

A Bistable [2]Catenane Switched by Hetero-Radical Pairing Interactions

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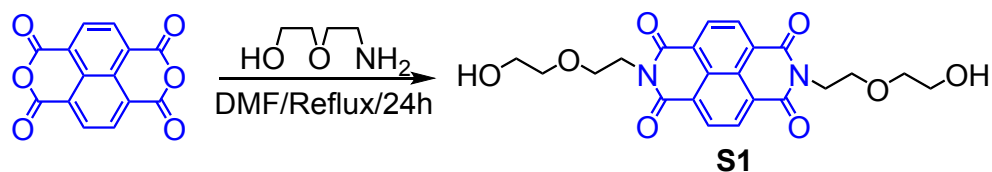
Supporting Information

1. Material, Instrumentation
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1. Material, Instrumentation

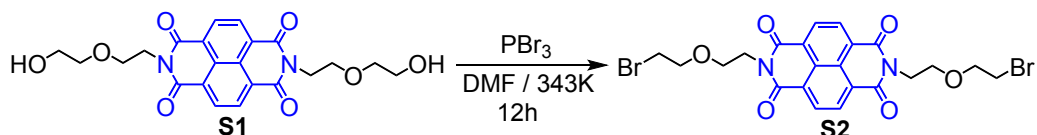
All reagents and solvents were purchased from commercial sources and used without further purification. All experiments involving radicals were handled in glove boxes. Cyclobis(paraquat-p-phenylene) tetrakis(hexafluorophosphate) ($\text{CBPQT}^{4+}\cdot 4\text{PF}_6^-$),¹ compound **1**² were prepared according to literature procedures. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature using Bruker AVANCE III 400/500 spectrometers, with working frequencies of 400/500 and 100/125 MHz for ^1H and ^{13}C , respectively. Chemical shifts are reported in ppm relative to the residual internal non-deuterated solvent signals (CD_3CN : $\delta = 1.94$ ppm; CDCl_3 : $\delta = 7.26$ ppm). High-resolution mass spectra (HRMS) were recorded on a fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Cyclic voltammetry experiments (CV) was carried out at room temperature in argon-purged solutions in MeCN with a Gamry multipurpose instrument (reference 600) interfaced to a PC. CV experiments were performed using a glassy carbon working electrode (0.018 cm^2 , Cypress system). The electrode surface was polished routinely with a $0.05\text{ }\mu\text{m}$ alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a Ag wire. The concentration of the sample and supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF_6) were $1.0 \times 10^{-3}\text{ mol L}^{-1}$ and 0.1 mol L^{-1} , respectively. The scan rate was set to 200 mV s^{-1} . UV-Vis absorption spectra were taken on a Cary series UV-Vis-NIR spectrophotometer.

2. Synthetic Procedures



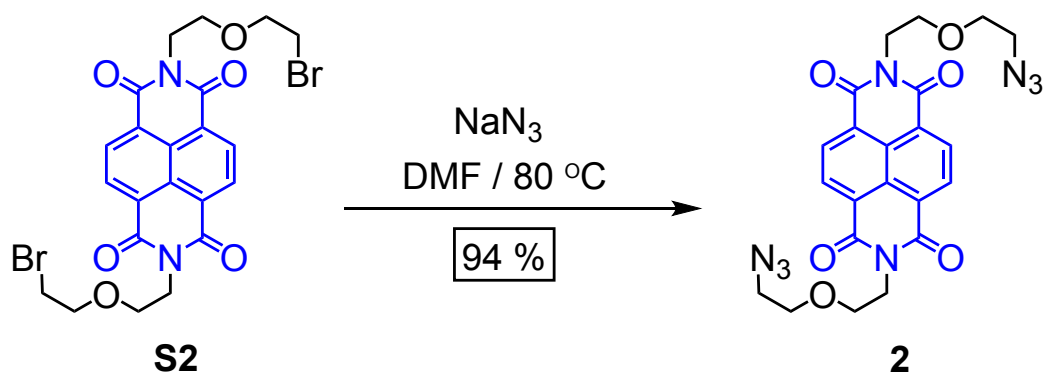
Supplementary Figure 1. Synthesis of **S1**

S1: 1,4,5,8-naphthalene tetracarboxylic dianhydride (500 mg, 1.86 mmol) and 2-(2-aminoethoxy)ethanol (488 mg, 4.65 mmol) were combined in DMF (15 mL). The reaction mixture was refluxed at 90 °C for 24 hours. After cooling to room temperature, the reaction mixture was poured into water. The precipitate was collected by filtration and washed with water (3 x 50 mL) and methanol (3 x 50 mL), before it dried in *vacuo* to afford the pure product **S1** as a pink solid (624 mg, 61%). ¹H NMR (400 MHz, CDCl₃): δ 8.77 (4H, s), 4.48 (4H, t, *J* = 5.6 Hz), 3.88 (4H, t, *J* = 5.6 Hz), 3.69-3.65 (8H, m). ¹³C NMR (100 MHz, CDCl₃): δ 163.1, 131.2, 126.8, 126.6, 76.7, 72.3, 68.2, 61.8, 40.0. (ESI-MS): *m/z* Calcd for C₂₂H₂₂N₂NaO₈: 465.1274, Found: 629.1924 (M + Na)⁺.



Supplementary Figure 2. Synthesis of **S2**

S2: PBr₃ (0.7 mL, 7.45 mmol) was added to a solution of compound **S1** (400 mg, 0.90 mmol) in dry DMF (20 mL). The mixture was stirred at 70 °C for 12 h. After cooling to room temperature, the reaction mixture was slowly poured into 5% aq. NaHCO₃, before it was dried in *vacuo* to afford compound **S2** (624 mg, 61%) as a white solid that was used in the next step without further purification.

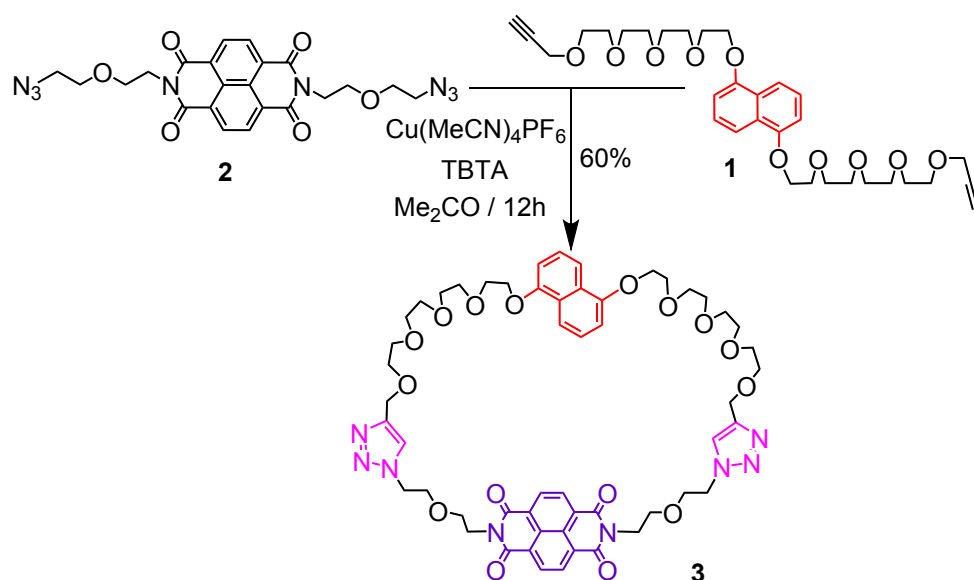


Supplementary Figure 3. Synthesis of 2

2: Compound **S2** (375 mg, 0.5 mmol) and NaN_3 (98 mg, 1.5 mmol) were dissolved in DMF (20 mL). The reaction mixture was stirred at 80 °C for 24 h. After cooling down to room temperature, the solution was poured into H_2O (50 mL). The resulting mixture was extracted with EtOAc (3 x 20 mL) and the combined organic solution was washed three times with saturated aqueous NaCl solution (3 x 100 mL). After dried with MgSO_4 , the solvent was removed in vacuo to afford the desired product **2** (231 mg, 94%) as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 8.68 (s, 4H), 4.49 (t, $J = 5.6$ Hz, 4H), 3.88 (t, $J = 5.6$ Hz, 4H), 3.71 (t, $J = 4.9$ Hz, 4H), 3.32 (t, $J = 4.9$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.0, 131.0, 126.8, 126.6, 69.8, 67.9, 50.7, 39.6. (ESI-MS): m/z Calcd for $\text{C}_{22}\text{H}_{20}\text{N}_8\text{NaO}_6$: 515.1404, Found: 515.1397 ($\text{M} + \text{Na}$) $^+$.

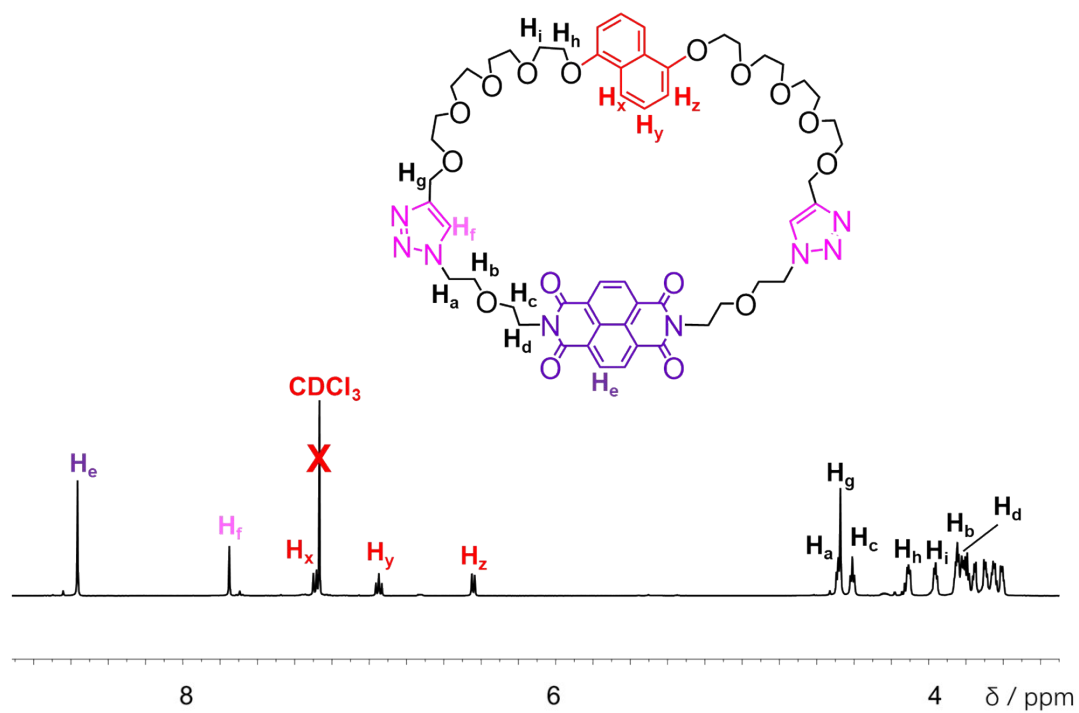
3. Synthesis, Separation and Characterization of Macrocycle 3 and [2]Catenane

$4^{4+} \cdot 4\text{PF}_6^{-}$

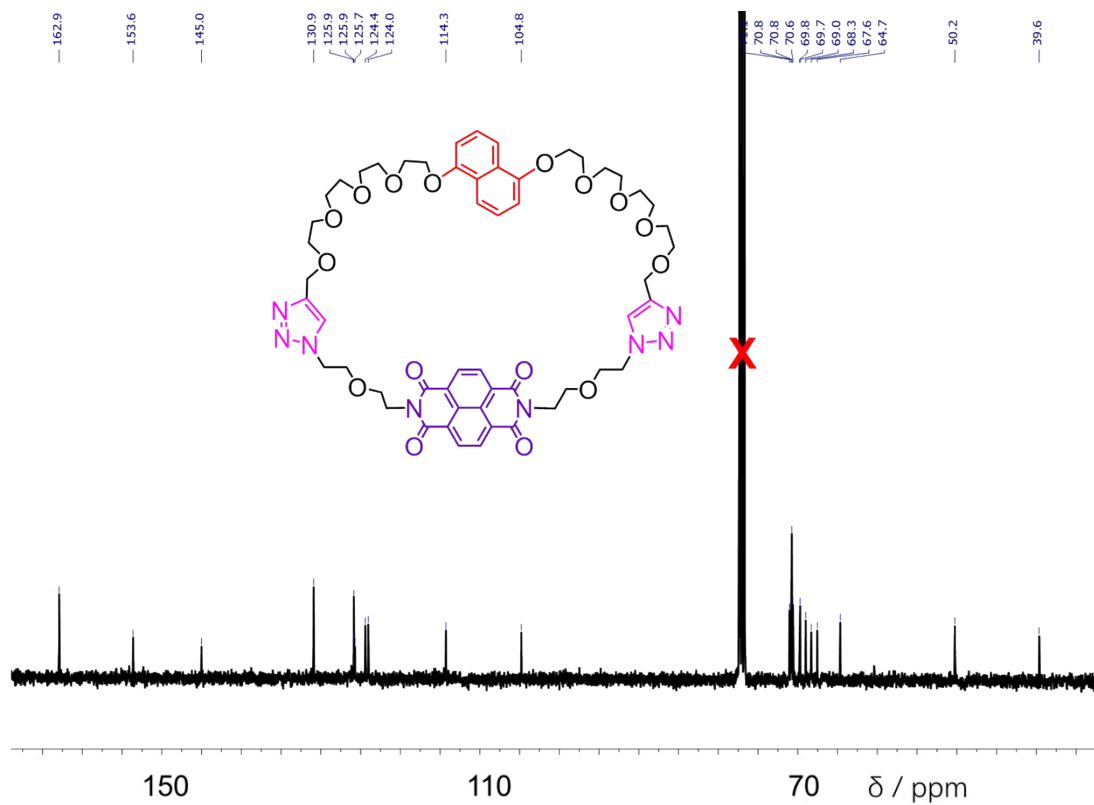


Supplementary Figure 5. Synthesis of macrocycle 3

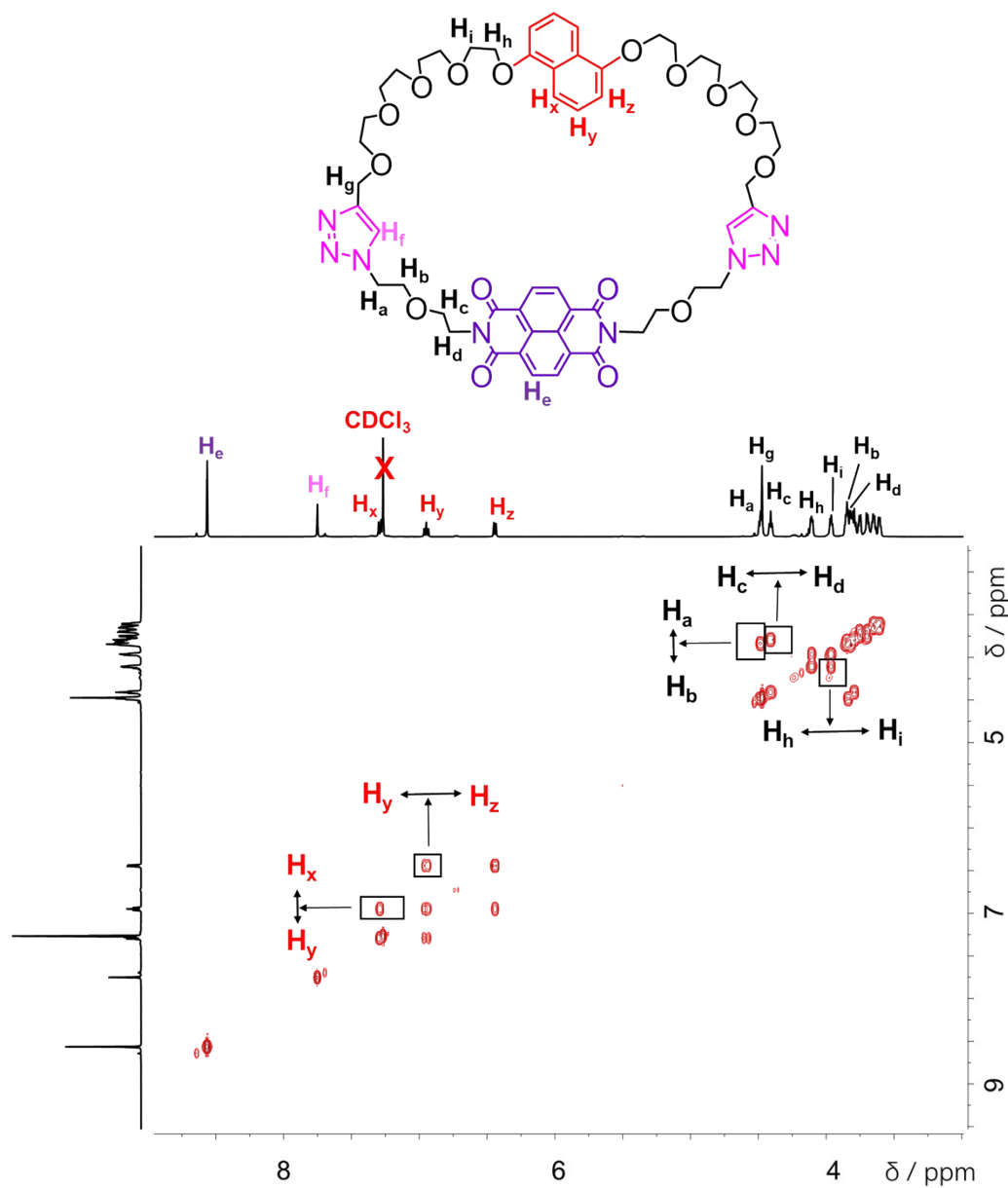
3: The diazide **2** (197 mg, 0.40 mmol), tris-(benzyltriazolylmethyl)amine (TBTA) (21 mg, 0.04 mmol), and the **1** (185 mg, 0.32 mmol) was placed in a round-bottomed flask (100 mL) and dissolved in dry Me_2CO . The flask was filled with a nitrogen atmosphere. $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (21 mg, 0.04 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. The solvent was then evaporated, yielding the crude product, which was purified by column chromatography [SiO_2 :EtOAc] to afford the pure macrocyclic compound **3** as a burgundy solid (130 mg, 36%). $^1\text{H NMR}$ (500 MHz, CDCl_3 , 298K): δ 8.56 (s, 4H), 7.75 (s, 2H), 7.29 (d, $J = 10.0$ Hz, 2H), 6.95 (t, $J = 5.0$ Hz, 2H), 6.44 (d, $J = 10.0$ Hz, 2H), 4.48 (t, $J = 5.0$ Hz, 4H), 4.47 (s, 4H), 4.41 (t, $J = 5.0$ Hz, 4H), 4.11 (t, $J = 5.0$ Hz, 4H), 3.96 (t, $J = 5.0$ Hz, 4H), 3.86-3.60 (m, 32H). $^{13}\text{C NMR}$ (600 MHz, CDCl_3 , 298K): $\delta = 162.9, 153.6, 145.0, 130.9, 125.9, 125.9, 125.7, 124.4, 124.0, 114.3, 104.8, 71.1, 70.8, 70.8, 70.6, 69.8, 69.7, 69.0, 68.3, 67.6, 64.7, 50.2, 39.6$. **ESI-HRMS** m/z calcd for $[\text{M}+\text{Na}]^+$ 1103.4181; found 1103.4179.



Supplementary Figure 6. Partial ^1H NMR spectra (500 MHz, CDCl_3 , 298 K) of **3**.

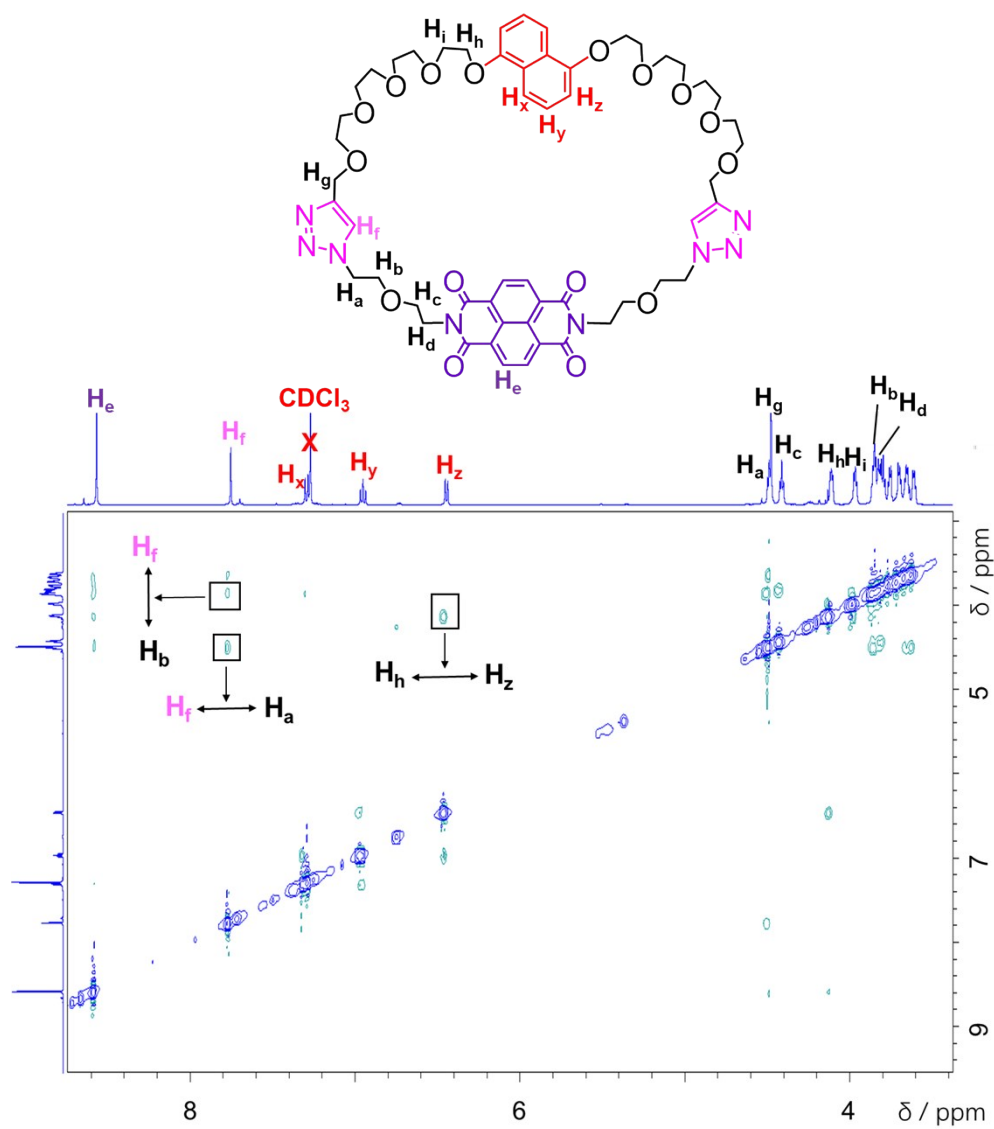


Supplementary Figure 7. ¹³C NMR spectra (150 MHz, CDCl₃, 298 K) of **3**.

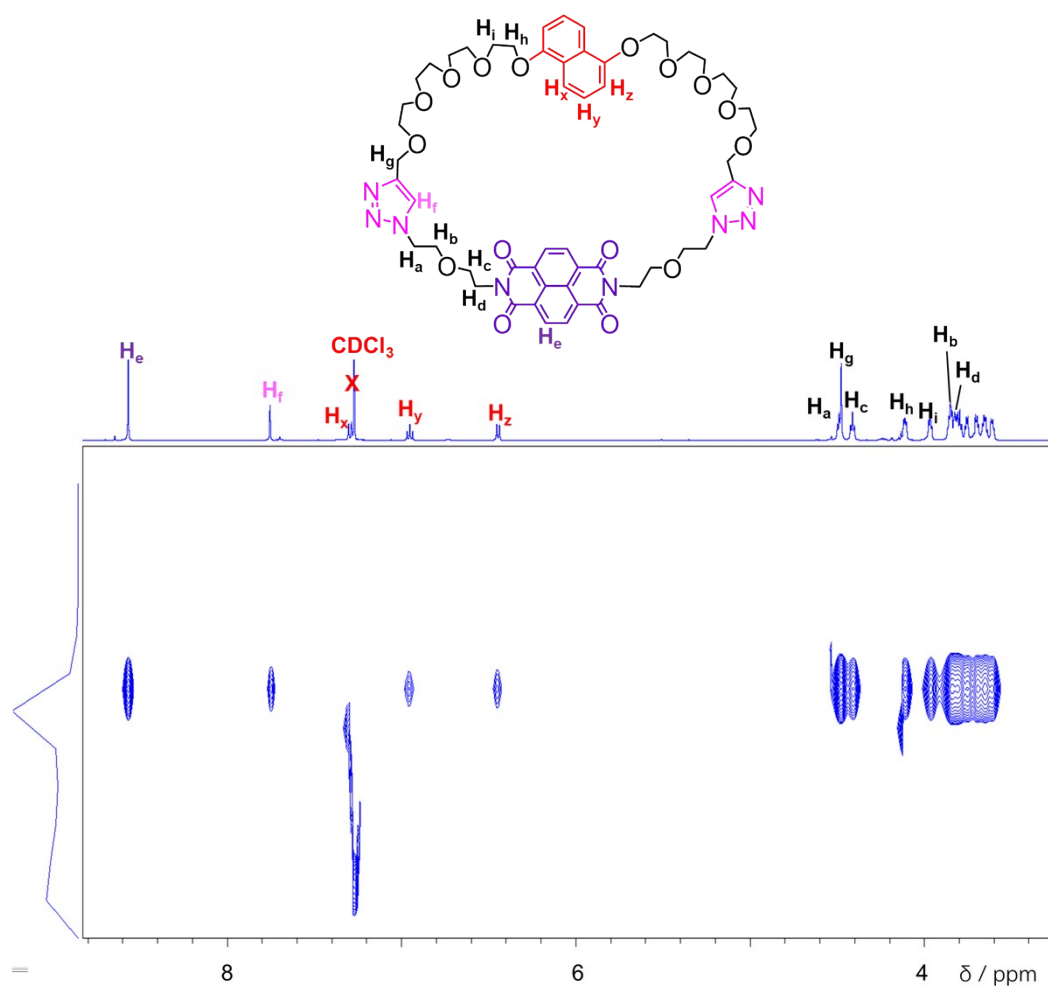


Supplementary Figure 8. ¹H-¹H COSY spectrum (500 MHz, CDCl₃, 298 K) of **3**.

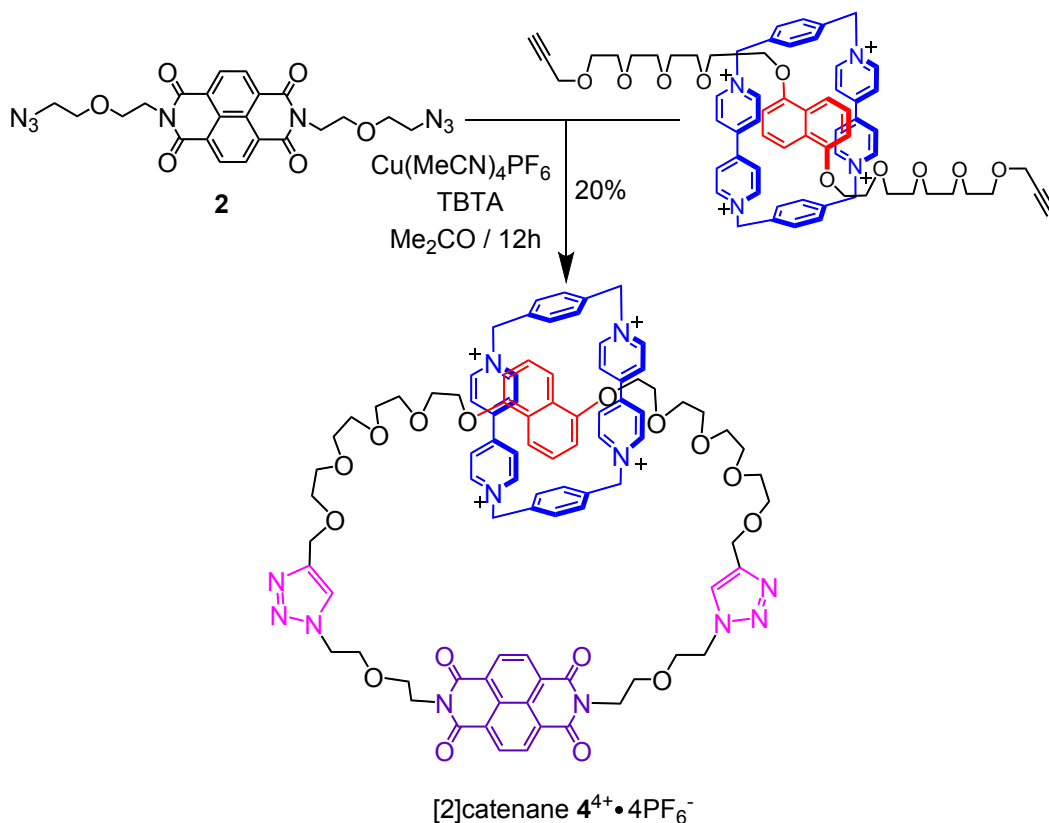
Key correlation peaks are labeled in the spectrum.



Supplementary Figure 9. ^1H - ^1H NOESY spectrum (500 MHz, CDCl_3 , 298 K) of 3. Key correlation peaks are labeled in the spectrum.

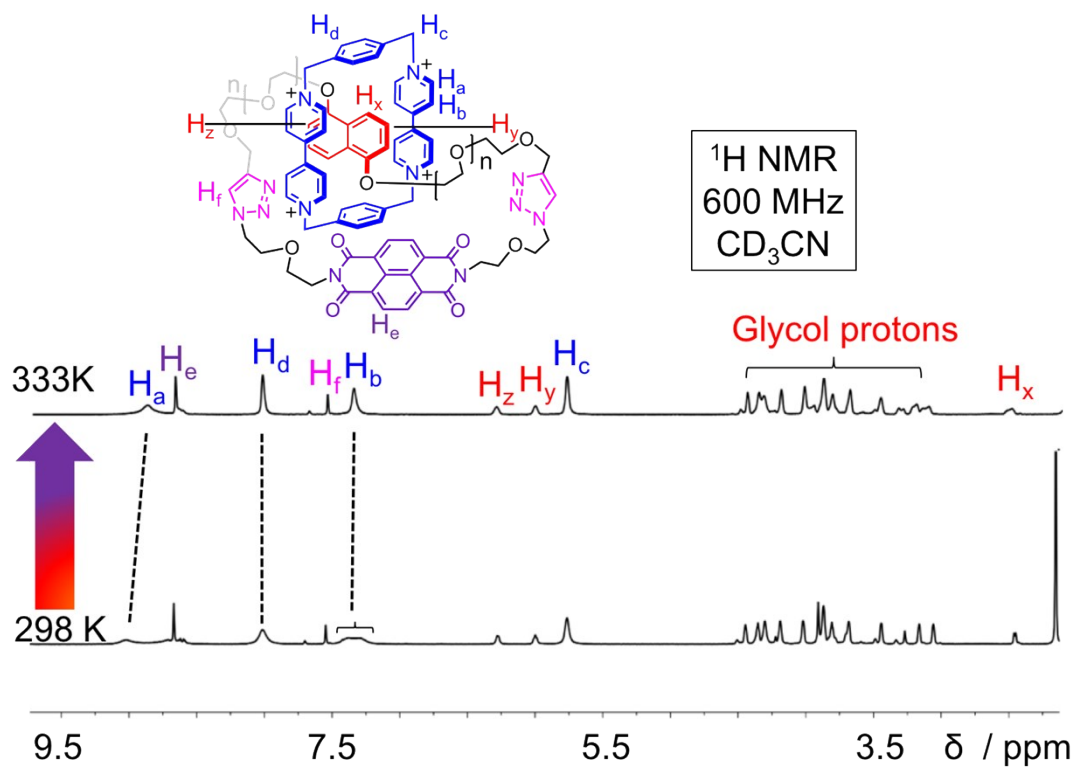


Supplementary Figure 10. DOSY spectrum (500 MHz, CDCl₃, 298 K) of **3**.

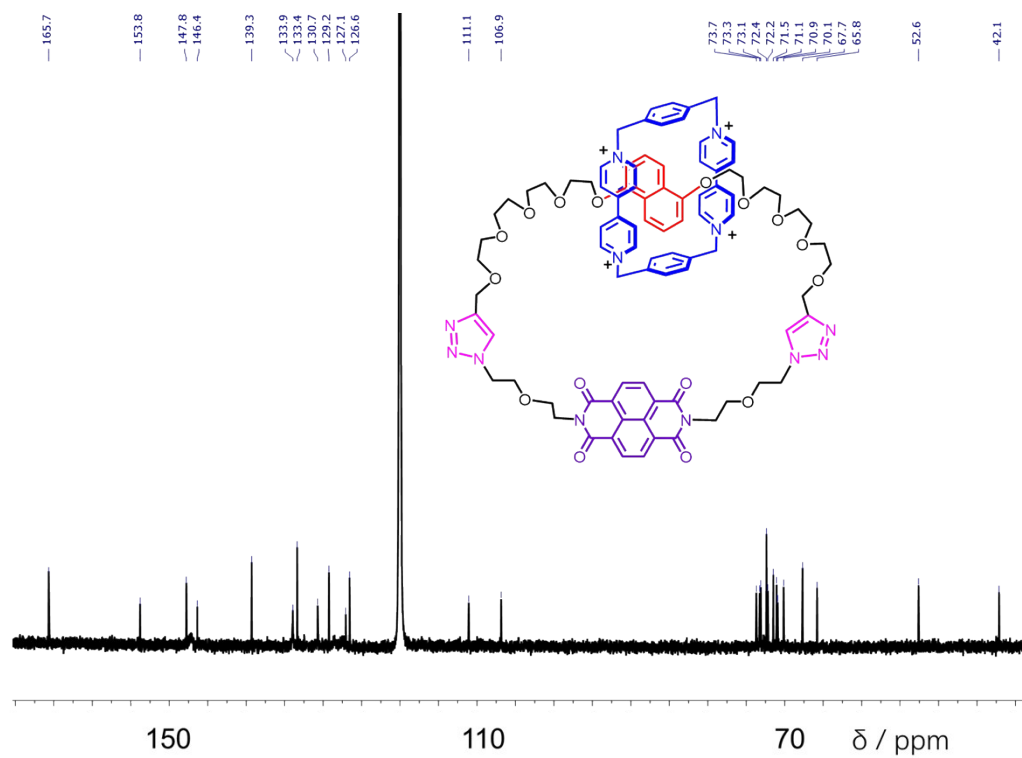


Supplementary Figure 11. Synthesis of [2]catenane $4^{4+} \cdot 4PF_6^-$

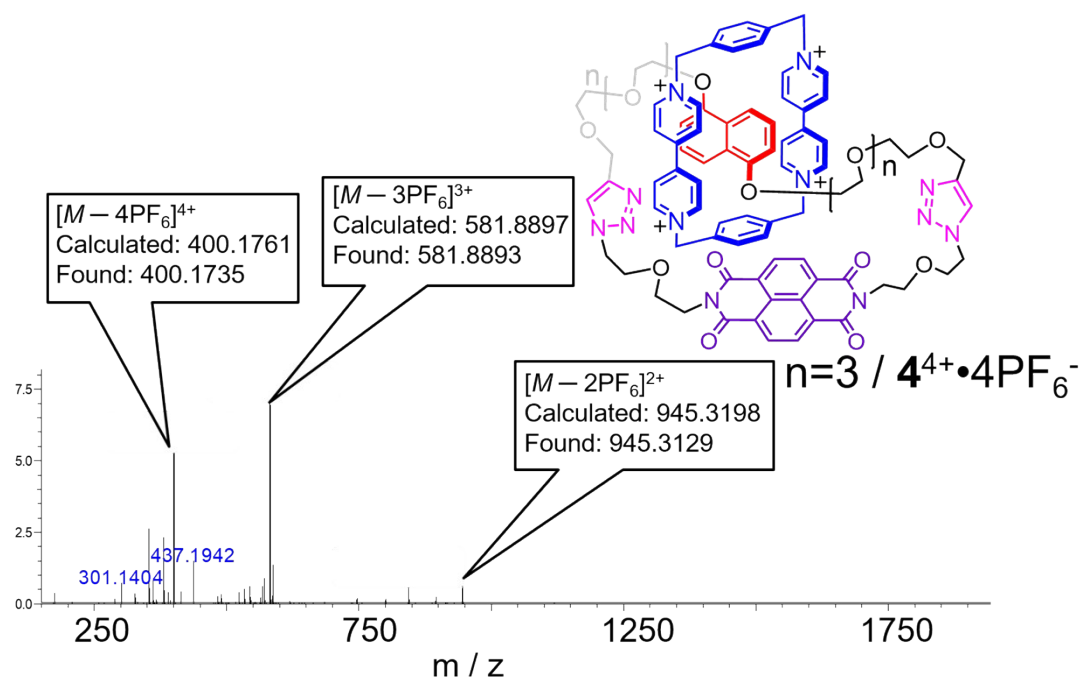
[2]catenane $4^{4+} \cdot 4PF_6^-$: The diazide **2** (80 mg, 0.16 mmol), compound **1** (129 mg, 0.21 mmol) and **CBPQT** $^{4+} \cdot 4PF_6^-$ (55 mg, 0.05 mmol), as well as $Cu(MeCN)_4PF_6$ (21 mg, 0.04 mmol) and TBTA (21 mg, 0.04 mmol), were dissolved in Me_2CO (20 mL) at room temperature. The reaction mixture was stirred overnight under argon. The solvent was evaporated off and the resulting purple solid was purified by column chromatography [SiO_2 : 2M NH_4Cl / MeOH / $MeNO_2$ (12 : 7 : 1)]. The solvent was then evaporated, followed by adding NH_4PF_6 (2 g) and water (100 mL). The purple solid was collected and washed with water to give $4^{4+} \cdot 4PF_6^-$ (23.5 mg, 20%). 1H NMR (600 MHz, CD_3CN , 333K): δ 8.88 (b, 8H), 8.68 (s, 4H), 8.03 (s, 8H), 7.55 (s, 2H), 7.36 (s, 8H), 6.28 (d, $J = 7.8$ Hz, 1H), 6.03 (t, $J = 8.4$ Hz, 1H), 5.78 (s, 8H), 4.45 (s, 4H), 4.37-3.11 (m, 48H), 2.5 (m, 2H). ^{13}C NMR (600 MHz, CD_3CN , 298K): δ = HRMS (ESI): m/z Calcd for $C_{90}H_{96}N_{12}O_{16}$: 400.1762, Found: 400.1735 ($M - 4PF_6$) $^{4+}$. m/z Calcd for $C_{90}H_{96}F_6N_{12}O_{16}P$: 581.8898, Found: 581.8893 ($M - 3PF_6$) $^{3+}$. m/z Calcd for $C_{90}H_{96}F_{12}N_{12}O_{16}P_2$: 945.3170, Found: 945.3129 ($M - 2PF_6$) $^{2+}$.



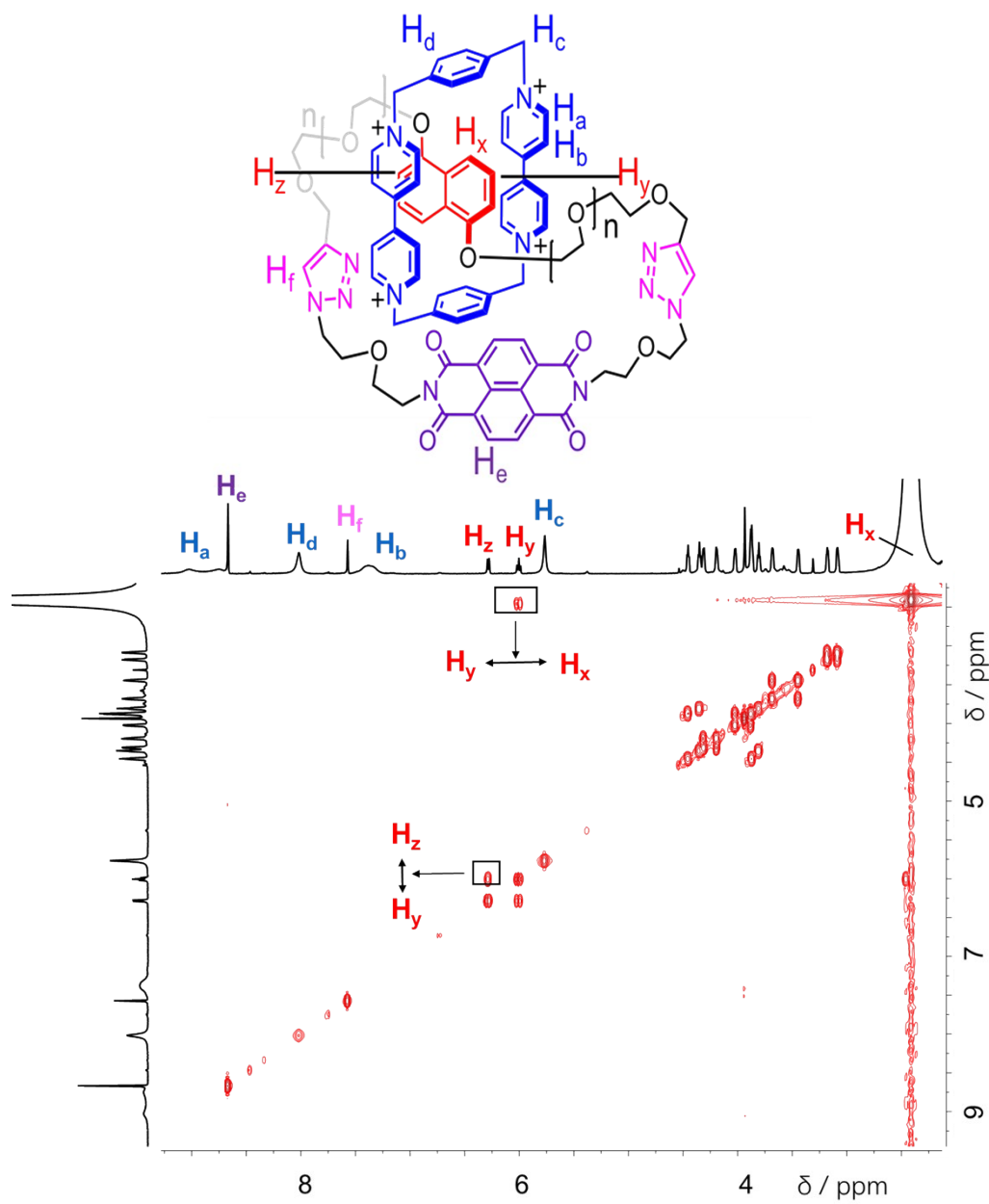
Supplementary Figure 12. Partial $^1\text{H NMR}$ spectrum of the [2]catenane $4^{4+} \cdot 4\text{PF}_6^-$ (600 MHz, CD_3CN), recorded at 298 K (bottom) and 333 K (top).



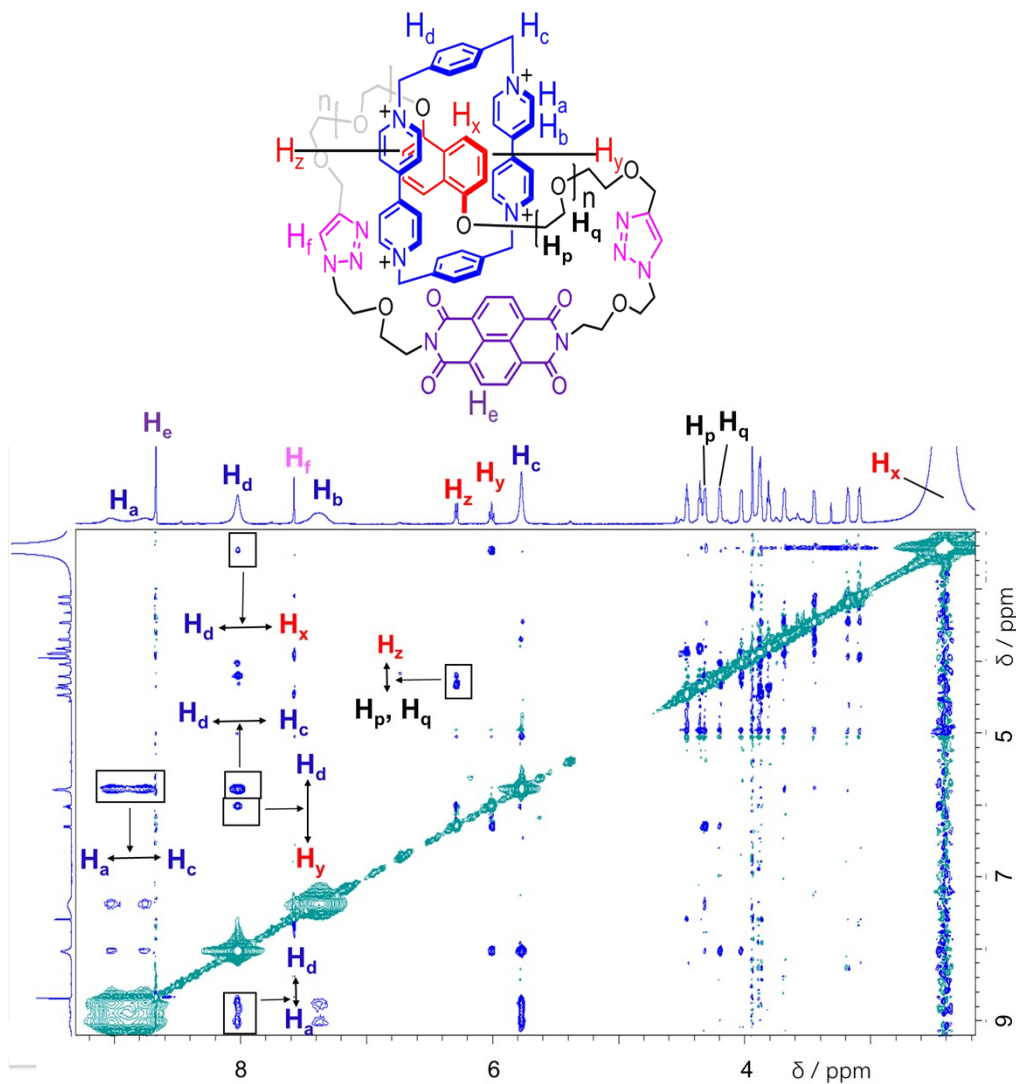
Supplementary Figure 13. ^{13}C NMR spectra (150 MHz, CD_3CN , 298 K) of [2]catenane $4^{4+}\cdot 4\text{PF}_6^-$.



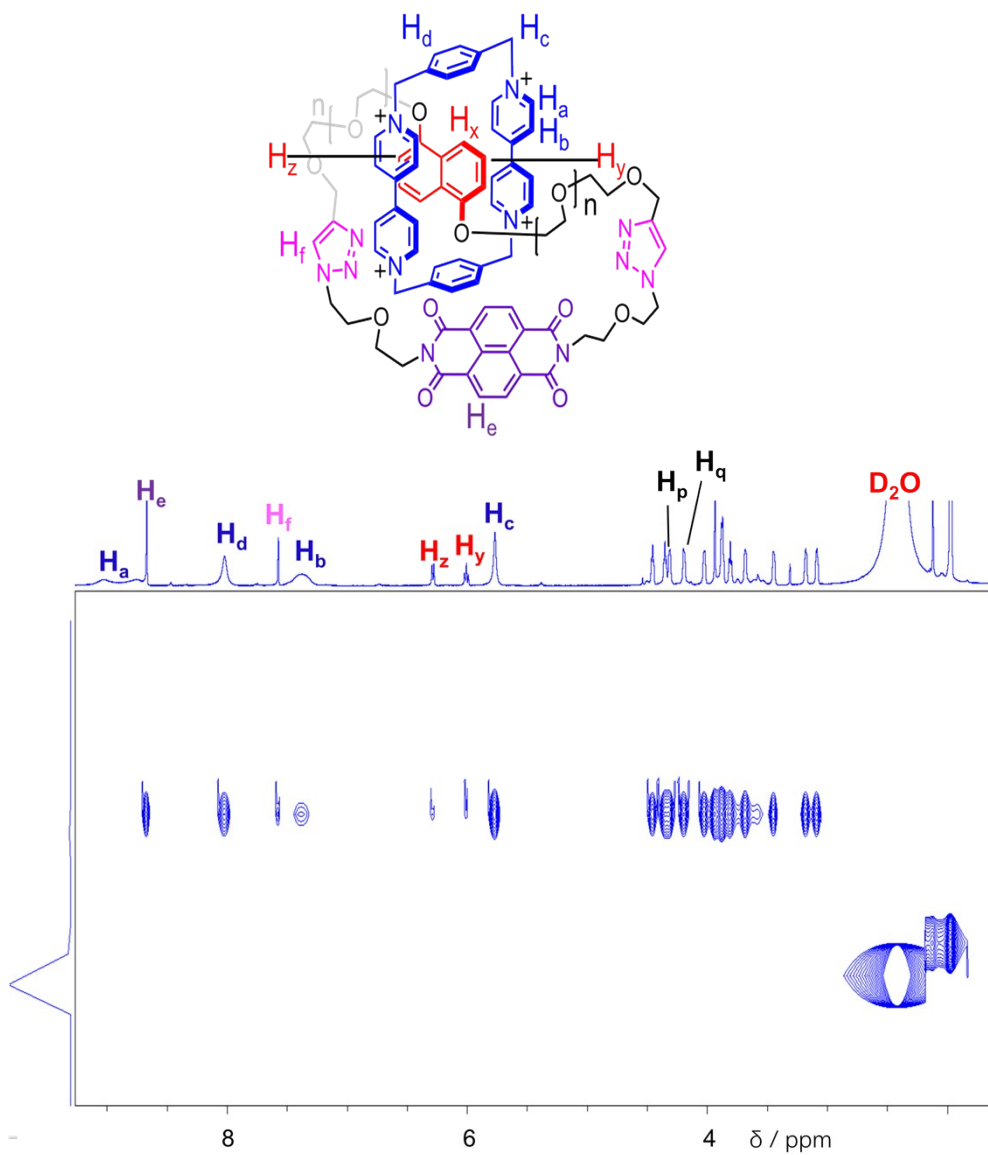
Supplementary Figure 14. ESI-MS of the [2]catenane $4^{4+} \cdot 4PF_6^{-}$. The signals labeled in the spectra correspond to molecular cations that contain four, three, and two positive charges, by losing corresponding amount of counteranions.



Supplementary Figure 15. 1H - 1H COSY spectrum (500 MHz, CD_3CN , 298K) of the [2]catenane $4^{4+} \cdot 4PF_6^{-}$. Key correlation peaks are labeled in the spectrum.

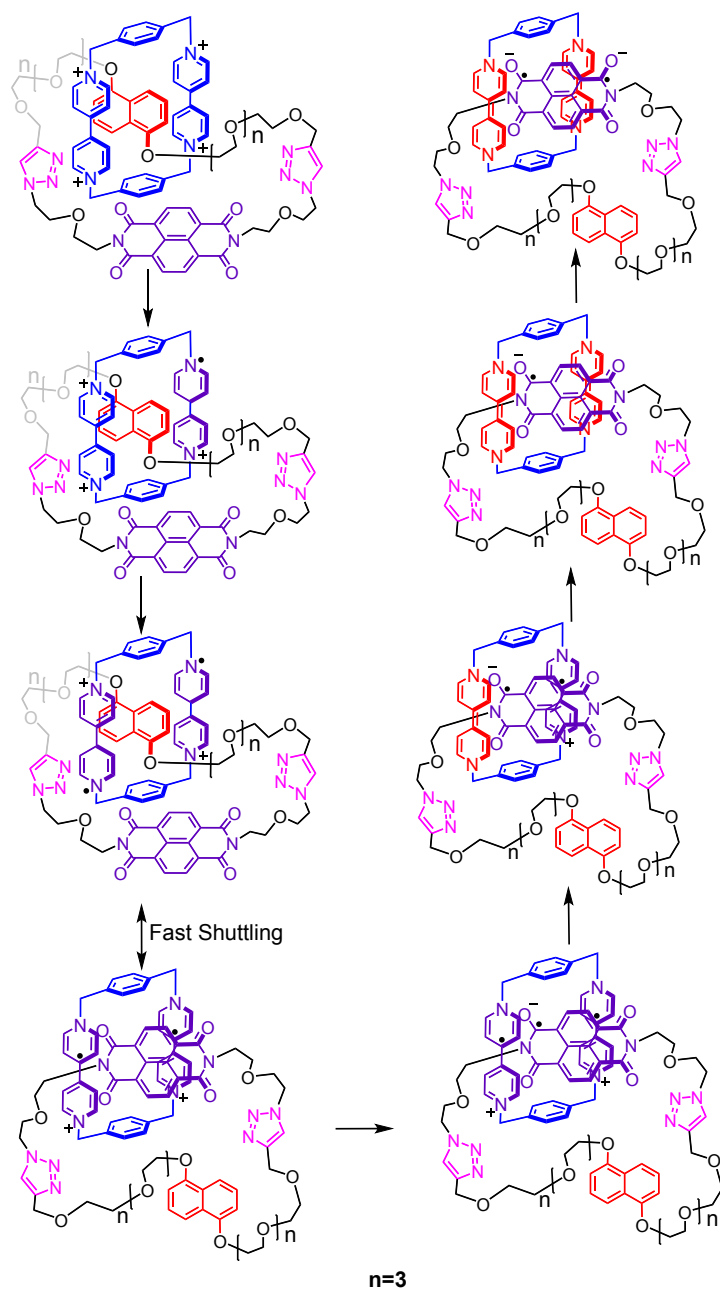


Supplementary Figure 16. 1H - 1H NOESY spectrum (500 MHz, CD_3CN , 298K) of the [2]catenane $4^{4+} \cdot 4PF_6^{-}$. Key correlation peaks are labeled in the spectrum.

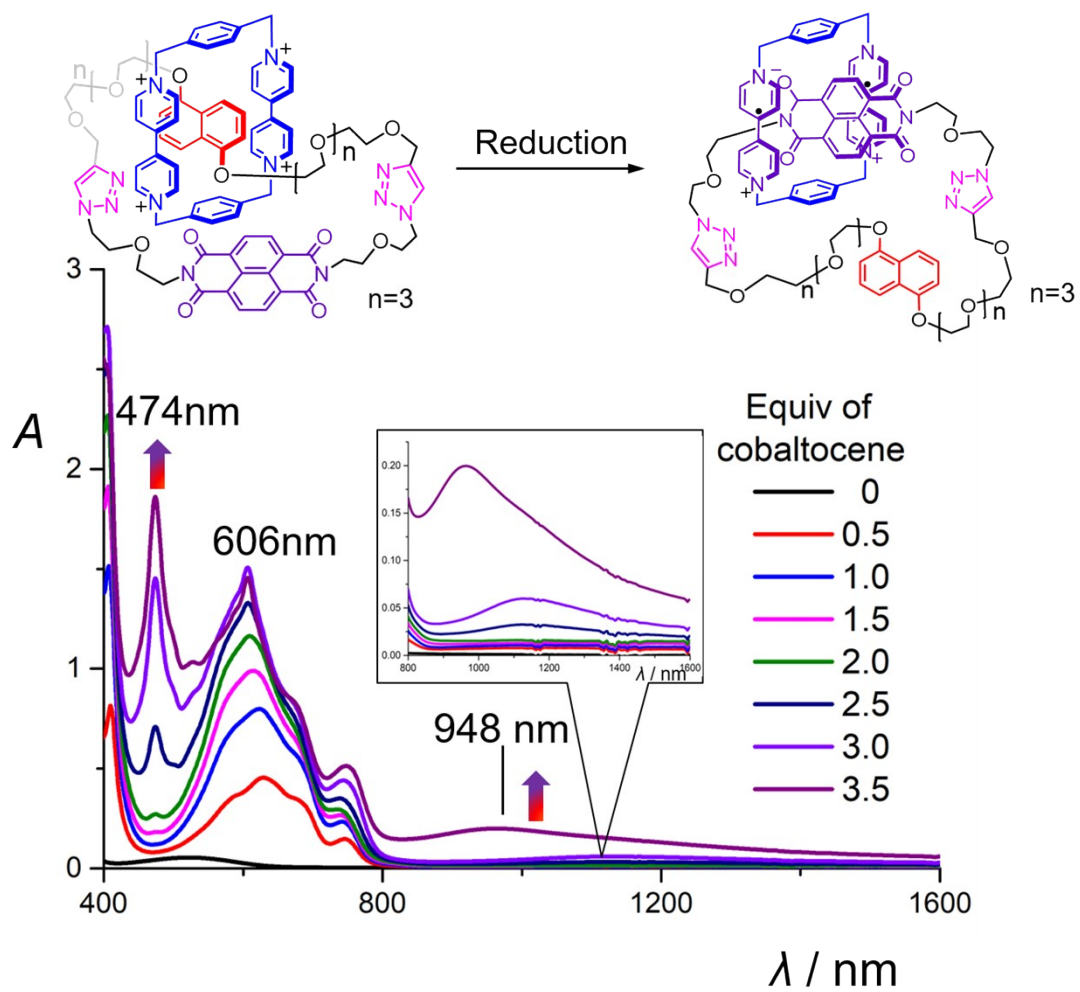


Supplementary Figure 17. ^1H - ^1H DOSY spectrum (500 MHz, CD_3CN , 298K) of the [2]catenane $4^{4+}\cdot 4\text{PF}_6^-$.

4. The Whole Reduction of Process of [2]Catenane $4^{4+}\cdot 4\text{PF}_6^-$ and UV/ Vis/ NIR Spectroscopy.

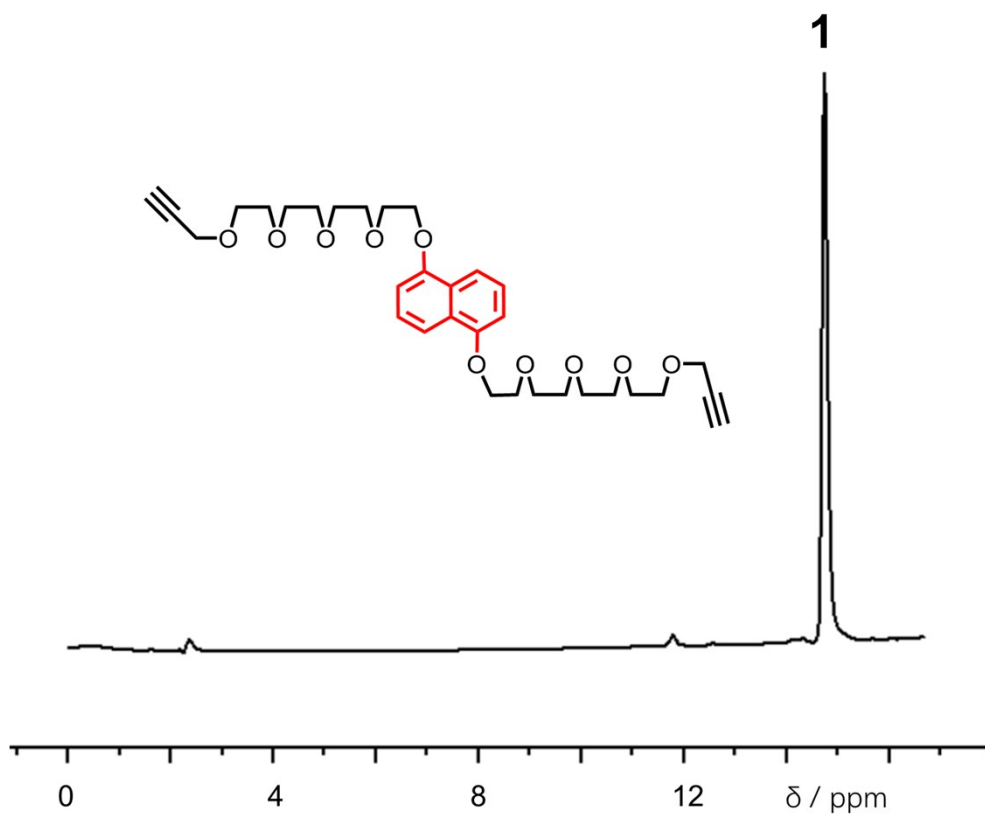


Supplementary Figure 18. Reduction of the [2]Catenane $4^{4+} \cdot 4PF_6^-$

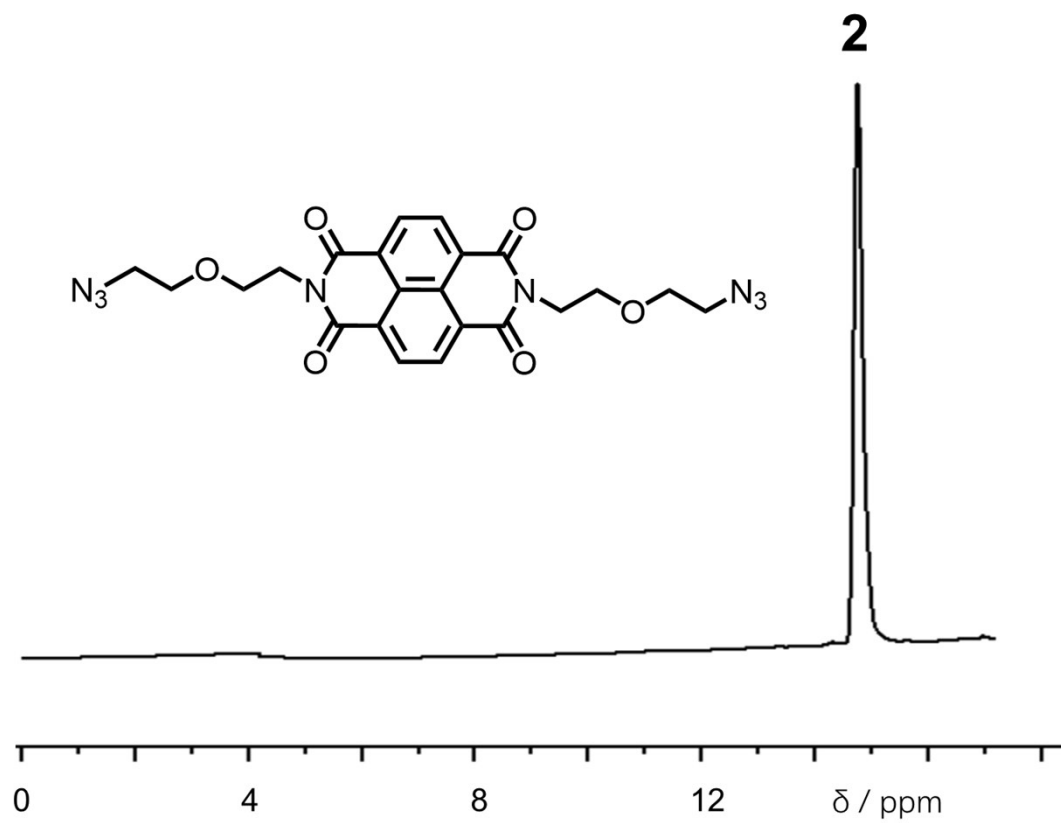


Supplementary Figure 19. The UV/Vis/NIR absorption spectra of the [2]Catenane $4^{4+} \cdot 4PF_6^-$, after adding different amount (from 0 to 3.5 equiv) of reductant, namely cobaltocene.

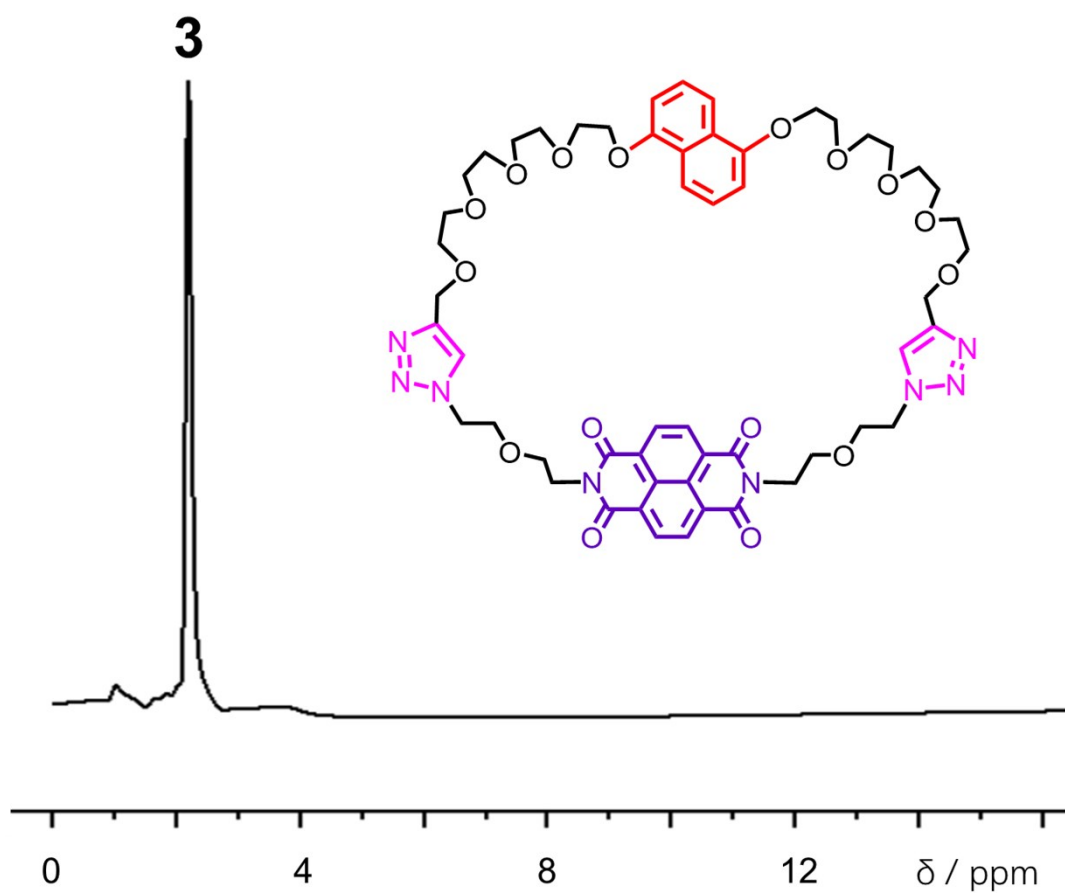
5. HPLC Analyses



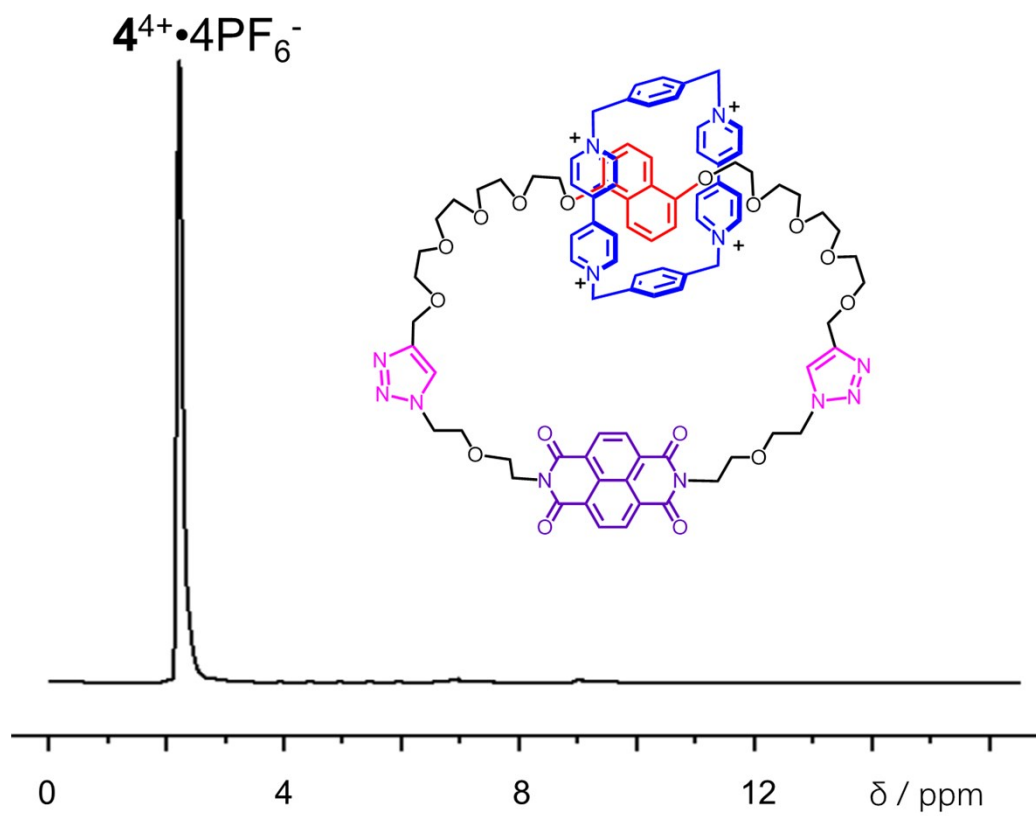
Supplementary Figure 20. Reversed-phase HPLC analysis of **1**.



Supplementary Figure 21. Reversed-phase HPLC analysis of **2**.



Supplementary Figure 22. Reversed-phase HPLC analysis of the macrocycle **3**.



Supplementary Figure 23. Reversed-phase HPLC analysis of the [2]catenane. $4^{4+} \cdot 4\text{PF}_6^-$.

6. Reference

- 1 M. Asakawa, W. Dehaen, G. L'abbé, S. Menzer, J. Nouwen, F. M. Raymo, J. F. Stoddart, D. J. Williams, *J. Org. Chem.* 1996, **61**, 9591-9595.
- 2 O. Š. Miljanić, W. R. Dichtel, S. I. Khan, S. Mortezaei, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* 2007, **129**, 26, 8236-8246.