

This is the peer-reviewed version of the following article:

N. H. Evans, Lanthanide-Containing Rotaxanes, Catenanes and Knots,

*ChemPlusChem*

DOI: 10.1002/cplu.202000135.

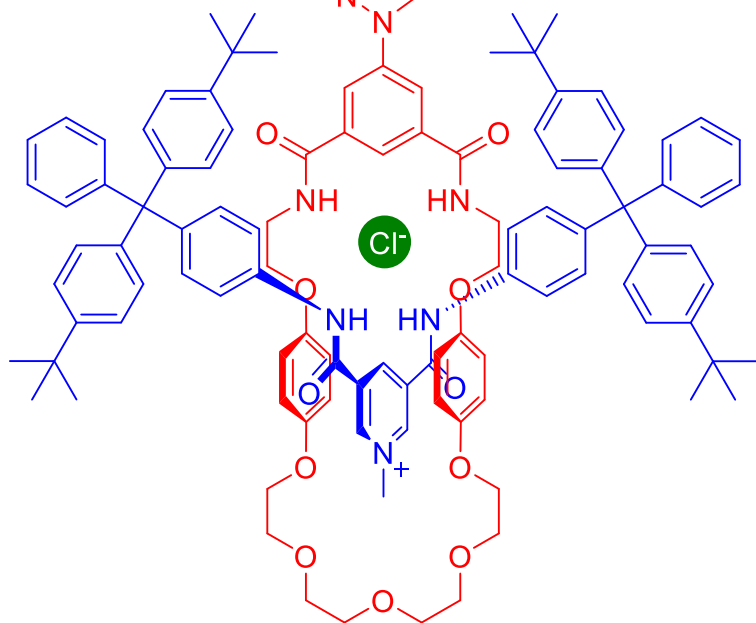
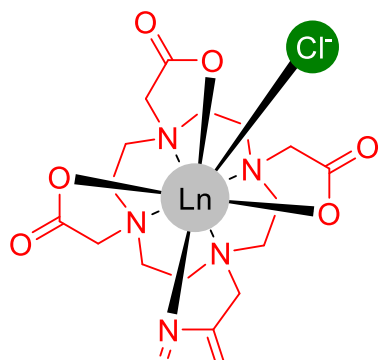
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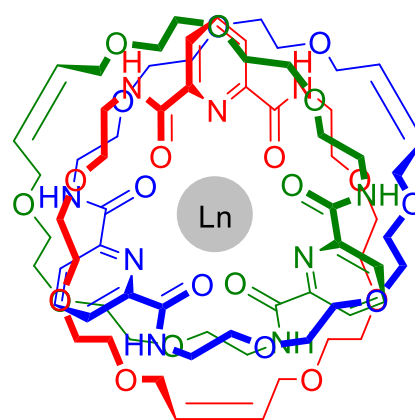
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# Lanthanide-Containing Rotaxanes, Catenanes and Knots

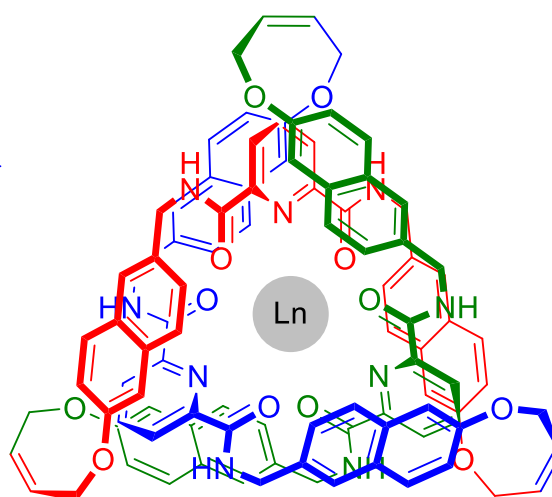
Nicholas H. Evans\*<sup>[a]</sup>



**ROTAXANES**



**CATENANES**



**KNOTS**

**Abstract:** The valuable luminescence, magnetic and catalytic properties of lanthanide cations are beginning to be exploited in conjunction with structurally exotic mechanically interlocked molecules (MIMs) such as rotaxanes, catenanes and knots. This mini-review provides an account of this rapidly developing research area commencing with the use of lanthanides in extended MIM containing frameworks. Then, attention turns to discrete lanthanide-containing pseudorotaxanes, followed by fully interlocked rotaxanes, catenanes and knots – where lanthanides have not only been incorporated into MIM architectures but have also been used to template formation of the interlocked structure. Particular focus is paid to examples where the lanthanide MIMs have been put to useful application, in what is still a relatively youthful avenue of research in both lanthanide coordination chemistry and the chemistry of mechanically interlocked molecules.

## 1. Introduction

Coordination complexes of lanthanide cations may be found in a range of applications, perhaps most notably as cellular imaging agents and responsive bioprobes.<sup>[1]</sup> For example, by use of well-chosen sensitizing chromophores, Ln(III) cations may be excited so that they then emit in the visible (e.g. Ln = Eu, Tb) or near-infrared (e.g. Ln = Nd, Yb) regions of the electromagnetic spectrum.<sup>[2]</sup> The Laporte forbidden nature of the *f-f* transitions leads to long lifetimes for the Ln(III) excited states, which allows for time-gated microscopy to remove interfering cellular autofluorescence. Furthermore, the narrow line-like bands of the Ln(III) emission spectra open up the possibility of deploying ratiometric measurements in cases of complexes that act as responsive probes.

Complexes of the highly paramagnetic  $4f^7$  Gd(III) cation are, of course, well-established in magnetic resonance imaging (MRI).<sup>[3]</sup> These traditional contrast agents improve the sensitivity of the technique by shortening the  $T_1$  and  $T_2$  relaxation times. More recently, lanthanide coordination complexes have been developed for alternative MRI techniques including PARACEST<sup>[4]</sup> and PARASHIFT.<sup>[5]</sup>

Lanthanide complexes have also proved useful as Lewis acids in the field of asymmetric catalysis.<sup>[6]</sup> The larger size of Ln(III) cations, compared to most other metal cations, permits for coordination of more sophisticated 3D chiral ligands whilst maintaining a degree of unsaturation at the metal centre, thus allowing the lanthanide cation to retain Lewis acid character.

Mechanically interlocked molecules (often abbreviated to MIMs),<sup>[7]</sup> such as rotaxanes,<sup>[8]</sup> catenanes<sup>[9]</sup> and knots<sup>[10]</sup> were once considered synthetic chemical curiosities but are increasingly being turned toward useful application.<sup>[11]</sup> The opportunities offered in the construction of molecular machines by the relative motion of the constituent parts of rotaxanes and catenanes has been recognized by the award of the 2016 Nobel Prize in Chemistry.<sup>[12]</sup> Transition metals<sup>[13]</sup> have been widely used as (passive<sup>[14]</sup> and active<sup>[15]</sup>) templates – alongside other templating interactions such as  $\pi$ - $\pi$  donor-acceptor interactions<sup>[16]</sup> and hydrogen bonding<sup>[17]</sup> in the construction of MIMs. In comparison, the use of lanthanide cations as templates for MIM synthesis is a much more recent development. Indeed, even incorporating lanthanide cations within MIMs has only been realized in the last decade or so. Nevertheless, the rapid pace of developments in this field warrants the writing of this mini-review.<sup>[18]</sup> In addition to discussion of synthetic progress, particular attention will be paid to where the prepared MIMs have been put to useful application.

Nick Evans graduated from Wadham College, University of Oxford with a First Class Masters in Chemistry (2006), before obtaining a DPhil in Inorganic Chemistry (2011), having worked on anion sensing rotaxanes and catenanes in the group of Prof Paul Beer. After undertaking postdoctoral research on chiral luminescent lanthanide complexes with Prof David Parker at Durham University, he became a lecturer at the newly re-opened Department of Chemistry at Lancaster University in 2013. His current research interests include both mechanically interlocked molecules and lanthanide coordination chemistry.



*This mini-review arises from my current research interest in lanthanide-containing interlocked molecules, which builds upon my experience working in the groups of Prof Paul Beer and Prof David Parker. Both Paul and David were inspirational mentors: I am very fortunate to have had the opportunity to work on world leading chemistry in their labs, where I was well-supported, both scientifically and pastorally.*

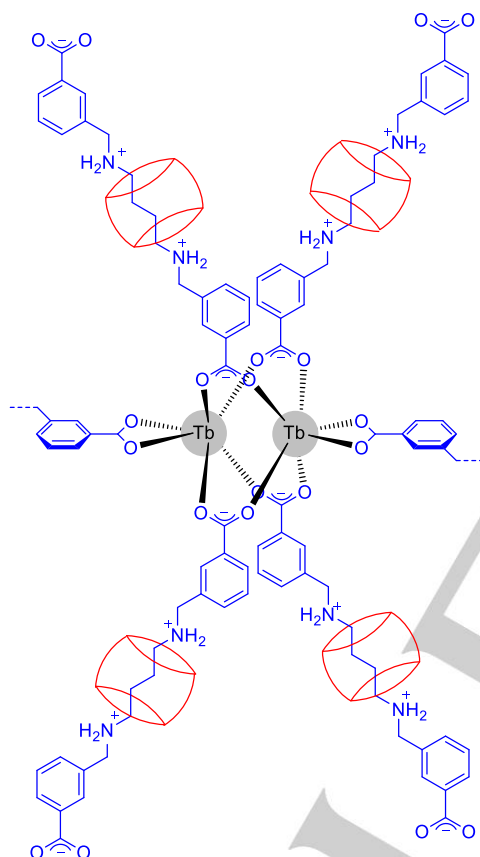
## 2. Lanthanides as Nodes in Metal Organic Frameworks (MORFs)

Whilst perhaps falling out of the principal focus of this review, it is felt appropriate to highlight the use of lanthanides as “nodes” in metal organic rotaxane frameworks (MORFs)<sup>[19]</sup> – in particular as much of this work pre-dates the incorporation of lanthanides in discrete MIMs.

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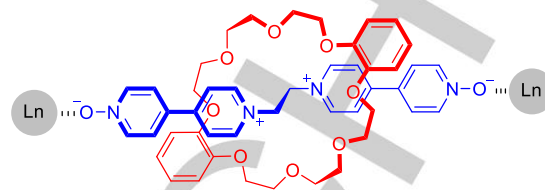
In 2000, Kim and co-workers reported the first use of Ln(III) cations as nodes in metal organic rotaxane frameworks (Figure 1).<sup>[20]</sup> Pseudorotaxane units containing cucurbiturils threaded upon *N,N*-bis(3-cyanobenzyl)-1,4-diammoniumbutane axes were treated with Tb(NO<sub>3</sub>)<sub>3</sub> to produce what was also the first 3D polyrotaxane network - previous efforts with transition metals having led solely to 2D networks. The basic building unit of the framework consists of a binuclear Tb(III) centre and six pseudorotaxane units. Under the reaction conditions the nitrile groups of the axes hydrolyze to form carboxylate groups that can coordinate to the Tb(III) cations.



**Figure 1.** Basic framework building unit in Kim's 3D lanthanide MORF (cucurbituril macrocycles are represented in red; coordinated water molecules not depicted for clarity).

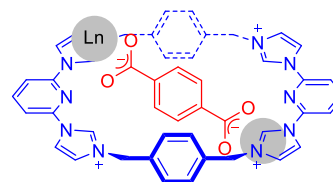
Subsequently, Hoffart and Loeb constructed MORFs with Ln(III) nodes by using a pseudorotaxane unit consisting of dibenzo-24-crown-8 ether threaded upon the bis-*N*-oxide of (4,4'-bipyridinium)ethane (Figure 2).<sup>[21]</sup> With Sm, Eu, Gd and Tb, the Ln(III) cation is found to be eight coordinate, with a square antiprismatic geometry consisting of six [2]rotaxane ligands, one water molecule and one coordinated triflate anion. Switching to the smaller Yb, yields an alternative structure: seven coordinate pentagonal bipyramid at Ln(III), with five *N*-oxide rotaxanes

occupying the equatorial positions, plus one of the axial sites (the other being occupied by a triflate counter-anion).



**Figure 2.** Pseudorotaxane unit found in Loeb's lanthanide MORFs.

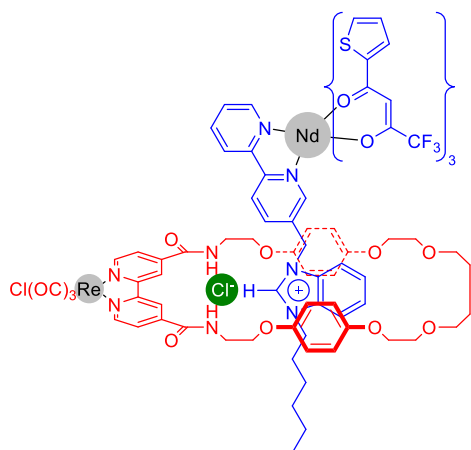
Sessler and co-workers have also reported upon the structures of MORFs and RSOFs (rotaxanated supramolecular organic frameworks) derived from a tetracationic macrocycle, terephthalate di-anion and Ln(III) cations (Figure 3).<sup>[22, 23]</sup> With larger lanthanide cations, a range of MORFs were prepared, with good correlation between the observed coordination number of the lanthanide and its ionic radius: Nd(III) (the largest) had two distinct 9 coordinate coordination geometries, Eu(III) one 9 coordinate, one 8 coordinate, while both Sm(III) and Tb(III) had two 8 coordinate. Notably, the Eu MORF exhibits bright visible fluorescence, that masks a background band arising from the macrocycle and terephthalate anion. In contrast, with smaller rare earth metal cations – Y(III), Gd(III), Er(III), Tm(III) and Lu(III) – essentially identical RSOFs were generated, where each lanthanide cation is 8 coordinate.



**Figure 3** Example of pseudorotaxane unit found in Sessler's lanthanide RSOFs and MORFs (NB: carboxylates of interpenetrated terephthalates are either mono- or bidentate depending on identity of lanthanide cation).

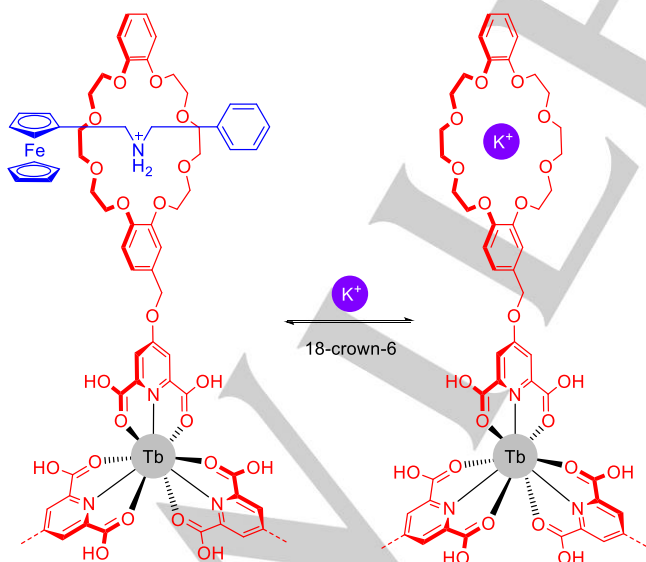
### 3. Lanthanide Pseudorotaxanes

In 2006, Beer and Faulkner reported the chloride anion templated assembly of a pseudorotaxane consisting of a Re(I) bipyridyl macrocycle and Ln(III) appended (benzo)imidazolium axle components (Figure 4).<sup>[24]</sup> Excitation of Re(I) and energy transfer from its <sup>3</sup>MLCT donor state to the Nd(III) or Yb(III) cation allows for near infrared emission from the lanthanide centre. Due to the 1/*r*<sup>6</sup> distance dependency of the Forster energy transfer process this can only occur for the assembled pseudorotaxane.



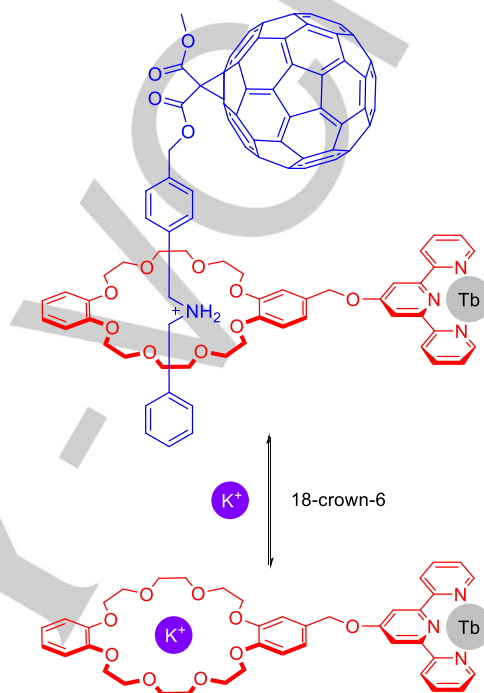
**Figure 4.** Example of chloride templated pseudorotaxane reported by Beer and Faulkner, that exhibits Förster energy transfer from Re(I) to Ln(III).

In a series of papers, Liu and co-workers have reported upon pseudorotaxane assemblies that exhibit switchable lanthanide luminescence.<sup>[25-27]</sup> In first instance they prepared a tris-dipicolinic acid complex of Tb(III), where each sensitizing ligand was appended with dibenzo-24-crown-8 (Figure 5).<sup>[25]</sup> Hydrogen bond supported threading of a ferrocene appended ammonium axle component through the crown ether leads to quenching of the terbium fluorescence. Addition of potassium cations restores lanthanide emission through displacement of the ferrocene/ammonium axle from the dibenzo-24-crown-8. This may be subsequently reversed by addition of 18-crown-6 to complex  $K^+$  and to allow re-threading of the axle component.



**Figure 5.** Liu's ferrocene quenching pseudorotaxane system.

In their second paper, the dibenzo-24-crown-8 was appended to a terpyridine moiety for binding to Tb(III), and the ammonium axle contained a  $C_{60}$  fullerene (Figure 6).<sup>[26]</sup> As before, threading of the axle leads to quenching of terbium fluorescence (due to the close proximity of the fullerene), that may be restored and re-quenched by addition of  $K^+$  and 18-crown-6 respectively.



**Figure 6.** Liu's fullerene quenching pseudorotaxane system.

Subsequently the same laboratory reported a more elaborate system where the axle component possess a diarylperfluorocyclopentene unit (Figure 7).<sup>[27]</sup> Formation of the pseudorotaxane leads to very modest quenching of the emission from the complexed Eu(III) cation. But exposure to 365 nm UV light leads to cyclization of the threaded diarylperfluorocyclopentene, and the excited Eu(III) cation acts as a donor, resulting in complete quenching of lanthanide emission whilst maintaining the pseudorotaxane assembly. This process may be reversed by exposure to 614 nm light, which leads to ring opening and restoration of the original diarylperfluorocyclopentene structure. Significantly, the system can be cycled multiple times by alternating UV and visible light. Once again, the fluorescence of this system may also be modulated by addition of potassium ions and 18-crown-6 mediating dethreading and threading events.

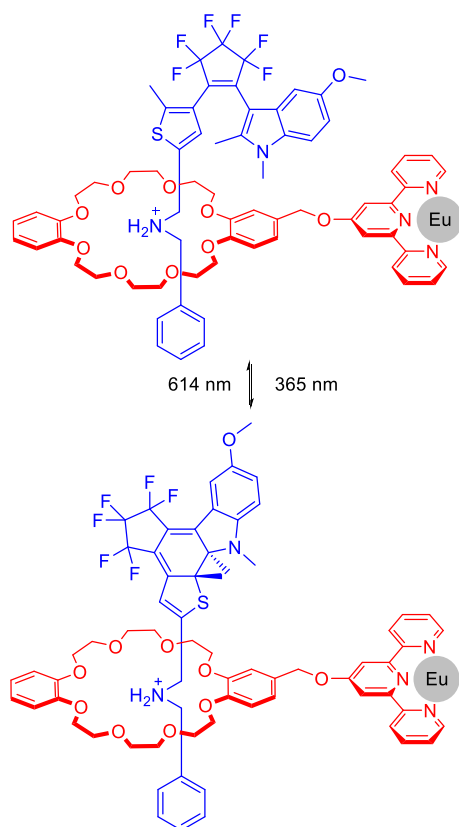


Figure 7. Liu's light modulated pseudorotaxane system.

#### 4. Lanthanide Rotaxanes

Discrete fully interlocked lanthanide rotaxanes have been investigated by the research team led by Beer and Faulkner.<sup>[28-30]</sup> In their first reported example, a lanthanide complex of propargyl DO3A (1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid) was attached by use of the CuAAC “click” reaction to an azido chloride templated rotaxane (Figure 8).<sup>[28]</sup> The resulting europium rotaxane exhibits chloride responsive luminescence in dichloromethane consistent with two independent binding sites – one on the lanthanide cation, the other in the rotaxane cavity. While chloride binding to Eu(III) leads to an initial quenching of the overall intensity of emission, subsequent binding in the rotaxane pocket leads to some restoration.

The first lanthanide templated fully interlocked molecule was reported almost contemporaneously by the group of Beer (Figure 9).<sup>[29]</sup> Incorporating a DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) cyclen into the macrocyclic structural framework, allows for generation of lanthanide macrobicycles (Ln = Lu, Eu). A pyridine-*N*-oxide axle precursor threaded through the metallated bimacrocyclic may be stoppered by the CuAAC “click” reaction in 20% yield. For the Eu(III) rotaxane, luminescence decay lifetime measurements in 1:1 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH and 1:1 CD<sub>2</sub>Cl<sub>2</sub>:CD<sub>3</sub>OD were used to calculate a tentative value of  $q = 0$

for the number of inner sphere solvent molecules bound to the lanthanide cation.

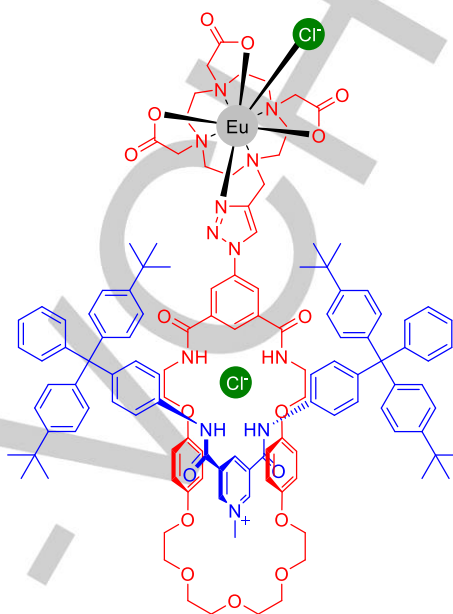


Figure 8. Beer and Faulkner's Eu(III) appended rotaxane responsive to chloride binding at Eu(III) and in the rotaxane cavity.

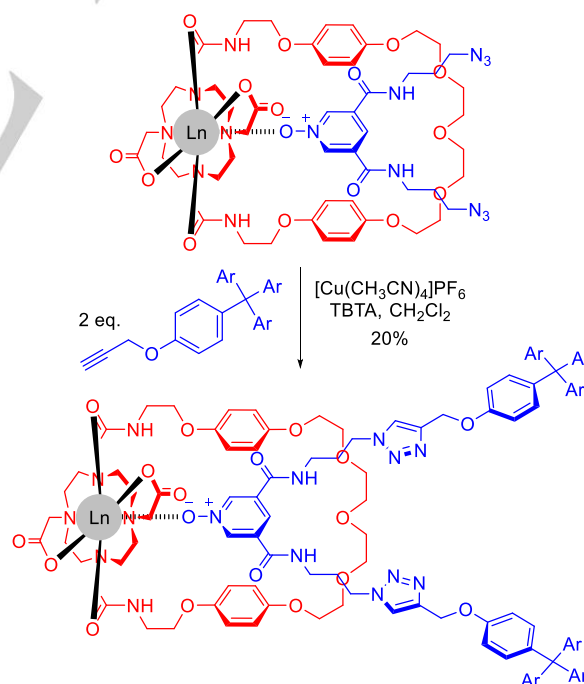
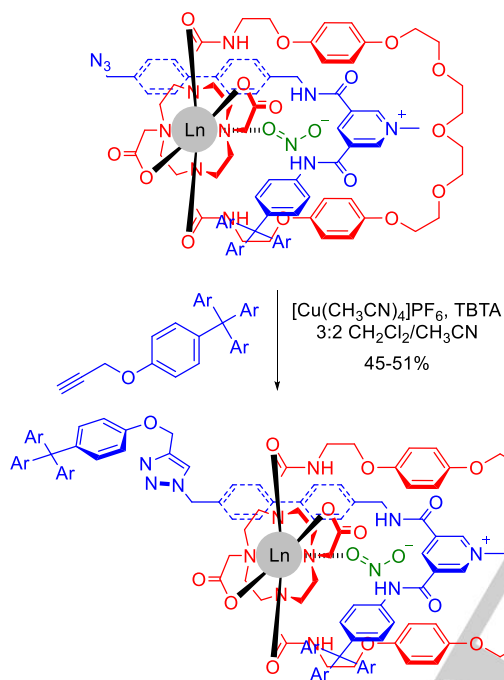


Figure 9. Synthesis of Beer's seminal lanthanide templated rotaxane.

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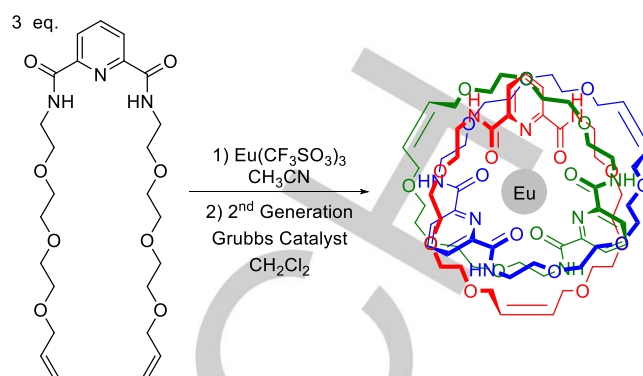
Subsequently Beer and Faulkner, described rotaxanes prepared by stoppering a methyl pyridinium axle threaded through the same macrobicyclic by use of a nitrite anion template, in significantly higher yields of 45-51% (Figure 10).<sup>[30]</sup> Notably, the use of chloride in place of nitrite, led only to trace formation of rotaxane. Upon anion exchange, the rotaxane was found - perhaps not surprisingly - to strongly bind fluoride, but interestingly more strongly than the non-interlocked lanthanide macrobicyclic. However, fluoride itself proved unable to template rotaxane formation.



**Figure 10.** Synthesis of Beer and Faulkner's lanthanide / nitrite templated rotaxane.

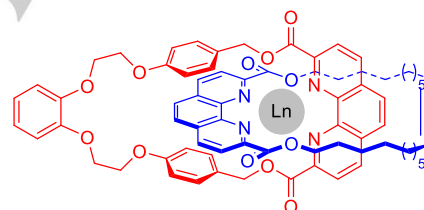
## 5. Lanthanide Catenanes

Gunnlaugsson and co-workers reported upon a study to use three equivalents of a 2,6-pyridinedicarboxamide ligand to achieve the lanthanide templated synthesis of a [3]catenane (Figure 11).<sup>[31]</sup> The researchers successfully prepared and characterized the Eu(III) precursor complex in solution. This was then subjected to Grubbs catalyzed ring closing metathesis (RCM) conditions at high dilution. After work-up, both metal-free and metallated ring-closed products were isolated. NMR and mass spectral analysis indicated the metal-free product was either a [3]catenane or knot. Mass spectral analysis of the Eu(III) containing material indicated the presence of the desired [3]catenane and a [2]catenane by-product.



**Figure 11.** Gunnlaugsson's synthesis of a lanthanide templated [3]catenane.

Very recently, Ghosh and co-workers have prepared a [2]catenane and studied its ability to bind lanthanide cations within its interlocked cavity (Figure 12).<sup>[32]</sup> The catenane was prepared by Sauvage-style passive Cu(I) cation templation in conjunction with Grubbs catalyzed RCM. Following removal of the Cu(I) template, complexes of the catenane with Eu(III), Gd(III) and diamagnetic Y(III) were then prepared. In the <sup>1</sup>H NMR spectrum of the Y(III) complex, downfield shifts of the phenanthroline proton environments are observed, imply binding of the rare earth cations at the phenanthroline N atoms.



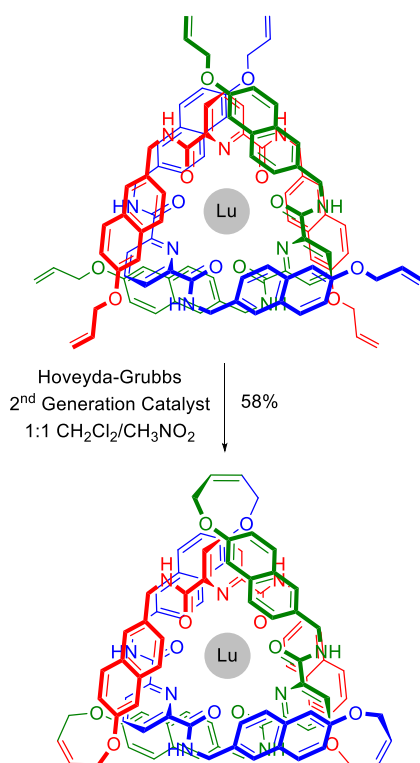
**Figure 12.** Ghosh's lanthanide binding [2]catenane.

## 6. Lanthanide Knots

Significant progress has been made in the preparation and chemical utilization of lanthanide templated knots, as reported by Leigh and co-workers.<sup>[33-37]</sup> This laboratory's first example of a lanthanide templated knot involved cyclizing three equivalents of a 2,6-pyridinedicarboxamide ligand around a Ln(III) cation (Figure 13).<sup>[33]</sup> In their system, careful design of the ligand introduced inter-ligand  $\pi$ - $\pi$  stacking in the precursor complex to arrange the end-groups such that cyclization would lead to the knot rather than unknotted macrocycle. RCM cyclization of the Lu(III) precursor complex (which in the case of the analogous Eu(III) complex had been characterized in the solid state by single crystal X-ray structure determination) led to production of two species in ~7:3 ratio. After work-up (using the chelating agent pentasodium diethylenetriaminepentaacetate, Na<sub>5</sub>DPTA), the major product (in 58% isolated yield) was identified by NMR and mass spectral analysis to be the target metallated trefoil knot, the

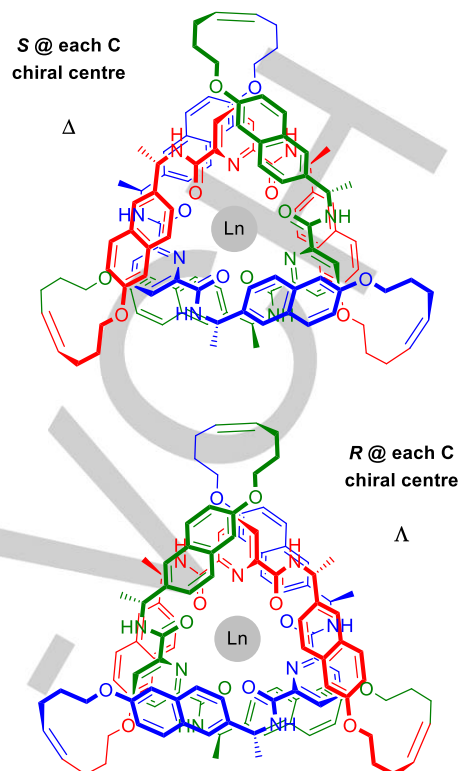
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minor product (in 17% yield) being the demetallated unknotted macrocycle isomer. It proved possible to demetallate the knot by use of tetraethylammonium fluoride.



**Figure 13.** Synthesis of Leigh's first lanthanide templated trefoil knot.

By inclusion of point chirality in the 2,6-pyridinedicarboxamide ligand, it proves possible to set the helical chirality of the resulting 3:1 ligand metal complex, and hence the helical chirality of the resulting trefoil knot (Figure 14).<sup>[34]</sup> Use of (*R, R*) ligand leads to a knot of  $\Delta$ -handedness and use of (*S, S*) ligand leads to a knot of  $\Lambda$ -handedness, as confirmed by X-ray crystallography. The ligands do not self-sort, i.e. solutions of racemic ligands form statistical mixtures of homoleptic and heteroleptic lanthanide complexes. Study by circular dichroism of the demetallated knots and their unknotted macrocyclic isomers, reveals that topological stereochemistry has a much greater influence on the asymmetry of the chromophore environment than the asymmetric carbon centres.



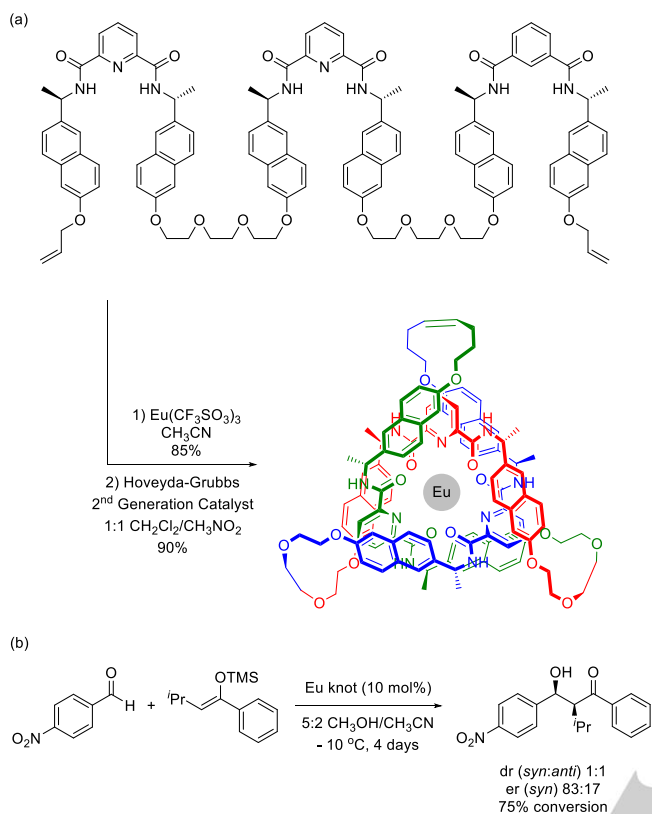
**Figure 14.** Control of helical chirality in lanthanide templated trefoil knots arising from point chirality in the precursor ligand.

Subsequently it was demonstrated that an enantiopure trefoil knot may be prepared in excellent yield by use of a single ligand containing three 2,6-pyridinedicarboxamides (Figure 15a).<sup>[35]</sup> The metallated pseudo-*D*<sub>3</sub>-symmetric  $\Lambda$  knot was then used as an asymmetric catalyst in Mukaiyama aldol reactions, with enantioselectivities of up to 83:17 er being observed (Figure 15b). Luminescence decay lifetime analysis in MeOH and MeOD, allowed for calculation of a value of  $q \sim 1$ , indicating the lanthanide cation may be accessible to the aldehyde substrate.

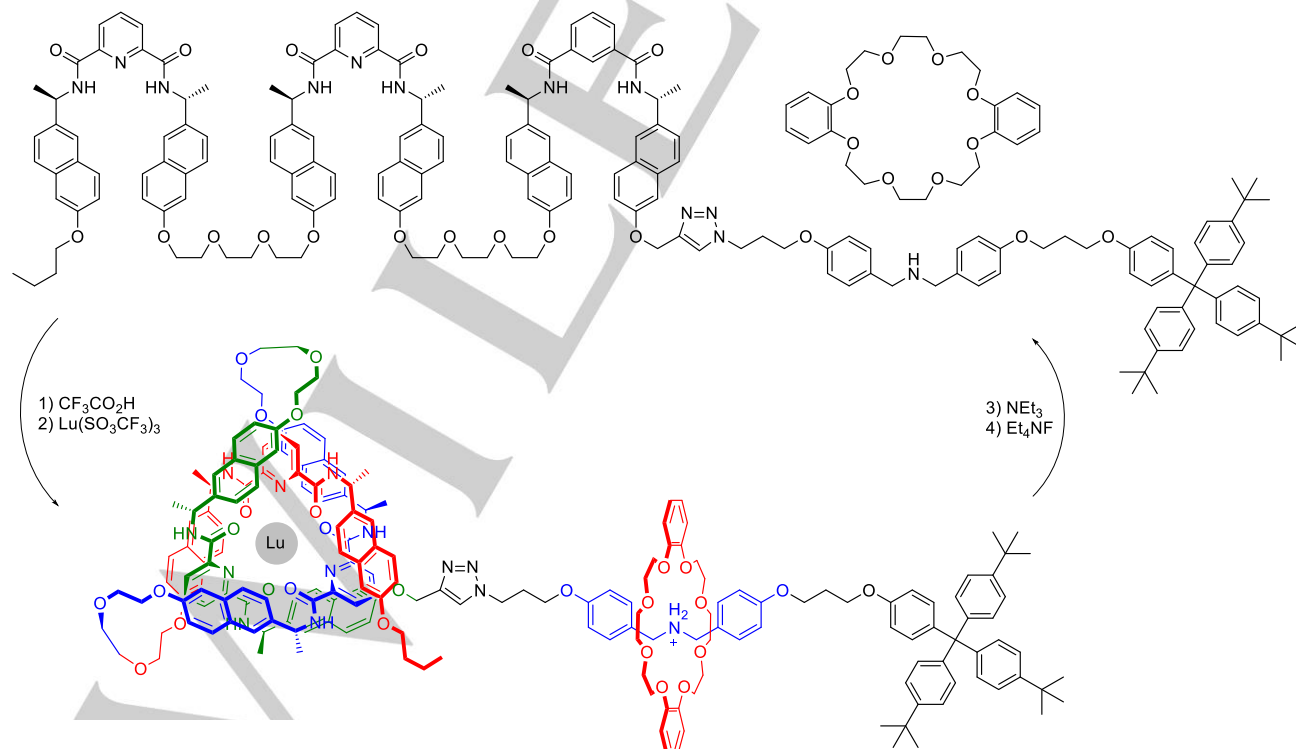
In a fascinating demonstration, incorporation of a tris(2,6-pyridyldicarboxamide) into an axle component of a rotaxane allows for the stoppering of the rotaxane by addition of Lu(III) cations (Figure 16).<sup>[36]</sup> Even after deactivation of the templating site (by deprotonation of a secondary ammonium) the macrocycle remains trapped on the axle. Untying of the knot – by use of tetraethylammonium fluoride – allows for dethreading of the macrocycle from the deprotonated axle.



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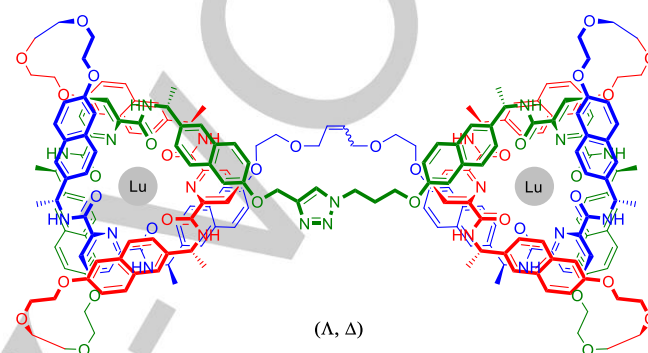


**Figure 15.** Lanthanide templated trefoil knot from a single strand ligand: (a) synthesis and (b) acting as an asymmetric catalyst in Mukaiyama aldol reactions.



**Figure 16.** Reversible stopping of a rotaxane by tying/untying a lanthanide trefoil knot.

The Leigh group has also reported upon the preparation of square and granny knots.<sup>[37]</sup> These were assembled by use of lanthanide complexed overhand knots of specific handedness, termed “entanglement synthons”. To prepare the target knots, appropriate entanglement synthons were first joined at one end by use of the CuAAC “click” reaction, then at the other end by Grubbs catalyzed RCM. The resulting composite knots can then be demetallated. If the two entangled synthons employed are of the same chirality a granny knot is isolated, whereas opposite handedness yields a square knot (as depicted in Figure 17).

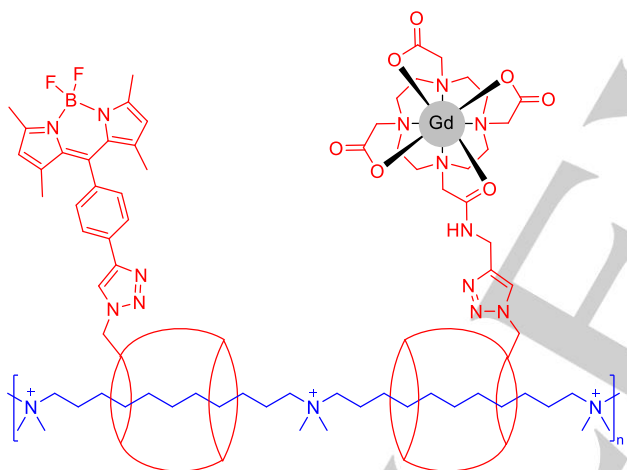


**Figure 17.** Lanthanide templated square knot.

## 7. An Application Case Study: Lanthanide Rotaxanes and Polyrotaxanes for Magnetic Resonance Imaging

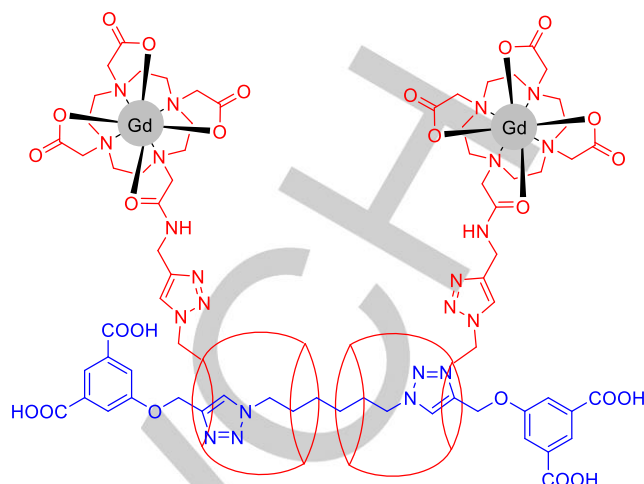
While chemical applications of lanthanide MIMs, e.g. in ion sensing and catalysis, have already been highlighted, the demonstration of a broader scientific and/or real-world application would underline the potential of lanthanide MIMs. Arguably, this is provided by work that involves incorporation of kinetically stable Gd(III) complexes into (poly)rotaxane structures for magnetic resonance imaging (MRI).<sup>[38-40]</sup>

For example, Vives, Hasenkopf and co-workers prepared cyclodextrin (CD) polyrotaxanes where each CD threaded upon a polymeric alkylammonium axle component is functionalized with either a Gd-DOTA derivative or fluorescent bodipy fragment to generate a target bimodal imaging agent (Figure 18).<sup>[38]</sup> The measured molar relaxivities for all the polyrotaxane samples prepared were greater than for the widely used Gd-DOTA, consistent with less rapid “tumbling” of the larger polyrotaxanes in solution. In principle, these increases in relaxivity should lead to a greater contrast in magnetic resonance images.



**Figure 18.** Representative structure of section of cyclodextrin polyrotaxane designed to be a bimodal imaging agent (simplified cyclodextrin macrocycles are represented in red for clarity).

While in this approach each threaded CD is molecularly defined, the threading is statistical and there is the potential for so-called “mechanicostereoisomers”. Also, the polyrotaxanes proved to be highly toxic, and so could not be used *in vivo*. To overcome these issues the same researchers looked at preparing simpler [3]rotaxanes (Figure 19).<sup>[39]</sup> These were constructed by stoppering pseudorotaxanes consisting of two “head-to-head” CD macrocycles functionalized with Gd complexes threaded upon a C<sub>12</sub> alkyl axle. In this case, *in vivo* studies could be undertaken in mice, with enhanced contrast and retention in the kidneys compared to Gd-DOTA.



**Figure 19.** Cyclodextrin [3]rotaxane MRI contrast agent (simplified cyclodextrin macrocycles are represented in red for clarity).

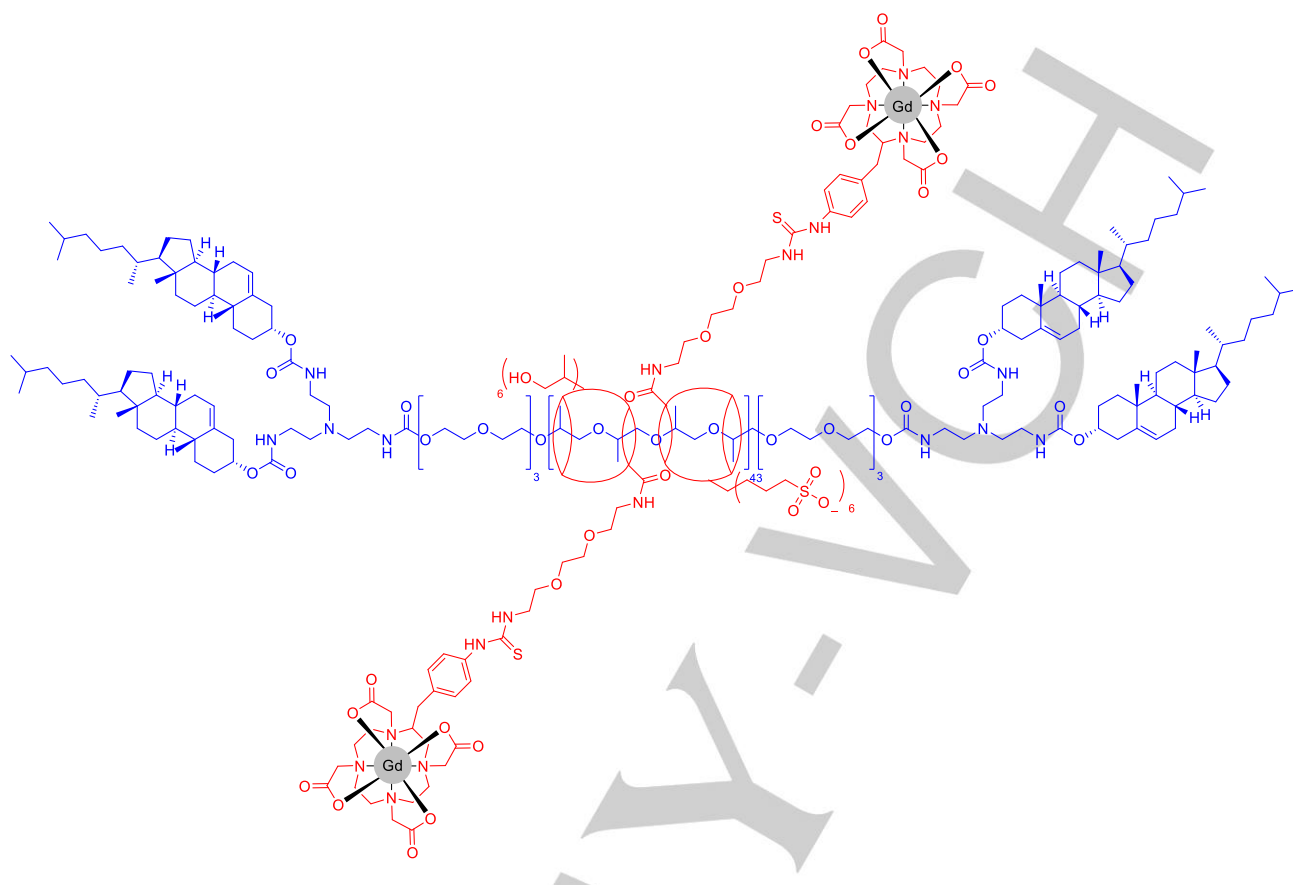
Separately, Thompson and co-workers have produced and studied a family of five water soluble CD polyrotaxanes, where the CD macrocycles have also been appended with Gd-DOTA derivatives (Figure 20).<sup>[40]</sup> When injected into mice, the polyrotaxanes exhibited increased T<sub>1</sub>-weighted MRI intensities compared to Gd-DOTA – consistent with less rapid solution “tumbling” of the larger polyrotaxanes.

## 8. Conclusions

It is apparent from this mini-review that the field of lanthanide MIMs is still in its infancy. To date much of the focus has been on simply preparing the MIMs rather than studying and exploiting their properties. However, the potential of lanthanide MIMs is clearly demonstrated by receptor rotaxanes, catalytic knots, and in particular (poly)rotaxanes for MRI. Considering the many synthetic methodologies to prepare interlocked molecules and the potential to append simple lanthanide complexes to MIMs, possibly the key synthetic challenge is to optimize purification of lanthanide-containing MIMs. In terms of applications, one can foresee exploitation of further properties arising from the mechanical bond, including the stimulus controlled, large amplitude molecular motion of interlocked components. These and other developments in lanthanide MIMs are warmly anticipated in the coming years.

## Acknowledgements

N. H. E. wishes to thank the Royal Society for funding of investigations into new lanthanide supramolecular assemblies (Research Grant: RGS/R2/180227).



**Figure 20.** An example of Thompson's cyclodextrin polyrotaxanes deployed as MRI contrast agents (simplified cyclodextrin macrocycles are represented in red for clarity).

**Keywords:** catenanes • knots • lanthanides • rotaxanes • template synthesis

- [1] a) E. Mathieu, A. Sipos, E. Demeyere, D. Phipps, D. Sakaveli, K. E. Borbas, *Chem. Commun.* **2018**, 54, 10021-10035; b) A. J. Amoroso, S. J. A. Pope, *Chem. Soc. Rev.* **2015**, 44, 4723-4742; c) M. C. Heffern, L. M. Matosziuk, T. J. Meade, *Chem. Rev.* **2014**, 114, 4496-4539.
- [2] a) J.-C. G. Bünzli, C. Piguët, *Chem. Soc. Rev.* **2005**, 34, 1048-1077; b) S. Shinoda, H. Tsukube, *Analyst* **2011**, 136, 431-435; c) S. J. Butler, D. Parker, *Chem. Soc. Rev.* **2012**, 42, 1652-1666; d) S. H. Hewitt, S. J. Butler, *Chem. Commun.* **2018**, 54, 6635-6647; e) Y. Ning, M. Zhu, J.-L. Zhang, *Coord. Chem. Rev.* **2019**, 399, 213028.
- [3] a) P. Caravan, *Chem. Soc. Rev.* **2006**, 35, 512-523; b) T. J. Clough, L. Jiang, K.-L. Wong, N. J. Long, *Nat. Commun.* **2019**, 10, 1420. c) J. Wahsner, E. M. Gale, A. Rodríguez-Rodríguez, P. Caravan, *Chem. Rev.* **2019**, 119, 957-1057.
- [4] M. Woods, D. E. Woessner, A. D. Sherry, *Chem. Soc. Rev.* **2006**, 35, 500-511.
- [5] A. C. Harnden, D. Parker, N. J. Rogers, *Coord. Chem. Rev.* **2019**, 383, 30-42.
- [6] a) K. Mikami, M. Terada, H. Matsuzawa, *Angew. Chem. Int. Ed.* **2002**, 41, 3554-3572; b) M. Shibasaki, N. Yoshikawa, *Chem. Rev.* **2002**, 102, 2187-2209; c) H. Pellissier, *Coord. Chem. Rev.* **2017**, 336, 96-151.
- [7] a) D. Sluysmans, J. F. Stoddart, *Trends in Chemistry* **2019**, 1, 185-197; b) C. J. Bruns, J. F. Stoddart, *The Nature of the Mechanical Bond: From Molecules to Machines*, Wiley & Sons, Hoboken, 2017.
- [8] M. Xue, Y. Yang, X. Chi, X. Yan, F. Huang, *Chem. Rev.* **2015**, 115, 7398-7501.
- [9] a) G. Gil-Ramírez, D. A. Leigh, A. J. Stephens, *Angew. Chem. Int. Ed.* **2015**, 54, 6110-6150; b) N. H. Evans, P. D. Beer, *Chem. Soc. Rev.* **2014**, 43, 4658-4683.
- [10] a) S. D. P. Fielden, D. A. Leigh, S. L. Woltering, *Angew. Chem. Int. Ed.* **2017**, 56, 11166-11194; b) K. E. Horner, M. A. Miller, J. W. Steed, P. M. Sutcliffe, *Chem. Soc. Rev.* **2016**, 45, 6432-6448.
- [11] a) S. F. M. van Dongen, S. Cantekin, J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, *Chem. Soc. Rev.* **2014**, 43, 99-122; b) N. Pairault, R. Barat, I. Tranoy-Opalinski, B. Renoux, M. Thomas, S. Papot, *C. R. Chim.* **2016**, 19, 103-112.
- [12] a) J.-P. Sauvage, *Angew. Chem. Int. Ed.* **2017**, 56, 11080-11093; b) J. F. Stoddart, *Angew. Chem. Int. Ed.* **2017**, 56, 11094-11125; c) B. L. Feringa, *Angew. Chem. Int. Ed.* **2017**, 56, 11060-11078.
- [13] J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh, R. T. McBurney, *Angew. Chem. Int. Ed.* **2011**, 50, 9260-9327.
- [14] a) J.-P. Sauvage, *Acc. Chem. Res.* **1990**, 23, 319-327; b) J.-C. Chambron, J.-P. Collin, V. Heitz, D. Jouvenot, J.-M. Kern, P. Mobian, D. Pomeranc, J.-P. Sauvage, *Eur. J. Org. Chem.* **2004**, 1627-1638.
- [15] a) J. D. Crowley, S. M. Goldup, A.-L. Lee, D. A. Leigh, R. T. McBurney, *Chem. Soc. Rev.* **2009**, 38, 1530-1541; b) M. Denis, S. M. Goldup, *Nat. Rev. Chem.* **2017**, 1, 0061.

## MINIREVIEW

- [16] G. Barin, A. Coskin, M. M. G. Fouda, J. F. Stoddart, *ChemPlusChem* **2012**, *77*, 159-185.
- [17] N. H. Evans, *Eur. J. Org. Chem.* **2019**, 3320-3343.
- [18] Some of the early work in this area has featured in a wider review on luminescent lanthanide supramolecular assemblies: J. Lehr, P. D. Beer, S. Faulkner, J. J. Davis, *Chem. Commun.* **2014**, *50*, 5678-5687.
- [19] S. J. Loeb, *Chem. Commun.* **2005**, 1511-1518.
- [20] E. Lee, J. Heo, K. Kim, *Angew. Chem. Int. Ed.* **2000**, *39*, 2699-2701.
- [21] D. J. Hoffart, S. J. Loeb, *Angew. Chem. Int. Ed.* **2005**, *44*, 901-904.
- [22] H.-Y. Gong, B. M. Rambo, C. A. Nelson, W. Cho, V. M. Lynch, X. Zhu, M. Oh, J. L. Sessler, *Dalton Trans.* **2012**, *41*, 1134-1137.
- [23] H.-Y. Gong, B. M. Rambo, C. A. Nelson, V. M. Lynch, X. Zhu, J. L. Sessler, *Chem. Commun.* **2012**, *48*, 10186-10188.
- [24] M. R. Sambrook, D. Curiel, E. J. Hayes, P. D. Beer, S. J. A. Pope, S. Faulkner, *New J. Chem.* **2006**, *30*, 1133-1136.
- [25] M. Han, H.-Y. Zhang, L.-X. Yang, Q. Jiang, Y. Liu, *Org. Lett.* **2008**, *10*, 5557-5560.
- [26] Z.-J. Ding, Y.-M. Zhang, X. Teng, Y. Liu, *J. Org. Chem.* **2011**, *76*, 1910-1913.
- [27] H.-B. Cheng, H.-Y. Zhang, Y. Liu, *J. Am. Chem. Soc.* **2013**, *135*, 10190-10193.
- [28] C. Allain, P. D. Beer, S. Faulkner, M. W. Jones, A. M. Kenwright, N. L. Kilah, R. C. Knighton, T. J. Sørensen, M. Tropicano, *Chem. Sci.* **2013**, *4*, 489-493.
- [29] F. Zapata, O. A. Blackburn, M. J. Langton, S. Faulkner, P. D. Beer, *Chem. Commun.* **2013**, *49*, 8157-8159.
- [30] M. J. Langton, O. A. Blackburn, T. Lang, S. Faulkner, P. D. Beer, *Angew. Chem. Int. Ed.* **2014**, *53*, 11463-11466.
- [31] C. Lincheneau, B. Jean-Denis, T. Gunnlaugsson, *Chem. Commun.* **2014**, *50*, 2857-2860.
- [32] M. Nandi, S. Bej, T. K. Ghosh, P. Ghosh, *Chem. Commun.* **2019**, *55*, 3085-3088.
- [33] J.-F. Ayme, G. Gil-Ramírez, D. A. Leigh, J.-F. Lemonnier, A. Markevicius, C. A. Muryn, G. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 13142-13145.
- [34] G. Zhang, G. Gil-Ramírez, A. Markevicius, C. Browne, I. J. Vitorica-Yrezabal, D. A. Leigh, *J. Am. Chem. Soc.* **2015**, *137*, 10437-10442.
- [35] G. Gil-Ramírez, S. Hoekman, M. O. Kitching, D. A. Leigh, I. J. Vitorica-Yrezabal, G. Zhang, *J. Am. Chem. Soc.* **2016**, *138*, 13159-13162.
- [36] D. A. Leigh, L. Pirvu, F. Schaufelberger, D. J. Tetlow, L. Zhang, *Angew. Chem. Int. Ed.* **2018**, *57*, 10484-10488.
- [37] D. A. Leigh, L. Pirvu, F. Schaufelberger, *J. Am. Chem. Soc.* **2019**, *141*, 6054-6059.
- [38] J. W. Fredy, J. Scelle, A. Guenet, E. Morel, S. A. de Beaumais, M. Ménand, V. Marvaud, C. S. Bonnet, E. Tóth, M. Sollogoub, G. Vives, B. Hasenknopf, *Chem. Eur. J.* **2014**, *20*, 10915-10920.
- [39] J. W. Fredy, J. Scelle, G. Ramniceanu, B.-T. Doan, C. S. Bonnet, E. Tóth, M. Ménand, M. Sollogoub, G. Vives, B. Hasenknopf, *Org. Lett.* **2017**, *19*, 1136-1139.
- [40] Y. A. Mondjinou, B. P. Loren, C. J. Collins, S.-H. Hyun, A. Demoret, J. Skulsky, C. Chaplain, V. Badwaik, D. H. Thompson, *Bioconjugate Chem.* **2018**, *29*, 3550-3560.

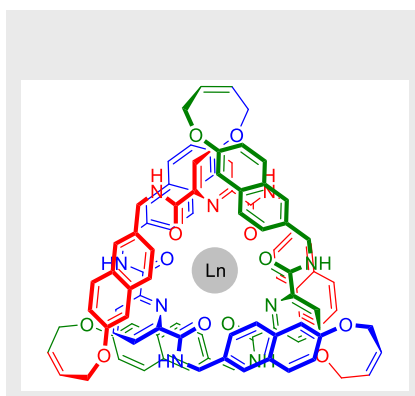
## MINIREVIEW

## Entry for the Table of Contents

Layout 1:

## MINIREVIEW

This review details progress in the rapidly developing field of lanthanide-containing mechanically interlocked molecules (MIMs). Examples of the appendage of coordination complexes and lanthanide templation are included, as well as emerging applications of the resulting MIMs.

*Nicholas H. Evans\****Page No. – Page No.****Lanthanide-Containing Rotaxanes,  
Catenanes and Knots**