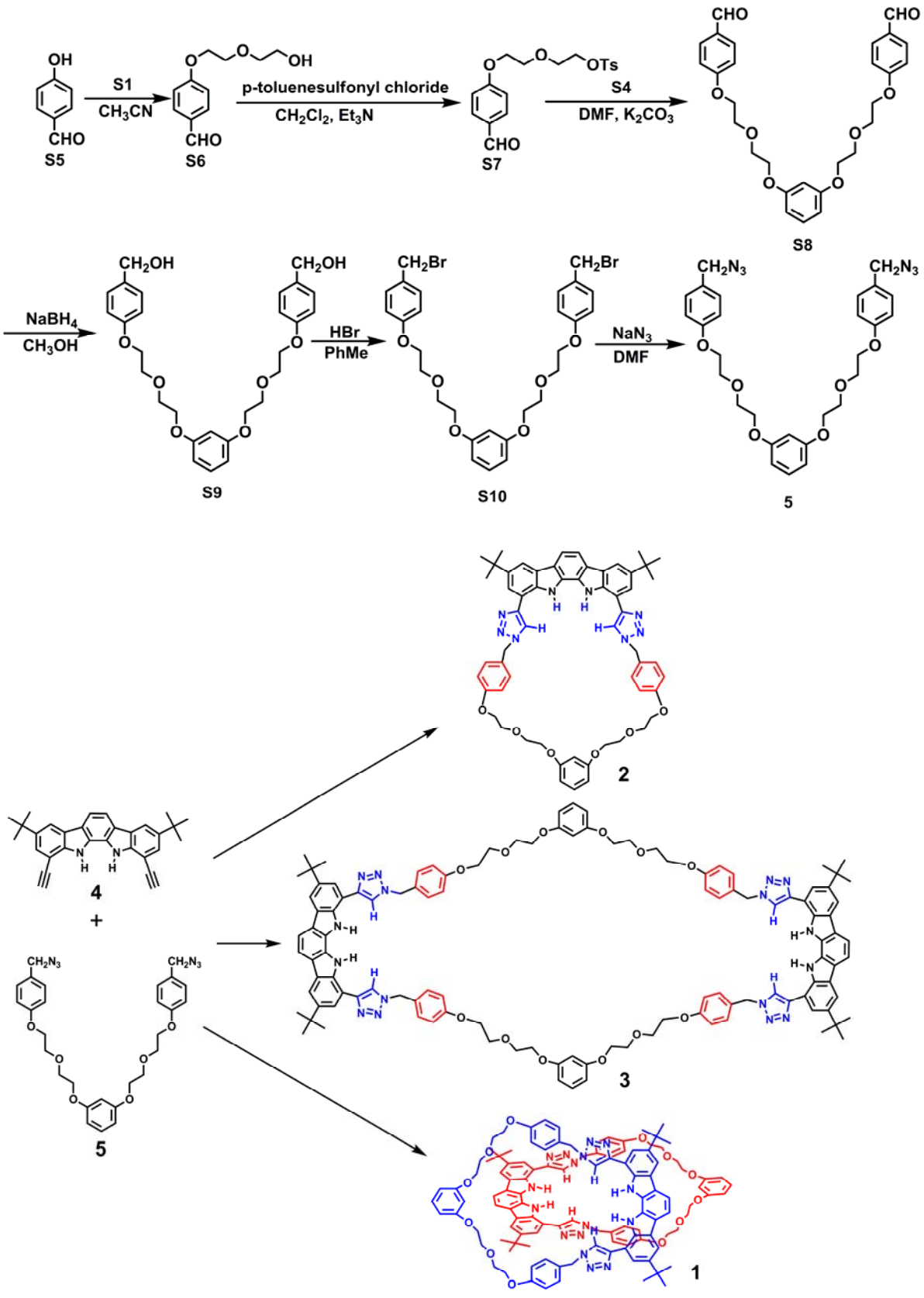
Supporting Information

Construction of an interpenetrated structure of macrocycles

Yingjie Zhao, Yuliang Li, Yongjun Li,* Haiyan Zheng, Xiaodong Yin and Huibiao Liu*

Table of contents

1. Synthesis of 1, 2, 3, 4 and 5



Compound 4 was synthesized in accordance with literature procedures.[1]

4-(2-(2-hydroxyethoxy)ethoxy)benzaldehyde, S6:

To a solution of 4-hydroxybenzaldehyde **S5** (2.44 g, 20 mmol) and 2-(2-chloroethoxy)ethanol **S1** (2.48 g, 20 mmol) in CH_3CN (150 mL), were added potassium carbonate (11.0 g , 80 mmol). The suspension was heated at 70°C for 3 d under an atmosphere of nitrogen. After cooling, the solution was concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 (200 mL), washed with H_2O (150 mL × 3), dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by column chromatography to give **S6** (3.3 g, yield = 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, J = 6.0, 1H), 7.82 (d, J = 9.3, 2H), 7.01 (d, J = 10.3, 2H), 4.21 (m, 2H), 3.88 (m, 2H), 3.76 (m, 2H), 3.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 162.8, 131.9, 129.3, 114.7, 72.6, 69.3, 67.6, 61.6. MS (EI) Calcd for $C_{11}H_{14}O_4$ (M) 210.09; Found 210.1 (M).

2-(2-(4-formylphenoxy)ethoxy)ethyl 4-methylbenzenesulfonate, S7:

A solution of **S6** (2.1 g, 10 mmol) and Et_3N (5.0 mL) in CH_2Cl_2 (50 mL) was cooled to 0°C. p-toluenesulfonyl chloride (2.17 g, 11.4 mmol) was added and the solution was stirred at R.T. for 18 h. The reaction was quenched with water (20 mL). The organic layer was separated, dried over $MgSO_4$, filtered, concentrated under reduced pressure and the resulting crude oil was purified by column chromatography (petroleum ether : CH_2Cl_2 1:4 as eluent) to yield 2-(2-(4-formylphenoxy)ethoxy)ethyl 4-methylbenzenesulfonate **S7** (2.8 g, yield = 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 4.20 (t, *J* = 4.4 Hz, 2H), 4.17 – 4.10 (m, 2H), 3.86 – 3.80 (m, 2H), 3.80 – 3.71 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 163.8, 145.0, 132.9, 132.0, 130.1, 129.9, 128.0, 114.9, 69.6, 69.3, 68.9, 67.7, 21.6. HRMS (ESI) Calcd for $C_{18}H_{20}O_6S$ $(M+Na)^+$ 387.0878; Found 387.0915 $(M+Na)^+$.

4,4'-(2,2'-(2,2'-(1,3-phenylenebis(oxy))bis(ethane-2,1-diyl))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)dibenzaldehyde S8:

To a solution of resorcinol **S4** (0.31 g, 2.8 mmol) in DMF (70 mL) was added K_2CO_3 (1.55 g, 11.2 mmol) and **S7** (2.55 g, 7 mmol), then the solution was heat to 70 °C for 10 h. After cooling, the solution was concentrated under reduced pressure. The residue was taken up in

CH_2Cl_2 (100 mL), washed with H_2O (100 mL × 3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether: ethyl acetate : CH_2Cl_2 1:1:1 as eluent) to yield **S8** (0.98 g, yield = 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 2H), 7.82 (d, *J* = 7.7 Hz, 4 H), 7.15 (t, *J* = 8.1Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 4H), 6.53 (s, 1H), 6.50 (d, *J* = 5.1 Hz, 2H), 4.23 (t, *J* = 4.2 Hz, 4H), 4.12 (t, *J* = 4.2 Hz, 4H), 3.95 (t, *J* = 4.2 Hz, 4H), 3.91 (t, *J* = 4.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 163.8, 159.9, 132.0, 130.1, 129.9, 114.9, 107.2, 101.9, 70.0, 69. 7, 67.8, 67.5. MALDI-TOF, Calcd for $C_{28}H_{30}O_8Na$ $(M+Na)^+$ 517.18; Found 517.2 $(M+Na)^+$. Anal. Calcd for $C_{28}H_{30}O_8$: C, 68.00; H, 6.11; Found: C, 67.92; H, 6.13.

(4,4'-(2,2'-(2,2'-(1,3-phenylenebis(oxy))bis(ethane-2,1-diyl))bis(oxy)bis(ethane-2,1-diyl)) bis(oxy)bis(4,1-phenylene))dimethanol, S9:

To a solution of **S8** (0.9 g, 1.8 mmol) in CH_3OH (30 mL) and CH_2Cl_2 (10 mL) was added $NaBH_4$ (0.14 g, 3.6 mmol), then was stirred at R.T. for 2h, the solution was concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 (100 mL), washed with HCl (5 %) (100 mL × 2), dried over anhydrous $MgSO_4$ and concentrated. The solution was concentrated under reduced pressure to yield **S9** (0.8 g, yield = 90%). ^{1}H NMR (400 MHz, CDCl3) δ 7.26 (d, *J* = 6.8 Hz, 4H), 7.15 (t, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.52 (s, 1H), 6.49 (d, *J* = 7.5 Hz, 2H), 4.60 (s, 4H), 4.18 – 4.05 (m, 8H), 3.95 – 3.84 (m, 8H), 1.68 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 158.4, 133.5, 129.9, 128.6, 114.8, 107.2, 101.9, 70.0, 67.6, 67.5, 65.0. MALDI-TOF, Calcd for $C_{28}H_{34}O_8Na$ $(M+Na)^+$ 521.22; Found 521.2 $(M+Na)^+$. Anal. Calcd for $C_{28}H_{34}O_8$: C, 67.45; H, 6.87; Found: C, 67.21; H, 6.82

1,3-bis(2-(2-(4-(azidomethyl)phenoxy)ethoxy)ethoxy)benzene, 5:

To a solution of **S9** (0.8 g, 1.6 mmol) in PhMe (30 mL) was added hydrogen bromide 33% acetic acid solution (3.9 g, 16 mmol), then was heated to 40 °C for 2 h under an atmosphere of nitrogen. After cooling, the solution was concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 (50 mL), washed with H_2O (50 mL × 3), dried over anhydrous $MgSO_4$ and concentrated. Without further purification, the product was dissolved in DMF (20 mL) containing NaN_3 (0.5 g, 7.7 mmol). The solution was heated to 70 °C for 10 h. After concentration, the residue was taken up in CH_2Cl_2 (50 mL), washed with H_2O (50 mL × 3),

dried over anhydrous $MgSO_4$ and concentrated, the residue was purified by column chromatography (ethyl acetate : petroleum ether 1:3 as eluent) to yield **7**. Two steps yield 0.3 g (35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 4H), 7.19 – 7.10 (m, 1H), 6.93 (d, *J* = 8.6 Hz, 4H), 6.53 (s, 1H), 6.52 (d, *J* = 2.8 Hz, 2H), 4.26 (s, 4H), 4.19 – 4.04 (m, 8H), 3.98 – 3.84 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 158.9, 129.8, 127.7, 115.0, 107.2, 101.9, 70.0, 69.9, 67.6, 67.5, 54.4. MALDI-TOF, Calcd for $C_{28}H_{32}N_6O_6Na$ $(M+Na)^+$ 571.23; Found 571.2 $(M+Na)^+$. Anal. Calcd for $C_{28}H_{32}N_6O_6$: C, 61.30; H, 5.88; N, 15.32; Found: C, 61.15; H, 6.01; N, 15.38

Synthesis of 1, 2 and **3**: 1, 8-Diaza [5.4.0] bicycloundec-7-ene (DBU) (4.0 mmol, 0.7 mL) was added to toluene (400 mL), degassed (argon) for 30 minutes and heated to 70 °C while flushing with argon. At 70 °C, CuI (0.05 mmol, 9.5 mg) and tetrabutyl ammonium chloride (0.5 mmol, 139 mg) was added to the mixture. A solution of the **4** (208 mg, 0.5 mmol) and **5** (274 mg, 0.5 mmol) in THF (5 mL) and toluene (50 mL) was added to the solution slowly over 12 h and stirred for another 18 h under argon. The reaction was quenched with water and washed with H_2O (100 mL × 3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was concentrated in vacuo. The product was purified via chromatography (SiO_2, CH_2Cl_2 : methanol 30 : 1) to afford **2** (310 mg, 65% yield) as a yellow solid, **3** (10 mg, <5% yeild), **3** (67 mg, 15% yield).

Compound 1: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 11.33 (s, 4H), 8.51 (s, 4H), 8.20 (s, 4H), 8.00 (s, 4H), 7.82 (s, 4H), 6.99 (t, *J* = 8.1, 2H), 6.77 (d, *J* = 7.6, 8H), 6.40 (s, 2H), 6.33 (d, *J* = 8.5, 4H), 6.29 (d, *J* = 7.5, 8H), 5.20 (s, 8H), 4.02 (s, 8H), 3.83 – 3.76 (m, 16H), 3.75 (s, 4H), 1.47 (s, 36H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 159.8, 158.6, 147.3, 142.4, 134.6, 129.7, 128.8, 127.5, 126.6, 125.24, 121.2, 120.6, 119.9, 116.2, 114.6, 113.2, 111.8, 106.6, 101.7, 69.6, 69.6, 67.3, 67.16, 54.1, 34.8, 31.9. MALDI-TOF (M), Calcd for $C_{116}H_{120}N_{16}O_{12}$ (M) 1928.9; Found 1929.1.

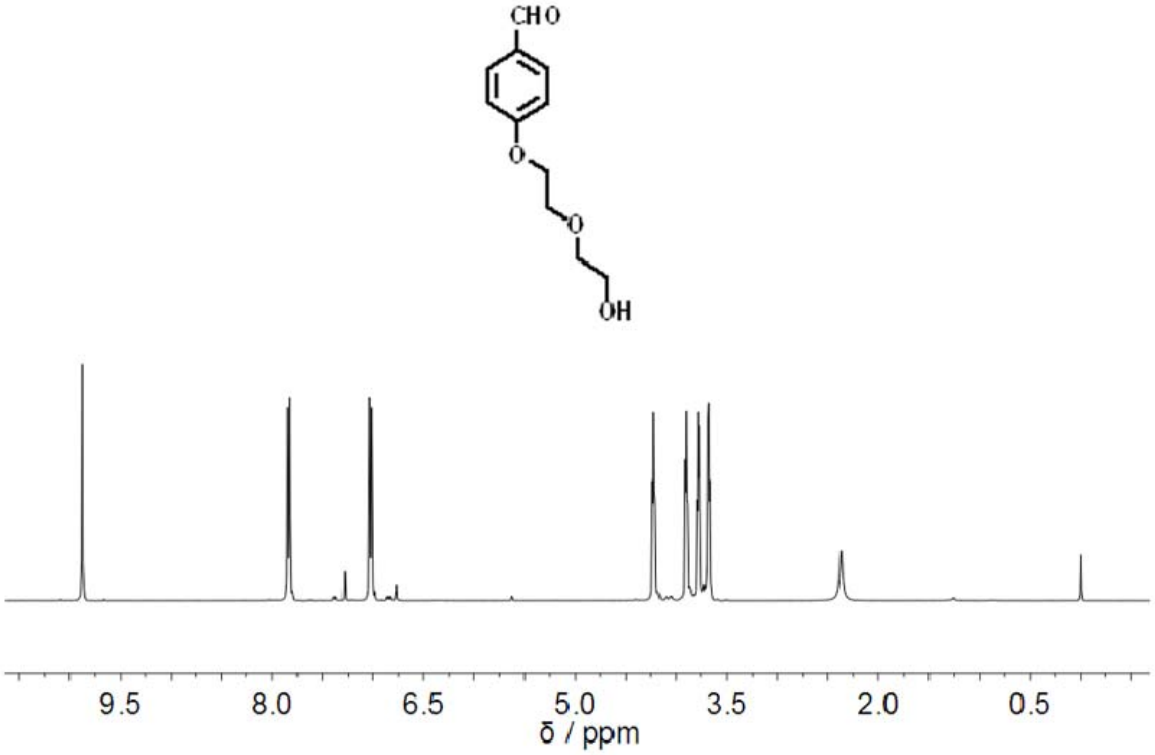
Compound 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 2H), 8.16 (s, 2H), 8.08 (s, 2H), 7.99 (s, 2H), 7.65 (s, 2H), 7.29 (d, *J* = 8.6 Hz, 4H), 7.11 (t, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 4H), 6.51 (s, 1H), 6.47 (d, *J* = 8.2, 2H), 5.60 (s, 4H), 4.17 – 4.03 (m, 8H), 3.86 (m, 8H), 1.50 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 159.0, 148.2, 142.3, 134.9, 129.8, 129.1,

127.6, 126.4, 125.3, 121.3, 119.5, 119.1, 116.3, 115.2, 112.7, 112.0, 107.0, 102.2, 69.8, 69.7, 67.6, 67.5, 53.9, 34.8, 32.1. MALDI-TOF (M), Calcd for $C_{58}H_{60}N_8O_6$ (M) 964.46; Found 964.8. HRMS (ESI) Calcd for $C_{58}H_{61}N_8O_6$ $(M+H)^+$ 965.47141; Found 965.46902 $(M+H)^+$

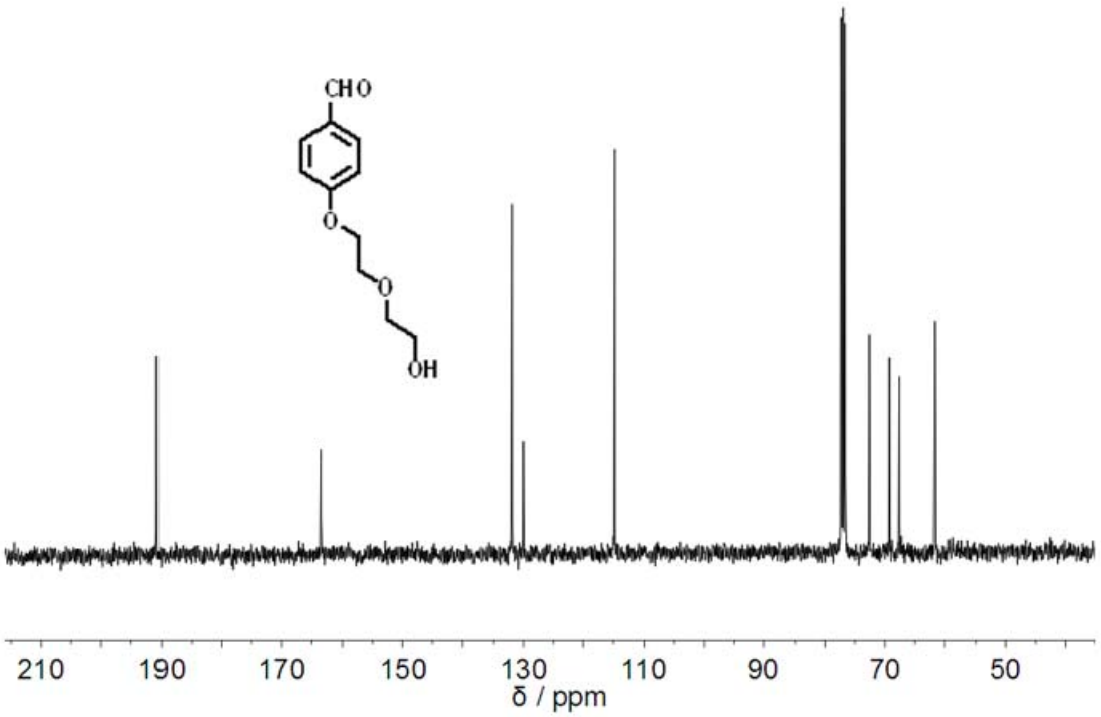
Compound 3: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 11.11 (s, 4H), 8.21 (s, 4H), 8.19 (s, 4H), 8.00 (s, 4H), 7.72 (s, 4H), 7.06 (d, J = 7.5, 8H), 7.02 (t, J = 8.3, 2H), 6.64 (d, J = 8.0, 8H), 6.38 (d, J = 8.4, 4H), 6.34 (s, 2H), 5.37 (s, 8H), 3.97 (s, 8H), 3.90 (s, 8H), 3.72 (d, J = 3.5, 16H), 1.48 (s, 36H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.0, 159.0, 147.1, 142.6, 134.6, 129.9, 129.6, 127.0, 126.5, 125.3, 121.3, 120.4, 119.9, 116.5, 115.0, 112.5, 112.0, 106.9, 101.8, 69.8, 69.8, 67.6, 67.6, 54.0, 34.8, 31.9. MALDI-TOF (M), Calcd for $C_{116}H_{120}N_{16}O_{12}$ (M) 1928.9; Found 1929.1.

2. ^{1}H NMR and ^{13}C NMR

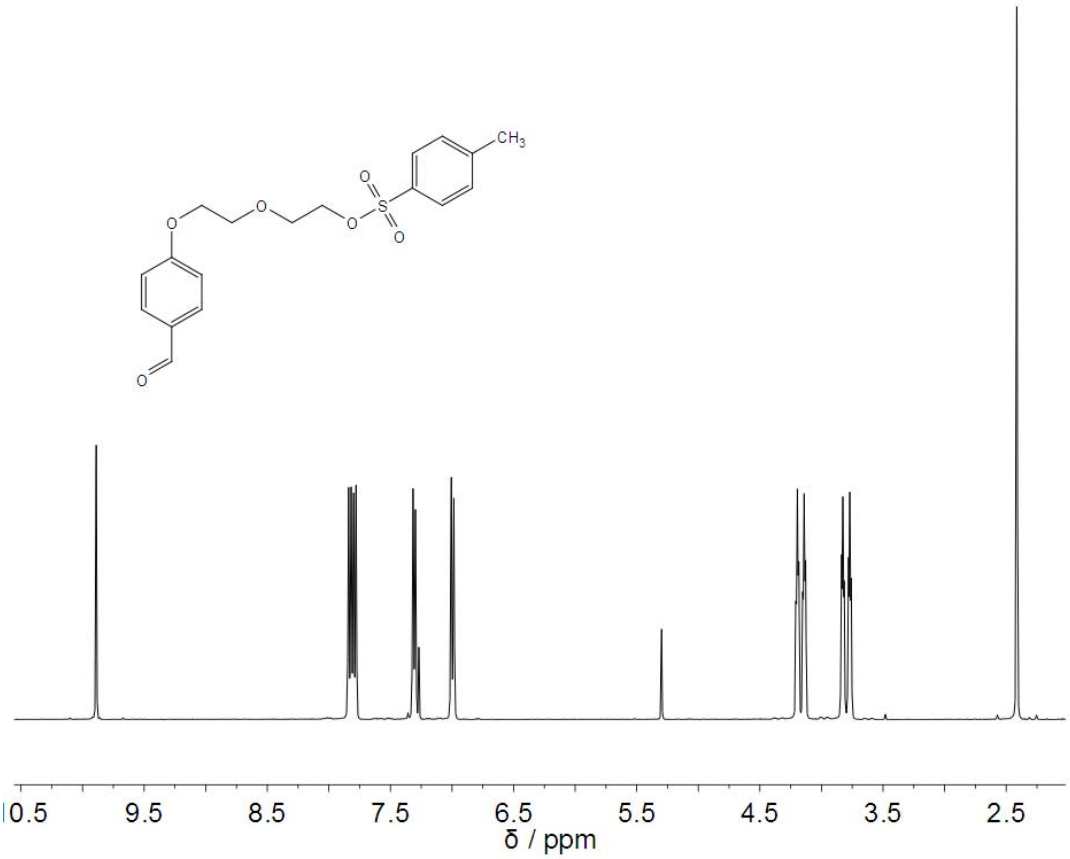
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **S6**



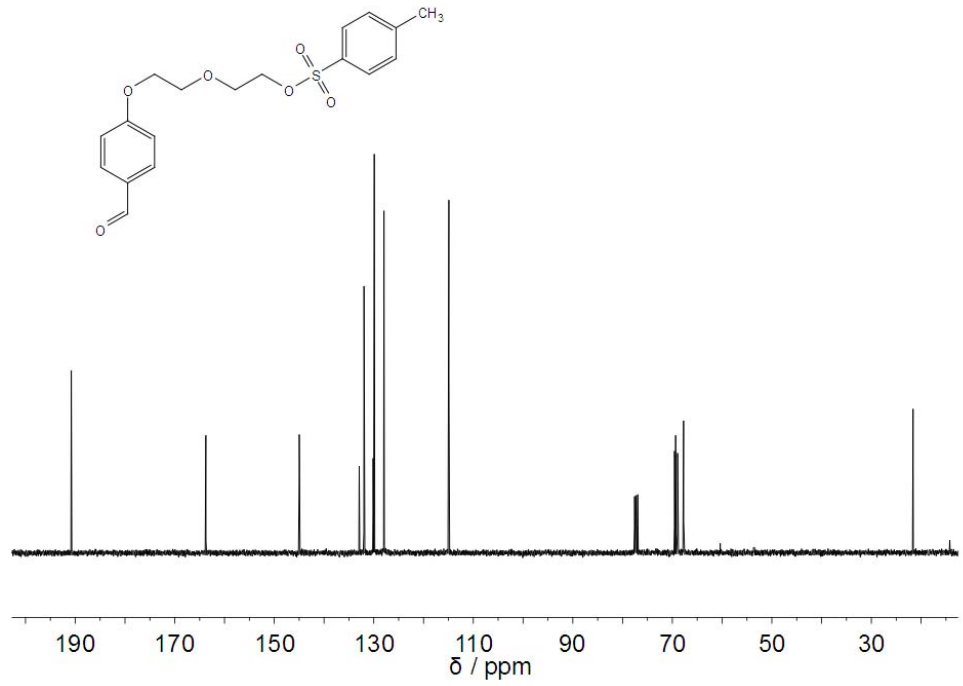
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **S6**



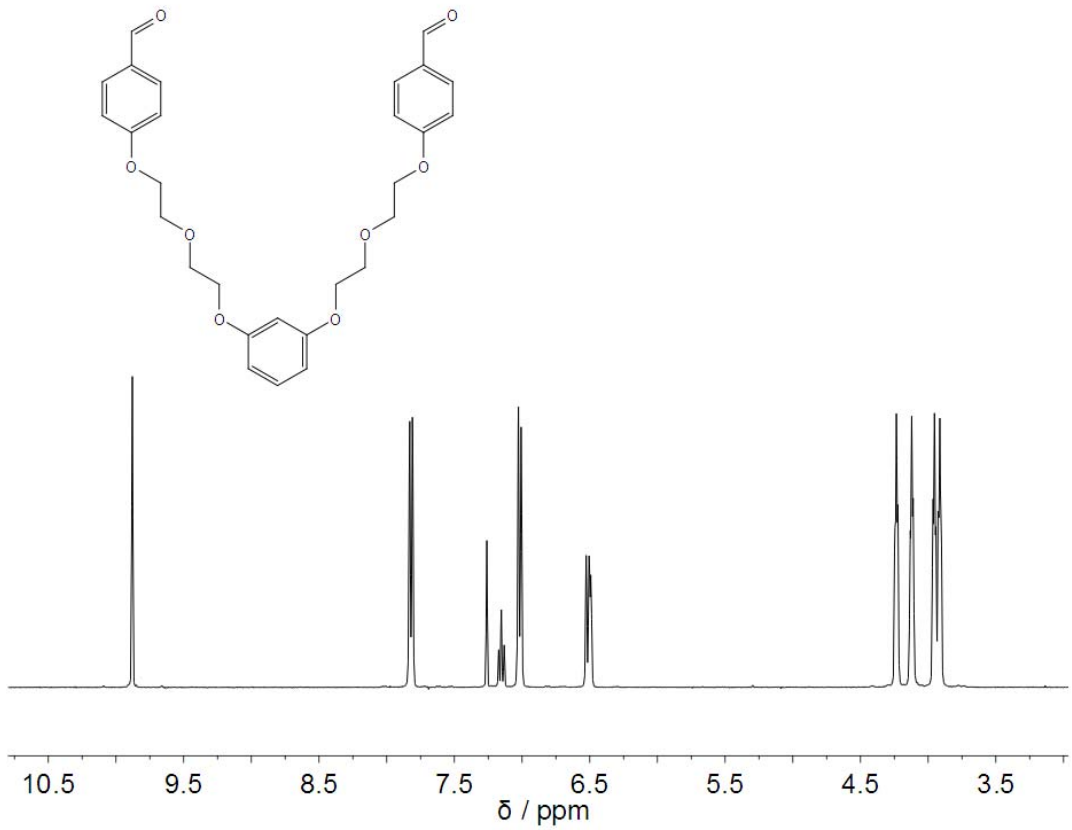
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **S7**



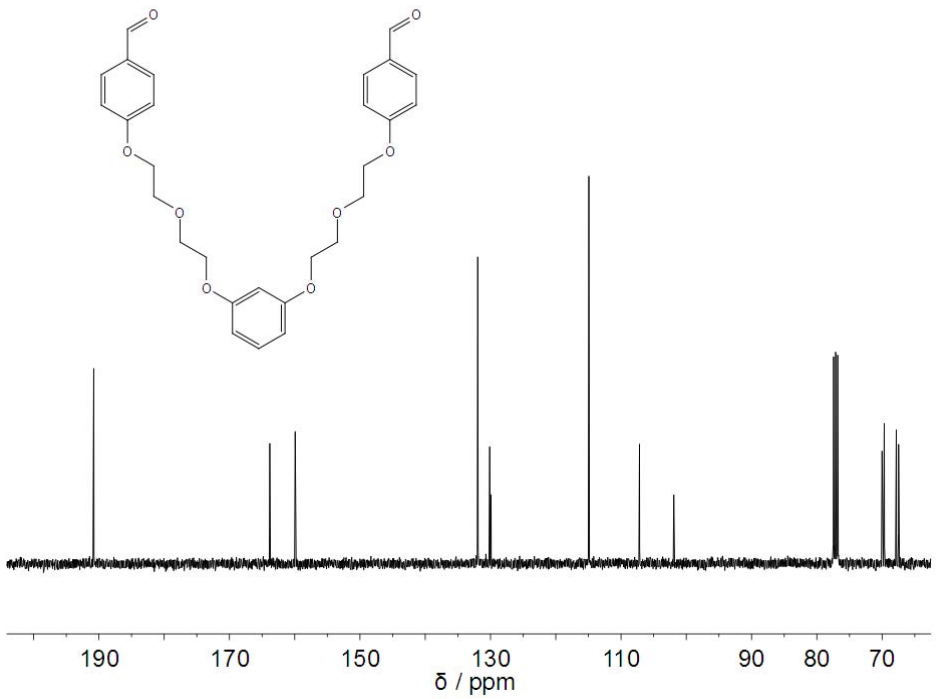
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **S7**



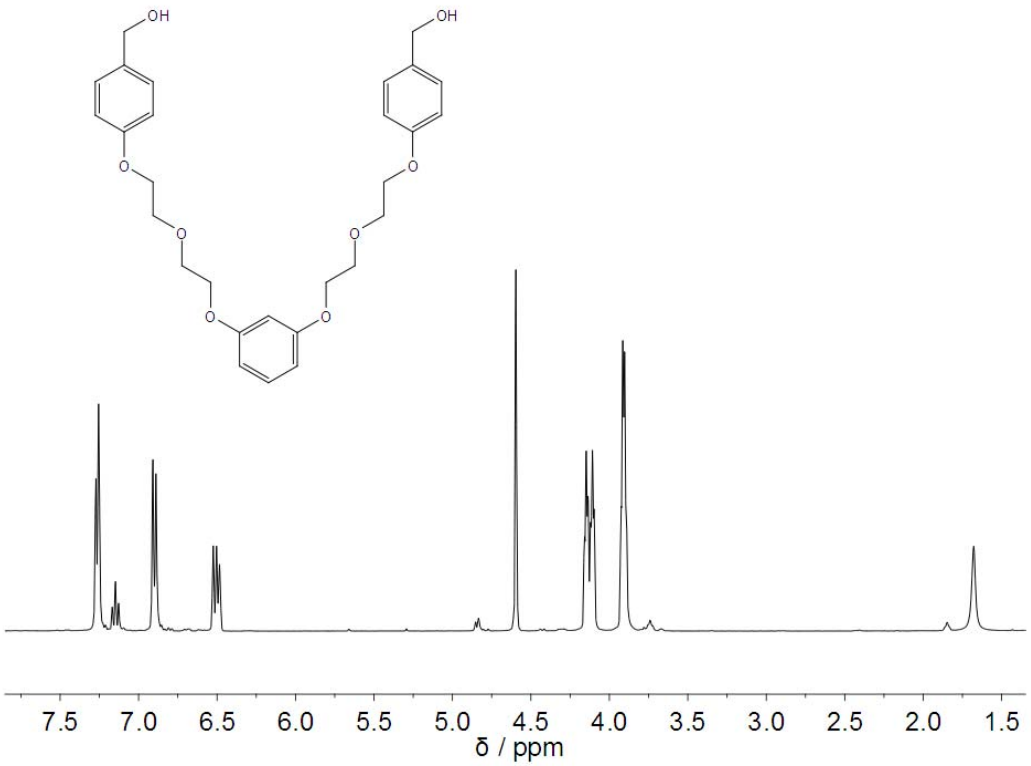
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **S8**



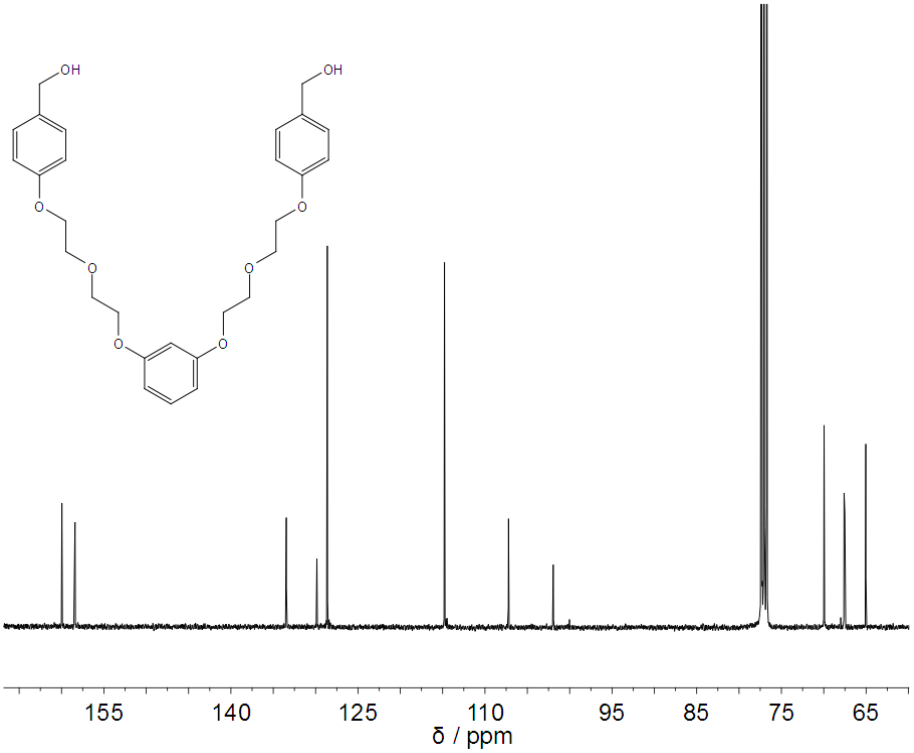
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **S8**



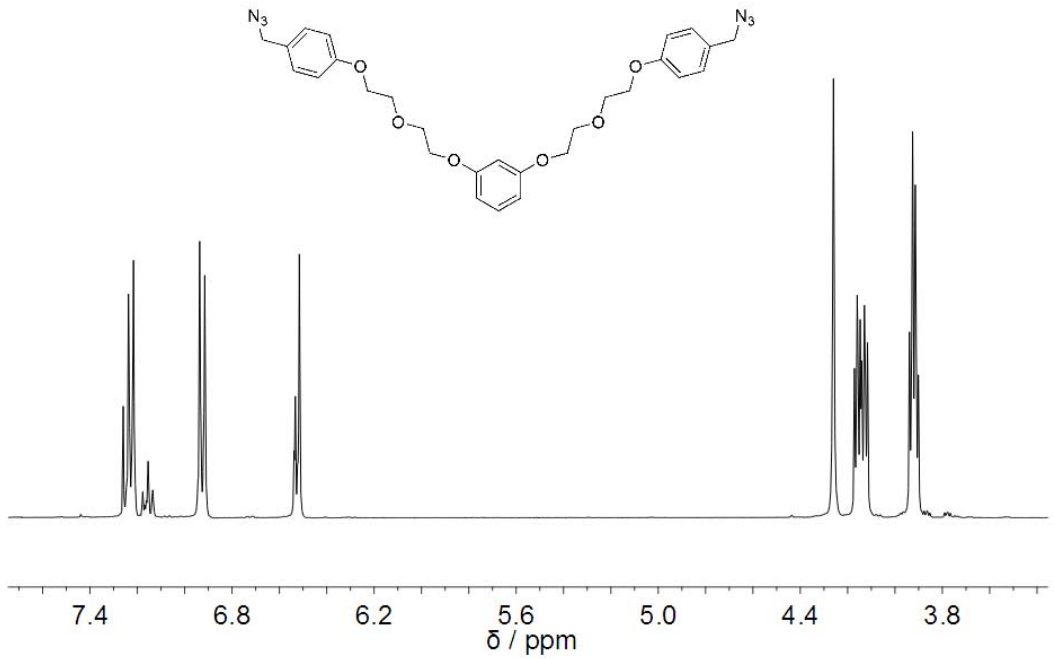
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **S9**



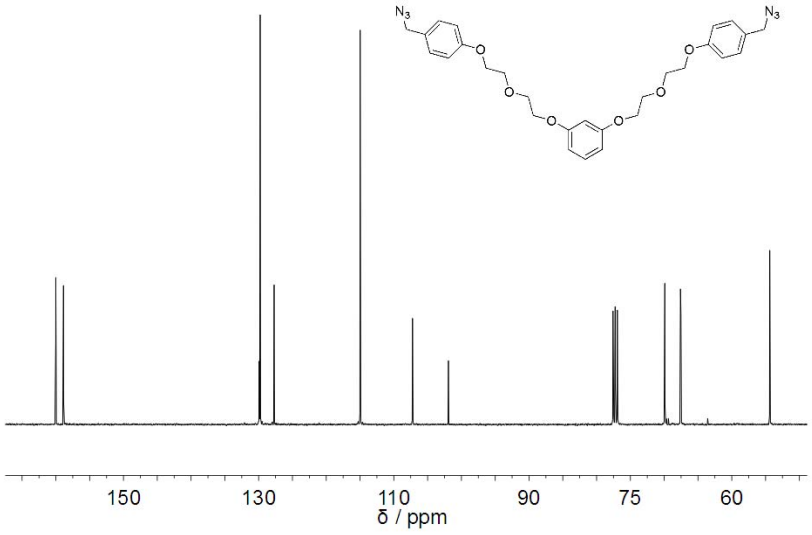
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **S9**



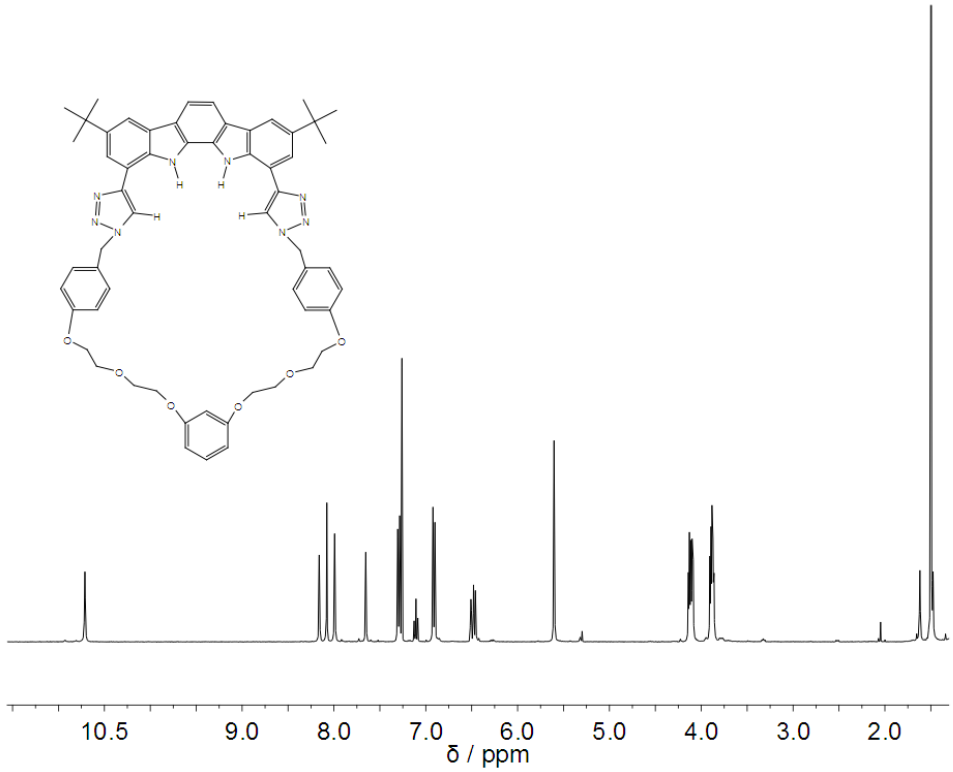
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **5**



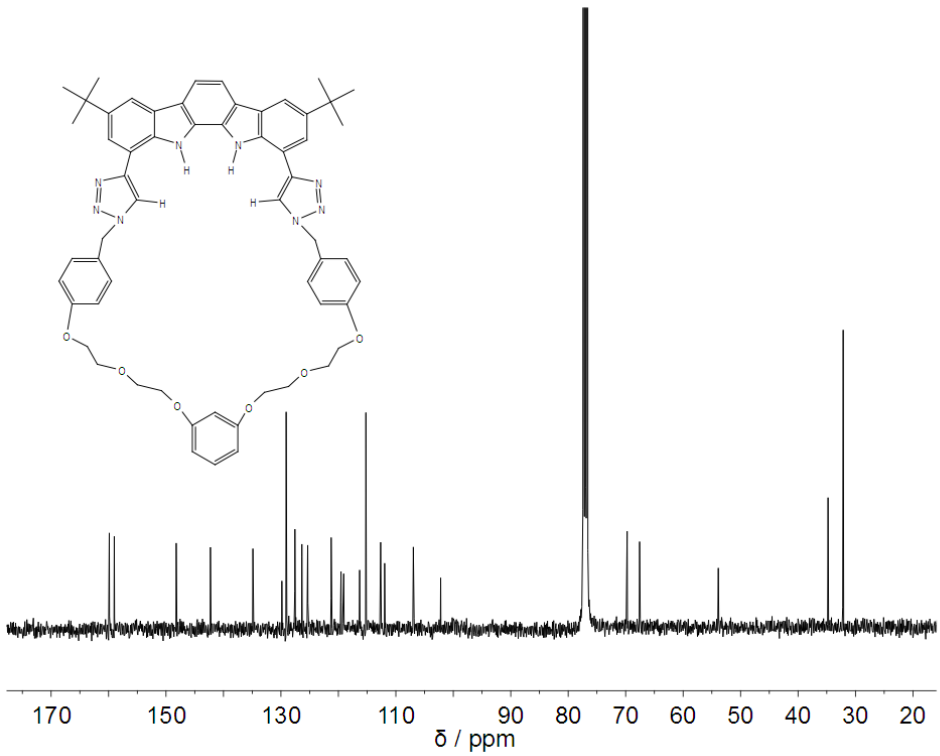
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **5**



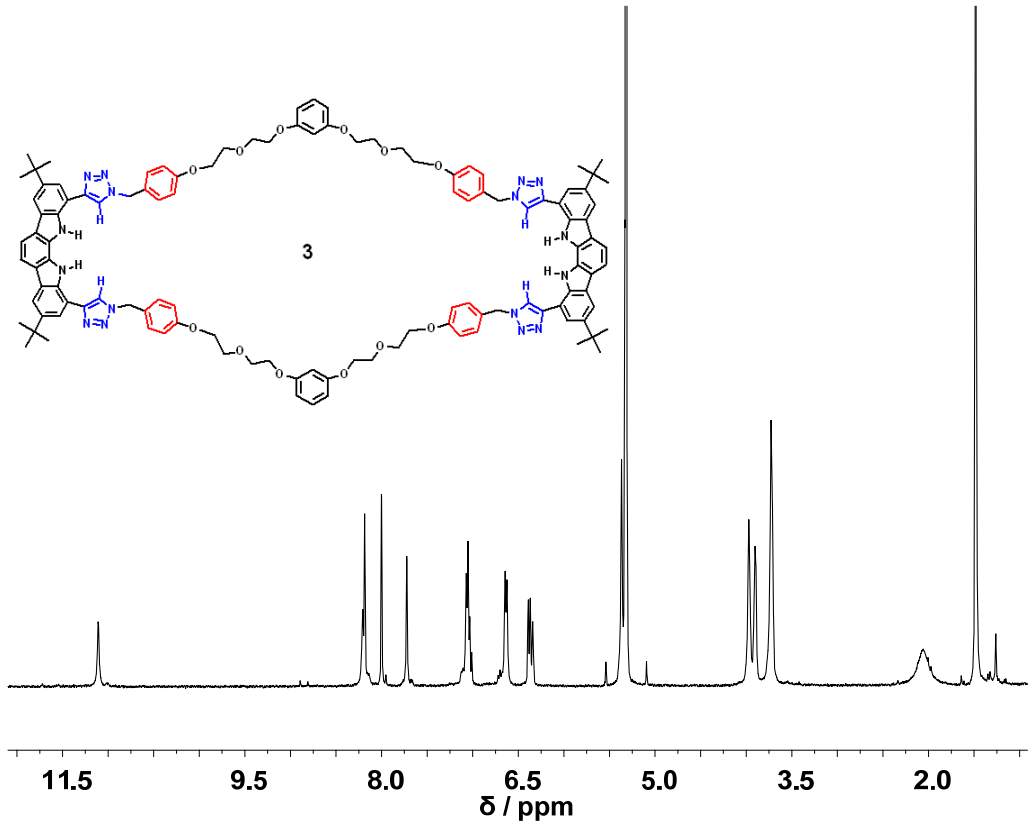
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **2**



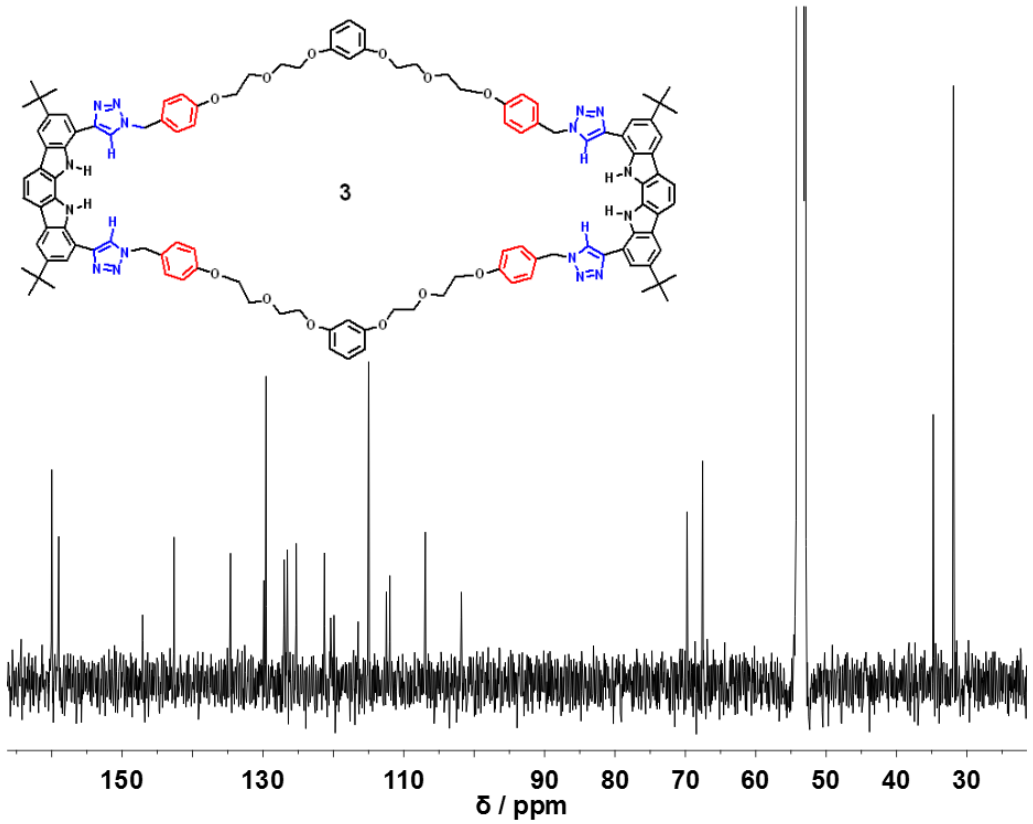
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **2**



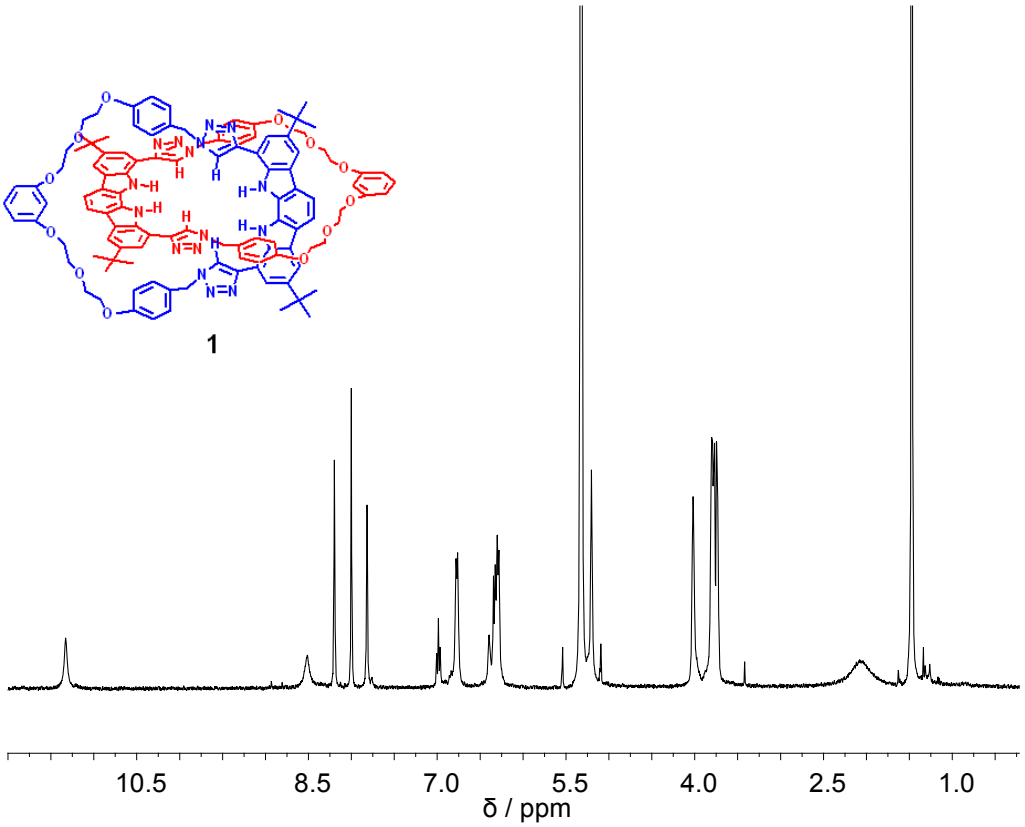
^{1}H NMR spectrum (400 MHz, 298 K, CD_2Cl_2) of **3**



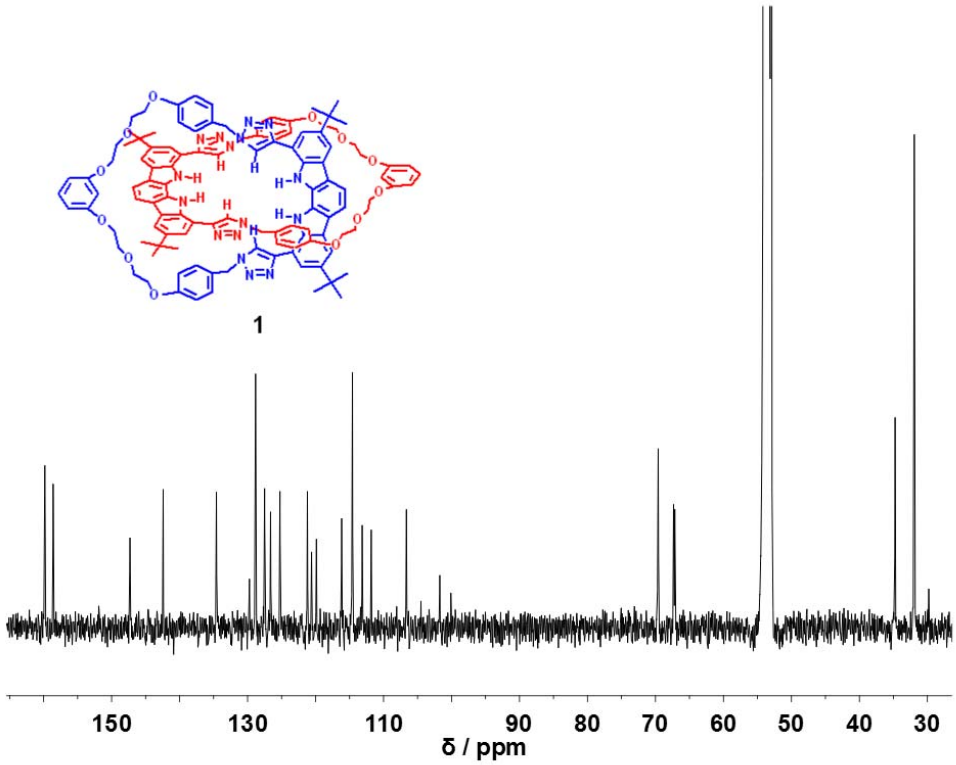
^{13}C NMR spectrum (100 MHz, 298 K, CD_2Cl_2) of **3**



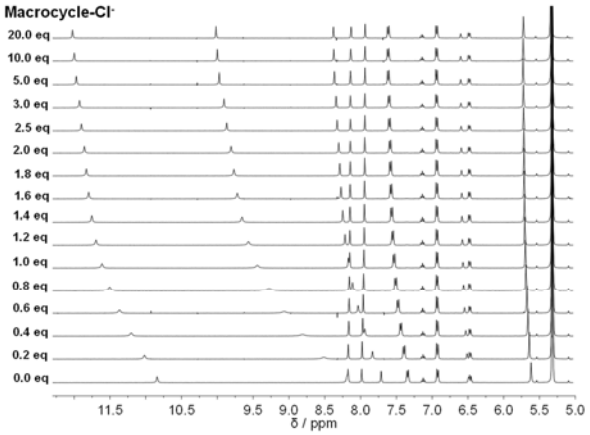
^{1}H NMR spectrum (400 MHz, 298 K, CD_2Cl_2) of **1**

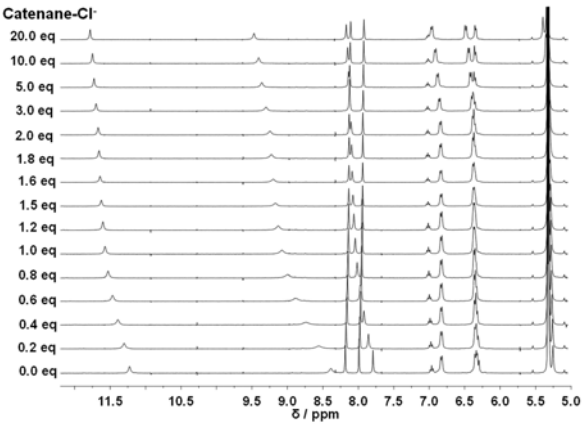


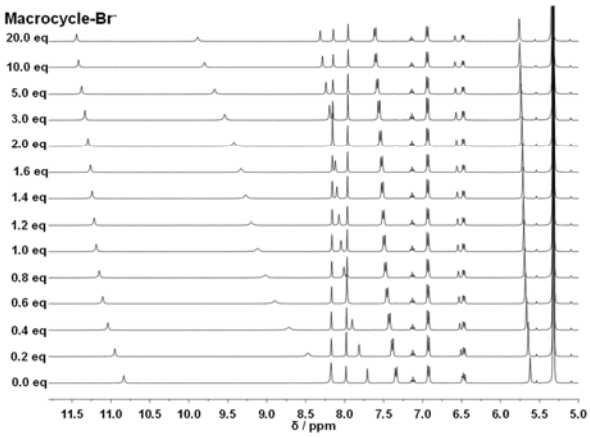
^{13}C NMR spectrum (100 MHz, 298 K, CD_2Cl_2) of **1**

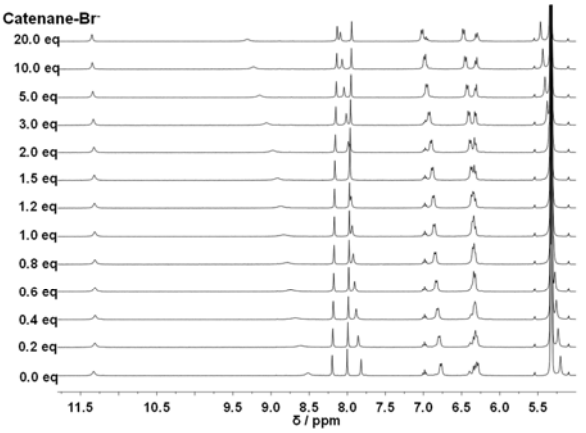


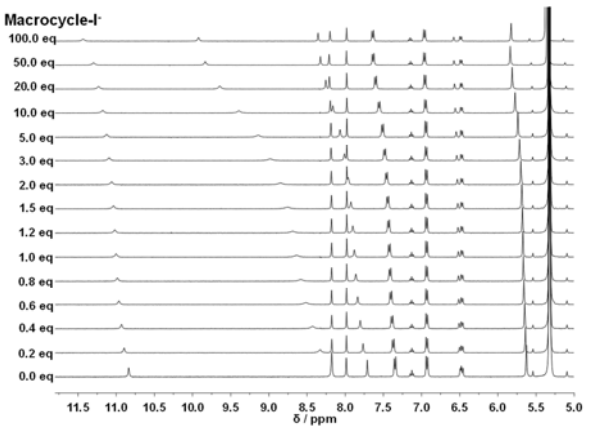
3. ^{1}H NMR Titration Studies

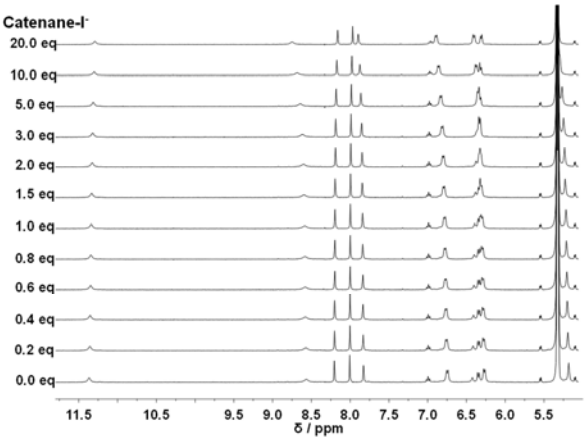


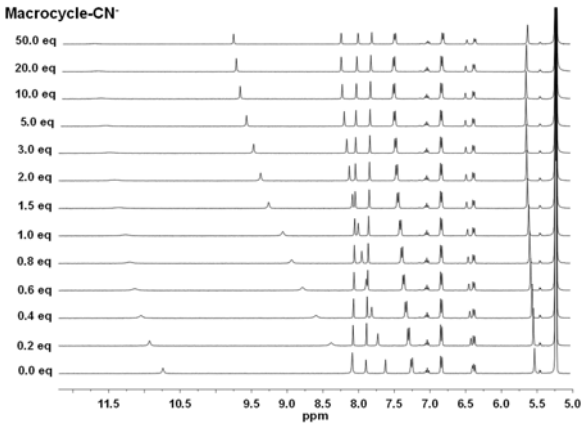


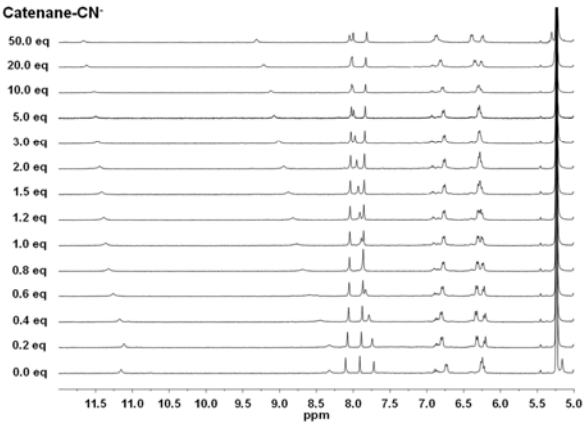


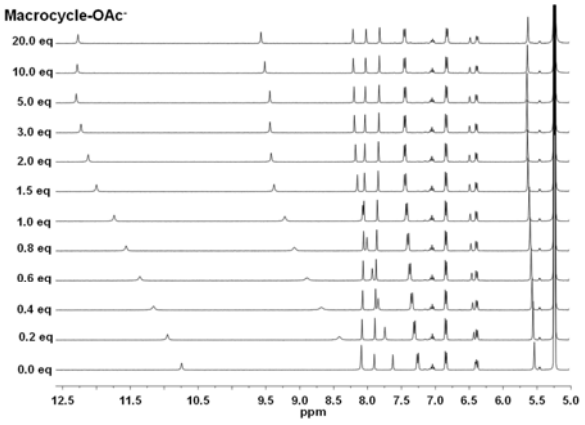


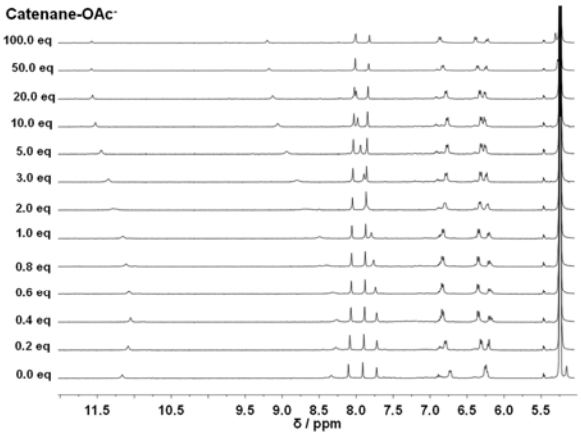


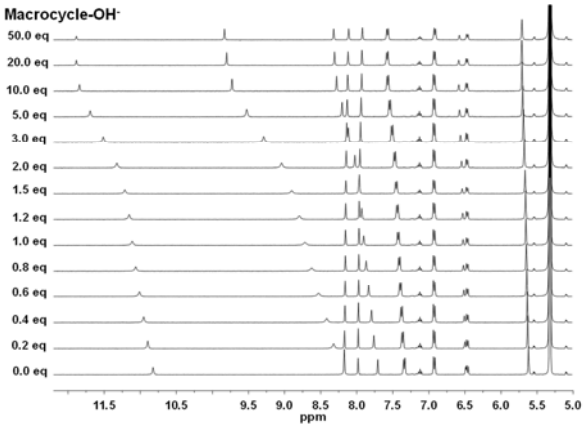


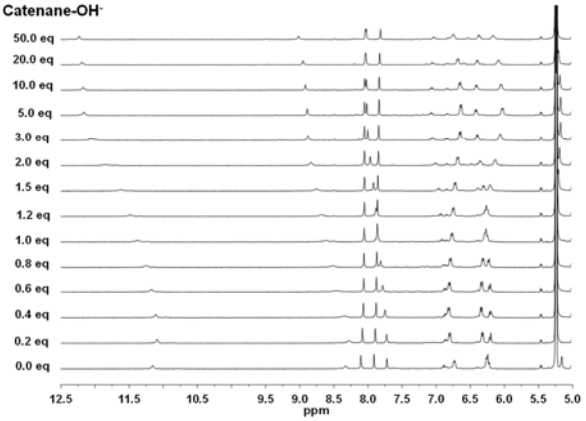

Macrocycle-CN⁻
50.0 eq
20.0 eq
10.0 eq
5.0 eq
3.0 eq
2.0 eq
1.5 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
ppm

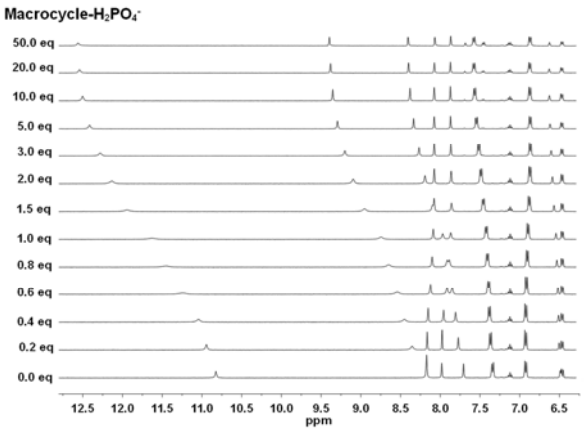

Catenane-CN⁻
50.0 eq
20.0 eq
10.0 eq
5.0 eq
3.0 eq
2.0 eq
1.5 eq
1.2 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
ppm


Macrocycle-OAc⁻
20.0 eq
10.0 eq
5.0 eq
3.0 eq
2.0 eq
1.5 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
ppm


Catenane-OAc⁻
100.0 eq
50.0 eq
20.0 eq
10.0 eq
5.0 eq
3.0 eq
2.0 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5
δ / ppm


Macrocycle-OH⁻
50.0 eq
20.0 eq
10.0 eq
5.0 eq
3.0 eq
2.0 eq
1.5 eq
1.2 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
ppm


Catenane-OH⁻
50.0 eq
20.0 eq
10.0 eq
5.0 eq
3.0 eq
2.0 eq
1.5 eq
1.2 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
ppm


Macrocycle-H2PO4⁻
50.0 eq
20.0 eq
10.0 eq
5.0 eq
3.0 eq
2.0 eq
1.5 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5
ppm

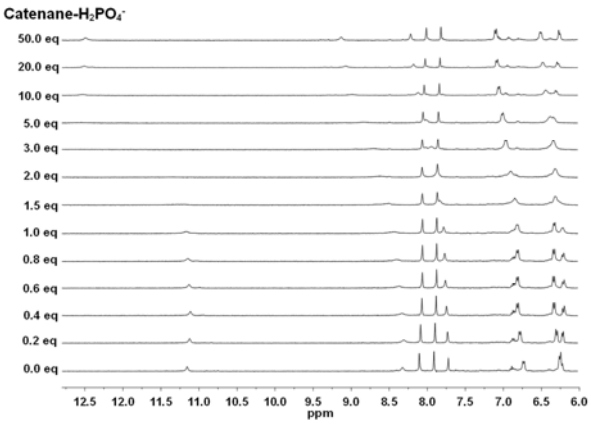

Catenane-H2PO4⁻
50.0 eq
20.0 eq
10.0 eq
5.0 eq
3.0 eq
2.0 eq
1.5 eq
1.0 eq
0.8 eq
0.6 eq
0.4 eq
0.2 eq
0.0 eq
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0
ppm

Figure S1 ^{1}H NMR spectra (aromatic region) of **1** and **2** in CD_2Cl_2 at 298 K upon titrational addition of TBA salts of Cl^-, Br^-, I^-, CN^-, OAc^-, OH^- and $H_2PO_4^-$ in CD_2Cl_2 solution

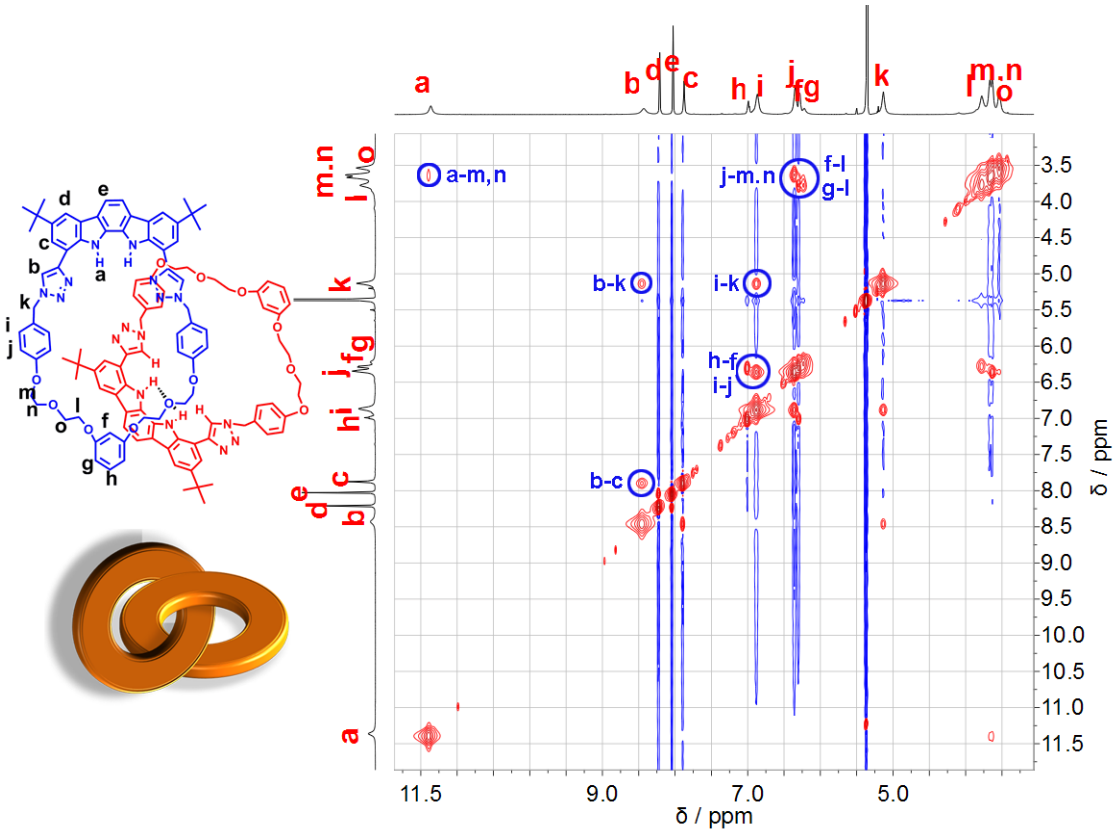
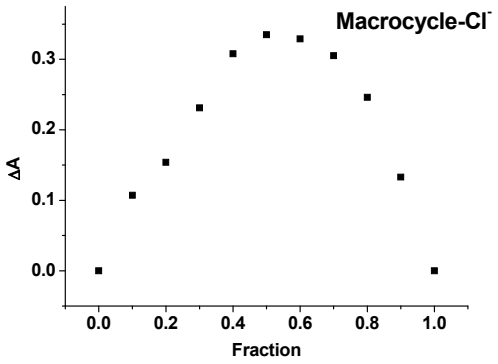
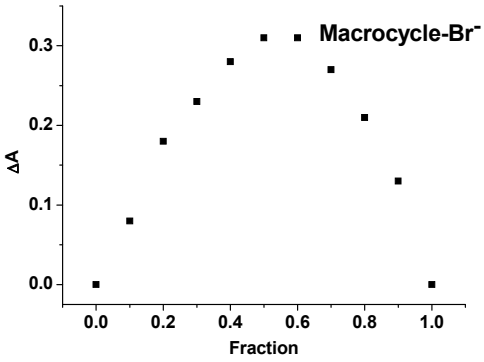


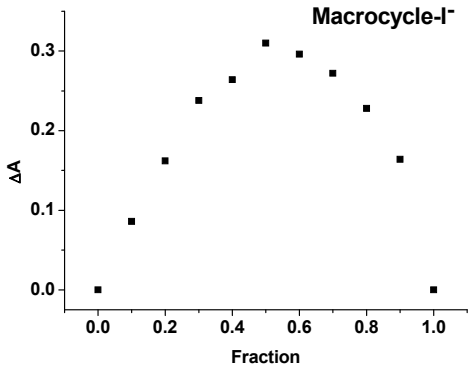
Figure S2. NOESY spectrum of **1** in CD_2Cl_2 at 258 K

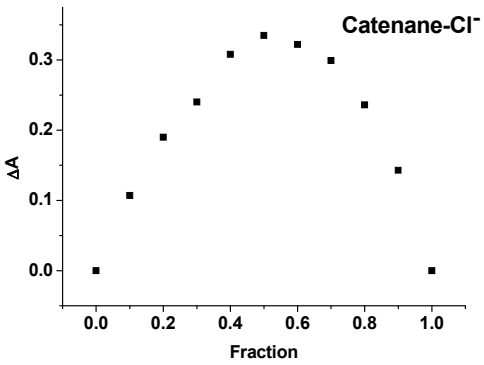
4. Binding Studies

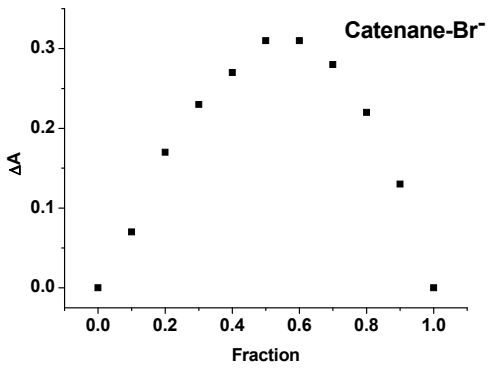
Job's plots[3]: Stock solutions of **1, 2** (1.0×10^{-4} M for **1** and 2.0×10^{-4} M for **2**) and an anion (1.0×10^{-4} M or 2.0×10^{-4} M) were separately prepared in CH_2Cl_2. The UV/Vis spectra was taken for each of 10 different solutions containing a total of 2.0 mL of the **1**, **2**, TBAX in the following ratios: 1:0, 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.3:0.7, 0.2:0.8, and 0.1:0.9. Job's plots were constructed by plotting $A_{obs}–A_M–A_x$ against the γ-coordinate.

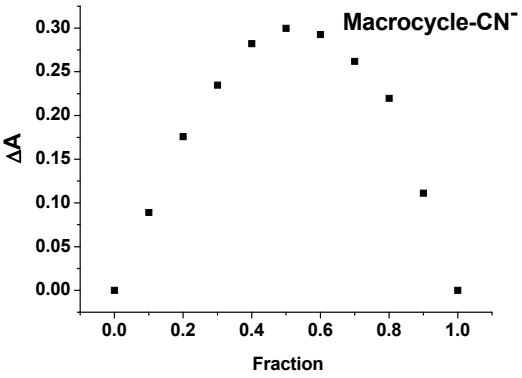

Macrocycle-Cl⁻
ΔA
Fraction

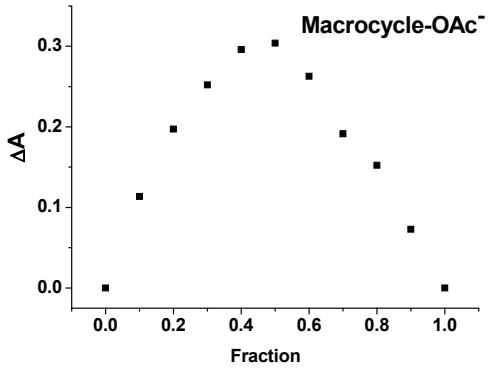

Macrocycle-Br⁻
ΔA
Fraction

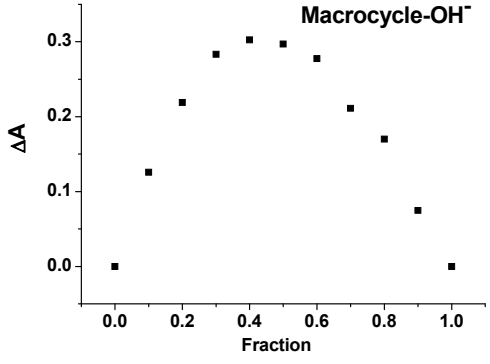

Macrocycle-I⁻
ΔA
Fraction


Catenane-Cl⁻
ΔA
Fraction


Catenane-Br⁻
ΔA
Fraction


Macrocycle-CN⁻
ΔA
Fraction


Macrocycle-OAc⁻
ΔA
Fraction


Macrocycle-OH⁻
ΔA
Fraction

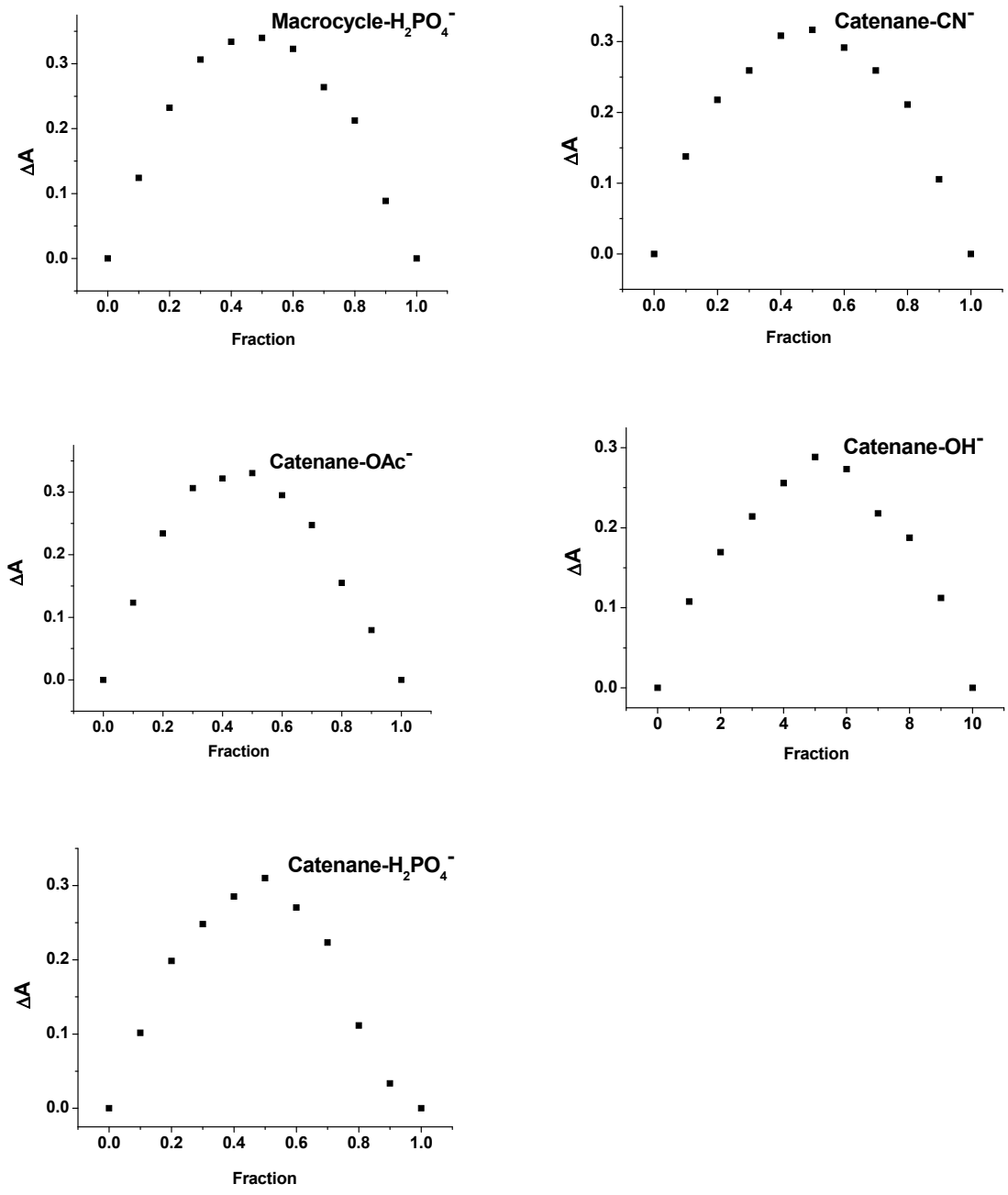
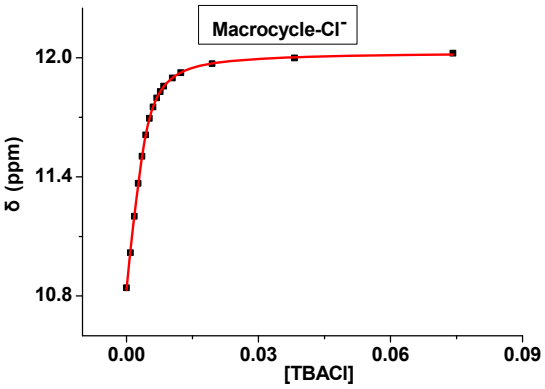
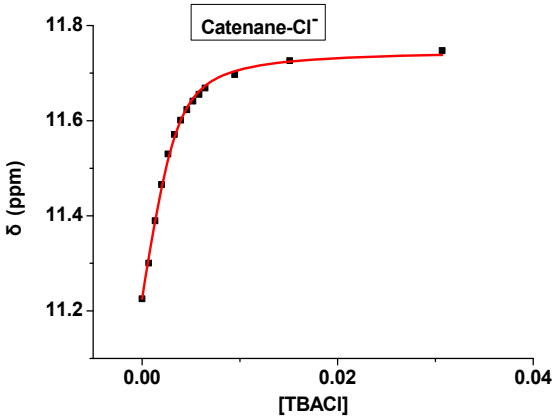
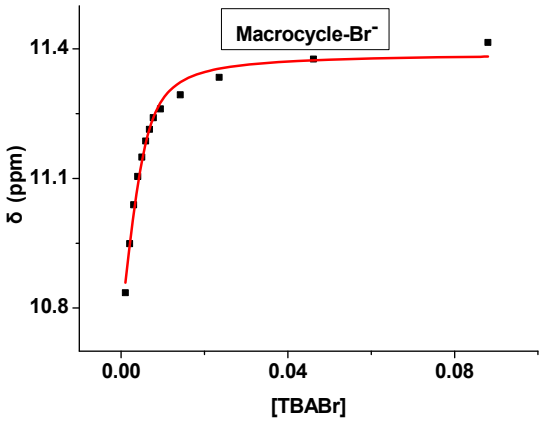
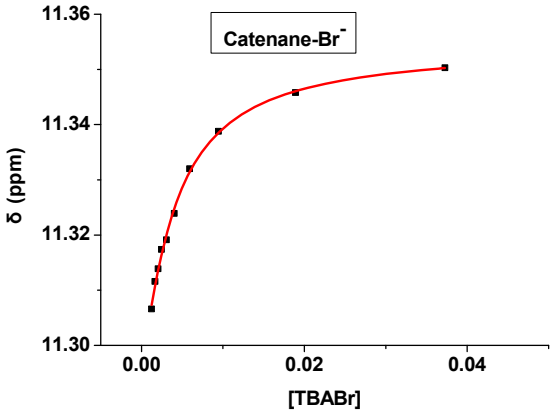


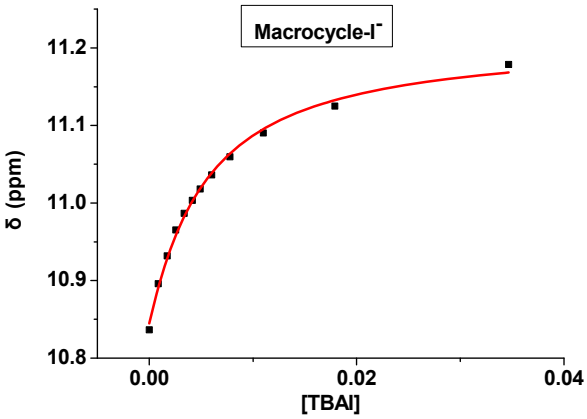
Figure S3. Job's Plot for complexation of the macrocycle, catenane and anion by UV spectroscopy.

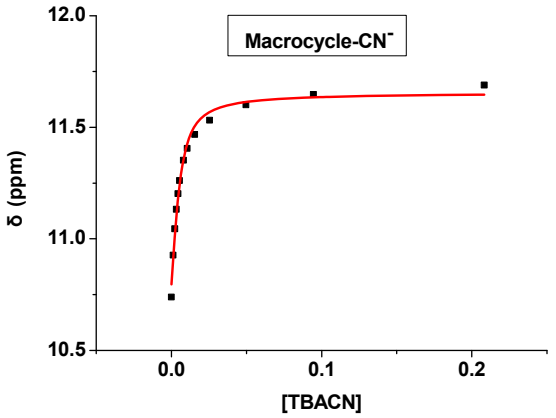

Macrocycle-Cl⁻
δ (ppm)
12.0
11.4
10.8
0.00
0.03
0.06
0.09
[TBACl]

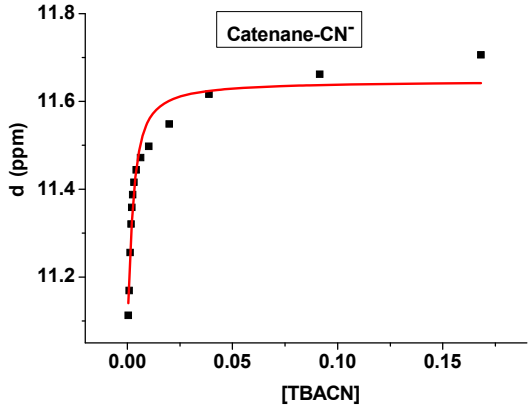

Catenane-Cl⁻
δ (ppm)
11.8
11.6
11.4
11.2
0.00
0.02
0.04
[TBACl]

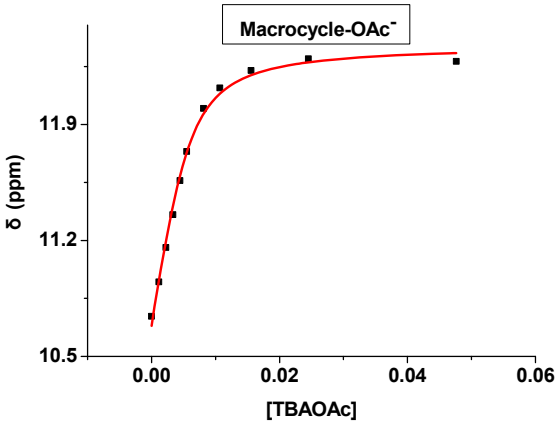

Macrocycle-Br⁻
δ (ppm)
11.4
11.1
10.8
0.00
0.04
0.08
[TBABr]

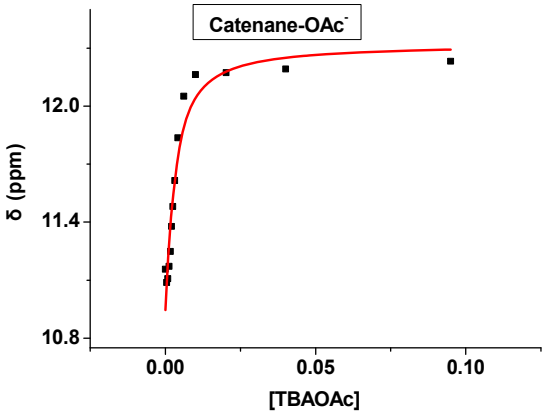

Catenane-Br⁻
δ (ppm)
11.36
11.34
11.32
11.30
0.00
0.02
0.04
[TBABr]

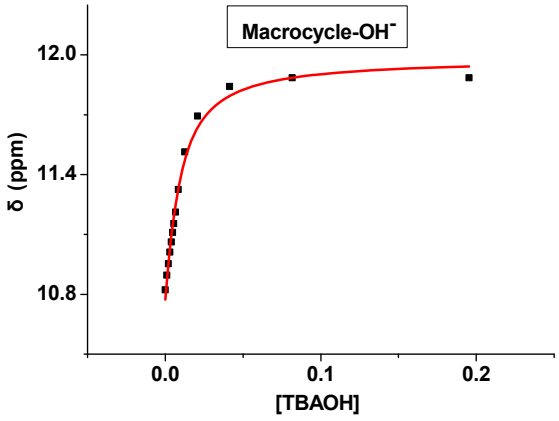

Macrocycle-I⁻
δ (ppm)
11.2
11.1
11.0
10.9
10.8
0.00
0.02
0.04
[TBAI]

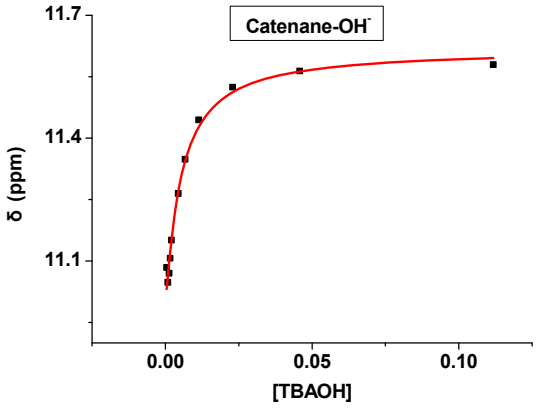

Macrocycle-CN-
δ (ppm)
12.0
11.5
11.0
10.5
0.0
0.1
0.2
[TBACN]


Catenane-CN-
d (ppm)
11.8
11.6
11.4
11.2
0.00
0.05
0.10
0.15
[TBACN]


Macrocycle-OAc-
δ (ppm)
11.9
11.2
10.5
0.00
0.02
0.04
0.06
[TBAOAc]


Catenane-OAc-
δ (ppm)
12.0
11.4
10.8
0.00
0.05
0.10
[TBAOAc]


Macrocycle-OH-
δ (ppm)
12.0
11.4
10.8
0.0
0.1
0.2
[TBAOH]


Catenane-OH-
δ (ppm)
11.7
11.4
11.1
0.00
0.05
0.10
[TBAOH]

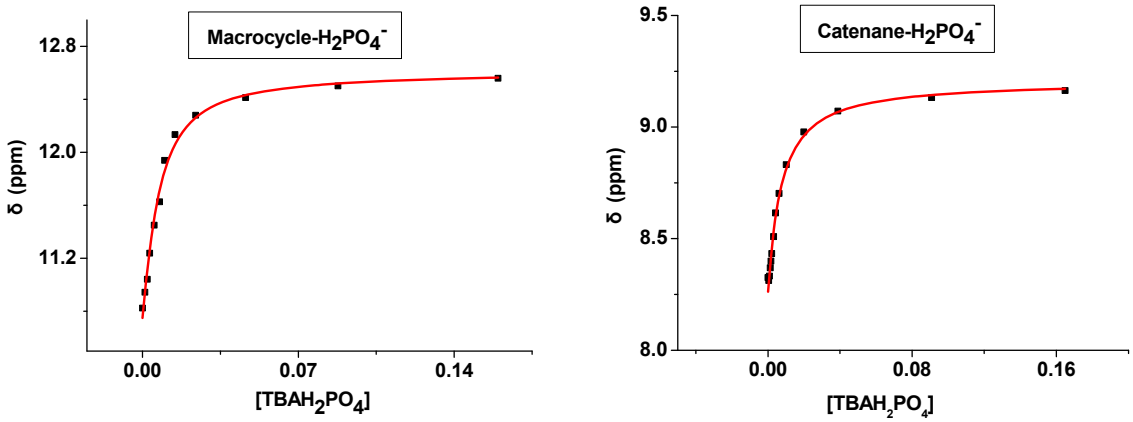


Figure S4. Change in the chemical shift of N-H_a or H_b (Catenane-$H_2PO_4^{2-}$) on addition of anions to a solution of **2** (macrocycle) and **1** (catenane) in CD_2Cl_2 at 298 K. Square symbols represent experimental data points; continuous lines represent calculated curves. All anions were added as their TBA salts.

[1] K. J. Chang, D. Moon, M. S. Lah, K. S. Jeong, *Angew. Chem. Int. Ed.* **2005**, *44*, 7926-7929.

[2] C. Schalley, *Analytical Methods in Supramolecular Chemistry*, WILEY-VCH Verlag, Weinheim 2007.