Supporting Information

Coordination Assisted Reversible Photoswitching of Spiropyran-Based Platinum Macrocycles

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Contents:

Experimental section

Materials and Methods

General methods. Building blocks were synthesized using standard Schlenk technique under N_2 atmosphere. All the starting materials and reagents were purchased from commercially available sources and were used without further purification. *trans*-$Pt(PEt_3)_2I_2$, 2,9-Bis[*trans*-$Pt(PEt_3)_2Br$]phenanthrene[1] and alkyne-spiropyran[2] were prepared according to known procedures. Solvents are distilled and purified according to the standard procedure. NMR spectra were recorded on a Bruker 400 and 500 MHz spectrometer. The chemical shifts (δ) in ^1H NMR spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the NMR solvents: CD_3OD (3.31) or $CDCl_3$ (7.26) or CD_2Cl_2 (5.32). ^{13}C NMR spectra were recorded using the same instrument at 100 MHz and all the chemical shifts (δ) were reported in ppm relative to external $CDCl_3$ at 77.8-77.2 ppm. The ^{31}P NMR spectra were recorded on a Bruker 500 MHz spectrometer at 202 MHz and the chemical shifts (δ) are reported in ppm relative to external 83% H_3PO_4 at 0.0 ppm. Electrospray ionization mass spectra were recorded using Agilent 6538 Ultra-High Definition (UHD) Accurate Mass Q-TOF spectrometer using standard spectroscopic grade solvents. Electronic absorption spectra were recorded on Shimadzu UV-2600 UV−visible spectrophotometer. The photochromic experiments were performed in a custom-made wood box decorated with 8 alternatively positioned 254 and 365 nm UV light source which were fitted vertically and was centered around the position of the cuvette.

Synthesis of 2,9-bis[*trans*-$Pt(PEt_3)_2(NO_3)$]phenanthrene (3):

2,9-bis[*trans*-$Pt(PEt_3)_2Br$]phenanthrene (120 mg, 0.1 mmol) and $AgNO_3$ (170 mg, 1 mmol) were taken in 3 mL of dichloromethane in a 10 mL round bottom flask. The reaction mixture was stirred at room temperature for 24 h under nitrogen atmosphere in dark. An off-white solid was formed, which was filtered off through celite bed, and the solvent was concentrated under reduced pressure. Cold *n*-pentane was slowly added to this solution to afford white precipitate. This precipitate was washed thoroughly with *n*-pentane thrice (3 ×10 mL). The supernatant was decanted, and the solid was dried in vacuo to afford white microcrystalline product (Yield: 86%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.48 (t, 2H), 7.58 (d, 2H), 7.50 (s, 2H), 7.42 (d, 2H), 1.53 (m, 24H), 1.18 (m, 36H) ppm. ^{31}P NMR ($CDCl_3$, 202 MHz): δ = 18.50 ppm (s, $^1J_{P\text{-}Pt}$ = 3565 Hz).

Synthesis of 1:

A 100 mL dry two-neck flask was charged with dibromo-spiropyran (**A**) (0.35 g, 0.8 mmol), pyridine-4-boronic acid (0.3g, 2.4 mmol) and K_2CO_3 (0.55g, 4 mmol). 40 mL dioxane and water (9:1 V/V) mixture was added and heated for 30 minutes at 50° C. $[Pd(PPh_3)_4]$ (0.09 g, 10 mol%) was added to this stirring solution and the reaction mixture was refluxed for 24 hours under N_2 atmosphere. After completion of the reaction the solvent was removed and extracted with chloroform and water. The organic layer was collected and dried over Na_2SO_4. Finally, the compound was purified by preparative TLC with THF/chloroform (15%) as eluent to obtain brown solid product (Yield: 58%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.6 (d, 4H), 7.53-7.49 (m, 3H). 7.45 (d, 4H), 7.38 (s, 2H), 6.97 (d, 1H), 6.84 (d, 1H), 6.63 (d, 1H), 5.78 (d, 1H), 2.81 (s, 3H), 1.39 (s, 3H), 1.23 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=155.7, 151.1, 150.7, 150.5, 149.6, 149.1, 148.1, 138.1, 130.5, 129.9, 129.5, 128.9, 127.5, 125.7, 121.3, 120.7, 120.2, 119.6, 116.6, 116.2, 107.6, 105.3, 52.3, 29.4, 26.4, 20.5 ppm. HRMS (ESI): $C_{29}H_{26}N_3O$, $[M+H]^+$ = 432.2076 (calcd) found: 432.2008(100%).

Synthesis of 2:

An oven-dried 100 mL two-neck round-bottom flask was charged with N,N-bis(4-pyridyl)-4-iodoaniline (**C**) (0.25 g, 0.67 mmol), spiropyranalkyne (0.3 g, 1 mmol), CuI (0.01 g, 5 mol %), and triphenylphosphine (0.02 g, 10 mol %). Freshly distilled triethylamine (40 mL) was added to the mixture, which was heated at 50° C for 15 min. $[Pd(PPh_3)_2Cl_2]$ (0.03 g, 3 mol %) was added to the hot solution and the mixture was heated at reflux for 24 h. After completion of the reaction (as monitored by TLC), the solvent was removed, and the compound was purified by preparative TLC with MeOH/ethyl acetate (10%) as eluent (Yield: 62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.44 (d, 4H), 7.52 (d, 2H). 7.25 (m, 2H), 7.20 (d, 1H), 7.13 (m, 2H), 7.08 (d, 1H), 6.97 (d, 4H), 6.86 (m, 2H), 6.69 (d, 1H), 6.54 (d, 1H), 5.73 (d, 1H), 2.73 (s, 3H), 1.30 (s, 3H), 1.17 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=155.4, 152.5, 151.4, 148.5, 143.9, 137.0, 133.7, 130.5, 129.2, 127.5, 122.6, 121.9, 120.8, 119.7, 119.4, 117.2, 115.8, 114.7, 107.3, 105.3, 91.1, 87.3, 52.4, 29.4, 26.3, 20.5 ppm. HRMS (ESI): $C_{37}H_{30}N_4O$, $[M+H]^+$ = 547.2497 (calcd) found: 547.1571 (100%).

Synthesis of 5:

An equimolar mixture of acceptor **3** (7 mg, 0.06 mmol) and newly prepared photochromic donor **1** (2.6 mg, 0.06 mmol) was dissolved in dry dichloromethane (3 mL) and stirred for 15 min. The reaction mixture was heated to reflux for another 12 h. The solvent was concentrated under vacuum and diethylether was added to afford solid product which was subjected to wash with ample amount of cold diethyl ether. Finally, the residual solid was dried to afford the desired final product **5** (Isolated yield: 75 %). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 9.03(br m, 2H), 8.70-

8.56 (m, 4H), 8.08 (s, 1H), 7.90 (s, 2H), 7.80 (d, 2H), 7.65-7.58 (m, 9H), 7.16 (d, 1H), 6.91 (d, 1H), 6.75 (d, 1H), 5.87 (d, 1H), 2.89 (s, 3H), 1.39 (br, 27H), 1.17-1.15 (m, 39H) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2): δ = 12.93 ppm. ($^{1}J_{P\text{-}Pt}$ = 3275 Hz); ESI-MS (m/z) = 1531.8307 [M-$2NO_3$]$^{2+}$, 1000.9058 [M-$3NO_3$]$^{3+}$, 734.9351 [M-$4NO_3$]$^{4+}$.

Synthesis of 6:

Donor **2** (0.005 mmol, 2.25 mg) was treated with 2,9-bis[*trans*-Pt$(PEt_3)_2NO_3$]phenanthrene (0.005 mmol, 5.9 mg) (**3**) in freshly distilled 1 mL dichloromethane. The resulting solution was stirred at 40°C for twelve hours. Within 10 minutes the solution changed its color to light violet. The solution was concentrated under vacuum and cold diethyl ether was slowly added to the solution to get off-white solid precipitate. The precipitate was washed three times with diethyl ether (3 × 10 mL). The supernatant liquid was decanted and the solid was dried in vacuo (yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, 2H), 8.66 (s, 2H), 8.31 – 8.27 (m, 4H), 7.77 (d, 2H), 7.58 – 7.53 (m, 8H), 7.31 (t, 2H), 7.21 – 7.19 (m, 1H), 7.09 (d, 1H), 6.90 – 6.84 (m, 4H), 6.71 (d, 1H), 6.55 (d, 1H), 5.75 (d, 1H), 2.75 (s, 3H), 1.44 – 1.37 (m, 24H), 1.32 (s, 3H), 1.22 – 1.14 (m, 39H) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, 295K, $CDCl_3$):13.83 ppm ($^{1}J_{P\text{-}Pt}$ = 3300 Hz). HRMS (ESI): m/z 1647.68, 1077.78 and 792.82 corresponding to [M – $2NO_3^-$]$^{2+}$, [M – $3NO_3^-$]$^{3+}$ and [M – $4NO_3^-$]$^{4+}$, respectively.

Synthesis of 7:

Donor **2** (0.01 mmol, 5.5 mg) and *cis*-(N,N,N',N'-tetramethylethane-1,2-diamine)Pt$(NO_3)_2$ (**4**) (0.01 mmol, 4.4 mg) were added to a mixture (1:1) of 1 mL acetone and methanol solution. Then the resulting pink solution was stirred at 50°C for twelve hours. After cooling the solution, it was concentrated, and cold diethyl ether was added to get light pink precipitate. The solid was washed multiple times with diethyl ether and dried (yield = 75%). ^{1}H NMR (400 MHz, $CDCl_3$: CD_3OD): δ = 8.95 – 8.76 (d, 4H), 7.58 – 7.52 (m, 3H), 7.19 – 7.17 (m, 3H), 7.11 – 7.07 (m, 5H), 6.98 (d, 1H), 6.77 (d, 2H), 6.59 (d, 1H), 6.45 (d, 1H), 5.65 (d, 1H), 2.93 (s, 4H), 2.79 – 2.72 (m, 12H), 2.64 (s, 3H), 1.20 (s, 3H), 1.08 (s, 3H) ppm. HRMS (ESI): m/z 592.57 and 1901.64 corresponded to [M − $3NO_3^-$]$^{3+}$ and [M − NO_3^-]$^{+}$, respectively.

Synthesis of 8:

A 100 mL round bottom flask was charged with **2** (0.1g, 0.18 mmol) and iodomethane (0.255g, 1.8 mmol) in acetonitrile. This mixture was heated to 60˚ C and kept for overnight. The solution turned yellow. After completion of the reaction, the solvent was concentrated, and cold diethyl ether was added to afford greenish yellow precipitate. It was washed three times with diethyl ether (10 mL) and finally dried to afford greenish yellow solid (0.1g, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.90 (d, 4H), 7.72 (d, 4H). 7.60 (d, 2H), 7.42 (d, 1H), 7.28-24 (m, 2H), 7.17 (t, 1H), 7.02 (d, 1H), 6.66 (m, 2H), 6.51 (d, 1H), 6.49 (d, 1H), 5.71 (d, 1H), 4.45 (s, 6H), 2.69 (s,

3H), 1.26 (s, 3H), 1.13 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =156.0, 155.7, 148.5, 147.2, 139.9, 136.9, 134.6, 133.9, 130.8, 129.2, 128.1, 125.9, 121.9, 120.8, 119.8, 119.6, 115.9, 114.0, 107.3, 105.4, 93.1, 87.0, 52.4, 49.0, 29.4, 26.3, 20.5 ppm. ESI-MS (m/z) = 703.1913 $[M-I]^+$ (calcd = 703.1900), 288.1395 $[M-2I]^{2+}$ (calcd = 288.1400).

Sample preparation for solution-state UV−Vis spectroscopy:

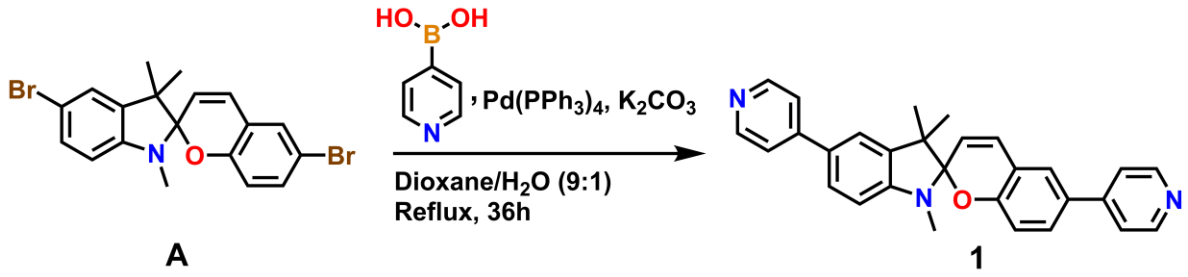
For the photochromic experiments, all the samples were prepared using spectroscopy grade DMSO as solvent and the concentration was maintained at 10^{-5}M. In a typical stock solution preparation, 1.6 mg **5** (1.7 mg for **6**, 0.98 mg for **7**, 0.43 mg for **1** and 0.54 mg for **2**) was added to a 5 mL of DMSO and stirred for a few minutes to obtain a clear solution (10^{-4} M for macrocycles and 2×10^{-4} M for donors in close form) at room temperature. In a quartz cuvette, 1800 μL of DMSO and 200 μL of stock solution of macrocycles were added to get 2 mL of 10^{-5} M solution. In separate 4 mL glass vial, 250 μL 16(N) HNO_3 and NEt_3 were added to which 1750 μL DMSO was added to prepare 2(N) acid and base solutions. During experiments, the samples (2 mL) were placed in an all transparent quartz cuvette and the cuvette was positioned into the sample chamber of the custom-made box decorated with 8 UV light source of 365 nm wavelength. For studying reversibility in photochromism, the sample was repeatedly exposed to the UV chamber and normal light source and their absorption spectra were recorded each time to verify the interconversion. For acid-base experiment, dilute nitric acid was chosen as the sample already contains nitrate counter ions and dilute triethylamine solution was used as the base. Addition of an equivalent amount of acid arrests the ring-opened form by protonation and the addition of base again deprotonates the ring to facilitate faster cyclisation.

Optimization methods:

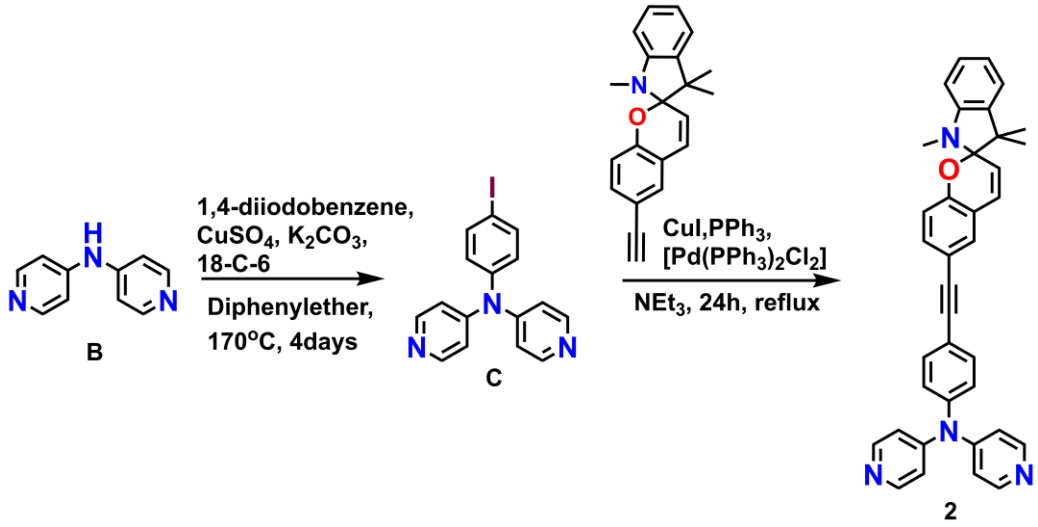
All the theoretical calculations were performed using Gaussian 09[3] package. The **5**, **6** and **7** were optimized using PM6 semi-empirical method. In all other calculations, the hybrid B3LYP functional has been used. The 6-31G basis set was used for all calculations. But for Pt centre the basis set was changed to LANL2DZ[4]. No symmetry constraints were used during the optimization procedure.

1. Synthesis and characterization of ligands and macrocycles:

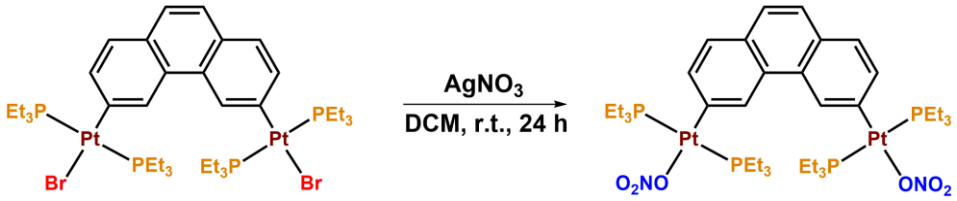
1.1 Synthesis and characterization of the ligands:



Scheme S1: Synthetic routes for the preparation of the donor **1.**



Scheme S2: Synthetic routes for the preparation of the donor **2.**



Scheme S3: Synthesis of the acceptor **3.**

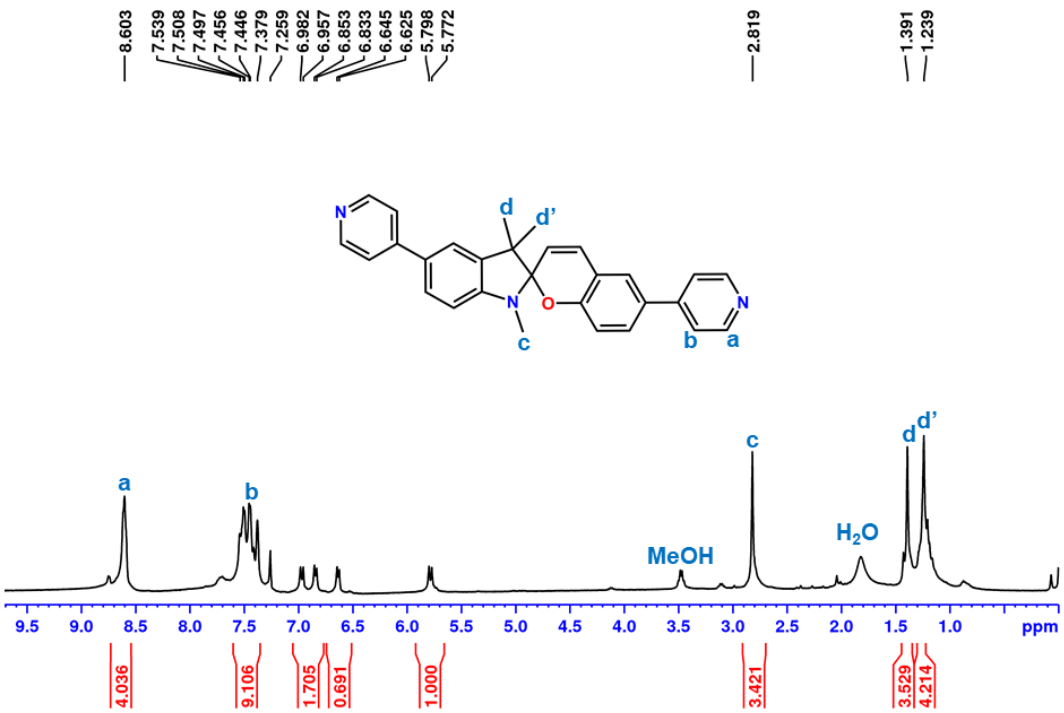


Figure S1. [1] H-NMR spectrum of donor **1** in $CDCl_3$.

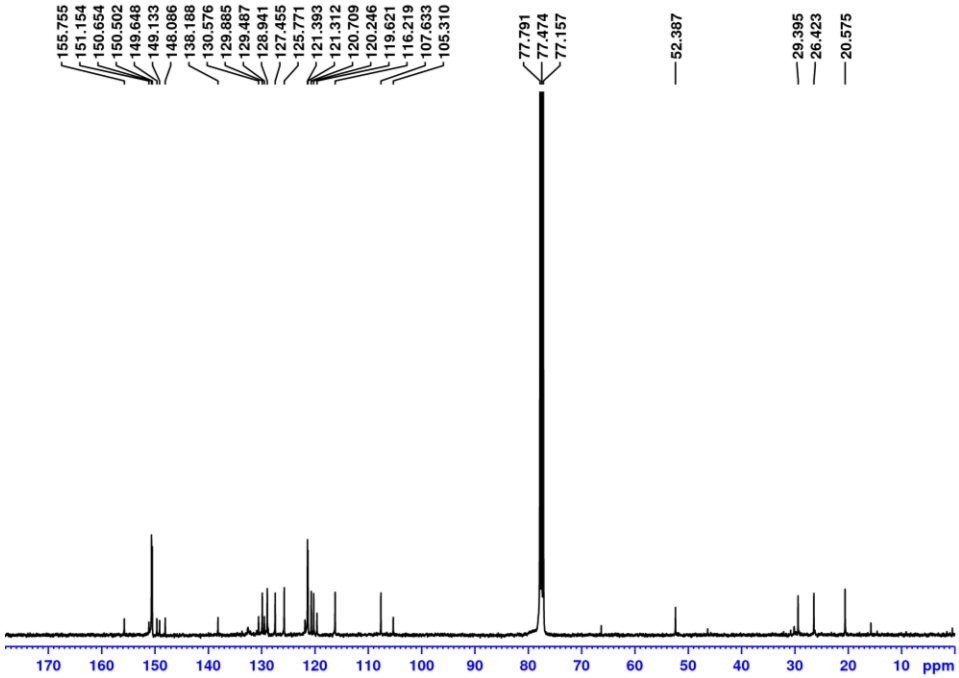


Figure S2. [13] C-NMR spectrum of donor **1** in $CDCl_3$.

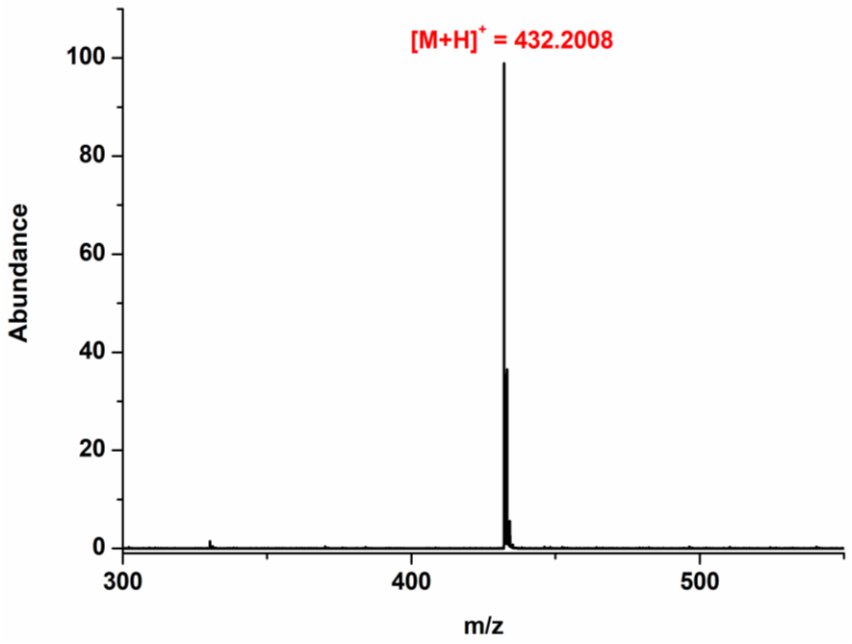


Figure S3: Mass spectrum of compound **1**.

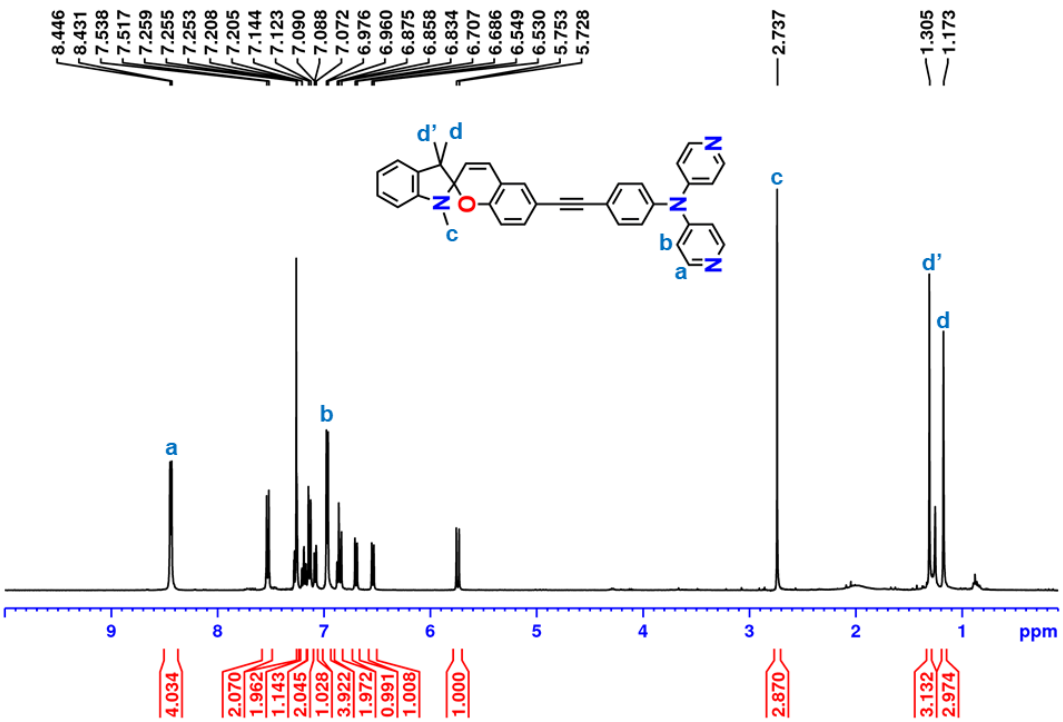


Figure S4. [1] H-NMR spectrum of the donor **2** in $CDCl_3$.

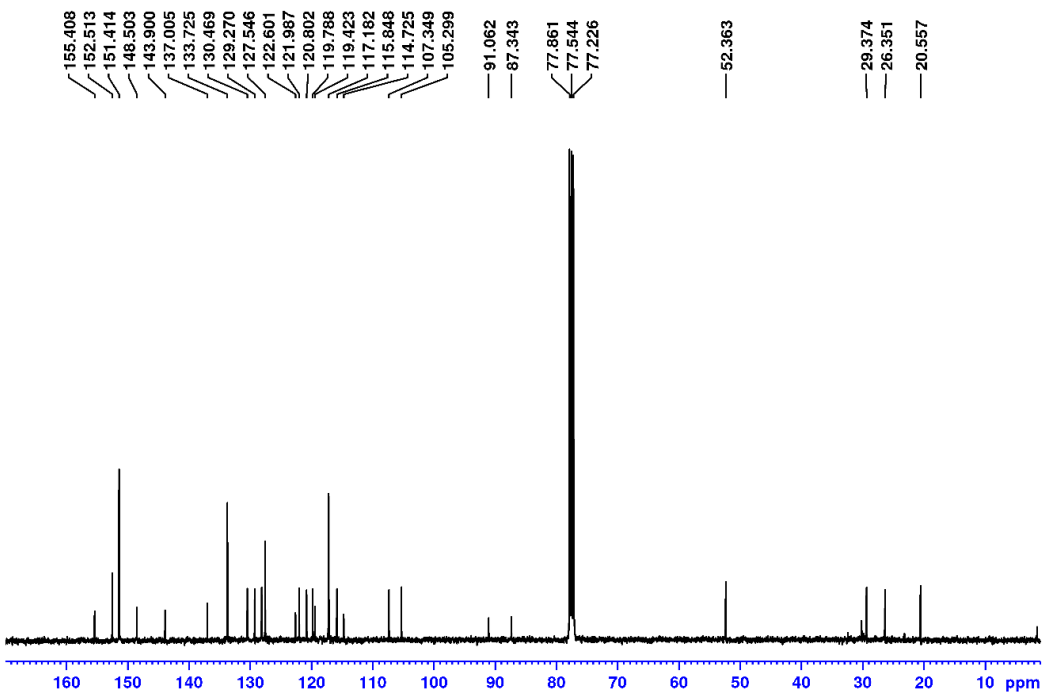


Figure S5. ^{13}C-NMR spectrum of donor **2** in $CDCl_3$.

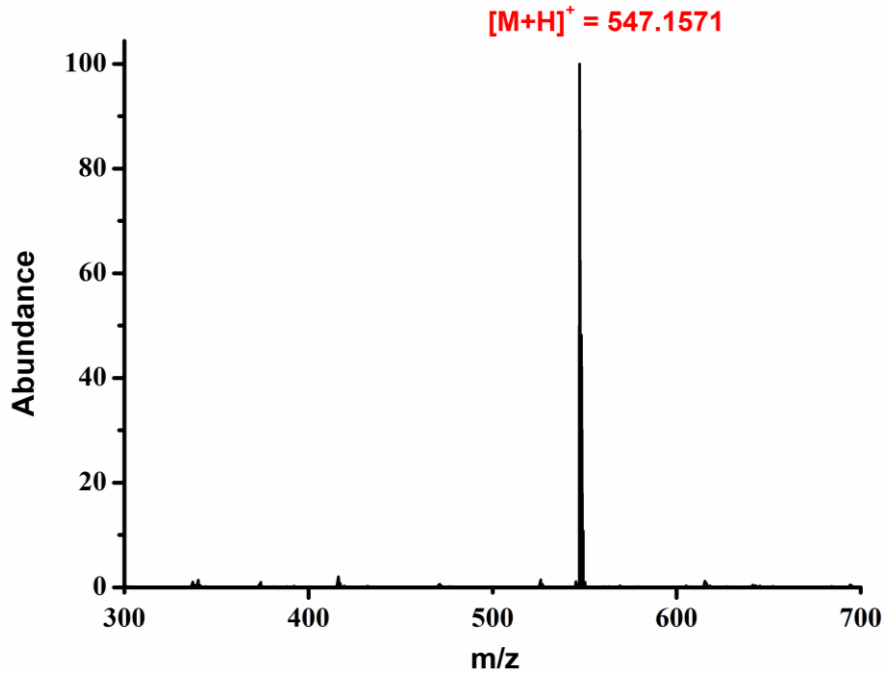


Figure S6: Mass spectrum of compound **2**.

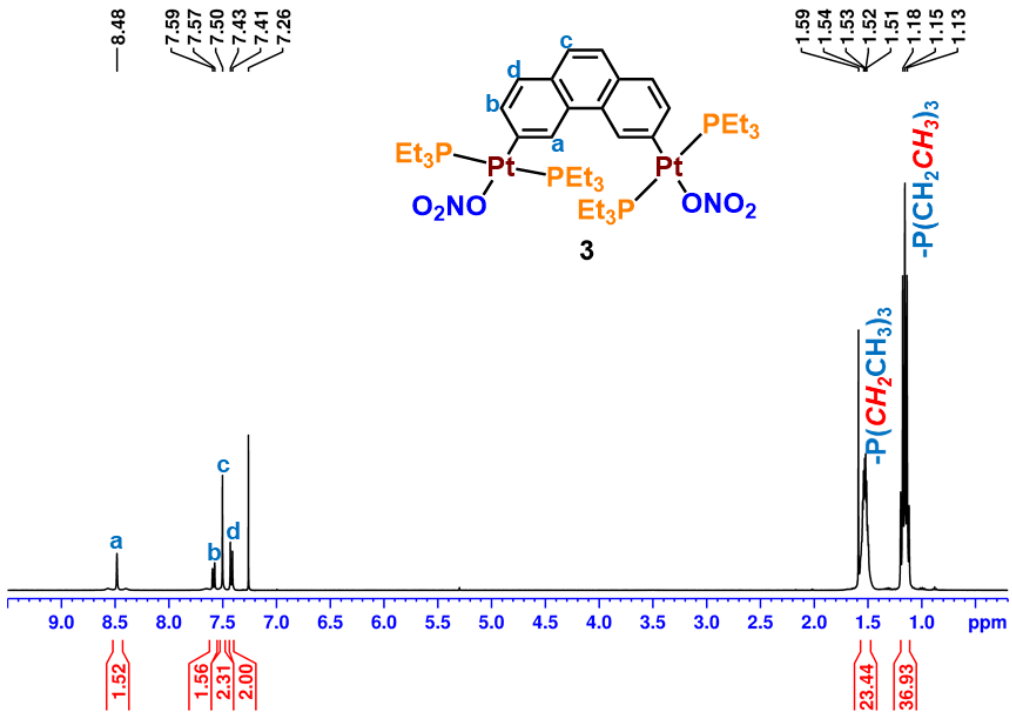


Figure S7. [1] H-NMR spectrum of acceptor **3** in $CDCl_3$.

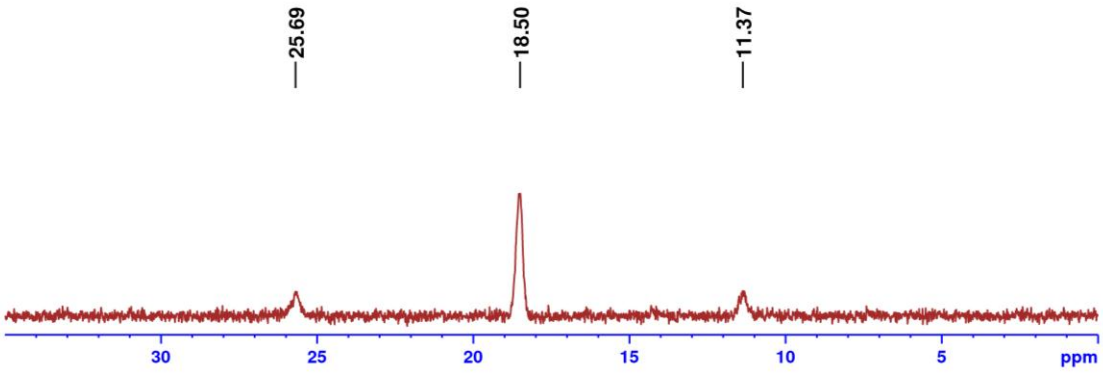
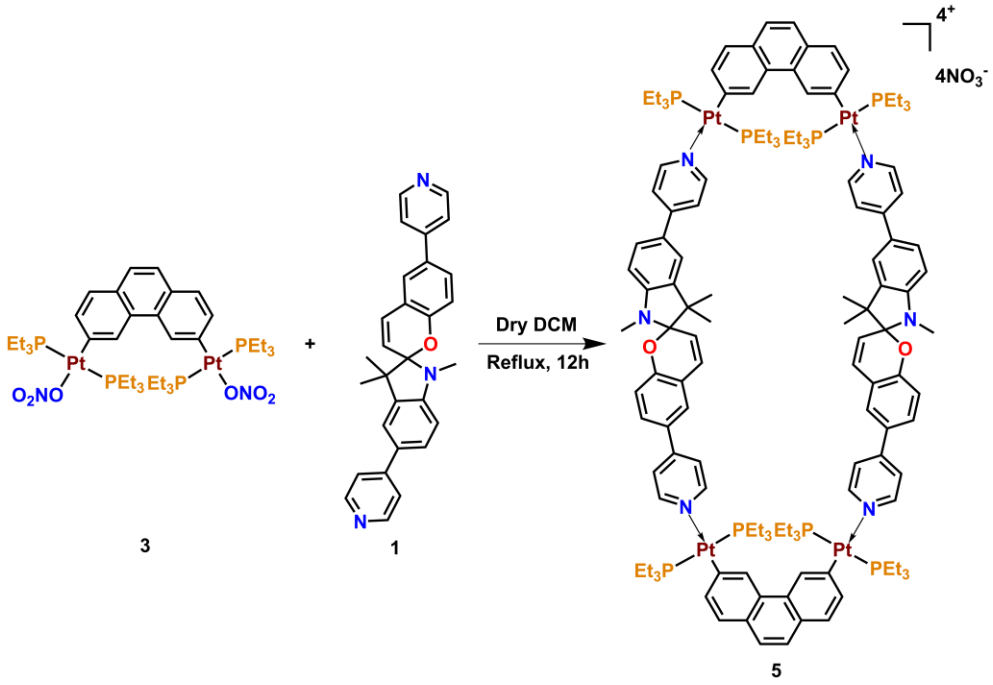


Figure S8. [31] P-NMR spectra of acceptor **3** in $CDCl_3$.

1.2 Self-assembly of 5:



Scheme S4: Synthetic scheme for **5.**

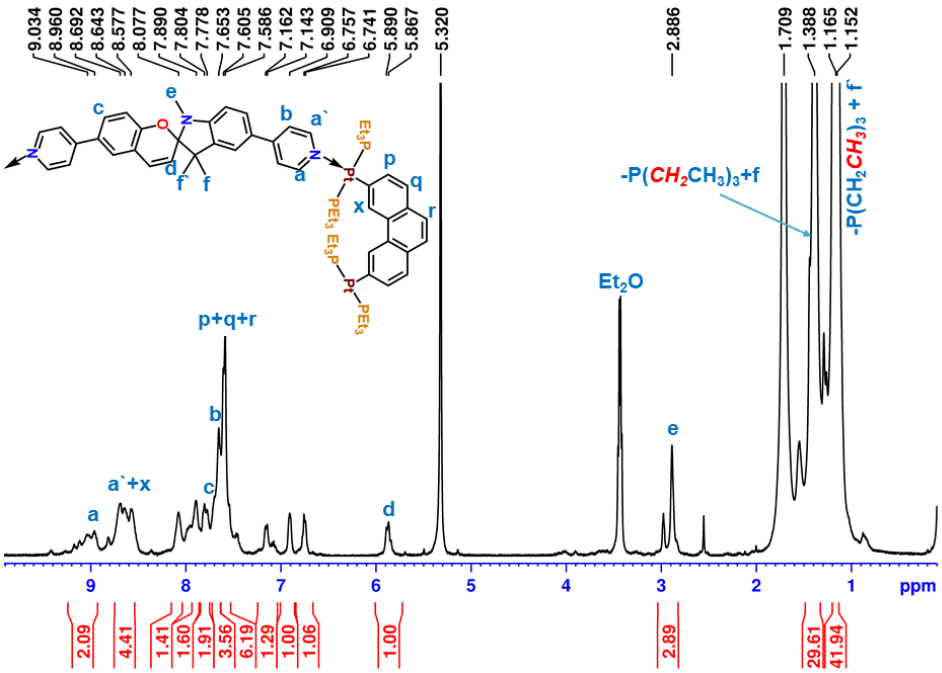


Figure S9. [1] H-NMR spectrum of macrocycle **5** in CD_2Cl_2 at 298 K.

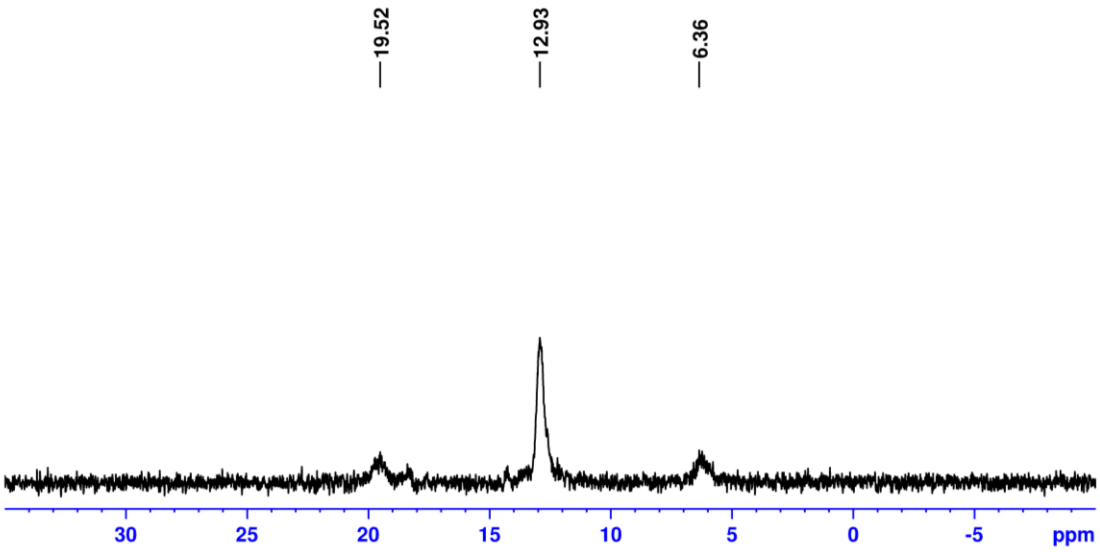


Figure S10: ^{31}P NMR spectrum of **5** (CD_2Cl_2, 298 K).

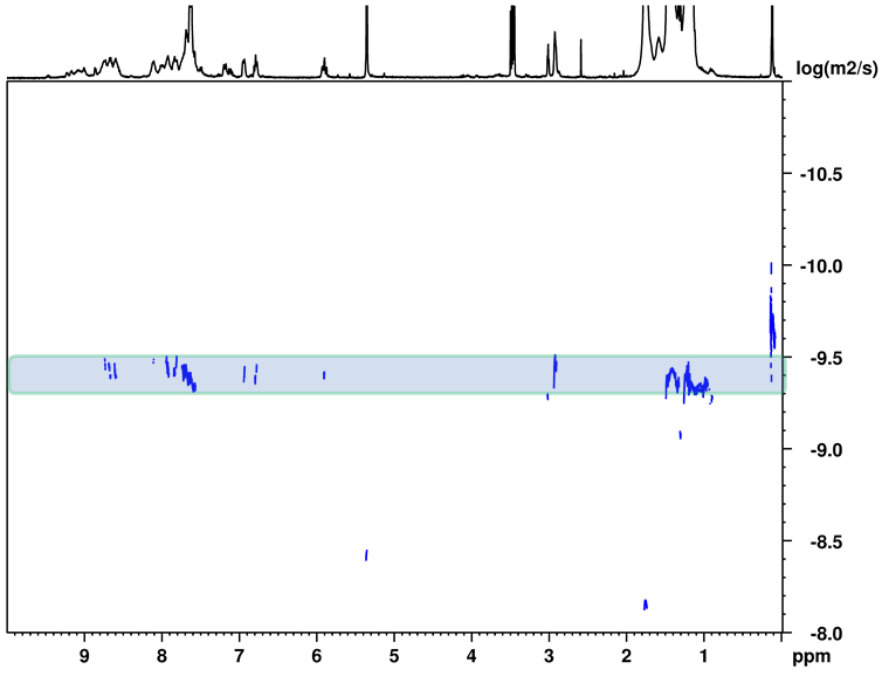
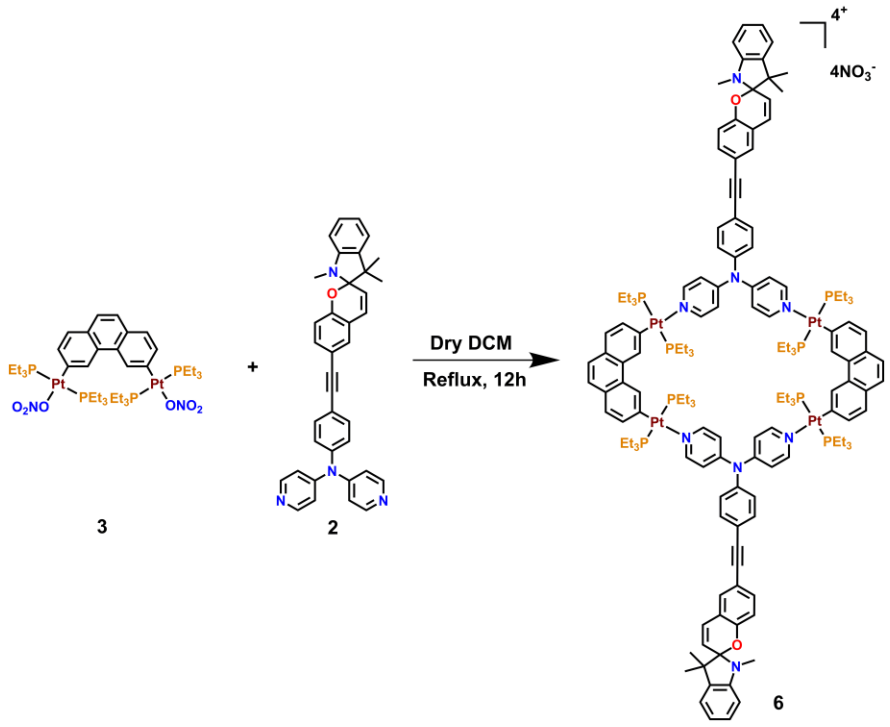


Figure S11: 2D ^{1}H -DOSY spectrum of **5** (CD_2Cl_2 at 298 K).

1.3 Self-assembly of 6:



Scheme S5: Schematic presentation of the synthesis of **6.**

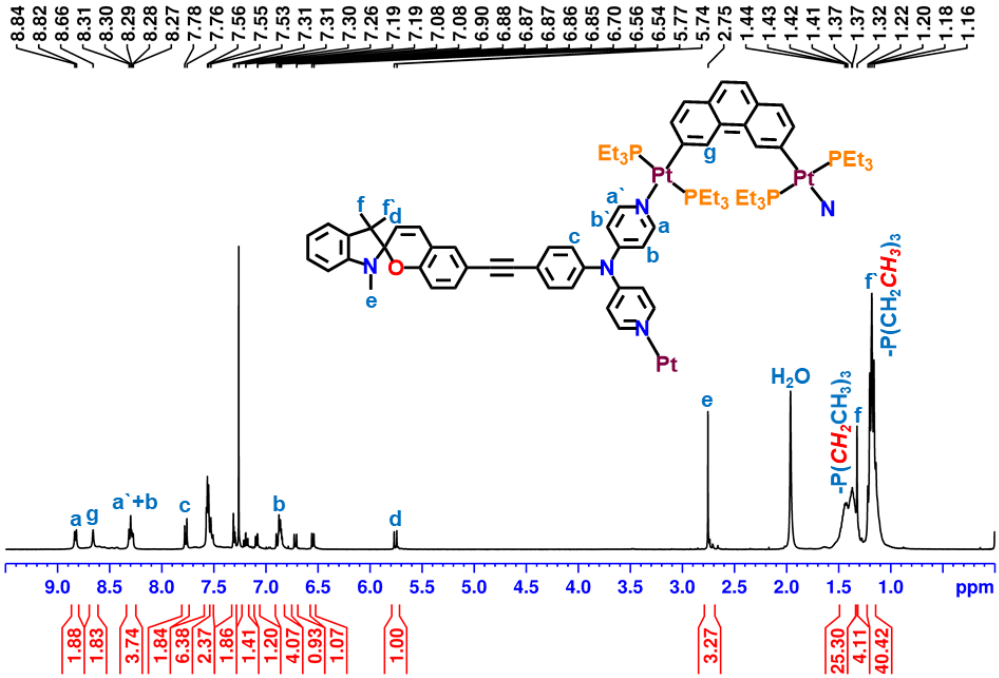


Figure S12. [1] H-NMR spectrum of macrocycle **6** in $CDCl_3$ at 298 K.

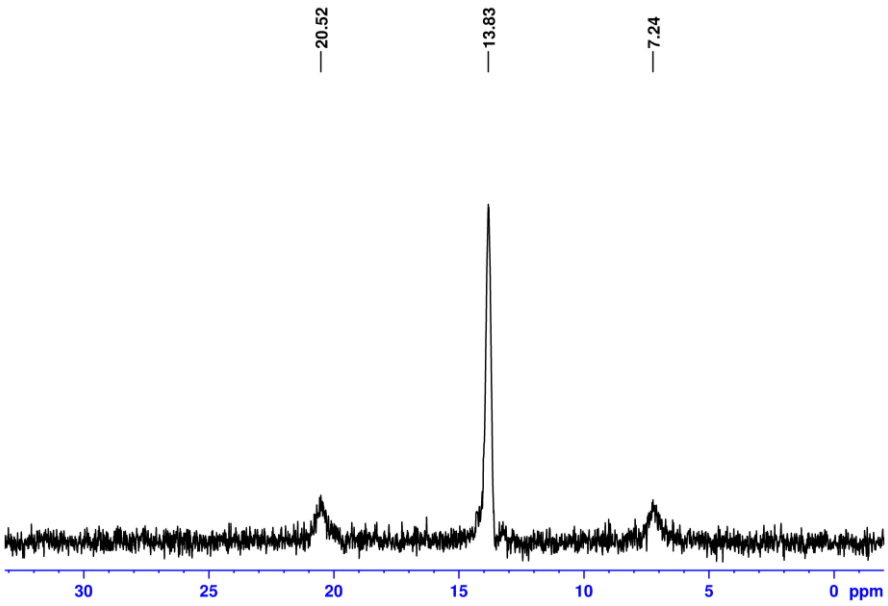


Figure S13: ^{31}P NMR spectrum of **6** ($CDCl_3$, 298 K).

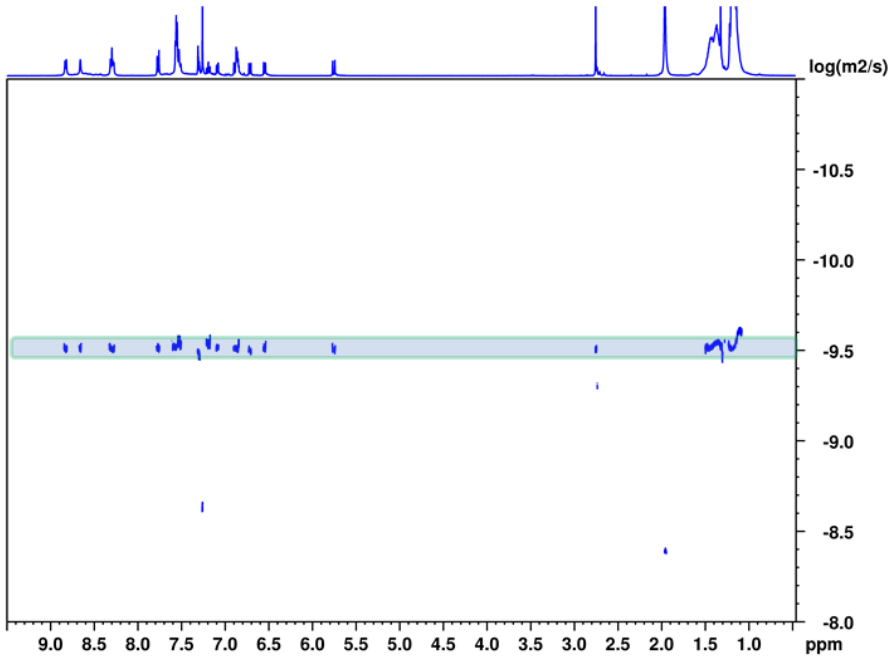
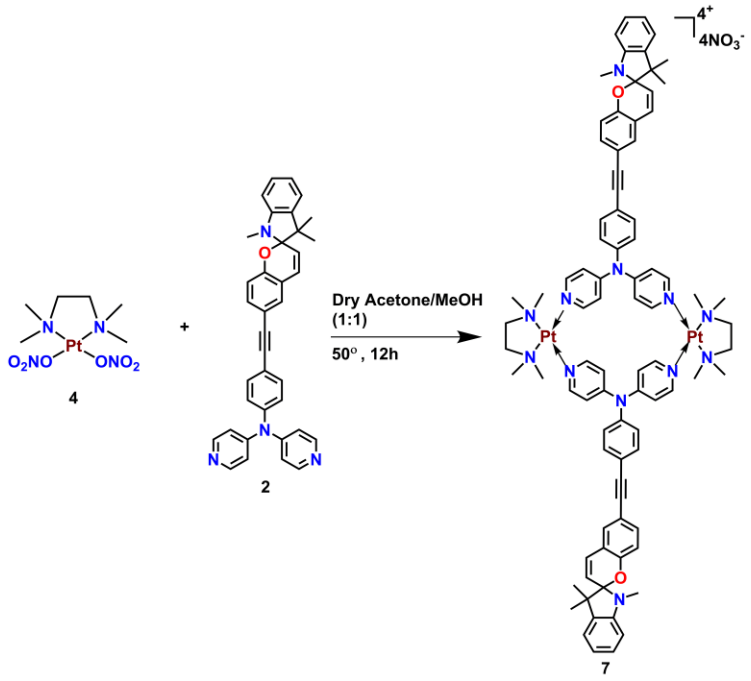


Figure S14: 2D ^{1}H-DOSY spectrum of **6** ($CDCl_3$ at 298 K).

1.4 Self-assembly of 7:



Scheme S6: Synthetic scheme for **7.**

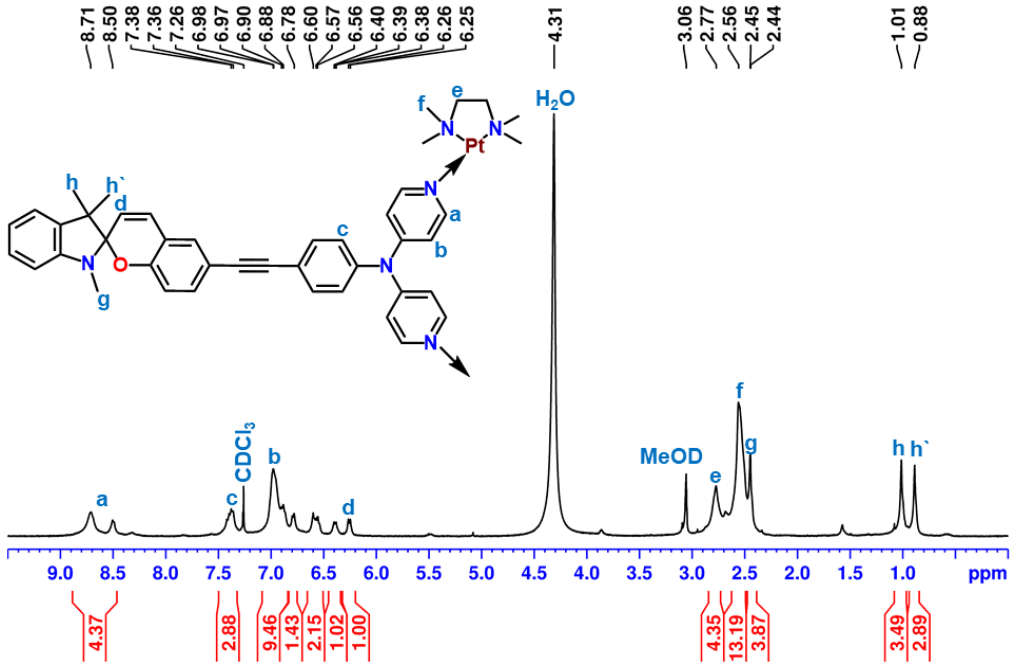


Figure S15. [1] H-NMR spectrum of macrocycle **7** in $CDCl_3$ + MeOD (1:1) at 298 K.

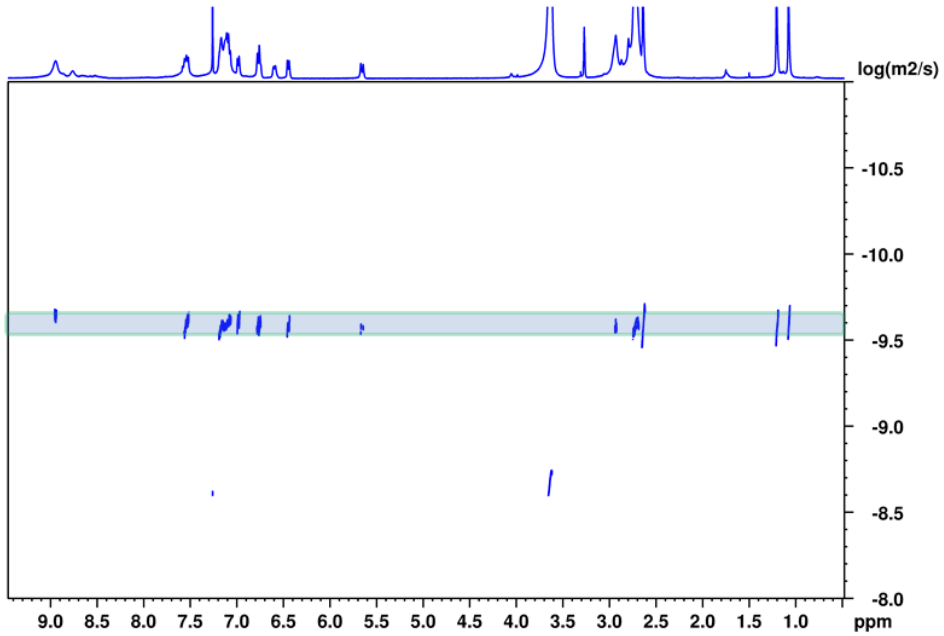


Figure S16: 2D ^{1}H-DOSY spectrum of **7** ($CDCl_3$ + MeOD at 298 K).

2. Mass spectra and isotopic patterns of different fragments:

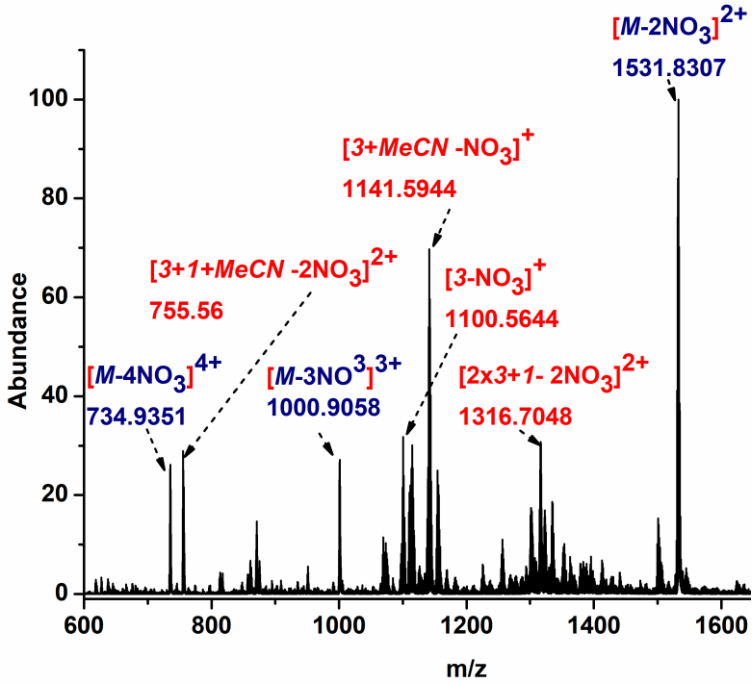


Figure S17: Electrospray ionization mass spectrum of **5** (**M = 5;** all compound numbers in italic)**.** Isotopic fragments are in blue and other fragments in red.

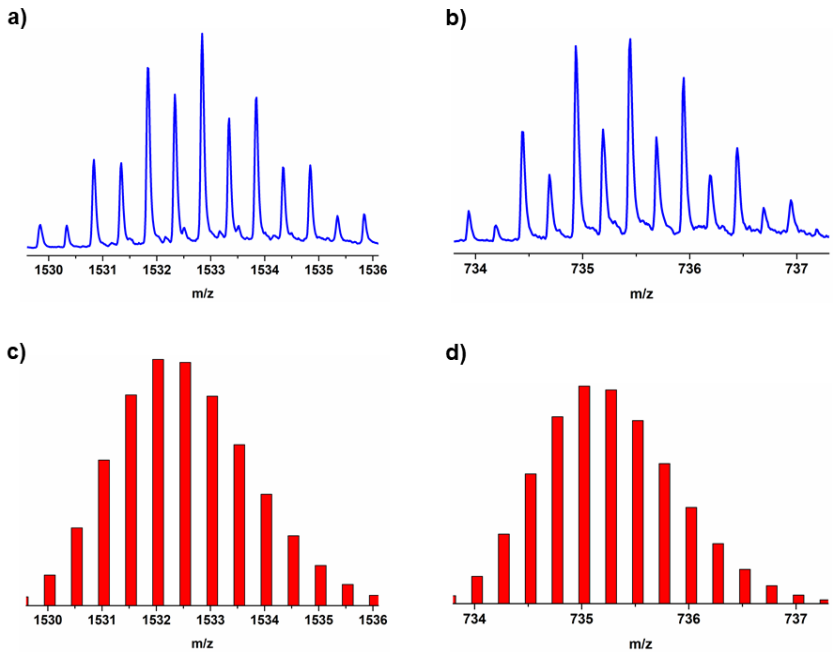


Figure S18: Experimental isotopic patterns of the fragments (a) [**M**-2NO_3]$^{2+}$, (b) [**M**-4NO_3]$^{4+}$ and their calculated patterns (c) and (d), respectively for macrocycle **5**. (These fragments may contain the mononeuclear fragment of the parent macrocycle.)

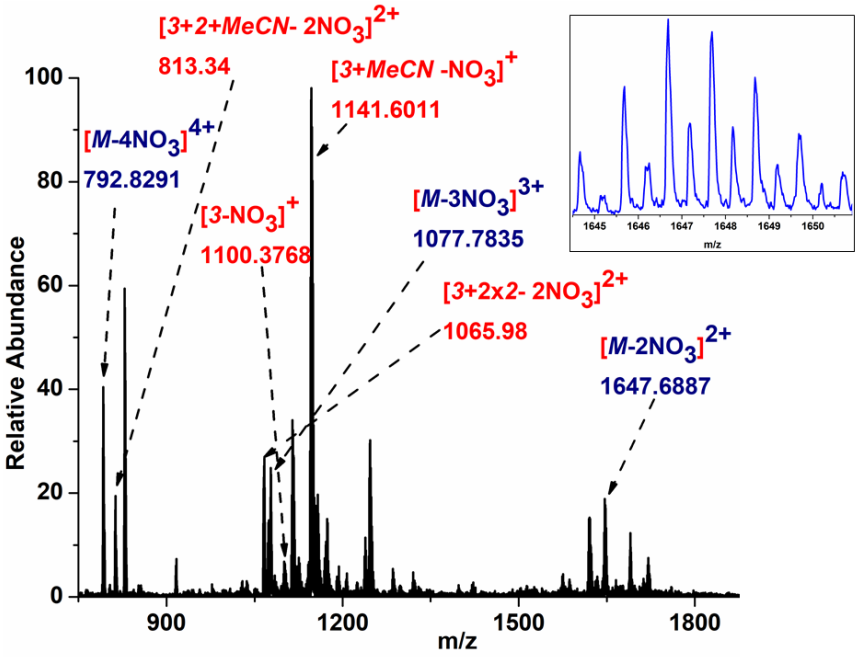


Figure S19: Electrospray ionization mass spectrum of **6.** (**M = 6;** all compound numbers in italic)**.** Experimental isotopic distribution pattern of [**M**-2NO_3]$^{2+}$ fragment (inset). Isotopic fragments are in blue and other fragments in red. (Doubly charged fragment pattern may contain the mononeuclear fragment of **6**).

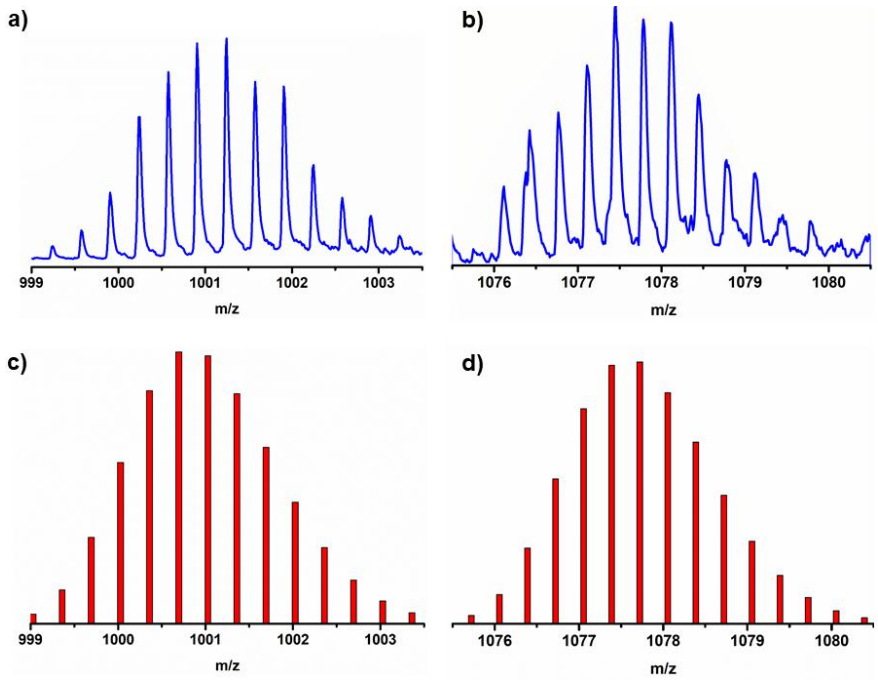


Figure S20. Experimental (blue) and calculated (red) isotopic distribution patterns of the peaks corresponding to [**5** - $3NO_3$]$^{3+}$ (m/z = 1000.9058) (left) and [**6** - $3NO_3$]$^{3+}$ (m/z = 1077.7835) (right).

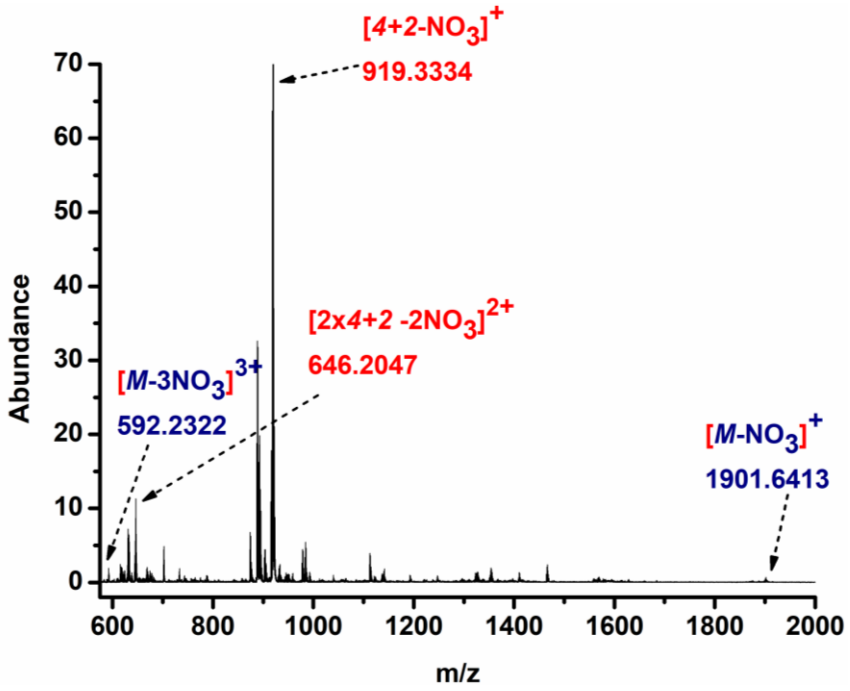


Figure S21: Electrospray ionization mass spectrum of **7** (**M = 7;** all compound numbers in italic)**.** Isotopic fragments are in blue and other fragments in red.

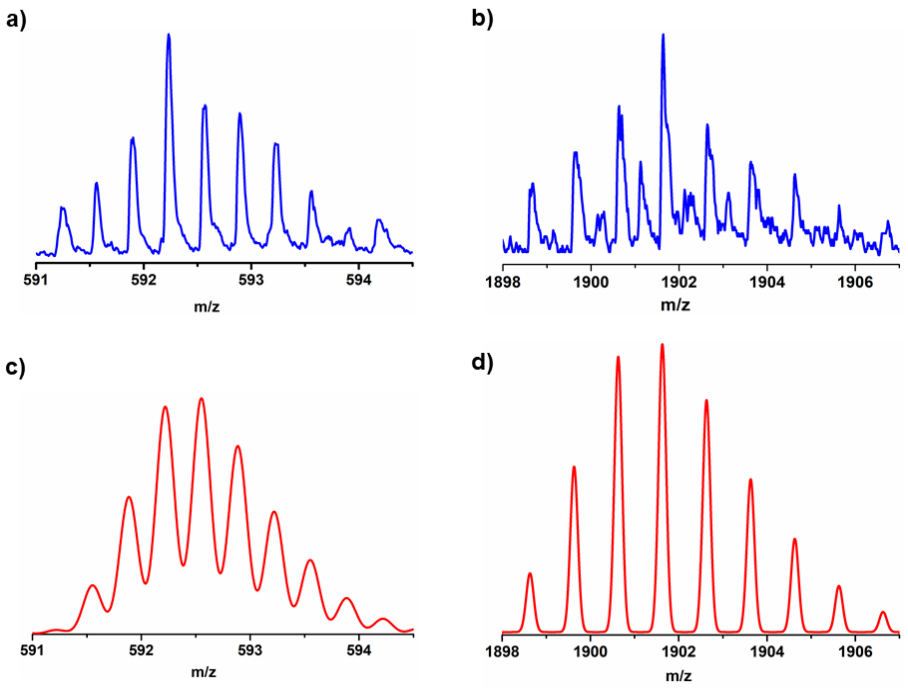


Figure S22: Experimental isotopic patterns of the fragments (a) [**M**-3NO_3]$^{3+}$, (b) [**M**-NO_3]$^{+}$ and their calculated patterns (c) and (d), respectively for macrocycle **7**.

3. Optimized geometries:

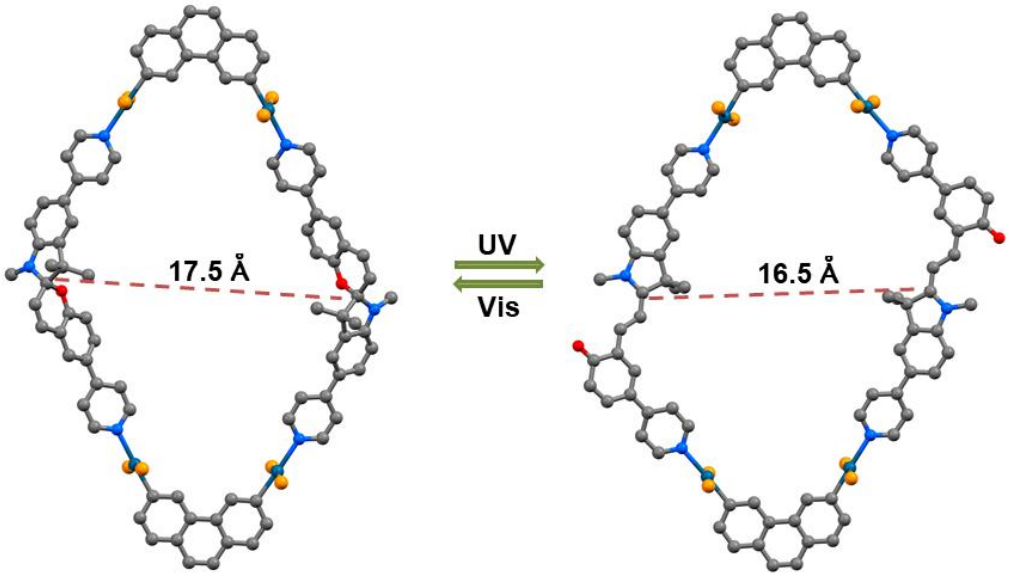


Figure S23: Optimized structures of **5**: ring-closed (left) and ring-opened isomer (right).

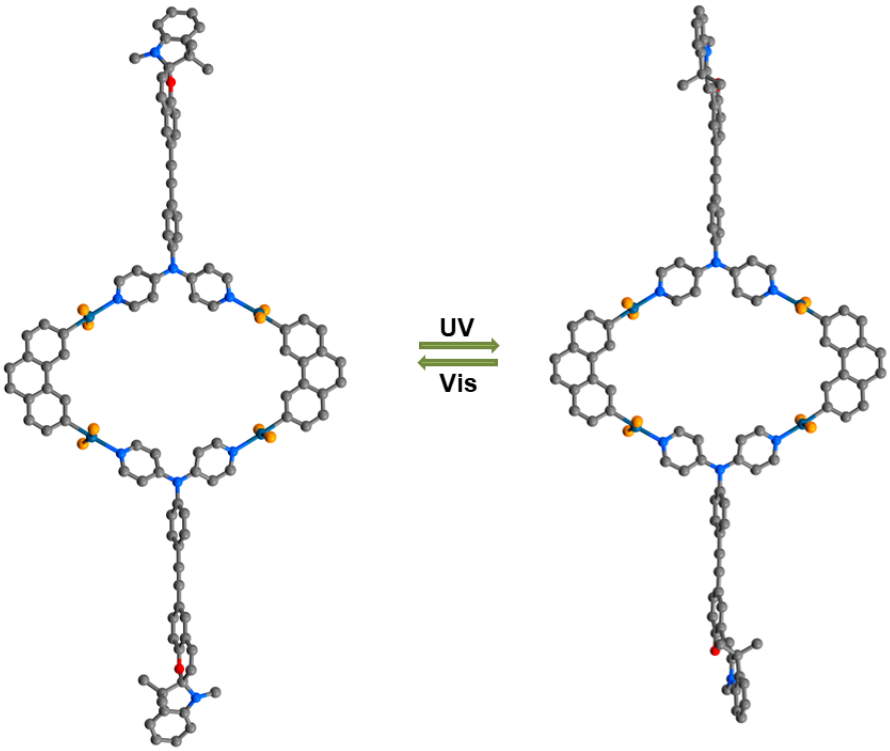
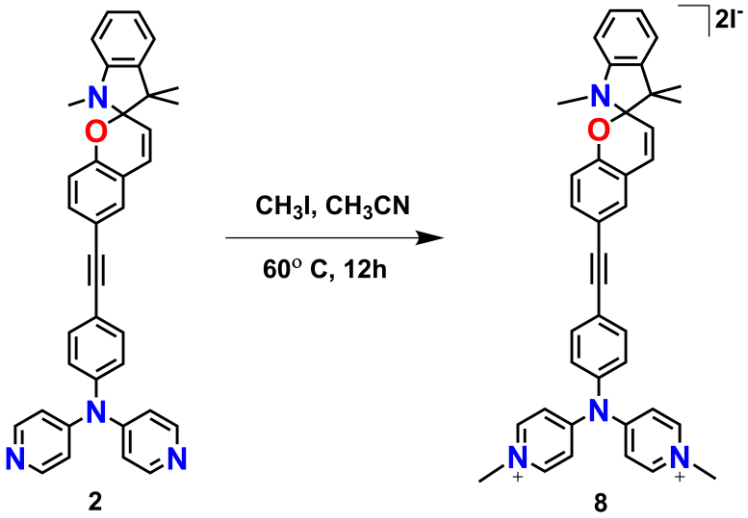


Figure S24: Optimized geometries of **6**: ring-closed (left) and ring-opened isomer (right).

4. Synthesis and characterization of N-methylated donor (8):



Scheme S7: Synthetic route for the preparation of **8.**

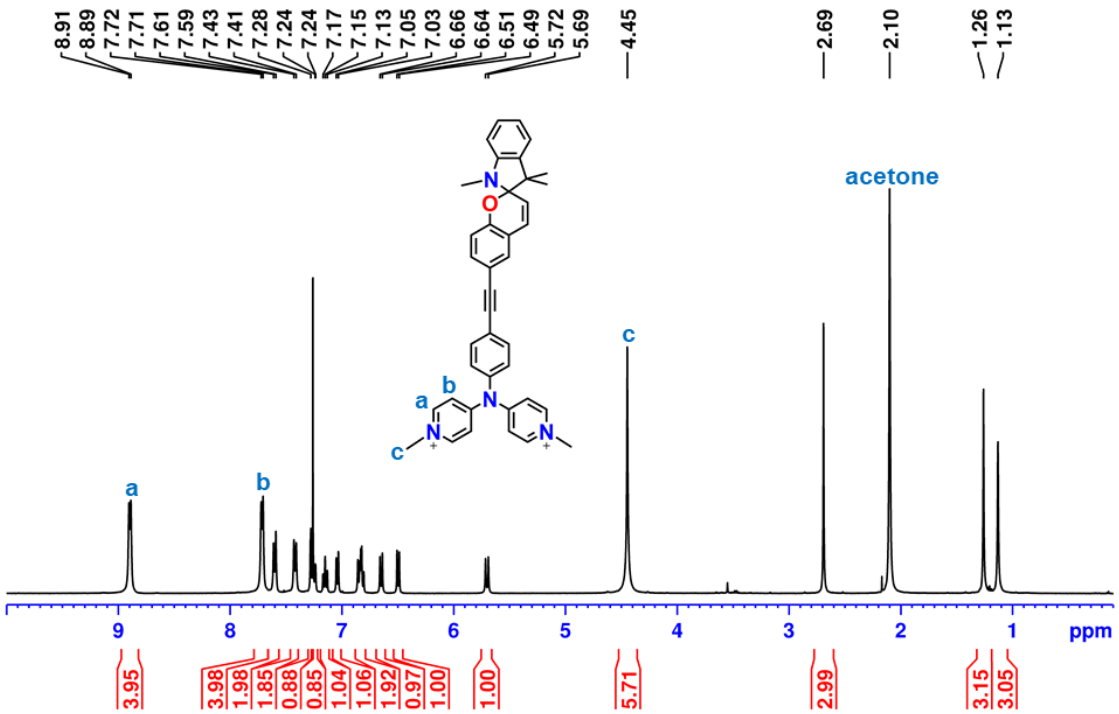


Figure S25. [1] H-NMR spectrum of methylated **2** (**8**) in $CDCl_3$ at 298 K.

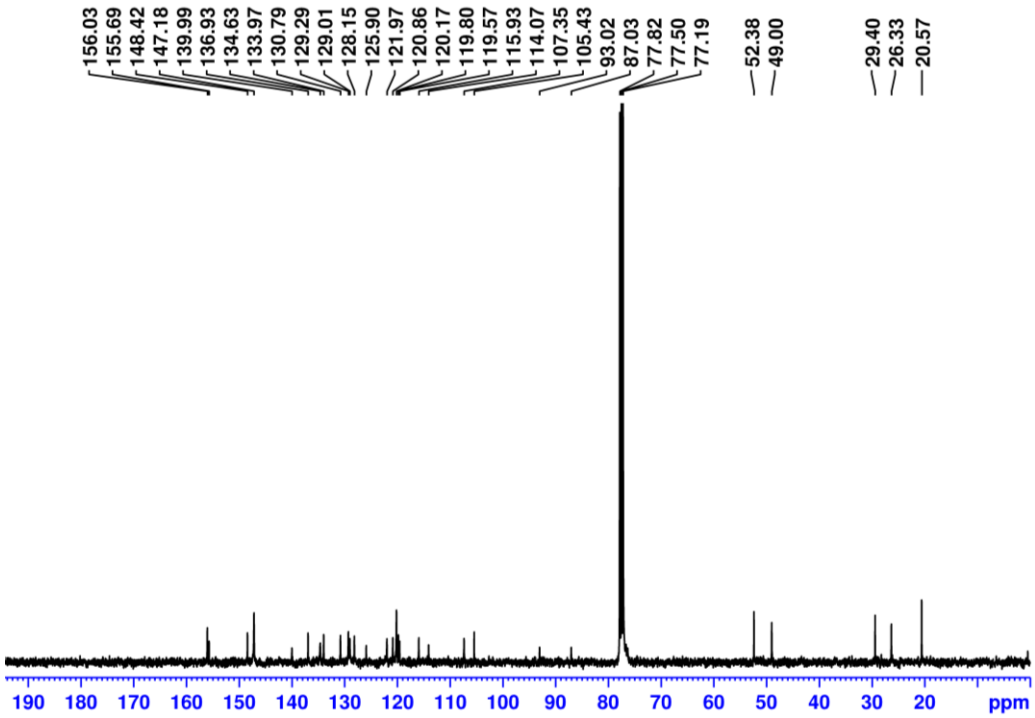


Figure S26. ^{13}C-NMR spectrum of methylated **2 (8)** in $CDCl_3$ at 298 K.

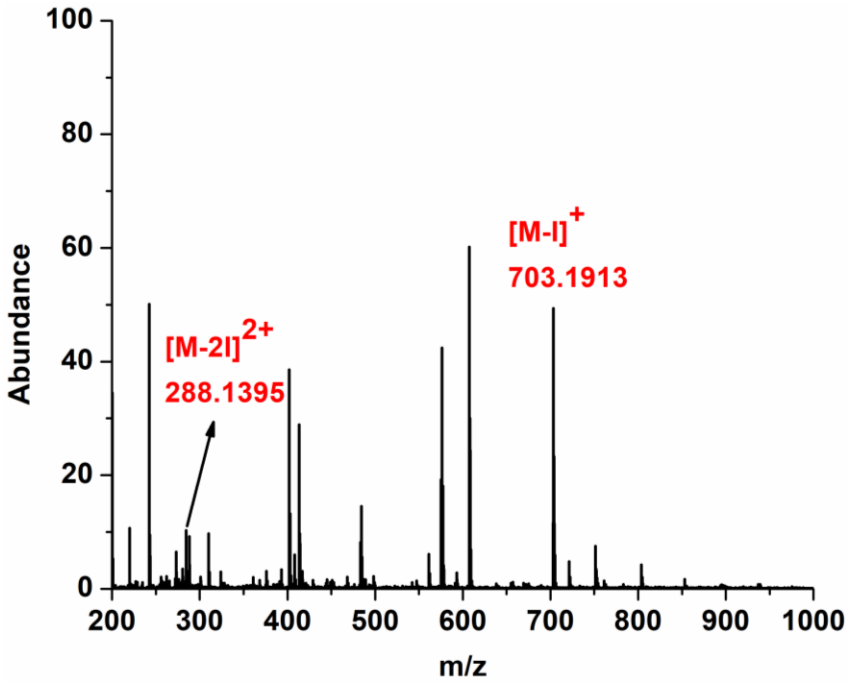


Figure S27: Electrospray ionization mass spectrum of **8.**

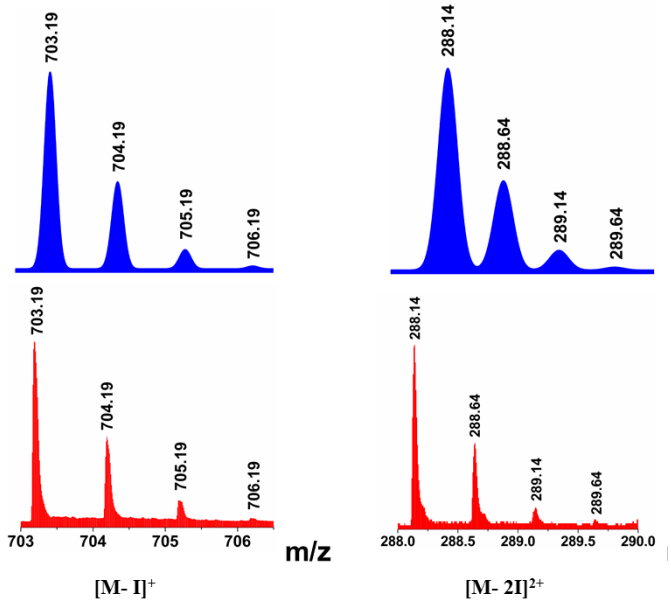


Figure S28. Experimental isotopic patterns of the fragments (red) [**M**-2I]$^{2+}$, [**M**-I]$^{+}$ of **8** and their calculated patterns (blue) respectively.

5. Photophysical experiments:

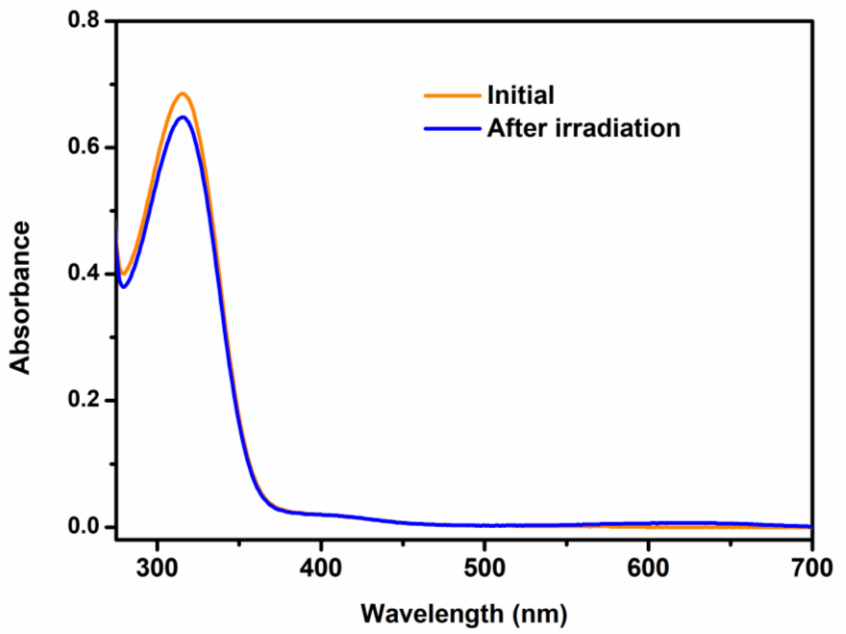


Figure S29: UV-Vis spectrum of the building block **1** (2×10^{-5}M in DMSO) upon exposure to 365 nm UV irradiation.

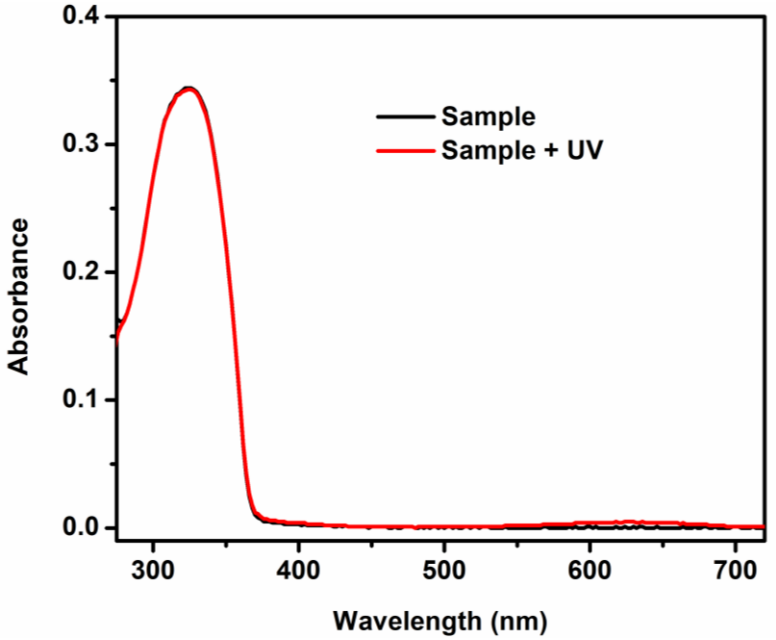


Figure S30: UV-Vis spectrum of the building block **2** (2×10^{-5}M in DMSO) upon exposure to 365 nm UV irradiation.

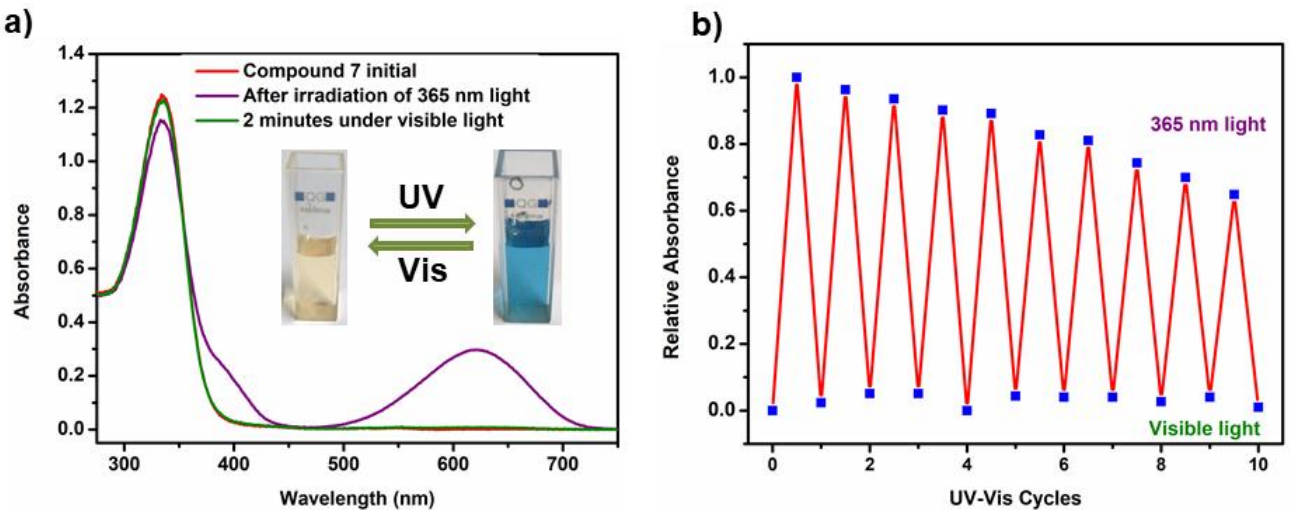


Figure S31: (a) Photochromic behavior of **7** (10^{-5}M in DMSO) after exposure to 365 nm UV irradiation. (b) Reversible photochromic behavior of **7.**

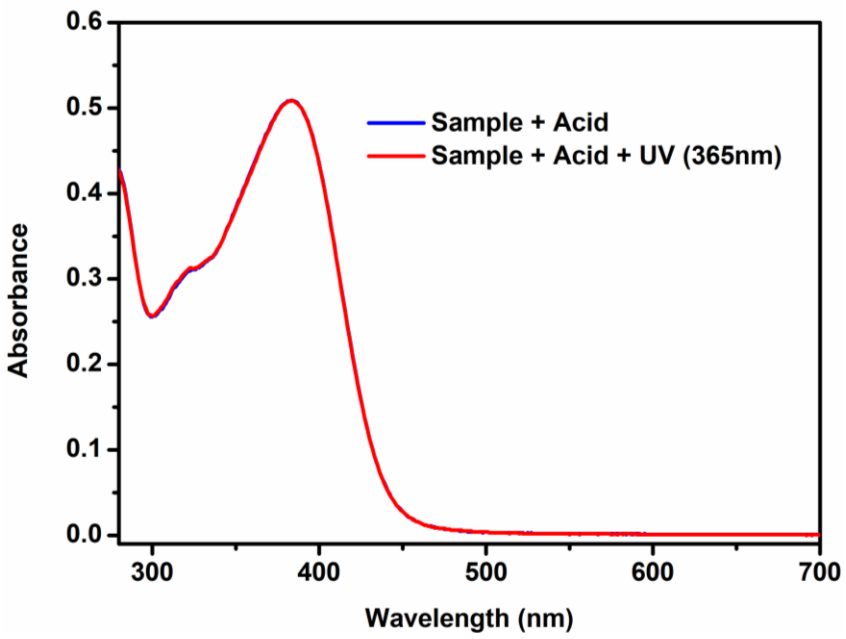


Figure S32: UV-Vis spectrum of the building block **1** (2×10^{-5}M in DMSO) with acid and after irradiation with 365 nm light in presence of acid.

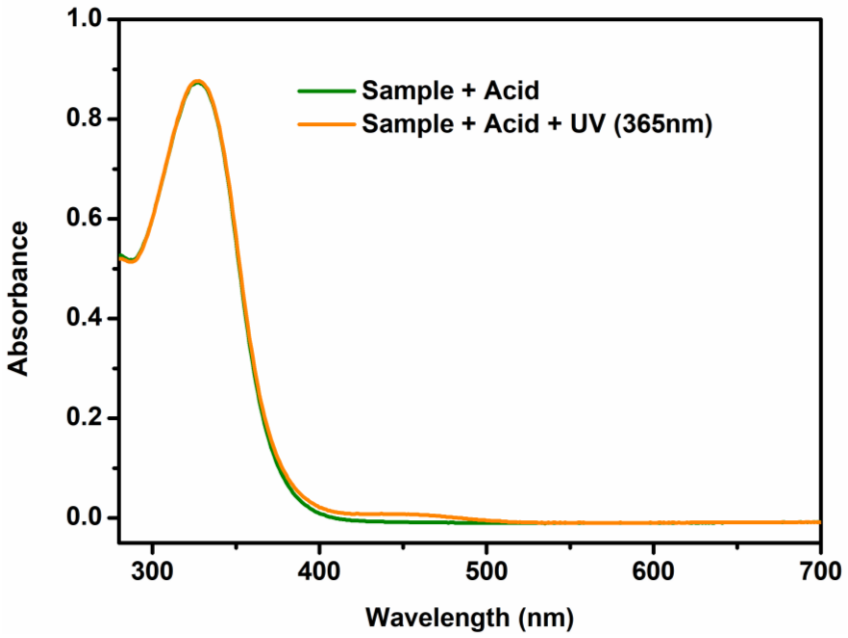


Figure S33: UV-Vis spectrum of the building block **2** (2×10^{-5}M in DMSO) with acid and after irradiation with 365 nm light in presence of acid.

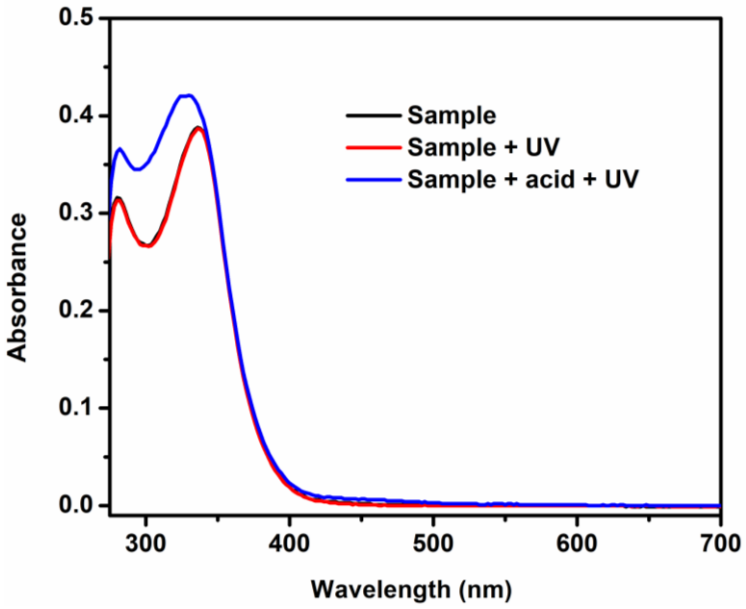
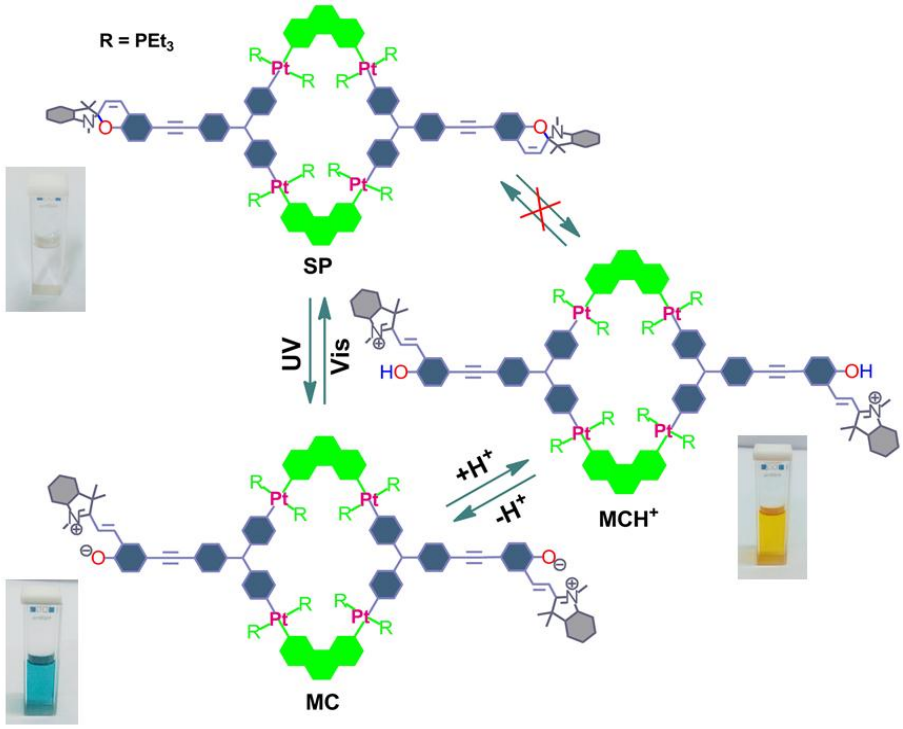


Figure S34: UV-Vis spectrum of the methylated **2 (8)** (2×10^{-5}M in DMSO) after exposure to 365 nm UV irradiation in absence and presence of acid.



Scheme S8: Schematic representation of acidochromic behavior of the macrocycles.

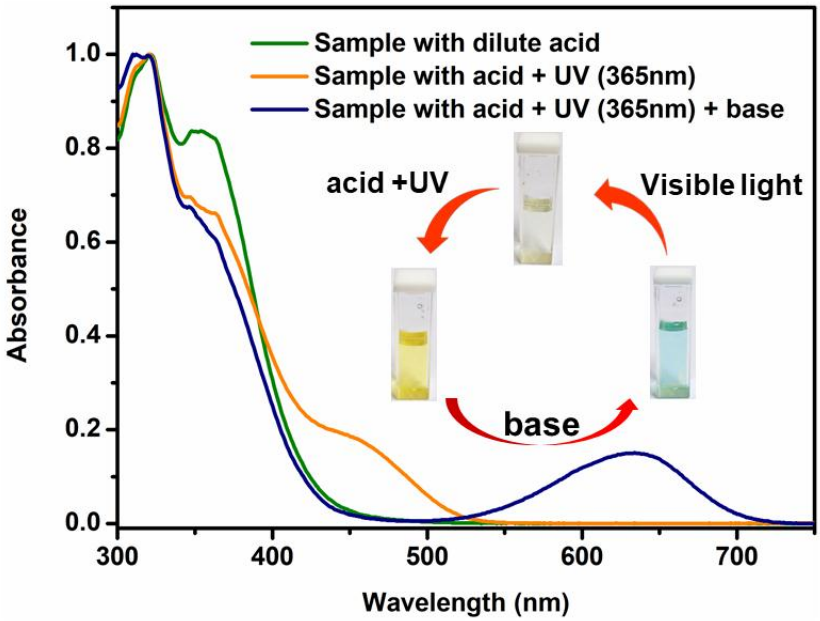


Figure S35: Acidochromic behavior **5** (10^{-5}M in DMSO).

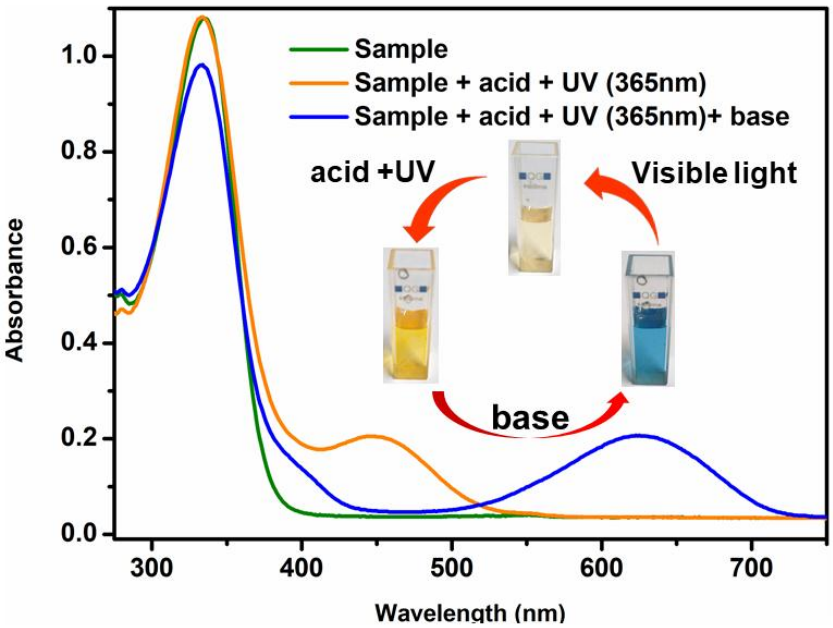


Figure S36: Acidochromic behavior **7** (10^{-5}M in DMSO)**.**

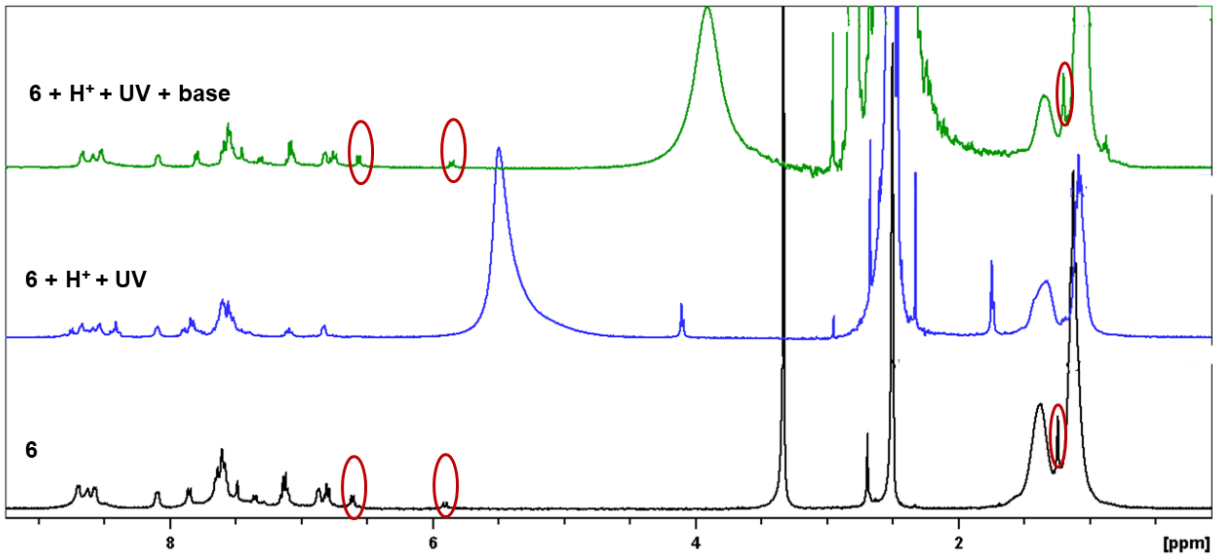


Figure S37: ^{1}H-NMR of **6** (bottom), **6 with acid + UV** (middle) and **6 with acid + UV + base** (top) in DMSO-d_6**.** (298K).

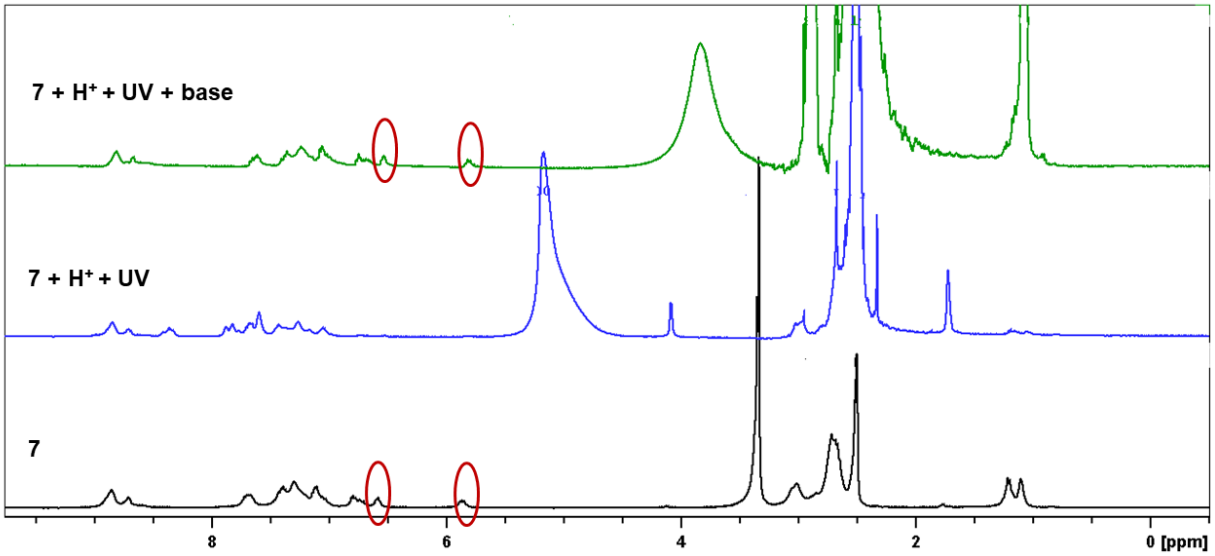


Figure S38: ^{1}H-NMR of **7** (bottom), **7 with acid + UV** (middle) and **7 with acid + UV + base** (top) in DMSO-d_6**.** (298K).

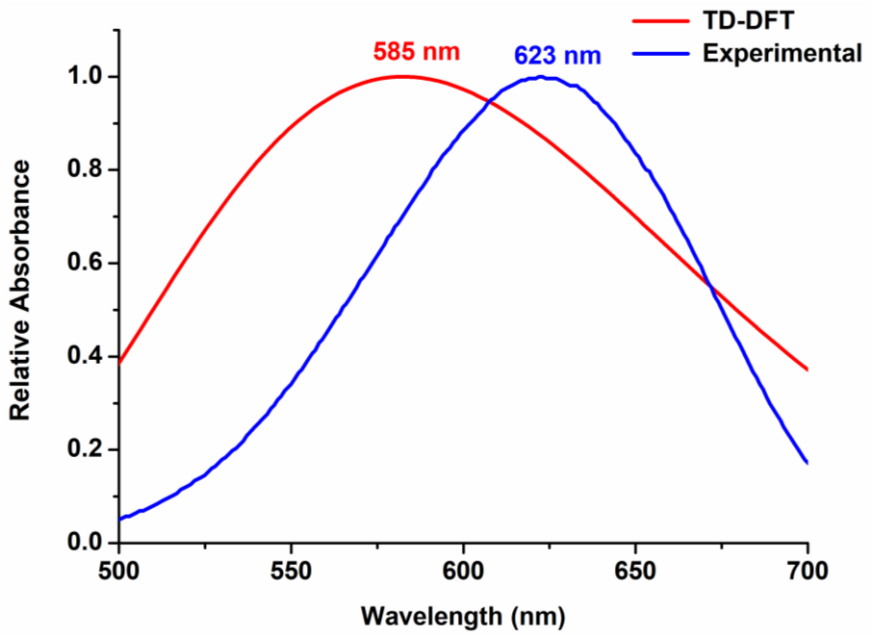


Figure S39. Comparison of experimental and theoretical (TD-DFT) UV-vis spectrum for the photochromic behaviour of **6.**

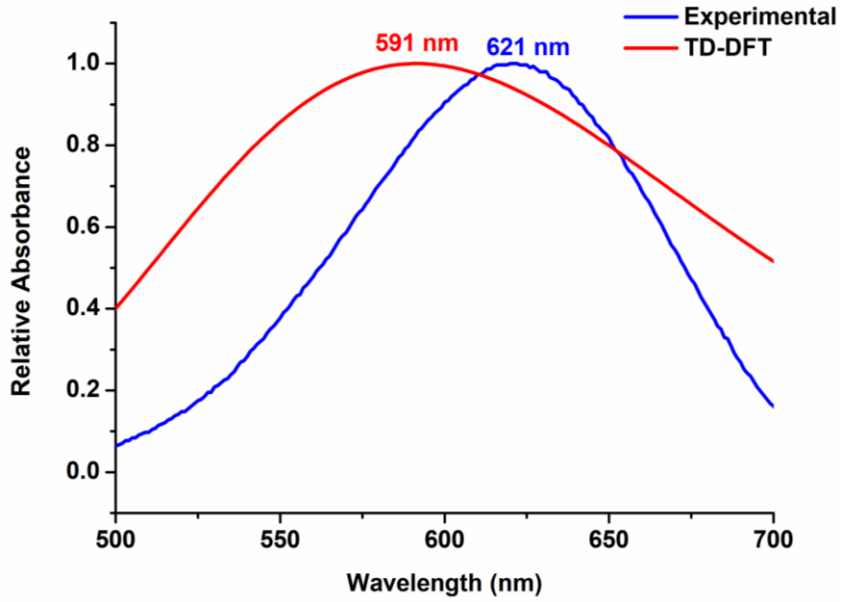


Figure S40. Comparison of experimental and theoretical (TD-DFT) UV-vis spectrum for the photochromic behaviour of **7.**

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