Formation of a Dicopper Platform Based Polyrotaxane Whose "String" and "Bead" Are Constructed from the Same Components

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S *Supporting Information*

ABSTRACT: The combination of the dicopper platform $[Cu_2(L)_2(THF)_2]$ (**1**·2THF), where H_2L is 1,1′-(1,3-phenylene)-bis-4,4-dimethylpentane-1,3-dione, and 1,4-bis(4-pyridyl)piperazine (bpp), afforded the first example of a one-dimensional polyrotaxane $\{[(1)(\mu_2\text{-bpp})]\text{-}[(1)_2(bpp)_2]\}_n$ whose *"string"* and *"bead"* are constructed from the same components. The *bead* of stoichiometry $[(1)_2(bpp)_2]$ has a large rectangular cavity of dimensions 7.40×15.64 Å and is threaded onto a stair-like *string* of composition $[(1)(\mu_2\text{-bpp})]_n$. The formation of the polyrotaxane is driven by $\pi{-}\pi$ stacking between the *string* and the *beads* with precise electronic and steric complementarity between these components. A pathway for the formation of the polyrotaxane is proposed.
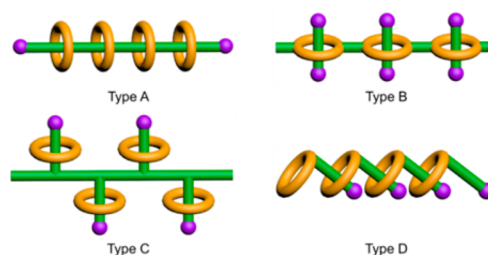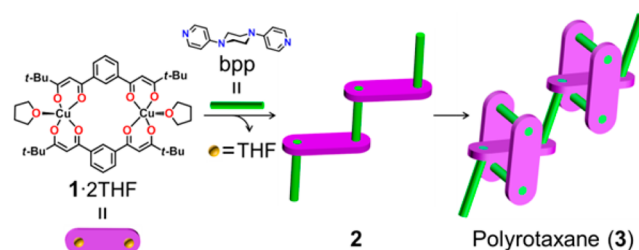
Figure 1. Four typical structures of polyrotaxanes.

Figure 2. Formation of polyrotaxane (**3**) whose *string* and *bead* are made from the same components: dicopper platform **1** and bpp.

Among entangled molecular systems, protocols for synthesizing mechanically interlocked catenane and rotaxane assemblies in reasonable yield have now been investigated for around three decades and a number of such systems have proved useful for constructing a varied range of molecular devices and machines.[1] Following pioneering work by Sauvage[2] and Stoddart[3] a number of approaches has been developed for synthesizing such products.[4] For rotaxanes, these have often involved the threading of macrocyclic ring *beads*, including crown ether, curcurbituril, cyclodextrins, and calixarene macrocycles onto linear *strings* of both fully organic or organic–inorganic composition employing a variety of synthetic protocols.[4] Alternatively, "clipping" in which the macrocyclic structure of the *bead* is generated around the *string*, using the latter as a template, has also been employed. Apart from discrete systems, a wide range of polyrotaxanes composed of repeating interlinked units have also been reported. Representative examples of the latter are given by A–D in Figure 1. Of these, straight chain systems of type A are the most common. In all of these systems the composition of the *beads* and *strings* differ.

Enhanced interest in organic–inorganic frameworks (MOFs) over recent years has also led to the increased development of new interlocked coordination compounds with, for example, polyrotaxane motifs being incorporated in a range of framework materials.[5]

In this work, we have shown that it is possible to prepare a polyrotaxane motif whose *string* and *bead* consist of the same components (Figure 2). For this, the dicopper platform $[Cu_2(L)_2(THF)_2]$ (abbreviated **1**·2THF)[6] and 1,4-bis(4-

pyridyl)piperazine (bpp) were employed as the building blocks. Each copper(II) center in **1**·2THF connects two L^{2-} ligands to give a planar arrangement, with each metal adopting an approximate square pyramidal geometry, being bound to four β-diketonato oxygen atoms in the basal plane and a THF molecule in the apical position.[6]

Previous studies have demonstrated that dinuclear copper platforms such as **1**·2THF react with linear bis-monodentate bridging ligands with replacement of the weakly bound axial THF ligands to yield either a discrete tetranuclear dibridged dimer or an infinite zigzag polymer with, in each case, the bridging ligand/copper platform ratio being 1:1.[7] Due to the extended dipyridyl structure incorporating a piperazine subunit, the bis-monodentate bpp ligand is expected to link different units to yield larger scale assemblies, including discrete or infinite forms.[8] As depicted in Figure 2, we found that a one pot reaction of the dicopper platform **1** with the difunctional bpp "pillar" ligand initially afforded a kinetically controlled (see later) one-dimensional (1D) stair-like coordination polymer **2**; this was

followed by the formation of a stable polyrotaxane **3** whose discrete *bead* and polymeric *string* are both constructed from the *same* components (each assembled from **1**·2THF and bpp).

The dicopper platform **1**·2THF (Figure 2) was prepared by reaction of the 1,3-phenylene-linked bis-*β*-diketone derivative (H$_2$**L**) with copper(II) chloride in THF under basic conditions as reported previously.[6] Complex **1**·2THF and bpp were dissolved in THF, and the reaction mixture was refluxed for 12 h. Slow evaporation of the solution over 3 days at room temperature afforded a small number of green crystals. A crystal from this batch was removed from the solution and used for an X-ray structure determination. The structure in Figure 3 shows a
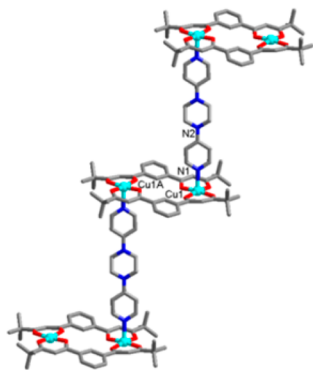

Figure 3. Stair-like one-dimensional structure of $\{(\mathbf{1})(\mu_2\text{-bpp})]\cdot 2\text{THF}\}_n$ (**2**). Noncoordinated solvent molecules are omitted.

1D stair-like coordination polymer of composition $\{(\mathbf{1})(\mu_2\text{-bpp})]\cdot 2\text{THF}\}_n$ (**2**) in which the two coordinated THF molecules associated with each dicopper platform (**1**·2THF) have been

replaced by pyridyl N atoms from μ_2-bpp bridging ligands (each with the central piperazine ring in its chair conformation). The asymmetric unit for **2** incorporates one copper(II) atom, one **L**$^{2-}$, and half a bpp ligand. The five-coordinated copper(II) center in **2** has a distorted square pyramidal environment (τ value = 0.078).[9] The copper(II) center is displaced from the O$_4$-plane by 0.16 Å toward the apical pyridyl nitrogen. Attempts to isolate **2** in higher yield were not successful.

To our surprise, we found that the zigzag polymeric product **2** transformed to the more complex 1D polyrotaxane **3** of formula $\{[(\mathbf{1})(\mu_2\text{-bpp})][(\mathbf{1})_2(\text{bpp})_2]\}_n\cdot(\text{bpp})_n$, when the reaction solution containing crystals of **2** was left undisturbed for 2 weeks; at the end of this period only crystals of the polyrotaxane were present, and these had formed in substantially higher yield (60%) than occurred initially for crystalline **2**. The X-ray structure of **3** is discussed below.

The observed conversion of crystalline **2** to **3** in the reaction solution on standing is in accord with the precursor complex **2** being a kinetic product, with the polyrotaxane **3** being the thermodynamic product. Comparison of the PXRD patterns for the synthesized polyrotaxane **3** with the simulated data for **2** and **3** confirmed the phase purity of the polyrotaxane **3** product (Figure S1); the purity of **3** was also confirmed by elemental analysis (see the Experimental Section in the Supporting Information).

The X-ray structure of polyrotaxane **3** clearly shows that the discrete near-rectangular *beads* $[(\mathbf{1})_2(\text{bpp})_2]$, each composed of two dicopper platforms of type **1** linked by two μ_2-bpp molecules in a parallel manner, are threaded onto the stair-like *string* (Figure 4a,b). As mentioned above, the *string* $[(\mathbf{1})(\text{bpp})]_n$ in the polyrotaxane **3** is also constructed from the same two components (a planar dicopper platform and a bpp ligand). In
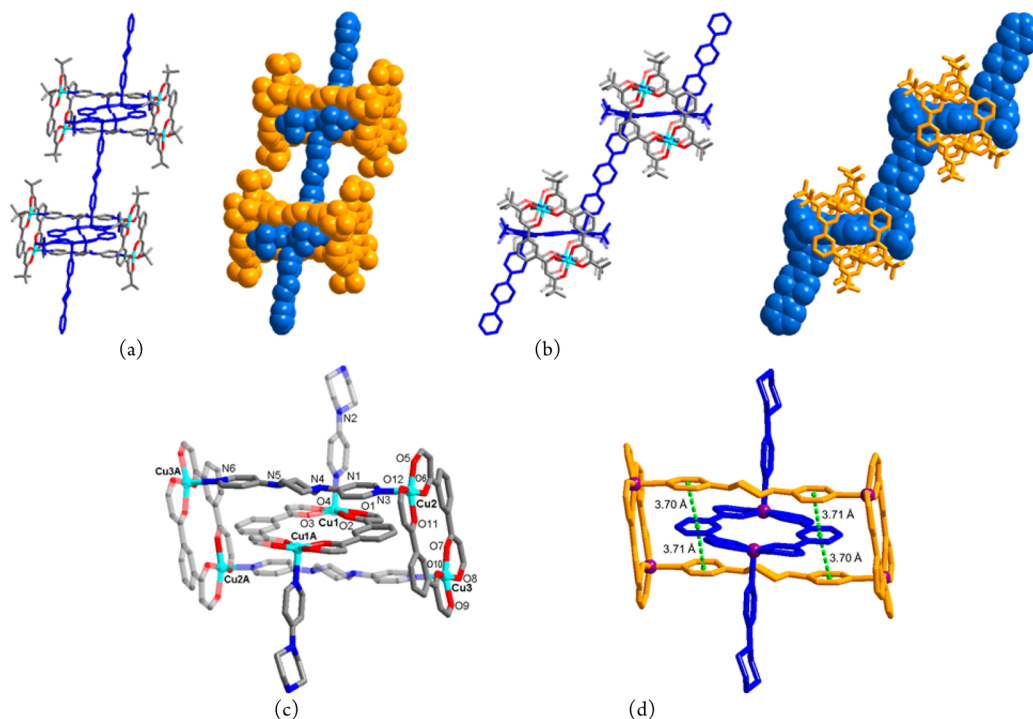

Figure 4. Polyrotaxane structure of $\{[(\mathbf{1})(\mu_2\text{-bpp})][(\mathbf{1})_2(\text{bpp})_2]\}_n\cdot(\text{bpp})_n$ (**3**): (a) a ball−stick (left) and space-filling (right) representations of two repeating units in the structure, (b) two further views of two repeating units in the structure, (c) a core unit showing the atom labeling, and (d) the face-to-face $\pi-\pi$ stacking interactions present in the structure. Uncoordinated bpp molecules and the terminal *t*-butyl groups on the bis-*β*-diketonato ligands are omitted.

the resulting alternating chain the dicopper platforms are linked via Cu−N bonds from the bpp ligands to yield the stair-like structure shown in blue in Figure 4a,b. The asymmetric unit of the polyrotaxane in **3** contains six copper(II) atoms, six L^{2-}, and three bpp ligands.

As expected, the $\pi-\pi$ stacking interactions between the aromatic rings of the *string* (blue) and *bead* (orange) are staggered with centroid−centroid distances of 3.70−3.71 Å, in accord with the presence of face-to-face $\pi-\pi$ stacking interactions (Figure S2). Notably, each molecular rectangle is involved in four $\pi-\pi$ stacking interactions, which clearly contribute to the stability of the rotaxane structure. The packing structure shows a herringbone pattern without significant interactions between 1D chains (Figure S3).

Comparison of the structure of the *string* component in the polyrotaxane **3** with that of the isolated stair-like kinetic product **2** shows that on polyrotaxane formation there is a change in the contact angle between the dicopper platform plane and each bpp ligand in the *string* from 84.9° to 115.0° (see Figure 5a,b), with
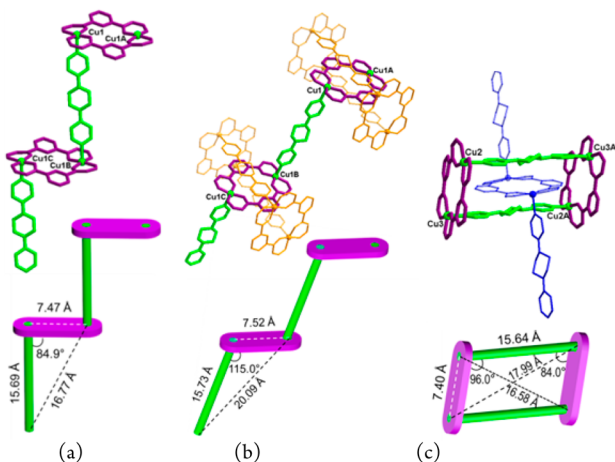
16.77 Å). The "opening up" of this angle minimizes the repulsion adjacent bpp linker units in *string* and *bead*, leading to enhanced offset of successive *beads* along the *string*.

In our previous studies, the reaction of **1**·2THF with shorter dipyridyl derivatives and other difunctional heterocyclic diamine ligands led to the stable formation of both discrete and 1D polymeric structures related to those discussed above.[7]

Consideration of these previous results along with the present ones indicates that the use of the longer semirigid bpp ligand in the present study leads to a *string* in which the stair-like structure has a higher step height as well as a larger rectangular *bead*. Both of these are geometrically and electronically ($\pi-\pi$ stacking) well matched to satisfy the precisely defined and mutually complementary conditions required for formation of polyrotaxane **3**.

The mass spectrum of polyrotaxane **3** dissolved in THF was not particularly informative, yielding only simple fragment ion peaks arising from $[(1)_2 + Na]^+$ and $[(1)_2 + K]^+$ (Figure S4c). However, the mass spectra of a mixture of **1**·2THF and the bpp ligand before and after refluxing in THF (Figure S4) in each case showed the presence of protonated species corresponding to $[(1)(bpp)+H]^+$ and $[(1)_2(bpp)+H]^+$ at m/z = 1022.83 and 1804.50, respectively. The isotopic patterns for these protonated ion peaks agree well with the theoretical distributions.

Although the detailed mechanism for polyrotaxane formation in this work remains uncertain, a stepwise pathway as shown in Figure 6 appears plausible. In this, initially the **1**·2THF platform undergoes THF ligand exchange by bpp to form a 2:1 $[(1)_2(bpp)]$ intermediate (*trans* form), which then propagates to form the 1D stair-like kinetic (see earlier discussion) product **2**; as mentioned the presence of a $[(1)_2(bpp)]$ species was identified in the mass spectra (Figure S4). The formation of polyrotaxane **3** may then proceed by the docking of **2** with $[(1)_2(bpp)]$. Following this, the *trans* configuration of $[(1)_2(bpp)]$ is simply converted to the *cis* form and threading of the *string* onto the rectangular *bead* is completed by clipping. The construction of the polyrotaxane thus involves a "docking− rotating−clipping" process (with the enthalpy gain from the effective $\pi-\pi$ stacking being weighed against the entropy loss associated with the aggregation).

In summary, we have demonstrated the one-pot synthesis of a polyrotaxane obtained via the self-assembly of the dicopper

Figure 5. Comparison of the structures and selected geometrical parameters for (a) **2**, (b) the *string* in **3**, and (c) the *bead* in **3**. *t*-Butyl groups are omitted.

the resulting diagonal distance (Cu1A···Cu1B 20.09 Å) in **3** being longer than the corresponding distance in **2** (Cu1A···Cu1B
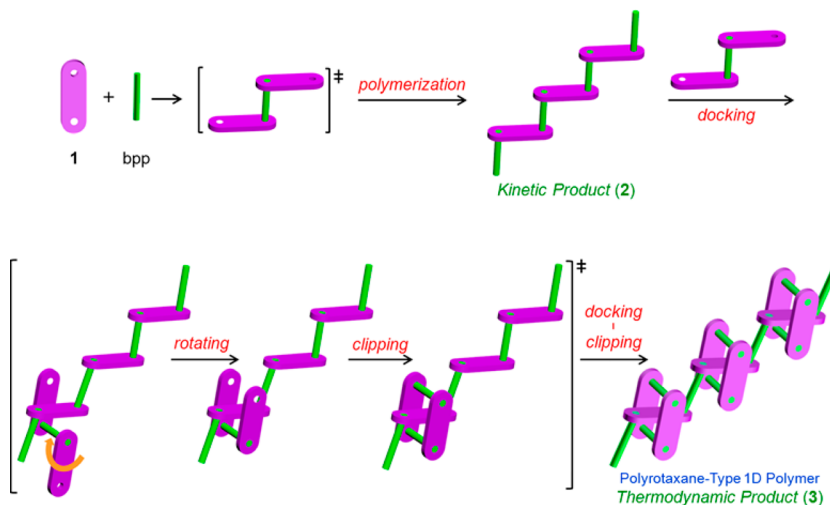

Figure 6. Proposed pathway for polyrotaxane formation from two components.

platform **1** and bpp. The product has a highly organized entangled polymeric structure that represents the first example of a polyrotaxane in which the *bead* and the *string* are constructed from the same components. In obtaining this outcome, the use of the longer bpp ligand for the generation of polyrotaxane **3** appears to be critical because it allows the formation of both a stair structure (*string*) with higher step height as well as a larger discrete rectangular framework (*bead*). Both products are precisely matched to satisfy the explicit steric and electronic conditions required for assembly of the intricate and highly complementary polyrotaxane arrangement that occurs in **3**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05770.

> Synthesis, PXRD patterns, crystal structures, and ESI-MS data (PDF)
> X-ray data of CCDC reference numbers 1404653 (**2**) and 1404654 (**3**) (CIF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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