

# **1.8-Dioxyanthracene-Derived Crown Ethers: Synthesis, Complexation with** Paraguat and Assembly of a Tetracationic Cyclophane-Crown Ether Based [2]Catenane

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1,8-Dioxyanthracene-based bisarylene crown ethers, composed of ethylene glycol chains and aromatic moieties, have been synthesized. Complexation studies revealed that these crown ethers could form 1:1 complexes with methyl viologen dication (N,N'-dimethyl-4,4'-bipyridinium dication;  $MV^{2+}$ ) in a mixed solvent of CDCl<sub>3</sub> and CD<sub>3</sub>CN (1:1 v/v) with association constants in a range of  $(1.2\pm0.1)\times10^3$  M<sup>-1</sup> to  $(1.6\pm0.2)\times10^4$  M<sup>-1</sup>. The structure of the complex and the strength of the  $\pi$ -donor/ $\pi$ -acceptor interactions between the 1,8-dioxyanthracene planes and the pyridinium rings of MV<sup>2+</sup> are highly dependent on the length of the polyether chains of the ethers. Structural analysis showed that the tetraethylene glycol-derived bis-1,8-dioxyanthracene-based crown ether 9 forms a U-shaped host-quest complex with MV<sup>2+</sup> by inserting the coplanar pyridinium rings of MV<sup>2+</sup> between the two parallel oriented 1,8-dioxyanthracene units of

## Introduction

Since Pedersen's pioneering work in the synthesis and group I metal complexation characteristics of crown ethers,<sup>[1]</sup> this class of molecules has been developed as the first generation of macrocyclic hosts and has played a significant role in the field of host-guest chemistry.<sup>[2]</sup> The identification of host-guest interactions between crown ether

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9, which is driven predominantly by  $\pi$ -donor/ $\pi$ -acceptor interactions. The pentaethylene glycol-derived bis-1,8-dioxyanthracene-based crown ether 10, however, adopts a crescent-shaped conformation in complex  $10 \supset MV^{2+}$  with the MV<sup>2+</sup> guest being encapsulated by the polyether chains, propelled mainly by the hydrogen-bonding interactions between the hydrogen atoms of MV<sup>2+</sup> and the oxygen atoms of the polyether chains of 10. Similarly, the hexaethylene glycol-derived bis-1,8-dioxyanthracene-based crown ether 11 forms a complex with  $MV^{2+}$ . However, only weak  $\pi$ -do $nor/\pi$ -acceptor interactions between the aromatic groups of the mixed bisarylene crown ethers 12 and 13, and MV<sup>2+</sup> were observed, and construction of tetracationic cyclophane [CBPQT<sup>4+</sup>] and crown ether **13** based [2]catenane **15** was achieved through supramolecular interactions between the [CBPQT<sup>4+</sup>] ring and naphtho unit in the crown ether.

hosts and secondary ammonium salts<sup>[3]</sup> or N,N'-dialkyl-4,4'-bipyridinium dication guests,<sup>[4]</sup> has led to the construction of various mechanically interlocked molecules. A range of crown ether hosts have since been designed, synthesized, and used for the creation of interlocked supramolecular architectures, including pseudorotaxanes, rotaxanes, and catenanes.<sup>[5]</sup> There are two approaches that are typically used to enhance the supramolecular interactions between the crown ether hosts and the N,N'-dialkyl-4,4'-bipyridinium dication or pyridinium guests. One is using preorganized structures, such as crown ether based cryptands<sup>[6]</sup> and shape-persistent molecular cages,<sup>[7,8]</sup> and the second is incorporating electron-rich aryl moieties, such as naphtho units, into the crown ether structures to enhance the chargetransfer interactions between the arylene functions and N, N'-dialkyl-4,4'-bipyridinium dications.<sup>[9]</sup> Anthracene, which is a highly electron-rich arylene, however, has much less frequently been incorporated into the structures of crown ethers,<sup>[10]</sup> possibly due to its unstable thermo- and photochemical nature. Indeed, reports on 1,8-dioxyanthracene-based crown ethers are almost completely absent.<sup>[11]</sup> In this report, the synthesis and characterization of five 1,8-dioxyanthracene-based bisarylene crown ethers are described, three of which are composed of two 1,8-dioxy-



Scheme 1. The synthesis of 1,8-dioxyanthracene-based bisarylene crown ethers. *Reagents and conditions:* (a) 1. CH<sub>3</sub>COCl/NEt<sub>3</sub>, 2. Zn/HAc, 3. NaOH; (b) oligoethylene glycol monotosylate/Cs<sub>2</sub>CO<sub>3</sub>, DMF, 90 °C; (c) TsCl/NaOH, THF; (d) **2**, (catechol or naphthalene-1,5-diol)/Cs<sub>2</sub>CO<sub>3</sub>, DMF, 90 °C.

anthracene units connected by two tetra-, penta- or hexaethylene glycol chains. Each of the other two crown ethers has one 1,8-dioxyanthracene unit connected through two tetraethylene glycol chains to a benzo or a naphtho moiety. We describe the results of our investigation on host-guest interactions of the synthesized crown ethers with methyl viologen dication (N,N'-dimethyl-4,4'-bipyridinium dication;  $MV^{2+}$ ) as well as the formation of the tetracationic cyclophane [CBPQT<sup>4+</sup>]-crown ether based [2]catenane.

## **Results and Discussion**

#### Synthesis of Anthracene-Based Crown Ethers

The 1,8-anthracene-based crown ethers were synthesized starting with the reduction of 1,8-dihydroxyanthracene-9,10-dione (1) to anthracene-1,8-diol (2)<sup>[12]</sup> (Scheme 1). The latter diol was alkylated by tetra-, penta- or hexaethylene glycol monotosylate under basic conditions to give diols **3**–**5**, respectively, which were then reacted with tosyl chloride to generate the corresponding bistosylates **6**–**8**. The [1+1] macrocyclization reaction of **6**–**8** with diol **2** gave the desired anthracene-based crown ethers **9**–**11**, respectively, in reasonable yields. Similarly, the [1+1] macrocyclization reaction of **6** with catechol or naphthalene-1,5-diol resulted in the formation of mixed bisarylene crown ethers **12** and **13**, respectively. The structures of the 1,8-anthracene-based crown ethers **9**–**13** were confirmed by <sup>1</sup>H, <sup>13</sup>C NMR and MS spectroscopy (see the Supporting Information).

It is known that [4+4] dimerization occurs for anthracene and its derivatives when irradiated at wavelengths above approximately 350 nm,<sup>[13]</sup> so it is quite reasonable to speculate that the 1,8-anthracene-based crown ethers would undergo dimerization. Although <sup>1</sup>H NMR spectra indicated that dimerization of the crown ether **9** did not occur in CDCl<sub>3</sub> solution, single-crystal structure analysis revealed that bis-1,8-dioxyanthracene-based crown ether **9** exists in an intramolecular dimerized state, as shown in Figure 1. Given that topochemical photoreaction of anthracenyl groups could take place only when they are positioned at suitable distances, this result suggests that the intramolecular dimerization of **9** probably occurred in the crystalline state.



Figure 1. Single-crystal structure of intramolecularly dimerized **9**; top: top view of the dimerized anthracene moieties; bottom: side view of the dimerized anthracene moieties. Hydrogen atoms are omitted for clarity.

# Complexation of the 1,8-Dioxyanthracene-Based Crown Ethers with Methyl Viologen Dications (MV<sup>2+</sup>)

The complexation of the 1,8-dioxyanthracene-based crown ethers with MV<sup>2+</sup> was investigated with 1D and 2D <sup>1</sup>H NMR spectroscopy, and by mass spectrometry as well as by single-crystal X-ray diffraction analysis. Mixing a yellow solution of 9 and a colorless solution of  $MV^{2+}\cdot 2PF_6^{-1}$ in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v) resulted in a clear dark-red solution immediately (Figure S1), which was attributed to the formation of a charge-transfer complex between the electron-rich anthracene planes of crown ether 9 and the electron-poor pyridinium rings of MV<sup>2+</sup>. The complexation behavior was further examined by using <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> and CD<sub>3</sub>CN (1:1 v/v). As shown in Figure 2, upfield shifts for the anthracene H-9 and H-10 signals  $(\delta = -0.79 \text{ and } -0.16 \text{ ppm})$  of 9, and  $\alpha$ - and  $\beta$ -pyridinium proton signals ( $\delta = -0.59$  and -1.00 ppm) of MV<sup>2+</sup>, were observed in the <sup>1</sup>H NMR spectrum of an equimolar mixture of 9 and MV<sup>2+</sup>, indicating the existence of  $\pi$ -donor/ $\pi$ acceptor interactions between the anthracene planes of 9 and the pyridinium rings of MV<sup>2+</sup>. Upfield shifts for the proton signals of the tetraethylene glycol chains on 9, and *N*-methyl protons of MV<sup>2+</sup> ( $\delta = -0.21$  ppm) were also observed (Figure 2), which were possibly caused by shielding effects. 2D <sup>1</sup>H NMR NOESY spectrum of the complex  $9 \supset MV^{2+}$  (Figure S2) clearly showed the correlations between the signals of  $\alpha$ - and  $\beta$ -pyridinium protons of MV<sup>2+</sup> and the signals of anthracene H-9 and H-10 protons on 9. The correlations between the signals of N-methyl protons of  $MV^{2+}$  and those of the tetraethylene glycol protons of 9 were also seen. The results indicated that face-to-face  $\pi$ stacking and charge transfer interactions between the anthracene planes of 9 and the pyridinium rings of  $MV^{2+}$ could be the main driving force for formation of the complex. Hydrogen-bonding interactions between the N-methyl groups of  $MV^{2+}$  and the ethylene glycol chains of 9 might also contribute to stabilizing the complex. A Job plot (Figure S3) based on <sup>1</sup>H NMR spectroscopic data demonstrated that crown ether 9 and  $MV^{2+}$  form a complex in a 1:1 ratio in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v), which was further confirmed by ESI-MS spectrometry  $\{m/z \ 1067.7 \ assigned$ to  $[9 \supset MV^{2+}-PF_6^{-}]^+$ ; Figure S4}. The association constant  $(K_a)$  of the complex  $9 \supset MV^{2+}$  in mixed solvent of CDCl<sub>3</sub> and CD<sub>3</sub>CN (1:1 v/v) was determined to be  $(1.6 \pm 0.2) \times$ 10<sup>4</sup> m<sup>-1</sup> with a <sup>1</sup>H NMR titration method (see the Supporting Information and Figure S6–S6).

Single crystals of the complex  $9 \supset MV^{2+}$  were obtained by slow evaporation of the complex solution in acetonitrile. In complex  $9 \supset MV^{2+}$  (Figure 3), the crown ether 9 is folded in a U-shaped conformation with the two anthracene planes being oriented parallel at a distance of 6.69 Å, and the two coplaner pyridinium rings of the  $MV^{2+}$  guest being intercalated between the two parallel anthracene planes of 9 in an offset manner, similar to those of anthracene-derived molecular tweezers for complexation of aromatic guests.<sup>[14]</sup> One  $\alpha$ -pyridinium hydrogen atom of  $MV^{2+}$  forms hydrogen bonds with three oxygen atoms of 9 (C–H···O distances:



Figure 2. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1:1 v/v): (a) free  $MV^{2+}$  (1.0 mM); (b) 9 (1.0 mM) +  $MV^{2+}$  (1.0 mM); (c) 9 (1.0 mM).

2.368, 2.559, and 2.559 Å), and the  $MV^{2+}$  guest does not thread the tetraethylene glycol chains of **9**. The complex  $9 \supset MV^{2+}$  is stabilized by  $\pi-\pi$  stacking, charge transfer, and by hydrogen-bonding interactions. In the crystal lattice, one  $MV^{2+}$  molecule was positioned between every two anthracene planes of different supramolecular complexes  $9 \supset MV^{2+}$ , resulting in a stacking array of alternated complex  $9 \supset MV^{2+}$  and  $MV^{2+}$  (see the Supporting Information).



Figure 3. Single-crystal structure of complex  $9 \supset MV^{2+}$ . Hydrogen atoms on host 9 and  $PF_6^-$  counterions are omitted for clarity.

Analogously, the complexation behavior between the penta- and hexaethylene glycol-derived bis-1,8-dioxyanthracene-containing crown ethers 10 and 11 with  $MV^{2+} \cdot 2PF_6^{-1}$ were studied in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v). It was found that the color of the complex  $10 \supset MV^{2+}$  and  $11 \supset MV^{2+}$  solutions was lighter than that of the complex  $9 \supset MV^{2+}$  solution, with the depth of the red color following a trend of  $9 \supset MV^{2+}$  (dark red) >  $10 \supset MV^{2+}$  (red) >  $11 \supset MV^{2+}$  (light red) (see the Supporting Information), which could be due to different strength of charge-transfer interactions between the pyridinium rings of  $MV^{2+}$  and the anthracene planes of the crown ethers. In the <sup>1</sup>H NMR spectra of equimolar mixtures of 10 and MV2+, and 11 and MV2+, upfield shifts for the anthracene H-9 and H-10 signals on 10 and 11, as well as for the  $\alpha$ - and  $\beta$ -pyridinium proton signals of MV<sup>2+</sup> (Figures 4 and 5), are smaller than those of the corresponding proton signals of the equimolar mixture of 9 and  $MV^{2+}$ . This result suggests a weaker  $\pi$ -donor/ $\pi$ -acceptor interaction between the anthracene planes of 10 or 11 with the pyridinium rings of MV<sup>2+</sup>, which is consistent with the lighter red color of  $10 \supset MV^{2+}$  and  $11 \supset MV^{2+}$  solutions. Upfield



Figure 4. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1:1 v/v): (a) free  $MV^{2+}$  (1.0 mM); (b) **10** (1.0 mM) +  $MV^{2+}$  (1.0 mM); (c) **10** (1.0 mM).

shifts for the N-methyl proton signals of  $MV^{2+}$ , as well as the proton signals of polyether chains, were also observed in the <sup>1</sup>H NMR spectra of the complex solutions of  $10 \supset MV^{2+}$  and  $11 \supset MV^{2+}$ , implying these protons are possibly shielded in the complexes. Furthermore, the 2D <sup>1</sup>H NMR NOESY spectrum (Figure S7) of the complex  $10 \supset MV^{2+}$  solution in CDCl<sub>3</sub> and CD<sub>3</sub>CN (1:1 v/v) revealed correlations of the  $\alpha$ - and  $\beta$ -pyridinium protons of MV<sup>2+</sup> with the anthracene and the pentaethylene glycol protons of 10, and correlations of N-methyl protons of  $MV^{2+}$  with the pentaethylene glycol protons of 10, which could indicate the existence of  $\pi$ -donor/ $\pi$ -acceptor interactions between the anthracene groups on 10 and the pyridinium rings on MV<sup>2+</sup>, as well as possible hydrogen-bonding interactions between the  $\alpha$ -,  $\beta$ -pyridinium and N-methyl protons of  $MV^{2+}$  and the oxygen atoms of the pentaethylene glycol chains of 10. However, in the 2D <sup>1</sup>H NMR NOESY spectrum (Figure S8) of the complex  $11 \supset MV^{2+}$  solution in CDCl<sub>3</sub> and CD<sub>3</sub>CN (1:1 v/v), only the correlation signals of  $\alpha$ -,  $\beta$ - and *N*-methyl protons of MV<sup>2+</sup> with the hexaethylene glycol protons of 11 can be observed, implying that the hydrogen-bonding interactions between the MV<sup>2+</sup> protons and the oxygen atoms of the hexaethylene glycol chains of 11 are the main propelling force for the formation of the supramolecular complex  $11 \supset MV^{2+}$ . Weak  $\pi$ -donor/ $\pi$ -acceptor interactions between the anthracene groups on 11 and the pyridinium rings of MV<sup>2+</sup> are also involved in the complex  $11 \supset MV^{2+}$ , based on the color change observed upon addition of MV<sup>2+</sup> dication to the host solution. Nonetheless, the supramolecular complex  $11 \supset MV^{2+}$  is presumed to be formed in a similar way to that of  $10 \supset MV^{2+}$ through the encapsulation of MV<sup>2+</sup> guest by hexaethylene glycol chains of 11. Job plots based on <sup>1</sup>H NMR spectroscopic data (Figure S9 and Figure S13), and on ESI-MS spectrometry  $\{m/z \ 1155.9 \text{ and } 1243.1, \text{ assigned to} \}$  $[10 \supset MV^{2+}-PF_6]^+$  and  $[11 \supset MV^{2+}-PF_6]^+$ , respectively; Figure S10 and S14} support structural assignment of 1:1 complexes  $10 \supset MV^{2+}$  and  $11 \supset MV^{2+}$  in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1

v/v). The association constants ( $K_a$ ) of the complexes  $10 \supset MV^{2+}$  and  $11 \supset MV^{2+}$  in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v) were determined to be  $(8.9 \pm 0.8) \times 10^3 \text{ m}^{-1}$  (Figure S11–S12) and  $(6.2 \pm 0.8) \times 10^3 \text{ m}^{-1}$  (Figure S115–S16), respectively (see the Supporting Information).



Figure 5. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1:1 v/v): (a) free  $MV^{2+}$  (1.0 mM); (b) **11** (1.0 mM) +  $MV^{2+}$  (1.0 mM); (c) **11** (1.0 mM).

As shown in Figure 6, single crystals of the complex  $10 \supset MV^{2+}$ , which were obtained in acetonitrile, reveal a host-guest complex that is structurally completely different from that of  $9 \supset MV^{2+}$ . In  $10 \supset MV^{2+}$ , the host crown ether 10 adopts a crescent-shaped conformation, the guest  $MV^{2+}$  dications are almost completely encapsulated by the polyether chains of the host 10 with its two pyridinium ring planes being twisted by  $30.5^{\circ}$ . The host-guest complex  $10 \supset MV^{2+}$  was stabilized by C–H··· $\pi$  and  $\pi$ - $\pi$  stacking interactions between the pyridinium rings of the  $MV^{2+}$  and the anthracene planes of 10, and further strengthened by multiple hydrogen bond (C–H···O distances ranged from 2.221 to 3.220 Å) interactions between the oxygen atoms



Figure 6. Single-crystal structure of complex  $10 \supset MV^{2+}$ : (a) top view; (b) side view. Hydrogen atoms on host 10 and PF<sub>6</sub><sup>-</sup> counterions are omitted for clarity.



of polyether chains on **10** and the hydrogen atoms of the pyridinium rings, as well as by the *N*-methyl protons of  $MV^{2+}$ . Unfortunately, attempts to grow single crystals of complex  $11 \supset MV^{2+}$  were unsuccessful.

The complexation behavior of mixed bisarylene crown ether 12 or 13 with MV<sup>2+</sup> was also examined in CDCl<sub>3</sub>/ CD<sub>3</sub>CN (1:1 v/v). Mixing a yellow solution of 12 in CDCl<sub>3</sub>/ CD<sub>3</sub>CN (1:1 v/v) and a colorless solution of  $MV^{2+} \cdot 2PF_6$ in 1:1 molar ratio resulted in immediate color change, implying the formation of a charge-transfer complex 12·MV<sup>2+</sup>. However, no clear color change was observed when the CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v) solutions of 13 and  $MV^{2+}\cdot 2PF_6^-$  were mixed in a 1:1 molar ratio, suggesting no charge transfer complex formation between 13 and  $MV^{2+}$ , possibly due to the unfavorable geometrical arrangement between the 1,5-dioxynaphthalene and 1,8-dioxyanthracene planes in 13, which resulted in less effective cooperative interaction with a MV<sup>2+</sup> guest. In the <sup>1</sup>H NMR spectrum of an equimolar mixture of 12 and MV<sup>2+</sup>·2PF<sub>6</sub><sup>-</sup> in CDCl<sub>3</sub>/ CD<sub>3</sub>CN (1:1 v/v), upfield shifts for the signals of H-9 and H-10 ( $\delta$  = -0.20 and -0.04 ppm) of anthracene, the signals of benzo protons ( $\delta = -0.15$  ppm) on 12, and  $\alpha$ - and  $\beta$ pyridinium proton signals of  $MV^{2+}$  ( $\delta = 0.21$  and 0.35 ppm), were observed (Figure 7), implying the existence of  $\pi$ -donor/ $\pi$ -acceptor interactions between the aryl planes of the crown ether 12 and the pyridinium rings of  $MV^{2+}$ . Correlations between the anthracene and benzo proton signals of 12 and signals of the MV<sup>2+</sup> pyridinium protons in the 2D <sup>1</sup>H NMR NOESY spectrum of the mixture 12 and MV<sup>2+</sup>·2PF<sub>6</sub><sup>-</sup> in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v) also supported the existence of  $\pi$ -donor/ $\pi$ -acceptor interactions between the aryl planes of 12 and the pyridinium ring planes of  $MV^{2+}$ . The existence for hydrogen-bonding interactions between the hydrogen atoms of  $MV^{2+}$  and the oxygen atoms of the polyether chains of 12 was supported by correlations between the protons of MV<sup>2+</sup> and the protons of polyether chains of 12 (Figure S17). A Job plot based on <sup>1</sup>H NMR spectroscopic data revealed that host 12 and guest MV<sup>2+</sup> form a 1:1 complex 12·MV<sup>2+</sup> in CDCl<sub>3</sub>/CD<sub>3</sub>CN (Figure S18), which was supported by ESI-MS spectrometry  $\{m/z \text{ 996.9 assigned to } [12 \cdot MV^{2+} - PF_6^{-}]^+; \text{ Figure S19} \}.$  The association constant ( $K_a$ ) of complex 12·MV<sup>2+</sup> in CDCl<sub>3</sub>/ CD<sub>3</sub>CN was determined to be  $(3.1 \pm 0.3) \times 10^3 \text{ m}^{-1}$  (Figure S20–S21). The <sup>1</sup>H NMR spectrum of an equimolar mixture of 13 and  $MV^{2+}\cdot 2PF_6^-$  in  $CDCl_3/CD_3CN$  (1:1 v/v) showed smaller upfield shifts for the proton signals of H-9 and H-10 ( $\delta$  = -0.12 and -0.02 ppm) of the anthracene moiety in 13, and  $\alpha$ - and  $\beta$ -pyridinium proton signals of MV<sup>2+</sup>  $(\delta = -0.11 \text{ and } -0.19 \text{ ppm})$  (Figure 8), compared with those in 12; and almost no shifts were observed for the proton signals of the naphtho moiety in 13, indicating the existence of weak interactions between the anthracene moiety of 13 and the pyridinium ring planes of MV<sup>2+</sup>. In the 2D <sup>1</sup>H NMR NOESY spectrum of the mixture of 13 and MV<sup>2+</sup>·2PF<sub>6</sub><sup>-</sup> in CDCl<sub>3</sub>/CD<sub>3</sub>CN (Figure S22), weak correlation signals between the anthracene protons of 13 and the  $\beta$ -pyridinium protons of MV<sup>2+</sup> were observed, hinting at the existence of weak  $\pi$ -donor/ $\pi$ -acceptor interactions between the anthracene planes of 13 and the pyridinium ring planes of  $MV^{2+}$ . The correlation signals between the polyether protons of 13 and the protons of  $MV^{2+}$  could be due to hydrogen-bonding interactions between the polyether oxygen atoms of 13 and the hydrogen atoms of  $MV^{2+}$ . A Job plot based on <sup>1</sup>H NMR spectroscopic data showed the formation of a 1:1 complex 13· $MV^{2+}$  (Figure S23), which was also supported by ESI-MS spectrometry {m/z 1016.9, assigned to [13· $MV^{2+}$ - $PF_6$ ]<sup>+</sup>; Figure S24}. The association constant ( $K_a$ ) of the complex 13· $MV^{2+}$  in CDCl<sub>3</sub>/CD<sub>3</sub>CN was determined to be (1.2 ± 0.1) × 10<sup>3</sup> M<sup>-1</sup> (Figure S25– S26).



Figure 7. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1:1 v/v): (a) free  $MV^{2+}$  (1.0 mM); (b) **12** (1.0 mM) +  $MV^{2+}$  (1.0 mM); (c) **12** (1.0 mM).



Figure 8. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 1:1 v/v): (a) free  $MV^{2+}$  (1.0 mM); (b) 13 (1.0 mM) +  $MV^{2+}$  (1.0 mM); (c) 13 (1.0 mM).

As revealed by the 1D and 2D <sup>1</sup>H NMR spectroscopic, mass spectrometric, and X-ray crystallographic data, all five 1,8-dioxyanthracene-based bisarylene crown ethers were found to form 1:1 complexes with N,N'-dimethyl-4,4'-bipyridinium dication (MV<sup>2+</sup>). In the tetraethylene glycol derived bis-1,8-dioxyanthracene-containing crown ether **9**,  $\pi$ donor/ $\pi$ -acceptor interactions are the dominant noncovalent bond interactions in the formation of the complex

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 $9 \supset MV^{2+}$  with the  $MV^{2+}$  guest being sandwiched by the two anthracene planes of the host. Nevertheless, in the cases of bis-1,8-dioxyanthracene-containing crown ethers with longer polyether chains, such as penta- or hexaethylene glycol-derived bis-1,8-dioxyanthracene-containing crown ethers 10 or 11, hydrogen-bonding interactions between the hydrogen atoms of the MV<sup>2+</sup> guest and the oxygen atoms of the penta- or hexaethylene glycol chains in 10 or 11 are the major driving force for the formation of complexes  $10 \supset MV^{2+}$  or  $11 \supset MV^{2+}$ , in which the MV<sup>2+</sup> guest is encapsulated by the polyether chains of the hosts. For the mixed bisarylene crown ether 12, the 1,8-dioxyanthracene and benzo planes of the host were postulated to interact with the MV<sup>2+</sup> guest in a similar way to that of the two 1,8dioxyanthracene planes in 9, but with a weaker binding affinity due to the less electron-rich nature of the benzo plane. The smaller association constant of the complex  $12 \cdot MV^{2+}$ , relative to that of  $9 \supset MV^{2+}$ , is consistent with such a hypothesis. Although <sup>1</sup>H NMR spectroscopic and mass spectrometric results suggested the formation of a 1:1 complex 13·MV<sup>2+</sup> upon mixing the 1,8-dioxyanthracene- and 1,5naphthalene-derived crown ether 13 and MV<sup>2+</sup> dications, the binding mode is not clear at this stage.

#### [2]Catenane Assembly

With the 1,8-dioxyanthracene-based crown ethers in hand, attempts were made to synthesize tetracationic cyclophane [cyclobis(paraquat-*p*-phenylene); CBPQT<sup>4+</sup>] aromatic crown ether-based [2]catenanes by utilizing charged  $\pi$ -donor/ $\pi$ -acceptor template methodology, as shown in Scheme 2. As the size and geometric parameters of the 1,8-dioxyanthracene moiety do not allow diparaguat 14 to thread into a tetracationic cyclophane ring, the synthesis of tetracationic cyclophane-crown ether based [2]catenanes were unsuccessful in the cases of 9, 10 and 11, which contain two 1,8-dioxyanthracene functions. However, in the case of the mixed bisarylene crown ether 13, the  $\pi$ electron-deficient aromatic diparaquat 14 could thread through the  $\pi$ -electron-rich crown ether ring 13 directed by the  $\pi$ -electron-rich naphtho moiety. Subsequent coupling of the complex 13.14 with a *p*-xylylene moiety afforded the  $[CBPQT^{4+}]$ -13 based [2]catenane 15.

The <sup>1</sup>H NMR spectrum of **15** in CD<sub>3</sub>CN confirmed its mechanically interlocked structure (Figure 9). The significant upfield shift of the H-4/8 protons of the 1,5-dioxynaphthalene (DNP) unit of the crown ether ring in 15 (relative to the corresponding proton signals of 13) indicates the CBPQT<sup>4+</sup> ring encircles the DNP unit through strong  $\pi$ donor/ $\pi$ -acceptor interactions. The encircling of the 1,8-dioxyanthracene unit by the CBPQT<sup>4+</sup> ring in [2]catenane 15 is prohibited due to the size and orientation of the 1,8-dioxyanthracene moiety. Small chemical shifts for the H-9 and H-10 protons of the 1,8-dioxyanthracene moiety of the crown ether in [2]catenane 15 showed the existence of weak supramolecular interactions between the CBPQT<sup>4+</sup> ring and the anthracene moiety. ESI-MS analysis also supports the formation of the CBPQT<sup>4+</sup>-13 based [2]catenane 15 by the presence of intense peaks at m/z 450.8 ([M-3PF<sub>6</sub>-]<sup>3+</sup>) and 748.7 ( $[M-2PF_6]^{2+}$ ). The structure of 15, which was unambiguously established by single-crystal X-ray diffraction analysis, revealed the formation of a CBPQT<sup>4+</sup>-13 based [2]catenane (Figure 10), in which the naphtho function of the crown ether subunit 13 is circulated by the CBPOT<sup>4+</sup> ring through mechanical linkage stabilized by  $\pi$ - $\pi$  stacking and hydrogen-bonding interactions, which is consistent with the results obtained in solution. In the solid



Figure 9. <sup>1</sup>H NMR spectra (CD<sub>3</sub>CN, 400 MHz): (top) [2]catenane **15** (1.0 mM); (bottom) **13** (1.0 mM).



Scheme 2.



state, the crown ether subunit 13 in [2]catenane 15 adopts a distorted U-shaped conformation, which resulted in the parallel arrangement of a bipyridinium plane of the CBPQT<sup>4+</sup> ring and the anthracene moiety, strengthened by  $\pi$ -donor/ $\pi$ -acceptor interactions.



Figure 10. Single-crystal structure of [CBPQT<sup>4+</sup>]-**13** based [2]-catenane **15**. Hydrogen atoms and  $PF_6^-$  counterions are omitted for clarity.

## Conclusions

By employing anthracene-1,8-diol as an aryl component, we have synthesized five novel 1,8-dioxyanthracene-based bisarylene crown ethers varied by either the length of polyether chains or by the aryl constituents. By means of <sup>1</sup>H NMR titration, mass spectrometry and X-ray single-crystal structural analysis, the 1,8-dioxyanthracene-based bisarylene crown ethers were found to form 1:1 complexes with N,N'-dimethyl-4,4'-bipyridinium dication (MV<sup>2+</sup>) in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1:1 v/v) with the association constants ranged from  $(1.2 \pm 0.1) \times 10^3 \text{ m}^{-1}$  to  $(1.6 \pm 0.2) \times 10^4 \text{ m}^{-1}$ . Results showed that the structures of the resulting supramolecular complexes formed between the bis-1,8-dioxyanthracene-derived crown ether hosts 9, 10, and 11, and MV<sup>2+</sup> guest are highly dependent on the lengths of the polyether chains connecting the two 1,8-dioxyanthracene moieties. For instance, the tetraethylene glycol-derived bis-1,8-dioxyanthracene-based crown ether 9 was found to form a sandwiched supramolecular complex  $9 \supset MV^{2+}$ driven predominantly by  $\pi$ -donor/ $\pi$ -acceptor interactions, whereas crescent-shaped conformations are adopted by the penta- and hexaethylene glycol-derived bis-1,8-dioxyanthracene-based crown ether hosts 10 and 11 in the supramolecular complexes  $10 \supset MV^{2+}$  and  $11 \supset MV^{2+}$ , respectively, with MV<sup>2+</sup> guest encapsulated by the polyether chains of these crown ether hosts through hydrogen-bonding interactions. Less stable supramolecular complex 12·MV<sup>2+</sup> was formed due to weaker  $\pi$ -contacts between the benzo plane of the crown ether 12 and MV<sup>2+</sup> dications, whereas the presence of geometrically mismatched 1,8-dioxyanthracene and 1,5naphthalene moieties in the crown ether 13 led to the formation of supramolecular complex  $13 \cdot MV^{2+}$  with a much smaller association constant. A tetracationic cyclophane [CBPQT<sup>4+</sup>]-crown ether based [2]catenane was successfully constructed through the recognition of naphthalene moiety in 13 and the [CBPQT<sup>4+</sup>] ring, although bis-1,8-dioxyanthracene-based crown ethers 9, 10, and 11 could not be used to construct [2]catenanes due to the size and orientation of the 1,8-dioxyanthracene planes.

# **Experimental Section**

**General Methods:** Commercially available chemicals were used without further purification unless stated otherwise. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with 400 MHz spectrometers in CDCl<sub>3</sub> or [D<sub>6</sub>] DMSO with TMS as the reference. Mass spectra (ESI analysis) were recorded with Waters ZQ 2000 and Bruker esquire 6000 instruments. Single-crystal X-ray diffraction data were collected with a SMART APEX 2 X-ray diffractometer equipped with a normal focus M-target X-ray tube. Data reduction included absorption corrections by the multi-scan method.

**Synthesis of 1,8-Dihydroxyanthracene (2):** Obtained from 1,8-dihydroxyanthracene-9,10-dione (1) by following a reported procedure. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta = 10.32$  (s, 2 H), 9.04 (s, 1 H), 8.34 (s, 1 H), 7.47 (d, J = 8.6 Hz, 2 H), 7.34–7.22 (m, 2 H), 6.79 (d, J = 7.1 Hz, 2 H) ppm. <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]DMSO):  $\delta = 153.5$ , 132.7, 126.2, 124.6, 123.4, 118.3, 115.7, 105.2 ppm. MS (ESI): *m/z* calcd. for C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>Na [M + Na]<sup>+</sup> 233.06; found 233.31.

Synthesis of Tetraethylene Glycol Monotosylate: To a mixture of tetraethylene glycol (3.88 g, 0.02 mol) in THF (40 mL) was added sodium hydroxide (2 m, 10 mL). After being stirred at r.t. for 10 min, tosyl chloride (3.8 g, 0.02 mol) in THF (20 mL) was added dropwise. The reaction mixture was stirred for 3 h, then dilute HCl was added to adjust the pH to 7. THF was then evaporated under reduced pressure and the residue was extracted with ethyl acetate and dried with anhydrous sodium sulfate. After the solvent was removed in vacuo, the crude product was purified by column chromatography over silica gel (ethyl acetate/petroleum ether, 1:2) to afford target compound (4.91 g, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.79 (d, J = 8.3 Hz, 2 H), 7.36 (d, J = 8.1 Hz, 2 H), 4.19–4.12 (m, 2 H), 3.73–3.56 (m, 14 H), 2.45 (s, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.84, 132.9, 129.8, 127.9, 72.5, 70.5, 70.3, 70.8, 69.3, 68.6, 61.5, 21.5 ppm. MS (ESI): m/z calcd. for  $C_{15}H_{24}O_7SNa [M + Na]^+ 371.11$ ; found 371.35.

**Synthesis of Pentaethylene Glycol Monotosylate:** Obtained as described for tetraethylene glycol monotosylate, yield 67%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.80 (d, *J* = 8.2 Hz, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 4.19–4.12 (m, 2 H), 3.73–3.67 (m, 4 H), 3.65 (d, *J* = 8.5 Hz, 8 H), 3.60 (d, *J* = 6.8 Hz, 6 H), 2.45 (s, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.9, 132.89, 129.9, 127.99, 70.6, 70.5, 70.4, 70.3, 70.2, 70.1, 69.3, 68.6, 61.5, 21.6 ppm. MS (ESI): *m/z* calcd. for C<sub>17</sub>H<sub>28</sub>O<sub>8</sub>SNa [M + Na]<sup>+</sup> 415.14; found 415.43.

**Synthesis of Hexaethylene Glycol Monotosylate:** Obtained as described for tetraethylene glycol monotosylate, yield 69%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.80 (d, *J* = 7.8 Hz, 2 H), 7.35 (d, *J* = 7.8 Hz, 2 H), 4.18–4.12 (m, 2 H), 3.76–3.52 (m, 22 H), 2.45 (s, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.8, 132.9, 129.9, 127.9, 72.6, 70.7, 70.6, 70.5, 70.3, 69.4, 68.7, 61.6, 21.6 ppm. MS (ESI): *m/z* calcd. for C<sub>19</sub>H<sub>32</sub>O<sub>9</sub>SNa [M + Na]<sup>+</sup> 459.17; found 459.41.

**Compound 3:** A mixture of 1,8-dihydroxyanthracene **2** (0.21 g, 1 mmol), tetraethylene glycol monotosylate (0.71 g, 2.1 mmol), and

Cs<sub>2</sub>CO<sub>3</sub> (0.98 g, 3 mmol) in anhydrous DMF (20 mL) was stirred at 90 °C for 16 h under an argon atmosphere. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (ethyl acetate/methanol, 10:1) to afford **3** (0.21 g, 37%). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 9.13 (s, 1 H), 8.45 (s, 1 H), 7.62 (d, *J* = 8.6 Hz, 2 H), 7.45–7.38 (m, 2 H), 6.91 (d, *J* = 7.4 Hz, 2 H), 4.57 (s, 2 H), 4.41–4.31 (m, 4 H), 4.00–3.92 (m, 4 H), 3.78–3.71 (m, 4 H), 3.63–3.59 (m, 4 H), 3.56–3.52 (m, 4 H), 3.47 (d, *J* = 19.7 Hz, 12 H) ppm. <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 154.2, 132.4, 126.1, 125.1, 123.2, 120.0, 115.0, 103.2, 72.3, 70.3, 69.9, 69.8, 69.7, 69.0, 67.8, 60.1 ppm. MS (ESI): *m/z* calcd. for C<sub>30</sub>H<sub>42</sub>O<sub>10</sub>Na [M + Na]<sup>+</sup> 585.27; found 585.51.

**Compound 4:** Obtained as described for **3**, yield 28%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.23 (s, 1 H), 8.29 (s, 1 H), 7.55 (d, *J* = 8.5 Hz, 2 H), 7.35 (t, *J* = 8.0 Hz, 2 H), 6.74 (d, *J* = 7.4 Hz, 2 H), 4.38 (t, *J* = 5.0 Hz, 4 H), 4.07 (t, *J* = 5.0 Hz, 4 H), 3.90–3.84 (m, 4 H), 3.74–3.70 (m, 4 H), 3.68 (dd, *J* = 9.3, 4.9 Hz, 8 H), 3.63–3.58 (m, 12 H), 3.56–3.52 (m, 4 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.9, 132.9, 125.6, 125.2, 124.4, 120.4, 115.9, 102.7, 77.4, 77.1, 76.8, 72.6, 71.1, 70.6, 70.2, 69.8, 67.9, 61.6 ppm. MS (ESI): *m/z* calcd. for C<sub>34</sub>H<sub>50</sub>O<sub>12</sub>Na [M + Na]<sup>+</sup> 673.32; found 673.51.

**Compound 5:** Obtained in as described for **3**, yield 35%. <sup>1</sup>H NMR (400 MHz,  $[D_7]DMF$ ):  $\delta = 9.32$  (s, 1 H), 8.51 (s, 1 H), 7.68 (d, J = 8.5 Hz, 2 H), 7.46 (t, J = 8.0 Hz, 2 H), 6.98 (d, J = 7.4 Hz, 2 H), 4.48–4.41 (m, 4 H), 4.12–4.06 (m, 4 H), 3.89–3.83 (m, 4 H), 3.73–3.70 (m, 4 H), 3.64–3.56 (m, 28 H), 3.51 (d, J = 5.2 Hz, 4 H) ppm. <sup>13</sup>C NMR (100 MHz,  $[D_7]DMF$ ):  $\delta = 155.1$ , 133.2, 126.3, 125.5, 124.5, 120.4, 115.7, 103.3, 73.0, 71.1, 70.6, 69.8, 68.5, 61.2 ppm. MS (ESI): m/z calcd. for  $C_{38}H_{58}O_{14}Na$  [M + Na]<sup>+</sup> 761.37; found 761.66.

Compound 6: To a solution of 3 (0.2 g, 0.36 mmol) in THF (15 mL) was added sodium hydroxide (2 M, 1 mL). After being stirred at r.t. for 10 min, tosyl chloride (0.15 g, 0.8 mmol) in THF (5 mL) was added dropwise. The reaction mixture was then stirred for 3 h. Dilute HCl was added to adjust the pH to 7. THF was then evaporated under reduced pressure and the residue was extracted with ethyl acetate and dried with anhydrous sodium sulfate. After the solvent was removed in vacuo, the crude product was purified by column chromatography over silica gel (ethyl acetate/petroleum ether, 2:1) to afford 6 (0.26 g, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.23 (s, 1 H), 8.28 (s, 1 H), 7.73 (d, J = 8.3 Hz, 4 H), 7.54 (d, J = 8.5 Hz, 2 H), 7.37–7.31 (m, 2 H), 7.26 (d, J = 8.1 Hz, 4 H), 6.72 (d, J = 7.4 Hz, 2 H), 4.36 (t, J = 5.0 Hz, 4 H), 4.09–4.02 (m, 8 H), 3.83 (dd, J = 5.6, 3.8 Hz, 4 H), 3.69–3.64 (m, 4 H), 3.59 (dd, J = 9.5, 5.0 Hz, 8 H), 3.54–3.48 (m, 4 H), 2.36 (s, 6 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.9, 144.8, 132.9, 129.8, 127.9, 125.6, 125.1, 124.4, 120.4, 115.9, 102.7, 71.0, 70.7, 70.6, 70.5, 69.7, 69.2, 68.6, 67.9, 21.5 ppm. MS (ESI): *m*/*z* calcd. for  $C_{44}H_{54}O_{14}S_2Na [M + Na]^+ 893.29$ ; found 893.51.

**Compound 7:** Obtained as described for **6**, yield 76%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.23 (s, 1 H), 8.30 (s, 1 H), 7.77 (d, *J* = 8.1 Hz, 4 H), 7.56 (d, *J* = 8.5 Hz, 2 H), 7.35 (t, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 4 H), 6.74 (d, *J* = 7.4 Hz, 2 H), 4.38 (t, *J* = 5.0 Hz, 4 H), 4.12–4.09 (m, 4 H), 4.07 (t, *J* = 5.0 Hz, 4 H), 3.88–3.84 (m, 4 H), 3.73–3.69 (m, 4 H), 3.65–3.57 (m, 12 H), 3.51 (m, 8 H), 2.41 (s, 6 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.9, 144.9, 132.9, 129.8, 127.9, 125.6, 125.2, 124.4, 120.4, 115.9, 102.6, 71.1, 70.7, 70.6, 70.5, 70.4, 69.7, 69.2, 68.6, 67.8, 21.6 ppm. MS (ESI): *m/z* calcd. for C<sub>48</sub>H<sub>62</sub>O<sub>16</sub>S<sub>2</sub>Na [M + Na]<sup>+</sup> 981.34; found 981.61.

**Compound 8:** Obtained as described for **6**, yield 78%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.23 (s, 1 H), 8.28 (s, 1 H), 7.76 (d, *J* = 6.5 Hz, 4 H), 7.54 (d, *J* = 7.6 Hz, 2 H), 7.33 (s, 2 H), 7.29 (s, 4 H), 6.72 (d, *J* = 5.8 Hz, 2 H), 4.36 (s, 4 H), 4.11 (s, 4 H), 4.06 (s, 4 H), 3.85 (s, 4 H), 3.71 (s, 5 H), 3.65 (s, 5 H), 3.61 (s, 8 H), 3.55 (d, *J* = 7.6 Hz, 8 H), 3.50 (s, 8 H), 2.38 (s, 6 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.9, 144.8, 132.9, 129.9, 127.9, 125.7, 125.2, 124.4, 120.4, 115.9, 102.7, 77.7, 77.6, 77.1, 70.9, 70.5, 69.8, 69.3, 68.6, 67.9, 21.6 ppm. MS (ESI): *m*/*z* calcd. for C<sub>52</sub>H<sub>70</sub>O<sub>18</sub>S<sub>2</sub>Na [M + Na]<sup>+</sup> 1069.39; found 1069.67.

**Compound 9:** A mixture of **2** (52 mg, 0.24 mmol), **6** (0.22 g, 0.24 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (0.4 g, 0.72 mmol) in anhydrous DMF (20 mL) was stirred at 90 °C for 16 h under an argon atmosphere. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (ethyl acetate/petroleum ether, 1:1) to afford **9** (43 mg, 25%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.26 (s, 1 H), 8.28 (s, 1 H), 7.54 (d, *J* = 8.6 Hz, 2 H), 7.35–7.28 (m, 2 H), 6.64 (d, *J* = 7.4 Hz, 2 H), 4.34–4.29 (m, 4 H), 4.10–4.06 (m, 4 H), 3.94–3.89 (m, 4 H), 3.82–3.76 (m, 4 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 155.0, 132.9, 125.6, 125.1, 124.4, 123.8, 116.0, 102.5, 71.2, 70.8, 69.9, 68.2 ppm. MS (ESI): *m/z* calcd. for C<sub>44</sub>H<sub>48</sub>O<sub>10</sub>Na [M + Na]<sup>+</sup> 759.31; found 759.65.

**Compound 10:** Obtained as described for **9**, yield 23%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.24$  (s, 1 H), 8.28 (s, 1 H), 7.55 (d, J = 8.5 Hz, 2 H), 7.33 (t, J = 8.0 Hz, 2 H), 6.68 (d, J = 7.4 Hz, 2 H), 4.34 (t, J = 4.8 Hz, 4 H), 4.06 (t, J = 4.8 Hz, 4 H), 3.93–3.84 (m, 4 H), 3.77–3.66 (m, 8 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 154.9$ , 132.9, 125.6, 125.1, 124.4, 120.4, 115.9, 102.5, 71.5, 70.7, 69.8, 68.1 ppm. MS (ESI): m/z calcd. for C<sub>48</sub>H<sub>56</sub>O<sub>12</sub>Na [M + Na]<sup>+</sup> 847.37; found 847.52.

**Compound 11:** Obtained as described for **9**, yield 18%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.23$  (s, 1 H), 8.27 (s, 1 H), 7.53 (d, J = 8.5 Hz, 2 H), 7.32 (t, J = 7.9 Hz, 2 H), 6.68 (d, J = 7.3 Hz, 2 H), 4.33 (t, J = 4.2 Hz, 4 H), 4.04 (t, J = 4.2 Hz, 4 H), 3.89–3.83 (m, 4 H), 3.73–3.68 (m, 4 H), 3.63 (d, J = 6.2 Hz, 8 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 155.0$ , 132.9, 125.6, 125.2, 124.4, 120.4, 116.0, 102.6, 70.8, 70.7, 70.6, 68.8, 68.0 ppm. MS (ESI): m/z calcd. for C<sub>52</sub>H<sub>64</sub>O<sub>14</sub>Na [M + Na]<sup>+</sup> 935.42; found 935.77.

**Compound 12:** A mixture of catechol (28 mg, 0.25 mmol), **6** (0.22 g, 0.25 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (0.25 g, 0.75 mmol) in anhydrous DMF (20 mL) was stirred at 90 °C for 16 h under an argon atmosphere. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (ethyl acetate/methanol, 50:1) to afford **12** (40 mg, 25%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.26 (s, 1 H), 8.29 (s, 1 H), 7.55 (d, *J* = 8.5 Hz, 2 H), 7.33 (t, *J* = 7.9 Hz, 2 H), 6.92–6.81 (m, 4 H), 6.68 (d, *J* = 7.4 Hz, 2 H), 4.38–4.31 (m, 4 H), 4.14–4.10 (m, 4 H), 4.10–4.05 (m, 4 H), 3.94–3.89 (m, 4 H), 3.89–3.84 (m, 4 H), 3.80–3.74 (m, 8 H), 3.72 (d, *J* = 5.2 Hz, 4 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 155.0, 148.9, 132.9, 125.6, 125.1, 124.4, 121.5, 120.4, 116.0, 114.3, 102.4, 71.1, 70.8, 69.8, 69.0, 68.1 ppm. MS (ESI): *m/z* calcd. for C<sub>36</sub>H<sub>44</sub>O<sub>10</sub>Na [M + Na]<sup>+</sup> 659.28; found 659.57.

**Compound 13:** A mixture of 1,5-dihydroxynaphthalene (64 mg, 0.4 mmol), **6** (0.23 g, 0.4 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (0.39 g, 1.2 mmol) in anhydrous DMF (20 mL) was stirred at 90 °C for 16 h under an argon atmosphere. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (ethyl acetate/petroleum ether, 1:1) to afford **13** (52 mg, 19%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.18$  (s, 1 H), 8.29 (s, 1 H), 7.89 (d, J = 8.4 Hz, 2 H), 7.55 (d,

 $J = 8.5 \text{ Hz}, 2 \text{ H}), 7.37-7.29 \text{ (m, 4 H)}, 6.83 \text{ (d, } J = 7.6 \text{ Hz}, 2 \text{ H}), 6.70 \text{ (d, } J = 7.4 \text{ Hz}, 2 \text{ H}), 4.29 \text{ (t, } J = 4.6 \text{ Hz}, 8 \text{ H}), 3.90 \text{ (dd, } J = 10.9, 5.5 \text{ Hz}, 8 \text{ H}), 3.75-3.70 \text{ (m, 4 H)}, 3.64-3.60 \text{ (m, 4 H)}, 3.56 \text{ (m, 8 H) ppm.}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{CDCl}_3): \delta = 155.0, 154.4, 132.9, 127.0, 125.6, 125.0, 124.5, 120.4, 116.0, 114.7, 106.7, 102.8, 71.2, 71.0, 70.7, 70.6, 69.9, 69.5, 69.3, 67.6 \text{ ppm. MS} (\text{ESI}): m/z \text{ calcd. for } C_{40}H_{46}O_{10}\text{Na} [\text{M} + \text{Na}]^+ 709.30; \text{ found } 709.61.$ 

Aromatic Diparaquat 14: A solution of 4,4'-bipyridine (0.31 g, 2 mmol), *p*-xylylene dibromide (0.26 g, 1 mmol) in anhydrous MeCN (10 mL) was stirred in a sealed tube at 60 °C for 8 h. After the solvent was removed in vacuo, the crude product was purified by column chromatography over silica gel (methanol/2 M NH<sub>4</sub>Cl/MeNO<sub>2</sub>, 10:7:1) to obtain a yellow solid. Then the solid was dissolved in hot water, and a saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added until no further precipitation was observed. The precipitate was filtered and dried to afford 14 (0.33 g, 45%). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 9.34 (d, *J* = 6.9 Hz, 4 H), 8.87 (d, *J* = 6.1 Hz, 4 H), 8.64 (d, *J* = 6.8 Hz, 4 H), 8.01 (d, *J* = 6.2 Hz, 4 H), 7.66 (s, 4 H), 5.88 (s, 4 H) ppm.

[2]Catenane 15: A mixture of 13 (68 mg, 0.1 mmol), 14 (36 mg, 0.05 mmol), and p-xylylene dibromide (13 mg, 0.05 mmol) in anhydrous DMF (5 mL) was stirred under 15 kbar of nitrogen for 8 d, the color of the solution gradually became purple. After the solvent was removed in vacuo, the crude product was purified by column chromatography over silica gel (methanol/2 M NH<sub>4</sub>Cl/MeNO<sub>2</sub>, 4:4:2) to obtain a purple solid. The solid was dissolved in hot water, and a saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added until no further precipitation was observed. The precipitate was filtered and dried to afford 15 (17 mg, 19%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$ = 8.78 (d, J = 6.5 Hz, 4 H), 8.45 (d, J = 6.0 Hz, 4 H), 8.30 (s, 1 H), 8.23 (s, 1 H), 7.98 (d, J = 0.5 Hz, 4 H), 7.85 (d, J = 0.9 Hz, 4 H), 7.52 (d, J = 8.7 Hz, 2 H), 7.39 (t, J = 7.9 Hz, 2 H), 7.10 (d, J = 6.0 Hz, 4 H), 6.97 (d, J = 5.4 Hz, 4 H), 6.84 (d, J = 7.4 Hz, 2 H), 4.22 (d, J = 3.1 Hz, 4 H), 4.19–4.15 (m, 4 H), 4.15–4.11 (m, 4 H), 3.97–3.91 (m, 4 H), 3.85–3.80 (m, 4 H), 3.79–3.74 (m, 4 H), 3.71-3.66 (m, 4 H), 3.66-3.58 (m, 4 H), 2.25 (d, J = 8.2 Hz, 2 H) ppm. <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN):  $\delta$  = 155.1, 151.8, 145.4, 144.9, 144.5, 137.1, 133.1, 131.9, 131.74, 128.37, 126.86, 126.19, 126.11, 124.85, 124.79, 124.42, 121.0, 115.5, 108.8, 105.6, 104.8, 71.4, 70.7, 70.5, 70.2, 69.5, 69.3, 68.6, 68.3, 65.5 ppm. MS (ESI): m/z calcd. for  $C_{76}H_{78}F_{12}N_4O_{10}P_2$  [M + 2PF<sub>6</sub>]<sup>2+</sup> 748.25; found 748.72; m/z calcd. for  $C_{76}H_{78}F_6N_4O_{10}P [M + 3PF_6]^{3+}$  450.51; found 450.82.

*N*,*N*'-Dimethyl-4,4'-bipyridinium Dications (MV<sup>2+</sup>·2PF<sub>6</sub>): A solution of 4,4'-bipyridine (0.16 g, 1 mmol) and iodomethane (155 µL, 2.5 mmol) in anhydrous MeCN (10 mL) was stirred in a sealed tube at 60 °C for 8 h. After the solution was cooled to room temperature, the yellow precipitate was filtered and washed with MeCN. The solid was then dissolved in hot water and a saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added until no further precipitation was observed. The precipitate was filtered and dried to afford MV<sup>2+</sup>·2PF<sub>6</sub> (0.26 g, 53%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN/CDCl<sub>3</sub>, 1:1):  $\delta$  = 8.87 (d, *J* = 6.2 Hz, 4 H), 8.40 (d, *J* = 5.7 Hz, 4 H), 4.43 (s, 6 H) ppm.

**Crystal Structure Data Collection and Refinement:** Intensity data were collected at 173(2) K with a Bruker SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ( $\lambda = 0.71073$  Å). Data reduction included absorption corrections by the multiscan method. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at their geometrically ideal positions and re-



fined isotropically. Experimental data for 9,  $9 \supset MV^{2+}$ ,  $10 \supset MV^{2+}$  and [CBPQT<sup>4+</sup>]-13 are shown below.

Single-Crystal Structure of 9:  $C_{48}H_{56}Cl_3O_{10}$ ;  $M_r = 899.27$ ; T = 173(2) K; triclinic; space group  $P\bar{1}$ ; a = 11.761(2), b = 13.549(3), c = 15.333(3) Å,  $a = 68.817(3)^\circ$ ,  $\beta = 82.684(3)^\circ$ ,  $\gamma = 81.438(3)^\circ$ ; V = 2245.7(7) Å<sup>3</sup>; Z = 2;  $\rho_{calcd.} = 1.330$  g/cm<sup>3</sup>; crystal size  $= 0.090 \times 0.060 \times 0.040$  mm;  $\mu = 0.262$  mm<sup>-1</sup>; reflections collected 13667; unique reflections 7810; data/restraints/parameters 7810/18/555; *GOF* on  $F^2$  1.016;  $R_{int}$  for independent data 0.0400; final  $R_1 = 0.0759$ ,  $wR_2 = 0.2168$ ; R indices (all data)  $R_1 = 0.11498$ ,  $wR_2 = 0.3001$ ; largest diff. peak and hole: 0.816 and -0.776 eÅ<sup>-3</sup>.

Single-Crystal Structure of 9⊃MV<sup>2+</sup>: C<sub>76</sub>H<sub>88</sub>F<sub>24</sub>N<sub>8</sub>O<sub>10</sub>P<sub>4</sub>; *M<sub>r</sub>* = 1853.42; *T* = 173(2) K; orthorhombic; space group *pbam*; *a* = 20.5094(5), *b* = 31.6190(8), *c* = 13.5291(4) Å, *a* = β = γ = 90°; *V* = 8773.4(4) Å<sup>3</sup>; *Z* = 4; ρ<sub>calcd.</sub> = 1.403 g/cm<sup>3</sup>; crystal size = 0.600 × 0.070 × 0.060 mm; μ = 1.768 mm<sup>-1</sup>; reflections collected 43207; unique reflections 7991; data/restraints/parameters 7991/88/ 690; *GOF* on *F*<sup>2</sup> 1.386; *R<sub>int</sub>* for independent data 0.0799; final *R*<sub>1</sub> = 0.1033, *wR*<sub>2</sub> = 0.3102; *R* indices (all data) *R*<sub>1</sub> = 0.1129, *wR*<sub>2</sub> = 0.3263; largest diff. peak and hole: 0.899 and -0.714 eÅ<sup>-3</sup>.

Single-Crystal Structure of 10⊃MV<sup>2+</sup>: C<sub>60</sub>H<sub>70</sub>F<sub>12</sub>N<sub>2</sub>O<sub>12</sub>P<sub>2</sub>;  $M_r$  = 1301.12; *T* = 173(2) K; trigonal; space group *R3.h*; *a* = *b* = 23.096(4), *c* = 59.589(9) Å, *a* = *β* = 90°, *γ* = 120°; *V* = 27527(9) Å<sup>3</sup>; *Z* = 18; *ρ*<sub>calcd</sub> = 1.413 g/cm<sup>3</sup>; crystal size = 0.490 × 0.400 × 0.360 mm; *μ* = 0.170 mm<sup>-1</sup>; reflections collected 33242; unique reflections 13849; data/restraints/parameters 13849/27/820; *GOF* on *F*<sup>2</sup> 1.226; *R*<sub>int</sub> for independent data 0.0389; final *R*<sub>1</sub> = 0.1089, *wR*<sub>2</sub> = 0.3105; *R* indices (all data) *R*<sub>1</sub> = 0.1573, *wR*<sub>2</sub> = 0.3535; largest diff. peak and hole: 2.465 and −1.189 e Å<sup>-3</sup>.

**Single-Crystal Structure of [2]Catenane 15:**  $C_{86}H_{93}F_{24}N_9O_{10}P_4$ ;  $M_r = 1992.57$ ; T = 173(2) K; monoclinic; space group Cc; a = 24.512(3); b = 14.1398(15); c = 27.513(3) Å,  $a = \gamma = 90^\circ$ ,  $\beta = 107.249(3)^\circ$ ; V = 9107.0(18) Å<sup>3</sup>; Z = 4;  $\rho_{calcd.} = 1.453$  g/cm<sup>3</sup>; crystal size =  $0.540 \times 0.380 \times 0.350$  mm;  $\mu = 0.194$  mm<sup>-1</sup>; reflections collected 31370; unique reflections 16643; data/restraints/parameters 16643/16/1202; *GOF* on  $F^2$  1.071;  $R_{int}$  for independent data 0.0353; final  $R_1 = 0.0594$ ,  $wR_2 = 0.1653$ ; R indices (all data)  $R_1 = 0.0737$ ,  $wR_2 = 0.1954$ ; largest diff. peak and hole: 1.013 and -0.420 eÅ<sup>-3</sup>.

**Supporting Information** (see footnote on the first page of this article): Synthesis and NMR spectra of 2–15 and complexes, details of association constant determination, Job plots and MS spectra. Solid-state packing of complex  $9 \supset MV^{2+}$ .

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