

## Supporting Information

### Diversiform Nanostructures Constructed from Tetraphenylethene and Pyrene-based Acid-Base Controllable Molecular Switching Amphiphilic [2]Rotaxanes with Tunable Aggregation-Induced Static Excimers

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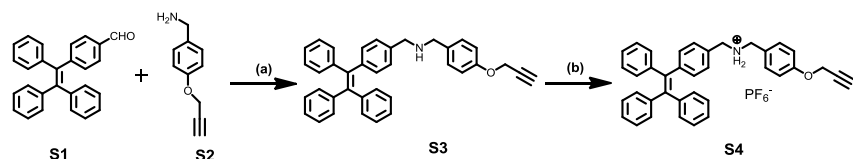
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## Synthesis overview and protocols

### Synthesis of S4

Compound **S4** was synthesized according to the reported procedures.<sup>S1</sup>

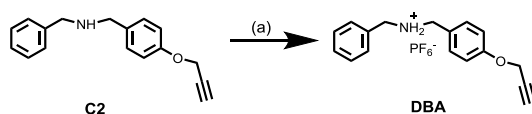


**Scheme S1:** Synthesis of **S4** with reagents and conditions: (a) MeOH, NaBH<sub>4</sub>, 0°C, 24 h, 63%; (b) Con. HCl, MeOH, NH<sub>4</sub>PF<sub>6</sub>, H<sub>2</sub>O, 70%.

To the solution of compound **S3** (3.32 g, 6.56 mmol) in MeOH (25 mL) was added conc. HCl to adjust pH < 2, and the solvent was then evaporated off under reduced pressure. The residue was suspended in acetone (25 mL). A saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added until the suspension became clear. The solvent was removed in vacuum, and water (50 mL) was added to the residue and the aqueous layer was extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure to provide the pure compound **S4** as a yellow glassy solid (3 g, 70%).

### Synthesis of DBA

Compound **C2** was synthesized according to the reported procedures.<sup>S2</sup>

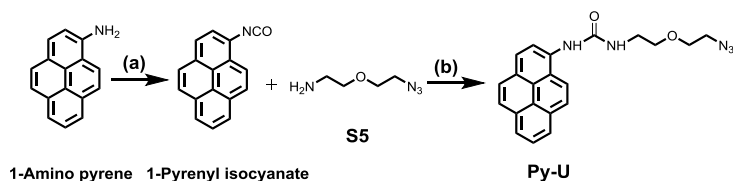


**Scheme S2:** Synthesis of **DBA** with reagents and conditions: (a) Con. HCl, MeOH, NH<sub>4</sub>PF<sub>6</sub>, H<sub>2</sub>O, 96%.

To the solution of compound **C2** (1.5 g, 3.77 mmol) in MeOH (25 mL) was added conc. HCl to adjust pH < 2, and the solvent was then evaporated off under reduced pressure. The residue was suspended in acetone (25 mL). A saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added until the suspension became clear. The solvent was removed in vacuum, and water (50 mL) was added to the residue and the aqueous layer was extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure to provide the pure compound **DBA** as a white solid (2.25 g, 96%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ<sub>H</sub> 7.48 (s, 5H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 4.78 (d, *J* = 2.4 Hz, 2H), 4.22 (d, *J* = 3.1 Hz, 2H), 4.20 (d, *J* = 4.5 Hz, 2H), 2.85 (t, *J* = 2.4 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN) δ (ppm) = 160.1, 133.5, 132.2, 131.7, 131.3, 130.7, 124.9, 116.8, 116.7, 80.0, 77.7, 57.2, 52.9, 52.7. HRMS–ESI (*m/z*): [M – PF<sub>6</sub>]<sup>+</sup> calcd for C<sub>17</sub>H<sub>18</sub>NO, 252.1383; found, 252.1383.

### Synthesis of Py-U

The following compounds of **1-Pyrenyl isocyanate** and **S5** were synthesized according to the reported procedures <sup>S3, S4</sup>

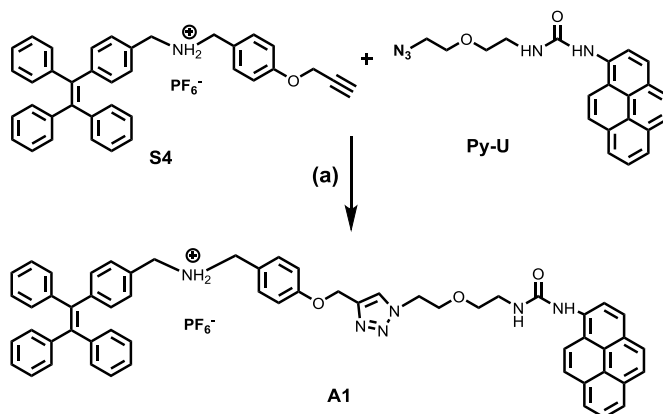


**Scheme S3:** Synthesis of **Py-U** with reagents and conditions: (a) trophosgene, Et<sub>3</sub>N, toluene, 80 °C, 5h, 71%; (b) DCM, rt, overnight, 61%.

In a round-bottomed flask compound **S5** (0.424 g, 3.2 mmol) was dissolved in dry DCM and 1-pyrenyl isocyanate (0.8 g, 3.26 mmol) added and stirred at room temperature for overnight. After that, the solvent was then removed under reduced pressure and the resulting crude compound

purified by chromatography on silica gel (DCM/MeOH, 9.8/0.2) to provide the desired product **Py-U** as a light green powder. (0.750 g, 61 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta_{\text{H}}$  8.35 (d,  $J = 8.3$  Hz, 1H), 8.23–8.1 (m, 4H), 8.12 (d,  $J = 9.32$  Hz, 1H), 8.08–8.01 (m, 3H), 7.73 (s, 1H), 5.74 (s, 1H), 3.69 (t,  $J = 4.8$  Hz, 2H), 3.62 (t,  $J = 5.4$  Hz, 2H), 3.45 (q,  $J = 5.5$  Hz, 2H), 3.4 (t,  $J = 5.0$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  (ppm) = 158.1, 134.6, 133.3, 133.3, 133.0, 132.6, 130.3, 130.2, 129.4, 128.9, 128.7, 127.9, 127.6, 126.8, 126.6, 126.2, 126.1, 123.6, 122.9, 118.9, 71.5, 71.0, 52.1, 41.4. HRMS–ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{20}\text{N}_5\text{O}_2$ , 374.1612; found, 374.1619.

### Synthesis of axle **A1**

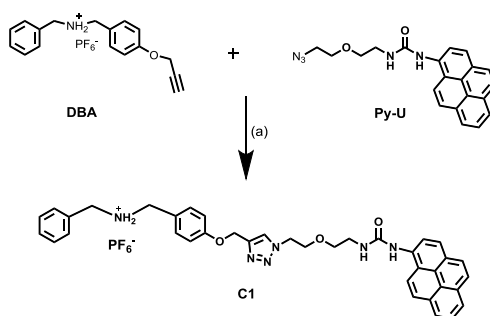


**Scheme S4.** Synthesis of **A1** with reagents and conditions: (a) NaAsc,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , THF/ $\text{H}_2\text{O}$  (3:1), 24 hr, 63%.

Compound **S4** (0.3 g, 4.6 mmol) and **Py-U** (0.17 g, 4.6 mmol) were dissolved in THF/ $\text{H}_2\text{O}$  (v/v = 3:1, 40 mL) in a round-bottomed flask under an inert atmosphere. An aqueous solution of copper (II) sulphate pentahydrate (0.229 g, 0.92 mmol) and sodium ascorbate (0.364 g, 1.8 mmol) was added to the reaction mixture and allowed to stir at room temperature for overnight. Completion of the reaction was monitored by TLC ( $\text{SiO}_2$ ). The solvent was removed under reduce pressure

and the crude product dissolved in DCM (100 mL). The organic phase was washed successively with an aqueous solution of  $\text{NH}_4\text{Cl}$  ( $2 \times 30$  mL) and  $\text{H}_2\text{O}$  (30 mL) and was separated, dried ( $\text{MgSO}_4$ ) and evaporated. The crude product was purified by silica gel chromatography (DCM / MeOH, 9.8/0.2) to afford the pure compound **A1** as a pale white solid in 63 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta_{\text{H}}$  8.26–8.01 (m, 6H), 8.03–8.01 (m, 3H), 7.92 (s, 1H), 7.73 (s, 1H), 7.13 (d,  $J = 2.0$  Hz, 2H) 7.12–7.10 (m, 4H), 7.08–7.03 (m, 3H), 7.01–6.91 (m, 10H), 6.85 (dd,  $J = 1.92$  , 6.5 Hz, 2H), 6.79 (dd,  $J = 2.0$ , Hz, 2H), 5.72 (t,  $J = 5.36$  Hz, 1H), 5.08 (s, 2H), 4.54 (t,  $J = 4.8$  Hz, 2H), 3.85 (t,  $J = 5.0$  Hz, 2H), 3.65 (s, 2H), 3.60 (s, 2H), 3.4 (t,  $J = 5.4$  Hz, 2H), 3.19 (q,  $J = 5.4$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  (ppm) = 159.4, 158.3, 145.0, 145.0, 144.8, 142.9, 134.0, 132.9, 132.3, 131.8, 129.9, 129.6, 129.3, 129.3, 128.8, 128.1, 128.0, 127.9, 127.8, 126.7, 126.7, 126.5, 126.3, 126.3, 126.0, 123.8, 122.9, 118.9, 116.3, 71.2, 70.4, 62.7, 52.8, 52.5, 51.7, 41.3. HRMS–ESI ( $m/z$ ):  $[\text{M}-\text{PF}_6^-]^+$  calcd for  $\text{C}_{58}\text{H}_{51}\text{N}_6\text{O}_3$ , 879.4017; found, 879.4030.

### Synthesis of control compound C1



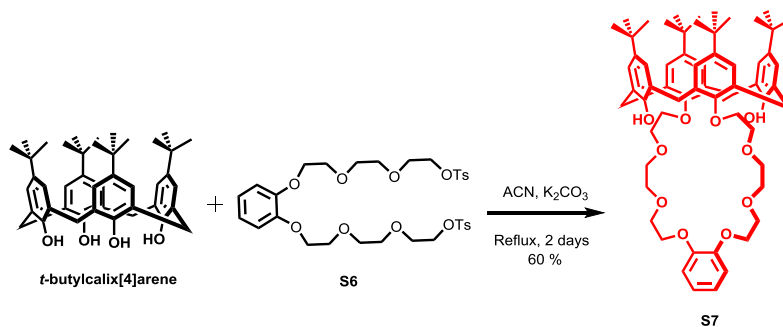
**Scheme S5.** Synthesis of **C1** with reagents and conditions: (a) NaAsc,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , THF/ $\text{H}_2\text{O}$  (3:1), 24 hr, 43%.

Compound **DBA** (0.3 g, 0.75 mmol) and **Py-U** (0.283 g, 0.75 mol) were dissolved in THF/ $\text{H}_2\text{O}$  (v/v = 3:1, 40 mL) in a round-bottomed flask under an inert atmosphere. An aqueous solution of

copper (II) sulphate pentahydrate (0.377 g, 1.51 mmol) and sodium ascorbate (0.600 g, 3.02 mmol) was added to the reaction mixture and allowed to stir at room temperature for overnight. Completion of the reaction was monitored by TLC (SiO<sub>2</sub>). The solvent was removed under reduce pressure and the crude product dissolved in DCM (100 mL). The organic phase was washed successively with an aqueous solution of NH<sub>4</sub>Cl (2 × 30 mL) and H<sub>2</sub>O (30 mL) and was separated, dried (MgSO<sub>4</sub>) and evaporated. The crude product was purified by silica gel chromatography (DCM / MeOH, 9.8/0.2) to afford the pure compound **C1** as a pale yellow solid in 43 % yield. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ<sub>H</sub> 8.39 (s, 1H), 8.24–8.14 (m, 4H), 8.09–7.98 (m, 4H), 7.94 (s, 1H), 7.74 (s, 1H) 7.35–7.30 (m, 5H), 7.02 (d, *J* = 8.72, 2H), 6.72 (d, *J* = 8.68, 2H), 5.73 (t, *J* = 5.36 Hz, 1H), 4.96 (s, 2H), 4.56 (t, *J* = 4.92 Hz, 2H), 3.89 (t, *J* = 5.12 Hz, 2H), 3.66 (s, 2H), 3.58–3.54 (m, 4H), 3.39 (q, *J* = 5.48 Hz, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN) δ (ppm) = 158.7, 157.8, 145.0, 142.5, 134.8, 134.8, 134.7, 133.1, 132.6, 130.7, 129.8, 129.7, 129.2, 128.9, 128.3, 127.9, 127.5, 126.8, 126.6, 126.2, 124.4, 123.2, 122.8, 118.4, 71.5, 70.4, 62.9, 54.1, 53.5, 51.6, 41.2. HRMS–ESI (*m/z*): [M–PF<sub>6</sub>]<sup>+</sup> calcd for C<sub>38</sub>H<sub>37</sub>N<sub>6</sub>O<sub>3</sub>, 625.2935; found, 625.2922.

### Synthesis of *t*-butylcalix[4]arene macrocycle **S7**.

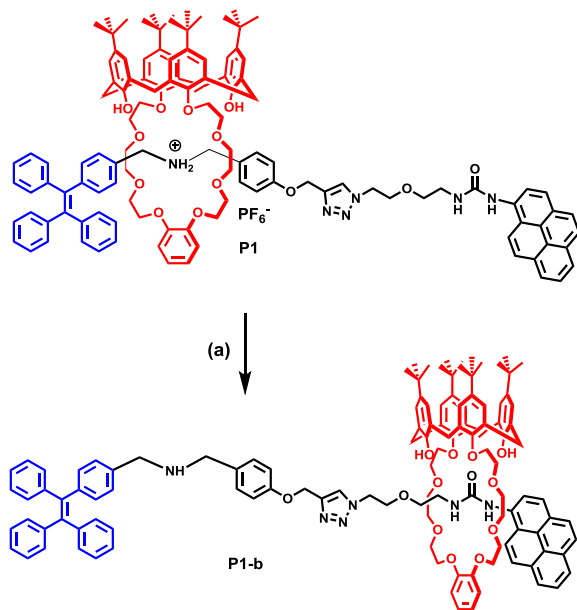
The following compounds of **S6** and *t*-butylcalix[4]arene macrocycle **S7** were synthesized according to the reported procedures.<sup>S1</sup>



**Scheme S6.** Synthesis of **S7** with reagents and conditions: (a) K<sub>2</sub>CO<sub>3</sub>, ACN, reflux, 3 days, 70%.

A mixture of calix[4]arene (1.00 g, 1.54 mmol), compound **S6** (1.05 g, 1.54 mmol) and  $K_2CO_3$  (0.426 g, 3.08 mmol) in dried acetonitrile (38 mL) was refluxed for 2 days. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product was purified by column chromatography ( $SiO_2$ , DCM/MeOH = 9.8/0.2) to afford a white solid compound **S7** (1.06 g, 1.08 mmol, 70%).  $^1H$  NMR (600 MHz,  $CD_3CN$ ):  $\delta_H$  8.12 (s, 2H), 7.23 (s, 4H), 7.16 (s, 4H), 6.94–6.92 (m, 4H), 4.38 (d,  $J$  = 12.6 Hz, 4H), 4.16–4.12 (m, 8H), 4.06–4.04 (m, 4H), 3.89–3.86 (m, 12H), 3.36 (d,  $J$  = 12.6 Hz, 4H), 1.22 (s, 18H), 1.17 (s, 18H).

### Synthesis of [2]rotaxane **P1-b**.



**Scheme S7.** Synthesis of [2]rotaxane **P1-b** with reagents and conditions: (a) DCM, aq. NaOH (0.1M), 2 hr, 50%.

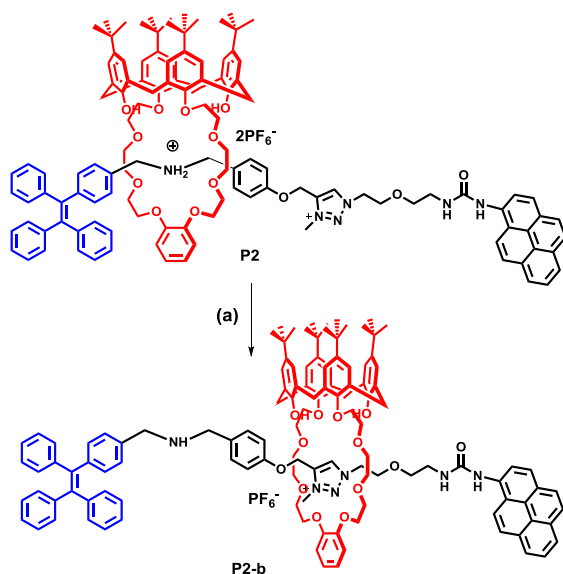
### Preparation of [2]rotaxane **P1-b**.

[2]Rotaxane **P1** (100 mg, 0.049 mmol) was dissolved in dichloromethane (10 mL). NaOH (aq 0.1 M (5 mL) was added and the mixture was stirred vigorously at room temperature for 30



minutes. The layers were separated, the organic phase dried over  $\text{MgSO}_4$ , filtered off and concentrated affording the rotaxane **P1-b** (50 mg, 50%) as a white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta_{\text{H}}$  8.77 (d,  $J = 8.32$  Hz, 1H), 8.40 (s, 1H), 8.27–8.02 (m, 5H), 7.99–7.87 (m, 6H), 7.72 (d,  $J = 9.68$  Hz, 2H), 7.58 (s, 1H), 7.16 (d,  $J = 8.0$  Hz, 2H), 7.09–6.95 (m, 14H), 6.89–6.77 (m, 10H), 6.63 (s, 4H), 6.44 (s, 2H), 6.35 (s, 1H), 5.48 (s, 1H), 5.03 (s, 2H), 4.41–4.28 (m, 8H), 4.16–4.05 (m, 6H), 3.96–3.89 (m, 8H), 3.79–3.67 (m, 10H), 3.62–3.50 (m, 8H), 3.26 (d,  $J = 13.36$  Hz, 4H), 1.31 (d,  $J = 3.12$  Hz, 18H), 0.84 (s, 18H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 157.8, 150.5, 149.7, 148.9, 143.7, 143.7, 132.8, 132.0, 131.8, 131.2, 131.0, 131.0, 130.8, 129.7, 129.2, 128.1, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.2, 126.4, 126.4, 126.3, 126.0, 125.6, 125.4, 125.3, 125.2, 125.2, 125.1, 124.9, 124.6, 123.8, 121.4, 121.3, 114.6, 114.5, 114.0, 71.2, 71.1, 70.5, 70.2, 70.1, 69.8, 69.6, 69.3, 68.8, 61.7, 52.5, 50.1, 33.9, 33.7, 31.7, 31.4, 31.2, 31.0, 30.8. HRMS–ESI ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{120}\text{H}_{133}\text{N}_6\text{O}_{13}$ , 1865.9925; found, 1865.9983.

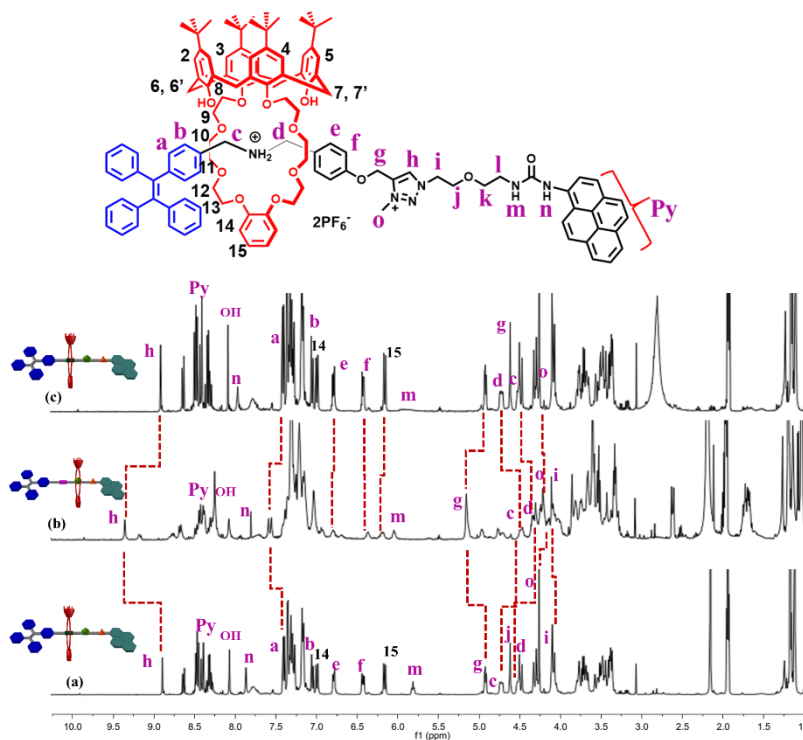
### Synthesis of [2]rotaxane **P2-b**.



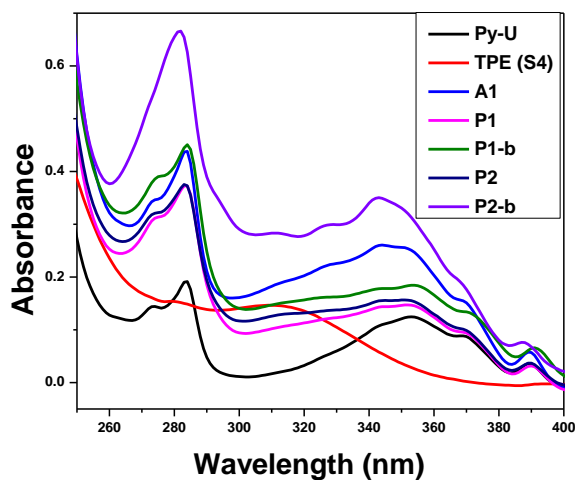
**Scheme S8.** Synthesis of [2]rotaxane **P2-b** with reagents and conditions: (a) DCM, aq. NaOH (0.1 M), 2 hr, 60%.

### Preparation of [2]rotaxane **P2-b**.

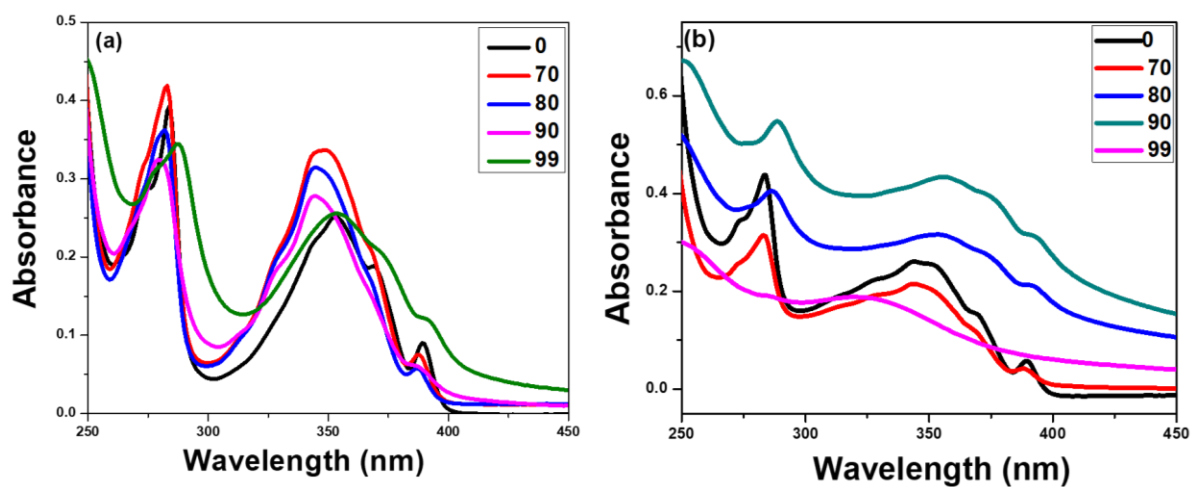
[2]Rotaxane **P2** (100 mg, 0.046 mmol) was dissolved in dichloromethane (10 mL). NaOH (aq 0.1 M (5 mL) was added and the mixture was stirred vigorously at room temperature for 30 minutes. The layers were separated, the organic phase dried over MgSO<sub>4</sub>, filtered off and concentrated affording the rotaxane **P2-b** (65 mg, 60%) as a white solid. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ<sub>H</sub> 9.10 (s, 1H), 8.44 (d, *J* = 8.36 Hz, 1H), 8.25–8.16 (m, 5H), 8.10–8.03 (m, 4H), 7.81 (s, 1H), 7.36 (d, *J* = 14.8 Hz, 2H), 7.20–7.03 (m, 29H), 6.97 (d, *J* = 7.88 Hz, 2H), 6.89–6.85 (m, 4H), 5.83 (s, 1H), 5.04 (s, 2H), 4.26 (t, *J* = 6.52 Hz, 2H), 4.16 (dd, *J* = 4.96, 12.8 Hz, 4H), 4.08–3.98 (m, 10H), 3.78 (s, 3H), 3.75 (t, *J* = 5.48 Hz, 2H), 3.69–3.68 (m, 4H), 3.61 (d, *J* = 5.12 Hz, 5H), 3.55 (s, 7H) 3.51 (d, *J* = 5.44 Hz, 2H), 3.41 (s, 2H), 3.32–3.24 (m, 6H), 1.22 (d, *J* = 1.92 Hz, 18H), 1.06 (s, 18H) ppm; <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN) δ (ppm) = 157.8, 151.2, 151.0, 149.4, 149.3, 145.4, 144.3, 144.1, 143.7, 142.6, 142.5, 141.2, 134.7, 134.7, 134.6, 133.1, 132.5, 132.4, 132.3, 131.0, 129.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.0, 128.0, 127.9, 127.7, 127.2, 127.1, 127.0, 126.9, 126.7, 126.2, 123.2, 122.8, 122.7, 118.9, 116.3, 114.0, 77.5, 72.2, 72.0, 71.7, 71.4, 70.8, 69.8, 68.6, 60.3, 54.5, 53.6, 53.3, 35.4, 35.2, 35.2, 32.5, 32.4, 32.3, 32.1, 31.9. HRMS–ESI (*m/z*): [*M*]<sup>+</sup> calcd for C<sub>121</sub>H<sub>135</sub>N<sub>6</sub>O<sub>13</sub>, 1880.0235; found, 1880.0082.



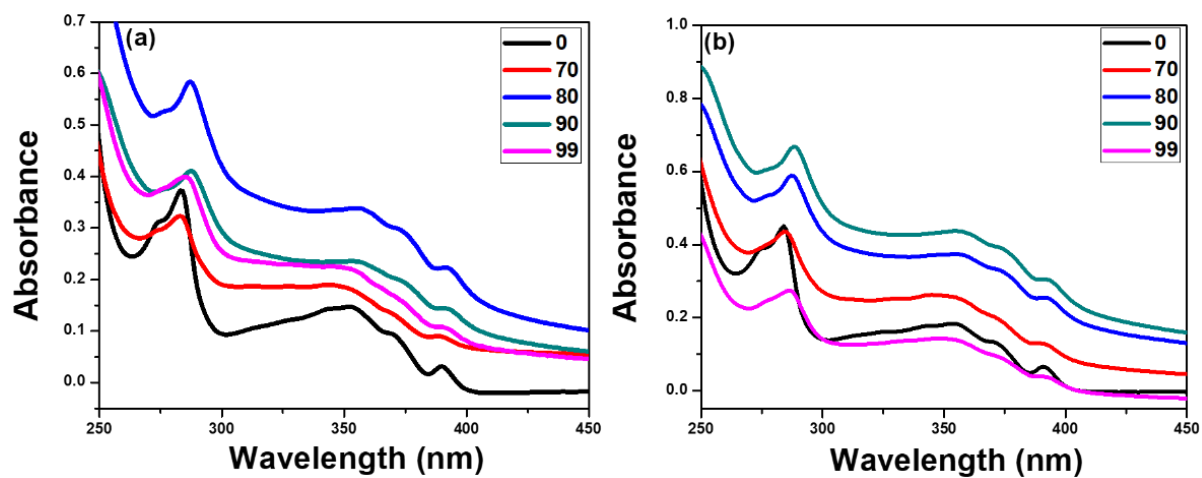
**Figure S1.**  $^1\text{H}$  NMR spectra (400 MHz, 298 K,  $\text{CD}_3\text{CN}$ ) of (a) [2]rotaxane **P2**, (b) deprotonation with addition of one equivalent NaOH to sample a, and (c) further addition of four equivalent of TFA to sample b.



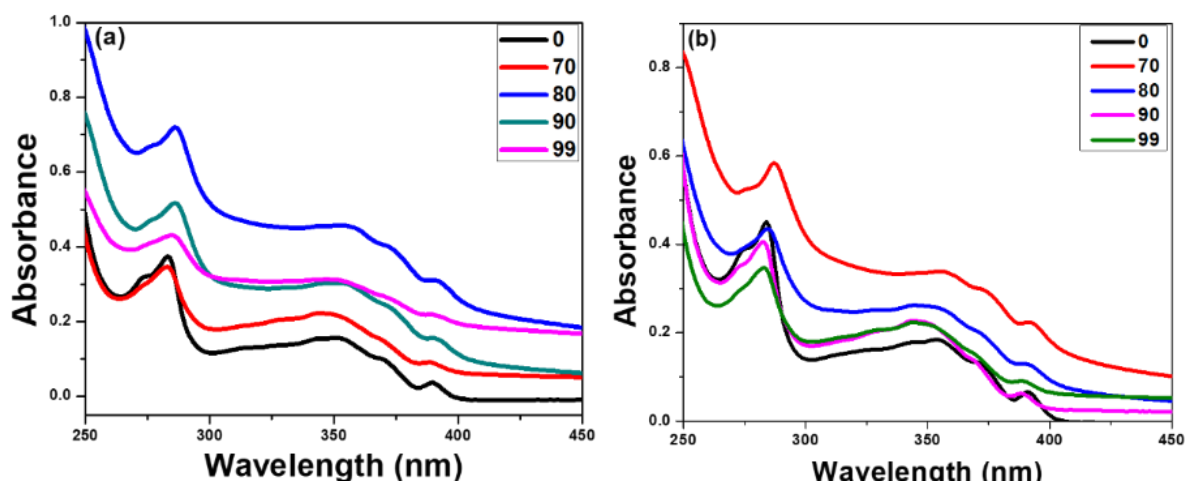
**Figure S2.** UV-vis absorption spectra of all [2]rotaxanes and its precursors in pure THF solvent ( $10\ \mu\text{M}$ ).



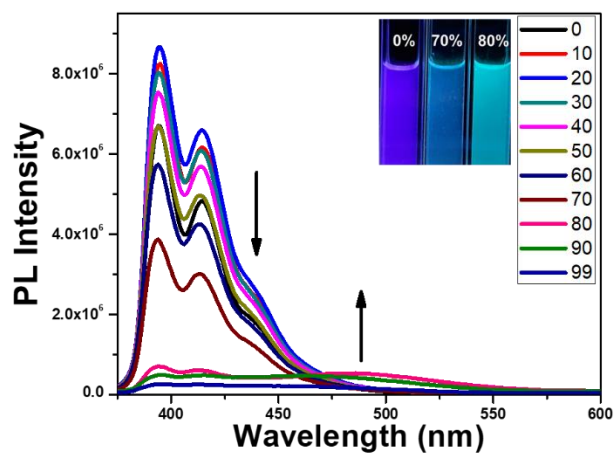
**Figure S3.** UV-vis absorption spectra of [2]rotaxanes (a) **C1** and (b) **A1** in THF/water mixtures (10  $\mu$ M) with different water fractions ( $f_w$ ).



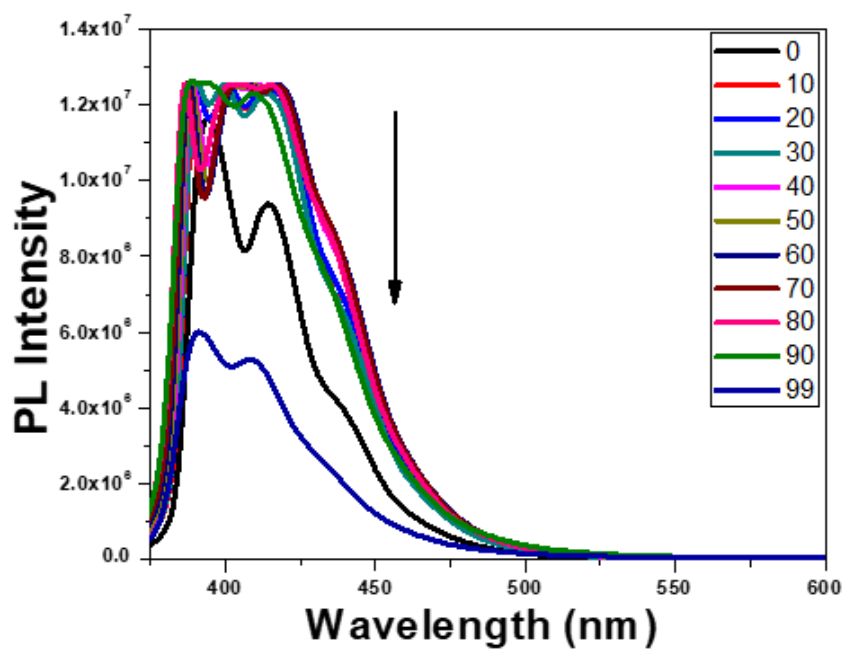
**Figure S4.** UV-vis absorption spectra of [2]rotaxanes (a) **P1** and (b) **P2** in THF/water mixtures (10  $\mu$ M) with different water fractions ( $f_w$ ).



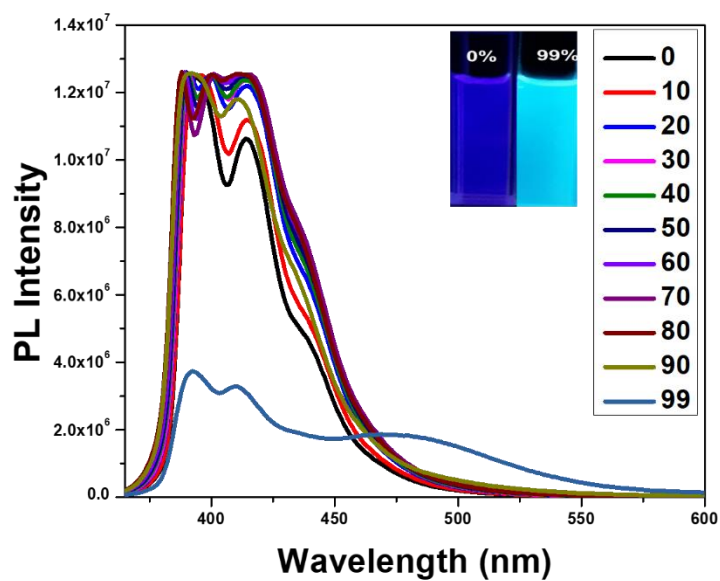
**Figure S5.** UV-vis absorption spectra of [2]rotaxanes (a) **P1-b** and (b) **P2-b** in THF/water mixtures (10  $\mu$ M) with different water fractions ( $f_w$ ).



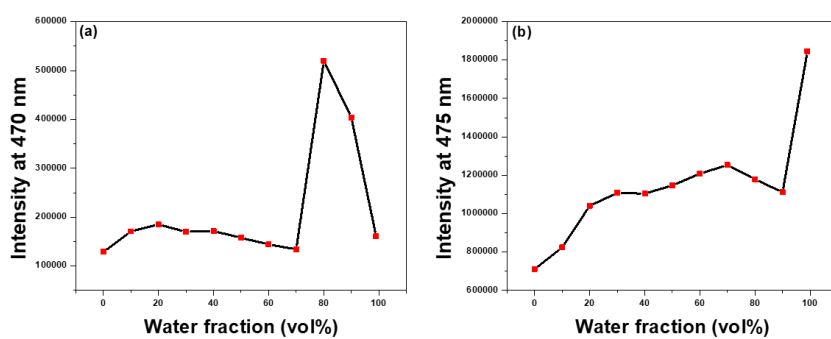
**Figure S6.** Fluorescence spectra of axle **A1** in THF/water mixtures (10  $\mu$ M) with different water fractions ( $f_w$ ) ( $\lambda_{ex} = 320$  nm); Inset figures: fluorescence photographs in THF/water mixtures with various water fractions ( $f_w$ ) taken under UV illumination ( $\lambda_{ex} = 365$  nm).



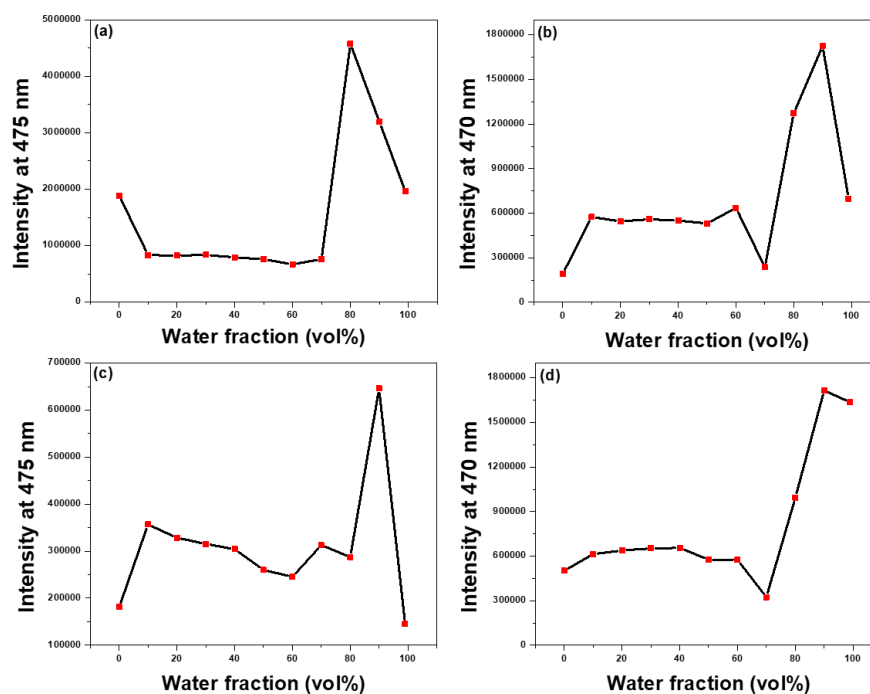
**Figure S7.** Fluorescence spectra of precursor **Py-U** in THF/water mixtures (10  $\mu\text{M}$ ) with different water fractions ( $f_w$ ) ( $\lambda_{\text{ex}} = 320$  nm).



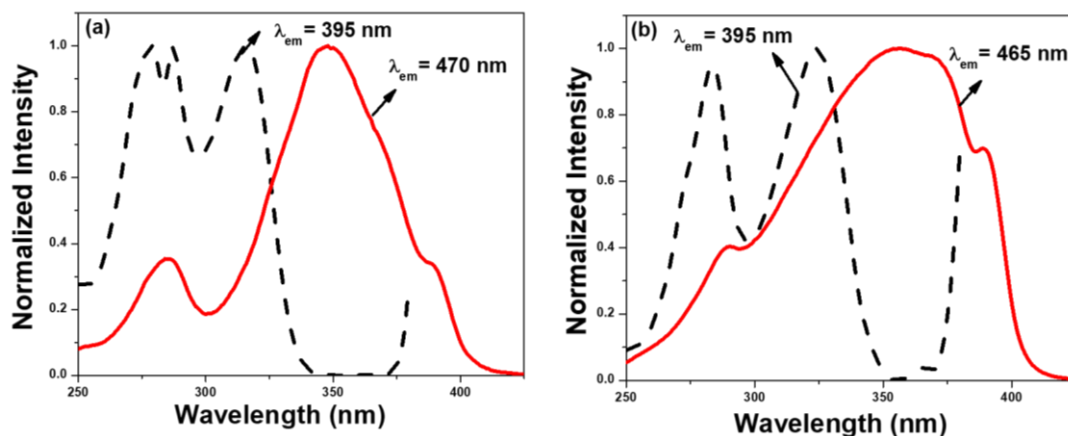
**Figure S8.** Fluorescence spectra of **C1** in THF/water mixtures (10  $\mu\text{M}$ ) with different water fractions ( $f_w$ ) ( $\lambda_{\text{ex}} = 320$  nm).



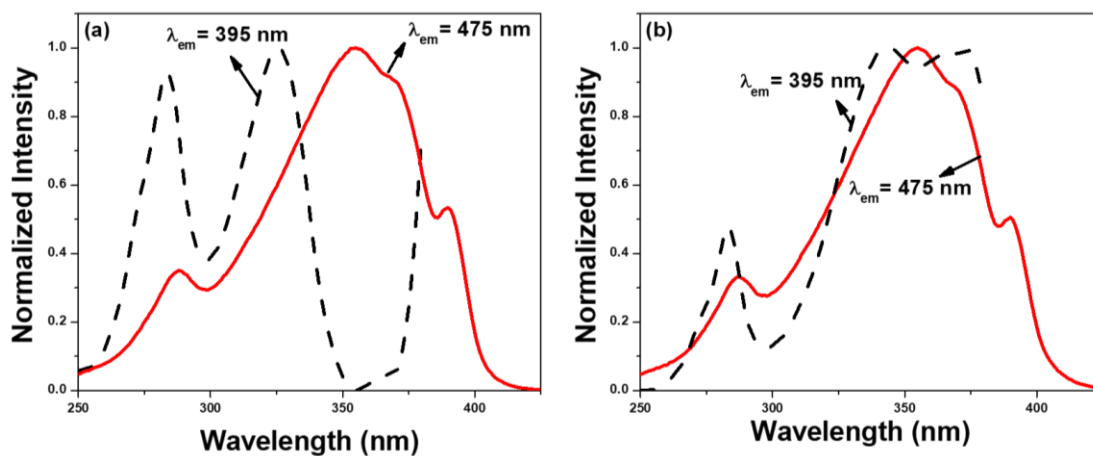
**Figure S9.** Plots of fluorescence intensity versus water fraction of (a) axle **A1**, (b) **C1** in THF/water mixture with different water fractions (from 0 to 99%).



**Figure S10.** Plots of fluorescence intensity versus water fraction of [2]rotaxanes (a) **P1**, (b) **P2**, (c) **P1-b**, and (d) **P2-b** in THF/water mixture with different water fractions (from 0 to 99%).



**Figure S11.** Normalized excitation spectra of (a) **C1** and (b) **A1** were monitored at 395 nm and 475 nm;  $f_w = 0\%$  (black dash line); (a)  $f_w = 99\%$  and (b)  $f_w = 80\%$  (red solid line) in THF/water mixtures (10  $\mu\text{M}$ ).

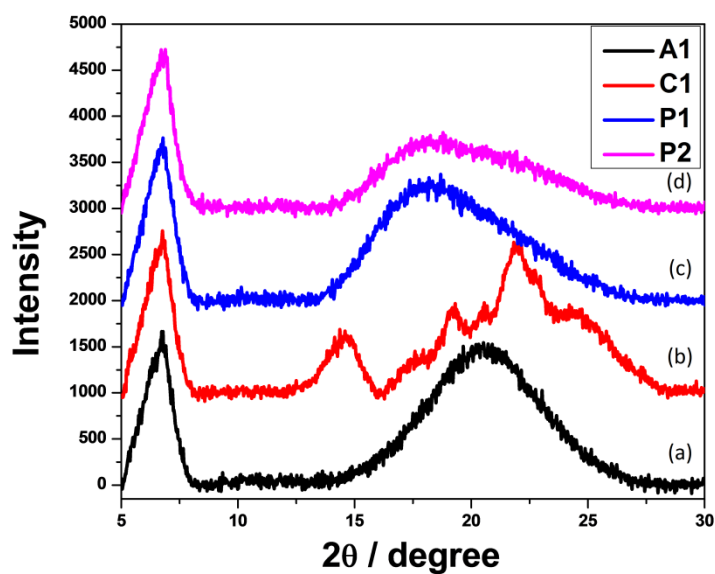


**Figure S12.** Normalized excitation spectra of [2]rotaxanes (a) **P1-b** and (b) **P2-b** were monitored at 395 nm,  $f_w = 0\%$  (black dash line) and 475 nm,  $f_w = 90\%$  (red solid line) in THF/water mixtures (10  $\mu\text{M}$ ).



**Table S1.** Optical properties of axle **A1** and [2]rotaxanes **P1**, **P2**, **P1-b** and **P2-b** (10  $\mu$ M) in AIE state (in THF/water mixture at water fraction  $f_w = 90\%$ ). AIE states using 9,10 diphenylanthracene ( $\Phi_F = 90\%$  in cyclohexane) as standard.<sup>S5</sup>

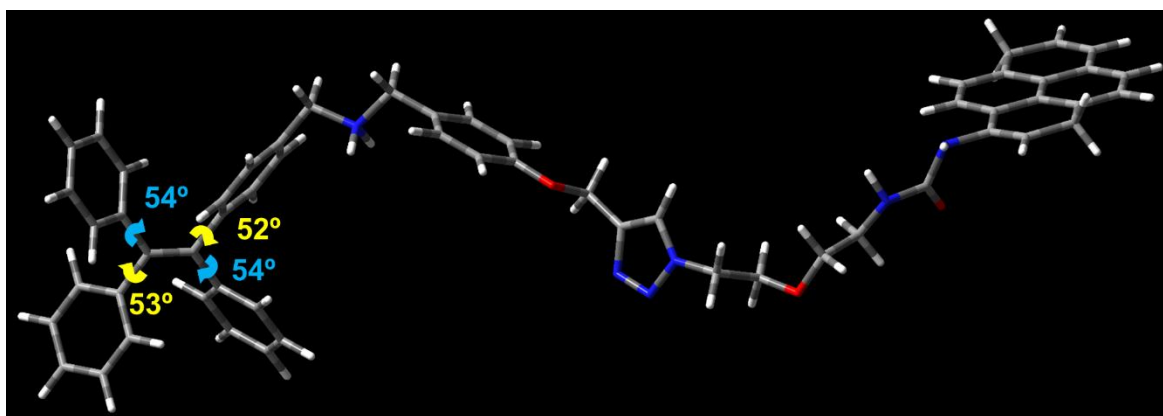
Compounds	$\lambda_{\text{abs}}$ (nm) Solution	$\lambda_{\text{emi}}$ (nm)		$\Phi_F$ AIE state
		Solution	AIE state	
<b>A1</b>	344	394/414	480	0.012
<b>P1</b>	344	394/414	486	0.023
<b>P2</b>	349	393/415	478	0.021
<b>P1-b</b>	350	394/414	480	0.017
<b>P2-b</b>	342	393/414	477	0.012



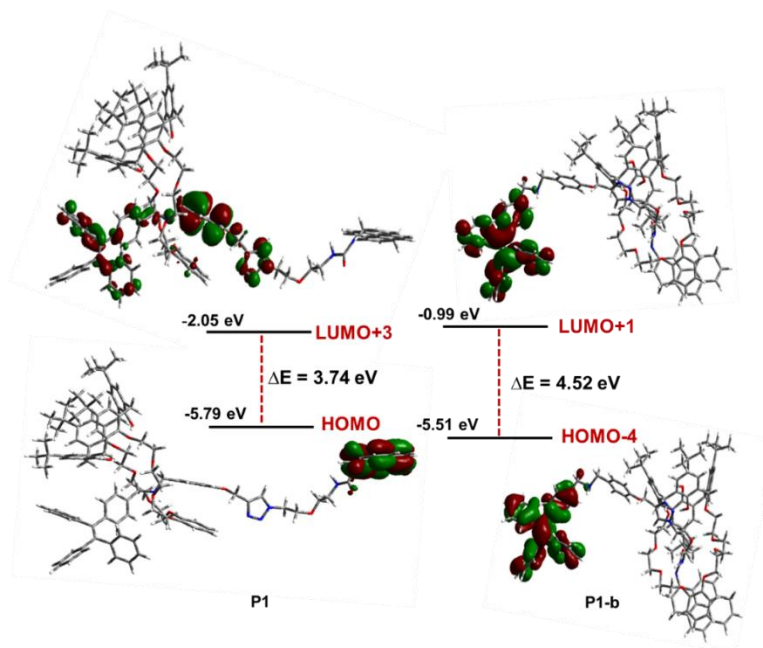
**Figure S13.** Powder X-ray diffraction patterns at room temperature of compounds (a) axle **A1**, (b) **C1**, (c) **P1**, and (d) **P2**.

**Table S2:** The results of frontier molecular orbital calculations and TD-DFT computed at B3LYP/6-31G (d,p)//HF level in gas phase.

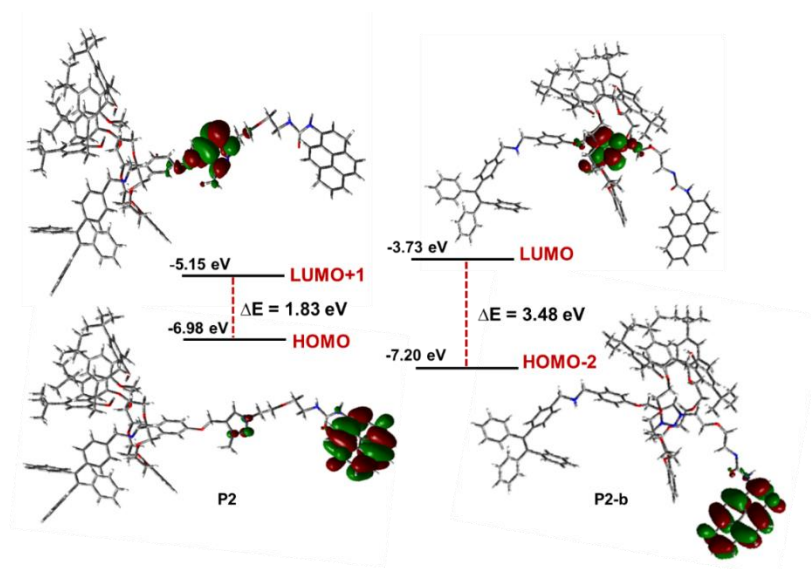
[2]rotaxanes	Oscillator Strength (f)	Band Gap (eV)	Electronic excitation
<b>P1</b>	0.2079	3.74	HOMO to LUMO+3
<b>P2</b>	0.0012	1.83	HOMO to LUMO+1
<b>P1-b</b>	0.3274	4.52	HOMO-4 to LUMO+1
<b>P2-b</b>	0.004	3.48	HOMO-2 to LUMO



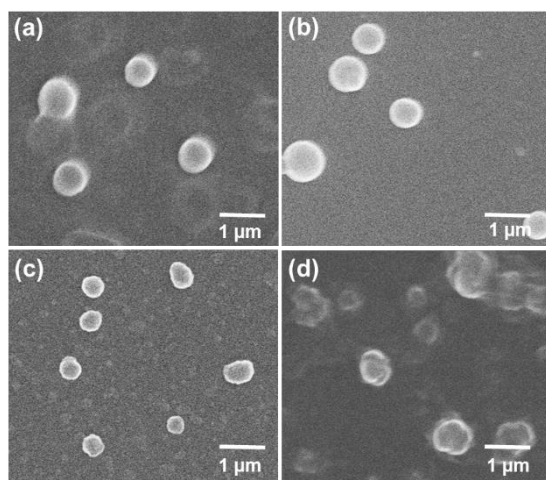
**Figure S14.** Geometries optimized at B3LYP/6-31G (d,p)//HF level of axle **A1**.



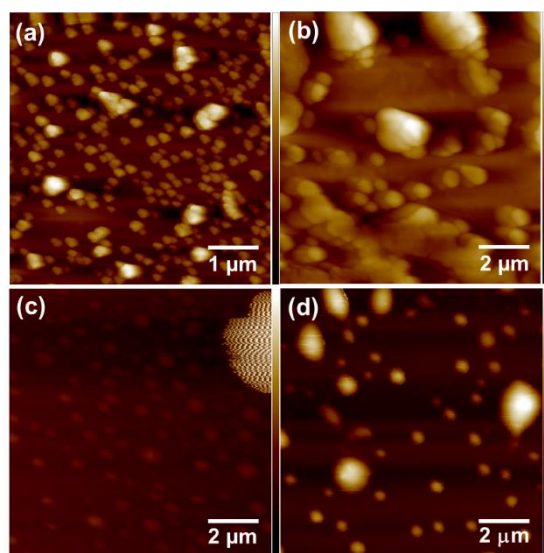
**Figure S15.** Frontier Molecular Orbitals of [2]rotaxanes **P1** and **P1-b** at the B3LYP/6-31G (d,p)//HF level in the gas phase.



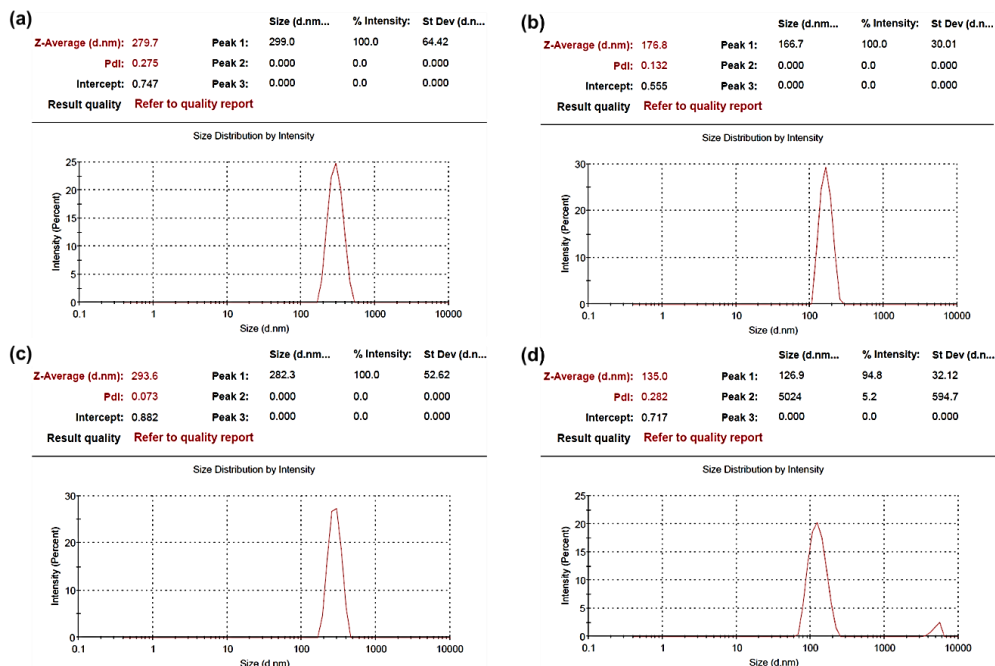
**Figure S16.** Frontier Molecular Orbitals of [2]rotaxanes **P2** and **P2-b** at the B3LYP/6-31G (d,p)//HF level in the gas phase.



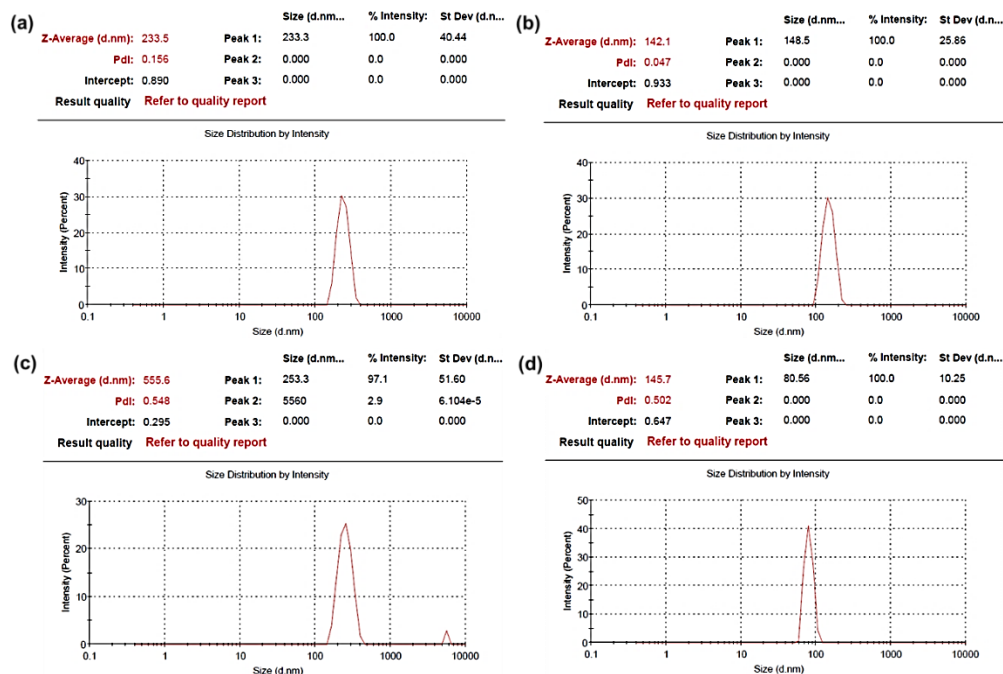
**Figure S17.** FE-SEM images of [2]rotaxanes (a) **P1**, (b) **P2**, (c) **P1-b**, and (d) **P2-b** in THF (10  $\mu\text{M}$ ). Scale bar for figures a, b, c, and d was 1  $\mu\text{m}$ .



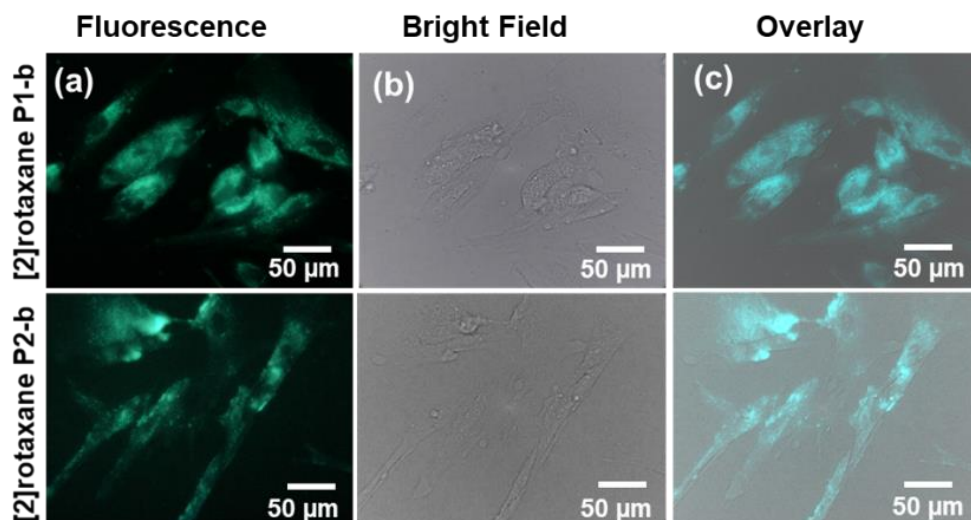
**Figure S18.** AFM images of [2]rotaxanes **P1** and **P1-b** in THF/water mixture (1  $\mu\text{M}$ ) with various water fractions ( $f_w$ ): (a) 70% of **P1**, (b) 80% of **P1**, (c) 70% of **P1-b**, and (d) 90% of **P1-b**. Scale bar for figures a = 1  $\mu\text{m}$ ; b, c, and d is 2  $\mu\text{m}$ .



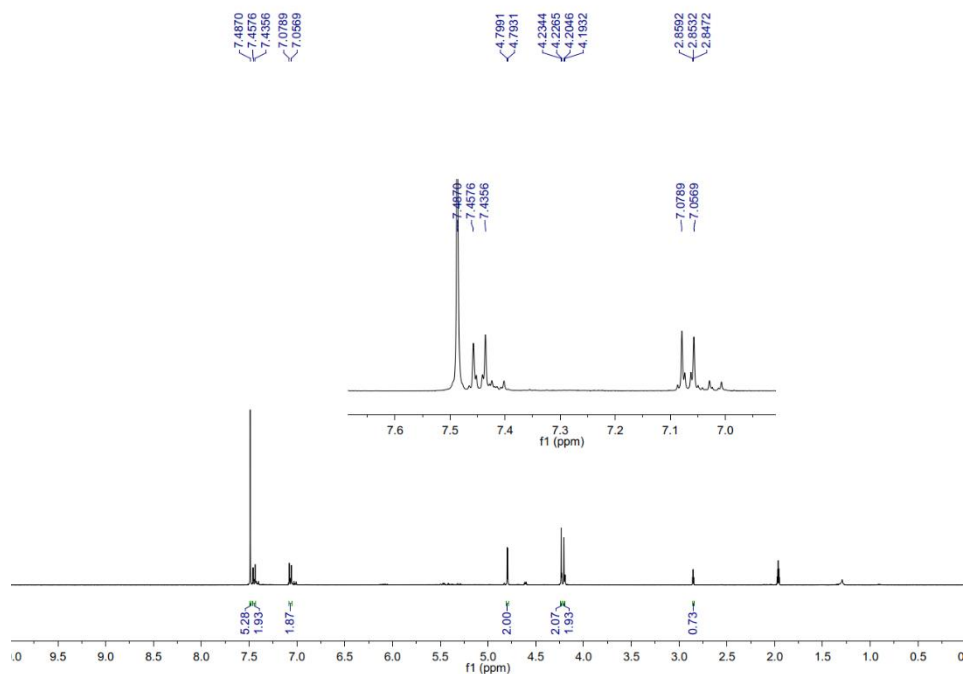
**Figure S19.** The particle size distribution of [2]rotaxanes **P1** and **P1-b** in THF/water mixtures (a) at 70%  $f_w$  of **P1**, (b) at 80%  $f_w$  of **P1**, (c) at 70%  $f_w$  of **P1-b**, and (d) at 90%  $f_w$  of **P1-b**.



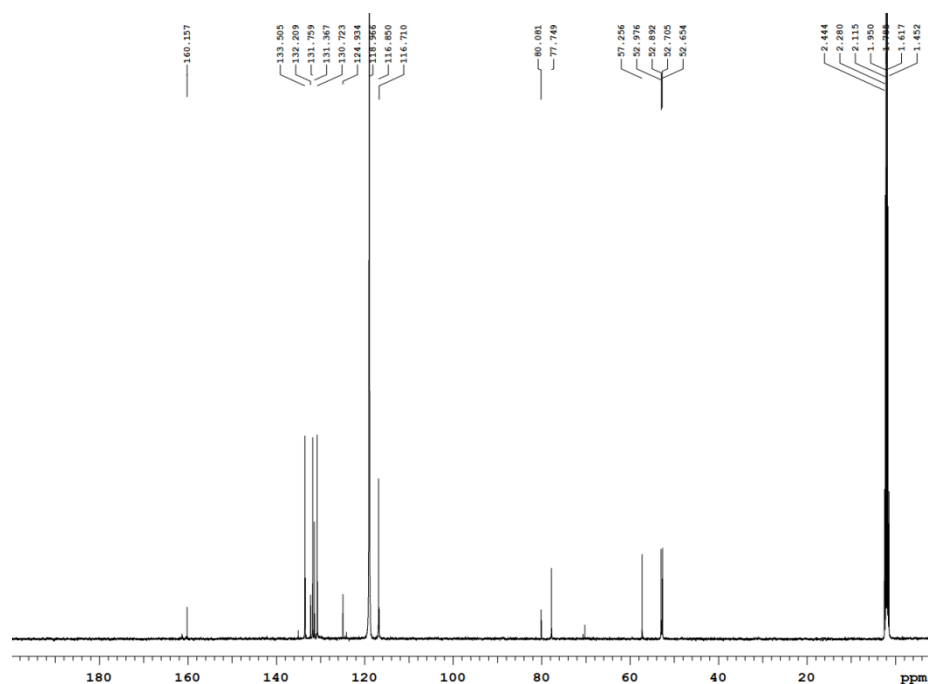
**Figure S20.** The particle size distribution of [2]rotaxanes **P2** and **P2-b** in THF/water mixtures (a) at 70%  $f_w$  of **P2**, (b) at 90%  $f_w$  of **P2**, (c) at 70%  $f_w$  of **P2-b**, and (d) at 90%  $f_w$  of **P2-b**.



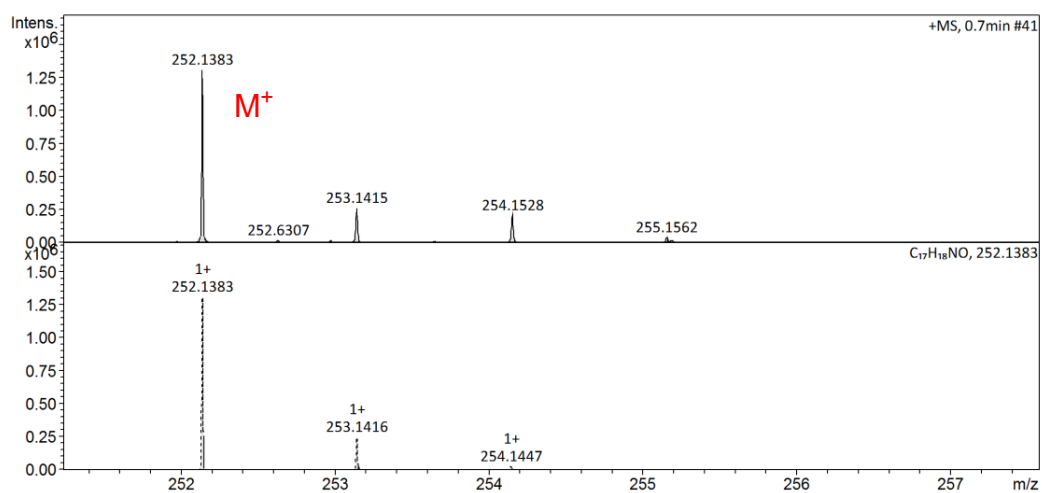
**Figure S21.** Fluorescence microscopy images of MRC-5 live cells incubated with [2]rotaxanes **P1-b** and **P2-b** in DMSO (10  $\mu\text{m}$ ); (a) Fluorescence images after cells were incubated for 5 hr (b) corresponding bright field images (c) overlay images of MRC-5. Scale bar is 50  $\mu\text{m}$ .



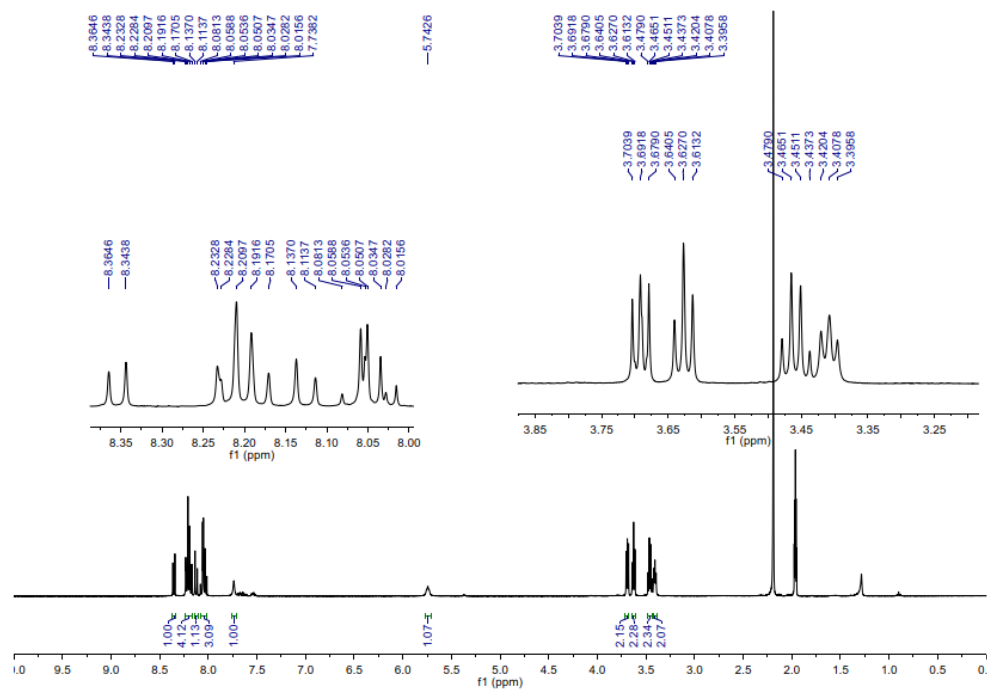
**Figure S22.**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound **DBA**



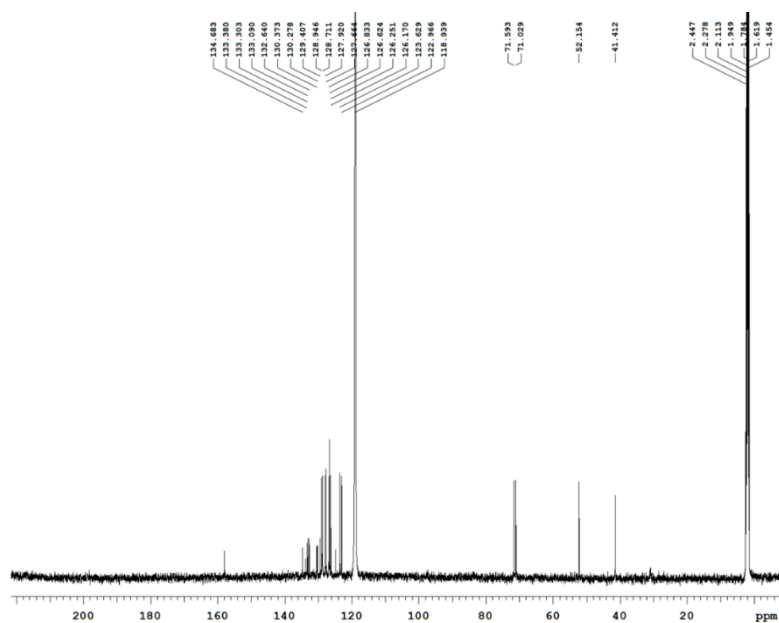
**Figure S23.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound **DBA**



**Figure S24.** HRMS ESI (+)-MS spectrum of compound **DBA**.

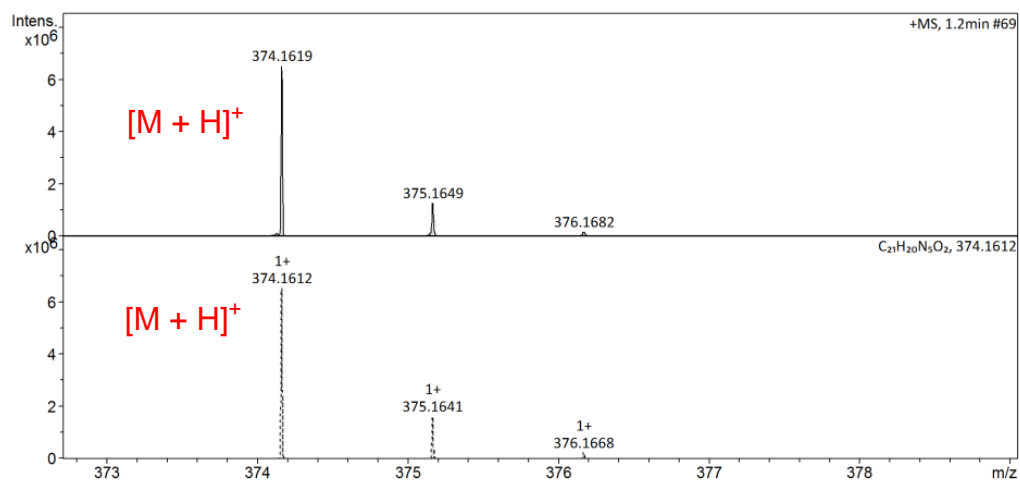


**Figure S25.** <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) spectrum of compound **Py-U**.

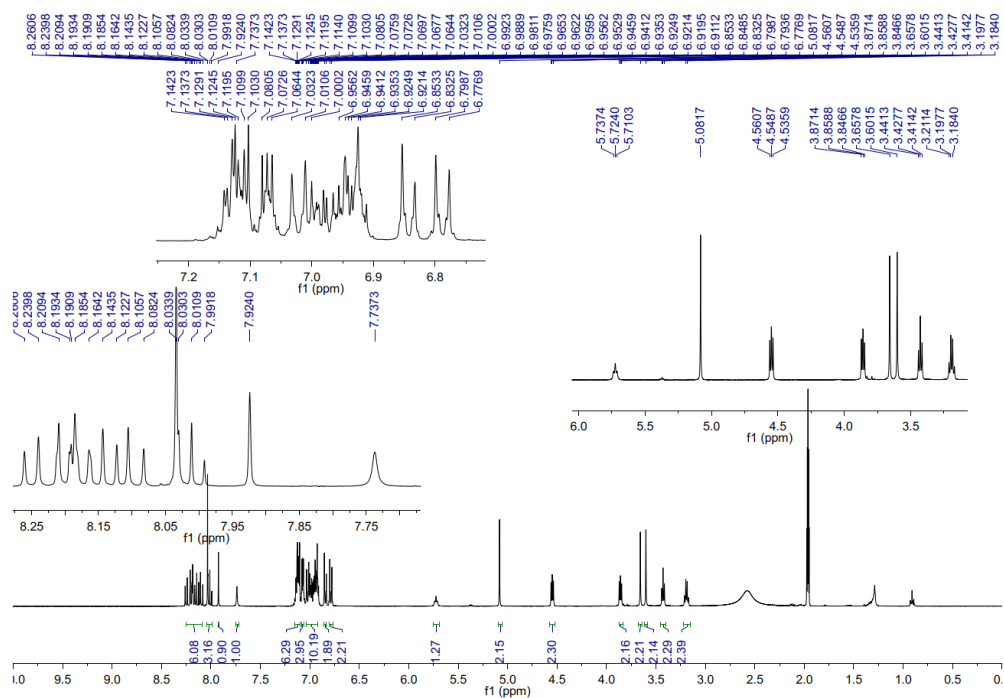


**Figure S26.** <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN) spectrum of compound **Py-U**.

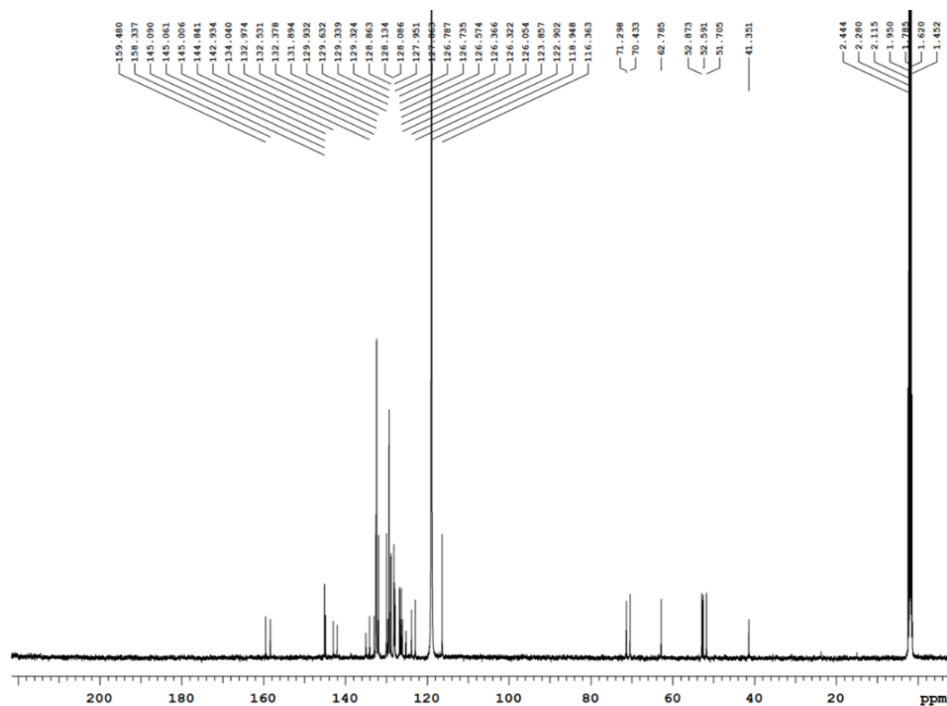




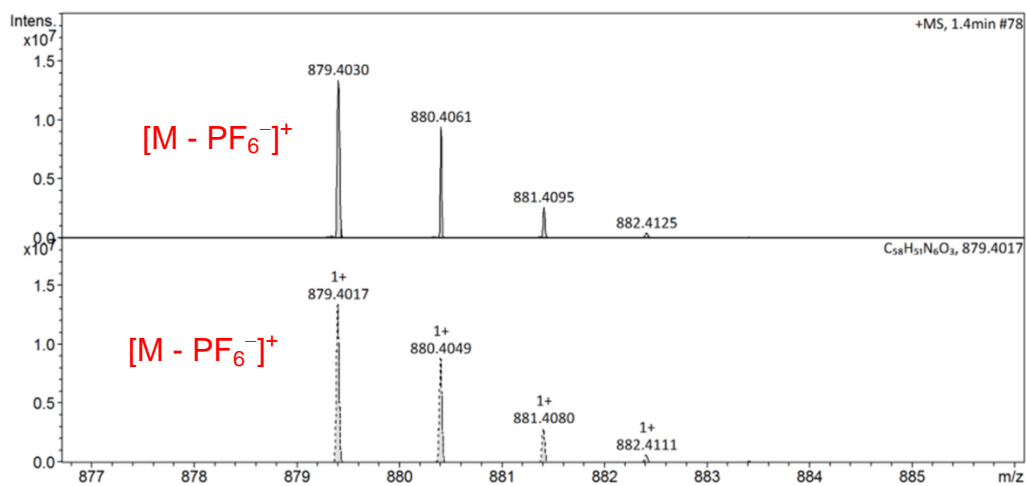
**Figure S27.** HRMS ESI (+)-MS spectrum of compound **Py-U**.



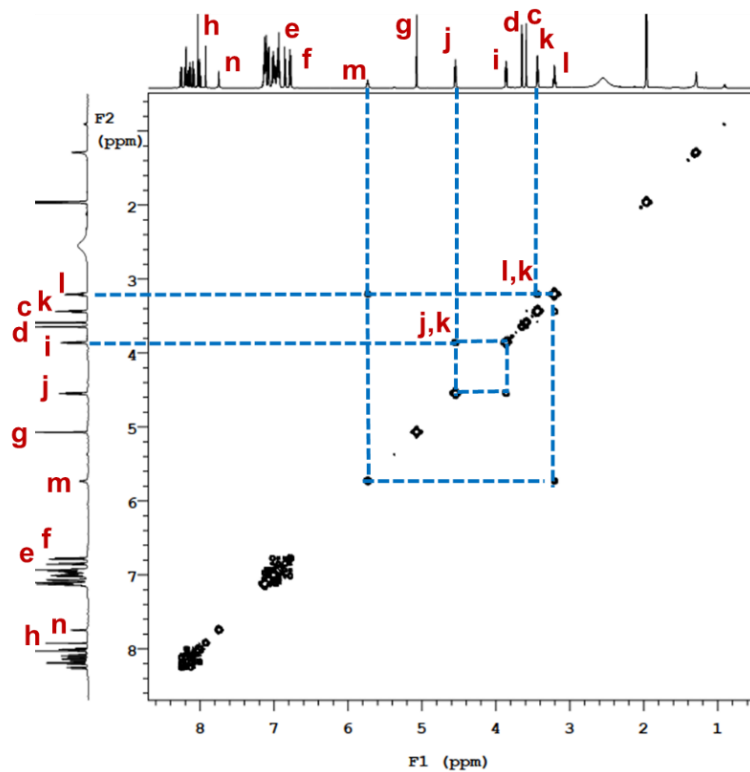
**Figure S28.**  $^1H$  NMR (400 MHz,  $CD_3CN$ ) spectrum of compound **A1**.



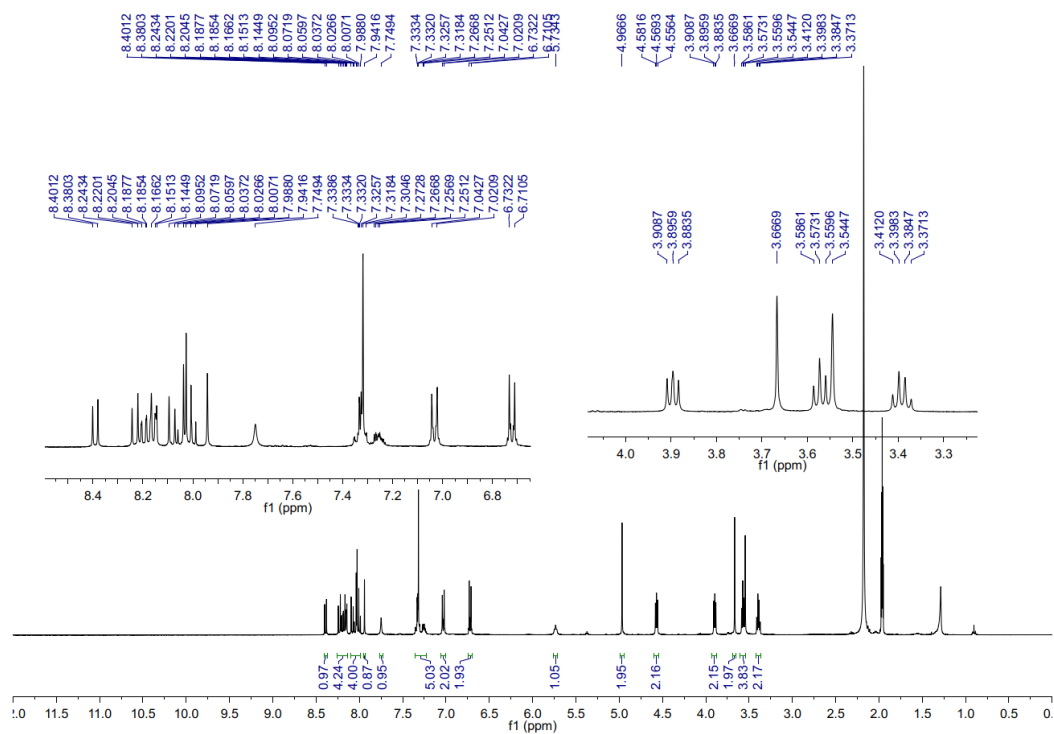
**Figure S29.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of compound **A1**.



**Figure S30.** HRMS ESI (+)-MS spectrum of compound **A1**.



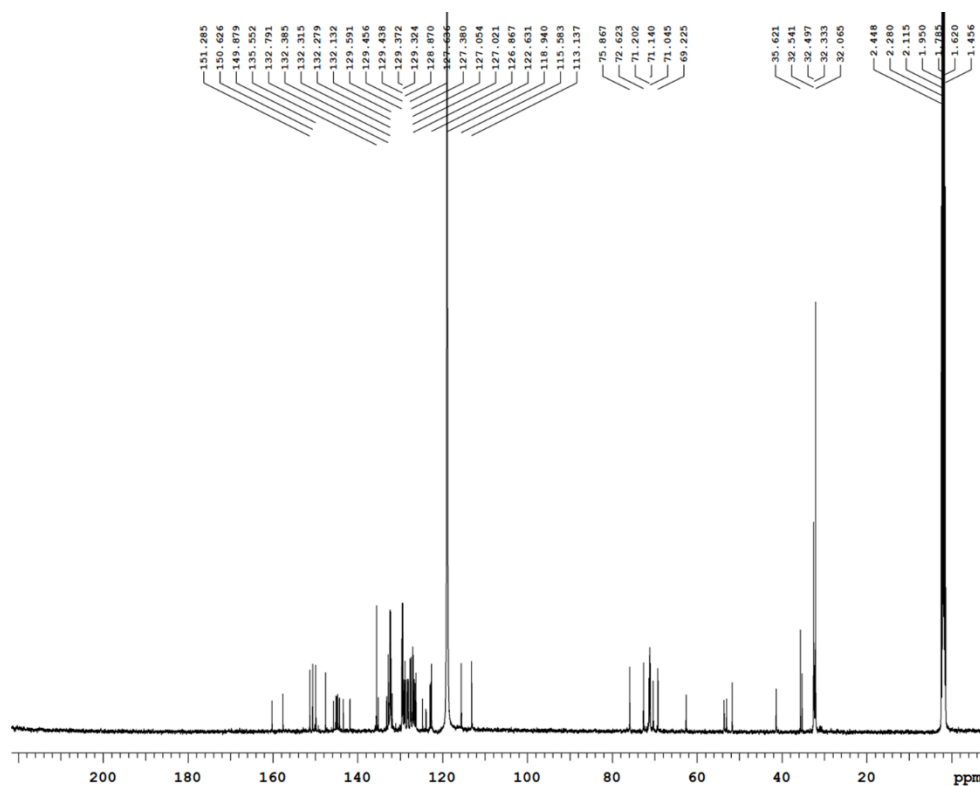
**Figure S31.** 2D-COSY spectrum (500 MHz, 298 K, CD<sub>3</sub>CN) of compound **A1**.



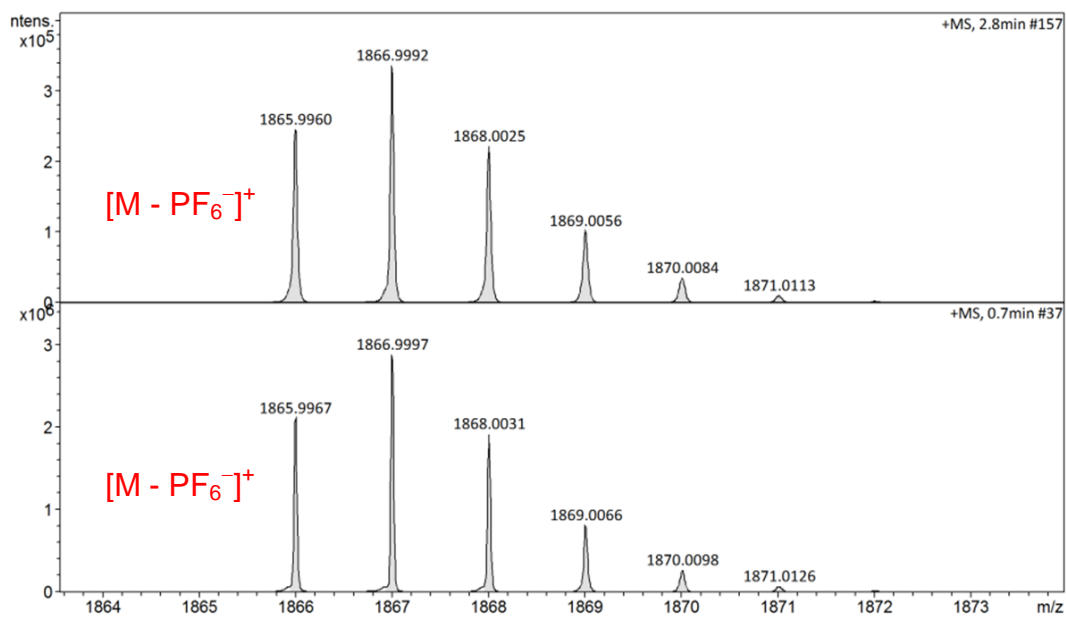
**Figure S32.** <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) spectrum of compound **C1**.



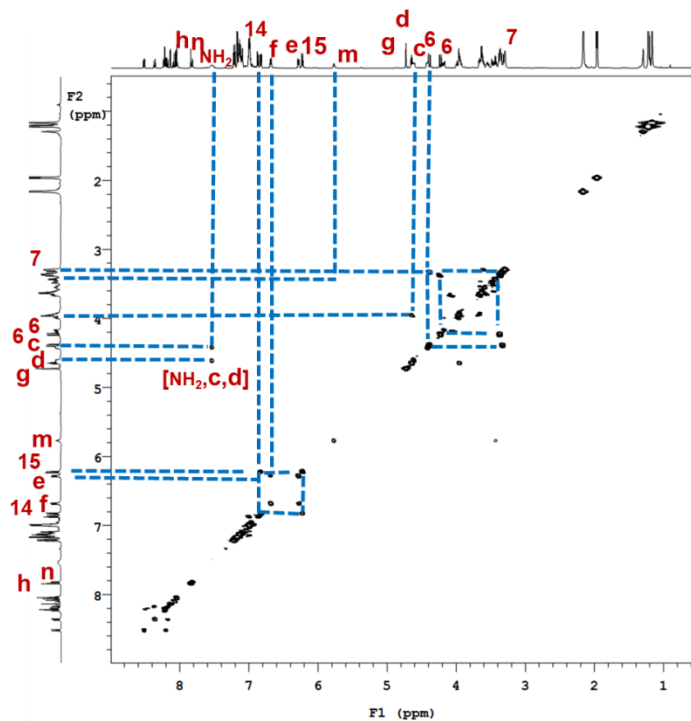




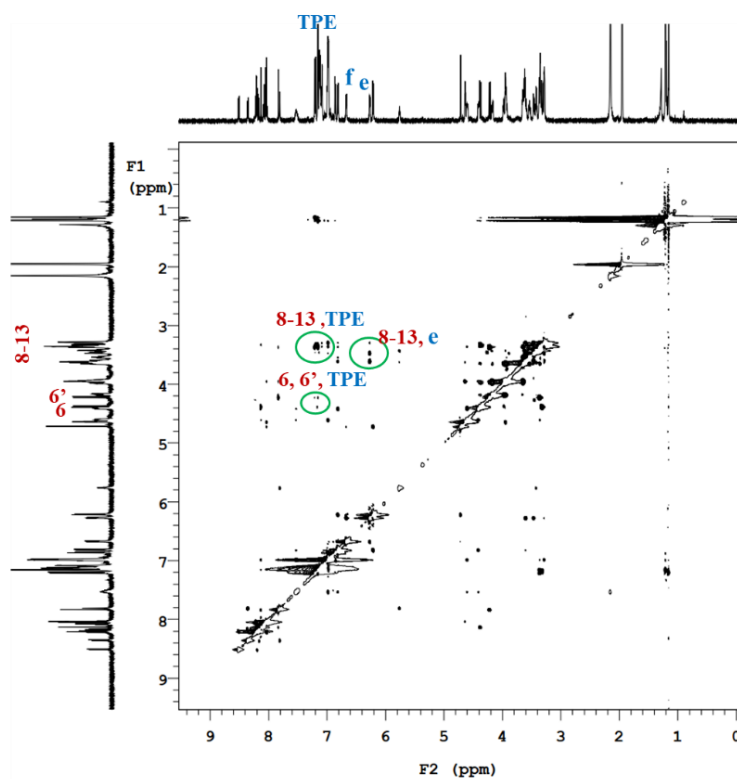
**Figure S37.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of [2]rotaxane **P1**.



**Figure S38.** HRMS ESI (+)-MS spectrum of [2]rotaxane **P1**.



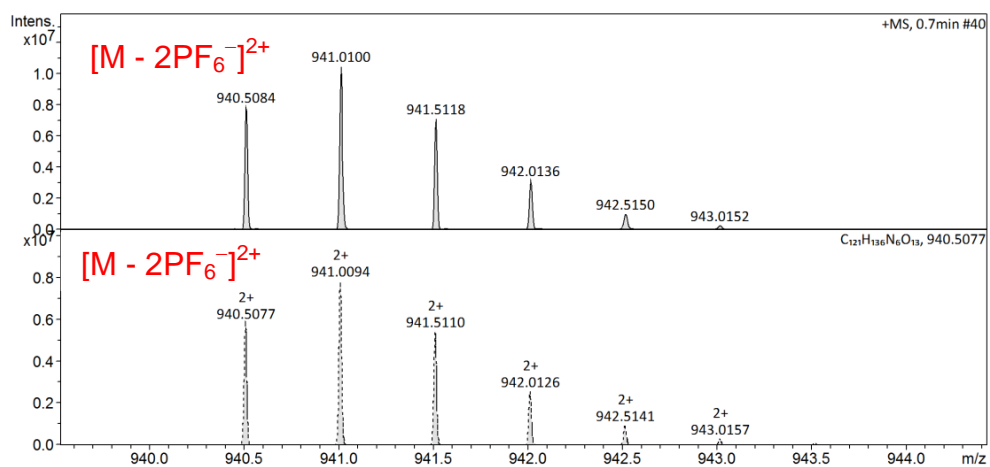
**Figure S39.** 2D-COSY spectrum (500 MHz, 298 K, CD<sub>3</sub>CN) of [2]rotaxane **P1**.



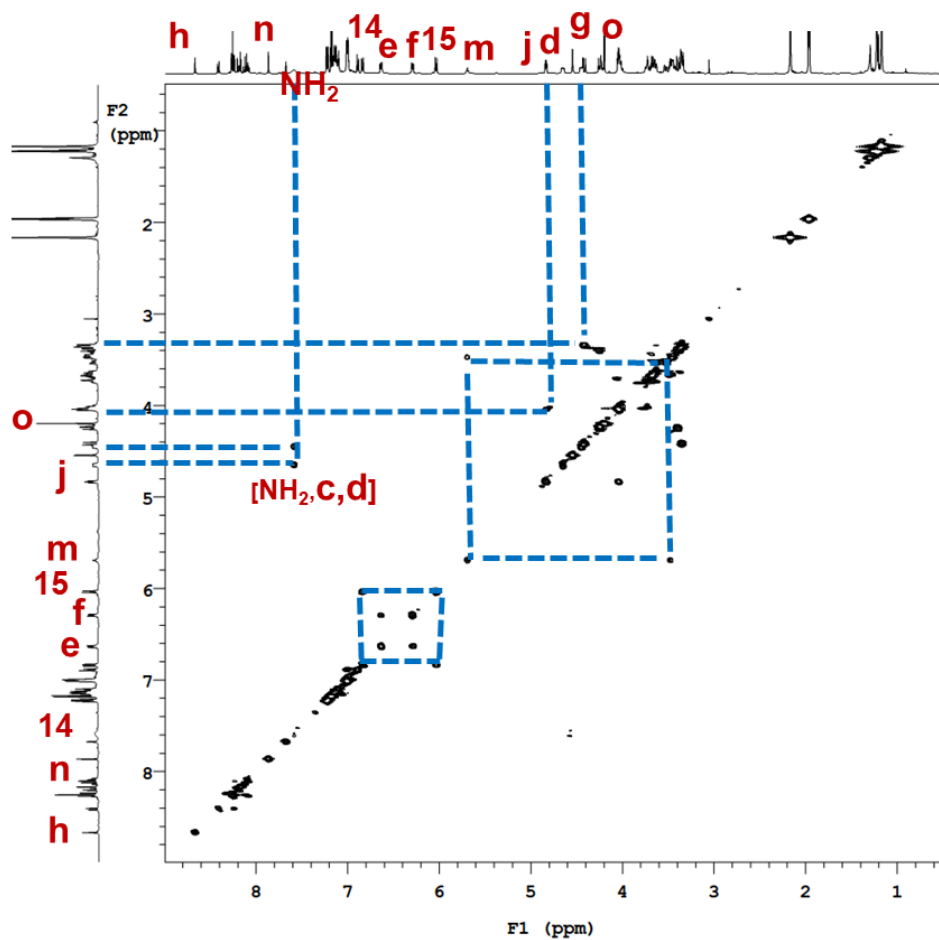
**Figure S40.** 2D ROESY spectrum (600 MHz, 298 K, CD<sub>3</sub>CN) of [2]rotaxane **P1**.



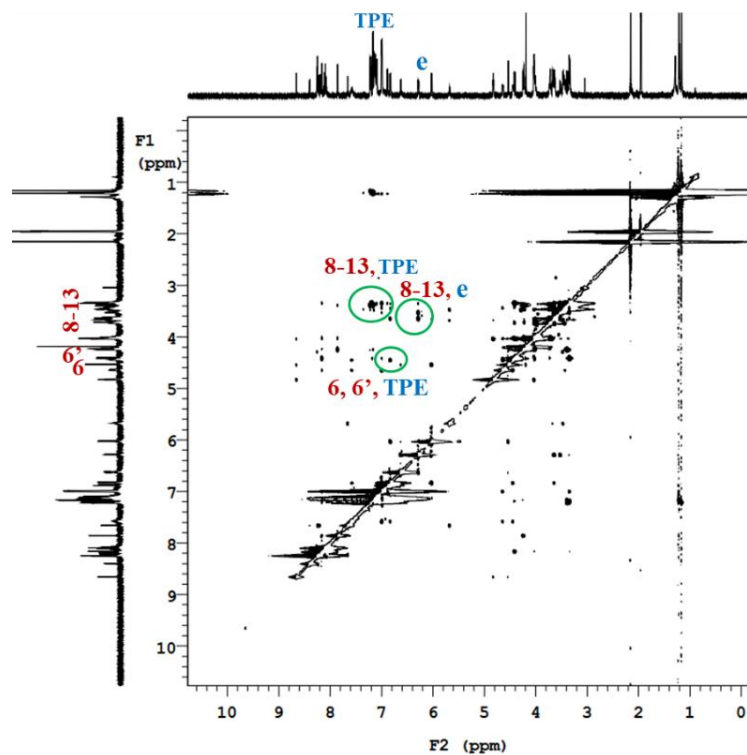




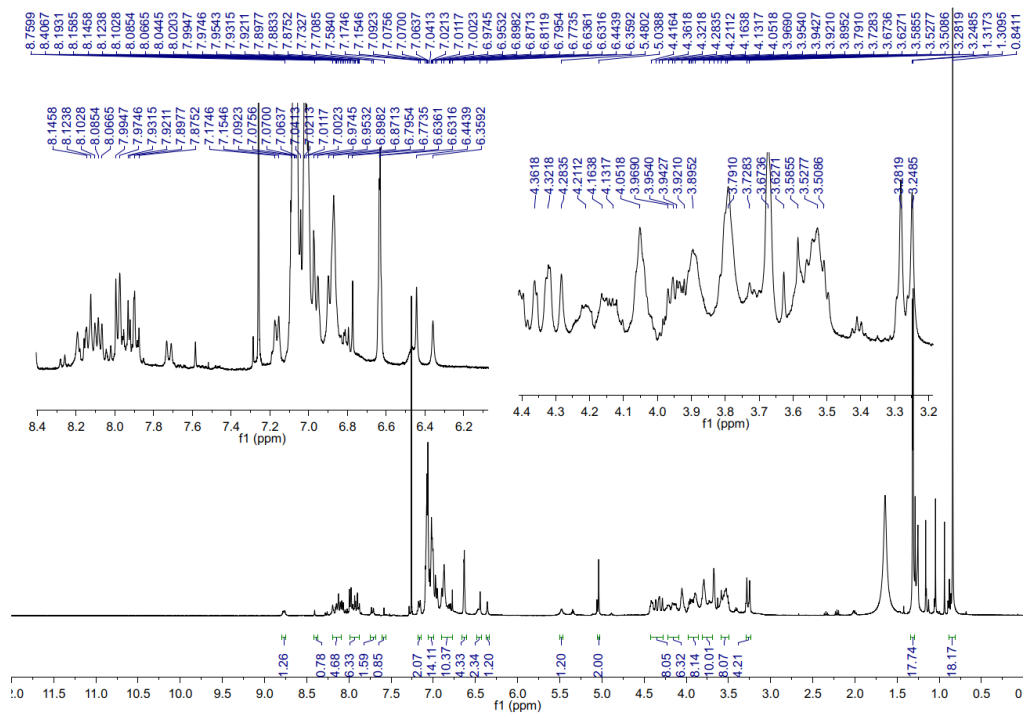
**Figure S43.** HRMS ESI (+)-MS spectrum of [2]rotaxane **P2**.



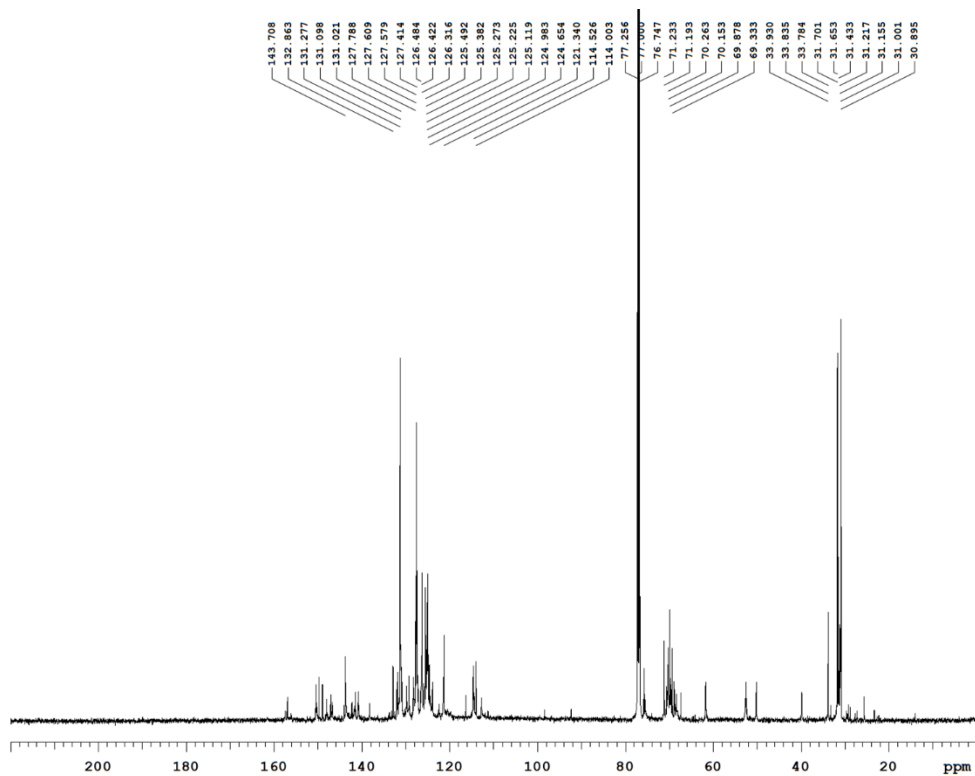
**Figure S44.** 2D-COSY spectrum (500 MHz, 298 K,  $CD_3CN$ ) of [2]rotaxane **P2**.



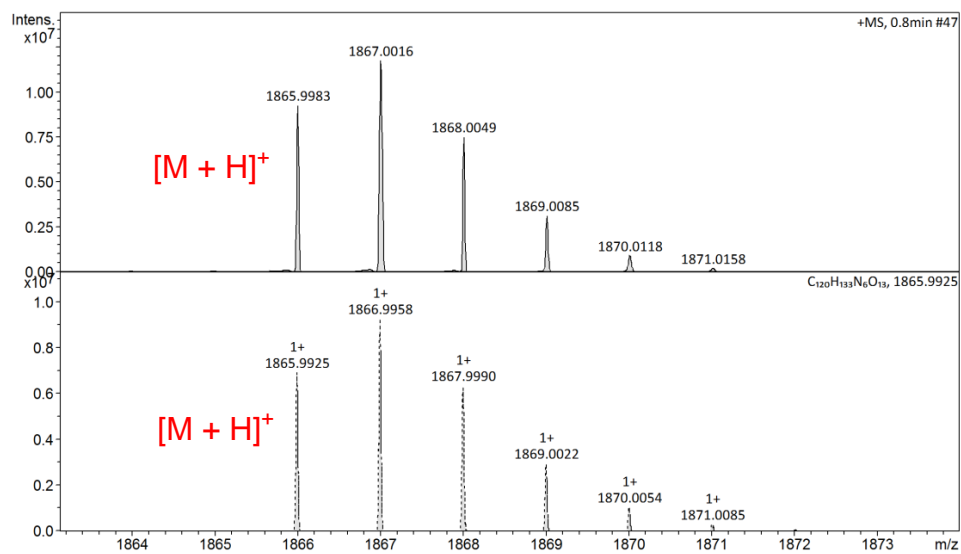
**Figure S45.** 2D ROESY spectrum (600 MHz, 298 K, CD<sub>3</sub>CN) of [2]rotaxane **P2**.



**Figure S46.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of [2]rotaxane **P1-b**.

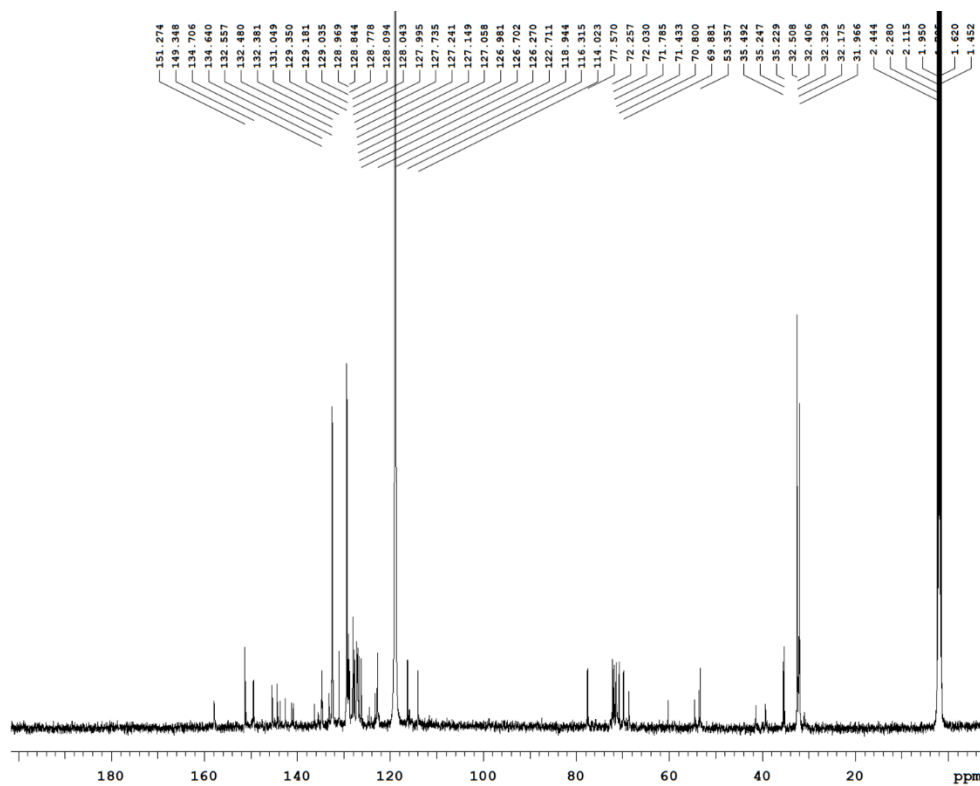


**Figure S47.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of [2]rotaxane **P1-b**.

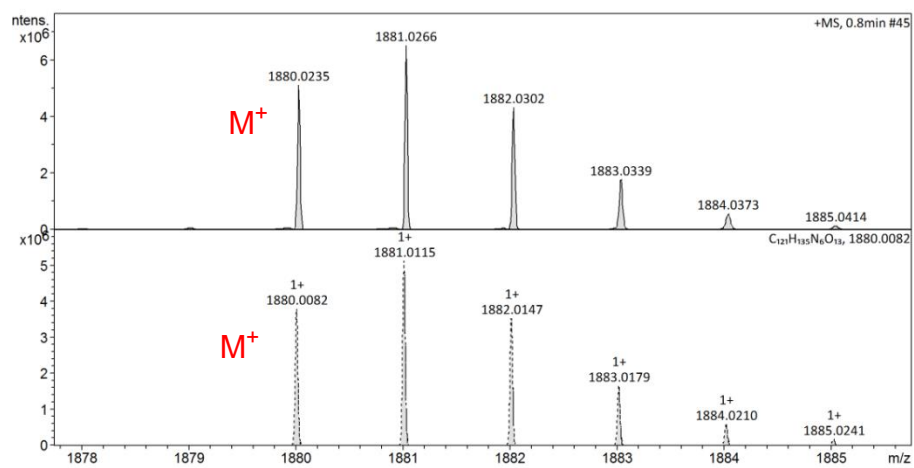


**Figure S48.** HRMS ESI (+)-MS spectrum of [2]rotaxane **P1-b**.

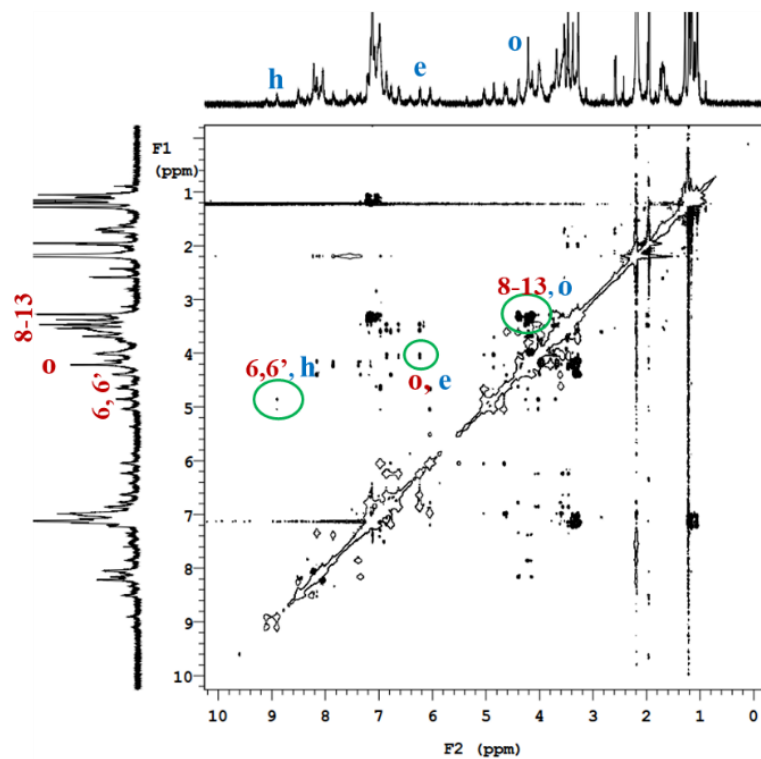




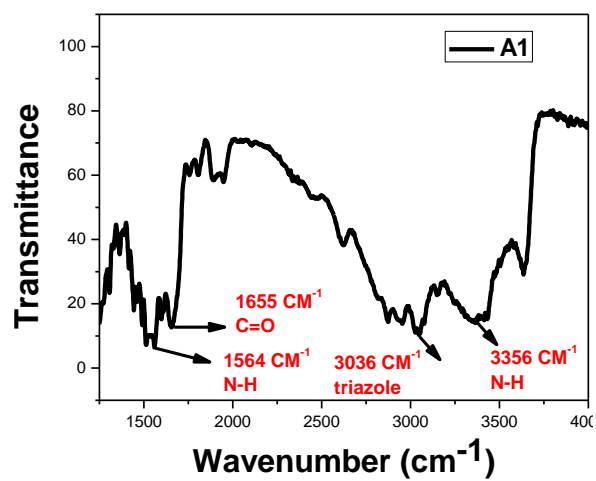
**Figure S51.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of [2]rotaxane **P2-b**.



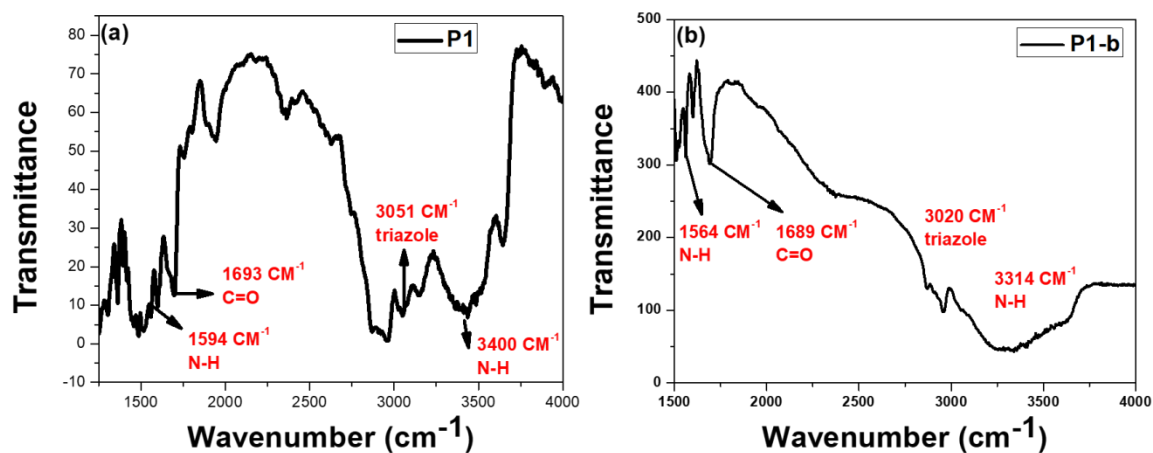
**Figure S52.** HRMS ESI (+)-MS spectrum of [2]rotaxane **P2-b**.



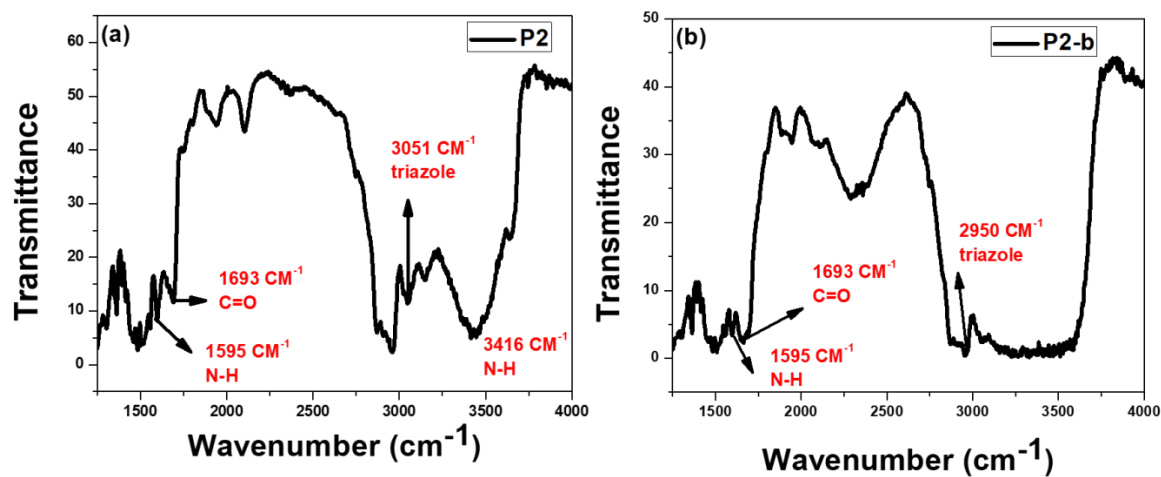
**Figure S53.** 2D ROESY spectrum (600 MHz, 298 K, CD<sub>3</sub>CN) of [2]rotaxane **P2**.



**Figures S54.** FTIR spectrum of compound **A1**.



Figures S55. FTIR spectra of compounds (a) **P1** and (b) **P1-b**.



Figures S56. FTIR spectra of compounds (a) **P2** and (b) **P2-b**.

## References

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