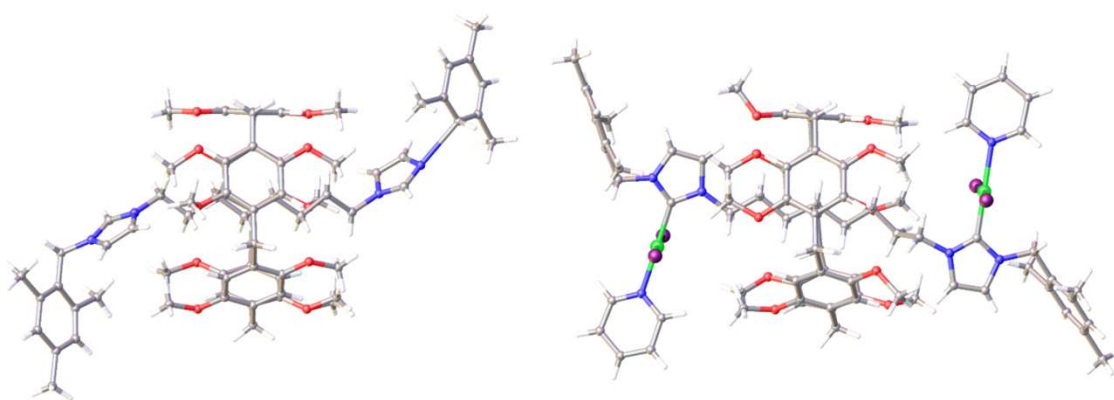




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Pillar[5]arene/Imidazolium Based [n]Rotaxanes



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Pillar[5]arene/Imidazolium Based [n]Rotaxanes

Thesis submitted to the University of Nottingham for the
Degree of Doctor of Philosophy

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Declaration

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, either in whole or in part, for any other degree. Some of the results have already been published.

Signed:

Philipp E. Langer

Date:

Abstract

Molecular machines and motors play a key role in numerous biological processes. Nature has thrown down the gauntlet regarding complexity and function of these systems. Over the last decade advances in synthetic and supramolecular chemistry have enabled chemists all over the world to make significant progress towards conquering the realm of nanomachines. At the forefront of this are mechanically interlocked molecules (MIMs), which have also added an additional dimension to various fields of both experimental and theoretical chemistry. The potential applications of molecular machines is undoubtedly immense and bridging the gap between the current generation of molecular machines and state of the art systems found in nature bears great reward. MIMs commonly feature members of the key macrocycle families. One of the most prominent recently discovered families of macrocycles are pillar[n]arenes. Their potential in the synthesis of MIMs is of great interest and is currently subject to substantial investigation.

Unlike in macroscopic machines where energy is typically converted to motion, in the realm of nanomachines Brownian motion results in continuous movement of the molecular components relative to each other. Therefore, one of the key challenges emerging in the field of molecular machines is controlling the motion of mechanically interlocked components relative to each other. A typical example of this are two station molecular shuttles, in which a macrocycle continuously moves back and forth between two identical stations. Metal coordination to a series of pillar[5]arene/*bis*-imidazolium [2]rotaxanes through the formation of metal-carbene bonds facilitates a new strategy to restrict the shuttling motion in two station molecular shuttles. Whilst pillar[5]arene exhibits fast shuttling along the entire *bis*-imidazolium axle in the parent [2]rotaxanes, Ag(I)- or Pd(II)-coordination to the imidazoliums through the formation of an N-heterocyclic carbene results in restricted motion. Ag(I)-coordination can be reversed to obtain the parent species and is a potential starting material for further transmetalation reactions with a

range of other metals. The asymmetric Pd(II)-coordination to only one imidazolium is achieved through fine tuning of the spacer length, separating the two imidazolium units.

In order to synthesise MIMs with specific functions for applications, it is necessary to develop a synthetic toolbox which allows the straightforward combination of different components to produce systems with desirable and predictable properties in high yields under mild conditions. Furthermore, it has to be possible to build up more complex [n]rotaxanes and include supramolecular building blocks such as porphyrins, carbazoles, NIs and BODIPYs. Such a toolbox approach is developed by demonstrating that the three constituents of a [n]rotaxane (the rod, the macrocycle and the stopper group) can all be functionalised to contain an array of desirable moieties. The complex interplay of components in MIMs and the significant impact threading can have on the overall properties of the system is demonstrated by fluorescence measurements, finding that regulation of the fluorescent response can be achieved through certain combinations of macrocycle and rod substitution.

The toolbox developed herein is employed in the synthesis of [2]rotaxanes with handcuff topology, which allows molecules to be loosely connected whilst positioning them in close proximity. This strategy is demonstrated by the production of rylene diimide dimers, connected through pillar[5]arene/imidazole mechanical bonds. The spectroscopic and electrochemical investigation of these compounds enables a rare insight into the manner in which these compounds interact and demonstrates some intriguing new properties. In particular, the perylene diimide dimer handcuff displays fascinating characteristics such as excimer emission and an unusual visible absorption profile, showing the formation of a radical anion π -dimer upon double reduction. Interesting interactions in a naphthalene diimide dimer and a mixed perylene/naphthalene diimide dimer are also observed, the second of which demonstrates the superior flexibility of this synthetic approach. The effect of Pd(II)-coordination to the imidazoliums of the handcuffs on the overall properties of the system is evaluated, showing small but important

changes in the way the rylene cores interact. The synthetic strategy described within this thesis facilitates the creation of unusual dimeric structures and the adaptability of this approach is demonstrated through the introduction of 1,5-dialkoxynaphthalene (DAN) units. The unique arrangement of redox active moieties in this way allows intermolecular interactions to be investigated and their effect on each other's electronic and magnetic properties to be probed. Demonstrated herein is that the pillar[5]arene-imidazole interaction can be used as a versatile motif in the synthesis of mechanically interlocked molecules with new and enhanced properties.

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Contents

Declaration	v
Abstract	vii
Acknowledgements	xi
Publication List	xiii
List of Symbols and Abbreviations	xxi
Chapter 1. Introduction.....	1
1.1. Macrocycles.....	3
1.1.1. Crown Ethers	3
1.1.2. Cyclodextrins	4
1.1.3. Calix[n]arenes	4
1.1.4. Cucurbit[n]urils	5
1.1.5. Other Macrocycles.....	5
1.1.6. Pillar[n]arenes	6
1.1.6.1. Structure.....	6
1.1.6.2. Synthesis.....	8
1.1.6.3. Functionalisation	10
1.1.6.4. Host-Guest Properties	12
1.2. Mechanically Interlocked Molecules (MIMs)	17
1.2.1. Synthesis Strategies for MIMs	18
1.2.2. Molecular Machines	19
1.2.3. Pillar[5]arene-based MIMs	19
1.2.3.1. Pillar[5]arene-based [n]rotaxanes	19
1.2.3.2. Pillar[5]arene-based Polyrotaxanes	21
1.3. Thesis Outline	23
1.4. References.....	24
Chapter 2. Pillar[5]arene/Imidazole-Based Molecular Shuttles	31
2.1. Introduction.....	33
2.1.1. Molecular Machines	33
2.1.2. Molecular Shuttles.....	33
2.1.2.1. Single Binding Site Molecular Shuttles	34
2.1.2.2. Degenerate Molecular Shuttles.....	35
2.1.2.3. Multiple Binding Site Molecular Shuttle.....	37
2.1.3. Pillar[5]arene-based Molecular Shuttles	38
2.2. Results and Discussion.....	42
2.2.1. Synthesis of a Series of Two Station Molecular Shuttles	42

2.2.2.	Synthesis of an Asymmetric One Station Shuttle	45
2.2.3.	Shuttling in [2]Rotaxanes 2.1a-2.1c	47
2.2.3.1.	Shielding Factor	49
2.2.3.2.	Variable Temperature ¹ H NMR Spectroscopy	51
2.2.3.3.	Solvent Effects	52
2.2.3.4.	Anion Exchange	54
2.2.4.	Confinement: Ag(I)-Coordination	55
2.2.4.1.	Synthesis	55
2.2.4.2.	Shuttling Confinement	56
2.2.4.3.	Confinement Reversal with TFA	59
2.2.5.	Confinement 2: Pd(II)-coordination	59
2.2.5.1.	Synthesis of Pd(II) complexes from Ag(I)-coordinated [2]Rotaxanes 2.2a-2.2c	59
2.2.5.2.	Synthesis from Organic [2]Rotaxanes	64
2.2.5.3.	Shuttling Confinement	64
2.2.6.	Crystallography	66
2.2.6.1.	[2]Rotaxanes 2.1a-2.1c	67
2.2.6.2.	Ag(I)-coordinated [2]Rotaxanes 2.2a-2.2c	67
2.2.6.3.	Pd(II)-coordinated [2]Rotaxanes 2.3a-2.3c	67
2.3.	Conclusions and Future Work	68
2.4.	Materials and Methods	70
2.4.1.	Synthesis	70
2.4.1.1.	General Procedure for <i>Bis</i> -imidazole Alkanes	70
2.4.1.2.	Decamethoxypillar[5]arene DMP[5]A	71
2.4.1.3.	2-(Iodomethyl)-1,3,5-trimethylbenzene	71
2.4.1.4.	General Procedure for [2]-Rotaxane 2.1a-2.1c	71
2.4.1.5.	General Procedure for Ag(I)-[2]Rotaxane 2.2a-2.2c	74
2.4.1.6.	General Procedure for Conversion of [2]Rotaxanes 2.2a-2.2c to 2.3a-2.2c	74
2.4.1.7.	General Procedure for Pd-[2]Rotaxane 2.3b , 2.3c and 2.6a from 2.1a-2.1c	76
2.4.1.8.	General Procedure for Unthreaded Stoppered Rods 2.4a-2.4c	76
2.4.1.9.	General Procedure for Ag(I)-coordination to Stoppered Rods 2.5a-2.5c	77
2.4.1.10.	General Procedure for Pd (II)-coordination to Stoppered Rods 2.6a-2.6c	78
2.4.1.11.	Ag(II) Protodemetalation with TFA	79
2.4.1.12.	2-((6-Bromohexyl)oxy)-1,3,5-trimethylbenzene	79
2.4.1.13.	1-(6-(Mesityloxy)hexyl)-1H-imidazole	80
2.4.1.14.	Procedure for [2]Rotaxane 2.7	80
2.4.1.15.	Procedure for Axle Equivalent of 2.7	81

2.5. References.....	82
Chapter 3. Expanding the Synthetic Scope of Pillar[5]arene/Imidazole [n]Rotaxanes.....	85
3.1. Introduction.....	87
3.1.1. Fluorescence in [n]Rotaxanes.....	87
3.1.1.1. Monitoring Shuttling with Fluorescence.	87
3.1.1.2. [n]Rotaxanes Including Fluorescent Moieties for Potential Applications	88
3.1.1.3. Complex Fluorescent [n]Rotaxane Switches	89
3.1.2. Fluorescence in Pillar[5]arenes	91
3.1.2.1. Fluorophore Functionalised Pillar[5]arenes in Pseudorotaxane Sensors.....	91
3.1.2.2. Fluorophore Functionalised Pillar[5]arenes in [n]Rotaxanes.....	92
3.2. Results and Discussion.....	94
3.2.1. Synthesis of Functionalised Pillar[5]arenes.....	94
3.2.1.1. Di-carbazole Pillar[5]arene DCP[5]A	95
3.2.1.2. Di-BODIPY Pillar[5]arene DBP[5]A	96
3.2.2. Effect of Threading on Fluorescence	97
3.2.2.1. Synthesis of Two Station DCP[5]A -based Molecular Shuttles	97
3.2.2.2. Synthesis of Asymmetric One Station DCP[5]A -based [2]Rotaxane	98
3.2.2.3. Fluorescence of DCP[5]A -Containing Series A in THF, Chloroform and DMSO..	99
3.2.3. Axle-Macrocycle Interactions	103
3.2.3.1. Carbazole Terminated Axle Compounds	104
3.2.3.2. Naphthalene Imide Terminated Axle Compounds	106
3.2.3.3. Dimmer Switch	113
3.2.4. Expanding Synthetic Scope.....	115
3.2.4.1. Asymmetric [2]Rotaxanes.....	116
3.2.4.2. Symmetric [3]Rotaxane	120
3.2.4.3. Di-Carboxylic Acid Stoppered [2]Rotaxane	121
3.2.4.4. Porphyrin-Based [n]Rotaxanes.....	125
3.2.5. Quasi[1]catenane - Pretzel-Like Molecule.....	130
3.3. Conclusions.....	135
3.4. Materials and Methods	136
3.4.1. Synthesis.....	136
3.4.1.1. Di-Bromo-Pillar[5]arene	136
3.4.1.2. Di-Carbazole-Pillar[5]arene DCP[5]A	137
3.4.1.3. Mono-Carbazole-Pillar[5]arene MCP[5]A	137
3.4.1.4. Di-BODIPY-Pillar[5]arene DBP[5]A	138
3.4.1.5. General Procedure for <i>Bis</i> -Imidazole DCP[5]A [2]Rotaxanes 3.1a-c and 3.2 ...	138

3.4.1.6.	[2]Rotaxane 3.3	140
3.4.1.7.	[2]Rotaxane 3.4	141
3.4.1.8.	Axle 3.5	142
3.4.1.9.	Ag(I)-Coordination to 3.3	142
3.4.1.10.	Pd(II)-Coordination in the Synthesis of 3.6	143
3.4.1.11.	[2]Rotaxane 3.7	144
3.4.1.12.	[2]Rotaxane 3.8	145
3.4.1.13.	Axle 3.9	145
3.4.1.14.	[2]Rotaxane 3.10	145
3.4.1.15.	[2]Rotaxane 3.11	146
3.4.1.16.	Axle 3.12	147
3.4.1.17.	[3]Rotaxane 3.13	147
3.4.1.18.	Tetra-Ester [2]Rotaxane 3.14	148
3.4.1.19.	Tetra-Ester [2]Rotaxane 3.15	148
3.4.1.20.	Porphyrin [2]Rotaxane 3.16	149
3.4.1.21.	Porphyrin [5]Rotaxane 3.17	149
3.4.1.22.	Porphyrin Tetra-Pillar[5]arene TP[5]AP	150
3.4.1.23.	[2]Rotaxane 3.18	150
3.4.1.24.	[2]Rotaxane 3.19	151
3.4.1.25.	Ag(I)-Coordinated [2]rotaxane 3.20	152
3.4.1.26.	Pd(II)-Coordinated [2]rotaxane 3.21	152
3.5.	References	154
Chapter 4.	Handcuff [2]Rotaxanes – Studying the Interactions Between Molecules	159
4.1.	Introduction	161
4.1.1.	Rylene Diimides	161
4.1.1.1.	Naphthalene Diimides (NDIs)	161
4.1.1.2.	Perylene Diimides (PDIs)	162
4.1.2.	NDI/PDI Stacking and Dimers	162
4.1.3.	Handcuff Topology	163
4.2.	Results and Discussion	166
4.2.1.	Molecular Design and Synthesis	166
4.2.2.	UV/vis Spectroscopy	171
4.2.3.	Emission Spectroscopy	172
4.2.4.	Electrochemistry	173
4.2.4.1.	CV	173
4.2.4.2.	Spectroelectrochemistry	179

4.2.4.3.	Mid- and Near-IR Spectroscopy.....	186
4.2.4.4.	EPR Spectroscopy	188
4.2.4.5.	Photophysics of 4.5	191
4.2.5.	Pd(II)-Coordinated to Handcuff [2]Rotaxanes	195
4.2.5.1.	Synthesis.....	195
4.2.5.2.	Emission Spectroscopy	199
4.2.5.3.	Electrochemistry.....	200
4.2.6.	Expanding Scope to Include Naphthalene.....	207
4.2.6.1.	Synthesis.....	208
4.2.6.2.	Electrochemistry.....	210
4.3.	Conclusions.....	213
4.4.	Materials and Methods	216
4.4.1.	Synthesis.....	216
4.4.1.1.	General Procedure for <i>Bis</i> -Imidazole PDI/NDI 4.1/4.2	216
4.4.1.2.	Pillar[5]arene butylamine.....	216
4.4.1.3.	General Procedure for <i>Bis</i> -Pillar[5]arene PDI/NDI 4.3/4.4	217
4.4.1.4.	General Procedure for Handcuff [2]Rotaxanes 4.5/4.6/4.7	218
4.4.1.5.	General Procedure for <i>Bis</i> -Imidazolium PDI/NDI 4.8/4.9	220
4.4.1.6.	General Procedure for Ag(I)-Coordination to Handcuffs 4.10/4.11	220
4.4.1.7.	General Procedure for Pd(II)-Coordination to Handcuff [2]Rotaxanes 4.13/4.14 and Axles 4.15/4.16	222
4.4.1.8.	General Procedure for Handcuff [2]Rotaxanes 4.16/4.17	224
4.5.	References.....	226
Chapter 5.	Conclusion	231
Chapter 6.	Materials and Methods	237
6.1.	Reagents and Purification.....	239
6.2.	General Equipment.....	239
6.2.1.	NMR Spectroscopy	239
6.2.2.	Mass Spectrometry.....	239
6.2.3.	Absorbance/Emission/ Spectroscopy.....	239
6.2.4.	Electrochemistry.....	239
6.2.4.1.	Cyclic Voltammetry.....	240
6.2.4.2.	Spectroelectrochemistry	240
6.2.4.3.	Bulk electrolysis and X-band EPR spectroscopy	241
6.2.5.	Photochemistry	241
6.2.5.1.	Ground State Absorption.....	241

6.2.5.2.	Ultrafast Transient Absorption and Time-Resolved Infrared Spectroscopy	241
6.3.	X-ray Crystallography	242
6.3.1.	Equipment and Software	242
6.3.2.	Crystal Data	242
6.4.	References	247

List of Symbols and Abbreviations

ϵ	Extinction Coefficient
$E_{1/2}$	Redox potential
Φ	Fluorescence Quantum Yield
$h\nu$	Photon
K	Association constant
K_{com}	Comproportionation Constant
λ	Wavelength
ν	Frequency
aq	Aqueous
BODIPY	Boron Dipyrromethene
CT	Charge-Transfer
c	Concentration
CB[n]s	Cucurbit[n]urils
CV	Cyclic Voltammetry
CBPQT	Cyclobis(paraquat- <i>p</i> -phenylene)
CDs	Cyclodextrin
DMP[5]A	Decamethoxy-pillar[5]arene
D-A	Donor-Acceptor
DAN	1,5-Dialkoxynaphthalene
DBP[5]A	Di-bodipy-pillararene
DCM	Dichloromethane
DCP[5]A	Di-carbazole-pillar[5]arene
DDQ	2,3-Dichloro-5,6-dicyanobenzoquinone
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic Acid
DOX	Doxorubicin
em	Emission
EPR	Electron Paramagnetic Resonance
ESI	Electrospray Ionisation

Fc/Fc ⁺	Ferrocene/Ferrocenium
HRMS	High Resolution Mass Spectrometry
ICT	Intramolecular Charge Transfer
MALDI	Matrix-Assisted Laser Desorption/Ionisation
MCP[5]A	Mono-carbazole-pillar[5]arene
MOF	Metal-Organic Framework
MORF	Metal-organic rotaxane framework
MeOH	Methanol
MIR	Mid Infra-Red
MIM	Mechanically Interlocked Molecule
MMIM	Multiple Mechanically Interlocked Molecule
MO	Molecular Orbital
MS	Mass Spectrometry
NI	Naphthalene imide
NHCs	N-heterocyclic carbenes
NDI	Naphthalene Diimide
NIR	Near Infrared
NOESY	Nuclear Overhauser Effect Spectroscopy
PDA	Perylene Dianhydride
PDI	Perylene Diimide
PET	Photoinduced Electron Transfer
ps	Picosecond
SWV	Square Wave Voltammetry
TA	Transient Absorbance
TEA	Triethylamine
TOF	Time of Flight
TP[5]AP	Tetra-pillar[5]arene porphyrin
TRIR	Time Resolved Infrared
UV	Ultraviolet
vis	Visible

Chapter 1

Introduction

1.1. Macrocycles

The design, synthesis and modification of macrocycle host molecules is an area of great significance. The rise of supramolecular chemistry over recent decades has made developing new aspects of macrocycle chemistry as important as ever. The most common and well defined macrocycle families have recently been joined by a new group known as pillararenes. The key properties, characteristics and structures of crown ethers, cyclodextrins, calixarenes, cucurbiturils and pillararenes are shown in Table 1.1 and are discussed below.

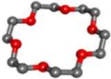
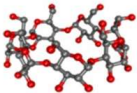
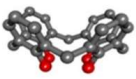
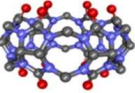
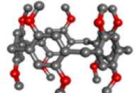
Macrocycle	Crown Ethers	Cyclodextrin	Calix[n]arene	Cucurbit[n]uril	Pillar[n]arene
Structure					
Shape	Crown	Cone	Basket	Barrel	Pillar
Discovery Date	1967	1891	1872/1942	1905/1981	2008
Homologues	12-24	6(α), 7(β), 8(γ)	4-8	5-8, 10, 14	5-10
Cavity Size	Flexible	4.4 Å (α), 5.8 Å (β), 7.4 Å (γ)	7.5-10 Å (4)	2.4 Å (5), 3.9 Å (6), 5.4 Å (7), 6.9 Å (8), 9-11 Å (10)	4.7 Å (5), 5.9 Å (6), 7.1 Å (7), 8.2 Å (8), 10.5 Å (10)
Synthesis	Metal templated	Enzymatic	Condensation polymerisation	Condensation polymerisation	Condensation polymerisation
Solubility	Good in a wide range	Polar solvents	Higher in non-polar solvents	Generally low solubility	Good in a range
Flexibility	High	Low	Moderate	Low	Moderate

Table 1.1: Comparing host macrocycles. Adapted from Ref.¹

1.1.1. Crown Ethers

Crown ethers were first reported by Charles Pedersen in 1967 and they have since been widely utilised in numerous areas of chemistry. They consist of a cyclic array of oxygen atoms separated by organic linkers, most commonly ethylene, $-\text{CH}_2-\text{CH}_2-$, spacers. This makes them very flexible and large crown ethers can adopt a wide range of conformations. Crown ether homologues can be readily synthesised in good yields, often by using a metal cation template.² As they have no reactive functional groups, any additional functionality has to be introduced before the cyclisation

reaction. Unlike most other macrocycles, they have excellent solubility in a wide range of solvents, which is due to the presence of both polar oxygen and non-polar aliphatic carbons. Their host-guest chemistry in organic solvents primarily originates from the coordination of the oxygen lone pairs to metal cations. Crown ethers have therefore found a particular foot-hold in cation complexation chemistry and have played a key role in the past and present development of MIMs.

1.1.2. Cyclodextrins

Cyclodextrins (CDs) are naturally occurring cyclic oligosaccharides consisting of six (α -CD), seven (β -CD) or eight (γ -CD) α -D-glucopyranose units linked at the 1- $\rightarrow$ 4 positions. Larger sizes are significantly less accessible and are therefore studied to a lesser extent. CDs have two inequivalent rims, giving them an overall truncated cone shape which is responsible for their unique complexation ability. Unlike most other macrocycles, CDs can be made on a large scale from starch using readily available enzymes making them commercially available at a modest price. The numerous hydroxyl groups on the rims are very reactive however, their reactivity is limited by CD's poor solubility in organic solvents.³ The hydroxyl groups nonetheless, make CDs highly soluble in polar solvents such as water and therefore their host-guest chemistry is dominated by hydrophobic effects and, to a lesser extent hydrogen bonding. CDs are biocompatible and are utilised across a wide range of applications in several industries including: pharmacy, food and mining.

1.1.3. Calix[n]arenes

Calix[n]arenes consist of phenolic units which are linked by methylene bridges at the *para*-position and are synthesised via a phenol-formaldehyde condensation. As shown in Table 1.1, this makes the two rims inequivalent giving them a basket shape. Both rims can be functionalised and their solubility depends on the degree of functionalisation. Due to the small, asymmetric nature of the calix[4]arene cavity, it is not big enough to fully thread a guest molecule however the open side can bind guests such as toluene. Calix[4]arene also has four fold symmetry which is relatively rare

in the realm of macrocycles.⁴ Larger calix[n]arenes exhibit rich host-guest chemistry because the individual phenolic units are electron rich and therefore form strong interactions with electron deficient guests such as cations. Due to their host-guest chemistry, tuneable size and rigid structure calix[n]arenes can be found in applications such as artificial receptors.⁵

1.1.4. Cucurbit[n]urils

Cucurbit[n]urils (CB[n]s) are highly symmetric, barrel shaped and consist of n-glycoluril units with two identical carbonyl-laced rims. They are prepared via an acid-catalysed condensation reaction of glycoluril and formaldehyde. Sizes 5-8, 10 and 14 are known and different mixtures of homologues can be accessed by varying the reaction temperature.⁶ The solubility and host-guest properties of CB[n]s is dependent on their size. The cavity is hydrophobic and therefore favours non-polar guests in polar solvents whilst the rims are laced with polar carbonyl groups which bind ions and molecules via hydrogen bonding and charge dipole interactions. Overall CB[n]s exhibit very high association constants with a large number of guests and are therefore attractive building blocks in the synthesis of MIMs, with the exception of CB[5]s where the cavity is too small for threading to occur.⁷

1.1.5. Other Macrocycles

In addition to the families of macrocycles described above there are other, less well defined groups of macrocycles such as cyclophanes, which are macrocyclic molecules containing aromatic rings linked by aliphatic bridges. The most famous cyclophane is cyclobis(paraquat-*p*-phenylene) (CBPQT4+), also known as the 'blue box'. This highly electron deficient host strongly binds π -electron-rich guests and has widely been used by Stoddart's research group. Another group of macrocycles are amide-based macrocycles such as cycle-tetralactam which are typically strong hydrogen bond acceptors and widely feature in the synthesis of MIMs.

1.1.6. Pillar[n]arenes

In 2008 a new family of macrocycles was first reported by Ogoshi et al.⁸ These compounds have become known as pillar[n]arenes due to their highly symmetric, pentagonal and cylindrical structure. Pillar[n]arenes are made up of five hydroquinone units linked at the *para* positions by methylene bridges. Although in structure they are similar to calix[n]arenes, the *para* bridges mean that the two rims are identical which gives them similar symmetry characteristics to CB[n]s. However, unlike CB[n]s the rim can easily be functionalised by either pre or post cyclisation modifications. These aspects along with their host-guest properties and planar chirality has made them a key player in the field of supramolecular chemistry in a relatively short period of time. The key structural features, synthesis, functionalisation and host-guest chemistry are discussed below.

1.1.6.1. Structure

1.1.6.1.1. *X-Ray Crystal Structure*

Pillar[5]arene was the first reported analogue and is still most widely used however, pillar[6]arene has also been well established and pillar[7-15]arene have been reported.⁹ The crystal structure of pillar[5]arene with ten methoxy groups on the rims was reported along with its discovery in 2008 and is shown in Figure 1.1. This structure highlights the high symmetry and illustrates the internal angles around the methylene bridges.

The crystal structure of pillar[6]arene shows similarly high symmetry to pillar[5]arene. The crystal structure of pillar[8-10]arene has also been reported, however to accommodate the additional ring strain these larger cycles have two cavities, for example pillar[8]arene has two pentagonal cavities in the crystalline phase.

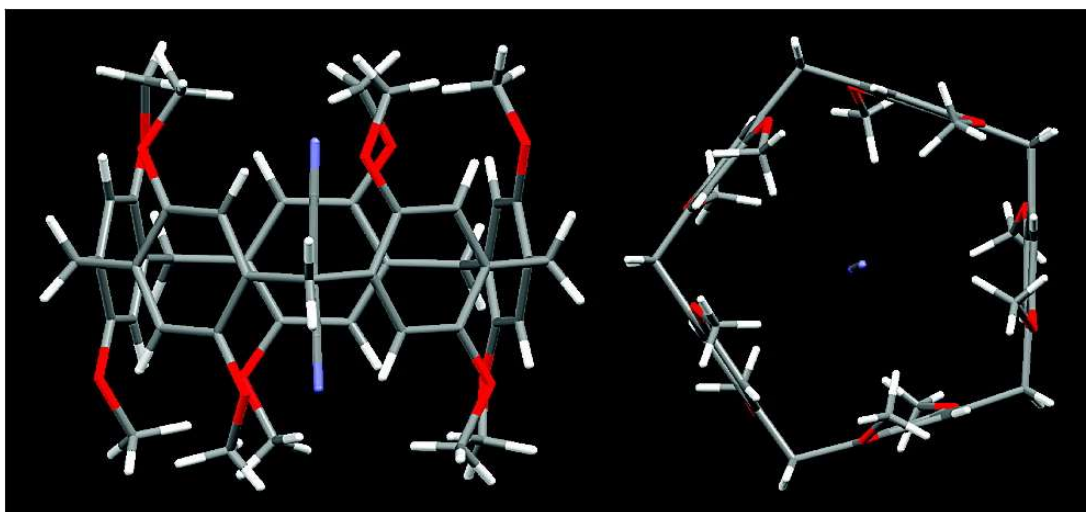


Figure 1.1: The crystal structure of pillar[5]arene from the side (left) and from the top (right) showing a guest acetonitrile molecule. Adapted from Ref.⁸

1.1.6.1.2. Conformational Isomers and Planar Chirality

When considering the conformational isomers of macrocycles; it is important to distinguish between firstly, macrocycles with fixed units which cannot rotate such as CB[n]s and secondly, flexible macrocycles where the units can rotate around 180° such as calix[n]arenes. Pillar[n]arenes fit in the second category and thus have conformational isomers. Pillar[5]arene has four diastereoisomers as well as four corresponding enantiomers which gives it eight conformers in total, shown in Figure 1.2. There has been a number of studies into the interconversion of these conformers and it has been found that the rim groups have a decisive effect on the stability of individual conformers. For example, both experimental¹⁰ and theoretical¹¹ results of per-hydroxylated pillar[5]arene showed that conformer d/d' was the most stable due to a network of hydrogen bonds. In per-alkylated pillar[5]arenes on the other hand, the steric bulk of the rim groups dominates conformer stability and as a result conformer a/a' is the most stable. Efforts have been made to prevent the rotation of units in order to lock the conformers and thus induce permanent chirality. In a series of pillar[5]arenes with rim alkyl chains of 1-6 and 12 carbons, the energy barrier of rotation increases with increasing chain length. However, it was not until the introduction of bulkier rim groups such as cyclo-hexylmethyl that the rotation was prevented

completely.¹² It has been possible to isolate the chiral components using chiral HPLC¹³ or a diastereomer method.¹⁴

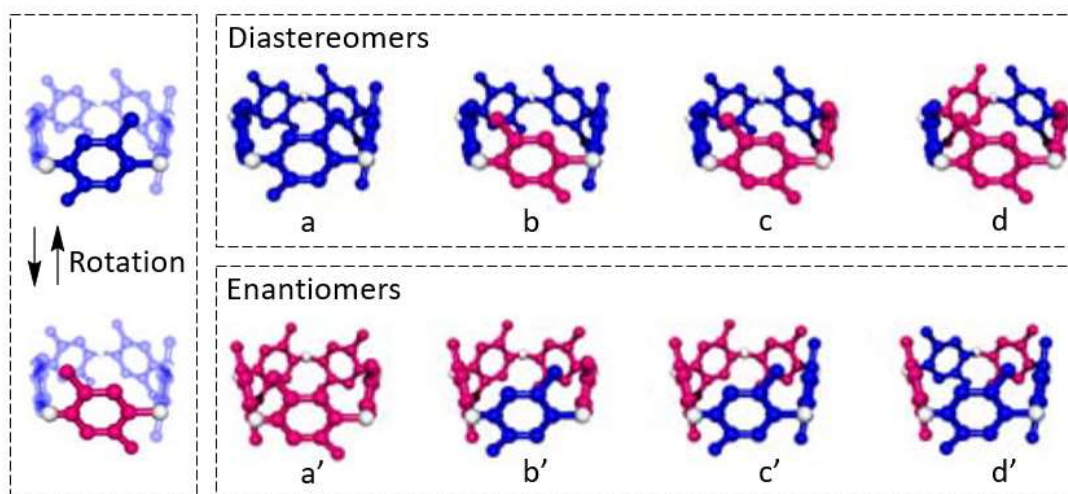


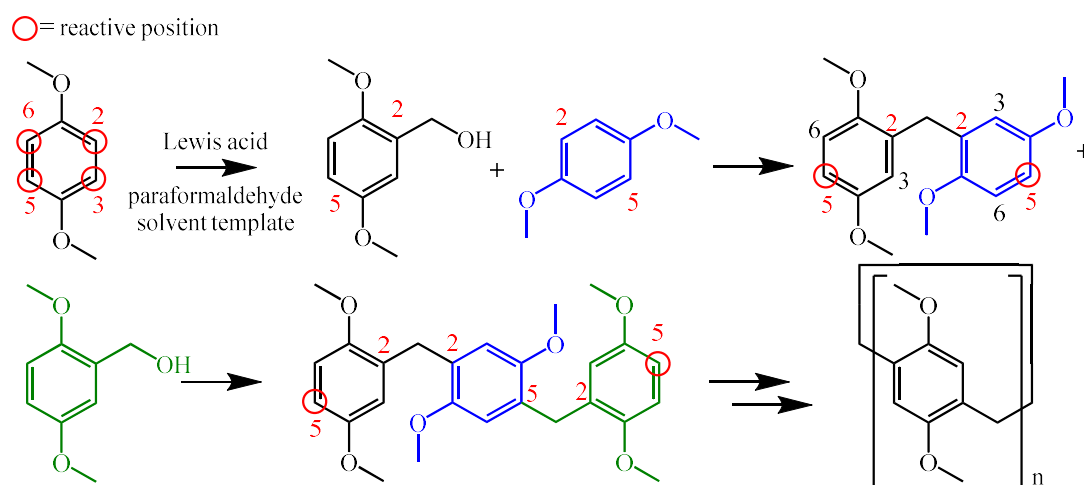
Figure 1.2: Rotational modes of the benzene units of pillar[5]arenes. Conformers of pillar[5]arene caused by rotation of the benzene units.¹⁵

1.1.6.2. Synthesis

Pillar[n]arenes were a product of chance during work done on phenol-paraformaldehyde resins. Similar to calix[n]arenes, they are made in a controlled condensation polymerisation. The key goal in these reactions is to minimise the formation of three-dimensional and linear polymers and to increase the rate of macrocycle formation. In calix[n]arenes the phenol substituent dominates the reactivity by electronically directing substitution to the ortho (2 and 6) positions. In the synthesis of pillar[n]arenes the initial monomer, for example 1,4-dimethoxybenzene, has 4 unsubstituted positions (2,3,5,6) which are equally reactive and are highlighted in Scheme 1.1. Once a paraformaldehyde and a monomer unit have reacted, sterics dominate the subsequent reactivity. Position 3 is clearly blocked by substitution at position 2 as well as the methoxy group at position 4. The steric inhibition of position 6 is more subtle, it arises from the methoxy group at position 1 being forced to face towards position 6 by substitution at position 2.¹

In macrocycle synthesis via controlled condensation polymerisation, the kinetic and thermodynamic driving forces have to be considered. Reactions under kinetic control favour

polymer formation whilst macrocycles are generally the thermodynamic product due to entropic energy contributions. It follows that within macrocycle families, the smallest sterically allowed ring size tends to be the most thermodynamically favourable. Pillar[5]arene can be synthesised selectively if the reaction is done under thermodynamic control whilst the synthesis of pillar[>5]arenes has to be done under kinetically dominated conditions, affected strongly by temperature and reaction time. It is worth noting however, that pillar[n]arenes can undergo reversible “dynamic” covalent bond formation in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ and a templating solvent. This has been demonstrated in the conversion of larger pillar[n]arenes to pillar[5]arene at elevated temperatures.¹⁶



Scheme 1.1: General proposed reaction pathway for the synthesis of pillar[n]arene from 1,4-dimethoxybenzene with paraformaldehyde in the presence of a Lewis acid and a solvent template.

One of the criteria for macrocycles to be useful in a wide range of applications is that they are readily available. Therefore the reaction condition optimisation of pillar[5]arene synthesis has been the subject of considerable investigation. The most significant factors are the catalyst and the solvent employed. Catalysts such as $\text{BF}_3 \cdot \text{OEt}_2$, FeCl_3 , AlCl_3 , *p*-TsOH and TFA have been investigated and it was found that $\text{BF}_3 \cdot \text{OEt}_2$ and TFA give the highest yield.¹⁷ In a similar fashion, solvents such as dichloromethane and dichloroethane were found to give higher yields than chloroform. Closer inspection of these observations resulted in the theory that some catalysts and

solvents acted as templates in the cyclisation process. This was confirmed by host-guest studies of pillar[5]arene with different solvents.¹⁸ The cost, sustainability and availability of catalysts and solvents have to be considered as well as the practicality and safety of scaling up pillar[5]arene synthesis.

1.1.6.3. Functionalisation

As previously mentioned, pillar[n]arenes can feature a range of substituents on both of their rims. These have a considerable influence on properties such as solubility and host-guest chemistry. Pillar[5]arene has received the most attention because it can be made in higher yields than its larger cousins. Mono-functionalised pillar[5]arene has only one constitutional isomer however, major issues arise when looking at multifunctional di-, tri- and tetra- pillar[5]arenes. The five possible conformational isomers of a di-functionalised pillar[5]arene are shown in Figure 1.3. For a tri-functionalised pillar[5]arene there are 10 conformational isomers. The position selective functionalisation of pillar[5]arene has been the subject of intense investigation. Two distinct approaches have been developed; firstly, deprotection and subsequent re-functionalisation and secondly, using different 1,4-dialkoxybenzene derivatives in the initial cyclisation.

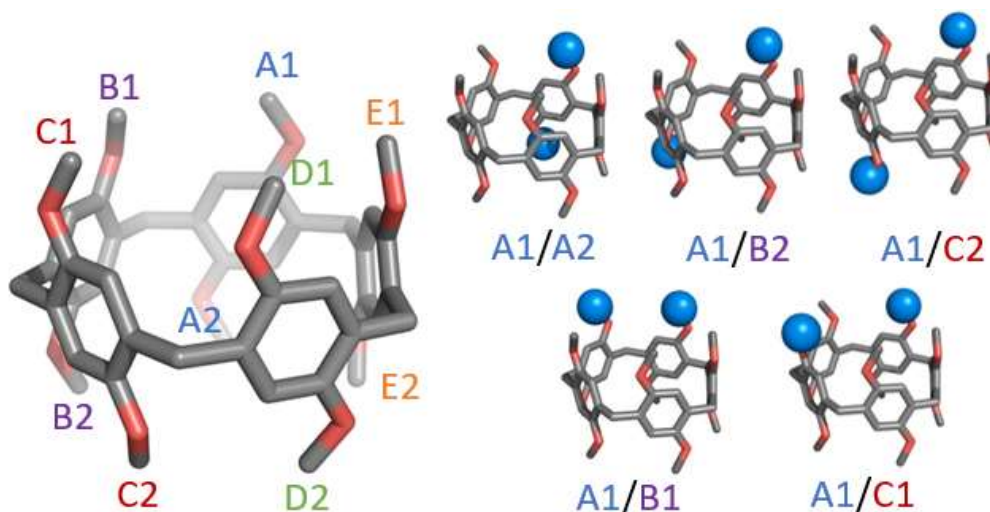


Figure 1.3: The five possible constitutional isomers of a di-functionalised pillar[5]arene. Generic functional groups are represented by blue spheres. The nomenclature shows each hydroquinone unit assigned a letter (A-E) and the two rims distinguished by numbers (1 and 2). Adapted from Ref.¹⁹

1.1.6.3.1. Method 1: Deprotection and Subsequent Re-functionalisation

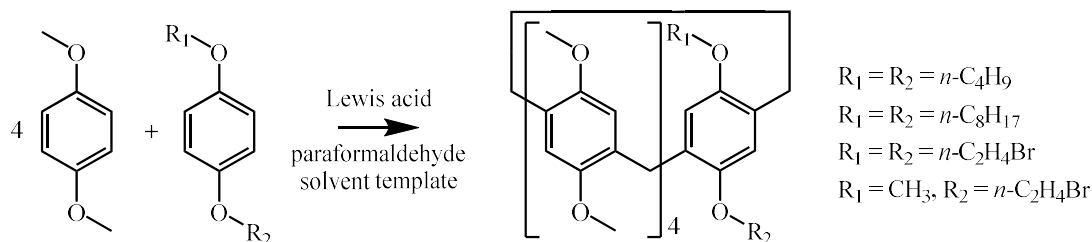
The first di-functionalised (A1/B2) conformational isomer was successfully isolated employing an *in situ* cyclisation and deprotection reaction with the Lewis acid AlBr_3 . Separating the mixture of isomers in this case was straight forward as the A1/B2 isomer was insoluble in methanol.²⁰ An alternative approach via a more conventional methoxy deprotection, using 0.9 equivalents of BBr_3 under optimised reaction time at room temperature, gave mono-hydroxylated pillar[5]arene at a yield of 22 %.²¹ Stoddart and co-workers²² developed this approach further by systematically varying the equivalents of BBr_3 and the reaction temperature. They found that the deprotection occurred in a stepwise manner under kinetic control at low temperature. Furthermore they converted the deprotected hydroxys to triflate groups which allowed the isomers to be separated using silica gel chromatography. In this manner the regioisomers mono-, di- and tri-triflated pillar[5]arene were isolated.

An alternative approach includes the oxidation of 1,4-dialkoxybenzene units to benzoquinone units and their subsequent reduction to afford pillar[5]arenes with hydroquinone units. The advantage of this approach over the deprotection using BBr_3 is that di-phenol pillar[5]arenes can be produced when two phenolic groups are on the same benzene unit (for example A1 and A2). The same applies to pillar[5]arenes with a higher number of hydroquinone units. In fact the oxidation reaction condition optimisation led to the preparation of pillar[5]arenes with two hydroquinone units (A/B and A/C) which, after reduction, gave the equivalent tetra-hydroxylated pillar[5]arenes (A1/A2/B1/B2 and A1/A2/C1/C2).²³

1.1.6.3.2. Method 2: Co-cyclisation of Two Different 1,4-Dialkoxybenzene Derivatives

Asymmetric pillar[5]arenes with different 1,4-dialkoxybenzenes, such as dimethoxy, dibutoxy, and dioctyloxy have been reported and are shown in Scheme 1.2. The introduction of reactive groups was first demonstrated by Stoddart and co-workers with the synthesis of a mono-functionalised pillar[5]arene with one 2-bromoethoxy and nine methoxy groups.²⁴ The selectivity for making

mono-functionalised product arises from fine tuning the ratio of the different monomers and the reaction time. Soon after, in a similar reaction using a 1,4-*bis*-(2-bromoethoxy)benzene monomer, the equivalent A1/A2 di-bromo functionalised pillar[5]arene has been reported.²⁵



Scheme 1.2: Co-cyclisation of two different 1,4-dialkoxybenzene derivatives.

The disadvantage of this reaction route is that the functionalities of the initial monomer units are limited as they may inhibit cyclisation or decompose under the polymerisation reaction conditions. In this regard, bromoalkoxy groups have shown great promise and have been the starting point for numerous subsequent modifications such the introduction of versatile amine²⁶ and azide²⁷ groups. This is additionally assisted by the post-cyclisation pillar[5]arene structure itself being relatively chemically robust.

1.1.6.4. Host-Guest Properties

Pillar[5]arenes exhibit interesting and diverse host-guest properties with a variety of guests. They consist of five electron rich aromatic rings and therefore bind electron accepting guests. During the formation of pillar[5]arene host-guest complexes, different types of interactions can contribute and come into play. These include coordination interactions between unpaired electrons and empty electron orbitals and electrostatic/charge-transfer (CT) interactions between electron donors and acceptors. Weak physical interactions such as van der Waals, π/π , and hydrogen-bonding interactions can also contribute significantly to complexation. The host-guest binding ability of pillar[5]arene has been utilised in the synthesis of catenanes, rotaxanes, rotaxane-dendrimers and polyrotaxanes.

1.1.6.4.1. *Rim Functionality Assisted Binding*

Rim functionality can have a significant effect on the host-guest properties of pillar[5]arene. Additional recognition sites can be tethered to the rim which can increase the binding of di-functional guests. This strategy has been employed to synthesise benzo-18-crown-6 functionalised pillar[5]arenes which formed a 1:1 inclusion complex with octane-1,8-diammonium di-cations. The aliphatic chain was found to thread the non-polar pillar[5]arene cavity whilst the ammonium cations bind the benzo-crown ethers.²⁸ In a similar system, a pillar[5]arene with ten electron-rich naphthyl rim groups was synthesised with strongly bound linear guests containing electron-deficient pyridinium units. It was found that size, charge density and C–H $\cdots$ π interactions all played a key role in the cooperative binding of these guests.²⁹ Yet another approach saw the synthesis of pillar[5]arene with one and two urea units tethered in the A1 and A1/A2 positions. These two functionalised pillar[5]arenes strongly bound alkylammoniums with varying chain length/counterion and linear alkyl dicarboxylates respectively.^{25a, 30}

1.1.6.4.2. *Water Soluble Pillar[5]arenes*

By further developing pillar[5]arene rim functionality, water soluble pillar[5]arenes have been developed and their guest binding properties have been studied. The first water soluble pillar[5]arene was reported in 2010 by Ogoshi and co-workers, who functionalised both rims with carboxylate groups. Subsequent studies showed that this deca-anion binds positively charged paraquat in water.³¹ Similarly, pillar[5]arene functionalised with trimethylammonium moieties was found to effectively bind sodium 1-octanesulfonate in aqueous media due to a combination of hydrophobic and electrostatic effects.³² By functionalising the rims with amino groups Yu, Hou and co-workers synthesised a neutral yet water soluble pillar[5]arene. This deca-amino pillar[5]arene encapsulated linear di-acids under acidic, neutral and basic conditions and formed ion pair bound [2]rotaxanes.³³

1.1.6.4.3. Organic Solvent Soluble Pillar[5]arenes

The majority of pillar[5]arenes are soluble in organic solvents and therefore the understanding of the host-guest interactions in this medium is key, especially for the synthesis of MIMs. The two most common interactions which drive complexation between neutral pillar[5]arenes and guests in organic solvents are cation/ π interactions and hydrogen bonding. Cationic guests which form stable complexes with pillar[5]arenes include paraquat and pyridinium derivatives,^{8,34} imidazolium cations,³⁵ *bis*-(imidazolium) dications,³⁶ secondary ammoniums³⁷ and *n*-octyltrimethylammonium hexafluorophosphate³⁸ shown in Figure 1.4/Table 1.2.

In the case of neutral guest, the dominant driving force for complexation is the formation of multiple hydrogen bonds. Stoddart and co-workers were the first to investigate the neutral guest recognition ability of pillar[5]arene. Neutral guests tend to have superior solubility in organic solvents which is advantageous for MIM synthesis. They investigated the guest binding ability of *per*-methylated pillar[5]arene with 1,8-diaminooctane and *n*-octylamine. The difference in the binding constant between these two guests suggested that the terminal amine groups assisted the binding.³⁹ Following this observation various other outer nitrogen-containing guests have been tested and especially short alkyl chains with small terminal nitrogen-containing heterocycles⁴⁰ and dibenzyl tetramethylene *bis*-carbamate derivatives⁴¹ have high association constants. In particular *bis*-imidazole butane forms very stable host-guest complexes with pillar[5]arene as shown in Table 1.2.⁴²

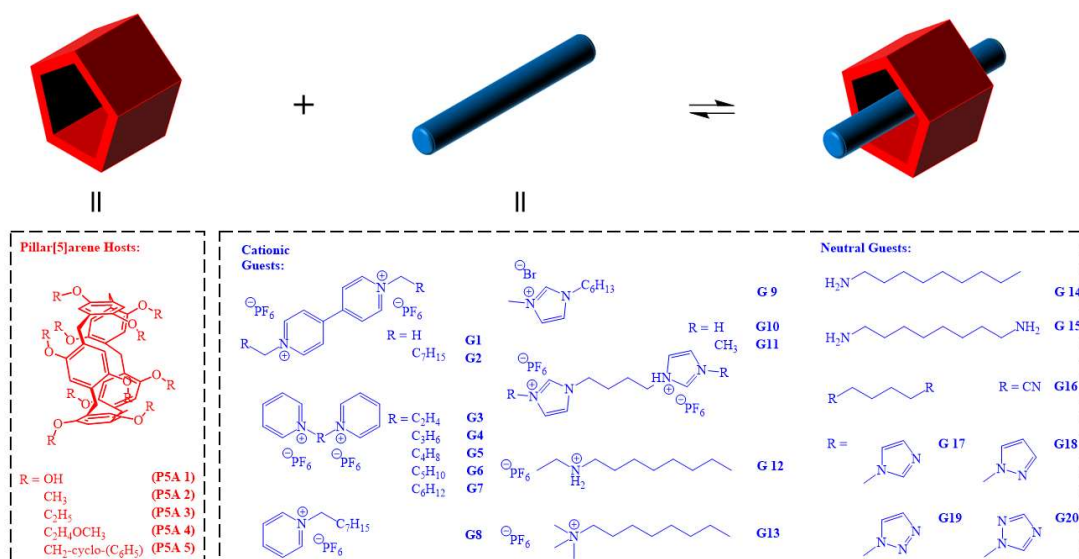


Figure 1.4: Cartoon representations of free pillar[5]arene (red), guest (blue) and host-guest complex. The structure of a selection of pillar[5]arenes (red) and cationic and neutral guests (blue).

Guest	Host	Solvent	Association constant K (M ⁻¹)	Method	Reference
G1	P5A 4	Acetonitrile	$(3.35 \pm 0.22) \times 10^4$	Isothermal Calorimetry	43
G2	P5A 1	Methanol	$(1.2 \pm 0.2) \times 10^4$	Fluorescence	8
G3	P5A 1	DMSO	Too small to be calculated	NMR	34
G4	P5A 1	DMSO	$(8.8 \pm 0.7) \times 10$	NMR	34
G5	P5A 1	DMSO	$(4.5 \pm 0.4) \times 10^2$	NMR	34
G6	P5A 1	DMSO	$(3.7 \pm 0.3) \times 10^2$	NMR	34
G7	P5A 1	DMSO	$(1.2 \pm 0.1) \times 10^2$	NMR	34
G8	P5A 1	Methanol	$(1.2 \pm 0.3) \times 10^3$	Fluorescence	8
G9	P5A 1	Acetone	$K_1 = 1.1 \times 10^2$, $K_2 = 2.0 \times 10$	NMR	35
G10	P5A 1	DMSO	$(5.5 \pm 0.2) \times 10$	NMR	36
		Acetone	$(4.6 \pm 0.6) \times 10^2$		
G11	P5A 1	DMSO	$(1.4 \pm 0.2) \times 10^2$	NMR	36
G12	P5A 2	Chloroform	$(1.09 \pm 0.41) \times 10^3$	NMR	37a
G13	P5A 5	Chloroform	8.3×10^2	NMR	12
G14	P5A 2	Chloroform	$(2.0 \pm 0.2) \times 10$	NMR	39

G15	P5A 2	Chloroform	$(7.0 \pm 1.0) \times 10$	NMR	39
G16	P5A 3	Acetone	$(2.4 \pm 0.3) \times 10^3$	NMR	44
G17	P5A 3	Chloroform	$(2.0 \pm 0.4) \times 10^4$	NMR	42
G18	P5A 3	Chloroform	$(6.6 \pm 0.2) \times 10$	NMR	40
G19	P5A 3	Chloroform	$(1.6 \pm 0.3) \times 10^4$	NMR	40
G20	P5A 3	Chloroform	$(6.6 \pm 0.4) \times 10^3$	NMR	40

Table 1.2: Host-Guest complexation between pillar[5]arenes (P5A 1-5) and guests (G1-20). Showing solvent, association constant and method used to calculate the binding.

The rich host-guest chemistry of pillar[5]arene has been utilised in the construction of various supramolecular architectures including pseudorotaxanes with di-guest and di-host systems.⁴⁵ Furthermore, co-pillar[5]arenes have been developed and shown to form temperature and concentration dependent dimers⁴⁶ and polypseudorotaxanes.⁴⁷ The synthesis of pillar[5]arene-based MIMs will be discussed in Section 1.2.3.

1.2. Mechanically Interlocked Molecules (MIMs)

Fundamentally a mechanical bond can be defined as “an entanglement in space between two or more component parts such that they cannot be separated without breaking or distorting the chemical bonds between atoms”.⁴⁸ As a consequence, these physically bonded molecules can possess topological isomers with distinct geometries. Examples of interlocked molecular architectures include knots, catenanes and rotaxanes. Besides offering new possibilities and challenges for chemists worldwide, MIMs are considered to have potential applications in very present topics such as information storage, processing and in molecular devices.⁴⁹ Rotaxane assemblies, in particular, have generated interest as the basis for development of functional and artificial nanomachines.⁵⁰

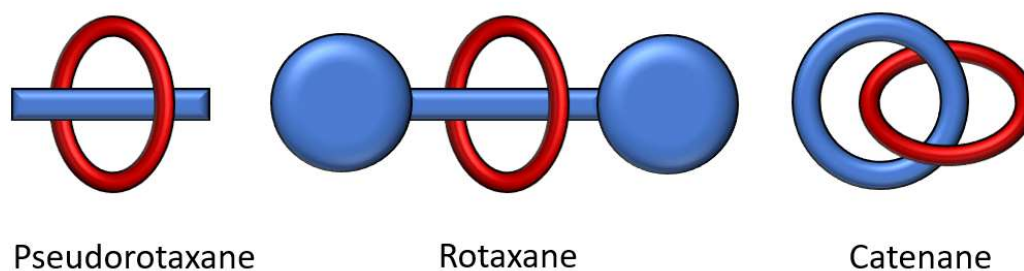


Figure 1.5: Cartoon representation of a pseudorotaxane, rotaxane and catenane.

Catenane is derived from the Latin *catena*, meaning chain. Catenanes consist of at least two topologically linked macrocycle (ring or host) components. Rotaxane is derived from the Latin *rota*, meaning wheel or axle. In a rotaxane there is at least one macrocycle and at least one linear component (rod or guest) which in turn is terminated with bulky end groups (stoppers) that prevent the macrocycle from slipping off the ends (dethreading). An un-stoppered rotaxane is referred to as a pseudorotaxane or host-guest complex. To clarify the terminology used within this thesis; rod is used to describe the unstoppered guest component whilst axle refers to the stoppered equivalent (threaded or unthreaded).

1.2.1. Synthesis Strategies for MIMs

Early efforts in the synthesis of MIMs saw Wasserman and co-workers develop a statistical threading method in which the interlocking of molecules was primarily due to chance. Without utilising any noncovalent bonding interactions, the yield of their reported [2]catenane was below 1 %.⁵¹ The statistical threading method was similarly employed in the synthesis of the first rotaxane in 1967 by Harrison and co-workers.⁵² An alternative approach using an 18 step synthesis, which involved the late cleavage of a covalent bond to separate two interlocked rings was developed by Gottfried Schill and Arthur Lüttringhaus in 1964.⁵³ There was a major transformation in the field of MIMs in 1983 when Jean-Pierre Sauvage and co-workers reported the use of a copper(I) ion to template the formation of catenanes.⁵⁴ This demonstrated that MIMs were readily available and paved the way for the use of noncovalent interaction in their synthesis. Since then, an assortment of strategies and methods have been developed for the synthesis of MIMs. This includes template methods,⁵⁵ utilising π - π stacking interactions,⁵⁶ hydrogen bonding,⁵⁷ hydrophobic interactions,⁵⁸ metal ion coordination,⁵⁹ anion templates⁶⁰ and more recently click chemistry.⁶¹ The breadth and diversity of these methods has led to the synthesis and construction of complex architectures such as olympiadane,⁶² Borromean rings⁶³ and polyrotaxanes.⁶⁴

In the synthesis of rotaxanes the template-directed synthetic method can be further subcategorised into different approaches: capping, snapping clipping and slipping. In the capping method the macrocycle encapsulates a rod (guest), forming a pseudorotaxane. The ends of the rod subsequently react with bulky stopper groups preventing the macrocycle from slipping off the ends. This method often yields symmetric rotaxanes. Non-symmetric rotaxanes can be synthesised by using the snapping method, in which the rod already has a bulky group on one end before threading and stoppering the other end. During clipping, the macrocycle forms around a dumbbell-like linear rod with bulky stoppers on both ends. Slipping is a more specific method in which the macrocycle can thread over an end group at an elevated temperature only and is then stuck once cooled.⁵⁶ Alternatively an active metal template can be used in which a metal centre is

both responsible for assembling the components and catalysing the covalent bond formation which results in rotaxane configuration.⁶⁵ Less common strategies have also been reported such as threading-followed-by-shrinking, where the macrocycle fits on the dumbbell rod easily but then reduces in size due to coordination⁶⁶ and threading-followed-by-swelling in which the stopper groups increase in size post threading.⁶⁷

1.2.2. Molecular Machines

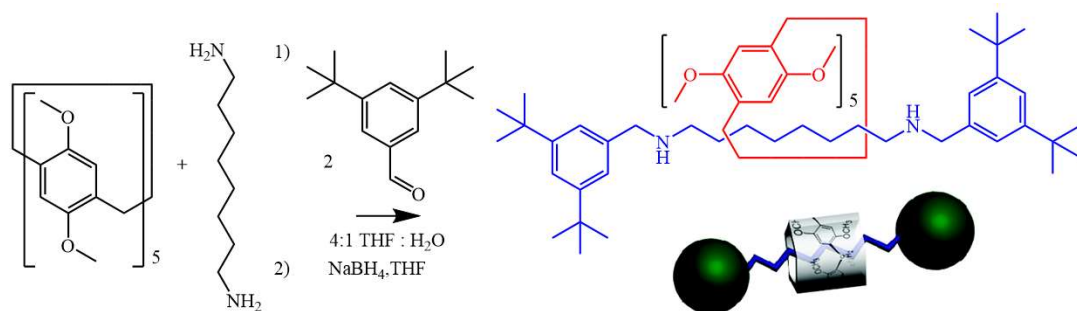
Due to the development of new synthesis strategies for MIMs, rotaxanes have attracted a lot of attention for possible applications. In particular, the high degree of freedom of the independent components and their motion relative to each other is a unique feature of these compounds. In a rotaxane there are two types of motion the macrocycle undergoes relative to the linear rod, rotation (spinning around the rod) and shuttling (along the rod). This motion has been limited and manipulated by external stimuli such as acid/base, choice of anion or cation, photochemistry, and electrochemistry⁶⁸ leading to the development of nanomotors,⁶⁹ molecular elevators⁷⁰ and ratchets.⁷¹ The intermolecular motion of rotaxanes has also been studied in the solid state,⁷² on surfaces⁷³ and within metal-organic frameworks (MOFs)⁷⁴ with the vision that they will one day feature in smart materials and molecular electronics.

1.2.3. Pillar[5]arene-based MIMs

1.2.3.1. Pillar[5]arene-based [n]rotaxanes

The binding properties of pillar[n]arenes has been the subject of intense investigation and a large quantity of guests have been reported and studied (Section 1.1.6.4.). Stoddart and co-workers contributed to this by looking at the binding affinity of pillar[5]arene for neutral guests such as alkanediamines which led to reporting the first pillar[5]arene-based [2]rotaxane shown in Scheme 1.3. They employed the capping strategy by using a condensation reaction between the terminal amine groups of the threaded rod and a bulky aldehyde. However, the di-amine guest used had a relatively low binding constant (Table 1.2) and therefore the reported yield of the [2]rotaxane

product was only 7 %.³⁹ Since then, recognition motifs with higher affinities for pillar[5]arene such as alkane⁷⁵ and triazole moieties⁷⁶ as well as cationic guests such as imidazolium⁷⁷ and pyridinium derivatives⁷⁸ have been used to synthesise pillar[5]arene-based [n]rotaxanes in higher yields. Although pillar[5]arene-based catenanes have been reported,⁷⁹ examples are rare and rotaxanes are the predominant pillararene-based MIMs.



Scheme 1.3: Preparation of the first pillar[5]arene-based [2]rotaxane by Stoddart and co-workers. Adapted from Ref.⁸⁰

Complex pillar[5]arene-based [n]rotaxane architectures have been reported. For example, Huang and co-workers have described a doubly threaded [3]rotaxane dimer based on an amino-modified co-pillar[5]arene which expanded and contracted in different solvents. This was because in non-polar solvents such as chloroform, the pillar[5]arene strongly interacts with the urea moiety via NH/ π interactions, while in polar solvents such as DMSO, these interactions are broken. Changes in the solvent therefore caused contraction/relaxation with a difference in length of the overall molecule of 6 Å.⁸¹ Similarly functionalised pillar[5]arenes have been used to synthesise self-threaded pillar[5]arene-based [1]rotaxanes with one⁸² and two⁸³ self-threaded units. Furthermore, amphiphilic pillar[5]arene-containing [2]rotaxanes with a good hydrophilic/hydrophobic balance have been synthesised and from these stable Langmuir films have been obtained. It was found that the pillar[5]arene alkyl chain lengths played a vital role on the reversibility of the compression–decompression cycles.⁸⁴ In an alternative approach, the heating and slipping approach has been effectively utilised in the synthesis of a pillar[5]arene-based [2]rotaxane using a cyclic host liquid.⁸⁵ In an effort to develop more complex topologies, a

novel [2]rota[2]catenane has been synthesised by including a pillar[5]arene/imidazolium-based [2]rotaxane subunit and a crown ether-tetracationic cyclophane [CBPQT]⁴⁺-based [2]catenane.⁸⁶ In a commendable demonstration of self-assembly Stoddart and co-workers have reported [4]rotaxanes and [5]rotaxanes in which pillar[5]arenes and cucurbit[6]urils interacted cooperatively with bipyridinium di-cations. Interestingly, pillar[5]arene modified the binding properties of cucurbit[6]uril resulting in a high level of pre-organisation. This was largely due to hydrogen bonding between hydroxyl groups on the rims of pillar[5]arene and carbonyl groups on the rims of cucurbit[6]uril.⁸⁷

1.2.3.2. Pillar[5]arene-based Polyrotaxanes

In an effort to strive towards using pillar[5]arene-based rotaxanes for applications, such as stimuli responsive materials for drug delivery and mimicking biological machines, a number of polyrotaxanes have been synthesised. The affinity of pillar[5]arene for cationic guests includes viologen polymers. These have been used as guests in the synthesis of pillar[5]arene-based polyrotaxanes stoppered with bulky adamantyl moieties.⁸⁸ A neutral polyrotaxane has also been reported using a liquid pillar[5]arene functionalised with tri(ethylene oxide) chains and azido-terminated polytetrahydrofuran with alkyne-stoppers.⁸⁹ In a similar system a non-ionic polyrotaxane was reported, based on pillar[5]arene threaded by star-poly(ϵ -caprolactone) and stoppered with adamantane end groups.⁹⁰ Additionally, a number of polypseudorotaxanes have been described⁹¹ including a stimulus responsive polyrotaxane gel, based on pseudorotaxanes linked by orthogonal metal-ligand coordination.⁹²

Dendrimers are highly branched macromolecules with perfectly defined and monodisperse structures. The high association constant of cyano groups and 1,4-methoxypillar[5]arene has been utilised in the assembly of pillar[5]arene-based supramolecular dendrimers.⁹³ More recently, Yang and co-workers reported dual stimuli-responsive dendrimers with reversible dimension modulation. The authors designed and synthesised 1,4-diethoxypillar[5]arene-rotaxane-branched

dendrimers up to the third generation with 21 switchable rotaxane moieties. The addition and removal of a DMSO molecule or acetate anion resulted in solvent- or anion-controlled molecular motions prompting a changing in dendrimer size.⁹⁴

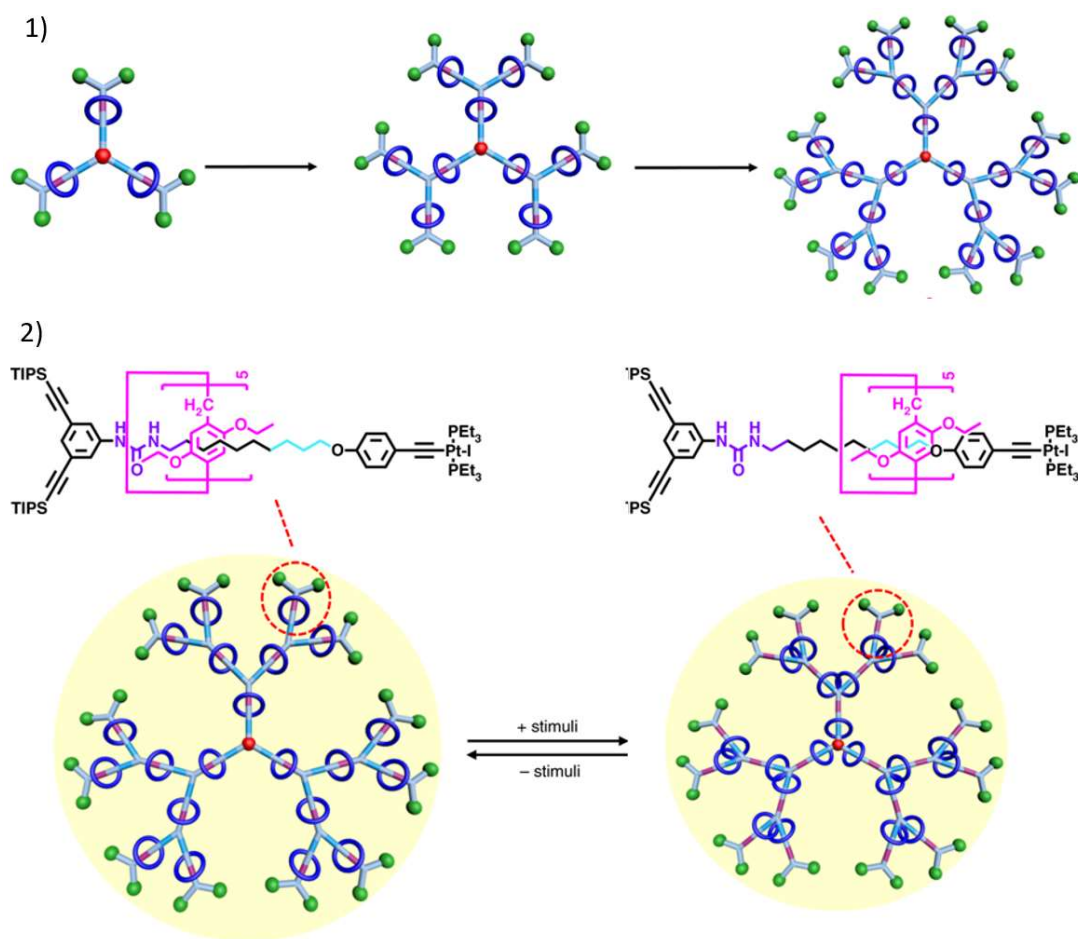


Figure 1.6: Cartoon representation of 1) the synthesis of the first, second and third generation of rotaxane-branched dendrimers and 2) the dimensional modulation of rotaxane-branched dendrimer upon the addition or removal of external stimuli. Adapted from Ref.⁹⁴

1.3. Thesis Outline

This thesis describes the synthesis of [n]rotaxane MIMs, utilising the favourable intermolecular interactions between pillar[5]arenes and imidazoles. The preferential position of the pillar[5]arene relative to the axle and the shuttling behaviour is determined. Furthermore, the effect of mechanically locking together different fluorescent/redox active moieties on the overall properties of a system are examined.

Following an introduction into mechanically interlocked molecules and pillar[n]arenes, Chapter 2 investigates the shuttling behaviour in one and two station molecular shuttles of different length using ^1H NMR spectroscopy and introduces a parameter (shielding factor), which shows the preferential position of the pillar[5]arene along the axle. The effect of coordinating metals (Ag(I) and Pd(II)) on the shuttling and the position of the pillar[5]arene is explored.

Chapter 3 looks at expanding the synthetic scope of pillar[5]arene/imidazole [n]rotaxanes by functionalising the pillar[5]arene, the imidazole and the stopper group component. The interactions between different components are investigated by fluorescence spectroscopy.

Chapter 4 explores a strategy for positioning, and loosely connecting, molecules in close proximity using mechanically interlocked handcuffs. The interactions between loosely connected pairs of redox active molecules are investigated using an array of spectroscopic and electrochemical techniques. The effect of metal (Pd(II)) coordination on these interactions is studied.

Chapter 5 summarises the results described in this thesis and reiterates the key findings as well as outlining their implications for future studies.

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Chapter 2

Pillar[5]arene/Imidazole- Based Molecular Shuttles

2.1. Introduction

2.1.1. Molecular Machines

The broad umbrella of molecular machines and motors includes both natural and synthetic molecules that convert chemical energy into mechanical force or motion. Renowned molecular motors in nature include the protein kinesin and enzymes DNA polymerase and ATP synthase. State of the art systems such as these have demonstrated the potential reward at stake for closing the gap between synthetic chemistry and the mechanical function of machines.¹ The quest to control and exploit molecular level motion began in the 1970s and rapidly expanded in the 1990s, making it the significant field it currently is. Today, research in this area focuses, in particular, on controlling the conformational and configurational changes of mechanical components and how their properties can be affected to perform complex tasks. Molecular mechanical motion has been shown to occur as a result of an external stimuli such as heat, solvent polarity, electrochemistry, cation or anion binding, light, pH and temperature.

Recently reported sophisticated molecular machines include a sequence-specific peptide synthesiser designed and built by Leigh and co-workers.² This complex, rotaxane-based system is able to “pick up” phenolic ester groups sequentially with a catalytic arm tethered to a macrocycle. The activated amino acid is then transferred to the end of a growing chain and the process is repeated. Using a different approach, Stoddart and co-workers built an artificial molecular pump which creates a local concentration gradient. Positively charged rings are pumped from solution and are kinetically trapped onto an oligomethylene chain. The ensnaring mechanism works based on a redox-active viologen which attracts and then repels rings during redox cycles.³

2.1.2. Molecular Shuttles

The nature of the mechanical bond allows for free but selective movement of the components relative to each other. For example, in a rotaxane the macrocycle is limited to orthogonal

movement along the axle. This leads to shuttling oscillation driven by random Brownian motion. The templating synthesis method (discussed in Section 1.2.1) often leaves behind moieties along the axle, which interact with the macrocycle. These recognition motives are commonly referred to as “stations” and their interaction with the macrocycle can be altered by external stimuli such as solvent,⁴ pH⁵ and anion binding.⁶ The rate of shuttling heavily depends on the strength of macrocycle-station interaction and the distance between the stations. Further macrocycle-axle interactions can also have an effect on the shuttling rate, for example moieties in between the two stations which repel the macrocycle (known as “speed bumps”). Molecular shuttles can be broadly put into three categories; firstly single binding site shuttles with only one station; secondly degenerate shuttles, with two equivalent stations (Figure 2.1) and finally multiple binding site shuttles with two or more inequivalent stations.

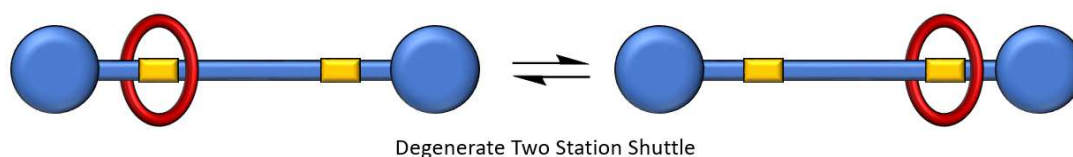


Figure 2.1: Cartoon representation of a [2]rotaxane molecular shuttle with two degenerate stations.

2.1.2.1. Single Binding Site Molecular Shuttles

In molecular shuttles with a single station there is no competition between stations to interact with the macrocycle and therefore shuttling is generally limited. In these systems, macrocycle movement away from the station can be induced by breaking the favourable station-macrocycle interactions. This has been achieved using a light-induced redox process⁷ such as isomerisation of an azobenzene station.⁸ Alternatively, when the macrocycle-station interaction is dominated by hydrogen bonding, the position and motion of the macrocycle is highly dependent on the solvent. In these cases shuttling can be induced by competitive, hydrogen bonding solvents.⁹

2.1.2.2. Degenerate Molecular Shuttles

The first degenerate molecular shuttle was reported by Stoddart and co-workers (Figure 2.2-1), who observed and followed the temperature dependent shuttling of a cyclophane macrocycle between two hydroquinol stations by NMR spectroscopy.¹⁰ In degenerate two station shuttles, the interaction between macrocycle and station must be broken during the shuttling cycle. This can be visualised in a basic energy diagram. The energy barrier between the two stations is proportional to the shuttling rate as shown in Figure 2.2-2. The shuttling rate can be manipulated by adding polar solvents^{4, 11} or by introducing/modifying a central “speed bump” moiety along the axle (in between the two stations).¹² Furthermore, the shuttling rate has been controlled by oxidation/reduction of hydrogen-bonding stations¹³ and photochemical ring contraction of a dianthrylethane-based macrocycle.¹⁴ Recently, a two station molecular shuttle has been reported by Berna and co-workers in which shuttling of the macrocycle was restricted through addition of external complementary hydrogen bonding molecules to both stations. Free shuttling was restored through the addition of a more competitive additive and subsequent competitive recognition event (Figure 2.3).¹⁵

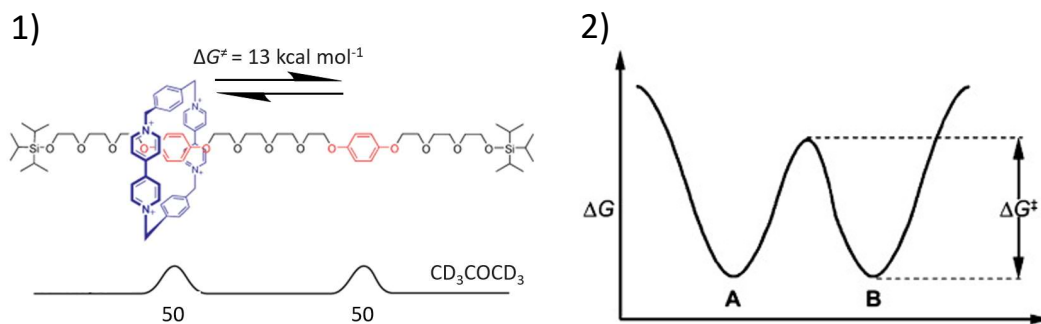


Figure 2.2: 1) The first molecular shuttle reported by Stoddart and co-workers showing degenerate shuttling by ^1H NMR spectroscopy. 2) General free energy profile of shuttling between two identical stations (A and B). The energy barrier ($\Delta G^\ddagger$) depends on the energy required to break the interactions holding the macrocycle at one station and a distance-dependent diffusional component. Adapted from Ref.^{1, 10}

The question of whether the distance between two stations has an effect on the rate of shuttling is an area of debate. Leigh and co-workers reported that in a peptide-based, two station molecular shuttle an increase in alkyl spacer length between the stations resulted in an additional shuttling energy barrier of ca. 5 kJmol^{-1} .¹⁶ However, a number of different systems with rigid linker units have been reported in which no correlation between spacer lengths and shuttling rate was observed.¹⁷ A possible explanation for this discrepancy came from Brouwer and Günbaşı who proposed that shuttling was facilitated by hydrogen bonding between the macrocycle and the station that it currently does not occupy. Therefore, as the linker length is increased, the dual binding conformation becomes increasingly less entropically favourable.¹⁸

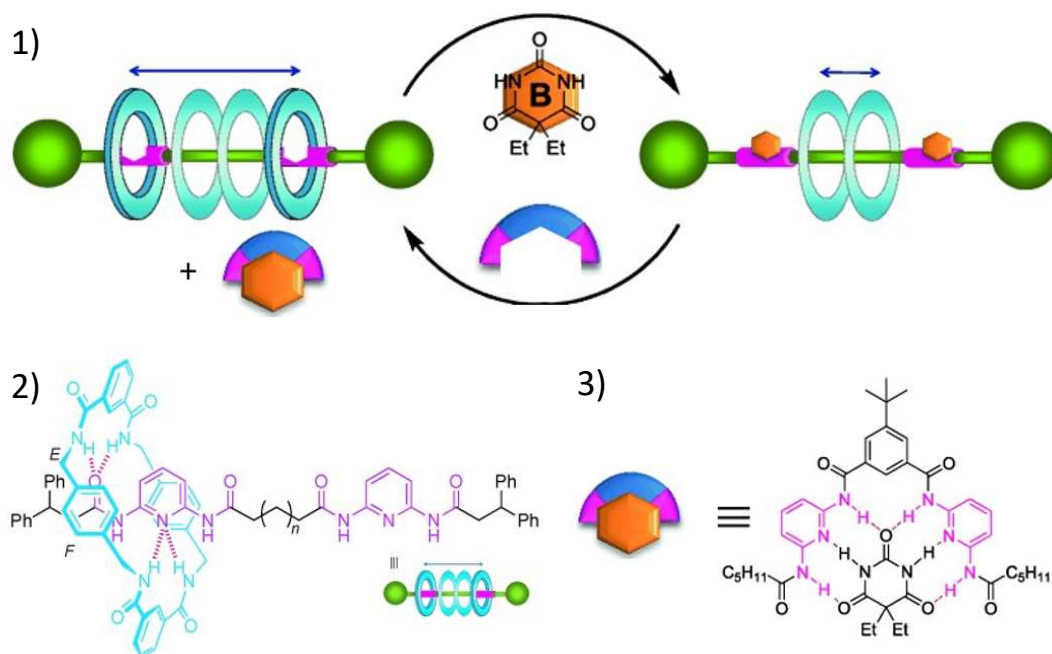


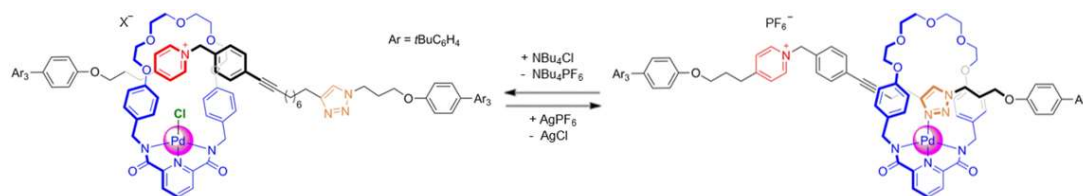
Figure 2.3: 1) Shows the reversible restriction of shuttling between two stations through the formation of a stronger acceptor-donor-acceptor to donor-acceptor-donor array. 2) Shows the structure of two station *bis*-(di(acylamino)pyridine) [2]rotaxane. 3) Structure of competitive acceptor-donor-acceptor to donor-acceptor-donor array which reverses shuttling restriction. Adapted from Ref.¹⁵

2.1.2.3. Multiple Binding Site Molecular Shuttle

In molecular shuttles with two different stations, at any given temperature, the macrocycle distribution over the different stations depends on the strength of station-macrocycle interaction. Upon disrupting this communication the macrocycle re-equilibrates and shifts its position. This change is driven by thermal motion and can be triggered by decreasing the binding energy of the occupied station or increasing the binding energy of the unoccupied station. In addition, shuttling can be altered by stimuli responsive modifications to the macrocycle.

Stimuli responsive molecular shuttles with driving forces such as light,¹⁹ redox-processes,²⁰ pH,⁵ cation/anion²¹ and reversible covalent bond formation²² have been reported. Furthermore, metal coordination has been used to prompt a change in macrocycle position as demonstrated by Leigh and co-workers, who reported a [2]rotaxane with a triazole and a pyridinium station in which palladium coordinated to both the macrocycle and the triazole station (Scheme 2.1). Upon the

addition of tetra-butylammonium chloride the triazole was replaced by a chloride and the crown ether moieties on the macrocycle coordinated to the pyridinium station. This process could be readily reversed by the addition of silver hexafluorophosphate which reacted with the chlorides forming silver chloride.⁶



Scheme 2.1: Palladium-based, chloride-switchable molecular shuttle. Adapted from Ref.^{1, 6}

2.1.3. Pillar[5]arene-based Molecular Shuttles

The first pillar[5]arene-based molecular shuttle was reported by Huang and co-workers in 2013. They took advantage of the strong interactions between pillar[5]arene and a semi-blocked rod containing an imidazolium motive. This [2]pseudorotaxane was reacted with a bulky stopper group to provide a [2]rotaxane with a single imidazolium station in a yield of 92 % (Figure 2.4-3). ¹H NMR and 2-D NMR spectroscopy showed that the pillar[5]arene was located around the imidazolium moiety in non-polar solvents such as chloroform. In more polar solvents however, the pillar[5]arene moved away from the imidazolium. Similarly, the shuttling could be adjusted by varying the temperature in DMSO. These [2]rotaxanes self-assembled to form supramolecular gels which showed similar multiple stimuli-responsiveness.²³

In 2014 Ogoshi and co-workers reported a pillar[5]arene-based [2]rotaxane, the synthesis of which included multiple copper(I)-catalyzed Huisgen alkyne–azide 1,3-dipolar cycloaddition reactions. This afforded a [2]rotaxane with an axle including two triazole stations of equal energy, between which continuous shuttling of the pillar[5]arene was observed.²⁴ A similar pillar[5]arene-based [2]rotaxane with two triazole stations has been described as part of a biologically active heteroglycocluster scaffold. In this case the authors did not comment on the position on the

pillar[5]arene along the rod, nevertheless shuttling in this system is very likely.²⁵ In a recent study, Ogoshi and Brouwer reported a series of neutral, pillar[5]arene-based [2]rotaxanes with two degenerate stations separated by flexible linkers of different length (Figure 2.4-1). The free energies of activation for the shuttling between the two stations were calculated and the shutting rates were found to be independent of spacer length. However, structural modification of the spacer by the introduction of repulsive oxygen atoms increased the shuttling energy barrier.²⁶

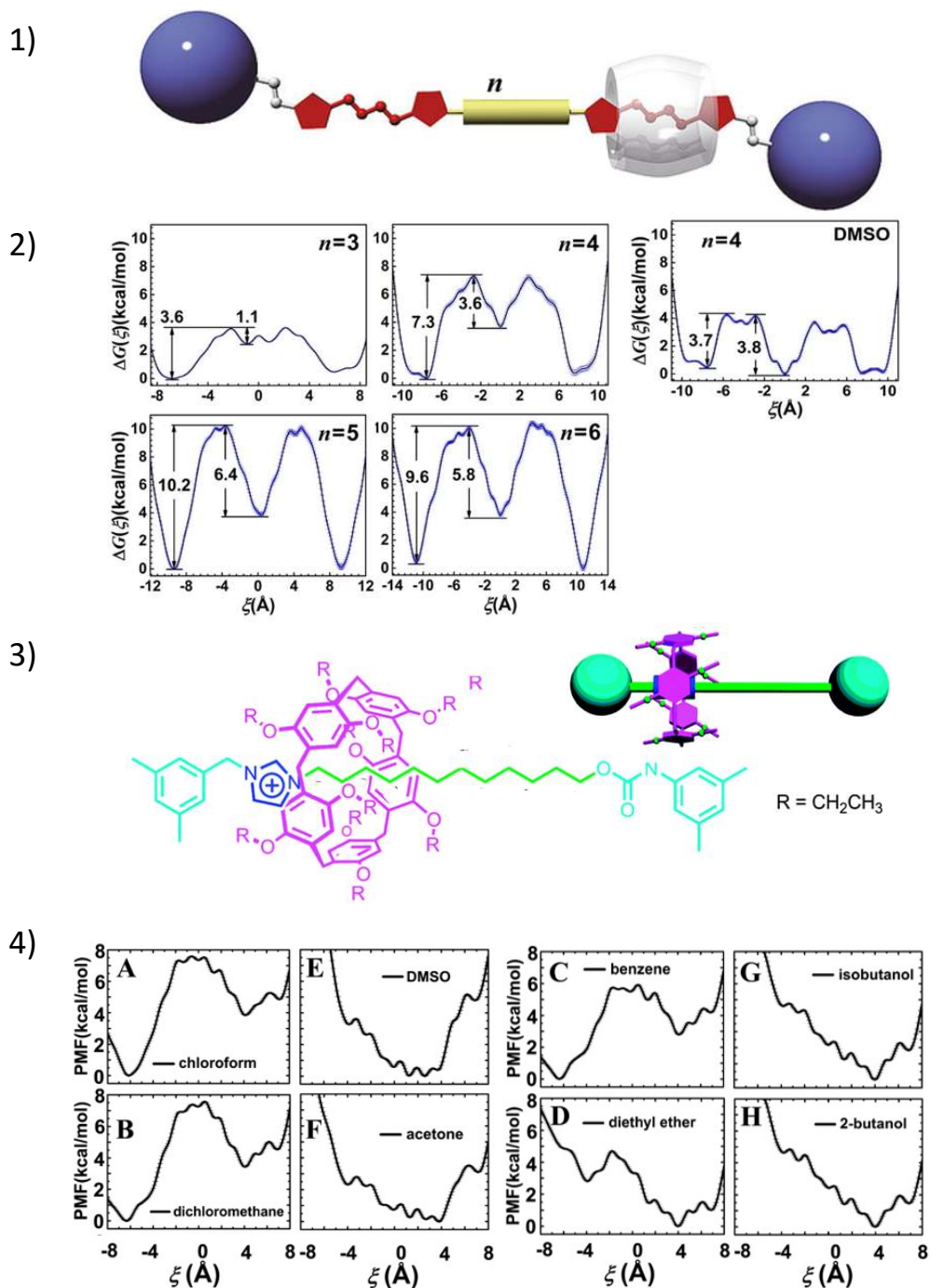


Figure 2.4: 1) Cartoon representation of a [2]rotaxane containing two di-triazole stations separated by alkyl linkers of varying length ($n = 4, 8, 12$ and 16).²⁶ 2) Free-energy profiles delineating shuttling in the rotaxane shown in (1) along ξ for $n = 3-6$ in chloroform and for $n=4$ in DMSO; where n is the alkyl linker separation length between the two stations.²⁷ 3) Chemical structure and cartoon representation of a [2]rotaxane containing one imidazolium station.²³ 4) Free energy profiles (potentials of mean force (PMF)) delineating the shuttling process along ξ in: (A) chloroform, (B) dichloromethane, (C) benzene, (D) diethyl ether, (E) DMSO, (F) acetone, (G) isobutanol, and (H) 2-butanol.²⁸

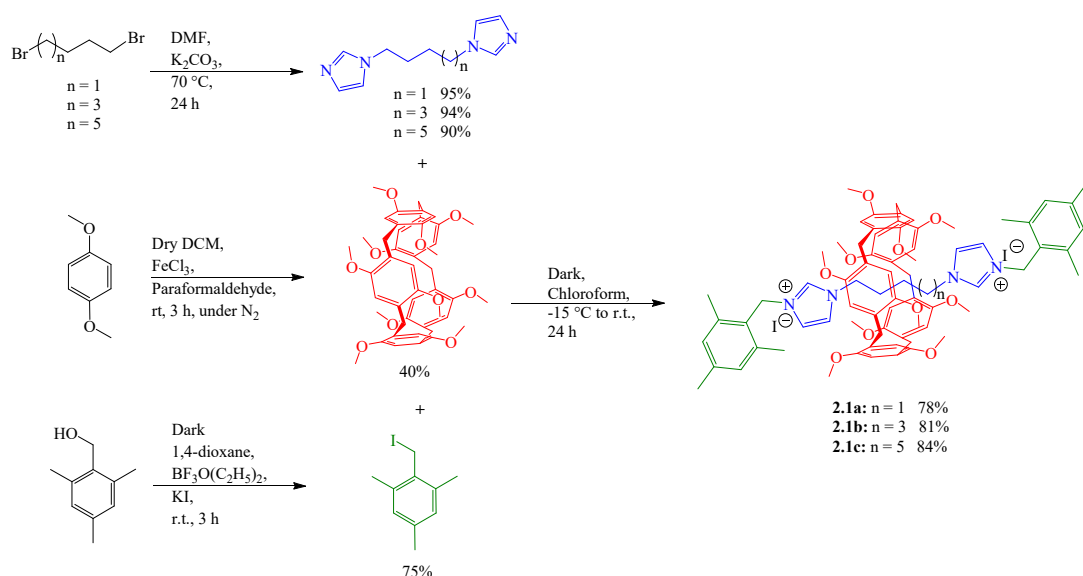
Shuttling in pillar[5]arene-based [n]rotaxanes is generating increasing interest and calculation-based studies have been developed to further understand these systems. Cai and co-workers used free energy calculations to investigate how solvents modulate shuttling in a pillar[5]arene-based [2]rotaxane with a single imidazolium station (Figure 2.4-3/4). The effects of polarity and hydrogen bonding ability of eight different solvents were considered. It was found that in low polarity solvents, pillar[5]arene strongly bound the imidazolium moiety (through hydrogen bonding) and its neighbouring methylene groups (through unusual C-H $\cdots\pi$ interactions).²⁸ On the other hand, in more polar solvents this was not the case and binding was minimal (Figure 2.4-4).

The same group recently reported similar calculations in an effort to model solvent and structural effects on shuttling in a pillar[5]arene-based [2]rotaxane with two degenerate di-triazole stations, separated by 3, 4, 5 and 6 carbon spacers (Figure 2.4-1). The shuttling rate dependence on the spacer length was investigated in chloroform by calculating the free-energy profiles and interestingly, spacer length 5 was found to have the slowest shuttling rate. Further free energy calculations of the [2]rotaxane with spacer length 4 in DMSO showed that the shuttling barrier in DMSO was significantly lower than in chloroform. This can be attributed to DMSO's higher polarity and ability to form hydrogen bonds with the triazole stations.²⁷

2.2. Results and Discussion.

Reported in this chapter is the synthesis of pillar[5]arene-based molecular shuttles with two imidazolium stations. Originating from the rising interest in pillar[5]arene-based molecular shuttles this provides further understanding of the shuttling mechanism and offers an alternative station to the far more common triazole moiety. The developments discussed herein will hopefully serve in the design of pillararene-based molecular machines.

2.2.1. Synthesis of a Series of Two Station Molecular Shuttles



Scheme 2.2: Synthesis of *bis*-imidazole rods (blue), decamethoxypillar[5]arene (**DMP[5]A**) wheel (red) and iodo-stopper group (green), and subsequent reaction of these components at $-15^\circ C$ to form [2]rotaxanes (**2.1a-2.1c**) via threading followed by stoppering.

A series of [2]rotaxanes with two equivalent stations (**2.1a-2.1c**) were synthesised via the capping synthetic approach. This first required the synthesis of three components; the rods, the wheel and the stopper group. Each of these was synthesised in one step from commercially available starting materials. Three *bis*-imidazole rods with different alkyl linker chain lengths (4, 6 and 8) were synthesised from the equivalent di-bromo alkyl compounds. In this procedure the di-bromo alkyl compounds were stirred overnight with imidazole and potassium carbonate in DMF at $80^\circ C$. A thorough aqueous work up afforded the pure products in excellent yields without further

purification. Deca-methoxy-pillar[5]arene (**DMP[5]A**) was synthesised using a Friedel-Crafts condensation polymerisation (discussed in Section 1.1.6.2). Anhydrous iron(III) chloride was used as the catalyst and anhydrous dichloromethane, which is known to act as a cyclisation template, was used as the solvent. To favour the formation of the macrocyclic product over polymers, the reaction was done under high dilution at room temperature and was quenched after three hours. The pure product was obtained as a white solid through multiple silica gel chromatography steps. The yield of this reaction was 40 %, which is not as high as other reported methods however, the reaction could be performed on a large scale giving up to 4.3 grams in one batch. The capping stopper group needs to firstly, contain a functional group to react with the ends of the rod components and secondly, be bulky enough to prevent dethreading. For this purpose, 2-(iodomethyl)-1,3,5-trimethylbenzene was synthesised from the equivalent primary alcohol using boron trifluoride diethyl etherate as a Lewis acid catalyst and potassium iodide as the iodine source.²⁹ The product was unstable in light and therefore both the reaction and the work up were shielded from light where possible. Furthermore, the product was stored in the fridge and subsequent reactions were performed whilst minimising the exposure to light.

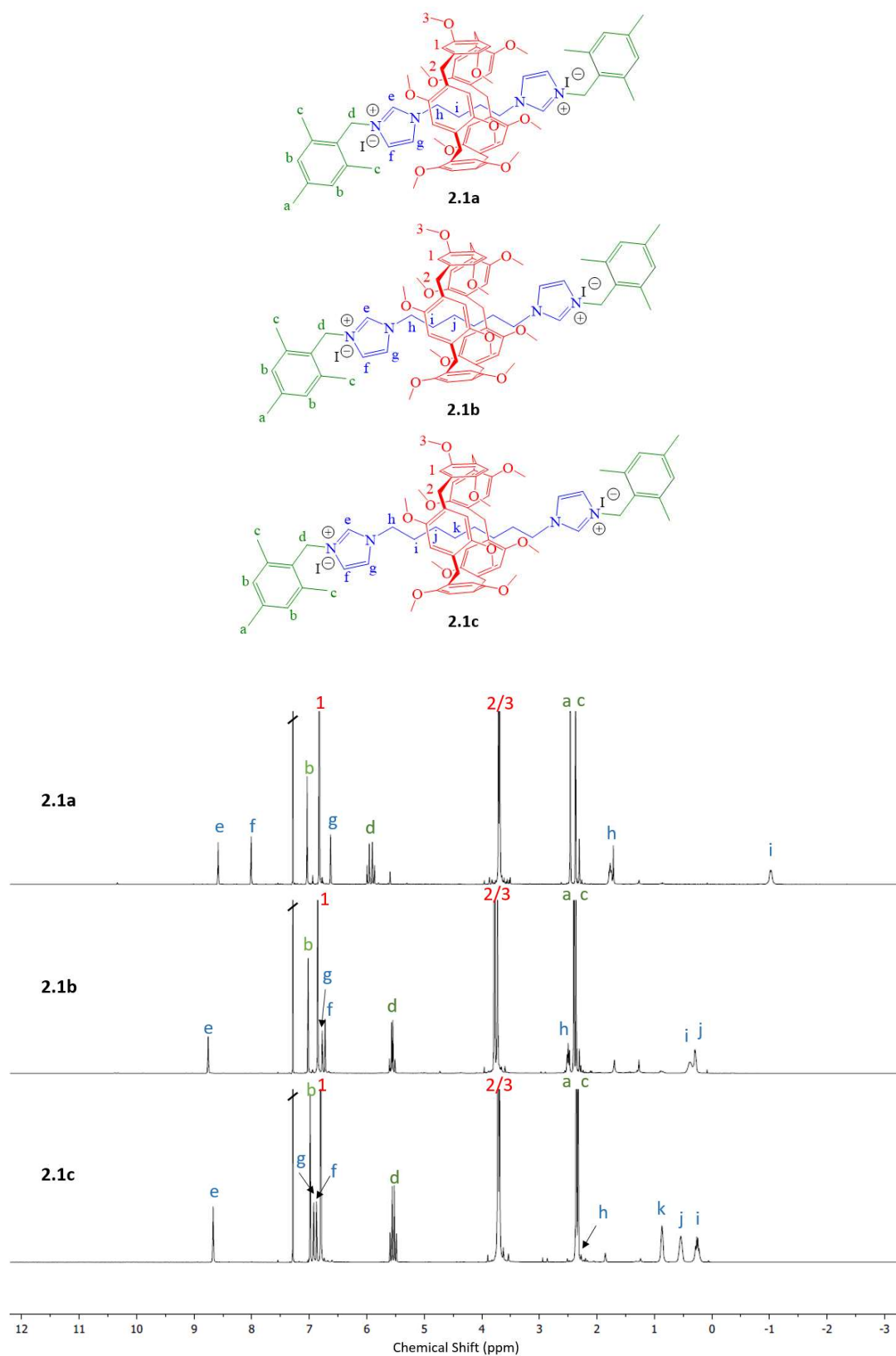
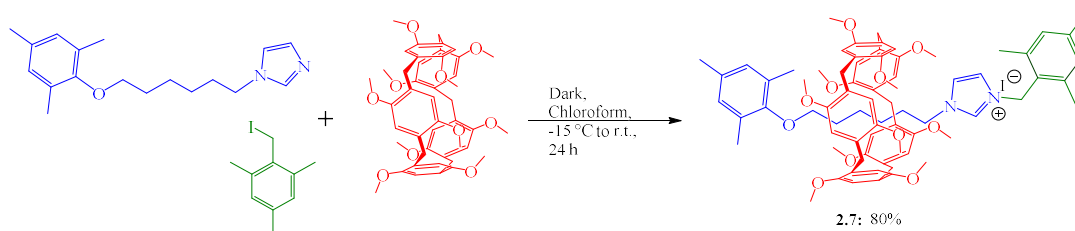


Figure 2.5: ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of [2]rotaxanes **2.1a-2.1c** (in descending order) showing the deshielding effect of **DMP[5]A** on the alkyl environments of the axle.

For the synthesis of [2]rotaxanes **2.1a-2.1c**, *bis*-imidazole rods (blue) and **DMP[5]A** (red) were dissolved in a minimum amount of chloroform and sonicated for 30 minutes. The mixture was then cooled to -15 °C, 2-(iodomethyl)-1,3,5-trimethylbenzene (green) was added and the reaction was left to stir overnight. The yellow solution was purified through silica gel chromatography to give [2]rotaxanes **2.1a-2.1c** in yields as high as 84 %. Characterisation was completed by ^1H , ^{13}C and ^1H - ^1H COSY NMR spectroscopy, high resolution mass spectrometry (HRMS) and single crystal X-ray crystallography. Despite the possibility of dethreading by dynamic nucleophilic substitution in the presence of an iodine counter anion, [2]rotaxanes **2.1a-2.1c** were bench stable.³⁰ Before looking at possible shuttling in these systems, it had to first be confirmed that the imidazolium moieties do in fact act as stations for **DMP[5]A**.

2.2.2. Synthesis of an Asymmetric One Station Shuttle



Scheme 2.3: Synthesis of asymmetric, one station [2]rotaxane **2.7** via the snapping method.

To experimentally establish that the imidazolium is in fact a station for **DMP[5]A**, an asymmetric [2]rotaxane containing only one imidazolium station was synthesised using the snapping method. For this purpose, a rod with a bulky group on one end and imidazole on the other end was synthesised in two steps. Subsequent threading and stoppering afforded [2]rotaxane **2.7** in a yield of 80 % (Scheme 2.3). The reaction was repeated in the absence of **DMP[5]A** to give the analogous unthreaded axle.

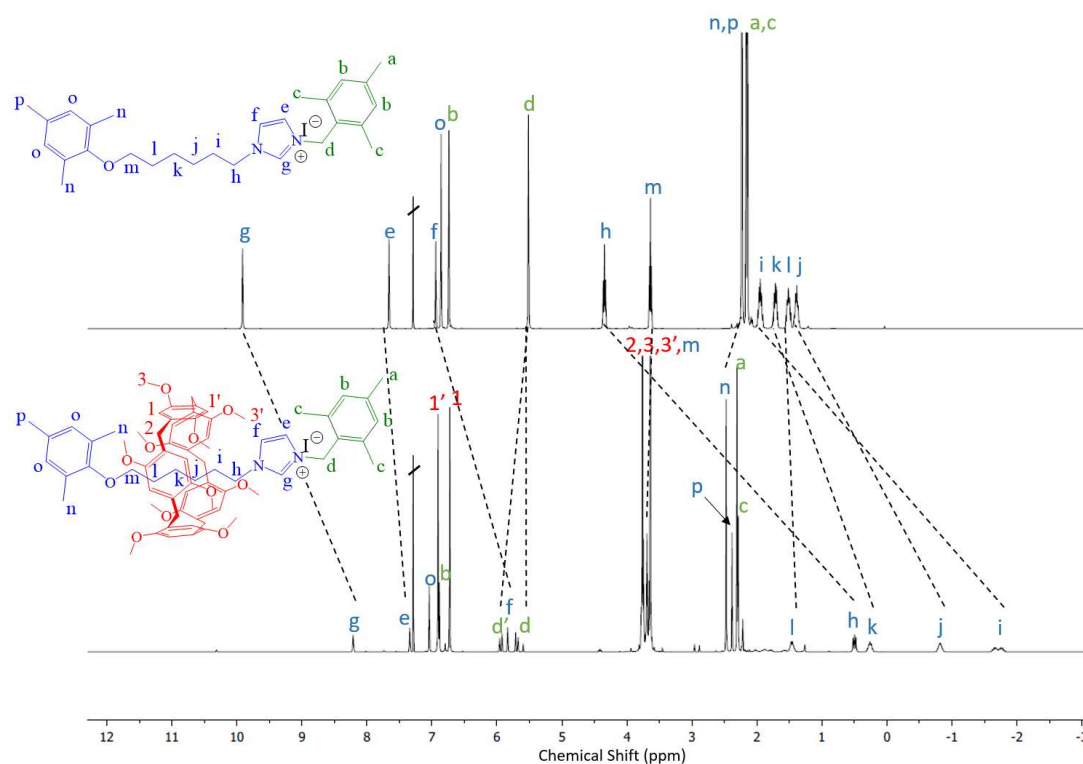


Figure 2.6: ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of [2]rotaxane **2.7** (bottom) and the unthreaded axle (top) showing the shielding effect **DMP[5]A** has on the axle environments $\text{H}_{\text{e-m}}$.

A ^1H NMR spectrum comparison between the threaded and non-threaded molecule is shown in Figure 2.6. The ^1H NMR spectrum shows peaks associated with stopper group (green), **DMP[5]A** (red) and axle (blue) environments. Threading was confirmed through the characteristic shielding effect of **DMP[5]A** on the alkyl environments of the axle. These environments are often shielded to such an extent that their associated ^1H NMR spectrum peaks are shifted upfield to below 1.00 ppm. The shielding effect which **DMP[5]A** has on individual axle proton environments can be analysed by comparing the chemical shifts of threaded and non-threaded axle components using Formula 2.1. A larger relative shielding factor indicates greater interaction of **DMP[5]A** with, and hence residency over, a given proton environment of the axle. The relative shielding factor provides a consistent method of comparison for the position of **DMP[5]A** across the [2]rotaxanes described within this chapter.

$$\text{Shielding} = \text{Unthreaded Axle Chemical Shift (ppm)} - \text{Rotaxane Axle Chemical Shift (ppm)}$$

Formula 2.1: Shielding factor; axle versus rotaxane ^1H NMR spectrum shift comparison.

When the shielding factors are plotted for axle environments $\text{H}_{\text{e-m}}$ in [2]rotaxane **2.7**, a graphical representation of the position of **DMP[5]A** along the axle can be created (Figure 2.7). This shows that proton environments H_{h} and H_{i} , which are adjacent to the imidazolium, are most affected by **DMP[5]A**. Therefore, **DMP[5]A** resides predominantly around these environments on the timescale of the NMR experiment, confirming that the imidazolium moiety acts as a station for **DMP[5]A**. The imidazolium environments $\text{H}_{\text{e-g}}$ are not affected by **DMP[5]A** to the same extent because the close proximity of the sterically bulky stopper group prevents **DMP[5]A** from fully encompassing the imidazolium.

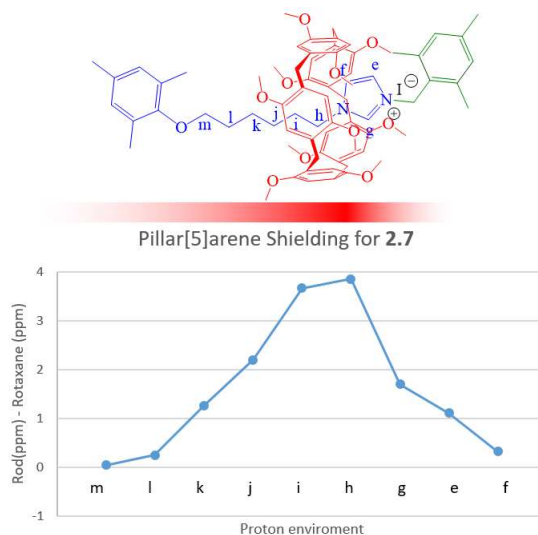


Figure 2.7: Calculated shielding factors (Formula 2.1) for [2]rotaxane **2.7** indicating the favoured residency of **DMP[5]A** along the axle in chloroform to be at $\text{H}_{\text{h-i}}$.

2.2.3. Shuttling in [2]Rotaxanes **2.1a-2.1c**

Having established that the imidazolium component acts as a station for **DMP[5]A** in [2]rotaxane **2.7**, the behaviour of **DMP[5]A** in [2]rotaxanes **2.1a-2.1c** was evaluated. The ^1H NMR spectra of [2]rotaxanes **2.1a-2.1c** showed a high degree of symmetry along the length of the axle which

indicates that **DMP[5]A** is either positioned in the centre of the alkyl chain or is shuttling along it faster than the timescale of the NMR experiment. Further analysis of the ^1H NMR spectra suggests the latter is the case as the signal observed for H_d exhibits an AB pattern. These methylene group protons, which link the imidazolium to the stopper group (H_d/H_d'), are diastereotopic and non-equivalent due to the chirality of **DMP[5]A**. This chirality transfer indicates that **DMP[5]A** is positioned in close proximity to these methylene protons despite a relatively small upfield shift in their ^1H NMR spectrum peak position. This shows that the **DMP[5]A** shuttles along the full length of the axle. This is further supported by ^1H - ^1H NOESY NMR spectroscopy of the longest axle [2]rotaxane **2.1c** (Figure 2.8) which confirms coupling between **DMP[5]A** (red) and axle (blue) protons (highlighted in red). These results confirm that [2]rotaxane **2.1c** is a two station molecular shuttle. The shuttling in [2]rotaxanes **2.1a-2.1c** was visualised using shielding factors (Formula 2.1). Furthermore, the effect of solvent polarity and change in anion on the shuttling behaviour of [2]rotaxane **2.1c** was investigated by ^1H NMR spectroscopy whilst variable temperature ^1H NMR spectroscopy was used to probe the effect of temperature on the shuttling.

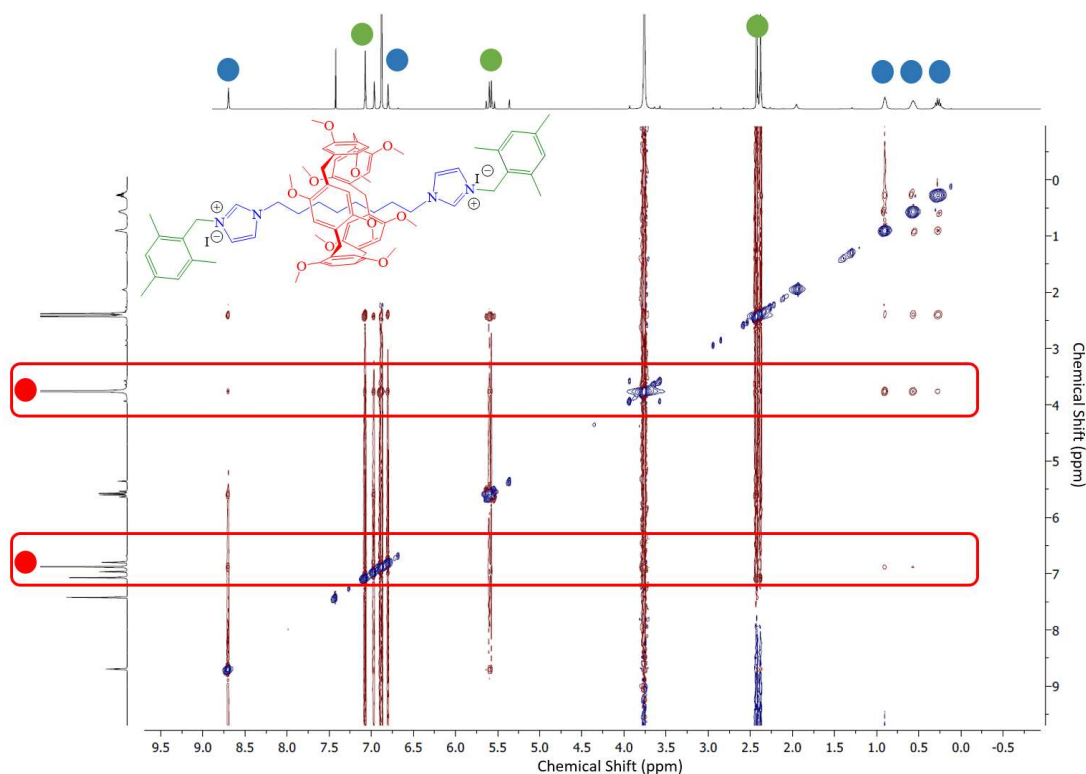
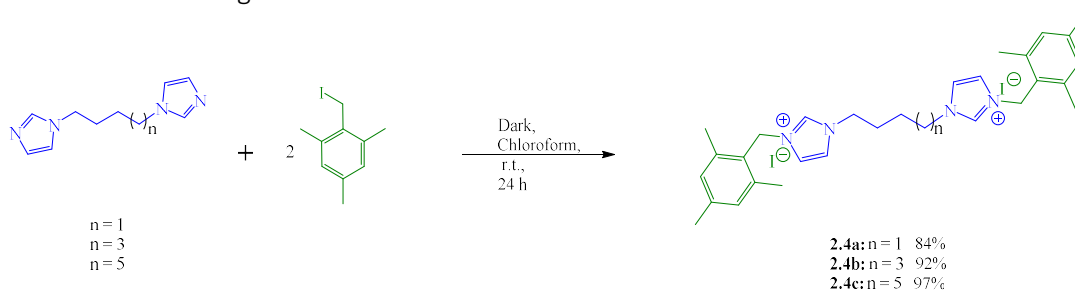


Figure 2.8: ^1H - ^1H NOESY (400 MHz, CDCl_3 , 298 K) spectrum of [2]rotaxane **2.1c**. Showing **DMP[5]A** environments highlighted in red coupling to axle protons shown in blue and green.

2.2.3.1. Shielding Factor



Scheme 2.4: Corresponding unthreaded *bis*-NHC rods, **2.4a-2.4c**, were synthesised using an analogous method to the one employed in the synthesis of [2]rotaxanes **2.1a-2.1c**.

In order to evaluate the shielding effect of [2]rotaxanes **2.1a-2.1c**, the corresponding *bis*-imidazolium rods (**2.4a-2.1c**) were prepared using an analogous procedure to the synthesis of [2]rotaxanes **2.1a-2.1c** (Scheme 2.4). The shielding factors of [2]rotaxanes **2.1a-2.1c** were calculated using Formula 2.1. The resulting plots, shown in Figure 2.9, contain a mirror plane which reflects their symmetrical nature. In [2]rotaxanes **2.1b** and **2.1c** the alkyl linker protons adjacent

to the imidazolium units, H_h and H_i , experience greater shielding from **DMP[5]A** than the more central protons, H_j and H_k . The butyl linker in [2]rotaxane **2.1a** on the other hand, is short enough that **DMP[5]A** provides effective shielding of all spacer protons. This confirms that two imidazoliums, separated by a butyl linker can be considered a single station, as previously reported and discussed in Section 2.1.3. Although no direct comparison between the plots in Figure 2.9-1 and free energy profiles of shuttling between two degenerate stations can be made, there is a considerable similarity between them. This is demonstrated by molecular dynamics simulations of a pillar[5]arene-based two station molecular shuttle described by Ogoshi, Brouwer and co-workers²⁶ (Figure 2.9-2/3), which displays a remarkable resemblance to the plots in Figure 2.9-1. This suggests that the shielding factor approach could be used to model the free energy profiles of conformational and configurational changes of mechanical components in MIMs.

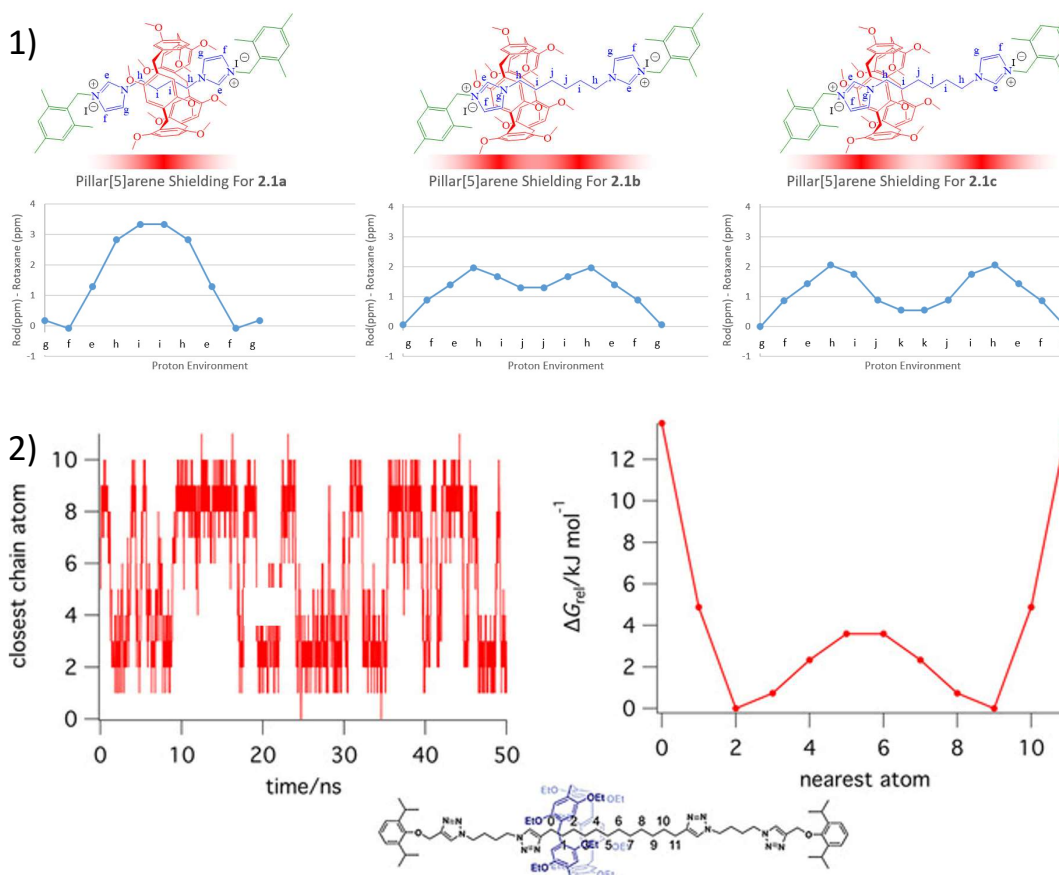


Figure 2.9: 1) Calculated shielding factors (Formula 2.1) for [2]rotaxanes **2.1a-2.1c**, indicating the favoured residency of **DMP[5]A** along the axle in chloroform. 2) Molecular dynamics simulations of Ogoshi and Brouwer's pillar[5]arene-based two station molecular shuttle (bottom); position of the pillar[5]arene on the axle as a function of time in a 50 ns run and 3) average free energy versus position over three 50 ns runs.²⁶

2.2.3.2. Variable Temperature ^1H NMR Spectroscopy

The shuttling in the [2]rotaxane with the longest alkyl linker, **2.1c**, was further investigated by variable temperature ^1H NMR spectroscopy. Over a temperatures range of 293 K – 193K no variation in the chemical shifts and only a small broadening of individual peaks was observed (Figure 2.10). This indicates that shuttling is faster than the timescale of the NMR experiment, even at low temperatures. An explanation for this rapid shuttling is that the alkyl linker provides no steric or electronic hindrance for the macrocycle, which is analogous with recent results published by Ogoshi and Brouwer discussed above.²⁶

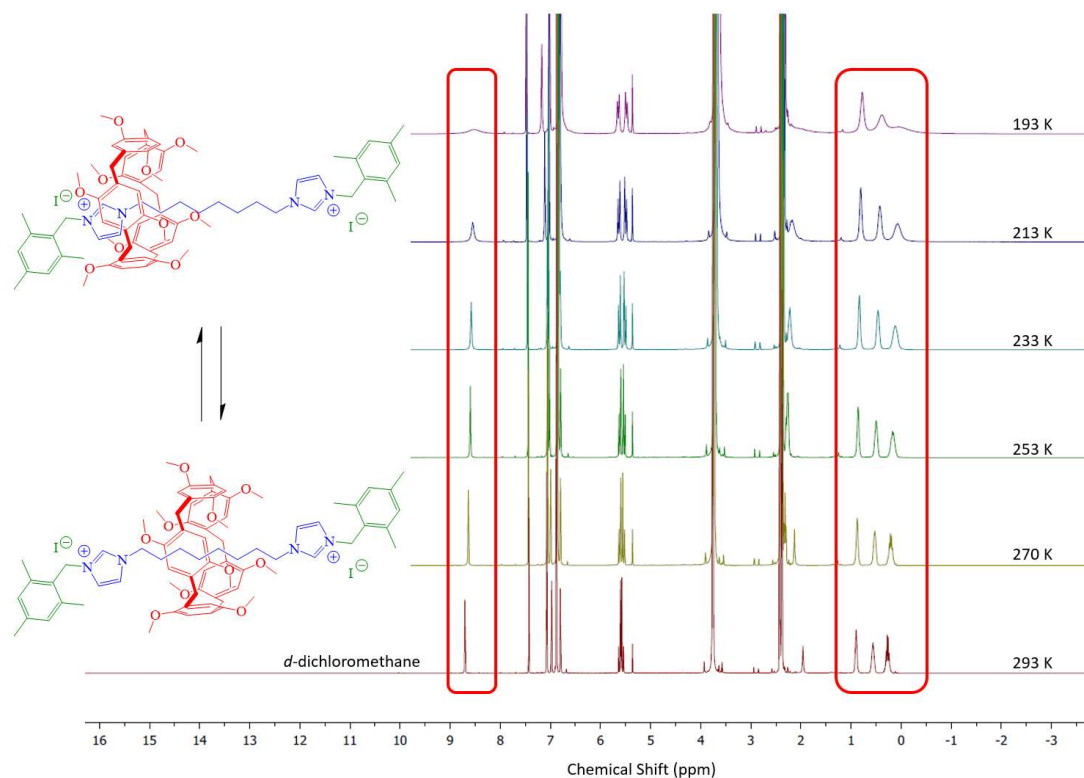


Figure 2.10: ^1H NMR (400 MHz, CD_2Cl_2 , VT) spectra of the [2]rotaxane **2.1c**. Showing no change in peak positions therefore indicating that shuttling of **DMP[5]A** is faster than the timescale of the NMR experiment, even at low temperature.

2.2.3.3. Solvent Effects

Previous work in the area of pillar[5]arene-based molecular shuttles, outlined in Section 2.1.3, shows the strong dependence of shuttling on the solvent. The shuttling motion in [2]rotaxane **2.1c** was investigated by ^1H NMR spectroscopy in chloroform, acetone and DMSO (Figure 2.11). In chloroform the axle termini are significantly more shielded whereas the central alkyl chain is less affected by **DMP[5]A**. Significantly different shifts are observed in DMSO, greater shielding is observed for the central alkyl chain whilst the termini experienced a reduced effect of **DMP[5]A** (Figure 2.11). This suggests that the cationic imidazolium groups interact with the polar DMSO solvent and are therefore more exposed which narrows the range of macrocycle shuttling. In acetone, the shuttling is in-between chloroform and DMSO as is its polarity (Figure 2.11). It was

not possible to investigate a greater range of solvents due to poor solubility of [2]rotaxanes **2.1a**-**2.1c** in less polar solvents.

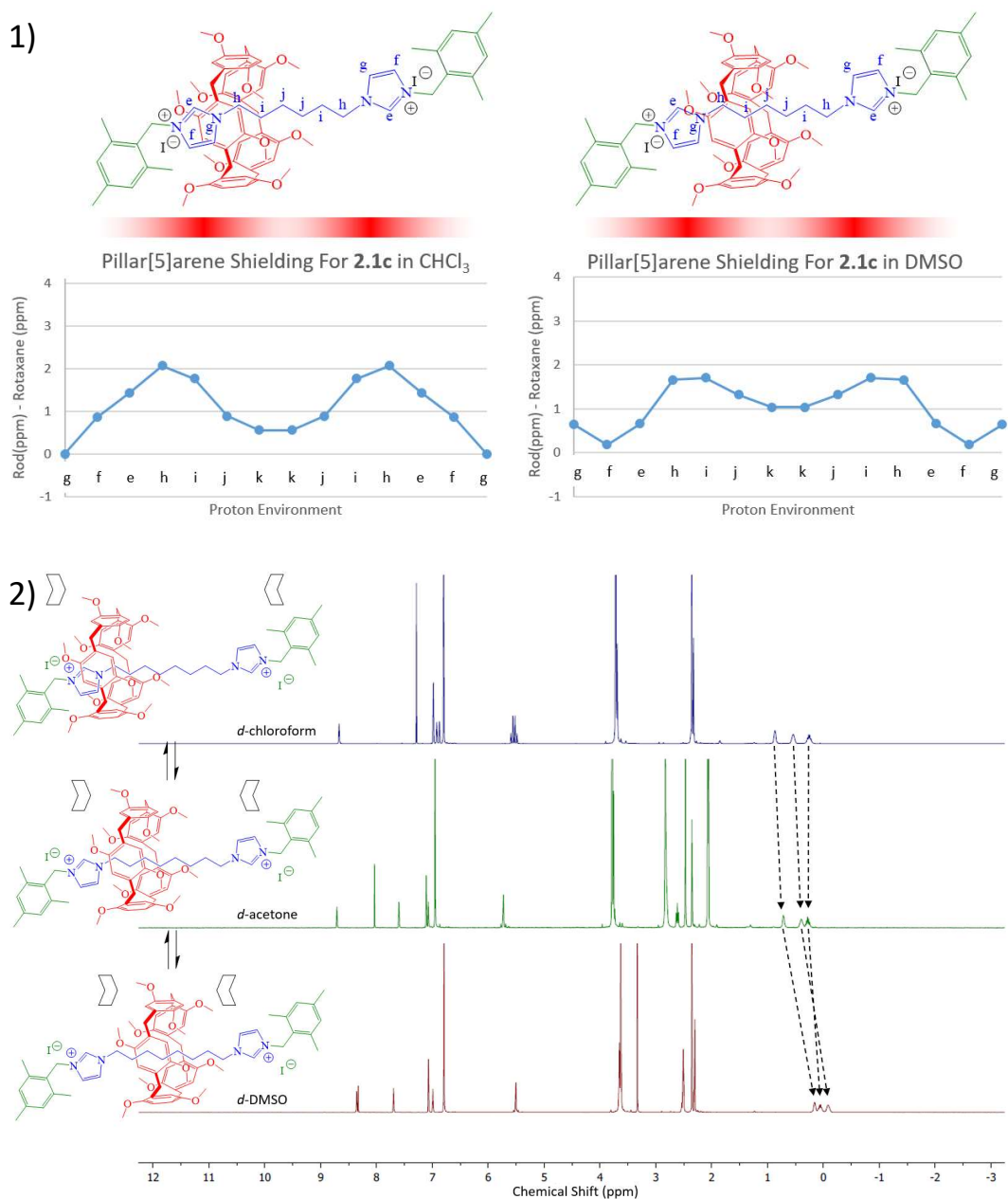


Figure 2.11: 1) Calculated shielding factors (Formula 2.1) for [2]rotaxane **2.1c**, indicating the favoured residency of **DMP[5]A** on the axle in chloroform and DMSO. 2) ^1H NMR spectra (400 MHz, 298 K) of [2]rotaxane **2.1c** in *d*-chloroform (top), *d*-acetone (middle) and *d*-DMSO (bottom) showing a narrowing in shuttling width with an increase in solvent polarity.

2.2.3.4. Anion Exchange

The influence of the counter anion on the shuttling was investigated by exchanging iodide for hexafluorophosphate. Anion exchange was carried out by heating [2]rotaxane **2.1c** and ammonium hexafluorophosphate salt in ethanol to reflux for 4 hours before filtering under reduced pressure to obtain the product. Successful anion exchange was confirmed by ^{19}F and ^{31}P NMR spectroscopy which showed typical spectral profiles for an imidazolium hexafluorophosphate moiety. ^1H NMR spectroscopy in chloroform revealed some subtle changes in the peak positions, in particular in the most downfield imidazolium proton environment, H_e . However, in contrast to the effects observed for solvent polarity, these changes to the shielding effects are negligible (Figure 2.12). This was even more pronounced in DMSO, where a comparison of the ^1H NMR spectra, showed no changes in the peak positions.

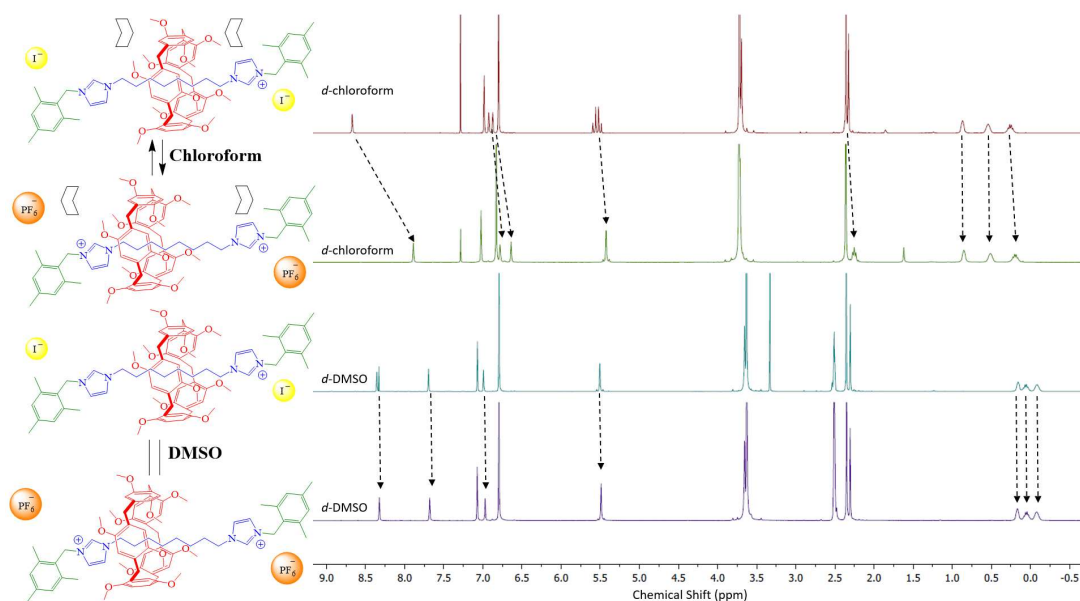
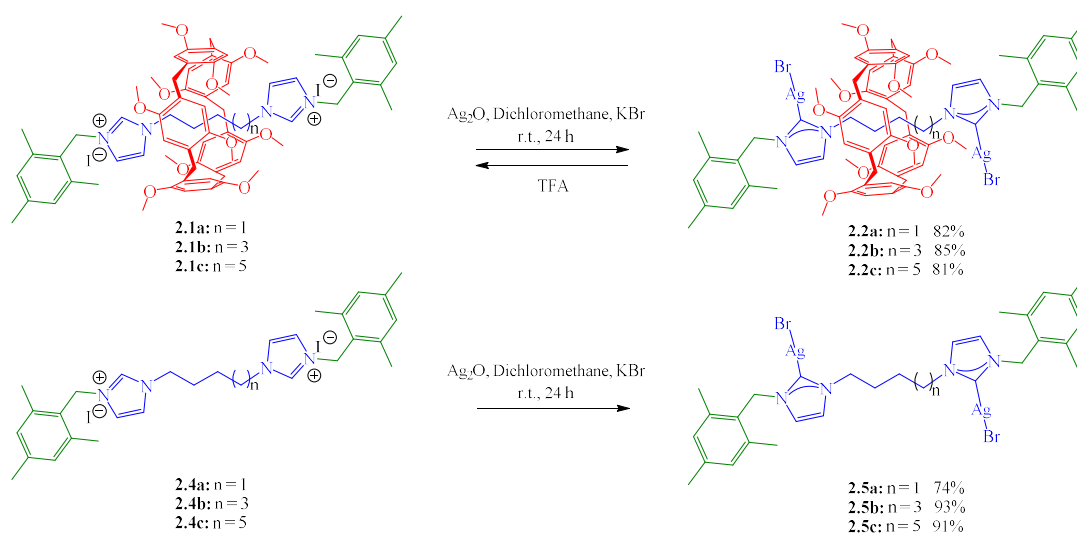


Figure 2.12: Schematic illustration showing the ^1H NMR spectra (400 MHz, 298 K) shifts in [2]rotaxane **2.1c** upon anion exchange with ammonium hexafluorophosphate in *d*-chloroform and *d*-DMSO.

2.2.4. Confinement: Ag(I)-Coordination

It was anticipated that metal coordination to the imidazolium rings, acting as N-heterocyclic carbenes (NHCs), would prevent the free shuttling of **DMP[5]A** along the entirety of the axle and instead confine it to a central position. Thus, a series of metal coordinated [2]rotaxanes were prepared by coordination of Ag(I) and Pd(II) to the imidazolium salts **2.1a-2.1c**, forming NHC complexes.

2.2.4.1. Synthesis



Scheme 2.5: Ag(I)-coordination to the imidazolium salts of [2]rotaxanes **2.1a-2.1c** as N-heterocyclic carbenes leads to restriction of **DMP[5]A** shuttling. Ag(I)-coordination can be readily achieved at room temperature and is reversible following addition of acid (TFA). Corresponding Ag(I) complexes of unthreaded *bis*-NHC rods, **2.5a-2.5c**, were synthesised using an analogous method from **2.4a-2.4c**.

The coordination of Ag(I) to imidazolium salts, as NHCs, is well established³¹ and silver NHCs have recently raised attention as potent antibacterial agents and chemotherapeutics.³² Ag-NHC coordination occurs at room temperature in dichloromethane and does not require additional reagents (such as additional bases). Thus, one equivalent of di-imidazolium salt [2]rotaxane, **2.1a-2.1c**, was reacted at room temperature with one equivalent of Ag₂O in the presence of potassium bromide (Scheme 2.5). Halide scrambling is possible in these systems so an excess of potassium bromide was added to ensure the exclusive formation of bromide complexes. Silver complexes

are known to be light sensitive and therefore the reaction was shielded from light. After stirring overnight the reaction mixture was filtered through celite. The crude product was redissolved in a minimum amount of dichloromethane and added dropwise into hexane. Filtration under suction gave Ag(I)-coordinated [2]rotaxanes **2.2a-2.2c** in high yields. Successful Ag(I)-coordination was evident in both NMR spectroscopy and single crystal X-ray crystallographic characterisation.

2.2.4.2. Shuttling Confinement

To determine the extent of shuttling in Ag(I)-coordinated [2]rotaxanes, **2.2a-2.2c**, compared to the nonmetalated [2]rotaxanes, **2.1a-2.2c**, ¹H NMR spectroscopy was employed to track the position of **DMP[5]A** with respect to the axle. As anticipated, the spectrum showed significant shifts in ¹H NMR signals (Figure 2.13), especially in signals associated with the central alkyl chain. In order to assess the relative shielding in the same way as for [2]rotaxanes **2.1a-2.1c**, the corresponding Ag(I) complexes of unthreaded *bis*-NHC rods were synthesised, **2.5a-2.5c**. These were readily prepared from **2.4a-2.4c** using an analogous reaction to the one used for the synthesis of **2.2a-2.2c** (Scheme 2.5).

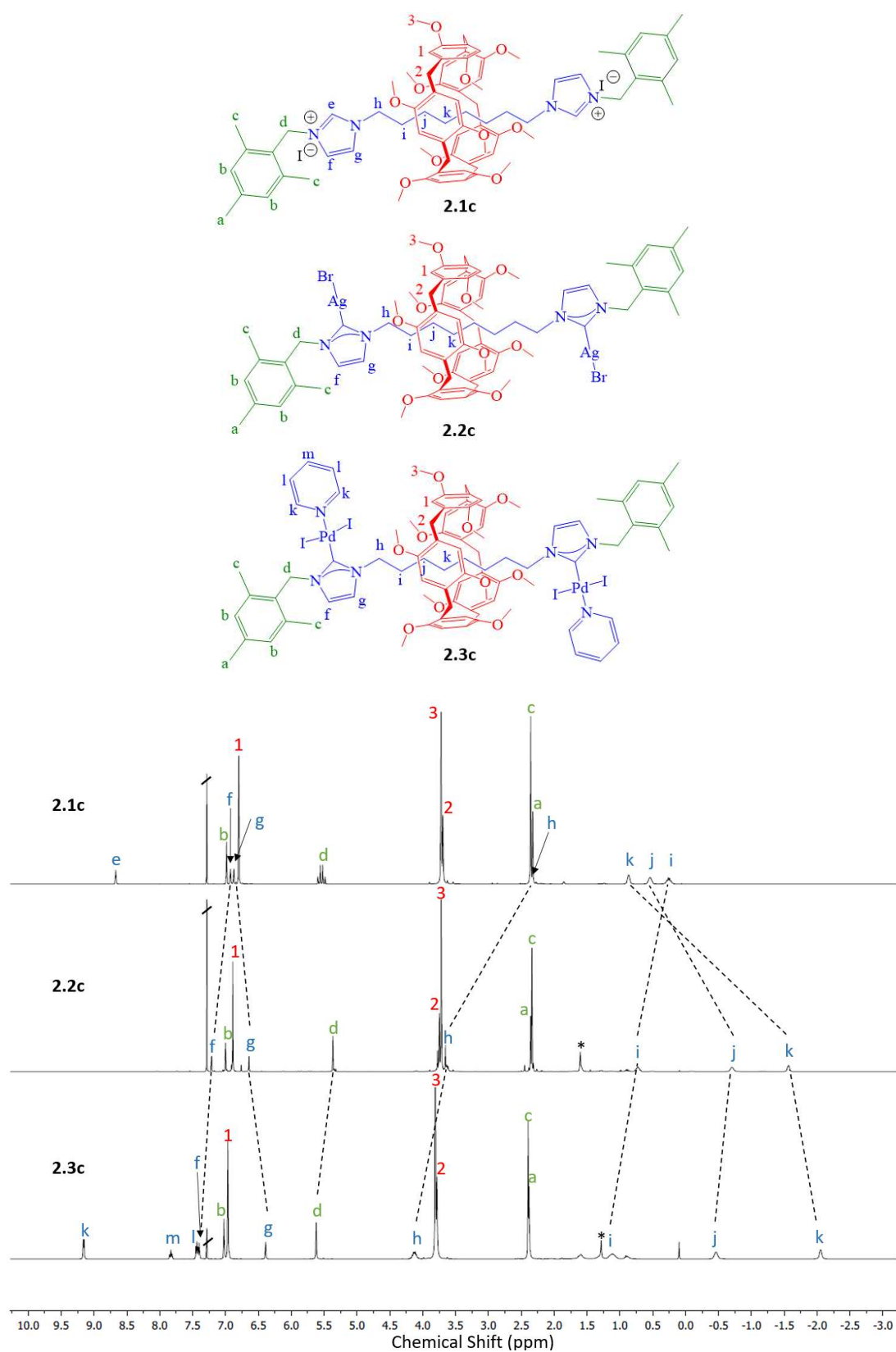


Figure 2.13: ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) showing the NMR shifts of [2]rotaxanes **2.1c** due to confinement of **DMP[5]A** by coordination of **Ag(I)** **2.2c** and **Pd(II)** **2.3c**.

When calculating the shielding effects in Ag(I)-coordinated [2]rotaxanes **2.2a-2.2c** (Figure 2.14), the central alkyl protons showed a significantly greater shift than the protons adjacent to the NHCs. The proton environments associated with the NHCs themselves on the other hand, showed only minor shifts despite Ag(I)-coordination to this group. Additionally, methylene bridge protons, H_d , no longer exhibit an AB pattern and is replaced by a sharp singlet. This indicates that **DMP[5]A** is no longer in close proximity to these protons and therefore no chiral information is transferred, unlike in [2]rotaxanes **2.1a-2.1c** where chiral transfer was observed. These results are illustrated by a change in the graph profiles for Ag(I)-coordinated [2]rotaxanes **2.2b-2.2c**, as seen in Figure 2.14. Rather than the bimodal shape exhibited by [2]rotaxanes **2.1b** and **2.1c**, Ag(I)-coordinated [2]rotaxanes **2.2b** and **2.2c** show a bell shaped curve. It is clear from these results that **DMP[5]A**-imidazolium interactions are broken and **DMP[5]A** is no longer able to shuttle along the full length of the axle in Ag(I)-coordinated [2]rotaxanes **2.2a-2.2c**. Ag(I)-coordination, therefore confines **DMP[5]A** to the central alkyl chain component of the rotaxane.

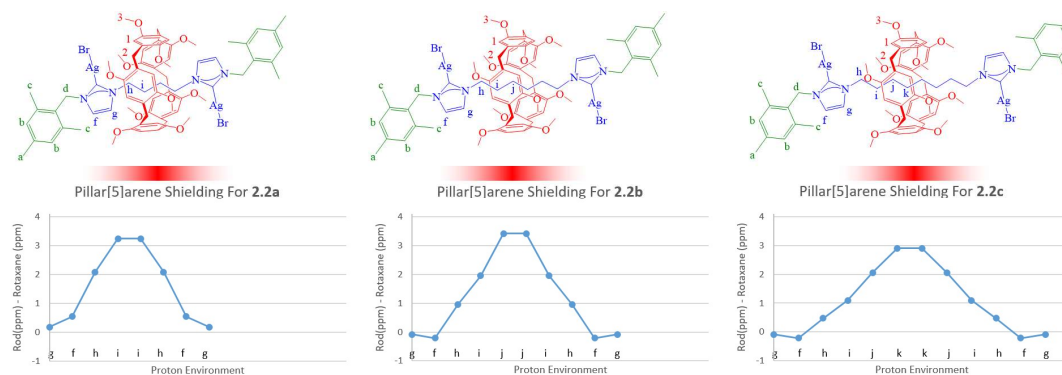


Figure 2.14: Position of the **DMP[5]A** along the axle in Ag(I)-coordinated [2]rotaxanes **2.2a-2.2c** (as calculated by Formula 2.1).

The protons adjacent to the NHCs are affected to a lesser extent than in [2]rotaxanes **2.1a-2.1c**, however enough to show that the **DMP[5]A** still has a degree of lateral mobility. This is due to Brownian motion however, after Ag(I)-coordination the most favourable position **DMP[5]A** can adopt is dominated by steric interactions with the end groups and no longer by electronic

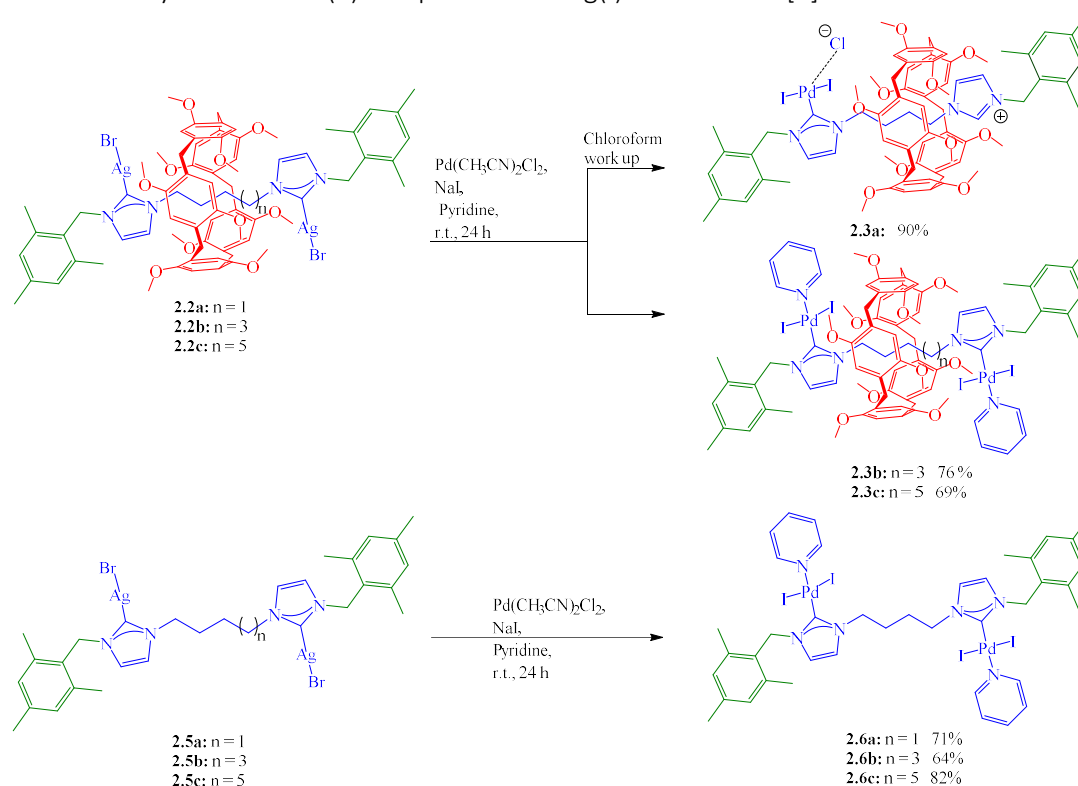
interactions with the axle. When **DMP[5]A** resides around the most central alkyl linker protons it has minimal steric clash with the end groups and hence this position is preferred.

2.2.4.3. Confinement Reversal with TFA

The confinement of **DMP[5]A** by Ag(I)-complexation can be readily reversed using an acid such as trifluoroacetic acid (TFA) shown in Scheme 2.5. Ag(I)-coordinated [2]rotaxanes **2.2a-2.2c** were dissolved in chloroform and TFA was added dropwise. The white precipitate which formed was removed by filtration and the filtrate was reduced to dryness. ^1H NMR spectroscopy showed peaks in conjunction with the original [2]rotaxanes **2.1a-2.1c**. This is evidence that **DMP[5]A** has been released to shuttle freely along the full length of the [2]rotaxane once again.

2.2.5. Confinement 2: Pd(II)-coordination

2.2.5.1. Synthesis of Pd(II) complexes from Ag(I)-coordinated [2]Rotaxanes **2.2a-2.2c**



Scheme 2.6: Pd(II)-coordination (**2.3b**, **2.3c**) is achieved by transmetalation of the corresponding Ag(I) complex resulting in further restriction of **DMP[5]A** shuttling. In [2]rotaxane **2.3a** only a mono-Pd(II) complex is observed due to steric restriction.

Ag(I) NHCs are useful starting materials for further functionalisations.^{31c} This reactivity was utilised in the conversion of Ag(I)-coordinated [2]rotaxanes **2.2a-2.2c** to related Pd(II)-coordinated [2]rotaxanes **2.3a-2.3c** through a reaction at room temperature with Pd(CH₃CN)₂Cl₂, NaI and anhydrous pyridine (Scheme 2.6). The resulting [2]rotaxanes are coordinated to Pd(II) via the NHC while the remaining coordination sites of the Pd(II) are occupied by a pyridine ligand and two iodides. For the Pd(II)-coordinated [2]rotaxanes with longer axle lengths, **2.3b-2.3c**, both the NHCs underwent transmetalation. However, in the case of Pd(II)-coordinated [2]rotaxane **2.3a**, with a shorter axle length, only one of the NHC groups transmetalates with palladium whilst the other is protonated. Although palladium-pyridine-coordination was observed in the ¹H NMR spectrum of the reaction mixture, after work up and purification only the zwitterionic complex **2.3a** could be isolated. In this compound the Pd(II) centre is coordinated to the NHC and two iodides as well as appearing to interact with the chloride anion. Mono-metalation is a result of the shorter linker between the two imidazolium groups, not allowing for two sterically demanding Pd(II) complexes and **DMP[5]A** on the same axle. Indeed, the presence of **DMP[5]A** can be considered to be controlling the reactivity of the axle in [2]rotaxane **2.3a** and is therefore acting as a protecting group for one of the imidazolium moieties.

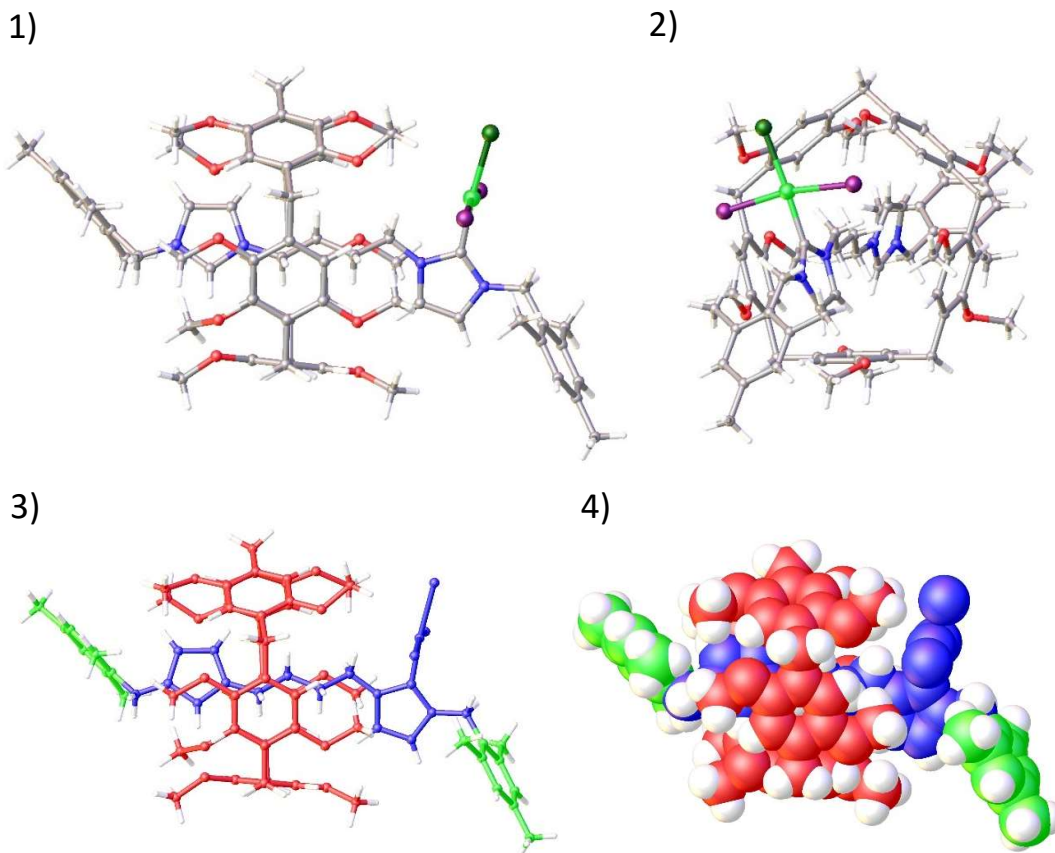


Figure 2.15: Crystal structure of Pd(II)-coordinated [2]rotaxane **2.3a** from the side (1) and down the end (2). Carbon atoms = grey, oxygen atoms = red, nitrogen atoms = blue, iodine atoms = purple and palladium atoms = green. Views of the crystal structures ball-and-stick (3) and spacefilled (4) representations. Blue = imidazolium/NHC rod, red = **DMP[5]A** wheel, and green = mestiyI stopper group.

During the characterisation of Pd(II)-coordinated [2]rotaxane **2.3a**, ^1H NMR spectroscopy revealed complex splitting patterns for signals attributed to the four axle alkyl chain protons, $\text{H}_{\text{h-k}}$ (Figure 2.15-1). Each of these protons was split into two distinct peaks with chemical shifts and coupling constants shown in Table 2.1. Furthermore, the ^1H NMR peaks associated with proton environments adjacent to the NHCs, H_{h} and H_{k} , were each split into a well-defined triplet of doublets. This splitting could be due to restriction in the rotatory motion of **DMP[5]A**, which renders the protons on each of the axle carbons in chemically inequivalent environments. Alternatively, it could be due to the transfer of chirality from **DMP[5]A** to the axle. In either case this unusual splitting is the result of drastic steric restriction in **DMP[5]A** manoeuvrability.

Proton environment	Chemical shift (ppm)	Splitting pattern	1J (Hz)	2J (Hz)
Hh	4.45 3.96	ABdt	240	5
Hi	1.43 1.07	ABm	180	-
Hj	0.72 0.59	ABm	115	-
Hk	-0.37 -0.60	ABdt	65	5

Table 2.1: ^1H NMR spectrum central chain proton environments, $\text{H}_{\text{h-k}}$, of Pd(II)-coordinated [2]rotaxane **2.3a** showing the chemical shifts, splitting patterns and coupling constants.

The splitting seen in the ^1H NMR spectrum of Pd(II)-coordinated [2]rotaxane **2.3a** showed no significant changes over a temperature range of 298 K – 323 K in chloroform. Furthermore the signals indicated no decomposition, once cooled the spectrum was identical to pre-heating. Due to the low solubility of Pd(II)-coordinated [2]rotaxane **2.3a** it was not possible to investigate **DMP[5]A** behaviour in a range of solvents and temperatures.

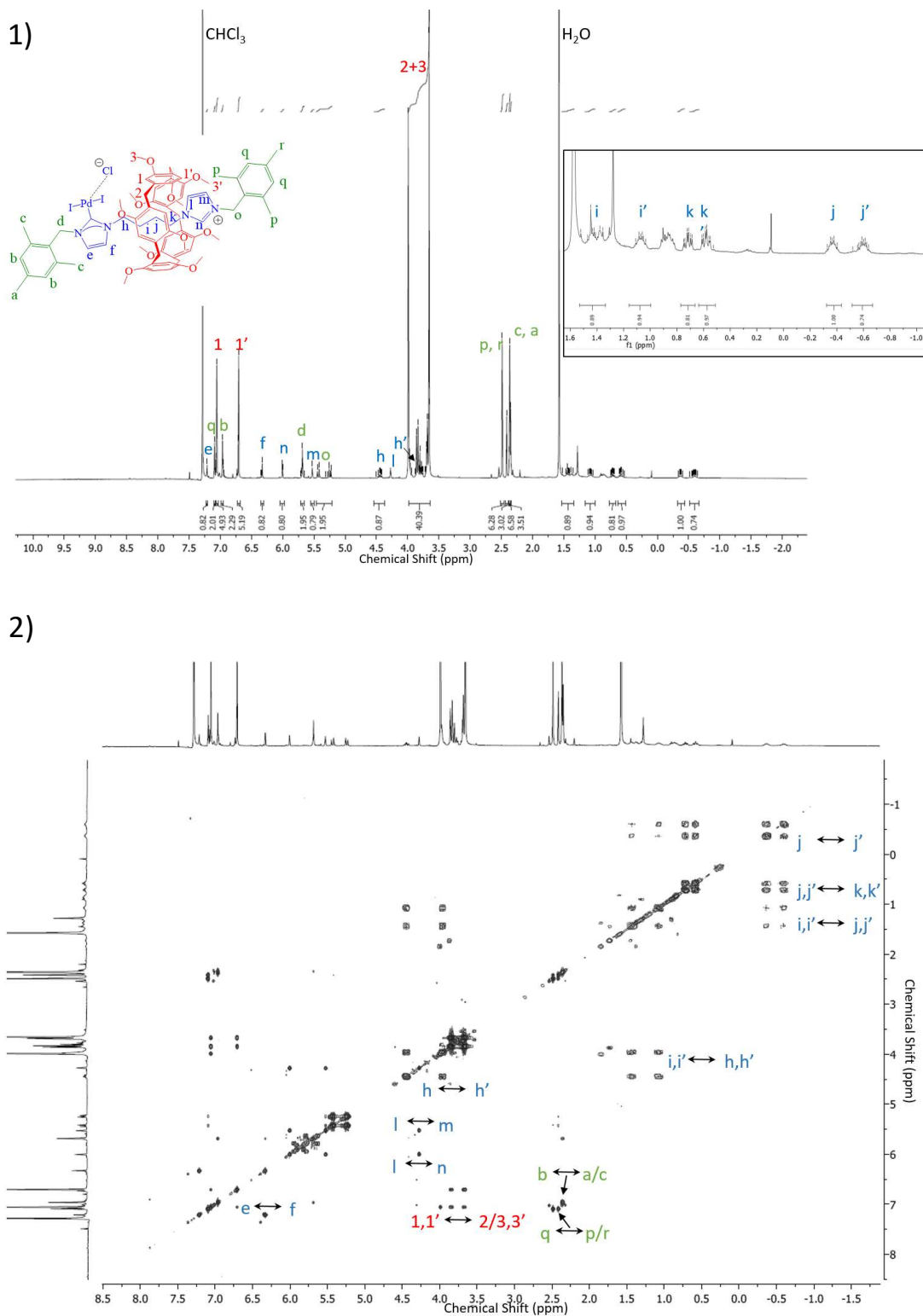


Figure 2.15: 1) ^1H NMR and ^1H – ^1H COSY NMR (500 MHz, CDCl_3 , 298 K) spectra of Pd(II)-coordinated [2]rotaxane **2.3a**.

2.2.5.2. Synthesis from Organic [2]]Rotaxanes

It was also possible to prepare Pd(II)-coordinated [2]rotaxanes **2.3b** and **2.3c** directly from [2]rotaxanes **2.1b** and **2.1c**, respectively, through heating solutions of the parent [2]rotaxanes to reflux in pyridine with Pd(CH₃CN)₂Cl₂, NaI and potassium carbonate. However, this reaction route gave significantly lower yields of 41 % and 45% for the Pd(II)-coordinated [2]rotaxanes **2.3b** and **2.3c**, respectively. In the case of the analogous reaction of [2]rotaxane **2.1a** the steric bulk and the elevated reaction temperature led to the dethreading of **DMP[5]A** which generated a dimetalated Pd(II)-*bis*-(NHC) species, **2.6a**, in a yield of 78%. Therefore, when considering the use of Pd(II)-coordination as a stimulus in more complex MIM switches, the reaction route via a Ag(I) complex is more advantageous, despite including an additional step.

2.2.5.3. Shuttling Confinement

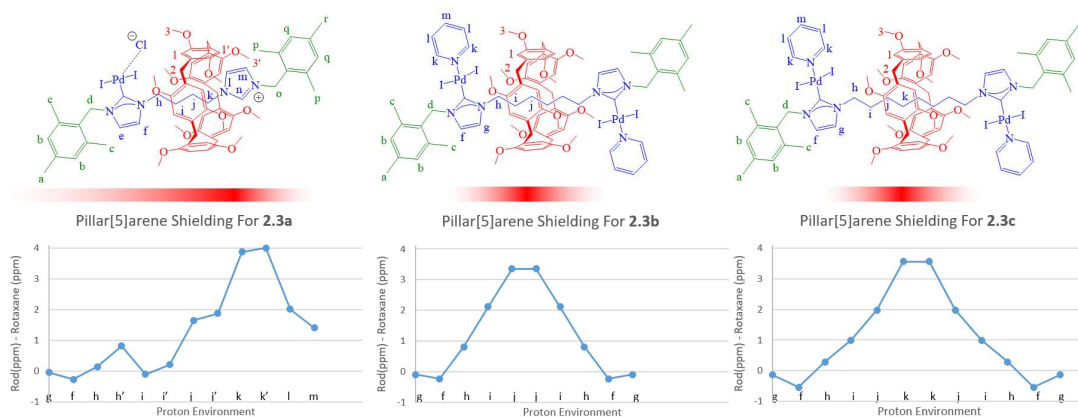


Figure 2.16: Calculated shielding effects (Formula 2.1) for Pd(II)-coordinated [2]rotaxane **2.3a-2.3c** indicating the favoured residency of **DMP[5]A** along the axle.

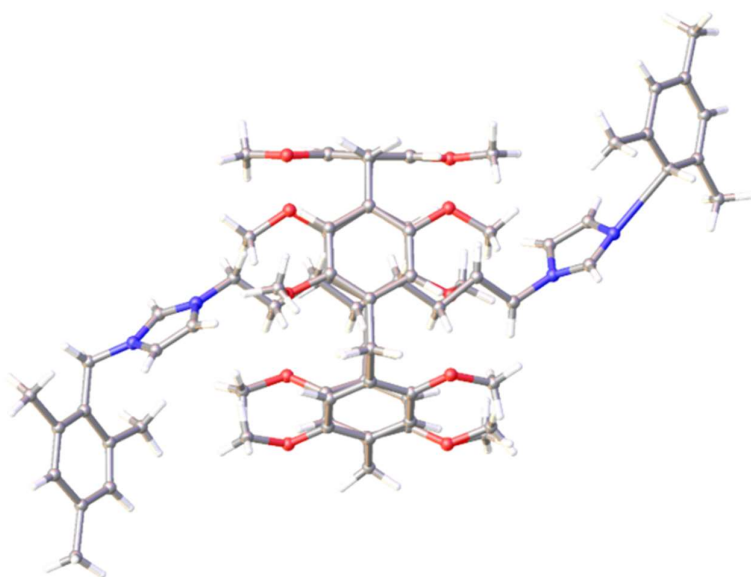
The shielding effect in Pd(II)-coordinated [2]rotaxanes **2.3a-2.3c** was evaluated using Formula 2.1 and plotted for each axle environment (Figure 2.16). This required the synthesis of unthreaded Pd(II) complexes of *bis*-NHC axles, **2.6a-2.6c**, which were readily prepared from **2.5a-2.5c** using an analogous reaction to the one used for the synthesis of Pd(II)-coordinated [2]rotaxanes **2.3a-2.3c** (Scheme 2.6). The shielding effects in Pd(II)-coordinated [2]rotaxanes **2.3b** and **2.3c** were similar to the equivalent Ag(I)-coordinated [2]rotaxanes, **2.2b** and **2.2c**. A significant upfield shift for ¹H

NMR peaks associated with the central alkyl chain was observed. However, the shifts were more pronounced due to the larger coordination sphere of the Pd(II) complex (Figure 2.13) indicating greater restriction of **DMP[5]A** movement along the [2]rotaxane axle. As with Ag(I)-coordinated [2]rotaxanes **2.2a-2.2c**, the signal for H_d was observed as a singlet due to the absence of an interaction with **DMP[5]A**.

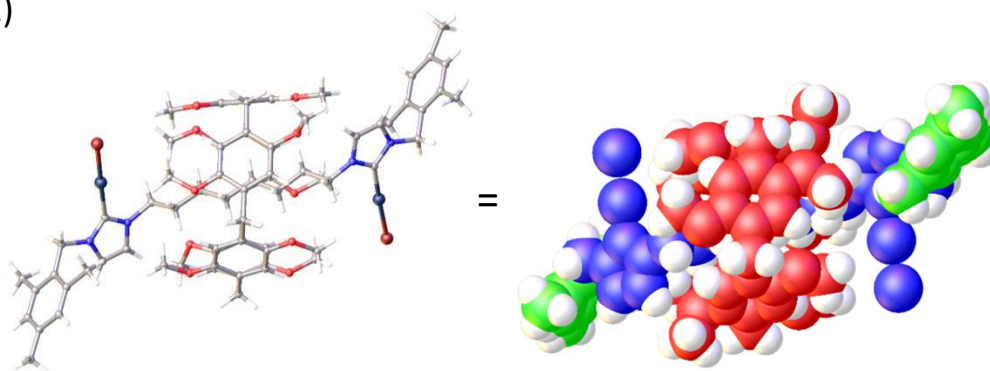
Pd(II)-coordinated [2]rotaxane **2.3a** behaves differently to the other [2]rotaxane Pd(II) complexes due to the asymmetric substitution of the axle. The shielding effect is calculated relative to the di-Pd(II) complex of the *bis*-NHC rod, **2.6a**, as an analogous axle cannot be synthesised because asymmetric substitution is only possible in the presence of **DMP[5]A**. The calculated shielding effects are shown in Figure 2.16 and clearly highlight the desymmetrisation in this complex. **DMP[5]A** shifts away from the Pd(II)-NHC complex, de-shielding the opposing end of the alkyl chain and the non-coordinated imidazolium group, H_{i-n}. When considering the discussion above, the axle component of Pd(II)-coordinated [2]rotaxane **2.3a** is expected to exhibit characteristics of both organic [2]rotaxanes **2.1a-2.1c** and Pd(II)-coordinated [2]rotaxane **2.3b-2.3c**. This is indeed the case; only one of the methylene proton environments demonstrates chirality transfer from **DMP[5]A**, H_o, whilst the other methylene proton environment, H_d, is a singlet. The asymmetric coordination and the extent of splitting indicate that in this complex there is minimal motion of **DMP[5]A** relative to the axle such as shuttling. It is therefore unlikely that the favourable interactions between **DMP[5]A** and the imidazolium are having an effect on **DMP[5]A** position. Instead, the position of **DMP[5]A** is determined entirely by the steric bulk of the stopper group on one end and the Pd(II) complex on the other end.

2.2.6. Crystallography

1)



2)



3)

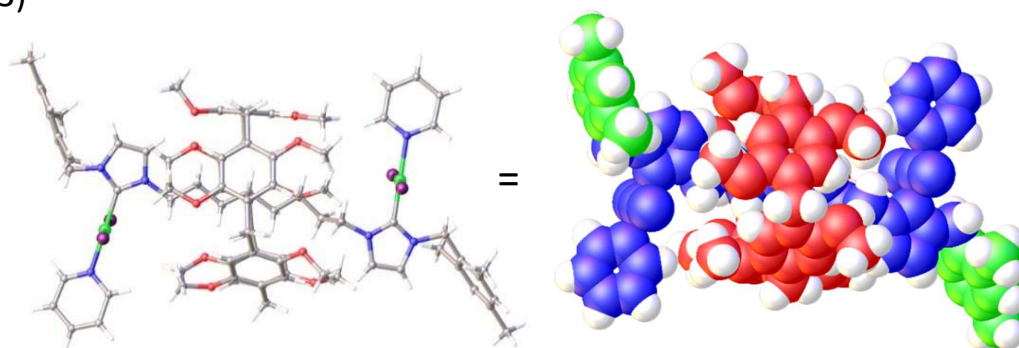


Figure 2.17: Crystal structure of [2]rotaxanes **2.1c** (1), **2.2c** (2) and **2.3c** (3). Carbon atoms = grey, oxygen atoms = red, nitrogen atoms = blue, silver atoms = dark blue, palladium atoms = green, bromine atoms = brown and iodide atoms = purple). Spacefilled representations of **2.2c** (2) and **2.3c** (3). Blue = imidazolium/NHC rod, red = **DMP[5]A** wheel, and green = mestiyI stopper group.

2.2.6.1. [2]Rotaxanes **2.1a-2.1c**

In each case single crystals were obtained by layering hexane onto a chloroform solution of [2]rotaxanes **2.1a-2.1c** and their structures were confirmed by single crystal X-ray diffraction studies. It is important to note that [2]rotaxanes **2.1a-2.1c** behave differently in the solid-state than in solution. The NMR studies showed the average position of the **DMP[5]A** along the axle to be around the imidazolium moieties, whilst the single crystal data shows **DMP[5]A** positioned in the centre of the axle over the linking alkyl chain (Figure 2.18-1). This discrepancy can be explained by solid state and packing effects of the molecules in the crystal phase.

2.2.6.2. Ag(I)-coordinated [2]Rotaxanes **2.2a-2.2c**

Ag(I)-coordinated [2]rotaxanes **2.2a-2.2c** crystallised readily from vapour diffusion of hexane into a solution of the complex in chloroform. Single crystal X-ray diffraction (Figure 2.18-2) along with ^1H , ^{13}C and ^1H - ^1H COSY NMR spectroscopy confirmed the structure of the target compounds. Notably, crystals of Ag(I)-coordinated [2]rotaxanes **2.2a-2.2c** appeared to be stable in light and at room temperature for long periods of time (up to months).

2.2.6.3. Pd(II)-coordinated [2]Rotaxanes **2.3a-2.3c**

Single crystals were obtained by vapour diffusion of hexane into a solution of Pd(II)-coordinated [2]rotaxanes **2.3a-2.3c** in chloroform. Their structures were confirmed by single crystal X-ray diffraction (see Figure 2.16/2.18-3).

2.3. Conclusions and Future Work

In summary, an **DMP[5]A**-based series of two station molecular shuttles has been synthesised in high yield through a new imidazole-iodo-methyl-benzene reaction route. It has been demonstrated that imidazolium units acts as stations for **DMP[5]A** through the synthesis of a single station [2]rotaxane, **2.7**. A relative shielding factor has been introduced as a consistent method for comparing **DMP[5]A** position along the axle in [2]rotaxanes described within this chapter. In [2]rotaxane molecular shuttles with linkers of 6 or more carbons, **2.1b** and **2.1c**, **DMP[5]A** exhibited continuous shuttling independent of chain length, temperature and anion. However the shuttling was found to be solvent dependent, with more polar solvents limiting the range of shuttling motion by competitively interacting with the imidazolium stations.

The shuttling behaviour of **DMP[5]A** along the full length of the axle can be restricted by coordination of silver and palladium (as Ag(I) and Pd(II)) to the imidazolium groups, acting as NHCs. This confines the shuttling movement of **DMP[5]A**, restricting it to the centre of the axle. In Ag(I)-coordinated [2]rotaxanes, **2.2a-2.2c**, the metalation process is reversible through the addition of TFA, allowing the release of **DMP[5]A** form confinement. In Pd(II)-coordinated [2]rotaxanes, **2.3a-2.3c**, movement of **DMP[5]A** is limited to a greater extent by the larger coordination sphere, as evidenced by NMR spectroscopy. With a [2]rotaxane of shorter axle length, **2.3a**, symmetry can be broken via Pd(II)-coordination because the **DMP[5]A** does not leave enough space for two palladium centres to coordinate. An interesting consequence of this is that the macrocycle topologically acts as a protecting group for the non-coordinated imidazole.

Transmetalation of Ag-NHC complexes has been shown to provide a versatile pathway for the coordination of a variety of metals, including Au,³³ Cu,³⁴ Fe³⁴ and Pd,³⁵ indicating a wide potential variety of target metal coordinated [n]rotaxane species allowing a mechanism for fine tuning shuttling in these systems and as a way of introducing additional functionality. The Ag(I)-coordinated [2]rotaxane, **2.2c**, has since been converted to a Rh(I) complex bearing [2]rotaxane

shown in Figure 2.18 through a transmetalation reaction with $\text{Rh}_2\text{Cl}_2(\text{COD})_2$. The catalytic properties of this system, in particular the effect the **DMP[5]A** has, are now being evaluated, but are beyond the scope of this chapter.

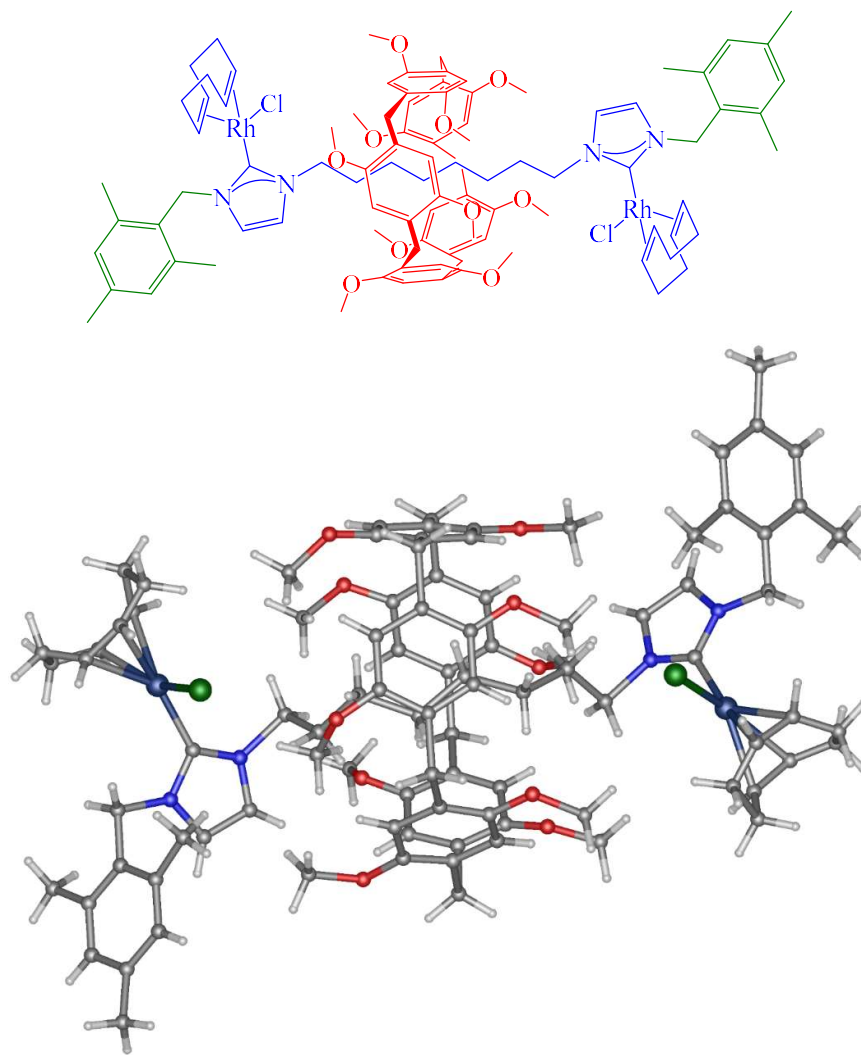


Figure 2.18: Chemical structure (top) and crystal structure (bottom) of Rh(I)-coordinated [2]rotaxane. Carbon atoms = grey, oxygen atoms = red, nitrogen atoms = blue, rhodium atoms = dark blue, chlorine atoms = green.

2.4. Materials and Methods

2.4.1. Synthesis

2.4.1.1. General Procedure for *Bis*-imidazole Alkanes

To a mixture of imidazole (30.88 mmol), potassium carbonate (36.96 mmol) in DMF (40 mL) was added dibromoalkane (6.20 mmol) and the mixture was stirred at 80 °C overnight. After letting the suspension cool to room temperature the solvent was removed under reduced pressure and the residue was taken up in dichloromethane. The organic layer was washed with water (3 x 100 mL) and brine (100 mL) and dried over anhydrous MgSO₄, filtered under gravity and concentrated under reduced pressure to afford the pure product as a pale-yellow oil which solidified at room temperature.

1,4-*bis*-imidazolebutane: 95 % ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 (s, 2H), 7.09 (t, *J* = 1.1 Hz, 2H), 6.88 (t, *J* = 1.3 Hz, 2H), 3.95 (t, *J* = 8 Hz 4H), 1.85 – 1.71 (m, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 137.01, 129.90, 118.57, 46.36, 28.14 ppm. HRMS (ESI+) *m/z*: 191.1299 [M]⁺, calc. for [C₁₀H₁₅N₄]⁺ = 191.1291.

1,4-*bis*-imidazolehexane: 94 % ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 (s, 2H), 7.04 (s, 2H), 6.87 (s, 2H), 3.90 (t, *J* = 7.0 Hz, 4H), 1.76 (d, *J* = 7.1 Hz, 4H), 1.29 (q, *J* = 3.8 Hz, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 137.03, 129.53, 118.67, 46.77, 30.85, 26.05 ppm. HRMS (ESI+) *m/z*: 219.1611 [M]⁺, calc. for [C₁₂H₁₉N₄]⁺ = 219.1604.

1,4-*bis*-imidazoleoctane: 90 % ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 (s, 2H), 6.98 (s, 2H), 6.83 (s, 2H), 3.85 (t, *J* = 6.3 Hz, 4H), 1.69 (t, *J* = 6.0 Hz, 4H), 1.26 – 1.16 (m, 8H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 136.98, 129.28, 118.72, 46.89, 30.92, 28.80, 26.32 ppm. HRMS (ESI+) *m/z*: 247.1926 [M]⁺, calc. for [C₁₄H₂₃N₄]⁺ = 247.1917.

2.4.1.2. Decamethoxypillar[5]arene **DMP[5]A**

1,4-Dimethoxybenzene (10 g, 72.46 mmol) was added to a flame dried flask which had been backfilled with dinitrogen three times. Anhydrous dichloromethane (500 mL) was added via cannula, followed by paraformaldehyde (7 g, 233.34 mmol). The mixture was stirred at room temperature for 10 minutes under a dinitrogen atmosphere after which anhydrous iron(III)chloride (2.5 g, 15.43 mmol) was added and the mixture was stirred at room temperature for 3 hours. The mixture was then quenched with water and the organic layer was separated, washed with water (3 x 200 mL) and concentrated under reduced pressure. The crude residue was subjected to column chromatography on silica gel (dichloromethane) to afford the product as a white solid (4.3 g, 40 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 6.79 (s, 10H), 3.80 (s, 10H), 3.68 (s, 30H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.80, 128.24, 114.08, 55.78, 29.67 ppm. HRMS (ESI+) m/z : 789.3006 [M]⁺, calc. for [C₄₅H₅₀O₁₀K]⁺ = 789.3041.

2.4.1.3. 2-(Iodomethyl)-1,3,5-trimethylbenzene

To a solution of mesitylmethanol (1.88 g, 13 mmol) in dioxane (20mL) was added to BF₃·Et₂O (1.78 g, 13 mmol) and potassium iodide (2.08 g, 13 mmol) and the solution was stirred at room temperature for 4 hours under the exclusion of light. The reaction mixture was poured into ice water and extracted with diethyl ether (3 x 50 mL). The organic layer was washed with brine (100 mL), dried over anhydrous MgSO₄, filtered under gravity and the solvent removed under reduced pressure. The crude product was purified by distillation to give the product as a pale-yellow solid (2.54 g, 75 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 6.87 (s, 2H), 4.50 (s, 2H), 2.36 (s, 6H), 2.29 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.97, 136.83, 129.42, 21.10, 19.27, 3.96.

2.4.1.4. General Procedure for [2]-Rotaxane **2.1a-2.1c**

Bis-imidazole alkanes (0.41 mmol) and **DMP[5]A** (0.82 mmol) were dissolved in chloroform (1 mL) and sonicated for 30 minutes. The solution was cooled to -15 °C and 2-(iodomethyl)-1,3,5-

trimethylbenzene (0.923 mmol) was added under the exclusion of light. The mixture was left to warm to room temperature and stirred under a dinitrogen atmosphere overnight. The crude residue was subjected to column chromatography on silica gel (chloroform:methanol 97.5:2.5) to afford **2.1a-2.1c** as pale yellow solids:

2.1a. 78 % ^1H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 8.00 (t, J = 1.8 Hz, 2H), 7.04 (s, 4H), 6.83 (s, 10H), 6.63 (t, J = 1.9 Hz, 2H), 5.88, 5.98 (ABq, 4H, J_{AB} = 16 Hz), 3.71 (s, 10H), 3.69 (s, 30H), 2.46 (s, 12H), 2.37 (s, 6H), 1.80 – 1.75 (m, 4H), -0.96 – -1.06 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.14, 140.18, 138.13, 133.53, 130.36, 130.08, 125.79, 123.31, 120.48, 116.02, 77.28, 58.49, 53.47, 49.31, 47.02, 29.16, 23.68, 21.17, 20.24 ppm. HRMS (ESI+) m/z : 1205.6625 [M]⁺, calc. for $[\text{C}_{75}\text{H}_{90}\text{N}_4\text{O}_{10}]^+ = 1205.6657$.

2.1b. 81 % ^1H NMR (400 MHz,) δ 8.77 (s, 2H), 6.64 (s, 2H), 7.03 (s, 4H), 6.87 (s, 10H), 6.78 (s, 2H), 5.53, 5.59 (ABq, 4H, J_{AB} = 16 Hz), 3.79 (s, 30H), 3.74 (s, 10H), 2.56 (t, J = 8.7 Hz, 4H), 2.40 (s, 12H), 2.38 (s, 6H), 0.45 (s, 4H), 0.31 (s, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.16, 140.20, 138.09, 134.47, 130.04, 129.94, 127.88, 122.69, 120.01, 115.80, 58.22, 52.80, 48.02, 29.16, 25.50, 21.13, 20.05, 19.86 ppm. HRMS (ESI+) m/z : 1233.6926 [M]⁺, calc. for $[\text{C}_{77}\text{H}_{94}\text{N}_4\text{O}_{10}]^+ = 1233.6970$.

2.1c 84 % ^1H NMR (400 MHz, Chloroform-*d*) δ 7.00 (s, 4H), 6.96 (s, 10H), 6.50 (d, J = 1.7 Hz, 2H), 6.37 (d, J = 1.7 Hz, 2H), 5.50, 5.58 (ABq, 4H, J_{AB} = 16 Hz), 3.75 (s, 10H), 3.60 (s, 30H), 2.40 (s, 12H), 2.37 (s, 6H), 2.19 – 1.98 (m, 4H), -1.23 – -1.48 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.95, 140.21, 138.01, 134.32, 130.09, 129.77, 125.12, 122.90, 119.52, 115.37, 77.26, 57.66, 48.54, 47.63, 29.81, 29.10, 28.74, 26.71, 21.13, 19.79 ppm. ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.36 (s, 2H), 7.69 (s, 2H), 7.07 (s, 4H), 6.99 (s, 2H), 6.79 (s, 10H), 5.57 – 5.44 (m, 4H), 3.65 (s, 10H), 3.63 (s, 30H), 2.52 – 2.50 (m, 7H), 2.36 (s, 12H), 2.30 (s, 6H), 0.23 – 0.11 (m, 4H), 0.11 – -0.01 (m, 4H), -0.03 – -0.17 (m, 4H) ppm. ^{13}C NMR (101 MHz, DMSO-*d*₆) δ 150.54, 139.39, 138.46, 134.43, 130.03, 128.78, 126.91, 122.93, 122.08, 114.32, 56.68, 48.61, 47.77, 29.18, 29.12, 28.31, 26.24, 21.14, 19.76 ppm. HRMS (ESI+) m/z : 1261.7263 [M]⁺, calc. for $[\text{C}_{79}\text{H}_{98}\text{N}_4\text{O}_{10}]^+ = 1261.7283$.

2.1c. (CD₃)₂SO

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.36 (s, 2H), 7.69 (t, *J* = 1.7 Hz, 2H), 7.07 (s, 4H), 6.99 (t, *J* = 1.7 Hz, 2H), 6.79 (s, 10H), 5.56 – 5.45 (m, 4H), 3.65 (s, 10H), 3.63 (s, 30H), 2.51 (m, DMSO+alkane, 10H), 2.36 (s, 12H), 2.30 (s, 6H), 0.16 (s, 4H), 0.05 (p, *J* = 13.9, 7.3 Hz, 4H), -0.09 (s, 4H) ppm. ¹³C NMR (101 MHz, DMSO-*d*₆) δ 150.54, 139.39, 138.46, 134.43, 130.03, 128.78, 126.91, 122.93, 122.08, 114.32, 79.68, 56.68, 48.61, 47.77, 29.18, 29.12, 28.31, 26.24, 21.14, 19.76 ppm.

2.1c. (CD₃)₂CO

¹H NMR (400 MHz, Acetone-*d*₆) δ 8.71 (s, 2H), 7.60 (t, *J* = 1.8 Hz, 2H), 7.11 (s, 4H), 7.07 (t, *J* = 1.8 Hz, 2H), 6.95 (s, 10H), 5.80 – 5.67 (m, 4H), 3.78 (s, 30H), 3.76 (s, 10H), 2.62 (t, *J* = 8.1 Hz, 4H), 2.47 (s, 12H), 2.35 (s, 6H), 0.72 (s, 4H), 0.40 (s, 4H), 0.33 – 0.19 (m, 4H) ppm.

2.1c. Anion effect (PF₆⁻)

2.1c (0.1 g, 0.0653 mmol) was dissolved in ethanol (20 mL) and ammonium hexafluorophosphate (0.43 g, 2.61 mmol) was added. The mixture was heated to reflux for 4 hours and left to cool to room temperature. The white precipitate was collected by filtration under reduced pressure, washed with ethanol and dried to afford the ion exchanged product as a white solid (0.09 g, 88 %).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 2H), 7.02 (s, 4H), 6.83 (s, 9H), 6.78 (s, 2H), 6.64 (s, 2H), 5.43 (s, 4H), 3.72 (s, 40H), 2.36 (s, 18H), 2.25 (t, *J* = 8.4 Hz, 4H), 0.84 (s, 4H), 0.51 (s, 4H), 0.35 – 0.00 (m, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.87, 140.25, 138.00, 133.78, 130.11, 129.64, 124.95, 122.43, 120.07, 115.13, 57.09, 48.66, 47.51, 29.64, 29.07, 28.31, 26.61, 21.11, 19.44 ppm. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -72.46 (d, *J* = 714.40 Hz) ppm. ³¹P NMR (162 MHz, Chloroform-*d*) δ -144.18 (sept, *J* = 712.80 Hz) ppm.

2.4.1.5. General Procedure for Ag(I)-[2]Rotaxane **2.2a-2.2c**

To solution of **2.1a-2.1c** (0.0810 mmol) in dichloromethane (25 mL) was added Ag₂O (0.0810 mmol) and the mixture was stirred at room temperature overnight under the exclusion of light. The mixture was filtered through a celite plug, washed with dichloromethane (2 x 50 mL) and the organic fractions were combined, dried over anhydrous MgSO₄, filtered under gravity and the solvent removed under reduced pressure to afford the crude product as an off-white solid. This was redissolved in dichloromethane (1mL) and added dropwise to cold hexane (20 mL). The white precipitate was collected by filtration under reduced pressure, washed with hexane and dried to afford **2.2a-2.2c** as white solids.

2.2a. 82 % ¹H NMR (400 MHz, Chloroform-*d*) δ 7.01 (s, 4H), 6.91 (s, 10H), 6.64 (d, *J* = 1.8 Hz, 2H), 5.40 (s, 4H), 3.75 (s, 10H), 3.69 (s, 30H), 2.36 (d, *J* = 5.8 Hz, 18H), -0.13 (s, 4H), -2.01 (s, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.16, 139.02, 137.58, 129.76, 129.73, 115.92, 77.22, 57.76, 50.02, 49.54, 29.12, 23.08, 21.12, 20.11 ppm.

2.2b. 85 % ¹H NMR (400 MHz,) δ 7.28 (d, *J* = 1.8 Hz, 2H), 6.98 (s, 4H), 6.88 (s, 10H), 6.61 (d, *J* = 1.8 Hz, 2H), 5.37 (s, 4H), 3.75 – 3.71 (m, 10H), 3.69 – 3.62 (m, 30H), 3.23 – 3.06 (m, 4H), 2.34 (s, 6H), 2.33 (s, 12H), -0.16 (s, 4H), -2.04 (s, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.87, 137.58, 129.87, 129.34, 120.64, 114.93, 57.46, 51.30, 49.68, 29.12, 23.55, 21.12, 19.99 ppm.

2.2c. 81 % ¹H NMR (400 MHz,) δ 7.19 (d, *J* = 1.8 Hz, 2H), 6.98 (s, 4H), 6.86 (s, 10H), 6.62 (d, *J* = 1.9 Hz, 2H), 5.34 (s, 4H), 3.74 (s, 10H), 3.69 (s, 30H), 3.63 – 3.57 (m, 4H), 2.33 (s, 6H), 2.32 (s, 12H), 0.78 – 0.63 (m, 4H), -0.73 (s, 4H), -1.59 (s, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.77, 137.66, 129.84, 128.98, 114.65, 56.84, 52.41, 49.71, 29.13, 25.62, 21.09, 19.96 ppm.

2.4.1.6. General Procedure for Conversion of [2]Rotaxanes **2.2a-2.2c** to **2.3a-2.2c**

2.2a-2.2c (0.062mmol) was added to a flame dried flask which had been backfilled with dinitrogen three times. Anhydrous pyridine (10 mL) was added via cannula, followed by Pd(CH₃CN)₂Cl₂ (0.130mmol) and potassium iodide (0.262mmol). The mixture was stirred at room temperature

overnight under a dinitrogen atmosphere and under the exclusion of light. All volatiles were evaporated under reduced pressure and the residue was taken up in chloroform and water. The organic layer was separated and washed with water (3 x 100 mL), 5 % CuSO₄ aq (100 mL) and brine (100 mL) and subsequently dried over MgSO₄ and filtered under gravity. The solvent was removed under reduced pressure and the residue subjected to a silica gel pad (dichloromethane) to afford **2.3a-2.3c** as orange solids.

2.3a. 90 % ¹H NMR (500 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 2.0 Hz, 1H), 7.09 (s, 2H), 7.06 (s, 5H), 6.96 (s, 2H), 6.71 (s, 5H), 6.33 (d, *J* = 2.0 Hz, 1H), 6.01 (s, 1H), 5.68 (s, 2H), 5.53 (s, 1H), 5.24, 5.43 (ABq, 2H, *J*_{AB} = 10 Hz), 3.96, 4.44 (ABtd, 2H, *J*_{AB} = 240, 5 Hz), 3.98 – 3.64 (m, 40H), 2.49 (s, 6H), 2.41 (s, 3H), 2.37 (s, 7H), 2.35 (s, 4H), 1.07, 1.43 (ABm, 2H, *J*_{AB} = 180 Hz), 0.59, 0.72 (ABtd, 2H, *J*_{AB} = 65, 5 Hz), -0.37, -0.60 (ABm, 2H, *J*_{AB} = 115 Hz) ppm. ¹³C NMR-sample was not sufficiently soluble to obtain good quality data. MALDI-TOF M/S *m/z*: 1565.366 [M]⁺, calc. for [C₇₅H₉₀N₄O₁₀I₂Pd]⁺ = 1565.372.

2.3b. 41 % ¹H NMR (400 MHz,) δ 9.17 (dt, *J* = 5.0, 1.6 Hz, 4H), 7.80 (tt, *J* = 7.7, 1.6 Hz, 2H), 7.46 – 7.38 (m, 4H), 7.08 (d, *J* = 2.1 Hz, 2H), 7.02 (s, 4H), 6.94 (s, 10H), 6.30 (d, *J* = 2.0 Hz, 2H), 5.66 (d, 4H), 3.76 (s, 10H), 3.72 (s, 30H), 3.66 – 3.56 (m, 4H), 2.37 (s, 18H), 0.01 – -0.19 (m, 4H), -1.68 – -1.83 (m, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 153.76, 150.98, 143.65, 138.95, 138.74, 137.65, 129.35, 129.15, 127.70, 124.54, 120.95, 118.50, 114.93, 58.38, 50.93, 50.75, 29.14, 27.10, 24.98, 21.16, 20.46 ppm.

2.3c. 45 % ¹H NMR (400 MHz,) δ 9.15 (dt, *J* = 5.0, 1.6 Hz, 4H), 7.84 (m, 2H), 7.47 – 7.40 (m, 4H), 7.39 (d, *J* = 2.1 Hz, 2H), 7.05 – 6.99 (m, 4H), 6.96 (s, 10H), 6.39 (d, *J* = 2.0 Hz, 2H), 5.62 (s, 4H), 4.15-4.09 (m, 4H), 3.80 (s, 30H), 3.78 (s, 10H), 2.39 (s, 12H), 2.38 (s, 6H), 1.16 – 1.04 (m, 4H), -0.45 (s, 4H), -2.04 (s, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 153.88, 150.78, 138.93, 137.76, 129.41, 128.78, 128.25, 124.59, 119.96, 119.53, 114.46, 114.06, 57.22, 55.80, 52.39, 50.40, 29.66, 29.22, 28.57, 27.09, 26.54, 21.16, 20.55, 1.06 ppm.

2.4.1.7. General Procedure for Pd-[2]Rotaxane **2.3b**, **2.3c** and **2.6a** from **2.1a-2.1c**

2.1a-2.1c (0.0810 mmol) was added to a flame dried flask which had been backfilled with dinitrogen three times. Anhydrous pyridine (10 mL) was added via cannula, followed by Pd(CH₃CN)₂Cl₂ (0.243 mmol), potassium iodide (1.215 mmol) and potassium carbonate (0.486 mmol). The mixture was heated to reflux and stirred overnight under a dinitrogen atmosphere and under the exclusion of light. All volatiles were evaporated under reduced pressure and the residue was redissolved in chloroform (25 mL) and water (25 mL). The organic layer was separated and washed with water (3 x 100 mL), 5 % CuSO₄ aq (100 mL) and brine (100 mL) and subsequently dried over MgSO₄ and filtered under gravity. The solvent was removed under reduced pressure and the residue subjected to a silica gel pad (dichloromethane) to afford the products as orange solids.

2.3b and **2.3c** in reported in Section 2.4.1.6

2.6a. 78 % ¹H NMR (400 MHz, Chloroform-*d*) δ 9.14 (dt, *J* = 5.0, 1.6 Hz, 4H), 7.73 (tt, *J* = 7.7, 1.6 Hz, 2H), 7.39 – 7.30 (m, 4H), 6.97 (s, 4H), 6.94 (d, *J* = 2.1 Hz, 2H), 6.29 (d, *J* = 2.1 Hz, 2H), 5.58 (s, 4H), 4.60 (s, 4H), 2.34 (s, 16H), 2.20 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 154.01, 144.72, 140.02, 138.91, 137.47, 129.33, 124.48, 109.99, 100.85, 66.39, 51.22, 21.08, 20.46, 19.34 ppm.

2.4.1.8. General Procedure for Unthreaded Stoppered Rods **2.4a-2.4c**

Bis-imidazole alkane (0.24 mmol) was dissolved in chloroform (10 mL) and 2-(iodomethyl)-1,3,5-trimethylbenzene (0.6 mmol) was added under the exclusion of light. The mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography (chloroform: methanol 90:10 -> 80:20) to give the final products as off-white solids.

2.4a. 84 % ¹H NMR (400 MHz, Chloroform-*d*) δ 9.88 (s, 2H), 7.92 (t, *J* = 1.8 Hz, 2H), 6.93 (s, 4H), 6.81 (s, 2H), 5.51 (s, 4H), 4.58 (s, 4H), 2.30 (s, 22H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ

140.04, 138.17, 135.74, 129.99, 125.07, 123.43, 120.57, 49.35, 48.26, 26.76, 21.07, 20.22 ppm.

HRMS (ESI+) m/z : 228.1631 [M]²⁺, calc. for [C₃₀H₄₀N₄]²⁺ = 228.1621).

2.4b. 92 % ¹H NMR (400 MHz, Chloroform-*d*) δ 10.16 (s, 2H), 7.65 (s, 2H), 6.96 (s, 4H), 6.78 (s, 2H), 5.57 (s, 4H), 4.47 (t, J = 7.4 Hz, 4H), 2.33 (s, 12H), 2.32 (s, 6H), 2.18 – 2.05 (m, 4H), 1.61 (t, J = 6.8 Hz, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 138.18, 136.24, 130.01, 125.13, 122.74, 120.49, 49.90, 48.20, 29.71, 24.66, 21.07, 20.14 ppm. HRMS (ESI+) m/z : 242.1790 [M]²⁺, calc. for [C₃₂H₄₄N₄]²⁺ = 242.1778.

2.4c. 97 % ¹H NMR (400 MHz, Chloroform-*d*) δ 10.10 (s, 2H), 7.78 (s, 2H), 6.92 (s, 4H), 6.84 (s, 2H), 5.55 (s, 4H), 4.41 (t, J = 7.5 Hz, 4H), 2.29 (s, 18H), 2.00 (s, 4H), 1.42 (s, 8H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 139.96, 138.09, 135.90, 129.97, 125.23, 123.10, 120.58, 50.14, 48.05, 29.71, 27.73, 25.32, 21.07, 20.11 ppm. HRMS (ESI+) m/z : 256.1958 [M]²⁺, calc. for [C₃₄H₄₈N₄]²⁺ = 256.1934.

2.4.1.9. General Procedure for Ag(I)-coordination to Stoppered Rods **2.5a-2.5c**

To solution of **2.4a-2.4c** (0.275 mmol) in dichloromethane (25 mL) was added Ag₂O (0.550 mmol) and the mixture was stirred at room temperature overnight under the exclusion of light. The mixture was filtered under gravity and the solvent removed under reduced pressure to afford the crude product as an off white solid. This was redissolved in dichloromethane (1mL) and added dropwise to cold hexane (20 mL). The white precipitate was collected by filtration under reduced pressure, washed with hexane and dried to afford **2.5a-2.5c** as white solids.

2.5a. 74 % ¹H NMR (400 MHz, Chloroform-*d*) δ 7.05 (d, J = 1.5 Hz, 2H), 6.91 (s, 4H), 6.59 – 6.54 (m, 2H), 5.29 (s, 4H), 4.18 (s, 4H), 2.29 (s, 6H), 2.24 (s, 12H), 1.89 (s, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 139.03, 137.77, 129.73, 127.58, 120.88, 120.31, 70.53, 51.36, 49.74, 28.36, 21.04, 20.03 ppm.

2.5b. 93 % ^1H NMR (400 MHz, Chloroform-*d*) δ 7.07 (d, J = 1.6 Hz, 2H), 6.91 (s, 4H), 6.56 (d, J = 1.5 Hz, 2H), 5.28 (s, 4H), 4.13 (t, J = 7.0 Hz, 4H), 2.28 (s, 6H), 2.25 (s, 12H), 1.86 – 1.78 (m, 4H), 1.45 – 1.36 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.98, 137.75, 129.71, 127.70, 121.02, 120.02, 53.49, 51.53, 49.62, 31.25, 25.28, 21.03, 20.00 ppm.

2.5c. 91 % ^1H NMR (400 MHz, Chloroform-*d*) δ 7.00 (d, J = 1.5 Hz, 2H), 6.92 (s, 4H), 6.57 (s, 2H), 5.27 (s, 4H), 4.10 (t, J = 7.2 Hz, 4H), 2.29 (s, 6H), 2.25 (s, 12H), 1.82 (p, J = 6.6, 6.2 Hz, 4H), 1.41 – 1.29 (m, 8H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.00, 137.77, 129.71, 127.66, 120.76, 119.98, 51.92, 49.65, 31.17, 28.46, 25.91, 21.03, 19.99 ppm.

2.4.1.10. General Procedure for Pd (II)-coordination to Stoppered Rods **2.6a-2.6c**

2.5a-2.5c (0.240mmol) was added to a flame dried flask which had been backfilled with dinitrogen three times. Anhydrous pyridine (10 mL) was added via cannula, followed by $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.577mmol) and potassium iodide (1.15mmol). The mixture was heated to reflux and stirred overnight under a dinitrogen atmosphere and under the exclusion of light. All volatiles were evaporated under reduced pressure and the residue was redissolved in chloroform (25 mL) and water (25 mL). The organic layer was separated and washed with water (3 x 100 mL), 5 % CuSO_4 aq (100 mL) and brine (100 mL) and subsequently dried over MgSO_4 and filtered under gravity. The solvent was removed under reduced pressure and the residue subjected to a silica gel pad (dichloromethane) to afford **2.6a-2.6c** as orange solids.

2.6a. 71 % ^1H and ^{13}C NMR analagous with spectra reported in Section 2.4.1.7.

2.6b. 64 % ^1H NMR (400 MHz, Chloroform-*d*) δ 9.10 (d, J = 5.7 Hz, 4H), 7.72 (t, J = 8.4 Hz, 2H), 7.34 (d, J = 6.1 Hz, 4H), 6.96 (s, 4H), 6.89 (s, 2H), 6.24 (s, 2H), 5.56 (s, 4H), 4.50 – 4.40 (m, 4H), 2.33 (s, 18H), 2.22 – 2.14 (m, 4H), 1.64 (s, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.88, 153.02, 138.87, 138.73, 137.68, 129.36, 127.38, 124.56, 121.01, 120.07, 51.70, 50.47, 29.16, 26.15, 21.20, 20.52 ppm.

2.6c. 82 % ^1H NMR (400 MHz, Chloroform-*d*) δ 9.10 (d, J = 4.9 Hz, 4H), 7.74 (t, J = 7.7 Hz, 2H), 7.35 (d, J = 7.6 Hz, 4H), 6.96 (s, 4H), 6.85 (d, J = 2.1 Hz, 2H), 6.25 (d, J = 2.0 Hz, 2H), 5.56 (s, 4H), 4.45 – 4.37 (m, 4H), 2.33 (s, 18H), 2.10 (s, 4H), 1.51 (s, 8H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.90, 153.04, 144.18, 138.88, 138.72, 137.68, 129.34, 127.39, 124.52, 120.85, 120.01, 51.86, 50.46, 29.42, 28.90, 26.58, 21.17, 20.50 ppm.

2.4.1.11. Ag(II) Protodemetalation with TFA

[2]Rotaxane (**2.2a-2.2c**) was dissolved in chloroform and TFA was added dropwise. A white precipitate formed which was removed by filtration. The filtrate was dried under reduced pressure to yield [2]rotaxane (**2.1a-2.1c**). The NMR spectra were analogous to spectra previously reported in Section 2.4.1.4.

2.4.1.12. 2-((6-Bromohexyl)oxy)-1,3,5-trimethylbenzene

To a mixture of 2,4,6-trimethylphenol (2 g, 14.7 mmol), potassium carbonate (2.0 g, 14.7 mmol) in DMF (35 mL) was added 1,6-dibromohexane (4.5 mL, 29.4 mmol) and the mixture was stirred at 70 °C overnight. After letting the suspension cool to room temperature the reaction mixture was taken up in dichloromethane and the organic layer was washed with water (3 x 100 mL) and brine (100 mL). The organic layer was dried over anhydrous MgSO_4 , filtered under gravity and concentrated under reduced pressure. The crude residue was subjected to column chromatography on silica gel (hexane:acetone 100:0 $\rightarrow$ 95:5) to afford 2-((6-bromohexyl)oxy)-1,3,5-trimethylbenzene as a colourless oil (3.25 g, 74 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 6.88 (s, 2H), 3.80 (t, J = 6.5 Hz, 2H), 3.49 (t, J = 6.8 Hz, 1H), 2.31 (s, 3H), 2.30 (s, 6H), 2.09 – 1.79 (m, 4H), 1.72 – 1.49 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.12, 153.87, 153.77, 132.91, 132.84, 130.54, 130.51, 129.40, 129.38, 77.32, 72.28, 72.06, 63.99, 63.82, 45.06, 33.86, 33.64, 32.83, 32.65, 32.58, 30.47, 30.33, 29.93, 28.41, 28.16, 27.77, 27.36, 26.89, 26.21, 25.89, 25.60, 25.49, 25.12, 20.72, 16.25 ppm.

2.4.1.13. 1-(6-(Mesityloxy)hexyl)-1H-imidazole

To a mixture of imidazole (0.51g, 7.53 mmol), potassium carbonate (1.04 g, 7.53 mmol) in DMF (20 mL) was added 2-((6-bromohexyl)oxy)-1,3,5-trimethylbenzene (1.5 g, 5.02 mmol) and the mixture was stirred at 70 °C overnight. After letting the suspension cool to room temperature the reaction mixture was taken up in dichloromethane and the organic layer was washed with water (3 x 100 mL) and brine (100 mL). The organic layer was dried over anhydrous MgSO₄, filtered under gravity and concentrated under reduced pressure. The crude residue was subjected to column chromatography on silica gel (hexane:acetone 90:10) to afford 1-(6-(mesityloxy)hexyl)-1H-imidazole as a pale yellow oil (1.15 g, 80 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 (s, 1H), 7.05 (s, 1H), 6.89 (s, 1H), 6.80 (s, 2H), 3.91 (t, *J* = 7.1 Hz, 2H), 3.70 (t, *J* = 6.4 Hz, 2H), 2.22 (s, 9H), 1.94 – 1.69 (m, 4H), 1.54 (p, *J* = 7.5 Hz, 2H), 1.36 (p, *J* = 7.6 Hz, 2H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.43, 153.68, 137.04, 132.84, 130.38, 129.38, 129.35, 118.73, 77.51, 71.90, 46.89, 36.38, 31.04, 30.24, 26.49, 25.75, 20.66, 16.18 ppm. HRMS (ESI+) *m/z*: 287.2115 [*M*]⁺, calc. for [C₁₈H₂₆N₂O]⁺ = 287.2079.

2.4.1.14. Procedure for [2]Rotaxane **2.7**

1-(6-(mesityloxy)hexyl)-1H-imidazole (0.1 g, 0.35mmol) and **DMP[5]A** (0.39 g, 0.53 mmol) were dissolved in chloroform (1 mL) and sonicated for 30 minutes. The solution was cooled to -15 °C and 2-(iodomethyl)-1,3,5-trimethylbenzene (0.18 g, 0.70 mmol) was added under the exclusion of light. The mixture was left to warm to room temperature and stirred overnight. The crude residue was subjected to column chromatography on silica gel (chloroform:methanol 98:2) to afford [2]rotaxane **2.7** as a pale yellow solid (0.36 g, 80 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.34 (s, 1H), 7.04 (s, 2H), 6.90 (s, 5H), 6.89 (s, 2H), 6.72 (s, 5H), 5.94 (d, *J* = 15.1 Hz, 1H), 5.83 (s, 1H), 5.69 (d, *J* = 15.1 Hz, 1H), 3.82 – 3.57 (m, 42H), 2.47 (s, 6H), 2.38 (s, 3H), 2.31 (s, 6H), 2.29 (s, 3H), 1.56 – 1.31 (m, 2H), 0.50 (t, 2H), 0.37 – 0.07 (m, 2H), -0.83 (dq, *J* = 11.7, 7.8, 5.8 Hz, 2H), -1.52 – -1.99 (m, 2H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 153.67, 151.17, 150.39, 139.92, 138.12, 138.04, 136.06, 133.21, 131.90, 130.51, 130.01, 129.91, 129.52, 129.28, 129.03, 125.92,

125.90, 123.01, 122.53, 122.50, 120.80, 115.97, 113.92, 77.52, 77.39, 77.20, 76.88, 72.50, 72.02, 70.55, 58.39, 55.87, 50.24, 48.87, 48.01, 47.17, 31.46, 30.31, 30.19, 29.69, 29.07, 26.20, 26.00, 25.69, 25.15, 24.28, 21.21, 21.06, 20.70, 20.66, 20.16, 20.07, 16.25 ppm. HRMS (ESI+) m/z: 1169.6491 [M]⁺, calc. for [C₇₃H₈₉N₂O₁₁]⁺ = 1169.6461.

2.7 (CD₃)₂SO

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.70 (s, 1H), 7.66 (s, 1H), 7.12 (s, 2H), 6.88 (s, 7H), 6.74 (s, 5H), 6.03 (s, 1H), 5.65 – 5.45 (m, 2H), 3.77 – 3.49 (m, 42H), 2.39 (s, 6H), 2.34 (s, 3H), 2.25 (s, 6H), 2.22 (s, 3H), 1.32 – 1.15 (m, 2H), 0.85 – 0.58 (m, 2H), 0.04 – -0.27 (m, 2H), -1.15 (dt, *J* = 16.7, 8.2 Hz, 2H), -1.56 – -1.88 (m, 2H) ppm. ¹³C NMR (101 MHz, DMSO-*d*₆) δ 153.80, 151.00, 150.22, 139.63, 139.02, 138.45, 136.03, 132.88, 132.72, 132.59, 130.25, 130.17, 130.12, 129.86, 129.68, 129.61, 129.28, 128.55, 127.91, 127.29, 126.51, 123.05, 122.93, 122.82, 121.02, 115.16, 113.77, 79.69, 72.43, 71.87, 70.26, 57.57, 55.91, 49.30, 47.99, 47.54, 47.46, 31.19, 30.16, 29.80, 29.50, 29.11, 25.84, 25.69, 25.63, 25.47, 23.81, 21.18, 21.08, 20.78, 19.74, 19.70, 16.41, 16.34 ppm.

2.4.1.15. Procedure for Axle Equivalent of 2.7

Procedure as per compounds **2.4a-2.4c**. column chromatography on silica gel (chloroform:methanol 98:2) to afford axle of **2.7** as a white solid (95 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 7.66 (s, 1H), 6.94 (s, 1H), 6.86 (s, 2H), 6.74 (s, 2H), 5.52 (s, 2H), 4.35 (t, *J* = 7.4 Hz, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.23 (s, 9H), 2.17 (s, 3H), 2.15 (s, 6H), 1.95 (p, *J* = 7.7 Hz, 2H), 1.79 – 1.65 (m, 2H), 1.60 – 1.45 (m, 2H), 1.45 – 1.31 (m, 2H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 153.57, 139.93, 138.00, 135.65, 132.82, 130.36, 129.96, 129.29, 125.17, 122.85, 121.01, 77.61, 71.89, 50.28, 48.07, 30.21, 30.14, 26.15, 25.66, 21.03, 20.64, 20.06, 16.22 ppm. HRMS (ESI+) m/z: 419.3083 [M]⁺, calc. for [C₂₈H₃₉N₂O]⁺ = 419.3057.

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Chapter 3

Expanding the Synthetic
Scope of
Pillar[5]arene/Imidazole
[n]Rotaxanes

3.1. Introduction

Fluorescent moieties have been used to great effect as components of MIM-based supramolecular architectures. Fluorescent markers such as naphthalimides, pyrenes and anthracenes have been used to monitor macrocycle shuttling and the binding of a macrocycle to specific stations. Fluorescent MIMs show promise in applications such as optical bio-imaging and in monitoring drug delivery.

3.1.1. Fluorescence in [n]Rotaxanes

3.1.1.1. Monitoring Shuttling with Fluorescence.

Absorbance and fluorescence have been used to monitor the progress of shuttling along rotaxanes in a number of systems.¹ Tian and co-workers reported a light driven molecular shuttle in which a rod, containing an azobenzene moiety, is stoppered by two different fluorescent naphthalimide end groups. *Cis-trans* photo-isomerisation of the azobenzene unit caused a change in the shuttling behaviour of a CD macrocycle, which altered the relative fluorescence emission intensity of the two end groups.² The same research group developed this methodology further and synthesised a [2]rotaxane which demonstrated properties that resemble a lockable, double INHIBIT logic gate.³ A [2]rotaxane-based molecular shuttle with two different recognition sites, amine/ammonium and amide, was reported by Li and co-workers. One of the end groups was a tetraphenylmethane unit, acting solely as a bulky stopper, whilst the other end group was a fluorescent anthracene moiety (Figure 3.1). The macrocycle showed high selectivity for the ammonium station when protonated and the amide station when deprotonated. Through the introduction of Li^+ and Zn^{2+} cations a similar switching of the macrocycle position was achieved. These independent movement processes were accompanied by distinct fluorescent responses from the anthracene. Fluorescence ranged from complete repression (protonated) to low level (deprotonated), medium level (presence of Li^+) and high level (presence of Zn^{2+}) emission.⁴ In a similar system, Li and co-workers utilised the photo-isomerisation of spiropyran to control molecular shuttling through

switching between photo-isomers that form hydrogen bonds of different strengths with an isophthalamide-based macrocycle.⁵ In this example, the movement of the macrocycle was accompanied by changes in the spiropyran absorbance which could be detected by the naked eye.

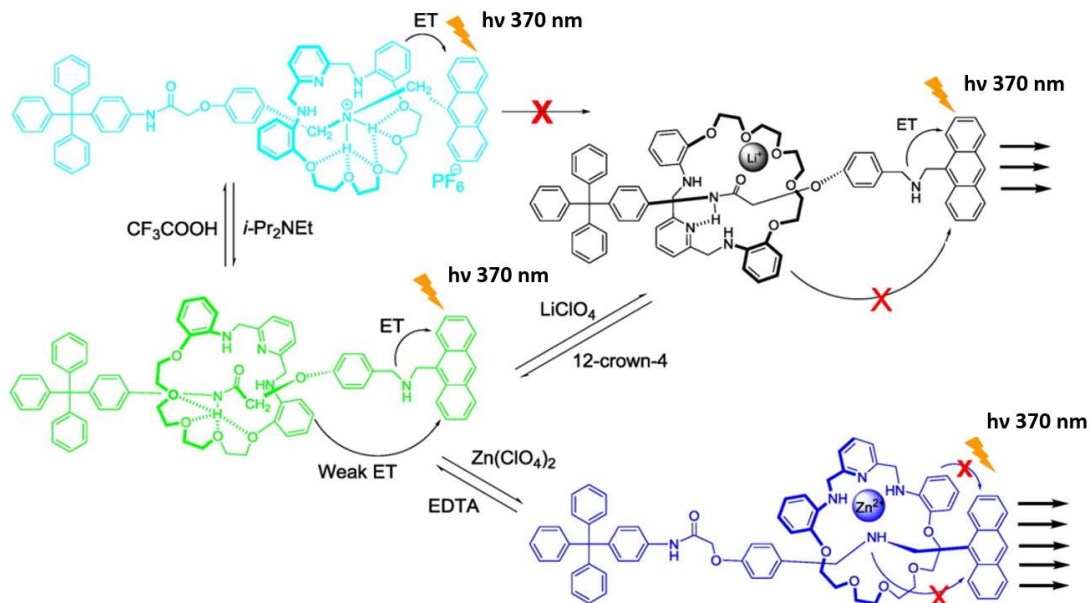


Figure 3.1: A molecular switch that can be operated by changing pH or by adding or removing Li^+ and Zn^{2+} ions. These changes are accompanied by multilevel expression of fluorescence. Adapted from Ref.⁶

3.1.1.2. [n]Rotaxanes Including Fluorescent Moieties for Potential Applications

Conjugated moieties have been integrated into [n]rotaxane architectures for a number of applications such as bio-imaging and light harvesting. For example, macrocycles have been designed to encapsulate fluorescent dyes such as squaraines. Squaraine-[2]rotaxanes have shown great potential as extremely stable near-infrared fluorescent probes for *in vitro* and *in vivo* optical imaging of live and fixed cells as well as in living mice. They are considered to be superior substitutes for currently used sulfonated carbocyanine dyes in numerous biotechnology and imaging applications.⁷ Mechanical bonds have been used in the design and synthesis of light-harvesting architectures. Pei and co-workers reported a mechanically interlocked, light-harvesting [3]rotaxane with hexyl-substituted truxene donor units tethered to a macrocycle and an oligo(*para*-phenylenevinylene) acceptor unit embedded into the axle. The interlocked topology of

the system promoted the intramolecular energy-transfer process as well as preventing intermolecular aggregation in the solid state.⁸ In a similar system, composed of a [2]rotaxane with two different chromophore stoppers (anthracene and hydroxylsubstituted tetraphenylimidazole), a dibenzo-24-crown-8 macrocycle was shown to reversibly move with changes in pH. This shuttling movement resulted in intramolecular photo-induced electron transfer from anthracene to a N-methyltriazolium station, which was accompanied by a fluorescent response.⁹

3.1.1.3. Complex Fluorescent [n]Rotaxane Switches

Different electrochemically and photochemically active components can be combined, using mechanical bonds, to build complex supramolecular architectures with multiple level stimuli responses.¹⁰ This requires a diverse toolbox of synthetic strategies which can accommodate various different components. Recently, Beer and co-workers designed and synthesised a complex four-station [3]rotaxane molecular shuttle, in which the axle component consisted of *bis*-naphthalene diimide (NDI) and *bis*-triazolium components with a central C₆₀ fullerene. The axle mechanically threaded two ferrocenyl-functionalised isophthalamide anion binding site-containing macrocycles. The relative positions of the electron donor and acceptor motifs could be altered through dynamic conformational anion recognition-mediated shuttling (Figure 3.2). Detailed photophysical analysis showed an on/off switchable emission response induced by anion binding. This was rationalised by considering the electron transfer processes and the formation of a C₆₀ fullerene/NDI-based charge-separated state.¹¹

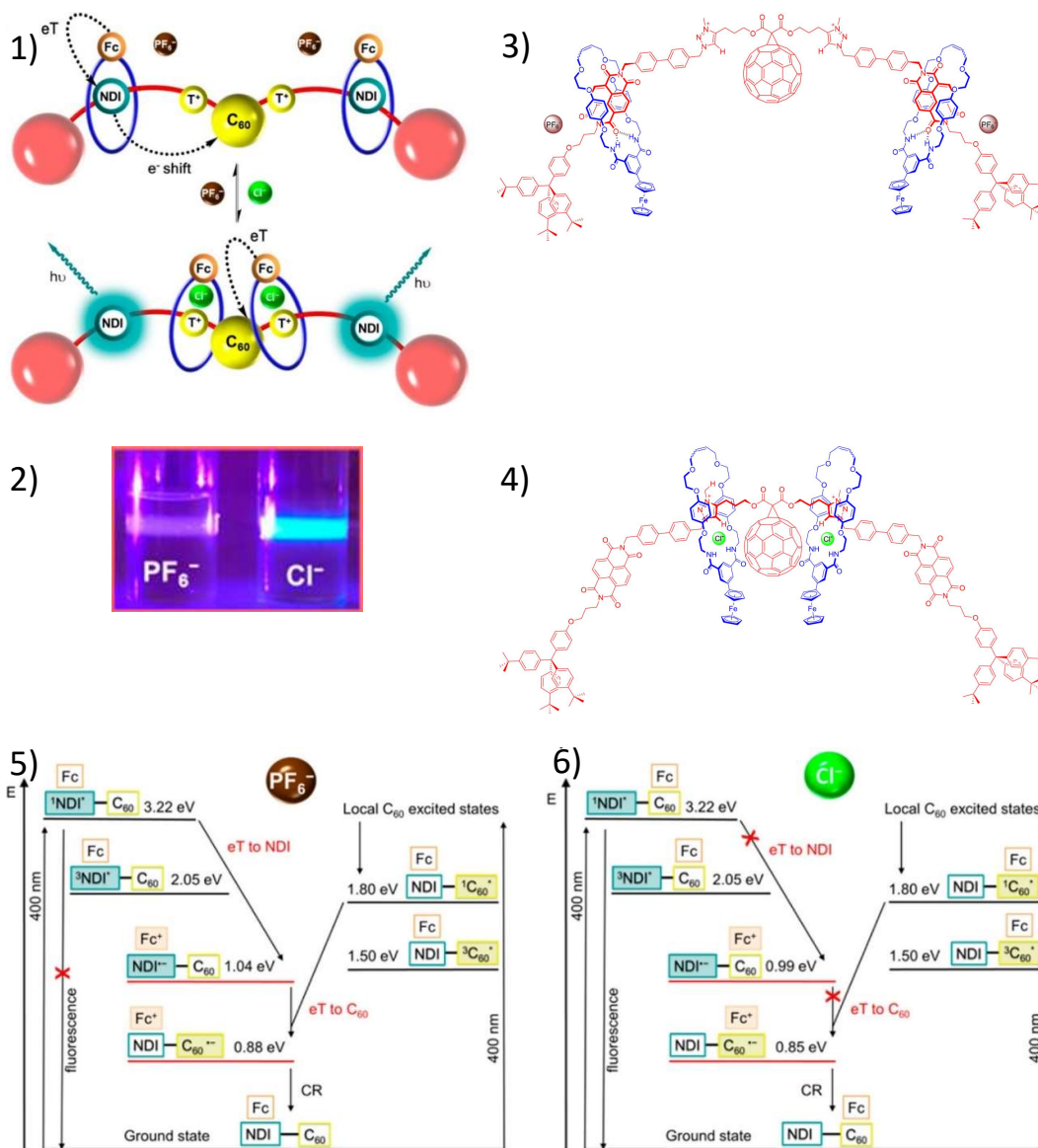


Figure 3.2: 1) Schematic of Beer and co-worker's dynamic, four station C_{60} fullerene-containing [3]rotaxane shuttle showing the NDI fluorescence response and electron transfer processes switchable via anion-induced molecular motion. 2) Visual difference in fluorescence between PF_6^- and Cl^- anions. Chemical structure and conformation of said [3]rotaxane with 3) PF_6^- and 4) Cl^- anions. Proposed energy level diagrams of the photoinduced processes with 5) PF_6^- and 6) Cl^- anions. NDI = naphthalene diimide, T⁺ = triazolium, Fc = ferrocene, CR = charge recombination, and eT = electron transfer. Adapted from Ref. ¹¹

Through the development of complex synthetic strategies, higher-order interlocked structures that include photochemical and electrochemical components can be developed. It is of particular importance that these systems exhibit large amplitude molecular motion and positional integrity

between conformations. Understanding the communication pathways between appropriately functionalised interlocked components and how these adjust with conformational changes plays a vital role in the development of photoactive switchable devices.¹²

3.1.2. Fluorescence in Pillar[5]arenes

3.1.2.1. Fluorophore Functionalised Pillar[5]arenes in Pseudorotaxane Sensors

Pillar[5]arenes functionalised with fluorescent moieties have been used as sensors for complexation. The first example of this was reported by Stoddart and co-workers who synthesised a pyrene mono-functionalised pillar[5]arene which was quenched by alkylamine binding.¹³ A more complex di-functionalised pillar[5]arene, bearing an ammonium and a fluorescent anthracene group, was reported by Yang and co-workers. Due to the dual-functionality of these pillar[5]arenes, they formed double-threaded supramolecular dimers (Figure 3.3). This specific conformation restricted the motion of the fluorescent dye moieties, which resulted in an enhanced fluorescence emission. Changes in solvent, pH, temperature or anion caused disassociation of this topology, followed by significant quenching.¹⁴ Recently, Ma and co-workers described a pillar[5]arene functionalised with two tetraphenyl ethylene moieties which formed [3]pseudorotaxanes with a dithienylethylene guest, containing two cyano-triazole branches. A photochromism reaction of the dithienylethylene unit resulted in on/off fluorescent switching.¹⁵

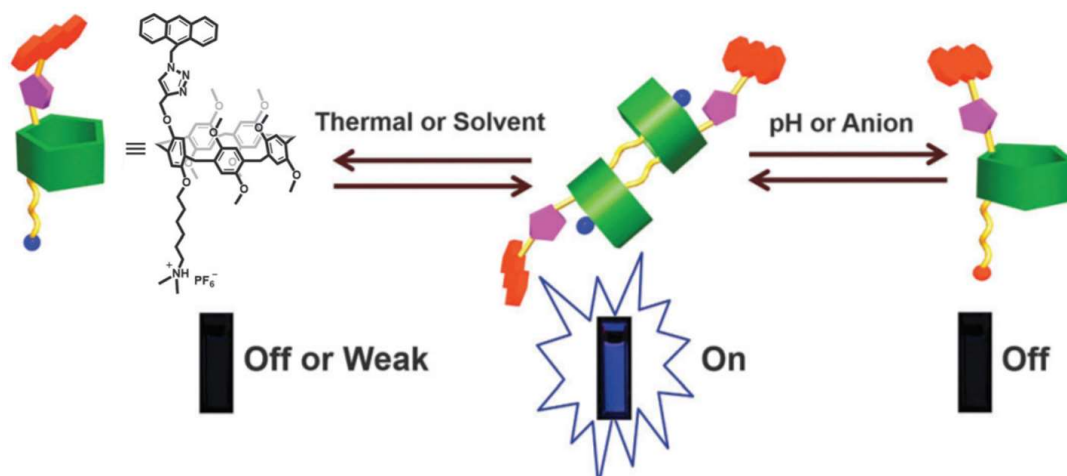


Figure 3.3: Structure and topology of a dual function pillar[5]arene showing switchable fluorescence emission upon exposure to different external stimuli: thermal, solvent composition, pH and anion. Adapted from Ref.¹⁴

Different fluorescent moieties have been included in the construction of pillar[5]arene-based supramolecular polymers, as part of both host and guest components. Variation of the fluorescent components has led to pillar[5]arene-based polymers that exhibit a range of different fluorescent colours.¹⁶ Similarly, Wang and co-workers reported linear pillar[5]arene-modified conjugated polymers showing anion-responsive fluorescence with an *n*-octylpyrazinium salt guest.¹⁷

3.1.2.2. Fluorophore Functionalised Pillar[5]arenes in [n]Rotaxanes

Despite the numerous examples of pillar[5]arenes bearing fluorescent moieties outlined above, examples of these utilised in MIMs are extremely rare. More commonly, fluorescent pillar[5]arene-based [n]rotaxanes make use of the fluorescent constituent as a bulky terminal group of the axle. A BODIPY chromophore has been used as such a terminal group in an imidazolium-pillar[5]arene-based [2]rotaxane which was used to fabricate a fluorescent supramolecular gel. Jiang and co-workers demonstrated that the fluorescence of this gel was dependent upon multiple stimuli such as temperature, solvent polarity and exposure to acid/base vapours.¹⁸ Neirengarten and co-workers reported a highly fluorescent [2]rotaxane in which the axle contained a porphyrin stopper and the pillar[5]arene component was functionalised with ten

peripheral Zn(II)-porphyrin moieties.¹⁹ In a more application orientated approach, Huang and co-workers described a complex [2]rotaxane in which tetraphenylethene (donor fluorophore) and triphenylphosphonium (mitochondria-targeting agent) moieties were employed as stoppering groups. The pillar[5]arene was functionalised with the anti-cancer therapeutic agent doxorubicin (DOX). The interlocked structure allowed the different components, each with a specific function, to be combined into one molecule. The product [2]rotaxane lit up mitochondria specifically, with excellent targeting ability and superior photostability (Figure 3.4).²⁰

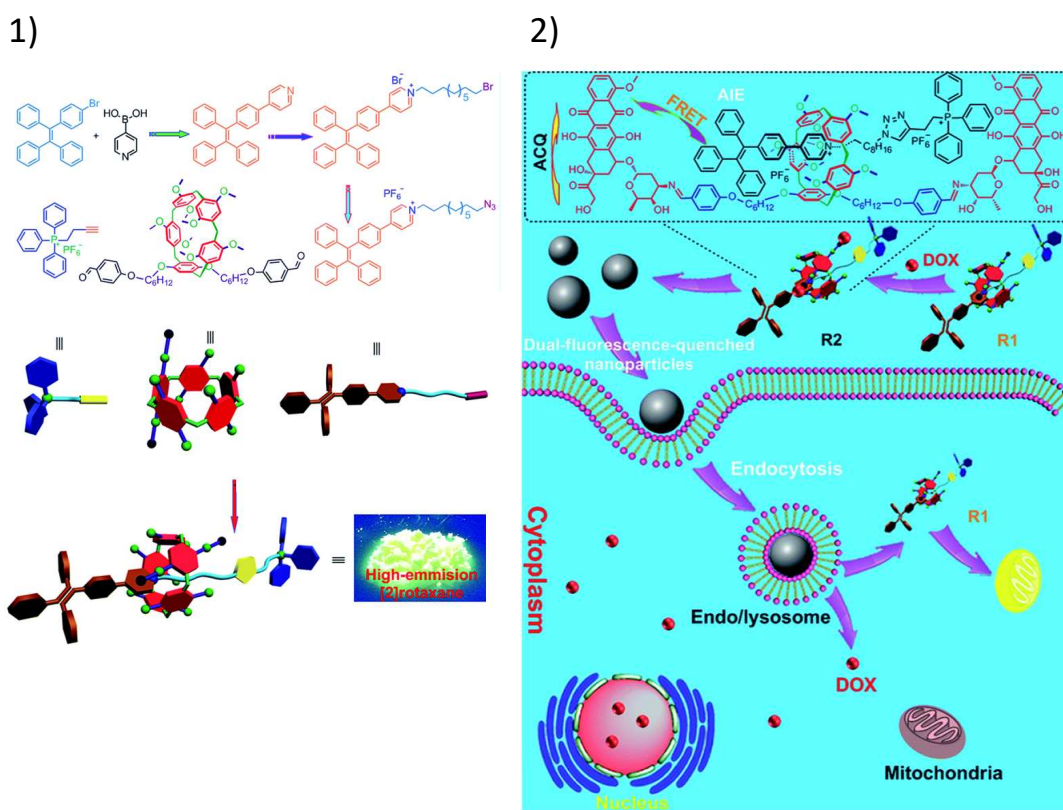


Figure 3.4: Synthetic route for the synthesis of a [2]rotaxane composed of tetraphenylethene and triphenylphosphonium moieties as stoppers as well as doxorubicin tethered to the pillar[5]arene. 2) Chemical structure of mitochondria-targeting probe-inspired prodrug (top) and the proposed cellular pathways of the dual-fluorescence-quenched nanoparticles it forms.

Adapted from Ref.²⁰

3.2. Results and Discussion

The interaction between pillar[5]arenes bearing fluorescent moieties with guest molecules can have a significant effect on the overall properties of the system. This led to the development of pillar[5]arene-based pseudorotaxanes as fluorescent switches and sensors, discussed in Section 3.1.2.3. However, the addition of stopper groups during rotaxane formation can also have a significant effect on the photophysical properties of these systems. This can be due to factors such as losing the dynamic association/dissociation of the host-guest complexes or the introduced confinement. Additionally, axle components such as stations and terminal groups can interact with the macrocycle and can have a significant effect on the properties of any moieties tethered to the pillar[5]arene. Unlike in pseudorotaxanes, there is no dynamic host-guest dissociation in MIMs due to external conditions such as solvent or temperature. However, there are significant interactions between the axle and the pillar[5]arene which can be affected by these external factors and have to be considered instead. In the development of fluorescent [n]rotaxanes for applications, investigating these effects is essential for building larger MIM systems with novel and predictable properties. The synthesis of a fluorescent di-carbazole pillar[5]arene (**DCP[5]A**) is described herein. Changes in the fluorescence upon threading with symmetric and asymmetric axles in different solvents were investigated using quantum yield measurements. These measurements revealed the complex interplay of different mechanically interlocked components. The synthetic scope for imidazole-pillar[5]arene [n]rotaxanes was developed further by varying both the rod and the stopper group components. Furthermore, supramolecular building blocks such as porphyrins, NIs and BODIPYs were utilised to build up more complex [n]rotaxanes.

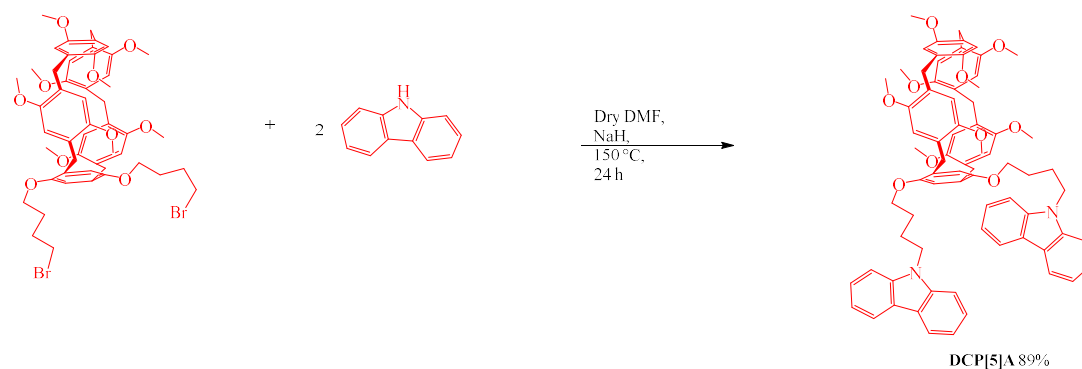
3.2.1. Synthesis of Functionalised Pillar[5]arenes

Methods for the synthesis of pillar[5]arenes, bearing a variety of functional groups, have been discussed in Section 1.1.6.3. Pillar[5]arene functionalised with two bromobutoxy groups was synthesised using a method adapted from that described in Scheme 2.2 (and discussed in Section

2.2.1). A 1:4 ratio of 1,4-*bis*-(4-bromobutoxy)benzene and 1,4-dimethoxybenzene monomers was used in the cyclisation polymerisation. In addition to the target di-functionalised product, the crude product also included unfunctionalised decamethoxypillar[5]arene (**DMP[5]A**) and pillar[5]arenes with multiple 1,4-*bis*-(4-bromobutoxy)benzene units. The desired product was successfully isolated from the mixture via multiple silica gel chromatography steps in an overall yield of 17 %.

3.2.1.1. Di-carbazole Pillar[5]arene **DCP[5]A**

Carbazole is a well-known heterocycle with unique photophysical²¹ and biological properties.²² The carbazole moiety can be functionalised at different positions²³ and carbazole-based materials are generally thermally and morphologically stable. Carbazole derivatives can possess both light emitting and hole transporting properties,²⁴ making them promising candidates for applications related to OLEDs.²⁵ Furthermore, carbazole moieties have been used in supramolecular structures such as mechanically interlocked coordination polymers. For example Zhou, Zhang and co-workers used a bent dipyridyl ligand (3,6-di(pyridin-4-yl)-9*H*-carbazole) to form complex coordination polymers with interlocked molecular rings.²⁶ Furthermore, Beer and co-workers used a 3,6-*bis*-triazolium carbazole unit as a receptor, rigid spacer and as an optical fluorescent probe for halide-selective anion recognition.²⁷ Despite the positive attributes of carbazole derivatives, examples of their use in the field of MIMs are scarce.

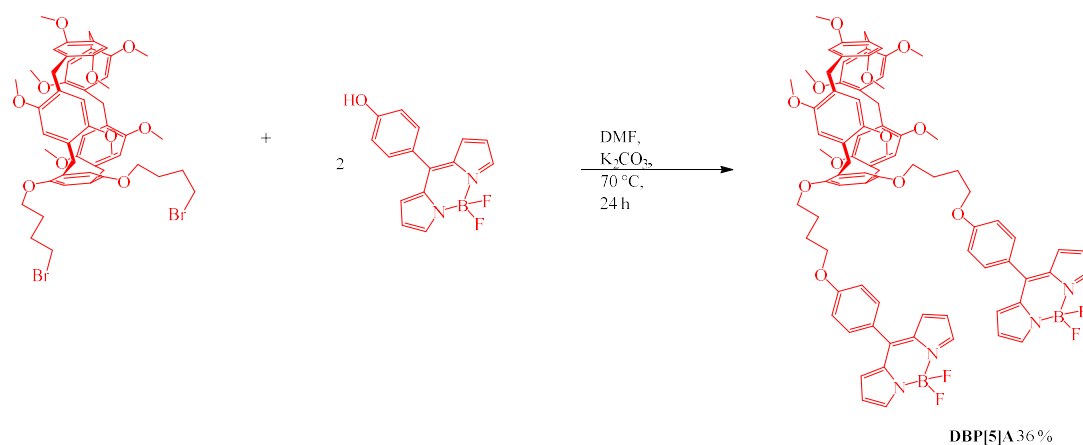


Scheme 3.1: Synthesis of di-carbazole-pillar[5]arene (**DCP[5]A**) from di-bromobutoxy-pillar[5]arene.

The pillar[5]arene cyclic structure is known to be relatively chemically stable which allows the reactivity of the alkyl-bromo groups to be exploited. Di-carbazole-pillar[5]arene (**DCP[5]A**) was synthesised from di-bromobutoxy-pillar[5]arene via a carbazole-sodium salt, generated *in situ* from sodium hydride and carbazole (Scheme 3.1). Due to the reactive nature of sodium hydride, the reaction was done under a dinitrogen atmosphere in a flame dried flask, backfilled with dinitrogen three times. Purification through silica gel chromatography gave the desired product as a white solid in a yield of 89 %. The high yield of this reaction and the commercial availability of carbazole makes this fluorescent pillar[5]arene an attractive starting point for further threading reactions.

3.2.1.2. Di-BODIPY Pillar[5]arene **DBP[5]A**

An alternative fluorescent moiety to carbazole is boron-dipyrromethene (BODIPY). BODIPY dyes are strongly UV-absorbing and emit sharp fluorescent peaks with high quantum yields. Furthermore, they are relatively robust to changes in polarity, pH and other physical conditions.²⁸ Modifications of their structure enables tuning of their photo-physical characteristics which has been utilised in applications such as protein and DNA labelling.²⁹



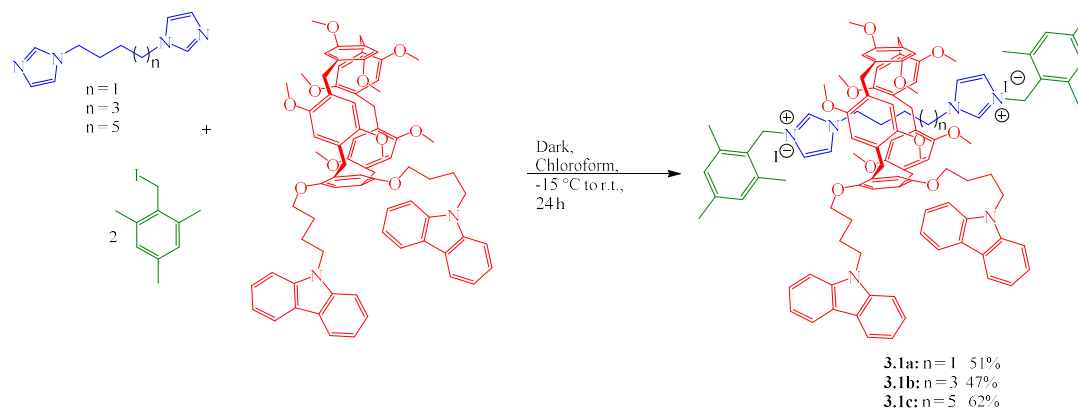
Scheme 3.2: Synthesis of di-BODIPY-pillar[5]arene (**DBP[5]A**) from di-bromobutoxy-pillar[5]arene and 4-hydroxyphenyl-BODIPY.

4-Hydroxyphenyl-BODIPY was synthesised in two steps via the 4-(hydroxyphenyl)-dipyrromethane intermediate, according to a known procedure,³⁰ in an overall yield of 28 %. 4-Hydroxyphenyl-BODIPY was reacted with di-bromobutoxy-pillar[5]arene in DMF in the presence of potassium carbonate at 70 °C to afford di-BODIPY-pillar[5]arene, **DBP[5]A**, in a 36 % yield (Scheme 3.2). **DBP[5]A** is a less attractive candidate for further threading reactions than **DCP[5]A** because it requires the synthesis of 4-hydroxyphenyl-BODIPY, making the overall yield of **DBP[5]A** significantly lower.

3.2.2. Effect of Threading on Fluorescence

The synthesis and behaviour of pillar[5]arene-based, two station molecular shuttles was discussed in Chapter 2. To investigate the effect of threading on the fluorescence of **DCP[5]A**, a series of **DCP[5]A**-containing two station molecular shuttles, analogous to **2.1a-2.1c**, were synthesised (Scheme 3.3). Our studies aim to establish the effect of threading on the fluorescence and any variation in emission across the different axle lengths or possible correlations between the shuttling motion and quantum yield.

3.2.2.1. Synthesis of Two Station **DCP[5]A**-based Molecular Shuttles



Scheme 3.3: Synthesis of **DCP[5]A**-based [2]rotaxanes, **3.1a-3.1c** (analogues to [2]rotaxanes **2.1a-2.1c**).

The **DCP[5]A**-containing [2]rotaxanes, **3.1a-3.1c**, were synthesised using an equivalent method to that employed in the synthesis of [2]rotaxanes **2.1a-2.1c**, however the yields were lower (Scheme

3.3). The ^1H NMR spectra of [2]rotaxanes **3.1a-3.1c** showed that the positional distribution of **DCP[5]A** along the axle was comparable to that in [2]rotaxanes **2.1a-2.1c**. Additionally, further variable temperature ^1H NMR spectroscopy studies of [2]rotaxane **3.1c** (Figure 3.5) showed similar changes upon cooling to the **DMP[5]A** equivalent [2]rotaxane **2.1c**. This suggests that similar shuttling behaviour is exhibited with and without carbazole moieties present.

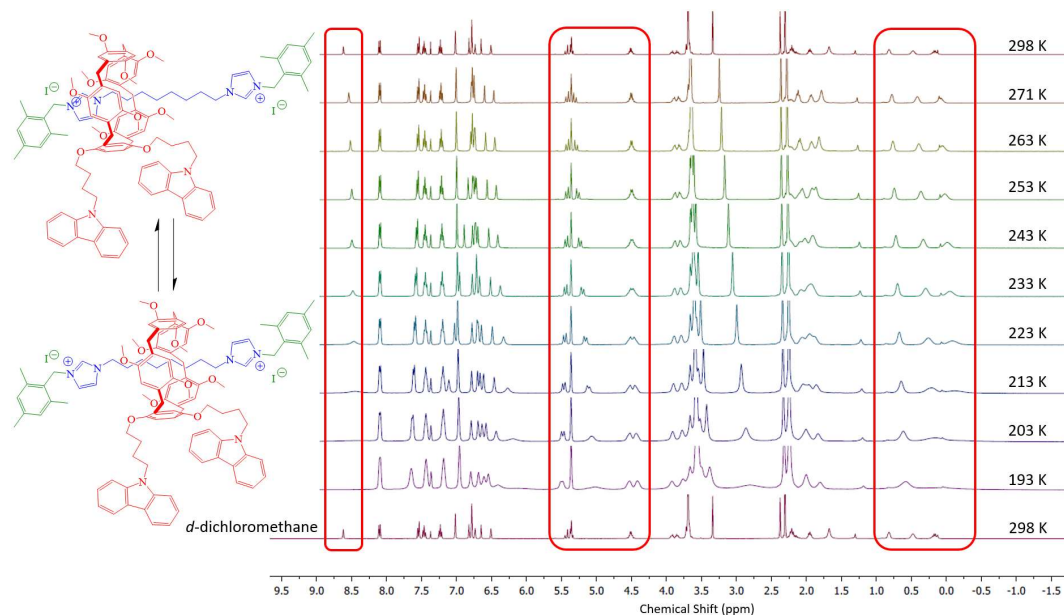
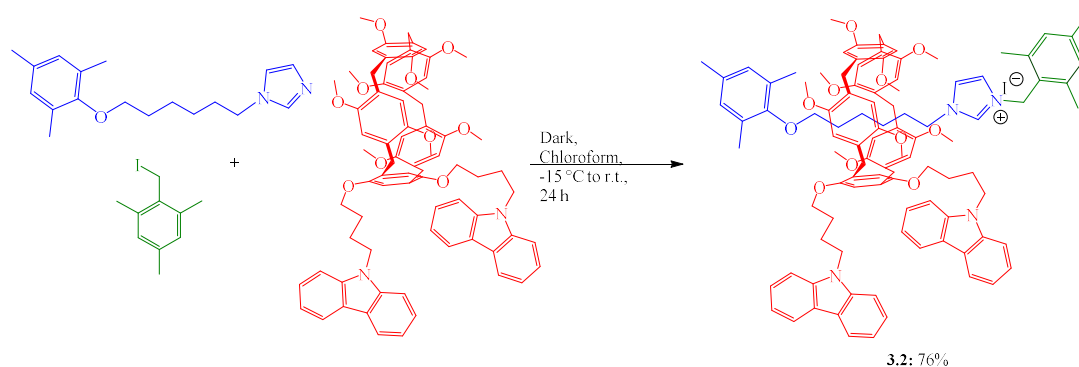


Figure 3.5: ^1H (400 MHz, CD_2Cl_2 , VT) spectra of the [2]rotaxane **3.1c** showing comparable changes in peak position to **DMP[5]A** equivalent **2.1c**, therefore indicating that shuttling of **DCP[5]A** is also faster than the timescale of the NMR experiment even at low temperature.

3.2.2.2. Synthesis of Asymmetric One Station **DCP[5]A**-based [2]Rotaxane



Scheme 3.4: Synthesis of asymmetric, one station **DCP[5]A**-based [2]rotaxane **3.2**.

One station **DCP[5]A**-based [2]rotaxane **3.2** (in which there is no shuttling) was synthesised to provide a comparison to the shuttling compounds **3.1a-3.1c**. The ^1H NMR spectrum of [2]rotaxane **3.2** showed **DCP[5]A** located around the imidazolium moiety, in a comparable position to the non-carbazole equivalent [2]rotaxane **2.7**. Together with free **DCP[5]A** and the two station [2]rotaxane **3.1a-3.1c**, a series of **DCP[5]A**-containing compounds has been synthesised and will be termed series A.

3.2.2.3. Fluorescence of **DCP[5]A**-Containing Series A in THF, Chloroform and DMSO

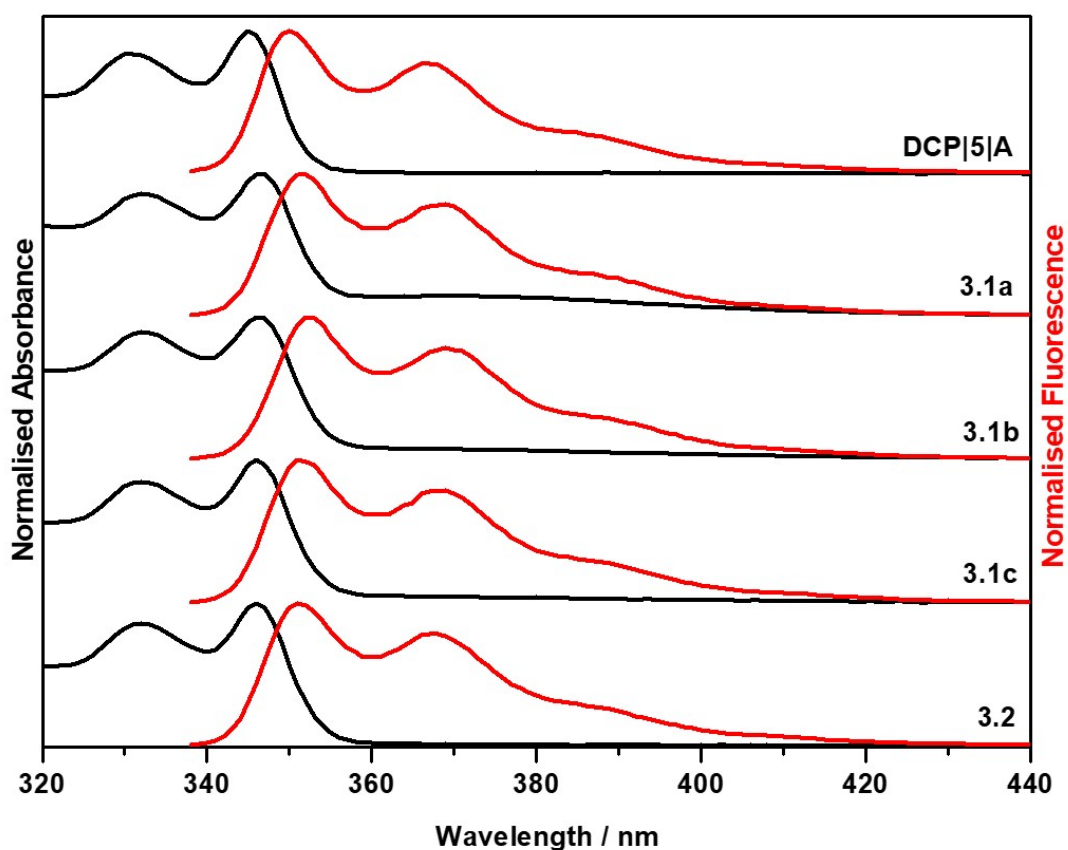
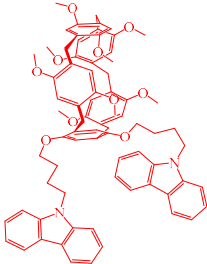
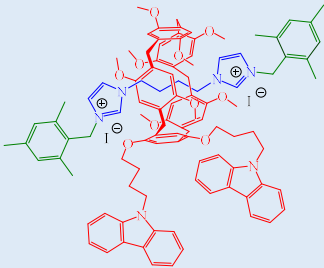
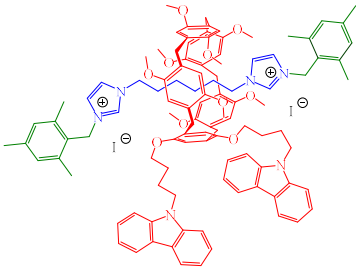
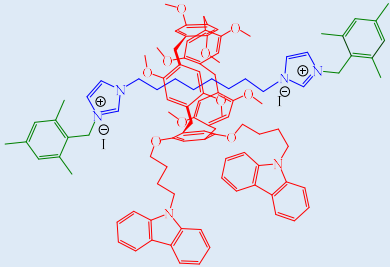


Figure 3.6: Absorbance (black) and emission (red) profiles of **DCP[5]A**-containing series A in THF (excitation 328 nm).

The absorbance spectrum of **DCP[5]A** (Figure 3.6-black) showed two distinct peaks at 346 and 332 nm. Excitation at 328 nm leads to emission (Figure 3.6-red) at 352 nm and 368 nm, with a Stokes shift of 6 nm between the most intense bands. The position, intensity and profile strongly resemble typical carbazole absorbance/emission data.³¹

Compound	Structure	Quantum Yield (Φ /%)		
		THF	Chloroform	DMSO
DCP[5]A		33	6.9	46
3.1a		4.0	3.9	45
3.1b		29	5.7	46
3.1c		6.0	4.8	47

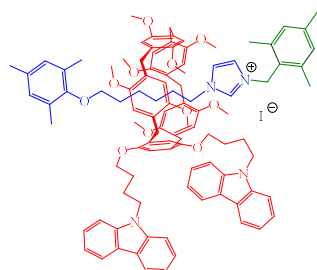


Table 3.1: Quantum yields (Φ) of series A (**DCP[5]A**) and [2]rotaxanes **3.1a-3.1c** and **3.2**) recorded in THF, chloroform and DMSO.

The quantum yields for series A were determined in THF, chloroform and DMSO (Table 3.1/Figure 3.7). A strong solvent dependant variation in the fluorescence was observed. In chloroform, the fluorescence is much weaker (with quantum yields of less than 0.1) than in THF and DMSO (with quantum yields of above 0.3). This solvatochromism of carbazole is known and has been studied extensively,³² especially in carbazole-based conjugated polymers.³³

Quantum yields of series A in THF, chloroform and DMSO

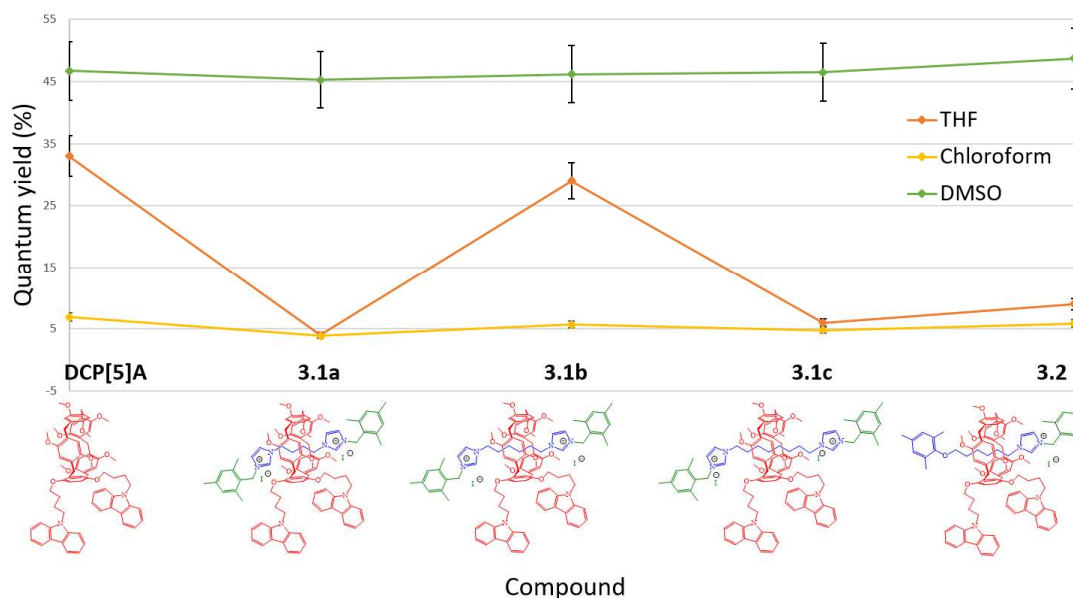


Figure 3.7: Quantum yield (Φ) of series A in THF (orange), chloroform (yellow) and DMSO (green) showing a 10 % error for each recorded value (however several values were recorded multiple times and gave values within 2 % of each other).

As anticipated, the quantum yields in chloroform are generally lower due to the aforementioned solvatochromic quenching of carbazole in this solvent. Additionally, there was little to no variation of the quantum yields in chloroform or DMSO across series A. Therefore, **DCP[5]A** and [2]rotaxanes **3.1a-3.1c** and **3.2** appear to exhibit “standard” carbazole fluorescence with no observable quenching (Figure 3.7). The fluorescence of [2]rotaxanes **3.1a**, **3.1c** and **3.2** was significantly quenched upon threading of the axle. On the other hand, in THF, [2]rotaxane **3.1b** exhibited a significantly higher quantum yield (0.29) than both [2]rotaxanes **3.1a** and **3.1c** (0.04 and 0.06 respectively). Interestingly, the carbazoles undergo significant quenching despite being separated from the conjugated system of the pillar[5]arene by four aliphatic carbons and the pillar[5]arene having no covalent attachment to the axle. This suggests that quenching occurs via a complex through-space mechanism.

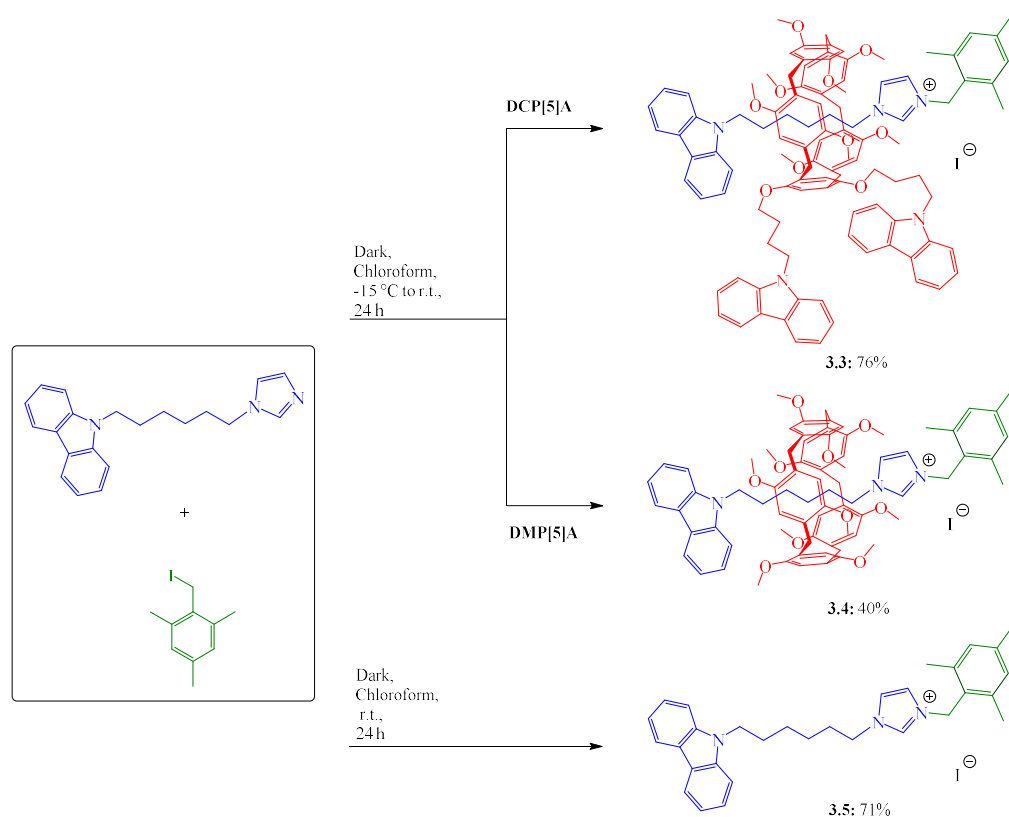
The fluorescence of [2]rotaxane **3.1b** appeared unaffected by threading and exhibited a quantum yield of similar magnitude to unthreaded **DCP[5]A**. This result was unexpected because the six carbon linker (**3.1b**) is in the middle of the series, whilst both the shorter (**3.1a**) and longer (**3.1c**) axle lengths showed significant quenching. A possible explanation can be derived by considering the shuttling motion in these systems. Cai and co-workers have recently reported a similar irregularity when calculating free energy profiles of pillar[5]arene-based, two station molecular shuttles with varying spacer lengths, discussed in Section 2.1.3. The authors evaluated the energy barrier of shuttling for spacer lengths 3-6 and found that spacer length 5 had the slowest shuttling rate.³⁴ There appears to be a correspondence between our results and these calculations, although the stations considered by Cai and co-workers were di-triazole moieties (not imidazoliums) and the solvent used for the calculations was chloroform. Nevertheless, the significant variation in carbazole fluorescence at different spacer lengths shows promise that **DCP[5]A** could be used to monitor shuttling rates in certain molecular shuttles. This is an intriguing prospect since it is currently difficult to monitor shuttling rates experimentally when they are too fast to be determined by NMR spectroscopy.

3.2.3. Axle-Macrocycle Interactions

The molecular shuttles described above demonstrate the complex interplay of components in MIMs and the significant impact threading can have on the overall properties of a system. Asymmetric [2]rotaxanes synthesised using the snapping method have been previously described in [2]rotaxanes **2.7** and **3.2**. It was envisioned that this strategy could be adapted to introduce asymmetric rods bearing additional aromatic moieties, thus providing a handle for including additional functionality to these systems. The interactions between these axle end groups and any functional groups tethered to the pillar[5]arene on the overall properties of the molecule can be profound. To investigate this, the snapping method was used to synthesise a series of [2]rotaxanes. Axles bearing carbazole and naphthalene imide moieties were combined with **DCP[5]A/DMP[5]A** and the unthreaded axle compounds were also synthesised. Interaction between the different components was evaluated, through quantum yield measurements.

3.2.3.1. Carbazole Terminated Axle Compounds

3.2.3.1.1. Synthesis



Scheme 3.5: The synthesis of [2]rotaxane **3.3** composed of three inequivalent carbazole moieties (top), [2]rotaxane **3.4** with carbazole terminated axle threading **DMP[5]A** macrocycle (middle) and carbazole terminated axle **3.5** (bottom).

The carbazole-imidazole rod (Scheme 3.5-blue) was synthesised in two steps from carbazole. Firstly a reaction of carbazole with sodium hydride and 1,6-dibromohexane in DMF at 80 °C, and secondly a reaction with potassium carbonate and imidazole in DMF at 80 °C. After each step silica gel chromatography was used to isolate the product in a yield of 55 % and 97 %, respectively. The carbazole-imidazole rod and 1.1 equivalents of **DCP[5]A** were dissolved in a minimum amount of chloroform and cooled to -15 °C. Subsequently, 2-(iodomethyl)-1,3,5-trimethylbenzene was added and the mixture was stirred overnight, under the exclusion of light at room temperature. Purification through silica gel chromatography gave [2]rotaxane **3.3** as a pale yellow solid in a yield of 76 %. [2]Rotaxane **3.4** and axle **3.5** were synthesised utilising the same method using **DMP[5]A** in a yield of 40 % and in the absence of a macrocycle in a yield of 71 %.

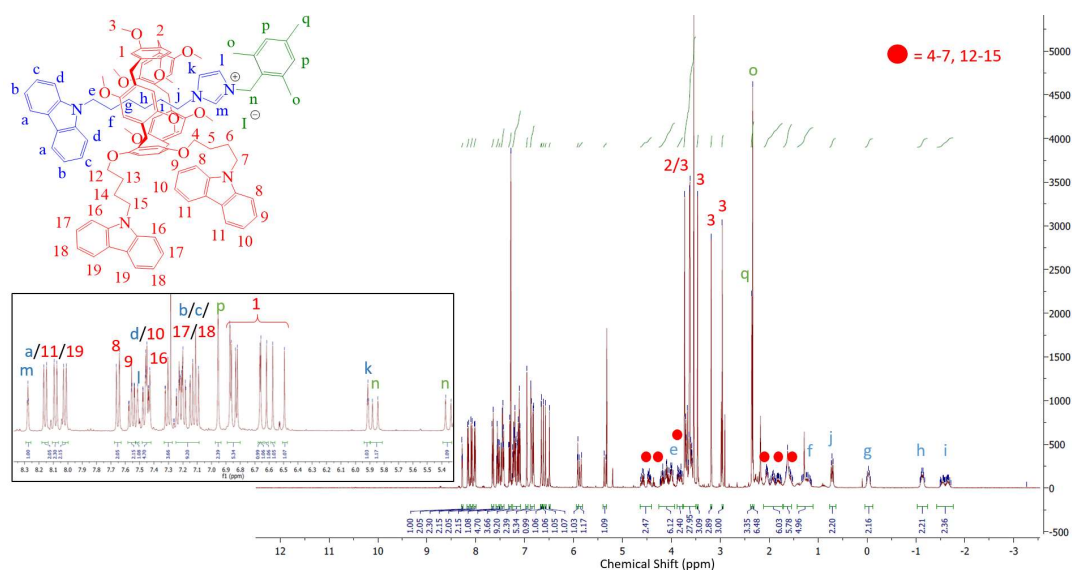
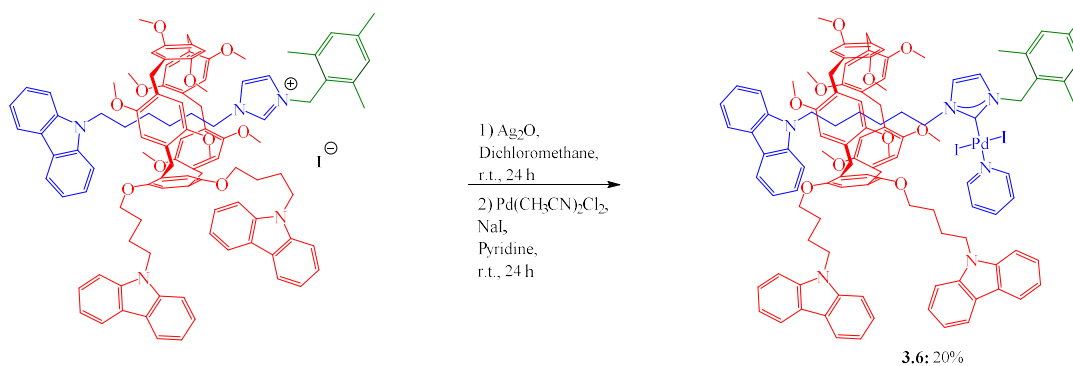


Figure 3.8: Assigned ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of [2]rotaxane **3.3**, inset shows aromatic region. (Blue/green: axle, red: DCP[5]A).

The ^1H NMR spectrum of [2]rotaxane **3.3** is shown in Figure 3.8. Due to the asymmetric nature of the axle, the two pillar[5]arene rims are different. Therefore the aromatic region shows the three carbazoles in inequivalent environments. Although this leads to a complex splitting pattern (Figure 3.8-inset), 2-D COSY NMR spectroscopy allowed the assignment of these peaks.

3.2.3.1.2. Pd(II)-Coordination



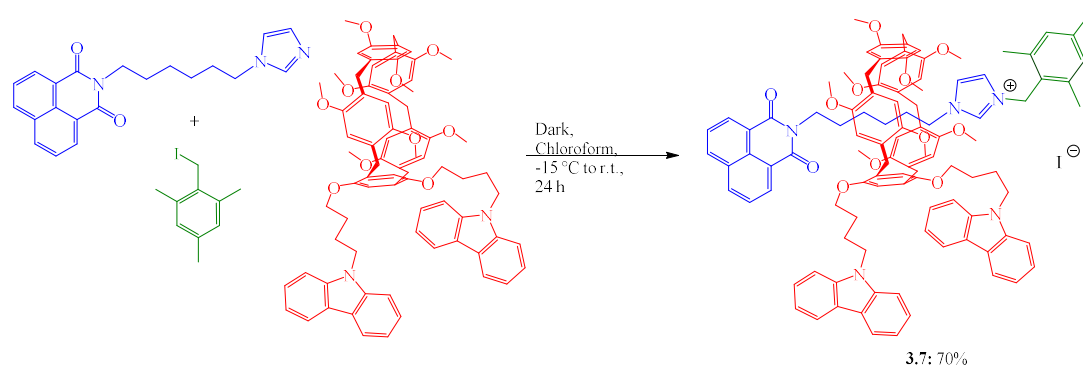
Scheme 3.6: Syntheses of Pd(II)-coordinated [2]rotaxane **3.6** through Ag(I)-coordination to the imidazolium, acting as an NHC, and subsequent transmetalation to Pd(II).

The Ag(I)/Pd(II)-coordination methodology discussed in Chapter 2 was utilised to coordinate Pd(II) to [2]rotaxane **3.3** to evaluate the robustness and investigate the effect of Pd(II)-coordination on

the fluorescence of this system (Scheme 3.6). Pd(II)-coordination was successful however, the yield in this case was 20 %, significantly lower than for Pd(II)-coordination in [2]rotaxanes **2.3a-2.3c**.

3.2.3.2. Naphthalene Imide Terminated Axle Compounds

3.2.3.2.1. Synthesis



Scheme 3.7: Synthesis of [2]rotaxane **3.7** with naphthalene imide (NI) terminated, asymmetric axle.

A third group of compounds (series C) was synthesised, containing naphthalene imide terminated axles to further probe the axle-macrocycle interactions. Naphthalene imide (NI)-imidazole rod (Scheme 3.7-blue) was synthesised in four steps from 1,6-dibromohexane using an adapted Gabriel synthesis.³⁵ Phthalimide potassium salt was reacted with an excess amount of 1,6-dibromohexane in DMF at 70 °C. The product was isolated through silica gel chromatography in a yield of 88 % before being reacted with imidazole and potassium carbonate in DMF at 80 °C. Purification by silica gel chromatography gave the product in a yield of 97 %. The phthalimide was converted to the amine using hydrazine mono-hydrate to afford the product without further purification in a yield of 91 %. Finally, the imidazole functionalised amine was reacted overnight with naphthalene anhydride in imidazole at 130 °C under a dinitrogen atmosphere. The product was isolated through silica gel chromatography as a light brown solid in a 60 % yield. [2]Rotaxane **3.7** was synthesised in an analogous procedure to the one used previously in the synthesis of [2]rotaxane **3.3** in a yield of 70 % (Scheme 3.7). The equivalent **DMP[5]A**-based NI-[2]rotaxane **3.8**

and unthreaded axle **3.9** were synthesised in yields of 77 % and 74 %, respectively. The ^1H NMR spectrum of [2]rotaxane **3.7** (Figure 3.9) exhibited a similar complex splitting to [2]rotaxane **3.3** (Figure 3.8).

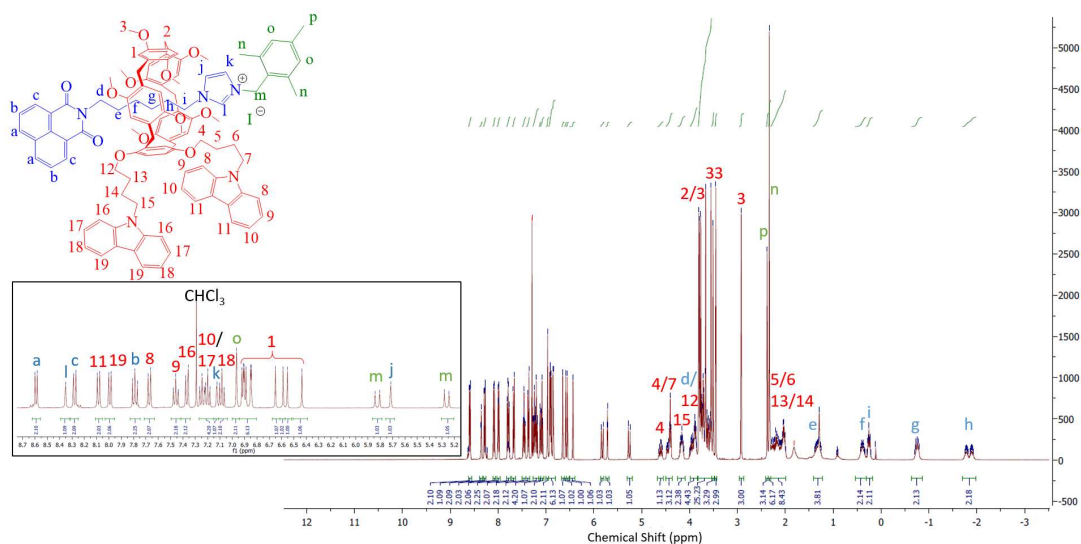


Figure 3.9: Assigned ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of [2]rotaxane **3.7**, inset shows aromatic region. (Blue/green: axle, red: **DCP[5]A**).

3.2.3.2.2. Fluorescence

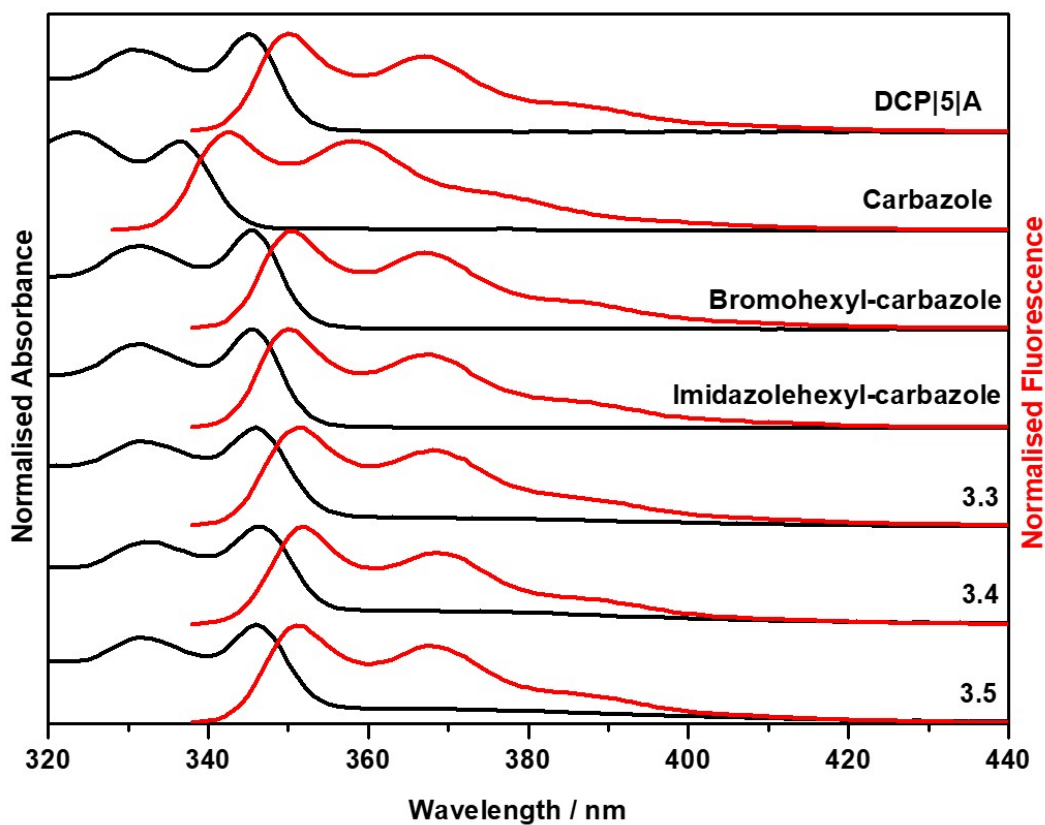
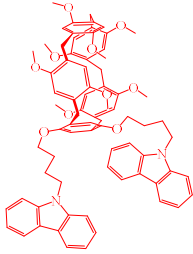
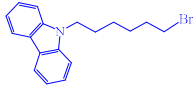
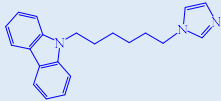
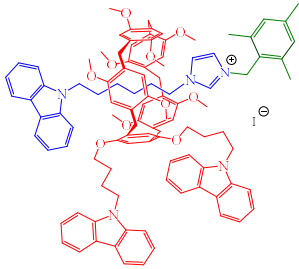
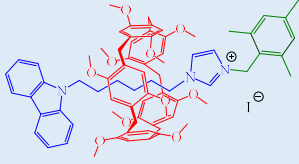
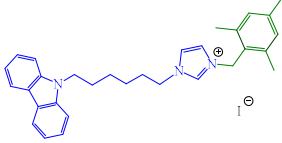


Figure 3.10: Absorbance (black) and emission (red) profiles of series B in THF (excitation 328 nm).

The absorbance and fluorescence emission spectra of **DCP[5]A**, carbazole, bromohexyl-carbazole, imidazolehexyl-carbazole, **3.3**, **3.4**, **3.5** and **3.6** were recorded in THF (Figure 3.10), DMSO and chloroform, series B. Each of the compounds in series B displayed two absorbance and two emission bands, analogous to those observed for series A.

Compound	Structure	Quantum Yield (Φ /%)		
		THF	Chloroform	DMSO
DCP[5]A		33	7.0	46
Carbazole		32	3.0	47
Bromohexyl-carbazole		30	6.0	47
Imidazolehexyl-carbazole		32	6.0	49
3.3		12	7.0	44
3.4		30	7.0	44
3.5		12	4.0	48

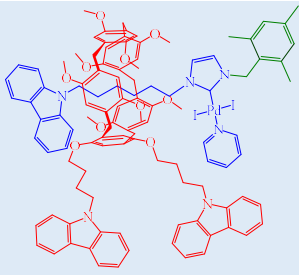
3.6		<0.1	0.2	<0.1
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Table 3.2: Quantum yields of series B (**DCP[5]A**, carbazole, bromohexyl-carbazole, imidazolehexyl-carbazole and compounds **3.3-3.6**) recorded in THF, chloroform and DMSO. (*=emission too low to record).

The quantum yields of series B were measured in THF, chloroform and DMSO (Table 3.2). In chloroform and DMSO the emission was comparable across all compounds (0.002-0.07 in chloroform and 0.44-0.49 in DMSO). Therefore, in these solvents no quenching was observed and series B exhibited typical carbazole fluorescence. This is consistent with results recorded for series A in chloroform and DMSO. On the other hand, in THF significant variation of the quantum yield across series B was observed. **DCP[5]A**, carbazole, bromohexyl-carbazole and imidazolehexyl-carbazole exhibited standard carbazole fluorescence in a range of 0.30-0.33, whilst [2]rotaxane **3.3** showed quenching to approximately 30 % of full carbazole emission with a quantum yield of 0.12. This suggests that out of the three carbazoles in this molecule, one emits fully whilst the other two are completely quenched. In contrast, [2]rotaxane **3.4** which contains a single carbazole moiety had a quantum yield of 0.30, similar to that of standard carbazole emission and therefore appears to undergo no quenching. Similar to [2]rotaxane **3.3**, the unthreaded axle **3.5**, showed partial quenching to approximately 30 % of standard carbazole emission. When considering these results, in conjunction with the fluorescence measurements for series A, it appears likely that a specific component of the system is responsible for carbazole quenching in these molecules. When the imidazolium moiety is considered as this quenching moiety, the quantum yields of series B can be rationalised as follows: in [2]rotaxane **3.3**, which exhibited absorbance of three carbazoles and emission from one carbazole, it is proposed that the imidazolium moiety quenches

the two carbazoles tethered to the pillar[5]arene. Therefore, the observed emission comes entirely from the remaining axle-based carbazole, which is too remote from the imidazolium to be quenched. Similarly, in the **DMP[5]A** equivalent [2]rotaxane **3.4** the carbazole terminating the axle is unquenched and therefore this compound exhibited full carbazole emission with no quenching. Axle **3.5** exhibited a quantum yield of approximately 30 % of full carbazole fluorescence. In the absence of **DMP[5]A** or **DCP[5]A** the alkyl linker appears to be flexible enough to allow the carbazole and imidazolium to come into close enough proximity of each other to induce partial quenching. It is therefore proposed that the quenching of fluorescence is related to the proximity of the carbazole/**DCP[5]A** to the imidazolium moiety. This is further supported by the consistent quantum yields in DMSO across series A and B. DMSO molecules strongly interact with the imidazolium moieties, preventing other components of the molecules to interact thus inhibiting any proximity dependent quenching mechanisms. It was not possible to identify any significant variations of quantum yields in chloroform because of the aforementioned lower emission of carbazole in this solvent. The fluorescence of Pd(II)-coordinated [2]rotaxane **3.6** is almost entirely quenched in THF, chloroform and DMSO. The quantum yield in chloroform was found to be 0.002 whilst in THF and DMSO the fluorescence was too weak for the quantum yield to be determined. This is likely due to the intrinsic quenching effect of heavy metals, which is well established.³⁶

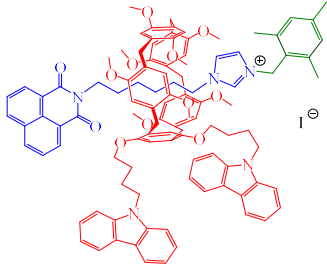
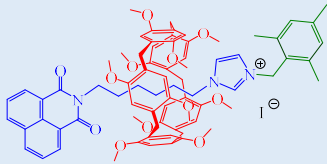
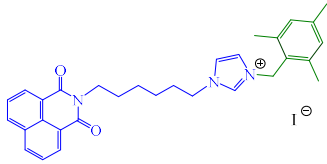
Compound	Structure	Quantum Yield (Φ /%)
		THF
3.7		0.4
3.8		0.1
3.9		0.4

Table 3.3: Quantum yields of series C (**3.7-3.9**) recorded in THF.

When considering fluorescence emission of series C, the quantum yields of systems containing NIs were found to be very low (Table 3.3). This includes the **DCP[5]A**-containing [2]rotaxane **3.7** in which exclusive emission from the NI is observed, despite excitation into the carbazole band. The introduction of an NI moiety appears to eradicate emission from all carbazoles present in the molecule, despite being on different, non-covalently bonded components. This demonstrates the great extent to which the components in [2]rotaxane **3.7** communicate and highlights the importance of carefully considering possible interactions when designing supramolecular MIMs with specific functions. NI emission is significantly lower than carbazole emission and therefore quantum yields were only recorded in THF.

3.2.3.3. Dimmer Switch

Photochromic switches are well established in the literature and frequently feature on/off modes, whilst structures with intermediate fluorescent stages are scarce.^{1, 37} Series A-C demonstrate that the arrangement of different components in specific constellations results in a specific “dimmed” fluorescence mode (30 % of full emission) as well as an on/off state (Figure 3.11). Although the system described herein is not dynamic, it does resemble a toolbox approach to building architectures with known and controllable functions, in this case fluorescence. This is further visualised by solutions of **3.7**, **3.3** and **3.4** in THF (Figure 3.12) exposed to visible and UV (355 nm) light.



Figure 3.11: Illustration showing how specific arrangements of components (top) result in off, dim and on modes of fluorescence in THF.

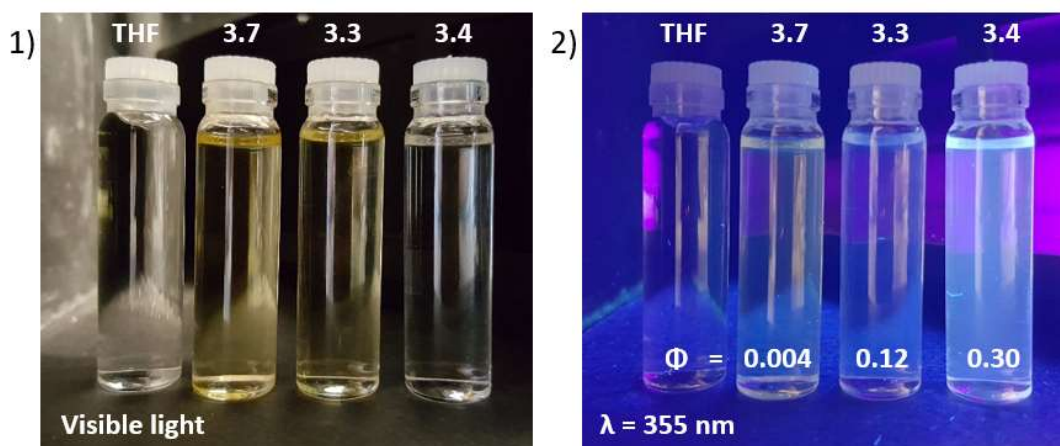
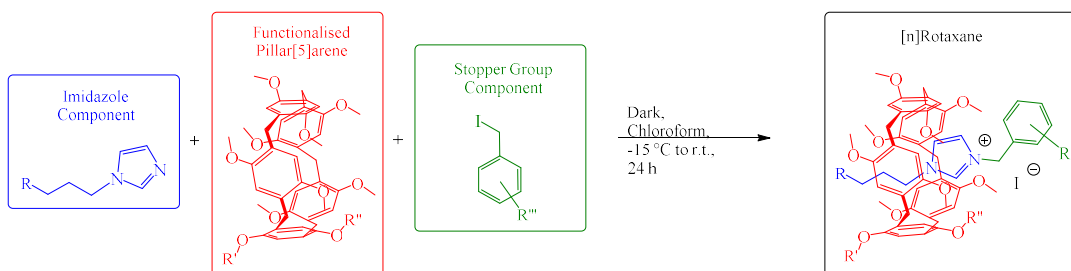


Figure 3.12: Left to right: THF, **3.7**, **3.3** and **3.4** as THF solutions ($1.91 \times 10^{-3} \text{ mol dm}^{-3}$) in 1) visible light and 2) long wave UV (355 nm).

3.2.4. Expanding Synthetic Scope

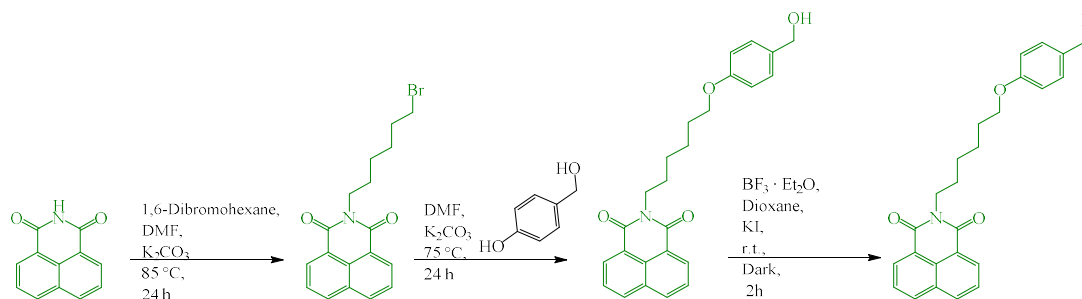
Thus far the possibility of functionalising pillar[5]arene macrocycles (with carbazole or BODIPY) and imidazole axles (with carbazole or NI) with different groups has been demonstrated. To further develop the synthetic method and complete the toolbox, varying the stopper group component was investigated (Scheme 3.8). In the imidazole-pillar[5]arene-based synthesis route, the stopper group component is required to possess two key features; firstly, sufficient steric bulk to prevent dethreading and secondly, iodo-methyl-benzene functionality to readily react with the nucleophilic dinitrogen of the imidazole.



Scheme 3.8: General synthetic strategy for the formation of pillar[5]arene/imidazolium-based-[n]rotaxanes. The imidazole (blue) and stopper group (green) components can be functionalised with different groups. Additional functionality can be introduced by using functionalised pillar[5]arenes (red).

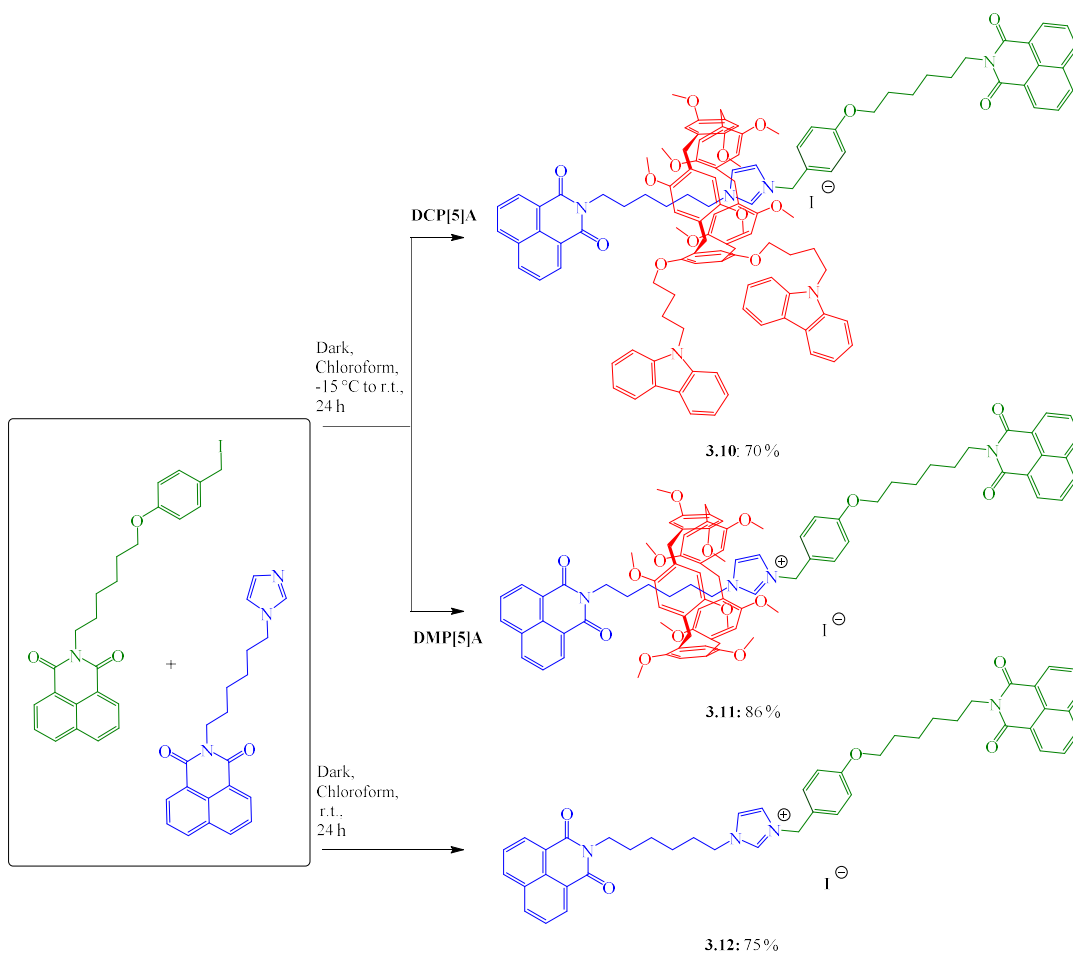
3.2.4.1. Asymmetric [2]Rotaxanes

3.2.4.1.1. Synthesis



Scheme 3.9: Three step synthesis of 1-(iodomethyl)-4-hydroxybenzyl-NI-hexane from 1,8-naphthalimide.

For the development of alternative stopper groups with easily varied terminating groups, commercially available 4-hydroxybenzyl alcohol was deemed a good starting point. The hydroxymethyl group is required for later conversion to the equivalent iodo group whilst the more reactive phenol can be selectively functionalised, for example with bromo-alkyls. To demonstrate this approach, 1-(iodomethyl)-4-alkyloxybenzene was synthesised in three steps (Scheme 3.9). Firstly, 1,8-naphthalimide was stirred at 85 °C with an excess amount of 1,6-dibromohexane and potassium carbonate to afford the product in a 40 % yield after purification through silica gel chromatography. Further reaction with 1.1 equivalents of 4-hydroxybenzyl alcohol and potassium carbonate in DMF at 75 °C and purification through silica gel chromatography gave the subsequent product as a white solid in a yield of 80 %. This was converted to the equivalent iodo compound using the same method as for the 2-(iodomethyl)-1,3,5-trimethylbenzene stopper group, previously described. To minimise decomposition, the product was used straight away in the synthesis of compounds **3.10-3.12** (Scheme 3.10), in an analogous procedure to that used in the synthesis of compounds **3.3-3.5** and **3.7-3.9**.



Scheme 3.10: Synthesis of [2]rotaxanes **3.10** (top) and **3.11** (middle), via the snapping method, and axle **3.12** using an NI terminated 1-(iodomethyl)-4-alkyloxybenzene stopper group component (green).

The assigned ^1H NMR spectrum of [2]rotaxane **3.10** (Figure 3.13) shows that **DCP[5]A** resides entirely on the imidazolium part of the rod (blue). The phenolic moiety is sterically not bulky enough to lock the pillar[5]arene on one side however it does act as a constraint. In conjunction with the strong pillar[5]arene/imidazolium interactions, this makes the energy barrier big enough to prevent **DCP[5]A** from slipping across to the other side (green).

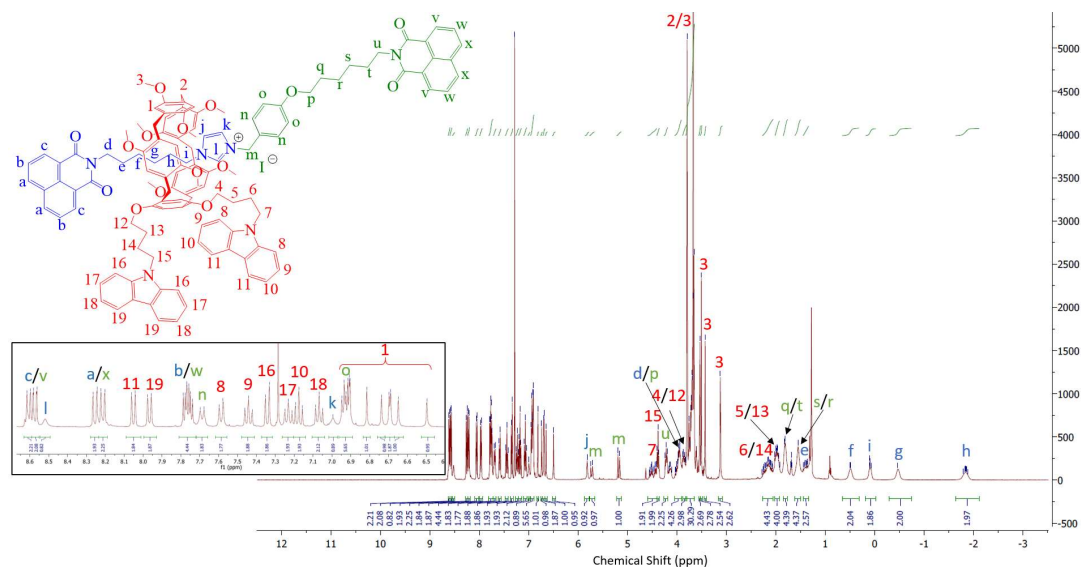


Figure 3.13: Assigned ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of [2]rotaxane **3.10**, inset shows aromatic region (blue/green: axle, red: DCP[5]A).

In this example NI was used as the terminal group however, this synthesis route demonstrates that the stopper group can be functionalised with a variety of functional groups. This method for the synthesis of asymmetric [2]rotaxanes shows great promise for introducing different moieties on each of the two end groups of the axle. Important for the design and synthesis of MIMs with multiple functionality, especially when tailoring them towards specific applications.

3.2.4.1.2. Fluorescence

Quantum yield measurements of compound **3.10-3.12** (series D) in THF showed emission exclusively from NI (Table 3.4). This includes [2]rotaxane **3.10**, which contains two carbazole moieties showing consistent quenching behaviour to [2]rotaxane **3.7** in series C.

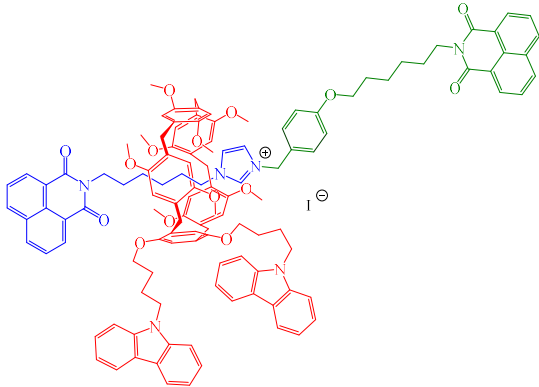
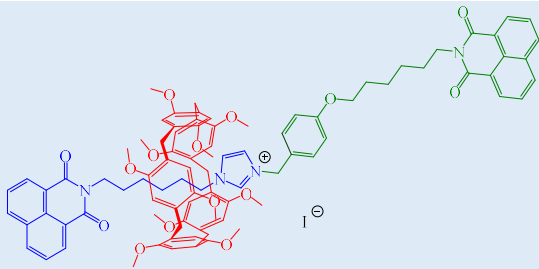
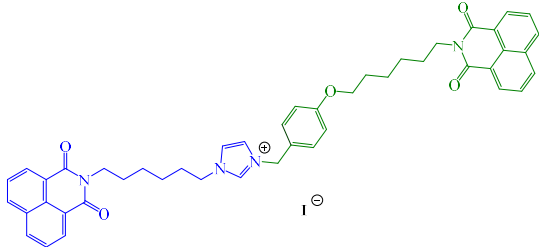
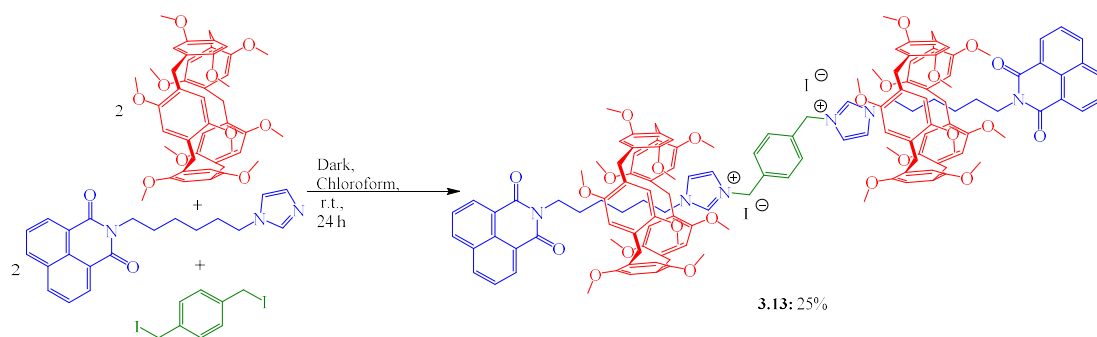
Compound	Structure	Quantum Yield (Φ /%)
		THF
3.10		0.4
3.11		0.4
3.12		0.4

Table 3.4: Quantum yields of series D (**3.10-3.12**) recorded in THF.

3.2.4.2. Symmetric [3]Rotaxane



Scheme 3.11: Synthesis of [3]rotaxane **3.13** using a 1,4-*bis*-(iodomethyl)benzene linker (green).

Following on from the encouraging results of using a 4-hydroxybenzyl alcohol-based stopper group, an alternative approach using a di-functional linking unit was considered (Scheme 3.11). The aim of this was to further develop the synthetic methodology and investigate the prospect of building higher order structures such as $[n > 2]$ rotaxanes and $[n]$ catenanes. A di-iodo group (1,4-*bis*-(iodomethyl)benzene, Scheme 3.11-green) was synthesised in one step from 1,4-phenylenedimethanol in a procedure analogous to previously used iodinations. Functionalised imidazoles provide a broad scope as terminating groups because they are easily accessible and robust. One equivalent of di-iodo-linker was added to two equivalents of imidazole functionalised NI (Scheme 3.11-blue) and three equivalents of **DMP[5]A** under the same conditions previously used for threading reactions. The product was isolated, using silica gel chromatography, as a pale yellow solid in a yield of 25 %. The structure of [3]rotaxane **3.13** was confirmed by ^1H NMR, ^{13}C NMR and 2-D NMR spectroscopy. The ^1H NMR spectrum of [3]rotaxane **3.13** (Figure 3.14) shows that the two NI terminating groups and the two **DMP[5]A**s are in identical environments, which demonstrates the high symmetry of the molecule.

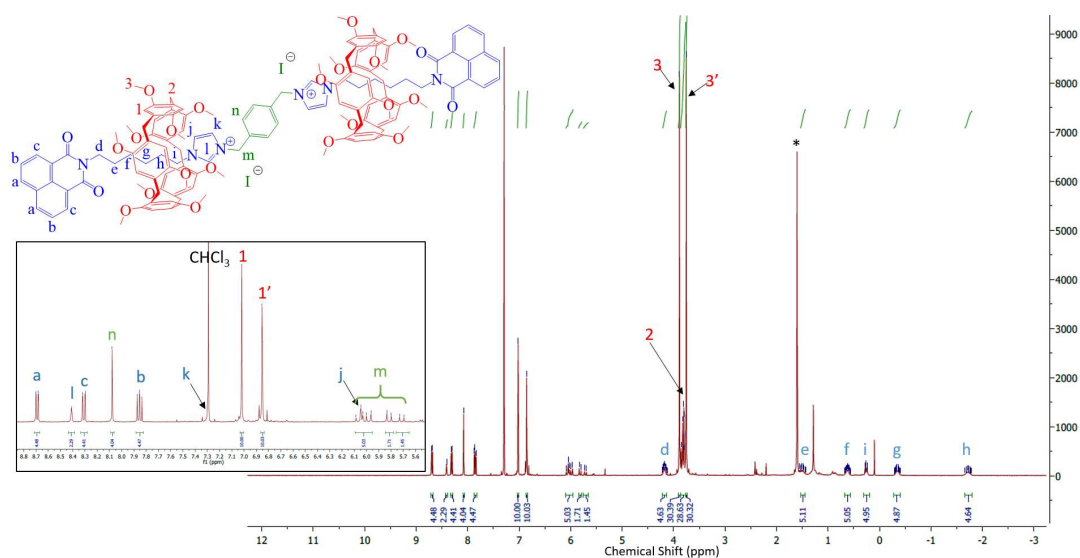


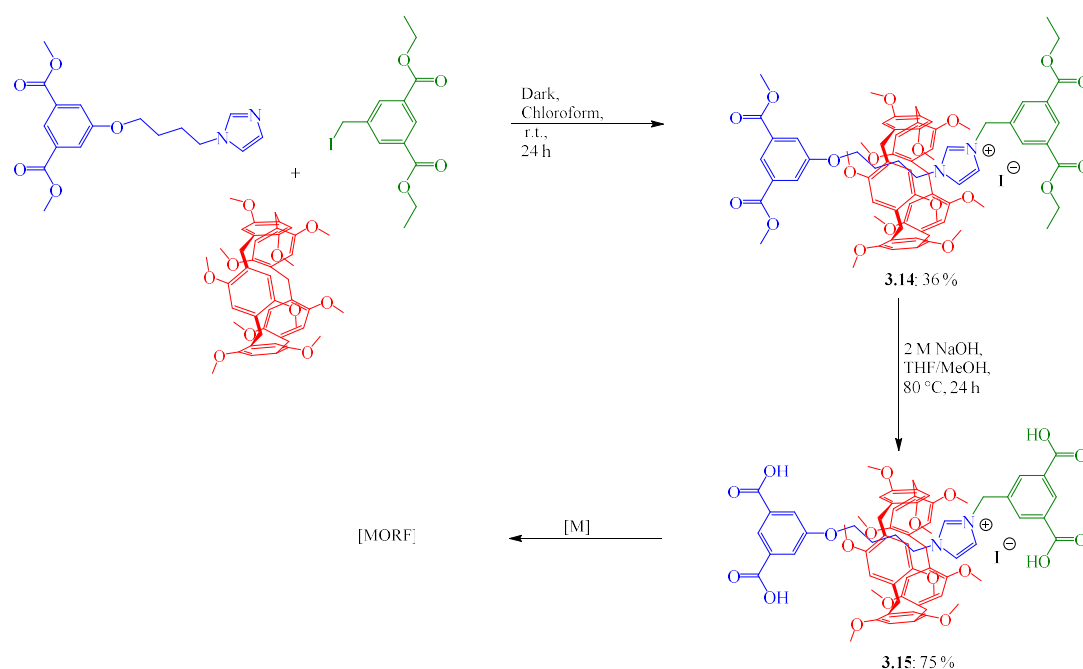
Figure 3.14: Assigned ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of [3]rotaxane **3.13**, inset shows aromatic region (blue/green: axle, red: **DMP[5]A**).

Despite the relatively low yield, this approach provides a good method for synthesising symmetric [n]rotaxanes with excellent control of axle end groups. Furthermore, there is the possibility of including functionalised pillar[5]arenes as a way to introduce additional scope to these compounds.

3.2.4.3. Di-Carboxylic Acid Stoppered [2]Rotaxane

One of the primary challenges faced by the MIM domain of chemistry is its relevance to real life applications. One way to address this is to use MIMs in conjunction with other areas of chemistry that have a high applicability. Such an area is metal-organic frameworks (MOFs). Similar to MIMs, MOFs are one of the most prominent areas of chemical research. It is therefore unsurprising that combining these areas of high interest is a very attractive proposition. Stoddart, Yaghi and co-workers demonstrated the formation of 2-D coordination polymers³⁸ and MOFs³⁹ using catenane linkers with carboxylic acid termini in 2010. Loeb and co-workers followed by publishing the first metal-organic rotaxane framework (MORF) in 2012⁴⁰ and have since gone on to publish a number of additional MORF systems,⁴¹ including a molecular shuttle which operates within a MORF.⁴² Although a variety of [2]rotaxane ligands have been demonstrated by Loeb and co-

workers, the macrocycle components used are all crown ether-based. Crown ethers have a rich history in supramolecular chemistry however, different functionalities and properties can be introduced by developing [n]rotaxane ligands composed of alternative macrocycles such as pillar[5]arenes. Recently, a step in this direction was made by Liu, Shi and co-workers who described [n]rotaxane coordination polymers composed of cucurbit[6]urils and *bis*-carboxylic acid linkers.⁴³ There is tremendous potential for systems combining MIMs and MOFs and imidazole-pillar[5]arene-based [n]rotaxanes allow excellent control over the axle terminating groups. It was therefore envisioned that the terminal axle groups could be tailored to include functional groups such as carboxylic acids, which can coordinate metals.



Scheme 3.12: Synthesis of tetra-ester-[2]rotaxane **3.14**, containing two di-ester groups and the conversion of these to di-carboxylic acids in the synthesis of tetra-carboxylic acid-[2]rotaxane **3.15**.

Tetra-ester-[2]rotaxane **3.14** was synthesised from di-ester-imidazole component (Scheme 3.12-blue) and di-ester stopper group component (Scheme 3.12-green). The ester groups were converted to the equivalent carboxylic acid groups through a sodium hydroxide deprotection. This synthetic route was chosen because the ester groups enhance solubility allowing for

straightforward purification of tetra-ester-[2]rotaxane **3.14** through silica gel chromatography. Tetra-carboxylic acid-[2]rotaxane **3.15** was not soluble in either pure chloroform or pure methanol, therefore NMR spectroscopy was performed in a 1:1 mixture of chloroform and methanol. This selective solubility is likely due to the presence of both non-polar (**DMP[5]A**) and highly polar groups (carboxylic acids) within the same molecule. Due to the presence of an imidazolium cation and carboxylic acid groups in the same molecule it is possible that this molecule exists as a zwitterion. Crystals were obtained by solvent evaporation from a solution containing **3.15** and zinc nitrate in acidified methanol and the crystal structure was determined by Mark Newman (Figure 3.15).

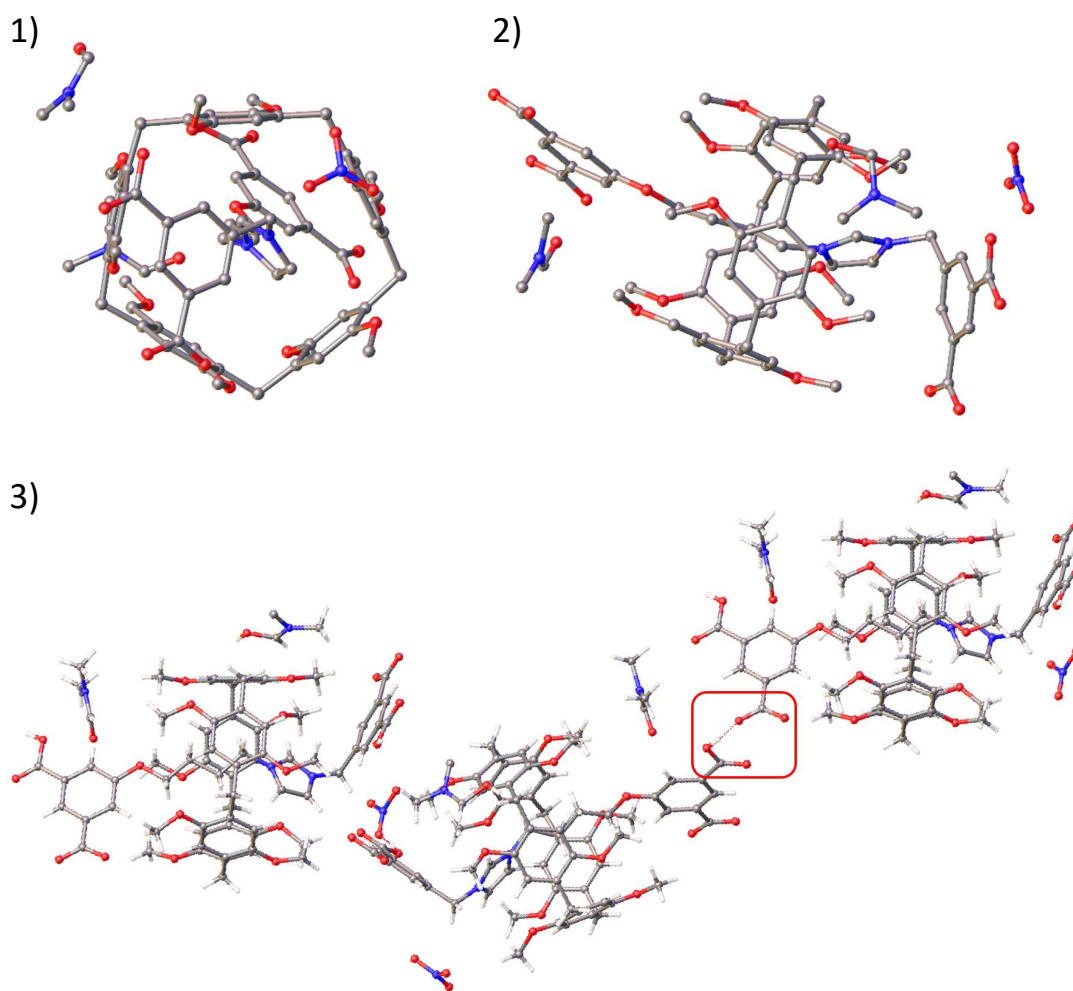


Figure 3.15: Crystal structure of tetra-carboxylic acid-[2]rotaxane **3.15** showing NO_3^- anions and DMF solvent molecules, hydrogens omitted for clarity. 1) end-on view, 2) side view and 3) packing and hydrogen bonding (highlighted) between the terminating carboxylic acid groups.

It was anticipated that tetra-carboxylic acid-[2]rotaxane **3.15** would form MORFs with a variety of metals. Thus, it would provide a versatile and novel synthesis method, enabling a range of [n]rotaxane linkers to be built. Additionally, functionalising the pillar[5]arene component could permit tuning of material properties and provide a handle for post-coordination reactions. Furthermore, pre- or post-coordination introduction of metals such as Ag(I) and Pd(II) (described in Chapter 2), to the imidazolium of the [2]rotaxane linker could provide an approach for synthesising materials with interesting properties for applications such as catalysis. Tetra-carboxylic acid-[2]rotaxane **3.15** exhibited pH dependent water solubility (Figure 3.16), making

it an interesting potential candidate for medical applications, for example in rotaxane-based drug delivery systems. The pH dependent water solubility provided by the di-carboxylic acid end groups, combined with the carbazole-containing pillar[5]arene (discussed early in this chapter) also bears the potential for a pH dependant fluorescence switch, in which fluorescence is switched on with an increase in solubility. Studies into the synthesis of MORFs are ongoing in the Champness research group.

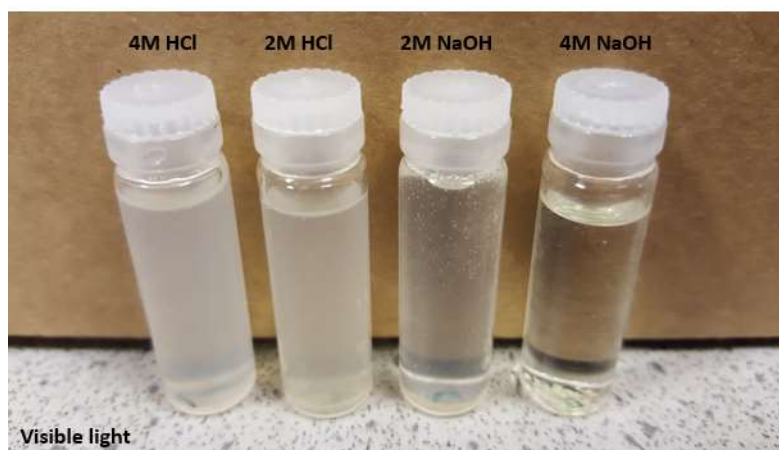
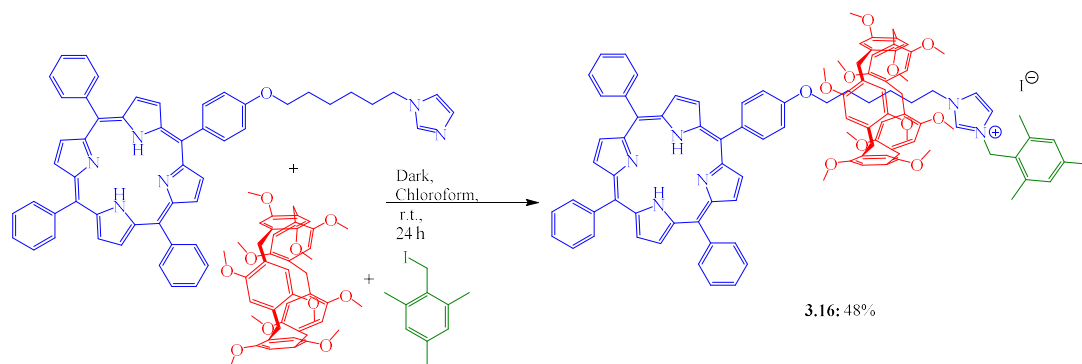


Figure 3.16: pH dependent water solubility of tetra-carboxylic acid-[2]rotaxane **3.15**.

3.2.4.4. Porphyrin-Based [n]Rotaxanes

Porphyrins are a strongly coloured group of heterocyclic macrocyclic compounds. They occur naturally, most famously in the protein haemoglobin.⁴⁴ Furthermore, porphyrins are key building blocks in the construction of supramolecular systems⁴⁵ and can be found at the forefront of research into applications such as artificial photosynthesis⁴⁶ and self-assembled nanoreactors.⁴⁷ Therefore, the incorporation of porphyrins into pillar[5]arene/imidazole-based [n]rotaxanes is an attractive proposition that opens the door to a number of potential applications.

3.2.4.4.1. Porphyrin-Based [2]Rotaxane **3.16**



Scheme 3.13: Synthesis of porphyrin [2]rotaxane **3.16**.

An asymmetric porphyrin, bearing a hexyl-imidazole and three phenyl groups was synthesised using a statistical approach (Scheme 3.13). Imidazole-hexyl-benzaldehyde was synthesised in two steps. Firstly, 4-hydroxybenzaldehyde was reacted with 1,6-dibromohexane and potassium carbonate in DMF at 80 °C. After purification, using silica gel chromatography, the product was reacted with imidazole under analogous conditions. Imidazole-hexyl-benzaldehyde and phenylbenzaldehyde were reacted in a 1:3 ratio following a known literature procedure.⁴⁸ Post-cyclisation manipulations are often low yielding and therefore the imidazole was introduced prior to porphyrin formation. Although imidazole and pyrrole have similar structures, the imidazole did not appear to interfere with the porphyrin cyclisation. The statistical approach is a one pot reaction in which the difficulty lies in the isolation of the products. However, the mono-imidazole isomer was successfully obtained through column chromatography on silica gel in a 10 % yield. The hexyl-imidazole bearing porphyrin showed good solubility in chloroform and reacted with pillar[5]arene and 2-(iodomethyl)-1,3,5-trimethylbenzene in an analogous manner to previously described threading reactions. The porphyrin-containing [2]rotaxane **3.16** was isolated as a purple solid through column chromatography on silica gel in a 48 % yield and the structure was confirmed by NMR spectroscopy (Figure 3.17).

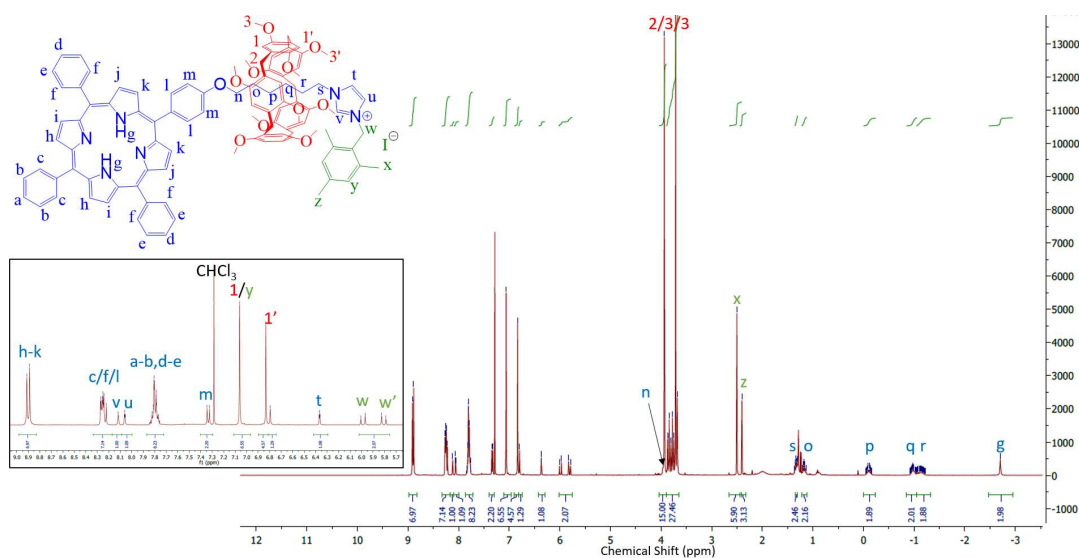
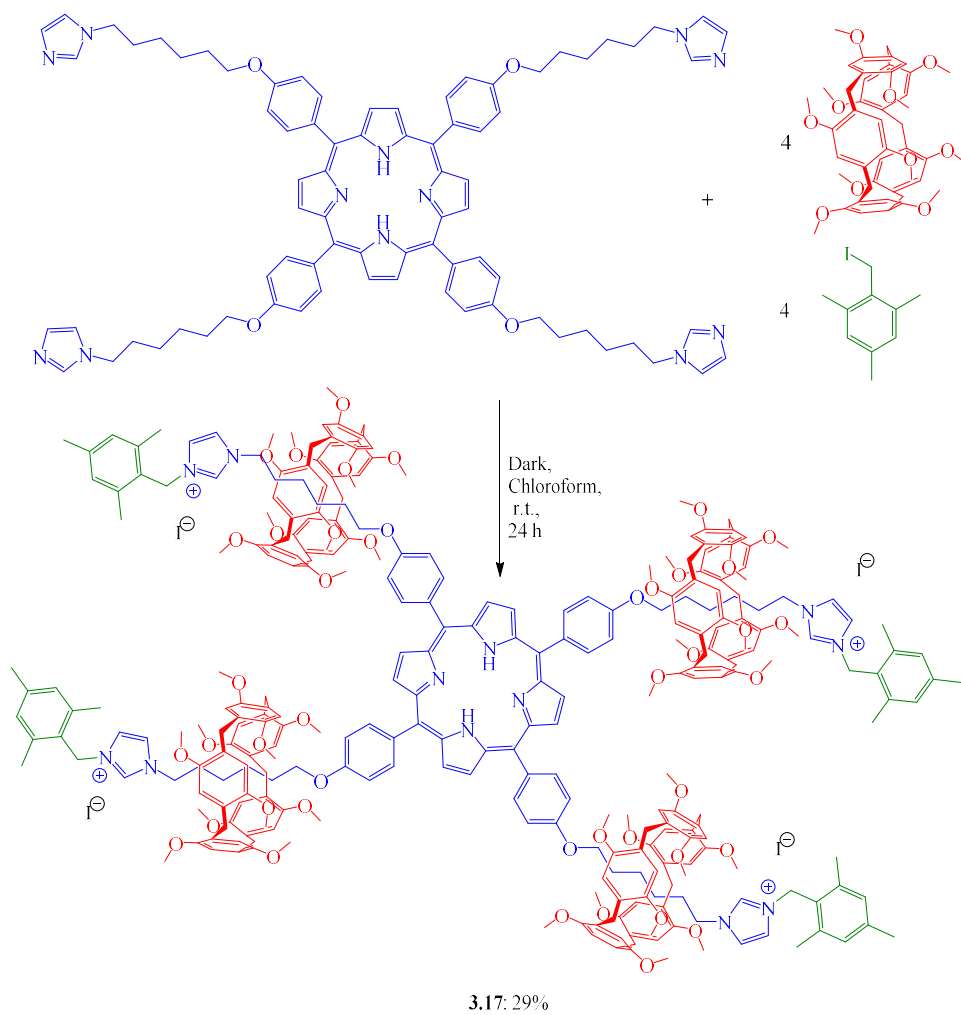


Figure 3.17: ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of porphyrin [5]rotaxane **3.16**.

3.2.4.4.2. Porphyrin-Based [5]Rotaxane **3.17**

Tetra-hexyl-imidazole-porphyrin was synthesised from imidazole-hexyl-benzaldehyde using the same methodology as described above for the mono-hexyl-imidazole porphyrin. Tetra-butyl-imidazole-porphyrin was also synthesised but showed poor solubility in chloroform which made purification and further threading reactions difficult. Tetra-hexyl-imidazole-porphyrin was reacted with five equivalents of **DMP[5]A** and 2-(iodomethyl)-1,3,5-trimethylbenzene under analogous conditions to previously described threading reactions. The product mixture was purified through column chromatography on silica gel to afford porphyrin [5]rotaxane **3.17** as a purple solid in a 29 % yield (Scheme 3.14). Threading and stoppering on all four imidazoles was evident from the ^1H NMR spectrum (Figure 3.18), which showed the corresponding integration ratios between peaks associated to the different components. Furthermore, relatively few peaks in the ^1H NMR spectrum and lack of more complex splitting patterns confirms the high symmetry of the molecule which is only possible if all four porphyrin arms are chemically equivalent.



Scheme 3.14: Synthesis of porphyrin [5]rotaxane **3.17**.

The synthesis of [5]rotaxane **3.17** provides a basis for building up higher order structures and shows that porphyrin functionality can be introduced into pillar[5]arene/imidazole-based [n]rotaxanes. It also further demonstrates the versatility of the synthesis approach described herein.

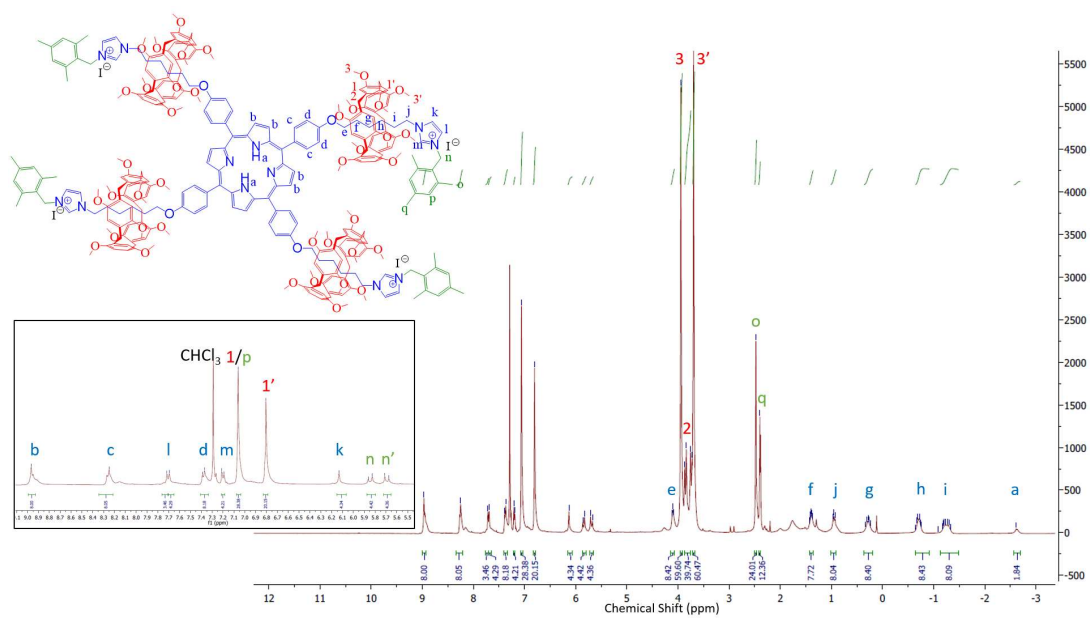
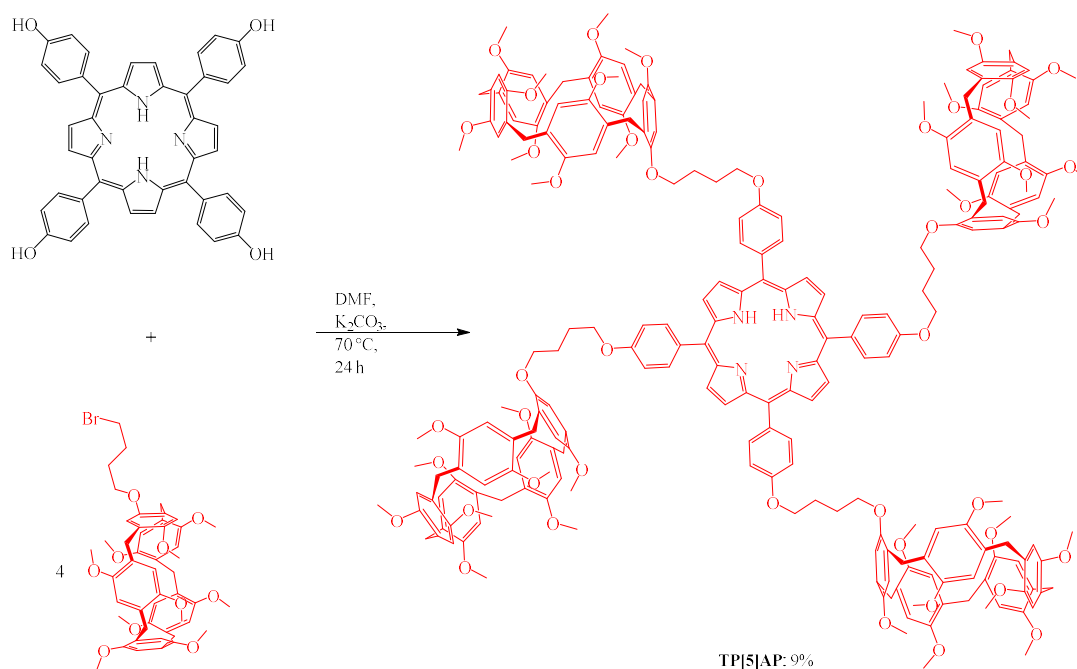


Figure 3.18: ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of porphyrin [5]rotaxane **3.17**.

3.2.4.4.3. Porphyrin Tetra-Pillar[5]arene **TP[5]AP**



Scheme 3.15: Synthesis of tetra-pillar[5]arene porphyrin **TP[5]AP**.

An alternative approach to the imidazole bearing porphyrins described above was used for the challenging synthesis of a porphyrin bearing four pillar[5]arenes. The porphyrin core was

synthesised prior to introducing the pillar[5]arene functionality because yields of both bromo-pillar[5]arene and porphyrin cyclisations are very low. Tetra-phenol-porphyrin was synthesised from 4-hydroxybenzaldehyde using an adapted literature procedure (Scheme 3.15).⁴⁸⁻⁴⁹ The reaction yield of 8 % was attributed to low solubility of the 4-hydroxybenzaldehyde starting material and the tetra-phenol product, which hindered purification. Bromo-pillar[5]arene was tethered to the phenol alcohols on the tetra-phenol-porphyrin using potassium carbonate in DMF at 80 °C. Tetra-pillar[5]arene-porphyrin (**TP[5]AP**) was isolated as a purple solid through column chromatography on silica gel in a 9 % yield. The structure of the product was confirmed through ¹H NMR (Figure 3.19), ¹³C NMR and 2-D NMR spectroscopy studies. However, due to the low overall yield of the synthesis it was not taken forward for further threading reactions.

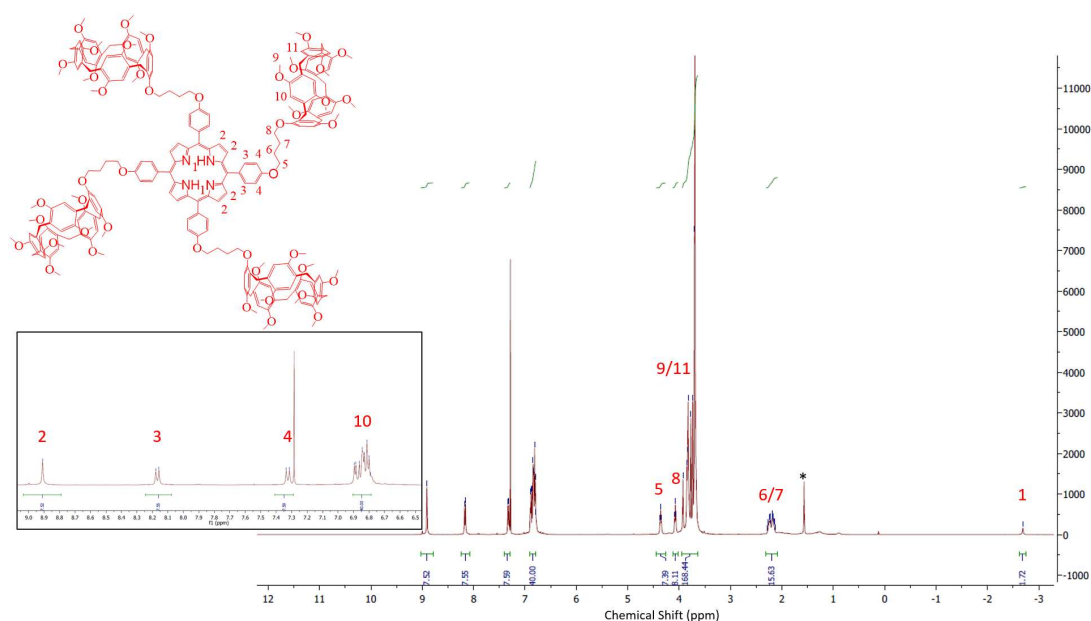


Figure 3.19: ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of **TP[5]AP**.

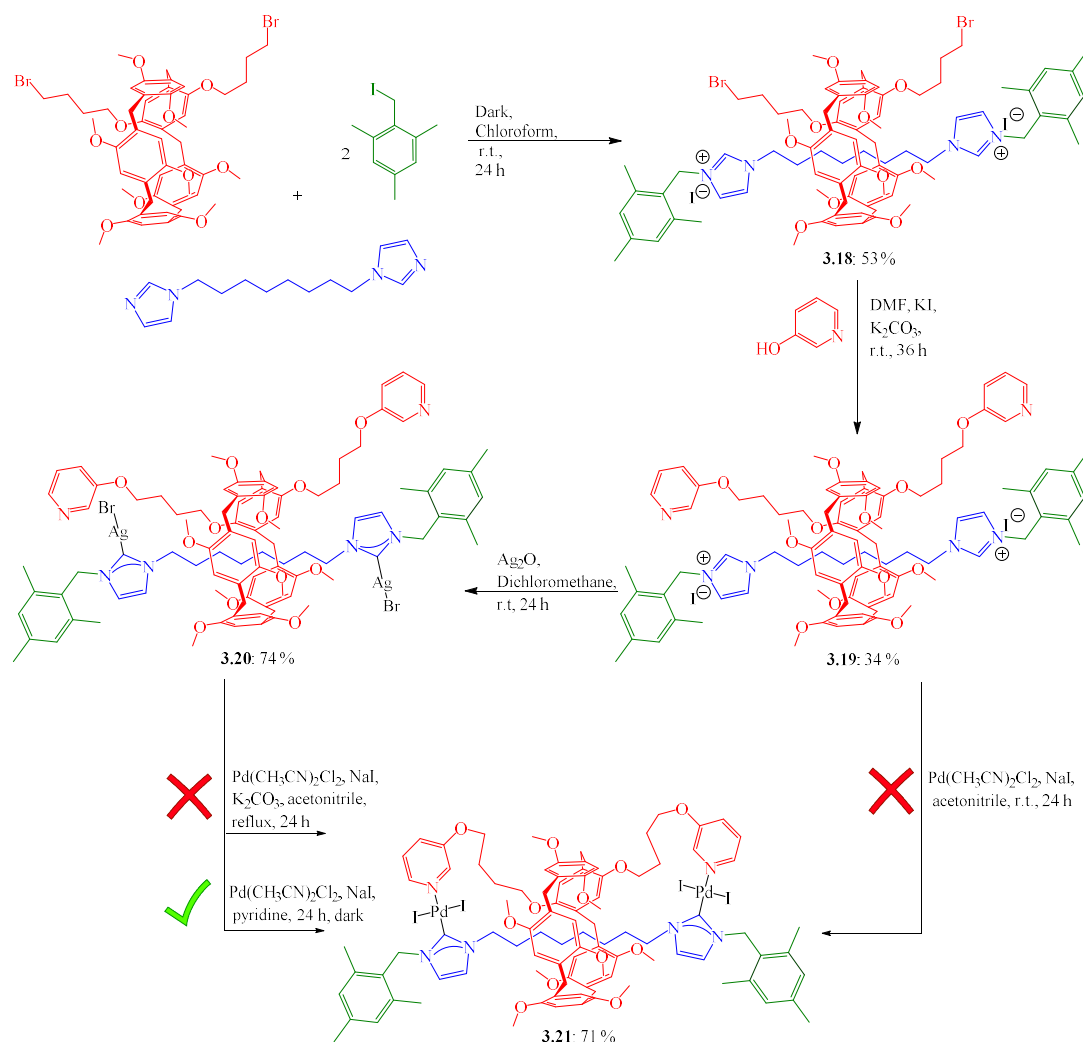
3.2.5. Quasi[1]catenane - Pretzel-Like Molecule

The name “quasi[1]catenane” was recently coined by Maarseveen and co-workers to describe a system which consists of two interlocked molecular rings, covalently linked at one position.⁵⁰ Although such a topology encompasses a mechanical bond, it is not a type of MIM since breaking the mechanical bond does not cause the components to dissociate.⁵¹ Similarly linked compounds

have previously been reported by Vögtle and co-workers, who referred to molecules of this topology as “pretzel-shaped molecules” or “pretzelanes”.⁵² Quasi[1]catenanes closely resemble lasso peptides, which are relatively common in the realm of bacteria and have been shown to have antimicrobial properties.⁵³ Therefore, quasi[1]catenanes are considered to have potential as a new class of antibiotics.

Considering the broad range of synthetic tools developed and described in this chapter, the synthesis of a quasi[1]catenane was attempted. It was envisioned that Pd(II) centres could be introduced as a covalent link between the two threaded components. For this purpose a [2]rotaxane (analogous to **2.1a** and **3.1a**) consisting of an 8-carbon *bis*-imidazole axle and a pillar[5]arene bearing two bromo-butyl arms was synthesised, **3.18** (Scheme 3.16). A subsequent reaction with a stoichiometric amount of 3-pyridinol in the presence of potassium carbonate and potassium iodide in DMF gave the [2]rotaxane **3.19**. 3-Pyridinol was considered to give an optimal angle between the Pd(II) and the pillar[5]arene during the metalation step. The pyridine moiety had to be added post-rotaxane formation to prevent the nucleophilic pyridine nitrogen reacting with the iodo-stopper group. Furthermore, this reaction was low yielding and several side products were observed, most likely due to the nucleophilic nitrogen of the 3-pyridinol reacting with the bromo-alkyl groups instead of the phenol group. To prevent competitive coordination of solvent pyridine, acetonitrile was used as the solvent for initial Pd(II)-coordination attempts. Firstly, di-pyridine [2]rotaxane **3.19** was heated to reflux overnight in acetonitrile with Pd(CH₃CN)₂Cl₂, potassium carbonate and potassium iodide. However, this reaction led to decomposition of the starting material. To avoid high temperatures, the synthetic strategy was adjusted to go via the equivalent Ag(I) complex. Ag(I)-coordination to the NHCs of **3.19** was achieved using similar reaction conditions to those previously described for the synthesis of **2.2a-2.2c**. Further reaction with Pd(CH₃CN)₂Cl₂ and potassium iodide in acetonitrile at room temperature overnight and subsequent aqueous work up showed that no Pd(II) transmetalation had occurred and the Ag(I) compound was still present. The equivalent reaction using pyridine as

the solvent was attempted; after an aqueous work up and a short silica gel pad, an orange solid was isolated in a 71 % yield.



Scheme 3.16: Synthesis of quasi[1]catenane **3.21**.

The successful tethering of pyridine to the pillar[5]arene was confirmed by NMR spectroscopy (Figure 3.20). ^1H NMR spectroscopy studies also confirmed Ag(I)-coordination, showing a significant shift in the central alkyl axle environments, H_{n-k} (Figure 3.20), as observed previously for **2.1c**. Furthermore, the signal associated with the imidazolium proton, H_e , between the nitrogen atoms was lost upon Ag(I)-coordination. The peaks associated to the pyridine environments (H_{8-11}) show no change in position, which indicates that there is no Ag(I)-pyridine

interaction. On the other hand, upon Pd(II)-coordination the ^1H NMR showed a significant shift in the position of the pyridine peaks downfield and broadening, which is a strong indication that the pyridine nitrogen is coordinated to a metal.⁵⁴ Furthermore, the peaks associated with the central alkyl axle environments, $\text{H}_{\text{j-k}}$, showed broadening and slight shifts in position. A possible explanation for this is that the pillar[5]arene is restrained in its shuttling and rotary motion, due to the pillar[5]arene now being covalently linked to the axle. These changes in the NMR peaks upon Pd(II)-coordination strongly indicate that Pd(II) is coordinated to both the NHC of the axle and the pyridine nitrogen of the pillar[5]arene suggesting that **3.21** is a quasi[1]catenane. A possible alternative is intermolecular Pd(II)-pyridine-nitrogen coordination, which would lead to the formation of a complex coordination polymer system. However, this is entropically unfavourable and a polymer would be expected to have very poor solubility, which was not observed. Unfortunately, the exact nature of this system could not be determined as it was not possible to obtain crystals of this compound.

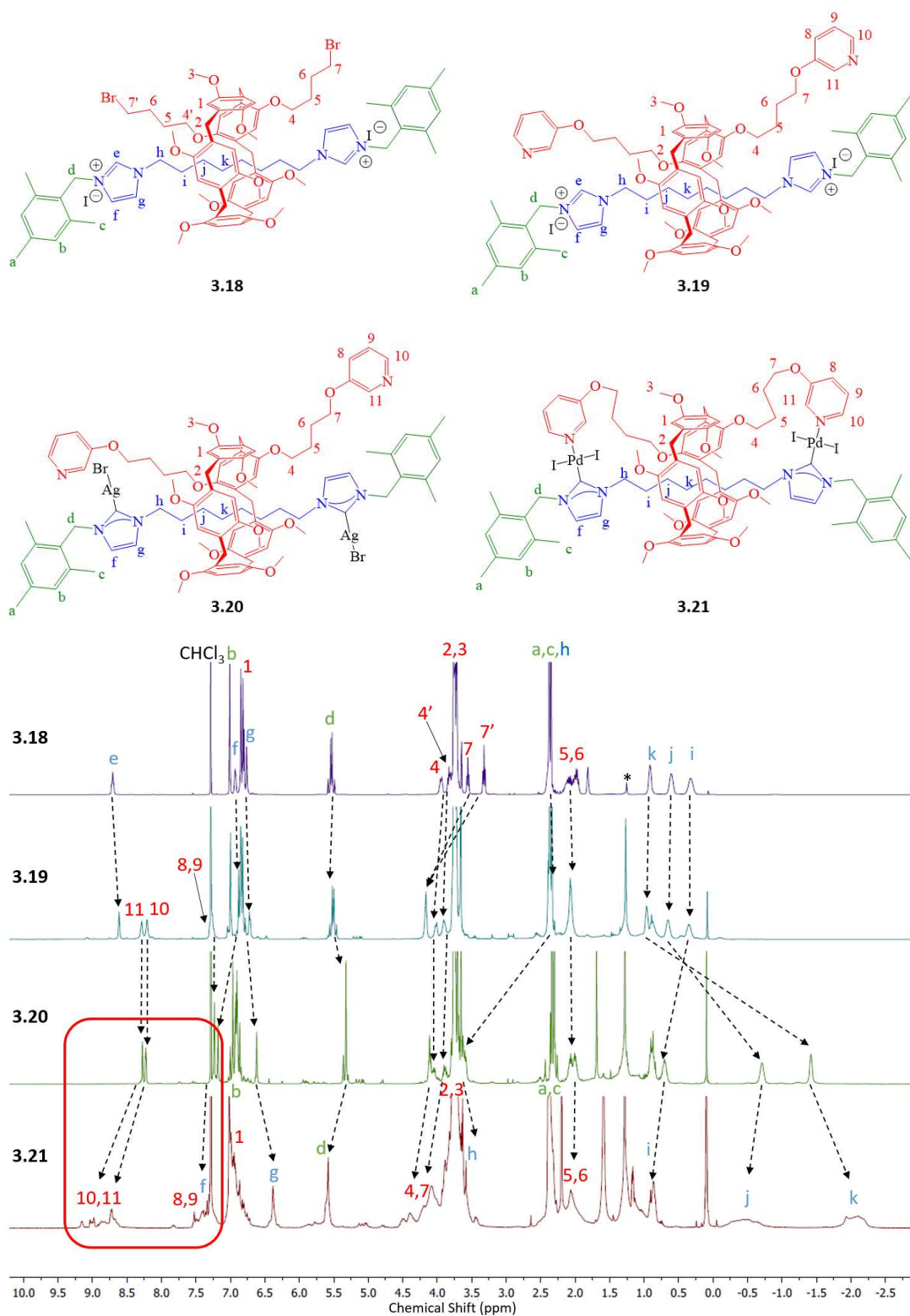


Figure 3.20: ^1H NMR (400 MHz, CDCl_3 , 298 K) spectra comparison between **3.18-3.21**, showing peak assignments and shifts.

3.3. Conclusions

Pillar[5]arenes di-functionalised with fluorescent moieties (carbazole and BODIPY) have been synthesised. The effect of threading on the fluorescence emission was investigated through the synthesis of one and two station [2]rotaxane molecular shuttles, based on **DCP[5]A**. The quantum yields of this series (A) were measured in THF, chloroform and DMSO. No variation in the quantum yield in DMSO or chloroform was observed. However, in THF threading caused significant quenching in all [2]rotaxanes except for the six carbon linker length. There is a possible correlation between this result and calculations recently reported by Cai and co-workers.³⁴ Therefore, there appears to be a connection between fluorescence and shuttling rate in these molecular shuttles.

The axle-macrocycle interactions were further investigated through the synthesis of asymmetric [2]rotaxanes, composed of axles terminated with carbazole and NI moieties. Through evaluating quantum yield measurements of different arrangements, it was concluded that the imidazolium was responsible for quenching carbazole fluorescence when in close proximity. The arrangement of different building blocks in specific constellations allows for full carbazole emission, dimming of fluorescence and complete quenching.

Expansion of the synthetic scope was demonstrated through the functionalisation of the stopper group component. This enables the synthesis of asymmetric [2]rotaxanes and opens up the possibility of introducing a wide variety of terminating moieties. An alternative approach has been discussed in which a di-iodo linking group is utilised. This enables two pillar[5]arenes units to be threaded as well as allowing great potential for varying the terminating groups of the dumbbell. A similar procedure led to the synthesis of a tetra-carboxylic acid-[2]rotaxane as a possible ligand for MORFs. Porphyrins have been introduced as a terminating group of an axle in a [2]rotaxane as well as in the centre of a [5]rotaxane. Furthermore, a tetra-pillar[5]arene-porphyrin has been synthesised. The synthetic mythology was further expanded to synthesise a quasi[1]catenane via Pd(II)-coordination to both the NHCs on the axle and a pyridine tethered to the pillar[5]arene.

3.4. Materials and Methods

3.4.1. Synthesis

3.4.1.1. Di-Bromo-Pillar[5]arene

1,4-Bis(4-bromobutoxy)benzene: 4-methoxyphenol (3.72g, 30 mmol), potassium carbonate (6 g, 43.41 mmol), 1,4-dibromobutane (10.795 g, 50 mmol) and acetone (70 mL) were stirred under reflux for 24 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. The crude product was recrystallized from methanol as a white solid (3.897 g, 50%). ^1H NMR (400 MHz, Chloroform-d) δ 6.84 (s, 4H), 3.97 (t, J = 6.1, Hz, 4H), 3.51 (t, J = 6.7, Hz, 4H), 2.15 – 2.04 (m, 4H), 2.00 – 1.89 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 153.08, 115.40, 67.46, 33.53, 29.51, 28.01. HRMS (ESI+) m/z : 380.9914 ($[\text{M}]^+$, calc. for $[\text{C}_{14}\text{H}_{21}\text{O}_2\text{Br}_2]^+$ = 380.9882).

Dibromo-pillar[5]arene: 1,4-bis(4-bromobutoxy)benzene (0.80 g, 3 mmol) and 1,4-dimethoxybenzene (6.64 g, 48 mmol) were dissolved in dry dichloromethane (500 mL) under a dinitrogen atmosphere. Paraformaldehyde (4.32 g, 144 mmol) was added and the mixture was left to stir at room temperature for 30 min before anhydrous iron (III) chloride (1.246 g, 7.69mmol) was added. The reaction mixture was left to stir at room temperature under dinitrogen for 3 hours. Water (250 mL) was added and extracted into dichloromethane (3 x 100 mL). The combined organic layers were dried over anhydrous MgSO_4 , filtered under gravity and solvent removed under reduced pressure. The residue was purified by silica gel chromatography (hexane:dichloromethane 30:70) to give the product as a white solid (0.45 g, 17%). ^1H NMR (400 MHz, Chloroform-d) δ 6.92 – 6.69 (m, 10H), 3.89 – 3.63 (m, 40H), 3.25 (t, J = 6.4 Hz, 4H), 1.95 – 1.72 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-d) δ 150.77, 128.24, 115.00, 114.05, 113.84, 67.34, 55.90, 33.47, 29.62, 29.44, 28.31. HRMS (ESI+) m/z : 1008.2533 ($[\text{M}+\text{H}]^+$, calc. for $[\text{C}_{51}\text{H}_{64}\text{Br}_2\text{NO}_{10}]^+$ = 1008.2553).

3.4.1.2. Di-Carbazole-Pillar[5]arene **DCP[5]A**

Carbazole (0.50 g, 3.01 mmol) and dry DMF (25 mL) were added to a flame dried flask which had been backfilled with dinitrogen three times. The solution was cooled to 0 °C before sodium hydride 60 % in mineral oil (0.133 g, 5.52 mmol) was added. The solution was warmed to room temperature and stirred for 1 h. Subsequently the solution was again cooled to 0 °C and dibromopillar[5]arene (1.50 g, 1.51 mmol) was slowly added. The mixture was refluxed overnight, then cooled, poured into water (300 mL) and extracted with dichloromethane (3 x 25 mL). The organic phase was dried over MgSO₄, filtered under gravity and concentrated under reduced pressure. The crude product was purified through silica gel chromatography (dichloromethane) to give the final product as a white solid (2.66 g, 89 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.8, Hz, 4H), 7.55 – 7.43 (m, 8H), 7.27 (t, *J* = 7.8, Hz, 4H), 6.77 (s, 4H), 6.73 (s, 4H), 6.63 (s, 2H), 4.45 (t, *J* = 7.0 Hz, 4H), 3.90 – 3.65 (m, 14H), 3.64 (s, 6H), 3.62 (s, 6H), 3.58 (s, 6H), 3.37 (s, 6H), 2.30 – 2.07 (m, 4H), 1.95 – 1.76 (m, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.81, 150.68, 150.03, 140.37, 128.43, 128.29, 128.13, 128.01, 125.70, 122.87, 120.43, 118.92, 115.12, 114.23, 113.90, 108.57, 68.11, 55.84, 55.80, 55.73, 55.52, 53.21, 42.82, 29.70, 29.58, 27.64, 26.08 ppm. HRMS (ESI+) *m/z*: 1182.5500 ([*M*+*H*]⁺, calc. for [C₇₅H₈₀N₃O₁₀]⁺ = 1182.5829).

3.4.1.3. Mono-Carbazole-Pillar[5]arene **MCP[5]A**

Procedure as per **DCP[5]A** (Section 3.4.1.2). (73 %) ¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.53 – 7.42 (m, 4H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.01 (s, 1H), 6.84 – 6.74 (m, 8H), 6.72 (s, 1H), 6.63 (s, 1H), 4.45 (t, *J* = 7.0 Hz, 2H), 3.86 (t, *J* = 6.1 Hz, 2H), 3.82 – 3.75 (m, 10H), 3.68 – 3.61 (m, 24H), 3.39 (s, 3H), 2.24 – 2.09 (m, 2H), 1.95 – 1.81 (m, 2H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.98, 150.87, 150.84, 150.78, 150.76, 149.92, 140.38, 128.46, 128.25, 128.22, 128.14, 128.10, 125.71, 122.88, 120.43, 118.91, 115.24, 114.21, 114.15, 114.08, 114.03, 113.93, 108.59, 68.22, 55.85, 55.77, 55.69, 55.52, 42.84, 30.35, 29.84, 29.75, 29.70, 29.65, 29.50, 27.64, 26.09 ppm.

3.4.1.4. Di-BODIPY-Pillar[5]arene **DBP[5]A**

Di-bromobutoxy-pillar[5]arene (0.15 g, 0.151 mmol), 4-hydroxyphenyl-BODIPY (0.113 g, 0.453 mmol) and potassium carbonate (0.125 g, 0.906 mmol) were dissolved in DMF (5 mL). The mixture was heated to 70 °C and stirred for 24 h under a dinitrogen atmosphere. Once TLC analysis showed the reaction had gone to completion (ca. 3 h), the solvent was removed under reduced pressure and dichloromethane (50 mL) and water (50 mL) were added. The organic layer was washed with water (3 x 100 mL) and brine (100 mL), dried over MgSO₄ and filtered under gravity. The resulting orange solution was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel (dichloromethane) to give the product as an orange solid (0.075 g, 36 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 4H), 7.57 (d, *J* = 8.7 Hz, 4H), 7.04 (d, *J* = 8.7 Hz, 4H), 6.99 (d, *J* = 4.1 Hz, 4H), 6.87 – 6.74 (m, 9H), 6.59 (d, *J* = 4.1 Hz, 4H), 4.11 (t, *J* = 5.9 Hz, 4H), 3.96 (t, *J* = 5.5 Hz, 4H), 3.92 – 3.72 (m, 10H), 3.69 (s, 6H), 3.68 (s, 6H), 3.65 (s, 6H), 3.64 (s, 6H), 2.14 – 1.90 (m, 8H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 161.55, 150.89, 150.82, 150.74, 149.97, 147.43, 143.40, 134.83, 132.46, 131.34, 128.41, 128.37, 128.33, 128.20, 128.11, 126.25, 118.32, 118.28, 115.08, 114.51, 114.33, 114.29, 114.15, 114.02, 67.95, 67.86, 55.92, 55.87, 55.81, 29.82, 29.75, 29.71, 29.62, 26.33, 26.21 ppm.

3.4.1.5. General Procedure for *Bis*-Imidazole **DCP[5]A** [2]Rotaxanes **3.1a-c** and **3.2**

Bis-imidazole (0.41 mmol) and **DCP[5]A** (0.82 mmol) were dissolved in chloroform (1 mL) and sonicated for 30 minutes. The solution was cooled to -15 °C and 2-(iodomethyl)-1,3,5-trimethylbenzene (0.923 mmol) was added under the exclusion of light. The mixture was left to warm to room temperature and stirred under a dinitrogen atmosphere overnight. The crude residue was subjected to column chromatography on silica gel (chloroform:methanol 97.5:2.5) to afford pure **3.1a-3.1c** as pale yellow solids.

3.1a (0.116 g, 51 %). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.34 (s, 2H), 8.07 (d, *J* = 7.7 Hz, 4H), 7.78 (s, 2H), 7.59 (d, *J* = 8.2 Hz, 4H), 7.45 (t, *J* = 8.2 Hz, 4H), 7.20 (t, *J* = 7.7 Hz, 4H), 6.97 (s, 4H), 6.83 (s,

2H), 6.68 (s, 2H), 6.64 (d, $J = 2.8$ Hz, 4H), 6.54 (s, 2H), 6.39 (s, 2H), 5.82 (d, $J = 15.1$ Hz, 2H), 5.43 (d, $J = 15.1$ Hz, 2H), 4.53 (dt, $J = 14.7, 7.3$ Hz, 2H), 4.48 – 4.36 (m, 2H), 4.17 – 4.04 (m, 2H), 3.84 (dt, $J = 9.6, 6.0$ Hz, 2H), 3.73 – 3.46 (m, 27H), 3.01 (s, 6H), 2.35 (s, 6H), 2.33 (s, 12H), 2.21 (dt, $J = 14.3, 7.9$ Hz, 2H), 2.13 (tt, $J = 13.4, 7.4$ Hz, 2H), 1.97 (p, $J = 6.7$ Hz, 4H), 1.64 – 1.56 (m, 4H), -1.16 (tq, $J = 14.2, 8.2, 6.0$ Hz, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 151.40, 151.00, 150.79, 150.72, 150.14, 140.28, 140.27, 140.03, 138.06, 133.36, 130.43, 130.37, 130.31, 130.25, 129.97, 129.74, 125.91, 125.86, 123.16, 122.69, 120.22, 120.14, 118.89, 116.86, 116.60, 115.58, 115.37, 115.20, 109.09, 77.25, 70.63, 58.71, 58.52, 57.82, 57.47, 48.99, 46.85, 42.83, 29.23, 29.11, 28.97, 27.65, 26.27, 23.61, 21.15, 20.26, 20.05 ppm. HRMS (ESI+) m/z : 810.9371 $[\text{M}]^{2+}$, calc. for $[\text{C}_{105}\text{H}_{116}\text{N}_6\text{O}_{10}]^{2+} = 810.9388$.

3.1b (0.106 g, 47 %). ^1H NMR (400 MHz, Chloroform- d) δ 9.24 (s, 2H), 8.06 (d, $J = 7.7$ Hz, 4H), 7.51 – 7.35 (m, 8H), 7.19 (t, $J = 7.8$ Hz, 4H), 6.95 (s, 4H), 6.83 – 6.73 (m, 8H), 6.71 (s, 2H), 6.65 – 6.58 (m, 4H), 5.57 – 5.39 (m, 4H), 4.45 (t, $J = 7.2$ Hz, 4H), 3.99 – 3.89 (m, 2H), 3.87 – 3.78 (m, 2H), 3.73 – 3.54 (m, 28H), 3.32 (s, 6H), 2.48 – 2.38 (m, 4H), 2.34 (s, 6H), 2.27 (s, 12H), 2.22 – 2.07 (m, 4H), 1.86 – 1.96 (m, 4H), 0.18 (s, 4H), -0.17 (s, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 151.02, 150.96, 150.90, 150.25, 140.32, 139.92, 137.96, 135.32, 130.14, 129.92, 129.75, 129.73, 129.69, 129.61, 125.72, 125.56, 122.75, 122.08, 120.33, 119.82, 118.90, 116.69, 115.64, 115.55, 115.49, 115.13, 108.69, 70.24, 57.88, 57.73, 57.61, 57.08, 48.27, 47.43, 42.75, 29.71, 29.13, 29.02, 26.14, 25.06, 21.11, 19.67 ppm. HRMS (ESI+) m/z : 824.4516 $[\text{M}]^+$, calc. for $[\text{C}_{107}\text{H}_{120}\text{N}_6\text{O}_{10}]^+ = 824.9544$.

3.1c (0.135 g, 62 %). ^1H NMR (400 MHz, Chloroform- d) δ 8.60 (s, 2H), 8.06 (d, $J = 7.7$ Hz, 4H), 7.51 (d, $J = 8.2$ Hz, 4H), 7.42 (t, $J = 7.7$ Hz, 4H), 7.20 (t, $J = 7.4$ Hz, 4H), 6.94 (s, 4H), 6.81 – 6.65 (m, 12H), 6.57 (s, 2H), 5.41 (d, $J = 14.6$ Hz, 2H), 5.30 (d, $J = 14.6$ Hz, 2H), 4.66 – 4.35 (m, 4H), 4.05 – 3.87 (m, 2H), 3.83 (s, 2H), 3.74 – 3.52 (m, 27H), 3.27 (s, 6H), 2.34 (s, 6H), 2.25 (s, 12H), 2.20 – 2.07 (m, 4H), 2.02 – 1.86 (m, 4H), 0.91 – 0.72 (m, 4H), 0.48 (s, 4H), 0.30 – 0.11 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 150.94, 150.85, 150.75, 150.73, 150.09, 140.32, 140.10, 137.90, 134.19, 130.01,

129.94, 129.73, 129.70, 129.48, 129.45, 125.75, 125.08, 122.75, 122.63, 120.33, 119.54, 118.89, 116.24, 115.43, 115.26, 115.21, 114.75, 108.80, 69.87, 57.67, 57.60, 56.81, 48.34, 47.48, 42.81, 29.71, 29.18, 29.07, 28.99, 28.61, 27.76, 26.57, 26.16, 21.13, 19.73 ppm. HRMS (ESI+) m/z : 838.9673 [M]²⁺, calc. for [C₁₀₉H₁₂₄N₆O₁₀]²⁺ = 838.9701.

3.2 (0.169 g, 76 %). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.41 – 8.32 (m, 1H), 8.09 (dd, J = 11.2, 7.7 Hz, 4H), 7.68 (d, J = 8.2 Hz, 2H), 7.49 – 7.39 (m, 4H), 7.36 (s, 1H), 7.35 (s, 1H), 7.26 – 7.16 (m, 5H), 6.96 (s, 2H), 6.85 (s, 2H), 6.84 (s, 1H), 6.83 (s, 2H), 6.81 (s, 1H), 6.79 (s, 1H), 6.73 (s, 1H), 6.64 (s, 1H), 6.58 (s, 1H), 6.54 (s, 1H), 6.42 (s, 1H), 5.85 (d, J = 17.4 Hz, 1H), 5.70 (s, 1H), 5.24 (d, J = 15.0 Hz, 1H), 4.61 (dt, J = 14.8, 7.1 Hz, 1H), 4.44 (ddd, J = 14.5, 8.7, 5.2 Hz, 1H), 4.35 (td, J = 7.0, 4.2 Hz, 2H), 4.16 (q, J = 6.4, 4.8 Hz, 1H), 3.95 (dt, J = 9.3, 5.8 Hz, 1H), 3.87 (dt, J = 9.6, 5.6 Hz, 1H), 3.82 – 3.75 (m, 2H), 3.75 – 3.51 (m, 28H), 3.43 (s, 3H), 3.39 (s, 3H), 2.89 (s, 3H), 2.37 (s, 3H), 2.33 (s, 6H), 2.28 (s, 3H), 2.23 (s, 6H), 2.21 – 2.12 (m, 2H), 2.10 – 2.00 (m, 2H), 1.87 – 1.79 (m, 2H), 1.34 (dt, J = 16.1, 9.0 Hz, 2H), 0.37 (t, J = 8.7 Hz, 2H), 0.26 – 0.07 (m, 2H), -0.82 – -1.05 (m, 2H), -1.65 – -1.81 (m, 1H), -1.88 (tt, J = 12.4, 7.0 Hz, 1H) ppm. ¹³C NMR (126 MHz, Chloroform-*d*) δ 153.70, 151.85, 151.05, 150.62, 150.55, 150.50, 150.33, 150.17, 149.76, 140.27, 139.66, 138.05, 133.20, 131.67, 130.71, 130.17, 129.93, 129.86, 129.82, 129.54, 129.36, 129.24, 129.10, 128.85, 128.65, 128.62, 125.82, 125.74, 122.85, 122.66, 120.43, 120.13, 118.98, 118.78, 118.20, 115.79, 115.71, 114.76, 114.56, 114.07, 113.62, 113.46, 109.28, 108.42, 72.43, 69.95, 68.91, 59.57, 58.06, 57.91, 56.92, 56.10, 55.64, 55.26, 48.58, 46.96, 42.94, 42.61, 31.44, 29.58, 29.19, 28.79, 28.40, 27.68, 27.57, 26.31, 25.94, 25.91, 24.97, 24.22, 21.20, 20.72, 20.25, 16.22 ppm. HRMS (ESI+) m/z : 1584.8535 [M]²⁺, calc. for [C₁₀₃H₁₁₅N₄O₁₁]²⁺ = 1584.8590).

3.4.1.6. [2]Rotaxane **3.3**

Carbazole-imidazole rod (0.03 g, 0.09 mmol) and **DCP[5]A** (0.12 g, 0.10 mmol) were dissolved in chloroform (1 mL) and the solution was cooled to -15 °C. 2-(iodomethyl)-1,3,5-trimethylbenzene (0.04 g, 0.15 mmol) was added under the exclusion of light and the mixture was let to stir at room

temperature overnight. The solvent was removed under reduced pressure and the crude product was purified through silica gel chromatography (chloroform:methanol 99:1) to give the final product as a pale yellow solid (0.12 g, 76 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.28 (t, J = 1.7 Hz, 1H), 8.16 (d, J = 7.6 Hz, 2H), 8.09 (d, J = 7.8 Hz, 2H), 8.02 (d, J = 7.8 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.56 (t, J = 8.2, 7.2, 1.1 Hz, 2H), 7.51 (s, 1H), 7.48 – 7.42 (m, 4H), 7.33 – 7.27 (m, 4H), 7.25 – 7.09 (m, 8H), 6.95 (s, 2H), 6.89 – 6.80 (m, 5H), 6.66 (s, 1H), 6.66 (s, 1H), 6.62 (s, 1H), 6.57 (s, 1H), 6.49 (s, 1H), 5.91 (t, J = 1.7 Hz, 1H), 5.86 (d, J = 15.1 Hz, 1H), 5.35 (d, J = 15.1 Hz, 1H), 4.64 – 4.41 (m, 2H), 4.26 – 3.93 (m, 6H), 3.88 – 3.77 (m, 2H), 3.75 – 3.50 (m, 25H), 3.46 (s, 3H), 3.18 (s, 3H), 2.96 (s, 3H), 2.36 (s, 3H), 2.34 (s, 6H), 2.11 – 1.73 (m, 6H), 1.71 – 1.54 (m, 6H), 1.43 – 1.10 (m, 2H), 0.77 – 0.64 (m, 2H), -0.03 (p, J = 7.9 Hz, 2H), -1.02 – -1.24 (m, 2H), -1.43 – -1.76 (m, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.78, 151.24, 150.74, 150.60, 150.54, 150.36, 150.28, 150.00, 140.30, 140.15, 140.13, 138.05, 132.03, 130.45, 130.27, 129.89, 129.86, 129.77, 129.33, 129.23, 129.11, 129.06, 128.96, 126.20, 125.82, 125.64, 125.61, 123.05, 122.94, 122.71, 122.69, 120.73, 120.35, 120.30, 120.16, 119.11, 118.85, 118.80, 117.59, 116.50, 115.46, 114.81, 114.67, 114.62, 114.44, 114.13, 109.20, 108.31, 108.22, 69.63, 59.11, 57.13, 56.89, 56.37, 56.04, 55.84, 48.73, 47.20, 42.92, 42.46, 28.80, 28.58, 27.61, 26.29, 25.49, 24.97, 21.16, 20.23 ppm. HRMS (ESI+) m/z : $[\text{M}+\text{H}]^+$ 1615.8435, calc. for $[\text{C}_{69}\text{H}_{74}\text{N}_2\text{O}_{19}]^+$ = 1615.8404.

3.4.1.7. [2]Rotaxane **3.4**

Procedure as per **3.3** with **DMP[5]A** instead of **DCP[5]A**, (0.060 g, 40 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 8.19 (d, J = 7.7 Hz, 2H), 7.61 (s, 1H), 7.60 – 7.56 (m, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 7.8 Hz, 2H), 7.05 (s, 2H), 6.93 (s, 5H), 6.77 (s, 5H), 6.02 – 5.92 (m, 2H), 5.76 (d, J = 15.1 Hz, 1H), 4.20 (t, J = 8.2 Hz, 2H), 3.80 – 3.65 (m, 40H), 2.49 (s, 6H), 2.39 (s, 3H), 1.45 – 1.30 (m, 2H), 0.84 – 0.76 (m, 2H), 0.22 – 0.10 (m, 2H), -0.87 – -1.06 (m, 2H), -1.35 – -1.62 (m, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.29, 150.68, 140.19, 139.88, 138.10, 132.13, 129.99, 129.93, 129.41, 126.09, 125.66, 122.92, 120.65, 119.05, 115.85, 114.82, 108.25, 58.29, 56.52,

49.03, 47.34, 43.07, 31.94, 29.71, 29.28, 29.12, 25.60, 25.54, 25.21, 21.20, 20.22 ppm. HRMS (ESI+) m/z : 1200.6281 [M]⁺, calc. for [C₇₆H₈₆N₃O₁₀]⁺ = 1200.6308.

3.4.1.8. Axle **3.5**

Procedure as per **3.3** with no macrocycle. (0.026 g, 71 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 10.21 (s, 1H), 8.09 (d, J = 7.7 Hz, 2H), 7.50 – 7.41 (m, 4H), 7.23 (t, J = 7.9 Hz, 2H), 7.08 (s, 1H), 6.93 (s, 2H), 6.75 (s, 1H), 5.52 (s, 2H), 4.34 (t, J = 6.8 Hz, 2H), 4.22 (t, J = 7.4 Hz, 2H), 3.66 (s, CD₃OD), 2.30 (s, 3H), 2.26 (s, 6H), 1.86 (m, 4H), 1.36 (m, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.37, 140.11, 138.10, 136.46, 130.00, 125.72, 125.00, 122.74, 121.62, 120.61, 120.29, 118.81, 108.84, 70.53, 50.08, 48.12, 42.80, 29.86, 29.71, 28.67, 26.48, 25.91, 21.06, 20.02 ppm. HRMS (ESI+) m/z : 450.2917 [M]⁺, calc. for [C₃₁H₃₆N₃]⁺ = 450.2904).

3.4.1.9. Ag(I)-Coordination to **3.3**

To solution of **3.3** (0.20 g, 0.113 mmol) in dichloromethane (25 mL) was added Ag₂O (0.053 g, 0.228 mmol) and the mixture was stirred at room temperature overnight under the exclusion of light. The mixture was filtered through a celite plug and the organic fractions were combined, dried over anhydrous MgSO₄, filtered under gravity and the solvent removed under reduced pressure to afford the crude product as an off white solid. This was redissolved in dichloromethane (1mL) and added dropwise to cold hexane (20 mL). The white precipitate was collected by filtration under reduced pressure, washed with hexane and dried to afford the product as a white solid (0.187 g, 92 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, J = 7.8 Hz, 4H), 8.04 (d, J = 7.6 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.62 (t, J = 8.2 Hz, 2H), 7.52 – 7.40 (m, 4H), 7.35 (t, J = 8.3 Hz, 2H), 7.27 – 7.18 (m, 6H), 7.14 (d, J = 8.2 Hz, 2H), 7.06 (s, 1H), 7.04 (s, 1H), 6.99 (d, J = 2.8 Hz, 2H), 6.96 (s, 2H), 6.93 – 6.84 (m, 6H), 6.81 (s, 1H), 6.65 (s, 1H), 6.46 (s, 1H), 5.25 – 5.11 (m, 2H), 4.39 (h, J = 7.9 Hz, 2H), 4.13 – 4.00 (m, 3H), 3.89 – 3.82 (m, 1H), 3.82 – 3.41 (m, 30H), 3.36 (s, 3H), 3.23 (s, 3H), 3.08 – 2.97 (m, 1H), 2.94 (s, 3H), 2.90 – 2.78 (m, 1H), 2.35 (s, 3H), 2.25 (s, 6H), 2.22 – 2.02 (m, 3H), 1.84 (p, J = 6.8 Hz, 2H), 1.77 – 1.63 (m, 2H), 1.41 – 1.16 (m, 3H), 0.95 – 0.83 (m, 1H), 0.42 – 0.24 (m,

2H), -0.34 – -0.62 (m, 2H), -1.61 – -1.89 (m, 2H), -2.25 – -2.52 (m, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.47, 151.46, 150.94, 150.62, 150.37, 150.19, 140.31, 140.25, 137.55, 130.45, 130.22, 130.01, 129.96, 129.79, 129.73, 129.35, 129.20, 128.96, 128.71, 128.69, 128.02, 125.81, 125.60, 125.39, 122.81, 122.76, 122.51, 120.36, 120.28, 118.91, 118.76, 118.56, 117.45, 116.85, 116.51, 115.94, 114.66, 114.09, 109.40, 108.68, 108.48, 69.93, 58.51, 58.23, 57.94, 57.86, 56.54, 56.02, 55.99, 55.86, 55.77, 42.81, 42.61, 29.08, 28.26, 27.81, 27.35, 26.11, 25.71, 24.77, 21.10, 19.94 ppm.

3.4.1.10. Pd(II)-Coordination in the Synthesis of **3.6**

Ag(I) coordinated **3.3** (0.2 g, 0.111 mmol), $\text{PdCl}_2 \cdot (\text{CH}_3\text{CN})_2$ (0.032 g, 0.124 mmol) and NaI (0.033 g, 0.220 mmol) were added to a flame dried flask which had been backfilled with dinitrogen three times. Anhydrous pyridine (10 mL) was added via cannula. The mixture was stirred overnight under a dinitrogen atmosphere and under the exclusion of light. All volatiles were evaporated under reduced pressure and the residue was redissolved in chloroform (25 mL) and water (25 mL). The organic layer was separated and washed with water (2 x 100 mL) and brine (1 x 100 mL) and subsequently dried over MgSO_4 and filtered under gravity. The solvent was removed under reduced pressure and the residue subjected to a silica gel pad (dichloromethane:hexane 50:50) to afford the product as an orange solid (0.045 g, 20 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.21 (d, J = 5.0 Hz, 2H), 8.12 (t, J = 7.7 Hz, 4H), 8.06 (d, J = 7.7 Hz, 2H), 7.87 (d, J = 8.1 Hz, 2H), 7.75 – 7.62 (m, 3H), 7.53 – 7.29 (m, 10H), 7.26 – 7.17 (m, 4H), 7.17 – 6.66 (m, 15H), 6.38 (s, 1H), 5.81 – 5.66 (m, 2H), 4.28 (t, J = 7.1 Hz, 2H), 4.21 – 3.93 (m, 4H), 3.91 – 2.89 (m, 44H), 2.41 (s, 6H), 2.34 (s, 3H), 2.09 – 1.87 (m, 2H), 1.87 – 1.77 (m, 2H), 1.77 – 1.68 (m, 2H), 1.45 – 1.33 (m, 2H), 0.40 – 0.17 (m, 2H), -0.02 – -0.27 (m, 2H), -1.59 – -1.79 (m, 1H), -1.79 – -1.94 (m, 1H), -1.96 – -2.13 (m, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.75, 151.92, 151.89, 151.02, 151.01, 150.89, 150.78, 150.56, 150.33, 140.65, 140.25, 138.93, 138.81, 130.75, 130.40, 130.06, 129.60, 129.39, 129.35, 129.02, 128.99, 128.71, 128.34, 127.68, 125.67, 125.58, 125.49, 124.46, 122.81, 122.73, 122.35, 120.60, 120.32, 120.25, 119.97, 118.82, 118.73, 118.39, 117.80, 117.64, 116.67, 115.91, 115.30,

114.47, 113.98, 113.94, 110.09, 108.69, 108.52, 70.36, 69.65, 58.83, 58.67, 58.65, 58.54, 58.42, 57.70, 56.04, 55.72, 43.10, 42.72, 42.56, 31.94, 29.72, 28.92, 27.74, 27.68, 27.49, 25.87, 25.59, 25.00, 23.20, 22.71, 21.10, 20.52, 17.49, 14.14 ppm.

3.4.1.11. [2]Rotaxane **3.7**

Naphthalene imide-imidazole rod (0.09 g, 0.26 mmol) and **DCP[5]A** (0.40 g, 0.34 mmol) were dissolved in chloroform (1 mL) and the solution was cooled to -15 °C. 2-(Iodomethyl)-1,3,5-trimethylbenzene (0.11 g, 0.42 mmol) was added under the exclusion of light and the mixture was let to stir at room temperature overnight. The solvent was removed under reduced pressure and the crude product was purified through silica gel chromatography (chloroform:methanol 98:2) to give the final product as a pale yellow solid. (0.30 g, 70 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 7.2 Hz, 2H), 8.35 (s, 1H), 8.28 (d, *J* = 7.6 Hz, 2H), 8.08 (d, *J* = 7.7 Hz, 2H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.79 (t, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.15 (m, 4H), 7.13 (s, 1H), 7.08 (t, *J* = 7.4 Hz, 2H), 6.97 (s, 2H), 6.94 – 6.81 (m, 6H), 6.65 (s, 1H), 6.59 (s, 1H), 6.55 (s, 1H), 6.44 (s, 1H), 5.82 (d, *J* = 15.1 Hz, 1H), 5.72 (s, 1H), 5.26 (d, *J* = 15.1 Hz, 1H), 4.67 – 4.55 (m, 1H), 4.49 – 4.36 (m, 3H), 4.25 – 4.09 (m, 2H), 3.99 – 3.84 (m, 4H), 3.82 – 3.54 (m, 25H), 3.51 (s, 3H), 3.45 (s, 3H), 2.92 (s, 3H), 2.38 (s, 3H), 2.33 (s, 6H), 2.30 – 1.99 (m, 8H), 1.42 – 1.22 (m, 2H), 0.54 – 0.31 (m, 2H), 0.31 – 0.18 (m, 2H), -0.64 – -0.86 (m, 2H), -1.70 – -1.99 (m, 2H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.73, 150.68, 150.27, 149.56, 140.27, 138.06, 134.10, 131.56, 131.02, 130.72, 129.85, 129.30, 129.23, 129.02, 128.81, 128.61, 128.49, 127.04, 125.82, 125.52, 122.73, 122.67, 120.47, 120.29, 120.11, 118.77, 113.44, 109.29, 108.40, 59.56, 58.12, 57.95, 56.84, 55.97, 55.65, 55.46, 42.96, 42.82, 40.37, 29.21, 28.82, 27.93, 26.07, 25.95, 25.68, 24.92, 20.23 ppm. HRMS (ESI+) *m/z*: 1645.8167 ([M+H]⁺, calc. for [C₆₉H₇₄N₂O₁₉]⁺ = 1645.8146).

3.4.1.12. [2]Rotaxane **3.8**

Procedure as per **3.7** with **DMP[5]A** instead of **DCP[5]A**, (0.114 g, 77 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, J = 7.3 Hz, 2H), 8.31 (d, J = 8.3 Hz, 2H), 8.23 (s, 1H), 7.84 (t, J = 8.3 Hz, 2H), 7.27 (s, 1H), 7.05 (s, 2H), 6.98 (s, 5H), 6.73 (s, 5H), 5.95 (d, J = 15.1 Hz, 1H), 5.85 (s, 1H), 5.70 (d, J = 15.0 Hz, 1H), 4.22 – 4.02 (m, 2H), 3.85 (s, 15H), 3.83 – 3.60 (m, 25H), 2.49 (s, 6H), 2.39 (s, 3H), 1.54 – 1.30 (m, 2H), 0.56 – 0.34 (m, 4H), -0.51 – -0.84 (m, 2H), -1.57 – -1.91 (m, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.90, 151.25, 150.27, 139.84, 138.10, 134.21, 131.85, 131.74, 131.10, 130.00, 129.93, 128.93, 128.15, 127.09, 122.66, 122.59, 120.87, 115.96, 113.73, 70.54, 58.39, 55.89, 48.85, 47.10, 40.58, 28.78, 26.06, 25.67, 25.19, 21.21, 20.17 ppm. HRMS (ESI+) m/z : 1230.6021 [M]⁺, calc. for $[\text{C}_{76}\text{H}_{84}\text{N}_3\text{O}_{12}]^+ = 1230.6050$.

3.4.1.13. Axle **3.9**

Procedure as per **3.7** with no macrocycle. (0.033 g, 74 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 8.56 (d, J = 7.3 Hz, 2H), 8.21 (d, J = 8.3 Hz, 2H), 7.81 – 7.68 (m, 2H), 7.33 (s, 1H), 6.91 (s, 3H), 5.58 (s, 2H), 4.35 (s, 2H), 4.18 – 4.05 (m, 2H), 2.29 (s, 6H), 2.25 (s, 3H), 1.96 (s, 2H), 1.77 – 1.69 (m, 2H), 1.45 (s, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.23, 140.04, 138.20, 136.53, 134.05, 131.60, 131.27, 129.98, 128.13, 126.98, 125.13, 122.55, 121.78, 120.90, 70.54, 50.38, 48.27, 39.77, 29.84, 29.70, 27.52, 26.10, 25.55, 21.05, 20.07 ppm. HRMS (ESI+) m/z : 480.2665 [M]⁺, calc. for $[\text{C}_{31}\text{H}_{34}\text{N}_3\text{O}_2]^+ = 480.2646$.

3.4.1.14. [2]Rotaxane **3.10**

Naphthalene imide-imidazole rod (0.03 g, 0.086 mmol) and **DCP[5]A** (0.170 g, 0.15 mmol) were dissolved in chloroform (1 mL) and the solution was cooled to -15 °C. (Iodomethyl)benzene NI Rod (0.05 g, 0.098 mmol) was added under the exclusion of light and the mixture was left to stir at room temperature overnight. The solvent was removed under reduced pressure and the crude product was purified through silica gel chromatography (chloroform:methanol 93:7) to give the final product as a pale yellow solid (0.12 g, 70 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, J =

7.3 Hz, 2H), 8.57 (d, $J = 7.3$ Hz, 2H), 8.52 (s, 1H), 8.25 (d, $J = 8.3$ Hz, 2H), 8.21 (d, $J = 8.2$ Hz, 2H), 8.05 (d, $J = 7.7$ Hz, 2H), 7.97 (d, $J = 7.7$ Hz, 2H), 7.81 – 7.72 (m, 4H), 7.69 (d, $J = 8.3$ Hz, 2H), 7.59 (d, $J = 8.2$ Hz, 2H), 7.44 (t, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.23 (t, $J = 7.6$ Hz, 2H), 7.17 (t, $J = 7.5$ Hz, 2H), 7.07 (t, $J = 7.4$ Hz, 2H), 6.99 (s, 1H), 6.96 – 6.89 (m, 6H), 6.82 (s, 1H), 6.74 (s, 1H), 6.69 (d, $J = 3.2$ Hz, 2H), 6.65 (s, 1H), 6.50 (s, 1H), 5.82 (s, 1H), 5.72 (d, $J = 14.2$ Hz, 1H), 5.18 (d, $J = 14.2$ Hz, 1H), 4.59 – 4.41 (m, 2H), 4.38 (t, $J = 7.0$ Hz, 2H), 4.22 (t, 2H), 4.05 – 3.91 (m, 4H), 3.89 – 3.81 (m, 3H), 3.82 – 3.65 (m, 24H), 3.54 (s, 3H), 3.51 (s, 3H), 3.43 (s, 3H), 3.12 (s, 3H), 2.27 – 2.05 (m, 4H), 2.02 – 1.93 (m, 4H), 1.85 – 1.76 (m, 4H), 1.55 (s, 4H), 1.45 – 1.34 (m, 3H), 0.49 (s, 2H), 0.18 – -0.02 (m, 2H), -0.47 (s, 2H), -1.84 (s, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 164.21, 163.78, 159.90, 151.25, 150.96, 150.88, 150.82, 150.23, 150.21, 150.19, 150.15, 150.12, 149.63, 140.29, 140.22, 134.07, 133.91, 132.10, 131.66, 131.58, 131.17, 131.02, 130.70, 129.91, 129.71, 129.52, 129.32, 129.20, 128.97, 128.92, 128.86, 128.81, 128.11, 127.01, 126.93, 125.86, 125.51, 122.70, 122.67, 122.65, 120.98, 120.29, 120.13, 118.77, 115.83, 115.25, 115.05, 114.61, 113.93, 113.78, 113.67, 113.63, 109.08, 108.36, 70.57, 70.05, 68.65, 68.08, 62.78, 58.17, 57.54, 57.11, 56.03, 55.83, 55.59, 52.26, 46.92, 42.92, 42.80, 40.31, 29.85, 29.71, 29.21, 29.14, 29.07, 29.00, 28.88, 28.02, 27.90, 27.76, 26.86, 26.19, 26.07, 26.02, 25.78, 25.70, 22.71, 14.15 ppm. HRMS (ESI+) m/z : 1898.8896 [M+H] $^{+}$, calc. for [C₆₉H₇₄N₂O₁₉] $^{+}$ = 1898.8884.

3.4.1.15. [2]Rotaxane **3.11**

Procedure as per **3.10** with **DMP[5]A** instead of **DCP[5]A**, (0.11 g, 86 %). ^1H NMR (400 MHz, Chloroform- d) δ 8.66 (dd, $J = 7.3$, 1.0 Hz, 2H), 8.61 (dd, $J = 7.3$, 1.1 Hz, 2H), 8.42 (s, 1H), 8.30 (dd, $J = 8.3$, 1.0 Hz, 2H), 8.24 (dd, $J = 8.4$, 1.0 Hz, 2H), 7.88 – 7.73 (m, 6H), 7.11 (s, 1H), 7.03 – 6.96 (m, 7H), 6.76 (s, 5H), 5.89 (d, $J = 14.1$ Hz, 2H), 5.52 (d, $J = 14.6$ Hz, 1H), 4.27 – 4.18 (m, 2H), 4.18 – 4.10 (m, 2H), 4.00 (s, 2H), 3.89 – 3.61 (m, 40H), 1.94 – 1.73 (m, 4H), 1.65 – 1.39 (m, 6H), 0.71 – 0.48 (m, 2H), 0.31 – 0.11 (m, 2H), -0.38 (s, 2H), -1.73 (s, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 164.22, 163.94, 159.94, 151.07, 150.28, 134.14, 133.95, 132.31, 131.72, 131.59, 131.19, 130.75, 129.68, 129.01, 128.15, 127.06, 126.95, 125.74, 122.71, 122.53, 121.10, 115.13, 113.90, 68.10,

57.96, 55.98, 52.42, 40.53, 29.71, 29.12, 28.84, 28.02, 26.84, 26.06, 25.83 ppm. HRMS (ESI+) m/z : 1483.6772 [M+H]⁺, calc. for [C₆₉H₇₃N₂O₁₉]⁺ = 1483.6788.

3.4.1.16. Axle **3.12**

Procedure as per **3.10** with no macrocycle. Yellow solid (75%). ¹H NMR (400 MHz, Chloroform-*d*) δ 10.29 (s, 1H), 8.67 – 8.58 (m, 4H), 8.28 – 8.20 (m, 4H), 7.78 (ddd, *J* = 9.0, 7.3, 1.8 Hz, 4H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.27 (s, 1H), 7.18 (s, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.51 (s, 2H), 4.33 (t, *J* = 7.3 Hz, 4H), 4.26 – 4.12 (m, 8H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.76 (m, 8H), 1.59 – 1.38 (m, 8H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 164.22, 161.18, 160.10, 136.54, 134.02, 133.94, 131.59, 131.26, 131.19, 130.77, 128.12, 126.97, 124.05, 122.67, 122.56, 121.73, 121.56, 115.36, 67.97, 53.27, 50.26, 40.30, 39.78, 29.78, 28.97, 28.22, 27.99, 27.49, 26.79, 26.09, 25.75, 25.59, 25.22 ppm. HRMS (ESI+) m/z : 733.4102 [M]⁺, calc. for [C₄₆H₄₅N₄O₅]⁺ = 733.3384.

3.4.1.17. [3]Rotaxane **3.13**

Naphthalene imide-imidazole rod (0.050 g, 0.144 mmol) and **DMP[5]A** (0.324 g, 0.432 mmol) were dissolved in chloroform (1 mL) and sonicated for 30 minutes. The solution was cooled to -15 °C and 1,4-*bis*-(iodomethyl)benzene (0.103 g, 0.288 mmol) was added under the exclusion of light. The mixture was left to warm to room temperature and stirred under a dinitrogen atmosphere overnight. The crude residue was subjected to column chromatography on silica gel (chloroform:methanol 99:1 -> 99:2) to afford the product as a pale yellow solid (0.091 g, 25 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 7.2 Hz, 4H), 8.41 (s, 2H), 8.31 (d, *J* = 8.3 Hz, 4H), 8.08 (s, 4H), 7.88 – 7.82 (m, 4H), 7.02 (s, 10H), 6.85 (s, 10H), 6.12 – 5.93 (m, 4H), 5.82 (d, *J* = 14.4 Hz, 2H), 5.71 (d, *J* = 14.4 Hz, 1H), 4.21 – 4.13 (m, 4H), 3.89 (s, 30H), 3.86 – 3.76 (m, 20H), 3.75 (s, 30H), 1.53 – 1.44 (m, 4H), 0.68 – 0.56 (m, 4H), 0.31 – 0.20 (m, 4H), -0.27 – -0.41 (m, 4H), -1.66 – -1.80 (m, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.16, 150.36, 131.16, 129.93, 129.13, 127.06, 115.80, 113.87, 58.71, 55.96, 29.17 ppm.

3.4.1.18. Tetra-Ester [2]Rotaxane **3.14**

Dimethyl 5-(4-(1H-imidazol-1-yl)butoxy)isophthalate (1.0 g, 0.692 mmol) and **DMP[5]A** (0.571 g, 0.761 mmol) were dissolved in chloroform (2 mL) and cooled to -15°C. Under the exclusion of light a solution of diethyl 5-(iodomethyl)isophthalate (0.181 g, 0.501 mmol) in chloroform (1 mL) was added and the mixture was left to warm to room temperature and stirred overnight. The product mixture was subjected to column chromatography on silica gel (chloroform:acetone 90:10) to afford the product as yellow solid (0.80 g, 36 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.84 – 8.75 (m, 2H), 8.73 (d, *J* = 1.6 Hz, 2H), 8.37 (t, *J* = 1.4 Hz, 1H), 7.80 (d, *J* = 1.5 Hz, 2H), 7.36 (t, *J* = 1.7 Hz, 1H), 7.03 (s, 5H), 6.81 (s, 5H), 6.12 (dd, *J* = 156, 14.5 Hz, 2H), 6.17 (t, *J* = 1.8 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 4H), 4.04 (s, 6H), 3.86 – 3.69 (m, 25H), 3.64 (s, 15H), 3.19 – 3.00 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 6H), 0.36 (t, 2H), 0.02 – -0.16 (m, 2H), -1.74 – -1.97 (m, 2H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.05, 165.11, 158.88, 151.18, 150.43, 135.04, 133.94, 132.93, 132.33, 132.06, 130.04, 129.46, 123.52, 123.11, 121.14, 119.53, 115.57, 114.38, 67.09, 61.97, 58.22, 56.11, 52.63, 47.31, 29.17, 25.70, 21.32, 14.53 ppm. HRMS (ESI+) *m/z*: 1317.5741 [M+H]⁺, calc. for [C₇₅H₈₅N₂O₁₉]⁺ = 1317.5747.

3.4.1.19. Tetra-Ester [2]Rotaxane **3.15**

3.14 (0.3 g, 0.23 mmol) was dissolved in methanol/tetrahydrofuran (24/12 mL) and 2 M sodium hydroxide (6 mL) was added dropwise to the stirring solution which was subsequently heated to reflux for 24 hours. Solvents were removed under reduced pressure and the residue was redissolved in water (30 mL). The pH of the solution was adjusted to 4 by the dropwise addition of 2 M HCl. The resulting mixture was left at 4 °C for 6 hours and the formed precipitate was filtered under gravity, washed with water (2 x 500 mL) and diethyl ether (2 x 50 mL) and dried to afford the product as a pale brown solid (0.21 g, 75 %). ¹H NMR (400 MHz, Methanol-*d*₄ : Chloroform-*d* 1:1) δ 8.79 (t, *J* = 1.6 Hz, 1H), 8.39 (t, *J* = 1.4 Hz, 1H), 8.32 (d, *J* = 1.5 Hz, 2H), 7.80 (d, *J* = 1.5 Hz, 2H), 7.72 (t, *J* = 1.8 Hz, 1H), 7.35 (s, 1H), 7.07 (s, 5H), 6.82 (s, 5H), 6.06 (t, *J* = 1.8 Hz, 1H), 5.58 (dd, *J* = 16, 14 Hz, 2H), 3.89 – 3.69 (m, 25H), 3.62 (s, 15H), 3.17 (dq, *J* = 23.4, 8.5 Hz, 2H), 0.41

(t, $J = 9.0$ Hz, 2H), 0.06 (s, 2H), 1.68 – 1.76 (m, 2H) ppm. ^{13}C NMR (101 MHz, Methanol- d_4 : Chloroform- d 1:1) δ 167.71, 158.63, 151.38, 150.29, 134.58, 134.07, 133.36, 132.56, 131.63, 130.07, 129.35, 123.49, 122.07, 119.28, 115.51, 114.17, 113.52, 66.95, 57.12, 55.63, 52.54, 28.77, 25.79, 21.40 ppm. HRMS (ESI+) m/z : 1233.4802 $[\text{M}+\text{H}]^+$, calc. for $[\text{C}_{69}\text{H}_{73}\text{N}_2\text{O}_{19}]^+ = 1233.4808$.

3.4.1.20. Porphyrin [2]Rotaxane **3.16**

1-Imidazole-porphyrin (0.01 g, 0.13 mmol) and **DMP[5]A** (0.14 g, 0.19 mmol) were dissolved in chloroform (1 mL) and sonicated for 30 minutes. The solution was cooled to -15 °C and 2-(iodomethyl)-1,3,5-trimethylbenzene (0.067 g, 0.26 mmol) was added under the exclusion of light. The mixture was left to warm to room temperature and stirred under a dinitrogen atmosphere overnight. The crude residue was subjected to column chromatography on silica gel (chloroform:methanol 99:1 $\rightarrow$ 98:2) to afford the product as a purple solid (0.109 g, 48 %). ^1H NMR (400 MHz, Chloroform- d) δ 8.90 (d, $J = 9.7$ Hz, 8H), 8.33 – 8.17 (m, 8H), 8.12 (s, 1H), 8.06 (t, $J = 1.6$ Hz, 1H), 7.87 – 7.72 (m, 9H), 7.33 (d, $J = 8.6$ Hz, 2H), 7.06 (s, 7H), 6.83 (s, 5H), 6.37 (t, $J = 1.7$ Hz, 1H), 6.02 – 5.76 (m, 2H), 3.93 (s, 15H), 3.89 – 3.65 (m, 27H), 2.50 (s, 6H), 2.40 (s, 3H), 1.36 – 1.30 (m, 2H), 1.22 – 1.12 (m, 2H), 0.00 – 0.24 (m, 2H), -0.85 – -1.05 (m, 2H), -1.05 – -1.33 (m, 2H), -2.70 (s, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 158.93, 151.19, 150.80, 150.51, 142.16, 142.10, 139.85, 138.18, 135.74, 134.65, 134.56, 132.91, 130.00, 129.83, 129.02, 128.24, 127.78, 126.72, 126.12, 122.57, 120.95, 120.19, 119.70, 115.87, 114.09, 113.90, 112.39, 68.30, 58.26, 55.95, 55.80, 48.94, 47.93, 30.09, 29.72, 29.18, 26.42, 25.43, 24.28, 20.20 ppm.

3.4.1.21. Porphyrin [5]Rotaxane **3.17**

Tetra-hexyl-imidazole-porphyrin (0.10 g, 0.078 mmol) and **DMP[5]A** (0.29 g, 0.391 mmol) were dissolved in chloroform (1 mL) and sonicated for 30 minutes. The solution was cooled to -15 °C and 2-(iodomethyl)-1,3,5-trimethylbenzene (0.10 g, 0.391 mmol) was added under the exclusion of light. The mixture was left to warm to room temperature and stirred under a dinitrogen atmosphere overnight. The crude residue was subjected to column chromatography on silica gel

(chloroform:methanol 97.5:2.5) to afford the product as a purple solid (0.087 g, 21 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.97 (s, 8H), 8.25 (s, 8H), 7.72 (s, 3H), 7.70 (s, 4H), 7.41 – 7.33 (m, 8H), 7.20 (d, J = 7.6 Hz, 4H), 7.06 (s, 28H), 6.80 (s, 20H), 6.13 (s, 4H), 5.84 (d, J = 13.5 Hz, 4H), 5.69 (d, J = 14.8 Hz, 4H), 4.14 – 4.07 (m, 8H), 3.94 (s, 60H), 3.80 (d, J = 32.4 Hz, 40H), 3.70 (s, 60H), 2.48 (s, 24H), 2.40 (s, 12H), 1.43 – 1.36 (m, 8H), 1.01 – 0.91 (m, 8H), 0.36 – 0.19 (m, 8H), -0.64 – -0.91 (m, 8H), -1.12 – -1.49 (m, 8H), -2.62 (s, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.31, 150.44, 140.12, 138.04, 135.82, 132.69, 130.12, 130.00, 129.06, 128.23, 125.61, 125.30, 121.77, 121.22, 119.82, 116.14, 113.87, 112.51, 112.48, 68.32, 58.46, 56.02, 48.62, 47.64, 30.36, 29.18, 26.21, 25.83, 24.88, 21.48, 21.23, 20.05 ppm.

3.4.1.22. Porphyrin Tetra-Pillar[5]arene **TP[5]AP**

Tetraphenol-porphyrin (0.040 g, 0.010 mmol), potassium carbonate (0.0087 g, 0.063 mmol) and bromo-pillar[5]arene (0.073 g, 0.083 mmol) in DMF (5 mL) was stirred at 70 °C for 24 h. The solvent was removed under reduced pressure. The residue was redissolved in ethyl acetate and washed with water (3 x 50 mL) and brine (1 x 50mL). The organic layer was dried over anhydrous MgSO_4 , filtered under gravity and concentrated. The crude product was purified through silica gel chromatography (dichloromethane: methanol 99:1) to give the product as a purple solid (0.020 g, 9 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.91 (s, 8H), 8.17 (d, J = 8.2 Hz, 8H), 7.32 (d, J = 8.4 Hz, 8H), 6.90 – 6.79 (m, 40H), 4.36 (t, J = 5.7 Hz, 8H), 4.07 (t, J = 5.7 Hz, 8H), 3.94 – 3.64 (m, 160H), 2.31 – 2.08 (m, 16H), -2.69 (s, 2H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.86, 150.90, 150.86, 150.81, 150.07, 135.65, 134.63, 128.42, 128.34, 128.30, 128.27, 128.26, 128.18, 119.79, 115.04, 114.27, 114.21, 114.14, 114.11, 114.07, 112.70, 68.15, 67.86, 55.95, 55.81, 55.78, 29.87, 29.85, 29.74, 29.66, 29.64, 26.66, 26.60 ppm.

3.4.1.23. [2]Rotaxane **3.18**

Bis-imidazole octane (0.083 g, 0.34mmol) and pillar[5]arene bearing two bromo-butyl arms (0.50 g, 0.50 mmol) were dissolved in chloroform (1 mL) and sonicated for 30 minutes. The solution was

cooled to -15 °C and 2-(iodomethyl)-1,3,5-trimethylbenzene (0.26 g, 1.00 mmol) was added under the exclusion of light. The mixture was left to warm to room temperature and stirred under a dinitrogen atmosphere overnight. The crude residue was subjected to column chromatography on silica gel (chloroform:methanol 99:1) to afford the product as a pale yellow solid (0.31 g, 53 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.71 (t, *J* = 5.7 Hz, 2H), 7.01 (s, 4H), 6.93 (s, 2H), 6.89 – 6.79 (m, 10H), 6.76 (s, 2H), 5.61 – 5.46 (m, 4H), 3.98 – 3.91 (m, 2H), 3.82 (dd, *J* = 11.0, 4.7 Hz, 2H), 3.56 (t, *J* = 6.4 Hz, 2H), 3.32 (t, *J* = 6.7 Hz, 2H), 2.37 (s, 12H), 2.35 (s, 6H), 2.03 (ddt, *J* = 39.5, 13.9, 6.3 Hz, 8H), 0.91 (s, 4H), 0.61 (s, 4H), 0.33 (s, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.09, 150.98, 150.88, 150.09, 140.18, 137.96, 134.37, 130.10, 130.04, 129.89, 129.80, 129.61, 125.13, 122.81, 119.58, 116.08, 115.76, 115.55, 115.40, 114.88, 70.53, 69.24, 69.07, 57.98, 57.82, 57.75, 57.48, 48.52, 47.64, 34.01, 30.82, 30.63, 30.37, 30.18, 29.95, 29.87, 29.26, 29.18, 29.01, 28.82, 28.54, 26.73, 21.16, 19.88 ppm.

3.4.1.24. [2]Rotaxane **3.19**

[2]Rotaxane **3.18** (0.5 g, 0.282 mmol), potassium iodide (0.122 g, 0.735 mmol) and potassium carbonate (0.184 g, 1.33 mmol) were suspended in DMF (30 mL). Pyridin-3-ol (0.076 g, 0.80 mmol) was added and the mixture stirred at room temperature for 36 hours. The mixture was cooled to room temperature, quenched with water (30 mL) and extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with water (3 x 30 mL) and brine (1 x 30 mL), dried over anhydrous MgSO₄ and filtered under gravity. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (chloroform:methanol 90:10) to give the product as an off white solid (0.17 g, 34 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.29 (s, 2H), 8.21 (s, 2H), 7.29 (s, 7H), 7.00 (s, 4H), 6.85 (d, *J* = 13.6, 10.3 Hz, 12H), 6.72 (d, *J* = 6.1 Hz, 2H), 5.57 – 5.43 (m, 4H), 4.17 (s, 4H), 4.02 (d, *J* = 5.2 Hz, 2H), 3.90 (d, *J* = 8.8 Hz, 2H), 3.79 – 3.63 (m, 40H), 2.37 (s, 12H), 2.34 (s, 6H), 2.13 – 2.01 (m, 8H), 0.96 (s, 4H), 0.65 (s, 4H), 0.45 – 0.21 (m, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.13, 151.07, 150.96, 150.94, 150.16, 141.87, 140.22, 137.96, 134.29, 130.08, 130.01, 129.97, 129.76,

129.69, 129.60, 125.08, 124.13, 122.82, 122.80, 121.17, 119.53, 119.46, 116.22, 115.71, 115.58, 115.45, 114.97, 70.53, 69.81, 68.08, 57.95, 57.75, 57.34, 48.53, 47.60, 29.89, 29.70, 29.26, 29.20, 29.04, 28.86, 26.75, 26.64, 26.36, 21.13, 19.85 ppm.

3.4.1.25. Ag(I)-Coordinated [2]rotaxane **3.20**

To solution of [2]rotaxane **3.19** (0.10 g, 0.0560 mmol) in dichloromethane (25 mL) was added Ag₂O (0.026 g, 0.112 mmol) and the mixture was stirred at room temperature overnight under the exclusion of light. The mixture was filtered through a celite plug and the organic fractions were combined, dried over anhydrous MgSO₄, filtered under gravity and the solvent removed under reduced pressure to afford the crude product as an off white solid. This was redissolved in dichloromethane (1mL) and added dropwise to cold hexane (20 mL). The white precipitate was collected by filtration under reduced pressure, washed with hexane and dried to afford di-pyridine 2Ag(I) [2]rotaxane (0.079 g, 74 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.28 (s, 2H), 8.23 (d, *J* = 3.8, Hz, 2H), 7.24 (s, 2H), 7.23 (s, 2H), 7.18 (d, *J* = 1.7 Hz, 2H), 6.96 (s, 4H), 6.95 – 6.82 (m, 10H), 6.65 – 6.56 (m, 2H), 5.32 (s, 4H), 4.11 (t, *J* = 5.7 Hz, 4H), 4.05 – 3.85 (m, 4H), 3.80 – 3.58 (m, 40H), 2.37 – 2.28 (m, 18H), 2.13 – 1.94 (m, 8H), 0.71 (m, 4H), -0.71 (s, 4H), -1.42 (s, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.07, 150.88, 150.84, 150.74, 150.68, 150.10, 142.09, 139.21, 138.08, 137.62, 129.82, 129.39, 129.16, 129.01, 128.89, 127.65, 123.92, 120.84, 120.61, 119.34, 115.10, 114.95, 114.20, 77.24, 69.12, 67.94, 57.19, 56.99, 56.53, 56.46, 52.37, 49.77, 31.16, 29.71, 29.23, 29.18, 27.57, 26.68, 26.52, 25.52, 21.08, 19.95 ppm.

3.4.1.26. Pd(II)-Coordinated [2]rotaxane **3.21**

Ag(I)-[2]rotaxane **3.20** (0.05 g, 0.0262 mmol) was added to a flame dried flask which had been backfilled with dinitrogen three times. Anhydrous pyridine (10 mL) was added via cannula, followed by Pd(CH₃CN)₂Cl₂ (0.015 g, 0.577 mmol) and NaI (0.017 g, 0.115 mmol). The mixture was heated to reflux and stirred overnight under a dinitrogen atmosphere and under the exclusion of light. All volatiles were evaporated under reduced pressure and the residue was redissolved in

chloroform (25 mL) and water (25 mL). The organic layer was separated and washed with water (3 x 100 mL), 5 % CuSO₄ aq. (100 mL) and brine (100 mL) and subsequently dried over MgSO₄ and filtered under gravity. The solvent was removed under reduced pressure and the residue subjected to a silica gel pad (dichloromethane) to afford the product as an orange solid (0.042 g, 71 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.29 – 8.51 (m, 3H), 7.61 – 7.30 (m, 3H), 7.09 – 6.62 (m, 14H), 6.44 – 6.24 (m, 2H), 5.60 (d, *J* = 14.2 Hz, 3H), 4.50 – 4.02 (m, 8H), 3.97 – 3.41 (m, 35H), 2.38 (d, *J* = 5.0 Hz, 17H), 2.13 – 1.95 (m, 4H), 0.95 – 0.76 (m, 4H), -0.11 – -0.91 (m, 4H), -1.73 – -2.45 (m, 4H) ppm. The limited solubility of this compound precluded the acquisition of a ¹³C NMR spectrum.

3.5. References

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Chapter 4

Handcuff [2]Rotaxanes – Studying the Interactions Between Molecules

4.1. Introduction

4.1.1. Rylene Diimides

Rylene diimides are polycyclic hydrocarbons consisting of naphthalene units, connected at the peri position with two imide groups (one on either end of the rylene). They are found in a wide range of applications; for example in dyes and organic semiconductors (n-type) due to their high electron affinities, large absorption coefficients, high fluorescence (up to 100 % quantum yields) and excellent chemical and thermal stability. These properties can be readily adjusted, enhanced and fine-tuned through symmetrical or asymmetrical modification of the substituents on the imide and core regions. The two smallest and most commonly used rylene diimide oligomers are composed of one and two naphthalene units and are called naphthalene-1,4,5,8-tetracarboxylic diimide (NDI) and perylene-3,4,9,10-tetracarboxylic diimide (PDI), respectively (Figure 4.1).¹

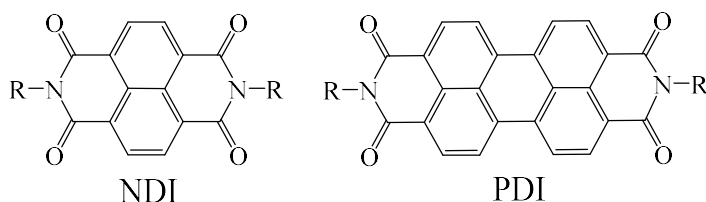


Figure 4.1: General structure of NDI and PDI.

4.1.1.1. Naphthalene Diimides (NDIs)

NDIs are the smallest member of the rylene diimide family. They are neutral, chemically robust and planar aromatic compounds. Due to their electron deficient cores, they are redox-active and have been utilised in a variety of applications such as in biomimetic/bioinspired artificial systems² as well as being considered promising candidates for organic electronics.³ NDI functionalisation through core-substitution has a direct influence on the aromatic network and therefore has a strong impact on the absorbance and fluorescence properties. Although functionalisation at the imide nitrogen has only little effect on the optical and electrochemical properties, imide substitution can have a significant effect on the aggregation behaviour and thus on the solubility

of NDIs.⁴ Furthermore, imide substitution is an effective synthetic handle in constructing NDI-based supramolecular architectures,⁵ donor-acceptor complexes⁶ and systems capable of artificial photosynthesis.⁷

4.1.1.2. Perylene Diimides (PDIs)

PDIs were the first reported rylene diimide⁸ and have since been utilised in a number of industrial applications such as in paints⁹ and as fluorescence emitters (for example in single molecule spectroscopy).¹⁰ To this day PDIs are the subject of intense study and research as they are strongly fluorescent, redox-active and absorb in the visible. These properties can be altered through functionalisation at the core and imide regions^{1a} allowing PDIs to be tailored into useful building blocks for self-assembly in supramolecular architectures.^{1c, 10-11}

4.1.2. NDI/PDI Stacking and Dimers

Functional dye-based materials are an area of increasing importance in many technological applications such as organic semiconductors. This has led to an increased interest in the nano- and bulk material properties of these molecules and therefore, understanding the intermolecular interactions which affect these properties is essential.^{1a} Through developing and understanding dye-based supramolecular assemblies, a greater understanding of the solid-state properties such as absorption, solid-state fluorescence and hole/electron transport can be derived.¹² One of the key factors influencing the properties of NDI and PDI bulk materials is π - π stacking. For example, face to face interactions between adjacent aromatic groups can have a dramatic effect on the redox properties and thus the conductivity of a material. Supramolecular architectures can constitute an intermediate state of matter allowing specific aspects of a bulk material (such as π - π stacking) to be studied. One strategy, which has shown interesting results, is the synthesis and study of dye-based dimers. Examples of these include; PDI-PDI dimers consisting of PDIs that are connected through one imide on each PDI¹³ and PDI-PDI dimers held together through hydrogen bonding interactions.¹⁴ PDI-PDI dimer cyclophanes have also been reported in which two PDIs are

linked at both imides with flexible¹⁵ or ridged¹⁶ bridging units. For example Lambert, Würthner and co-workers reported a cyclophane consisting of PDIs linked with dynamic phenylene ethynylene bridging units, allowing for a pronounced conformational transition upon tetra-reduction (Figure 4.2).¹⁷ Similar strategies have been applied in the synthesis and study of NDI-NDI dimers¹⁸ and more recently terrylene-diimide dimers.¹⁹

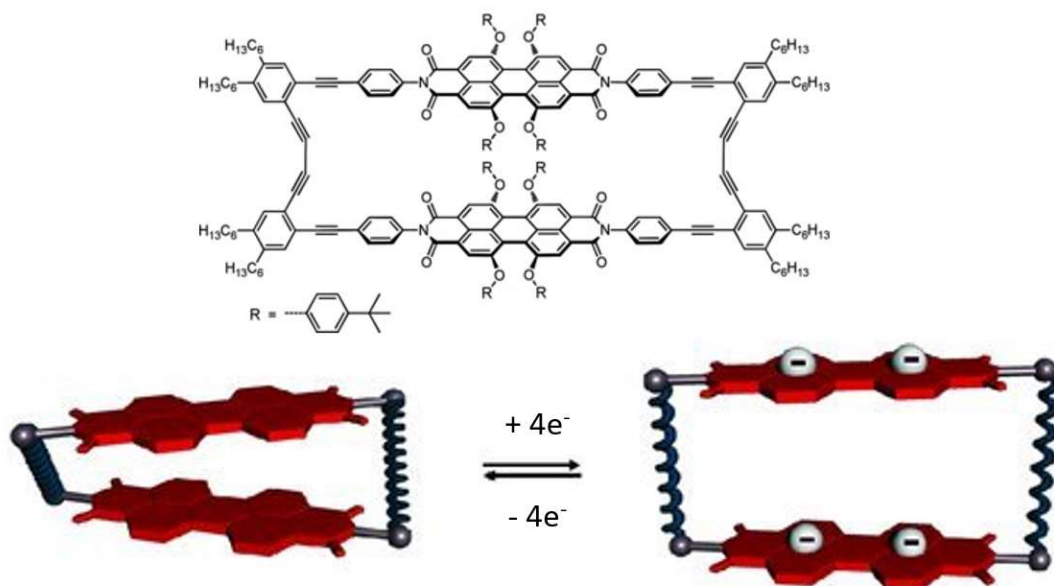


Figure 4.2: A PDI cyclophane dimer exhibiting a pronounced reversible conformational transition upon tetra-reduction. Adapted from Ref.¹⁷

4.1.3. Handcuff Topology

As described in Chapter 1, MIMs with numerous components and a broad range of topologies have been reported. Multiple mechanically interlocked molecules (MMIMs) are a way of accessing higher order architectures and building more complex topologies such as handcuff MIMs.²⁰ Handcuff MIMs consist of covalently linked macrocycles, mechanically interlocked by a third macrocycle (handcuff catenane) or axle (handcuff rotaxane) that threads both rings (Figure 4.3-1). An early example of a handcuff [2]catenane was described by Becher and co-workers, who utilised donor-acceptor interactions between an electron-rich tetra-thiafulvalene-based *bis*-macrocycle and an electron-deficient-cyclo-*bis*-(paraquat-*p*-phenylene) to drive assembly.²¹ Other

reported strategies include the use of templates such as Cu(I) derivatives coordinated to 1,10-phenanthroline (Sauvage and co-workers)²² and chloride anions (Beer and co-workers).²³ Similarly, Stoddart and co-workers employed a template-directed approach in the synthesis of a handcuff [2]catenane by utilising interactions between a π -electron-rich *bis*-1,5-dioxynaphtho[50]crown-14 and a π -electron-deficient cyclo-*bis*-(paraquat-*p*-phenylene) cyclophane.²⁴ Handcuff [2]rotaxanes with three macrocycles, covalently linked together have been developed by Stoddart and co-workers as part of a molecular elevator,²⁵ whilst doubly²⁶ and triply²⁷ stacked four-fold handcuff [n]rotaxanes based on a porphyrin template have been reported by Tanaka and co-workers. More typical handcuff [2]rotaxanes consist of only two covalently linked macrocycles, both of which are threaded by an axle. Liu and co-workers utilised donor-acceptor interactions between an electron-rich anthracene and an electron-deficient NDI unit to synthesise a double-leg-two-station molecular elevator (Figure 4.3-1).²⁸ In this example the macrocycles are planar crown ethers, therefore threading through either side is indistinguishable and as a result there are no topological isomers. Topological isomers induce chirality in [n]rotaxanes and [n]catenanes which is an area of increasing significance²⁹ however this isomerisation can also present problems in the design and synthesis of MIMs and MMIMs.³⁰ A handcuff with a single topological isomer, based on a double-calix[6]arene system with a *bis*-ammonium axle, was reported by Gaeta, Neri and co-workers. The authors took advantage of the “*endo*-alkyl rule”³¹ to control the threading directionality of alkylbenzylammonium axles with calix[6]arene macrocycles (Figure 4.3-2)³² however, this method is very specific. Recently, a helical chiral handcuff [2]rotaxane featuring two ammonium ion recognition sites in the axle component and di-macrocyclic calix-*bis*-crown ethers was reported by Tokunaga and co-workers. The authors observed the enantiomeric character of the isomers through CD spectroscopy and were able to isolate them using chiral HPLC.³³

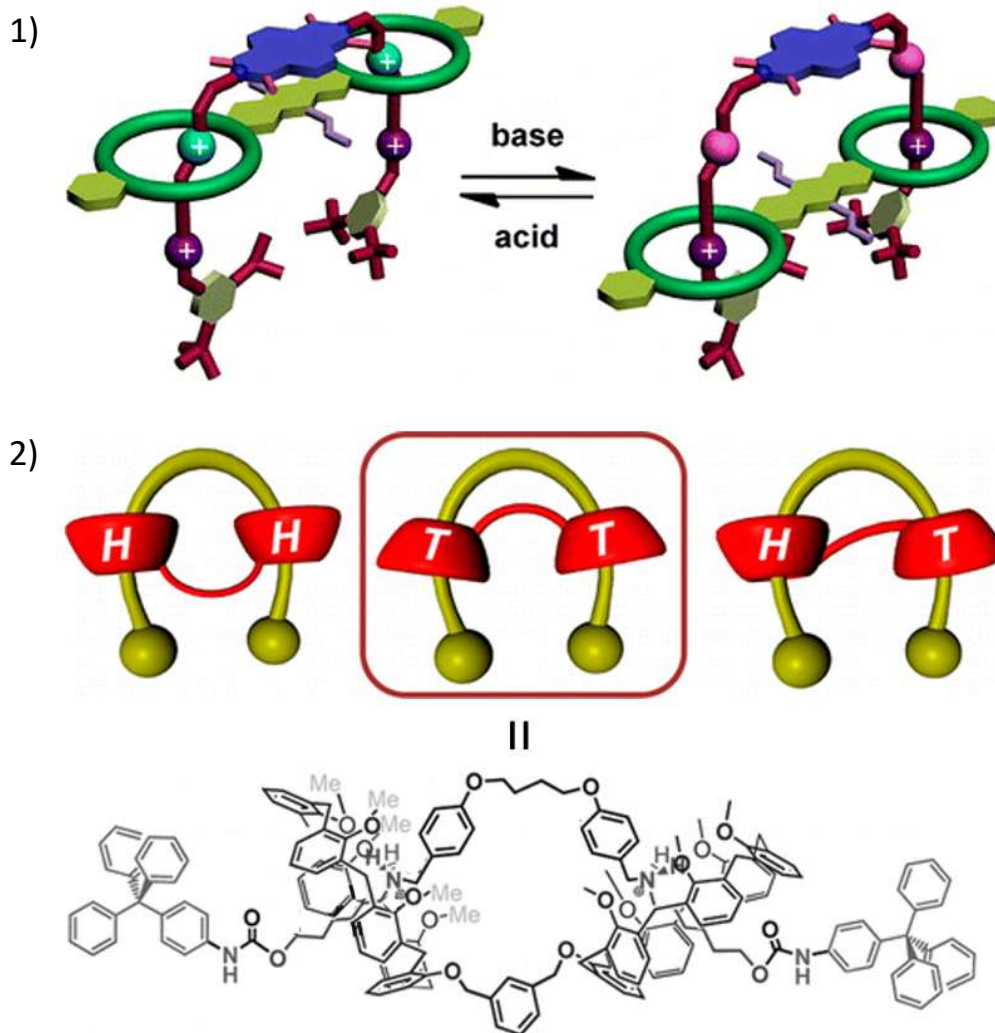
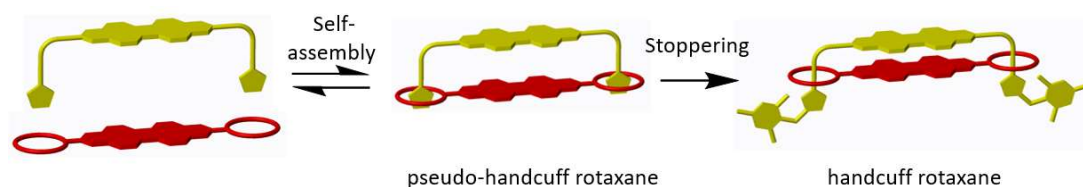


Figure 4.3: 1) Cartoon representation of a double-leg molecular elevator handcuff [2]rotaxane. Adapted from Ref.²⁸ 2) Cartoon depiction of the three possible topological isomers of a handcuff [2]rotaxane with asymmetric macrocycles and chemical structure of an orientated handcuff [2]rotaxane. Adapted from Ref.³²

4.2. Results and Discussion

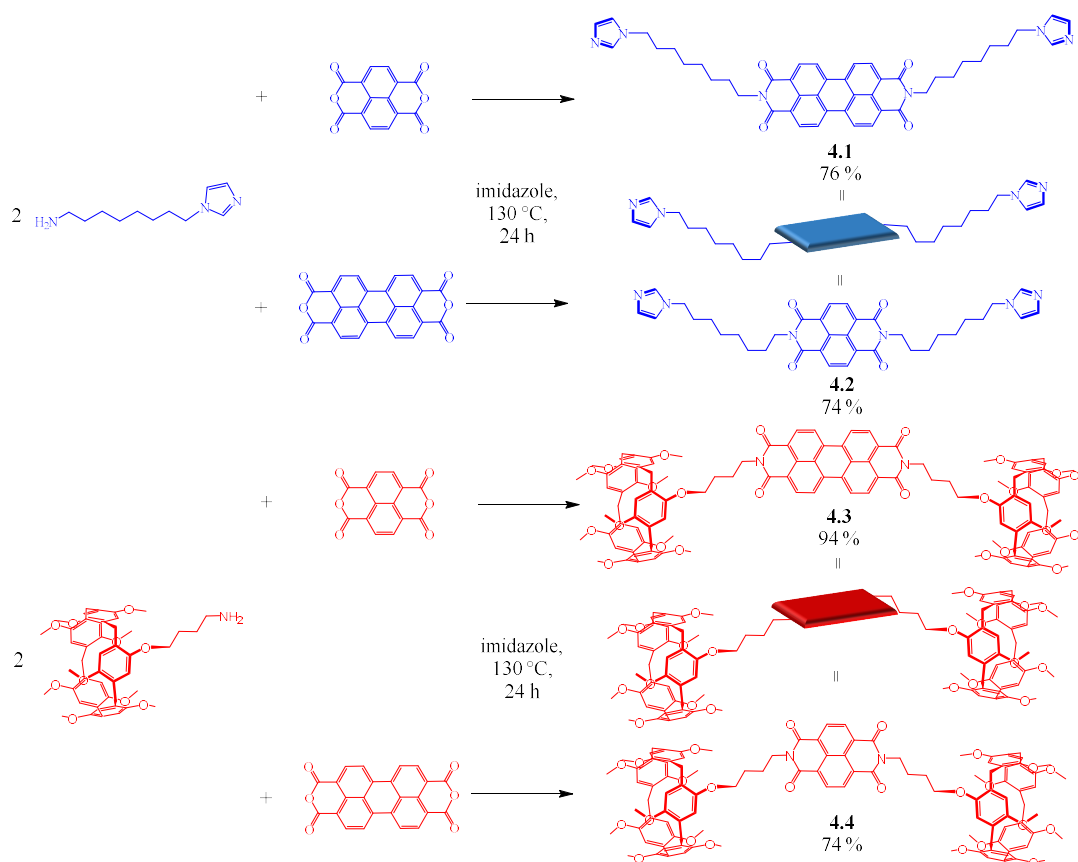
4.2.1. Molecular Design and Synthesis

In the PDI and NDI cyclophanes (described in Section 4.1.2) the aromatic cores are linked by covalent or coordination bonds, which restrict the arrangement the aromatic moieties can take relative to each other. Mechanical bonds can be exploited to provide a large degree of flexibility whilst not allowing the aromatic moieties to fully disassociate. Additionally, the topological arrangement induced by handcuff [2]rotaxanes situates the rylene diimides in a co-facial arrangement, potentially allowing for communication between the two aromatic cores (Scheme 4.1).



Scheme 4.1: Cartoon representation of handcuff synthesis. Pseudo-handcuff [2]rotaxane assembly is driven by pillar[5]arene/imidazole interactions and π - π stacking between the two aromatic cores.

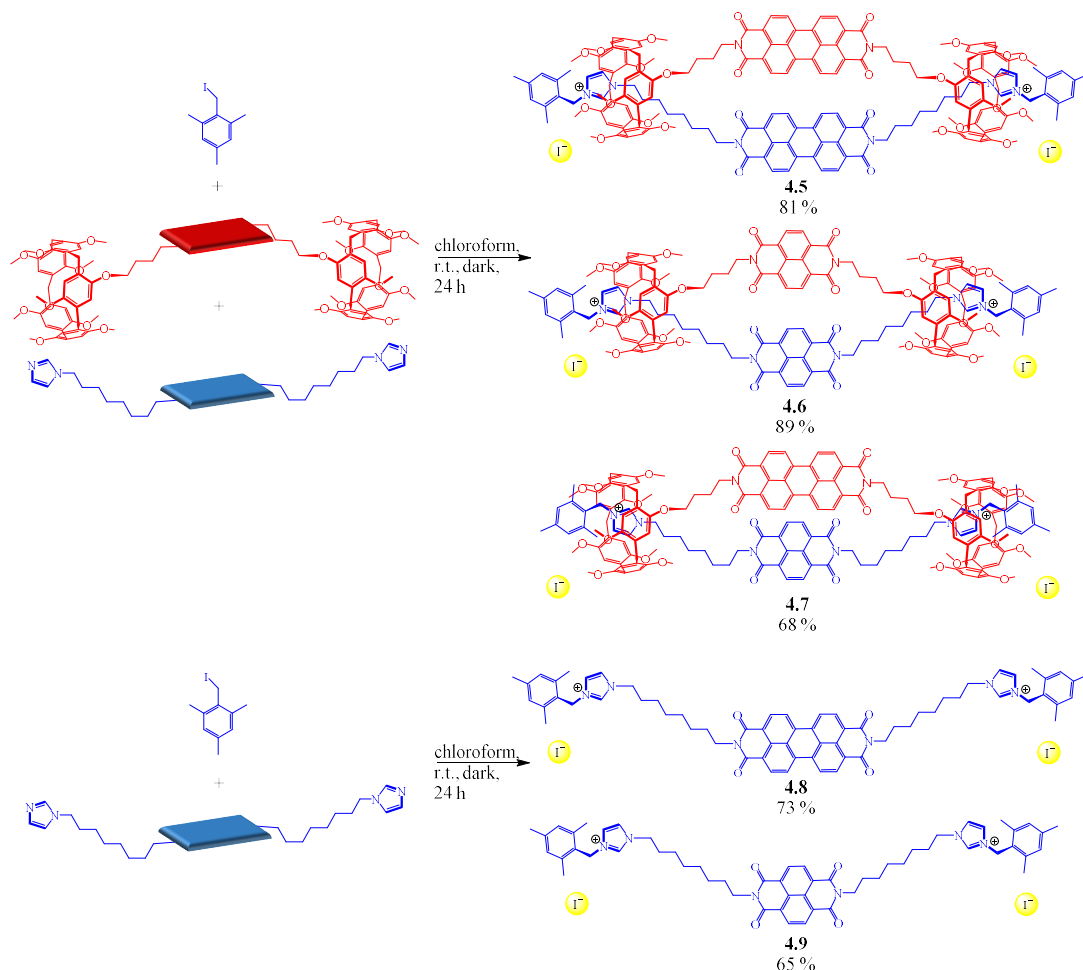
The same methodology discussed and developed in Chapters 2 and 3 was used in the synthesis of PDI/NDI-containing [2]rotaxanes with handcuff topology. This required the synthesis of the desired aromatic groups, functionalised with two imidazoles on one component and two pillar[5]arenes on the other component (Scheme 4.2). Reaction of the appropriate rylene dianhydride with an imidazole group, functionalised with an alkylamine arm led to the formation of PDI and NDI units with pendant imidazoles (**4.1** and **4.2**, respectively). An analogous reaction with amine-functionalised pillar[5]arene, led to the formation of *bis*-pillar[5]arene-functionalised PDI and NDI (**4.3** and **4.4** respectively). In both the *bis*-imidazole and the *bis*-pillar[5]arene species, the two pendant arms are separated by the aromatic PDI/NDI core.



Scheme 4.2: Synthesis of *bis*-imidazole, **4.1-4.2**, and *bis*-pillar[5]arene, **4.3-4.4**, PDI/NDI.

The reaction of one equivalent of *bis*-imidazole component with one equivalent of *bis*-pillar[5]arene component led to the formation of stable pseudo-rotaxanes. This is driven by favourable pillar[5]arene/imidazole and rylene π - π stacking interactions in chloroform. The components were readily locked together using the proven 2-(iodomethyl)-1,3,5-trimethylbenzene stopper group, under analogous conditions to previously described threading reactions (Scheme 4.3). The combination of monomer units in such a manner led to the formation of PDI-PDI, NDI-NDI and PDI-NDI handcuff dimers (**4.5**, **4.6** and **4.7**, respectively). This synthetic strategy provides a widely applicable way of selectively locking different components together co-facially, allowing their interactions to be studied. In principle, this simple approach only requires the components to feature the necessary functionality for locking them together (imidazoles/pillar[5]arenes). The unthreaded PDI and NDI axle components (**4.8** and **4.9**

respectively) were also synthesised to provide a viable comparison in the evaluation of handcuff [2]rotaxane properties. They were readily prepared using an analogous procedure to the handcuff [2]rotaxanes, in the absence of the *bis*-pillar[5]arene component (Scheme 4.3).



Scheme 4.3: Synthesis of PDI-PDI, NDI-NDI and PDI-NDI handcuff [2]rotaxanes, **4.5-4.7**, as well as PDI and NDI *bis*-imidazolium axles, **4.8** and **4.9**.

Formation of the handcuff [2]rotaxane structures was confirmed through NMR spectroscopy and HRMS. A strong upfield shift of peaks associated with the imidazolium and the alkyl chain (linking the imidazolium to the PDI/NDI core) was observed due to the shielding effect of the pillar[5]arene (Figure 4.4). Additionally, H₀ (the CH₂ linking the stopper group to the imidazolium) shows the characteristic splitting, due to pillar[5]arene chirality, previously observed in Chapters 2 and 3. The high degree of symmetry shown in the ¹H NMR spectra indicates dual threading, confirming

handcuff topology. The asymmetric functionalisation of the pillar[5]arene units, on either end of the aromatic cores, makes their rims inequivalent. Threading can occur through either rim which results in two different threading modes for each pillar[5]arene. Therefore there are three possible threading arrangements resulting in three possible stereoisomers (Figure 4.3-2). Evidence of this additional isomerism is seen in further splitting of peaks in the ^1H NMR, for example in H_i and H_h . However, assignment of individual peaks to a specific stereoisomers was not possible. The nature of interactions between the two rylene diimides in **4.5-4.7** was investigated through exploring the electrochemical properties of the three handcuff [2]rotaxane systems and comparing them to their unthreaded constituents, **4.3-4.4** and **4.8-4.9**. To do so, a combination of electroanalytical techniques were employed; including UV/vis spectroscopy, fluorescence spectroscopy, cyclic voltammetry (CV), spectroelectrochemistry and electron paramagnetic resonance (EPR) spectroscopy. This comprehensive analysis was done in conjunction with Dr. Stephen Davies.

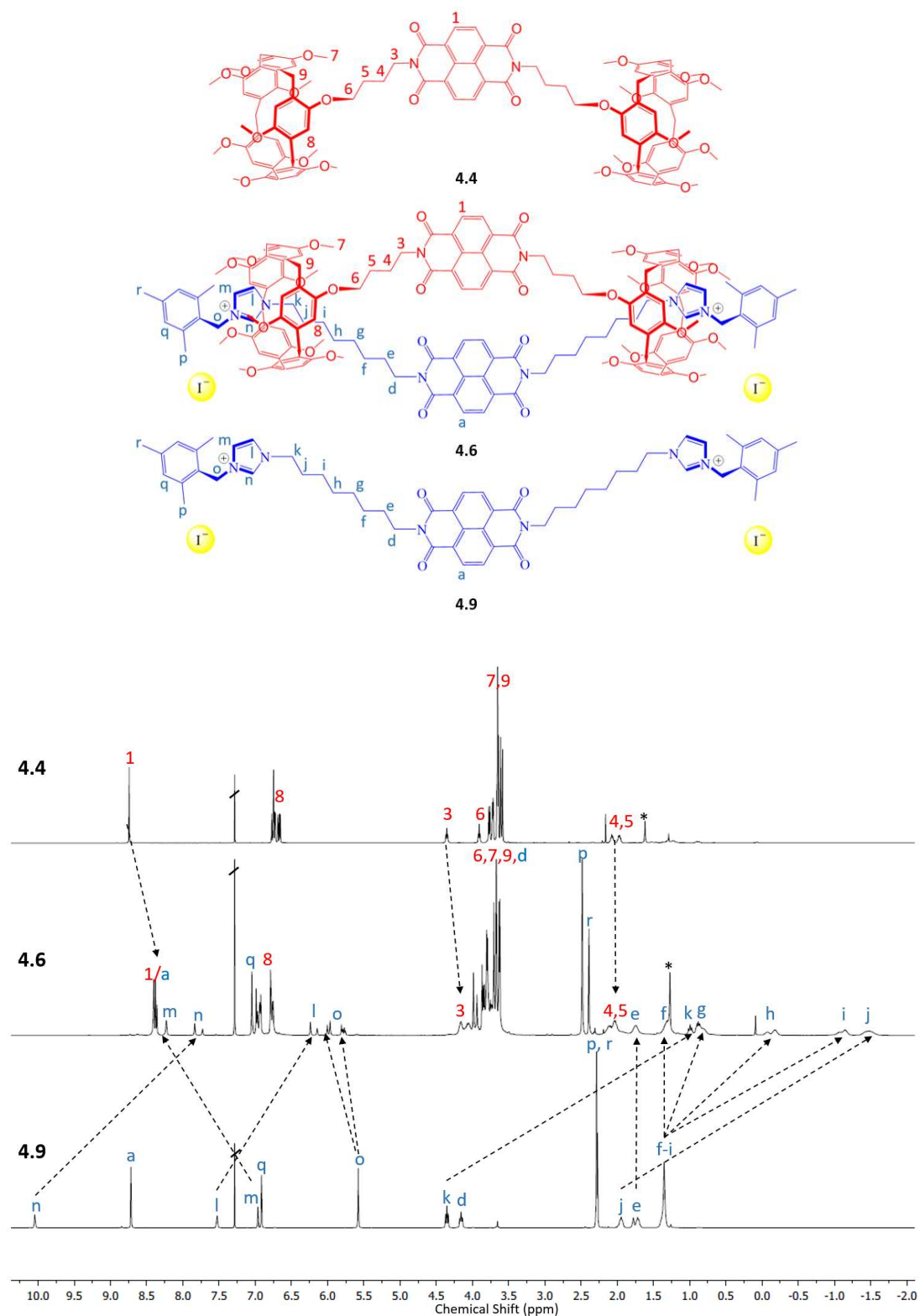


Figure 4.4: ^1H NMR (400 MHz, CDCl_3 , 298 K) spectra of **4.4** (top), **4.6** (middle) and **4.9** (bottom). Showing handcuff [2]rotaxane formation through the arising shifts in the alkyl-peaks of the axle due to the shielding effect of the pillar[5]arene.

4.2.2. UV/vis Spectroscopy

The UV/vis spectra of PDI monomer components (**4.3** and **4.8**) in chloroform (Table 4.1) showed three bands of increasing intensity and overall absorption profiles consistent with monomeric PDIs in solution.^{14b} However, the visible absorbance spectrum of **4.5** showed a reordering of the intensity of these bands and the spectral profile was consistent with that of a π -stacked chromophore.³⁴ The dominant absorption band (at 493 nm) exhibited a blue shift of 32 nm relative to the monomers. Although this shift is relatively small, it may be the consequence of a transition into an exciton-split LUMO which forms due to π - π interactions between PDI cores orientated in a face-to-face arrangement.^{16c, 35} In contrast, the UV/vis spectrum of a 1:1 mixture of **4.3** and **4.8** showed no significant differences and was essentially a sum of the individual components. Unlike for **4.5**, the UV/vis spectra of **4.6** resembled that of a 1:1 monomer mixture. There was no change in the relative transition intensities, nor was there a shift in the peak positions. This varies from a H-aggregated NDI-NDI dimer, previous report by Wasielewski, Stoddart and co-workers, in which a significant blue shift in the NDI bands of a was observed.^{18c} The UV/vis spectrum of **4.7** also showed an absorption profile similar to that of the monomers, in which the relative transition intensities suggested no stacking interactions and no significant shifts were observed.

Solvent		Absorption (λ_{abs} / nm)				Emission (λ_{em} / nm)				$\lambda_{\text{Excitation}}$ / nm	Φ
		NDI bands		PDI bands							
4.3	CHCl ₃	-	-	458	489	525	533	574	-	485	0.002
4.4	CH ₂ Cl ₂	361	381	-	-	-	-	-	-	-	-
4.5	CHCl ₃	-	-	-	493	533	622	-	-	533	-
	CH ₂ Cl ₂	-	-	-	492	531	627	-	-	490	0.016
	MeCN	-	-	-	489	528	655	-	-	529	-
4.6	CH ₂ Cl ₂	361	382	-	-	-	-	-	-	-	-
4.7	CHCl ₃	364	385	464	495	533	-	-	-	-	-
	CH ₂ Cl ₂	365	384	463	494	532	544	585	-	490	0.004
	MeCN	363	384	462	493	530	532	574	627	490	-
4.8	CHCl ₃	-	-	458	489	525	534	575	624	490	0.800
4.9	CHCl ₃	360	381	-	-	-	385	408	-	360	0.001

Table 4.1: Absorption and emission data for compounds **4.3-4.9** (bold indicates the most intense band).

4.2.3. Emission Spectroscopy

The emission spectrum of monomer **4.8** in chloroform showed typical PDI fluorescence (Figure 3.5) with a small Stokes shift, vibronic features and a quantum yield of 0.800. Although the emission spectrum of **4.3** showed similar characteristics, it was substantially quenched to a quantum yield of 0.002. This is evidence for a very efficient non-radiative decay pathway between the PDI core and the pillar[5]arenes. The emission spectrum of **4.5** exhibited significant differences from its monomer components. Excitation of **4.5** at 490 nm in dichloromethane showed a broad featureless transition centred at 627 nm. Furthermore, this peak displayed a larger Stokes shift ($\nu_{\text{abs}} - \nu_{\text{em}} = 2883 \text{ cm}^{-1}$) and slightly enhanced fluorescence (quantum yield of 0.016) relative to **4.3**. These attributes correspond to characteristic features associated with emission from an excimer-like state in molecules containing π -stacking, where the π -systems are electronically coupled in the excited state.^{16d} Emission from **4.5** was found to be solvent dependant. Going from dichloromethane/chloroform to acetonitrile, the increase in polarity resulted in a red-shift of the emission band to 655 nm, accompanied by an increased Stokes shift ($\nu_{\text{abs}} - \nu_{\text{em}} = 3672 \text{ cm}^{-1}$). However, in the ground state the spectral profile remained essentially unaffected by the change in solvent and therefore these effects appear to be limited to the excited state. The observed emission characteristics in **4.5** can be rationalised by considering electron delocalisation between the π^* orbitals of the two PDI units. For this type of electron sharing to occur, the close proximity of the two PDI units is essential. This was confirmed by the emission spectrum of a 1:1 mixture of **4.3** and **4.8** which gave a typical PDI fluorescence response, with no emission of an excimer-like state. Unlike in **4.8**, the emission spectrum of **4.9** exhibited very weak fluorescence (quantum yield of 0.001), however weak vibronic coupling was still observed. **4.4** showed heavy quenching (similar to **4.3**) and no quantum yield could be determined. Similarly, the emission spectrum of **4.6** only showed weak fluorescence and there was no evidence of an excimer-like state. In **4.7** weak fluorescence was also observed (quantum yield of 0.004 in dichloromethane) however the emission profile showed some vibronic coupling. The emission band was centred at 544 nm which

corresponds to emission from a typical localised PDI orbital and therefore **4.7** exhibits no evidence for the presence of an excimer-like state in dichloromethane, chloroform or acetonitrile. This could be due to a lack of π - π interactions between the PDI and the NDI cores in the ground state (of which there was no evidence for in the UV/vis spectrum) or due to the disparity in excitation energies between the PDI and NDI cores.

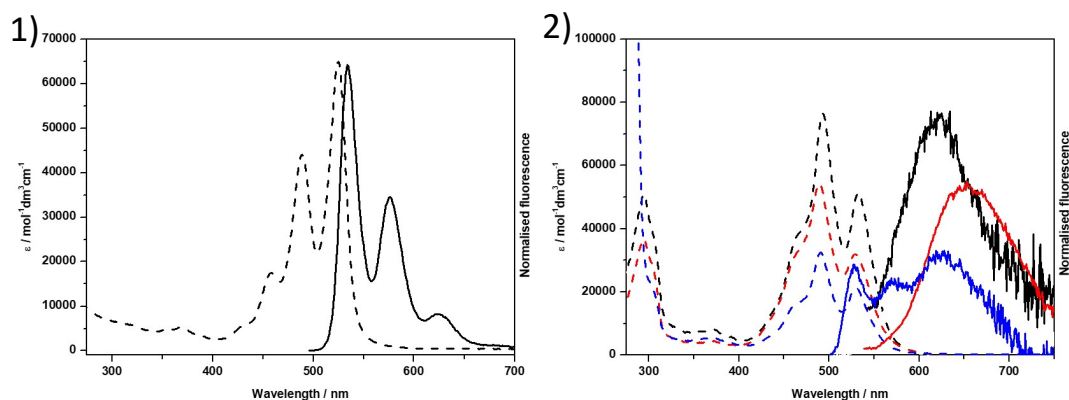


Figure 4.5: UV/vis absorption (dashed) and emission (solid) of 1) **4.8** in chloroform and 2) **4.5** in chloroform (black), acetonitrile (red) and THF (blue).

4.2.4. Electrochemistry

Encouraged by the evidence for communication between the two rylene diimides (apparent in the emission profile of **4.5**) the molecular orbitals of **4.3-4.9** at each accessible oxidation state were probed using cyclic (CV) and square-wave (SW) voltammetry and spectroelectrochemistry. Only sweeps to negative potential were considered for these compounds in order to eliminate problems associated with the oxidation of the iodide counter ions in **4.5-4.9**.³⁶

4.2.4.1. CV

The CVs of **4.3** and **4.8** each showed two one-electron reductions (separated by ca. 0.2 V), consistent with other PDIs that have no bay substitutions (Table 4.2).³⁷ By contrast the CV of **4.5** showed three distinct redox couples; two one-electron reductions at -0.93 and -1.07 V as well as one two-electron reduction at -1.25 V. Compared to **4.3** and **4.8**, the first one-electron reduction

of **4.5** was shifted positively (by 0.03 and 0.01 V respectively), whilst the second one-electron reduction was shifted to a more negative potential (by 0.11 and 0.13 V respectively). The third reduction was found to be a single two-electron process which was shifted to more negative potential by 0.10 and 0.13 V (relative to **4.3** and **4.8**) and corresponds to the addition of one electron to each of the two PDI cores (Figure 4.6-1). The observation of three well separated redox couples, despite the molecule containing two essentially equivalent redox centres, indicates that there is electronic communication between the two PDI cores (on the experimental timescale). The co-facial arrangement of the PDI units and the absence of an electronic pathway through covalent bonds suggests that this communication occurs via a through-space shared π -framework. The CV of a 1:1 mixture of **4.3** and **4.8** showed only the sum of the components, excluding the possibility of intermolecular interactions being responsible for the complex CV response of **4.5**. In a molecule containing two equivalent redox centres, in which the electrons are interacting through a shared π system, the presence of one electron makes the addition of a second electron more energetically unfavourable. This is due to increased repulsive (coulombic) interactions between the already added electron and the second electron. The extent of this interaction can be quantified using the difference between the first and second redox potential ($\Delta E = E_2 - E_1$) and is proportional to the magnitude of delocalisation. Although the first reduction (to generate [**4.5**] $^-$) occurs at only slightly more positive potential than for either **4.3** or **4.8**, this could be an indication that the electron enters a lower energy molecular-based orbital derived from the combination of the two PDI π systems. Addition of a second electron to this (already occupied) molecular orbital is more difficult due to the aforementioned coulombic repulsion between the electrons. The increased energy required for this process results in a more negative reduction potential of the second one-electron redox couple (to generate [**4.5**] $^{2-}$). The difference between the first and second reduction allows the calculation of the comproportionation constant ($K_{com} = 10^{\frac{F\Delta E}{2.303RT}}$), a measure of delocalisation. The CV of **4.5** showed a difference between the first and second reduction of 0.14 V which gives a comproportionation constant of ca. 10^2 . This indicates limited

delocalisation and makes **4.5** a Robin-Day Class II mixed valent species (on the electrochemical timescale).³⁸ The third reduction occurred in a single step (generating [**4.5**]⁴⁻) and suggests that communication between the two PDI units is considerably reduced or lost completely, resulting in two separate localised PDI-based π -orbitals (Robin-Day Class I). The non-rigid framework, with which the PDI cores are connected, allows for the reorientation of the two PDIs to minimise any repulsive interactions within the tetra-anionic species. It is likely that in [**4.5**]⁴⁻ the repulsive forces dominate over the energetically favourable π - π interactions and thus the delocalised framework is significantly disturbed or lost all together. This redox behaviour considerably varies from that observed by Würthner and co-workers¹⁷ for a rigid PDI-PDI dimer, in which the PDIs are separated by diacetylene spacers (Figure 4.2). Due to the rigidity of these linkers, the third reduction is immediately followed by a chemical reaction resulting in separation of the PDI cores and consequential opening of the cyclophane cavity. This is shown by the fourth reduction occurring at a formally more positive potential than the third reduction due to diminished Coulomb repulsion between the PDIs in the widened cyclophane configuration. Therefore the third and fourth reductions were found to be electrochemically irreversible, unlike in the PDI-PDI handcuff [2]rotaxane which is sufficiently dynamic for the PDI cores to adjust their relative position and thus exhibit electrochemically reversible behaviour.

The CVs of **4.4** and **4.9** each showed an initial one-electron reduction at -0.99 V and -1.01 V followed by a second one-electron reduction, at significantly lower potentials of -1.39 V and -1.45 V. These are typical reduction potentials for NDIs.³⁹ However the CV of **4.6** showed a similar profile to the CV of **4.5**, with two one-electron redox processes at -0.94 V and -1.16 V as well as one two-electron reduction at -1.46 V (Figure 4.6-2). The difference between the first and the second reduction is 0.22 V and therefore the comproportionation constant is ca. 5×10^3 . This shows that **4.6**, similar to **4.5**, exhibits Robin-Day Class II mixed valent character with limited delocalisation (on the electrochemical timescale). The third two-electron reduction occurred in a single step and correlates to one electron being added to each of the NDI cores for a total of two sections on each

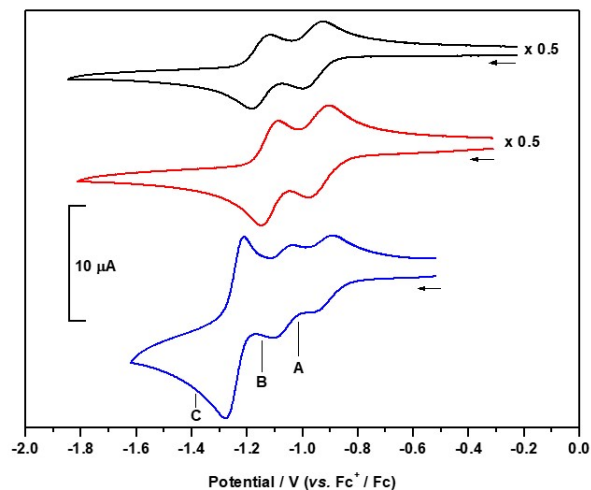
NDI. Similar to **4.5**, this is most likely accompanied by reorientation of the NDI units relative to each other, minimising the repulsive interactions between the NDIs in the tetra-anionic redox state and leading to a loss of delocalisation. Further evidence for the reorientation of the NDIs is that the third reduction of **4.6** exhibited a scan rate dependence, with peak separation dropping to 0.05 V (at slower scan rates of 0.20 Vs⁻¹). This is significantly lower than that of the ferrocene couple under identical conditions (0.07 V) and is indicative of an EE-type mechanism; which occurs when there are favourable interactions associated with adding the second electron (in this case adding a 4th electron overall) and typically requires a significant structural change or large solvation or ion-pairing effect. Although the CV of **4.6** is consistent with results obtained for **4.5**, it differs substantially from a rigid doubly-bridged covalently linked NDI cyclophane reported by Wasielewski, Stoddart and co-workers, which showed high level delocalisation across a π -based molecular orbital up to and including the tetra-anionic redox state (shown in the CV experiments).^{18c}

The CV of **4.7** is considerably more complex than that of **4.5** and **4.6**, exhibiting five individual reduction steps (Figure 4.6-3). The first two reductions overlap and are only resolved by the SW voltammogram to occur at -0.88 V and -1.11 V. They appear to be of equal intensity however lower than successive processes. Furthermore, the CV of **4.7** showed that the first reduction starts to develop at a less negative potential than in **4.3** and **4.9**, suggesting that the first electron added is shared across the π -systems of the PDI and NDI cores and therefore there is communication between them (on the CV timescale). A possible explanation for the splitting of the first reduction could be the presence of handcuff [2]rotaxane stereoisomers (described in Section 4.1.3). In this case in one arrangement the two central cores are orientated in such a way that they interact, whilst in the other arrangement there is little or no communication. The three subsequent redox processes fall within the potential range of the reductions observed for the monomer components and therefore are considered to show no significant communication.

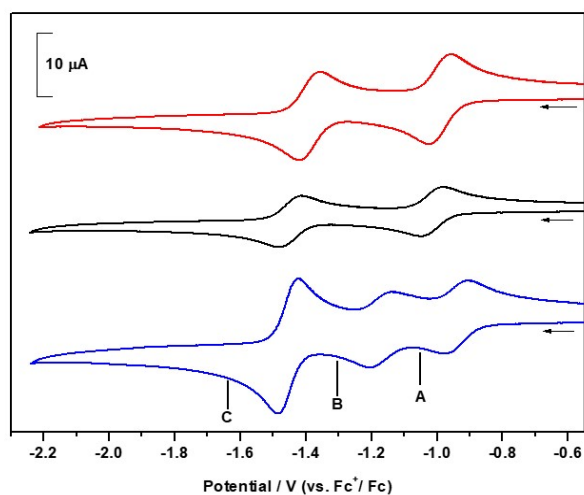
Compound	1 st reduction		2 nd reduction		3 rd reduction		4 th reduction	
	CV	SW	CV	SW	CV	SW	CV	SW
	$E_{1/2}$ / V	/ V	$E_{1/2}$ / V	/ V	$E_{1/2}$ / V	/ V	$E_{1/2}$ / V	/ V
4.3	-0.96	-0.97	-1.15	-1.16	-	-	-	-
4.4	-1.01	-1.01	-1.45	-1.44	-	-	-	-
4.5	-0.93	-0.94	-1.07	-1.07	-1.25	-1.25	-	-
4.6	-0.94	-0.95	-1.16	-1.18	-1.46	-1.47	-	-
4.7	^a	-0.88 ^b	-1.12	-1.11	-1.28	-1.28	^a	-1.40
4.8	-0.94	-0.97	-1.12	-1.14	-	-	-	-
4.9	-0.99	-0.99	-1.39	-1.40	-	-	-	-

Table 4.2: Reduction potentials of compounds **4.3-4.9**. Potentials quoted against $E_{1/2}$ Fc⁺/Fc at 0.1 Vs⁻¹ used as the internal standard. Recorded in dichloromethane at ambient temperature containing [nBu₄N][BF₄] (0.4 M) as the supporting electrolyte. ^a Peak potentials were not resolved; ^b additional unresolved shoulder to negative potential.

1)



2)



3)

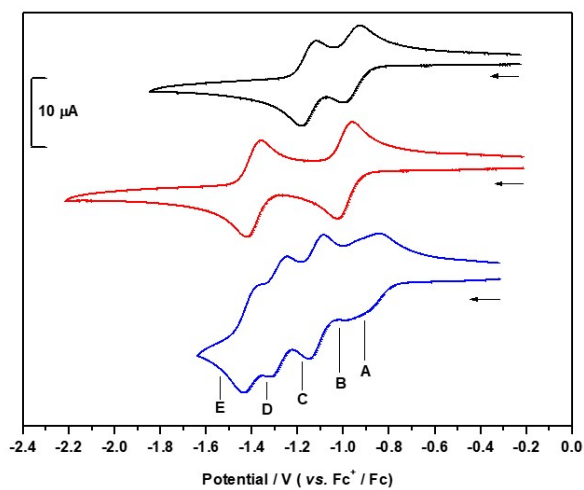


Figure 4.6: Cyclic Voltammetry of: 1) **4.5** (blue) and monomers **4.3** (black) and **4.8** (red), 2) **4.6** (blue) and monomers **4.4** (black) and **4.9** (red), 3) **4.7** (blue) and monomers **4.3** (black) and **4.9** (red). Recorded in dichloromethane containing 0.4 M $[\text{nBu}_4\text{N}][\text{BF}_4]$ as the supporting electrolyte, with a scan rate of 0.10 V s^{-1} . Points marked A-E represent potentials used in spectroelectrochemical reduction experiments.

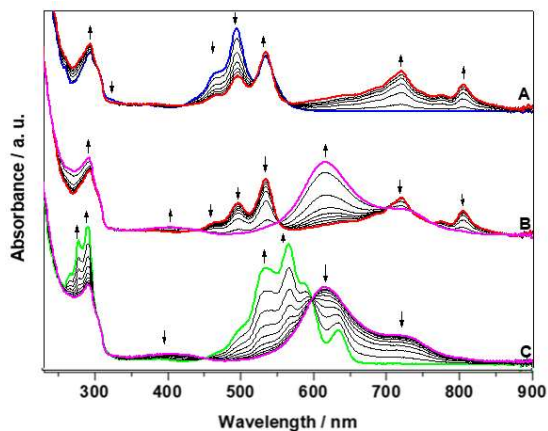
4.2.4.2. Spectroelectrochemistry

Both PDIs and NDIs have characteristic UV/vis absorbance traces in the neutral, one-electron and two-electron reduced states. Therefore, the reduction behaviours of **4.5-4.7** were probed using spectroelectrochemical measurements, based on reduction potentials found in the CVs. Monomer components **4.3**, **4.4**, **4.8** and **4.9** were also studied in this way and showed consistent UV/vis profiles at each reduction step to typical PDI/NDIs.^{1a, 6b}

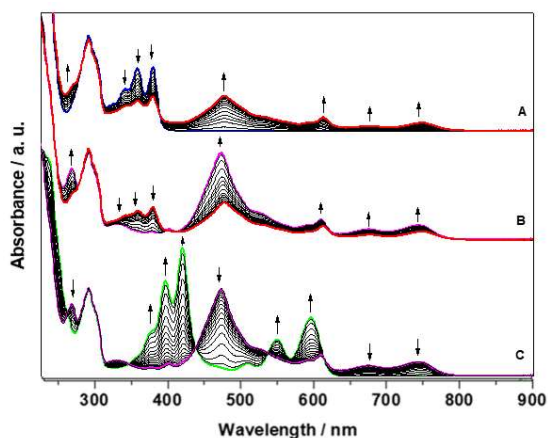
The UV/vis spectral profile of neutral **4.5** (Figure 4.5) showed evidence of H-aggregation within the handcuff [2]rotaxane structure. Upon the first reduction (to give $[\mathbf{4.5}]^{\cdot-}$) the UV/vis spectrum showed bands consistent with both mono-reduced PDI and non-aggregated neutral PDI (Figure 4.7-1-A). This suggests that the electron is localised on just one of the PDIs ($[\text{PDI}]^{\cdot-}-[\text{PDI}]^{\cdot-}$). Following the second reduction (to give $[\mathbf{4.5}]^{2-}$) there is a major change in the UV/vis spectrum. Features associated with the first reduction are replaced by a broad absorption at 615 nm which varies significantly from both mono- and di-reduced PDI spectral profiles, observed for PDI monomer units **4.3** and **4.8**. If each of the two electrons was located on one of the PDI units ($[\text{PDI}]^{\cdot-}-[\text{PDI}]^{\cdot-}$), then a UV/vis spectrum similar to that of mono-reduced **4.3/4.8** would be expected. However, the unique spectrum of $[\mathbf{4.5}]^{2-}$ suggests the presence of a ' π -dimer' ($[\text{PDI-PDI}]^{2-}$) in which the electrons occupy a molecular-based orbital manifold (Figure 4.8). A similar observation was made for the covalently linked NDI-NDI dimer described by Wasielewski, Stoddart and co-workers, noted previously.^{18c} The third two-electron reduction process (to give $[\mathbf{4.5}]^{4-}$) gave rise to a UV/vis spectrum in agreement with the spectra of typical di-reduced PDI (consistent with $[\mathbf{4.1}]^{2-}$ and $[\mathbf{4.2}]^{2-}$). This indicates that each of the PDIs in the handcuff [2]rotaxane is occupied by two electrons ($[\text{PDI}]^{2-}-[\text{PDI}]^{2-}$) and suggests that there is no longer any communication between them. Furthermore, it is feasible that the like charges repel one another and therefore the PDI^{2-} moieties move apart. Movement with minimal constraint is possible due to the extensive flexibility provided by the mechanical bonds, linking the PDIs together.

For **4.6**, the first reduction (to generate $[\mathbf{4.6}]^{\cdot-}$) showed absorption features consistent with both neutral and mono-reduced NDI, coherent with spectral profiles observed for mono-reduced **4.4** and **4.9** (Figure 4.7-2). This suggests that the electron is localised on one of the NDI units ($[\text{NDI}]^{\cdot-}$ -[NDI]) and is comparable to the arrangement in $[\mathbf{4.5}]^{\cdot-}$. However, following the second reduction (to give $[\mathbf{4.6}]^{2-}$) the UV/vis spectrum showed no broad absorbance (as seen in $[\mathbf{4.6}]^{2-}$) and instead showed features associated with typical mono-reduced NDI. This suggests that each of the two electrons is localised on one of the NDI units ($[\text{NDI}]^{\cdot-}$ - $[\text{NDI}]^{\cdot-}$) and there is no delocalisation occurs (on the experimental timescale). Despite the CV showing two separate one-electron processes (similar to **4.5**) suggesting electron sharing. The discrepancy between CV and spectroelectrochemistry could be due to the difference in experimental timescales and indicates that an equilibrium exists between the delocalised ($[\text{NDI-NDI}]^{2-}$) and the localised ($[\text{NDI}]^{\cdot-}$ - $[\text{NDI}]^{\cdot-}$) states (Figure 4.8). Upon the third two-electron reduction (to give $[\mathbf{4.6}]^{4-}$) the UV/vis spectrum was consistent with the spectrum observed for typical di-reduced NDIs ($[\mathbf{4.3}]^{2-}$ and $[\mathbf{4.4}]^{2-}$). This indicates that in $[\mathbf{4.6}]^{4-}$ each NDI moiety has accepted two electrons and therefore the NDIs move apart. This conformational change is supported by the scan rate dependence observed for this reduction process in the CV.

1)



2)



3)

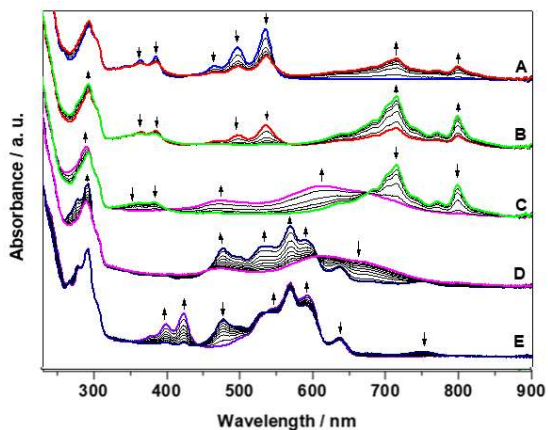


Figure 4.7: UV/vis absorption spectra showing the inter-conversion of redox states in: 1) **4.5** between neutral (blue), mono-reduced (red), di-reduced (magenta) and tetra-reduced (green); 2) **4.6** between neutral (blue), mono-reduced (red), di-reduced (magenta) and tetra-reduced (green); 3) **4.7** between neutral (blue), semi-mono-reduced (red), mono-reduced (green), di-reduced (magenta), tri-reduced (dark blue) and tetra-reduced (purple). Arrows indicate the progress of reduction. See Figure 4.6/Table 4.2 for potentials applied (A-E). Spectra were recorded in dichloromethane containing $[\text{nBu}_4\text{N}][\text{BF}_4]$ (0.4 M) as the supporting electrolyte at 273 K.

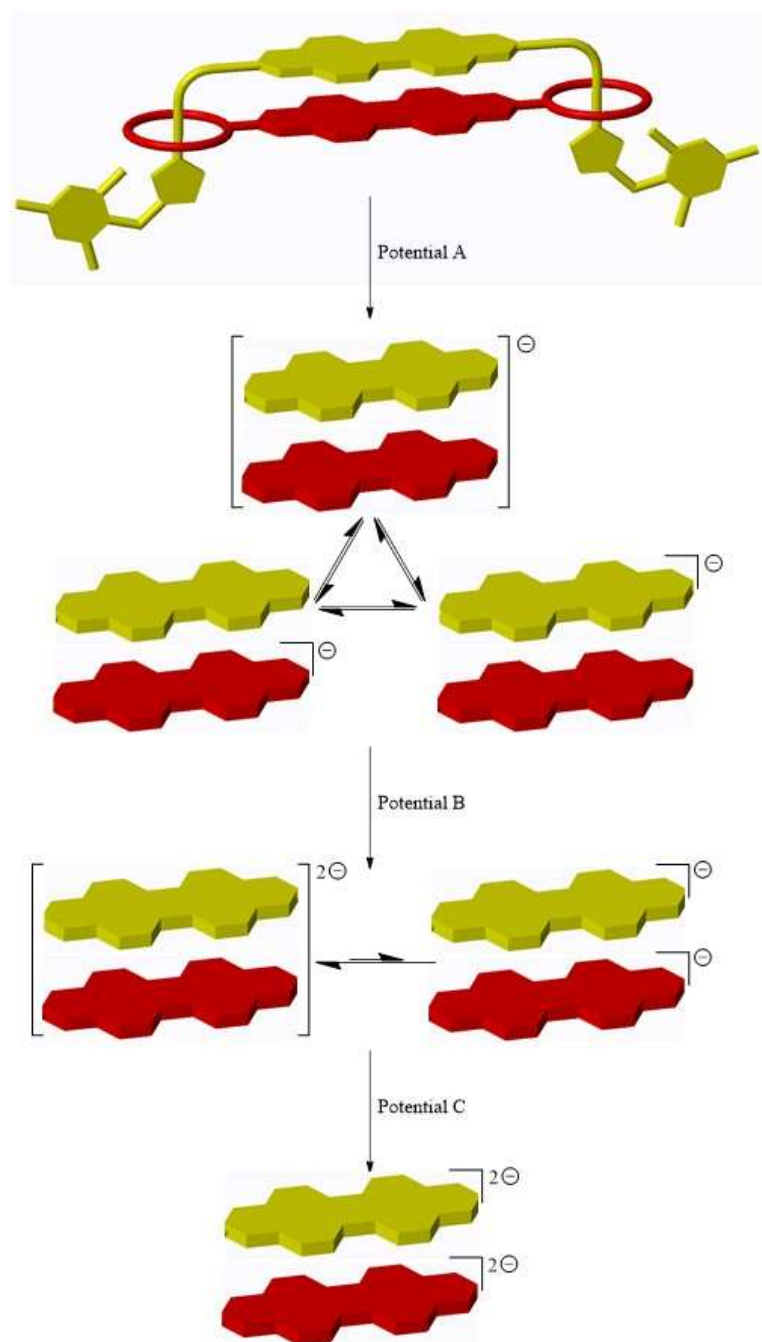
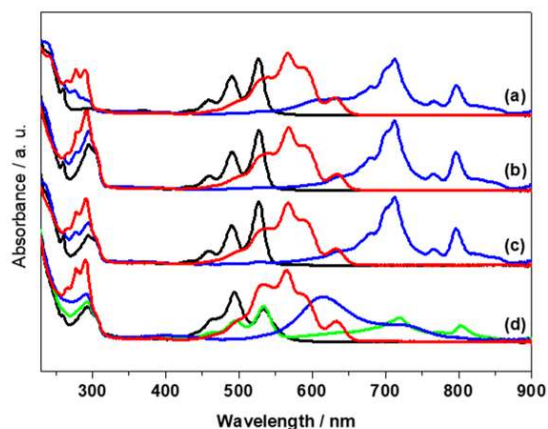


Figure 4.8: Schematic representation showing the location of the electron(s) upon reduction of **4.5** at potentials A, B and C.

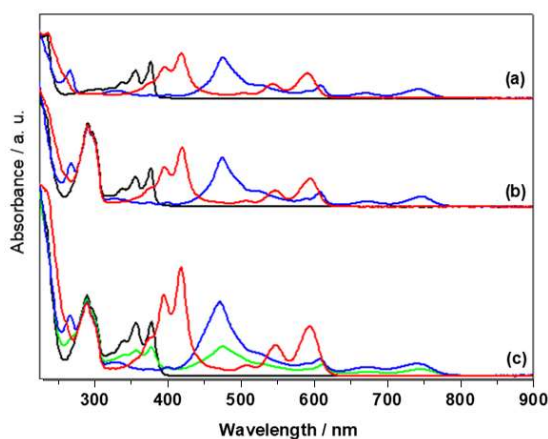
Applying a constant potential of -0.88 V (A) to **4.7** resulted in the formation of bands associated with mono-reduced PDI, at the expense of neutral PDI bands (Figure 4.7-3). Although the first PDI and NDI reductions in **4.3** and **4.9** occurred at almost identical potentials, no mono-reduced NDI

bands were observed at potential A in **4.7** (despite a slight loss of intensity in the parent NDI bands). Upon reduction at potential B, there was a complete loss of bands associated with neutral PDI, however there was still no indication of bands associated with mono-reduced NDI. This suggests that the two initial redox processes in the CV correspond solely to the mono-reduction of the PDI moiety. Therefore, at potential B the electron is localised on the PDI ($[PDI^{\cdot-}-NDI]$). The NDI appears to be largely unaffected by reduction potential B, indicating that the reduction properties of **4.7** are different to the NDI monomer component (**4.4**). The second one-electron reduction (at potential C) resulted in the loss of bands associated with neutral NDI and mono-reduced PDI, accompanied by the introduction of a broad absorbance at 612 nm. This band strongly resembled the broad absorbance feature observed for $[4.5]^{2-}$ and was therefore also attributed to the presence of a ' π -dimer' ($[PDI-NDI]^{2-}$), in which the electrons occupy a molecular-based orbital manifold. Following further reduction at potential D (to give $[4.7]^{3-}$) the broad feature was lost and was replaced with bands comparable to those observed for $[4.3]^{2-}$ and $[4.9]^{1-}$ states. This indicates that communication between the PDI and the NDI units is lost and the electrons are now localised on the individual π -systems ($[PDI]^{2-}-[NDI]^{\cdot-}$). The final reduction at potential E (to give $[4.7]^{4-}$) resulted in a loss of bands associated with mono-reduced NDI and brought forth the evolution of bands comparable to those observed for $[4.9]^{2-}$. This indicates that the fourth electron enters into a localised NDI-based orbital, resulting in two electrons localised on each of the PDI and NDI π -systems. This indicates that there is no communication between the PDI and the NDI in the tetra-reduced species, as previously observed in $[4.5]^{4-}$ and $[4.6]^{4-}$.

1)



2)



3)

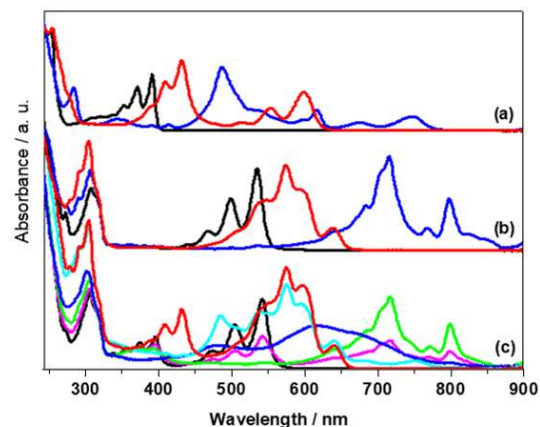


Figure 4.9: Comparison of UV/vis spectral profiles at different redox states for: 1) a) **4.8** (black), **[4.8]⁻** (blue) and **[4.8]²⁻** (red); b) **4.3** (black), **[4.3]⁻** (blue) and **[4.3]²⁻** (red); c) 1:1 mixture of **4.3** and **4.8** (black), first reduction (blue) and second reduction (red); d) **4.5** (black), **[4.5]⁻** (green), **[4.5]²⁻** (blue) and **[4.5]⁴⁻** (red). 2) a) **4.9** (black), **[4.9]⁻** (blue) and **[4.9]²⁻** (red); b) **4.4** (black), **[4.4]⁻** (blue) and **[4.4]²⁻** (red); c) **4.6** (black), **[4.6]⁻** (green), **[4.6]²⁻** (blue) and **[4.6]⁴⁻** (red). 3) a) **4.9** (black), **[4.9]⁻** (blue) and **[4.9]²⁻** (red); b) **4.3** (black), **[4.3]⁻** (blue) and **[4.3]²⁻** (red); c) **4.7** (black), semi-**[4.7]⁻** (magenta), **[4.7]⁻** (green), **[4.7]²⁻** (blue), **[4.7]³⁻** (cyan) and **[4.7]⁴⁻** (red). Spectra were recorded in dichloromethane containing **[ⁿBu₄N][BF₄]** (0.4 M) as the supporting electrolyte at 273 K.

UV/vis λ_{abs} / nm ($\epsilon \times 10^{-3}$ / mol ⁻¹ dm ³ cm ⁻¹)					
Compound	Neutral	Mono-anion	Dianion	Trianion	Tetraanion
4.3	260 (31.9), 295 (51.5), 371 (3.7), 460 (15.6), 491 (42.6), 528 (68.6)	295 (66.8), 350 (4.6), 529 (3.7), 680 (37.1), 713 (78.4), 766 (18.6), 796 (42.7)	292 (91.7), 389 (2.7), 568 (71.0), 635 (18.6)	-	-
4.4	296 (54.0), 342 (11.4), 361 (19.4), 381 (24.7)	273 (28.4), 296 (52.3), 331 (5.1), 380 (2.5), 404 (2.7), 478 (31.5), 592 (4.9), 611 (9.4), 678 (3.4), 750 (6.2)	295 (52.8), 400 (25.7), 423 (38.5), 510 (3.6), 550 (10.2), 598 (17.8)	-	-
4.5	294 (5.6), 494 (7.9), 534 (5.2)	293 (6.4), 495 (3.2), 534 (5.6), 719 (3.7), 803 (2.4)	292 (7.6), 399 - (0.8), 615 (7.2)	-	278 (11.9), 291 (13.3), 533 (9.2), 565 (11.6), 634 (3.1)
4.6	294 (52.5), 345 (23.0), 361 (34.8), 382 (35.0)	294 (50.3), 361 (16.6), 382 (18.8), 479 (19.1), 595 (4.5), 614 (7.4), 676 (2.7), 747 (4.3)	272 (39.2), 295 (48.5), 331 (9.0), 379 (4.5), 404 (5.8), 474 (48.0), 593 (8.1), 610 (11.2), 675 (5.8), 742 (7.9)	-	294 (47.7), 399 (52.6), 422 (70.6), 511 (7.0), 550 (20.1), 596 (32.2)
4.7	294 (7.9), 365 (2.8), 386 (3.4), 466 (2.0), 497 (4.7), 535 (7.4)	294 (8.5), 364 (2.5), 384 (2.6), 498 (2.0), 535 (3.5), 714 (3.0), 798 (1.9), 293 (9.4), 364 (2.2), 381 (2.3),	289 (10.3), 473 (2.5), 612 (4.6)	278 (12.8), 292 (15.0), 476 (5.7), 532 (6.0), 569 (8.9), 589 (6.9), 635 (3.0), 751 (0.9)	265 (10.7), 292 (15.6), 399 (4.7), 423 (6.3), 569 (10.7), 591 (8.8), 636 (2.5)

		714 (7.6), 770 (2.4)			
4.8	260 (24.2), 292 (6.1), 370 (4.4), 459 (13.4), 491 (34.9), 527 (51.2)	236 (66.2), 276 (22.1), 352 (3.6), 382 (3.0), 635 (15.4), 680 (25.6), 713 (50.4), 767 (12.6), 797 (26.8)	266 (31.0), 278 (41.0), 289 (40.8), 387 (2.4), 567 (56.0), 632 (15.7)	-	-
4.9	240 (41.4), 309 (6.1), 342 (10.6), 360 (18.4), 381 (23.7)	271 (18.0), 332 (4.8), 381 (2.1), 404 (2.5), 479 (26.5), 612 (8.4), 673 (3.4), 745 (5.9)	242 (42.7), 399 (20.3), 423 (29.4), 507 (3.5), 546 (9.3), 594 (16.2)	-	-

Table 4.3: Summary of UV/vis Spectroscopic data for **4.3-4.9**. Obtained in dichloromethane containing [ⁿBu₄N][BF₄] (0.4 M) at 273 K over a spectral range of 230-900 nm.

4.2.4.3. Mid- and Near-IR Spectroscopy

Following the telling insights into the different redox states of **4.5**, **4.6** and **4.7** using UV/Vis spectroscopy, mid- and near-IR spectroscopic measurements were used to investigate these states further. IR spectra of **4.3**/[**4.3**]⁻, **4.8**/[**4.8**]⁻ and **4.5**/[**4.5**]⁻/[**4.5**]²⁻ were recorded in a range of 1500-4000 cm⁻¹ (Figure 4.10). No significant peaks could be observed at lower energy than 1900 cm⁻¹ as this region was partially obscured by dichloromethane and [ⁿBu₄N][BF₄] electrolyte bands. The mid-IR of neutral **4.3**, **4.8** and **4.5** exhibited bands at ca. 1695 and 1655 and 1595 cm⁻¹, typical for bay-unsubstituted PDIs⁴⁰ (Figure 4.10-black). Following the first reduction of monomer components (**4.3** and **4.8**) these bands were replaced by lower energy bands at ca. 1640, 1585 and 1530 cm⁻¹, typical for mono-reduced PDIs. Upon the first reduction of **4.5** (potential B), bands associated with both neutral and mono-reduced PDI were observed (Figure 4.10-blue). This suggests that the electron exhibits localised character (on the timescale of this experiment),

analogous with observations made in the UV/vis spectrum of $[4.5]^-$. Following the second full reduction of **4.5** (potential C), which is equivalent to a one-electron reduction of each PDI unit in the handcuff [2]rotaxane, there was a complete loss the neutral PDI bands and only mono-reduced PDI bands were observed. However, these new bands appeared broader and their relative intensities were subtly shifted (Figure 4.10-red) compared to mono-reduced **4.3** and **4.8**.

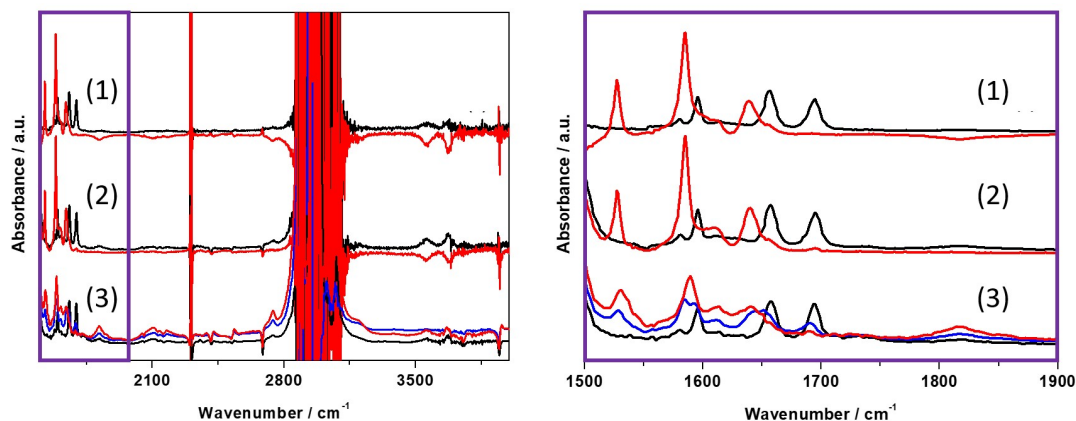


Figure 4.10: FT-IR spectra of 1) **4.8** (black) and $[4.8]^-$ (red), 2) **4.3** (black) and $[4.3]^-$ (red) and 3) (a) **4.5** (black) $[4.5]^-$ (blue) and $[4.5]^{2-}$ (red).

Further investigation of the $[4.5]^{2-}$ state by near-IR (NIR) spectroscopy showed a broad absorbance at 1527 nm (Figure 4.11-1-red). The re-oxidation of this species to mono-reduced **4.5** was followed by NIR and the loss of the broad band at ca. 1527 nm was observed (Figure 4.11-1-black). The bands which formed during the re-oxidation to the $[4.5]^-$ species were consistent with typical mono-reduced PDI. This is in conjunction with the UV/vis spectra and suggests that there is no communication between the two PDIs in the monoreduced state, which is unexpected considering the strong interaction observed for the di-reduced species ($[4.5]^{2-}$). Di-reduced **4.7** ($[4.7]^{2-}$) showed a similar broad absorbance at ca. 1550 nm in the NIR to $[4.5]^{2-}$ (Figure 4.11-2). Therefore, it is likely that similar communication exists within these two compounds at this redox state. Unlike in $[4.5]^{2-}$ and $[4.7]^{2-}$, no broad absorbance feature was observed in the UV/vis spectrum of $[4.6]^{2-}$, therefore the NIR region was not investigated further for this species.

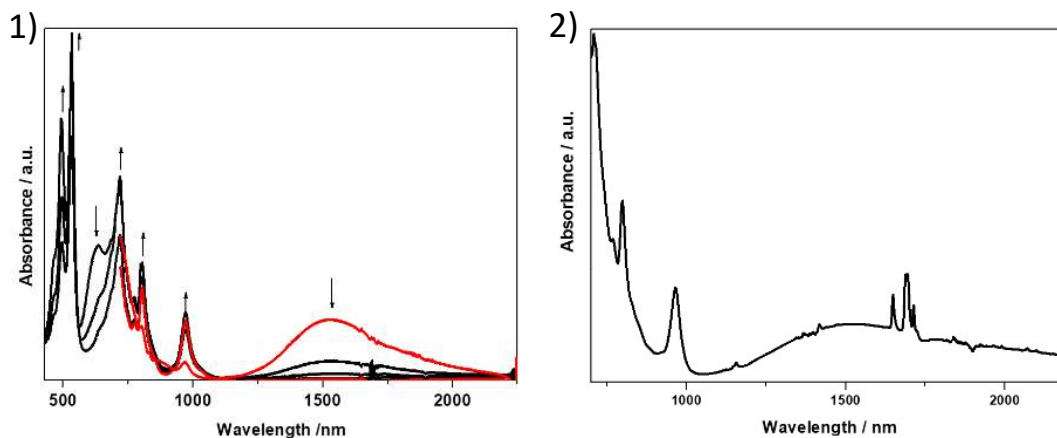


Figure 4.11: NIR spectra of 1) oxidation of [4.5]²⁻ (red) to [4.5][•] (black), progress is shown by the arrows, and 2) [4.7]²⁻.

4.2.4.4. EPR Spectroscopy

The localisation of the radical electron in handcuff [2]rotaxanes [4.5][•], [4.6][•] and [4.7][•] was investigated using EPR spectroscopy and compared to EPR spectra of monomers [4.3][•], [4.4][•], [4.8][•] and [4.9][•] (Figure 4.12). The radical species were generated by coulometric reductions using bulk electrolysis of solutions in dichloromethane containing 0.4 M [ⁿBu₄N][BF₄]. The EPR spectra of [4.5][•] was significantly less well resolved than that of the monomer components [4.3][•]/[4.8][•] and the line width was reduced by ca. 72 % (9.4 G for [4.5][•] and 13.0 G for [4.3][•] and [4.8][•]). The reduced spectral width and spectral characteristics of [4.5][•] could be simulated using three sets of eight hydrogen atoms and four equivalent nitrogen atoms, each at a magnitude of half that required in the simulation of [4.3][•] and [4.8][•]. This indicates either full delocalisation of the electron across both PDI cores or hopping of the electron between the two PDI cores (faster than the timescale of the EPR experiment).^{18c, 34} The electrochemical reduction of [4.5][•] to [4.5]²⁻ saw a loss of signal, eliminating the possibility of a bi-radical, in which each of the electrons is located on one of the PDIs. Furthermore, cooling the solution of [4.5]²⁻ to 77 K showed no evidence for the presence of a ground state triplet. Instead, this result suggests the presence of a ground state singlet in which

the two electrons are occupying a shared π -based molecular orbital, consistent with the UV/vis results for this redox state.

The EPR spectra of $[4.4]^-$ and $[4.9]^-$ could be accurately simulated using couplings of the unpaired electron to two sets of four hydrogen atoms and two equivalent nitrogen atoms (typical parameters for simulating mono-anionic NDI). The electrochemical reduction of $[4.6]$ to $[4.6]^-$ gave an EPR active species, which showed features consistent with the presence of mono-anionic NDI. These features were simulated with identical hyperfine coupling parameters to those used in the reproduction of $[4.4]^-$ and $[4.9]^-$. However, due to the low intensity of these features relative to the overall spectrum, they only contribute ca. 2 % to the overall spectral area. The remaining spectral contribution came from the electron being in a delocalised/hopping environment, comparable to that observed in $[4.5]^-$. The EPR spectrum of $[4.6]^-$ was successfully simulated using a 98:2 mixture of fully delocalised and localised components, respectively. Upon the electrochemical reduction of $[4.6]$ to $[4.6]^{2-}$, the EPR signal was lost and cooling the sample to 77 K showed no indication of a triplet state. These results suggest the presence of a ground state singlet, consistent with the two electrons entering a π -based molecular orbital shared between the two NDIs. Although this conclusion is consistent with results observed for **4.5**, it does not align with the UV/vis spectra recorded for $[4.6]^{2-}$ in which the electrons were considered to have localised character and each appeared to occupy one NDI core. This discrepancy highlights the difference in timescale between these spectroscopic techniques and suggests that the electron hopping rate in $[4.6]^{2-}$ is slower than in $[4.5]^{2-}$, possibly due to NDIs smaller aromatic area and therefore reduced π - π interaction surface.

The electrochemical reduction of **4.7** to $[4.7]^-$ gave an EPR active species. The spectral profile and position indicated that the electron was predominantly localised on the PDI component. However the spectral width was slightly narrowed compared to $[4.3]^-$ (ca. 96 %), suggesting that some degree of delocalisation/hopping may be occurring (on the timescale of the experiment). Similar

to $[4.5]^{2-}$ and $[4.6]^{2-}$, the electrochemical reduction of $[4.7]^-$ to $[4.7]^{2-}$ showed a significant reduction in the EPR signal and there was no indication of a triplet state at 77 K. This is consistent with the electrons entering a shared π -based molecular orbital, supporting observations made in the UV/vis and NIR spectra of this redox state. These results suggest that the electron sharing properties of **4.7** are closer related to those of **4.5** than **4.6**. Further electrochemical reduction to $[4.7]^{3-}$ brought about the return of an EPR signal. The spectral profile closely resembled that of a mono-anionic NDI (such as $[4.4]^-$ and $[4.9]^-$) suggesting that the added electron occupies a localised NDI-based orbital. This is consistent with results observed for the UV/vis spectrum of this redox state. These results indicate that in $[4.7]^{3-}$ two electrons are localised in a PDI-based orbital and the remaining electron is localised in a NDI-based orbital ($[PDI]^{2-}$ - $[NDI]^-$). Upon further electrochemical reduction to $[4.7]^{4-}$, the EPR signal associated with $[4.7]^{3-}$ was significantly reduced in intensity. This result, in conjunction with the loss of the mono-anionic NDI band in the UV/vis of $[4.7]^{4-}$, shows that the fourth electron occupies a localised NDI-based orbital ($[PDI]^{2-}$ - $[NDI]^{2-}$).

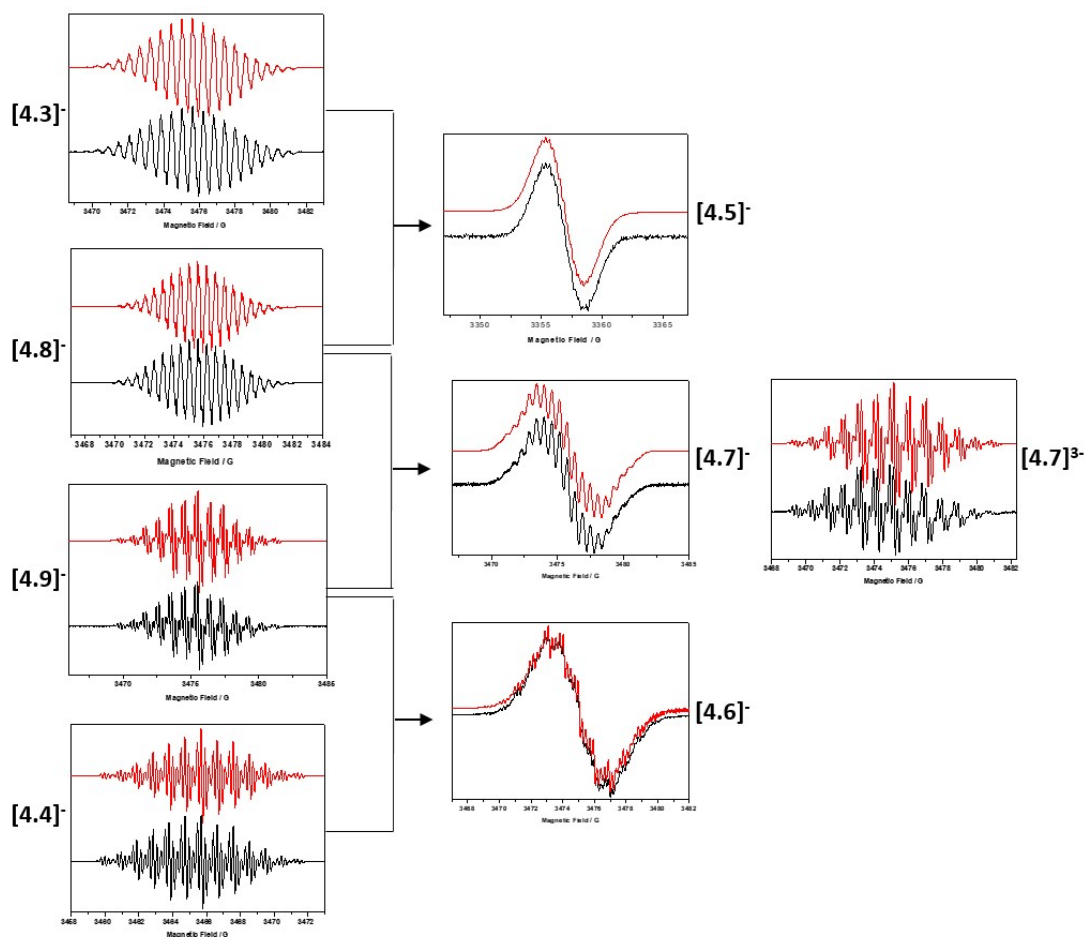


Figure 4.12: EPR spectra of mono-reduced **4.3-4.9** and tri-reduced **4.7**. Experimental data (black), simulated data (red).

4.2.4.5. Photophysics of **4.5**

The photophysical properties of **4.3**, **4.5** and **4.8** were probed by Katherine Reynolds using picosecond transient absorption (psTA) and picosecond time-resolved infrared (psTRIR) spectroscopy (Figure 4.13 and Figure 4.14, respectively). Upon excitation of **4.3** at 520 nm, defined transient bands at 753 nm and 949 nm formed. The excited state dynamics showed a fast solvent relaxation process (ca. 8 ps) which could be distinguished from a PDI singlet state (^1PDI - ca. 60 ps). Although this assignment is in conjunction with literature reports, the observed lifetime is significantly shorter than that of typical PDIs (ca. 1.4 ns).⁴¹ This suggests that ^1PDI is being quenched, which correlates to the low quantum yield observed for this compound. Following excitation of **4.8** at 520 nm, defined bands at 751 nm and 939 nm were observed. Similar to **4.3**

there were two processes: solvent relaxation (ca. 19 ps) and a ^1PDI excited state (ca. 600 ps). Although the decay of the ^1PDI excited state in **4.8** is slower than in **4.3**, it is still faster than in typical PDIs. These lifetimes suggest that whilst both the pillar[5]arene and the imidazolium have a quenching effect on the ^1PDI excited state, the pillar[5]arene's is more significant. Following excitation of **4.5** at 520 nm a broad band centred at ca. 695 nm formed, which subsequently underwent a blue shift to ca. 620 nm. This corresponds to the formation of an excimer between two PDI cores^{13c} and significantly differs from features detected in the monomer components **4.3** and **4.8**.

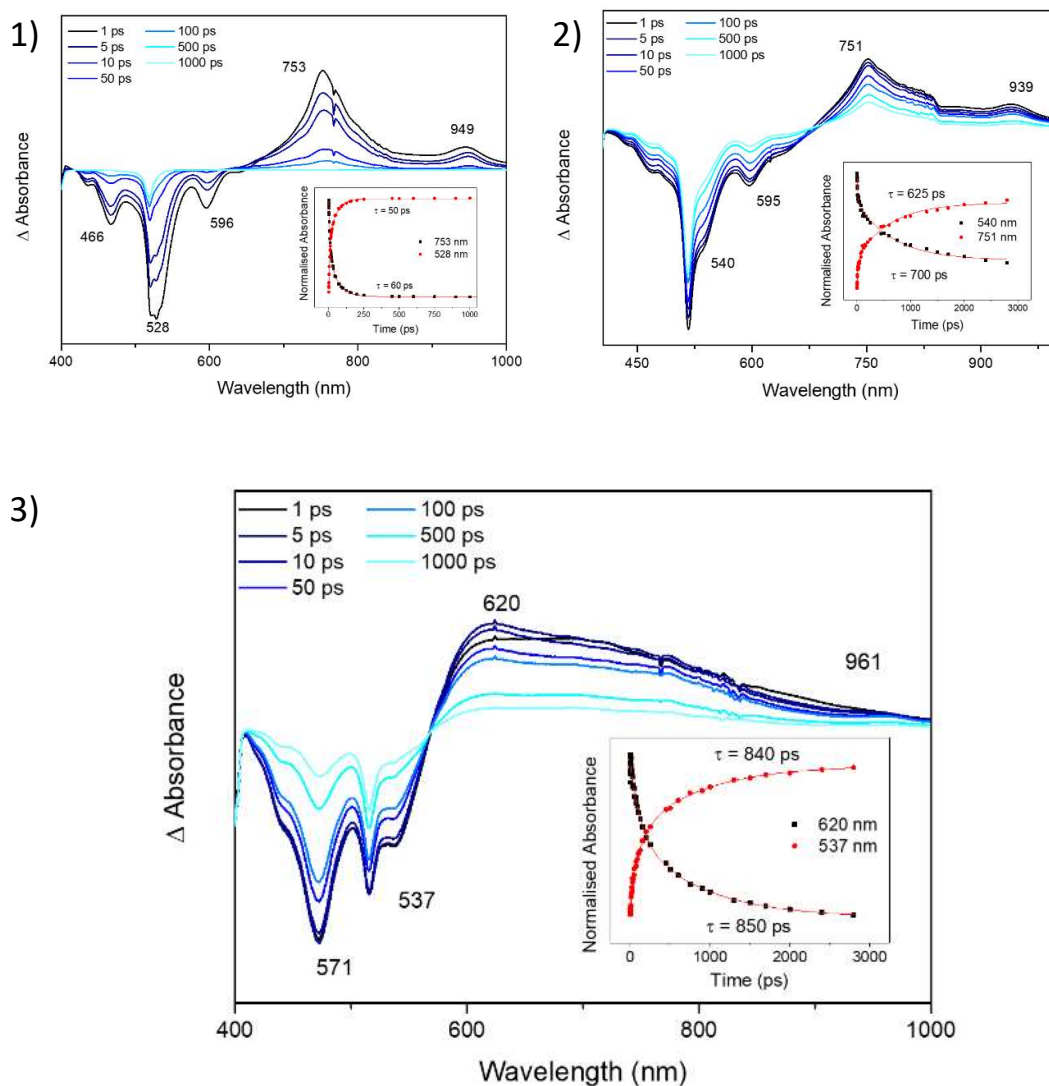


Figure 4.13: Picosecond TA spectra and decay profiles (insets) upon excitation at 520 nm in dichloromethane for 1) **4.3**, 2) **4.8** and 3) **4.5**.

TRIR spectra of **4.3** showed defined transient C=O bands at 1645 cm^{-1} and 1620 cm^{-1} (indicative of a ^1PDI excited state⁴²) as well as other peaks (associated with the pillar[5]arenes). The ^1PDI excited state was short lived (ca. 80 ps) compared to equivalent PDIs, which usually decay after ca. 4 ns.⁴³ This is further evidence for a pillar[5]arene-related quenching process in **4.3**, indicated by the low quantum yield and psTA measurements. Similar to **4.3**, the TRIR spectra of **4.8** showed defined transient C=O bands at 1647 cm^{-1} and 1623 cm^{-1} , which are in conjunction with a ^1PDI excited state. Although this state was longer lived (ca. 400 ps) than in **4.3**, it was shorter than equivalent literature examples (consistent with the trend observed for the lifetimes of **4.3** and **4.8** in psTA measurements). The TRIR spectra of **4.5** showed no new peaks (compared to **4.3** and **4.8**) however a broadening of the C=O bands at ca. 1640-1620 cm^{-1} was observed. This is evidence for the presence of an excimer state.⁴³ The excimer state in **4.5** is short lived compared to other covalently linked dimers,⁴³ which could be a feature associated with the non-covalent mature in which the PDI cores are connected.

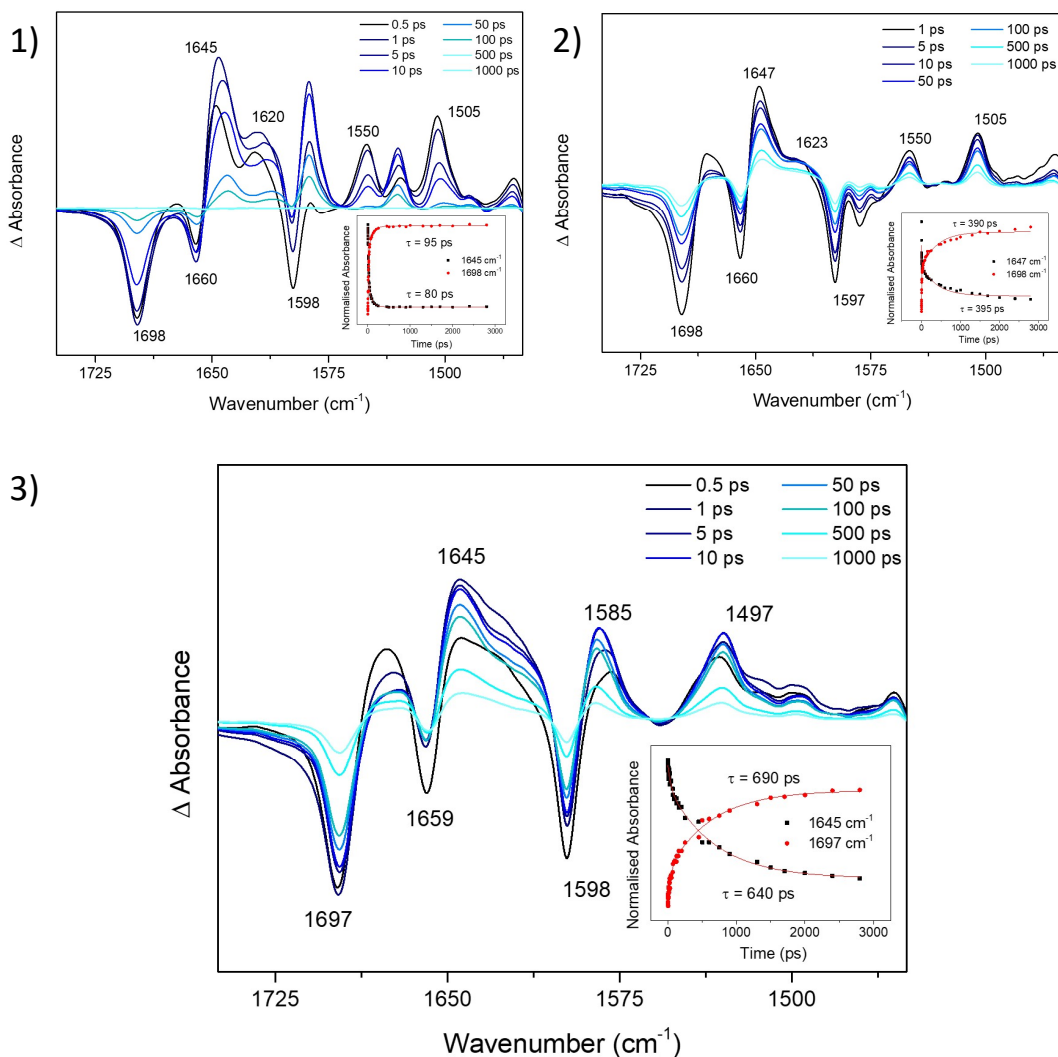


Figure 4.14: Picosecond TRIR spectra and decay profiles (insets) of 1) **4.3**, 2) **4.8** and 3) **4.5**, following excitation at 520 nm in dichloromethane.

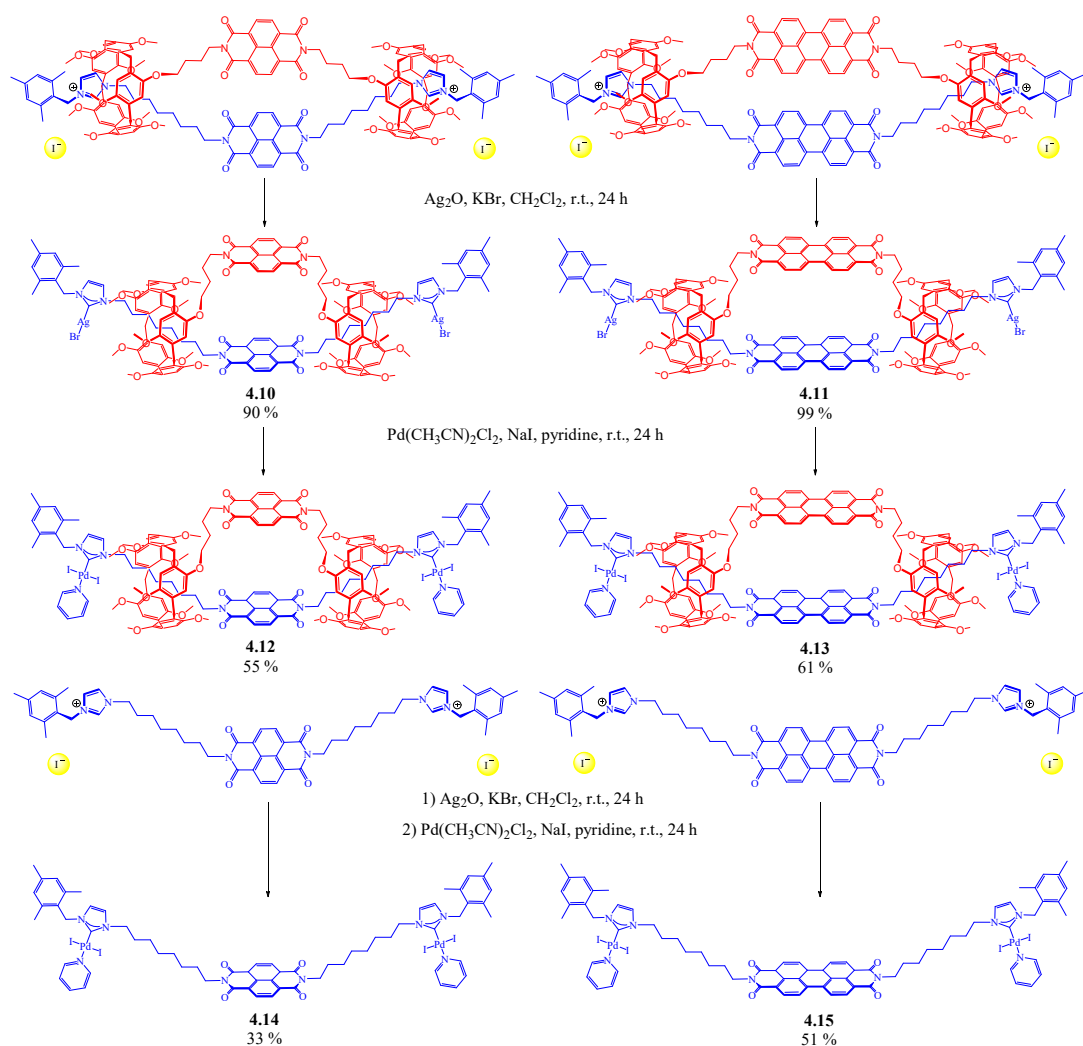
The psTA and psTRIR appear to tell a similar story. Both of these techniques confirm the quenching effect of the pillar[5]arenes and the imidazoliums (too a lesser extent) on the PDI excited states. Furthermore, they confirm the presence of an excimer in the excited state of **4.5** and highlight the discrepancy between the monomeric PDIs (**4.3** and **4.8**) and the handcuff [2]rotaxane structure (**4.5**). A similar study of **4.7** was not possible as the psTA and psTRIR spectra were too complex for peaks to be reliably assigned.

4.2.5. Pd(II)-Coordinated to Handcuff [2]Rotaxanes

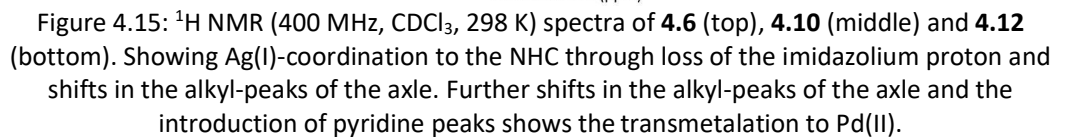
The coordination of Ag(I) and Pd(II) to the imidazolium of pillar[5]arene/imidazole-based [2]rotaxanes and the accompanying positional change of the pillar[5]arene relative to the axle was described in Chapter 2. It was envisioned that a comparable metalation of handcuff [2]rotaxanes would result in positional adjustments of the components relative to each other, causing changes in communication between the rylene diimides and thus a variation of their electrochemical properties.

4.2.5.1. Synthesis

Pd(II)-containing NDI-NDI (**4.12**) and PDI-PDI (**4.13**) handcuff [2]rotaxanes were synthesised from **4.6** and **4.5** via the corresponding Ag(I) complexes **4.10** and **4.11** (Scheme 4.4). In the first step **4.5/4.6** was dissolved in dichloromethane followed by the addition of Ag₂O and potassium bromide. The mixture was stirred under the exclusion of light for 24 h before being filtered through celite. The solvent was then removed under reduced pressure and the crude product was re-dissolved in a minimum volume of dichloromethane and added dropwise to hexane. The precipitate was collected by filtration and dried under suction to give **4.10** and **4.11** in yields of 90 % and 99 %, respectively. Subsequent reaction of these compounds with Pd(CH₃CN)₂Cl₂ and NaI in anhydrous pyridine overnight at room temperature, under the exclusion of light and purification through a short silica gel plug gave the equivalent di-Pd(II) handcuff [2]rotaxanes **4.12** and **4.13** in a yield of 55 % and 61 %, respectively. Using the same methodology the di-Pd(II)-coordinated NDI and PDI axle components (**4.14** and **4.15**) were synthesised (Scheme 4.4) as a comparison for assessing the hybrid properties of the handcuff [2]rotaxane systems.



Scheme 4.4: Synthesis of Ag(I)- (**4.10-4.11**) and Pd(II)- (**4.12-4.13**) coordinated NDI-NDI/PDI-PDI handcuff [2]rotaxanes. Synthesis of Pd(II)-coordinated axle compounds (**4.14-4.15**).



Ag(I)-coordination in **4.10** and **4.11** was confirmed by ^1H NMR, 2-D NMR and ^{13}C spectroscopy. Although there was no evidence to suggest any instability in these compounds, **4.10** and **4.11** were used in their subsequent reactions as soon as possible and no attempt to electrochemically characterise these compounds was made. Pd(II)-coordinated compounds **4.12**, **4.13**, **4.16** and **4.17** were characterised by ^1H NMR, 2-D NMR and ^{13}C spectroscopy and appeared to be bench stable. Despite numerous attempts, it was not possible to obtain crystal structures of metalated handcuff [2]rotaxane complexes because crystals large enough and/or of sufficient quality were not attainable. The ^1H NMR spectra of **4.5** and **4.6** showed significant shifts upon Ag(I)- and Pd(II)-coordination (shown for **4.6** in Figure 4.15). Ag(I)-coordination was confirmed by the loss of imidazolium environment (H_n) and by shifts in the remaining NHC environments ($\text{H}_{\text{l-m}}$) as well as a loss of the AB pattern for the signal associated with the methylene group protons, H_o (linking the imidazolium to the stopper group). Significant shifts in the alkyl environments closer to the imidazolium ($\text{H}_{\text{e-k}}$) were also observed, demonstrating that the pillar[5]arene/imidazolium interactions are broken and that the pillar[5]arene now resides on the alkyl chain. Pd(II)-coordination was confirmed through the introduction of peaks associated with pyridine ($\text{H}_{\text{s-u}}$) and was accompanied by subtle changes in peak positions for signals associated with the threaded alkyl chain. Similar to observations made for Pd(II) transmetalation in Chapter 2, axle environments closer to the imidazoliums ($\text{H}_{\text{i-k}}$) are shifted downfield whilst environments further away from the imidazoliums ($\text{H}_{\text{e-g}}$) are shifted upfield. These shifts imply that Pd(II) complexation sterically confines the pillar[5]arenes to a smaller region of the axle than in the Ag(I) equivalents, likely due to the increased coordination sphere of the Pd(II) complex. Whilst the position of the pillar[5]arene can be determined from the ^1H NMR spectrum, it is difficult to assess if metal coordination has an effect on the relative position aromatic cores.

The photophysical and electrochemical properties of Pd(II)-coordinated handcuff [2]rotaxanes (**4.12** and **4.13**) and their unthreaded axles (**4.14** and **4.15**) were investigated. In particular to determine if the complex communication previously observed for **4.5** and **4.6** was affected by the

introduction of Pd(II) complexes and the associated changes in pillar[5]arene position. To do so a combination of electroanalytical techniques including CV, absorption/emission spectroscopy, spectroelectrochemistry and EPR spectroscopy were employed.

4.2.5.2. Emission Spectroscopy

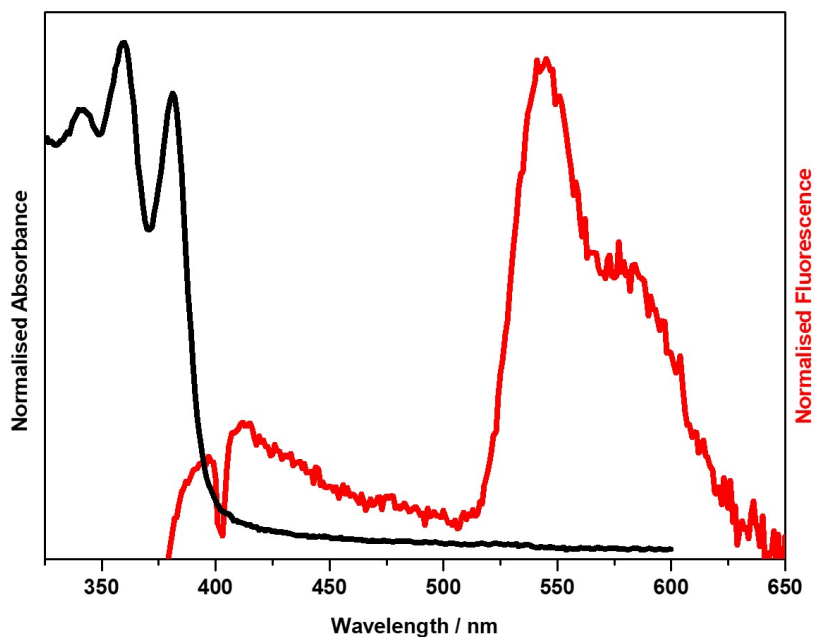


Figure 4.16: UV/vis absorption (black) and emission (red) of **4.12** showing weak excimer type emission.

The UV/vis spectroscopy of **4.12-4.15** are described and further discussed in the spectroelectrochemistry section of this chapter (Section 4.2.5.3.2). The emission spectra of **4.14** and **4.15** were recorded in dichloromethane and showed fluorescence and typical NDI/PDI vibronic coupling. However, the quantum yield of **4.15** (0.077) was much lower than in the equivalent Pd(II)-free analogue **4.8** (0.800), showing that a significant quenching effect is associated with the presence of Pd(II) (previously observed for [2]rotaxane **3.6** in Chapter 3). Although **4.4** and **4.6** were essentially non-emissive, **4.12** showed a weak emission band at 545 nm indicating the presence of a weak excimer type state (Figure 4.16). This change in the fluorescence signifies Pd(II) complex introduction has a subtle effect on the nature of communication between the NDI cores in **4.12**. This is surprising as the presence of the

pillar[5]arene moiety tends to significantly reduce emission, even in strongly emitting compounds such as PDIs (for example in **4.3**). In contrast to **4.12**, the PDI analogue **4.13** was non-emissive therefore Pd(II)-coordination quenches excimer type emission. Overall there appears to be a significant change in the rylene diimide interactions within the handcuff [2]rotaxanes upon Pd(II)-coordination however emission spectroscopy reveals only limited information regarding the nature of these changes.

4.2.5.3. Electrochemistry

Encouraged by the changes of the emission spectra upon Pd(II) complexation in **4.12** and **4.13**, CV and spectroelectrochemistry were used to further probe the effect of Pd(II)-coordination on the interaction between the two rylene diimides.

4.2.5.3.1. CV

Compound	1 st reduction		2 nd reduction		3 rd reduction	
	CV	SW	CV	SW	CV	SW
	E _{1/2} / V	/ V	E _{1/2} / V	/ V	E _{1/2} / V	/ V
4.5	-0.93	-0.94	-1.07	-1.07	-1.25	-1.25
4.6	-0.94	-0.95	-1.16	-1.18	1.46	-1.47
4.12	-0.97	-0.97	-1.24	-1.24	-1.56 ^{a,b}	-1.56
4.13	-0.98	-0.98	-1.16	-1.16	-1.30	-1.31
4.14	-1.04	-1.04	-1.46	-1.46	-	-
4.15	-1.00	-1.00	-1.18 ^c	-1.20	-	-

Table 4.4: Reduction potentials of compounds **4.5**, **4.6** and **4.12-4.15**. Potentials quoted against E_{1/2} Fc⁺/Fc at 0.1 Vs⁻¹ used as the internal standard. Recorded in dichloromethane at ambient temperature containing [nBu₄N][BF₄] (0.4 M) as the supporting electrolyte. ^a Does not show scan rate dependence seen for other handcuff [2]rotaxanes; ^b additional broad reduction at E_p^c -2.11 V; ^c additional broad reduction at E_p^c -2.10 V.

The CVs of **4.12-4.15** were recorded as dichloromethane solutions containing [nBu₄N][BF₄] (0.4 M) as the supporting electrolyte. The CV of **4.12** consisted of three distinct redox couples, indicating a similar communication between the two redox-active NDIs to the Pd(II)-free analogue, **4.6**. However, an additional broad reduction process at -2.11 V was observed (Figure 4.17-1). The monomeric axle component, **4.14**, exhibited a similar broad reduction process at -2.04 V,

suggesting that this redox couple is associated with the $[\text{PdI}_2(\text{C}_5\text{H}_5\text{N})]$ complexes in these molecules. Compared to **4.6**, the CV of **4.12** showed slight shifts in the reduction potentials which increased in magnitude from reduction to reduction (-0.02, -0.06 and -0.09 V for 1st, 2nd and 3rd reductions). The potential difference between the first and the second reduction (ΔE) is therefore increased to 0.27 V, giving an increased comproportionation constant of ca. 4×10^4 . Although this is larger than in **4.6** (ca. 5×10^3), it shows that **4.12** is still a Robin-Day Class II mixed valent species, exhibiting limited communication between the NDI cores (on the experiment timescale). The third reduction appeared as a two-electron process however, unlike **4.6** no scan rate dependence was observed and the separations were consistent with those of the ferrocene standard. Overall, the characteristic electrochemical profile of the handcuff motif appears to be largely unaffected by Pd(II)-coordination, with the exception of an additional broad reduction process at lower potential (associated with the $[\text{PdI}_2(\text{C}_5\text{H}_5\text{N})]$ complexes) and a slight increase in electron density on the NDIs, making the addition of electrons more energetically unfavourable. Furthermore, the difference in the scan rate dependence suggests that there is a subtle change in the way the electrons are interacting.

The CV of **4.13** showed a similar profile to **4.5**, with the addition of a broad reduction process at ca. -2.0 V (Figure 4.17-2). A similar broad reduction at ca. -2.0 V was also observed for the monomeric axle component (**4.15**) and is associated with the presence of $[\text{PdI}_2(\text{C}_5\text{H}_5\text{N})]$ complexes. The presence of Pd(II) in **4.13** results in shifts of each of the reductions to less negative potentials (by 0.05, 0.09, 0.05 V for 1st, 2nd and 3rd reductions) compared to the Pd(II)-free analogue, **4.5**. Interestingly, this trend is opposite to the one observed for the NDI analogue, **4.12**. Furthermore, the two-electron reduction exhibits comparable scan rate dependence to the Pd(II)-free analogue, **4.5**. Although there appears to be some minor changes in the electrochemical properties of **4.5** upon Pd(II)-coordination, these are subtle and less pronounced than in the NDI analogue, **4.12**.

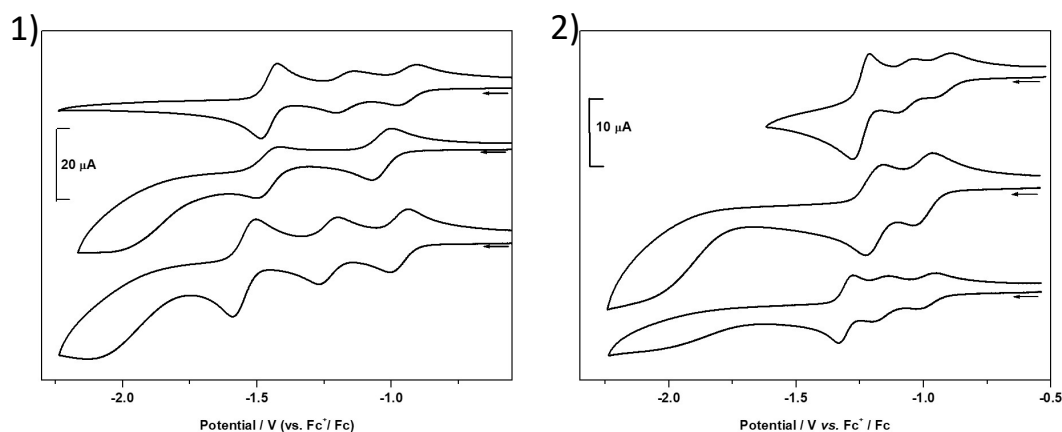


Figure 4.17: Cyclic Voltammetry of: 1) **4.6** (top), monomer **4.14** (middle) and **4.12** (bottom) and 2) **4.5** (top) and monomer **4.15** (middle) and **4.3** (bottom). Recorded in dichloromethane containing 0.4 M $[\text{nBu}_4\text{N}][\text{BF}_4]$ as the supporting electrolyte, with a scan rate of 0.10 Vs^{-1} .

4.2.5.3.2. Spectroelectrochemistry

The UV/vis spectra of neutral monomer components **4.14** and **4.15** showed an absorption profile consistent with that of their Pd(II)-free analogues, **4.9** and **4.8**, typical for bay un-substituted NDIs and PDIs (Figure 4.18). A comparable similarity was observed in the UV/vis spectra of the one- and two-electron reduced states of these compounds. The UV/vis spectrum of **4.13** showed a similar intensity reversal of the spectral bands between 450 nm and 550 nm to the Pd(II)-free analogue (**4.5**), consistent with an H-aggregated chromophore (Figure 4.18/Table 4.5). Following the first reduction of **4.13** (to give $[\mathbf{4.13}]^{\cdot-}$) the UV/vis spectrum was consistent with that observed for $[\mathbf{4.5}]^{\cdot-}$, showing bands associated with both typical mono-reduced and neutral (non-aggregated) PDI. This indicates that the electron is localised on one of the PDI units and the aggregation is disrupted. Upon the second reduction (to give $[\mathbf{4.13}]^{2-}$) a broad band at 626 nm was observed, which is characteristic for the presence of a ' π -dimer' (seen before in $[\mathbf{4.5}]^{2-}$). The third (two-electron) reduction process (to give $[\mathbf{4.13}]^{4-}$) gave rise to a UV/vis spectrum consistent with typical di-reduced PDI. This indicates that each of the PDI units is occupied by two localised electrons and there is no significant communication between the two aromatic moieties. Overall, the spectroelectrochemical study of **4.13** shows very similar behaviour to the Pd(II)-free analogue

(**4.5**) and provides no evidence for a change in communication between the two PDI units following Pd(II)-coordination.

In **4.12** the neutral UV/vis spectrum showed evidence for a subtle change in the relative ratios between the bands at 320 nm and 400 nm compared to the Pd(II)-free analogue (**4.6**). A similar, however more drastic intensity change in these bands was noted by Wasielewski, Stoddart and co-workers in an NDI dimer cyclophane.^{18c} Such changes in the relative intensities are an indication of H-type aggregation⁴⁴ and suggest that the two NDI cores in **4.12** are interacting more strongly, in the neutral state, than in **4.6**. The first reduction of **4.12** (to give [**4.12**]^{•-}) exhibited absorption features consistent with both neutral and mono-reduced NDI, analogues with [**4.6**]^{•-} (Figure 4.18-1/Table 4.5). The second reduction (to give [**4.12**]²⁻) and the third (two-electron) reduction (to give [**4.12**]⁴⁻) showed UV/vis spectra comparable to those recorded for Pd(II)-free analogous [**4.6**]²⁻ and [**4.6**]⁴⁻. These results indicate that (similar to **4.13**) Pd(II)-coordination has little to no effect on the spectroelectrochemical properties of **4.6** (on the timescale of the experiment). Following the first oxidation of **4.12** (to give [**4.12**]⁺), the UV/vis spectra showed this process to be spectroelectrochemically non-reversible and therefore no further oxidations were investigated.

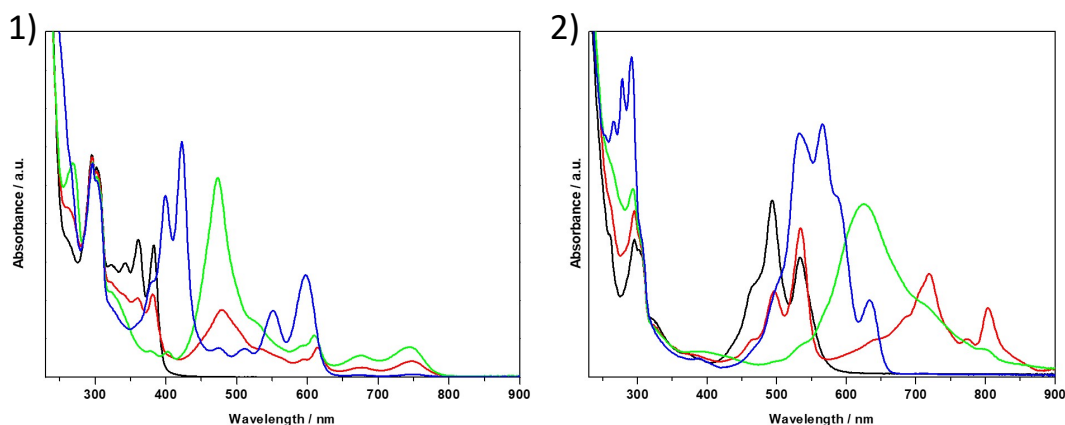


Figure 4.18: UV/vis absorption spectra of neutral (black), mono-reduced (red), di-reduced (green) and tetra-reduced (blue) for 1) **4.12** and 2) **4.13**. Spectra were recorded in dichloromethane containing [ⁿBu₄N][BF₄] (0.4 M) as the supporting electrolyte at 273 K.

UV/vis λ_{abs} / nm ($\epsilon \times 10^{-3}$ / mol ⁻¹ dm ³ cm ⁻¹)				
Compound	Neutral	Mono-anion	Dianion	Tetraanion
4.12	295 (59.5), 302 (56.1), 332 (30.1), 342 (30.5), 361 (36.8), 383 (35.3)	295 (58.8), 302 (55.1), 360 (21.1), 381 (22.2), 479 (18.0), 595 (4.7), 614 (8.0), 677 (2.6), 747 (4.3)	269 (57.2), 296 (57.5), 302 (53.6), 322 (22.9), 378 (7.0), 403 (6.8), 473 (53.3), 610 (11.2), 677 (5.8), 746 (8.0)	296 (57.2), 302 (52.6), 399 (48.6), 422 (63.1), 474 (7.8), 510 (7.6), 551 (17.8), 597 (27.3)
4.13	260 (33.9), 295 (32.7), 302 (30.3), 370 (5.7), 494 (42.0), 534 (28.4)	295 (39.5), 497 (20.4), 534 (35.4), 719 (24.6), 773 (9.1), 804 (16.5)	293 (44.6), 387 (6.1), 626 (41.0), 798 (6.7)	266 (60.6), 278 (70.8), 291 (76.0), 377 (4.3), 532 (57.8), 566 (60.1), 633 (18.2)
4.14	262 (36.9), 322 (29.6), 389 (24.5), 360 (26.7)	267 (47.9), 319 (26.4), 376 (5.5), 404 (4.3), 478 (32.0), 591 (5.4), 610 (9.9), 674 (3.9), 747 (6.7)	383 (13.7), 400 (16.8), 423 (19.5), 477 (6.8), 509 (6.4), 549 (9.4), 596 (11.0), 676 (2.7) ^a	-
4.15	261 (67.5), 318 (28.1), 460 (19.1), 491 (49.9), 527 (72.6)	262 (72.3), 296 (29.5), 318 (27.2), 455 (1.7), 494 (2.5), 637 (19.2), 680 (39.7), 712 (80.9), 766 (19.3), 797 (43.4)	265 (75.8), 277 (71.9), 291 (64.6), 317 (28.2), 542 (47.9), 568 (78.3), 589 (58.6), 634 (21.5)	-

Table 4.5: Summary of UV/vis Spectroscopic data for **4.12-4.15**. Obtained in dichloromethane containing [ⁿBu₄N][BF₄] (0.4 M) at 273 K over a spectral range of 230-900 nm.

4.2.5.3.3. EPR Spectroscopy

The X-band EPR spectra of [**4.12**]⁻, [**4.13**]⁻, [**4.14**]⁻ and [**4.15**]⁻ (generated by coulometric reduction of **4.12-4.15**) were recorded as fluid solutions at ambient temperature in dichloromethane containing 0.4 M [ⁿBu₄N][BF₄]. The EPR spectrum of [**4.14**]⁻ was comparable to those recorded for other NDI mono-reduced species (such as [**4.4**]⁻ and [**4.9**]⁻) and was reasonably simulated using couplings of the unpaired electron to two sets of four hydrogen atoms and two equivalent nitrogen atoms. The mono-reduction of **4.12** to [**4.12**]⁻ also gave an EPR active species (similar to [**4.6**]⁻) however, substantial broadening meant that any hyperfine at low field was unresolved

(Figure 4.19-1/2). The electrochemical reduction of $[\mathbf{4.6}]^{\cdot -}$ to $[\mathbf{4.6}]^{2-}$ (discussed in Section 4.2.4.4) showed the EPR signal significantly diminished (leaving only a 7 % residual signal). Furthermore, cooling of the sample showed no evidence to support the presence of a triplet state. This suggests that $[\mathbf{4.6}]^{2-}$ forms a ground state singlet in which the two electrons enter a shared π -based molecular orbital. By comparison, the frozen (77 K) solution EPR spectrum of $[\mathbf{4.12}]^{2-}$ showed a structureless band in the half-field region (Figure 4.19-3, g_{av} 4.009), which is evidence for the presence of a ground state triplet ($\Delta m_s = 2$ transition). In addition to this signal at half-field, the signal at full-field ($\Delta m_s = 1$ transition) was complex and could be reasonably simulated by using a combination of multiple triplet states and a doublet state (Figure 4.19-3). The considerable difference in the magnetic properties between $[\mathbf{4.12}]^{2-}$ and $[\mathbf{4.6}]^{2-}$ shows that there is a substantial transformation in the way the NDI units interact and communicate upon Pd(II)-coordination, on the EPR timescale.

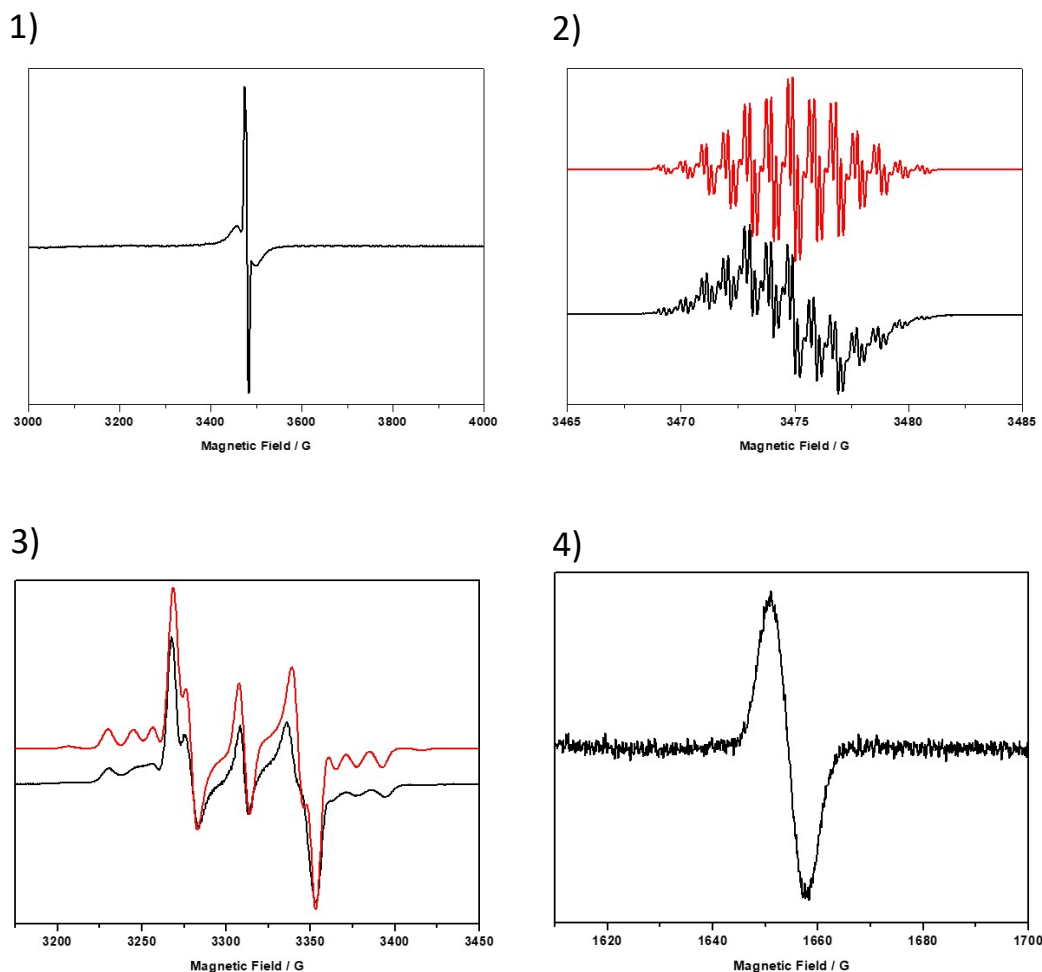


Figure 4.18: EPR spectra of $[4.12]^-$: 1) wide scan range and 2) narrow scan range, at ambient temperature. EPR spectra of $[4.12]^{2-}$: 3) wide scan range and 4) half-field feature, at 77 K. Experimental data (black), simulated data (red).

The EPR spectrum of $[4.15]^-$ was analogous to typical bay unsubstituted mono-reduced PDI spectra (for example $[4.1]^-$ and $[4.2]^-$) and was reasonably simulated using couplings of the unpaired electron to three sets of four hydrogen atoms and two equivalent nitrogen atoms (Figure 4.20-1/2). The electrochemical reduction of **4.13** gave the EPR active species $[4.13]^-$, which showed significant line broadening as well as a narrowing of the spectral width (comparable to the Pd(II)-free analogue $[4.5]^-$). This similarity suggests that the electron delocalisation/hopping between the two PDIs is unaffected by Pd(II)-coordination (on the timescale of the experiment). Upon the second reduction (to give $[4.13]^{2-}$) there was a significant reduction in the EPR signal which

indicates the presence of a ground state singlet. Similar to **[4.5]**²⁻, this is consistent with the electrons entering a shared π -based molecular orbital. Furthermore, cooling the solution to 77 K showed no evidence of a ground state triplet, apparent in the NDI equivalent **[4.12]**²⁻ species. Unlike for **4.6**, there appeared to be no change in the magnetic properties of **4.5** upon Pd(II)-coordination (**4.13**). This could be the result of the larger aromatic framework of PDIs allowing for stronger π - π interactions and greater overlap, which are less affected by Pd(II)-coordination than in the NDI analogue, **4.12**.

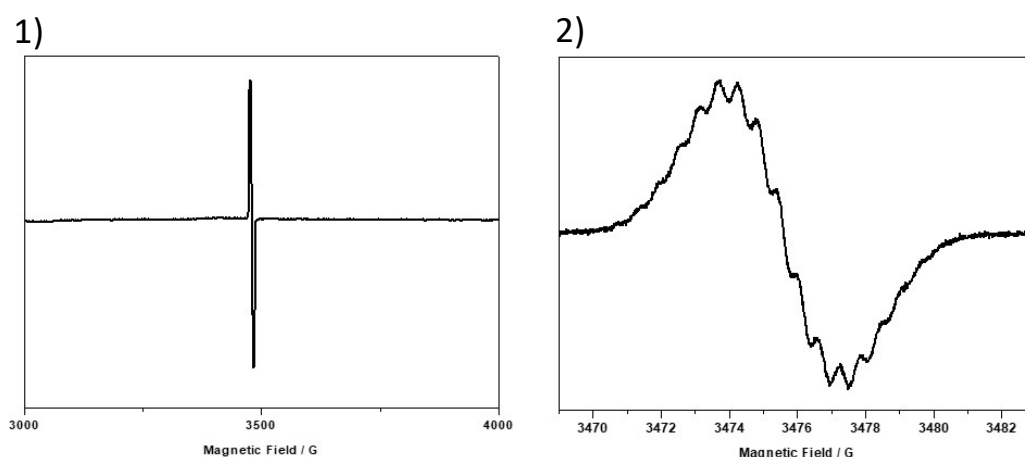


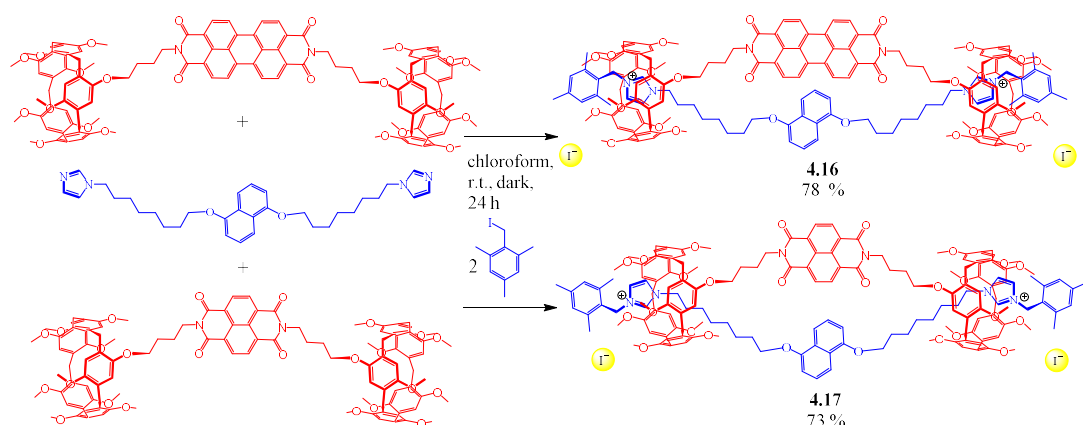
Figure 4.20: EPR spectra of **[4.13]**^{•-}: 1) wide scan range and 2) narrow scan range, at ambient temperature.

4.2.6. Expanding Scope to Include Naphthalene

Following the encouraging results of synthesising [2]rotaxanes with handcuff topology using PDI and NDI moieties, it was envisioned that the pillar[5]arene-imidazole synthesis method could be used to readily assemble a wide range of molecules with handcuff tropology, featuring different combinations of interesting moieties. This possibility was investigated by introducing 1,5-dialkoxynaphthalene (DAN) units. DANs are electron-rich (donor) aromatic moieties that are commonly utilised in the construction of supramolecular architectures, especially in conjunction with electron deficient acceptor units (such as NDIs and PDIs). For example, DANs have been shown to form alternative donor-acceptor stacks through self-sorting assembly⁴⁵ aided by

hydrogen bonding⁴⁶ or through solid-state grinding.⁴⁷ Furthermore, DANs have been used in the assembly of [2]catenane-containing struts in catenated metal-organic frameworks⁴⁸ and have been co-crystallised with pyromellitic diimide derivatives to form organic charge transfer complexes⁴⁹ which exhibit ferroelectric behaviour.⁵⁰ In addition to the applications in which DANs are employed, they are also cheap and can be readily functionalised with a variety of substituents. This makes DANs an attractive aromatic moiety to expand the scope of handcuff [2]rotaxanes and demonstrate how a library of compounds can be built up.

4.2.6.1. Synthesis



Scheme 4.5: Synthesis of PDI-DAN and NDI-DAN handcuff [2]rotaxanes **4.16** and **4.17**.

The reaction of naphthalene-1,5-diol with an excess amount of di-bromooctane in the presence of potassium carbonate, led to the formation of a DAN bearing two bromo-alkyl chains. Further reaction with imidazole led to the formation of a *bis*-imidazole species in which the two arms are separated by the naphthalene aromatic core, similar to *bis*-imidazole PDI and NDI, **4.1** and **4.2**. Subsequent mixing of *bis*-imidazole DAN with rylene di-pillar[5]arenes (**4.3** and **4.4**) in chloroform and reaction with 2-(iodomethyl)-1,3,5-trimethylbenzene led to the formation of PDI-DAN and NDI-DAN handcuff [2]rotaxanes **4.16** and **4.17**, respectively (Scheme 4.5). The structure of **4.16** and **4.17** was confirmed by ¹H, 2-D and ¹³C NMR spectroscopy studies (¹H and ¹H-¹H COSY NMR spectra of **4.16** is shown in Figure 4.21) and HRMS. The impact of having an electron-rich

component adjacent to the PDI/NDI cores on their redox properties was investigated using electrochemical techniques including CV, spectroelectrochemistry and EPR spectroscopy.

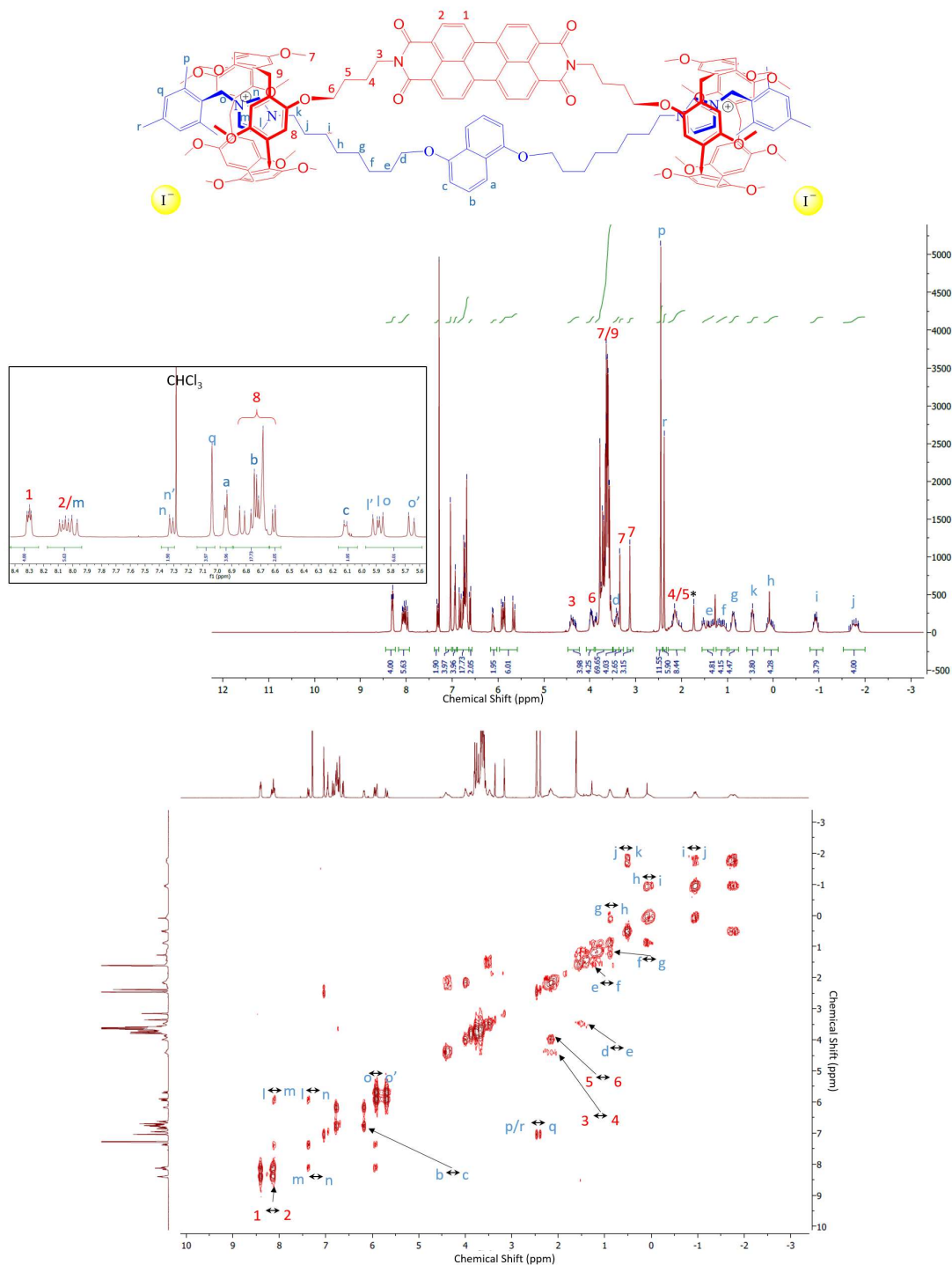


Figure 4.21: ^1H NMR and ^1H - ^1H COSY NMR (400 MHz, CDCl_3 , 298 K) spectra of **4.16**.

4.2.6.2. Electrochemistry

4.2.6.2.1. CV

The CVs of **4.16** and **4.17** were recorded under analogous conditions to the handcuff [2]rotaxanes previously described (Table 4.6). **4.16** showed two reduction processes (-1.01, -1.24 V) which were subtly shifted to more negative potential compared to the PDI monomer **4.3** (-0.96, -1.15 V). Although DAN (like NDI) has a naphthalene core, the CV showed no evidence for electron sharing (which was observed for PDI-NDI handcuff [2]rotaxane **4.7**). This illustrates the importance of matching the orbital energies of the two handcuff [2]rotaxane components for there to be a significant interaction between them. The CV of **4.15** also showed two reductions which only exhibited a very minor negative shift in reduction potentials (≤ 0.03 V) compared to the NDI monomer (**4.4**).

Compound	1 st reduction		2 nd reduction	
	CV	SW	CV	SW
	$E_{1/2}$ / V	/ V	$E_{1/2}$ / V	/ V
4.3	-0.96	-0.97	-1.15	-1.16
4.4	-1.01	-1.01	-1.45	-1.44
4.16	-1.01	-1.01	-1.24	-1.24
4.17	-1.06	-1.07	-1.48	-1.48

Table 4.6: Reduction potentials of PDI and NDI monomer compounds **4.3** and **4.4** as well as DAN-incorporated handcuff [2]rotaxanes **4.16** and **4.17**. Potentials quoted against $E_{1/2}$ Fc⁺/Fc at 0.1 Vs⁻¹ used as the internal standard. Recorded in dichloromethane at ambient temperature containing [nBu₄N][BF₄] (0.4 M) as the supporting electrolyte.

4.2.6.2.2. Spectroelectrochemistry

DANs electron dense planar π framework in close proximity to the PDI and NDI units was anticipated to have an effect on the electrochemical properties of the PDI and NDI moieties in **4.16** and **4.17**. However, the CV of **4.16** and **4.17** only showed minor deviations in the reduction potentials compared to the monomer equivalents **4.3** and **4.4**. This was further investigated using spectroelectrochemical measurements (Figure 4.22/Table 4.7). The UV/vis spectra of both neutral

and mono-reduced **4.16** and **4.17** were consistent with spectra of typical bay unsubstituted PDIs and NDIs (with the absence of any aggregation).

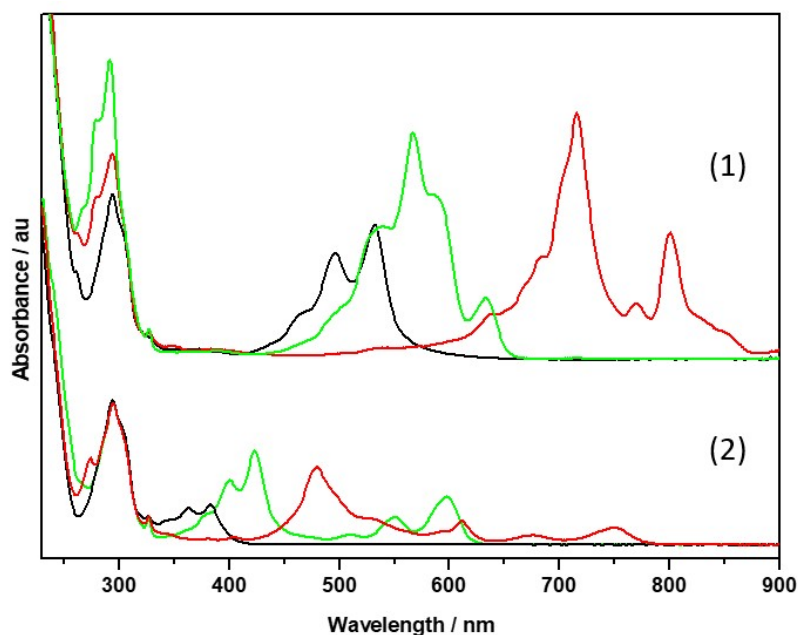


Figure 4.22: UV/vis absorption spectra of neutral (black), mono-reduced (red) and di-reduced (green) for 1) **4.17** and 2) **4.16**. Spectra were recorded in dichloromethane containing $[\text{nBu}_4\text{N}][\text{BF}_4]$ (0.4 M) as the supporting electrolyte at 273 K.

UV/vis λ_{abs} / nm ($\epsilon \times 10^{-3} / \text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$)			
Compound	Neutral	Mono-anion	Dianion
4.16	261 (31.7), 294 (59.6), 496 (38.2), 532 (48.4)	294 (74.2), 346 (4.7), 383 (3.6), 539 (4.0), 638 (16.2), 684 (36.8), 716 (88.6), 769 (20.0), 801 (45.5)	279 (86.4), 292 (107.9), 327 (10.9), 540 (47.7), 568 (81.6), 586 (59.2), 633 (22.0)
4.17	295 (52.3), 326 (10.3), 363 (13.2), 509 (0.3)	274 (31.4), 295 (50.9), 327 (10.2), 381 (2.1), 479 (28.0), 593 (4.7), 611 (8.6), 676 (3.4), 749 (6.0)	295 (51.0), 327 (9.3), 400 (23.3), 423 (33.8), 510 (3.6), 550 (10.1), 597 (17.4)

Table 4.7: Summary of UV/vis Spectroscopic data for **4.16** and **4.17**. Obtained in dichloromethane containing $[\text{nBu}_4\text{N}][\text{BF}_4]$ (0.4 M) at 273 K over a spectral range of 230-900 nm.

4.2.6.2.3. EPR Spectroscopy

The X-band EPR spectra of $[4.16]^-$ and $[4.17]^-$ were recorded as fluid solutions at ambient temperature in dichloromethane containing 0.4 M $[n\text{Bu}_4\text{N}][\text{BF}_4]$ (Figure 4.23). Similar to the CV and spectroelectrochemistry results, the EPR spectra of $[4.16]^-$ and $[4.17]^-$ were comparable to the ones recorded for mono-reduced monomer components $[4.3]^-$ and $[4.4]^-$. They were reasonably simulated using parameters consistent with PDI-based and NDI-based reductions, respectively.

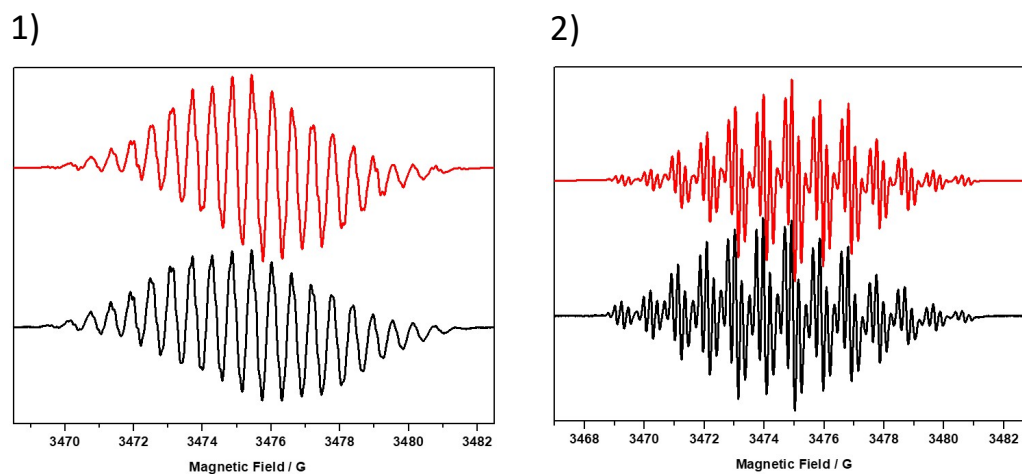


Figure 4.23: EPR spectra of $[4.16]^-$ and $[4.17]^-$. Experimental data (black), simulated data (red).

4.3. Conclusions

The pillar[5]arene/imidazole-based MIM synthesis method (described in Chapter 2 and 3) has been utilised in the synthesis of dual threaded [2]rotaxanes with handcuff topology. Using the handcuff structure, dimers of aromatic moieties have been locked in a co-facial manner. The nature of the mechanical bonds linking the aromatic units together, provides sufficient flexibility for them to move with a greater degree of freedom than covalently linked systems. This allows the aromatics groups to move together or apart upon applied stimuli such as a change in redox state and therefore the handcuff [2]rotaxanes appear to closely mimic freely stacked molecules. Rylene diimides (PDIs and NDIs) have been combined in PDI-PDI, NDI-NDI and PDI-NDI handcuff [2]rotaxanes. The nature of interactions between the π -orbital manifolds held in close proximity, was probed through full electrochemical characterisation. In the PDI-PDI handcuff [2]rotaxane (**4.5**) the formation of H-aggregate in the ground state and fluorescence emission from an excimer-like state was observed. This was evidence for stacking in the ground state and strong electron delocalisation between the PDI cores in the excited state. By contrast, the NDI-NDI handcuff [2]rotaxane (**4.6**) showed no H-aggregation and was found to be non-fluorescent. Similarly, the PDI-NDI handcuff [2]rotaxane (**4.7**) exhibited no H-aggregation and the fluorescence showed only weak emission (and features typical for localised PDI orbital). However, interaction between the two π -systems in **4.5**, **4.6** and **4.7** was apparent in their CVs, which showed splitting of the first reduction into two well separated one-electron processes for **4.5** and **4.6** as well as showing additional splitting for **4.7**. Probing mono-reduced **4.5**, using spectroelectrochemical measurements, showed bands associated with both neutral and mono-reduced PDI whilst the EPR spectrum showed delocalisation (or fast hopping) of the electron. Mono-reduced **4.6** showed a similar discrepancy between spectroelectrochemical and EPR measurements whilst mono-reduced **4.7** exhibited no evidence for delocalisation of the electron on the EPR timescale. Di-reduced **4.5** exhibited unusual broad bands at 615 nm and 1527 nm, not present in either mono-

or di-reduced PDI monomer components (**4.3** and **4.8**). These broad absorbance features are evidence for the formation of a ' π -dimer'. Although the electronic spectrum of **[4.6]**²⁻ showed no such bands, **[4.7]**²⁻ exhibited analogous bands suggesting similar π - π stacking interactions between NDI and PDI-based orbitals. Complete reduction of **4.5** and **4.6** to give **[4.5]**⁴⁻ and **[4.6]**⁴⁻ species revealed spectroscopic and electrochemical profiles consistent with typical **[PDI]**²⁻ and **[NDI]**²⁻ species, respectively. This differs from covalently linked dimers and demonstrates the flexible nature of the interlocked structure. Reduction of **4.7** to give **[4.7]**³⁻ showed the unpaired electron localised on the NDI moiety (**[PDI]**²⁻-**[NDI]**^{·-}), which demonstrates that electrons can be sequentially added to specific components of the interlocked molecule by carefully selecting electron accepting sites with appropriate reduction potentials. These investigations into the reduced species of **4.5-4.7** revealed unusual behaviour which enhances and reinforces the understanding of the interactions between rylene diimides.

PsTA measurements of *bis*-pillar[5]arene PDI, **4.3**, revealed a short lived ¹PDI excited state, quenched by the pillar[5]arenes, which is in agreement with the low quantum yield observed for this compound. The equivalent measurements done on *bis*-imidazolium PDI, **4.8**, showed a longer lived ¹PDI excited state than in **4.3**, however still shorter than for typical PDIs, suggesting that the imidazoliums also have a quenching effect. Further psTRIR measurements confirmed these results. psTA and psTRIR measurements of **4.5** showed compelling evidence for the formation of an excimer between the two PDIs, which supports observations made in the spectroelectrochemical characterisation of the reduced states. The excimer lifetime was found to be significantly shorter than in covalently linked dimers, which is likely to be a feature associated with the non-covalent nature the PDI cores are linked together.

Ag(I) was coordinated to the imidazolium of **4.5**, **4.6**, **4.14** and **4.15** to form NHCs, and subsequent transmetalation with Pd(II) gave di-[PdI₂(C₅H₅N)] complex-containing handcuff [2]rotaxanes **4.12/4.13** and axles **4.14/4.15**. NMR spectroscopy studies showed a similar shift in the

pillar[5]arene position along the axle as described in Chapter 2 following metal coordination. The fluorescence of **4.13** was quenched, showing no excimer type emission. By contrast, fluorescence measurements of **4.12** showed a weak emission band at 545 nm indicating the presence of an excimer type state, not present in the Pd(II)-free analogue. The CVs of **4.12** and **4.13** exhibited the same spectral profile as **4.6** and **4.5** respectively, however each of the reductions showed a slight shift in reduction potential. An additional broad reduction process at ca. -2.0 V was observed in all Pd(II)-coordinated compounds. Although the fluorescence and CV measurements indicate some change in the nature of interaction between the aromatic moieties upon Pd(II)-coordination, the spectroelectrochemistry of **4.13** and **4.12** showed little to no change at any redox state. Furthermore, the EPR spectrum of [**4.13**]⁻ showed the presence of a ground state singlet, consistent with the Pd(II)-free analogue in which the electron occupies a shared π -based molecular orbital. By contrast, the EPR spectrum of [**4.12**]²⁻ exhibits a band at half-field, indicating the presence of a ground state triplet as well as a complex feature at full-field composed of multiple triplet states and a doublet state. Pd(II)-coordination appears to have a subtle yet significant effect on the nature of interactions occurring in the handcuff [2]rotaxanes.

The interlocked synthesis approach for handcuff [2]rotaxanes provides a straight forward method for combining different aromatic groups within a handcuff molecule, of which literature examples are rare. Furthermore, a large library of handcuff molecules with varying properties can be built up by combining a newly synthesised monomer with every, already known counterpart. To demonstrate this, a DAN moiety bearing two alkyl-imidazoles was synthesised and combined in a handcuff [2]rotaxane with di-pillar[5]arene PDI and NDI. Although DANs are electron-rich, the close proximity of a DAN moiety to a PDI/NDI unit appeared to have only a minor effect on the spectroscopic and electrochemical properties of these systems. Transient measurements would be useful to identify any charge-transfer between the DAN and rylene diimide units. Although these are beyond the scope of this project, they would be a good starting point for future investigations.

4.4. Materials and Methods

4.4.1. Synthesis

4.4.1.1. General Procedure for *Bis*-Imidazole PDI/NDI **4.1/4.2**

8-Imidazolyloctylamine (9.20 mmol) and rylene *peri*-tetracarboxylic dianhydride (4.50 mmol) were dissolved in DMF (40 mL) and heated to 160 °C under a dinitrogen atmosphere for 24 h. The solvent was removed under reduced pressure and the residue was taken up in chloroform (50 mL) and washed with water (4 x 50 mL) and dried over anhydrous MgSO₄ and filtered under gravity. The organic solvent was removed under reduced pressure and the residue was redissolved in a minimum volume of chloroform and added dropwise to cold hexane (300 mL). The formed precipitate was collected by filtration under reduced pressure and dried to afford the product.

4.1. Red solid (76 %) ¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 8.0 Hz, 4H), 8.56 (d, *J* = 8.1 Hz, 4H), 7.49 (s, 2H), 7.07 (s, 2H), 6.93 (s, 2H), 4.21 (t, 4H), 3.95 (t, *J* = 7.2 Hz, 4H), 1.84 – 1.74 (m, 8H), 1.48 – 1.31 (m, 16H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.34, 137.08, 134.53, 131.36, 129.35, 129.29, 126.35, 123.28, 123.07, 118.80, 47.01, 40.58, 31.04, 29.05, 28.90, 27.96, 26.96, 26.48 ppm. HRMS (ESI-) *m/z*: 747.3629 [M+H]⁺, calc. for [C₄₆H₄₆N₆O₄]⁺ = 746.3581.

4.2. Light brown solid (74 %) ¹H NMR (400 MHz, Chloroform-*d*) δ 8.76 (s, 4H), 7.51 (s, 2H), 7.06 (s, 2H), 6.92 (s, 2H), 4.19 (t, 4H), 3.94 (t, *J* = 7.1 Hz, 4H), 1.86 – 1.66 (m, 8H), 1.51 – 1.21 (m, 16H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.86, 137.08, 130.98, 129.38, 126.65, 118.78, 46.99, 40.87, 31.03, 29.02, 28.88, 27.94, 26.89, 26.47 ppm. HRMS (ESI-) *m/z*: 623.3329 [M+H]⁺, calc. for [C₃₆H₄₂N₆O₄]⁺ = 622.3268.

4.4.1.2. Pillar[5]arene butylamine

Pillar[5]arene-butylphthalimide: di-bromobutoxy-pillar[5]arene (0.436 g, 0.5 mmol) was dissolved in dry DMF (5 mL). Phthalimide (0.11 g, 0.72 mmol) and potassium carbonate (0.11 g, 0.80 mmol) were added to the solution and the reaction mixture was stirred overnight at 60 °C. The mixture was cooled to room temperature and reduced under reduced pressure. Water (50 mL) was added

and the resulting mixture was extracted with dichloromethane (3 x 50 mL). The organic layer was dried over anhydrous MgSO_4 , filtered under gravity and the solvent removed under reduced pressure. The crude product was purified using silica gel chromatography (dichloromethane) to give the product as a pale yellow solid (0.301 g, 64%). ^1H NMR (400 MHz, Chloroform- d) δ 7.91 – 7.87 (m, 2H), 7.75 (m, 3H), 6.87 – 6.71 (m, 10H), 3.90 (t, J = 6.1 Hz, 2H), 3.85 – 3.61 (m, 39H), 2.05 – 1.93 (m, 2H), 1.89 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 168.43, 167.96, 166.85, 150.79, 150.75, 150.72, 149.86, 134.39, 134.30, 133.99, 132.66, 132.09, 131.68, 128.41, 128.31, 128.28, 128.24, 128.19, 128.12, 123.76, 123.59, 123.24, 114.94, 114.10, 114.03, 113.99, 113.94, 113.86, 67.82, 55.83, 55.80, 55.77, 55.69, 52.60, 40.45, 37.83, 29.73, 29.65, 29.62, 29.44, 27.28, 25.63. HRMS (ESI+) m/z : 955.4340 ($[\text{M}+\text{H}_4\text{N}]^+$, calc. for $[\text{C}_{56}\text{H}_{63}\text{N}_2\text{O}_{12}]^+ = 955.4376$).

Pillar[5]arene-butylamine: pillar[5]arene-butylphthalimide (0.30 g, 0.320 mmol) was dissolved in dry THF (20 mL) and hydrazine monohydrate (0.16 g, 320 mmol) was added. The reaction mixture was heated to reflux and stirred overnight. After cooling, aqueous sodium carbonate was added and the product was extracted into dichloromethane (3 x 50 mL). After drying over anhydrous MgSO_4 and filtering under gravity the solvent was removed under reduced pressure to give the product, without further purification, as a pale yellow solid (0.21 g, 87%). ^1H NMR (400 MHz, Chloroform- d) δ 6.95 – 6.67 (m, 10H), 4.10 – 3.37 (m, 40H), 1.50 (s, 4H). ^{13}C NMR (101 MHz, Chloroform- d) δ 150.90, 150.79, 150.74, 150.70, 150.66, 149.93, 128.57, 128.42, 128.38, 128.30, 128.25, 128.19, 128.13, 114.93, 114.49, 114.14, 114.08, 114.03, 113.97, 113.71, 68.62, 56.08, 55.91, 55.86, 55.81, 55.75, 55.72, 55.69, 30.34, 30.06, 29.79, 29.68, 29.46, 29.39, 26.84, 1.05. HRMS (ESI+) m/z : 808.4121 ($[\text{M}+\text{H}]^+$, calc. for $[\text{C}_{48}\text{H}_{58}\text{NO}_{10}]^+ = 808.4055$).

4.4.1.3. General Procedure for *Bis*-Pillar[5]arene PDI/NDI **4.3/4.4**

Pillar[5]arene butylamine (0.25 mmol), rylene-3,4,9,10-tetracarboxylic dianhydride (0.12 mmol) and imidazole (7.2 mmol) were heated at 130 °C under a dinitrogen atmosphere for 24 h. The mixture was taken up in chloroform (50 mL) and the organic layer was washed with water (4 x 50

mL) and dried over anhydrous MgSO_4 and filtered under gravity. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (methanol/chloroform 0.5:100) to give the product.

4.3 Red solid (0.235 g, 94 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, J = 7.9 Hz, 2H), 8.51 (d, J = 8.0 Hz, 2H), 6.83 – 6.63 (m, 10H), 4.35 (t, J = 6.9 Hz, 2H), 3.92 (t, J = 6.0 Hz, 2H), 3.83 – 3.51 (m, 37H), 2.14 – 1.90 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.38, 150.79, 150.66, 149.95, 134.59, 131.36, 129.27, 128.40, 128.29, 128.25, 128.18, 128.12, 128.09, 127.93, 126.34, 125.53, 123.18, 123.04, 114.97, 114.19, 114.11, 114.06, 114.03, 113.95, 113.84, 68.08, 55.82, 55.78, 55.73, 55.72, 55.66, 55.65, 53.20, 30.34, 29.73, 29.71, 29.41, 27.53, 25.11 ppm. HRMS (ESI+) m/z : 1970.8147 [M]⁺, calc. for $[\text{C}_{120}\text{H}_{118}\text{N}_2\text{O}_{24}]^+ = 1970.8069$.

4.4 Brown solid (74 %). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.74 (s, 2H), 6.80 – 6.59 (m, 10H), 4.35 (t, J = 7.1 Hz, 2H), 3.91 (t, J = 6.1 Hz, 2H), 3.82 – 3.56 (m, 36H), 2.08 (p, J = 7.7, 6.6 Hz, 2H), 1.97 (p, J = 12.8, 6.1 Hz, 2H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.94, 150.82, 150.77, 150.73, 150.71, 150.61, 149.83, 130.75, 128.32, 128.24, 128.14, 128.02, 127.91, 126.58, 126.45, 114.86, 114.22, 114.19, 114.02, 113.89, 113.74, 67.83, 40.65, 29.78, 29.63, 29.31, 27.45, 25.00 ppm. HRMS (ESI+) m/z : 1870.7613 [M+Na]⁺, calc. for $[\text{C}_{110}\text{H}_{114}\text{N}_2\text{O}_{24}\text{Na}]^+ = 1870.7687$.

4.4.1.4. General Procedure for Handcuff [2]Rotaxanes **4.5/4.6/4.7**

Bis-imidazole PDI/NDI (**4.1/4.2**) (0.05 mmol) and *bis*-pillar[5]arene PDI/NDI (**4.3/4.4**) (0.05 mmol) were dissolved in chloroform (1 mL) and cooled to -15 °C. 2-(iodomethyl)-1,3,5-trimethylbenzene (0.15 mmol) was added and the mixture was left to warm to room temperature and stirred overnight under the exclusion of light. The crude residue was subjected to column chromatography on silica gel (chloroform: methanol 98:2 -> 90:10) to afford the product.

4.5 Red solid (0.140 g, 81 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 7.80 (m, 16H), 7.52 (s, 1H), 7.43 (s, 1H), 7.07 (s, 4H), 7.05 – 6.86 (m, 10H), 6.84 – 6.62 (m, 10H), 6.07 (s, 1H), 5.99 (s, 1H), 5.95 – 5.58 (m, 4H), 4.26 – 3.44 (m, 82H), 2.48 (s, 12H), 2.40 (s, 6H), 2.17 – 1.96 (m, 8H), 1.85 –

1.62 (m, 8H), 1.14 – 0.87 (m, 4H), 0.67 (dt, J = 29.8, 8.8 Hz, 4H), 0.29 – -0.05 (m, 4H), -0.64 – -1.10 (m, 4H), -1.36 – -1.74 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 162.45, 162.43, 151.45, 151.29, 150.68, 150.28, 150.23, 150.19, 140.05, 138.05, 133.02, 132.98, 132.40, 130.18, 130.11, 130.07, 129.95, 129.03, 128.94, 128.86, 128.83, 125.77, 123.13, 123.11, 122.29, 122.05, 122.02, 121.09, 58.59, 58.30, 58.03, 55.77, 55.67, 29.06, 25.89, 21.21, 20.02 ppm. HRMS (ESI+) m/z : 1491.6826 [M-H] $^{2+}$, calc. for $[\text{C}_{186}\text{H}_{190}\text{N}_8\text{O}_{28}]^{2+}$ = 1492.6873.

4.6. Light brown solid (0.167 g, 68 %). ^1H NMR (400 MHz, Chloroform- d) δ 8.55 – 8.29 (m, 8H), 8.23 (s, 2H), 7.84 (s, 1H), 7.73 (s, 1H), 7.05 (s, 4H), 7.01 – 6.61 (m, 21H), 6.24 (s, 1H), 6.14 (s, 1H), 6.04 – 5.71 (m, 4H), 4.25 – 4.05 (m, 8H), 4.01 – 3.49 (m, 82H), 2.48 (s, 12H), 2.39 (s, 6H), 2.14 – 1.99 (m, 8H), 1.80 – 1.69 (m, 4H), 1.33 (m, 4H), 1.05 – 0.96 (m, 2H), 0.93 – 0.79 (m, 6H), 0.04 – -0.35 (m, 4H), -1.17 (s, 4H), -1.28 – -1.63 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 162.09, 162.02, 151.24, 151.11, 151.02, 150.53, 150.30, 139.88, 138.09, 132.39, 132.28, 130.52, 130.00, 129.83, 129.75, 129.04, 128.94, 128.91, 128.71, 126.06, 126.04, 125.96, 122.67, 120.85, 116.19, 115.96, 115.88, 115.59, 115.51, 114.85, 114.59, 113.69, 113.61, 68.07, 58.42, 58.21, 58.11, 58.02, 55.99, 55.79, 55.62, 48.88, 47.72, 47.60, 40.96, 40.67, 30.51, 29.71, 29.14, 29.07, 28.70, 28.33, 27.79, 25.96, 25.81, 25.54, 25.38, 24.73, 21.20, 20.15 ppm. HRMS (ESI+) m/z : 1368.1509 [M] $^{2+}$, calc. for $[\text{C}_{166}\text{H}_{182}\text{N}_8\text{O}_{28}]^{2+}$ = 1368.1543.

4.7. Red solid (0.161 g, 89 %). ^1H NMR (400 MHz, Chloroform- d) δ 8.37 (t, J = 6.6 Hz, 4H), 8.07 (d, J = 8.1 Hz, 4H), 7.99 (s, 1H), 7.94 (s, 1H), 7.92 (s, 3H), 7.55 (s, 1H), 7.45 (s, 1H), 7.08 (s, 4H), 7.06 – 6.62 (m, 18H), 6.07 (s, 1H), 5.98 (s, 1H), 5.96 – 5.63 (m, 4H), 4.43 (s, 4H), 4.17 – 3.48 (m, 78H), 2.50 (s, 12H), 2.42 (s, 6H), 2.38 – 2.16 (m, 8H), 1.52 – 1.36 (m, 4H), 1.32 – 1.19 (m, 4H), 0.98 – 0.83 (m, 4H), 0.71 (t, J = 8.8 Hz, 2H), 0.61 (t, 2H), 0.24 – -0.11 (m, 4H), -0.67 – -1.09 (m, 4H), -1.42 – -1.82 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform- d) δ 162.80, 151.54, 151.33, 151.17, 151.08, 150.89, 150.50, 150.37, 139.93, 138.11, 132.69, 132.45, 130.74, 130.12, 130.01, 129.76, 128.89, 128.83, 125.14, 123.29, 122.87, 122.15, 121.03, 116.29, 115.73, 113.79, 58.60, 58.50, 58.39, 58.21, 58.14,

58.01, 55.72, 55.64, 48.72, 29.16, 28.60, 27.75, 25.73, 25.42, 21.13, 20.01 ppm. HRMS (ESI+) m/z: 1429.6723 [M]²⁺, calc. for [C₁₇₆H₁₈₆N₈O₂₈]²⁺ = 1430.1700.

4.4.1.5. General Procedure for *Bis*-Imidazolium PDI/NDI **4.8/4.9**

Bis-imidazole PDI/NDI (**4.1/4.2**) (0.24 mmol) was dissolved in chloroform (10mL) and 2-(iodomethyl)-1,3,5-trimethylbenzene (0.6 mmol) was added under the exclusion of light. The mixture was stirred over night at room temperature. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography (chloroform: methanol 90:10 -> 80:20).

4.8. Red solid (73 %). ¹H NMR (400 MHz, Chloroform-*d*/Methanol-*d*) δ 9.32 (s, 2H), 8.16 (d, *J* = 7.9 Hz, 4H), 8.07 (d, *J* = 8.2 Hz, 4H), 7.45 (d, *J* = 1.9 Hz, 2H), 6.98 (d, *J* = 1.9 Hz, 2H), 6.86 (s, 4H), 5.43 (s, 4H), 4.25 (t, *J* = 7.5 Hz, 4H), 3.95 (t, *J* = 7.4 Hz, 4H), 2.22 (s, 12H), 2.19 (s, 6H), 1.93 – 1.81 (m, 4H), 1.68 – 1.56 (m, 4H), 1.33 (m, 16H) ppm. ¹³C NMR (126 MHz, Chloroform-*d*/Methanol-*d*) δ 163.32, 140.06, 137.83, 134.38 (2C, one from imidazolium and one from PDI core), 131.22, 129.82, 128.86, 125.94, 124.85, 123.29, 122.68, 122.38, 121.64, 49.94, 47.78, 40.22, 29.80, 28.60, 28.32, 27.50, 26.54, 25.77, 20.65, 19.32 ppm. HRMS (ESI+) m/z: 506.2808 [M]²⁺, calc. for [C₆₆H₇₂N₆O₄]²⁺ = 506.2802.

4.9. Light brown solid (65 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 10.05 (s, 2H), 8.72 (s, 4H), 7.53 (s, 2H), 6.96 (s, 2H), 6.91 (s, 4H), 5.58 (s, 4H), 4.35 (t, *J* = 7.5 Hz, 4H), 4.16 (t, *J* = 7.3 Hz, 4H), 2.29 (s, 12H), 2.27 (s, 6H), 2.02 – 1.89 (m, 4H), 1.75 – 1.65 (m, 4H), 1.35 (s, 16H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.78, 140.01, 138.11, 135.98, 130.97, 129.98, 126.62, 126.51, 125.17, 122.41, 120.99, 50.32, 48.17, 40.67, 30.14, 28.89, 28.61, 27.81, 26.69, 26.03, 21.07, 20.10 ppm. HRMS (ESI+) m/z: 444.2659 [M]²⁺, calc. for [C₅₆H₆₈N₆O₄]²⁺ = 444.2646.

4.4.1.6. General Procedure for Ag(I)-Coordination to Handcuffs **4.10/4.11**

To a solution of handcuff [2]rotaxanes (**4.5/4.6**) (0.131 mmol) in dichloromethane (25 mL) was added Ag₂O (1.31 mmol) and the mixture was stirred at room temperature overnight under the

exclusion of light. The mixture was filtered under gravity and the solvent removed under reduced pressure to afford the crude product. This was redissolved in dichloromethane (1 mL) and added dropwise to cold hexane (20 mL). The precipitate was collected by filtration under reduced pressure, washed with hexane and dried to afford the product.

4.10. Dark brown solid (90 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.50 – 8.27 (m, 8H), 7.10 – 6.73 (m, 26H), 6.64 (s, 2H), 5.41 (s, 4H), 4.19 (s, 4H), 4.13 – 3.50 (m, 90H), 3.27 (s, 4H), 2.12 (s, 8H), 1.39 (s, 4H), 0.65 – 0.41 (m, 4H), 0.04 – -0.23 (m, 4H), -0.61 – -0.81 (m, 4H), -1.84 – -2.06 (m, 4H), -2.06 – -2.24 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.24, 162.06, 161.97, 161.74, 151.12, 150.91, 150.81, 150.45, 150.42, 150.33, 150.26, 150.18, 139.09, 137.64, 130.45, 130.00, 129.82, 129.71, 129.08, 129.04, 128.98, 128.90, 128.83, 128.76, 128.65, 128.59, 128.54, 128.45, 128.34, 128.29, 128.24, 128.21, 127.98, 125.96, 125.91, 125.88, 120.75, 118.91, 114.98, 114.82, 114.65, 113.43, 113.20, 112.98, 68.22, 58.29, 58.24, 58.08, 57.98, 57.83, 57.58, 57.52, 57.43, 57.38, 57.26, 57.22, 57.10, 55.93, 55.83, 55.74, 55.70, 55.61, 55.59, 55.54, 55.52, 55.49, 55.27, 51.70, 49.72, 41.56, 40.41, 40.26, 30.53, 30.43, 29.71, 29.06, 28.95, 28.92, 27.72, 27.62, 27.35, 27.22, 27.16, 25.06, 23.90, 21.21, 21.13, 20.18, 20.00 ppm. (Some decomposition was observed in solution over 24 hours).

4.11. Red solid (99 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, J = 7.1 Hz, 8H), 8.19 – 7.90 (m, 8H), 7.26 (d, J = 1.6 Hz, 1H), 7.13 – 6.85 (m, 25H), 6.62 (t, J = 1.8 Hz, 2H), 5.40 (d, J = 2.3 Hz, 4H), 4.28 – 4.17 (m, 4H), 4.15 – 3.52 (m, 87H), 3.34 – 3.05 (m, 4H), 2.38 (s, 6H), 2.37 (s, 11H), 2.21 – 2.09 (m, 8H), 1.54 – 1.39 (m, 4H), 0.70 – 0.43 (m, 4H), -0.00 – -0.25 (m, 4H), -0.45 – -0.71 (m, 4H), -1.89 – -2.22 (m, 8H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.65, 162.44, 151.06, 150.97, 150.87, 150.82, 150.73, 150.69, 150.65, 150.55, 150.38, 150.36, 150.32, 150.25, 150.21, 139.09, 137.65, 133.36, 130.45, 129.82, 129.30, 129.02, 128.88, 128.78, 128.58, 128.54, 128.19, 128.00, 122.82, 120.79, 118.79, 115.05, 115.00, 114.77, 114.73, 113.31, 113.27, 112.95, 57.64, 57.52,

57.41, 57.30, 57.18, 56.96, 55.90, 55.81, 55.61, 55.54, 55.23, 51.67, 49.72, 29.71, 29.37, 29.24, 29.17, 29.13, 28.95, 27.92, 27.83, 27.29, 27.17, 23.84, 21.12, 19.99 ppm.

4.4.1.7. General Procedure for Pd(II)-Coordination to Handcuff [2]Rotaxanes **4.13/4.14** and Axles **4.15/4.16**

Ag(I)-coordinated handcuff [2]rotaxane/axle (**4.10/4.11**) (0.016 mmol) was added to a flame dried flask which had been backfilled with dinitrogen three times. Anhydrous pyridine (10 mL) was added via cannula, followed by Pd(CH₃CN)₂Cl₂ (0.035 mmol) and potassium iodide (0.040 mmol). The mixture was heated to reflux and stirred overnight under a dinitrogen atmosphere and under the exclusion of light. All volatiles were evaporated under reduced pressure and the residue was redissolved in chloroform (25 mL) and water (25 mL). The organic layer was separated and washed with water (3 x 50 mL), 5 % CuSO₄ aq. (50 mL) and brine (50 mL) and subsequently dried over MgSO₄ and filtered under gravity. The solvent was removed under reduced pressure and the residue subjected to a silica gel pad (dichloromethane) to afford the product.

4.12. Brown/orange solid (55 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.17 (d, *J* = 5.0 Hz, 4H), 8.50 – 8.40 (m, 4H), 8.39 (d, *J* = 4.4 Hz, 4H), 7.83 (t, *J* = 7.6 Hz, 2H), 7.51 (s, 2H), 7.48 – 7.37 (m, 4H), 7.16 – 6.70 (m, 25H), 6.46 – 6.32 (m, 2H), 5.64 (s, 4H), 4.18 (s, 4H), 4.10 (s, 4H), 4.05 – 3.58 (m, 81H), 2.41 (s, 12H), 2.40 (s, 6H), 2.18 – 1.98 (m, 8H), 1.17 (s, 4H), 1.01 – 0.83 (m, 4H), 0.83 – 0.49 (m, 4H), 0.08 – -0.28 (m, 4H), -0.79 – -1.33 (m, 4H), -1.45 – -1.93 (m, 4H), -2.34 (s, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.03, 161.98, 161.70, 161.66, 161.62, 153.83, 153.05, 153.01, 151.13, 151.08, 151.05, 150.91, 150.75, 150.68, 150.58, 150.54, 150.46, 150.39, 150.31, 149.94, 145.18, 143.49, 138.96, 138.88, 138.82, 138.76, 137.94, 137.72, 130.42, 130.34, 129.49, 129.39, 129.28, 128.99, 128.93, 128.89, 128.84, 128.72, 128.64, 128.59, 128.52, 128.42, 128.35, 128.31, 128.25, 128.22, 128.16, 128.14, 127.63, 126.03, 125.98, 125.91, 125.84, 124.59, 120.10, 119.12, 116.94, 115.82, 115.61, 115.11, 115.01, 114.70, 114.37, 114.29, 114.11, 113.81, 113.65, 113.54, 113.29, 113.20, 112.91, 69.59, 68.78, 58.04, 57.80, 57.76, 57.57, 57.39, 57.35, 57.32, 57.14, 57.02, 55.80, 55.68, 55.57, 55.46, 52.17, 52.14, 50.45, 41.80, 40.48, 40.17, 33.96, 33.48, 32.75, 31.95,

30.97, 29.73, 29.68, 29.39, 29.31, 29.03, 28.59, 28.46, 28.36, 28.29, 28.06, 27.79, 27.75, 27.68, 27.59, 27.49, 27.19, 27.02, 25.92, 25.87, 25.26, 25.17, 24.79, 22.72, 21.54, 21.18, 20.57, 20.28, 20.23 ppm.

4.13. Red solid (61 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.18 (d, 4H), 8.34 – 7.70 (m, 18H), 7.53 (s, 2H), 7.46 (s, 4H), 7.20 – 6.64 (m, 25H), 6.40 (s, 2H), 5.65 (s, 4H), 4.12 (s, 8H), 4.07 – 3.47 (m, 81H), 2.41 (d, J = 6.2 Hz, 18H), 2.15 (dd, J = 27.9, 16.1 Hz, 8H), 1.25 – 1.02 (m, 4H), 0.84 – 0.55 (m, 4H), 0.07 (s, 4H), -0.80 – -1.33 (m, 4H), -1.43 – -1.82 (m, 4H), -2.11 – -2.50 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.49, 162.43, 162.37, 162.32, 162.26, 153.82, 153.05, 153.01, 151.16, 151.01, 150.95, 150.87, 150.79, 150.73, 150.62, 150.52, 150.49, 150.45, 150.41, 150.31, 150.27, 150.20, 149.97, 143.46, 143.41, 138.95, 138.87, 138.78, 137.99, 137.77, 133.20, 133.01, 132.84, 130.20, 129.49, 129.41, 129.25, 128.85, 128.74, 128.70, 128.64, 128.46, 128.40, 128.37, 128.33, 128.23, 128.17, 128.15, 128.05, 128.00, 127.62, 125.29, 125.22, 124.90, 124.63, 122.93, 122.75, 122.60, 122.37, 120.15, 119.14, 119.10, 116.70, 115.73, 115.42, 115.10, 114.66, 114.12, 113.75, 113.13, 112.77, 69.66, 68.47, 58.17, 57.96, 57.72, 57.59, 57.40, 57.36, 57.29, 57.25, 57.16, 57.01, 55.86, 55.78, 55.72, 55.64, 55.58, 55.45, 55.40, 55.33, 52.20, 52.12, 50.47, 41.51, 40.38, 39.64, 29.73, 29.69, 29.65, 29.51, 29.39, 29.35, 29.17, 29.00, 28.55, 28.27, 27.98, 27.75, 27.08, 26.87, 25.93, 25.80, 25.50, 25.23, 22.73, 21.19, 21.02, 20.97, 20.59, 20.30, 20.24, 20.07 ppm.

4.14. Brown/orange solid (33 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.11 (d, J = 5.0 Hz, 4H), 8.75 (s, 4H), 7.76 (t, J = 7.7 Hz, 2H), 7.46 – 7.32 (m, 4H), 6.95 (s, 4H), 6.83 (d, J = 2.0 Hz, 2H), 6.27 (d, J = 1.6 Hz, 2H), 5.54 (s, 4H), 4.55 – 4.33 (m, 4H), 4.33 – 4.13 (m, 4H), 2.32 (s, 18H), 2.13 – 2.03 (m, 4H), 1.79 (s, 4H), 1.46 (s, 16H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.84, 153.95, 144.26, 138.91, 138.72, 137.57, 130.94, 129.30, 127.37, 126.61, 124.45, 120.65, 120.04, 51.86, 50.44, 40.92, 29.44, 29.15, 29.07, 28.04, 26.97, 26.71, 21.10, 20.46 ppm.

4.15. Red solid (51 %). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.11 (d, J = 4.4 Hz, 4H), 8.23 (d, J = 6.8 Hz, 4H), 7.99 (s, 4H), 7.75 (t, J = 7.3 Hz, 2H), 7.35 (s, 4H), 6.94 (s, 4H), 6.87 (s, 2H), 6.27 (s, 2H), 5.55

(s, 4H), 4.56 – 4.33 (m, 4H), 4.13 (s, 4H), 2.32 (s, 18H), 2.11 (s, 4H), 1.78 (s, 4H), 1.51 (s, 16H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ 162.72, 153.93, 153.08, 144.19, 138.89, 138.70, 137.61, 133.43, 130.58, 129.31, 128.52, 127.39, 125.30, 124.48, 122.80, 122.57, 120.78, 120.03, 51.87, 50.44, 40.59, 29.71, 29.50, 29.21, 29.14, 28.01, 27.08, 26.76, 21.11, 20.47 ppm.

4.4.1.8. General Procedure for Handcuff [2]Rotaxanes **4.16/4.17**

Synthesised following the same procedure as for (**4.5/4.6/4.7**).

4.16. Red solid (78 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.44 – 8.24 (m, 4H), 8.17 – 7.94 (m, 6H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.04 (s, 4H), 6.94 (d, *J* = 6.9 Hz, 4H), 6.89 – 6.64 (m, 18H), 6.61 (d, *J* = 7.3 Hz, 2H), 6.11 (d, *J* = 7.2 Hz, 2H), 5.97 – 5.58 (m, 6H), 4.48 – 4.23 (m, 4H), 4.08 – 3.91 (m, 4H), 3.88 – 3.50 (m, 70H), 3.39 (s, 4H), 3.34 (s, 3H), 3.13 (s, 3H), 2.45 (s, 12H), 2.38 (s, 6H), 2.15 (s, 8H), 1.53 (s, 5H), 1.24 – 1.01 (m, 4H), 0.97 – 0.75 (m, 4H), 0.45 (t, *J* = 10.6 Hz, 4H), 0.15 (s, 4H), -0.94 (s, 4H), -1.77 (s, 4H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.17, 153.41, 153.31, 151.28, 151.17, 151.13, 151.10, 150.72, 150.65, 150.42, 150.35, 150.25, 150.21, 150.18, 149.75, 139.95, 138.04, 136.06, 133.77, 132.02, 130.72, 130.05, 130.01, 129.94, 129.90, 129.85, 129.79, 129.75, 129.68, 129.07, 129.03, 128.99, 128.83, 128.77, 128.26, 125.85, 125.21, 125.16, 124.37, 123.77, 123.21, 122.22, 122.14, 121.98, 121.95, 120.88, 116.16, 115.61, 115.52, 114.94, 113.99, 113.78, 113.51, 113.41, 112.78, 104.27, 70.58, 68.95, 68.82, 67.41, 58.49, 58.44, 58.39, 58.35, 58.12, 58.03, 56.00, 55.93, 55.75, 55.55, 55.48, 55.45, 48.67, 47.28, 40.41, 40.20, 31.03, 30.83, 29.92, 29.84, 29.71, 28.76, 28.48, 28.44, 28.11, 26.92, 26.85, 26.25, 26.00, 25.73, 25.53, 25.37, 25.31, 21.20, 20.07, 1.03 ppm. HRMS (ESI+) *m/z*: 1377.1763 [M]²⁺, calc. for [C₁₇₂H₁₈₈N₆O₂₆]²⁺ = 1377.1798.

4.17. Light brown solid (73 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.32 (s, 4H), 8.05 (s, 2H), 7.62 (s, 1H), 7.56 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.09 – 6.66 (m, 28H), 6.40 (t, *J* = 8.6 Hz, 2H), 6.07 (s, 1H), 6.03 (s, 1H), 5.97 – 5.65 (m, 4H), 4.41 – 4.20 (m, 4H), 4.02 (s, 4H), 3.97 – 3.46 (m, 88H), 2.46 (s, 12H), 2.38 (s, 6H), 2.21 – 2.08 (m, 8H), 2.08 – 1.95 (m, 4H), 1.95 – 1.73 (m, 4H), 1.66 – 1.42 (m, 3H), 1.42 – 1.19 (m, 8H), 0.97 – 0.68 (m, 8H), 0.38 – -0.10 (m, 4H), -0.76 – -1.09 (m, 4H), -1.35 – -

1.83 (m, 4H) ppm. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.67, 162.61, 153.82, 151.19, 151.15, 151.12, 151.05, 151.00, 150.52, 150.42, 150.35, 150.29, 139.93, 132.30, 132.23, 130.08, 130.02, 129.90, 129.84, 129.69, 129.01, 128.99, 128.85, 128.80, 128.63, 125.92, 125.84, 125.70, 125.62, 125.32, 124.96, 122.36, 120.94, 116.47, 116.06, 115.65, 115.49, 114.77, 114.27, 113.87, 113.57, 113.45, 113.41, 112.75, 104.98, 70.53, 68.46, 68.27, 68.07, 67.98, 58.55, 58.45, 58.31, 58.23, 58.15, 58.10, 57.93, 55.72, 55.64, 55.54, 55.51, 48.78, 47.62, 47.56, 40.42, 31.65, 31.35, 30.47, 30.36, 29.69, 29.27, 29.16, 29.07, 28.90, 28.65, 28.49, 27.86, 27.72, 27.41, 26.10, 25.99, 25.57, 25.52, 25.32, 25.08, 21.20, 20.12 ppm. HRMS (ESI+) m/z : 1315.1643 ($[\text{M}]^{2+}$, calc. for $[\text{C}_{162}\text{H}_{184}\text{N}_6\text{O}_{26}]^{2+} = 1315.1641$).

4.5. References

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Chapter 5

Conclusion

Research into MIMs has been expanding rapidly for several years and has provided an additional dimension to numerous other areas of chemistry. The results described and discussed within this thesis have contributed towards exploring key aspects of pillar[5]arene-based MIMs. These include pillar[5]arene shuttling in a series of two station molecular shuttles, developing synthetic methodologies to synthesise [n]rotaxanes whilst including key supramolecular building blocks and [2]rotaxanes with handcuff topology. Analytical techniques such as NMR and fluorescence spectroscopy have been used to provide an insight into the dynamic properties of these systems; whilst electrochemical analysis has revealed unusual reduced states, resulting from mechanically interlocking molecules in specific positions relative to each other. Prior to this work there have been limited reports of strategies for the synthesis of pillar[5]arene-based MIMs therefore, the pillar[5]arene/imidazole approach introduced and described within this thesis provides a powerful toolbox for future pillar[5]arene-based MIM investigations. Specifically, the high yield, mild reaction conditions and wide scope make this approach very attractive for future research, such as building larger supramolecular architectures or synthesising compounds for organo-electronic applications.

In Chapter 1 a series of symmetrical [2]rotaxanes with varying axle lengths was synthesised. Comparing the ^1H NMR spectroscopy shifts of threaded and unthreaded axle environments was used to determine the preferred position of pillar[5]arene along the axle (shielding factor), thus visualising the shuttling behaviour in these systems. It was found that the pillar[5]arene shuttles continuously between the two imidazolium stations for axle lengths >4 carbon atoms. The shuttling behaviour was successfully restricted through the coordination of metals (Ag(I) and Pd(II)) to the imidazolium groups, acting as NHCs. Due to the symmetric metal coordination, in all but one case, this process confined the shuttling motion of the pillar[5]arene to the centre of the axle. The Ag(I) metalation process could be reversed through the addition of acid, which allowed the release of pillar[5]arene from confinement. Asymmetric Pd(II)-coordination was achieved in the shortest axle compound (4 carbons separating the imidazoliums) as a result of steric

hindrance. This elegant strategy paves the way for a new and potentially diverse class of [n]rotaxane molecular shuttles, whilst metal coordination provides an effective approach for limiting motion within these systems. Furthermore, transmetalation of Ag-NHCs provides a handle for the introduction of other metals and provides the basis for the synthesis of a variety of metal coordinated [n]rotaxane species for potential applications, such as rhodium for catalysis.

Combining components bearing functional groups and moieties with interesting properties to achieve supramolecular functionality is one of the most prominent ways of utilising mechanical bonds. The pillar[5]arene-imidazole interaction was used to synthesise more complex pillar[5]arene-based [n]rotaxanes, including prominent supramolecular building blocks. This demonstrates the large scope of this approach and makes a promising case for its use in the synthesis of more application-orientated targets. Fluorescent carbazole units were tethered to pillar[5]arene and threading reactions with symmetric and asymmetric rods gave a series of [2]rotaxanes. The effect of inter-component interactions on the overall fluorescence properties of these systems was investigated using quantum yields. The relative proximity of the different components was found to have a drastic solvent specific quenching effect on the carbazole emission. This highlights the importance of carefully considering the possible interactions that may occur within a MIM system and demonstrates the necessity of synthesising and analysing MIMs to gain a better understanding of the way different components interact. Selectively combining different components allowed systems with specific 'off', 'dim' and 'on' fluorescent outputs to be synthesised. The development of functional stopper group components opens up the synthesis of further asymmetric [2]rotaxanes as well as symmetric [3]rotaxanes. Additionally, further functionalisation of the imidazole component led to the synthesis of porphyrin-based [2]- and [5]-rotaxanes. In an attempt to combine pillar[5]arene and the axle functionality, pillar[5]arene was functionalised with pyridine and subsequent Pd(II)-coordination resulted in the formation of a quasi[1]catenane. Conceivably the development of symmetric and asymmetric

pillar[5]arene/imidazole-based [n]rotaxanes will allow for the design and synthesis of systems with specific, desirable and predictable properties.

Although a number of MIMs with handcuff topology have been reported, this confirmation has not been utilised to combine two electrochemically interesting components to study how they interact. Described within this thesis is the use of the handcuff motif to probe the fundamental interactions between PDIs and NDIs, which have previously only been addressed using covalently linked dimer cyclophanes. A thorough investigation into the electrochemical properties of PDI-PDI, NDI-NDI and PDI-NDI handcuff [2]rotaxanes revealed the complex through space interactions resulting from the close proximity and the face-to-face arrangement of these aromatic moieties. Most significantly the mechanical bonds provide a high degree of flexibility, which allows the redox active components to move together or apart at different reduced states with a high degree of freedom. This means that handcuff structures more closely resemble the behaviour of freely stacked molecules, which is a key advantage compared to similar covalently linked systems.

The UV/vis spectrum of a neutral PDI-PDI handcuff showed a rearrangement of the relative band intensities, indicating face-to-face stacking, whilst the fluorescence spectrum revealed a broad emission band from an excimer-like state. Although these techniques revealed no such interactions for the NDI-NDI and PDI-NDI, cyclic voltammetry of all three handcuff [2]rotaxanes showed communication between the two nylene diimides through splitting of the first reduction into two well separated one-electron processes. Spectroelectrochemical investigation of the individual reduced states provided further evidence of electron sharing between the two redox active moieties in the PDI-PDI and PDI-NDI. The UV/vis spectra of the di-reduced states showed a broad absorbance, indicating a ' π -dimer'. This was confirmed by the presence of broad bands in the NIR spectra of these compounds. In all cases complete reduction resulted in spectra typical for di-reduced species of the monomer components, unlike in covalently linked dimers found in literature. This demonstrates that the two aromatic cores are no longer interacting and the

mechanical bonds allow them to move apart. EPR spectra of the mono-reduced PDI-PDI and NDI-NDI handcuffs showed narrowing of the spectral width, evidence for delocalisation/fast-hopping of the electron whilst no evidence for this was observed in the mono-reduced PDI-NDI. This shows that the delocalisation/electron hopping in this redox state is faster than the timescale of the UV/vis experiment, however slower than that of the EPR experiment. These extensive studies enhance and reinforce the understanding of the interactions between freely rylene diimides. Metal coordination was employed to perturb the relative rylene diimide position within the PDI-PDI and NDI-NDI handcuff [2]rotaxanes. Following Pd(II)-coordination analysis using UV/vis, emission, CV and spectroelectrochemistry showed only minor changes in the compounds properties, with the exception of the EPR spectrum of Pd(II)-coordinated NDI-NDI handcuff, which exhibited a significant transformation showing a ground state triplet. Interestingly, Pd(II)-coordination therefore has a profound effect on the magnetic properties of this specific system. The MIM handcuff approach provides a new strategy allowing the systematic investigation of interactions between molecules placed in close proximity. To demonstrate the versatility of this method, PDI and NDI handcuff [2]rotaxanes including a DAN moiety were synthesised.

The results described in this thesis have gone some way towards exploring the fundamental interactions between PDIs, NDIs and DANs. This broadens the underlying understanding of these redox active moieties which is necessary for building functional compounds and materials for applications. More generally, the methodology developed and discussed within this thesis contributes towards building supramolecular architectures which allow further fundamental insight into how molecular components can interact in topologically confined systems and provide a firm basis for the construction of pillararene-imidazolium molecular machines.

Chapter 6

Materials and Methods

6.1. Reagents and Purification

All chemicals and dry solvents were used as-purchased from Alfa Aesar, Fisher Scientific, Sigma-Aldrich, or VWR International. Column chromatography was performed on silica gel 60. Ferrocene was purchased from Aldrich and used as received. Reactions sensitive to air and moisture were performed using a standard Schlenk line, with dinitrogen as the inert atmosphere. Glassware used was flame dried under vacuum and backfilled with dinitrogen.

6.2. General Equipment

6.2.1. NMR Spectroscopy

NMR spectra were recorded at room temperature using Bruker DPX400, AV400, AV(III)400 or AV(III)500 instruments. Deuterated solvents were used as specified. Chemical shifts were recorded referenced to solvent residue.

6.2.2. Mass Spectrometry

Mass Spectrometry were recorded using Bruker microTOF II, JEOL GCv4G, Bruker Impact II or Bruker Ultraflex III.

6.2.3. Absorbance/Emission/ Spectroscopy

Standard UV/vis spectra were collected on a Perkin Elmer Lambda 16 spectrophotometer using a 1 cm path length quartz cuvette. Fluorescence spectra were recorded as aerated solutions using a Jobin Yvon Horiba FluoroMax-3 spectrometer at ambient temperature in a 1 cm path length quartz cuvette. Quantum yields were measured using a standard method published by Williams, Winfield and Miller.¹

6.2.4. Electrochemistry

All electrochemical studies were completed in conjunction with Dr. Stephen Davies.

6.2.4.1. Cyclic Voltammetry

Cyclic and square wave voltammetry experiments were carried out using an Autolab PGSTAT20 under an argon atmosphere using a three-electrode arrangement in a single compartment cell. A glassy carbon working electrode, a platinum wire secondary electrode and a saturated calomel reference electrode were used in the cell. The reference electrode was chemically isolated from the test solution using a bridge tube terminated with a Vycor frit and containing a solution of electrolyte in dichloromethane. An analyte concentration of ca. 0.5 mM was used with $[\text{nBu}_4\text{N}][\text{BF}_4]$ (0.4 M) as a supporting electrolyte. Redox potentials are referenced to the ferrocenium/ferrocene couple used as the internal standard. Decamethylferrocene, using the $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}]^+ / [(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}]$ couple, was also employed as the internal standard under certain circumstances. When this was the case the redox processes of the test compounds were referenced to the Fc^+/Fc couple by an independent calibration. The separation between the $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}]^+ / [(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}]$ couple and the Fc^+/Fc couple recorded under identical conditions was 0.52 V. No compensation was applied for internal resistance.

6.2.4.2. Spectroelectrochemistry

UV/vis spectroelectrochemical measurements were performed using an optically transparent electrochemical cell, consisting of a modified quartz cuvette with a 0.5 mm path length. A three-electrode configuration of a platinum/rhodium gauze working electrode, platinum wire secondary electrode and a saturated calomel reference electrode (chemically isolated as above) were used in the cell. The potential at the working electrode was controlled with a Sycopel Scientific Ltd DD10M potentiostat. Temperature control was achieved by passing a stream of chilled dinitrogen across the surface of the cell. $[\text{nBu}_4\text{N}][\text{BF}_4]$ (0.4 M) was used as the supporting electrolyte for the experiments. Concentrations of analyte were chosen to give a maximum absolute absorbance of 0.7, in dichloromethane containing 0.4 M $[\text{nBu}_4\text{N}][\text{BF}_4]$.

6.2.4.3. Bulk electrolysis and X-band EPR spectroscopy

X-band EPR spectroscopic data were recorded on a Bruker EMX spectrometer as fluid (ambient temperature) or frozen (77 K) solutions in quartz tubes. Spectra were simulated using WINEPR SimFonia software. Bulk electrolysis was performed to generate samples for study by FT-IR, NIR and EPR spectroscopies. Samples were prepared under an argon atmosphere at 0 °C in a two-component cell: a platinum/rhodium gauze working electrode and secondary electrode were separated by a glass frit. A saturated calomel reference electrode was bridged to the test solution through a Vycor frit, oriented at the center of the working electrode. The working electrode compartment, containing analyte (1 mM), was stirred rapidly with a magnetic stirrer bar during electrolysis. $[\text{tBu}_4\text{N}][\text{BF}_4]$ (0.4 M) was used as the supporting electrolyte for the experiments. After electrolysis was completed, the prepared solution was transferred by Teflon cannula for analysis.

6.2.5. Photochemistry

Ultrafast TRIR spectra were collected by Katherine Reynolds as dichloromethane solutions, using the Nottingham ultrafast TRIR apparatus and measurements performed.

6.2.5.1. Ground State Absorption

Ground state absorption spectra were obtained using a Perkin-Elmer Lambda 950 spectrometer at room temperature in dichloromethane. IR solution cells (Harrick Corp) with calcium fluoride (CaF_2) windows (25x2 mm, Crystran) with a path length of 0.2 μm were used for the measurement.

6.2.5.2. Ultrafast Transient Absorption and Time-Resolved Infrared Spectroscopy

The samples for the TA and TRIR spectra were collected by Katherine Reynolds at Rutherford Appleton Laboratories on the ULTRA apparatus described in detail previously.² 1,2 Briefly, a Ti:sapphire laser amplifier (Thales Laser ALPHA 10 000), which was cryogenically cooled, provided 800 nm pulses with a duration of 50 fs at 10 kHz. The output from the laser amplifier was split to provide pump and probe beams. A computer controlled OPAs (Light Conversion) was used to generate both the 520 nm pump beam and a tuneable mid-IR probe and white light continuum

for TA. The pump and probe beams were focussed to overlap at the sample with diameters of 0.2 mm for TA and TRIR. The IR probe beam was dispersed onto two linear 128 element MCT detector arrays acquiring spectra at 10 kHz. Difference spectra were generated by modulating the pump laser output at 5 kHz using a chopper and energy/spectral instabilities of the laser were accounted for by taking a portion of the probe before the sample and dispersing it onto a third MCT detector array, used as a reference. For TA the white light continuum was detected at 10 kHz on a 512 element silicon array with no reference. Both TA and TRIR measurements were carried out in static IR solution cells (Harrick Corp) with calcium fluoride (CaF₂) windows (25x2 mm, Crystran) with a path length of 0.2 µm in dichloromethane. During the measurement the sample was in constant movement by the use of a raster, moving it in a horizontal and vertical directions to ensure no photodecomposition occurred during the experiment.

6.3. X-ray Crystallography

6.3.1. Equipment and Software

Single crystals were selected and mounted using fomblin film on a micromount. Data was collected with a SuperNova, Atlas S2 diffractometer or a XtalLAB PRO MM007, PILATUS3 R 200K diffractometer. The crystals were kept at 120(±2) K during data collection. Using Olex2,³ the structures were solved by Dr. C. Pfeiffer (**2.1a-2.1c**, **2.2a-2.2c** and **2.3b-2.3c**), Dr. W. Lewis (**2.3a**) and Mr. M. Newman (**3.15**) with the ShelXT⁴ structure solution program using Intrinsic Phasing and refined with the ShelXL⁵ refinement package using Least Squares minimisation.

6.3.2. Crystal Data

2.1a C₇₈H₉₃Br_{0.72}Cl_{10.28}N₄O₁₀ (*M* = 1668.43 g/mol): monoclinic, space group C2/c (no. 15), *a* = 49.652(3) Å, *b* = 12.0617(4) Å, *c* = 27.909(2) Å, *β* = 102.619(6)°, *V* = 16310.8(16) Å³, *Z* = 8, *T* = 120(2) K, *μ*(CuKα) = 4.092 mm⁻¹, *D*_{calc} = 1.359 g/cm³, 50074 reflections measured (6.716° ≤ 2*θ* ≤ 130.176°), 13868 unique (*R*_{int} = 0.1578, *R*_{sigma} = 0.1099) which were used in all calculations. The final *R*₁ was 0.0963 (*I* > 2σ(*I*)) and *wR*₂ was 0.2799 (all data). GoF = 1.291.

2.1b $C_{79}H_{98}Cl_4I_2N_4O_{10}$ ($M=1659.21$ g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 20.0828(3)$ Å, $b = 12.8444(2)$ Å, $c = 31.5223(5)$ Å, $\beta = 102.9695(15)^\circ$, $V = 7923.8(2)$ Å³, $Z = 4$, $T = 120(2)$ K, $\mu(\text{CuK}\alpha) = 7.939$ mm⁻¹, $D_{\text{calc}} = 1.391$ g/cm³, 95903 reflections measured ($7.46^\circ \leq 2\theta \leq 133.198^\circ$), 14000 unique ($R_{\text{int}} = 0.0850$, $R_{\text{sigma}} = 0.0356$) which were used in all calculations. The final R_1 was 0.1494 ($I > 2\sigma(I)$) and wR_2 was 0.3340 (all data). GoF = 1.085.

2.1c $C_{81}H_{98}Cl_3I_2N_4O_{10}$ ($M=1647.78$ g/mol): monoclinic, space group $P2_1$ (no. 4), $a = 16.3045(5)$ Å, $b = 12.8881(3)$ Å, $c = 20.4913(5)$ Å, $\beta = 107.067(3)^\circ$, $V = 4116.31(19)$ Å³, $Z = 2$, $T = 120(2)$ K, $\mu(\text{CuK}\alpha) = 7.346$ mm⁻¹, $D_{\text{calc}} = 1.329$ g/cm³, 55391 reflections measured ($8.212^\circ \leq 2\theta \leq 133.178^\circ$), 14052 unique ($R_{\text{int}} = 0.3012$, $R_{\text{sigma}} = 0.1382$) which were used in all calculations. The final R_1 was 0.1536 ($I > 2\sigma(I)$) and wR_2 was 0.4041 (all data). GoF = 1.535.

Disordered counterion iodine and solvent chloroform could not be sensibly modelled and the structure was processed using PLATON SQUEEZE,⁶ which gave an estimate of 424 e⁻ per cell, corresponding to one iodide ion and three chloroform molecules. These molecules were included in the sum formula and calculation of derived parameters.

2.2a Br $C_{77}H_{90}Ag_2Br_2Cl_6N_4O_{10}$ ($M=1819.78$ g/mol): triclinic, space group $P-1$ (no. 2), $a = 12.5204(10)$ Å, $b = 16.9379(8)$ Å, $c = 19.2586(7)$ Å, $\alpha = 77.409(4)^\circ$, $\beta = 80.515(5)^\circ$, $\gamma = 80.739(5)^\circ$, $V = 3898.2(4)$ Å³, $Z = 2$, $T = 120(2)$ K, $\mu(\text{CuK}\alpha) = 7.601$ mm⁻¹, $D_{\text{calc}} = 1.550$ g/cm³, 53950 reflections measured ($7.22^\circ \leq 2\theta \leq 163.492^\circ$), 15508 unique ($R_{\text{int}} = 0.2027$, $R_{\text{sigma}} = 0.1838$) which were used in all calculations. The final R_1 was 0.0860 ($I > 2\sigma(I)$) and wR_2 was 0.2767 (all data). GoF = 1.055.

2.2a Cl $C_{77}H_{90}Ag_2Cl_8N_4O_{10}$ ($M=1730.86$ g/mol): triclinic, space group $P-1$ (no. 2), $a = 12.4582(3)$ Å, $b = 16.8795(4)$ Å, $c = 19.1895(5)$ Å, $\alpha = 77.554(2)^\circ$, $\beta = 80.633(2)^\circ$, $\gamma = 80.930(2)^\circ$, $V = 3856.37(17)$ Å³, $Z = 2$, $T = 120(2)$ K, $\mu(\text{CuK}\alpha) = 7.107$ mm⁻¹, $D_{\text{calc}} = 1.491$ g/cm³, 42843 reflections measured ($4.758^\circ \leq 2\theta \leq 133.194^\circ$), 13599 unique ($R_{\text{int}} = 0.0400$, $R_{\text{sigma}} = 0.0355$) which were used in all calculations. The final R_1 was 0.0547 ($I > 2\sigma(I)$) and wR_2 was 0.1774 (all data). GoF = 1.354.

2.2b $C_{81}H_{93}Ag_2Br_2Cl_{12}N_4O_{10}$ ($M=2083.55$ g/mol): monoclinic, space group $P2_1$ (no. 4), $a = 12.1948(5)$ Å, $b = 28.7424(6)$ Å, $c = 12.6578(4)$ Å, $\beta = 101.327(4)^\circ$, $V = 4350.2(3)$ Å³, $Z = 2$, $T = 120(2)$ K, $\mu(\text{CuK}\alpha) = 8.549$ mm⁻¹, $D_{\text{calc}} = 1.591$ g/cm³, 20543 reflections measured ($7.394^\circ \leq 2\theta \leq 153.392^\circ$), 11419 unique ($R_{\text{int}} = 0.0668$, $R_{\text{sigma}} = 0.0709$) which were used in all calculations. The final R_1 was 0.0986 ($I > 2\sigma(I)$) and wR_2 was 0.3002 (all data). GoF = 1.139.

Disordered solvent chloroform molecules could not be sensibly modelled and the structure was processed using PLATON SQUEEZE,⁶ which gave an estimate of 136 e⁻ per cell, corresponding to two chloroform molecules. These molecules were included in the sum formula and calculation of derived parameters.

2.2c $C_{81}H_{98}Ag_2BrCl_7N_4O_{10}$ ($M=1831.43$ g/mol): monoclinic, space group $P2_1$ (no. 4), $a = 16.4695(4)$ Å, $b = 12.8394(4)$ Å, $c = 20.6024(6)$ Å, $\beta = 107.615(3)^\circ$, $V = 4152.3(2)$ Å³, $Z = 2$, $T = 120(2)$ K, $\mu(\text{CuK}\alpha) = 6.886$ mm⁻¹, $D_{\text{calc}} = 1.465$ g/cm³, 18124 reflections measured ($5.63^\circ \leq 2\theta \leq 147.426^\circ$), 10970 unique ($R_{\text{int}} = 0.0684$, $R_{\text{sigma}} = 0.0652$) which were used in all calculations. The final R_1 was 0.0577 ($I > 2\sigma(I)$) and wR_2 was 0.1452 (all data). GoF = 0.974.

The crystal collected was a 2-component twin. The orientations of the two twin components were determined in CrysAlisPro,⁷ and integrated to provide a single component HKL file which was used for the initial solution, and a multi-component HKL file which was used for subsequent structure refinement.

2.3a $C_{79.25}H_{93.25}Cl_{13.84}I_{1.91}N_4O_{10}Pd$ ($M=2101.46$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 16.515(2)$ Å, $b = 22.093(3)$ Å, $c = 24.313(2)$ Å, $\beta = 92.023(10)^\circ$, $V = 8952.2(18)$ Å³, $Z = 4$, $T = 120(2)$ K, $\mu(\text{CuK}\alpha) = 11.106$ mm⁻¹, $D_{\text{calc}} = 1.559$ g/cm³, 25705 reflections measured ($5.378^\circ \leq 2\theta \leq 133.202^\circ$), 14455 unique ($R_{\text{int}} = 0.2595$, $R_{\text{sigma}} = 0.3588$) which were used in all calculations. The final R_1 was 0.2550 ($I > 2\sigma(I)$) and wR_2 was 0.6260 (all data). GoF = 0.930.

Equivalent bond lengths and angle of the organic portion of the structure were restrained to be approximately equal. Five- and six-membered rings were constrained to idealised geometries, and restrained to be coplanar with their flanking atoms. Enhanced rigid bond and similarity restraints were applied to the thermal parameters of all non-hydrogen atoms.

The halogen sites coordinated to the palladium atom are statistically disordered between iodide and chloride. The occupancy of each site was refined competitively, converging to iodide:chloride ratios of 0.27:0.73, 0.78:0.22 and 0.86:0.14, for the axial and two equatorial sites respectively. The major component was set to that of the most highly occupied atom at each site, corresponding to two equatorial iodides and an axial chloride, however it is possible that all six arrangements of iodide and chloride are present in the crystal. Pd-Cl distances and Pd-I distances were separately restrained to be approximately equal.

Hydrogen atoms were placed in calculated positions and refined with a riding model. Methyl groups, in general, were refined with a fixed orientation, determined by adjacent groups. For carbon atoms C13B, C36B and C90A, it was necessary to refine as rigid rotors, to prevent close H..H inter- and intra-molecular interactions. For C13B and C90A it was necessary to add H..H relative distance restraints to stabilise the rotation position of the group during refinement.

2.3b $\text{C}_{87}\text{H}_{102}\text{I}_4\text{N}_6\text{O}_{10}\text{Pd}_2$ ($M = 2112.14$ g/mol): monoclinic, space group $P2_1$ (no. 4), $a = 16.2495(7)$ Å, $b = 12.2253(6)$ Å, $c = 21.1205(7)$ Å, $\beta = 92.453(4)^\circ$, $V = 4191.8(3)$ Å³, $Z = 2$, $T = 120(2)$ K, $\mu(\text{CuK}\alpha) = 15.514$ mm⁻¹, $D_{\text{calc}} = 1.673$ g/cm³, 17866 reflections measured ($6.726^\circ \leq 2\theta \leq 148.888^\circ$), 12242 unique ($R_{\text{int}} = 0.0518$, $R_{\text{sigma}} = 0.0416$) which were used in all calculations. The final R_1 was 0.0666 ($I > 2\sigma(I)$) and wR_2 was 0.2143 (all data). GoF = 0.995.

The crystal collected was a 2-component twin. The orientations of the two twin components were determined in CrysAlisPro⁷ and integrated to provide a single component HKL file which was used for the final refinement of the structure.

2.3c $C_{89}H_{106}I_4N_6O_{10}Pd_2$ ($M=2140.19$ g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 20.0957(6)$ Å, $b = 12.1538(3)$ Å, $c = 37.0911(11)$ Å, $\beta = 103.157(3)^\circ$, $V = 8821.3(4)$ Å³, $Z = 4$, $T = 120(2)$ K, $\mu(\text{MoK}\alpha) = 1.867$ mm⁻¹, $D_{\text{calc}} = 1.612$ g/cm³, 542213 reflections measured ($5.798^\circ \leq 2\theta \leq 57.81^\circ$), 22446 unique ($R_{\text{int}} = 0.2245$, $R_{\text{sigma}} = 0.0927$) which were used in all calculations. The final R_1 was 0.1116 ($I > 2\sigma(I)$) and wR_2 was 0.3418 (all data). GoF = 1.049.

3.15 $C_{78}H_{84}N_2O_{18}Zn$ ($M = 1402.84$ g/mol): monoclinic, space group $P2_1$, $a = 16.5043(2)$ Å, $b = 12.08540(10)$ Å, $c = 19.2985(2)$ Å, $\beta = 108.0460(10)^\circ$, $V = 3659.94(7)$ Å³, $Z = 2$, $T = 120(2)$ K, $\mu(\text{CuK}\alpha) = 15.184$ mm⁻¹, $D_{\text{calc}} = 1.273$ g/cm³, 30775 reflections measured ($8.474^\circ \leq 2\theta \leq 147.822^\circ$), 13771 unique ($R_{\text{int}} = 0.0213$, $R_{\text{sigma}} = 0.0241$) which were used in all calculations. The final R_1 was 0.0560 ($I > 2\sigma(I)$) and wR_2 was 0.1647 (all data). GoF = 1.054.

6.4. References

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