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A chemical-responsive bis(*m*-phenylene)-32-crown-10/2,7-diazapyrenium salt [2]pseudorotaxane†

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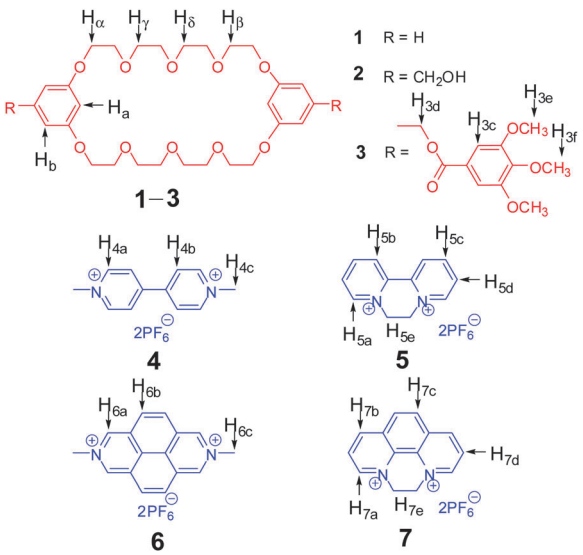
A chemical-responsive bis(*m*-phenylene)-32-crown-10/2,7-diazapyrenium salt [2]pseudorotaxane was prepared. It was found to form a supramolecular poly[2]pseudorotaxane in the solid state driven by π–π stacking interactions.

Of continuing interest in the field of supramolecular chemistry, in particular, in the design of molecular machines,[1] supramolecular polymers,[2] and functional supramolecular materials,[3] is the bottom-up construction of externally addressable supramolecular structures.[4] As a result, host–guest chemistry based on macrocyclic compounds (such as crown ethers, cyclodextrins, pillararenes *etc.*) has seen mighty progress in various aspects of supramolecular chemistry due to its good selectivity, high efficiency, and stimuli-responsiveness.[5] In host–guest chemistry, pseudorotaxanes,[6] the fundamental building blocks for the preparation of advanced mechanically interlocked supramolecular architectures with fascinating properties, are host–guest complexes in which linear molecular components (guests) are encircled by macrocyclic components (hosts). Therefore, the fabrication and preparation of pseudorotaxanes, especially with novel topologies and using new host–guest recognition motifs which can exhibit response to external stimuli, have been a topic of great interest and challenge.

2,7-Diazapyrenium (DAP) derivatives, which integrate the features of pyrene, viologens, and nucleic acid intercalators, have been proved to be versatile building blocks in supramolecular chemistry.[7] The π-electron-deficient character and extended π-surface ensure efficient supramolecular associations with various π-electron-rich counterparts, thereby facilitating the construction of advanced supramolecular architectures. For example, Stoddart and coworkers prepared functional molecular machines based on the recognition of crown ether derivatives to DAP derivatives.[8] Kaifer *et al.* designed and prepared DAP-based fluorescence probes for the detection of ions and neurotransmitters due to their good host–guest association and luminescence properties.[9] However, up to now, the host–guest complexation and self-assembled structures from bis(*m*-phenylene)-32-crown-10 and 2,7-diazapyrenium derivatives have not been exploited yet, possibly because of the preconception that the cavity of bis(*m*-phenylene)-32-crown-10 was not large enough to allow the DAP derivatives to thread.



Herein, a novel bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivative bearing two electron-rich pyrogallol trimethyl ether groups (**3**) was synthesized. By the self-assembly of **3** with dimethyldiazapyrenium (DMDAP) dication **6**, a threaded [2]pseudorotaxane was obtained, and then a supramolecular poly[2]pseudorotaxane was formed in the solid state driven by π–π stacking interactions. More interestingly, the assembly and disassembly of this [2]pseudorotaxane can be reversibly controlled by the sequential addition of basic and acidic chemicals (Et_2NH and TFA, respectively). For comparison, the host–guest chemistry between host **3** and guests **4**, **5**, and **7** was also addressed.

Equimolar acetone solutions of host **3** with guests **4–7** are yellow because of charge transfer interactions between electron-rich aromatic rings of the host and electron-poor pyridinium rings of the guests, which is direct evidence for complexation. Job's plots[10] (Fig. S4, ESI†) based on UV–vis spectroscopy absorbance data in acetone demonstrated that all these host–guest complexes were of 1 : 1 stoichiometry in solution.

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† Electronic supplementary information (ESI) available: Compound characterization, synthetic details, determination of association constants, ESIMS, X-ray crystallographic files (CIF) for **3**⊃**6** and **3**⊃**7**, X-ray analysis data on **3**⊃**6** and **3**⊃**7**, and other materials. CCDC 879994. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33783e

This was further confirmed by electrospray ionization mass spectrometry (ESIMS): m/z 1315.6 for $[\mathbf{3}\supset\mathbf{4} - PF_6]^+$, m/z 585.5 for $[\mathbf{3}\supset\mathbf{4} - 2PF_6]^{2+}$, m/z 1313.7 for $[\mathbf{3}\supset\mathbf{5} - PF_6]^+$, m/z 584.6 for $[\mathbf{3}\supset\mathbf{5} - 2PF_6]^{2+}$, m/z 1364.1 for $[\mathbf{3}\supset\mathbf{6} - PF_6]^+$, m/z 1337.6 for $[\mathbf{3}\supset\mathbf{7} - PF_6]^+$, and m/z 596.6 for $[\mathbf{3}\supset\mathbf{7} - 2PF_6]^{2+}$ (Fig. S5–S8, ESI†). No peaks with other complexation stoichiometries were found. The association constants (K_a) were determined in acetone by using a UV–vis titration method to be 1.67×10^2 M^{-1} for **3**⊃**4**, 63.6 M^{-1} for **3**⊃**5**, 2.17×10^3 M^{-1} for **3**⊃**6**, 3.91×10^2 M^{-1} for **3**⊃**7**. It is worth noting that the K_a values of **3**⊃**6** (or **7**) are about 13 (or 6) times higher than that of **3**⊃**4** (or **5**), indicating that the π-electron-deficient character and extended π-surface of **6** and **7** can enhance the binding affinity of the crown ether portion for their heterocyclic cores.

The proton NMR spectra of equimolar (1.00 mM) acetone solutions of **3** and **6** (Fig. 1d) showed that the complexation is fast exchange. In the spectrum of the complex **3**⊃**6**, pronounced upfield shifts in the signals of the aromatic protons of **3** (H_{3a}, H_{3b}) and **6** (H_{6a}, H_{6b}) suggest that stacking occurs between these electronically complementary aromatic rings. The proton NMR spectrum of an equimolar (1.00 mM) acetone solution of **3** and **4** (Fig. 1a–c) was also investigated for comparison and only slight chemical shift changes were observed for the protons of both **3** and **4**, indicating that the binding ability of complex **3**⊃**6** was stronger than that of **3**⊃**4**. Similar chemical shift changes were also observed in the cases of **3**⊃**5** and **3**⊃**7** (Fig. S13, ESI†). These results are consistent with the association constant difference between these complexes.

To further study the host–guest complexation and self-assembled structures, a yellow crystal of **3**⊃**6** with 1 : 1 stoichiometry was grown by a vapor diffusion method. The X-ray crystal structure of complex **3**⊃**6** demonstrated that host **3** and guest **6** form a [2]pseudorotaxane-type threaded structure in the solid state (Fig. 2a) instead of the common taco complex structures observed in the BMP32C10–paraquat complexation, possibly because the two big pyrogallol trimethyl ether groups make the complex **3**⊃**6** assume a "zig–zig" geometry (Fig. 2a), as observed by Gibson *et al.*[6a] The complex **3**⊃**6** is stabilized by hydrogen bonding and face-to-face π-stacking

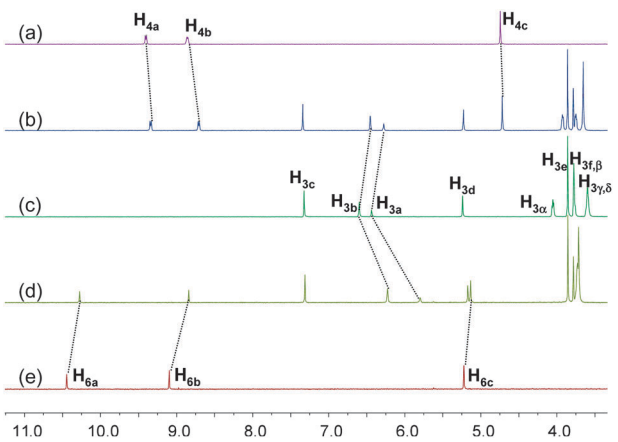

Fig. 1 Partial ^1H NMR spectra (acetone-d_6, 293 K, 400 MHz): (a) 1.00 mM **4**; (b) 1.00 mM **3** and **4**; (c) 1.00 mM **3**; (d) 1.00 mM **3** and **6**; (e) 1.00 mM **6**.

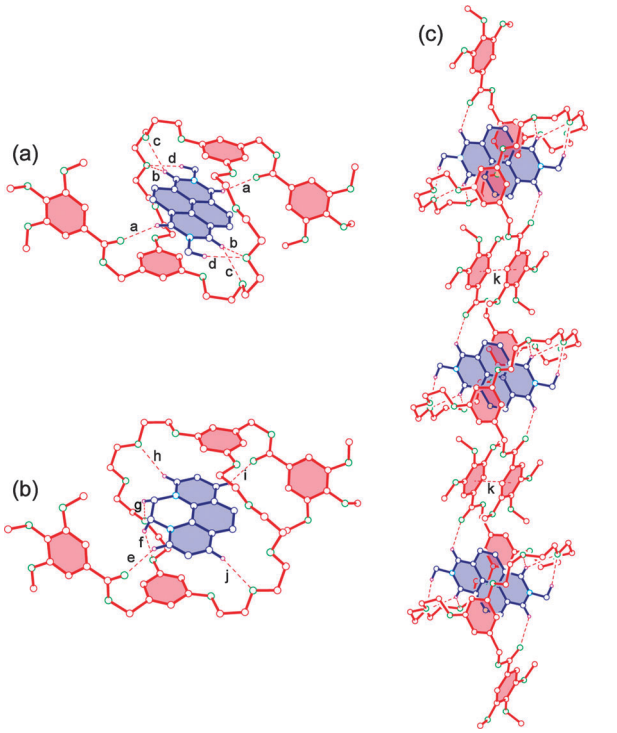

Fig. 2 Ball–stick views of the X-ray structures of **3**⊃**6** (a) and **3**⊃**7** (b). Host **3** is red, guests **6** and **7** are blue, hydrogens are purple, oxygens are green, and nitrogens are sky blue. PF_6^- counterions, solvent molecules, and hydrogens except the ones involved in hydrogen bonding between **3** and **6** (or **7**) are omitted for clarity. Hydrogen bond parameters are as follows: C···O distance (Å), H···O distance (Å), C–H···O angles (°): a, 3.05, 2.36, 130.8; b, 3,35, 2.57, 134.0; c, 3.32, 2.53, 143.4; d, 3.27, 2.34, 162.3; e, 3.19, 2.31, 154.4; f, 3.48, 2.62, 145.5; g, 3.25, 2.48, 134.1; h, 3.37, 2.60, 138.5; i, 3.12, 2.24, 154.1; j, 3.45, 2.62, 146.0. Face to face π-stacking parameters: centroid–centroid distance (Å) k, 3.78; ring plane–ring plane inclination (°): 0. (c) Supramolecular poly[2]pseudorotaxane structure of **3**⊃**6** in the solid state driven by π–π stacking interactions.

interactions. The crystal structure shows that eight hydrogen bonds are formed between six hydrogen atoms of guest **6** and six oxygen atoms of host **3**. Four α-pyridinium hydrogen atoms (a, b, and c) and two *N*-methyl hydrogen atoms (d) are involved in these hydrogen bonding interactions (Fig. 2a). What is more interesting is that a supramolecular poly[2]pseudorotaxane structure forms driven by π–π stacking interactions between the electron-rich pyrogallol trimethyl ether groups on host **3** molecules in different **3**⊃**6** complexes in the solid state (Fig. 2c). The dihedral angle between two neighbouring phenyl rings is 0°, which maximizes the π–π stacking interactions in this supramolecular poly[2]pseudorotaxane structure. From a control experiment, the single crystal structure of the complex **3**⊃**7** was also obtained and the supramolecular poly[2]pseudorotaxane structure was not observed in the solid state, indicating that the formation of supramolecular polypseudorotaxane structure is guest-dependent (Fig. 2b).

Moreover, the assembly and disassembly of the [2]pseudorotaxane between **3** and **6** can be reversibly controlled by the sequential addition of diethylamine (DEA) and trifluoroacetic acid (TFA). When DEA was added into the yellow solutions of **3** and **6**, they became dark green because the more stable

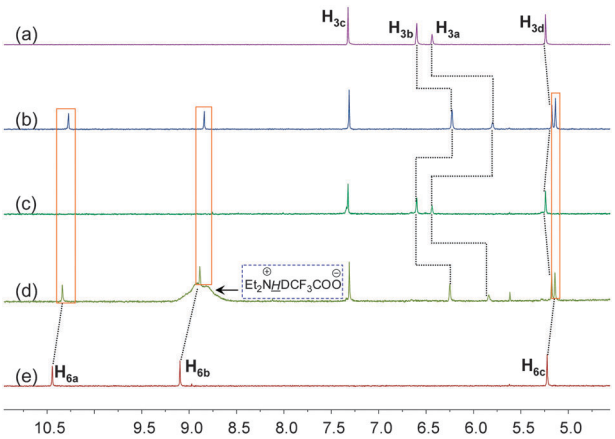

Fig. 3 Partial ^{1}H NMR spectra (acetone-d_6, 293 K, 400 MHz): (a) 1.00 mM **3**; (b) 1.00 mM **3** and **6**; (c) after addition of DEA to b; (d) after addition of TFA to c; (e) 1.00 mM **3**.

adduct between **6** and DEA was formed while the complex **3**⊃**6** was dissociated. Subsequently, the complex **3**⊃**6** can form again when enough TFA was added to neutralize DEA. Meanwhile, the dark green solution gradually reverted to yellow. This reversible process was confirmed by proton NMR experiments (Fig. 3) and UV–vis spectroscopy (Fig. S14, ESI†). When DEA (10.0 equiv.) was added to a solution of **3** (1.00 mM) and **6** (1.00 mM) in acetone-d_6 (0.5 mL), the intensity of the arene signals of **6** disappeared substantially and the protons of **3** returned to almost their uncomplexed values (Fig. 3c). However, after addition of TFA (10.0 equiv.) to this solution, the complexation between **3** and **6** was recovered; large chemical shift changes corresponding to the protons of **3** and **6** were observed again (Fig. 3d). This reversible complexation process provides a simple on–off switch which can be used in the construction of controllable molecular switches.

In summary, we have synthesized a novel bis(*m*-phenylene)-32-crown-10 derivative bearing two electron-rich pyrogallol trimethyl ether groups and studied its binding abilities to guests **4**–**7**. We found that the π-electron-deficient character and extended π-surfaces of **6** and **7** can enhance the binding affinity of the crown ether portion for their heterocyclic cores compared to the cases of **3**⊃**4** (or **5**). By the self-assembly of **3** with **6**, a threaded [2]pseudorotaxane was obtained instead of a folded taco complex, and then a supramolecular poly[2]-pseudorotaxane was formed in the solid state driven by π–π stacking interactions. More interestingly, we demonstrated that the assembly and disassembly of this [2]pseudorotaxane can be reversibly controlled by the sequential addition of diethylamine and trifluoroacetic acid. Our current efforts are focused on extending this chemical-responsive recognition motif to fabricate molecular switches and mechanically interlocked molecular machines.

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