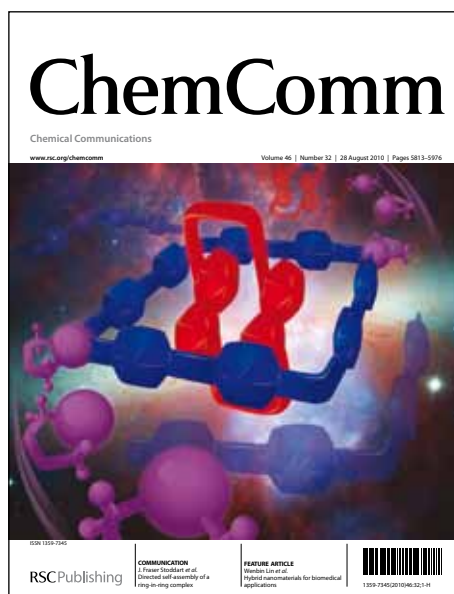


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## COMMUNICATION

## Engineering Entanglement: Controlling the Formation of Polycatenanes and Polyrotaxanes by $\pi$ Interactions

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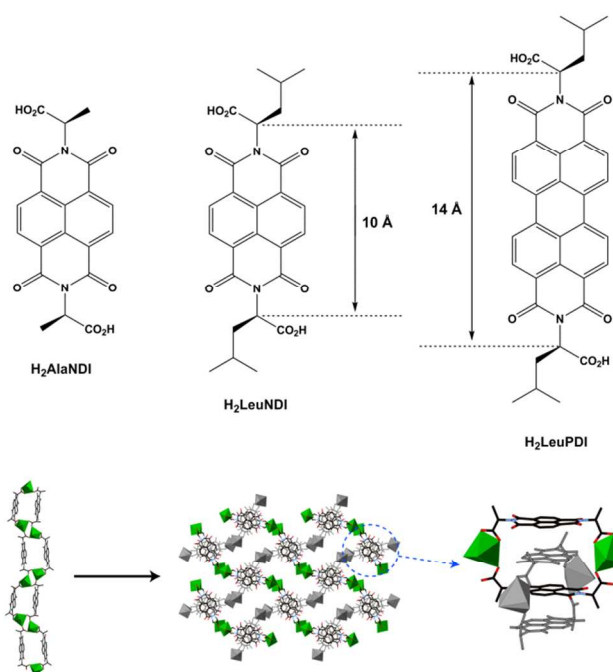
**A reproducible metallocyclic motif containing amino-acid functionalised aromatic diimides has been employed to demonstrate remarkable control over entanglement topologies. [2]-Catenane and pseudo-rotaxane units give rise to 1D→2D polycatenation, the formation of which can be sterically prevented, and a unique 1D→3D polyrotaxane.**

The use of  $\pi$  interactions to form either discrete or infinite supramolecular assemblies takes advantage of directional electrostatic interactions between aromatic surfaces.<sup>1</sup> Such interactions, present between adjacent base-pairs in DNA strands, have been shown to play a vital role in the formation and development of mechanically interlocked complexes.<sup>2</sup> The importance and potential of this approach to topologically non-trivial materials has been recently highlighted, showing the myriad of supramolecular assemblies that can be constructed using macrocycles containing aromatic groups to form catenanes and the combination of these macrocycles with linear guests to form rotaxanes.<sup>3</sup> Such systems are known using both purely organic macrocycles<sup>4</sup> and using metallocycles with ligands containing  $\pi$ -systems.<sup>5</sup>

The formation of interlocking macrocycles through designed supramolecular interactions in the solid-state, as opposed to discrete supramolecular complexes, is a less explored area, with many reports of polycatenane and polyrotaxane frameworks being *ex post facto* descriptions of network topologies.<sup>6</sup> There is a concerted research effort towards being able to control interpenetration topologies by altering synthetic conditions, using templates and tailoring ligand systems.<sup>7</sup> Given the large base of work in discrete supramolecular  $\pi$  systems, it follows that this logic should be able to be extended into infinite, solid-state assemblies with the utilisation of 'discrete' motifs to form entangled networks.

We have reported the ability of an alanine-substituted naphthalenediimide (NDI), H<sub>2</sub>AlaNDI, to form the one-dimensional coordination polymer *poly*-[Cd<sub>2</sub>(AlaNDI)<sub>2</sub>(DMF)<sub>4</sub>].<sup>8</sup> This polymeric compound consists of conjoined bis-NDI metallocycles,

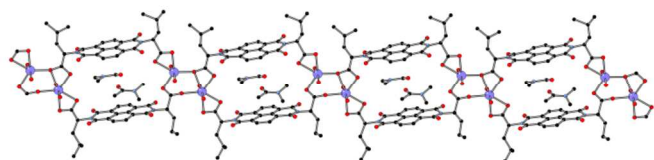
{Cd<sub>2</sub>(AlaNDI)<sub>2</sub>}, and assembles into a 1D→2D polycatenated structure by interlocking of the rings between perpendicular, topologically linear chains (Figure 1).



**Figure 1.** (top) Diimide ligands with amino-acid end-groups that differ in the steric bulk of the alkyl chain (methyl or isobutyl) and the length of the core unit, greatly affecting the interlocked supramolecular assemblies that can form. (bottom) The formation of a 1D→2D polycatenated structure in [Cd<sub>2</sub>(AlaNDI)<sub>2</sub>(DMF)<sub>4</sub>] containing interlocked {Cd<sub>2</sub>(AlaNDI)<sub>2</sub>} metallocycles.

The size and geometry of the metallocycle is ideal for forming a self-complementary catenane with a mean plane distance between NDIs of  $\sim 7$  Å, *i.e.* preorganised to accept a planar, aromatic guest in the cavity with face-to-face  $\pi$ -interactions of *ca.* 3.5 Å. NDIs are well known in discrete systems to associate through  $\pi$  interactions.<sup>9</sup> The presence of a substituent at the chiral centres of the ligand appears essential for formation of the cyclic motif by controlling the ligand conformation, evidenced by the 1D chains using H<sub>2</sub>GlyNDI with only a CH<sub>2</sub> bridge between the carboxylate and the NDI core.<sup>10</sup>

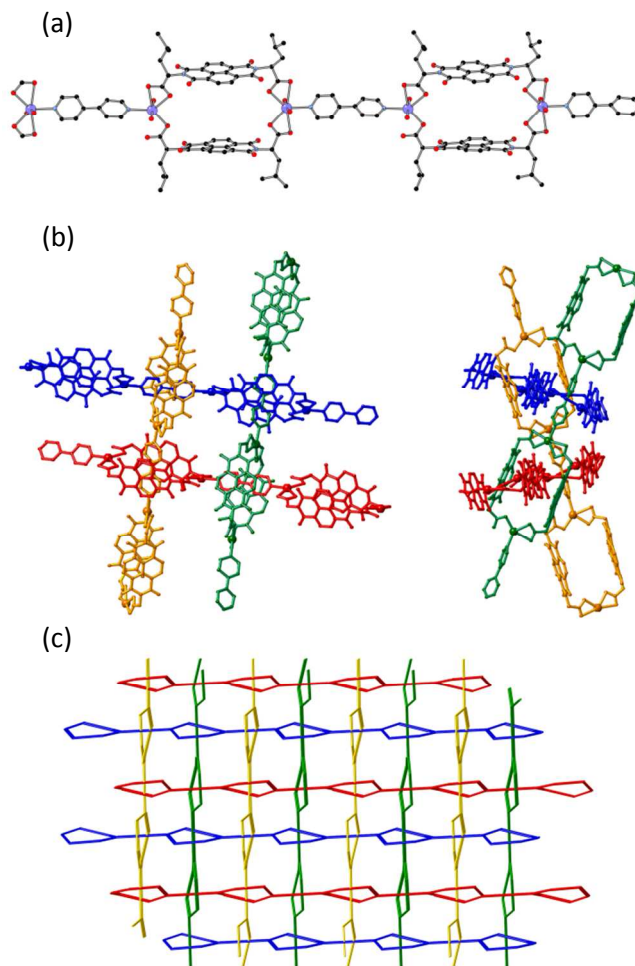
Our initial observation led us to explore whether the assembly of interlocked structures utilising the metallocyclic motif of amino-acid-NDIs (aaNDIs) could be directed in order to control the entanglement of the resulting structure. Herein we demonstrate a remarkable control of the self-assembly of such systems to exploit sterically bulky groups to prevent self-association, to form novel 1D $\rightarrow$ 3D polyrotaxanes by inserting bipyridyl spacers between the NDI-metalloccycles and to form polycatenanes using a larger perylene-3,4,9,10-tetracarboxylic diimide (PDI) core group which overrides the presence of additional steric bulk. The 1D $\rightarrow$ 2D polycatenation in [Cd<sub>2</sub>(AlaNDI)<sub>2</sub>(DMF)<sub>4</sub>] is built around a catenane motif between two {Cd<sub>2</sub>(AlaNDI)<sub>2</sub>} metalloccycles which form a stack of four NDI units with three face-to-face  $\pi$  interactions (Figure 1). The AlaNDI ligand is not sterically demanding as the methyl substituents on the chiral centres point away from the NDI core, thereby allowing catenation of the two metalloccycles. When the AlaNDI ligand is replaced with the more sterically crowded LeuNDI ligand, which possesses isobutyl groups in place of methyl groups, a material (**1**) containing similar 1D chains of *poly*-{[Cd<sub>2</sub>(LeuNDI)<sub>2</sub>(DMA)<sub>4</sub>]}·DMA is obtained that shows no interpenetration between metalloccycles (Figure 2).



**Figure 2.** The 1D chains of [Cd(LeuNDI)(DMA)<sub>2</sub>] contain solvent within the metalloccycles, rather than form an interpenetrating motif, postulated to be due to the steric bulk of the isobutyl chains

The 1D chains formed with AlaNDI and LeuNDI are of identical composition, [Cd<sub>2</sub>(aaNDI)<sub>2</sub>(DMx)<sub>4</sub>] (DMx = DMA or DMF), with the same connectivity and a slight difference in morphology which is thought to arise from crystal packing effects (*vide supra*). The LeuNDI ligands adopt the expected geometry, allowing the formation of the metallocycle, and the dinuclear cadmium linker between the metalloccycles retains the same coordination environment with both chelating and bridging carboxylates and solvent molecules completing the octahedral coordination spheres. The isobutyl groups are situated over the faces of the NDI cores, thereby not leaving enough space for the catenane motif to form due to the steric clash that would occur between the isobutyl chains of one macrocycle and the aromatic protons of the other (Figure 2). In place of interpenetration, two disordered DMA molecules reside within the macrocyclic cavities. The steric bulk of the isobutyl groups also prevents any  $\pi$  interactions between chains, which dominate the crystal packing in [Cd<sub>2</sub>(AlaNDI)<sub>2</sub>(DMF)<sub>4</sub>]. The absence of interpenetration in **1** demonstrates that the self-association of 1D chains can be 'switched off' by the use of bulkier side chains on the aaNDI ligand. This raises the interesting prospect of whether less sterically demanding aromatic co-ligands can be

passed through the macrocycles in the [Cd<sub>2</sub>(LeuNDI)<sub>2</sub>] chain in place of catenation.

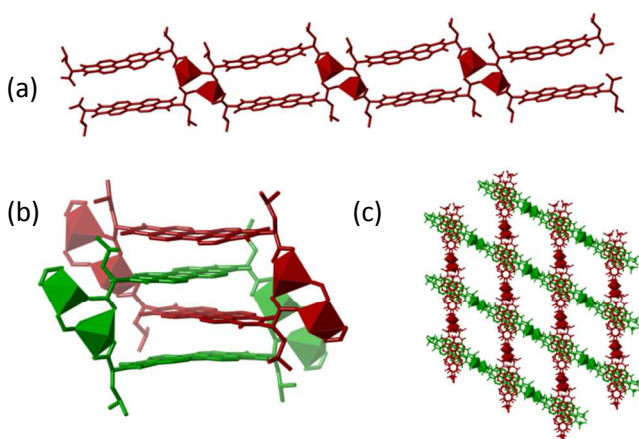


**Figure 3.** (a) A portion of one of the 1D chains in the structure of **2** with the metallocycle motif separated by bipyridine linkers. (b) Two views showing the chains forming a polyrotaxane network with the bipyridine ligands passing through the {Cd<sub>2</sub>(LeuNDI)<sub>2</sub>} metalloccycles to give (c) the overall 1D $\rightarrow$ 3D polyrotaxane structure.

Reaction of H<sub>2</sub>LeuNDI with Cd(NO<sub>3</sub>)<sub>2</sub> in the presence of 4,4'-bipyridine (bipy) yields the compound *poly*-{[Cd<sub>2</sub>(LeuNDI)<sub>2</sub>(bipy)(DMF)<sub>3</sub>(H<sub>2</sub>O)]·DMF·H<sub>2</sub>O} (**2**) as a pure crystalline product.<sup>11</sup> The compound contains a 1D coordination polymer that once again has the desired {Cd<sub>2</sub>(LeuNDI)<sub>2</sub>} metalloccycles. However, the metalloccycles are now bridged by a 4,4'-bipyridine ligand rather than being directly connected through a Cd<sub>2</sub>-carboxylate node (Figure 3a). The macrocycles themselves are the same as those in the structure of **1**, with a separation of  $\sim 7$  Å between the NDI groups which are slightly deviated from being parallel to each other within each loop ( $\sim 9^\circ$ ). The macrocycles are sterically prevented from forming catenanes, due to the isobutyl chains of the leucine, which allows the bipyridine ligands of perpendicular 1D chains to pass through the metallocycle. Overall this arrangement gives, to the best of our knowledge, an unprecedented example of a 1D $\rightarrow$ 3D polyrotaxane, with the linear

bipyridine ligand being threaded through the  $\{Cd_2(LeuNDI)_2\}$  macrocycles. The 1D chains, when viewed in isolation, are topologically linear, as are those in **1**, with the two NDI ligands that connect the  $Cd_2$  nodes conventionally reduced to a single linkage for topological analysis. To accurately attribute topological connectivity within the structure, the chain must be described with an expanded topology to describe the ring, thereby fitting the definition of a polyrotaxane as recently put forward by Yang, Ma and Batten.<sup>6e</sup>

The presence of 4,4'-bipyridine as a bridging ligand in **2** introduces an additional degree of freedom compared to the chains in **1**, with free rotation of the bipyridine along the  $Cd \cdots Cd$  vector. This extra freedom means that the interpenetration is not restricted to the 1D chains being co-planar, as is the case in  $[Cd_2(AlaNDI)_2(DMF)_4]$ , and the chains in **2** are able to form a 1D $\rightarrow$ 3D polyrotaxane structure (Figure 3c). The chains intersect at an angle of approximately 35° with closest C $\cdots$ C contacts between the NDI and the 4,4'-bipyridine of 3.28 Å. The crystallographic 2-fold axis passes through the point of intersection between four chains (Figure 3b).



**Figure 4.** (a) A portion of the 1D coordination polymer from the structure of **3**, (b) the catenane motif between two metallocycles and (c) the overall 1D $\rightarrow$ 2D polycatenation of the chains.

The steric clash between ligands that prevents the formation of a polycatenane in **1** can potentially be overcome in one of two ways; the size of the alkyl substituent could be reduced (*c.f.*  $[Cd_2(AlaNDI)_2(DMF)_4]$ ) or the length of the aromatic core could be increased. Towards the latter goal we synthesised the larger perylene-derived species  $H_2LeuPDI$  (Figure 1). The two connected naphthalene rings in  $H_2LeuPDI$  make the ligand approximately 4 Å longer than the NDI analogue whilst retaining the same width, thereby ensuring that the two isobutyl chains are far enough apart that two perpendicular PDI ligands can easily form  $\pi$ -stacking interactions. Reaction of  $H_2LeuPDI$  with  $Cd(NO_3)_2$  afforded a single crystalline product that consists of poly- $\{[Cd_2(LeuPDI)_2(H_2O)_4] \cdot 3DMF\}$  (**3**).<sup>11</sup> The 1D polymer in **3** has an analogous composition to that in **1**, with the longer ligands forming a larger metallocycle between  $Cd_2$  nodes (Figure 4a). Given the larger distance between the isobutyl side chains, the catenane motif recurs in the structure of **3** giving an overall 1D $\rightarrow$ 2D polycatenated structure akin to that of  $[Cd_2(AlaNDI)_2(DMF)_4]$  (Figure 4, *c.f.* Figure 1). Given the increased size of the ligands, the core unit is slightly bowed towards the middle of the metallocycle with the four ligands that form the catenane being non-parallel (Figure 4b). The closest C $\cdots$ C distance between PDI groups within the catenane is  $\sim 3.4$  Å. With the length of the ligand overcoming the steric bulk of the

isobutyl groups, there are also face-to-face  $\pi$  interactions between the sheets giving rise to infinite  $\pi$  stacking parallel to the unique axis of the hexagonal structure.

## Conclusions

The metallomacrocycle formed between cadmium and either aaNDIs or aaPDI is a robust supramolecular tecton for engineering entangled networks through the formation of discrete catenane or rotaxane motifs. Adjusting the size of the peripheral alkyl groups can prevent self-complementary polycatenation of 1D chains (**1**). Less bulky aromatic guest species, such as 4,4'-bipyridine, can be threaded through the macrocycle as shown in the polyrotaxane **2**. Expanding the aromatic core used in the macrocycle overrides the steric bulk and once again allows a polycatenane motif to be formed.

## Notes and references

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Electronic Supplementary Information (ESI) available: CIFs of structures **1-3** (CCDC 971846-971848), synthetic details, detailed crystal and refinement information, powder X-ray patterns, thermogravimetric traces. See DOI: 10.1039/c000000x/

1. a) J. K. Klosterman, Y. Yamauchi and M. Fujita, *Chem. Soc. Rev.*, 2009, **38**, 1714-1725; b) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525-5534; c) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885-3896; d) E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem. Int. Ed.*, 2003, **42**, 1210-1250.
2. C. G. Claessens and J. F. Stoddart, *J. Phys. Org. Chem.*, 1997, **10**, 254-272.
3. a) G. Barin, A. Coskun, M. M. G. Fouda and J. F. Stoddart, *Chempluschem*, 2012, **77**, 159-185; b) R. S. Forgan, J.-P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434-5464.
4. a) D. G. Hamilton, J. K. M. Sanders, J. E. Davies, W. Clegg and S. J. Teat, *Chem. Commun.*, 1997, 897-898; b) C. A. Hunter, *J. Am. Chem. Soc.*, 1992, **114**, 5303-5311; c) D. G. Hamilton, J. E. Davies, L. Prodi and J. K. M. Sanders, *Chem.-Eur. J.*, 1998, **4**, 608-620; d) G. D. Fallon, M. A. P. Lee, S. J. Langford and P. J. Nichols, *Org. Lett.*, 2004, **6**, 655-658.
5. a) L. Loots and L. J. Barbour, *Chem. Commun.*, 2013, **49**, 671-673; b) C. Alvarino, A. Terenzi, V. Blanco, M. D. Garcia, C. Peinador and J. M. Quintela, *Dalton Trans.*, 2012, **41**, 11992-11998; c) M. Fujita, *Acc. Chem. Res.*, 1999, **32**, 53-61; d) J. Lu, D. R. Turner, L. P. Harding, L. T. Byrne, M. V. Baker and S. R. Batten, *J. Am. Chem. Soc.*, 2009, **131**, 10372-+; e) S. P. Black, A. R. Stefankiewicz, M. M. J. Smulders, D. Sattler, C. A. Schalley, J. R. Nitschke and J. K. M. Sanders, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 5749-5752; f) A. C. Try, M. M. Harding, D. G. Hamilton and J. K. M. Sanders, *Chem. Commun.*, 1998, 723-724.
6. a) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *J. Solid State Chem.*, 2005, **178**, 2452-2474; b) D. M. Proserpio, *Nat. Chem.*, 2010, **2**, 435-436; c) L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2003, **5**, 269-279; d) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247-289; e) J. Yang, J.-F. Ma and S. R. Batten, *Chem. Commun.*, 2012, **48**, 7899-7912; f) S. R. Batten, *CrystEngComm*, 2001, **3**, 67-72; g) S.

- R. Batten, S. M. Neville and D. R. Turner, *Coordination polymers - design, analysis and application*, The Royal Society of Chemistry, Cambridge, 2009.
7. H. L. Jiang, T. A. Makal and H. C. Zhou, *Coord. Chem. Rev.*, 2013, **257**, 2232-2249.
  8. L. J. McCormick and D. R. Turner, *CrystEngComm*, 2013, **15**, 8234-8236.
  9. a) S. V. Bhosale, C. H. Jani and S. J. Langford, *Chem. Soc. Rev.*, 2008, **37**, 331-342; b) S. Gabutti, S. Schaffner, M. Neuburger, M. Fischer, G. Schafer and M. Mayor, *Organic & biomolecular chemistry*, 2009, **7**, 3222-3229; c) S. Guha, F. S. Goodson, R. J. Clark and S. Saha, *CrystEngComm*, 2012, **14**, 1213-1215; d) M. S. Khoshbin, M. V. Ovchinnikov, K. S. Salaita, C. A. Mirkin, C. L. Stern, L. N. Zakharov and A. L. Rheingold, *Chem.-Asian J.*, 2006, **1**, 686-692.
  10. L. Qin, W. N. Zhao, G. J. Yu, L. P. Xu and L. Han, *Inorg. Chem. Commun.*, 2013, **34**, 47-50.
  11. See supporting information for characterisation.