

Electronic Supplementary Information

Tristable [n]Rotaxanes: From Molecular Shuttles to Molecular Cable Car

Zheng Meng,^{a,b} Jun-Feng Xiang,^a and Chuan-Feng Chen^{a,*}

^aBeijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; ^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

E-mail: cchen@iccas.ac.cn

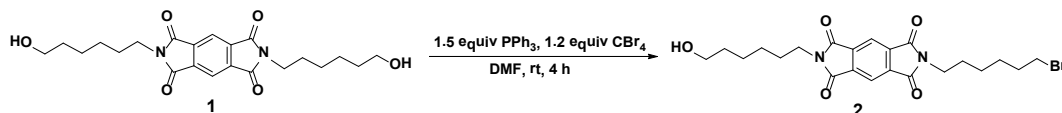
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1. Materials and methods

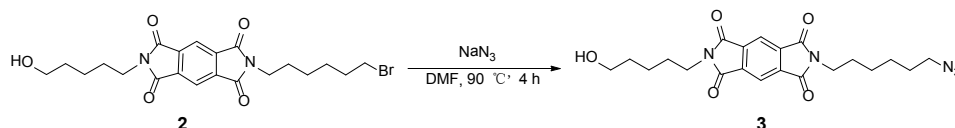
All reactions were performed in open atmosphere unless otherwise stated. All reagents, unless otherwise indicated, were obtained from commercial sources. Compounds **1**,^[1] **4**,^[2] **6**,^[3] oct-7-yn-1-ol and 8-bromooct-1-yne^[4] were synthesized as the literature procedures. Anhydrous CH₂Cl₂ and DMF were obtained by 5 Å molecular sieves activated under 500 °C for 6 hours. Melting points were determined using a Focus X-4 apparatus and were not corrected. All yields were given as isolated yields. Analytical thin-layer chromatography (TLC) was performed on Merck silicagel 60 F254 plates. NMR spectra were recorded on a Bruker DPX 300 MHz or BRUKER AVANCE 600 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and *J* values were given in Hz. 2D-ROESY, HSQC, HMBC experiments were performed on a BRUKER AVANCE 600 MHz spectrometer. Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), m (multiplet). High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific ExactiveTM spectrometer.

2. Synthesis of new compounds **2**, **3**, **5**, **7**, **S0**, **S1**, **S2**, **A2**, **S3**, **S4**



Scheme S1. Synthesis of **2**.

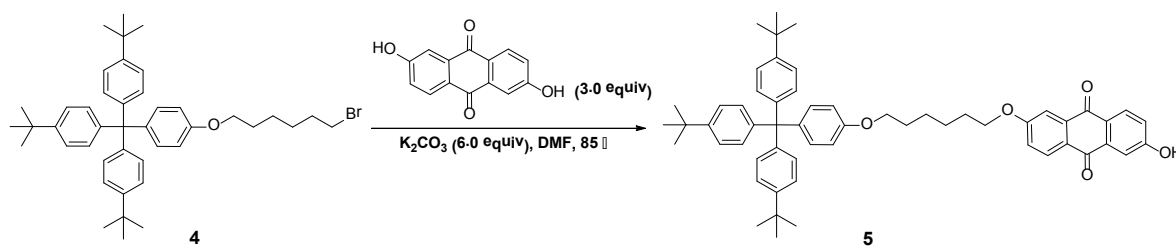
Synthesis of 2. To a solution of **1** (4.17 g, 10 mmol) and CBr₄ (3.27 g, 12 mmol) in anhydrous DMF (100 mL) was slowly added the solution of PPh₃ (4.0 g, 15 mmol) in DMF (20 mL) in one hour, and the mixture was then stirred at r.t. for another 4 h. After the reaction mixture was concentrated under reduced pressure, the residue was purified by silica-gel column chromatography (CH₂Cl₂ → CH₂Cl₂/EtOAc=10:1) to afford **2** as white solid (2.78 g, 58 %). M.p.: 164–165 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.27 (s, 2H), 3.75 (t, *J* = 7.2 Hz, 4H), 3.64 (dd, *J* = 11.9, 6.3 Hz, 2H), 3.40 (t, *J* = 6.7 Hz, 2H), 1.92–1.81 (m, 2H), 1.79–1.67 (m, 4H), 1.63–1.51 (m, 4H), 1.51–1.44 (m, 2H), 1.44–1.33 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 166.3, 137.3, 137.2, 118.2, 62.5, 38.6, 38.5, 33.6, 32.5, 28.4, 28.2, 27.6, 26.6, 26.0, 25.3. HRMS (ESI): *m/z* = 479.1169 [M+H]⁺ (calcd. 479.1178 for C₂₂H₂₈O₅N₂Br).



Scheme S2. Synthesis of **3**.

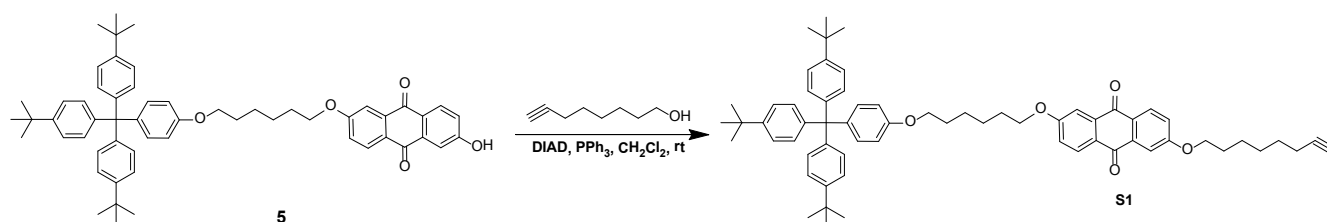
Synthesis of 3. To a solution of **2** (0.96 g, 2 mmol) in DMF (50 mL) was added NaN₃ (650 mg, 10 mmol). The mixture was heated up to 90 °C for 4 hours, and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure to give a residue, which was then dissolved in CH₂Cl₂ (100 mL), washed by H₂O for three times (3 × 60 mL). The organic phase was collected and concentrated under reduced pressure to give white solid (829 mg, 97%), which was without further purification and pure enough for the characterization and follow-up reaction. M.p.: 150–151 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.27 (s, 2H), 3.75 (t, *J* = 7.2 Hz, 4H), 3.63 (t, *J* = 5.4 Hz, 2H), 3.27 (t, *J* =

6.8 Hz, 2H), 1.80–1.66 (m, 4H), 1.66–1.52 (m, 4H), 1.50–1.32 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3): δ = 166.3, 137.2, 137.2, 118.2, 62.7, 51.3, 38.6, 38.5, 32.5, 28.7, 28.4, 28.3, 26.5, 26.4, 26.2, 25.2; HRMS (ESI): m/z = 464.1905 $[\text{M}+\text{Na}]^+$ (calcd. 464.1904 for $\text{C}_{22}\text{H}_{27}\text{O}_5\text{N}_5\text{Na}$).



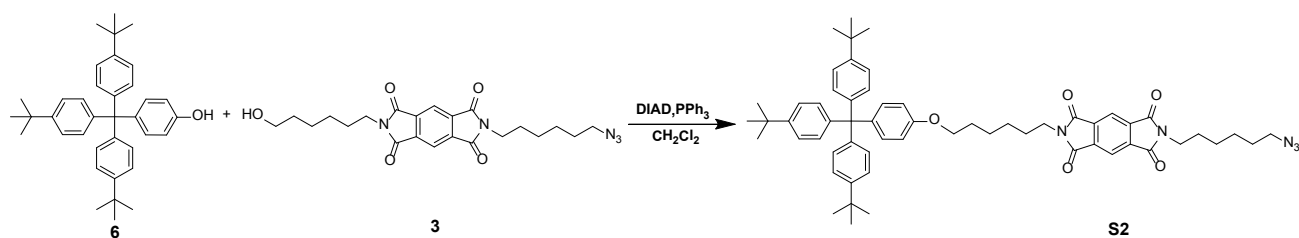
Scheme S3. Synthesis of **5**.

Synthesis of 5. Compound **4** (1.33 g, 2.0 mmol), 2,6-dihydroxyanthracene-9,10-dione (1.44 g, 6.0 mmol) and K_2CO_3 (1.66 g, 12.0 mmol) were mixed in dry DMF (80 mL). The mixture was stirred under 85°C overnight, then cooled to room temperature, and filtrated. The filtered cake was washed by a large amount of CH_2Cl_2 . The filtrate was collected and concentrated under reduced pressure to give a residue, which was then purified by silica-gel column chromatography ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}=100:1$) to yield 695 mg (42 %) of **5** as yellow solid. M.p.: $282\text{--}283^\circ\text{C}$; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ = 8.09 (dd, J = 12.4, 8.7 Hz, 2H), 7.57 (d, J = 2.5 Hz, 1H), 7.49 (d, J = 2.5 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.29 (d, J = 8.5 Hz, 6H), 7.21 (d, J = 11.1 Hz, 1H), 7.06 (d, J = 8.5 Hz, 6H), 7.01 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 4.20 (t, J = 6.4 Hz, 2H), 3.94 (t, J = 6.4 Hz, 2H), 1.86–1.68 (m, 4H), 1.43–1.55 (m, 4H), 1.25 (s, 27H); ^{13}C NMR spectra is not available because of the very poor solubility of **5** in common solvents; HRMS (APCI): m/z = 825.4520 $[\text{M}-\text{H}]^-$ (calcd. 825.4514 for $\text{C}_{57}\text{H}_{61}\text{O}_5$).



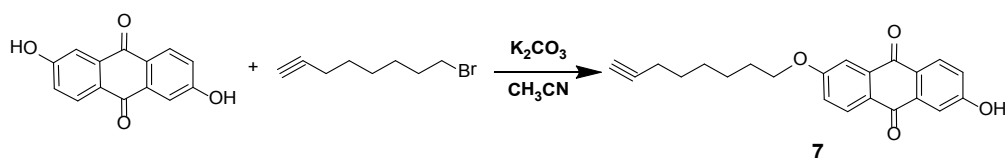
Scheme S4. Synthesis of **S1**.

Synthesis of S1. To a mixture of **5** (320 mg, 0.39 mmol), oct-7-yn-1-ol (60 mg, 0.47 mmol) and PPh_3 (160 mg, 0.6 mmol) in dry CH_2Cl_2 (15 mL) under an Ar atmosphere was added dropwise DIAD (130 mg, 0.6 mmol) at room temperature, which afforded a yellowish-brown solution. After the reaction mixture was stirred at room temperature for 10 h, the solvent was then evaporated in vacuo to give a crude product, which was purified by silica-gel column chromatography ($\text{CH}_2\text{Cl}_2/\text{petroleum ether}=1:1$) to afford **S1** as light yellow solid (321 mg, 88 %). M.p.: $205\text{--}206^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ = 8.22 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 2.5 Hz, 2H), 7.22 (dd, J = 8.6, 4.3 Hz, 8H), 7.08 (d, J = 8.5 Hz, 8H), 6.76 (d, J = 8.9 Hz, 2H), 4.15 (dd, J = 6.4, 4.7 Hz, 4H), 3.96 (t, J = 6.3 Hz, 2H), 2.29–2.16 (m, 2H), 1.96 (t, J = 2.6 Hz, 1H), 1.93–1.76 (m, 6H), 1.67–1.43 (m, 12H), 1.30 (s, 27H); ^{13}C NMR (75 MHz, CDCl_3): δ = 182.2, 180.5, 172.9, 164.0, 156.9, 153.7, 148.3, 144.2, 139.4, 135.8, 132.2, 130.8, 129.7, 127.0, 124.0, 120.9, 113.0, 110.5, 84.5, 68.66, 68.4, 67.6, 63.1, 34.3, 31.4, 29.3, 29.0, 28.9, 28.4, 28.3, 26.0, 25.8, 25.5, 18.4; HRMS (ESI): m/z = 957.5427 $[\text{M}+\text{Na}]^+$ (calcd. 957.5428 for $\text{C}_{65}\text{H}_{74}\text{O}_5\text{Na}$).



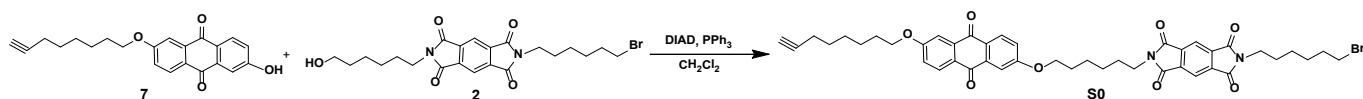
Scheme S5. Synthesis of **S2**.

Synthesis of S2. To a solution of **6** (320 mg, 0.60 mmol), **3** (318 mg, 0.72 mmol) and PPh₃ (240 mg, 0.90 mmol) in dry CH₂Cl₂ (25 mL) under an Ar atmosphere was added dropwise DIAD (185 mg, 0.90 mmol) at room temperature. The reaction mixture was stirred at room temperature for 12 h, and then concentrated in vacuo to give a residue, which was further purified by silica-gel column chromatography (CH₂Cl₂/petroleum ether=2:1) to afford **S2** as white solid (350 mg, 53 %). M.p.: 209-210 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.27 (s, 2H), 7.22 (d, *J* = 8.5 Hz, 6H), 7.13–7.02 (m, 8H), 6.73 (d, *J* = 8.8 Hz, 2H), 3.91 (t, *J* = 6.2 Hz, 2H), 3.75 (t, *J* = 7.0 Hz, 4H), 3.26 (t, *J* = 6.7 Hz, 2H), 1.76 (dd, *J* = 12.4, 5.6 Hz, 6H), 1.61 (dd, *J* = 13.7, 6.9 Hz, 2H), 1.52 (dd, *J* = 11.5, 6.6 Hz, 2H), 1.42 (t, *J* = 9.9 Hz, 6H), 1.30 (s, 27H); ¹³C NMR (75 MHz, CDCl₃): δ = 166.3, 156.8, 148.3, 144.2, 139.4, 137.3, 137.2, 132.2, 130.7, 124.0, 118.2, 112.9, 67.5, 63.0, 51.3, 38.6, 38.5, 34.3, 31.4, 29.2, 28.7, 28.4, 28.3, 26.7, 26.4, 26.2, 25.7; HRMS (ESI): *m/z* = 950.5171 [M+Na]⁺ (calcd. 950.5196 for C₅₉H₆₉N₅O₅Na).



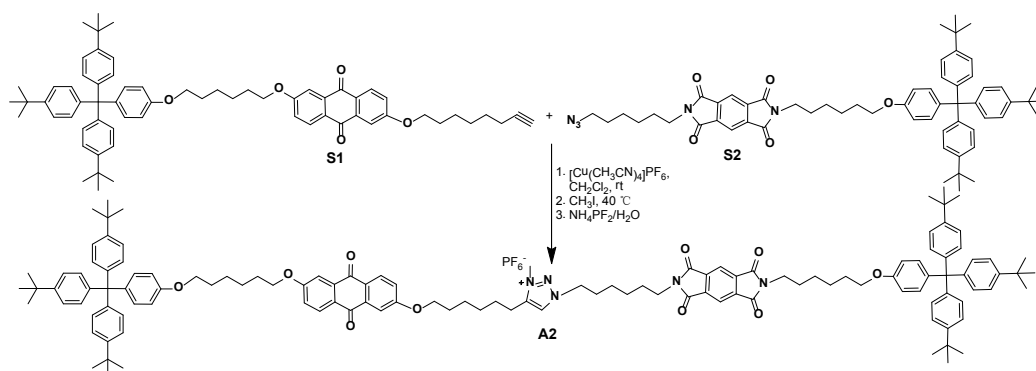
Scheme S6. Synthesis of **7**.

Synthesis of 7. To a solution of 1.30 g (5.50 mmol) of 2,6-dihydroxyanthracene-9,10-dione in dry DMF (180 mL) was added 1.75 g (11.0 mmol) of anhydrous potassium carbonate, 520 mg (2.75 mmol) of 8-bromooct-1-yne and a catalytic amount of sodium iodide, respectively. The mixture was heated to 90 °C for 18 hours, and then cooled to room temperature. The reaction mixture was filtrated, and the filtered cake was washed with CH₂Cl₂. The filtrate was collected and concentrated under reduced pressure to give a residue, which was purified by silica-gel column chromatography (dichloromethane/methanol = 80:1) to yield 470 mg (49 %) of **7** as a yellow solid. M.p.: 135-136 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ = 11.03 (s, 1H), 8.09 (dd, *J* = 10.7, 8.7 Hz, 2H), 7.52 (dd, *J* = 21.5, 2.5 Hz, 2H), 7.30 (ddd, *J* = 51.4, 8.6, 2.5 Hz, 2H), 4.18 (t, *J* = 6.4 Hz, 2H), 2.75 (t, *J* = 2.6 Hz, 1H), 2.24–2.11 (m, 2H), 1.88–1.68 (m, 2H), 1.57–1.30 (m, 6H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 181.2, 181.2, 180.9, 177.8, 163.6, 163.3, 163.1, 157.9, 143.0, 135.3, 135.2, 131.4, 129.7, 129.2, 127.3, 126.2, 125.2, 125.1, 121.9, 121.0, 120.2, 119.0, 112.1, 110.4, 103.6, 99.5, 89.7, 84.5, 82.2, 73.2, 71.1, 68.2, 66.5, 28.3, 27.9, 24.8, 17.6; HRMS (ESI): *m/z* = 347.1295 [M-H][−] (calcd. 347.1278 for C₂₂H₁₉O₄).



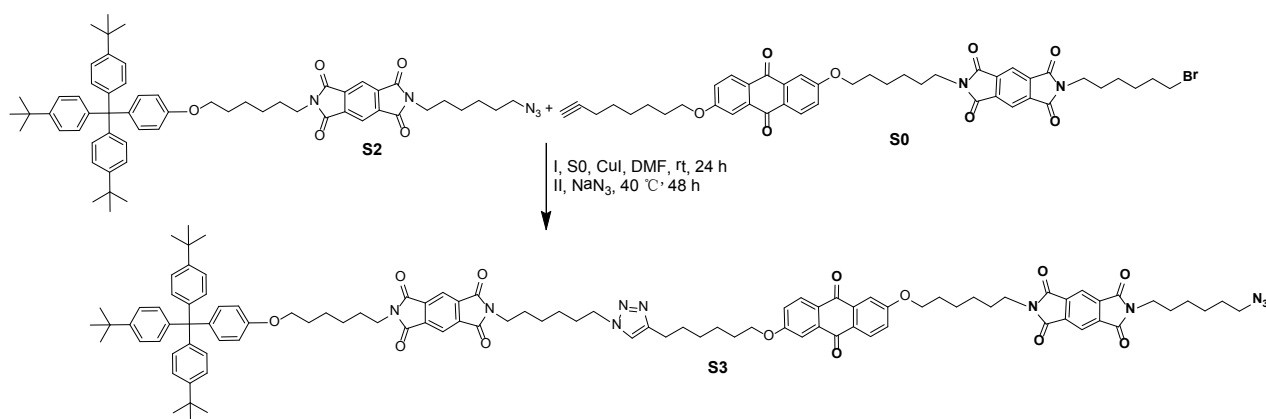
Scheme S7. Synthesis of **S0**.

Synthesis of S0. To a mixture of **7** (122 mg, 0.35 mmol), **2** (198 mg, 0.41 mmol) and PPh₃ (163 mg, 0.62 mmol) in dry CH₂Cl₂ (15 mL) under an Ar atmosphere was added dropwise DIAD (130 mg, 0.62 mmol) at room temperature. The mixture was stirred at room temperature for 12 h, and then concentrated in vacuo. The residue was purified by silica-gel column chromatography (CH₂Cl₂) to give **S2** as a yellow solid (250 mg, 88 %). M.p.: 156-157 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.25 (s, 2H), 8.20 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.67 (dd, *J* = 6.8, 2.5 Hz, 2H), 7.24–7.16 (m, 2H), 4.20–4.09 (m, 4H), 3.75 (dt, *J* = 11.0, 7.3 Hz, 4H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.23 (td, *J* = 6.6, 2.5 Hz, 2H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.93–1.81 (m, 6H), 1.73 (dt, *J* = 22.1, 7.3 Hz, 4H), 1.63–1.35 (m, 14H); ¹³C NMR (75 MHz, CDCl₃): δ = 182.1, 166.2, 164.0, 137.2, 135.8, 129.6, 127.0, 120.9, 118.1, 110.5, 100.0, 99.0, 84.4, 68.7, 68.5, 68.3, 38.5, 33.6, 32.5, 28.9, 28.3, 27.6, 26.5, 26.0, 25.5, 18.3; HRMS (ESI): *m/z* = 831.2251 [M+Na]⁺ (calcd. 831.2251 for C₄₄H₄₅O₈N₂BrNa).



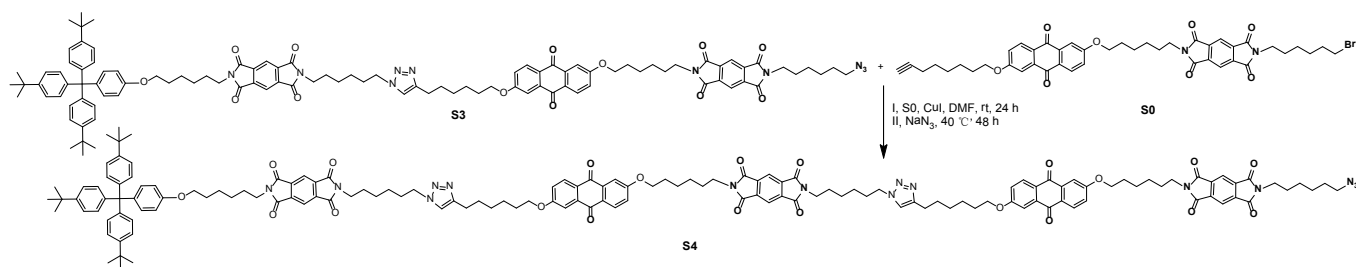
Scheme S8. Synthesis of **A2**.

Synthesis of A2. To a solution of **S1** (35 mg, 0.037 mmol) and **S2** (35mg, 0.038 mmol) in dried and degassed CH₂Cl₂ (10 mL) under an Ar atmosphere was added 3 mg (0.01 mmol) of [Cu(CH₃CN)₄]PF₆ at room temperature. After the solution was stirred for 12 h, 1 mL of CH₃I was added, and the mixture was then heated to 40 °C for another two days. The reaction mixture was cooled to room temperature, poured into saturated aqueous NH₄PF₆ (10 mL), and then vigorously stirred for 0.5 h. The organic phase was dried over anhydrous MgSO₄, and the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography (CH₂Cl₂/CH₃OH = 50:1) to give **A2** as a light yellow solid (73 mg, 98%). M.p.: 221-222 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.28–8.12 (m, 5H), 7.64 (d, *J* = 14.4 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 14H), 7.07 (d, *J* = 7.7 Hz, 16H), 6.74 (t, *J* = 7.7 Hz, 4H), 4.52 (t, *J* = 7.1 Hz, 2H), 4.20 (s, 3H), 4.14 (t, *J* = 5.2 Hz, 4H), 3.93 (dt, *J* = 12.5, 6.4 Hz, 4H), 3.72 (dd, *J* = 12.2, 5.5 Hz, 4H), 2.86 (t, *J* = 7.3 Hz, 2H), 1.96–2.09 (m, 2H), 1.80–1.93 (m, 8H), 1.66–1.77 (m, 6H), 1.50–1.63 (m, 12H), 1.47–1.37 (m, 6H), 1.29 (s, 54H); ¹³C NMR (75 MHz, CDCl₃): δ = 182.0, 178.3, 166.3, 164.0, 156.9, 148.3, 145.8, 144.9, 144.2, 139.5, 137.2, 135.6, 132.3, 130.8, 129.7, 129.6, 127.96, 126.9, 124.0, 120.8, 120.5, 118.0, 117.0, 113.0, 110.9, 110.6, 68.7, 68.6, 67.6, 63.1, 57.0, 55.7, 53.9, 39.8, 38.6, 38.2, 37.3, 34.3, 31.8, 31.4, 29.3, 29.1, 28.9, 28.7, 28.4, 27.9, 26.7, 26.6, 26.0, 25.9, 25.7, 25.4, 23.2; HRMS (ESI): *m/z* = 1878.1085 [M-PF₆]⁺ (calcd. 1878.1142 for C₁₂₅H₁₄₇ O₁₀N₅).



Scheme S9. Synthesis of **S3**.

Synthesis of S3. To a solution of **S2** (162 mg, 0.20 mmol) and **S0** (186 mg, 0.20 mmol) in dry and degassed DMF (20 mL) under an Ar atmosphere was added 7 mg (0.02 mmol) of CuI at room temperature. After the solution was stirred for 24 h, 65 mg (1.0 mmol) of NaN₃ was added. And the mixture was then heated to 40 °C for two days, cooled to room temperature, and concentrated in vacuo to remove most of the solvent. The residue was subjected to CH₂Cl₂/H₂O, washed with water for 5 times (5×15 mL). The organic layer was dried over anhydrous MgSO₄, and then concentrated in vacuo to give the crude product, which was further purified by silica-gel column chromatography (CH₂Cl₂/CH₃OH = 50:1) to give **S4** as a light yellow solid (259 mg, 76 %). M.p.: 177–178 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.17–8.29 (m, 6H), 7.67 (s, 2H), 7.22 (d, *J* = 8.4 Hz, 8H), 7.07 (d, *J* = 8.5 Hz, 8H), 6.74 (d, *J* = 8.7 Hz, 2H), 4.30 (t, *J* = 7.0 Hz, 2H), 4.14 (t, *J* = 6.2 Hz, 4H), 3.91 (t, *J* = 6.2 Hz, 2H), 3.80–3.69 (m, 8H), 3.26 (t, *J* = 6.7 Hz, 2H), 2.74 (t, *J* = 7.0 Hz, 2H), 1.93–1.82 (m, 6H), 1.74 (dd, *J* = 6.5, 4.9 Hz, 12H), 1.58 (dd, *J* = 13.3, 7.9 Hz, 12H), 1.35–1.51 (m, 18H), 1.29 (s, 27 H); ¹³C NMR (75 MHz, CDCl₃): δ = 182.1, 166.2, 164.0, 163.9, 156.8, 148.3, 144.2, 139.5, 137.3, 137.2, 137.2, 135.8, 132.2, 130.7, 129.6, 127.0, 124.0, 120.9, 118.1, 112.9, 110.6, 110.5, 68.7, 68.5, 67.5, 63.1, 51.3, 50.0, 38.6, 38.5, 38.4, 34.3, 32.5, 31.4, 30.1, 29.3, 29.2, 28.8, 28.7, 28.4, 28.31, 28.26, 28.2, 26.6, 26.5, 26.4, 26.2, 26.0, 25.7, 25.5; HRMS (ESI): *m/z* = 1722.8477 [M+Na]⁺ (calcd. 1722.8498 for C₁₀₃H₁₁₄N₁₀O₁₃Na).

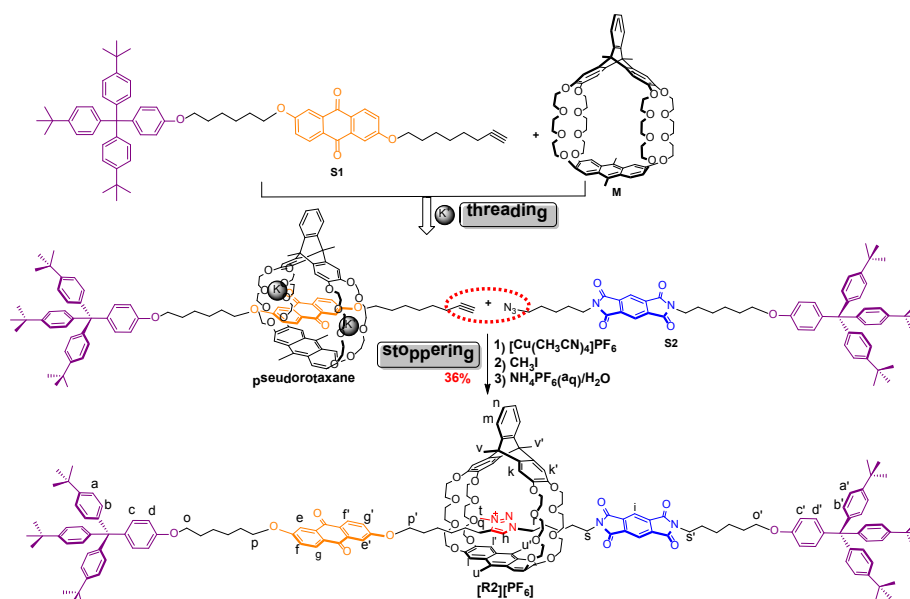


Scheme S10. Synthesis of **S4**.

Synthesis of S4. To a solution of **S3** (170 mg, 0.10 mmol) and **S0** (93 mg, 0.10 mmol) in dry and degassed DMF (15 mL) under an Ar atmosphere was added 7 mg (0.02 mmol) of CuI at room temperature. After the solution was stirred for 24 h, 33 mg (0.50 mmol) of NaN₃ was added. The mixture was then heated to 40 °C for two days, cooled to room temperature, and concentrated in vacuo to remove most of the solvent. The residue was subjected to CH₂Cl₂/H₂O, washed with water for 5 times (5×15 mL). The organic layer was then concentrated in vacuo to give the crude product, which was further purified by silica-gel column chromatography (CH₂Cl₂/CH₃OH = 50:1→40:1) to give **S4** as a light yellow solid (132 mg, 51 %). M.p.: 202–203 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.22 (dd, *J* = 16.3, 7.2 Hz, 10H), 7.67 (s, 4H), 7.21 (t, *J* = 8.5 Hz, 10H), 7.13–7.03 (m, 8H), 6.74 (d, *J* = 8.8 Hz, 2H), 4.30 (t, *J* = 7.1 Hz, 4H), 4.13 (t, *J* = 6.3

Hz, 8H), 3.91 (t, $J = 6.2$ Hz, 2H), 3.81–3.68 (m, 12H), 3.26 (t, $J = 6.8$ Hz, 2H), 2.73 (t, $J = 7.6$ Hz, 4H), 1.95–1.80 (m, 12H), 1.79–1.65 (m, 18H), 1.63–1.52 (m, 18H), 1.51–1.44 (m, 12H), 1.42–1.34 (m, 12H), 1.29 (s, 28H); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 182.11, 182.09, 166.2, 164.0, 163.9, 156.8, 148.3, 148.2, 144.2, 139.5, 137.3, 137.2, 137.2, 135.8, 132.2, 130.7, 129.6, 129.6, 127.0, 126.9, 124.0, 120.8, 120.8, 120.4, 118.1, 112.9, 110.6, 110.5, 77.4, 77.2, 77.0, 76.6, 68.7, 68.5, 67.5, 63.0, 51.3, 49.9, 38.6, 38.5, 38.5, 38.4, 34.3, 31.4, 30.1, 29.3, 29.2, 28.9, 28.9, 28.8, 28.6, 28.4, 28.3, 28.2, 28.2, 26.6, 26.5, 26.4, 26.2, 26.2, 26.0, 25.7, 25.6, 25.5$; HRMS (ESI): $m/z = 2494.1693$ $[\text{M}+\text{Na}]^+$ (calcd. 2494.1766 for $\text{C}_{147}\text{H}_{159}\text{N}_{15}\text{O}_{21}\text{Na}$).

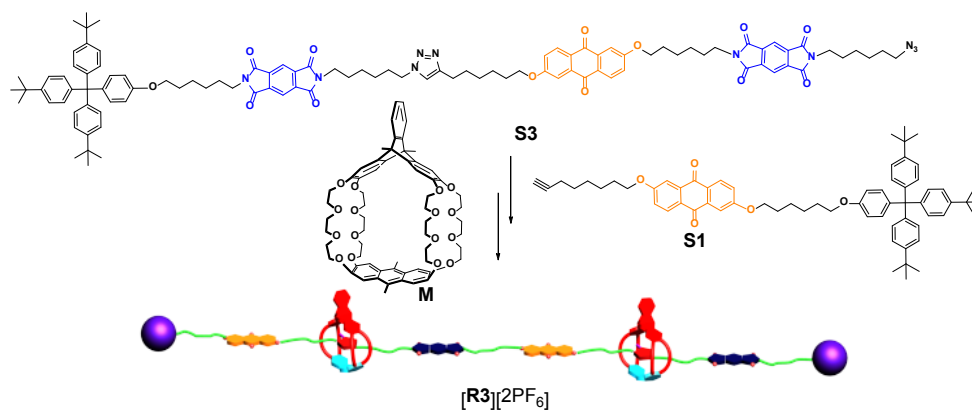
3. Synthesis of $[\text{R2}][\text{PF}_6]$, $[\text{R3}][2\text{PF}_6]$ and $[\text{R4}][3\text{PF}_6]$



Scheme S12. Synthesis of $[\text{2}]$ rotaxane $[\text{R2}][\text{PF}_6]$.

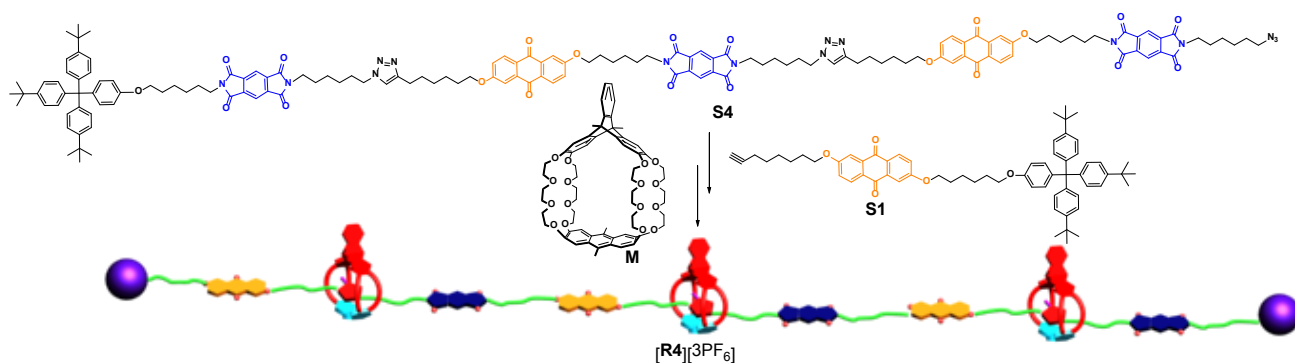
Synthesis of the $[\text{2}]$ rotaxane $[\text{R2}][\text{PF}_6]$. To the solution of **S1** (60.0 mg, 0.062 mmol) and **M** (75.4 mg, 0.070 mmol) in dry CH_2Cl_2 (15 mL) was added 60 mg KPF_6 , and the mixture was ultrasonic oscillated for at least 10 min. until the solution turned to brown for formation of the pseudorotaxane. Then the mixture was stirred under room temperature and bubbled with Ar for 0.5 h. After that, to the above mixture was successively added **S2** (71.2 mg, 0.076 mmol), a drop of lutidine and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (14.2 mg, 0.038 mmol) under Ar atmosphere. After being stirred for two days, the mixture was concentrated in vacuo to give a residue. To the residue was added 5 mL of $\text{CH}_3\text{I}/\text{CH}_3\text{CN}$ (1:4, v/v), and the resulted mixture was then stirred at 40 °C for another two days in a sealed tube. After being cooled to room temperature, the reaction mixture was diluted with CH_2Cl_2 (30 mL), and then washed with saturated aqueous NH_4PF_6 (20 mL $\times$ 3) and H_2O (20 mL $\times$ 3). The organic layer was concentrated in vacuo, and the crude product was purified by silica-gel column chromatography ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 100:1 \rightarrow 70:1$) to give $[\text{R2}][\text{PF}_6]$ as a pink solid (69 mg, 36 %). M.p.: > 300 °C; ^1H NMR (600 MHz, $\text{CDCl}_3:\text{CD}_3\text{CN}=1:1$, 278 K): $\delta = 8.30\text{--}8.05$ (m, 4H), 7.78–7.58 (m, 2H), 7.41–7.30 (m, 2H), 7.30–7.00 (m, 31H), 6.86 (s, 2H), 6.75 (dd, $J = 17.5, 8.5$ Hz, 4H), 6.58 (d, 4H), 6.29 (br, 1H), 4.48–4.35 (m, 4H), 4.30 (s, 2H), 4.22–4.12 (m, 5H), 4.10–4.03 (m, 4H), 4.02–3.90 (m, 8H), 3.90–3.64 (m, 30H), 3.53–3.63 (m, 4H), 3.31 (s, 2H), 2.63 (d, 6H), 2.17–2.11 (m, 2H), 2.11–2.00 (m, 5H), 1.93–1.88 (m, 2H), 1.88–1.80 (m, 4H), 1.79–1.74 (m, 2H), 1.73–1.63 (m, 4H), 1.53 (s, 6H), 1.48–1.36 (m, 6H), 1.28 (s, 54H); ^{13}C NMR (150 MHz, $\text{CDCl}_3:\text{CD}_3\text{CN}=1:1$, 278 K): $\delta = 181.7, 166.6, 166.4, 163.9, 156.82, 156.78, 149.1, 148.2, 147.7, 147.6, 145.1, 144.7, 144.5, 143.1, 141.4, 141.3, 139.3, 137.19, 136.9,$

135.6, 131.8, 130.3, 129.7, 129.6, 126.8, 126.7, 125.9, 125.12, 125.07, 124.4, 123.3, 122.8, 120.6, 119.8, 118.1, 117.2, 113.2, 113.1, 110.6, 110.6, 107.9, 107.1, 103.0, 102.8, 70.9, 70.8, 70.20, 70.16, 69.3, 69.2, 68.94, 68.8, 68.7, 68.6, 68.5, 68.3, 67.6, 67.5, 63.0, 51.9, 47.6, 47.5, 38.4, 38.1, 37.6, 34.2, 31.0, 30.0, 29.6, 29.4, 29.2, 29.1, 29.00, 28.9, 28.83, 28.80, 28.3, 28.2, 26.5, 25.9, 25.9, 25.7, 25.6, 25.5, 22.6, 22.5, 14.4, 14.3, 13.9, 13.4, 13.5; HRMS (ESI): $m/z = 2951.5957$ [$M-PF_6$]⁺ (calcd. 2951.5951 for $C_{187}H_{218}N_5O_{26}$).



Scheme S12. Synthesis of [3]rotaxane **[R3][2PF₆]**.

Synthesis of the [3]rotaxane [R3][3PF₆]. To the solution of **S3** (55 mg, 0.032 mmol), **S1** (18 mg, 0.032 mmol) and **M** (76 mg, 0.070 mmol) in dry CH_2Cl_2 (15 mL) was added 94 mg (0.51 mmol) KPF_6 . The mixture was ultrasonic oscillated for 20 min., and then stirred at room temperature under Ar atmosphere for 4 h. To the above mixture was successively added a drop of lutidine and $[Cu(CH_3CN)_4]PF_6$ (12 mg, 0.032 mmol). After being stirred for two days, the mixture was concentrated in vacuo. The residue was dissolved in 5 mL of CH_3I/CH_3CN (1:4, v/v), and the resulted mixture was then stirred at 40 °C for another two days in a sealed tube. After being cooled to room temperature, the reaction mixture was diluted with CH_2Cl_2 (30 mL), and then washed with saturated aqueous NH_4PF_6 (20 mL×3) and H_2O (20 mL×3). The organic layer was concentrated in vacuo, and the crude product was purified by thin-layer silica-gel chromatography (eluent: $CH_2Cl_2/CH_3OH = 15:1$) to give **[R3][2PF₆]** as a pink solid (44 mg, 27 %). M.p.: > 300 °C; 1H NMR (600 MHz, $CDCl_3:CD_3CN=1:1$, 278 K): $\delta = 8.36-7.99$ (m, 8H), 7.76 (s, 2H), 7.63 (s, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.34–7.06 (m, 46H), 6.90 (s, 4H), 6.78 (dd, $J = 14.5, 8.7$ Hz, 4H), 6.72–6.54 (m, 8H), 6.43 (br, 2H), 4.51–4.39 (m, 8H), 4.32 (s, 4H), 4.26–4.17 (m, 9H), 4.17–4.11 (m, 5H), 4.11–4.04 (m, 9H), 4.04–3.94 (m, 16H), 3.94–3.69 (m, 77H), 3.67–3.58 (m, 11H), 3.37–3.30 (s, 4H), 2.81–2.51 (m, 12H), 2.13–2.05 (m, 14H), 1.97–1.91 (m, 5H), 1.90–1.80 (m, 9H), 1.79–1.66 (m, 10H), 1.61–1.53 (m, 7H), 1.53–1.49 (m, 5H), 1.48–1.41 (d, 11H), 1.32 (s, 56H); HRMS (ESI): $m/z = 2405.7156$ $1/2[M-2PF_6]^{2+}$ (calcd. 2405.7157 for $1/2 C_{294}H_{338}N_{10}O_{50}$).



Scheme S13. Synthesis of [4]rotaxane [R4][3PF₆].

Synthesis of the [4]rotaxane [R4][3PF₆]. To the solution of **S4** (50 mg, 0.019 mmol), **S1** (18 mg, 0.021 mmol) and **M** (80 mg, 0.075 mmol) in dry CH₂Cl₂ (15 mL) was added 84 mg (0.046 mmol) KPF₆. The mixture was ultrasonic oscillated for 20 min. under Ar atmosphere, then stirred at room temperature for 6 h to give a dark brown solution. To the above solution was successively added a drop of lutidine and [Cu(CH₃CN)₄]PF₆ (15 mg, 0.040 mmol). After being stirred for two days, the reaction mixture was concentrated in vacuo. To the residue was added 5 mL of CH₃I/CH₃CN (2:3, v/v), and the resulted mixture was stirred at 40 °C for another two days in a sealed tube. After work-up as described as above, [R4][3PF₆] as a pink solid (31 mg, 23 %) could be obtained by thin-layer silica-gel chromatography (eluent: CH₂Cl₂/CH₃OH = 13:1). M.p.: > 300 °C; ¹H NMR (600 MHz, CDCl₃:CD₃CN=1:1, 278 K): δ = 8.32–8.06 (m, 12H), 7.74 (s, 3H), 7.60 (s, 3H), 7.39 (s, 3H), 7.33–7.27 (d, 13H), 7.25–7.12 (m, 28H), 7.12–7.05 (m, 6H), 6.90 (s, 6H), 6.77 (dd, *J* = 16.1, 8.4 Hz, 4H), 6.72–6.54 (d, 12H), 6.49 (br, 3H), 4.52–4.39 (m, 12H), 4.31 (s, 6H), 4.25–4.16 (m, 13H), 4.15–4.04 (s, 19H), 4.04–4.95 (m, 21H), 3.93–3.69 (m, 97H), 3.67–3.58 (m, 14H), 3.42 (s, 6H), 2.66 (d, 18H), 2.13–2.02 (m, 20H), 1.94 (s, 7H), 1.89–1.78 (m, 13H), 1.78–1.64 (s, 13H), 1.63–1.50 (d, 14H), 1.50–1.41 (m, 16H), 1.32 (s, 55H); HRMS (ESI): *m/z* = 2223.7512 1/3[M-3PF₆]³⁺ (calcd. 2223.7557 for 1/3C₄₀₁H₄₅₈N₁₅O₇₄).

4. ^1H NMR, ^{13}C NMR, HSQC, HMBC, and ROESY spectra of three stable states of the [2]rotaxane.

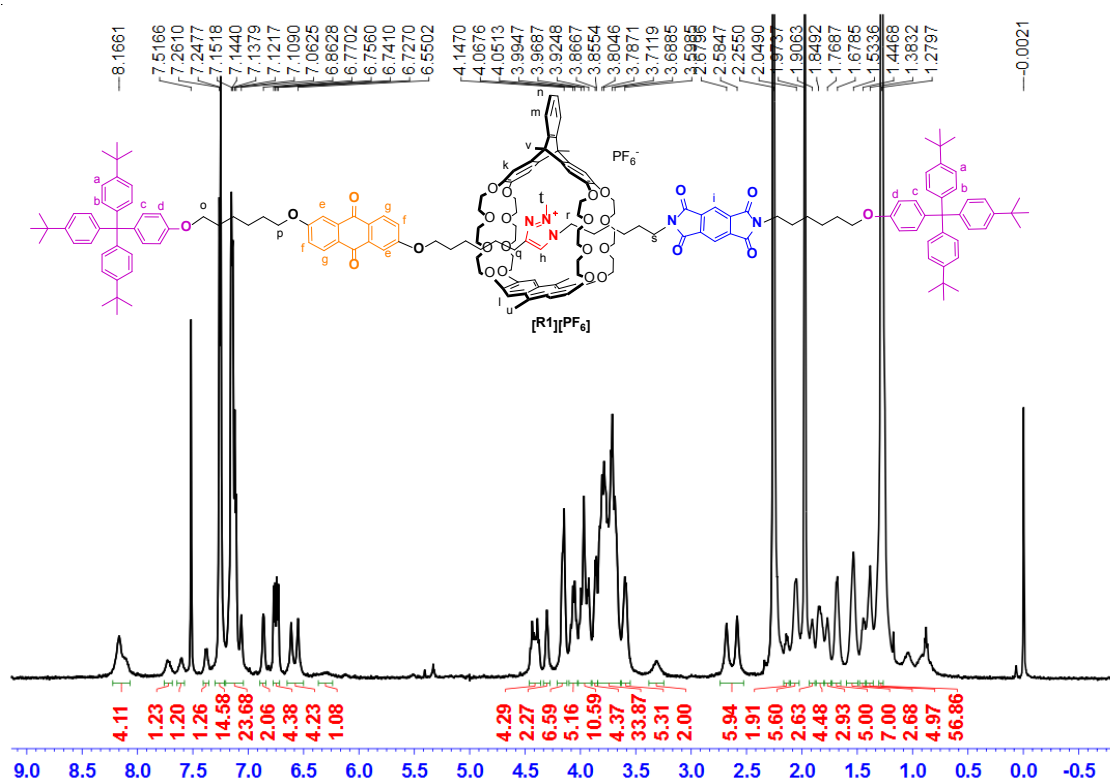


Fig. S1. ^1H NMR spectrum(CDCl₃/CD₃CN=1:1, 600 MHz, 278 K) of [2]rotaxane $[\text{R2}][\text{PF}_6]$.

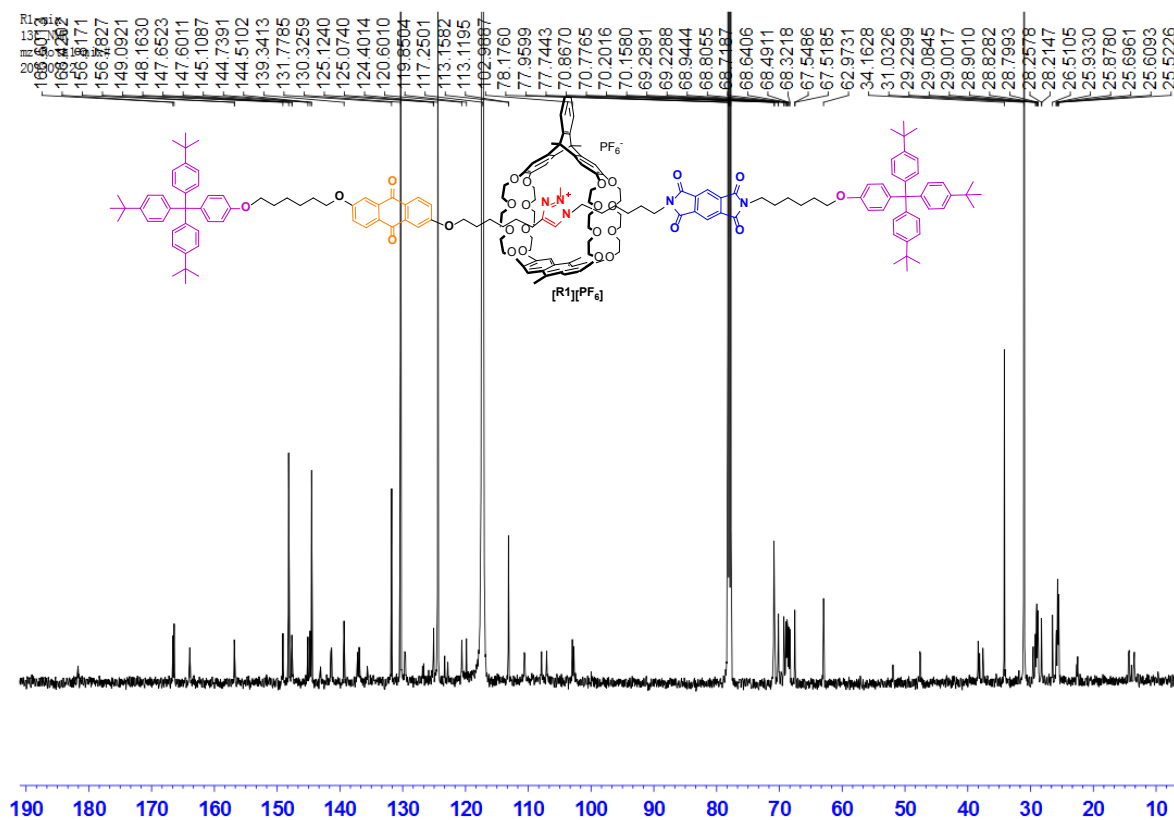


Fig. S2. ^{13}C NMR spectrum(CDCl₃/CD₃CN=1:1, 150 MHz, 278 K) of [2]rotaxane $[\text{R2}][\text{PF}_6]$.

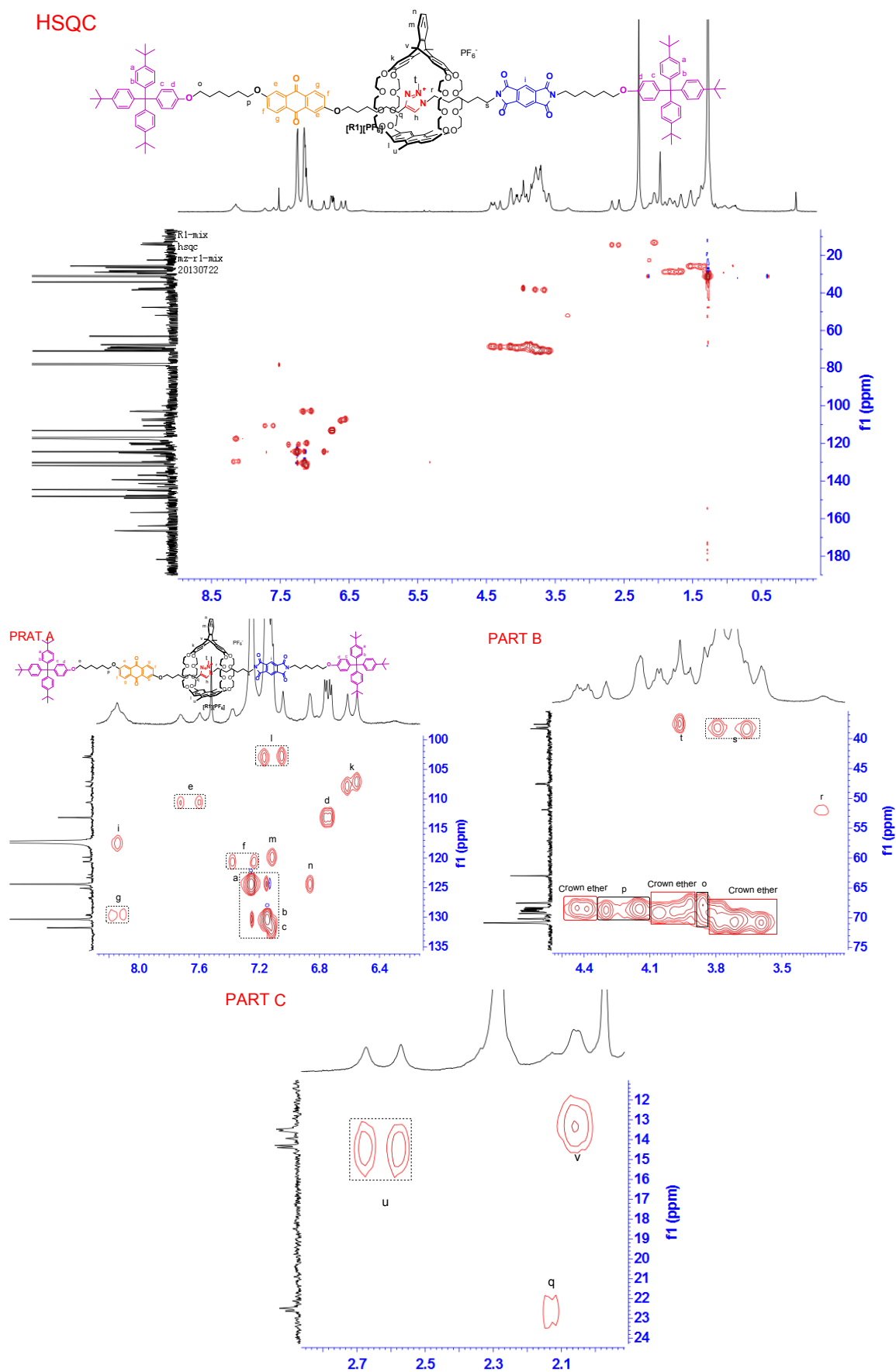


Fig. S3. HSQC spectrum ($\text{CDCl}_3/\text{CD}_3\text{CN}=1:1$, 600 MHz, 278 K) of [2]rotaxane **[R2]**[PF_6].

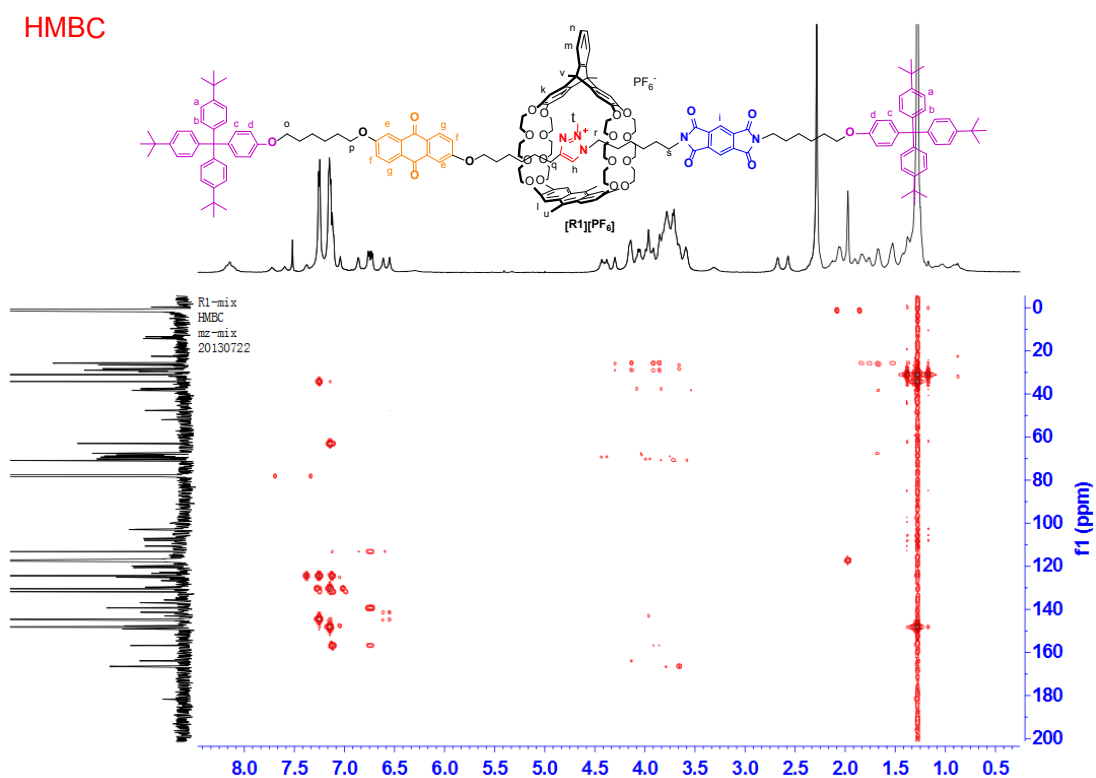


Fig. S4. HMBC spectrum ($CDCl_3/CD_3CN=1:1$, 600 MHz, 278 K) of [2]rotaxane **[R2]** $[PF_6]$.

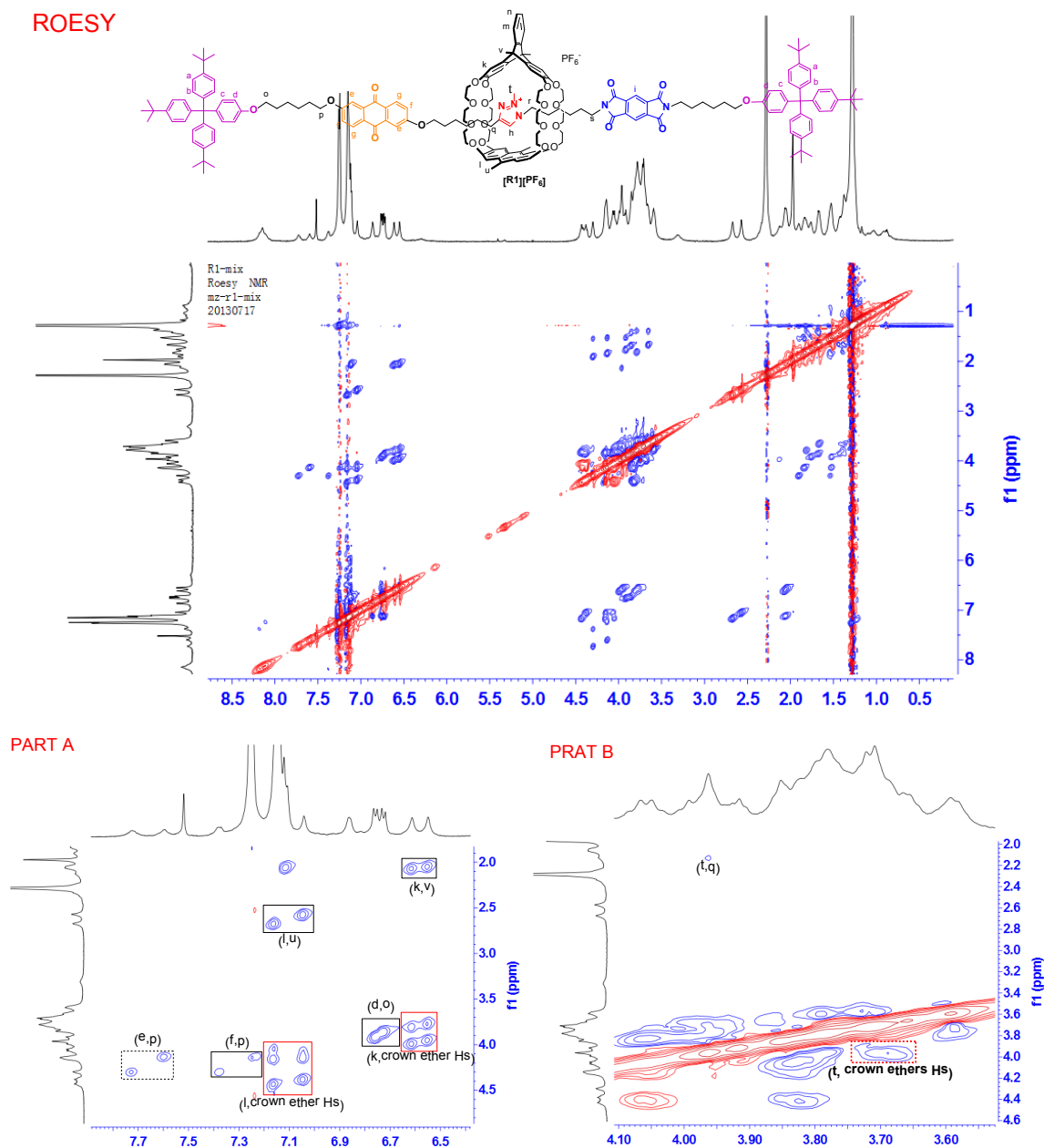


Fig. S5. ROESY spectrum ($\text{CDCl}_3/\text{CD}_3\text{CN}=1:1$, 600 MHz, 278 K) of [2]rotaxane [R2][PF₆].

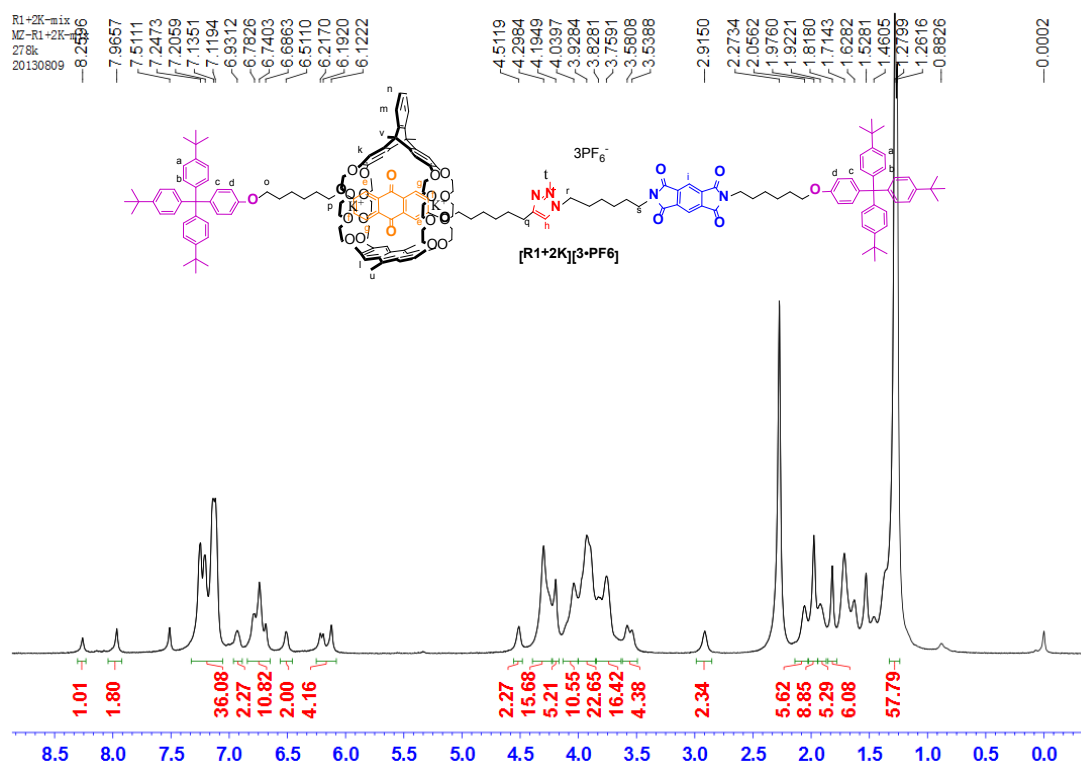


Fig. S6. ¹H NMR spectrum (CDCl₃/CD₃CN=1:1, 600 MHz, 278 K) of [2]rotaxane [R₂][PF₆] after the addition of 6 equivalents of KPF₆.

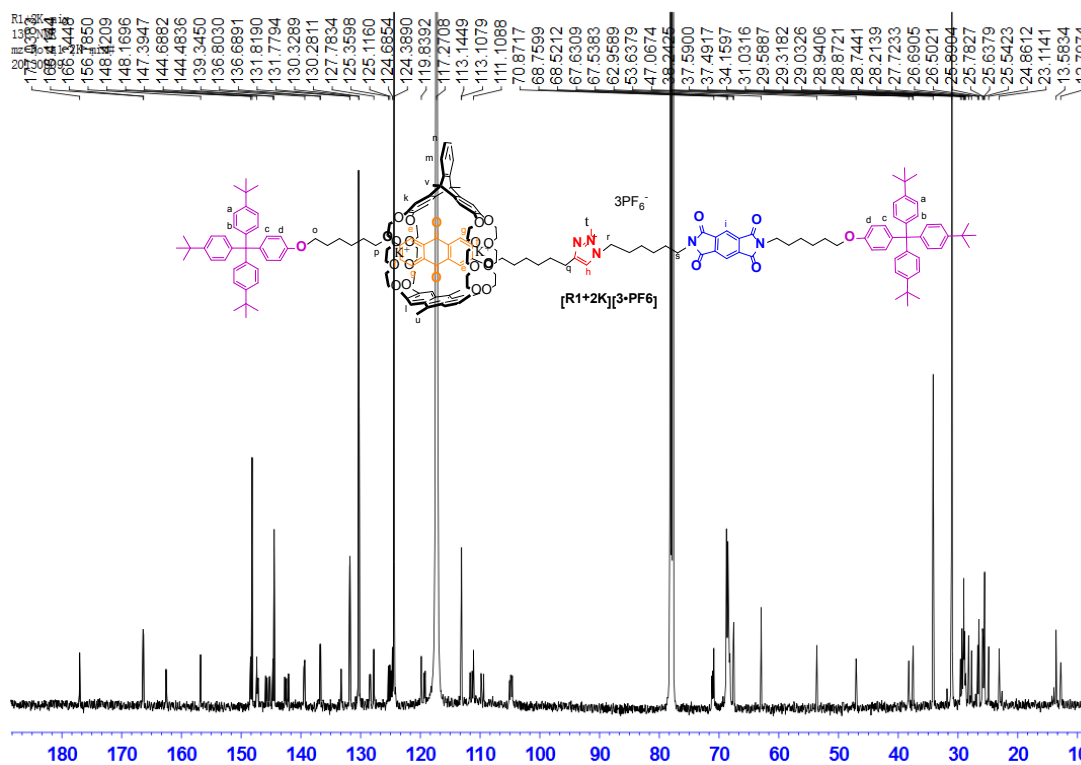


Fig. S7. ¹³C NMR spectrum (CDCl₃/CD₃CN=1:1, 150 MHz, 278 K) of [2]rotaxane [R₂][PF₆] after the addition of 6 equivalents of KPF₆.

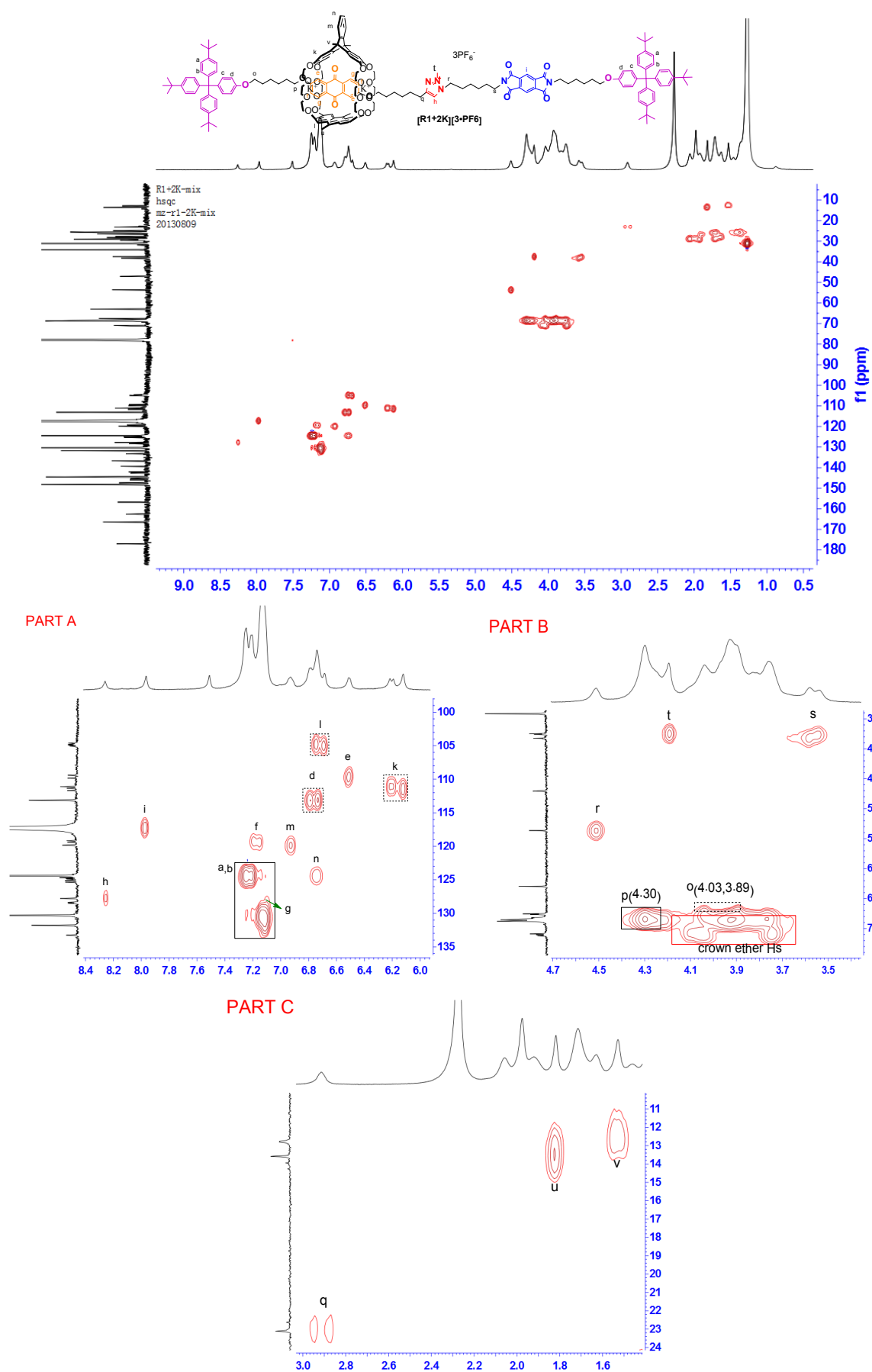


Fig. S8. HSQC spectrum (CDCl₃/CD₃CN=1:1, 600 MHz, 278 K) of [2]rotaxane [R2][PF₆] after the addition of 6 equivalents of KPF₆.

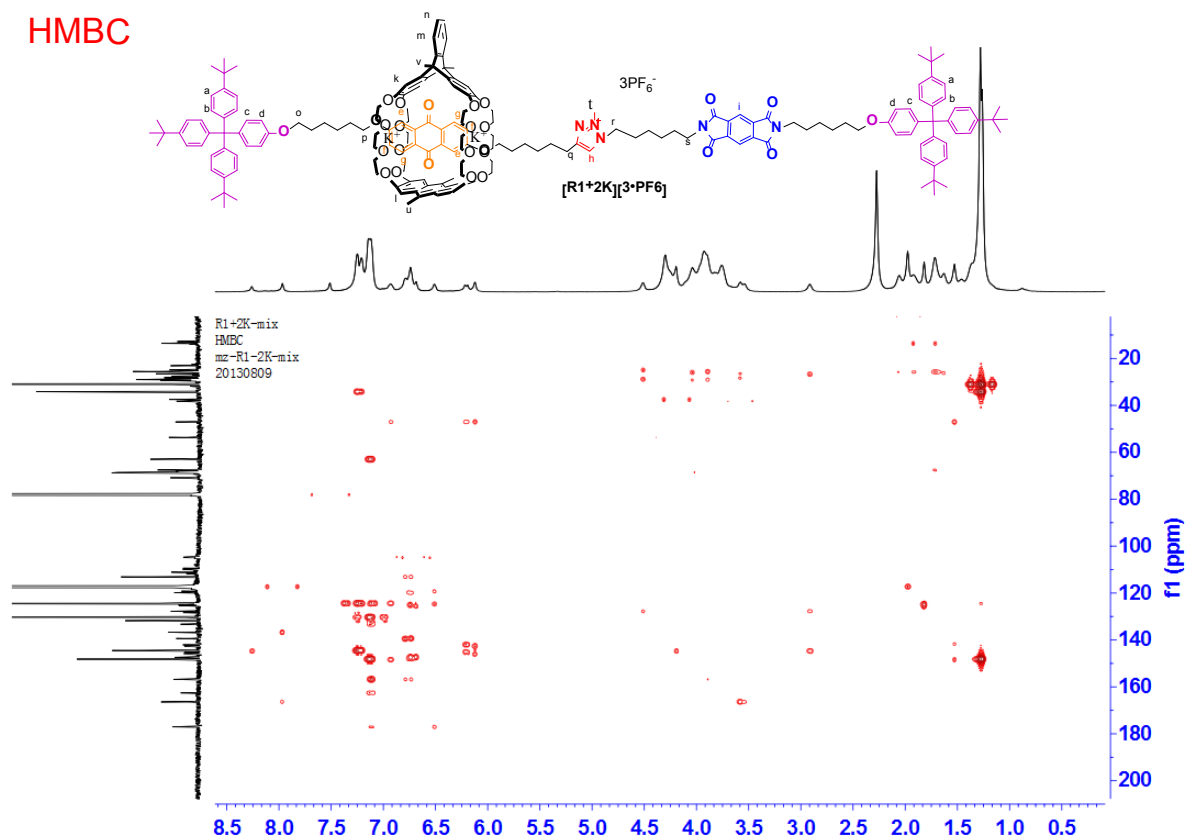
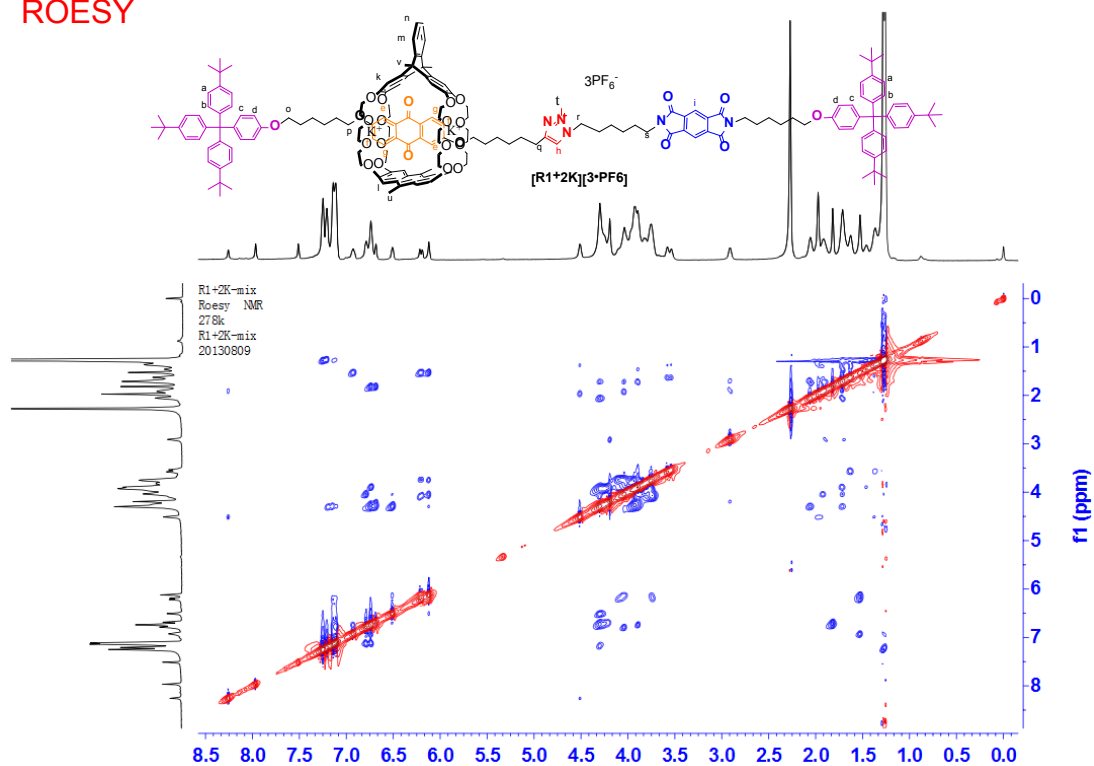
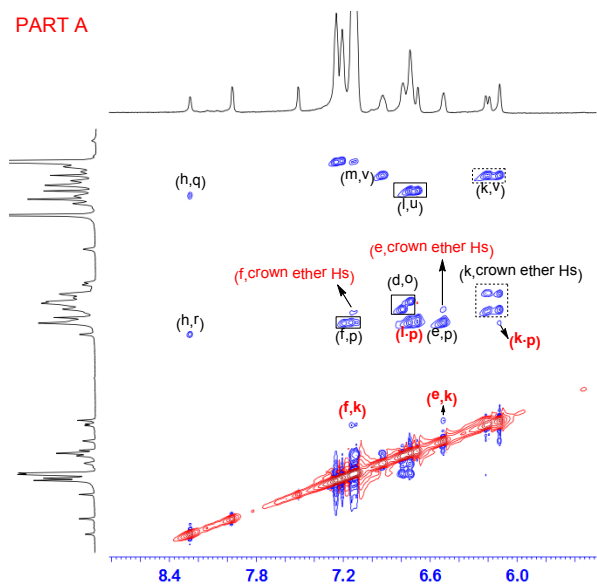


Fig. S9. HMBC spectrum ($CDCl_3/CD_3CN=1:1$, 600 MHz, 278 K) of [2]rotaxane $[R2][PF_6]$ after the addition of 6 equivalents of KPF_6 .

ROESY



PART A



PART B

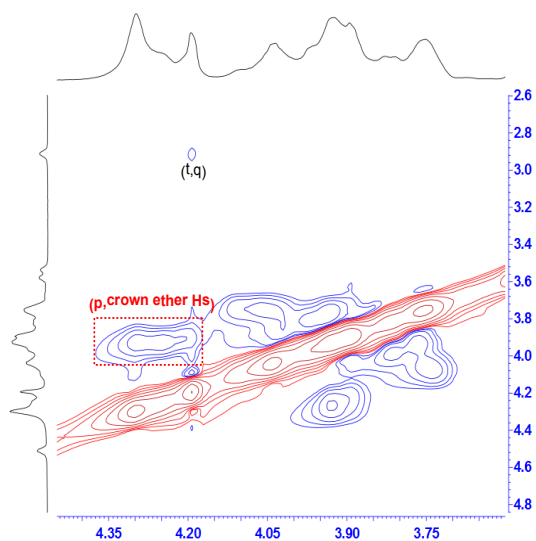


Fig. S10. ROESY spectrum ($\text{CDCl}_3/\text{CD}_3\text{CN}=1:1$, 600 MHz, 278 K) of [2]rotaxane **[R2]**[PF₆] after the addition of 6 equivalents of KPF₆.

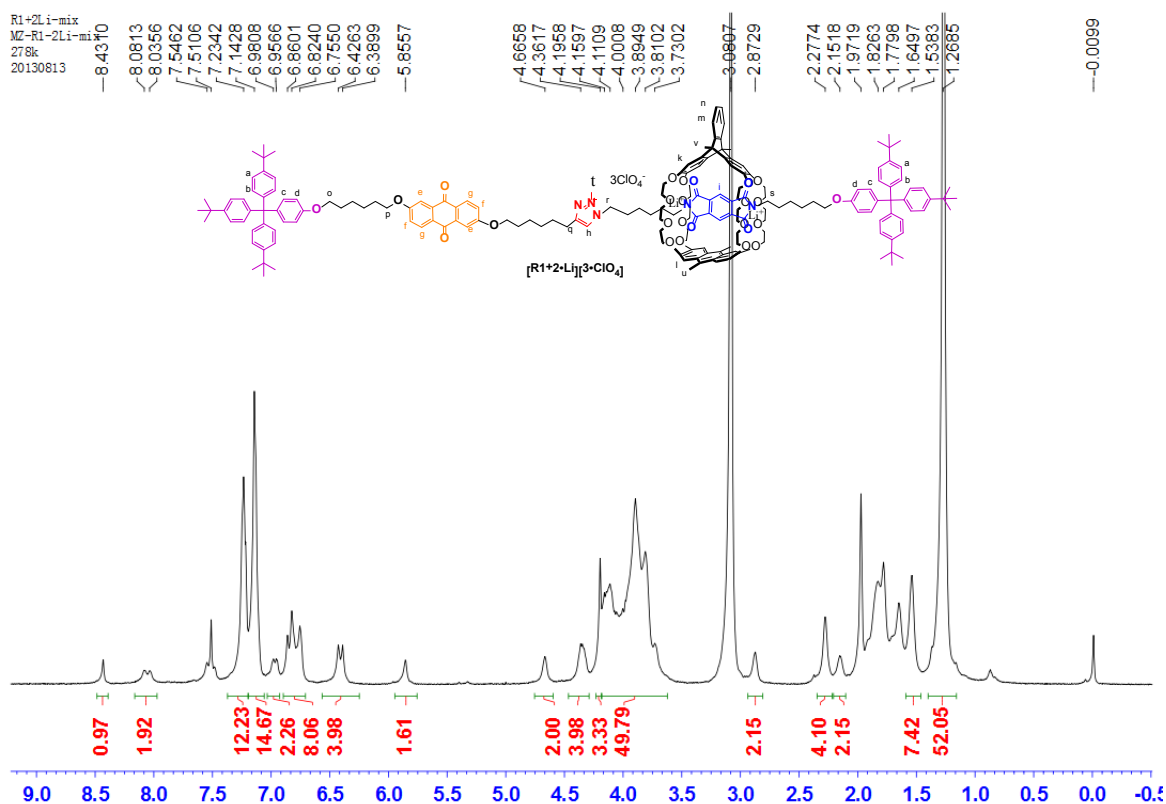


Fig. S11. ¹H NMR spectrum (CDCl₃/CD₃CN=1:1, 600 MHz, 278 K) of [2]rotaxane [R₂][PF₆] after the addition of 6 equivalents of LiClO₄.

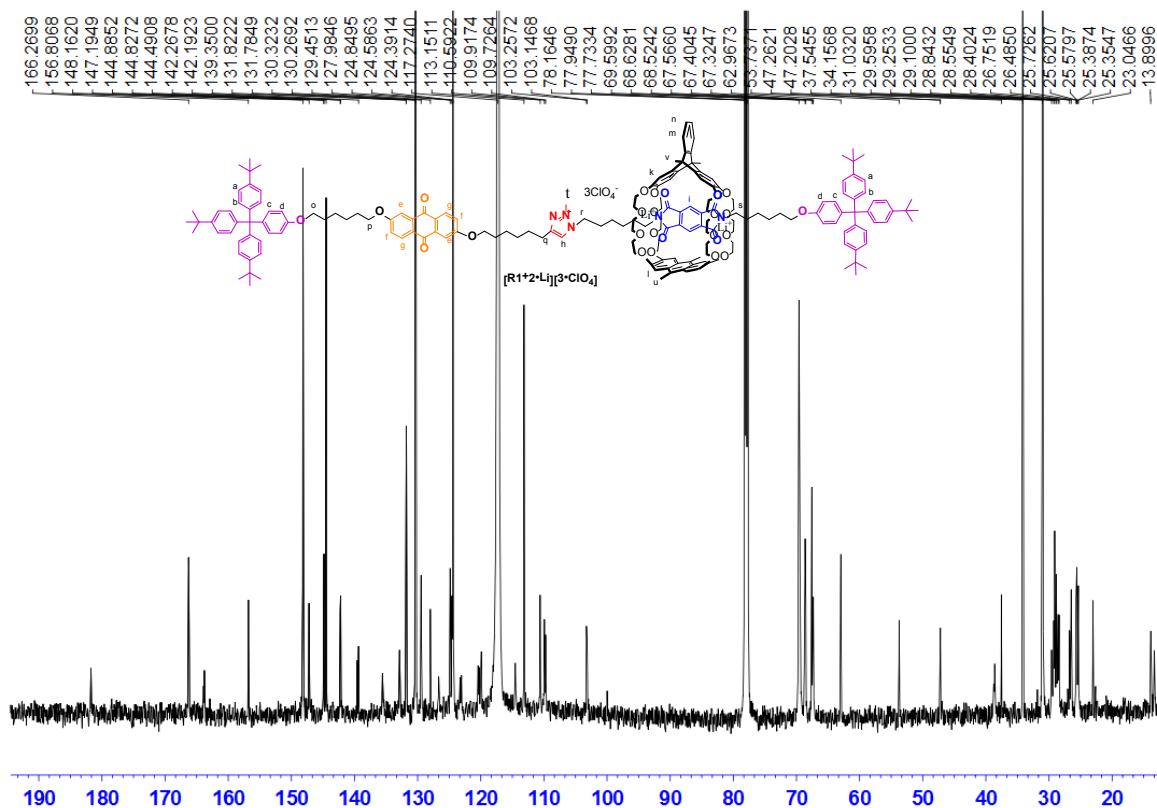


Fig. S12. ¹³C NMR spectrum (CDCl₃/CD₃CN=1:1, 150 MHz, 278 K) of [2]rotaxane [R₂][PF₆] after the addition of 6 equivalents of LiClO₄.

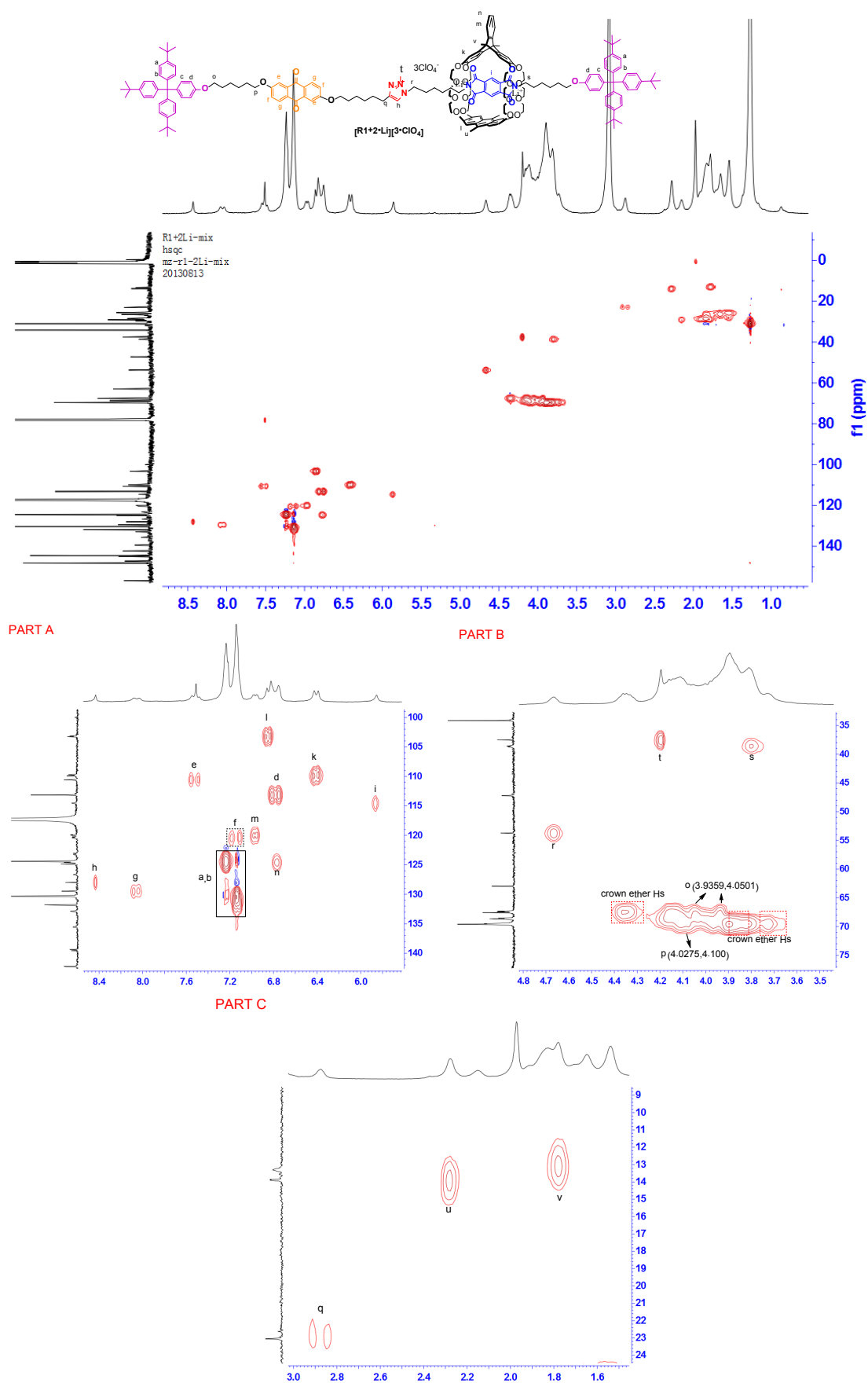


Fig. S13. HSQC spectrum ($CDCl_3/CD_3CN=1:1$, 600 MHz, 278 K) of [2]rotaxane $[R2][PF_6]$ after the addition of 6 equivalents of $LiClO_4$.

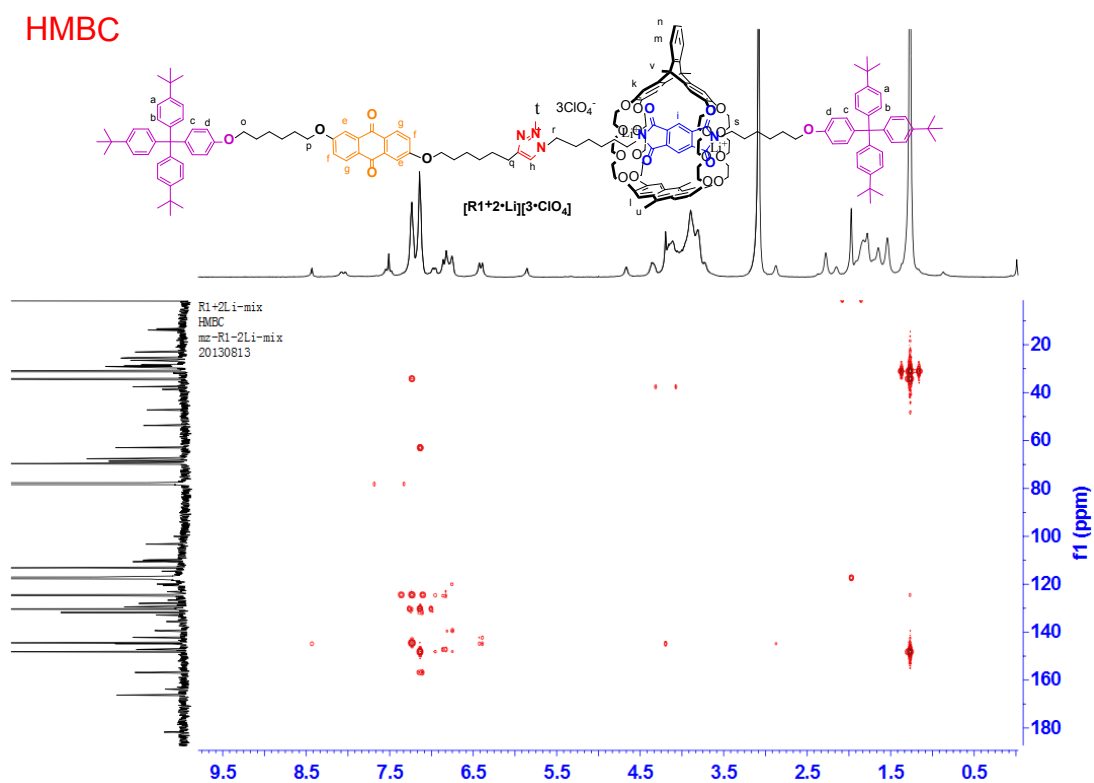


Fig. S14. HMBC spectrum (CDCl₃/CD₃CN=1:1, 600 MHz, 278 K) of [2]rotaxane **[R2]**[PF₆] after the addition of 6 equivalents of LiClO₄.

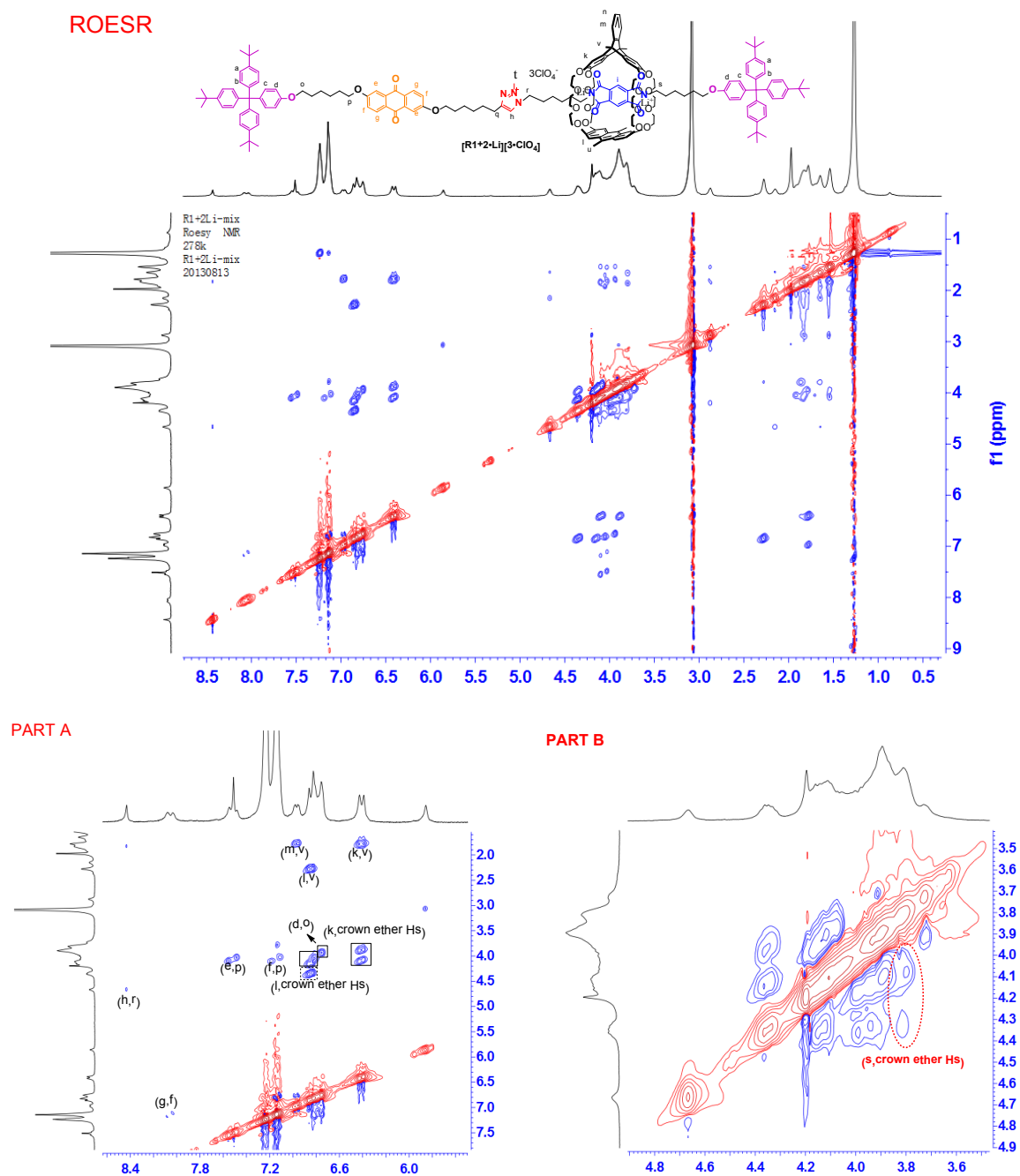


Fig. S15. ROESY spectrum ($\text{CDCl}_3/\text{CD}_3\text{CN}=1:1$, 600 MHz, 278 K) of [2]rotaxane **[R2]**[PF₆] after the addition of 6 equivalents of LiClO₄.

5. HRMS spectra for three states of the [2]rotaxane

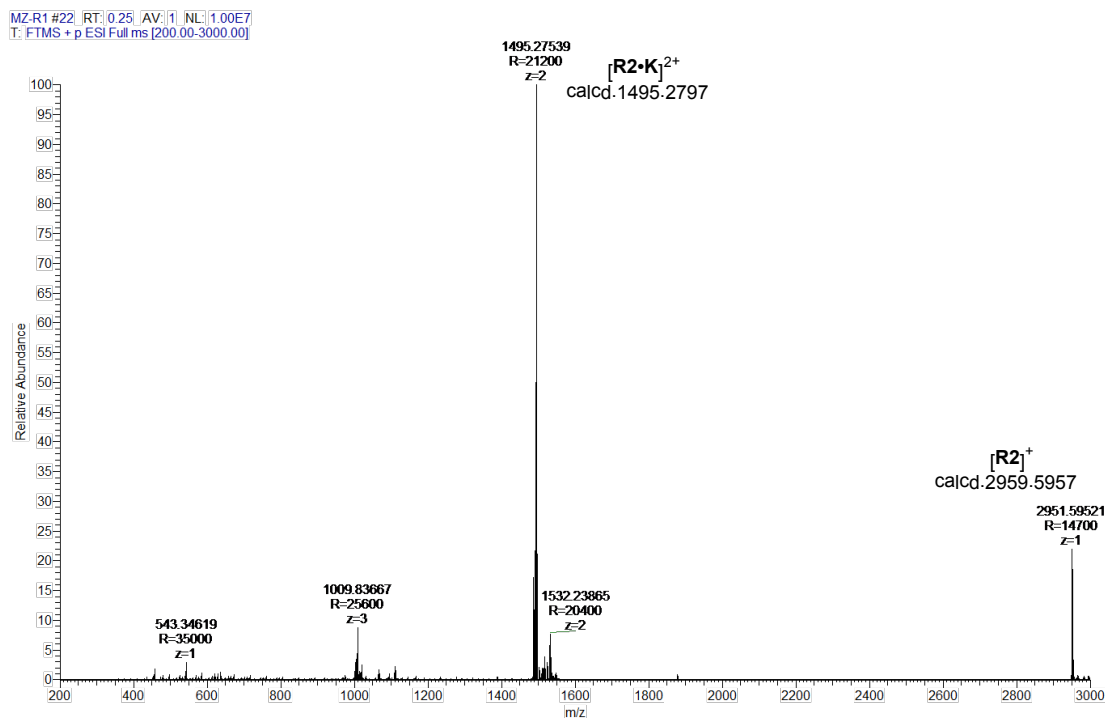


Fig. S16. HRMS spectrum of [2]rotaxane [R2][PF₆].

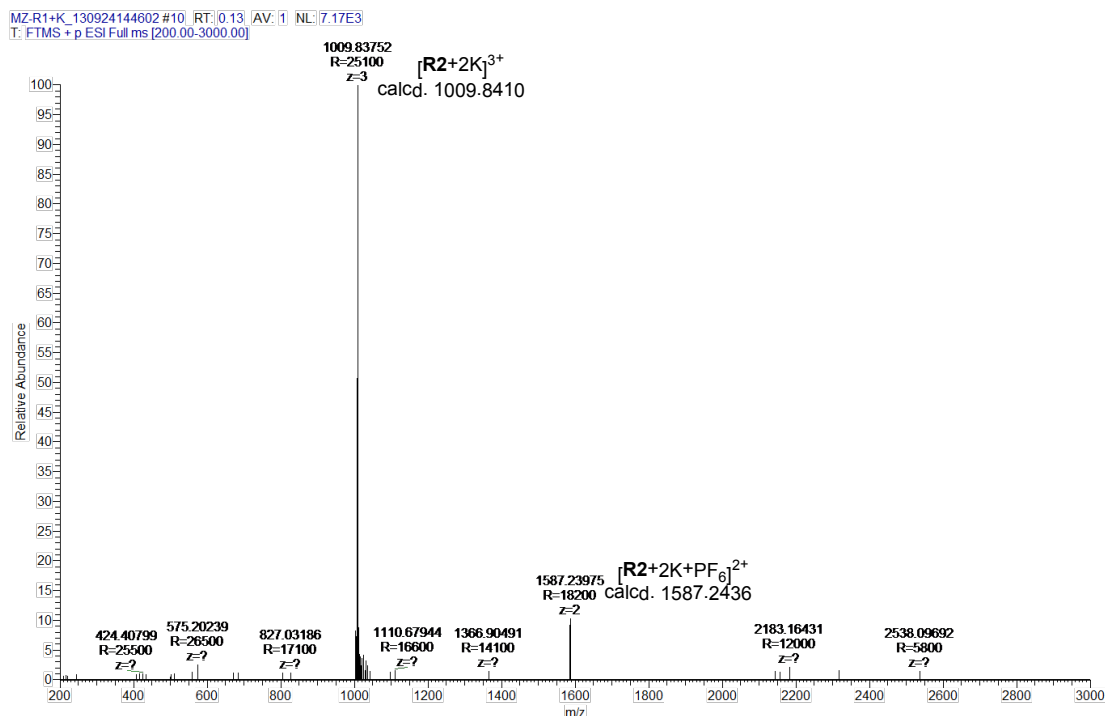


Fig. S17. HRMS spectrum of [2]rotaxane [R2][PF₆] after 6 equivalents of KPF₆ were added.

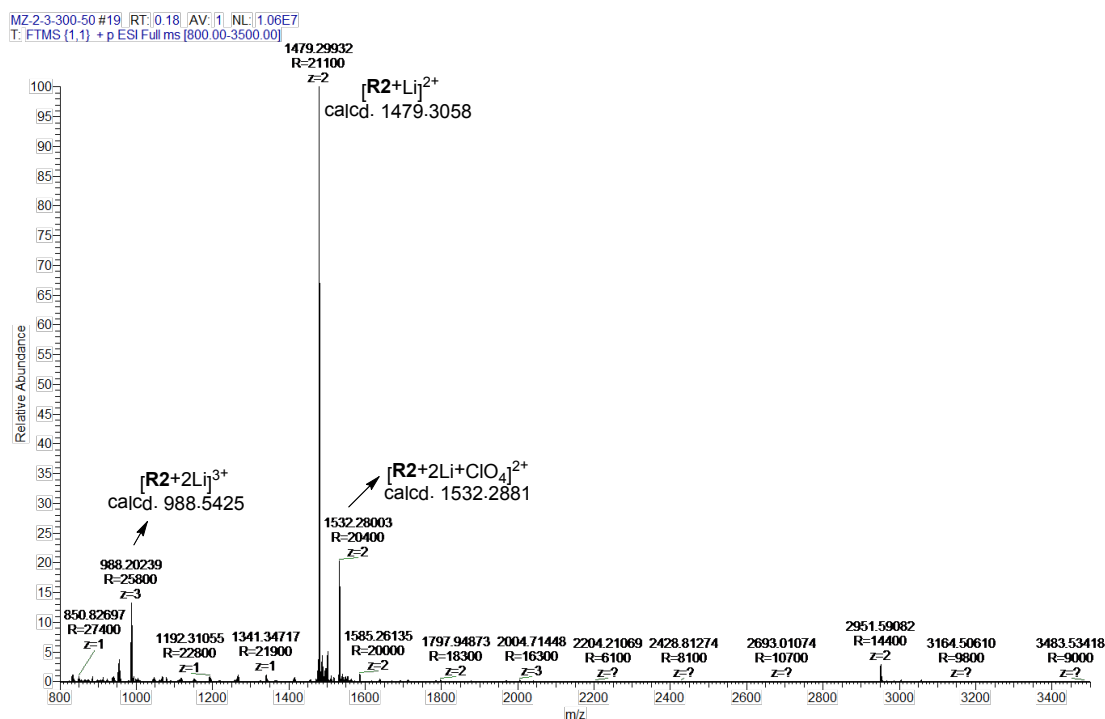


Fig. S18. HRMS spectrum of [2]rotaxane [R2][PF₆] after 6 equivalents of LiClO₄ were added.

6. UV-Vis and thin-layer chromatography experiments

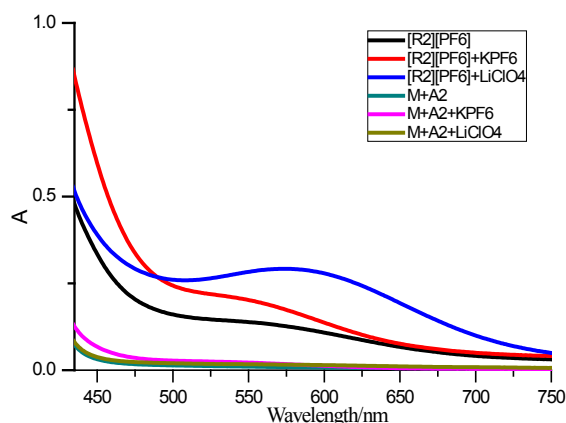


Fig. S19. The three stable states of [2]rotaxane shuttle as monitored by UV-Vis spectroscopy. ($c=0.50$ mM, CHCl₃/CH₃CN=1:1 (v/v), $\lambda=1.0$ cm, 298 K).

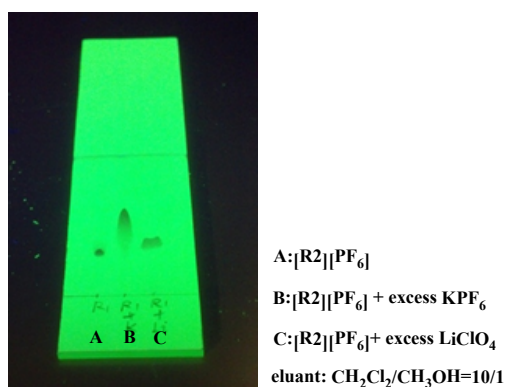


Fig. S20. Thin-layer chromatography of three stable states of the [2]rotaxane [R2][PF₆].

7. ^1H NMR for the shuttling process of the [2]rotaxane

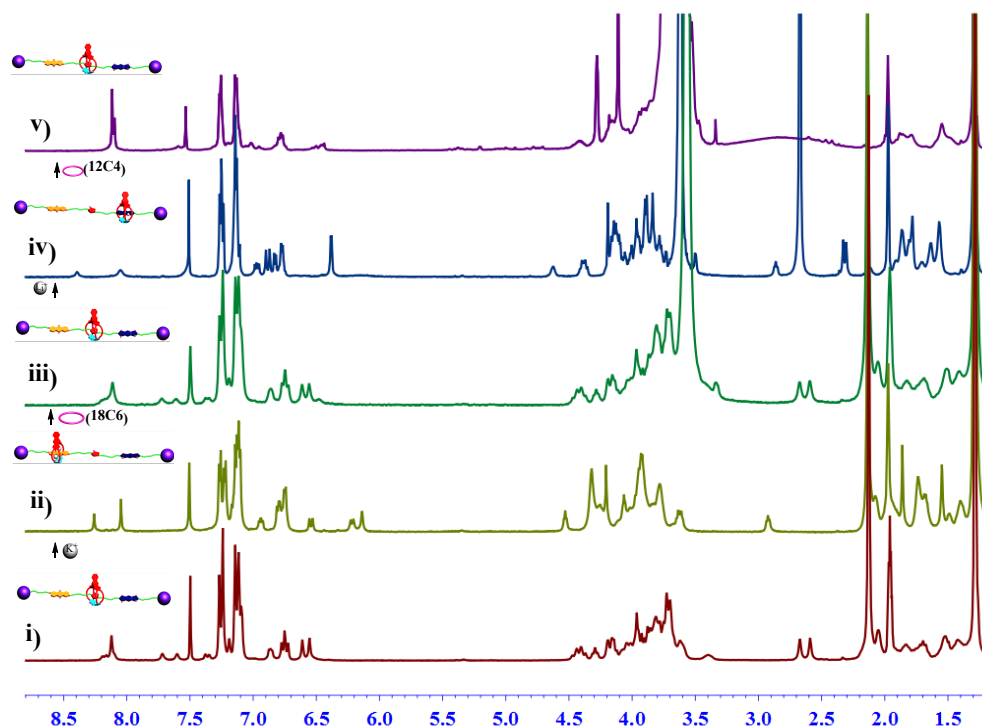


Fig. S21. The shuttling movement of the macrocycle **M** in the [2]rotaxane controlled by chemical stimuli. ^1H NMR spectra (600 MHz, 298 K, $\text{CD}_3\text{CN}/\text{CDCl}_3=1:1$) of (i) $[\text{R2}][\text{PF}_6]$; (ii) the solution obtained after adding 4.0 equivalents of KPF_6 to $[\text{R2}][\text{PF}_6]$; (iii) the solution obtained after adding 6.0 equivalents of 18C6 to solution in (ii); (iv) the solution obtained after adding 3.0 equivalents of LiClO_4 to solution in (iii); (v) the solution obtained after adding excess to 12C4 to solution in (iv).

8. HRMS spectra for three states of [3]-, [4]rotaxanes

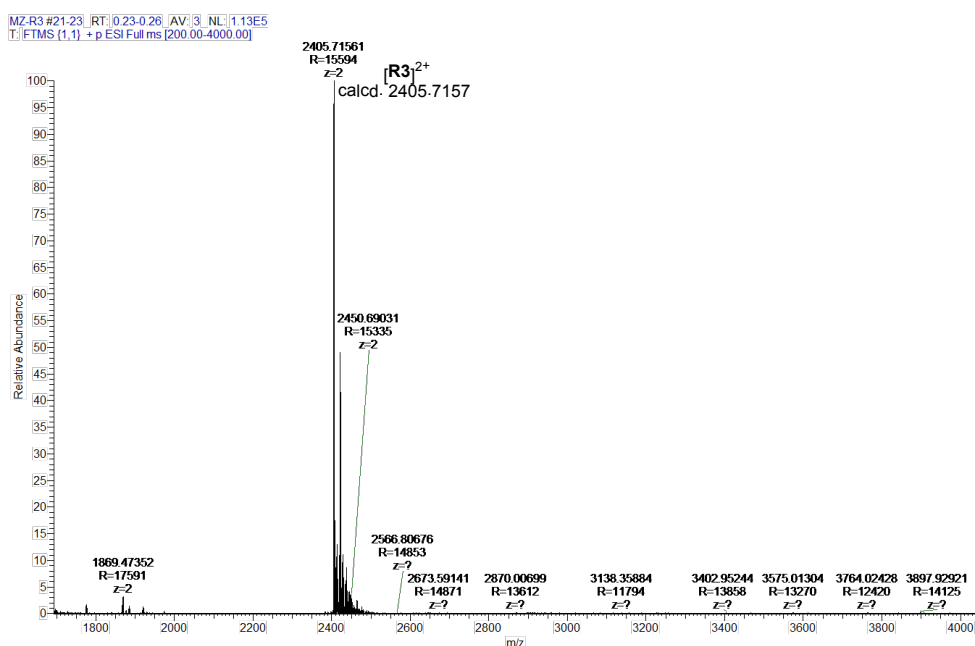


Fig. S22. HRMS spectrum of [3]rotaxane $[\text{R3}][2\text{PF}_6]$.

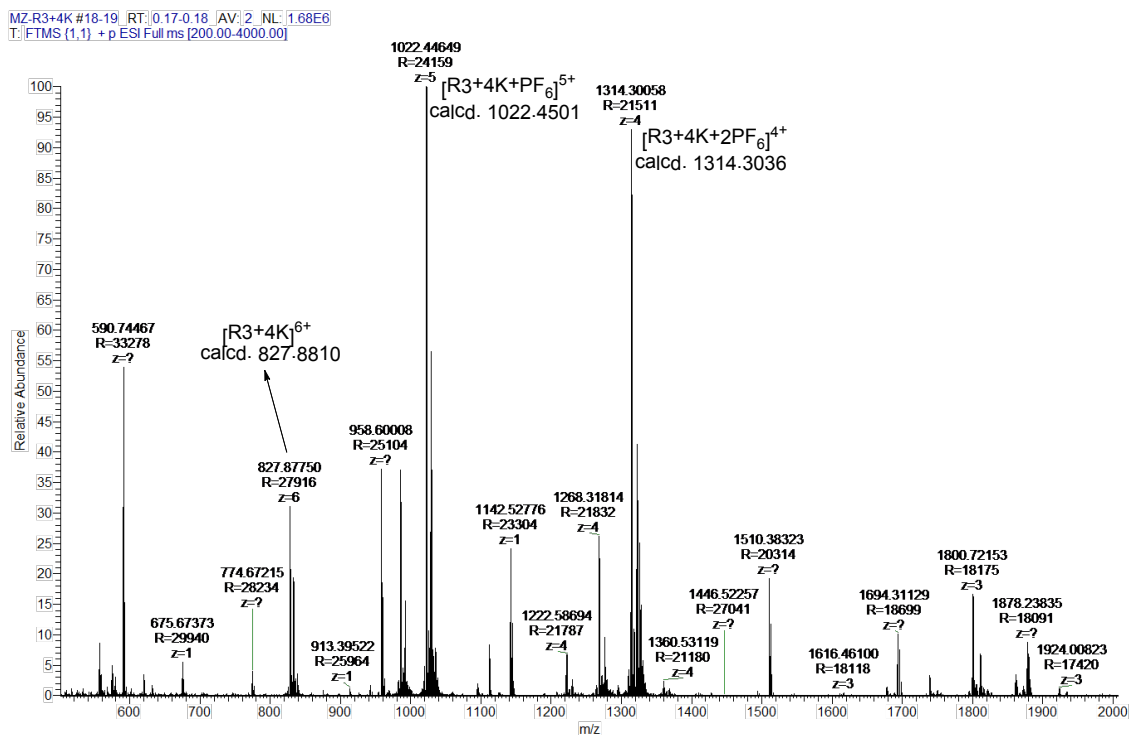


Fig. S23. HRMS spectrum of [3]rotaxane [R3][2PF₆] after 12 equivalents of KPF₆ were added.

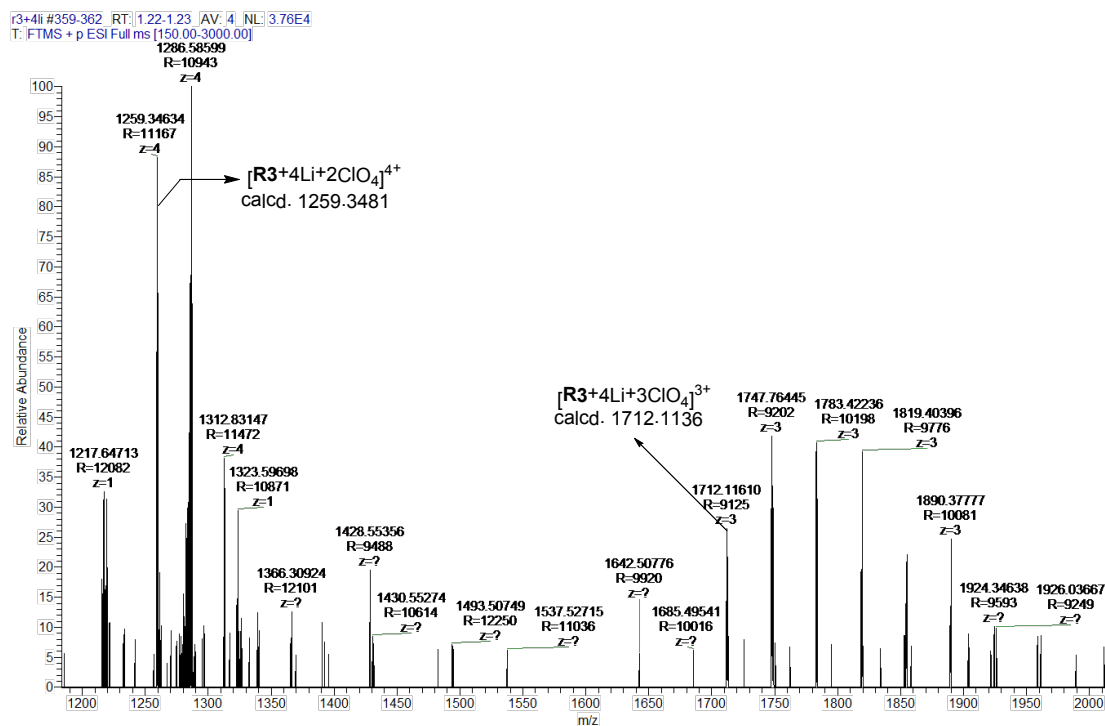


Fig. S24. HRMS spectrum of [3]rotaxane [R3][2PF₆] after 12 equivalents of LiClO₄ were added.

MZ-R4-01_130916143401 #10 RT: 0.13 AV: 1 NL: 1.99E6
T: FTMS + p ESI Full ms [200.00-4000.00]

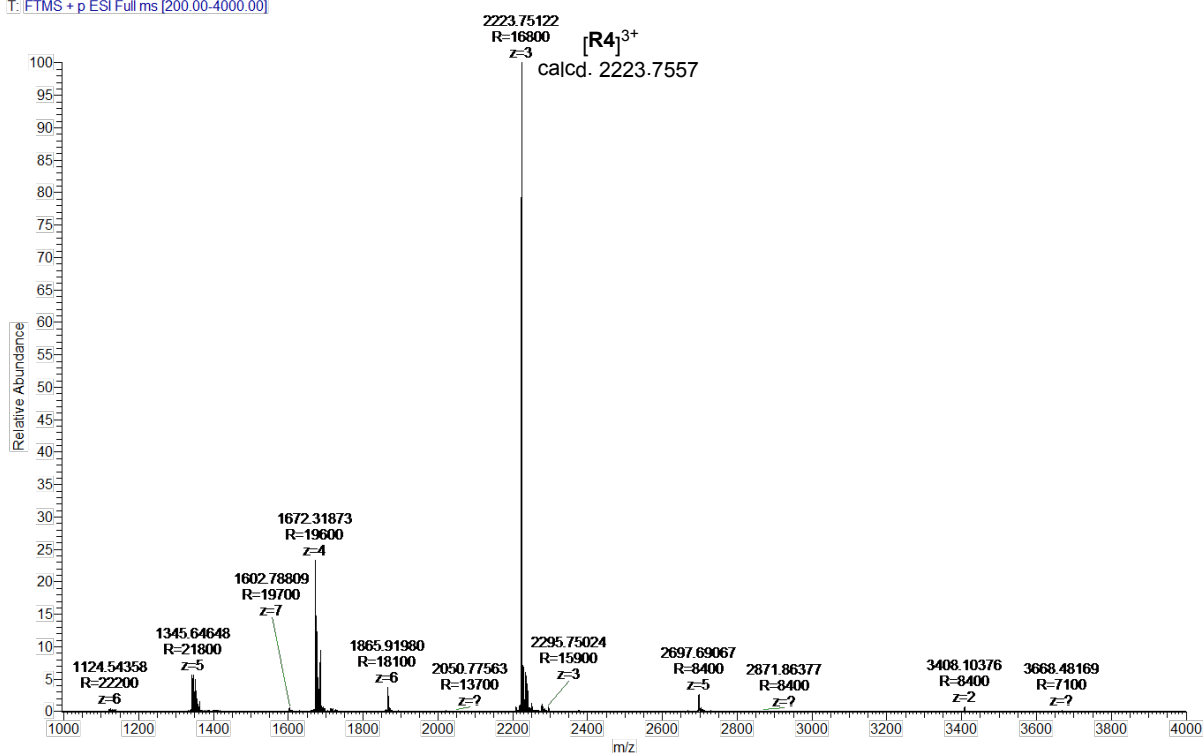


Fig. S25. HRMS spectrum of [4]rotaxane [R4][3PF₆].

MZ-R4-02 #11-12 RT: 0.09-0.10 AV: 2 NL: 8.93E5
T: FTMS + p ESI Full ms [200.00-4000.00]

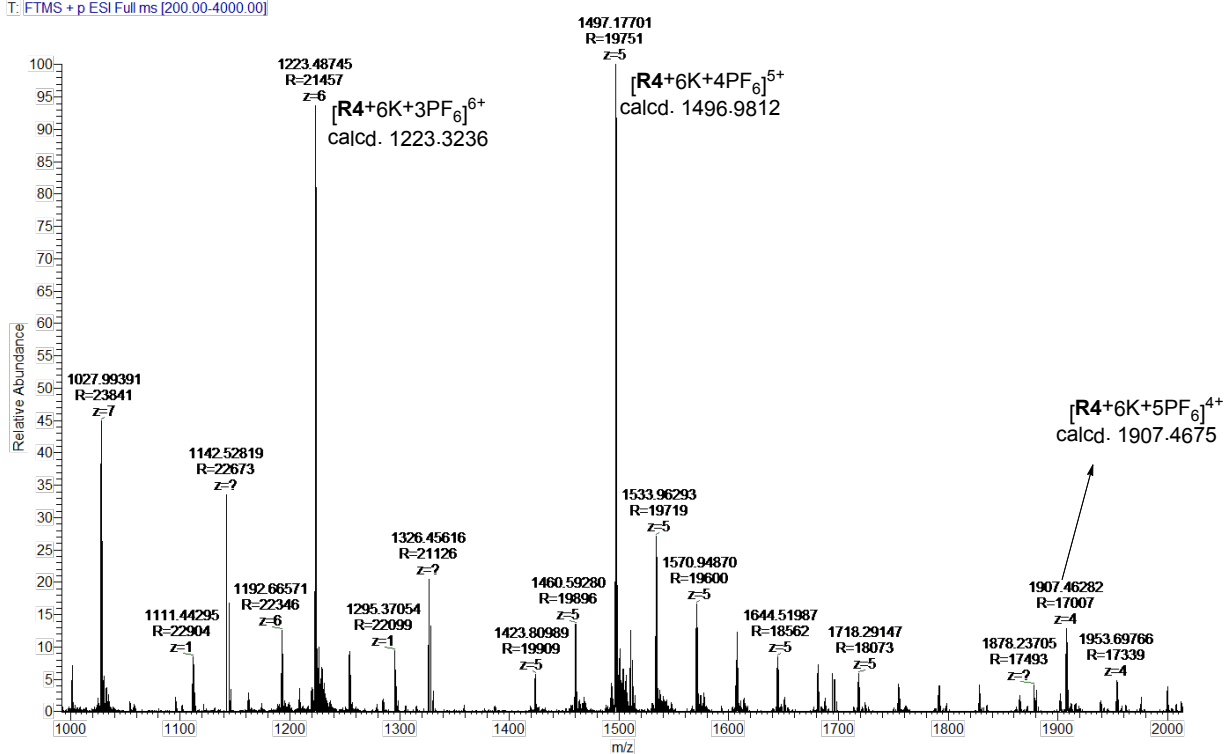


Fig. S26. HRMS spectrum of [4]rotaxane [R4][3PF₆] after 18 equivalents of KPF₆ were added.

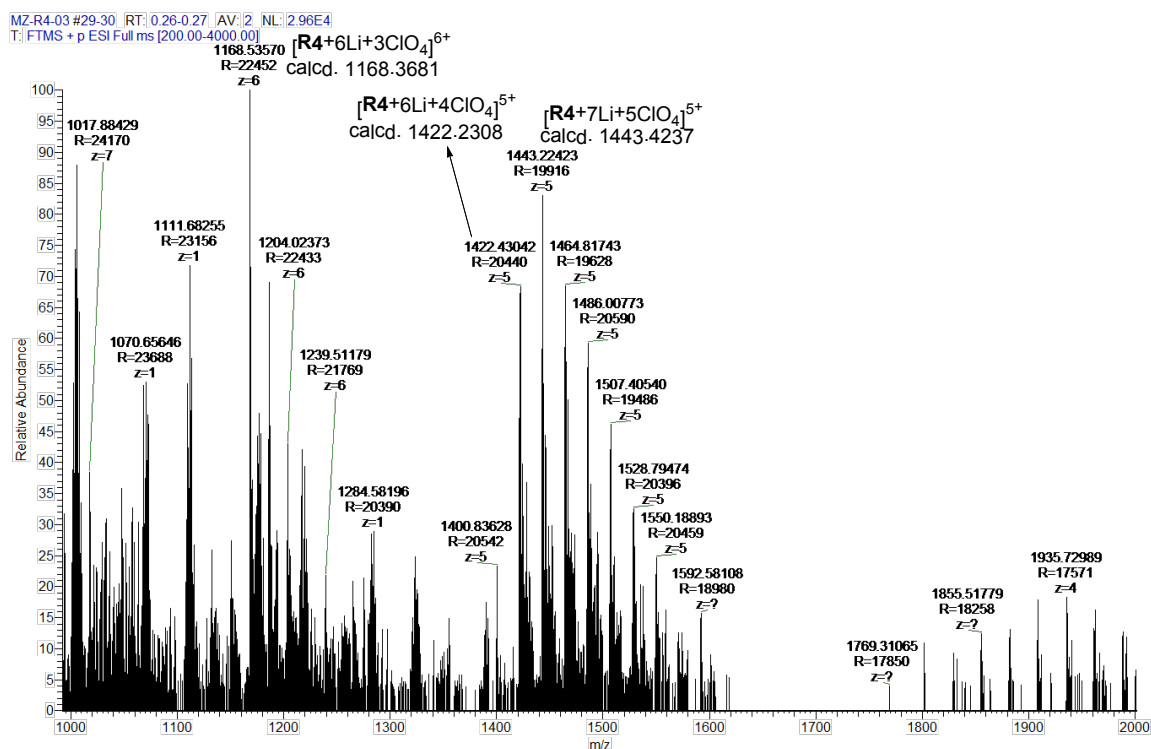


Fig. S27. HRMS spectrum of [4]rotaxane [R4][3PF₆] after 18 equivalents of LiClO₄ were added.

9. ¹H NMR spectra for the shuttling process of [3], [4]rotaxanes

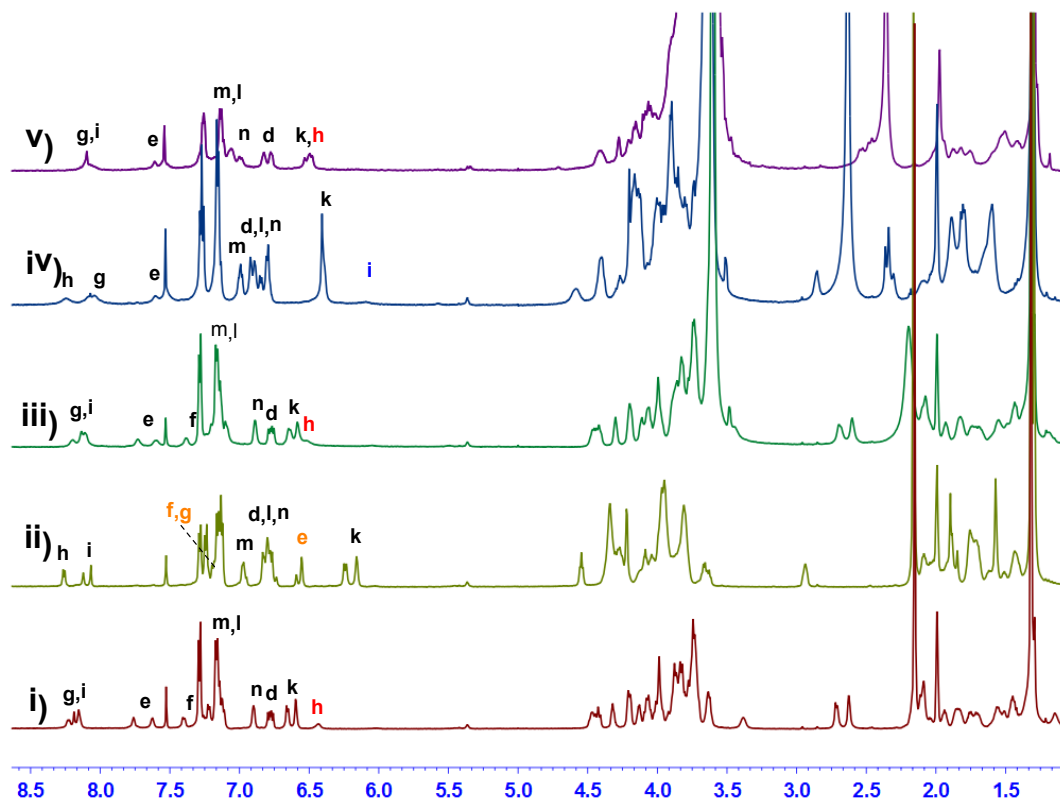


Fig. S28. The shuttling movement of the two macrocycles (**M**) in the [3]rotaxane by chemical stimuli. ¹H NMR spectra (600 MHz, 298 K, CD₃CN/CDCl₃=1:1) of (i) [R3][2PF₆]; (ii) the solution obtained after adding 8.0 equivalents of KPF₆ to [R3][2PF₆]; (iii) the solution obtained after adding 12.0 equivalents of 18C6 to solution in (ii); (iv) the solution obtained after adding 6.0 equivalents of LiClO₄ to solution in (iii); (v) the solution obtained after adding excess to 12C4 to solution in (iv).

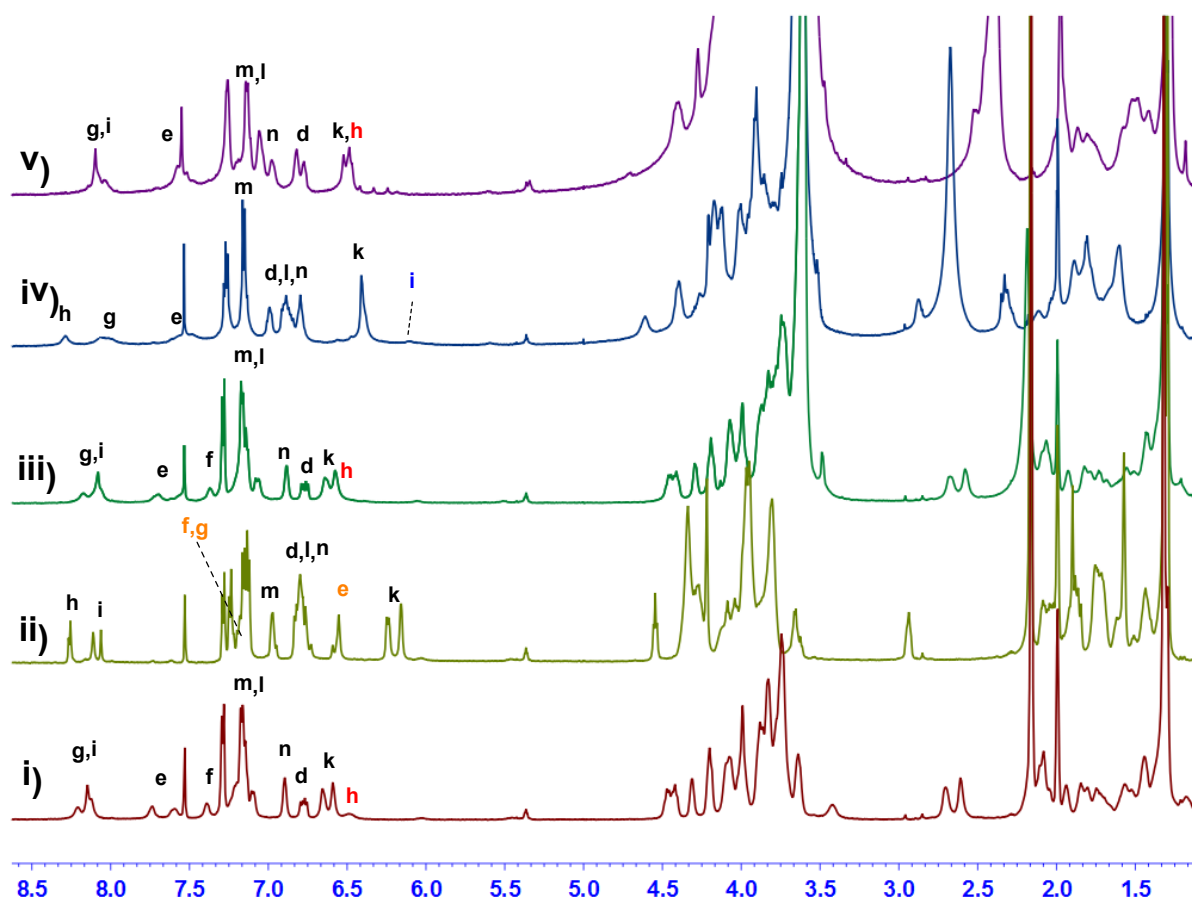


Fig. S29. The shuttling movement of the three macrocycles (**M**) in the [4]rotaxane controlled by chemical stimuli. ^1H NMR spectra (600 MHz, 298 K, $\text{CD}_3\text{CN}/\text{CDCl}_3=1:1$) of (i) $[\mathbf{R4}][3\text{PF}_6]$; (ii) the solution obtained after adding 12.0 equivalents of KPF_6 to $[\mathbf{R4}][3\text{PF}_6]$; (iii) the solution obtained after adding 18.0 equivalents of 18C6 to solution in (ii); (iv) the solution obtained after adding 9.0 equivalents of LiClO_4 to solution in (iii); (v) the solution obtained after adding excess 12C4 to solution in (iv).

10. NMR spectra for other new compounds

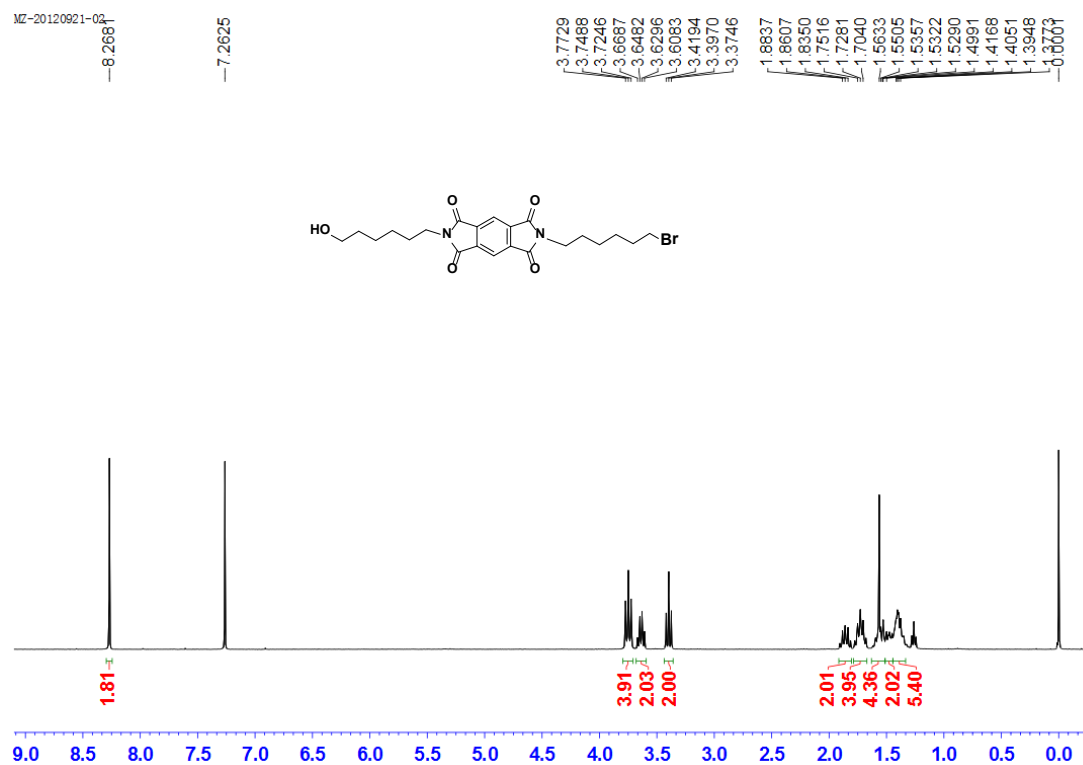


Fig. S30. ¹H NMR spectrum (CDCl₃, 300 MHz, 298 K) of 2.

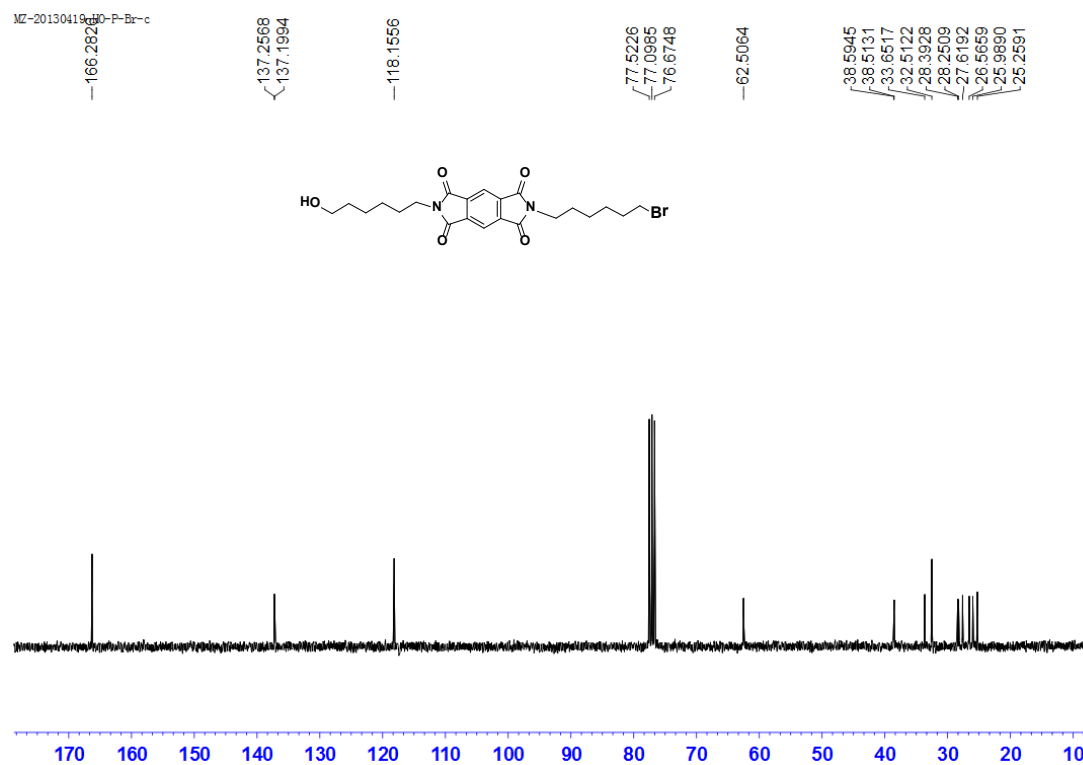


Fig. S31. ¹³C NMR spectrum (CDCl₃, 75 MHz, 298 K) of 2.

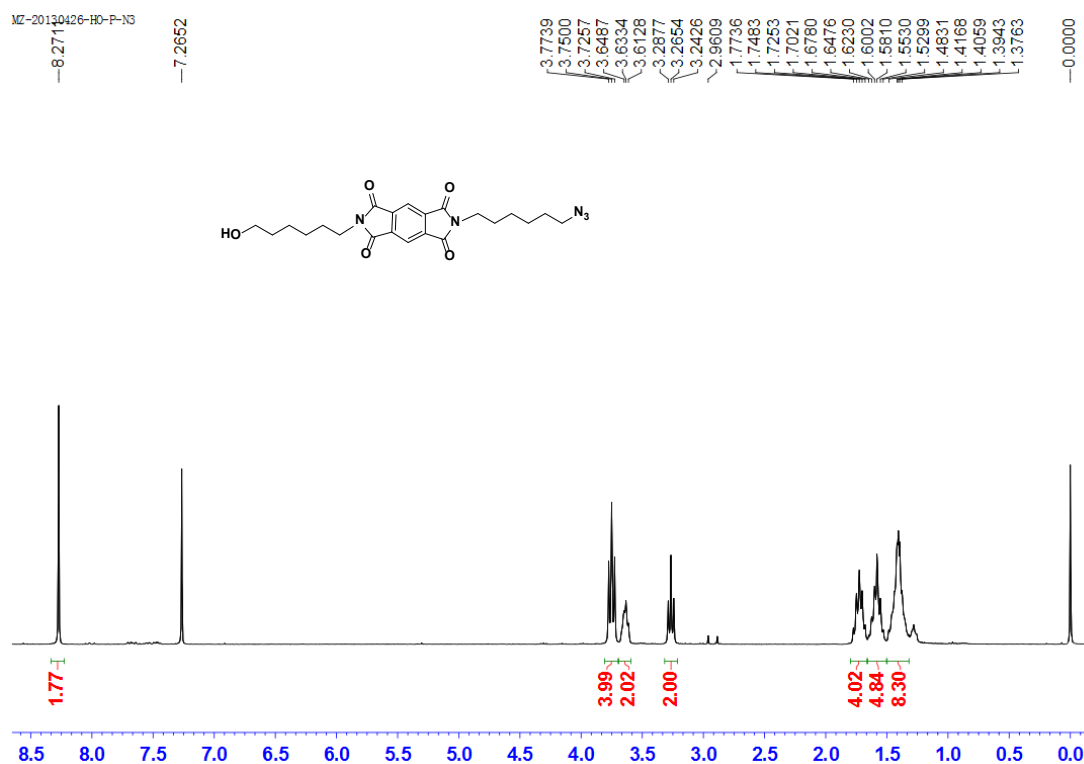


Fig. S32. ¹H NMR spectrum (CDCl₃, 300 MHz, 298 K) of **3**.

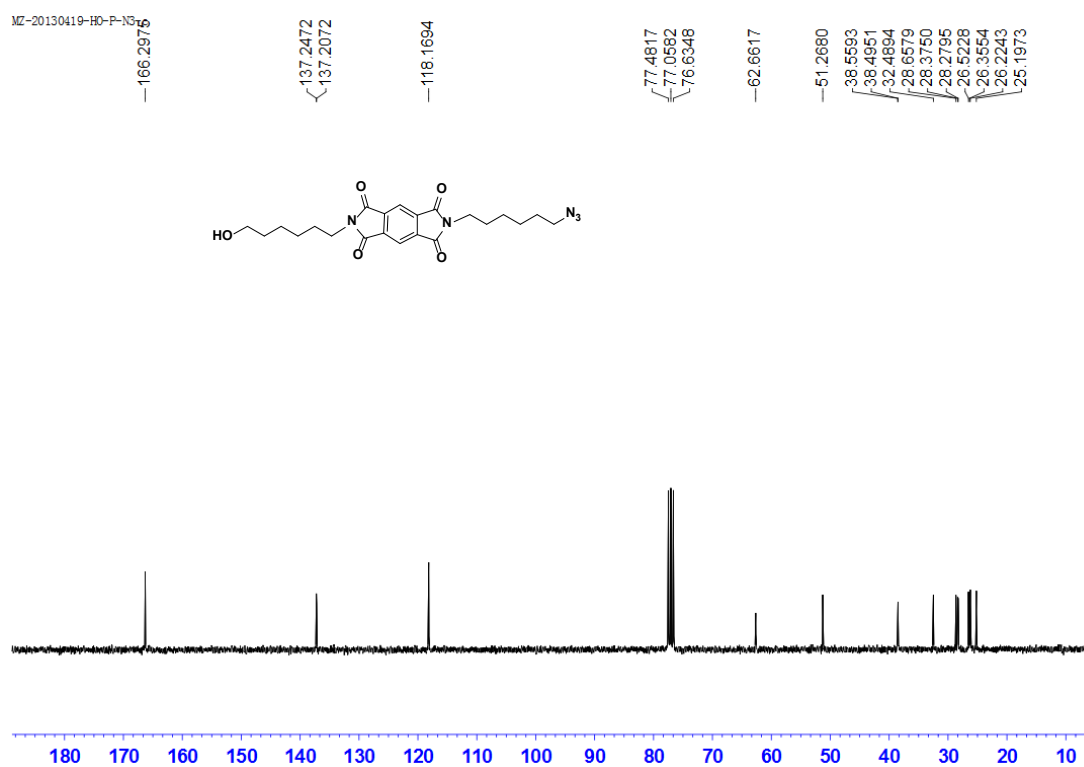


Fig. S33. ¹³C NMR spectrum (CDCl₃, 75 MHz, 298 K) of **3**.

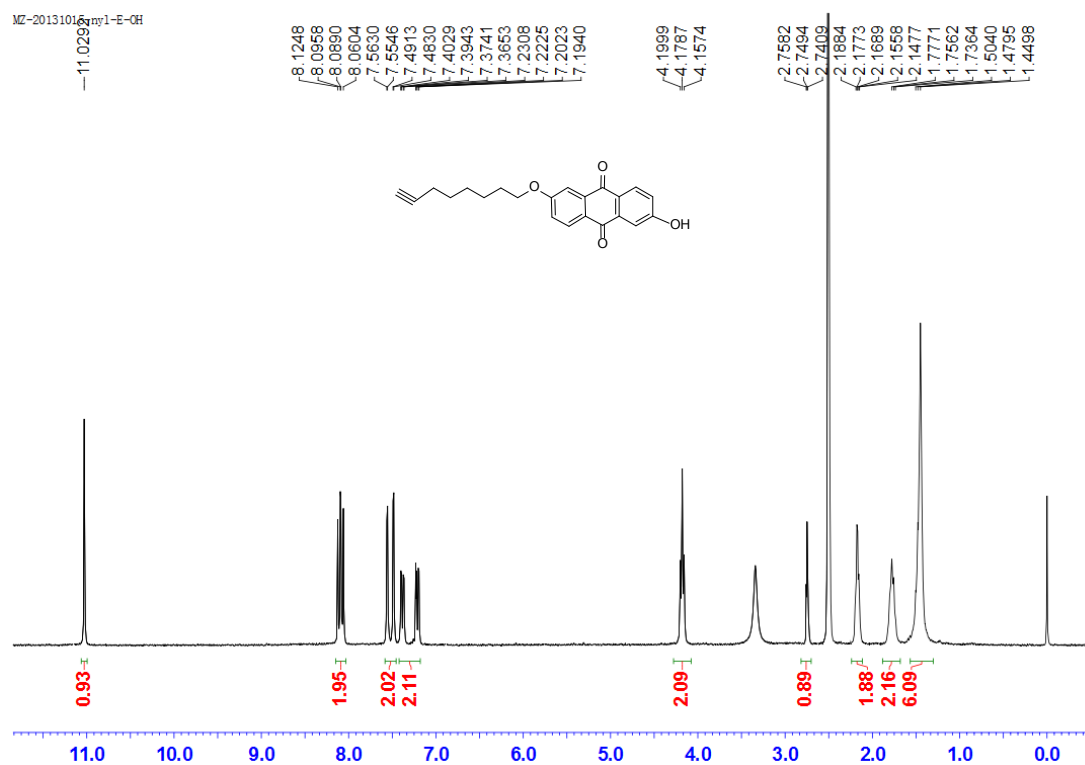


Fig. S34. ¹H NMR spectrum (DMSO-*d*₆, 300 MHz, 298 K) of 7.

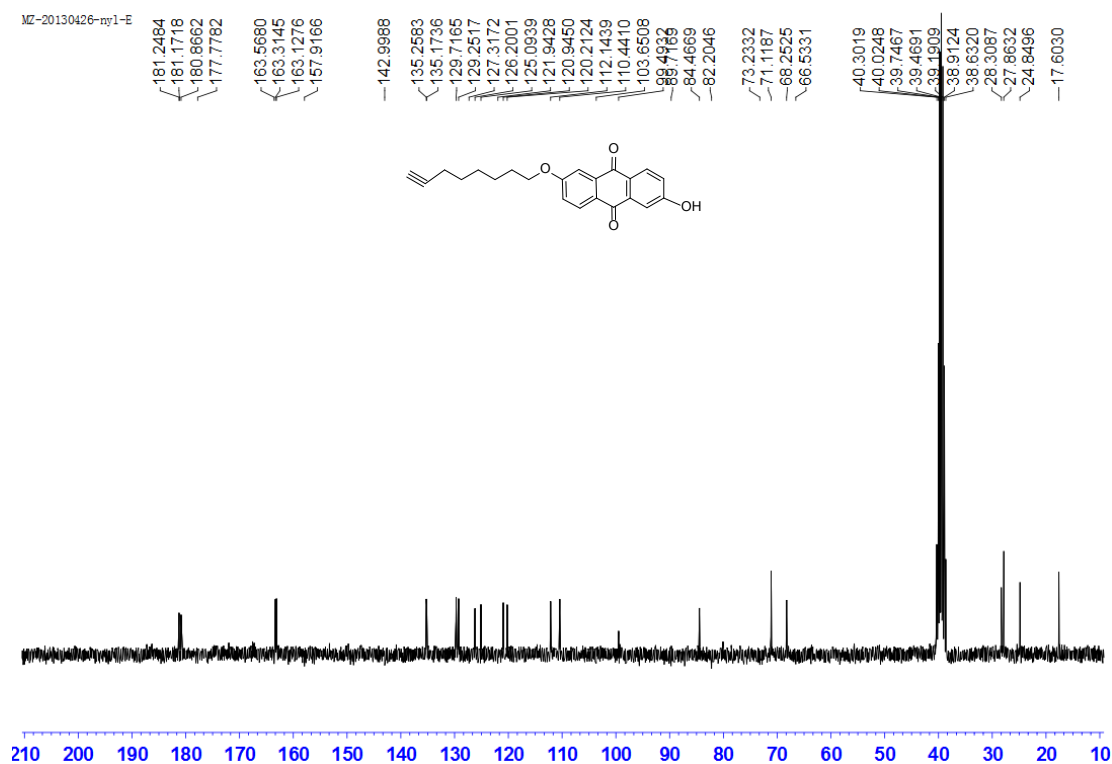


Fig. S35. ¹³C NMR spectrum (DMSO-*d*₆, 75 MHz, 298 K) of 7.

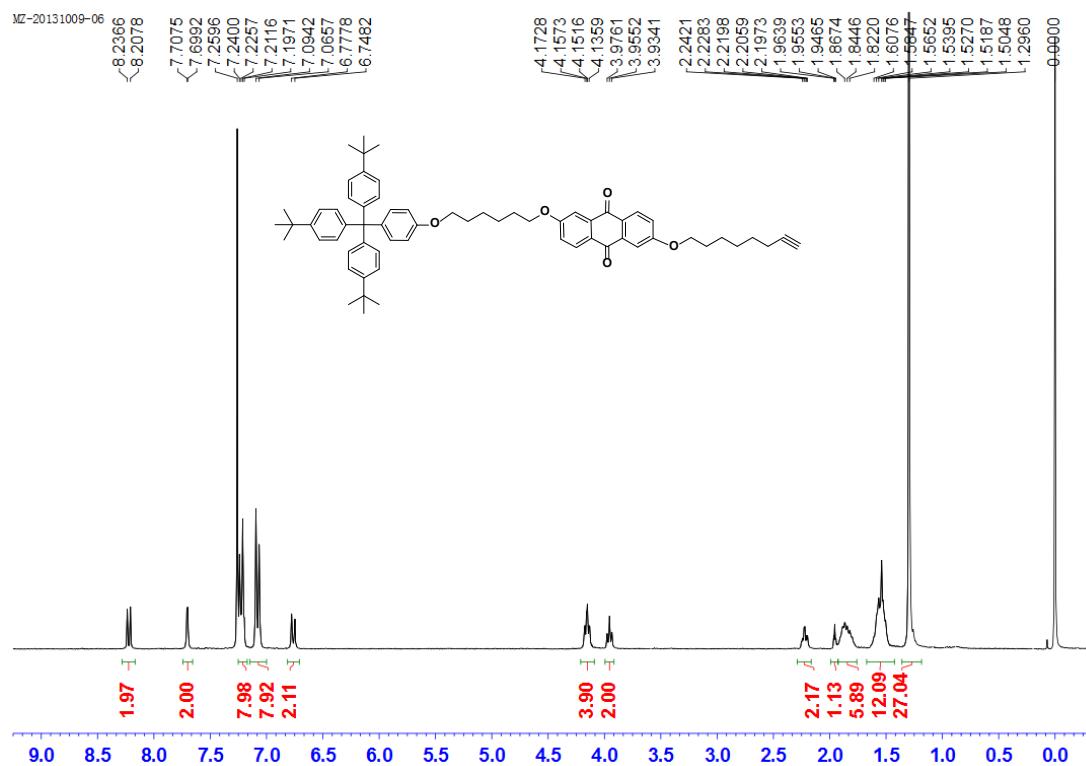


Fig. S36. ^1H NMR spectrum (CDCl_3 , 300 MHz, 298 K) of S1.

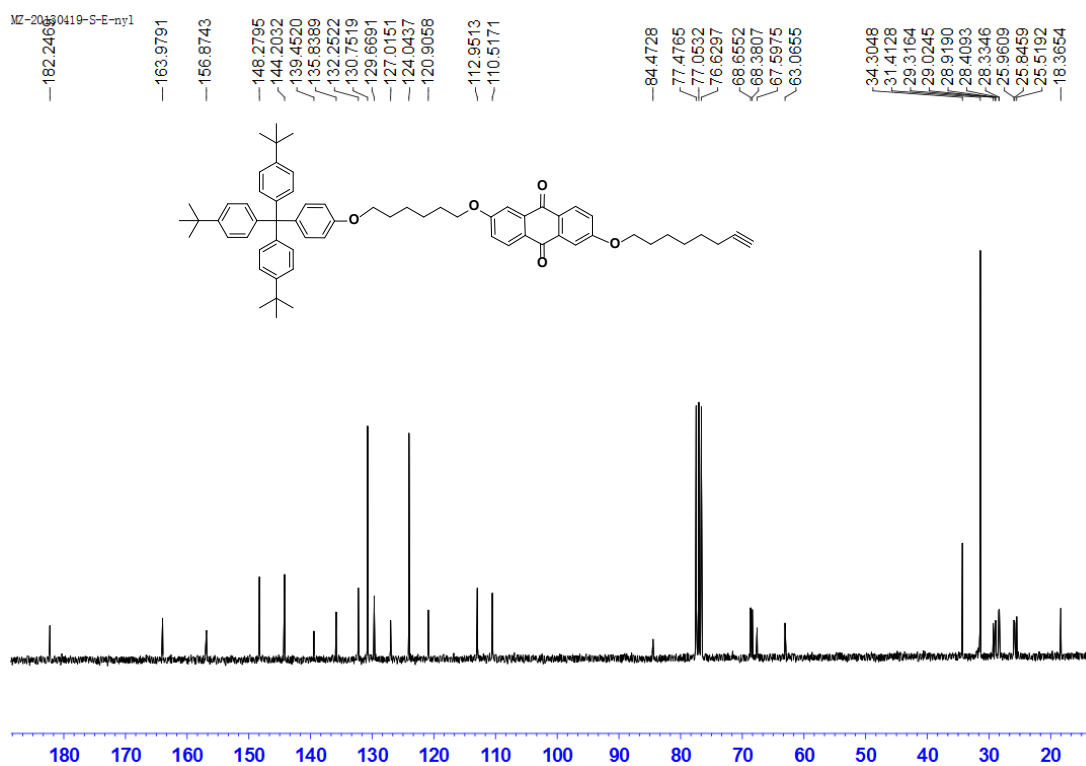


Fig. S37. ^{13}C NMR spectrum (CDCl_3 , 75 MHz, 298 K) of S1.

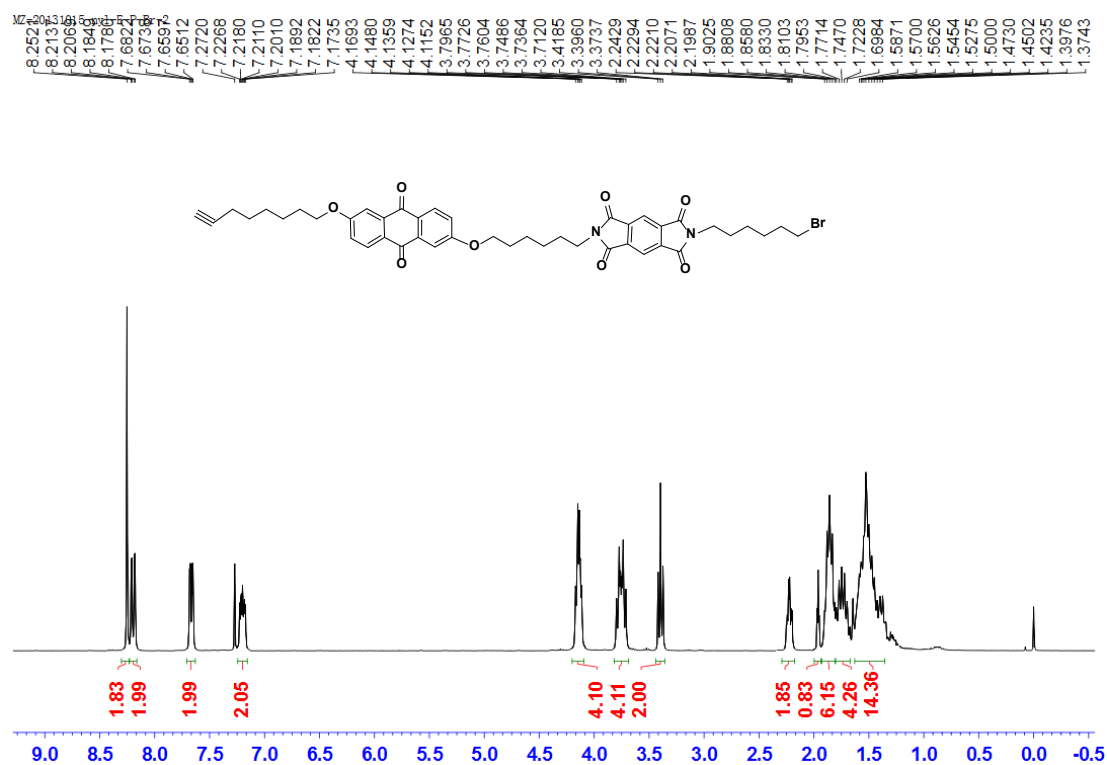


Fig. S38. ¹H NMR spectrum (CDCl₃, 300 MHz, 298 K) of S0.

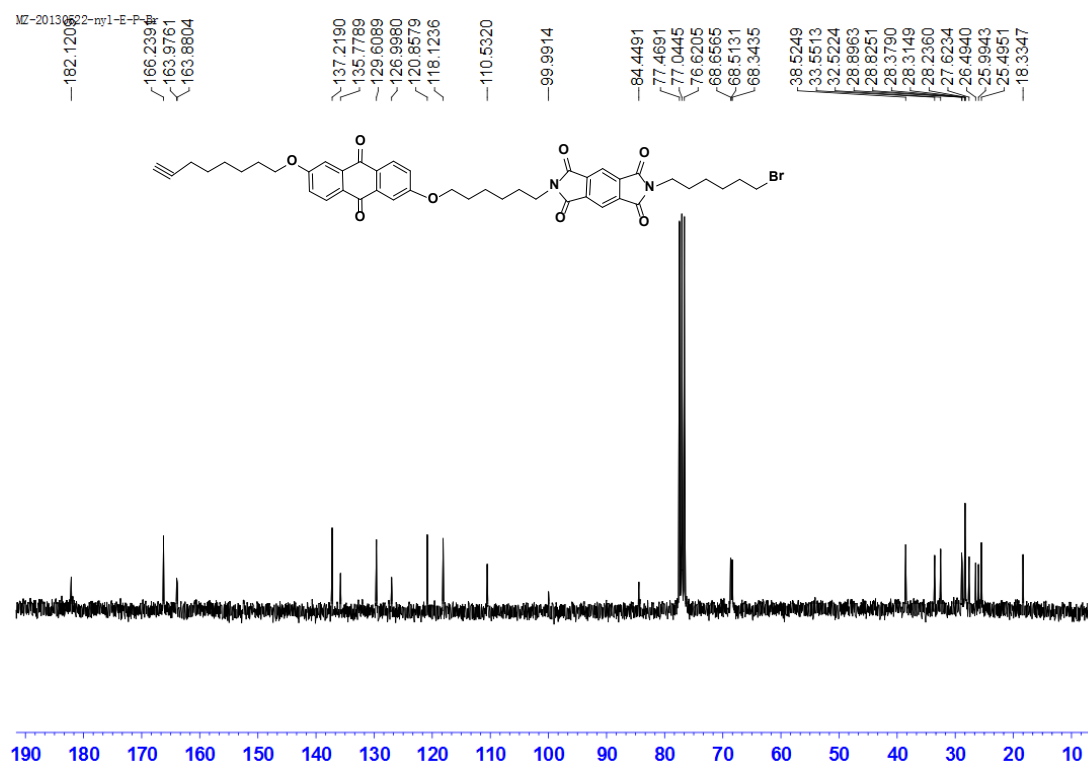


Fig. S39. ¹³C NMR spectrum (CDCl₃, 75 MHz, 298 K) of S0.

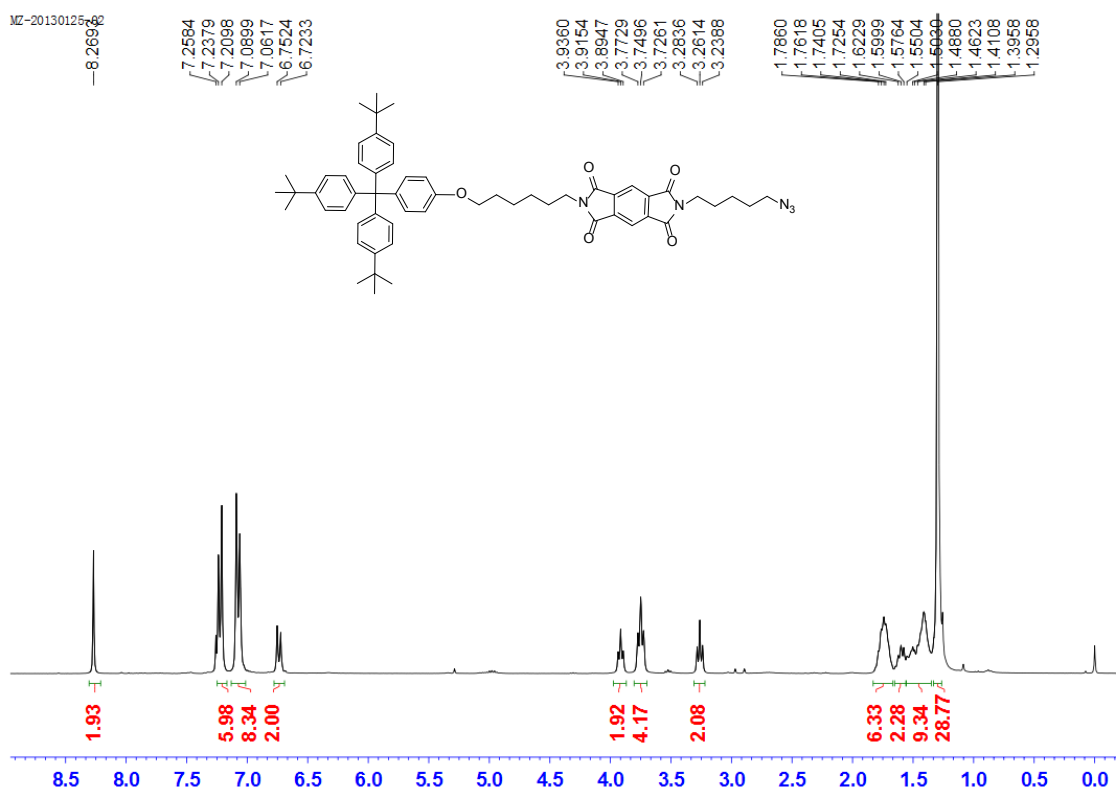


Fig. S40. ¹H NMR spectrum (CDCl₃, 300MHz, 298 K) of S2.

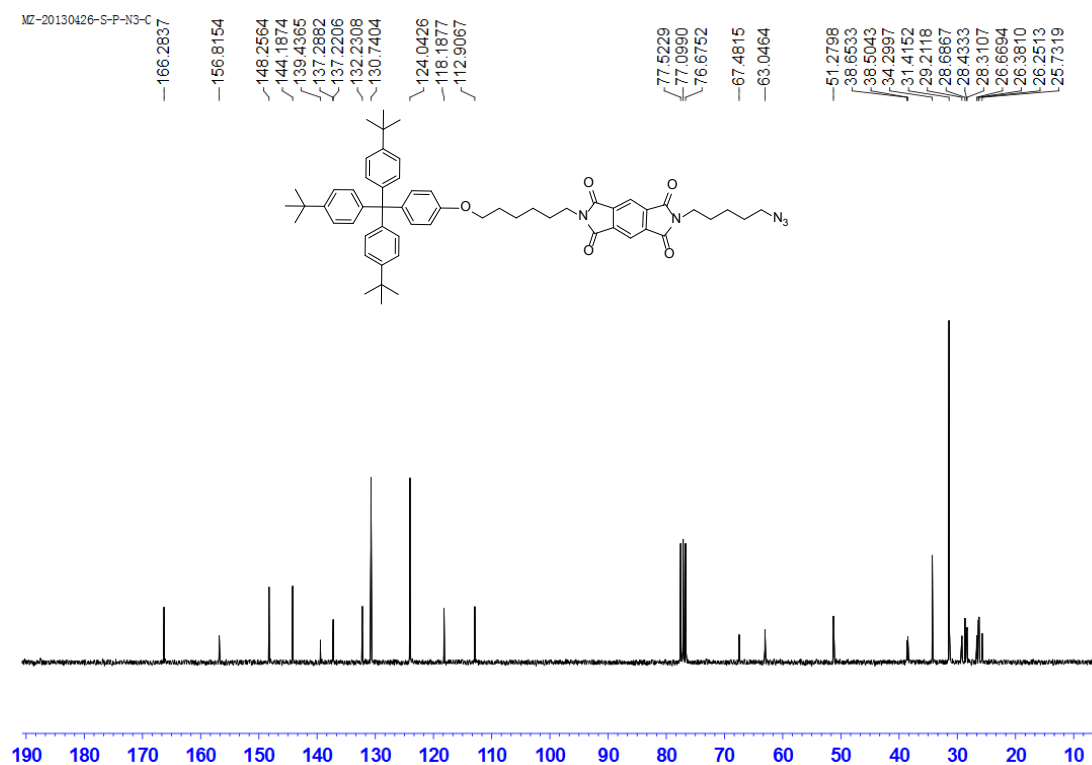


Fig. S41. ¹³C NMR spectrum (CDCl₃, 75 MHz, 298 K) of S2.

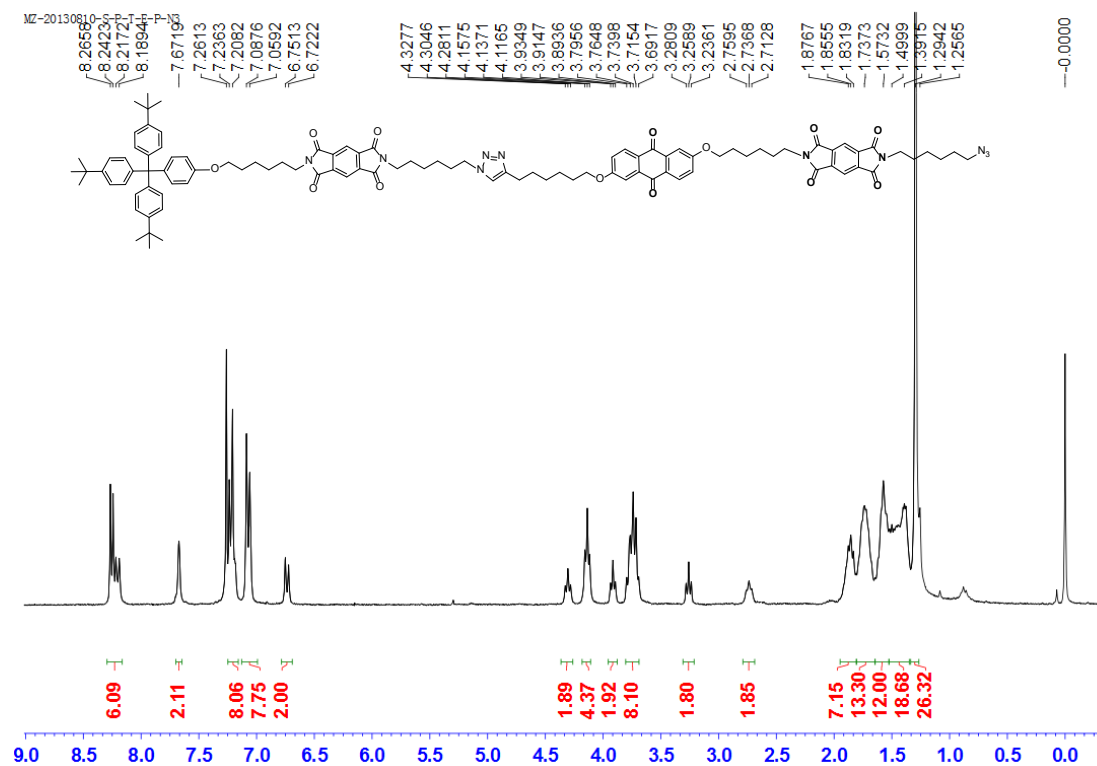


Fig. S42. ¹H NMR spectrum (CDCl₃, 300 MHz, 298 K) of S3.

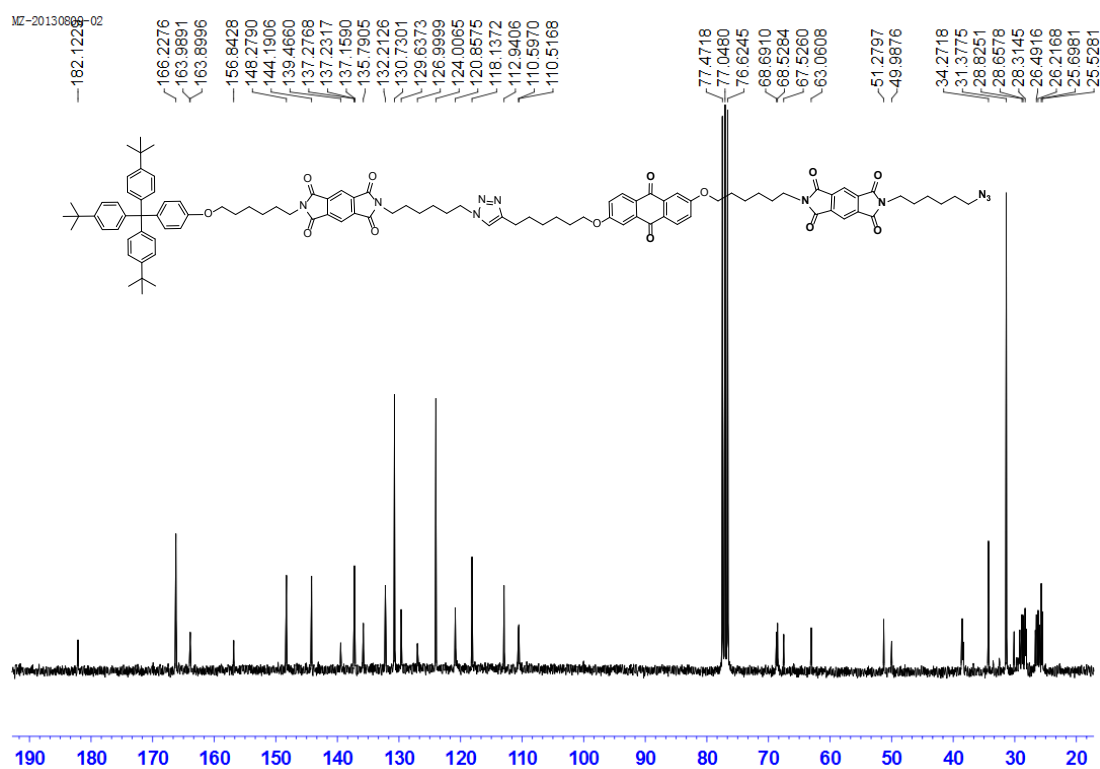


Fig. S43. ¹³C NMR spectrum (CDCl₃, 75 MHz, 298 K) of S3.

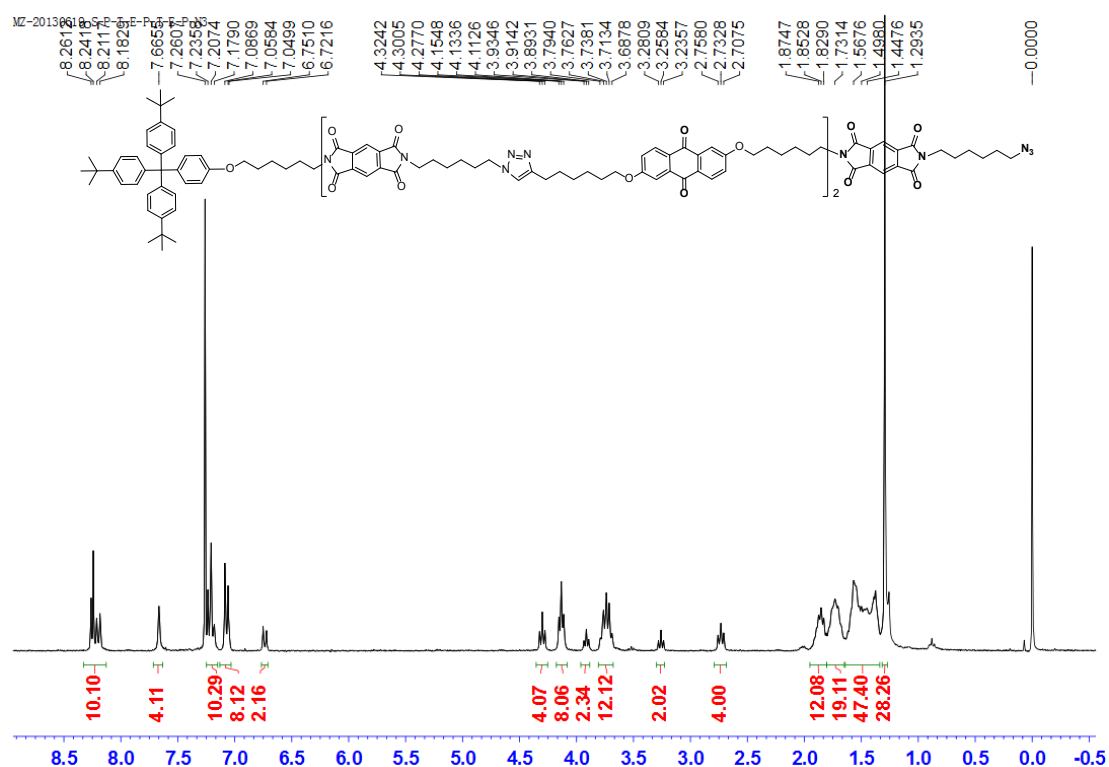


Fig. S44. ^1H NMR spectrum (CDCl_3 , 300 MHz, 298 K) of **S3**.

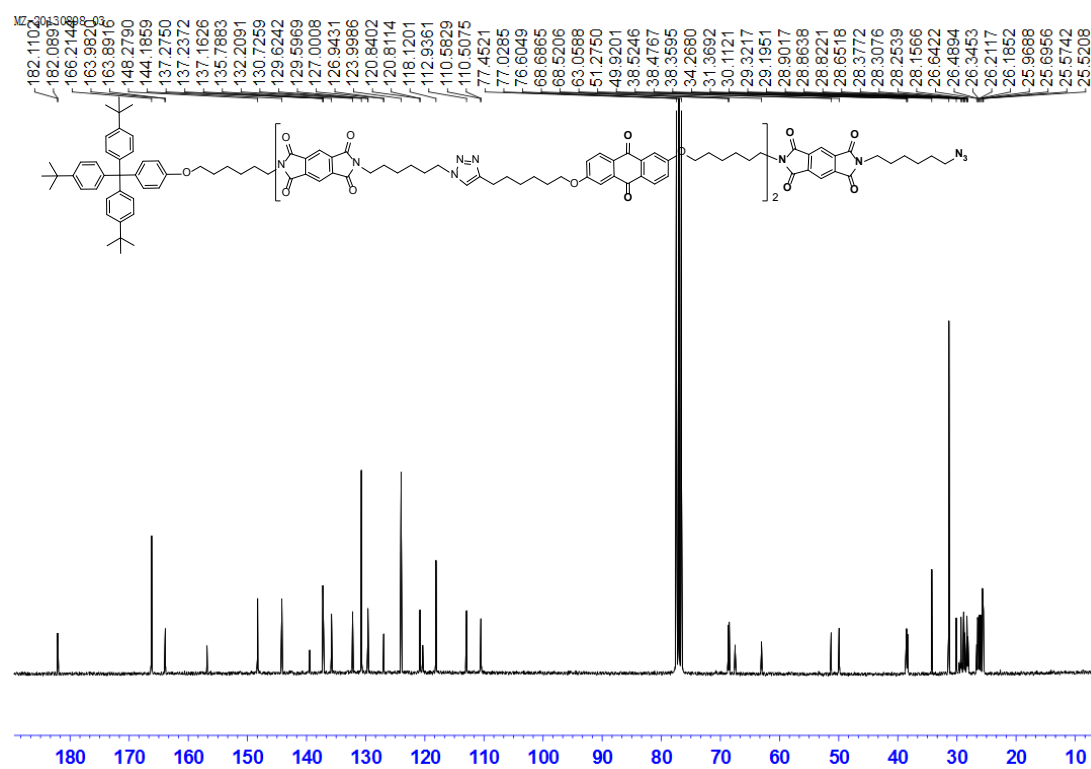
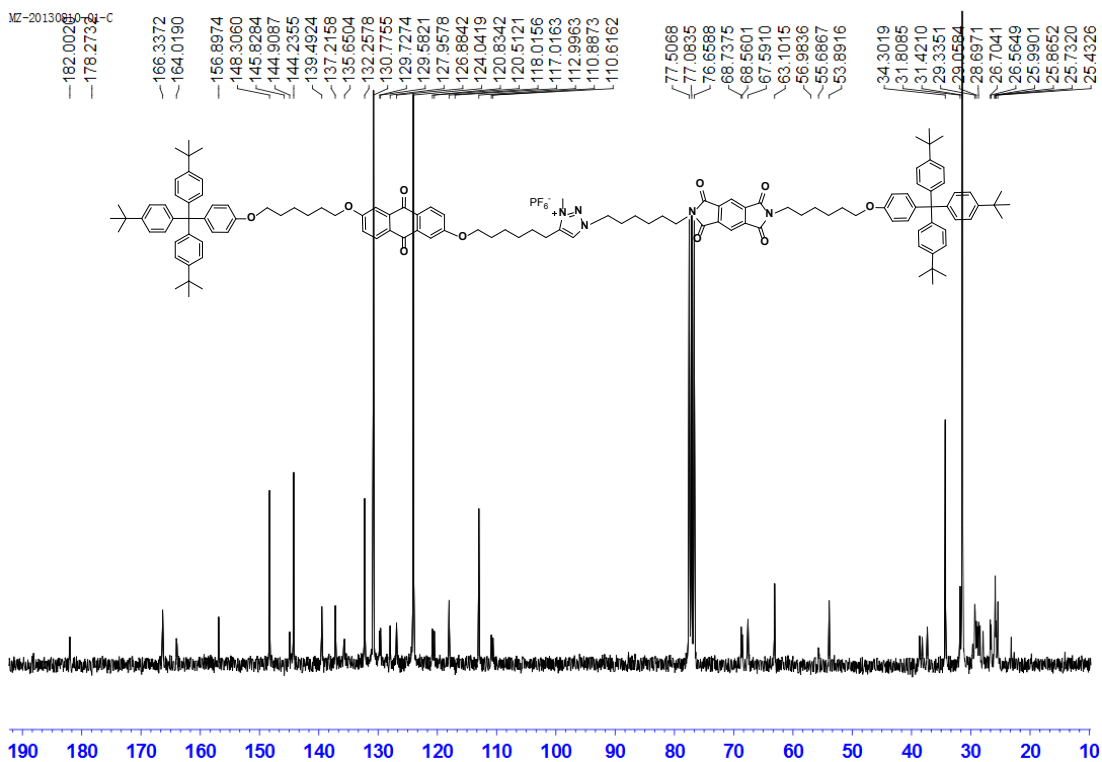


Fig. S45. ^{13}C NMR spectrum (CDCl_3 , 75 MHz, 298 K) of **S4**.



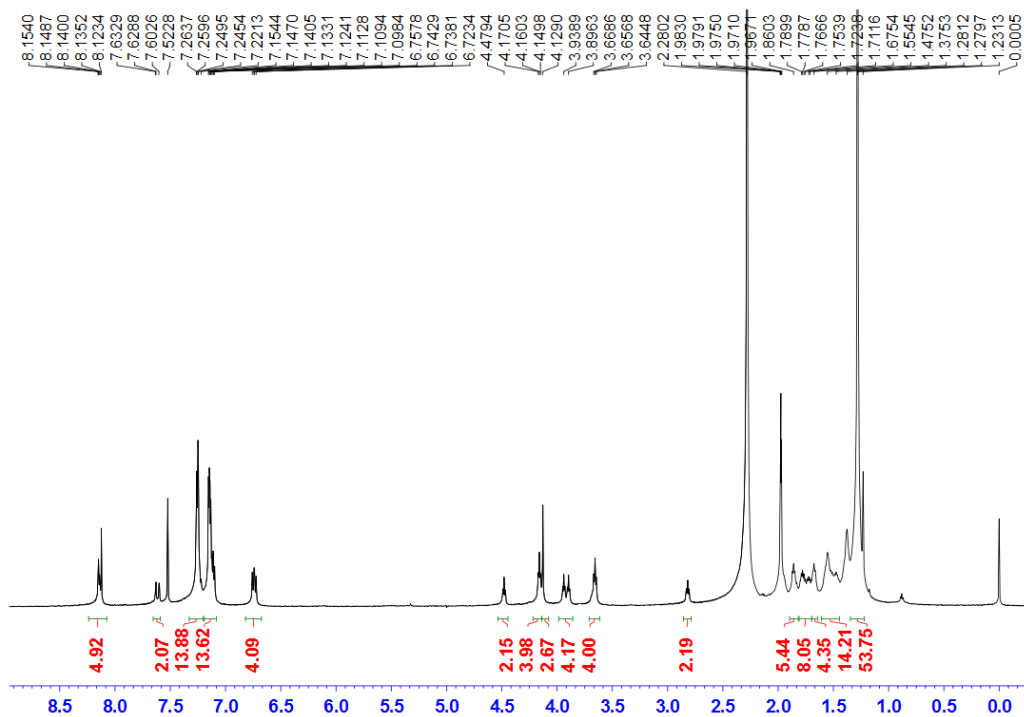


Fig. S48. ¹H NMR spectrum (CDCl₃:CD₃CN=1:1, 600 MHz, 298 K) of **A2**.

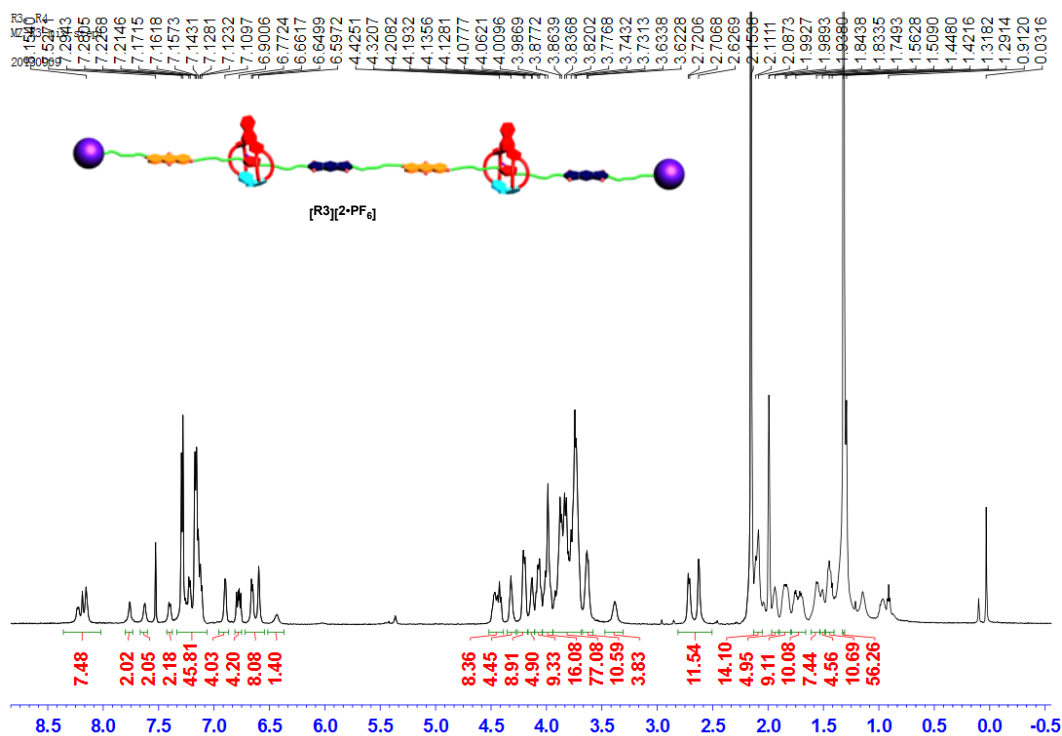


Fig. S49. ¹H NMR spectrum (CDCl₃/CD₃CN=1:1, 600 MHz, 298 K) of [3]rotaxane [**R3**][2PF₆].

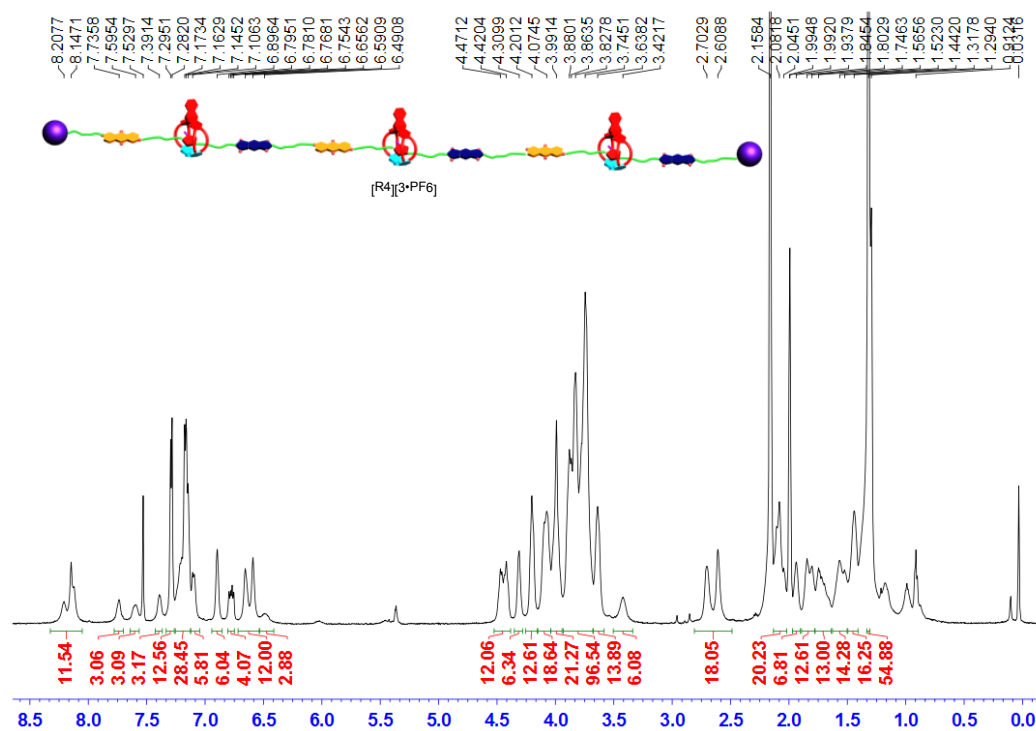


Fig. S50. ^1H NMR spectrum ($\text{CDCl}_3/\text{CD}_3\text{CN}=1:1$, 600 MHz, 298 K) of [4]rotaxane [R4][3PF₆].

11. References

1. S. De, S. Ramakrishnan, *Macromolecules*, 2009, **42**, 8599-8603.
2. L. M. Klivansky, G. Koshkakaryan, D. Cao, Y. Liu, *Angew. Chem., Int. Ed.*, 2009, **48**, 4185-4189.
3. H. W. Gibson, S. H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bheda, *J. Org. Chem.*, 1993, **58**, 3748-3756.
4. F. Havas, N. Leygue, M. Danel, B. Mestre, C. Galaup, C. Picard, *Tetrahedron*, 2009, **65**, 7673-7686.