DOI: 10.1002/ejoc.201000910

Improved Pseudorotaxane and Catenane Formation from a Derivative of Bis(*m*-phenylene)-32-crown-10

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Keywords: Catenanes / Host-guest systems / Crown compounds / Pseudorotaxanes / Complexation geometry

2,2′-Dihydroxy-bis(*m*-phenylene)-32-crown-10 (2,2′-dihydroxy-BMP32C10, **1a**) was synthesized and used to prepare the [2]catenane **4** in an unexpected yield of 68 %, three times the corresponding value for the case in which BMP32C10 (**1b**) was used and close to the corresponding value for the case in which bis(*p*-phenylene)-34-crown-10 was used. This indicated that **1a** and paraquat derivatives formed pseudorotaxanes rather than the previously reported "taco complexes" between BMP32C10 and paraquat derivatives. Another unique feature of **1a** in relation to other previously reported BMP32C10 derivatives was that its binding to paraquat derivatives in solution could be switched off and back on by addition of K^+ and then dibenzo-18-crown-6. In the solid state, a 2:1 [3]pseudorotaxane of **1a** with a paraquat derivative was formed.

Introduction

Mechanically interlocked molecules (MIMs) have been widely applied in the preparation of molecular machines[1] and mechanically bonded macromolecules or polymers.[2] For the efficient construction of MIMs, control of the complexation geometry is very important because the syntheses of MIMs are based on the preorganization of the different components to form threaded structures in solution. Leigh et al.[3] developed active metal template synthesis in order to construct interlocked structures such as rotaxanes and catenanes, efficiently based on the formation of a pseudorotaxane geometry when a metal ion was incorporated into precisely designed molecule systems, acting as both a template and as a catalyst. Fujita et al.[4] observed that the distortion of a cyclodextrin cavity could significantly restrict the guest rotation. Schalley et al.[5] found that small structural changes such as the simple exchange of a CH group for an isoelectronic N atom could have unexpectedly large effects on the deslipping reactions of rotaxanes. We have previously reported a paraquat (*N*,*N*′-dimethyl-4,4′-bipyridium) substituent effect on complexation with a dibenzo-24-crown-8-based cryptand[6] and control of the complexation geometry of a bis(*m*-phenylene)-32-crown-10 (BMP32C10) heteroditopic host and paraquat through the use of different anions.[7]

The recognition motifs of bis(*p*-phenylene)/bis(*o*-phenylene) crown ethers, such as bis(*p*-phenylene)-34-crown-10 (BPP34C10), with respect to paraquat derivatives make them good candidates for the construction of MIMs,[8] not only because of the excellent oxidation/reduction properties of paraquat derivatives, but also because of the effective formation of pseudorotaxane-type complexes between them in solution.

However, if two or more functionalized bis(*p*-phenylene) or bis(*o*-phenylene) crown ether hosts are used in the fabrication of MIMs, a stereoisomeric problem emerges, limiting the further applications of these recognition motifs.[9] One strategy for solving this symmetry-based problem is the introduction of bis(*m*-phenylene) crown ethers, such as BMP32C10.[9a,b,10] However, BMP32C10 and paraquat derivatives mainly form "taco complexes", in which the guest molecules are surrounded by the folded hosts to form sandwich structures, rather than threading into the cavities of the hosts to form pseudorotaxanes in solution.[11] This makes it hard to construct MIMs efficiently from them,[12] and so the use of BMP32C10 derivatives in the construction of MIMs is greatly limited.

Here we report the synthesis of 2,2′-dihydroxy-BMP32C10 (**1a**, Scheme 1), its unexpected pseudorotaxane formation with paraquat derivatives not only in solution but also in the solid state, and its application in the efficient preparation of a [2]catenane.

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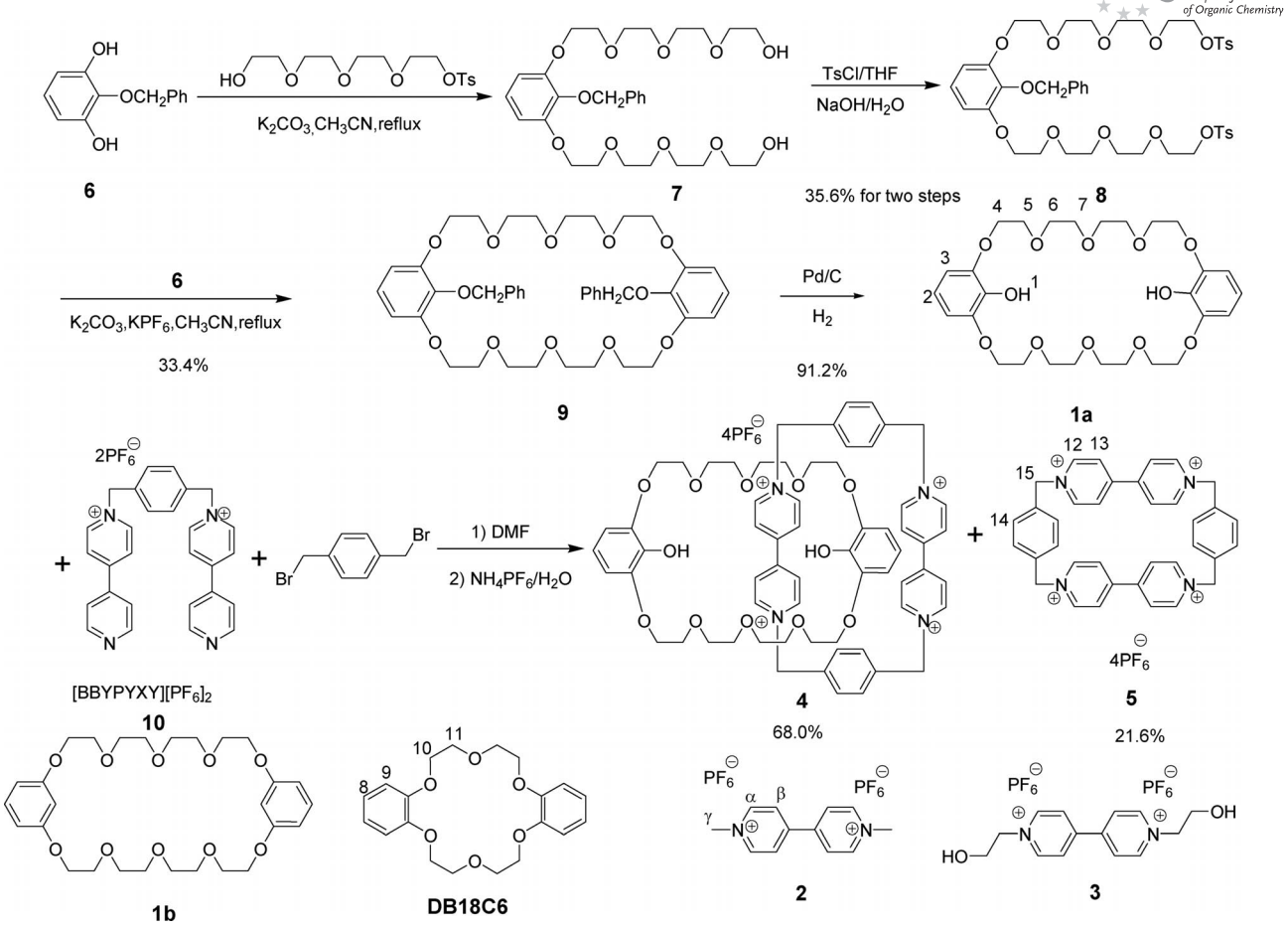
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900xxx.



Scheme 1. Syntheses of 2,2′-dihydroxy-BMP32C10 (**1a**) and the [2]catenane **4**, together with the chemical structures of BMP32C10 (**1b**), DB18C6, and the paraquat derivatives **2** and **3**.

Results and Discussion

Although **1a** had been synthesized by Bartsch and coworkers in 1989,[13] we synthesized it in a more efficient way from pyrogallol in five steps. Complexation between it and the paraquat derivatives **2** and **3**[14] (Scheme 1) was then studied.

When equimolar (2.00 mM) acetone solutions of **1a** and either **2** or **3** were prepared, a bright yellow color appeared, as a result of charge-transfer interactions between the electron-rich aromatic rings of the crown ether host and the electron-poor pyridinium rings of the paraquat derivative guest. Job plots[15] based on UV/Vis absorbance data for the charge-transfer band (λ = 403 nm) demonstrated that the complexes of **1a** with **2** and **3** were both of 1:1 stoichiometry in solution. The association constants (K_a) of the complexes **1a**⊃**2** and **1a**⊃**3** in acetone were determined by probing the charge-transfer band of the complexes by a UV/Vis titration method to be 980 ± 28 M^{-1} and 926 ± 50 M^{-1}, respectively, higher than the corresponding values for BMP32C10⊃**2**[16] and BMP32C10⊃**3** (487 M^{-1} and 223 M^{-1}, respectively).

The 1:1 stoichiometries of both **1a**⊃**2** and **1a**⊃**3** were confirmed by electrospray ionization mass spectrometry (ESI MS). Peaks were found at *m*/*z* 899.7 (45.8%) and 959.2 (66.4%) for the complexes **1a**⊃**2** and **1a**⊃**3**, respectively, corresponding to $[\mathbf{1a}\supset\mathbf{2} - PF_6]^+$ and $[\mathbf{1a}\supset\mathbf{3} - PF_6]^+$.

To investigate the complexation between **1** and either **2** or **3** further, proton NMR spectra of separate equimolar (8.00 mM) CD_3COCD_3 solutions of **1a** with **2** and **3** were examined (Figure 1 and Figure S16 in the Supporting Information). Both complexation systems **1a**⊃**2** and **1a**⊃**3** exist in fast exchange on the proton NMR timescale. The chemical shift changes of protons on the host **1a** and on the guests **2** or **3** after complexation are similar, so only the complexation between **1a** and **2** is discussed here. Upfield shifts were observed for the H^α and H^β pyridinium protons in the paraquat **2** after complexation (spectra a and b in Figure 1). The H^2 and H^3 aromatic protons and the H^4 and H^5 ethylenoxy protons in the host **1a** shifted upfield after complexation whereas the H^6 and H^7 ethylenoxy protons in **1a** moved downfield (spectra b and e in Figure 1).

Unlike BMP32C10, **1a** can bind K^+.[17] We then checked whether the complexation of **1a** with either **2** or **3** could be controlled by addition or removal of K^+ in solution. When 2 molar equiv. of KPF_6 were added to an equimolar solution of **1a** and **2** (8.00 mM) in CD_3COCD_3, the chemical shifts of the protons on **2** returned to their uncomplexed values (spectra a and c in Figure 1) and correspondingly the yellow color of the solution totally disappeared, indicating

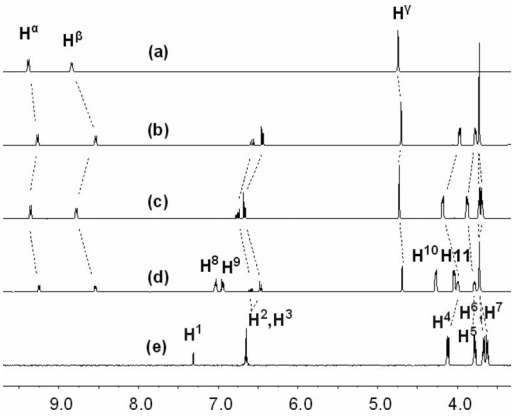


Figure 1. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 295 K) of: a) **2**, b) **1a** and **2** (8.00 mM), c) **1a** and **2** (8.00 mM) and KPF_6 (16.0 mM), d) **1a** and **2** (8.00 mM), KPF_6 (16.0 mM), and DB18C6 (16.0 mM), and e) **1a**.

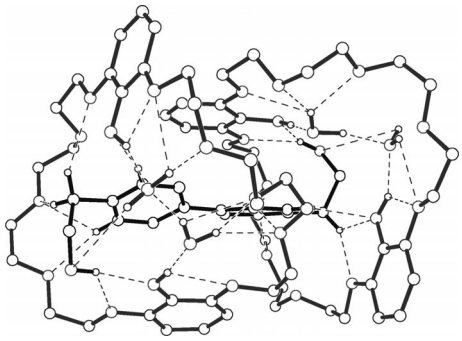


Figure 2. A ball-and-stick view of the X-ray crystal structure of $\mathbf{1a}_2\supset\mathbf{3}$. PF_6^- counterions, other solvent molecules, and hydrogens other than those involved in hydrogen bonding between **1** and **3** are omitted for clarity. Hydrogen bond parameters are provided in the Supporting Information.

the total dissociation of the complex $\mathbf{1a}\supset\mathbf{2}$. However, when 2 molar equiv. of dibenzo-18-crown-6 (DB18C6) were subsequently added, chemical shift changes of the protons on **2** were again observed (spectra b and d in Figure 1) and the yellow color of the solution correspondingly recovered, indicating the reformation of the complex $\mathbf{1a}\supset\mathbf{2}$.

The complexation between **1a** and **3** has 1:1 stoichiometry not only in solution but also in the gas phase, as shown above. A yellow single crystal of $\mathbf{1a}_2\supset\mathbf{3}$ suitable for X-ray diffraction analysis was obtained by vapor diffusion of pentane into an acetone solution of **1a** and **3**. The $\mathbf{1a}_2\supset\mathbf{3}$ complex is a [3]pseudorotaxane in the solid state (Figure 2). This is noteworthy because all previously reported complexes based on BMP32C10 and paraquat derivatives are taco [2]complexes.[10b,c,11] The [3]pseudorotaxane $\mathbf{1a}_2\supset\mathbf{3}$ is mainly stabilized by hydrogen bonding (Figure 2). The solid-state structure of $\mathbf{1a}_2\supset\mathbf{3}$ is not symmetric: the hydrogen bonding parameters for corresponding hydrogen atoms on the two pyridinium rings are not equal. There are four water bridges in the $\mathbf{1a}_2\supset\mathbf{3}$ complex, and these are involved in 17 hydrogen bonds, which further stabilize the structure. At each end of the paraquat guest **3**, two water molecules link the two phenol groups of a **1a** molecule, forming a supramolecular cryptand,[10b,18] increasing the interactions between host **1a** and guest **3**. The [3]pseudorotaxane formation between **1a** and **3** in the solid state indicates that the host **1a** and paraquat derivatives might also form pseudorotaxanes in solution.

To investigate further whether **1a** and paraquat derivatives can form pseudorotaxanes in solution, we used the recognition of paraquat derivatives by **1a** to synthesize the [2]catenane **4** (Scheme 1). The yield of the [2]catenane **4** was 68%, three times the corresponding value (17%) for the case in which BMP32C10 was used.[12a] This indicated that **1a** and paraquat derivatives formed pseudorotaxanes rather than the previously reported "taco complexes" between **1b** and paraquat derivatives.[11] The yield of the [2]catenane **4** was close to the corresponding value (70%) for the case in which BPP34C10 was used.[12a] This further demonstrated that **1a**, like BPP34C10, formed pseudorotaxanes with paraquat derivatives.[19]

Partial proton NMR spectra of **1a**, **4**, and **5** in CD_3SOCD_3 are shown in Figure 3. After the formation of the [2]catenane **4**, the signals of the H^2 and H^3 aromatic protons and the H^4 ethylenoxy protons of **1a** were dramatically shifted upfield. Significant upfield shifts were also observed for the signals of the H^{12} and H^{13} pyridinium protons on the cyclophane **5**, whereas the H^{14} aromatic H signals were shifted downfield.

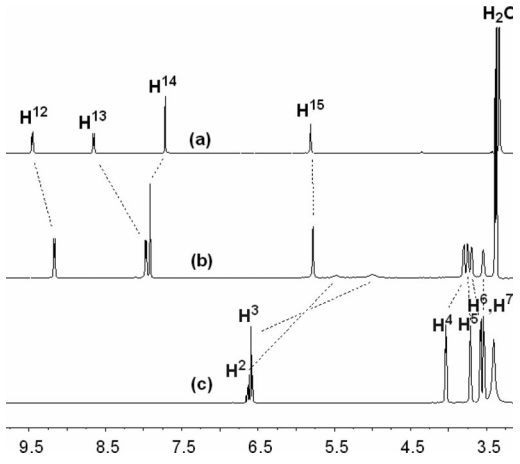


Figure 3. ^{1}H NMR spectra (400 MHz, $[D_6]$DMSO, 295 K) of: a) the cyclophane **5**, b) the [2]catenane **4**, and c) **1a**.

The formation of the [2]catenane **4** was further confirmed by ESIMS. Peaks were found at *m*/*z* 689.1 (100%), 411.1 (40%), and 272.1 (96%) for the [2]catenane **4**, corresponding to $[\mathbf{4} - 2PF_6]^{2+}$, $[\mathbf{4} - 3PF_6]^{3+}$ and $[\mathbf{4} - 4PF_6]^{4+}$, respectively.

The generation of the [2]catenane **4** was further confirmed by X-ray diffraction analysis (Figure 4) of a red single crystal grown by vapor diffusion of diisopropyl ether into an acetonitrile solution of **4**. The solid-state structure

of **4** is stabilized by hydrogen bonding, face-to-face π-stacking interactions, and aromatic edge-to-face π-stacking interactions. It seems that face-to-face π-stacking interactions are important in this structure because there are only one hydrogen bond and two C(O)–H···π bonds between **1a** and **5** here.

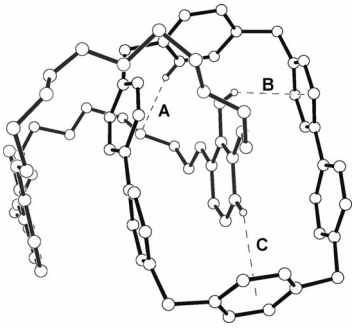


Figure 4. A ball-and-stick view of the X-ray crystal structure of the [2]catenane **4**. PF_6^- counterions, solvent molecules, and hydrogens other than those involved in hydrogen bonding and O(C)–H···π edge-to-face interactions between **1a** and **5** are omitted for clarity. Hydrogen bond parameters: H···O distance [Å], C–H···O angle [°], C···O distance [Å] **A**, 2.48, 160, 3.37. Face-to-face π-stacking parameters: centroid-centroid distances [Å] 3.55, 3.97, 3.73; ring plane/ring plane inclinations [°]: 2.3, 11.4, 4.8. The O(C)–H···π edge-to-face interactions **B** and **C** are defined by H···pyridine (benzene) centroid distances [Å] of 3.00 and 2.82 and O(C)–H···centroid angles [°] of 98 and 135, respectively.

Conclusions

In summary, we found that although **1a** shows only subtle structure changes in relation to **1b**, their binding properties to paraquat derivatives are very different. Firstly, **1a** shows better affinity than **1b** towards paraquat derivatives because the two additional electron-donating phenol groups increase the face-to-face π-stacking and charge-transfer interactions between the host and guest. Secondly, in solution **1a** forms pseudorotaxanes rather than "taco complexes" with paraquat derivatives, so it is possible to use **1a** in the efficient construction of MIMs with paraquat derivatives. Because of their symmetrical natures, (2,2′-)-difunctional derivatives of BMP32C10 can easily be prepared as pure compounds without tedious isomer separation and have simpler NMR spectra than their substituted bis(*p*-phenylene)/bis(*o*-phenylene) analogues.[9a–c,10a,12b] The symmetry-based problem discussed above can therefore be solved if we use (2,2′-)-difunctional BMP32C10 derivatives instead of functionalized bis(*p*-phenylene)/bis(*o*-phenylene) crown ethers to prepare MIMs with paraquat derivatives. Thirdly, because of the introduction of the two *endo*-phenol groups, complexation between **1a** and paraquat derivatives can be easily controlled by addition or removal of K^+. Further work will be directed towards application of the recognition of paraquat derivatives by **1a** for the efficient fabrication of more complicated MIMs, including molecular machines.

Experimental Section

General: All reagents were purchased from commercial suppliers and used as received. BMP32C10 (**1b**),[20] 1,1′-[1,4-phenylenebis(methylene)]bis-4,4′-bipyridinium bis(hexafluorophosphate) ([BBIPYXY][PF_6]$_2$, **10**),[21] 2-(benzyloxy)benzene-1,3-diol (**6**),[22] tetraethylene glycol monotosylate,[23] and the paraquat derivatives **2** and **3**[14] were prepared by literature procedures. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. CCDC-781942 (**1a**$_2$⊃**3**) and -781943 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses of 7 and 8: K_2CO_3 (13.8 g, 100 mmol), 2-(benzyloxy)-benzene-1,3-diol (**6**, 4.32 g, 20.0 mmol), and tetraethylene glycol monotosylate (17.4 g, 50.0 mmol) were placed in a 500 mL round-bottomed flask. The flask was evacuated and nitrogen was introduced. After this process had been carried out for three times, CH_3CN (250 mL) was added. The solution was stirred at reflux for 24 h. The mixture was then filtered and the filtrate was concentrated to give **7**, which was used in the next step without further purification.

The unpurified **7** (18.1 g, 32.1 mmol) and sodium hydroxide solution (3.00 M, 100 mL) were placed in a 500 mL round-bottomed flask. A THF (100 mL) solution of *p*-toluenesulfonyl chloride (19.1 g, 100 mmol) was added dropwise to the mixture, which was stirred mechanically for about 3 h at 6 °C and then for 24 h at room temperature. When the reaction was complete, the water phase was extracted with ethyl acetate (3 × 100 mL). The organic phases was combined, dried with anhydrous Na_2SO_4, and then concentrated. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether 4:5) to give **8** (6.24 g, 35.6% for two steps) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 7.78 (d, J = 8.0 Hz, 4 H, Ar-H), 7.51 (d, J = 6.8 Hz, 2 H, Ar-H), 7.27–7.35 (m, 7 H, Ar-H), 6.94 (t, J = 8.4 Hz, 1 H, Ar-H), 6.60 (d, J = 8.4 Hz, 2 H, Ar-H), 5.02 (s, 2 H, benzyl-H), 4.13–4.16 (m, 8 H, α-OCH_2 and β-OCH_2), 3.84 (t, J = 5.0 Hz, 4 H, –CH_2OTs), 3.69 (t, J = 5.0 Hz, 4 H, –CH_2CH_2OTs), 3.66 (t, J = 4.8 Hz, 4 H, γ-OCH_2), 3.60 (t, J = 4.8 Hz, 4 H, δ-OCH_2), 3.53–3.57 (m, 8 H, ε-OCH_2 and ζ-OCH_2), 2.44 (s, 6 H, Ts-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ = 153.2, 145.0, 138.4, 133.1, 130.0, 128.5, 128.3, 128.1, 127.9, 123.9, 107.7, 75.0, 71.0, 70.8, 70.7, 69.9, 69.5, 69.4, 68.9, 68.8, and 21.8 ppm. LRESI-MS: m/z (%) = 894.3 (100) [**8** + NH_4]$^+$. HRESI-MS: calcd. for $C_{43}H_{56}NaO_{15}S_2$ [**8** + Na]$^+$: 899.2953; found 899.2985, error 3.6 ppm.

Synthesis of the Crown Ether 9: K_2CO_3 (9.66 g, 70.0 mmol) and CH_3CN (500 mL) were placed in a 1000 mL round-bottomed flask. The flask was evacuated and nitrogen was introduced. A CH_3CN (50.0 mL) solution of 2-(benzyloxy)benzene-1,3-diol (**6**, 1.64 g, 7.12 mmol) and **8** (6.24 g, 7.12 mmol) was added at the rate of 1.00 mL h^{-1} at reflux. After addition, the mixture was stirred at reflux for seven days, allowed to cool, and filtered. The filtrate was concentrated to give a pale yellow crude product, which was purified by flash column chromatography (ethyl acetate/petroleum 2:1) to give **9** (1.75 g, 33.4%) as a white solid; m.p. 88.8–88.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 7.42 (d, J = 7.4 Hz, 4 H, Ar-H), 7.20 (d, J = 7.4 Hz, 4 H, Ar-H), 7.12 (t, J = 7.4 Hz, 2 H, Ar-

H), 6.85 (t, J = 8.4 Hz, 2 H, Ar-H), 6.50 (d, J = 8.4 Hz, 4 H, Ar-H), 4.90 (s, 4 H, benzyl-H), 4.05 (t, J = 4.8 Hz, 8 H, α-OCH_2), 3.75 (t, J = 4.8 Hz, 8 H, β-OCH_2), 3.58–3.60 (m, 8 H, γ-OCH_2), 3.50–3.54 (m, 8 H, δ-OCH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ = 153.3, 138.5, 128.5, 128.2, 127.8, 123.7, 107.6, 74.9, 71.2, 70.9, 70.0, 69.1 ppm. LRESI-MS: m/z (%) = 766.8 (48.0) [**9** + NH_4]$^+$, 771.9 (100) [**9** + Na]$^+$, 787.8 (50.0) [**9** + K]$^+$. HRESI-MS: calcd. for $C_{42}H_{52}NaO_{12}$ [**9** + Na]$^+$: 771.3351; found 771.3376, error 3.2 ppm.

Synthesis of the Crown Ether 1a: Pd/C (100 mg) and **9** (1.00 g, 1.35 mmol) were placed in a 150 mL round-bottomed flask. The flask was evacuated and then hydrogen was introduced. After this process had been carried out three times, CH_3Cl/CH_3OH (1:1 v/v, 100 mL) was added. The reaction mixture was heated at 60 °C for 24 h, the solution was filtered, and the filtrate was concentrated to give a pale yellow crude product, which was purified by flash column chromatography (ethyl acetate/methanol 1:10) to give **1a** (700 mg, 91.2%) as a white solid; m.p. 92.3–94.8 °C. ^{1}H NMR (400 MHz, CD_3COCD_3, 295 K): δ = 7.32 (s, 2 H, –OH), 6.64–6.67 (m, 6 H, Ar-H), 4.13 (t, J = 4.8 Hz, 8 H, α-OCH_2), 3.80 (t, J = 4.8 Hz, 8 H, β-OCH_2), 3.62–3.70 (m, 16 H, γ-OCH_2 and δ-OCH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ = 147.4, 138.2, 118.5, 109.1, 70.9, 70.6, 69.8, 69.6 ppm. LRESI-MS: m/z (%) = 569.3 (82.0) [**1a** + H]$^+$, 591.6 (100) [**1a** + Na]$^+$. HRESI-MS: calcd. for $C_{28}H_{40}NaO_{12}$ [**1a** + Na]$^+$: 591.2412; found 591.2406, error –1.0 ppm.

Synthesis of the [2]Catenane 4: A solution of [BBIPYXY][PF_6]$_2$ (**10**, 70.6 mg, 0.100 mmol) in dry DMF (5 mL) was added under N_2 to a solution of **1a** (142 mg, 0.250 mmol) in dry DMF (5 mL). The color of the mixture quickly changed to faint yellow. 1,4-Bis(bromomethyl)benzene (26.4 mg, 0.100 mmol) in DMF (5 mL) was then added to the mixture at room temperature. A red deposit gradually appeared. The reaction mixture was then stirred at room temperature for 5 d. The solvent was removed in vacuo, and the resulting residue was dissolved in a mixture of MeOH/2 N $NH_4Cl/MeNO_2$ (7:2:1) and subjected to column chromatography (SiO_2, MeOH/2 N $NH_4Cl/MeNO_2$ 25:2:1). The fractions containing the product (TLC monitoring) were combined and concentrated under vacuum to give a residue, which was dissolved in H_2O. A red solid, the [2]-catenane **4** (113 mg, 68.0%), was precipitated from this solution by addition of a saturated aqueous NH_4PF_6 solution; m.p. >200 °C (dec.). ^{1}H NMR (500 MHz, CD_3SOCD_3, 295 K): δ = 9.17 (d, J = 6.8 Hz, 8 H, α-pyridinium-H), 7.97 (d, J = 6.8 Hz, 8 H, β-pyridinium-H), 7.91 (s, 8 H, Ar-H of cyclophane **5**), 5.77 (s, 8 H, benzyl-H of cyclophane **5**), 5.48 (br., 2 H, Ar-H of crown ether **1a**), 5.00 (br., 4 H, Ar-H of crown ether **1a**), 3.78–3.81 (m, 8 H, α-OCH_2), 3.72–3.76 (m, 8 H, β-OCH_2), 3.68–3.72 (m, 8 H, γ-OCH_2), 3.52–3.58 (m, 8 H, δ-OCH_2) ppm. ^{13}C NMR (125 MHz, CD_3CN, 295 K): δ = 147.0, 145.5, 137.3, 131.9, 126.6, 120.7, 71.1, 71.0, 70.2, 69.5, 65.9 ppm. LRESI-MS: m/z (%) = 689.1 (100) [**4** – 2PF_6]$^{2+}$, 411.1 (40) [**4** – 3PF_6]$^{3+}$, 272.1 (96) [**4** – 4PF_6]$^{4+}$. HRESI-MS: calcd. for $C_{64}H_{72}F_{12}N_4O_{12}P_2$ [**4** – 2PF_6]$^{2+}$: 689.2210; found 689.2262, error 7.6 ppm.

Supporting Information (see also the footnote on the first page of this article): Characterizations, Job plots, UV/Vis data, and crystal data for **1a**$_2$⊃**3** and **4**.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20774086, 20834004, and J0830413) and the Fundamental Research Funds for the Central Universities (China) (2010QNA3008).

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Received: June 24, 2010
Published Online: October 27, 2010

