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Crystalline Materials Incorporating Rotaxanes and Porphyrins

Pablo Alen Martinez Bulit
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Crystalline Materials Incorporating Rotaxanes and Porphyrins

By

Pablo Alen Martinez Bulit

A Dissertation
Submitted to the Faculty of Graduate Studies
through the Department of Chemistry and Biochemistry
in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy
at the University of Windsor

Windsor, Ontario, Canada

2019

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Crystalline Materials Incorporating Rotaxanes and Porphyrins

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Declaration of Co-authorship/Previous Publications

I. Co-Authorship

I hereby declare that this thesis incorporates material that is result of joint research, as follows:

I am the primary author on three of the publications that have resulted, or will result from the work outlined in this thesis. I acknowledge my supervisor, Stephen J. Loeb, for his contributions to the writing and editing of this thesis.

Chapter one, Section 1.4 is based on a review article that has been submitted for publication. I am the primary author of this manuscript. I acknowledge contributions form Alexander J. Stirk for the production of the final figures and from S.J Loeb in editing the manuscript.

Chapter two is a manuscript in preparation and it contains joint research with Kelong Zhu. It was also conducted in collaboration with Christopher A. O’Keefe under the supervision of Robert W. Schurko. S.J. Loeb, K. Zhu, and I designed the project. I conducted the experimental synthesis and characterization; Janeen Auld assisted running the mass spectrometry experiments. S.J. Loeb assisted in the solution of single-crystal X-ray diffraction structures. C.A. O’Keefe performed the solid-state NMR spectroscopy experiments and data analysis with input from R.W. Schurko.

Chapter three is a manuscript in preparation and it contains joint research with Kelong Zhu. It was also conducted in collaboration with Christopher A. O’Keefe under the supervision of Robert W. Schurko. S.J. Loeb, K. Zhu, and I designed the project. I conducted the experimental synthesis and characterization; Janeen Auld assisted running the mass spectrometry experiments. S.J. Loeb assisted in the solution of single-crystal X-ray diffraction structures. C.A. O’Keefe performed the solid-state NMR spectroscopy experiments and data analysis with input from R.W. Schurko.
Chapter four is a manuscript in preparation and it contains joint research with Kelong Zhu. S.J. Loeb, K. Zhu, and I designed the project. I conducted the experimental synthesis and characterization; Janeen Auld assisted running the mass spectrometry experiments. S.J. Loeb assisted in the solution of single-crystal X-ray diffraction structures.

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II. Previous Publication

This thesis includes one original paper that has been previously published/submitted for publication in a peer reviewed journal, as follows:

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Abstract

The work herein describes the synthesis and characterization of rotaxane molecules, the incorporation of a selection of these molecules into metal-organic frameworks (MOFs), and the study of how these rotaxanes respond to external stimuli such as changes in temperature and chemical environment, both in solution and when immobilized inside a MOF.

Chapter 1 introduces the concepts utilized during this work and presents a general overview of the state of the field.

Chapter 2 describes the fabrication of the first porphyrin-based MOFs incorporating a rotaxane linker, UWDM-7 and -8. Their structures were analyzed by single-crystal X-ray diffraction (SC-XRD), powder X-ray diffraction (PXRD), and the rotational dynamics of the crown ether rings were studied with variable temperature (VT) $^2$H solid-state nuclear magnetic resonance spectroscopy (SSNMR). It was found that the rotation of these rings could be controlled by modifying the rigidity of the framework and by adding/removing guest solvent molecules within the pores of the materials.

Chapter 3 presents an initial approach to the use of reticular chemistry applied to MOFs containing mechanically interlocked molecules and porphyrins. The synthesis of two porphyrin linkers is described. Another example of a mixed-linker MOF, UWDM-9, is presented and its structural features are described. The topological analysis of UWDM-9 resulted in the report of the first occurrence of the tui topology. Preliminary VT $^2$H SSNMR studies are presented, and they show a lower activation energy for the partial rotation of the crown ether macrocycles compared to other UWDM MOFs.
Chapter 4 describes a new method for the synthesis of rotaxanes with high compositional complexity. Rotaxanes were synthesized using a capping method in a one-pot reaction that also creates a porphyrin core. This new synthetic route allows for the incorporation of various substituent groups on these molecules, different crown ether molecules, as well as recognition sites. Six rotaxanes are presented and characterized using XRD, NMR spectroscopy, and mass spectrometry.

In Chapter 5, some of these rotaxanes are tested as linkers in the synthesis of MOFs. The process to decide the conditions to test and which structures to target is described, along with simulations supporting some of the findings.

Finally, Chapter 6 puts the findings of this work in retrospect and analyzes potential future work derived from this dissertation and contemplates the directions the broader field might take.
I dedicate this work to the three bravest women I know: my mother, my aunt, and my grandmother.
“They don’t think it be like it is but it do”

Oscar Gamble
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<th>Full Form</th>
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<td>24C6</td>
<td>24-Crown-6 ether</td>
</tr>
<tr>
<td>24C8</td>
<td>24-Crown-8 ether</td>
</tr>
<tr>
<td>ADC</td>
<td>4,4’-Azodiphenyldicarboxylic acid</td>
</tr>
<tr>
<td>ASAP</td>
<td>Atmospheric solid analysis probe</td>
</tr>
<tr>
<td>B24C6</td>
<td>Benzo-24-crown-6 ether</td>
</tr>
<tr>
<td>BDC</td>
<td>1,4-Benzenedicarboxylate</td>
</tr>
<tr>
<td>BPDC</td>
<td>4,4’-Biphenyldicarboxylic acid</td>
</tr>
<tr>
<td>bipy</td>
<td>4,4’-Bipyridine</td>
</tr>
<tr>
<td>BODCA</td>
<td>1,4-Bicyclo[2.2.2]octane dicarboxylic acid</td>
</tr>
<tr>
<td>br</td>
<td>Broad</td>
</tr>
<tr>
<td>CBPQT</td>
<td>Cyclobis(paraquat-p-phenylene)</td>
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<td>CH-TCPP</td>
<td>5,10,15,20-Tetrakis(4-carboxyphenyl)-tetracyclohexenoporphyrin</td>
</tr>
<tr>
<td>COSY</td>
<td>Correlation Spectroscopy</td>
</tr>
<tr>
<td>CSD</td>
<td>Cambridge Structural Database</td>
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<td>d</td>
<td>Doublet</td>
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<tr>
<td>DB24C8</td>
<td>Dibenzo-24-crown-8 ether</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DEF</td>
<td>N,N-Diethylformamide</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DOSY</td>
<td>Diffusion Ordered Spectroscopy</td>
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<tr>
<td>DPNI</td>
<td>$N-N'$-Di-(4-pyridyl)-1,4,5,8-naphtalenetetracarboxydiimide</td>
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<td>DPT</td>
<td>3,6-Di-4-pyridyl-1,2,4,5-tetraazine</td>
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<tr>
<td>$E_a$</td>
<td>Activation Energy</td>
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<td>Electric-field gradient</td>
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<td>ESI</td>
<td>Electrospray ionization</td>
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<td>FML</td>
<td>Fast motion limit</td>
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<tr>
<td>GoF</td>
<td>Goodness of fit</td>
</tr>
<tr>
<td>HR-MS</td>
<td>High resolution mass spectrometry</td>
</tr>
<tr>
<td>IMR</td>
<td>Intermediate motion regime</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>MAS</td>
<td>Magic-angle spinning</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>MIM</td>
<td>Mechanically interlocked molecule</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal-organic framework</td>
</tr>
<tr>
<td>Mp</td>
<td>Melting point</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NOESY</td>
<td>Nuclear Overhauser Enhancement Spectroscopy</td>
</tr>
<tr>
<td>NU-#</td>
<td>Northwestern University MOF series</td>
</tr>
<tr>
<td>OE-TCPP</td>
<td>$\beta$-Octaethyl-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition/Description</td>
</tr>
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<td>--------------</td>
<td>-----------------------</td>
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<tr>
<td>PCN-#</td>
<td>Porous coordination network MOF series</td>
</tr>
<tr>
<td>PPF-#</td>
<td>Porphyrin paddlewheel framework MOF series</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-ray diffraction</td>
</tr>
<tr>
<td>q</td>
<td>Quartet</td>
</tr>
<tr>
<td>RCM</td>
<td>Ring closing metathesis</td>
</tr>
<tr>
<td>RCSR</td>
<td>Reticular Chemistry Structure Resource</td>
</tr>
<tr>
<td>RPM</td>
<td>Robust porphyrin material</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>SALE</td>
<td>Solvent-assisted ligand exchange</td>
</tr>
<tr>
<td>SALI</td>
<td>Solvent-assisted ligand incorporation</td>
</tr>
<tr>
<td>SBU</td>
<td>Secondary building unit</td>
</tr>
<tr>
<td>SC-XRD</td>
<td>Single-crystal X-ray diffraction</td>
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<td>SML</td>
<td>Slow motion limit</td>
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<tr>
<td>S/N</td>
<td>Signal-to-noise</td>
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<td>SSNMR</td>
<td>Solid-state Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
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<tr>
<td>TCPB</td>
<td>1,2,4,5-Tetrakis(4-carboxyphenyl)benzene</td>
</tr>
<tr>
<td>TCBPP</td>
<td>5,10,15,20-Tetrakis(4-carboxybiphenyl)-porphyrin</td>
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<td>5,10,15,20-Tetrakis(4-carboxyl)-21H,23H-porphyrin</td>
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<td>TDC</td>
<td>Tryptcene-9,10-dicarboxylate</td>
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<td>Description</td>
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<td>TDCPP</td>
<td>5,10,15,20-Tetrakis(3,5-dicarboxyphenyl)-porphyrin</td>
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<tr>
<td>THF</td>
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<td>TMS</td>
<td>Tetramethylsilane</td>
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<td>TOCSY</td>
<td>Total Correlation Spectroscopy</td>
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<td>ToF</td>
<td>Time-of-flight</td>
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<td>University of California-Los Angeles MOF series</td>
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<tr>
<td>UWDM-#</td>
<td>University of Windsor Dynamic Material MOF series</td>
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<td>VT-</td>
<td>Variable temperature</td>
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Chapter 1. Key Concepts, Definitions, and State of the Field

1.1 Introduction

The research contained in this work combines two fields of chemistry: supramolecular chemistry and reticular chemistry. The first emerged as a new area in the late 70s and it is defined as “the chemistry of molecular assemblies and of the intermolecular bond”. Supramolecular chemistry gained relevance after the 1987 Nobel Prize in Chemistry for the “development and use of molecules with structure-specific interactions of high selectivity” was awarded to Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen, and it was recognized again recently, with the 2016 Nobel Prize in Chemistry for the “the design and synthesis of molecular machines” awarded to Jean-Pierre Sauvage, J. Fraser Stoddart and Bernard Feringa.

The second area, reticular chemistry, is much younger but it has also been internationally recognized. The 2018 Wolf Prize in Chemistry was awarded to Omar Yaghi, for pioneering reticular chemistry via metal-organic frameworks and covalent organic frameworks, and Makoto Fujita for conceiving metal-directed assembly principles leading to large highly porous complexes.

By working between these two disciplines, we aim to find a point where we can synergistically combine their core concepts and apply them for the design and study of porous materials with components capable of dynamic behaviours. The fundamental concepts to put this work in context are described below, as well as some of the most recent findings by our research group and others working in the same field.
1.2 Mechanically Interlocked Molecules

A mechanically interlocked molecule (MIM) consists of two or more molecular entities joined by a mechanical bond, which is defined as an entanglement in space between two or more molecular entities, resulting in the need for the breakage of chemical bonds between atoms to separate these components. Catenanes (from the Latin *catena*, chain) and rotaxanes (from *rota*, wheel; and *axis*) are the most common MIMs, and one of their most exciting characteristics is their ability to exhibit a dynamic behaviour (*vide infra*). Catenanes are formed by two or more ring-like molecules interlocked in the same way as the links of a chain. Rotaxanes are formed by a dumbbell-shaped axle with ring-like molecules wrapped around it. The groups at ends of the axle, called stoppers, are bulky enough to prevent the dissociation of the components. Cartoons of these two types of molecule, and other dynamic molecules, are shown on Scheme 1.4.1, and real examples are shown throughout this introductory chapter.

Our understanding of the processes involved in molecular recognition - *i.e.* specific, non-covalent interactions between molecules- has made the synthesis of some MIMs a quotidian task. There are three recognized pathways to make rotaxanes: capping, clipping, and slipping. All these methods require a molecular recognition step between the two components that will form the MIM and directing this recognition event can be achieved through precise control of the electrostatic interactions present on the separate components. Supramolecular chemistry is the discipline that studies all these phenomena and interactions. It relies on organic chemistry, to build these molecules, on physical chemistry, to determine how they associate and behave, and on materials chemistry, to incorporate these molecules into *functional* materials.
1.3 Metal-organic Frameworks

For the last three decades, extensive research focused on the synthesis, characterization, and prediction of structural properties on metal-organic frameworks (MOFs) has been published. These materials are a subclass of coordination polymers, defined by having an open framework and potential voids. They can be deconstructed into two components: (i) a metal cluster or secondary building unit (SBU) and (ii) one or more organic linkers. The study of how these two components interact and result in chemical nets is known as reticular chemistry. Reticular chemistry relies heavily in the topological analysis of nets, and it has appropriated a variety of mathematical terms that do not necessarily mean the same for a mathematician as for a materials scientist. For the purpose of this work, topology is understood as the underlying representation of a molecule or chemical net, which focuses on its connectedness and continuity. Or, in other words, it only analyzes the coordination bonds between SBUs and linkers, and the geometric features of the linkers. To help visualize such features, augmented representations consisting of replacing these components by polyhedra are used. Topological nets are identified by a three-letter code, and each code represents a net of minimal transitivity.

1.3.1 Metal-Organic Frameworks with Porphyrin Linkers

Porphyrin molecules have transcended from being studied as dyes and biomolecules to fields like catalysis, functional materials, solar energy, etc. Whereas the porphyrins present in living organisms are challenging to synthesize artificially, there are a vast number of synthetic porphyrins that can be fabricated and tailored in the laboratory. These molecules have been used in a variety of nanomaterials, including
MOFs. They have key characteristics as organic linkers: high thermal and chemical stability, facile synthesis, and attractive chemical properties.

The study of these materials has resulted in the production of porous materials capable of extremely high gas uptake, outstanding catalytic activity, and new topological networks, just to mention a few examples. Various coordination motifs have been used in the construction of these frameworks. Carboxylic acids are, by far, the most extensively used donor groups; however, other donor groups such as imidazole, sulphone, and pyridine have been successfully utilized in the synthesis of MOFs.

1.4 The Challenge of Organizing Mobile Molecules in the Solid State

Utilizing a combination of supramolecular chemistry and organic synthesis, scientists have created a variety of molecular systems that crudely imitate the workings of macroscopic machinery (or at least machine-like components). Some notable examples include gates/doors, pumps, elevators, and nanocars as well as those that mimic biological systems such as muscles, a DNA walker, and peptide synthesizers. While these sophisticated molecular systems are capable of rudimentary operation in solution, our inability to organize them in a coherent manner and amplify their function renders most of them simple curiosities, for now. One approach to achieving the next level of molecular organization is to arrange these mobile units in close proximity to each other in infinite periodic arrays, i.e. in crystalline networks. A class of solid-state materials that is well suited for this application is MOFs. MOFs can be very robust materials if the right combination of organic linkers and metal nodes is used and can potentially provide the large void space necessary for unimpeded motion in the solid-state. In 2010, Stoddart, Yaghi, and coworkers introduced the term robust dynamics
This section recounts where this approach of organizing “machines” in the solid-state has taken the field in the intervening years and attempts to identify where we see it going in the future (Scheme 1.4.1).

Scheme 1.4.1. Installing dynamic linkers – those containing rotor units, rotaxanes, catenanes, molecular shuttles and unidirectional propellers – inside crystalline, metal-organic frameworks, allows for the organization of these mobile molecules into materials with a packing high density.

The use of MOFs as the construct for the organization of large dynamic molecules in the solid-state has many advantages: (i) the robust composition and chemical diversity of MOFs allow for tremendous versatility in linker design, (ii) MOFs have well defined
structures and the data available on the structure and topology of these materials enables the use of reticular synthesis,\textsuperscript{7,32–34} (iii) their large internal void space has the potential to permit large amplitude motions and (iv) this inherent porosity enables the diffusion of sizable molecules inside these materials creating the potential for actuation, sensing and host-guest chemistry.

1.4.1 Metal-organic Frameworks and Molecular Rotors

A molecular motion that caught the early attention of material scientists was the simple rotation of a phenyl ring of a MOF linker (strut)\textsuperscript{35–42} as these units can be thought of as molecular rotors. For example, rotation of the phenyl group of the 1,4-benzenedicarboxylate (BDC) linker in iconic MOF-5 was characterized by $^2$H solid-state NMR (SSNMR) spectroscopy and shown to have a barrier to rotation of 47.3 kJ/mol, with a pre-exponential factor of $1.6 \times 10^{12}$ s$^{-1}$. This means that at room temperature, rotation is occurring at a rate of 6700 Hz. With this information in hand, Garcia-Garibay and coworkers sought out a related linker that could exhibit the same dynamics, but in a much more efficient manner. In an elegant study, they reported the first example of a barrierless molecular rotor functioning in a MOF.\textsuperscript{43} To achieve extremely rapid motion, the rotational barrier of the rotor component needed to be smaller than the thermal energy ($E_a \leq 2.495$ kJ/mol at 300 K) and the MOF structure required enough free volume to allow for completely unhindered motion. Four architectural features were seen as key: (i) the size and shape of the rotator unit – this determines the surface area and moment of inertia, (ii) the free volume available for rotation – this must be larger than the revolution volume of the rotator, (iii) the chemical nature and torsional barriers of the bonds for both the rotator and the stator – these effect
the activation energy of the rotation and (iv) the orientation of the rotator with respect to the stator – which should be axially symmetric. Bicyclo[2.2.2]octane was selected as the rotator since its rotary volume is a cylinder with a diameter >5.6 Å which is very close to that of a phenyl ring and previous studies had determined an activation energy for this group to be between 4.8 and 11.3 kJ/mol.\textsuperscript{44} Linker 1,4-bicyclo[2.2.2]octane dicarboxylic acid (BODCA) allowed direct incorporation of the rotor into a MOF with \textit{pcu} (primitive cubic, 6-c) topology (\textbf{Figure 1.4.1}).\textsuperscript{45} The rotor dynamics of BODCA-MOF were studied by \textit{\textsuperscript{1}H} and \textit{\textsuperscript{2}H} SSNMR. First, spin-lattice relaxation experiments were used to determine the activation energy of the rotation of the linker, giving a value of 0.774 kJ/mol. Variable temperature (VT) \textit{\textsuperscript{2}H} SSNMR showed that between 292 and 50 K the sample is at the fast-motion limit (FML, motion occurring at >10 MHz, increasing rates further does not affect the powder patterns). Lowering the temperature to between 50 and 12 K resulted in coalescence of the Pake doublet (distinctive, mirror symmetric powder pattern arising from dipole coupling between two $\frac{1}{2}$ spin nuclei or the first order quadrupolar interaction for integer spin nuclei). Between 12 and 9 K intermediate-motion regime rates (IMR, motion occurring at rates between $10^3$-$10^7$ Hz, the shape of the patterns varies greatly with rates) for a two-site jump are observed while at 6 K, the motion is at the slow-motion limit (SML, motion occurring at rates $<10^3$ Hz). Calculated activation energies and rotation frequencies showed that for BODCA-MOF, rotation in this solid is comparable to that expected in high-density gases or low-density liquids.
Figure 1.4.1. (A) Augmented representation of BODCA-MOF (pcu net) with rotator fragment shown in blue, stator in red, and SBUs as octahedra. (B) BODCA linker. (C) VT $^2$H SSNMR of BODCA-MOF (black, experimental; blue, simulated) showing rotation at the FML above 21 K, Adapted from [42].

Although we sometimes (incorrectly) think of these molecular systems in terms of macroscopic objects, molecules confined in nanoscopic environments often behave in unexpected ways. A common analogy to describe these conditions is that operating molecular machines at the nanoscale is like trying to “swim in molasses or walk in a hurricane”. In this respect, Garcia-Garibay was able to study the effect of solvent on the rotation rates of a molecular rotor inside a MOF. A pillaring linker consisting of a central triptycene unit, alkynyl spacers and pyridine donors that can bind to an SBU was designed and incorporated into the UCLA-R# (University of California Los Angeles – Rotor) series of MOFs. Linear dicarboxylate linkers were used to form a 2D grid; BDC for UCLA-R1, 4,4’-biphenyldicarboxylate (BPDC) for UCLA-R2, and tryptcene-9,10-dicarboxylate (TDC) for UCLA-R3. The resulting MOFs (Figure 1.4.2) are isoreticular to MOF-5 and exhibit varying degrees of interpenetration; UCLA-R2 (4-fold), UCLA-R1 (2-fold) and UCLA-R3 (non-interpenetrated). SC-XRD analysis showed that the only
structure with enough void space to allow free motion of the rotator was UCLA-R3 which was studied by VT $^2$H SSNMR using a deuterium-labeled linker.

For UCLA-R3, the blades of the TDC groups interdigitate which restricts their mobility but the triptycene units of the linker have enough void space between adjacent rotators (~10.3 Å) to accommodate the volume of their revolution. VT $^2$H SSNMR experiments showed that the rotation rates of the triptycene units vary from 800 kHz at 293 K to the FML above 333 K. The activation energy for the rotation was calculated to be 56.5 kJ/mol with a pre-exponential factor of $8.7 \times 10^{15}$ Hz. When comparing this pre-exponential factor to the expected value (ca. $5 \times 10^{11}$ Hz), the authors proposed that the difference could be explained using hydrodynamic theory and determined the viscosity of the DMF molecules confined in the pores to be $13.3 \text{ N}\cdot\text{s}\cdot\text{m}^{-2}$; a value four orders of magnitude larger than the viscosity of bulk DMF and comparable to that of honey.

Figure 1.4.2. (A) Augmented representation of UCLA-R3 (pcu net) with rotator fragment shown in blue, stator in red, and SBUs as octahedra. (B) Rotor linker R3. (C) VT $^2$H SSNMR of UCLA-R3 showing the different motions observed. Adapted from [46].
1.4.2 Metal-organic Frameworks Containing Mechanically Interlocked Molecules

Early attempts to make materials that might exhibit robust dynamics resulted in several MOFs that incorporated mechanically-interlocked molecules (MIMs) such as rotaxanes\textsuperscript{49-52} and catenanes\textsuperscript{53-55}, but the mobility of the interlocked components – large macrocyclic wheels such as cucurbiturils and crown ethers – was severely limited by a lack of sufficient void space. However, since those early reports, some sophisticated examples of MOFs incorporating MIMs capable of undergoing large amplitude conformational changes have been reported.

1.4.2.1 Rotation (Pirouetting) of a Wheel

Rotaxanes exhibit two primary types of dynamic behaviour. The macrocyclic wheel can rotate about the axle (often called pirouetting), or it can move between recognition sites, displaying a to-and-fro, translational motion (known as shuttling). The first pirouetting motion of a macrocyclic wheel of a [2]rotaxane incorporated into a MOF was reported by Loeb and Schurko.\textsuperscript{56}

A tetracarboxylate [2]rotaxane linker with a 24-crown-6 ether (24C6) macrocycle was prepared using ring-closing metathesis\textsuperscript{57} by clipping a polyether precursor around an anilinium recognition site; a \textsuperscript{2}H label was inserted into the macrocycle by reduction of the resulting double bond (Figure 1.4.3a). The rotaxane linker (R\textsubscript{124}) was used to prepare a MOF designated UWDM-1\textsubscript{24} (University of Windsor Dynamic Material). The structure of UWDM-1\textsubscript{24} (Figure 1.4.3b) consists of copper paddlewheels linked by rotaxanes with an fog topology (3,4-c).\textsuperscript{58} VT \textsuperscript{2}H SSNMR spectra showed that at low temperatures, the macrocycle is static, but upon raising the temperature three different motion regimes can
be accessed: (i) two-site jumps of the deuterons in the flexible alkyl portion of the ring, (ii) partial rotation of the crown ether and (iii) full rotation of the crown ether.

Following the study on UWDM-1\textsubscript{24}, two analogous linkers were prepared to determine the influence of ring size and shape on the rotational dynamics; UWDM-1\textsubscript{22} and UWDM-1\textsubscript{B24} with 22-crown-6 (22C6) or benzo-24-crown-6 (B24C6) respectively.\textsuperscript{59} Both MOFs showed reduced rotational dynamics for the wheels. It was proposed that the strain in the macrocycle and the stronger intermolecular interactions between the smaller ring and axle were responsible for the lower mobility in UWDM-1\textsubscript{22}, while the bulkier benzo group in UWDM-1\textsubscript{B24} produced unfavorable steric hindrance within the MOF that reduced motional freedom.

![Figure 1.4.3](image)

**Figure 1.4.3.** (A) Rotaxane linker R1\textsubscript{24} used in the construction of UWDM-1. (B) Augmented representation of UWDM-1 (fog net) with the rotaxane axle in blue, 24C6 rings in red, and Cu paddlewheels in green.

Loeb and co-workers also reported the synthesis and characterization of a series of pillared MOFs in which a reversible phase change could be used to effect the mobility of the macrocyclic wheel – toggling the rotation ON and OFF.\textsuperscript{60} The pillaring ligand (R2)
was constructed with an anilinium-based axle containing \textit{meta}-xylene substituents as stops, a 24C6 macrocycle and pyridyl groups for coordination to the SBUs (Figure 1.4.4). The dicarboxylate linkers 4,4’-azodiphenyldicarboxylate (ADC) and BPDC were used to create 2D grids which were then pillared with the rotaxane ligand to create UWDM-2 and UWDM-3 with 3- and 2-fold interpenetrated \textit{pcu} nets respectively.

The same deuterium labeling strategy employed for UWDM-1 was used to study the rotation of the 24C6 ring by VT \textsuperscript{2}H SSNMR spectroscopy. The high degree of interpenetration observed for the as-synthesized materials UWDM-2 and UWDM-3 was shown to create a closely packed structure with very limited space for rotation of the ring. SSNMR studies showed that increasing temperature resulted in only two-site jumps and partial rotation of the ring. However, VT PXRD experiments on as-synthesized UWDM-3 showed that a phase change occurs (\textit{\alpha}-UWDM-3 to \textit{\beta}-UWDM-3) upon heating and solvent loss which can be reversed by re-solvation. Interestingly, while \textit{\alpha}-UWDM-3 showed restricted mobility, \textit{\beta}-UWDM-3 showed full rotation of the macrocyclic ring above 381 K. The authors described the position of the macrocyclic ring with respect to the MOF framework in \textit{\alpha}-UWDM-3 as a “round peg in a square hole” and rationalized the increased mobility of \textit{\beta}-UWDM-3 as being a result of removing this constraint – the ring is released from the square grid – resulting in an increased volume for motion.
Loeb also studied the dynamics of a MOF with an unsymmetrical benzimidazole-based rotaxane linker\textsuperscript{61}. With this linker, described as Y-shaped (Figure 1.4.5a), it was possible to study the influence of changing the recognition motif on the rotational dynamics of an interlocked 24C6 macrocycle. R3 was synthesized using the clipping method described for R1 and R2 (vide supra). This linker provides much stronger interactions between the axle and wheel components, as there are two charge-assisted hydrogen bonds between the protonated recognition site and the 24C6 ring. Note: as the nitrate counterion was an integral part of the SBU it was not possible to remove the template to reduce these interactions.

UWDM-5 contains an atypical SBU formed by two Zn\textsuperscript{II} ions, four carboxylate groups of R3, a coordinated nitrate ion, and a coordinated DEF molecule. The final
structure adopts a *pts* topology (cooperite, 4,4-c), with 18% void space. The packing of the structure shows that the distance between adjacent macrocyclic rings is enough to avoid ring-ring interactions (Figure 1.4.5). Rotation of the 24C6 ring monitored by VT \(^3\)H SSNMR confirms the unconstrained environment of the rings with full rotation occurring at 381 K. A comparison between the motions observed in UWDM-1 and UWDM-5 suggests that the influence of having a bulkier and stronger recognition site is only appreciable at low temperatures. When enough energy is provided to the system for the rotation of the macrocycles to occur, the energetic differences between the sets of non-covalent interactions become negligible.

![Diagram](image)

**Figure 1.4.5.** (A) Rotaxane linker R3. (B) Augmented representation of UWDM-5 (*pts* net) with the rotaxane axle in blue, 24C6 rings in red, and the SBUs in green and yellow. (C) VT \(^2\)H SSNMR of UWDM-1 showing static behaviour at 160 K, a combination of a two-site jumps and partial rotation at 324 K and full rotation at 423 K. Simulated spectra in red. (D) Schematic representations of the motions observed for a 24C6 ring.
A different approach to the synthesis of MOFs that contain internal MIMs is post-synthetic modification (PSM). 63 Although this method has many advantages, not all MOFs are suitable and only a single example has been reported that gives rise to a dynamic MIM in MOF. Stoddart, Farha, Hupp and co-workers successfully incorporated a [2]catenane into NU-1000 64,65 using the PSM protocol known as solvent-assisted ligand incorporation (SALI). 66 NU-1000 was constructed using 4,4’,4’’,4’’’-(pyrene-1,3,6,8-tetraaryl) tetrabenzoate (TBAPy) linkers and Zr$_6$ SBUs. The geometry of the linker results in an 8-connected Zr-cluster with a csq (4,8-c) topology (Figure 1.4.6b). 13,67 This topology cannot form interpenetrated structures and the arrangement of the linkers produces distinct triangular and hexagonal channels with dimensions of ~12 Å and ~30 Å respectively. The mesoporous hexagonal channel allows for the diffusion of large molecules and the terminal hydroxo ligands on the zirconium cluster are conveniently accessible. The stability of this material is remarkable, being able to withstand pH ranges from 1-12 and temperatures up to 500 °C. 66,68
**Figure 1.4.6.** (A) Catenane ligand FC$^{n+}$. (B) Augmented representation of a section of the hexagonal pore in NU-1000 (csq net) with Zr SBU’s in green, TBAPy linkers in red and cartoons representing attached FC$^{n+}$ ligands. (C) UV-Vis-NIR spectra showing circumrotation in NU-1000-FC$^{n+}$; cartoons show the two possible co-conformations of the catenane ligand. (D) Cyclic voltammograms showing the accessible redox states of FC$^{n+}$. Adapted from [64].

A bistable [2]catenane formed by a cyclobisparaquat (CBPQT) ring functionalized with a triazole group, a 4-methoxybenzoate chain and an interlocked ring with both tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) units was synthesized (Figure 1.4.6a). Phase-pure NU-1000 was mixed with a solution of the catenane ligand, in acetonitrile at 60 °C for 48 h, producing the MOF designated as NU-1000-FC$^{n+}$. The material was characterized by solution $^1$H NMR spectroscopy of a
digested sample of the MOF and elemental analysis. Adsorption isotherms indicate the added ligands are located in the hexagonal channels. With the assistance of molecular mechanics modeling, a structure of the solid was proposed and is depicted in Figure 1.4b.

Circumrotation of the TTF/DNP macrocycle was monitored in solution by cyclic voltammetry. A system that is only redox active towards TTF and not TBAPy was chosen to avoid decomposition of the framework and it was possible to observe the interactions of both TTF and DNP with the CBPQT static fragment. UV-Vis spectroscopy confirmed the observations that NU-1000-FCn+ behaves as a bistable molecular switch – a true example of robust dynamics.

1.4.2.2 Translation (Shuttling) of a Wheel

While the void required for a macrocycle to freely rotate inside the pore of a MOF is substantial, creating enough space for an analogous macrocycle to be displaced back and forth from its original position to a new position approximately a nanometer away along a rigid track is considerably more challenging. Expanding their work on MOFs with MIMs, Loeb, Zhu and coworkers reported the fabrication of a MOF with a molecular shuttle that operates inside the pores.69

Linker R4 incorporates two benzimidazole recognition sites and an interlocked 24-crown-8 ether (24C8) macrocycle (Figure 1.4.7). Triphenyl units act as stoppers and also create a shield around the wheel, providing the required empty space for the shuttling motion to occur. Carboxylate groups installed in the para position of the triphenylene units provide the coordinating units to the SBUs. A 13C label was installed at both the recognition sites which allowed occupied and unoccupied sites to be
distinguished by NMR spectroscopy. The shuttling behaviour of the linker was first studied in solution; an energy barrier of 32.2 kJ/mol and a rate of $1.4 \times 10^7$ Hz at 298 K were determined by VT $^{13}$C NMR spectroscopy. The linker was then incorporated into a Zn-based MOF. While the structure superficially resembles the two-fold interpenetrated lattices of IRMOF-15, the linker used for this material produces a covalently link between the lattices resulting in an *hea* topology (heazlewoodite, 4,6-c),\(^3\) with 47% void space. The translational shuttling motion of the 24C8 ring in UWDM-4 was monitored by VT $^{13}$C SSNMR. These experiments showed that the shuttling capacity of the linker is preserved after its incorporation into the MOF. The rate of shuttling in the solid-state was calculated to be 283 Hz, with an energy barrier of 59.0 kJ/mol. The origin of the higher barrier to shuttling in UWDM-4 relative to that observed in solution for the ligand is not clear. Although there could undoubtedly be both enthalpic (steric) and entropic (solvent organization) reasons, with only one example available it is too early to offer a physically realistic explanation.
**Figure 1.4.7.** (A) Rotaxane linker R4. $^{13}$C enriched sites are represented by *. (B) Augmented representation of UWDM-4; green and yellow cubes are connected by the crossbar of the H-shaped linker, to give an *hea* topology rather than an interpenetrated *pcu* topology. (C) VT $^1$H-$^{13}$C CP/MAS SSNMR spectra of a $^{13}$C enriched sample of UWDM-4 with shuttling rates. (D) $^{13}$C 2D EXSY spectrum of UWDM-4 showing cross-peaks due to exchange between the two $^{13}$C sites.

### 1.4.3 Metal-organic Frameworks Incorporating Molecular Motors

Perhaps the most iconic examples of molecular machinery in solution, on surfaces and attached to soft materials are the unidirectional rotors (motors) pioneered by Feringa and coworkers. $^{70}$ Most recently, these researchers have turned their attention to the crystalline solid state and shown that a second-generation light-driven unidirectional motor, can be incorporated into a pillared MOF $^{71}$ The pillaring linker (L, **Figure 1.4.8a**)
was designed to undergo a solvent-assisted linker exchange (SALE)\textsuperscript{72} replacing dipyridynaphtalenediimide (DPNI) in a MOF consisting of 1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene (TCPB) and zinc paddlewheels. By using SALE instead of solvothermal synthesis, linker L is not subject to conditions under which the fairly sensitive olefinic bond of the rotor might result in fatigue and/or decomposition. \textsuperscript{1}H NMR spectroscopy, elemental analysis, and inductively coupled plasma atomic emission spectroscopy (ICP-AES) were used to confirm the complete substitution of the DPNI by L. PXRD confirmed the isoreticular structure of M-MOF to the parent BrYO-MOF. The single crystal analysis only provided a partial solution of the structure; the 2D grid was resolved, but the portion corresponding to the pillaring ligand and molecular motor was highly disordered. The structure of M-MOF was determined to have a non-interpenetrated \textit{fsc} (4,6-c) topology (Figure 1.4.8b)\textsuperscript{73} and the crystallinity was only maintained when saturated with solvent. Considering the unit cell dimensions and composition of M-MOF, one cubic centimeter contains \textit{ca.} $4 \times 10^{20}$ motor units.
**Figure 1.4.8.** (A) Molecular motor linker M and auxiliary linker TCBP. (B) Augmented representation of M-MOF ($f_{sc}$ net) with rotary motor fragment in red, stator in blue, TCBP linker in green and Zn paddlewheels as octahedra. (C) Schematic representation of the unidirectional rotary cycle. PEZI: photochemical E/Z isomerization, THI: thermal helix inversion. (D) Raman spectra showing photochemical and thermal isomerization in M-MOF. Adapted from [70].
The unidirectional rotation of the motor was studied by Raman spectroscopy in a single-crystal saturated with solvent (Figure 1.4.8c and d). These studies showed the linker inside M-MOF can undergo the same motion as in solution. The material could be cycled through the photoisomerization-relaxation steps required for a full rotary cycle without any indication of fatigue/failure. The energetic barrier for the thermal helix inversion was determined to be 88.6 kJ/mol, a value essentially identical to the barrier determined in solution (87.7 kJ/mol in DMF @ 20 °C). The fact that incorporation into a solid-state material does not affect the dynamics of the system is remarkable and highlights that similar photodynamic systems might be ideal targets for displaying robust dynamics.

1.4.4 Future Perspectives and Outstanding Questions

Today – in a fairly short timeframe, chemists have adapted molecular switches and machinery once confined to solution and organized them to operate in the highly condensed solid phase of metal-organic framework materials. It is a combination of advances in both the areas of porous crystalline (MOF) materials and molecular machines that has allowed this amalgamation to occur. These initial forays into the solid-state have established unequivocally that this is an area rich for exploration and one that can organize extremely complex, large amplitude motions at high density.

Tomorrow – even in highly ordered systems, it is not currently feasible to address individual molecules as separate units, so it unlikely that near-future applications will be those that involve computer memory or RAM. However, the ability to organize, switch, or align groups of molecules – or solid-state domains of dynamic molecules – can have a
significant impact on bulk material properties (electrical, optical) that rely on their orientation. This is very likely where the first true applications for robust dynamics lie.

An optimistic future – one of the exciting advances in MOF materials has been the demonstration that multiple functionalities can be assembled into the same material – 2 and 3 components very precisely\textsuperscript{74–76} and many more randomly\textsuperscript{77,78} – providing optimism for the possibility of using MOFs as a platform for arranging multiple machinery components. The idea of creating factory-like, nano-scale assembly lines with multiple molecular machine components working together to achieve a unified goal is somewhere on the horizon – not quite reality, but no longer the realm of science-fiction.

Not everything in science is certainty, so after presenting these recent developments, we have formulated some questions, and decided to leave them unanswered, for the readers to contemplate:

- Is there an ideal solid-state material (maybe not a MOF) for robust dynamics that combines the best of topology, free volume, and stability to optimize machine operation? If so, how do we go about determining what that might be?

- The current methods to analyze crystalline solids are often incompatible, or perform poorly, with materials that are porous and have highly mobile components. Are there alternate (existing?) analytical techniques that can be applied to better characterize these types of materials?

- To date, the field – as described herein – has progressed from systems with restricted movement to those with precise unidirectional motion by taking its cue from molecular systems developed to operate in solution. Are there fundamentally different types of machines that would be better suited for the solid-state?
• If we can order the mobile components in densely packed arrays, how can coherent motion in the solid state be converted into work?

• What “fuel” (e.g. chemical, electro-chemical, photo-chemical) is best for powering molecular machines imbedded inside solid-state materials?

1.5 Context of the Research

The chemical systems described above represent the most sophisticated examples of dynamic MOFs reported to this day. Unfortunately, we still require a higher number of these systems, i.e. data points, to start making strong correlations between topology, linker structure, and function. The work in this dissertation provides a few more data points in the hope of contributing to the advance of such endeavours. It also describes the thought process behind designing and fabrication creating these systems and identifies their strengths and weaknesses.

Chapters 2 and 3 describe the efforts and results of incorporating rotaxane linkers into porphyrin-based MOFs. The rotational dynamics of 24C6 ether rings were studied and the results show that the combinations of these two types of linker result in materials that preserve the characteristic features of both.

Chapter 4 focuses on the design of increasingly complex linkers, where instead of rotational dynamics a switching behaviour can be observed. This chapter consists only of studies in solution, but it lays the foundations for the translation of these characteristics into solid-state materials.

Chapter 5 describes the process of combining linker design, reticular chemistry, and computational simulations to produce MOFs of known topologies but unconventional linkers.
1.6 References


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Chapter 2. Solvent and Steric Influence on Rotational Dynamics in Porphyrinic Metal-Organic Frameworks with Mechanically Interlocked Pillars

2.1 Introduction

Organizing mechanically interlocked molecules (MIMs) into crystalline arrays allows for the investigation of motional modes and the corresponding rates that are not accessible when studying these molecules in solution. Eliminating the random tumbling of the molecules in the liquid phase and minimizing the thermal vibrations of the static components by placing them in a rigid framework, also allows for the study of the effects that the framework structure, nature of the guest molecules, and external stimuli have on the dynamics of these materials. This information can then be used in the bottom-up design of molecular systems capable of ordered, switchable rotational motion, and their eventual incorporation into molecular machinery.

Following the guidelines proposed by Garcia-Garibay\textsuperscript{1} and Loeb\textsuperscript{2}, our objective is to integrate rotaxanes into crystalline materials with a rigid framework that minimizes the motion of all the components except that of the interlocked macrocycles, and with sufficient void space around these mobile components to allow for their unhindered motion or \textit{amphidynamic}\textsuperscript{3} character. Metal-organic frameworks (MOFs) are an ideal class of materials for this purpose\textsuperscript{4} and have been actively used with this goal in mind.\textsuperscript{2,5-7} The emblematic MOF \textbf{UWDM-1}\textsuperscript{2} (University of Windsor Dynamic Material), containing a rotaxane with a 24-crown-6 ether (24C6) macrocycle and an \textit{fog} topology is
the first example of rotational dynamics inside a metal-organic framework. Three other MOFs in this series, UWDM-2,6 UWDM-3,6 and UWDM-58 also have macrocyclic rings that undergo pirouetting motions. UWDM-2 and -3 form interpenetrated pcu lattices, which decreases their available free volume and severely restricts the dynamics of the rings. A phase change that occurs for UWDM-3 results in full rotation of the ring but unfortunately the structure of the new phase is unknown, limiting our understanding of the correlation between structure and dynamics. In this work, we attempt to address some of the problems encountered when studying these pcu MOFs, while advancing the understanding of the influence of structure and guest molecules on rotational dynamics in solid-state materials.

We decided to investigate porphyrin linkers to determine if they would produce a stable, non-interpenetrated structure. These molecules have been used as robust building blocks for the synthesis of MOFs for more than two decades.9–11 The rigidity as well as the thermal and chemical stability of porphyrins are ideal characteristics for MOF linkers and they can be incorporated both as a structural unit and as active linkers (e.g. catalytic linkers12). One of the most prevalent porphyrins in MOF synthesis, meso-tetrakis(4-carboxyphenyl)porphyrin (TCPP), produces a wide variety of topologies and networks, both as a single linker13–21 or in the construction of pillared 3D structures.22–27 The predictability of the resulting structure when combining this porphyrin, a linear bipyridine-like strut, and metal paddlewheel as secondary building has been used in studies regarding the formation of particular stacking arrangements,28–30 making light-harvesting materials,26,27 and in photochromic MOFs.22
Herein, we report the synthesis of two new MOFs (UWDM-7 and UWDM-8) which were fabricated from linear pillaring rotaxane linkers, a porphyrin tetracarboxylate, and Zn\textsuperscript{II} ions. The rotational dynamics of the rings on the pillaring linkers and the influence of different solvent guest molecules inside the frameworks were studied using variable temperature (VT) \textsuperscript{2}H solid-state NMR spectroscopy (SSNMR). UWDM-7 and UWDM-8 have a high stability compared to other pillared MOFs, and can undergo activation and solvent exchange without collapsing. By increasing the available data on rotational dynamics inside of MOFs and exploring the role that secondary linkers, guest molecules, and structural variation have on such dynamics, we hope to make advances in the realization of molecular machines which function in the solid state.

2.2 Results and Discussion

Scheme 2.2.1 shows the synthesis of the pillaring linkers L1 and L2 used in this work. The dibromo-substituted [2]rotaxane synthon was synthesized via ring-closing metathesis\textsuperscript{31} of a preorganized polyethylene glycol precursor around an axle incorporating an anilinium recognition site. As previously shown,\textsuperscript{6} the methyl groups on the 3,5- positions of the aromatic core are bulky enough to prevent the slippage of the macrocyclic ring during the solvothermal conditions required for MOF synthesis. Suzuki coupling between the dibromo synthon and 4-pyridinyl boronic acid (L1) or 2-methyl-4-pyridinyl boronic acid (L2) was used to incorporate the coordinating pyridine groups. Finally, the double bond on the macrocyclic ring (E/Z isomers) was reduced using D\textsubscript{2} gas and Pd/C, giving the linkers L1 or L2 as a mixture of isotopomers. The crystal structure of L2 was determined by single-crystal X-ray diffraction (SC-XRD) and compared with the previously reported structure for L1.\textsuperscript{6} Figure 2.2.1 shows the ball-and-stick
representation of the rotaxane linkers \textbf{L1} and \textbf{L2}. Both linkers have the same pillaring length (N_{py}...N_{py} distance \sim 17.8 \text{ Å}), however the addition of methyl groups \textit{ortho} to the pyridine nitrogen in \textbf{L2} makes this linker sterically more hindered around the pyridyl nitrogen. Although structurally similar, \textbf{L1} and \textbf{L2} crystallize in different space groups and the crystal packing is less efficient in \textbf{L2} due to the disruption of \pi-stacking interactions by the additional methyl group. The non-covalent interactions between the crown ether and the axle are similar in both cases, with a single N–H…O interaction (\textbf{L1}: 3.44 Å, 160°; \textbf{L2}: 3.36 Å, 148.7°)

\begin{center}
\includegraphics[width=\textwidth]{scheme.png}
\end{center}

\textbf{Scheme 2.2.1.} Synthesis of MIM linkers \textbf{L1} and \textbf{L2}. (i) Grubbs catalyst 1\textsuperscript{st} Gen, CH\textsubscript{2}Cl\textsubscript{2}/CH\textsubscript{3}NO\textsubscript{2} (9:1); (ii) Pd(PPh\textsubscript{3})\textsubscript{4}, DMF/Tol (1:1); (iii) Pd/C, D\textsubscript{2}, CH\textsubscript{3}OH. See Experimental Section for detailed synthetic conditions.
The combination of a planar, square tetratopic linker, a metal paddlewheel, and a linear, bipyridine-like pillaring linker is known to produce an fsc topology. Varying the nature of the pillaring linker gives rise to isostructural networks with varying sizes and layering patterns. Conversely, different tetratopic linkers can be used in the construction of the 2D grid, resulting in interpenetrated and non-interpenetrated structures. Two new MOFs, labeled UWDM-7 and UWDM-8, were synthesized under solvothermal conditions, by combining one equivalent of PdTCPP, two equivalents of Zn(NO₃)₂·6H₂O, and four equivalents of the respective rotaxane linker, L₁ or L₂, in DMF. The MOF materials were isolated in good yields, >80% based on porphyrin, and their structures were determined by SC-XRD (Figure 2.2.2) to have formulae 

\[ \text{[Zn}_2(\text{PdTCPP}) \text{(L1)}_{2}](\text{DMF})_x \] 
and 

\[ \text{[Zn}_2(\text{PdTCPP}) \text{(L2)}_{2}](\text{DMF})_x \].

Isostructural MOFs are also obtained with NiTCPP and ZnTCPP (Figure 2.5.7). While these two metals offer open metal centres that have the potential to be used for actuating the rotation of the
macrocycle by coordination of ancillary ligands, they also create additional problems. If ZnTCPP is used the metal centre can be 5-coordinate and it is possible to obtain structures where the layering is AA or ABBA, and controlling which one is formed is not straightforward. For NiTCPP, while only the AA structure forms, the presence of a paramagnetic metal centre results in efficient $T_2$ relaxation of the $^2$H nuclides yielding spectra with low signal-to-noise ratios even under magic-angle spinning (MAS) conditions (Figure 2.5.9) and complicating the analysis of the dynamics via SSNMR (vide infra).

![Figure 2.2.2](image)

**Figure 2.2.2.** Ball-and-stick representations of the single-crystal X-ray structures of UWDM-7 (left) containing rotaxane linker L1 and UWDM-8 (right) containing rotaxane linker L2. Colour key: blue = rotaxane axle, red = 24C6 macrocycle, green = PdTCPP linker, dark green = zinc atoms.

UWDM-7 and UWDM-8 both adopt a two-fold interpenetrated fsc net, as expected, where the porphyrins form a two-dimensional grid with the zinc paddlewheels distributed at ~17 Å intervals, which is pillared by the [2]rotaxane linkers, producing an interlayer distance of 24.7 Å. Although it has been shown that when using large pillaring linkers, the structures tend to be interpenetrated, it was thought that the combination of
these two particular linkers might prevent interpenetration due to the steric bulk of the interlocked 24C6 rings. Further structural analysis shows that although the macrocyclic ring does not fit through the openings in the 2D grid (an ~8 Å wide opening vs. an ~11 Å wide macrocycle) the narrower section of the axle can reside in this opening. This allows a second framework to grow within the original structure and as a result, the thermodynamically favoured 2-fold interpenetrated structure is obtained. In the resulting structure, the rotaxane linkers are spaced by about 8 Å along the crystallographic axis $a$ and about 14 Å apart along the $b$ axis. Consequently, the crown ether rings are also spaced at 8 Å intervals, and sit 4 Å from the closest axle fragment. Due to the interpenetration, the macrocyclic rings reside between two planes determined by the porphyrin linkers of the two independent frameworks (Figure 2.2.3b). Even with this structural arrangement, there is no obvious steric hindrance that could prevent the rotation of these molecular fragments (Figure 2.2.3c). The analysis of the void space in these structures using $PLATON^{34}$ shows accessible spaces of 49% and 47% for UWDM-7 and UWDM-8, respectively. There are two different pores, centered at [0.5, 0.85, 0] and [0.5, 0.85, 0.5] (Figure 2.2.4); the small pore is located between two planes separated by 8 Å, while the large pore is located around 4 crown ether rings. Thermal gravimetric analysis is consistent with this space being occupied by DMF molecules, with an initial weight loss of 10% above 110 °C (not observed for the evacuated samples) followed by the decomposition of the crown ether rings around 200 °C, and finally the decomposition of the framework above 350 °C (Figure 2.5.5 and Figure 2.5.6).
Figure 2.2.3. A) Augmented net of UWDM-8 showing a 2-fold interpenetrated fsc network. The 24C6 rings are omitted for clarity. B) View along b axis, showing the spatial distribution of crown ether rings (in space-filling representation) in UWDM-8. C) View along c axis.

The stabilities of both as-synthesized and activated samples of UWDM-7 and UWDM-8 were studied by variable temperature powder X-ray diffraction (VT-PXRD) (See Experimental Section for activation details). The activation process involved exchanging DMF for CH₂Cl₂ and air-drying to produce desolvated material. It was found that UWDM-7 has three different phases in the temperature range studied. The first, α-UWDM-7, corresponds to the as-synthesized material with DMF inside the cavities. Upon heating this sample, a gradual phase change to β-UWDM-7 is observed which is attributed to a deformation or tilting of the pillars in the framework. Although the structure of this new phase is unknown this hypothesis is consistent with observations
made for similar pillared systems. β-UWDM-7 reverts to the α-UWDM-7 form upon re-exposure to DMF (Figure 2.5.8). On the other hand, full activation does not produce β-UWDM-7. The activated material has a powder pattern at room temperature that does not match that simulated for α-UWDM-7 or observed for β-UWDM-7, so a third phase is assigned for this material, namely γ-UWDM-7. This crystalline phase remains unchanged in the temperature range of 295-473 K. The activation process does not reduce the crystallinity of the sample but it does affect the quality of the single crystals (cracking), making unambiguous determination of the structure of γ-UWDM-7 difficult (See Table 2.3.1 for unit cell comparison). Despite the structural changes that must be occurring for these materials, none of the phases of UWDM-7 show evidence of irreversible collapse of the framework and total loss of crystallinity which is common in other pillared structures, and would greatly hinder the dynamics of the macrocycles.

Figure 2.2.4. Ball-and-stick representation of the X-ray crystal structure of α-UWDM-8 showing the two different pores in the structure, represented by gray and purple spheres. View along a (left) and b (right).
For UWDM-8, a different behaviour is observed; the as-synthesized sample does not undergo any structural changes upon heating and the PXRD pattern only exhibits broadening at higher temperature as a result of increased strain. After activation, the powder pattern of UWDM-8 exhibits changes in the intensity of some peaks. However, the crystallinity and stability are retained and in this case, it was possible to determine the SC-XRD structure of the activated sample, β-UWDM-8. The structure shows that the difference in the PXRD patterns correspond to a distortion of the framework that causes a change in the space group due to loss of symmetry (Figure 2.2.6) but preserves the overall topology. The single-crystal-to-single-crystal transformation is helpful in understanding the effect of guest removal for this porous material, as well as the effect that such small changes can have on the rotational dynamics inside the MOF (vide infra).

![Figure 2.2.5. VT PXRD patterns of A) α-UWDM-7, B) γ-UWDM-7, C) α-UWDM-8, and D) β-UWDM-8.](image)
Figure 2.2.6. Single-crystal-to-single-crystal transformation in UWDM-8 upon removal of the solvent molecules in the framework. A) α-UWDM-8 along crystallographic axis a. B) α-UWDM-8 along crystallographic axis b. C) β-UWDM-8 along crystallographic axis a. The distortion of the framework caused by the removal of the solvent can be seen in the tilted framework D) β-UWDM-8 along crystallographic axis b. Colour key: blue: rotaxane axle, red: 24C6 ring, green: PdTCPP, dark green: Zn atoms.

2.3 Solid-state dynamics

$^2$H SSNMR is an excellent tool to monitor rotational dynamics in mechanically interlocked molecules, as the powder patterns are highly sensitive to molecular motion.
and their corresponding rates. Three motional regimes are defined based on the relative magnitudes of the $^2$H quadrupolar frequency ($\nu_Q$) and the exchange rate ($\nu_{ex}$): the slow motion limit (SML), where $\nu_{ex} \ll \nu_Q$ (i.e., $\nu_{ex} < 10^3$ Hz); the intermediate motion regime (IMR), where $\nu_{ex} \approx \nu_Q$ (i.e., $10^3$ Hz $\leq \nu_{ex} \leq 10^7$ Hz); and the fast motion limit (FML), where $\nu_{ex} \gg \nu_Q$ (i.e., $\nu_{ex} > 10^7$ Hz). Motions with rates in the SML are too slow to produce changes in the $^2$H powder patterns, whereas motions with rates in the FML do not result in any further changes in the powder patterns. However, motions with rates in the IMR result in powder patterns that change drastically with temperature and can be diagnostic in the determination of motional models. As previously demonstrated,\textsuperscript{2,5,6} the 24C6 macrocyclic rings can undergo three distinct types of motion in the solid-state: 1) a two-site jump of the deuterons about an axis that is collinear with the C–C bonds, 2) partial rotation of the ring in which the hydrogen-bond donor on the axle interacts with each of the oxygen atoms on the ring and 3) full (but non-directional) rotation of the ring about the axle. Details of the data collection and simulation of the $^2$H powder patterns can be found in the Experimental Section.

Although both \textbf{UWDM-7} and \textbf{UWDM-8} materials have a two-fold interpenetrated network, the analysis of the structure shows the macrocycles are located in relatively unhindered positions. Following PXRD analysis, it was decided to investigate the dynamics of both as-synthesized and activated samples, \textit{i.e.} \textbf{$\alpha$-UWDM-7}, \textbf{$\gamma$-UWDM-7}, \textbf{$\alpha$-UWDM-8}, and \textbf{$\beta$-UWDM-8}. The spectra for \textbf{UWDM-7} and \textbf{UWDM-8} phases are shown in \textbf{Figure 2.3.1} and \textbf{Figure 2.3.2}, and the rates and modes of motion are summarized in \textbf{Table 2.5.4} to \textbf{Table 2.5.7} respectively. In all cases, the spectra
acquired at 185 K were simulated with the absence of motions, or equivalently, motions occurring at rates within the SML.

2.3.1 α-UWDM-7

For the as-synthesized sample α-UWDM-7 (Figure 2.3.1a), the $^2$H SSNMR spectrum acquired at 208 K was simulated as a two-site jump motion with a jump angle of $\beta = 75^\circ$. The onset of the partial rotational motion is observed in the spectrum acquired at 253 K. The spectrum collected at 285 K was simulated as the FML of the combined two-site jump and partial rotational motions. Increasing the temperature to 411 K (i.e., the highest temperature to which the sample could be heated) does not produce any significant changes to the $^2$H powder patterns and therefore, no additional modes of motion occur in α-UWDM-7. It is important to remember that α-UWDM-7 is converted to β-UWDM-7 upon heating so the SSNMR does not represent the motions of a phase pure material.

2.3.2 γ-UWDM-7

$^2$H SSNMR spectra acquired above 185 K were simulated as the two-site jump motion with rates in the IMR. The FML for the two-site jump motion occurs at 321 K. Increasing the temperature further results in the onset of the partial rotational motion and the spectrum acquired at 366 K was simulated as the FML of the combined two-site jump and partial rotational motions (Figure 2.3.1b).
Figure 2.3.1. (A) Experimental VT $^2$H SSNMR spectra for α-UWDM-7 and corresponding simulations showing the (i) SML, (ii) onset of the two-site jump ($\beta = 75^\circ$), (iii) FML of the two-site jump and onset of partial rotation, and (iv) FML of the two-site jump and partial rotation. (B) Experimental VT $^2$H SSNMR spectra for γ-UWDM-7 and corresponding simulations showing the (i) SML, (ii) IMR for the two-site jump, (iii) FML of the two-site jump, (iv) onset of partial rotation, and (v) FML of the two-site jump and partial rotation.
2.3.3 \( \alpha \)-UWDM-8

Increasing the temperature above 185 K results in drastic changes in the \(^2\text{H}\) powder patterns (Figure 2.3.2a), indicating the rapid onset of the two-site jump motion. The spectrum acquired at 253 K was simulated with the FML of the two-site jump and the onset of the partial rotational motion, the rate of which increases with temperature. At 343 K, an axially symmetric pattern is obtained, indicating the FML of the full rotational motion. Increasing the temperature further (up to 411 K) results in no further changes to the spectra.

2.3.4 \( \beta \)-UWDM-8

The spectrum acquired at 273 K was simulated with the two-site jump motion with a jump angle of 70° and rates in the FML. Increasing the temperature to 298 K results in an increase in the jump angle (\(\beta = 75°\)) and the onset of partial rotation. The FML of the combined two-site jump and partial rotational motions occurs at 343 K and increasing the temperature does not result in any further changes in the \(^2\text{H}\) powder patterns (Figure 2.3.2b).
Figure 2.3.2. (A) Experimental VT $^2$H SSNMR spectra for $\alpha$-UWDM-8 and corresponding simulations showing the (i) SML, (ii) FML of the two-site jump ($\beta = 78^{\circ}$) and onset of partial rotation, (iii) FML of the two-site jump and partial rotation, and (iv) FML of the two-site jump and full rotation. (B) Experimental VT $^2$H SSNMR spectra for $\beta$-UWDM-8 and corresponding simulations showing the (i) SML, (ii) FML for the two-site jump ($\beta = 70^{\circ}$), (iii) FML of the two-site jump ($\beta = 75^{\circ}$) and onset of partial rotation, and (iv) FML of the two-site jump and partial rotation.
At this point, it is important to summarize the factors that affect ring dynamics in **UWDM-7** and **UWDM-8**. This series of MOFs are made using similar components and only differ in the presence of a methyl substituent on the 2-position of the pyridine group of the axle in **UWDM-8**. The MOFs were found to have similar structures and XRD analysis suggests that activation does not produce drastic changes or collapsing of the framework structure; however, the dynamics of the crown ether macrocycles in these systems are very different.

The structural changes induced by removal of the solvent have pronounced effects on the motion. For **α-UWDM-7**, the onset temperature of the two-site jump motion is 208 K and the FML is reached by 253 K (similar to the onset temperature observed for **UWDM-1**). Conversely, for **γ-UWDM-7**, the FML of the two-site jump occurs at 321 K (a difference of almost 75 K). An analogous observation is made for the partial rotational motion with FML temperatures of 285 and 366 K for **α-UWDM-7** and **γ-UWDM-7**, respectively. The effect is less pronounced for **UWDM-8**, where the FML for the two-site jump and partial rotation occur at same temperatures; however, increasing the temperature further results in full rotation of the macrocyclic rings in **α-UWDM-8**, but no additional motion for **β-UWDM-8**.

Activation also results in a decrease in the rates of motion of the rings in both **UWDM-7** and **UWDM-8**, but it is unclear whether this is driven by structural changes or is a consequence of the different chemical environments of the rings (*i.e.*, interactions with solvent molecules). To address this, solvent-exchange reactions were conducted on **α-UWDM-8**, where solvents were chosen to reflect a variety of polarities and viscosities. It is known that some of these solvent properties might change substantially from those of
the bulk liquids when confined in small cavities,\textsuperscript{36} however, they can still provide valuable information about the interactions happening at the nanoscopic level. The solvent-exchange process was carried out in a similar way to the activation process: the samples were submerged in the solvent of choice and the solvent was replaced every 2-3 hours, for at least 24 h. Samples were filtered and air-dried briefly before running the experiments.

VT \textsuperscript{2}H SSNMR spectra were acquired and are shown in Figure 2.3.3. With the exception of some of the lower temperature spectra (with poor S/N), it appears that the motion of the rings in \textit{a}-UWDM-8 is the same (\textit{i.e.}, full rotation occurs at higher temperatures) regardless of the solvent within the pores. Therefore, it was concluded that while desolvation produces only minor changes in structure, this is sufficient to cause significant changes in the motion of the rings, and can be attributed to a tilting of the framework structure such that the rings of one [2]rotaxane linker come into close contact with the static portion of the framework. Moreover, the dynamic behaviour of \textit{a}-UWDM-8 can be described in an analogous fashion to the macroscopic \textit{stick-slip} phenomenon, in which a moving object momentarily drags the objects surrounding it, followed by the relaxation of these objects to their original position.

In comparing UWDM-7 and UWDM-8, it is evident that the motion of the macrocyclic rings is more hindered in the former. The FML for partial rotation occurs at 343 K for \textit{a}-UWDM-7, which is comparable to other UWDM systems described herein (\textit{vide supra}); however, increasing the temperature does not result in full rotation in \textit{a}-UWDM-7. It is proposed that the addition of the methyl group on L2 increases the rigidity of the pillars and reduces the possibility for thermally-induced structural
transformations (i.e., framework tilting) that increase the steric interactions between the rings and the framework, thereby allowing for unhindered motions of the rings in $\alpha$-UWDM-8 in comparison to those in UWDM-7.

![Figure 2.3.3](image)

Figure 2.3.3. Experimental VT $^2$H SSNMR spectra of UWDM-8 with (A) no solvent, or the addition of (B) dimethylformamide, (C) mesitylene, (D) dioxane, (E) 1-butanol, (F) ethylene glycol, or (G) triethylene glycol within the pores of the framework.

This new data contributes to the available information of rotational dynamics of aniline-based rotaxanes in MOFs. Table 2.3.1 summarizes the temperatures at which the three distinct types of motion start happening in five different UWDM MOFs. It can be seen that it is not always possible for the 24C6 rings to reach full rotation, but the new UWDM-8 has the lowest onset temperature for that motion reported to date. Additionally, the onset temperature for the two-site jump and partial rotation vary substantially and no correlation between structure and onset temperature is apparent.

**Table 2.3.1.** Summary of onset temperatures for the three distinct motion modes observed in UWDM MOFs with an aniline-based rotaxane linkers.

<table>
<thead>
<tr>
<th>MOF</th>
<th>2-site jump onset (K)</th>
<th>Partial rotation onset (K)</th>
<th>Full rotation onset (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UWDM-1</td>
<td>251</td>
<td>324</td>
<td>373</td>
</tr>
<tr>
<td>UWDM-2</td>
<td>255</td>
<td>255</td>
<td>--</td>
</tr>
<tr>
<td>$\alpha$-UWDM-3</td>
<td>247</td>
<td>255</td>
<td>--</td>
</tr>
<tr>
<td>$\beta$-UWDM-3</td>
<td>234</td>
<td>255</td>
<td>339</td>
</tr>
<tr>
<td>$\alpha$-UWDM-7</td>
<td>208</td>
<td>253</td>
<td>--</td>
</tr>
<tr>
<td>$\gamma$-UWDM-7</td>
<td>273</td>
<td>330</td>
<td>--</td>
</tr>
<tr>
<td>$\alpha$-UWDM-8</td>
<td>223</td>
<td>253</td>
<td>323</td>
</tr>
<tr>
<td>$\beta$-UWDM-8</td>
<td>248</td>
<td>298</td>
<td>--</td>
</tr>
</tbody>
</table>
Previous studies have shown that small modifications to the organic linker structure, for example, change substituents from H to Me or CH$_2$OH, can result in structural changes such as formation of a different SBU,$^{37}$ varying the degrees of interpenetration, or modifying the layering of a structure.$^{29}$ This work represents another example of how these seemingly small alterations of organic linkers can play a key role in the final properties of materials, and should be carefully considered in their design.

2.4 Conclusions

A new rotaxane linker and two new MOFs showing rotational dynamics were synthesized, adding to the UWDM series. Both UWDM-7 and UWDM-8 are mixed-linker, pillared frameworks, and the first examples of structures that combine a metalloporphyrin and a MIM linker. The use of the new rotaxane linker L$_2$ produces a rigid framework structure that allows for full rotation of the 24C6 macrocycle when there is solvent present in the pores of the material. The nature of the guest molecules does not affect the rotational dynamics, however their presence is required to avoid the deformation of the framework resulting in a material where the ring cannot freely rotate. With the study of these pillared MOFs, we have gained an understanding of how the rigidity of the static framework influences the capability of the rotaxane components to reach full mobility.

This study paves the way for the design and synthesis of porphyrin-containing MOFs with mobile MIM components. Future studies will be focused on the variation of the metal centre in the porphyrin, in order to investigate its effects on the rotational dynamics of the MIM component. This can potentially create systems where the
actuation of the rotational motion is controlled not only thermally but also by the introduction of additional ligands coordinated to the porphyrin metal centre.

2.5 Experimental Section

2.5.1 General Comments

4-Bromo-3,5-dimethylaniline,\textsuperscript{38} 4-bromo-3,5-dimethylbenzaldehyde,\textsuperscript{39} and pentaethyleneglycol-dipent-4-enyl ether\textsuperscript{31} were synthesized following modified literature methods. Solvents and reagents were obtained from Millipore-Sigma, Tokyo Chemical Industry Co. Ltd., Frontier Scientific, or Strem Chemicals and used without further purification. Solvents were dried using an Innovative Technologies Solvent Purification System. High-resolution mass spectrometry data were recorded on a Waters Xevo GS-XS ToF instrument in electrospray ionization (ESI) or atmospheric solids analysis probe (ASAP) mode.

2.5.2 Synthesis of pillaring linkers

\textbf{Scheme 2.5.1.} Compound 1.

(1). A mixture of 4-bromo-3,5-dimethylaniline (1.36 g, 6.8 mmol) and 4-bromo-3,5-dimethylbenzaldehyde (1.53 g, 7.2 mmol) was dissolved in a minimum amount of chloroform and sufficient MgSO\textsubscript{4} was added to make a slurry. The reaction mixture was
stirred for 18 h, filtered and the solvent removed under reduced pressure. The crude product was rinsed with cold methanol to yield a yellow-white powder. Yield: 2.56 g, 95%. Mp: 161-164 °C. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta$ (ppm) = 8.34 (s, 1H, c), 7.61 (s, 2H, b), 6.96 (s, 2H, d), 2.48 (s, 6H, a), 2.44 (s, 6H, e). $^{13}$C NMR (125 MHz, CDCl$_3$, 298 K) $\delta$ (ppm) = 159.7, 150.4, 139.2, 139.1, 134.5, 131.4, 129.6, 128.3, 124.8, 120.7, 24.1, 24.0 HR-MS (ASAP): Calculated for [M-H]$^+$ [C$_{17}$H$_{18}$Br$_2$N]$^+$ m/z = 393.9801; found m/z = 393.9794

Scheme 2.5.2. Compound 2.

(2). Compound 1 (2.56 g, 6.5 mmol) was dissolved in THF/EtOH (80 mL, 1:1) and sodium borohydride (285 mg, 7.2 mmol) slowly added. After stirring the reaction mixture for 18 h, the solvents were removed under reduced pressure and the crude product dissolved in chloroform (100 mL), washed with water (2 x 25 mL), and dried over MgSO$_4$. After removal of the solvent a white powder was obtained. 2.57 g, quantitative yield Mp: 134-136 °C. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta$ (ppm) = 7.05 (s, 2H, e), 6.37 (s, 2H, b), 4.17 (s, 2H, d), 3.87 (b, 1H, c), 2.40 (s, 6H, f), 2.32 (s, 6H, a). Values match those previously reported.$^6$
Scheme 2.5.3. Compound [2-H][BF₄].

[2-H][BF₄] Compound 2 (2.53 g, 6.4 mmol) was dissolved in diethyl ether (100 mL). Tetrafluoroboric acid diethyl ether complex (0.91 mL, 6.7 mmol) was slowly added, the solution stirred for 30 minutes and filtered. After recrystallization from acetonitrile a pale yellow powder was obtained. Yield: 2.80 g, 90% Mp: 239-242 °C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ (ppm) = 8.59 (b, 2H, c), 7.13 (s, 2H, e), 7.10 (s, 2H, b), 4.44 (s, 2H, d), 2.42 (s, 6H, f), 2.40 (s, 6H, a). Values match those previously reported.

Scheme 2.5.4. Compound 3.

(3). Compound [2-H][BF₄] (1.355 g, 2.8 mmol) and pentaethyleneglycol-dipent-4-enyl ether (1.567 g, 4.2 mmol) were dissolved in DCM/MeNO₂ (9:1) (250 mL) under N₂ atmosphere. After stirring for 10 min, Grubbs Catalyst 1st (230 mg, 0.28 mmol) was added and the reaction mixture heated at 45 °C for 24 hours. Subsequent catalyst additions were done after 24 h (115 mg) and 72 h (115 mg). After a total reaction time of
120 hours the solvents were removed and Et₂O was added to the residue. The mixture was then sonicated for 10 min, the solvent was decanted, and the residue was dissolved in methanol. The resultant solution was neutralized with triethylamine and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (SiO₂, ethyl acetate/ hexanes, 1:4 v/v). Rf: 0.4. Recrystallization from methanol gave mixed E and Z isomers from the desired product. Yield: 1.01 g, 50%. Mp: 204-207 °C. ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 7.45-7.44 (m, 2H, e), 6.69-6.63 (m, 2H, b), 5.27-5.16 (m, 3H, c, o), 4.39-4.37 (m, 2H, d), 3.56-3.21 (m, 24H, g-l), 2.42-2.39 (m, 6H, f), 2.34-2.33 (m, 6H, a), 2.00-1.92 (m, 4H, n), 1.63-1.45 (m, 4H, m). Values match those previously reported.⁶

Scheme 2.5.5. Compound 4.

(4). Compound 3 (400 mg, 0.54 mmol, E/Z mixture) was dissolved in DMF/Toluene (1:1) (20 mL) under N₂ atmosphere. 4-pyridyl boronic acid (220 mg, 1.6 mmol), Cs₂CO₃ (526 mg, 1.6 mmol), and Pd(PPh₃)₄ (62 mg, .05 mmol) were added and the reaction mixture was heated at 110 °C for 12 hours. The reaction mixture was cooled down, filtered, and the solid residue was rinsed with chloroform. The solvents were removed under reduced pressure and the crude product was purified by column
chromatography (SiO$_2$, ethyl acetate/ dichloromethane/ methanol 1:1:0.1 v/v). Yield: 357 mg, 90%. Mp: 229-230 °C $^1$H NMR (500 MHz, CD$_3$CN, 298 K) δ (ppm) = 8.65-8.64 (m, 2H, $j$), 8.58-8.57 (m, 2H, $a$), 7.52-7.51 (m, 2H, $i$), 7.16-7.14 (m, 4H, $b$, $g$), 6.73-6.69 (m, 2H, $d$), 5.40-5.22 (m, 3H, $e$, $s$), 4.56-4.45 (m, 2H, $f$), 3.62-3.19 (m, 24H, $k$-$o$), 2.02 (sb, 6H, $h$), 1.98(sb, 6H, $c$), 1.65-1.39 (m, 4H, $q$, $r$). Values match those previously reported.$^6$

Scheme 2.5.6. Compound L1-D$_2$.

(L1-D$_2$). Compound 4 (350 mg, 0.47 mmol, E/Z mixture) was dissolved in methanol (25 mL) and added to a Schlenk flask charged with 10% Pd/C (150 mg) under N$_2$ atmosphere. The flask was degassed and flushed with D$_2$ gas introduced via balloon. The mixture was stirred for 3 h under ambient conditions. The reaction mixture was filtered through a Celite pad and the solvent removed under reduced pressure. Recrystallization from hexanes gave the pure product as a white solid consisting of a mixture of isotopomers. Yield: 345 mg, 95%. Mp: 227-228 °C. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) δ (ppm) = 8.68-8.67 (m, 2H, $j$), 8.60 (sb, 2H, $a$), 7.51 (s, 2H, $g$), 7.19-7.18 (m, 2H, $i$), 7.12-7.10 (m, 2H, $b$), 6.71 (s, 2H, $d$), 5.24 (t, 1H, $J= 4.5$ Hz, $e$), 4.50 (d, 2H, $J= 4.5$ Hz, $j$), 3.59-3.27 (m, 24H, $k$-$p$), 2.04 (s, 6H, $h$), 2.00 (s, 6H, $c$), 1.49-1.41 (m, 4H, $r$).
$^1$H NMR (77 MHz, CDCl$_3$, 298 K) $\delta$ (ppm) = 1.11. Values match those previously reported.$^6$

Scheme 2.5.7. Compound 6.

(6). Compound 3 (200 mg, 0.27 mmol, E/Z mixture) was dissolved in DMF/Toluene (1:1) (20 mL) under N$_2$ atmosphere. 2-methylpyridine-4-boronic acid (177 mg, 0.81 mmol), Cs$_2$CO$_3$ (263 mg, 0.81 mmol), and Pd(PPh$_3$)$_4$ (32 mg, 0.03 mmol) were added and the reaction mixture was heated at 110 °C for 12 hours. The reaction mixture was cooled down, filtered, and the solid residue was rinsed with chloroform. The solvents were removed under reduced pressure and the crude product was purified by column chromatography (SiO$_2$, ethyl acetate/ dichloromethane/ methanol 1:1:0.1 v/v) Yield: 170 mg, 90%. Mp: 99-103 °C. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta$ (ppm) = 8.55-8.54 (m, $^1$H, $n$), 8.49-8.48 (m, $^1$H, $b$), 7.48-7.47 (m, 2H, $i$), 7.01-7.00 (m, 1H, $l$), 6.96-6.95 (m, 2H, $d$, $k$), 6.90-6.89 (m, 1H, $c$), 6.71-6.66 (m, 2H, $f$), 5.32-5.22 (m, 3H, $g$, $w$), 4.52-4.42 (m, 2H, $h$), 3.60-3.30 (m, 24H, o-t), 2.61 (s, 3H, $m$), 2.58 (s, 3H, $a$), 2.28-1.90 (m, 16H, e, j, t, v), 1.71-1.38 (m, 4H, $u$). $^{13}$C NMR (500 MHz, CDCl$_3$, 298 K) $\delta$ (ppm) = 158.6, 158.0, 151.5, 151.4, 150.4, 149.4, 149.3, 148.8, 140.4, 140.0, 137.5, 137.4, 134.8, 134.6, 134.2, 130.3, 129.8, 129.4, 129.1, 126.7, 125.6, 124.3, 123.4, 122.0, 113.0, 112.7, 72.2,
HR-MS (ESI+): Calculated for [M-H]+ [C_{47}H_{66}N_{3}O_{6}]^+ m/z = 768.4946; found m/z = 768.4929

**Scheme 2.5.8.** Compound L2-D2

(L2-D2). Compound 6 (1.00 g, 1.3 mmol, E/Z mixture) was dissolved in methanol (50 mL) and added to a Schlenk flask charged with 10% Pd/C (200 mg) under N₂ atmosphere. The flask was degassed and flushed with D₂ gas introduced via balloon. The mixture was stirred for 3 h under ambient conditions. The reaction mixture was filtered through a Celite pad and the solvents removed under reduced pressure. Recrystallization from hexanes gave the pure product as a white solid consisting of a mixture of isotopomers. Yield: 820 mg, 82 %. Mp: 114-117 °C. 

\[ ^1H \text{NMR} (500 \text{ MHz, CDCl}_3, 298 \text{ K}) \delta \text{ (ppm)} = 8.55 (d, 1H, J = 5.0 \text{ Hz, } n), 8.48 (d, 1H, J = 5.0 \text{ Hz, } b), 7.49 (s, 2H, i), 7.00 (s, 1H, k), 6.95 (s, 1H, c), 6.94 (d, 1H, J = 5 Hz, l), 6.89 (d, 1H, J = 5 Hz, d), 6.69 (s, 2H, j), 5.19 (t, 1H, J = 4.5 Hz, g), 4.48 (d, 2H, J = 4.5 Hz, h), 3.60-3.25 (m, 24H, o-t), 2.57 (s, 3H, m) 2.54 (s, 3H, a), 2.03 (s, 6H, j), 1.96 (s, 6H, c), 1.51-1.06 (m, 10H, u-w). \]

\[ ^2H \text{NMR} (77 \text{ MHz, CDCl}_3, 298 \text{ K}) \delta \text{ (ppm)} = 1.13. \]

\[ ^{13}C \text{NMR} (125 \text{ MHz, CDCl}_3, 298 \text{ K}) \delta \text{ (ppm)} = 158.6, 157.9, 151.5, 150.5, 149.3, 149.2, 148.8, 140.2, 137.4, 134.6, 134.2, 129.2, 126.6, 121.2, 20.7. \]
125.7, 124.3, 123.4, 122.1, 112.9, 77.4, 75.1, 71.8, 71.1, 70.7, 70.6, 70.4, 47.3, 29.8, 28.9, 28.5, 25.7, 25.0, 24.7, 24.6, 21.1, 20.7. HR-MS (ESI+): Calculated for [M-H]$^+$ $[\text{C}_{47}\text{H}_{66}\text{N}_3\text{O}_6]^+$ $m/z = 772.5228$; found $m/z = 772.5234$.

2.5.3 Porphyrin linkers

Scheme 2.5.9. Structure of PdTCPP.

PdTCPP. Meso-tetra-(4-carboxyphenyl)porphyrin (250 mg, 0.3 mmol) and PdCl$_2$ (225 mg, 1.2 mmol) were added into an 80 mL microwave tube. DMF (25 mL) was added, the tube was placed inside the microwave reactor and heated at 155 °C for three cycles of 5 min. After cooling down, THF (50 mL) was added and the reaction was filtered. The resultant organic layer was washed with water, centrifuged, and filtered to yield a purple powder. Yield: 250 mg, 89 %. Mp: >400 °C. $^1$H NMR (500 MHz, DMSO-d$_6$, 298 K) $\delta$ (ppm) = 8.82 (s, 8H, $a$), 8.39 (d, 8H, $J = 8.3$ Hz, $b$), 8.32 (d, 8H, $J = 8.3$ Hz, $c$). Values match those previously reported.\textsuperscript{26}
Scheme 2.5.10. Structure of NiTCPP.

NiTCPP. *Meso*-tetra-(4-carboxyphenyl)porphyrin tetramethyl ester (85 mg, 0.1 mmol) and NiCl$_2$·6H$_2$O (304 mg, 1.2 mmol) were dissolved in DMF (10 mL). The reaction was refluxed for 6 h, quenched with water (15 mL) and centrifuged. The resultant solid was washed with water, dissolved in chloroform, and washed with HCl (1 M, 20 mL × 2) and water (20 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure and the bright red solid was transferred to a 10 mL microwave tube. THF (2 mL), MeOH (2 mL), and KOH (6 M, 2 mL) were added to the tube, placed inside the microwave reactor and heated at 85 °C for 2 cycles of 10 min. The organic solvents were removed under reduced pressure, water was added to the resultant solution, and HCl (1 M) was used to acidify the reaction until no further precipitate was formed. After filtration a red powder was obtained. Yield: 75 mg, 90%. Mp: >400 °C. $^1$H NMR
(500 MHz, DMSO-d<sub>6</sub>, 298 K) δ (ppm) = 8.77 (s, 8H, <i>a</i>), 8.32 (d, 8H, <i>J</i> = 8.3 Hz, <i>b</i>), 8.16 (d, 8H, <i>J</i> = 8.3 Hz, <i>c</i>). Values match those previously reported.<sup>40</sup>

2.5.4 Synthesis of Pillared MOFs

**UWDM-7.** Ten 20 mL scintillation vials were loaded with Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (6 mg, 0.02 mmol), L<sub>1</sub> (30 mg, 0.04 mmol), and PdTCPP (9 mg, 0.01 mmol). DMF (2 mL) and HBF<sub>4</sub>·Et<sub>2</sub>O (1 drop) were added to each vial and the mixture sonicated for 1 minute. The mixture was heated in a programmable oven at 85 °C for 48 h and cooled to room temperature over 6 h. Red plate crystals were collected by filtration and stored in fresh DMF. Yield based on porphyrin: 231 mg, 90%. To confirm the composition of the MOF a small amount of the sample was digested in DMSO-<i>d</i><sub>6</sub> using deuterated triflic acid (CF<sub>3</sub>SO<sub>3</sub>D). The ratio of porphyrin linker to rotaxane linker matches the expected value of 1:2 (Figure 2.5.1)
**Figure 2.5.1.** Partial $^1$H NMR spectrum of digested **UWDM-7** showing a porphyrin:rotaxane ratio of 1:2. Rotaxane peaks in blue, porphyrin peaks in red.

![NMR spectrum](image)

**Figure 2.5.2.** Optical micrograph of **α-UWDM-7** crystals showing their plate morphology.

**UWDM-8.** Ten 20 mL scintillation vials were loaded with Zn(NO$_3$)$_2$·6H$_2$O (6 mg, 0.02 mmol), **L2** (30 mg, 0.04 mmol), and PdTCPP (9 mg, 0.01 mmol). DMF (2 mL) and HBF$_4$·Et$_2$O (1 drop) were added to each vial and the mixture sonicated for 1 minute. The mixture was heated in a programmable oven at 80 °C for 48 h and cooled to room temperature over 6 h. Red plate crystals were collected by filtration and stored in fresh DMF. Yield based on porphyrin: 210 mg, 80%. The same digestion procedure used for **UWDM-7** confirms the composition of the material.

**UWDM-8-Ni.** A 20 mL scintillation vial was loaded with Zn(NO$_3$)$_2$·6H$_2$O (6 mg, 0.02 mmol), **L2** (30 mg, 0.04 mmol), and NiTCPP (8 mg, 0.01 mmol). DMF (2 mL) and HBF$_4$·Et$_2$O (1 drop) were added to each vial and the mixture sonicated for 1 min. The mixture was heated in a programmable oven at 80 °C for 48 h and cooled to room
temperature over 6 h. Red plate crystals were collected by filtration and stored in fresh DMF.

**UWDM-8-Zn.** A 20 mL scintillation vial was loaded with Zn(NO$_3$)$_2$·6H$_2$O (9 mg, 0.03 mmol), L$_2$ (30 mg, 0.04 mmol), and TCPP (8 mg, 0.01 mmol). DMF (2 mL) and HBF$_4$·Et$_2$O (1 drop) were added to each vial and the mixture sonicated for 1 min. The mixture was heated in a programmable oven at 80 °C for 48 h and cooled to room temperature over 6 h. Purple plate crystals were collected by filtration and stored in fresh DMF.

![Figure 2.5.3](image_url)

**Figure 2.5.3.** Partial $^1$H NMR spectrum of digested UWDM-8. Showing a porphyrin:rotaxane ratio of 1:2. Rotaxane peaks in blue, porphyrin peaks in red.
Figure 2.5.4. Optical micrograph of α-UWDM-8 crystals showing their plate morphology.

Desolvation/activation process: After the solvothermal synthesis, the supernatant solution was replaced with fresh DMF until no colour change in the solvent was perceptible. The crystals were then soaked in dichloromethane for at least 24 h, replacing the solvent every 2-3 h. Finally, the crystals were filtered and air-dried before collecting the VT SSNMR spectra. The $^1$H NMR spectra of the digestion of the activated samples confirm the absence of DMF guest molecules in the framework.

2.5.5 Thermogravimetric Analysis

Thermogravimetric analyses were collected on a Mettler Toledo STDA 851e instrument. Samples were stabilized at 25 °C for 30 minutes and then heated to 550 °C at a rate of 5 °C per minute. As expected, the activated sample does not show any weight loss corresponding to water, dimethylformamide, or dichloromethane inside the cavities of the MOF. At around 450 K the macrocyclic ring starts to break off and decompose followed by the complete degradation of the organic linkers above 600 K. In the as-synthesized sample, an initial weight loss corresponding to the loss of
dimethylformamide molecules residing in the pores of the material is observed between room temperature and 400 K, followed by the decomposition of the macrocycle and finally the degradation of the rest of the organic linkers above 600 K.

**Figure 2.5.5.** Thermal gravimetric curves of UWDM-7
Figure 2.5.6. Thermal gravimetric curves of UWDM-8.

2.5.6 Single Crystal X-ray Diffraction Studies

Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer, equipped with a PHOTON 100 detector, kappa goniometer, and collected using a Cu high brilliance IµS microfocus source. Crystals were mounted on MiTeGen MicroMounts and frozen in paratone oil under a cold stream of N$_2$ from an Oxford Cryostream 700 from Oxford Cryosystems. Reflection data were integrated using APEX III software.

Crystals of L2 were grown from slow diffusion of hexanes into nitromethane. The crystals were of good size and quality however the diffraction was not great as is common with some mechanically interlocked molecules. Different solvent mixtures were tried, all resulting in crystals with the same unit cell and quality. After data collection,
using Olex2, the structure was solved with the XT solution program and the Intrinsic Phasing method, and refined with the XL package using Least Squares minimization.

**Table 2.5.1.** Crystal data, solution, and refinement parameters for L2.

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<tr>
<th>Chemical formula</th>
<th>C_{47}H_{65}D_{2}N_{3}O_{6}</th>
<th>μ (mm⁻¹)</th>
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<td>Crystal system</td>
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<td>Radiation</td>
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<td>Space group</td>
<td>𝑃̅</td>
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<td>4.62 to 101.14</td>
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<tr>
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<td>Reflections collected</td>
<td>127210</td>
</tr>
<tr>
<td>T (K)</td>
<td>173(2)</td>
<td>Unique reflections</td>
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</tr>
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</tr>
<tr>
<td>b (Å)</td>
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<td>Restraints</td>
<td>34</td>
</tr>
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</tr>
<tr>
<td>α (°)</td>
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<td>R_{1} [I &gt; 2σ(I)]</td>
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</tr>
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<td>R_{1} all</td>
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<td>γ (°)</td>
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<td>ρ (g·cm⁻³)</td>
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</table>

\[
R_1 = \frac{\sum |F_{\text{obs}} - F_{\text{calc}}|}{\sum |F_{\text{obs}}|}; \quad wR_2 = \left(\frac{\sum w|F_{\text{obs}}^2 - F_{\text{calc}}^2|}{\sum wF_{\text{obs}}^2}\right)^{1/2}, \quad w = q[σ^2(F_{\text{obs}}^2) + (ap)^2 + bP]^{-1}
\]

Crystals of UWDM-7 and UWDM-8 were of good quality, with an unfavourable aspect ratio typical of porphyrin-based arrangements. As is common with porous materials and mechanically interlocked molecules, the crystals were weakly diffracting (max. resolution ~1.0-1.4 Å). Different batches of crystals were tried with all of them giving similarly poor diffraction intensity. A sample of UWDM-7 was sent to the Canadian Light Source for synchrotron X-ray diffraction without successful results. The asymmetric unit for both MOFs consists of one zinc paddlewheel, one porphyrin ligand, and one rotaxane pillar.
Table 2.5.2. Crystal data, solution, and refinement parameters for UWDM-7 and UWDM-8.

<table>
<thead>
<tr>
<th>Compound</th>
<th>α-UWDM-7</th>
<th>α-UWDM-8</th>
<th>β-UWDM-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>Zn_{2}Pd(C_{48}H_{24}N_{4}O_{8})</td>
<td>Zn_{2}Pd(C_{48}H_{24}N_{4}O_{8})</td>
<td>Zn_{2}Pd(C_{48}H_{24}N_{4}O_{8})</td>
</tr>
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<td>1830.28</td>
<td>1791.98</td>
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<td>Crystal system</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2</td>
<td>P2/2</td>
<td>P2/c</td>
</tr>
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<td>Metallic red</td>
<td>Metallic red</td>
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<td>90</td>
<td>90</td>
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<tr>
<td>β (°)</td>
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<tr>
<td>γ (°)</td>
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<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>
| V (Å³) | 6851(3) | 6817.6(3) | 13562.9(9) *
| Z | 2 | 2 | 4 |
| ρ (g·cm⁻³) | 0.838 | 0.892 | 0.840 |
| μ (mm⁻¹) | 1.802 | 1.838 | 1.6809 |
| F (000) | 1638 | 1804 | 2488 |
| Radiation (Å) | 1.54178 | 1.54178 | 1.54178 |
| 2θ range (°) | 3.74 to 103.59 | 5.25 to 133.60 | 5.26 to 89.28 |
| Reflections collected | 33230 | 47274 | 41797 |
| Unique reflections | 13065 | 12328 | 10602 |
| Parameters | 693 | 447 | 672 |
| Restraints | 96 | 0 | 52 |
| Rint | 5.53% | 8.49% | 14.63% |
| R1 [I > 2σ(I)] | 11.67% | 13.78% | 18.77% |
| R1 all | 14.62% | 17.91% | 23.90% |
| wR2 [I > 2σ(I)] | 33.47% | 36.20% | 47.56% |
| wR2 all | 38.71% | 40.08% | 51.17% |
| GoF on F² | 1.617 | 1.131 | 1.776 |
| Flack | 0.497(5) | | |

*R₁ = \frac{\sum{w_F}_o-b_F}{{\sum{w_F}_o}^2} \frac{1}{1/2} ; w_R_2 = \left( \frac{\sum{w_F}_o-b_F}{{\sum{w_F}_o}^2} \right)^{1/2} , w = q[σ^2(F_o)+aP]+bP, P = \frac{F_o^2+2F_c^2}{3}

Table 2.5.3. Unit cell comparison for UWDM-7 and UWDM-8.

<table>
<thead>
<tr>
<th>Compound</th>
<th>α-UWDM-7</th>
<th>γ-UWDM-7</th>
<th>α-UWDM-8</th>
<th>β-UWDM-8</th>
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<tbody>
<tr>
<td>a (Å)</td>
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<tr>
<td>b (Å)</td>
<td>16.225(4)</td>
<td>16.390(3)</td>
<td>16.4056(4)</td>
<td>16.4164(6)</td>
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<tr>
<td>c (Å)</td>
<td>24.722(6)</td>
<td>24.5774(4)</td>
<td>24.7321(7)</td>
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</tr>
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<td>SG</td>
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<td>P2</td>
<td>P2</td>
<td>P2/c</td>
</tr>
<tr>
<td>β (°)</td>
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<td>94.169(2)</td>
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</tr>
<tr>
<td>V (Å³)</td>
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<td>6808(2)</td>
<td>6817.6(3)</td>
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* Value normalized to the other unit cells for comparison purposes
2.5.7 Powder X-ray Diffraction Patterns

Powder X-ray diffraction patterns were collected on a Bruker D8 Discover equipped with an Oxford Cryosystems Cryostream 700 and using a borosilicate capillary tube. The samples were heated at a rate of 120 °C/h and held at the target temperature for 15 minutes prior to data collection.

![Powder patterns showing isostructural α-UWDM-7 MOFs with a) PdTCPP b) NiTCPP c) ZnTCPP](image)

**Figure 2.5.7.** Powder patterns showing isostructural α-UWDM-7 MOFs with a) PdTCPP b) NiTCPP c) ZnTCPP
Figure 2.5.8. Powder patterns showing UWDM-7 a) α-UWDM-7 b) γ-UWDM-7 c) γ-UWDM-7 resolvated with DMF d) α-UWDM-7 after VT-SSNMR experiments e) α-UWDM-7 after VT-SSNMR, resolvated with DMF.

2.5.8 Solid-State NMR Spectroscopy and Simulations

All SSNMR experiments were performed using a Bruker Avance III HD console, equipped with a 9.4 T Oxford magnet with resonance frequencies of: $\nu_0(^1\text{H}) = 399.73$ MHz, and $\nu_0(^2\text{H}) = 61.4$ MHz.

A 5 mm double resonance (HX) static probe was used. Optimized 90° pulse lengths of either 3 or 3.25 µs and recycle delays of 1 s were used. Temperatures of the VT unit and probe were calibrated using the temperature-dependent chemical shift of PbNO$_3$.$^{44,45}$ The quadrupolar-echo pulse sequence (90°-τ$_1$-90°-τ$_2$-acquire) was used with
30, 50, 60 or 90 µs pulse spacings. The quadrupolar parameters of the SML spectra were
determined with simulations using WSolids. Simulations of the IMR and FML spectra
were conducted using EXPRESS.

![Figure 2.5.9. 2H MAS SSNMR spectrum of α-UWDM-7-Ni. \( v_{\text{rot}} = 14 \text{ kHz} \). Number of
scans: 64600. Experimental time: 18 h.](image)

**Table 2.5.4.** Rates and modes of motion used in the simulation of experimental VT 2H
SSNMR data for α-UWDM-7.

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<thead>
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<th>Temperature (K)</th>
<th>Two-site Jump Rate (kHz)</th>
<th>Partial Rotation Rate</th>
</tr>
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<tbody>
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<td>0</td>
</tr>
<tr>
<td>208</td>
<td>&lt;500</td>
<td>0</td>
</tr>
<tr>
<td>253</td>
<td>&gt;10000</td>
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<tr>
<td>411</td>
<td>&gt;10000</td>
<td>&gt;10000</td>
</tr>
</tbody>
</table>
Table 2.5.5. Rates and modes of motion used in the simulation of experimental VT \(^2\)H SSNMR data for \(\gamma\)-UWDM-7.

<table>
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<th>Two-site Jump Rate (kHz)</th>
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Table 2.5.6. Rates and modes of motion used in the simulation of experimental VT \(^2\)H SSNMR data for \(\alpha\)-UWDM-8.

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<td>0</td>
</tr>
<tr>
<td>253</td>
<td>&gt;10000</td>
<td>10(5)</td>
<td>0</td>
</tr>
<tr>
<td>273</td>
<td>&gt;10000</td>
<td>1000(500)</td>
<td>0</td>
</tr>
<tr>
<td>343</td>
<td>&gt;10000</td>
<td>&gt;10000</td>
<td>&gt;10000</td>
</tr>
<tr>
<td>411</td>
<td>&gt;10000</td>
<td>&gt;10000</td>
<td>&gt;10000</td>
</tr>
</tbody>
</table>

Table 2.5.7. Rates and modes of motion used in the simulation of experimental VT \(^2\)H SSNMR data for \(\beta\)-UWDM-8.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Two-site Jump Rate (kHz)</th>
<th>Partial Rotation Rate (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>185</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>273</td>
<td>&gt;10000</td>
<td>0</td>
</tr>
<tr>
<td>298</td>
<td>&gt;10000</td>
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</tr>
<tr>
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<td>&gt;10000</td>
<td>&gt;10000</td>
</tr>
<tr>
<td>411</td>
<td>&gt;10000</td>
<td>&gt;10000</td>
</tr>
</tbody>
</table>
2.6 References


Férey, Series of porous 3-d coordination polymers based on iron(iii) and porphyrin derivatives, *Chem. Mater.*, 2011, **23**, 4641–4651.


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Chapter 3: Structural Analysis and Rotational Dynamics

Inside a Porphyrin MOF with \textit{tui} Topology

3.1 Introduction

Reticular synthesis of metal-organic frameworks (MOFs) is a powerful tool for the development of new materials with predictable structure and properties.\textsuperscript{1} Using this approach, it is possible to incorporate functionalities into organic linkers (e.g. catalytic or molecular recognition sites) without compromising the robustness of the frameworks and while taking advantage of their pore distribution. In Chapter 2, we reported the synthesis, characterization, and study of the rotational dynamics of mixed linker metal-organic frameworks (MOFs), \textbf{UWDM-7} and \textbf{UWDM-8} (University of Windsor Dynamic Material) containing a porphyrin (palladium(II)-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin, PdTCPP) and a pillaring rotaxane linker that adopts a doubly-interpenetrated \textit{fsc} topology. In an effort to obtain a non-interpenetrated version of this material, we applied the principles of reticular synthesis and modified the porphyrin linker in order to sterically block the interpenetrated network from growing; this approach has been demonstrated successfully by Hupp and collaborators.\textsuperscript{2}

Although it is known that porphyrin molecules with substituents in the \(\beta\)-pyrrolic position tend to adopt a saddle or ruffle conformation,\textsuperscript{3–5} it has also been demonstrated that the directing geometry of a secondary building unit (SBU) can overcome this distortion and organize these porphyrins in a planar fashion.\textsuperscript{6–8} After the successful incorporation of three dodeca-substituted porphyrin linkers into a series of isoreticular MOFs by Zhou and coworkers,\textsuperscript{9} we decided to use a similar linker design. In this
Chapter, we report the synthesis of two dodeca-substituted porphyrins and our attempts at incorporating these porphyrins into a non-interpenetrated pillared MOF with an \textit{fsc} topology. One new MOF, \textbf{UWDM-9}, was synthesized and characterized, giving rise to an unprecedented \textit{tui} topology.\textsuperscript{10} The structural features of this new material and the factors that determine the success of reticular synthesis are discussed.

\subsection*{3.2 Results and Discussion}

Two porphyrin linkers with substituents in both \(\beta\)-pyrrolic and \textit{meso} positions were targeted for this work (\textbf{Scheme 3.2.1} and \textbf{Scheme 3.2.2}). The substituents selected for the \(\beta\)-positions, diethyl or cyclohexyl, have similar steric bulk, but the latter has a more rigid structure. While it was hoped that this steric effect would prevent interpenetration of the frameworks, it was noted that it could also have a direct influence on the conformation adopted by the carboxyphenyl substituents at the \textit{meso} positions. If the bulk is substantial, it forces the phenyl rings to deviate from their normal 90° angle with respect to the porphyrin core and this might prevent formation of the framework. By using a soft SBU that allows for flexible coordination, like zinc paddlewheels,\textsuperscript{11–13} it was expected that these deviations could be overcome and still produce the desired topology.
Scheme 3.2.1. Overall synthetic scheme for Pd-CH-TCPP.

**M-CH-TCPP.** 5,10,15,20-Tetrakis(4-carboxyphenyl)-tetracyclohexenoporphyrin (CH-TCPP) and its metallated derivatives, Ni-CH-TCPP and Pd-CH-TCPP, were synthesized following a modified literature procedure (Scheme 3.2.1, see Experimental Section for detailed synthesis).⁵

Scheme 3.2.2. Synthetic route for Ni-OE-TCPP.

**M-OE-TCPP.** 5,10,15,20-Tetrakis(4-carboxyphenyl)-octaethylporphyrin (OE-TCPP) and Ni-OE-TCPP were synthesized following a modified literature procedure.⁹ (Scheme 3.2.2, see Experimental Section for detailed synthesis).
The single-crystal X-ray structures of the methyl ester of Pd-CH-TCPP, the free-base OE-\textit{m}-TPPCOO\textit{Me}, and the metallated Ni-OE-TCPP were determined (See Experimental Section for details). Figure 3.2.1 shows that even when the metalloloporphyrins adopt a saddle conformation, the four carbonyl carbon atoms only deviate from planarity by 9.6° and 1.9° respectively. These values support the hypothesis that it might be possible to overcome the distortion on these molecules when incorporating them into MOFs that require a planar linker.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig321.png}
\caption{Ball-and-stick representation of the single crystal X-ray crystal structures of a) Ni-OE-TCPP, front view, b) Pd-CH-TPPCOO\textit{Me}, front view, c) Ni-OE-TCPP, side view, and b) Pd-CH-TPPCOO\textit{Me}, side view. The saddle conformation can be observed in the side view images.}
\end{figure}
**L1.** The [2]Rotaxane linker was synthesized following the reported procedure (Scheme 3.4.1, see also Chapter 2, Experimental Section).\(^{14}\)

**Scheme 3.2.3.** Synthetic pathway for **UWDM-9.** The 24C6 macrocycles are omitted for clarity, since they do not affect the topology of the material

**UWDM-9** was synthesized under solvothermal conditions by combining one equivalent of M-CH-TCPP, two equivalents of Zn(NO\(_3\))\(_2\)·6H\(_2\)O, and four equivalents of the rotaxane linker **L1.** The materials were isolated in moderate yields, 60% with respect to porphyrin, and the structure of **UWDM-9-Ni** was determined by SC-XRD to have formula \([\text{Zn}_2(\text{Ni-CH-TCPP})(\text{L1})_2]\)·xDMF. Despite the crystals being of good size and quality, it was not possible to fully solve the structure without the assistance of molecular
modeling. The porphyrin linker can be fully located from the electron density maps, however the rotaxane linkers cannot be adequately refined. The partial solution for the structure was imported into Materials Studio B2017 and using the Forcite module the structures of the linkers were completed and the geometry of the resulting MOF was optimized, with the unit cell dimensions constrained to the experimental values. The 24C6 rings were placed in idealized positions. If Pd-CH-TCPP is used instead, an isostructural material is obtained (Figure 3.4.5). Lastly, despite our best efforts, it was not possible to obtain a MOF with M-OE-TCPP and the rotaxane linker.

![Figure 3.2.2. Ball-and-stick representation of the coordination environment around the SBU of UWDM-9. Colour key: blue: rotaxane axle, teal: porphyrin linkers, black: Zn centres, red: 24C6 wheel.](image)

The combination of TCPP, a bipyridine-like linear linker, and a paddlewheel SBU is known to produce the $fsc$ topology. In our attempt to obtain a non-interpenetrated $fsc$ structure containing porphyrin and rotaxane linkers, UWDM-9 was synthesized. The
resulting structure presents the first example of the \textit{tui} topology. The asymmetric unit consists of two tetrahedral zinc centres as secondary building units, two rotaxane linkers, and one porphyrin linker. Each zinc atom is coordinated to two rotaxane linkers and two oxygen atoms from the porphyrin (Figure 3.2.2). The unexpected monodentate coordination of the porphyrin carboxylate groups, combined with the curvature in these molecules, creates a complex net instead of the target structure. The porphyrin linkers in UWDM-9 adopt a saddle conformation with deviations from planarity of $+23^\circ$ and $-18^\circ$ and are arranged in a helical fashion (Figure 3.4.4).

\textbf{Figure 3.2.3.} 3D framework structure and augmented representation of \textbf{UWDM-9} (A) along the \textit{c} axis without showing the 24C6 rings, (B) along the \textit{c} axis with 24C6, (b) along the \textit{b} axis, 24C6 rings hidden, (D) along the \textit{b} axis with 24C6, rings. Colour key: blue struts: rotaxane axle, teal: porphyrin linkers, black: Zn centres, red: 24C6 wheel. The unit cell is shown in black.

At first glance, the structure of \textbf{UWDM-9} seems to be related to the \textit{qtz} or \textit{dia} nets, since it is formed by tetrahedral SBUs following a helical pattern in a chiral net;
however, the topological analysis of the structure revealed this to be a new topology, classified as *tui* and deposited in the Topos Topological Database (TTD).\(^{10}\)

The *tui* topology consists of a (4,4)-connected net with point symbol \((7^4.8.9)(7^5.8)_2\). While angles and distances are irrelevant for the topological analysis of nets, in this case, they can help understand why the *tui* topology was obtained instead of the target *fsc* or another, simpler, net. **Figure 3.2.4** shows the augmented representation of the linkers used and it can be seen how the theoretically linear rotaxane linker is kinked (this is a conformation in the intermediate point between the linear conformation exhibited in **UWDM-2** and **UWDM-3** and the reported behaviour of the naked rotaxane axle).\(^{14,16}\) Moreover, the tetratopic linker, which was expected to adopt a planar conformation, instead adopts a distorted tetrahedral conformation. These two deformations allow for the growth of an intricate 3D network. Additionally, the use of a mixed linker system adds to the complexity in the final framework.

Despite the large volume occupied by the linkers as seen in **Figure 3.2.3**, **UWDM-9** is quite porous, with *Mercury*\(^{17}\) calculations showing the structure consists of 38.9% void space (15.6% is solvent accessible). **UWDM-9** has channels running perpendicular to the *a* and *b* crystallographic axes. The 24C6 rings are distributed evenly and seem to be in close proximity to each other (The exact position of the macrocycles could not be determined; therefore, this observation is based solely on the model used). Regardless of this fact, we were interested in the study of rotational dynamics of the 24C6 macrocycle.
Figure 3.2.4. Augmented representation of the linkers in UWDM-9. The distortion of the linkers from their idealized geometry can be observed.

To this extent, the stability of UWDM-9 was determined with variable temperature (VT) powder X-ray diffraction (PXRD). Even with the lack of a metal cluster as an SBU, UWDM-9 is stable in the range of 295 K to 398 K, and the intensity of the patterns starts decreasing only above this temperature (Figure 3.2.5). The thermal gravimetric analysis shows an initial loss of solvent contained in the material at 330 K, followed by its complete decomposition starting at 530 K (Figure 3.4.6).
Variable temperature PXRD patterns of as-synthesized UWDM-9.

$^2$H solid-state NMR (SSNMR) is a very sensitive technique to probe dynamics in the solid-state. Due to the nature of the packing in this structure, and the limited stability at higher temperatures it was not expected that full rotation of the macrocycle would be attainable, nevertheless the motions occurring in this material might provide insight on how close proximity of the components affects the rotational dynamics of the macrocyclic rings.

UWDM-9 was treated with fresh solvent for 2 days before running the NMR experiments in order to ensure the pores only contained guest solvent molecules and not
free, unbound linkers. $^2$H solid-state NMR spectra were acquired for UWDM-9 over a temperature range of 173 K to 373 K (Figure 3.2.6). In comparison to previously reported spectra of analogous UWDM species, the signal-to-noise (S/N) levels in these spectra are low; this could arise from several factors, including i) the low wt% of $^2$H in this sample (ca. 0.3% D w/w) ii) partial sample decomposition (vide infra), and/or iii) some semi-coherent interference arising from an unknown source proximate to the solid-state NMR spectrometer (these spectra will have to be reacquired as a result of this interference). Though the patterns cannot be simulated with accuracy due to the low S/N, the variations in the pattern shapes with temperature are similar to that of UWDM-2, and can be interpreted in an analogous fashion

The pattern acquired at 173 K has a splitting between the two outer discontinuities of ca. 120 kHz (the “feet” of these spectra are not visible due to poor S/N), corresponding to a $^2$H nucleus in a C-D bond with a quadrupolar coupling constant of $C_Q = 165 \pm 15$ kHz and $\eta_Q = 0.05 \pm 0.05$. This pattern indicates that there are no substantial motions of the C-D deuterons at 173 K, and is representative of the slow motion limit (SML). At 198 K, the S/N worsens, and some sharper features emerge in the centre of the pattern, indicating the onset of dynamic motion (this is representative of dynamics in the intermediate motional regime, IMR). These motions likely correspond to a two-site jump of the CD$_2$ group. At 298 K, the overall pattern narrows substantially, and is composed of two overlapping patterns: i) a broader underlying pattern (major component) that is ca. 100 kHz wide at its base, corresponding to partial ring rotation in the fast motion limit (FML) (i.e., the ring moves in 45° steps, due to repeated formation and breaking of a single hydrogen bond between the pillar and the macrocycle); and ii) a sharp peak (minor...
component), which likely indicates the presence of an isotropically reorienting macrocycle that is disconnected from the framework. This latter feature has relatively low integrated intensity in comparison to the aforementioned broader pattern, and could arise from minor sample decomposition. Finally, the patterns acquired at 323 K and 373 K are similar to that acquired at 298 K; full ring rotation, which would cause further narrowing of this pattern, is never observed. It should be noted that the problems encountered during the acquisition of these spectra resulted in a limited number of temperatures where the S/N permitted the collection of spectra within reasonable experimental times.
Figure 3.2.6. Experimental VT $^2$H SSNMR spectra of **UWDM-9**. The low S/N and the presence of interference on the right side of these patterns impede the accurate simulation.
The three stages of dynamics, SML (no motion), IMR (two-site CD$_2$ jumps), and FML (partial ring rotation), are the same in UWDM-2 and UWDM-9. However, the temperatures over which these motions occur are distinct. In UWDM-2, the onset of motions in the IMR occurs at ca. 255 K, substantially higher in temperature than the 198 K observed for UWDM-9. In addition, the onset of the partial ring rotation in the FML is observed at ca. 338 K for UWDM-2, which is also higher than the onset for UWDM-9, which occurs at ca. 298 K. These results indicate that UWDM-9 requires much less energy (i.e., lower temperatures) to produce similar modes of motions to those observed in UWDM-2. One possible explanation for the change in the energetic barriers for partial rotation of the crown ether macrocycles in UWDM-9 could be the deformation of the rotaxane linker (vide supra), affecting the directionality, and therefore strength, of the hydrogen-bonding interactions.

The information gathered from the NMR data complements the structural analysis derived from the X-ray data and the topological analysis of UWDM-9. The complementarity of these techniques enables the correlation of the unusual structural features in this new material with its rotational dynamics and demonstrates the application of these techniques in tandem for the characterization of advanced materials.

3.3 Conclusions

The combination of a rotaxane linker and a dodeca-substituted porphyrin linker resulted in a new MOF, UWDM-9, with a tui topology. UWDM-9 is only the third structure reported of a porphyrinic MOF with a rotaxane linker and the first reported occurrence of the tui topology. UWDM-9 displays permanent porosity and it is stable up to 100 °C. The rotational dynamics inside this MOF were studied, but only preliminary
results were obtained due to the poor S/N of the $^2$H spectra. These preliminary results indicate that the energetic barrier for rotational motion in UWDM-9 is considerably lower than all the previous MOFs in the UWDM series, but further SSNMR studies are required to fully characterize this behaviour and are ongoing.

In the introduction to this chapter, it was stated that the target structure for this project was a non-interpenetrated $fsc$ net, and that according to the principles of reticular synthesis, it should be obtainable from the combination of a zinc paddlewheel SBU, a tetracarboxylate porphyrin linker, and a linear rotaxane linker. Unfortunately, in this case the linkers deviate from the ideal geometry required for the $fsc$ net, and it was not possible to overcome these variations during the self-assembly process. This is a good example of the limitations of reticular synthesis, since it is not always possible to preserve the shape of a molecule when introducing new functionalities. In order to make a dodeca-substituted porphyrin behave like a completely planar molecule, further elongation on the meso substituents would be required and that defeats the purpose of modifying the linker to block the open space available for the formation of an interpenetrated framework. This is a valuable lesson for the future use of reticular synthesis and crystal engineering in the design of MIMs in MOFs or other structures where molecular motion is expected to occur and interpenetration represents an obstacle for the observation of unhindered motion.
3.4 Experimental Section

3.4.1 1. General Comments

Solvents and reagents were obtained from Millipore-Sigma, Tokyo Chemical Industry Co., Ltd., Frontier Scientific, or Strem Chemicals. Solvents were dried over molecular sieves for at least 24 h. Deuterated solvents were obtained from Cambridge Isotope Laboratories and stored over molecular sieves after opening. Solution $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III console equipped with an 11.7 T magnet. All peak shifts are listed in ppm relative to TMS using the residual solvent peak as a reference standard.

Column chromatography was performed using Silicycle Ultra Pure Silica Gel (230-400 mesh) or Sigma-Aldrich Aluminum oxide (Activated, neutral, Brockmann I, ~150 mesh). High-resolution mass spectrometry data were recorded on a Waters Xevo GS-XS ToF instrument in electrospray ionization (ESI) or atmospheric solids analysis probe (ASAP) mode. UV-Vis spectra were recorded using a Varian Cary 50E Spectrometer using a quartz glass cuvette of 10x10 mm. Topological analysis of the crystal structure was carried on using the ToposPro package version 5.3.0.3. 

10
3.4.2 Rotaxane synthesis

Scheme 3.4.1. Synthetic pathway for the rotaxane linker L1. (i) Grubbs catalyst 1st Gen, CH₂Cl₂/CH₃NO₂ (9:1); (ii) Pd(PPh₃)₄, DMF/Tol (1:1); (iii) Pd/C, D₂, CH₃OH.

Experimental details for the synthesis of L1 are described in Chapter 2, Section 2.5.2.
3.4.3 Porphyrin synthesis

Scheme 3.4.2. 5,10,15,20-Tetrakis(4-carboxyphenyl)-ocaethylporphyrin methyl ester (OE-m-TPPCOOME).

Methyl 4-formylbenzoate (1.333 g, 8 mmol) was dissolved in dry dichloromethane (450 mL) under N₂ atmosphere and the flask was protected from the light. 3,4-Diethylpyrrole (1.000 g, 8 mmol) was then added and the reaction mixture was stirred for 10 min. Boron trifluoride diethyl etherate (200 µL) was then added and the reaction mixture stirred for an additional 2 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.270 g, 5.6 mmol) was added to the reaction and the mixture was refluxed for 2 h. After cooling down the reaction mixture, it was transferred to a separatory funnel and the organic phase was washed with saturated sodium bisulfite (2 x 200 mL) and brine (200 mL), dried over Na₂SO₄ and the solvent removed under reduced pressure. The crude product was acidified using acetic acid and purified by column chromatography (SiO₂, CHCl₃(1% AcOH) → CHCl₃:THF:AcOH 100:10:1.5) to give a bright green powder. Yield: 0.970 g, 42%. Mp: 283 °C (decomp). ¹H NMR (500 MHz, C₆D₆, 298 K) δ (ppm) = 8.44 (d, J = 8.3 Hz, 8H, a), 8.29 (d, J = 8.3 Hz, 8H, b), 3.58 (s, 12H, c), 2.57 (sextet, J =
7.05 Hz, 8H, d), 2.1 (b, 8H, e), 0.49 (t, J = 7.2 Hz, 24H, f). $^{13}$C NMR (125 MHz, C$_6$D$_6$, 298 K) $\delta$ (ppm) = 166.7, 145.3, 130.6, 128.7, 128.3, 128.2, 128.0, 118.0, 51.8, 19.8, 17.1.

Scheme 3.4.3. Nickel(II)-5,10,15,20-tetrakis(4-carboxyphenyl)-octaethylporphyrin (Ni-OE-TPPCOOME).

The free-base porphyrin OE-$m$-TPPCOOME (100 mg, 0.01 mmol) and NiCl$_2$·6H$_2$O (50 mg, 0.20 mmol) were loaded in a microwave reaction tube with a stir bar and DMF (7 mL) added. The tube was sealed and heated at 155 °C for 15 min. The resulting red solution was diluted with THF:Et$_2$O (2:1 v/v, 30 mL) and washed with water (10 mL). The organic phase was dried over MgSO$_4$ and the solvent removed under reduced pressure. The resulting purple powder was then dissolved in tetrahydrofuran (2 mL) and transferred into a microwave reaction tube. Methanol (2 mL) and sodium hydroxide (6 M, 2 mL) were added and the reaction heated at 85 °C for 20 min. The organic solvents were removed under reduced pressure and the aqueous phase was acidified with HCl (1 M) until no further precipitation was observed. After centrifuging and drying under vacuum, a red-brown powder was isolated. Yield 60 mg, 60%. Mp: 320 °C (decomp). $^1$H NMR (500 MHz, MeOD, 298 K) $\delta$ (ppm) = 8.34 (d, J = 7.2
Hz, 8H, a), 8.19 (d, J = 7.2 Hz, 8H, b), 2.55 (b, 8H, c), 1.91 (b, 8H, d), 0.48 (t, J = 7.3 Hz, 24H, e).

Scheme 3.4.4. [Trans-(2-iodocyclohexyl)sulfonyl]benzene.

Benzenesulfinic acid (284 mg, 2 mmol) was added to a solution of N-iodosuccinimide (450 mg, 2 mmol) in dichloromethane (50 mL). After stirring at room temperature for 5 h, cyclohexene (164 mg, 2 mmol) was added and the reaction mixture stirred for additional 2 h. The reaction mixture was then washed with saturated NaHCO₃ (50 mL) and NaHSO₃ (50 mL) solutions. The organic phase was dried over MgSO₄ and the solvent removed under reduced pressure. The crude product was then purified by column chromatography (SiO₂, hexanes:ethyl acetate 1:1 v/v, Rf: 0.38). Yield: 640 mg, 80%. ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 7.88 (d, J = 7.9 Hz, 2H, c), 7.67 (t, J = 7.9 Hz, 1H, a), 7.58 (t, J = 8.0 Hz, 2H, b), 5.10 (m, 1H, e), 3.36 (m, 1H, d), 2.29-2.15 (m, 2H,f), 2.05-1.96 (m, 3H, i+h) 1.77- 1.60 (m, 2H, g) 1.55-1.49 (m, 1H, h). Values match those previously reported.⁵

Scheme 3.4.5. (1-Cyclohexen-1-ylsulfonyl)benzene
[Trans-(2-iodocyclohexyl)sulfonyl]benzene (6.54 g, 18.7 mmol) was dissolved in dichloromethane (50 mL) and Al₂O₃ (50 mL) added. The reaction mixture was stirred at room temperature for 24 h, filtered, and the solvent removed under reduced pressure. The crude product was purified by column chromatography (SiO₂, hexanes:ethyl acetate 1:9 – 1:1 v/v). Yield: 3.20 g, 77%. ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 7.85 (d, J = 7.9 Hz, 2H, c), 7.59 (t, J = 7.8 Hz, 1H, a), 7.51 (t, J = 8.0 Hz, 2H, b), 7.05 (tt, J = 3.9 Hz 1.6 Hz, 1H, d), 2.27-2.23 (m, 2H, e), 2.16-2.13 (m, 2H, h), 1.65-1.60 (m, 2H, f), 1.57-1.53 (m, 2H, g). Values match those previously reported.⁵

Scheme 3.4.6. 4,5,6,7-Tetrahydro-2H-isoindole.

A solution of tert-butyl isocynoacetate (1.81 mL, 16.5 mmol) in tetrahydrofuran (100 mL) was added to a suspension of potassium tert-butoxide (1.90 g, 16.5 mmol) in tetrahydrofuran (100 mL) at 0 °C under N₂ atmosphere. (1-Cyclohexen-1-ylsulfonyl)benzene (3.20 g, 14.4 mmol) was dissolved in tetrahydrofuran (50 mL) and added dropwise to the reaction mixture, maintaining the temperature at 0 °C. After stirring for 12 h, the reaction mixture volume was reduced to approx. 50 mL and dissolved in chloroform (100 mL). The combined organic phase was washed with water (2 x 100 mL) and brine (100 mL) and filtered through a silica pad. Ethyl 4,5,6,7-tetrahydro-2H-isoindole-1-carboxylate was dissolved in degassed ethylene glycol (40 mL) and sodium hydroxide (3.0 g) added. The reaction mixture was heated under reflux for 30 min and then poured onto crushed ice. The aqueous phase was extracted with
chloroform (100 mL) and dried over Na$_2$SO$_4$. The crude product was then filtered through a silica pad and immediately used for the next reaction.

Scheme 3.4.7. 5,10,15,20-Tetrakis(4-carboxyphenyl)-tetracyclohexenoporphyrin methyl ester (CH-$m$-TPPCOOMe)

Methyl formyl benzoate (1.56 g, 9.5 mmol) was charged into a Schlenk flask under N$_2$. A solution of 4,5,6,7-tetrahydro-2H-isoindole (1.13 g, 9.5 mmol) in degassed chloroform was added to the flask, the final volume adjusted to 500 mL and the flask was protected from light. After stirring the reaction mixture for 10 min, BF$_3$·Et$_2$O (0.250 mL) was added. After 3 h, DDQ (0.70 g, 3 mmol) was added and the reaction mixture was stirred overnight. The volume of the reaction mixture was then reduced to approx. 50 mL and acidified with acetic acid. The crude product was loaded into a chromatography column (SiO$_2$, CHCl$_3$:THF:AcOH 100:10:1 v/v) and the green fraction was collected and recrystallized as the triflate salt. Yield: 600 mg, 24 %. Mp: 340 °C (decomp.). $^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta$ (ppm) = 8.56 (d, $J = 8.1$ Hz, 8H, a), 8.51 (d, $J = 8.1$ Hz, 8H, b), 4.13 (s, 12H, c), 2.48 (dt, $J = 17.2$, 5.6 Hz, 8H, d or g), 2.01 (dt, $J = 17.2$, 5.6 Hz, 8H, d or g), 1.66 (q, $J = 6$ Hz, 8H, e or f), 1.16 (q, $J = 6$ Hz, 8H, e or f), -1.41 (s, 4H, h). HR-
MS (ESI +): Calculated for [M-H₂]^{2+} [C_{68}H_{66}N_{4}O_{8}]^{2+} m/z = 532.2362; found m/z = 532.2365. Values match those previously reported.⁵

![Scheme 3.4.8. Palladium(II)-5,10,15,20-tetrakis(4-carboxyphenyl)-tetracyclohexenoporphyrin](image)

Porphyrrin CH-m-TPPCOOMe (0.110 g, 0.08 mmol) was dissolved in N,N-dimethylformamide (7 mL) and transferred into a microwave reaction tube. PdCl₂ (60 mg, 0.4 mmol) was added and the reaction mixture heated at 155 °C for 15 min. The resulting red solution was diluted with THF:Et₂O (2:1 v/v, 30 mL) and washed with water (10 mL). The organic phase was dried over MgSO₄ and the solvent removed under reduced pressure. The resulting purple powder was then dissolved in tetrahydrofuran (2 mL) and transferred into a microwave reaction tube. Methanol (2 mL) and sodium hydroxide (6 M, 2 mL) were added and the reaction heated at 85 °C for 20 min. The organic solvents were removed under reduced pressure and the aqueous phase was acidified with HCl (1 M) until no further precipitation was observed. After filtration a red powder was obtained. Yield 57 mg, 52%. Mp: >400 °C. ¹H NMR (500 MHz, DMSO-d₆, 298 K) δ (ppm) = 8.29 (d, J = 7.9 Hz, 8H, a), 8.13 (d, J = 7.9 Hz, 8H, b), 2.26 (b, 16H, c),
1.44 (b, 16H, d). HR-MS (ESI +): Calculated for [M-H]$^+$ [PdC$_{64}$H$_{53}$N$_4$O$_8$]$^+$ \( m/z = 1111.2920 \); found \( m/z = 1111.2900 \).

Ni-CH-TCPP. Same procedure as above using NiCl$_2$·6H$_2$O. Yield 76 mg, 70%.

Mp: >400 °C. $^1$H NMR (500 MHz, DMSO-$d_6$, 298 K) \( \delta \) (ppm) = 13.28 (b, 4H), 8.21 (d, \( J = 7.6 \) Hz, 8H), 7.96 (d, \( J = 7.6 \) Hz, 8H), 2.17 (b, 16H), 1.40 (b, 16H).

3.4.4 MOF Synthesis

**UWDM-9-Ni.** Zn(NO$_3$)$_2$·6H$_2$O (2.0 mg, 6.7 µmol), L1 (10.0 mg, 13.4 µmol), and Ni-CH-TCPP (3.5 mg, 3.3 µmol) were dissolved in 0.75 mL of N,N-dimethylformamide in a 1 dram vial to which 2 drops HBF$_4$·Et$_2$O were added. The vial was placed inside a scintillation vial and the mixture heated at 90 °C for 5 days to yield hexagonal red crystals.

**Figure 3.4.1.** Optical micrograph of **UWDM-9-Pd** crystals. Their hexagonal morphology can be seen.

**UWDM-9.** The synthesis was scaled up as follows in order to perform SSNMR experiments. Zn(NO$_3$)$_2$·6H$_2$O (31 mg, 0.102 mmol), Pd-CH-TCPP (57 mg, 0.051 mmol),
and L1 (152 mg, 0.205 mmol) were placed in a 20 mL scintillation vial and dissolved in 12 mL of N,N-dimethylformamide to which 6 drops of HBF₄ were added. The vial was sonicated, the mixture divided equally on 5 more vials and heated at 90 °C for 5 days to yield hexagonal red crystals (76 mg, 75% based on porphyrin). To further corroborate the composition of **UWDM-9**, a small amount of crystals was suspended in DMSO-d₆ followed by addition of triflic acid-d₆.

**Figure 3.4.2.** Partial ¹H NMR spectrum of digested **UWDM-9**. The porphyrin (red) to rotaxane (blue) ratio is 1:2.

### 3.4.5 3. Single-crystal X-ray Studies

Single crystal X-ray data were collected on a Bruker D8 Venture diffractometer, equipped with a PHOTON 100 detector, kappa goniometer, and collected using a Cu high brilliance 1µS microfocus source or a MoKα source. Crystals were mounted on MiTeGen
MicroMounts and frozen in paratone oil under a cold stream of N\textsubscript{2} from an Oxford Cryosystems Cryostream 700. Reflection data were integrated using APEX III software.

Single crystals of OE-\textit{m}-TPPCOO\textsubscript{Me} were grown from slow diffusion of methanol into a solution of OE-\textit{m}-TPPCOO\textsubscript{Me} in dichloromethane. Single crystals of Ni-OE-TCPP were grown by slow evaporation of a dimethylformamide solution. Single crystals of Pd-CH-TPPCOO\textsubscript{Me} were grown by slow evaporation of an ether solution. Using Olex2,\textsuperscript{18} the structures were solved with the \textit{olex2.solve}\textsuperscript{19} or \textit{XT}\textsuperscript{20} solution program and the Charge Flipping or Intrinsic Phasing method, respectively, and refined with the XL\textsuperscript{21} package using Least Squares minimization. Solvent masks were applied Ni-OE-TCPP and Pd-CH-TPPCOO\textsubscript{Me}.\textsuperscript{22} Figures were created using the Diamond suite.\textsuperscript{23}
Figure 3.4.3. Hydrogen bonded network in Ni-OE-TCPP. Colour key: green: nickel, gray: carbon, blue: nitrogen, red: oxygen. Dashed bonds represent the hydrogen bonding interactions.

The X-ray crystal structure of Ni-OE-TCPP was determined and it was found that the porphyrin molecules are arranged in a hydrogen-bonding network. The packing of the molecules generates a supramolecular structure with 48% accessible void space, occupied by disordered solvent molecules. A solvent mask was applied in order to consider their contribution to the electron density during the structure refinement.\(^{18}\)

Table 3.4.1. Crystal data, solution, and refinement parameters for porphyrins OE-\(m\)-TPPCOOMe, Ni-OE-TCPP, and Pd-CH-TPPCOOMe.

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<thead>
<tr>
<th>Compound</th>
<th>OE-(m)-TPPCOOMe</th>
<th>Ni-OE-TCPP</th>
<th>Pd-CH-TPPCOOMe</th>
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<tr>
<td>Chemical formula</td>
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<td>(NiC_{68}H_{60}N_4O_8)</td>
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<td>Formula weight (g·mol(^{-1}))</td>
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<td>Crystal system</td>
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<td>Space group</td>
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<td>(P_{2_1}/n)</td>
<td>(P\overline{1})</td>
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<tr>
<td>Colour</td>
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<td>Metallic red</td>
<td>Metallic red</td>
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<tr>
<td>(T) (K)</td>
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<td>100(2)</td>
<td>170(2)</td>
</tr>
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<td>(b) (Å)</td>
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<td>(c) (Å)</td>
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<td>(R_1) all</td>
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<td>8.97%</td>
<td>6.21%</td>
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<tr>
<td>(wR_2) ([I &gt; 2\sigma(I)])</td>
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<td>23.55%</td>
<td>8.69%</td>
</tr>
<tr>
<td>(wR_2) all</td>
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<td>25.09%</td>
<td>9.24%</td>
</tr>
<tr>
<td>GoF on (F^2)</td>
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<td>1.059</td>
<td>1.056</td>
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\[ R_1 = \frac{\sum|F_{obs} - F_{calc}|}{\sum F_{obs}}; wR_2 = \left(\frac{\sum w(F_{obs} - F_{calc})^2}{\sum wF_{obs}^2}\right)^{1/2}, w = q[\sigma^2(F_{obs}) + (aP)^2 + bP]^{-1}, P = \frac{F_{obs}^2 + 2F_{calc}^2}{3} \]

109
Table 3.4.2. Crystal data, solution, and refinement parameters for UWDM-9.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Zn₂(NiC₆₈N₄O₈)</th>
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<td>Radiation (Å)</td>
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<td>P₆₅</td>
<td>Reflections collected</td>
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<td>Colour</td>
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<td>Unique reflections</td>
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<td>c (Å)</td>
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<td>α (°)</td>
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<td>5 to 89</td>
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<td>β (°)</td>
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<td>V (Å³)</td>
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<td>Z</td>
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<td>5 to 89</td>
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<td>ρ (g·cm⁻³)</td>
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<td>Θ range (°)</td>
<td>5 to 89</td>
</tr>
</tbody>
</table>

\[ R_1 = \frac{\sum|F_{obs} - F_{calc}|}{\sum|F_{obs}|} ; wR_2 = \left( \frac{\sum[w|F_{obs}^2 - F_{calc}^2|^2]}{\sum[w|F_{obs}|^2]} \right)^{1/2} , w = q[σ²(F_{obs}) + (aP)² + bP]^{-1} \]

Figure 3.4.4. Helical arrangement of the porphyrin linkers observed in UWDM-9. Rotaxane linkers shown as blue sticks, 24C6 rings omitted for clarity.

3.4.6 Powder X-ray Diffraction Studies

Powder X-ray diffraction data were collected using a capillary tube on a Bruker D8 Discover diffractometer equipped with a 140 mm 2-D Vantec 500 detector, and a
conventional copper source set to 40 kV and 40 mA. VT-PXRD data were collected on the same instrument, using an Oxford Cryostream 700.

![X-ray diffraction patterns](image)

**Figure 3.4.5.** Powder X-ray diffraction patterns for a) simulated UWDM-9, b) UWDM-9-Pd, c) UWDM-9-Ni.

3.4.7 Thermogravimetric Analysis Studies

Thermogravimetric analysis was performed on a Mettler Toledo STDA 851e instrument. The sample were stabilized at 25 °C for 30 min and then heated to 550 °C at a rate of 5 °C per min.
3.4.8 Solid-state NMR Spectroscopy

All SSNMR experiments were performed using a Bruker Avance III HD console, equipped with a 9.4 T Oxford magnet with resonance frequencies of: \( \nu_0(\text{H}) = 399.73 \) MHz, and \( \nu_0(\text{D}) = 61.4 \) MHz. A 5 mm double resonance (HX) static probe was used. Optimized 90° pulse lengths of 3 \( \mu \)s and recycle delays of 1 s were used. Temperatures of the VT unit and probe were calibrated using the temperature-dependent chemical shift of \( \text{PbNO}_3 \).\(^{24,25}\) The quadrupolar-echo pulse sequence (90°-\( \tau_1 \)-90°-\( \tau_2 \)-acquire) was used with 30 \( \mu \)s pulse spacings.

As mentioned above, the \( ^2\text{H} \) SSNMR spectra will have to be reacquired for a fresh sample; recent elimination of the problem of interference on the 5 mm HX static
Chemagnetics/Varian solid-state NMR probe should greatly improve S/N, and allow refinement of this model via accompanying simulations.

3.5 References


Chapter 4. One-Pot Synthesis of Porphyrin-[5]Rotaxanes

4.1 Introduction

The synthesis of mechanically interlocked molecules (MIMs) with higher degrees of complexity and an increased number of components has gained attention in recent years. \([n]\)Rotaxanes with porphyrin moieties have been synthesized as molecular compressors/receptors,\(^1\) tweezers,\(^2\) mechanical picket-fences,\(^3\) scaffolds to pre-organize polyynes,\(^4\) precursors for the synthesis of porphyrin nanorings,\(^5\) molecules for anion recognition,\(^6\) systems for electron-transfer,\(^7,8\) catalytic models,\(^9\) and potential molecular switches.\(^10\) Other interesting MIMs with porphyrins and/or high compositional complexity have also been reported in the literature.\(^5,11–20\) Most of the examples mentioned above require a multi-step pathway, or even a synthetic \textit{tour de force}, where the interlocked components are first individually assembled and then fused together to form the final product. If more efficient methods for the synthesis of sophisticated MIM architectures could be found, the potential to explore their chemistry and to develop functional systems with these molecules would be increased.

The incorporation of porphyrin cores into mechanically interlocked architectures has been of interest due to the wide range of applications of porphyrins (\textit{e.g.} artificial photosynthesis, catalysis, light harvesting, molecular photonics) and their robustness as supramolecular building blocks. J. P. Sauvage and colleagues have proposed that systems with mechanical bonds and chromophores might be used to understand and replicate electron-transfer in photosynthetic systems.\(^21,22\) Goldup and co-workers also believe that
MIMs with porphyrins can be incorporated into “smart” materials and have potential to be used in catalysis.\textsuperscript{3}

Lindsey’s method for the preparation of \textit{meso}-substituted porphyrins has a high tolerance for the functionalization of the aldehyde precursor and the yields are higher (up to 50\% yield) compared to other synthetic methods.\textsuperscript{23,24} Here, we employ this method for the synthesis of symmetrical [5]rotaxanes in a one-pot reaction. This reaction works as a multi-capping method, where commonly used recognition sites are employed to direct the molecular recognition in conjunction with simple crown ether wheels to create [5]rotaxanes with the potential to be incorporated into solid-state materials. Considering the reported synthetic pathways for similar molecules, we believe this procedure represents one of the most direct routes for obtaining interlocked architectures with a high number of components.

4.2 Results and Discussion

4.2.1 Synthesis and characterization of 5R1-5R6

\textbf{Scheme 4.2.1} shows the general procedure followed for the synthesis of [5]rotaxanes. First, an aldehyde axle with a recognition site is prepared (\textbf{Scheme 4.2.2}) and then in a one-pot reaction, it is combined with a suitable macrocyclic ring and pyrrole to form a porphyrinogen that can be oxidized to give the final [5]rotaxane. Using this method, it is possible to vary the nature of the stopper groups or the crown ether without altering the overall synthetic pathway.

Porphyrin-[5]rotaxanes 5R1-5R6 (Scheme 4.2.3 and Scheme 4.2.4) were isolated in moderate yields (10-30%) from the reaction between the aldehyde axles 1-6, dibenzo-24-crown-8 ether (DB24C8), and pyrrole in dichloromethane. The use of DCM as solvent allows for the maximization of the association constant between the crown ether ring and the protonated axle; DB24C8 was selected for this work due to its crystallinity, and it is used in excess to ensure complete complexation of the axles. Finally, oxidation with DDQ makes the porphyrinogen permanently interlocked.
We investigated three different structural variations in the components and the effect they have on pseudorotaxane and rotaxane formation: i) the substituent groups on the axle, ii) the crown ether wheel, and iii) the recognition sites (Table 4.2.1). The substituents on the axle effect the association constant by modifying the electronic properties of this interaction (e.g. EWG on aldehyde 1 vs. EDG on aldehyde 4), but the effect is minor. The nature of the macrocyclic wheel also influences the association
interactions, with the electron-rich DB24C8 showing a higher affinity than 24-crown-8 ether (24C8) for all the axles tested. Finally, and as previous studies in our research group have shown, the nature of the recognition site has the most noticeable impact on the pseudorotaxane formation. The benzimidazolium motif is much more efficient than the anilinium in the molecular recognition process, with association constants at least two orders of magnitude higher. It should be noted that the condensation reaction between the pseudorotaxane aldehydes and pyrrole does not seem to be greatly affected by any of the modifications studied, and the differences in yield are primarily attributed to the efficiency and ease of the purification procedure.

**Table 4.2.1.** Association constants for [2]pseudorotaxane formation between different cationic axles and two crown ether rings.

<table>
<thead>
<tr>
<th>Axle</th>
<th>24C8</th>
<th>DB24C8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>210</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>1550</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
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<td>4</td>
<td>840</td>
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<tr>
<td>5</td>
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<td>&gt;10000</td>
</tr>
<tr>
<td>6</td>
<td>N/D</td>
<td>&gt;10000</td>
</tr>
</tbody>
</table>

*a* Determined by $^1$H NMR spectroscopy (0.5-1.0 x $10^{-3}$ M, 298 K). All anions are BF$_4^{-}$. Errors are estimated to be less than 10%. *b* An approximation at the upper limit of the value measurable by $^1$H NMR spectroscopy.

The [5]rotaxanes were characterized by NMR and UV-Vis spectroscopy, mass spectrometry, and the crystal structure of 5R1 was obtained. The mass spectra of rotaxanes 5R1-5R6 show a molecular ion corresponding to [M + 4H]$^{4+}$ and the isotope
patterns are in good agreement with simulations (Experimental Section, Figure 4.4.7). Additional molecular ions corresponding to [M + 2H]^{2+}, [M + 3H]^{3+}, [M + 5H]^{5+}, and [M + 6H]^{6+} were observed in some cases and provide additional evidence that the macrocycle, and not a polymeric chain, is the isolated product. For 5R1, an additional spectrum using matrix-assisted laser desorption ionization (MALDI) was collected and the molecular ion corresponding to [M – H]^+ was observed (Experimental Section, Figure 4.4.6).

With the exception of 5R4, for which it was not possible to completely assign all the peaks, possibly due to aggregation effects, the rotaxanes were successfully characterized by ^1^H NMR spectroscopy. They exhibit the characteristic peaks of a meso-substituted porphyrin where, due to symmetry, one quarter of the molecule is sufficient to describe all the proton environments present. The integration of the peaks in these spectra further corroborates the formation of the porphyrin and the incorporation of four interlocked crown ether macrocycles per porphyrin unit. Characteristic splitting due to rotaxane formation is observed for \(-\text{NH}–\) and \(-\text{CH}_2–\) peaks on the axle, as well as shifting and splitting of the various proton environments on the crown ether rings, indicating hydrogen bonding and \(\pi\)-stacking interactions with the recognition site. The resonances of the porphyrin core (\(\beta\)-pyrrole and core pyrrolic protons) on the aniline-based rotaxanes do not change substantially upon rotaxane formation, however they are very sensitive to protonation changes of both the recognition sites and the central pyrrole units. For the benzimidazole-based MIMs, substantial shifting of the \(\beta\)-pyrrole and aryl protons adjacent to the porphyrin core is observed. This is in agreement with the
additional electron density that a protonated benzimidazole motif incorporates into the molecule.

Scheme 4.2.3. Aniline-based [5]rotaxanes
Scheme 4.2.4. Benzimidazole-based [5]rotaxanes

The single-crystal X-ray structure of [5R1-H6][BF$_4$]$_6$ was determined and it is shown in Figure 4.2.1. It consists of a saddled porphyrin with the four crown ether rings π-stacked over the isophthalic fragments. Disordered BF$_4^-$ anions sit on the top and the bottom of the pocket formed by the pyrrole nitrogen atoms, and between each porphyrin arm. There are two hydrogen-bonding interactions between the axle anilinium NH$_2^+$ group and DB24C8 oxygen atoms (2.72 Å, 2.84 Å, 158°, 139°) and two additional CH---O interactions (3.02 Å, 3.11 Å, 140°, 135°). The crown ether adopts a C-conformation allowing π-stacking interactions with the electron-deficient isophthalic fragment (3.8 Å). Attempts to obtain the crystal structure of neutral 5R1 and the other [5]rotaxanes for comparison purposes were unsuccessful (Experimental Section, Figure 4.4.4).
Figure 4.2.1. Ball-and-stick representation of the single-crystal X-ray structure of cationic 5R1. The porphyrin core is shown in blue and DB24C8 rings in red. Hydrogen atoms on the crown ether rings and BF$_4^-$ counterions are omitted for clarity.

A characteristic UV-Vis-NIR spectrum for a porphyrin with meso-substitution was observed for rotaxanes 5R1-5R6. The porphyrin P1 (same core as 5R1 but without interlocked crown ether rings) was synthesized in order to compare its spectrum to that of 5R1; the two spectra are almost identical, with only minor changes (<5 nm) in the absorption maxima (Experimental section, Figure 4.4.5). Upon protonation or metallation, the spectrum is simplified to two $Q$ bands instead of four, as expected. The titration of 5R1 with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) shows the classic profile for a porphyrin, with the blue shifting of the Soret band and the appearance of the $Q_{II}$ and
$Q_{III}$ bands because of the deprotonation of the central pyrrole nitrogen atoms (symmetry is reduced from $D_{4h}$ to $D_{2h}$). No additional equilibria from the deprotonation of the –NH– recognition sites are observed. The analysis of the data suggests that this is a cumulative equilibrium and no stepwise binding equilibria are detected.

Figure 4.2.2. UV-Vis titration curve for cationic 5R1 with DBU (top). Photographs of the change in colour upon deprotonation (bottom).

5R4 was also studied by UV-Vis spectroscopy and the addition of the electron-rich trityl groups has an effect on the energy levels of the porphyrin. The $Q_{IV}$ band is red shifted by about 125 nm, and some additional bands are observed. This has been
described as the *hyperporphyrin* effect and is caused by charge transfer transitions from the electron-rich trityl $\pi$ orbital to the porphyrin $\pi^*$ orbital.\textsuperscript{27,28}

**Figure 4.2.3.** UV-Vis titration curve for [5R4-H$_6$][BF$_4$]$_6$ with DBU.

Finally, the titration curve for cationic 5R5 with DBU shows the same type of behaviour as 5R1, with the benzimidazole core $\pi$-$\pi^*$ transition observed in the 330–360 nm region.
Figure 4.2.4. UV-Vis titration curve for 5R5 with DBU.

4.2.2 Conformational switching in porphyrin-[5]rotaxanes.

Previous studies of MIMs having DB24C8 or other rings capable of π-stacking have shown that the conformation of the macrocycle (i.e. folded S- or C-shape or open) can be inferred from the $J$-couplings and chemical shifts of characteristic protons.\textsuperscript{25,29} Additionally, if the macrocycle is desymmetrized it can be incorporated into a flip-switch system where these conformations can be interconverted.\textsuperscript{30–32} If such large amplitude conformational switches could be organized into arrays – e.g. four per porphyrin platform – and could operate over a large spatial area, this would represent a realistic starting point for their incorporation into ordered systems where they might function coherently and possibly in a concerted fashion.
After studying the cationic structure of 5R1, we decided to investigate if there were any conformational changes occurring in this molecule with variation in pH (acid-base chemistry). First, a titration plot of the cationic form of 5R1 with DBU, monitored by $^1$H NMR, was performed. **Figure 4.2.6** shows the resulting spectra where the peaks corresponding to the aromatic environments on the crown ether are more deshielded upon neutralization of the recognition site. The chemical shift of the glycolic crown ether protons and the splitting patterns are also influenced by the protonation state and upon neutralization these peaks are shifted slightly upfield, consistent with the loss of hydrogen bonding interactions and the different environments are better resolved indicating an open conformation similar to that of the free crown ether. The peaks corresponding to the isophthalic stopper groups are more shielded by approximately one ppm compared to the neutral species, with a concomitant change in the second-order coupling constant providing additional evidence that π-stacking over this fragment is occurring.
Following these studies, Nuclear Overhauser Effect Spectroscopy (NOESY) $^1$H NMR experiments were conducted to determine if through space correlations could be used as an additional probe for the conformation of the crown ether macrocycles. Figure 4.2.7 shows the comparison between $^1$H NOESY spectra of protonated and neutral 5R1. Although no direct NOE crosspeaks are observed between the aromatic protons of DB24C8 and the axle, likely since these distances are >4 Å, the intensity of the NOE correlations between the glycolic protons and the protons near or on the recognition site infer a tighter (i.e. folded) conformation of the ring in this region. For these close interactions to be possible, it would likely require that the crown ether is in the C-conformation, wrapping around either the isophthalic groups or the meso-aryl rings. The absence of NOE crosspeaks between the β-pyrrole protons and the aromatic DB24C8
and the positive crosspeaks with the glycolic protons indicates the former arrangement is
the more likely structure.

The same study was performed with 5R3, but using the peaks corresponding to
the methyl group stoppers as reference, and the same correlations can be made (Figure
4.2.8). Thus, this type of primitive (conformational) switching can be exploited if the
molecules are organized and immobilized on an acid-base-resistant template.

Figure 4.2.7. ^1^H-^1^H NOESY spectra (500 MHz, CDCl$_3$, 298 K, mixing time 400 ms) of
neutral (left) and protonated (right) 5R1.
Figure 4.2.8. $^1$H-$^1$H NOESY spectra (500 MHz, CDCl$_3$, 298 K, mixing time 400 ms) of neutral (left) and protonated (right) 5R3.

For 5R5, other well-resolved proton signals can be used to indirectly determine the conformation of the macrocycle. The sharp peaks corresponding to the backbone protons on the benzimidazole core and the protons on the T-shape phenyl groups are in close spatial proximity to those of the aromatic rings of a DB24C8 molecule if it adopts a C-conformation. If the crown is in an open conformation, the protons on the backbone should have no through-space correlation to any protons on the ring. First, Correlation Spectroscopy (COSY) and Total Correlation Spectroscopy (TOCSY) were used to fully assign the peaks of the $^1$H spectrum (See Experimental Section, Figure 4.4.1 and Figure 4.4.2). After the assignment was complete, $^1$H-$^1$H NOESY was used to determine if it is possible to use the selected resonances as probes of the conformational changes in the macrocycle. Figure 4.2.9 shows the changes in the spectra indicating the conformation adopted by the DB24C8 rings. Broadening of peaks due to aggregation makes the interpretation of the protonated spectrum more challenging, but the spectroscopic evidence infers that conformational switching also occurs for 5R5.
Figure 4.2.9. \(^1\)H–\(^1\)H NOESY spectra (500 MHz, CD\(_2\)Cl\(_2\), 298 K, mixing time 400 ms) of neutral (left) and protonated (right) 5R5.

Table 4.2.2 summarizes selected spectroscopic data for the rotaxanes. The chemical shift and splitting patterns of the glycolic and aromatic protons of DB24C8 are shown and a trend is observed for the shielding of glycolic protons and deshielding of aromatic protons upon deprotonation.

Table 4.2.2. Chemical shift and splitting patterns of DB24C8 protons for some porphyrin-[5]rotaxanes.

<table>
<thead>
<tr>
<th>Rotaxane</th>
<th>Protonated</th>
<th>Neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glycolic</td>
<td>Aromatic</td>
</tr>
<tr>
<td>5R1</td>
<td>4.30</td>
<td>6.63</td>
</tr>
<tr>
<td></td>
<td>3.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.80</td>
<td>multiplet</td>
</tr>
<tr>
<td>5R2</td>
<td>4.24</td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td>4.02</td>
<td>multiplet</td>
</tr>
<tr>
<td></td>
<td>3.74</td>
<td></td>
</tr>
<tr>
<td>5R3</td>
<td>4.28</td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td>3.95</td>
<td>multiplet</td>
</tr>
<tr>
<td></td>
<td>3.72</td>
<td></td>
</tr>
<tr>
<td>5R5</td>
<td>3.84</td>
<td>6.64</td>
</tr>
<tr>
<td></td>
<td>3.38</td>
<td>6.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>multiplets</td>
</tr>
</tbody>
</table>
In addition to the NMR studies, the fluorescence of protonated benzimidazoles can be used to visually identify the protonation state of these molecules and, in these systems, indirectly determine the conformation of the crown ethers. Figure 4.2.10 shows a photograph of neutral 5R5 and protonated 5R5 under long wave (365 nm) UV light radiation. The optical switching properties of interlocked molecules have been reported and used in the construction of a molecular abacus\textsuperscript{33} and non-linear optic devices.

Figure 4.2.10. Photograph of 5R5 (left) and [5R5-H\textsubscript{6}][BF\textsubscript{4}]\textsubscript{6} (right) under UV light (365 nm) radiation.

Unfortunately, the spectroscopic evidence does not allow for a determination of the extent of the switching behaviour of the DB24C8 units inside these [5]rotaxanes. One aspect worth considering is the fact that in solution, interconversion between the two possible C- or S-conformations (Figure 4.2.11) might have a low energetic barrier. Moreover, if the S-conformation is rapidly alternating sides (flipping), this can result in NOE cross peaks that might be misleading. It would be interesting to observe if the same ambiguous behaviour occurs in the solid state, and if it does, the use of unsymmetrical crown ethers (e.g. benzo, naphtho24C8 rather than dibenzo24C8) might be a way of eliminating this ambiguity.
Figure 4.2.11. Cartoon representation of the two possible stacked conformations –C (left) and S (right)– of DB24C8 (red). The blue and yellow sites represent two different aromatic rings on the rotaxane axle.

4.3 Conclusions

We developed a synthetic pathway for the fabrication of large multi-switchable, porphyrin-based MIMs using only a few synthetic steps for axle formation and a one-pot reaction for the final formation of the [5]rotaxanes. This methodology allows for variation of the recognition sites, the substituent groups on the meso position, and the macrocyclic wheels. With this degree of versatility, it should be possible to build a wide range of mechanically interlocked architectures and fine-tune their electronic properties for specific applications.

Future studies will be aimed at the incorporation of [5]rotaxanes into crystalline solids, in order to further study the conformational changes occurring in these molecules upon protonation. If the switching behaviour observed in solution can be translated into a solid-state material, systems with emerging photophysical and dynamic properties could be achievable.
4.4 Experimental section

4.4.1 General comments

Solvents and reagents were obtained from Millipore-Sigma, Tokyo Chemical Industry Co. Ltd., Lancaster Synthesis, Frontier Scientific, or Strem Chemicals. Diethyl-5-aminoisophtalate,\textsuperscript{34} 3,5-dibromoaniline,\textsuperscript{35} 4-(5,5-dimethyl-1,3-dioxan-2-yl) benzaldehyde,\textsuperscript{36} 4,7-dibromo-2,1,3-benzothiadiazole,\textsuperscript{37} 1,2-diamino-3,6-di(4’-t-butyl phenyl)-benzene,\textsuperscript{29} and 4,7-bis(4-bromophenyl)-2,1,3-benzothiadiazole\textsuperscript{38} were synthesized according to literature methods. Solvents were dried over molecular sieves for at least 24 h. Deuterated solvents were obtained from Cambridge Isotope Laboratories and stored over molecular sieves after opening. Solution $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III console equipped with an 11.7 T magnet. All chemical shifts are listed in ppm relative to TMS using the residual solvent peak as a secondary reference standard. Column chromatography was performed using Silicycle Ultra Pure Silica Gel (230-400 mesh) or Sigma-Aldrich Aluminum oxide (Activated, neutral, Brockmann I, ~150 mesh). IR spectra were collected on a Bruker Alpha-T ATR-FTIR spectrometer.
4.4.2 Synthesis

Scheme 4.4.1. Diethyl 5-((4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)amino)isophthalate (1a).

To a solution of diethyl-5-aminoisophthalate (1.58 g, 6.7 mmol) and 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (1.47 g, 6.7 mmol) in dichloroethane (35 mL), under N₂, was added sodium triacetoxyborohydride (1.98 g, 9.3 mmol). The solution was stirred for 16 h and quenched with saturated sodium bicarbonate solution. The organic phase was isolated and washed with water (50 mL) and brine (10 mL), dried over MgSO₄, and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (SiO₂, dichloromethane/ethyl acetate/triethylamine 100:2:0.5 v/v, Rf = 0.60). Yield: 1.8 g white solid, 62%. Mp: 109-116 °C. ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 7.99 (1H, c), 7.47 (d, 2H, J = 7.9 Hz, h), 7.45 (s, 2H, d), 7.35 (d, 2H, J = 7.9 Hz, g), 5.38 (s, 1H, i), 4.37 (s, 2H, f), 4.35 (q, 4H, J = 7.1 Hz, b), 3.75 (d, 2H, J = 10.9 Hz, j, k), 3.63 (d, 2H, J = 10.9 Hz, j, k), 1.37 (t, 6H, J = 7.1 Hz, a), 1.28 (s, 3H, l), 0.79 (s, 3H, m). ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm) = 166.3, 148.1, 139.2, 138.0, 131.7, 127.6, 126.7, 119.6, 117.6, 101.5, 77.7, 61.2,
48.0, 30.3, 23.1, 22.0, 14.4. HR-MS (ESI +): Calculated for [M-H]$^+$ [C$_{25}$H$_{32}$NO$_6$]$^+$ m/z = 442.2230; found m/z = 442.2224.

Scheme 4.4.2. Diethyl-5-((4-formylbenzyl)amino)isophthalate (Aldehyde 1).

1a (1.8 g, 4.1 mmol) was dissolved in THF (75 mL) and HCl (5 mL conc. HCl in 25 mL water) was added. The reaction mixture was refluxed for 16 h. After cooling down to room temperature, sodium bicarbonate was added until no further CO$_2$ evolution was observed. The organic solvent was removed under reduced pressure and the aqueous residue extracted with ethyl acetate. After drying over anhydrous MgSO$_4$ the solvent was removed under reduced pressure and the resulting solid was washed with methanol to yield a white crystalline powder. Yield: 1.2 g, 83%. Mp: 112-116 °C. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) δ (ppm) = 10.00 (s, 1H, i), 8.05 (s, 1H, c), 7.88 (d, J = 8.0 Hz, 2H, h), 7.55 (d, J = 8.0 Hz, 2H, g), 7.48 (s, 2H, d), 4.52 (s, 2H, f), 4.36 (q, 4H, J = 7.2 Hz, b), 1.38 (t, 6H, J = 7.2 Hz, a). $^{13}$C NMR (125 MHz, CDCl$_3$, 298 K) δ (ppm) = 191.9, 166.2, 147.8, 145.8, 135.8, 131.9, 130.3, 127.9, 120.0, 117.7, 61.3, 47.9, 14.4. HR-MS (ESI +): Calculated for [M-H]$^+$ [C$_{20}$H$_{22}$NO$_5$]$^+$ m/z = 356.1498; found m/z = 356.1500.

To a solution of aldehyde 1 (200 mg, 0.56 mmol) in dry, degassed dichloromethane (50 mL) was added tetrafluoroboric acid diethyl ether complex (76.6 µL, 0.56 mmol). After stirring for 30 min at room temperature, dibenzo-24-crown-8 ether (1.01 g, 2.24 mmol) was added and the solution stirred for and additional 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (39.0 µL, 0.56 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (7.5 µL) was added. After 2 h of stirring at room temperature, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 96 mg, 0.42 mmol) was added. After heating at 40 °C for 2 h, the reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude product was washed with hot toluene (100 mL),
dissolved in dichloromethane (50 mL), and washed with saturated sodium bicarbonate solution (50 mL). Further purification by flash column chromatography (SiO₂, dichloromethane/methanol 95:5 v/v, Rₚ = 0.45) followed by recrystallization from acetonitrile/diisopropyl ether gave pure green crystals of the desired product in the form of its tetrafluoroborate salt. Yield: 85 mg, 18%. Mp: 207 °C (decomp). ¹H NMR for [5R1-H₆][BF₄]₆ (500 MHz, CD₂Cl₂, 298 K) δ (ppm) = 9.87 (b, 8H), 8.81 (s, 8H), 8.80 (d, 8H, J = 7.6 Hz), 8.55 (s, 8H), 8.33 (s, 4H), 8.32 (d, 8H, J = 7.6 Hz), 6.72 (s, 32H), 5.95-5.92 (m, 8H), 4.44 (q, 16H, J = 7.0 Hz), 4.23 (b, 32H), 4.18 (d, 16H, J = 9.1 Hz), 4.00 (d, 16H, J = 9.1 Hz), 3.85-3.80 (b, 32H), 1.47 (t, 24H, J = 7.0 Hz), -2.78 (s, 4H). ¹³C NMR (125 MHz, CD₂Cl₂, 298 K) δ (ppm) = 164.4, 147.6, 146.2 139.9, 139.5, 136.1, 134.5, 132.6, 131.1, 130.4, 129.1, 128.0, 123.1, 121.8, 112.5, 71.4, 70.9, 68.6, 624, 54.3, 53.8, 53.6, 53.4, 14.6. HR-MS (ESI +): Calculated for [M-H₄]⁴⁺ [C₁₉₂H₂₂₂N₈O₄₈]⁴⁺ m/z = 852.3810; found m/z = 852.3811. IR (cm⁻¹): 3392.9, 3313.8, 3067.4, 2917.6, 2872.3, 1713.5, 1593.7, 1503.3, 1451.6, 1368.5, 1350.8, 1231.8, 1104.5, 1051.2, 1024.2, 950.0, 856.0, 801.8, 757.6, 671.4. UV-Vis (CH₂Cl₂, λₛₑᵣ) = 420 (Soret), 519, 556, 595, 650
Scheme 4.4.4. 5,10,15,20-Tetrakis(4-(diethyl-N-(3,5-aminomethylisophtalate)-phenyl)porphyrin (P1)

To a solution of aldehyde 1 (355 mg, 1.0 mmol) in dry, degassed dichloromethane (100 mL) and protected from light was added freshly distilled pyrrole (69.4 µL, 1.0 mmol). After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (12.6 µL) was added. After 6 h of stirring at room temperature more boron trifluoride diethyl etherate (20.0 µL) was added and let stir at room temperature overnight. Then, DDQ (170 mg, 0.75 mmol) was added and stirred at room temperature for 4 h followed by removal of the solvent under reduced pressure. The crude mixture was then purified via column chromatography (Al₂O₃, dichloromethane/methanol 100:1 v/v). The fluorescent red band was collected and the solvent removed under reduced pressure. The
crude product was then purified via column chromatography (SiO$_2$, dichloromethane/methanol 100:1 v/v, $R_f$ = 0.26) to yield a red solid (105 mg, 26%). Mp: 228 °C (decomp). $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ (ppm) = 8.85 (s, 8H, b), 8.15 (d, $J$ = 7.7 Hz, 8H, c), 8.06 (t, $J$ = 1.4 Hz, 4H, h), 7.7 (d, $J$ = 7.7 Hz, 8H, d), 7.68 (d, $J$ = 1.4 Hz, 8H, g), 4.77 (b, 4H, f), 4.70 (s, 8H, e), 4.41 (q, $J$ = 7.1 Hz, 16H, i), 1.43 (t, $J$ = 7.1 Hz, 24H, j), -2.82 (s, 2H, a). $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ (ppm) = 166.5, 148.9, 141.5, 138.8, 135.2, 132.4, 126.3, 120.3, 119.6, 117.9, 61.6, 48.4, 14.6. HR-MS (ESI +): Calculated for [M-H]$^+$ [C$_{96}$H$_{91}$N$_8$O$_{16}$]$^+$ m/z = 1612.6586; found m/z = 1612.6616. IR (cm$^{-1}$): 3390.3, 3314.0, 2977.9, 2929.2, 2901.2, 2869.2, 2848.4, 1708.2, 1599.2, 1507.5, 1452.7, 1394.7, 1227.8, 1125.7, 1092.4, 1024.1, 966.7, 860.2, 796.1, 754.6 671.3. UV-Vis (CH$_2$Cl$_2$, $\lambda_{nm}$) = 419 (Soret), 515, 550, 590, 646.

**Scheme 4.4.5.** Diethyl-3,5-carboxyphenylaniline (2a).

3,5-Dibromoaniline (0.50 g, 2.0 mmol) and 4-(ethoxycarbonyl)phenylboronic acid (0.97 g, 5.0 mmol) were added to a Schlenk flask under N$_2$ atmosphere. Degassed THF (100 mL) and degassed Na$_2$CO$_3$ solution (2 M, 50 mL) were added and the reaction mixture stirred for 10 min. Tetrakis(triphenylphosphine)palladium (230 mg, 0.2 mmol) was added and the reaction mixture refluxed at 80 °C for 3 days. After cooling to room temperature, the organic fraction was isolated and the aqueous fraction was extracted.
with ethyl acetate (2 x 50 mL). All the organic fractions were combined, washed with water (2 x 50 mL) and brine (50 mL), and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product recrystallized from CH₃CN to yield a pale yellow solid (0.64 g, 82%). Mp: 175-177 °C. ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 8.12 (d, 2H, J = 8.4 Hz, c), 7.68 (d, 2H, J = 8.4 Hz, d), 7.23 (s, 1H, e), 6.95 (s, 2H, f), 4.40 (q, 4H, J = 7.1 Hz, b), 3.94 (b, 2H, g), 1.42 (t, 6H, J = 7.1 Hz, a). ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm) = 166.6, 147.5, 145.6, 142.1, 130.2, 129.6, 127.2, 117.1, 113.7, 61.1, 14.5. HR-MS (ESI +): Calculated for [M-H]⁺ [C₂₄H₂₄NO₄]⁺ m/z = 390.1705; found m/z = 390.1711.

Scheme 4.4.6. Diethyl 5'-((4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)amino)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (2b).

To a solution of 2a (1.10 g, 2.8 mmol) and 4-(5,5-dimethyl-1,3-dioxan-2-yl)-benzaldehyde (0.62 g, 2.8 mmol) in dichloroethane (25 mL), under N₂, was added sodium triacetoxyborohydride (0.90 g, 4.2 mmol). The solution was stirred overnight and
quenched with saturated sodium bicarbonate solution. The organic phase was isolated and washed with water (2 x 50 mL) and brine (10 mL), dried over MgSO₄, and the solvent removed under reduced pressure. The crude product was used for the next reaction without further purification. Mp: 144-148 °C. ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 8.08 (d, 4H, J = 8.2 Hz, c), 7.61 (d, 4H, J = 7.7 Hz, d), 7.50 (d, 2H, J = 8.1 Hz, j), 7.42 (d, 2H, J = 8.1 Hz, i), 7.20 (s, 1H, e), 6.91 (s, 2H, f), 5.39 (s, 1H, g), 4.46 (s, 2H, h), 4.40 (q, 6H, J = 7.1 Hz, b), 3.76 (d, 2H, J = 10.9 Hz, l,m), 3.64 (d, 2H, J = 10.9 Hz, l,m), 1.41 (t, 6H, J = 7.1 Hz, a), 1.29 (s, 3H, n), 0.80 (s, 3H, o). ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm) = 166.6, 145.8, 142.0, 139.2, 138.1, 130.1, 129.5, 127.7, 127.2, 126.7, 116.7, 112.1, 101.6, 77.8, 61.1, 48.6, 30.3, 23.1, 22.0, 14.5. HR-MS (ESI +): Calculated for [M-H]⁺ [C₃₇H₄₀N O₆]⁺ m/z = 594.2856; found m/z = 594.2866.

Scheme 4.4.7. Diethyl 5′-((4-formylbenzyl)amino)-[1,1′:3′,1″-terphenyl]-4,4″-dicarboxylate (Aldehyde 2).

2b (1.1 g, 1.8 mmol) was dissolved in THF (60 mL) and HCl (5 mL conc. HCl in 30 mL water) was added. The reaction mixture was refluxed overnight. After cooling to room temperature, sodium bicarbonate was added until no further CO₂ evolution was
observed. The organic solvent was removed under reduced pressure and the aqueous residue extracted with ethyl acetate. After drying over anhydrous MgSO₄ the solvent was removed under reduced pressure and the resulting solid was washed with methanol to yield a pale yellow solid (770 mg, 82%). Mp: 144-147 °C. ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 10.00 (s, 1H, k), 8.08 (d, 4H, J = 8.2 Hz, c), 7.87 (d, 2H, J = 8.0 Hz, j), 7.59 (m, 6H, d,i), 7.22 (s, 1H, e), 6.88 (s, 2H, f), 4.57 (s, 2H, h), 4.39 (q, 4H, J = 7.1 Hz, b), 1.41 (t, 6H, J = 7.1 Hz, a). ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm) = 191.9, 166.5, 148.6, 146.5, 145.7, 142.0, 135.7, 130.3, 130.1, 129.5, 127.8, 127.1, 116.4, 111.5, 61.1, 48.0, 14.4. HR-MS (ESI +): Calculated for [M-H]+ [C₃₂H₃₀NO₅]⁺ m/z = 508.2124; found m/z = 508.2131.


To a solution of aldehyde 2 (250 mg, 0.5 mmol) in dry, degassed dichloromethane (50 mL) was added tetrafluoroboric acid diethyl ether complex (67 µL, 0.5 mmol). After
stirring for 30 min at room temperature, dibenzo-24-crown-8 ether (442 mg, 1.0 mmol) was added and the solution stirred for additional 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (34.0 µL, 0.5 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (15 µL) was added. After 3 h of stirring at room temperature, DDQ (85 mg, 0.38 mmol) was added and the reaction mixture stirred for a further 2 h. After removal of the solvent under reduced pressure, the crude mixture was purified via column chromatography (Al₂O₃, dichloromethane/methanol 100:2.5 v/v). The fluorescent red band was collected and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO₂, dichloromethane/methanol 100:2.5 v/v, Rf = 0.32), neutralized with triethylamine, washed several times with hot acetonitrile, and recrystallized from toluene to give bright red crystals. Yield: 150 mg, 30%. Mp: 210 °C (decomp). ¹H NMR for (500 MHz, CDCl₃, 298 K) δ (ppm) = 8.73 (s, 8H, b), 7.99-7.96 (m, 32H, c,d,j), 7.69 (d, J = 8.4 Hz, 16H, i), 7.48 (s, 8H, g), 7.14 (s, 4H, h), 7.70 (s, 4H), 6.68 (m, 32H, m,n), 6.17 (t, J = 3.8 Hz, 4H, f), 5.32 (d, J = 3.8 Hz, 8H, e) 4.40 (q, J = 7.1 Hz, 16H, k), 4.23 (m, 32H, o), 3.85 (m, 32H, p), 3.51 (m, 32H, q,r), 1.47 (t, J = 7.1 Hz, 24H, l), -2.78 (s, 2H, a). HR-MS (ESI +): Calculated for [M-H₄]⁴⁺ [C₂₄₀H₂₅₄N₈O₄₈]⁴⁺ m/z = 1004.4437; found m/z = 1004.4454. IR (cm⁻¹): 3385.8, 3308.7, 3061.4, 2959.5, 2922.0, 2869.8, 1708.5, 1594.2, 1502.3, 1451.4, 1397.3, 1366.0, 1252.5, 1213.8, 1181.2, 1099.4, 1050.6, 1017.7, 948.8, 930.4, 851.7, 800.6, 770.6, 738.2, 702.9, 599.4, 497.7. UV-Vis (CH₂Cl₂, λmax) = 419 (Soret), 517, 552, 591, 647.
Scheme 4.4.9. 4-Bromo-N-(4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)-3,5-dimethylaniline (3a).

4-Bromo-3,5-dimethylaniline (400 mg, 2.0 mmol) and 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (463 mg, 2.1 mmol) were dissolved in chloroform and MgSO₄ was added to make a slurry. After stirring at RT for 48 h, the reaction mixture was filtered and the solvent removed under reduced pressure. The resultant solid was then dissolved in THF:ethanol (1:1, 40 mL), sodium borohydride (227 mg, 6.0 mmol) was added portion-wise and the reaction mixture was stirred overnight at room temperature. After removal of the solvents under reduced pressure, the crude mixture was dissolved in ethyl acetate and washed with water and brine. The organic phase was dried over MgSO₄ and the solvent removed under reduced pressure to yield a yellow oil. Yield: 710 mg, 88%.

$^{1}$H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 7.55 (d, 2H, J = 8.0 Hz, f), 7.37 (d, 2H, J = 8.0 Hz, e), 6.37 (s, 2H, b), 5.43 (s, 1H, c), 4.27, (s, 2H, d), 3.83 (d, 2H, J = 10.9 Hz, h,i), 3.70 (d, 2H, J = 10.9 Hz, h,i), 2.36 (s, 6H, a), 1.36 (s, 3H, j), 0.85 (s, 3H, k).

$^{13}$C NMR (125 MHz, CDCl₃, 298 K) δ (ppm) = 146.7, 140.0, 138.5, 137.5, 127.1, 126.6, 114.7, 112.8, 101.5, 77.6, 47.8, 30.2, 24.0, 23.0, 21.8. HR-MS (ESI +): Calculated for [M-H]$^+$ [C₂₁H₂₇BrNO₂]$^+$ m/z = 404.1223; found m/z = 404.1225.
Scheme 4.4.10. Methyl 4'-((4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)amino)-2',6'-dimethyl-[1,1'-biphenyl]-4-carboxylate (3b).

To a solution of 3a (717 mg, 1.8 mmol) in degassed DMF (10 mL) cesium carbonate (722 mg, 2.2 mmol), 4-(methoxycarbonyl)phenylboronic acid (399 mg, 2.2 mmol), and tetrakis(triphenylphosphine) palladium (205 mg, 0.2 mmol) were added. The reaction mixture was heated at 110 °C for 48 h. After cooling the mixture, it was partitioned between water (100 mL) and ethyl acetate (100 mL). The organic phase was then washed with more water and brine, and dried over MgSO₄. The crude product was purified by column chromatography (SiO₂, hexanes/ethyl acetate 10:1 v/v, Rₜ = 0.32) to yield a white powder (490 mg, 60%). Mp: 101-104 °C. ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 8.07 (d, 2H, J = 8.3 Hz, b), 7.51 (d, 2H, J = 8.1 Hz, i), 7.41 (d, 2H, J = 8.1 Hz, c), 7.24, (d, 2H, 8.3 Hz, h), 6.39 (s, 2H, e), 5.41 (s, 1H, f), 4.35 (s, 2H, g), 3.94 (s, 3H, a), 3.79 (d, 2H, J = 10.7 Hz, k,j), 3.68 (d, 2H, J = 10.7 Hz, k,j), 1.94 (s, 6H, d), 1.31 (s, 3H, m), 0.81 (s, 3H, n). ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm) = 167.4, 147.4, 146.8, 140.4, 137.7, 136.8, 130.7, 130.3, 129.7, 128.2, 127.5, 126.6, 111.9,101.7, 77.8, 52.2, 48.2, 30.4, 23.2, 22.0, 21.2. HR-MS (ESI +): Calculated for [M-H]⁺ [C₂₉H₃₄NO₄]⁺ m/z = 460.2483; found m/z = 460.2488. NOTE: The ethyl ester was also prepared and used for some of the reactions.
**Scheme 4.4.11.** Methyl 4'-((4-formylbenzyl)amino)-2',6'-dimethyl-[1,1'-biphenyl]-4-carboxylate (Aldehyde 3).

3b (850 mg, 1.7 mmol) was dissolved in THF and HCl (3 mL in 10 mL of water) was added. After refluxing the reaction mixture for 12 h, sodium bicarbonate was added until no CO₂ evolution was observed. The organic solvent was removed under reduced pressure and ethyl acetate was added to the aqueous phase. The organic phase was washed with water and brine, dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was washed with cold methanol to yield an off-white solid (572 mg, 57%). Mp: 250 °C (decomp). ¹H NMR (500 MHz, CDCl₃, 298 K) δ (ppm) = 10.01 (s, 1H, j), 8.05 (d, J = 8.5 Hz, 2H, b), 7.87 (d, J = 8.3 Hz, 2H, i), 7.56 (d, J = 8.1 Hz, 2H, h), 7.21 (d, J = 8.5 Hz, 2H, c), 6.38 (s, 2H, e), 4.46 (s, 2H, g), 3.93 (s, 3H, a), 2.04 (s, 6H, d). ¹³C NMR (125 MHz, CDCl₃, 298 K) δ (ppm) = 192.2, 147.2, 147.0, 146.6, 136.9, 135.6, 131.9, 130.3, 130.2, 129.7, 128.3, 127.8, 115.4, 112.0, 52.3, 48.1, 21.1. HR-MS (ESI +): Calculated for [M-H]⁺ [C₂₄H₂₄NO₃]⁺ m/z = 374.1755; found m/z = 374.1756.

To a solution of 3c (230 mg, 0.6 mmol) in dry, degassed dichloromethane (65 mL) was added tetrafluoroboric acid diethyl ether complex (84 µL, 0.6 mmol). After stirring for 30 min at room temperature, dibenzo-24-crown-8 ether (1.105 g, 2.5 mmol) was added and the solution stirred for an additional 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (42.7 µL, 0.6 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (15 µL) was added. After 4 h of stirring at room temperature, DDQ (105 mg) was added and the reaction mixture stirred for a further 2 h. The solvent removed under reduced pressure and the crude mixture was then purified via column chromatography (Al₂O₃, dichloromethane/ methanol 100:2 v/v). The fluorescent red band was collected and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO₂, dichloromethane/methanol 100:3 v/v, Rₜ = 0.44). After removal of
the solvent under reduced pressure, the product was neutralised with triethylamine, washed several times with hot acetonitrile, and recrystallized from toluene to give bright red crystals. Yield: 180 mg, 33%. Mp: 221 °C (decomp). $^1$H NMR [5R3-H$_6$][BF$_4$]$_6$ (500 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ (ppm) = 9.60 (bs, 8H, f), 8.80 (s, 8H, b), 8.78 (d, $J = 7.8$ Hz, 8H, c), 8.30 (d, $J = 7.8$ Hz, 8H, d), 8.13 (d, $J = 8.1$ Hz, 8H, j), 7.34 (s, 8H, g), 7.05 (d, $J = 8.1$ Hz, 8H, i), 6.86 (m, 32 H, m,n), 5.88 (m, 8H, e), 4.41 (q, $J = 7.1$ Hz, 16H, k), 4.30 (m, 32H, p), 4.19 (m, 16H, q), 3.98 (m, 16H, r), 3.72 (m, 32H, o), 1.84 (s, 24H, h), 1.43 (t, $J = 7.1$ Hz, 24H, I), -2.77 (s, 4H, a). HR-MS (ESI +): Calculated for [M-H$_4$]$^{1+}$ [C$_{208}$H$_{230}$N$_8$O$_{40}$]$^{4+}$ $m/z =$; found $m/z = 870.4069$. IR (cm$^{-1}$): 3512.6, 3126.2, 3053.8, 2918.5, 2877.2, 1715.1, 1609.0, 1592.2, 1566.6, 1503.6, 1453.4, 1436.7, 1415.0, 1352.9, 1285.2, 1248.7, 1208.0, 1093.5, 1049.6, 1004.8, 985.8, 947.3, 915.1, 858.9, 822.4, 776.8, 742.0 712.1, 598.9, 580.2, 518.5. UV-Vis (CH$_2$Cl$_2$, $\lambda_{nm}$) = 423 (Soret), 518, 555, 592, 650, 734

**Scheme 4.4.13.** N-(4-(5,5-dimethyl-1,3-dioxan-2-yl)benzyl)-4-tritylaniline (4a).

4-Tritylaniline (335 mg, 1.0 mmol) and 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (220 mg, 1.0 mmol) were dissolved in chloroform and MgSO$_4$ was added to make a slurry. After stirring at RT for 48 h, the reaction mixture was filtered and the solvent removed under reduced pressure. The resultant solid was then dissolved in
THF: ethanol (1:1, 40 mL), sodium borohydride (114 mg, 3.0 mmol) was added portion-wise and the reaction mixture was stirred at room temperature for 48 h. After removal of the solvents under reduced pressure, the crude mixture was dissolved in ethyl acetate, washed with water and brine. The organic phase was dried over MgSO₄ and the solvent removed under reduced pressure to yield a beige fluffy powder (400 mg, 74%). Mp: 160-164 °C. \(^1\)H NMR (500 MHz, CD₂Cl₂, 298 K) \(\delta \) (ppm) = 7.50 (d, 2H, \(J = 8.1 \) Hz, i), 7.40 (d, 2H, \(J = 8.1 \) Hz, h), 7.32-7.18 (m, 15H, a-c), 7.03 (d, 2H, \(J = 8.8 \) Hz, e), 6.54 (d, 2H, \(J = 8.8 \) Hz, d), 4.32 (s, 2H, g), 4.17 (s, 1H, f), 3.78 (d, 2H, \(J = 11.1 \) Hz, j,k), 3.68 (d, 2H, \(J = 10.5 \) Hz, j,k), 1.30 (s, 3H, m), 0.82 (s, 3H, n). \(^{13}\)C NMR (125 MHz, CDCl₃, 298 K) \(\delta \) (ppm) = 147.8, 146.5, 140.7, 138.3, 136.1, 132.2, 131.3, 127.8, 127.6, 126.8, 126.0, 112.1, 101.8, 77.9, 64.6, 48.4, 30.4, 23.2, 22.0. HR-MS (ESI +): Calculated for [M-H]+ \([C_{38}H_{38}NO_{2}]^+\) \(m/z\) = 540.2903; found \(m/z\) = 540.2905.

Scheme 4.4.14. 4-(((4-Tritylphenyl)amino)methyl)benzaldehyde (Aldehyde 4).

4a (400 mg, 0.7 mmol) was dissolved in THF and HCl (3 mL in 10 mL of water) was added. After refluxing the reaction mixture for 12 h, NaHCO₃ was added until no CO₂ evolution was observed. The organic solvent was removed under reduced pressure and ethyl acetate was added to the aqueous phase. The organic phase was washed with water and brine, dried over MgSO₄ and the solvent was removed under reduced pressure.
The crude product was washed with cold methanol to yield an off-white solid (310 mg, 92%). Mp: 196-198 °C. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ (ppm) = 9.99 (s, 1H, j), 7.86 (d, $J = 8.2$ Hz, 2H, i), 7.57 (d, $J = 8.0$ Hz, 2H, h), 7.25-7.17 (m, 15H, a-c), 7.00 (d, $J = 8.8$ Hz, 2H, e), 6.50 (d, $J = 8.8$ Hz, 2H, d), 4.43 (s, 2H, g), 3.44 (s, 1H, f). $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ (ppm) = 192.1, 147.8, 147.5, 146.1, 136.5, 132.2, 131.3, 130.3, 128.1, 127.8, 127.3, 126.1, 112.2, 48.4. HR-MS (ESI +): Calculated for [M-H]$^+$ [C$_{33}$H$_{28}$NO]$^+$ $m/z = 454.2171$; found $m/z = 454.2161$.


To a solution of aldehyde 4 (453 mg, 1.0 mmol) in dry, degassed dichloromethane (100 mL) was added tetrafluoroboric acid diethyl ether complex (161.0 µL, 1.0 mmol). After stirring for 30 min at room temperature, dibenzo-24-crown-8 ether (897 mg, 2.0 mmol) was added and the solution stirred for an additional 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (69.4 µL, 1.0 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (40 µL)
was added. After 3 h of stirring at room temperature, DDQ (170 mg, 0.8 mmol) was added and the reaction mixture stirred for a further 2 h. The solvent removed under reduced pressure and the crude mixture was then purified via column chromatography (Al₂O₃, dichloromethane/methanol 100:5 v/v). The fluorescent red band was collected and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO₂, dichloromethane/methanol 100:5 v/v, Rf = 0.74). The crude product was then neutralised with triethylamine, washed several times with hot acetonitrile, and recrystallized from toluene to give bright red crystals. Yield: 155 mg, 16%. Mp: 255 °C (decomp). The acquisition of ¹H NMR spectrum where individual peaks could be resolved was not possible due to aggregation of the sample. Spectra roughly matching the total number of protons on this molecule were collected in different solvents and at different temperatures without significant improvement of the resolution. The acquisition of a ¹³C NMR spectrum with reasonable S/N from which individual carbon assignments could be made was not possible due to the limited solubility and aggregation phenomena of this material in common organic solvents. HR-MS (ESI): Calculated for [M-H₄]⁴⁺ [C₂₄H₂₄₆N₈O₃₂]⁴⁺ m/z = 950.4484; found m/z = 950.4498. IR (cm⁻¹): 3636.6, 3562.6, 3058.4, 3032.9, 2924.3, 2877.6, 1593.8, 1503.6, 1450.2, 1353.9, 1323.8, 1288.4, 1249.9, 1209.0, 1051.6, 948.0, 851.6, 746.3, 702.2, 629.2, 599.7, 550.3, 520.4, 498.8. UV-Vis (CH₂Cl₂, λₑm) = 423 (Soret), 443 (Soret), 519, 552, 652, 732.
Scheme 4.4.16. 4-(4,7-Bis(4-(tert-butyl)phenyl)-1H-benzo[d]imidazol-2-yl)benzaldehyde (Aldehyde 5).

1,2-Diamino-3,6-di(4′-t-butylphenyl)-benzene (350 mg, 0.1 mmol) and terephthalaldehyde (626 mg, 0.5 mmol) were dissolved in acetonitrile/chloroform (125 mL/25 mL) and ZrCl$_4$ (22 mg, 0.01 mmol) was added. The mixture was stirred at room temperature for 24 h and filtered. The solvents were removed under reduced pressure and the crude product was dissolved in ether. HCl•Et$_2$O (0.250 mL, 2 M) was added and the precipitate was filtered. After an anion exchange reaction with HBF$_4$, the product was isolated as a yellow powder. Yield: 300 mg, 62%. Mp: 196-200 °C. $^1$H NMR (500 MHz, CD$_3$CN, 298 K) δ (ppm) = 10.05 (s, 1H), 8.35 (d, $J$ = 8.3 Hz, 2H), 8.02 (d, $J$ = 8.4 Hz, 2H), 7.89 (d, $J$ = 8.2 Hz, 4H), 7.59 (d, $J$ = 8.4 Hz, 4H), 7.45 (s, 2H), 1.40 (s, 18H). $^{13}$C NMR (75 MHz, DMSO-$d_6$, 298 K) δ (ppm) = 192.8, 150.9, 150.3, 137.4, 135.1, 134.2, 132.5, 129.6, 129.1, 128.5, 127.5, 125.6, 124.1, 34.5, 31.2. HR-MS (ESI +): Calculated for [M-H]$^+$ [C$_{34}$H$_{35}$N$_2$O$]^+$ m/z = 487.2744; found m/z = 487.2745.
Scheme 4.4.17. [5]Rotaxane 5R5

To a solution of [Aldehyde 5][HBF₄] (150 mg, 0.3 mmol) in dry, degassed dichloromethane (30 mL) was added dibenzo-24-crown-8 ether (184 mg, 0.4 mmol) and the solution stirred for 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (19.0 µL, 0.3 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (15 µL) was added. After 4 h of stirring at room temperature, DDQ (45 mg, 0.2 mmol) was added and the reaction mixture stirred for a further 2 h. The solvent removed under reduced pressure and the crude mixture was then purified via column chromatography (Al₂O₃, dichloromethane/methanol 100:3 ν/ν). The fluorescent red band was collected and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO₂,
dichloromethane/methanol 95:3 v/v, \( R_f = 0.24 \)). The crude product was then neutralised with triethylamine, washed several times with hot acetonitrile, and recrystallized from toluene to give bright red crystals. Yield: 45 mg, 18%. Mp: 245 °C (decomp). \(^1\)H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) \( \delta \) (ppm) = 11.90 (s, 4H), 9.61 (d, \( J = 8.1 \) Hz, 8H), 9.04 (s, 8H), 8.48 (d, \( J = 8.5 \) Hz , 8H), 8.24 (d, \( J = 8.3 \) Hz , 8H), 7.62 (d, \( J = 7.9 \) Hz , 4H), 7.54 (d, \( J = 8.3 \) Hz , 8H), 7.29-7.26 (m, 12H), 7.19 (d, \( J = 8.4 \) Hz , 8H), 6.75 (s, 32H), 4.10-3.99 (m, 32H), 3.76-3.70 (m, 32H), 3.27-3.25 (m, 16H), 3.03-3.01 (m, 16H), 1.26-1.26 (m, 72H), -2.88 (s, 2H). \(^{13}\)C DEPTQ135 NMR (125 MHz, CD$_2$Cl$_2$, 298 K) \( \delta \) (ppm) = 154.1 (n), 150.3 (n), 150.2 (n), 148.7 (n), 143.1 (n), 142.8 (n), 136.5 (n), 136.1 (n), 135.0 (p), 133.8 (n), 130.5 (n), 130.3 (p), 130.2 (n), 129.5 (p), 128.5 (p), 125.8 (p), 125.5 (n), 125.4 (p), 123.6 (p), 121.0 (p), 120.9 (p), 112.0 (p), 69.8 (n), 69.4 (n), 68.6 (n), 34.7 (n), 31.5 (p), 31.5 (p). HR-MS (ESI +): Calculated for [M-H$_4$]$^{4+}$ [C$_{248}$H$_{274}$N$_{12}$O$_{32}$]$^{4+}$ m/z = 983.5057; found m/z = 983.5062. IR (cm$^{-1}$): 3539.9, 3240.7, 3101.5, 2948.9, 2903.5, 2871.1, 1636.3, 1615.5, 1580.0, 1502.5, 1454.8, 1391.5, 1364.4, 1353.0, 1318.9, 1286.7, 1246.3, 1208.5, 1122.3, 1097.4, 1051.2, 948.9, 821.4, 776.7, 740.7, 670.2, 599.7, 562.4, 518.. UV-Vis (CH$_2$Cl$_2$, \( \lambda_{\text{nm}} \)) = 230-320, 436 (Soret), 518, 560, 598, 650, 695.
Figure 4.4.1. Partial $^1$H-$^1$H COSY NMR spectrum of 5R5.
**Figure 4.4.2.** Partial $^1$H-$^1$H TOCSY NMR spectrum of 5R5.
To a solution of 4,7-bis(4-bromophenyl)-2,1,3-benzotriazolate (1.70 g, 3.8 mmol) in THF/Ethanol (1:3, 120 mL) was added sodium borohydride (500 mg, 13.2 mmol) and cobalt(II) chloride (50 mg, 0.2 mmol). The reaction mixture was heated to reflux for 5 h, filtered while hot, and the solvents removed under reduced pressure. The crude product was dissolved in dichloromethane (100 mL) and washed with water (2 x 100 mL) and brine (50 mL), dried over MgSO$_4$, and the solvent removed under reduced pressure to give a white solid. Yield: 1.45 g, 95%. Mp: 200 °C (decomp). $^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta$ (ppm) = 7.60 (d, $J = 8.5$ Hz, 4H, a), 7.36 (d, $J = 8.5$ Hz, 4H, b), 6.73 (s, 2H, c), 3.57 (bs, 4H, d).
To a solution of 1,2-diamino-3,6-bis(4-bromophenyl)benzene (1.45 g, 3.5 mmol) in chloroform (100 mL) was added terephthaldehyde (2.50 g, 18.5 mmol) and zirconium tetrachloride (90 mg, 0.4 mmol). The reaction mixture was stirred at RT for 48 h and filtered. After removal of the solvent under reduced pressure, the crude product was washed with chloroform to give a pale-yellow powder. 1.59 g, 86%. Mp: 175 °C (decomp). $^1$H NMR (500 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 12.94 (bs, 1H, d), 10.08 (s, 1H, g), 8.53 (d, $J = 8.1$ Hz, 2H, f), 8.28-7.86 (b, 4H, b,b’), 8.05 (d, $J = 8.1$ Hz, 2H, e), 7.73 (d, $J = 8.3$ Hz, 4H, a,a’), 7.43 (bs, 2H, c,c’). $^{13}$C NMR (125 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 193.11, 152.1, 151.4, 141.9, 139.7, 137.0, 135.7, 135.0, 132.9, 132.3, 131.8, 131.6, 131.4, 131.3, 131.1, 130.9, 130.8, 129.9, 129.5, 129.0, 128.6, 128.4, 127.9, 127.4, 124.8, 123.8, 121.8, 121.5, 121.1, 120.8. HR-MS (ESI +): Calculated for [M]$^+$ [$C_{26}H_{17}Br_2N_2O]^+ m/z = 532.9682$; found $m/z = 532.9689$.

Scheme 4.4.20. n-Butyl ester 4-carboxyphenyl boronic acid.

4-Carboxyphenyl boronic acid (3.0 g, 18 mmol) was suspended in n-butanol (20 mL) and concentrated hydrochloric acid (0.5 mL) added to the mixture and refluxed for 5 h. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was dissolved in ethyl acetate (100 mL) and washed with water (3 x 50 mL). The organic phase was dried over MgSO$_4$ and the solvent removed under
reduced pressure to give a white powder 3.98 g, Quantitative yield. Mp: 86-89 °C. $^1$H NMR (500 MHz, DMSO-$d_6$, 298 K) δ (ppm): 8.01 (d, $J = 7.9$ Hz, 2H, f), 7.97 (d, $J = 8.1$ Hz, 2H, e), 7.91* (s, 4H), 4.27 (q, $J = 6.4$ Hz, 2H, d), 1.73-1.65* (m, 2H, c), 1.47-1.38* (m, 2H, b), 0.97-0.90* (m, 3H, a). *The integration was done considering the monomer and dimer species. $^{13}$C DEPTQ135 NMR (125 MHz, DMSO-$d_6$, 298 K) δ (ppm): 166.0 (n), 165.9 (n), 134.2 (p), 133.6 (p), 131.0 (n), 130.7 (n), 128.1 (p), 127.9 (p), 64.3 (n), 64.3 (n), 30.3 (n), 18.7 (n), 13.6 (p). The carbon atom attached to the boron could not be observed due to quadrupolar relaxation effects. HR-MS (ESI −): Calculated for [M$^-$ $[C_{11}H_{14}BO_4]$] $m/z = 221.0991$; found $m/z = 221.1021$.


To a solution of 6b (1.40 g, 2.6 mmol) in degassed toluene (50 mL) was added butyl ester 4-carboxyphenyl boronic acid (1.46 g, 6.6 mmol, 2.5 eq), caesium carbonate (2.15 g, 6.6 mmol), and Pd($PPh_3$)$_4$ (300 mg, 0.26 mmol) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was filtered and the product was recrystallized twice from toluene to give a bright yellow powder. Yield: 800 mg, 58%. Mp: 154 °C (decomp). $^1$H NMR (500 MHz, DMSO-$d_6$, 298 K) δ
13.04 (bs, 1H, j), 10.09 (s, 1H, m), 8.58 (d, $J = 8.3$ Hz, 2H, l), 8.50-7.74 (b, 22H, e-i, e′-i′, k), 4.32 (t, $J = 6.4$ Hz, 4H, d), 1.73 (q, $J = 7.8$ Hz, 4H, c), 1.47 (sextet, $J = 7.5$ Hz, 4H, b), 0.97 (t, $J = 7.4$ Hz, 6H, a). $^{13}$C NMR (125 MHz, DMSO-$d_6$, 298 K) δ (ppm): 192.7, 165.6, 144.2, 129.9, 129.8, 129.4, 128.7, 127.9, 126.8, 126.4, 68.0, 64.4, 39.0, 30.3, 18.8, 13.6. Resonances for quaternary carbons could not be observed due to low receptivity.

HR-MS (ESI +): Calculated for [M]$^+$ [C$_{11}$H$_{14}$BO$_4$]$^-$ m/z = 727.3166; found m/z = 727.3172.

Scheme 4.4.22. Pseudorotaxane equilibrium for aldehyde 6 and DB24C8.

The low solubility of aldehyde 6 results in a poorly resolved $^1$H NMR spectrum; however, when a pseudorotaxane is formed, it is possible to resolve all the proton environments. Figure 4.4.3 shows a comparison between the $^1$H NMR spectra of the pure aldehyde and the pseudorotaxane.
Figure 4.4.3. Partial $^1$H NMR spectra for aldehyde 6 (bottom, DMSO-$d_6$) and pseudorotaxane with aldehyde 6 and DB24C8 (top, CD$_2$Cl$_2$).

To a solution of [Aldehyde 6][HBF₄] (450 mg, 0.55 mmol) in dry, degassed dichloromethane (60 mL) was added dibenzo-24-crown-8 ether (279 mg, 0.60 mmol) and the solution stirred for 10 min. The reaction mixture was then protected from light and freshly distilled pyrrole (38.3 µL, 0.55 mmol) added. After stirring for 15 min at room temperature, boron trifluoride diethyl etherate (20 µL) was added. After 2.5 h of stirring at room temperature, DDQ (94 mg, 0.41 mmol) was added and the reaction mixture stirred for a further 2 h. The solvent removed under reduced pressure and the crude mixture was then purified via column chromatography (Al₂O₃,
dichloromethane/methanol 100:2.5 v/v). The fluorescent red band was collected and the solvent removed under reduced pressure. The crude product was then purified via column chromatography (SiO$_2$, dichloromethane/methanol 95:5 v/v, $R_f = 0.63$). After removal of the solvent under reduced pressure and recrystallization from acetonitrile-ethyl ether the product was isolated as a dark red solid. Yield: 295 mg, 39%. Mp: 261 °C (decomp). $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) $\delta$ (ppm) = 11.90 (s, 4H), 9.61 (d, $J = 8.1$ Hz, 8H), 9.04 (s, 8H), 8.48 (d, $J = 8.5$ Hz, 8H), 8.24 (d, $J = 8.3$ Hz, 8H), 7.62 (d, $J = 7.9$ Hz, 4H), 7.54 (d, $J = 8.3$ Hz, 8H), 7.29-7.26 (m, 12H), 7.19 (d, $J = 8.4$ Hz, 8H), 6.75 (s, 32H), 4.10-3.99 (m, 32H), 3.76-3.70 (m, 32H), 3.27-3.25 (m, 16H), 3.03-3.01 (m, 16H), 1.26-1.26 (m, 72H), -2.88 (s, 2H). HR-MS (ESI +): Calculated for [M – 4H]$^{4+}$ [C$_{304}$H$_{304}$N$_{14}$O$_{48}$]$^{4+}$ $m/z = 1223.7932$; found $m/z = 1223.7993$. IR (cm$^{-1}$): 3498.2, 3199.0, 3066.5, 2926.8, 2871.3, 1708.2, 1633.5, 1553.0, 1501.9, 1468.1, 1452.2, 1383.4, 1352.4, 1273.5, 1247.5, 1205.5, 1098.2, 1047.6, 1003.8, 945.8, 820.0, 771.3, 737.1, 700.2, 598.3, 550.8, 518.0, 506.2. UV-Vis (CH$_2$Cl$_2$, $\lambda_{nm}$): 350, 432 (Soret), 521, 561, 606, 654.

4.4.3 Single crystal X-ray diffraction

X-ray data were collected on a Bruker D8 Venture diffractometer, equipped with a PHOTON 100 detector, kappa goniometer, and collected using a Cu high brilliance IµS microfocus source. Crystals were mounted on MiTeGen MicroMounts™ and frozen in paratone oil under a cold stream of N$_2$. Reflection data were integrated using APEX III software.

Even though these [5]rotaxanes tend to crystallize, it was not possible to obtain single crystals of sufficient size for SC-XRD analysis. Samples of some of these crystals
were sent to the Canadian Light Source, but the diffraction was too poor to allow the
determination of their unit cell parameters and structure.

Figure 4.4.4. Optical micrographs of crystals of 5R3 (left) and 5R5 (right).

Crystals of [5R1-H6][BF₄]₆ were grown by slow diffusion of diisopropyl ether
into an acetonitrile solution of the rotaxane. Data was collected for several crystals from
different batches, and the quality of all these data sets is comparable. The BF₄⁻ could not
be refined and are the main source of disorder on this structure. Using Olex2, the
structure was solved with the XT solution program using the Intrinsic Phasing method,
and refined with the XL package using Least Squares minimization. Figures were
created using the Diamond suite.
Table 4.4.1. Crystal data, solution, and refinement parameters for 5R1.

<table>
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</tr>
<tr>
<td>Formula weight (g·mol⁻¹)</td>
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</tr>
<tr>
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<td>25.0888(5)</td>
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<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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<td>2θ range (°)</td>
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<tr>
<td>Unique reflections</td>
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</tr>
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</tr>
<tr>
<td>Restraints</td>
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</tr>
<tr>
<td>Rᵢ [I &gt; 2σ (I)]*</td>
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</tr>
<tr>
<td>R₁ all</td>
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</tr>
<tr>
<td>wR₂ [I &gt; 2σ (I)]*</td>
<td>56.52%</td>
</tr>
<tr>
<td>wR₃ all</td>
<td>62.79%</td>
</tr>
<tr>
<td>GoF on F²</td>
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</tr>
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</table>

\[
R₁ = \frac{\sum|F_{obs} - F_{calc}|}{\sum|F_{obs}|}; \quad wR₂ = \left(\frac{\sum[w|F_{obs}² - F_{calc}²|]}{\sum[wF_{obs}²]}\right)^{1/2}, \quad w = q[σ²(F_{obs})² + (aP)² + bP]^{-1}
\]

4.4.4 UV-Vis Studies

UV-Vis-NIR spectra were recorded on a Varian Cary 50E Spectrometer using a quartz glass cuvette of 10 × 10 mm. Solutions were prepared using solvents containing oxygen and moisture from the atmosphere.

Figure 4.4.5. Comparison of the UV-Vis spectra of 5R1 (orange) and P1 (purple) in DCM.
4.4.5 Mass Spectrometry

High-resolution mass spectrometry experiments were performed on a Waters XEVO G2-XS ToF instrument in electrospray ionization (ESI) or atmospheric solids analysis probe (ASAP) mode. For **5R1**, an additional spectrum was collected using a Waters SYNAPT G2-Si instrument in matrix-assisted laser desorption ionization (MALDI) mode.

![Experimental mass spectrum](image)

**Figure 4.4.6.** Experimental mass spectrum (black) and calculated isotope pattern (red) of **5R1** in MALDI mode, showing the [**5R1**-H]**⁺** molecular ion.
Figure 4.4.7. Experimental mass spectra (black) and calculated isotope pattern (red) of [5]rotaxanes 5R1 – 5R6 showing the $[5\text{R}^{\#}-\text{H}_4]^{4+}$ molecular ion.
4.5 References


N. Noujeim, K. Zhu, V. N. Vukotic and S. J. Loeb, Pseudorotaxanes from T-


Chapter 5. Incorporation of [5]Rotaxanes into Crystalline Materials

5.1 Introduction

With the guidelines for the application of reticular chemistry in mind, we decided to investigate routes for the synthesis of MOFs which incorporate the [5]rotaxanes presented in Chapter 4. In order to do this, we first needed to identify an existing MOF, or crystalline material, where a simple linker could be conceptually substituted for by one of these newly designed molecules. While porphyrinic MOFs have been studied extensively due to their potential catalytic activity, gas capture ability, and even therapeutic properties,1–5 not all these frameworks are stable under the conditions required for: a) fast, unhindered rotation of the macrocyclic crown ethers, or b) acid-base controlled switching of the crown ether conformation. In the first screening process to identify target structures and apply the principles of reticular chemistry, all MOFs constructed utilizing SBUs that decompose under the required conditions were eliminated from the list of candidates.6 After narrowing down the search to only MOFs fabricated with a stable SBU, the next step was to identify potential positions for functionalization of the linkers. The addition of: i) a recognition site for the rotaxane assembly, ii) stopper groups to prevent slippage, and iii) donor groups for the coordination to the SBU are all requirements for successful dynamic linkers. In some cases, these last two functions can be performed by the same substituent. Finally, it is necessary to ensure the synthesis of the designed linkers is feasible and that the stability of the final molecules is enough to withstand solvothermal synthesis conditions.
This chapter will be presented utilizing the conceptual steps described above; each subsection is an iteration in the process towards (potentially) obtaining a MOF with a [5]rotaxane linker. The reader should be aware of the limited success this approach has yielded so far. The scale of each attempted MOF synthesis was limited by the complexity of the [5]rotaxane linkers being used; the amounts of material available were never enough to allow for optimizing any promising synthetic conditions and prevented the use of high-throughput screening methods commonly employed in the reticular synthesis of MOFs.

5.2 Isophthalic octatopic linkers

A reasonable starting point for ligand design is the smallest possible porphyrin linker. Porphyrins with substituents in the \textit{meso} position are relatively easy to synthesize, and the degree of complexity of the substituent arms can be varied without altering the condensation step to obtain the porphyrin macrocycle. A porphyrin previously shown in this work (\textit{Chapters} 2 and 3), \textit{meso}-tetrakis(4-carboxyphenyl)porphyrin (TCPP), is one of the simplest \textit{meso}-substituted macrocycles. In order to install a recognition site, stopper groups, and have enough space to incorporate a crown ether in this molecule, it is necessary to extend the structure by the addition of at least one phenyl group. This results in \textit{meso}-tetrakis(4-carboxybiphenyl)porphyrin (TCBPP, \textbf{Scheme 5.2.1}), but this porphyrin would require additional structural modifications to accommodate the recognition site and stopper groups. In order to incorporate tetra-substituted porphyrin linkers into a MOF, the coordinating group has to be unhindered and able to coordinate to the SBU. One way to do this would be to design a TCBPP-like molecule and install stopper groups to prevent the slippage of the macrocyclic crown ether (positions, 3,5- of
the outermost phenyl ring), however this would result in an inability to coordinate to an SBU due to steric crowding. An alternative approach would be to make the coordinating group double as a stopper group, i.e. installing the carboxylate groups in the 3,5-positions instead of in the 4-position. There are examples in the literature showing the incorporation of porphyrin linkers with this substitution pattern into MOFs. In particular, *meso*-tetrakis(3,5-dicarboxyphenyl)porphyrin (TDCPP) and *meso*-tetrakis(3,5-dicarboxybiphenyl)porphyrin (TDCBPP, **Scheme 5.2.1**) produce the highly porous MOFs MMPF-2\(^7\) (MMPF: metal-metalloporphyrin framework) and MMPF-9\(^8\) (**Figure 5.2.1**) when combined with a cobalt trigonal SBU or a copper paddlewheel, respectively. TDCPP also forms MOFs with rare-earth metals, gallium, indium, iron, manganese, and sodium SBUs.\(^9,10\) Ultimately, taking TDCBPP and installing an aniline/anilinium recognition site between the two phenyl rings gives the porphyrin-based [5]rotaxane linker we hope to incorporate into a MOF (see **Scheme 5.2.2**).

**Scheme 5.2.1.** TCBPP, TDCPP, TDCBPP porphyrinic linkers.
Figure 5.2.1. Augmented representations of MMPF-2 (left) and MMPF-9 MOFs (right). Colour code: Porphyrin linker in red and yellow, Co₃O SBU in blue, Cu paddlewheels in green.

The rotaxane linker 5R₁-OA is shown in Scheme 5.2.2 and the synthetic procedure followed to make it can be found in Chapter 4. The ester groups were hydrolyzed to obtain 5R₁-OA and allow the coordination to metal centres of an SBU.

Scheme 5.2.2. Rotaxane linker 5R₁-OA (octa-acid).

Following the reported synthetic procedure for MMPF-9,⁸ 5R₁-OA was combined with copper nitrate and acetic acid in DMF, and heated in a programmable oven at
temperatures between 75 and 120 °C for varying periods of time. Other metal sources like zinc and indium were also tested based on the potential of the linker to form SBUs with these metals; however, the original Co$_3$O cluster was not targeted due to its limited stability. After several unsuccessful attempts at MOF synthesis, molecular modelling simulations were performed using the crystallographic data available for MMPF-9 (See Experimental Section for details). These studies showed that the addition of crown ethers in the vicinity of the isophthalic group causes a very crowded region around the SBU (Figure 5.2.2), potentially preventing the MOF from forming as designed.

Figure 5.2.2. Molecular mechanics modelling of the target MOF with 5R1-OA. The DB24C8 rings are shown in space filling model and it can be seen how two rings are superimposed, making the structure unviable.
After these findings, no further efforts to screen synthetic conditions for the incorporation of 5R1-OA into a MOF were conducted. If a less bulky crown ether ring (e.g. 24C8, 22C6) is used during the synthesis, the steric hindrance problem might be solved, but in the process the switching potential of the linker is also lost.

5.3 **Extended isophthalic-like octatopic linkers**

Elongation of the linkers is a common tool used in reticular synthesis. The use of a linker where instead of a diisophthalic motif, two 4-carboxyphenyl groups are installed has been successfully implemented by Eddaoudi,\textsuperscript{11,12} Zhang,\textsuperscript{13} and also by our research group.\textsuperscript{14} The new linker designed after the first iteration of this process can be seen in Scheme 5.3.1. This molecule has the same shape as meso-tetrakis{3,5-bis[(4-carboxy)phenyl]}porphyrin (TBCPPP), used by Zhang and coworkers to make UNLPF-1\textsuperscript{13} and -10\textsuperscript{15} (University of Nebraska-Lincoln Porous Framework, Figure 5.3.1), so we were hopeful about incorporating into a material isostructural with these MOFs.
Figure 5.3.1. A) TBCPPP linker, B) Augmented representation of TBCPPP, C) UNLPF-1, with zinc paddlewheels shown in teal, D) UNLPF-10, with indium SBU's shown in gray.
Inclusion of octatopic linkers, especially porphyrins, into MOFs can be problematic due to the tendency of these ligands to precipitate before the self-assembly process is complete. To remedy this issue, Goldberg\textsuperscript{9,16} developed a two-step synthetic procedure that takes this phenomenon into account. After the precipitation occurs, sodium hydroxide is added as a modulator; this addition allows dissolution of the precipitate and slows down the rate of formation of the coordination polymer, thus providing a better self-healing process resulting in MOF formation with increased crystallite size. Unfortunately, even using this approach, only amorphous material could be isolated from the solvothermal reactions between 5R2-OA and various metal salts. It should be noted that the addition of crown ethers drastically influences the solubility of the porphyrins; non-interlocked porphyrins usually require acidic conditions, high-polarity solvents, and high temperatures to be completely dissolved, while the [5]rotaxane linkers might be too soluble, making the crystallization process unfavourable.
5.4 Extended tetratopic linkers

Due to the unsuccessful attempts at fabricating a MOF with the octa-acid linkers, and the interest in obtaining an acid-base stable MOF, we turned our attention to a family of zirconium based MOFs. The MOFs with a Zr$_6$ cluster (UiO-66 family), first reported by Lillerud and colleagues,$^{17}$ are known for their robustness and good stability in pH ranges from 1 to 12.$^6,18$ Yaghi and collaborators reported the synthesis of two zirconium MOFs using TCPP as a linker, namely MOF-525 and MOF-545, with ftw or csq topology respectively. The number of equivalents of porphyrin used determines which topology is formed, and the number of $\mu_3$-oxo bridges in the SBU changes accordingly to balance the overall charge.$^{19}$ Both materials are highly porous (pore sizes of 20 and 36 Å, respectively) and are stable under acidic conditions and high relative humidity. Following this study, Zhou$^{20}$ and Farha$^{21}$ independently reported the successful implementation of isoreticular chemistry for the fabrication of porphyrin Zr MOFs with an ftw-a topology. In the first report, three different porphyrins of varying length were used to produce the MOF series PCN-228, -229, -230, with pore sizes ranging from the nano- to the meso-scale (Figure 5.4.1).
**Figure 5.4.1.** Porphyrin linkers (top) and augmented representations of zirconium MOFs with *ftw*-a topology (bottom left) and *csq* topology (bottom right).

The linker designed based of these groups of MOFs is shown in **Scheme 5.4.1**. In this case, the length of our rotaxane linker **5R3-TA** is shorter than the largest linker used by Zhou and co-workers, so we expect to obtain a material with a unit cell having dimensions somewhere between those of PCN-229 and PCN-230.
One downside of working with Zr₆ clusters is that by increasing the strength of the O–Zr interactions (760 kJ/mol vs 284 kJ/mol for Zn–O), the self-healing process that makes it possible to grow single crystals of these materials is perturbed. When synthesizing Zr MOFs, it is very common to obtain microcrystalline powder, forcing the structure determination to rely heavily on obtaining well-resolved PXRD measurements and their refinement instead of SC-XRD data. Several different solvothermal conditions were tested, unfortunately none of them yielded unambiguously crystalline material. **Figure 5.4.2** shows a Scanning Electron Microscopy (SEM) image of the powder isolated from the solvothermal reaction. No crystalline domains can be clearly identified, indicating the material either consists of very tiny microcrystals or the powder is amorphous. The IR spectrum of the isolated powder is missing the asymmetric C–O stretch of the carbonyl group, consistent with coordination to a metal centre (**Figure 5.4.3**), while the distinctive features indicate the presence of a porphyrin and a crown ether.
One of the advantages of using reticular chemistry is the possibility of simulating an X-ray powder pattern of the target material based on data from an isoreticular MOF available in the literature. **Figure 5.4.4** shows a comparison between the experimental patterns of the powder isolated from the solvothermal reaction with ZrCl$_4$ and a simulated powder pattern of the target MOF (See Experimental Section for details). The broadness of the experimental pattern severely restricts the possibility of correlating these patterns, and while these data are inconclusive, they suggest this material could potentially be a microcrystalline Zr MOF with **5R3-TA** as a linker.

**Figure 5.4.2.** SEM image of the isolated powder from the reaction of ZrCl$_4$ and **5R3-TA**.
Figure 5.4.3. Comparison of the IR spectra of 5R3-TA and the powder isolated from the solvothermal reaction with ZrCl₄.

Figure 5.4.4. Experimental (black) and simulated (green, no broadening; red, 0.1 µm crystallites) PXRD patterns for a Zr MOF with ftw-a topology and linker 5R3-TA.
Different metal sources (ZrCl$_4$, ZrOCl$_2$), the pre-assembled cluster Zr$_6$O$_4$(OH)$_4$(OMc)$_{12}$, various solvothermal conditions and modulators, and alternative mechanochemical synthesis routes$^{23,24}$ were tested but all of them produced the same type of powders. Again, the limited quantities of the linker restricted the number of conditions that could be screened.

5.5 Benzimidazole as directing unit

The final linker in this chapter was not designed based on existing linkers, but with the goal of incorporating a benzimidazole-based [5]rotaxane into a MOF. In this case, it is the geometry of the recognition site and the accessible chemical modifications that determined the final linker design. Scheme 5.5.1 shows the possible substitution patterns and geometries directed by the benzimidazole core. The T-shaped substitution pattern at the 4,7-positions was selected, and this requires functionalization with two additional phenyl rings on each side in order to satisfy the dimensions necessary for suitable tessellation.
Scheme 5.5.1. Possible designs for a benzimidazole-based [5]rotaxane linker. The red circles indicate donor groups for coordination to SBUs, the green circles denote the need for stopper groups.

Scheme 5.5.2. Rotaxane linker [5]R5-OA.
After designing the rotaxane linker, molecular modeling was used to build a credible MOF. Using the Forcite module on Materials Studio B2017, a structure was built and the dihedral angles on the T-shape fragments were constrained so a divergent coordination to SBUs was achievable (See Experimental Section for details). According to the geometry of the linker, it is required to use a 4-connected SBU and the resulting structure is shown in Figure 5.5.1.

Since the resulting structure appeared to be viable, the linker was combined with copper, zinc, and zirconium salts. The first two metals can produce a paddlewheel SBU where the rotaxane linker will occupy the four blades of the cluster and an additional ligand, potentially water, would complete the coordination sphere for the apical positions of the SBU. While there are few reported examples of a four-connected Zr₆ cluster, this SBU is known for its versatility when it comes to connectivity, with the possibility of forming 3-, 4-, 6-, 8-, 9-, 10- and 12-connected clusters.²⁵⁻²⁷ At this point, a material incorporating linker 5R5-OA has not been isolated, but efforts to screen various synthetic conditions are still underway.
Figure 5.5.1. A) Ball-and-stick model of a MOF incorporating 5R5-OA and a paddlewheel SBU, B) Augmented representation of 5R5-OA, C) Augmented representations of a MOF incorporating 5R5-OA.
5.6 **An alternative to MOFs: The trityl embrace**

In his search of supramolecular interactions that could allow for the incorporation of molecular rotors into crystalline materials, Garcia Garibay\textsuperscript{28} has exploited what Scudder and Dance aptly named the trityl (or phenyl) embrace.\textsuperscript{29,30} This interaction is the one occurring between two triphenylmethane groups due to interdigitation and edge-to-face \( \pi \)-stacking. It has an estimated stabilizing energy of around 54.4 kJ/mol, and is a strongly ordering and well-known director for the crystal packing of molecules.

\textbf{Figure 5.6.1.} Schematic representation of a trityl embrace.

We were interested in investigating the effect of these interactions in the crystal packing of a porphyrin-[5]rotaxane. The inclusion of the trityl groups into the [5]rotaxane scaffold is straightforward, however it was not clear if the stabilizing energy of these interactions would be enough to overcome other competing interactions present in porphyrin systems (\textit{i.e.} aggregation, stacking).

Characterizing 5R4 was problematic, indicating that the addition of trityl groups either favours aggregation of these molecules or considerably decreases their solubility. Various crystallization efforts were conducted, using pure 5R4, a metallated porphyrin core, and in the presence of other molecules (co-crystallization) like triphenylmethane and 1,4-diazabicyclo[2.2.2]octane, but the aggregation and precipitation of the rotaxane could not be overcome.

5.7 Conclusions

The implementation of reticular chemistry for the fabrication of MOFs with porphyrin-[5]rotaxanes as linkers was not successful despite numerous trials. During the design of the first linker, 5R1-OA, the contribution of the crown ethers to the steric bulk of the molecule was neglected and this omission proved to be central to the failure of that first approach. This is the only case where it is evident that the formation of a MOF is not possible giving the structure of the linker used. The improvements on the linker design and the variations investigated, unfortunately, have not yielded satisfactory results and
the cause for this is not clear. It was mentioned already that the limited available quantities of these linkers restrict the number of synthetic conditions that were screened. While the use of reticular chemistry is a common approach for MOF chemistry, more often than not its success results from a brute force approach instead of a rational progression of the conditions tested. This turns to be very problematic when the complexity of the linkers is increased and gram quantities are not available. Finally, rotaxane formation affects the solubility of the scaffolds used and it might prevent the initial nucleation step required for the propagation of the MOF net.

It is the opinion of the author that the linkers presented in this chapter have all the required characteristics to be integrated into a MOF, and that the lack of results is just a consequence of the particular conditions tested and not a reflection of problematic linker design.

5.8 Experimental Section

5.8.1 General comments

Methacrylic acid, metal salts, trifluoroacetic acid, acetic acid, and solvents were acquired from commercial sources and used without further purification. The cluster Zr₆O₄(OH)₄(OMc)₁₂ was prepared following the reported procedure. Scanning Electron Microscopy images were collected on a FEI Quanta 200 FEG microscope. IR spectra were collected on a Bruker Alpha-T ATR-FTIR spectrometer.

5.8.2 Synthesis of rotaxane linkers

Linkers 5R1-OA, 5R2-OA, 5R3-TA, and 5R5-OA were obtained following the same general hydrolysis protocol. A 10 mL microwave tube with a stir bar was charged
with the respective rotaxane 5R#, THF (2 mL) and methanol (2 mL), and NaOH (6 M, 2 mL) were added and the reaction heated to 85 °C for two periods of 10 min. After cooling down, the organic phase was removed under reduced pressure and HCl (2 M) was added until no further precipitation was observed. After centrifuging and drying under vacuum, the linkers were isolated in quantitative yields.

5.8.3 Powder X-ray Diffraction Analysis

Powder X-ray diffraction data were collected using a capillary tube on a Bruker D8 Discover diffractometer equipped with a 140 mm 2-D Vantec 500 detector, and a conventional copper source set to 40 kV and 40 mA. PXRD simulations were conducted using the Reflex module of Materials Studio B2017, and the model MOF (vide infra), and with varying crystallite sizes to account for broadening of the patterns.

5.9 Molecular Mechanics Modeling

All the molecular modeling simulations were performed using the Forcite module on Materials Studio B2017. For the modelling of isoreticular MOFs, the available crystallographic data was used as a starting point. The CIF files (MMPF-98 CSD Refcode BIPSUQ; PCN-23020 CSD Refcode TOVGES) were imported into the software and altered to accommodate the structure of the rotaxane linkers. The structures were allowed to relax, and using the Smart algorithm a geometry optimization with the Universal Force Field was performed. The unit cell parameters were allowed to refine to account for the difference in size between these linkers, but the crystal system and space group were preserved.

For the construction of a MOF incorporating 5R5-OA, the structure was build with the visualizer incorporated into Materials Studio B2017. After this step, the dihedral
angle for two of the meso substituents (5 and 15, or 10 and 20) was fixed to 0° and the remaining two angles were fixed to 90°. Various SBUs were tested for the construction of a MOF, and a four-bladed paddlewheel was chosen due to the apparent compatibility between the geometries of this cluster and of the linkers. The final MOF was built using the space group $P-1$ and its geometry optimized in the same way described above. The chosen SBU and the linker showed a good compatibility and the model refined satisfactorily.

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Chapter 6. Conclusions and Future Work

6.1 Overview

Throughout the chapters of this dissertation, the synthesis and study of [n]rotaxanes, porphyrins, and metal-organic frameworks were described. The nature of mechanically interlocked molecules has inspired supramolecular chemists to investigate these molecules and to push the boundaries of molecular design and functionality. There are only a few examples of real life applications for the materials designed with supramolecular chemistry, but their potential certainly exists. On the other hand, MOF chemists have already realized commercial applications for their objects of study, perhaps due to the more collaborative contact with engineers. MOFs are used today mostly for their storage purposes, with MOF Technologies\textsuperscript{2} anti-ripping technology being used in supermarkets, and NuMat Technologies\textsuperscript{3} devices for transport and safe storage of difficult-to-handle chemicals being some of the most notable examples. While our motivation to develop the research presented in this work is not the creation of a start-up company (although a hypothetical company named SpinnyBits could be imagined), the knowledge assembled herein may help chemists in the design and synthesis of materials with fine-tuned motions and functions.

Chapter 1 placed the synthetic efforts in the context of a broader, collective attempt at establishing a basis for the incorporation of mechanically interlocked molecules into solid-state materials, and potentially, molecular machinery. The number of solid-state materials capable of robust dynamics is still very limited, and nowhere near the production of a molecular machine. Regarding this aspect, the careless use of terms
like molecular machines out of context might harm the field and has already resulted in famous controversies. True molecular machines that operate inside a metal-organic framework are not yet a reality, and those capable of operating in solution are few and far between, so extreme care should be used when discussing these systems as to not misrepresent our findings. The end of Chapter 1 posed a series of open questions to the reader. Perhaps, after reading this dissertation and the work cited herein, some of the answers may come to mind. As for the existence of an ideal material for robust dynamics, we will keep working on the development of porous materials with mechanically interlocked molecules, and trying to answer this aspect in the process.

Chapters 2 and 3 described the incorporation of two types of linkers, porphyrins and rotaxanes, into MOFs, producing three new members of the UWDM MOF series, UWDM-7, -8, and -9. By having a porphyrin scaffold, a MOF with a higher stability than those previously reported was obtained, and this new linker not only increases the stability, but also has the potential to influence the dynamic behaviour of the rotaxane linker. The interpenetrated fsc nets in UWDM-7 and -8 do not hinder the rotational dynamics of the crown ethers. With respect to the use of the porphyrin linkers beyond their structural-directing properties, the techniques used to probe the dynamic behaviour of the crown ether, unfortunately, are not compatible with the presence of paramagnetic species (e.g. metal ions capable of coordinating to additional ligands) severely limiting our capacity to explore this avenue of research. Due to the known motional modes of the crown ether molecules in the rotaxanes which have been incorporated into MOF structures, attempts are being made to develop experimental techniques and simulation methodologies to investigate the dynamics in more challenging...
systems (e.g., α-UWDM-7-Ni). In the meantime, the possibility of using different metalloporphyrins to make a non-interpenetrated version of either of these MOFs can be explored. Ru(CO)-TCPP has been successfully incorporated into porphyrinic MOFs without the loss of the apical carbonyl ligand. This simple modification might be enough to disrupt the growth of the second framework, as the structure of UWDM-7 and 8 shows that the porphyrin linkers from the independent frameworks are in close proximity.

The topological analysis of chemical nets is, by itself, a captivating topic. By using a dodeca-substituted porphyrin and a rotaxane linker, the first occurrence of the tui net, UWDM-9, was reported.

Chapter 4 combined the two types of linkers used in the previous chapters to form porphyrin-[5]rotaxanes. By taking advantage of the compatibility between Lindsey’s method for the fabrication of meso-substituted porphyrins, and the self-assembly of crown ethers with anilinium or benzimidazolium recognition motifs, a one-pot synthesis was developed and resulted in six symmetrical [5]rotaxanes 5R1 – 5R6. The characterization of these new MIMs revealed that some may be able to operate as rudimentary acid-base molecular switches. The versatility of the synthetic process described should be further explored in order to incorporate different crown ethers and other molecular fragments of interest (e.g. introduction of dipole moments, coordination pockets, photoswitches). Additionally, the electronic properties of these molecules should be the subject of future studies, and perhaps collaborations with other research groups working on the photophysical aspects of MIMs.

In Chapter 5, the steps to incorporate [5]rotaxane linkers in MOFs were presented. Agreeably, this section is the one where future work is more needed. It was shown that
despite the linker design following the principles of reticular chemistry, the screening and optimization of synthetic conditions requires high throughput methods incompatible with the scale at which these [5]rotaxanes can be synthesized. With this in mind, the implementation of molecular mechanics modeling in the design of materials with robust dynamics should be routinely applied. The existence of the computation-ready experimental (CoRE)\textsuperscript{8} MOF database, and its constant expansion, provides a plethora of available idealized structures to screen, without the need to synthesize the linkers until a few target structures can be identified. An alternative option for the continuation of this work is the modification of the synthetic pathway to produce [3]rotaxanes where only two of the four meso positions have an interlocked ring. Reactions to produce such molecules are well-known and only add a few more synthetic steps. By doing this, the remaining two meso positions can be functionalized with donor groups that are not surrounded by stopper groups or crown ethers, and then incorporated into MOFs by either direct solvothermal synthesis, or post-synthetic modification. Another possible conduit for this project is the incorporation of two different substitution patterns into the porphyrin core in order to increase the complexity, and introduce self-sorting mechanism into the systems.

Finally, two more ambitious ventures can be envisioned. (i) covalent-organic frameworks (COFs) are an emerging class of materials where reticular chemistry can be readily applied.\textsuperscript{9,10} Modifying the [5]rotaxane linkers to be compatible with COF synthesis is an easy transformation and maybe one worth investigating. The fabrication of metal-free, crystalline solids with MIMs could be one of the answers to where the future directions of robust materials with dynamic components are going. (ii) Conductive MOFs
have been reported recently\textsuperscript{11–15}, offering yet another external stimulus that can be used in the control of dynamic properties. If a MIM linker can be designed to either (a) be doped into these conductive structures or (b) be conductive itself, then the synthesis of materials where the interlocked wheels can be aligned upon the application of an electric field should be achievable. The aligning of MIM components in a solid-state material has been a long-sought goal in our research group.

Almost sixty years after Feynmann’s seminal lecture “There is plenty of room at the bottom”\textsuperscript{16}, the progress in the development of theoretical frames, synthetic techniques, and instrumentation have shown us that not only Feynmann was right, but that he might have underestimated the amount of space available for the development of nanostructures. May there be more scientists willing to keep expanding this realm.

6.2 References


2 MOF Technologies\textsuperscript{TM}, \url{http://www.moftechnologies.com/}.

3 NuMat Technologies, \url{https://www.numat-tech.com/}.


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