

Synthesis of a metal-free coordinating ring *via* formation of a cleavable [2]catenane

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Synthetic procedures and products characterizations

General methods:

All reagents and solvents were purchased at the highest commercial quality from chemical suppliers (Sigma-Aldrich, Merck, Fluka) and used without further purification unless otherwise noted. All reactions were carried out under nitrogen atmosphere with dry solvents under anhydrous conditions. Dry solvents were obtained using a double column SolvTech purification system. Water was deionized using a Millipore Elix 10 filtration system (Millipore, Molsheim, France). Yields refer to spectroscopically purified (¹H NMR) homogeneous materials.

Thin Layer Chromatographies were performed using TLC silica plastic sheets (Polygram SIL G/UV254, Macherey-Nagel) or TLC alox plastic sheets (Polygram Alox N/UV254, Macherey-Nagel). In most cases, irradiation using a *Bioblock VL-4C* UV-Lamp (6 W, 254 nm and/or 365 nm). *Preparative Adsorption Flash Column Chromatographies* were performed using silica gel (Geduran, silica gel 60 (230 – 400 mesh, 40 – 63 μm, Merck)) or aluminium oxide 90 (standardized activity II, 70 – 230 mesh, Merck).

¹H NMR spectra were recorded on a *Bruker Avance 400* spectrometer at 400 MHz and ¹³C spectra at 100 MHz. The spectra were internally referenced to the residual proton solvent signal. Residual solvent peaks were taken as reference (CDCl₃: 7.26 ppm, CD₂Cl₂: 5.30 ppm). For ¹H NMR assignments, the chemical shifts are given in ppm. Coupling constants *J* are given in Hz. Peaks are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br).

ElectroSpray High Resolution Mass Spectrometry (ESI-TOF) analyses were performed on a Bruker *Micro-TOF* mass spectrometer at the Service de Spectrométrie de Masse, Université de Strasbourg (sample solutions were introduced into the mass spectrometer source with a syringe pump with a flow rate of 40 $\mu\text{l}\cdot\text{min}^{-1}$).

Synthesis of Macrocycle 3

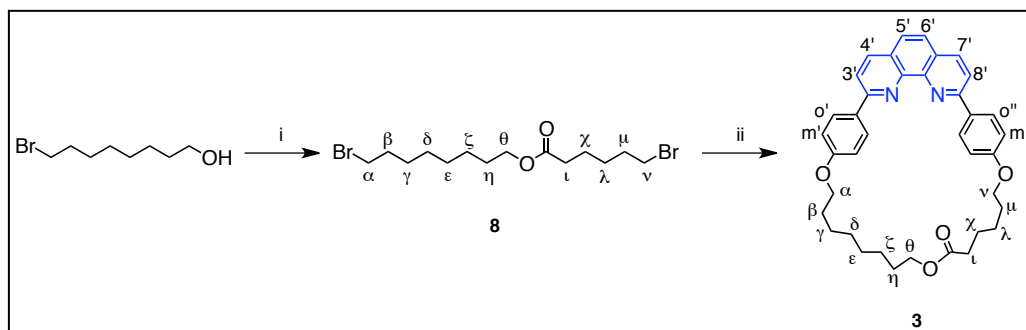
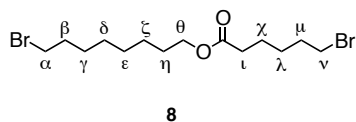


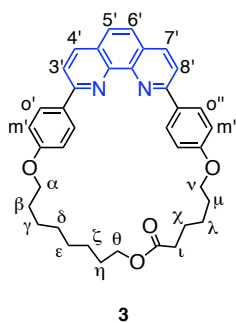
Figure S11. Synthesis of macrocycle 3: (i) 6-bromohexanoyl chloride, pyridine, r.t., 1 h, 70 %; (ii) 2,9-diphenol-1,10-phenanthroline, Cs_2CO_3 , DMF, 60°C, 3 d, 96 %.

Compound 8



A solution of 6-bromohexanoyl chloride (4.90 g, 23 mmol), 8-bromo-1-octanol (3.14 g, 15 mmol), in pyridine (100 mL) was stirred 1 h at room temperature. After that, the mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (3*20 mL). The organic phases were combined, washed with HCl (6N) (20 mL), $\text{NaHCO}_{3\text{sat}}$ (20 mL), water (20 mL) and dried over MgSO_4 . Concentration under reduced pressure followed by column chromatography (SiO_2 , CH_2Cl_2 /pentane: 50/50) afforded compound 8 (4.05 g, 70 %) as a white solid. ^1H NMR (CDCl_3 , 400 MHz, 25°C): δ = 4.01 (t, 3J = 6.4 Hz, 2H, H_θ), 3.43-3.29 (m, 4H, $\text{H}_{\alpha,\nu}$), 2.27 (t, 3J = 7.6 Hz, 2H, H_ν), 1.92-1.18 (m, 18H, $\text{H}_{\beta,\gamma,\delta,\varepsilon,\zeta,\eta,\chi,\lambda,\mu}$); ^{13}C NMR (CDCl_3 , 100 MHz, 25°C): δ = 173.5, 64.4, 34.1, 33.9, 33.5, 32.7, 32.4, 29.0, 28.6, 28.6, 28.0, 27.6, 25.8, 24.1.

Macrocycle 3



To a suspension of Cs_2CO_3 (1 g, 3.069 mmol) in DMF (135 mL) at 60°C was added over 24 h a solution of 2,9-di(*p*-phenol)-1,10-phenanthroline (0.348 g, 0.956 mmol) and 5-bromopentyl-11-bromoundecanoate **8** in DMF (50 mL). After the addition, the solution was stirred 72 h at 60°C . DMF was then removed under vacuum and the residue taken up in a mixture of $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3*50 mL), the organic phases were combined, dried over MgSO_4 , and filtered. Concentration under reduced pressure followed by column chromatography (SiO_2 , CH_2Cl_2) afforded macrocycle **3** (540 mg, 96%) as a white solid. ^1H NMR (CD_2Cl_2 , 400 MHz, 25°C): δ = 8.42-8.30 (m, 6H, $\text{H}_{\text{o}',\text{o}'',4',7'}$), 8.10 (d, 3J = 8.4 Hz, 2H, $\text{H}_{3',8'}$), 7.80 (s, 2H, $\text{H}_{5',6'}$), 7.12 (d, 3J = 8.8 Hz, 4H, $\text{H}_{\text{m}',\text{m}''}$), 4.17-4.02 (m, 6H, $\text{H}_{\alpha,\nu,\theta}$), 2.34 (d, 3J = 7.6 Hz, 2H, H_l), 1.95-1.79 (m, 4H, $\text{H}_{\beta,\mu}$), 1.78-1.34 (m, 14H, $\text{H}_{\gamma,\delta,\varepsilon,\zeta,\eta,\chi,\lambda}$); ^{13}C NMR (CDCl_3 , 100 MHz, 25°C): δ = 173.9, 160.8, 156.4, 146.4, 137.0, 132.6, 132.5, 129.3, 127.9, 126.0, 119.5, 115.4, 68.8, 68.6, 64.0, 35.0, 30.0, 29.4, 29.2, 29.1, 29.0, 26.4, 26.4, 26.2, 25.1; MS (ES): calcd for $\text{C}_{38}\text{H}_{40}\text{N}_2\text{O}_4$: 611.29 $[\text{M}+\text{Na}]^+$, found 611.30.

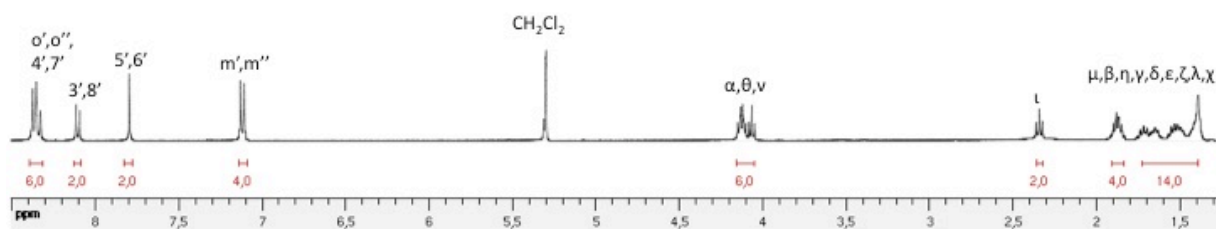
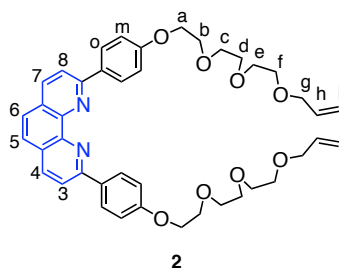


Figure SI2. ^1H NMR spectrum of macrocycle **3** in CD_2Cl_2 .

Compound 2



A solution of 2,9-di(*p*-phenol)-1,10-phenanthroline (500 mg, 1.37 mmol), 1-bromo-3,6,9-trioxadodec-11ene (763 mg, 3.00 mmol), and cesium carbonate (4.5 g, 13.7 mmol) in DMF (10 mL) was stirred overnight at 60°C. After cooling down to room temperature, the mixture was filtered to remove cesium carbonate. Concentration under reduced pressure followed by column chromatography (SiO₂, CH₂Cl₂ → CH₂Cl₂/MeOH: 99/1; afforded compound **2** (796 mg, 82 %) as a yellow solid. ¹H NMR (CD₂Cl₂, 400 MHz, 25°C): δ = 8.45 (d, ³*J* = 8.8 Hz, 4H, H_o), 8.32 (d, ³*J* = 8.4 Hz, 2H, H_{4,7}), 8.14 (d, ³*J* = 8.4 Hz, 2H, H_{3,8}), 7.80 (s, 2H, H_{5,6}), 7.18 (d, ³*J* = 8.8 Hz, 4H, H_m), 6.04-5.89 (m, 2H, H_h), 5.43-5.15 (m, 4H, H_i), 4.29 (t, ³*J* = 4.4 Hz, 4H, H_a), 4.11-4.00 (m, 4H, H_g), 3.99-3.51 (m, 20H, H_{b,c,d,e,f}); ¹³C NMR (CD₂Cl₂, 100 MHz, 25°C): δ = 160.2, 155.8, 146.0, 136.7, 135.1, 132.2, 128.8, 127.6, 125.6, 119.2, 116.4, 114.8, 72.0, 70.8, 70.6, 70.6, 69.6, 69.6, 67.6; HR-MS (ES): calcd for C₄₂H₄₈N₂O₈: 709.349 [M+H]⁺, found 709.356.

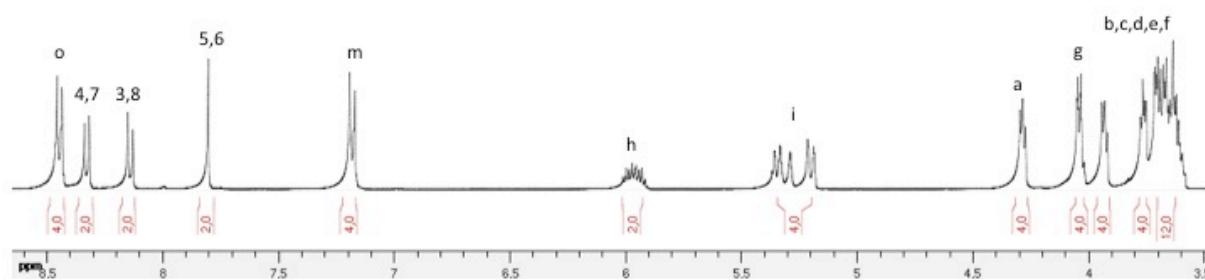


Figure SI3. ¹H NMR spectrum of compound **2** in CD₂Cl₂.

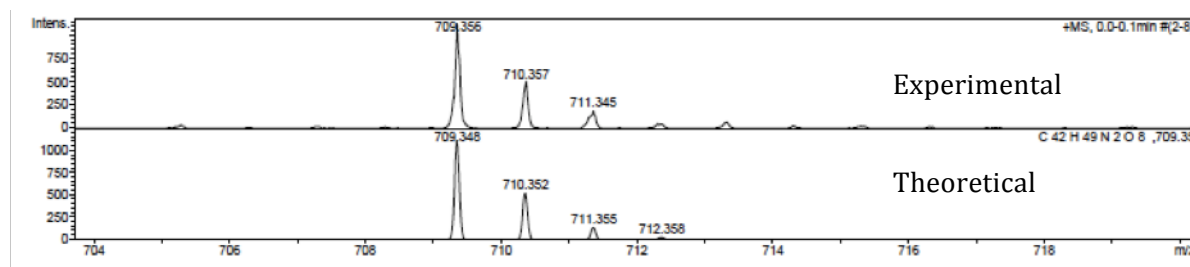
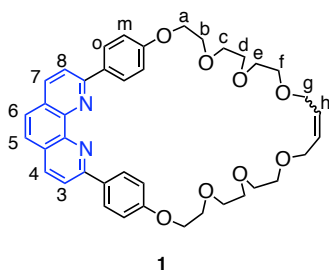


Figure SI4. HR ES-MS spectrum of compound **2** (top) and the corresponding simulation (bottom).

Macrocycle 1



Method A

Grubb's 1st generation catalyst (5.8 mg, 7.0 μmol) was added to a solution of **2** (100.0 mg, 0.14 mmol) in CH_2Cl_2 (14 mL). After 6h at room temperature, an additional portion of catalyst (5.8 mg, 7.0 μmol) was added. After 5 days, concentration under reduced pressure followed by column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2/\text{MeOH}$: 99/1; afforded compound **1** (68.6 mg, 72 %) as a yellow solid.

Method B

To a solution of catenand **6** (64.7 mg, 0.051 mmol) in THF / MeOH (1 / 1, 6 mL) was added a solution of KOH (5.7 mg, 0.102 mmol) in MeOH (1 mL) and the solution was stirred for 1 h. The solvents were removed under vacuum, the residue taking up in CH_2Cl_2 and filtrate, leaving an insoluble potassium salt of opened macrocycle **3**. The organic layer was concentrated under vacuum to give compound **1** as (34.7 mg, 100%) as a colorless solid.

Analysis

^1H NMR (CD_2Cl_2 , 400 MHz, 25°C): δ = 8.42 (d, 3J = 8.8 Hz, 4H, H_o), 8.27 (d, 3J = 8.4 Hz, 2H, $\text{H}_{4,7}$), 8.10 (d, 3J = 8.4 Hz, 2H, $\text{H}_{3,8}$), 7.75 (s, 2H, $\text{H}_{5,6}$), 7.14 (d, 3J = 8.8 Hz, 4H, H_m), 5.87-5.81 (m, 2H, H_h), 4.24 (t, 3J = 4.4 Hz, 4H, H_a), 4.07-3.99 (m, 4H, H_g), 3.94-3.50 (m, 20H, $\text{H}_{b,c,d,e,f}$); ^{13}C NMR (CD_2Cl_2 , 100 MHz, 25°C): δ = 160.2, 155.8, 146.0, 136.6, 132.2, 129.5, 128.8, 127.6, 125.6, 119.0, 114.8, 71.1, 70.9, 70.7, 70.6, 69.7, 69.6, 67.6; HR-MS (ES): calcd for $\text{C}_{40}\text{H}_{44}\text{N}_2\text{O}_8$: 681.317 $[\text{M}+\text{H}]^+$, found 681.316.

= 7.6 Hz, 2H, H_l), 2.01-1.32 (m, 18H, H_{β,γ,δ,ε,ζ,η,χ,λ,μ}); HR-MS (ES): calcd for C₈₀H₈₈CuN₄O₁₂:
1359.569 [M]⁺, found 1359.562.

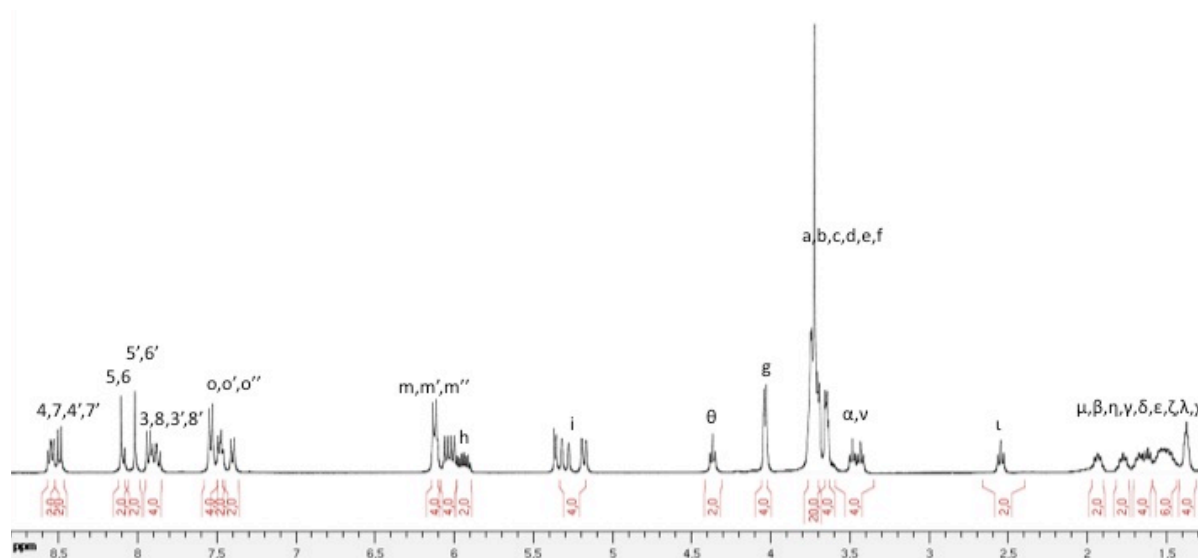


Figure SI7. ¹H NMR spectrum of Pseudo-Cu(I)-[2]catenane **4**⁺ in CD₂Cl₂.

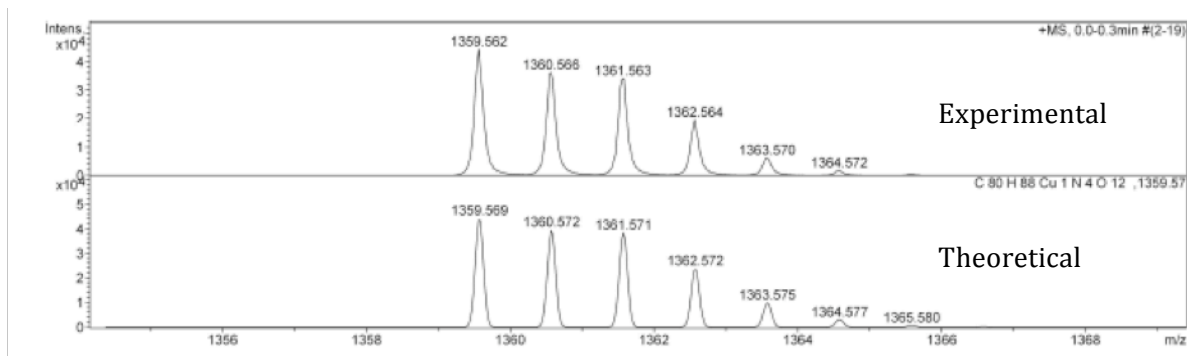
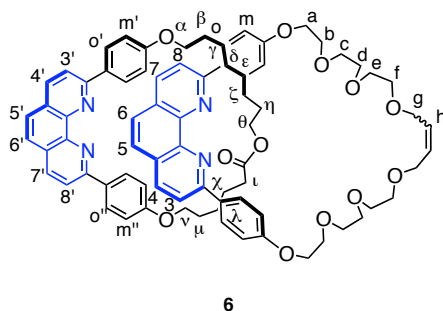


Figure SI8. HR ES-MS spectrum of pseudo-Cu(I)-[2]catenane **4**⁺ (*top*) and the corresponding simulation (*bottom*).

[2]catenand **6**



6

To a solution of catenane **5**⁺ (75.4 mg, 0.051 mmol) in a mixture of CH₂Cl₂ (3 mL) and CH₃CN (1.5 mL) was added a solution of saturated KCN in water (0.5 mL) and the solution was stirred for 30 min. Water (20 mL) was added and the aqueous layer was extracted with CH₂Cl₂ (3*20 mL). The organic phases were combined and concentrated under vacuum to give, without further purification, the desired catenand **6** (64.7 mg, 0.051 mmol, 100%) as a pale yellow solid. ¹H NMR (CD₂Cl₂, 400 MHz, 25°C): δ = 8.60-8.34 (m, 8H, H_{o,o',o''}), 8.35-8.15 (m, 4H, H_{4,7,4',7'}), 8.15-7.99 (m, 4H, H_{3,8,3',8'}), 7.83-7.60 (m, 4H, H_{5,6,5',6'}), 7.23-6.91 (m, 8H, H_{m,m',m''}), 5.88-5.72 (m, 2H, H_h), 4.20-4.11 (m, 2H, H_θ), 4.11-4.03 (m, 4H, H_a), 4.03-3.96 (m, 4H, H_{α,v}), 3.96-3.90 (m, 4H, H_g), 3.84-3.73 (m, 4H, H_b), 3.70-3.48 (m, 16H, H_{c,d,e,f}), 2.37 (t, ³J = 7.6 Hz, 2H, H_l), 1.91-1.18 (m, 18H, H_{β,γ,δ,ε,ζ,η,χ,λ,μ}); HR-MS (ES): calcd for C₇₈H₈₄N₄O₁₂: 1269.616 [M+H]⁺, found 1269.615.

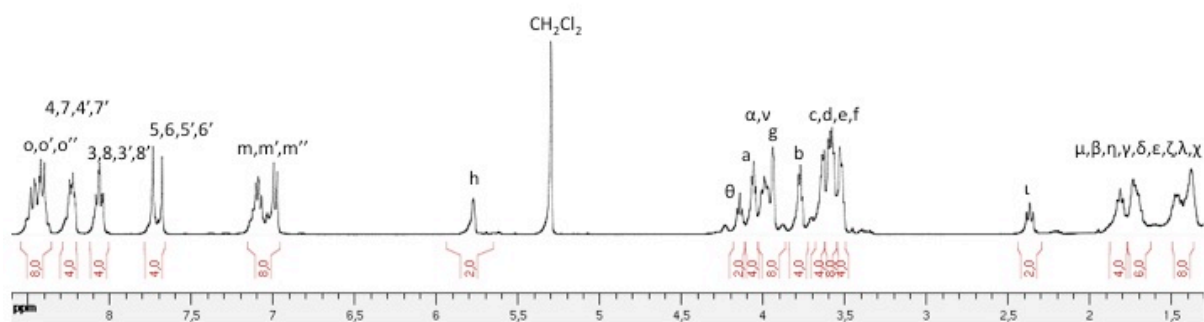


Figure SI11. ¹H NMR spectrum of [2]catenand **6** in CD₂Cl₂.

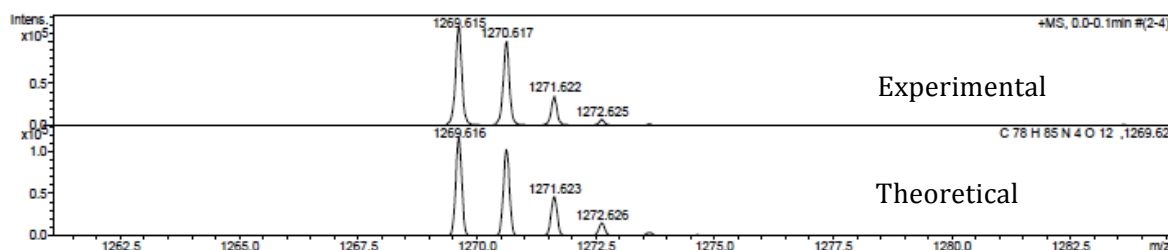
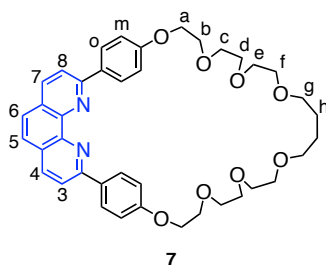


Figure S112. HR ES-MS spectrum of [2]catenane **6** (*top*) and the corresponding simulation (*bottom*).

Macrocycle 7



A mixture of **1** (100 mg, 0.147 mmol) and Pd/C (10 wt. % loading, 10 mg) in THF (50 mL) was stirred at room temperature under positive H₂ atmosphere. After 12 h, the mixture was filtered on celite. Concentration under reduced pressure followed by column chromatography (SiO₂, CH₂Cl₂ → CH₂Cl₂/MeOH: 97/3) afforded compound **7** (92.3 mg, 92% yield) as a colorless glassy product. ¹H NMR (CD₂Cl₂, 400 MHz, 25°C): δ = 8.45 (d, ³J = 8.8 Hz, 4H, H_o), 8.31 (d, ³J = 8.4 Hz, 2H, H_{4,7}), 8.13 (d, ³J = 8.4 Hz, 2H, H_{3,8}), 7.79 (s, 2H, H_{5,6}), 7.19 (d, ³J = 8.8 Hz, 4H, H_m), 4.28 (t, ³J = 4.4 Hz, 4H, H_a), 3.94-3.89 (m, 4H, H_b), 3.80-3.60 (m, 16H, H_{b,c,d,e,f}), 3.55-3.51 (m, 4H, H_g), 1.76-1.68 (m, 4H, H_h); ¹³C NMR (CD₂Cl₂, 100 MHz, 25°C): δ = 160.3, 155.9, 146.1, 136.8, 132.3, 128.9, 127.7, 125.7, 119.1, 114.9, 71.1, 71.0, 70.8, 70.7, 70.3, 69.7, 67.7, 26.5; HR-MS (ES): calcd for C₄₀H₄₆N₂O₈: 683.333 [M+H]⁺, found 683.332.

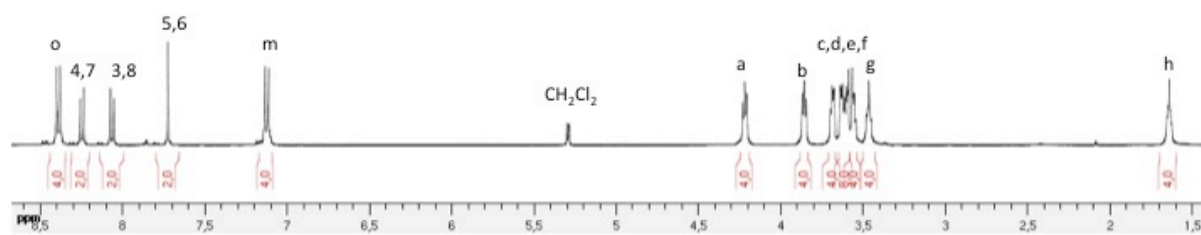


Figure SI13. ^1H NMR spectrum of macrocycle **7** in CD_2Cl_2 .

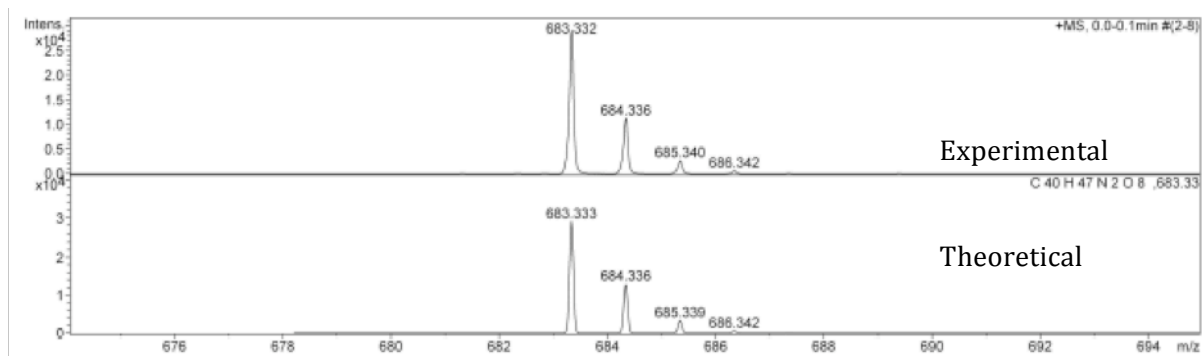


Figure SI14. HR ES-MS spectrum of macrocycle **7** (*top*) and the corresponding simulation (*bottom*).