - $\text{AlCl}_3/\text{CuCl}_2$ route and **Method C** - DDQ/H^+ route.

Method A discussed in Section 4.3.5 was followed using a solution of iron(III) trichloride (602 mg, 3.70 mmol), in nitromethane (3 mL) was added dropwise to a stirred solution of **88** (100 mg, 0.14 mmol) in CH_2Cl_2 (40 mL). A similar work up was followed and preparative thin layer chromatography (SiO_2 , C_7H_8 : CH_3OH , 10:0.4) resulted in successful isolation of $5/6$ -Sym-HASB (**91**) as a yellow solid in 23 % yield. (23 mg, 0.03 mmol).

$5/6$ -Sym-HASB (**91**)



¹H-NMR (600 MHz, 20 °C, CDCl₃, δ in ppm): 10.37 (s, 2H, H¹ and H⁴), 10.29 (s, 2H, H² and H³), 10.18 (s, 1H, H⁹), 9.76 (s, 1H, H⁵), 9.66 (s, 1H, H¹⁰ or H¹¹), 8.98 (d, J = 8.1 Hz, 1H, H⁷), 8.85 (s, 1H, H⁸), 7.85 (m, 2H, H⁶ and H¹⁰ or H¹¹), 1.88 (s, 9H, C(CH₃)₃), 1.67 (s, 9H, C(CH₃)₃), 1.64 (s, 9H, C(CH₃)₃).

HRMS (ESI-MS, C₇H₈): calculated for C₄₈H₃₈N₆, [M+H]⁺ *m/z*, 699.3236; found 699.3236.

UV-Vis (C₇H₈, nm): 323 (λ_{max}^{abs}), 352, 385, 440, 468.

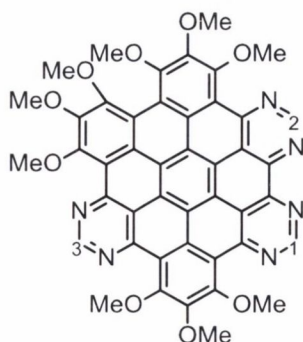
Fluorescence (C₇H₈, nm, λ_{exc} = 360 nm, RT): 495 (λ_{max}^{em}).

Method B and **Method C** were also attempted for **88**, however was not successful. For more details refer the discussion.

4.3.7 Cyclodehydrogenation of **95**

Method A discussed in section 4.3.5 was followed using a solution of iron(III) trichloride (602 mg, 3.70 mmol), in nitromethane (3 mL), which was added dropwise to a stirred solution of **95** (100 mg, 0.12 mmol) in CH₂Cl₂ (40 mL). After 24 hrs the reaction was quenched with CH₃OH and was stirred for 30 min. The solvent was removed *in vacuo*, and yielded a brownish red solid. Preliminary mass spectral analysis of the crude material indicated the presence of a mixture of products, showing mainly the presence of the fully-fused product (six C-C bonds closed) **97** as the predominant product, along with a ⁵/₆th-fused product (five C-C bonds closed). Thin layer preparative plate (SiO₂, C₇H₈:CH₃OH, 20:1) resulted in isolation of the fully fused **97** in 10 % yield. (10 mg, 0.012 mmol).

7, 8, 9, 10, 11, 12, 16, 17, 18-Non-(methoxy)-1, 3, 4, 6, 13, 15 –hexaazasuperbenzene (97)



$^1\text{H-NMR}$ (600 MHz, 20 °C, CDCl_3 , δ in ppm): 10.49 (s, 1H, H1 or H2), 10.46 (s, 1H, H1 or H2), 10.33 (s, 1H, H3), 4.56 - 4.20 (27 H, -OCH₃).

HRMS (ESI-MS, CHCl_3): calculated for $\text{C}_{45}\text{H}_{31}\text{N}_6\text{O}_9$, $[\text{M}+\text{H}]^+$ m/z 799.2147; found 799.2144.

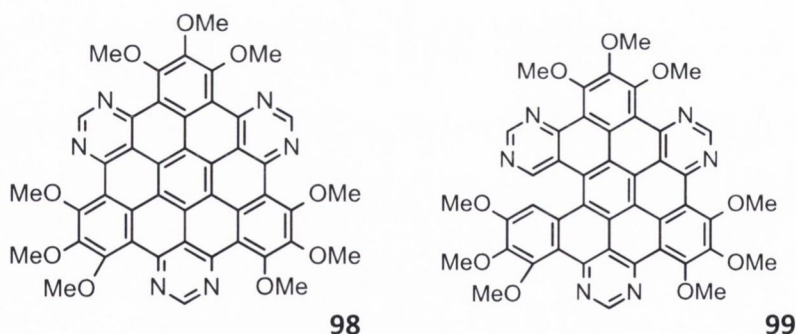
UV-Vis (C_7H_8 , nm): 325, 365 ($\lambda_{\text{max}}^{\text{abs}}$), 386, 462, 492.

Fluorescence (C_7H_8 , nm, $\lambda_{\text{exc}} = 360$ nm, RT): 514 ($\lambda_{\text{max}}^{\text{em}}$).

4.3.8 Cyclodehydrogenation of **96**

Method A discussed in section 4.3.5 was followed using a solution of iron(III) trichloride (602 mg, 3.70 mmol) in nitromethane (3 mL) which was added dropwise to a stirred solution of **96** (100 mg, 0.12 mmol) in CH_2Cl_2 (40 mL). A similar work up was carried out as discussed for **95**. The preliminary mass spectral analysis of the crude product resulted in both the fully-fused **98** and $5/6^{\text{th}}$ -fused **99**. However, despite several attempts using thin layer preparative plate in various solvent systems ($\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$, 10:0.1)/ $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$, 10:0.2)/ ($\text{C}_7\text{H}_8:\text{CH}_3\text{OH}$, 20:1) the two products could not be separated.

4, 5, 6, 10, 11, 12, 16, 17, 18-Non-(methoxy)-1, 3, 7, 9, 13, 15 –hexaazasuperbenzene (98) and $5/6^{\text{th}}$ -Sym-HASB (99)



HRMS (ESI-MS, CHCl_3): calculated for $\text{C}_{45}\text{H}_{31}\text{N}_6\text{O}_9$, $[\text{M}+\text{H}]^+$ m/z , 799.2153; found 799.2134 (**98**).

HRMS (ESI-MS, CHCl_3): calculated for $\text{C}_{45}\text{H}_{33}\text{N}_6\text{O}_9$, $[\text{M}+\text{H}]^+$ m/z , 801.2309; found 801.2332 (**99**).

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6. Annex

Crystal data and structure refinement for 73.

Identification code	73	
Empirical formula	C60 H60 N2	
Formula weight	653.73	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.1443(13) Å	$\alpha = 77.004(2)^\circ$.
	b = 17.7841(18) Å	$\beta = 84.724(2)^\circ$.
	c = 24.953(3) Å	$\gamma = 79.400(2)^\circ$.
Volume	5154.3(9) Å ³	
Z	4	
Density (calculated)	1.053 Mg/m ³	
Absorption coefficient	0.060 mm ⁻¹	
F(000)	1768	
Theta range for data collection	0.84 to 23.26°.	
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -27 ≤ l ≤ 26	
Reflections collected	34984	
Independent reflections	14660 [R(int) = 0.0695]	
Completeness to theta = 23.26°	98.8 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14660 / 0 / 1148	
Goodness-of-fit on F ²	1.000	
Final R indices [I > 2σ(I)]	R1 = 0.0943, wR2 = 0.2567	
R indices (all data)	R1 = 0.1808, wR2 = 0.3188	
Largest diff. peak and hole	1.176 and -0.683 e.Å ⁻³	

Crystal data and structure refinement for 74.

Identification code	74	
Empirical formula	C59 H66 N2O3	
Formula weight	851.14	
Temperature	256(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 15.7194(5)$ Å	$\alpha = 90^\circ$.
	$b = 17.5813(6)$ Å	$\beta = 110.498(2)^\circ$.
	$c = 17.9395(6)$ Å	$\gamma = 90^\circ$.
Volume	$4644.0(3)$ Å ³	
Z	4	
Density (calculated)	1.217 Mg/m ³	
Absorption coefficient	0.569 mm ⁻¹	
F(000)	1832	
Theta range for data collection	3.64 to 60.00°.	
Index ranges	$-17 \leq h \leq 17$, $-19 \leq k \leq 19$, $-20 \leq l \leq 17$	
Reflections collected	30796	
Independent reflections	6864 [R(int) = 0.0348]	
Completeness to theta = 60.00°	99.5 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6864 / 0 / 536	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2sigma(I)]	R1 = 0.0628, wR2 = 0.1602	
R indices (all data)	R1 = 0.0680, wR2 = 0.1650	
Extinction coefficient	0.00018(7)	
Largest diff. peak and hole	0.952 and -0.841 e.Å ⁻³	

Crystal data and structure refinement for 82.

Identification code	82	
Empirical formula	C ₅₉ H ₅₄ N ₂ O ₃	
Formula weight	839.04	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 17.8254(6) Å	$\alpha = 90^\circ$.
	<i>b</i> = 10.8398(4) Å	$\beta = 124.420(2)^\circ$.
	<i>c</i> = 29.3462(9) Å	$\gamma = 90^\circ$.
Volume	4677.6(3) Å ³	
Z	4	
Density (calculated)	1.191 Mg/m ³	
Absorption coefficient	0.564 mm ⁻¹	
F(000)	1784	
Crystal size	0.16 x 0.14 x 0.08 mm ³	
Theta range for data collection	3.65 to 58.40°.	
Index ranges	-19 ≤ <i>h</i> ≤ 14, -10 ≤ <i>k</i> ≤ 11, -23 ≤ <i>l</i> ≤ 32	
Reflections collected	15062	
Independent reflections	6139 [<i>R</i> (int) = 0.0359]	
Completeness to theta = 58.40°	93.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9563 and 0.9151	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	6139 / 21 / 623	
Goodness-of-fit on <i>F</i> ²	1.087	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0681, <i>wR</i> 2 = 0.1911	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0802, <i>wR</i> 2 = 0.2003	
Largest diff. peak and hole	0.693 and -0.358 e.Å ⁻³	

Crystal data and structure refinement for 84.

Identification code	84	
Empirical formula	C44 H32 N2	
Formula weight	588.71	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	<i>P</i> c a 2 ₁	
Unit cell dimensions	a = 9.5909(7) Å	α = 90°.
	b = 14.2441(10) Å	β = 90°.
	c = 22.2623(11) Å	γ = 90°.
Volume	3041.3(3) Å ³	
Z	4	
Density (calculated)	1.286 Mg/m ³	
Absorption coefficient	0.569 mm ⁻¹	
F(000)	1240	
Crystal size	0.370 x 0.210 x 0.010 mm ³	
Theta range for data collection	3.102 to 68.061°.	
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 16, -24 ≤ l ≤ 22	
Reflections collected	6501	
Independent reflections	3726 [R(int) = 0.0463]	
Completeness to theta = 67.679°	94.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7530 and 0.5813	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3726 / 1 / 419	
Goodness-of-fit on F ²	1.004	
Final R indices [I > 2σ(I)]	R1 = 0.0549, wR2 = 0.1333	
R indices (all data)	R1 = 0.0718, wR2 = 0.1445	
Absolute structure parameter	n/a	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.220 and -0.297 e.Å ⁻³	

Crystal data and structure refinement for 88.

Identification code	88	
Empirical formula	C96 H98 N12	
Formula weight	1435.86	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 11.426(2) Å	α = 72.93(3)°.
	<i>b</i> = 17.891(4) Å	β = 89.89(3)°.
	<i>c</i> = 21.730(4) Å	γ = 73.92(3)°.
Volume	4065.0(14) Å ³	
<i>Z</i>	2	
Density (calculated)	1.173 Mg/m ³	
Absorption coefficient	0.070 mm ⁻¹	
<i>F</i> (000)	1532	
Crystal size	0.60 x 0.50 x 0.40 mm ³	
Theta range for data collection	1.81 to 25.12°.	
Index ranges	-13 ≤ <i>h</i> ≤ 13, -21 ≤ <i>k</i> ≤ 21, -25 ≤ <i>l</i> ≤ 25	
Reflections collected	43311	
Independent reflections	14451 [<i>R</i> (int) = 0.0431]	
Completeness to theta = 25.12°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9723 and 0.9589	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	14451 / 0 / 982	
Goodness-of-fit on <i>F</i> ²	1.013	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0472, <i>wR</i> 2 = 0.1199	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0807, <i>wR</i> 2 = 0.1403	
Largest diff. peak and hole	0.368 and -0.548 e.Å ⁻³	