Supporting Information

Control of the cavity size of flexible covalent cages by silver coordination to the peripheral binding sites

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Contents

1 General procedures

1.1 Materials and reagents

All chemicals were of the best commercially available grade and used without further purification. $Ag(SbF_6)$ and Ag(OTf) were purchased from Alfa Aesar and used as received. Lithium bis(trimethylsilyl)amide, DABCO and TIPSCl were purchased from Sigma-Aldrich and used as received. Spectroscopic grade DCM and methanol, anhydrous DMF were used for the synthesis. DCM was distilled over CaH_2 before use. THF was dried using dry-station GT S100 before use. Thin layer chromatography was carried out using aluminium sheets of silica gel (Merck, 60 F_{254}). Column chromatography was carried out using silica gel (Merck, silica gel 60, 0.063– 0.200 mm), fine silica gel (Merck, silica gel 60, 40-63 μm) or aluminium oxide (Merck, aluminium oxide 90 standardized).

1.2 General methods

Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ES-MS). Nuclear Magnetic Resonance (NMR) spectra for ^{1}H, ^{13}C were acquired on Bruker AVANCE 300, 400, 500 or 600 spectrometers. The ^{1}H and ^{13}C spectra were referenced to residual solvent peak. In the assignments, the chemical shift (in ppm) is given first, followed in brackets, by the number of protons implied, the multiplicity of the signal (s: singlet, br: broad, d: doublet, q: quadruplet, m: multiplet), the value of the coupling constants in Hertz if applicable, and finally the assignment. Measures of self-diffusion coefficients were performed on a BRUKER 600 MHz spectrometer - Avance III, equipped with a high strength z gradient probe DOTY Scientific, developing a pulse field gradient of 50 G/cm/A. The gradient coil is cooled by air flow and the sample was thermostated at 298 K. Diffusion NMR data were acquired using a Stimulated Echo pulse sequence with bipolar z gradients. Limited Eddy current Delay was fixed to 5 ms. The gradient strength varied linearly between 6 and 305 G / cm in 30 experiments. The diffusion time and the duration of the sinusoidal gradients were optimized for each sample. Typically the diffusion time was set between 8 and 10 ms, and the half-gradient delay between 600 and 900 s. The gradient recovery delay was set to 100 s. A recycling delay of 3 s was respected between scans. DOSY NMR Processing: DOSY spectra are generated by the DOSY module of the software NMRNotebook, using Inverse Laplace Transform (ILT) driven by maximum entropy, to build the diffusion dimension. An exponential line broadening apodization of 1 Hz was applied to the spectral axis and baseline offset was corrected before DOSY calculation. Intensities of selected NMR peaks were processed by ILT. The final DOSY spectra were obtained with 128 points in the diffusion dimension and 1000 MaxEnt iterations.
UV-visible spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at 21°C with a 1 cm path cell.

2 Experimental procedures and characterization

2.1 Synthesis, ^{1}H and ^{13}C NMR spectra of compound 4

A solution of Lithium bis(trimethylsilyl)amide (1 M in THF, 1.65 mmol, 1.65 mL) was added to a stirred solution of α,ω-bis(O-propargyl)diethyleneglycol (1.1 mmol, 200 mg) in dry THF (120 mL) at room temperature under argon. After 10 min, TIPSCl (1.1 mmol, 235 µL) was added to the reaction mixture. After 25 min, aqueous KOH (1 M, 120 mL) was added. After removal of THF under reduced pressure, and the aqueous layer was extracted with CH_2Cl_2. The organic phase was dried over sodium sulfate, filtrated and evaporated. The residue was purified by silica column chromatography (petroleum ether/AcOEt from 99/1 to 9/10) to afford a colorless oil (123 mg, 33% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 4.22 (2H, s, CH_2-C≡TIPS), 4.18 (2H, d, ^{4}J = 2.4 Hz, CH_2-C≡), 3.67 (8H, m, CH_2-O), 2.40 (1H, t, ^{4}J = 2.4 Hz, HC≡C), 1.04 (21H, br s, Si(iPr)$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) = 103.4 (C_{17}), 87.9 (C_{18}), 79.8 ($C_{18'}$), 74.7 ($C_{17'}$), 70.7 (C_{13},C_{14}), 70.6 (C_{13},C_{14}), 69.3 (C_{12}), 68.9 (C_{15}), 59.4 (C_{16}), 58.6 (C_{11}), 18.8 (C_{20}), 11.3 (C_{19}). **ES-MS**: m/z (%) calcd for $[C_{19}H_{34}N_{16}O_3SiNa]^+$: 361.217; found: 361.220 (100).

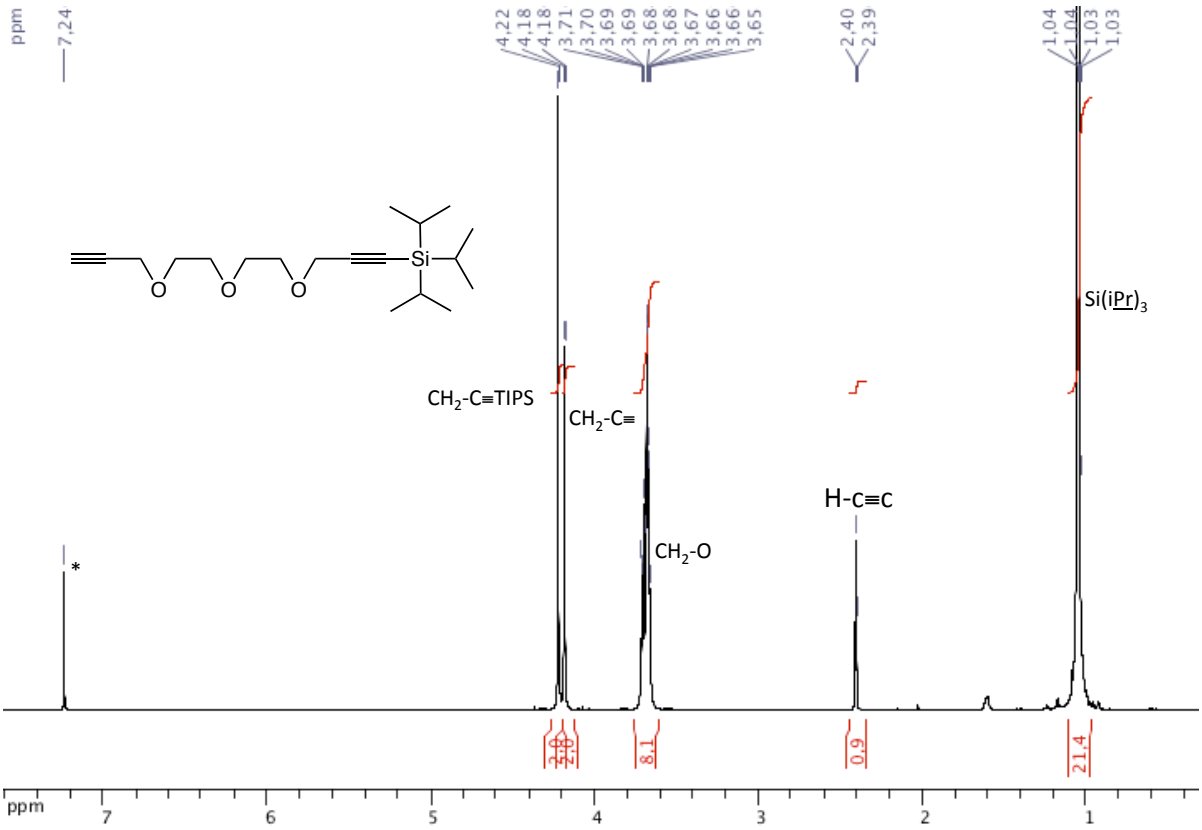

Figure SI1. ^{1}H NMR ($CHCl_3$, 500 MHz, 298K) spectrum of **4**, *: $CHCl_3$.

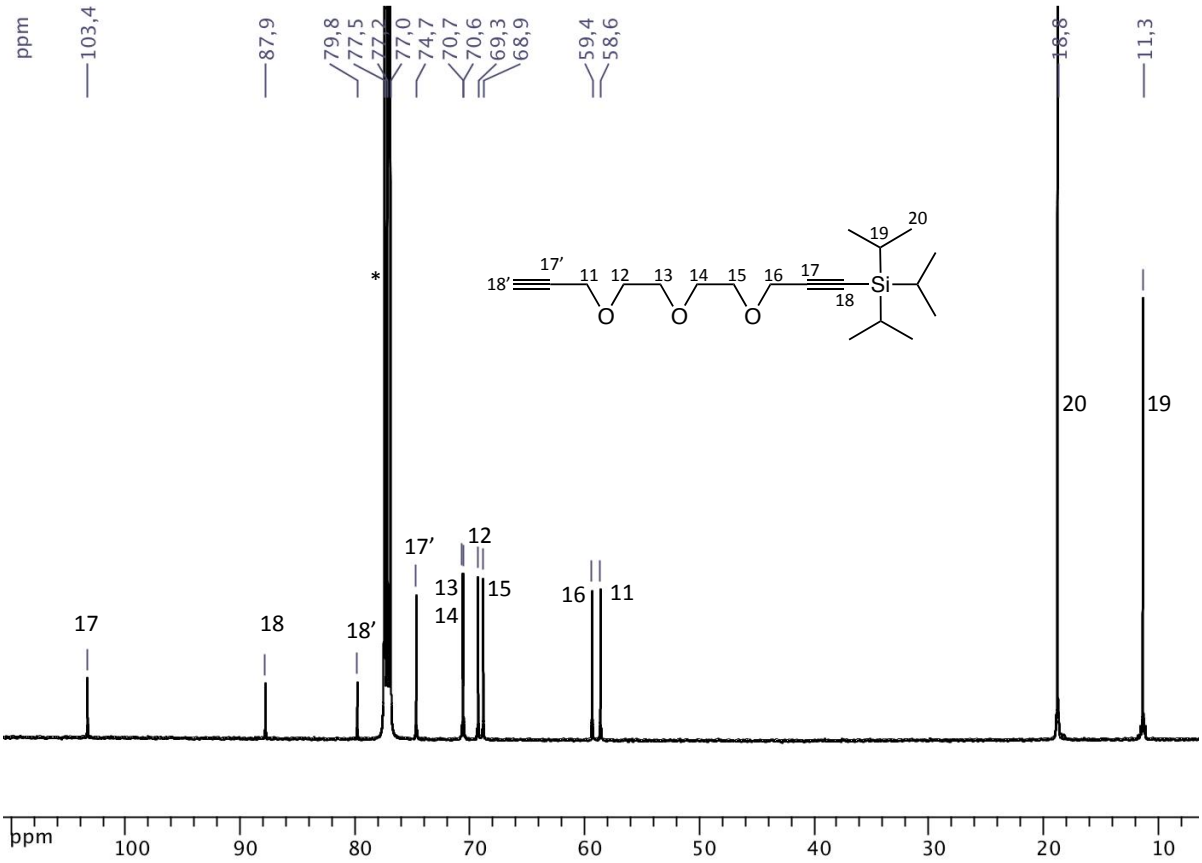

Figure SI2. ^{13}C NMR ($CDCl_3$, 126 MHz, 298K) spectrum of **4**, *: $CHCl_3$.

2.2 Synthesis, ^{1}H and ^{13}C NMR spectra of compound 5

To a stirred solution of **4** (1.80 mmol, 608 mg) and zinc [5,10,15,20-tetrakis(*p*-(azidomethyl)phenyl)porphyrin] **3** (0.39 mmol, 352 mg) in anhydrous DMF (39 mL) were added $CuSO_4.5H_2O$ (0.39 mmol, 98 mg) and sodium ascorbate (1.36 mmol, 270 mg). The reaction mixture was degassed (3 vacuum-argon cycles) and stirred at 50°C overnight under argon. The solvent was evaporated and the residue was dissolved in CH_2Cl_2. The organic layer was washed with water and brine and dried over sodium sulfate. After filtration and evaporation, the residue was purified by silica column chromatography (CH_2Cl_2/MeOH from 100/0 to 90/10) to afford a purple solid (974 mg, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.76 (8H, s, H_{py}), 8.13 (8H, d, ^{3}J=7.4 Hz, H_o), 7.45 (4H, br s, H_t), 7.32 (8H, br d, ^{3}J=7.4 Hz, H_m), 5.49 (8H, br s, H_1), 4.19 (8H, s, H_7), 3.75 (8H, br s, H_2), 3.67 (8H, m, H_6), 3.61 (8H, m, H_5), 3.56 (8H, m, H_4), 3.44 (8H, br s, H_3), 1.01 (84H, br s, Si(iPr)$_3$). **^{1}H NMR** (300 MHz, $CDCl_3$+pyridine-d_5): δ (ppm) = 8.61 (8H, s, H_{py}), 7.93 (8H, d, ^{3}J=8.0 Hz, H_o), 7.66 (4H, s, H_t), 7.35 (8H, d, ^{3}J=8.0 Hz, H_m), 5.60 (8H, s, H_1), 4.19 (8H, s, H_7), 3.98 (8H, s, H_2), 3.49 (32H, m, $H_{3\text{-}6}$), 0.80 (84H, s, Si(iPr)$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) = 150.1 (C_2), 145.0 (C_{10}), 144.2 (C_4), 135.1 (C_5), 133.5 (C_7), 131.8 (C_1), 126.9 (C_6), 122.6 (C_9), 120.0 (C_3), 103.3 (C_{17}), 88.0 (C_{18}), 70.5 (C_{13},C_{14}), 69.8 (C_{12}), 68.8 (C_{15}), 63.9 (C_{11}), 59.3 (C_{16}), 54.2 (C_8), 18.8 (C_{20}), 11.3 (C_{19}). **ES-MS**: m/z (%) calcd for $[C_{124}H_{168}N_{16}O_{12}Si_4ZnNa_2]^{2+}/2$: 1147.5590; found: 1147.5535 (100) $[M+2Na^+]/2$; calcd for $[C_{248}H_{337}N_{32}O_{24}Si_8Zn_2Na_2]^{3+}/3$: 1515.0883; found: 1515.0654 (78) $[M+2Na^+ + H^+]/3$.

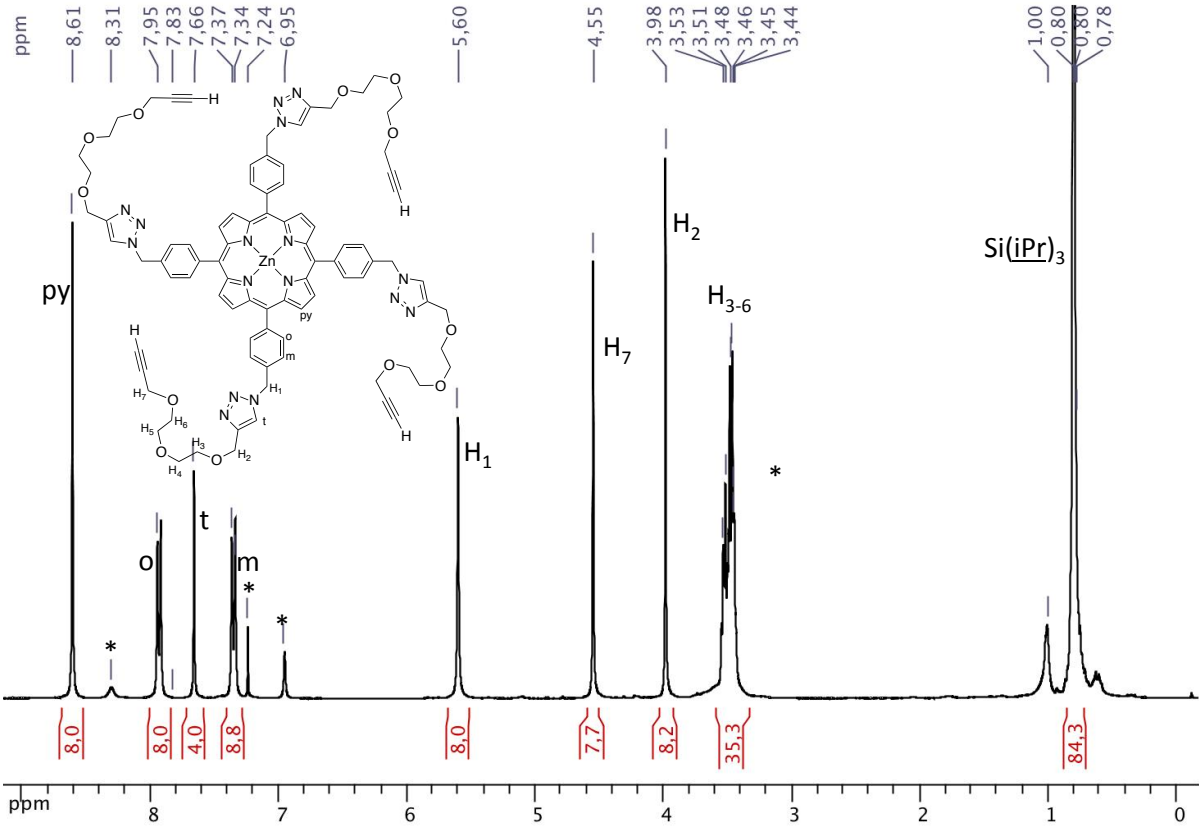

Figure SI3. ^{1}H NMR ($CDCl_3$+pyridine-d_5, 300 MHz, 298K) spectrum of **5**, *: pyridine or $CHCl_3$.

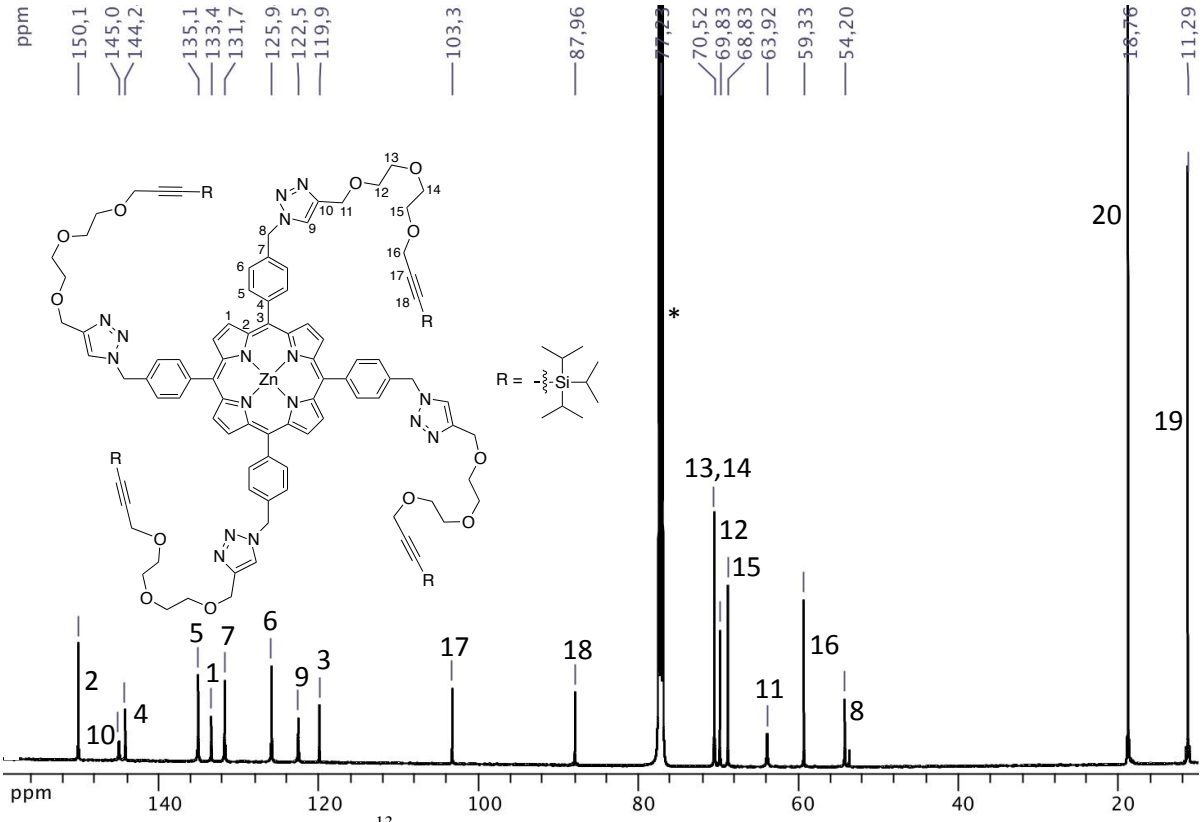

Figure SI4. ^{13}C NMR ($CDCl_3$, 126 MHz, 298K) spectrum of **5**.

2.3 Synthesis, ^{1}H and ^{13}C NMR spectra of compound 6

TBAF.$3H_2O$ (320 µmol, 100 mg) was added to a stirred solution of **5** (67 µmol, 150 mg) in dry THF (25 mL). The reaction mixture protected from light was stirred overnight at room temperature. After removal of THF under reduced pressure, the residue was dissolved in CH_2Cl_2. The organic layer was washed with water, the aqueous phase was extracted several times with CH_2Cl_2 and the combined organic phases were dried over sodium sulfate, filtrated and evaporated. The residue was purified by silica column chromatography (CH_2Cl_2/MeOH from 100/0 to 93/7) to afford a purple solid (68 mg, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.75 (8H, s, H_{py}), 8.12 (8H, d, ^{3}J=8.0 Hz, H_o), 7.43 (4H, br s, H_t), 7.32 (8H, br d, ^{3}J=8.0 Hz, H_m), 5.48 (8H, br s, H_1), 4.14 (8H, d,^{4}J=2,4 Hz, H_7), 3.72 (8H, br s, H_2), 3.64 (8H, m, H_6), 3.60 (8H, m, H_5), 3.55 (8H, m, H_4), 3.41 (8H, br s, H_3), 2.36 (4H, t, ^{4}J=2,4 Hz, H-c≡c). **^{1}H NMR** (300 MHz, $CDCl_3$+pyridine-d_5): δ (ppm) = 8.70 (8H, s, H_{py}), 8.05 (, d, ^{3}J=7.9 Hz, H_o), 7.75 (4H, s, H_t), 7.48 (8H,d, ^{3}J=7.9 Hz, H_m), 5.73 (8H, s, H_1), 4.67 (8H, s, H_2), 4.05 (8H, d, ^{3}J=2,4 Hz, H_7), 3.62 (32H, m, $H_{3\text{-}6}$), 2.29 (4H, t, ^{3}J=2,4 Hz, HC≡C). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) = 150.1 (C_2), 145.0 (C_{10}), 144.2 (C_4), 135.1 (C_5), 133.5 (C_7), 131.8 (C_1), 126.0 (C_6), 122.6 (C_9), 120.0 (C_3), 79.8 (C_{17}), 74.9 (C_{18}), 70.5 (C_{13},C_{14}), 69.8 (C_{12}), 69.3 (C_{15}), 63.9 (C_{11}), 58.6 (C_{16}), 54.2 (C_8). **ES-MS**: m/z (%) calcd for $[C_{88}H_{88}N_{16}O_{12}Zn_2]^{+}$: 1625.61; found: 1625.61 (100) [M+H^{+}]; calcd for $[C_{88}H_{88}N_{16}O_{12}ZnH_2]^{2+}$/2 : 813.31; found: 813.31 (22) [M+$2H^{+}$]/2.

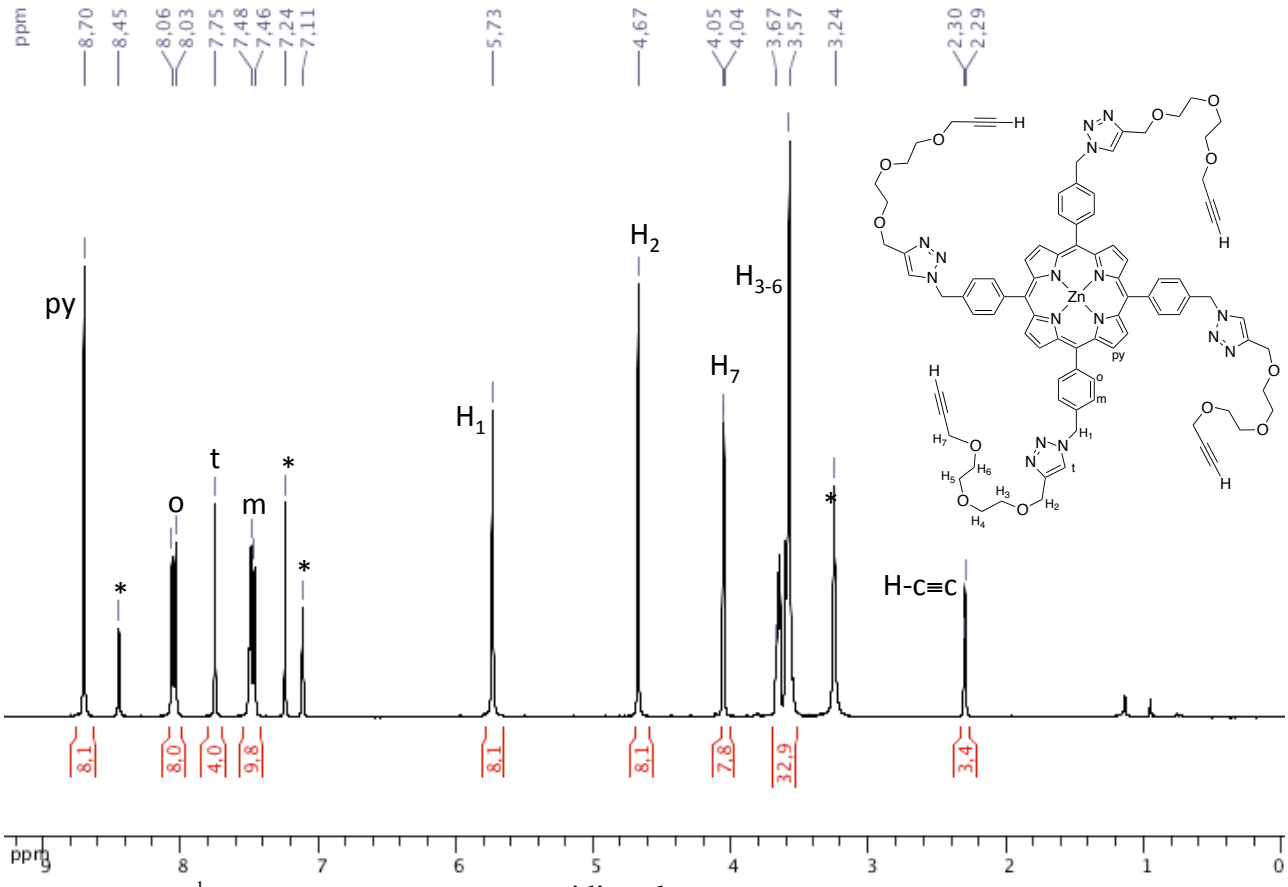

Figure SI5. ^{1}H NMR spectrum ($CDCl_3$+pyridine-d_5, 300 MHz, 298K) of **6**, *: pyridine or methanol.

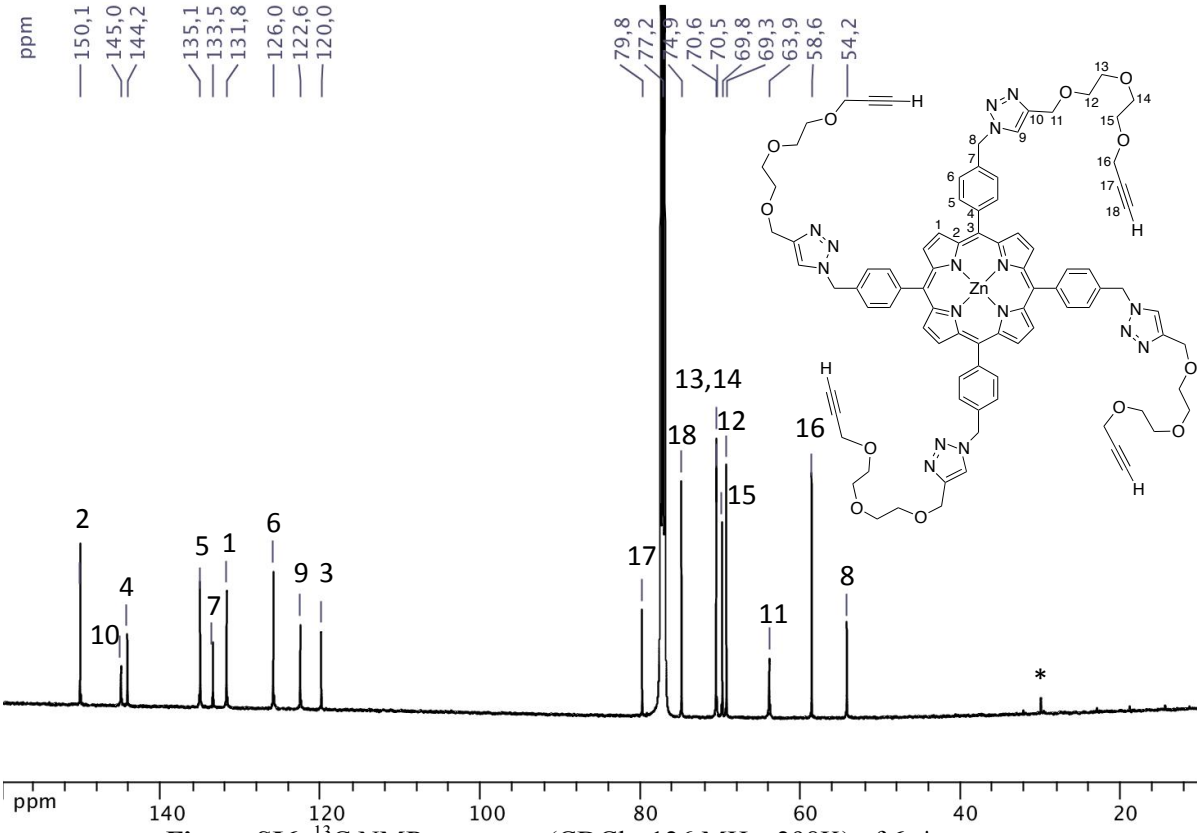

Figure SI6. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz, 298K) of **6**, *: grease.

2.4 Synthesis of cages 1 and 1•DABCO

To a stirred solution of **6** (295 µmol, 480 mg) and zinc [5,10,15,20-tetrakis(*p*-(azidomethyl)phenyl)porphyrin] **3** (295 µmol, 265 mg) in dried and degassed CH_2Cl_2 (320 mL), a solution of DABCO in CH_2Cl_2 was added (133.5 mM, 2.21 mL, 295 µmol). The reaction mixture, protected from light, was stirred at room temperature under argon for 2 hours. [Cu(tren')]Br (354 µmol, 639 mg) and Na_2CO_3 (1.65 mmol, 175 mg) were added, and the reaction mixture was refluxed under argon for 5 days. The mixture was cooled at room temperature, and washed with water and brine. The organic phase was dried over sodium sulfate and evaporated. The residue was purified by consecutive column chromatographies first on standardized alumina (CH_2Cl_2/MeOH 2%) then on fine silica (CH_2Cl_2/MeOH 90/10 then $CHCl_3$/MeOH 90/10 with 1% pyridine) to afford a mixture of **1** and **1•DABCO**.

Removal of DABCO from 1•DABCO to afford 1: To a solution of cage **1•DABCO** in CH_2Cl_2 MeOH in excess was added. The solution was stirred overnight to afford a suspension. The solvent was separated by centrifugation and the residue was dried under vacuum to afford a purple solid.

The yield of the reaction based on the amount of cage **1** obtained (185 mg) was 25%.

Cage **1**: **^{1}H NMR** (500 MHz, DMF-d_7): δ 8.49 (16 H, s, H_{py}), 8.20 (8 H, s, H_t), 8.12 (8 H, d, ^3J = 7.6 Hz, $H_{o\ out}$), 7.66 (8 H, d, ^3J = 7.6 Hz, $H_{m\ out}$), 7.26 (8 H, br s, $H_{o\ in}$), 6.53 (8 H, br s, $H_{m\ in}$), 5.66 (16 H, s, H_1), 4.62 (16 H, s, H_2), 3.69 (16 H, m, H_3), 3.66 (16 H, m, H_4). **^{13}C NMR** (126 MHz, DMF-d_7): δ 150.6 (C_2), 146.0 (C_{10}), 143.6 (C_4), 136.1 ($C_{5\ in}$), 135.6 (C_7), 135.5 ($C_{5\ out}$), 132.5 (C_1), 127.0 ($C_{6\ out}$), 126.3 ($C_{6\ in}$), 125.1 (C_9), 121.0 (C_3), 71.3 (C_{13}), 70.5 (C_{12}), 65.0 (C_{11}), 54.8 (C_8). **ES-MS**: m/z (%) calcd for $[C_{136}H_{120}N_{32}O_{12}Zn_2Na_2]^{2+}$/2: 1283.4065; found: 1283.4089 (100) [M+2Na$^+$]/2; calcd for $[C_{136}H_{120}N_{32}O_{12}Zn_2Na_3]^{3+}$/3: 863.2674; found: 863.2537 (88) [M+3Na$^+$]/3.

Cage **1•DABCO**: **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.45 (16 H, s, H_{py}), 8.11 (8 H, s, H_t), 8.00 (8 H, dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, $H_{o\ out}$), 7.69 (8 H, dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, $H_{m\ out}$), 7.62 (8 H, dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, $H_{m\ in}$), 7.47 (8 H, dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, $H_{o\ in}$), 5.93 (16 H, s, H_1), 4.84 (16 H, s, H_2), 3.82 (16 H, m, H_3), 3.76 (16 H, m, H_4), -5.04 (12 H, s, H_{DABCO}). **^{13}C NMR** (126 MHz, CD_2Cl_2): δ 149.7 (C_2), 146.2 (C_{10}), 143.4 (C_4), 135.2 ($C_{5\ in}$), 134.9 (C_7), 134.4 ($C_{5\ out}$), 131.7 (C_1),

127.0 ($C_{6\,out}$), 126.2 ($C_{6\,in}$), 123.6 (C_9), 119.8 (C_3), 71.3 (C_{13}), 70.4 (C_{12}), 65.5 (C_{11}), 53.8 (C_8), 38.7 (C_{DABCO}). **ES-MS**: m/z (%) calcd for $[C_{136}H_{121}N_{32}O_{12}Zn_2Na_2]^{3+}/3$: 855.939; found: 855.608 (100) $[M\text{-}DABCO+H^+{+}2Na^+]/3$; calcd for $[C_{142}H_{133}N_{34}O_{12}Zn_2Na_2]^{3+}/3$: 893.307; found: 893.306 (89) $[M+H^+{+}2Na^+]/3$; calcd for $[C_{136}H_{121}N_{32}O_{12}Zn_2Na]^{2+}/2$: 1272.417; found: 1274.416 (64) $[M\text{-}DABCO+H^+{+}Na^+]/2$; calcd for $[C_{142}H_{133}N_{34}O_{12}Zn_2Na]^{2+}/2$: 1328.466; found: 1328.468 (55) $[M+H^+{+}Na^+]/2$.

Coordination of DABCO inside 1 to afford 1•DABCO: DABCO (5.9 mM, 248 µL) was added to a stirred suspension of cage **1** (1.46 µmol, 3.7 mg) in distilled CH_2Cl_2 (10 mL) at room temperature. The purple solution, protected from light, was stirred for 20 minutes. The solvent was removed under reduced pressure and the residue was dried under vacuum to afford a purple solid (3.8 mg) in quantitative yield.

2.4.1 NMR characterization of compound 1•DABCO

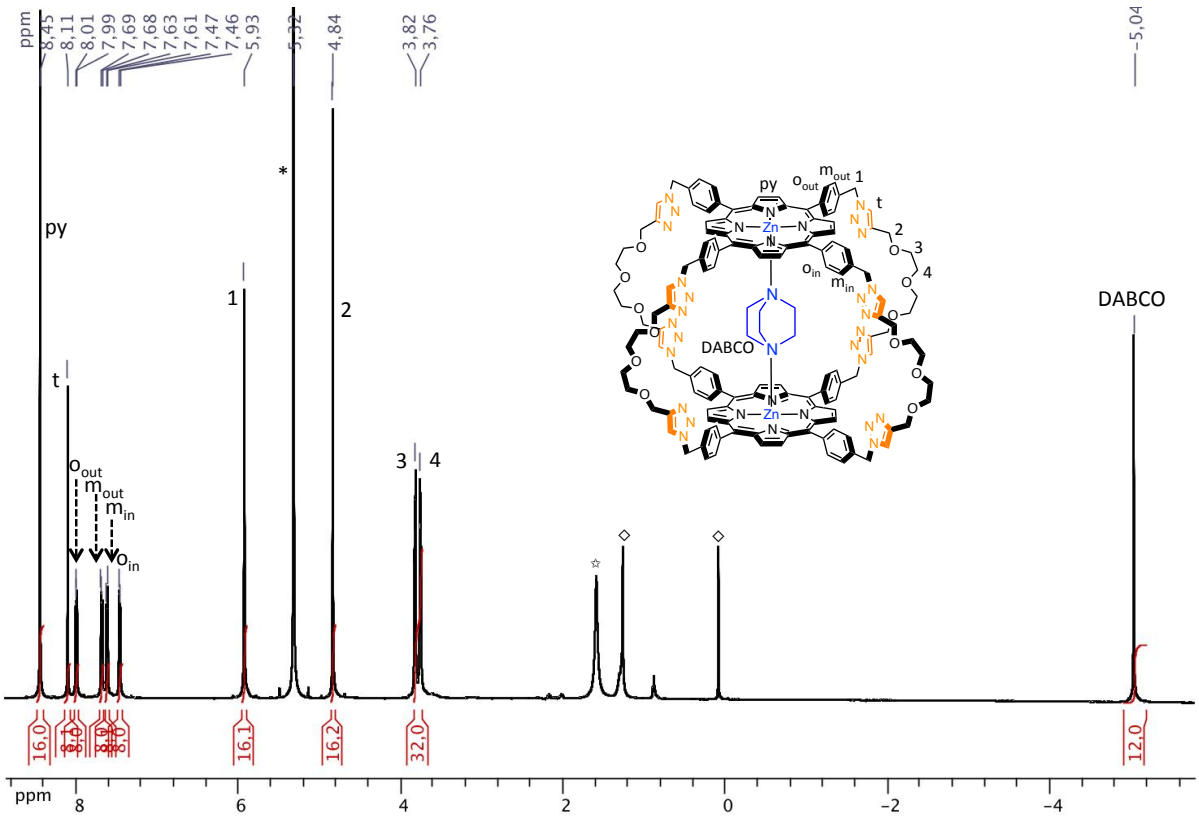

Figure SI7. ^1H NMR (CD_2Cl_2, 500 MHz, 298K) spectrum of cage **1•DABCO**, *: CH_2Cl_2, ☆: H_2O, ◇: grease.

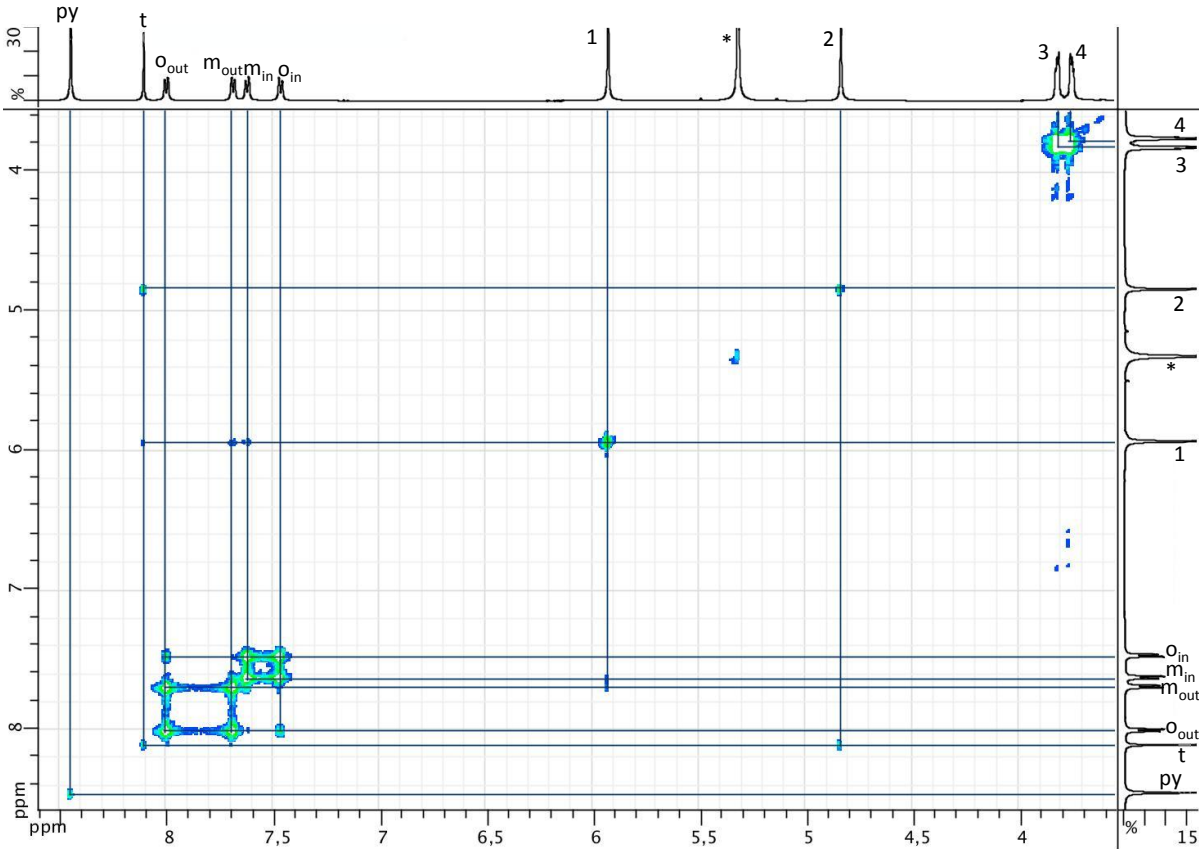

Figure SI8. COSY spectrum (CD_2Cl_2, 500 MHz, 298K) of cage **1•DABCO**, *: CH_2Cl_2.

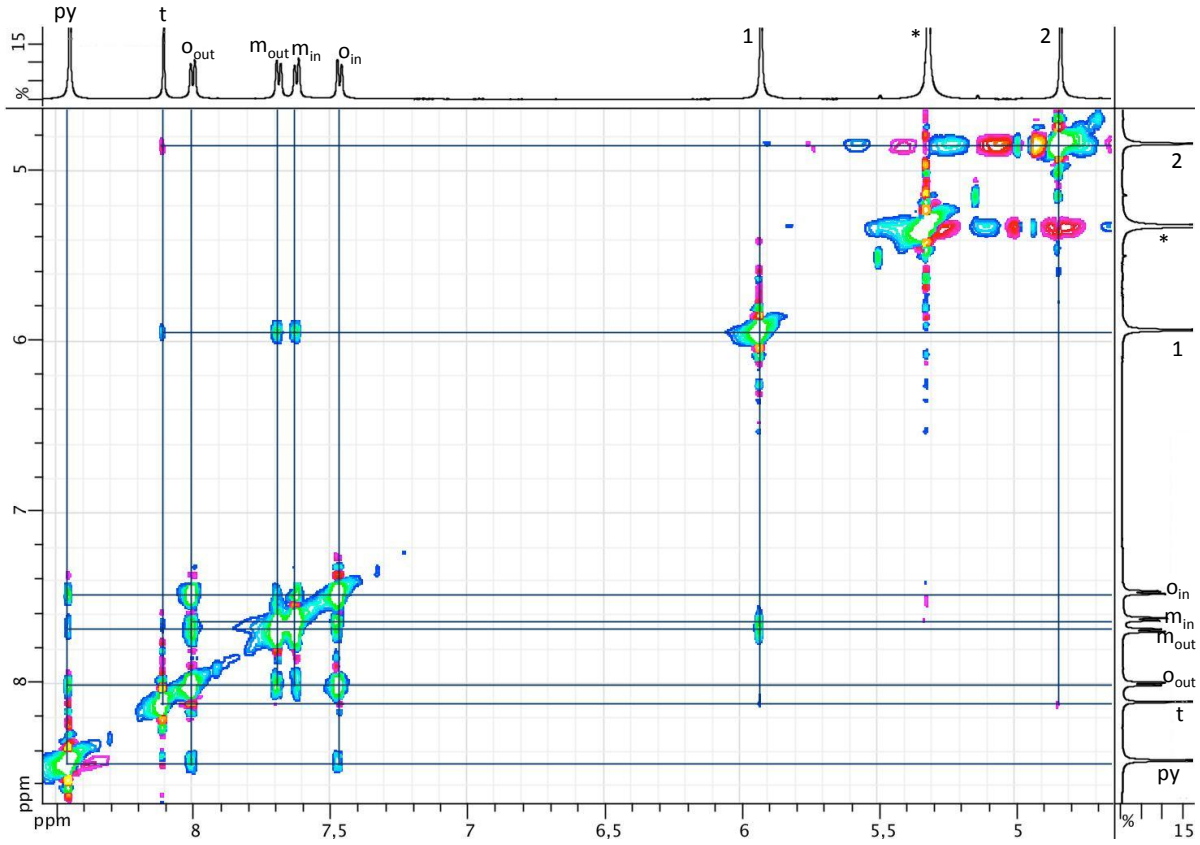

Figure SI9. ROESY spectrum (CD_2Cl_2, 500 MHz, 298K) of cage **1•DABCO**, *: CH_2Cl_2.

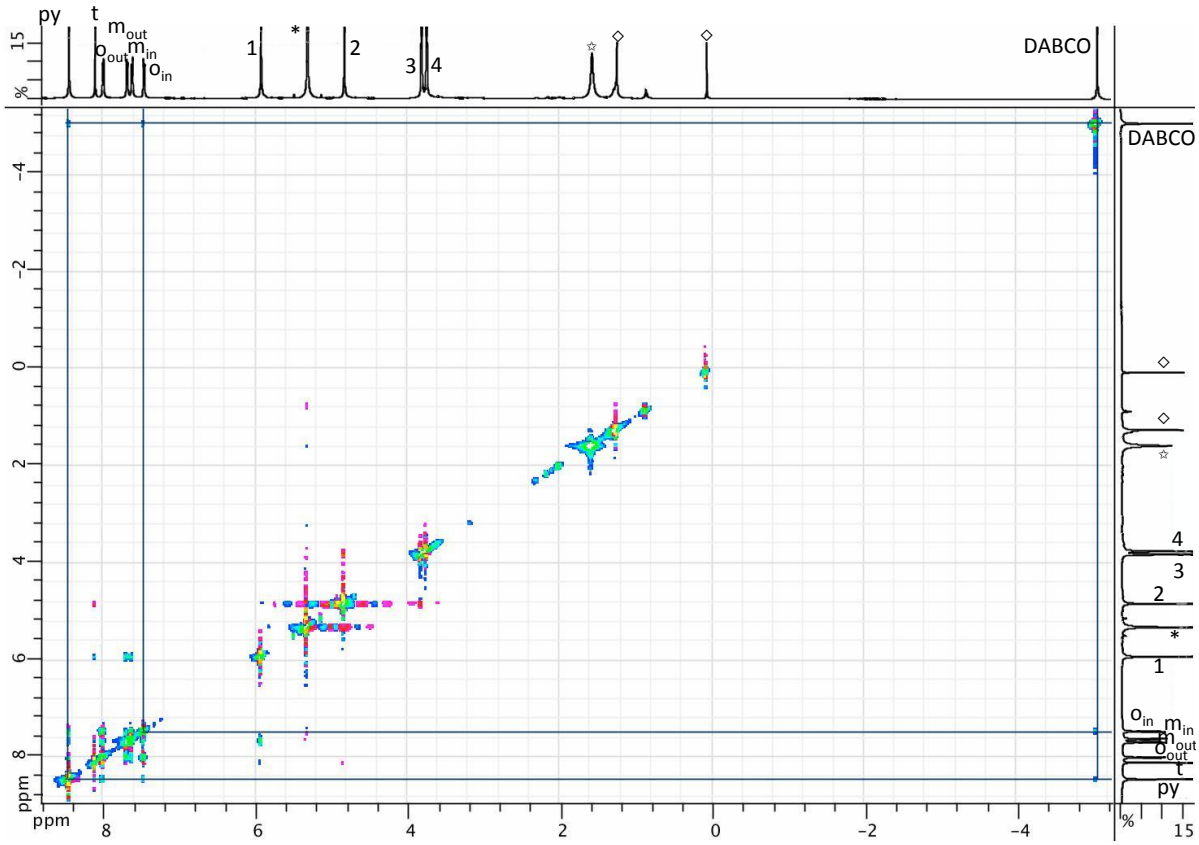

Figure SI10. ROESY spectrum (CD_2Cl_2, 500 MHz, 298K) of cage **1•DABCO**, *: CH_2Cl_2, ☆: H_2O, ◇: grease.

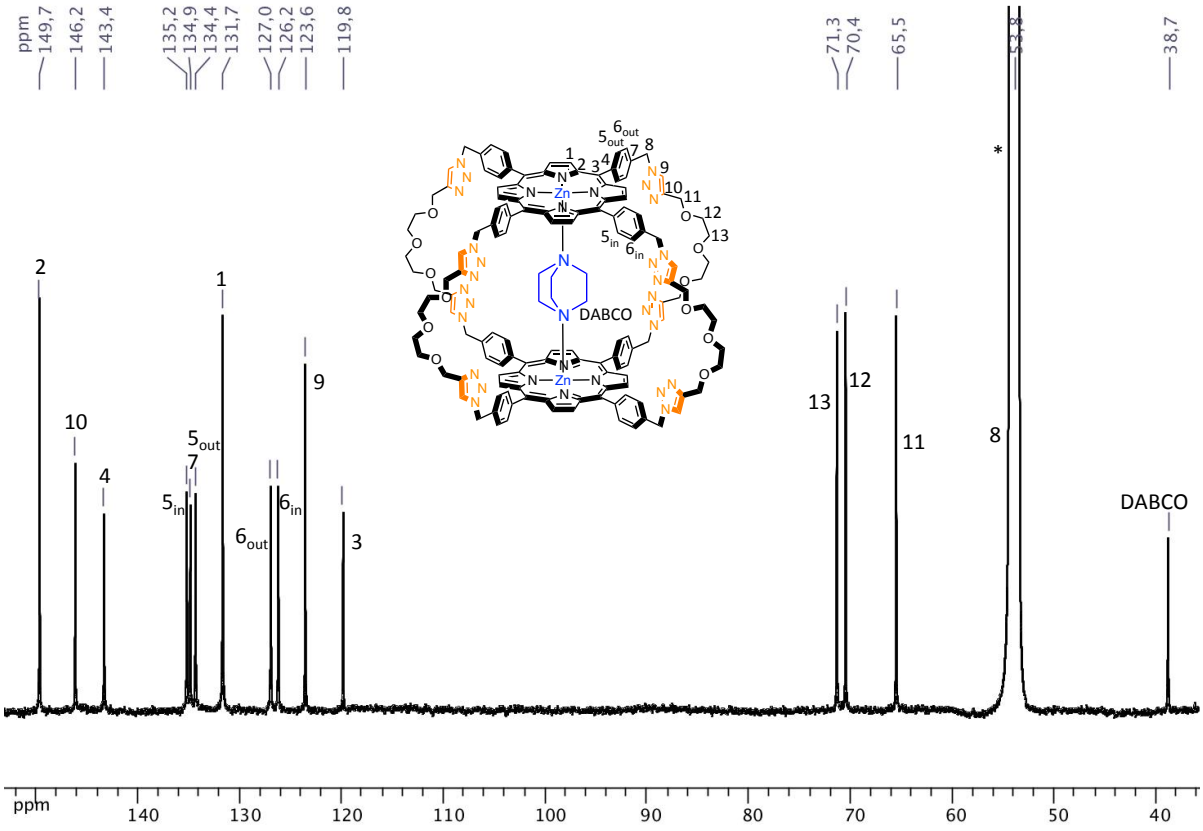

Figure SI11. ^{13}C spectrum (CD_2Cl_2, 126 MHz, 298K) of cage **1•DABCO**, *: CH_2Cl_2.

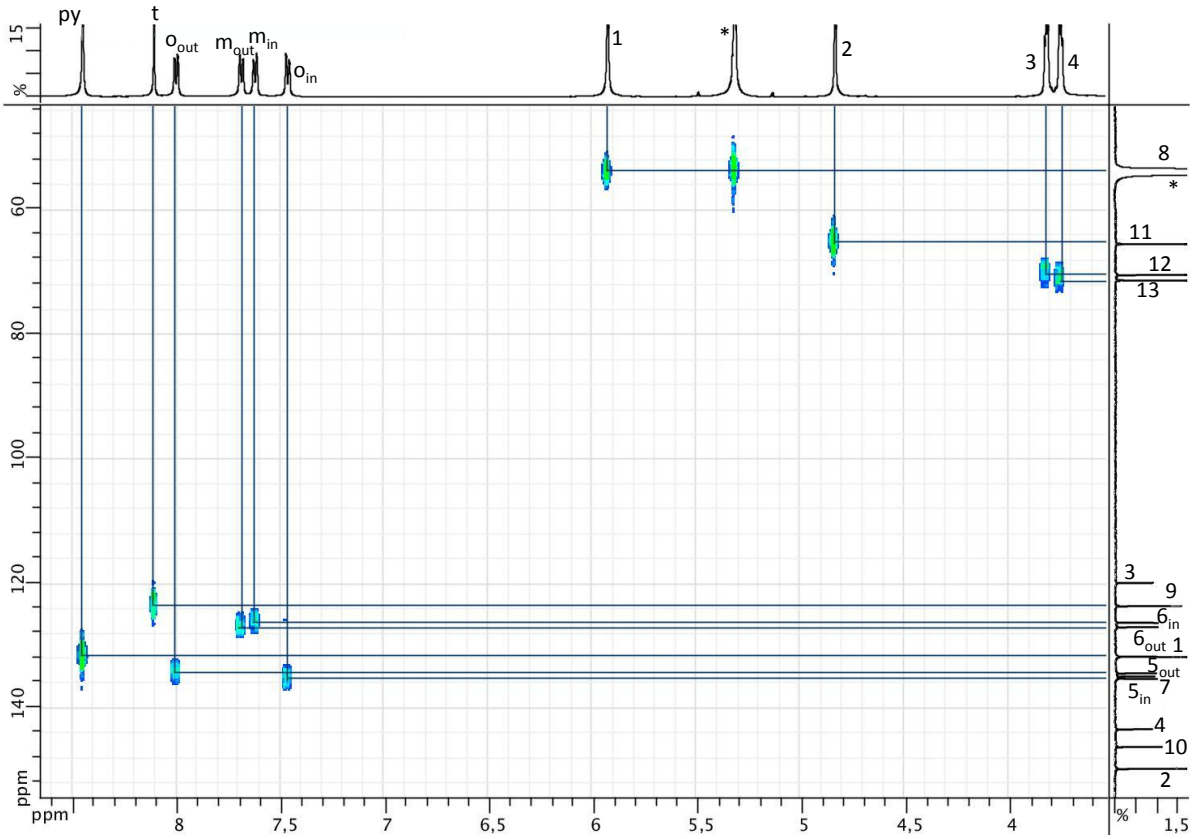

Figure SI12. HSQC spectrum (CD_2Cl_2, ^1H 500 MHz; ^{13}C 126 MHz, 298K) of cage **1•DABCO**, *: CH_2Cl_2.

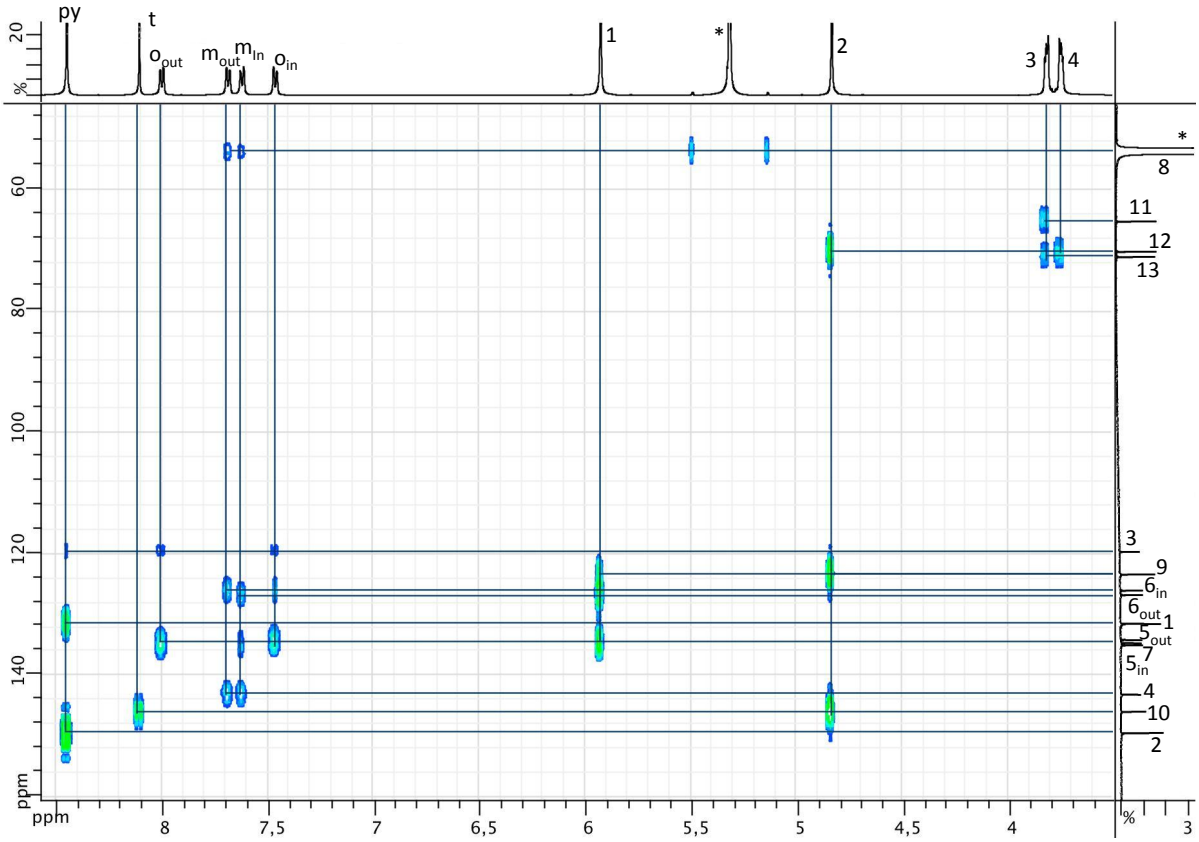

Figure SI13. HMBC spectrum (CD_2Cl_2, ^1H 500 MHz; ^{13}C 126 MHz, 298K) of cage **1•DABCO**, *: CH_2Cl_2.

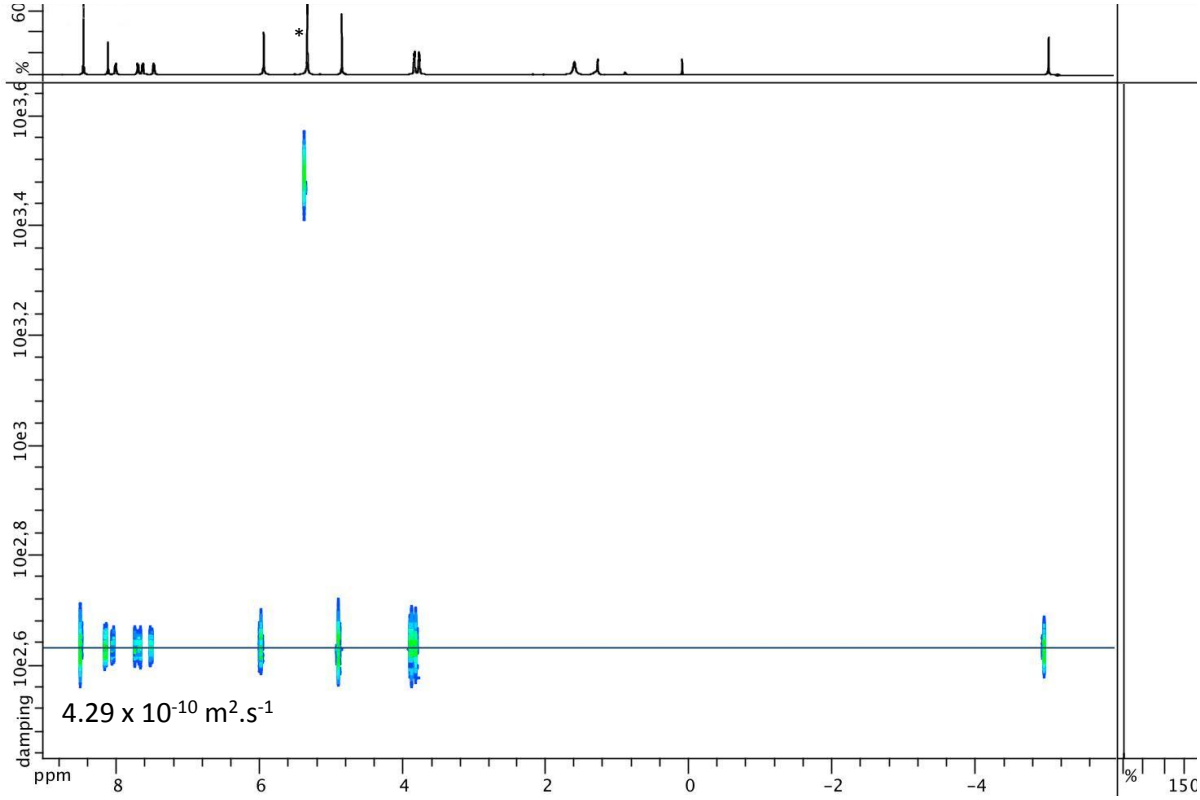

Figure SI14. DOSY NMR spectrum (CD_2Cl_2, 600 MHz, 298K) of cage **1•DABCO**, *: CH_2Cl_2.

2.4.2 ESI-MS spectrum of 1•DABCO

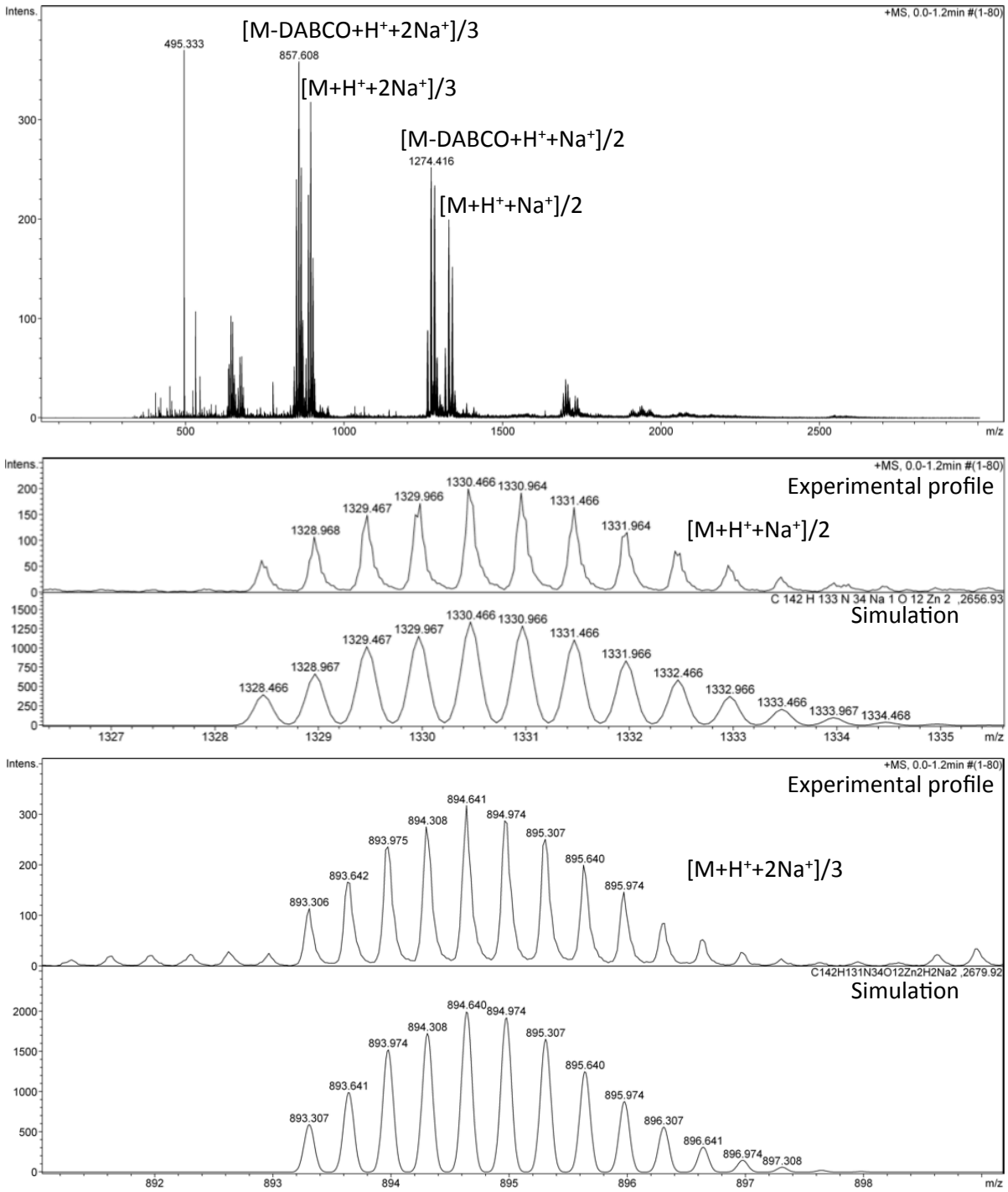

Figure SI15. ES-MS spectrum of cage **1•DABCO**.

2.4.3 X-ray structure of 1•DABCO

The X-ray crystal structure obtained for **1•DABCO** was not of sufficient quality:
Alerts level A:
RFACG01_ALERT_3_A The value of the R factor is > 0.20: R factor given = 0.217
RFACR01_ALERT_3_A The value of the weighted R factor is > 0.45: Weighted R factor given = 0.554
PLAT082_ALERT_2_A High R1 Value: 0.22
PLAT084_ALERT_3_A High wR2 Value (i.e. > 0.25): 0.55
Author Response:
The diffraction quality was very poor. Rmerge is over 30 for a resolution higher than 1.05 A-1. Various crystals were measured with no improvement in the data quality.

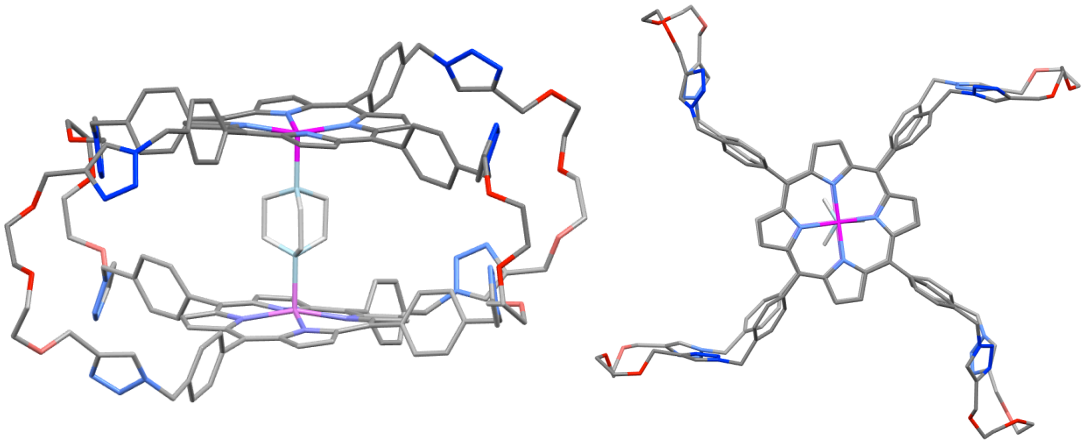

Figure SI16. Crystal structure of cage **1•DABCO**: side view (left) and top view (right).

2.4.4 UV-Vis. Spectra of 1 after addition of DABCO

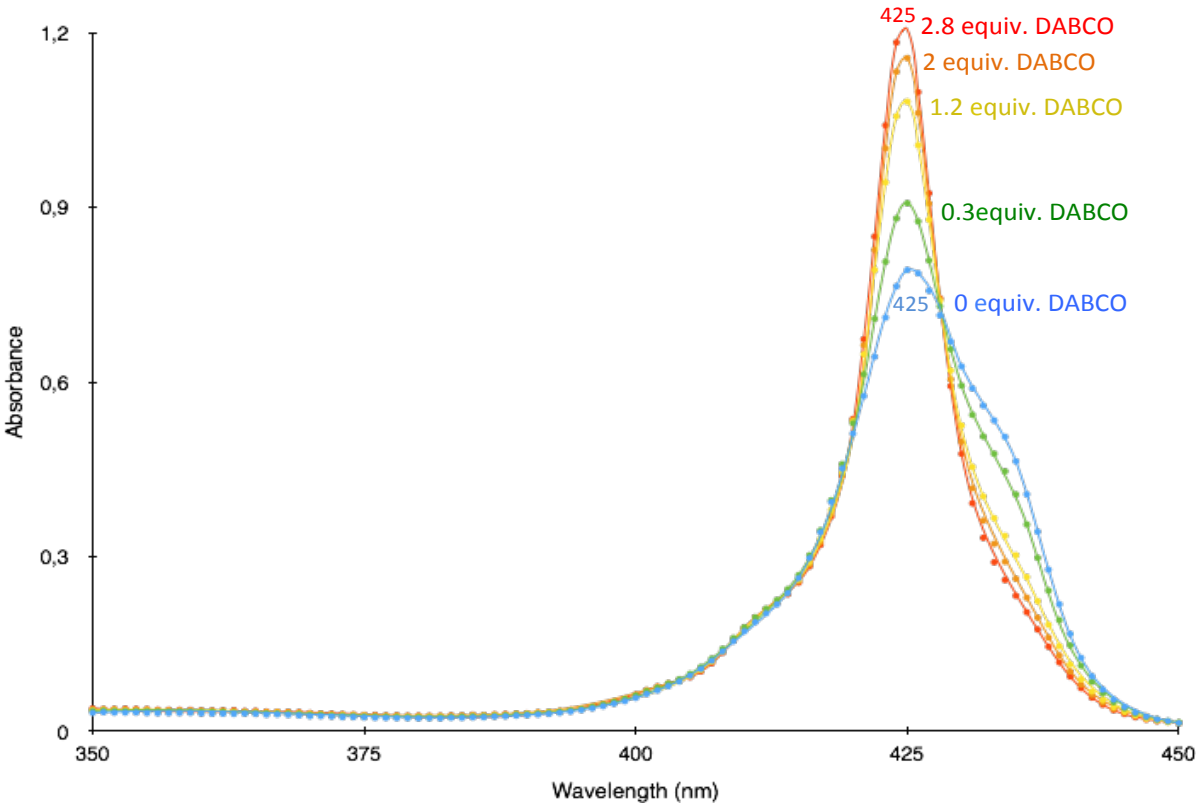

Figure SI17. UV-Vis. spectra of **1** ($1.1.10^{-6}$ $mol.L^{-1}$) in $CHCl_3$/10% MeOH (blue) and after addition of 0.3, 1.2, 2 and 2.8 equiv. of DABCO.

2.4.5 UV-Vis. Spectra of 1 and ZnTTP

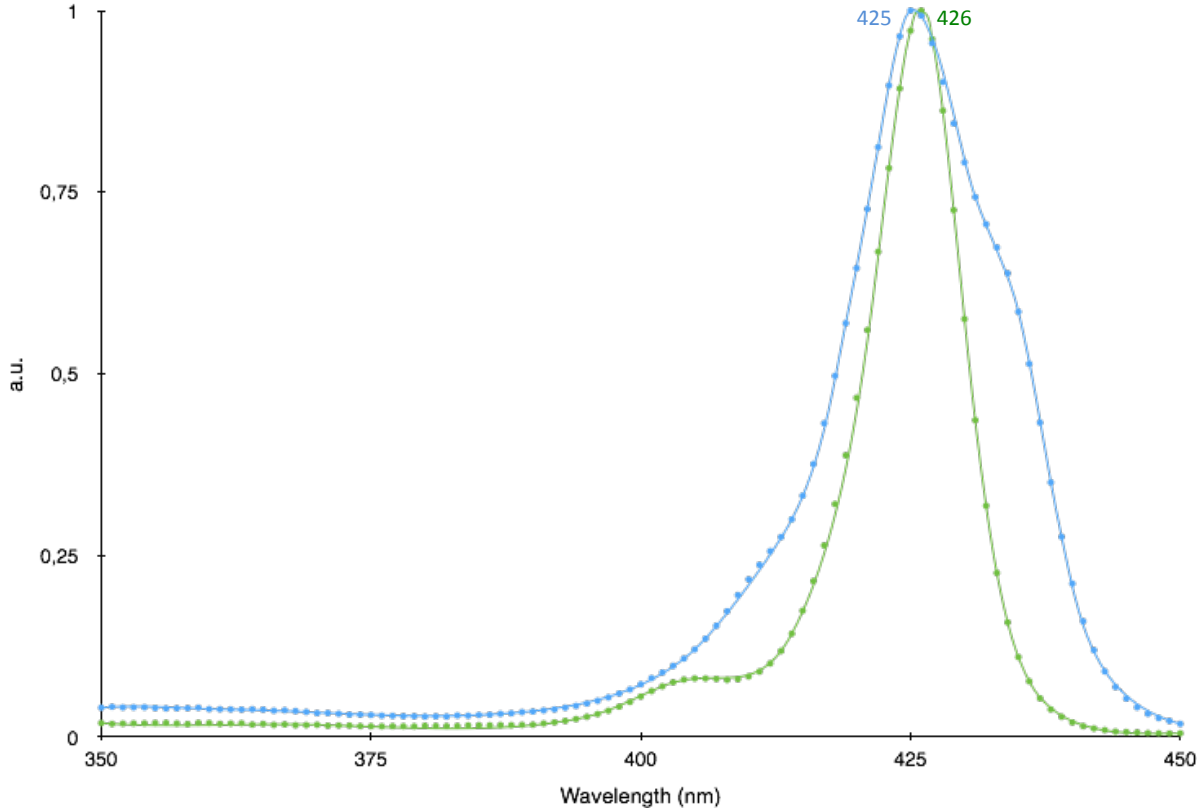

Figure SI18. UV-Vis. spectra of **ZnTTP** (green) and **1** (blue) in $CHCl_3$/10% MeOH.

2.4.6 NMR characterization of compound 1

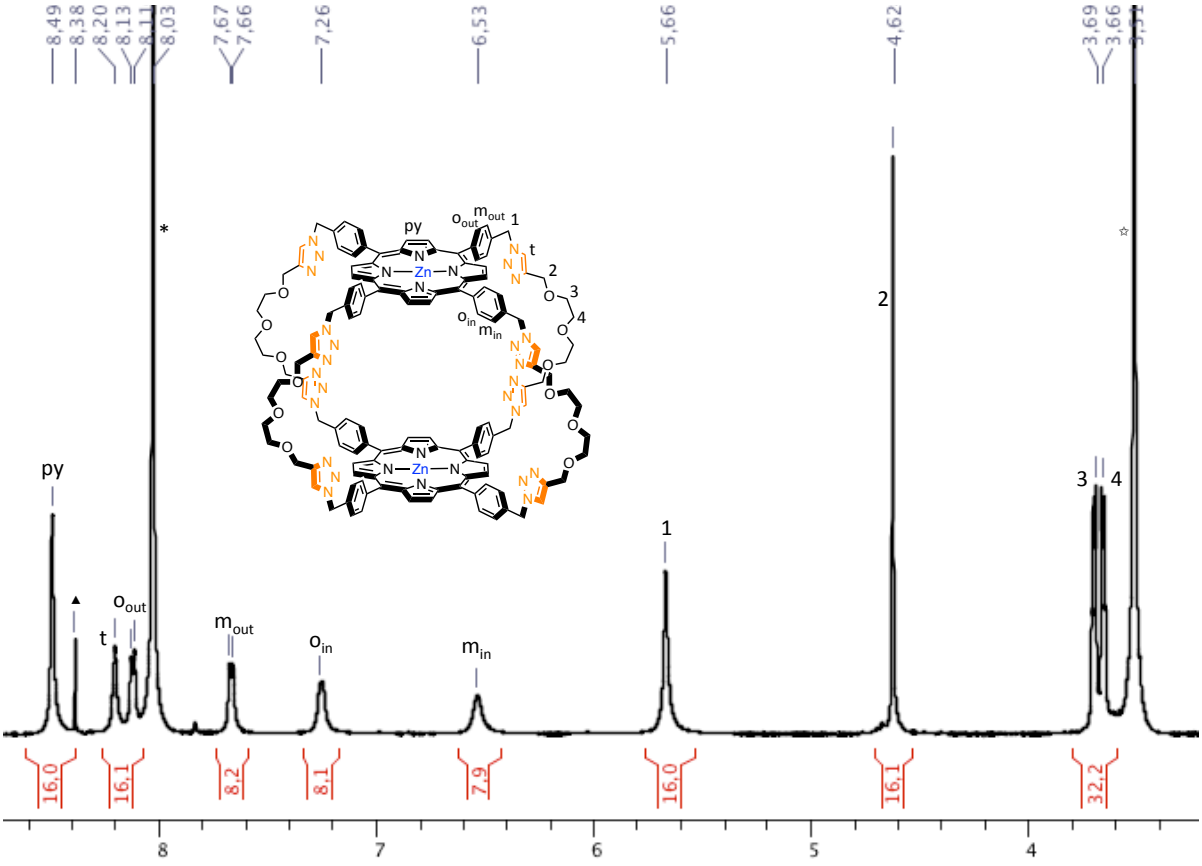

Figure SI19. ^{1}H NMR spectrum (DMF-d_7, 500 MHz, 298K) of cage **1**, *: DMF, ▲: $CHCl_3$, ☆: H_2O.

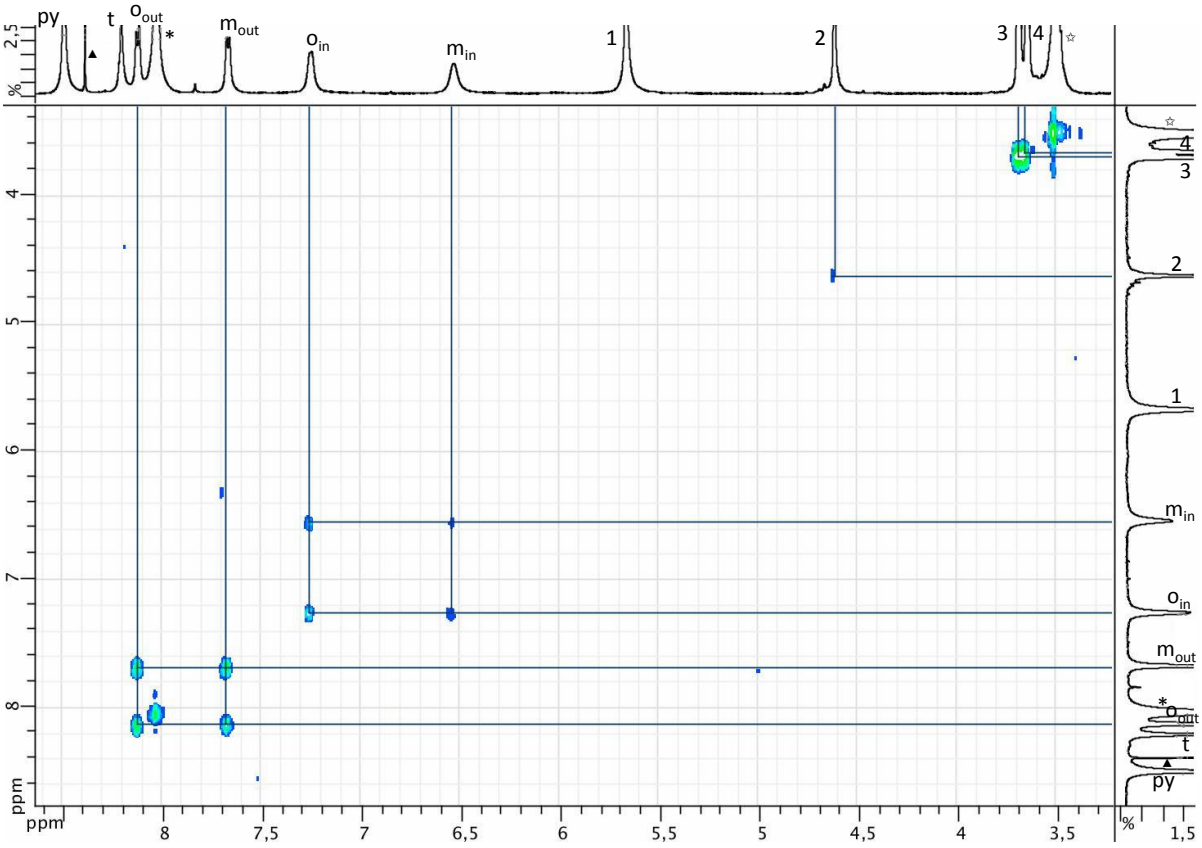

Figure SI20. COSY spectrum (DMF-d_7, 500 MHz, 298K) of cage **1**, *: DMF, ▲: $CHCl_3$, ☆: H_2O.

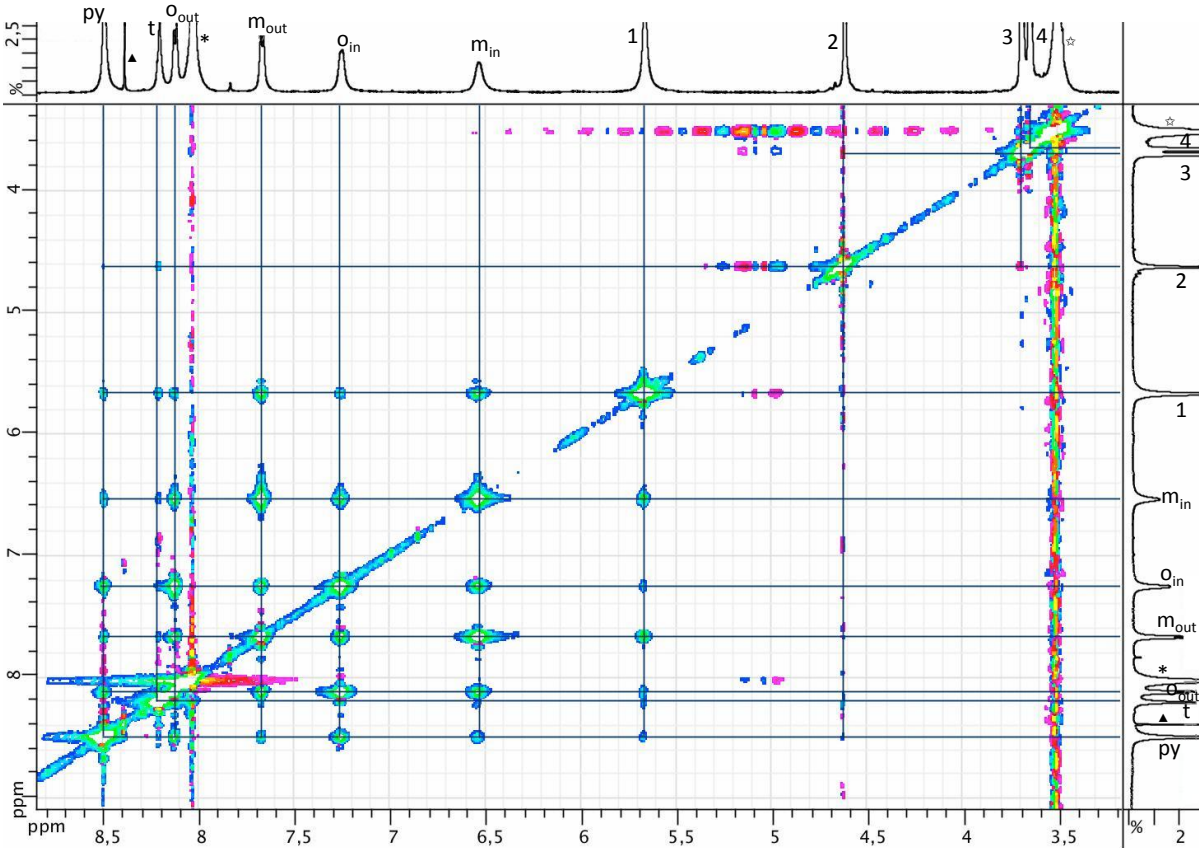

Figure SI21. NOESY spectrum (DMF-d_7, 500 MHz, 298K) of cage **1**, *: DMF, ▲: $CHCl_3$, ☆: H_2O.

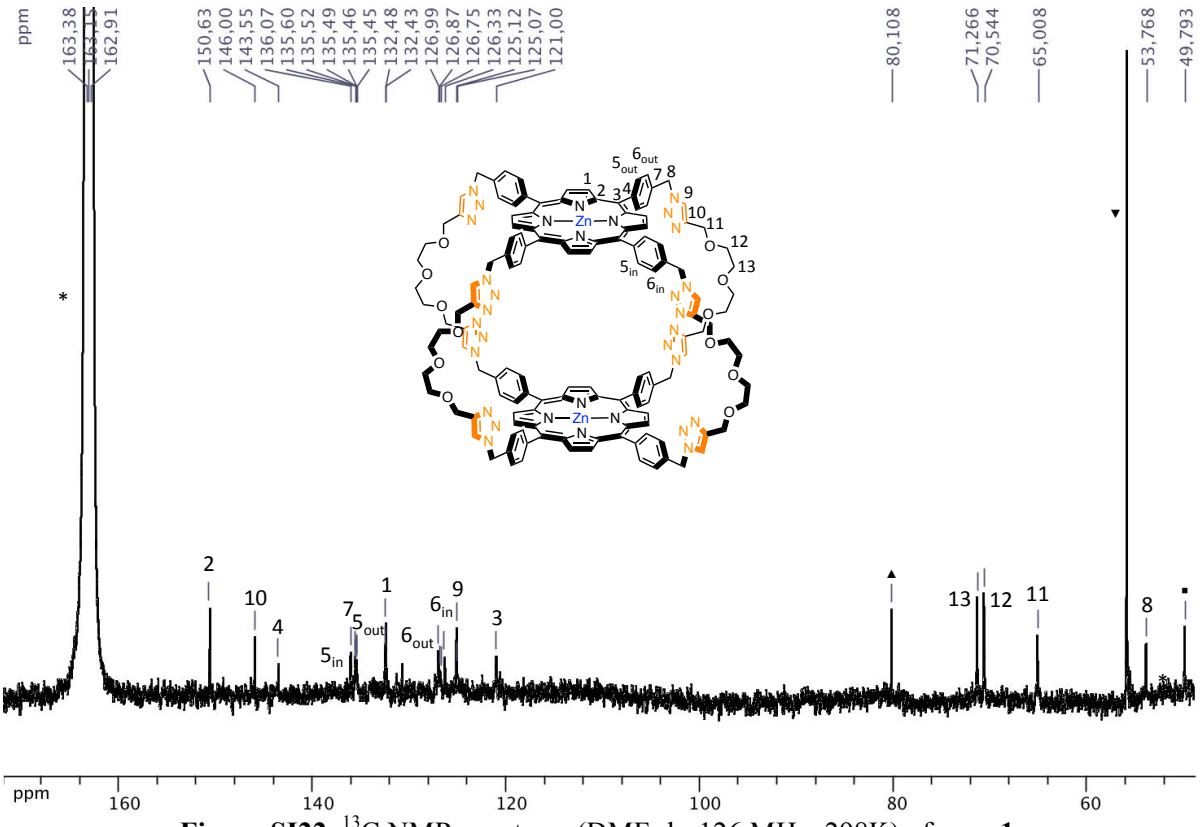

Figure SI22. ^{13}C NMR spectrum (DMF-d_7, 126 MHz, 298K) of cage **1**, *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ■: MeOH.

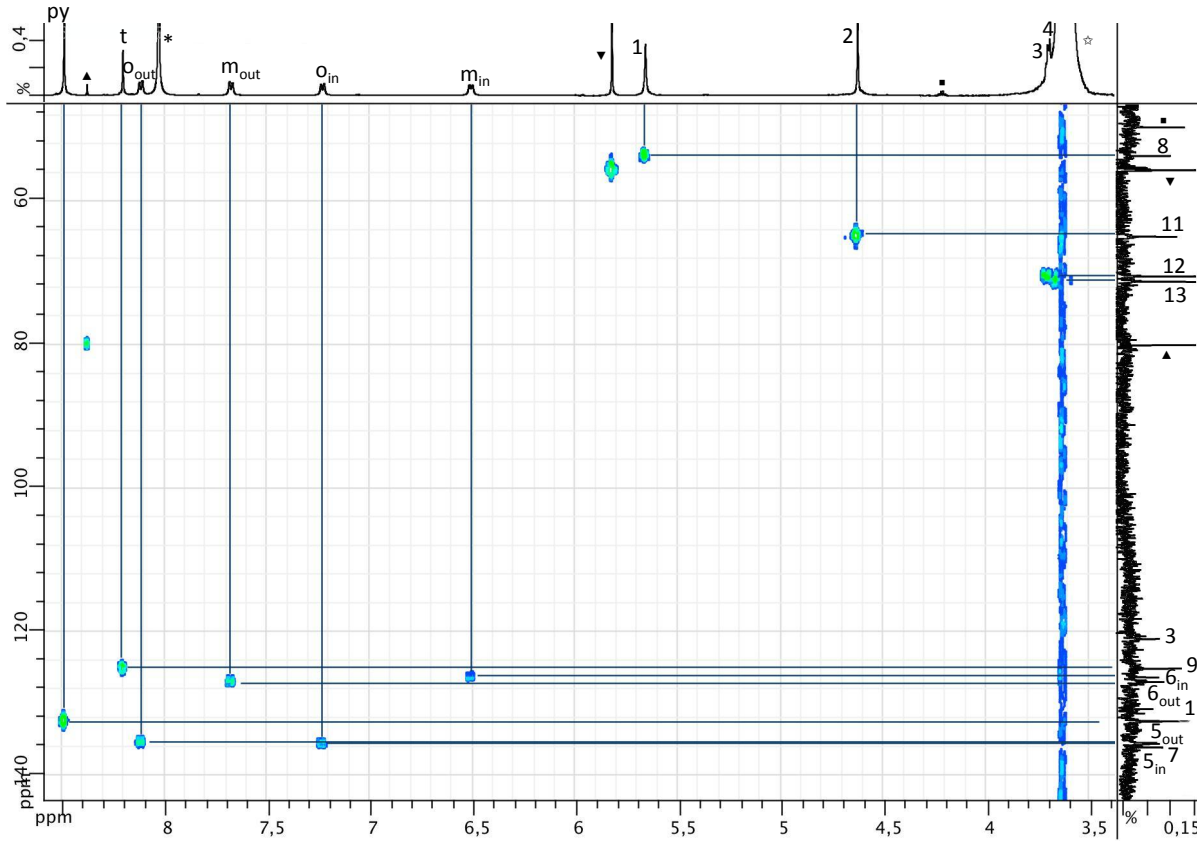

Figure SI23. HSQC spectrum (DMF-d_7, ^{1}H 500 MHz; ^{13}C 126 MHz, 298K) of cage **1**, *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ■: MeOH, ☆: H_2O.

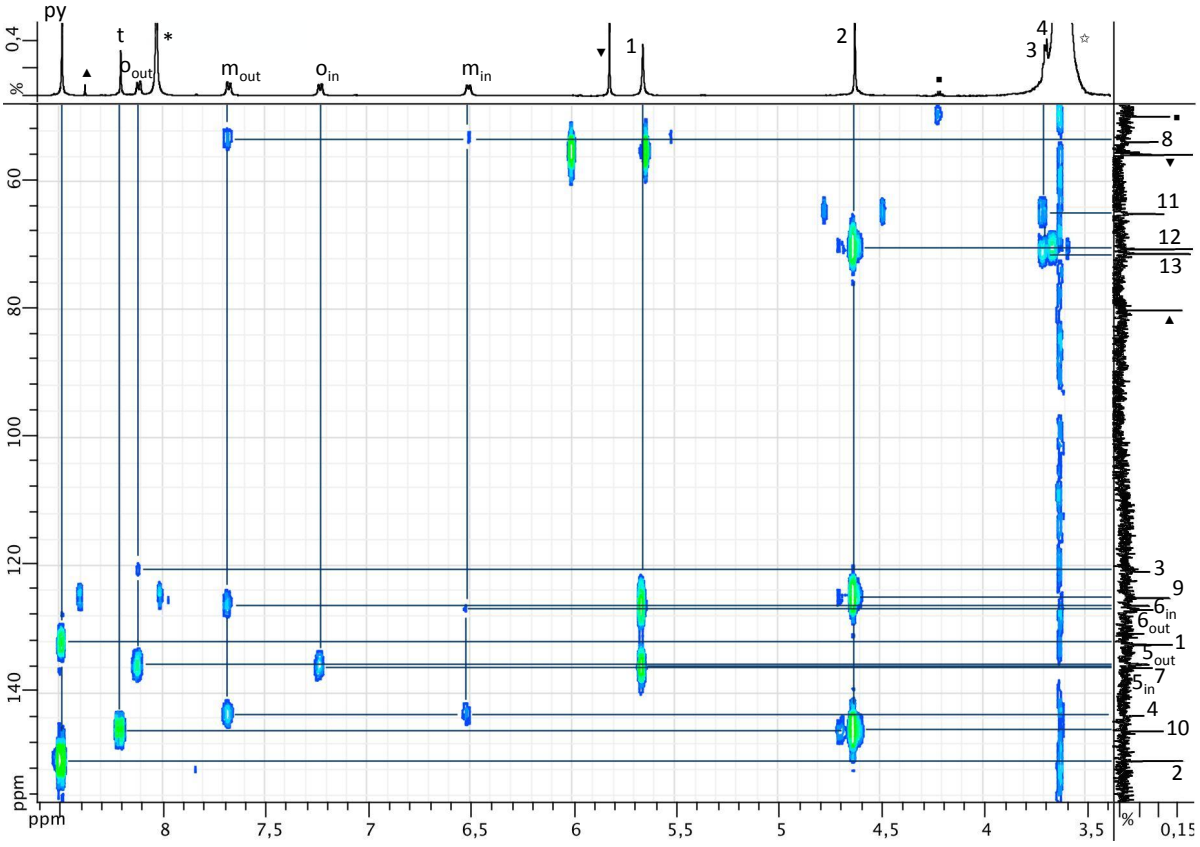

Figure SI24. HMBC spectrum (DMF-d_7, ^{1}H 500 MHz; ^{13}C 126 MHz, 298K) of cage **1**, *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ■: MeOH, ☆: H_2O.

2.4.7 ^{1}H NMR spectrum of ZnTTP

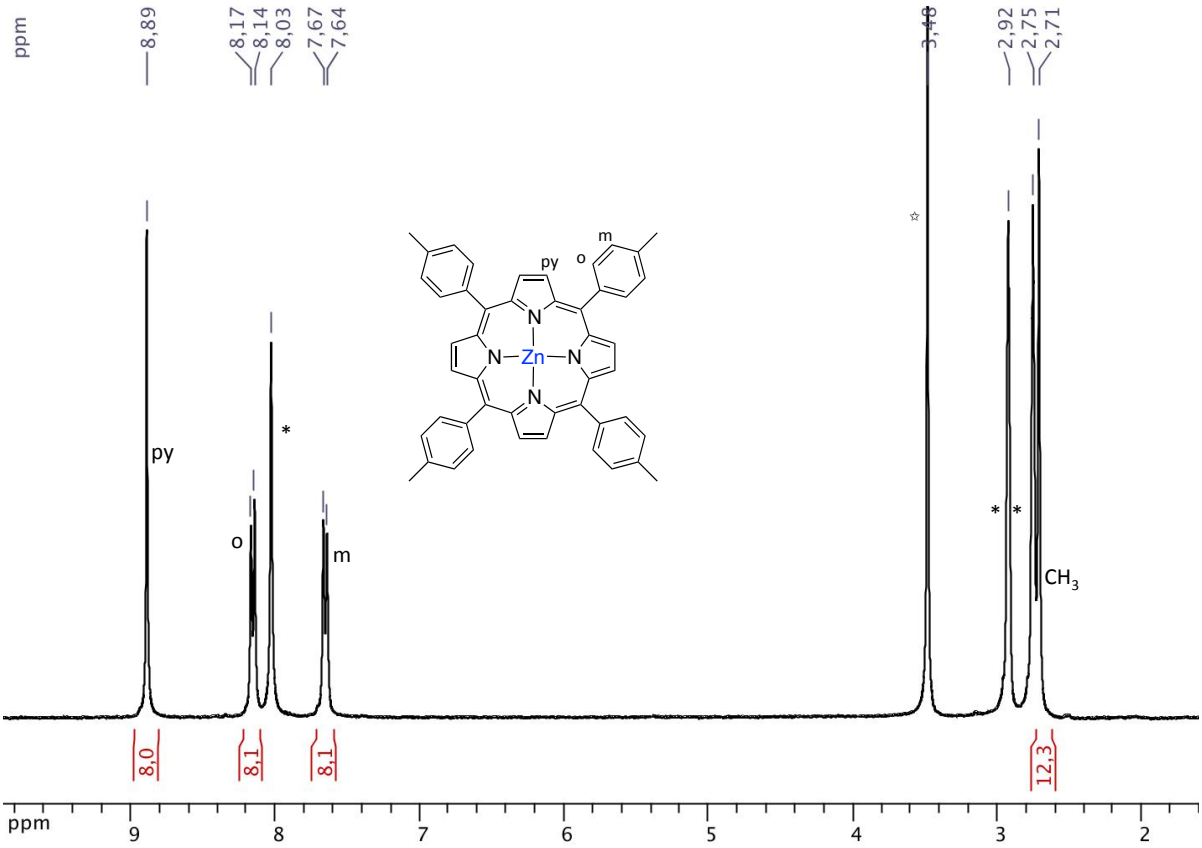

Figure SI25. ^{1}H NMR spectrum (DMF-d_7, 300 MHz) of **ZnTTP**, *: DMF, ☆: H_2O.

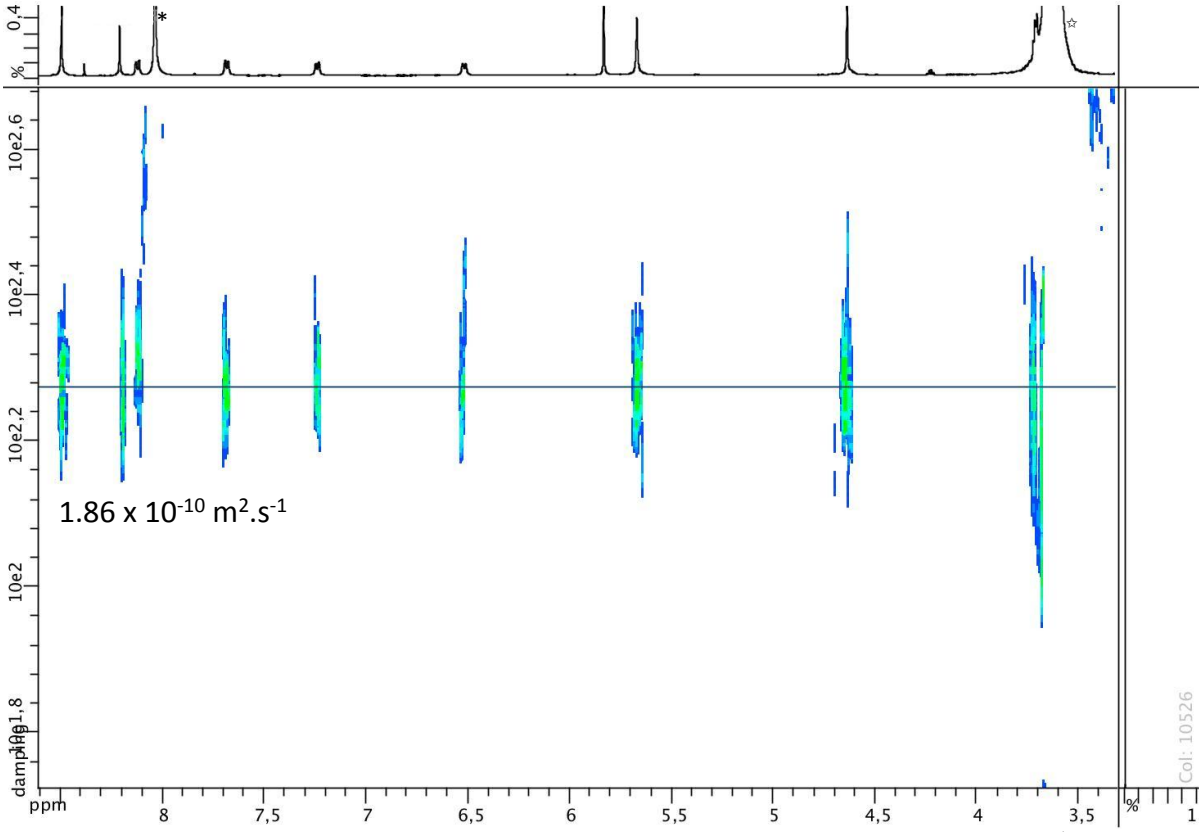

Figure SI26. DOSY NMR spectrum (DMF-d_7, 600 MHz, 298K) of cage **1**, *: DMF, ☆: H_2O.

2.4.8 ESI-MS spectrum of 1

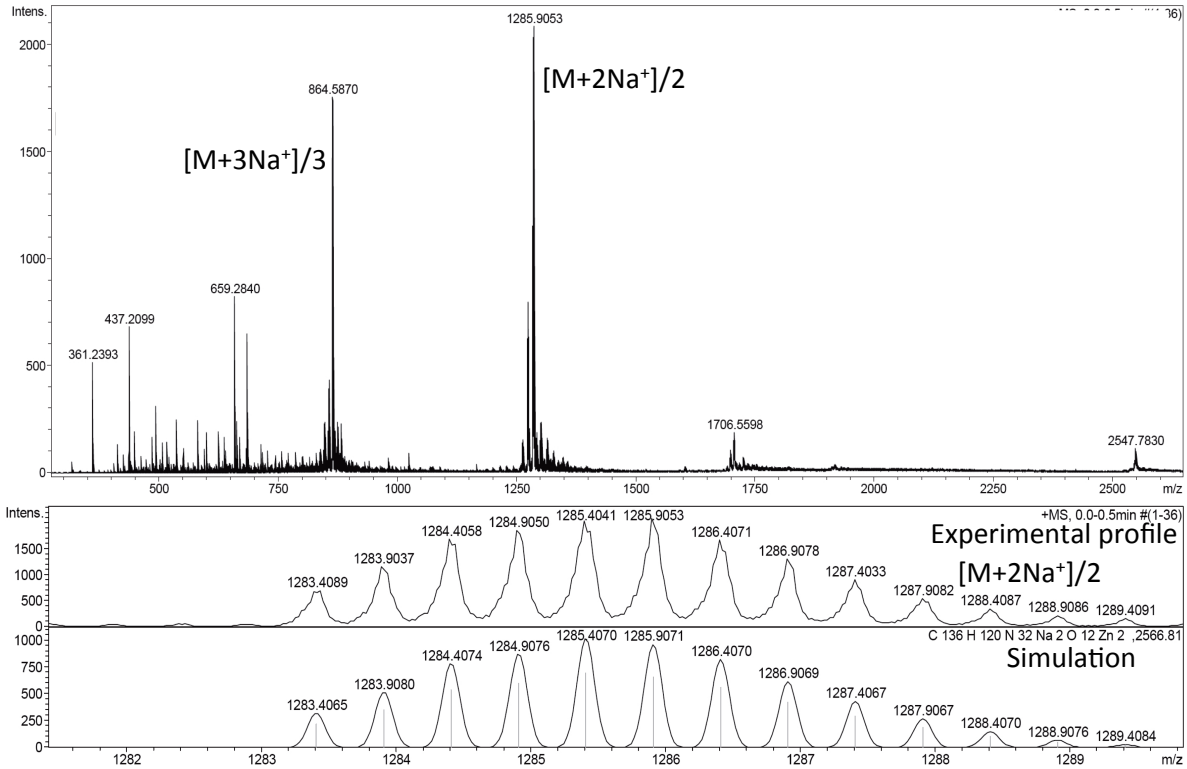

Figure SI27. ES-MS spectrum of cage **1**

2.4.9 Variable temperature ^{1}H NMR of 1

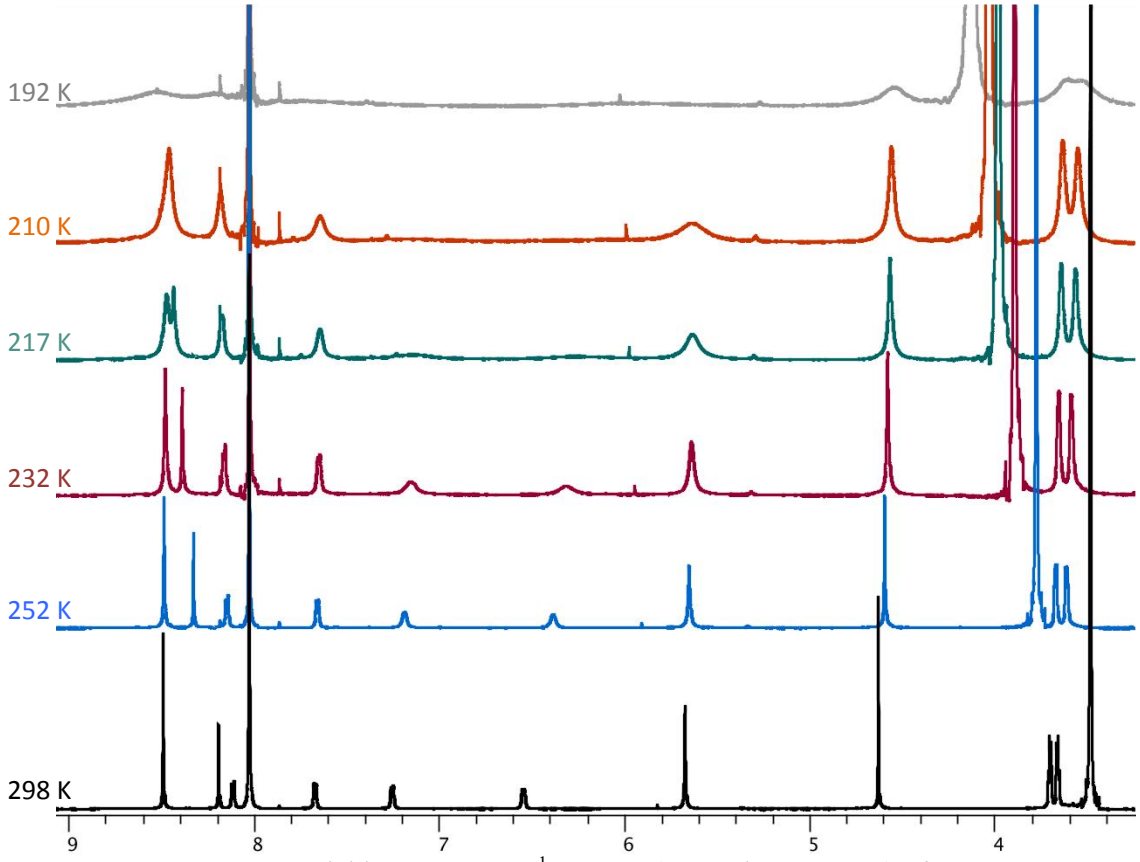

Figure SI28. Variable temperature ^{1}H-NMR (DMF-d_7, 600 MHz) of cage **1**.

2.4.10 Crystallographic data of 1

Experimental data:

Single crystals of Zn complex were grown in DMSO/MeOH. The crystals were placed in oil, and a red prism single crystal of dimensions 0.32 x 0.25 x 0.20 mm was selected, mounted on a glass fibre and placed in a low-temperature N_2 stream.
X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38mm. The cell parameters were determined (APEX2 software) [1] from reflections taken from tree sets of 12 frames, each at 10s exposure. The structure was solved by Direct methods using the program SHELXS-2013 [2]. The refinement and all further calculations were carried out using SHELXL-2013 [3]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX2 [1]; transmission factors: T_{min}/T_{max} = 0.7030/0.7456. The SQUEEZE instruction in PLATON [4] was applied. The residual electron density was assigned to four molecules of methanol.
CCDC 1403732.

[1] "M86-E01078 APEX2 User Manual", Bruker AXS Inc., Madison, USA, 2006.
[2] G. M. Sheldrick, Acta Cryst. **1990**, A46, 467-473.
[3] G. M. Sheldrick, Acta Cryst. **2008**, A64, 112-122.
[4] A. L. Spek, J.Appl.Cryst. **2003**, 36, 7-13.

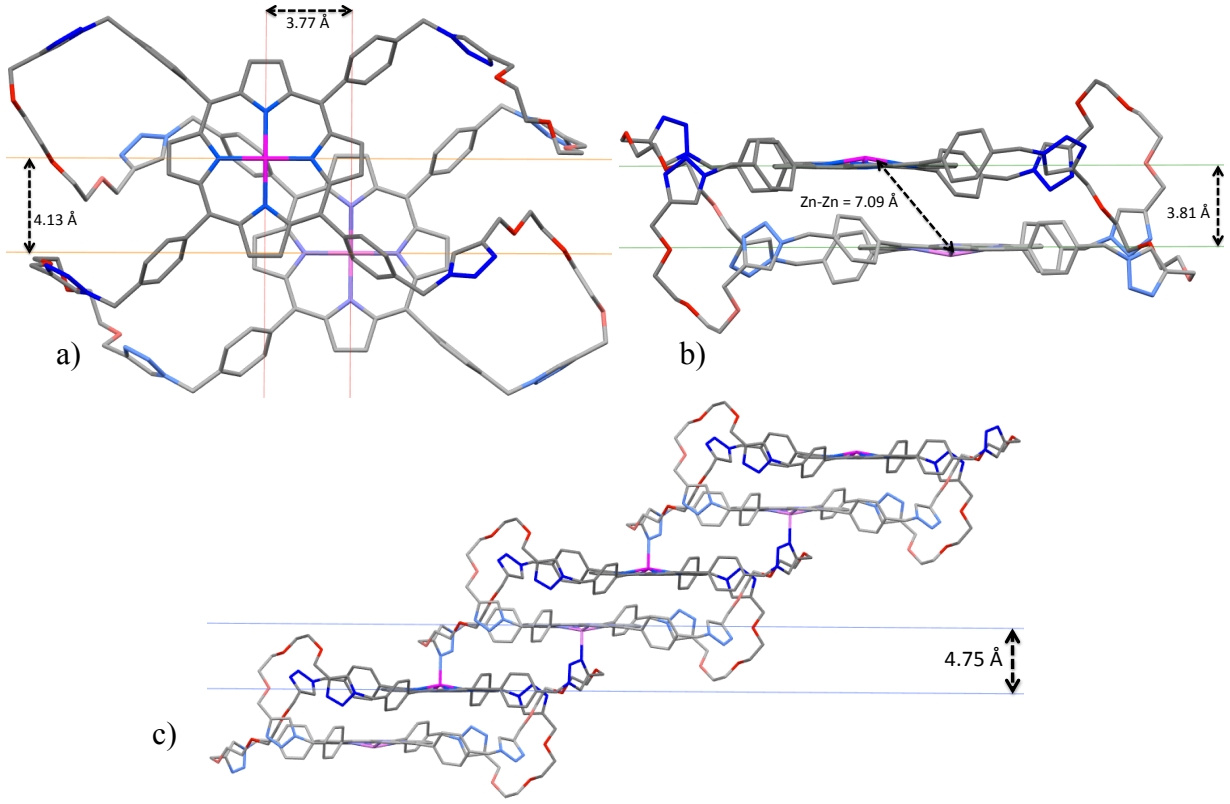

Figure SI29. Crystallographic structure of **1**: a) top view; horizontal (red) and vertical (orange) offsets between the porphyrins are indicated, b) side view of **1**, c) side view of the 1D coordination network. Significant distances are indicated on the pictures. H atoms and solvent molecules are omitted for clarity.

2.5 Synthesis of cage 2

A solution of TFA/CH_2Cl_2 1:1 was added dropwise to a stirred suspension of cage **1** (9.3 µmol, 23.4 mg) in CH_2Cl_2 until the reaction mixture became a green solution. After 15 min of stirring at room temperature, the solution was treated with K_2CO_3 to obtain a dark red solution. The organic phase was washed with water, dried over sodium sulfate, evaporated under vacuum to afford a dark red solid. (22 mg, quantitative yield). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.34 (16 H, s, H_{py}), 7.90 (8 H, d, ^3J = 7.6 Hz, $H_{o\ out}$), 7.76 (8 H, s, H_t), 7.46 (8 H, d, ^3J = 7.6 Hz, $H_{m\ out}$), 6.81 (8 H, d, ^3J = 7.6 Hz, $H_{o\ in}$), 6.36 (8 H, d, ^3J = 7.6 Hz, $H_{m\ in}$), 5.51 (16 H, s, H_1), 4.70 (16 H, s, H_2), 3.75 (16H, m, H_3), 3.68 (16 H, m, H_4), -3.04 (4 H, s, NH). **^{13}C NMR** (125 MHz, CD_2Cl_2): δ 145.2 (C_{10}), 141.9 (C_4), 135.0 ($C_{5\ out}$), 134.7 (C_7), 134.7 ($C_{5\ in}$), 126.4 ($C_{6\ out}$), 125.9 ($C_{6\ in}$), 123.6 (C_9), 129.5 (C_3), 71.0 (C_{13}), 70.3 (C_{12}), 65.0 (C_{11}), 53.8 (C_8); pyrrolic ^{13}C are too enlarged to be observed at 298K **ES-MS**: m/z (%) calcd for $[C_{136}H_{124}N_{32}O_{12}Na_2]^{2+}$/2: 1221.4930; found: 1221.4991 (100) $[M+2Na^+]$/2.

2.5.1 NMR characterization of compound 2

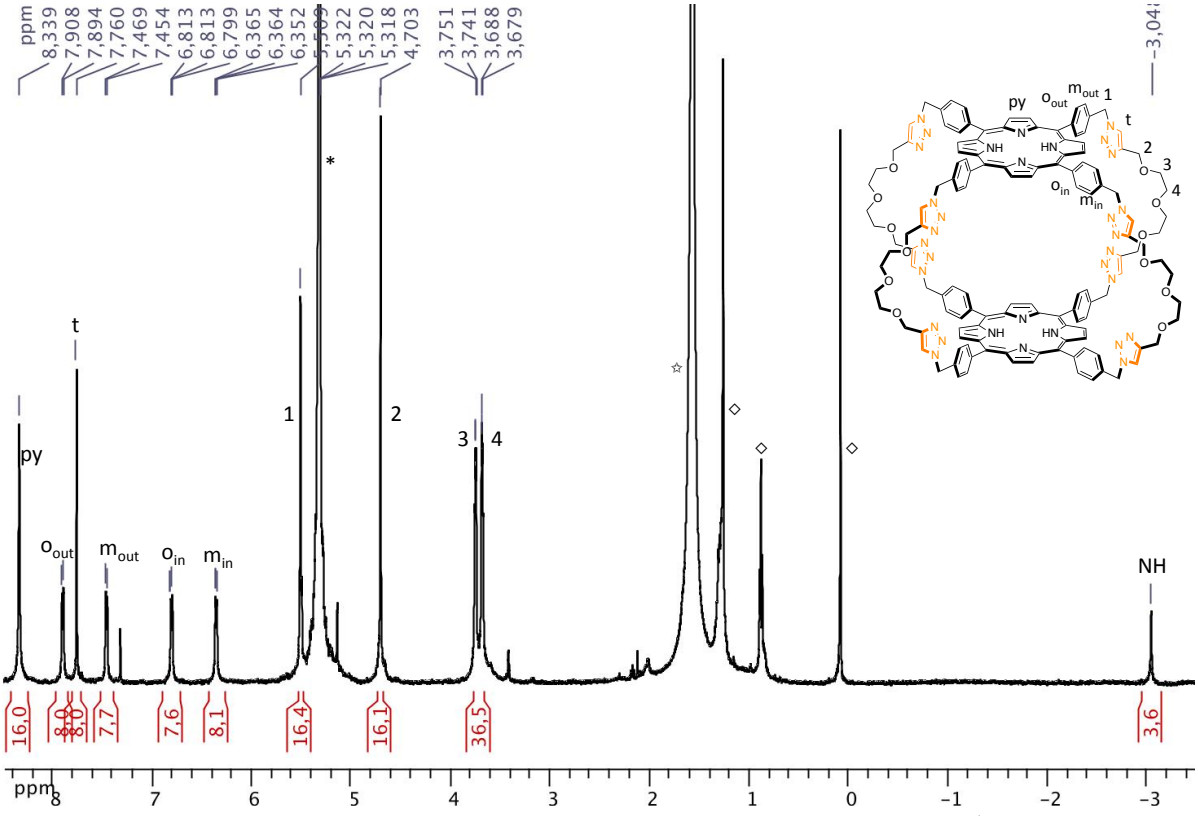

Figure SI30. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz, 298K) of cage **2**, *: CH_2Cl_2, ☆: H_2O, ◇: grease.

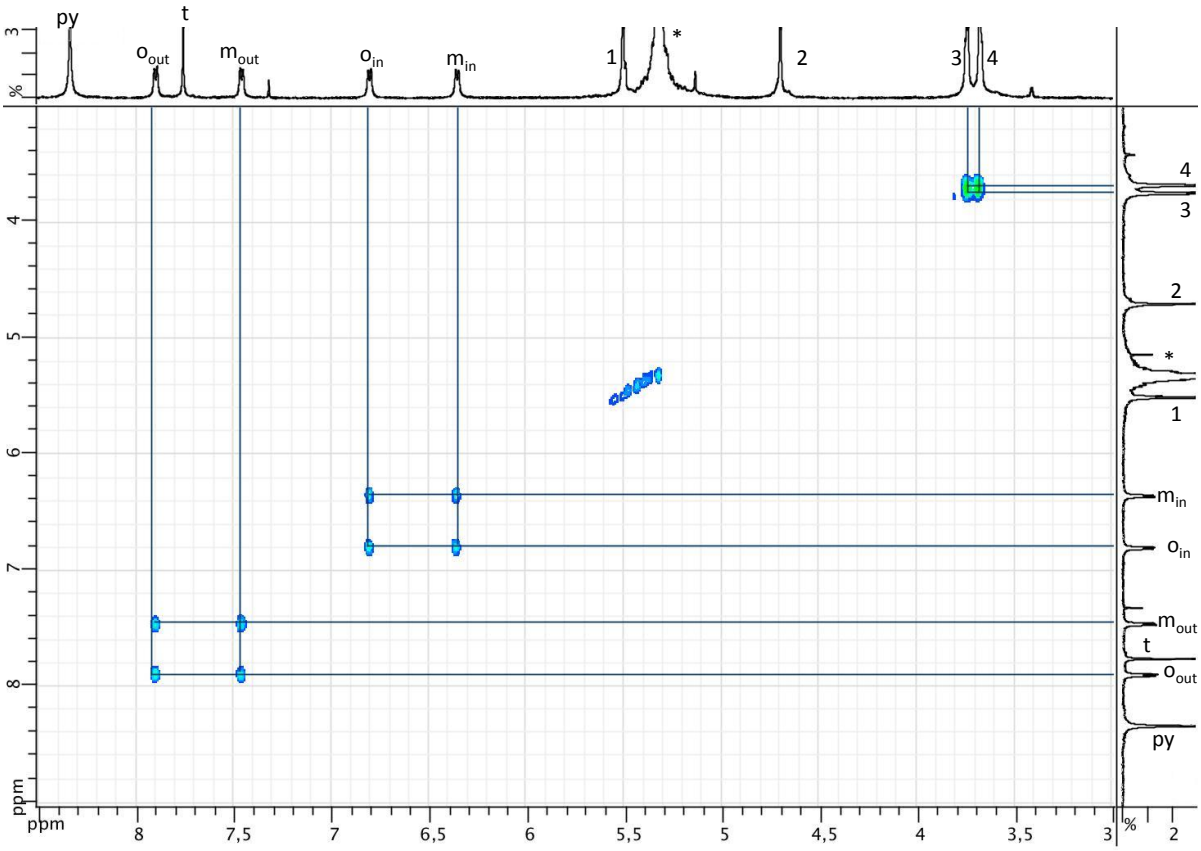

Figure SI31. COSY spectrum (CD_2Cl_2, 500 MHz, 298K) of cage **2**, *: CH_2Cl_2.

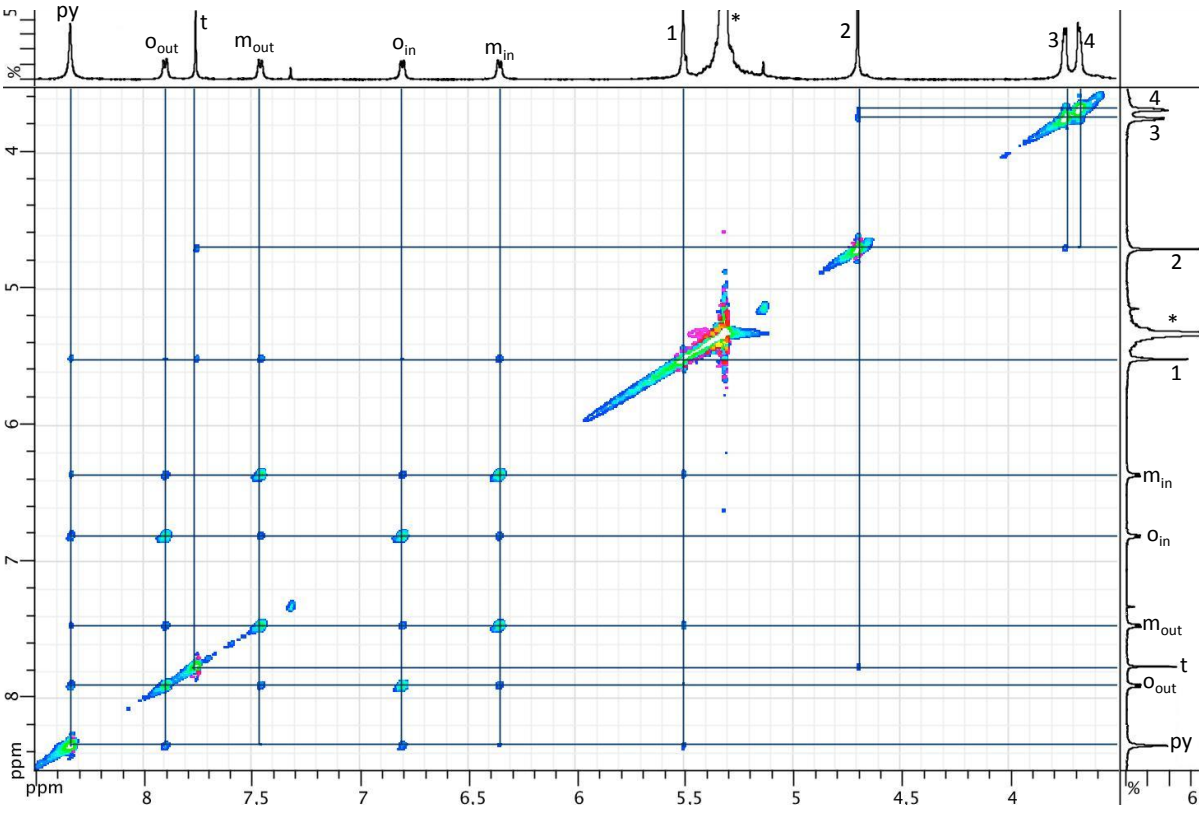

Figure SI32. NOESY spectrum (CD_2Cl_2, 500 MHz, 298K) of cage **2**, *: CH_2Cl_2.

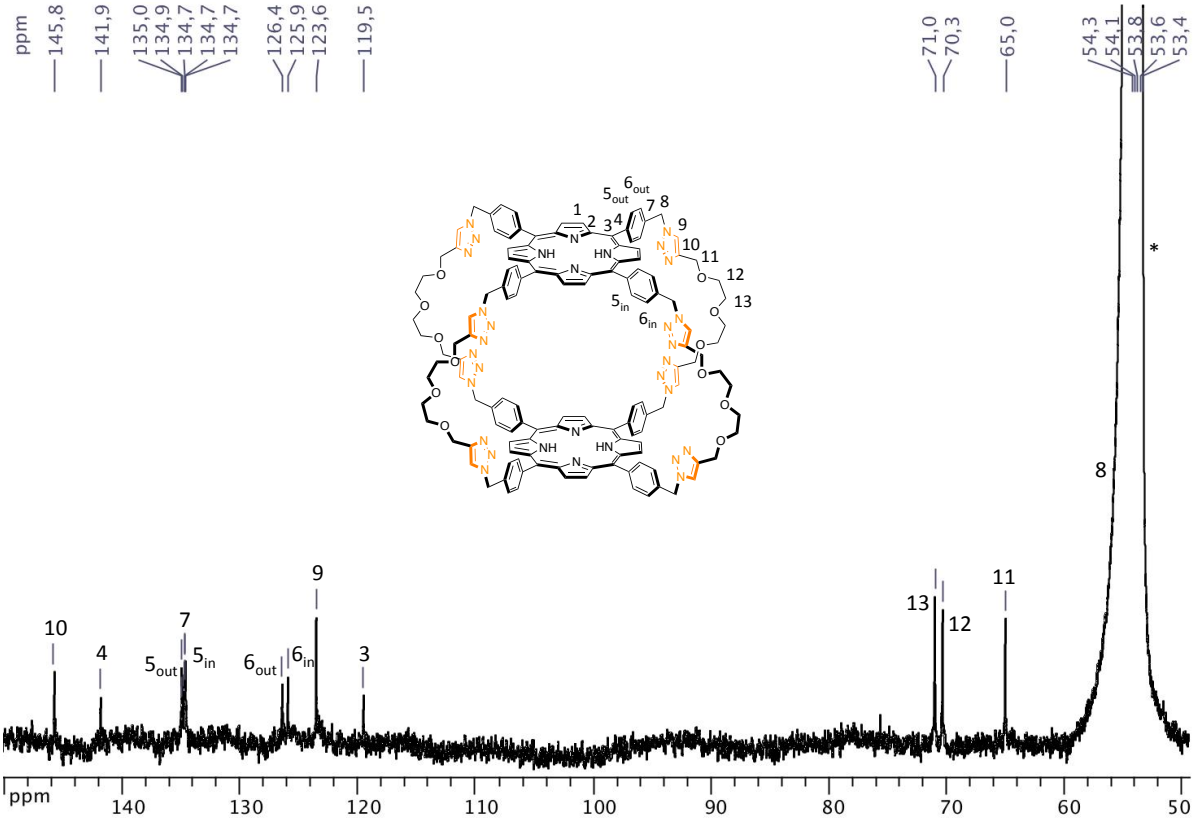

Figure SI33. ^{13}C NMR spectrum (CD_2Cl_2, 126 MHz, 298K) of cage **2**, *: CH_2Cl_2.

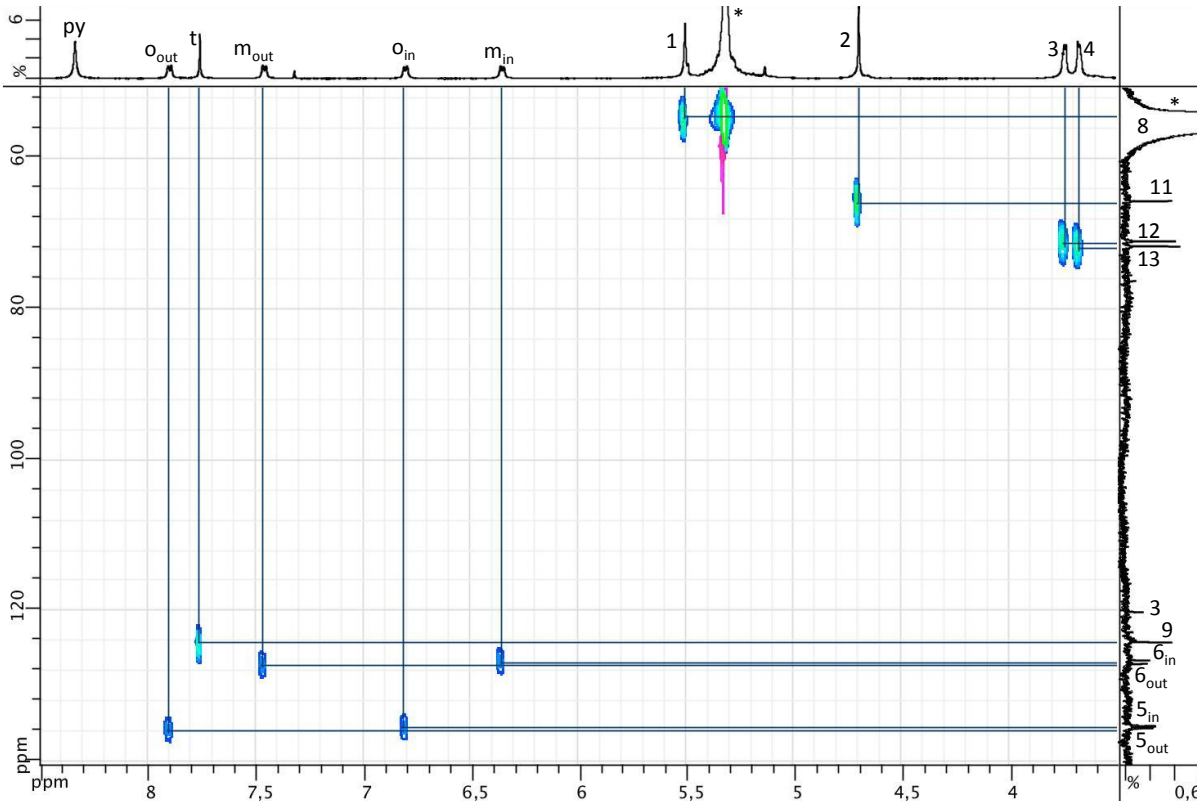

Figure SI34. HSQC spectrum (CD_2Cl_2, ^{1}H 500 MHz; ^{13}C 126 MHz, 298K) of cage **2**, *: CH_2Cl_2.

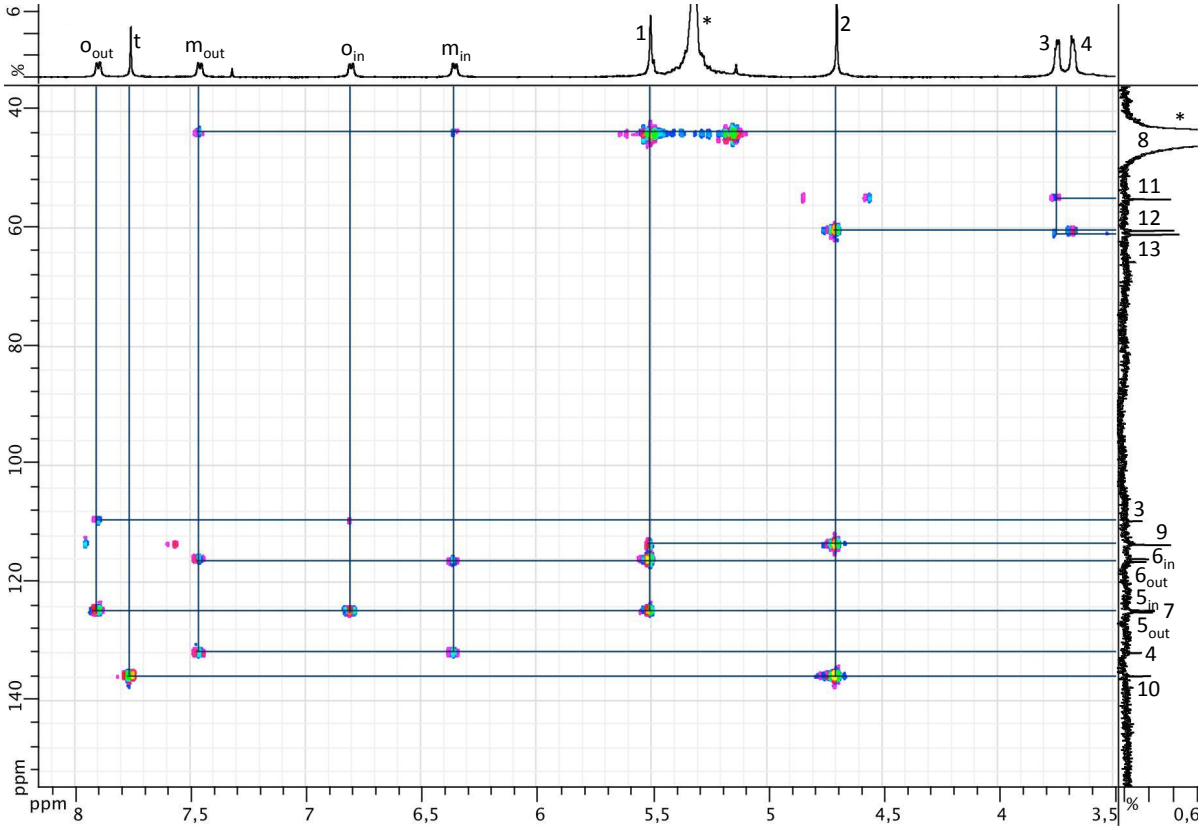

Figure SI35. HMBC spectrum (CD_2Cl_2, ^{1}H 500 MHz; ^{13}C 126 MHz, 298K) of cage **2**, *: CH_2Cl_2.

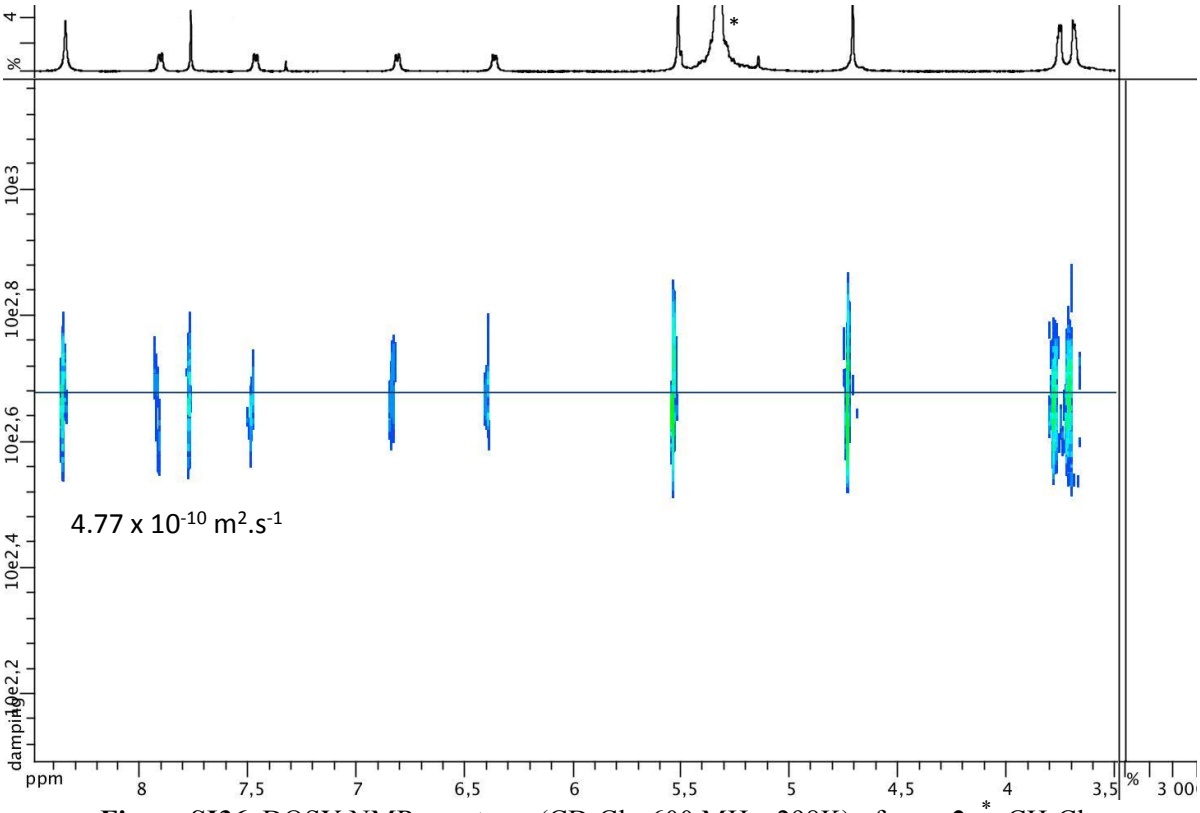

Figure SI36. DOSY NMR spectrum (CD_2Cl_2, 600 MHz, 298K) of cage **2**, *: CH_2Cl_2.

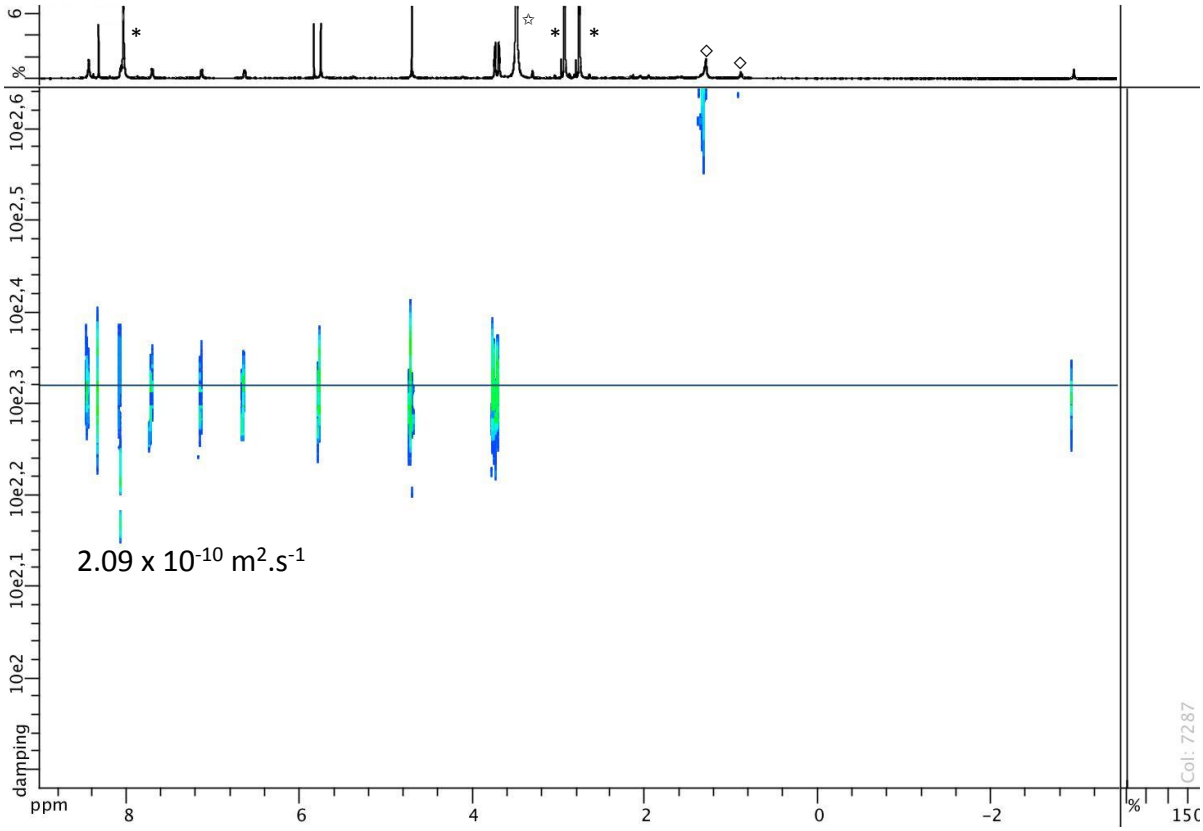

Figure SI37. DOSY NMR spectrum (DMF-d_7, 600 MHz, 298K) of cage **2**, *: DMF, ☆: H_2O, ◇: grease.

2.5.2 ESI-MS spectrum of 2

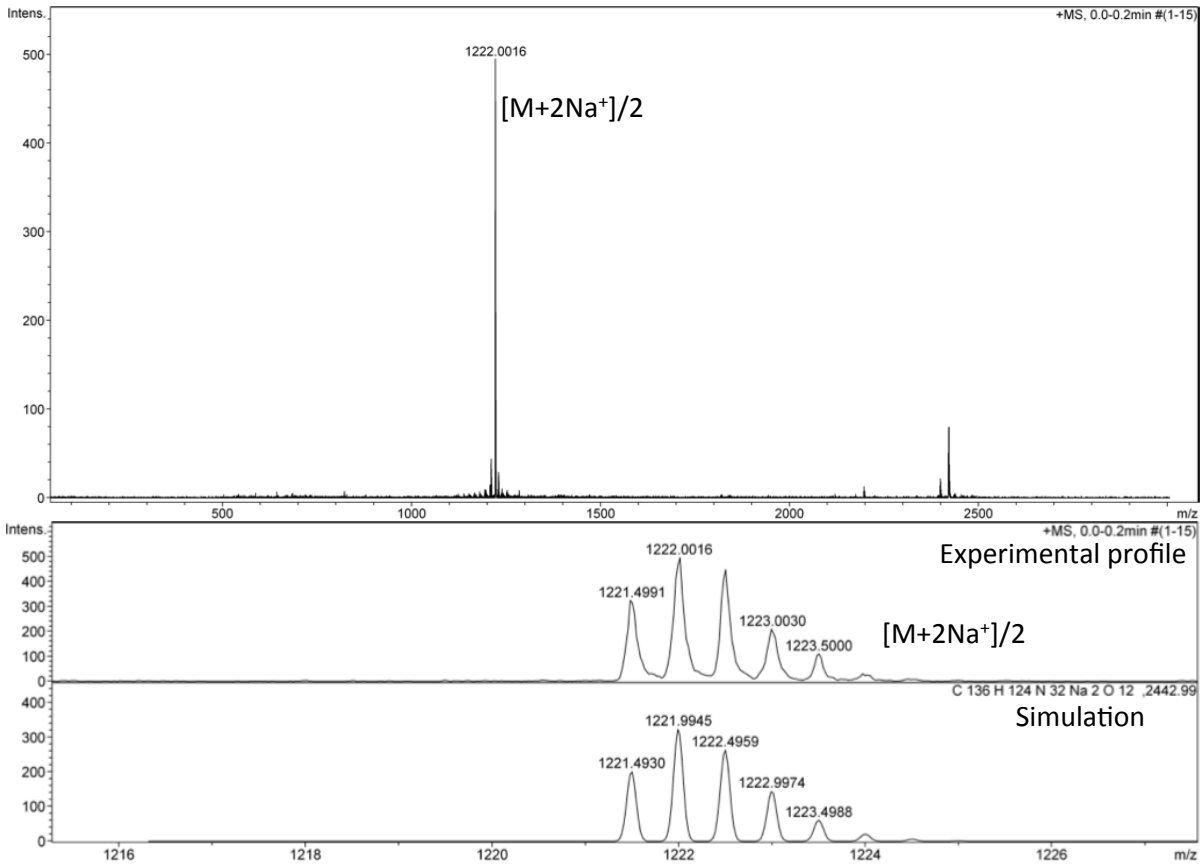

Figure SI38. ES-MS spectrum of cage **2**.

2.6 Synthesis of the silver-complexed cage [Ag$_4$(1)](SbF$_6$)$_4$

A solution of $AgSbF_6$ (4 equiv., 8.4 mM, 1.17 mL) in $CHCl_3$/MeOH 90/10 was added at room temperature to a stirred solution of cage **1** (2.45 µmol, 6.18 mg) in distilled $CHCl_3$/MeOH (90/10, 25 mL), protected from light. A purple precipitate formed immediately. After 20 minutes, the solvent was removed and the residue was dried under vacuum to afford a purple solid (9.5 mg, quantitative yield). **^{1}H NMR** (500 MHz, DMF-d_7): δ 8.82 (8 H, s, H_t), 8.49 (16 H, s, H_{py}), 8.15 (8 H, dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, $H_{o\ out}$), 7.96 (8 H, d, ^3J = 7.6 Hz, $H_{m\ out}$), 7.74 (8 H, d, ^3J = 7.6 Hz, $H_{o\ in}$), 7.53 (d, ^3J = 7.6 Hz, 8 H, $H_{m\ in}$), 6.15 (s, 16 H, H_1), 4.98 (s, 16 H, H_2), 3.85 (m, 16 H, H_3), 3.80 (16 H, m, H_4). **^{13}C NMR** (126 MHz, DMF-d_7): δ 150.3 (C_2), 146.9 (C_{10}), 144.0 (C_4), 136.4 ($C_{5\ in}$), 135.6 (C_7), 135.5 ($C_{5\ out}$), 132.2 (C_1), 127.8 ($C_{6\ out}$), 127.2 ($C_{6\ in}$), 126.0 (C_9), 120.7 (C_3), 71.6 (C_{13}), 70.5 (C_{12}), 64.2 (C_{11}), 55.1 (C_8). **ES-MS**: m/z (%) calcd for $[C_{136}H_{120}Ag_4N_{32}O_{12}Zn_2]^{4+}$/4: 737.3639; found: 737.3615 (100) [**Ag$_4$(1)$^{4+}$**]/4; calcd for $[C_{136}H_{120}Ag_3N_{32}O_{12}Zn_2]^{3+}$/3: 947.1833; found: 947.1771 (89) [**Ag$_3$(1)$^{3+}$**]/3; calcd for $[C_{136}H_{120}Ag_2N_{32}O_{12}Zn_2]^{2+}$/2: 1367.3200; found: 1367.3167 (15) [**Ag$_2$(1)$^{2+}$**]/2.

2.6.1 NMR characterization of [Ag$_4$(1)](SbF$_6$)$_4$

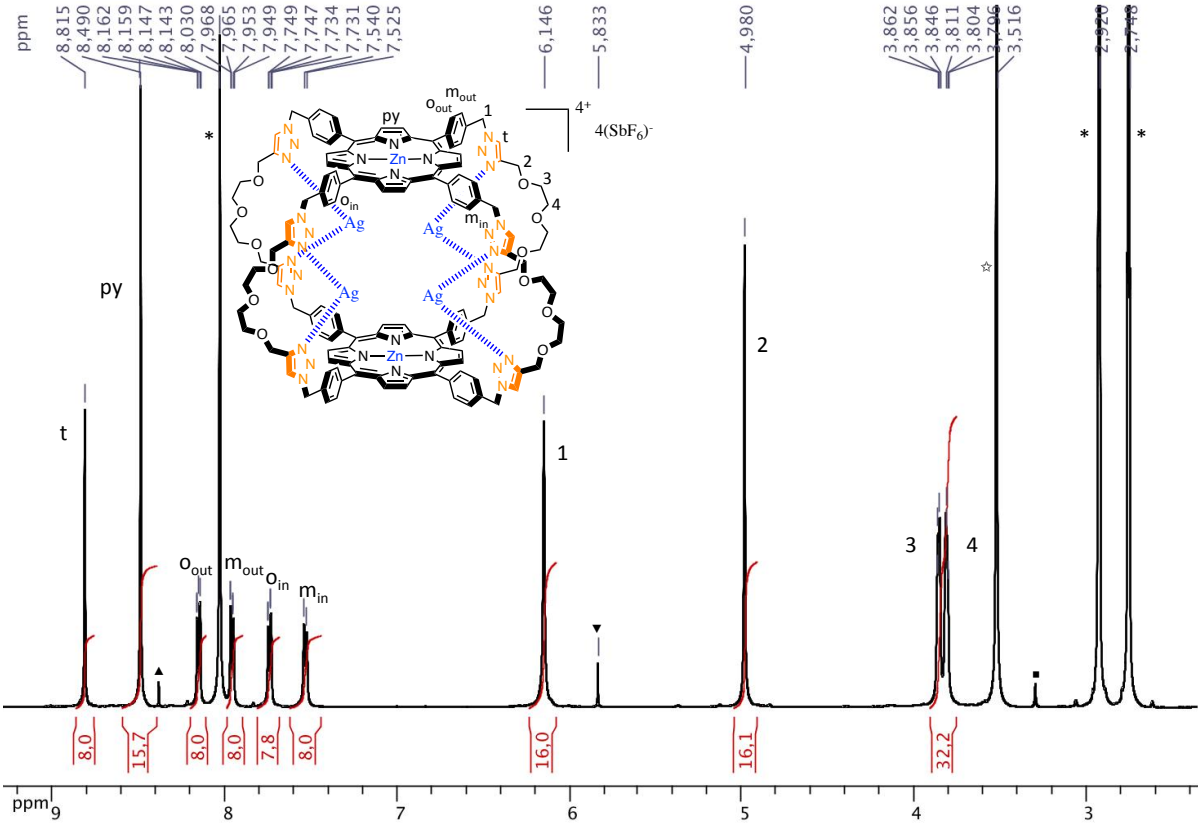

Figure SI39. ^{1}H NMR spectrum (DMF-d_7, 500 MHz, 298K) of complex **[Ag$_4$(1)](SbF$_6$)$_4$**, *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ▪: MeOH, ☆: H_2O.

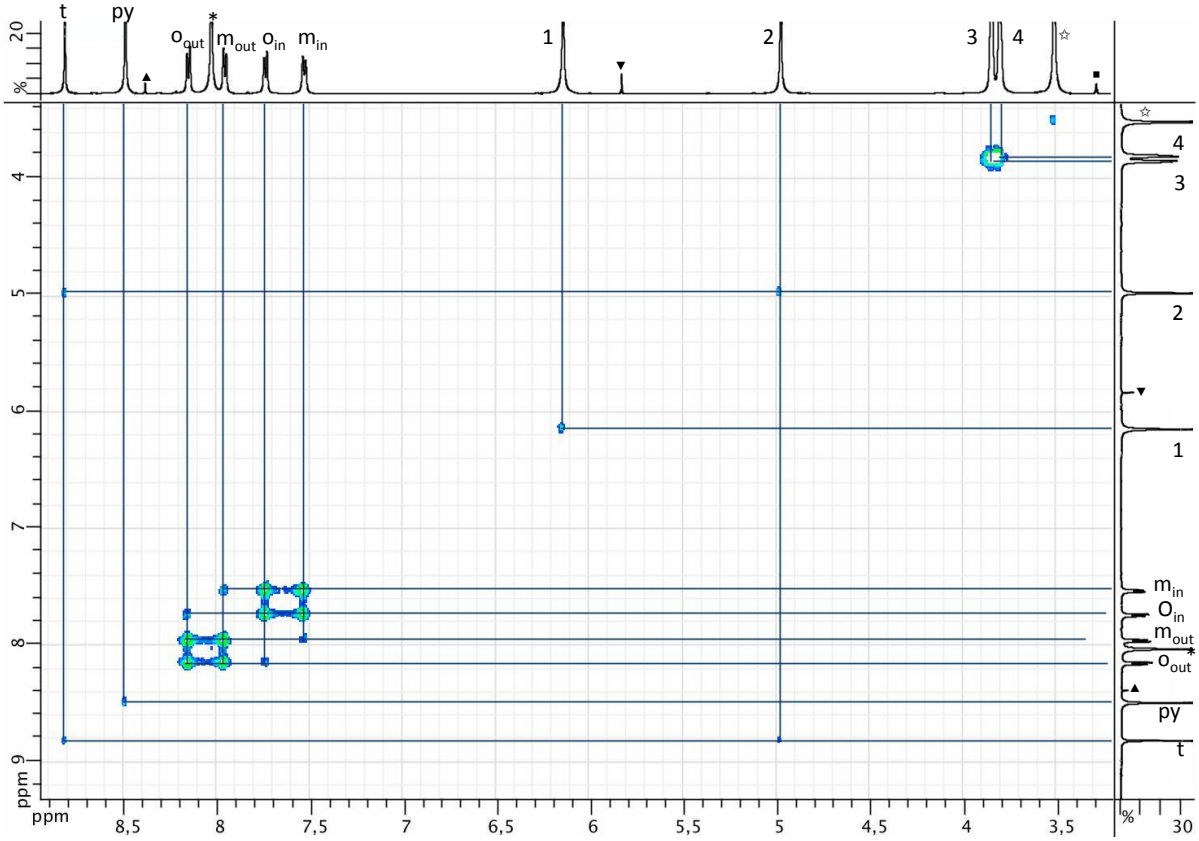

Figure SI40. COSY spectrum (DMF-d_7, 500 MHz, 298K) of complex **$[Ag_4(1)](SbF_6)_4$**, *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ▪: MeOH, ☆: H_2O.

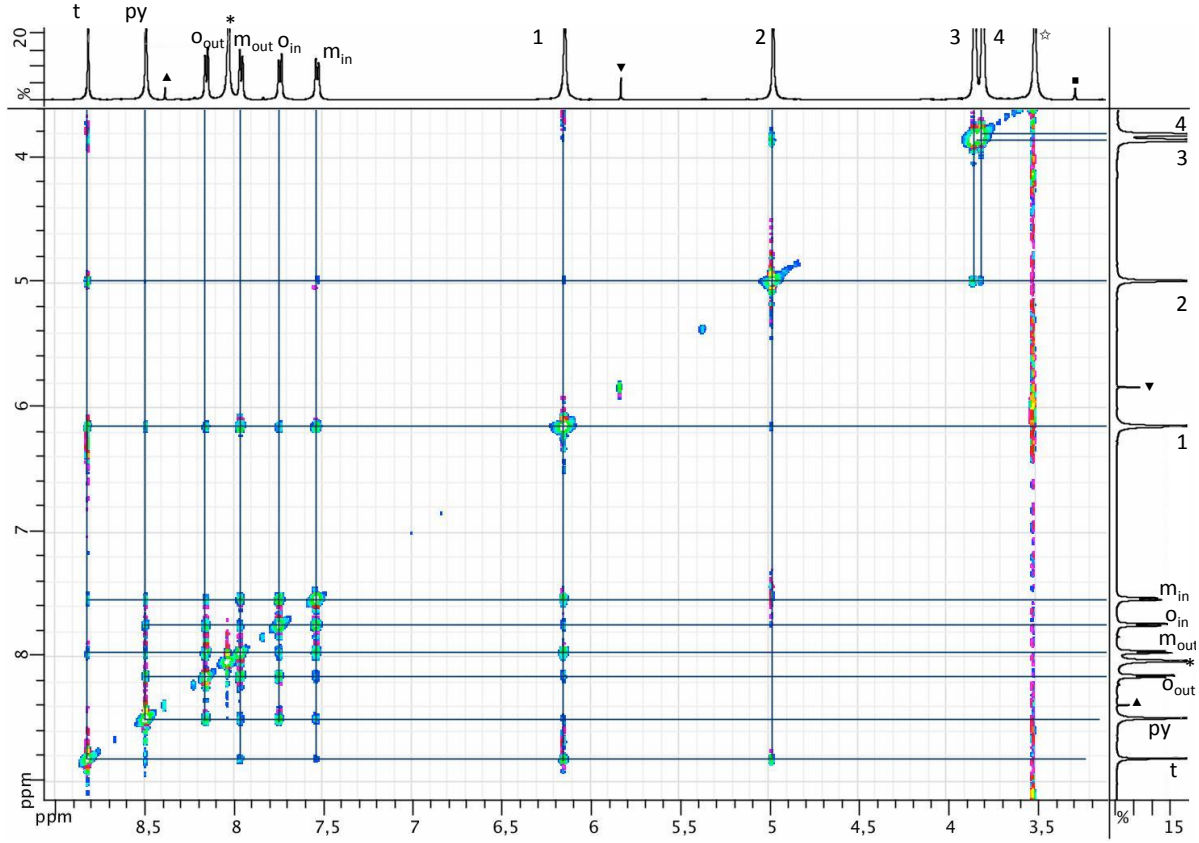

Figure SI41. NOESY spectrum (DMF-d_7, 500 MHz, 298K) of complex **$[Ag_4(1)](SbF_6)_4$**, *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ▪: MeOH, ☆: H_2O.

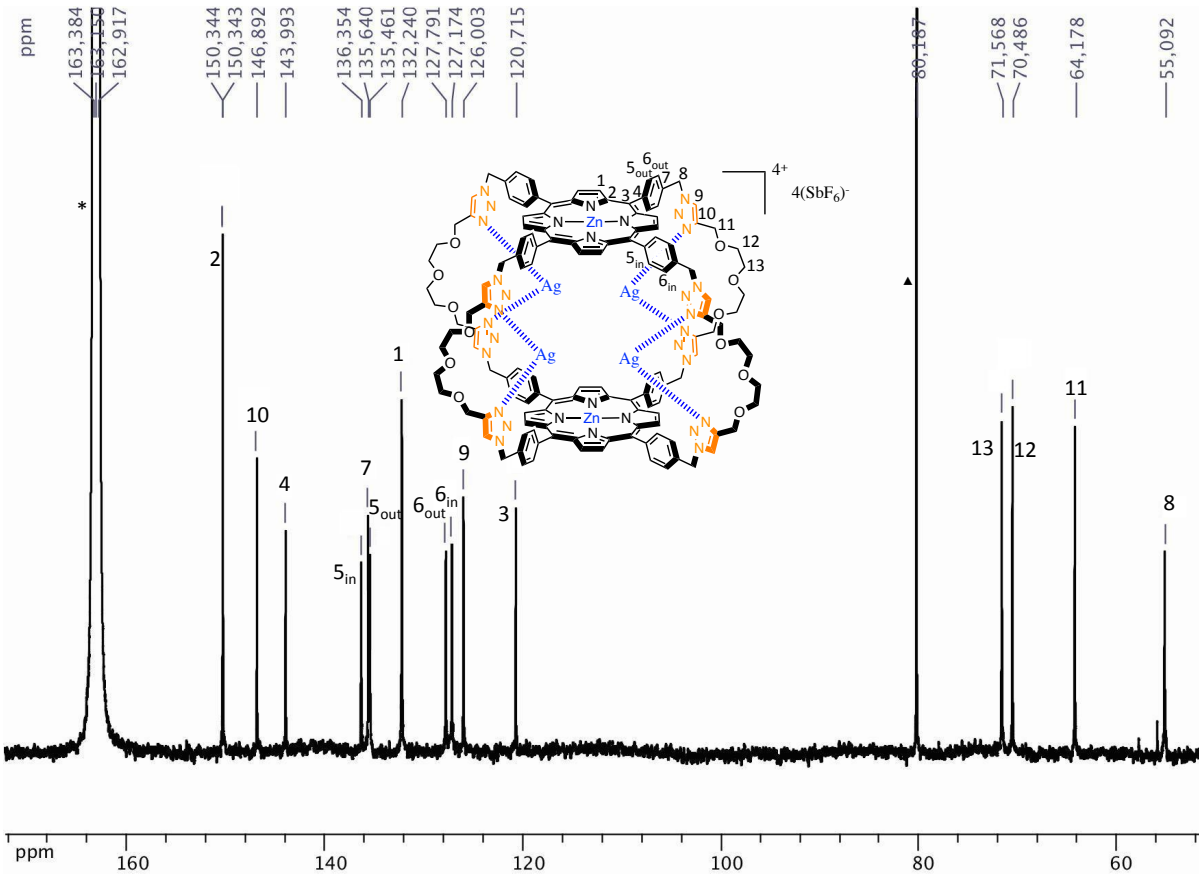

Figure SI42. ^{13}C NMR spectrum (DMF-d_7, 126 MHz, 298K) of **[Ag_4(1)][SbF_6)$_4$**, *: DMF, ▲: $CHCl_3$.

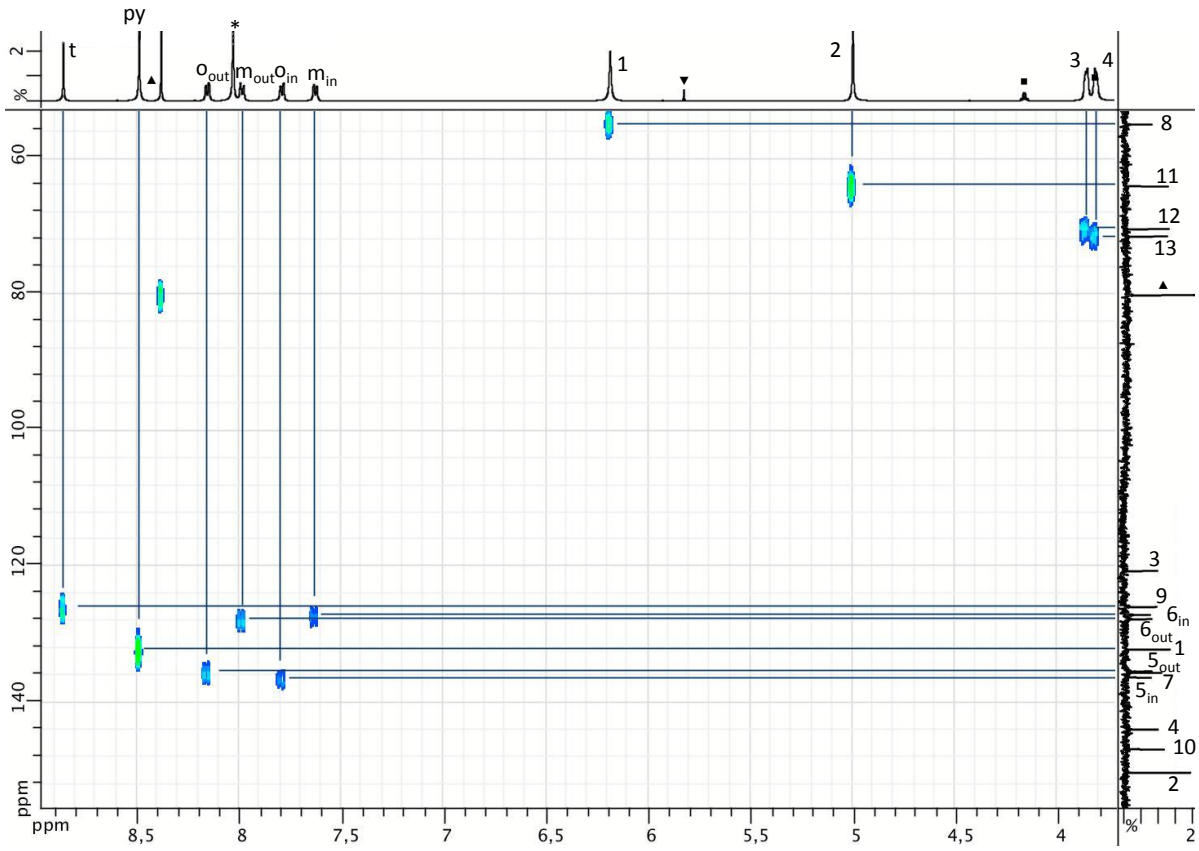

Figure SI43. HSQC spectrum (DMF-d_7, ^1H 500 MHz; ^{13}C 126 MHz, 298K) of complex **[Ag_4(1)][SbF_6)$_4$**, *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ▪: MeOH.

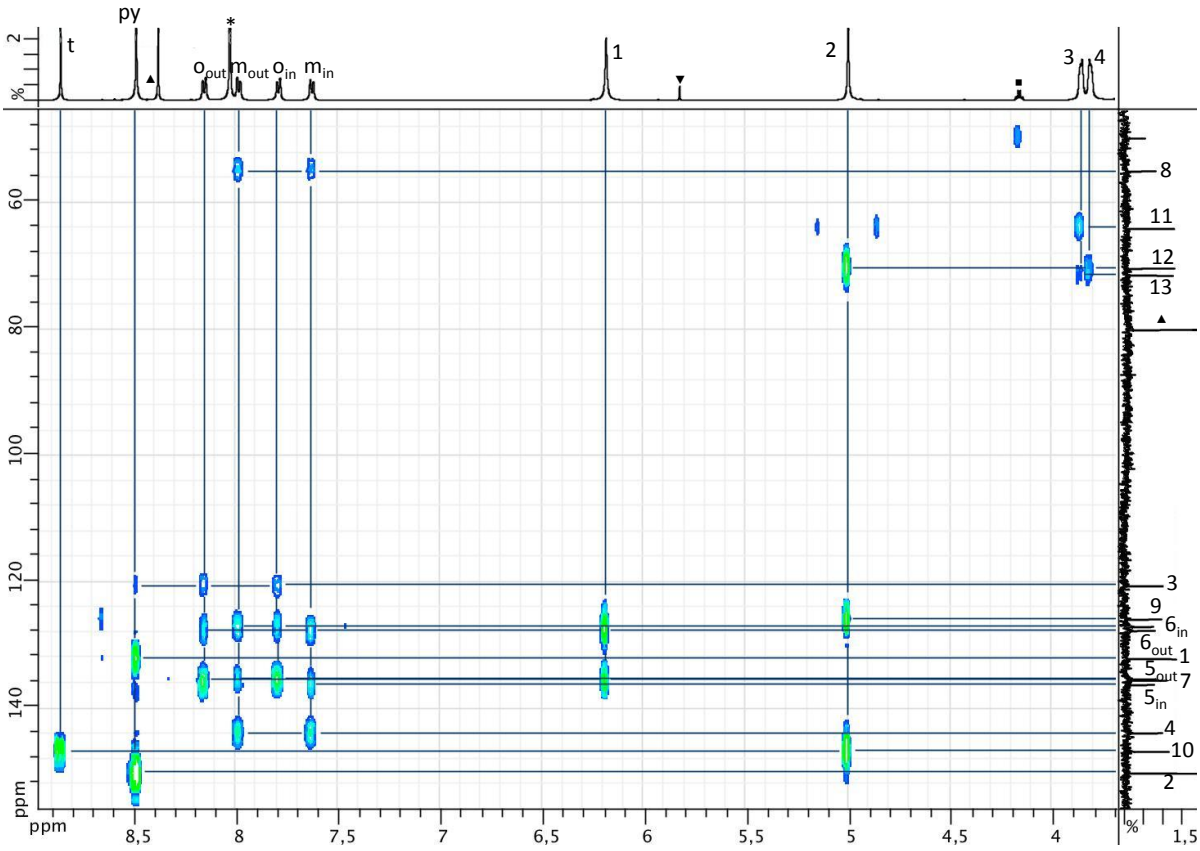

Figure SI44. HMBC spectrum (DMF-d_7, ^{1}H 500 MHz; ^{13}C 126 MHz, 298K) of complex **[Ag_4(1)](SbF_6)$_4$**, *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ▪: MeOH.

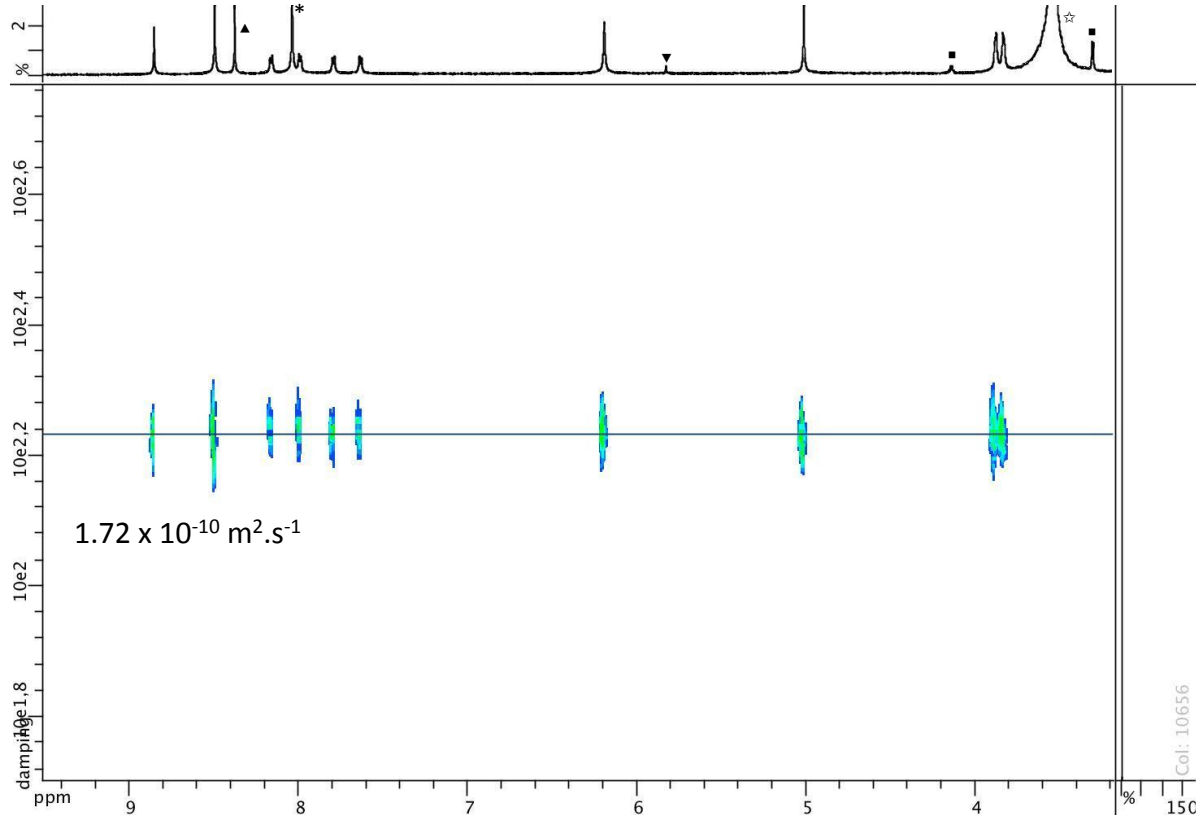

Figure SI45. DOSY NMR spectrum (DMF-d_7, 600 MHz, 298K) of complex **[Ag_4(1)](SbF_6)$_4$**, *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ▪: MeOH, ☆: H_2O.

2.6.2 ESI-MS spectrum of $[Ag_4(1)](SbF_6)_4$

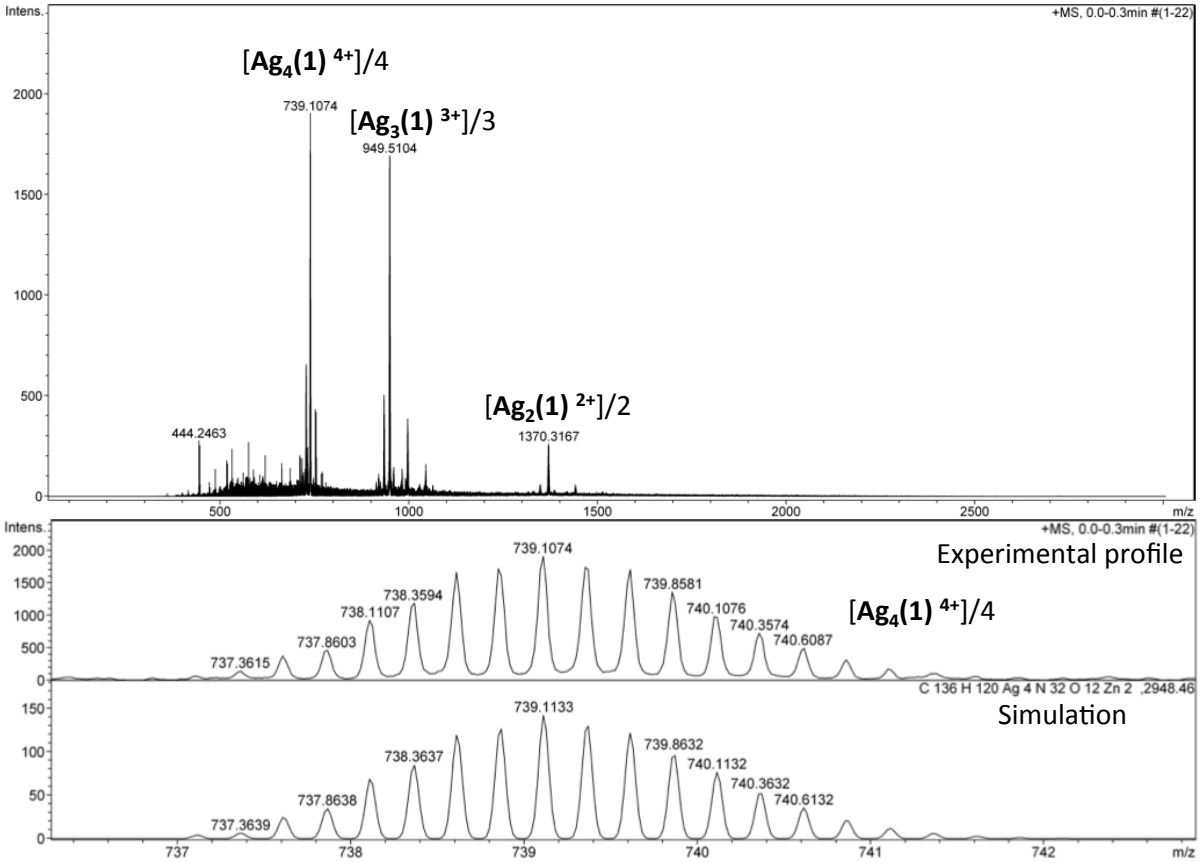

Figure SI46. ES-MS spectrum of complex $[Ag_4(1)](SbF_6)_4$.

2.6.3 Decoordination of Ag(I) from $[Ag_4(1)](SbF_6)_4$

To a solution of **$[Ag_4(1)](SbF_6)_4$** in DMF was added 10 equiv. of LiCl as a solid. The solvent was removed under reduced pressure, and the residue was washed several times with MeOH, dissolved in $CHCl_3$/MeOH 90/10 and filtrated. The ^{1}H NMR spectra of the purple solid dissolved in DMF-d_7 (Figure SI47 b) was identical to the one of cage **1** (Figure SI47 c).

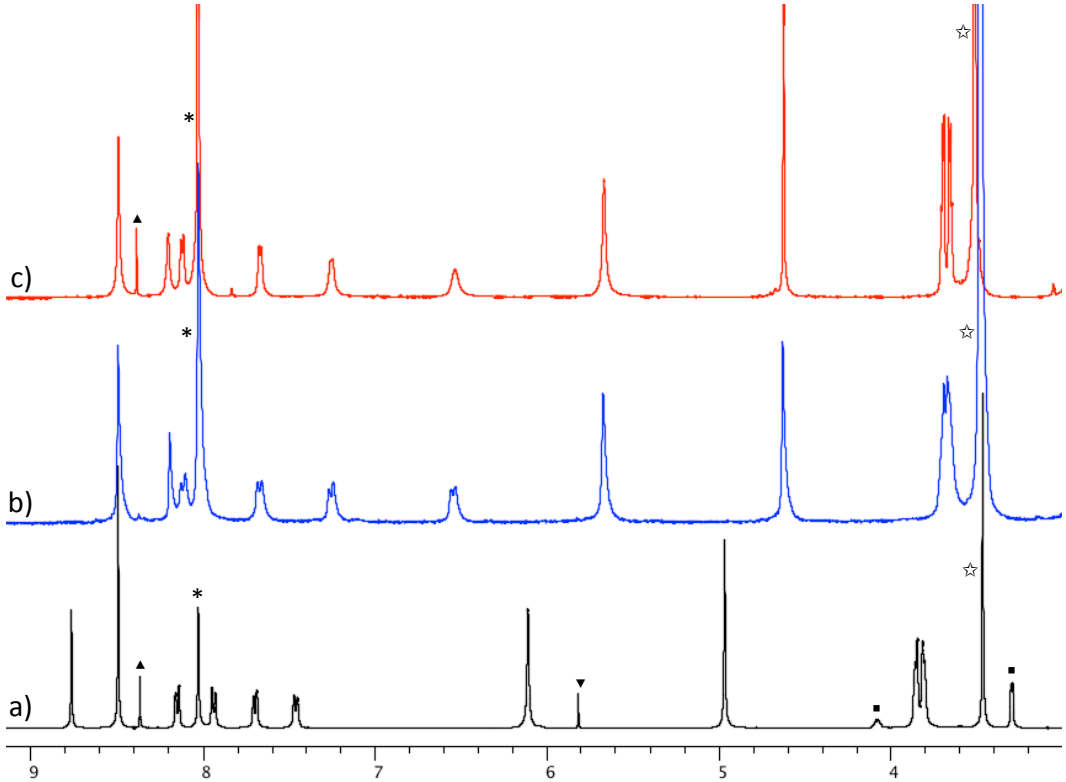

Figure SI47. ^{1}H NMR spectrum (DMF-d_7, 400 MHz) of a) complex **$[Ag_4(1)](SbF_6)_4$** b) after addition of 10 equiv. of LiCl and removal of AgCl c) cage **1**; *: DMF, ▲: $CHCl_3$, ▼: CH_2Cl_2, ▪: MeOH, ☆: H_2O.

2.6.4 UV-Vis. Spectra of 1 after addition of AgOTf

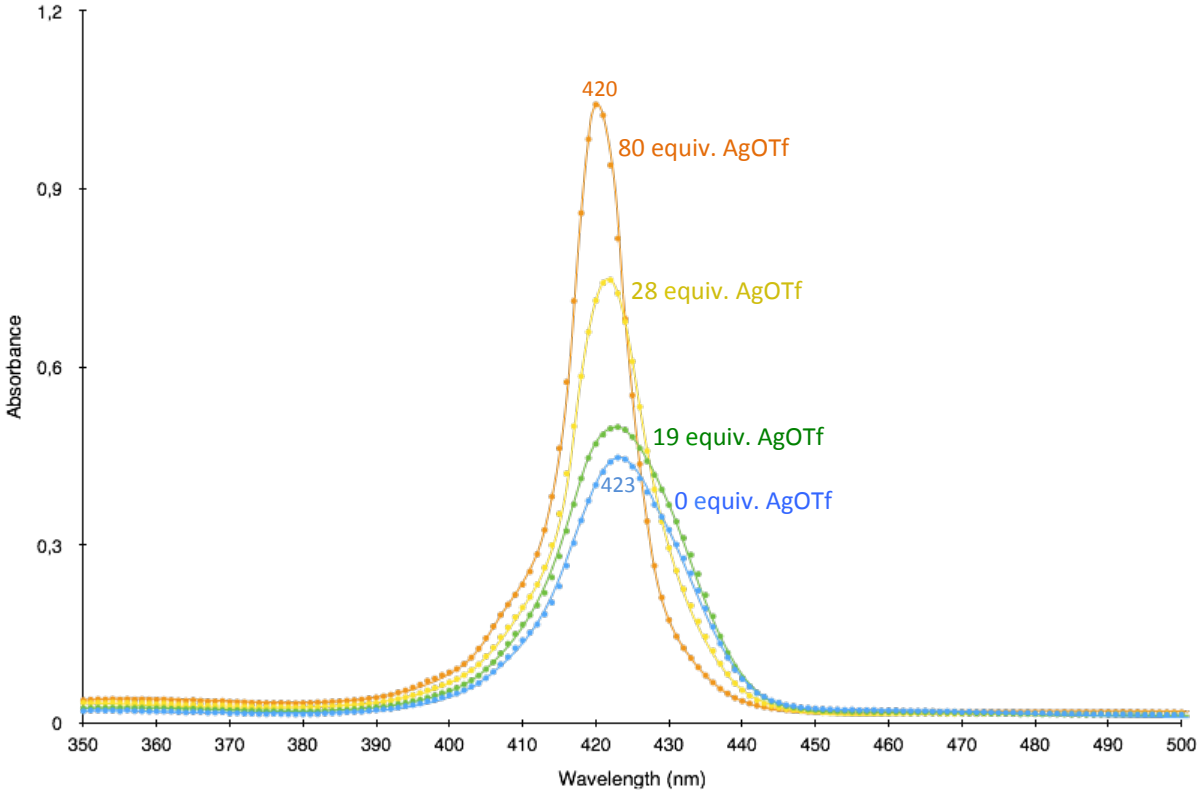

Figure SI48. UV-Vis. spectra of **1** ($7.7.10^{-7}$ $mol.L^{-1}$) in CH_2Cl_2/15% MeOH (blue) and after addition of 19, 28 and 80 equiv. of AgOTf.

2.6.5 UV-Vis. Spectra of 1 and ZnTTP

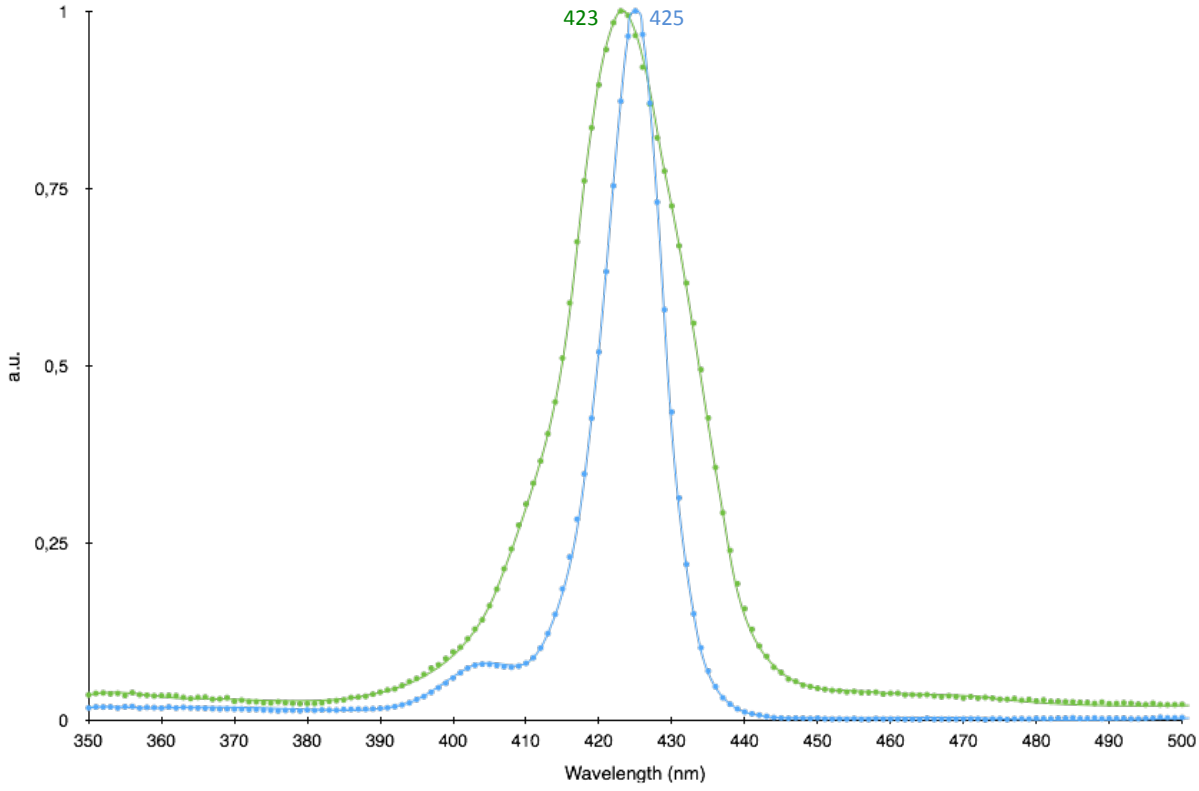

Figure SI49. UV-Vis. spectra of **ZnTTP** (blue) and **1** (green) in CH_2Cl_2/15% MeOH.

2.7 Synthesis of the silver-complexed cage [Ag$_4$(2)](OTf)$_4$

A solution of AgOTf (4 equiv., 1.45 mM, 3.92 mL) in $CHCl_3$/MeOH 90/10 was added at room temperature to a stirred solution of cage **2** (1.42 µmol, 3.4 mg) in distilled CH_2Cl_2/MeOH (80/20, 3 mL), protected from light. After 20 minutes, the solvent was removed from the purple solution and the residue was dried under vacuum to afford a purple solid (4.0 mg, quantitative yield). **^{1}H NMR** (500 MHz, DMF-d$_7$): δ 8.75 (8 H, s, H$_t$), 8.53 (16 H, s, H$_{py}$), 8.19 (8 H, dd, ^{3}J = 7.5 Hz, ^{4}J = 1.2 Hz, H$_{o\ out}$), 7.95 (8 H, d, ^{3}J = 7.6 Hz, H$_{m\ out}$), 7.57 (8 H, d, ^{3}J = 7.1 Hz, H$_{o\ in}$), 7.31 (8 H, d, ^{3}J = 7.1 Hz, H$_{m\ in}$), 6.06 (16 H, s, H$_1$), 4.94 (16 H, s, H$_2$), 3.84 (16 H, m, H$_3$), 3.79 (16 H, m, H$_4$), -3.39 (4 H, s, NH). **ES-MS**: m/z (%) calcd for $[C_{136}H_{124}Ag_4N_{32}O_{12}Zn_2]^{4+}$/4: 706.1565; found: 706.1551 (100) [**Ag$_4$(2)$^{4+}$**]/4; calcd for $[C_{136}H_{120}Ag_3N_{32}O_{12}Zn_2]^{3+}$/3: 905.9071; found: 905.8994 (53) [**Ag$_3$(2)$^{3+}$**]/3.

2.7.1 NMR characterization of [Ag$_4$(2)](OTf)$_4$

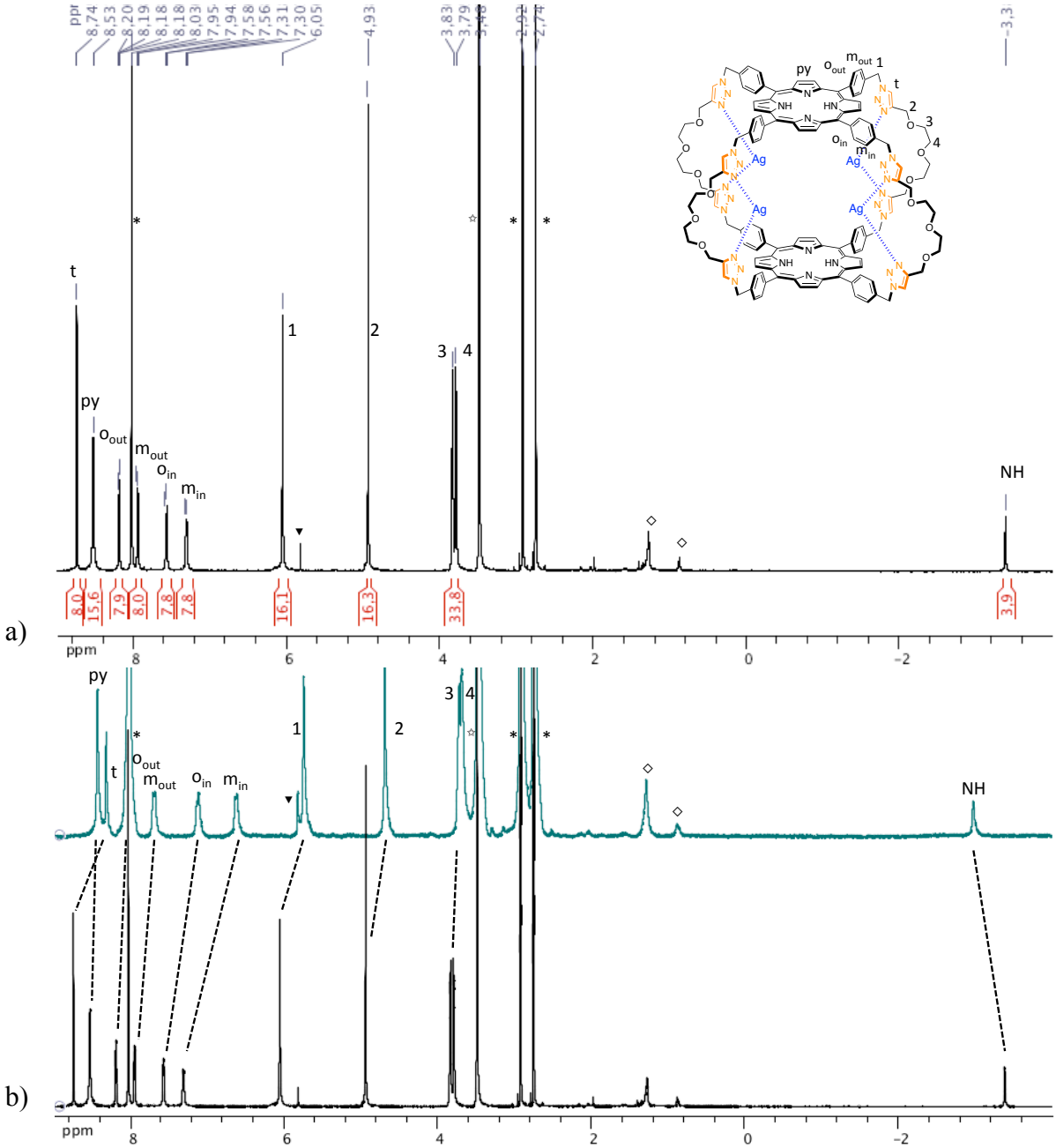

Figure SI50. ^{1}H NMR spectra (DMF-d$_7$, 500 MHz, 298K) of a) complex **[Ag$_4$(2)](OTf)$_4$**, b) superposition of **2** (top) and **[Ag$_4$(2)](OTf)$_4$** (bottom) in DMF-d$_7$, *: DMF, ▾: CH_2Cl_2, ☆: H_2O, ◇: grease.

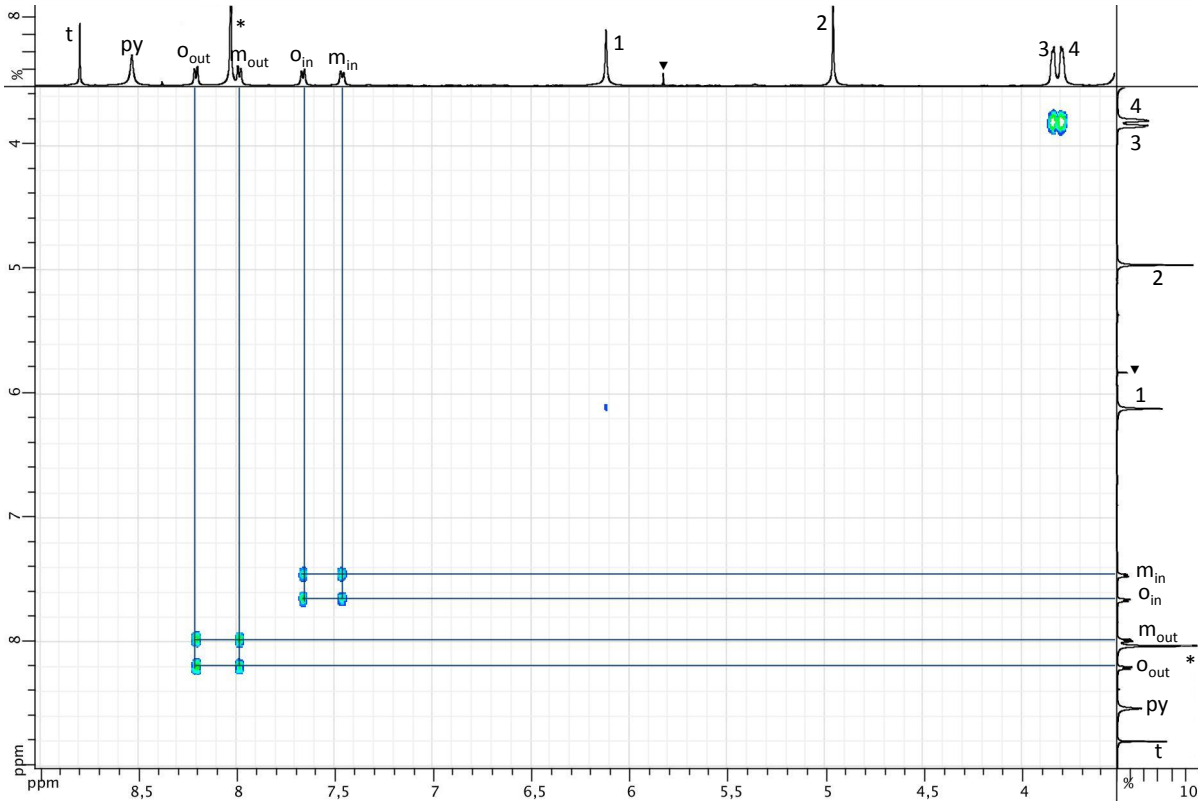

Figure SI51. COSY spectrum (DMF-d_7, 500 MHz, 298K) of complex **[Ag_4(2)](OTf)$_4$**, *: DMF, ▾: CH_2Cl_2.

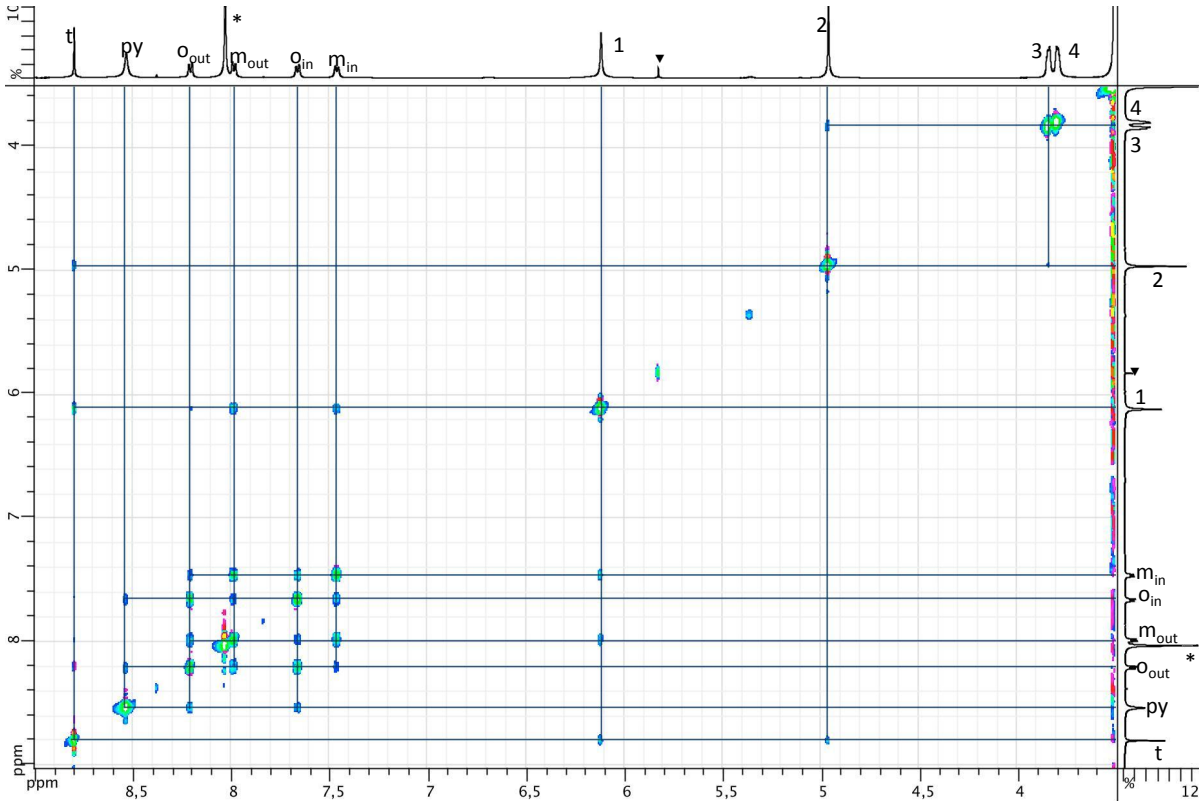

Figure SI52. NOESY spectrum (DMF-d_7, 500 MHz, 298K) of complex **[Ag_4(2)](OTf)$_4$**, *: DMF, ▾: CH_2Cl_2.

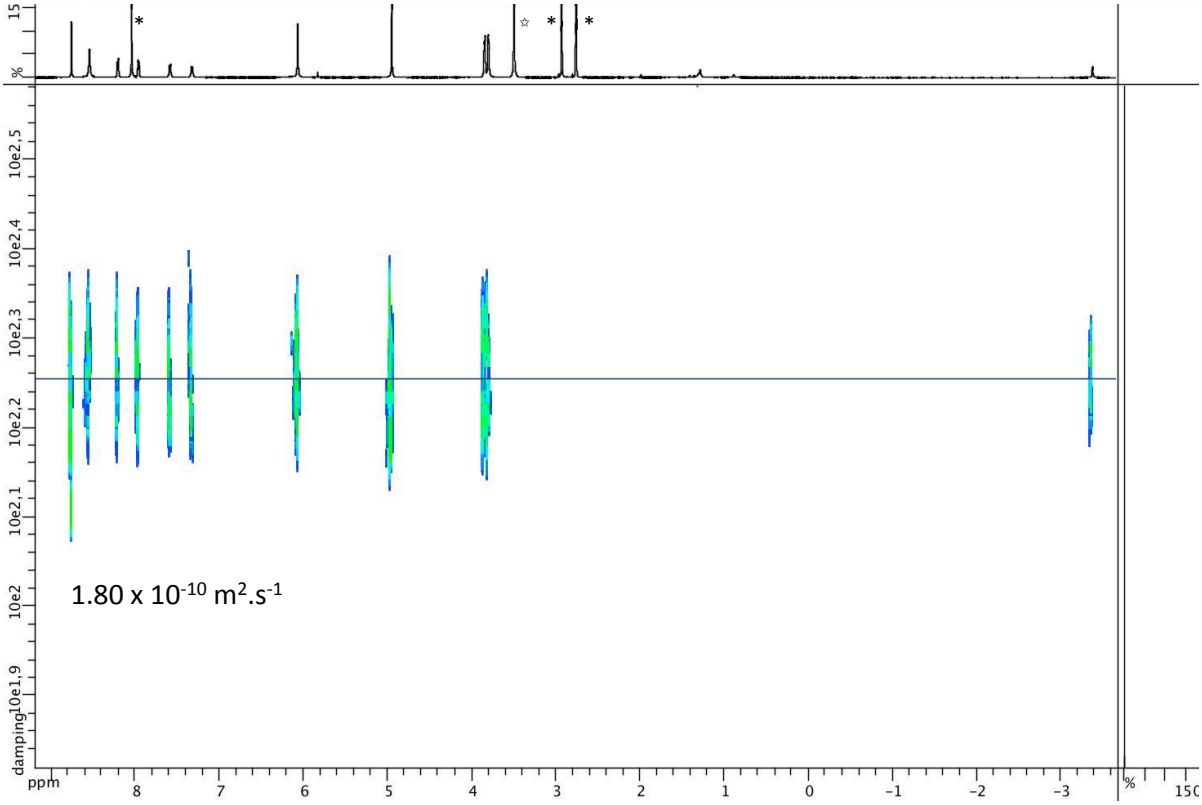

Figure SI53. DOSY spectrum (DMF-d_7, 600 MHz, 298K) of complex **[Ag_4(2)](OTf)$_4$**, *: DMF, ☆: H_2O.

2.7.2 ESI-MS spectrum of [Ag_4(2)](OTf)$_4$

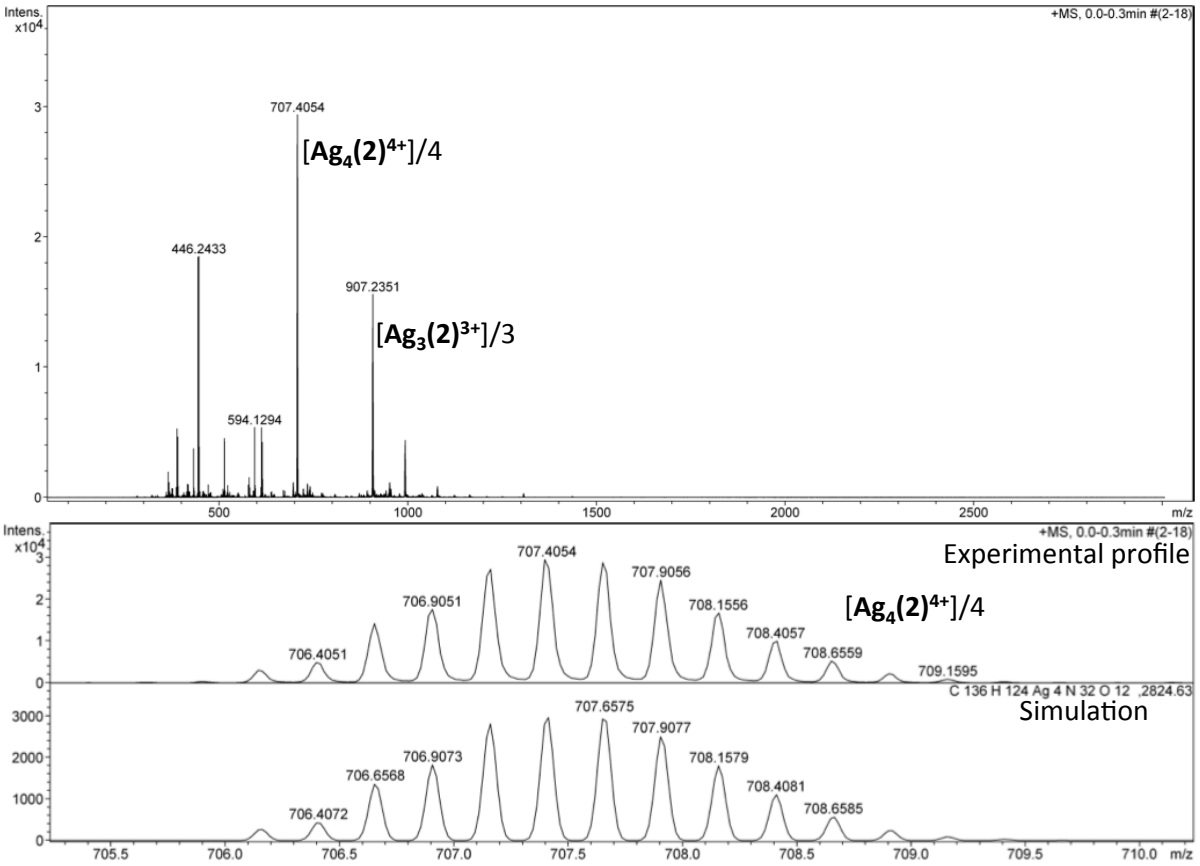

Figure SI54. ES-MS spectrum of complex **[Ag_4(2)](OTf)$_4$**.