Electronic Supplementary Information

Toward bidirectional photoswitchable colored photochromic molecules with visible light stability

Tian-Guang Zhan, Huan-Huan Yin, Si-Tai Zheng, Wei-Cheng Lin, Nan-Li Shen, Jiecheng Cui, Li-Chun Kong, Li-Juan Liu, and Kang-Da Zhang*

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Science, Zhejiang Normal University, 688 Yingbin Road, Jinhua 321004 (P. R. China), E-mail: Kangda.Zhang@zjnu.cn

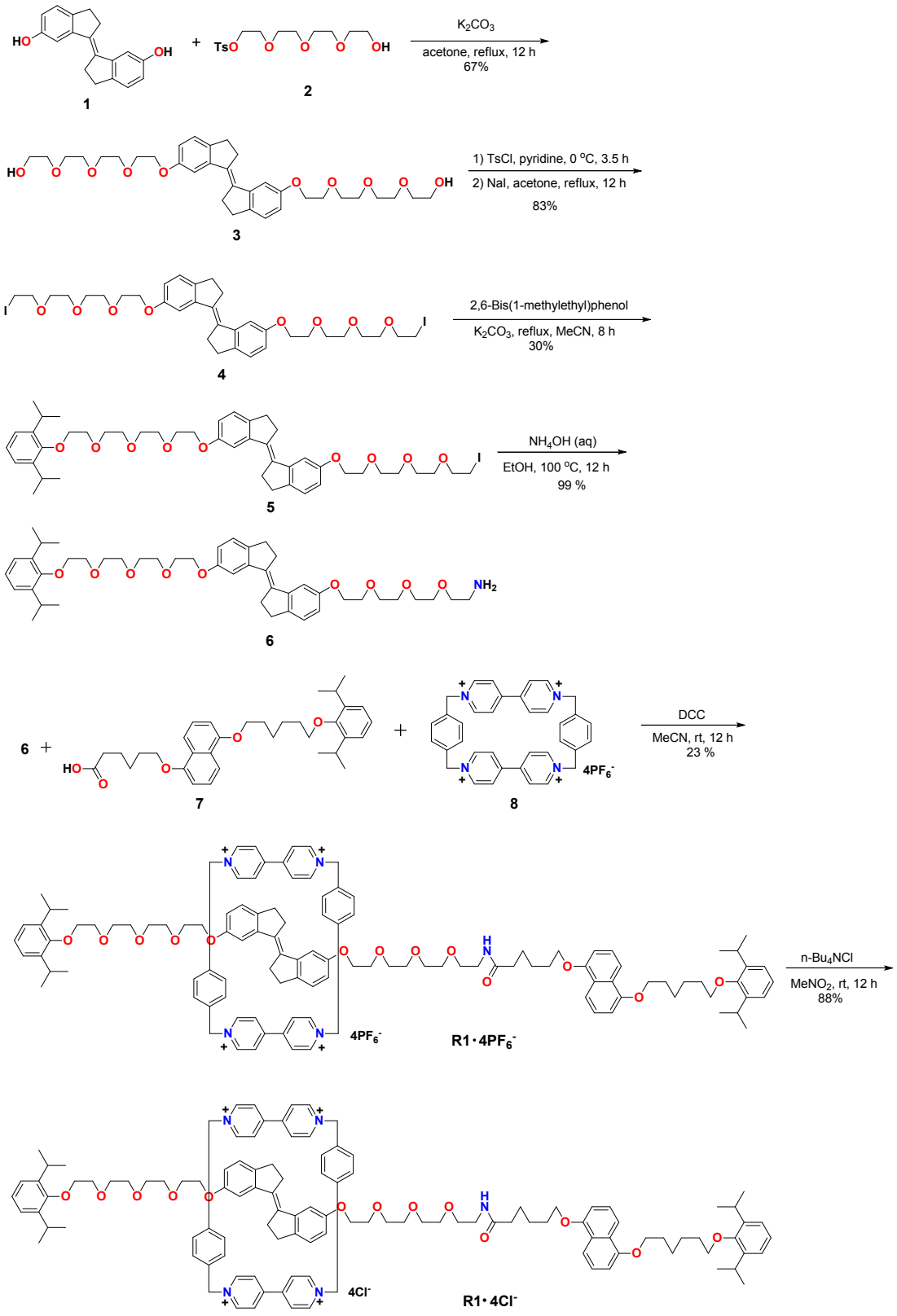
Table of Contents

Section 1: Materials and general methods

All reagents were used as received from the commercial suppliers without further purification; the solvents have been purified by standard procedures before use. Compounds **1**[1], **2**[2], **7**[3], **8**[4], **9**[3], **15**[5] and 1, 5-bis(2-(2-methoxyethoxy)ethoxy) naphthalene (**G1**) [4] were synthesized according to the literatures.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 600 spectrometer. UV-Vis absorption spectra were recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer.

Section 2: Synthetic procedures



Scheme S1. Synthetic route of **R1**.

Compound 3. Compound **1**[2] (2.00 g, 7.57 mmol) and compound **2**[3] (6.59 g, 18.9 mmol) were dissolved in 30 mL acetone, to which K_2CO_3 (6.28 g, 45.4 mmol) was added and the resulting mixture was refluxed for 12 hours under nitrogen atmosphere. After the reaction was completed (monitored by TLC), the reaction mixture was cooled down to room temperature and filtrated. The filtrate was evaporated under vacuum to remove the solvent, and the resulting residue was further purified by flash column chromatography with the binary eluent of PE/EtOAc = 3/1. Compound **3** (3.13 g, 5.08 mmol) could be isolated as yellow solid in the yield of 67%. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.19 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 2.4 Hz, 2H), 6.79 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 2H), 4.18 (t, J = 4.8 Hz, 4H), 3.88 (t, J = 4.8 Hz, 4H), 3.77-3.75 (m, 4H), 3.73-3.69 (m, 8H), 3.68-3.67 (br, 8H), 3.18-3.15 (m, 4H), 3.06-3.02 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 157.69, 144.37, 139.74, 135.75, 125.21, 113.61, 111.03, 72.91, 72.61, 70.75, 70.63, 70.55, 70.51, 70.26, 69.95, 69.87, 67.72, 61.69, 61.53, 32.47, 30.22. MS (ESI) *m/z*: 639.2 $[M + Na]^+$. HRMS (ESI): Calcd for $C_{34}H_{48}NaO_{10}$ $[M + Na]^+$: 639.3140. Found: 639.3179.

Compound 4. The obtained compound **3** (2.00 g, 3.24 mmol) was dissolved in 15 mL anhydrous pyridine together with *p*-toluenesulfonyl chloride (8.02 g, 42.1 mmol), and the resulting mixture was stirred at 0 ^{o}C for 3.5 hours until the reaction was complete. 200 mL water was then added to quench the reaction; the generated sticky liquid was isolated by centrifugation and dissolved in 30 mL CH_2Cl_2. After washing by water (2 × 80 mL) and brine (80 mL) continuously, the organic phase was dried with anhydrous sodium sulfate. The desiccant and solvent were removed by filtration and concentration, respectively, and light yellow solid was obtained. This light yellow compound was further dissolved in 30 mL acetone and refluxed for 12 hours in the presence of NaI (5.06 g, 33.7 mmol). When the iodine substitution reaction was complete as monitored by TLC, the reaction mixture was cooled down and filtrated; the resulting filtrate was then concentrated to remove the solvent. The obtained yellow solid was dissolved in 40 mL CH_2Cl_2 and then washed with water (2 × 80 mL) and brine (80 mL), respectively; the organic phase was dried with anhydrous sodium

sulfate. Filtration was further performed to remove the desiccant and the filtrate was concentrated. The resulting residue was further purified by flash column chromatography using a binary eluent of PE/EtOAc = 3/1. Compound **4** (2.24 g, 2.68 mmol) could be obtained as yellow solid in the yield of 83%. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.19 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 1.8 Hz, 2H), 6.79 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 2H), 4.18 (t, J = 4.2 Hz, 4H), 3.88 (t, J = 4.8 Hz, 4H), 3.77-3.73 (m, 8H), 3.72-3.70 (m, 4H), 3.69-3.65 (m, 8H), 3.25 (t, J = 7.2 Hz, 4H), 3.18-3.14 (m, 4H), 3.06-3.02 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 157.80, 144.37, 139.68, 135.76, 125.21, 113.63, 111.07, 72.00, 70.86, 70.76, 70.68, 70.25, 69.93, 67.77, 32.52, 30.25, 2.99. MS (ESI) *m/z*: 859.2 $[M + Na]^+$. HRMS (ESI): Calcd for $C_{34}H_{46}I_2NaO_8$ $[M + Na]^+$: 859.1174. Found: 859.1187.

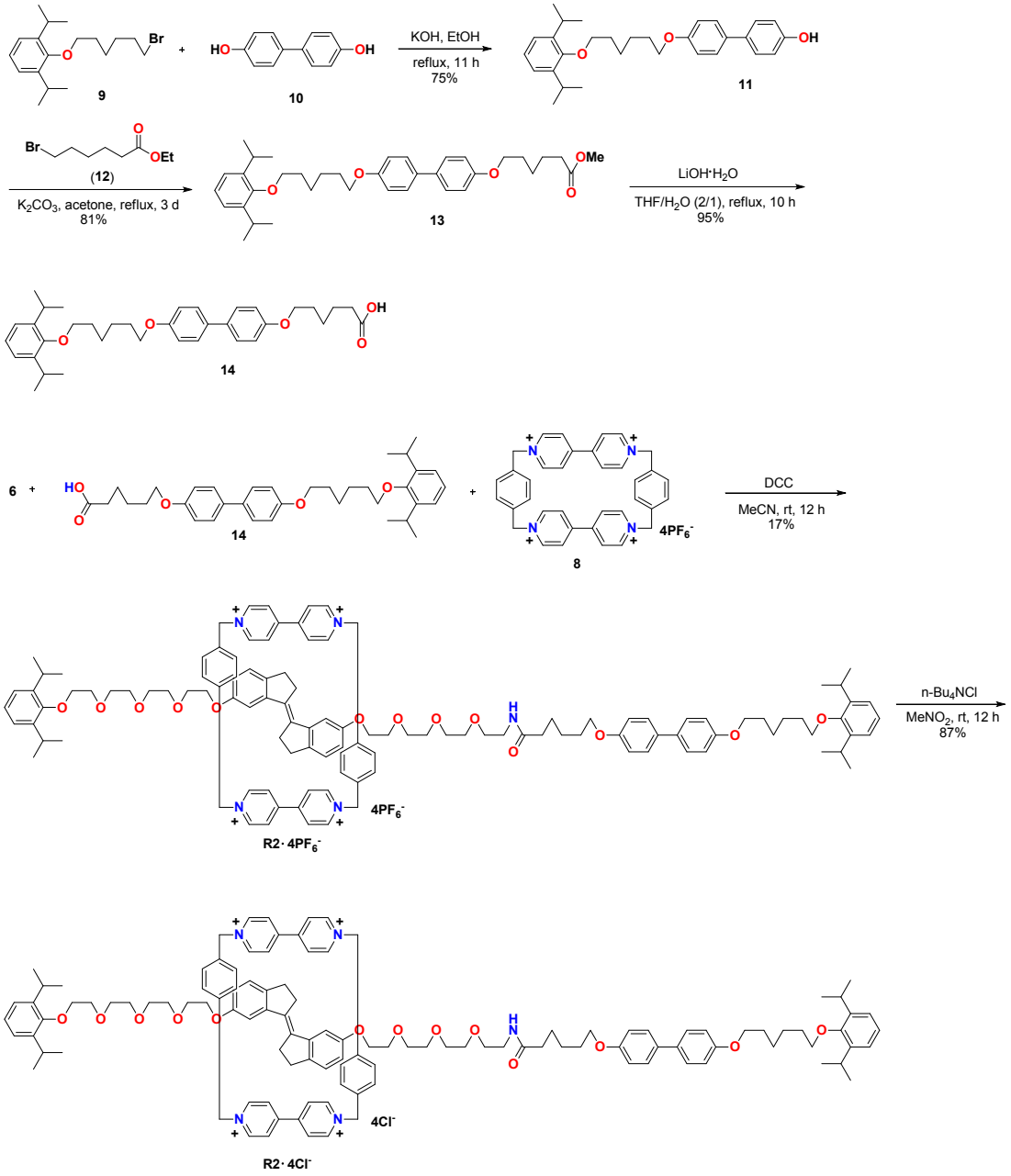
Compound 5. Compound **4** (1.00 g, 1.20 mmol) and 2, 6-bis (1-methylethyl)phenol (0.214 g, 1.20 mmol) were dissolved in 15 mL anhydrous acetonitrile, and K_2CO_3 (0.985 g, 7.13 mmol) was further added, the resulting mixture was refluxed for 8 hours. 60 mL ethyl acetate was further added after the reaction solution was cooled down. The resulting mixture was washed by water (3 × 100 mL) and brine (100 mL), respectively; and the organic phase was dried by Na_2SO_4. The desiccant was removed by filtration and the filtrate was evaporated under vacuum to discard the solvent. The resulting residue was further purified by flash column chromatography using a binary eluent of PE/EtOAc = 2/1. Compound **5** (0.316 g, 0.356 mmol) could be obtained as yellow oil in the yield of 30%. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.20-7.16 (m, 4H), 7.09 (br, 3H), 6.81-6.78 (m, 2H), 4.18 (t, J = 4.8 Hz, 4H), 3.92-3.88 (m, 6H), 3.86-3.84 (m, 2H), 3.78-3.70 (m, 14H), 3.69-3.65 (m, 4H), 3.38 (septet, J = 7.2 Hz, 2H), 3.25 (t, J = 7.2 Hz, 2H), 3.18-3.14 (m, 4H), 3.06-3.02 (m, 4H), 1.21 (d, J = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 157.79, 153.04, 144.38, 144.37, 141.85, 139.69, 139.68, 135.77, 135.75, 125.20, 124.63, 124.01, 113.63, 111.07, 73.86, 72.00, 71.04, 70.86, 70.79, 70.75, 70.67, 70.57, 70.25, 69.93, 69.91, 67.78, 67.76, 32.51, 30.23, 26.23, 24.15, 2.96. MS (ESI) *m/z*: 887.4 $[M + H]^+$. HRMS (ESI): Calcd for $C_{46}H_{63}INaO_9$ $[M + Na]^+$: 909.3414. Found: 909.3431.

Compound 6. Compound **5** (0.039 g, 0.044 mmol) was dissolved in the binary solvent of ethanol and aqueous ammonia (v/v, 6 ml / 2 ml), the resulting mixture was sealed in a tube and heated at 100 °C for 12 hours. After cooling down to room temperature, the reaction mixture was evaporated to remove the solvent. The remaining yellow solid was dissolved in 10 mL ethyl acetate and subsequently washed by saturated $NaHCO_3$ aqueous solution (3 × 30 mL), then dried with Na_2SO_4. The desiccant and solvent were removed by filtration and concentration, respectively. After dried under vacuum, compound **6** (0.0337 g, 0.0434 mmol) was prepared as yellow solid in the yield of 99%. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.21-7.16 (m, 4H), 7.09 (br, 3H), 6.81-6.77 (m, 2H), 4.19-4.16 (m, 4H), 3.92-3.83 (m, 8H), 3.78-3.73 (m, 10H), 3.72-3.69 (m, 2H), 3.68-3.63 (m, 4H), 3.57 (t, *J* = 4.8 Hz, 2H), 3.38 (septet, *J* = 7.2 Hz, 2H), 3.19-3.13 (m, 4H), 3.06-3.01 (m, 4H), 2.91 (t, *J* = 4.8 Hz, 2H), 1.21 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 157.81, 157.70, 153.06, 144.42, 144.34, 141.84, 139.81, 139.68, 135.82, 135.69, 125.26, 125.19, 124.62, 124.00, 113.71, 113.66, 111.08, 111.06, 73.86, 71.93, 71.03, 70.79, 70.78, 70.73, 70.56, 70.55, 70.27, 69.91, 69.87, 67.90, 67.77, 41.39, 32.50, 32.49, 30.23, 30.22, 26.23, 24.13. MS (ESI) *m/z*: 776.5 $[M + H]^+$. HRMS (ESI): Calcd for $C_{46}H_{66}NO_9$ $[M + H]^+$: 776.4732. Found: 776.4749.

Bistable [2]Rotaxane R1·4PF$_6$. Compound **6** (0.240 g, 0.309 mmol), compound **7**[4] (0.182 g, 0.340 mmol) and compound **8**[5] (0.500 g, 0.454 mmol) were dissolved in 3 mL anhydrous CH_3CN, the resulting mixture was stirred at room temperature for 20 min. DCC (0.100 g, 0.485 mmol) was then added and keep stirring for another 12 hours. The solvent was removed by evaporating under vacuum, and the remaining residue was further purified by flash column chromatography using a ternary solvent of MeOH / H_2O / saturated NH_4Cl (a.q) = 6/3/1 as the eluent. The blue solid was collected and dissolved in 30 mL of the binary solvent of MeOH / H_2O (v/v, 1/2), to which saturated NH_4PF_6 aqueous solution was added. The blue precipitates were collected by filtration and washed with 20 mL water. After dried under vacuum, [2]rotaxane **R1·4PF$_6$** (0.170 g, 0.0711 mmol) was offered as blue solid in the yield of

23%. ^{1}H NMR (600 MHz, CD_3CN, 298 K) δ: 8.72 (s, 8H), 7.98 (s, 8H), 7.35 (s, 8H), 7.22-7.18 (m, 2H), 7.16-7.07 (m, 4H), 6.90-6.50 (m, 5H), 6.42 (br, 2H), 6.14 (br, 2H), 5.74 (m, 8H), 4.17-4.01 (m, 8H), 3.84 (t, *J* = 6.0 Hz, 2H), 3.86-3.82 (m, 6H), 3.77-3.59 (m, 16H), 3.55 (t, *J* = 4.8 Hz, 2H), 3.50-3.44 (m, 6H), 3.02-2.78 (m, 8H), 2.41 (t, *J* =6.6 Hz, 2H), 2.25 (m, 2H), 2.15-2.05 (m, 4H), 1.91 (m, 4H), 1.78-1.66 (m, 4H), 1.29 (d, *J* = 6.6 Hz, 12H), 1.19 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (150 MHz, CD_3CN, 298 K) δ: 173.48, 157.55, 153.47, 153.46, 153.08, 153.07, 152.02, 151.87, 145.01, 144.19, 143.87, 143.82, 141.89, 141.88, 139.60, 139.56, 136.63, 135.67, 1.35.62, 131.22, 127.84, 125.34, 125.22, 124.74, 124.64, 124.10, 124.05, 113.48, 110.47, 104.55, 104.38, 74.88, 73.96, 70.52, 70.48, 70.39, 70.37, 70.32, 70.13, 69.98, 69.48, 69.46, 69.29, 68.54, 68.52, 67.75, 67.73, 64.88, 39.04, 35.58, 32.11, 32.02, 30.50, 29.58, 29.57, 29.43, 29.18, 26.27, 25.98, 25.95, 25.91, 25.59, 25.59, 25.16, 23.46, 23.38. MS (ESI) *m/z*: 652.4 $[M\text{-}3PF_6^-]^{3+}$. HRMS (ESI): Calcd for $C_{116}H_{141}F_6N_5O_{13}P$ $[M\text{-}3PF_6^-]^{3+}$: 652.3391. Found: 652.3424.

Bistable [2]Rotaxane R1·4Cl. The obtained [2]rotaxane **R1·4PF$_6$** (0.100 g, 0.0418 mmol) was dissolved in 5 mL CH_3NO_2, to which a solution of NH_4Cl (0.800 g, 2.88 mmol) in 3 mL CH_3NO_2 was added. The resulting suspension was stirring for 12 hours at room temperature. The blue precipitates were then collected by filtration and further washed 10 mL CH_3NO_2. After dried under vacuum, [2]rotaxane **R1·4Cl** (0.0719 g, 0.0368 mmol) was prepared as blue solid in the yield of 88%.



Scheme S2. Synthetic route of **R2**.

Compound 11. Compound **9**[4] (1.57 g, 4.60 mmol) and compound **10** (5.56 g, 29.9 mmol) were dissolved in 60 mL anhydrous ethanol, and KOH (1.67 g, 29.8 mmol) was further added. The resulting mixture was refluxed under nitrogen atmosphere for 11 hours until the reaction was complete. After cooling down, 50 mL ethyl acetate was added to quench the reaction. The solid in the mixture was removed by filtration and the filtrate was further washed by water (3 × 40 mL), and the organic phase was dried with Na_2SO_4. After discarding the desiccant by filtration, the solvent was

evaporated under vacuum and the remaining reside was further purified by flash column chromatography eluted with a binary solvent of PE / EtOAc (v/v, 10/1). Compound **11** (1.54 g, 3.40 mmol) could be obtained as white solid in the yield of 75%. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.15-7.10 (m, 3H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.26 (s, 1H), 4.04 (t, *J* = 6.6 Hz, 2H), 3.79 (t, *J* = 6.6 Hz, 2H), 3.35 (septet, *J* = 7.2 Hz, 2H), 1.93-1.87 (m, 4H), 1.67-1.57 (m, 4H), 1.26 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 158.20, 154.69, 153.31, 141.88, 133.68, 133.34, 127.96, 127.73, 124.50, 124.03, 115.65, 114.79, 74.88, 68.01, 30.40, 29.32, 26.45, 26.09, 25.97, 24.20. MS (ESI) *m/z*: 439.3 $[M + Na]^+$. HRMS (ESI): Calcd for $C_{30}H_{38}NaO_3$ $[M + Na]^+$: 469.2713. Found: 469.2738.

Compound 13. Compound **11** (1.47 g, 3.29 mmol) and compound **12** (0.827 g, 3.96 mmol) were dissolved in 60 mL acetone, to which K_2CO_3 (1.82 g, 13.2 mmol) was added, the resulting mixture was then refluxed under nitrogen atmosphere for 3 days. After the completion of the reaction suggested by TLC monitoring, it was allowed to cool down. Filtration was performed and the filtrate was concentrated by evaporation under vacuum. The remaining white solid was further dissolved in 50 mL CH_2Cl_2 and washed with water (3 × 50 mL) and brine (50 mL) consecutively, and the organic phase was then dried by Na_2SO_4. The desiccant and solvent were removed by filtration and concentration, respectively. The resulting residue was further purified by flash column chromatography using binary solvent of PE/EtOAc (v/v, 10/1) as eluent. Compound **13** (1.53 g, 2.66 mmol) was prepared as white solid in the yield of 81%. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.50-7.47 (m, 4H), 7.14-7.08 (m, 3H), 6.99-6.94 (m, 4H), 4.04 (t, *J* = 6.6 Hz, 2H), 4.01 (t, *J* = 6.6 HZ, 2H), 3.78 (t, *J* = 6,6 Hz, 2H), 3.70 (s, 3H), 3.35 (septet, *J* = 7.2 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.93-1.82 (m, 6H), 1.76-1.71 (m, 2H), 1.66-1.58 (m, 4H), 1.57-1.51 (m, 2H), 1.26 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 174.13, 158.22, 158.15, 153.43, 141.85, 133.43, 133.38, 127.72, 127.71, 124.42, 123.98, 114.75, 74.77, 67.95, 67.72, 51.56, 34.03, 30.44, 29.35, 29.03, 26.45, 25.99, 25.73, 24.75, 24.18. MS (ESI) *m/z*: 575.4 [M

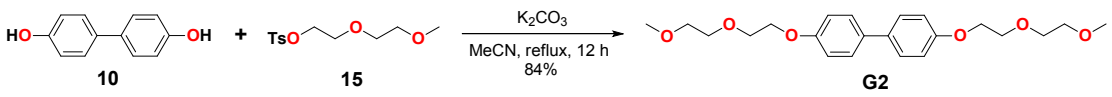
+ H]$^+$. HRMS (ESI): Calcd for $C_{37}H_{54}NO_5$ [M + NH_4]$^+$: 592.3997. Found: 592.4049.

Compound 14. Compound **13** (1.31 g, 2.28 mmol) were dissolved in 40 mL THF, to which 20 mL aqueous solution containing LiOH·H_2O (2.14 g, 52.2 mmol) was added, and the resulting mixture was refluxed for 10 hours. After the reaction was completed as monitored by TLC, cooling down and the reaction mixture was acidified to pH = 2~3 with aqueous 1 M HCl (a.q.) solution. The acidic mixture was further extracted by 60 mL ethyl acetate, and the organic phase was then washed with water (3 × 50 mL) and brine (50 mL) consecutively, and then dried with Na_2SO_4. The desiccant and solvent were removed by filtration and concentration, respectively. After drying, compound **14** (1.21 g, 2.17 mmol) could be obtained as white solid in the yield of 95%. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.48-7.45 (m, 4H), 7.12-7.08 (m, 3H), 6.95 (t, *J* = 8.4 Hz, 4H), 4.03 (t, *J* = 6.0 Hz, 2H), 4.00 (t, *J* = 6.0 Hz, 2H), 3.76 (t, *J* = 6.6 Hz, 2H), 3.33 (septet, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.91-1.81 (m, 6H), 1.74 (quintet, *J* = 7.8 Hz, 2H), 1.65-1.53 (m, 6H), 1.23 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 158.19, 158.11, 153.40, 141.84, 133.45, 133.36, 127.71, 124.39, 123.97, 114.74, 74.76, 67.95, 67.69, 33.89, 30.41, 29.33, 29.00, 26.43, 25.97, 25.65, 24.46, 24.15. MS (ESI) *m/z*: 561.3 [M + H]$^+$. HRMS (ESI): Calcd for $C_{36}H_{48}NaO_5$ [M + Na]$^+$: 583.3394. Found: 583.3438.

Bistable [2]Rotaxne R2·4PF$_6$. Compound **6** (0.240 g, 0.309 mmol), compound **14** (0.198 g, 0.353 mmol) and compound **8** (0.500 g, 0.454 mmol) were dissolved in 3 mL anhydrous CH_3CN, the resulting mixture was stirred at room temperature for 20 min. DCC (0.106 g, 0.515 mmol) was then added and keep stirring for another 12 hours. The solvent was removed by evaporating under vacuum, and the remaining residue was further purified by flash column chromatography using a ternary solvent of MeOH / H_2O / saturated NH_4Cl (a.q) = 6/3/1 as the eluent. The gray solid was collected and dissolved in 30 mL of the binary solvent of MeOH / H_2O (v/v, 1/2), to which saturated NH_4PF_6 aqueous solution was added. The gray precipitates were collected by filtration and washed with 20 mL water, then dried under vacuum.

[2]rotaxane **R2·4PF$_6$** (0.127 g, 0.0525 mmol) was produced as gray solid in the yield of 17%. ^{1}H NMR (600 MHz, CD_3COCD_3, 298 K) δ: 9.45 (s, 8H), 8.25 (s, 8H), 8.14 (br, 8H), 7.39 (s, 1H), 7.18-7.15 (m, 2H), 7.13-7.06 (m, 4H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.56 (br, 3H), 6.18-6.10 (m, 8H), 5.76 (br, 3H), 4.16-4.06 (m, 6H), 3.95 (t, *J* = 6.0 Hz, 2H), 3,91-3.88 (m, 6H), 3.86-3.65 (m, 20H), 3.59 (t, *J* = 6.0 Hz, 2H), 3.47-3.38 (m, 6H), 2.98 (br, 8H), 2.35 (t, *J* = 6.0 Hz, 2H), 1.99-1.91 (m, 4H), 1.85 (quintet, *J* = 6.6 Hz, 2H), 1.80-1.66 (m, 6H), 1.64-1.59 (m, 2H), 1.27 (d, *J* = 6.6 Hz, 12H), 1.20 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (150 MHz, CD_3CN, 298 K) δ: 173.60, 158.98, 158.05, 157.57, 153.46, 153.08, 147.28, 144.50, 143.96, 143.91, 141.88, 139.63, 139.59, 137.23, 135.68, 130.76, 128.98 (br), 126.66, 126.59, 126.44, 125.46, 125.35, 125.19 (br), 125.06, 124.75, 124.59, 124.05, 115.03, 114.51, 113.45, 110.53, 74.76, 73.99, 73.97, 70.49, 70.35, 70.30, 70.13, 70.11, 70.06, 70.01, 69.49, 69.48, 69.25, 68.29, 67.75, 64.72, 39.10, 35.70, 32.14, 32.10, 30.23, 29.64, 29.63, 29.28, 28.41, 26.24, 25.96, 25.92, 25.90, 25.39, 25.03, 23.45, 23.43. MS (ESI) *m/z*: 459.8 [M-4PF$_6^-$]$^{4+}$. HRMS (ESI): Calcd for $C_{118}H_{143}F_{12}N_5O_{13}P_2$ [M-2PF$_6^-$]$^{2+}$: 1063.9989. Found: 1064.0039.

Bistable [2]Rotaxne R2·4Cl. The obtained [2]rotaxane **R2·4PF$_6$** (0.0820 g, 0.0339 mmol) was dissolved in 4 mL CH_3NO_2, to which CH_3NO_2 solution containing NH_4Cl (0.600 g, 2.16 mmol) was added. The resulting mixture suspension was stirring for 12 hours at room temperature. The gray precipitates were then collected by filtration and further washed 10 mL CH_3NO_2. After dried under vacuum, [2]rotaxane **R2·4Cl** (0.0584 g, 0.0295 mmol) was prepared as gray solid in the yield of 87%.



Scheme S3. The synthesis of **G2**.

4, 4'-bis(2-(2-methoxyethoxy)ethoxy)-1, 1'-biphenyl (G2). Compound **10** (0.681 g, 3.66 mmol), compound **15**[5] (2.00 g, 0.454 mmol) and K_2CO_3 (3.04 g, 22.0 mmol)

were mixed in 20 mL anhydrous CH_3CN, the resulting suspension was refluxed for 12 hours. After the reaction was complete as monitored by TLC, the reaction mixture was cooling down to room temperature. The precipitates was discard by filtration and the filtrate was concentrated to offer white solid, which was further dissolved in 50 mL ethyl acetate and washed with water (3 × 80 mL) and brine (100 mL) successively, and the organic phase was dried by Na_2SO_4. The desiccant and solvent were removed by filtration and evaporation, respectively. The resulting residue was further purified by flash column chromatography with a binary eluent of PE / EtOAc = 3:1, compound 4, 4'-bis(2-(2-methoxyethoxy)ethoxy)-1, 1'-biphenyl (**G2**) (1.20 g, 3.07 mmol) was prepared as white solid in the yield of 84%. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ: 7.45 (d, *J* = 8.4 Hz, 4H), 6.96 (d, *J* = 8.4 Hz, 4H), 4.17 (t, *J* = 4.8 Hz, 4H), 3.89-3.86 (m, 4H), 3.74-3.72 (m, 4H), 3.60-3.57 (m, 4H), 3.39 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ: 157.92, 133.59, 127.66, 114.91, 71.98, 70.78, 69.81, 67.52, 59.10. MS (ESI) *m/z*: 391.3 $[M + H]^+$. HRMS (ESI): Calcd for $C_{22}H_{31}O_6$ $[M + H]^+$: 391.2115. Found: 391.2109.

Section 3: Temperature-varied ^{1}H NMR spectra of R1·4PF$_6$ and R2·4PF$_6$

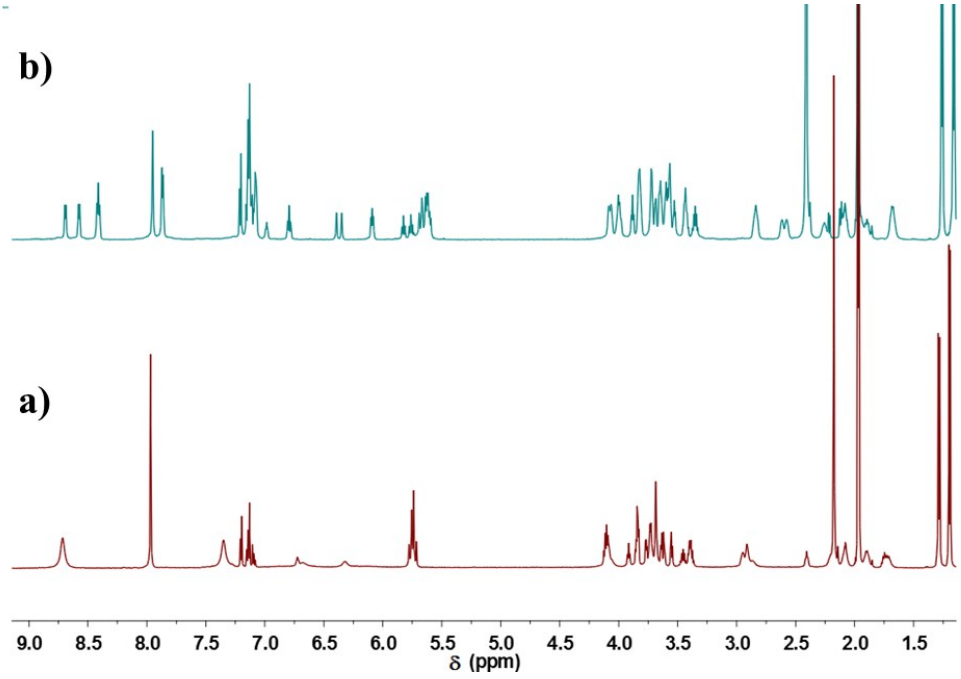


Fig. S1 Temperature-varied ^{1}H NMR spectra (600 MHz, 2.0 mM) of recorded the [2] rotaxane **R1·4PF$_6$** at a) 298 K; and b) 233 K in CD_3CN.

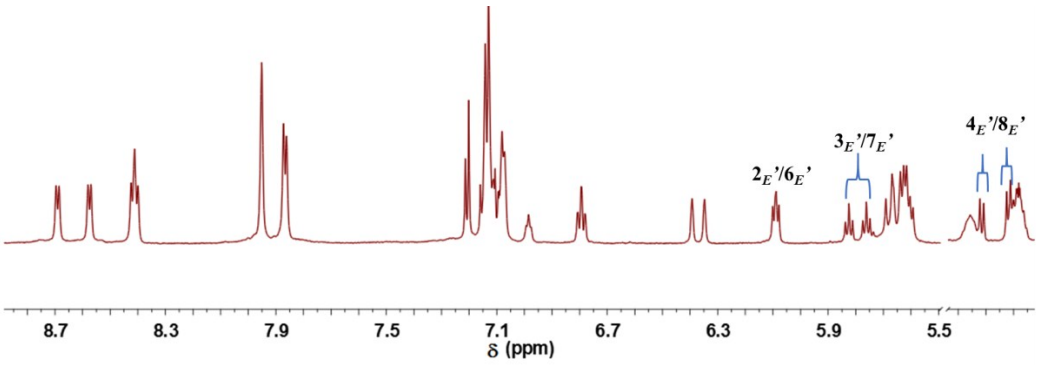


Fig. S2 Partial ^{1}H NMR spectra (600 MHz, 5 mM) of **R1·4PF$_6$** at 233 K in CD_3CN.

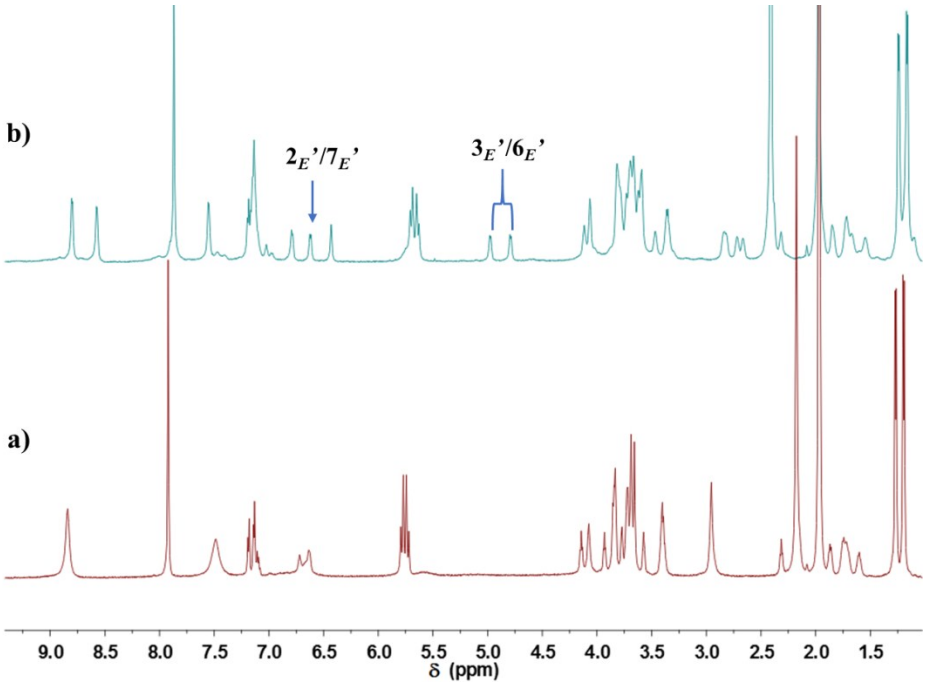


Fig. S3 Temperature-varied ^{1}H NMR spectra (600 MHz, 2.0 mM) of recorded the [2] rotaxane **R2·4PF$_6$** at a) 298 K; and b) 233 K in CD_3CN.

Section 4: Solvent-dependent spectral properties of R1·4PF$_6$ and R2·4PF$_6$

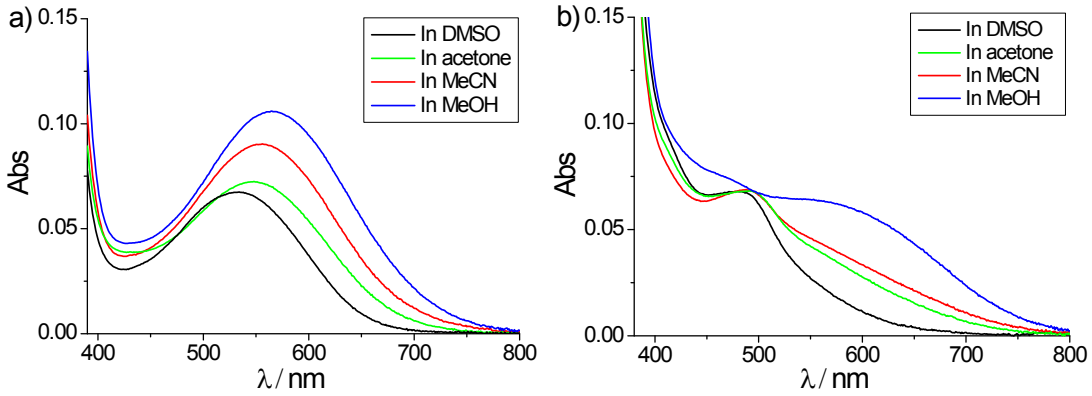


Fig. S4 UV/Vis absorption spectra of a) **R1·4PF$_6$** (0.10 mM) and (b) **R2·4PF$_6$** (0.10 mM) in DMSO (black line), acetone (green line), MeCN (red line) and MeOH (blue line) at 20 °C.

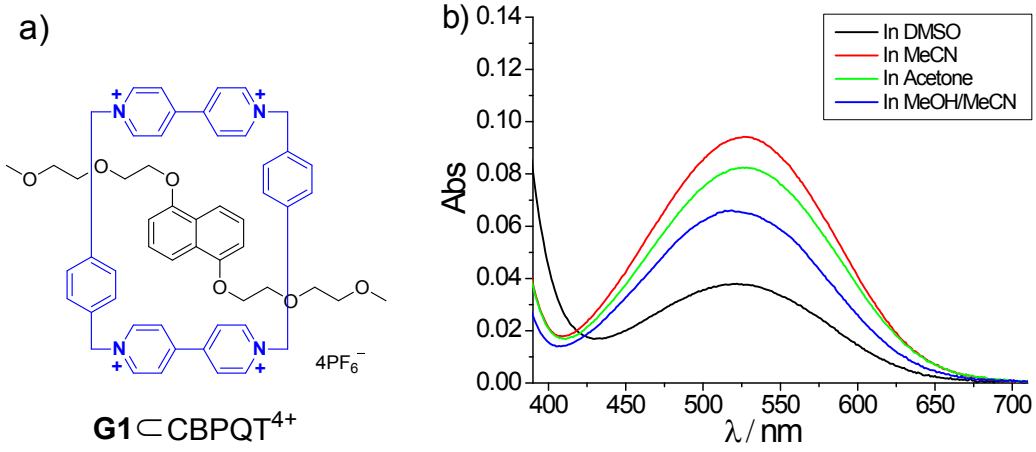


Fig. S5 (a) The structure of **G1**⊂CBPQT·4PF$_6$ complex and (b) the UV/Vis absorption spectra for the mixture of **G1** (0.20 mM) and CBPQT·4PF$_6$ (0.20 mM) in DMSO (black line), MeCN (red line), acetone (green line), and MeOH / MeCN (v/v, 4 / 1) (blue line) at 20 °C.

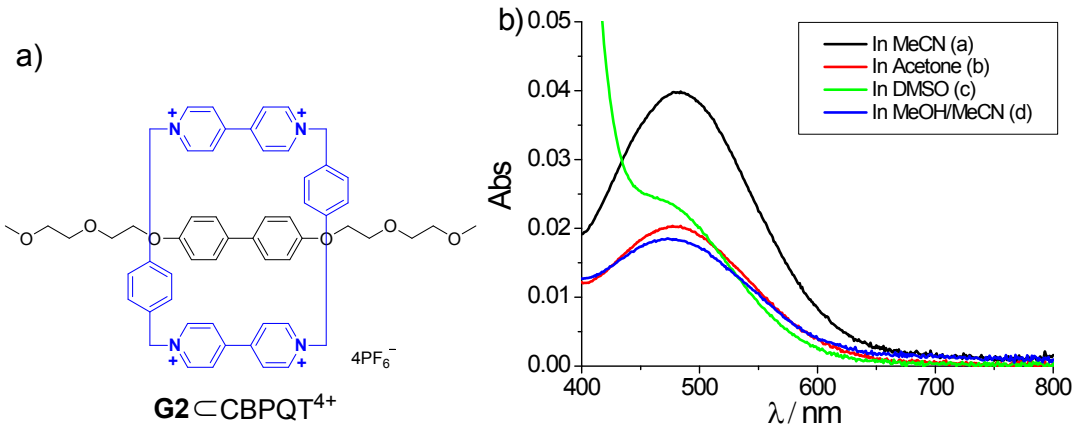


Fig. S6 (a) The structure of **G2**⊂CBPQT·4PF_6 complex and (b) the UV/Vis absorption spectra for the mixture of **G2** (1.0 mM) and CBPQT·4PF_6 (0.60 mM) in MeCN (black line), acetone (red line), DMSO (green line), and MeOH/MeCN (v/v, 4/1) (blue line) at 20 °C.

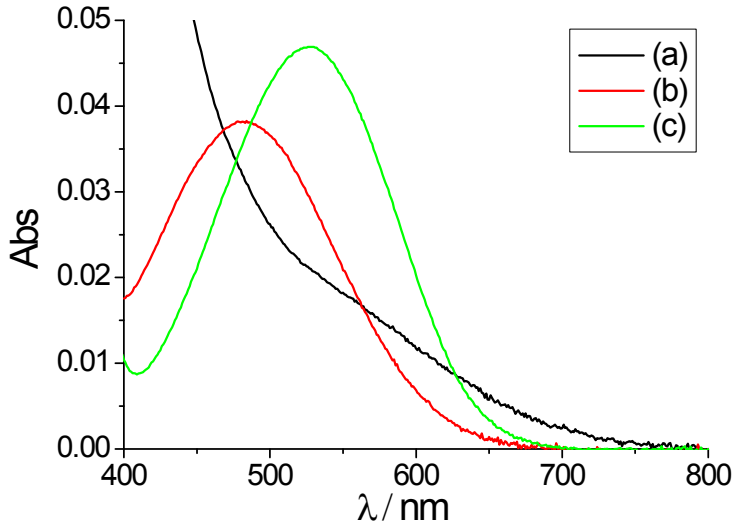


Fig. S7 UV/Vis absorption spectra for the mixtures of a) compound **3** (1.0 mM) and CBPQT·4PF_6 (0.60 mM), b) **G2** (1.0 mM) and CBPQT·4PF_6 (0.60 mM), and c) **G1** (0.12 mM) and CBPQT·4PF_6 (0.12 mM) in MeCN at 20 °C.

Section 5: Temperature-varied ^{1}H NMR spectra of R1·4Cl and R2·4Cl

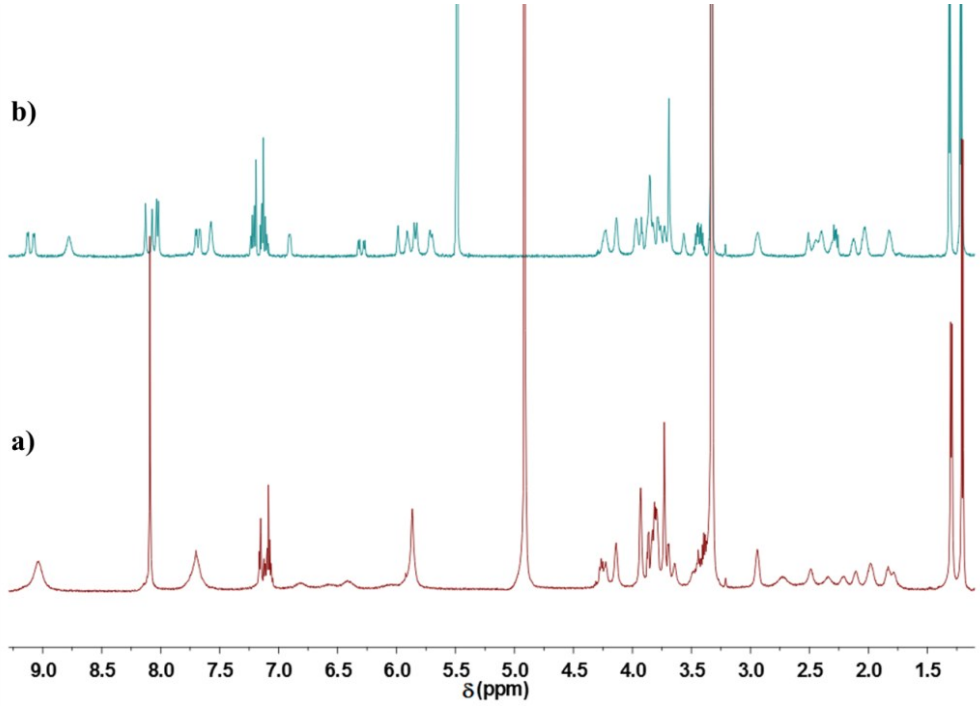


Fig. S8 Temperature-varied ^{1}H NMR spectra (600 MHz, 2.0 mM) of recorded **R1·4Cl** at a) 298 K; and d) 233 K in CD_3OD.

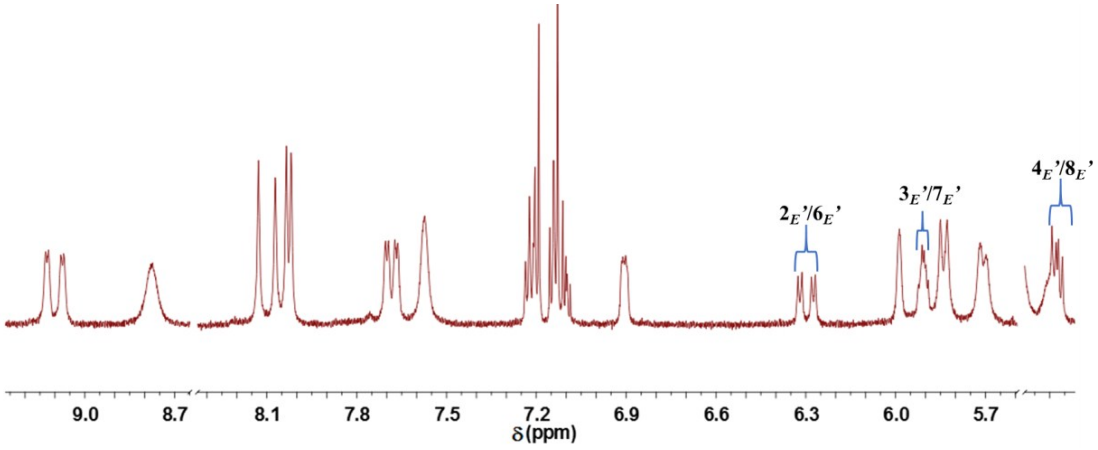


Fig. S9 Partial ^{1}H NMR spectra (600 MHz, 5 mM) of **R1·4Cl** at 233 K in CD_3OD.

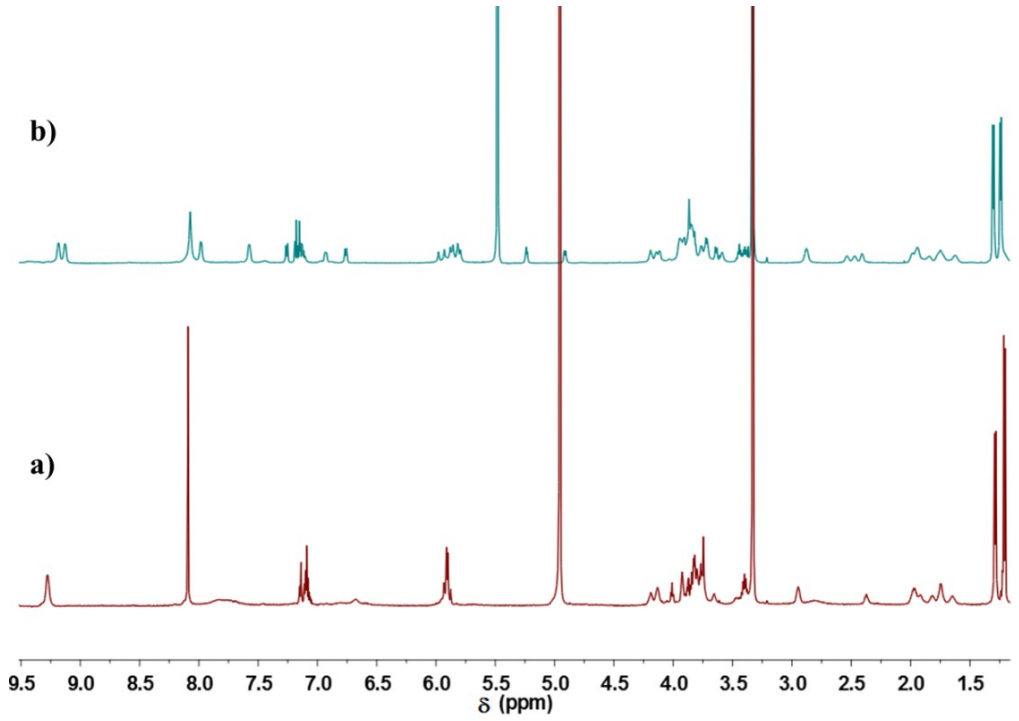


Fig. S10 Temperature-varied ^{1}H NMR spectra (600 MHz, 2.0 mM) of recorded **R2·4Cl** at a) 298 K; and d) 233 K in CD_3OD.

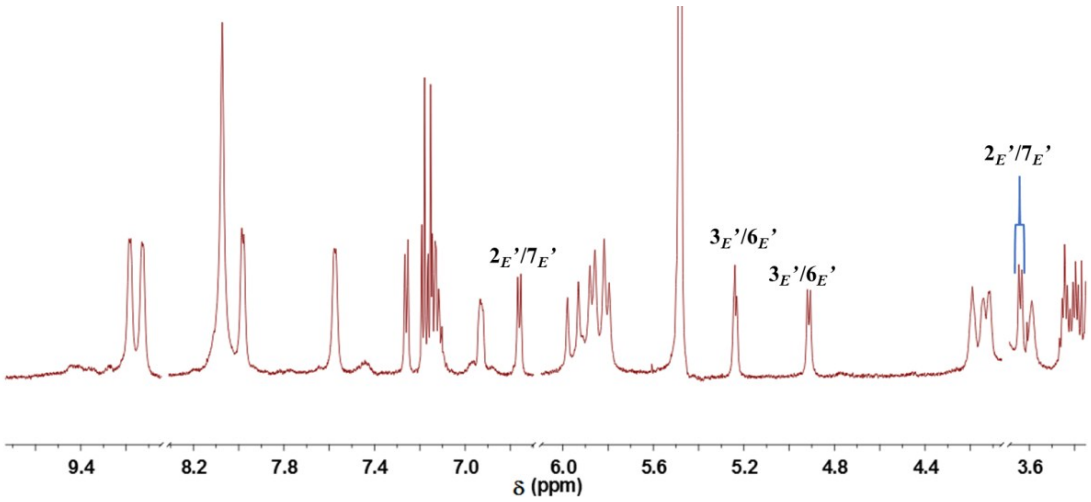


Fig. S11 Partial ^{1}H NMR spectra (600 MHz, 5 mM) of **R2·4Cl** at 233 K in CD_3OD.

Section 6: Photochromic behaviors of R1·4Cl and R2·4Cl in methanol

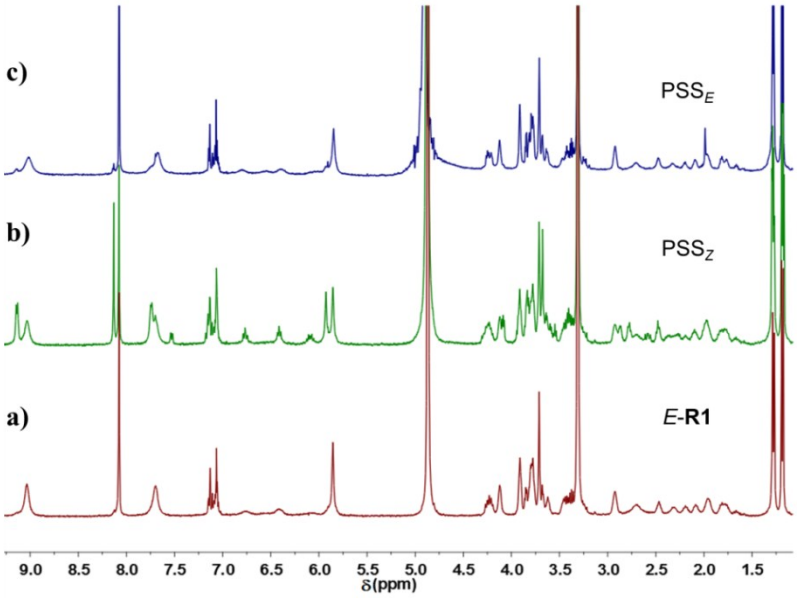


Fig. S12 Partial ^{1}H NMR spectra (600 MHz, CD_3OD, 2.0 mM, 298K) of **R1·4Cl** recorded (a) before irradiation; (b) after irradiation by UV light (λ = 340 nm 1.1 mW / cm^2) for 1.5 h; and (c) the UV-irradiated samples after irradiation with another UV light (λ = 375 nm, 5.2 mW / cm^2) for 1 h.

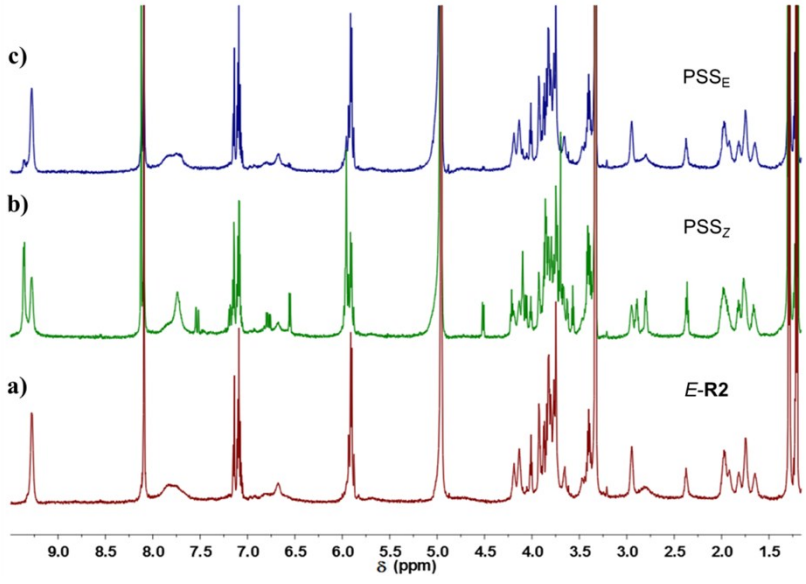


Fig. S13 Partial ^{1}H NMR spectra (600 MHz, CD_3OD, 2.0 mM, 298K) of **R2·4Cl** recorded (a) before irradiation; (b) after irradiation by UV light (λ = 340 nm 1.1 mW / cm^2) for 1.5 h; and (c) the UV-irradiated samples after irradiation with another UV light (λ = 375 nm, 5.2 mW/cm^2) for 1 h.

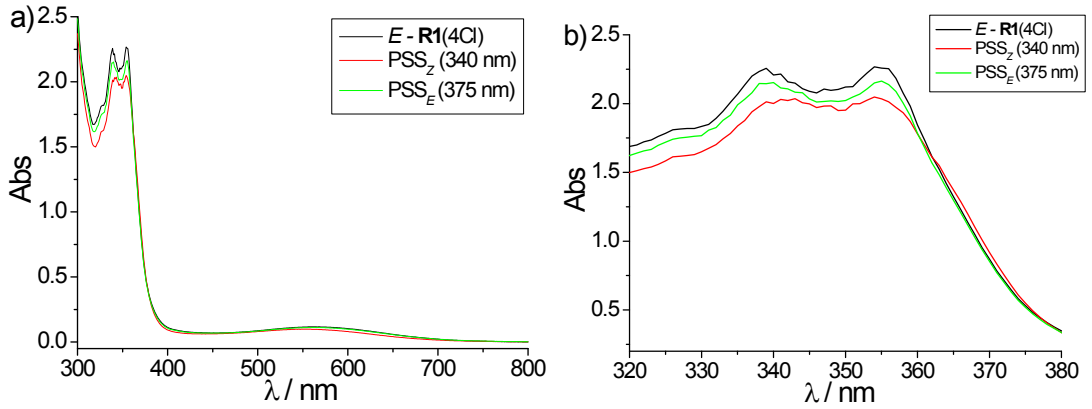


Fig. S14 The (a) full and (b) partial magnified UV/Vis absorption spectra of **R1· 4Cl** (0.10 mM) recorded in MeOH at 20 °C. Black line: before UV irradiation; red line: after UV light (λ = 340 nm, 1.1 mW / cm^2) irradiation of the solution for 20 min; green line: the above UV-irradiated **R1· 4Cl** solution after irradiation with another UV light (λ = 375 nm, 5.2 mW / cm^2) for 15 min.

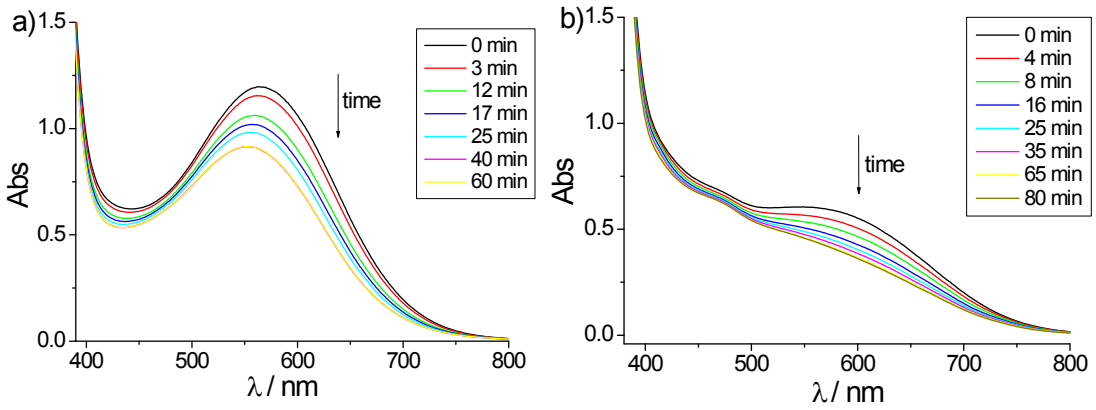


Fig. S15 Time-resolved UV/Vis absorption spectra of 1.0 mM *E*-isomer to PSS$_Z$ of (a) **R1·4Cl** and (b) **R2·4Cl** in MeOH under irradiation at λ = 340 nm at 20 °C.

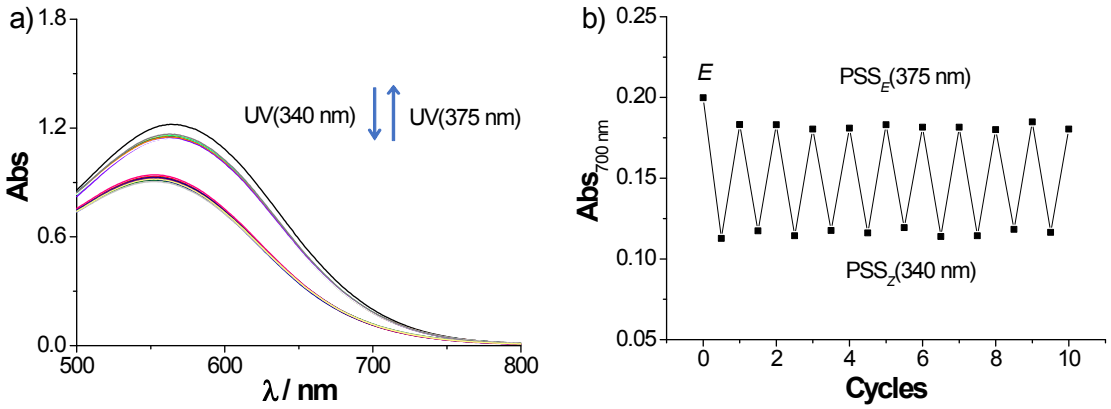


Fig. S16 UV/Vis absorption spectra of **R1•4Cl** (1.0 mM) and (b) plot of corresponding absorption λ at 700 nm after UV irradiation (λ = 340 nm, 1.1 mW / cm^2) in MeOH for 1 h, and UV-irradiated **R1•4Cl** solution after irradiation by another UV light (λ = 375 nm, 5.2 mW / cm^2) for 1 h. The absorption spectra were record at 20 °C, and there is about 10 min interval between each irradiation experiments.

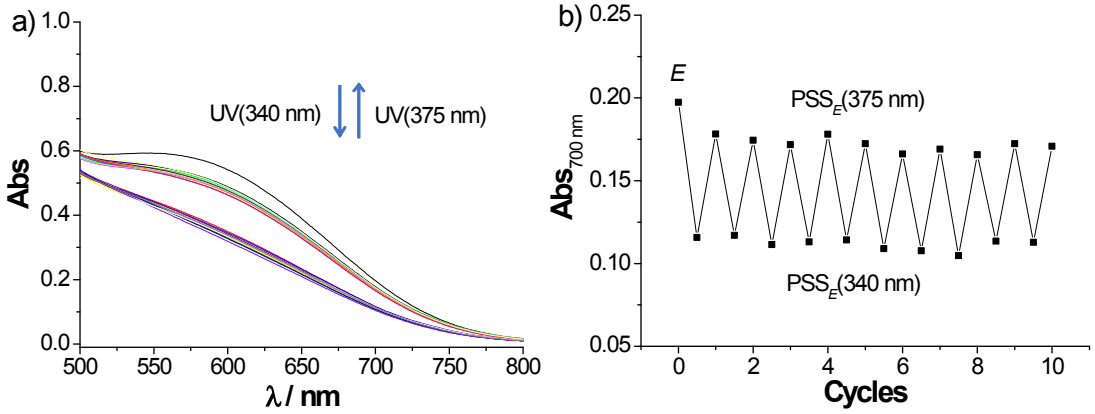


Fig. S17 UV/Vis absorption spectra of **R2•4Cl** (1.0 mM) and (b) plot of corresponding absorption λ at 700 nm after UV irradiation (λ = 340 nm, 1.1 mW / cm^2) in MeOH for 1 h, and UV-irradiated **R2•4Cl** solution after irradiation by another UV light (λ = 375 nm, 5.2 mW / cm^2) for 1 h. The absorption spectra were record at 20 °C, and there is about 10 min interval between each irradiation experiments.

Section 7: Visible light stability of UV-irradiated R1·4Cl and R2·4Cl

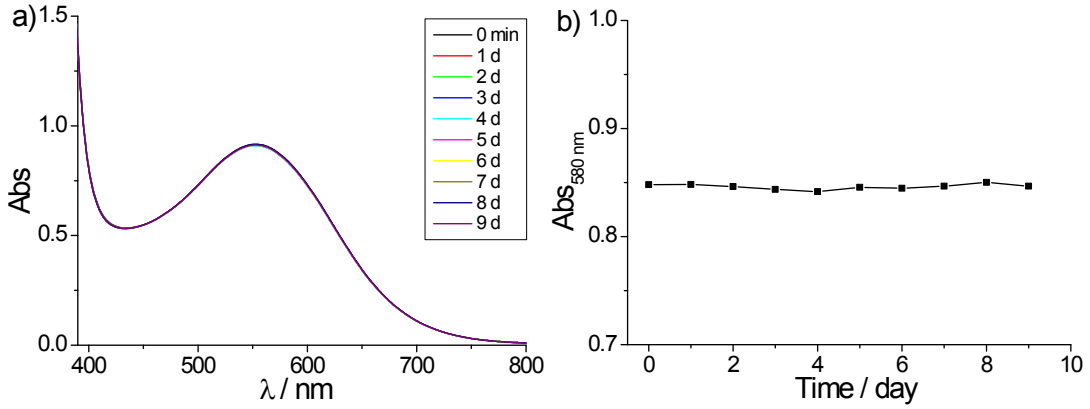


Fig. S18 (a) Time lapse absorption spectra of the PSS_Z solution of **R1·4Cl** (1.0 mM) in MeOH at 20°C under irradiation (λ > 400 nm, 40 mW / cm^2); (b) plot of corresponding absorption at λ = 580 nm versus the recording time.

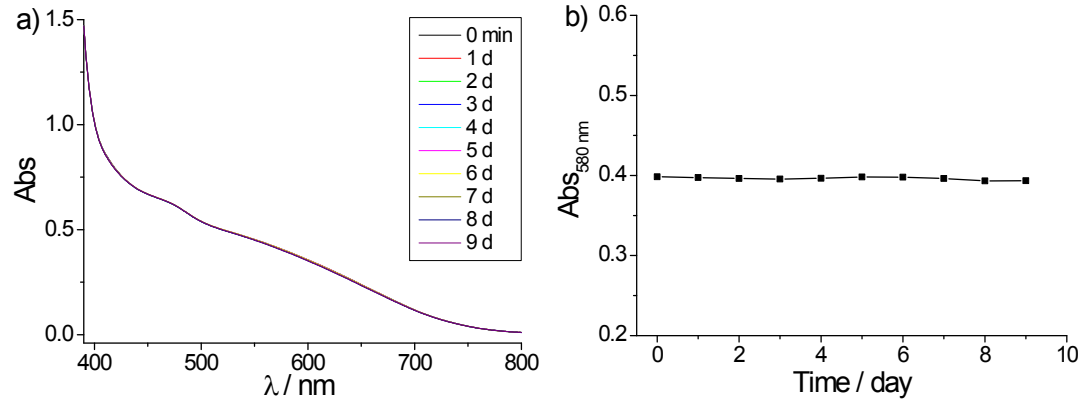


Fig. S19 (a) Time lapse absorption spectra of the PSS_Z solution of **R2·4Cl** (1.0 mM) in MeOH at 20°C under irradiation (λ > 400 nm, 40 mW / cm^2); (b) plot of corresponding absorption at λ = 580 nm versus the recording time.

Section 8: The detailed calculation of thermodynamically stable states of $R1_E$ and $R2_E$

For $\mathbf{R1}_E$:

$$\mathbf{R1}_E\text{(I)} \rightleftharpoons \mathbf{R1}_E\text{(II)}$$

$[1/(1+x)]C^0$ $[x/(1+x)]C^0$

$C^0[R1_E(II)] + C^0[R1_E(I)] = C^0$

$C^0[R1_E(II)] / C^0[R1_E(I)] = x$

$\eta\ [R1_E(I)] = 1/(1+x)$

$A^0_{700\ nm}\ (R1_E) = \varepsilon^{CT}_{700\ nm}\ [R1_E(I)] \times C^0[R1_E(I)] + \varepsilon^{CT}_{700\ nm}[R1_E(II)] \times C^0[R1_E(II)]$

$= \varepsilon^{CT}_{700\ nm}\ [R1_E(I)] \times C^0[R_E(I)]$

($\varepsilon^{CT}_{700\ nm}[R1_E(II)] = 0$, because the CT band of DNP@CBPQT^{4+} in $R1_E$ doesn't have absorption at 700 nm, see Figure S4b)

$A^0_{620\ nm}\ (R1_E) = \varepsilon^{CT}_{620\ nm}\ [R1_E(I)] \times C^0[R1_E(I)] + \varepsilon^{CT}_{620\ nm}[R1_E(II)] \times C^0[R1_E(II)]$

$A^0_{700\ nm}\ (R1_E)/A^0_{620\ nm}\ (R1_E) = \{\varepsilon^{CT}_{700\ nm}\ [R1_E(I)] \times C^0[R_E(I)]\}/\{\ \varepsilon^{CT}_{620\ nm}\ [R1_E(I)] \times C^0[R1_E(I)] + \varepsilon^{CT}_{620\ nm}[R1_E(II)] \times C^0[R1_E(II)]\}$

$= \varepsilon^{CT}_{700\ nm}\ [R1_E(I)]/\{\ \varepsilon^{CT}_{620\ nm}\ [R1_E(I)] + \varepsilon^{CT}_{620\ nm}[R1_E(II)] \times x\}$

$\varepsilon^{CT}_{700\ nm}\ [R1_E(I)] = \{\varepsilon^{CT}_{620\ nm}[R1_E(II)] \times x\}/\{[A^0_{620\ nm}\ (R1_E)/\ A^0_{700\ nm}\ (R1_E)] - \varepsilon^{CT}_{620\ nm}\ [R1_E(I)]/\ \varepsilon^{CT}_{700\ nm}\ [R1_E(I)]\}$

$A^0_{700\ nm}\ (R1_E) = \varepsilon^{CT}_{700\ nm}\ [R1_E(I)] \times C^0[R_E(I)]$

$= [(1/1+x) \times C^0] \times \{\varepsilon^{CT}_{620\ nm}[R1_E(II)] \times x\}/\{[A^0_{620\ nm}\ (R1_E)/\ A^0_{700\ nm}\ (R1_E)] - \varepsilon^{CT}_{620\ nm}\ [R1_E(I)]/\varepsilon^{CT}_{700\ nm}\ [R1_E(I)]\}$

For $\mathbf{R1}_E$ in MeOH, x = 0.65, $\eta\ [R1_E(I)] = 0.61$, $\varepsilon^{CT}_{700\ nm}\ [R1_E(I)] = 322\ L{\cdot}mol^{-1}{\cdot}cm^{-1}$.

Notes:

(1) C^0 is the total concentration of $\mathbf{R1}_E$ which has not been irradiated by UV light;

(2) $C^0[\mathbf{R1}_E(I)]$ represents the concentration of $\mathbf{R1}_E$ isomer I;

(3) $C^0[\mathbf{R1}_E(II)]$ refers to the concentration of $\mathbf{R1}_E$ isomer II;

(4) "x" is the ratio of $C^0[\mathbf{R1}_E(II)]$ to $C^0[\mathbf{R1}_E(I)]$;

(5) "η [$R1_E$(I)]" is the ratio of $\mathbf{R1}_{\boldsymbol{E}}$ isomer I in $\mathbf{R1}_{\boldsymbol{E}}$;

(6) $A^0_{700\ nm}$ and $A^0_{620\ nm}$ correspond to absorbance at 700 nm and 620 nm of the solution of $\mathbf{R1}_{\boldsymbol{E}}$, respectively;

(7) $\varepsilon^{CT}_{700\ nm}$ [$R1_E$(I)] is the molar extinction coefficient of the CT absorption band at 700 nm of stiff stilbene@CBPQT^{4+} in $\mathbf{R}_{\boldsymbol{E}}$ isomer I. $\varepsilon^{CT}_{700\ nm}$[$R1_E$(II)] is the molar extinction coefficient of the CT absorption band at 700 nm of DNP@CBPQT^{4+} in $\mathbf{R}_{\boldsymbol{E}}$ isomer II. The absorption at 700 nm generates from the CT absorption band of stiff stilbene@CBPQT^{4+} in $\mathbf{R}_{\boldsymbol{E}}$ isomer I. The CT absorption band of DNP@CBPQT^{4+} doesn't have absorption at 700 nm;

(8) $\varepsilon^{CT}_{620\ nm}$[$R_E$(I)] is the molar extinction coefficient of the CT absorption band at 620 nm of stiff stilbene@CBPQT^{4+} in $\mathbf{R}_{\boldsymbol{E}}$ isomer I. $\varepsilon^{CT}_{620\ nm}$[$R_E$(II)] is the molar extinction coefficient of the CT absorption band at 620 nm of DNP@CBPQT^{4+} in $\mathbf{R}_{\boldsymbol{E}}$ isomer II;

(9) The ratio of $\varepsilon^{CT}_{620\ nm}$ [$R1_E$(I)] to $\varepsilon^{CT}_{700\ nm}$ [$R1_E$(I)] could be measured through the UV/Vis absorption spectra of the complexes of compound **3** and CBPQT^{4+};

(10) $\varepsilon^{CT}_{620\ nm}$[$R1_E$(II)] is approximately equal to $\varepsilon^{CT}_{620\ nm}$[**G1**@CBPQT^{4+}], which is the molar extinction coefficient of the CT absorption band at 620 nm of DNP@CBPQT^{4+} in complexes of **G1** and CBPQT^{4+}.

For $\mathbf{R2}_{\boldsymbol{E}}$:

$$\mathbf{R2}_{\boldsymbol{E}}\text{(I)} \rightleftharpoons \mathbf{R2}_{\boldsymbol{E}}\text{(II)}$$

$$[1/(1+x)]C^0 \qquad [x/(1+x)]C^0$$

$C^0[R2_E(II)] + C^0[R2_E(I)] = C^0$

$C^0[R2_E(II)] / C^0[R2_E(I)] = x$

$\eta\ [R2_E(I)] = 1/(1+x)$

$A^0_{700\ nm}\ (R2_E) = \varepsilon^{CT}_{700\ nm}\ [R2_E(I)] \times C^0[R2_E(I)] + \varepsilon^{CT}_{700\ nm}[R2_E(II)] \times C^0[R2_E(II)]$

$= \varepsilon^{CT}_{700\ nm}\ [R2_E(I)] \times C^0[R2_E(I)]$

(here $\varepsilon^{CT}_{700\ nm}[R2_E(II)] = 0$, because the CT band of BP@CBPQT^{4+} in $R2_E$ doesn't have absorption at 700 nm)

$= \varepsilon^{CT}_{700\ nm}\ [R2_E(I)] \times [1/(1+x)] \times C^0$

For $\mathbf{R2}_{\boldsymbol{E}}$ in MeOH, x = 0.56, η [$R2_E$(I)] = 0.64.

Notes:

(1) C^0 is the total concentration of $\mathbf{R2}_{\boldsymbol{E}}$ which has not been irradiated by Uv light;

(2) C^0[$\mathbf{R2}_{\boldsymbol{E}}$(I)] represents the concentrations of $\mathbf{R2}_{\boldsymbol{E}}$ isomer I;

(3) C^0[$\mathbf{R2}_{\boldsymbol{E}}$(II)] refers to the concentration of $\mathbf{R2}_{\boldsymbol{E}}$ isomer II;

(4) "x" is the ratio of C^0[$\mathbf{R2}_{\boldsymbol{E}}$(II)] to C^0[$\mathbf{R2}_{\boldsymbol{E}}$(I)];

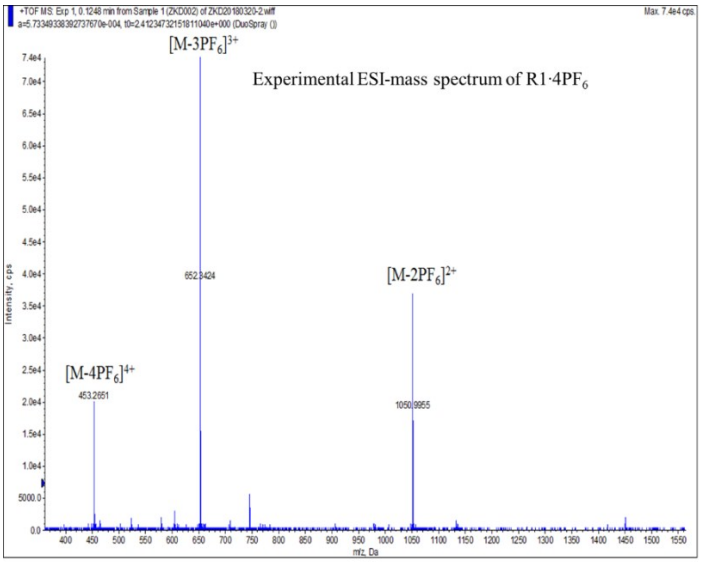
(5) "η [$R2_E$(I)]" is the of $\mathbf{R2}_{\boldsymbol{E}}$ isomer I in $\mathbf{R2}_{\boldsymbol{E}}$;

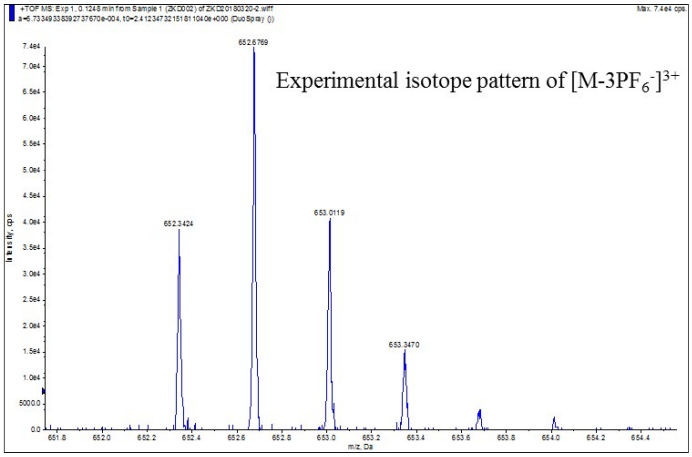
(6) $A^0_{700\ nm}$ corresponds to absorbance at 700 nm of the solution of $\mathbf{R2}_{\boldsymbol{E}}$;

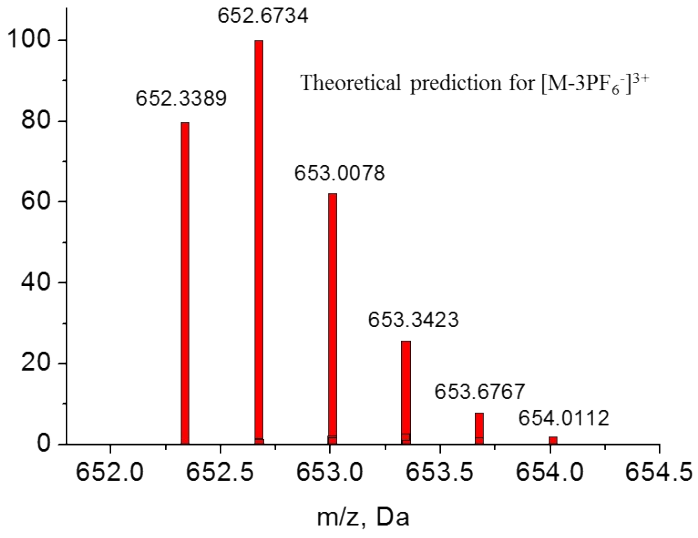
(7) $\varepsilon^{CT}_{700\ nm}$ [$R2_E$(I)] is the molar extinction coefficient of the CT absorption band at 700 nm of stiff stilbene@$CBPQT^{4+}$ in $\mathbf{R}_{\boldsymbol{E}}$ isomer I. $\varepsilon^{CT}_{700\ nm}$[$R2_E$(II)] is the molar extinction coefficient of the CT absorption band at 700 nm of BP@$CBPQT^{4+}$ in $\mathbf{R}_{\boldsymbol{E}}$ isomer II. The absorption at 700 nm generates from the CT absorption band of stiff stilbene@$CBPQT^{4+}$ in $\mathbf{R}_{\boldsymbol{E}}$ isomer I. The CT absorption band of BP@$CBPQT^{4+}$ doesn't have absorption at 700 nm;

(8) $\varepsilon^{CT}_{700\ nm}$[$R2_E$(I)] is approximately equal to $\varepsilon^{CT}_{700\ nm}$[$R1_E$(I)].

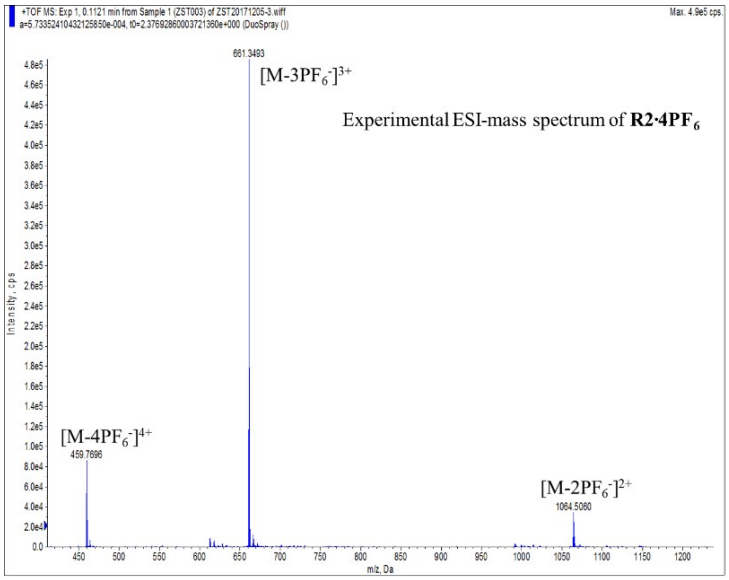
Section 9: Characterization data (MS, ^{1}H NMR and ^{13}C NMR spectra) for the new compounds

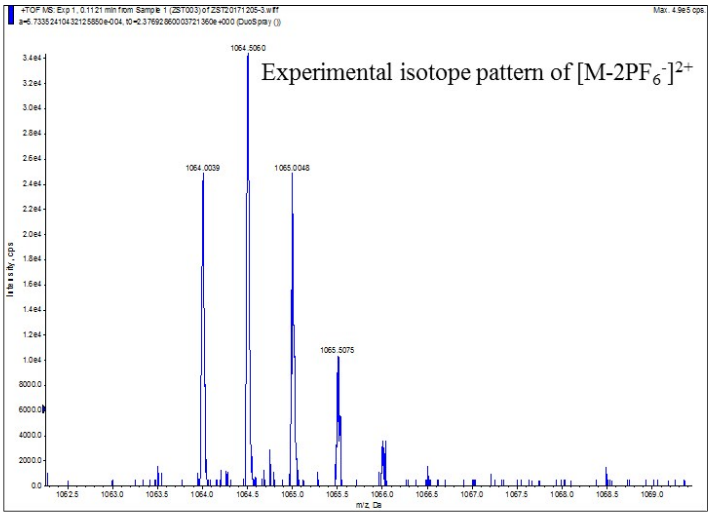


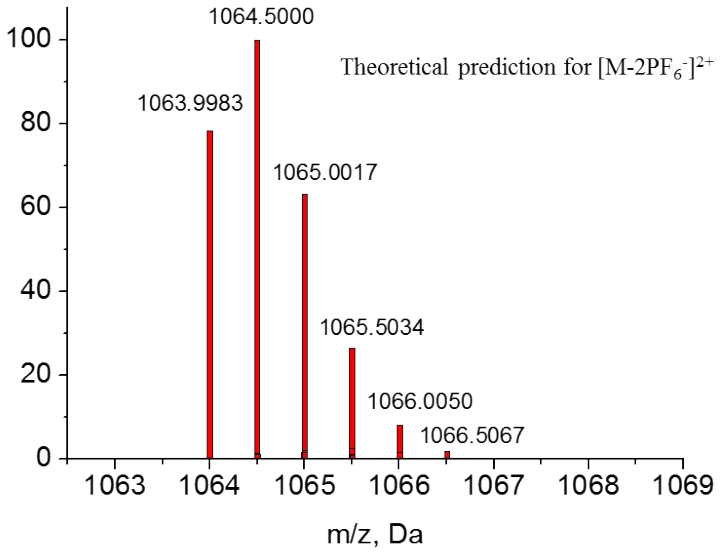




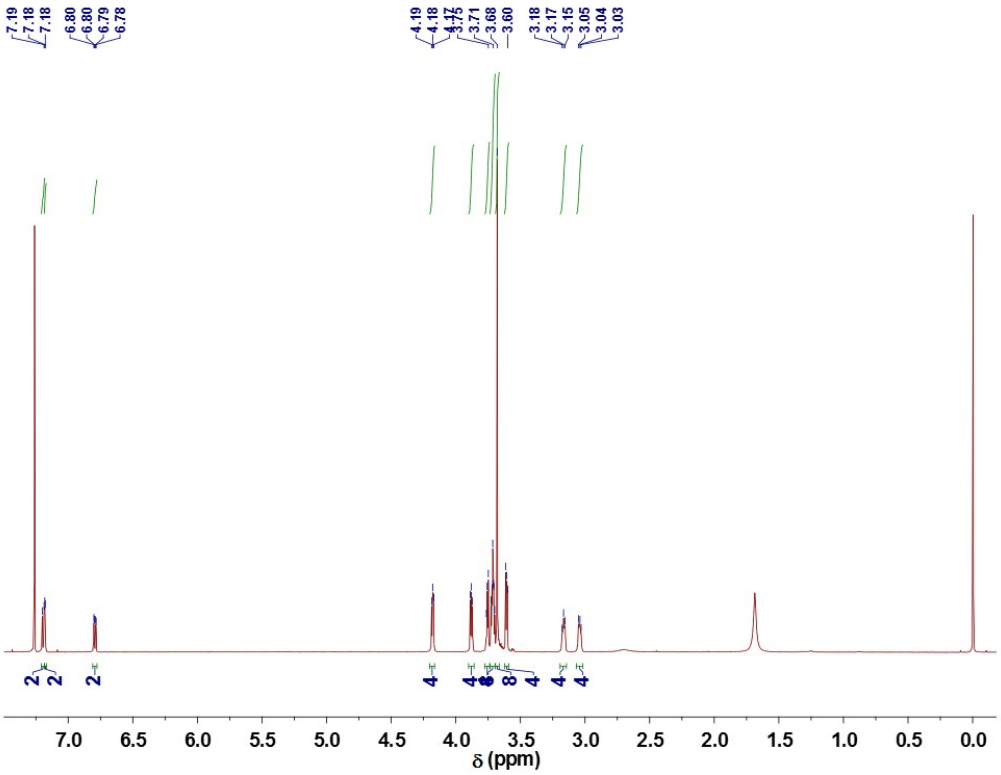
ESI mass spectrum of [2] rotaxane **R1·4PF$_6$**.



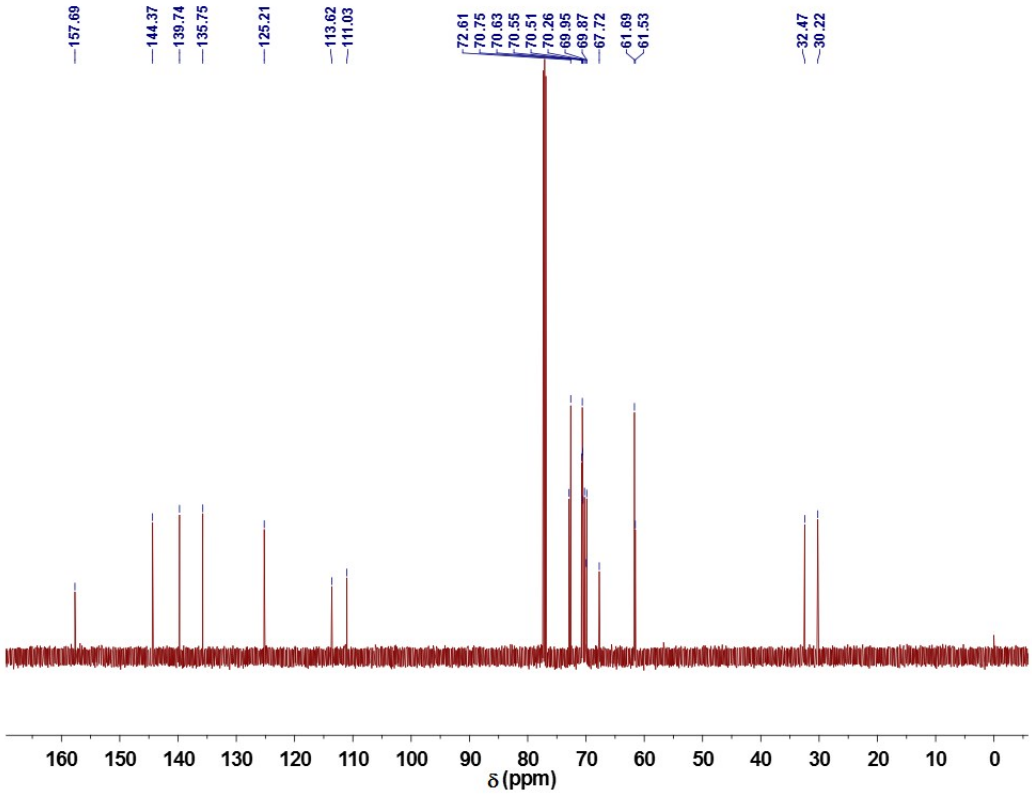




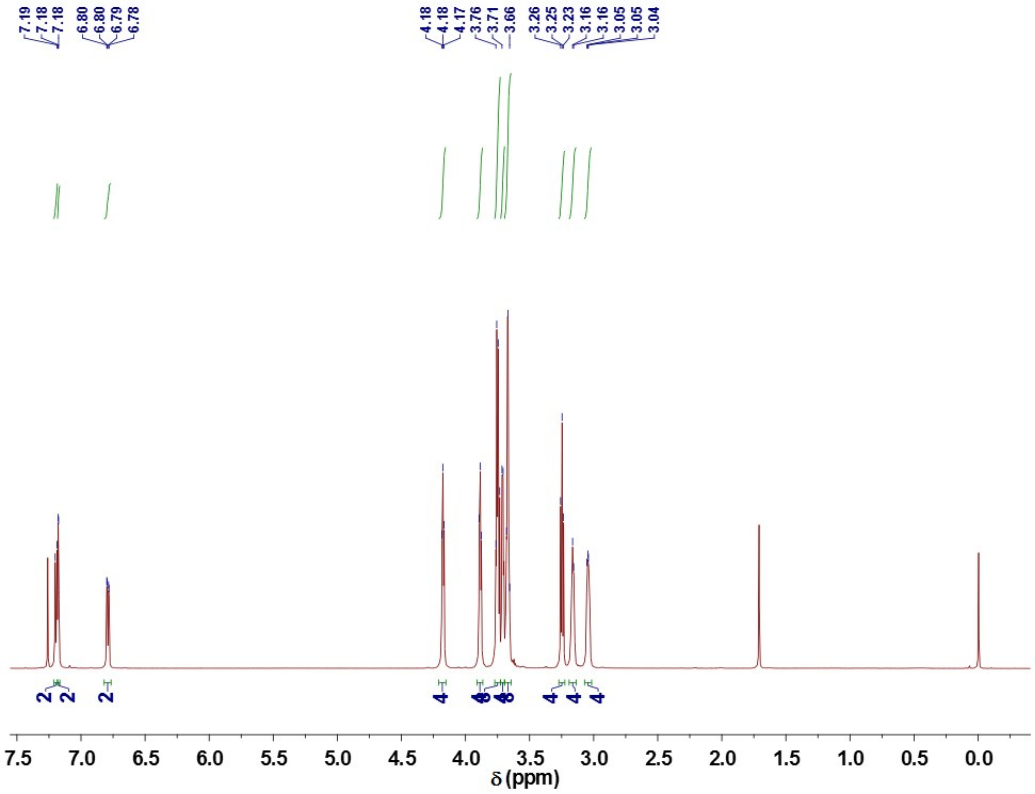
ESI mass spectrum of [2] rotaxane **R2·4PF$_6$**.



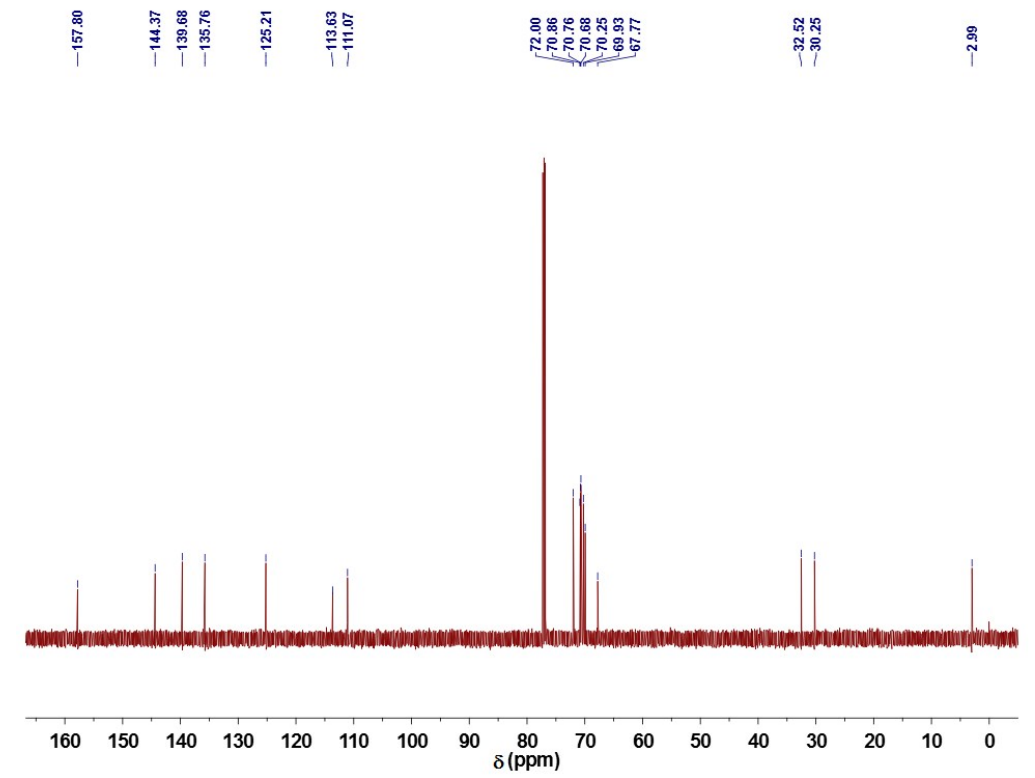
^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 298 K) of compound **3**.



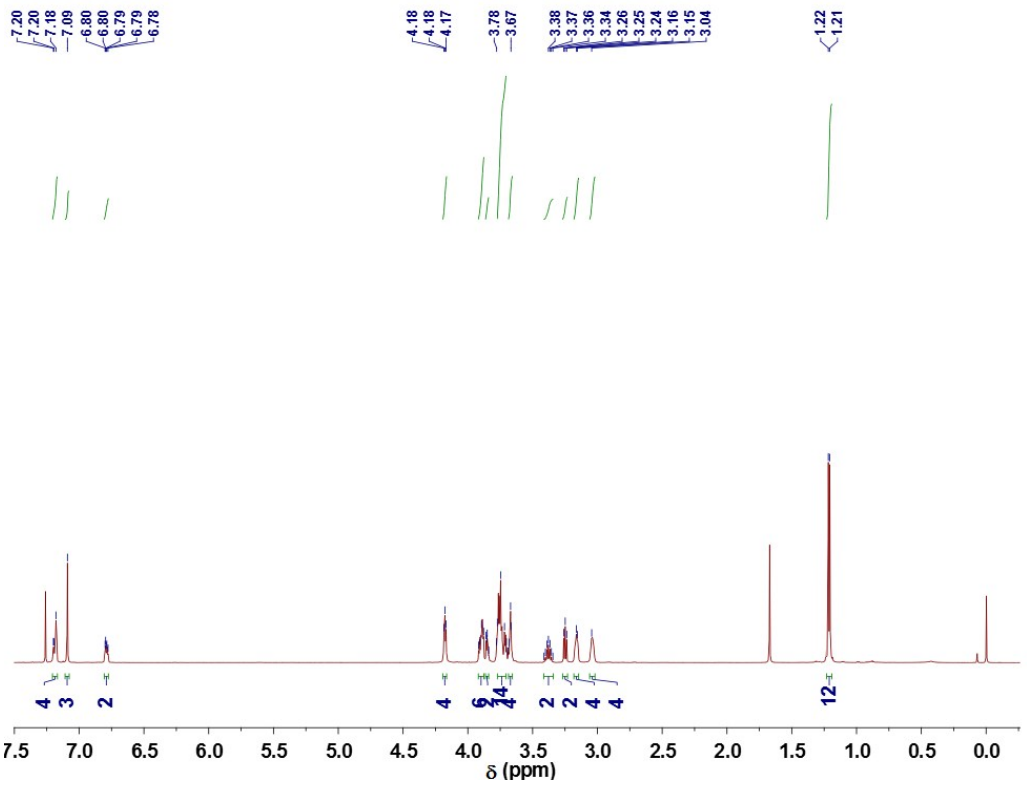
^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of compound **3**.



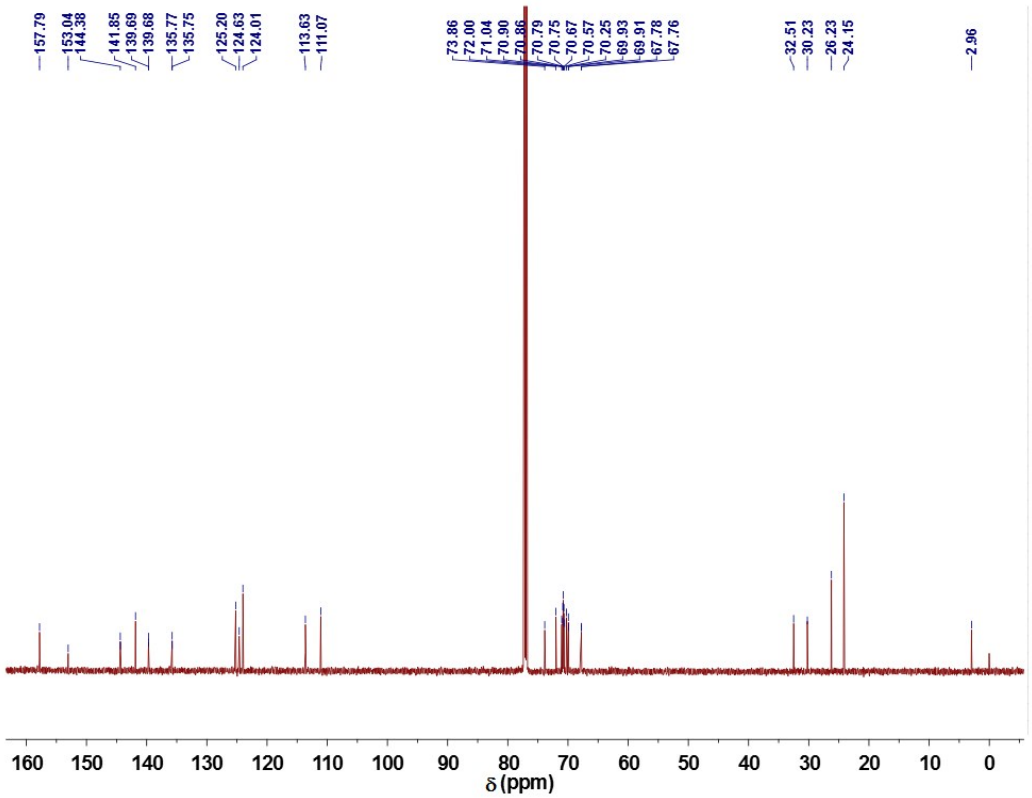
^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 298 K) of compound **4**.



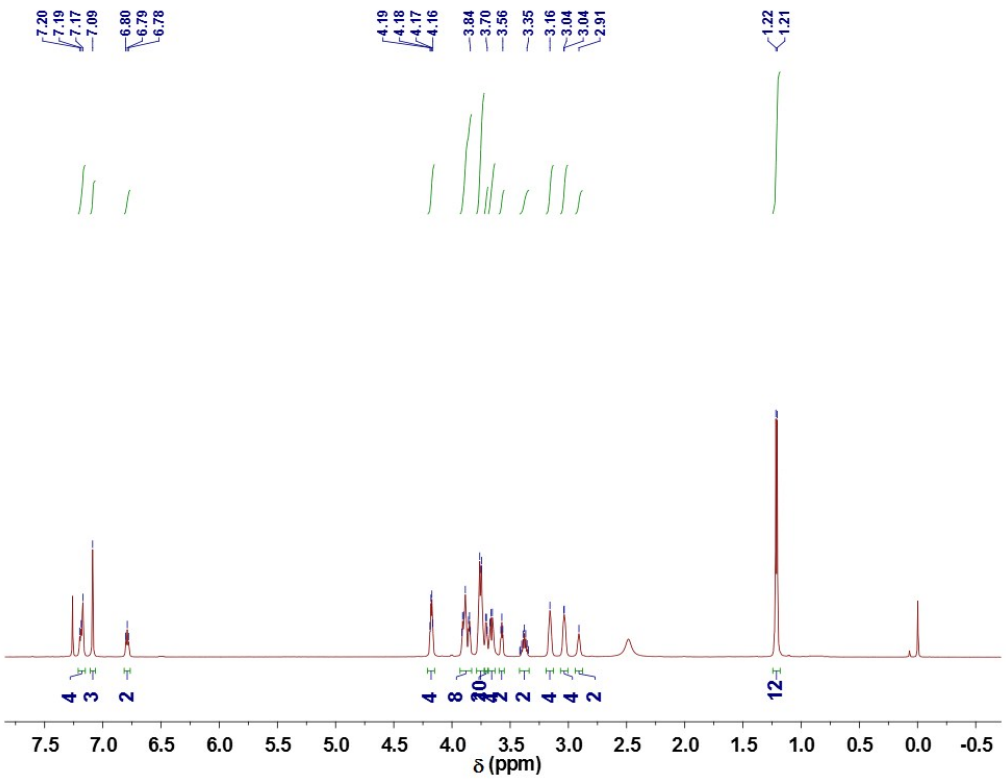
^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of compound **4**.



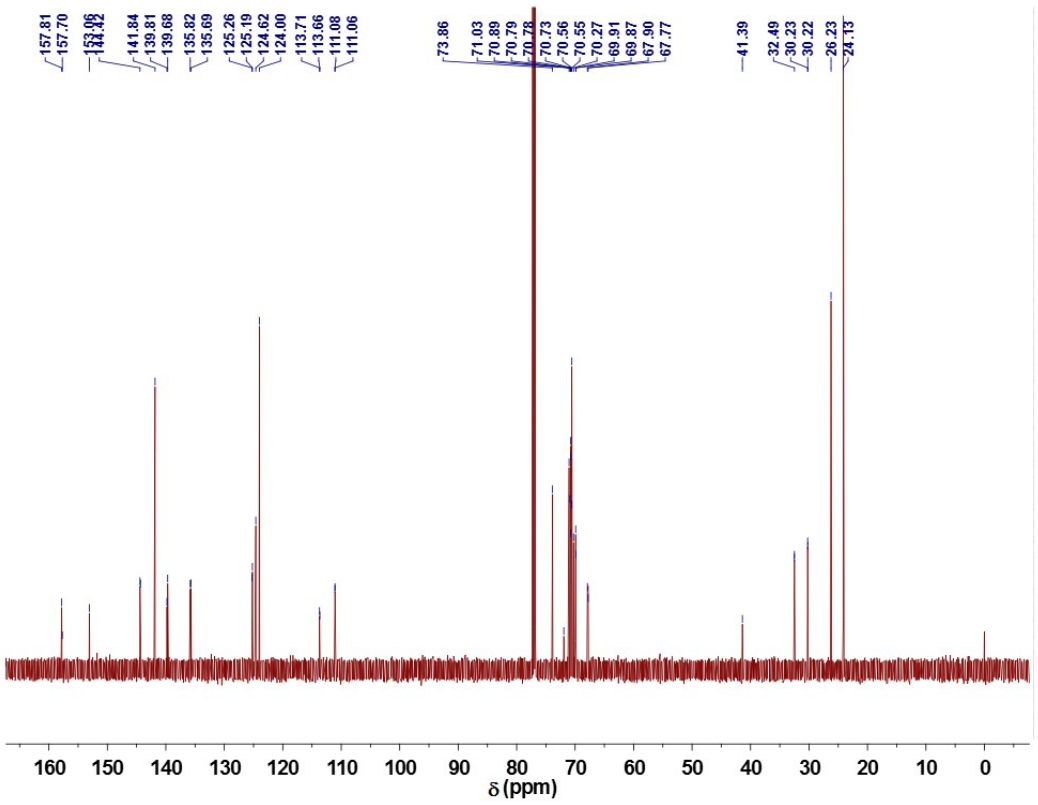
^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 298 K) of compound **5**.



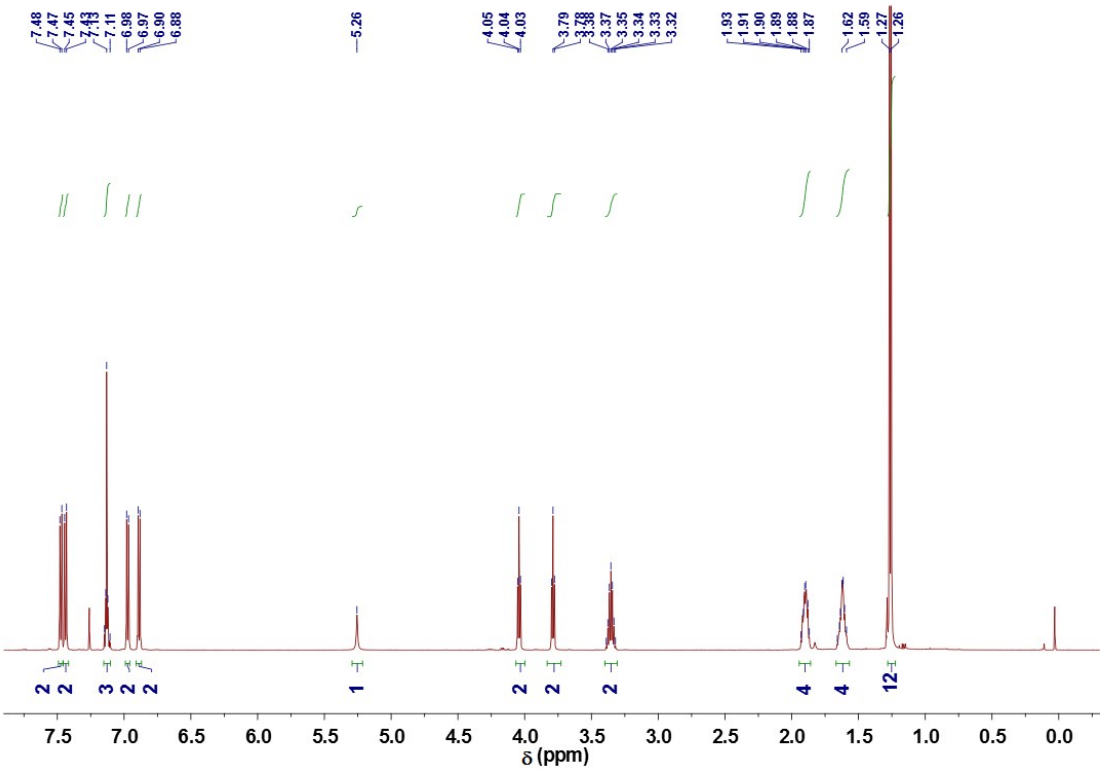
^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of compound **5**.



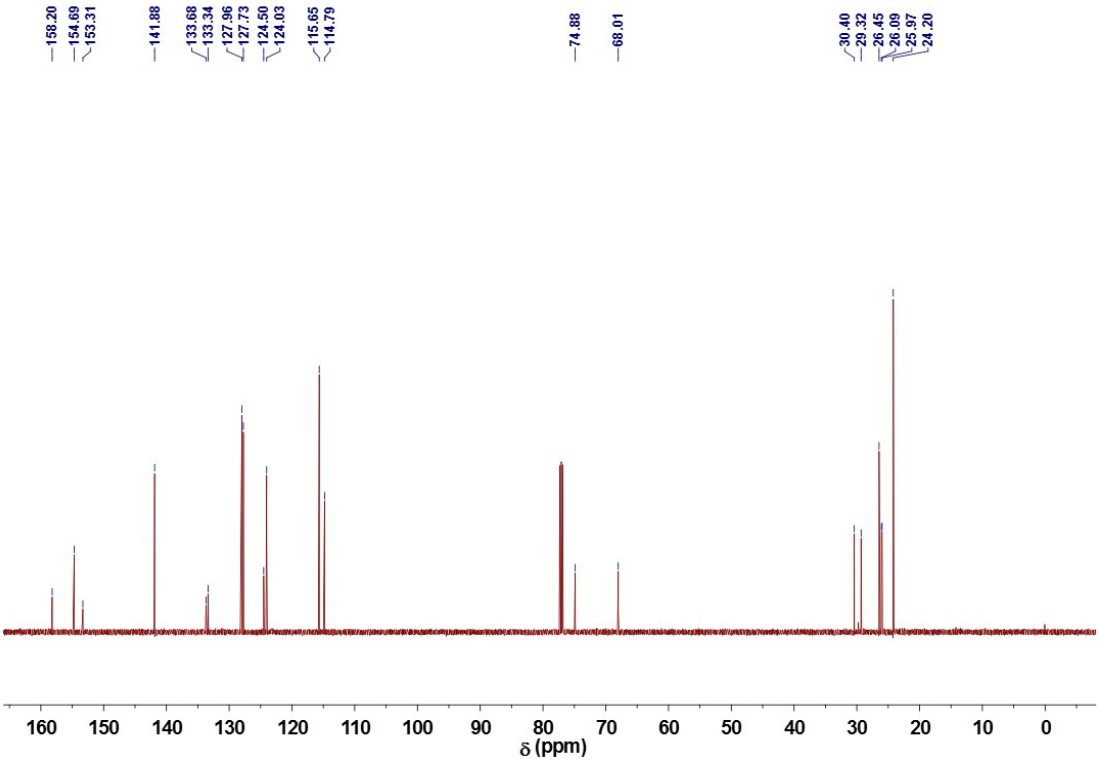
^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 298 K) of compound **6**.



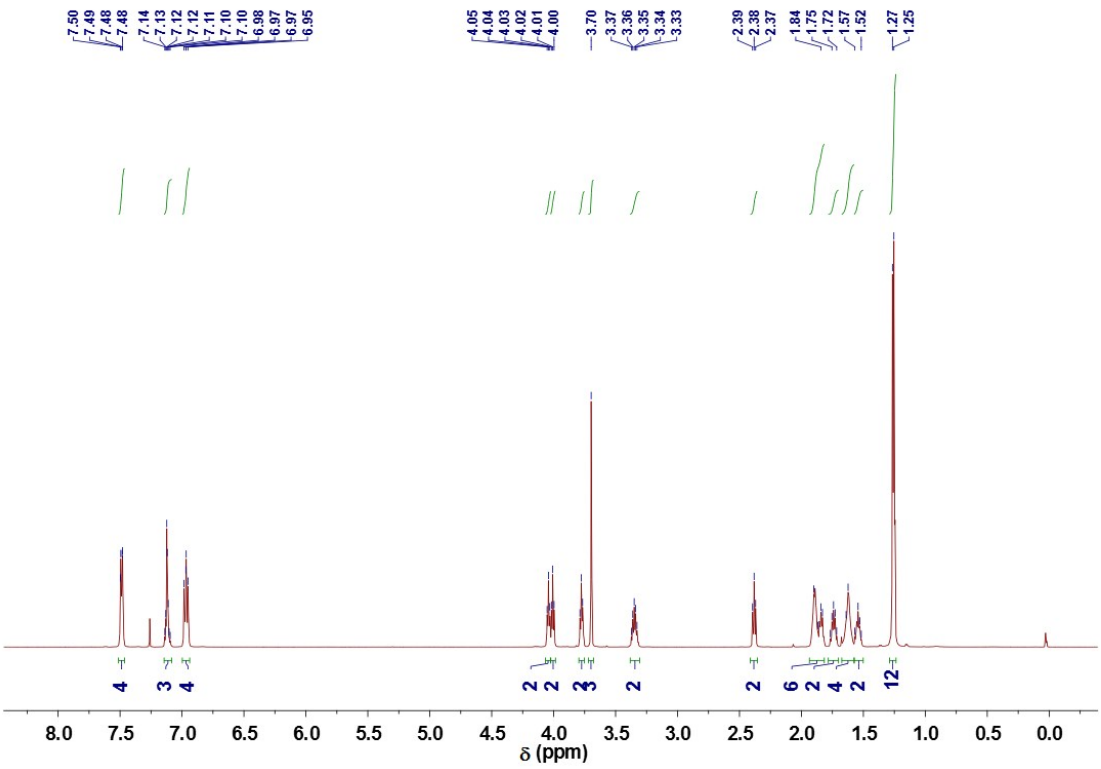
^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of compound **6**.



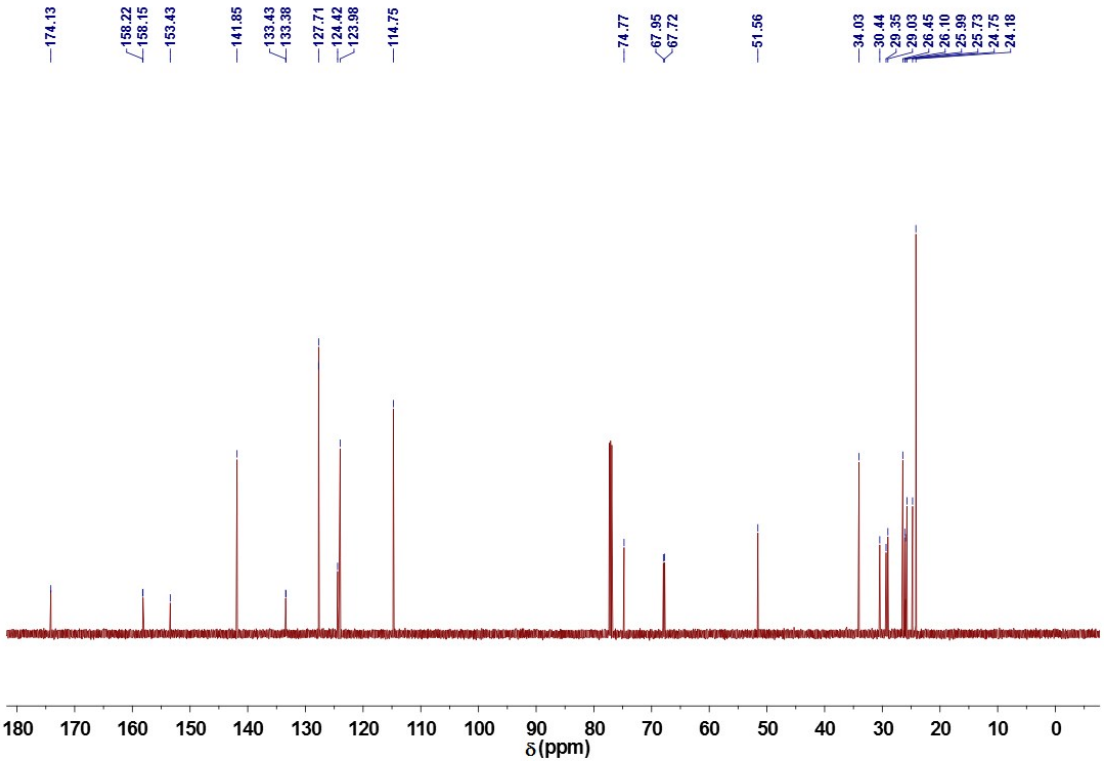
^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 298 K) of compound **11**.



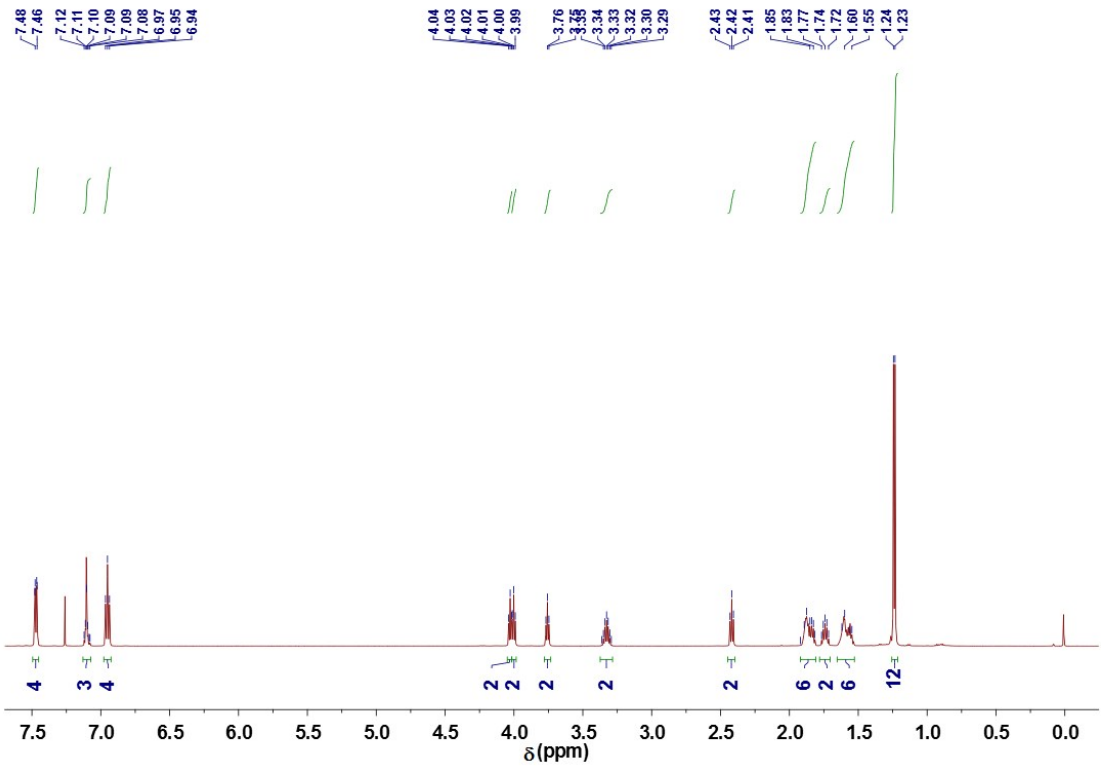
^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of compound **11**.



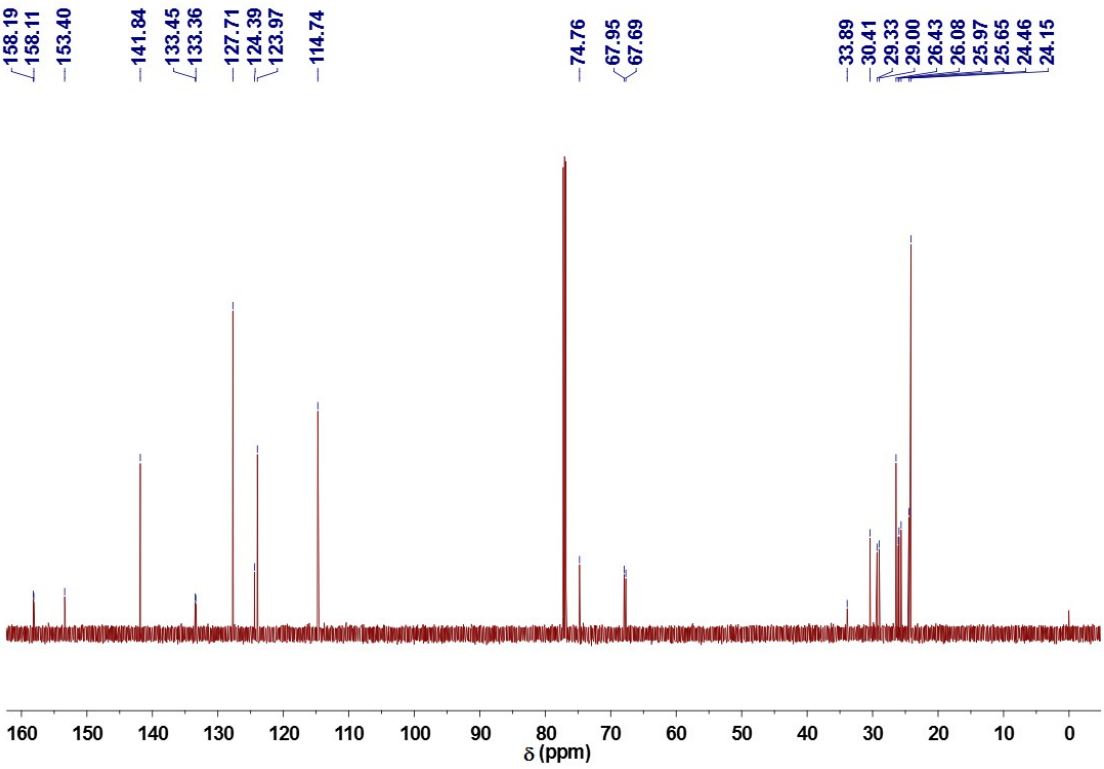
^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 298 K) of compound **13**.



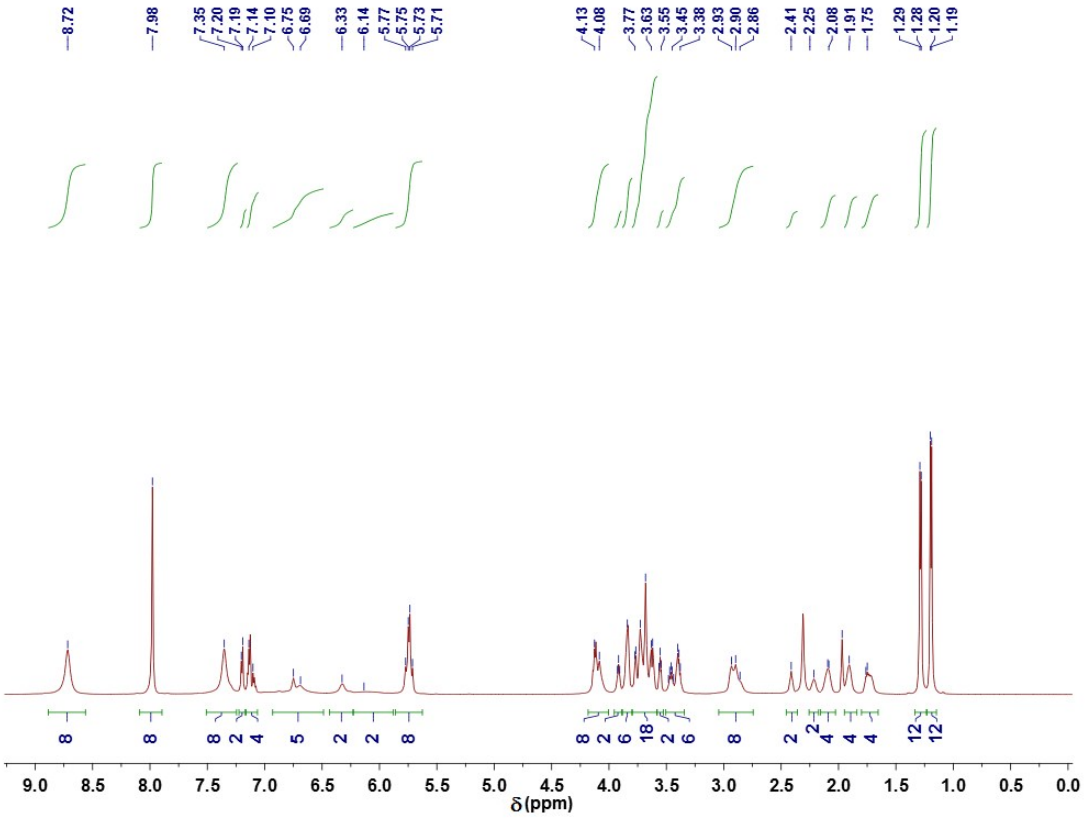
^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of compound **13**.



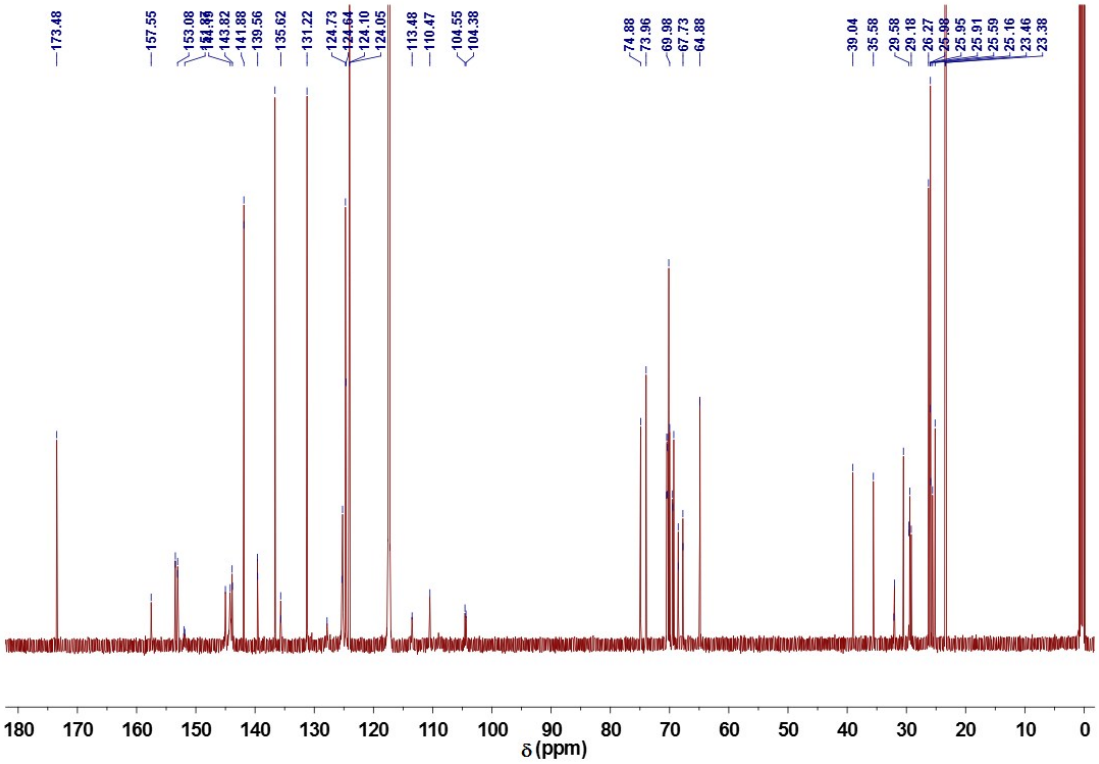
^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 298 K) of compound **14**.



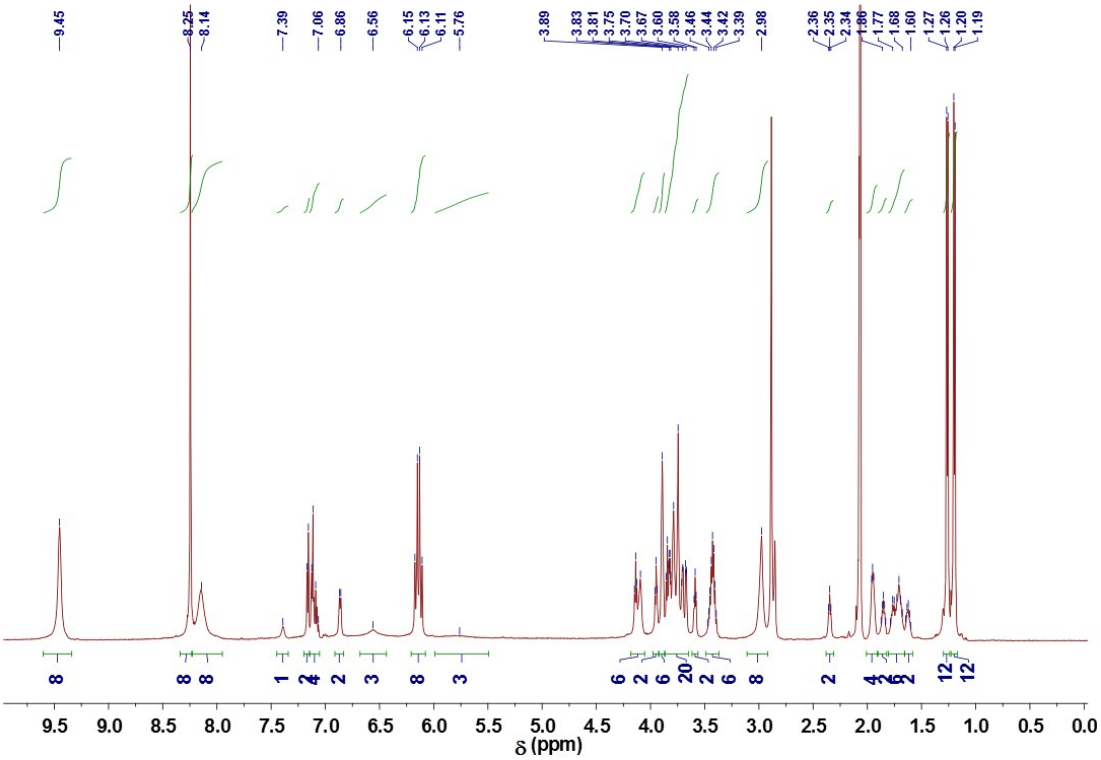
^{13}C NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of compound **14**.



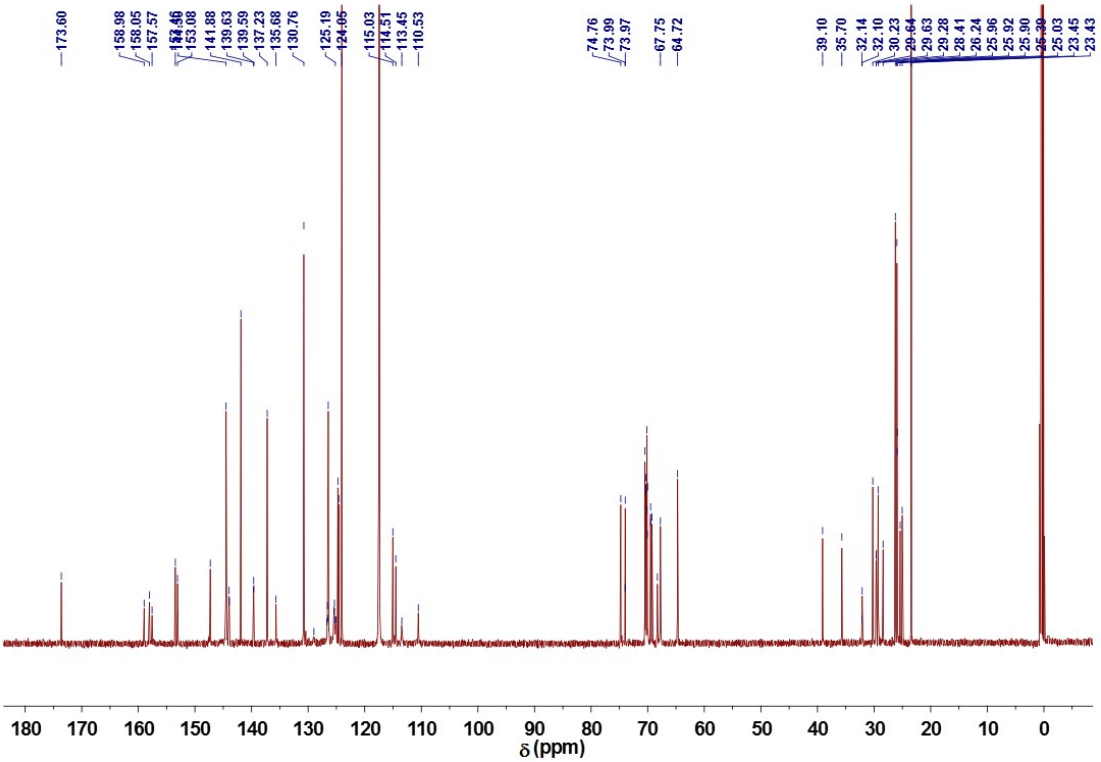
^{1}H NMR spectrum (CD_3CN, 600 MHz, 40 mM, 298 K) of bisatble [2]rotaxane **R1·4PF$_6$**.



^{13}C NMR spectrum (CD_3CN, 150 MHz, 40 mM, 298 K) of bisatble [2]rotaxane **R1·4PF$_6$**.



^{1}H NMR spectrum (CD_3COCD_3, 600 MHz, 15 mM, 298 K) of bisatble [2]rotaxane **R2·4PF$_6$**.



^{13}C NMR spectrum (CD_3CN, 150 MHz, 40 mM, 298 K) of bisatble [2]rotaxane **R2·4PF$_6$**.

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