Metal–organic *rotaxane* frameworks; MO*R*Fs

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Linear exodentate pyridinium ligands such as 1,2-bis(4,4′-bipyridinium)ethane or its bis *N*-oxide derivative can be used as axles for the formation of [2]pseudorotaxanes utilising 24-membered crown ethers such as dibenzo-24-crown-8 ether (DB24C8) as the wheel. These [2]pseudorotaxanes can be used to construct coordination networks using transition or lanthanide metal ions as the connecting nodes. 1-, 2- and 3D metal–organic *rotaxane* frameworks (MO*R*Fs) are possible. The resulting materials contain mechanically interlocked units and may be the forerunners of unique solids which contain machine-like components in an ordered array.

Introduction

Mechanically interlocked molecules such as rotaxanes and catenanes have shown to be particularly useful for the construction of molecular machines.[1] Although a great deal of information about the dynamic nature and fundamental switching properties of these systems has been derived from solution studies,[2] there is a need for strategies which could lead to the fabrication of solid state nanoscale devices from these molecules. A number of methodologies for imposing higher order on individual rotaxanes have been investigated; for example i) attachment to a surface,[3] ii) tethering between two electrodes,[4] iii) incorporation into organic polymers[5] or dendrimers[6] and iv) assembling into the repeating framework of a crystalline lattice.[7] Ultimately, higher degrees of ordering have the potential to produce materials that contain functional components that are individually addressable and controllable. This review describes our initial investigations into the fourth strategy listed above; the formation of metal-based polyrotaxanes which we term metal–organic *rotaxane* frameworks (MO*R*Fs).[8] The only other well defined set of metal-based polyrotaxanes known are those of Kim *et al.* in which diaminoalkane axles and a cucurbituril (CB[6]) wheel are used.[9] In general, many aspects of the chemistry described herein for our system can also be attributed to the CB[6] materials. The biggest difference is probably the ease of chemical modifications possible for a rotaxane linker using simple crown ethers rather than CB[6].

The use of [2]rotaxanes as linkers in metal–ligand self-assembly reactions should provide a blueprint for the eventual organising of rotaxane based molecular machines into 1-, 2- or 3-dimensional frameworks. The challenge of creating metal–organic frameworks (MOFs) involving rotaxanes as linkers involves designing appropriate ligands and devising protocols for self-assembly synthesis and crystallisation. One defining attribute of a conventional MOF is the ability to modify the linker unit by organic synthesis.[8] Herein, an additional degree of flexibility is available as the rotaxane linker can be modified by retaining the bridging axle unit, and therefore the basic metal–ligand framework, but exchanging the wheel component. This supramolecular modification is a potentially powerful way to tune the internal properties of the material by simply changing the 24-membered crown ether employed in the self-assembly synthesis. Although all the examples in this review utilise commercially available DB24C8, the facile synthesis of various substituted 24C8 ethers should make a library of this type of material easily accessible.

Rotaxanes as bridging ligands

We recently demonstrated that simple 1,2-bis(pyridinium)-ethane dications can act as axles for the efficient formation of [2]pseudorotaxanes when employing 24-membered crown ethers as the wheel component.[10] The two components are held together by a series of eight C–H···O interactions and significant ion–dipole interactions between the positive charge on the pyridinium nitrogen atoms and the electronegative oxygen atoms of the crown ether; Fig. 1. The strength of the interaction was shown to be sensitive to the nature of the substituents on the pyridinium ring with electron-withdrawing groups resulting in increased binding.[10] Using crown ethers with aromatic rings also increased the association by the introduction of π-stacking between the electron-poor pyridinium rings and the electron-rich catechol rings. Association constants for [2]pseudorotaxane formation, measured in MeCN solution at 298 K, varied from ~50 to ~3000 M^{-1}.[10]

This basic [2]pseudorotaxane motif was then used to construct fully interlocked [2]rotaxanes by using the 1,2-bis(4,4′-bipyridinium)ethane dication, $\mathbf{1}^{2+}$ shown in Fig. 1.[11] The presence of terminal pyridine groups facilitated [2]rotaxane formation by either alkylation with bulky *tert*-butylbenzyl groups or coordination by transition metal complexes of suitable size.[12] To date, we have used this motif to construct a

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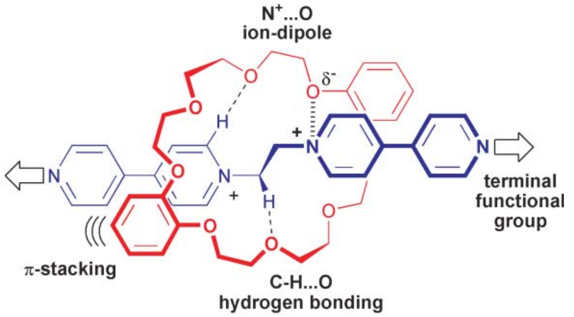

Fig. 1 A linear 1,2-bis(4,4′-bipyridinium)ethane dication, $\mathbf{1}^{2+}$ (blue) and a DB24C8 macrocycle (red), act as axle and wheel to form the interpenetrated [2]pseudorotaxane, $\mathbf{2}^{2+}$. Examples of the three non-covalent interactions are shown: 1) ion–dipole interactions between the pyridinium N-atoms and the electronegative ether O-atoms, 2) C–H···O hydrogen bonds from the π-pyridinium and ethylene protons to the crown ether oxygen atoms (two of eight are shown) and 3) π-stacking between electron-poor pyridinium and electron-rich catechol rings.

variety of interlocked molecules including [2]rotaxanes,[12,13] [3]rotaxanes,[14] [3]catenanes[15] and [2]rotaxane molecular shuttles.[16] It has also been used by Stoddart, in combination with a secondary ammonium binding site, to create an acid–base controlled molecular shuttle.[17] Fig. 2 shows the crystal structure of the [2]pseudorotaxane $\mathbf{2}^{2+}$. It is clear that the non-alkylated nitrogen atoms of the pyridine functional groups extend out past the crown ether and are accessible for coordination. The intramolecular distance between these terminal pyridine nitrogen atoms is 17.7 Å making this linker over twice the length of the ubiquitous bridging ligand 4′4-bipyridine (7.0 Å). In addition, this ligand has significant width and breadth (6.6 and 10.2 Å) making it a ligand with uncommon girth.[12]

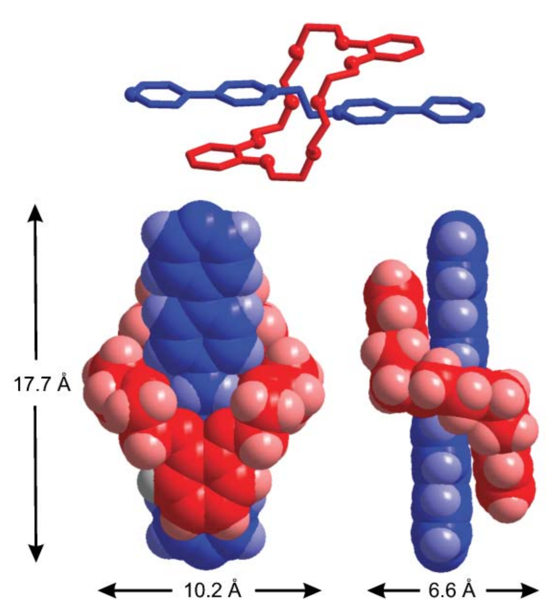

Fig. 2 X-ray structure of the [2]pseudorotaxane "ligand" $\mathbf{2}^{2+}$ formed from a 1,2-bis(4,4′-bipyridinium)ethane axle (blue) and a DB24C8 wheel (red). Top: a ball-and-stick representation showing the threading of the two components. Bottom: space-filling models emphasising the width and breadth of this unit and the π-stacking.

Almost any metal complex with a single open coordination site is bulky enough to be used as an effective stopper and form a metal-based [2]rotaxane from $\mathbf{2}^{2+}$. Our initial study involved the self-assembly reaction constituting $\mathbf{1}^{2+}$, DB24C8 and the palladated pincer fragment $[Pd(C_6H_3(CH_2SPh)_2)]^+$ in MeCN.[12] The ^1H NMR spectrum of the reaction mixture showed quantitative formation of the metal stoppered [2]rotaxane which could be isolated from solution by crystallisation. An X-ray crystal structure determination verified the interlocked nature of the product. Subsequently, Branda *et al.* showed that the stoppers could be larger more sophisticated metal units by using the porphyrin complex [Ru(CO)(TTP)] with $\mathbf{2}^{2+}$ to create an analogous [2]rotaxane.[18] Perhaps, the most elegant metal-based [2]rotaxane derived from $\mathbf{2}^{2+}$ is that capped by the very simple anionic metal fragments $[MBr_3]^-$ (M = Mn, Co).[19] The structure of the resulting neutral zwitterionic species is shown in Fig. 3.

One dimensional coordination polymers

The evolution from interlocked molecules with metal complexes as capping units to a 1D metal–organic *rotaxane* framework (MO*R*F) was fairly straightforward. Mixing $\mathbf{1}^{2+}$ as the BF_4 salt, with a 2-fold excess of DB24C8 in MeCN resulted in a solution which contained an equivalent of the [2]pseudorotaxane ligand $\mathbf{2}[BF_4]_2$. Diffusion of this solution into an MeCN solution of $[M(H_2O)_6][BF_4]_2$ (M = Co, Zn) resulted in isolation of crystalline material with formula $\{[Co(H_2O)_2(MeCN)_2(\mathbf{2})][BF_4]_4.(MeCN)_2(H_2O)_2\}_x$ in good yield; 71% (Co), 92% (Zn).[20] Fig. 4 shows that the use of Co(II) ions in the presence of a coordinating solvent such as MeCN results in an octahedral coordination sphere comprised of two equivalents of $\mathbf{2}^{2+}$, two MeCN molecules and two water molecules with each set of ligands having a *trans* orientation. The resulting linear 1D coordination polymer propagates along an axis in which every linker is a [2]rotaxane. The linearity of the framework is due to the fact that the linker $\mathbf{1}^{2+}$

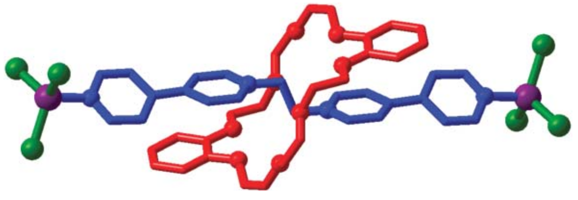

Fig. 3 Adding two bulky $[CoBr_3]^-$ stoppers to $\mathbf{2}^{2+}$ traps the wheel on the axle and creates a permanently interlocked and neutral [2]rotaxane.

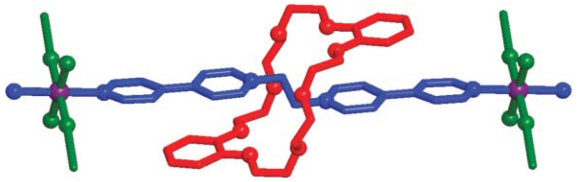

Fig. 4 Using a transition metal node such as $[Co(MeCN)_2(H_2O)_2]^{2+}$ which can bind two equivalents of $\mathbf{2}^{2+}$ forms a 1D MO*R*F in which every bridging linker is a [2]rotaxane.

can only adopt an *anti* conformation at the central ethylene unit when threaded through the crown ether. This combined with a *trans* geometry at the metal ion produces a linear 1D MO*R*F with a repeat distance of 22.1 Å.[20]

A 1D MO*R*F can be viewed as a metal–ligand "wire" in which the mechanically linked crown ether wheels act as a protective coating analogous to the use of long-chain hydrocarbons attached to phosphine ligands reported by Gladysz for surrounding metal polyacetylene linkages.[21] The 1D MO*R*Fs also contain infinite channels parallel to the polymer chains which are filled with anions and the two solvents of crystallisation, water and MeCN. Fig. 5 shows several strands of the framework in space-filling mode. It is likely that the girth of this rotaxane ligand contributes to both the parallel organisation of the chains as well as the channels between them. As evidence for this, we have crystallised two 1D polymers utilising only $\mathbf{1}^{2+}$ as a linker; *i.e.* without the crown ethers. In both cases, we found a classic herringbone pattern was formed and in one of these the linker actually adopted the *gauche* conformation resulting in a bent geometry and a sinusoidal rather than linear strand. There was no parallel alignment of chains and neither compound contained void channels for solvent occlusion.

Two dimensional grids

Since, the linear 1D MO*R*Fs contained an octahedral metal ion in which the ancillary ligands were solvent molecules (H_2O and MeCN), we reasoned it should be possible to induce higher orders of dimensionality by simply employing a greater amount of [2]pseudorotaxane ligand in a non-coordinating solvent such as $MeNO_2$ The reaction of two equivalents of $\mathbf{1}[BF_4]_2$ with four equivalents of DB24C8 and one equivalent of $[M(H_2O)_6][BF_4]_2$ (M = Cu, Cd, Ni) in $MeNO_2$ produced X-ray quality crystalline material in good yield (>80%).[20] Fig. 6 shows that the use of these metal ions in a non-coordinating solvent allows for a an octahedral coordination geometry comprising four [2]pseudorotaxane ligands in a square planar arrangement, along with one water molecule and one coordinated BF_4^- anion.

Fig. 7 shows how propagation of these units results in a 2D MO*R*F with square nets and formula $\{[Cd(H_2O)(BF_4)(\mathbf{2})_2].[BF_4]_5(MeNO_2)_{15}\}_x$, in which every bridging ligand is a [2]rotaxane. The sides of the square are defined by Cd···Cd

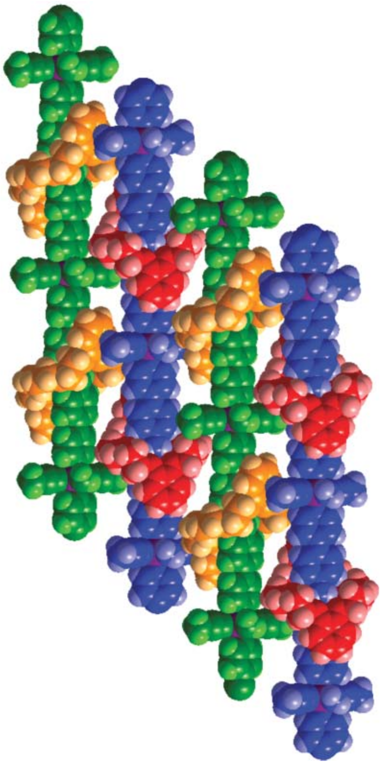

Fig. 5 The individual chains of the linear 1D MO*R*F run parallel through the solid and form infinite channels between the strands. Anions and solvents have been removed for clarity.

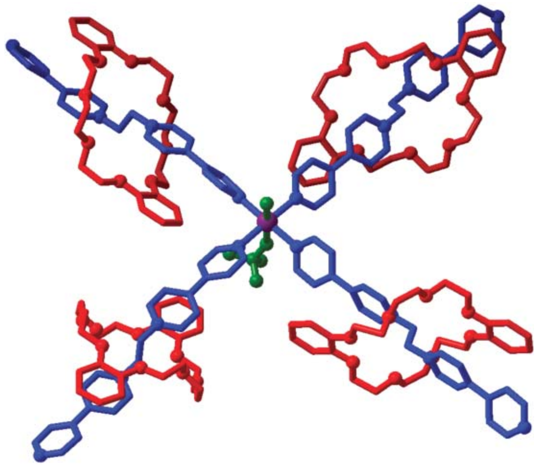

Fig. 6 Using a transition metal fragment such as $[Cd(H_2O)(BF_4)]^{2+}$ which can bind four equivalents of $\mathbf{2}^{2+}$ a 2D square net MO*R*F is formed in which every bridging linker is a [2]rotaxane. The axial sites are occupied by a tetrafluoroborate anion and a water molecule.

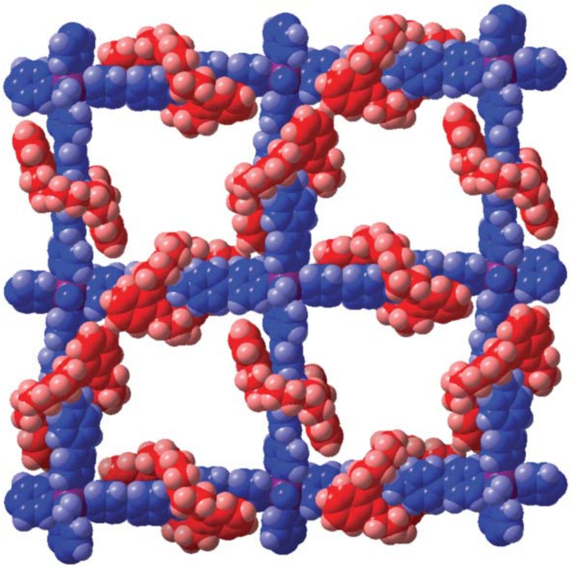

Fig. 7 The square grid does not allow for interpenetration to occur resulting in large cavities and channels that are lined with units of DB24C8. Anions and solvent have been removed for clarity.

distances of 22.2 Å. The interlayer spacings are 12.0 and 10.0 Å with the layers stacked in an alternating pattern knitted together by a H···F and H···O hydrogen bonds from the Cd–OH_2 unit of one layer to the neighbouring Cd–BF_4 group of an adjacent layer. Fig. 8 shows how this pattern gives rise to an open framework material with large infinite channels. Uniquely, these channels are lined with crown ethers as well as being filled with solvent and anions; there are 15 molecules of $MeNO_2$ per metal ion. Calculations estimate that the accessible void space occupied by anions and solvent is 50%; 38% for solvent only.[20]

Three dimensional frameworks

Regardless of the metal to ligand ratio employed, a two dimensional square net was the highest order MO*R*F that could be attained using the [2]pseudorotaxane $\mathbf{2}^{2+}$ as the bridging ligand. We ascribed this apparent failure to the crowding required to place six of these sterically demanding ligands around a single metal ion. In order to avoid crowding at the metal centre, we synthesised the bis *N*-oxide analogue of $\mathbf{1}^{2+}$ a new axle $\mathbf{3}^{2+}$; Fig. 9. We rationalised that the addition of two N–O functional groups would extend the length of the axle by a sum of two N–O bonds (~2.6 Å). Thus, moving the bulk away from the metal centre but retaining all the recognition elements important to the integrity of the pseudorotaxane.

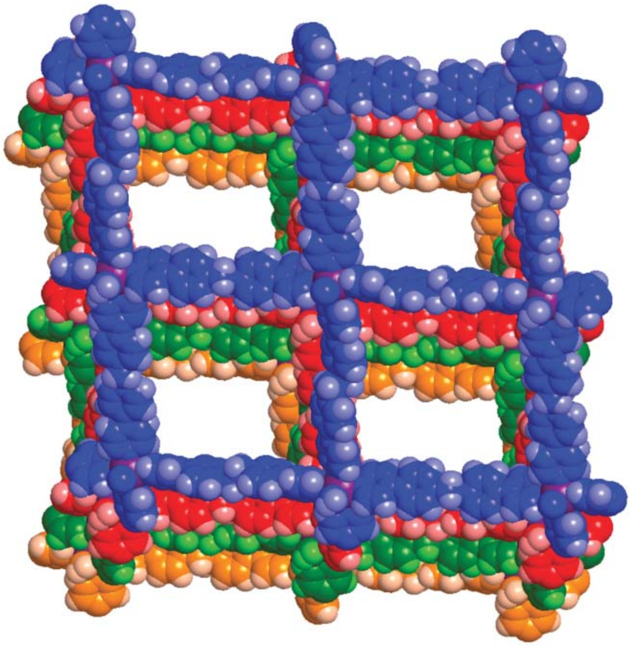

Fig. 8 The square grids align to form infinite channels that are lined with units of DB24C8. Anions, solvents and crown ethers have been removed for clarity.

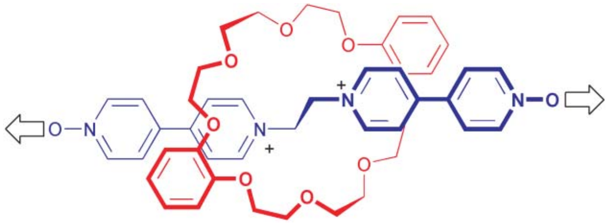

Fig. 9 The bis(*N*-oxide) version of the 1,2-bis(4,4′-bipyridinium)-ethane dication, $\mathbf{3}^{2+}$ (blue) can also form a [2]pseudorotaxane $\mathbf{4}^{2+}$ with DB24C8 (red).

Our first attempt at constructing a 3D MO*R*F from this new axle involved repeating the previous self-assembly strategy using Cd(II) ions in $MeNO_2$ that had been successful in giving us the 2D MO*R*F. The resulting material was indeed a polyrotaxane but the desired 3D framework was not attained. Instead, a 2D network was created with only one of the directions utilising the rotaxane linker $\mathbf{4}^{2+}$ and the other simply employing $\mathbf{3}^{2+}$ as a linker with no crown ether wheel.[22] Fig. 10 shows the basic coordination sphere around the Cd(II) centre.†

The structure actually has more in common with our 1D MO*R*F and is probably best described as a 1D polyrotaxane in which the individual polymer strands are further bridged by an ancillary linker; in this case the "naked" axle $\mathbf{3}^{2+}$. Interestingly, we had attempted to construct exactly such a system from the Co(II) 1D MO*R*F by replacing the two bound MeCN ligands by a bridging nitrile but were unsuccessful. Fig. 11 shows how the two different linkers are used to create a 2D network. Note

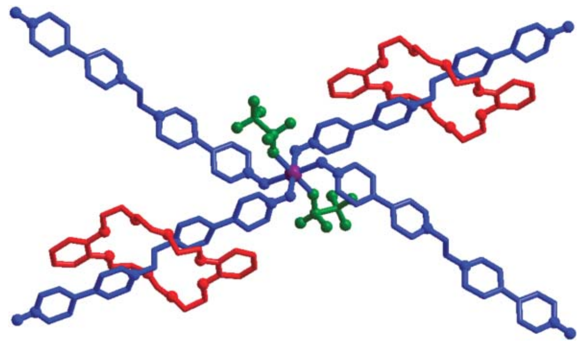

Fig. 10 Two different ligands, the pseudorotaxane $\mathbf{4}^{2+}$ and the naked axle $\mathbf{3}^{2+}$ combine in the square plane of an octahedral Cd(II) centre to produce a 2D network in which only one direction is a polyrotaxane. Two triflate anions occupy the axial coordination sites; all other anions and solvents are omitted or clarity.

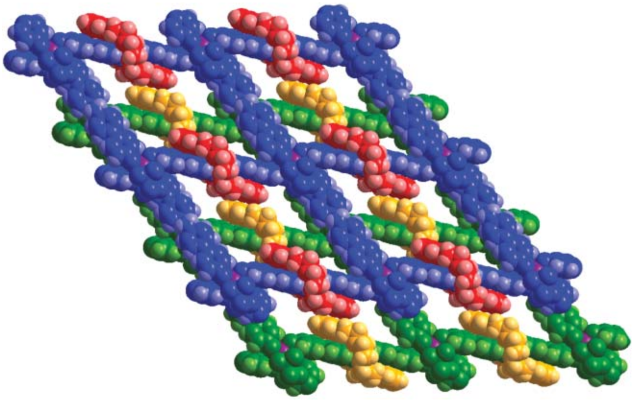

Fig. 11 Crown ethers on alternating layers (blue framework with red crowns and green framework with orange crowns are shown) completely fill the void space created by bridging the 1D polyrotaxanes. Anions and solvent have been removed for clarity.

that the ~120° angle of the Cd–O–N linkage creates sheets of parallelograms rather than squares. In this structure, the openings created by bridging in two dimensions are substantial but the space is completely filled by the rotaxane linker from an adjacent layer. These sheets alternate in a pattern which eliminates the kind of infinite channel observed when all the linkers were rotaxanes. This observation may have significant consequences for the design of open framework structures with polyrotaxanes. It may be that mixing and matching rotaxane linkers with common bridging ligands will not be a satisfactory way to build MO*R*Fs with appreciable void space.

Since, the use of a Cd(II) metal centre did not yield the desired 3D MO*R*F, we decided to employ larger metal ions in a further effort to decrease crowding in the coordination sphere and induce higher order dimensionality. To this end, we reacted three equivalents of **3**$[OTf]_2$ with nine equivalents of DB24C8 and one equivalent of $[M(OTf)_3]$ (M = Sm, Eu, Gd, Tb) in MeCN. X-ray quality crystalline material was produced in moderate yield (~50% on average). Fig. 12 shows that the use of Ln(III) ions as nodes results in an eight-coordinate metal centre with a square *anti*-prismatic geometry comprised of six [2]rotaxane ligands, one water molecule and one coordinated triflate anion.[23]

Fig. 13 shows how propagation of these units results in 3D, MO*R*Fs with formula $\{[M(H_2O)(OTf)(\mathbf{4})_3][Cl][OTf]_7\}_x$, (M = Sm, Eu, Gd, Tb) in which every bridging ligand is a [2]rotaxane. The edges of the net are defined by Sm···Sm distances of ~23.5 Å. Although the cavity of this framework has a volume of ~10,000 Å^3, this apparently void space is filled by the single interpenetration of a parallel net. (See Fig. 16 for diagrams depicting single interpenetration of these two lattices.) As envisioned, the combination of a longer axle and larger metal ions resulted in the coordination of six [2]rotaxane ligands to create a 3D MO*R*F structure. An obvious side-effect of employing the longer axles is that there is a concomitant elongation of the metal–metal distance. This in turn creates an expanded cavity with larger "windows" which can now accommodate the girth of the [2]rotaxane ligand through interpenetration.

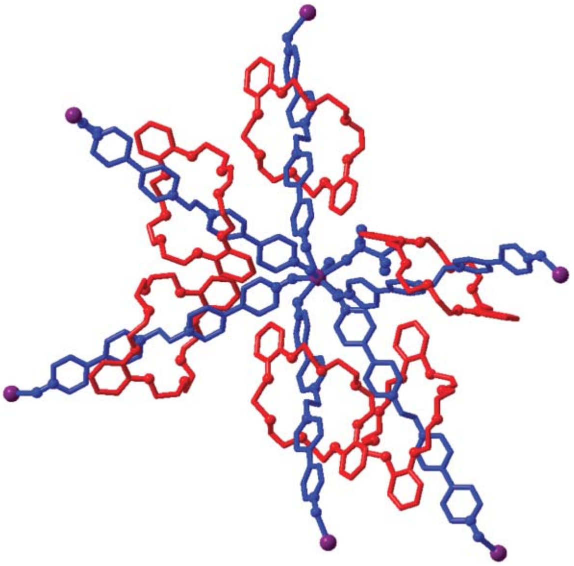

Fig. 12 Using a Ln(III) ion such as Sm, Eu, Gd or Tb allows for the coordination of six rotaxane ligands as part of an eight-coordinate *anti*-prismatic geometry. The other two sites are occupied by a triflate anion and a water molecule.

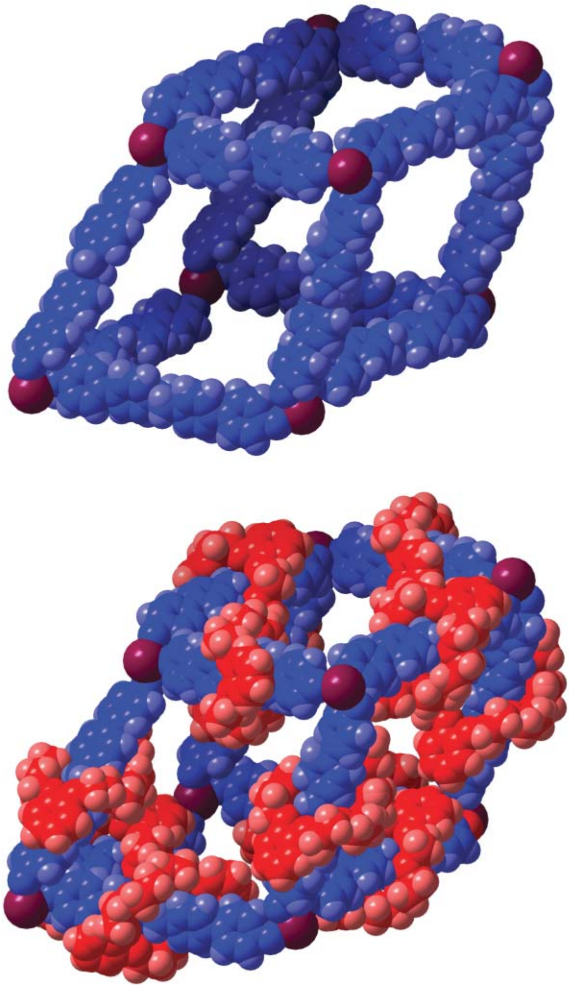

Fig. 13 A combination of Ln(III) ions (Sm, Eu, Gd, Tb) and the pyridine-*N*-oxide linker $\mathbf{4}^{2+}$ produces a 3D MO*R*F structure in which every linker is a [2]rotaxane. Top: a single "cube" section of the 3D skeleton (blue) shown without the crown ether units. Bottom: as above with the crown ether units (red).

It was gratifying to be able to produce an isomorphous series (Sm, Eu, Gd, Tb) of 3D MO*R*Fs based upon eight coordinate metal centres, but we found that changing to a slightly smaller lanthanide metal ion, Yb(III) (2.40 Å *vs.* 2.51 Å, for Tb), yielded another 3D MO*R*F with a completely different framework. A material with formula $\{[Yb(OTf)(\mathbf{4})_3][Cl][OTf]_7\}_x$, was isolated in moderate yield using the same diffusion procedure used to produce the other 3D MO*R*Fs. In this case, a seven-coordinate pentagonal bipyramidal geometry is adopted by the smaller Yb(III) centre. Five *N*-oxide based rotaxanes occupy the equatorial sites of the pentagonal plane with one further rotaxane and a single triflate ion positioned in the axial sites; Fig. 14. On reducing the size of the Ln(III) node, a single water molecule is removed and the coordination number decreased from 8 to 7. This

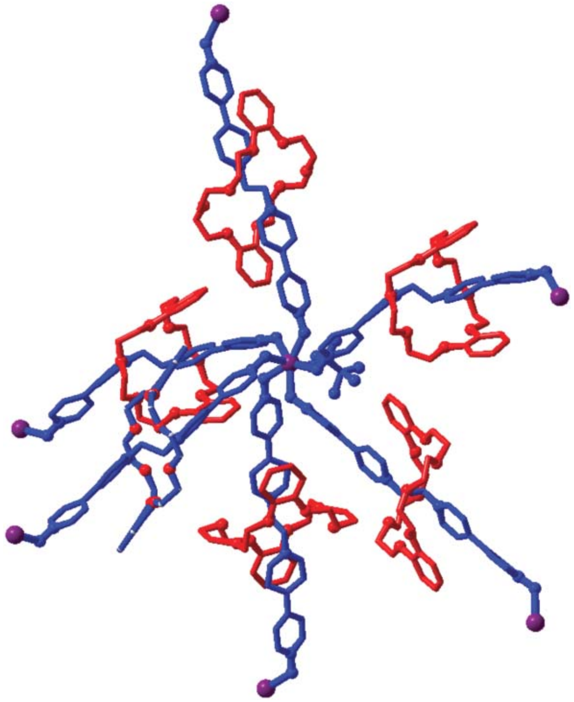

Fig. 14 Using a smaller Yb(III) metal centre, a seven-coordinate, pentagonal bipyramidal geometry is formed comprised of six rotaxane ligands a single triflate ion.

subtle change has a dramatic effect on the nature of the resulting MO*R*F structure.[23]

Since the novel seven-coordinate geometry at Yb(III) contains a pentagonal equatorial plane, we were immediately confronted with the question of how Nature would tessellate a five-coordinate node into a two dimensional network; formally such a pattern is impossible with pentagons. However, since each *N*-oxide ligand can ''bend'' at the Yb–O–N linkage a (3/4,5) net is formed which solves the problem by utilising a combination of alternating triangles and squares. Until very recently, even this two dimensional pattern was unknown in chemical systems.[24] Fig. 15 shows the tiling in the pentagonal plane. This network propagates one step further into a full 3D MO*R*F by pillaring to alternating layers utilising the 6th [2]rotaxane ligand in the apical position. This results in a previously unknown chemical topology which takes the form of a (3/4/6,6) 6-connected net comprised of triangles, squares and hexagons. The square openings are used for interpenetration as this is not possible through the more crowded triangular cavities. Fig. 16 shows how these two independent lattices are interpenetrated.

Stability of the MO*R*F structure

All of the metal–organic *rotaxane* frameworks prepared in this study show the same basic stability. They are all highly crystalline materials that occlude solvent to some degree. Each material loses some portion of its trapped solvent rapidly upon removal from the mother liquor at room temperature. Thermogravimetric analysis showed that all residual solvent was removed after heating to ~100 °C. Each MO*R*F studied then showed a stable phase until ~225–250 °C, at which point decomposition of the metal ligand framework was indicated by loss of DB24C8. It should be remembered that the interlocked crown ether, although it is originally held in place by weak non-covalent bonds, can only be removed by breaking a bond in the metal ligand backbone. Thus, the loss of DB24C8 is

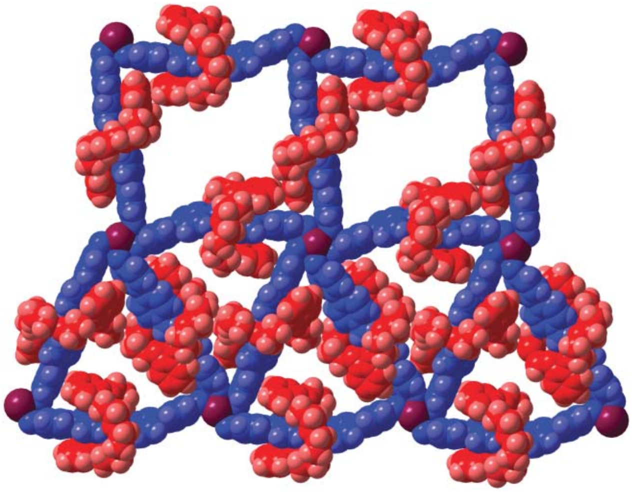

Fig. 15 The pentagonal equatorial plane of the Yb(III) MO*R*F has a tiling pattern that involves alternating squares and triangle centred about a five-coordinate node. The squares have openings that allow for interpenetration of an adjacent net but the more crowded triangles do not.

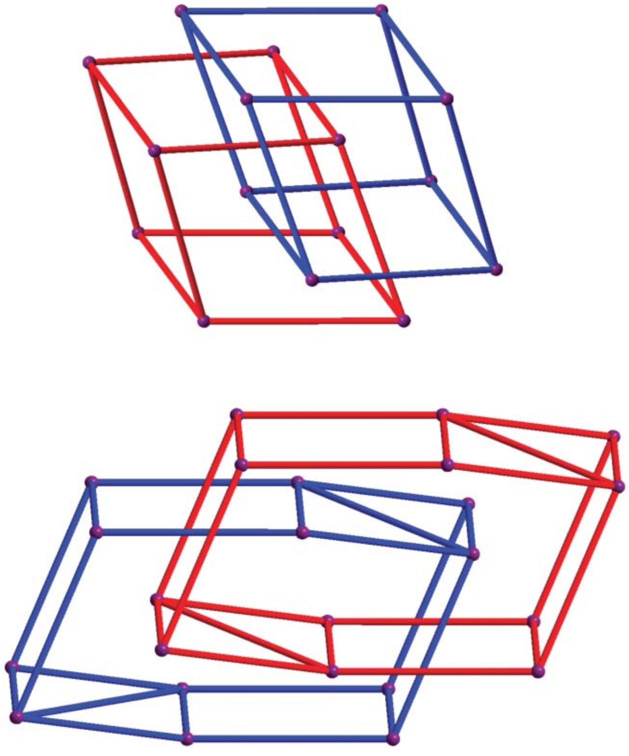

Fig. 16 Each of the 3D MO*R*F structures is singly interpenetrated. Top: The eight coordinate Sm(III) material, Bottom: The seven coordinate Yb(III) material. Nodes are metal ions with rods representing the rotaxane linkages. The two separate interpenetrating nets are coloured red and blue.

actually a sensitive and unambiguous detection of framework breakdown. In the case of the 3D MO*R*Fs, powder XRD patterns of the stable desolvated phase were consistent with retention of the 3D framework observed in the single crystal structures. For the 1D and 2D materials it was not possible to make such a claim but retention of the polyrotaxane backbone is inferred by observation of a stable phase over a broad temperature range of >150 °C following solvent removal and prior to loss of crown ether. We can confidently conclude that these new materials are at least as stable as basic coordination polymers constructed from these metal ions and pyridine donor ligands. There is nothing inherently unstable about a MO*R*F structure.

Conclusion and outlook

For this chemistry to evolve, we must be able to prepare truly robust MO*R*Fs. This is an issue that can be addressed in the same manner as it was for conventional MOFs.[8] However, there are extra considerations that must be taken into account due to the mechanically linked nature of the rotaxane component. For example, a straightforward modification that would stabilise the metal ligand interaction and can easily be implemented is the replacement of the monodentate pyridine or pyridine-*N*-oxide donors of the present axles by a multidentate chelator. However, a problem that is unique to using a pseudorotaxane as a ligand is the need to conduct the self-assembly reaction under conditions which favour pseudorotaxane formation. This precludes the use of strongly donating polar solvents that compete with the non-covalent interactions holding the pseudorotaxane together and obviously rules out the use of any type of solvothermal conditions involving polar solvents, heat and/or pressure. The solution to this dilemma is to pre-prepare the rotaxane linker such that unthreading of the mechanical linkage is not a possibility. That is, construct a linker that is a permanently interlocked [2]rotaxane prior to metal–ligand self-assembly.

We have recently reported the preparation and preliminary coordination chemistry with Fe(II) of the terpyridine-based [2]rotaxane ligand shown in Fig. 17.[25] Since the ligand is already a permanently interlocked [2]rotaxane the conditions under which chelation to a metal centre is conducted are almost irrelevant to the integrity of the mechanical linkage. For example, we have also prepared heteroleptic Ru(II) complexes of these ligands at reflux in polar solvents with no decomposition of the [2]rotaxane ligands.[26] This type of approach to bridging rotaxane ligands should greatly expand the synthetic conditions under which MO*R*F assembly can be conducted and allow the preparation of MO*R*Fs with increased stability.

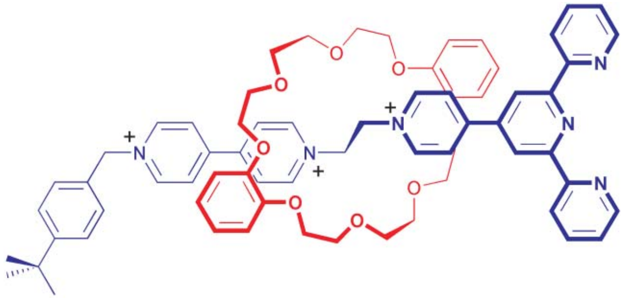

Fig. 17 The terpy-based [2]rotaxane is a permanently interlocked molecule and can be manipulated as a ligand under a variety of reactions conditions without unthreading of the mechanically linked components.

One of the ultimate goals for this chemistry is to create solid state materials that contain arrays of ordered molecular machines based on mechanically interlocked species. We have already created the molecules and observed their properties as individual entities in solution. The major challenges for the future will be to i) prepare MO*R*Fs with mechanically switchable components and internal frameworks that make molecular motion feasible and ii) determine the driving forces (chemical, electrochemical, photochemical, *etc.*) that are compatible with the chemical make-up of the material.

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References

† The X-ray structure of this compound has not been reported previously. $C_{78}H_{84}CdF_{12}N_{12}O_{38}S_6$, M = 2444.33, triclinic, $P\bar{1}$, a = 11.5792(10), b = 12.4592(11), c = 19.0001(17) Å, α = 88.380(2)° β = 84.943(2)°, γ = 65.788(2)° U = 2490.2(4) Å^3, T = 100.0(2) K, Z = 1, μ = 0.471 mm^{-1}, 19918 independent reflections (R_{int} = 0.0703). R_1 = 0.1017, wR_1 = 0.1555, (8735 reflections, $I > 2\sigma I$), R_2 = 0.2645, wR_2 = 0.3085 (all data), GoF(F^2) = 1015. Data were collected on a Bruker APEX CCD instrument and solutions performed using the SHELXTL 5.03 Program Library, Bruker Analytical Instrument Division, Madison, WI, USA, 1997. CCDC 263332. See http://www.rsc.org/suppdata/cc/b4/b416609d/ for crystallographic data in .cif or other electronic format. All diagrams are constructed from X-ray data using the program DIAMOND.[27]

1 (*a*) J. F. Stoddart, *Acc. Chem. Res.*, 2001, **34**, 410; (*b*) A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier and J. R. Heath, *Acc. Chem. Res.*, 2001, **34**, 433; (*c*) J-.P. Collin, C. Dietrich-Buchecker, P. Gaviña, M. C. Jiminez-Molero and J.-P. Sauvage, *Acc. Chem. Res.*, 2001, **34**, 477; (*d*) A. N. Shipway and I. Willner, *Acc. Chem. Res.*, 2001, **34**, 421.
2 (*a*) V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem. Int. Ed.*, 2000, **39**, 3348; (*b*) R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi and M. Venturi, *Acc. Chem. Res.*, 2001, **34**, 445.
3 (*a*) I. C. Lee, C. W. Frank, T. Yamamoto, H.-R. Tseng, A. H. Flood, J. F. Stoddart and J. O. Jeppesen, *Langmuir*, 2004, **20**, 5809; (*b*) D. Steuerman, H.-R. Tseng, S. Vignon, Y. Luo, J. F. Stoddart and J. R. Heath, *Polym. Mat. Sci. Eng.*, 2004, **90**, 209; (*c*) H.-R. Tseng, D. Wu, N. X. Fang, X. Zhang and J. F. Stoddart, *ChemPhysChem*, 2004, **5**, 111.
4 H. Yu, Y. Luo, K. Beverly, J. F. Stoddart, H.-R. Tseng and J. R. Heath, *Angew. Chem. Int. Ed.*, 2003, **42**, 5706.

5 H. W. Gibson, D. S. Nagvekar, M. Yamaguchi, S. Bhattacharjee, H. Wang, M. J. Vergne and D. M. Hercules, *Macromolecules*, 2004, **37**, 7514 and references therein.

6 J. W. Lee and K. Kim, *Top. Curr. Chem.*, 2003, **228**, 111.

7 (*a*) M. Albrecht, M. Lutz, A. L. Spek and G. van Koten, *Nature*, 2000, **406**, 970; (*b*) O. M. Yaghi, M. O'Keefe, N. W. Ockwing, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.

8 The term MO*R*F is used in this article to designate a sub-class of MOF as defined by Yaghi. See: J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3.

9 The preparation of these materials pre-dates those described herein. For an excellent review of this chemical system see: K. Kim, *Chem. Rev.*, 2002, **31**, 96.

10 S. J. Loeb and J. A. Wisner, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2838.

11 M. I. Attalla, N. S. McAlpine and L. A. Summers, *Z. Naturforsch., Teil B*, 1984, **39**, 74.

12 S. J. Loeb and J. A. Wisner, *Chem. Commun.*, 1998, 2757.

13 N. Georges, S. J. Loeb, J. Tiburcio and J. A. Wisner, *Org. Biomol. Chem.*, 2004, **2**, 2751.

14 S. J. Loeb and J. A. Wisner, *Chem. Commun.*, 2000, 845.

15 A. L. Hubbard, G. J. E. Davidson, R. H. Patel, J. A. Wisner and S. J. Loeb, *Chem. Commun.*, 2004, 138.

16 S. J. Loeb and J. A. Wisner, *Chem. Commun.*, 2000, 1939.

17 A. M. Elizarov, S.-H. Chiu and J. F. Stoddart, *J. Org. Chem.*, 2002, **67**, 9175.

18 TTP is the 5,10,15,20-tetratolylporphyrinato dianionic ligand. The Ru(CO) complex is neutral but easily coordinates a sixth axial ligand. See: K. Chichak, M. C. Walsh and N. R. Branda, *Chem. Commun.*, 2000, 847.

19 G. J. E. Davidson, S. J. Loeb, N. A. Parekh and J. A. Wisner, *Dalton Trans.*, 2001, 3135.

20 G. J. E. Davidson and S. J. Loeb, *Angew. Chem. Int. Ed.*, 2003, **42**, 74.

21 (*a*) J. Stahl, J. C. Bohling, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martín-Alvarez, F. Hampel and J. A. Gladysz, *Angew. Chem. Int. Ed.*, 2002, **41**, 1872; (*b*) C. R. Horn, J. M. Martín-Alvarez and J. A. Gladysz, *Organometallics*, 2002, **21**, 5386.

22 D. J. Hoffart and S. J. Loeb, unpublished results.

23 D. J. Hoffart and S. J. Loeb, *Angew. Chem. Int. Ed.*, 2005, **117**, 901.

24 (*a*) J.-R. Li, X.-H. Bu and R.-H. Zhang, *Inorg. Chem.*, 2004, **43**, 237; (*b*) X.-H. Bu, W. Weng, W. Chen and R.-H. Zhang, *Inorg. Chem.*, 2002, **41**, 413.

25 G. J. E. Davidson and S. J. Loeb, *Dalton Trans.*, 2003, 4319.

26 G. J. E. Davidson and S. J. Loeb, unpublished results.

27 Ball-and-stick and space filling diagrams were prepared using DIAMOND 3.0 – Visual Crystal Structure Information System CRYSTAL IMPACT, Postfach 1251, D-53002 Bonn.