

Electronic Supplementary Information

Dual absorption spectral changes by light-triggered shutting in bistable [2]rotaxanes with non-destructive readout

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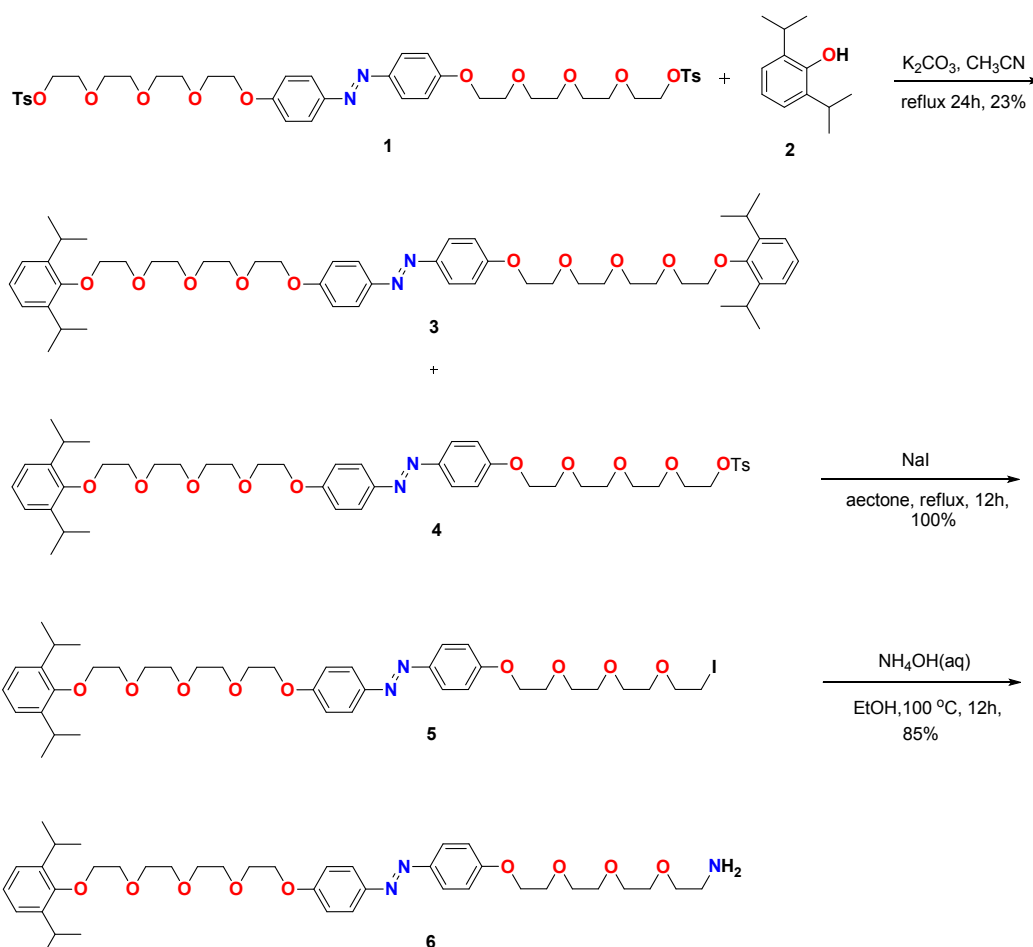
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Section 1: Materials and General Methods

All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise; the solvents have been purified by standard procedures before use ^[1]. Compound **1**^[2], **14**^[3] and **15**^[4] were synthesized according to the literatures. ¹H NMR and ¹³C NMR, 2D COSY and 2D NOESY spectra were recorded on a Bruker AVANCE 600 spectrometer.

UV-Vis absorption spectra for the compounds were recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer. A LABINO UV light lamp ($\lambda = 365$ nm, 35 mW/cm²) and an ULP-L20-D optical light source LED lamp ($\lambda > 400$ nm, 100 mW/cm²) were used for the UV/Vis irradiation experiments.

Section 2: Synthesis and Characterizations



Compound 3 and 4. Compound **1**¹ (0.874 g, 1.00 mmol) and **2** (0.178 g, 1.00 mmol) were dissolved in 50 mL anhydrous CH₃CN, and K₂CO₃ (2.50 g, 18.1 mmol) was added, the resulting mixture was heated to reflux for 24 hours. After the reaction was complete monitored by TLC, cooling down to room temperature, the precipitate was removed by filtering and filtrate was gathered and concentrated. The resulting residue was further dissolved in 50 mL ethyl acetate, which was washed by water (30 mL × 3) and brine (30 mL × 3) sequentially and dried by MgSO₄. The crude compound was further purified by flash column chromatography on silica using a petroleum ether/ethyl acetate mixture as eluent (3/1 ~ 1/1), compound **3** (0.201 g) and **4** (0.264 g) were obtained as yellow solid in the yield of 23% and 30%, respectively.

3. ¹H NMR (600 MHz, CDCl₃, 298 K) δ: 7.85 (d, *J* = 9.0 Hz, 4.0 H), 7.09 (s, 6H), 7.00 (d, *J* = 9.0 Hz, 4H), 4.21 (t, *J* = 4.8 Hz, 4H), 3.91 (m, 8H), 3.85 (t, *J* = 4.8 Hz, 4H), 3.78-3.71 (m, 16H), 3.38 (septet, *J* = 7.2 Hz, 4H), 1.21 (d, *J* = 7.2 Hz, 24H).

¹³C NMR (150 MHz, CD₃CN, 298 K) δ: 161.89, 153.96, 147.72, 142.72, 125.55, 125.06, 124.87,

115.75, 74.84, 71.40, 71.34, 71.19, 71.03, 70.06, 68.72, 26.80, 24.28.

MS (ESI) m/z : 887.5 $[M + H]^+$. HRMS (ESI): Calcd for $C_{52}H_{75}N_2O_{10}$ $[M + H]^+$: 887.5486. Found: 887.5506.

4. 1H NMR (400 MHz, $CDCl_3$, 298 K) δ : 8.02 (d, $J = 8.8$ Hz, 4H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.09 (s, 3H), 7.03 (d, $J = 8.8$ Hz, 4H), 4.24-4.20 (m, 4H), 4.17-4.14 (m, 2H), 3.93-3.85 (m, 8H), 3.79-3.64 (m, 14H), 3.62-3.57 (m, 4H), 3.38 (septet, $J = 7.2$ Hz, 2H), 2.43 (s, 3H), 1.22 (d, $J = 7.2$ Hz, 12H).

^{13}C NMR (150 MHz, CD_3CN , 298 K) δ : 162.01, 162.00, 154.07, 147.83, 146.27, 142.83, 133.83, 130.97, 128.73, 125.65, 125.15, 124.97, 115.87, 74.95, 71.50, 71.44, 71.29, 71.13, 71.03, 70.91, 70.16, 70.14, 69.17, 68.84, 68.82, 26.90, 24.36, 21.66.

MS (ESI) m/z : 881.5 $[M + H]^+$. HRMS (ESI): Calcd for $C_{47}H_{65}N_2O_{13}$ $[M + H]^+$: 881.4253. Found: 881.4309.

Compound 6. Compound **4** (0.200 g, 0.227 mmol) was dissolved in 20 mL acetone and NaI (0.340 g, 2.27 mmol) was added, the resulting mixture was heated to reflux for 12 hours. After the reaction was complete monitored by TLC, cooling down to room temperature and the precipitate was removed by filtering, the filtrate was gathered and concentrated by evaporating, and the remained yellow solid was further dissolved in 20 mL ethyl acetate, which was washed by water (30 mL \times 3) and brine (30 mL \times 3) sequentially. The organic layer was further evaporated and dried under vacuum, compound **5** (0.190 g) was obtained as yellow solid in a quantitative yield and used directly for the next step without further purification.

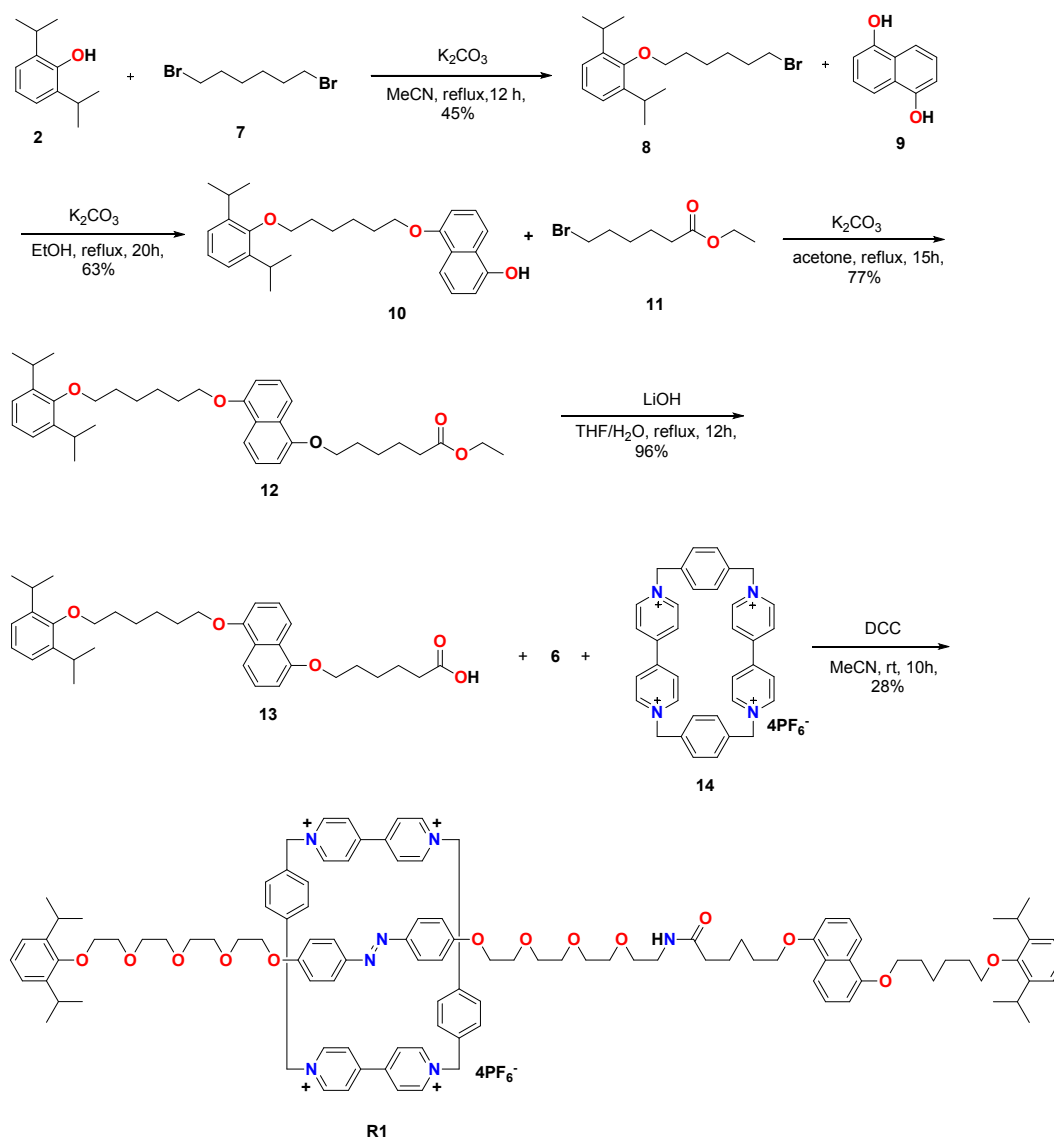
Compound **5** (0.190 g, 0.227 mmol) was dissolved in 30 mL ethanol, and 10 mL ammonia (25%) was added, the resulting mixture was heated at 100°C in a sealed tube for 12 hours. After the reaction was complete monitored by TLC, cooling down to room temperature, the solvent was removed by evaporation lead to yellow viscous liquid, which was further dissolved in 20 mL ethyl acetate and washed with saturated $NaHCO_3$ aqueous (30 mL \times 3) and brine (30 mL \times 3), respectively before to be dried with Na_2SO_4 . After removing the solvent by evaporation, 0.141 g compound **6** was obtained as yellow solid in a yield of 85%.

1H NMR (600 MHz, CD_3CN , 298 K) δ : 7.86 (m, 4H), 7.14-7.05 (m, 7H), 4.21-4.18 (m, 4H), 3.89-3.86 (m, 2H), 3.84-3.81 (m, 4H), 3.79 (m, 2H), 3.69-3.64 (m, 10H), 3.62-3.58 (m, 4H), 3.57-3.55

(m, 2H), 3.44-3.37 (m, 4H), 2.74 (t, $J = 5.4$ Hz, 2H), 1.20 (d, $J = 7.2$ Hz, 12H).

^{13}C NMR (150 MHz, CD_3CN , 298 K) δ : 161.94, 154.00, 147.78, 142.77, 125.62, 125.12, 124.92, 115.82, 74.89, 74.05, 71.44, 71.38, 71.32, 71.25, 71.23, 71.11, 71.85, 70.85, 70.11, 70.10, 68.76, 42.42, 26.86, 24.35.

MS (ESI) m/z : 726.5 $[\text{M} + \text{H}]^+$. HRMS (ESI): Calcd for $\text{C}_{40}\text{H}_{60}\text{N}_3\text{O}_9$ $[\text{M} + \text{H}]^+$: 726.4324. Found: 726.4341.



Compound 8. Compound 2 (0.630 g, 3.53 mmol) and 7 (2.23 g, 9.15 mmol) were dissolved in 30 mL anhydrous CH_3CN , and K_2CO_3 (0.980 g, 7.07 mmol) was added, the resulting mixture was reflux for 12 hours. After the reaction was complete monitored by TLC, cooling down to room temperature and the solvent was removed by evaporation, the remained residues was dissolved

with 30 mL ethyl acetate, which was washed by water (30 mL \times 3) and brine (30 mL) sequentially and dried by Na₂SO₄. The crude compound was further purified by flash column chromatography on silica using petroleum ether as eluent, and compound **8** (0.542 g, 1.54 mmol) was obtained as colorless oil in a yield of 45%.

¹H NMR (600 MHz, CDCl₃, 298 K) δ : 7.12-7.07 (m, 3H), 3.25 (t, J = 6.6 Hz, 2H), 3.46 (t, J = 6.6 Hz, 2H), 3.32 (septet, J = 6.6 Hz, 2H), 1.94 (quintet, J = 6.6 Hz, 2H), 1.86 (quintet, J = 6.6 Hz, 2H), 1.61-1.53 (m, 4H), 1.24 (d, J = 6.6 Hz, 12H).

¹³C NMR (150 MHz, CDCl₃, 298 K) δ : 153.39, 141.81, 124.41, 123.97, 74.58, 33.85, 32.78, 30.27, 28.10, 26.45, 25.36, 24.13.

MS (EI) m/z : 340 [M]⁺. HRMS (EI): Calcd for C₁₈H₂₉BrO [M]⁺: 340.1396. Found: 340.1400.

Compound 10. Compound **8** (0.522 g, 1.53 mmol) and **9** (1.59 g, 9.93 mmol) were dissolved in 40 mL ethanol and KOH (0.556 g, 9.93 mmol) was added, the resulting mixture was reflux for 4 hours. After the reaction was complete monitored by TLC, cooling down to room temperature and the solvent was removed by evaporation, the remained residues was dissolved with 30 mL CH₂Cl₂, the precipitate was removed by filtering and the filtrate was gathered, washed with 1 M diluted HCl (30 mL \times 3) and brine (30 mL \times 3) before to be dried over Na₂SO₄. The crude compound was further purified by flash column chromatography on silica using a binary solvent of petroleum ether / ethyl acetate (80/3) as eluent, compound **10** (0.404 g, 0.961 mmol) was obtained as yellow solid in a yield of 63%.

¹H NMR (600 MHz, CDCl₃, 298 K) δ : 7.89 (d, J = 9.0 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.31-7.27 (m, 1H), 7.12-7.08 (m, 3H), 6.85 (d, J = 7.8 Hz, 2H), 5.35-5.29 (m, 1H), 4.16 (t, J = 6.6 Hz, 2H), 3.77 (t, J = 6.6 Hz, 2H), 3.34 (septet, J = 7.2 Hz, 2H), 2.00 (quintet, J = 6.6 Hz, 2H), 1.91 (quintet, J = 6.6 Hz, 2H), 1.70-1.65 (m, 4H), 1.24 (d, J = 7.2 Hz, 12H).

¹³C NMR (150 MHz, CDCl₃, 298 K) δ : 154.94, 153.52, 151.32, 141.98, 127.25, 125.49, 125.47, 125.16, 124.53, 124.10, 114.97, 113.54, 109.52, 105.34, 74.94, 68.21, 30.56, 29.46, 26.56, 26.44, 26.14, 24.26, 30.56, 29.46, 26.56, 26.44, 26.14, 24.26.

MS (ESI) m/z : 421.3 [M + H]⁺. HRMS (ESI): Calcd for C₂₈H₃₇O₃ [M + H]⁺: 421.2737. Found: 421.2733.

Compound 12. Compound **10** (0.260 g, 0.618 mmol) and **11** (0.220 g, 0.986 mmol) were dissolved in 6 mL acetone, K_2CO_3 (0.380 g, 2.75 mmol) was added, the resulting mixture was reflux for 4 hours. After the reaction was complete monitored by TLC, cooling down to room temperature and the solvent was removed by evaporation, the remained residues was dissolved with 30 mL CH_2Cl_2 . The precipitate was removed by filtrated and the filtrate was gathered, washed with water (30 mL \times 3) and brine (30 mL \times 3) sequentially before to be dried over Na_2SO_4 . The crude compound was further purified by flash column chromatography on silica using a binary solvent of CH_2Cl_2 / petroleum ether (1/1 ~ 2/1) as eluent, compound **10** (0.270 g, 0.480 mmol) was obtained as white solid in a yield of 77%.

1H NMR (600 MHz, $CDCl_3$, 298 K) δ : 7.85 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.35 (m, 2H), 7.10 (m, 3H), 6.84 (d, J = 7.8 Hz, 1H), 6.82 (d, J = 7.8 Hz, 1H), 4.18-4.10 (m, 6H), 3.76 (t, J = 6.0 Hz, 6H), 3.33 (septet, J = 6.6 Hz, 2H), 2.37 (t, J = 7.2 Hz, 2H), 2.01-1.88 (m, 6H), 1.76 (quintet, J = 7.2 Hz, 2H), 1.68-1.60 (m, 6H), 1.26 (t, J = 7.2 Hz, 3H), 1.23 (d, J = 6.6 Hz, 12H).

^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ : 173.81, 154.77, 154.70, 153.55, 141.95, 126.92, 126.90, 125.21, 124.48, 124.06, 114.26, 114.20, 105.40, 74.89, 68.17, 67.93, 60.38, 34.45, 30.56, 29.47, 29.16, 26.54, 26.42, 26.12, 26.02, 24.92, 24.24, 14.38.

MS (ESI) m/z : 585.3 $[M + Na]^+$. HRMS (ESI): Calcd for $C_{36}H_{50}O_5Na$ $[M + Na]^+$: 585.3550. Found: 585.3559.

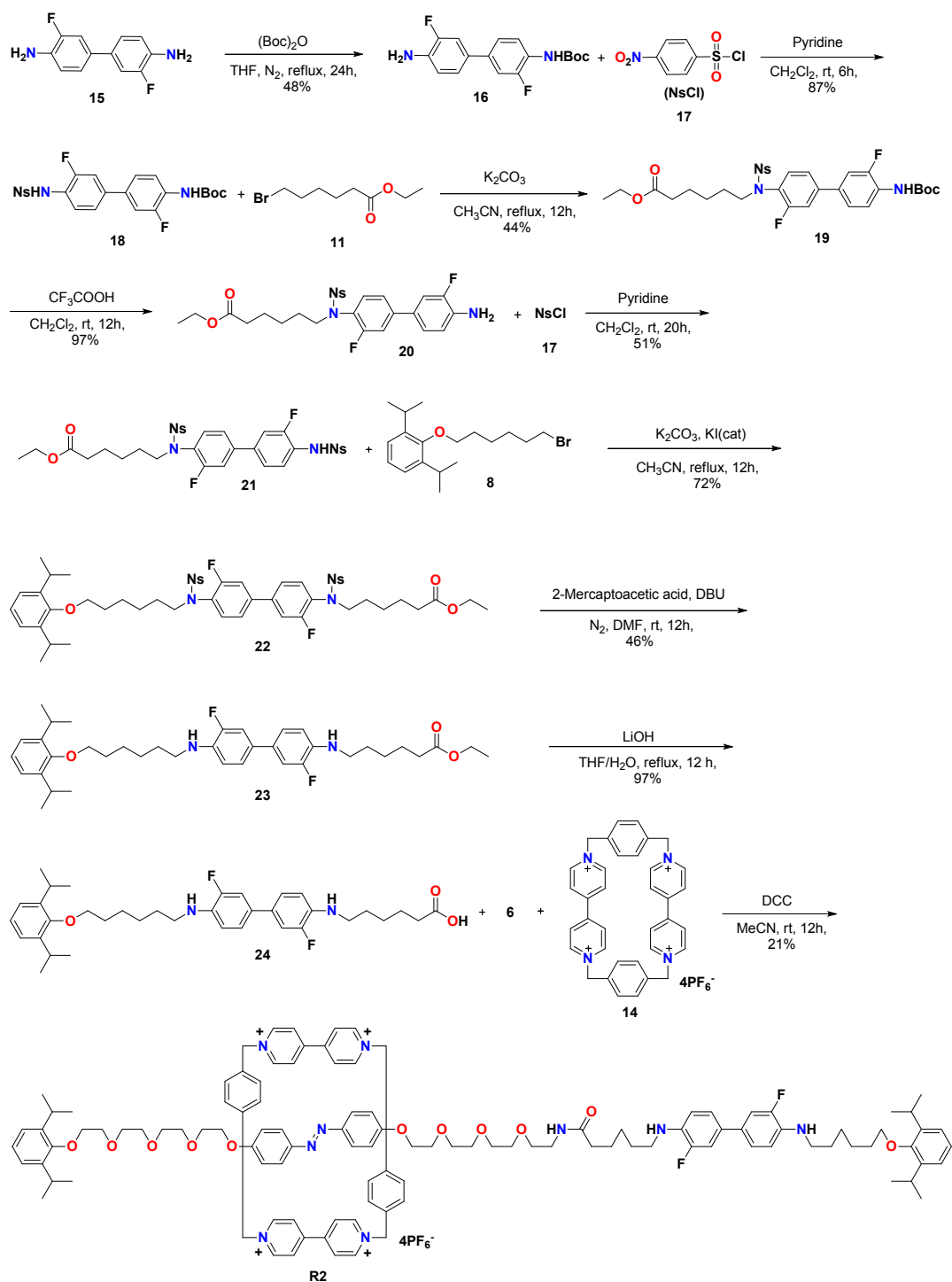
Compound 13. Compound **12** (0.210 g, 0.373 mmol) was dissolved in 15 mL THF, $LiOH \cdot H_2O$ (0.600 g, 14.3 mmol) was dissolved in 7.5 mL and added into above THF solution, the resulting mixture was refluxed for 15 hours under argon atmosphere. After the reaction was complete monitored by TLC, cooling down to room temperature and 30 mL ethyl acetate was added to quench the reaction. 10% diluted HCl aqueous was used to acidified the mixture to $pH \approx 2$, then organic phase was washed with water (30 mL \times 2) and brine (30 mL \times 3) sequentially before to be dried over Na_2SO_4 . The organic solvent was removed by evaporation and dried under vacuum; compound **12** (0.190 g) was obtained as white solid in a yield of 96%, which was further used directly for the next step.

Bistable [2]Rotaxane R1. Compound **13** (110 mg, 0.206 mmol), compound **6** (150 mg, 0.207 mmol) and compound **14**^[3] (300 mg, 0.273 mmol) were dissolved in 2 mL anhydrous CH₃CN. The resulting mixture was allowed to be stirred at room temperature for 10 min under an argon atmosphere and then DCC (0.494 mg, 0.240 mmol) was added. After stirring for another 10 hours, 15 mL CH₃NO₂ solution that containing tetrabutylammonium chloride (1.00 g, 3.60 mmol) was poured into the reaction solution, the precipitate was filtrated and the filter cake was collected and washed by 20 mL diethyl ether. The resulting crude compound was further purified by flash column chromatography on silica using a mixed solvent of methanol/water/saturated NH₄Cl (6/3/1) as eluent, compound **R1** (130 mg, 0.0555 mmol) was obtained as orange solid in a yield of 27%.

¹H NMR (400 MHz, CD₃CN, 5 mM, 298 K) δ : 8.81/8.74 (d, $J = 6.4$ Hz, 8H), 7.99/7.87 (s, 8H), 7.62/7.34 (br, 7.5H; d, $J = 6.4$ Hz, 0.5 H), 7.19-7.05 (m, 6H), 6.85-6.15 (m, 8H), 6.10-5.65 (m, 12H), 4.15 (t, $J = 6.8$ Hz, 2H), 4.11-4.05 (m, 6H), 3.92-3.86 (m, 4H), 3.84-3.69 (m, 18H), 3.66-3.61 (m, 2H), 3.60-3.55 (m, 2H), 3.45 (t, $J = 6.0$ Hz, 2H), 3.39-3.30 (m, 4H), 3.24 (q, $J = 6.0$ Hz, 2H), 2.39/2.21 (t, $J = 6.0$ Hz, 2H), 2.01 (br, 2H), 1.91 (br, 4H), 1.70 (m, 6H), 1.62-1.53 (m, 2H), 1.27/1.20 (d, $J = 7.2$ Hz, 12H), 1.70 (d, $J = 7.2$ Hz, 12H).

¹³C NMR (150 MHz, CD₃CN, 298 K) δ : 174.09, 161.28, 154.35, 153.96, 147.19, 146.64, 145.48, 142.75, 137.74, 131.82, 126.99, 125.66, 125.43, 124.98, 124.91, 124.62, 124.58, 115.19, 106.29, 75.58, 74.79, 71.57, 71.47, 71.36, 71.29, 71.26, 71.18, 70.98, 70.79, 70.21, 70.17, 70.13, 69.17, 69.02, 68.88, 68.85, 65.62, 39.81, 36.61, 31.09, 30.00, 29.74, 27.10, 26.85, 26.73, 26.63, 26.56, 26.14, 24.29, 24.27.

HRMS (ESI): Calcd for C₁₁₀H₁₃₅F₁₂N₇O₁₃P₂ [M - 2PF₄]²⁺: 1025.9701, Found: 1025.9746



Compound 16: A three-necked bottle was charged with compound **15**^[4] (1.5 g, 6.82 mmol), which was then degassed and recharged with argon, 25 mL anhydrous THF was added and the resulting solution was heated to reflux. Boc_2O (1.93 g, 8.85 mmol) was dissolved in another 25 mL anhydrous THF and added into above bottle dropwise through a constant pressure funnel, and the resulting mixture was then allowed to reflux overnight. After the reaction was completed,

cooled down and poured into 100 mL H₂O, extracted with ethyl acetate (50 mL × 3) and the organic layers were then gathered, and washed with water and brine sequentially before to be dried over MgSO₄. The crude compound was further purified by flash column chromatography on silica using a petroleum ether / ethyl acetate mixture as eluent (10/1~3/1), and 1.06 g compound **16** was obtained as a brown solid in a yield of 48%.

¹H NMR (600 MHz, CD₃CN, 298 K) δ: 7.88 (t, *J* = 6.0 Hz, 1H), 7.35-7.33 (m, 2H), 7.32 (t, *J* = 6.0 Hz, 1H), 7.28-7.26 (dd, *J*₁ = *J*₂ = 6.0 Hz, 1H), 7.22-7.20 (dd, *J*₁ = 6.0 Hz, *J*₂ = 6.0 Hz, 1H), 6.87-8.84 (quartet, *J*₁ = 12 Hz, *J*₂ = 6.0 Hz, 1H), 4.31 (s, 2H), 1.50 (s, 9H).

¹⁹F NMR (600 MHz, DMSO-*d*₆, 298 K) δ: -123.73, -134.18.

¹³C NMR (150 MHz, DMSO-*d*₆, 298 K) δ: 155.19, 153.56, 153.00, 151.55, 149.98, 136.27, 136.07, 135.98, 126.35, 124.42, 124.34, 122.31, 120.87, 116.33, 112.73, 112.60, 112.25, 112.11, 79.24, 27.92.

MS (ESI) *m/z*: 343.1 [M+Na]⁺. HRMS (ESI): Calcd for C₁₇H₁₈F₂N₂O₂Na [M+Na]⁺: 343.1234. Found: 343.1243.

Compound 18: Compound **16** (0.16 g, 0.5 mmol) and compound **17** (0.12 g, 0.55 mmol) were dissolved in a binary solvent of 5 mL CH₂Cl₂ and 1 mL pyridine, the resulting mixture was stirred for 6 hours at room temperature. After the reaction was completed, poured into 50 mL diluted HCl and extracted with ethyl acetate (50 mL × 3), the organic layers were then gathered, and washed with water and brine sequentially before to be dried over MgSO₄. The crude compound was further purified by flash column chromatography on silica using a petroleum ether / ethyl acetate mixture as eluent (10/1~4/1), and 0.22 g compound **18** was obtained as a pale powder in a yield of 87%.

¹H NMR (600 MHz, DMSO-*d*₆, 298 K) δ: 10.68 (s, 1H), 9.07 (s, 1H), 8.40 (d, *J* = 12 Hz, 2H), 8.02 (d, *J* = 6.0 Hz, 2H), 7.71 (t, *J* = 6.0 Hz, 1H), 7.56-7.55 (dd, *J*₁ = *J*₂ = 6.0 Hz, 1H), 7.54-7.53 (dd, *J*₁ = *J*₂ = 6.0 Hz, 1H), 7.49-7.47 (dd, *J*₁ = *J*₂ = 6.0 Hz, 1H), 7.45-7.43 (dd, *J*₁ = *J*₂ = 6.0 Hz, 1H), 7.32 (t, *J* = 6.0 Hz, 1H), 1.45 (s, 9H).

¹⁹F NMR (600 MHz, DMSO-*d*₆, 298 K) δ: -121.71, -123.49.

¹³C NMR (150 MHz, DMSO-*d*₆, 298 K) δ: 156.87, 155.23, 154.64, 153.01, 152.80, 149.76, 145.41, 138.22, 134.03, 128.15, 127.28, 126.41, 126.34, 124.53, 123.78, 122.68, 122.59, 122.50,

122.16, 113.92, 113.78, 113.48, 113.34, 79.48, 27.89.

MS (ESI) m/z : 528.1 [M+Na]⁺. HRMS (ESI): Calcd for C₂₃H₂₁F₂N₃O₆SNa [M+Na]⁺: 528.1017.

Found: 528.1001.

Compound 19: Compound **18** (0.13 g, 0.26 mmol) and K₂CO₃ (1.0 g, 7.25 mmol) were mixed in a 100 mL three-necked bottle, which was then degassed and recharged with argon and 40 mL anhydrous CH₃CN was added. Compound **11** (0.15 g, 0.68 mmol) was dissolved in 10 mL anhydrous CH₃CN then added into the above bottle, and the resulting mixture was allowed to reflux overnight. After the reaction was completed, cooled down and poured into 100 mL H₂O, extracted with ethyl acetate (50 mL × 3) and the organic layers were then gathered, washed with brine before to be dried over MgSO₄. The crude compound was further purified by flash column chromatography on silica using a petroleum ether/ethyl acetate mixture as eluent (50/1~10/1), and 0.073 g compound **19** was obtained as a pale solid in a yield of 44%.

¹H NMR (600 MHz, CDCl₃, 298 K) δ: 8.28 (d, J = 12 Hz, 2H), 8.14 (s, 1H), 8.74 (d, J = 12 Hz, 2H), 7.31-7.26 (m, 3H), 7.23 (d, J = 12 Hz, 1H), 1.16 (d, J = 12 Hz, 1H), 6.84 (d, J = 6.0 Hz, 1H), 4.07-4.04 (quartet, J = 6.0 Hz, 2H), 3.56 (t, J = 6.0 Hz, 2H), 2.22 (t, J = 12 Hz, 2H), 1.58-1.52 (quintet, J = 12 Hz, 2H), 1.49 (s, 9H), 1.48-1.43 (quintet, J = 12 Hz, 2H), 1.38-1.32 (m, 2H), 1.18 (t, J = 6.0 Hz, 3H).

¹⁹F NMR (600 MHz, CDCl₃, 298 K) δ: -118.03, -131.74.

¹³C NMR (150 MHz, CDCl₃, 298 K) δ: 173.50, 160.53, 158.86, 152.98, 152.31, 151.37, 150.18, 144.90, 142.50, 133.35, 133.18, 128.68, 127.37, 127.30, 124.27, 124.13, 124.05, 123.08, 122.94, 120.33, 114.91, 114.77, 113.36, 113.22, 81.41, 60.34, 50.64, 34.10, 28.30, 25.89, 24.44, 14.29.

MS (ESI) m/z : 670.2 [M+Na]⁺. HRMS (ESI): Calcd for C₃₁H₃₅F₂N₃O₈SNa [M+Na]⁺: 670.2011.

Found: 670.2082.

Compound 20: Compound **19** (0.073 g, 0.11 mmol) was dissolved in 5 mL CH₂Cl₂ in a 10 mL bottle, and 1 mL CF₃COOH was further added. The resulting mixture was then stirred for 12 hours at room temperature. After the reaction was completed, poured into 50 mL saturated NaHCO₃, extracted with ethyl acetate (30 mL × 3) and the organic layers were then gathered, washed with brine and dried by MgSO₄. 0.060g compound **20** was obtained as yellow oil in a yield of 44%.

¹H NMR (600 MHz, DMSO-*d*₆, 298 K) δ: 8.42 (d, *J* = 6.0 Hz, 2H), 7.95 (d, *J* = 6.0 Hz, 2H), 7.54-7.52 (dd, *J*₁ = *J*₂ = 6.0 Hz, 1H), 7.45 (t, *J* = 6.0 Hz, 1H), 7.43 (t, *J* = 6.0 Hz, 1H), 7.31-7.30 (dd, *J*₁ = *J*₂ = 6.0 Hz, 1H), 7.11 (t, *J* = 12 Hz, 1H), 6.83 (t, *J* = 12 Hz, 1H), 5.44 (s, 2H), 4.02-3.99 (quartet, 2H), 3.53 (t, *J* = 6.0 Hz, 2H), 2.20 (t, *J* = 6.0 Hz, 2H), 1.45 (quintet, 2H), 1.35-1.26 (m, 4H), 1.14 (t, *J* = 6.0 Hz, 3H).

¹⁹F NMR (600 MHz, DMSO-*d*₆, 298 K) δ: -117.83, -133.94.

¹³C NMR (150 MHz, DMSO-*d*₆, 298 K) δ: 172.66, 160.46, 158.80, 149.89, 149.82, 143.67, 142.00, 136.98, 136.90, 131.31, 128.76, 125.10, 124.57, 122.89, 122.54, 121.55, 116.20, 116.17, 113.19, 113.14, 113.05, 113.01, 59.59, 50.07, 33.23, 27.36, 24.96, 23.77, 13.98.

MS (ESI) *m/z*: 570.1 [M+Na]⁺. HRMS (ESI): Calcd for C₂₆H₂₇F₂N₃O₆SNa [M+Na]⁺: 570.1486. Found: 570.1483.

Compound 21: Compound **20** (1.65 g, 3.02 mmol) and compound **17** (0.8 g, 3.61 mmol) were dissolved in a binary solvent of 30 mL CH₂Cl₂ and 6 mL pyridine, the resulting mixture was then stirred for 20 hours. After the reaction was completed, poured into 100 mL diluted HCl (a.q), extracted with CH₂Cl₂ (60 mL × 3) and the organic layers were then gathered, washed with saturated NaHCO₃ and brine sequentially before to be dried over MgSO₄. The crude compound was further purified by flash column chromatography on silica using a petroleum ether/ethyl acetate mixture as eluent (10/1~3/1), and 1.12 g compound **21** was obtained as an orange oil in the yield of 51%.

¹H NMR (600 MHz, DMSO-*d*₆, 298 K) δ: 10.76 (s, 1H), 8.42-8.39 (dd, *J*₁ = *J*₂ = 6.0 Hz, 4H), 8.01 (d, *J* = 12 Hz, 2H), 7.94 (d, *J* = 12 Hz, 2H), 7.69-7.66 (dd, *J*₁ = *J*₂ = 6.0 Hz, 2H), 7.64-7.62 (dd, *J*₁ = *J*₂ = 6.0 Hz, 2H), 7.55 (t, *J* = 12 Hz, 2H), 7.35 (t, *J* = 12 Hz, 1H), 7.22 (t, *J* = 6.0 Hz, 1H), 4.01-3.98 (quartet, *J* = 6.0 Hz, 2H), 3.55 (t, *J* = 6.0 Hz, 2H), 2.19 (t, *J* = 6.0 Hz, 2H), 1.44 (quintet, *J* = 6.0 Hz, 2H), 1.36-1.25 (m, 4H), 1.13 (t, *J* = 6.0 Hz, 3H).

¹⁹F NMR (600 MHz, DMSO-*d*₆, 298 K) δ: -117.08, -121.45.

¹³C NMR (150 MHz, DMSO-*d*₆, 298 K) δ: 172.76, 160.49, 158.82, 156.69, 155.05, 150.03, 149.91, 145.37, 143.57, 140.36, 137.18, 131.66, 128.87, 128.25, 127.03, 124.80, 124.69, 124.67, 123.76, 123.67, 123.22, 123.10, 59.70, 50.14, 33.31, 27.44, 25.04, 23.84, 14.06.

MS (ESI) *m/z*: 755.1 [M+Na]⁺. HRMS (ESI): Calcd for C₃₂H₃₀F₂N₄O₁₀S₂Na [M+Na]⁺: 755.1269.

Found:755.1268.

Compound 22: Compound **21** (1.12 g, 1.53 mmol), K₂CO₃ (11.40 g, 82.61 mmol) and KI (0.20 g, 1.20 mmol) were mixed in a 100 mL three-necked bottle, which was then degassed and charged with argon gas. Compound **8** was dissolved in 35 mL anhydrous CH₃CN, and added into above bottle. The resulting mixture was then allowed to reflux for 12 hours, cooling down and poured into 200 mL H₂O, extracted with ethyl acetate (100 mL × 3) and the organic layers were then gathered, washed with brine and dried by MgSO₄. The crude compound was further purified by flash column chromatography on silica using a petroleum ether/ethyl acetate mixture as eluent (20/1~4/1), and 1.09 g compound **22** was obtained as an orange oil in the yield of 72%.

¹H NMR (600 MHz, DMSO-*d*₆, 298 K) δ: 8.43-8.41 (dd, *J*₁ = *J*₂ = 6 Hz, 4H), 7.97-7.95 (dd, *J*₁ = *J*₂ = 6.0 Hz, 4H), 7.78-7.77 (dd, *J*₁ = *J*₂ = 6.0 Hz, 1H), 7.76-7.75 (dd, *J*₁ = *J*₂ = 6.0 Hz, 1H), 7.62 (t, *J* = 6.0 Hz, 2H), 7.30-7.25 (quartet, *J* = 6.0 Hz, 2H), 7.08-7.02 (m, 3H), 4.03-3.99 (quartet, *J* = 6.0 Hz, 2H), 3.64-3.57 (m, 6H), 3.21-3.17 (quintet, *J* = 6.0 Hz, 2H), 2.21 (t, *J* = 12 Hz, 2H), 1.68 (quartet, *J* = 6.0 Hz, 2H), 1.48-1.28 (m, 12H), 1.14 (t, *J* = 6.0 Hz, 3H), 1.13/1.12 (d, *J* = 6.0 Hz, 12H).

¹⁹F NMR (600 MHz, DMSO-*d*₆, 298 K) δ: -116.85.

¹³C NMR (150 MHz, DMSO-*d*₆, 298 K) δ: 172.92, 160.73, 159.07, 153.18, 150.25, 143.81, 140.39, 131.98, 129.10, 125.51, 125.41, 125.32, 124.53, 123.99, 123.59, 74.36, 59.89, 50.56, 50.37, 33.53, 29.83, 28.07, 27.70, 26.07, 25.67, 25.30, 25.22, 24.06, 14.26.

MS (ESI) *m/z*: 1015.3 [M+Na]⁺. HRMS (ESI): Calcd for C₅₀H₅₈F₂N₄O₁₁S₂Na [M+Na]⁺: 1015.3409. Found: 1015.3403.

Compound 23: Compound **22** (0.21 g, 0.21 mmol), 2-Mercaptoacetic acid (0.07 g, 0.76 mmol) and DBU (0.232 g, 1.20 mmol) were dissolved in 5 mL anhydrous DMF, and the resulting mixture was stirred at room temperature under argon atmosphere for 12 hours. After the reaction was completed, poured into 100 mL diluted HCl (a.q), extracted with CH₂Cl₂ (60 mL × 3) and the organic layers were then gathered, washed with brine and dried by MgSO₄. The crude compound was further purified by flash column chromatography on silica using a petroleum ether/ethyl acetate mixture as eluent (20/1 ~ 10/1), and 0.06 g compound **23** was obtained as a yellow oil in

the yield of 46%.

^1H NMR (600 MHz, $\text{CD}_3\text{CN}-d_3$, 298 K) δ : 7.22-7.19 (m, 4H), 7.12 (d, $J = 6.0$ Hz, 1H), 7.10 (s, 1H), 7.07-7.05 (quartet, $J = 6.0$ Hz, 1H), 4.35 (s, 2H), 4.09-4.05 (quartet, $J = 6.0$ Hz, 2H), 3.73 (t, $J_1 = 6.0$ Hz, $J_2 = 12$ Hz, 2H), 3.35-3.28 (septet, $J = 6.0$ Hz, 2H), 3.20-3.13 (m, 4H), 2.29 (t, $J_1 = 6.0$ Hz, $J_2 = 12$ Hz, 2H), 1.84-1.79 (quintet, $J = 6.0$ Hz, 2H), 1.70-1.54 (m, 8H), 1.52-1.47 (m, 2H), 1.43-1.38 (m, 2H), 1.20 (t, $J_1 = J_2 = 6.0$ Hz, 3H), 1.19 (d, $J = 6.0$ Hz, 12H).

^{19}F NMR (600 MHz, $\text{CD}_3\text{CN}-d_3$, 298 K) δ : -136.39, -136.41.

^{13}C NMR (150 MHz, $\text{CD}_3\text{CN}-d_3$, 298 K) δ : 174.68, 154.83, 153.86, 152.29, 143.23, 137.22, 137.16, 137.14, 137.08, 129.61, 125.86, 125.35, 123.31, 113.65, 113.62, 113.25, 113.13, 75.95, 61.24, 44.46, 44.28, 35.13, 31.43, 30.36, 30.02, 28.02, 27.55, 27.03, 25.90, 24.72, 14.98.

MS (ESI) m/z : 645.4 $[\text{M}+\text{Na}]^+$. HRMS (ESI): Calcd for $\text{C}_{38}\text{H}_{52}\text{F}_2\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 645.3844. Found: 645.3850.

Compound 24: Compound **23** (0.245 g, 0.385 mmol) was dissolved in 15 mL THF, LiOH (0.600 g, 14.3 mmol) was dissolved in 7.5 mL H_2O , then added into above THF solution. The resulting mixture was heated to reflux under argon atmosphere for 12 hours. After the reaction was completed, cooling down and poured into 30 mL ethyl acetate, acidified to pH = 2.0 by diluted HCl (a.q), the organic layers were then washed with water (30 mL \times 2) and brine (30 mL \times 3) sequentially before to be dried by Na_2SO_4 . The organic solvent was further removed by evaporation and dried under vacuum; compound **24** (0.222 g) was obtained as white solid in the yield of 97%, which was further used directly for the next step.

Bistable [2]Rotaxane R2: Compound **24** (0.130 g, 0.219 mmol), compound **6** (0.191 g, 0.263 mmol) and compound **14** (0.300 g, 0.273 mmol) were dissolved in 2 mL anhydrous CH_3CN . The resulting mixture was stirred at room temperature under argon atmosphere for 10 mins, and DCC (0.494 g, 0.240 mmol) was added. After being stirred for another 10 hours, 15 mL CH_3NO_2 solution that containing tetrabutylammonium chloride (1.00 g, 3.60 mmol) was poured into the reaction solution. The precipitate was filtrated and the filter cake was collected and washed by 20 mL diethyl ether, which was further purified by flash column chromatography on silica using a methanol/water/ saturated NH_4Cl mixture (6/3/1) as eluent, 0.111 g compound **R2** was obtained as

orange solid in the yield of 21%.

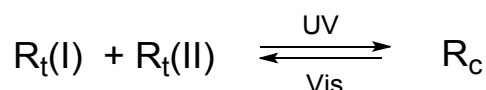
^1H NMR (600 MHz, CD_3CN , 5 mM, 298 K) δ : 8.90/8.86 (d, $J = 6.6$ Hz, 8H), 7.89/7.85 (s, 8H), 7.71/7.66 (d, $J = 6.6$ Hz, 8H), 7.17-7.06 (m, 6H), 6.90-6.62 (m, 7H), 5.91 (br, 2H), 5.82-5.70 (m, 10H), 4.41 (br, 1H), 4.26 (br, 1H), 4.10-4.05 (m, 4H), 3.92-3.87 (m, 4H), 3.82-3.70 (m, 18H), 3.67-3.64 (m, 2H), 3.60-3.56 (m, 2H), 3.44 (t, $J = 6.6$ Hz, 2H), 3.37-3.30 (m, 4H), 3.24-3.20 (m, 2H), 3.18 (t, $J = 6.6$ Hz, 2H), 3.04 (br, 2H), 2.29/2.15 (t, $J = 6.6$ Hz, 2H), 1.84 (quintet, $J = 6.6$ Hz, 2H), 1.71 (quintet, $J = 6.6$ Hz, 2H), 1.63-1.57 (m, 6H), 1.55-1.49 (quintet, $J = 6.6$ Hz, 2H), 1.40 (quintet, $J = 6.6$ Hz, 2H), 1.24/1.20 (d, $J = 7.2$ Hz, 12H), 1.17 (d, $J = 6.6$ Hz, 12H).

^{13}C NMR (150 MHz, CD_3CN , 298 K) δ : 174.12, 161.27, 161.17, 154.32, 153.93, 153.14, 151.56, 147.69, 146.62, 145.59, 142.72, 137.83, 136.81, 136.73, 136.49, 136.41, 131.71, 127.27, 125.65, 125.39, 124.96, 124.87, 124.60, 124.54, 122.43, 115.16, 115.09, 113.11, 112.90, 112.23, 75.49, 74.76, 71.56, 71.45, 71.26, 71.22, 71.16, 71.13, 70.94, 70.76, 70.20, 70.16, 70.12, 68.86, 68.83, 65.57, 44.02, 43.80, 39.73, 36.55, 30.97, 29.88, 29.47, 27.59, 27.11, 27.06, 26.84, 26.58, 26.07, 24.38, 24.23.

HRMS (ESI): Calcd for $\text{C}_{112}\text{H}_{137}\text{F}_{14}\text{N}_9\text{O}_{11}\text{P}_2$ [$\text{M} - 2\text{PF}_6$] $^{2+}$: 1055.9839. Found: 1055.9837.

Section 3:

The rates of the isomers of **R1** and **R2** were calculated based on the combination of their UV-Vis and ^1H NMR spectra before and after UV irradiation, the detailed calculation of thermodynamically stable states and photostationary states are described as follows:



Before irradiation with UV light: $x\eta^0_{(\text{R}(\text{II}))}$ $\eta^0_{(\text{R}(\text{II}))}$ $\eta^0_{(\text{R}_c)}$

After irradiation with UV light: $x\eta_{(\text{R}(\text{II}))}$ $\eta_{(\text{R}(\text{II}))}$ $\eta_{(\text{R}_c)}$

$$\eta^0_{(R_t(II))} = (1 - \eta^0_{(R_c)}) / (1 + x)$$

$$\eta_{(R_t(II))} = (1 - \eta_{(R_c)}) / (1 + x)$$

$$\begin{aligned} N &= \varepsilon_{CT}(\eta_{(R_t(II))} + \eta_{(R_c)}) / \varepsilon_{CT}(\eta^0_{(R_t(II))} + \eta^0_{(R_c)}) \\ &= (\eta_{(R_t(II))} + \eta_{(R_c)}) / (\eta^0_{(R_t(II))} + \eta^0_{(R_c)}) \\ &= [(1 - \eta_{(R_c)}) / (1 + x) + \eta_{(R_c)}] / [(1 - \eta^0_{(R_c)}) / (1 + x) + \eta^0_{(R_c)}] \\ &= (1 + x\eta_{(R_c)}) / (1 + x\eta^0_{(R_c)}) \end{aligned}$$

$$x = (N - 1) / (\eta_{(R_c)} - N\eta^0_{(R_c)})$$

$$\eta^0_{(R_t(II))} = (1 - \eta^0_{(R_c)}) / (1 + x) = (1 - \eta^0_{(R_c)}) / [1 + (N - 1) / (\eta_{(R_c)} - N\eta^0_{(R_c)})]$$

$$\eta^0_{(R_t(I))} = x\eta^0_{(R_t(II))}$$

$$\eta_{(R_t(II))} = (1 - \eta_{(R_c)}) / (1 + x) = (1 - \eta_{(R_c)}) / [1 + (N - 1) / (\eta_{(R_c)} - N\eta^0_{(R_c)})]$$

$$\eta_{(R_t(I))} = x\eta_{(R_t(II))}$$

Notes:

(1) $\eta^0_{(R_t(I))}$, $\eta_{(R_t(I))}$ represent the percentages of R_t isomer I before and after UV irradiation, respectively;

(2) $\eta^0_{(R_t(II))}$, $\eta_{(R_t(II))}$ refer to the percentages of R_t isomer II before and after UV irradiation, respectively;

(3) $\eta^0_{(R_c)}$, $\eta_{(R_c)}$ correspond to the percentages of R_c before and after UV irradiation, respectively, which can be obtained by the integrals of the corresponding peaks in the 1H NMR spectra.

(4) $x = \eta^0_{(R_t(I))} / \eta^0_{(R_t(II))} = \eta_{(R_t(I))} / \eta_{(R_t(II))}$;

(5) “N” refers to the enhancement times of the charge-transfer bands before and after UV irradiation, which can be obtained directly by reading the spectral changes of the CT bands before and after UV irradiation.

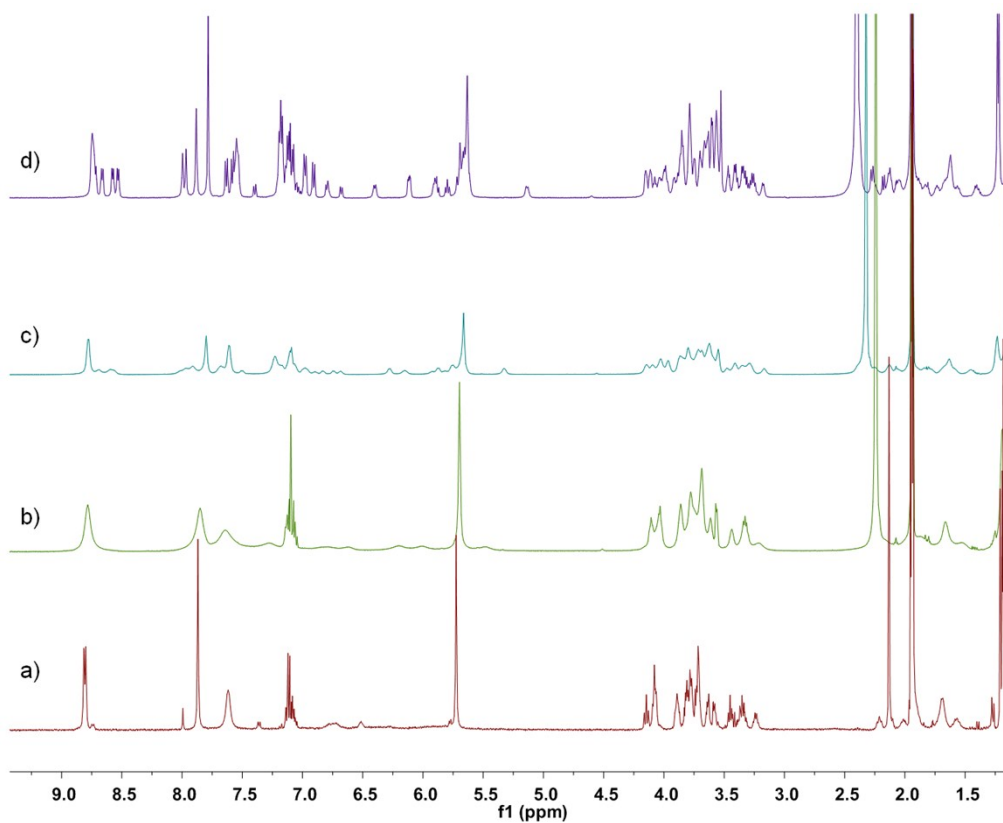


Figure S1. Variable-temperature ^1H NMR spectra (600 MHz, 5mM) of recorded the [2] rotaxane **R1** at a) 298 K; b) 273 K; c) 253 K and d) 233 K in CD_3CN .

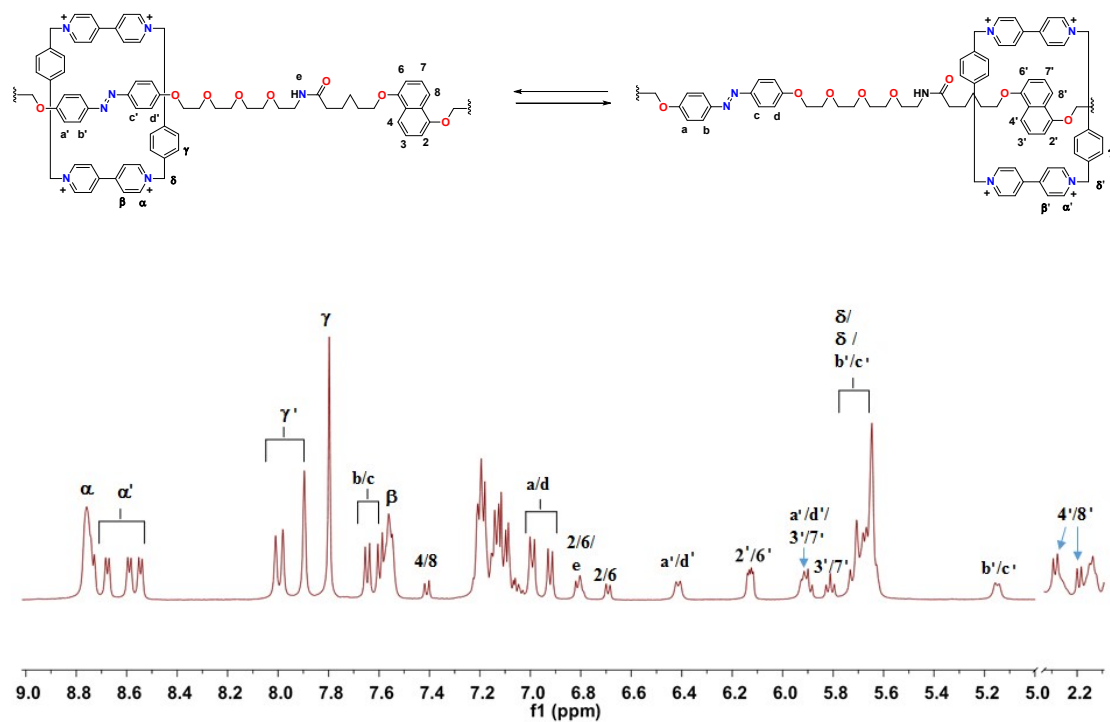


Figure S2. Partial ^1H NMR spectra (600 MHz, 5 mM) of the [2] rotaxane **R1** at 233 K in CD_3CN .

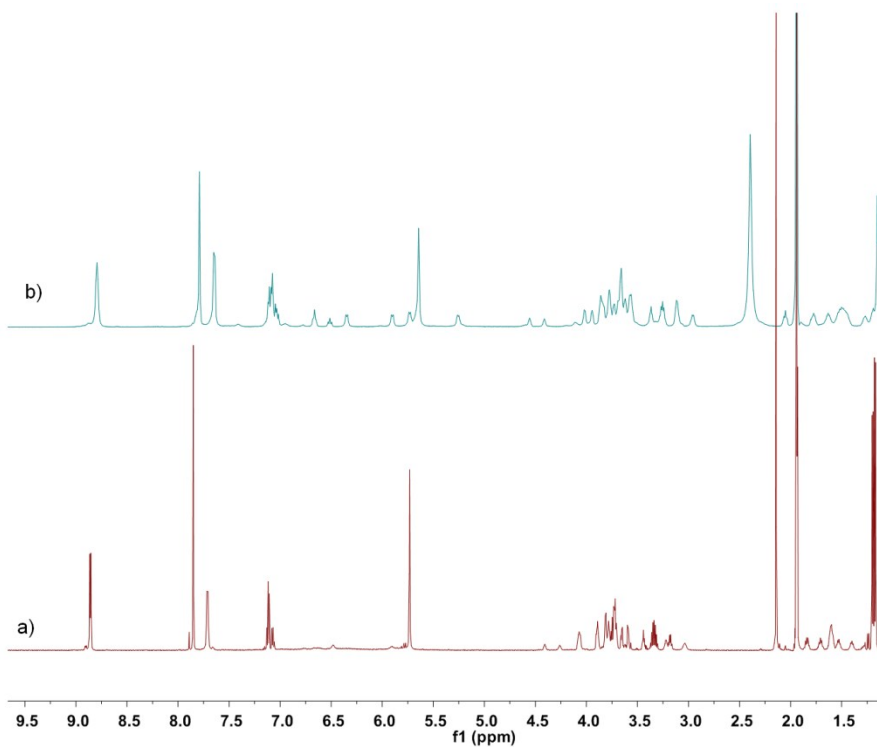


Figure S3. Variable-temperature ^1H NMR spectra (600 MHz, 5 mM) of recorded the [2] rotaxane **R2** at a) 298 K and b) 233 K in CD_3CN .

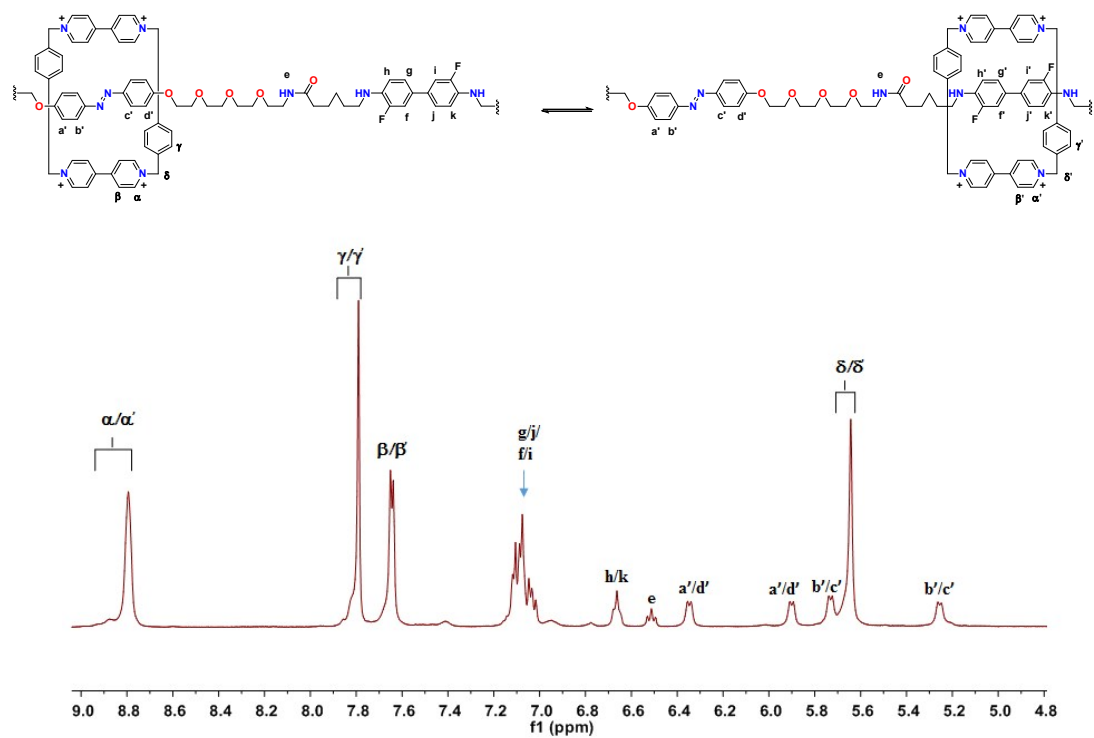


Figure S4. Partial ^1H NMR spectra (600 MHz, 5 mM) of the [2] rotaxane **R2** at 233 K in CD_3CN .

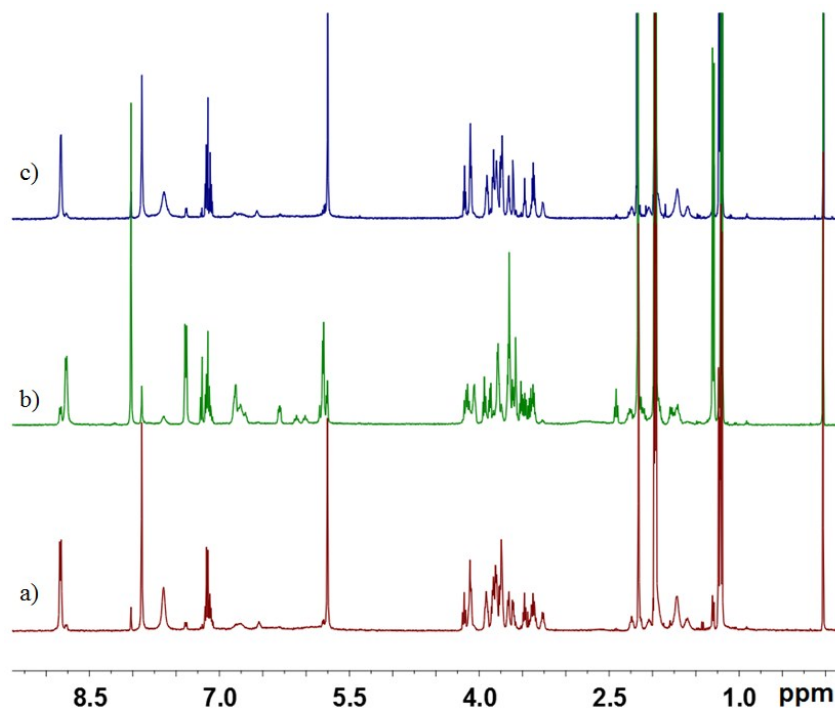


Figure S5. ^1H NMR spectra (600 MHz, CD_3CN , 5 mM, 298K) of the [2] rotaxane **R1** a) before and b) after irradiation ($\lambda = 365$ nm, 35 mW/cm 2) of the solution for 15 min; and the UV-irradiated [2] rotaxane **R1** solution c) after irradiation by broadband visible light ($\lambda > 400$ nm, 100 mW/cm 2) for 5 min.

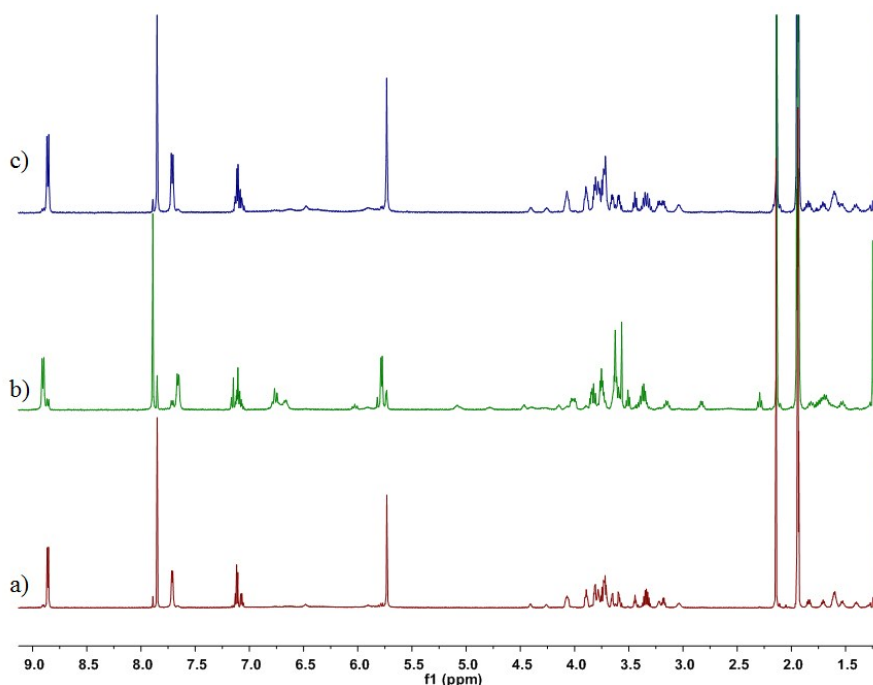


Figure S 6. ^1H NMR spectra (600 MHz, CD_3CN , 5 mM, 298K) of the [2] rotaxane **R2** a) before and b) after irradiation ($\lambda = 365$ nm, 35 mW/cm 2) of the solution for 10 min; and the UV-irradiated [2] rotaxane **R1** solution c) after irradiation by broadband visible light ($\lambda > 400$ nm, 100 mW/cm 2) for 5 min.

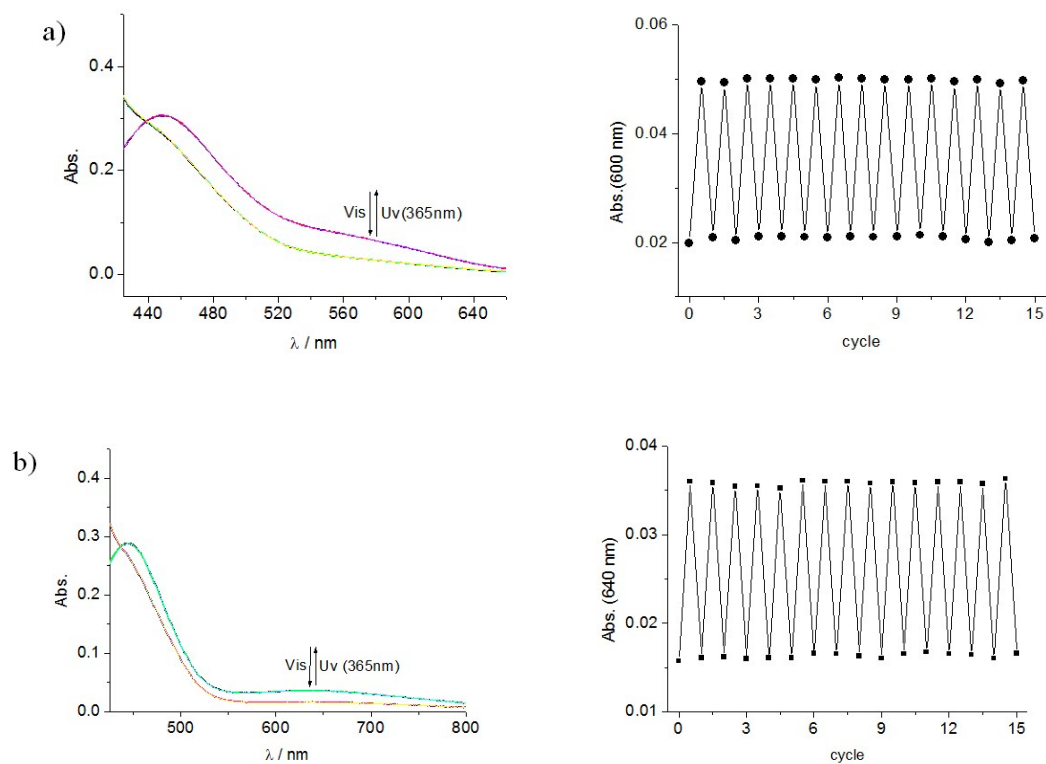
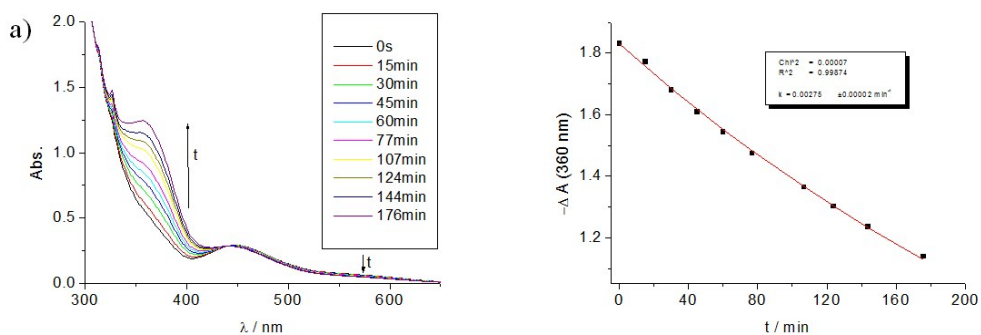


Figure S7. a) UV/Vis absorption spectra of [2] rotaxane **R1** (0.1 mM) (left) and plot of corresponding absorption λ at 600 nm (right) after UV irradiation ($\lambda = 365 \text{ nm}$, 35 mW/cm^2) in MeCN at room temperature for 1min, and UV-irradiated [2] rotaxane **R1** solution after visible light irradiation ($\lambda > 400 \text{ nm}$, 100 mW/cm^2) at room temperature for 5min before next UV irradiation. b) UV/Vis absorption spectra of [2] rotaxane **R2** (0.1 mM) (left) and plot of corresponding absorption λ at 640 nm (right) after UV irradiation ($\lambda = 365 \text{ nm}$, 35 mW/cm^2) in MeCN at room temperature for 1min, and UV-irradiated [2] rotaxane **R2** solution after visible light irradiation ($\lambda > 400 \text{ nm}$, 100 mW/cm^2) at room temperature for 5min for next UV irradiation.



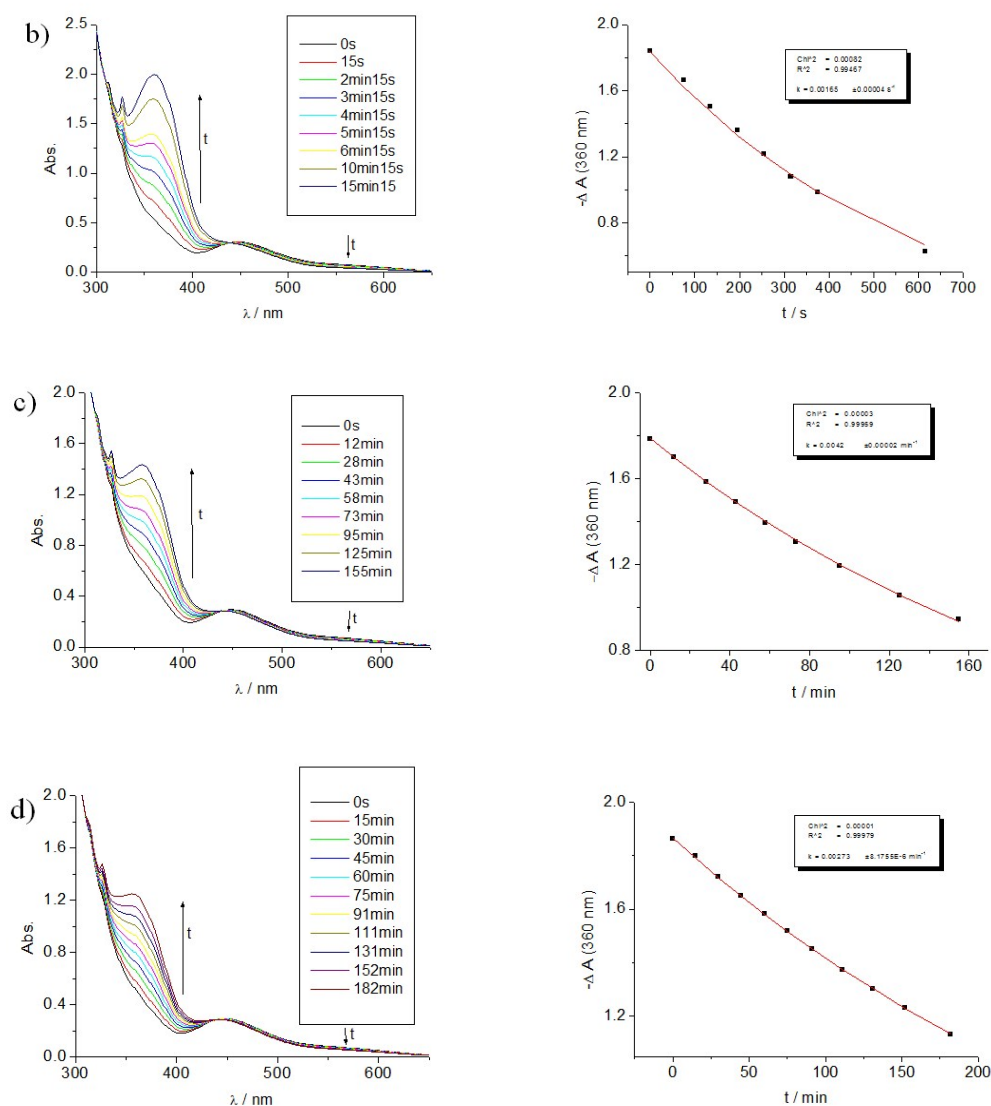


Figure S8. a) time lapse absorption spectra of UV-irradiated [2] rotaxane **R1** (0.1 mM) (left) in MeCN at room temperature under dark and plot of change in absorption $-\Delta A_{360 \text{ nm}} = A_{360 \text{ nm}} - A_{360 \text{ nm}}$ (before UV irradiation) (right) versus the recording time. b) time lapse absorption spectra of UV-irradiated [2] rotaxane **R1** (0.1 mM) (left) in MeCN at room temperature under irradiation ($\lambda = 450 \text{ nm}$, 0.5 mW/cm^2) and plot of change in absorption $-\Delta A_{360 \text{ nm}} = A_{360 \text{ nm}} - A_{360 \text{ nm}}$ (before UV irradiation) (right) versus the recording time. c) time lapse absorption spectra of UV-irradiated [2] rotaxane **R1** (0.1 mM) (left) in MeCN at room temperature under irradiation ($\lambda = 550 \text{ nm}$, 0.5 mW/cm^2) and plot of change in absorption $-\Delta A_{360 \text{ nm}} = A_{360 \text{ nm}} - A_{360 \text{ nm}}$ (before UV irradiation) (right) versus the recording time. d) time lapse absorption spectra of UV-irradiated [2] rotaxane **R1** (0.1 mM) (left) in MeCN at room temperature under irradiation ($\lambda = 600 \text{ nm}$, 0.5 mW/cm^2) and plot of change in absorption $-\Delta A_{360 \text{ nm}} = A_{360 \text{ nm}} - A_{360 \text{ nm}}$ (before UV irradiation) (right) versus the recording time.

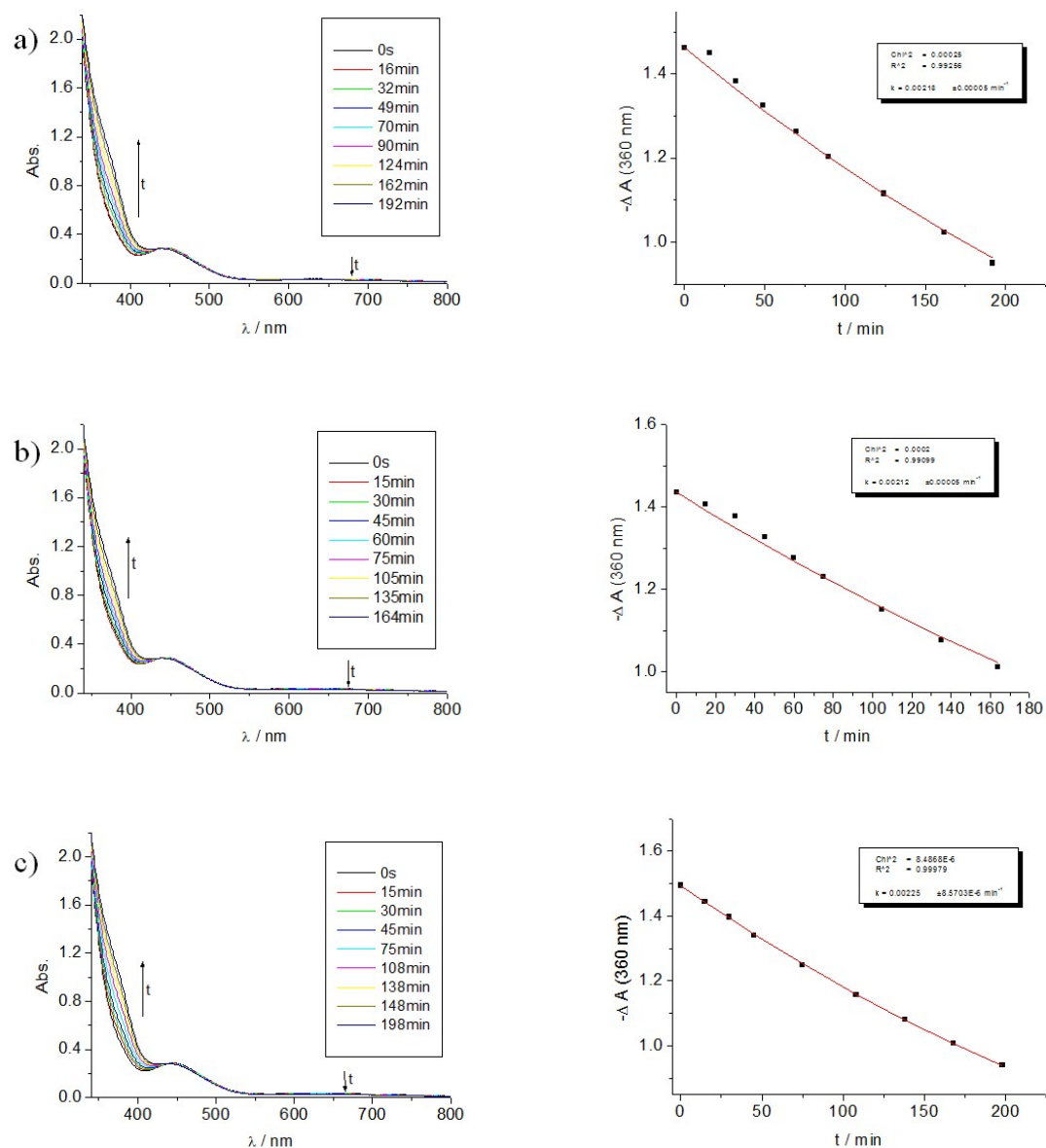


Figure S9. a) time lapse absorption spectra of UV-irradiated [2] rotaxane **R2** (0.1 mM) (left) in MeCN at room temperature under dark and plot of change in absorption $-\Delta A_{360 \text{ nm}} = A_{360 \text{ nm}} - A_{360 \text{ nm}}$ (before UV irradiation) (right) versus the recording time. b) time lapse absorption spectra of UV-irradiated [2] rotaxane **R2** (0.1 mM) (left) in MeCN at room temperature under irradiation ($\lambda = 650 \text{ nm}$, 0.5 mW/cm^2) and plot of change in absorption $-\Delta A_{360 \text{ nm}} = A_{360 \text{ nm}} - A_{360 \text{ nm}}$ (before UV irradiation) (right) versus the recording time. c) time lapse absorption spectra of UV-irradiated [2] rotaxane **R2** (0.1 mM) (left) in MeCN at room temperature under irradiation ($\lambda = 700 \text{ nm}$, 0.5 mW/cm^2) and plot of change in absorption $-\Delta A_{360 \text{ nm}} = A_{360 \text{ nm}} - A_{360 \text{ nm}}$ (before UV irradiation) (right) versus the recording time.

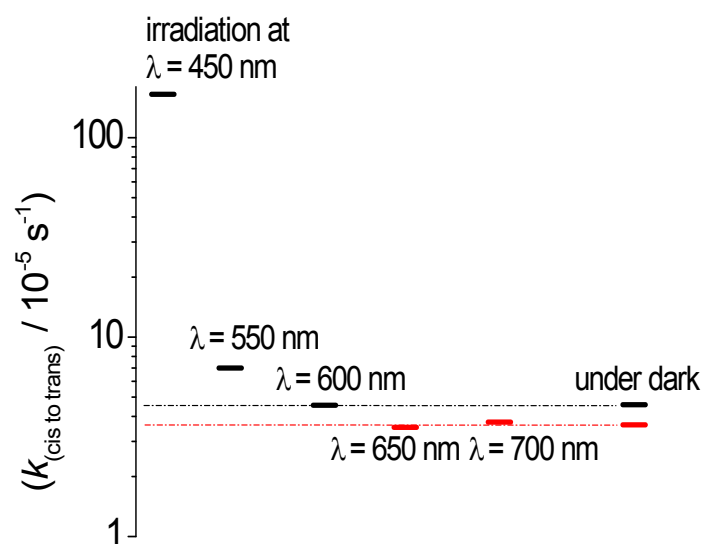


Figure S10. The diagram of the rate constants for the *cis* \rightarrow *trans* isomerization of AB units of **R1_c** (black) and **R2_c** (red) under different irradiation conditions.

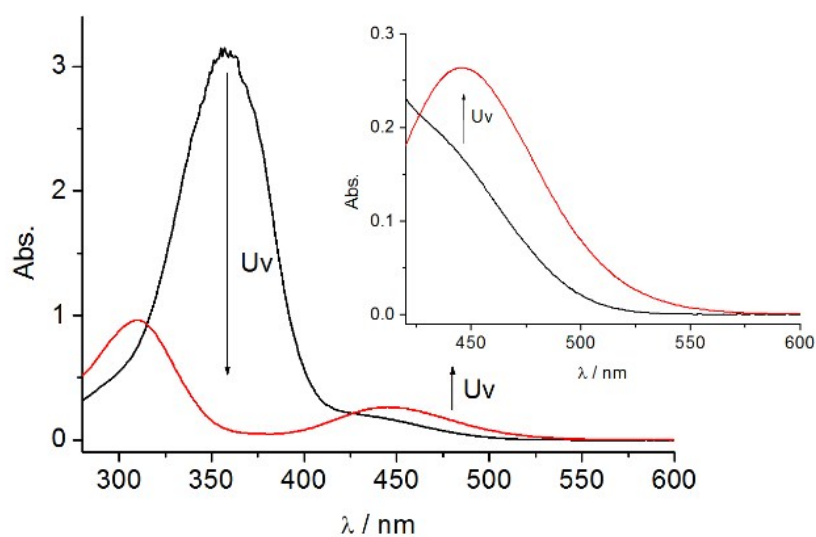


Figure S11. UV/Vis absorption spectra of compound **1** (0.1 mM) before (black line) and after irradiation ($\lambda = 365$ nm, 35 mW/cm²) (red line) in MeCN at room temperature for 30 s.

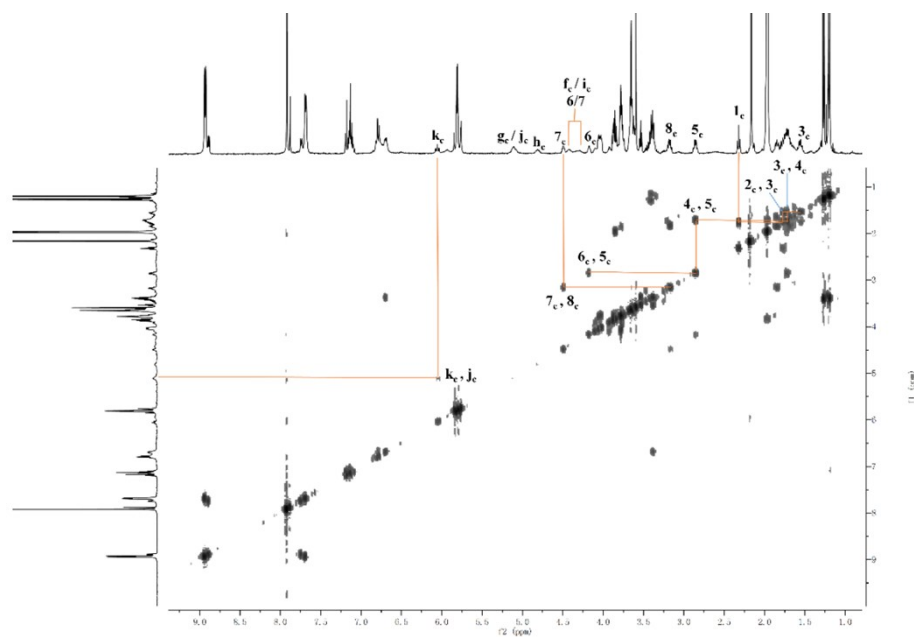


Figure S12. 2D COSY NMR spectrum (600 MHz, CD₃CN, 5 mM, 298K) of the [2] rotaxane **R2** after irradiation ($\lambda = 365$ nm, 35 mW/cm²) for 10 min.

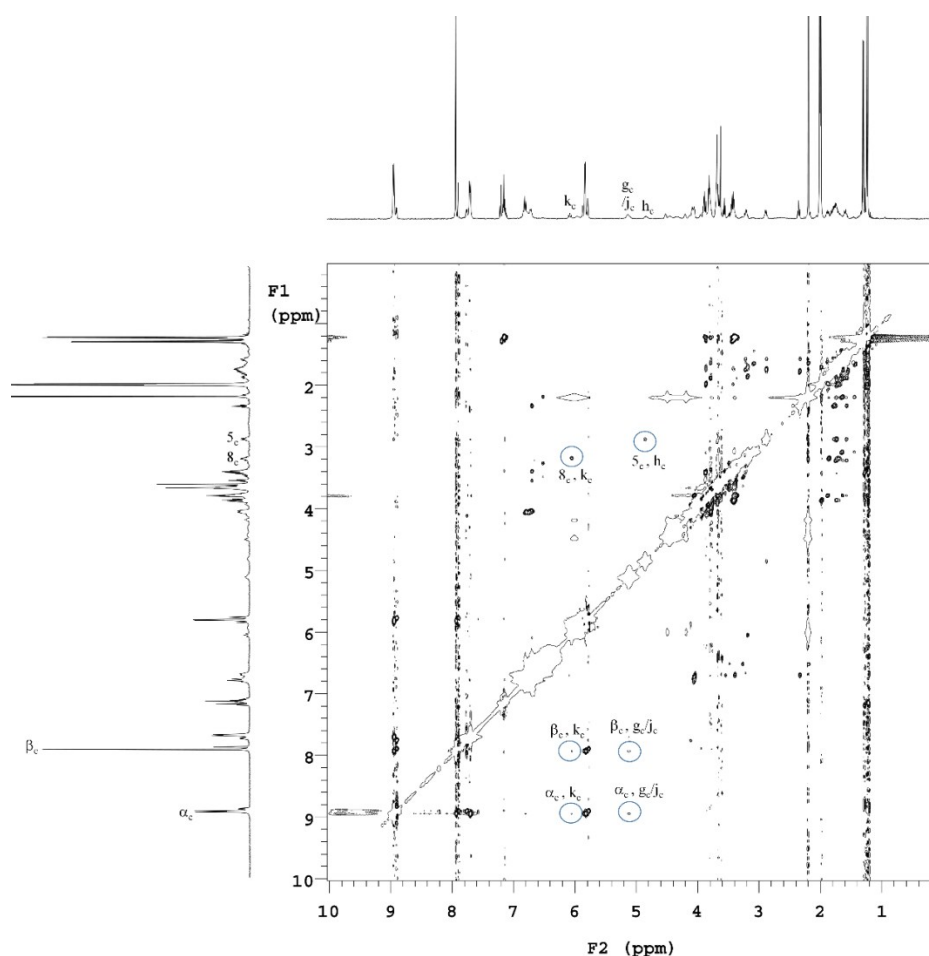


Figure S13. 2D NOESY NMR spectrum (600 MHz, CD₃CN, 5 mM, 298K) of the [2] rotaxane **R2** after irradiation ($\lambda = 365$ nm, 35 mW/cm²) for 10 min.

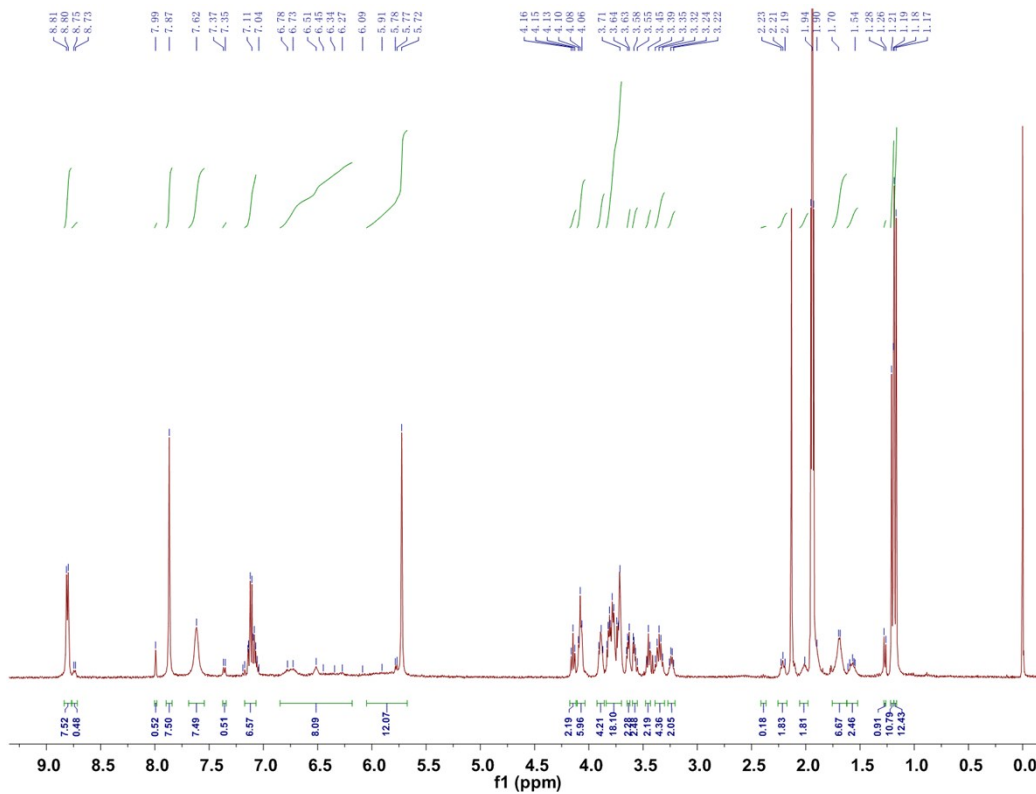


Figure S14. ^1H NMR (600 MHz, CD_3CN , 5 mM, 298K) spectrum of [2] rotaxane **R1**.

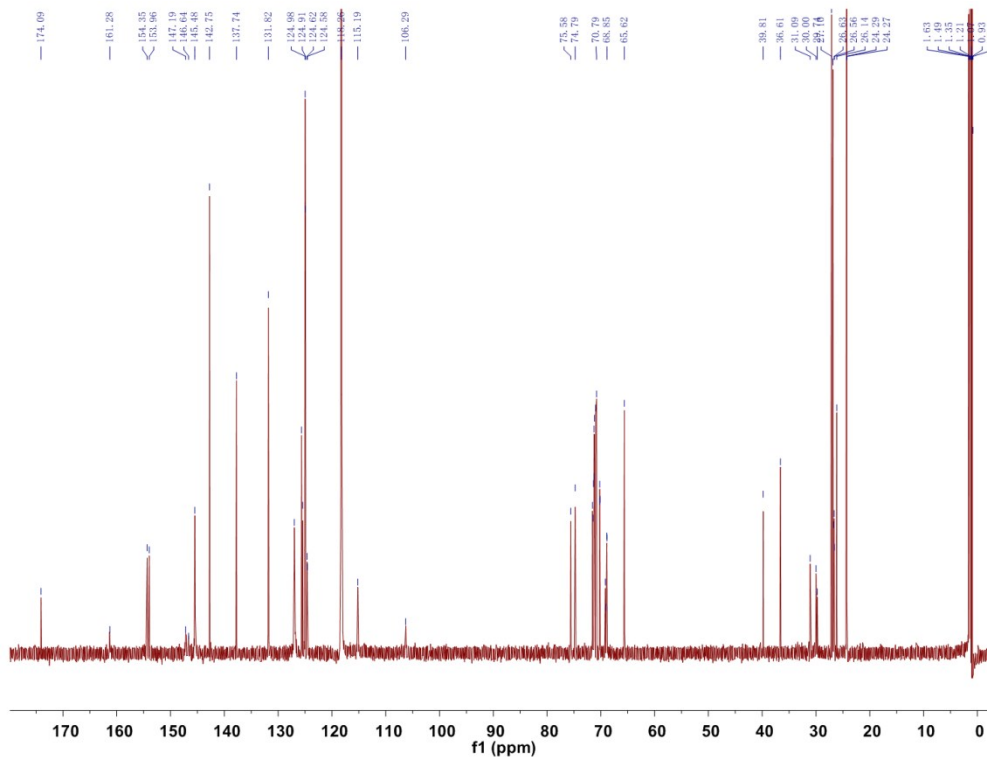


Figure S15. ^{13}C NMR (600 MHz, CD_3CN , 40 mM, 298K) spectrum of [2] rotaxane **R1**.

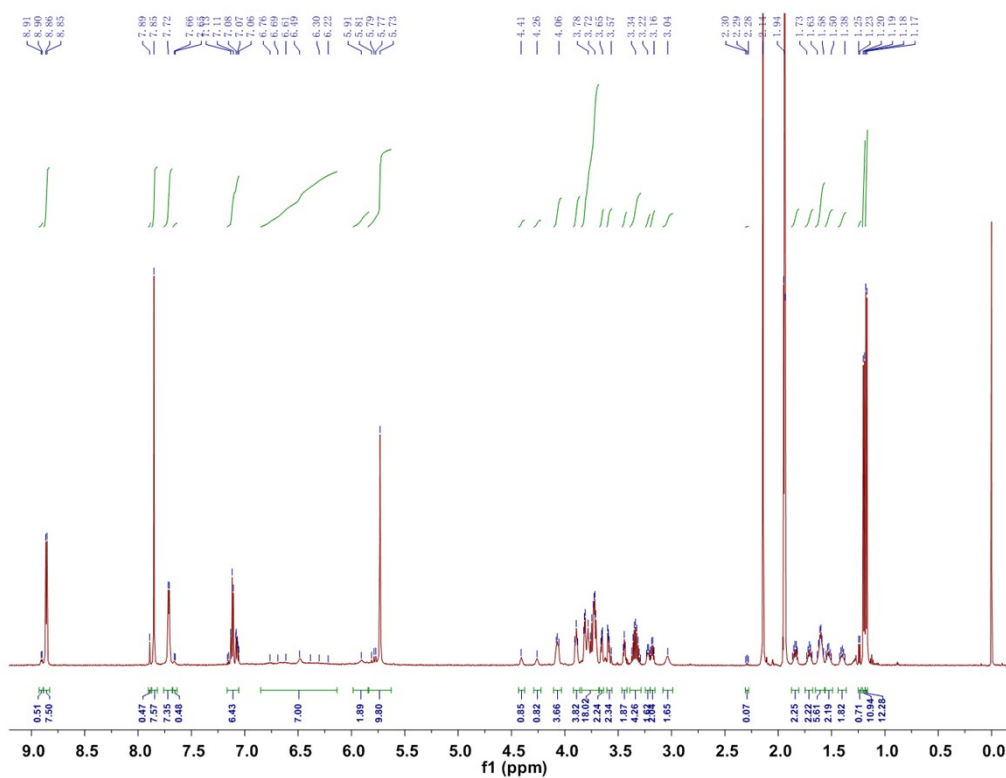


Figure S16. ^1H NMR (600 MHz, CD_3CN , 5 mM, 298K) spectrum of [2] rotaxane **R2**.

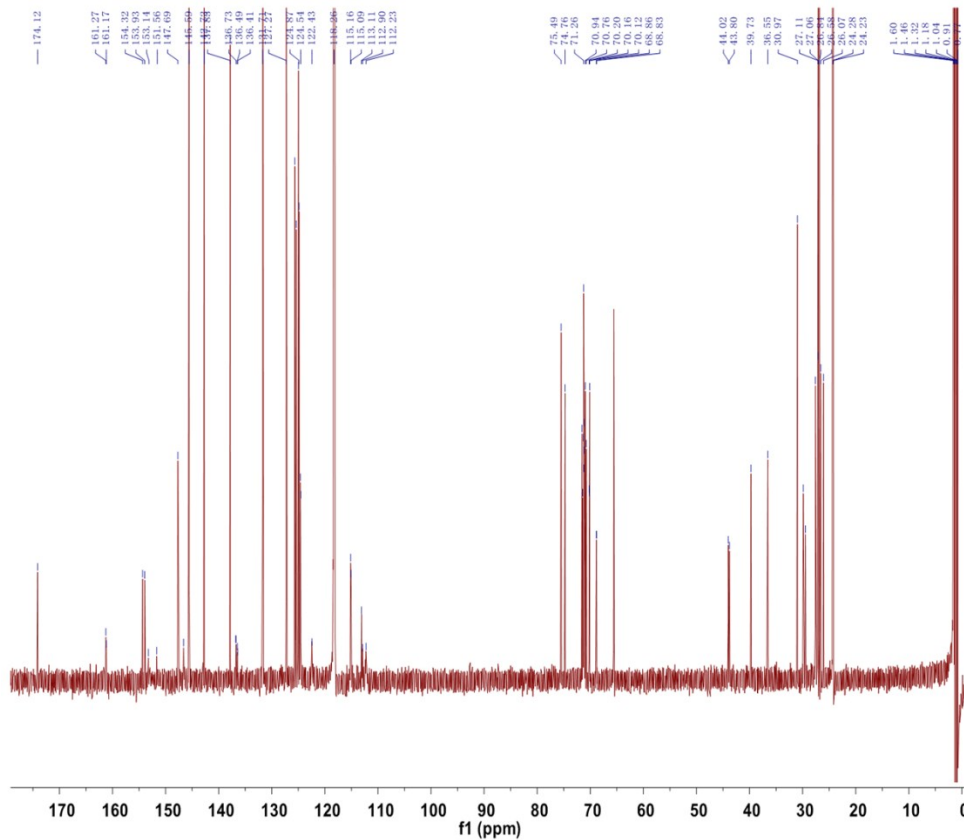


Figure S17. ^{13}C NMR (600 MHz, CD_3CN , 40 mM, 298K) spectrum of [2] rotaxane **R2**.

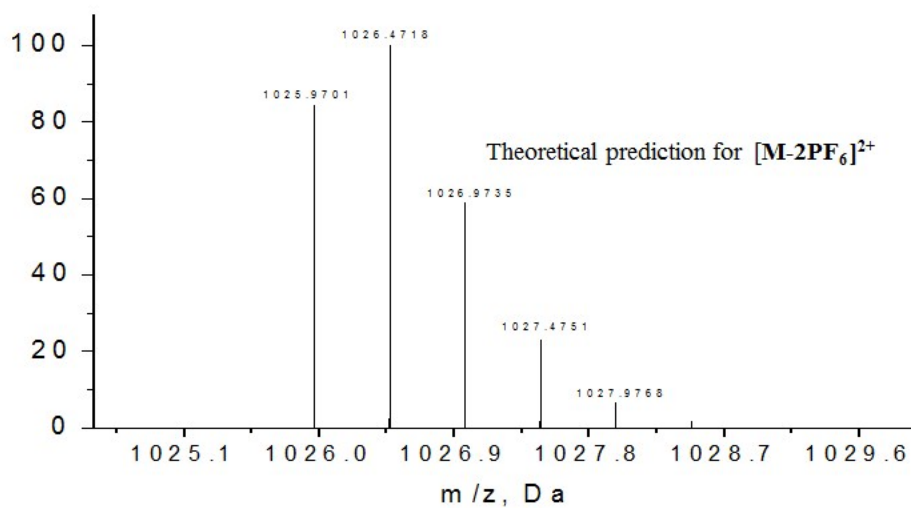
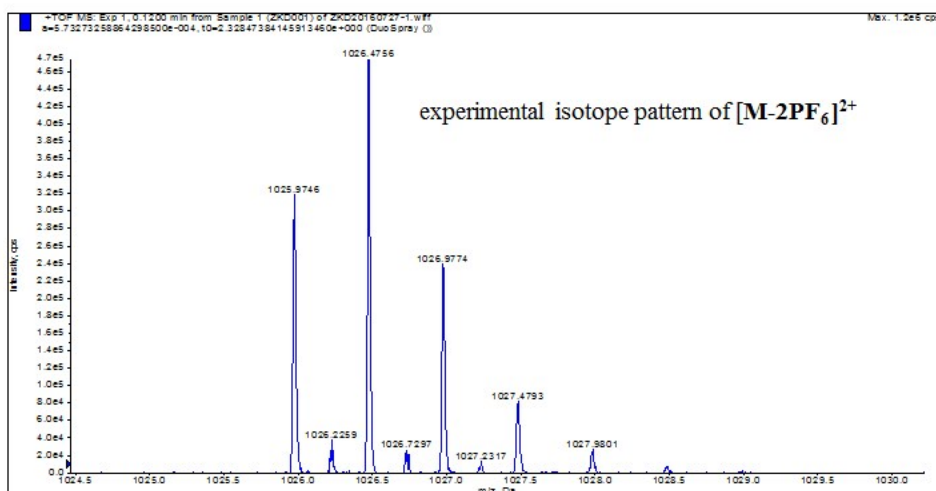
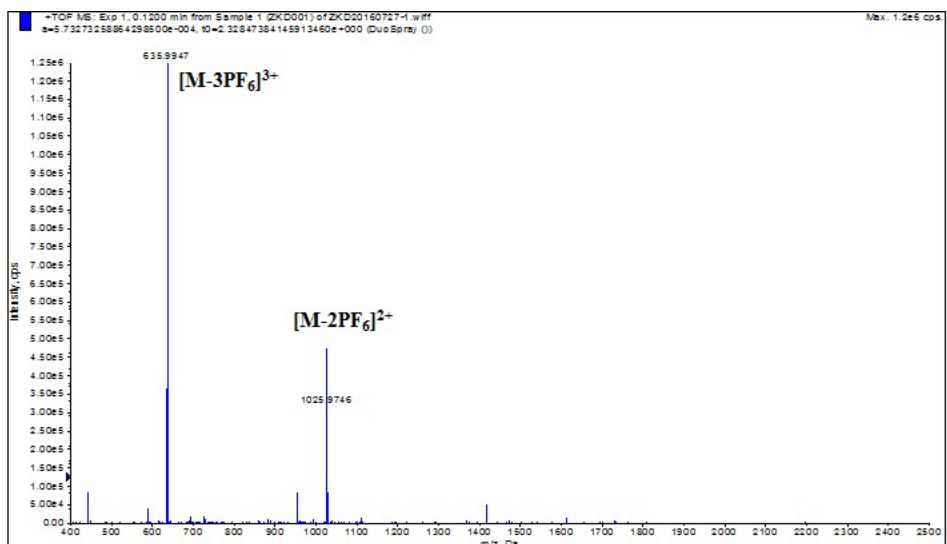


Figure S18. ESI-mass spectrum of [2] rotaxane R1.

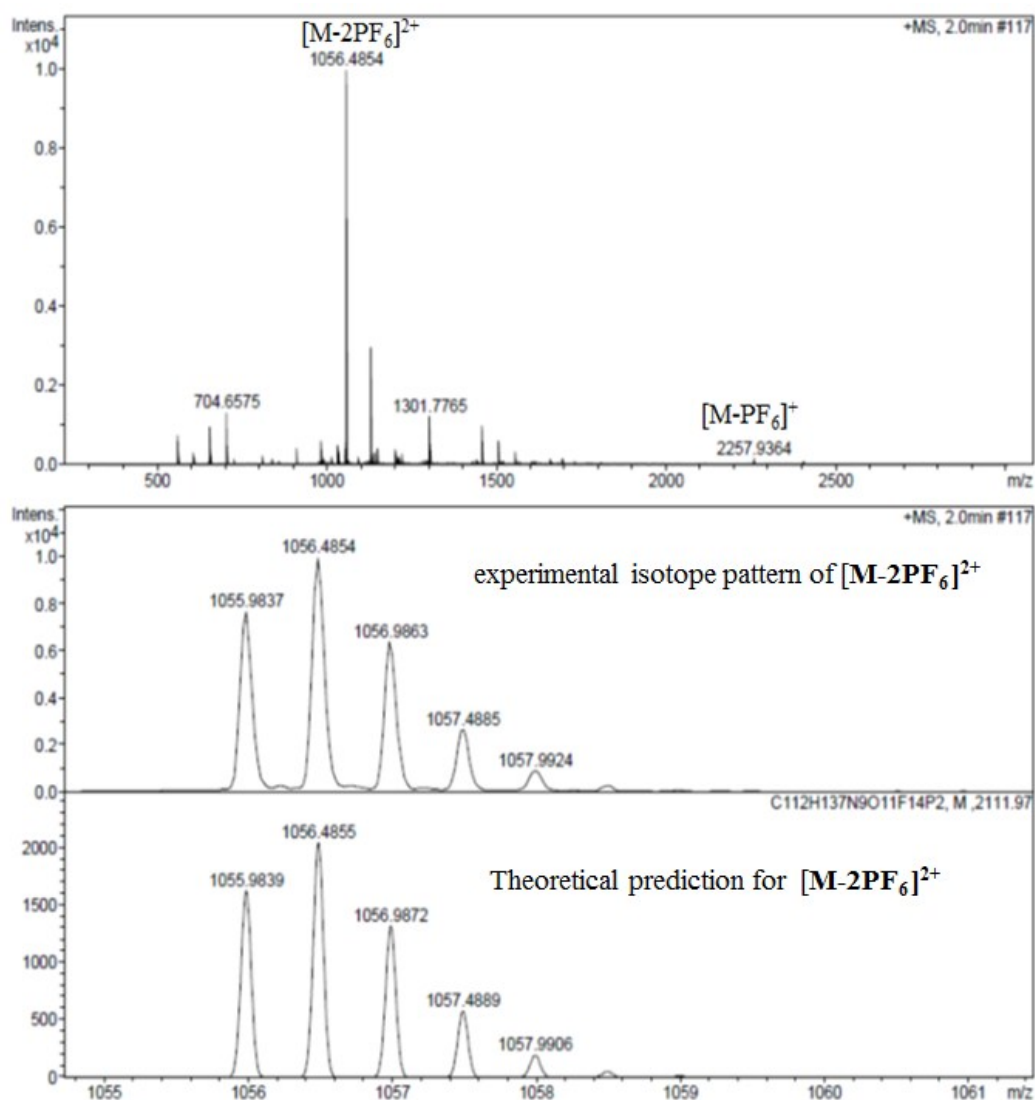


Figure S19. ESI-mass spectrum of [2] rotaxane **R2**.

Referees

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