Metal-Organic and Supramolecular Architectures Based on Mechanically Interlocked Molecules

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METAL-ORGANIC AND SUPRAMOLECULAR ARCHITECTURES BASED ON MECHANICALLY INTERLOCKED MOLECULES

by

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A dissertation submitted to the Graduate College in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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April 2013

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The focus of this work is on mechanically interlocked molecules (MIMs), which have unusual physicochemical and mechanical properties with potential applications in nano-scale/molecular devices and high strength materials.

Rotaxanes, for example, consist of an axle-like molecule threaded through a wheel-like molecule, with bulky groups at the two ends of the axle preventing the wheel from dissociating. The position of the wheel along the axle can be switched in a controllable and reversible manner by applying external stimuli, a feature that might lead to the next generation of computers. Molecularly woven materials (MWMs), another example of molecules with mechanically interlocked features, are predicted to be unprecedentedly strong while being lightweight and flexible.

With the ultimate goal of achieving control over the functioning of molecular devices in the solid state, a variety of pseudorotaxane building blocks were prepared and characterized, including a novel, rare blue-colored motif. The temperature-dependent assembly/disassembly of pseudorotaxanes was exploited for the construction of single-wavelength colorimetric temperature sensors over a 100 °C window. Pseudorotaxanes based on aromatic crown ether wheels and disubstituted 4,4’-bipyridinium axles were
converted into rotaxanes upon binding to metal complexes (zinc, cadmium, mercury, copper, cobalt), and the formation of ordered crystalline arrays was studied in the solid state. The columnar organization of pseudorotaxanes by \( \text{Hg}_2\text{X}_6^{2-} \) complexes (\( \text{X} = \text{Cl, Br, I} \)), leading to unprecedented dichroic (blue/red) rotaxane crystals, was demonstrated for the first time. From the crystal structures studied it became apparent that negatively charged metal complexes are needed for successful assembly with the positively charged pseudorotaxane units. To be able to use the more common, positively charged metal ions for rotaxane framework construction, neutral and negatively charged pseudorotaxanes were synthesized, by attaching anionic substituents (carboxylates, sulfonates) to either the wheel or the axle component. It was found that pseudorotaxane formation also enabled resolution of two sulfonated crown ether isomers, which were inseparable by conventional methods.

Organic ligands for MWM precursors were designed and synthesized according to multi-step schemes. Helical metal-complexes based on these ligands were prepared and characterized.

Chromatography, Nuclear Magnetic Resonance and UV-Visible spectroscopy, Mass spectrometry, Electrochemistry, Thermogravimetric Analysis and X-ray crystallography were used in identification, purification and characterization of the compounds involved.
ACKNOWLEDGEMENTS

It is my pleasure to acknowledge everyone who is behind my success and accomplishments. First and foremost, I am sincerely and heartily grateful to my advisor, Dr. Gellert Mezei for his continuous support, motivation, enthusiasm, patience, guidance and advice to move my doctoral research forward throughout the last five years. I greatly appreciate the immense chemistry knowledge and good human qualities I have gained from him which will definitely make a good impact on my professional life as well as my personal life.

In addition to my advisor, I would like to thank my dissertation committee, Dr. Ekkehard Sinn, Dr. Guda Ramakrishna and Dr. Daniel Kujawski for their collaborative studies, insightful comments, suggestions and discussions. I would like to show my sincere gratitude to Dr. Carla Schmiesing for her initial help with the X-ray diffraction measurements, Dr. Christopher Ziegler (University of Akron) for his support with the initial low temperature crystallographic measurements, and Dr. Andrew Maverick (Louisiana State University) for collaborating on the metallo-ligand project.

I would like to thank two graduate advisors, Dr. John Miller and Dr. Sherine Obare for their guidance to complete my studies.

I greatly appreciate Ms. Pamela McCartney and Ms. Robin Lenkart for their support in administrative matters.
Acknowledgements – continued

I owe sincere and earnest thankfulness to the Department of Chemistry at Western Michigan University for accepting me as a doctoral student and giving this valuable opportunity to travel across the world and be exposed to the fast paced research environment in the western world while pursuing my graduate studies. In addition, I am grateful to the Graduate College at Western Michigan University for their financial support. The dissertation completion fellowship helped me a lot in focusing on my dissertation writing.

I would like to extend my thanks to two group members, Samuel Barajas for contributing to the molecularly woven material project, and Joseph Kreft for his help with proofreading the early drafts of my dissertation. I am also thankful to my fellow chemist Semere Bairu for his help with variable temperature UV-Vis spectroscopic studies and Dr. Obare’s and Dr. Guda’s groups for letting me use the electrochemical workstation and the UV-Visible spectrophotometer without any hesitation.

The doctoral research life would have been more difficult without the support of a couple of my close friends, Dr. Piyadarsha Amarthunga, Dr. Aruna Weerasinghe, Wajira Ariyadasa and Shino Toma. I greatly appreciate them being with me in all my victories and difficulties throughout my studies.

Last but not least, I would like to thank my mother and brother back home in Sri Lanka for their support throughout my life.

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<td>[C4BP][PF₆]₂</td>
<td>N,N'-bis[(4-carboethoxy)propyl]-4,4′-bipyridinium hexafluorophosphate</td>
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<tr>
<td>[CBPQT]⁺⁺⁺</td>
<td>Cyclobis-(paraquat-ₚ-phenylene)</td>
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<td>[Cu(CH₃CN)₄]PF₆</td>
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<td>[DSBPP34C10][TBA]₂</td>
<td>Tetrabutylammonium bis-ₚ-phenylene-34-crown-10-1²,15²-disulfonate</td>
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<td>[PyBP][NO₃]₂</td>
<td>N,N'-bis(4-pyridyl)-4,4′-bipyridinium nitrate</td>
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<tr>
<td>Bu₃SnCl</td>
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<td>'Pr₂O</td>
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<td>KSnF₆</td>
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<td>LDA</td>
<td>Lithium diisopropylamide</td>
</tr>
<tr>
<td>LiCl</td>
<td>Lithium Chloride</td>
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<tr>
<td>LSPR</td>
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<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
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<td>NH₄PF₆</td>
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<td>Tetrahydrofuran</td>
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<td>TLC</td>
<td>Thin Layer Chromatography</td>
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List of Abbreviations – continued

TPDB24C8  Tetra-\textit{p}-anisyl dibenzo-24-crown-8

TSBN38C10  Tetrasulphonated binaphtho-38-crown-10

TTF  Tetrathiafulvalene

UV-Vis  UV-Visible

\textit{V}^{\ast\ast}  Mono-radical viologen cation

\textit{V}^{\circ}  Di-reduced viologen

\textit{V}^{2+}  Dicationic viologen

\Delta\delta  Chemical shift change

\delta  Chemical shift

\varepsilon  Molar extinction coefficient

\lambda_{\text{max}}  Wavelength at the absorbance maxima
CHAPTER 1

INTRODUCTION

1.1. Mechanically interlocked molecules (MIMs)

MIMs contain components which are held together by a mechanical bond. To separate the components, at least one covalent bond has to be broken. Therefore, MIMs are considered to be molecules rather than complexes or supramolecular entities.\textsuperscript{1,2}

Catenanes, rotaxanes, pretzelanes, molecular knots, and molecular Borromean rings are examples of MIMs (Figure 1.1).\textsuperscript{3,4}

![Figure 1.1: Schematics (from left to right) of a catenane, rotaxane, pretzelane, pentafoil knot and Borromean ring.](image)

1.1.1. Pseudorotaxanes and rotaxanes

Pseudorotaxanes consist of an axle–like molecule threaded through a wheel–like molecule (Figure 1.2A). These two components interact with each other via non-covalent intermolecular interactions such as $\pi–\pi$ stacking,\textsuperscript{1,5,6} hydrogen bonding,\textsuperscript{2} and electrostatic interactions.\textsuperscript{7,8} In pseudorotaxanes, the wheel-like molecule can dissociate from the axle due to threading/dethreading equilibrium between the two components. By attaching bulky groups at both ends of the axle of a pseudorotaxane, the wheel is
mechanically locked onto the axle. The resulting assembly is called a rotaxane (Figure 1.2B). In both pseudorotaxanes and rotaxanes, the wheel-like molecule can slide along or pirouette around the axle.\textsuperscript{3,9–12}

Figure 1.2: Schematics of A) a pseudorotaxane and B) a rotaxane.

The most commonly used axles for the construction of pseudorotaxanes and rotaxanes contain one of the following cores: 4,4' -bipyridinium,\textsuperscript{13} 1,2-bis(pyridinium) ethane,\textsuperscript{14} perylenediimide,\textsuperscript{15,16} naphthalenediimide\textsuperscript{15,16} or diaminoalkane (Figure 1.3).\textsuperscript{17,18}

Figure 1.3: Commonly used axle cores for pseudorotaxane construction A) 4,4' -bipyridinium, B) 1,2-bis(pyridinium) ethane, C) perylenediimide, D) naphthalenediimide and E) diaminoalkane.

Crown ethers,\textsuperscript{13,14,19} cucurbiturils,\textsuperscript{17,18} cyclodextrins,\textsuperscript{11,13} cyclo[2](2,6-di(1H-imidazol-1-yl)pyridine)[2](1,4-dimethylenebenzene) (‘Texas sized’ molecular box – [TSMB]\textsuperscript{4+}),\textsuperscript{20} cyclobis-(paraquat-p-phenylene) ([(CBPQT)]\textsuperscript{4+})\textsuperscript{13,21} and pillarenes\textsuperscript{22,23} have been most often used as wheel components for pseudorotaxanes (Figure 1.4).
Figure 1.4: Commonly used wheel-like molecules for pseudorotaxane construction A) crown ethers, B) cucurbiturils, C) pillarenes, D) cyclodextrins, E) cyclobis(paraquat-p-phenylene) and F) (cyclo[2](2,6-di(1H-imidazol-1-yl)pyridine)[2](1,4-dimethylenebenzene).

The first generation of pseudorotaxanes reported by J. Fraser Stoddart, a pioneer in MIMs, and his coworkers consist of [CBPQT]\(^{4+}\) (wheel E) and aromatic axles (Figure 1.5A), or aromatic crown ethers and 4,4′-bipyridinium core.\(^{13,24}\) The pseudorotaxanes reported by Harry W. Gibson et. al consist of 1,3-dibenzo crown ethers and 4,4′-bipyridinium core containing axles.\(^{10}\) The self assembly processes of these systems are driven by the \(\pi-\pi\) stacking– and charge transfer (CT)– interactions between the \(\pi-\)
electron rich, \( \pi \)-donor units and the \( \pi \)-electron deficient, \( \pi \)-acceptors units. In addition, \( N^+\cdots O \) electrostatic interactions and \( C-H\cdots O \) hydrogen bonds between two components contribute to the robustness of the assembly.

Jeremy K. M. Sanders and coworkers proposed a number of neutral pseudorotaxane systems which consist of neutral crown ethers and naphthalenediimide or perylenediimide core containing axles (Figure 1.5B).\(^{15,16}\) Since both axle and wheel components are neutral, \( \pi-\pi \) stacking interactions between two components are the main driving force for pseudorotaxane formation.

To amplify the interactions between the axle and the wheel and obtain highly stable pseudorotaxanes, Stephen J. Loeb’s and Donald Fitzmaurice’s groups synthesized \([2]\)pseudorotaxanes with (+2) positively charged axles and (–2) negatively charged disulphonated aromatic crown ether wheels (Figure 1.5C).\(^7,8\) Feihe Huang’s research group in China has reported the pillarene wheel and the 4,4′-bipyridinium core containing pseudorotaxanes (Figure 1.5D).\(^{22,23}\)

\[ \text{Figure 1.5: Representative examples of [2]pseudorotaxanes.} \]
A number of synthetic approaches have been employed to lock the wheel onto the axle to form a rotaxane. The first reported rotaxane synthesis attempts were based on statistical approaches which provided very low yields.\textsuperscript{25–28} Later on, a covalent bond directed approach was employed, which consists of multi-step organic synthesis, and again resulted in a low overall yield.\textsuperscript{29–31} To overcome these drawbacks, in 1983 Jean-Pierre Sauvage and his coworkers reported a ground breaking approach called the metal-ligand coordination directed molecular recognition approach.\textsuperscript{32} This approach has been widely used not only for rotaxane synthesis but also for a wide variety of other MIMs.\textsuperscript{33}

Among the rotaxanes synthesized according to the above mentioned methods and reported in the literature, two major types of bulky stoppers can be recognized.\textsuperscript{3} One type consist of bulky organic moieties, such as tris(1-methylethyl)silyl,\textsuperscript{34} anthracenyl,\textsuperscript{35} 3,5-bis(dimethylethyl)phenyl,\textsuperscript{33} 1,3-dicarboxyphenyl,\textsuperscript{33,36} 3,5-bis(4-carboxypheyl)phenyl, tris(4-tert-butylphenyl)-4-phenoxy\textsuperscript{33} (Figure 1.6A–F) while the other type consist of bulky metal complexes, such as a ruthenium polypyridine complex\textsuperscript{37} or metal (Zn(II), Au(II), Rh(II), Ru(II)) porphyrins (Figure 1.6G–J).\textsuperscript{38,39} The two bulky stoppers used in rotaxane synthesis can be identical or different.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Diagram of bulky stoppers used in rotaxane synthesis.}
\end{figure}
**Figure 1.6:** Representative examples of bulky organic stoppers (A-F), metal complex stoppers (G-J).

Two examples of rotaxanes with bulky organic stopper and the metal complex are given in Figure 1.7.\textsuperscript{39,40}

![Rotaxane Diagram](image)

\( M = \text{Zn(II), Ru(CO), RhI} \)

**Figure 1.7:** [2]rotaxane with a) bulky organic group– and b) metal complex– as a stopper.
1.1.2. Bistable (two station) rotaxanes

Bistable rotaxanes are rotaxanes which have axles with two different accommodation sites for the wheel molecule or wheels with two different accommodation sites for the axle molecule.\textsuperscript{16,34,41} By applying external stimuli such as a chemical (pH, metal ions), photochemical or electrochemical changes, the wheel can move along the axle, from one station to the other or pirouette around the axle.\textsuperscript{42} This molecular level movement is a result of changing the binding affinity of one component (axle or wheel) of the rotaxane towards the first or second station on the other component and it has been very useful property in constructing artificial molecular machines (AMMs).\textsuperscript{42}

Stoddart and coworkers reported a pH-driven bistable rotaxane based molecular machine in 1994, the axle of which has two recognition sites for the tetra cationic wheel molecule (dibenzo-ride and biphenol) (Figure 1.8).\textsuperscript{34} In one conformation, the wheel molecule is located on stays in the dibenzo-ride site. The addition of trifluoroacetic acid leads to the protonation of the dibenzo-ride site, which then repels the cationic wheel. Subsequently, the wheel moves along the axle to the biphenyl site. Upon addition of pyridine (base), the dibenzo-ride site is regenerated and the wheel molecule moves back to the original position. The wheel molecule can therefore move back and forth as a shuttle, driven by changes of the medium is pH.\textsuperscript{34}
Figure 1.8: a) Schematics of a bistable rotaxane which has two recognition sites on the axle. b) A representative example of pH driven bistable rotaxanes. Figure (b) was reproduced with permission from reference 34. Copyright 1994 Nature Publishing Group.

In 2004, Jean Pierre Sauvage and coworkers reported a redox driven molecular machine based on a bistable rotaxane. The wheel molecule was designed to have two metal binding sites: 1,10-phenanthroline and 2,6-bis(2-pyridyl)pyridine (terpyridine). The axle molecule contains a 2,2′-bipyridinium core (Figure 1.9). In the presence of Cu(I) ions, the bidentate 1,10-phenanthroline group of the wheel together with the 2,2′-bipyridinium group of the axle chelate to the Cu(I) ion in a tetrahedral coordination geometry. Upon oxidation of Cu(I) to Cu(II) electrochemically, the terpyridine group of the wheel coordinates to the Cu(II) ion, replacing 1,10-phenanthroline to provide the preferred trigonal bipyramidal conformation around the Cu(II) ion. A pirouetting motion of the wheel around the axle can therefore be induced by altering the redox stimuli of the medium. 41
Figure 1.9: a) Schematics of a bistable rotaxane possessing two recognition sites on the wheel and b) A representative example of a redox driven bistable rotaxane. The figure (b) was reproduced with permission from reference 41. Copyright 2004 the Royal Society of Chemistry (RSC).

1.1.3. Metal-organic rotaxane frameworks (MORFs)

1.1.3.1. Metal-organic frameworks

Organic ligand molecules can bind to metal ions or complex nodes via metal–ligand coordination bonds to form extended one–, two– or three– dimensional networks called metal-organic frameworks (MOFs). $^{43}$

Figure 1.10: Schematic representation of extended 1D, 2D and 3D MOFs.
The dimensionality of MOFs is determined by the coordination geometry of the metal ion/cluster and the denticity of the ligand (Figure 1.10). Ligands containing carboxylate, pyridyl and nitrile functional groups are widely used in the MOFs’ construction. Both pyridine and nitrile ligands bind to the metal ions in a monodentate fashion while carboxylate ligands bind in a monodentate, bis-monodentate or bidentate pattern (Figure 1.11). The high porosity and the organic-inorganic hybrid nature of the MOFs make them very useful in a vast range of applications. The porous nature of MOFs utilized in selective separation of compounds, catalytic reactions, guest exchange and gas storage applications. The organic component of the MOFs provides tunable cavity sizes and shapes based on the shape (ligand coordinating angle), size and the functionality of the ligand, while inorganic component provides the optical, electronic and magnetic properties.

Figure 1.11: Coordination geometries of a) pyridine based ligands, b) nitrile based ligands and c) carboxylate based ligands. (M = metal ion).

A sub class of MOFs consists of (pseudo)rotaxanes as linkers between metal ions called metal-organic rotaxane frameworks (MORFs) (Figure 1.12). The MORFs are not as widely explored as MOFs. Kimoon Kim, Stephen J. Loeb, Jonathan Sessler, J. Fraser
Stoddart and their coworkers reported the known examples of MORFs. According to the dimensionality of the structure, MORFs can be divided into three groups: 1D, 2D and 3-D MORFs. Appropriate selection of coordinating groups at the two ends of the (pseudo)rotaxane linkers, the nature of solvents (coordinating or non-coordinating), metal ions and counter ions are very important factors that determine the final dimensionality of MORFs. 

![Image of 1D, 2D, and 3D MORFs]

**Figure 1.12:** Schematic representation of extended 1D, 2D and 3D metal–organic rotaxane frameworks.

1.1.3.2. 1D MORFs

A number of 1D MORFs with different shapes such as straight chain, zig–zag shaped, square wave shaped or helical structure have been reported by pioneers in MORFs. They have designed and synthesized pseudorotaxane linkers with pyridine or carboxylate functionalities at the two ends, which are essential for the preparation of extended structures.
The very first 1D metal–organic rotaxane structure was reported by Kimoon Kim and his co-workers in 1996. In their studies various combinations of diamino alkane derivatives and cucurbit[6]uril (CB(6)) were used as the axle molecule and the wheel molecule, respectively, to construct [2]pseudorotaxanes (Figure 1.13). The highly symmetric nature of the (CB(6)) wheel shows a higher affinity of forming pseudorotaxanes even in the highly polar aqueous medium. Transition metal ions have been used as metal ion nodes due to their relatively strong bond forming capacity and the large number of preferred coordination geometries. All 1D MORFs reported by Kim’s laboratory were grown at room temperature.

\[
\begin{align*}
\text{A1; } & n = 1, R = & \text{n} & \text{H}_2 \text{R} \\
\text{A2; } & n = 1, R = & \text{N} & \text{N} \\
\text{A3; } & n = 2, R = & \text{N} & \text{N} \\
\text{CB(6)} & & \\
\text{P1} = & [\text{A1/CB(6)}]^{2+} \\
\text{P2} = & [\text{A2/CB(6)}]^{2+} \\
\text{P3} = & [\text{A3/CB(6)}]^{2+}
\end{align*}
\]

**Figure 1.13:** Various pseudorotaxanes used by Kim’s group for 1D and 2D MORFs.

Layering of a solution of Cu(NO₃)₂ in methanol over an aqueous solution of [P1][NO₃]₂ [2]pseudorotaxanes leads to crystals that contain a zig–zag shaped extended 1D metal–organic rotaxane chain, **MORF–1**. The crystal structure of **MORF–1** shows that each Cu(II) ion has square pyramidal coordination geometry. The terminal pyridyl groups of two **P1** [2]pseudorotaxane linkers are coordinated to one equatorial and one axial position of a Cu(II) ion in a *cis* geometry. The remaining three coordination sites of the Cu(II) ion are occupied by three water molecules (Figure 1.14.a).
The slow reaction of an aqueous solution of M(NO$_3$)$_2$ (M = Co(II) or Ni(II)) with the same [2]pseudorotaxane linker in an aqueous medium produces iso-structural, square wave shaped 1D MORFs, MORF–2 and MORF–3, respectively (Figure 1.14.b). In contrast, layering an aqueous solution of Co(NO$_3$)$_2$ or Ni(NO$_3$)$_2$ with a solution of [P2][NO$_3$]$_2$ [2]pseudorotaxanes (which have terminal 3-pyridyl groups instead of 4-pyridyl) yields zig-zag shaped iso-structural 1D MORFs, MORF–4 and MORF–5, respectively (Figure 1.14.c). In the last four cases, the metal ion centers are found in octahedral coordination geometries. In the case of MORF–2 and MORF–3, four water molecules coordinate to the equatorial positions of the metal ion, while axial positions are occupied by the terminal pyridine group of the P1 [2]pseudorotaxane linker. This \textit{trans} binding geometry of two [2]pseudorotaxane ligands to the metal ion and the sigmoidal shape of the P1 [2]pseudorotaxane unit give the square wave shape to MORF–2 and MORF–3. In contrast, two sites of the metal centers of MORF–4 and MORF–5 are coordinated by the 3–pyridine groups of two P2 [2]pseudorotaxane linkers in a \textit{cis} geometry, while the remaining sites are coordinated by water molecules to give a zig–zag shaped 1D MORF.

Kim and coworkers also reported a number of 1D MORFs with second row transition metals such as Ag(I) and Cd(II). Layering a solution of Ag(CH$_3$(C$_6$H$_4$)SO$_3$) in methanol over an aqueous solution of a [P1][NO$_3$]$_2$ [2]pseudorotaxane yields a 1D linear chain, MORF–6 (Figure 1.14.d). In contrast, changing the metal salt from Ag(CH$_3$(C$_6$H$_4$)SO$_3$) to AgNO$_3$ and the [2]pseudorotaxane from [P1][NO$_3$]$_2$ to [P3][NO$_3$]$_2$ yields a 1D helical structure, MORF–7 (Figure 1.14.e). Crystal structures of MORF–6 and MORF–7 both show coordination of the Ag(I) ion node with two P1 or P3 [2]pseudorotaxane linkers,
respectively, in a trans geometry. The helical structure, MORF–7, contains two Ag(I) ions and two P3 [2]pseudorotaxane linkers per one turn of the helix.48

The 1D helix of MORF–8 was obtained by layering an aqueous solution of Cd(NO$_3$)$_2$ over an aqueous solution of [P3][NO$_3$]$_2$ [2]pseudorotaxane. The crystal structure of MORF–8 shows that each turn of the helix consists of four Cd(II) ions of two types and four P3 [2]pseudorotaxane linkers (Figure 1.14.f). Both Cd(II) ion types show distorted octahedral geometry. The first type of Cd(II) ions are coordinated in a cis geometry by 3-pyridyl groups of two [2]pseudorotaxane linkers, while the other four coordination sites are occupied by water molecules. The second type of Cd(II) ions are coordinated by the [2]pseudorotaxane linkers in a trans geometry, while the remaining sites are occupied by three water molecules and one nitrate ion. The MORF–7 and MORF–8 are racemic mixtures, since the same crystal contains both left handed and right handed helixes.18

**Figure 1.14:** Crystal structures (space filling representation) of 1D rotaxane coordination polymers reported by Kim’s group: a) zig–zag shaped MORF–1; b) square wave shaped MORF–2; c) zig–zag shaped MORF–5; d) straight chain MORF–6; e) helical MORF–7.17 Solvent molecules and hydrogens are omitted for clarity. Color code: O, red; N, light purple; C, grey, metal ions, green. This figure was reproduced with permission from reference 18. Copyright 2002 John Wiley and Sons, Inc.

Stephen J. Loeb and coworkers used positively charged axles and neutral dibenzo-24-crown-8 (DB24C8) or anionic disulphonated dibenzo-24-crown-8 (DSDB24C8) crown
ether wheels to construct [2]pseudorotaxanes (Figure 1.15). The axles (A4 and A5) have two pyridine groups at the two ends that can coordinate to metal ions. All 1D MORFs reported by Loeb’s group were grown at room temperature.

![Diagram showing the construction of pseudorotaxanes](image)

**Figure 1.15:** The various pseudorotaxanes used by Loeb’s group for 1D MORFs.

Loeb and coworkers reported a 1D metal–organic rotaxane structure which consists of 2+ charged P4 [2]pseudorotaxanes and Co(II) or Zn(II) metal ion centers. Evaporation of a solution containing a 1:2:1 mixture of [A4][BF4]2, DB24C8 and [M(H2O)6][BF4]2 (M = Co(II), Zn(II)) in acetonitrile yields the isomorphous 1D polyrotaxane chains MORF-9 and MORF-10, respectively (Figure 1.16a). Both Co(II) and Zn(II) metal ions possess octahedral coordination geometry with two pyridyl groups from two [P4] [2]pseudorotaxane linkers bound in a *trans* geometry. The remaining coordination sites are occupied by two *trans* water molecules and two *trans* acetonitrile (solvent) molecules. Tetrafluoroborate anions in the crystal structures of MORF–9 and MORF–10 balance the positive charge of the P4 [2]pseudorotaxanes.49

Layering a solution of zinc tetrakis(carboxyphenyl)porphyrin in methanol over a solution of P4 [2]pseudorotaxane in chloroform yields a 1D MORF, MORF–11 (Figure 1.16b).
The crystal structure of **MORF–11** shows that each Zn(II) ion acquires distorted octahedral geometry. The four equatorial sites of the Zn(II) ion are chelated by the porphyrin ring and the axial positions are occupied by the terminal pyridine groups of the P4 [2]pseudorotaxane linkers.

To eliminate the counterions and obtain neutral MORFs, Loeb *et. al.* used [Me₄N]₂[DSDB24C8] crown ether wheel and [A₄][BF₄]₂ axle molecule to form neutral dizwitterionic P5 [2]pseudorotaxanes. Neutral, paddle wheel copper benzoate was used as a metal ion node. A neutral **MORF–12** was obtained by layering a solution of [A₄][BF₄]₂ and copper benzoate in dimethylformamide (DMF) with a methanolic solution of [Me₄N]₂[DSDB24C8]. The axial coordination sites of the copper paddle wheel structure was coordinated by terminal pyridyl groups of two neutral P5 [2]pseudorotaxane linkers to form a 1D linear chain of polyrotaxane (Figure 1.1c).

An equimolar mixture of negatively charged P6 [2]pseudorotaxane and Zn(NO₃)₂·4H₂O in methanol yielded a 1D coordinated polyrotaxane chain, **MORF–13** (Figure 1.16d). Its crystal structure shows that each Zn(II) ion has octahedral coordination geometry. Terminal pyridyl groups of two P6 [2]pseudorotaxanes coordinate to the Zn(II) ion node in a *trans* geometry. In addition, three methanol molecules and the SO₃⁻ group from DSDB24C8 of the neighboring pseudorotaxane chain coordinate to the Zn(II) ion node. As a result, the parallel polyrotaxane chains in the crystal structure are arranged in a head-to-tail fashion. The non-coordinating nitrate ions are present in the crystal structure for charge balance.
Jonathan L. Sessler and coworkers prepared on pseudorotaxanes which consist of a large molecular box, \([\text{TSMB}]^{4+}\), and a 1,6-naphthalene dicarboxylate anion axle. The positively charged (+4) wheel interacts with the negatively charged (−2) axle to form a (±2) charged pseudorotaxane (Figure 1.17).

![Figure 1.17: The [2]pseudorotaxane used by Sessler’s group to build 1D MORFs.](image)

The addition of triethyl amine to a mixture of AgNO₃ (or AgPF₆), [TSMB][PF₆]₄ and the acid form of NDC in a 1:1:1 mixture of dimethylformamide, acetonitrile and water
forms a precipitate. Slow evaporation of the filtrate yields a 1D MORF, **MORF–14**. The crystal structure of **MORF–14** shows that each Ag(I) ion is coordinated by two carboxylate groups, one from a [2]pseudorotaxane linker and one from a naked axle, in a linear monodentate fashion (Figure 1.18). Naked axles and [2]pseudorotaxanes are arranged in an alternative manner in the consecutive layers which facilitates strong donor–acceptor–donor interactions between axles and wheels of neighboring chains. Naked [NDC]$^{2–}$ molecules in the **MORF–14** crystal structure balance the charge.$^{53}$

![Figure 1.18: Crystal structure (wire frame representation) of 1D MORF, **MORF–14**, reported by Sessler’s group. Solvent molecules, hydrogens and counter ions are omitted for clarity. Color code: C, black; O, red; Ag(I), golden yellow; [TSMB]$^{4+}$, light green.](image)

### 1.1.3.3. 2D MORFs

Binding of [2]pseudorotaxane linkers to more than two coordination sites on the same metal ion in a trigonal planar or square planar geometry yields extended 2D MORFs. The reported 2D MORFs have hexagonal or square shaped cavities.

Kimoon Kim and his coworkers have reported the first 2D MORF in 1997. Layering a solution of AgNO$_3$ in methanol with an aqueous solution of [P1][NO$_3$]$_2$ [2]pseudorotaxanes yields a 2D MORF, **MORF–15**, which contains large edge-sharing chair-shaped hexagons (Figure 1.19a). Each corner of the lattice consist of a Ag(I) ion with a distorted tetrahedral geometry. Three coordination sites of the Ag(I) ion are coordinated by terminal pyridyl groups of P1 [2]pseudorotaxane linkers, while the
remaining site is coordinated by a nitrate ion. The void space of the hexagons are filled with an interpenetrated 2D hexagonal shaped MORF, in an almost perpendicular geometry.47

The [P2][NO3]2 [2]pseudorotaxanes react with AgCF3SO3 to form a 2D square grid, MORF-16 (Figure 1.19b). Similarly, the reaction between Cu(NO3)2 and [P2][NO3]2 [2]pseudorotaxanes produces a 2D square grid, MORF-17. The Ag(I) ions in MORF-16 have distorted tetrahedral geometry with all their coordination sites occupied by the P2 [2]pseudorotaxane linkers. In contrast, the Cu(II) ion centers of MORF-17 have distorted square pyramidal geometry with four sites coordinated by P2 [2]pseudorotaxanes and one site coordinated by a water molecule.18

Figure 1.19: Crystal structures (space filling representation) of 2D MORFs reported by Kim’s group. a) hexagonal shaped MORF-15 and b) square grid shaped MORF-16. Solvent molecules, hydrogens and counter ions are omitted for clarity. Color code: O, red; N, light purple; C, grey; Ag(I), green. Reproduced with permission from reference 18. Copyright 2002 John Wiley and Sons, Inc.

Since coordinating solvents such as water and acetonitrile coordinate to the metal ion centers of 1D MORF-9 and MORF-10, Loeb et. al. used non-coordinating solvents (nitromethane), anhydrous metal salts and high concentration of [2]pseudorotaxane to
obtain MORFs with higher dimensionality. The 2D non-interpenetrated iso-structural square grid shaped MORF-18, MORF-19 and MORF-20 were synthesized by diffusing isopropyl ether into a 2:4:1 mixture of [A1][BF₄]₂ axle, DB24C8 and [M(H₂O)₆][BF₄] (M = Cu(II), Cd(II), Ni(II)), respectively in nitromethane (Figure 1.20a). Each metal ion center shows octahedral coordination geometry with four square planar sites occupied by four P1 [2]pseudorotaxane linkers, while the remaining coordination sites are occupied by one water molecule and one BF₄⁻ anion (Figure 1.20a).⁴⁴,⁴⁹

![Crystal structures](image)

**Figure 1:20:** Crystal structures (wire frame representation) of 2D MORFs reported by Loeb’s group. a) MORF-19; b) MORF-21; c) MORF-22. Solvent molecules and counter ions are omitted for clarity. Color code: O, red; N, blue; C, black; Cd(II), orange; crown ethers, red. Reproduced with permission of the RSC from reference 45.

Later on, Loeb’s group studied the effect of changing the axle or wheel on the MORFs’ synthesis and their dimensionality. The N-oxide analogue of A1 axle (1,2-bis(4,4'-dipyridinium N-monoxide) ethane - A7) was used in MORF-21 instead of A1, while the tetra-p-anisyl derivative of DB24C8 (TPDB24C8) wheel was used in MORF-22 instead of DB24C8 under the same crystal growing conditions (Figure 1.21). In both cases, P8 or P9 [2]pseudorotaxane linkers are connected via Cd(II) ion nodes in a *trans* geometry to
form 1D strands. The 1D strands are connected to each other via naked axles to produce a 2D square grid (Figure 1.20b and c).44,54

![Diagram of 1D strands connected to form a 2D grid](image)

**Figure 1.21.** The various [2]pseudorotaxanes used by Loeb’s group for the construction of 2D MORFs.

So far, these 2D MORFs reported by Loeb’s groups contain (+2) positively charged [2]pseudorotaxanes (P4, P8 or P9). In an attempt to eliminate counter ions from the MORFs’ structure, an interesting square grid shaped non-interpenetrated 2D MORF, MORF-23, was obtained. It consists of negatively charged P6 [2]pseudorotaxanes and Zn(II) ion nodes. After standing for 5 days at room temperature, a 2:1 mixture of P6 [2]pseudorotaxane and Zn(NO₃)₂·(H₂O)₆ in methanol yields a neutral 2D MORF, MORF-23. The crystal structure of MORF-23 shows that four P6 [2]pseudorotaxanes are coordinated to the Zn(II) ion in a square planar arrangement (Figure 1.22a). The remaining two sites of the octahedral coordination sphere of Zn(II) ion are occupied by two water molecules. Since DSDB24C8 is positioned in the same direction along the axle within the same layer, each layer of the square grid is enantiomerically pure. The DSDB24C8 wheels in the neighboring layers have an opposite chirality. The neighboring
layers form hydrogen bonds between the axial water molecules on the Zn(II) ions and the
SO$_3^-$ groups of the DSDB24C8 crown ether to yield a racemic solid (Figure 1.22b).}

**Figure 1.22**: Crystal structure (wire frame representation) of a neutral 2D MORF
reported by Loeb’s group: a) square grids of MORF-23; b) side view showing hydrogen
bonding between two layers of MORF-23. Solvent molecules and hydrogens are omitted
for clarity. Color code: O, red; N, blue; C, black; S, yellow; Zn(II), silver; crown ethers,
red. Reproduced with the permission of the RSC from reference 45.

1.1.3.4. 3D MORFs
The coordination of [2]pseudorotaxane linkers to metal ions with tetrahedral, trigonal
bipyramidal, octahedral or square antiprismatic coordination geometry yields 3D
MORFs.
Kimoon Kim and coworkers have employed three strategies to obtain 3D MORFs.
Lanthanide metal ion nodes were used instead of transition metal ions since they have
larger ionic radii and higher coordination number compared to the transition metal ions.
[2]Pseudorotaxanes with terminal nitrile functional groups were used. The reactions were
carried out under hydrothermal conditions, because the nitrile groups are easily converted
into carboxylate groups under those conditions, which then react with Tb(III) ions to
produce 3D MORFs (Figure 1.23). By employing the above mentioned strategies, Kimoon Kim’s reported 3D MORFs in 2000.\textsuperscript{17,55}

![Figure 1.23: Various pseudorotaxanes used by Kim’s group for 3D MORFs construction.](image)

A reaction of an aqueous mixture of $[\text{P10}]\text{[NO}_3\text{]}_2$ [2]pseudorotaxanes, Tb(NO$_3$)$_2$·5H$_2$O and triethyl amine in a sealed container at 150 °C for three days, produces a 3D MORF, **MORF-24**. The building block of the **MORF-24** consists of a binuclear Tb(III) center and six P12 [2]pseudorotaxane units. The crystal structure of **MORF-24** shows that the 3-phenylcarboxylate terminal functional groups of [2]pseudorotaxanes function both as bridging ligand and chelating ligand. Each Tb(III) ion center shows distorted square antiprismatic coordination geometry with coordination by four bridging [2]pseudorotaxanes, one chelating [2]pseudorotaxane and two water molecules (Figure 1.24).
Stephen J. Loeb and coworkers’ attempt to obtain 3D MORFs with first row transition metal ion nodes and P4 [2]pseudorotaxane linkers were unsuccessful due to the steric hindrance arising from coordinating six bulky [2]pseudorotaxanes around one transition metal ion node. To overcome this problem, they used [P8]2+ [2]pseudorotaxane which has a longer axle (A7) than A1. In addition, lanthanide metal ions were employed, since they are more oxophilic and prefer higher coordination numbers. The lanthanide ions are hard acids while oxide groups are hard bases which drives the metal-ligand binding. A mixture of 3:9:1 axle/wheel/lanthanide ion [M(OTf)3] (M = Sm(III) (MORF-25), Eu(III) (MORF-26), Gd(III) (MORF-27), Tb(III) (MORF-28)) in acetonitrile yields isomorphous series of interpenetrated 3D MORFs at room temperature (Figure 1.25a). All lanthanide(III) ion nodes show distorted square antiprismatic coordination geometry. Six out of eight coordination sites are occupied by P8 [2]pseudorotaxane linkers, while the remaining sites are coordinated by one water molecule and one triflate anion.56
Figure 1.25: Crystal structures (wire frame representation) of 3D MORFs reported by Loeb’s group. a) MORF-25; b) MORF-29; c) square grid of MORF-30; d) side view of MORF-30 showing pillaring between two layers. Solvent molecules, hydrogens and counter ions are omitted for clarity. Color code: O, red; N, blue; C, black; S, yellow; Zn(II), silver; Sm(III), lime green; Y(III), golden yellow; crown ethers, red. Reproduced with the permission of the RSC from reference 45.

The second row transition metal ion, Y(III), which has slightly smaller radius than lanthanides, produces a slightly different 3D MORF, MORF-29, at room temperature. Slow diffusion of a solution of Yb(OTf)₃ in acetonitrile into a solution of [P₈][OTf]₃ [2]pseudorotaxane in acetonitrile produces MORF-29. The coordination geometry around the Y(III) is pentagonal bipyramidal. All equatorial sites are coordinated by five P₈ [2]pseudorotaxane linkers, while the axial sites coordinated by one [2]pseudorotaxane linker and a triflate anion. The equatorial [2]pseudorotaxanes form an alternating triangle- and square- shaped 2D network, while the axial [2]pseudorotaxanes act as connectors to yield a 3D structure (Figure 1.25b). The square-shaped-cavities show interpenetration, while the triangle shaped cavities do not, due to steric hindrance.⁵⁶

Loeb and coworkers also obtained a 3D MORF, MORF-30, during the synthesis of MORF-23. Similarly to MORF-23, MORF-30 consists of 2D square grids that contain Zn(II) ions and P₆ [2]pseudorotaxanes (Figure 1.25c). In contrast to MORF-23, in MORF-30 the 2D layers are pillared by robust [Zn(CH₃OH)₂(H₂O)₂(SO₄)₂] instead of
forming hydrogen bonding with water molecules (Figure 1.2d). As a result, the distance between two layers in MORF-30 is larger than in MORF-23. Each layer of MORF-30 is a racemic mixture, while MORF-23 has alternating enantiomeric layers.

A groundbreaking 3D MORF with dynamic interlocked components was reported by Loeb’s group in 2012. They used a compact and rigid [2]rotaxane linker instead of a [2]pseudorotaxane as building block in the construction of 3D MORFs. The [2]rotaxane unit consists of a 24-crown-6 [24C6] wheel, a benzyl aniline recognition site on the crossbar and 3,5-benzene-dicarboxylic groups at the two ends of the axle, which function as bulky stoppers as well as coordinating groups (Figure 1.26a). After heating, a 2:1 mixture of Cu(NO₃)₂·3H₂O and R₁ in a 3:2:2 mixture of DMF, EtOH and H₂O with two drops of HNO₃ at 65 °C over 48 h, followed by slow cooling to room temperature produces a 3D MORF, MORF-31 (Figure 1.26b), with a rare β-phase NbO topology. Each Cu(II) ion in MORF-31 forms a paddle-wheel structure. Upon binding to the Cu(II) ion, the rotaxane building block (R₁) are assembled into large polyhedra (Figure 1.26c).

![Figure 1.26](image)

**Figure 1.26:** a) Schematics of the [2]rotaxane used by Loeb’s group to synthesize 3D MORFs with dynamic interlocked components; b) crystal structure of MORF-31; c) polyhedron comprised of six paddle-wheel units and 24C6 wheels. Solvent molecules omitted for the clarity. Color code: axle, blue; wheel, red; Cu(II), green. Reproduced with permission from reference 36. Copyright 2012 Nature Publishing Group.
In 2011, Jonathan L. Sessler and coworkers reported a 3D MORF, MORF-32. X-ray quality crystals of MORF-32 were obtained from a mixture of P7 [2]pseudorotaxane, Zn(NO$_3$)$_2$(H$_2$O)$_6$ and triethylamine in a 1:1 mixture of diethylformamide (DEF) and water. The crystal structure of MORF-32 shows each Zn(II) center coordinated by three naked axles and one P7 [2]pseudorotaxane linker in a tetrahedral geometry, which form an interpenetrated bicyclic adamantane-type network (Figure 1.27).

![Figure 1.27](image)

**Figure 1.27:** Crystal structure of MORF–32, an adamantane type 3D MORF reported by Sessler’s group. Solvent molecules and hydrogen atoms are omitted for clarity. Color code: [TSMB]$^{4+}$, blue; [NDC]$^-$, black; carboxylate O, red; Zn(II), silver. Reproduced with the permission of the RSC from reference 45.

P14 [2]pseudorotaxanes (Figure 1.28) and lanthanide cations, Nd(III), Eu(III), Sm(III), or Tb(III), yield luminescent 3DMORFs, MORF-33, MORF-34, MORF-35 and MORF-36, respectively. These four different MORFs were obtained by slow diffusion of layered solutions at room temperature. An aqueous solution of two equivalents of the nitrate salt of the metal (M(NO$_3$)$_2$; M = Nd(III), Sm(III), Eu(III), or Tb(III)) was layered with a 1:1 mixture of DMF and water. The resulting solution was further layered with a 1:5:10 mixture of the [TSMB]$^{4+}$ wheel, terephthalic acid and tetramethyl ammonium hydroxide pentahydrate (Me$_4$NOH·5H$_2$O) in a 1:1 mixture of DMF and water.
In **MORF-33** to **MORF-36**, lanthanide(III) ions were found in two different coordination environments. The coordination number of the Nb(III) ions in both environments is nine, while the one of the Eu(III) ions is eight and nine. Isostructural **MORF-35** and **MORF-36** show two different types of Sm(III) and Tb(III) ions with the same coordination number, eight. The monomeric unit of **MORF-33** to **MORF-36** is comprised of two **P14** [2]pseudorotaxane linkers, seven terephthalate anions and four lanthanide(III) metal ions (Figure 29a). The carboxylate groups at the two ends of the **P14** [2]pseudorotaxanes are either chelated in a bidentate fashion or coordinated in a monodentate fashion to lanthanide(III) nodes. In the crystal structures of **MORF-33** to **MORF-36**, terephthalate anions bridge the 1D monomeric units to form extended 2D networks. The 2D networks are further connected via the oxygen atoms of the terephthalate dianions to form a 3D network (Figure 1.29).\(^5\)
Figure 1.29: Crystal structures of 3DMORFs reported by Sessler’s group. a) the monomeric unit of MORF-33; b) 3D structure of MORF-33; c) the monomeric unit of MORF-35; d) 3D structure of MORF-35. Solvent molecules, hydrogens and counter ions omitted for clarity. Color code: [TSMB]$^{4+}$, yellow; [BDC]$^{2-}$, purple; blue, black and green, O, red. Reproduced with the permission of the RSC from reference 58.

J. Fraser Stoddart, Jean-Pierre Sauvage and Omar M. Yaghi and coworkers reported the incorporation of copper-coordinated pseudorotaxane linkers P15 into MOFs to obtain 3D MORFs (Figure 1.30).\textsuperscript{59}

Figure 1.30: Schematics of copper coordinated [P15]$^{2+}$ [2]pseudorotaxane linker.
A solution of [P13][PF₆]₂ and Zn(NO₃)₂·6H₂O in diethylformamide (DEF) in a sealed vessel in an isothermal oven at 100 °C over 48 h followed by cooling to room temperature yielded a 3D MORF, MORF-37. The crystal structure of MORF-37 shows that each corner of the 3D MORF consists of the secondary building unit Zn₄O. Each Zn(II) ion is coordinated by the terminal carboxylate group of the axle to form a 3D structure (Figure 1.31). ⁵⁹

![Figure 1.31: Crystal structure of copper complex rotaxane incorporated 3D MORF, MORF-37. Solvent molecules and hydrogens omitted for clarity. Color code: O, red; N, blue; C, black; Zn(II), grey; Cu(II), yellow, W1, lime green. Reproduced with the permission of the RSC from reference 45.](image)

1.1.4. Molecularly woven materials (MWMs)

Molecularly woven materials are organic polymers which consist of polymeric interwoven molecular strands. Even though a number of interwoven structures have been reported in the literature, they cannot be considered as actual MWMs since their organic molecular strands are interconnected via metal-metal bonds or coordinative bonds or other weak intermolecular interactions instead of covalent bonds.

Daryle H. Busch and Timothy J. Hubin have reported a ‘tile’ approach ⁶⁰, ⁶¹ for the synthesis of interwoven polymers, which is somewhat similar to our approach. Since four
ditopic ligand and four metal ion containing coordination complexes show an irreversibly interlocked cross-over interwoven pattern,⁶²,⁶³ they are promising building blocks for the synthesis of molecularly woven materials. Hubin’s and Busch’s ‘tile’ approach consists of polymerization of building blocks (metal complex) via metal-ligand coordination (Figure 1.32) or covalent bond formation to obtain the truly interlocked, ‘infinite’ size molecularly interwoven material.

**Figure 1.32**: Schematics of the ‘tile’ approach to molecularly interwoven polymers.

MWMs comprised of individual molecular strands that consist of metal-free, covalent organic skeletons are expected to have a high strength and light weight. In addition, demetallated cross-over interwoven strands are also expected to possess high flexibility. MWMs could be utilized where there is a need for more durable materials for objects subjected to heavy use, such as medical implants, stronger materials for airplane and
automobile construction, improved body-armor or armored vehicles, longer lasting bridges and roads, more resistant buildings in areas with frequent earthquakes.

1.1.5. Applications of MIMs

Since MIMs such as rotaxanes and catenanes can be used in artificial molecular machines (AMMs) due to their precisely controllable motion at the molecular level, a number of research groups studied the synthesis of MIMs as well as the fabrication of nano scale devices/AMMs from MIMs over the last two decades. The reported nano-scale devices have a number of applications in various fields including molecular electronics-based random access memories, drug delivery methodologies, light harvesting devices and molecular switches.

As discussed in section 1.1.1.1., bistable rotaxanes and catenanes have more than one stable co-conformation, which can be accessed in a reversible manner by applying external stimuli (chemical, photochemical or electrochemical). Most of the early research on MIMs and AMMs was carried out in solution, where molecules move randomly. Later on, several research groups explored a number of methods to obtain highly organized MIMs on solid surfaces and to fabricate AMMs.

A few representative examples of applications of MIMs are explained in this section.
1.1.5.1. Molecular electronics\textsuperscript{64,65}

One of the very interesting examples of molecular electronics reported by Stoddart, Heath and coworkers is a crossed bar memory circuit based on a bistable [2]rotaxane.

**Figure 1.33:** Scanning electron microscopy images of a) entire crossed bar memory circuit; b) cross-point of top- (red) and bottom- (yellow) nanowire electrodes; c) approximately 2500 junctions of crossed bar memory; d) the bistable [2]rotaxane used for the fabrication of crossbar memory.\textsuperscript{64} Reproduced with permission from reference 64. Copyright 2007 Nature Publishing Group.
The molecular memory circuit was fabricated in such a way that a monolayer of bistable [2]rotaxanes is sandwiched between the Ti top nano–wire electrode and the Si bottom nano–wire electrode. Each bit of the crossed bar memory consists of Ti top wire, Si bottom wire and approximately 100 bistable [2]rotaxane units (Figure 1.33a–c).64

The bistable [2]rotaxane consists of two recognition sites – tetrathiafulvalene (TTF - green site) and dioxynapthalene site (DNP - red site) – for the tetracationic [CBPQT]^{4+} wheel (Figure 1.33d). In the fabricated device, the hydrophilic stopper (light blue) is in contact with the Si bottom nano-wire, while the hydrophobic stopper (black) is in contact with the Ti top nano-wire. In the ground state co-conformation the wheel molecules are located on the TTF recognition site, which corresponds to the low conductance or ‘0’ co-conformation. Upon oxidation of the TTF site to TTF^{1+} or TTF^{2+}, the [CBPQT]^{4+} wheel moves to the DNP site to form a meta-stable co-conformation, which corresponds to the high-conductance or ‘1’ co-conformation. The reduction of TTF^{1+} back to the TTF^{0} allows the bistable [2]rotaxanes to return to the ground state co-conformation, which has a half-life of about an hour.64

The bistability and the switching mechanism of the bistable [2]rotaxanes were studied by determining the thermodynamic and kinetic parameters of the fabricated crossed bar memory.64

1.1.5.2. Nano-scale drug delivery vehicles66–68

MIMs-based nano-scale drug delivery vehicles attracted considerable attention over the last decade due to their promising potential of precise delivery of drugs and controlled release. J. Fraser Stoddart, Jeffery I. Zink and coworkers explored the biomedical applications of bistable rotaxane-coated mechanized silica nano-particles (MSNP) as
nano-scale drug delivery vehicles. Most of the MIM-based drug delivery vehicles reported so far consist of three main units: 1) a solid support, b) a payload of cargo (or the therapeutics), and c) the molecular machinery (MIMs) (Figure 1.34a). Since in vivo studies of MSNPs demonstrate a lack of cytotoxicity and a great extent of biocompatibility, MSNPs have been used as a solid support for the MIMs. MSNPs are uniform spheres ~ 100 nm in size, which have highly ordered pores with approximately diameter of 2 nm. Typically, cargo molecules with easily detectable properties, such as fluorescence, have been used, since the release of cargo molecules from nano-particles can be easily detected. A monolayer of MIMs on the MSNPs is responsible for the controlled delivery of the therapeutic molecules. One of the representative examples of MIMs-based drug delivery methodologies and its mechanism are shown below.

![Schematics of a) the structural formula of the bistable [2]rotaxanes and the monolayered MSNPs and b) proposed mechanism for loading and releasing cycle of cargo molecules. The silica particles are not drawn to scale, and only a few of the ordered pores are shown.](image)

**Figure 1.34:** Schematics of a) the structural formula of the bistable [2]rotaxanes and the monolayered MSNPs and b) proposed mechanism for loading and releasing cycle of cargo molecules. The silica particles are not drawn to scale, and only a few of the ordered pores are shown.68,69 Reproduced with the permission of the RSC from reference 68.
Similarly to the earlier molecular electronics example, a bistable [2]rotaxane consisting of an axle with two recognition sites (TTF and DNP) and the tetracationic [CBPQT]$^{4+}$ wheel were used as a MIM in this case. The [CBPQT]$^{4+}$ wheel shuttles between the two sites depending on the redox stimuli. In the ground state co-conformation of the bistable rotaxane, the [CBPQT]$^{4+}$ wheel is located on the TTF recognition site, leaving openings as cylindrical pores on the MSNPs. Cargo molecules are loaded by diffusion in this conformation. Upon oxidation, the [CBPQT]$^{4+}$ wheels move to the DNP recognition sites and the openings close. The addition of ascorbic acid reduces the TTF sites and the [CBPQT]$^{4+}$ wheels move back to the original ground state co-conformation, allowing the cargo molecules to be released. In this conformation, the cylindrical pore is ready for recharging. This representative example demonstrated that the cylindrical pore of the MSNP can be closed and opened in a reversible manner for controlled drug release purposes (Figure 1.34b).

1.1.5.3. Light harvesting AMMs

In 2005, Stoddart and coworkers reported a pseudorotaxane-based light harvesting device, which mimics the photosynthetic energy transduction process. Basically, it consists of a molecular triad and a [2]pseudorotaxane unit. The triad was designed to contain three different functional units: a) an electron-donating TTF unit, b) a chromophoric porphyrin unit, and c) an electron-accepting C$_{60}$ unit. The disulphide terminal group on the triad was anchored on the gold working electrode to make a self-assembled monolayer (SAM) of triads. The [2]pseudorotaxane unit consists of the $\pi$-
electron-rich 1,5-bis[(2-hydroxyethoxy)ethoxy]naphthalene (BHEEN) axle and the electron deficient [CBPQT]$^{4+}$ wheel (Figure 1.35).

By applying an external photochemical stimulus (413 nm laser light) to a SAM of a triad on gold electrode, the porphyrin unit undergoes a photoinduced electron transfer (PET) process, which transfers electrons to the electron-accepting C$_{60}$ unit. This process is followed by the charge shift (CS) from the TTF unit to the cationic radical phorphyrin unit. The resulting charge on the TTF$^{1+}$ unit is then neutralized by the Au electrode in the closed circuit. Subsequently, the electron generated from this molecular level energy supply dethreads the [2]pseudorotaxane by reducing the wheel to a radical form of [CBPQT]$^{73+}$ before its electron is passed onto the Pt counter electrode. In the meantime, [CBPQT]$^{73+}$ undergoes oxidation and forms pseudorotaxane while the electrons transfer via the Pt electrode to complete the circuit.$^{70}$

**Figure 1.35:** Schematic representation of a light harvesting molecular machine and its mechanism. The electron transfer processes are indicated by arrows.$^{70}$ Reproduced with permission from reference 70. Copyright 2005 John Wiley and Sons, Inc.
1.1.5.4. Molecular switches

Huang, Stoddart and coworkers reported surface plasmon-based reversible molecular motions in molecular machineries such as bistable rotaxanes on a gold nanodisk (Figure 1.36a). Surface-plasmon-based nanophotonics or ‘plasmonics’ can potentially be applied in future generation nanophotonics integrated circuits. Similarly to the examples in chapters 1.1.5.1 and 1.1.5.2, the bistable [2]rotaxanes used in the molecular switch explained below consist of an axle with TTF and DNP recognition sites and the [CBPQT]$^{4+}$ wheel. The disulfide terminal group at one end of the axle is anchored to the gold nanodisk surface (Figure 1.36b).

Figure 1.36: a) Schematics of bistable [2]rotaxane-based molecular switches and b) the bistable[2]rotaxane used for the fabrication of the molecular machine. Reproduced with permission from reference 71. Copyright 2009 American Chemical Society.
In this example, the oxidation state of the monolayer of bistable [2]rotaxanes immobilized onto the gold nanodisks’ surface reversibly controls the localized surface plasmon resonance (LSPR) of the Au nanodisk. In the ground state co-conformation of the [2]rotaxanes, the wheel components are located on the TTF recognition site. Upon oxidation, the TTF station converts into TTF$^{2+}$, which repels the [CBPQT]$^{4+}$ electrostatically. As a result, the [CBPQT]$^{4+}$ wheel moves to the DNP recognition site to form a metastable co-conformation of bistable rotaxane. Upon reduction, the [CBPQT]$^{4+}$ wheel returns back to the TTF recognition site.
1.2. Objectives and goals

1.2.1. MORFs

Our **long term goal** is to construct MORFs and supramolecular architectures using pseudorotaxanes as building blocks and develop functional devices/molecular machines (Figure 1.37) based on the chemical and physical properties of the incorporated materials.

![Figure 1.37: Schematics of a 3D MORF built from [2]pseudorotaxane building blocks. The two recognition sites on the axle have different binding affinities for the wheel. External stimuli can drive the motion of the wheel from one station to the other resulting in different properties of the MORF.](image)

In working towards the long term goal, we have set a number of **short term goals**:

1) Synthesize and characterize various axle- and wheel- components.

2) Synthesize and crystallize pseudorotaxanes with different combinations of axles and wheels.
3) Characterize pseudorotaxanes in solution using UV-Vis, \(^1\)H-NMR and electrochemistry as well as in the solid state, by single crystal X-ray diffraction, and study their stability.

4) Construct and characterize metal-organic rotaxane architectures using rigid-linear pseudorotaxanes as building blocks

Even though supramolecules such as rotaxanes and catenanes are very useful for the fabrication of nano-scale functional devices, the large amount of information about their dynamic behavior and the switching properties was obtained from solution studies. In solution, the molecules show random motion and the output of the individual molecular machines is averaged out resulting in no net work. Therefore, it is essential to arrange them in a higher order form and interlock the components. Strategies such as deposition on a surface,\(^72\) tethering between two electrodes,\(^65,73\) incorporation into an organic polymers\(^10,11\) or dendrimers,\(^74,75\) and incorporation into crystalline lattices (MOFs)\(^17,45\) have been used. All these strategies produce materials with higher degrees of ordering, which have individually addressable and controllable components. The most promising strategy is the linking of pseudorotaxane units via metal ions to obtain crystalline lattices, since the synthesis and characterization of MOFs is a thoroughly studied field. In addition, MOFs are potential candidates for improved gas storage, sensing, catalysis, chemical separation and drug delivery applications.\(^43,76\) Compared to MOFs, MORFs have a number of interesting features: the volume of the wheel molecules is useful in avoiding interpenetration of crystalline lattices and in forming cavities with larger capacity; 2) the ability to change the position of the wheel molecules without affecting the basic skeleton of the crystalline lattice provides structural flexibility and allows
control over cavity properties and function; 3) the movement of the wheel along or around the axle is useful in designing addressable and controllable devices.\textsuperscript{49}

The binding geometry of previously used axle molecules is unpredictable due to their non-linear and non-rigid nature. Therefore, we used [2]pseudorotaxanes with rigid linear axle molecules, which were unprecedented when this project began (Figure 1.38). We have chosen aromatic crown ethers, such as bis-\( p \)-phenyl-34-crown-10 (BPP34C10), bis-naphtho-38-crown-10 (BN38C10) and the novel crown ether, bis-naphtho-32-crown-8 (BN32C8) as wheel components, and N,N'-bis(4-pyridyl)-4,4'-bipyridinium nitrate ([PyBP][NO\textsubscript{3}]\textsubscript{2}) and N,N'-bis(4-carboxyphenyl)-4,4'-bipyridinium chloride ([CpBP]Cl\textsubscript{2}) as axle components, since the [4,4'-bipyridinium/ aromatic crown ether] motif produces colored CT complexes which facilitate the visual monitoring of pseudorotaxane formation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.38.png}
\caption{Proposed axles and wheels for the linear, rigid [2]pseudorotaxanes.}
\end{figure}

In addition to forming colored complexes, the 4,4'-bipyridinium moiety of the axle is also able to form non-covalent interactions, such as \( \pi-\pi \) stacking, N\textsuperscript{+}⋯O electrostatic interactions and C–H⋯O hydrogen bonding with aromatic crown ethers, which contribute to the stability of the resulting pseudorotaxanes. Pyridine or carboxylate groups at the two
ends of the axles have the ability to form metal-ligand coordination bonds, which is an essential element in building MORFs.

1.2.2. MWMs

The long term goal of this research project is to synthesize and characterize molecularly woven materials which are expected to have high strength, light weight and high flexibility.

The short term goal is to develop and optimize a synthetic methodology for the preparation of appropriate ligands, and their helical metal complexes, which can then be polymerized to yield MWMs.

To prepare a material which combines high strength, lightweight and flexibility, we proposed to polymerize double stranded, dinuclear helical building blocks, as illustrated in Figure 1.39.

**Figure 1.39:** Proposed scheme for MWM synthesis.
Double stranded helicates are metal-ligand coordination complexes in which two strands of organic ligand molecules are arranged in a helical geometry around templating metal ions. Single,\textsuperscript{77,78} double,\textsuperscript{79–81} triple,\textsuperscript{82–85} quadruple\textsuperscript{86–88} stranded and circular\textsuperscript{89–91} helicates have been reported in the literature. The most commonly used ligands for helicates contain 2,2′-bipyridine, 1,10-phenanthroline, catechol, thiocatechol, 1,3-dicarbonyl, o-hydroxy-carbonyl, 8-hydroxyquinoline and hydroxamate moieties. Transition metal ions, such as Ti(II), Ni(II), Cu(II), Zn(II), Ag(I), Co(II), Pd(II), Cd(II) and lanthanides, such as Eu(III), have been used in metal helicate synthesis.\textsuperscript{92–96}

We have designed a new ligand \textbf{L1} (Figure 1.40a), as starting material for the double stranded, dinuclear helicates, which has geometrical features that allow only for intermolecular and no intramolecular polymerization (Figure 1.40b). The 2,2′-bipyridinium core was used, because it is expected to form a helical core based on the literature.\textsuperscript{2,94} The phenyl groups attached to the 2,2′-bipyridinium core are expected to provide rigidity to the ligand skeleton, orienting the terminal allyl groups away from the helical core. The allyl groups are far enough from each other so that they cannot undergo intramolecular alkene metathesis. The –CH$_2$–CH$_2$– spacer group is expected to facilitate double stranded helicate formation based on the literature.\textsuperscript{2,94}
**Figure 1.40:** Schematics of a) ligand L1, and b) the expected double stranded, dinuclear, helical metal complex of L1.

The alkene metathesis reaction is a transition metal catalyzed organic reaction which involves cleavage of two carbon-carbon double bonds and formation of a new carbon-carbon double bond. Both Grubbs’ and Schrock’s catalyst can be used as the transition metal catalyst for the alkene metathesis reaction.
CHAPTER 2

EXPERIMENTAL

2.1. General procedures and instrumentation

General procedures: All commercially available chemicals were used as received. Acetone and THF were dried using CaSO$_4$ and sodium, respectively, and distilled under N$_2$ and stored over 4Å molecular sieves before use. Toluene was degassed by purging N$_2$ over 20 min. DMF was dried using 3Å molecular sieves and vacuum distilled before use. Thin layer chromatography (TLC) was performed on Sigma–Aldrich silica gel plates and viewed under UV light (256 nm and/or 354 nm wavelengths) or an iodine bath. Column chromatography was performed using flash silica gel from Dynamic Adsorbents.

Tri(ethylene glycol) ditosylate, $^{97}$ tetra(ethylene glycol) ditosylate, $^{97}$ bis-$p$-phenylene-34-crown-10 (BPP34C10), $^{98,99}$ bis-naphtho-38-crown-10 (BN38C10), $^{100}$ bis-naphtho-32-crown-8 (BN32C8), $^{101}$ tetrabutylammonium bis-paraphenylene-34-crown-10-1$^2$,15$^3$-disulphonate ([TBA]$_2$DSBPP34C10), $^7$ N,N$'$-bis(2,4-dinitrophenyl)-4,4$'$-bipyridinium dichloride ([DNPBP]Cl$_2$), $^{102}$ [PyBP][NO$_3$]$_2$, $^{103}$ [CpBP]Cl$_2$, $^{104}$ N,N$'$-bis[(4-carboethoxy)propyl]-4,4$'$-bipyridinium hexafluorophosphate ([C4BP][PF$_6$]$_2$), $^{105}$ S-4-bromobutyl ethanethioate, $^{106}$ tributyl dimethyl silyloxy (TBDMS) 4-bromophenol (2), $^{107}$ 2-tributyltin-6-methyl pyridine (5), $^{108}$ 6-bromo-6$'$-methyl-2,2$'$-bipyridine (7), $^{109}$ 2-(methoxyphenyl)-1,10-phenanthroline (14), $^{110-112}$ 3-(4-pyridyl)pentane-2,4-dione, $^{113,114}$ bis[3-(4-pyridyl)pentane-2,4-dionato] copper (II) (Cu(Pyacac)$_2$), $^{115}$ and bis(3-phenyl
pentane-2,4-dionato) copper (II) \( \text{(Cu(Phacac)}_2 \)\(^{116} \) were synthesized according to modified literature procedures.

General Instrumentation: Melting points were measured using Mel–Temp II laboratory devices. UV–Vis spectra were obtained on a Shimadzu UV 2101 PC spectrophotometer. \(^1\text{H–NMR}\) and \(^{13}\text{C–NMR}\) spectra were recorded on a Jeol JNM-ECP400 instrument operating at 400 MHz at room temperature using deuterated solvents. Mass spectra were recorded using a Waters–Synapse mass spectrometer using LC–MS grade solvents. Electrochemistry measurements were performed using a Bioanalytical Systems (BAS) CV–50W electrochemical workstation. X–ray diffraction data were collected on a Bruker SMART APEX II diffractometer using graphite-monochromated Mo-K\(\alpha\) \((\lambda = 0.71073 \ \text{Å})\) radiation at 100 K.

2.2. Synthesis

2.2.1. Starting materials and ligands

2.2.1.1. BPP34C10: A solution of 1,4-dihydroxynaphthalene (20.92 g, 0.19 mol) in dry acetone (500 mL) was added to a refluxing suspension of \( \text{K}_2\text{CO}_3 \) (89 g, 0.64 mol) in dry acetone (250 mL). Tetraethylene glycol ditosylate (82.94 g, 0.165 mol) in dry acetone (750 ml) was added and the resulted mixture was refluxed 5 days under \( \text{N}_2 \). The mixture was cooled to room temperature, filtered, and evaporated to dryness under reduced pressure. The dark brown color viscous liquid (53.5 g) was purified using column chromatography (column height-45 cm, diameter-10 cm) over 1887 g (a mixture of 70–230 mesh 60 Å – 1675 g and 70–270 mesh 60 Å – 212 g) of silica gel using
Et₂O:CHCl₃:CH₃OH – 68:30:2 (9L) and Et₂O:CHCl₃:CH₃OH – 68:30:2.5 (8L) as an eluting solution. 620 fractions were collected into 20 ml test tubes.

Fractions number 341-531 were collected and evaporated under reduced pressure. The resulting light pinkish orange powder was washed with Et₂O (50 mL x 3) to obtain a white solid (4.83 g, 10.9 %). The combined Et₂O filtrate was evaporated under reduced pressure and washed with Et₂O to recover another crop of pure BPP34C10 (0.370 g, 0.97 %).

Fractions number 251–340 (which contained unreacted tetraethylene glycol ditosylate and crown ether) and 532-591 (which contained crown ether and byproduct) were combined and evaporated under reduced pressure. The resulting light brown colored solid (1.1445 g) was purified by column chromatography over 20 g of silica gel (70–270 mesh 60 Å). 18 x 6 mL fractions were collected. Fractions number 6-15 were combined and evaporated and washed with Et₂O to obtain a third crop of pure BPP34C10 (1.1250 g, 2.54 %). Rᵣ = 0.21 (Et₂O:CHCl₃:CH₃OH – 68:30:2 ); m.p. 94-95 ºC. (Lit. 93-94 ºC) ¹H NMR (400 MHz, CDCl₃); δ = 6.75 (s, 8H), 3.98 (t, 8H, J = 4.7 Hz), 3.83 (t, 8H, J = 4.7 Hz), 3.70 (m, 16H). ¹³C-NMR (D₂O, 400 MHz): δ (ppm) = 153.16, 115.60, 70.95, 70.82, 69.88, 68.23. λₘₐₓ (CH₃OH:CHCl₃ = 1:1) = 290 nm.

Scheme 2.1: Synthesis of bis-<i>p</i>-phenylene-34-crown-10 (BPP34C10).
2.2.1.2. BN32C8

The synthetic procedure of BN32C8 was originally published in *New J. Chem.* 2010, 34, 2097–2100101 and reproduced by permission of The RSC on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

Step 1 - 1,5-Bis[10-(p-toluenesulfonyl)-1,4,7,10-tetraoxadecyl]naphthalene: A solution of 1,5-dihydroxynaphthalene (9.20 g, 58 mmol) and triethylene glycol ditosylate (132.06 g, 288 mmol) in dry acetone (1.5 L) were added under N₂ to a refluxing suspension of K₂CO₃ (250 g, 1.8 mol) in dry acetone (1.5 L) over 2 h. After 6 days of refluxing, the mixture was cooled to room temperature, filtered, and evaporated to dryness under reduced pressure. The dark brown colored viscous liquid (129.6 g) was purified by column chromatography (height-1.5’, diameter- 4”) over 1850 g of flash silica using 6:1 (6 L), 3:1 (4 L), 2:1 (1.8 L) and 1:2 (20L) mixtures of hexane:EtOAc as eluent.

Fractions containing both unreacted triethylene glycol ditosylate and the product were collected and evaporated using a rotary evaporator to obtain a brown-red viscous liquid (57.7 g). It was purified by column chromatography (height-1.5’, diameter- 4”) over 1775 g of flash silica using 3:2 (23.5 L) and 1:1 (22.5 L) mixtures of hexane:EtOAc as eluent. 1,5-Bis[10-(p-toluenesulfonyl)-1,4,7,10-tetraoxadecyl]naphthalene containing fractions were collected and evaporated under reduced pressure to obtain the pure product (21.4 g, 50.3 %). Rf = 0.44 (EtOAc:Hexane – 3:2 ); ¹H-NMR (400 MHz, CDCl₃); δ = 7.84 (d, J = 8.40 Hz, 2H), 7.78 (d, J = 8.40 Hz, 4H), 7.33 (t, J = 8.40 Hz, 2H), 7.30 (d, J = 8.40 Hz, 4H), 6.83 (d, J= 7.70 Hz, 2H), 4.27 (t, J = 4.4 Hz, 4H), 4.14 (t, J = 4.76 Hz, 4H), 3.95 (t, J= 4.4 Hz, 4H), 3.71 (m, 8H), 3.62 (t, J = 4.4 Hz, 4H), 2.39 (s, 6H).
Scheme 2.2: First step of BN32C10 synthesis: 1,5-Bis[10-(p-toluenesulfonyl)-1,4,7,10-tetraoxadecyl]naphthalene.

Step 2 - BN32C8: A solution of 1,5-dihydroxynaphthalene (4.67 g, 29.2 mmol) and 1,5-bis[p-toluenesulfonyl]-1,4,7,10-tetraoxadecyl]naphthalene (21.4 g, 29.2 mmol) in dry acetone (1.0 L) was added under N$_2$ to a refluxing suspension of K$_2$CO$_3$ (150 g, 1.08 mol) in dry acetone (3 L) over 3 h.

The mixture was refluxed for 5 days under N$_2$, cooled to room temperature, filtered, and evaporated to dryness under reduced pressure. The dark brown colored viscous liquid (26.9 g) was purified by column chromatography (height-1.5’, diameter- 4”) over 1850 g of flash silica gel using a 1:1 (12 L) mixture of hexane:EtOAc as eluent. Fractions containing only crown ether were collected and evaporated using a rotary evaporator. It was treated with Et$_2$O (150 mL) and filtered to obtain a yellowish brown product (2.1 g) which was dissolved in CHCl$_3$ (50 mL) and a maroon-brown solid was removed by filtration. The filtrate was concentrated under N$_2$ flow and Et$_2$O (250 mL) was added. It was kept in a refrigerator at –4 °C for a slow precipitation overnight. The precipitate was filtered and dried to obtain pure BN32C8 (1.88 g, 11.7 %).

Fractions containing unreacted 1,5-bis[(p-toluenesulfonyl)-1,4,7,10-tetraoxadecyl] naphthalene and the product were combined and evaporated under reduced pressure and
treated with a 1:1 (150 mL) mixture of hexane:EtOAc and filtered. The residue was dissolved in CHCl$_3$ (100 mL). The maroon-brown solid was filtered out and the filtrate was evaporated to 3/4 of the initial volume under N$_2$ flow. Et$_2$O (250 mL) was added to the concentrated filtrate and kept it in a refrigerator at –4 °C overnight for slow precipitation. The precipitate was filtered and a white colored BN32C8 (2.1 g, 13.1 %) was obtained as a second crop. R$_f$ = 0.60 (EtOAc:Hexane – 2:1); m.p. 163-164 °C. $^1$H-NMR (400 MHz, CDCl$_3$); δ = 7.60 (d, J = 8.44 Hz, 4H), 6.96(t, J = 8.44 Hz, 4H), 6.53(d, J = 7.32 Hz, 4H), 4.12(t, J = 4.4 Hz, 8H), 3.92 (t, J = 4.4 Hz, 8H), 3.80(s, 8H). $^{13}$C NMR (400 MHz, CDCl$_3$); δ = 154.11 (4C), 126.68 (4C), 124.84 (4C), 114.45 (4C), 105.75 (4C), 71.30 (4C), 69.89 (4C), 67.94 (4C). $\lambda_{\text{max}}$(CH$_3$OH:CHCl$_3$ – 1:1) = 298 nm.

Scheme 2.3: Synthesis of BN32C8 (second step).

2.2.1.3. syn-DSBPP34C10 and anti-DSBPP34C10

Maroon-red colored crystals of [PyBP/syn-DSBPP34C10] and orange colored crystals of [PyBP/anti-DSBPP34C10] were grown as explained in Section 2.2.2.11 and they were separated manually. The following procedure was carried out for both [PyBP/syn-DSBPP34C10] and [PyBP/anti-DSBPP34C10] pseudorotaxane crystals separately to isolate two isomers, syn- and anti-DSBPP34C10.
Crystals were dissolved in H_2O (4.0 mL) and treated with 65% aqueous HPF_6. The white precipitate ([PyBP][PF_6]_2) was filtered, washed with water (~1.50 mL) and the filtrate was evaporated to dryness to obtain pure syn- or anti-DSBPP34C10 as a sticky colorless solid.

In the case of [PyBP/syn-DSBPP34C10] crystals, 7.0 mg of crystals (0.007 mmol) was treated with 20 μL (0.14 mmol) of HPF_6 solution to obtain syn-DSBPP34C10 (4.2 mg, 88 %). ¹H-NMR (D_2O, 400 MHz): δ (ppm) = 7.04 (d, J = 2.56 Hz, 2H), 6.72 (m, 4H), 4.01 (t, J = 4.4 Hz, 4H), 3.95 (t, J = 4.2 Hz, 4H), 3.79 (t, 8H), 3.66 (s, 16H).

In the case of [PyBP/anti-DSBPP34C10] crystals, 8.0 mg of crystals (0.008 mmol) was treated with 23 μL (0.16 mmol) of HPF_6 solution to obtain anti-DSBPP34C10 (6.4 mg, 88 %). ¹H-NMR (MeOD, 400 MHz): δ (ppm) = 7.43 (d, J = 2.92 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 6.88 (dd, J = 3.10 Hz, J = 9.00 Hz, 2H), 4.16 (t, J = 5.08 Hz, 4H), 3.99 (t, J = 4.58 Hz, 4H), 3.86 (t, J = 4.96, 4H), 3.80 (t, J = 4.4 Hz, 4H), 3.71 (t, J = 3.3 Hz, 4H), 3.65 (s, 12H).

2.2.1.4. N,N’-bis(4-carboxyphenyl)-4,4’-bipyridinium chloride ([CpBP]Cl_2): An aqueous solution (15.40 mL) of 1,1’-bis(2,4-dinitrophenyl)-4,4’-bipyridinium chloride (2.15 g, 3.83 mmol) was added dropwise over 25 min to a refluxing aqueous solution (10.40 mL) of 4-aminobenzoic acid (2.62 g, 19.1 mmol). After refluxing for 1 h at 105 °C, it was cooled down to room temperature and transferred to acetone (154 mL). The resulting yellowish-orange colored precipitate was filtered and washed with a 1:6 mixture of H_2O: acetone (40 mL). The residue was redissolved in water and treated with activated carbon. The mixture was boiled for 5 min and was filtered. The filtrate was concentrated using a rotary evaporator to obtain a light yellow solid (0.340 g, 19 %). ¹H-NMR (CD_3OD, 400
MHz): $\delta$ (ppm) = 9.62 (d, $J = 6.96$ Hz, 4H), 8.95 (d, $J = 6.96$ Hz, 4H), 8.38 (d, $J = 8.40$ Hz, 4H), 8.01 (d, $J = 8.40$ Hz, 4H). $^{13}$C-NMR (CD$_3$OD, 400 MHz): $\delta$ (ppm) = 145.93, 131.58, 127.15, 124.49. $\lambda_{\text{max}}$(CH$_3$OH:CHCl$_3$ = 1:1) = 310 nm.

Scheme 2.4: Synthesis of [CpBP]Cl$_2$.

2.3.1.5. N,N'-bis[3-(carboethoxy)propyl]-4,4'-bipyridinium hexafluorophosphate ([C4BP][PF$_6$]$_2$): The synthetic procedure of [C4BP][PF$_6$]$_2$ was originally published in New J. Chem. 2010, 34, 2097–2100$^{101}$ and reproduced by permission of The RSC on behalf of the CNRS and the RSC.

A solution of N,N'-bis[3-(carboethoxy)propyl]-4,4'-bipyridinium bromide (2.32 g, 4.23 mmol) in H$_2$O (6.5 ml) was treated with a solution of NH$_4$PF$_6$ (2.79 g, 17.1 mmol) in H$_2$O (10 ml). The resulting white precipitate was filtered off, washed with an aqueous solution of NH$_4$PF$_6$ (2.79 g, 17.1 mmol, 10 mL) and then with ice-cold water (10 mL). Recrystallization from hot H$_2$O followed by washing with Et$_2$O and drying in vacuum yielded pure [C4BP][PF$_6$]$_2$ (2.64 g, 92 %). m.p. 225-227 °C. $^1$H-NMR (400 MHz, DMSO-d6): 9.37 (d, 4H, 6.6 Hz), 8.78 (d, 4H, 6.6 Hz), 4.71 (t, 4H, 7.1Hz), 4.05 (q, 4H, 7.1 Hz), 2.46 (t, 4H, 7.5 Hz), 2.25 (m, 4H), 1.17 (t, 6H, 7.1 Hz) ppm.
2.2.1.6. Multi-step synthesis of 1-(4-thiolbutyl)-1'-[4-(carboxy)butyl]-4,4′-bipyridinium bromide (compound 5)

This synthetic procedure was originally published in *Sensors and Actuators B, 2013, 176, 768-774* and reproduced with permission. Copyright 2013 Elsevier B.V.

![Scheme 2.5: Multi-step synthesis of compound 5.](image)

2.2.1.6.1. N-(4-acetylthiolbutyl)-4,4′-bipyridinium bromide (compound 2): A solution of compound 1 (500 mg, 2.368 mmol) in dried acetonitrile (4 mL) was added to the refluxing solution of 4,4′-bipyridine (1.109 g, 7.104 mmol) in dried acetonitrile (8 mL) under nitrogen. After refluxing for two days, the reaction mixture was added to Et₂O (60 mL). The solution was filtered and the residue was washed with a 1:5 mixture of acetonitrile and Et₂O (20 mL) to obtain a brown solid, compound 2 (653 mg, 75 %). ¹H-NMR (D₂O, 400 MHz): δ (ppm) = 8.95 (d, J = 6.24 Hz, 2H), 8.76 (s, 2H), 8.40 (d, J = 6.20 Hz, 2H), 7.92 (d, J = 5.16 Hz, 2H), 4.67 (t, J = 7.32 Hz, 2H), 2.92 (t, J = 7.14 Hz, 2H), 2.33 (s, H), 2.10 (m, 2H), 1.67 (m, 2H).
2.2.1.6.2. 1-(4-acetylthiolbutyl)-1’-[4-(carboethoxy)butyl]-4,4’-bipyridinium bromide (compound 4): Ethyl-4-bromobutyrate (1.039 g, 5.332 mmol) in dry acetonitrile (3.0 mL) was transferred under nitrogen into a solution of compound 2 (653 mg, 1.77 mmol) in dry acetonitrile (3 mL). After refluxing for two days it was cooled to room temperature. The resulting yellow precipitate was collected by filtration and dissolved in a minimum amount of methanol. A large excess of Et\(_2\)O (CH\(_3\)OH:Et\(_2\)O ~ 1:10 ) was added to the solution and filtration afforded a yellow solid (757 mg, 76 %). \(^1\)H-NMR (D\(_2\)O, 400 MHz): \(\delta\) (ppm) = 9.09 (m, 4H), 8.51 (m, 4H), 4.72 (m, 4H), 4.09 (q, J = 7.21 Hz, 2H), 2.90 (t, J = 7.14 Hz, 2H), 2.53 (t, J = 7.14 Hz, 2H), 2.33 (m, 5H), 2.11 (m, 2H), 1.64 (m, 2H), 1.88 (t, J = 7.14 Hz, 3H).

2.3.1.6.3. 1-(4-Thiolbutyl)-1’-[4-(carboxy)butyl]-4,4’-bipyridinium bromide (compound 5): A solution of 2 M HBr (0.88 mL) was added to the solid compound 4 (378 mg, 0.67 mmol). The resulting solution was evaporated at 100 \(^\circ\)C using house vacuum to obtain a yellow solid (297 mg, 90 %). \(^1\)H NMR (D\(_2\)O, 400 MHz): \(\delta\) (ppm) = 9.10 (t, J = 6.78Hz, 4H), 8.52 (d, J = 3.62 Hz, 4H), 4.74 (m, 4H), 2.56 (m, 4H), 2.35 (m, 2H), 2.16 (m, 2H), 1.66 (m, 2H).
2.2.1.7. Multi-step synthesis of ligand L1 for MWMs

Scheme 2.6: Multi-step synthesis of L1.
2.2.1.7.1. Compound 8: nBuLi (23.95 mL, 38.32 mmol) was added drop wise under N₂ to a solution of TBDMS 4-bromophenol 7 (10.0 g, 34.8 mmol) in THF (83 mL) at -78 °C. The reaction mixture was stirred for 90 min at the same temperature. After adding Bu₃SnCl (9.88 mL, 34.9 mmol), the reaction mixture was gradually warmed to room temperature and was stirred. Then, it was filtered and the filtrate was concentrated under reduced pressure to obtain a slightly yellow colored viscous liquid (18.9 g). GC-MS analysis was carried out on a crude mixture (78.6 % of the crude is compound 8). The crude mixture was used in the synthesis of compound 13 without further purification.

2.2.1.7.2. Compound 13 (6-4-[1,1-dimethylethyl]dimethylsilyloxy]phenyl-6′-methyl-2,2′-bipyridine): Degassed toluene (102 mL) was added to a mixture of compound 8 (14.5 g, 29 mmol), compound 12 (7.26 g, 29 mmol), LiCl (2.27 g, 53 mmol) and Pd(PPh₃)₄ (0.526 g, 0.45 mmol) under N₂. After refluxing for 24 h at 120 °C, the solution was cooled to room temperature and filtered. The evaporated filtrate was recrystallized from methanol to obtain a white solid (5.6 g, 51 %), m.p. 98-100 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.39 (d, J = 7.68 Hz, 1H), 8.32 (d, J = 7.72 Hz, 1H), 8.04 (d, J = 8.80 Hz, 2H), 7.83 (t, J = 7.70 Hz, 1H), 7.70 (t, J = 7.94 Hz, 2H), 7.16 (d, J= 7.36 Hz, 1H), 6.95 (d, J = 8.76 Hz, 2H), 2.63 (s, 3H), 1.00 (s, 9H), 0.23 (s, 6H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) = 157.82 (1C), 156.87 (1C), 156.18 (1C), 155.96 (1C), 137.61 (1C), 137.06 (1C), 132.77 (1C), 128.24 (1C), 132.29 (1C), 120.44 (1C), 119.53 (1C), 118.75 (1C), 118.34 (1C), 25.81 (1C), 24.78 (1C), 18.38 (1C), –4.26 (1C).

2.2.1.7.3. Compound 14: LDA (1000 µL, 2 mmol) was added into a solution of compound 13 (500 mg, 1.32 mmol) in dried THF under N₂ at -78 °C. After 4 h stirring at -78 °C, a solution of dibromoethane (130 µL, 1.5 mmol) in degassed THF (10 mL) was
transferred to it over 10 min. After 1 h it was warmed up to room temperature and stirred overnight. The evaporated reaction mixture was purified by chromatography over silica with a 5:1 mixture of hexane: EtOAc as an eluting mixture to obtain a white powder (130 mg, 26%). m.p. 200-201 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) = 8.42 (d, J = 8.00 Hz, 2H), 8.38 (d, J = 8.04 Hz, 2H), 8.04 (d, J = 8.80 Hz, 4H), 7.83 (t, J = 7.88 Hz, 2H), 7.70 (t, J = 7.70 Hz, 4H), 7.16 (d, J= 7.32 Hz, 2H), 6.95 (d, J = 8.80 Hz, 4H), 3.46 (s, 4H), 1.04 (s, 18H), 0.23 (s, 12H). $^{13}$C- NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) = 160.67 (2C), 156.85 (2C), 156.14 (2C), 156.07 (2C), 155.91 (2C), 137.58 (2C), 137.03 (2C), 132.80 (2C), 128.23 (4C), 123.08 (2C), 120.43 (4C), 119.52 (2C), 118.89 (2C), 118.62 (2C), 37.83 (2C), 25.81 (6C), 18.38 (2C), −4.25 (4C).

2.2.1.7.4. Compound 15: Tetrabutylammonium fluoride (TBAF) (154 mg, 0.59 mmol) was added to a solution of compound 14 in dry THF (8 mL). After overnight stirring, the resulting solid was filtered off and dissolved in CHCl$_3$:CH$_3$OH = 1:1 mixture (10 mL). It was filtered through a silica bed and the filtrate was evaporated to obtain a white colored powder (110 mg, 79%). $^1$H-NMR (DMSO-$d_6$, 400 MHz): $\delta$ (ppm) = 8.36 (d, J = 7.72 Hz, 2H), 8.27 (d, J = 7.32 Hz, 2H), 8.07 (d, J = 8.44 Hz, 4H), 7.90 (t+d+t, 6H), 7.38 (d, J = 7.36 Hz, 2H), 6.90 (d, J = 8.80 Hz, 4H), (2.50, J = 1.64 Hz, 4H). $^{13}$C- NMR (DMSO-$d_6$, 400 MHz): $\delta$ (ppm) = 160.94 (2C), 159.25 (2C), 156.07 (2C), 155.47 (2C), 155.42 (2C), 138.60 (2C), 138.06 (2C), 129.99 (2C), 128.62 (4C), 123.85 (2C), 119.71 (4C), 118.61 (2C), 116.13 (2C), 37.32 (2C).

2.2.1.7.5. Compound 16 (L1): A solution of allyl bromide (36 µL, 0.42 mmol) and compound (15) (100 mg, 0.19 mmol) in dry DMF (85 mL) was added to Cs$_2$CO$_3$ under
N₂. After stirring for 3 h at 80 °C, the solvent was vacuum distilled. The white residue was dissolved in water (20 mL) and extracted into CH₂Cl₂ (3 x 20 mL). The combined organic extracts were dried using MgSO₄ and filtered through a silica bed. The filtrate was evaporated to obtain a white solid (100 mg, 86 %). m.p. 180-181 °C. ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) = 8.42 (d, J = 8.04 Hz, 2H), 8.38 (d, J = 7.72 Hz, 2H), 8.10 (d, J = 8.80 Hz, 4H), 7.83 (t, J = 7.88 Hz, 2H), 7.70 (t, J = 7.70 Hz, 4H), 7.16 (d, J = 7.72 Hz, 2H), 7.03 (d, J = 8.80 Hz, 4H), 6.09 (m, 2H), 5.45 (td, J = 17.24 Hz, 2H), 5.31 (td, J = 10.6 Hz, 2H), 4.61 (d, J = 3.64 Hz, 4H), 3.44 (s, 4H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) = 160.68 (2C), 159.54 (2C), 156.09 (2C), 156.03 (2C), 155.90 (2C), 137.60 (2C), 137.04 (2C), 133.22 (2C), 132.36 (2C), 128.26 (2C), 123.09 (2C), 119.44 (2C), 118.89 (2C), 118.62 (2C), 117.95 (2C), 114.95 (2C), 77.74 (2C), 77.31 (2C), 68.96 (2C), 37.82 (2C).

2.2.1.8. Multi-step synthesis of Ligand L2 for MWMs

2.2.1.8.1. Compound 19: nBuLi (1.6 M in hexane, 35.00 mL, 56.00 mmol) was added drop-wise under N₂ over 10 min to a solution of 4-bromoanisole (17) (10.0 g, 53.46 mmol) in THF (80 mL) at -78 °C. After 90 min stirring at -78 °C, it was added under N₂ using a cannula to a solution of 1,10-phenanthroline (8.00 g, 44.39 mmol) at -78 °C over 2 h. After 3 h stirring at -78 °C, the reaction mixture was gradually warmed up to room temperature and stirred overnight. The dark brown colored reaction mixture was transferred to a beaker containing 200 cm³ of ice cubes. Organic and aqueous layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were dried over MgSO₄ and rearomatized by successive addition of MnO₂ (20g at a time, total of 90g). This oxidation reaction was monitored.
with TLC and the disappearance of the color of the solution. After stirring for 5 days, the solution was filtered, and the solvent was evaporated using a rotary evaporator. The resulting dark brown colored crude material (10.94 g) was chromatographed over silica using an EtOAc:Hexane mixture as an eluent (EtOAc:Hexane (1/5) – 840 mL, EtOAc:Hexane (1/4) – 750 mL, EtOAc:Hexane (1/3) – 240 mL, EtOAc:Hexane (1/1) – 200 mL, EtOAc:Hexane (2/1) – 900 mL, EtOAc – 1800 mL). The pinkish-yellow colored compound (1.93 g) was washed with Et₂O to yield very slightly pink colored compound 3 (1.43 g, 11.2 %). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) = 9.23 (dd, J = 4.40 Hz, 1H), 8.32 (d, J = 8.76 Hz, 2H), 8.26 (t, J = 8.06 Hz, 2H), 8.06 (d, J = 8.44 Hz, 1H), 7.76 (q, J = 9.88 Hz, 2H), 7.62 (q, J = 4.15 Hz, 1H), 7.06 (d, J = 8.80 Hz, 2H), 3.89 (s, 3H).

Scheme 2.7: Synthesis of compound 19.

2.2.2. Supramolecules and their metal complexes

2.2.2.1. [PyBP/BPP34C10][NO₃]₂ [2]pseudorotaxane: Maroon-red colored, X-ray quality, single crystals of [PyBP/BPP34C10][NO₃]₂ [2]pseudorotaxanes (7.0 mg, 72 %) were obtained from a 1:1 mixture of [PyBP][NO₃]₂ (4.0 mg, 0.009 mmol) and BPP34C10 (5.0 mg, 0.009 mmol) in CH₃OH (2.0 mL) by slow diffusion of iPr₂O vapor at –20 °C. ¹H-NMR (CD₃OD:CDCl₃ = 1:1, 400 MHz): δ (ppm) = 9.47 (d, J = 6.96 Hz, 4H),
9.02 (d, J = 5.12 Hz, 4H), 8.68 (d, J = 6.96 Hz, 4H), 8.06 (d, J = 6.20 Hz, 4H), 6.55 (s, 8H), 3.84 (m, 8H), 3.74 (m, 8H), 3.61 (s, 16H). λ_{max} (CH$_3$OH:CHCl$_3$ = 1:1) = 500 nm.

2.2.2.2. [PyBP/BN38C10][SbF$_6$]$_2$ [2]pseudorotaxane: Blue colored, X-ray quality, single crystals of [PyBP/BN38C10][SbF$_6$]$_2$ [2]pseudorotaxanes (5.2 mg, 60%) were obtained by layering a solution of K$_2$SbF$_6$ (3.8 mg, 0.014 mmol) in CH$_3$OH (1.4 mL) over a solution comprised of a 1:1 mixture of [PyBP][NO$_3$]$_2$ (3.0 mg, 0.007 mmol) and BN38C10 (4.3 mg, 0.007 mmol) in a 1:1 mixture of CH$_3$OH and CHCl$_3$ (1.4 mL) at room temperature. $^1$H-NMR (CD$_3$OD:CDCl$_3$ = 1:1, 400 MHz): δ (ppm) = 9.58 (d, J = 6.96 Hz, 4H), 9.35 (d, J = 6.24 Hz, 4H), 8.47 (d, J = 6.96 Hz, 4H), 8.39 (d, J = 6.24 Hz, 4H), 7.76 (d, J = 8.08 Hz, 4H), 7.40 (t, J = 8.06 Hz, 4H), 6.74 (d, J = 7.72 Hz, 4H), 4.28 (t, J = 4.22 Hz, 8H), 4.19 (t, d = 4.04 Hz, 8H), 4.01 (m, 16H). λ_{max} (CH$_3$OH:CHCl$_3$ = 1:1) = 590 nm.

2.2.2.3. [PyBP/BN32C8][NO$_3$]$_2$ [2]pseudorotaxane: Blue colored, X-ray quality, single crystals of [PyBP/BN32C8][PF$_6$]$_2$ [2]pseudorotaxanes (5.0 mg, 62%) were obtained by layering a solution of K$_2$SbF$_6$ (3.8 mg, 0.014 mmol) in CH$_3$OH (1.2 mL) over a solution comprised of a 1:1 mixture of [PyBP][NO$_3$]$_2$ (3.0 mg, 0.007 mmol) and BN32C8 (3.7 mg, 0.007 mmol) in a 1:1 mixture of CH$_3$OH and CHCl$_3$ (1.6 mL) at room temperature. $^1$H-NMR (CD$_3$OD:CDCl$_3$ = 1:1, 400 MHz): δ (ppm) = 9.43 (d, J = 6.60 Hz, 4H), 9.34 (d, J = 5.88 Hz, 4H), 8.40 (d, J = 6.96 Hz, 4H), 8.29 (d, J = 6.24 Hz, 4H), 7.63 (d, J = 8.44 Hz, 4H), 7.20 (t, J = 8.06 Hz, 4H), 6.78 (d, J = 7.72 Hz, 4H), 4.37 (t, J = 4.40 Hz, 8H), 4.23 (t, J = 4.20 Hz, 8H), 4.13 (s, 8H). λ_{max} (CH$_3$OH:CHCl$_3$ = 1:1) = 610 nm.
2.2.2.4. [PyBP/DB24C8][NO₃]₂ [3]pseudorotaxane: Yellow colored, X-ray quality, single crystals of [PyBP/DB24C8][NO₃]₂ [3]pseudorotaxanes (6.0 mg, 50 %) were obtained by slow diffusion of iPr₂O vapor into a 1:1 mixture of [PyBP][NO₃]₂ (4.0 mg, 0.009 mmol) and DB24C8 (4.1 mg, 0.009 mmol) in a 1:1 mixture of CH₃OH and CHCl₃ (1.6 mL) at –20 °C. ¹H NMR (CD₃OD:CDCl₃ = 1:1, 400 MHz): δ (ppm) = 9.77 (s, 4H), 8.98 (d, J = 5.12 Hz, 8H), 8.34 (s, 4H), 6.82 (m, 8H), 4.03 (m, 8H), 3.87 (m, 8H), 3.79 (m, 8H). ʎₘₐₓ (CH₃OH:CHCl₃ = 1:1) = 440 nm.

2.2.2.5. [CpBP-2H⁺/BPP34C10] [2]pseudorotaxane: Maroon-red colored, X-ray quality, single crystals of [CpBP-2H⁺/BPP34C10] [2]pseudorotaxanes (4.0 mg, 37 %) were obtained by slow diffusion of Et₂O vapor into a 1:1 mixture of [CpBP]Cl₂ (5.0 mg, 0.011 mmol) and BPP34C10 (5.7 mg, 0.011 mmol) in CH₃OH (1.6 mL) at –20 °C. ¹H-NMR (CD₃OD:CDCl₃ = 2:1, 400 MHz): δ (ppm) = 9.48 (d, J = 6.60 Hz, 4H), 8.70 (d, J = 5.84 Hz, 4H), 8.40 (d, J = 8.40 Hz, 4H), 8.04 (d, J = 8.04 Hz, 4H), 6.54 (s, 8H), 3.83 (m, 8H), 3.73 (m, 8H), 3.59 (m, 16H). ʎₘₐₓ (CH₃OH:CHCl₃ = 3:1) = 484 nm.

2.2.2.6. [CpBP/BN38C10]Cl₂ [2]pseudorotaxane: A blue colored powder of [CpBP/BN38C10]Cl₂ [2]pseudorotaxanes (5.3 mg, 45 %) was obtained by slow diffusion of iPr₂O vapor into a 1:1 mixture of [CpBP]Cl₂ (5.0 mg, 0.011 mmol) and BN38C10 (6.7 mg, 0.011 mmol) in a 3:1 mixture of CH₃OH and CHCl₃ (1.6 mL) at –20 °C. ¹H-NMR (CD₃OD:CDCl₃ = 2:1, 400 MHz): δ (ppm) = 9.32 (d, J = 5.12 Hz, 4H), 8.44 (d, J = 8.44 Hz, 4H), 8.26 (s, 4H), 8.07 (d, J = 8.04 Hz, 4H), 7.41 (d, J = 8.40 Hz, 4H), 7.08 (t, J = 8.06 Hz, 4H), 6.46 (t, J = 7.72 Hz, 4H), 3.91 (m, 8H), 3.85 (m, 8H), 3.70 (m, 16H). ʎₘₐₓ (CH₃OH:CHCl₃ = 3:1) = 550 nm.
2.2.2.7. [CpBP-2H⁺/BN32C8] [2]pseudorotaxane: Bluish purple colored, X-ray quality, single crystals of [CpBP-2H⁺/BN32C8] [2]pseudorotaxanes (6.6 mg, 60 %) were obtained by slow diffusion of Et₂O vapor into a 1:1 mixture of [CpBP]Cl₂ (5.0 mg, 0.011 mmol) and BN32C8 (5.8 mg, 0.011 mmol) in a 3:1 mixture of CH₃OH and CHCl₃ (1.6 mL) at –20 °C. ¹H-NMR (CD₃OD:CDCl₃ = 2:1, 400 MHz): δ (ppm) = 9.23 (s, 4H), 8.44 (d, J = 8.04 Hz, 4H), 8.00 (d, J = 8.04 Hz, 8H), 7.24 (s, 4H), 6.89 (t, J = 7.88 Hz, 4H), 6.49 (s, 4H), 4.05 (s, 8H), 3.94 (s, 8H), 3.84 (s, 8H). λₘₐₓ (CH₃OH:CHCl₃ = 3:1) = 571 nm.

2.2.2.8. [C4BP/BPP34C10][PF₆]₂ [2]pseudorotaxane: Dark orange colored, X-ray quality, single crystals of [C4BP/BPP34C10][PF₆]₂ [2]pseudorotaxanes (8.5 mg, 95 %) were obtained by iPr₂O vapor diffusion into a 1:1 mixture of [C4BP][PF₆]₂ (5.0 mg, 0.008 mmol) and BPP34C10 (4.0 mg, 0.008 mmol) in a 1:1 mixture of (CH₃)₂CO:CH₃OH at –20 °C. ¹H-NMR (acetone-d₆:CDCl₃ = 2:1, 400 MHz): δ (ppm) = 9.26 (d, J = 6.60 Hz, 4H.), 8.50 (d, J = 6.60 Hz, 4H), 6.49 (s, 8H), 4.95 (t, 4H, J = 7.50 Hz), 4.10 (q, J = 7.20 Hz, 4H), 3.79 (m, 8H), 3.74 (m, 8H), 3.73 (s, 16H), 2.56 (t, J = 7.3 Hz, 4H), 2.47 (m, 4H), 1.20 (t, J = 7.1 Hz, 6 H). λₘₐₓ (CH₃)₂CO:CHCl₃ = 2:1) = 448 nm.

2.2.2.9. [C4BP/BN38C10]Br₂ [2]pseudorotaxane: Dark bright red colored, X-ray quality, single crystals of [C4BP/BN38C10]Br₂ [2]pseudorotaxane (1.0 mg, 10%) were obtained by Et₂O vapor diffusion into a 1:1 mixture of [C4BP]Br₂ (5.0 mg, 0.009 mmol) and BN38C10 (5.8 mg, 0.009 mmol) in a 1:1 mixture of CHCl₃:CH₃OH at –20 °C. ¹H-NMR (acetone-d₆:CDCl₃ = 2:1, 400 MHz): δ (ppm) = 9.05 (d, J = 6.20 Hz, 4H), 7.99 (s, 4H), 7.22 (d, J = 8.4 Hz, 4H), 7.05 (t, J = 8.10 Hz, 4H), 6.54 (d, J = 7.70 Hz, 4H), 4.93 (t, J =
7.40 Hz, 4H), 4.13 (q, J = 7.20 Hz, 4H), 3.99 (d, J = 4.40 Hz, 8H), 3.90 (d, J = 4.00 Hz, 8H), 3.80 (s, 16H), 2.60 (t, J = 7.3 Hz, 4H), 2.46 (m, 4H), 1.22 (t, J = 7.1 Hz, 6H). $\lambda_{\text{max}}$ (CH$_3$)$_2$CO:CHCl$_3$ = 2:1) = 490 nm.

2.2.2.10. [C4BP/BN32C10][PF$_6$]$_2$ [2]pseudorotaxane: All crystallization attempts yielded a light-pink colored solution and no crystals. $^1$H-NMR (acetone-d$_6$: CDCl$_3$ = 2:1, 400 MHz): $\delta$ (ppm) = 9.13 (s, 4H), 8.16 (s, 4H), 7.30 (s, 4H), 6.94 (t, J = 8.10 Hz, 4H), 6.60 (d, J = 7.7 Hz, 4H), 4.90 (s, 4H), 4.12 (m, 4H), 4.02 (d, J = 4.4 Hz, 8H), 3.95 (d, J = 4.0 Hz, 8H), 3.85 (s, 4H), 2.56 (t, J = 7.3 Hz, 4H), 2.48 (m, 4H), 1.21 (t, J = 7.10 Hz, 6H). $\lambda_{\text{max}}$ (CH$_3$)$_2$CO:CHCl$_3$ = 2:1) = 501 nm.

2.2.2.11. [PyBP/syn-DSBPP34C10] [2]pseudorotaxane and [PyBP/anti-DSBPP34C10] [2]pseudorotaxane: Crystals were obtained by both diffusion and layering methods.

Diffusion method: $^3$Pr$_2$O vapor was diffused into a solution of [PyBP][NO$_3$]$_2$ (20.0 mg, 0.045 mmol) and [TBA]$_2$[DSBPP34C10] (54.0 mg, 0.046 mmol) in CH$_3$OH (5.0 mL). Maroon-red (10.0 mg, 22 %) and orange (8.0 mg, 17 %) colored, X-ray quality crystals were obtained at –20 °C after one week.

Layering: A solution of [PyBP][NO$_3$]$_2$ (7.4 mg, 0.017 mmol) and [TBA]$_2$[DSBPP34C10] (20.0 mg, 0.017 mmol) in CH$_3$OH (3.6 mL) was layered over $^3$Pr$_2$O (2.0 mL). Maroon-red (2.4 mg, 14 %) and orange (2.2 mg, 13 %) colored, X-ray quality crystals were obtained at room temperature after one week.

Maroon-red colored crystals: $^1$H-NMR (CD$_3$OD, 400 MHz): $\delta$ (ppm) = 9.45 (d, J = 6.60 Hz, 4H), 9.03 (d, J = 6.24 Hz, 4H), 8.39 (d, J = 6.96 Hz, 4H), 8.31 (d, J = 6.20 Hz, 4H),
6.99 (d, J = 3.28 Hz, 2H), 6.45 (d, J = 8.80 Hz, 2H), 6.24 (dd, J = 8.96, 3.12 Hz, 2H),
3.81 (t, J= 3.64 Hz, 4H), 3.75 (d, J = 4.04 Hz, 4H), 3.71 (m, 4H), 3.66 (m, 4H), 3.53 ( d,
J = 4.76 Hz, 4H), 3.49 (d, J = 5.48 Hz, 4H), 3.47 (s, 8H). \( \lambda_{\text{max}} \) (CH\(_3\)OH) = 461 nm.

Orange colored crystals: \(^1\)H-NMR (CD\(_3\)OD, 400 MHz): \( \delta \) (ppm) = 9.45 (d, J = 6.60 Hz,
4H), 9.04 (dd, J = 4.38, 1.44 Hz, 4H), 8.40 (d, J = 6.56 Hz, 4H), 8.31 (dd, J = 4.72, 1.48 Hz,
4H), 6.98 (d, J = 3.28 Hz, 2H), 6.46 (d, J = 8.8 Hz, 2H), 6.24 (dd, J = 8.76, 2.94 Hz,
2H), 3.81 (t, J = 3.48 Hz, 4H), 3.76 (d, J = 4.40 Hz, 4H), 3.70 (m, 4H), 3.66 (m, 4H), 3.54
(d, J = 6.08 Hz, 4H), 3.51 (d, J = 5.76 Hz, 4H), 3.48 (s, 8H). \( \lambda_{\text{max}} \) (CH\(_3\)OH) = 458 nm.

(20.0 mg, 0.043 mol) and [TBA]\(_2\)DSBPP34C10 (50.0 mg, 0.043 mol) in CH\(_3\)OH (3.0 mL) was layered over \(^i\)Pr\(_2\)O (3.0 mL). A mixture of red and orange colored, X-ray quality crystals of [CpBP/syn-, anti-DSBPP34C10] pseudorotaxanes (16.8 mg, 36.2 %)
were obtained at room temperature after one week. \(^1\)H-NMR (CD\(_3\)OD, 400 MHz): \( \delta \)
(ppm) = 9.43 (d, J = 6.96 Hz, 4H), 8.35 (d, J = 6.96 Hz, 4H), 8.40(d, J = 8.76 Hz, 4H),
8.30 (d, J = 8.30 Hz, 4H), 6.93(d+d, J = 3.14 Hz, 2H), 6.49, (d+d, J = 2.38 Hz, 2H),
6.37(dd+dd, J = 3.32, 6.40 Hz, 2H), 3.83(m, 4H), 3.77(m, 4H), 3.70(m, 8H), 3.59(m, 4H),
3.53(m, 8H), 3.46(m, 4H). \( \lambda_{\text{max}} \) (CH\(_3\)OH) = 436 nm.

2.2.2.13. [C4BP/syn-, anti-DSBPP34C10] [2]pseudorotaxane: A solution of
[C4BP][PF\(_6\)]\(_2\) (5.0 mg, 0.0074 mmol) and [TBA]\(_2\)DSBPP34C10 (8.7 mg, 0.0074 mol) in
a 1:1 mixture of CH\(_3\)COCH\(_3\):CH\(_3\)OH (3 mL) was layered over \(^i\)Pr\(_2\)O (3 mL). A mixture
of yellow and orange colored, X-ray quality [C4BP/syn-, anti-DSBPP34C10] [2]pseudorotaxanes crystals (5.1 mg, 64 %) were obtained at room temperature after one week. \(^1\)H-NMR (\(d_6\)-acetone:CD\(_3\)OD =1:1, 400 MHz): \( \delta \) (ppm) = 9.05 (d, J = 6.60 Hz,
4H), 8.10 (d, J = 6.60 Hz, 4H), 6.75 (s, 2H), 6.23 (s, 4H), 4.84 (t, J = 7.70 Hz, 4H), 4.12 (q, J = 7.20 Hz, 4H), 3.74 (m, 24H), 3.71 (d, J = 4.04 Hz, 8H), 2.59 (t, J = 7.52 Hz, 4H), 2.45 (m, 4H), 1.22 (t, J = 7.14 Hz, 6H). $\lambda_{\text{max}}$ (CH$_3$OH) = 407 nm.

2.2.2.14. [PyBP/BN38C10](ZnCl$_3$)$_2$: A solution of ZnCl$_2$ (0.8 mg, 0.0057 mmol) in CH$_3$OH (1.5 mL) was layered over a solution of PyBP-[NO$_3$]$_2$ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2 mg, 0.0051 mmol) in a 1:1 mixture of CH$_3$OH:CHCl$_3$ (1.5 mL). Dark blue colored, rhombic shaped, X-ray quality crystals were obtained after two weeks.

2.2.2.15. [PyBP/BN32C8](ZnCl$_3$)$_2$: A solution of ZnCl$_2$ (0.8 mg, 0.0057 mmol) in CH$_3$OH (1.8 mL) was layered over a solution of [PyBP][NO$_3$]$_2$ (5 mg, 0.011 mmol) and BN32C8 (5.5 mg, 0.010 mmol) in a 1:1 mixture of CH$_3$OH:CHCl$_3$ (1.8 mL). Dark blue colored, rhombic shaped, X-ray quality crystals were obtained after two weeks.

2.2.2.16. [PyBP/BN38C10](ZnBr$_3$)$_2$: A solution of ZnBr$_2$ (1.3 mg, 0.0057 mmol) in CH$_3$OH (1.8 mL) was layered over a solution of [PyBP][NO$_3$]$_2$ (1.3 mg, 0.0028 mmol) and BN38C10 (1.6 mg, 0.0025 mmol) in a 1:1 mixture of CH$_3$OH:CHCl$_3$ (0.75 mL). Dark blue colored, rhombic shaped, X-ray quality crystals were obtained after two weeks.

2.2.2.17. [PyBP/BN32C8](ZnBr$_3$)$_2$: A solution of ZnBr$_2$ (1.3 mg, 0.0057 mmol) in CH$_3$OH (1.5 mL) was layered over a solution of [PyBP][NO$_3$]$_2$ (2.5 mg, 0.0057 mmol) and BN32C8 (2.8 mg, 0.0050 mmol) in a 1:1 mixture of CH$_3$OH:CHCl$_3$ (1.5 mL). Dark blue colored, X-ray quality crystals (2.8 mg, 57 %) were obtained after two weeks.

2.2.2.18. [PyBP/BPP34C10][CdBr$_4$]: A solution of CdBr$_2$ (3.1 mg, 0.0091 mmol) in CH$_3$OH (1.5 mL) was layered over a 1:1 mixture of [PyBP][NO$_3$]$_2$ (2.0 mg, 0.0046 mmol) and BPP34C10 (2.0 mg, 0.0037 mmol) in a 1:1 mixture of CH$_3$OH:CHCl$_3$ (1.5
mL). Dark maroon-red colored, X-ray quality, needle shaped crystals were obtained after two weeks.

2.2.2.19. [PyBP/BN38C10][CdBr₄]: A solution of CdBr₂ (3.9 mg, 0.0114 mmol) in CH₃OH (1.5 mL) was layered over a 1:1 mixture of [PyBP][NO₃]₂ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2 mg, 0.0051 mmol) in a 1:1 mixture of CH₃OH:CHCl₃ (1.5 mL). Dark blue colored, X-ray quality, rhombic shaped crystals were obtained after two weeks.

2.2.2.20. [PyBP/BPP34C10][CdI₄]: A solution of CdI₂ (4.2 mg, 0.0114 mmol) in CH₃OH (1.5 mL) was layered over a solution of [PyBP][NO₃]₂ (2.5 mg, 0.0057 mmol) and BPP34C10 (2.5 mg, 4.7 mmol) in CH₃OH (1.5 mL). X-ray quality, dark maroon-red colored, needle shaped crystals were obtained after two weeks.

2.2.2.21. [PyBP/BN38C10][CdI₄]: A solution of CdI₂ (2.1 mg, 0.0057 mmol) in CH₃OH (1.5 mL) was layered over a solution of [PyBP][NO₃]₂ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2 mg, 0.0051 mmol) in a 1:1 mixture of CH₃OH:CHCl₃ (1.5 mL). Dark maroon-red colored, X-ray quality, rhombic shaped crystals were obtained after one month.

The same crystal was obtained by another method as follows. The solution of CdI₂ (4.2 mg, 0.0114 mmol) in CH₃OH (1.5 mL) was layered over a solution of [PyBP][NO₃]₂ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2 mg, 0.0051 mmol) in a 1:1 mixture of CH₃OH:CHCl₃ (1.5 mL). X-ray quality, dark maroon-red colored, rhombic shaped crystals were obtained after one month.
2.2.2.2. [PyBP/BN32C8](CdI$_3$)$_2$: A solution of CdI$_2$ (4.2 mg, 0.0114 mmol) in CH$_3$OH (1.5 mL) was layered over a 1:1 mixture of [PyBP][NO$_3$]$_2$ (2.5 mg, 0.0057 mmol) and BN32C8 (2.8 mg, 0.0057 mmol) in a 1:1 mixture of CH$_3$OH:CHCl$_3$ (1.5 mL). After two weeks, the resulting clear solution was layered over $^i$Pr$_2$O to obtain X-ray quality, dark maroon-red colored, needle shaped crystals.

2.2.2.3. [PyBP/BN38C10](Hg$_2$Cl$_6$)$_2$: A solution of HgCl$_2$ (3.2 mg, 0.0114 mmol) in CH$_3$OH (1.5 mL) was layered over a solution of [PyBP][NO$_3$]$_2$ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2 mg, 0.0051 mmol) in a 1:1 mixture of CH$_3$OH:CHCl$_3$ (1.5 mL). X-ray quality, dark blue colored, rhombic shaped crystals were obtained after two weeks.

2.2.2.4. [PyBP/BN32C8](Hg$_2$Cl$_6$)$_2$: A solution of HgCl$_2$ (3.2 mg, 0.0114 mmol) in CH$_3$OH (1.5 mL) was layered over a solution of [PyBP][NO$_3$]$_2$ (2.5 mg, 0.0057 mmol) and BN32C10 (2.7 mg, 0.0051 mmol) in a 1:1 mixture of CH$_3$OH:CHCl$_3$ (1.5 mL). X-ray quality, dark blue colored, rhombic shaped crystals were obtained after two weeks.

2.2.2.5. [PyBP/BN38C10](Hg$_2$Br$_6$)$_2$: A solution of HgBr$_2$ (4.2 mg, 0.0114 mmol) in CH$_3$OH (1.5 mL) was layered over a solution of [PyBP][NO$_3$]$_2$ (2.5 mg, 0.0057 mmol) and BN38C10 (3.2mg, 0.0051 mmol) in a 1:1 mixture of CHCl$_3$:CH$_3$OH (1.5 mL). Dark blue color, rhombic shaped X-ray quality crystals resulted after three weeks.

2.2.2.6. [PyBP/BN32C8][Hg$_2$Br$_8$]: A solution of HgBr$_2$ (4.2 mg, 0.0115 mmol) in CH$_3$OH (1.5 mL) was layered over a solution of [PyBP][NO$_3$]$_2$ (2.5 mg, 0.0057 mmol) and BN32C8 (2.8mg, 0.0057 mmol) in a 1:1 mixture of CHCl$_3$:CH$_3$OH (1.5 mL). Greenish-blue colored, very small crystals formed after one week. They were not high enough quality for X-ray diffraction. Upon standing, the greenish-blue colored crystals
disappeared. Dichroic (blue and red), rhombic shaped X-ray quality crystals were obtained after five weeks.

2.2.2.27. [PyBP/BN38C10][Hg2I6]: A 3:2 mixture of CHCl3:CH3OH was layered over a solution of [PyBP][NO3]2 (2.5 mg, 5.7 mmol) and BN38C10 (3.2 mg, 0.0051 mmol) in a 1:1 mixture of CHCl3:CH3OH (1.5 mL). After that the solution of HgI2 (5.2 mg, 0.0114 mmol) in CH3OH (1.5 mL) was layered over the resulted two layer solution. The vial was kept in the freezer at −20 °C for one week. White, needle shaped crystalline material were on the bottom of the vial. After warming it up to room temperature, the white crystalline material disappeared within 30-40 min. Upon standing at room temperature it gave dark blue rhombic shaped, X-ray quality crystals after two weeks.

2.2.2.28. [PyBP/BN32C8][Hg2I6]: A 3:2 mixture of CHCl3:CH3OH was layered over a solution of [PyBP][NO3]2 (2.0 mg, 0.0046 mmol) and BN32C8 (2.8 mg, 0.0057 mmol) in a 1:1 mixture of CHCl3:CH3OH (1.5 mL). After that the solution of HgBr2 (4.2 mg, 0.0092 mmol) in CH3OH (1.5 mL) was layered over the resulted two layer solution. The vial was kept in the freezer at −20 °C for seven days. No crystals were obtained. It was taken out from the freezer and kept at room temperature. Upon standing at room temperature dark blue rhombic shaped, X-ray quality crystals formed after two weeks.

2.2.2.29. Cu(II) complex-1 of L1: A solution of [Cu(CH3CN)4]PF6 (1.6 mg, 0.004 mmol) in CH3CN:CH3OH = 1:1 (1.0 mL) was mixed with L1 (3.0 mg, 0.005 mmol) in CHCl3 (1.0 ml) to obtain a maroon-red colored solution. Slow evaporation of the resulting mixture of [Cu(CH3CN)4]PF6: L1 provided dichroic (blue and purple), X-ray quality, flake-like crystals.
2.2.2.30. Cu(II) complex-2 of L1: Blue colored, X-ray quality single crystals were obtained by iPr₂O vapor diffusion into a 1:1 mixture of L1 (3.0 mg, 0.005 mmol) and [Cu(CH₃CN)₄]PF₆ (1.6 mg, 0.004 mmol) in a 1:1 mixture of CHCl₃:CH₃CN.

2.2.2.31. Cu(Pyacac)₂ metallo-ligand (ML polymorph 1): iPr₂O was layered over a mixture of Cu(Pyacac)₂ (5.0 mg, 0.012 mmol) and diaza-18-crown-6 (6.3 mg, 0.024 mmol) in a 1:1 mixture of CHCl₃:CH₃OH. Cubic shaped, green colored, X-ray quality crystals of ML polymorph 1 were obtained after three days.

Another polymorph of Cu(Pyacac)₂ metallo-ligand (ML polymorph 2) was obtained as follows. iPr₂O was layered over a solution of Cu(Pyacac)₂ (5.0 mg, 0.012 mmol) and diaza-18-crown-6 (6.3 mg, 0.024 mmol) in C₂H₅OH. Cubic shaped, green colored, X-ray quality crystals of ML polymorph 2 were obtained after three days.

2.2.2.32. [diaza-18-crown-6][CuCl₂] complex (ML3): Cubic shaped, dark blue colored, X-ray quality crystals of ML3 were obtained from the same crystal growing vial of ML1 (2.2.2.31) after three weeks.

2.2.2.33. Cu(Phacac)₂ and diaza-18-crown-6 complex (ML4): iPr₂O vapor was diffused into a 1:1 mixture of Cu(Phacac)₂ (5.0 mg, 0.012 mmol) and diaza-18-crown-6 (3.2 mg, 0.008 mmol) in CHCl₃ at room temperature. The resulting transparent light greenish-blue solution was slowly evaporated to obtain blue colored, X-ray quality single crystals of ML4 after one week.
2.3. Solution preparation for UV-visible spectroscopy

The standard solutions of 3.000(± 0.006) x 10⁻³ M [PyBP][NO₃]₂, [CpBP]Cl₂, [C₄BP][PF₆]₂, BPP34C₁₀, BN₃₈C₁₀ and BN₃₂C₈ were prepared in 10.00(± 0.02) mL volumetric flasks by dissolving 13.083(±0.001), 14.041(±0.001), 20.290(±0.001), 16.098(±0.001), 19.088(±0.001) and 16.459(±0.001) mg, respectively. In the case of a syn- and anti- mixture of [TBA]₂DSBPP34C₁₀, the standard solutions were prepared in 5.00(± 0.01) mL volumetric flasks by dissolving 17.687(±0.001) mg of [TBA]₂DSBPP34C₁₀.

The standard solutions of 1.50(± 0.01) x 10⁻³ M [2]pseudorotaxanes were prepared by mixing 1.50(± 0.01) mL of 3.000(± 0.006) x 10⁻³ M standard solutions of the axle and the wheel using a micropipette.

A 1:1 mixture of CH₃OH:CHCl₃ was used as the solvent for [PyBP/wheel][NO₃]₂ and [CpBP/wheel]Cl₂ [2]pseudorotaxanes while 2:1 mixture of acetone:CH₂Cl₂ was used for [C₄BP/wheel]Cl₂ [2]pseudorotaxanes. All [axle/DSBPP34C₁₀] [2]pseudorotaxane solutions were prepared in milli-Q H₂O.

2.3.1. Variable temperature (VT) UV-Vis measurements for [C₄BP/wheel][PF₆]₂ [2]pseudorotaxanes

The standard solutions of 1.0(± 0.1) x 10⁻³ M [C₄BP/wheel][PF₆]₂ [2]pseudorotaxane solutions were prepared in 25.00(+ 0.03 mL) volumetric flasks by dissolving 16.9(+ 0.1) mg of [C₄BP][PF₆]₂ together with 13.4(+ 0.1) mg of BPP34C₁₀ or 15.9(+ 0.1) mg of BN₃₈C₁₀ or 13.7(+ 0.1) mg of BN₃₂C₈ respectively in a 2:1 mixture of acetone: CH₂Cl₂.
2.4. Solution preparation for \(^1\)H-NMR spectroscopy

2.4.1. \([\text{PyBP/neutral crown ether}][\text{NO}_3]_2\) [2]pseudorotaxanes

A 1:1 mixture of CD\(_3\)OD:CDCl\(_3\) was used as a solvent mixture for NMR solution for \([\text{PyBP/neutral crown ether}][\text{NO}_3]_2\) [2]pseudorotaxanes.

The solutions of \(3.82(\pm 0.01) \times 10^{-3}\) M of the axle and wheel components were prepared by dissolving \(1.000(\pm 0.001)\) mg of \([\text{PyBP}][\text{NO}_3]_2\), \(1.230(\pm 0.001)\) mg of BPP34C10, \(1.460(\pm 0.001)\) mg of BN38C10 and \(1.258(\pm 0.001)\) mg of BN32C8, respectively in 600(\pm 1) \(\mu\)L of NMR solvent mixture.

The solutions of \(3.82(\pm 0.01) \times 10^{-3}\) M of \([\text{PyBP/wheel}]\) pseudorotaxanes were prepared by mixing \(1.000(\pm 0.001)\) mg of \([\text{PyBP}][\text{NO}_3]_2\) together with either \(1.230(\pm 0.001)\) mg of BPP34C10 or \(1.460(\pm 0.001)\) mg of BN38C10 or \(1.258(\pm 0.001)\) mg of BN32C8 in 600(\pm 1) \(\mu\)L of the NMR solvent mixture.

2.4.2. \([\text{CpBP/neutral crown ether}]\text{Cl}_2\) [2]pseudorotaxanes

A 2:1 mixture of CD\(_3\)OD:CDCl\(_3\) was used as the solvent mixture for NMR solutions for \([\text{CpBP/wheel}]\text{Cl}_2\) [2]pseudorotaxanes.

Solutions of \(3.56(\pm 0.01) \times 10^{-3}\) M of the axle and wheel components were prepared by dissolving \(1.000(\pm 0.001)\) mg of \([\text{CpBP}]\text{Cl}_2\), \(1.146(\pm 0.001)\) mg of BPP34C10, \(1.359(\pm 0.001)\) mg of BN38C10 and \(1.172(\pm 0.001)\) mg of BN32C8, respectively in 600(\pm 1) \(\mu\)L of the NMR solvent mixture.

The solutions of \(3.56(\pm 0.01) \times 10^{-3}\) M of \([\text{CpBP/wheel}]\text{Cl}_2\) [2]pseudorotaxanes were prepared by mixing \(1.000(\pm 0.001)\) mg of \([\text{CpBP}]\text{Cl}_2\) together with either \(1.146(\pm 0.001)\)
mg of BPP34C10 or 1.359(±0.001) mg of BN32C8 or 1.172(±0.001) mg of BN38C10 in 600(±1) μL of the NMR solvent mixture.

2.4.3. [C4BP/ neutral crown ether][PF₆]₂ [2]pseudorotaxanes

A 1:1 mixture of d-acetone:CDCl₃ was used as a solvent mixture for NMR solutions. The 4.0(±0.4) x 10⁻³ M [C4BP][PF₆]₂, BPP34C10 and [BPP34C10/C4BP][PF₆]₂ [2]pseudorotaxane solutions were prepared by dissolving 1.5(± 0.1) mg [C4BP][PF₆]₂, 1.1(±0.1) mg of BPP34C10 and 2.6(±0.1) mg of [BPP34C10/C4BP][PF₆]₂ [2]pseudorotaxane crystals, respectively, in 500(± 1) µL of the NMR solvent mixture. The 3.7(±0.3) x 10⁻³ M [C4BP][PF₆]₂ and BN38C10 solutions were prepared by dissolving 1.5(± 0.1) mg of [C4BP][PF₆]₂, 1.4(± 0.1) mg BN38C10, respectively in 600(± 1) µL of the NMR solvent mixture. The 3.7(±0.1) x 10⁻³ M [C4BP/BN38C8][PF₆]₂ [2]pseudorotaxane solution was prepared by dissolving 1.4(± 0.1) mg of [C4BP][PF₆]₂ and 1.5(± 0.1) mg of BN38C10 in 600(± 1) µL of the NMR solvent mixture.

The 3.7(±0.3) x 10⁻³ M [C4BP][PF₆]₂ and BN32C8 were prepared by dissolving 1.5(± 0.1) mg of [C4BP][PF₆]₂, 1.2(± 0.1) mg of BN38C10, respectively in 600(± 1) µL of the NMR solvent mixture. The 3.7(±0.1) x 10⁻³ M [C4BP/BN32C8][PF₆]₂ [2]pseudorotaxane solution was prepared by dissolving 1.5(± 0.1) mg of [C4BP][PF₆]₂ and 1.2(± 0.1) mg of BN32C8, respectively, in 600(± 1) µL of the NMR solvent mixture.
2.4.4. [4,4’-bipyridinium axle/DSBPP34C10] [2]pseudorotaxanes

The solutions of 3.69(±0.01) mM of [C4BP][PF₆]₂, [C4BP/syn- and anti-DSBPP34C10] [2]pseudorotaxanes and [TBA]₂DSBPP34C10 were prepared by dissolving 1.500(±0.001) mg, 2.398(±0.001) mg and 2.616(±0.001) mg, respectively, in 600(±1) μL of a 1:1 mixture of d₆-acetone and CD₃OD.

The solutions of 6.90(±0.01) mM of [PyBP/syn- and anti-DSBPP34C10], [PyBP/syn-DSBPP34C10] and [PyBP/anti-DSBPP34C10] pseudorotaxanes were prepared by dissolving 3.500(±0.001) mg of [2]pseudorotaxane crystals in 500(±1) μL of CD₃OD.

The solutions of 6.90(±0.01) mM [PyBP][NO₃]₂ and [TBA]₂DSBPP34C10 were prepared by dissolving 1.516(±0.001) mg of [PyBP][NO₃]₂ and 4.100(±0.001) mg of [TBA]₂DSBPP34C10, respectively, in 500(±1) μL of CD₃OD.

The solutions of 5.34(±0.01) mM of [CpBP/ syn- and anti-DSBPP34C10] was prepared by dissolving 1.500(±0.001) mg of [CpBP]Cl₂ and 3.780(±0.001) mg of syn- and anti-[TBA]₂DSBPP34C10 in 600(±1) μL of CD₃OD. The standard solutions of 5.34(±0.01) mM syn- and anti-[TBA]₂DSBPP34C10 and [CpBP]Cl₂ were prepared by dissolving 3.780(±0.001) mg and 1.500(±0.001) mg, respectively, in 600(±1) μL of CD₃OD.

2.5. Axle-to-wheel molar ratios of pseudorotaxanes

The Job’s plot method¹¹⁸ was employed to determine the axle:wheel stoichiometry in pseudorotaxane solutions using UV-Visible spectroscopy or ¹H-NMR spectroscopy.

Equimolar standard solutions of the axle and the wheel were prepared. In the case of UV-Vis spectroscopic method, as shown in Table 2.1, the standard solutions were mixed using a micropipette to obtain the different molar ratios of wheel:axle in a final volume of
3.00(± 0.1) mL. The absorbance of each solution was measured at its $\lambda_{\text{max}}$. The plot of absorbance at $\lambda_{\text{max}}$ vs. mole fraction was used to obtain the stoichiometry between the wheel and the axle.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Wheel:axle molar ratio</th>
<th>Volume of axle/ mL</th>
<th>Volume of wheel / mL</th>
<th>Concentration of axle/ (± 0.1) x 10^{-4} M</th>
<th>Concentration of wheel/ (± 0.1) x 10^{-4} M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10:0</td>
<td>3.00</td>
<td>0.00</td>
<td>10</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>9:1</td>
<td>2.70</td>
<td>0.30</td>
<td>9.0</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>8:2</td>
<td>2.40</td>
<td>0.60</td>
<td>8.0</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>7:3</td>
<td>2.10</td>
<td>0.90</td>
<td>7.0</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>6:4</td>
<td>1.80</td>
<td>1.20</td>
<td>6.0</td>
<td>4.0</td>
</tr>
<tr>
<td>6</td>
<td>5:5</td>
<td>1.50</td>
<td>1.50</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>7</td>
<td>4:6</td>
<td>1.20</td>
<td>1.80</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>8</td>
<td>3:7</td>
<td>0.90</td>
<td>2.10</td>
<td>3.0</td>
<td>7.0</td>
</tr>
<tr>
<td>9</td>
<td>2:8</td>
<td>0.60</td>
<td>2.40</td>
<td>2.0</td>
<td>8.0</td>
</tr>
<tr>
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<td>2.70</td>
<td>1.0</td>
<td>9.0</td>
</tr>
<tr>
<td>11</td>
<td>0:10</td>
<td>0.00</td>
<td>3.00</td>
<td>0.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

**Table 2.1:** Solutions preparation for molar ratio measurements of pseudorotaxanes by UV-Vis spectroscopic method.

In the case of the $^1$H-NMR method, the standard solutions of the axle and the wheel were mixed using a micropipette according to Table 2.2 to obtain the different molar ratios of the axle and the wheel in the total volume of 600(±1) μl to determine the stoichiometry. The concentration of the axle and the wheel solutions were identical. $^1$H-NMR spectra of each sample were taken at room temperature.
Table 2.2: Solution preparation for molar ratio measurements of pseudorotaxanes by $^1$H-NMR spectroscopic method.

UV-Visible spectroscopy was used to determine the molar ratios of all pseudorotaxanes except [PyBP/BPP34C10][NO$_3$]$_2$ and [CpBP/BPP34C10]Cl$_2$. $^1$H-NMR spectroscopy was used to determine the molar ratio of [PyBP/BPP34C10][NO$_3$]$_2$ and [CpBP/BPP34C10]Cl$_2$.

A 1:1 mixture of CH$_3$OH:CHCl$_3$ was used as the solvent for [PyBP/wheel][NO$_3$]$_2$ and [CpBP/wheel]Cl$_2$ [2]pseudorotaxanes, while a 1:1 mixture of CH$_3$CN:CHCl$_3$ was used for [C4BP/wheel][PF$_6$]$_2$ [2]pseudorotaxanes. All [axle/DSBPP34C10] [2]pseudorotaxane solutions were prepared in milli-Q H$_2$O. In the case of the determination of the molar ratio of [C4BP]$^{2+}$ and [TBA]$_2$DSBPP34C10 pseudorotaxanes, [C4BP]Br$_2$ was used instead [C4BP][PF$_6$]$_2$ due to solubility problems.

For UV-Vis spectra, standard solutions of 1.00(± 0.01) x 10$^{-3}$ M [PyBP][NO$_3$]$_2$, [CpBP]Cl$_2$, [C4BP][PF$_6$]$_2$, [C4BP]Br$_2$, BPP34C10, BN38C10, BN32C8 and [TBA]$_2$DSBPP34C10 were prepared in 25.00(± 0.03) mL volumetric flasks, by dissolving 10.910(± 0.001) mg, 11.701(± 0.001) mg, 16.951(± 0.001) mg, 13.703(±
0.001) mg, 13.436(± 0.001) mg 15.907(± 0.001) mg, 13.715(± 0.001) mg and 29.479(± 0.001) mg, respectively.

For $^1$H–NMR spectra, standard solutions of $2.00(±0.02) \times 10^{-3}$ M [PyBP][NO$_3$]$_2$, [CpBP]Cl$_2$ and BPP34C10 were prepared by dissolving 1.832(±0.001) mg, 2.055(±0.001) mg and 2.252(±0.001) mg, respectively in 2.10(±0.02) mL of a 1:1 mixture of CDCl$_3$:CD$_3$OD.

2.6. Binding constant measurements

The Benensi-Hilderbrand method$^{119}$ was used to obtain the association constant between the axle and the wheel of [2]pseudorotaxanes using UV-Visible spectroscopy or $^1$H-NMR spectroscopy. Spectroscopic method and the solvent selection were similar to the section 2.5 unless otherwise mentioned.


For NMR spectra, the standard solution of $2.00(±0.01)$ mM [PyBP][NO$_3$]$_2$ was prepared by dissolving 3.053(±0.001) mg in the total volume of $3.50(±0.03)$ mL while the standard solutions of $5.00(±0.03)$ mM BPP34C10 were prepared by dissolving 4.022(±0.001) mg in the total volume of $1.50(±0.01)$ mL of the deuterated solvent mixture. The standard [PyBP][NO$_3$]$_2$ solution was titrated with the standard BPP34C10 solution to obtain the final axle:wheel ratio of 1:5. After each addition, $^1$H-NMR spectra were recorded.
For UV-Vis spectra, standard solutions of 0.50(± 0.01) x 10^{-3} M and 1.00(± 0.01) x 10^{-3} M [PyBP][NO_3]_2 were prepared in 10.00(± 0.02) mL volumetric flasks by dissolving 2.182(± 0.001) mg and 4.363(± 0.001) mg of [PyBP][NO_3]_2, respectively.

The standard [PyBP/BN38C10][NO_3]_2 and [PyBP/BN32C8][NO_3]_2 [2]pseudorotaxane solutions was prepared to obtain a 1:10 axle:wheel ratio by dissolving 7.953(±0.001) mg of BN38C10 and 6.858(±0.001) mg of BN32C8 in 2.50(±0.01) mL of standard 0.50(± 0.01) x 10^{-3} M and 1.00(± 0.01) x 10^{-3} M [PyBP][NO_3]_2 solutions, respectively.

The volume of 2.00(±0.01) mL of standard [PyBP][NO_3]_2 solution was transferred to a cuvette and titrated with the standard pseudorotaxane solution up to a wheel:axle ratio of 5:1 in the total volume of 4.00(±0.03) mL.

2.6.2. [CpBP/neutral crown ether]Cl_2 [2]pseudorotaxanes

The dilution method^{120,121} was used to determine the binding constants of [CpBP/BN38C10]Cl_2 and [CpBP/BN38C10]Cl_2 [2]pseudorotaxanes.

The standard solution of 3.00(±0.01) x 10^{-3} M [CpBP]Cl_2 was prepared by dissolving 5.140(±0.001) mg in the total volume of 3.50(±0.03) mL while the standard solutions of 7.50(±0.01) x 10^{-3} M BPP34C10 were prepared by dissolving 6.033(±0.001) mg in the total volume of 1.50(±0.01) mL of CD_3OD. The standard [CpBP]Cl_2 solution was titrated with standard BPP34C10 solution to obtain a final axle:wheel ratio of 1:5. After each addition, ^1H-NMR spectra were recorded.
The standard solution of 3.00(±0.01) x 10^{-3} M [CpBP/BN38C10]Cl₂ [2]pseudorotaxane solutions were prepared by dissolving 14.042(±0.001) mg of [CpBP]Cl₂ and 19.089(±0.001) mg of BN38C10 in a 10.00(±0.02) mL volumetric flask.

The standard solution of 1.50(±0.01) x 10^{-3} M [CpBP/BN32C8]Cl₂ [2]pseudorotaxane solutions were prepared by dissolving 7.021(±0.001) mg of [CpBP]Cl₂ and 8.229(±0.001) mg of BN32C8 in a 10.00(±0.02) mL volumetric flask.

The standard solution of pseudorotaxanes were transferred to a cuvette and diluted with a 1:1 mixture of CH₃OH:CHCl₃ by successive addition of 125 µL to obtain the final volume of 4.00(±0.03) mL. After each addition absorbance at λ_{max} was measured using a UV-Vis spectrometer.

2.6.3. [C4BP/neutral crown ether][PF₆]₂ [2]pseudorotaxanes

A standard solution of 1.0(±0.1) x 10^{-3} M [C4BP][PF₆]₂ was prepared in 10.00(± 0.02) mL volumetric flasks by dissolving 6.8(± 0.1) mg of [C4BP][PF₆]₂ in a 1:1 mixture of CH₃CN:CHCl₃.

The standard [C4BP/wheel][PF₆]₂ pseudorotaxane solutions were prepared to obtain 1.0(± 0.1) x 10^{-3} M [C4BP][PF₆]₂ concentration and 10.0(± 0.1) x 10^{-3} M wheel concentration in the same solution by dissolving 13.4(±0.1) mg of BPP34C10, 15.9(± 0.1) mg of BN38C10, 13.7(± 0.1) mg of BN32C8, respectively in 2.50(± 0.01) mL of standard [C4BP][PF₆]₂ solution.

The volume of 2.00(±0.01) mL standard [C4BP][PF₆]₂ solution was transferred to a cuvette and titrated with standard pseudorotaxane solution up to a wheel:axle ratio of 5:1 in a total volume of 4.00(±0.03) mL.
2.6.4. [4,4′-bipyridinium axle/DSBPP34C10] [2]pseudorotaxanes

The dilution method was used to determine the binding constant and extinction coefficient of [axle/DSBPP34C10] [2]pseudorotaxanes. Water was used as the solvent.

The 3.0(± 0.1) x 10^{-3} M solutions of the axle and the wheel were prepared in 5.00(±0.01) mL volumetric flasks. The UV-visible spectrum of each solution was recorded and the λ_{max} was determined. The solutions were diluted by adding 200 μL of the solution at a time and the new absorbance was measured at the λ_{max}. The dilution followed by absorbance measurements were carried out to obtain 12 data points.

2.7. Electrochemistry

A composite electrode system containing two platinum wires (0.04 mm) as working and counter electrodes and a silver wire as a quasi-reference electrode was used. It was polished using 0.05 μm Al₂O₃ on a felted surface. Tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) was used as a supporting electrolyte unless otherwise mentioned. The sample solutions were degassed by purging purified nitrogen and kept under an inert atmosphere throughout the measurements. Ferrocene was used as an internal standard. Potential values were reported versus the ferrocene/ferrocenium (Fc/Fc^+) redox couple. The volume of 2.00 (± 0.01) mL of standard solution was transferred to a shell vial which contains 77.5(± 0.1) mg of TBAPF₆ (supporting electrolyte) and few crystals of ferrocene (reference). Solvent-saturated N₂ was purged through the electrochemical solution over 30 min. This procedure was followed for all standard solutions prior to the electrochemical measurements.
2.7.1. [PyBP/neutral crown ether][PF₆]₂ pseudorotaxanes

The standard solutions of the axle, wheel and [PyBP/wheel][PF₆]₂ [2]pseudorotaxane were prepared in a 1:1 mixture of CH₃CN:CH₂Cl₂.

The standard solutions of 0.50(± 0.01) x 10⁻³ M [PyBP][PF₆]₂, BPP34C10, BN38C10 and BN32C8 were prepared in 10.00(±0.02) mL volumetric flasks by dissolving 3.010(±0.001) mg, 2.683(±0.001) mg, 3.181(±0.001) mg and 2.743(±0.001) mg, respectively.

The standard solutions of 0.50(± 0.01) x 10⁻³ M [PyBP/wheel][PF₆]₂ [2]pseudorotaxanes were prepared by 3.010(±0.001) mg of [PyBP][NO₃]₂ together with 2.683(±0.001) mg of BPP34C10, 3.181(±0.001) mg of BN38C10 and 2.743(±0.001) mg of BN32C8 in 10.00 mL volumetric flasks.

2.7.2. [CpBP/neutral crown ether]Cl₂ [2]pseudorotaxanes

Tetrabutylammonium chloride (TBACl) (55.6 mg, 0.1 M) was used as the supporting electrolyte. The standard solutions of the axle, wheel and [CpBP/wheel]Cl₂ [2]pseudorotaxane were prepared in a 2:1 mixture of CH₃OH:CH₂Cl₂.

The standard solutions of 1.00(± 0.01) x 10⁻³ M [CpBP]Cl₂, BPP34C10, BN38C10 and BN32C8 were prepared in 10.00(±0.02) mL volumetric flasks by dissolving 4.681(±0.001) mg, 5.366(±0.001) mg, 6.362(±0.001) mg and 5.486(±0.001) mg respectively.

The standard solutions of 1.00(± 0.01) x 10⁻³ M [CpBP/wheel]Cl₂ pseudorotaxanes were prepared by dissolving 4.681(±0.001) mg of [CpBP]Cl₂ together with 5.366(±0.001) mg
of BPP34C10 or 6.362(±0.001) mg of BN38C10 or 5.486(±0.001) mg of BN32C8 in 10.00(± 0.02) mL volumetric flasks.

2.7.3. [C4BP/neutral crown ether][PF₆]₂ pseudorotaxanes

A 1:2 mixture of CH₃CN:CH₂Cl₂ were used as the solvent mixture for the axle, wheel and [C4BP/wheel][PF₆]₂ [2]pseudorotaxane solutions.

The standard solutions of 1.0(± 0.1) x 10⁻³ M [C4BP][PF₆]₂, BPP34C10, BN38C10 and BN32C10 were prepared in 10.00(± 0.02) mL volumetric flasks by dissolving 6.7(± 0.1) mg, 5.3(± 0.1) mg, 6.3(± 0.1) mg and 5.4(± 0.1) mg, respectively.

The standard solution of 1.0(± 0.1) x 10⁻³ M [C4BP/BPP34C10][PF₆]₂ [2]pseudorotaxane was prepared in 10.00(± 0.02) mL volumetric flask by dissolving 6.7(± 0.1) mg of [C4BP][PF₆]₂ and 5.3(± 0.1) mg of BPP34C10.

2.7.4. [4,4′-bipyridinium axle/DSBPP34C10] [2]pseudorotaxanes

The standard solutions of 0.50(± 0.01) x 10⁻³ M [PyBP/syn-DSBPP34C10] and [PyBP/anti-DSBPP34C10] were prepared in a 10.00(± 0.02) mL volumetric flask by dissolving 5.032(± 0.001) mg in a 2:1 mixture of CH₃OH:CH₃CN.

The standard solutions of 1.00(± 0.01) x 10⁻³ M [CpBP/syn- and anti-DSBPP34C10] were prepared in a 10.00(± 0.02) mL volumetric flask by dissolving 10.904(± 0.001) mg of [CpBP/syn- and anti-DSBPP34C10] crystals in a 2:1 mixture of CH₃OH:CH₂Cl₂.
2.8. Metal binding studies of [PyBP/neutral crown ether]\(^{2+}\) by UV-Vis spectroscopy

Standard solutions of 2.00(± 0.01) x 10\(^{-3}\) mM [PyBP][NO\(_3\)]\(_2\), BPP34C10, BN38C10 and BN32C8 were prepared in 5.00(±0.01) mL volumetric flasks by dissolving 4.361(±0.001) mg, 5.366(±0.001) mg, 6.363(±0.001) mg and 5.486(±0.001) mg, respectively. Standard solutions of 4.00(± 0.01) x 10\(^{-3}\) mM ZnCl\(_2\), ZnBr\(_2\), ZnI\(_2\), CdCl\(_2\), CdBr\(_2\), CdI\(_2\), HgCl\(_2\), HgBr\(_2\) and HgI\(_2\) were prepared in 10.00(±0.02) mL volumetric flasks by dissolving 5.484(±0.001) mg, 9.008(±0.001) mg, 12.767(±0.001) mg, 9.133(±0.001) mg, 10.888(±0.001) mg, 14.650(±0.001) mg, 10.860(±0.001) mg, 14.416(±0.001) mg and 18.176(±0.001) mg, respectively.

Standard solutions of 4.00(± 0.01) x 10\(^{-3}\) mM ZnCl\(_2\)/KCl, ZnBr\(_2\)/KBr and ZnI\(_2\)/KI were prepared by adding 5.452(±0.001) mg of KCl, 9.008(±0.001) mg of KBr, 12.767(±0.001) mg of KI in standard solutions of 4.00(± 0.01) x 10\(^{-3}\) mM ZnCl\(_2\), ZnBr\(_2\) and ZnI\(_2\), respectively. As shown in Table 2.3, standard solutions were mixed and UV-Vis spectra of each solution were recorded.

<table>
<thead>
<tr>
<th>Volume of [PyBP](^{2+}) solution/ mL</th>
<th>Volume of the crown ether solution/ mL</th>
<th>Volume of MX(_2) or MX(_2)/KX / mL</th>
<th>Volume of the solvent/ mL</th>
<th>Pseudorotaxane: M(^{2+}) ratio</th>
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<td>1.00</td>
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*Table 2.3:* Solution preparation for the metal binding studies.

2.9. Metal binding studies of [PyBP/neutral crown ether]\(^{2+}\) by \(^{1}\)H-NMR spectroscopy

All pseudorotaxane solutions were prepared in a 1:1 mixture of CH\(_3\)OH:CH\(_2\)Cl\(_2\) while all MX\(_2\)/KX (1/1) (M = Zn(II), Cd(II), Hg(II), X = Cl\(^{-}\), Br\(^{-}\), I\(^{-}\)) solutions were prepared in
CH$_3$OH. Always a solution of MX$_2$/KX (1/1) was layered over a solution of pseudorotaxane. Each pseudorotaxane layer consisted of a 1:1 mixture of [PyBP][NO$_3$]$_2$ axle (2.5 mg, 0.0057 mmol) and crown ether (BPP34C10 (3.1 mg, 0.0057 mmol) or BN38C10 (3.6 mg, 0.0057 mmol) or BN32C8 (3.2 mg, 0.0057 mmol)). The MX$_2$/KX (1/1) layer consisted of two molar equivalents of pseudorotaxanes.

After one week, the resulting solution and crystals/precipitate were separated by decanting the solution. Crystals or precipitates were washed with a 3:1 mixture of CH$_3$OH and CH$_2$Cl$_2$ and dried under air. The decanted solution was evaporated. $^1$H-NMR spectra of evaporated solution and dried crystal/precipitates were recorded in DMSO-$d_6$. 
### 2.10. Crystallographic data

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Table 2.4 continued.

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<th>2([PyBP/BN38C10][CdI₄])CHCl₃·4CH₃OH</th>
<th>[PyBP/BN32C8][CdI₃]₂2CH₂OH</th>
<th><a href="Hg%E2%82%82Cl%E2%82%86">PyBP/BN38C10</a>₂PyBP·2CH₂OH</th>
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<td>P ̅</td>
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<td>[Cu(L1)][PF$_6$]$_2$</td>
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<td><strong>R(F), R_w(F) [I &gt; 2σ(I)]</strong></td>
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<td>0.135611/0.4094</td>
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Table 2.4: Crystallographic data of starting materials, ligands and their supramolecules.
CHAPTER 3

RESULTS AND DISCUSSION

3.1. Characterization of pseudorotaxanes

3.1.1. UV-visible spectroscopic studies

[PyBP][NO$_3$]$_2$, [CpBP]Cl$_2$ and [C4BP]Br$_2$ axles are very slightly yellow in color while [C4BP][PF$_6$]$_2$ axle, BPP34C10, BN38C10, BN32C8 and [TBA]$_2$DSBPP34C10 crown ethers are colorless in the solution regardless of the solvent. Upon mixing the solutions of the axle and the wheel, colored pseudorotaxane solutions formed instantaneously.

In [4,4′-bipyridinium/aromatic crown ether] [2]pseudorotaxanes, the π-electron rich wheel interacts with the π-electron deficient axle via CT interaction to form a colored host-guest complex. The color of [2]pseudorotaxanes depends on the energy gap between the highest occupied molecular orbital (HOMO) of the donor unit (crown ethers) and the lowest unoccupied molecular orbital (LUMO) of the acceptor unit (4,4′-bipyridinium core). Therefore, using different crown ethers with the same axle produces a series of colors due to the change in the HOMO energy level while the LUMO energy level remains constant. Table 3.1 summarizes the absorbance maxima of the pseudorotaxane solutions studied.
<table>
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<th>Axle</th>
<th>Wheel</th>
<th>Solvent</th>
<th>(\lambda_{\text{max}})/ nm</th>
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<td>[PyBP][NO(_3)](_2)</td>
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<td>CH(_3)OH: CHCl(_3) = 1:1</td>
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<td>BN38C10</td>
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<td>590</td>
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<td>BN32C8</td>
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<td>610</td>
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<td>[CpBP]Cl(_2)</td>
<td>BPP34C10</td>
<td>CH(_3)OH: CHCl(_3) = 1:1</td>
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<td></td>
<td>BN38C10</td>
<td></td>
<td>556</td>
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<td></td>
<td>BN32C8</td>
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<td>585</td>
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<td>[C4BP][PF(_6)](_2)</td>
<td>BPP34C10</td>
<td>Acetone: CH(_2)Cl(_2) = 2:1</td>
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<td>BN38C10</td>
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<td>503</td>
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<td>501</td>
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<td>[C4BP][PF(_6)](_2)</td>
<td>[TBA](_2)DSBPP34C10</td>
<td>CH(_3)OH</td>
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<td>CH(_3)OH</td>
<td>440</td>
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<td>[CyBP]Cl(_2)</td>
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**Table 3.1:** Absorption spectral data for [2]pseudorotaxanes.

3.1.1.1. [PyBP/neutral crown ether][NO\(_3\)]\(_2\) [2]pseudorotaxanes

A mixture of [PyBP][NO\(_3\)]\(_2\) axle with crown ethers, BPP34C10, BN38C10 or BN32C8 in a 1:1 mixture of CH\(_3\)OH and CHCl\(_3\) produced red, purple and blue colored solutions with absorption maxima at 495, 590 and 610 nm, respectively (Figure 3.1).
Figure 3.1: a) Pseudorotaxane solutions; b) UV-Visible spectra of [PyBP/neutral crown ether][NO$_3$]$_2$ [2]pseudorotaxanes (in a 1:1 mixture of CH$_3$OH and CHCl$_3$).
3.1.1.2. [CpBP/neutral crown ether]Cl₂ [2]pseudorotaxanes

Upon mixing a solution of [CpBP]Cl₂ axle in a 1:1 mixture of CH₃OH and CHCl₃ with solutions of crown ethers, BPP34C10, BN38C10 or BN32C8 in the same solvent mixture produced red, purple and blue colored solutions with absorption maxima at 484, 556 and 585 nm, respectively (Figure 3.2).
3.1.1.3. [C4BP/neutral crown ether][PF₆]₂ [2]pseudorotaxanes

Addition of the axle solution to a BPP34C10 wheel solution (2:1 mixture of acetone and CH₂Cl₂) instantaneously produced a light orange colored solution with absorption maximum at 451 nm, while both BN38C10 or BN32C8 wheel solutions produced light magenta colored solutions with absorption maxima at 503 and 501 nm, respectively (Figure 3.3).

**Figure 3.2:** a) Pseudorotaxane solutions; b) UV-Visible spectra of [CpBP/neutral crown ether]Cl₂ [2]pseudorotaxanes (in a 1:1 mixture of CH₃OH and CHCl₃).
Figure 3.3: UV-Visible spectra of [C4BP/neutral crown ether][PF₆]₂ [2] pseudorotaxanes (in a 1:1 mixture of acetone and CH₂Cl₂).

3.1.1.4. [DSBPP34C10/axle] [2] pseudorotaxanes

Both [PyBP][NO₃]₂ and [CpBP]Cl₂ instantaneously produced maroon–red solutions with the wheel in CH₃OH, which show absorption maxima at 440 nm, while [C4BP]Br₂ produces an orange solution with absorption maximum at 393 nm (Figure 3.4).

Figure 3.4: UV-Visible spectra of [axle/DSDBPP34C10] [2] pseudorotaxanes (in CH₃OH).
In the case of the pseudorotaxanes discussed in Section 3.1.1., the CT transitions between
the \( \pi \)-electron rich wheel and the \( \pi \)-electron deficient axle, and similar color changes
were observed. \([4,4^\prime\text{-bipyridinium/BPP34C10}]^{2+}\) [2]pseudorotaxane analogs with benzyl\(^{123}\) or methyl\(^{21}\) instead of pyridyl, 4-carboxyphenyl or 3-(carboethoxy)propyl
groups show \( \lambda_{\text{max}} \) values at 450 nm and 436 nm, respectively (in acetone). These slight
changes are attributed to the change in LUMO level of the axle due to different
substituent groups and the polarity of the medium (solvent).

The absorbance maxima of both \([\text{C4BP/BN38C10}]^{2+}\) and \([\text{C4BP/BN38C10}]^{2+}\)
[2]pseudorotaxane systems lie in the same region as similar \([4,4'\text{-bipyridinium/}
\text{binaphtho}] \) chromophores (501 nm).\(^{105}\) Compared to the \([\text{C4BP}]^{2+}\) axle, aromatic
substituents – pyridyl and 4-carboxyphenyl – at the two ends of the \([\text{PyBP}]^{2+}\) and
\([\text{CpBP}]^{2+}\) axles shift the absorption band to higher wavelengths by means of reducing the
HOMO-LUMO energy gap of the naphthalene donor group and the 4,4\(^\prime\)-bipyridinium
core acceptor of pseudorotaxanes.

The absorption maxima of \([4,4'\text{-bipyridinium/DSBPP34C10}]^{2+}\) [2]pseudorotaxanes appear
in a lower wavelength region than those of \([4,4'\text{-bipyridinium/BPP34C10}]^{2+}\), even in
highly polar solvents, such as water or \(\text{CH}_3\text{OH}\). This difference is attributed to the
decrease in the HOMO energy level of the \([\text{DSBPP34C10}]^{2-}\), compared to BPP34C10
which results in an increase in the HOMO-LUMO energy gap.
3.1.2. $^1\text{H}$-NMR spectroscopic studies

$^1\text{H}$–NMR spectra of the individual axle, individual wheel, equimolar mixture of the two or crystals of [2]pseudorotaxanes were recorded in the same deuterated solvent/solvent mixtures at room temperature. The peaks of both the axle and the wheel shift from their original chemical shift value upon pseudorotaxane formation. The $^1\text{H}$–NMR spectra of the [2]pseudorotaxanes discussed below show only a single set of resonances, even after the addition of excess axle or wheel. This observation revealed that [2]pseudorotaxanes undergo a fast exchange equilibrium with their individual axle and wheel components on the NMR time scale. The relative chemical shift of the individual components of the [2]pseudorotaxane depends on the $\pi-\pi$ stacking, C–H⋯O hydrogen bonds and N$^+\delta$⋯O$^-\delta$ electrostatic interactions involved in [2]pseudorotaxanes.


The $^1\text{H}$–NMR spectra of [PyBP/neutral crown ether] pseudorotaxanes were recorded in a 1:1 mixture of CD$_3$OD and CDCl$_3$. The upfield shifts of the axle protons in the $\delta = 8.28$–9.82 ppm region and the downfield shifts of neutral crown ether peaks in the $\delta = 6.71$–8.01 ppm region are a result of pseudorotaxane formation (Table 3.2). A representative example of stacked $^1\text{H}$-NMR spectra of the axle, [2]pseudorotaxane and the wheel is shown below (Figure 3.5). Proton assignments are given in Figure 3.6.
Figure 3.5: $^1$H-NMR spectra (400 MHz) of 3.88 mM solutions of [PyBP][NO$_3$]$_2$ (blue), BPP34C10 (red), and [PyBP/BPP34C10][NO$_3$]$_2$ (green) in a 1:1 mixture of CH$_3$OH and CHCl$_3$ at 25 °C.

3.1.2.2. [CpBP/neutral crown ether][NO$_3$]$_2$ [2]pseudorotaxanes

The $^1$H–NMR spectra of [CpBP/neutral crown ether] pseudorotaxanes were recorded in a 2:1 mixture of CD$_3$OD and CDCl$_3$. Similarly to the chemical shift changes of the [PyBP]$^{2+}$ pseudorotaxanes, the NMR peaks of the [CpBP]$^{2+}$ axle in the $\delta = 7.98$–9.56 ppm region shifted upfield, while the ones of the wheel in the $\delta = 6.72$–7.71 ppm region shifted downfield due to pseudorotaxane formation (Table 3.3).

3.1.2.3. [C4BP/neutral crown ether][PF$_6$]$_2$ [2]pseudorotaxanes

The $^1$H–NMR spectra of [C4BP/neutral crown ether] pseudorotaxanes were recorded in a 2:1 mixture of acetone–d$_6$ and CDCl$_3$. The significant upfield shifts of the NMR
resonances of the [C4BP]^{2+} axle in the δ = 8.77–9.38 ppm region (H_a and H_b protons) and the downfield shifts of the wheel peaks in the δ = 6.72–7.72 ppm region (H_h, H_i and H_j protons) are an indication of the interaction between the 4,4′-bipyridinium core of the [C4BP]^{2+} axle and the neutral crown ether wheels (Table 3.4).

3.1.2.4. [axle/DSBPP34C10] [2]pseudorotaxanes

The $^1$H–NMR spectra of [C4BP/DSBPP34C10] pseudorotaxanes were recorded in a 2:1 mixture of acetone-d_6:CDCl_3, while the ones of the [PyBP/DSBPP34C10] and the [CpBP/DSBPP34C10] [2]pseudorotaxanes were recorded in CD_3OD (Table 3.5 and 3.6). Since a mixture of syn– and anti– isomers of DSBPP34C10 were used, two distinct sets of aromatic peaks were observed in the aromatic region of the crown ethers (but only one set in the aliphatic region). Similar to the previous [2]pseudorotaxanes, with neutral crown ethers, the peaks of the axle shifted upfield, while the peaks of the crown ether peaks shifted downfield.

![Proton assignment of axles and wheels.](image)

**Figure 3.6:** Proton assignment of axles and wheels.
In the case of the [2]pseudorotaxanes discussed above, π–π stacking interactions between the 4,4′-bipyridinium core and aromatic rings (bis-phenyl or bis-naphtho) of the crown ethers shield the axle protons. As a result, the axle protons shift upfield, while the crown ether peaks shift downfield.


In the case of the [PyBP/neutral crown ether]^{2+} [2]pseudorotaxanes, the chemical shift of H_d proton increases as follows: [PyBP/BPP34C10][NO_3]_2 (0.49) < [PyBP/BN38C10][NO_3]_2 (0.70) < [PyBP/BN328][NO_3]_2 (0.77). The magnitude of the chemical shift change of the H_d proton in each [2]pseudorotaxane system is given within parentheses and they are correlated to the association constant measurements discussed in Section 3.1.4. As with the [PyBP/neutral crown ether]^{2+} [2]pseudorotaxanes, the same correlation of the chemical shift change and the binding constant values were observed for all other [2]pseudorotaxanes studied here.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>δ (Δδ) for H₆/ppm</th>
<th>δ (Δδ) for H₇/ppm</th>
<th>δ (Δδ) for H₈/ppm</th>
<th>δ (Δδ) for H₉/ppm</th>
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<td>[PyBP][NO₃]₂</td>
<td>CD₃OD:CDCl₃ = 1:1</td>
<td>9.82</td>
<td>9.30</td>
<td>9.17</td>
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<td></td>
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<tr>
<td>[PyBP/BPP34C10][NO₃]₂</td>
<td>CD₃OD:CDCl₃ = 1:1</td>
<td>9.47 (-0.35)</td>
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</tr>
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<td>[PyBP/BN38C10][NO₃]₂</td>
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<td>8.39 (+0.11)</td>
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<td>(d, J = 6.96 Hz, 4H)</td>
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<td>[PyBP/BN32C8][NO₃]₂</td>
<td>CD₃OD:CDCl₃ = 1:1</td>
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<td>(d, J = 6.60 Hz, 4H)</td>
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<table>
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<th>δ (Δδ) for H₇/ppm</th>
<th>δ (Δδ) for H₈/ppm</th>
<th>δ (Δδ) for H₉/ppm</th>
<th>δ (Δδ) for H₁₀/ppm</th>
<th>δ (Δδ) for H₁₁/ppm</th>
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<td>BPP34C10</td>
<td>CD₃OD:CDCl₃ = 1:1</td>
<td>6.71 (s, 8H)</td>
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<td></td>
<td>(m, 8H)</td>
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<td>[PyBP/BPP34C10][NO₃]₂</td>
<td>CD₃OD:CDCl₃ = 1:1</td>
<td>6.55 (-0.16)</td>
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<td></td>
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<tr>
<td>BN38C10</td>
<td>CD₃OD:CDCl₃ = 1:1</td>
<td>8.01 (d, J = 8.84 Hz, 4H)</td>
<td>7.45 (d, J = 8.06 Hz, 4H)</td>
<td>6.76 (d, J = 7.72 Hz, 4H)</td>
<td>4.22 (d, J = 3.12 Hz, 8H)</td>
<td>4.15 (d, J = 3.30 Hz, 8H)</td>
<td>4.01 (d, J = 3.30 Hz, 8H)</td>
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<td>(m, 8H)</td>
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<td>[PyBP/BN38C10][NO₃]₂</td>
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<td>7.76 (-0.25)</td>
<td>7.40 (-0.05)</td>
<td>6.74 (-0.02)</td>
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<td>CD₃OD:CDCl₃ = 1:1</td>
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<td>7.24 (d, J = 8.06 Hz, 4H)</td>
<td>6.81 (d, J = 7.72 Hz, 4H)</td>
<td>4.39 (d, J = 4.22 Hz, 8H)</td>
<td>4.21 (d, J = 4.04 Hz, 8H)</td>
<td>4.09 (s, 8H)</td>
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<td>(d, J = 8.44 Hz, 4H)</td>
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<tr>
<td>[PyBP/BN32C8][NO₃]₂</td>
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<td>7.63 (-0.21)</td>
<td>7.20 (-0.04)</td>
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<td>4.23 (+0.02)</td>
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<td>(d, J = 8.44 Hz, 4H)</td>
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**Table 3.2:** ¹H-NMR chemical shifts and chemical shift changes for the [PyBP][NO₃]₂ axle and its corresponding [2]pseudorotaxanes (top) and wheels and their [2]pseudorotaxanes (bottom), which undergo fast exchange on the NMR time scale.
<table>
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<tr>
<th>Compound</th>
<th>Solvent</th>
<th>δ (Δδ) for H₆/ppm</th>
<th>δ (Δδ) for H₅/ppm</th>
<th>δ (Δδ) for H₄/ppm</th>
<th>δ (Δδ) for H₃/ppm</th>
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<tr>
<td>[CpBP]Cl₂</td>
<td>CD₃OD:CDCl₃ = 2:1</td>
<td>9.56 (d, J = 5.48 Hz, 4H)</td>
<td>8.95 (d, J = 5.48 Hz, 4H)</td>
<td>8.39 (d, J = 8.04 Hz, 4H)</td>
<td>7.98 (d, J = 8.04 Hz, 4H)</td>
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<td>[CpBP/BPP34C10]Cl₂</td>
<td>CD₃OD:CDCl₃ = 2:1</td>
<td>9.48 (-0.08) (d, J = 6.60 Hz, 4H)</td>
<td>8.70 (-0.25) (d, J = 5.84 Hz, 4H)</td>
<td>8.40 (+0.01) (d, J = 8.40 Hz, 4H)</td>
<td>8.04 (+0.06) (d, J = 8.04 Hz, 4H)</td>
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<tr>
<td>[CpBP/BN38C10]·Cl₂</td>
<td>CD₃OD:CDCl₃ = 2:1</td>
<td>9.32 (-0.24) (d, J = 5.12 Hz, 4H)</td>
<td>8.44 (-0.51) (d, J = 8.44 Hz, 4H)</td>
<td>8.26 (-0.13) (s, 4H)</td>
<td>8.07 (+0.09) (d, J = 8.04 Hz, 4H)</td>
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<tr>
<td>[CpBP/BN32C8]Cl₂</td>
<td>CD₃OD:CDCl₃ = 2:1</td>
<td>9.23 (-0.33) (s, 4H)</td>
<td>8.44 (-0.51) (d, J = 8.04 Hz, 4H)</td>
<td>(-0.39) 8.00 (+0.02) (d, J = 8.04 Hz, 8H)</td>
<td>(-0.39) 8.00 (+0.02) (d, J = 8.04 Hz, 8H)</td>
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</table>

<table>
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<th>Compound</th>
<th>Solvent</th>
<th>δ (Δδ) for H₆/ppm</th>
<th>δ (Δδ) for H₅/ppm</th>
<th>δ (Δδ) for H₄/ppm</th>
<th>δ (Δδ) for H₃/ppm</th>
<th>δ (Δδ) for H₂/ppm</th>
<th>δ (Δδ) for H₁/ppm</th>
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</thead>
<tbody>
<tr>
<td>BPP34C10</td>
<td>CD₃OD:CDCl₃ = 2:1</td>
<td>6.72 (s, 8H)</td>
<td>3.94 (m, 8H)</td>
<td>3.81 (m, 8H)</td>
<td>3.68 (m, 16H)</td>
<td></td>
<td></td>
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<tr>
<td>[CpBP/BPP34C10]Cl₂</td>
<td>CD₃OD:CDCl₃ = 2:1</td>
<td>6.54 (-0.18) (s, 8H)</td>
<td>3.83 (-0.11) (m, 8H)</td>
<td>3.73 (-0.09) (m, 8H)</td>
<td>3.59 (-0.09) (m, 16H)</td>
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<td>BN38C10</td>
<td>CD₃OD:CDCl₃ = 2:1</td>
<td>7.71 (d, J = 8.44 Hz, 4H)</td>
<td>7.15 (t, J = 8.06 Hz, 4H)</td>
<td>6.48 (t, J = 8.06 Hz, 4H)</td>
<td>3.98 (t, J = 7.72 Hz, 4H)</td>
<td>3.89 (m, 8H)</td>
<td>3.72 (m, 16H)</td>
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<td>[CpBP/BN38C10]Cl₂</td>
<td>CD₃OD:CDCl₃ = 2:1</td>
<td>7.41 (-0.30) (d, J = 8.40 Hz, 4H)</td>
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<td>3.70 (-0.02) (m, 16H)</td>
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<td>BN32C8</td>
<td>CD₃OD:CDCl₃ = 2:1</td>
<td>7.52 (d, J = 8.44 Hz, 4H)</td>
<td>6.94 (t, J = 8.04 Hz, 4H)</td>
<td>6.54 (d, J = 7.68 Hz, 4H)</td>
<td>4.09 (m, 8H)</td>
<td>3.91 (m, 8H)</td>
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<td>[CpBP/BN32C8]Cl₂</td>
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<td>6.49 (-0.05) (s, 4H)</td>
<td>4.05 (-0.04) (s, 4H)</td>
<td>3.94 (+0.03) (s, 8H)</td>
<td>3.84 (+0.05) (s, 8H)</td>
</tr>
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</table>

**Table 3.3:** ¹H-NMR chemical shifts and chemical shift changes for the [CpBP]Cl₂ axle and its corresponding [2]pseudorotaxanes (top) and wheels and their [2]pseudorotaxanes (bottom), which undergo fast exchange on the NMR time scale.
<table>
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<th>δ (Δδ) for H_3/ ppm</th>
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<th>δ (Δδ) for H_6/ ppm</th>
<th>δ (Δδ) for H_7/ ppm</th>
<th>δ (Δδ) for H_8/ ppm</th>
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<td>Acetone-d6:</td>
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<td>8.77</td>
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<td>4.06</td>
<td>2.52</td>
<td>2.44</td>
<td>1.18</td>
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<td>CDCl_3 = 2:1</td>
<td>(d, J = 7.00 Hz, 4H)</td>
<td>(d, J = 6.20 Hz, 4H)</td>
<td>(t, J = 7.40 Hz, 4H)</td>
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<td>(t, J = 7.10 Hz, 4H)</td>
<td>(q, J = 7.10 Hz, 4H)</td>
<td>(t, J = 7.30 Hz, 6H)</td>
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<td>Acetone-d6:</td>
<td>9.26 (-0.12)</td>
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<td>(d, J = 6.60 Hz, 4H)</td>
<td>(d, J = 6.60 Hz, 4H)</td>
<td>(t, J = 7.50 Hz, 4H)</td>
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<td>CDCl_3 = 2:1</td>
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<td>(s, 4H)</td>
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<td>3.77</td>
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<td>(m, 8H)</td>
<td>(m, 8H)</td>
<td>(m, 16H)</td>
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<td>4.04</td>
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<td>(t, J = 8.10 Hz, 4H)</td>
<td>(t, J = 7.70 Hz, 4H)</td>
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</tr>
<tr>
<td>[C4BP/BN38C10][PF_6]_2</td>
<td>Acetone-d6:</td>
<td>7.22 (-0.50)</td>
<td>7.05 (-0.10)</td>
<td>6.54 (+0.02)</td>
<td>3.99 (-0.05)</td>
</tr>
<tr>
<td></td>
<td>CDCl_3 = 2:1</td>
<td>(d, J = 8.08 Hz, 4H)</td>
<td>(t, J = 8.10 Hz, 4H)</td>
<td>(t, J = 7.70 Hz, 4H)</td>
<td>(d, J = 4.40 Hz, 8H)</td>
</tr>
<tr>
<td>BN32C8</td>
<td>Acetone-d6:</td>
<td>7.55</td>
<td>6.93</td>
<td>6.59</td>
<td>4.12</td>
</tr>
<tr>
<td></td>
<td>CDCl_3 = 2:1</td>
<td>(d, J = 8.40 Hz, 4H)</td>
<td>(t, J = 8.10 Hz, 4H)</td>
<td>(t, J = 7.70 Hz, 4H)</td>
<td>(d, J = 4.80 Hz, 8H)</td>
</tr>
<tr>
<td>[C4BP/BN32C8][PF_6]_2</td>
<td>Acetone-d6:</td>
<td>7.30 (-0.25)</td>
<td>6.94 (-0.01)</td>
<td>6.60 (+0.01)</td>
<td>4.12 (0.00)</td>
</tr>
<tr>
<td></td>
<td>CDCl_3 = 2:1</td>
<td>(s, 4H)</td>
<td>(t, J = 8.10 Hz, 4H)</td>
<td>(d, J = 7.70 Hz, 4H)</td>
<td>(d, J = 4.40 Hz, 8H)</td>
</tr>
</tbody>
</table>

Table 3.4: 1H-NMR chemical shifts and chemical shift changes for the [C4BP][PF_6]_2 axle and its corresponding [2]pseudorotaxanes (top) and wheels and their [2]pseudorotaxanes (bottom), which undergo fast exchange on the NMR time scale.
Table 3.5: $^1$H-NMR chemical shifts and chemical shift changes for the syn- and anti- [TBA]$_2$DSBPP34C10 wheels and their corresponding [2]pseudorotaxanes.
Table 3.6: $^1$H-NMR chemical shifts and chemical shift changes for the [axle/syn- and anti-DSBPP34C10] pseudorotaxane with the axle, which undergo fast exchange on the NMR time scale.
3.1.3. Axle-to-wheel molar ratio of pseudorotaxanes

The Job’s plot method\textsuperscript{118} is commonly used in determination of reaction stoichiometries. It can also be used to determine the molar ratio between the axle and the wheel components of the pseudorotaxane. In solution, ‘a’ number of moles of axles undergo self assembly with ‘b’ number of moles of wheels to yield \([a+b]\) pseudorotaxanes (Equation 1):

\[
 a\text{Axle} + b\text{Wheel} \rightleftharpoons [a+b]\text{Pseudorotaxane} \tag{1}
\]

Pseudorotaxane solutions were prepared by mixing different volumes of the axle and the wheel so that the total number of moles of the axle and the wheel, \([\text{Axle}]_0+[	ext{Wheel}]_0 = M\), remain constant, while \([\text{Axle}]_0/[\text{Wheel}]_0\) varies (where \([\text{Axle}]_0\) and \([\text{Wheel}]_0\) are initial concentrations of the axle and the wheel, respectively). Monitoring the change of a physical or chemical property which is proportional to the concentration of pseudorotaxanes allows us to construct a plot of \([\text{pseudorotaxane}]\) against \([\text{Wheel}]/([\text{Wheel}]+[\text{Axle}])\) or \([\text{Axle}]/([\text{Wheel}]+[\text{Axle}])\). This plot shows that the concentration of the pseudorotaxane has a maximum for the axle to wheel molar ratio which is equal to \(alb\). In the case of UV-Vis spectroscopic method, the absorbance of the pseudorotaxane solution is proportional to the pseudorotaxane concentration while the product of chemical shift change and initial concentration of the axle or wheel of the pseudorotaxane solution is proportional to the pseudorotaxane in the NMR spectroscopic method.\textsuperscript{124,125}

The UV–visible spectroscopic method has been used for all pseudorotaxanes except \([\text{PyBP/BPP34C10}]\text{[NO}_3\text{]}_2\) and \([\text{CpBP/BPP34C10}]\text{Cl}_2\), because the absorbance that arises from axles and pseudorotaxanes appeared at similar wavelength. Therefore, the NMR
spectroscopic method was employed for [PyBP/BPP34C10][NO₃]₂ and [CpBP/BPP34C10]Cl₂ pseudorotaxanes. Representative Job’s plots for each pseudorotaxane system are shown in Figure 3.7; all other Job’s plots are shown in Appendix B.

![Figure 3.7: Job’s plots of A) [PyBP/BPP34C10][NO₃]₂, B) [CpBP/BPP34C10]Cl₂, C) [C₄BP/BPP34C10][PF₆]₂ and D) [PyBP/DSBPP34C10] [2]pseudorotaxanes.](image)

Figure 3.7a and b show the maxima of (chemical shift change x [axle or wheel]), while Figure 3.7c and d show the highest absorbance (at their λ_max) at 1:1 molar ratio of
axle:wheel. It indicates that in pseudorotaxanes the axle and the wheel form a 1:1 complex.

Table 3.7 summarizes the axle-to-wheel molar ratios and solvents for all pseudorotaxanes studied. The pseudorotaxanes that consist of a 4,4′-bipyridinium core and bis-naphtho or bis-p-phenylene crown ethers show 1:1 complexation in solution. In contrast, the pseudorotaxanes with 4,4′-bipyridinium axles and dibenzo-24-crown-8 (DB24C8) show a 1:2 axle:wheel ratio both in solution\textsuperscript{126} and in the solid state (discussed in Section 3.1.5).

<table>
<thead>
<tr>
<th>Axle</th>
<th>Wheel</th>
<th>Solvent/ solvent mixture</th>
<th>Axle: Wheel molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C4BP][PF₆]₂</td>
<td>BPP34C10</td>
<td>CH₃CN: CHCl₃ = 1:1</td>
<td>1:1</td>
</tr>
<tr>
<td></td>
<td>BN38C10</td>
<td>CH₃CN: CHCl₃ = 1:1</td>
<td>1:1</td>
</tr>
<tr>
<td></td>
<td>BN32C8</td>
<td>CH₃CN: CHCl₃ = 1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>[PyBP][NO₃]₂</td>
<td>BPP34C10</td>
<td>CD₂OD: CDCl₃ = 1:1</td>
<td>1:1</td>
</tr>
<tr>
<td></td>
<td>BN38C10</td>
<td>CH₃OH: CHCl₃ = 1:1</td>
<td>1:1</td>
</tr>
<tr>
<td></td>
<td>BN32C8</td>
<td>CH₃OH: CHCl₃ = 1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>[CpBP]Cl₂</td>
<td>BPP34C10</td>
<td>CD₂OD: CDCl₃ = 1:1</td>
<td>1:1</td>
</tr>
<tr>
<td></td>
<td>BN38C10</td>
<td>CH₃OH: CHCl₃ = 1:1</td>
<td>1:1</td>
</tr>
<tr>
<td></td>
<td>BN32C8</td>
<td>CH₃OH: CHCl₃ = 1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>[C4BP][PF₆]₂</td>
<td>DSBPP34C10</td>
<td>CH₃OH</td>
<td>1:1</td>
</tr>
<tr>
<td>[PyBP][NO₃]₂</td>
<td>BPP34C10</td>
<td>CH₃OH</td>
<td>1:1</td>
</tr>
<tr>
<td>[CpBP]Cl₂</td>
<td>BPP34C10</td>
<td>CH₃OH</td>
<td>1:1</td>
</tr>
</tbody>
</table>

Table 3.7: Axle: wheel molar ratios of pseudorotaxanes.
3.1.4. Association constant studies

The Benesi-Hildebrand method\textsuperscript{119} or the dilution method\textsuperscript{120,121} was employed to determine the association constant of [2]pseudorotaxanes. UV–Visible spectroscopy or $^1\text{H}$–NMR spectroscopy techniques were used to collect the data.

3.1.4.1. Benesi-Hildebrand method using UV-vis spectroscopy

In solution, the axle and the wheel undergo an equilibrium process to form [2]pseudorotaxane (Equation 2):

$$\text{Axle} + \text{Wheel} \rightleftharpoons \text{Pseudorotaxane}$$

where $K_a$ is the equilibrium constant. Then, $K_a$ can be written as:

$$K_a = \frac{[\text{Pseudorotaxane}]}{[\text{Axle}][\text{Wheel}]}$$

$$K_a = \frac{c_p}{(c_A^0 - c_p)(c_W^0 - c_p)}$$

where $c_p$ is the concentration of the [2]pseudorotaxane, $c_A^0$ is the initial concentration of the axle and $c_W^0$ is the initial concentration of the wheel.

When $c_W^0 \gg c_A^0$, $(c_W^0 - c_p) = c_W^0$ and and $c_p = A/\varepsilon l$, equation (4) can be rearranged as:

$$\frac{c_W^0}{A} = \frac{1}{(K_a\varepsilon)} \frac{1}{c_A^0} + \frac{1}{\varepsilon}$$

The plot of $\frac{c_W^0}{A}$ vs $\frac{1}{c_A^0}$ gives a straight line with a slope of $\frac{1}{(K_a\varepsilon)}$ and an intercept of $\frac{1}{\varepsilon}$.

When $c_A^0 \gg c_W^0$ and $c_p = A/\varepsilon l$, equation (4) can be rearranged as:

$$\frac{c_A^0}{A} = \frac{1}{(K_a\varepsilon)} \frac{1}{c_W^0} + \frac{1}{\varepsilon}$$
The plot of $\frac{c_A^2}{A}$ vs $\frac{1}{c_{WP}^0}$ gives a straight line with a slope of $\frac{1}{(K_a \epsilon)}$ and an intercept of $\frac{1}{\epsilon}$.

Association constants and molar extinction coefficients for the different pseudorotaxanes were determined using equation (6).

1.1.4.2. Benesi-Hildebrand method using $^1$H–NMR spectroscopy

The NMR version of the Benesi-Hildebrand method was independently derived by Norman C. Li$^{127}$ and Alan L. Ahsbaugh$^{128}$. Gibson and coworkers$^{129}$ used this method to determine association constants of pseudorotaxanes. The [2]pseudorotaxane equilibrium represented by equation (2) depends on the association constant $K_a$ and the rate of the threading–dethreading process. The following equations are derived for the [2]pseudorotaxane which undergoes a fast equilibrium process on NMR time scale and shows only one set of time averaged peaks of the axle, the wheel and the [2]pseudorotaxane. Under these circumstances, the observed chemical shift ($\delta_{obs}$) of any species present in the mixture is the weight average of the characteristic frequencies of the free and complexed molecules.

$$\delta_{obs} = X_A \delta_F + X_P \delta_C$$

(7)

$$\delta_{obs} = \delta_A + X_P \Delta_0$$

(8)

where $X_A$ and $X_P$ are molar fractions of the free axle and the pseudorotaxane.

$$\Delta_0 = \delta_F - \delta_C$$

$$\Delta = \delta_F - \delta$$

where $\delta_F$ is the chemical shift of the free guest, $\delta_C$ is the chemical shift of the fully complexed guest and $\delta$ is the time averaged chemical shift of the titrant.
When \( X_A \gg X_W \), equation (9) can be obtained after a number of refinement steps:

\[
\frac{1}{\Delta} = \frac{1}{K_{A\Delta}} X \frac{1}{[Axle]} + \frac{1}{\Delta} \tag{9}
\]

The concentration of the guest can be obtained as:

\[
[Axle] = [Axle]_0 - \left( \frac{\Delta}{\Delta_0} [Wheel]_0 \right) \tag{10}
\]

The double reciprocal plot of \( \frac{1}{\Delta} \) vs \( \frac{1}{[\text{tritrant}]_0} \) gives a straight line with a slope of \( \frac{1}{(K_{A\Delta})} \) and an intercept of \( \frac{1}{\Delta_0} \).

1.1.4.3. Dilution method by UV-vis spectroscopy

The dilution method was originally developed by Ray\textsuperscript{130} and adopted by Stoddart\textsuperscript{120} for pseudorotaxanes. A 1:1 complexation of the axle and the wheel is essential when using this method, as well as equimolar solution of the axle and the wheel. Sequential dilution followed by the recording of optical absorption spectra is involved in this method.

\[
[Axle] + [Pseudorotaxane] = C_T \tag{11}
\]

\[
[Wheel] + [Pseudorotaxane] = C_T \tag{12}
\]

where \( C_T \) is the total concentration of the axle or the wheel in the solution.

When the equilibrium concentration of the pseudorotaxane is \( C_p \), equation (2) can be rearranged as:

\[
K_a = \frac{C_p}{(C_T-C_p)^2} \tag{13}
\]

The measured total absorbance \( A_T \) of the pseudorotaxane solution at a particular wavelength is the sum of the absorbance of the free axle, free wheel and the [2]pseudorotaxane.

\[
A_T = A_P + A_W + A_A \tag{14}
\]
where \( A_p \) is the absorbance of the [2]pseudorotaxane, \( A_w \) is the absorbance of the uncomplexed wheel and \( A_a \) is the absorbance of the uncomplexed axle. Assuming that all species obey the Beer-Lambert law:

\[
A_T = \varepsilon_p C_p l + \varepsilon_w (C_T - C_p) l + \varepsilon_a (C_T - C_p) l
\]  \hspace{1cm} (15)

where, \( \varepsilon_p \), \( \varepsilon_a \) and \( \varepsilon_w \) are molar extinction coefficients of the pseudorotaxane, the axle and the wheel, respectively. Crown ethers show no absorbance at the \( \lambda_{\text{max}} \) of the pseudorotaxane. Therefore,

\( \varepsilon_a (C_T - C_p) l = 0 \) and equation (13) can be rearranged as:

\[
C_p = \frac{A_T - \varepsilon_a C_T l}{(\varepsilon_p - \varepsilon_a) l}
\]  \hspace{1cm} (16)

For convenience, \( A = A_T - \varepsilon_a C_T l \) and \( \varepsilon = (\varepsilon_p - \varepsilon_a) l \). Then equation (18) can be written as:

\[
C_p = \frac{A}{\varepsilon l}
\]  \hspace{1cm} (17)

By combining equations (15) and (19), equation (20) can be obtained:

\[
\frac{C}{A} = \frac{1}{(K_a \varepsilon l)^{1/2}} \times \frac{1}{A^{1/2}} + \frac{1}{\varepsilon l}
\]  \hspace{1cm} (18)

The plot of \( \frac{C}{A} \) vs \( \frac{1}{A^{1/2}} \) gives a straight line with a slope of \( \frac{1}{(K_a \varepsilon l)} \) and an intercept of \( \frac{1}{\varepsilon l} \). Association constants and molar extinction coefficients for the different pseudorotaxanes were determined using equation (18).
3.1.4.4. [PyBP/neutral crown ether][NO₃]₂ [2]pseudorotaxanes

Since the [PyBP][NO₃]₂ axle has a low solubility in a 1:1 mixture of CH₃OH and CHCl₃ compared to the neutral crown ethers, the axle solution was always titrated with the [2]pseudorotaxane solution. The [PyBP/BN32C10][NO₃]₂⁺ [2]pseudorotaxane shows the highest association constant compared to the other two [2]pseudorotaxanes (Table 3.8).

<table>
<thead>
<tr>
<th>[2]Pseudorotaxane</th>
<th>Solvent mixture</th>
<th>Association constant/ M⁻¹</th>
<th>Molar extinction coefficient/ Lmol⁻¹cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PyBP/BPP34C10][NO₃]₂</td>
<td>CD₃OD: CDCl₃ (1/1)</td>
<td>1.69 (±0.23) x 10²</td>
<td>–</td>
</tr>
<tr>
<td>[PyBP/BN38C10][NO₃]₂</td>
<td>CH₃OH: CHCl₃ (1/1)</td>
<td>4.20 (± 0.20) x 10²</td>
<td>7.90 (± 0.40) x 10²</td>
</tr>
<tr>
<td>[PyBP/BN32C8][NO₃]₂</td>
<td>CH₃OH: CHCl₃ (1/1)</td>
<td>8.70 (± 0.70) x 10²</td>
<td>1.20 (± 0.10) x 10³</td>
</tr>
</tbody>
</table>


The Benesi-Hildebrand plots of [PyBP/BPP34C10]²⁺ [2]pseudorotaxanes are shown in Figure 3.8A. (See Appendix B for all other Benesi-Hildebrand plots.)
Figure 3.8: Benesi-Hildebrand plots of A) [PyBP/BPP34C10][NO$_3$]$_2$, B) [CpBP/BPP34C10]Cl$_2$, C) [C4BP/BPP34C10][PF$_6$]$_2$ and D) [PyBP/DSBPP34C10] [2]pseudorotaxanes

3.1.4.5. [CpBP/neutral crown ether]Cl$_2$ [2]pseudorotaxanes

The [CpBP]Cl$_2$ axle was titrated with BPP34C10 in pure CD$_3$OD since both compounds are soluble in CH$_3$OH. Since the BN38C10 and BN32C8 crown ethers are not soluble in pure CH$_3$OH, a 1:1 mixture of CH$_3$OH and CHCl$_3$ was used as the solvent in this case. Because the axle and the wheel have low solubility, in the CH$_3$OH:CHCl$_3$ mixture, the dilution method was employed instead of the Benesi-Hildebrand method to prevent the precipitation at higher concentrations.
The association constant values of [CpBP/neutral crown ether]Cl₂ show the same trend as the ones of the [PyBP/neutral crown ether][NO₃]₂ [2]pseudorotaxanes (Table 3.9). The Benesi-Hildebrand plot of [CpBP/BPP34C10]²⁺ [2]pseudorotaxanes are shown in Figure 3.8B.

<table>
<thead>
<tr>
<th>[2]pseudorotaxane</th>
<th>Solvent mixture</th>
<th>Association constant/ M⁻¹</th>
<th>Molar extinction coefficient/ Lmol⁻¹cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpBP/BPP34C10]Cl₂</td>
<td>CD₂OD</td>
<td>1.62 (±0.49) x 10²</td>
<td>–</td>
</tr>
<tr>
<td>[CpBP/BN38C10]Cl₂</td>
<td>CH₃OH:CHCl₃ (1/1)</td>
<td>4.80 (± 0.20) x 10²</td>
<td>7.00 (± 0.30) x 10²</td>
</tr>
<tr>
<td>[CpBP/BN32C8]Cl₂</td>
<td>CH₃OH:CHCl₃ (1/1)</td>
<td>9.70 (± 0.70) x 10²</td>
<td>1.04 (± 0.11) x 10³</td>
</tr>
</tbody>
</table>

**Table 3.9:** Association constants and molar extinction coefficient values of [CpBP/neutral crown ether]Cl₂ [2]pseudorotaxanes.

3.1.4.6 [C4BP/neutral crown ether][PF₆]₂ [2]pseudorotaxanes

The axle solution was titrated with the [2]pseudorotaxane solution which has the same axle concentration and 10 times higher wheel concentration. Constant axle concentration was maintained throughout the titration and a 1:5 ratio of axle:wheel was obtained at the end.

Among the [C4BP/neutral crown ethers][PF₆]₂ pseudorotaxanes, the association constant decreases in the order: [C4BP/BN32C8][PF₆]₂ > [C4BP/BN38C10][PF₆]₂ > [C4BP/BPP34C10][PF₆]₂. These results reveal that the bis-naphtho crown ethers bind stronger than the bis-\(\beta\)-phenylene crown ether, BPP34C10 (Table 3.10). The Benesi-Hildebrand plots of [C4BP/BPP34C10]²⁺ [2]pseudorotaxanes are shown in Figure 3.8C.
<table>
<thead>
<tr>
<th>[2]pseudorotaxane</th>
<th>Solvent mixture</th>
<th>Association constant/ M$^{-1}$</th>
<th>Molar extinction coefficient/ Lmol$^{-1}$cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C4BP/BPP34C10][PF$_6$]$_2$</td>
<td>CH$_3$CN:CHCl$_3$ (1/1)</td>
<td>1.0 (±0.2) x 10$^2$</td>
<td>6.3 (±0.8) x 10$^2$</td>
</tr>
<tr>
<td>[C4BP/BN38C10][PF$_6$]$_2$</td>
<td>CH$_3$CN:CHCl$_3$ (1/1)</td>
<td>2.4 (±0.3) x 10$^2$</td>
<td>1.0 (±0.1) x 10$^3$</td>
</tr>
<tr>
<td>[C4BP/BN32C8][PF$_6$]$_2$</td>
<td>CH$_3$CN:CHCl$_3$ (1/1)</td>
<td>1.7 (±0.3) x 10$^2$</td>
<td>1.3 (±0.1) x 10$^4$</td>
</tr>
</tbody>
</table>

**Table 3.10:** Association constants and molar extinction coefficients of [C4BP/neutral crown ether][PF$_6$]$_2$ [2]pseudorotaxanes.

3.1.4.7. [syn- and anti-DSBPP34C10/axle] [2]pseudorotaxanes

The interactions between sulphonated crown ethers and positively charged axles are complicated in less polar solvents by ion-pairing effects.\(^8\) Even though non-covalent interactions are less prominent in highly polar solvents, the TBA salt of syn- and anti-DSBPP34C10 crown ethers forms [2]pseudorotaxanes with 4,4′-bipyridinium-based axles even in pure water. Association constant measurements of [syn- and anti-DSBPP34C10/axle] [2]pseudorotaxanes were carried out in water. [Syn- and anti-DSBPP34C10/axle] [2]pseudorotaxanes show stronger interactions compared to the non-sulphonated analog of the crown ether (Table 3.11). Benesi-Hildebrand plots of [PyBP/BPP34C10]$^{2+}$ [2]pseudorotaxanes are shown in Figure 3.8A. Loeb,\(^8\) Fitzmaurice\(^7\) and coworkers have shown that addition of an anionic group such as SO$_3^{-}$ or CO$_2^{-}$ increases the association with a di-cationic axle. This significant change in the association constants is a result of electrostatic ion-ion interactions in addition to hydrogen bonds, ion-dipole interactions and π–π stacking between the axle and the wheel components of [2]pseudorotaxanes.
Axle  | $K_a$ of [axle/BPP34C10] [2]pseudorotaxane / M$^{-1}$ | $K_a$ of [axle/syn- and anti-DSBPP34C10] [2]pseudorotaxane in H$_2$O/ M$^{-1}$ | Molar extinction coefficient of [axle/syn- and anti-DSBPP34C10] [2]pseudorotaxane in H$_2$O/ Lmol$^{-1}$cm$^{-1}$ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[C4BP][PF$_6$]$_2$</td>
<td>1.0 ($\pm 0.2$) x $10^4$ in CH$_3$CN:CHCl$_3$ (1/1)</td>
<td>7.39 ($\pm 0.91$) x $10^2$</td>
<td>4.20 ($\pm 0.42$) x $10^2$</td>
</tr>
<tr>
<td>[PyBP][NO$_3$]$_2$</td>
<td>1.69 ($\pm 0.23$) x $10^2$ in CH$_3$OH:CHCl$_3$ (1/1)</td>
<td>2.63 ($\pm 0.23$) x $10^3$</td>
<td>1.82 ($\pm 0.03$) x $10^2$</td>
</tr>
<tr>
<td>[CpBP]Cl$_2$</td>
<td>1.62 ($\pm 0.49$) x $10^2$ in CH$_3$OH:CHCl$_3$ (1/1)</td>
<td>1.34 ($\pm 0.07$) x $10^3$</td>
<td>1.87 ($\pm 0.12$) x $10^2$</td>
</tr>
</tbody>
</table>

Table 3.11: Association constants and molar extinction coefficients of [syn- and anti-DSBPP34C10/axle] [2]pseudorotaxanes compared to their non-sulphonated analogs.

In the case of the [4,4′-bipyridinium/neutral crown ether] [2]pseudorotaxanes, the [4,4′-bipyridinium/binaphtho] [2]pseudorotaxanes show stronger association than the [4,4′-bipyridinium/bis-p-phenylene] [2]pseudorotaxanes, due to stronger $\pi-\pi$ interactions between the naphtho groups of the wheel and the 4,4′-bipyridinium core of the axle.

Table 3.10 shows a comparison of the association constants of [4,4′-bipyridinium/BPP34C10] and [4,4′-bipyridinium/DSBPP34C10] [2]pseudorotaxanes. By introducing two negative charges on the wheel, a tenfold increase of the association constant was observed, even in a highly polar aqueous medium. This is a consequence of the strong electrostatic interaction between the (+2) positively charged axle and the (−2) negatively charged wheel.
3.1.5. Electrochemistry studies

The pseudorotaxanes discussed in this section exhibit interesting electrochemical behavior due to the redox-active character of the 4,4′-bipyridinium core of the axle. The electrochemistry of viologens (diquaternized form of 4,4′-bipyridine: disubsituted-4,4′-bipyridinium salts) is well understood and is comprised of two consecutive single electron reductions (Figure 3.9).

![Figure 3.9: Three common redox forms of viologens: V^{2+}, bipyridinium dication; V^{+*}, bipyridinium radical cation; V^0, di-reduced bipyridinium compound.](image)

Electrochemistry studies of [2]pseudorotaxanes provide the half–wave reduction potential of the axle and the oxidation potential of the wheel, which are measures of the strength of inter-component interactions. Upon complexation of crown ethers with 4,4′-bipyridinium-containing axles, the reduction potential of the viologen moiety shifts towards more negative values, revealing that the presence of the crown ether facilitates the reduction. The stronger the inter-component interactions, the larger the shift of the reduction potential.

The cyclic voltammograms of the [4,4′-bipyridinium/crown ether]^{2+} [2]pseudorotaxanes show two reductions for the axle and an oxidation for the crown ether. The first and second reduction potentials are related to radical cation V^{+*} and di-reduced V^0 formation, respectively (Figure 3.10).

The cyclic voltagrams of [PyBP][PF$_6$]$_2$, crown ethers and its [2]pseudorotaxanes show two reversible reduction peaks for the 4,4$'$-bipyridinium core of the axle (Figure 3.11). The reduction potentials of pure [PyBP][PF$_6$]$_2$ axle appear at $-481$ mV and $-720$ mV. The half-wave reduction potentials of the viologen moieties of [2]pseudorotaxanes shifted to less negative values compared to those of the pure axle. This may be due to the low [2]pseudorotaxane percentage in the solution at low concentration (0.5 mM). However, the reduction potential values (Table 3.12) decrease in the order [PyBP/BPP34C10][PF$_6$]$_4$ $>$ [PyBP/BN38C10][PF$_6$]$_4$ $>$ [PyBP/BN32C8][PF$_6$]$_4$, which correlates with the association constant values discussed in Section 3.1.4.1.
Figure 3.11: Overlaid cyclic voltammograms of [PyBP][PF$_6$]$_2$ (black), [PyBP/BN38C10][PF$_6$]$_2$ (red) and [PyBP/BN32C8][PF$_6$]$_2$ (blue).


<table>
<thead>
<tr>
<th>Axle</th>
<th>wheel</th>
<th>[2]pseudorotaxane</th>
<th>$V^{2+}/V^{**}$ potential/ mV</th>
<th>$V^{**}/V^0$ potential/ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PyBP][PF$_6$]$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1.5.2. [CpBP/neutral crown ether]Cl$_2$ [2]pseudorotaxanes

The cyclic voltammogram of [CpBP/neutral crown ether]Cl$_2$ shows that as expected, the first and the second reduction potential of the axle in [2]pseudorotaxanes shifted towards more negative values compared to the pure axle (–535 mV and –957 mV). [CpBP/BN32C8]Cl$_2$ [2]pseudorotaxane shows the lowest reduction potentials while [CpBP/BPP34C10]Cl$_2$ [2]pseudorotaxane shows the highest reduction potential among [2]pseudorotaxanes (Table 3.13), which is correlated with the association constant values
discussed in Section 3.1.4.2. Interestingly, the second oxidation peak of the [2]pseudorotaxanes (Figure 3.12a-c) is sharp which reveals the strong adsorption of the fully reduced species on the electrode surface.\(^{133}\)

![Cyclic voltammograms](image)

**Figure 3.12:** Overlaid cyclic voltammograms of A) [CpBP/BPP34C10]Cl\(_2\) [2]pseudorotaxanes (golden brown) B) [CpBP/BN38C10]Cl\(_2\) [2]pseudorotaxanes (brownish red), C) [CpBP/BN32C8]Cl\(_2\) pseudorotaxane (magenta) and D) [CpBP/syn- and anti- DSBP34C10] (black), with [CpBP]Cl\(_2\) (blue).

<table>
<thead>
<tr>
<th>Axle</th>
<th>wheel</th>
<th>[2]pseudorotaxane</th>
<th>(V^{2+}/V^{+}) potential/ mV</th>
<th>(V^{+}/V^{0}) potential/ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpBP]Cl(_2)</td>
<td>–</td>
<td>–</td>
<td>(-535)</td>
<td>(-957)</td>
</tr>
<tr>
<td>[CpBP]Cl(_2)</td>
<td>BPP34C10</td>
<td>[CpBP/BPP34C10]Cl(_2)</td>
<td>(-543.5)</td>
<td>(-959)</td>
</tr>
<tr>
<td>[CpBP]Cl(_2)</td>
<td>BN38C10</td>
<td>[CpBP/BN38C10]Cl(_2)</td>
<td>(-543.5)</td>
<td>(-960)</td>
</tr>
<tr>
<td>[CpBP]Cl(_2)</td>
<td>BN32C8</td>
<td>[CpBP/BN32C10]Cl(_2)</td>
<td>(-561.5)</td>
<td>(-989)</td>
</tr>
</tbody>
</table>

As shown in Figure 3.12d, the second oxidation peak of the [CpBP/syn- and anti-DSBPP34C10] [2]pseudorotaxanes is not easily recognizable as [CpBP/neutral crown ether]Cl₂ [2]pseudorotaxanes.

3.1.5.3. [C4BP/neutral crown ether][PF₆]₂ [2]pseudorotaxanes

As expected, the reduction potentials of the axle shift towards more negative values in [2]pseudorotaxanes, while the oxidation potentials of the crown ethers shift towards less positive values. The oxidation/reduction potential values (Table 3.14) decrease in the order [C4BP/BPP34C10][PF₆]₄ > [C4BP/BN38C10][PF₆]₄ > [C4BP/BN32C8][PF₆]₄, which correlates with the association constant values discussed in Section 3.1.4.3.

<table>
<thead>
<tr>
<th>Axle</th>
<th>wheel</th>
<th>[2]pseudorotaxane</th>
<th>( V^{2\text{+}}/V^{2\text{+}}^* ) potential/ mV</th>
<th>( V^{*2\text{+}}/V^{*2\text{+}}^\circ ) potential/ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C4BP][PF₆]₂</td>
<td>–</td>
<td>–</td>
<td>–760</td>
<td>–1200</td>
</tr>
<tr>
<td>[C4BP][PF₆]₂</td>
<td>BPP34C10</td>
<td>[C4BP/BPP34C10][PF₆]₂</td>
<td>–842</td>
<td>–960</td>
</tr>
<tr>
<td>[C4BP][PF₆]₂</td>
<td>BN38C10</td>
<td>[C4BP/BN38C10][PF₆]₂</td>
<td>–853</td>
<td>–972</td>
</tr>
<tr>
<td>[C4BP][PF₆]₂</td>
<td>BN32C8</td>
<td>[C4BP/BN32C10][PF₆]₂</td>
<td>–869</td>
<td>–991</td>
</tr>
</tbody>
</table>

3.1.6. Crystallographic studies

A number of pseudorotaxane crystals suitable for X-ray diffraction analysis were grown at −20 °C, for the following reasons: at low temperatures, 1) the equilibrium between individual components and pseudorotaxanes shifts to more pseudorotaxane formation, yielding a higher percentage of pseudorotaxane in the solution, and 2) the rate of the solution diffusion and crystal growing process becomes slower, which results in higher quality crystals.


X-ray quality, maroon-red, single crystals of [PyBP/BPP34C10][NO\textsubscript{3}]\textsubscript{2} [2]pseudorotaxane were grown by diffusing \textsuperscript{t}Pr\textsubscript{2}O into a [2]pseudorotaxane solution in CH\textsubscript{3}OH. All attempts to obtain X-ray quality single crystals of [PyBP/bis-naphtho crown ether][NO\textsubscript{3}]\textsubscript{2} [2]pseudorotaxanes at −20 °C or room temperature yielded light yellow precipitates of [PyBP][NO\textsubscript{3}]\textsubscript{2} and colorless crystals of the respective crown ethers. Fortunately, layering a solution of [PyBP/bis-naphtho crown ether][NO\textsubscript{3}]\textsubscript{2} [2]pseudorotaxanes in a 1:1 mixture of CH\textsubscript{3}OH:CH\textsubscript{3}Cl with methanolic solution of either NH\textsubscript{4}PF\textsubscript{6} or KSBF\textsubscript{6} yielded X-ray quality crystals of [PyBP/bis-naphtho crown ether]^{2+} [2]pseudorotaxanes as PF\textsubscript{6}− or SbF\textsubscript{6}− salt. Apparently, the exchange of the smaller NO\textsubscript{3}− ions to larger PF\textsubscript{6}− or SbF\textsubscript{6}− ions facilitates the crystal packing and the crystallization process.

Crystal structures of all [PyBP/bis-\textit{p}-phenylene or bis-naphtho neutral crown ether]^{2+} [2]pseudorotaxanes indicate a 1:1 complexation of the axle and the wheel in the solid state. In contrast, 1:2 complexation ratio of axle:wheel was observed in [PyBP/(DB24C8)\textsubscript{2}][NO\textsubscript{3}]\textsubscript{2} pseudorotaxanes in the solid state (Figure 3.13). The same 1:2
complexation behavior of the DB24C8 crown ether with 4,4′-bipyridinium cations bearing different aliphatic and aromatic substituents was reported by Nikitin et al.\textsuperscript{126}

**Figure 3.13**: Thermal ellipsoid plots of a) [PyBP/BPP34C10][NO\textsubscript{3}]\textsubscript{2} (50 %), b) [PyBP/BN32C8][SbF\textsubscript{6}]\textsubscript{2} (50 %), c) [PyBP/BN38C10][SbF\textsubscript{6}]\textsubscript{2} (30 %) and d) [PyBP/DB24C8][NO\textsubscript{3}]\textsubscript{2} (30 %) \textsuperscript{2}pseudorotaxanes. Hydrogen atoms and solvent molecules omitted for clarity. Color code: C, gray; N, blue; O, red; Sb, bluish gray; F, green.

In the crystal structures of [PyBP/neutral crown ether]\textsuperscript{2+} \textsuperscript{2}pseudorotaxanes, the pseudorotaxane units lie on inversion centers except for [PyBP/BPP34C10][NO\textsubscript{3}]\textsubscript{2}. The 4,4′-bipyridinium core of the axle is symmetrically located between the two aromatic
groups of bis-naphtho crown ethers, but it is asymmetrically located in bis-\( p \)-phenyl crown ethers. The centroid–centroid distances (\( \pi-\pi \) stacking interactions) between the aromatic rings of the crown ethers and the 4,4′-bipyridinium core of the axle are 3.630–3.714 \( \text{Å} \), 3.371(2) \( \text{Å} \) and 3.294(2) \( \text{Å} \) for [PyBP/BPP34C10]\(^{2+}\), [PyBP/BN38C10]\(^{2+}\) and [PyBP/BN32C8]\(^{2+}\), respectively. Multiple C–H···O hydrogen bonds with C–H···O angle larger than 120° and H···O distances of 2.527(2)–2.693(2) \( \text{Å} \), 2.438(2)–2.694(2) \( \text{Å} \) and 2.291(5)–2.979(5) \( \text{Å} \) were observed in [PyBP/BPP34C10]\(^{2+}\), [PyBP/BN38C10]\(^{2+}\) and [PyBP/BPP32C8]\(^{2+}\), respectively (Table 3.15 shows the summary of hydrogen bonding data of [PyBP/dis-naphtho crown ether]\(^{2+}\) [2]pseudorotaxanes). All [2]pseudorotaxane crystal structures show similar terminal N···N distances within the axle. The shortest N···N distance, 15.405(4) \( \text{Å} \), was observed in [PyBP/BPP34C10]\(^{2+}\), while the longest N···N distance, 15.421(4) \( \text{Å} \) was observed in [PyBP/BN38C10]\(^{2+}\). The N···N distance in [PyBP/BN32C8]\(^{2+}\) is 15.414(7) \( \text{Å} \). In all three crystal structures, the four aromatic groups of the axle are arranged in a non-planar geometry. Crystal structures of [PyBP/bis-naphtho crown ether]\(^{2+}\) [2]pseudorotaxanes show linear axle and co-planar 4,4′-bipyridinium core. The axle in [PyBP/BPP34C10]\(^{2+}\) is non-linear and the 4,4′-bipyridinium core is non-planar, with an inter-planar angle of 18.58°. The two terminal pyridine groups are rotated in the same direction by 39.47–39.88°, 47.98(9)° and 43.39(19)° degrees in [PyBP/BPP34C10]\(^{2+}\), [PyBP/BN32C8]\(^{2+}\) and [PyBP/BN34C10]\(^{2+}\), respectively. Two nitrate ions found in the crystal structure of [PyBP/BPP34C10]\(^{2+}\) counter balance the two positive charges of the [2]pseudorotaxane unit. In the case of [PyBP/naphtho crown ether]\(^{2+}\) [2]pseudorotaxanes, two SbF\(_6^-\) anions are responsible for
charge balance. No solvent molecules were incorporated in any of these crystal structures.

<table>
<thead>
<tr>
<th>Pseudorotaxane</th>
<th>C-H···A</th>
<th>C-H/(Å)</th>
<th>H···O/(Å)</th>
<th>C···O/(Å)</th>
<th>C-H···O°</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PyBP/BN38C10]²⁺</td>
<td>C2 H2 O2</td>
<td>0.931(5)</td>
<td>2.692(4)</td>
<td>3.567(4)</td>
<td>156.7(3)</td>
</tr>
<tr>
<td></td>
<td>C6 H6 O3</td>
<td>0.930(4)</td>
<td>2.438(3)</td>
<td>3.332(3)</td>
<td>161.1(3)</td>
</tr>
<tr>
<td></td>
<td>C6 H6 O4</td>
<td>0.930(4)</td>
<td>3.072(3)</td>
<td>3.716(3)</td>
<td>127.9(3)</td>
</tr>
<tr>
<td>[PyBP/BN32C8]²⁺</td>
<td>C6 H6 O3</td>
<td>0.89(6)</td>
<td>2.558(4)</td>
<td>3.303(7)</td>
<td>136.7(3)</td>
</tr>
<tr>
<td></td>
<td>C6 H6 O2</td>
<td>0.89(6)</td>
<td>2.291(5)</td>
<td>3.078(7)</td>
<td>141.9(4)</td>
</tr>
<tr>
<td></td>
<td>C2 H2 O3</td>
<td>0.78(7)</td>
<td>2.979(5)</td>
<td>3.798(7)</td>
<td>147.5(4)</td>
</tr>
</tbody>
</table>


In the case of [PyBP/(DB24C8)₂][NO₃]₂ [3]pseudorotaxane, a linear, non-planar axle with non co-planar aromatic groups was observed. The terminal pyridine groups of the axle are rotated by 69.27° and 22.09° degrees in the same direction, while the two aromatic rings of the 4,4′-bipyridinium core of the axle are rotated by 47.25° degrees to facilitate the formation of stronger π–π interactions between the axle and the wheel. In each [3]pseudorotaxane unit, two threaded crown ether molecules are packed in a horseshoe shape (Figure 3.13.d) around the axle. The angles between the corresponding aromatic ring of the axle and the crown ether lie within 23.35–28.99° degrees. The centroid–centroid distances, 4.133–4.422 Å, are longer than those of the other three [2]pseudorotaxanes with a [PyBP]²⁺ axle. A terminal N···N distance of 15.319(4) Å was observed. Similar to the other [PyBP/neutral crown ether]²⁺ [2]pseudorotaxanes explained above, [PyBP/DB24C8]²⁺ [3]pseudorotaxanes show C–H···O hydrogen bonding with C–H···O angle greater than 120° and H···O distances ranging from 2.086(2)
to 2.860(2) Å. Two nitrate ions balance the (+2) positive charge of the [3]pseudorotaxane unit. One CHCl₃ molecule was also found in the asymmetric unit of the crystal structure.

3.1.6.2. [CpBP/neutral crown ether]²⁺ [2]pseudorotaxanes

From the [CpBP/neutral crown ether]²⁺ [2]pseudorotaxanes, [CpBP–2H⁺/BPP34C10] and [CpBP–2H⁺/BN32C8] crystallized as X-ray quality single crystals, while all the crystal growing attempts of [CpBP/BN38C10]²⁺ yielded either a blue or a light yellow precipitate ([CpBP]Cl₂), and colorless crystals of BN38C10. Interestingly, the axle was deprotonated in both crystal structures during [2]pseudorotaxane crystallization. The crystal structures of [CpBP/BPP34C10]²⁺ and [CpBP/BN32C8]²⁺ confirm the 1:1 complexation of the axle to the wheel in the solid state (Figure 3.14).

The asymmetric unit of the [CpBP–2H⁺/BPP34C10] [2]pseudorotaxane consists of two [2]pseudorotaxanes sitting on inversion centers. In the case of [CpBP–2H⁺/BN32C8], the [2]pseudorotaxane unit does not lie on an inversion center. The π–π separations between the aromatic rings of the crown ethers and the 4,4'-bipyridinium core of the axle range from 3.468 to 3.730 Å in [CpBP–2H⁺/BPP34C10], while in [CpBP–2H⁺/BN32C8], they range from 3.217 to 3.436 Å. The C–H···O hydrogen bondings with C–H···O angle greater than 120° and H···O distance range from 2.231(2) to 2.988(2) and 2.270(5) to 2.390(5) Å were observed in [CpBP–2H⁺/BPP34C10] and [CpBP–2H⁺/BN32C8], respectively. A planar 4,4'-bipyridinium core was observed in the crystal structure of [CpBP–2H⁺/BPP34C10], while the two pyridinium planes are rotated by 12.80° degrees in [CpBP–2H⁺/BN32C8]. The axle is slightly curved in both crystal structures. The 4-carboxyphenyl substituents at the two ends of the 4,4'-bipyridinium core are rotated in the
same direction by 49.67° and 50.23° degrees in the two [2]pseudorotaxane units of [CpBP–2H+/BPP34C10]. In the case of [CpBP–2H+/BN32C8], the terminal substituent groups are rotated in opposite direction by 52.37° and 48.03° degrees. The carboxylate groups at the two ends of the axle render the [CpBP]^{2+} axle longer than the [PyBP]^{2+} axle. The C⋅⋅⋅C distances between the two terminal COO{−} groups are 18.354(4) and 18.713(5) Å in the two [CpBP–2H+/BPP34C10] units, respectively, and 18.23(1) Å in [CpBP–2H+/BN32C8]. CH_{3}OH solvent molecules were observed in both crystal structures. In [CpBP–2H+/BPP34C10], an additional crown ether molecule was also found in the asymmetric unit.

![Thermal ellipsoid plots (50%) of a) [CpBP–2H+/BPP34C10] and b) [CpBP–2H+/BN32C8] [2]pseudorotaxanes. Hydrogen atoms and solvent molecules omitted for clarity. Color code: C, gray; N, blue; O, red.](image)

**Figure 3.14:** Thermal ellipsoid plots (50%) of a) [CpBP–2H+/BPP34C10] and b) [CpBP–2H+/BN32C8] [2]pseudorotaxanes. Hydrogen atoms and solvent molecules omitted for clarity. Color code: C, gray; N, blue; O, red.

3.1.6.3. [C4BP/neutral crown ether]^{2+} [2]pseudorotaxanes

[C4BP][PF_{6}]_{2} is soluble in acetone and acetonitrile, while all neutral crown ethers are soluble in CHCl_{3} and CH_{2}Cl_{2}. Therefore, initial crystal growing attempts were carried out in a 1:1 mixture of acetone or acetonitrile and CHCl_{3} or CH_{2}Cl_{2}. Crystals of [C4BP/BPP34C10][PF_{6}]_{2} were thus obtained, while attempts to crystallize [C4BP/BN38C10]^{2+} and [C4BP/BN32C8]^{2+} yielded elongated hexagonal, very light blue
crystals of [C4BP][PF₆]₂ and cubic or elongated crystals of BN32C8 and BN38C10, respectively.

The crystal structure of [C4BP/BPP34C10][PF₆]₂ shows 1:1 complexation of the axle and the wheel in the solid state (Figure 1.15). The [2]pseudorotaxane unit is located on an inversion center. The planar 4,4′-bipyridinium core of the axle is symmetrically located between the two phenyl rings of the crown ether, with π–π stacking distances of 3.556(1) Å. A summary of hydrogen bonding data of [C4BP/BPP34C10]²⁺ is shown in Table 3.16. The aliphatic substituent groups at the two ends of the 4,4′-bipyridinium core are arranged in a way that maximizes the hydrogen bond formation. The terminal C···C distance of the axle molecule is 16.252(3) Å. Two PF₆⁻ counterions balance the positive charge of the [2]pseudorotaxane unit.

**Figure 3.15:** a) Thermal ellipsoid plots of [C4BP/BPP34C10][PF₆]₂ (50%) [2]pseudorotaxanes and b) ball-and-stick representation showing the terminal C···C distance of the axle. Hydrogen atoms are omitted for clarity. Color code: C, gray; N, blue; O, red; P, purple; F, green.
<table>
<thead>
<tr>
<th>C-H···A</th>
<th>C-H/(Å)</th>
<th>H···O/(Å)</th>
<th>C···O/(Å)</th>
<th>C-H···A°</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1 H24 C24</td>
<td>0.930(1)</td>
<td>2.8937(8)</td>
<td>3.722(1)</td>
<td>149.00(9)</td>
</tr>
<tr>
<td>O2 H14A C14</td>
<td>0.970(1)</td>
<td>3.093(1)</td>
<td>3.723(2)</td>
<td>124.05(8)</td>
</tr>
<tr>
<td>O2 H13B C13</td>
<td>0.970(1)</td>
<td>2.447(1)</td>
<td>3.318(2)</td>
<td>149.20(8)</td>
</tr>
<tr>
<td>O3 H5A C5</td>
<td>0.970(2)</td>
<td>3.172(1)</td>
<td>3.798(2)</td>
<td>123.80(8)</td>
</tr>
<tr>
<td>O4 H7 C7</td>
<td>0.930(1)</td>
<td>2.896(1)</td>
<td>3.560(2)</td>
<td>129.41(9)</td>
</tr>
<tr>
<td>O5 H6A C6</td>
<td>0.970(1)</td>
<td>2.786(1)</td>
<td>3.533(2)</td>
<td>134.34(8)</td>
</tr>
<tr>
<td>O5 H7 C7</td>
<td>0.930(1)</td>
<td>2.9328(8)</td>
<td>3.765(1)</td>
<td>149.65(9)</td>
</tr>
<tr>
<td>O5 H5A C5</td>
<td>0.970(2)</td>
<td>3.123(1)</td>
<td>3.618(2)</td>
<td>113.33(8)</td>
</tr>
<tr>
<td>O7 H6A C6</td>
<td>0.970(1)</td>
<td>2.5124(9)</td>
<td>3.321(2)</td>
<td>140.83(8)</td>
</tr>
<tr>
<td>O4 H5A C5</td>
<td>0.970(2)</td>
<td>2.414(1)</td>
<td>3.380(2)</td>
<td>173.83(8)</td>
</tr>
</tbody>
</table>

Table 3.16: Summary of hydrogen bonding data of [C4BP/BPP34C10]^{2+} pseudorotaxanes.

3.1.6.4. [axle/DSBPP34C10] [2] pseudorotaxanes

The [Axle/DSBPP34C10] [2] pseudorotaxanes show 1:1 complexation of the axle and the wheel in the solid state (Figure 3.16–3.18). iPr₂O vapor diffusion or layering over a methanolic solution of syn and anti mixture of [PyBP/DSBPP34C10] yields [PyBP/syn–DBPP34C10] as maroon–red colored crystals within one day at room temperature, or within 3–4 days at –20 ºC. The orange colored [PyBP/anti-DSBPP34C10] [2] pseudorotaxane crystallizes slower than [PyBP/syn-DSBPP34C10]. It takes one week at room temperature and 2-3 weeks at –20 ºC freezer to crystallize. The different color of the crystals and the different crystal growing rate facilitate the separation of the two different isomers of [PyBP/DSBPP34C10].
Figure 3.16: Thermal ellipsoid plots of a) [PyBP/anti-DSBPP34C10] (50%) and [PyBP/anti-DSBPP34C10] (30%) [2]pseudorotaxanes. Solvent molecules and hydrogen atoms are omitted for clarity. Color code: C, gray; N, blue; O, red; S, yellow.

In the crystal structures of the syn and anti isomers of [PyBP/DSBPP34C10], only the [2]pseudorotaxane unit of [PyBP/anti-DSBPP34C10] lies on the inversion center of the unit cell. These crystal structures show shorter $\pi-\pi$ stacking distances, 3.525–3.657 Å and 3.582 Å, respectively, compared to the non-sulphonated [2]pseudorotaxane analog, [PyBP/BPP34C10]$^{2+}$ (3.630–3.714 Å). Linear, non-planar axle structures were observed in both crystal structures. The 4,4’-bipyridinium core of the axle in [PyBP/anti-DSBPP34C10] is planar, while the two pyridinium planes are rotated by 7.45° degrees in [PyBP/syn-DSBPP34C10]. The terminal pyridine groups of the axle in [PyBP/anti-DSBPP34C10] are rotated by 54.05° degrees in a same direction, while they are rotated by 43.29° and 47.51° in [PyBP/anti-DSBPP34C10]. The terminal N···N distance of the axle (15.400(5) and 15.414(2) Å in the syn and anti isomers,
respectively) is similar to those in [PyBP/BPP34C10]^{2+}. CH₃OH molecules were found in both crystal structures.

The [CpBP−2H⁺/anti-DSBPP34C10] [2]pseudorotaxane crystallizes very easily as maroon-red cubes from a concentrated pseudorotaxane solution in methanol at room temperature, without iPr₂O or Et₂O diffusion. All attempts to crystallize [CpBP−2H⁺/syn-DSBPP34C10] yielded a microcrystalline material not suited for the single crystal X-ray diffraction analysis.

![Thermal ellipsoid plot](image)

**Figure 3.17:** Thermal ellipsoid plot of [CpBP/anti-DSBPP34C10] (30%). Solvent molecules and hydrogen atoms omitted for clarity. Color code: C, gray; N, blue; O, red; S, yellow.

The asymmetric unit of [CpBP/anti-DSBPP34C10] consists of two [2]pseudorotaxane units lying on inversion centers. The planar 4,4'-bipyridinium core forms π−π stacking interactions (3.561–3.636 Å) with the sulphonated phenyl rings of the crown ether. The terminal pyridine groups of the axle molecule are rotated by 38.59° and 72.04° degrees in the same direction, in the two [2]pseudorotaxane units. The terminal C···C distances between the two terminal COO⁻ units are 18.319(2) and 18.418 (2). Five CH₃OH molecules are found in the asymmetric unit.
Both syn- and anti-DSBPP34C10 crystallize as orange X-ray quality crystals with [C4BP][PF₆]₂, which were difficult to distinguish by the naked eye. Similarly to the in non-sulphonated analog, both syn and anti [C4BP/DSBPP34C10] crystal structures show π–π interactions between the aromatic rings of the axle and the wheel, which range from 3.625 to 3.724 Å and 3.546 to 3.559 Å, respectively. Both isomers of [C4BP/DSBPP34C10] show a large number of C–H····O hydrogen bonds between the axle and the wheel compared to the non-sulphonated analog, [C4BP/BPP34C10][²⁺]. The SO₃⁻ groups of the crown ether form addition hydrogen bonds with the 4,4’-bipyridinium core, as well as with the aliphatic chain of the axle. C–H····O hydrogen bonds with C–H····O angle greater than 120° and H····O distances ranging from 2.510(4) to 2.723(4) Å and 2.441(2) to 2.654(2) Å were observed in [C4BP/anti-DSBPP34C10] and [C4BP/syn-DSBPP34C10], respectively. The terminal C····C distance of the axle shows a dramatic difference compared to the axle in the non-sulphonated pseudorotaxane analogue (Figure 3.3.15b). It is 23.229(7) Å in [C4BP/syn-DSBPP34C10] [2] pseudorotaxanes which is larger than that of the [C4BP/anti-DSBPP34C10] [2] pseudorotaxanes, 21.34(1) Å (Figure 3.18.b). Both crystal structures show a non-planar 4,4’-bipyridinium core with 22.36° and 1.62° degrees rotation. Two CH₃OH and two water molecules were found in the asymmetric unit of [C4BP/syn-DSBPP34C10].
Figure 3.18: Thermal ellipsoid plots of a) [C4BP/syn-DSBPP34C10] (50%), b) [C4BP/anti-DSBPP34C10] (30%) and c) end-end distances of the axles in the two [2]pseudorotaxane isomers. Solvent molecules and hydrogen atoms omitted for clarity. Color code: C, gray; N, blue; O, red; S, yellow.
3.2. Temperature sensing behavior of [2]pseudorotaxanes

The results discussed in this section were published as “Single color pseudorotaxane based temperature sensing” in *New J. Chem.* **2010**, *34*, 2097–2100 and are reproduced by permission of The RSC on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

In solution, the wheel and the axle components of the pseudorotaxanes undergo a threading/dethreading equilibrium process. At different temperatures, pseudorotaxane solutions show different color intensities depending on the actual amount of [2]pseudorotaxane. At higher temperatures, the axle dissociates from the wheel, resulting in a lower percentage of [2]pseudorotaxane in solution and a lower color intensity. At lower temperatures, the pseudorotaxane formation equilibrium shifts towards a higher percentage of [2]pseudorotaxane and more intensely colored solutions (Figure 3.19).

![Figure 3.19](image)

**Figure 3.19:** Temperature dependent association and dissociation of individual components of pseudorotaxanes.

This observation prompted us to carry out VT UV-Vis spectroscopic studies, to understand the temperature sensing behavior of pseudorotaxanes in solution. The colorless axle, [C4BP][PF$_6$]$_2$ and colorless aromatic wheels, BPP34C10, BN38C10 and BN28C8 (Figure 3.20) were used in the VT UV-Visible spectroscopic studies.
3.2.1. Variable temperature UV-visible spectroscopic studies

As discussed in Section 3.1.1.3, [C4BP/BPP34C10]$^{2+}$ [2]pseudorotaxane shows a CT band in the visible region of the UV-Visible spectrum ($\lambda_{\text{max}} = 451$ nm in a 2:1 mixture of acetone:CH$_2$Cl$_2$). Since the axle and wheel are colorless in solution, they did not show any absorbance within the visible region of the electronic spectra. The electronic spectra of [C4BP/neutral crown ether]$^{2+}$ [2]pseudorotaxanes were recorded over a 100 °C temperature window ranging from 223 K (−50 °C) to 323 K (+50 °C) (Figure 3.21A). The absorbance of the [2]pseudorotaxane solution increases when temperature decreases, with no change in the $\lambda_{\text{max}}$ value. The other two [2]pseudorotaxane systems, [C4BP/BN38C10]$^{2+}$ and [C4BP/BN32C8]$^{2+}$ also show the same behavior and their electronic spectra are shown in Figure 3.21.B and C. The reversible and continuous change of the absorbance value of [2]pseudorotaxanes with temperatures is an indication of the equilibrium between [2]pseudorotaxanes and their individual components in

Figure 3.20: Schematics of the axle and wheels used in the VT UV-Vis studies.
solution. Interestingly, the color of [C4BP/BPP34C10][PF₆]₂ crystals is lost at 107–109 °C, before its melting point at 191–193 °C.

The plot of the variation of the extinction coefficient of each [2]pseudorotaxane solution as a function of temperature (Figure 3.21.D. – calibration plot) shows that the extinction coefficient is inversely proportional to the temperature of the [2]pseudorotaxanes studied. Therefore, the temperature sensing behavior of [2]pseudorotaxanes could be used to measure temperature. The calibration plot can be used as scale for colorimetric thermometers.

Thermochromic pigments based on liquid crystals have been used in most known colorimetric thermometers. The color change in liquid crystals, as in most inorganic and organic thermochromic compounds, occurs at specific temperatures over a very narrow range. Only a few examples of individual chemical systems are known today where the color change spans a large temperature range. In these systems, the temperature dependent color change often involves a shift in the absorption maximum. For application purposes, such as in microfluidic devices and other complex systems, where conventional thermometers are inappropriate, it would be advantageous to have a colorimetric thermometer that can be read at a single wavelength.
By analyzing the temperature dependent absorption spectra, the thermodynamic parameters of [2]pseudorotaxanes used in this study were calculated.

\[ \Delta G = \Delta H - T\Delta S \]  
\[ \Delta G = -RT\ln K_a \]
where $\Delta G, \Delta H, \Delta S$ are the Gibbs’ free energy change, enthalpy and entropy for pseudorotaxane formation, respectively. $R$ is the universal gas constant and $T$ is the temperature in K.

The equilibrium constant of pseudorotaxanes which show 1:1 axle:wheel complexation is shown by equation (3) in Section 3.1.4:

$$K_a = \frac{C_p}{(C_A^{0} - C_P)(C_W^{0} - C_P)}.$$  

According to the Beer-Lambert law, $A = \varepsilon C l$, then equation (3) can be written as:

$$K_a = \frac{A/\varepsilon l}{(C_W^{0}/A_{\varepsilon l})^2}$$  

(21)

where $A$ is the absorbance of the pseudorotaxane as a function of temperature and $\varepsilon$ is the extinction coefficient of the [2]pseudorotaxane, which is obtained from the Benesi-Hildebrand analysis explained in Section 3.1.4.

$K_a$ values as a function of temperature were obtained using equation (22).

$$lnK_a = - \frac{\Delta H}{RT} + \frac{\Delta S}{R}$$  

(22)

The slope and the intercept of the plot of $lnK_a$ vs $1/T$ gives $(-\frac{\Delta H}{R})$ and $(\frac{\Delta S}{R})$, respectively; the entropy and enthalpy values calculated using the $lnK_a$ vs $1/T$ plot (Figure 3.22) are tabulated in Table 3.17.
**Figure 3.22:** Plot of \( \ln K_a \) versus \( 1/T \) for [C4BP/neutral crown ether]\(^{2+} \) [2]pseudorotaxanes.

<table>
<thead>
<tr>
<th>Wheel component</th>
<th>( K_a ) (( 10^2 )M(^{-1} ))</th>
<th>( \varepsilon ) (( 10^3 ) M(^{-1} ) cm(^{-1} ))</th>
<th>( \Delta H ) (kcal/mol)</th>
<th>( \Delta S ) (cal/mol K)</th>
<th>( \Delta G^\circ ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPP34C10</td>
<td>1.0 (±0.2)</td>
<td>0.63 (±0.08)</td>
<td>−11 (±0.2)</td>
<td>−26 (±1)</td>
<td>−3.2 (±0.1)</td>
</tr>
<tr>
<td>BN38C10</td>
<td>2.4 (±0.3)</td>
<td>1.0 (±0.1)</td>
<td>−8.1 (±0.2)</td>
<td>−16 (±1)</td>
<td>−3.4 (±0.1)</td>
</tr>
<tr>
<td>BN32C8</td>
<td>1.7 (±0.3)</td>
<td>1.3 (±0.1)</td>
<td>−7.1 (±0.2)</td>
<td>−13 (±1)</td>
<td>−3.2 (±0.1)</td>
</tr>
</tbody>
</table>

**Table 3.17:** Thermodynamic parameters of the formation of [C4BP/neutral crown ether]\(^{2+} \) [2]pseudorotaxanes studied using 1.0 (±0.1) mM [2]pseudorotaxanes in a 2:1 mixture of \((\text{CH}_3)\text{2}\text{CO}\) and \(\text{CH}_2\text{Cl}_2\).

The thermodynamic parameters obtained are consistent with reported values for similar systems.\(^{24,144}\) Pseudorotaxane formation from its components in the [C4BP/neutral crown ether]\(^{2+} \) systems is barrierless and is driven by entropy, with higher temperatures favoring dissociation. It is important to note that a temperature-dependent color intensity change would not be observable in the case of related rotaxanes, where dissociation of the wheel from the axle is prevented by bulky stoppers.
3.3. Metal-organic (pseudo)rotaxanes

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After complete characterization of [2]pseudorotaxanes in the solid state as well as in solution, the metal binding properties of [PyBP/neutral crown ether]\(^{2+}\) [2]pseudorotaxanes were studied. In the solid state, MX\(_2\) (M = Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\); X = Cl\(^{-}\), Br\(^{-}\) and I\(^{-}\)) binding properties of [PyBP/neutral crown ether]\(^{2+}\) [2]pseudorotaxanes were studied by using single crystal X-ray diffraction, while the solution state studies were carried out using UV-Vis and \(^1\)H-NMR spectroscopy.

3.3.1. X-ray diffraction studies

3.3.1.1. Crystal growing

Metal-organic (pseudo)rotaxane crystals suitable for X-ray diffraction were obtained by layering a solution of (+2) charged [2]pseudorotaxanes with a solution of neutral metal halides, MX\(_2\) (M = Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\); X = Cl\(^{-}\), Br\(^{-}\), I\(^{-}\)) at room temperature. All [PyBP/BN38C10][NO\(_3\)]\(_2\) and [PyBP/BN32C8][NO\(_3\)]\(_2\) pseudorotaxane solutions were prepared in CH\(_3\)OH and CHCl\(_3\) mixtures, while [PyBP/BPP34C10][NO\(_3\)]\(_2\) pseudorotaxane and metal halide solutions were prepared in CH\(_3\)OH. After slow mixing of the layers containing [2]pseudorotaxane [PyBP/BN38C10][NO\(_3\)]\(_2\) or [PyBP/BN32C8][NO\(_3\)]\(_2\) and metal halide, the final solution contained a 3:1 mixture of CH\(_3\)OH and CHCl\(_3\). During crystal growing, the neutral metal salts were transformed into singly charged anionic species of MX\(_3^{-}\) (M = Zn\(^{2+}\), Cd\(^{2+}\), X = Cl\(^{-}\), Br\(^{-}\)) or doubly
charged anionic species of CdBr$_4^{2-}$ or M$_2$X$_6^{2-}$ (M = Hg$^{2+}$, X = Cl$^-$, Br$^-$, I$^-$) by anion scrambling.

3.3.1.2. Zinc metal-organic rotaxanes

From the fifteen X-ray quality metal-organic (pseudo)rotaxane crystals, four were obtained from ZnX$_2$ (X = Cl$^-$, Br$^-$) and [PyBP/BN38C10][NO$_3$]$_2$ or [PyBP/BN32C8][NO$_3$]$_2$. In the case of [PyBP/BN38C10][NO$_3$]$_2$ and [PyBP/BN32C8][NO$_3$]$_2$, two ZnCl$_3^-$ or ZnBr$_3^-$ anions bind to the two ends of (+2) charged, ditopic [2]pseudorotaxanes to form the dizwitterionic metal-organic rotaxanes [PyBP/BN38C10](ZnX$_3$)$_2$ and [PyBP/BN32C8](ZnX$_3$)$_2$, regardless of the metal/pseudorotaxane ratio in the layered solutions. The iso-structural crystals of [PyBP/BN38C10](ZnX$_3$)$_2$ and [PyBP/BN32C8](ZnX$_3$)$_2$ (X = Cl$^-$, Br$^-$), respectively, show that neutral zinc halides of ZnCl$_2$ and ZnBr$_2$ were transformed into singly charged ZnCl$_3^-$ and ZnBr$_3^-$ anions, respectively, during crystallization.

Since BPP34C10 is soluble in CH$_3$OH, crystal growing attempts of [PyBP/BPP34C10][NO$_3$]$_2$ with ZnX$_2$ (X = Cl$^-$, Br$^-$) were carried out either in CH$_3$OH or CH$_3$OH/CHCl$_3$ mixtures. In both cases, [PyBP][NO$_3$]$_2$ precipitated as a light yellow powder, while BPP34C10 crystallized as colorless prisms. This observation indicates that the dissociation of the axle from the wheel occurs during the slow mixing of the pseudorotaxane and metal halide containing layers regardless of the solvent.

To force the pseudorotaxane equilibrium towards more pseudorotaxane formation and to facilitate the formation of the MX$_3^-$ anions, the following two strategies were employed one at a time or as a combination of both. Since [PyBP/BPP34C10][NO$_3$]$_2$ has a lower
association constant than [PyBP/BN38C10][NO₃]₂ or [PyBP/BN32C8][NO₃]₂, a 10-fold excess of BPP34C10 was used to force the threading-dethreading equilibrium towards more pseudorotaxane formation. In this attempt, only the crown ether crystallized and the color of the solution turned from red to light yellow (the color of the axle). The use of a MX₂/KX (1:1) mixture and a pseudorotaxane/(MX₂/KX) ratio of 1:2 facilitates the formation of the MX₃⁻ ions and provides the optimum stoichiometry required for metal-pseudorotaxane formation (equation 25). In this attempt, the axle precipitated due to the higher ionic strength generated by KX. Upon using a [PyBP][NO₃]₂:BPP34C10:ZnX₂:KX ratio of 1/10/2/2 (employing both strategies at the same time), the axle precipitated and the wheel crystallized alone. These results show that during slow mixing of the metal halide solution and the [2]pseudorotaxane solution, the [PyBP/BPP34C10][NO₃]₂ [2]pseudorotaxane equilibrium shifts toward dissociation regardless of the axle/wheel or pseudorotaxane/metal ion ratio.

\[
[\text{PyBP/BPP34C10}][\text{NO}_3]_2 + [\text{ZnX}_2/\text{KX}] \rightarrow [\text{PyBP/BPP34C10}(\text{ZnX}_2)_3 + 2\text{KNO}_3 \quad (23)
\]

The same strategy was employed in an attempt to obtain metal-organic rotaxanes with ZnI₂ and [2]pseudorotaxanes in CH₃OH/CHCl₃ mixtures. During slow mixing of the [2]pseudorotaxane and metal halide containing layers, the [PyBP]²⁺ axle crystallized as the dizwitterionic [PyBP](ZnI₃)₂ (Figure 3.23). Again, the [2]pseudorotaxane formation equilibrium shifted towards dissociation.

**Figure 3.23:** Crystal structure (ball and stick representation) of [PyBP](ZnI₃)₂. Solvent molecules are omitted for clarity. Color code: Zn, magenta; I, purple; N, blue; C, black; H, white.
3.3.1.3. Cadmium metal organic rotaxanes

Five single crystals suitable for X-ray diffraction studies were obtained with \([\text{PyBP/BPP34C10}][\text{NO}_3]_2\), \([\text{PyBP/BN38C10}][\text{NO}_3]_2\) or \([\text{PyBP/BN32C8}][\text{NO}_3]_2\) pseudorotaxanes and cadmium halides (Br\(^-\) or I\(^-\)). The only structure showing pseudorotaxane-metal binding is metal pseudorotaxane binding behavior was observed with \([\text{PyBP/BN38C10}][\text{NO}_3]_2\) and cadmium iodide. Its binding pattern is similar to the zinc-bound rotaxanes: one unit of ditopic \([\text{PyBP/BN32C8}]^{2+}\) pseudorotaxane binds to two singly charged CdBr\(_3^-\) anions to yield a dizwitterionic metal-organic rotaxane.\(^{145}\)

The crystal structure shows that neutral CdI\(_2\) was converted into singly charged anionic species of CdI\(_3^-\) during self assembly. In the other four structures, doubly charged CdX\(_4^{2-}\) anions act as counter ions for the (+2) charged \([2]\)pseudorotaxane units, without metal-pseudorotaxane binding. During the initial preparation of metal-pseudorotaxane crystals, significant amounts of \([\text{PyBP}][\text{CdI}_4]\) crystals (Figure 3.24) were isolated from each vial. This observation indicates that the equilibrium between each \([2]\)pseudorotaxane and its individual components shifts towards dissociation due to the crystallization of \([\text{PyBP}][\text{CdI}_4]\).

\[
\begin{align*}
\text{[PyBP][NO}_3\] + \text{neutral crown ether} & \rightleftharpoons \text{[PyBP/neutral crown ether][NO}_3\]_2 \quad (24) \\
\text{[PyBP]}^{2+} + 2 \text{CdI}_2 & \longrightarrow \text{[PyBP][CdI}_4\] + \text{Cd}^{2+} \quad (25)
\end{align*}
\]

**Figure 3.24:** Crystal structure (ball and stick representation) of \([\text{PyBP}][\text{CdI}_4]\). Solvent molecules are omitted for clarity. Color code: Cd, green; I, purple; N, blue; C, black; H, white.
3.3.1.4. Mercury metal-organic rotaxanes

Six X-ray quality crystals were obtained with the combination of [PyBP/BN38C10]^{2+} and [PyBP/BN32C8]^{2+} [2]pseudorotaxanes and mercury halides. Crystal structures show that rearrangement of mercury halides for the anion formation is slightly different from zinc and cadmium halides. The neutral mercury halides underwent not only anion scrambling but also dimerization to form doubly charged anionic species of Hg_{2}X_{6}^{2-} (X = Cl^-, Br^-, I^-), which have two bridging halide ions connecting two mercury ions. Two anions of doubly charged Hg_{2}X_{6}^{2-} (X = Cl^-, Br^-) bind to the two ends of the ditopic axle of [PyBP/BN38C10][NO_{3}]_{2} [2]pseudorotaxanes to yield two negatively charged metal-organic rotaxanes, while the corresponding analog of the [PyBP/BN38C10]^{2+} [2]pseudorotaxanes show metal-pseudorotaxane non-binding behavior. [PyBP/BN38C10]^{2+} and [PyBP/BN32C8]^{2+} [2]pseudorotaxanes crystallize with Hg_{2}I_{6}^{2-} in which both structures Hg_{2}I_{6}^{2-} behaves as a counter ion in crystallization with doubly charged pseudorotaxanes. It shows similar behavior to the CdX_{4}^{2-} anion in the [2]pseudorotaxane crystal structure. The [PyBP/BPP34C10]^{2+} [2]pseudorotaxane did not crystallize as metal-organic (pseudo)rotaxane with mercury halides.

3.3.2. Crystallographic description

3.3.2.1. Zinc metal-organic rotaxanes

The asymmetric units of [PyBP/BN38C10](ZnCl_{3})_{2} and [PyBP/BN38C10](ZnBr_{3})_{2} consist of two metal-organic rotaxane (MOR) units, while the ones of [PyBP/BN32C8](ZnCl_{3})_{2} and [PyBP/BN32C8](ZnBr_{3})_{2} consist of only one (Figure 3.25). In all four cases, the pseudorotaxane units are located on inversion centers. The 4,4′-
bipyridinium core of the axle interacts with the two naphthalene rings of the crown ether via $\pi-\pi$ stacking. [PyBP/BN32C8](ZnCl$_3$)$_2$ and [PyBP/BN32C8](ZnBr$_3$)$_2$ show $\pi-\pi$ stacking distances of 3.375(3) Å and 3.414(3) Å, while [PyBP/BN38C10](ZnCl$_3$)$_2$ and [PyBP/BN38C10](ZnBr$_3$)$_2$ show $\pi-\pi$ stacking distances ranging from 3.293(2) to 3.679(3) and 3.345(2) to 3.668(2)Å, respectively. The multiple C–H···O hydrogen bonds ranging from 3.057(5) to 3.496(6) Å contribute to the association between the axle and the wheel of the [2]pseudorotaxane units. Planar 4,4$'$-bipyridinium cores and linear [PyBP]$^{2+}$ axles were observed in all four crystal structures. The terminal N···N distances of the axles of the four [2]pseudorotaxanes are similar. Identical N···N distances, 15.437(3) Å and 15.437(9) Å were observed in [PyBP/BN32C8](ZnCl$_3$)$_2$ and [PyBP/BN32C8](ZnBr$_3$)$_2$, respectively. The terminal N···N distances of the two axles in the asymmetric unit of [PyBP/BN38C10](ZnCl$_3$)$_2$ and [PyBP/BN38C10](ZnBr$_3$)$_2$ are 15.417(8) and 15.432(7) Å, and 15.378(4) and 15.403(6) Å, respectively. The two terminal pyridine units of [PyBP/BN32C8](ZnCl$_3$)$_2$ and [PyBP/BN32C8](ZnBr$_3$)$_2$ were rotated relative to the 4,4$'$-bipyridinium core by 23.65 and 29.6(2)$^\circ$ in the same direction. In the case of [PyBP/BN38C10](ZnCl$_3$)$_2$, the terminal pyridine rings of the two pseudorotaxane units in the asymmetric unit one rotated by 26.8(2)$^\circ$ and 43.01(2)$^\circ$ in opposite directions while in [PyBP/BN38C10](ZnBr$_3$)$_2$ They are rotated by 27.19(17)$^\circ$ and 45.64(17)$^\circ$ in the same direction. In all four structures, distorted tetrahedral coordination geometry of zinc ion was observed. The Zn–N distances of MORs derived from [PyBP/BN38C10]$^{2+}$ (2.083(2)–2.088(1) Å) were smaller than those of derived from [PyBP/BN32C8]$^{2+}$ (2.095(5)–2.107(3) Å). Methanol molecules were found only in the crystal structure of [PyBP/BN32C8](ZnBr$_3$)$_2$. 
Figure 3.25: Thermal ellipsoid plot (30 %) of a) [PyBP/BN38C10](ZnCl$_3$)$_2$, b) [PyBP/BN32C8](ZnCl$_3$)$_2$, c) (40 %) [PyBP/BN38C10](ZnBr$_3$)$_2$ and d) [PyBP/BN32C8](ZnBr$_3$)$_2$. Hydrogen atoms and solvent molecules are omitted for clarity. Color code: Zn, magenta; Cl, green; Br, orange; O, red; N, blue; C, black.

3.2.2.2. Cadmium metal-organic rotaxanes

In the cadmium metal-organic rotaxane crystal structures, the [2]pseudorotaxane units are not located on inversion centers except for [PyBP/BN38C10][CdI$_4$]. The $\pi-\pi$ stacking interactions between the 4,4′-bipyridinium core of the axle and the bis-naphtho rings of the wheel are 3.421(1) Å. The $\pi-\pi$ stacking interactions range from 3.451(2) to 3.479(3)Å, 3.549(2) to 3.664(2) Å, 3.433(4) to 3.607(1) Å and 3.249(3) to 3.215(4) Å in [PyBP/BPP34C10][CdBr$_4$], [PyBP/BPP34C10][CdI$_4$], [PyBP/BN38C10][CdBr$_4$] and [PyBP/BN32C8][CdI$_4$], respectively. The [PyBP]$^{2+}$ axles are linear in all structures except for [PyBP/BN32C8](CdI$_3$)$_2$ (Figure 3.26).

A co-planar 4,4′-bipyridinium core was only observed in the case of [PyBP/BN38C10][CdI$_4$]. The two pyridinium rings of the 4,4′-bipyridinium core of [PyBP/BPP34C10]$^{2+}$ are rotated by 14.11(16)$^\circ$ and 19.88$^\circ$ in [PyBP/BPP34C10][CdBr$_4$]...
and [PyBP/BPP34C10][CdI₄], respectively. These angles are more than twice as large as those in [PyBP/BN38C10][CdBr₄] (6.26° and 7.11°). The angle between the two rings of the 4,4′-bipyridinium core of [PyBP/BN32C8](CdI₃)₂ is 6.2°. This non-planarity of the 4,4′-bipyridinium core of the axle apparently leads to a better overlapping of the π orbitals of the electron-rich crown ether and the electron-deficient axle, which leads to a lower energy state of the structure. [PyBP/BPP34C10][CdBr₄] and [PyBP/BPP34C10][CdI₄] show N⋯N distances of 15.462(6) and 15.45(1) Å, respectively. The two [PyBP/BN38C10] units in the asymmetric unit of [PyBP/BN38C10][CdBr₄] have N⋯N distances of 15.36(4) and 15.43(4) Å. The [PyBP/BN38C10][CdI₄] and [PyBP/BN32C8](CdI₄) crystal structures show 15.49(1) and 15.38(1) terminal N⋯N distances, respectively. Multiple C–H⋯O hydrogen bonds between the axle and the wheel are observed in all five structures. Two CH₃OH and one CHCl₃ molecule are observed in the asymmetric unit of [PyBP/BN38C10] [CdBr₄]. Distorted tetrahedral geometry of cadmium ion was observed in all five structures. The Cd–N bond lengths of 2.320(7) and 2.345(7) Å lie within the 2.266–2.421 Å range for Cd–N distances found in complexes reported in the CSD containing the PyCdI₃ unit.
Figure 3.26: Thermal ellipsoid plots (30 %) of a) [PyBP/BPP34C10][CdBr₄], b) [PyBP/BPP34C10][CdI₄], c) [PyBP/BN38C10][CdBr₄], d) [PyBP/BN38C10][CdI₄] and e) [PyBP/BN32C8][CdI₄]. Hydrogen atoms and solvent molecules omitted for clarity. Color code: Cd, dark green; Br, orange; I, purple; O, red, N, blue; C, black.
3.3.2.3. Mercury metal-organic rotaxanes

Only the [PyBP/BN38C10]^{2+} and [PyBP/BN32C8]^{2+} pseudorotaxanes crystallized with mercury halides to yield X-ray quality single crystals (Figure 3.27). The mercury metal-organic rotaxanes sit on inversion centers. Linear axles with co-planar 4,4'-bipyridinium cores were observed in all crystal structures. The terminal N···N distances of the axles were found to be 15.42(1), 15.49(1), 15.43(1), 15.49(1), 15.469(6) and 15.48(2) Å in [PyBP/BN38C10](Hg_{2}Cl_{6})_{2}, [PyBP/BN32C8][Hg_{2}Cl_{6}], [PyBP/BN38C10](Hg_{2}Br_{6})_{2}, [PyBP/BN32C8][Hg_{2}Br_{6}], [PyBP/BN38C10][Hg_{2}I_{6}] and [PyBP/BN32C8][Hg_{2}I_{6}], respectively. The mercury metal-organic rotaxanes derived from [PyBP/BN32C8]^{2+}[2]pseudorotaxanes, [PyBP/BN32C8][Hg_{2}Cl_{6}], [PyBP/BN32C8][Hg_{2}Br_{6}] and [PyBP/BN32C8][Hg_{2}I_{6}], show shorter π–π stacking distances (3.24(1), 3.283(1) and 3.298(4) Å, respectively) than those derived from [PyBP/BN38C10]^{2+}[2]pseudorotaxanes, [PyBP/BN38C10](Hg_{2}Cl_{6})_{2}, [PyBP/BN38C10](Hg_{2}Br_{6})_{2} and [PyBP/BN38C10][Hg_{2}I_{6}] (3.39(1), 3.460(3) and 3.730(2) Å, respectively). This observation goes along with the higher association constant value of [PyBP/BN32C8]^{2+}[2]pseudorotaxanes discussed in Section 3.1.4. The 4,4'-bipyridinium core of the axle is planar, while the terminal pyridine group are rotated to the same direction by 38.0(1)^{o}, 31.0(1)^{o}, 39.3(3)^{o}, 29.2(1)^{o}, 36.5(2)^{o} and 32.62(5)^{o} in [PyBP/BN38C10](Hg_{2}Cl_{6})_{2}, [PyBP/BN32C8][Hg_{2}Cl_{6}], [PyBP/BN38C10](Hg_{2}Br_{6})_{2}, [PyBP/BN32C8][Hg_{2}Br_{6}], [PyBP/BN38C10][Hg_{2}I_{6}] and [PyBP/BN32C8][Hg_{2}I_{6}], respectively. The asymmetric units of [PyBP/BN38C10](Hg_{2}Cl_{6})_{2} and [PyBP/BN38C10](Hg_{2}Cl_{6})_{2} contain an additional axle molecule to neutralize the (−2) charge of the metal-rotaxane unit. In addition, they contain one methanol (solvent) molecule. In all six structures, the mercury
ion is found in the distorted tetrahedral environment. The Hg–N bond length of 2.317(4) Å also lies within the 2.113–2.445 Å range found in other reported PyHgCl$_3$-containing complexes.

**Figure 3.27**: Thermal ellipsoid plots (30 %) of a) [PyBP/BN38C10](Hg$_2$Cl$_6$)$_2$, b) [PyBP/BN32C8][Hg$_2$Cl$_6$], c) [PyBP/BN38C10](Hg$_2$Br$_6$)$_2$, d) [PyBP/BN32C8][Hg$_2$Br$_6$], e) [PyBP/BN38C10][Hg$_2$I$_6$] and f) [PyBP/BN32C8][Hg$_2$I$_6$]. Hydrogen atoms and solvent molecules omitted for clarity. Color code: Hg, brown; Cl, green; Br, orange; I, purple; O, red; N, blue; C, black.
3.2.2.3.1. Blue-red dichroism

Interestingly, optical absorption micrographs of [PyBP/BN32C8][Hg₂Cl₆] taken under polarized light show that the crystal drastically changes color from blue to red (and vice versa) upon rotation around the perpendicular axis (Figure 3.28a).

![Figure 3.28: a) Optical micrographs of the same crystal of [PyBP/BN32C8][Hg₂Cl₆] in two different orientations (under Paratone-N oil) b) Columnar arrangement of the [PyBP/BN32C8]²⁺ and [Hg₂Cl₆]²⁻ units in the crystal structure.](image)

A closer examination of the packing diagram reveals a columnar arrangement of the pseudorotaxane units and [Hg₂Cl₆]²⁻ units (Figure 3.28b). A similar blue/red linear dichroic emission from a triarylmethane dye has recently been reported.¹⁴⁶
3.3.3. UV-visible spectroscopic studies

Zinc halide binding studies of [PyBP/neutral crown ether]2+ [2]pseudorotaxanes were carried out in a 1:1 mixture of CH3OH and CHCl3. Separate solutions with 1:1, 1:2, 1:3 and 1:4 [2]pseudorotaxane:ZnX2 molar ratios were prepared and the corresponding UV-Visible spectra were recorded. None of the mixtures yields a precipitate.

The UV-Visible spectra of ZnCl2/[2]pseudorotaxane and ZnBr2/[2]pseudorotaxane were similar to that of the corresponding [2]pseudorotaxane, and provide no evidence for metal-pseudorotaxane binding (Figure 3.29a and b). The ZnI2/[2]pseudorotaxane system shows a slightly different behavior from ZnCl2/[2]pseudorotaxane and ZnBr2/[2]pseudorotaxane. The absorbance value of ZnI2/[2]pseudorotaxane solutions increased with the [2]pseudorotaxanes:ZnI2 molar ratio compared to the corresponding [2]pseudorotaxane (Figure 3.29c). The increased absorbance is an indication of CT transition between iodide ions and the [2]pseudorotaxane unit and it does not provide a direct indication of metal-pseudorotaxane binding.

According to the solid state characterization of zinc metal-organic rotaxanes, the [2]pseudorotaxane units are coordinated by two ZnX3– anions. Therefore, to provide an additional halide ion and facilitate ZnX3– formation, zinc halide solutions were prepared by using equimolar amounts of ZnX2 and KX, which is expected to produce ZnX3– ions.

\[
\text{ZnX}_2 + \text{KX} \rightarrow \text{ZnX}_3^- + \text{K}^+ \quad (26)
\]

In all cases, the mixtures of [ZnX2/KX]/[2]pseudorotaxanes yielded a light yellow precipitate, regardless of the [ZnX2/KX]:[2]pseudorotaxanes ratio.

CdI2 and [2]pseudorotaxane mixtures show a behavior similar to the ZnI2/[2]pseudorotaxanes. In a similar way, mercury halide binding experiments of
[PyBP/ neutral crown ether]$^{2+}$ [2]pseudorotaxanes were carried out. The mixtures of [2]pseudorotaxane and HgCl$_2$ or HgBr$_2$ gave precipitates immediately after mixing, even at low concentrations such as 0.66 mM for both the [2]pseudorotaxane and the mercury halide. In the case of HgI$_2$/[2]pseudorotaxane mixtures, no precipitation occurs and the absorbance maxima remain constant regardless of the metal:[2]pseudorotaxane ratio (Figure 3.29d).

**Figure 3.29:** a) ZnCl$_2$, b) ZnBr$_2$, c) ZnI$_2$ and d) HgI$_2$ binding studies of [PyBP/BPP34C10]$^{2+}$ [2]pseudorotaxanes in a 1:1 mixture of CH$_3$OH:CHCl$_3$ using UV-Visible spectroscopy. Color code: [PyBP][NO$_3$]$_2$ axle, blue; [PyBP/BPP34C10]$^{2+}$: MX$_2$ (M = Zn(II) or Hg(II), X = (Cl$^-$, Br$^-$, I$^-$)) = 1:1 (red), 1:2 (purple), 1:3 (black), 1:4 (yellow), 1:5 (green).

The UV-Visible spectra of ZnCl$_2$, ZnBr$_2$, ZnI$_2$, HgI$_2$ binding studies with [PyBP/BN38C10]$^{2+}$ and [PyBP/BN32C8]$^{2+}$ [2]pseudorotaxanes are given in Appendix C.
3.3.4. $^1$H-NMR spectroscopic studies

[2]Pseudorotaxanes and [MX$_2$/KX] solutions were layered to obtain the optimum ratio of [2]pseudorotaxane:[MX$_2$/KX] of 1:2 at the end of the slow mixing of the two layers. All [2]pseudorotaxane solutions were prepared in a 1:1 mixture of CH$_3$OH:CH$_2$Cl$_2$, while [MX$_2$/KX] solutions were prepared in CH$_3$OH to obtain a 2:1 CH$_3$OH:CH$_2$Cl$_2$ ratio at the end. Within one week, either precipitation or crystallization took place in each vial. The solution was decanted and the precipitates/crystals as well as the residues obtained by evaporating the decanted solutions were analyzed by $^1$H-NMR.

Observations of each vial and the $^1$H-NMR analysis results are tabulated in Tables 3.18 and 3.19, respectively.
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<td>solution</td>
</tr>
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<td>Light yellow precipitate</td>
<td>Light yellow solution</td>
</tr>
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<td>Colorless solution</td>
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<td>Red crystals</td>
<td>Light yellow solution</td>
</tr>
<tr>
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<td>Light yellowish-brown precipitate</td>
<td>Colorless solution</td>
</tr>
<tr>
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<td>Light yellow precipitate</td>
<td>Colorless solution</td>
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</tr>
<tr>
<td>HgI₂/KI</td>
<td>Light yellow solution</td>
<td>Maroon-red precipitate</td>
<td>Light yellow solution</td>
</tr>
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**Table 3.18:** Observations of crystal growing vials after one week.

Since Zn$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$ are diamagnetic cationic species, peak broadening in the NMR, an indication of presence of metal ion, cannot be observed. Even though NMR spectra provide information about the composition of the precipitate/crystalline solid, the presence/absence of the neutral metal halide, cationic metal ion or anionic metal halide clusters cannot be concluded based on the NMR results.

Table 3.19: Results of NMR analysis of solids/crystals from each crystal growing vial.
3.4. Isomer separation of syn- and anti-DSBPP34C10 using pseudorotaxane crystals

Crystal structures of [PyBP/neutral crown ether]$^{2+}$ [2]pseudorotaxanes show that the metal-organic (pseudo)rotaxanes always assemble so that the net charge of the entity is zero. Reduction of the charge of the pseudorotaxanes has a potential to obtain MORFs with higher order of dimensionalities with positively charged metal ions. Therefore to be able to use the more common, positively charged metal ions for rotaxane framework construction, neutral and negatively charged pseudorotaxanes were synthesized by introducing anionic sulphonate groups to the BPP34C10 wheel component.

Neutral [2]pseudorotaxane formation

$$[\text{PyBP}][\text{NO}_3]_2 + [\text{TBA}]_2\text{DSBPP34C10} \rightarrow [\text{PyBP/DSBPP34C10}] + 2[\text{TBA}]\text{NO}_3$$  (27)

Negatively charged [2]pseudorotaxane formation

$$[\text{CpBP–2H}^+] + [\text{TBA}]_2\text{DSBPP34C10} \rightarrow [\text{CpBP–2H}^+/\text{DSBPP34C10}]^{2–} + 2\text{TBA}^+$$  (28)

The acidic form of DSBPP34C10 was converted to the corresponding TBA salt ([TBA]$_2$DABPP34C10) by reacting a colorless solution of DSBPP34C10 in methanol with a colorless aqueous solution of TBAOH. The final solvent mixture consists of a H$_2$O:CH$_3$OH in 1:10 ratio, which yields a white precipitate at room temperature. Although the $^1$H–NMR spectrum of the evaporated filtrate could be assigned to the syn– and anti– [TBA]$_2$DSBPP34C10, the ratio between the anti– and syn– isomers is found to be different than 1:1. Crystallization of the white precipitate as X–ray quality, prismatic,
colorless crystals reveals that it consist of the SO$_2$Cl derivative of anti-DSBPP34C10 (Figure 3.30).

![Crystal structure of the SO$_2$Cl derivative of anti-DSBPP34C10](image)

**Figure 3.30:** Crystal structure of the SO$_2$Cl derivative of anti-DSBPP34C10. Color code: C, black; O, red; S, yellow; Cl, green.

To obtain a better percentage of anti–TBA$_2$DSBPP34C10 in the DSBPP34C10 isomer mixture, the reaction was carried out at 50 ºC instead of room temperature which yields no precipitate of the SO$_2$Cl derivative.

Fitzmaurice$^7$ and coworkers used TBA$_2$DSBPP34C10 in rotaxanes and pseudorotaxanes, as a mixture of the syn- and anti- isomers. Using conventional methods, such as recrystallization, precipitation or chromatographic methods, they were unable to separate the acid or TBA$^+$ salt form of the syn– and anti–DSBPP34C10. We achieved the separation of the two isomers via the [PyBP/syn- and anti-DSBPP34C10] pseudorotaxane formation.

As explained in Section 2.2.2.11., the syn– and anti–TBA$_2$DSBPP34C10 crown ethers crystallize with the [PyBP][NO$_3$]$_2$ axle as red and orange crystals, respectively (Figure 3.31a). The red and orange crystals show different crystallization rates, which facilitates the manual separation of the [PyBP/syn-DSBPP34C10] and [PyBP/anti-DSBPP34C10]
crystals. The addition of HPF$_6$ to the manually separated [2]pseudorotaxane crystals dethreads the axle from the wheel and precipitates the [PyBP]$^{2+}$ axle as its PF$_6^-$ salt, leaving the acid form of the crown ether in solution (Figure 3.31b). Evaporation of the filtrate yields the acid form of pure isomers.


The $^1$H–NMR spectra of the acidic form of the pure anti– and syn–DSBPP34C10 are shown in Figure 3.32.
Figure 3.32: $^1$H NMR of anti-DSBPP34C10 and syn-DSBPP34C10.
3.5. Metallo- ligands for MORFs

The pseudorotaxane building blocks reported so far consist of either a) an organic axle and an organic wheel,\textsuperscript{13,10} b) an organic axle and a hybrid organic-inorganic wheel\textsuperscript{147,148} or c) a hybrid organic-inorganic axle and an organic wheel.\textsuperscript{149} The use of both organic axles and wheels for pseudorotaxane construction is widely explored, while studies on the combination of organic axles/wheels and hybrid wheels/axles are yet to be performed. Interestingly, none of the research groups have used hybrid axles or wheels for MORFs construction yet.

An interesting organic-inorganic hybrid metallo-ligand, Cu(Pyacac)\textsubscript{2} was synthesized and characterized by Halliwell \textit{et. al.} in 1997. Cu(Pyacac)\textsubscript{2} is a linear, rigid ligand with two pyridine groups at the two ends (Figure 3.33a).\textsuperscript{150} Later on, Maverick and coworkers synthesized Cu-Cd mixed metal-organic frameworks (MMOFs).\textsuperscript{151} The reaction of Cd(NO\textsubscript{3})\textsubscript{2} with Cu(Pyacac)\textsubscript{2} yields a ladder type 1D structure (Figure 3.33.b) while the reaction of CuCl\textsubscript{2} and Cu(Pyacac)\textsubscript{2} yields a square grid type 2D structure (Figure 3.33.c). Therefore, we proposed to test whether Cu(Pyacac)\textsubscript{2} can to form pseudorotaxanes and ultimately MORFs.

\textbf{Figure 3.33}: a) Schematic of the linear, rigid metallo-ligand, Cu(Pyacac)\textsubscript{2}; b) ladder type 1D structure and c) square grid type 2D MMOFs of Cu(Pyacac)\textsubscript{2}. Color code: C, black; O, red; N, blue; Cd, yellow; Cu, orange. Reproduced with permission from reference 151. Copyright 2007 American Chemical Society.
The Cu(Pyacac)$_2$ ligand is insoluble in common organic solvents except THF and CHCl$_3$. It is very slightly soluble in C$_2$H$_5$OH. Mixing a solution of light yellowish-green Cu(Pyacac)$_2$ in CHCl$_3$ with a colorless solution of BPP34C10, BN38C10 or BN32C8 in CHCl$_3$ yields a solution with a similar color as that of Cu(Pyacac)$_2$. Attempts to crystallize pseudorotaxanes with a Cu(Pyacac)$_2$ axle and a BPP34C10, BN38C10 or BN32C8 wheel yielded only Cu(Pyacac)$_2$ as green, cubic crystals (Figure 3.34 a).

**Figure 3.34:** Thermal ellipsoid plot (80 %) of Cu(Pyacac)$_2$ (polymorph1) and b) it’s packing diagram showing weak Cu-N coordination bonds. Solvent molecules omitted for clarity. Color code: C, black; O, red; N, blue; Cu, light blue.

The crystal structure of Cu(Phacac)$_2$ (polymorph 1) shows that terminal pyridine nitrogens from two axles coordinate to the square planar Cu(II) center of another axle in between the two, via Cu-N co-ordination bonds, resulting in a 2D sheet of [Cu(Pyacac)$_2$]$_\infty$. The Cu···N distance (2.591(2)Å) is longer than the usual Cu–N distance of 2.57(1). The terminal N···N distance is 15.128(2) Å.

From the crystal structure of Cu(Pyacac)$_2$ it became apparent that the formation of Cu-N coordination bonds might prevent the formation of [Cu(Pyacac)$_2$/neutral crown ether]
pseudorotaxanes. Therefore, for the next crystal growing attempt, a diaza crown ether was employed instead of the aromatic crown ethers (Figure 3.35). The interior diameter between two nitrogen atoms of diaza-18-crown-6 reported in CSD lie within 5.314(2) to 5.740(2) Å while the H⋯H distance of the CH$_3$ groups are 6.121(2). Apparently, it is sufficiently large to allow threading of the Cu(Phacac)$_2$ axle via slippage mechanism$^{152}$. In addition, the two N atoms located at opposite side of the macrocycle can potentially coordinate to the Cu(II) ion center of the axle and lead to pseudorotaxane formation.

Attempts to grow pseudorotaxane crystals with Cu(Pyacac)$_2$ and diaza-18-crown-6 yielded the X-ray quality, green cubic crystals of a different polymorph of Cu(Pyacac)$_2$ (Figure 3.36). The crystal structure of the polymorph 2 indicates that the Cu-N distance (2.438(6) Å) is slightly shorter than the corresponding one in polymorph 1. The terminal N⋯N distance is 15.213(8) Å. The shape and the size of the cavity in the polymorph 1 and polymorph 2 are different from the ones in a third, known polymorph of Cu(Phacac)$_2$.$^{150}$
These results show that the pyridine nitrogen has a higher coordination affinity than the diaza-18-crown-6 nitrogen towards the Cu(II) metal center. Since phenyl groups have no potential to coordinate to the Cu(II) center of the another axle, the phenyl analog of the Cu(Pyacac)$_2$ axle, bis[3-(4-phenyl)pentane-2,4-dionato]copper(II) (Cu(Phacac)$_2$), was used in the next experiment (Figure 3.37).

**Figure 3.37:** Schematics of the formation of the proposed [2]pseudorotaxanes of [Cu(Phacac)$_2$/diaza-18-crown-6].
Evaporation of a mixture of Cu(Phacac)$_2$ and diaza-18-crown-6 in CH$_3$OH produced X-ray quality, prismatic, blue crystals. The crystal structure reveals no pseudorotaxane formation from Cu(Phacac)$_2$ and diaza-18-crown-6. In contrast, one molecule of diaza-18-crown-6 is sandwiched between two axles, with the two N atoms of the diaza-18-crown-6 coordinating to two Cu(II) centers of two axles yielding penta-coordinated Cu(II) centers (ML$_3$) (Figure 3.38).

**Figure 3.38:** Crystal structure of ML$_3$. Color code: C, black; O, red; N, blue; Cu, light blue.

Proposed improvements to obtain the hybrid axle containing [2]pseudorotaxanes are described in Section 4.2.2.
3.6. Molecularly woven materials

The \textbf{L1} molecule (See Figure 1.40 in Chapter 1.2.2) was designed to have all the basic elements required to form a double stranded, dinuclear helix with metal ions. The 2,2′-bipyridinium unit is a well known chelating group. The length of the connecting \(-\text{CH}_2-\text{CH}_2-\) group is long enough to allow the helical dimer formation between two \textbf{L1} molecules. The rigid phenyl groups attached to the 2,2′-bipyridinium unit places the allyl groups away from each other, preventing the intramolecular alkene metathesis reactions. The terminal allyl groups are expected to undergo intermolecular alkene metathesis reaction.

The multistep synthesis (see Scheme 2.6 in Chapter 2.3.1.7) of \textbf{L1} started by protecting the OH group of 4-bromophenol (compound 6). The OH group is converted into a tert-butyl dimethyl silyloxy (TBDMS) group which is not affected by lithiation reagents or by the conditions in the next steps. The synthesis of compound 8 was carried out in a one-pot, two-step reaction, comprised of lithiation followed by introduction of the SnBu\textsubscript{3} group. Compound 10 was synthesized similarly. Both compound 8 and 10 are starting materials for the Stille cross-coupling reaction. The palladium catalyzed cross-coupling between compound 10 and 11 yields 3-bromo-3′-methyl-2,2′-bipyridine, compound 12. The Stille coupling reaction between the organotin compound 8, and aromatic bromo compound 12, yields compound 13. Lithium diisopropyl amide (LDA) was used as the lithiation reagent in the synthesis of compound 14. LDA shows greater selectivity over BuLi in proton abstraction vs. nucleophilic addition. Deprotection of the OTBDMS protecting group using TBAF is a common procedure. Therefore, compound 14 was
deprotected using TBAF. The last step of the multi-step is the attachment of the allyl group onto compound 15.

Since L1 is soluble in CHCl₃ and [Cu(CH₃CN)₄]PF₆ is soluble in CH₃CN, a mixture of CHCl₃ and CH₃CN was used in crystal growing. After evaporation of the solvent, X-ray quality single crystals were obtained. The crystal growing attempts with L1 and other tetrahedral metal ions (Ag(I)) always yielded a white precipitate or microcrystalline powder. ¹H-NMR analysis showed that the precipitate is pure L1.

![Figure 3.39: Crystal structure (ball and stick representation) of the Cu(II) complex of L1. Hydrogen and solvents omitted for clarity. Color code, C; black, O; red, N; blue, P; purple; F; lime green, Cu(II); light blue.](image)

The crystal structure of the Cu(II) complex of L1 (Figure 3.39) shows that L1 forms a single stranded helical structure with Cu(II) ions. Rings A and B, and A' and B' show π–π stacking distances 3.527(2) Å and 3.540(5) Å, respectively. The Cu(II) ion has a distorted tetrahedral coordination geometry. The two 2,2'-bipyridinium cores are not planar. Two PF₆⁻ counter ions balance the charge of the Cu(II) complex of L1.
This crystal structure reveals that the $\pi-\pi$ stacking interactions between the aromatic rings and the freely rotating –CH$_2$–CH$_2$– single bond between two pyridine units of the two 2,2’-bipyridinium groups form a mononuclear Cu(I) complex, instead of a double stranded, dinuclear complex. Therefore, we proposed a new multi-step synthetic route (Scheme 5.1) to synthesize ligand L2, which has a rigid –C$_6$H$_4$– linker instead of –CH$_2$–CH$_2$– between the two 2,2’-bipyridinium groups, and rigid 1,10-phenantholine groups instead of the 2,2’-bipyridinium groups.
CHAPTER 4
CONCLUSIONS

UV-Visible spectroscopic studies of the [4,4′-bipyridinium/crown ether] [2]pseudorotaxanes show the effect of the HOMO-LUMO energy gap between the electron rich crown ether and the electron deficient 4,4′-bipyridinium axle on the energy of the charge transfer transition and the resulting color of the pseudorotaxanes and their stability.

The NMR studies performed on [4,4′-bipyridinium/neutral crown ether]2+ pseudorotaxane solutions show that in solution the pseudorotaxane is in fast equilibrium with its individual components.

The Job’s plots of pseudorotaxanes show that a 1:1 complexation between the axle and the wheel of all pseudorotaxanes in solution.

The Benesi-Hildebrand plots of [4,4′-bipyridinium/neutral crown ether]2+ [2]pseudorotaxanes show that bis-naphtho crown ethers (BN38C10 and BN32C8) bind to the axle molecules more strongly than the bis-p-phenyl crown ether (BPP34C10). Attachment of two negative charges onto the crown ether was achieved by sulfonating BPP34C10. The DSBPP34C10 crown ether binds to axles 10 times more strongly than the non-sulphonated analog (BPP34C10) in water.

Electrochemical studies of [2]pseudorotaxanes show that the reduction potential of the 4,4′-bipyridinium core decreases and the oxidation potential of the wheel increases upon
pseudorotaxane formation, due to the interaction of the electron-rich wheel with the electron-deficient axle.

Crystallographic studies of pseudorotaxanes show \( \pi-\pi \) stacking and C–H⋯O hydrogen bonding interactions in the solid state. All pseudorotaxanes except \([\text{PyBP/DB24C8}]^{2+}\) show a 1:1 complexation between the axle and the wheel in the solid state. \([\text{PyBP/DB24C8}]^{2+}\) shows an axle:wheel ratio of 1:2.

We have shown that the combinations of the linear-rigid \([\text{PyBP}]\text{[NO}_3\text{]}_2\) or \([\text{CpBP}]\text{Cl}_2\) axles with BPP34C10, BN38C10, BN32C8 or DSBPP34C10 crown ethers are versatile templating motifs for pseudorotaxane formation and are potential building blocks for the construction of MORFs.

The interactions between the axle and the wheel at low temperatures are stronger than at high temperatures. The stronger the interactions between the axle and the wheel, the higher the intensity of the corresponding pseudorotaxane solution. Variable temperature UV-vis studies of \([\text{C4BP/neutral crown ether} ]^{2+}\) \([2\]pseudorotaxanes show temperature sensing behavior of \([2\]pseudorotaxanes over a 100 °C window without changes in the \(\lambda_{\text{max}}\) value.

Metal binding studies of \([\text{PyBP/neutral crown ether} ]^{2+}\) pseudorotaxanes indicate that they have different binding affinities towards zinc, cadmium and mercury metal halides. Among the (+2) charged linear, rigid axle \([2\]pseudorotaxanes, only \([\text{PyBP/BN38C10}]^{2+}\) or \([\text{PyBP/BN32C8}]^{2+}\) yield dizwitterionic metal-organic rotaxanes with \(\text{ZnCl}_2\) and \(\text{ZnBr}_2\). Two (–1) charged \(\text{ZnX}_3^-\) moieties (\(X=\text{Cl}^-, \text{Br}^-, \Gamma\)) bind to the two ends of the \([2\]pseudorotaxanes. Attempts to grow crystals of MORFs with \([\text{PyBP/BPP34C10}]^{2+}\) \([2\]pseudorotaxanes and \(\text{ZnX}_2\) (\(X=\text{Cl}^-, \text{Br}^-, \Gamma\)) yield to the separation of the individual
components of the pseudorotaxanes. The wheel crystallizes, while the axle precipitates in
the case of ZnCl$_2$ or ZnBr$_2$. With ZnI$_2$, the axle crystallizes as [PyBP](ZnI$_3$)$_2$ instead of
forming a metal-pseudorotaxane complex.

All (+2) charged linear, rigid axle [2]pseudorotaxanes of [PyBP/BPP34C10]$^{2+}$ or
[PyBP/BN38C10]$^{2+}$ crystallize with (–2) charged CdBr$_4^{2–}$ and CdI$_4^{2–}$ counter ions; only

HgX$_2$ (X = Cl$^–$, Br$^–$, I$^–$), while [PyBP/BN38C10]$^{2+}$ [2]pseudorotaxanes show metal-
rotaxane binding with HgX$_2$ (X = Cl$^–$, Br$^–$) but not with HgI$_2$. During crystallization,
the neutral mercury halides convert into (–2) charged dimerized species, Hg$_2$X$_6^{2–}$ The
pseudorotaxane unit binds to two (–2) charged Hg$_2$X$_6^{2–}$ moieties to yield (–2) charged
metal-organic rotaxanes when X = Cl$^–$ and Br$^–$.

Metal-organic rotaxanes derived from [PyBP/BN38C10][NO$_3$]$_2$ and Hg$^{2+}$ halides (Cl$^–$,
Br$^–$, I$^–$) show blue/red dichroism due to the columnar arrangement of the
[PyBP/BN38C10]$^{2+}$ pseudorotaxane units in the crystals.

To use the most common cationic metal nodes for metal binding studies,
[2]pseudorotaxanes with negatively charged DSBPP34C10 wheel was prepared.
Differences in crystallization rate and color of [PyBP/syn–DSBPP34C10] and
[PyBP/anti–DSBPP34C10] facilitate the manual separation of the two isomeric, neutral
[2]pseudorotaxane crystals. It enables the separation of pure syn and anti isomers of
DSBPP34C10, which were inseparable by conventional methods.
The pyridine nitrogens of the metallo-ligand Cu(Pyacac)2 bind to the Cu(II) centers instead of forming pseudorotaxanes with diaza-18-crown-6 and lead to a 2D square grid. The shape and the size of the cavities of the 2D structure depend on the solvents used in the crystal growing attempts. The use of Cu(Phacac)2 prevents the square grid formation of metallo-ligand itself. Diaza-18-crown-6 forms a sandwiched structure with two Cu(Phacac)2 metallo-ligands. The N atoms of the diaza-18-crown-6 wheel coordinate to square planar Cu(II) centers of two adjacent axles and lead to penta-coordinated, square pyramidal Cu(II) coordination geometries.

Ligand L1 binds to Cu(II) to form a tetrahedral mononuclear metal complex which is driven by π–π interactions between the terminal phenyl group and the pyridine group of the 2,2’-bipyridinium core.
CHAPTER 5

FUTURE WORK

5.1. Synthesis of tetrasulphonated BN38C10

Negatively charged (–2) [2]pseudorotaxanes could be synthesized using tetrasulphonated BN38C10 (TSBN38C10), [CpBP]Cl₂ or [PyBP][NO₃]₂ axles (Figure 5.1). Negatively charged pseudorotaxanes have a high potential to undergo self-assembly with positively charged metal ions to yield neutral MORFs with different dimensionality. This approach facilitates the elimination of counter ions from the cavity space of the MORFs.

![Figure 5.1: Schematics of a) TSBN38C10 and b) negatively charged pseudorotaxane formation.](image)

5.2. Synthesis of larger diaza crown ethers and metallo-ligands with hexacoordinated metal centers.

The crystal structure of diaza-18-crown-6 bound Cu(Phacac)₂ (Figure 3.38) shows that diaza-18-crown-6 binds to Cu(Phacac)₂ from outside, instead of wrapping around it. Apparently, even at higher temperatures (65 °C) the barrier for the wheel to slip onto the axle is too high. To lower this barrier, larger wheel molecules, such as 1,13-diaza-24-crown-6 or dipyrido-24-crown-8 can be used (Figure 5.2a and b). Also, bis[3-
(4-phenyl)pentane-2,4-dionato[nickel(II) (Ni(Phacac)₂) can be used as the axle, since nickel is more likely to become hexacoordinate than copper.

Figure 5.2: Schematics of a) diaza-24-crown-8, b) dipyrido-24-crown-8 and c) Ni(Phacac)₂.

5.3. Molecularly woven materials

Ligand L₂ was designed to have favorable features to facilitate double stranded, dinuclear helicate formation. The Cu complex of L₁ shows that the –CH₂–CH₂– spacer and the C–C single bond between the two pyridinium rings of 4,4′-bipyridine provides enough flexibility to L₁ to adopt a confirmation that leads to a helical mononuclear complex. To impart rigidity to the structure, a m–C₆H₄ spacer and 1,10-phenanthroline groups are proposed (Figure 5.3).

Figure 5.3: Schematics of L₂.
The proposed multistep synthetic route for L2 is given in Scheme 5.1

Scheme 5.1: Multi-step synthesis of ligand L2
REFERENCES


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Appendix A

$^1$H-NMR and $^{13}$C-NMR spectral data of selected compounds
$^1$H-NMR of BPP34C10 in CDCl$_3$

$^{13}$C-NMR of BPP34C10 in CDCl$_3$
$^1$H-NMR of BN32C8 in CDCl$_3$

$^{13}$C-NMR of BN32C8 in CDCl$_3$
$^1$H-NMR of [CpBP]Cl$_2$ in CD$_3$OD

$^{13}$C-NMR of [CpBP]Cl$_2$ in CD$_3$OD
$^1$H-NMR of compound 13 in CDCl$_3$
$^1$H-NMR of compound 14 in CDCl$_3$
$^1$H-NMR of compound 15 in $d_6$-DMSO

$^{13}$C-NMR of compound 15 in $d_6$-DMSO
$^1$H-NMR of compound 16 in CDCl$_3$

$^{13}$C-NMR of compound 16 in CDCl$_3$
$^1$H-NMR of compound 19 in CDCl$_3$
Appendix B

Molar ratio plots and Benesi-Hildebrand plots of pseudorotaxanes
Molar ratio plots


Job’s plots of A) [PyBP/BN38C10][NO₃]₂ and B) [PyBP/BN32C8][NO₃]₂ pseudorotaxanes


Job’s plots of A) [CpBP/BN38C10]Cl₂ and B) [CpBP/BN32C8]Cl₂ pseudorotaxanes
Job’s plots of A) [C4BP/BN38C10][PF$_6$]$_2$ and B) [C4BP/BN32C8][PF$_6$]$_2$ pseudorotaxanes

Job’s plots of A) [CpBP/DSBPP34C10] and B) [C4BP/DSBPP34C10] pseudorotaxanes
Benesi-Hildebrand plots

\([\text{PyBP/neutral crown ether}][\text{NO}_3]_2\) [2]pseudorotaxanes

Benesi-Hilderbrand plots for A) \([\text{PyBP/DN38C10}][\text{NO}_3]_2\) and B) \([\text{C4BP/DN32C8}][\text{NO}_3]_2\) pseudorotaxanes

\([\text{CpBP/neutral crown ether}]\text{Cl}_2\) [2]pseudorotaxanes

Benesi-Hilderbrand plots for A) \([\text{CpBP/BN38C10}]\text{Cl}_2\) and B) \([\text{CpBP/BN32C8}]\text{Cl}_2\) pseudorotaxanes

Bensesi-Hilderbrand plots for A) [C4BP/DN38C10][PF₆]₂ and B) [C4BP/DN32C8][PF₆]₂ pseudorotaxanes

[DSBPP34C10/axle] [2]pseudorotaxanes

Bensesi-Hilderbrand plots for A) [C4BP/syn- and anti-DSBPP34C10]; B) [PyBP/ syn- and anti-DSBPP34C10][NO₃]₂; C) [CpBP/ syn- and anti-DSBPP34C10].
Appendix C

Solution state metal binding studies of [PyBP/BN38C10]$^{2+}$ and [PyBP/BN32C8]$^{2+}$ pseudorotaxanes
Solution state metal binding studies of [PyBP/BN38C10]$^{2+}$

A) ZnCl$_2$, B) ZnBr$_2$, C) ZnI$_2$ and D) HgI$_2$ binding studies of [PyBP/BN38C10]$^{2+}$[2]pseudorotaxanes in a 1:1 mixture of CH$_3$OH: CHCl$_3$ using UV-Visible spectroscopy
Solution state metal binding studies of [PyBP/BN32C8]^{2+}

A) ZnCl$_2$, B) ZnBr$_2$, C) ZnI$_2$ and D) HgI$_2$ binding studies of [PyBP/ BN32C8]^{2+} [2]pseudorotaxanes in a 1:1 mixture of CH$_3$OH: CHCl$_3$ using UV-Visible spectroscopy
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