Three-dimensional bis(*m*-phenylene)-32-crown-10-based cryptand/paraquat catenanes

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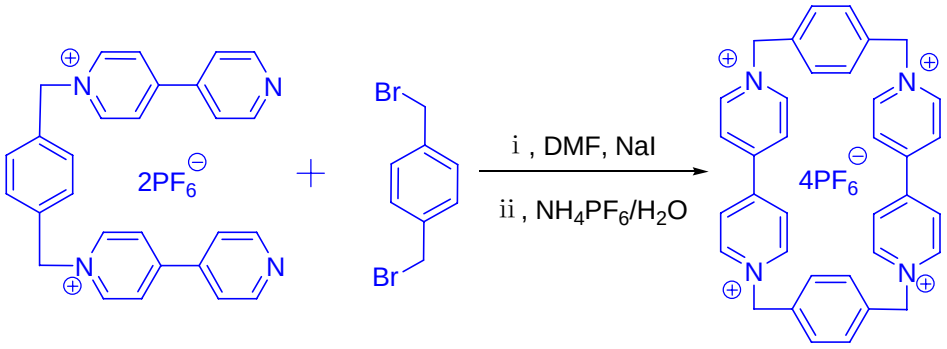
Supporting Information (16 pages)

1. Materials and methods

Bis(*m*-phenylene)-32-crown-10-based cryptand **1**,[S1] 1,1'-[1,4-phenylenebis(methylene)]bis-4,4'-bipyridinium bis(hexafluorophosphate) (**[BBIPYXY][PF$_6$]$_2$**)[S2] and 1,1'-[4,4'-biphenylenedimethylene]bis-4,4'-bipyridinium bis(hexafluorophosphate) (**[BBIPYBT][PF$_6$]$_2$**)[S3] were prepared according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer with internal standard TMS. ^{13}C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometry at 125 MHz. Low-resolution electrospray ionization mass spectra (LRESIMS) were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Breman, Germany) equipped with ESI interface and ion trap analyzer. High-resolution electrospray ionization mass spectra (HRMS) were obtained on a Bruker 7-tesla FT-ICRMS equipped with an electrospray source (Billelica, MA, USA).

2. Synthesis of cyclophane ***2***



[BBIPYXY][PF_6]$_2$ **2**

1,4-Bis(bromomethyl)benzene (264 mg, 1.00 mmol) and **[BBIPYXY][PF_6]$_2$** (706 mg, 1.00 mmol) were dissolved in dry DMF (50 mL). NaI (10 mg) was added to the solution at room temperature. A red precipitate appeared gradually. Then the reaction mixture was stirred at room temperature for 7 days. The solvent was removed under vacuum. The resultant 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-$MeNO_2$ (7:2:1)]. The fractions containing the product (as monitored by TLC) were combined and concentrated under vacuum to give a residue which was dissolved in H_2O. A white solid was precipitated from this solution by addition of a saturated aqueous NH_4PF_6 solution. It was then recrystallized from acetone-H_2O to give **2** (151 mg, 13.7 %).[S2] The proton NMR spectrum of **2** is shown in Figure S1. ^{1}H NMR (400 MHz, acetone-d_6, room temperature) δ (ppm): 9.32 (d, J = 5.6 Hz, 8H), 8.52 (d, J = 5.6 Hz, 8H), 7.70 (s, 8H), 6.09 (s, 8H).

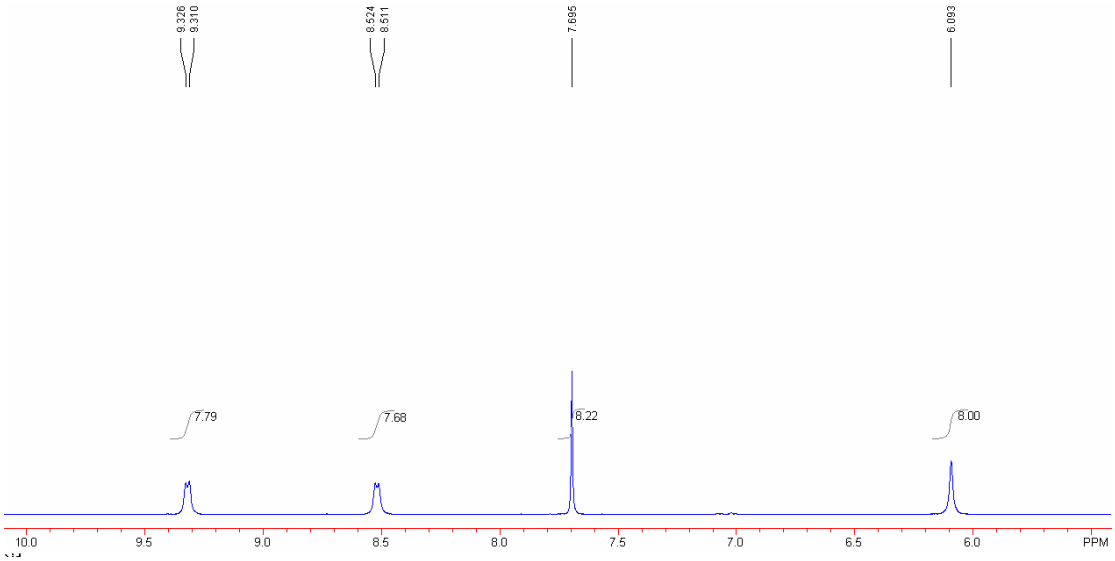
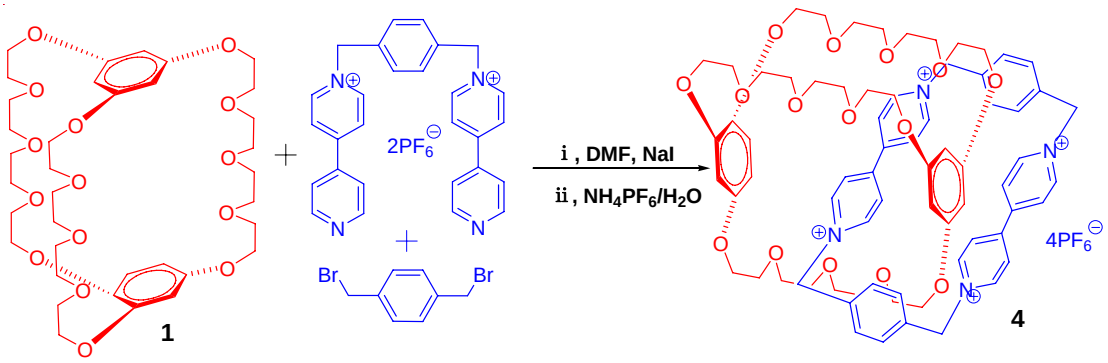


Figure S1. ^{1}H NMR spectrum (400 MHz, acetone-d_6, room temperature) of cyclophane **2**.

3. Synthesis of [2]catenane ***4***



A solution of **[BBIPYXY][PF$_6$]$_2$** (140 mg, 0.2 mmol) in dry DMF (5 mL) was added to a solution of **1** (363 mg, 0.5 mmol) in dry DMF (5 mL) under N_2 protection. The color of the mixture changed to yellow quickly. Then 1,4-bis(bromomethyl)benzene (56.0 mg, 0.2 mmol) and NaI (10.0 mg) in DMF (5 mL) was added to the mixture and stirred at room temperature. A red deposit appeared gradually. Then the reaction was stirred at room temperature for 3 days.[S2] The solvent was removed under vacuum. The resultant 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-$MeNO_2$ (10:2:1)]. The fractions containing the product (as monitored by TLC) were combined and concentrated under vacuum to give a residue which was dissolved in H_2O. A red solid, [2]catenane **4** (134 mg, 37.0 %) was precipitated from this solution by addition of a saturated aqueous NH_4PF_6 solution. m.p. 251–253 °C The proton NMR spectrum of **4** is shown in Figure S2. ^{1}H NMR (acetone-d_6, 400 M HZ): 9.10–9.50 (m, 8H), 7.90–8.30 (m, 16H), 6.00–6.10 (m, 8H), 5.40–5.55 (m, 4H), 3.40–4.30 (m, 50H). The ^{13}C NMR spectrum of **4** is shown in Figure S3. ^{13}C NMR (125 MHz, acetone-d_6, room temperature) δ (ppm): 160.3, 159.4, 150.5 147.9 146.4, 146.3 145.1, 144.7 144.4, 136.6, 134.9, 131.6, 131.2, 130.5, 129.3, 127.6, 126.6, 125.8, 125.5, 125.3, 93.7, 93.1, 89.3, 70.9, 69.5, 68.9, 68.0, 67.6, 65.0, 64.7, 64.2, 63.1. LRESIMS is shown in Figure S4: *m/z* 258.9 [**S2** – HPF_6 – $C_{10}H_8N_2$]$^+$ (30%), 561.0 [**S2**]$^+$ (81%), 659.4 [M – 2PF_6 – **S1** – $CH_2C_6H_4CH_2$]$^{2+}$ (66%), 711.2 [M – 2PF_6 – **S1**]$^{2+}$ (100%), [S3] 768.2 [M – 2PF_6]$^{2+}$ (67%), 1681.1 [M – PF_6]$^+$ (35%). HRMS: *m/z* calcd for [M – PF_6]$^+$ $C_{72}H_{86}F_{18}N_4O_{15}P_3$, 1681.5010, found 1681.5074, error 3.8 ppm. *m/z* calcd for [M – 2PF_6]$^{2+}$ $C_{72}H_{86}F_{12}N_4O_{15}P_2$, 768.2681, found 768.2674, error 0.9 ppm.

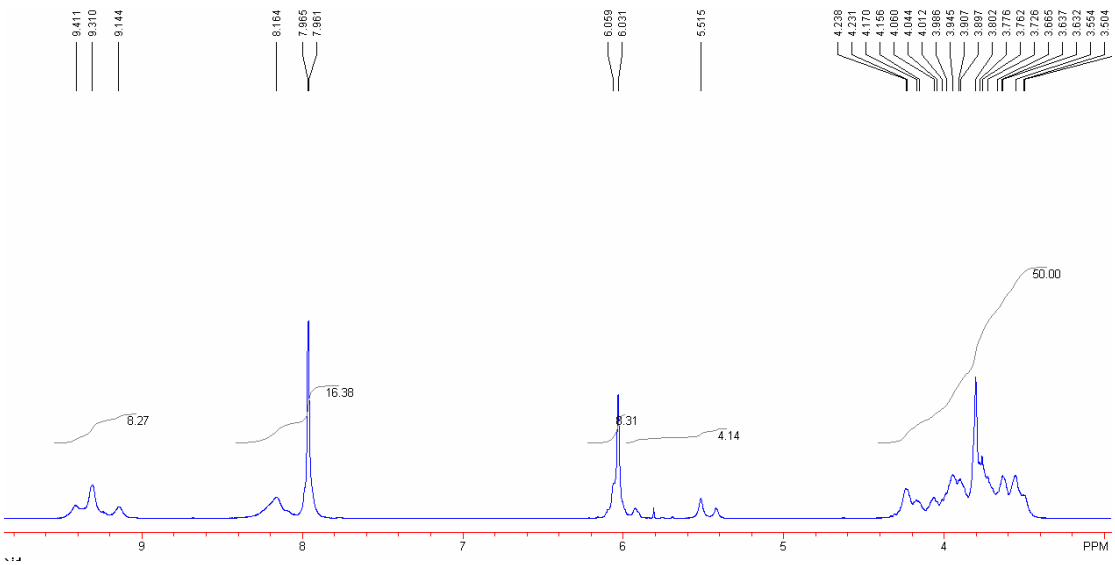


Figure S2. ^{1}H NMR spectrum (400 MHz, (acetone-d_6, room temperatur) of [2]catenane **4**.

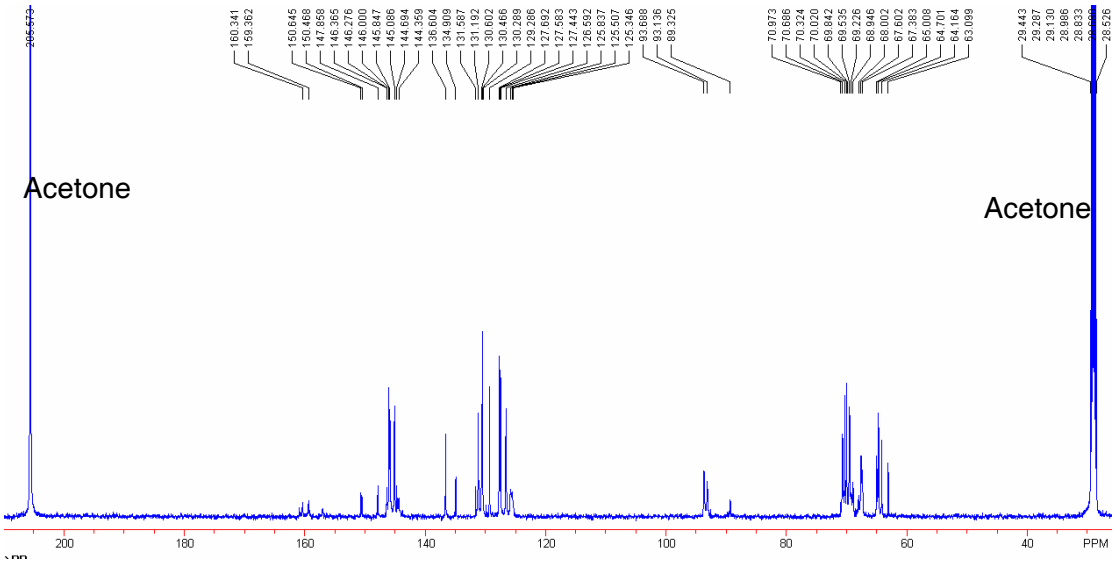
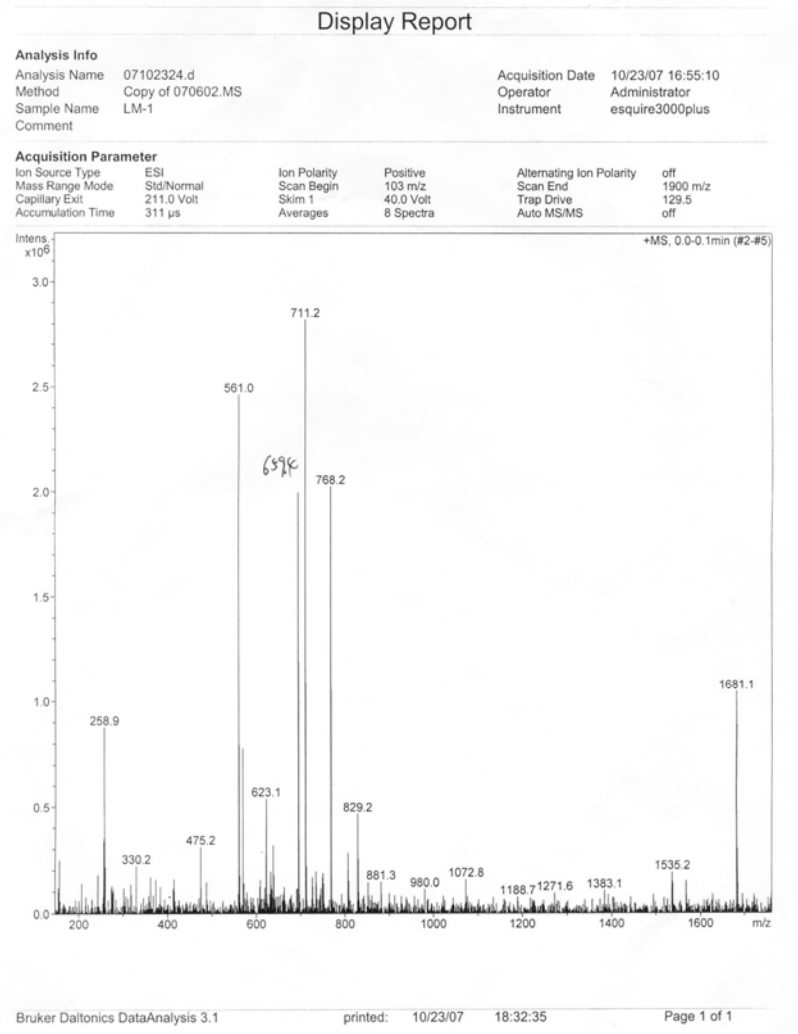
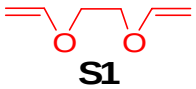


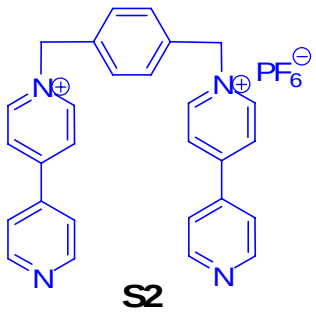
Figure S3. ^{13}C NMR spectrum (125 MHz, (acetone-d_6, room temperature) of **4**.





S1

$C_6H_{10}O_2$
Exact Mass: 114.0681

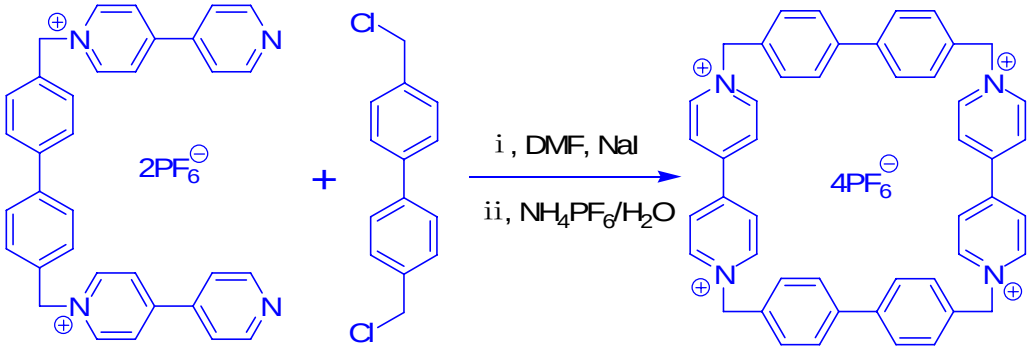


S2

$C_{28}H_{24}F_6N_4P^+$
Exact Mass: 561.1637

Figure S4. Electrospray ionization mass spectrum of **4**. Assignment of main peaks: *m*/*z* 258.9 [**S2** – HPF_6 – $C_{10}H_8N_2$]$^+$ (30%), 561.0 [**S2**]$^+$ (81%), 659.4 [M – $2PF_6$ – **S1** – $CH_2C_6H_4CH_2$]$^{2+}$ (66%), 711.2 [M – $2PF_6$ – **S1**]$^{2+}$ (100%), 768.2 [M – $2PF_6$]$^{2+}$ (67%), 1681.1 [M – PF_6]$^+$ (35%).

4. Synthesis of cyclophane ***4***



[BBIPYBT][PF_6]$_2$ **3**

A solution of **[BBIPYBT][PF_6]$_2$** (313 mg, 0.40 mmol) in DMF (20 mL) was added to a solution of 4,4'-bis(chloromethyl) biphenyl (100 mg, 0.40 mmol) and NaI (50 mg) in DMF (20 mL) at room temperature. After complete addition, the mixture was stirred at reflux for another 7 days. The color of the mixture changed to red gradually. The solvent was removed under vacuum. The resultant 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 new product (as monitored by TLC) were combined and concentrated under vacuum to give a residue which was dissolved in H_2O. Cyclophan**e 3** (14 mg, 2.8 %) was precipitated from this solution by addition of a saturated aqueous NH_4PF_6 solution as a white solid. The proton NMR spectrum of **3** is shown in Figure S5. ^{1}H NMR (400 MHz, acetone-d_6, room temperature) δ (ppm): 9.49 (d, J = 7.2 Hz, 8H), 8.73 (d, J = 7.2 Hz, 8H), 7.67 (d, J = 8.4 Hz, 8H), 7.63 (d, J = 8.4 Hz, 8H), 6.16 (s, 8H).

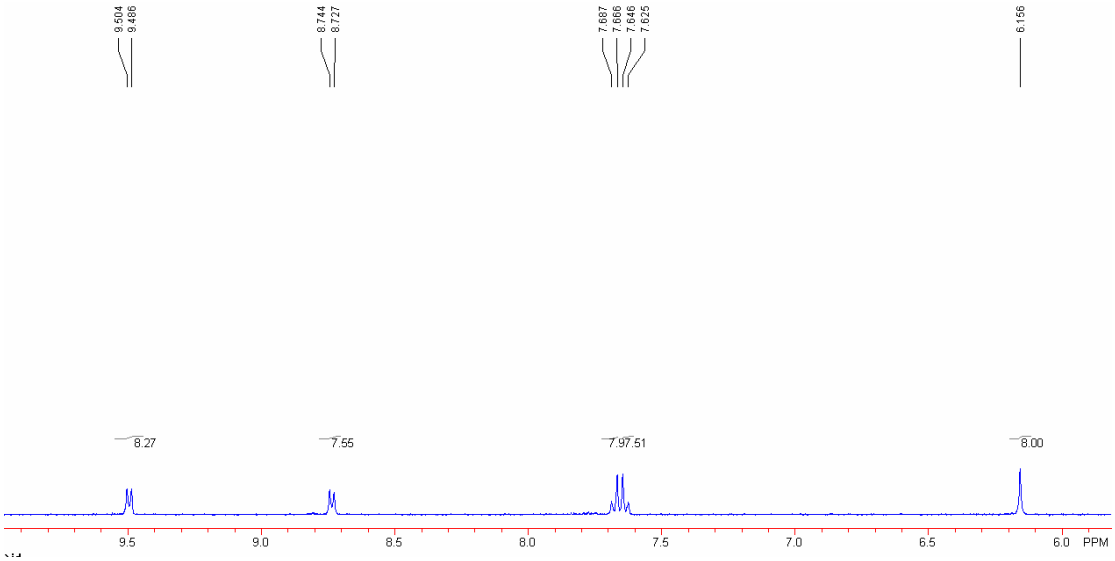
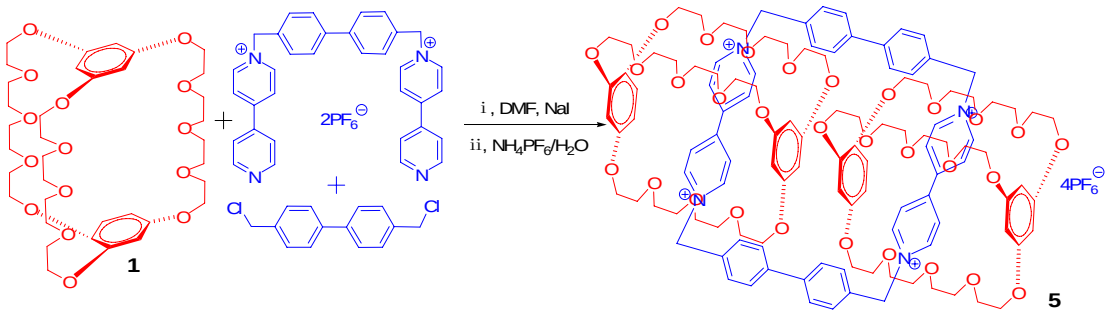


Figure S5. ^{1}H NMR spectrum (400 MHz, acetone-d_6, room temperatur) of cyclophane **3**.

5. Synthesis of [3]catenane **5**



A solution of **[BBIPYBT][PF_6]$_2$** (117 mg, 0.16 mmol) in dry DMF (5 mL) was added to a solution of cryptand **1** (280 mg, 0.39 mmol) in dry DMF (5 mL) under N_2 protection. The color of the mixture changed to deep yellow quickly. Then 4,4'-bis(chloromethyl)biphenyl (45.2 mg, 0.16 mmol) and NaI (10.0 mg) in DMF (5 mL) was added to the mixture and stirred at room temperature. The reaction mixture was stirred at room temperature for 7 days.[S4] The color of the reaction mixture turned deep red gradually. The solvent was removed under vacuum. The resultant 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 (as monitored by TLC) were combined and concentrated under vacuum to give a residue which was dissolved in H_2O. [3]catenane **5** (75 mg, 16.3 %), an orange solid, was precipitated from this solution by addition of a saturated aqueous NH_4PF_6 solution. m.p. 263–265 °C The proton NMR spectrum of **5** is shown in Figure S6. ^{1}H NMR (400 MHz, acetone-d_6, room temperature) δ (ppm): 9.20 (d, J = 6.0 Hz, 8H), 8.02 (d, J = 6.0 Hz, 8H), 7.90 (d, J = 8.0 Hz, 8H), 7.82 (d, J = 8.0 Hz, 8H), 6.08 (s, 8H), 5.49–5.77 (br, 6H), 3.50–4.10 (m, 96H), 3.43 (br, 6H). The ^{13}C NMR spectrum of **5** is shown in Figure S7.^{13}C NMR (125 MHz, $(CD_3)_2CO$, room temperature) δ (ppm): 160.1, 146.7, 145.3, 140.8, 134.7, 130.8, 128.0, 125.6, 93.7, 70.4, 70.2, 69.8, 67.6, 64.6. LRESIMS is shown in Figure S8: m/z 756.9 $[M - 3PF_6]^{3+}$ (100%), 1207.9 $[M - 2PF_6]^{2+}$ (90%), 531.5 $[M - 4PF_6]^{4+}$ (9.7%). HRMS: m/z calcd for $[M - 2PF_6]^{2+}$ $C_{120}H_{148}F_{12}N_4O_{30}P_2$, 1207.4726, found 1207.4681, error 3.7 ppm. m/z calcd for $[M - 3PF_6]^{3+}$ $C_{120}H_{148}F_6N_4O_{30}P$, 756.6601, found 756.6595, error 0.8

ppm. *m*/*z* calcd for $[M - 4PF_6]^{4+}$ $C_{120}H_{148}N_4O_{30}$, 531.2539, found 531.2526, error 2.4 ppm.

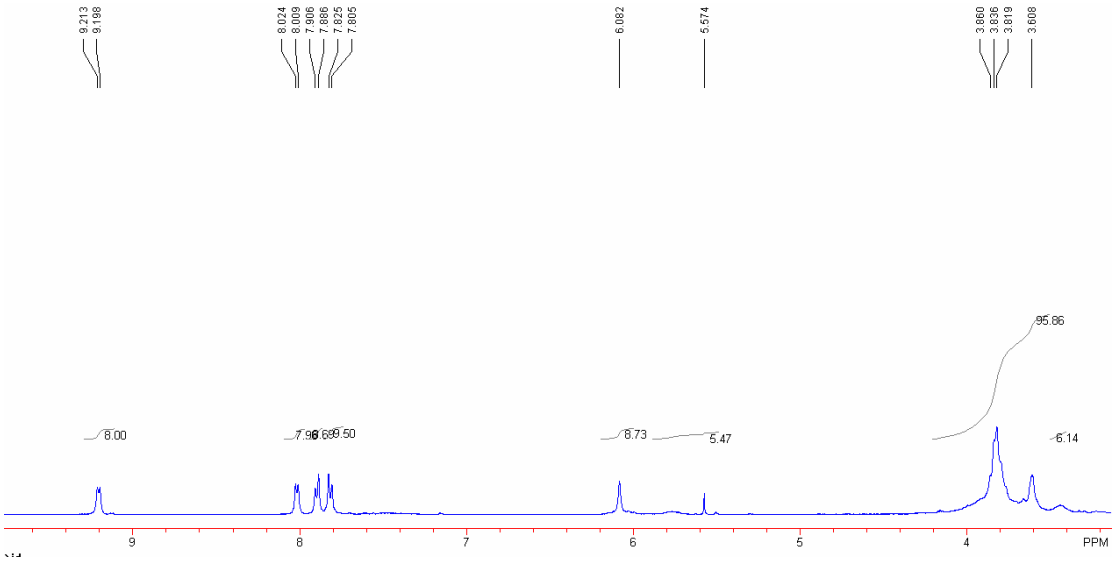


Figure S6. ^{1}H NMR spectrum (400 MHz, acetone-d_6, room temperatur) of [3]catenane **5**

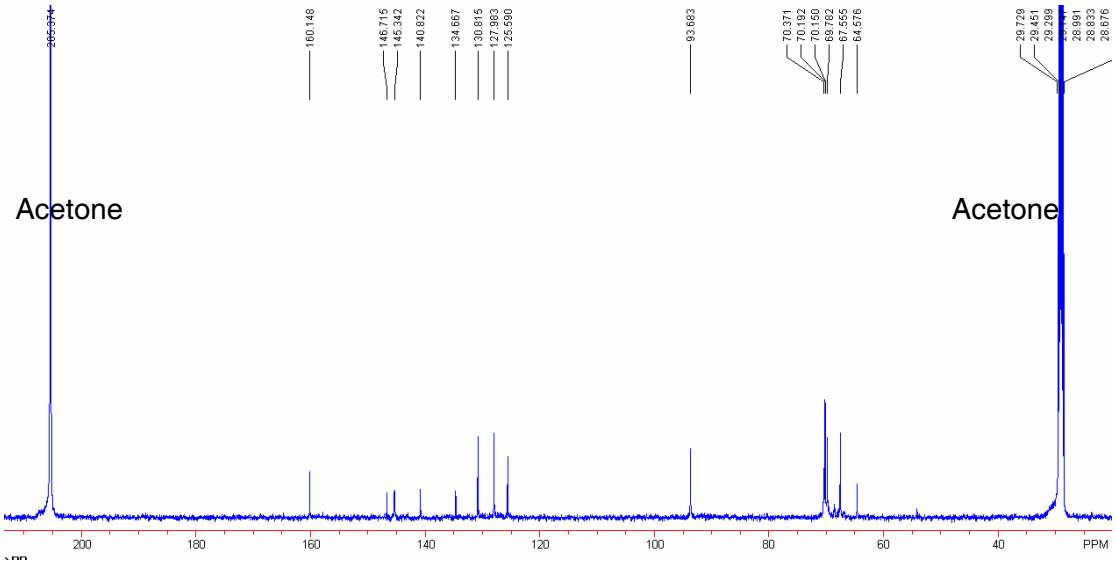


Figure S7. ^{13}C NMR spectrum (125 MHz, acetone-d_6, room temperature) of **5**

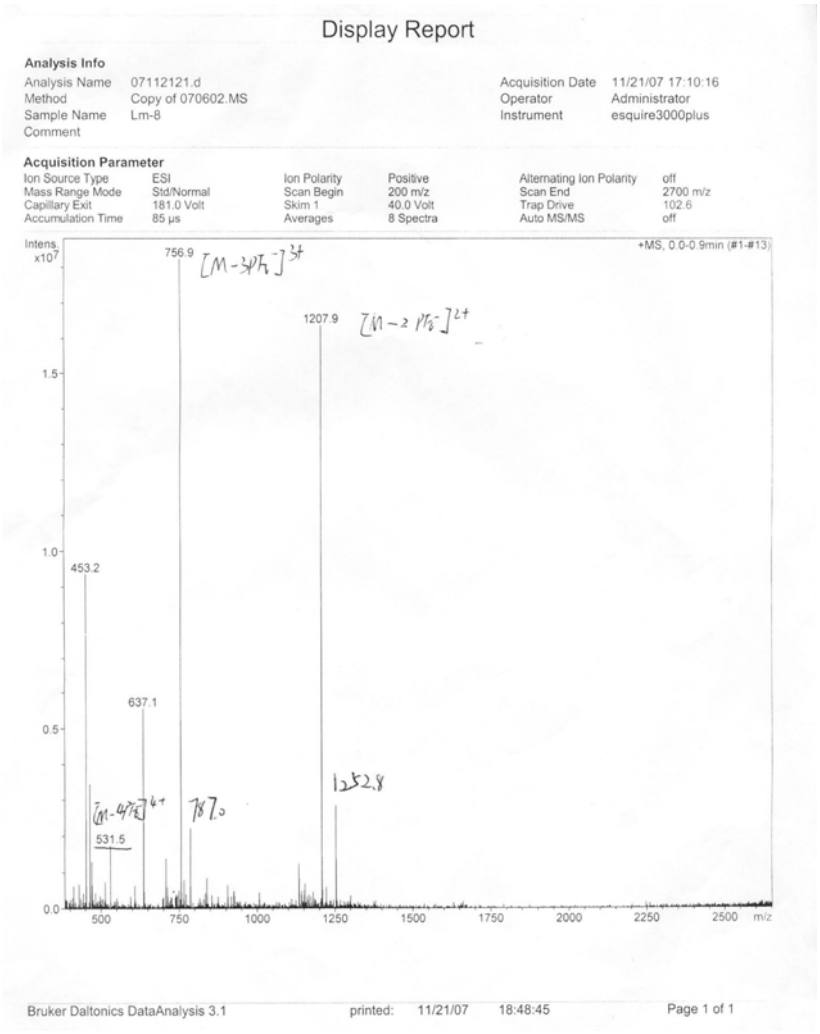


Figure S8. Electrospray ionization mass spectrum of **5**. Assignment of main peaks: *m*/*z* 531.5 $[M - 4PF_6]^{4+}$ (9.7%), 756.9 $[M - 3PF_6]^{3+}$ (100%), 1207.9 $[M - 2PF_6]^{2+}$ (90%).

*6. UV-vis spectra of catenanes **4** and **5***

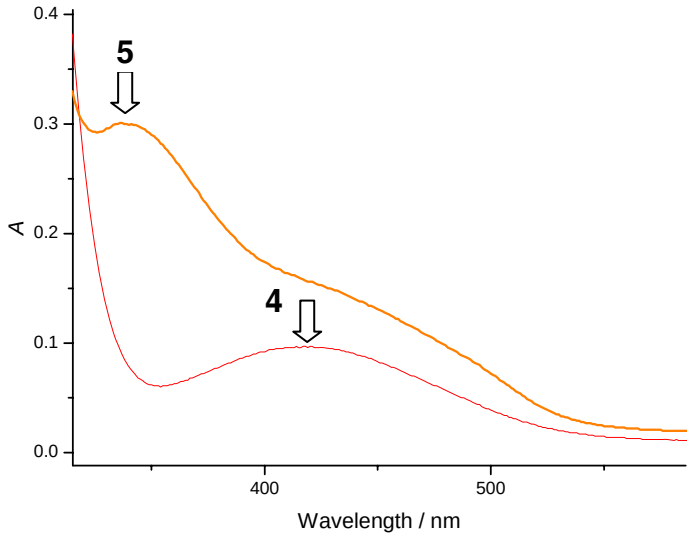


Figure S9. UV-vis spectra of catenanes **4** (5×10^{-4} M) and **5** (5×10^{-4} M) in MeCN, showing the charge-transfer absorption maximums at λ = 418 nm (ε = 194 $M^{-1}\,dm^{-1}$) and λ = 337 nm (ε = 602 $M^{-1}\,dm^{-1}$), respectively.

7. X-ray crystal data and packing structure of [2]catenane ***4***

Crystallographic data: prism, red, 0.27 × 0.25 × 0.20 mm^3, $C_{82}H_{102.925}F_{24}I_{0.075}N_9O_{16}P_4$, *FW* 2060.06, triclinic, space group $P\,\bar{1}$, a = 13.9005(15), b = 14.0323(11), c = 26.137(2) Å, α = 75.665(4)°, β = 81.887(4)°, γ = 74.949(5)°, V = 4753.9(7) $Å^3$, Z = 2, D_c =1.439 g cm^{-3}, T = 100(2) K, μ = 0.217 mm^{-1}, 30619 measured reflections, 17056 independent reflections, 1250 parameters, 0 restraints, $F(000)$ = 2132.0, R_1 = 0.1168, wR_2 = 0.2700 (all data), R_1 = 0.0927, wR_2 = 0.2500 [$I > 2\sigma(I)$], max. residual density 2.135 e•$Å^{-3}$, and goodness-of-fit (F^2) = 1.035.

Three H atoms from one of the benzene rings appeared to be partly substituted by iodine atoms. All these H and I atoms were refined anisotropically and the occupancies of three iodine atoms converged to 0.0390(17), 0.0254(16) and 0.0094(15) for I1, I2 and I3, respectively. It can be supposed that the NaI we used in the reaction have been degraded over time, producing I_2 which may have reacted with the phenyl rings of compound **1**.

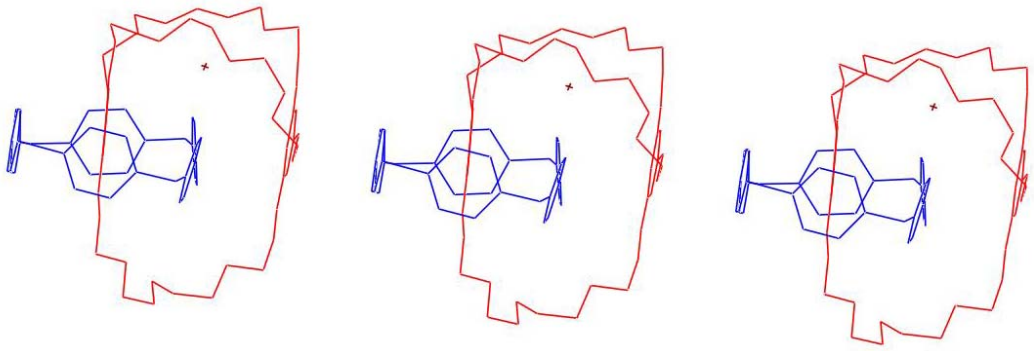


Figure S10. Part of the polar stack of [2]catenane **4** in the crystal, illustrating the alternating sequence of π-electron deficient and π-electron rich aromatic moieties. Cryptand **1** is red, cyclophane **2** is blue. PF_6 counterions, solvent molecules and hydrogens were omitted for clarity. The [2]catenane **4** forms a continuous polar π-electron donor/π-electron acceptor stacking in its crystal structure, the planes of the lattice translated alongside phloroglucinol ring and alongside bipyridinium unit being separated by 3.4086(17) Å.

8. X-ray crystal data and packing structure of [3]catenane ***5***

Crystallographic data: prism, orange, 0.58 × 0.45 × 0.17 mm^3, $C_{70}H_{99}F_{12}N_7O_{20}P_2$, *FW* 1648.50, monoclinic, space group *P* $2_1/c$, *a* = 20.196(4), *b* = 14.757(3), *c* = 28.726(6) Å, $\alpha = 90°$, $\beta = 92.64(3)°$, $\gamma = 90°$, *V* = 8552.2(3) $Å^3$, *Z* = 4, D_c=1.280 g cm^{-3}, *T* = 100 K, μ = 0.145 mm^{-1}, 62628 measured reflections, 15437 independent reflections, 969 parameters, 0 restraints, *F*(000) = 3464.000, R_1 = 0.0740, wR_2 = 0.1528 (all data), R_1 = 0.0537, wR_2 = 0.1413 [$I > 2\sigma(I)$], max. residual density 0.555 e•$Å^{-3}$, and goodness-of-fit (F^2) = 1.047.

The PLATON/SQUEEZE was used to remove the contributions of disordered water molecules, leaving two large voids at the coordinates of (1.000, -0.069, 0.250) and (1.000, -0.026, 0.750) with the same volumes of 617 $Å^3$. 80 electrons were effectively removed in each void, which corresponds with 16 water molecules in the unit cell, or 4 per asymmetric unit. After L.S.-convergence, a proper final FCF file was produced by running PLATON/CALC FCF.

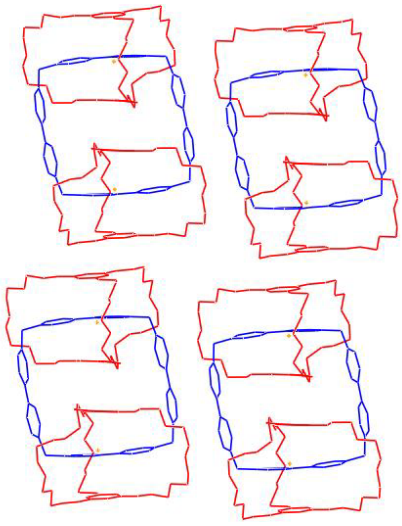


Figure S11. Part of the continuously stacked array of [3]catenane **5** in the crystal. Cryptand **1** is red, cyclophane **3** is blue. PF_6 counterions, solvent molecules and hydrogens were omitted for clarity. Unlike the stacking format in [2]catenane **4**, [3]catenane **5** loses the alternating π- donor/π-acceptor sequence but through a continuously phloroglucinol-to-phloroglucinol stacked array. The interplanar

separation between neighboring alongside phloroglucinol rings is 3.3009(10) Å, the centroid-centroid separation being 5.0712(25) Å. Adjacent stacks are positioned with one phenylene ring of each biphenylene unit in one stack parallel to (interplanar separation 3.7423(9) Å, centroid-centroid distance 3.9961(14) Å) a centrosymmetrically related one in another. These two modes of π-stacking result in the formation of a three-dimensional network of face-to-face and edge-to-face π systems.

References:

S1. Bryant, W. S.; Jones, J. W.; Mason, P. E.; Guzei, I. A.; Rheingold, A. L.; Nagvekar, D. S.; Gibson, H. W. *Org. Lett.* **1999**, *1*, 1001−1004.

S2. Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slwain, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc*. **1992**, *114*, 193−218.

S3. We have found the similar unusual mass spectra fragments in the same bis(*m*-phenylene)-32-crown-10-based cryptand complex in the paper: F. Huang, F. R. Fronczek, M. Ashraf-Khorassani and H. W. Gibson. *Tetrahedron. Lett*., 2005, **46**, 6765–6769

S4. Amabilino, D. B.; Ashton, P. R.; Brown, C. L.; Cordora, E.; Godinez, L. A.; Godinez, L. A.; Kaifer, A. E.; Newton, S. P.; Pietraszkiewicz, M.; Philp, D.; Raymo, F. M.; Reder, A. S.; Rutland, M. T.; Slawin, A. M. E.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc*. **1995**, *117*, 1271−1293.