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Complexation between Pentiptycene Derived Bis(crown ether)s and CBPQT^{4+} Salt: Ion-Controlled Switchable Processes and Changeable Role of the CBPQT^{4+} in Host−Guest Systems

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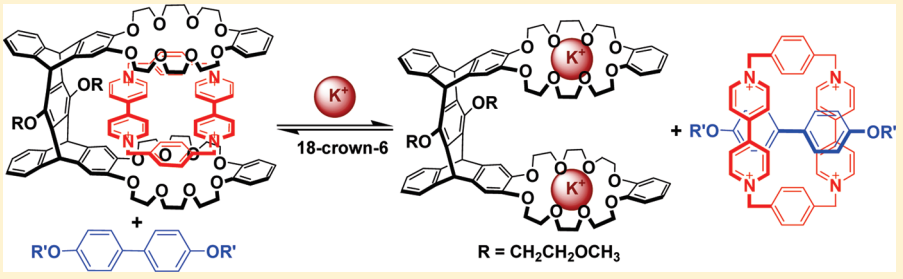
Supporting Information

ABSTRACT: The pentiptycene derived bis(crown ether)s with two 24-crown-8 moieties in the cis position could include the CBPQT^{4+} ring inside their cavities to form 1:1 complexes, and the naphthalene groups connected in the crown ether moieties showed less effective complexation ability toward the CBPQT^{4+} ring than the host containing two terminal benzene rings. This result was probably due to the stereohindrance effect of the naphthalene groups, and it was obviously different from that of the pentiptycene derived mono(crown ether)s. For the pentiptycene derived bis(crown ether) with two 24-crown-8 moieties in the trans position, it formed a 1:2 stable complex with the CBPQT^{4+} salt in solution and in the solid state, in which the pentiptycene moiety played an important role in stabilizing the complex. Moreover, binding and release of the CBPQT^{4+} ring in the complexes based on the pentiptycene-derived crown ethers could be chemically controlled by adding and removing potassium ions, in which the complexation modes played the key role. Interestingly, it was further found that switching the role of the CBPQT^{4+} ring in host and guest systems based on the pentiptycene derived bis(crown ether)s was easily achieved, which represents a new kind of supramolecular system.



INTRODUCTION

In host−guest chemistry, the development of new supramolecular systems based on novel synthetic hosts that have the efficient binding abilities toward specific substrates is a permanent and challenging topic.[1] Consequently, different synthetic hosts[1,2] including crown ethers, cryptands, calixarenes, cucurbiturils, cyclophanes, calixpyrroles, and others have been reported, and they have resulted in various new supramolecular systems with specific structures and properties.

Pentiptycene and its derivatives[3] are a class of structurally unique compounds with the rigid, aromatic, and H-shaped scaffold, and they have found various specific applications in materials science,[4] fluorescent chemosensors,[5] and conformational regulator.[6] Recently, Yang et al.[7] reported a photocontrollable molecular brake based on the pentiptycene scaffold, which represents the first example of a room temperature light-driven molecular brake. Although pentiptycene derivatives have attracted increased interest in recent years, most of their applications were based on the central ring functionalized pentiptycenes, and only a few examples on the peripheral functionalized pentiptycenes have so far been reported.[3b] In particular, compared with those of triptycene derivatives with the Y-shaped scaffold,[8] little is still known about pentiptycene-derived hosts and their applications in supramolecular chemistry.[9]

Tetracationic cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+})[10] (**1**) is a rigid macrocycle with a π-electron deficient cavity, and it has been proved to be a useful host to form complexes with different electron-rich aromatic guests, such as dioxynaphthalene, tetrathiafulvalene, benzidine, biphenol, and dihydroquinone units.[11] Consequently, various supramolecular systems based on the interlocked structures of the CBPQT^{4+} ring have hitherto been developed.[12] However, few examples on the CBPQT^{4+} ring used as a guest have been reported.[9a,13] Recently, we[9a] reported a novel pentiptycene-derived host **6** containing two DB24C8 moieties (Figure 1), which was shown to accommodate the CBPQT^{4+} ring to form a 1:1 stable complex. Moreover, we found that the pentiptycene derived mono(crown ether)s **4** and **5** could also form 1:1 stable complexes with the CBPQT^{4+} ring.[9c] It was further interestingly found that not only the pentiptycene-derived mono(crown ether) but also the CBPQT^{4+} ring in the complexes act as the host as well as the guest, which belongs to a

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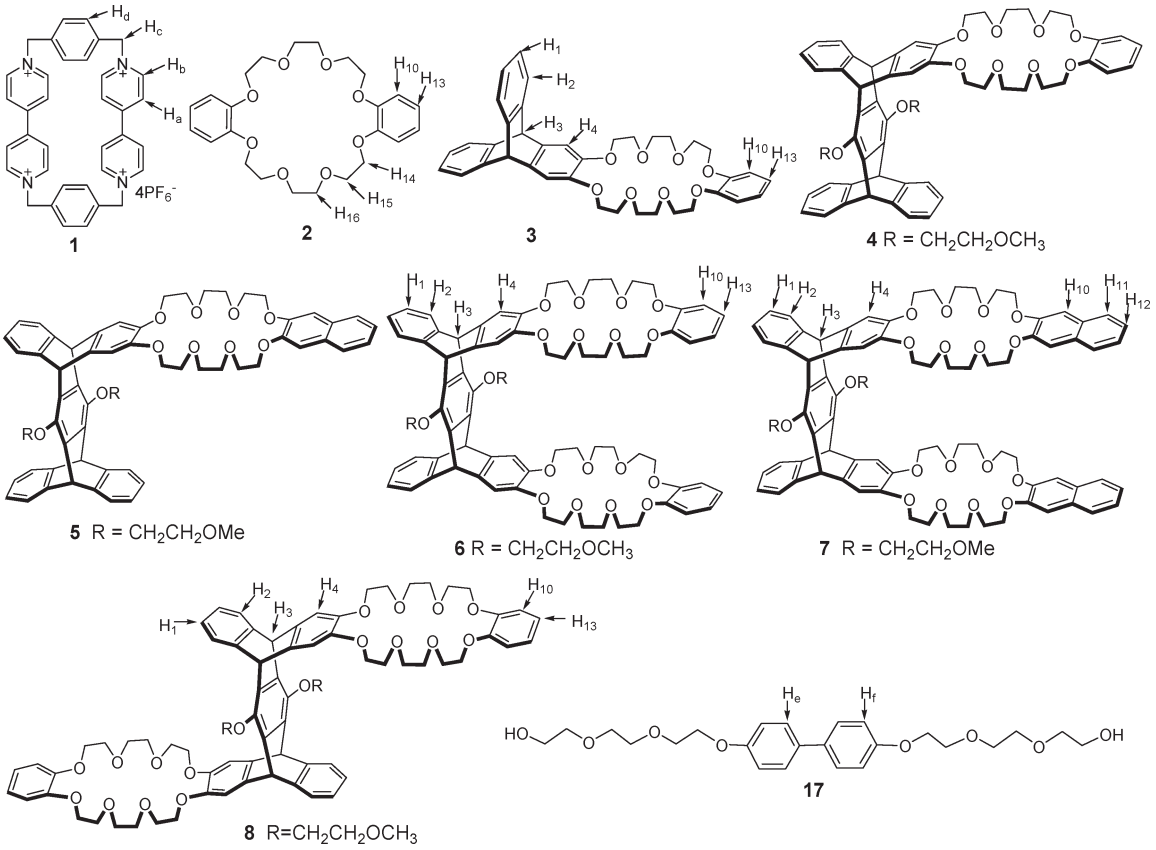

Figure 1. Structures and proton designations of compounds **1**−**8** and **17**.

new kind of supramolecular system. In this paper, we report the complexation between the pentiptycene-derived bis(crown ether)s with two 24-crown-8 moieties in cis or trans position and the $CBPQT^{4+}$ ring in detail, which resulted in the formation of 1:1 or 1:2 stable complexes with different complexation modes in solution and in the solid state. Moreover, binding and release of the $CBPQT^{4+}$ ring in the complexes based on the pentiptycene-derived crown ethers could be chemically controlled by adding and removing potassium ions. Interestingly, we further found that the switchable process between two different complexes **1**·**17** and **6**·**1** could be efficiently performed, and the role of the $CBPQT^{4+}$ ring acting as a host or a guest could thus be changeable in the supramolecular system.

RESULTS AND DISCUSSION

Synthesis of the Pentiptycene or Triptycene Derived Crown Ethers. The pentiptycene-derived crown ethers **4**,[9c] **5**,[9c] and **6**[9a] were prepared by the previously described methods. Similarly, the crown ether **3** was synthesized in 38% yield by the reaction of triptycene derivative **9**[14] and the bistosylate **10** under a high dilution condition in the presence of cesium carbonate (Scheme 1a). The pentiptycene-derived bis(crown ether) **7** was easily obtained in 35% yield by the reaction of pentiptycene derivative **11**[9a] and the bistosylate **12** with cesium carbonate as the base (Scheme 1b). Starting from pentiptycene quinone **13**,[3b] the pentiptycene derivative **16** containing two catechol moieties was synthesized by reduction of the quinone moiety of **13** with $Na_2S_2O_4$, reaction with 2-methoxyethyl 4-methylbenzenesulfonate in the presence of potassium carbonate, oxidation with cerium ammonium nitrate (CAN) in aqueous acetonitrile, and then reduction of the *o*-quinone moieties of **15** with catalytic hydrogenation. Finally, the reaction of **16** with the bistosylate **10** under a high dilution condition in the presence of cesium carbonate gave the pentiptycene-derived bis(crown ether) **8** in 35% yield (Scheme 1c). The structures of **3**, **7**, and **8** were confirmed by ^1H NMR, ^{13}C NMR, MALDI-TOF MS, and elemental analyses.[15]

Complexation between $CBPQT^{4+}$ Ring and the Pentiptycene-Derived Bis(crown ether)s. In the previous communication,[9a] we showed that pentiptycene-derived bis(crown ether) **6** was a highly efficient host for formation of 1:1 stable complex **6**·**1** with the $CBPQT^{4+}$ ring in solution and in the solid state, in which the $CBPQT^{4+}$ ring acted as a guest. Previously, we[9c] also found that the pentiptycene-derived mono(crown ether) **5** with a stronger donor naphthalene group connected in the crown ether moiety showed more effective complexation ability toward the $CBPQT^{4+}$ ring than the mono(crown ether) **4** with a terminal benzene ring. To know if the stronger donor group would affect the complexation ability in the pentiptycene-derived bis(crown ether) systems, we then studied the complexation between the pentiptycene-derived bis(crown ether) **7** with naphthalene groups in the 24-crown-8 moieties and the $CBPQT^{4+}$ ring in solution by the ^1H NMR method. Similar to the case of **6**, the ^1H NMR spectrum of a 1:1 mixture of **7** and **1** in $CD_3CN/CDCl_3$ (2:1, v/v) exhibited a great difference from those of free **7** and free **1** (Figure 2). Not only the protons H_a and H_b of the $CBPQT^{4+}$ ring but the protons H_{10}, H_{11}, and H_{12} of the naphthalene groups showed upfield shifts, which may be caused by the shielding effect of the adjacent aromatic rings. Moreover, obvious changes in the chemical shifts of the protons H_c and H_d of the $CBPQT^{4+}$ ring

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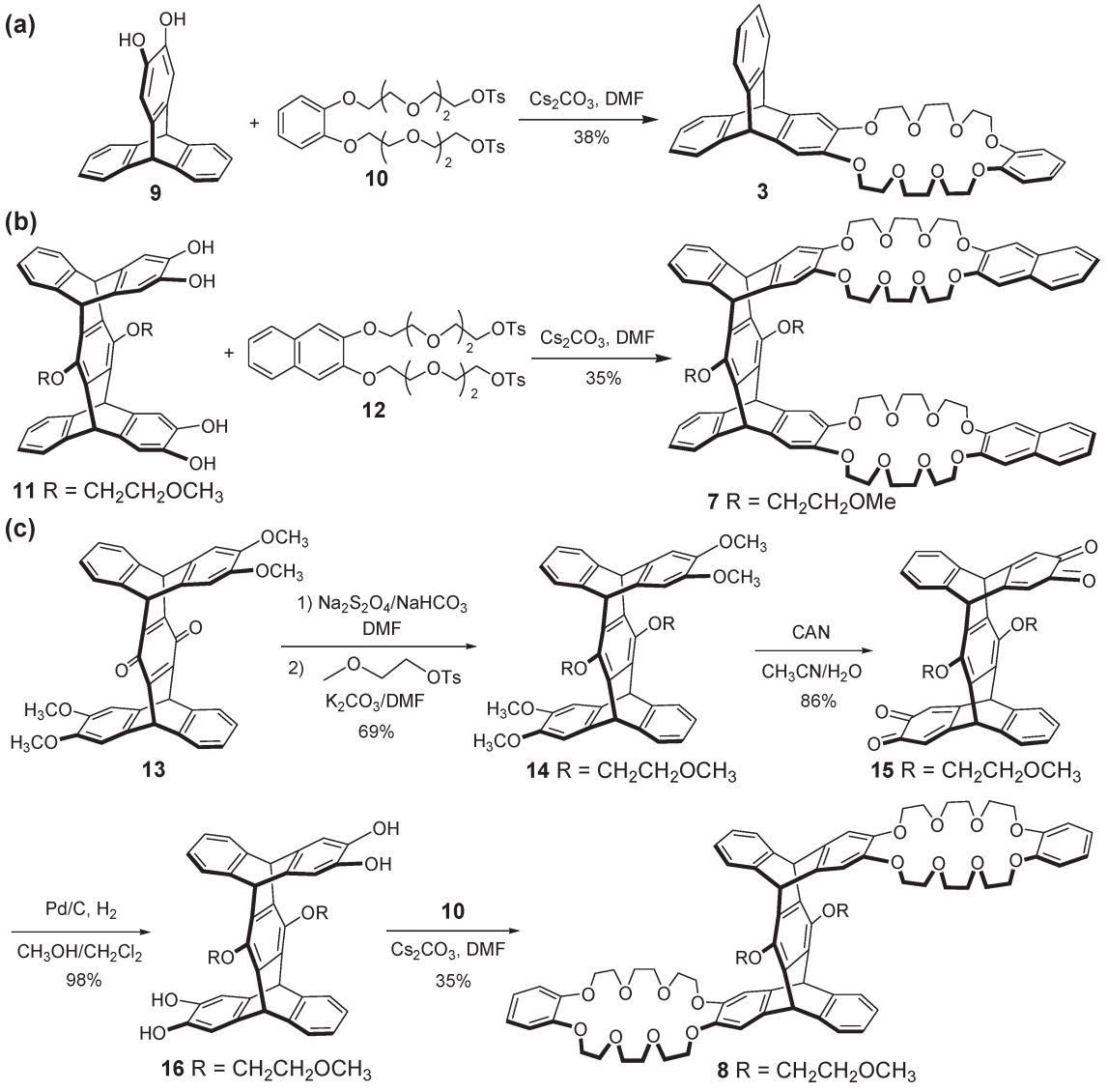
Scheme 1. Synthesis of the Pentiptycene- or Triptycene-Derived Crown Ethers



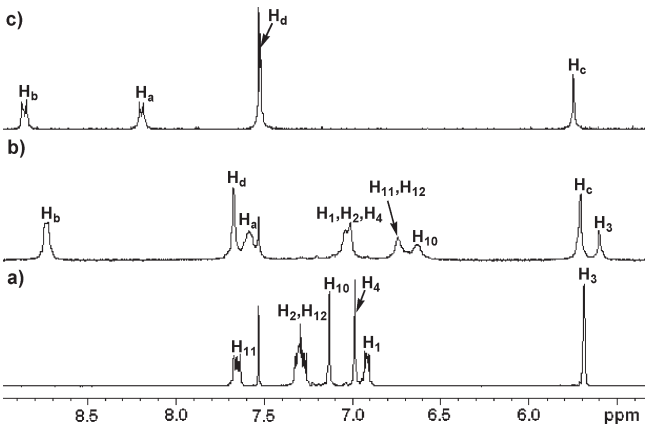


Figure 2. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 2, 298 K) of (a) free **7**, (b) **7** and 1.0 equiv of **1**, and (c) free **1**. $[7]_0$ = 2.0 mM.

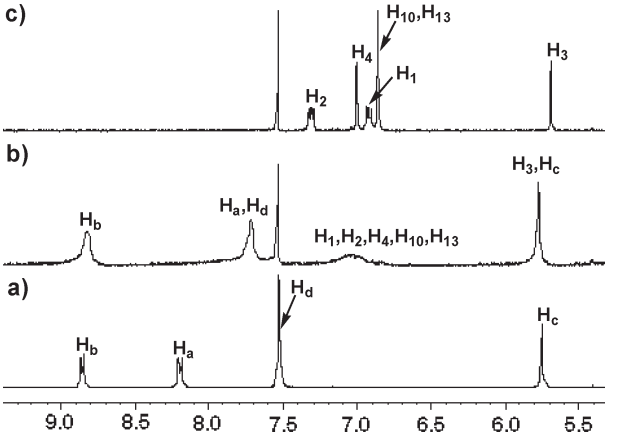


Figure 3. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 2, 298 K) of (a) free **1**, (b) **1** and 2.0 equiv of **8**, and (c) free **8**. $[8]_0$ = 1.0 mM.

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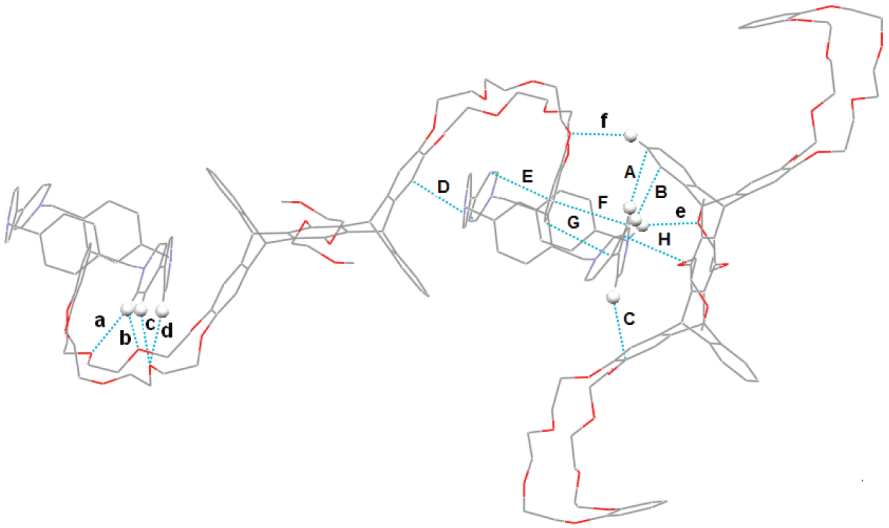

Figure 4. View of the crystal structure of complex **8**·**1**$_2$. Blue lines denote the noncovalent interactions between **8** and **1**. The C−H···O hydrogen bond distances (Å): a = 2.49 Å, b = 2.49 Å, c = 2.60 Å, d = 2.66 Å, e = 2.66 Å, f = 2.72 Å. Solvent molecules, PF_6^- counterions, two CBPQT^{4+} rings, and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

and the bridgehead proton H_3 of the pentipycene scaffold were also observed. These observations suggested that pentiptycene-derived bis(crown ether) **7** formed a 1:1 complex with the CBPQT^{4+} ring, and the complexation mode is nearly the same as that of complex **6**·**1**. Moreover, the association constant[16] for complex **7**·**1** was calculated to be 1.4(±0.1) × 10^3 M^{-1}, which was smaller than that for complex **6**·**1** (2.7 × 10^3 M^{-1}).[9a] This result might be caused by the stereohindrance effect of the naphthalene moieties in **7**, which was obviously different from that of the pentiptycene-derived mono(crown ether)s.[9c] Formation of the 1:1 complex between **7** and **1** was further evidenced by its electrospray ionization mass spectrum (ESI-MS), in which the peak at m/z 695.21 for [**7**·**1**-3PF_6^-]$^{3+}$ was found. Since changes of the CV curves, to some extent, could reflect the complexation abilities of the complexes, we further investigated the electrochemical behaviors of the CBPQT^{4+} ring in the absence and presence of **7**. Similar to that of **6**, upon the addition of **7** to the solution of **1** in CH_3CN, the first two-electron reduction peak became broad and low, while the second two-electron reduction peak moved to a more negative value.[15] However, the changes were smaller than those upon the addition of **6**, which was consistent with the results of ^{1}H NMR experiments.

We further investigated the complexation between the CBPQT^{4+} ring and the pentiptycene-derived bis(crown ether) **8** with two dibenzo-24-crown-8 moieties in trans position in detail. Consequently, it was found that when 1.0 mM **8** and 2 equiv of **1** were mixed in acetonitrile/chloroform (2:1, v/v), they gave an orange solution immediately due to the charge transfer interaction between the electron-rich aromatic rings of **8** and the electron-poor paraquat rings of **1**. As shown in Figure 3, the ^{1}H NMR spectrum of a 1:2 mixture of **1** and **8** in CD_3CN and $CDCl_3$ (2:1, v/v) showed a great difference from those for **8** and **1**, and only one set of peaks were found, which indicated the fast-exchange complexation between **8** and **1**. Consequently, the protons H_b and H_a of the CBPQT^{4+} ring showed significant upfield shifts ($\Delta\delta$ 0.44 ppm for H_b, and 0.06 ppm for H_a), which might be due to the strong shielding effect of the aromatic rings in **8**. Similarly, the signal of proton H_2 of **8** also shifted upfield, which was attributed to its position in the shielding region of the paraquat moieties of **1**. In contrast, a considerable downfield shift of the aromatic proton H_d in **1** was observed, which might be attributed to its position in the deshielding region of the aromatic ring of **8**. These observations suggested that **1** and **8** formed a stable complex. Furthermore, ^{1}H NMR spectroscopic titrations afforded a quantitative estimate between **1** and **8** by monitoring the changes of the chemical shift of the proton H_d. The results showed that a 1:2 complex **8**·**1**$_2$ was formed by a mole ratio plot, which was different from that of complex **6**·**1**.[9a]Accordingly, the average association constant $K_{a,exp}$ for 1:2 complex **8**·**1**$_2$ was calculated to be 7.4(±0.2) × 10^2 M^{-1} by the Scatchard plot.[16]

The ESI-MS provided more evidence for the formation of complex **8**·**1**$_2$. As a result, the peaks at m/z 1065.11, 1028.68, and 661.83 for [**8**·**1**-2PF_6^-]$^{2+}$, [**8**·**1**$_2$-3PF_6^-]$^{3+}$, and [**8**·**1**-3PF_6^-]$^{3+}$, respectively, were observed, which indicated that the 1:2 stable complex formed. Further support for the formation of complex **8**·**1**$_2$ came from its X-ray diffraction result. As shown in Figure 4, it was found that the triptycene-like crown ether moiety of one side of molecule **8** and the pentiptycene scaffold of its adjacent molecule formed an open cavity, in which one CBPQT^{4+} ring was included. Meanwhile, the terminal benzene ring of each DB24C8 moiety of **8** was positioned inside the cavity of the CBPQT^{4+} ring. This complexation mode is obviously different from that between **6** and **1** in the solid state since in complex **6**·**1** the CBPQT^{4+} ring is positioned inside the cavity of one molecule **6**.[9a] In complex **8**·**1**$_2$, there existed multiple C−H···O hydrogen bonding interactions between protons H_a, H_b of the CBPQT^{4+} ring and polyether oxygen atoms of the DB24C8 moiety and the oxygen atom in the central benzene ring of **8**, and also between the proton H_1 and the polyether oxygen atoms of the DB24C8 moiety. Moreover, there existed multiple $\pi\cdots\pi$ stacking interactions between the paraquat rings and the benzene rings of the pentiptycene scaffold, and also between the benzene rings of the DB24C8 moieties with the distances of 3.40 (D), 3.28 (E), 3.39 (F), 3.37 (G), and 3.27 Å (H), respectively. Multiple C−H···π interactions between the aromatic hydrogen atoms (H_a, H_b) in the CBPQT^{4+} ring and the benzene rings of the pentiptycene scaffold with the distances of 2.85 (A), 2.61 (B), and 2.86 Å (C), respectively, were also observed. These multiple

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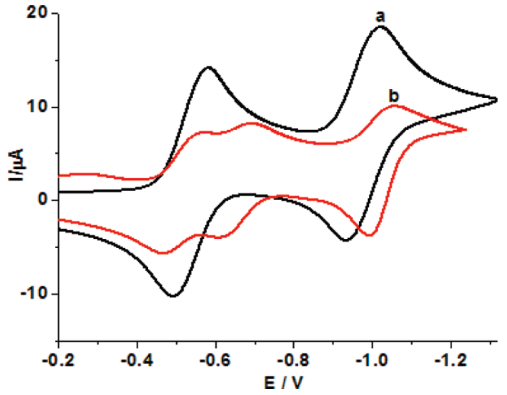

Figure 5. CV curves for a solution of $\mathbf{1}^{4+}$ (1.0×10^{-3} M) in CH_3CN-(Bu_4N)PF_6 (0.1 M) in the absence (black line) and the presence (red line) of **8** (1.0×10^{-3} M). Working electrode: Pt. Scan rate: 0.1 V s^{-1}.

noncovalent interactions played an important role in the formation of the stable complex $\mathbf{8}\cdot\mathbf{1}_2$.

The electrochemical behaviors of the $CBPQT^{4+}$ ring in the absence and presence of **8** were also studied. As shown in Figure 5, the $CBPQT^{4+}$ ring showed two reversible two-electron redox processes in CH_3CN with the half-wave potential values at −0.536 and −0.977 V vs $Ag/AgNO_3$, respectively.[17] It was found that upon the addition of **8**, the CV patterns for reduction of the $CBPQT^{4+}$ ring were remarkably affected. Particularly, the first two-electron reduction peak split into two parts with the gap of 138 mV, and the shift of the first reduction of the split peak (−511 mV) to less negative potentials than for free $CBPQT^{4+}$ (−536 mV) was observed, which means that the CT interaction mixing the HOMO of **8** and the LUMOs of bipyridinium ring together might be responsible for splitting the degeneracy of the bipyridinium-based LUMOs.[18] The second two-electron reduction peak shifts to the more negative potential and does not show broadening, which implies a decrease in electron affinity as the $CBPQT^{4+}$ ring strongly hinders the generation of the dication in the limited available space.[19] Such behaviors suggested that **8** and **1** formed a stable complex, and the complexation was caused by the charge transfer interactions.

Since dibenzo[24]crown-8 (**2**) is an important moiety of the pentiptycene-derived (crown ether)s, we then tested the complexation between **2** and $CBPQT^{4+}$ ring. Consequently, when **1** and 1.0 equiv of **2** were mixed in 2:1 acetonitrile/chloroform, they gave a pale yellow solution immediately due to the charge transfer interaction between the electron-rich aromatic rings of **2** and the electron-deficient bipyridinium rings of the $CBPQT^{4+}$ salt. The ^{1}H NMR spectrum of a 1:1 mixture of **1** and **2** showed a little difference from those for free **2** and free **1**.[15] But the aromatic protons H_{10} and H_{13} of **2** showed significant upfield shifts ($\Delta\delta$ = 0.22 ppm for H_{10}, and 0.37 ppm for H_{13}), which might be due to the shielding effect of the paraquat moieties of **1**. The results indicated that the $CBPQT^{4+}$ ring might serve as a host to include the aromatic ring of **2** in its cavity. Formation of the 1:1 complex between **1** and **2** was also confirmed by its ESI-MS, in which a strong peak at m/z 371.31 for $[\mathbf{1}\cdot\mathbf{2}\text{-}3PF_6^-]^{3+}$ was observed. The electrochemical behavior of the $CBPQT^{4+}$ ring in the absence and presence of **2** was also studied. Consequently, it was found that upon the addition of **2**, the CV patterns for reduction of the $CBPQT^{4+}$ ring were nearly unaffected, a little shift of the first reduction peak to the less negative potential was

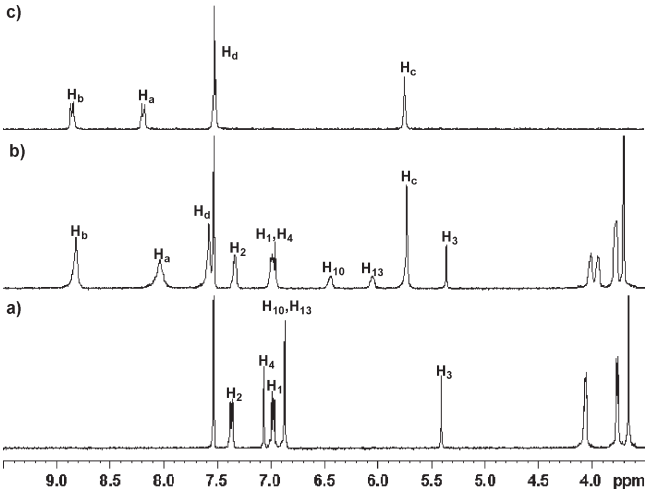

Figure 6. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 2, 298 K) of (a) free **3**, (b) **3** and 1.0 equiv of **1**, and (c) free **1**. $[\mathbf{1}]_0$ = 2.0 mM.

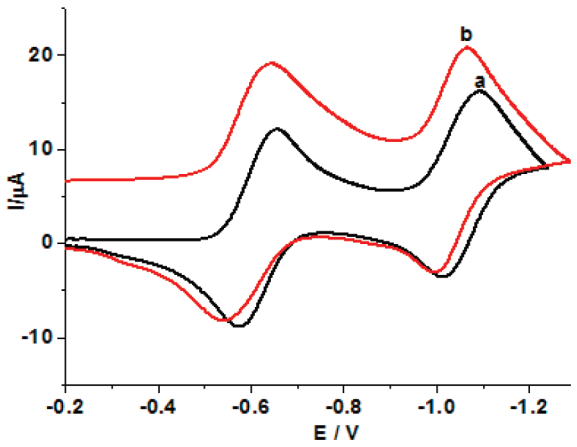

Figure 7. CV curves for a solution of $\mathbf{1}^{4+}$(1.0×10^{-3} M) in CH_3CN-(Bu_4N)PF_6 (0.1 M) in the absence (black line) and the presence (red line) of **6** (3.0×10^{-3} M). Working electrode: Pt. Scan rate: 0.1 V s^{-1}.

only observed. Such behaviors implied that the weak complexation between **1** and **2** occurred, which was caused by the charge transfer interaction.

As a comparison, we also investigated the complexation between the $CBPQT^{4+}$ ring and triptycene-derived mono(crown ether) **3** in solution by ^{1}H NMR experiments in 2:1 (v/v) acetonitrile/chloroform. As shown in Figure 6, it was found that the signals of protons H_{10} and H_{13} of **3** shifted upfield probably due to their positions in the shielding region of the paraquat moieties of the $CBPQT^{4+}$ ring. Meanwhile, the upfield shifts of protons H_a and H_b were also observed. These observations suggested that the terminal benzene ring of the DB24C8 moiety in **3** might be positioned inside the cavity of the $CBPQT^{4+}$ ring to form a 1:1 stable complex with the $CBPQT^{4+}$. Accordingly, the association constant between **1** and **3** was calculated to be $4.9(\pm0.2) \times 10^2$ M^{-1} by the Scatchard plot.[16] Furthermore, we studied the complexation mode between **1** and **3** by the ^{1}H−^{1}H ROESY NMR spectrum. Consequently, the NOE effects between the bridgehead proton H_3 and the methylene proton of the $CBPQT^{4+}$ ring, and also between the aromatic proton H_2 of the triptycene

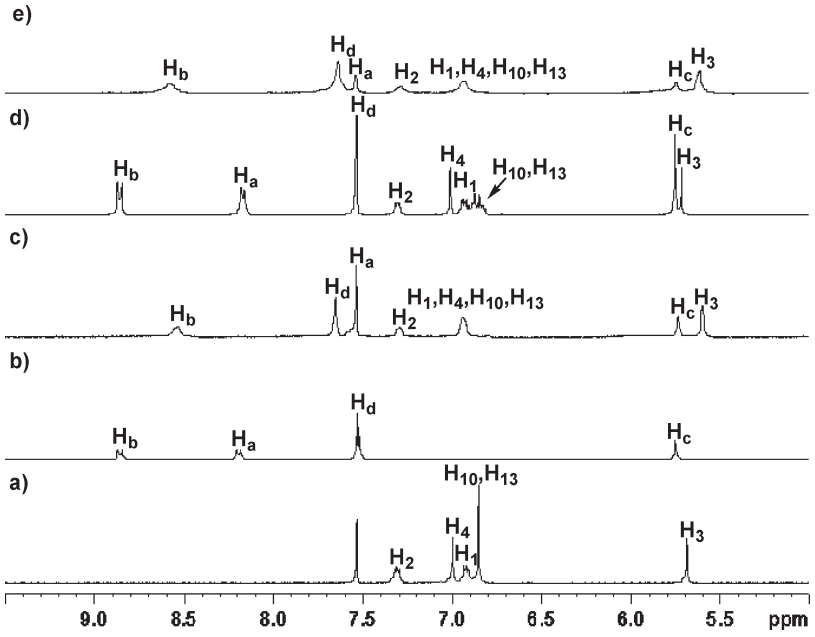

Figure 8. Partial ^{1}H NMR spectra (300 MHz, 1:2 v/v $CDCl_3/CD_3CN$, 298 K) of (a) free **6**, (b) free **1**, (c) **6** and 1.0 equiv of **1**, (d) the mixture obtained after adding KPF_6 (4 equiv of **1**) to solution from part c, and (e) the mixture obtained after adding 18-crown-6 (6 equiv of **1**) to solution from part d. $[\mathbf{1}]_0$ = 2.0 mM.

moiety and the aromatic proton H_d of the $CBPQT^{4+}$ ring were observed. These results indicated that the $CBPQT^{4+}$ ring adopts a symmetric structure in the complex, meanwhile the terminal benzene ring of the DB24C8 moiety was selectively included in the cavity of the $CBPQT^{4+}$ ring, which is similar to that of dibenzo-24-crown-8, and the $CBPQT^{4+}$ ring also served the role as a host in complex **1**·**3**.

In the ESI mass spectrum of a solution of **1** and **3**, the strongest peak was found at m/z 717.7 for $[\mathbf{1}\cdot\mathbf{3}\text{-}2PF_6^-]^{2+}$, which provided another evidence for formation of 1:1 complex **1**·**3**. Moreover, the electrochemical behaviors of the $CBPQT^{4+}$ ring in the absence and presence of **3** were also investigated. Upon the addition of **3** to the solution of $CBPQT^{4+}$ salt in CH_3CN, both the cathodic and anodic peaks corresponding to the first and second two-electron reduction process of the paraquat moieties moved to the less negative values (Figure 7), which was different from those cases in the presence of other compounds. Such behaviors suggested that formation of the complex between **1** and **3** was caused by a charge transfer interaction, and the complex dissociated upon two-electron reduction of the $CBPQT^{4+}$ ring.[14] Moreover, no split or broad peaks were observed, which means that the two paraquat moieties of **1** in complex **1**·**3** were in the same chemical environment.

Since the electrochemical behaviors of complex $\mathbf{8}\cdot\mathbf{1}_2$ are obviously different from that of complex **1**·**3**, and the two paraquat moieties of the $CBPQT^{4+}$ ring in $\mathbf{8}\cdot\mathbf{1}_2$ are situated in different chemical environment, we speculated that molecule **8** in complex $\mathbf{8}\cdot\mathbf{1}_2$ was not the mechanical combination of two molecules of **3**, and that the $CBPQT^{4+}$ ring was situated in the cavity of two pentiptycene scaffolds. Moreover, the ^{1}H NMR spectra of the complex $\mathbf{8}\cdot\mathbf{1}_2$ at low temperatures[15] were further recorded, which showed that with lowering of the temperature, the signals corresponding to the protons of the $CBPQT^{4+}$ ring, and the aromatic protons of **8** broadened gradually, and then split into multiple signals at 238 K. These results indicated that the $CBPQT^{4+}$ ring showed an unsymmetric structure in the complex, which also suggested that the complexation mode of $\mathbf{8}\cdot\mathbf{1}_2$ was different from those of **1**·**2** and **1**·**3** in solution.

Potassium Ion Controlled Binding and Release of the $CBPQT^{4+}$ Ring. Since the pentiptycene-derived bis(crown ether)s contain two 24-crown-8 moieties, they could form complexes with cations, such as potassium ions, and the subsequent complexation of the cations would introduce extra electrostatic repellent force to the cationic $CBPQT^{4+}$ ring(s), and dissociate the previously formed host−guest complexes between the pentiptycene derived crown ethers and the $CBPQT^{4+}$ ring(s). Moreover, it was known that 18-crown-6 is a very strong sequestering agent for potassium ion, which thus encouraged us to further investigate the potassium ion-controlled binding and release of the $CBPQT^{4+}$ ring(s) in the complexes based on the pentiptycene-derived bis(crown ether)s.[20] First, we found that a solution of **6** and 2 equiv of KPF_6 showed a single strong peak at m/z 698.77 in the ESI-MS,[15] which indicated that two potassium ions could bind to the crown ether moieties to form the complex $\mathbf{6}\cdot 2KPF_6$. Then, we carried out a series of ^{1}H NMR experiments. As shown in Figure 8, the ^{1}H NMR spectrum of a 1:1 mixture of **6** and **1** showed a well-defined resonance. When excess KPF_6 salts were added to the above solution, it was found that the proton signals of complex **6**·**1** totally disappeared (Figure 8d), while the proton signals of the $CBPQT^{4+}$ ring shifted downfield or upfield almost to the original positions of free **1** (Figure 8b). Moreover, the aromatic proton signals of molecule **6** had a slight difference while the peak shape of the crown ether region had a big change. These observations indicated that the potassium ion bound to the crown ether moiety, which resulted in the release of the $CBPQT^{4+}$ ring from the cavity of host **6**. When 18-crown-6 was added into the above system, it was found that the proton signals of complex **6**·**1** recovered (Figure 8e), which suggested that complex **6**·**1** formed again. Thus, the binding and release of the $CBPQT^{4+}$ ring in complex **6**·**1** could be efficiently controlled by the potassium ions. Similarly, we found that binding and release

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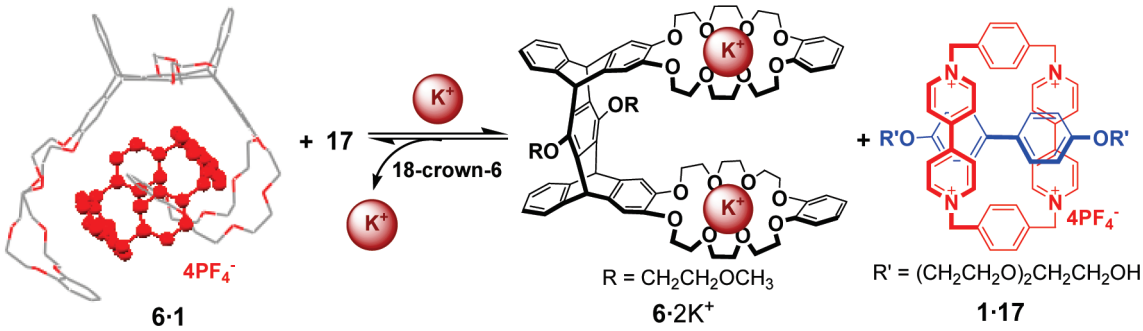

Figure 9. Scheme representation of the changeable role of CBPQT^{4+} ring controlled by adding and removing the potassium ions.

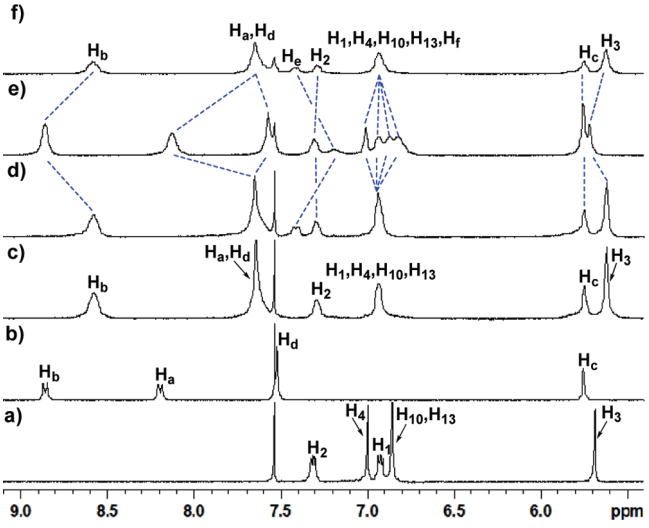

Figure 10. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 2, 298 K) of (a) free **6**, (b) free **1**, (c) **6** and 1.0 equiv of **1**, (d) **6** and 1.0 equiv of **1**, and 1.0 equiv of **17**, (e) the mixture obtained after adding KPF_6 (4 equiv of **1**) to solution from part d, and (f) the mixture obtained after adding 18-crown-6 (6 equiv of **1**) to the solution from part e. $[\mathbf{1}]_0$ = 2.0 mM.

of the CBPQT^{4+} ring(s) in the complexes **7**·**1**, and **8**·$\mathbf{1}_2$ could also be easily controlled by the potassium ions.[15]

It was different from those of the potassium ion controlled binding and release of the CBPQT^{4+} ring described above, we found that when excess KPF_6 was added to the solution of pentiptycene-derived mono(crown ether) **4** and 1 equiv of CBPQT^{4+} salt **1**, the proton signals of complex **4**·**1** did not disappear, only the signals of protons H_a and H_b of the CBPQT^{4+} ring shifted a little downfield, and proton H_c a little upfield, which was far from the original position.[15] Moreover, the aromatic protons of molecule **4** in the complex showed different signals from those of both the free **4** and complex **4**·**1**, while the peak shape of the crown ether region also had a big change. These observations might be due to the different complexation mode from those of the other complexes based on the pentiptycene-derived bis(crown ether)s, and the formation of a ternary complex composed of **4**, **1**, and K^+ ion.

The Changeable Role of CBPQT^{4+} Ring in Host−Guest Systems. In complex **6**·**1**, the CBPQT^{4+} ring acts as a guest. It was also known that the CBPQT^{4+} ring can be used as a host to form a 1:1 stable complex with guest **17**.[11a] Moreover, the presence of guest **17** cannot influence formation of complex **6**·**1** in solution, furthermore, binding and release of **1** in complex **6**·**1** can be controlled by adding and releasing the potassium ions. Therefore, we envisioned that the switchable process between two different complexes **6**·**1** and **1**·**17** could be efficiently performed by adding and releasing the potassium ions, and the role of the CBPQT^{4+} ring acting as a host or a guest could thus be changeable in the supramolecular system (Figure 9).

As shown in Figure 10, the ^{1}H NMR spectrum of a 1:1:1 mixture of **6**, **1**, and **17** displayed the characteristic proton signal patterns of complex **6**·**1** and compound **17** (Figure 10d), which indicated that there is no obvious complexation between **1** and **17** in the presence of **6**. But when 4 equiv of KPF_6 was added to the above solution, it was found that the aromatic and bridgehead proton signals of **6** shifted nearly to the original positions, while the peak shape of the crown ether region had a big change. Moreover, the signals of protons H_e, H_f in **17** broadened and shifted upfield, and the signals of aromatic protons H_a and H_b of the CBPQT^{4+} ring shifted upfield while the signal of proton H_c shifted downfield (Figure 10e). These observations suggested that complex **6**·**1** decomposed, while complex **1**·**17** formed. When 6 equiv of 18-crown-6 was added into the above system, it was found that complex **1**·**17** dissociated while complex **6**·**1** formed again (Figure 10f). Consequently, changing the role of the CBPQT^{4+} ring between guest and host in a supramolecular system based on pentiptycene crown ether could be easily achieved. Under similar conditions, the changeable role of the CBPQT^{4+} ring in the supramolecular system composed of **8**, **1**, and **17** was also observed.[15]

CONCLUSIONS

In conclusion, we have proved that the pentiptycene-derived bis(crown ether)s containing one pentiptycene scaffold and two 24-crown-8 moieties in cis or trans position could form 1:1 or 1:2 stable complexes with the CBPQT^{4+} ring in different complexation modes in both solution and solid state, in which the pentiptycene subunit played an important role in stabilizing the complexes. Moreover, it was also found that the binding and release of the CBPQT^{4+} ring in the complexes based on the pentiptycene-derived bis(crown ether)s could be efficiently controlled by adding and removing potassium ions, and the complexation mode played the key role in carrying out this process. Interestingly, we further found that switching the role of the CBPQT^{4+} ring between guest and host in a supramolecular system based on the pentiptycene bis(crown ether)s was easily achieved. This switchable process represents a new kind of supramolecular system, and we believe that it will be useful in the construction of new functional supramolecular systems.

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EXPERIMENTAL SECTION

The tetracationic cyclobis(paraquat-*p*-phenylene) salt **1**,[11a] the pentiptycene derived crown ethers **4**,[9c] **5**,[9c] **6**,[9a] and guest **17**[11a] were prepared by the previously described methods.

Compound 3. A suspension of cesium carbonate (1.28 g, 4.0 mmol) in anhydrous DMF (60 mL) under argon atmosphere was stirred vigorously for 10 min and then heated to 100 °C. To the mixture was added dropwise a solution of **9** (0.29 g, 1.00 mmol) and bistosylate **10** (0.68 g, 1.00 mmol) in anhydrous DMF (50 mL) over 12 h. The reaction mixture was stirred at 100 °C for another 3d. After cooling to ambient temperature, the mixture was filtered and washed with CH_2Cl_2 (50 mL). The filtrate was concentrated under reduced pressure to give a gray solid, which was dissolved in CH_2Cl_2 (250 mL) and washed with diluted HCl. The organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the resulting oil was subjected to successive column chromatography over silica gel (eluent: 150:1 CH_2Cl_2/CH_3OH) to give **3** (0.24 g, 38%) as an off-white solid. Mp 69−70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 8H), 3.82−3.87 (m, 8H), 4.08−4.11 (m, 8H), 5.29 (s, 2H), 6.85 (s, 4H), 6.95−6.97 (m, 4H), 6.98 (s, 2H), 7.32−7.35 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.7, 69.4, 69.90, 69.95, 70.0, 71.1, 71.2, 111.7, 114.2, 121.4, 123.3, 125.0, 138.7, 145.6, 146.1, 149.0. MALDI-TOF MS *m*/*z* 647.2 $[M + Na]^+$. Anal. Calcd for $C_{38}H_{40}O_8 \cdot 0.8H_2O$: C, 71.41; H, 6.56. Found: C, 71.50; H, 6.48.

Compound 7. A suspension of cesium carbonate (2.51 g, 7.7 mmol) in anhydrous DMF (70 mL) under argon atmosphere was stirred vigorously for 10 min and then heated to 100 °C. To the mixture was added dropwise a solution of **11** (0.60 g, 0.93 mmol) and bistosylate **12** (1.37 g, 1.86 mmol) in anhydrous DMF (70 mL) over 12 h. The reaction mixture was stirred at 100 °C for another 3 d. After cooling to ambient temperature, the mixture was filtered and washed with CH_2Cl_2 (60 mL). The filtrate was concentrated under reduced pressure to give a gray solid, which was dissolved in CH_2Cl_2 (250 mL) and washed with diluted HCl. The organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the resulting oil was subjected to successive column chromatography over silica gel (eluent: 150:1 CH_2Cl_2/CH_3OH) to give **7** (0.46 g, 35%) as an off-white solid. Mp 77−78 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (s, 7H), 3.73−3.80 (m, 8H), 3.80−3.85 (m, 15H), 3.85−3.88 (m, 4H), 3.88−3.92 (m, 8H), 3.92−4.04 (m, 12H), 4.17−4.19 (m, 8H), 5.63 (s, 4H), 6.89−6.92 (m, 4H), 6.93 (s, 4H), 7.05 (s, 4H), 7.25−7.30 (m, 8H), 7.61−7.64 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 47.7, 59.4, 69.2, 69.7, 69.9, 70.0, 71.1, 71.4, 71.9, 74.8, 107.9, 111.7, 123.3, 124.1, 125.0, 126.3, 129.3, 136.8, 138.7, 145.7, 145.9, 146.0, 149.0. MALDI-TOF MS *m*/*z* 1442.1 $[M + Na]^+$. Anal. Calcd for $C_{84}H_{90}O_{20} \cdot H_2O$: C, 70.18; H, 6.45. Found: C, 69.94; H, 6.57.

Compound 14. To a solution of **13** (0.58 g, 1 mmol) in DMF (30 mL) was added $NaHCO_3$ (0.59 g, 7 mmol) and $Na_2S_2O_4$ (5.7 g, 33 mmol). The mixture was heated under Ar at 100 °C overnight. The cooled solution was poured into water (300 mL), and the white precipitate was collected and dried under vacuum, which was used without further purification. A mixture of pentiptycene hydroquinone (508 mg, 0.87 mmol), 2-methoxyethyl 4-methylbenzenesulfonate (431 mg, 1.87 mmol), and K_2CO_3 (972 mg, 7.04 mmol) in dry DMF (60 mL) was refluxed under Ar for 2 days. The mixture was filtered, and the filtration was concentrated under reduced pressure. Then, CH_2Cl_2 (50 mL) was added and the solution was washed with diluted HCl, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was subjected to column chromatography with 20:1 (v/v) CH_2Cl_2/ethyl acetate as eluent to afford **14** (481 mg, 69%) as a white solid. Mp 138−139 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 6H), 3.78 (s, 12H), 3.89−3.91 (t, 4H), 4.05−4.06 (t, 4H), 5.67 (s, 4H), 6.90−6.92 (m, 4H), 6.96 (s, 4H), 7.25−7.30 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 47.8, 56.3, 59.4, 71.9, 74.8, 108.9, 123.3, 125.0, 136.9, 138.2, 145.7, 145.9, 146.1. MALDI-TOF MS *m*/*z* 698.3 $[M]^+$, 721.3 $[M + Na]^+$, 737.2 $[M + K]^+$. Anal. Calcd for $C_{44}H_{42}O_8 \cdot 0.75H_2O$: C, 74.19, H, 6.16. Found: C, 74.47; H, 6.51.

Compound 15. A mixture of **14** (156 mg, 0.22 mmol) and CAN (735 mg, 1.34 mmol) in acetonitrile (15 mL) and water (5 mL) was stirred at room temperature for 30 min. The reaction mixture was extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate, and then concentrated under reduced pressure. The crude product was further purified by column chromatography over silica gel (eluent: 20:1 CH_2Cl_2/ethyl acetate) to give **15** (122 mg, 86%) as an orange solid. Mp >300 °C. IR ν 1644 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 6H), 3.83−3.87 (m, 4H), 4.01−4.08 (m, 4H), 5.63 (s, 4H), 6.33 (s, 4H), 7.26−7.28 (m, 4H), 7.42−7.48 (m, 4H). MALDI-TOF MS *m*/*z* 642.3 $[M + 4H]^+$. Anal. Calcd for $C_{40}H_{30}O_8 \cdot 1.2H_2O$: C, 72.76; H, 4.95. Found: C, 72.54; H, 5.04.

Compound 8. Reduction of the *o*-quinone **15** (0.35 g, 0.55 mmol) with catalytic hydrogenation gave **16** (0.35 g, 0.55 mmol) as a white solid in 98% yield, which was used in the next reaction without further purification. A suspension of cesium carbonate (1.47 g, 4.5 mmol) in anhydrous DMF (70 mL) under argon atmosphere was stirred vigorously for 10 min and then heated to 100 °C. To the mixture was added dropwise a solution of **16** (0.35 g, 0.55 mmol) and bistosylate **10** (0.752 g, 1.1 mmol) in anhydrous DMF (50 mL) over 12 h. The reaction mixture was stirred at 100 °C for another 3 d. After cooling to ambient temperature, the mixture was filtered and washed with CH_2Cl_2 (60 mL). The filtrate was concentrated under reduced pressure to give a gray solid, which was dissolved in CH_2Cl_2 (250 mL) and washed with diluted HCl. The organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the resulting oil was subjected to successive column chromatography over silica gel (eluent: 100:1 CH_2Cl_2/CH_3OH) to give **8** (0.25 g, 35%) as an off-white solid. Mp 72−73 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59−3.65 (m, 22H), 3.73−3.75 (m, 16H), 3.86−3.87 (m, 4H), 4.03−4.05 (m, 20H), 5.68 (s, 4H), 6.89 (s, 8H), 6.91−6.94 (m, 4H), 6.98 (s, 4H), 7.29−7.32 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 47.7, 59.4, 69.4, 69.9, 70.1, 71.0, 71.1, 71.9, 74.8, 76.6, 100.0, 112.0, 114.3, 121.4, 123.3, 125.0, 136.8, 138.9, 145.7, 145.8, 146.1. MALDI-TOF MS *m*/*z* 1341.7 $[M + Na]^+$. Anal. Calcd for $C_{76}H_{86}O_{20}$: C, 69.18; H, 6.57. Found: C, 68.81; H, 6.96.

ASSOCIATED CONTENT

Supporting Information. Copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds, copies of ESI-MS, ^{1}H−^{1}H COSY, and ^{1}H−^{1}H ROESY spectra for the complexes, determination of the association constants, and X-ray crystallographic file (CIF) for complex **8**·**1**$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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