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Supplementary Information

Reversible fluorescence and Förster resonance energy transfer switching behaviours of bistable photo-switchable [*c*2] daisy chain rotaxanes and photo-patterning applications

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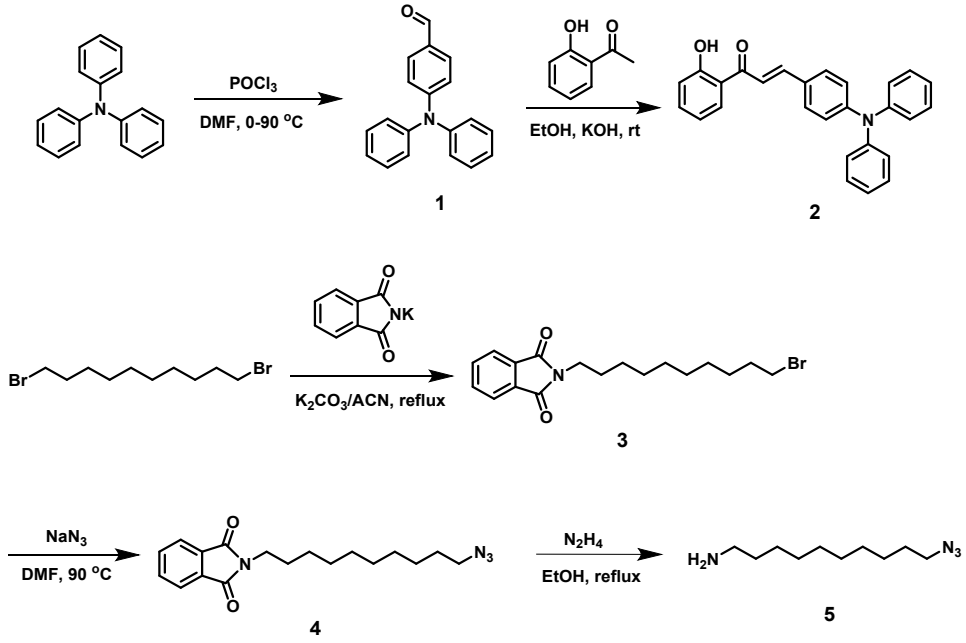
1. Synthetic procedures



Scheme S1 Synthetic routes of triphenylamine (TPA)-chalcone derivative **2** and compound **5**

Synthesis of compound 1.[S1] Triphenylamine (10 g, 40.8 mmol) was dissolved in DMF (100 mL), then $POCl_3$ (7.5 mL, 80.2 mmol) was slowly added and stirred at 0-5 °C for 30 min. Subsequently, the reaction mixture was allowed to warm up to 90 °C and stirred to react overnight. The resultant solution was quenched by water, then the residue was filtered out and washed with water for several times. The solid was dissolved in DCM, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (Hex:EtOAc = 100:1, v/v) to afford compound **1** as a white solid (8.92 g, yield 80%). ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 9.81 (s, 1H); 7.69-7.66 (m, 2H); 7.36-7.32 (m, 4H); 7.18-7.15 (m, 6H); 7.03-7.00 (m, 2H).

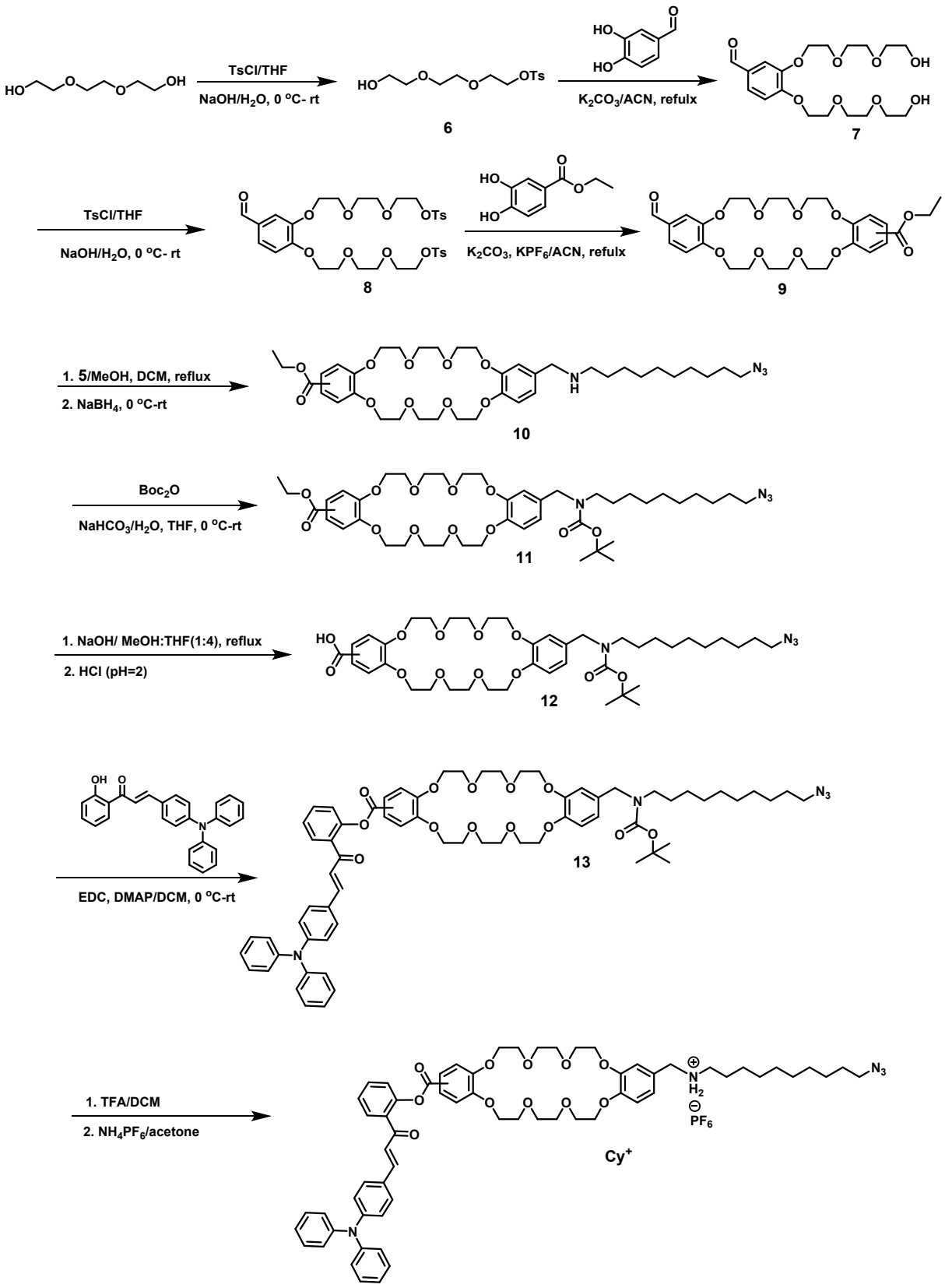
Synthesis of compound 2.[S2] A solution of 2'-hydroxyacetophenone (3.6 g, 26.4 mmol) in EtOH (100 mL) was added 30 mL KOH solution (4.35 g, 66.0 mmol), followed by the addition of compound **1** (6.0 g, 22 mmol) at 0 °C and stirred for 30 min. The reaction mixture was continuously stirred at 70 °C for 3 h. After removal of EtOH, water was added and the solution was neutralized with diluted HCl to pH = 4. The precipitate was filtered out, washed with water and pentane for several times. The solid was dried in vacuum at 60 °C for 6 h to obtain compound **2** as an orange-red solid (6.11 g, yield 71%). ^{1}H NMR (400 MHz, $CDCl_3$, δ

ppm): 13.01 (s, 1H); 7.92-7.87 (m, 2H); 7.54-7.46 (m, 4H); 7.34-7.30 (m, 4H); 7.18-7.11 (m, 6H); 7.05-7.01 (m, 2H); 6.95-6.91 (m, 1H).

Synthesis of compound 3.[S3] Potassium phthalimide (7.5 g, 40 mmol) and K_2CO_3 (13.8 g, 100 mmol) were mixed in ACN (400 mL) and stirred at 90 °C for 15 min. Then, 1,10-dibromodecane (60 g, 200 mmol) was added and refluxed under N_2 atmosphere for 3 h. The solid was removed by filtration, the filtrate was concentrated under reduced pressure and the residue was extracted with DCM (2×50 mL). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated by rotary evaporator. The crude product was purified by column chromatography using Hex:EtOAc = 100:1 to 25:1 (v/v) eluent to acquire compound **3** as a white solid (13 g, yield 89%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.85-7.80 (m, 2H); 7.72-7.67 (m, 2H); 3.66 (t, J = 7.4 Hz, 2H); 3.38 (t, J = 7.0 Hz, 2H); 1.86-1.79 (m, 2H); 1.43-1.37 (m, 2H); 1.36-1.24 (m, 12H).

Synthesis of compound 4.[S3] A solution of compound **3** (6 g, 16.38 mmol) in DMF (100 mL) was added NaN_3 (2.7 g, 41.54 mmol) and stirred at 90 °C under N_2 atmosphere overnight. The reaction was quenched by water, followed by extraction with EtOAc (3×50 mL). The organic layer was dried over anhydrous Na_2SO_4 and solvents were removed under reduced pressure to yield compound **4** as a pale yellow solid (5.11 g, yield 95%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.86-7.81 (m, 2H); 7.72-7.68 (m, 2H); 3.67 (t, J = 7.4 Hz, 2H); 3.24 (t, J = 6.8 Hz, 2H); 1.70-1.64 (m, 2H); 1.61-1.54 (m, 2H); 1.37-1.25 (m, 12H).

Synthesis of compound 5.[S3] Compound **4** (4.0 g, 12.18 mmol) and $N_2H_4{\cdot}H_2O$ (4 ml, 128.8 mmol) were dissolved in EtOH (200 mL), then refluxed under N_2 gas protection overnight. The resultant solution was filtered, washed with cool EtOH and the filtrate was concentrated under reduced pressure, followed by the extraction with DCM (3×50 mL) and washed with water twice. The organic layer was dried over anhydrous Na_2SO_4 and DCM was removed by rotary evaporator to afford compound **5** (10-azidodecan-1-amine) as a slight yellow oil (2.1 g, yield 87%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.23 (t, J = 6.6 Hz, 2H); 2.66 (t, J = 7.0 Hz, 2H); 1.61-1.54 (m, 2H); 1.44-1.38 (m, 2H); 1.36-1.23 (m, 12H).



Scheme S2 Synthetic routes of TPA-chalcone host-bearing ammonium guest **Cy**$^{+}$

Synthesis of compound 6.[S4] An aqueous NaOH (40 g, 1.0 mol, 200 mL) solution was added into the solution of triethylene glycol (75 g, 0.5 mol) in THF (200 mL) at 0-5 °C. Then, *p*-toluenesulfonyl chloride (115 g, 0.6 mol) in THF (200 mL) was added dropwise, maintaining the reaction temperature below 5 °C. Subsequently, the reaction mixture was stirred at room temperature for further 3 h under N_2 atmosphere. The solvent was removed, the residue was extracted with EtOAc, dried over anhydrous Na_2SO_4 and the obtained solution was concentrated under reduced pressure. The crude product was purified by column chromatography with Hex:DCM = 4:1 to EtOAc:DCM = 4:1 (v/v) to achieve compound **6** as a pale yellow oil (92.8 g, yield 61%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.76 (d, J = 10.0 Hz, 2H); 7.33-7.30 (m, 2H); 4.15-4.12 (m, 2H); 3.68-3.66 (m, 4H); 3.57 (s, 4H); 3.55-3.52 (m, 2H); 2.47-2.46 (m, 1H); 2.41 (s, 3H).

Synthesis of compound 7.[S5] A mixture of 3,4-dihydroxybenzaldehyde (5 g, 36.2 mmol) and K_2CO_3 (20.2 g, 144.8 mmol) in ACN (100 mL) was stirred at 90 °C under N_2 atmosphere for 15 min, followed by the addition of compound **6** (27.6 g, 90.7 mmol) and the reaction mixture was refluxed for 24 h. After filtering off solids, the filtrate was concentrated under reduced pressure, the residue was extracted with DCM (3×50 mL) and washed with brine. The solution was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using an eluent of EtOAc:DCM:MeOH = 25:25:1 (v/v/v) to obtain compound **7** as a pale yellow oil (11.5 g, yield 79%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.79 (s, 1H); 7.42-7.39 (m, 2H); 7.95 (d, J = 8.0 Hz, 1H); 4.22-4.18 (m, 4H); 3.90-3.85 (m, 4H); 3.74-3.71 (m, 4H); 3.69-3.66 (m, 4H); 3.65-3.63 (m, 4H); 3.57-3.55 (m, 4H); 3.11 (s, 2H).

Synthesis of compound 8.[S5] A solution of NaOH (4.82 g, 120.6 mmol) was added to compound **7** (8.1 g, 20.1 mmol) in THF (100 mL) at 0-5 °C, followed by the addition of TsCl (15.33 g, 80.4 mmol) in THF (100 mL). Subsequently, the reaction mixture was allowed to warm up to room temperature and stirred for further 3 h under N_2 gas protection. The solvent was removed, the residue was extracted with EtOAc, dried over anhydrous Na_2SO_4 and the solution was concentrated under reduced pressure. The crude product was purified by column chromatography with Hex:EtOAc = 1:1 to 1:1.5 (v/v) mixed solvents to obtain compound **8** as a pale yellow oil (12.86 g, yield 90%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.80 (s, 1H); 7.76-7.75 (m, 4H); 7.43-7.41 (m, 1H); 7.40 (d, J = 1.5 Hz, 1 H); 7.30 (d, J = 3.0 Hz, 4H);

6.98 (d, J = 8.5 Hz, 1H); 4.20 (t, J = 5.0 Hz, 2H); 4.16 (t, J = 4.75 Hz, 2H); 4.13-4.11 (m, 4H); 3.85 (t, J = 4.75 Hz, 2H); 3.82 (t, J = 5.0 Hz, 2H); 3.67-3.64 (m, 8H); 3.59-3.57 (m, 4H); 2.40 (s, 6H).

Synthesis of compound 9.[S5] Compound **8** (5.83 g, 8.2 mmol) was added to a mixture of ethyl 3,4-dihydroxybenzoate (1.5 g, 8.2 mmol), K_2CO_3 (3.4 g, 24.6 mmol) and KPF_6 (2.27 g, 12.3 mmol) in ACN (200 mL). The reaction mixture was stirred at reflux under N_2 atmosphere for 24 h. The resultant solution was filtered and concentrated under reduced pressure. Then, the residue was further extracted with EtOAc (3×50 mL) and washed with water for several times. The organic layer was dried over anhydrous Na_2SO_4, then EtOAc was evaporated under reduced pressure and the crude product was purified by column chromatography using DCM:EtOAc = 1:5 (v/v) eluent to afford compound **9** as a white solid (3.02 g, yield 67%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 9.78 (s, 1H); 7.62 (dd, J = 2.0 Hz, J = 8.4 Hz, 1H); 7.49 (d, J = 1.6 Hz, 1H); 7.40 (dd, J = 2.0 Hz, J = 8.4 Hz, 1H); 7.35 (d, J = 1.6 Hz, 1H); 6.91(dd, J = 2.4 Hz, J = 8.0 Hz, 1H); 6.82 (d, J = 8.4 Hz, 1H); 4.31 (q, J = 7.2 Hz, 2H); 4.20-4.16 (m, 8H); 3.94-3.90 (m, 8H); 3.84-3.78 (m, 8H); 1.34 (t, J = 7.0 Hz, 3H).

Synthesis of compound 10. Compound **9** (3.0 g, 5.5 mmol) and compound **5** (1.31 g, 6.6 mmol) were dissolved in 100 mL of MeOH:DCM (1:1, v/v), then a few drops of catalytic CH_3COOH were added. The reaction mixture was refluxed for 24 h under N_2 gas protection. The obtained solution was cooled down to 0 °C, then $NaBH_4$ (1.25 g, 33.0 mmol) was slowly added and stirred at room temperature for 3 h. Water was added to quench reaction, then organic solvents were removed under reduced pressure and pH of solution was adjusted to 5 by HCl solution. Then, the solution was extracted with DCM (2×50 mL), DCM layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography using a gradient solvent system from DCM:EtOAc:MeOH = 40:40:1 (v/v/v) to DCM:MeOH = 5:1 (v/v) to get compound **10** as a white solid (3.32 g, yield 83%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.65-7.62 (m, 1H); 7.52 (d, J = 2.0Hz, 1H); 7.13 (t, J = 2.4 Hz, 1H); 6.90 (d, J = 8.0 Hz, 1H); 6.84 (dd, J = 1.2 Hz, J = 8.4 Hz, 1H); 6.78-6.79 (dd, J = 2 Hz, J = 8.4 Hz, 1H); 4.33 (q, J = 7 Hz, 2H); 4.21-4.17 (m, 6H); 4.12-4.09 (m, 2H); 3.94-3.92 (m, 8H); 3.83-3.81 (m, 8H); 3.26-3.22 (m, 2H); 2.81 (t, J = 7.6 Hz, 1H); 2.66 (t, J = 7.8 Hz, 2H); 1.68-1.62 (m, 2H); 1.60-1.53 (m, 2H); 1.36 (t, J = 7.2 Hz, 3H); 1.34-1.23 (m, 12H).

Synthesis of compound 11. Compound **10** (3.0 g, 4.1 mmol) was dissolved in THF (50 mL), a solution of $NaHCO_3$ (1.04 g, 12.3 mmol) in water (50 mL) was then added and stirred around 0 °C for 10 min. Subsequently, *di-tert*-butyl dicarbonate (1.35 g, 6.2 mmol) was added, the reaction mixture was allowed to warm up to room temperature and stirred for 2 h under N_2 atmosphere. The resultant solution was neutralized to pH = 5 by citric acid solution, THF was then removed, the solution was extracted with DCM (2×50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was washed with pentane for several times and dried for 5 h under vacuum to afford compound **11** as a white solid (3.0 g, yield 88%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.65-7.63 (m, 1H); 7.52 (d, J = 2.0 Hz, 1H); 6.84 (d, J = 8.5 Hz, 1H); 6.84 (d, J = 8.5 Hz, 1H); 6.79-6.71 (m, 3H); 4.35-4.30 (3, 4H); 4.20-4.18 (m, 4H); 4.13-4.11 m, 4H); 3.94-3.90 (m, 8H); 3.87-3.82 (m, 8H); 3.24 (t, J = 7.0 Hz, 2H); 3.15-3.05 (m, 2H); 1.75 (s, 2H); 1.61-1.55 (m, 2H); 1.46 (s, 9H); 1.37 (t, J = 7.0 Hz, 3J); 1.33-1.20 (m, 12H).

Synthesis of compound 12. A 20 mL aqueous solution of NaOH (0.24 g, 6.0 mmol) was added to a solution of compound **11** (2.5 g, 3.0 mmol) in 100 ml MeOH:THF (1:4, v/v), then the reaction mixture was stirred and refluxed at 80 °C overnight. The organic solvents were removed under reduced pressure, then water and HCl solution were added to adjust pH = 2. The precipitate was filtered, washed with water a few times and the obtained solid was dissolved in DCM, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield compound **12** as a white solid (2.18 g, yield 91%). ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 12.63 (s, 1H); 7.54 (dd, J = 2.0 Hz, J = 8.5Hz, 1H); 7.43 (d, J = 2.0 Hz, 1H); 7.03 (d, J = 8.0 Hz, 1H); 6.84 (d, J = 8.5 Hz, 1H); 6.89 (d, J = 8.5 Hz, 1H); 6.82 (s, 1H); 6.74 (dd, J = 2.0 Hz, J = 8.0 Hz,1H); 4.25 (s, 1H); 4.14 (t, J = 4 Hz, 2H); 4.10 (t, J = 4.25 Hz, 2H); 4.05-4.02 (m, 4H); 3.79-3.73 (m, 8H); 3.68-6.64 (m, 8H); 3.29 (t, J = 7.0 Hz, 2H); 3.06 (s, 2H); 1.53-1.48 (m, 2H); 1.41-1.36 (m, 11H); 1.32-1.14 (m, 12H).

Synthesis of compound 13. Compound **12** (2.0 g, 2.5 mmol), EDC (1.06 g, 5.5 mmol) and DMAP (0.15 g, 1.23 mmol) were dissolved in dry DCM (50 mL) and stirred at 0 ºC for 1 h. Then, compound **2** (1.57 g, 4.0 mmol) was added and the mixture was stirred at room temperature overnight. Water was added to the resultant solution, the organic layer was collected and concentrated under reduced pressure. The crude product was purified by column chromatography (DCM to DCM:EtOAc = 4:1, v/v) to obtain compound **13** as a yellowish-orange solid (2.68 g, yield 91%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.78-7.75

(m, 1H); 7.69 (dd, J = 1.6 Hz, J = 7.6 Hz, 1H); 7.57-7.53 (m, 2H); 7.50-7.46 (m, 2H); 7.38-7.33 (m, 1H); 7.32-7.25 (m, 7H); 7.12-7.12 (m, 6H); 6.99-6.95 (m, 1H); 6.93-6.89 (m, 2H); 6.83 (dd, J = 1.2 Hz, J = 8.8 Hz, 1H); 6.82-6.72 (m, 3H); 4.32 (s, 2H); 4.19-4.11 (m, 8H); 3.94-3.87 (m, 8H); 3.83-3.81 (m, 8H); 3.24 (t, J = 7.0 Hz, 2H); 3.15-3.07 (m, 2H); 1.62-1.55 (m, 2H); 1.47-1.43 (m, 11H); 1.37-1.19 (m, 12H).

Synthesis of Cy^+. Compound **13** (2.0 g, 1.7 mmol) was dissolved in DCM (100 mL), followed by the addition of trifluoroacetic acid (3 mL) at 0 ºC. The mixture was allowed to warm up to room temperature and stirred for 3 h. Then, water was added to the resultant solution, the organic layer was collected and concentrated under reduced pressure after extraction by DCM. The intermediate salt was dispersed in 50 mL acetone, the saturated solution of NH_4PF_6 in 10 mL H_2O was then added and stirred at room temperature for 1 h. The solvent was removed, the residue was filtered and washed with de-ionized water for several times. The solid was re-dissolved in DCM, dried over anhydrous Na_2SO_4 and the solution was concentrated under reduced pressure to obtain compound $\mathbf{Cy}^+$ as an orange solid (1.72 g, yield 83%). ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 8.54 (s, 2H); 7.86-7.75 (m, 1H); 7.72-7.64 (m, 2H); 7.52-7.41 (m, 4H); 7.39-7.29 (m, 5H); 7.20-7.13 (m, 3H); 7.09-7.04 (m, 6H); 7.01-6.97 (m, 3H); 6.82-6.72 (m, 2H); 4.15-4.02 (m, 10H); 3.80-3.70 (m, 8H); 3.67-6.63 (m, 8H); 3.29 (t, J = 6.5 Hz, 2H); 2.86-2.81 (m, 2H); 1.60-1.53 (m, 2H); 1.53-1.48 (m, 2H); 1.30-1.24 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 192.02, 191.95, 164.64, 152.52,152.37, 150.46, 148.96, 147.74, 147.61, 146.79, 146.53, 146.33, 146.28, 145.96, 132.94, 132.27, 129.90, 129.81, 129.74, 129.52, 129.38, 127.36, 126.49, 126.10, 125.93, 125.69, 124.87, 124.80, 124.53, 124.51, 123.69, 123.06, 121.93, 121.30, 121.27, 113.25, 112.79, 111.36, 72.50, 72.04, 71.10, 70.95, 70.73, 70.54, 70.33, 70.14, 67.83, 67.32, 67.16, 52.33, 51.63, 51.58, 49.10, 29.50, 29.48, 29.40, 29.27, 29.18, 28.96, 26.94, 26.84. HRMS (ESI$^+$) [M-PF_6^-]$^+$: calcd. for $C_{63}H_{974}N_5O_{11}^+$, 1076.5379; found, 1076.5413.

Stopper **SP-C_3H_3** was synthesized according to our previous publication.[S6] ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.04-8.02 (m, 2H); 7.25-7.22 (m, 1H); 7.13-7.11 (m, 1H); 6.98-6.93 (m, 2H); 6.82 (d, J = 6.4 Hz, 1H); 6.76-6.74 (m, 1H); 6.23 (d, J = 6.4 Hz, 1H); 5.89 (d, J = 8.4 Hz, 1H); 4.07-4.03 (m, 1H); 3.88-3.84 (m, 1H); 2.10 (t, J = 2.0 Hz, 1H); 1.31 (s, 3H); 1.21 (s, 3H).

2. Characterizations of intermediate compounds and photo-switchable [*c2*] daisy chain rotaxane [*c2*]-SP-Ext

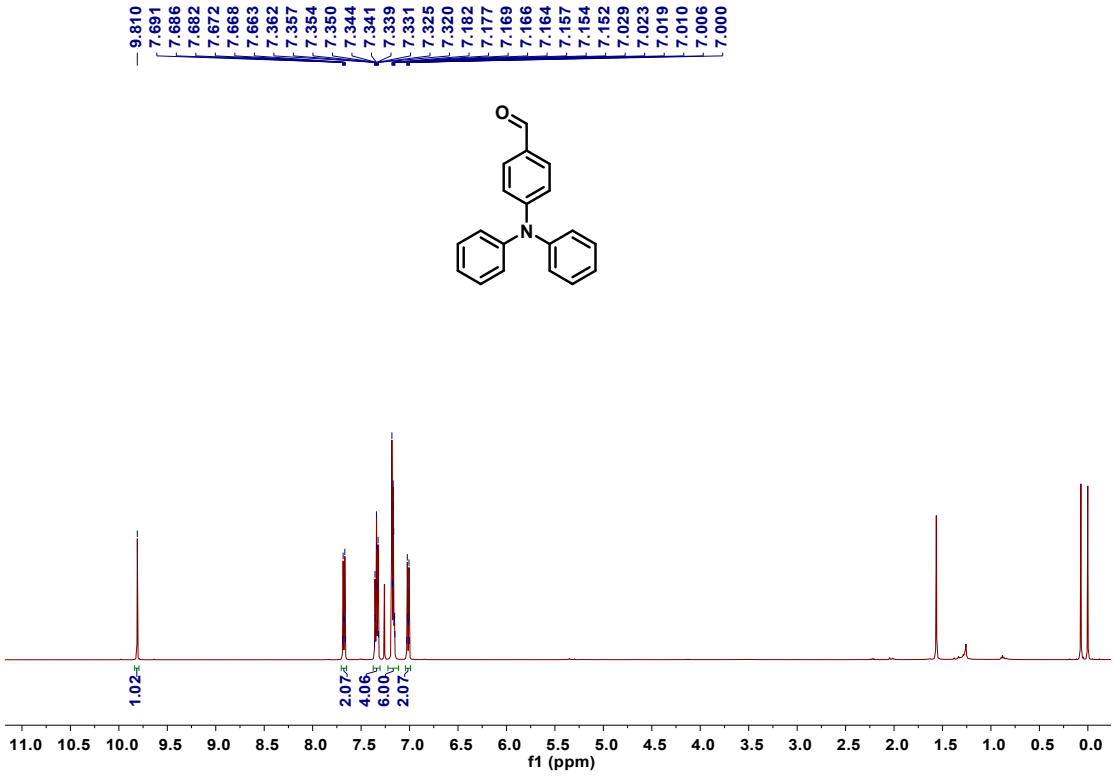


Fig. S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **1**.

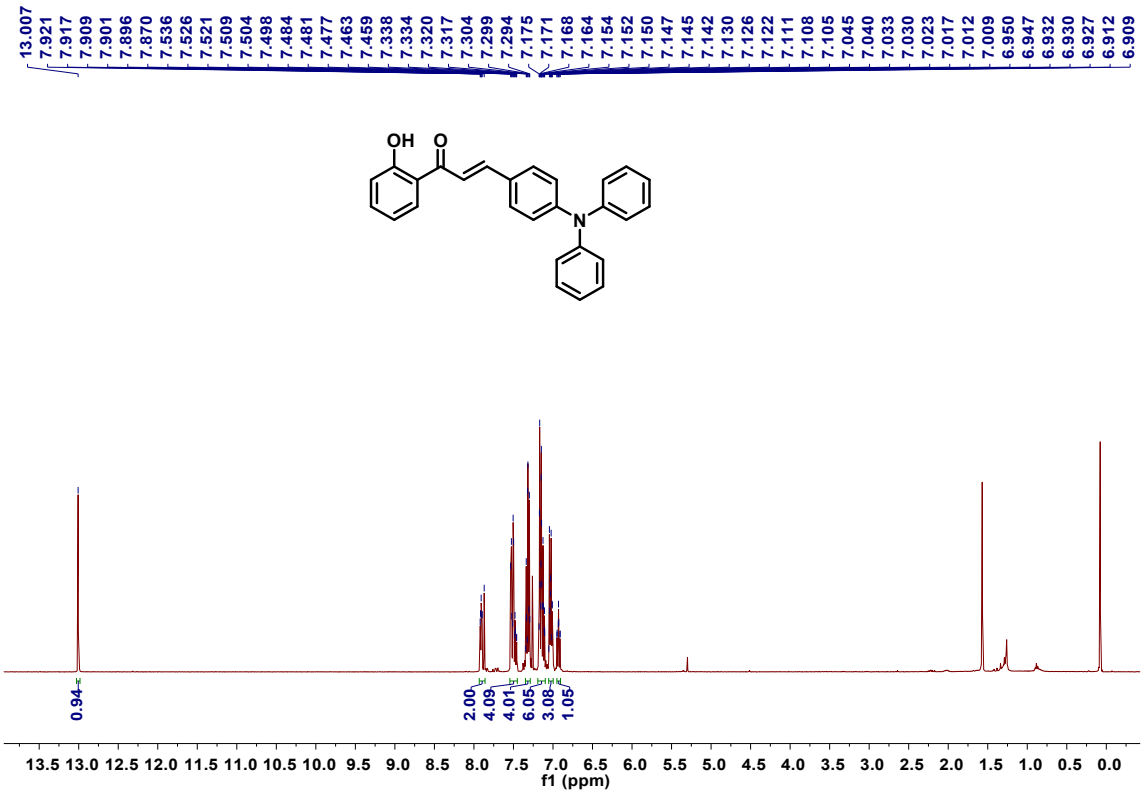


Fig. S2 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2**.

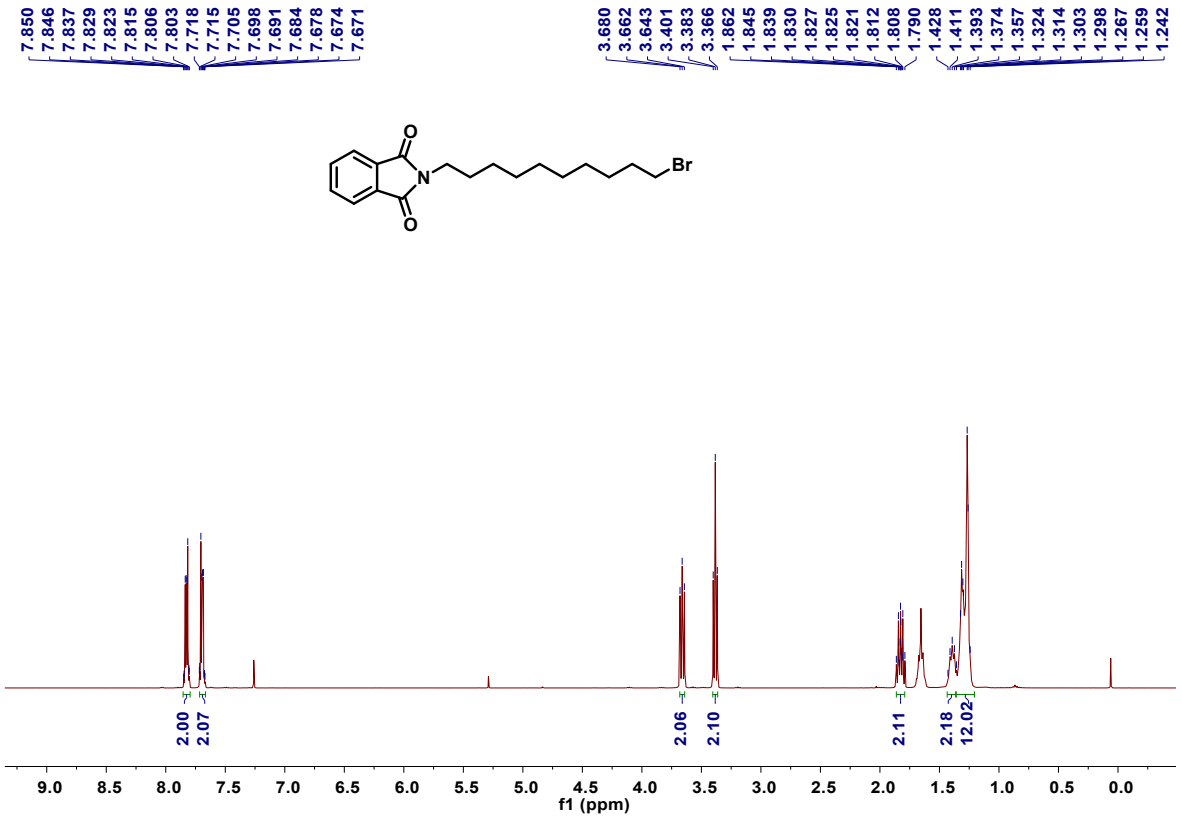


Fig. S3 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3**.

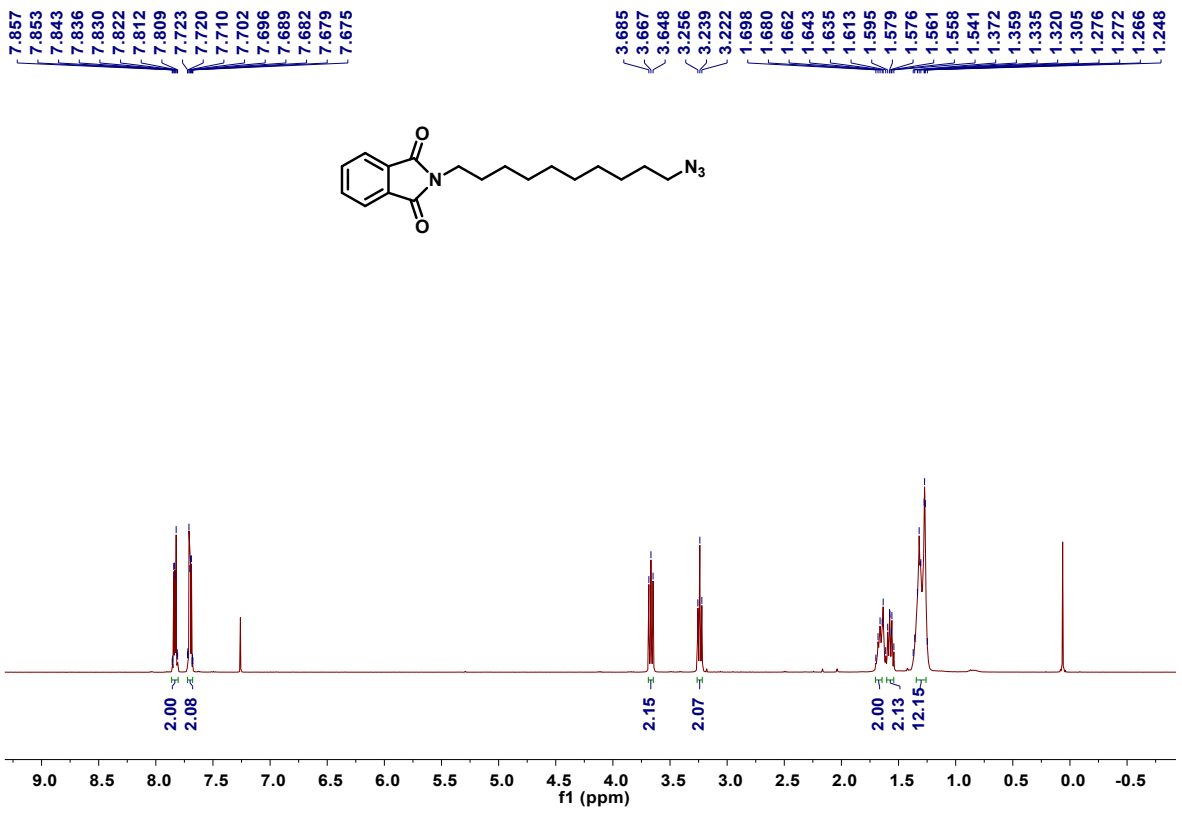


Fig. S4 ^{1}H NMR spectrum 500 MHz, $CDCl_3$) of compound **4**.

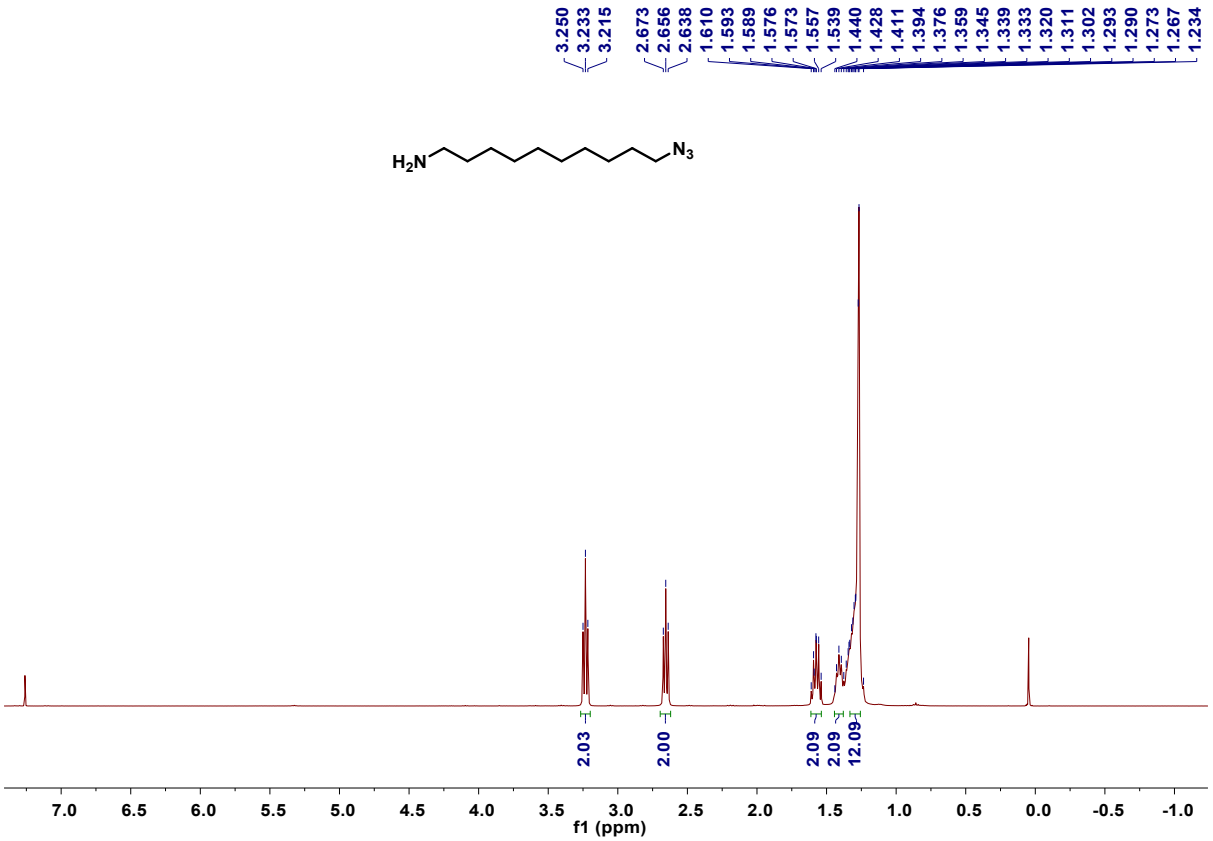


Fig. S5 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5**.

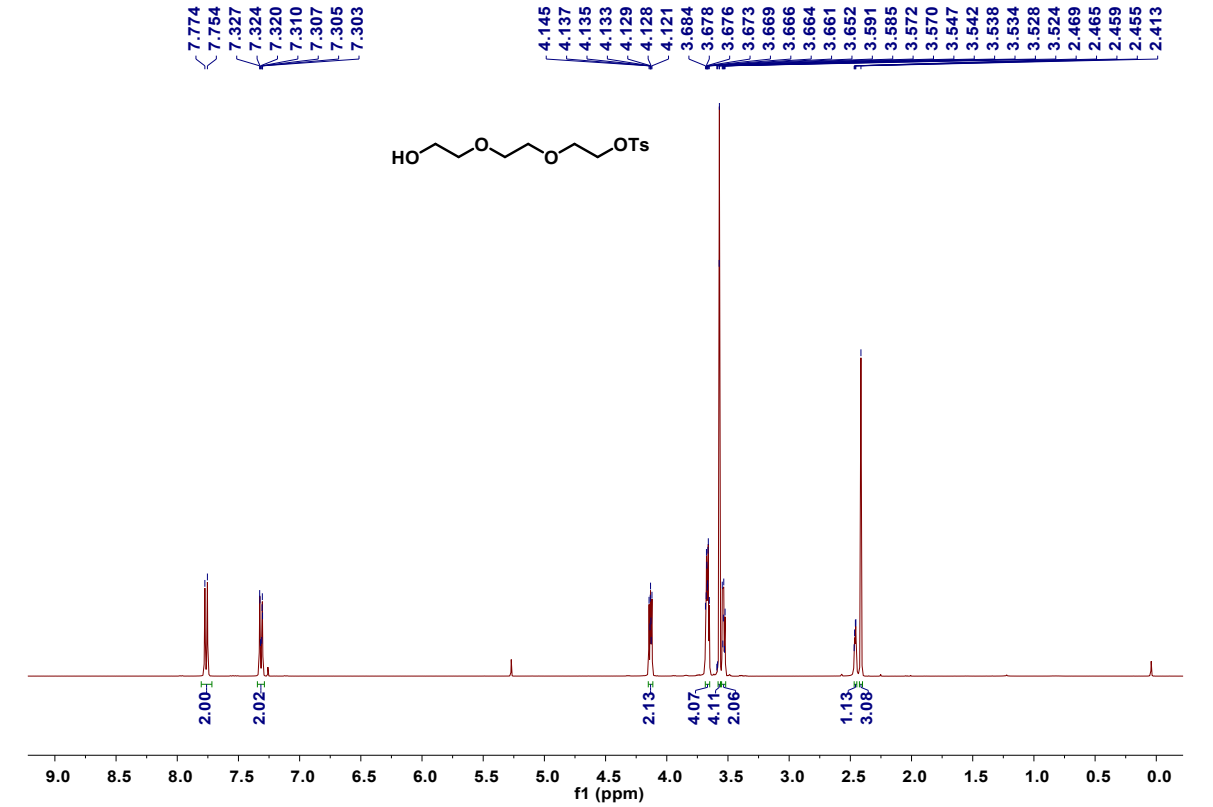


Fig. S6 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6**.

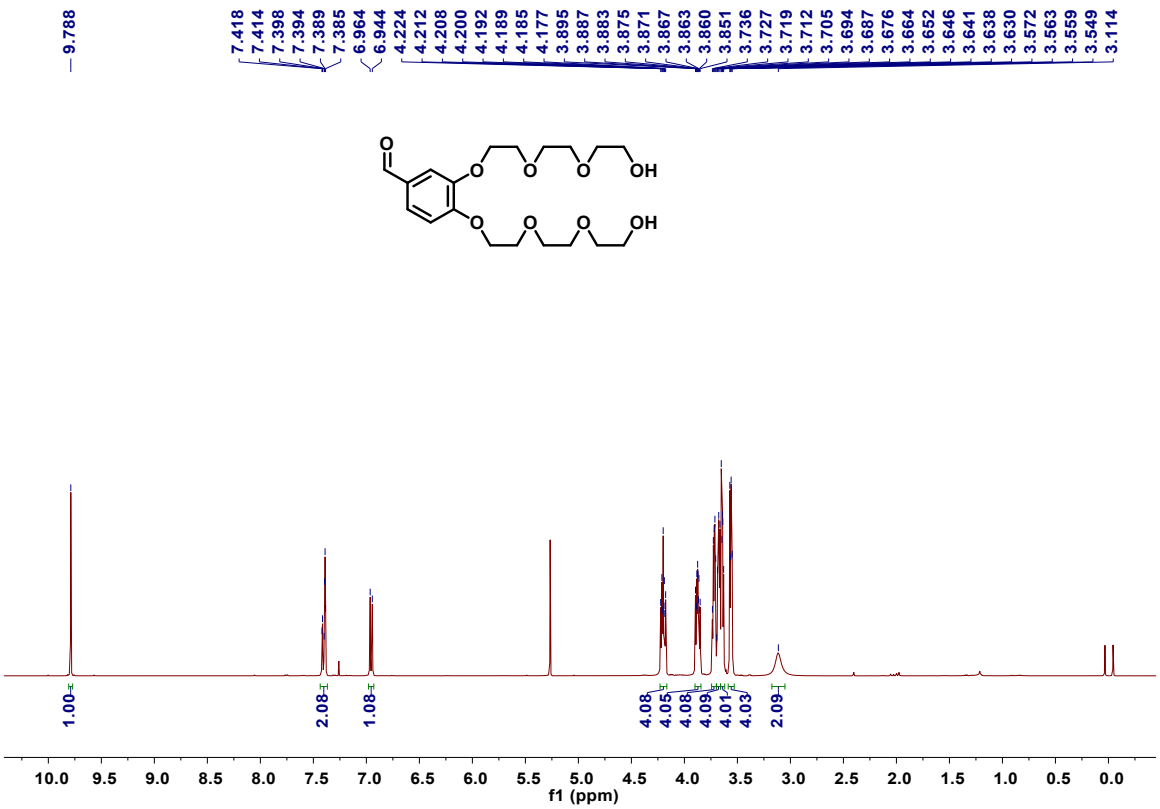


Fig. S7 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**.

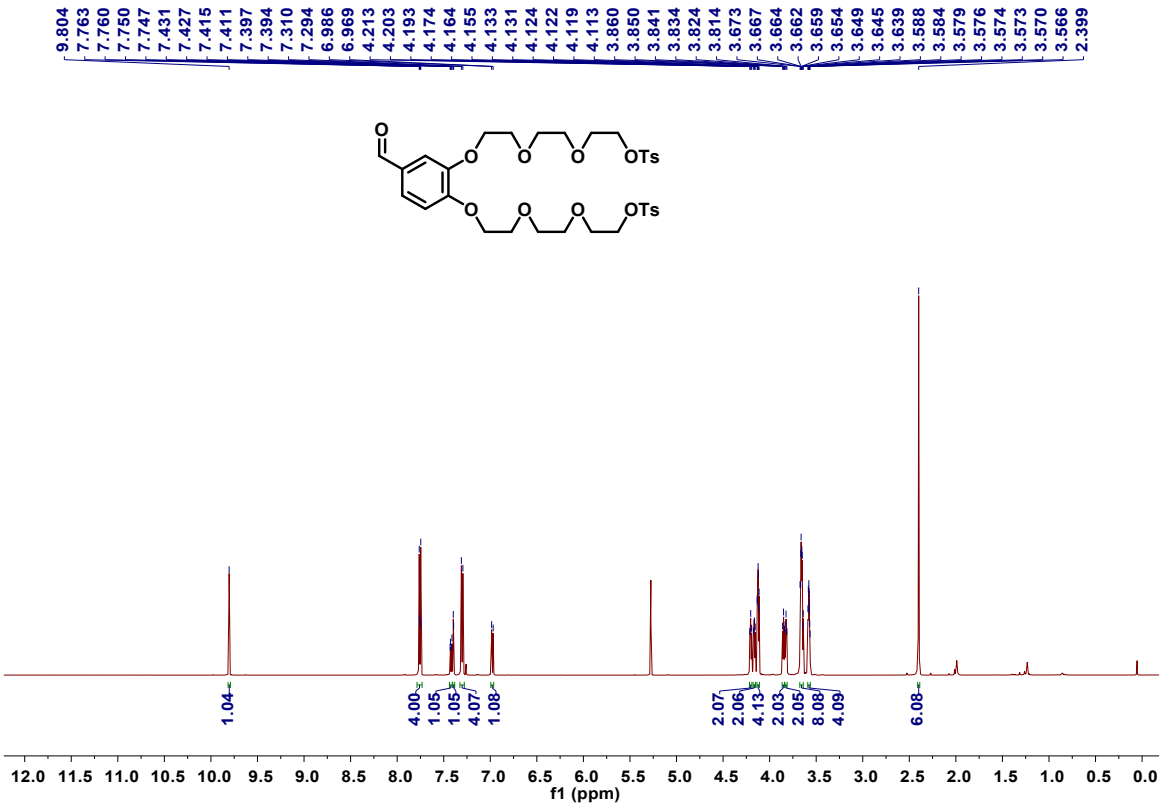


Fig. S8 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **8**.

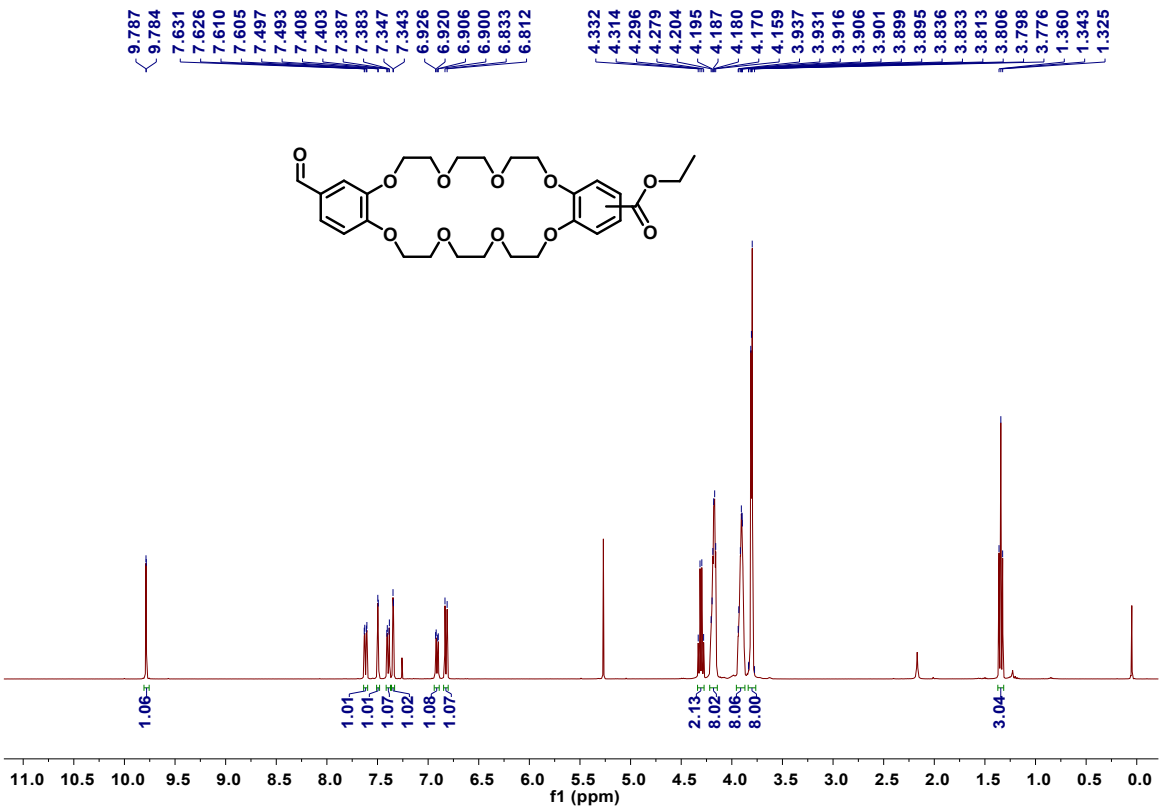


Fig. S9 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **9**.

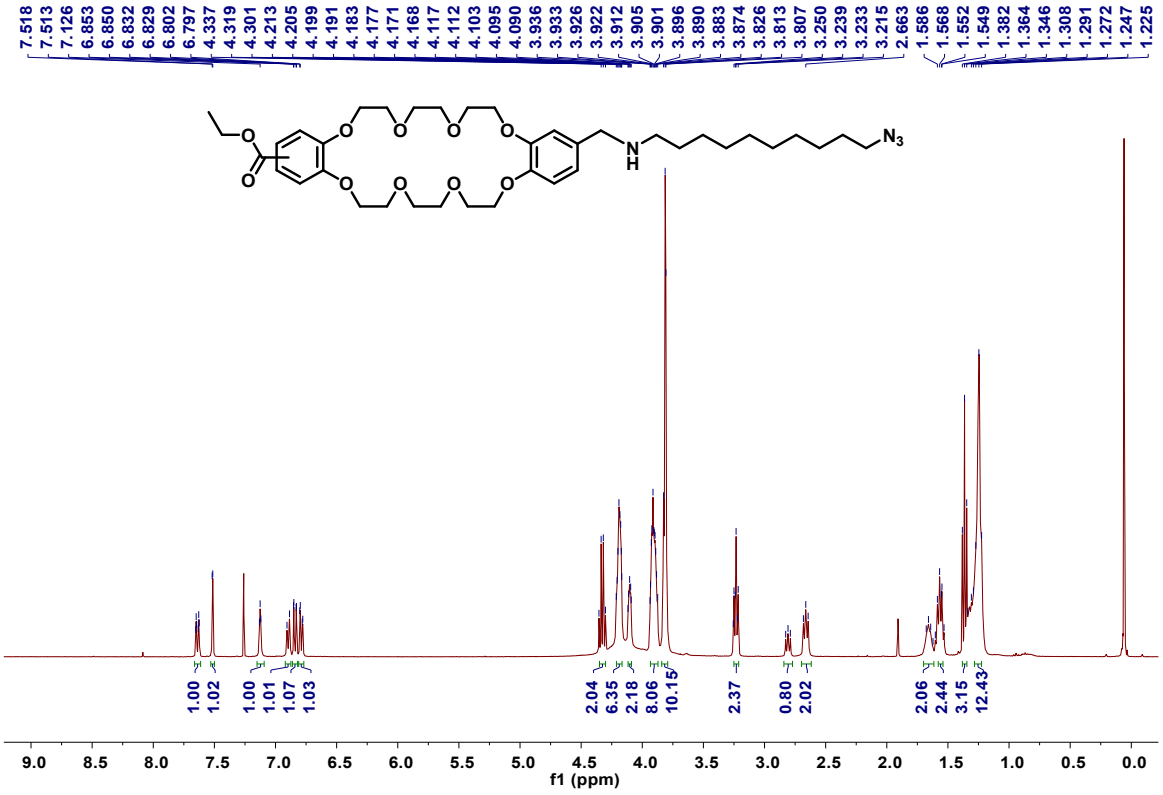
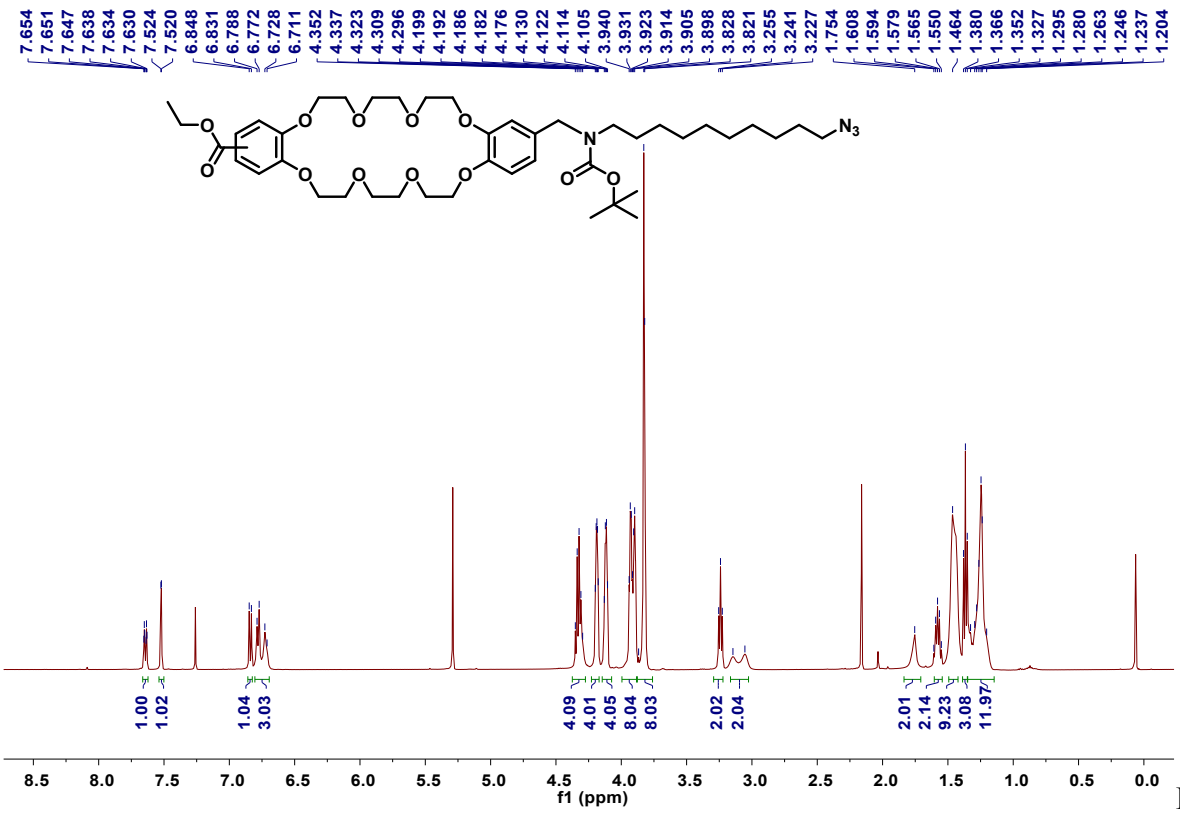


Fig. S10 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10**.



Fi

g. S11 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **11**.

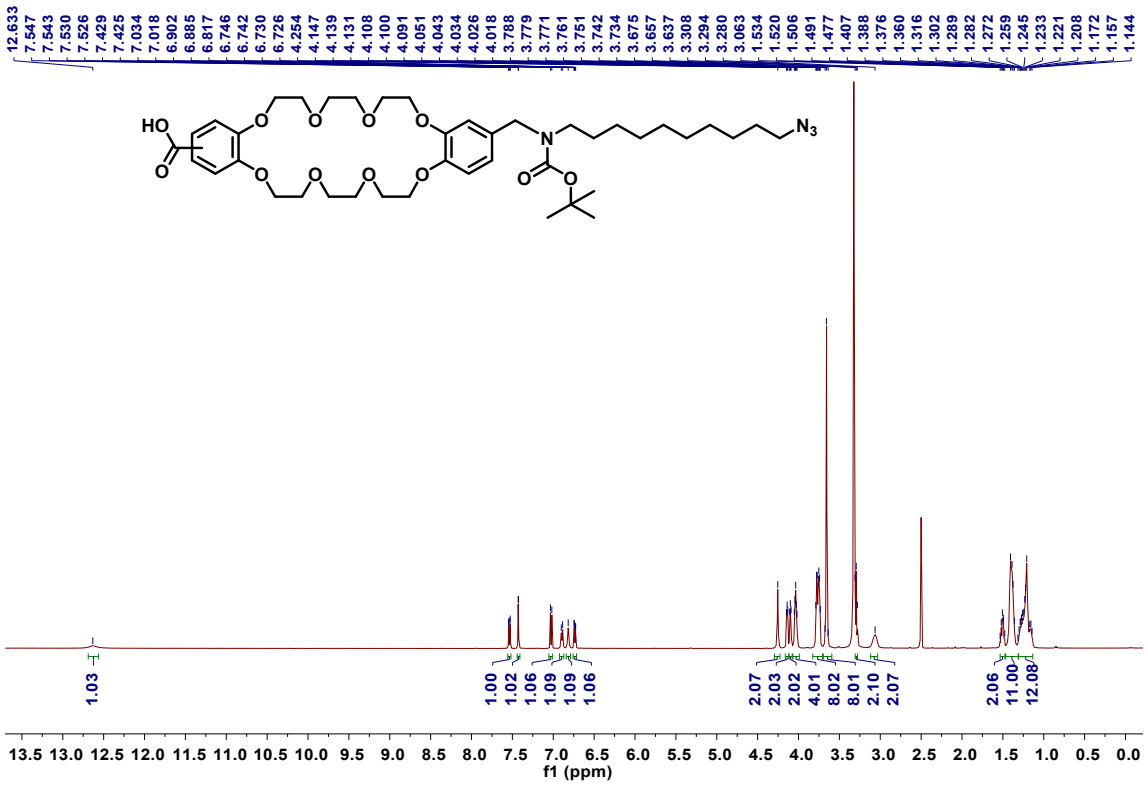


Fig. S12 ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of compound **12**.

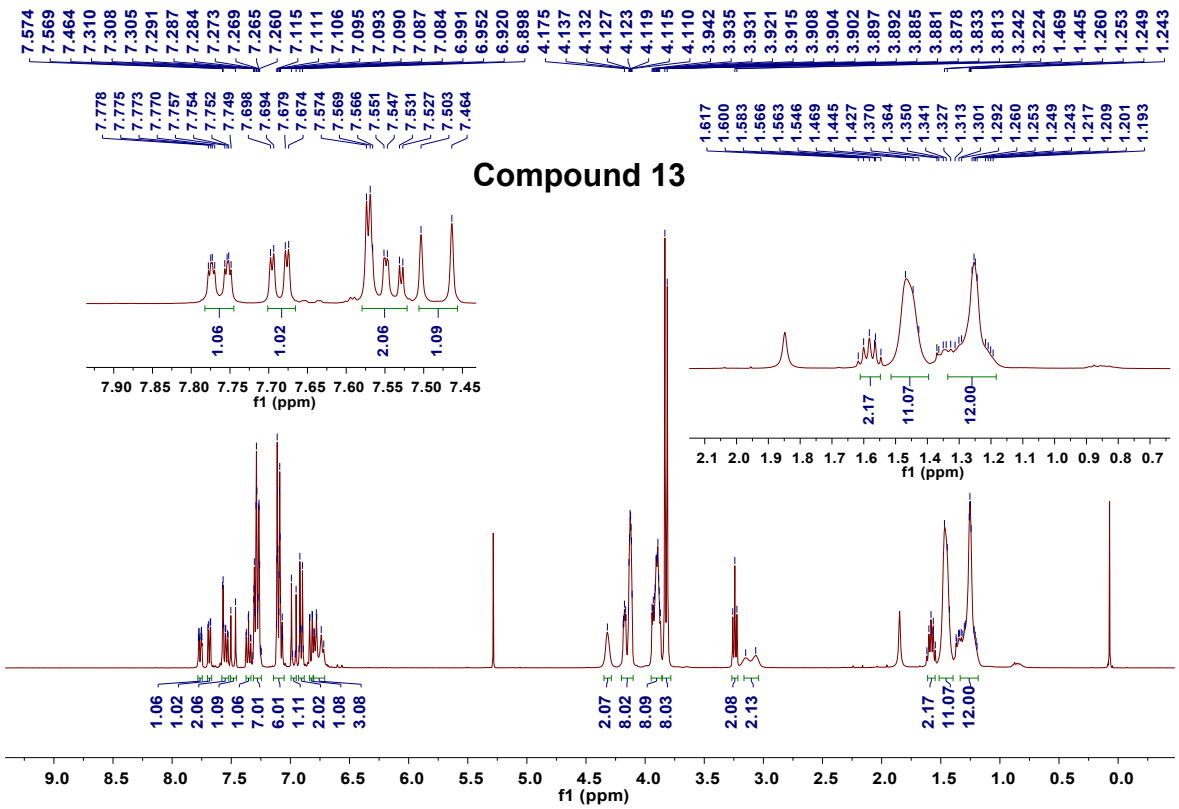


Fig. S13 ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **13**.

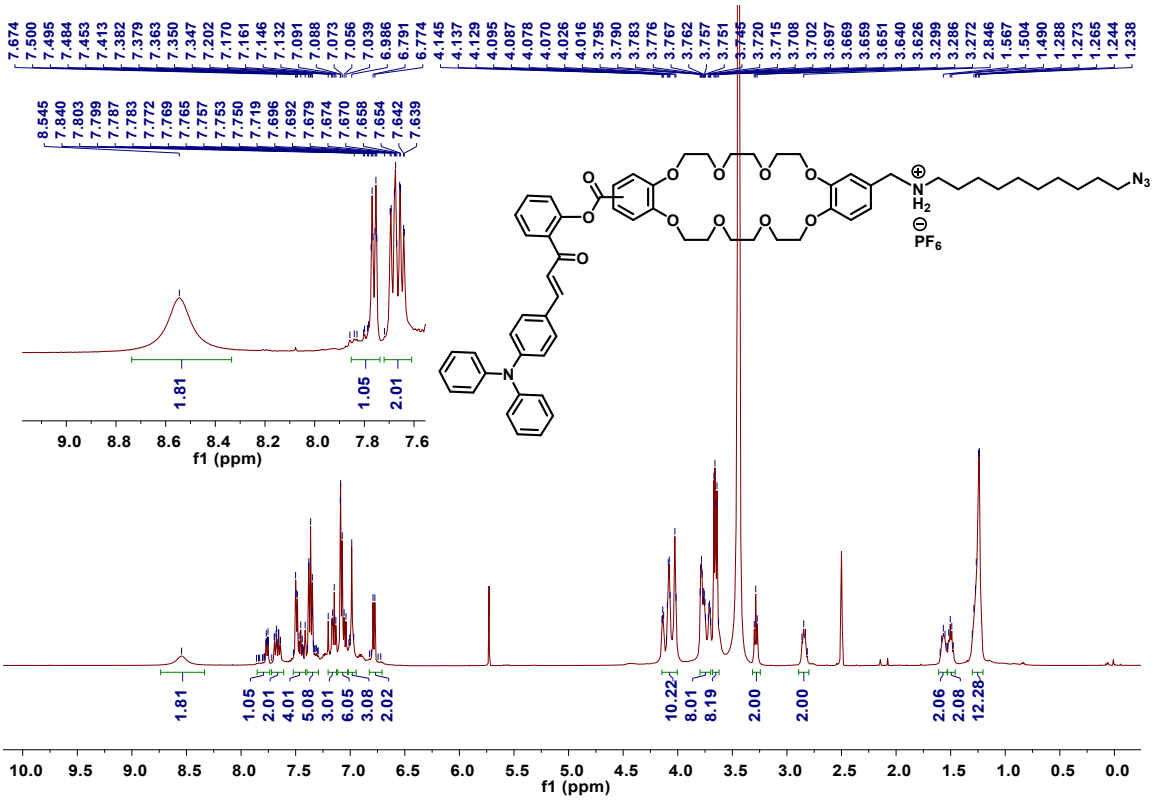


Fig. S14 ^{1}H NMR spectra (500 MHz, DMSO-d_6) of compound **Cy**$^{+}$.

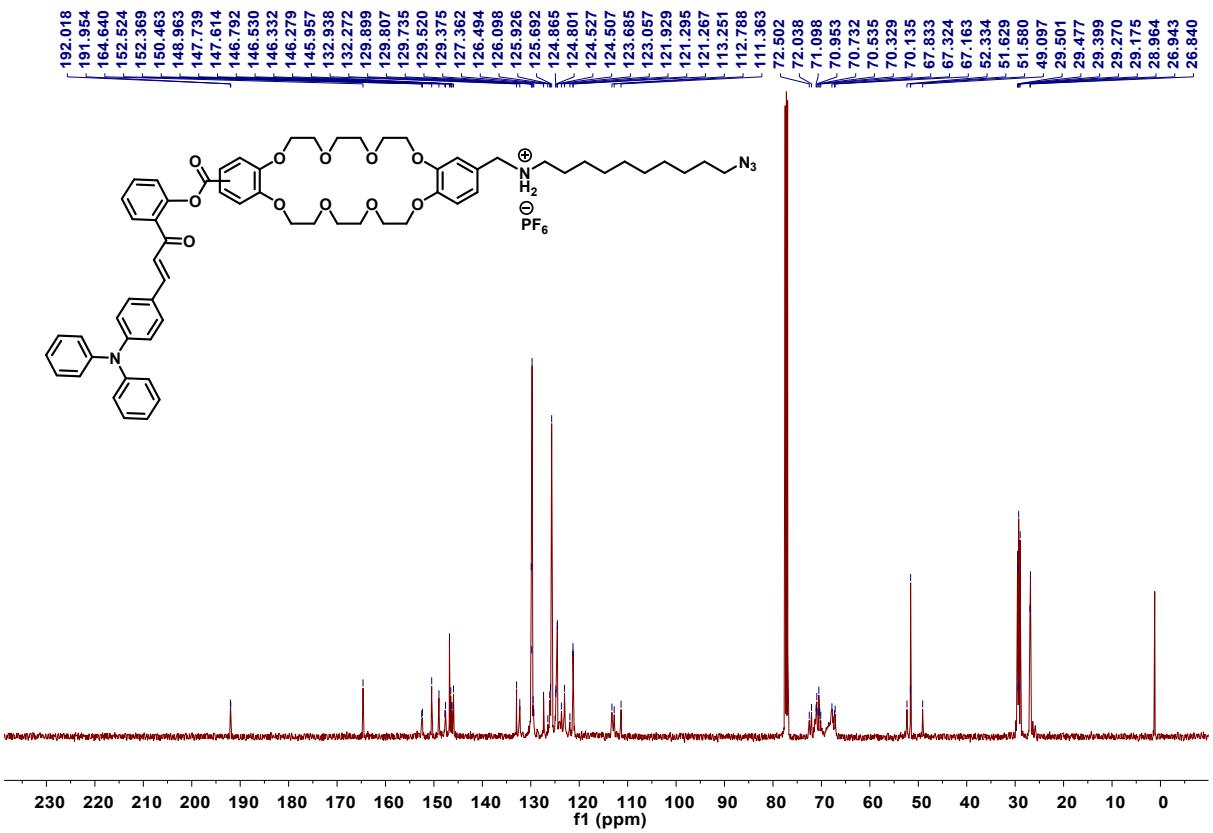


Fig. S15 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **Cy**$^+$.

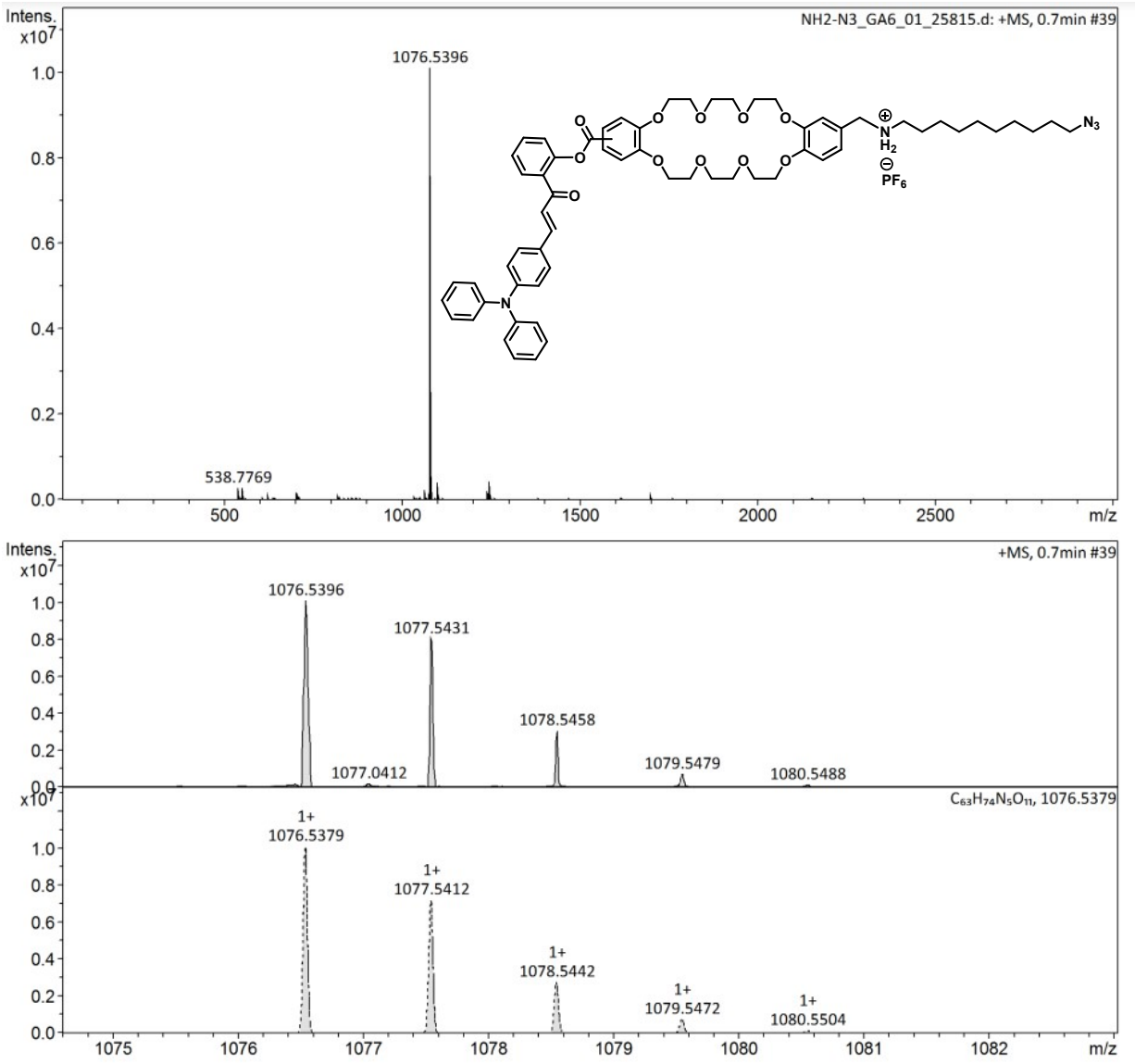


Fig. S16 HRMS-ESI spectra of compound **Cy**$^{+}$.

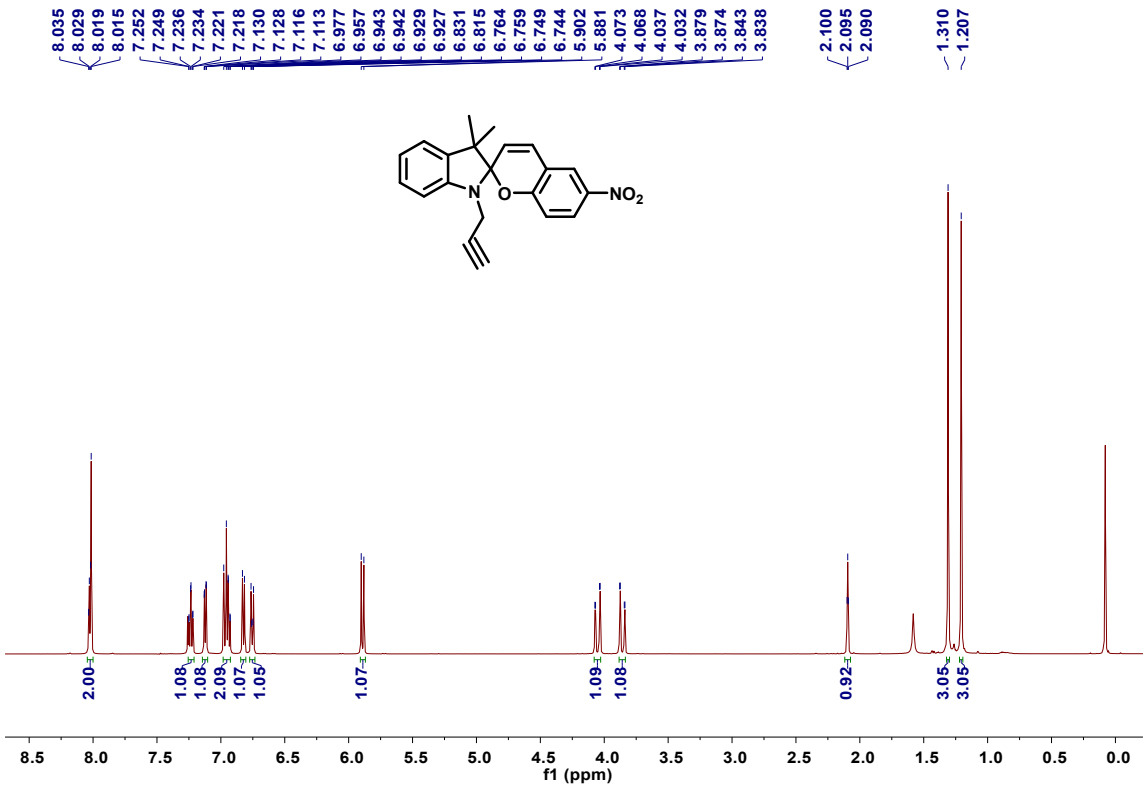


Fig. S17 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **SP-C_3H_3**.

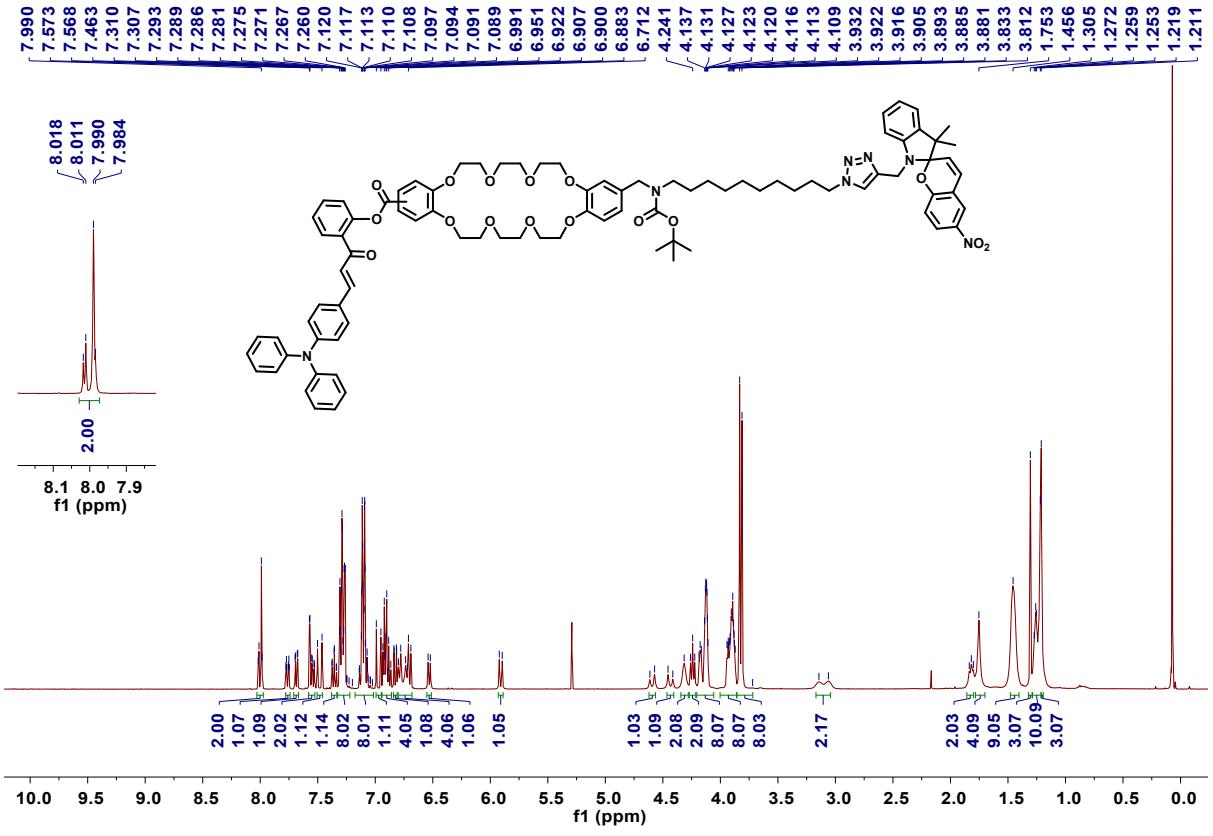


Fig. S18 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **14**.

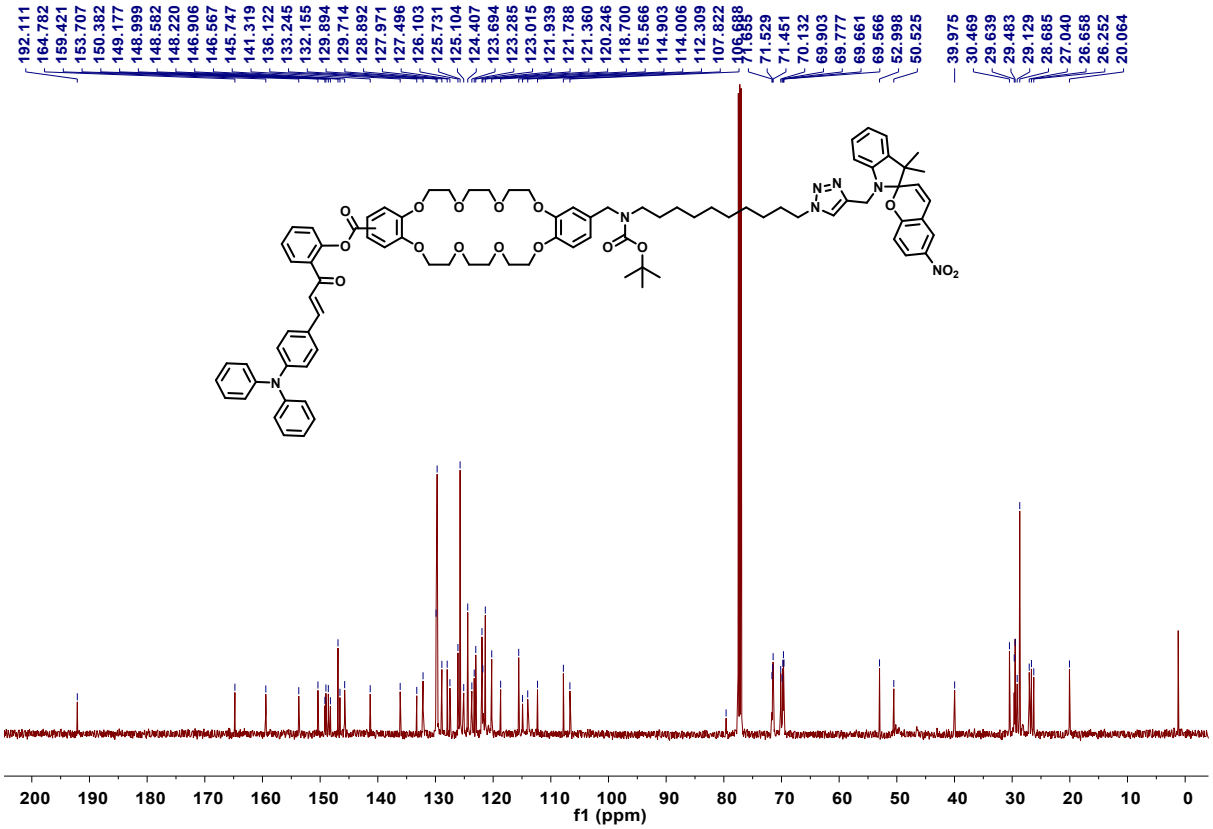


Fig. S19 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **14**.

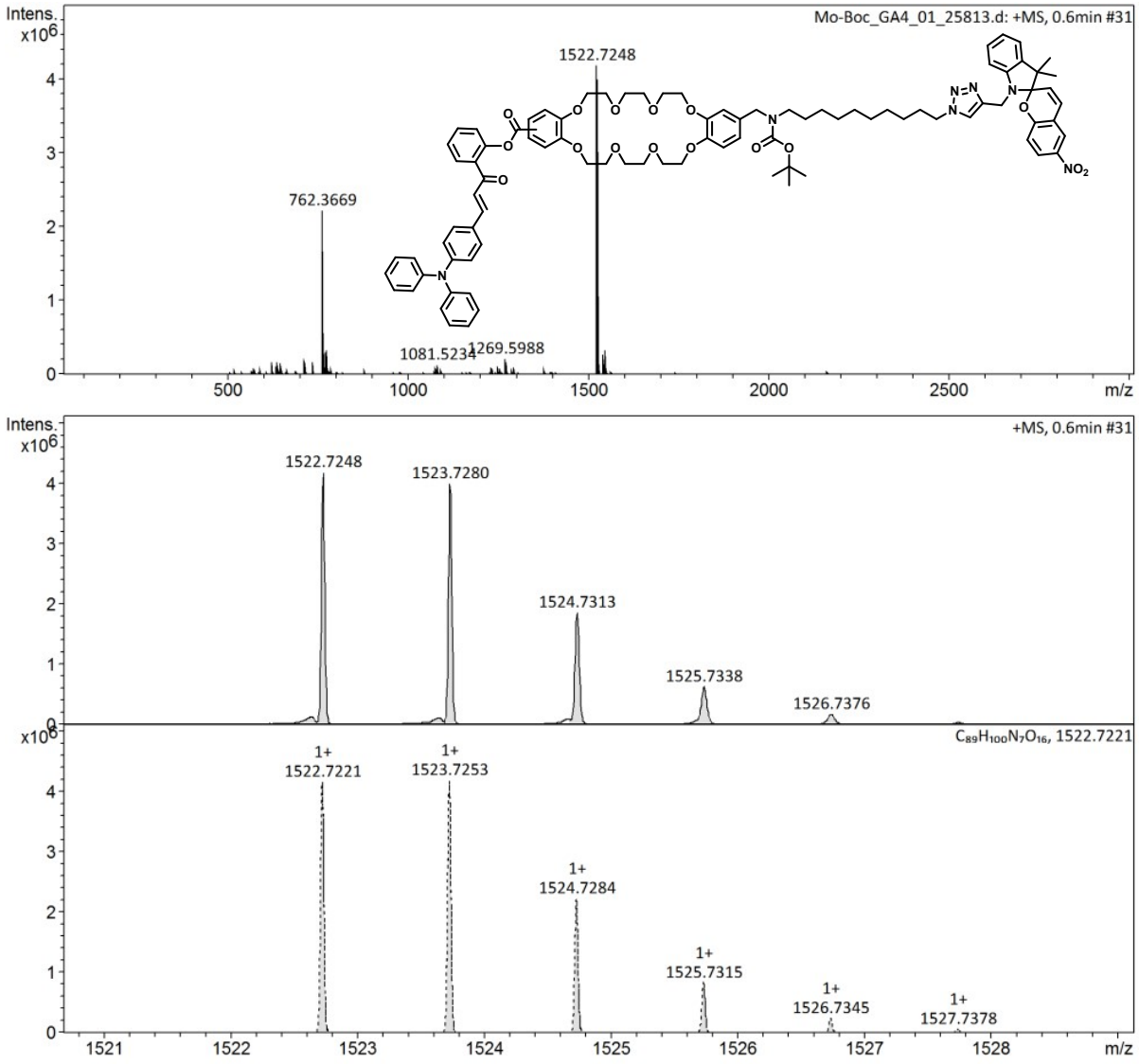


Fig. S20 HRMS-ESI spectra of compound **14**.

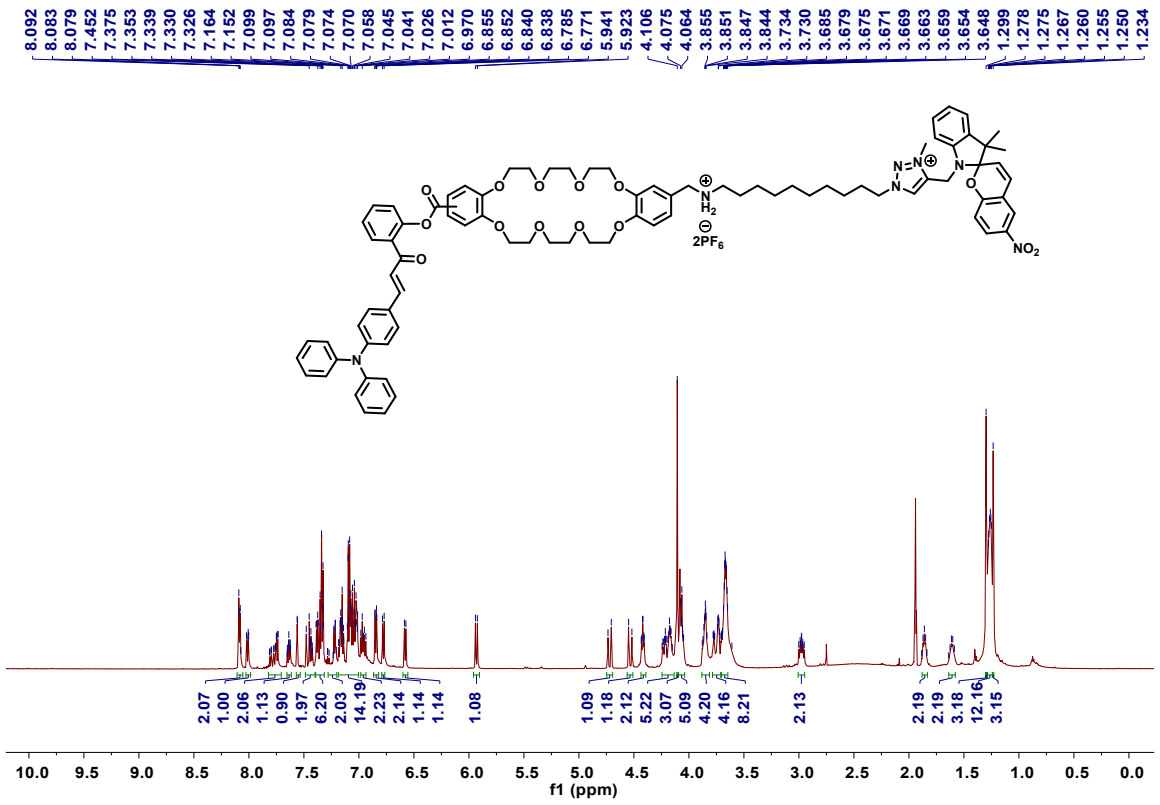


Fig. S21 ^{1}H NMR spectrum (600 MHz, CD_3CN) of **Cy-SP**.

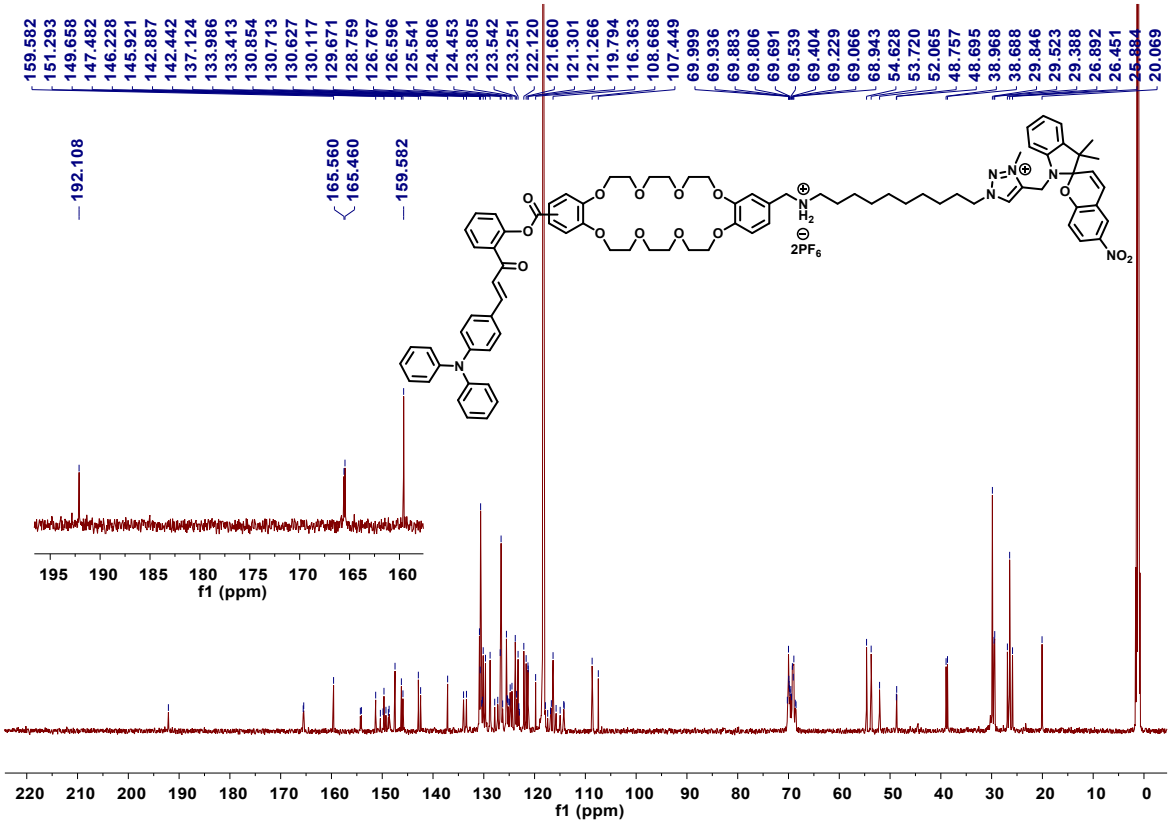


Fig. S22 ^{13}C NMR spectrum (150 MHz, CD_3CN) of **Cy-SP**.

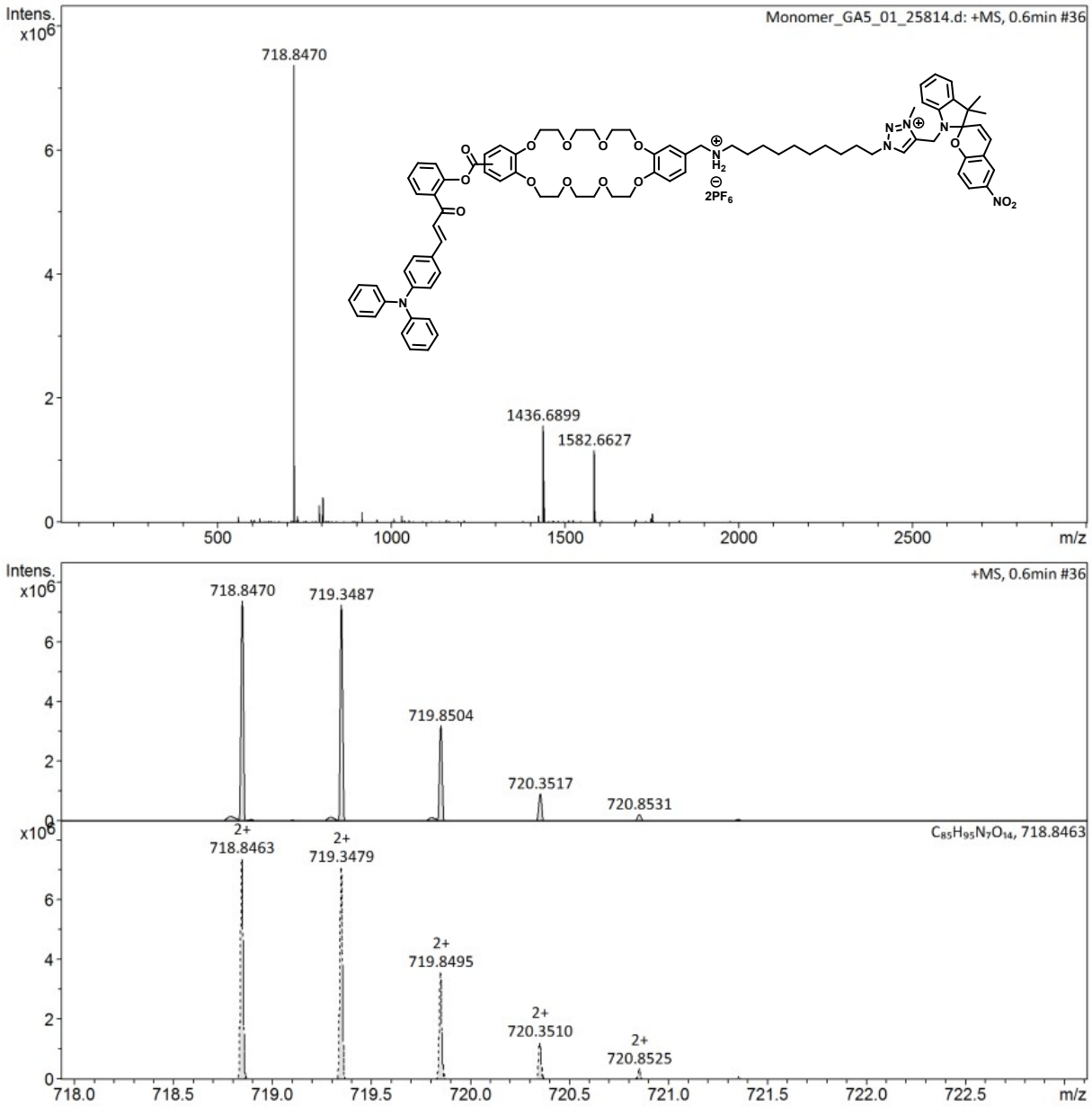


Fig. S23 HRMS-ESI spectra of **Cy-SP**.

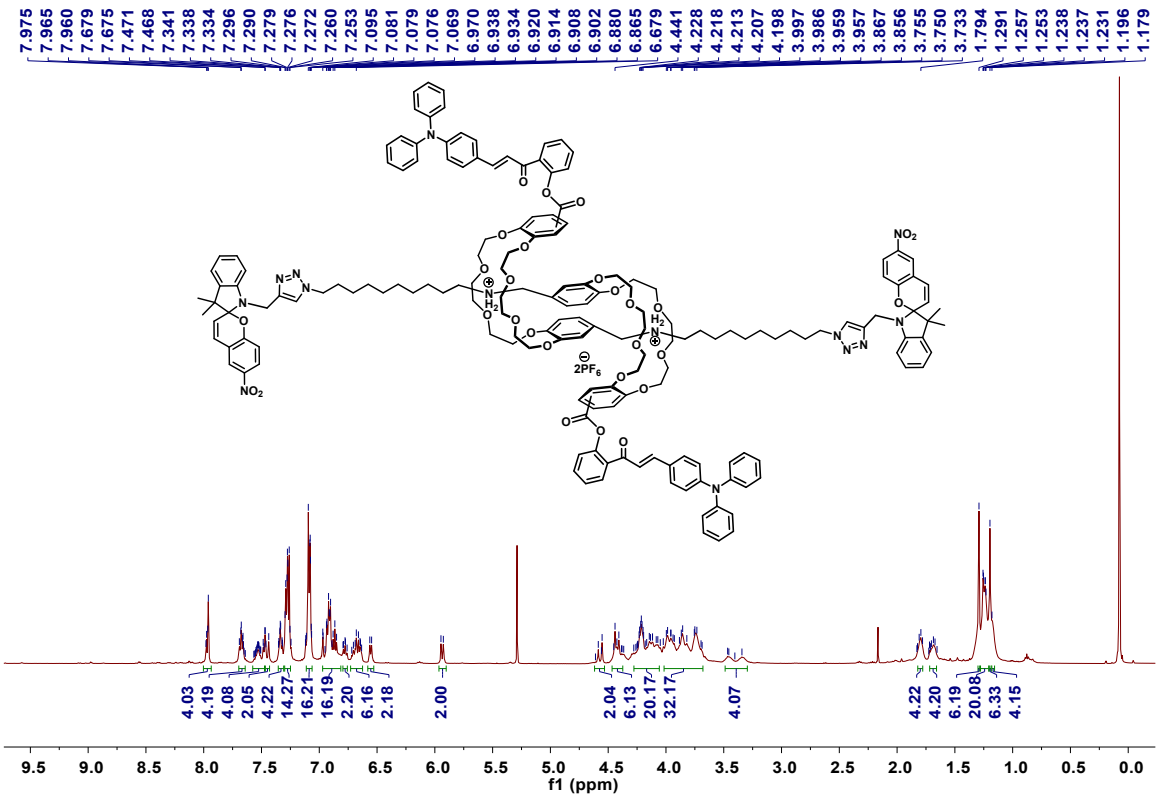


Fig. S24 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **[*c2*]-SP**.

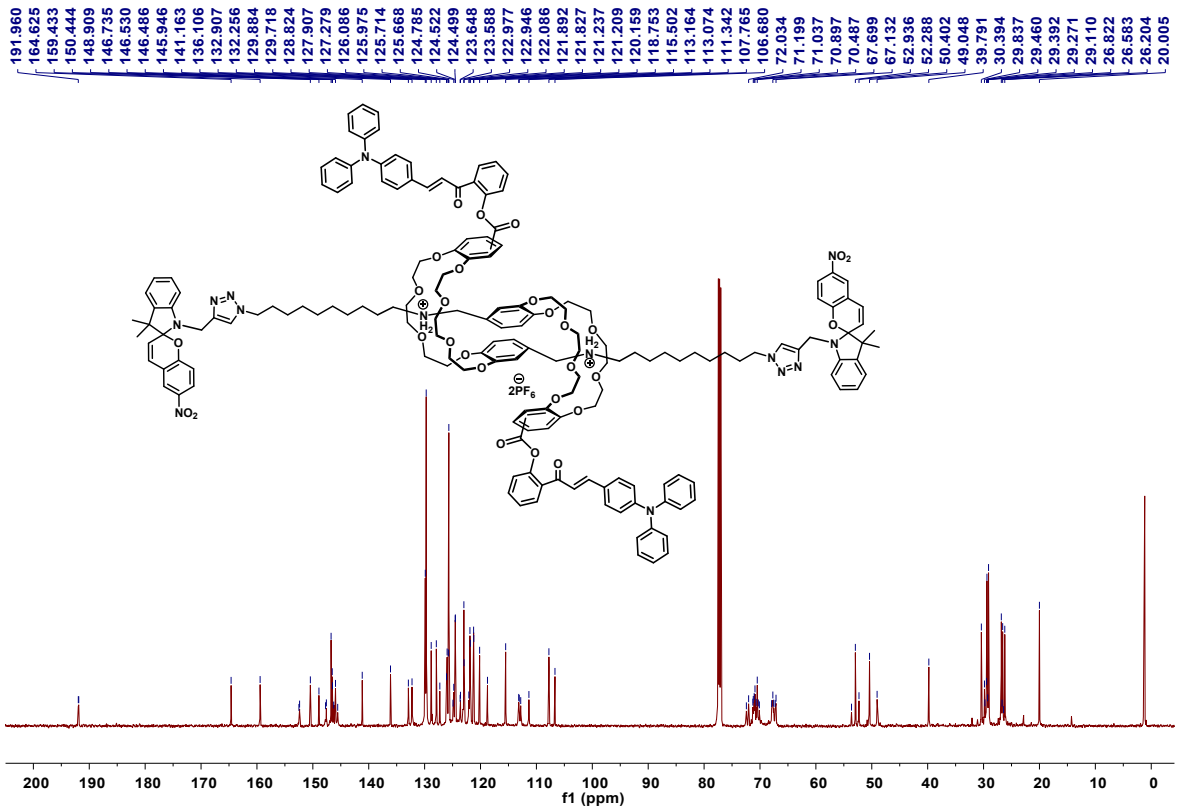


Fig. S25 ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of **[*c2*]-SP**.

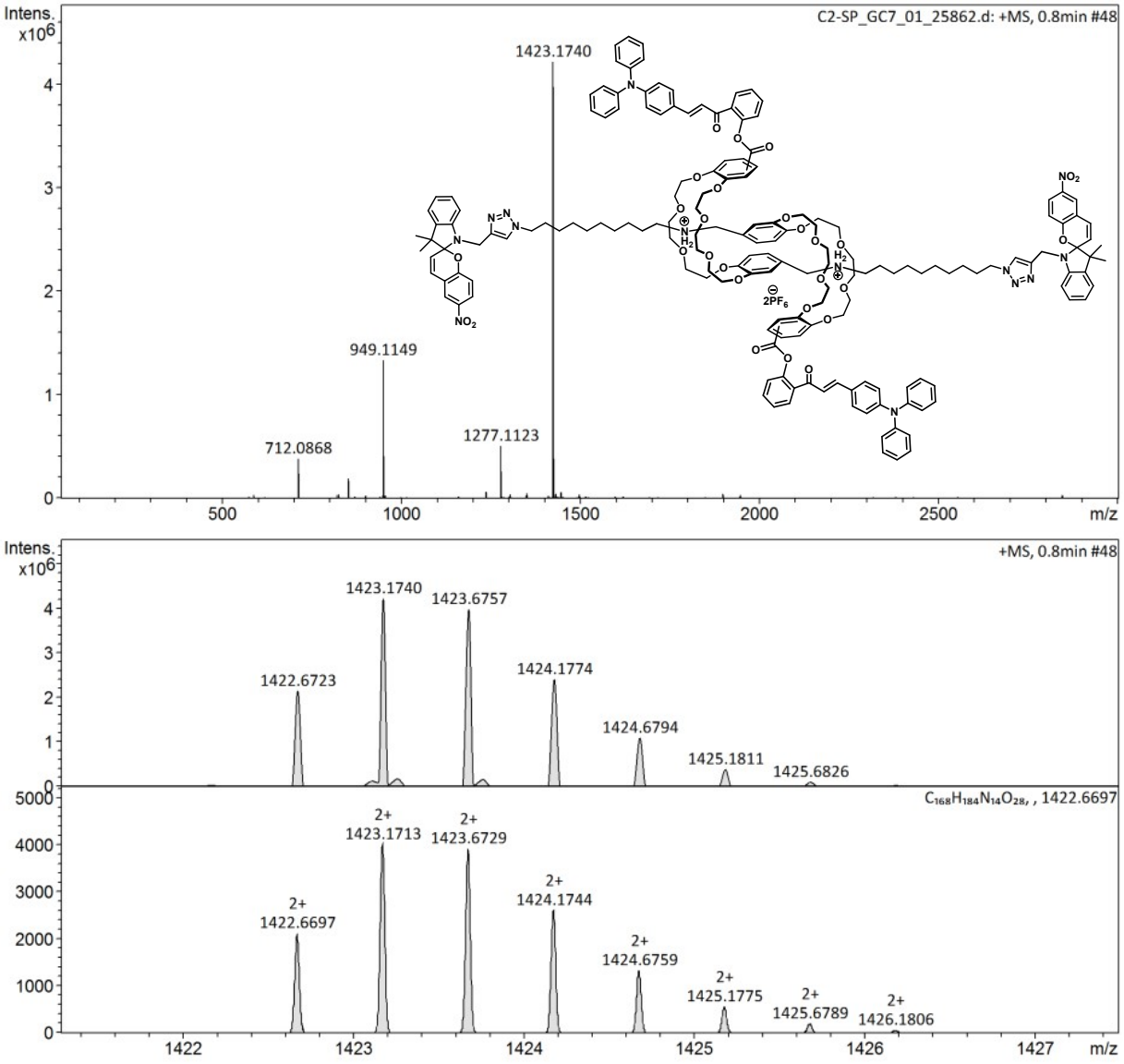


Fig. S26 HRMS-ESI spectra of **[*c2*]-SP**.

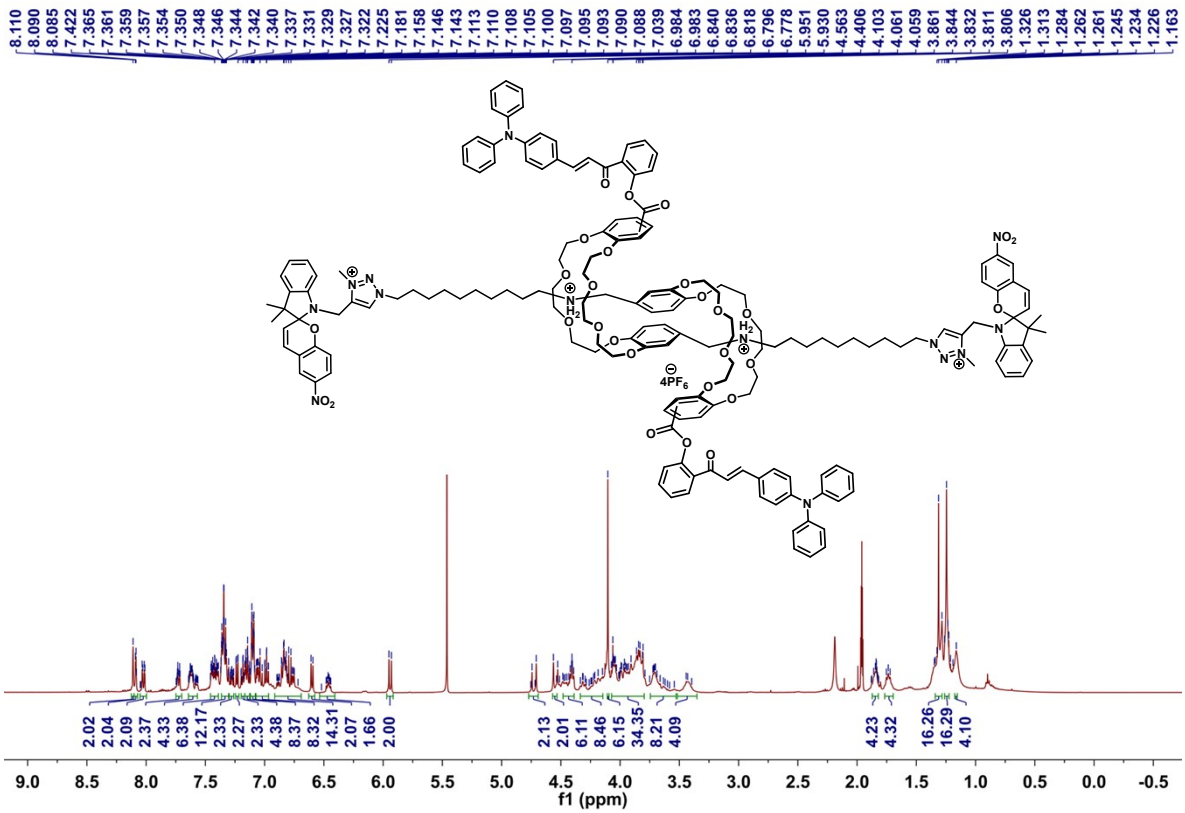


Fig. S27 ^{1}H NMR spectrum (500 MHz, CD_3CN) of **[*c2*]-SP-Ext**.

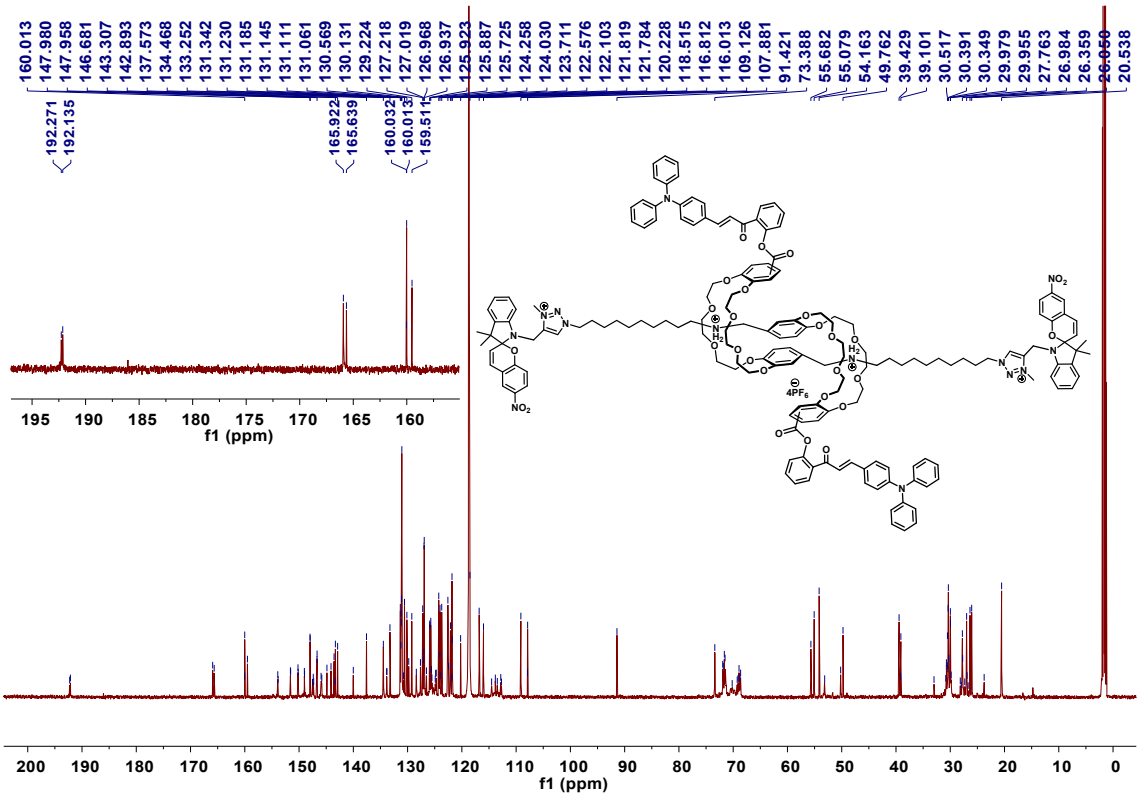


Fig. S28 ^{13}C NMR spectra (150 MHz, CD_3CN) of **[*c2*]-SP-Ext**.

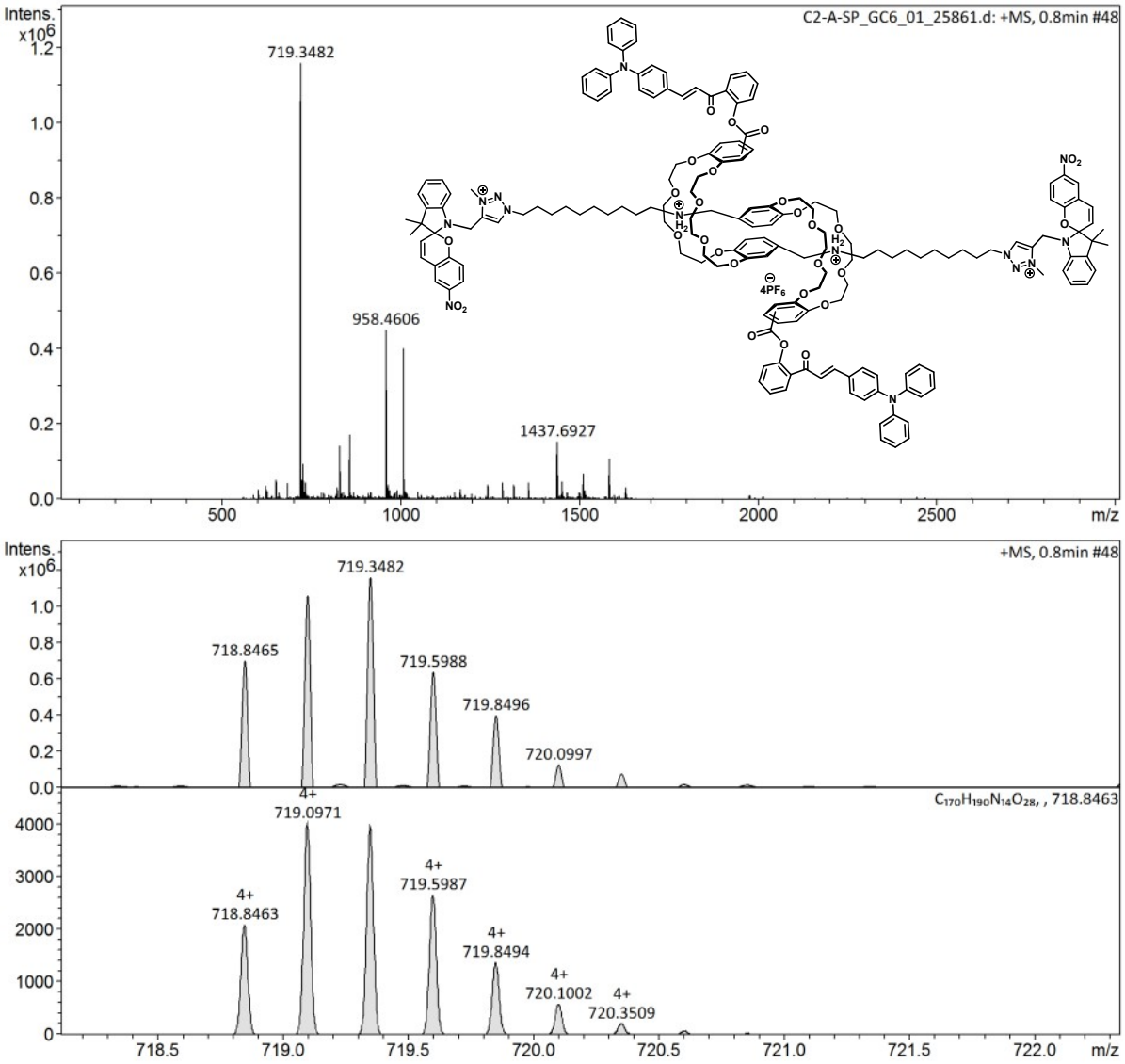


Fig. S29 HRMS-ESI spectra of **[*c2*]-SP-Ext**.

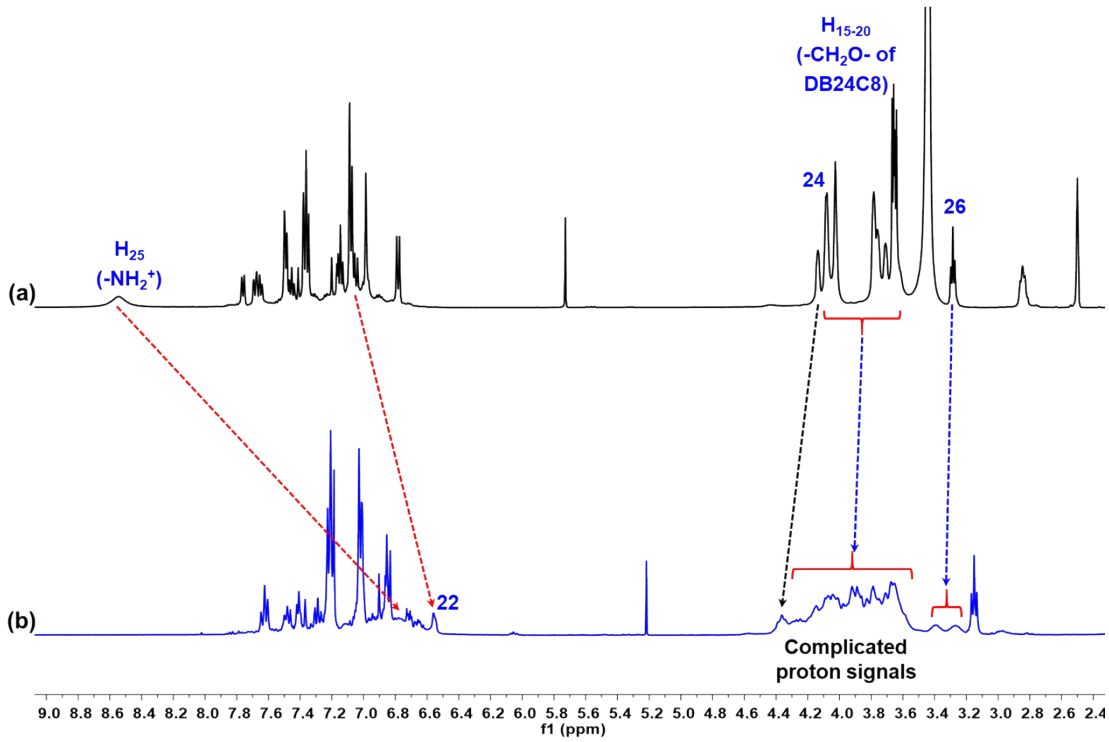


Fig. S30 Partial ^{1}H NMR spectra (400 MHz, 298 K) of compound **Cy**$^{+}$ in (a) DMSO-d_6 (**Cy**$^{+}$ monomer) and (b) $CDCl_3$ (**Cy**$^{+}$ dimer, ***pseudo*-[*c*2]**).

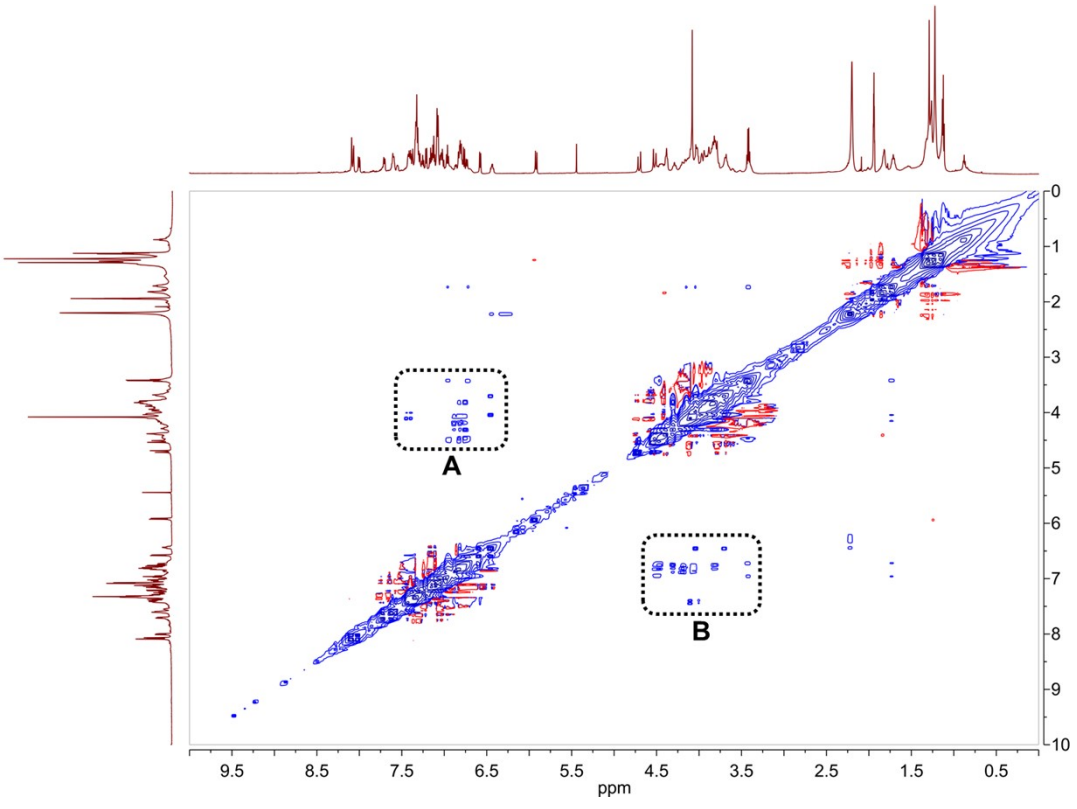


Fig. S31 2D NOESY NMR spectrum (600 MHz, CD_3CN) of **[*c*2]-SP-Ext**.

3. Photo-physical studies of compounds

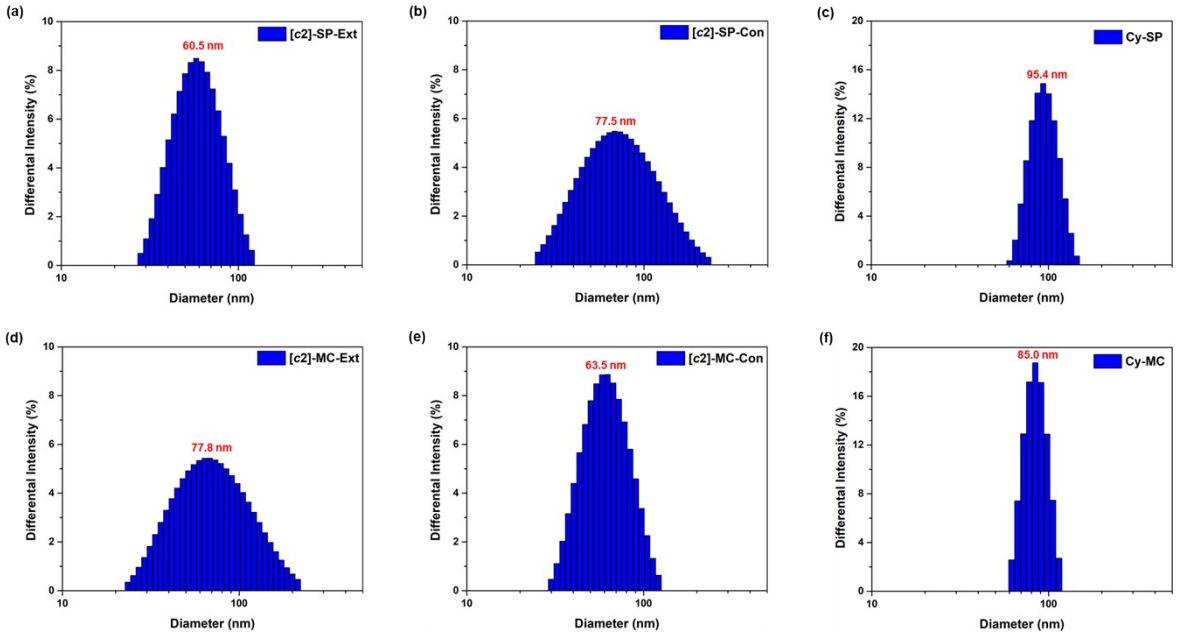


Fig. S32 DLS results of (a,d) **[*c*2]-SP-Ext** and **[*c*2]-MC-Ext**, (b,e) **[*c*2]-SP-Con** and **[*c*2]-MC-Con** and (c,f) **Cy-SP** and **Cy-MC** in THF/H_2O solutions (90% H_2O). Concentrations: [*c*2] daisy chains = 20 μM, **Cy-SP** = 40 μM.

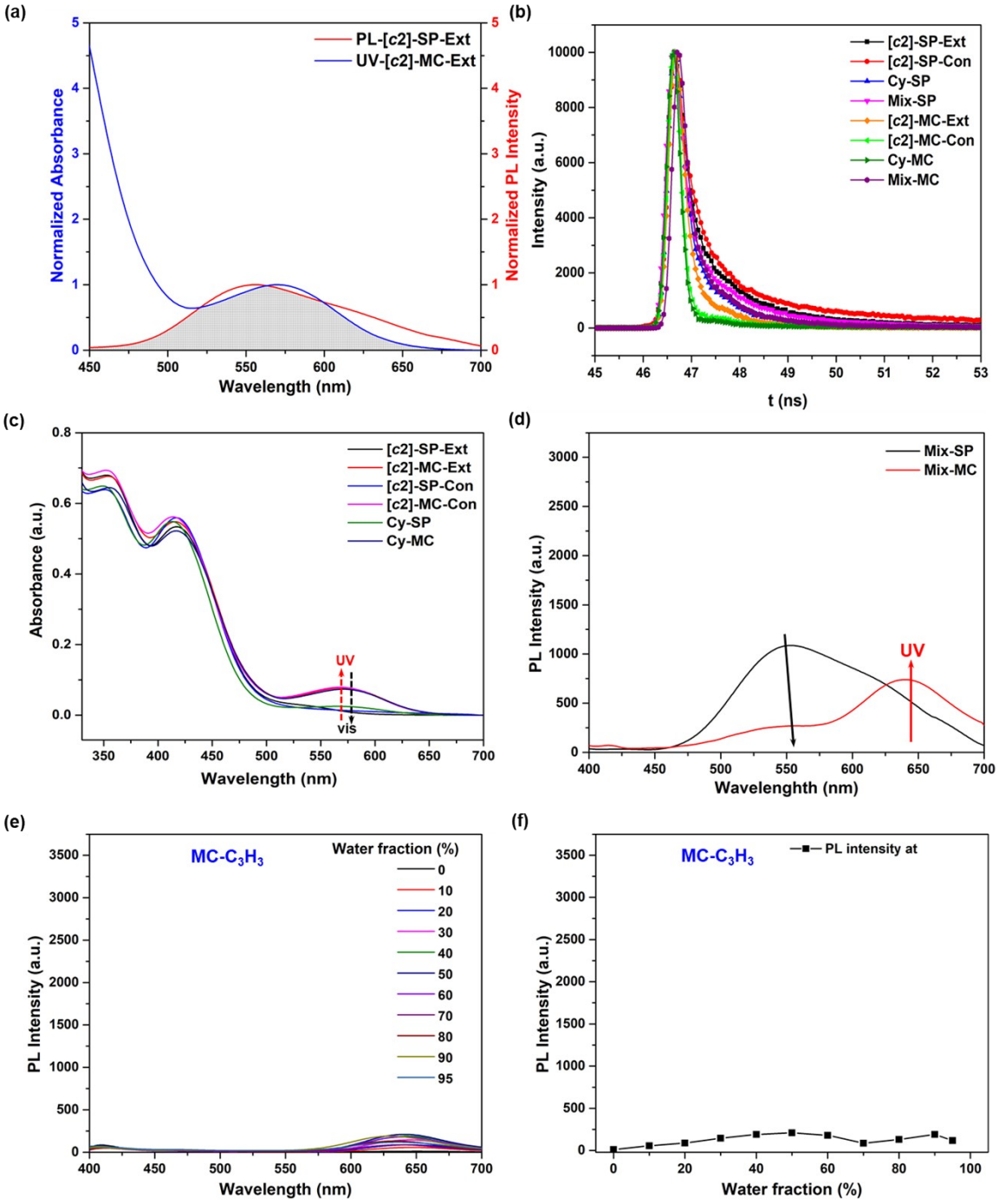


Fig. S33 (a) Spectral overlap of **[*c*2]-SP-Ext** emission (λ_{ex} = 365 nm) and **[*c*2]-MC-Ext** absorbance in THF/H_2O solutions (90% H_2O, v/v), (b) TRPL spectra of [*c*2] daisy chain rotaxanes, non-interlocked analogues and mixtures (λ_{ex} = 375 nm, λ_{em} = 556 nm), (c) absorption spectra of [*c*2] daisy chain rotaxanes and non-interlocked analogues, (d) PL spectra of mixtures under UV/Vis lights, (e) PL spectra and (f) relative PL intensities of **MC-C_3H_3** in THF/H_2O with different water fractions. Concentrations: [*c*2] daisy chains = 20 μM, **Cy-SP** = **MC-C_3H_3** = 40 μM, λ_{ex} = 365 nm.

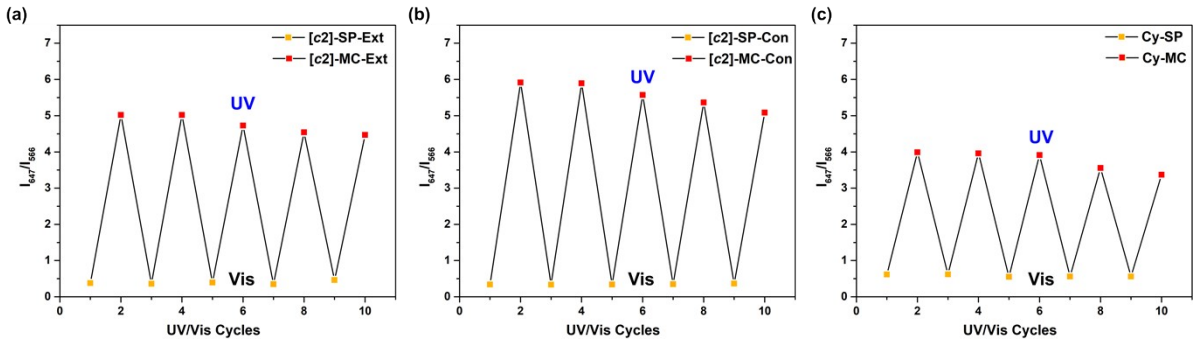


Fig. S34 Reversible fluorescence switching of (a) **[*c*2]-SP-Ext ↔ [*c*2]-MC-Ext**, (b) **[*c*2]-SP-Con ↔ [*c*2]-MC-Con** and (c) **Cy-SP ↔ Cy-MC** under alternative UV/Vis exposures.

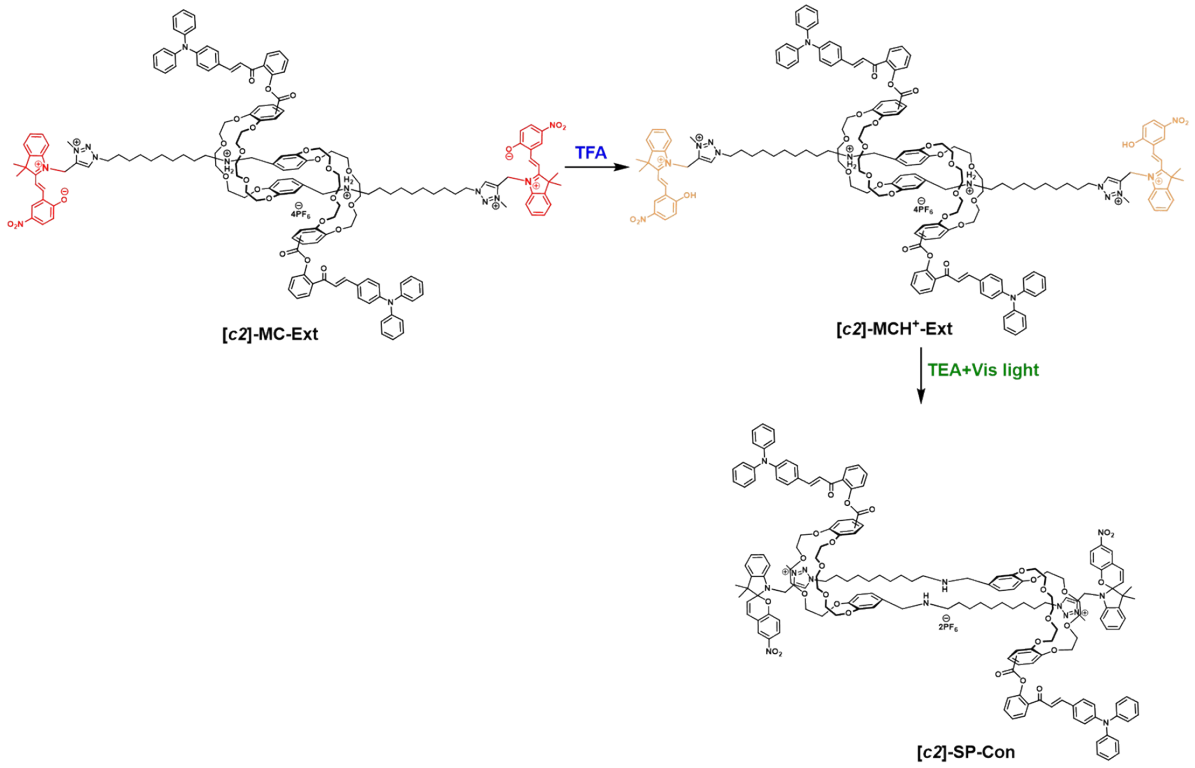


Fig. S35 Acid-base responses of **[*c*2]-MC-Ext** upon TFA/TEA treatments.

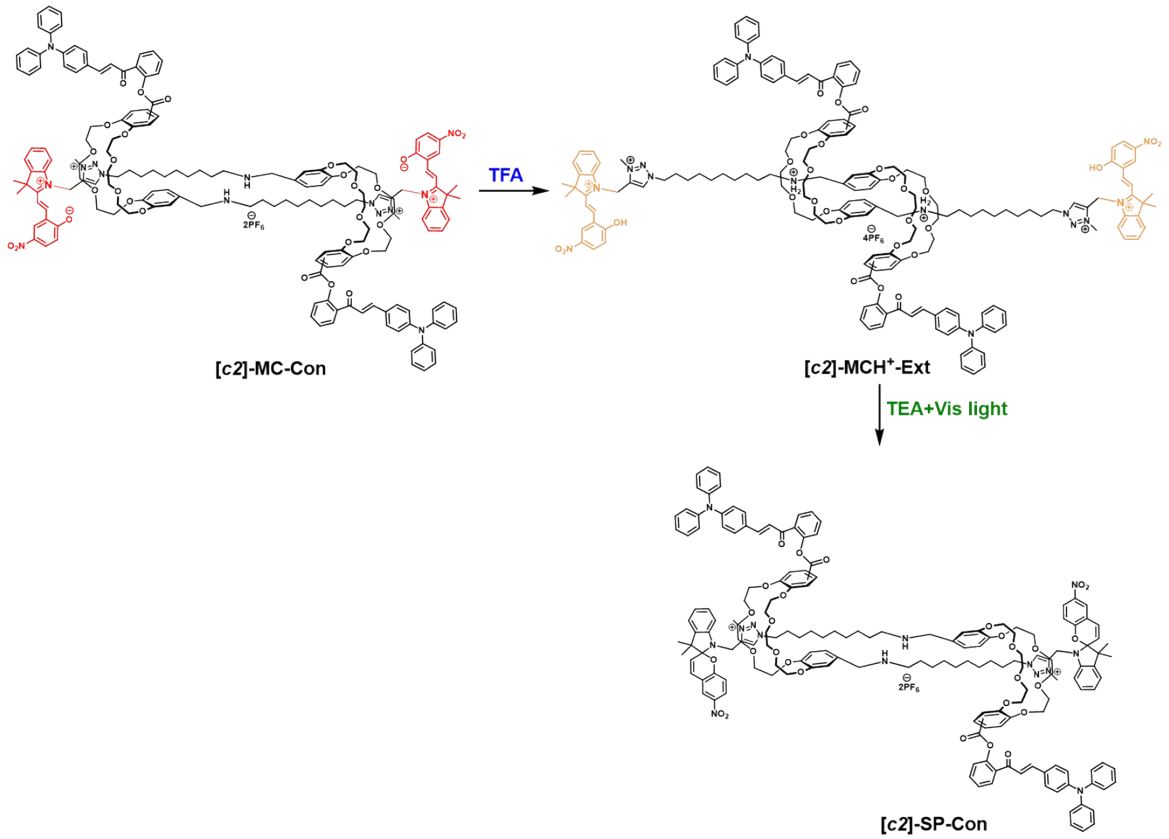


Fig. S36 Acid-base responses of **[*c*2]-MC-Con** upon TFA/TEA treatments.

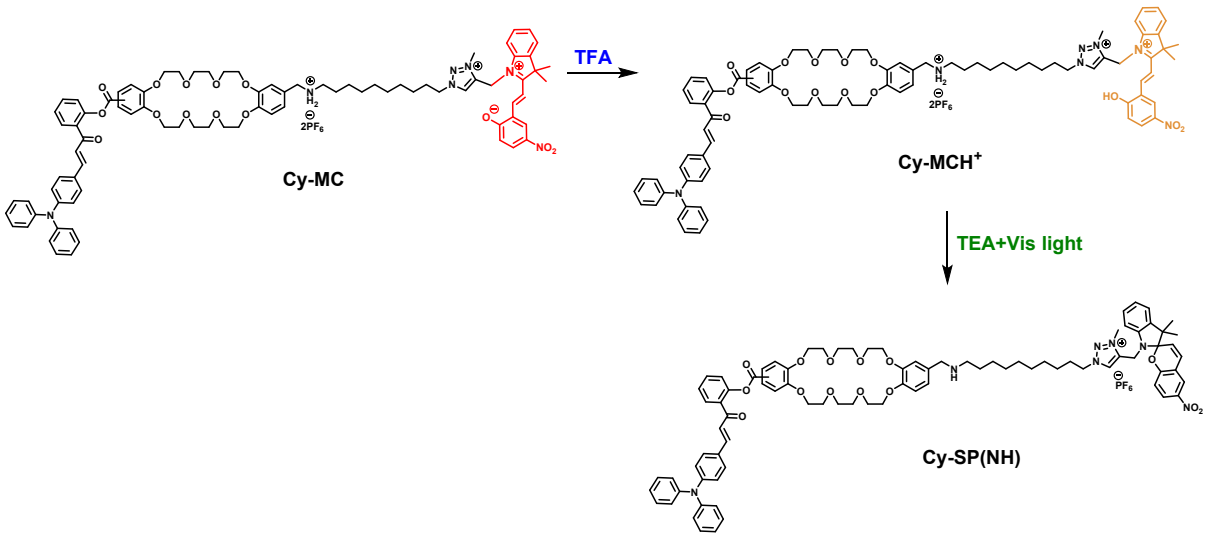


Fig. S37 Acid-base responses of **Cy-MC** upon TFA/TEA treatments.

4. References

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(S6) T. T. K. Cuc, P. Q. Nhien, T. M. Khang, C.-C. Weng, C.-H. Wu, B.-t. B. Hue, Y.-K. Li, J. I. Wu and H.-C. Lin, *Chem. Mater.*, 2020, **32**, 9371-9389.