

Supporting Materials

Cyclophane Capsule Motifs with Side Pockets

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Synthesis:

Triad 2. A 3-neck round bottom flask equipped with two dropping funnels was filled with dry CH₂Cl₂ (500 mL) under argon in a dry ice/acetone bath. The funnels were charged with 1,3,5-benzenetricarbonyl trichloride (1.00 g, 3.77 mmol) in CH₂Cl₂ (150 mL), N'-methyl-2,2'-diaminodiethylamine (0.66 g, 5.65 mmol), and NEt₃ (1.58 mL, 11.3 mmol) in CH₂Cl₂ (150 mL). The reagents in the two dropping funnels were added into the flask simultaneously at equal rates over 1 h and the reaction mixture was stirred for 24 h. The solvent was evaporated and the residue was redissolved in 300 mL of CH₂Cl₂. The organic phase was washed with saturated NaHCO₃ solution (200 mL), dried with Na₂SO₄, and concentrated. The crude product was purified by column chromatography (basic Al₂O₃, 3% MeOH in CH₂Cl₂) to give pure **2** (yield: 15 %). ¹H NMR (400 MHz, DMSO-*d*₆, 23 °C, TMS): δ = 7.94 (br s, 6H, NH), 7.92 (s, 6H, ArH), 3.37 (q, *J* (H,H) = 4.5 Hz, 12H, CH₂), 2.57 (t, *J* (H,H) = 4.5 Hz, 12H, CH₂), 2.34 (s, 9H, CH₃); ¹³C NMR (400 MHz, DMSO-*d*₆) δ 165.3 (C=O), 134.1, and 127.6 (Ar), 54.6, and 42.4 (CH₂), 36.7 (CH₃). FAB MS *m/z* 664.4 [MH]⁺.

Tetrad 3-E and 3-S. N'-Methyl-2,2'-diaminodiethylamine (0.72 g, 6.14 mmol) was added to a solution of tetramethyl 1,2,4,5-benzenetetracarboxylate (0.95 g, 3.07 mmol) in MeOH (110 mL). The reaction mixture was stirred under reflux condition for 5 days. After the reaction, the precipitates were removed by filtration and the filtrate was evaporated. This crude product was purified by column chromatography (neutral Al₂O₃, 5% MeOH in CH₂Cl₂) to give the pure isomers **3-E** and **3-S** (yield: 7% for each). **3-E:** ¹H NMR (400 MHz, DMSO-*d*₆, 23 °C, TMS): δ = 7.94 (br s, 8H, NH), 7.21 (s, 4H, ArH), 3.36 (m, 8H, CH₂), 3.25 (m, 8H, CH₂), 2.56 (m, 8H, CH₂), 2.45 (m, 8H, CH₂), 2.22 (m, 12H, CH₃); ¹³C NMR (400 MHz, DMSO-*d*₆) δ 167.2 (C=O), 135.8, and 126.5 (Ar), 55.6, and 41.1 (CH₂), 36.7 (CH₃). FAB MS *m/z* 833.5 [MH]⁺. **3-S:** ¹H NMR (400 MHz,

DMSO- d_6 , 23 °C, TMS): δ = 8.35 (br s, 8H, NH), 7.20 (s, 4H, ArH), 3.69 (m, 8H, CH₂), 2.90 (m, 8H, CH₂), 2.64 (m, 8H, CH₂), 2.48 (m, 8H, CH₂), 2.28 (m, 12H, CH₃); ¹³C NMR (400 MHz, DMSO- d_6) δ 167.6 (C=O), 136.7, and 127.4 (Ar), 55.1, and 41.2 (CH₂), 36.7 (CH₃). FAB MS m/z 833.5 [MH]⁺.

NMR studies:

¹H NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz. Each titration was performed by 20 measurements in DMSO- d_6 at room temperature. Aliquots from a stock solution of the $n\text{Bu}_4\text{N}^+$ salts (20 mM) were gradually added to the initial solution of ligand (2 mM). Up to ten anion equivalents were added during the titrations. All proton signals were referenced to a TMS standard. The association constants K were calculated by EQNMR. All titration curves fit best in 1:1 or 1:2 binding modes of the ligand to anions.

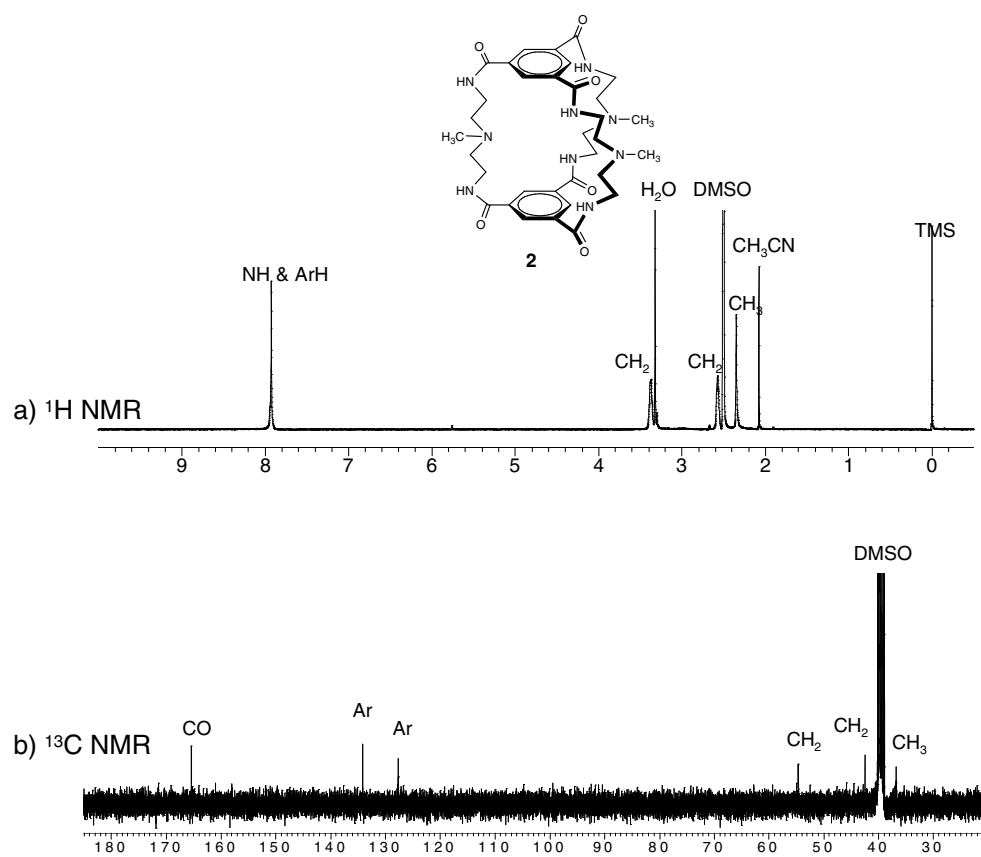
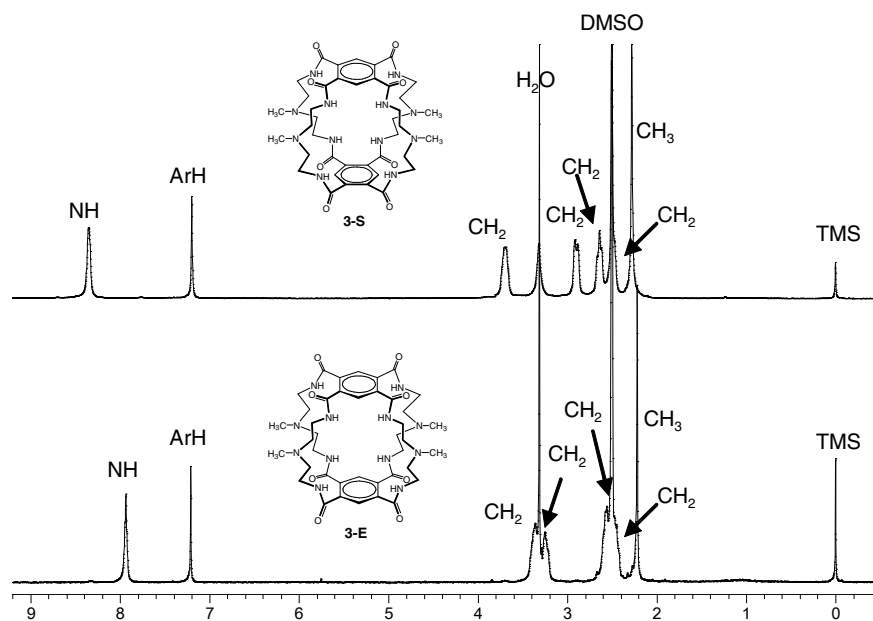
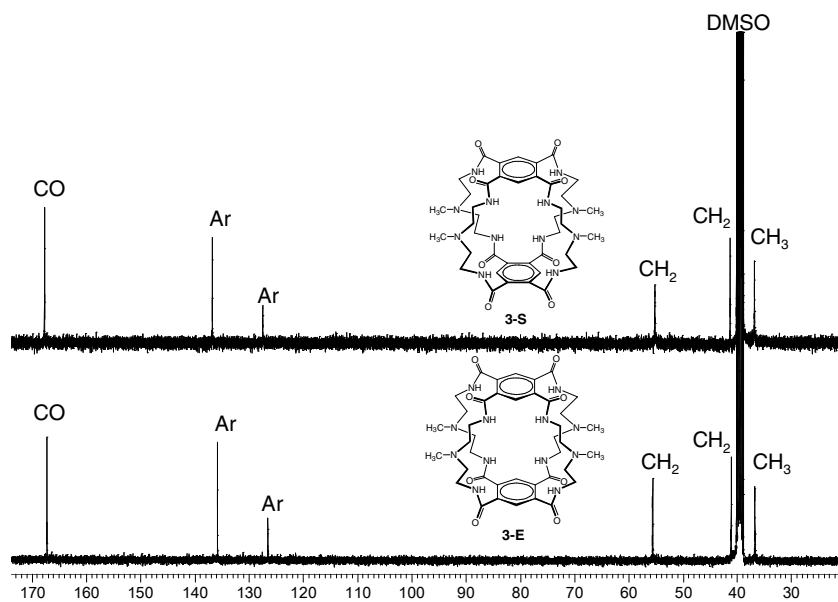


Figure S1. ^1H and ^{13}C NMR spectra of **2** in $\text{DMSO}-d_6$.



A



B

Figure S2. (A) ^1H NMR and (B) ^{13}C NMR spectra of the 3-E and 3-S isomers in $\text{DMSO}-d_6$.

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