

Supporting Information

Dual and sequential locked/unlocked photo-switching effects on FRET processes by tightened/loosened nano-loops of diarylethene-based [1]rotaxanes

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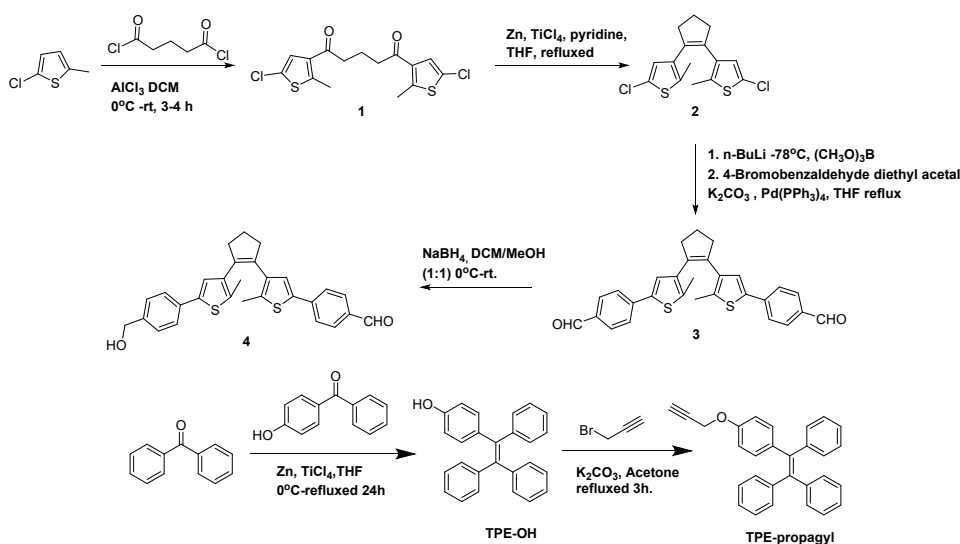
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1. Experimental procedures

Materials. All reagents for reaction were purchased from commercial sources of ACROS, TCI Japan, J. T. Baker, Alfa Aesar and Sigma-Aldrich and directly used without any further purification. For some specific reactions, the solvents were dried by the drying solvent system and deionized water was produced by passing through a water ultra-purification system before using. Nitrogen gas protection condition and vacuum-line manipulation are required for all reactions.

Instruments. NMR measurements were performed on Agilent 400 MHz, Bruker Advance 500 and 600 MHz instruments at 298K. High resolution mass spectra (HRMS) were obtained from Impact HD Q-TOF mass spectrometer (Bruker, Germany) using an electrospray ionization (ESI) source operated for positive ion mode. The elemental analyses (EA) of compounds were performed by Elementar Vario CUBE (CHN-OS Rapid, German). A DelsaNano C particle analyzer (BECKMAN COULTER) was used to determine the average sizes of target compounds based on the dynamic light scattering (DLS) technique. The fluorescence and absorbance spectra of all compounds were recorded on a fluorescence spectrophotometer (HITACHI F-4500) and an ultraviolet/visible near-infrared spectrophotometer (Lambda 950, PerkinElmer), respectively. PDL 200 Pulsed Diode Laser was used to determine time-resolved photoluminescence (TRPL) data (lifetime values) of all compounds.

Synthetic procedures.



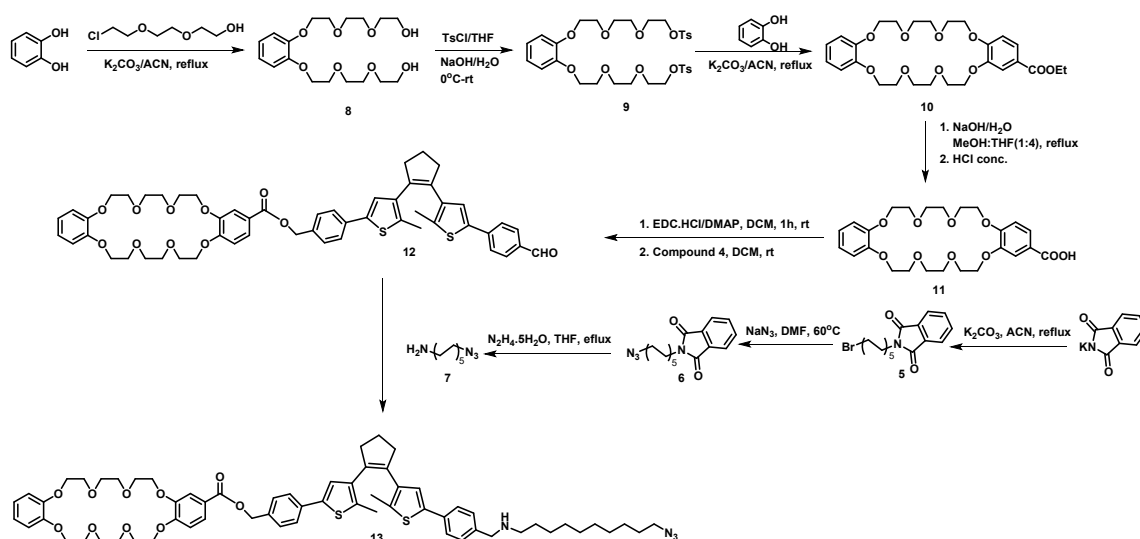
Scheme S1 Synthetic routes of compounds **4** and **TPE-propagyl**.

Compounds **1-2** and **TPE-OH** were synthesized according to the previous literature¹⁻³ with modifications.

Synthesis of compound TPE-Propagyl: **TPE-OH** (5 g, 14.70 mmol), propargyl bromide (2.66 mL, 35.28 mmol) and K_2CO_3 (4.8 g, 35.28 mmol) were added in the same portion with 50 mL of acetone. Then, the reaction solution was stirred and refluxed for 3 h under nitrogen gas protection. The reaction was filtered and washed with water solution, dried with anhydrous Na_2SO_4 and further purified by column chromatography using Hex/DCM (4:1, v/v) to afford compound **TPE-propagyl** as a white solid (4.26 g, yield 76.48%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.12 – 7.06 (m, 9H), 7.05 – 7.00 (m, 6H), 6.97 – 6.92 (m, 2H), 6.72 – 6.68 (m, 2H), 4.60 (d, J = 2.5 Hz, 2H), 2.48 (t, J = 2.5 Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 156.14, 143.88, 143.85, 140.35, 140.32, 136.98, 132.48, 131.34, 131.30, 131.28, 127.70, 127.58, 126.36, 126.27, 126.25, 113.96, 78.56, 75.37, 55.74.

Synthesis of compound 3: To a solution of compound **2** (5 g, 15.18 mmol) in anhydrous tetrahydrofuran (50 mL), $n\text{-BuLi}$ (13 mL of 2.5 M solution in hexane, 33.4 mmol) was slowly added at -78°C and continuously stirred for 2 h under nitrogen atmosphere. Then, trimethyl borate (4.35 mL, 39 mmol) was added dropwise and stirred for another 6 h at room temperature. The reddish solution was added dropwise to a flask containing 4-bromobenzaldehyde diethyl acetal (7.86 g, 30.36 mmol), $\text{Pd(PPh}_3)_4$ (150 mg, 0.123 mmol) and K_2CO_3 solution (10 mL, 2 M) in tetrahydrofuran (10 mL). The mixture was stirred and refluxed for 24 h under nitrogen atmosphere. The reaction was cooled to room temperature, quenched with 5 mL conc. HCl, extracted with ethyl acetate (3 \times 50 mL) and dried over anhydrous Na_2SO_4 . The solution was concentrated under reduced pressure and the crude product was purified by column chromatography using Hex/EtOAc (4:1) to afford compound **3** as a light yellow solid (4.26 g, yield 60%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.88 (s, 2H), 7.75 (d, J = 6.8 Hz, 4H), 7.55 (d, J = 6.4 Hz, 4H), 7.11 (s, 2H), 2.79 (t, J = 6 Hz, 4H), 2.07-2.00 (m, 2H), 1.96 (s, 6H). $^{13}\text{C NMR}$ 191.37, 140.08, 138.17, 137.17, 137.06, 134.80, 134.67, 130.41, 126.03, 125.30, 38.43, 22.98, 14.59.

Synthesis of compound 4: Compound **3** (4.68 g, 10 mmol) was dissolved in 100 mL DCM/MeOH (1:1) and stir at 0°C under nitrogen atmosphere. Then, NaBH₄ (380 mg, 3.33 mmol) was consecutively added to this solution, which was continued to stir for 30 minutes. The reaction was quenched by 50 mL H₂O solution, which was extracted with ethyl acetate (3×50 mL) and dried with anhydrous Na₂SO₄. The solvents were removed under vacuum, and then the crude product was purified by column chromatography using Hex/EtOAc (2:1) to afford **4** as a light purple solid (1.88 g, yield 40%). ¹H NMR (400 MHz, CDCl₃) δ 9.96 (s, 1H), 7.83 (d, J = 6.8 Hz, 2H), 7.62 (d, J = 6.8 Hz, 2H), 7.47 (d, J = 6.8 Hz, 2H), 7.33 (d, J = 6.4 Hz, 2H), 7.18 (s, 1H), 7.03 (s, 1H), 4.68 (s, 2H), 2.85 (t, J = 6 Hz, 4H), 2.13-2.07 (m, 2H), 2.04 (s, 3H), 2.01 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 191.43, 140.23, 139.67, 139.50, 137.98, 137.35, 137.12, 136.53, 135.31, 134.63, 134.55, 134.22, 130.43, 127.51, 126.21, 125.45, 125.32, 123.96, 65.04, 38.46, 38.40, 23.02, 14.60, 14.41.



Scheme S2 Synthetic routes of compound **13**.

Compounds **8-12** were synthesized according to the previous literature⁴ with modifications.

Synthesis of compound 5: To a mixture of phthalimide potassium salt (11.14 g, 60 mmol) and K₂CO₃ (30 g, 370 mmol) in CH₃CN (200 mL), 1,10-dibromodecane (99.88 g, 370 mmol) was added to react and reflux for 10 h under nitrogen atmosphere. The mixture was filtered and ACN was removed by a rotary evaporator. The residue was further purified by column chromatography using Hex/EA (6:1) to give a white solid (20.44 g, 93 %). ¹H NMR (400 MHz, CDCl₃): δ 7.85-7.80 (m, 2H), 7.72-7.67 (m, 2H), 3.66 (t, J = 7.2 Hz, 2H), 3.38 (t, J = 7.2 Hz, 2H), 1.86-1.79 (m, 2H), 1.43-1.37 (m, 2H), 1.36-1.24 (m, 12H).

Synthesis of compound 6: Compound **5** (14.6 g, 40 mmol) was dissolved in anhydrous DMF (50 mL), and NaN₃ (4.5 g, 70 mmol) was added consecutively. After stirred at 60°C for 48 h, the obtained mixture was extracted with EA, washed with water (3×50 mL) and dried over anhydrous Na₂SO₄, then the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography using Hex/EA (9:1) resulting in a yellow solid (12.53 g, 95.72 %). ¹H NMR (400 MHz, CDCl₃): δ 7.86-7.81 (m, 2H), 7.72-7.68 (m, 2H), 3.67 (t, J = 7.2 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 7: To a solution of compound **6** (8 g, 24 mmol) in EtOH (40 mL), hydrazine hydrate (3.04 g, 60 mmol) was added and continuously refluxed overnight under nitrogen gas protection. The acquired mixture was filtered, then the excess of hydrazine hydrate and EtOH was removed by vacuum at 65 °C to yield compound **7** as a pale yellow liquid (3.25 g, 67.28 %). ¹H NMR (400 MHz, CDCl₃): δ 3.23 (t, J = 6.8 Hz, 2H), 2.66 (t, J = 6.8 Hz, 2H), 1.61-1.54 (m, 2H), 1.44-1.38 (m, 2H), 1.36-1.23 (m, 12H).

Synthesis of compound 10: A mixture of ethyl 3,4-dihydroxybenzoate (2.02 g, 10.86 mmol), K₂CO₃ (4.55 g, 32.6 mmol) and KPF₆ (3.06 g, 16.29 mmol) were dissolved in anhydrous ACN (150 mL), then compound **9** (7.42 g, 10.86 mmol) in anhydrous ACN was added quickly. This mixture was stirred and refluxed under nitrogen atmosphere for 24 h. Upon cooling, the reaction mixture was filtered to remove K₂CO₃ and the solvent was removed, then the residue was further extracted with EtOAc (3×50 mL). The organic phase was dried with anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by column

chromatography using Hex/ EtOAc (1:4) to attain compound **10** as a white solid (4.24 g, yield 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.65 (dd, J = 2.8 Hz, J = 11.2 Hz, 1H), 7.53 (d, J = 2.8 Hz, 1H), 6.92-6.84 (m, 5H), 4.33 (q, J = 9.6 Hz, 2H), 4.21-4.14 (m, 8H), 3.95-3.88 (m, 8H), 3.82-3.81 (m, 8H), 1.37 (t, J = 9.6 Hz, 3H).

Synthesis of compound 11: A mixture of compound **10** (2.6 g, 5 mmol) in 50 mL MeOH/THF (1:4, v/v) and 20 mL NaOH 1 M (0.8 g, 20 mmol) in H₂O was prepared and refluxed overnight. After cooling to room temperature, the solvents were removed under vacuum and then 10 mL conc. HCl was added to the solution until pH < 1. The precipitate was filtered, washed with water three times and dried at 80 °C over 12 h to yield compound **11** as a white solid (4.87 g, yield 90%). ¹H NMR (400 MHz, DMSO) δ 7.53 (dd, J = 2 Hz, J = 8.4 Hz, 1H), 7.41 (d, J = 2 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.94-6.91 (m, 2H), 6.90-6.82 (m, 2H), 4.13-4.07 (m, 4H), 4.04-4.02 (m, 4H), 3.77-3.72 (m, 8H), 3.64 (s, 8H). ¹³C NMR (125 MHz, DMSO) δ 167.27, 152.43, 148.59, 147.87, 123.69, 123.29, 121.37, 121.34, 114.23, 114.18, 114.08, 112.59, 70.63, 70.57, 70.53, 69.31, 69.17, 69.05, 68.99, 68.86.

Synthesis of compound 12: Compound **11** (4 g, 8 mmol) was dispersed in 100 mL of anhydrous DCM. Then, EDC.HCl (1.69 g, 8.8 mmol) followed by DMAP (270 mg, 2.3 mmol) was added directly to the solution and stirred for another 1 h at room temperature under N₂ gas protection. The solution of compound **4** (3.76 g, 8 mmol) in anhydrous DCM was slowly added dropwise to be reacted and stirred for 12 h at room temperature. After that, the residue was extracted with DCM and washed with brine. The organic layer was dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using DCM/EA (3:2) to afford compound **12** as a slight purple solid (6.8 g, yield 90%). ¹H NMR (500 MHz, CDCl₃) δ 9.89 (s, 1H), 7.75 (d, J = 8.5 Hz, 2H), 7.60 (dd, J = 2.5 Hz, J = 8.5 Hz, 1H), 7.55 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 2.5 Hz, 1H), 7.42 (d, J = 8 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.11 (s, 1H), 6.96 (s, 1H), 6.82-6.76 (m, 5H), 5.23 (s, 2H), 4.11 (q, J = 4 Hz, 4H), 4.08-4.06 (m, 4H), 3.87-3.83 (m, 8H), 3.76 (d, J = 5 Hz, 8H), 2.78 (t, J = 7.5 Hz, 4H), 2.06-2.00 (m, 2H), 1.96 (s, 3H), 1.93 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 191.41, 166.14, 153.05, 148.92, 148.28, 137.33, 137.11, 136.58, 134.98, 134.64, 134.26, 130.42, 128.79, 126.17, 125.42, 125.32, 124.15, 124.08, 123.88, 122.75, 121.43, 121.41, 114.50, 114.30, 114.07, 112.03, 71.43, 71.33, 71.25, 69.93, 69.75, 69.61, 69.52, 69.46, 69.39, 69.33, 69.27, 66.22, 51.94, 38.45, 23.01, 14.59, 14.43.

Synthesis of compound 13: Compounds **7** (2.38 g, 12 mmol) and **12** (7.56 g, 8 mmol) were dissolved in DCM/MeOH (1:4, v/v), and refluxed overnight under nitrogen atmosphere. Then, the reaction mixture was cooled to 0°C, NaBH₄ (0.91 g, 24 mmol) was further added in the portion under ice bath and stirred for another 6 h at room temperature. Thereafter, the reaction solution was poured into water (100 mL), and the solvent was removed under reduced pressure. Thereafter, the residue was extracted with DCM (3x50 mL), and washed with water (3x50 mL) and brine (100 mL). Then, the organic layer was dried over anhydrous Na₂SO₄ and concentrated by vacuum. The crude product was purified via column chromatography with DCM/MeOH (25:1) to give compound **13** as a purple solid (4.8 g, 53.27%). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, J = 2 Hz, J = 8.4 Hz, 1H), 7.56-7.36 (m, 9H), 7.04 (s, 1H), 7.00 (s, 1H), 6.90-6.82 (m, 5H), 5.29 (s, 2H), 4.19-4.17 (m, 4H), 4.16-4.13 (m, 4H), 3.94-3.90 (m, 8H), 3.87 (s, 2H), 3.83 (d, J = 4 Hz, 8H), 3.23 (t, J = 7.2 Hz, 2H), 2.82 (q, J = 7.2 Hz, 4H), 2.69 (t, J = 8 Hz, 2H), 2.10-2.04 (m, 2H), 1.95 (d, J = 3.2 Hz, 6H), 1.72-1.65 (m, 2H), 1.60-1.53 (m, 2H), 1.34-1.29 (m, 4H), 1.28-1.24 (m, 8H). ¹³C NMR (125 MHz, CDCl₃) δ 166.15, 148.92, 148.28, 134.48, 129.07, 128.78, 127.21, 125.41, 124.23, 124.08, 123.93, 122.78, 121.42, 114.49, 114.07, 112.03, 71.43, 71.32, 71.25, 69.94, 69.76, 69.61, 69.51, 69.39, 69.33, 69.28, 66.26, 51.47, 38.49, 29.68, 29.37, 29.09, 28.81, 27.19, 26.68, 22.98, 14.40.

Synthesis of compound 14: To a solution of compound **13** (1.13 g, 1 mmol) in mixture of THF/H₂O (9:1, v/v) (100 mL) and NaHCO₃ (203 mg, 2.4 mmol), di-*tert*-butyl dicarbonate (262 mg, 1.2 mmol) was added consecutively at 0 °C. After 30 min, the solution was stirred overnight at room temperature. The milky solution was extracted with EA (2x50 mL). The aqueous layer was acidified to pH = 4-5 by a careful addition of citric acid at 0 °C, and then extracted with EA (3x50 mL). The combined organic phase was washed with water (3x50 mL) and brine (3x50 mL), dried over anhydrous Na₂SO₄ and evaporated under reduced pressure, then the crude product was purified by flash column chromatography using Hex/EA (9:1) to yield compound **14** (0.94 g, 76.6 %). ¹H NMR (400 MHz, CD₃CN) δ 7.89-7.88 (m, 1H), 7.74-7.72 (m, 1H), 7.68-7.57 (m, 4H), 7.54-7.48 (m, 3H), 7.45-7.38 (m, 3H), 7.31 (d, J = 6.4 Hz, 1H), 7.19-7.11 (m, 9H), 7.02-6.98 (m, 3H), 6.95-6.86 (m, 7H), 6.77-6.75 (m, 2H), 5.26 (s, 2H), 5.03 (s, 2H), 4.42 (s, 1H), 4.35 (s, 2H), 4.31 (t, J = 5.6 Hz, 2H), 4.16-4.11 (m, 4H), 4.08-4.06 (m, 4H), 3.83-3.77 (m, 8H), 3.69-3.67 (m, 8H), 3.13 (s, 2H), 2.81 (t, J = 5.6 Hz, 3H), 2.09-2.04 (m, 2H), 2.02-1.99 (m, 4H), 1.82-1.79 (m, 2H), 1.43-1.39 (m, 11H), 1.27-1.19 (m, 15H). ¹³C NMR (125 MHz, CDCl₃) δ 166.12, 153.01, 148.89, 148.26, 139.42, 128.76, 128.61, 125.39, 125.30, 124.21, 124.05, 123.78, 122.75, 121.41, 121.38, 114.47, 114.05, 112.00, 71.40, 71.30, 71.22, 69.91, 69.73, 69.58, 69.48, 69.36, 69.30, 69.25, 66.23, 51.44, 38.47, 29.41, 29.34, 29.24, 29.07, 28.78, 28.44, 26.78, 26.66, 22.96, 14.40, 14.36.

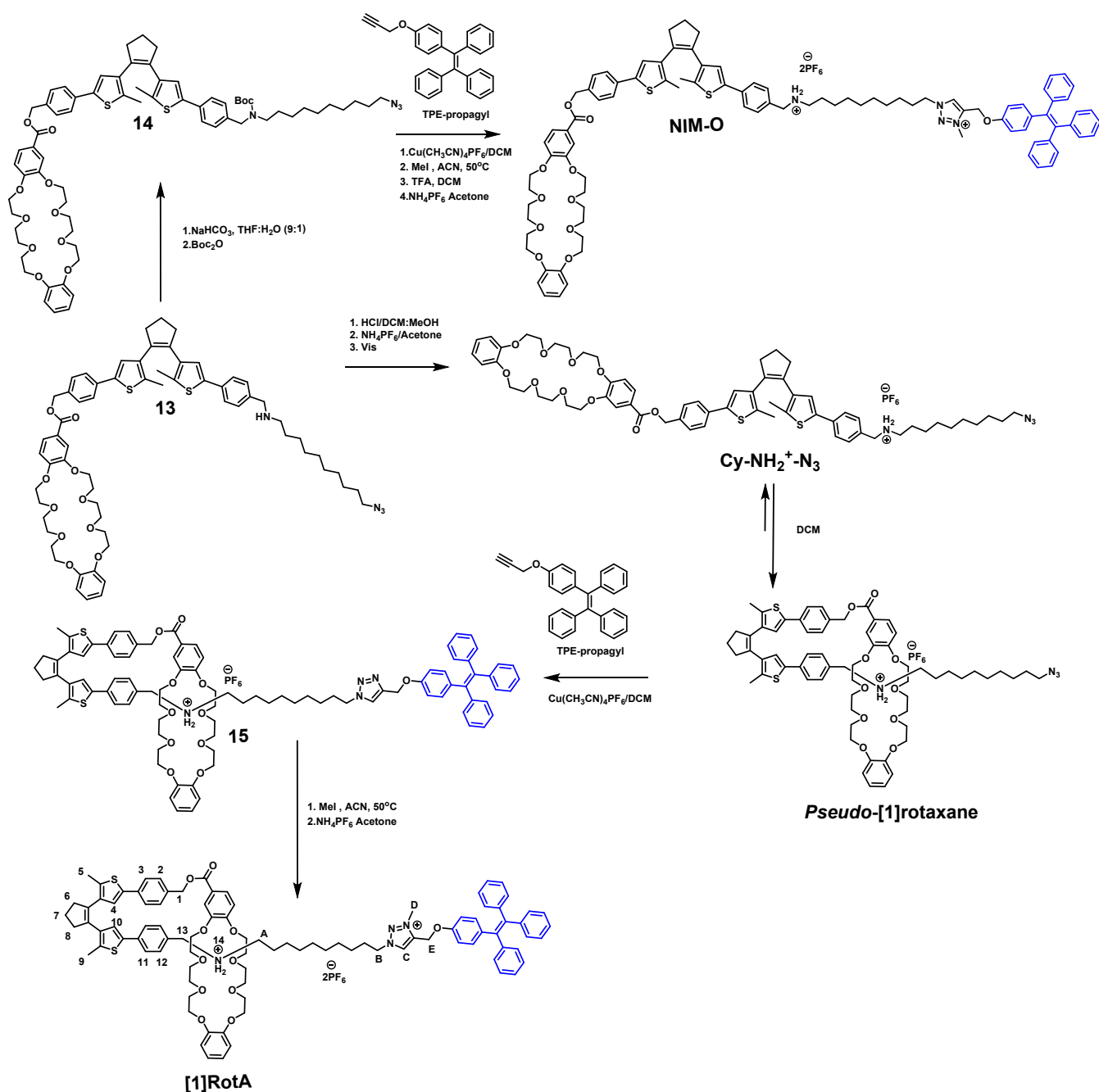
Synthesis of compound Cy-NH₂⁺-N₃: Compound **13** (2.25 g, 1.99 mmol) was dissolved in DCM/MeOH (1:1, v/v), then HCl conc. (2 mL) was added and stirred overnight at room temperature. The reaction mixture was extracted with DCM, washed with DI water (2×50 mL), and the solvent was removed to gain chloride salt of compound **13**. Then, the chloride salt of compound **13** was dispersed in 50 mL of acetone, and the saturated NH₄PF₆ solution (10 mL) was added and stirred at room temperature overnight. The solvent was removed, and the residue was filtered washed with DI water (3×50 mL). Then, the solid compound was dried under vacuum for 24 h to produce **Cy-NH₂⁺-N₃** as a slight purple solid (2.08 g, 82.21 %), which was directly used for next steps.

Synthesis of [1]rotaxane 15. Compound **Cy-NH₂⁺-N₃** (700 mg, 0.49 mmol) was dissolved in degassed and dry dichloromethane (50 mL) and continuously stirred at room temperature for 24 h, then compound **TPE-propagyl** (213 mg, 0.55 mmol) and [Cu(CH₃CN)₄]PF₆ (205 mg, 0.55 mmol) were slowly added to the reaction solution. The reaction mixture was stirred for another 24 h at room temperature under nitrogen gas protection. Subsequently, the solution was diluted with DCM (100 mL), then the aqueous solution of Na₂EDTA (100 mL) was added and stirred for 1 h. The organic layer was collected, washed with water (2×50 mL), dried over anhydrous Na₂SO₄ and the DCM was evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel with an eluent of DCM/MeOH (100:1, v/v) to obtain [1]rotaxane **15** as a slight yellow solid (372 mg, 45.3%). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (dd, J = 8.5, 2.0 Hz, 1H), 7.66 (s, 1H), 7.50 (d, J = 2.0 Hz, 1H), 7.50 – 7.40 (m, 1H), 7.14 – 7.06 (m, 15H), 7.04 – 7.00 (m, 7H), 6.95 – 6.92 (m, 3H), 6.91-6.87 (m, 2H), 6.85 – 6.81 (m, 3H), 6.73 – 6.69 (m, 4H), 6.40 (s, 1H), 5.42 – 5.32 (m, 3H), 5.10 (s, 2H), 4.54 – 4.43 (m, 3H), 4.36 (t, J = 7.5 Hz, 2H), 4.34-4.27 (m, 3H), 4.20 – 3.64 (m, 25H), 3.44 (s, 2H), 2.92 – 2.83 (m, 2H), 2.76 – 2.73 (m, 2H), 2.43 (s, 3H), 2.12-2.06 (m, 2H), 2.03 (s, 3H), 1.92-1.91 (m, 3H), 1.69-1.63 (m, 3H), 1.43-1.37 (m, 3H), 1.34-1.32 (m, 5H), 1.29 – 1.24 (m, 8H). ¹³C NMR (125 MHz, CDCl₃) δ 168.78, 166.32, 156.06, 154.03, 152.71, 152.71, 148.01, 147.39, 147.24, 144.40, 144.34, 144.29, 141.43, 140.69, 140.10, 139.45, 138.80, 138.31, 138.13, 136.75, 136.34, 136.32, 136.13, 135.89, 135.85, 135.29, 134.74, 133.50, 132.77, 131.99, 131.96, 131.91, 131.17, 130.94, 130.19, 130.14, 129.56, 129.29, 129.19, 128.50, 128.38, 128.34, 128.27, 127.31, 127.25, 127.17, 127.13, 127.00, 126.74, 126.53, 126.37, 125.90, 125.34, 124.78, 123.54, 122.58, 122.47, 122.05, 121.64, 114.57, 113.00, 112.88, 111.93, 72.08, 71.65, 71.59, 71.13, 70.88, 70.82, 70.69, 69.30, 68.82, 68.66, 68.04, 66.52, 65.84, 58.39, 55.03, 52.50, 49.72, 39.27, 38.26, 37.24, 30.36, 29.74, 29.37, 29.34, 29.21, 29.12, 27.88, 27.29, 26.90, 26.30, 24.05, 23.35, 16.61, 15.93, 15.51, 14.78, 14.39, 1.68. HRMS (ESI⁺) [M-PF₆]⁺: calcd. for C₉₃H₁₀₁N₄O₁₁S₂⁺, 1514.6935; found, 1514.6982.

Synthesis of [1]rotaxane [1]RotA. In a sealed tube, a solution of [1]rotaxane **15** (350 mg, mmol) in MeCN (10 mL) and CH₃I (5 mL) was stirred to react at 50 °C overnight. The resultant solution was cooled to room temperature, and all volatiles were removed by the vacuum rotary evaporator, where the residue was suspended in acetone (20 mL). Then, an excess of saturated aqueous solution of NH₄PF₆ was added to the suspension, and the mixture was stirred at room temperature overnight. Acetone was removed under reduced pressure, and the residue was then extracted with DCM (2×100 mL), washed with DI water (2×40 mL), dried with Na₂SO₄ anhydrous and further concentrated by a rotary evaporator. The crude product was purified on silica gel by column chromatography using an eluent of DCM/MeOH (100:2) to afford [1]RotA as a slight yellow solid (361 mg, 95%). ¹H NMR (600 MHz, CDCl₃) δ 8.41 (s, 1H), 7.69 – 7.67 (m, 1H), 7.48 – 7.47 (m, 1H), 7.45-7.29 (m, 4H), 7.14-7.04 (m, 15H), 7.03 – 6.98 (m, 6H), 6.95 (d, J = 8.4 Hz, 2H), 6.90-6.87 (m, 3H), 6.84 – 6.79 (m, 3H), 6.6.76-6.67 (m, 5H), 6.38 (s, 1H), 5.41- 5.31 (m, 2H), 5.16 (s, 2H), 4.52 (t, J = 7.8 Hz, 2H), 4.45 (t, J = 10.8 Hz, 2H), 4.32-4.27(m, 3H), 4.24 (s, 3H), 4.19-4.13 (m, 3H), 4.10-3.99 (m, 6H), 3.95-3.89 (m, 3H), 3.86-3.61 (m, 15H), 3.44-3.37 (m, 3H), 2.91-2.77 (m, 5H), 2.73 (t, J = 7.8 Hz, 2H), 2.42 (s, 2H), 2.10-2.05 (m, 3H), 2.00-1.96 (m, 4H), 1.67-1.59 (m, 6H), 1.40-1.36 (m, 4H), 1.29-1.24 (m, 11H). ¹³C NMR (125 MHz, CDCl₃) δ 166.31, 156.06, 152.71, 148.01, 147.38, 147.24, 144.40, 144.32, 144.28, 141.42, 140.69, 140.11, 139.46, 138.78, 138.30, 138.12, 136.73, 136.34, 136.10, 135.88, 135.27, 134.73, 133.48, 133.32, 131.97, 131.95, 131.90, 131.22, 130.94, 130.13, 128.49, 128.43, 128.33, 128.27, 127.31, 127.24, 127.17, 127.12, 126.99, 126.73, 126.55, 126.36, 126.15, 125.89, 125.70, 125.33, 124.77, 123.52, 122.56, 122.46, 114.58, 112.98, 112.87, 111.93, 72.08, 71.63, 71.12, 70.87, 70.81, 70.69, 69.28, 68.80, 68.65, 68.03, 66.51, 65.82, 58.39, 54.99, 52.50, 49.70, 39.22, 38.25, 38.11, 37.76, 37.24, 32.59, 32.17, 31.07, 30.70, 30.36, 30.31, 30.02, 29.91, 29.74, 29.38, 29.25, 29.13, 27.75, 27.28, 26.92, 26.32, 24.04, 23.35, 15.93, 15.50, 14.78, 14.38, 1.68. HRMS (ESI⁺) [M-2PF₆]²⁺: calcd. for C₉₄H₁₀₄N₄O₁₁S₂²⁺, 764.8582; found, 764.8590. Elemental analysis (EA): calcd. for C₉₄H₁₀₄N₄O₁₁S₂P₂F₁₂, C 62.04, H 5.76, N 3.08%, S 3.52%; found, C 60.36, H 6.08, N 3.04%, S 3.52%.

Synthesis of compound NIM. A mixture of compounds **TPE-propagyl** (213 mg, 0.55 mmol) and [Cu(CH₃CN)₄]PF₆ (205 mg, 0.55 mmol) in 20 mL of anhydrous and degassed DCM was stirred for 15 min, followed by the addition of compound **14** (600 mg, 0.49 mmol), then the reaction mixture was stirred at room temperature for 24 h under nitrogen gas protection. After the completely reaction,

the solution was diluted with DCM (20 mL), and 50 mL of aqueous Na₂EDTA solution was added. Then, the organic layer was collected, washed with water twice, and dried upon anhydrous Na₂SO₄. The filtrate was concentrated and dried under vacuum for 1 h to obtain the intermediate compound for next step without further purification. For the methylation reaction, the intermediate compound was dissolved in anhydrous ACN (10 mL) and MeI (5 mL), then the solution was stirred at 50 °C for 24 h under nitrogen atmosphere. After the removal of MeI and ACN excess under reduced pressure, the residue was washed with Et₂O (3×30 mL), and the solid was re-dissolved in DCM for further de-protection reaction of Boc-group by adding 1 mL TFA. After 1 h for reaction, water was added, and the solution was extracted with DCM (2×20 mL). The organic layer was collected, then dried and evaporated by a vacuum rotary evaporator. Subsequently, the resultant solid was suspended in 20 mL acetone, followed by adding an excessive saturated aqueous solution of NH₄PF₆, and stirred at room temperature overnight. Acetone was removed under vacuum, and de-ionized water (50 mL) was added into the obtained residue. Then, the precipitate was filtered, followed by water and pentane (2×30 mL) washing twice. The resultant solid was further purified on silica gel by column chromatography with an eluent of DCM/MeOH (25:1) to yield **NIM** as a pale yellow solid (530 mg, 89.5 %). ¹H NMR (500 MHz, CDCl₃) δ 8.44 (s, 1H), 7.75-7.69 (m, 1H), 7.59 (d, *J* = 13.5 Hz, 1H), 7.46 – 7.36 (m, 7H), 7.10 – 7.05 (m, 9H), 7.02 – 6.95 (m, 15H), 6.70 – 6.68 (m, 2H), 5.28 (s, 2H), 5.18 (s, 2H), 4.49 (t, *J* = 7.5 Hz, 2H), 4.26-4.24 (m, 4H), 4.21-4.13 (m, 8H), 3.87 – 3.84 (m, 5H), 3.76-3.73 (m, 5H), 3.68 (br, 6H), 2.97 (br, 2H), 2.83-2.80 (m, 4H), 2.08 (s, 3H), 2.03 (s, 3H), 2.00 – 1.96 (m, 2H), 1.26 – 1.23 (m, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 166.83, 156.04, 153.68, 149.52, 148.89, 144.36, 144.29, 141.47, 140.6, 138.73, 137.58, 135.96, 135.57, 135.42, 135.19, 135.09, 133.50, 131.94, 131.43, 130.89, 129.47, 129.13, 128.47, 128.34, 128.29, 127.13, 127.4, 126.46, 126.08, 125.35, 124.87, 123.4, 122.17, 115.17, 114.74, 114.55, 112.73, 72.06, 71.95, 71.88, 70.62, 70.44, 70.29, 70.14, 69.96, 66.95, 39.22, 30.38, 29.43, 28.50, 28.34, 28.22, 26.03, 25.93, 23.65, 15.13. HRMS (ESI⁺) [M-2PF₆⁻]²⁺: calcd. for C₉₄H₁₀₄N₄O₁₁S₂⁺, 764.8582; found, 764.8599.



Scheme S3 Synthetic routes of **NIM** and **[1]RotA**.

In some aprotic solvents (e.g. CH₂Cl₂, CHCl₃, (CH₃)₂CO, CH₃CN), the linear thread component was mechanically self-trapped into macrocycle DB24C8 at BAA as a template to produce *pseudo*-[1]rotaxane followed by end-capping of TPE stopper, resulting in the formation of **[1]RotA**. In detail, a *pseudo*-[1]rotaxane was carefully prepared by dissolving the photochromic compound **Cy-NH₂⁺-N₃** in a suitable amount of DCM under ambient light at room temperature. By using Cu(I)-catalyzed Huisgen alkyne-azide 1,3-dipolar cycloaddition (CuAAC) reaction, the conversion of *pseudo*- to [1]rotaxane was carried out upon the addition of **TPE-propargyl** stopper in the presence of [Cu(CH₃CN)₄]PF₆ catalyst to obtain [1]rotaxane **15** (yield = 45.3%). The further methylation reaction of triazole group using CH₃I/CH₃CN at 50 °C was produced as the auxiliary station of [1]rotaxane in the methyltri-azolium form (MTA), continuously exchanged ion with a saturated NH₄PF₆ solution in acetone to yield a desired compound **[1]RotA** with a high yield (95%).

Besides, a similar synthetic pathway of **[1]RotA** was also employed to synthesize the unthread compound (**NIM-O**) by using a tert-butyloxycarbonyl (Boc) compound (**Cy-NBoc-N₃**), which was integrated with a bulky Boc-protection group in the ammonium

recognition site to inhibit the mechanically molecular self-tightening between DB24C8 and NH_2^+ via the host-guest interaction (Scheme S3).

It could be easily observed that certain proton signals of the methylene groups H_{13} and H_A directly-linked to BAA station were shifted downfield ($\Delta\delta = 0.62\text{-}0.73$ ppm, $\Delta\delta = 0.21$ ppm, respectively) due to their hydrogen-bonding interactions with crown ether-oxygen atoms of DB24C8 (Fig. 2b). In addition, the resonance signals of symmetric protons in DTE unit, such as $\text{H}_{4/10}$, $\text{H}_{6/8}$ and $\text{H}_{9/5}$, were shifted and split into multiple peaks, which may be attributed to the spatially asymmetrical structures of parallel conformers in DTE moiety formed during the self-threading processes and the end-capping of [1]rotaxane. The characteristic proton signals of **[1]RotA** were further confirmed by ^1H - ^1H COSY (Fig. S28) and the self-thread structure was further proven by 2D ROESY spectra (Fig. S29) between protons in BAA station and DB24C8.

Indeed, a significant downfield shift of triazolium proton H_C ($\Delta\delta = 0.75$ ppm) along with a minor downfield shift of H_B ($\Delta\delta = 0.27$ ppm) were obviously observed in Fig. 2c. Furthermore, the proton signals of H_A and H_{13} bonded to BAA station were remarkably shifted upfield ($\Delta\delta = -0.95$ ppm and $-0.62, -0.73$ ppm, respectively) because of the disappearance of their H-bonding interactions with DB24C8, along with the resonance of proton H_D being slightly upfield-shift ($\Delta\delta = -0.10$ ppm) caused by macrocyclic shielding effects. Interestingly, the proton signals ($\text{H}_{4/10}$, $\text{H}_{9/5}$ and $\text{H}_{6/8}$) of DTE moiety were coupling each other with closer-chemical shifts due to the transformation from asymmetric to symmetric DTE structures during the departure of macrocycle ring from BAA site to MTA station, leading to the formation of loosened [1]rotaxane architecture. Subsequently, the shuttling back of DB24C8 to BAA station to reproduce the initial **[1]RotA** could be obtained through the re-protonation of NH group in **[1]RotB** by using TFA (2.2 equiv.), which was proven by the re-emergence of all proton signals (H_A , H_B , H_C , H_D , $\text{H}_{4/10}$, $\text{H}_{9/5}$ and $\text{H}_{6/8}$) in the ^1H NMR spectrum (Fig. 2d).

Initially, we considered the protocol to construct the major product of **[1]RotA** in self-tightened architecture resulting from the self-recognition between DB24C8 and BAA station in the flexible bent structure with a parallel (p) DTE-O conformer (open form) with the highest yield of 45% (Fig. 3a). In the meanwhile, the linear structure of **Cy-NH₂⁺-N₃** coexisted in an anti-parallel (ap) DTE-O conformer to produce unthread compound **NIM-O** by the end capping procedure to achieve a minor yield of 35%. Moreover, upon the UV irradiation to carry out the mentioned synthesis of major product has been switched to the linear rigid structure of DTE-C isomer (close form) and generate single unthread compound **NIM-C** by the end capping procedure to achieve a high yield of 85% with 10 min UV exposure time. Therefore, by the thin layer chromatography (TLC) inspection in Fig. 3b we can prove the UV-Vis tunable synthesis of major productions for **[1]RotA** with DTE-O and **NIM-C** with DTE-C isomeric intermediate reactions under Vis and UV exposure conditions, respectively. Different periods of UV exposure time have been approached to obtain different yield ratios of isomers **[1]RotA** and **NIM-C** and the related results are summarized in Fig. 3c, where the longer UV exposure time induce higher yields of **NIM-C** accompanied with lower yields of **[1]RotA** due to the higher rigidity of DTE-C isomer (close form) in the linear structure of unconstrained **NIM-C**. Therefore, the controllable synthetic yields of both isomers **[1]RotA** and **NIM-C** can be manipulated by the flexible bent DTE-O conformer (open form) and rigid DTE-C isomer (close form) via different UV exposure time. Based on these results, we can conclude that the photo-controllable unthreaded behaviour from self-tightened **[1]RotA** to linear **NIM-C** through the synthetic efficiencies of isomeric MIM and **NIM** structures by the end capping procedure with significantly different yields (45 % and 85 % for **[1]RotA** and **NIM-C**, respectively).

2. Characterizations of intermediate compounds and AIE photo-switchable [1]rotaxanes

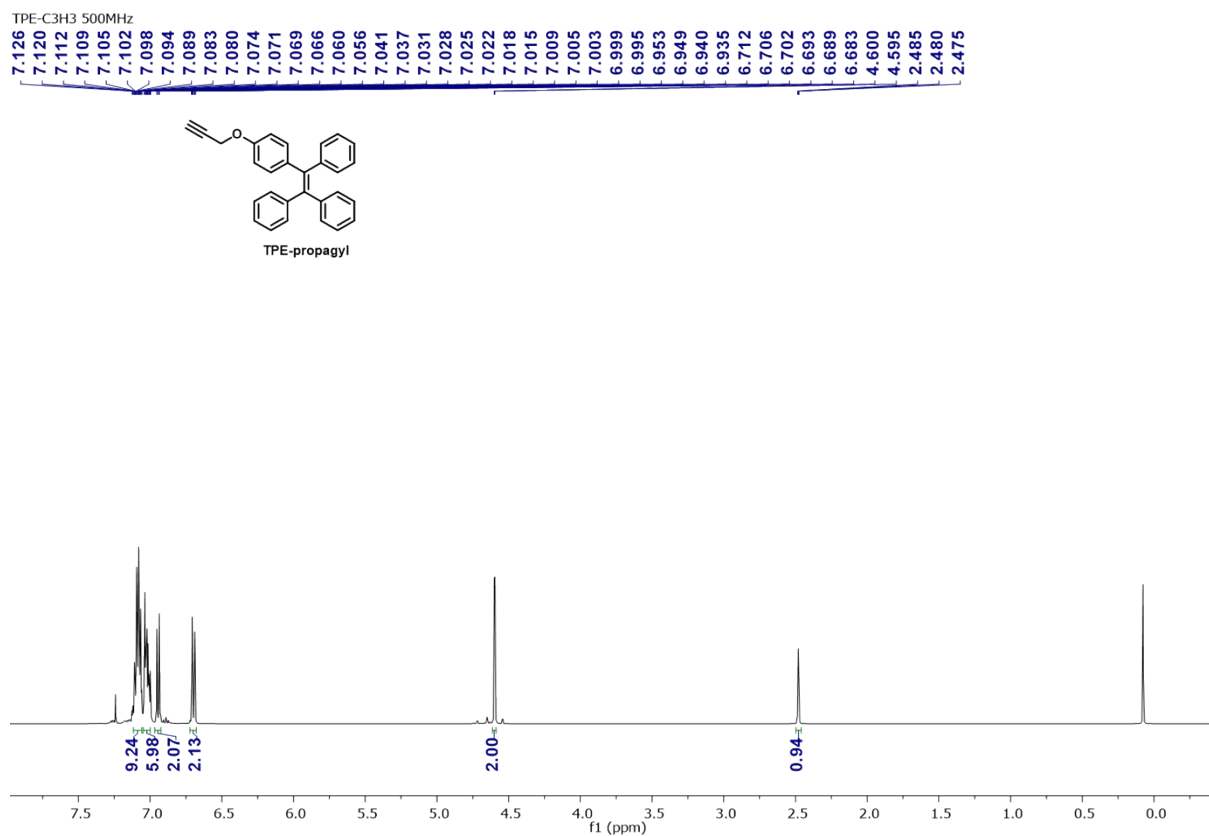


Fig. S1 ^1H NMR spectrum (500 MHz, CDCl_3) of compound TPE-propagyl.

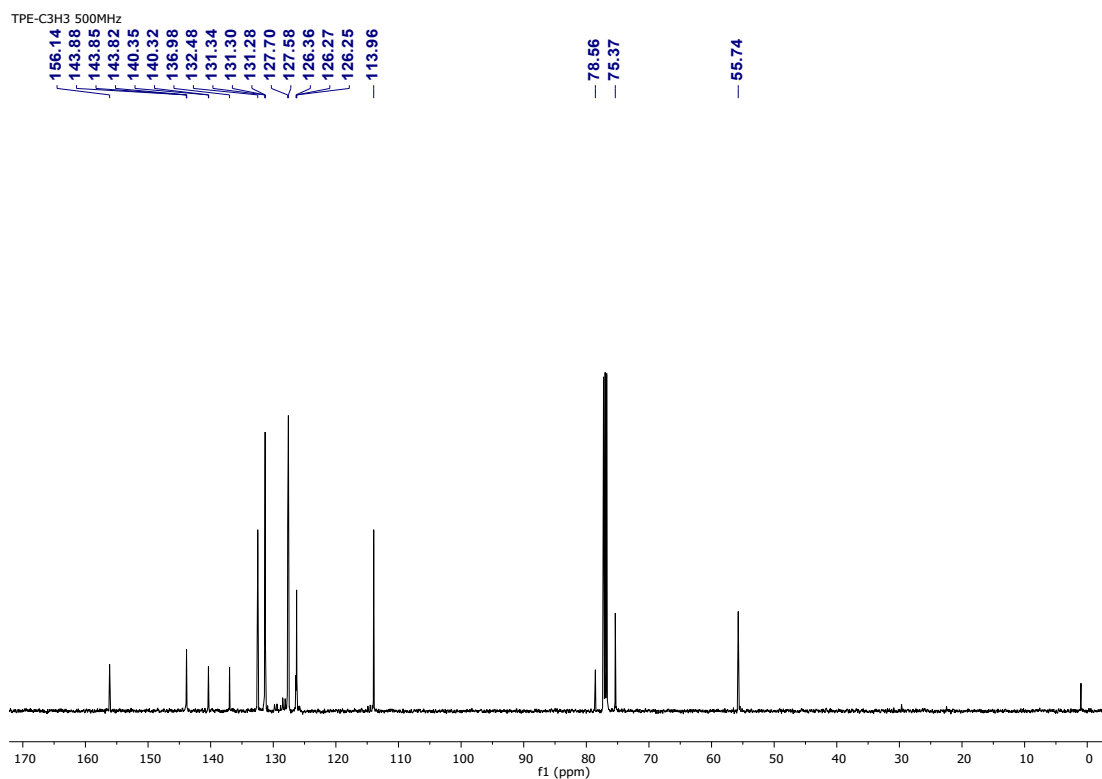


Fig. S2 ^{13}C NMR spectrum (125 MHz, CDCl_3) of compound TPE-propagyl.

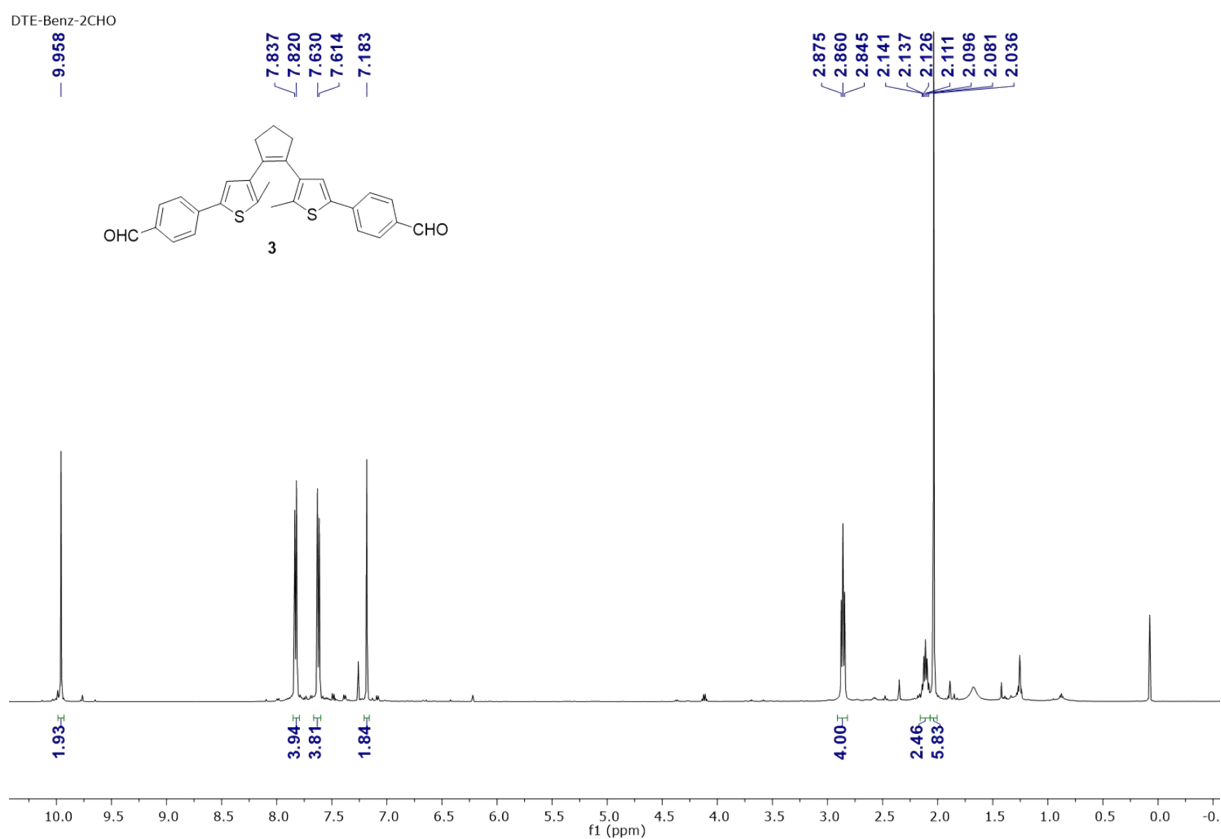


Fig. S3 ¹H NMR spectrum (400 MHz, CDCl₃) of compound 3.

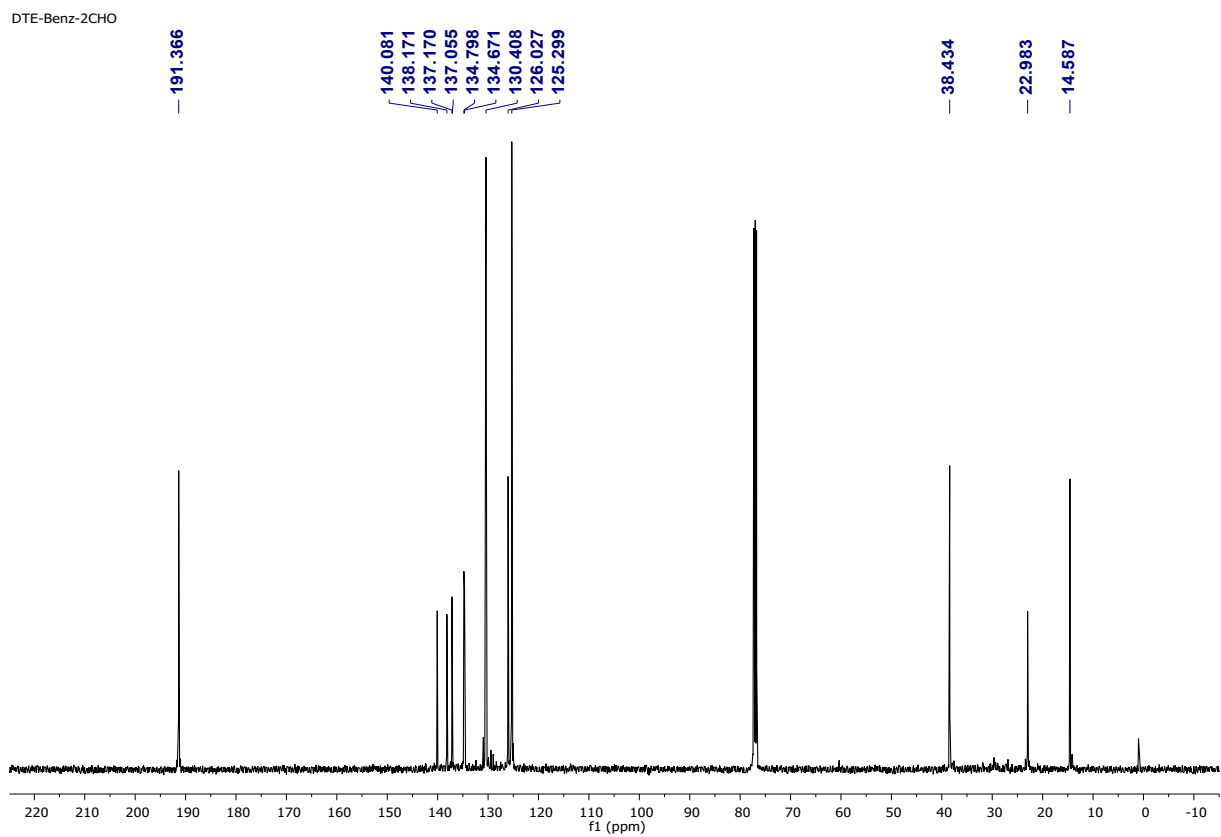


Fig. S4 ¹³C NMR spectrum (100 MHz, CDCl₃) of compound 3.

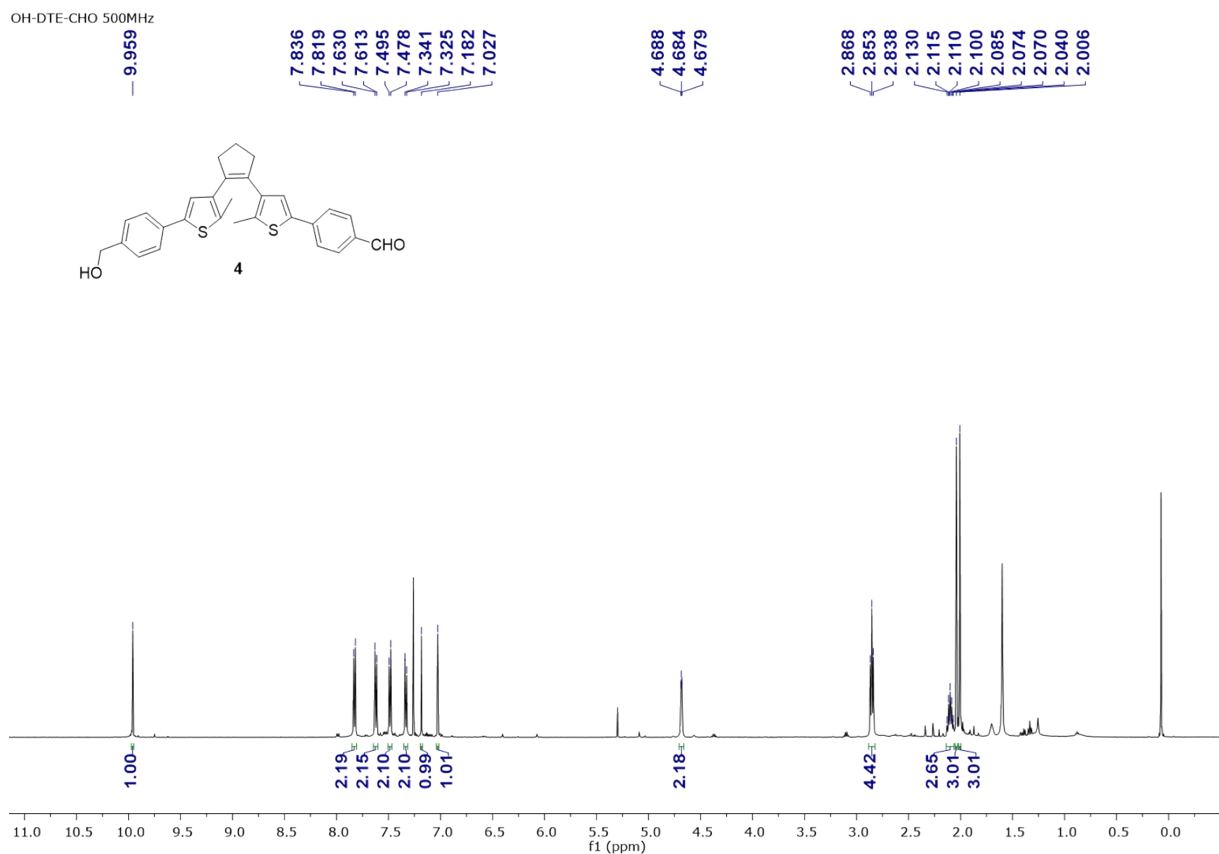


Fig. S5 ^1H NMR spectrum (400 MHz, CDCl_3) of compound 4.

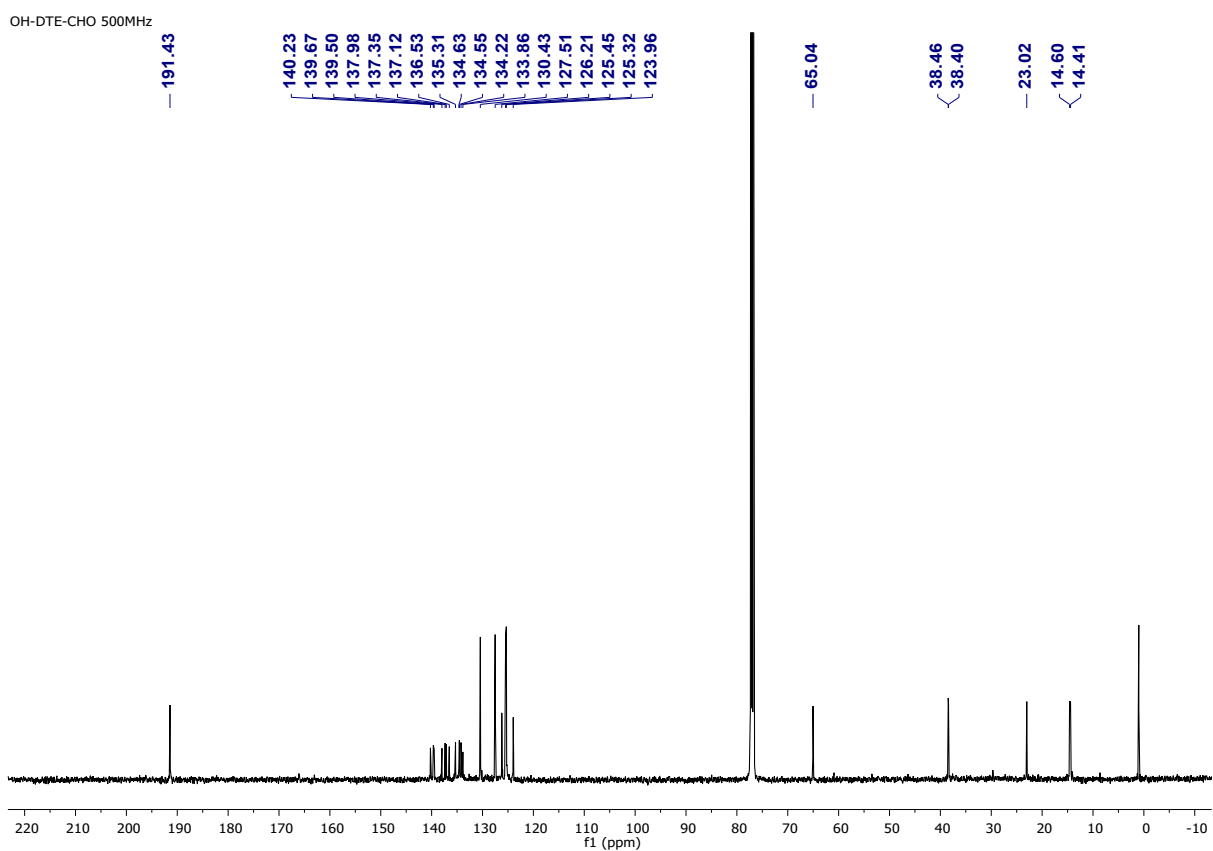


Fig. S6 ^{13}C NMR spectrum (125 MHz, CDCl_3) of compound 4.

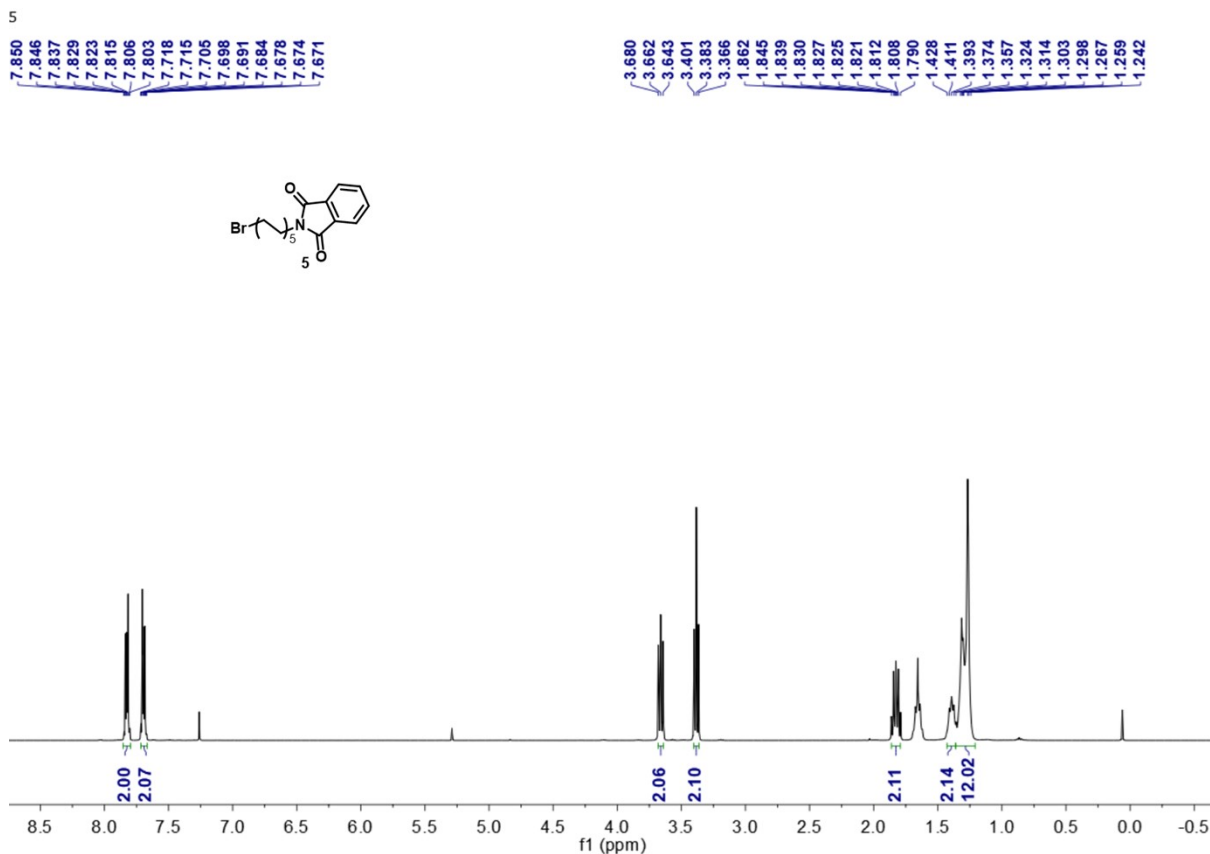


Fig. S7 ^1H NMR spectrum (400 MHz, CDCl_3) of compound 5.

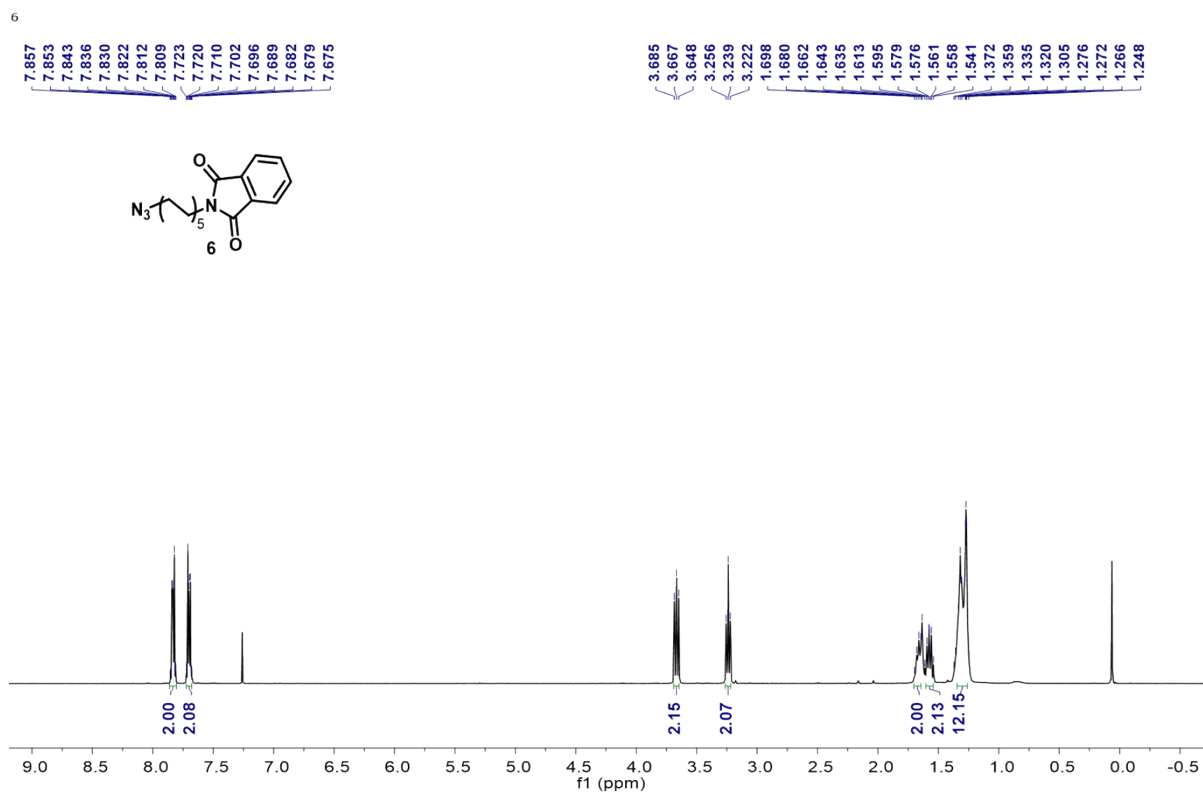


Fig. S8 ^1H NMR spectrum (500 MHz, CDCl_3) of compound 6.

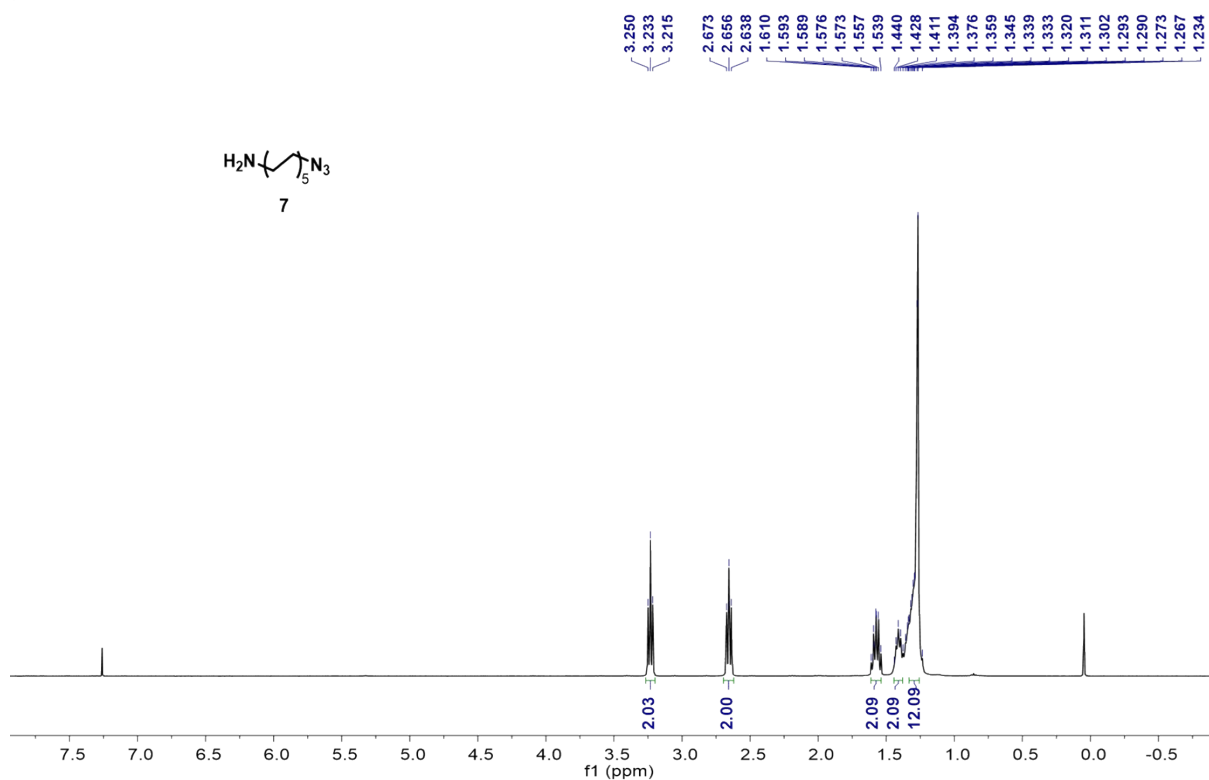


Fig. S9. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **7**.

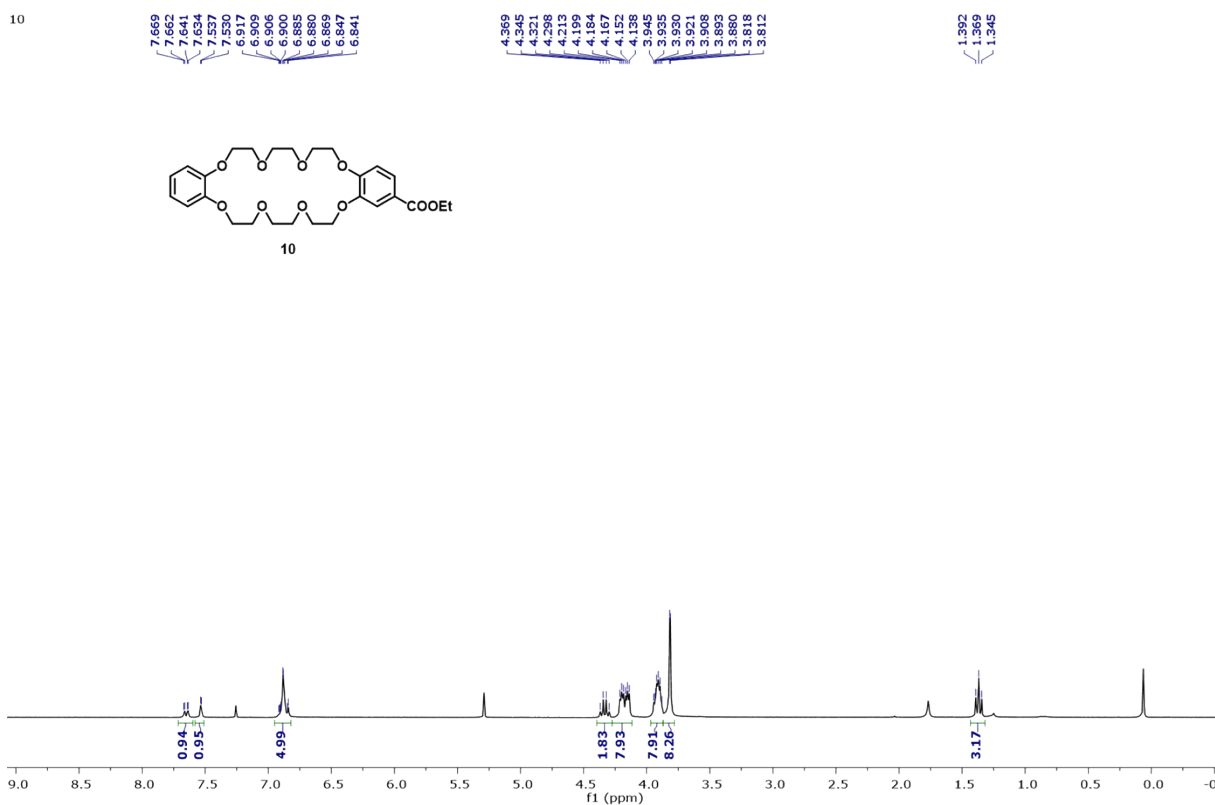


Fig. S10. ^1H NMR spectrum (400 MHz, CDCl_3) of compound **10**.

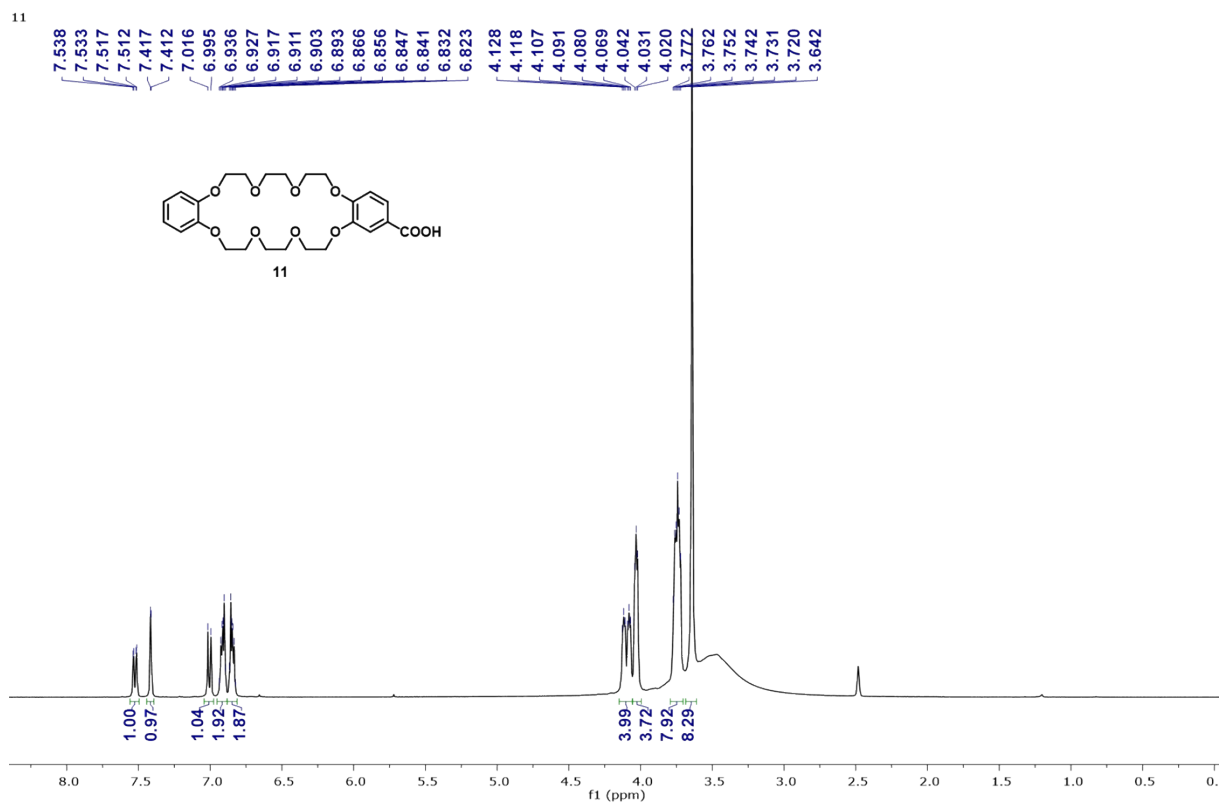


Fig. S11 ^1H NMR spectrum (400 MHz, DMSO) of compound 11.

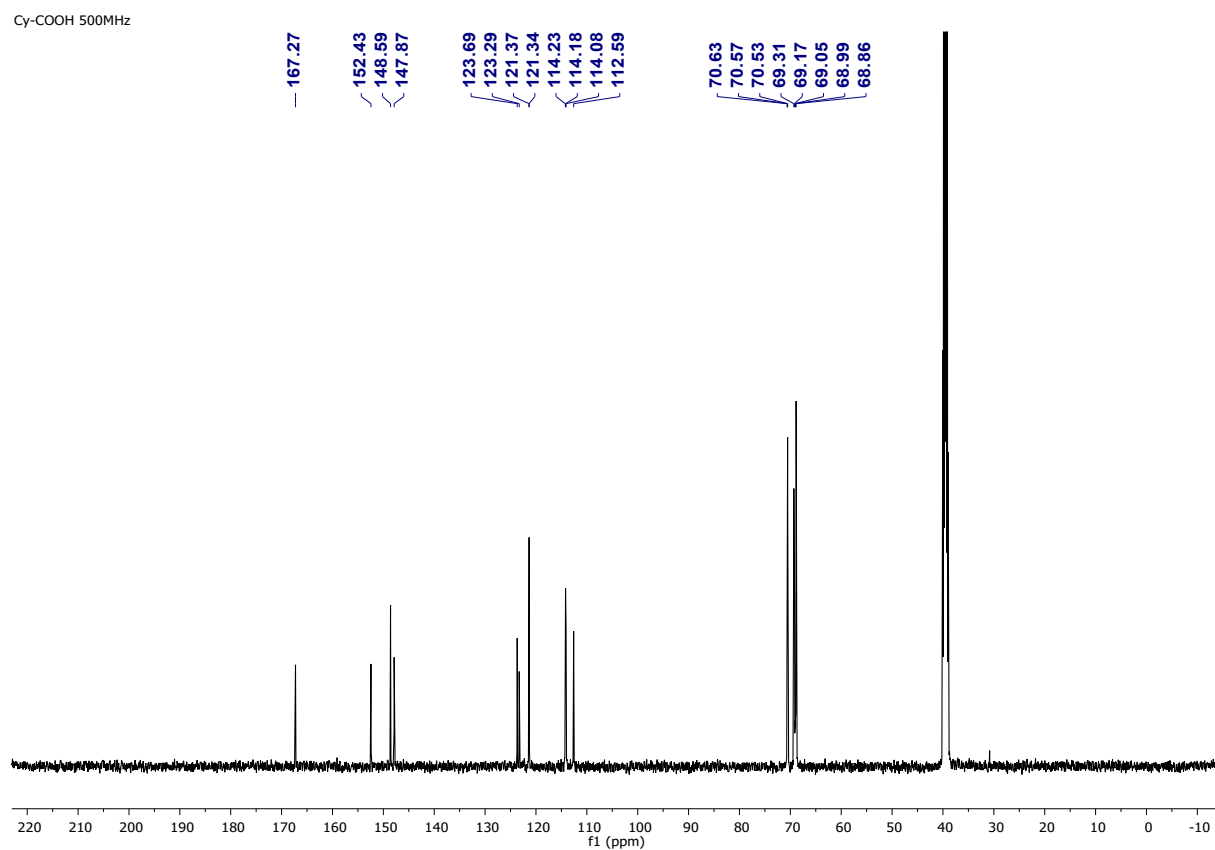
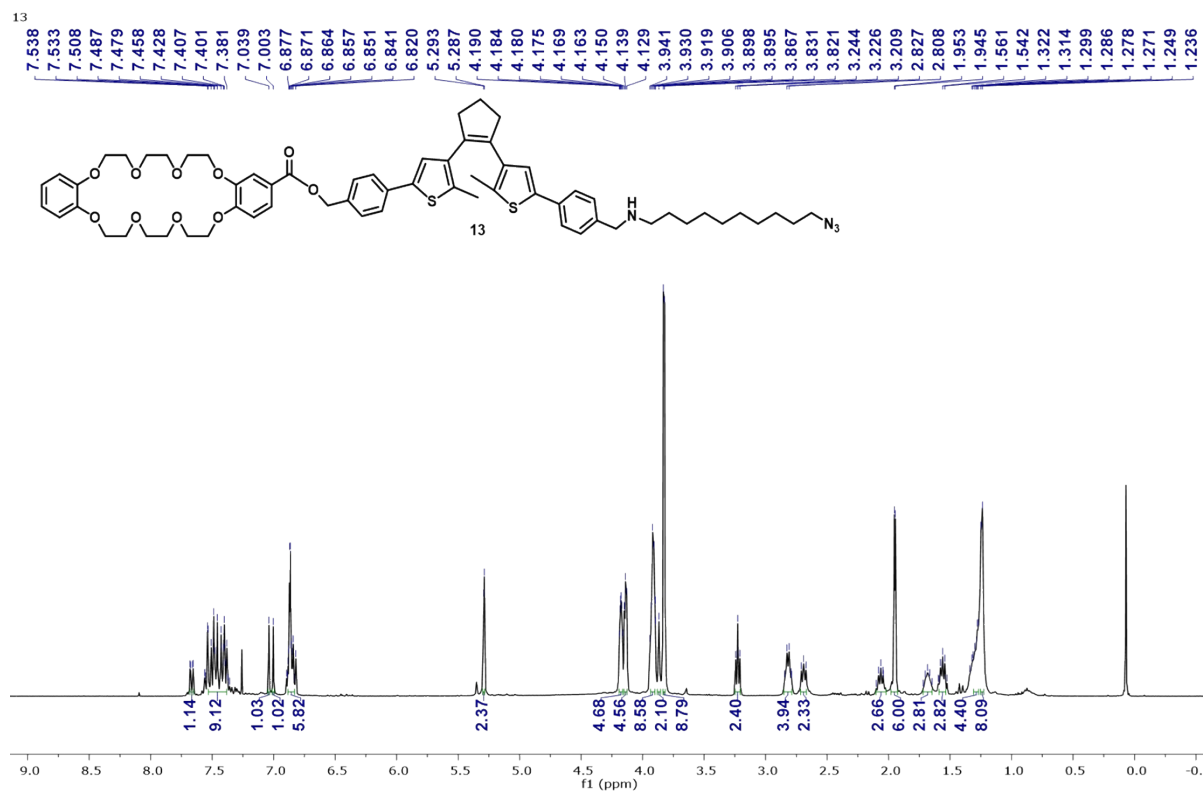


Fig. S12 ^{13}C NMR spectrum (125 MHz, DMSO) of compound 11.



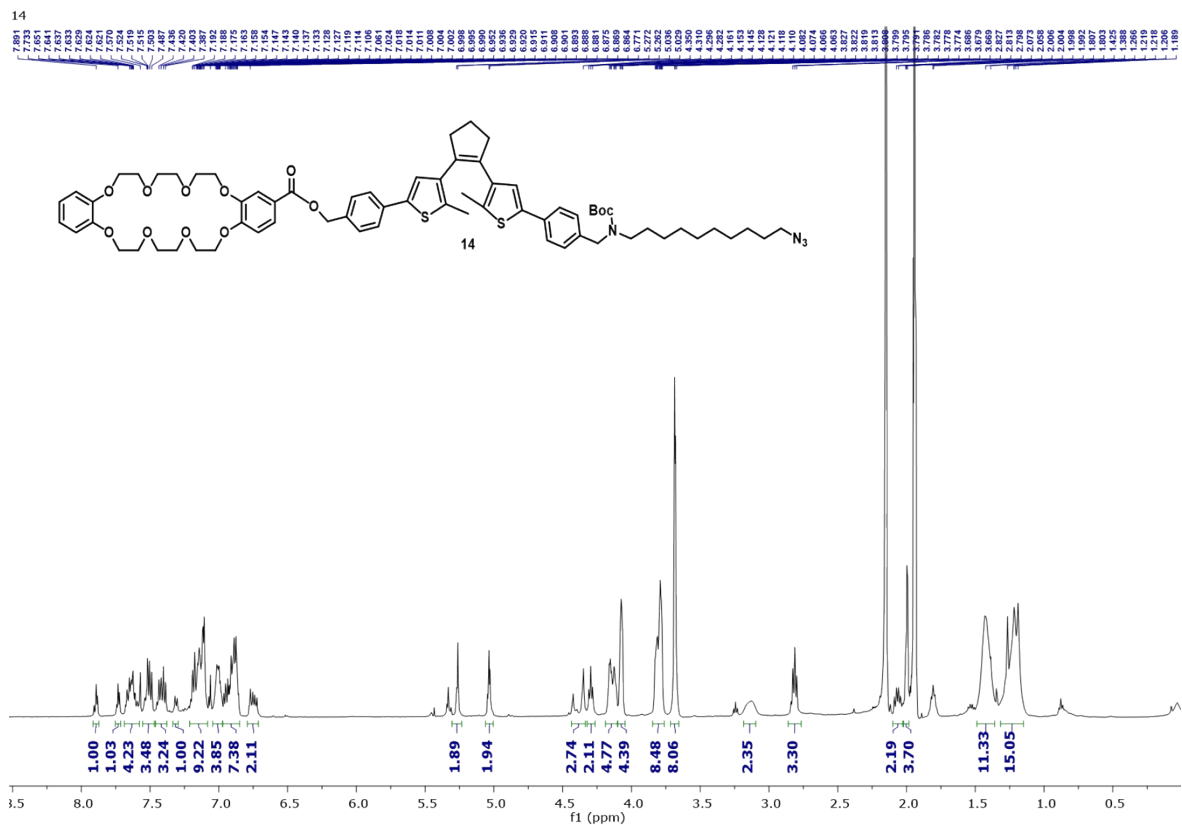


Fig. S17 ¹H NMR spectrum (400 MHz, CD₃CN) of compound 14.

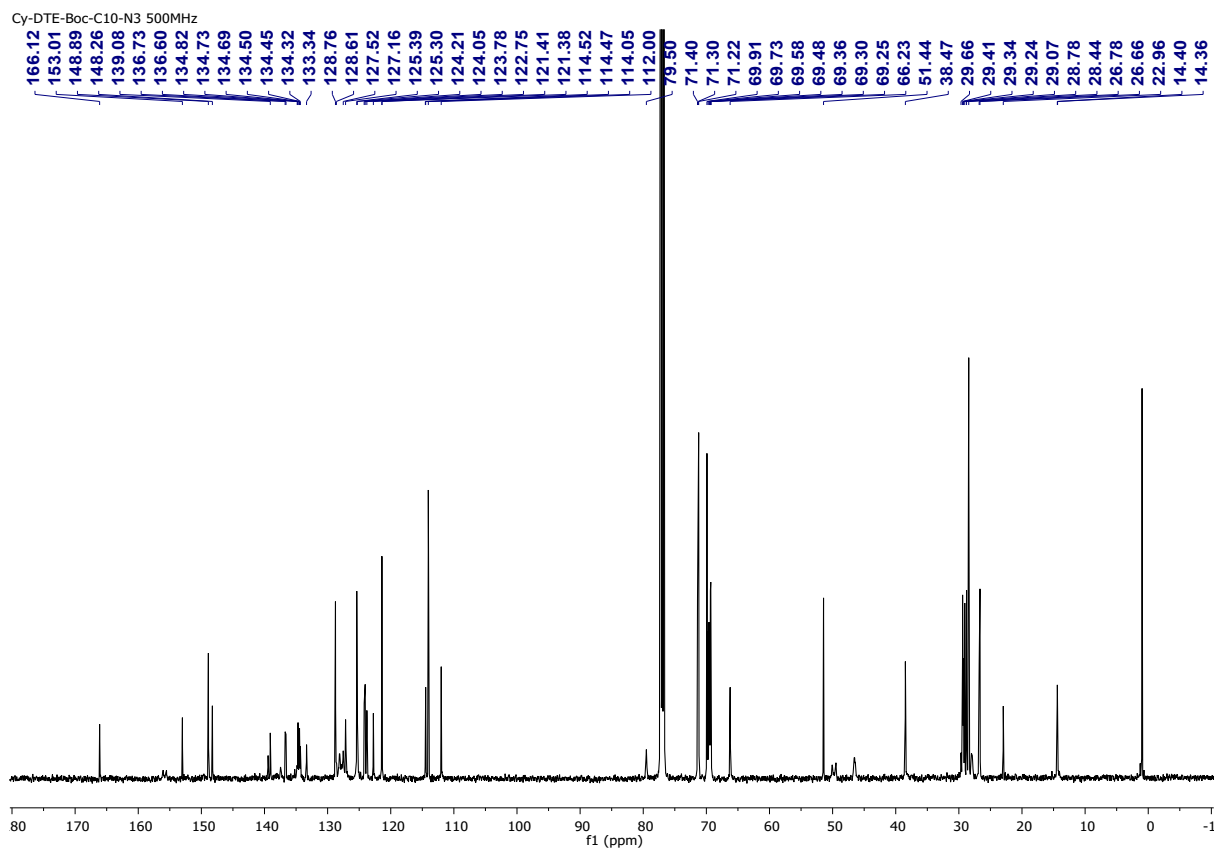


Fig. S18 ¹³C NMR spectrum (125 MHz, CDCl₃) of compound 14.

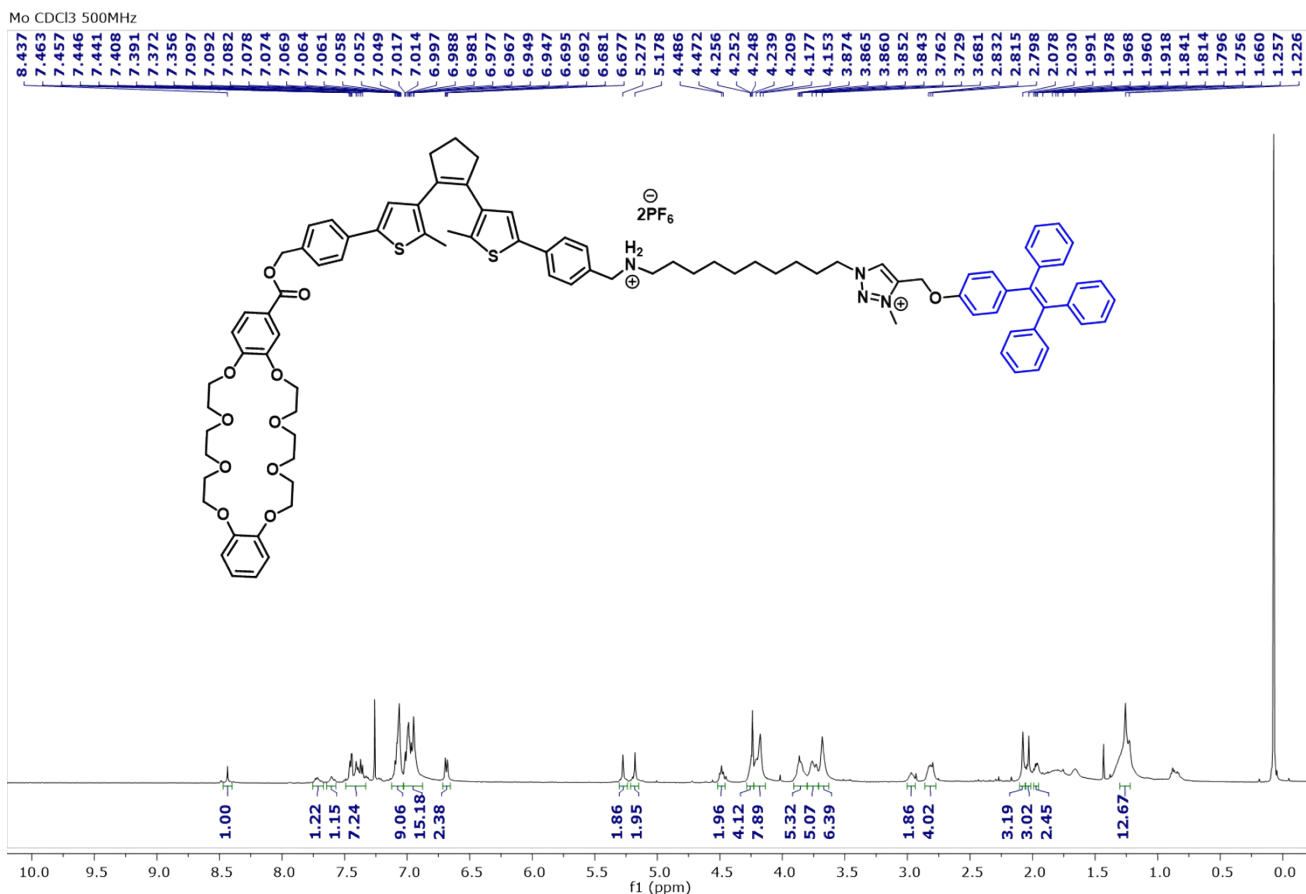


Fig. S19 ¹H NMR spectrum (500 MHz, CDCl₃) of NIM.

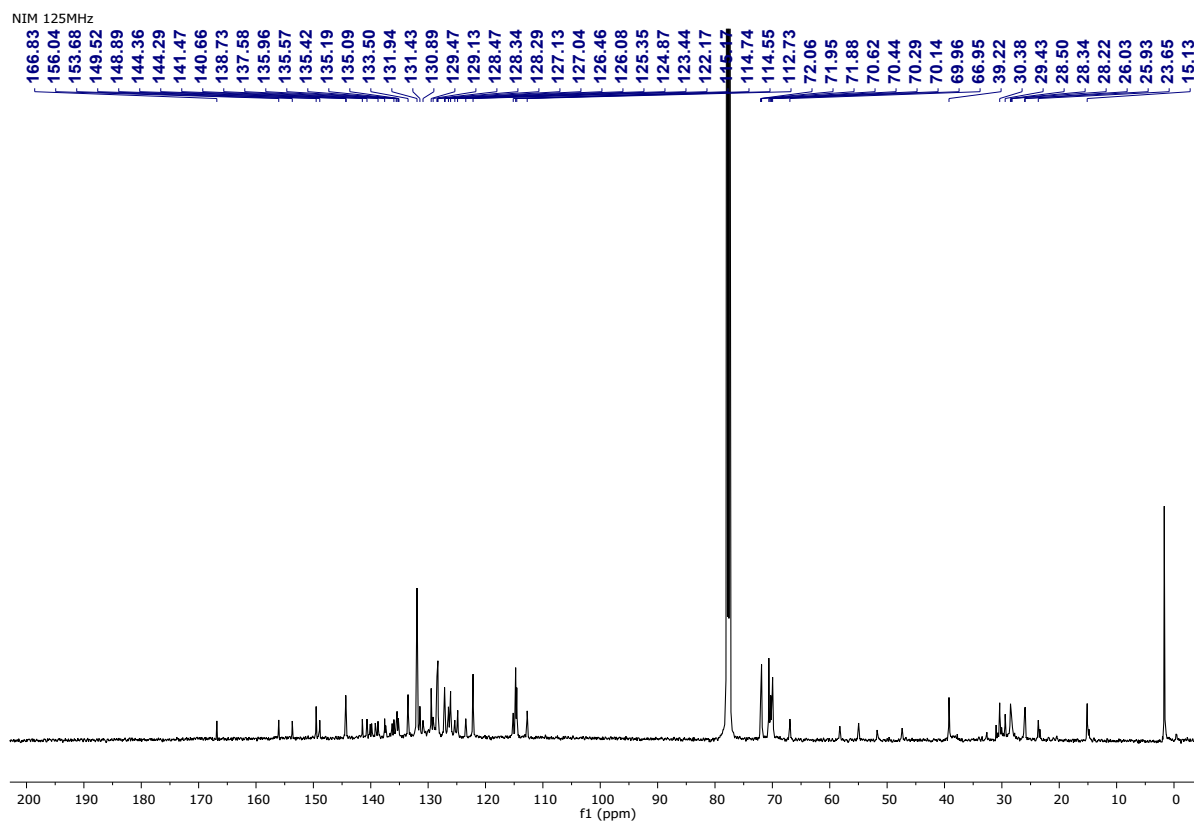


Fig. S20 ¹³C NMR spectrum (125 MHz, CDCl₃) of NIM.

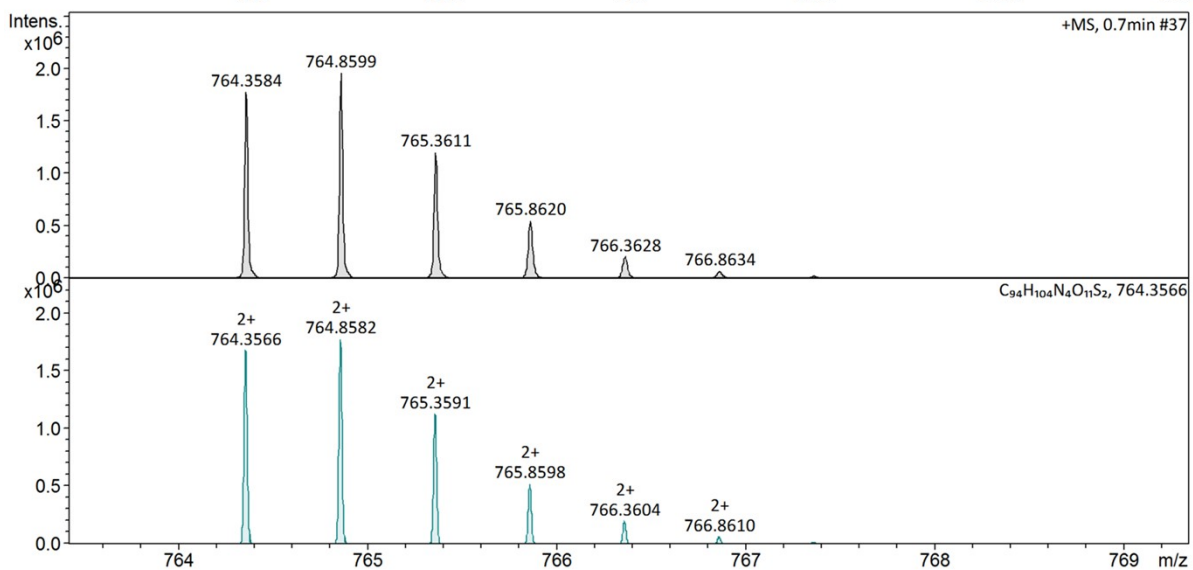
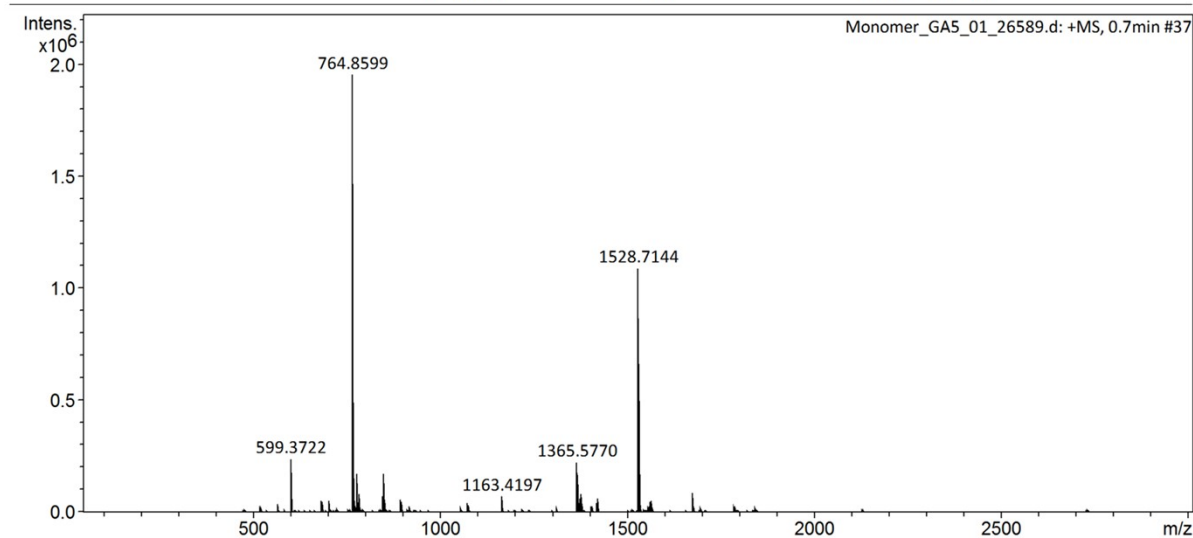
Display Report

Analysis Info

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Method	MW600-3000.m	Operator	NCTU
Sample Name	NIM	Instrument	impact HD
Comment			1819696.00164

Acquisition Parameter

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Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
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Fig. S21 HRMS-ESI spectra of **NIM**.

Display Report

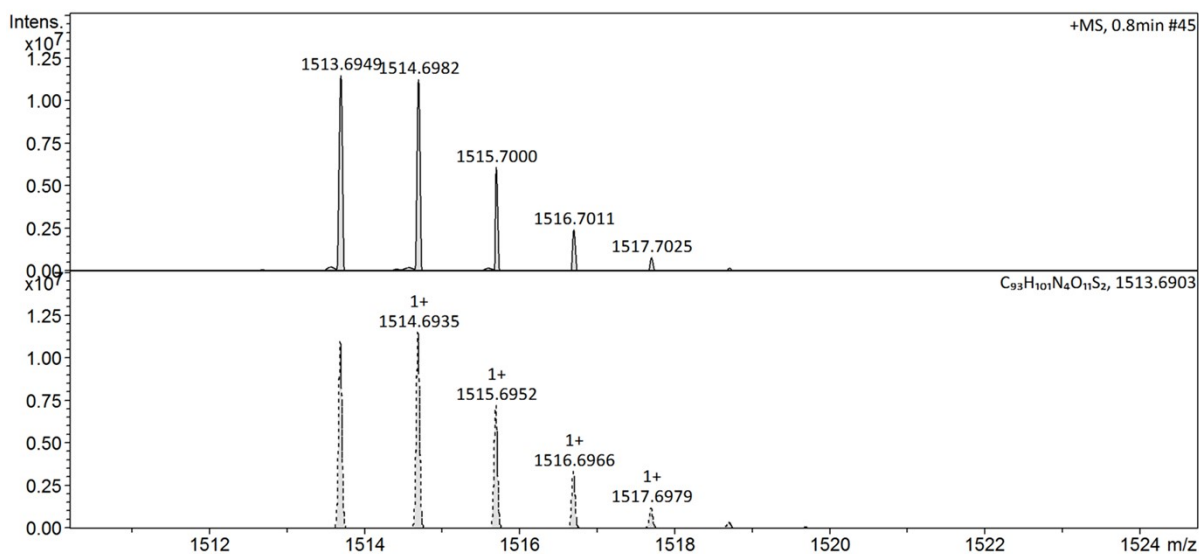
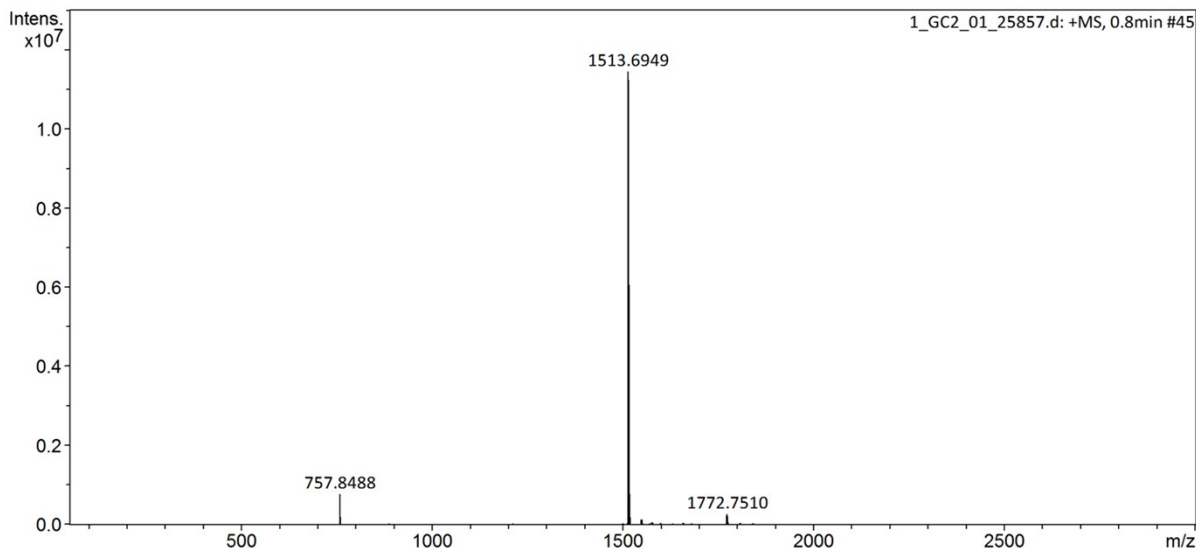
Analysis Info

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Sample Name 15
Comment

Acquisition Date 7/6/2021 12:52:39 PM
Operator NCTU
Instrument impact HD 1819696.00164

Acquisition Parameter

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Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
1513.6949	1	C ₉₃ H ₁₀₁ N ₄ O ₁₁ S ₂	1513.6903	-3.1	54.4	1	100.00	45.5	even	ok	M

Fig. S24 HRMS-ESI spectra of compound 15.

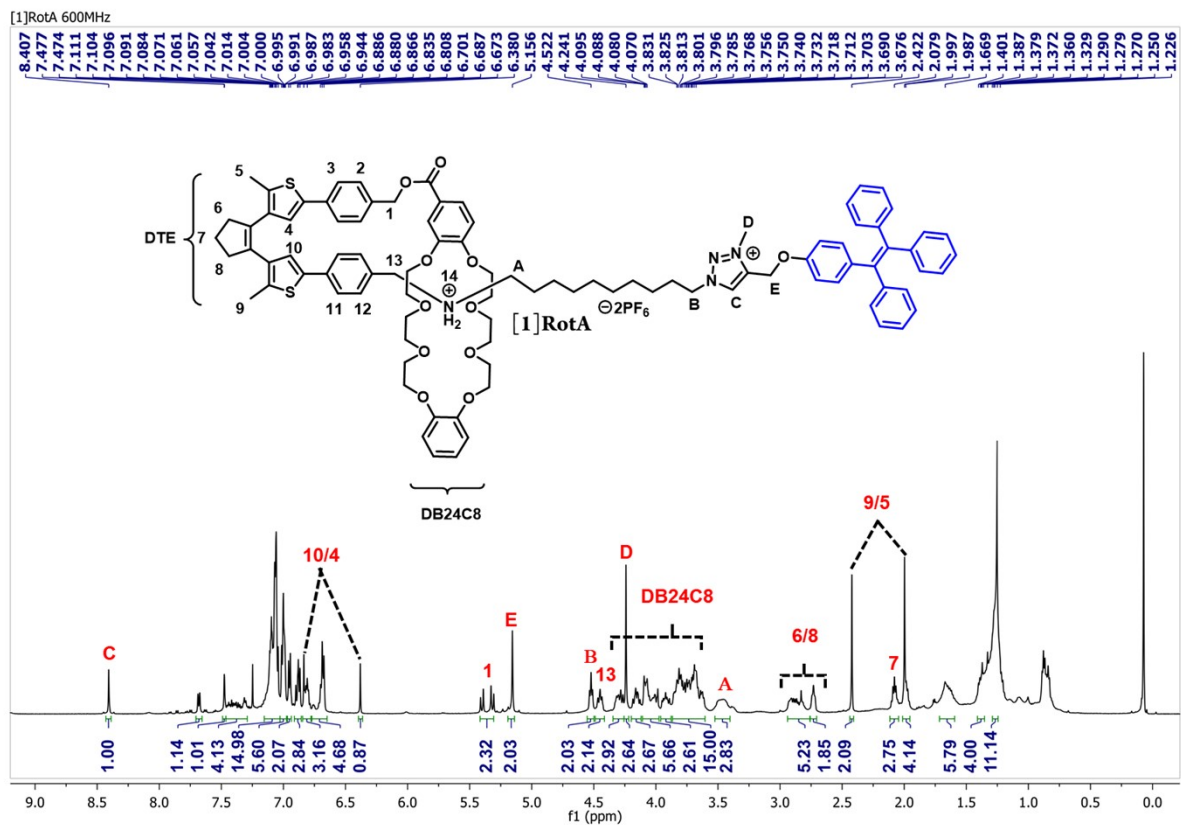


Fig. S25 1H NMR spectrum (600 MHz, $CDCl_3$) of [1]RotA.

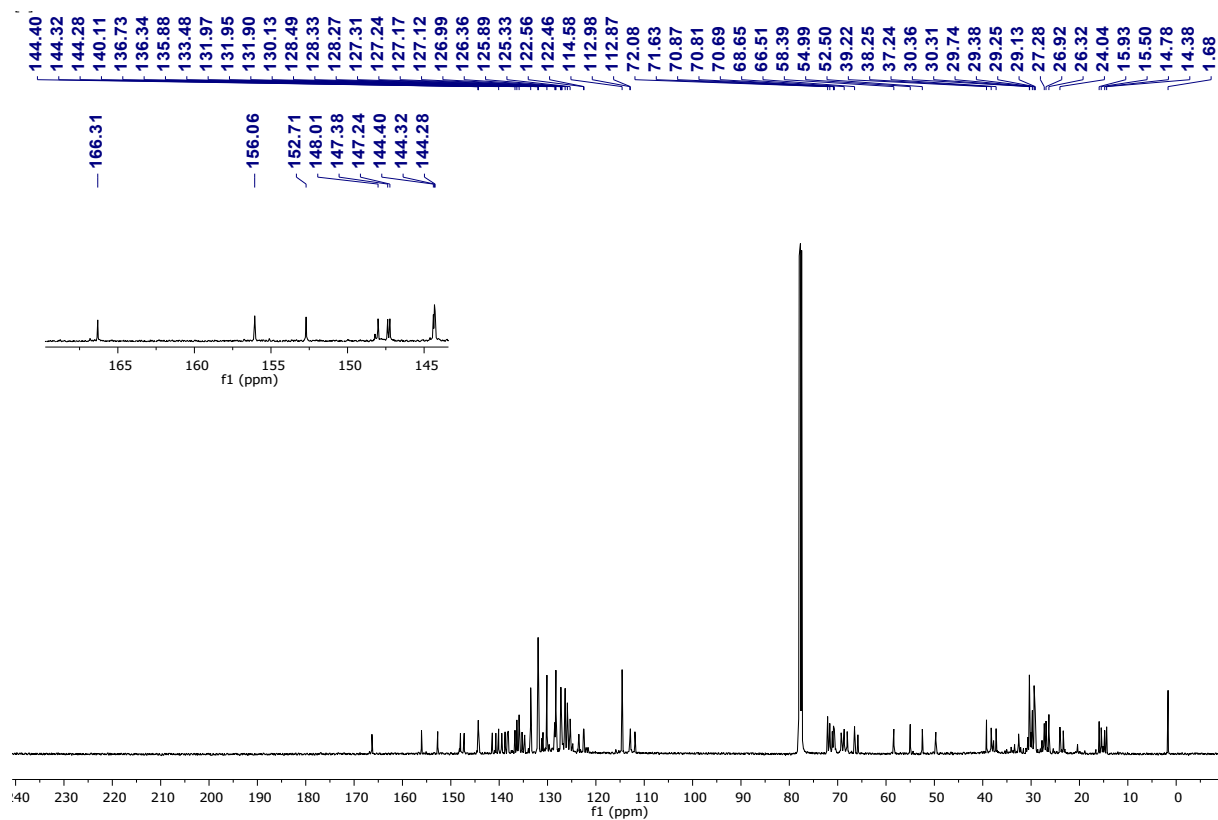


Fig. S26 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of [1]RotA.

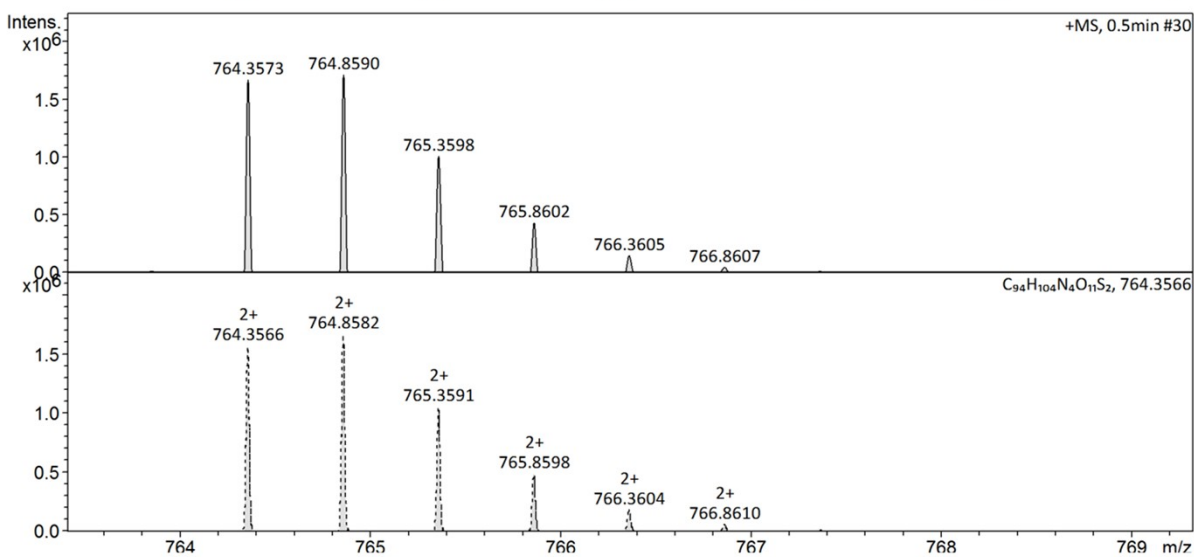
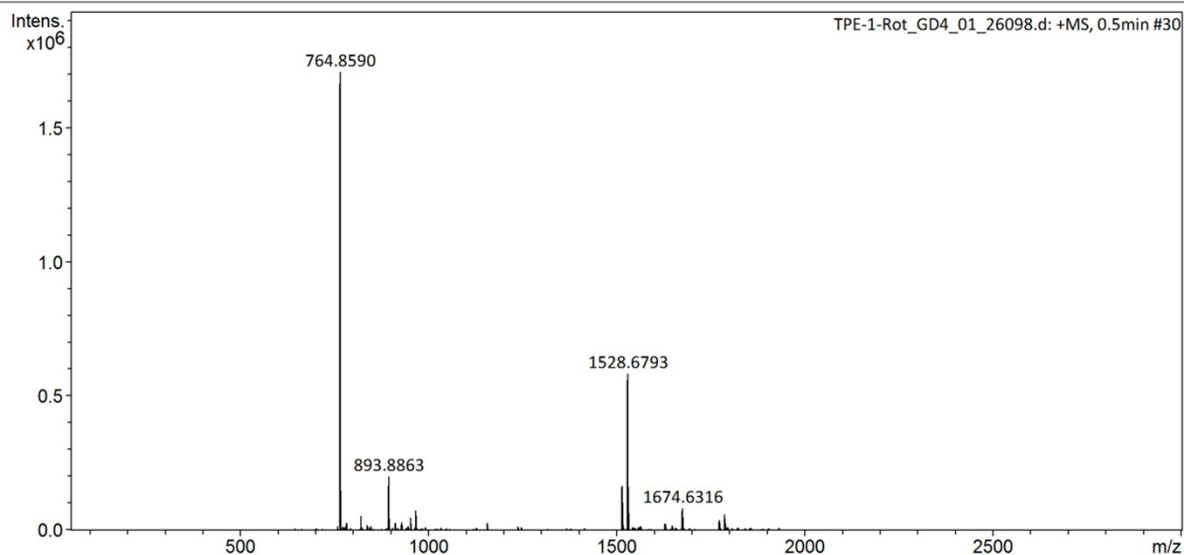
Display Report

Analysis Info

Analysis Name	D:\Data\Nctu service\data\2021\20210720\TPE-1-Rot_GD4_01_26098.d	Acquisition Date	7/20/2021 12:59:50 PM
Method	MW600-3000.m	Operator	NCTU
Sample Name	TPE-1-Rot	Instrument	impact HD 1819696.00164
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
764.3573	1	C ₉₄ H ₁₀₄ N ₄ O ₁₁ S ₂	764.3566	-0.9	28.2	1	100.00	45.0	even	ok	M

Fig. S27 HRMS-ESI spectra of **[1]RotA**.

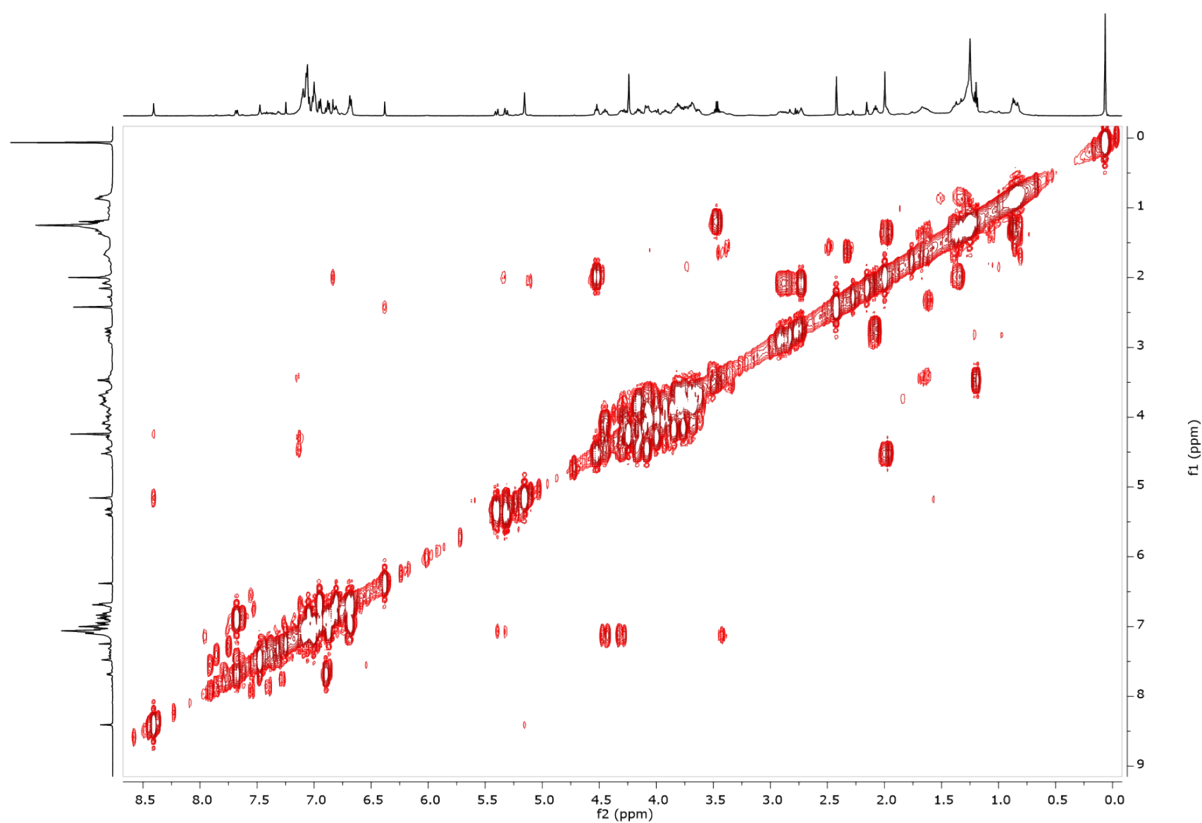


Fig. S28 2D COSY spectrum (600 MHz, CDCl₃) of **[1]RotA**.

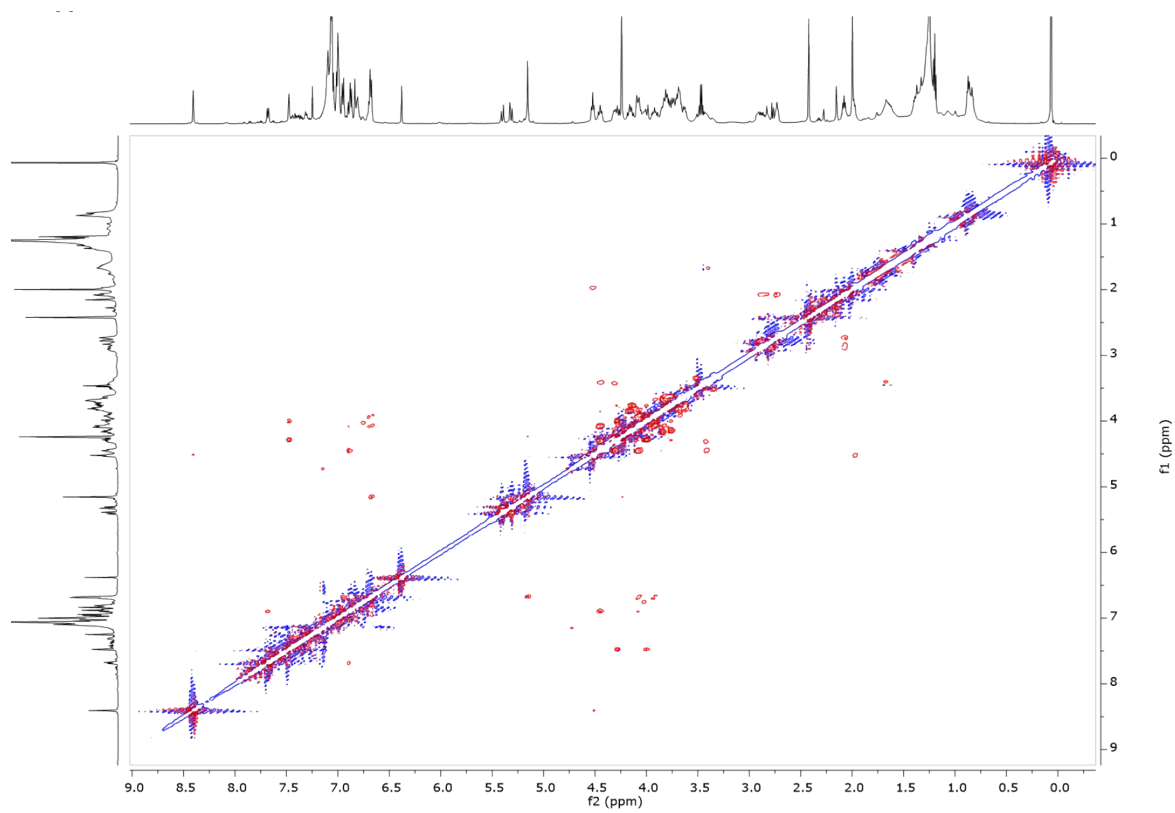


Fig. S29 2D ROESY spectrum (600 MHz, CDCl₃) of **[1]RotA**.

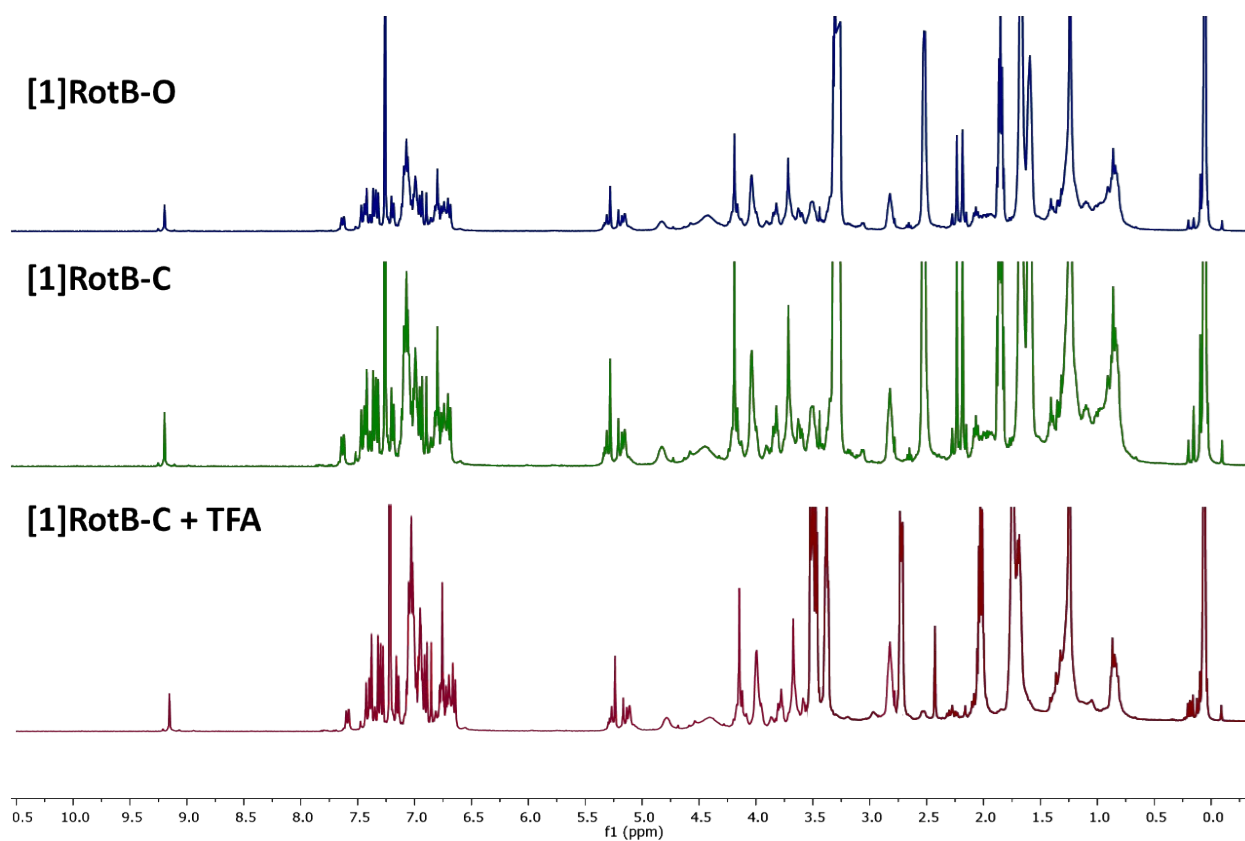


Fig. S30 ¹H NMR spectra (400 MHz, CDCl₃) of **[1]RotB-O**, **[1]RotB-C** and **[1]RotB-C+TFA**.

Since we wonder what will happen to [1]RotB-C by adding TFA to see if its macrocycle can shuttle back to its original ammonium station, the ¹H NMR data of **[1]RotB-O**, **[1]RotB-C** and **[1]RotB-C+TFA** are added and compared in Fig. S30. As expected, there is no obvious difference in the ¹H NMR data of **[1]RotB-C** and **[1]RotB-C+TFA** (i.e., before/after adding TFA), because **[1]RotB-C** would prohibit the shuttling of its macrocycle back to its original ammonium station due to the rigid and bulky DTE closure form in **[1]RotB-C**.

3. Photo-physical and morphological studies of novel compounds

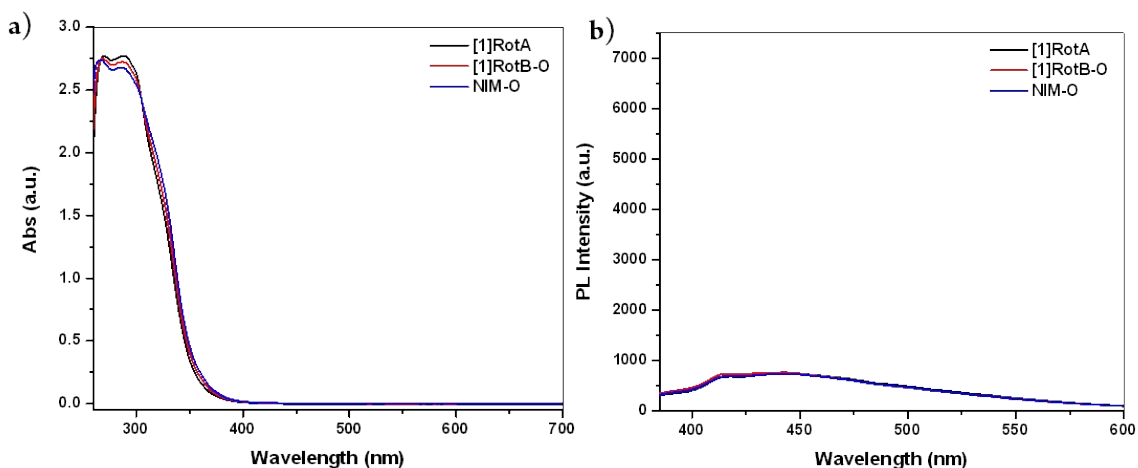


Fig. S31 Absorption spectra (a) and PL intensities of **[1]RotA**, **[1]RotB-O** and **NIM-O** in DMSO solutions. Compound concentration: 50 μM , λ_{ex} : 310 nm.

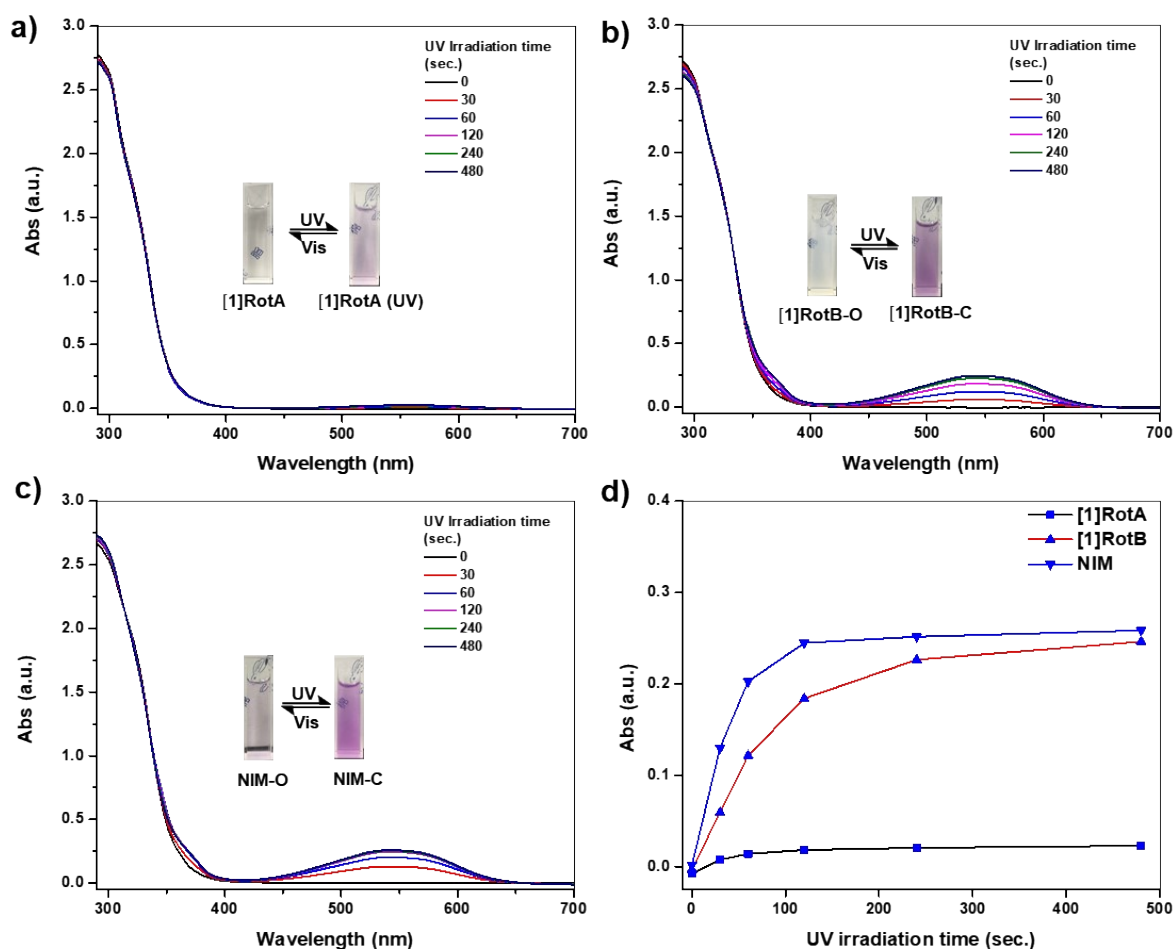


Fig. S32 Absorption spectra of (a) **[1]RotA**, (b) from **[1]RotB-O** to **[1]RotB-C** upon UV exposure, (c) from **NIM-O** to **NIM-C** upon UV exposure, (d) Relative absorbance of **[1]RotA**, **[1]RotB-O** and **NIM-O** upon UV exposure. *Insets*: photo-images of (a) **[1]RotA**, (b) **[1]RotB-O** and (c) **NIM-O** before and after UV irradiation for 480 s, in solution DMSO. Compound concentration: 50 μM , λ_{ex} : 310 nm.

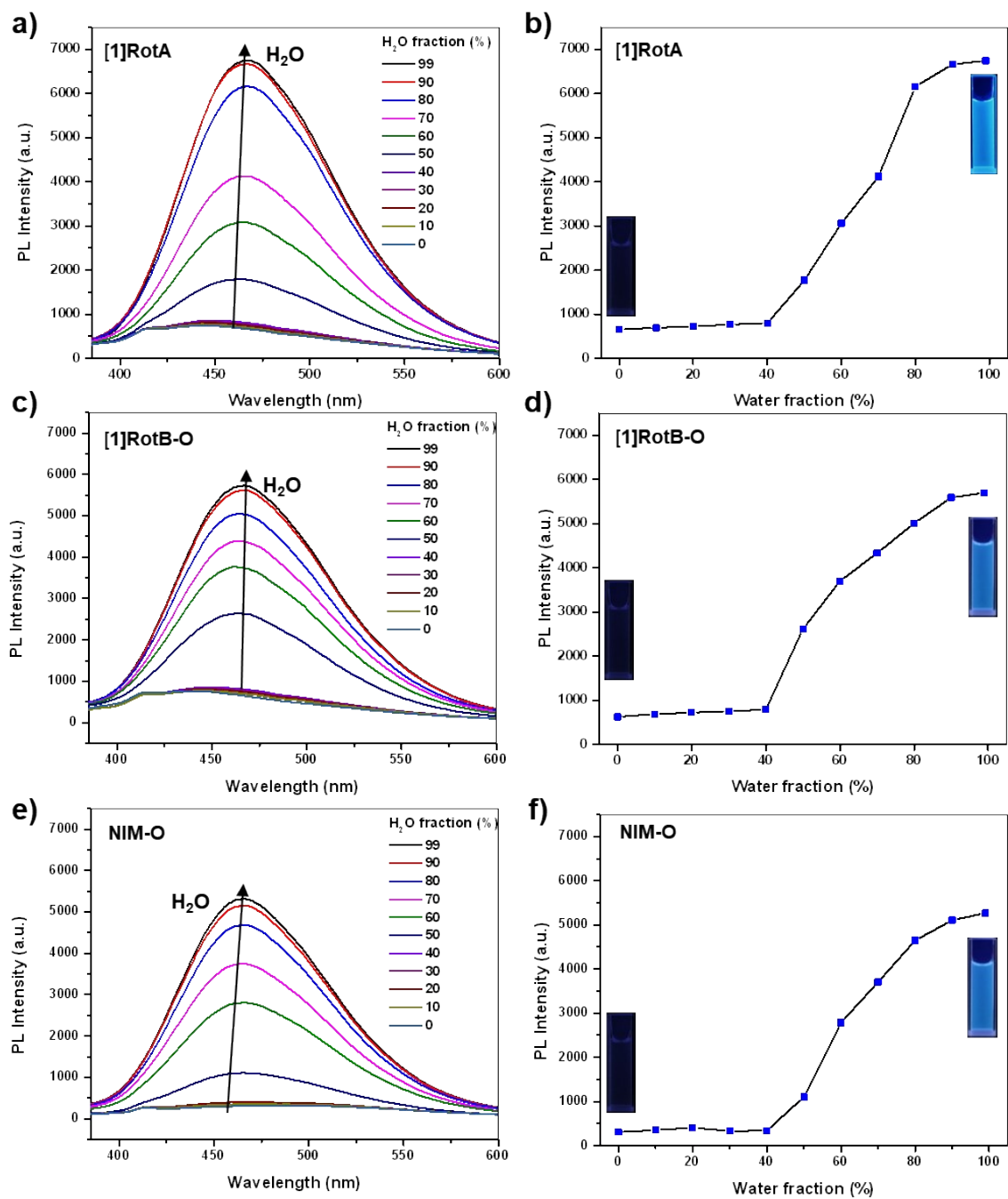


Fig. S33 PL spectra and relative emission intensities of (a) and (b) [1]RotA, (c) and (d) [1]RotB-O, (e) and (f) NIM-O with different water fractions. *Insets:* Fluorescence photo-images of (b) [1]RotA, (d) [1]RotB-O and (f) NIM-O in pure DMSO (left) and DMSO/H₂O (1/99, v/v) (right) under UV lamp. Concentration: 50 μ M, λ_{ex} : 310 nm.

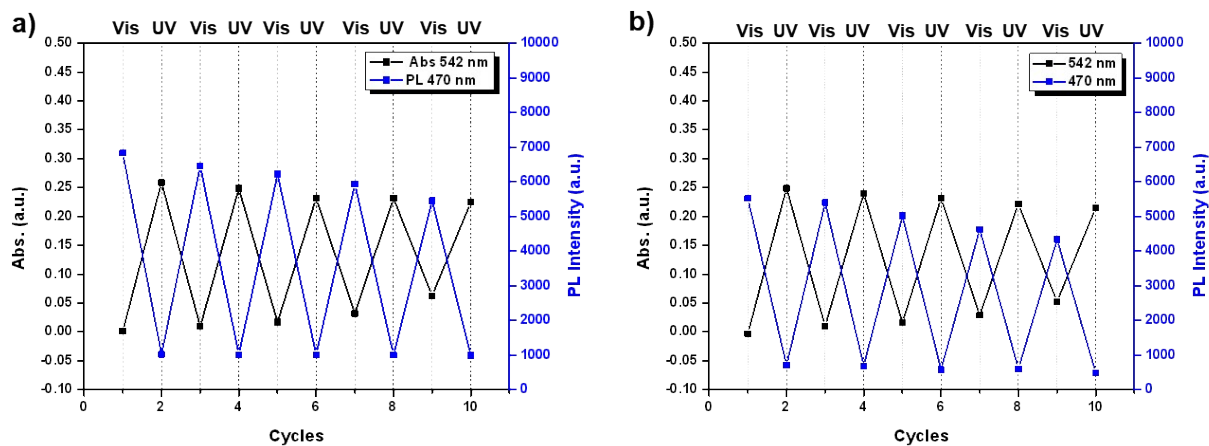


Fig. S34 Photo-fatigue resistance from absorption and PL profiles of (a) **[1]RotB** and (b) **NIM** alternating UV (365 nm, 60 s) and visible light (>500 nm, 600 s) irradiation. Compound concentration: 50 μ M, λ_{ex} : 310 nm.

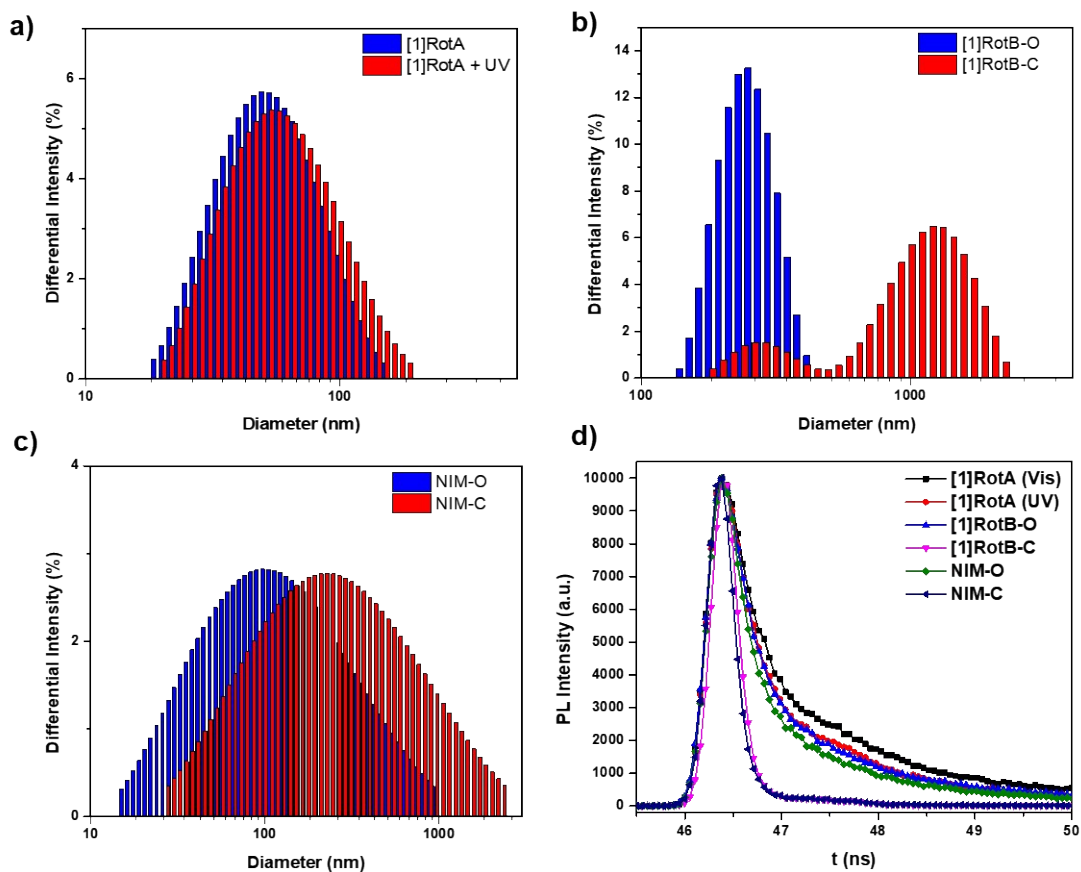


Fig. S35 DLS results of (a) **[1]RotA**, (b) **[1]RotB** and (c) **NIM** in DMSO/H₂O co-solvent (1/99, v/v) before and after UV exposure. (d) TRPL profiles of **[1]RotA**, **[1]RotA(UV)**, **[1]RotB-O**, **[1]RotB-C**, **NIM-O** and **NIM-C**. Concentration: 50 μ M, λ_{ex} : 310 nm.

Besides, the alternative ring-opening and closure of [1]rotaxanes and related structures (i.e. from open form of [1]RotB-O and NIM-O to close form of [1]RotB-C and NIM-C) can be proceeded by optical switchable UV/Vis irradiation leading to reversible FRET-OFF/ON processes, i.e. TPE emission on/off within ten cycles (Fig. S34), suggesting not only good reversibilities and stabilities of photochromism signatures but also strong relationship between photochromism and FRET behaviours. In addition, the average particles sizes of [1]RotA, [1]RotB-O and NIM-O in Figs. S35a-c were examined by DLS technique to be 55, 251 and 158 nm, respectively. Surprisingly, upon UV exposure the average particle size of NIM-C and [1]RotB-C were enormously become 2 and 4-fold increase (395 and 1080 nm), respectively, due to the stronger $\pi - \pi$ stacking of photo-isomerization of DTE for both NIM-C and [1]RotB-C along with a larger loop effect for [1]RotB-C, which was proposed in Figs. S35c and S35d, while the sizes of [1]RotA(UV) in Fig. 4a was only slightly enhanced (64 nm) owing to the less aggregation in the flexible open form of DTE. Besides, their self-assembly properties are visualized by the SEM images (Fig. S36) with similar sizes of DLS results.

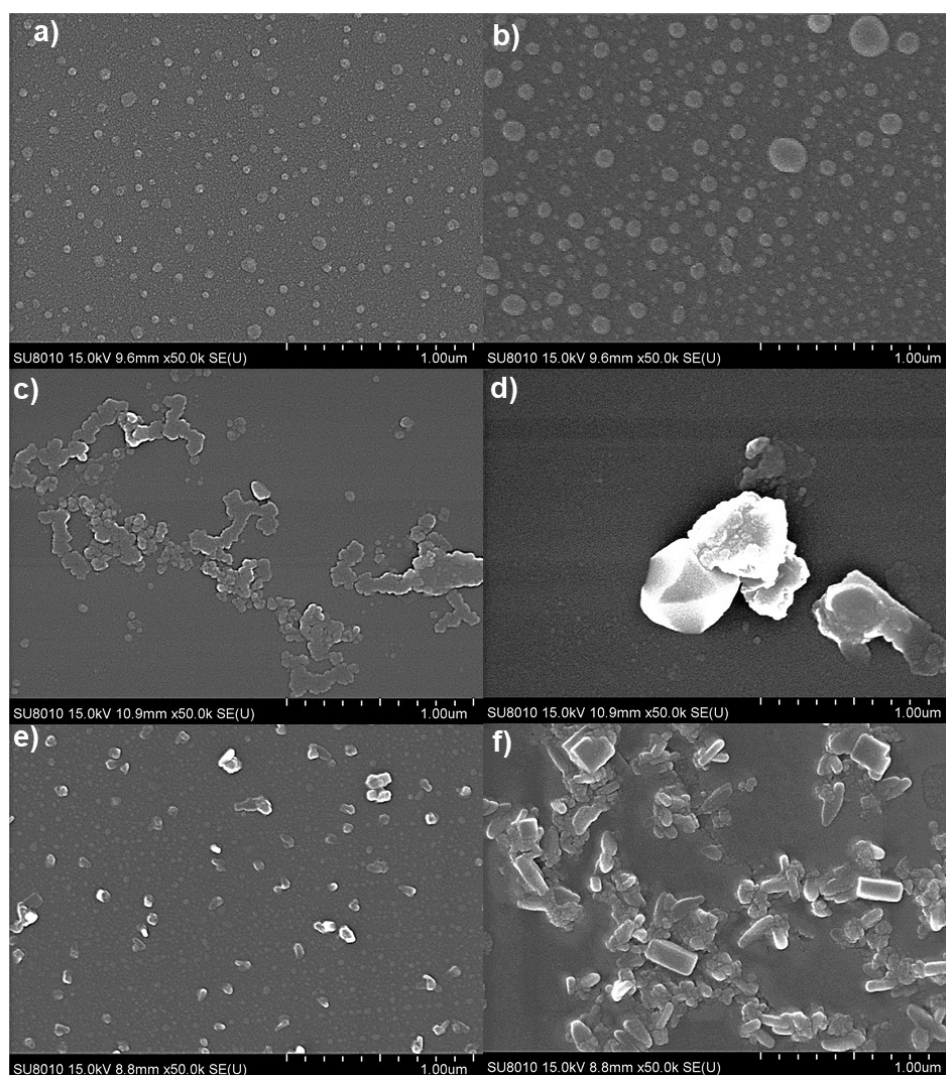


Fig. S36 SEM images before and after UV exposure of (a), (b) [1]RotA, (b), (c) [1]RotB and (c), (d) NIM in THF/H₂O solutions with 99% water fraction. Concentration: 100 μ M.

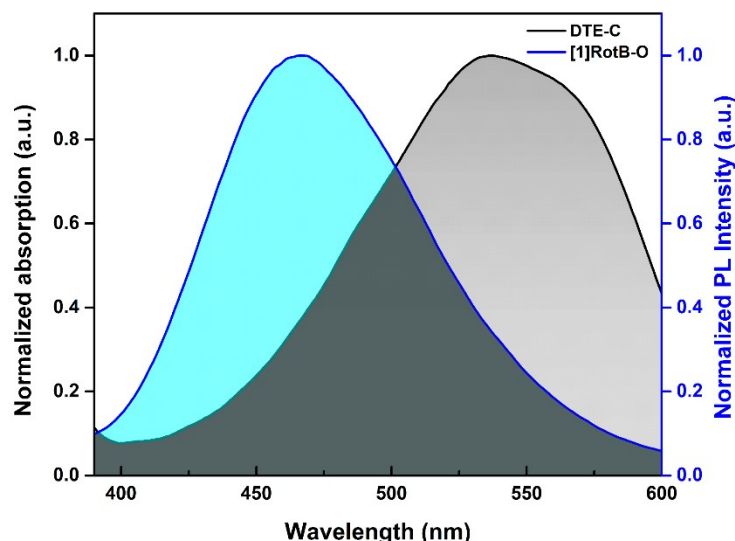


Fig. S37 Spectral overlap between [1]RotB-O emission and DTE-C absorbance. Concentration: 50 μ M, λ_{ex} : 310 nm.

Indeed, the **DTE-C** absorption spectrum ($\lambda_{\text{abs}} = 542$ nm) was partially overlapped with the **TPE** emission spectrum ($\lambda_{\text{ex}} = 470$ nm), resulting in Förster resonance energy transfer (FRET)⁵ processes of releasing emission energy from **TPE** donor to be absorbed by **DTE-C** acceptor in [1]RotB-C and NIM-C (Fig. S37). Furthermore, the fluorescence lifetime values and FRET efficiencies of [1]RotA, [1]RotA(UV), [1]RotB-O, [1]RotB-C, NIM-O and NIM-C were also obtained by TRPL measurements in order to approve the FRET processes of **TPE** donor transfer emitting energy to **DTE-C** acceptor (Fig. S35d). Concerning the DTE open form of [1]RotA, [1]RotB-O and NIM-O without FRET phenomena, we observed respective longer lifetime values of **TPE** donor at 470 nm to be 2.51, 2.06 and 2.06 ns. (see Table S1). However, with FRET processes, [1]RotA(UV), [1]RotB-C and NIM-C exhibited corresponding shorter lifetime values of 2.02, 0.6 and 0.58 ns. Notably, the FRET efficiencies of [1]RotA(UV), [1]RotB-C and NIM-C (19.4%, 70.6% and 71.8%, respectively) revealed that the efficient FRET processes consist with our design in the switchable FRET behaviours based on molecular machine tuned by acid-base, where [1]RotA is FRET-OFF locked and inert to UV exposure due to the DTE p-conformer, compared with unlocked and flexible transformation between p-conformer and ap-conformer of DTE open form in [1]RotB-O/[1]RotB-C and NIM-O/NIM-C.

Table S1 Average Sizes (d, nm) and Lifetime Values (τ , ns) of [1]RotA, [1]RotA(UV), [1]RotB-O, [1]RotB-C, NIM-O and NIM-C in DMSO/H₂O (99%)

Entry	[1]RotA	[1]RotA (UV)	[1]RotB-O	[1]RotB-C	NIM-O	NIM-C
D _h (nm) ^[a]	57	64	251	1080	158	395
τ (ns) ^[b]	2.51	2.02	2.02	0.60	2.06	0.58
E (%) ^[c]		19.4		70.6		71.8

^[a] Determined by DLS with compound concentration: 50 μ M in DMSO/H₂O (1:99, v/v). ^[b] Determined by TRPL ($\lambda_{\text{ex}} = 375$ nm and $\lambda_{\text{em}} = 470$ nm).

^[c] Determined by
$$E = 1 - \frac{\tau_{DA}}{\tau_D}$$

4. pH-Gated on FRET phenomena

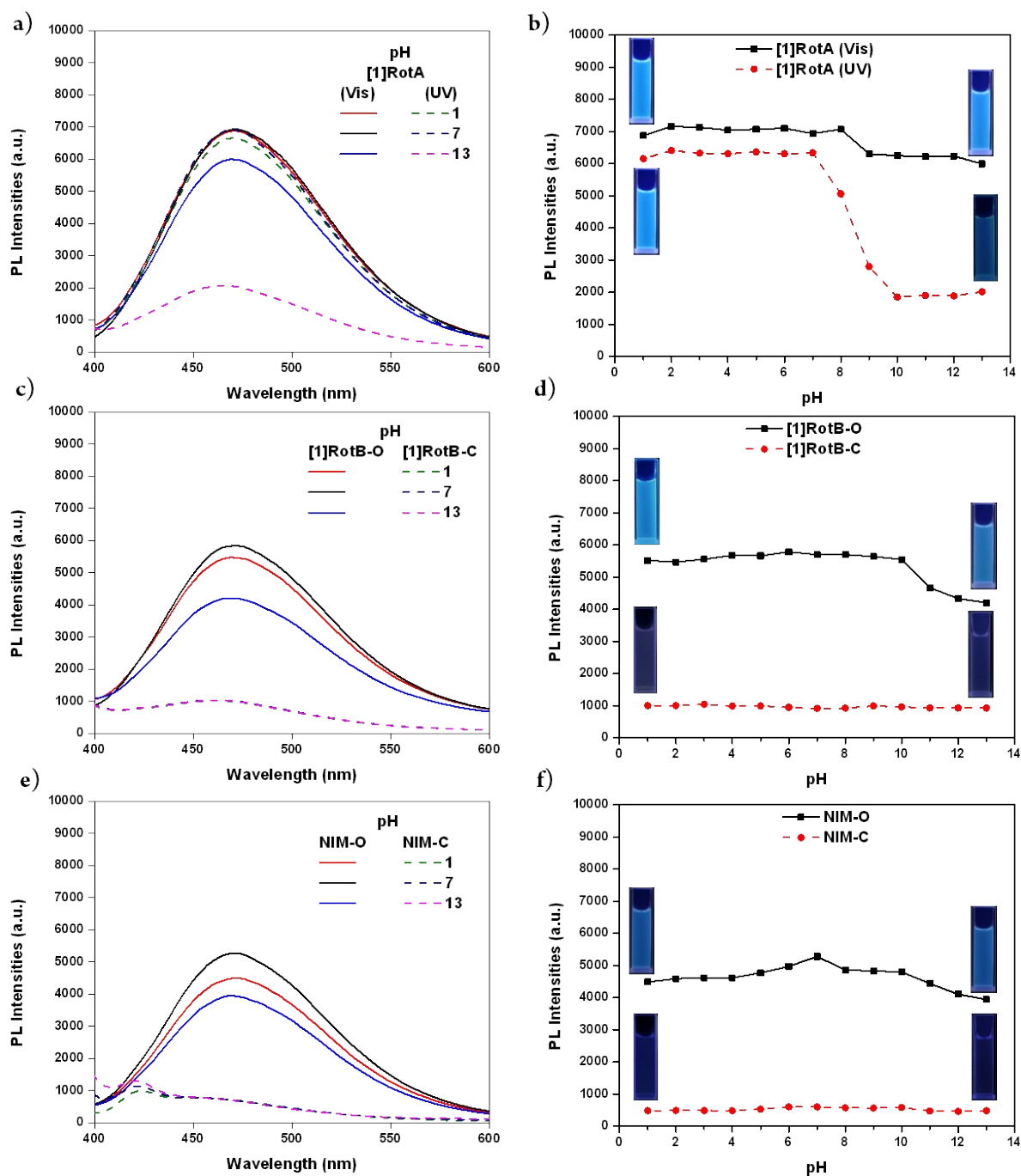


Fig. S38 PL spectra and relative PL intensities of (a) and (b) **[1]RotA** under UV/Vis exposures, (c) and (d) **[1]RotB-O**, **[1]RotB-C** and (e) and (f) **NIM-O**, **NIM-C** in DMSO/H₂O (1:99, v/v) at various pH values. *Insets*: PL photo-images of (b) **[1]RotA**, (d) **[1]RotB** and (f) **NIM** upon UV/Vis irradiations at pH=1 and 13. Concentration: 50 μ M, λ_{ex} : 310 nm.

Since the motion of MIMs (i.e., molecular shuttling) would be adjusted by the protonated and deprotonated BAA station to become tightened and loosened structures (i.e., **[1]RotA** and **[1]RotB**, respectively) resulting in different locked and unlocked FRET behaviors, thus different acid-base conditions were investigated by the pH effects on FRET processes of bistable **[1]rotaxane** and related structures (i.e., **[1]RotA**, **[1]RotB** and **NIM-O**). Hydrochloride (HCl) and sodium hydroxide (NaOH) solutions were used as an acid and base to control pH from 1 to 13 in semi-aqueous solution (DMSO/H₂O, 1/99, v/v), where their aggregation sizes did not change too much in the DLS measurements (Fig. S35). As shown in Figs. S38a-f, **[1]RotA**, **[1]RotB-O** and **NIM-O** emitted bright

fluorescence in acid and neutral environments ($\text{pH} \leq 7$) but only decreased slightly in base conditions ($\text{pH} > 7$). Interestingly, **[1]RotA**(UV) displayed stable blue PL emissions in acid and neutral conditions ($\text{pH} \leq 7$), while its PL intensity was steadily dropped in basic conditions (at $\text{pH} = 8-10$) and stabilized up to $\text{pH} = 13$ upon UV irradiation (Figs. S38a-b) due to the prominent shuttling of the macrocycle from **[1]RotA** to **[1]RotB-O** under base condition and converting to **[1]RotB-C** under UV exposure. Regarding to **[1]RotB-C** and **NIM-C**, no PL emissions were observed under all pH conditions (Fig. 37c-e) indicating ideal FRET-ON processes between TPE unit and close form of DTE moiety. Accordingly, **[1]RotA** displayed pH-dependent effects on PL properties in comparison with **[1]RotB** and **NIM** due to the macrocycle shuttling motion in **[1]RotA** to be transformed into **[1]RotB** under basic conditions. Owing to the controllable FRET processes by pH-gated photochromic behaviors, **[1]RotA** is demonstrated as an output signaling MIMs from the nanoscale loop design with a large bending structure of DTE open form by programmable external stimuli inputs (i.e., base and UV).

5. DFT stimulation

The optimized structure of **[1]RotA** by Gaussian 16 program ⁷ (see Fig. 5) clearly showed that the structure of open form DTE *p*-conformer was "self-trapped" by the recognition between macrocycle DB24C8 and BAA station to induce a tightened loop with a constrained structure. Since **[1]RotB-O** (loosened loop) and **NIM-O** (non-interlocked structure) offered more spatial flexibilities in the DTE unit after DB24C8 was shuttled to the MTA site, both potentially reactive C1 to C6 distances (denoted as $r_{\text{C1-C6}}$) were calculated as 3.67Å (marked in red colour in Fig. 5), which was suitable to involve the photoisomerization and further to facilitate the ring closure reactions. However, in contrast to **[1]RotB-O** and **NIM-O**, the much longer $r_{\text{C1-C6}}$ distance of 5.49Å (shown in Fig. 5 and Table S2) in the *p*-conformeric structure of **[1]RotA** was induced due to its largest bending structure leading to the largest repulsion of $-\text{CH}_3$ group (attached to both C1 and C6 atoms) and thus to inhibit the ring closure reaction of **[1]RotA** upon UV radiation. According to Fig. 3d, the UV facilitated DTE ring closure reaction speeds and kinetics through the quenching of TPE emission in **[1]RotA**, **[1]RotB-O** and **NIM-O** by following the conformational freedoms of their loop and non-constrained structures in the sequence of **[1]RotA** (tightened loop) < **[1]RotB-O** (loosened loop) < **NIM-O** (non-interlocked molecule). Therefore, the photoisomerization by UV exposure between open and close forms of DTE was operative in **[1]RotB-O** and **NIM-O** but not **[1]RotA**. The FRET distances between DTE and TPE were 1.87 nm in **[1]RotB-C** and 2.62 nm in **NIM-C**, within the range of suitable donor-acceptor distance (1-10 nm) for FRET process.⁵⁻⁶ In addition, the distinct difference was found in the computed absorption profiles of DTE-C and DTE-O *ap*-conformers (see Table S3). The absorption peak at 575 nm in DTE-C provided a good spectral overlap to the TPE emission (470 nm, PL experiment in Fig. S37), leading to an effective FRET process. On the contrary, the absorption profiles in DTE-O resulted in the large spectral separation between DTE-O and TPE. Therefore, the isomerization between DTE-O and DTE-C offered the photo-switchable mechanism for the FRET phenomena. The Cartesian coordinates (in Å) for optimized structures of **[1]RotA**, **[1]RotB-O**, **[1]RotB-C**, **NIM-O**, and **NIM-C** in B3LYP/6-31G(d) are also illustrated in Table S4.

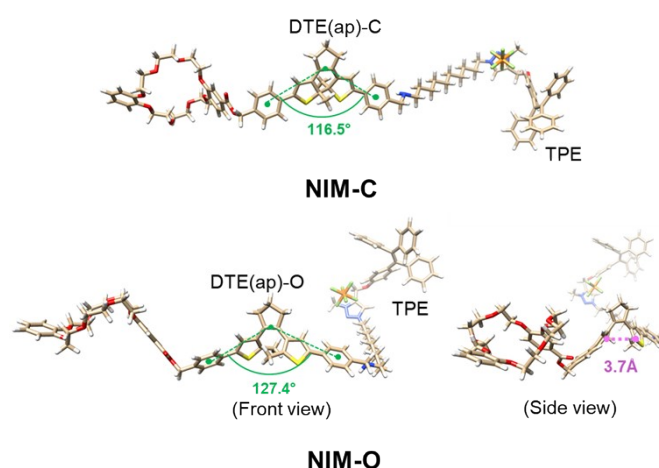


Fig. S39 Optimized structures for **NIM-O** and **NIM-C**, DTE(*p*) and DTE(*ap*) referred to parallel- and antiparallel- conformers, while -C and -O indicated the close and open forms of DTE. The C1 to C6 distances ($r_{\text{C1-C6}}$) for the C1-C6 bond formations in photoisomerization were marked in pink in the side view for open form compounds (**NIM-O** and **NIM-C**).

Table S2 Potentially Reactive C1 to C6 Distances (rC1-C6) and Dihedral Angles (ϕ) for Optimized Structures of **[1]RotA**, **[1]RotB-O** and **NIM-O**

Compound	rC1-C6 (Å)	ϕ (C1, C2, C3, C4) °	ϕ (C3, C4, C5, C6) °
[1]RotA	5.49	127.5	137.3
[1]RotB-O	3.67 ^[a]	48.0	52.7
NIM-O	3.67 ^[a]	49.9	48.8

^[a] rC1-C6 distance in **[1]RotB-O** and **NIM-O** are 3.672 and 3.666 Å, respectively.

Table S3 Computed Absorption Spectra of DTE-C and DTE-O (AP-Conformers), Computed at TD-B3LYP/6-31G⁶

Compounds	Absorptance (oscillator strength) ^[a] nm
DTE-C	575 (0.46) 307 (0.44)
DTE-O	289 (0.73) 273 (0.47)

^[a] The values of absorption wavelengths are given in nm and oscillator strength values were given in parentheses. Only the transitions with oscillator strength > 0.20 were listed.

Table S4. Cartesian coordinates (in Å) for optimized structures of **[1]RotA**, **[1]RotB-O**, **[1]RotB-C**, **NIM-O**, and **NIM-C** in B3LYP/6-31G(d)**[1]RotA**

	X	Y	Z
C	5.30826	-3.23874	-1.3646
C	5.74137	-2.77356	-2.62037
C	4.1005	-2.72479	-0.85613
C	5.02257	-1.81439	-3.32751
H	6.64419	-3.18189	-3.06616
C	3.37333	-1.7772	-1.57226
H	3.74239	-3.0567	0.11403
C	3.8321	-1.28911	-2.80322
H	5.38265	-1.4838	-4.2947
H	2.43241	-1.41145	-1.16888
C	3.08607	-0.22493	-3.57123
H	3.25195	-0.34471	-4.64164
H	2.01203	-0.24758	-3.36743
C	7.24867	2.60014	4.82867
C	6.01686	2.34525	4.01812
O	8.22454	3.1324	4.34596
C	6.24986	2.00596	2.67348

C	4.70453	2.43997	4.47011
C	5.21404	1.66623	1.80978
H	7.27754	1.99931	2.33811
C	3.65029	2.11739	3.61264
H	4.47683	2.77113	5.4766
C	3.88128	1.67951	2.3066
O	5.40262	1.29425	0.50728
H	2.63535	2.1914	3.98343
O	2.88942	1.25151	1.46976
C	6.75293	1.29438	0.02845
C	1.62635	0.9318	2.06712
C	6.81903	0.75668	-1.39394
H	7.36685	0.63413	0.65661
H	7.16999	2.30833	0.09347
C	0.77266	0.14738	1.07327
H	1.10663	1.84781	2.37859
H	1.80398	0.31383	2.95756
H	7.87836	0.56542	-1.62482
H	6.28605	-0.19506	-1.4489
O	6.25275	1.58082	-2.40233
H	0.08026	-0.49033	1.64488
H	1.43475	-0.50851	0.50015
O	0.04617	0.92889	0.14136
C	6.99816	2.73998	-2.78571
C	-1.24811	1.33595	0.59278
C	6.66927	3.13325	-4.21659
H	8.07425	2.51997	-2.7296
H	6.77746	3.57253	-2.10315
C	-2.11448	1.80281	-0.57168
H	-1.75377	0.47966	1.06894
H	-1.17003	2.14141	1.34035
O	5.30657	3.53654	-4.3028
H	7.33115	3.97279	-4.49232
H	6.86501	2.2995	-4.89689
O	-1.82758	3.12279	-1.02411
H	-3.15713	1.83251	-0.24695
H	-2.05066	1.07762	-1.391
C	4.89002	3.7996	-5.64089
C	-0.71815	3.23603	-1.9047

C	3.40495	4.11482	-5.652
H	5.42364	4.68173	-6.03634
H	5.10437	2.94397	-6.28544
C	-1.04606	2.87994	-3.35362
H	0.11146	2.62187	-1.54939
H	-0.40307	4.2831	-1.86754
O	2.622	2.98706	-5.2088
H	3.18524	4.95674	-4.98274
H	3.10766	4.38727	-6.6696
O	0.18647	3.06021	-4.06071
H	-1.3912	1.84562	-3.44914
H	-1.8351	3.53163	-3.74459
C	1.51819	2.61724	-5.96969
C	0.24463	2.64044	-5.36263
C	1.66972	2.15726	-7.27505
C	-0.86879	2.22577	-6.10199
C	0.55097	1.75578	-8.00944
H	2.66985	2.06599	-7.68514
C	-0.71126	1.79591	-7.42254
H	-1.85673	2.23722	-5.65456
H	0.67778	1.39214	-9.02456
N	3.55441	1.18136	-3.23188
H	4.58245	1.19524	-3.10874
C	2.89125	1.80411	-2.03335
H	1.8419	1.91112	-2.31002
H	2.97657	1.10198	-1.20237
C	3.51233	3.15509	-1.66185
H	4.49127	2.96723	-1.21408
H	3.68847	3.74199	-2.56696
C	2.65179	3.96867	-0.68288
H	1.74978	4.30942	-1.20201
H	2.31883	3.32875	0.14366
C	3.41103	5.17868	-0.11981
H	4.2993	4.81939	0.4182
H	3.7878	5.78776	-0.95525
C	2.60011	6.08523	0.82443
H	3.28466	6.83807	1.23473
H	2.25578	5.49592	1.68697
C	1.39248	6.79802	0.16558

H	1.38136	7.85664	0.45814
H	1.52199	6.79546	-0.9265
C	0.02389	6.18951	0.51207
H	-0.17548	6.33697	1.58385
H	0.04183	5.10412	0.35252
C	-1.12102	6.79378	-0.31221
H	-1.12591	7.88744	-0.19288
H	-0.92607	6.60476	-1.37789
C	-2.50086	6.22834	0.06037
H	-2.77288	6.54443	1.0748
H	-2.47521	5.13375	0.03239
C	-3.5611	6.71897	-0.9291
H	-3.54335	7.80823	-1.03478
H	-3.42145	6.264	-1.91215
N	-4.93956	6.356	-0.53086
C	-8.5423	3.05914	0.78922
C	-9.21104	2.55774	1.91164
C	-7.61018	2.27386	0.11203
C	-8.95775	1.26133	2.34177
H	-9.93212	3.18743	2.42419
C	-7.35775	0.9796	0.56724
H	-7.07203	2.62364	-0.7568
C	-8.03068	0.43944	1.67347
H	-9.4867	0.87616	3.20762
H	-6.63076	0.38487	0.02277
C	-7.73205	-0.94201	2.14927
C	-8.71384	-1.85165	2.43361
C	-10.14339	-1.64216	2.0459
C	-10.49643	-1.31439	0.72595
C	-11.17286	-1.8235	2.98609
C	-11.83323	-1.15643	0.36303
H	-9.71569	-1.1864	-0.01742
C	-12.50903	-1.65483	2.62566
H	-10.92043	-2.09258	4.00836
C	-12.8444	-1.32104	1.31184
H	-12.08426	-0.90893	-0.6649
H	-13.28877	-1.7886	3.37088
H	-13.88598	-1.19696	1.02814
C	-8.44126	-3.13292	3.14302

C	-7.65355	-3.17884	4.31169
C	-9.02471	-4.33555	2.69983
C	-7.43373	-4.36379	4.99559
H	-7.2141	-2.26193	4.68913
C	-8.79656	-5.52686	3.37091
H	-9.65397	-4.32878	1.81545
C	-7.99621	-5.57575	4.5346

[1]RotB-O

	X	Y	Z
C	5.50756	6.23762	0.30737
C	5.34251	6.55582	1.66861
C	4.41588	6.45026	-0.5539
C	4.13352	7.05261	2.14372
H	6.15962	6.38063	2.36199
C	3.20351	6.93545	-0.07231
H	4.52065	6.23799	-1.61456
C	3.04154	7.23799	1.28603
H	4.02799	7.27691	3.20289
H	2.36555	7.06877	-0.74975
C	12.04075	-0.94093	-0.61224
C	12.92318	-0.92352	-1.70621
C	11.7655	-2.18727	-0.01616
C	13.51027	-2.09975	-2.17267
H	13.13345	0.01466	-2.21178
C	12.34099	-3.35653	-0.49574
H	11.10196	-2.23676	0.84314
C	13.22929	-3.33458	-1.57965
H	14.18745	-2.05548	-3.02342
H	12.10171	-4.3089	-0.03178
C	1.70771	7.68526	1.82915
H	1.8275	8.30993	2.71699
H	1.12121	8.21792	1.07872
C	13.86414	-4.62708	-2.06186
H	14.49577	-4.4176	-2.94512
H	14.53903	-5.00472	-1.28211
O	0.9364	6.54491	2.30067
C	0.16236	5.91588	1.38411

C	-0.41553	4.65125	1.90187
O	-0.01651	6.33497	0.25255
C	-1.19354	3.88795	1.01139
C	-0.16443	4.1682	3.18556
C	-1.69291	2.65048	1.38586
H	-1.36232	4.29166	0.02087
C	-0.66554	2.9243	3.57581
H	0.43385	4.75062	3.87605
C	-1.40923	2.14421	2.68698
O	-2.43434	1.8226	0.58974
H	-0.4639	2.56053	4.57621
O	-1.88679	0.90288	2.9501
C	-3.01787	2.31049	-0.61304
C	-1.57839	0.27679	4.20412
C	-2.13354	2.18756	-1.84681
H	-3.32331	3.35829	-0.49483
H	-3.91512	1.70392	-0.75858
C	-1.92028	-1.19852	4.12483
H	-2.14813	0.77108	5.00167
H	-0.50557	0.3666	4.41574
H	-2.68319	2.64501	-2.6861
H	-1.18771	2.73687	-1.72759
O	-1.86427	0.8181	-2.13025
H	-1.6223	-1.6564	5.08024
H	-1.32402	-1.68088	3.34626
O	-3.31081	-1.36002	3.89376
C	-1.33853	0.63644	-3.43339
C	-3.84397	-2.60688	4.30857
C	-0.94596	-0.8109	-3.66007
H	-0.44028	1.25954	-3.57931
H	-2.08135	0.93554	-4.18993
C	-3.30514	-3.86563	3.63548
H	-3.6767	-2.73101	5.3926
H	-4.92256	-2.53764	4.13401
O	-2.09882	-1.63848	-3.67564
H	-0.42391	-0.87065	-4.62975
H	-0.23943	-1.14166	-2.88243
O	-3.869	-4.05939	2.33408
H	-3.60109	-4.71474	4.27726

H	-2.21229	-3.86378	3.5893
C	-1.83037	-2.94495	-4.1516
C	-3.51013	-5.32482	1.81252
C	-3.1151	-3.74594	-4.2372
H	-1.39795	-2.89273	-5.16521
H	-1.1032	-3.46344	-3.50792
C	-4.47598	-5.75867	0.72354
H	-3.58681	-6.08968	2.60486
H	-2.46775	-5.3368	1.46476
O	-3.51148	-4.19677	-2.94261
H	-3.89712	-3.11728	-4.68228
H	-2.94968	-4.6123	-4.89296
O	-4.16031	-5.17454	-0.55165
H	-4.43506	-6.85168	0.6229
H	-5.48971	-5.46903	1.0248
C	-4.64237	-4.97921	-2.8754
C	-4.9838	-5.50138	-1.60087
C	-5.44525	-5.27869	-3.97622
C	-6.11719	-6.30798	-1.48246
C	-6.5792	-6.08777	-3.83983
H	-5.19826	-4.88381	-4.9539
C	-6.91275	-6.60131	-2.59587
H	-6.39405	-6.71639	-0.51916
H	-7.18739	-6.3055	-4.71259
N	12.86031	-5.6677	-2.30523
H	13.2927	-6.58421	-2.21414
C	12.19981	-5.57474	-3.61133
H	12.00934	-4.51229	-3.80841
H	12.85153	-5.93067	-4.43082
C	10.86285	-6.3288	-3.62986
H	10.5387	-6.4481	-4.67364
H	11.01216	-7.34552	-3.23652
C	9.7742	-5.60304	-2.83144
H	10.14523	-5.41638	-1.8163
H	9.61974	-4.61179	-3.28403
C	8.42305	-6.32725	-2.76182
H	8.10987	-6.63081	-3.7724
H	8.52604	-7.2558	-2.1813
C	7.33797	-5.43653	-2.14287

H	7.23826	-4.53224	-2.76208
H	7.67686	-5.08557	-1.15732
C	5.95495	-6.08471	-1.99089
H	5.65165	-6.54293	-2.94425
H	6.00522	-6.90289	-1.25812
C	4.90117	-5.05667	-1.55973
H	4.83336	-4.28066	-2.33719
H	5.24745	-4.54221	-0.65236
C	3.49754	-5.61871	-1.29483
H	3.16574	-6.22342	-2.15209
H	3.5271	-6.29141	-0.42704
C	2.50285	-4.47876	-1.03717
H	2.41356	-3.86082	-1.94106
H	2.88276	-3.83663	-0.23861
C	1.11889	-4.97267	-0.62115
H	0.68686	-5.66195	-1.35331
H	1.15264	-5.44874	0.36074
N	0.15982	-3.85344	-0.50289
C	-4.67659	-0.75241	0.53984
C	-5.09491	-0.01696	1.6599
C	-5.53193	-0.87926	-0.56401
C	-6.35173	0.56793	1.6697
H	-4.42404	0.05311	2.50646
C	-6.78527	-0.2654	-0.54211
H	-5.24718	-1.4552	-1.43636
C	-7.22429	0.47414	0.56464
H	-6.66782	1.11931	2.55078
H	-7.43828	-0.37898	-1.40166
C	-8.58474	1.0751	0.60719
C	-9.10973	1.79489	-0.43494
C	-8.2681	2.30877	-1.56062
C	-8.64202	2.09164	-2.89797
C	-7.12418	3.08525	-1.3089
C	-7.88525	2.61014	-3.94824
H	-9.53321	1.50815	-3.11333

NIM-O

X	Y	Z
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C	-11.49558	-6.1961	-2.81098
C	-10.55387	-5.38525	-1.94176
C	-9.575	-6.26866	-1.33299
C	-9.73874	-7.65907	-1.90928
H	-11.39214	-8.37592	-3.20039
H	-12.54861	-5.92003	-2.68198
H	-11.2584	-6.0446	-3.87465
H	-9.52838	-8.45764	-1.18959
H	-9.05808	-7.80674	-2.76162
H	-11.86409	-7.93405	-1.55591
C	-8.70905	-5.81543	-0.38382
C	-7.60437	-6.48212	0.23825
C	-8.92809	-4.39848	0.18054
C	-6.78373	-5.68787	0.98435
H	-7.41707	-7.54258	0.10143
S	-7.30378	-3.98068	1.01871
C	-10.49895	-4.03749	-1.74956
C	-11.37374	-3.00759	-2.22347
C	-9.29184	-3.4563	-0.98922
C	-11.16803	-1.76913	-1.68662
H	-12.17589	-3.20763	-2.92684
S	-9.86096	-1.74868	-0.46681
C	-10.01219	-4.47325	1.28163
C	-8.1401	-3.259	-2.0069
H	-10.1381	-3.51157	1.78389
H	-10.97308	-4.76925	0.84936
H	-9.71845	-5.22032	2.02395
H	-8.50042	-2.65134	-2.84115
H	-7.28509	-2.7565	-1.55052
H	-7.80921	-4.22669	-2.39718
C	-5.54821	-6.08031	1.66968
C	-5.06259	-5.36301	2.77979
C	-4.78667	-7.17067	1.20744
C	-3.87174	-5.72497	3.40123
H	-5.63417	-4.52363	3.16474
C	-3.58978	-7.51937	1.82382
H	-5.1128	-7.71696	0.32765
C	-3.11354	-6.80229	2.92714

H	-3.51585	-5.15228	4.25341
H	-3.00163	-8.34142	1.42365
C	-11.86549	-0.52444	-2.01856
C	-12.50291	-0.36192	-3.26316
C	-11.88104	0.56701	-1.12874
C	-13.10433	0.84577	-3.60587
H	-12.481	-1.17123	-3.987
C	-12.48859	1.76869	-1.47454
H	-11.40977	0.47102	-0.15428
C	-13.0981	1.93455	-2.72539
H	-13.559	0.95403	-4.58845
H	-12.46831	2.60909	-0.78762
C	-1.81128	-7.18477	3.59209
H	-1.97824	-7.6128	4.58499
H	-1.25975	-7.90226	2.9797
C	-13.71095	3.26925	-3.11705
H	-13.89685	3.26656	-4.20825
H	-14.69296	3.37751	-2.63583
O	-0.97402	-6.03545	3.85739
C	-0.32962	-5.51429	2.78117
C	0.4036	-4.26599	3.11131
O	-0.37243	-6.01391	1.67307
C	0.92414	-3.52582	2.0348
C	0.56496	-3.79571	4.41327
C	1.57906	-2.3217	2.24873
H	0.77769	-3.92463	1.03889
C	1.23219	-2.59052	4.64212
H	0.16992	-4.36157	5.24875
C	1.72532	-1.83161	3.57737
O	2.09366	-1.51913	1.26499
H	1.35589	-2.24074	5.65967
O	2.33044	-0.62074	3.70436
C	2.16617	-2.00255	-0.08236
C	2.61737	-0.12898	5.02266
C	0.90561	-1.69997	-0.89854
H	2.37199	-3.07962	-0.08722
H	3.03299	-1.4944	-0.5118
C	3.17834	1.27623	4.93236
H	3.33246	-0.80485	5.50852

H	1.69547	-0.09035	5.61716
H	0.94112	-2.29024	-1.82866
H	0.01465	-2.01021	-0.3428
O	0.73225	-0.32115	-1.19334
H	3.30679	1.64373	5.96207
H	2.46199	1.94101	4.444
O	4.42708	1.25022	4.25133
C	1.49279	0.10902	-2.31832
C	5.3045	2.32653	4.55499
C	1.25959	1.5987	-2.54628
H	1.19796	-0.46062	-3.21369
H	2.566	-0.05011	-2.15911
C	4.89516	3.704	4.04599
H	5.43947	2.39896	5.6471
H	6.26401	2.05051	4.10632
O	2.21308	1.98758	-3.53032
H	0.23575	1.78472	-2.9071
H	1.41017	2.14458	-1.61223
O	4.95956	3.72794	2.62019
H	5.61811	4.42926	4.45933
H	3.89728	3.98953	4.39405
C	2.11437	3.31402	-4.01418
C	4.8441	5.03884	2.08349
C	2.80312	4.38335	-3.16831
H	2.61175	3.29792	-4.99119
H	1.06341	3.60189	-4.17292
C	5.08779	4.9722	0.56961
H	5.61038	5.68793	2.54251
H	3.86084	5.46837	2.31352
O	1.92367	4.85268	-2.12871
H	3.72677	3.98814	-2.73034
H	3.05661	5.232	-3.81943
O	3.8973	4.94646	-0.23534
H	5.72381	5.79993	0.23561
H	5.59555	4.03162	0.34565
C	2.29159	6.05977	-1.56309
C	3.30418	6.13033	-0.57691
C	1.60879	7.21393	-1.94261
C	3.60245	7.37225	-0.00276

C	1.91216	8.44933	-1.36508
H	0.8381	7.12001	-2.7026
C	2.91296	8.52115	-0.39961
H	4.35791	7.44981	0.77061
H	1.37159	9.34065	-1.66864
N	-12.88626	4.393	-2.66971
H	-13.4277	5.25324	-2.72267
C	-11.63045	4.54443	-3.40932
H	-11.17084	3.55074	-3.46188
H	-11.78636	4.86909	-4.45638
C	-10.65861	5.48718	-2.69252
H	-11.02654	6.52315	-2.73395
H	-10.64894	5.20343	-1.63232
C	-9.23134	5.40284	-3.25257
H	-8.95211	4.34069	-3.31619
H	-9.20072	5.78528	-4.28306
C	-8.18247	6.12354	-2.39163
H	-8.31063	7.21304	-2.46466
H	-8.3596	5.86641	-1.33705
C	-6.74256	5.72786	-2.7496
H	-6.50103	6.05706	-3.77063
H	-6.68759	4.62921	-2.76671
C	-5.68466	6.24801	-1.76383
H	-5.54869	7.33221	-1.88417
H	-6.05451	6.09943	-0.73871
C	-4.33977	5.52022	-1.9011
H	-3.90867	5.70335	-2.89583
H	-4.53367	4.43872	-1.85102
C	-3.31604	5.87903	-0.81235
H	-2.9129	6.88703	-0.98267
H	-3.82597	5.91237	0.16095
C	-2.18144	4.84844	-0.72995
H	-1.60897	4.81668	-1.66619
H	-2.62486	3.85504	-0.59385
C	-1.22959	5.10981	0.44158
H	-0.53465	5.9278	0.24164
H	-1.7638	5.33469	1.36688
N	-0.39988	3.92807	0.73393
C	4.38275	1.12277	-0.00403

C	5.06901	0.57225	1.08534
C	4.95493	1.07696	-1.28679
C	6.31658	-0.01394	0.87504
H	4.661	0.6078	2.08854
C	6.18868	0.46904	-1.47618
H	4.41251	1.51532	-2.11895
C	6.89834	-0.09899	-0.40078
H	6.84513	-0.42749	1.72936
H	6.61628	0.43936	-2.47338
C	8.23896	-0.71646	-0.59282
C	8.5043	-1.60318	-1.60409
C	7.42039	-2.25629	-2.40241
C	7.46733	-2.26788	-3.80709
C	6.36335	-2.93057	-1.76744
C	6.47731	-2.90704	-4.55258
H	8.28543	-1.76601	-4.31687
C	5.38033	-3.58059	-2.51222
H	6.32155	-2.94637	-0.68263
C	5.42969	-3.56736	-3.90797
H	6.52795	-2.89393	-5.63812
H	4.58033	-4.10981	-2.00034
H	4.66395	-4.07528	-4.48805
C	9.88559	-2.00488	-1.98401
C	10.18804	-3.35221	-2.27607
C	10.91838	-1.05834	-2.13197
C	11.45981	-3.74882	-2.65823
H	9.40566	-4.09961	-2.18955
C	12.188	-1.4462	-2.52727
H	10.71263	-0.01112	-1.93915
C	12.49824	-2.79943	-2.79461
H	11.64457	-4.79799	-2.85303
H	12.96417	-0.69321	-2.64121
C	9.27266	-0.31423	0.40719
C	10.05049	-1.27499	1.0761
C	9.45378	1.03945	0.74336
C	10.99343	-0.89474	2.02994
H	9.90449	-2.32675	0.84969
C	10.40656	1.42097	1.68611
H	8.84416	1.79318	0.25332

C	11.18069	0.45504	2.33359
H	11.57842	-1.65505	2.54059
H	10.54118	2.47378	1.92029
H	11.91705	0.75163	3.07564
C	13.8569	-3.09449	-3.19392
H	14.50443	-2.22238	-3.25593
C	14.47975	-4.27467	-3.50594
C	13.86177	-5.56504	-3.49966
C	15.86577	-4.25624	-3.87246
N	13.37833	-6.62418	-3.50064
N	16.99098	-4.23373	-4.16942
P	0.68072	4.53103	4.47239
F	0.43664	2.9476	4.02485
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F	-0.5073	4.4108	5.55675
F	1.8919	4.59412	3.33263
F	-0.38663	4.99151	3.31247
F	0.96272	6.07486	4.85501
H	3.15816	9.4712	0.0661
C	2.53177	1.84663	1.35645
H	2.39929	0.86798	1.82061
H	3.15514	2.47062	2.00368
O	3.15303	1.71646	0.06875
N	-0.01456	1.98072	1.37043
N	-0.99863	2.82267	1.13412
C	0.94336	3.80923	0.73209
C	1.21483	2.52581	1.14829
H	1.6081	4.60959	0.46977
C	-0.34792	0.68031	1.94519
H	0.28047	-0.07429	1.48021
H	-0.1751	0.73125	3.02102
H	-1.4005	0.49456	1.73613
C	-11.21042	-7.66013	-2.39262
C	-11.49558	-6.1961	-2.81098
C	-10.55387	-5.38525	-1.94176
C	-9.575	-6.26866	-1.33299
C	-9.73874	-7.65907	-1.90928
H	-11.39214	-8.37592	-3.20039
H	-12.54861	-5.92003	-2.68198

H	-11.2584	-6.0446	-3.87465
H	-9.52838	-8.45764	-1.18959
H	-9.05808	-7.80674	-2.76162
H	-11.86409	-7.93405	-1.55591
C	-8.70905	-5.81543	-0.38382
C	-7.60437	-6.48212	0.23825
C	-8.92809	-4.39848	0.18054
C	-6.78373	-5.68787	0.98435
H	-7.41707	-7.54258	0.10143
S	-7.30378	-3.98068	1.01871
C	-10.49895	-4.03749	-1.74956
C	-11.37374	-3.00759	-2.22347
C	-9.29184	-3.4563	-0.98922
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