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Metallosupramolecular Poly[2]pseudorotaxane Constructed by Metal Coordination and Crown-Ether-Based Molecular Recognition

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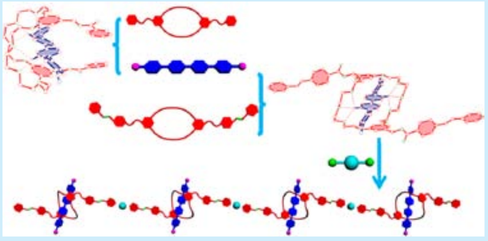
Supporting Information

ABSTRACT: A novel bis(*m*-phenylene)-32-crown-10 derivative bearing two π-extended pyridyl groups was synthesized, and its host−guest complexation with a paraquat derivative to form a threaded [2]pseudorotaxane was studied. Subsequently, a poly[2]pseudorotaxane was constructed with a metallosupramolecular polymer backbone via metal coordination, which was comprehensively confirmed by the combination of ^{1}H NMR, ^{31}P{^{1}H} NMR, DOSY NMR, DLS, and EDX techniques.



Self-assembly[1] is a key process in the natural world. As intriguing and advanced self-assembled architectures, polypseudorotaxanes,[2] in which repeated macrocyclic hosts (such as crown ethers,[3] cyclodextrins,[4] pillararenes,[5] etc.) or pseudorotaxane units are introduced into a long-chain polymeric backbone, have captured great attention in the scientific community, not only because of their fascinating topologies but also due to their potential applications in materials science, nanotechnology, etc.[6] However, the threading efficiency of macrocyclic hosts or self-complementary guests to the covalent polymeric backbone is somewhat influenced by various factors, such as polymeric chain length, etc.[7] Alternatively, supramolecular polymers,[8] which are polymeric arrays of monomeric units linked together by noncovalent interactions, can serve as more preferable backbones for the construction of polypseudorotaxanes, since the novel structures would be endowed with unique topology and adaptive properties. For example, in 2009, Huang and co-workers reported the preparation of linear main-chain polypseudorotaxanes with supramolecular polymer backbones via two self-sorting host−guest recognition motifs.[9] In 2011, Wang and co-workers reported the formation of polypseudorotaxane networks by cross-linking quadruple hydrogen-bonded linear supramolecular polymers.[10]

Coordination-driven self assembly is a versatile methodology to construct supramolecular coordination complexes (SCCs) based on the spontaneous formation of metal−ligand bonds.[11] Therefore, the preparation of polypseudorotaxanes by metal−ligand self assembly is a viable method for the programmed organization of mechanically linked molecular components into advanced architectures with considerable stability and hierarchical complexity.[12] However, to the best of our knowledge, such interesting metallosupramolecular self assemblies have rarely been reported. In other words, polypseudorotaxanes with metallosupramolecular polymer backbones are underexplored yet present a powerful way to develop supramolecular materials. Therefore, we are interested in the preparation of metallosupramolecular poly[2]pseudorotaxane via metal coordination and crown-ether-based molecular recognition.

Bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivatives, which have symmetric chemical structures, can form taco or threaded host−guest complexes with paraquat derivatives with good binding ability, showing interesting geometries.[13] To efficiently prepare metallosupramolecular poly[2]pseudorotaxanes via BMP32C10-based molecular recognition, two factors should be considered: (1) the introduction of Lewis basic donors on BMP32C10 to coordinate with metal acceptors and (2) the formation of threaded structures instead of taco complexes between BMP32C10 and paraquat derivatives. Herein, we report the construction of a metallosupramolecular poly[2]pseudorotaxane via metal coordination and BMP32C10-based molecular recognition.

Previously, Gibson and Huang et al. demonstrated that a BMP32C10 derivative bearing two pyridyl groups (**1**) can form taco complexes with paraquat derivatives, which made it impossible to prepare polypseudorotaxanes based on **1**.[13] To overcome this barrier, we designed a novel BMP32C10 derivative bearing two π-extended pyridyl groups (**2**), which not only forms a threaded [2]pseudorotaxane with paraquat derivative **3** but also offers pyridyl ligands to coordinate with metal acceptors, making it possible to prepare a metallosupramolecular poly[2]pseudorotaxane (Scheme 1).

Job plots[14] (Figure S4, Supporting Information) based on UV−vis spectroscopy absorbance data demonstrated that both $\mathbf{1}\supset\mathbf{3}$ and $\mathbf{2}\supset\mathbf{3}$ were of 1:1 stoichiometry in acetone. Furthermore, electrospray ionization mass spectrometry (ESI-MS) also confirmed this: m/z 1311.3 for $[\mathbf{1}\supset\mathbf{3} - \mathrm{PF}_6]^+$ and 583.4 for $[\mathbf{1}\supset\mathbf{3} - 2\mathrm{PF}_6]^{2+}$ (Figure S5, Supporting Information), m/z 1515.5 for $[\mathbf{2}\supset\mathbf{3} - \mathrm{PF}_6]^+$ and 685.7 for $[\mathbf{2}\supset\mathbf{3} - 2\mathrm{PF}_6]^{2+}$

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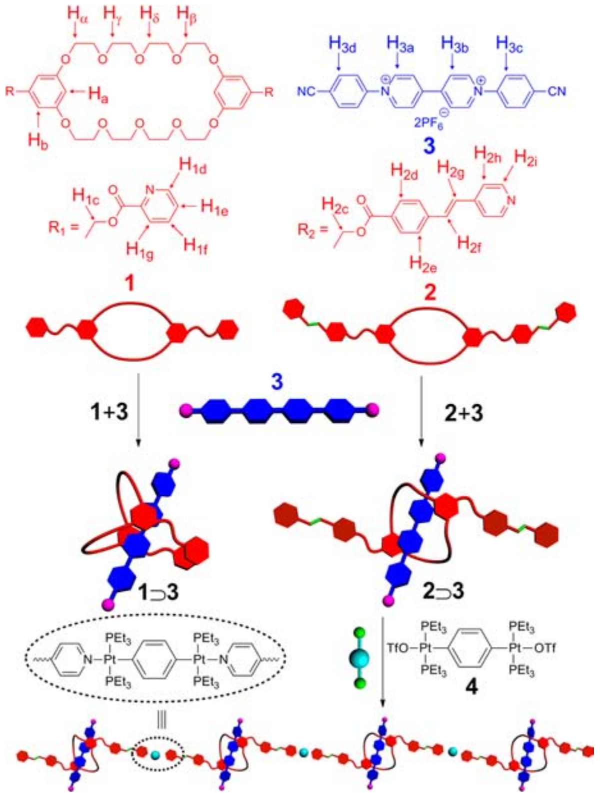
Scheme 1. Compounds Used in This Study and Cartoon Representation of the Formation of Metallosupramolecular Poly[2]pseudorotaxane Diven by Metal Coordination



(Figure S6, Supporting Information). There are no peaks with other complexation stoichiometries. The association constants (K_a) were determined in acetone by using a UV−vis titration method to be $(3.91 \pm 0.24) \times 10^3$ M^{-1} for **1**⊃**3** and $(5.68 \pm 0.27) \times 10^2$ M^{-1} for **2**⊃**3** (Figures S7 and S8, Supporting Information). It is worth noting that the K_a value for **1**⊃**3** is about 7 times higher than that of **2**⊃**3**, indicating that the formation of a supramolecular cryptand (as shown in crystal structure) enhances the host−guest complexation.[13b]

The ^{1}H NMR spectra of an equimolar (5.00 mM) mixture of **1** (or **2**) and **3** in acetone-d_6 at room temperature showed that the complexation is a fast exchange on the NMR time scale (Figure 1). In the spectrum of the complex, pronounced upfield shifts of the aromatic protons of **1** (H_{1a}, H_{1b}), **2** (H_{2a}, H_{2b}), and **3** (H_{3b}) suggest that stacking occurs between these electronically complementary aromatic rings. What is more, peaks corresponding to H_{3c-d} for **1**⊃**3** split into two peaks, while they almost remain the same for **2**⊃**3** (Figure 1, spectra b and d). This phenomenon may be ascribed to the asymmetrical host−guest binding between **1** and **3**.

The host−guest complexation and self-assembled structures were further studied by single-crystal X-ray analysis. Yellow single crystals of **1**⊃**3** and **2**⊃**3** with 1:1 stoichiometries were obtained by vapor diffusion of diisopropyl ether into their solutions in CH_3CN. The structure of **1**⊃**3** demonstrates that host **1** and guest **3** form a taco complex structure (Figure 2a). Three driving forces stabilize this supramolecular cryptand-based complex: charge-transfer interactions, hydrogen bonding (four hydrogen bonds formed between two hydrogen atoms of guest **3** and four oxygen atoms of host **1**), and π-stacking interaction between the two pyridyl groups on **1**. However, complex **2**⊃**3** shows a [2]pseudorotaxane-type threaded structure in the solid state (Figure 2b), which is consistent with our expectation. Furthermore, guest **3** in the complex **2**⊃**3** is much more symmetrical than that of **1**⊃**3**, which can account for their different behaviors (Figure 1).

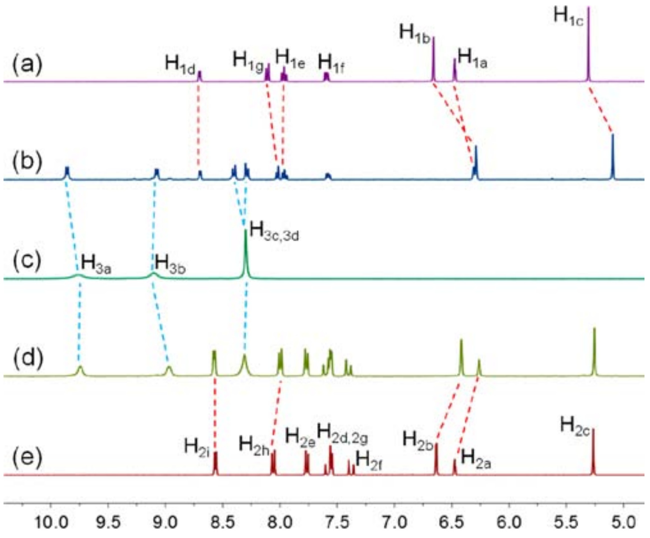


Figure 1. Partial ^{1}H NMR spectra (400 MHz, acetone-d_6, 293 K): (a) **1**; (b) **1** + **3**; (c) **3**; (d) **2** + **3**; (e) **2**. c = 5.00 mM.

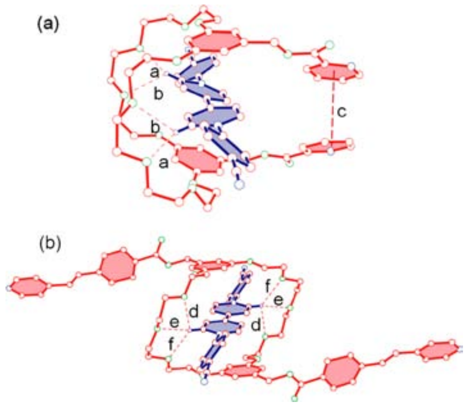


Figure 2. Ball-and-stick views of the X-ray structures of **1**⊃**3** (a) and **2**⊃**3** (b). Hosts **1** and **2** are red, guest **3** is blue, hydrogens are purple, oxygens are green, and nitrogens are sky blue. PF_6^- counterions and hydrogens except the ones involved in hydrogen bonding were omitted for clarity. Hydrogen bond parameters are as follows, C···O distance (Å), H···O distance (Å), C−H···O angles (deg): **a**, 3.31, 2.41, 159.5; **b**, 3.32, 2.63, 129.7; **d**, 2.95, 2.59, 103.2; **e**, 3.25, 2.31, 171.7; **f**, 3.17, 2.62, 117.6. Face to face π-stacking parameters: centroid−centroid distance (Å) **c**, 3.92; ring plane−ring plane inclination (deg), 11.4.

From the crystal structure of **2**⊃**3**, we find that the pyridine nitrogen atoms on BMP32C10 are located outside, which makes them easy to coordinate with metal acceptors. Therefore, we constructed a poly[2]pseudorotaxane with a metallosupramolecular polymer backbone based on metal-coordination interaction with 180° diplatinum(II) acceptor **4**. When equimolar **4** was added into the acetone-d_6 solution of **2** and **3** at 5.00 mM, higher than the critical precipitation concentration (2.00 mM), some flocculent precipitate formed immediately that can be attributed to the formation of a metallosupramolecular poly[2]pseudorotaxane with high molecular weight (Figure 3b). After several minutes of standing, the solid

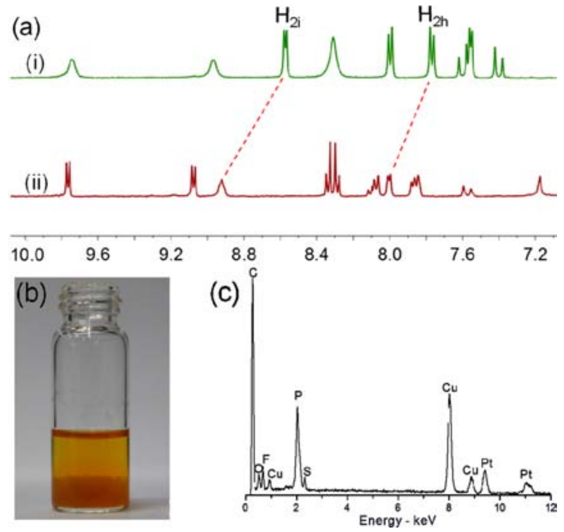


Figure 3. (a) Partial ^{1}H NMR spectra (400 MHz, acetone-d_6, 293 K): (i) **2** + **3**; (ii) **2** + **3** + **4**. (b) Optical image of (ii) after standing for several minutes. (c) EDX spectrum of (ii). c = 5.00 mM.

precipitate fell to the bottom of the bottle, and the supernate was used to perform ^{1}H NMR, ^{31}P{^{1}H} NMR, two-dimensional diffusion-ordered NMR (DOSY), and dynamic light scattering (DLS) experiments.

In the ^{1}H NMR spectrum, pronounced downfield shifts of the pyridine protons of host **2** (H_{2h} and H_{2i}) were observed because the N-atom on the pyridyl group coordinates to the electron-withdrawing platinum(II) center, leading to a loss of electron density (Figure 3a). What is more, the chemical shifts of an equimolar (5.00 mM) solution of **2** and **4** are almost the same as the equimolar (5.00 mM) mixture of **2**, **3**, and **4**. This phenomenon indicates that the cyano groups on the guest have no influence on the coordination (Figure S12, Supporting Information). The ^{31}P{^{1}H} NMR spectrum of the supernate consists of one major ^{31}P signal at δ = 12.95 ppm with two concomitant ^{195}Pt satellites. Moreover, an additional ^{31}P signal (δ = 12.70 ppm) of lower intensity was also observed, which probably arises from ^{31}P resonances of the end group (Figure S10, Supporting Information). The peak shifted upfield from the starting diplatinum(II) acceptor **4** by ca. 5.30 ppm (Figure S11, Supporting Information), indicating coordination-driven self assembly. DOSY NMR experiments displayed that the addition of equimolar **4** into the solution of **2** and **3** (5.00 mM) changed the D values from 7.08×10^{-10} to 2.51×10^{-10} m^{2}s^{-1}, which indicated the formation of a supramolecular polymer (Figures S13−15, Supporting Information). The DLS result revealed the solution of **2⊃3** has a size of about 2.20 nm (Figure 4a). Though the crystal structure shows the length of the molecule is 3.20 nm, the difference is reasonable because of averaging over all directions. After the addition of **4**, the average diameter of the assembly was about 342 nm (Figure 4b), providing convincing proof to support the formation of high molecular weight metallosupramolecular poly[2]-pseudorotaxane. A characteristic energy-dispersive X-ray spectroscopy (EDX) profile of both the flocculent precipitate and the supernate shows the presence of Pt and P (Figure 3c), further indicating the formation of a metallosupramolecular poly[2]pseudorotaxane driven by metal coordination.

In summary, we have synthesized a novel BMP32C10 derivative bearing two π-extended pyridyl groups, **2**, and studied its binding to paraquat derivative **3**. The X-ray crystal structure showed that the host−guest complex **2⊃3** adopted a threaded geometry with pyridyl nitrogen atoms outside, a sharp contrast to the reported pyridine-functionalized BMP32C10 derivative **1**, which formed a supramolecular cryptand-based taco complex with **3**. The outside pyridyl nitrogen atoms on **2⊃3** endow this complex with post-self-assembly behavior by metal coordination. Subsequently, we constructed a poly[2]-pseudorotaxane with a metallosupramolecular polymer backbone via metal coordination. The combination of various techniques, such as ^{1}H NMR, ^{31}P{^{1}H} NMR, DOSY NMR, DLS, and EDX comprehensively confirmed the formation of this unique metallopoly[2]pseudorotaxane. The dynamic and reversible supramolecular polymer backbone endows the novel polypseudorotaxane structure with adaptive properties. Furthermore, monodisperse polyrotaxanes and stimuli-responsive materials can be constructed by using such a one-dimensional metallosupramolecular polypseudorotaxane, which is now carried out in our group.

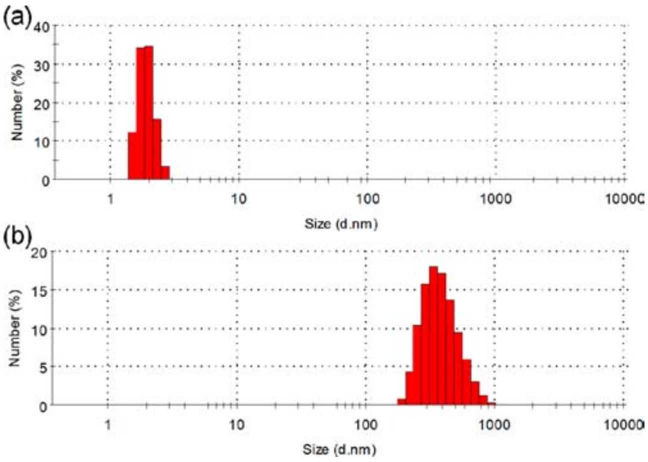


Figure 4. Size distributions of (a) **2** + **3** and (b) **2** + **3** + **4**. c = 5.00 mM.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis of **2**, ESI-MS, X-ray crystallographic files (CIF) for **1⊃3** and **2⊃3** (CCDC 963240 and 963241), and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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