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Synthesis of a Bis(1,2,3-phenylene) Cryptand and Its Dual-Response Binding to Paraquat and Diquat

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Keywords: Cryptands / Crown compounds / Host-guest systems / Taco complexes / Controllable assembly

A bis(1,2,3-phenylene) cryptand has been synthesized and used to prepare 1:1 complexes with paraquat and diquat, with association constants of 2.2×10^3 M^{-1} and 3.7×10^3 M^{-1}, respectively, in $CHCl_3/CH_3CN$ (1:1). In the solid state this cryptand forms a taco complex with paraquat, which has never been found before in cryptand/paraquat complexes. Furthermore, its binding to paraquat and diquat in solution can be switched off (and back on) by addition of acid or K^+ (and then base or 18-crown-6).

Introduction

The design and preparation of novel hosts featuring strong host–guest interactions and controllable binding properties is a hot topic in supramolecular chemistry, due to their applications in the fabrication of molecular switches,[1] molecular machines,[2] drug delivery materials,[3] supramolecular polymers,[4] and other interesting host–guest systems.[5] Paraquat (*N*,*N*′-dimethyl-4,4′-bipyridinium) and diquat (1,1′-ethylene-2,2′-bipyridinium) derivatives are commonly used guests in supramolecular chemistry.[2h,6,7] Gibson et al. designed and synthesized crown ether-based cryptand hosts for paraquat and diquat derivatives for the efficient preparation of mechanically interlocked structures and large supramolecular systems from small molecules with the aid of host–guest recognition motifs.[6a–6d,7] They showed that these cryptands can complex paraquat and diquat derivatives much more strongly than the corresponding simple crown ethers. Later, we demonstrated that mechanically interlocked structures such as rotaxanes[8] and catenanes[8c,9] could be constructed in high yields with the aid of such cryptand/paraquat recognition motifs and that supramolecular polymers[4d] could be fabricated efficiently. Liu et al. developed an excellent one-pot [2+3] clipping method to obtain a cryptand and a related [2]rotaxane through sixfold imine bond formation.[10] Recently, Jiang et al. demonstrated that diacetylene-containing cryptands could be made with high yields through copper(II)-mediated Eglinton coupling.[11] However, all of the previously reported cryptands are bis(1,3,5-phenylene) or bis(1,2,4-phenylene) ones;[6–11] no bis(1,2,3-phenylene) analogues had been reported until now. We became interested in preparing bis(1,2,3-phenylene) cryptands and studying their complexation with paraquat in order to investigate how the differences in the positions of the ether chains on the two phenyl rings affect the binding of bisphenylene cryptands to paraquat. Here we report the synthesis of the bis(1,2,3-phenylene) cryptand **1** (Scheme 1) and its dual-responsive binding to paraquat **3** and diquat **4**.[12]

Results and Discussion

The design of the bis(1,2,3-phenylene) cryptand **1** was inspired by the crystal structure of a taco complex **2a**⊃**3** formed between the bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivative **2a** and paraquat **3** (Scheme 1).[6a] Note from the crystal structure of **2a**⊃**3** that an F atom of the PF_6 counterion is hydrogen-bonded to the two β-pyridinium hydrogen atoms of **3**. On the basis of this observation we designed the bis(1,2,3-phenylene) cryptand **1** with a hydrogen-bond acceptor site – the pyridyl nitrogen atom – in approximately the right location for interaction with the two β-pyridinium hydrogen atoms of **3**. The cryptand **1** was synthesized from the commercially available starting material propyl gallate in seven steps and in reasonable yields (Scheme 1). Complexation between the cryptand **1** and paraquat **3** or diquat **4** was then studied. When equimolar (8.00 mM) $CHCl_3/CH_3CN$ (1:1 *v*:*v*) solutions of **1** and either **3** or **4** were prepared, a bright yellow color appeared as a result of charge-transfer interactions between the electron-rich aromatic rings of **1** and the electron-poor pyridinium rings of **3** or **4**.

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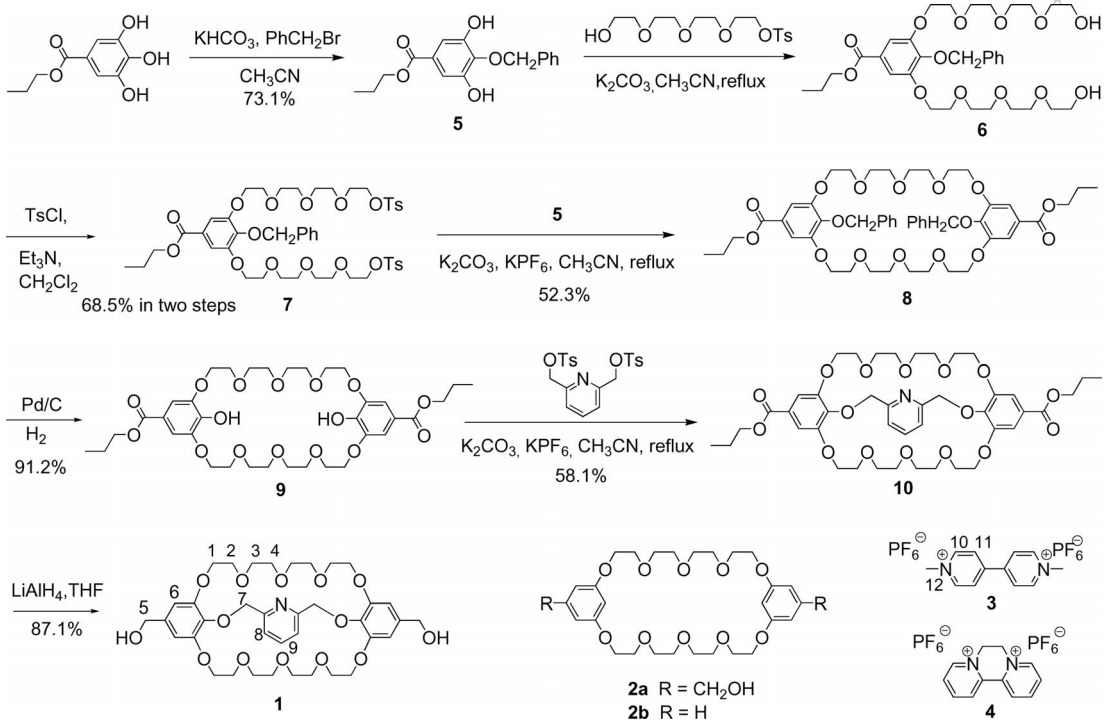

Scheme 1. Synthesis of the bis(1,2,3-phenylene) cryptand **1**, together with the chemical structures of the bis(*m*-phenylene)-32-crown-10 derivatives **2a** and **2b**, paraquat **3**, and diquat **4**.

Job plots[13] based on UV/Vis spectroscopic absorbance data for the charge-transfer bands (λ = 403 nm) demonstrated that the complexes of **1** with **3** or **4** in solution were each of 1:1 stoichiometry. It was previously reported that the complex formed in solution between BMP32C10 (**2b**, Scheme 1) and **3** was also of 1:1 stoichiometry.[6c] The association constants (K_a) of the complexes **1**⊃**3**, **1**⊃**4**, and **2b**⊃**3** in $CHCl_3/CH_3CN$ (1:1 *v*:*v*) were determined by examination of the charge-transfer bands of the complexes by UV/Vis spectroscopy and by a titration method to be $2.2(\pm0.5)\times10^3$ M^{-1}, $3.7(\pm1.0)\times10^3$ M^{-1}, and $917(\pm70)$ M^{-1}, respectively. Therefore, an increase in association constants was observed on going from the crown ether-based complex **2b**⊃**3** to the cryptand-based complex **1**⊃**3**.

The electrospray ionization mass spectra also confirmed the 1:1 complexation between the cryptand **1** and paraquat (**3**) or diquat (**4**). Peaks were found at *m*/*z* 458.8 (100%) and 1062.4 (12.5%) for **1**⊃**3** and at *m*/*z* 457.7 (100%) and 1059.9 (21.5%) for **1**⊃**4**, corresponding to $[\mathbf{1}\supset\mathbf{3} - 2PF_6]^{2+}$, $[\mathbf{1}\supset\mathbf{3} - PF_6]^{+}$, $[\mathbf{1}\supset\mathbf{4} - 2PF_6]^{2+}$, and $[\mathbf{1}\supset\mathbf{4} - PF_6]^{+}$, respectively.

The 1:1 stoichiometry of the cryptand **1** and paraquat **3** was further confirmed by X-ray diffraction analysis of a yellow single crystal grown by vapor diffusion of diisopropyl ether into a $CHCl_3/CH_3CN$ (1:1 *v*:*v*) solution of **1** and **3**. The **1**⊃**3** complex has a taco complex geometry (Figure 1),[14] never found before in cryptand/paraquat complexes, which have previously all been of the inclusion or pseudorotaxane types.[6,7a–7c,8–11] The complex is stabilized by hydrogen bonding, charge transfer, and aromatic edge-to-face π-stacking interactions in the solid state (Figure 1). The crystal structure shows that four hydrogen bonds (**a**, **b**, **c**, and **d**) are formed between the hydrogen atoms on the same side of paraquat **3** with oxygen or nitrogen atoms on the cryptand **1**. Most notably, in accordance with our design, a β-pyridinium hydrogen of the guest **3** is directly hydrogen-bonded to the pyridine nitrogen atom of the host in **1**⊃**3**. The crystals of the **1**⊃**3** complex have a yellow color due to charge-transfer interactions between the electron-rich aromatic rings of **1** and the electron-poor pyridinium rings of **3**. Interestingly, an aromatic edge-to-face interaction (**e**) between a β-pyridinium hydrogen and the pyridine moiety on the cryptand **1** is found in the solid structure

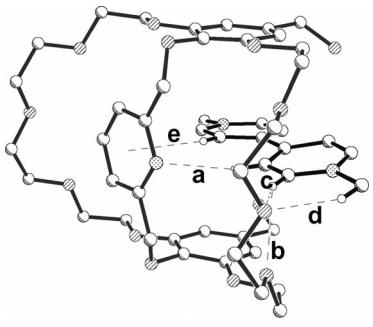

Figure 1. A ball-and-stick view of the X-ray crystal structure of **1**⊃**3**. PF_6^- counterions, solvent molecules, and hydrogens other than those involved in hydrogen bonding between the cryptand **1** and paraquat **3** are omitted for clarity. Hydrogen bond parameters: H···O (N) distance [Å], C–H···O (N) angle [°], C···O (N) distance [Å] **a**) 2.50, 156, 3.37; **b**) 2.57, 118, 3.12; **c**) 2.46, 155, 3.32; **d**) 2.50, 157, 3.40. The C–H···π edge-to-face interaction **e** is defined by an H···pyridine centroid distance [Å] of 2.69 and a C–H··· centroid angle [°] of 155.

(Figure 1), increasing the host–guest interactions between **1** and **3**.

Further investigation of the complexation between **1** and **3** or **4** was carried out by proton NMR spectroscopy (spectra a, b, and e in Figure 2 and Figure S21 in the Supporting Information). The complexation systems **1⊃3** and **1⊃4** are fast-exchange on the proton NMR timescale. A significant upfield shift was observed for the H^{11} β-pyridinium protons of paraquat **3**, whereas no obvious chemical shift changes were observed after complexation for the H^{10} α-pyridinium protons or the H^{12} *N*-methyl protons of **3** (spectra a and b in Figure 2). This is noteworthy because obvious chemical shift changes after complexation have usually been seen for H^{10} α-pyridinium protons in previously reported cryptand/paraquat complexes.[6,7a–7c,8–11] The H^6 aromatic protons, the H^5 benzyl protons, and the H^1 α-ethylenoxy protons of **1** moved upfield after complexation (spectra b and e in Figure 2). Other protons of the cryptand **1** did not undergo obvious chemical shift changes after complexation (spectra b and e in Figure 2). Chemical shift changes could also be observed for the complexation system between the cryptand **1** and diquat **4** (Figure S21 in the Supporting Information).

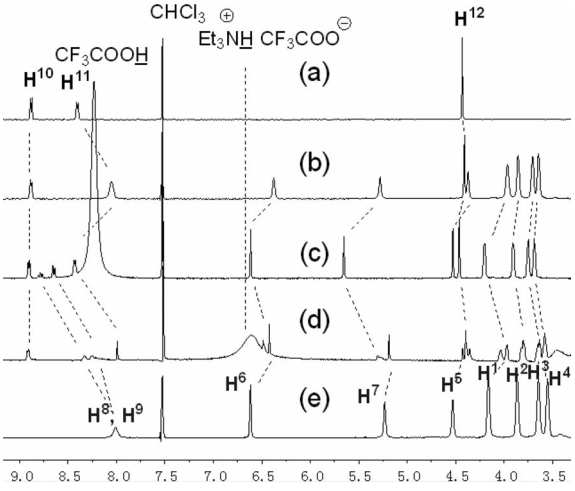

Figure 2. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ 1:1, 295 K) of: a) **3**, b) **1** and **3** (8.00 mM), c) a solution of trifluoroacetic acid (3 drops) and **1** and **3** (8.00 mM, 0.5 mL), d) a solution of trifluoroacetic acid (3 drops), triethylamine (6 drops), and **1** and **3** (8.00 mM, 0.5 mL), and e) **1**.

We next turned to the control of the binding between the cryptand **1** and paraquat **3**. From crown ether **2b** to cryptand **1**, a chain containing seven atoms, a pyridyl nitrogen atom located in its center, was introduced into the crown ether **2a** to form the cryptand **1**. The introduced pyridyl nitrogen atom can be protonated by addition of acid, which will cause the complex to disassemble. Later, when enough base is added to deprotonate the pyridinium moiety completely, the complex **1⊃3** can form again.[7a] This was confirmed by proton NMR experiments (Figure 2). When trifluoroacetic acid (3 drops) was added to **1** and **3** (each 8.00 mM) in $CDCl_3/CD_3CN$ (1:1, 0.5 mL), the chemical shift corresponding to the H^{11} β-pyridinium protons of paraquat **3** returned almost to their uncomplexed value (spectra a and c in Figure 2), indicating that the complexation between the cryptand host **1** and paraquat **3** was essentially totally quenched; consistently with this, the color of the solution changed from yellow to colorless. After addition of triethylamine (6 drops) to this solution, complexation between **1** and **3** was recovered; a large change in the chemical shift corresponding to H^{11} of **3** was again observed (see spectra b and d of Figure 2).[15] The color of the solution changed to yellow again. Additionally, the H^8 and H^9 pyridyl protons and the H^7 methylene protons of **1** had clearly shifted downfield after addition of trifluoroacetic acid (spectra b and c in Figure 2), indicating that the pyridyl nitrogen atom of **1** was protonated.

On the other hand, from crown ether **2a** to the cryptand **1**, the introduction of a seven-atom third chain divides the BMP32C10 cavity into two asymmetric 24-crown-8 cavities (Scheme 1). When K^+ is added, the cryptand **1** should form a more stable 1:2 complex with K^+, which can cause the complex between the cryptand **1** and paraquat **3** to disassemble. Later, when enough 18-crown-6 (18C6) is added to trap the K^+, the complex **1⊃3** can reform. This was also confirmed by proton NMR experiments (Figure 3). When KPF_6 (2 molar equiv.) was added to an equimolar solution of **1** and **3** (8.00 mM) in $CDCl_3/CD_3CN$ (1:1), the chemical shifts of the paraquat **3** protons returned to their uncomplexed values (spectra a and c in Figure 3) and correspondingly the yellow color of the solution totally disappeared, indicating the total dissociation of the **1⊃3** complex. However, when 18C6 (2 mol-equiv.) was subsequently added, chemical shift changes of the protons on **3** were again observed (see spectra b and d of Figure 3) and correspondingly the yellow color of the solution recovered, indicating the reformation of the **1⊃3** complex.[15]

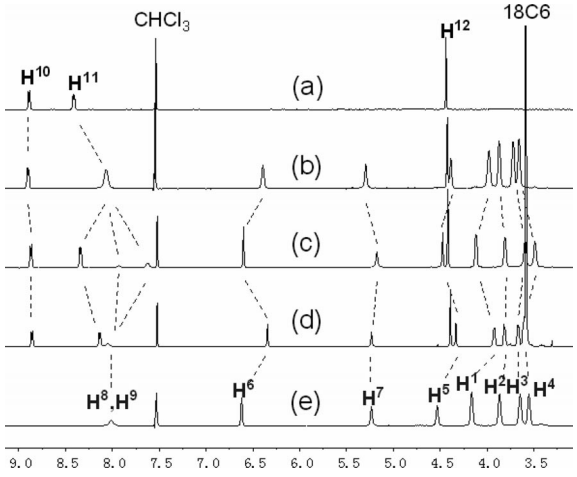

Figure 3. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ 1:1, 295 K) of: a) **3**, b) **1** and **3** (8.00 mM), c) **1** and **3** (8.00 mM) and KPF_6 (16.0 mM), d) **1** and **3** (8.00 mM), KPF_6 (16.0 mM) and 18C6 (16.0 mM), and e) **1**.

Similarly, the binding of the cryptand **1** to diquat **4** in solution also could be switched off (and back on) by addition of acid or K^+ (and then base or 18C6).

Conclusions

In summary, we have synthesized a novel bis(1,2,3-phenylene) cryptand and studied its dual-response binding to paraquat and diquat. We found that the cryptand **1** forms a taco complex with paraquat **3** in the solid state. More importantly, we demonstrated that the complexation between the cryptand **1** and paraquat **3** or diquat **4** could be controlled either by changing the solution pH or by addition of small molecules such as KPF_6 and 18C6. This dual-responsive host–guest binding property is a unique feature of the bis(1,2,3-phenylene) cryptand **1** in relation to previously reported bis(1,3,5-phenylene) and bis(1,2,4-phenylene) cryptands. The cryptand **1** can be used in efficient taco-complex-templated syntheses of mechanically interlocked structures such as rotaxanes and catenanes[8c] and its dual-response binding to paraquat and diquat could be employable in the fabrication of advanced functional supramolecular systems such as molecular switches and molecular machines.

Experimental Section

General: All reagents were purchased from commercial suppliers and used as received. BMP32C10 (**2b**), BMP32C10 diol (**2a**),[16] and (2,6-pyridinediyl)bismethylene ditosylate[17] were synthesized by published literature procedures. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance 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. The high-resolution electron impact (HREI) mass spectrum of **5** was obtained with a GCT Premier CAB170 mass spectrometer. CCDC-773275 (**1⊃3**) contains 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.

Synthesis of 5: $KHCO_3$ (7.50 g, 75.0 mmol) was cooled in an ice bath under nitrogen. A solution of propyl gallate (10.6 g, 50.0 mmol) in CH_3CN (75.0 mL) was added dropwise. Benzyl bromide (8.50 g, 50.0 mmol) was then added, and the reaction mixture was allowed to warm to room temperature. After 16 h, the solvent was removed in vacuo. The residue was dissolved in ethyl acetate and water. The aqueous layer was separated and extracted with ethyl acetate (100 mL × 3). The organic layers were combined, washed with brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to afford a dark oil, which was purified by flash column chromatography (ethyl acetate/petroleum ether 8:100 followed by ethyl acetate/petroleum ether 15:100) to give **5** (11.1 g, 73.1%) as a white solid; m.p. 109.3–110.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 7.40 (s, 5 H, Ar-H), 7.22 (s, 2 H, Ar-H), 5.51 (s, 2 H, benzyl-H), 5.13 (s, 2 H, –OH), 4.24 (t, J = 5.4 Hz, 2 H, α-CH_2), 1.76 (m, 2 H, β-CH_2), 1.02 (t, J = 5.4 Hz, 3 H, γ-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 295 K): δ = 166.8, 149.0, 137.2, 136.4, 128.8, 126.0, 109.6, 75.4, 66.9, 21.9, 10.4 ppm. LRESI-MS: m/z (%) = 303.2 (100) [**5** + H]$^+$. HREI-MS: calcd. for $C_{17}H_{18}O_5$ [**5**]$^+$ 302.1154; found 302.1143, error –3.6 ppm.

Synthesis of 6 and 7: K_2CO_3 (13.8 g, 100 mmol), compound **5** (6.05 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 then nitrogen was introduced. After this process had been carried out three times, CH_3CN (250 mL) was added. The solution was stirred mechanically at reflux for 24 h. The mixture was then filtered and the filtrate was concentrated to give **6**, which was used in the next step without further purification.

The unpurified **6** (25.6 g, 39.0 mmol) and *p*-toluenesulfonyl chloride (19.1 g, 100 mmol) were dissolved in CH_2Cl_2 (400 mL). Triethylamine (14.2 mL, 100 mmol) was added dropwise to the solution. The whole mixture was stirred mechanically for 3 h at 6 °C and for another 24 h at room temperature. When the reaction was complete, the mixture was washed with brine (200 mL × 3). The aqueous layer was separated and extracted with CH_2Cl_2 (200 mL × 3). The organic phase was combined, dried with anhydrous Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether 2:3) to give **7** (13.2 g, 68.5%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 7.77 (d, J = 7.0 Hz, 4 H, Ar-H), 7.48 (d, J = 7.0 Hz, 2 H, Ar-H), 7.26–7.32 (m, 9 H, Ar-H), 5.09 (s, 2 H, benzyl-H), 4.24 (t, J = 7.4 Hz, 2 H, α-CH_2), 4.16 (t, J = 4.8 Hz, 4 H, α-OCH_2), 4.12 (t, J = 4.8 Hz, 4 H, –CH_2OTs), 3.84 (t, J = 5.0 Hz, 4 H, β-OCH_2), 3.68 (t, J = 5.0 Hz, 4 H, –C$H_2$$CH_2$OTs), 3.63 (t, J = 5.0 Hz, 4 H, γ-OCH_2), 3.59 (t, J = 5.0 Hz, 4 H, –C$H_2$$OCH_2CH_2$OTs), 3.54 (m, 8 H, δ-$OCH_2$), 2.42 (s, 6 H, Ts-H), 1.76 (m, 2 H, β-CH_2), 1.00 (t, J = 7.2 Hz, 3 H, γ-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 295 K): δ = 166.1, 152.4, 144.7, 141.8, 137.6, 132.8, 129.7, 128.1, 125.5, 108.5, 74.7, 70.6, 69.5, 69.2, 68.6, 66.6, 22.0, 21.6, 10.5 ppm. LRESI-MS: m/z (%) = 985.3 (100) [**7** + Na]$^+$. HRESI-MS: calcd. for $C_{47}H_{62}NaO_{17}S_2$ [**7** + Na]$^+$ 985.3321; found 985.3323, error 0.2 ppm.

Synthesis of the Crown Ether 8: K_2CO_3 (2.76 g, 20.0 mmol), KPF_6 (1.84 g, 10.0 mmol), and CH_3CN (350 mL) were placed in a 1000 mL round-bottomed flask. The flask was evacuated and then nitrogen was introduced. The flask was heated and a CH_3CN solution (50.0 mL) of **7** (1.81 g, 1.88 mmol) and **5** (0.570 g, 1.88 mmol) was added at a speed of 1.00 mL h^{-1} when the solution in the flask began to reflux. After the solution had been completely added, the mixture was stirred at reflux for a further seven days. The solution was filtered and concentrated to give a pale yellow crude product, which was purified by flash column chromatography (ethyl acetate/petroleum ether 1:1) to give **8** (0.800 g, 52.3%) as a white solid; m.p. 79.6–81.1 °C. ^{1}H NMR (400 MHz, CD_3COCD_3, 295 K): δ = 7.44 (d, J = 7.0 Hz, 4 H, Ar-H), 7.17–7.21 (m, 8 H, Ar-H), 7.07–7.11 (m, 2 H, Ar-H), 4.94 (s, 4 H, benzyl-H), 4.16 (t, J = 7.0 Hz, 4 H, α-CH_2), 4.05 (t, J = 4.0 Hz, 8 H, α-OCH_2), 3.76 (t, J = 4.0 Hz, 8 H, β-OCH_2), 3.55–3.58 (m, 8 H, γ-OCH_2), 3.50–3.54 (m, 8 H, δ-OCH_2), 1.68–1.73 (m, 4 H, β-CH_2), 0.95 (t, J = 7.2 Hz, 6 H, γ-CH_3) ppm. ^{13}C NMR (100 MHz, CD_3COCD_3, 295 K): δ = 165.3, 152.3, 128.5, 127.7, 125.5, 108.1, 74.4, 70.1, 69.3, 68.6, 66.1, 59.6, 21.8, 19.8, 13.5, 9.8 ppm. LRESI-MS: m/z (%) = 943.7 (100) [**8** + Na]$^+$, 959.2 (18%) [**8** + K]$^+$. HRESI-MS: calcd. for $C_{50}H_{64}NaO_{16}$ [**8** + Na]$^+$ 943.4087; found 943.4066, error –2.2 ppm.

Synthesis of the Crown Ether 9: Pd/C (130 mg) and **8** (540 mg, 0.586 mmol) were placed in a 250 mL round-bottomed flask. The flask was evacuated and then hydrogen was introduced. After this process had been carried out three times, $CHCl_3$/CH_3OH (1:1 v/v, 170 mL) was added. The system was heated at 60 °C for 24 h. The solution was filtered and concentrated to give a crude product, which was purified by flash column chromatography (ethyl acetate/methanol 10:1) to give **9** (396 mg, 91.2%) as a white solid; m.p. 89.0–90.7 °C. ^{1}H NMR (400 MHz, CD_3COCD_3, 295 K): δ = 7.32 (s, 4 H, Ar-H), 4.16–4.21 (m, 12 H, α-CH_2 and α-OCH_2), 3.82 (t,

J = 4.0 Hz, 8 H, β-OCH_2), 3.69 (t, J = 4.0 Hz, 8 H, γ-OCH_2), 3.62–3.64 (m, 8 H, δ-OCH_2), 1.72–1.77 (m, 4 H, β-CH_2), 1.00 (t, J = 7.2 Hz, 6 H, γ-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 295 K): δ = 162.2, 144.4, 142.6, 120.5, 110.9, 70.7, 70.4, 69.9, 69.3, 66.3, 22.0, 10.4 ppm. LRESI-MS: m/z (%) = 758.4 (35) [**9** + NH_4]$^+$, 763.3 (100) [**9** + Na]$^+$. HRESI-MS: calcd. for $C_{36}H_{52}NaO_{16}$ [**9** + Na]$^+$ 763.3148; found 763.3166, error 2.4 ppm.

Synthesis of the Cryptand 10: K_2CO_3 (552 mg, 4.00 mmol), KPF_6 (184 mg, 1.00 mmol), and CH_3CN (160 mL) were placed in a 500 mL round-bottomed flask under nitrogen. A CH_3CN (50.0 mL) solution of **9** (300 mg, 0.400 mmol) and (2,6-pyridinediyl)bismethylene ditosylate (180 mg, 0.400 mmol) was added at a speed of 1.00 mL h^{-1} at reflux. The mixture was then stirred at reflux for a further 5 d. The solution was filtered and concentrated to give a crude product, which was purified by flash column chromatography (ethyl acetate) to give **10** (179 mg, 58.1%) as a white solid; m.p. 159.7–160.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 7.91 (m, 3 H, pyridine-H), 7.28 (s, 4 H, Ar-H), 5.31 (s, 4 H, benzyl-H), 4.25 (t, J = 7.0 Hz, 4 H, α-CH_2), 4.15–4.22 (m, 8 H, α-OCH_2), 3.85–3.89 (m, 8 H, β-OCH_2), 3.60–3.66 (m, 8 H, γ-OCH_2), 3.52–3.58 (m, 8 H, δ-OCH_2), 1.74–1.81 (m, 4 H, β-CH_2), 1.01 (t, J = 7.2 Hz, 6 H, γ-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ = 166.0, 157.3, 151.9, 141.9, 137.3, 125.4, 119.5, 107.9, 75.2, 70.5, 69.4, 68.6, 66.5, 29.5, 21.9, 10.3 ppm. LRESI-MS: m/z (%) = 844.3 (30) [**10** + H]$^+$, 866.3 (100) [**10** + Na]$^+$. HRESI-MS: calcd. for $C_{43}H_{57}NNaO_{16}$ [**10** + Na]$^+$ 866.3570; found 866.3535, error –4.0 ppm.

Synthesis of the Cryptand 1: $LiAlH_4$ (230 mg, 6.06 mmol) was placed in a 150 mL round-bottomed flask. Compound **10** (150 mg, 0.124 mmol) in anhydrous THF (20.0 mL) was added slowly. Water was then added to quench the remaining $LiAlH_4$. The reaction mixture was filtered under vacuum and the filtrate was concentrated to give a crude product, which was purified by flash column chromatography (ethyl acetate/methanol 10:1) to give **1** (78.9 mg, 87.1%) as a white solid; m.p. 130.8–131.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ = 7.92 (m, 3 H, pyridinium-H), 6.47 (s, 4 H, Ar-H), 5.22 (s, 4 H, benzyl-H), 4.45 (s, 4 H, α-CH_2), 4.10 (br., 8 H, α-OCH_2), 3.83 (br., 8 H, β-OCH_2), 3.60 (t, J = 4.4 Hz, 8 H, γ-OCH_2), 3.50 (t, J = 4.4 Hz, 8 H, δ-OCH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 295 K): δ = 157.9, 152.5, 137.9, 137.3, 136.4, 120.3, 104.9, 75.2, 70.8, 69.9, 68.8, 65.0 ppm. LRESI-MS: m/z (%) = 629.5 (35) [**1** + H – $CH_2C_5H_3NCH_2$]$^+$, 732.7 (40) [**1** + H]$^+$, 754.7 (100) [**1** + Na]$^+$, 770.6 (10) [**1** + K]$^+$. HRESI-MS: calcd. for $C_{37}H_{49}NNaO_{14}$ [**1** + Na]$^+$ 754.3045; found 754.3031, error –2.0 ppm.

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

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