

Selectivity Algorithm for the Formation of two Cryptand/Paraquat Catenanes

Ming Liu, Shijun Li, Menglong Hu, Feng Wang, and Feihe Huang^{*}

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

Fax: +86-571-8795-1895; Tel: +86-571-8795-3189; Email address:

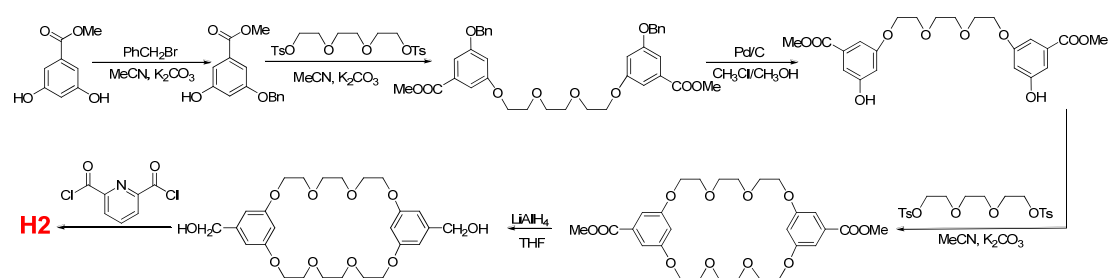
fhuang@zju.edu.cn.

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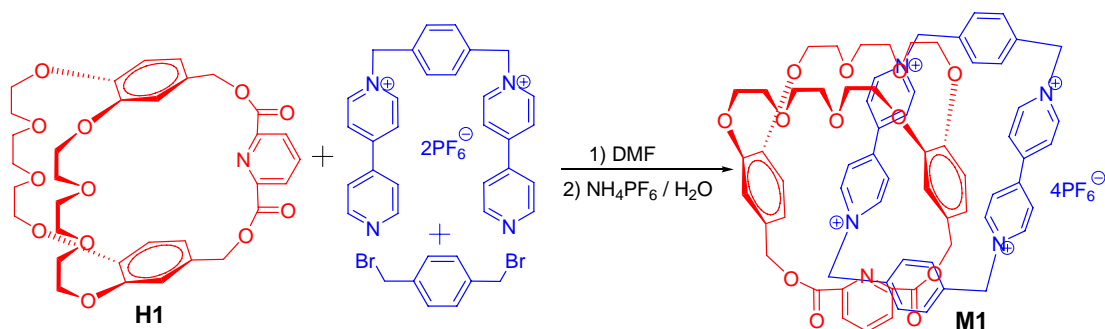
1. Materials and methods

Bis(*m*-phenylene)-26-crown-8-based cryptand **H2** was synthesized as shown in Scheme S1,^{11b} dibenzo-24-crown-8-based cryptand **H1** was synthesized by a similar route, employing methyl 3,4-dihydroxybenzoate as the starting material.^{10b,11a} 1,1'-[1,4-Phenylenebis(methylene)]bis-4,4'-bipyridinium bis(hexafluorophosphate) ([**BBIPYXY**][PF₆]₂)^{12a} was prepared according to a literature procedure. Solvents were either employed as purchased or dried according to procedures described in the literature. ¹H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer with internal standard TMS. ¹³C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer at 125 MHz. Low-resolution electrospray ionization mass spectra (LRESIMS) were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, 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 (Billerica, MA, USA).

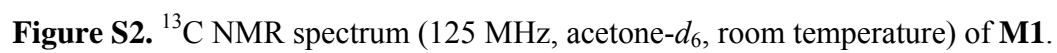
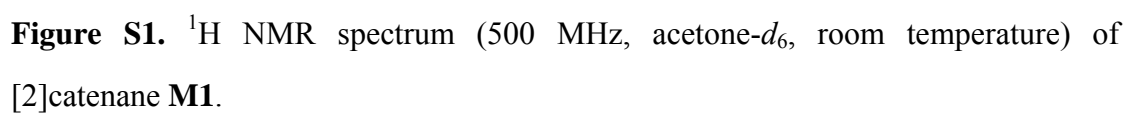


Scheme 1. General procedure to synthesize cryptand hosts.

2. Synthesis of [2]catenane **M1**



A solution of **[BBIPYXY][PF₆]₂** (63.5 mg, 0.09 mmol) in dry DMF (3 mL) was added to a solution of **H1** (120 mg, 0.19 mmol) in dry DMF (3 mL) under N₂ protection. The color of the mixture changed to faint yellow quickly. Then 1,4-bis(bromomethyl)benzene (26.5 mg, 0.09 mmol) in DMF (3 mL) was added to the mixture at room temperature. A red deposit appeared gradually. Then the reaction was stirred at room temperature for 7 days.^{S2} The solvent was removed in vacuum. The resultant residue was dissolved in a mixture of MeOH:2 N NH₄Cl:MeNO₂ (7:2:1) and subjected to column chromatography [SiO₂: MeOH:2 N NH₄Cl:MeNO₂ (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 H₂O. A deep yellow solid, [2]catenane **M1** (48 mg, 30.6 %), m.p. 267–271 °C, was precipitated from this solution by addition of a saturated aqueous NH₄PF₆ solution. The proton NMR spectrum of **M1** is shown in Figure S1. ¹H NMR (acetone-*d*₆, 500 MHz): δ 9.51–9.34 (m, 10H), 9.03–8.45 (m, 10H), 8.31–7.82 (m, 16H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.44 (s, 1H), 6.33 (d, *J* = 8.0 Hz, 1H), 6.20–5.91 (m, 10H), 5.54 (d, *J* = 11.5 Hz, 1H), 5.13 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 11.5 Hz, 1H), 4.71–4.63 (m, 2H), 4.40–3.73 (m, 24H). The ¹³C NMR spectrum of **M1** is shown in Figure S2. ¹³C NMR (125 MHz, acetone-*d*₆, room temperature): δ 148.6, 147.1, 146.3, 145.9, 143.5, 136.6, 130.7, 129.6, 127.1, 126.7, 124.2, 108.7, 106.1, 70.8, 70.4, 69.5, 68.4, 67.7, 68.5, 65.2, 64.4, 64.0, 63.3. LRESIMS is shown in Figure S3: *m/z* 1595.0 [**M** – PF₆]⁺ (96%), 725.1 [**M** – 2PF₆]²⁺ (14%). HRMS: *m/z* calcd for [**M** – PF₆]⁺ C₆₉H₆₉F₁₈N₅O₁₂P₃, 1594.3863, found 1594.3875, error 1.0 ppm; *m/z* calcd for [**M** – 2PF₆]²⁺ C₆₉H₆₉F₁₂N₅O₁₂P₂, 724.7108, found 724.7112, error 1.0 ppm.



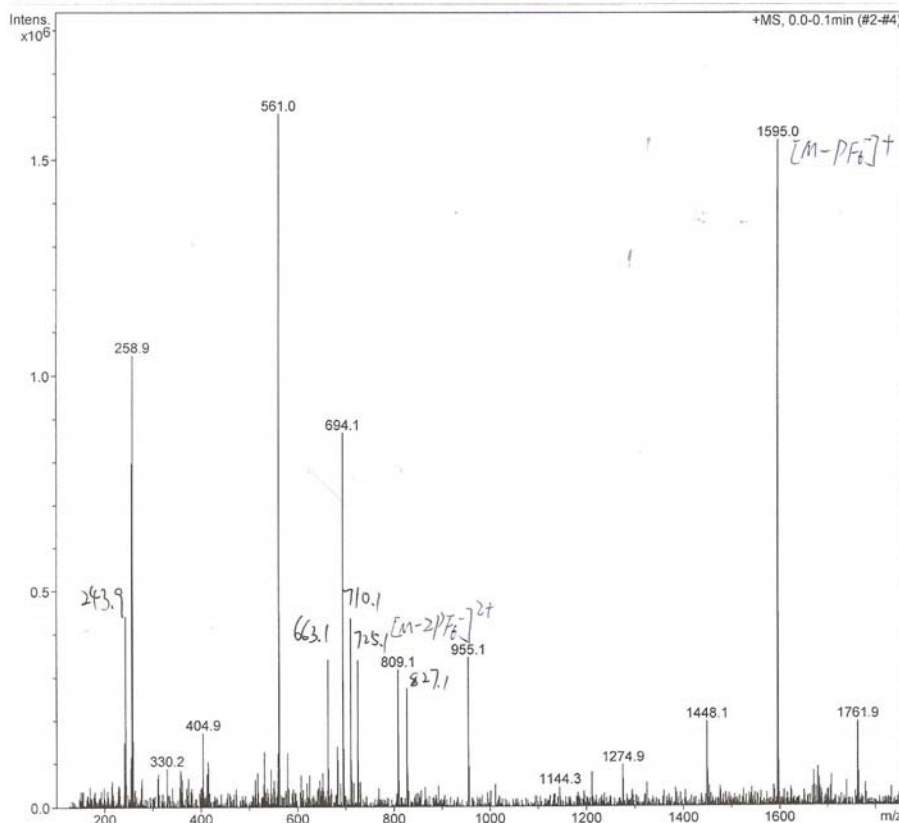
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Acquisition Parameter

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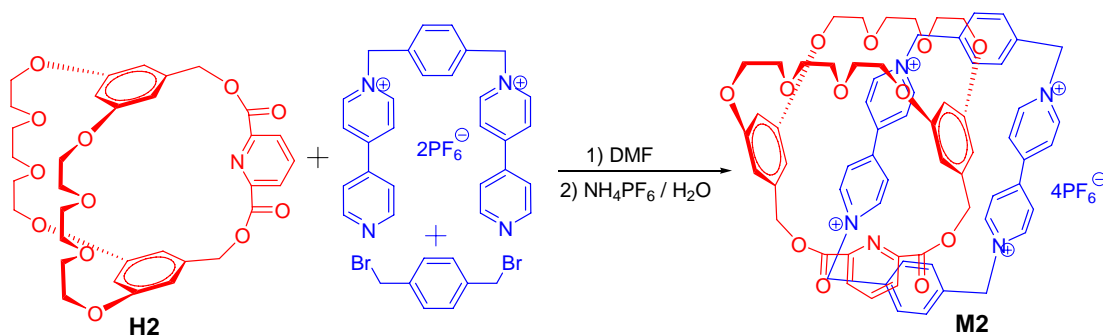
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Figure S3. Electrospray ionization mass spectrum of **M1**. Assignment of main peaks: m/z 1595.0 $[M - PF_6]^+$ (96%), 725.1 $[M - 2PF_6]^{2+}$ (14%), 561.0 $[G - CH_2PhCH_2 - PF_6]^+$ (100%).

3. Synthesis of [2]catenane **M2**



A solution of **[BBIPYXY][PF₆]₂** (106 mg, 0.15 mmol) in dry DMF (5 mL) was added to a solution of **H2** (123 mg, 0.19 mmol) in dry DMF (5 mL) under N₂ protection. The color of the mixture changed to faint yellow quickly. Then 1,4-bis(bromomethyl)benzene (44.0 mg, 0.15 mmol) in DMF (5 mL) was added to the mixture at room temperature. A red deposit appeared gradually. Then the reaction was stirred at room temperature for 7 days.^{S2} The solvent was removed in vacuum. The resultant residue was dissolved in a mixture of MeOH:2 N NH₄Cl:MeNO₂ (7:2:1) and subjected to column chromatography [SiO₂: MeOH:2 N NH₄Cl:MeNO₂ (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 H₂O. A orange solid, [2]catenane **M2** (66 mg, 25.4 %), m.p. 251–253 °C, was precipitated from this solution by addition of a saturated aqueous NH₄PF₆ solution. The proton NMR spectrum of **M2** is shown in Figure S4. ¹H NMR (acetone-*d*₆, 500 MHz): δ 10.10 (d, *J* = 8.0 Hz, 1H), 9.61–9.02 (m, 8H), 8.58–7.91 (m, 14H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 6.39 (s, 1H), 6.25–5.81 (m, 8H), 5.56–5.52 (m, 8H), 5.39 (1H), 4.38–3.39 (m, 24H). The ¹³C NMR spectrum of **M2** is shown in Figure S5. ¹³C NMR (125 MHz, acetonitrile-*d*₃, room temperature): δ 166.2, 165.8, 159.0, 160.1, 156.9, 149.7, 147.2, 146.3, 145.9, 142.5, 135.6, 131.7, 129.5, 127.2, 126.3, 125.6, 106.1, 106.1, 72.8, 71.4, 69.3, 68.4, 67.1, 65.2, 64.0, 63.5. LRESIMS is shown in Figure S6: 725.0 [M – 2PF₆]²⁺ (60%), 1595.5 [M – PF₆]⁺ (16%). HRMS: *m/z* calcd for [M – PF₆]⁺ C₆₉H₆₉F₁₈N₅O₁₂P₃, 1594.3863, found 1594.3862, error 0.06 ppm; *m/z* calcd for [M – 2PF₆]²⁺ C₆₉H₆₉F₁₂N₅O₁₂P₂, 724.7108, found 724.7106, error 0.3 ppm.

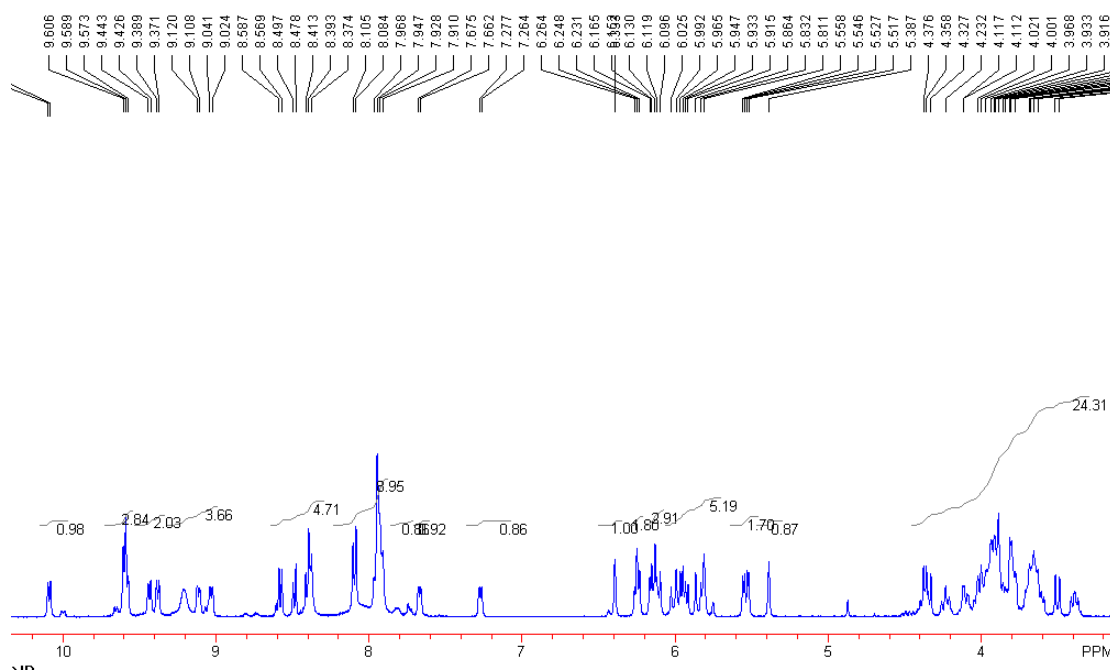


Figure S4. ^1H NMR spectrum (500 MHz, acetone- d_6 , room temperature) of **M2**.

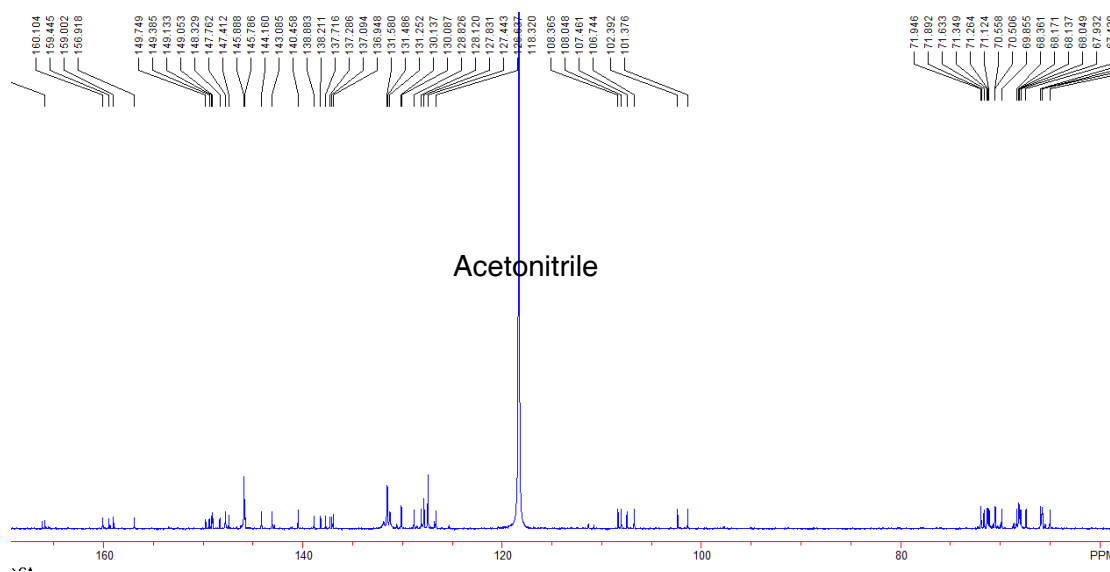


Figure S5. ^{13}C NMR spectrum (125 MHz, acetonitrile- d_3 , room temperature) of **M2**.

Spectrum 1A Plot - 2009-3-26 21:37

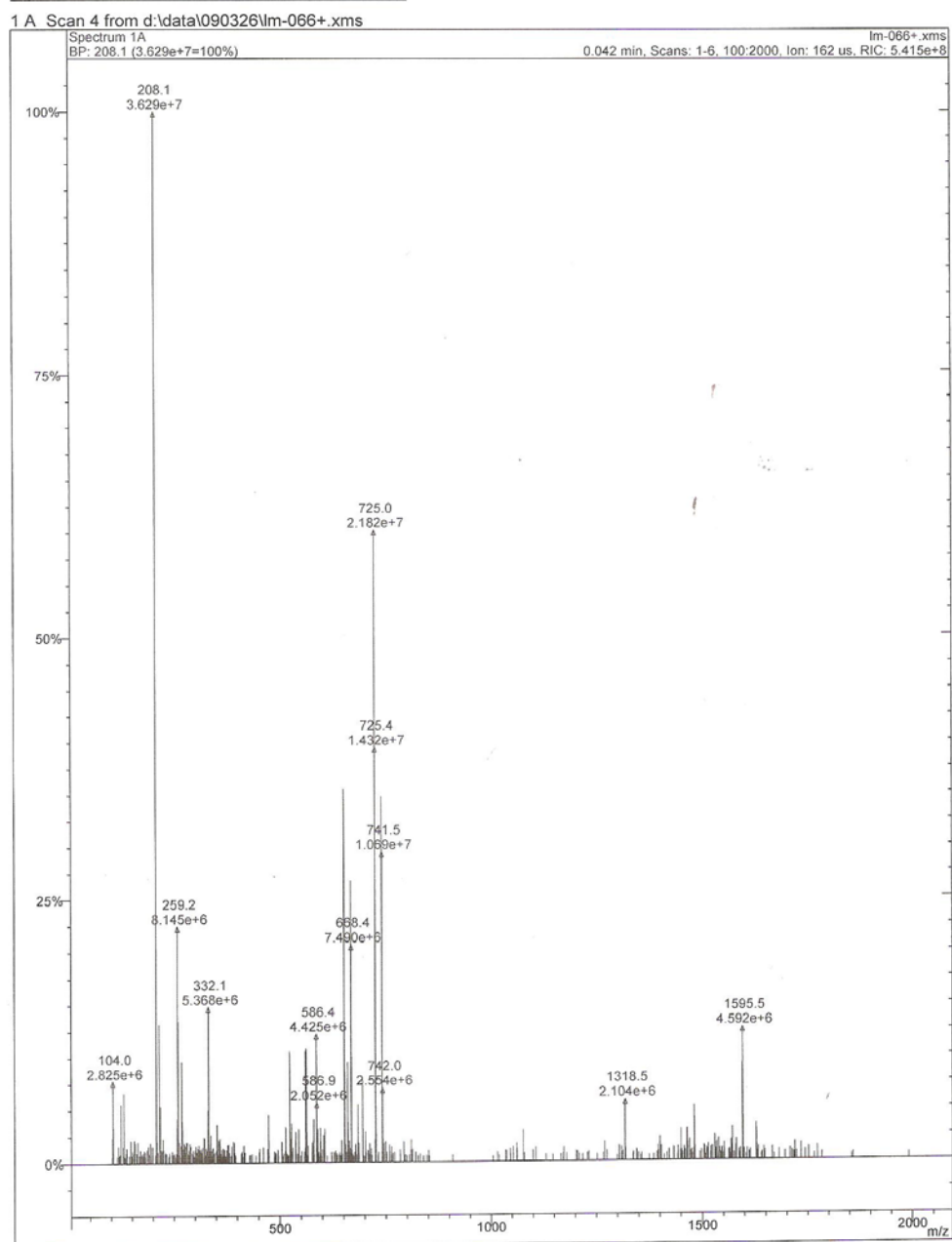


Figure S6. Electrospray ionization mass spectrum of **M2**. Assignment of main peaks:
 m/z 1595.5 [**M2** – PF₆]⁺ (14%), 725.0 [**M2** – 2PF₆]²⁺ (60%).

4. Variable-temperature NMR spectra of **M2**

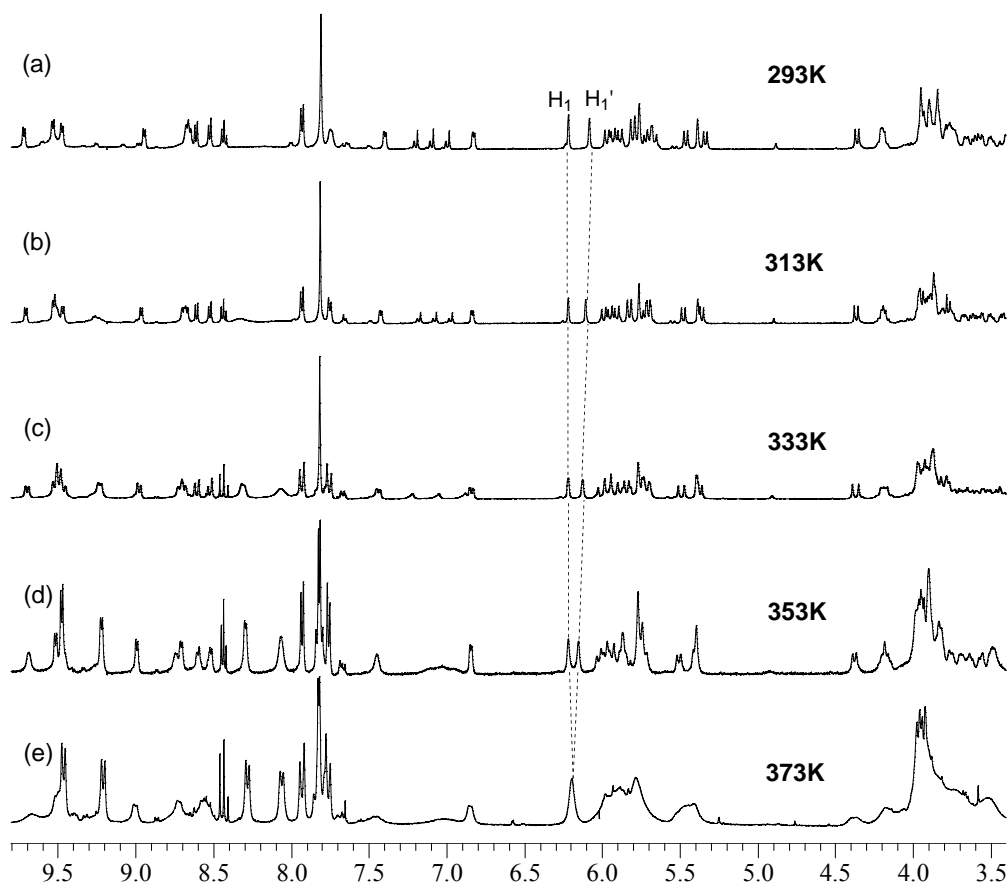


Figure S7. Partial temperature-dependent ¹H NMR spectra of **M2** recorded in DMSO-*d*₆ at (a) 20 °C, (b) 40 °C, (c) 60 °C, (d) 80 °C, (e) 100 °C.

Two rotational temperature-dependent processes of related catenanes have been identified by Stoddart et al.^{S1} Their corresponding activation barriers can be calculated using the “coalescence method”.^{S2} We also supposed that there are two possible dynamic processes in **M2**: a pirouetting process of the ethylene glycol chains of the cryptand around the cyclophane **G**, and the exchange process of the two bipyridinium units of cyclophane **G**. We investigated the protons (H₁, H₁') at around 6.2 ppm, which was attributed to the “inside” and “alongside” protons on the benzene rings of the cryptand host. The coalescence temperature (100 °C) and frequency difference of exchanging sets of signals were used to calculate the activation barrier. The calculated activation barrier (19.3 kcal·mol⁻¹) was related to the process of the ethylene glycol chains around the cyclophane **G**.

5. UV-vis spectra of catenanes **M1** and **M2**

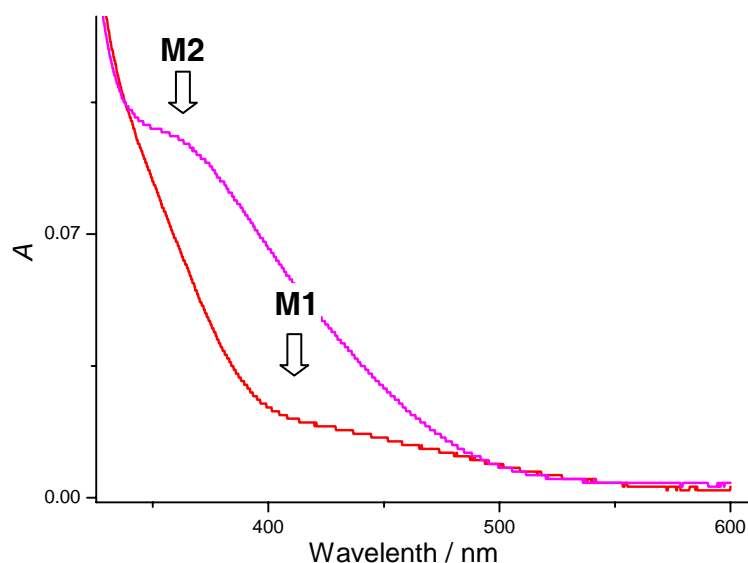


Figure S8. UV-vis spectra of catenanes **M1** (3×10^{-5} M) and **M2** (3×10^{-5} M) in MeCN, showing the charge-transfer absorption maxima at $\lambda = 410$ nm ($\epsilon = 640$ M⁻¹·dm⁻¹) and $\lambda = 352$ nm ($\epsilon = 3080$ M⁻¹·dm⁻¹), respectively.

6. X-ray crystal data for [2]catenane **M1**

Crystallographic data: red, C₇₇H₈₁F₂₄N₉O₁₂P₄, *FW* 1904.39, triclinic, space group *P1*, $a = 13.474(3)$, $b = 13.507(3)$, $c = 14.013(3)$ Å, $\alpha = 103.97^\circ$, $\beta = 99.34(3)^\circ$, $\gamma = 118.61(3)^\circ$, $V = 2053.8(7)$ Å³, $Z = 1$, $D_c = 1.540$ g cm⁻³, $T = 293$ K, $\mu = 0.213$ mm⁻¹, 11899 measured reflections, 8133 independent reflections, 1139 parameters, 3 restraints, $F(000) = 978$, $R_1 = 0.1095$, $wR_2 = 0.1228$ (all data), $R_1 = 0.0689$, $wR_2 = 0.1090$ [$I > 2\sigma(I)$], max. residual density 0.334 e·Å⁻³, and goodness-of-fit (F^2) = 1.051.

7. X-ray crystal data for [2]catenane **M2**

Crystallographic data: orange, C₈₃H₉₀F₂₄N₁₂O₁₃P₄, *FW* 2043.53, monoclinic, space group *P 2₁/c*, $a = 26.682(5)$, $b = 16.661(3)$, $c = 21.761(4)$ Å, $\alpha = 90^\circ$, $\beta = 106.67(3)^\circ$, $\gamma = 90^\circ$, $V = 9267(3)$ Å³, $Z = 4$, $D_c = 1.465$ g cm⁻³, $T = 293$ K, $\mu = 0.196$ mm⁻¹, 15354 measured reflections, 9897 independent reflections, 1234 parameters, 0 restraints,

$F(000) = 4208.000$, $R_1 = 0.1329$, $wR_2 = 0.2988$ (all data), $R_1 = 0.0989$, $wR_2 = 0.2633$ [$I > 2\sigma(I)$], max. residual density $1.125 \text{ e}\cdot\text{\AA}^{-3}$, and goodness-of-fit (F^2) = 1.100. In **M2**, the atom O50 on the isolated water molecule has a relative high thermal parameter (0.51), which means it vibrates at a large scale. Therefore the hydrogen atoms on O50 would have an even larger vibration scale. Therefore, we didn't add hydrogen atoms on it.

References:

- S1. 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.
- S2. (a) Sutherland, I. O. *Annu. Rep. NMR Spectrosc.* **1971**, *4*, 71–235. (b) Friebolin, H. P. *Basic 1D and 2D NMR Spectroscopy*; VCH Publishers: New York, 1991; Chapter 11, pp 271–272.