Supplementary Material (ESI) for Journal of Materials Chemistry

Optmizing Reaction Conditions for Synthesis of Electron Donor [60]Fullerene Interlocked Multiring Systems

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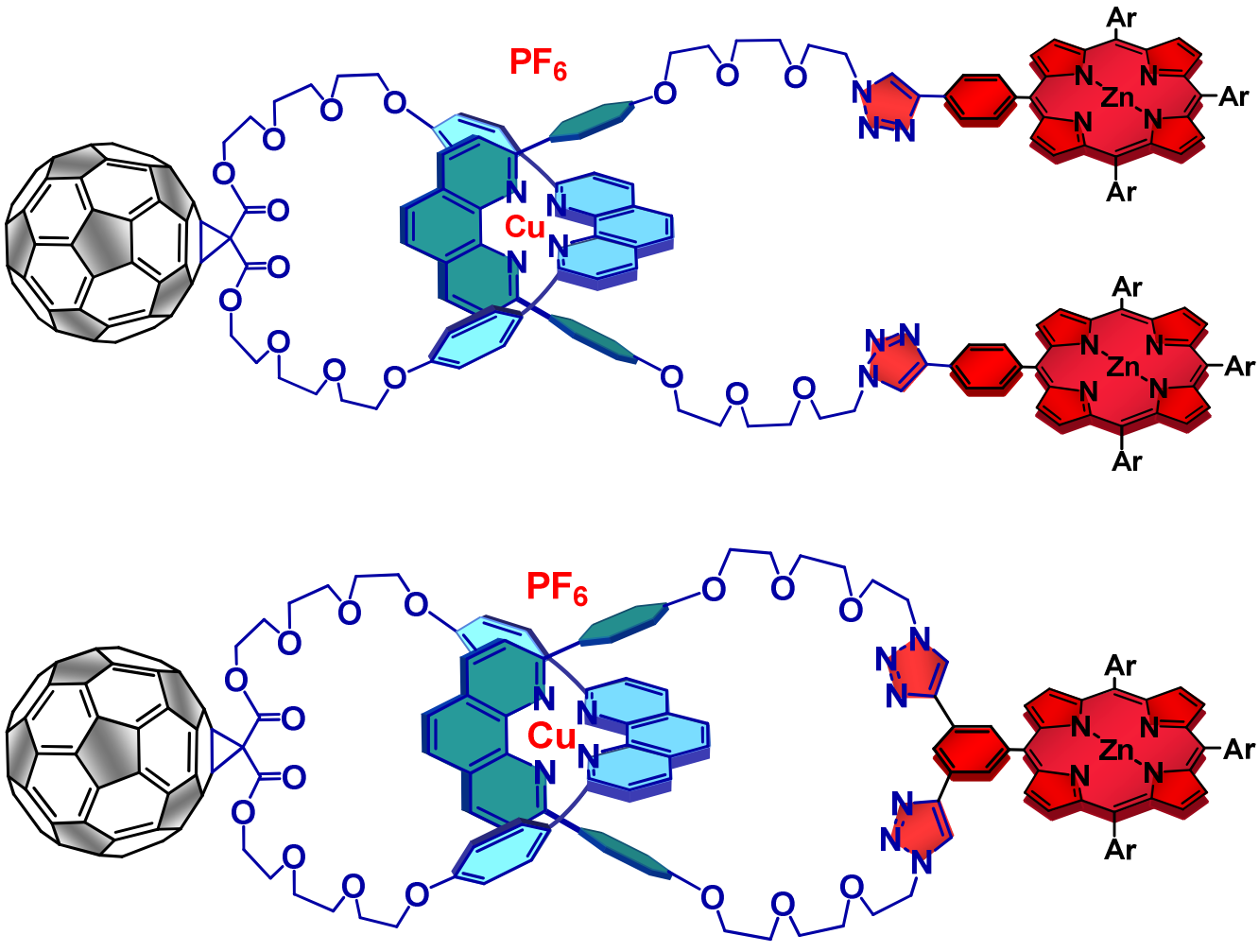

SUPPORTING INFORMATION

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General Information

NMR spectra were obtained on either a Bruker AVANCE 400 (400 MHz) or an AVANCE 800 (800 MHz) spectrometer using deuterated solvents as the lock. The spectra were collected at 25 ^{o}C and chemical shifts (δ, ppm) were referenced to residual solvent peak.

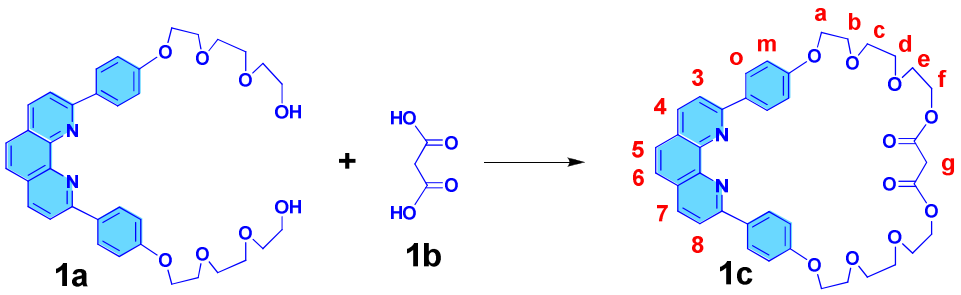
Mass spectra were obtained on an Agilent 1100 Series Capillary LCMSD Trap XCT Spectrometer in positive or negative-ion mode and ThermoFinnigan PolarisQ ion-trap GCMS Spectrometer.

MALDI-TOF mass spectra were obtained using a Bruker OmniFLEX MALDI-TOF MS Spectrometer. This instrument was operated at an accelerating potential of 20kV in linear mode. The mass spectra represent an average of over 256 consecutive laser shots. The mass scale was calibrated using the matrix peaks and the calibration software available from Bruker OmniFLEX. Reported *m/z* values correspond to monoisotopic masses. The compound solutions (10^{-3} mol/L) were prepared in THF. Matrix compounds were purchased from Aldrich and used without further purification. The matrix, α-cyano-4-hydroxy-cinnamic acid (CCA) was dissolved (10 g/L) in a solvent mixture composed of H_2O/CH_3CN/TFA (25/75/1, v/v), while 2,5-dihydroxybenzoic acid (DHB) was dissoved in CH_3CN. Two microliters of compound solution were mixed with 10 μL of matrix solution. The final solution was deposited onto the sample target and allowed to air dry.

Materials

All chemicals were purchased from Sigma/Aldrich and Alfa Aesar and used without further purification. Prior to moisture sensitive reactions, solvents were freshly distilled. Methylene chloride (CH_2Cl_2) and acetonitrile (CH_3CN) were dried over calcium hydride while tetrahydrofuran (THF) was dried using sodium/benzophenone. Anhydrous dimethylformamide (DMF) was used as received. All syntheses were carried out using Schlenk techniques. Moisture sensitive liquids were transferred using a cannula or syringe. The progress of a reaction was monitored by thin-layer chromatography (TLC) whenever possible. TLC was performed using precoated glass plates (Silica gel 60, 0.25 mm thickness) containing a 254 nm fluorescent indicator. Column chromatography was carried out using Merck Silica gel 60 (0.063-0.200 mm) and neutral alumina (Brockmann I, activated, 150 mesh, 58Å). Compound **1a** was prepared following literature procedure.[1]

Synthesis of Macrocycle **1c**:

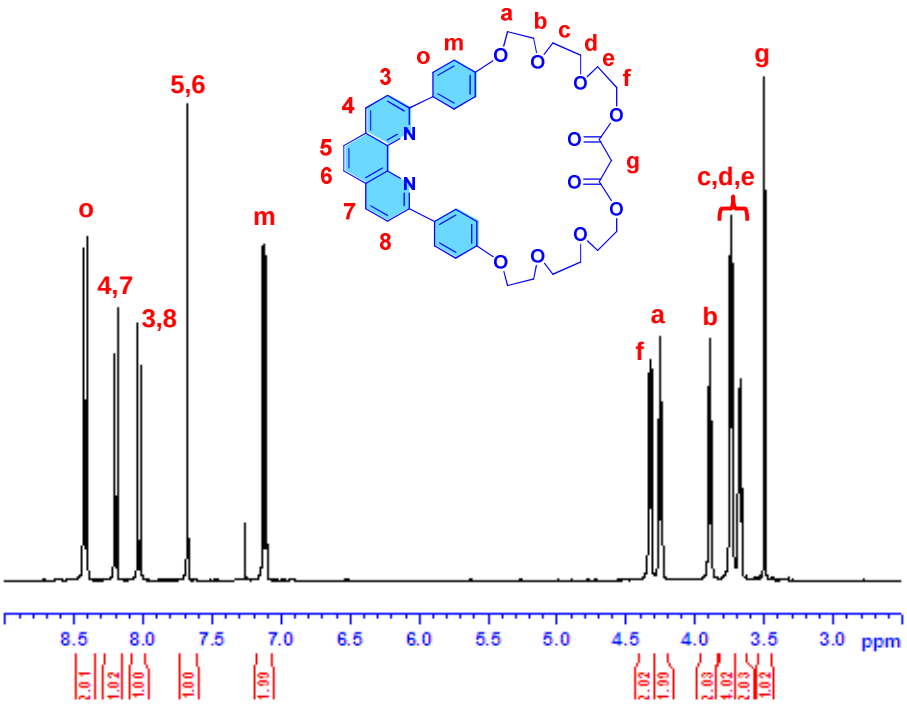


Compound **1a** (2.00 g, 3.18 mmol) and malonic acid **1b** (0.33 g, 3.18 mmol) were dissolved in 100 mL of CH_2Cl_2. Triethylamine (Et_3N) (1.61 g, ~2.25 mL, 16 mmol) and bis(2-oxo-3-oxazolidinyl)phosphonic chloride (BOP-Cl) (0.81 g, 3.18 mmol) were added and the reaction mixture was stirred at room temperature for 2 h. Another portion of BOP-Cl (0.81 g, 3.18 mmol) and Et_3N (0.80 g, ~1.15 mL, 8 mmol) were added and the magnetic stirring was kept for 12 h at rt to complete the macrocyclization reaction. The crude mixture was neutralized with HCl_{aq} (10%), the organic phase was separated, washed with water (3 x 100 mL), dried over Na_2SO_4, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO_2) using EtOAc as eluent, affording **1c** as a colorless oil (~1.00 g, 45% yield).

^{1}H NMR ($CDCl_3$), δ ppm: 8.44 (d, *J* = 8.8 Hz, 4H, H_o); 8.20 (d, *J* = 8.5 Hz, 2H, H_4 and H_7); 8.05 (d, *J* = 8.5 Hz, 2H, H_3 and H_8); 7.69 (s, 2H, H_5 and H_6); 7.14 (d, *J* = 8.8 Hz, 4H, H_m); 4.34 (t, *J* = 4.9 Hz, 4H, Ph–O–CH_2); 4.26 (t, *J* = 4.9 Hz, 4H, CH_2–O–C=O); 3.90-3.60 (m, 16H, O–CH_2–CH_2–O); 3.51 (s, 2H, COO–CH_2–COO).

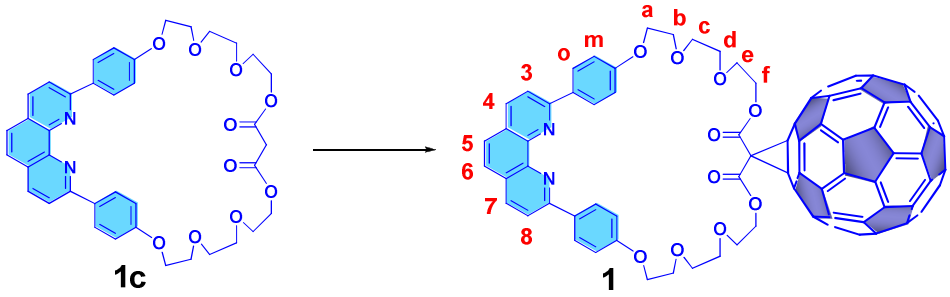
^{13}C NMR ($CDCl_3$), δ ppm: CH_2 malonic acid group: 207 ppm. Phenanthroline nuclei: 159.5, 156.4, 146.0, 136.9, 132.7, 129.0, 127.6, 125.6, 119.2, 114.8. Polyoxo-ethylene linker: 72.7, 69.7, 69.5, 69.2, 67.6, 66.0.

LC-MSD: m/z found 697.55 $[M+H]^+$, calculated 696.27 for $C_{39}H_{40}N_2O_{10}$.



^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$, 300K).

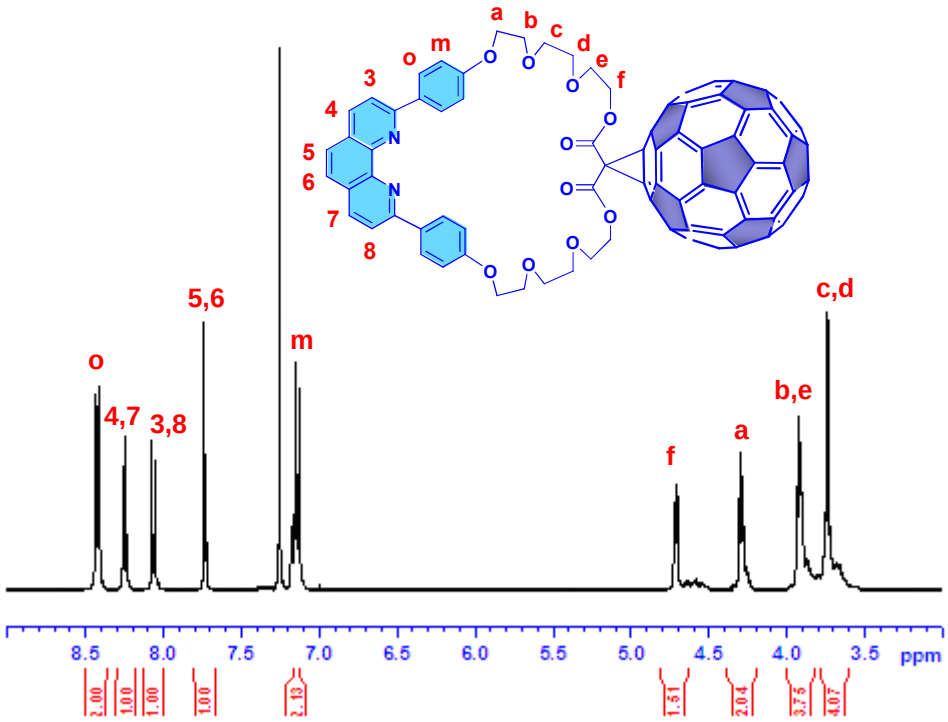
Synthesis of Macrocycle **1**:



Macrocycle **1c** (0.100 g, 0.143 mmol), C_{60} (0.162 g , 0.225 mmol) and I_2 (0.070 g, 0.272 mmol) were dissolved in 160 mL of toluene under magnetic stirring. DBU (0.081 g, 0.080 mL, 0.531 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. The crude mixture was neutralized with HCl_{aq} (10%), the organic phase was separated, washed with water (3 x 100 mL), dried over Na_2SO_4, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO_2) using toluene/MeOH (97:3, v/v) as the eluent, affording **1** as a brown solid in 55% yield.

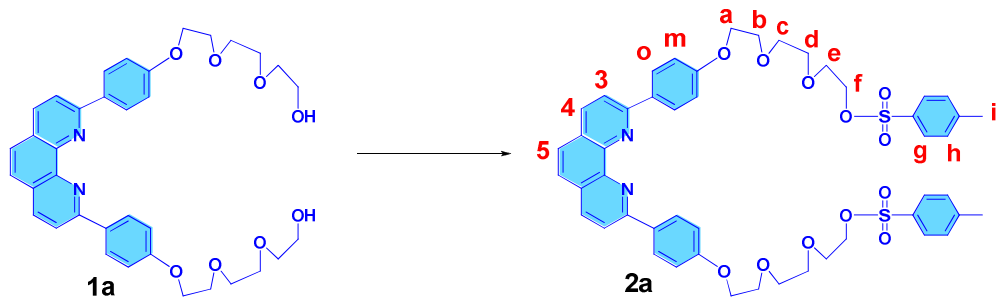
^{1}H NMR ($CDCl_3$), δ ppm: 8.36 (d, *J* = 8.8 Hz, 4H, H_o); 8.17 (d, *J* = 8.5 Hz, 2H, H_4 and H_7); 8.00 (d, *J* = 8.5 Hz, 2H, H_3 and H_8); 7.67 (s, 2H, H_5 and H_6); 7.08 (d, *J* = 8.8 Hz, 4H, H_m); 4.64 (t, *J* = 4.9 Hz, 4H, H_f); 4.22 (t, *J* = 4.9 Hz, 4H, H_a); 3.92 (m, 8H, H_b and H_e); 3.74 (s, 8H, H_c and H_d).

MALDI-TOF: m/z found 1415.15 $[M+H]^+$, calculated, 1414.25 for $C_{99}H_{38}N_2O_{10}$.



^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$, 300K).

Synthesis of di-tosylate phenanthroline derivative **2a**:

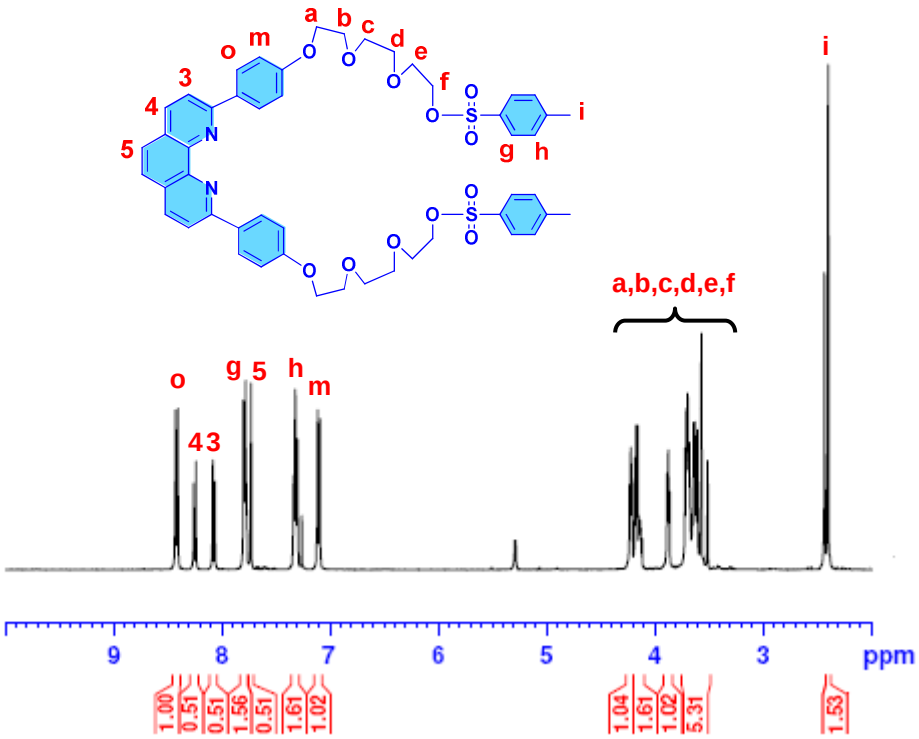


In a three necked round bottom flask, compound **1** (2.60 g, 7.55 mmol) and triethylamine (5.80 g, 57.50 mmol) were dissolved in 50 mL of dry CH_2Cl_2 under N_2 atmosphere and magnetic stirring. In an addition funnel, *p*-tosyl chloride (p-Ts) (7.00 g, 36.84 mmol) was dissolved in 50 mL of dry CH_2Cl_2. The round bottom flask was cooled to 0^{o}C and the p-TsCl solution was added dropwise (over 10 min) under N_2 atmosphere with magnetic stirring. After addition, the reaction mixture was kept at 0 ^{o}C for 4 h and then allowed to warm to rt and stirred for 12 h. The reaction was carefully quenched at 0 ^{o}C by addition of 10% aqueous HCl. The red organic phase was decanted, washed with water (3x 100 mL), dried over Na_2SO_4, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO_2) using CH_2Cl_2/MeOH as the eluent (gradient from 0 to 5%, v/v), affording **2a** as a red oil (5.30 g, 75% yield).

^{1}H NMR ($CDCl_3$), δ ppm: 8.34 (d, *J* = 9.0 Hz, 4H, H_o); 8.26 (d, *J* = 9.0 Hz, 2H, H_4 and H_7); 8.08 (d, *J* = 9.0 Hz, 2H, H_3 and H_8); 7.80 (d, *J* = 9.0 Hz, 4H, H_g); 7.73 (s, 2H, H_5 and H_6); 7.32 (d, *J* = 9.0 Hz, 4H, H_h); 7.11 (d, *J* = 9.0 Hz, 4H, H_m); 4.30-3.40 (m, 24H, H_{a-f}); 2.39 (s, 6H, H_i).

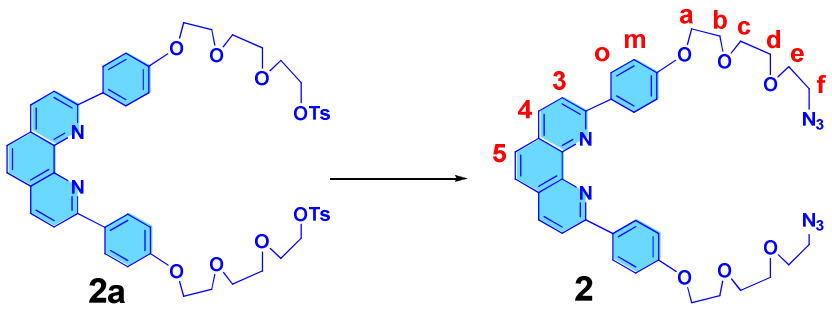
^{13}C NMR ($CDCl_3$), δ ppm: phenanthroline nuclei: 159.5, 156.4, 146.0, 136.9, 132.7, 129.0, 127.6, 125.6, 119.2, 114.8. Polyoxo-ethylene linker: 72.7, 69.7, 69.5, 67.6, 66.0, 61.6. Tosyl group: 144.4, 140.3, 130.3, 128.1, 67.4, 21.3.

LC-MSD: m/z found 937.43 $[M+H]^+$, calculated 936.30 for $C_{50}H_{52}N_2O_{12}S_2$.



^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$, 300K).

Synthesis of di-azido phenanthroline derivative **2**:



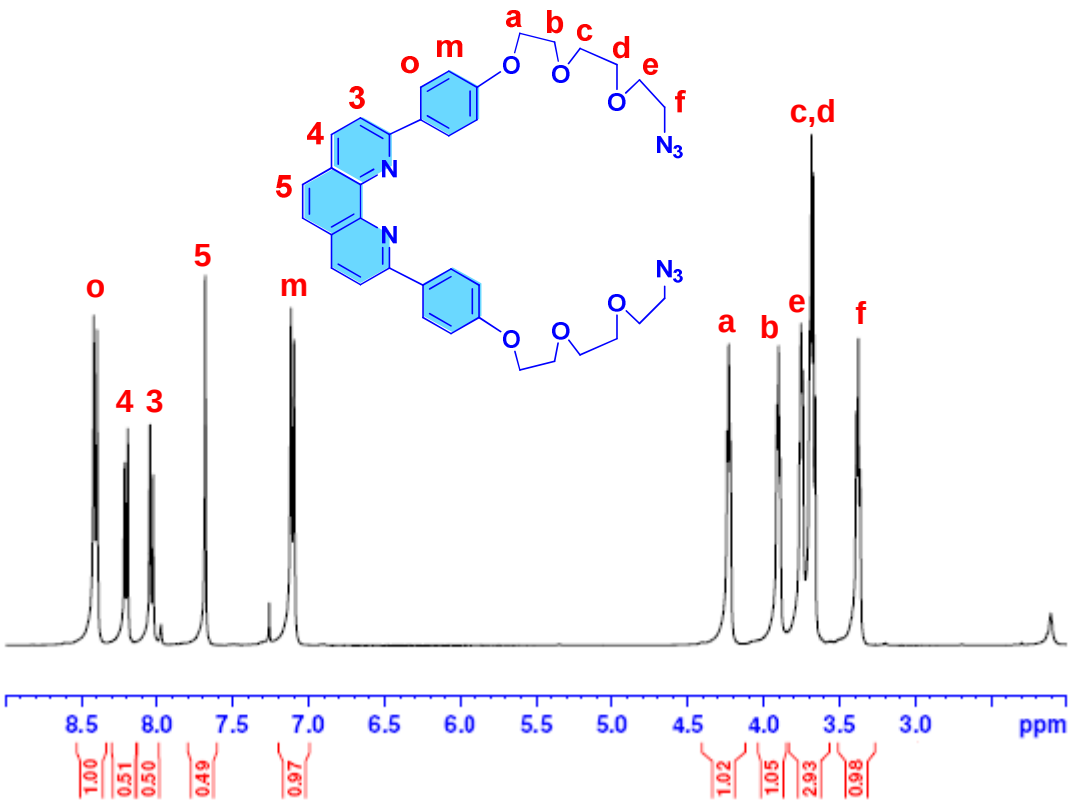
* Organic azides have been reported in literature as potential explosives. The authors suggest the use of standard PVC blast shield while handling organic azides.

Compound **2** (1.00 g, 1.07 mmol) and NaN_3 (0.40 g, 6.00 mmol) were dissolved in 50 mL of anhydrous DMF and the reaction mixture was heated to 80 ^oC for 12 h. The mixture was cooled to rt and the DMF was evaporated under reduced pressure. CH_2Cl_2 (200 mL) and H_2O (50 ml) were added, the organic phase was separated, washed with water (3 x 100 mL), dried over Na_2SO_4, filtered through paper and concentrated under reduced pressure. Final purification was achieved by flash chromatography (SiO_2) using CH_2Cl_2/MeOH as the eluent (98:2, v/v), affording **2** as a waxy product (0.650 g, 93% yield).

^{1}H NMR ($CDCl_3$), δ ppm: 8.41 (d, *J* = 8.0 Hz, 4H, H_o); 8.21 (d, *J* = 8.0 Hz, 2H, H_4 and H_7); 8.04 (d, *J* = 8.0 Hz, 2H, H_3 and H_8); 7.68 (s, 2H, H_5 and H_6); 7.11 (d, *J* = 8.0 Hz, 4H, H_m); 4.23 (t, 4H, H_a); 3.95 (t, 4H, H_b); 3.77 (t, 4H, H_e); 3.65 (t, 8H, H_c and H_d); 3.37 (t, 4H, H_f).

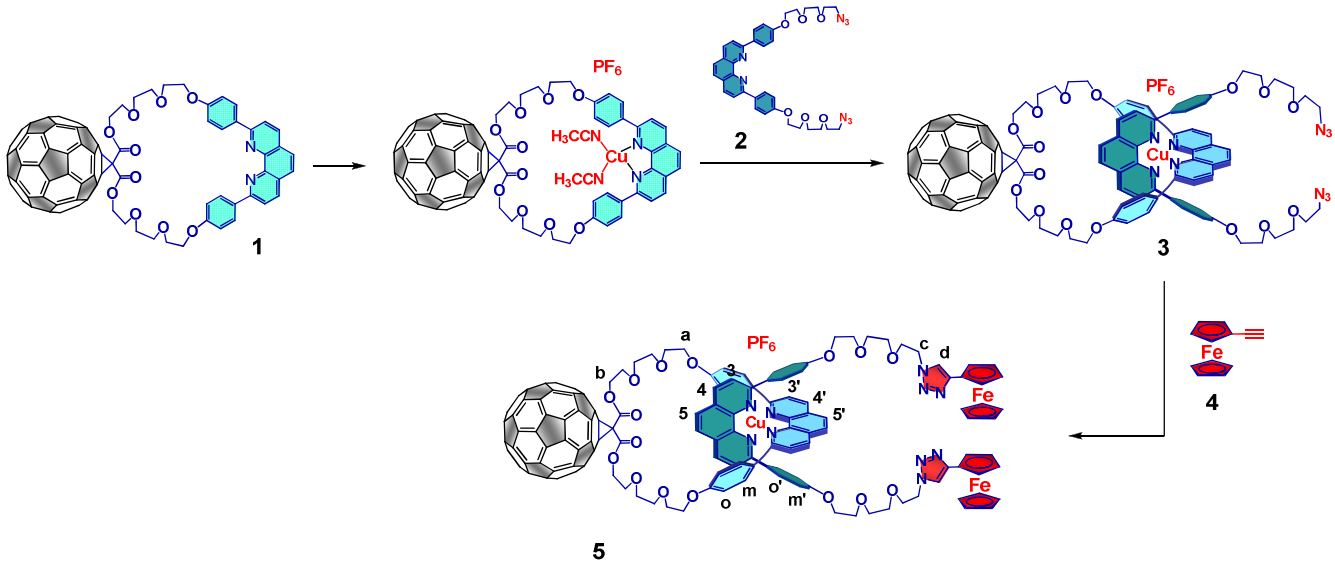
^{13}C NMR ($CDCl_3$), δ ppm: phenanthroline nuclei: 159.5, 156.4, 146.0, 136.9, 132.7, 129.0, 127.6, 125.6, 119.2, 114.8. Polyoxo-ethylene linker: 72.7, 69.7, 69.5, 67.6, 66.0. CH_2N_3: 41.2.

IR (KBr) ν cm^{-1}: 2098 (N=N stretch).



^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$, 300K).

One-Pot Procedure for Preparation of Ferrocene-Stoppered Fullerene Rotaxane **5**:

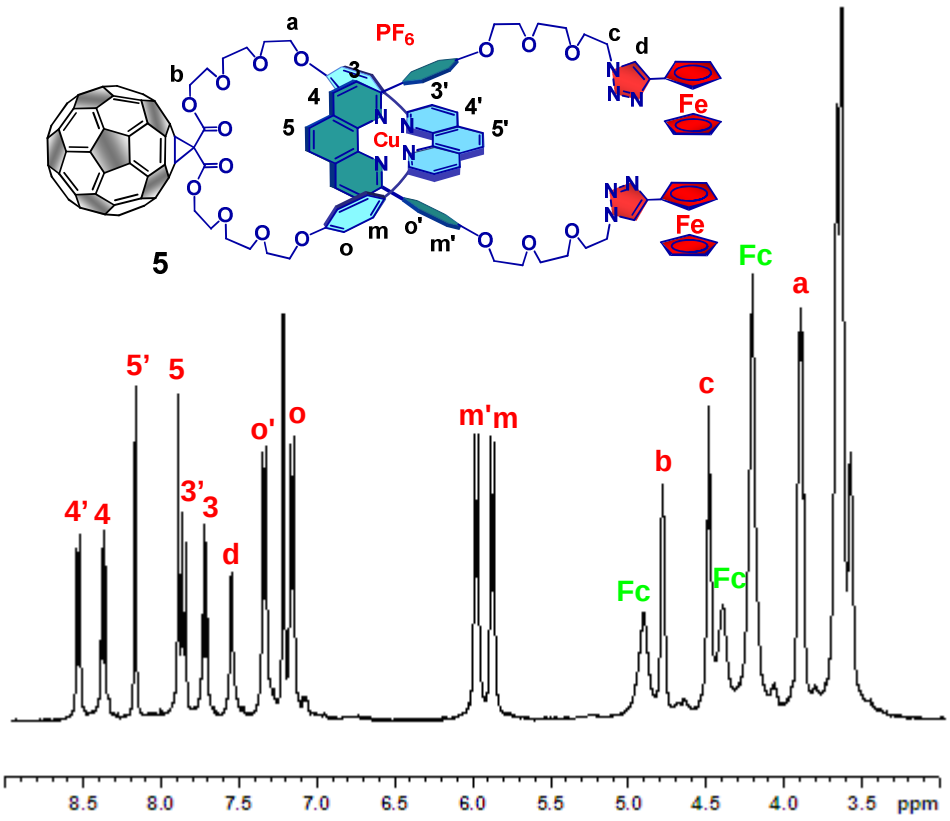


In the reaction flask, macrocycle **1** (0.0265 g, 0.0188 mmol) was dissolved in 3 mL of degassed CH_2Cl_2/CH_3CN (7:3, v/v) to which $[Cu(CH_3CN)_4][PF_6]$ (0.0071 g, 0.0188 mmol) was added under N_2. The dark orange solution was stirred for 30 min at rt. The di-azidophenanthroline ligand **2** (0.0128 g, 0.0188 mmol) was then added as a solid to the flask and the deep red solution was stirred under N_2 at rt for 3 h to afford precursor **3**. Meanwhile, CuI (0.0071 g, 0.0376 mmol), sodium

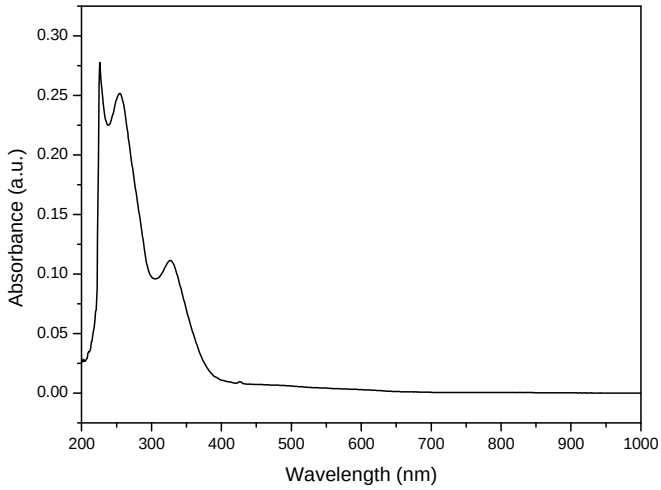
ascorbate (0.030 g, 0.150 mmol) and sulphonated bathophenanthroline (0.0433 g, 0.0734 mmol) were added to 3 mL of a degassed and solvent mixture composed of H_2O/EtOH (1:1, v/v) under N_2 atmosphere. The suspension was heated to reflux, cooled to rt and added by syringe to the flask containing **3**. Finally, alkynyl ferrocene **4** (~ 0.012 g, 0.0564 mmol, added as a solid) and DBU (0.019 g, 19μL, 0.127 mmol) were added and the red mixture was stirred under N_2 for 12 h at rt. The crude mixture was neutralized by adding 5 mL of 10% HCl aqueous solution and extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was washed with water (3 x 50 mL), concentrated to a volume of 10 mL and then stirred for 2 h with saturated MeOH solution of KPF_6 to effect the anion exchange. The solvents were evaporated under reduced pressure, and the remaining insoluble light brown solid was extracted with CH_2Cl_2 (3 x 100 mL) and then filtered through paper. The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography (SiO_2), first using CH_2Cl_2 to elute unreacted alkynyl ferrocene **4** (which had been added in slight excess) and then CH_2Cl_2/CH_3OH (97/3 v/v) to afford rotaxane **5** as a brown solid in 92% yield.

^{1}H NMR ($CDCl_3$), δ ppm: 8.56 (d, *J* = 8.6 Hz, 2H, H_4' and H_7'); 8.40 (d, *J* = 8.6 Hz, 2H, H_4 and H_7); 8.21 (s, 2H, H_5' and H_6'); 7.93 (s, 2H, H_5 and H_6); 7.89 (d, *J* = 8.6 Hz, 2H, H_3' and H_8'); 7.75 (d, *J* = 8.6 Hz, 2H, H_3 and H_8); 7.75 (s, 2H, H_b); 7.60 (d, *J* = 8.8 Hz, 4H, H_o'); 7.37 (d, *J* = 8.8 Hz, 4H, H_o); 6.03 (d, *J* = 8.8 Hz, 4H, H_m'); 5.90 (d, *J* = 8.8 Hz, 4H, H_m); 4.94 (br, 2H, ferrocene substituted ring); 4.82 (br, 4H, H_f); 4.52 (m, 4H, H_a); 4.40 (br, 2H, ferrocene substituted ring); 4.25 (br, 5H, non-substituted ferrocene ring); 4.00-3.50 (m, 40H, polyoxo-ethylene linkers).

MALDI-TOF: m/z found 2577.36 $[M - PF_6]^+$, calculated, 2722 for $C_{159}H_{98}N_{10}O_{16}Fe_2CuPF_6$.

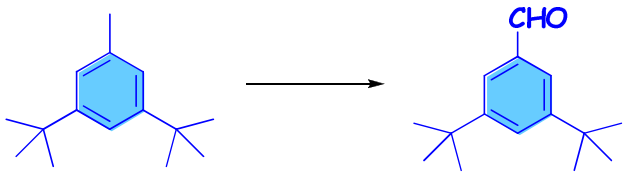


^{1}H NMR spectrum of rotaxane **5** (400 MHz, $CDCl_3$, 300K).



Absorption spectrum of Rotaxane **5** (10^{-6} M in $CHCl_3$)

Synthesis of 3,5-di-*tert*-butylbenzaldehyde:



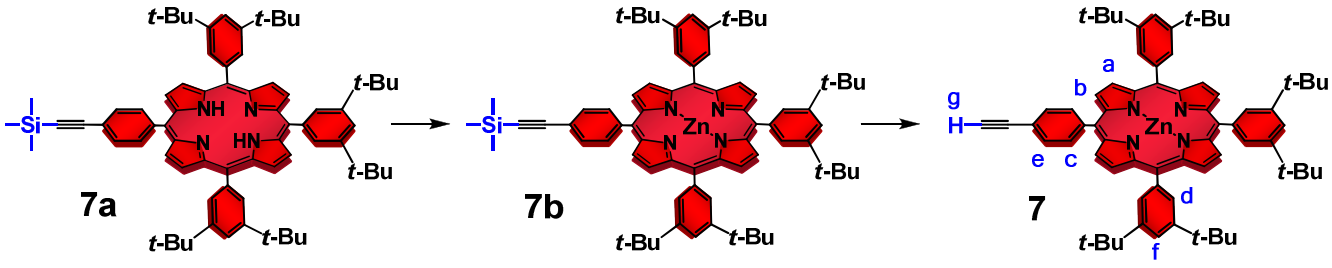
A solution of 3,5-di-*tert*-butyltoluene (25.0 g, 0.122 mol), *N*-bromosuccinimide (33.0 g, 0.185 mol) and azobisisobutyronitrile (AIBN) (0.900 g, 0.0055 mol) in benzene was heated at reflux under magnetic stirring for 4 h. The reaction mixture was cooled, filtered through paper and the solvents was evaporated under reduced pressure. The residue was dissolved in 70 mL of a solvent mixture composed by EtOH/H_2O (1:1) and hexamethylenetetramine (50.0 g, 0.357 mol) was added and the solution was heated at reflux for 4 h. Concentrate HCl was added (21 mL) and heating at reflux was continued for 30 min. The ethanol was removed under reduced pressure, and the remaining aqueous layer was extracted with ether. The ether layer was dried over Na_2SO_4 and the solvent removed. Recrystallization from EtOH afforded the desired product as white crystals (19.10 g, 72% yield).

^{1}H NMR ($CDCl_3$), δ ppm: 10.01 (s, 1H, CHO); 7.72 (d, *J* = 8.5 Hz, 2H, H_o); 7.71 (m, *J* = 8.5 Hz,1H, H_p); 1.36 (s, 18H, CH_3).

^{13}C NMR ($CDCl_3$), δ ppm: 192 (CHO); 146.9 (C_3 and C_5); 137.2 (C_1); 129.7 (C_4); 122.6 (C_2 and C_6); 34.5 (C–CH_3); 31.4 (C–CH_3).

GC-MS: m/z found 219.02 $[M+H]^+$, calculated 218.17 for $C_{15}H_{22}O$.

Synthesis of Alkynylphenyl-zinc(II) porphyrin **7**:[3]

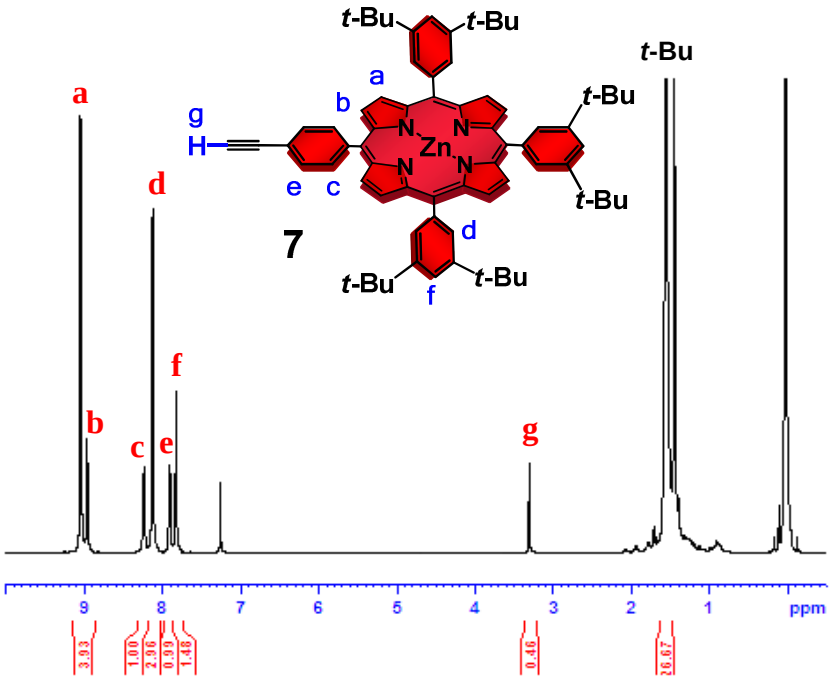


Pyrrole (1.49 g, 1.50 mL, 22.5 mmol), 3,5-di-*tert*-butyl benzaldehyde (3.30 g, 15.0 mmol), tetraphenyl-phosphonium chloride (0,05 g, 0.134 mmol) and 4-((trimethylsilyl)-ethynyl)benzaldehyde (1.01 g, 5.0 mmol), were dissolved in 200 mL of freshly distilled CH_2Cl_2 and stirred under N_2 at rt for 10 min. $BF_3.OEt_2$ (0.5 equiv) was added, the reaction flask covered with aluminium foil and the red solution was stirred at rt for 1 h. DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) (3.5 equiv) was then added and the reaction mixture was stirred for another 12 h. Reduction of the volume to ~100 mL under reduced pressure and filtration through celite eliminated undesirable polymeric materials. The porphyrinic products were first

separated from the byproducts by flash chromatography using hexanes/CH_2Cl_2 (1:1, v/v) as the eluent. Without any workup, the porphyrin mixture was metallated by dissolving the porphyrin mixture in 50 mL of CH_2Cl_2, followed by addition of a MeOH saturated solution of zinc acetate and heating at reflux for 1 h. The mixture was washed with water, dried over Na_2SO_4, filtered through paper and dried under reduced pressure. The crude mixture was then redissolved in 50 mL of THF. Tetrabutylammonium fluoride (TBAF) (0.22 g, 0.81 mmol) was added and the solution was stirred at rt for 30 min. The solvent was evaporated, CH_2Cl_2 (100 mL) was added and the organic layer was washed with water (3 x 100 ml), dried over Na_2SO_4, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO_2) using hexanes/CH_2Cl_2 (90:10, v/v) as the eluent, affording **7** as a purple solid in 9% overall yield.

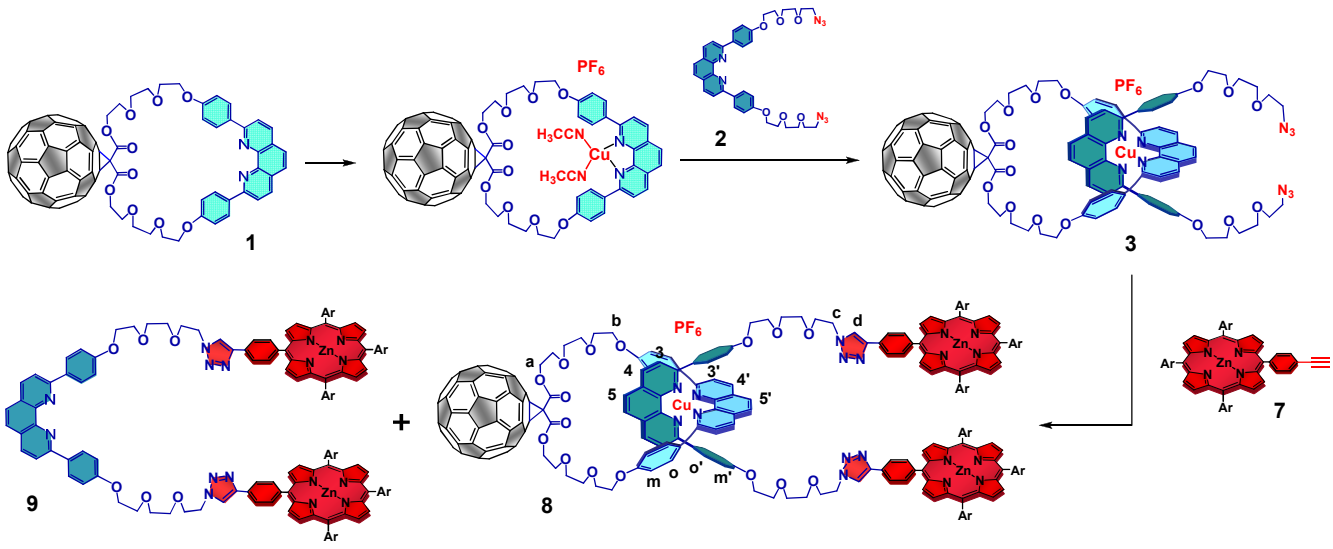
^{1}H NMR ($CDCl_3$), δ ppm: 9.12 (s, 6H, H_a); 8.91 (d, *J* = 8.0 Hz, 2H, H_b); 8.31 (d, *J* = 8.0 Hz, 2H, H_c); 8.15 (s, 6H, H_d of *tert*-butyl aromatic rings); 7.90 (d, *J* = 8.0 Hz, 2H, H_e); 7.81 (s, 3H, H_f); 3.25 (s, 1H, H_g); 1.56 (s, 54H, H_h).

MALDI-TOF: m/z found 1037.01 $[M + H]^+$, calculated, 1036.54 for $C_{70}H_{76}N_4Zn$.



^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$, 300K).

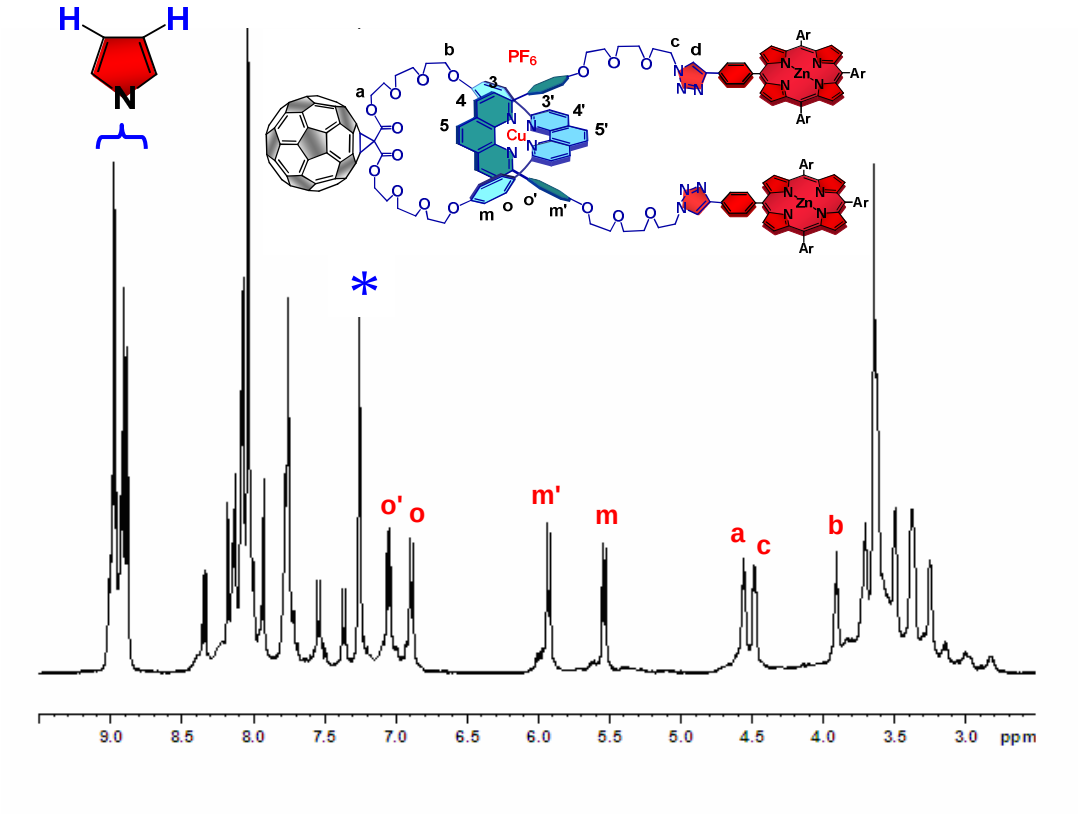
One-Pot Procedure for Preparation of Porphyrin-Stoppered Fullerene Rotaxane **16**:



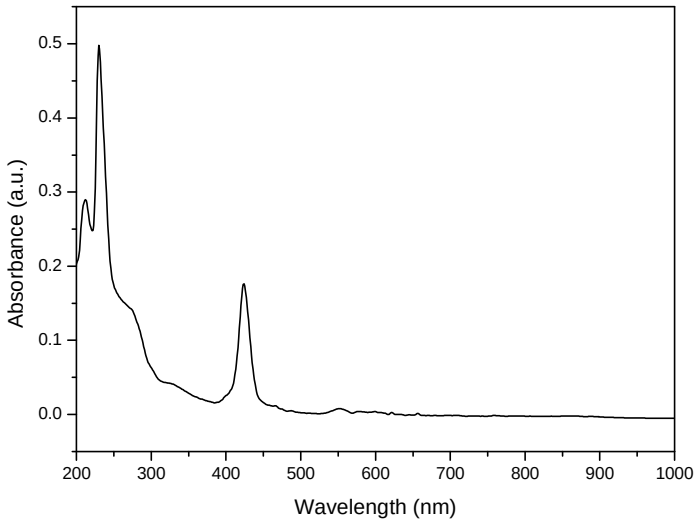
Rotaxane **16** was prepared following the same procedure described for rotaxane **9**. Final purification was achieved by column chromatography (SiO_2), using gradient CH_2Cl_2/CH_3OH (from 0 to 3%, v/v): CH_2Cl_2 eluted the first product, which was identified as unreacted porphyrin (added in slight excess); CH_2Cl_2/CH_3OH (99:1, v/v) eluted the second product (purple solid, 20% yield), identified as the non-interlocked *bis*-porphyrin phenanthroline dumbbell compound (MALDI-TOF *m*/z 2752, $[M + H]^+$. The target rotaxane **16** was then eluted using CH_2Cl_2/CH_3OH (97:3, v/v) and isolated as a purple solid in 70% yield.

^{1}H NMR ($CDCl_3$), δ ppm: 9.10-8.80 (m, 16H, pyrrolic protons) 8.28 (d, *J* = 8.0 Hz, 2H, $H_{4'}$ and $H_{7'}$); 8.20-7.60 (m, 28H, H_4, H_7, $H_{5'}$, $H_{6'}$, H_5, H_6, H_o of ZnP *t*-butyl aromatic ring, H of triazole rings, $H_{o\ and\ m}$ aromatic ring attached to the triazole rings); 7.76 (s, 6H, H_p of ZnP *t*-butyl aromatic rings); 7.55 (d, *J* = 8.0 Hz, 2H, $H_{3'}$ and $H_{8'}$); 7.37 (d, *J* = 8.0 Hz, 2H, H_3 and H_8); 7.06 (d, *J* = 8.0 Hz, 4H, $H_{o'}$); 6.90 (d, *J* = 8.0 Hz, 4H, H_o); 5.94 (d, *J* = 8.0 Hz, 4H, $H_{m'}$); 5.55 (d, *J* = 8.0 Hz, 4H, H_m); 4.56 (s, 4H, H_b); 4.48 (s, 4H, H_c); 4.00-3.00 (m, O–CH_2–CH_2–O).

MALDI-TOF: m/z found 4230.16 $[M - PF_6]^+$, calculated, 4375.28 for $C_{275}H_{230}N_{18}O_{16}Zn_2CuPF_6$.

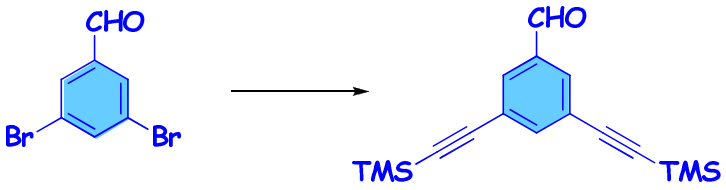


^{1}H NMR spectrum of rotaxane **8** (400 MHz, $CDCl_3$, 300K).



Absorption spectrum of Rotaxane **8** (10^{-7} M in $CHCl_3$)

Synthesis of 3,5-Di-(trimethylsilylethynyl)benzaldehyde:



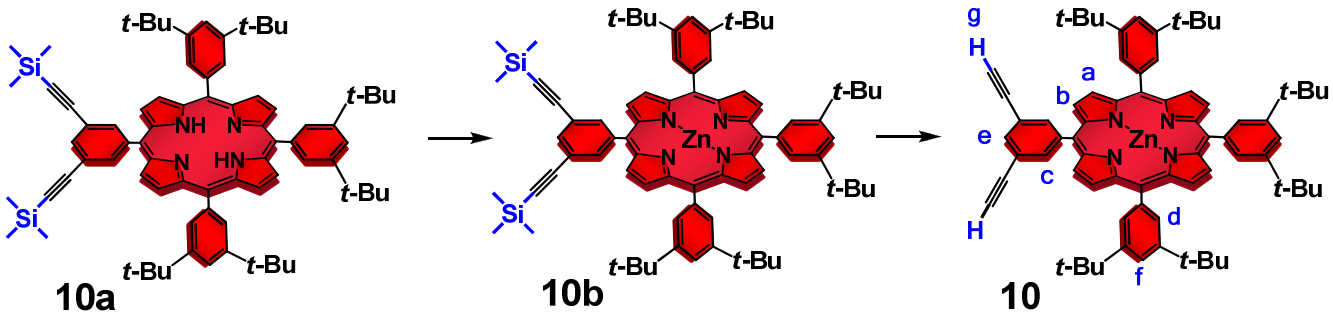
In a round bottomed reaction flask, bis(benzonitrile)-dichloropalladium(II) (0.130 g, 0.325 mmol) and CuI (0.042 g, 0.216 mmol) was dissolved in 11 mL of oxygen-free dioxane under N_2 atmosphere and at rt. A 2.2 mL aliquot of a 0.27 M solution of tri-phenylphosphine in dioxane was then added followed by addition of di-isopropylamine (1.8 mL, 13 mmol), 3,5-di-bromobenzaldehyde (1.42 g, 5.4 mmol) and trimethylsilylacetylene (1.8 mL, 13 mmol). The reaction mixture was stirred under N_2 atmosphere and at rt. After ~30 min the solution became warm and a black precipitate formed, turning the reaction solution nearly solid. The reaction was run for 7 h before being diluted with ethyl acetate and filtered through Celite. The product was purified by flash chromatography (SiO_2) using hexanes as eluent to afford a colorless oil (1.53 g, 95% yield).

^{1}H NMR ($CDCl_3$), δ ppm: 9.74 (s, 1H, C<u>H</u>O); 7.65 (d, *J* = 2.0 Hz, 2H, H_o); 7.56 (m, *J* = 2.0 Hz, 21, H_p); 0.074 (s, 18H, Si(C<u>H</u>$_3$)$_3$.

^{13}C NMR ($CDCl_3$), δ ppm: 191 (<u>C</u>HO); 142 (C_4); 136.3 (C_1); 132.6 (C_2 and C_6); 125.6 (C_3 and C_5); 102.0 (<u>C</u>≡C–Si(CH$_3$)$_3$); 52.4 (C≡<u>C</u>–Si(CH$_3$)$_3$); 3.3 (C≡C–Si(<u>C</u>H$_3$)$_3$).

GC-MS: m/z found 299.0 [M + H]$^+$, calculated 298. 12 for $C_{17}H_2OSi_2$.

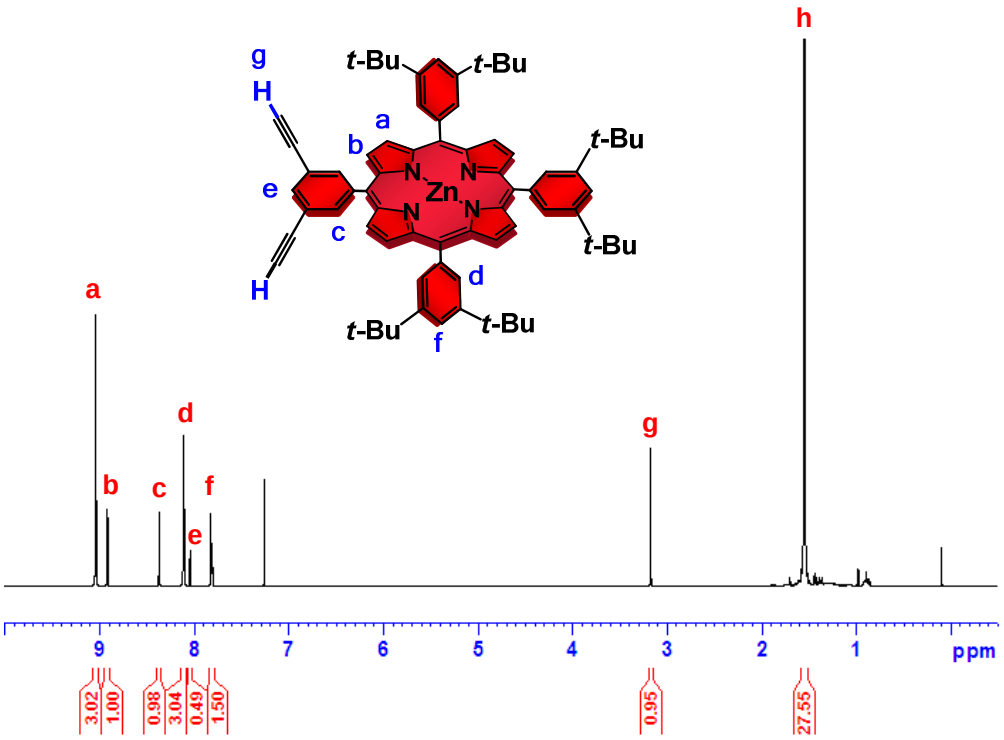
Synthesis of Alkynylphenyl-zinc(II) porphyrin **10**:[3]



ZnP **10** was prepared following the same procedure described for ZnP **7**. Final purification was achieved by column chromatography (SiO_2), using hexanes/CH_2Cl_2 (80:20 v/v) as eluent, affording **10** as a purple solid (0.480g, 9 % yield).

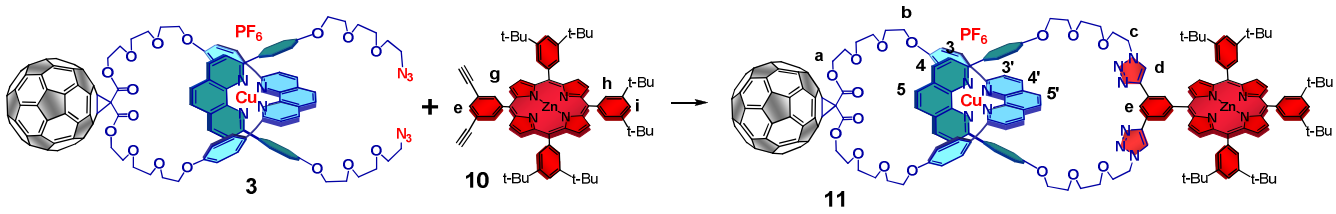
^{1}H NMR ($CDCl_3$), δ ppm: 9.04 (m, 6H, pyrrolic protons); 8.92 (d, 2H, pyrrolic protons); 8.37 (d, 2H, H_o of TMS-alkyne-containing aromatic ring); 8.11 (s, 6H, H_o of *tert*-butyl aromatic rings); 8.04 (s, 1H, H_p of TMS-alkyne-containing aromatic ring); 7.82 (s, 3H, H_p of *tert*-butyl aromatic rings); 3.17 (s, 2H, C≡C<u>H</u>); 1.54 (s, 54H, C<u>H</u>$_3$);

MALDI-TOF: m/z found 1061.53 [M + H]$^+$, calculated 1060.64 for $C_{72}H_{76}N_4Zn$.



^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$, 300K).

One-Pot Procedure for Preparation of Porphyrin-Fullerene-[2]Catenanes **11**:

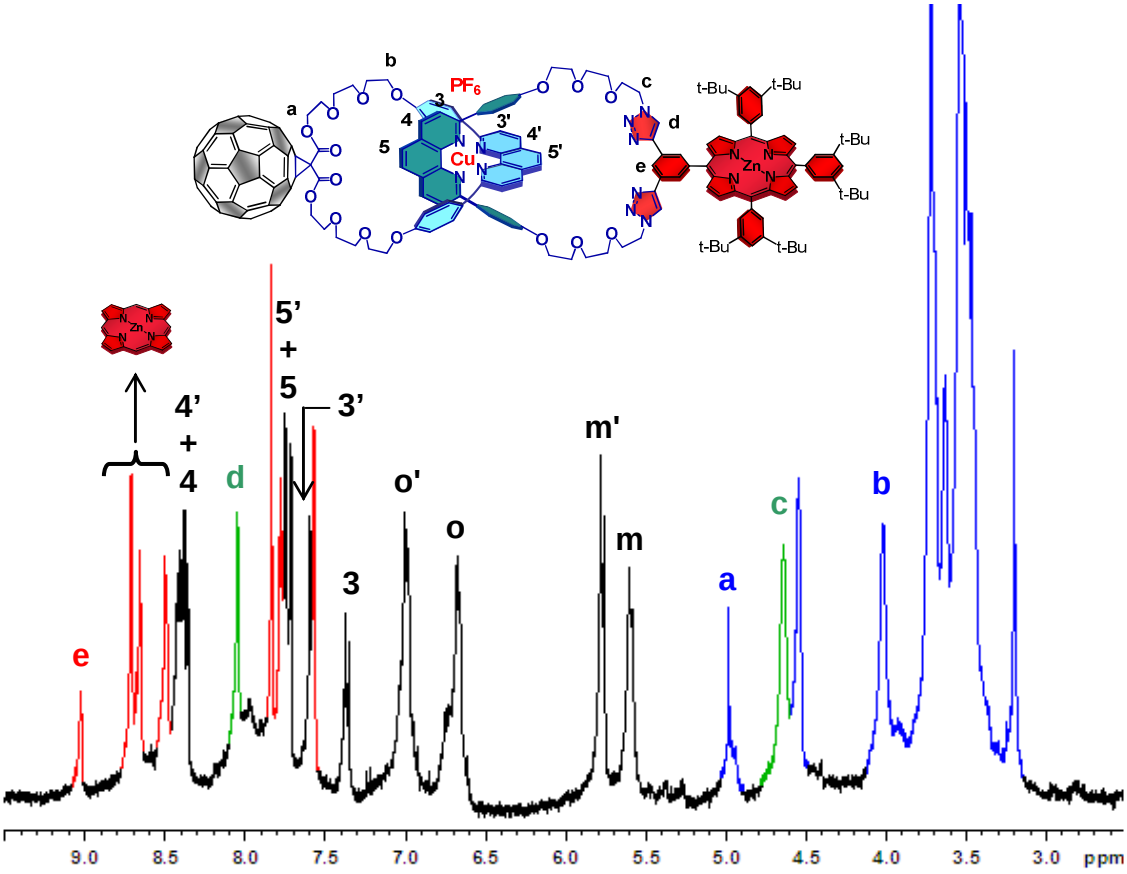


In flask A, macrocycle **1** (0.058 g, 0.041 mmol) was dissolved in 3 mL of degassed CH_2Cl_2/CH_3CN (7:3, v/v) to which $[Cu(CH_3CN)_4][PF_6]$ (0.015 g, 0.041 mmol) was added under N_2 and the solution was stirred at rt for 30 min. The azidophenanthroline ligand **2** (0.028 g, 0.041 mmol) was then added as a solid to flask A and the brown solution was stirred under N_2 at rt for 3 h to generate precursor **3**. Meanwhile, in the reaction flask, CuI (0.016 g, 0.082 mmol), sodium ascorbate (0.066 g, 0.331 mmol) and sulphonated bathophenathroline (0.098 g, 0.165 mmol) were dissolved in 20 mL of degassed H_2O/EtOH (1:1, v/v). The pink suspension was heated at reflux and cooled back to rt. The deep red solution in the flask A containing **3** was then diluted to 10 mL with degassed CH_2Cl_2 and added by syringe to the reaction flask. Finally, porphyrin **10** (0.044 g, 0.041 mmol), dissolved in 3 mL of degassed CH_2Cl_2, and DBU (0.018 g, 0.124 mmol) were added and the resulting purple mixture was stirred under N_2 for 12 h at rt. The crude mixture was neutralized by adding 5 mL of 10% HCl_{aq} solution and extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was washed with water (3 x 100 mL), concentrated to a

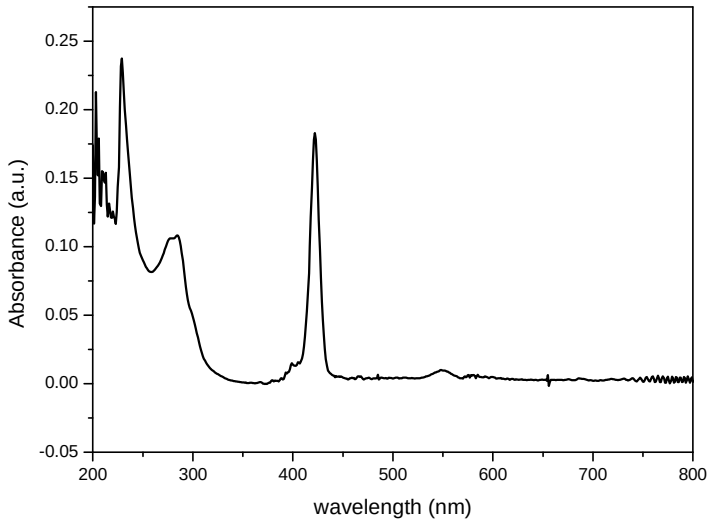
volume of 10 mL and then stirred for 3 h with a saturated MeOH solution of KPF_6 to effect the anion exchange. The solvents were evaporated under reduced pressure, the remaining insoluble purple solid was extracted with CH_2Cl_2 (3 x 100 mL) and filtered through paper. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2) using CH_2Cl_2/CH_3OH (99/1 v/v) as eluent, affording **11** as a purple solid (0.078 g, 57% yield).

^{1}H NMR (CD_3CN), δ ppm: 8.98 (s, 1H, H_p of triazole-containing aromatic ring); 8.77 (d, 4H, pyrrolic protons); 8.69 (d, 2H, pyrrolic protons); 8.57 (d, 2H, pyrrolic protons); 8.45 (dd, 4H, $H_{4'}$, $H_{7'}$, H_4, and H_7); 8.11 (s, 2H, H on triazole rings); 7.85 (s, 6H, H_o of ZnP *tert*-butyl aromatic rings); 7.81 (s, 2H, H_o of triazole-containing aromatic ring); 7.80 (s, 2H, $H_{5'}$ and $H_{6'}$); 7.79 (s, 2H, H_5 and H_6); 7.64 (d, 2H, $H_{3'}$ and $H_{8'}$); 7.63 (s, 3H, H_p of ZnP-*tert*-butyl aromatic rings); 7.36 (d, 2H, H_3 and H_8); 7.07 (d, 4H, $H_{o'}$); 6.74 (d, 4H, H_o); 5.82 (d, 4H, $H_{m'}$); 5.67 (d, 4H, H_m); 5.04 (s, 4H, H_b); 4.69 (s, 4H, CH_2-triazole rings); 4.80-3.00 (m, polyoxo-ethylene linker); 1.54 (s, 54H, CH_3 *t*-butyl groups).

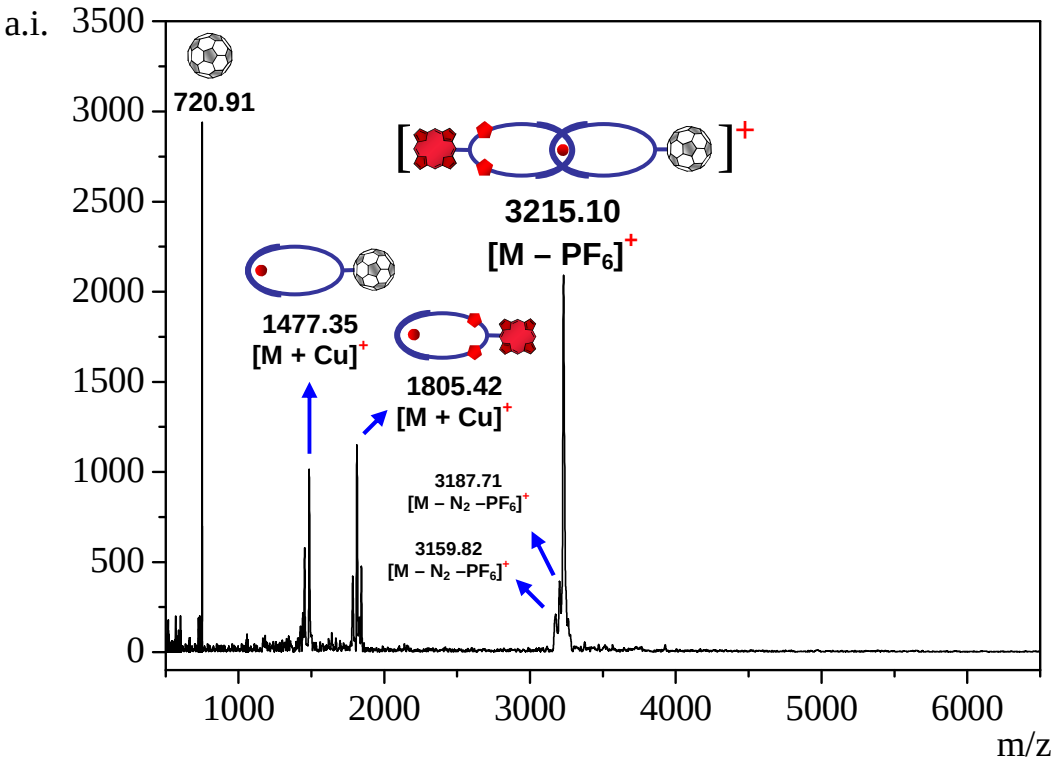
MALDI-TOF: m/z found 3215.12 $[M - PF_6]^+$, calculated, 3215.97 for $C_{207}H_{152}N_{14}O_{16}$ ZnCu.



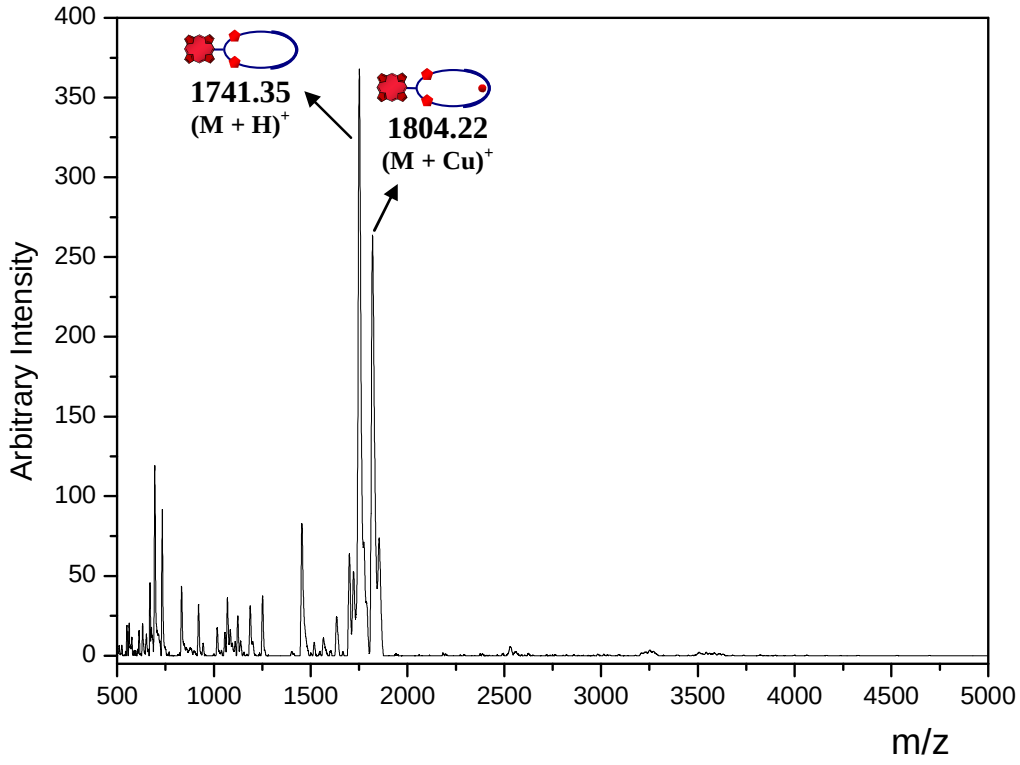
^{1}H NMR spectrum of ZnP-C_{60}-[2]Catenanes **11** (800 MHz, CD_3CN, 300K).



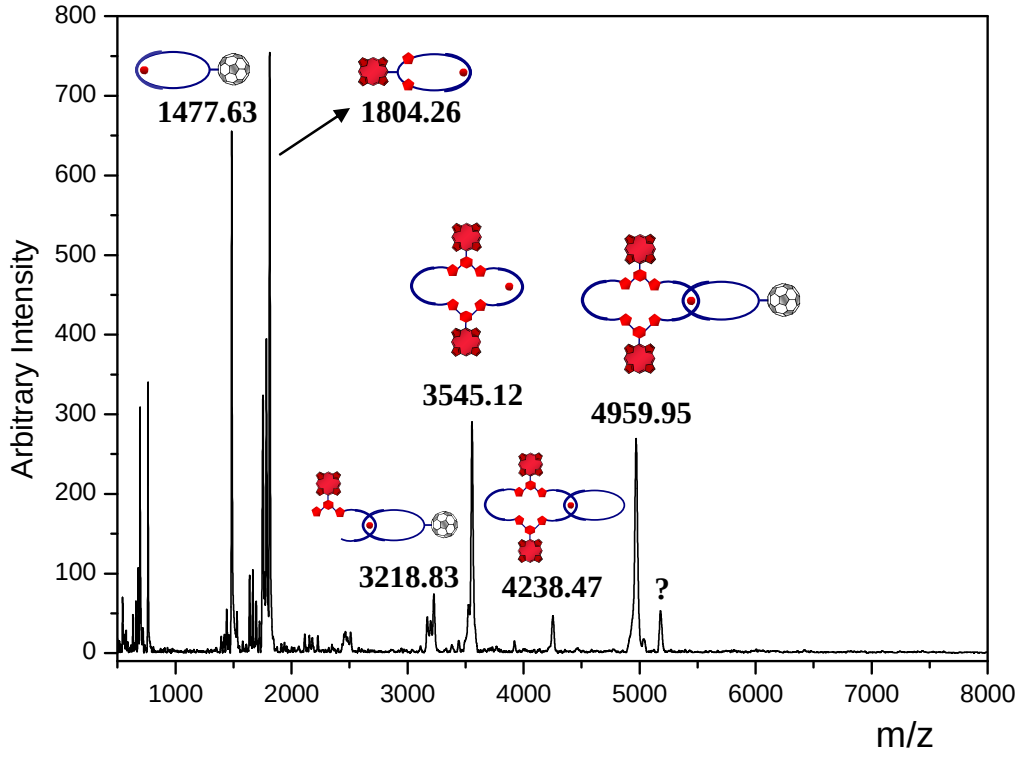
Absorption spectrum of ZnP-C_{60}-[2]Catenanes **11** (10^{-7} M in $CHCl_3$)



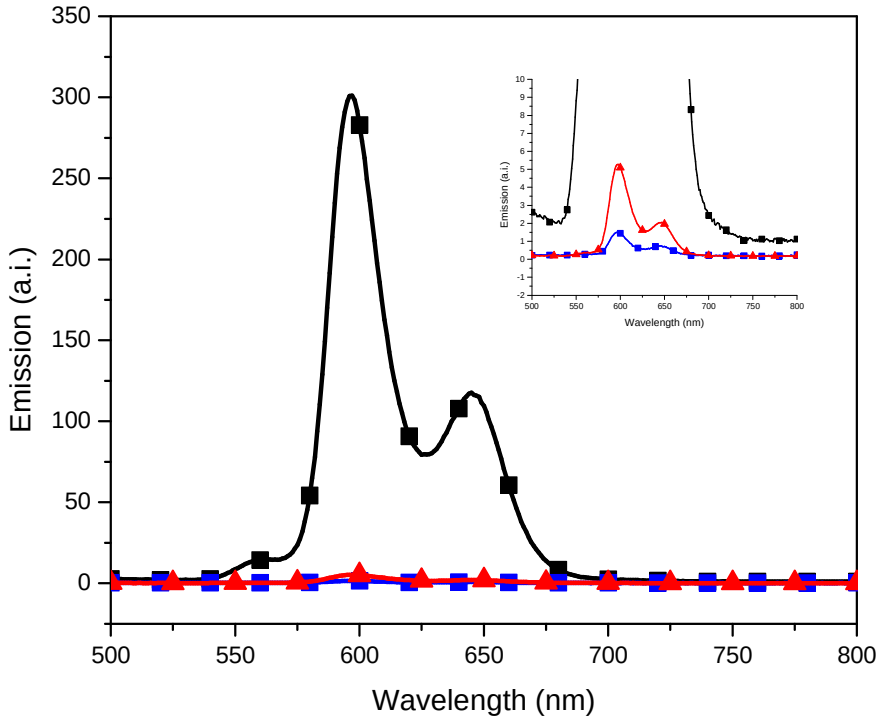
MALDI-TOF mass spectrum of triazole-linked ZnP-C_{60}-[2]catenate **11** (positive mode, α-cyano-4-hydroxycinnamic acid matrix). The absence of peaks between the molecular ion peak and the peaks corresponding to the individual macrocycles is characteristic of catenane structures. Loss of N_2 molecules indicates rupture of the ZnP-macrocycle through the triazole rings.[4-9]



MALDI-TOF spectrum of cyclic byproduct **12** isolated from reaction mixture of ZnP-C_{60}-[2]catenate **11**. Positive mode, universal matrix (DHB/CCA 1:1 mixture).

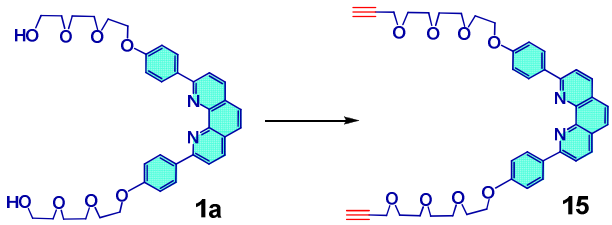


MALDI-TOF spectrum of cyclic byproduct **13** isolated from reaction mixture of ZnP-C_{60}-[2]catenate **11**. Positive mode, universal matrix (DHB/CCA 1:1 mixture).



Fluorescence spectra of alkynyl zinc porphyrin **7** (black), rotaxane **8** (red) and catenate **11** (blue) in dichloromethane with matching absorption (OD =0.20) at the 424 nm excitation wavelength.

Synthesis of di-alkyne phenanthroline derivative **15**:



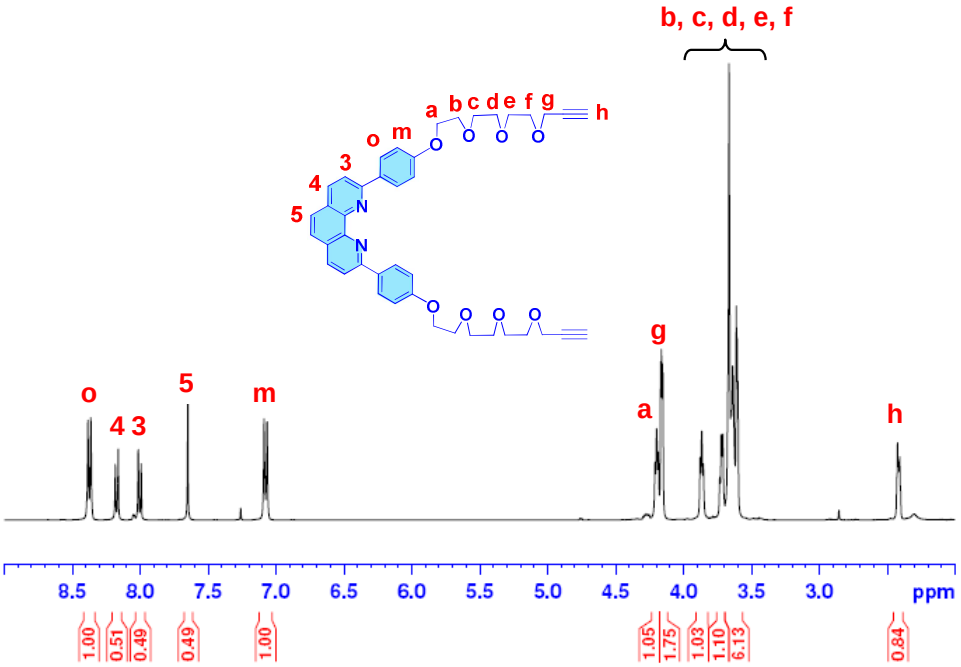
Phenanthroline diol derivative **1a** (4.00 g, 6.380 mmol) and propargyl bromide (15.00 g, 12.740 mmol) were dissolved in 200 mL of dry DMF and stirred for 15 min under argon atmosphere at rt. Sodium hydride (0.450 g, 18.90 mmol) was then added and the reaction mixture was heated to 80 °C. After 4 h, another portion of NaH (0.220 g, 9.450 mmol) and propargyl bromide (7.50 g, 6.370 mmol) were added and the reaction mixture was stirred for an additional 8 h at 80 °C. The reaction was carefully quenched with cold water and concentrated under reduced pressure. CH_2Cl_2 (300 mL) was added and the organic layer was then separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with water (3 x 150 ml), dried over magnesium sulphate, filtered through paper and concentrated. Final

purification was achieved by column chromatography (SiO_2) using CH_2Cl_2/MeOH as the eluent (gradient from 0 to 3%, v/v), affording 3.60 g of **15** as a brown oil. Isolated yield 85%.

^{1}H NMR ($CDCl_3$), δ ppm: 8.34 (d, *J* = 8.8 Hz, 4H, H_o); 8.27 (d, *J* = 8.5 Hz, 2H, H_4 and H_7); 8.11 (d, *J* = 8.5 Hz, 2H, H_3 and H_8); 7.76 (s, 2H, H_5 and H_6); 7.08 (d, *J* = 8.8 Hz, 4H, H_m); 4.20 (t, *J* = 4.9 Hz, 4H, H_a); 4.16 (t, *J* = 4.9 Hz, 4H, H_g); 3.86 (t, 4H, H_f); 3.85-3.55 (m, 16H, H_b, H_c, H_d, H_e); 2.42 (m, 2H, H_h).

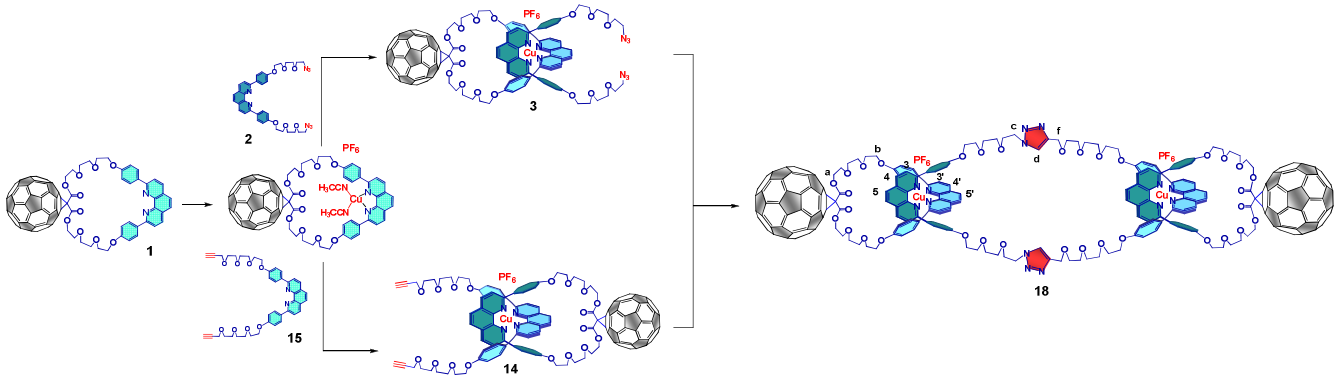
^{13}C NMR ($CDCl_3$), δ ppm: phenanthroline nuclei: 159.5, 156.4, 146.0, 136.9, 132.7, 129.0, 127.6, 125.6, 119.2, 114.8. Polyoxo-ethylene linker: 72.7, 69.7, 69.5, 69.2, 67.6, 66.0. Alkynyl group: 78.2 (CH_2-C≡CH); 76.2 (CH_2-C≡CH); 59.9 (CH_2-C≡CH).

LC-MSD: m/z found 705.40 $[M+H]^+$, calculated, 704.31 for $C_{42}H_{44}N_2O_8$.



^{1}H NMR spectrum of di-alkyne phenanthroline derivative **15** (400 MHz, $CDCl_3$, 300K).

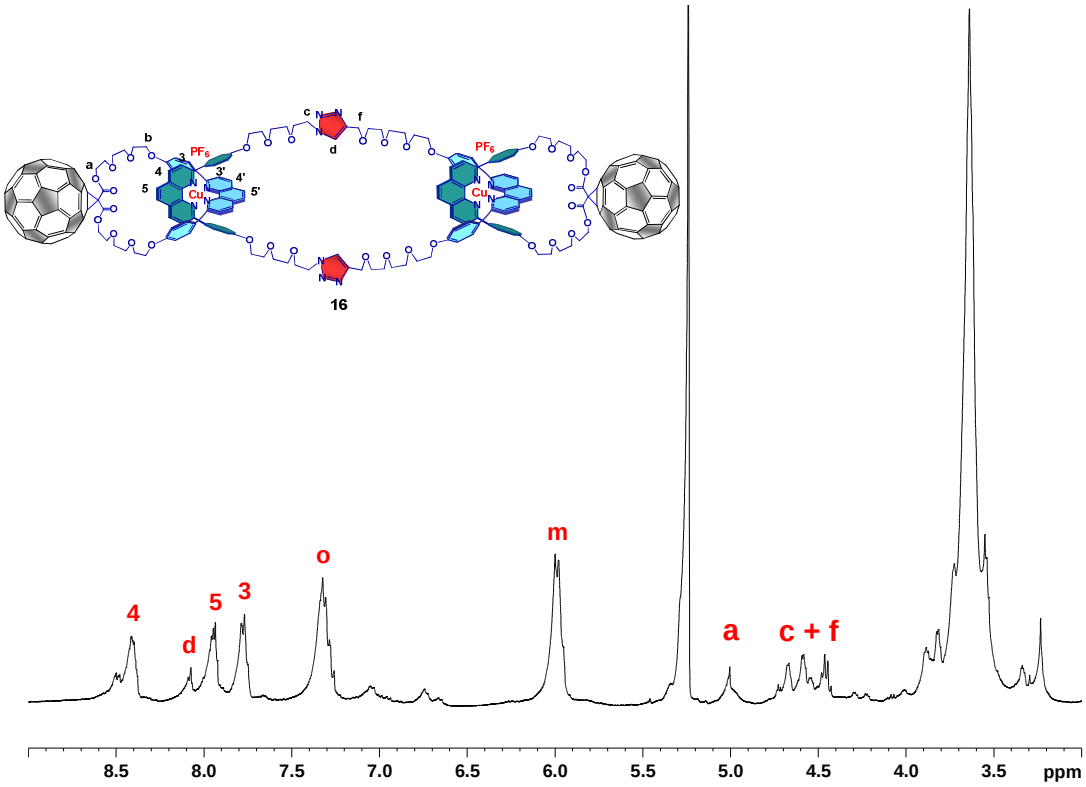
Preparation of *bis*-[60]Fullerene-[3]Catenanes **18**:



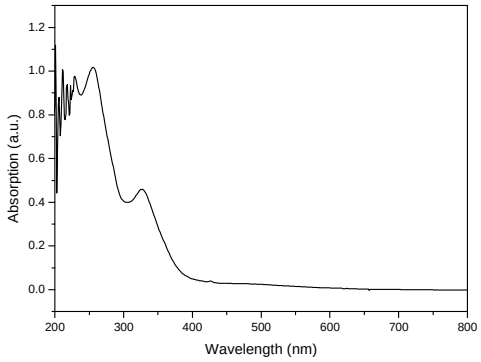
In two separate flasks A and B, macrocycle **1** (0.047 g, 0.0618 mmol) was dissolved in 3 mL of degassed CH_2Cl_2/CH_3CN (7:3, v/v) and $[Cu(CH_3CN)_4][PF_6]$ (0.023 g, 0.0618 mmol) was added under N_2 at rt in both flasks. In flask A, the diazidophenanthroline ligand **2** (0.042 g, 0.0618 mmol) was added, while the dialkyne phenanthroline derivative **15** was added to flask B. Both brown solutions were stirred under N_2 at rt for 3 h. Meanwhile, in the reaction flask, CuI (0.024 g, 0.123 mmol), sodium ascorbate (0.195 g, 0.988 mmol) and sulphonated bathophenanthroline (0.146 g, 0.247 mmol) were dissolved in 20 mL of degassed H_2O/EtOH (1:1, v/v). The pink suspension was heated at reflux for 2 min and cooled back to rt. The deep brown solutions in the flasks A and B were each diluted to 10 mL with degassed CH_2Cl_2 and added by syringe to reaction flask. Finally, DBU (0.146 g, 0.247 mmol) was added and the red mixture was stirred under N_2 for 12 h at rt. The crude mixture was neutralized by adding 5 mL of 10% HCl aqueous solution and extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was washed with water (3 x 100 mL), concentrated to a volume of 10 mL and then stirred for 2 h with a saturated MeOH solution of KPF_6 to effect the anion exchange. The solvents were evaporated under reduced pressure, the remaining insoluble light brown solid was extracted with CH_2Cl_2 (3 x 100 mL) and filtered through paper. The solvent was evaporated under reduced pressure and the crude product was repeated purified by column chromatography (SiO_2) using CH_2Cl_2/CH_3OH (99/1 v/v) as eluent, affording **18** as a brown solid (0.114 g, 40% yield).

^{1}H NMR (CD_2Cl_2), δ ppm: 8.40 (d, 2H, $H_{4'}$ and $H_{7'}$); 8.30 (d, 2H, H_4 and H_7); 7.90 (d, 2H, $H_{5'}$ and $H_{6'}$); 7.80 (d, 2H, H_5 and H_6); 7.85 (d, 2H, H–triazole rings) 7.63 (m, 2H, $H_{3'}$ and $H_{8'}$); 7.54 (d, 2H, H_3 and H_8); 7.26 (d, 4H, $H_{o'}$); 7.12 (d, 4H, $H_{o'}$); 7.00 (d, 4H, H_o); 6.28 (d, 2H, $H_{m'}$); 6.10 (d, 2H, H_m); 4.53 (s, 2H, CH_2-C-triazole rings); 4.49 (s, 2H, CH_2-N-triazole rings); 4.40-3.40 (m, polyoxo-ethylene linkers).

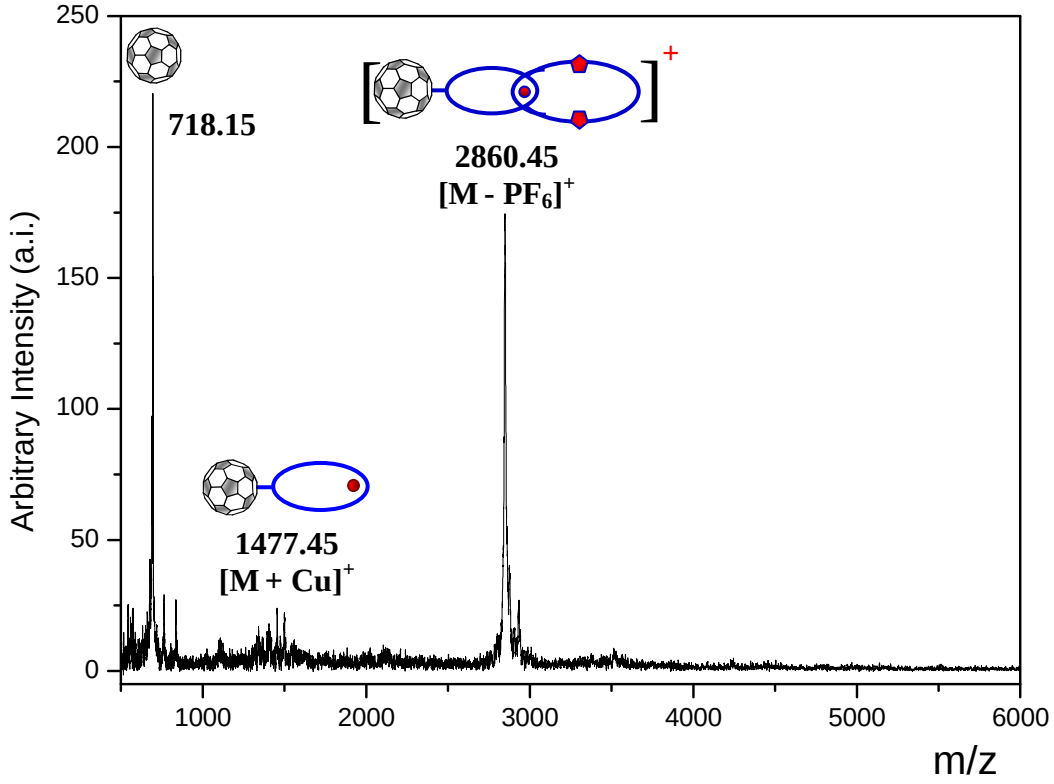
MALDI-TOF: m/z found 2167.90 $[M - 2PF_6]^{2+}$, calculated 4336.50 for $C_{276}H_{158}N_{14}O_{34}Cu_2$.



^{1}H NMR spectrum of *bis*-C_{60}-[3]Catenanes **18** (400 MHz, CD_2Cl_2, 298K).



Absorption spectrum of *bis*-C_{60}-[3]Catenanes **18** (10^{-7} M in $CHCl_3$)



MALDI-TOF spectrum of related-C_{60}-[2]catenates **17** isolated from reaction mixture of *bis*-C_{60}-[3]catenate **18**. Positive mode, α-cyano-4-hydroxycinnamic acid matrix.

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