

An unprecedented 2D \rightarrow 3D metal–organic polyrotaxane framework constructed from cadmium and a flexible star-like ligand†

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Received 1st November 2010, Accepted 23rd November 2010

DOI: 10.1039/c0cc04724d

An unprecedented 2D \rightarrow 3D metal–organic polyrotaxane framework, based on a new star-like tri(4-imidazolylphenyl)-amine ligand, has been synthesized and characterized, which represents the first example of 2D \rightarrow 3D polyrotaxane entangled in a parallel fashion.

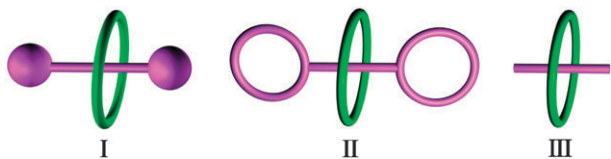
Entangled systems of metal–organic frameworks (MOFs) have undergone revolutionary growth over the past decades because of their undisputed aesthetic topological structures, fascinating properties such as molecular machines and sensor devices, and potential biological applications.¹ Polyrotaxane, as an intriguing branch of the entanglement system, is regarded as particularly significant, which has provided a long-standing fascination for chemists.² As elucidated in several comprehensive reviews, the polyrotaxane family can be described as regularly ordered infinite versions of the finite molecular motifs.² Actually, by means of ‘ideal’ continuous deformations, we could separate the components of any finite portion of a polyrotaxane.³ Although the extended polymeric analogues of the species can be characterized by the presence of the rings as stoppers and side arms as the rods, this is at present a largely unexplored area of chemical topology.^{3,4}

On the other hand, as mentioned by Ciani and coworkers in their reviews, pseudo-rotaxanes (Scheme 1), which can be entangled *via* rotaxane-like links and the rods that can be withdrawn from the loops, have been investigated widely from 1D to 3D frameworks.^{3,5} However, the real polyrotaxane arrays are exceedingly rare.⁴ As far as we know, so far, only a few fascinating examples showing 1D \rightarrow 1D, 1D \rightarrow 2D and 2D \rightarrow 2D polyrotaxane associations have been documented

involving loops and rods (Scheme S1†).⁴ In particular, only one example of 2D \rightarrow 3D polyrotaxane has been reported very recently.^{4c}

Since the pioneering work by Sauvage and Stoddart, admirable synthetic strategies initiated by Kim and Robson *et al.* have been developed to assemble rotaxanes into polyrotaxanes with highly repeated structures in the field of metal–organic polyrotaxane framework.² Nevertheless, the construction of 3D polyrotaxane remains a challenging and unexplored issue in coordination chemistry. As mentioned in previous works, the synthetic strategy for the polyrotaxane networks is mainly dependent on the ligands selected with both flexible and long rigid characters. In these cases, conformationally flexible ligands have the ability to give unusual entanglements involving a loop, while long rigid ligands are good candidates for a rod in the assembly, and insertion of a linear rod through those loops. Typically, conformationally flexible 1,4-bis(imidazol-1-ylmethyl)benzene (bix), 1,3-bis(4-pyridyl)propane, 1,2-bis(4,4'-bipyridinium)-ethane and 4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl have been used to construct polyrotaxane architectures.⁴ Taking inspiration from the aforementioned points, in this work, we synthesized a conformationally flexible star-like tridentate ligand, tri(4-imidazolylphenyl)amine (Tipa) (Scheme S2, ESI†). The Ph-imidazole arms of the Tipa ligand can rotate freely and adjust itself sterically around the central N moiety when coordinating to the metal centers. Thus, the star-like Tipa ligand is a good candidate for the construction of metal–organic polyrotaxane frameworks. Herein, we report an intriguing 2D \rightarrow 3D framework [Cd(Tipa)Cl₂]_n·1.07nH₂O (**1**) based on the star-like Tipa ligand. Remarkably, this framework represents the first example of 2D \rightarrow 3D polyrotaxane entangled in a parallel fashion.

Compound [Cd(Tipa)Cl₂]_n·1.07nH₂O (**1**) was prepared by solvothermal reaction of CdCl₂·2.5H₂O (0.068 g, 0.3 mmol), Tipa (0.044 g, 0.1 mmol), CH₃OH (8 mL) and water (2 mL) at 150 °C for three days.† Single-crystal X-ray diffraction reveals that **1** is a unique 2D \rightarrow 3D polyrotaxane entangled in a parallel fashion. The asymmetric unit of **1** contains one unique Cd(II) atom, one unique Tipa ligand, one point zero seven uncoordinated water molecules and two unique chlorine anions, where the O2W atom lies on an inversion center (Fig. S1, ESI†). The Cd(II) ion is five-coordinated by three N atoms from three Tipa ligands and two chlorine anions in a distorted square pyramidal geometry with a τ value of 0.11.⁶ The Cd–N bond lengths vary from 2.276(2) to 2.346(2) Å, and N–Cd–N angles range from 94.95(8)° to 153.05(8)°. Each Tipa ligand bridges three Cd(II) centers to generate a highly undulant 2D sheet with a thickness of *ca.* 9.53 Å (Fig. 1). From a topological viewpoint, the sheet can be considered as a



Scheme 1 (I) Schematic representations of the finite molecular motifs of rotaxane with the presence of bulky stoppers; (II) the presence of the rings as stoppers; (III) pseudorotaxane with no stopper.

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† Electronic supplementary information (ESI) available: Crystallographic data and complementary drawings for crystal structures. CCDC 799006. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc04724d

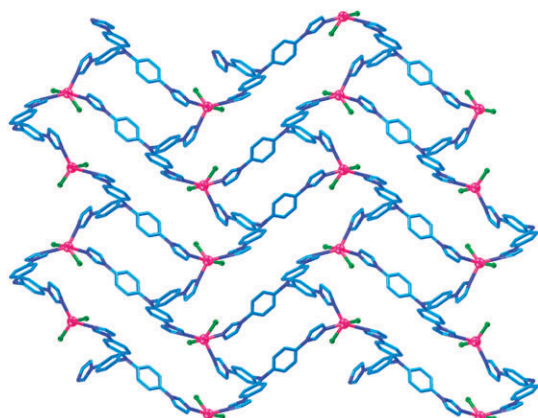


Fig. 1 A view of a single sheet in **1**.

3-connected network with a Schläfli symbol of $4 \cdot 8^2$ (Fig. S2, ESI†). There are two kinds of large windows of $\text{Cd}_2(\text{Tipa})_2$ and $\text{Cd}_4(\text{Tipa})_4$ in the resulting layers. The $\text{Cd}_2(\text{Tipa})_2$ window is built up by two Cd atoms and four Ph-imidazole arms of two different Tipa ligands with the dimension of $9.52 \times 9.75 \text{ \AA}$, while the $\text{Cd}_4(\text{Tipa})_4$ unit is built up by four Cd atoms and eight Ph-imidazole arms of four ligands with the dimension of $18.56 \times 16.02 \text{ \AA}$ (Fig. S3, ESI†). It is noteworthy that every one $\text{Cd}_2(\text{Tipa})_2$ unit of each layer is threaded through simultaneously by two armed rods of the ligands from two adjacent layers in a parallel fashion as highlighted in Fig. 2.

Each green armed rod of the above layer passes through one of the $\text{Cd}_2(\text{Tipa})_2$ unit (blue one), and each orange armed rod of the below layer passes through the same one $\text{Cd}_2(\text{Tipa})_2$ unit (Fig. 2).

All sheets are identical, and entangled in an ABC fashion (Fig. S4, ESI†). As a result, an unprecedented $2\text{D} \rightarrow 3\text{D}$

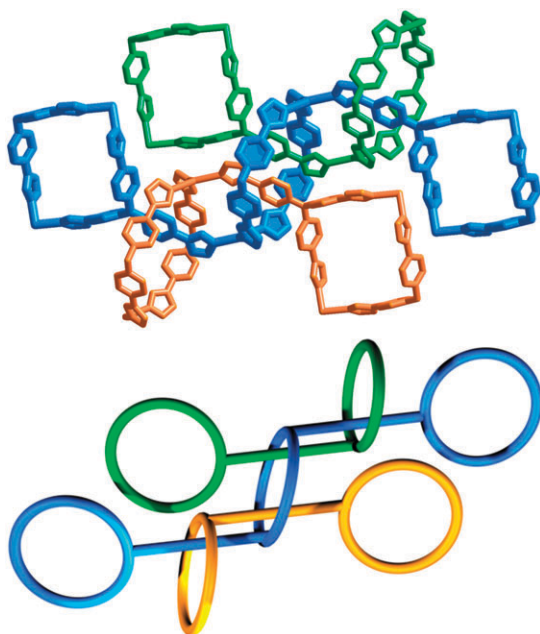


Fig. 2 (top) One blue $\text{Cd}_2(\text{Tipa})_2$ unit is threaded through by two armed rods of the adjacent layers, where all chloride ions are omitted for clarity and (bottom) schematic representation of one ring threaded by two rods.

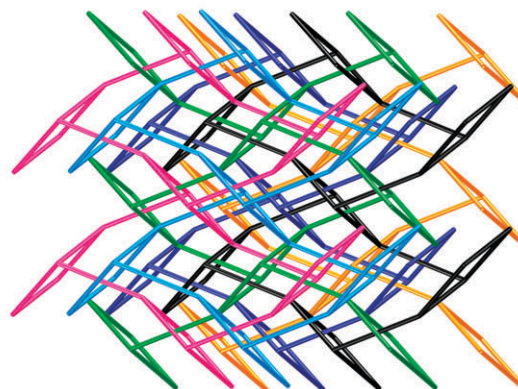
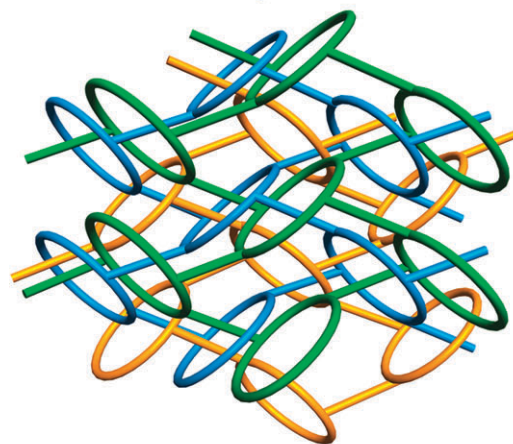
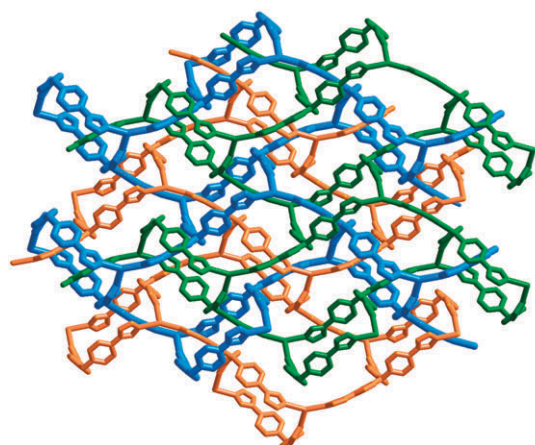


Fig. 3 (top) A view of the three entangled nets in **1** (blue sheet lies in middle, and green and orange sheets lie above and below, respectively); (middle) schematic representation of the three entangled nets in a parallel mode in **1** and (below) schematic representation of the $2\text{D} \rightarrow 3\text{D}$ polyrotaxane in **1**.

entanglement is generated, originating from the three adjacent polymeric sheets at one time (Fig. 3). Actually, if we regard each $\text{Cd}_2(\text{Tipa})_2$ unit as a loop and one arm of the ligand as a single rod, undoubtedly, the entanglement in **1** is an unquestionable polyrotaxane. The way the networks entangled, however, is very different from previous reported examples, and is in fact the first example of its particular entangled topology.⁴

Notably, further study into the nature of the intricate architecture of **1** is that all loops of $\text{Cd}_2(\text{Tipa})_2$ are equivalent. However, the planes of adjacent $\text{Cd}_2(\text{Tipa})_2$ rings within the

layer are almost close to perpendicular with the dihedral angle being 89.43° . Without a doubt, the results afford a high feasibility of the entangled $2D \rightarrow 3D$ polyrotaxane array. On the other hand, another important factor for the construction of this intriguing polyrotaxane is the large $Cd_2(Tipa)_2$ loops of a single network. Thus, every two rods from two independent sheets can pass through one ring of another sheet simultaneously and every one ring encircles two rods of two adjacent sheets, thus giving an unprecedented type of $3D$ polyrotaxane by one ring with four stoppers rather than a common rotaxane with two stoppers.³

So far, only a few $1D$ and $2D$ polyrotaxane frameworks have been reported.⁴ Robson and co-workers have reported the first unusual $2D \rightarrow 2D$ polyrotaxane network $[Zn(bix)_2(NO_3)_2] \cdot 4.5H_2O$ ($bix = 1,4$ -bis(imidazol-1-ylmethyl)-benzene).^{4b} In that reported example, there are two independent $2D$ polymeric layers, in which the layers contain the bix rods and the $Zn_2(bix)_2$ loops. The bix rods pass through the loops of another layer in a parallel fashion to give an unusual $2D \rightarrow 2D$ polyrotaxane, where one rod only passes through one ring of another layer. Taking inspiration from the example, several polyrotaxanes of $2D \rightarrow 2D$ based on different N-donor ligands and transition metals have been reported.^{4f,g} However, so far, only one fascinating example of $2D \rightarrow 3D$ polyrotaxane $[Cd_4(bix)_4(bpea)_4] \cdot 4H_2O$ ($bpea =$ biphenylethene-4,4'-dicarboxylate), involving $Cd_2(bix)_2$ loop and $bpea$ rod, has been documented,^{4e} where one loop of an independent layer is penetrated by one rod of the adjacent layer. In these modes, each $2D$ network is entangled with four inclined networks, giving an aesthetic $3D$ polyrotaxane in an inclined fashion. It should be pointed out that although both the reported $[Cd_4(bix)_4(bpea)_4] \cdot 4H_2O$ and compound **1** show the $2D \rightarrow 3D$ polyrotaxanes, their entangled modes are completely different. The sheets of $[Cd_4(bix)_4(bpea)_4] \cdot 4H_2O$ are entangled in an inclined fashion, while the ones of **1** are entangled in a parallel fashion. In addition, only one rod passes through one loop in $[Cd_4(bix)_4(bpea)_4] \cdot 4H_2O$, whereas, in **1**, two rods pass through one loop simultaneously.

The emission spectrum of **1** exhibits an intense emission at 426 nm in the blue region upon excitation at 320 nm, which is a slightly red-shifted 6 nm compared with the $Tipa$ ligand ($\lambda_{ex} = 365$ nm, $\lambda_{em} = 420$ nm) (Fig. S5, ESI†). Therefore, the emission peak of **1** may be assigned to the intraligand fluorescent emission. The red-shift of luminescence may be attributed to the ligand coordinating to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay.

In summary, an unprecedented $2D \rightarrow 3D$ polyrotaxane framework based on the star-like $Tipa$ ligand has been prepared by using $Cd_2(Tipa)_2$ as the loop and the long Ph -imidazole arm as the rod. The entangled modes observed in **1** are unique in the metal–organic polyrotaxane framework. Also, it is the first time for the construction of a polyrotaxane

framework from a star-like ligand. The synthetic strategy presents a progressive evolution for the construction of high dimensional polyrotaxane frameworks.

We thank the National Science Foundation of China (21001023 and 21071028), Program for Changjiang Scholars and Innovative Research Teams in Chinese University, the Specialized Research Fund for the Doctoral Program of Higher Education, the Science Foundation of Jilin Province (20090137 and 20100109), the Training Fund of NENU'S Scientific Innovation Project, and the Fundamental Research Funds for the Central Universities for support.

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