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Chemically-Responsive Complexation of A Diquaternary Salt with Bis(*m*-phenylene)-32-Crown-10 Derivatives and Host Substituent Effect on Complexation Geometry

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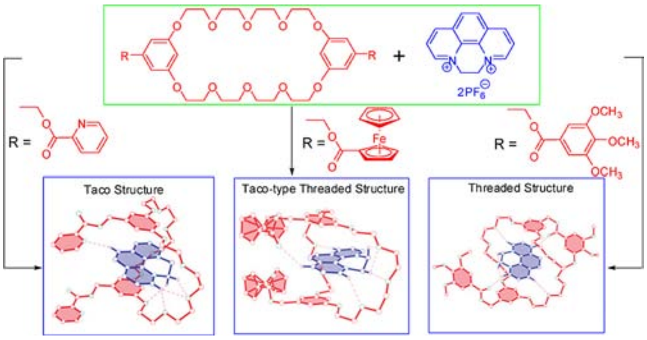
ABSTRACT



A chemically responsive diquaternary salt with π-extended surface was made. The host−guest complexation with chemo-responsiveness between three bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivatives and this diquaternary salt guest was studied through the sequential addition of basic and acidic reagents (diethylamine and trifluoroacetic acid, respectively). Furthermore, the host-substituent effect on the complexation geometries of these three host−guest complexes, from taco to taco-type threaded to threaded structures by changing the substituent on BMP32C10 as shown by crystal structures, was also addressed.

In host−guest chemistry, available recognition motifs with stimuli-responsiveness are the genesis of a diverse range of responsive supramolecular assemblies, such as molecular machines,[1] supramolecular polymers,[2] and other functional supramolecular materials.[3] Therefore, exploring novel responsive recognition motifs will undoubtedly push forward the development of supramolecular chemistry.[4] The diquaternary salt of phenanthroline **4** (Figure 1), which possesses the features of rigidity, planarity, aromaticity, etc., has been proven to be a useful building block in supramolecular chemistry.[5] Furthermore, its π-electron-deficient character

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and extended π-surface ensure efficient supramolecular associations with various π-electron-rich counterparts.[5c] Meanwhile, by comparing the structural characteristics of **4** with 2,7-diazapyrenium derivative **5** (Figure 1), we speculate that this salt can also respond to chemical stimuli. However, up to now, this issue has never been addressed.

On the other hand, control of the binding behavior of a guest into a host and the relative positional changes that occur within host−guest complexes are of extreme importance for the preparation of advanced functional supramolecular assemblies.[6] Generally, small structural changes (for example different substituent groups) can cause large effects on the host−guest binding behaviors. Schalley et al. reported that the simple exchange of a CH group by an isoelectronic N atom could cause large effects on the deslipping reaction of rotaxanes.[7] Recently, we found that the replacement of a bromo atom at the end of the alkyl guest part of a copillar[5]arene with a hydrogen atom can make the conformation change between a cyclic dimer and a linear supramolecular polymer in the solid state.[8] Therefore, disclosing substituent effects on host−guest binding behaviors facilitates the efficient construction of advanced supramolecular assemblies. Herein, we report chemically responsive complexation of diquaternary salt **4** with three bis(m-phenylene)-32-crown-10 derivatives and host substituent effect on the complexation geometry.

The addition of 10.0 equiv of diethylamine (DEA) to a colorless solution of **4** in acetone gave a deep red solution (inserted picture in Figure 2) as a result of the charge-transfer (CT) interactions between electron-accepting **4** and the electron-donating amine, indicating the formation of an adduct between them. Meanwhile, the formation of the adduct causes the appearance of a broad CT absorption band (λ_{max} = 490 nm, trace b in Figure 2). Then, the addition of trifluoroacetic acid (TFA, 10.0 equiv) resulted in the loss of the deep red color, giving back the original color (traces b and c in Figure 2). The spectrum acquired after this chemical transformation gave signals of **4** without any appreciable sign of degradation. Furthermore, an isothermal titration calorimetric (ITC) experiment (Figure S4, Supporting Information) was performed in acetone to show the formation of a 2:1 adduct between **4** and DEA with association constants (K_a) of 1.48 ($\pm$0.15) $\times$ 10^5 M^{-1} (K_{a1}) and 3.53 ($\pm$0.21) $\times$ 10^4 M^{-1} (K_{a2}).

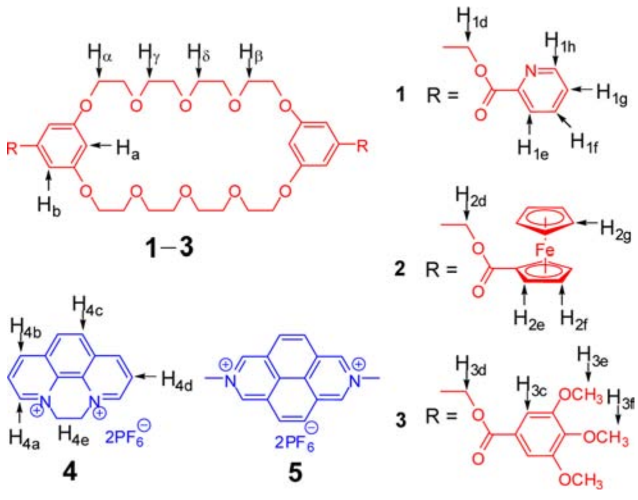

Figure 1. Chemical structures of bis(m-phenylene)-32-crown-10 derivatives **1**−**3** and guest salts **4** and **5**.

With this unique guest in hand, we then conducted host−guest complexation between guest **4** and hosts **1**, **2**, and **3**. Equimolar acetone solutions of hosts **1**−**3** with guest **4** are yellow due to charge transfer interactions between the electron-rich aromatic rings of the hosts and the electron-poor pyridinium rings of the guest, direct evidence for complexation. Furthermore, Job plots[9] (Figure S5, Supporting Information) based on UV−vis spectroscopy and electrospray ionization mass spectrometry (ESI-MS) (Figures S6−8, Supporting Information) demonstrated that the three host−guest complexes were of 1:1 stoichiometry. The association constants (K_a) were determined in acetone by using a UV−vis titration method to be 3.13 ($\pm$0.20) $\times$ 10^3 M^{-1} for **1**$\supset$**4**, 4.42 ($\pm$0.25) $\times$ 10^2 M^{-1} for **2**$\supset$**4**, and 2.32 ($\pm$0.10) $\times$ 10^2 M^{-1} for **3**$\supset$**4** (Figures S9−11, Supporting Information). The difference in K_a indicates that the substituent groups on hosts have an influence on the host−guest complexation in solution.

The proton NMR spectra of equimolar (2.00 mM) acetone solutions of hosts **1**−**3** with guest **4** (Figure 3) showed that these complexations are fast exchange. After complexation between **1** and **4**, peaks corresponding to H_{1a}, H_{1b}, H_{1d}, and H_{1e} of host **1** and H_{4a}, H_{4c}, and H_{4d} of guest **4** shifted upfield, while H_{1f}, H_{1g}, and H_{1h} of host **1** and H_{4b} and H_{4e} of guest **4** moved downfield (Figure 3a−c). Similar chemical shift changes were also observed for the cases of **2**$\supset$**4** and

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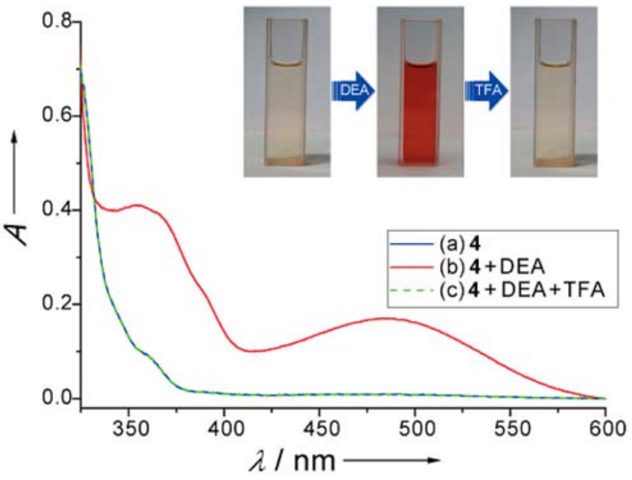

Figure 2. UV−vis absorption spectra of (a) 1.00 × 10^{-4} M **4**, (b) after addition of DEA (10.0 equiv) to a, and (c) after addition of TFA (10.0 equiv) to b.

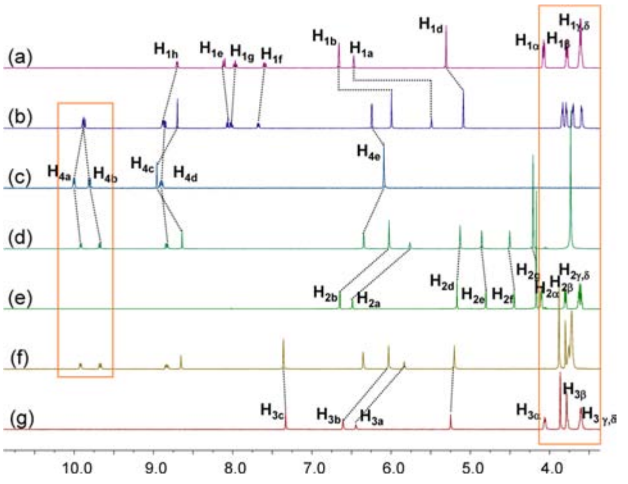

Figure 3. Partial ^{1}H NMR spectra (400 MHz, acetone-d_6, 293 K) of (a) 2.00 mM **1**; (b) 2.00 mM **1** + 2.00 mM **4**; (c) 2.00 mM **4**; (d) 2.00 mM **2** + 2.00 mM **4**; (e) 2.00 mM **2**; (f) 2.00 mM **3** + 2.00 mM **4**; (g) 2.00 mM **3**.

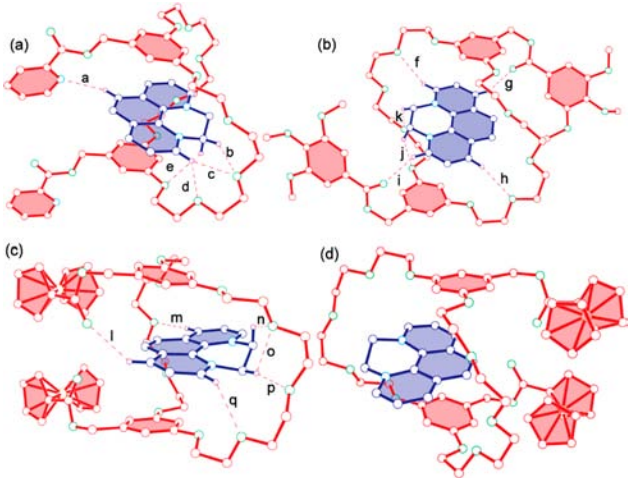

Figure 4. Ball-and-stick views of the X-ray structures of **1**⊃**4** (a), **3**⊃**4** (b), and **2**⊃**4** (c, d). Hosts **1**−**3** are red, guest **4** is blue, hydrogens are purple, oxygens are green, and nitrogens are sky blue. PF_6^- counterions, solvent molecules, and hydrogens except the ones involved in hydrogen bonding between the three host−guest complexes were omitted for clarity. Hydrogen bond parameters are as follows: C···O (N) distance (Å), H···O (N) distance (Å), C−H···O (N) angles (deg): a, 3.24, 2.47, 138.0; b, 3,33, 2.46, 145.8; c, 3.20, 2.32, 154.4; d, 3.05, 2.68, 103.9; e, 3.46, 2.67, 136.5; f, 3.37, 2.60, 138.5; g, 3.12, 2.24, 154.1; h, 3.45, 2.62, 146.0; i, 3.19, 2.31, 154.4; j, 3.48, 2.62, 145.5; k, 3.25, 2.48, 134.1; l, 3.30, 2.53, 139.3; m, 3.36, 2.42, 168.4; n, 3.20, 2.56, 121.8; o, 3.16, 2.54, 120.1; p, 3.50, 2.52, 170.1; q, 3.25, 2.54, 130.8.

3⊃**4** (Figure 3c−g). However, interestingly, there were obvious differences among these three sets of NMR spectra. First, two peaks corresponding to aromatic protons H_{4a} and H_{4b} of guest **4** shifted upfield upon complexation of **2** or **3** with **4** (Figure 4c−g), while for **1**⊃**4**, one signal of **4** (H_{4a}) moved upfield and the other (H_{4b}) shifted downfield. Second, the four peaks corresponding to ethyleneoxy protons ($H_{3\alpha}$, $H_{3\beta}$, $H_{3\gamma}$, and $H_{3\delta}$) of **3** merged together and the same ones of **2** merged together to became one sharp and broad peak upon complexation of **2** or **3** with **4**, while clearly four separate peaks were observed for these ethyleneoxy protons after the complexation of **1** with **4**. These interesting differences indicated that the complexation of **1** with **4**, **2** with **4**, and **3** with **4** in solution might have different host−guest geometries respectively, presumably as a result of the difference in the end substituent groups of BMP32C10 derivatives **1**−**3**.

To clarify the reason for the different host−guest complexation geometries, three high-quality yellow crystals of **1**⊃**4**, **2**⊃**4**, and **3**⊃**4** with 1:1 stoichiometry were grown by vapor diffusion. Although the three complexes are all stabilized by hydrogen bonding (Figure 4, **a**−**q**) and face-to-face π-stacking interactions, their self-assembled geometries are different in the solid state. The crystal structure of **1**⊃**4** demonstrates that host **1** and guest **4** form a taco-type structure in which guest **3** is wrapped by host **1** (Figure 4a). However, in the crystal structure of **2**⊃**4**, although the host **2** adopts a taco-type geometry, the guest **4** threads through the cavity of host **2**, forming a taco-type threaded structure (Figure 4, c and d). Meanwhile, in the case of **3**⊃**4**, host **3** and guest **4** form a [2]pseudorotaxane-type threaded structure in which guest **4** threads through the cavity of host **3** (Figure 4b), possibly because the two big pyrogallol trimethyl ether groups make **3**⊃**4** assume a "zig-zig" geometry (Figure 4b), as also observed by Gibson et al.[10] Therefore, by changing the end substituent groups of BM32C10 derivatives, we can control the complexation geometry of these derivatives with diquaternary salt **4**.

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Moreover, as shown in Figure 4, the guest **4** adopted different geometries in hosts **1**–**3** which further explained the different behaviors of the three sets of NMR spectra in Figure 3.

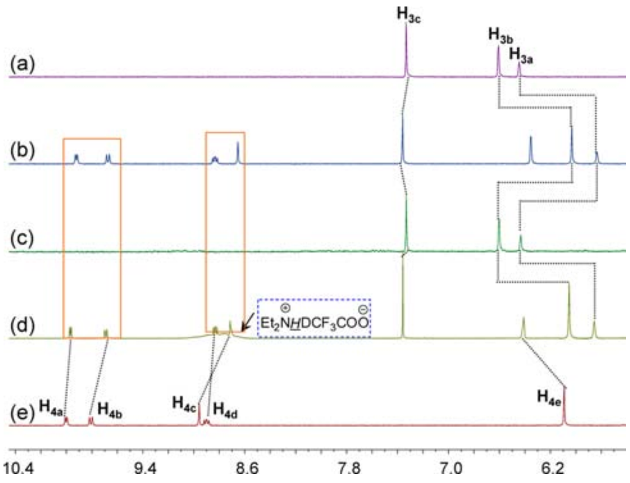

Figure 5. Partial ^{1}H NMR spectra (400 MHz, acetone-d_6, 293 K): (a) 2.00 mM **3**; (b) 2.00 mM **3** and **4**; (c) after addition of DEA to b; (d) after addition of TFA to c; (e) 2.00 mM **4**.

Moreover, the complexation between **3** and **4** can be reversibly controlled by the sequential addition of DEA and TFA. When enough DEA was added into the yellow solutions of **3** and **4**, they became deep red because the more stable adduct between **4** and DEA formed while complex **3**⊃**4** was dissociated. Subsequently, complex **3**⊃**4** formed again when enough TFA was added to neutralize DEA. Meanwhile, the solution color gradually reverted to yellow. This reversible process was confirmed by proton NMR experiments (Figure 5). When DEA (10.0 equiv) was added to a solution of 2.00 mM **3** and **4** in acetone-d_6, the intensity of the arene signals of **4** disappeared substantially and the signals of **3** returned to almost their uncomplexed values (Figure 5c). However, after addition of TFA (10.0 equiv) to this solution, the complexation between **3** and **4** was recovered; large chemical shift changes corresponding to the protons on **3** and **4** were observed again (Figure 5d). This chemically responsive process was also observed in the case of **2**⊃**4** (Figure S12, Supporting Information). The reversible complexation process provides a simple on–off switch which can be used in the construction of controllable molecular switches.

In summary, we report the reversible formation of an adduct between a diquaternary salt and DEA and the employment of this adduct formation to construct chemically responsive host–guest complexes between this salt and three BMP32C10 derivatives. Furthermore, we disclose the host substituent effect on the complexation geometry of the three resultant host–guest complexes. The fundamental knowledge gained from the study of these chemically responsive host–guest complexes prompts us to extend this new recognition motif to fabricate responsive and functional supramolecular assemblies.

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Supporting Information Available. Determination of stoichiometries, ESI-MS, ITC data, X-ray crystallographic files (CIF) for **1**⊃**4**, **2**⊃**4**, and **3**⊃**4**, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.