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Supramolecular Side-Chain Poly[2]pseudorotaxanes Formed by Orthogonal Coordination-Driven Self-Assembly and Crown-Ether-Based Host–Guest Interactions

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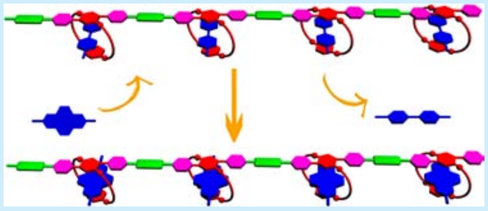
S *Supporting Information*

ABSTRACT: The themes of coordination-driven self-assembly, host–guest interactions, and supramolecular polymerization are unified in an orthogonal noninterfering fashion to deliver side-chain poly[2]pseudorotaxanes. Specifically, a bis(*p*-phenylene)-34-crown-10 derivative **1** bearing two pyridyl groups polymerizes into a side-chain poly[2]pseudorotaxane upon the addition of di-Pt(II) acceptor **4** in the presence of paraquat. Interestingly, by adding a competitive guest **3**, the poly[2]pseudorotaxane can realize a conversion in one pot.



In supramolecular chemistry and polymer science, the formation of mechanically bonded polymers, such as polyrotaxanes and polycatenanes, has captured increasing attention from the scientific community because of the reversibility of mechanical bonds, along with the processability and unique mechanical and physical characteristics of such superstructures, which ensure their potential applications in molecular devices, materials science, *etc.*[1] Polypseudorotaxanes, the supramolecular precursors of polyrotaxanes and polycatenanes, are polymeric architectures having pseudorotaxanes as repeated units.[2] Generally, there are two main approaches for the formation of polypseudorotaxanes. Route I is the incorporation of repeated macrocyclic hosts (such as crown ethers,[3] cyclodextrins and calixarenes,[4] pillararenes,[5] *etc.*) into polymeric backbones. Harada et al. first utilized this strategy to construct polypseudorotaxanes by incorporating cyclodextrins into linear poly(ethylene glycol) or poly(propylene glycol) chains.[6] Route II is the incorporation of discrete pseudorotaxane moieties into the polymeric main-chain or side-chain part. This methodology was well investigated by the Gibson group who recently reported a supramolecular pseudorotaxane graft copolymer from a crown ether polyester and a complementary paraquat-terminated polystyrene guest.[7] As defined by Gibson et al., for polypseudorotaxanes and polyrotaxanes, at least one covalent polymer should be used as a component.[8] However, many intrinsic and extrinsic factors such as chain length and the density of mechanically linked subunits may influence the threading efficiency of macrocyclic hosts or self-complementary guests to the covalent polymeric backbone.[9] Alternatively, supramolecular polymers[10] assembled from monomeric units are reversible and stimuli-responsive, which can demonstrate traditional polymeric properties in solutions as well as in the bulk. Therefore, many scientists are pursuing effective methods to construct novel polypseudorotaxanes with supramolecular polymer backbones instead of traditional covalent ones, which might possess some unique and adaptive properties that are unachievable via traditional polypseudorotaxanes. For example, Huang et al. reported the formation of main-chain polypseudorotaxane with crown ether-based supramolecular polymer backbones.[11] Recently, Wang et al. reported a pillar[5]arene-based supramolecular polypseudorotaxane polymer networks constructed by quadruple H-bonding interfaces.[12]

Coordination-driven self-assembly, which is based on the formation of metal–ligand bonds, has been proven to be a powerful methodology to construct supramolecular coordination complexes (SCCs).[13] By directing by this convenient and efficient means, a plethora of complicated supramolecular architectures with considerable stability and hierarchical complexity have been successfully prepared.[14] Recently, in their pioneering works, Huang and Stang et al. realized hierarchical supramolecular polymerization of discrete metallacycles to access novel supramolecular polymeric materials.[15] Their efforts imply the importance of coordination-driven self-assembly for the formation of supramolecular materials. While up to now, to the best of our knowledge, metal-coordination-driven supramolecular polymerization of pseudorotaxanes in a hierarchical orthogonal fashion to construct supramolecular side-chain polypseudorotaxanes with metallosupramolecular polymer backbone has not been reported yet.

Bis(*p*-phenylene)-34-crown-10 (BPP34C10) derivatives can form threaded host–guest complexes with paraquat derivatives with good binding ability.[16] Moreover, they show much better binding ability with more electron-deficient organic guest molecules, such as 2,7-diazapyrenium derivatives. Herein, we present a facile strategy to construct complexed supramolecular architectures on the basis of such recognition motifs. Our approach involves the unification of coordination-driven self-assembly and BPP34C10-based host–guest interactions in an orthogonal fashion to deliver desired supramolecular side-chain

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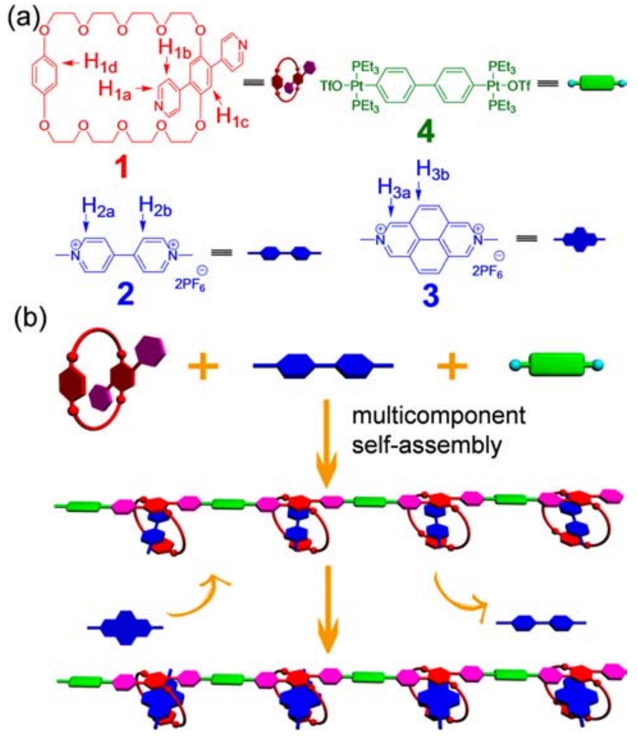
poly[2]pseudorotaxanes with the same metallosupramolecular polymer backbone. Specifically, a BPP34C10 derivative **1** bearing two pyridyl groups was synthesized by Suzuki coupling, which not only shows good binding ability toward the paraquat derivative but also offers pyridyl ligands to coordinate with metal acceptors, which make it a good candidate to prepare a metallosupramolecular side-chain poly[2]pseudorotaxane (Scheme 1b). In addition, the dynamic nature of host−guest interactions offers an opportunity to realize the transformation of poly[2]pseudorotaxanes by adding a competitive guest, 2,7-diazapyrenium derivative (DAP) **3**, which can expel paraquat **2** from the cavity of BPP34C10 **1** (Scheme 1b).

Scheme 1. (a) Compounds Used in This Study and (b) Cartoon Representation of the Formation of Metallosupramolecular Poly[2]pseudorotaxanes Driven by Metal Coordination and Host−Guest Interactions



Job plots[17] (Figure S4, Supporting Information (SI)) confirmed that both **1**⊃**2** and **1**⊃**3** were of 1:1 stoichiometries in acetone. The electrospray ionization mass spectrometry (ESI-MS) experiments further demonstrated this: m/z 1021.1 for $[\mathbf{1}\supset\mathbf{2} - PF_6]^+$ and m/z 438.3 for $[\mathbf{1}\supset\mathbf{2} - 2PF_6]^{2+}$ (Figure S5, SI); m/z 1069.2 for $[\mathbf{1}\supset\mathbf{3} - PF_6]^+$ and m/z 462.4 for $[\mathbf{1}\supset\mathbf{3} - 2PF_6]^{2+}$ (Figure S6, SI). No peaks related to the complexes with other stoichiometries were found. Based on a UV−vis titration method, the association constants (K_a) were determined in acetone to be 7.04×10^2 M^{-1} for **1**⊃**2** and 2.70×10^3 M^{-1} for **1**⊃**3** (Figures S7 and S8, SI). It is noteworthy that the K_a value of **1**⊃**3** is about 4 times higher than that of **1**⊃**2**, which makes it possible to realize the competitive binding between them and host **1**.

The proton NMR spectra of equimolar (5.00 mM) acetone solutions of **1** and **2** (or **3**) (Figure 1) showed that the complexation is a fast exchange process. In the spectrum of complex **1**⊃**2**, obvious upfield shifts in the signals of the aromatic protons of **1** (H_{1b-d}) and **2** (H_{2a} and H_{2b}) indicate that π-stacking occurs between these electronically complementary aromatic rings (Figure 1a−c). The proton NMR spectrum of equimolar (5.00 mM) acetone solutions of **1** and **3** (Figure 1d) was also studied and displayed more significant changes in the chemical shifts of the protons of the complex (H_{1b-d} on **1** and H_{3a} and H_{3b} on **3**), indicating that the binding ability of complex **1**⊃**3** was stronger than that of **1**⊃**2**. These results are consistent with the association constant difference between these two complexes.

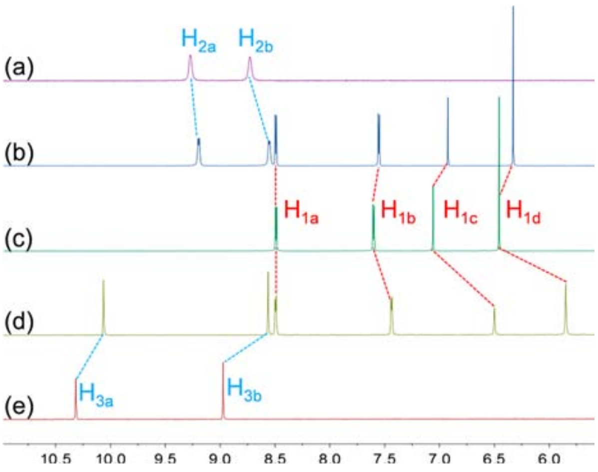


Figure 1. Partial ^1H NMR spectra (500 MHz, acetone-d_6, 293 K): (a) **2**; (b) **1** + **2**; (c) **1**; (d) **1** + **3**; (e) **3**. c = 5.00 mM.

Single-crystal X-ray analysis was used to further validate the host−guest complexation and self-assembled structure. A yellow single crystal of **1**⊃**2** with 1:1 stoichiometry was obtained by a vapor diffusion method. Complex **1**⊃**2** shows a pseudorotaxane-type threaded structure in the solid state (Figure 2), which is consistent with our expectation. Two driving forces stabilize this supramolecular complex: charge-transfer interactions and H-bonds (five H-bonds formed between four H-atoms of guest **2** and four O-atoms of host **1**).

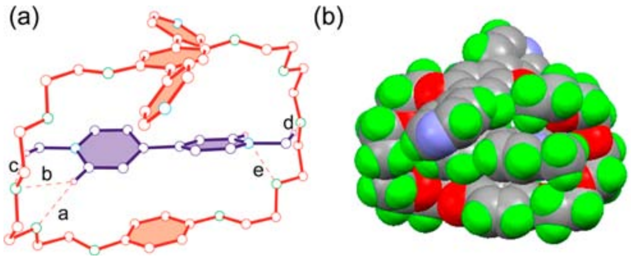


Figure 2. (a) Ball-and-stick view of the X-ray structure of **1**⊃**2**. Host **1** is red, guest **2** is blue, hydrogens are purple, oxygens are green, and nitrogens are sky blue; PF_6^- counterions and hydrogens except the ones involved in H-bonding were omitted for clarity. H-bond parameters are as follows, C···O distance (Å), H···O distance (Å), C−H···O angles (deg): **a**, 3.05, 2.56, 112.3; **b**, 3.50, 2.66, 147.6; **c**, 3.30, 2.36, 162.0; **d**, 3.45, 2.54, 154.2; **e**, 3.18, 2.55, 124.1. (b) Space-filling view of the X-ray structure of **1**⊃**2**.

The X-ray crystal structure of **1**⊃**2** clearly shows that the pyridine N-atoms are located on the same phenyl ring of BPP34C10 **1** and oriented in the opposite directions, which makes it facile to realize metal coordination, thereby forming side-chain poly[2]pseudorotaxane. After the addition of an equimolar 180° diplatinum(II) acceptor **4** into an acetone-d_6 solution of **1** and **2** at 5.00 mM, the resultant solution of **1**, **2**, and **4** 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 order to investigate the competitive transformation from the paraquat-based polypseudorotaxane to the DAP-based polypseudorotaxane, equimolar guest **3** was then added into the above acetone-d_6 solution of **1**, **2**, and **4**, and the resultant solution of **1**, **2**, **4**, and **3** was also used to perform ^{1}H and $^{31}P\{^{1}H\}$ NMR studies.

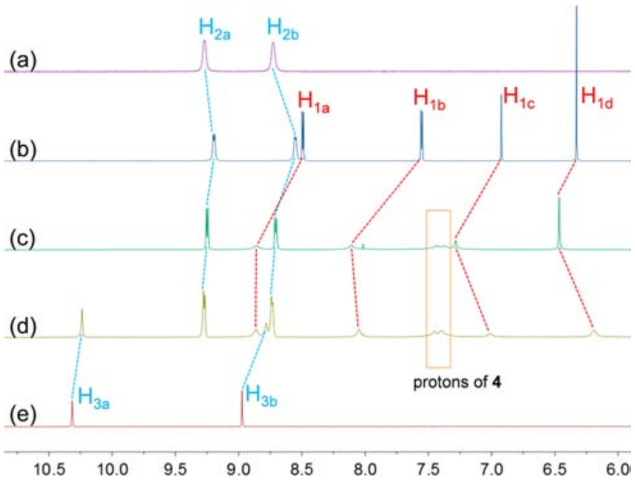


Figure 3. Partial ^{1}H NMR spectra (500 MHz, acetone-d_6, 293 K): (a) **2**; (b) **1** + **2**; (c) **1** + **2** + **4**; (d) **1** + **2** + **4** + **3**; (e) **3**. c = 5.00 mM.

In the ^{1}H NMR spectrum of the solution of **1**, **2**, and **4**, the pyridine protons exhibited downfield shifts (H_{1a} and H_{1b}), resulting from the loss of electron density upon coordination of the pyridine N-atom with the Pt(II)-center (Figure 3c). The $^{31}P\{^{1}H\}$ NMR spectrum of the solution of **1**, **2**, and **4** consists of one major sharp ^{31}P signal at δ = 18.62 ppm with two concomitant ^{195}Pt satellites, which corresponded to a single phosphorus environment (Figure S11, spectrum c). The peak shifted upfield from the starting diplatinum(II) acceptor **4** by ca. 5.09 ppm (Figure S11, spectrum a), indicating coordination-driven self-assembly. The multiple NMR analysis of the reaction mixture of **1**, **2**, and **4** supported the formation of metallosupramolecular poly[2]pseudorotaxane based on the BPP34C10/paraquat recognition motif. Moreover, despite these observable changes in the ^{1}H NMR spectra, no significant changes are notable in the $^{31}P\{^{1}H\}$ NMR spectra of system **1** and **4**, and system **1**, **2**, and **4**, which indicated that the phosphorus environment was not affected by the host−guest interactions that have little bearing on the Pt−N bonding.

To further confirm the formation of the metallosupramolecular polymer backbone, a DOSY NMR experiment was performed to study the self-assembly between **1** and **4** (Figures S9 and S10, SI). Upon the addition of **4** into a solution of **1** (5.00 mM), the measured weight-average diffusion D values decreased from 9.77×10^{-10} to 3.55×10^{-11} m^2 s^{-1}, indicating the formation of a high-molecular-weight aggregate (Figure 4a). In addition, DLS experiments were conducted to study the size distributions of the assemblies. The average hydrodynamic diameter (D_h) of [2]pseudorotaxane **1**⊃**2** was determined to be 1.45 nm (Figure 4b), which is close to the maximum length of its X-ray crystal structure (Figure 2a). After di-Pt(II) acceptor **4** was added into the solution of **1**⊃**2**, the corresponding D_h value increased significantly to 615 nm (Figure 4b), which showed the presence of metallosupramolecular poly[2]pseudorotaxane. A similar increase in D_h values was also observed in the cases of **1** + **4** and **1** + **3** + **4** (Figure S12). Furthermore, cyclic voltammetry experiments of the assemblies were conducted to study their electrochemical activities. It was found that the electrochemical property of paraquat was influenced significantly when it was recognized to form side-chain poly[2]-pseudorotaxane (Figure S13, SI).

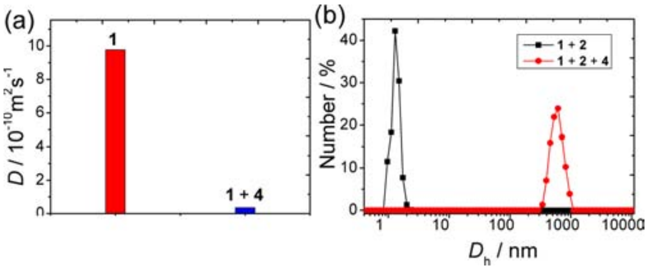


Figure 4. (a) Diffusion coefficient D values (500 MHz, acetone-d_6, 293 K) of **1** and **1** + **4**. (b) Size distributions of **1** + **2** and **1** + **2** + **4**. c = 5.00 mM.

Interestingly, the dynamic nature of host−guest interactions offers an opportunity to realize the transformation of the paraquat-based polypseudorotaxane by adding a competitive guest. For instance, after the addition of guest **3** into the acetone-d_6 solution of **1**, **2**, and **4**, pronounced upfield shifts in the signals of the aromatic protons of **3** (H_{3a} and H_{3b}) were observed (Figure 3d), along with the chemical shifts corresponding to the paraquat protons (H_{2a} and H_{2b}) restored to their uncomplexed values, suggesting that more stable DAP-based polypseudorotaxane formed while the paraquat-based polypseudorotaxane dissociated. Moreover, the pronounced upfield shifts in the signals of the aromatic protons of **1** (H_{1b-d}) were also observed, which further indicated the formation of the DAP-based polypseudorotaxane since the π-electron-deficient character of **3** can enhance the π-stacking interactions.

In summary, we have synthesized a BPP34C10 derivative bearing two pyridyl groups and studied its binding to paraquat **2** and DAP **3**. It was found that the binding ability of **1** to **3** is stronger than that of **1** to **2**. The X-ray crystal structure showed that the host−guest complex **1**⊃**2** adopted a threaded geometry with pyridyl N-atoms outside, which endowed this complex with post-self-assembly behavior by metal coordination. Subsequently, we constructed the paraquat-based side-chain polypseudorotaxane with a metallosupramolecular polymer backbone via metal coordination. This was confirmed by the combination of various techniques, such as ^{1}H NMR, $^{31}P\{^{1}H\}$ NMR, DOSY NMR, and DLS. Interestingly, after guest **3** was added into the solution of **1**, **2**, and **4**, the more stable DAP-based polypseudorotaxane formed while the paraquat-polypseudorotaxane dissociated due to the competitive host−guest complexation. The design methodology established here includes orthogonal noninterfering self-assembly with metal coordination, host−guest interactions, and supramolecular polymerization. It is highly expected that this design principle would benefit the construction of complexed supramolecular materials with reversibility and adaptability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of **1**, ESI-MS, Job plots, X-ray crystallographic files (CIF) for **1**⊃**2** (CCDC 982064), and other materials. These materials are 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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