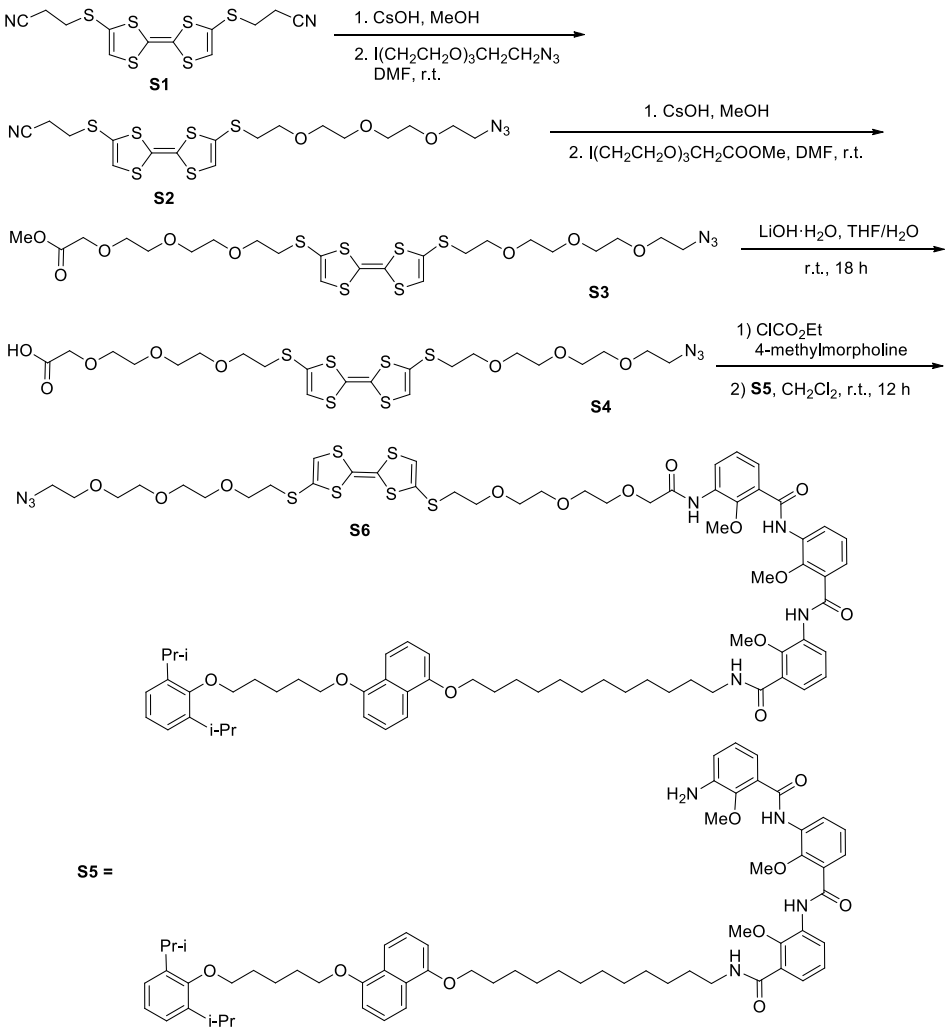
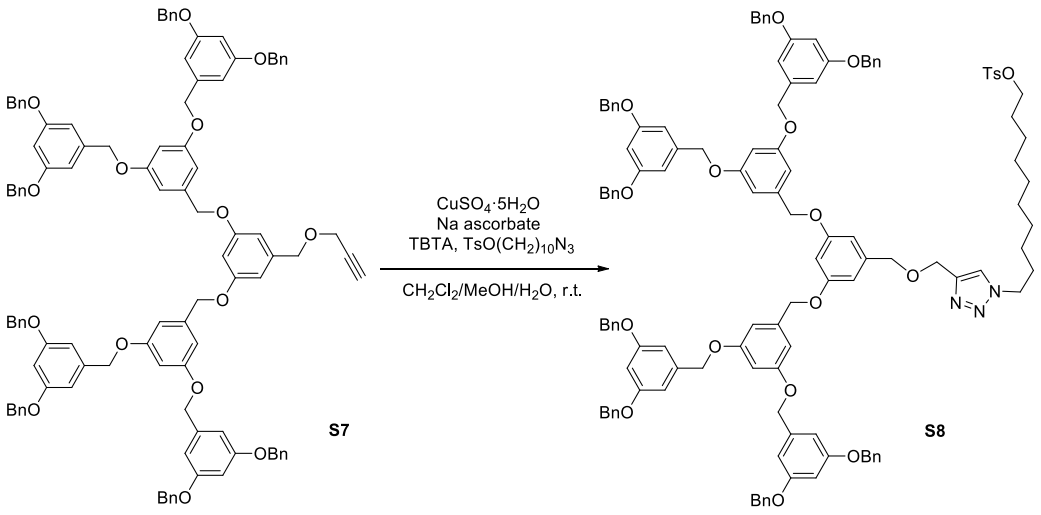


Compound S2. To a solution of compound **S1**[1] (0.48 g, 1.28 mmol) in DMF (30 mL) was added dropwise a solution of cesium hydroxide monohydrate (0.24 g, 1.43 mmol) in methanol (10 mL). The solution was stirred for 30 min and then a solution of $I(CH_2CH_2O)_3CH_2CH_2N_3$[2] (0.84 g, 2.56 mmol) in 10 mL DMF was added in one portion. Stirring was continued for another 12 h and the solvent was then evaporated under vacuum. The resulting slurry was re-dissolved with dichloromethane (50 mL). The solution was washed with water (25 mL × 2) and brine (25 mL), and dried over anhydrous sodium sulfate. The solvent was then removed and the resulting crude product was subjected to column chromatography (n-hexane/ethyl acetate 4:1) to give compound **S2** as a brown oil (0.34 g, 50%). ^{1}H NMR (400 MHz, CD_3CN) δ: 6.67 (s, 1H), 6.56 (s, 1H), 3.68-3.50 (m, 12H), 3.38-3.33 (m, 2H), 2.98 (t,d, J_1 =6.7 Hz, J_2 = 1.2 Hz, 2H), 2.94 (t,d, J_1 = 6.2 Hz, J_2 = 1.2 Hz, 2H), 2.72 (t,d, J_1 = 6.7 Hz, J_2 = 1.7 Hz, 2H). ^{13}C NMR (100 MHz, CD_3CN) δ: 127.0, 125.0, 124.1, 124.0, 119.2, 71.2, 71.1, 70.5, 70.2, 51.5, 36.2, 31.6, 19.1 HRMS (ESI): Calcd for $C_{17}H_{22}N_4O_3S_6$: 522.0016 $[M]^+$. Found: 522.0020.

Compound S3. To a solution of compound **S2** (0.34 g, 0.64 mmol) in DMF (20 mL) was added dropwise a solution of cesium hydroxide monohydrate (0.13 g, 0.77 mmol) in methanol (5 mL). After stirring for another 30 min, a solution of $I(CH_2CH_2O)_3CH_2CO_2Me$[3] (0.43 g, 1.29 mmol) in 6 mL DMF was added. The solution was stirred for 12 h and the solvent was evaporated under vacuum. The resulting residue was triturated with dichloromethane (50 mL). The solution was washed with water (25 mL × 2) and brine (25 mL), and dried over sodium sulfate. After the solvent was removed, the resulting crude product was subjected to column chromatography (n-hexane/ethyl acetate 1:1) to afford

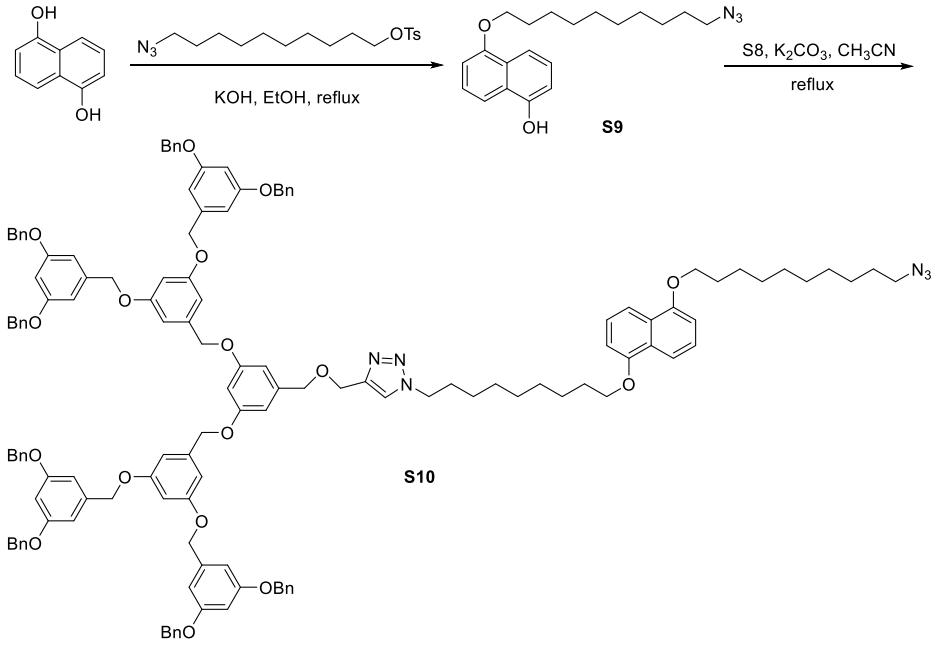
compound **S3** as a brown oil (0.33 g, 77%). ^{1}H NMR (400 MHz, CD_3CN): δ 6.56 (s, 2H), 4.10 (s, 2H), 3.68 (s, 3H), 3.65-3.50 (m, 22H), 3.42-3.24 (m, 2H), 2.94 (t,d, J_1 = 6.2 Hz, J_2 =1.2 Hz, 4H). ^{13}C NMR (100 MHz, CD_3CN): δ 171.7, 127.2, 124.1, 124.0, 71.4, 71.2, 71.1, 71.0, 70.5, 70.1, 68.9, 52.1, 51.5, 36.1. HRMS(ESI): Calcd for $C_{23}H_{35}N_3O_8S_6$: 673.0748 $[M]^+$. Found: 673.0722.

Compound S6. To a solution of compound **S3** (0.33 g, 0.50 mmol) in THF (32 mL) was added a solution of lithium hydroxide monohydrate (0.81 g, 0.02 mol) in water (8 mL). The mixture was stirred at room temperature for 18 hours and then acidified with aqueous hydrochloric acid to pH = 3 and then concentrated under vacuum. The resulting residue was triturated with dichloromethane (20 mL). The solution was washed with water (10 mL × 2) and brine (10 mL), and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure yielded compound **S4** as a yellow oil. Without further purification, the crude product was dissolved in dichloromethane (10 mL). To the solution were added *N*-methylmorpholine (61 mg, 0.60 mmol) and ethyl chloroformate (54 mg, 0.50 mmol). After stirring for 40 min at room temperature, a solution of compound **S5**[3] (0.53 g, 0.5 mmol) in dichloromethane (10 mL) was added. Stirring was continued for another 12 h and then the solution was washed with water (10 mL × 2) and brine (10 mL), and dried over sodium sulfate. Upon removal of the solvent with rotavapor, the resulting crude product was subjected to column chromatography (n-hexane/ethyl acetate 1:2) to afford compound **S6** as an orange solid (0.61 g, 73%). ^{1}H NMR (400 MHz, acetone-d_6): δ 10.34 (s, 1H), 10.24 (s, 1H), 9.19 (s, 1H), 8.78 (d,d, J_1 = 8.1 Hz, J_2 = 1.3 Hz, 1H), 8.69 (d,d, J_1 = 8.1 Hz, J_2 = 1.3 Hz, 1H), 8.53 (d,d, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 7.87-7.78 (m, 4H), 7.71 (t, J = 5.5 Hz, 1H), 7.45 (d,d, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.36 (m, 4H), 7.23 (t, J = 8.0 Hz, 1H), 7.14-7.02 (m, 3H), 6.99-6.88 (m, 2H), 6.68 (s, 1H), 6.60 (s, 1H), 4.26-4.19 (m, 4H), 4.15 (t, J = 6.2 Hz, 2H), 4.08 (s, 6H), 3.97 (s, 3H), 3.89-3.75 (m, 6H), 3.74-3.69 (m, 2H), 3.69-3.54 (m, 18H), 3.48-3.32 (m, 6H), 2.96 (t, J = 6.3 Hz, 2H), 1.99-1.80 (m, 6H), 1.71-1.62 (m, 2H), 1.61-1.52 (m, 2H), 1.48-1.30 (m, 16H), 1.20 (d, J = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, acetone-d_6): δ 169.0, 166.19, 163.7, 163.6, 155.6, 154.5, 148.8, 148.7, 148.1, 142.5, 133.8, 133.4, 132.8, 130.6, 129.9, 128.0, 127.8, 127.7, 127.3, 127.2, 126.7, 126.6, 126.1, 126.0, 125.9, 125.5, 125.4, 125.3, 125.1, 124.7, 124.1, 124.0, 123.8, 123.4, 123.3, 114.8, 114.7, 106.4, 106.3, 75.4, 72.1, 71.5, 71.4, 71.3, 71.2, 70.7, 70.4, 70.3, 68.9, 68.8, 63.9, 63.4, 63.0, 51.5, 40.4, 36.1, 36.0, 31.0, 30.5, 30.4, 30.2, 27.9, 27.2, 27.1, 24.4, 23.8. HRMS (ESI): Calcd for $C_{85}H_{111}N_7O_{16}S_6Na$: 1700.6309 $[M+Na]^+$. Found: 1700.6312.



Compound S8. A solution of $CuSO_4$▪$5H_2O$ (4 mg), TBTA (2 mg), sodium ascorbate (0.38 g, 1.96

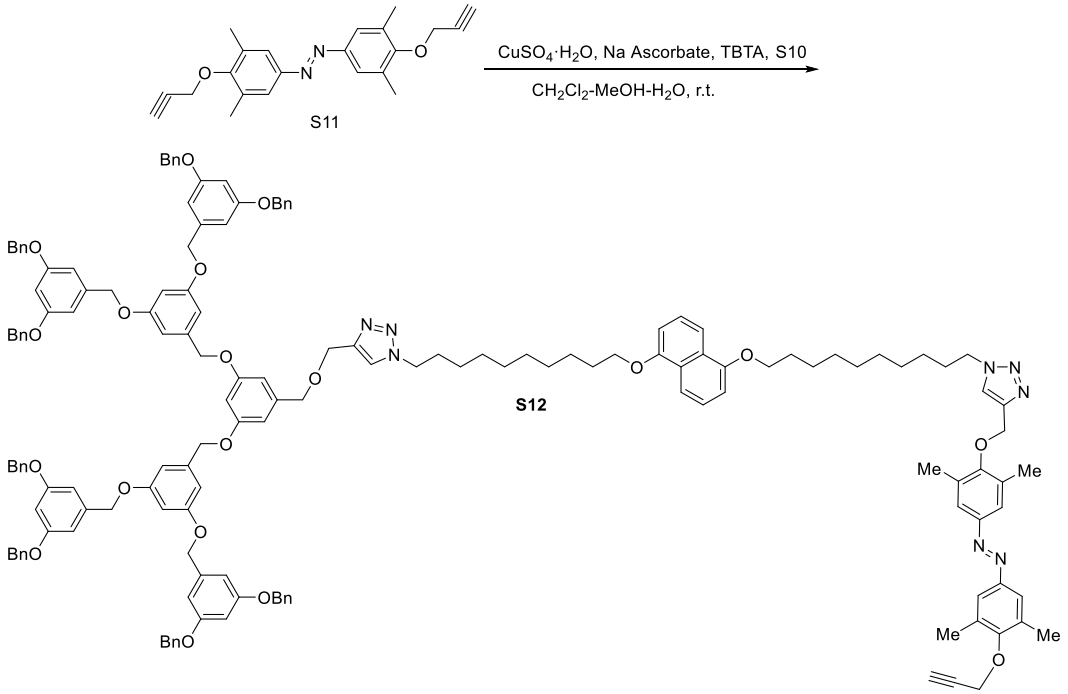
mmol), compound **S7**[4] (0.16 g, 0.098 mmol), $TsO(CH_2)_{10}N_3$[5] (45 mg, 0.098 mmol), and K_2CO_3 (40 mg, 0.29 mmol) in water/dicholoromethane/methanol (1.5 mL/5 mL/2.5 mL) was stirred for 12 h at room temperature and then concentrated under reduced pressure. The resulting residue was triturated with dichloromethane (10 mL). The organic phase was washed with water (50 mL × 3) and brine (5 mL), and dried over anhydrous sodium sulfate. Upon removal of the solvent, the resulting residue was subjected to column chromatography (DCM/MeOH 100:1) to give compound **S8** as a pale yellow oil (0.15 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.50-7.26 (m, 43H), 6.68-6.63 (m, 12H), 6.61 (d, *J* = 1.5 Hz, 2H), 6.56 (t, *J* = 2.2 Hz, 4H), 6.55-6.52 (m, 3H), 5.01 (s, 16H), 4.95 (s, 12H), 4.65 (s, 2H), 4.52 (s, 2H), 4.27 (t, *J* = 7.2 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 2.42 (s, 3H), 2.06-1.96 (m, 2H), 1.89-1.79 (m, 2H), 1.34-1.12 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 160.1, 160.0, 144.6, 140.4, 139.3, 139.2, 136.8, 133.2, 129.8, 128.5, 128.2, 127.9, 127.8, 127.5, 127.1, 106.7, 106.4, 101.6, 101.4, 72.3, 70.6, 70.0, 69.9, 63.7, 50.3, 30.2, 29.6, 29.2, 28.9, 28.8, 28.7, 26.4, 25.2, 21.6. HRMS (ESI): Calcd for $C_{125}H_{122}N_3O_{18}S$: 1984.8444 $[M+H]^+$. Found: 1984.8423.



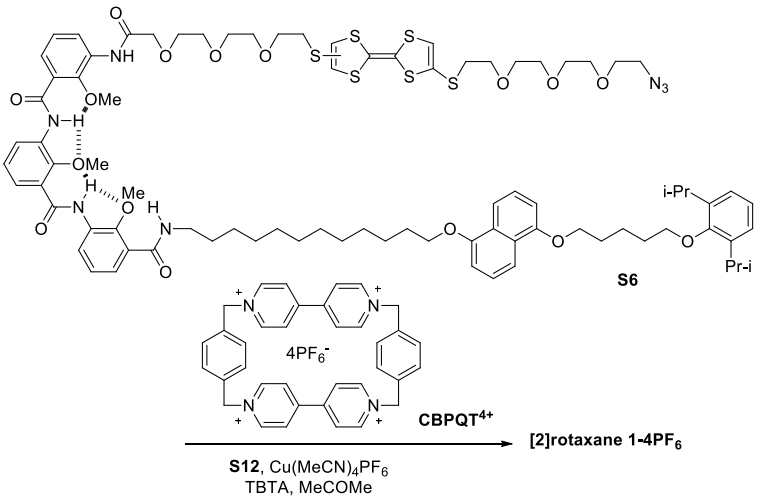
Compound S9. A solution of $TsO(CH_2)_{10}N_3$[5] (0.56 g, 1.53 mmol), 1,5-dihydroxy naphthalene (1.6 g, 9.9 mmol) and potassium hydroxide (0.56 g, 9.9 mmol) in ethanol (40 mL) was heated under reflux for 24 h and then cooled to room temperature. Diluted hydrochloric acid was added to pH = 2. The solvent was then evaporated and the resulting residue was triturated dichloromethane (10 mL). The organic phase was washed with water (5 mL × 3) and brine (5 mL), and dried over sodium sulfate. The solvent was then removed and the crude product subjected to column chromatography (n-hexane/ethyl acetate 80:7) to afford compound **S9** as a brown solid (0.34 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.41-7.35 (m, 1H), 7.33-7.27 (m, 1H), 6.84 (t, *J* = 7.6 Hz, 2H), 5.20 (s, 1H), 4.13 (t, *J* = 6.4 Hz, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 1.96-1.87 (m, 2H), 1.58 (s, 6H), 1.40-1.31 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.5, 125.1, 115.1, 113.4, 109.5, 105.3, 68.3, 51.6, 29.6, 29.5, 29.5, 29.4, 29.2, 28.9, 26.8, 26.4. HRMS (ESI): Calcd for $C_{20}H_{28}N_3O_2$: 342.2182 $[M+H]^+$. Found: 342.2165.

Compound S10. A solution of compounds **S9** (29 mg, 0.075 mmol), **S8** (150 mg, 0.075 mmol), K_2CO_3 (26 mg, 0.19 mmol) and 18-crown-6 (20 mg) in MeCN (10 mL) was heated under reflux for 24 h and then concentrated. The resulting residue was triturated with dichloromethane (10 mL). The organic

phase was washed with water (5 mL × 3) and brine (5 mL), and dried over by sodium sulfate. After the solvent was removed, the resulting residue was subjected to column chromatography (n-hexane/ethyl acetate 2:1) to afford compound **S10** as a white solid (0.11 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.56-7.26 (m, 43H), 6.87 (d, *J* = 7.5 Hz, 2H), 6.75 (s, 12H), 6.70 (s, 2H), 6.67-6.58 (m, 7H), 5.06 (s, 16H), 5.01 (s, 12H), 4.73 (s, 2H), 4.60 (s, 2H), 4.30 (t, *J* = 7.0 Hz, 2H), 4.20-4.10 (m, 4H), 3.29 (t, *J* = 6.9 Hz, 2H), 2.00-1.87 (m, 6H), 1.69-1.57 (m, 6H), 1.51-1.25 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.3, 160.2, 160.1, 154.7, 145.1, 140.5, 139.4, 139.3, 136.8, 128.6, 128.0, 127.6, 127.2, 126.9, 125.2, 122.4, 114.2, 106.8, 106.5, 105.3, 101.7, 101.5, 72.4, 70.2, 70.1, 68.2, 63.8, 51.5, 50.4, 30.3, 29.8, 29.6, 29.5, 29.4, 29.4, 29.2, 29.0, 28.9, 26.8, 26.5, 26.3. HRMS (ESI): Calcd for $C_{138}H_{141}N_6O_{17}$: 2154.0353 $[M+H]^+$. Found: 2154.0364.



Compound S12. A solution of $CuSO_4$▪$5H_2O$ (6 mg), TBTA (1.8 mg), sodium ascorbate (0.28 g, 1.39 mmol), compounds **S10** (0.15 g, 0.070 mmol) and **S11**[6] (0.13 g, 0.42 mmol), and K_2CO_3 (35 mg, 0.21 mmol) in water/dicholoromethane/methanol (3 mL/10 mL/5 mL) was stirred for 12 h at room temperature and then concentrated under reduced pressure. The resulting slurry was triturated with dichloromethane (10 mL). The organic layer was washed with water (5 mL × 3) and brine (5 mL), and dried over anhydrous sodium sulfate. The solvent was then removed and the resulting residue was subjected to column chromatography (n-hexane/ethyl acetate 1:1) to give compound **S12** as an orange solid (59.3 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.65-7.55 (m, 5H), 7.47 (s, 1H), 7.43-7.28 (m, 42H), 6.82-6.77 (m, 2H), 6.70-6.62 (m, 12H), 6.62-6.57 (m, 2H), 6.57-6.50 (m, 7H), 5.03 (s, 2H), 5.01 (s, 16H), 4.95 (s, 12H), 4.66 (s, 2H), 4.57 (d, *J* = 2.4 Hz, 2H), 4.52 (s, 2H), 4.36 (t, *J* = 7.3 Hz, 2H), 4.26 (t, *J* = 7.2 Hz, 2H), 4.12-4.01 (m, 4H), 2.52 (t, *J* = 2.4 Hz, 1H), 2.41 (s, 6H), 2.37 (s, 6H), 1.95-1.80 (m, 10H), 1.58-1.45 (m, 6H), 1.35-1.25 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.3, 160.2, 160.1, 157.5, 154.8, 149.2, 149.1, 145.1, 144.3, 140.5, 139.4, 139.3, 136.9, 132.2, 132.1, 128.7, 128.1, 127.7, 126.9, 125.2, 123.5, 123.4, 122.5, 122.4, 114.2, 106.9, 106.5, 105.4, 101.8, 101.6, 75.5, 72.5, 70.2, 70.1, 68.2, 65.9, 63.9, 60.0, 50.5, 50.4, 30.5, 30.4, 29.8, 29.5, 29.4, 29.1, 26.6, 26.3, 16.9, 16.8. HRMS (ESI): Calcd for $C_{160}H_{163}N_8O_{19}$: 2500.2035 $[M+H]^+$. Found: 2500.2012.



[2]Rotaxane 1^{4+}▪$4PF_6^-$. A solution of compounds **S12** (100 mg, 0.04 mmol), **S6** (67.4 mg, 0.04 mmol), $CBPQT^{4+}$▪$4PF_6^-$[7] (44 mg, 0.04 mmol), TBTA (4.3 mg) and $Cu(MeCN)_4PF_6$ (5.9 mg) in acetone (7 mL) was stirred for 24 h at room temperature. The solvent was evaporated and the resulting solid was triturated with dichloromethane (5 mL). The organic layer was washed with water (2 mL × 3) and then concentrated. The resulting residue was subjected to column chromatography (2% NH_4PF_6 in acetone) to afford [2]rotaxane **1**▪$4PF_6$ as a green solid (45 mg, 21%). ^{1}H NMR (400 MHz, CD_3CN): δ 9.97 (s, 2H), 8.96 (s, 8H), 8.85 (s, 1H), 8.60 (d, *J* = 7.9 Hz, 1H), 8.55 (d, *J* = 7.9 Hz, 1H), 8.35 (d, *J* = 7.9 Hz, 1H), 7.91 (s, 8H), 7.78-7.55 (m, 16H), 7.46 (d, *J* = 6.1 Hz, 4H), 7.35 (s, 6H), 7.27-7.09 (m, 46H), 7.01 (s, 2H), 6.81-6.72 (m, 2H), 6.63-6.57 (m, 2H), 6.50 (s, 12H), 6.43 (s, 2H), 6.38 (s, 7H), 6.01-5.85 (m, 2H), 5.64 (s, 8H), 5.01-4.76 (m, 19H), 4.73 (s, 12H), 4.42 (d, *J* = 18.8 Hz, 4H), 4.26 (s, 2H), 4.18-4.06 (m, 4H), 4.05-3.87 (m, 12H), 3.84-3.60 (m, 26H), 3.60-3.49 (m, 4H), 3.40-3.17 (m, 6H), 3.00 (s, 3H), 2.23 (d, *J* = 18.8 Hz, 12H), 1.88-1.77 (m, 4H), 1.76-1.45 (m, 16H), 1.33-1.10 (m, 38H), 1.10 (s, 12H). ^{13}C NMR (126 MHz, CD_3CN): δ 169.4, 166.7, 164.2, 164.1, 160.9, 160.8, 160.7, 158.9, 158.8, 155.5, 155.4, 154.4, 149.6, 149.5, 149.0, 148.9, 148.2, 146.6, 146.5, 146.1, 145.4, 144.6, 142.7, 142.0, 140.7, 140.6, 138.0, 137.0, 136.9, 133.4, 133.2, 133.1, 132.4, 132.3, 131.8, 131.5, 130.8, 129.7, 129.6, 129.4, 128.8, 128.5, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 126.8, 126.3, 126.2, 126.1, 126.0, 125.9, 125.8, 125.7, 125.5, 125.3, 124.9, 124.7, 124.1, 124.0, 123.9, 120.9, 120.5, 120.1, 114.7, 109.3, 109.2, 109.1, 107.4, 106.6, 106.5, 102.3, 75.5, 72.5, 71.8, 71.5, 71.2, 71.1, 71.0, 70.9, 70.7, 70.5, 70.1, 69.8, 69.1, 69.0, 66.3, 65.5, 64.3, 63.9, 63.4, 63.0, 50.9, 50.8, 50.7, 40.5, 36.2, 36.1, 31.6, 30.9, 30.8, 30.7, 30.5, 30.3, 30.2, 30.1, 30.0, 29.9, 29.6, 27.8, 27.2, 27.1, 26.9, 26.9, 26.8, 24.5, 24.4, 23.7, 17.0. HRMS (ESI): Calcd for $C_{281}H_{305}F_{12}N_{19}O_{35}P_2S_6$: 2495.0174 $[M\text{-}2PF_6^-]^{2+}$. Found: 2495.0173. HRMS (ESI): Calcd for $C_{281}H_{305}F_6N_{19}O_{35}PS_6$: 1615.0234 $[M\text{-}3PF_6^-]^{3+}$. Found:1615.0268.

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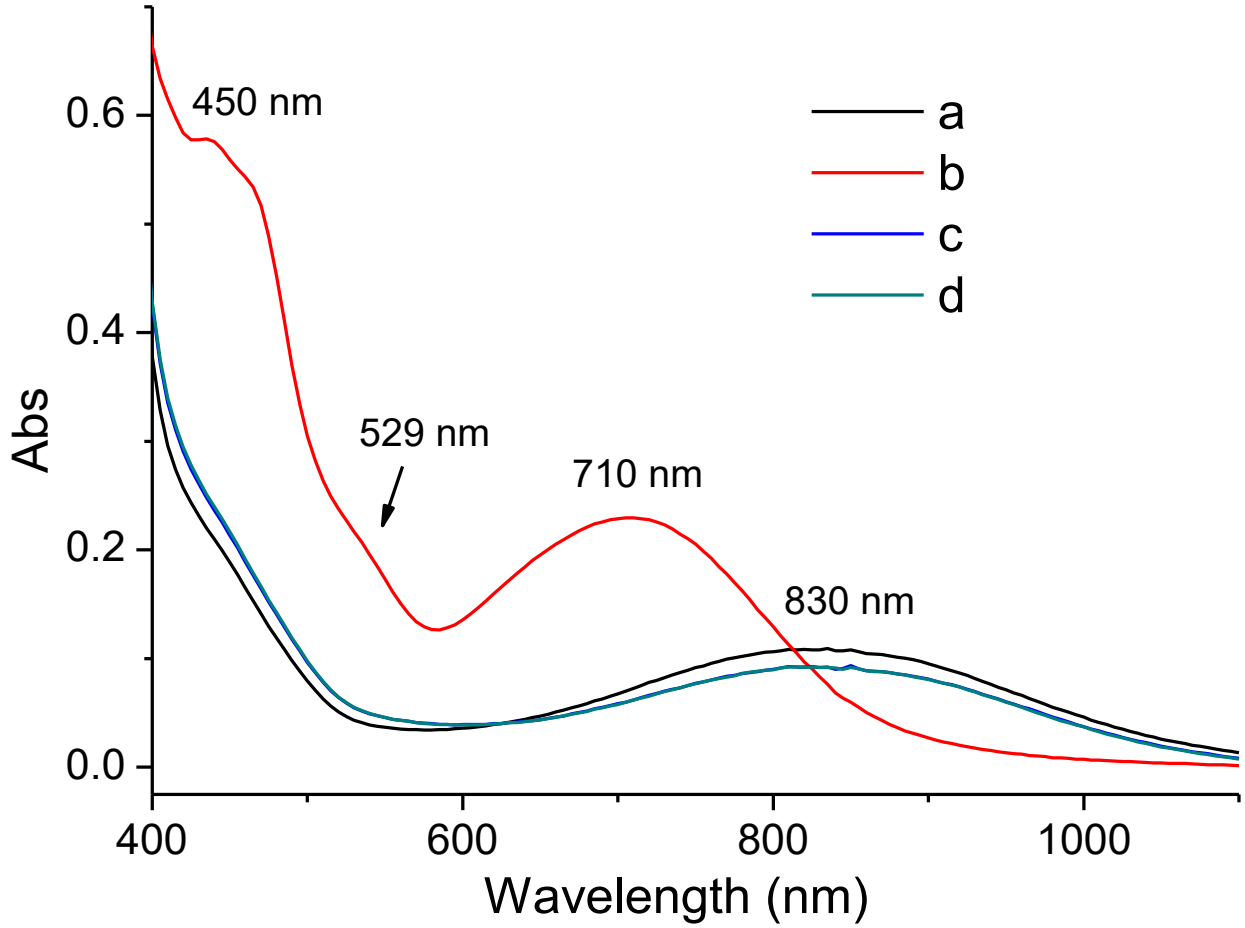

Figure S1. Absorption spectra of [2]rotaxane **1**·4PF_6 (50 μM) in MeCN and $CHCl_3$ (1:1) at 298 K: a) The original solution; b) After $Fe(ClO_4)_3$ (1 equiv) was added; c) After NEt_3 (25 equiv) was added; and d) Recorded after 20 min.

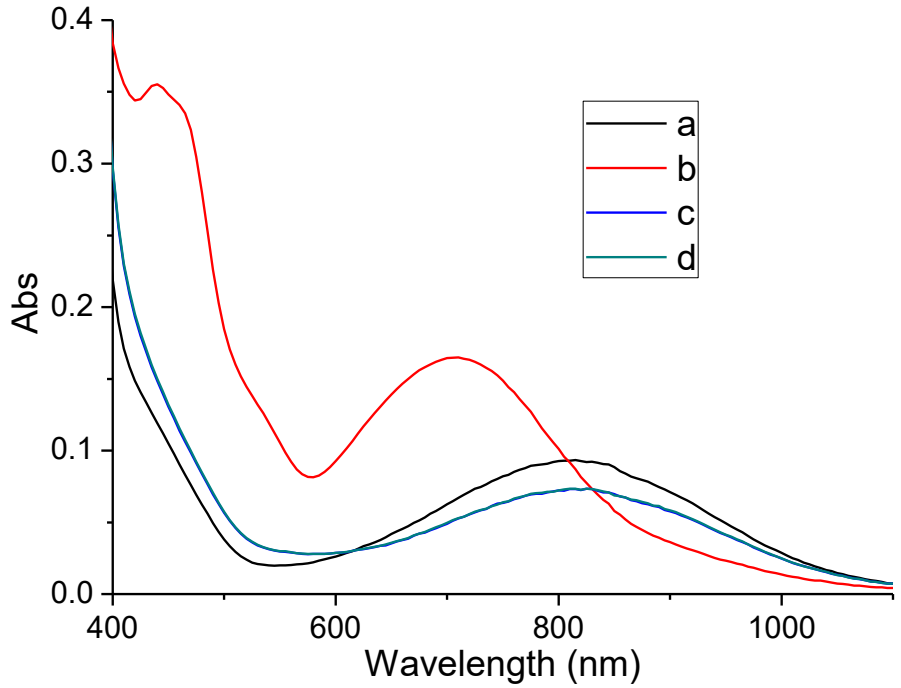

Figure S2. Absorption spectra of [2]rotaxane **1**·4PF_6 (50 μM) in MeCN at 298 K: a) The original solution; b) After $Fe(ClO_4)_3$ (1 equiv) was added; c) After NEt_3 (25 equiv) was added; and d) Recorded after 20 min.

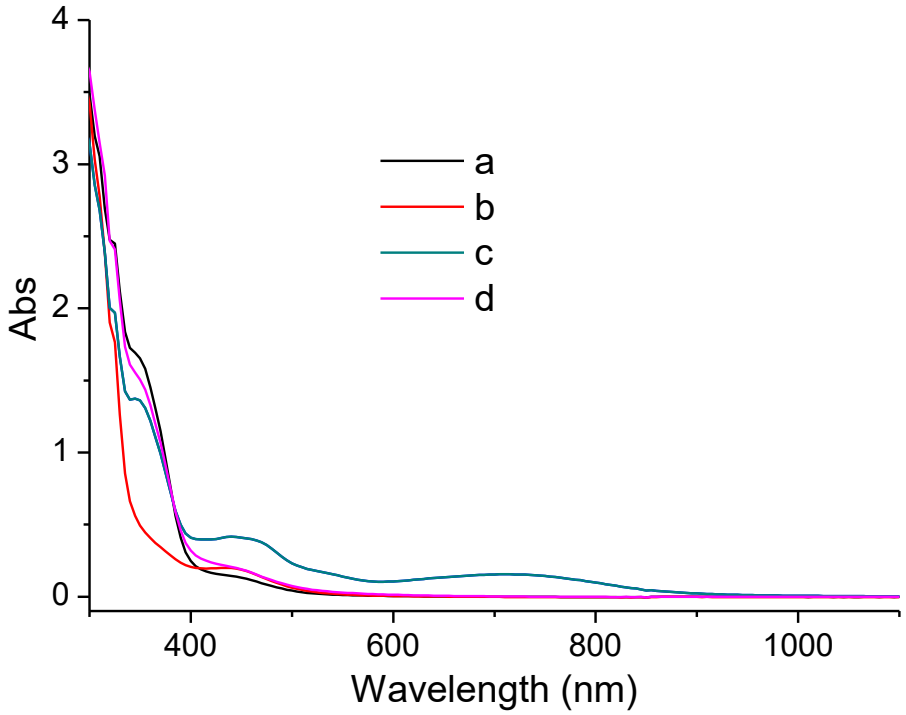

Figure S3. The UV/Vis spectra of the linear component (**LC**) (50 μM) in MeCN and $CHCl_3$ (1:1) at 298 K: a) The original solution; b) After irradiating the solution with 365 nm light for 10 min; c) After $Fe(ClO_4)_3$ (1.0 equiv) was added; and d) After NEt_3 (25 equiv) was added.

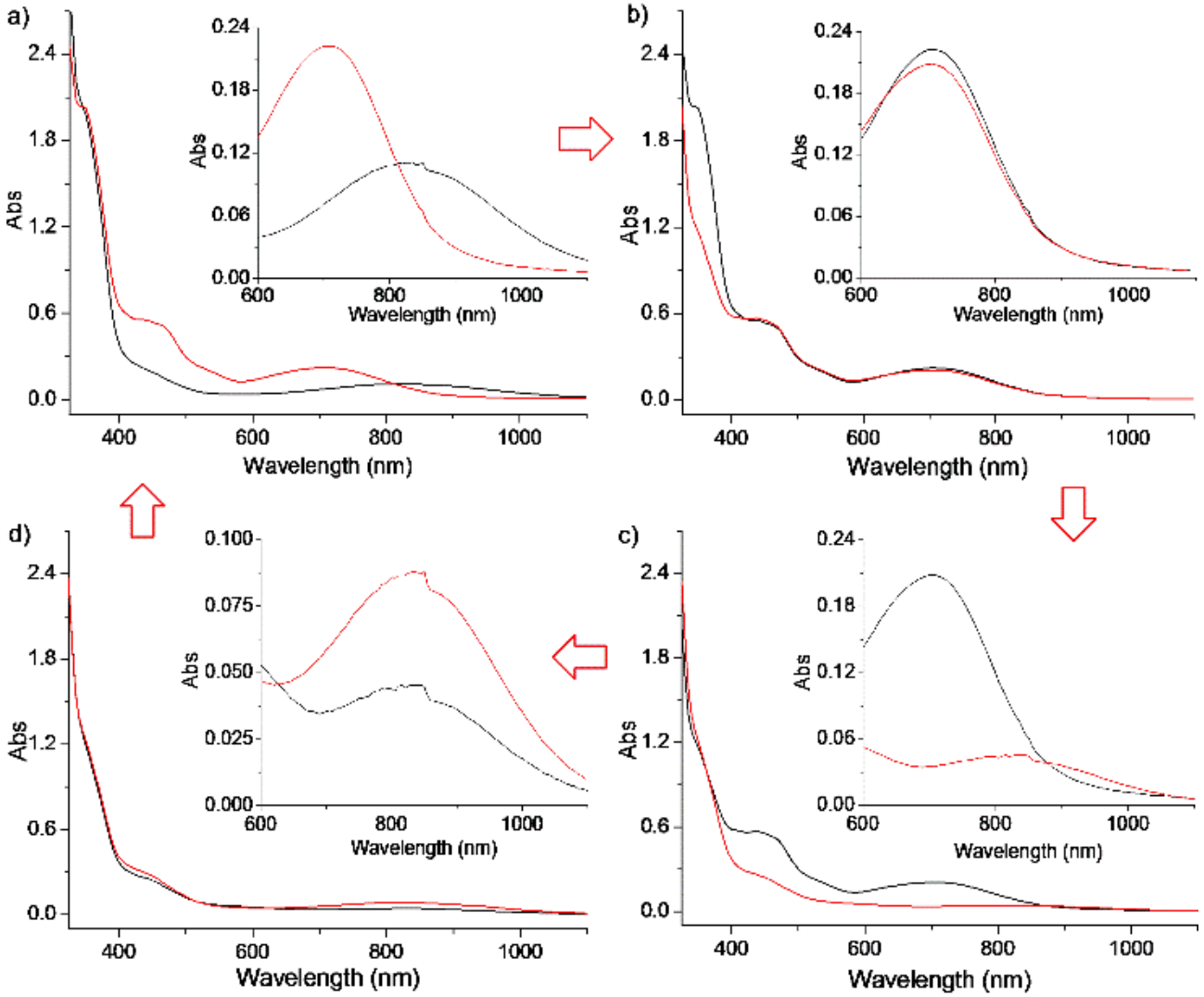

Figure S4. UV/vis spectra of [2]rotaxane $\mathbf{1}^{4+}$•$4PF_6^-$ (50 μM) in MeCN and $CHCl_3$ (1:1) at 298 K: a) Before (black) and after (red) $Fe(ClO_4)_3$ (1.0 equiv) was added; b) Before (black) and after (red) irradiation with 365 nm light; c) Before (black) and after (red) NEt_3 (25 equiv) was added and recorded immediately; and d) Recorded immediately (black) and 3 h later (red) after NEt_3 was added.

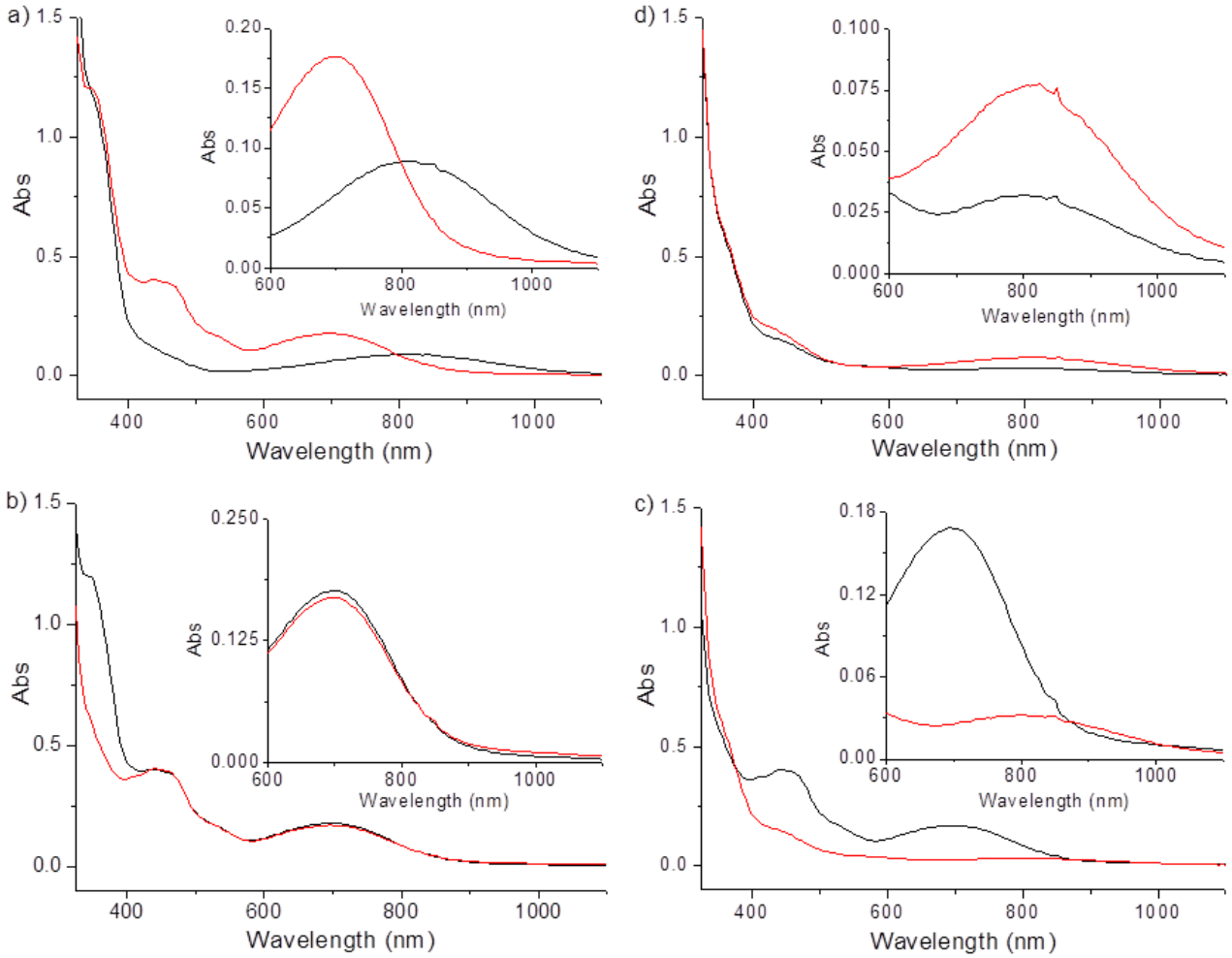

Figure S5. UV/vis spectra of [2]rotaxane $\mathbf{1}^{4+}$•$4PF_6^-$ (50 μM) in MeCN at 298 K: a) Before (black) and after (red) $Fe(ClO_4)_3$ (1.0 equiv) was added; b) Before (black) and after (red) irradiation with 365 nm light; c) Before (black) and after (red) NEt_3 (25 equiv) was added and recorded immediately; and d) Recorded immediately (black) and 2 h later (red) after NEt_3 was added.

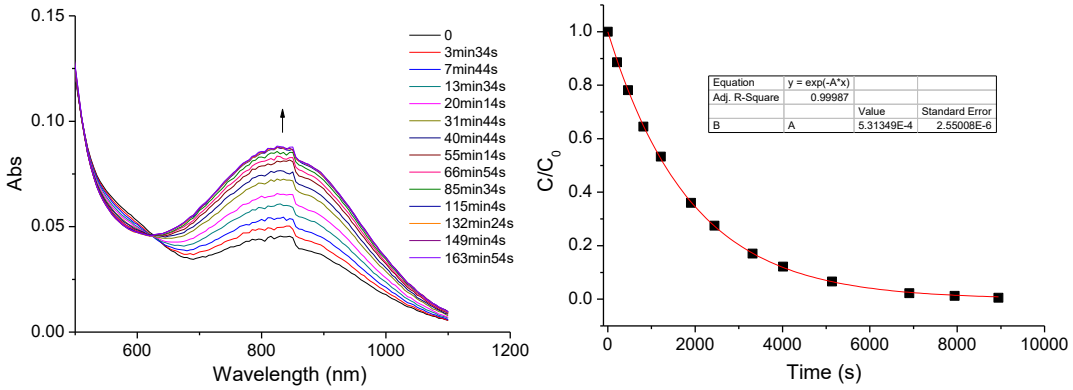

Figure S6. Left: Time-dependent UV/Vis spectra of [2]rotaxane **1**·$4PF_6$ in MeCN and $CHCl_3$ (1:1) at 298 K obtained after NEt_3 (25 equiv) was added to the sample shown in Figure S4. Right: The plot of the C/C_0 (C_0 was the initial concentration of MSCC after reduction and C was the concentration of MSCC after time t) ratio versus the recording time.

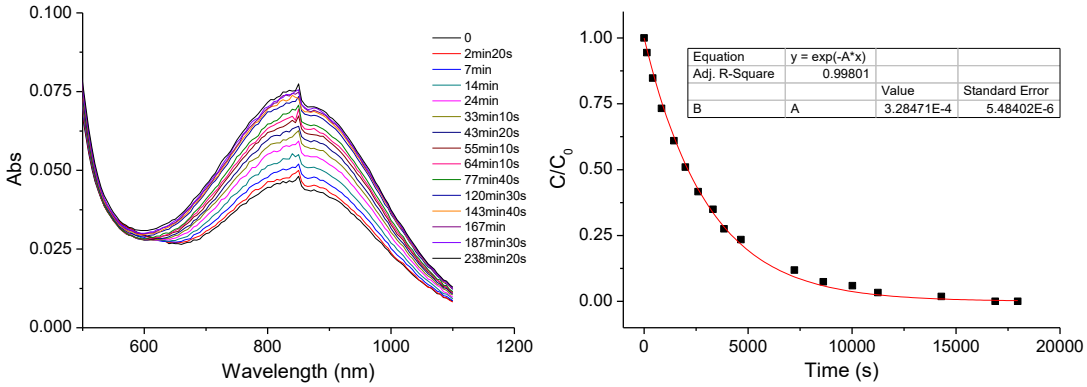

Figure S7. Left: Time-dependent UV/Vis spectra of [2]rotaxane **1**·4PF_6 in MeCN and $CHCl_3$ (1:3) at 298 K obtained after NEt_3 (25 equiv) was added to the sample shown in Fig. 3 in the text. Right: The plot of the C/C_0 (C_0 was the initial concentration of MSCC after reduction and C was the concentration of MSCC after time t) ratio versus the recording time.

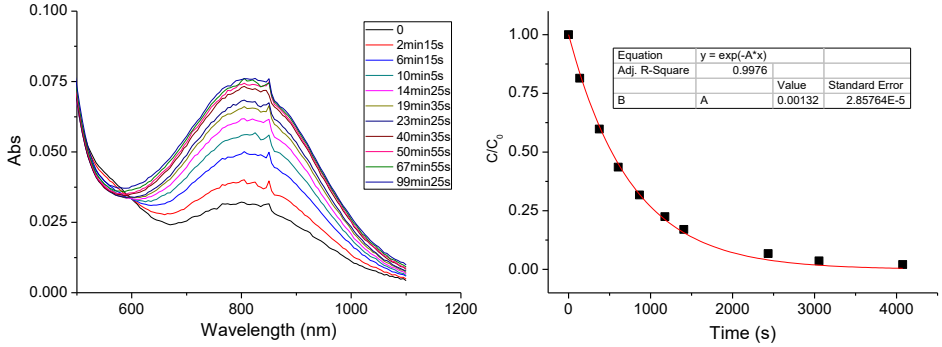

Figure S8. Left: Time-dependent UV/Vis spectra of [2]rotaxane **1**·4PF_6 in MeCN at 298 K obtained after NEt_3 (25 equiv) was added to the sample shown in Figure S5. Right: The plot of the C/C_0 (C_0 was the initial concentration of MSCC after reduction and C was the concentration of MSCC after time t) ratio versus the recording time.

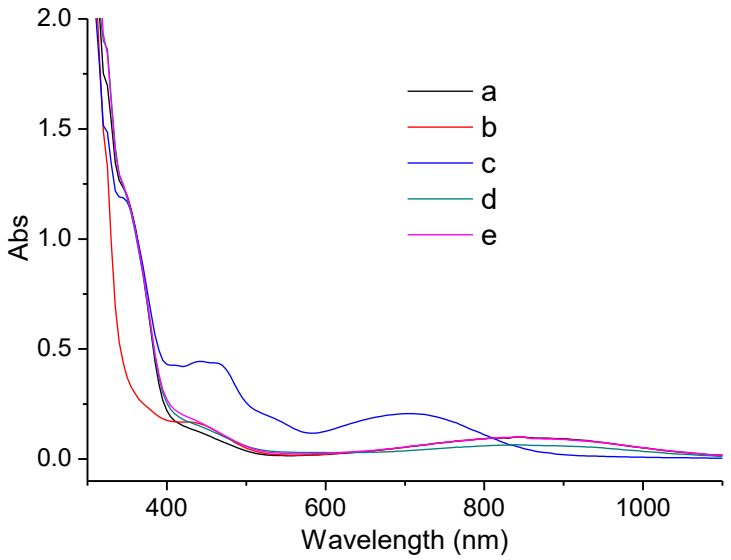

Figure S9. The UV/Vis spectra of [2]rotaxane **1**·4PF_6 (50 μM) in MeCN and $CHCl_3$ (1:3) at 298 K: a) The original solution; b) After irradiating the solution with 365 nm light for 10 min; c) After $Fe(ClO_4)_3$ (1.0 equiv) was added; and d) Recorded immediately and e) 3 h later after NEt_3 (25 equiv) was added.

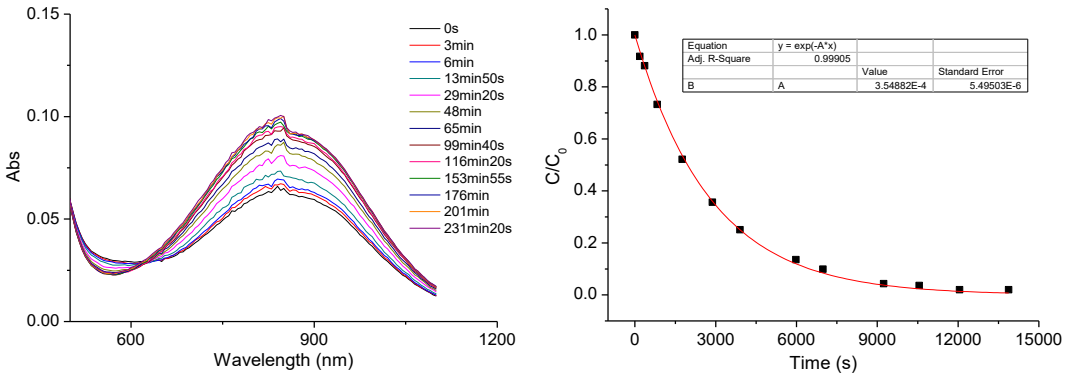

Figure S10. Left: Time-dependent UV/Vis spectra of [2]rotaxane **1**·4PF_6 in MeCN and $CHCl_3$ (1:3) at 298 K obtained after NEt_3 (25 equiv) was added to the sample shown in Figure 4. Right: The plot of the C/C_0 (C_0 was the initial concentration of MSCC after reduction and C was the concentration of MSCC after time t) ratio versus the recording time.

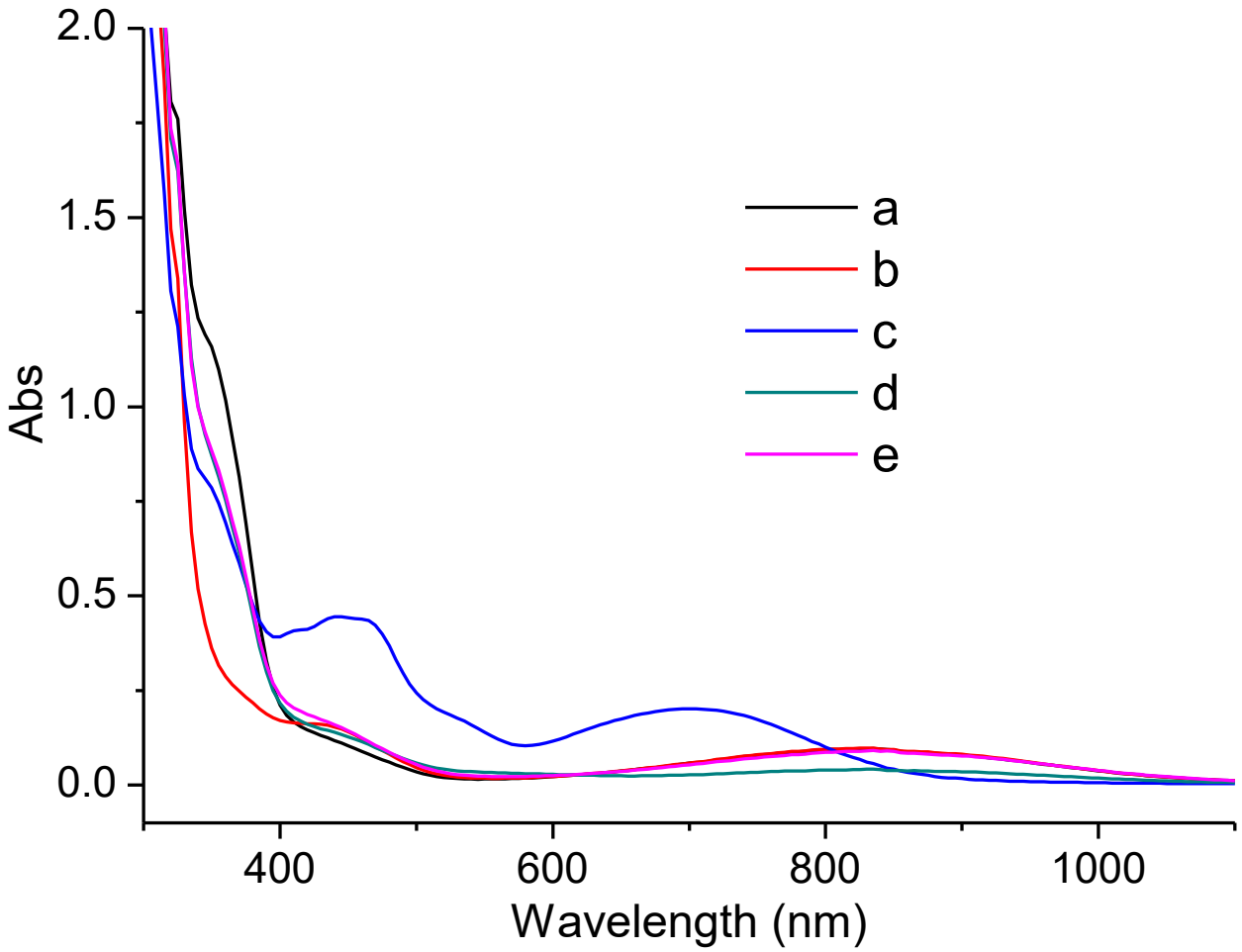

Figure S11. The UV/Vis spectra of [2]rotaxane **1**·4PF_6 (50 μM) in MeCN and $CHCl_3$ (1:1) at 298 K: a) The original solution; b) After irradiating the solution with 365 nm light for 10 min; c) After $Fe(ClO_4)_3$ (1.0 equiv) was added; and d) Recorded immediately and e) 3.5 h later after NEt_3 (25 equiv) was added.

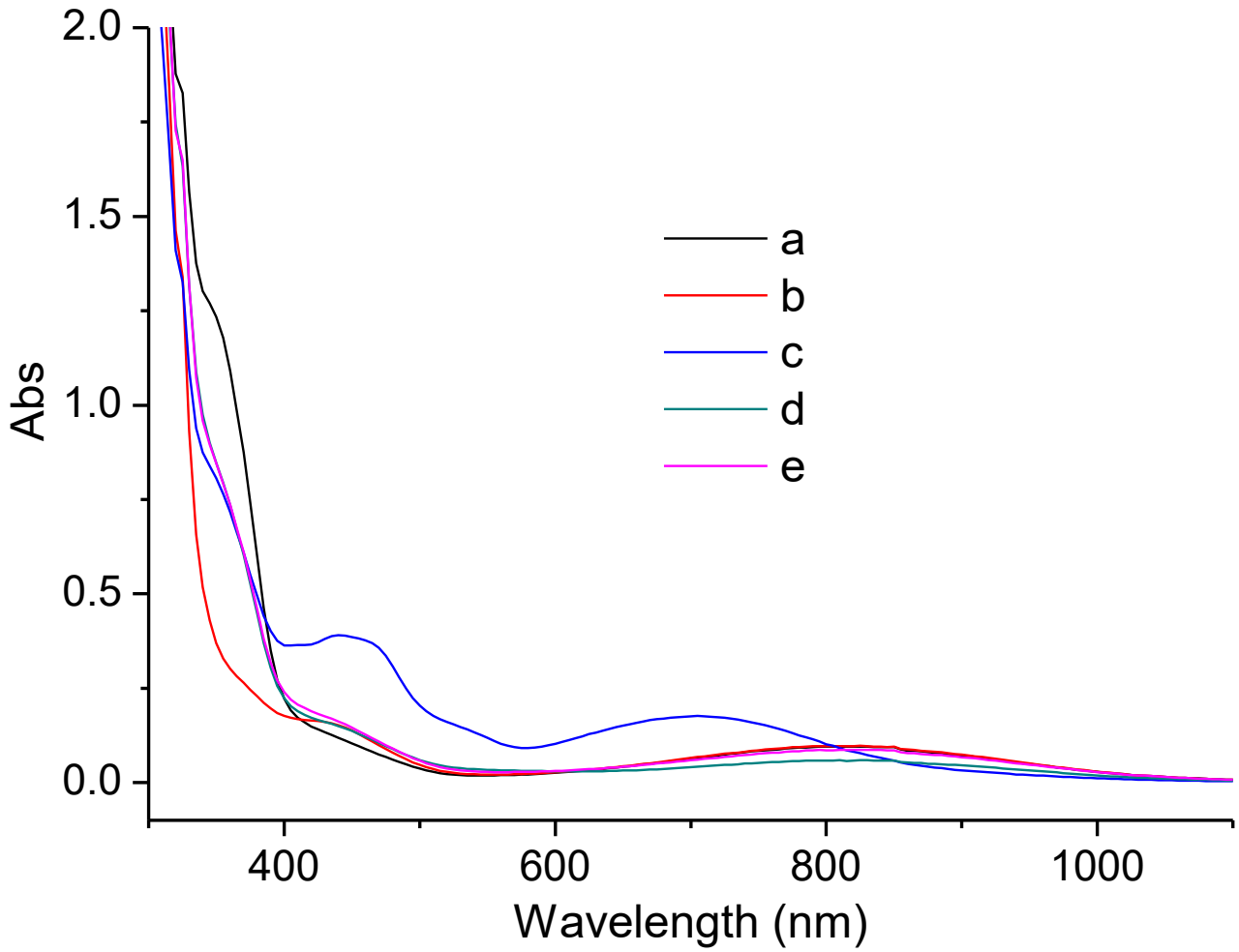

Figure S12. The UV/Vis spectra of [2]rotaxane **1**·4PF_6 (50 μM) in MeCN at 298 K: a) The original solution; b) After irradiating the solution with 365 nm light for 10 min; c) After $Fe(ClO_4)_3$ (1.0 equiv) was added; and d) Recorded immediately and e) 3 h later after NEt_3 (25 equiv) was added.

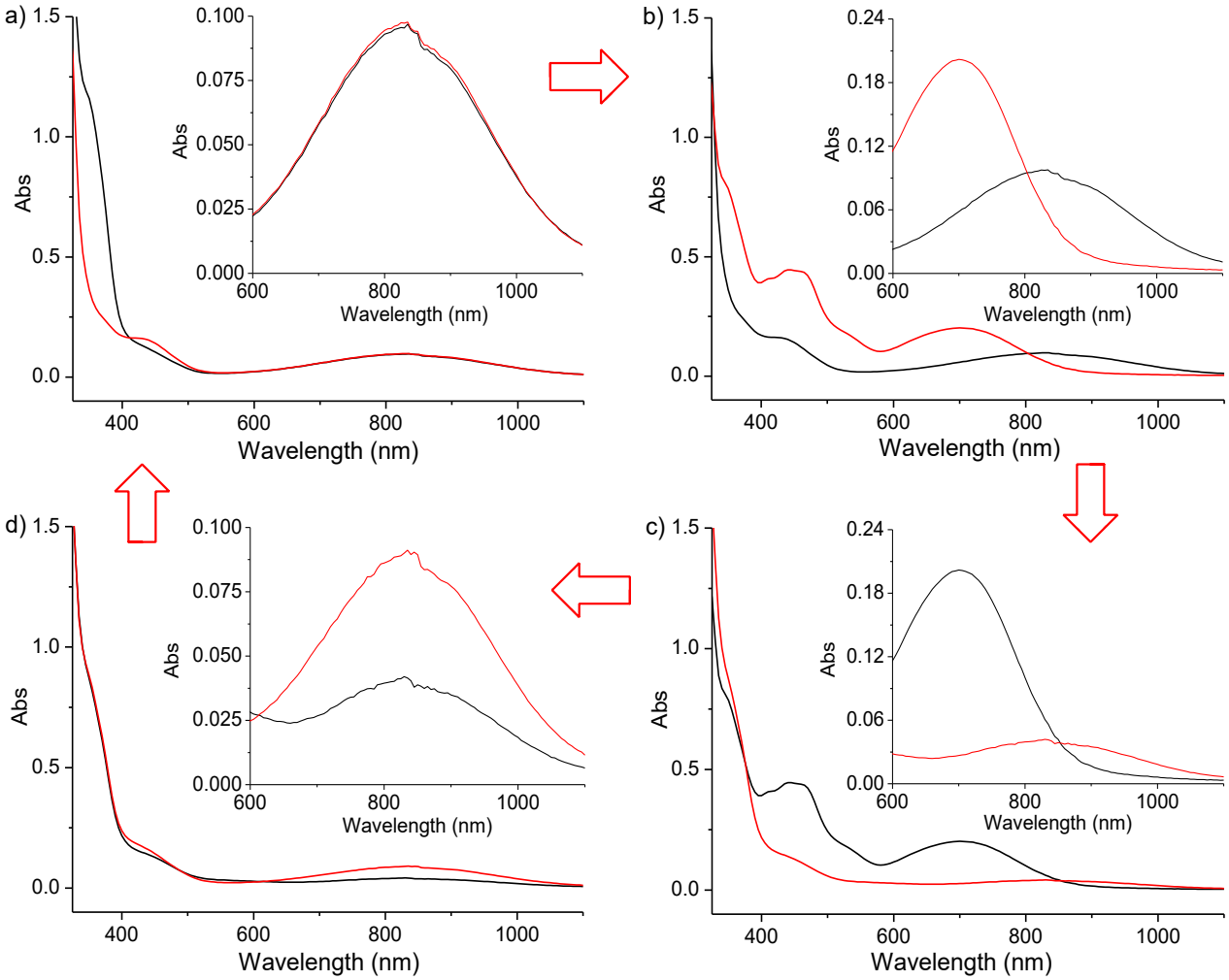

Figure S13. UV/vis spectra of [2]rotaxane $\mathbf{1}^{4+}$•$4PF_6^-$ (50 μM) in MeCN and $CHCl_3$ (1:1) at 298 K: a) Before (black) and after (red) irradiation with 365 nm light for 10 min; b) Before (black) and after (after) $Fe(ClO_4)_3$ (1.0 equiv) was added; c) Before (black) and after (red) NEt_3 (25 equiv) was added and recorded immediately; and d) Recorded immediately (black) and 3.5 h later (red) after NEt_3 was added.

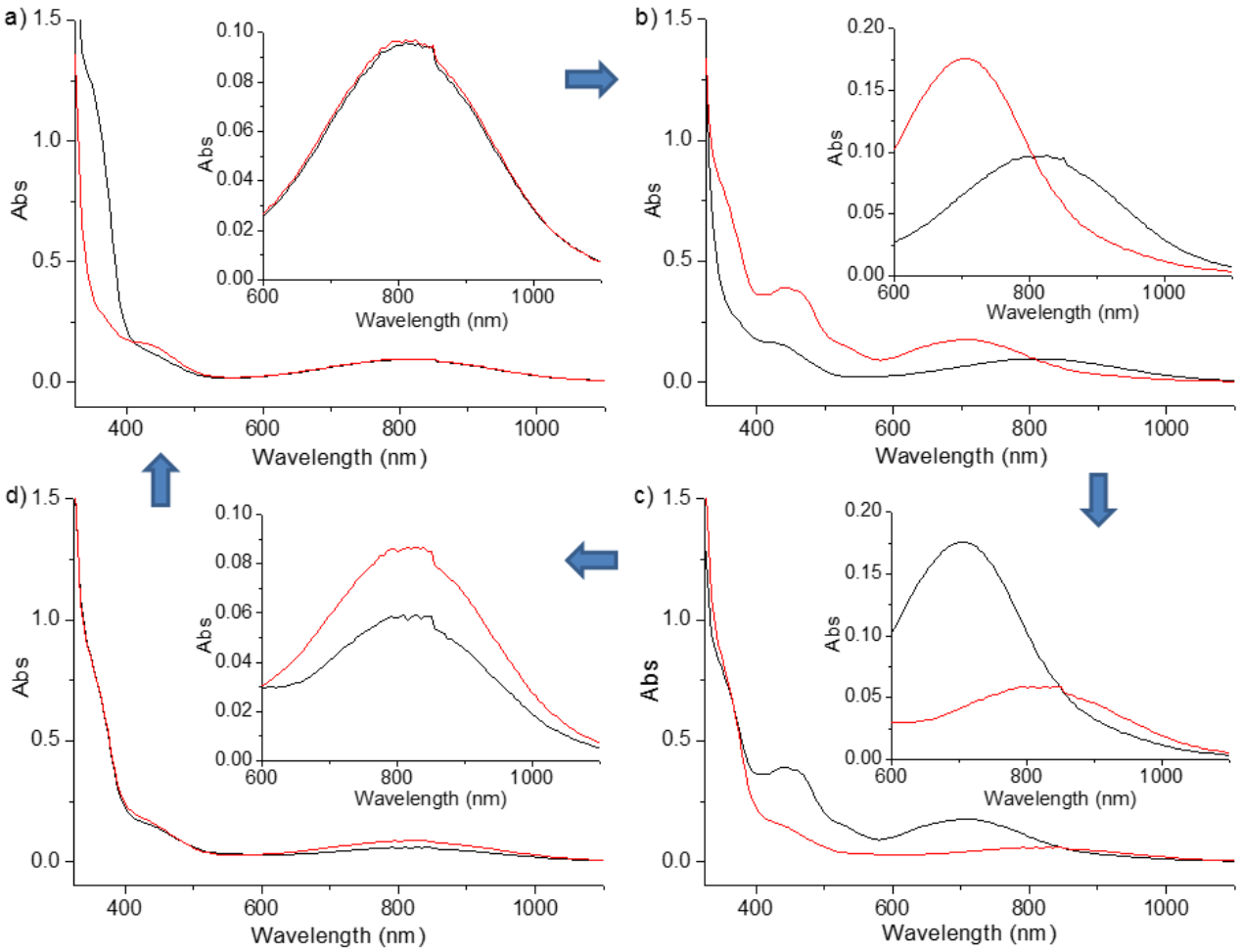

Figure S14. UV/vis spectra of [2]rotaxane $\mathbf{1}^{4+}\bullet 4PF_6^-$ (50 μM) in MeCN at 298 K: a) Before (black) and after (red) irradiation with 365 nm light; b) Before (black) and after (after) $Fe(ClO_4)_3$ (1.0 equiv) was added; c) Before (black) and after (red) NEt_3 (25 equiv) was added and recorded immediately; and d) Recorded immediately (black) and 90 min later (red) after NEt_3 was added.

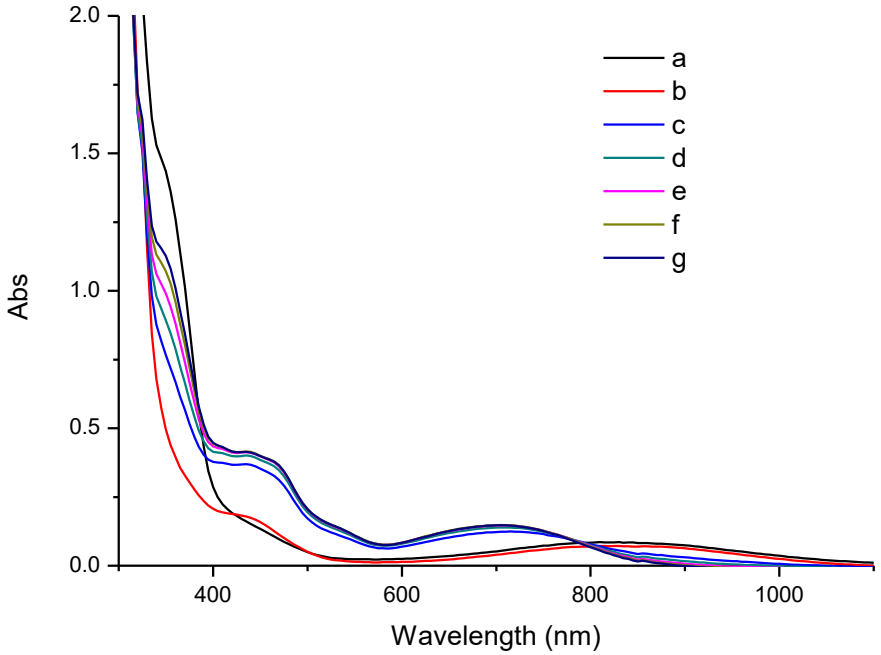

Figure S15. The UV/Vis spectra of [2]rotaxane **1**·4PF_6 (50 μM) in MeCN and $CHCl_3$ (1:1) at 298 K: a) The original solution; b) After irradiating the solution with 365 nm light for 10 min; c) After $Fe(ClO_4)_3$ (1.0 equiv) was added and recorded immediately; and recorded after d) 131 s, e) 260 s, f) 400 s and g) 525 s.

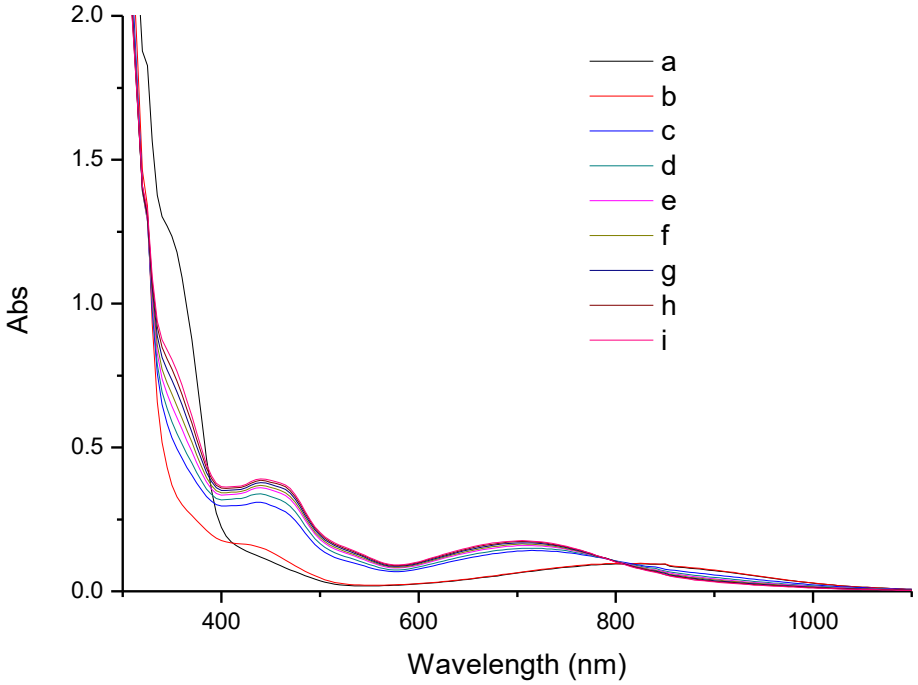

Figure S16. The UV/Vis spectra of [2]rotaxane **1**·4PF_6 (50 μM) in MeCN at 298 K: a) The original solution; b) After irradiating the solution with 365 nm light for 10 min; c) After $Fe(ClO_4)_3$ (1.0 equiv) was added and recorded immediately and recorded after d) 156 s, e) 299 s, f) 448s, g) 628 s and h) 758s, i) 892 s.

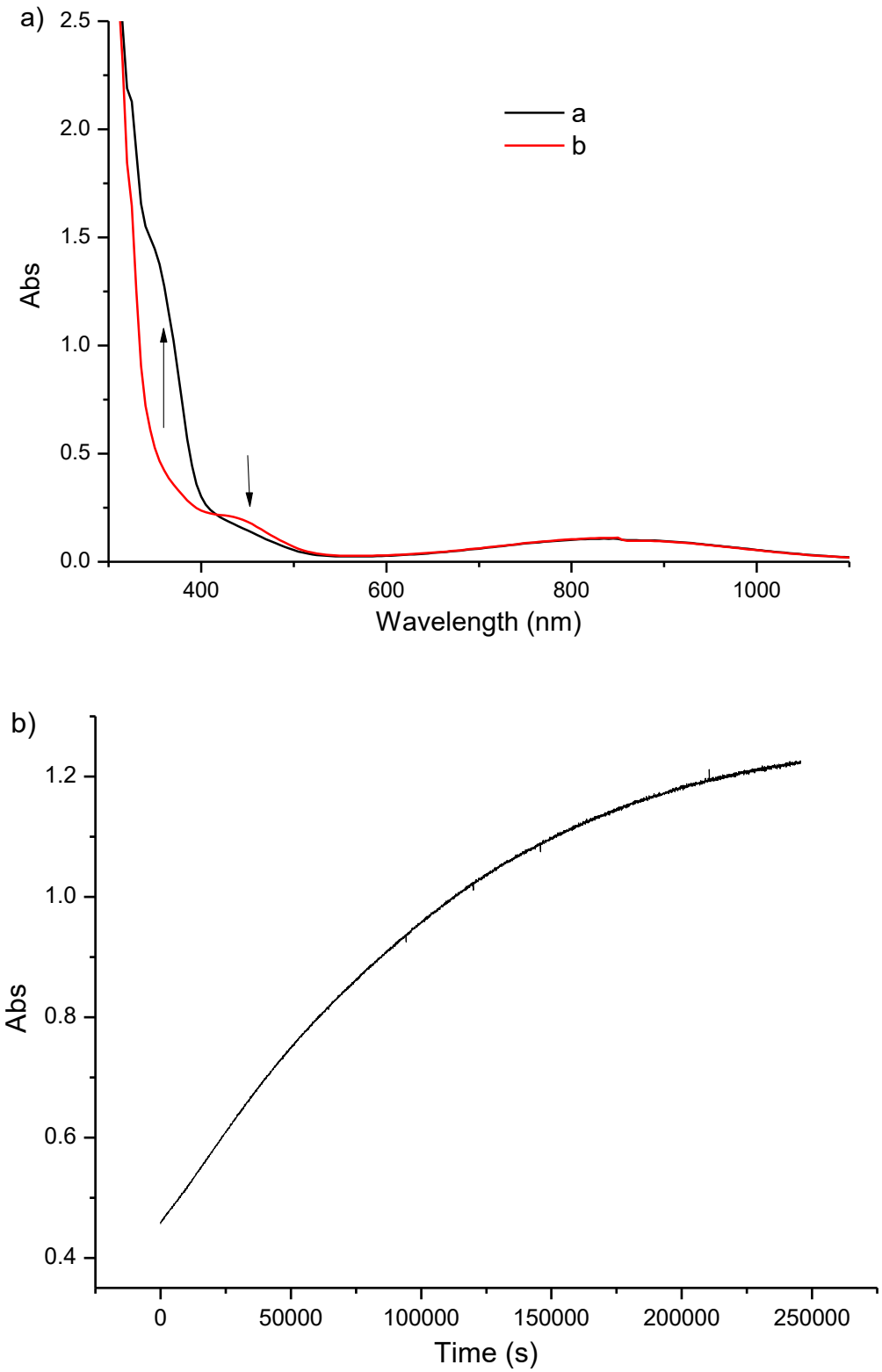

Figure S17. Top: UV/vis spectra of [2]rotaxane $\mathbf{1}^{4+}$•$4PF_6^-$ (50 μM) in MeCN and $CHCl_3$ (1:3) at 298 K: a) Before (black) and after (red) irradiation with 365 nm light. Bottom: Time-dependent absorption changes at 360 nm observed upon leaving the irradiated solution in the dark.

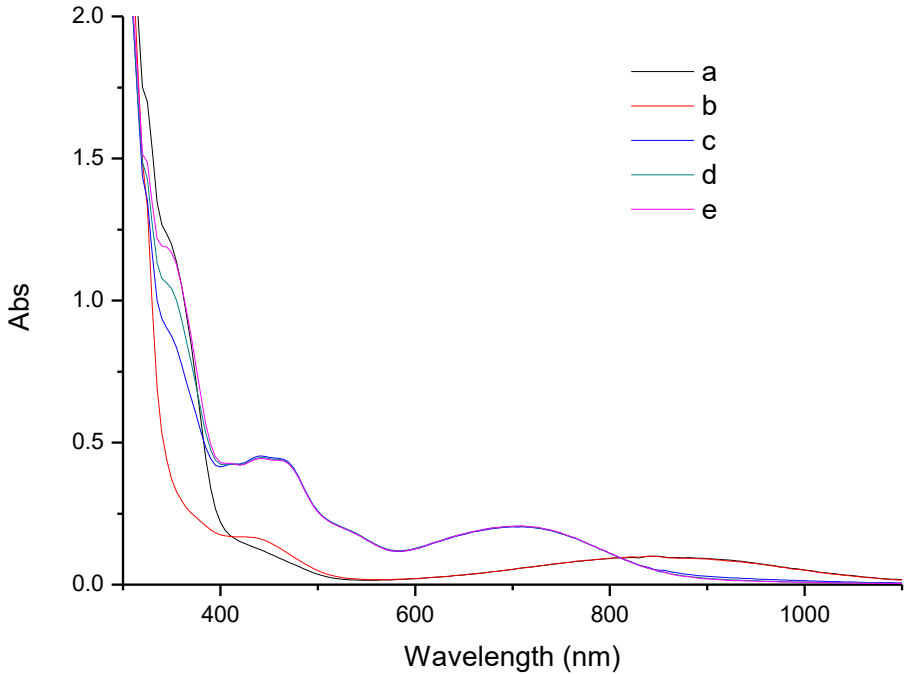

Figure S18. The UV/Vis spectra of [2]rotaxane **1**·4PF_6 (50 μM) in MeCN and $CHCl_3$ (1:3) at 298 K: a) The original solution; b) After irradiating the solution with 365 nm light for 10 min; c) After $Fe(ClO_4)_3$ (1.0 equiv) was added and recorded immediately; and Recorded after d) 2min10s and e) 6min40s.

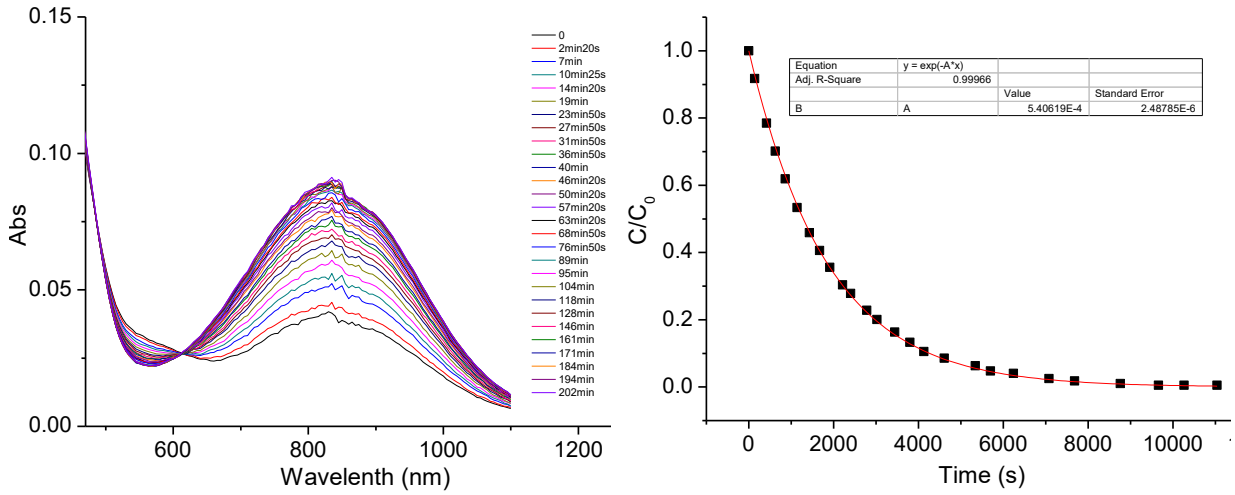

Figure S19. Left: Time-dependent UV/Vis spectra of [2]rotaxane **1**·4PF_6 in MeCN and $CHCl_3$ (1:1) at 298 K obtained after NEt_3 (25 equiv) was added to the sample shown in Figure S13. Right: The plot of the C/C_0 (C_0 was the initial concentration of MSCC after reduction and C was the concentration of MSCC after time t) ratio versus the recording time.

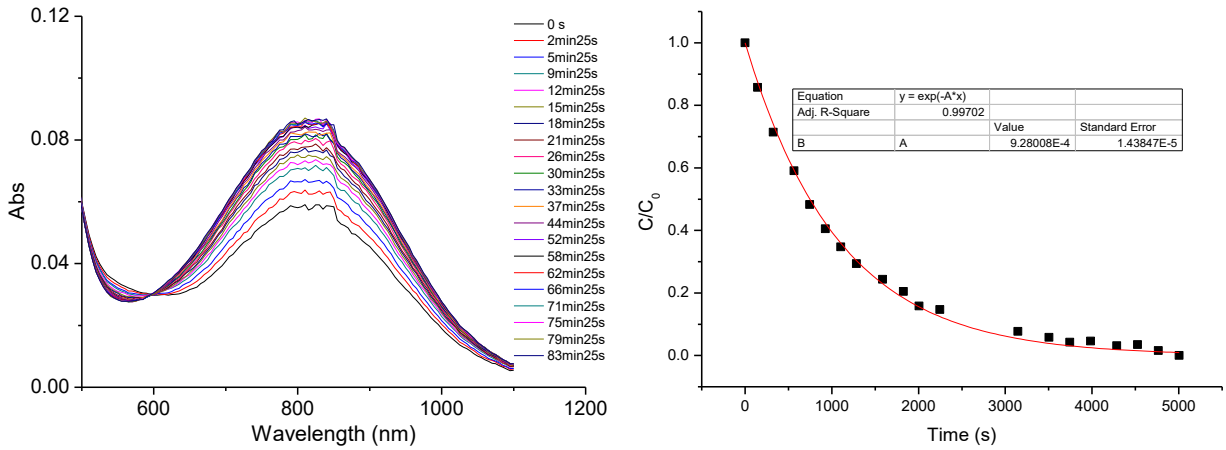

Figure S20. Left: Time-dependent UV/Vis spectra of [2]rotaxane **1**·4PF_6 in MeCN at 298 K obtained after NEt_3 (25 equiv) was added to the sample shown in Figure S14. Right: The plot of the C/C_0 (C_0 was the initial concentration of MSCC after reduction and C was the concentration of MSCC after time t) ratio versus the recording time.

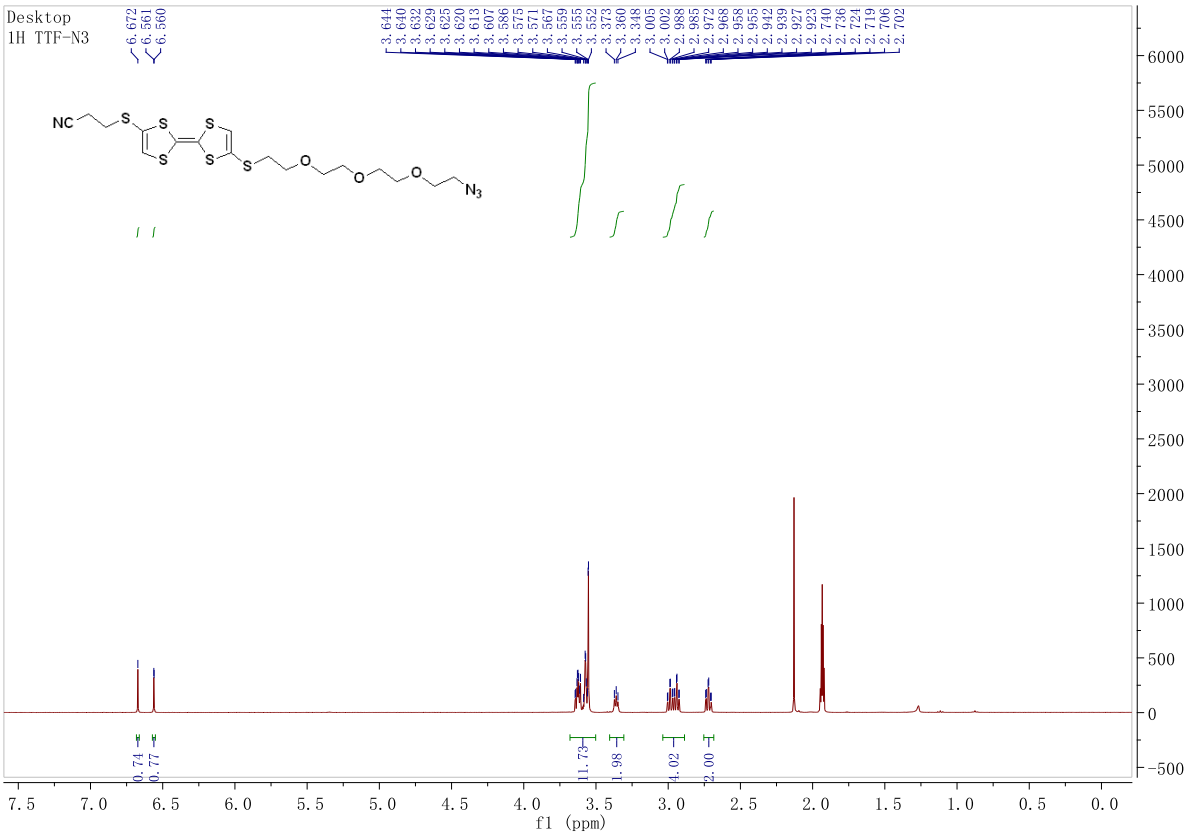

Figure S21. ^{1}H NMR spectrum (400 MHz) of compound **S2** in CD_3CN at 298 K.

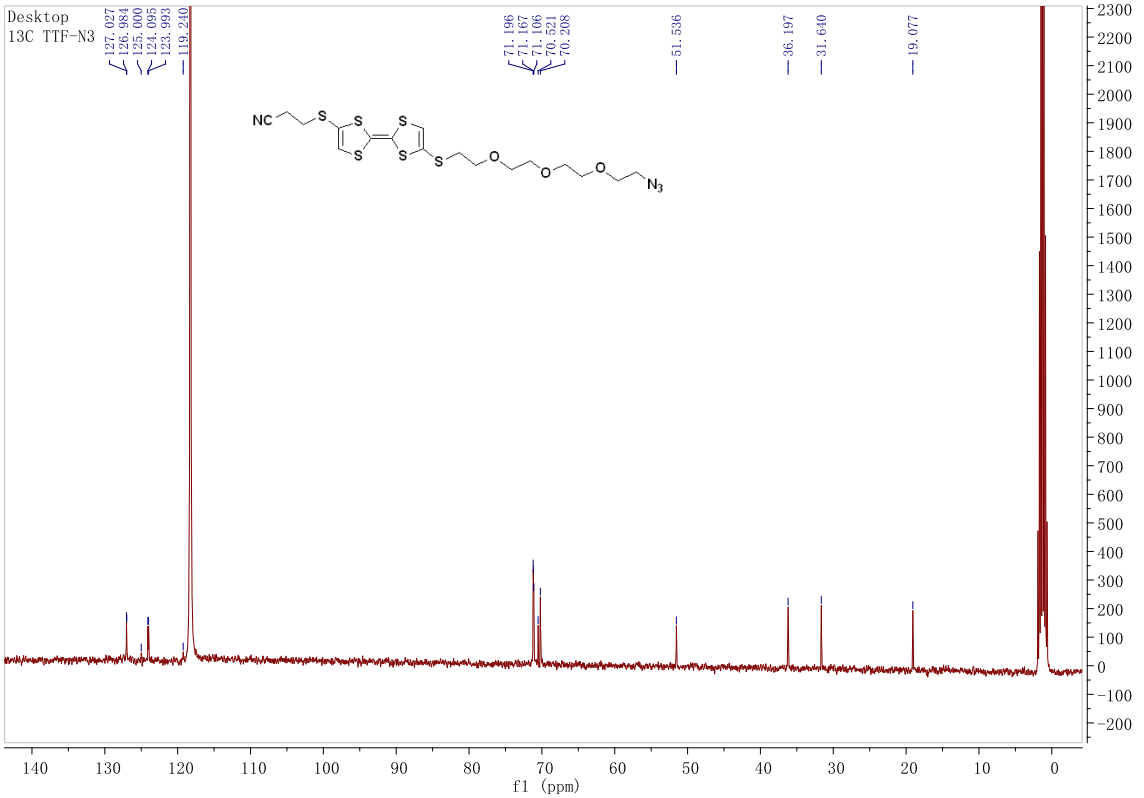

Figure S22. ^{13}C NMR spectrum (100 MHz) of compound **S2** in CD_3CN at 298 K.

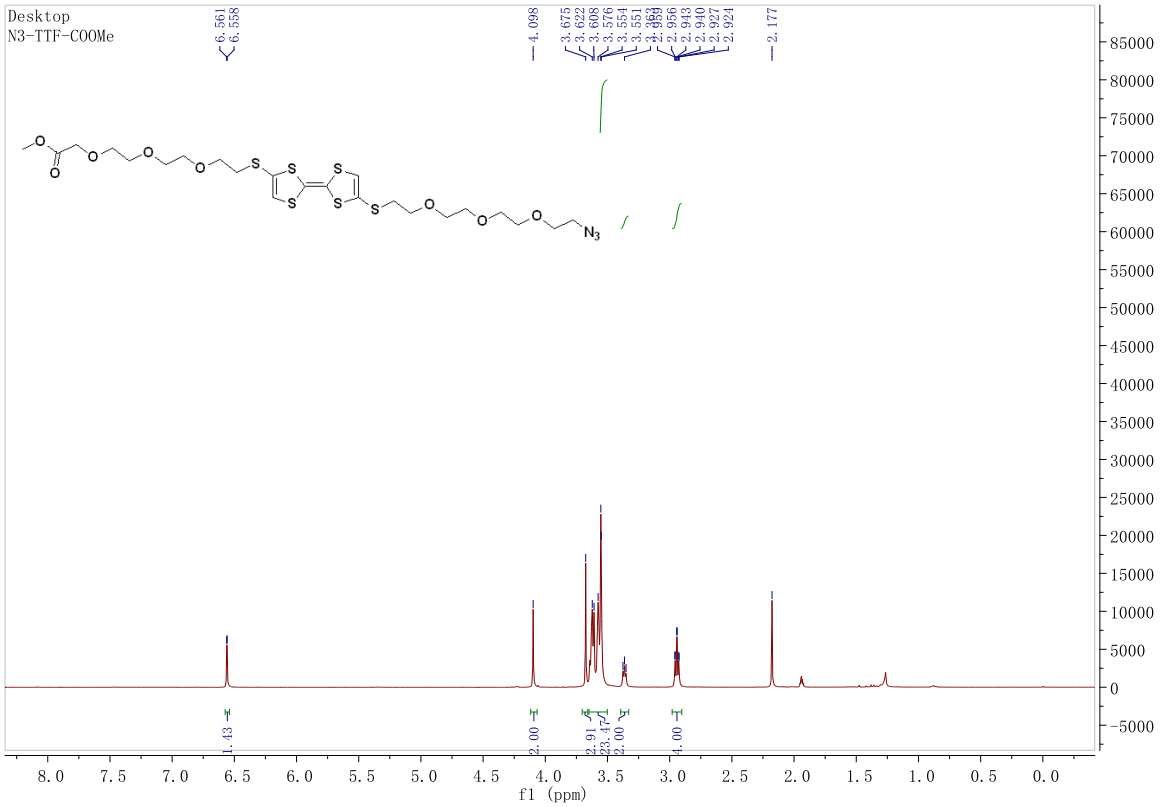

Figure S23. ^{1}H NMR spectrum (400 MHz) of compound **S3** in CD_3CN at 298 K.

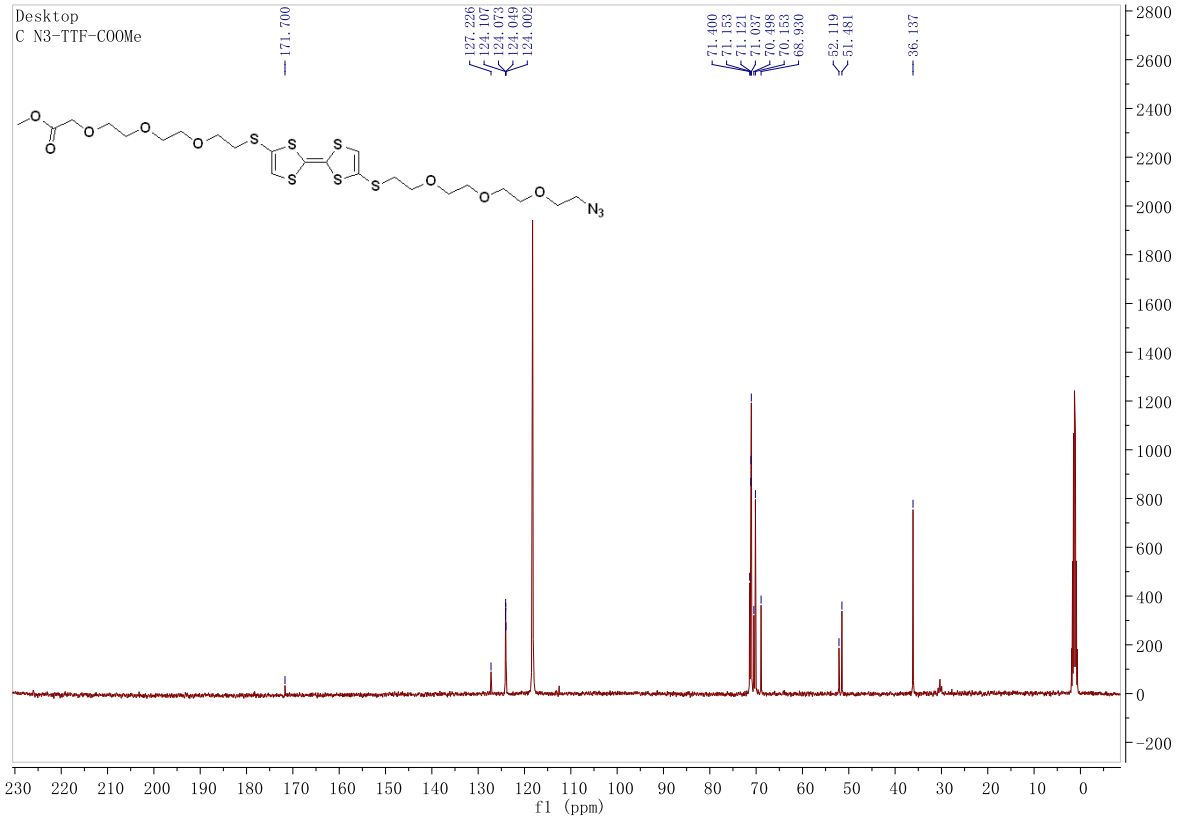

Figure S24. ^{13}C NMR spectrum (100 MHz) of compound **S3** in CD_3CN at 298 K.

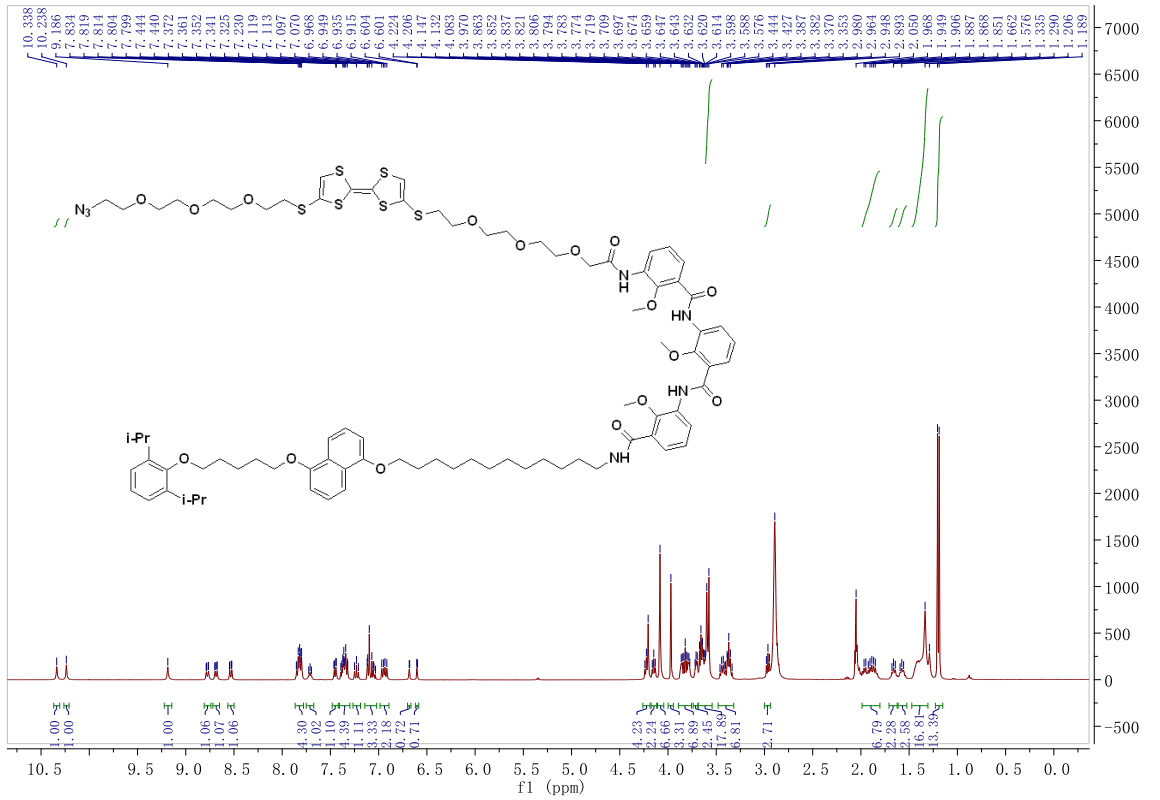

Figure S25. ^{1}H NMR spectrum (400 MHz) of compound **S6** in acetone-d_6 at 298 K.

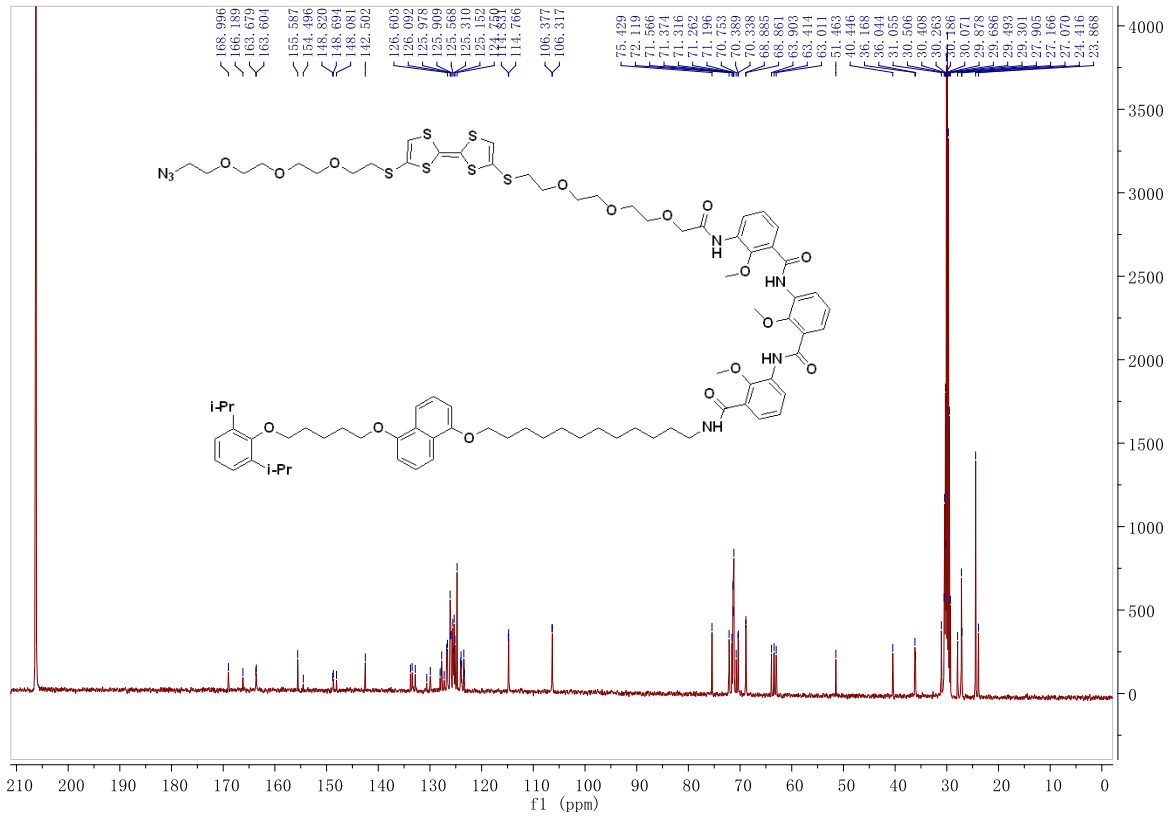

Figure S26. ^{13}C NMR spectrum (100 MHz) of compound **S6** in acetone-d_6 at 298 K.

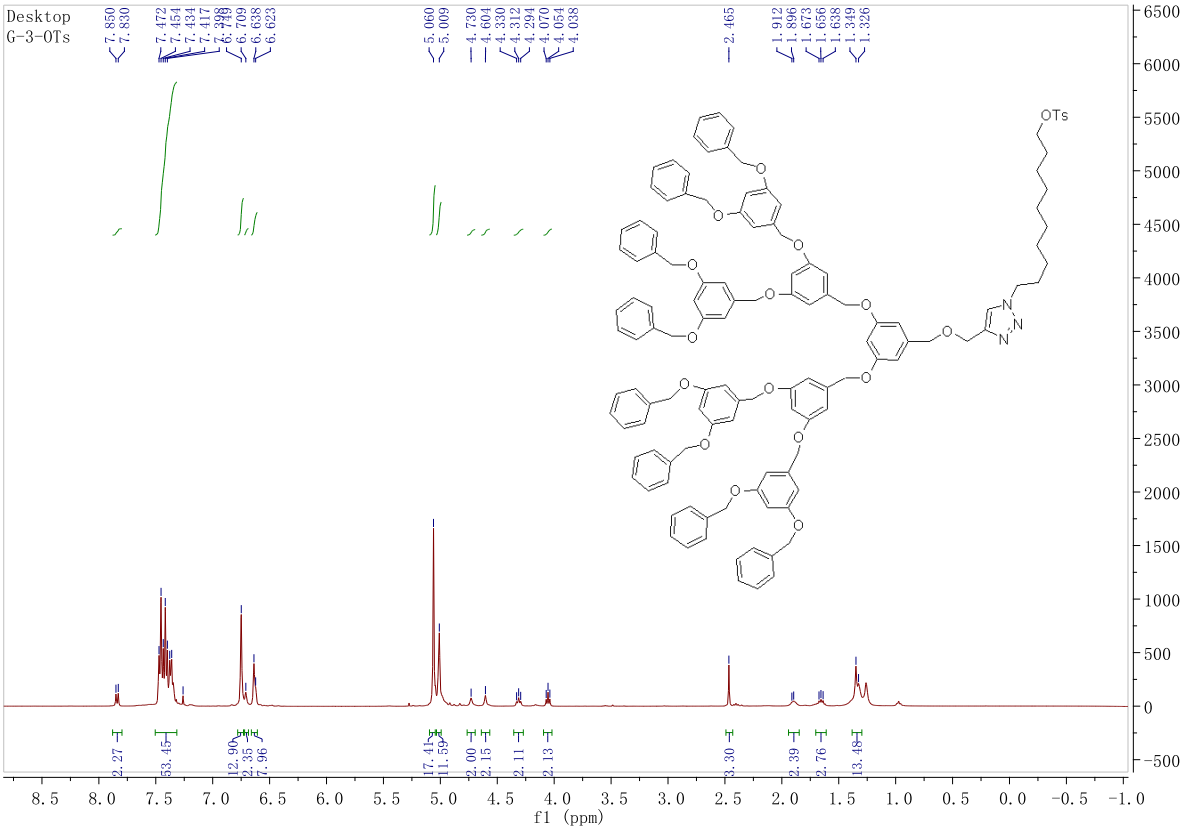

Figure S27. ^{1}H NMR spectrum (400 MHz) of compound **S8** in $CDCl_3$ at 298 K.

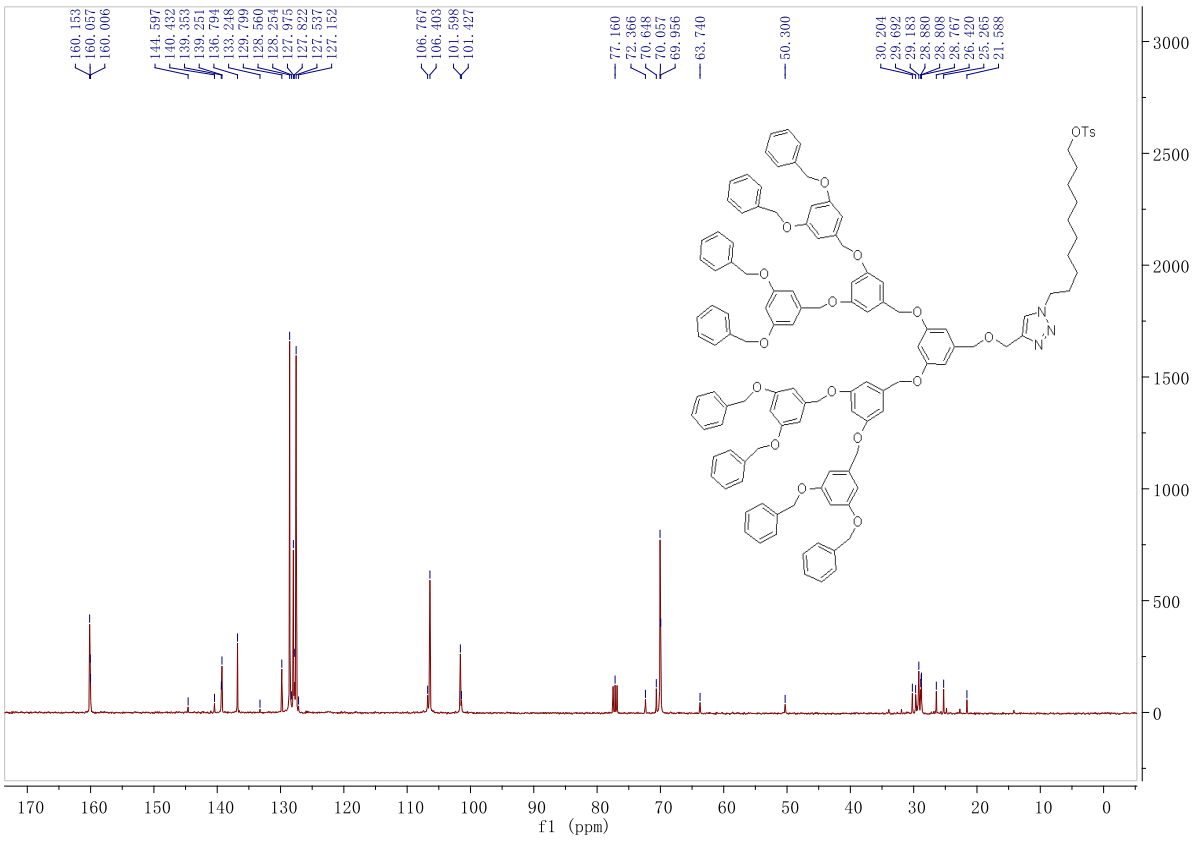

Figure S28. ^{13}C NMR spectrum (100 MHz) of compound **S8** in $CDCl_3$ at 298 K.

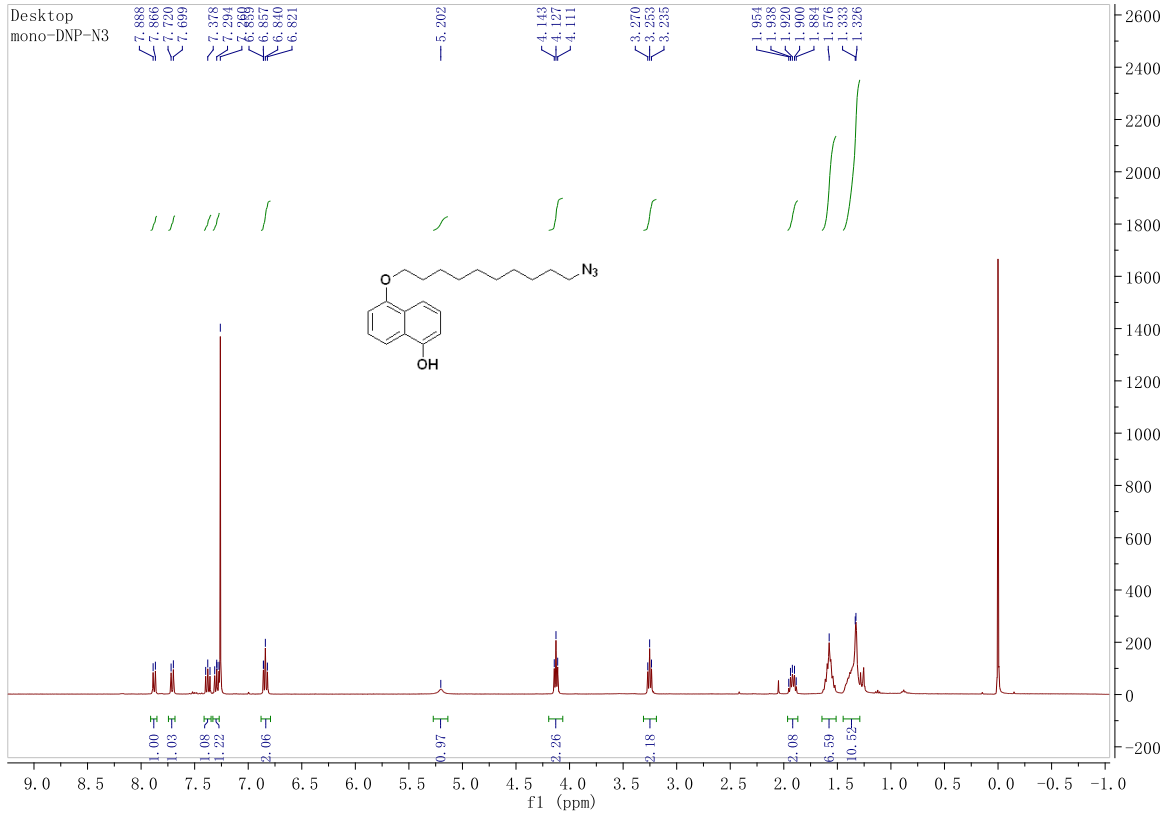

Figure S29. ^{1}H NMR spectrum (400 MHz) of compound **S9** in $CDCl_3$ at 298 K.

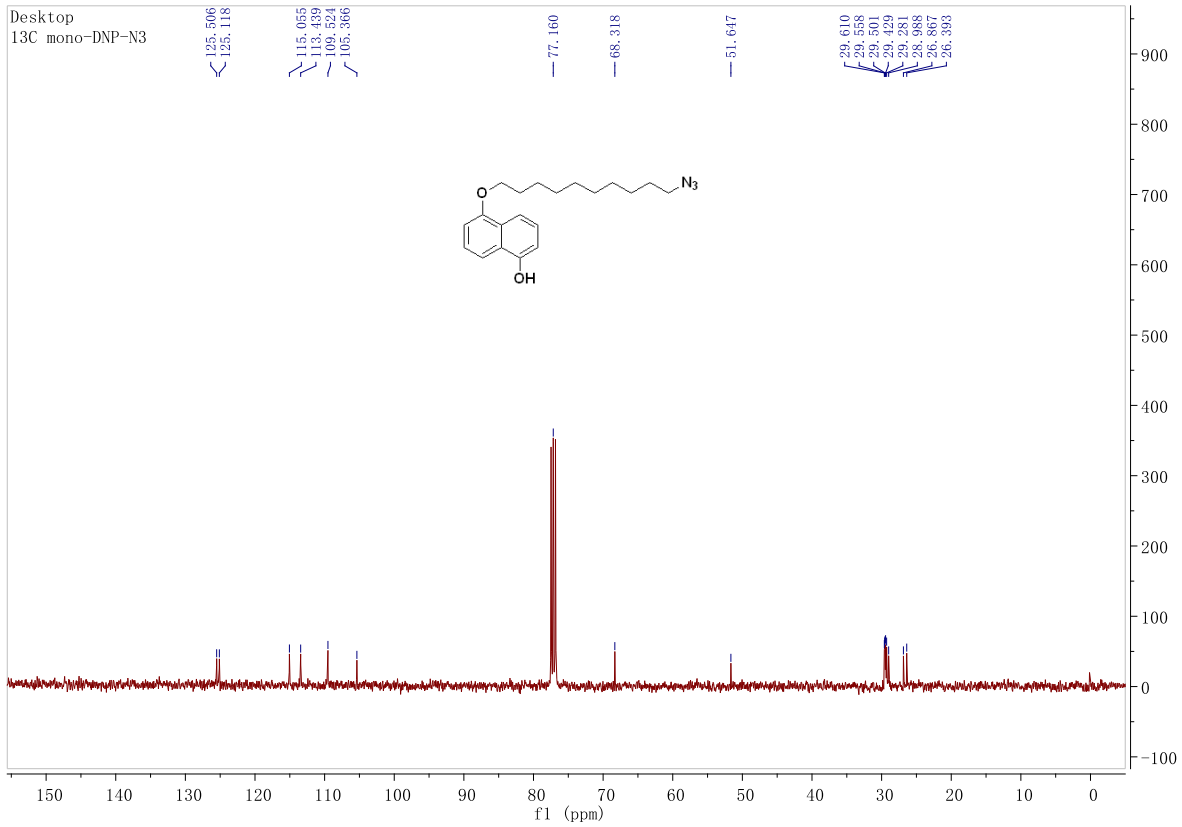

Figure S30. ^{13}C NMR spectrum (100 MHz) of compound **S9** in $CDCl_3$ at 298 K.

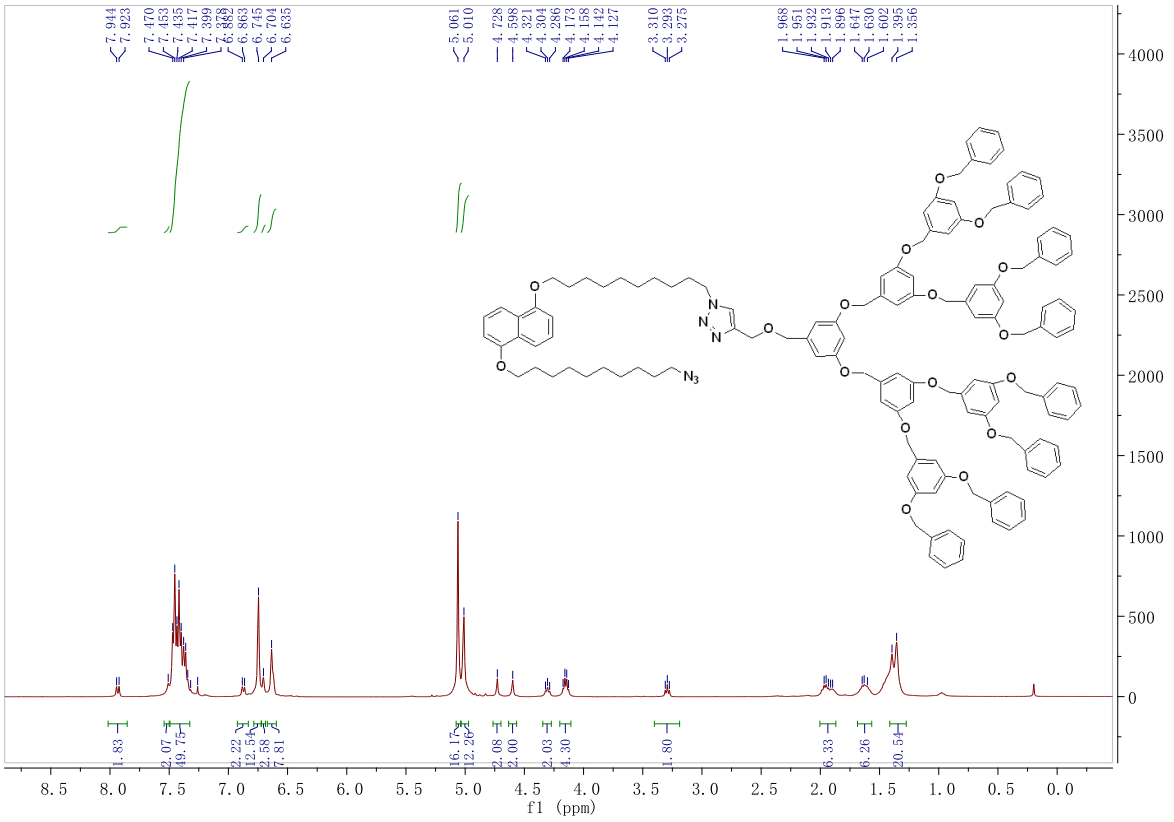

Figure S31. ^{1}H NMR spectrum (400 MHz) of compound **S10** in $CDCl_3$ at 298 K.

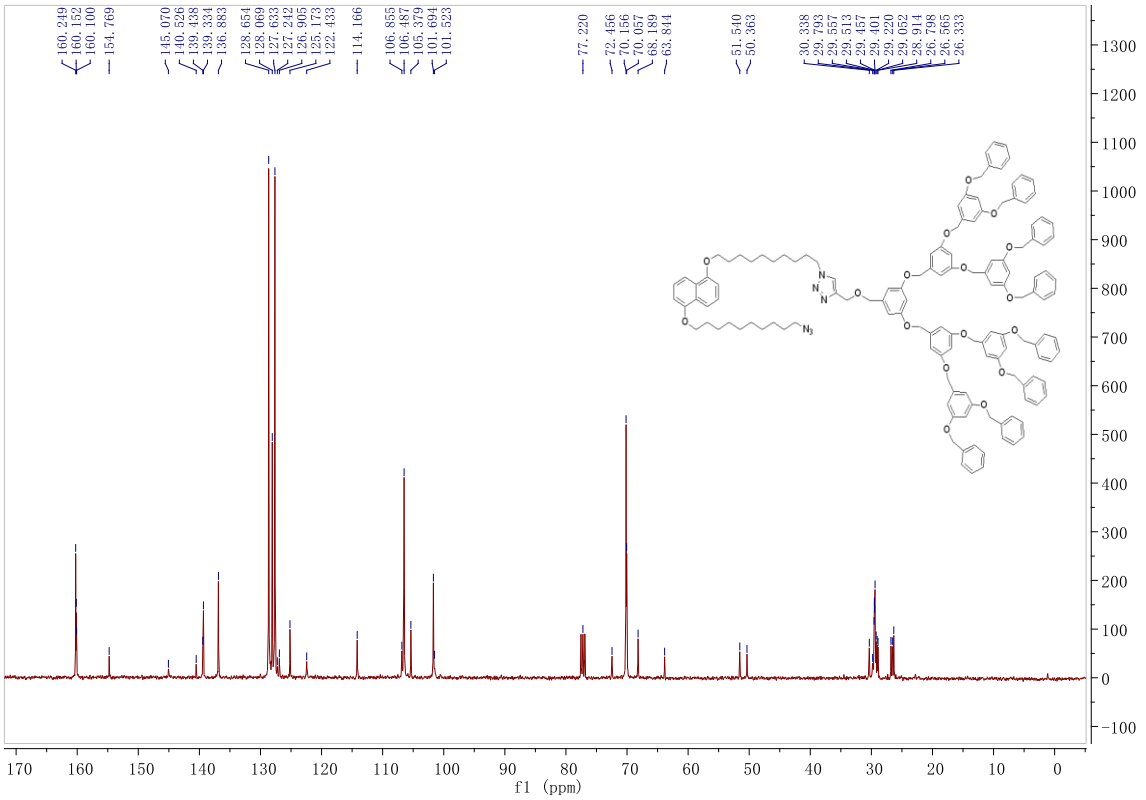

Figure S32. ^{13}C NMR spectrum (100 MHz) of compound **S10** in $CDCl_3$ at 298 K.

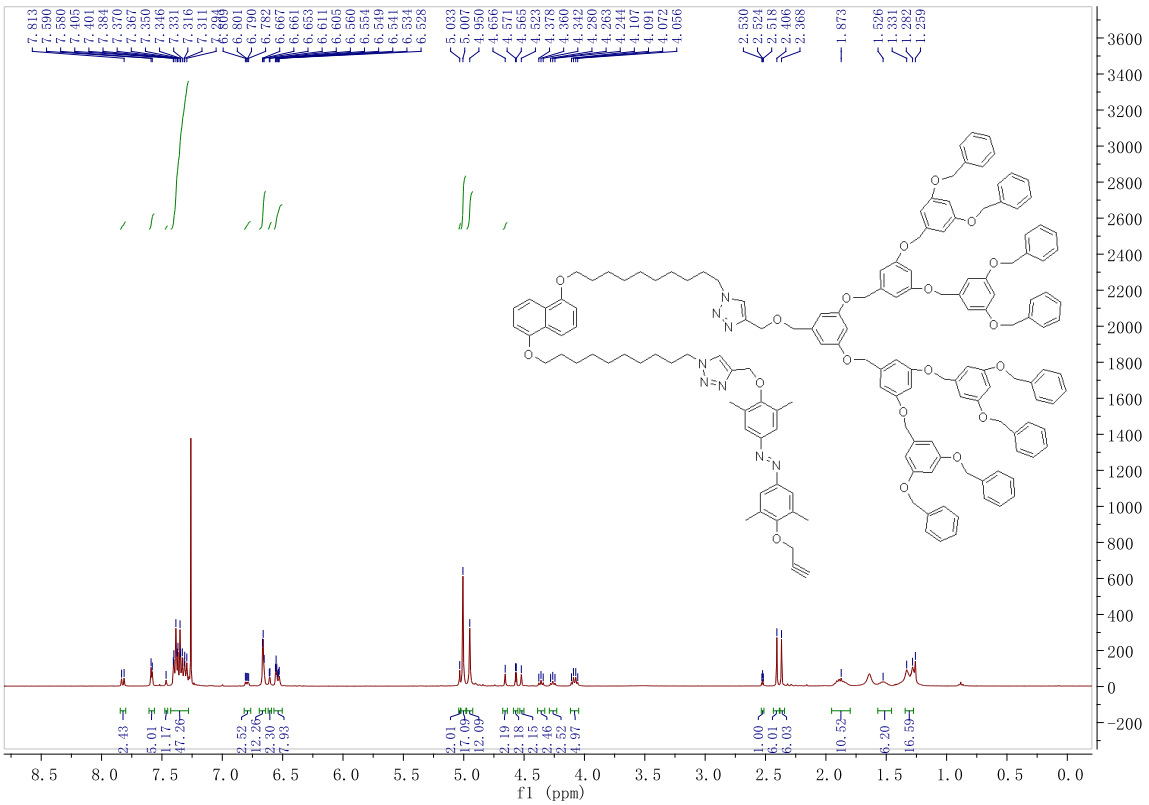

Figure S33. ^{1}H NMR spectrum (400 MHz) of compound **S12** in $CDCl_3$ at 298 K.

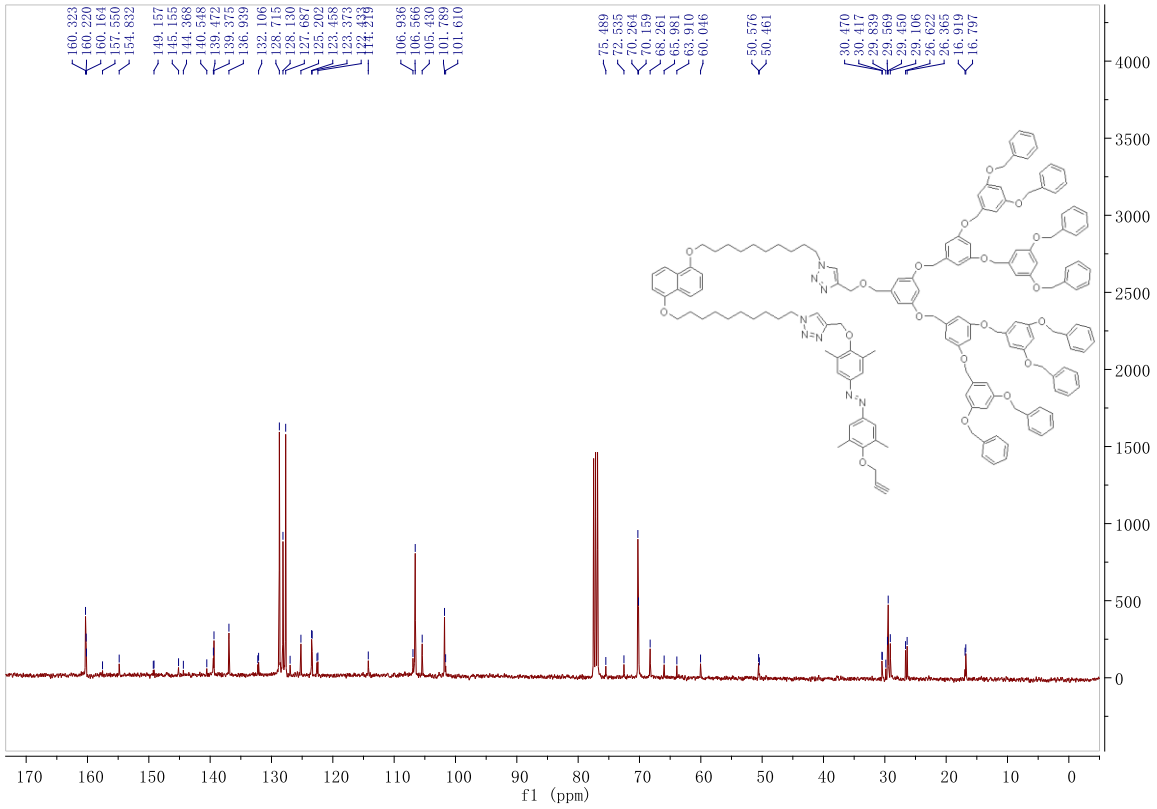

Figure S34. ^{13}C NMR spectrum (100 MHz) of compound **S12** in $CDCl_3$ at 298 K.

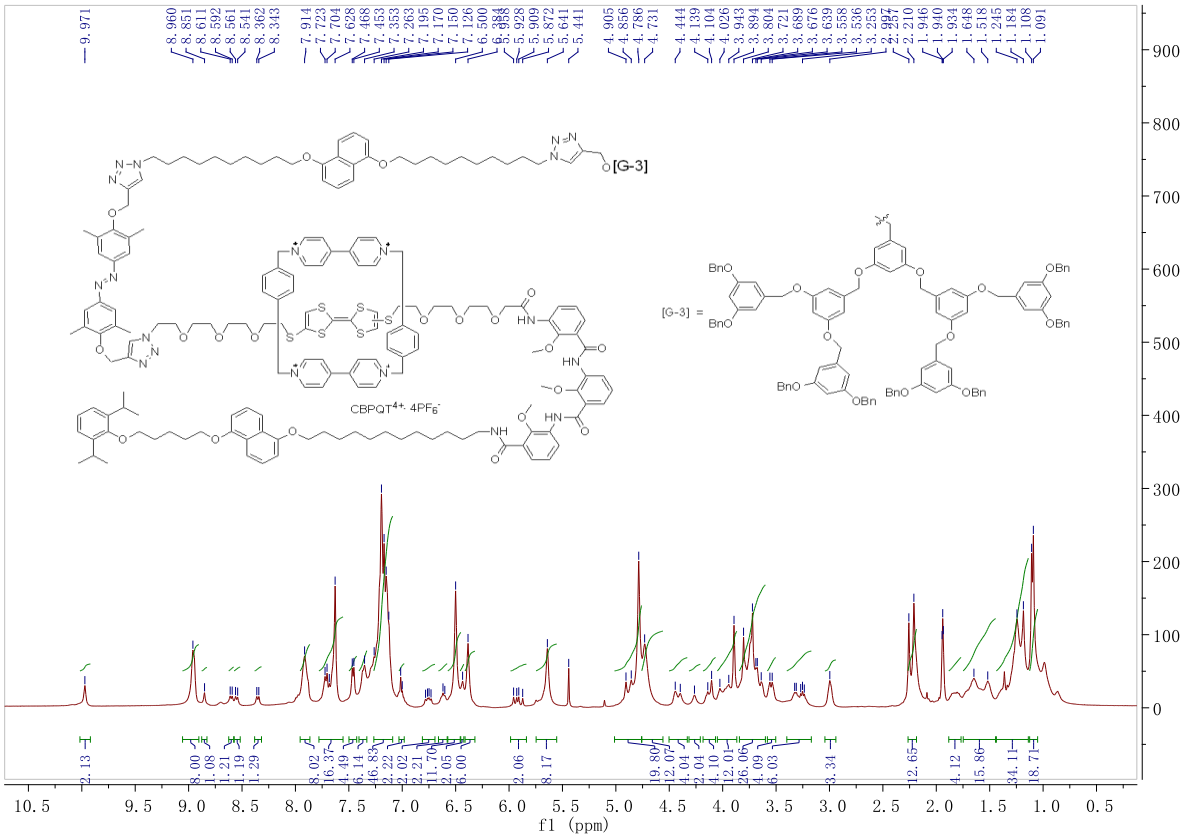

Figure S35. ^{1}H NMR spectrum (400 MHz) of [2]rotaxane $\mathbf{1}^{4+}\cdot 4PF_6^-$ in CD_3CN at 298 K.

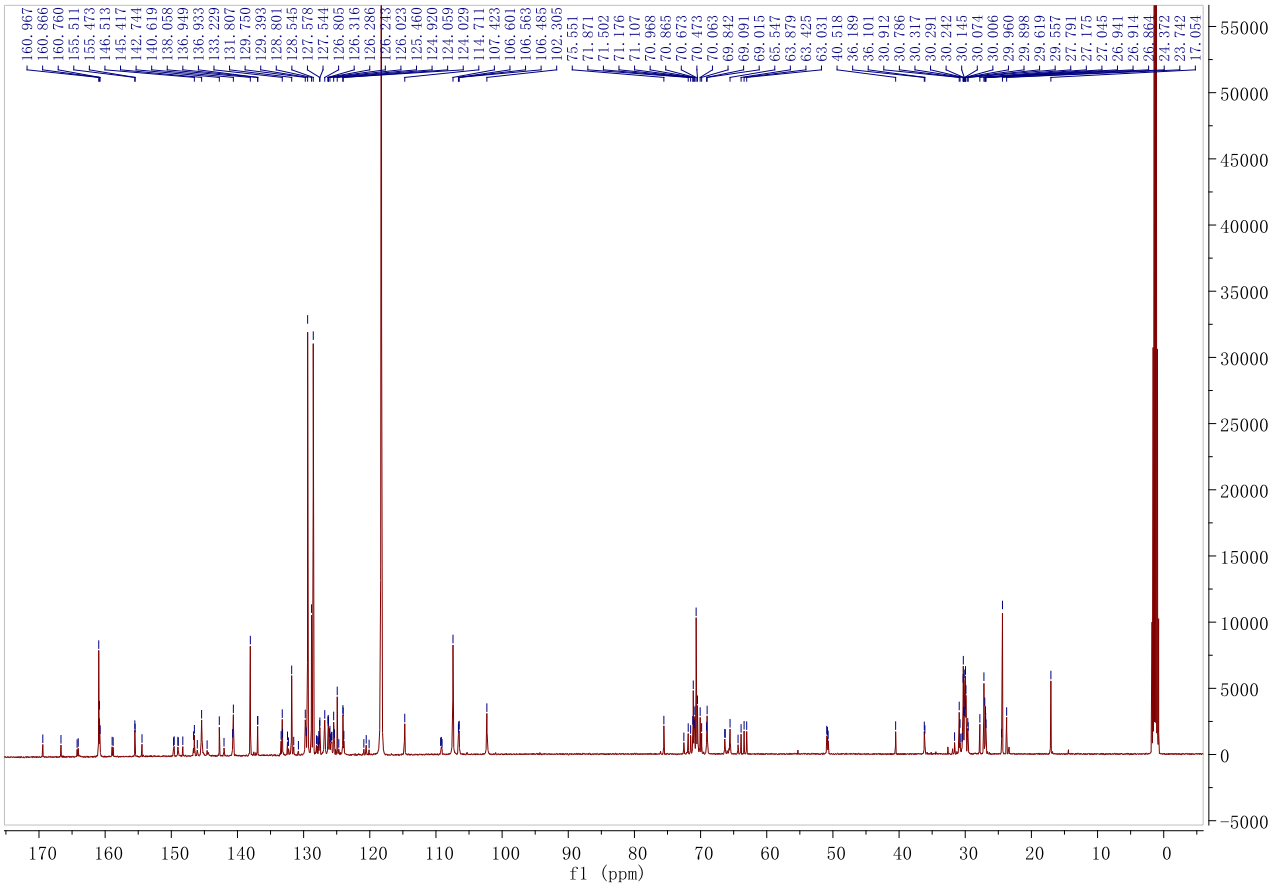

Figure S36. ^{13}C NMR spectrum (100 MHz) of [2]rotaxane $\mathbf{1}^{4+}\cdot 4PF_6^-$ in CD_3CN at 298 K.