Supporting Information

Construction of a functional [2]rotaxane with multilevel fluorescence responses

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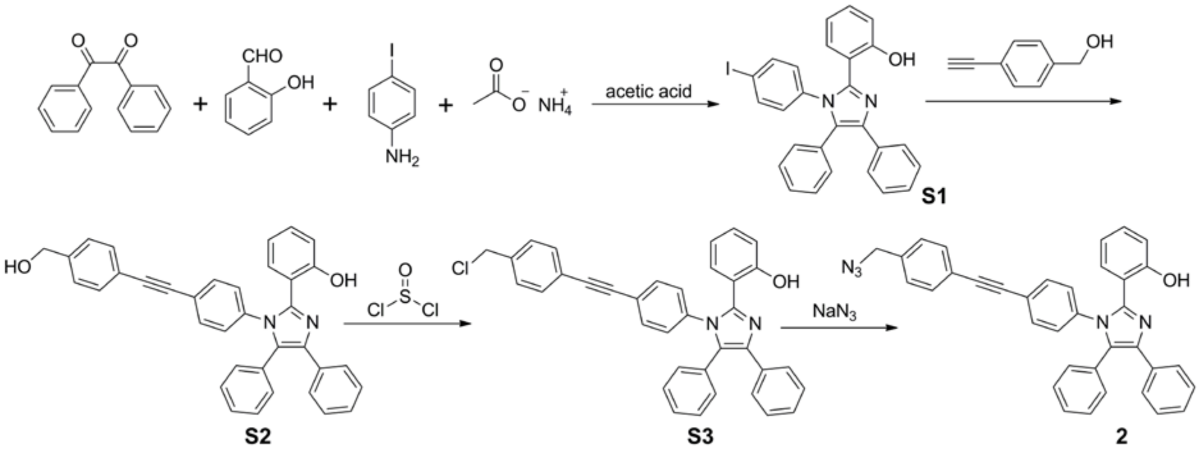
1. Synthesis of 2:



2-(1-(4-iodophenyl)-4,5-diphenyl-1H-imidazol-2-yl)phenol, S1:

5.0 g of benzil (23.8 mmol) and 2.55 mL of salicylaldehyde (23.8 mmol) were dissolved in 120 mL of glacial acetic acid at room temperature. 5.2 g (23.8 mmol) of 4-iodoaniline was added and 9.17 g of ammonium acetate (119 mmol) was added subsequently. The mixture was heated at 110 ^{o}C for 12 h. After termination of reaction, the dark solution was poured into copious amount of water. the mixture was filtered and dried. After the silica-gel column purification, 2.59 g white powder was obtained (Yeild = 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.27 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 7.1 Hz, 2H), 7.36 – 7.04 (m, 10H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.89, 146.33, 140.34, 138.37, 137.00, 134.38, 132.85, 132.82, 131.88, 131.72, 131.67, 131.11, 131.01, 130.22, 130.18, 129.99, 129.85, 129.82, 128.67, 128.42, 127.54, 119.62, 119.33, 114.23, 96.38. MALDI-TOF, Calcd for: $C_{27}H_{20}IN_2O$ $[M+H]^+$ 515.1; Found 515.2; Elemental Analysis calcd (%) for $C_{27}H_{19}IN_2O$: C 63.05, H, 3.72, N 5.45; Found C 62.96, H 3.75, N 5.48.

2-(1-(4-((4-(hydroxymethyl)phenyl)ethynyl)phenyl)-4,5-diphenyl-1H-imidazol-2-yl)phenol, S2:

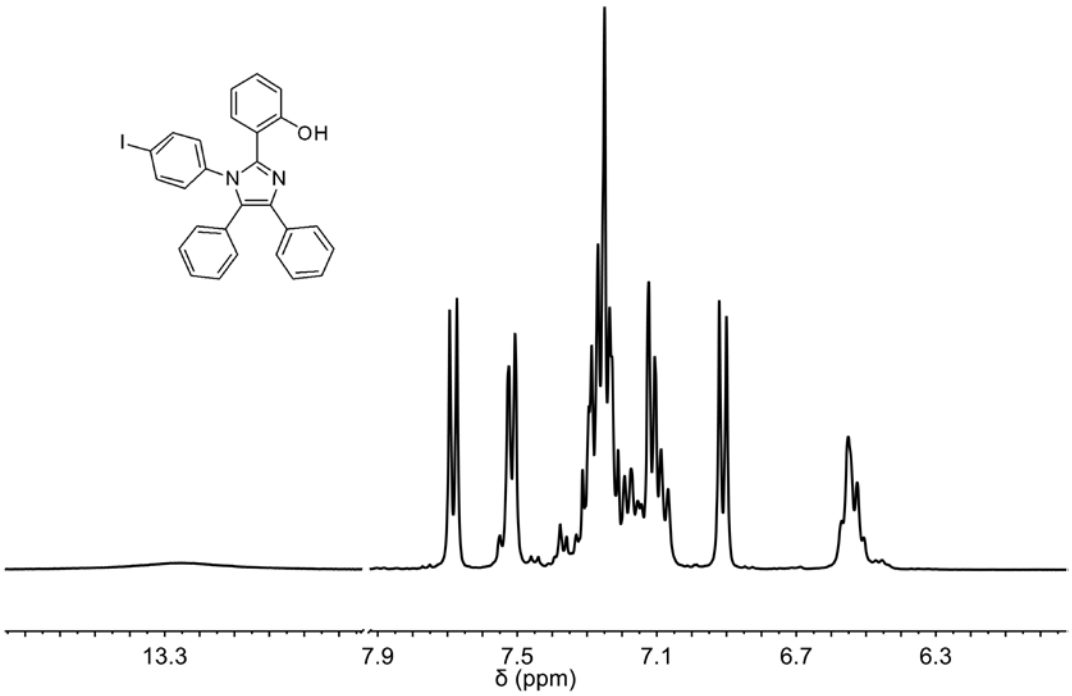
5.0 g **S1** (9.7 mmol) and 1.3g (4-ethynylphenyl)methanol (9.7 mmol) were dissolved in degassed tetrahydrofuran (THF, 150 mL), triethylamine (Et_3N, 50 mL). CuI (18 mg, 0.1 mmol), and $Pd(PPh_3)_2Cl_2$ (63 mg, 0.1 mmol) were added. The solution was stirred at R.T. for 12 h under an atmosphere of nitrogen. The reaction was quenched with water (20 mL). The organic layer was separated, dried over $MgSO_4$, filtered, concentrated under reduced pressure and the resulting crude oil was purified by column chromatography to yield **S2** (4.3 g, yield = 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 13.30 (s, 1H), 7.49-7.55 (t, 6H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.21 (m, 6H), 7.18-7.12 (m, 6H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.51 (t, *J* = 7.6 Hz, 1H), 4.72 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.37, 144.86, 141.63, 136.74, 135.40, 132.89, 132.75, 131.83, 131.33, 130.35, 130.13, 129.60, 128.69, 128.64, 128.32, 127.14, 126.93, 126.89, 126.15, 124.32, 121.73, 118.09, 117.81, 112.82, 91.28, 88.07, 64.86; MALDI-TOF, Calcd for: $C_{36}H_{27}N_2O_2$ $[M+H]^+$ 519.2; Found 519.2; Elemental Analysis calcd (%) for $C_{36}H_{26}N_2O_2$: C 83.37, H, 5.05, N 5.40; Found C 83.35, H 5.08, N 5.45.

2-(1-(4-((4-(azidomethyl)phenyl)ethynyl)phenyl)-4,5-diphenyl-1H-imidazol-2-yl)phenol, 2:

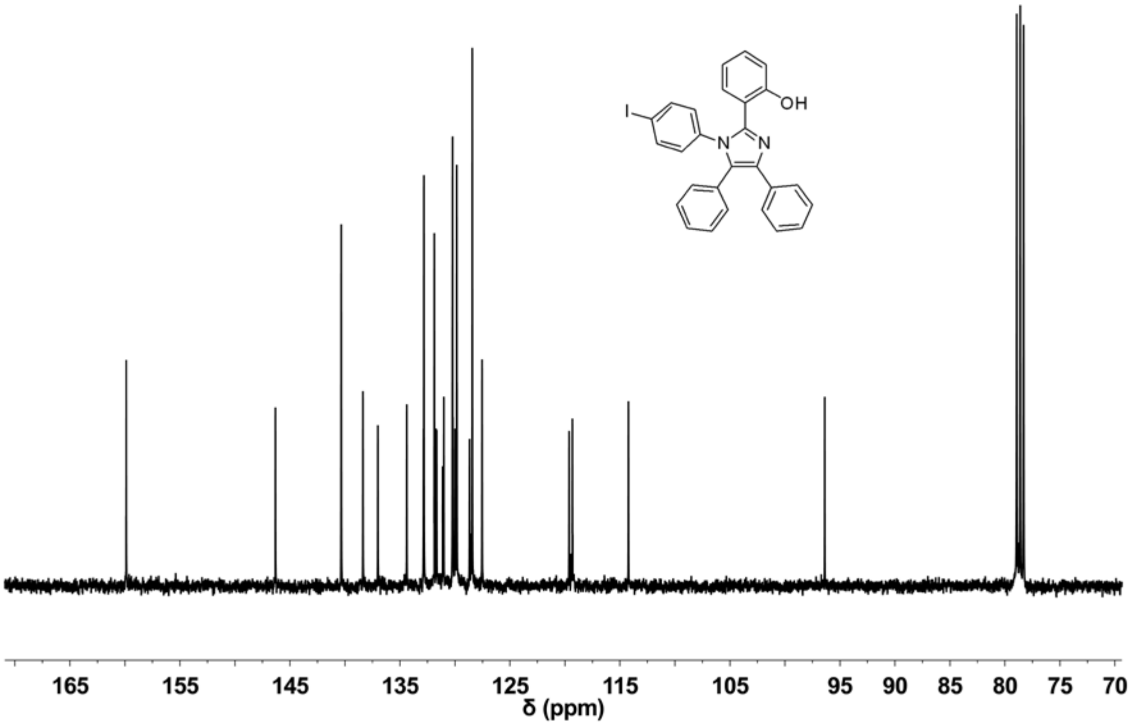
To a solution of **S2** (5.0 g, 9.7 mmol) in CH_2Cl_2 (100 mL) was added sulfurous dichloride (2.3 g, 20 mmol), then was stirred at R.T. for 2 h. Washed with H_2O (100 mL × 3), dried over anhydrous $MgSO_4$ and concentrated. Without further purification, the product was dissolved in DMF (100 mL) containing NaN_3 (1.0 g, 15 mmol). The solution was heated to 70 °C for 12 h. After concentration, the residue was taken up in CH_2Cl_2 (100 mL), washed with H_2O (100 mL × 3), dried over anhydrous $MgSO_4$ and concentrated, the residue was purified by column chromatography to yield **2**. Two steps yield 2.9 g (55%). ^1H NMR (400 MHz, $CDCl_3$) δ 13.29 (s, 1H), 7.49-7.55 (m, 6H), 7.20-7.31 (m, 8H), 7.11-7.16 (m, 5H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.50 (t, *J* = 7.5 Hz, 1H), 4.35 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.43, 144.90, 136.90, 136.11, 135.45, 132.95, 132.80, 132.08, 131.35, 130.36, 129.63, 128.74, 128.67, 128.34, 128.24, 127.15, 126.95, 126.15, 124.15, 122.60, 118.09, 117.82, 112.83, 90.89, 88.68, 54.45; MALDI-TOF: Calcd for $C_{36}H_{26}N_5O$ $[M+H]^+$ 544.2; Found 544.2; Elemental Analysis calcd (%) for $C_{36}H_{25}N_5O$: C 79.54, H 4.64, N 12.88; Found C 79.45, H 4.77, N 12.75.

2. ^{1}H NMR and ^{13}C NMR

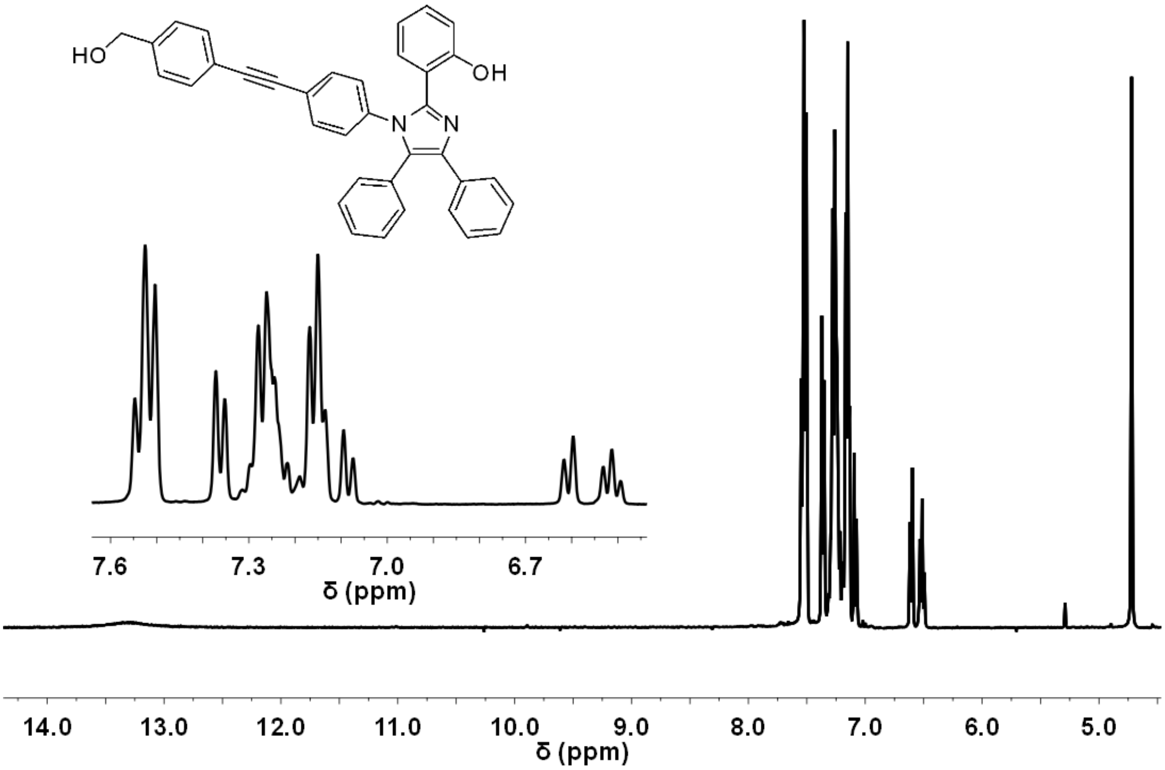
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **S1**



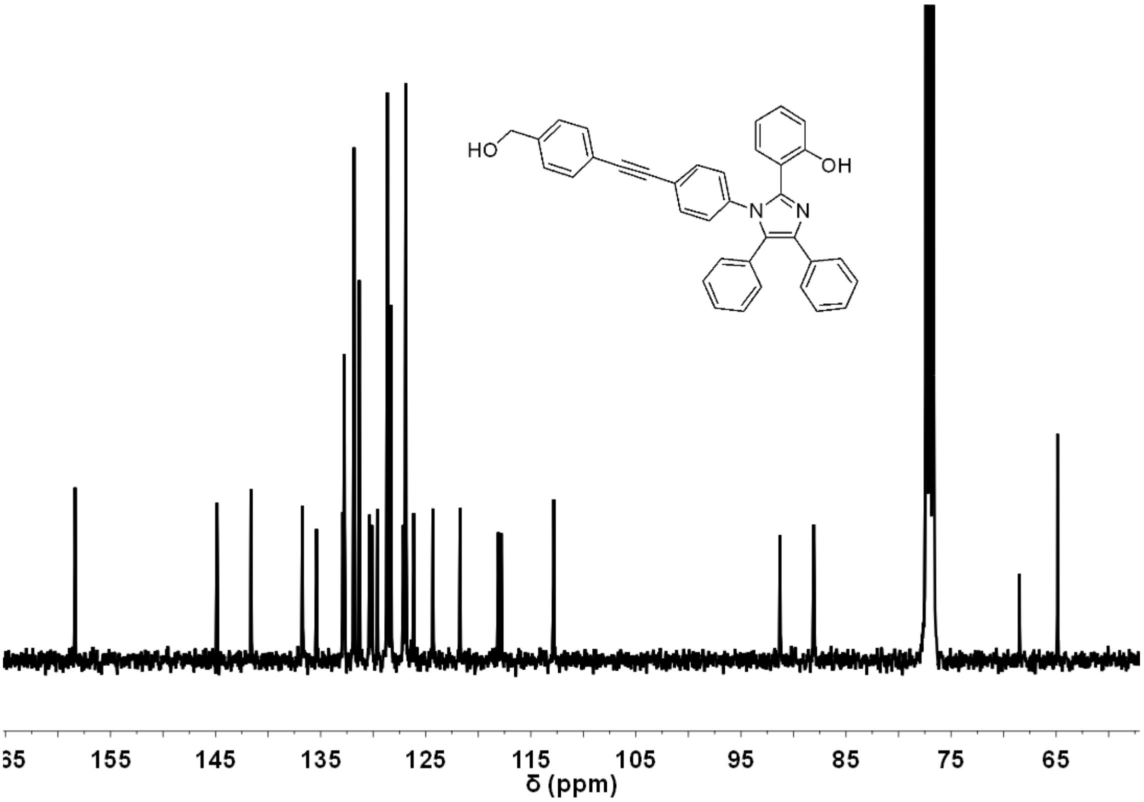
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **S1**



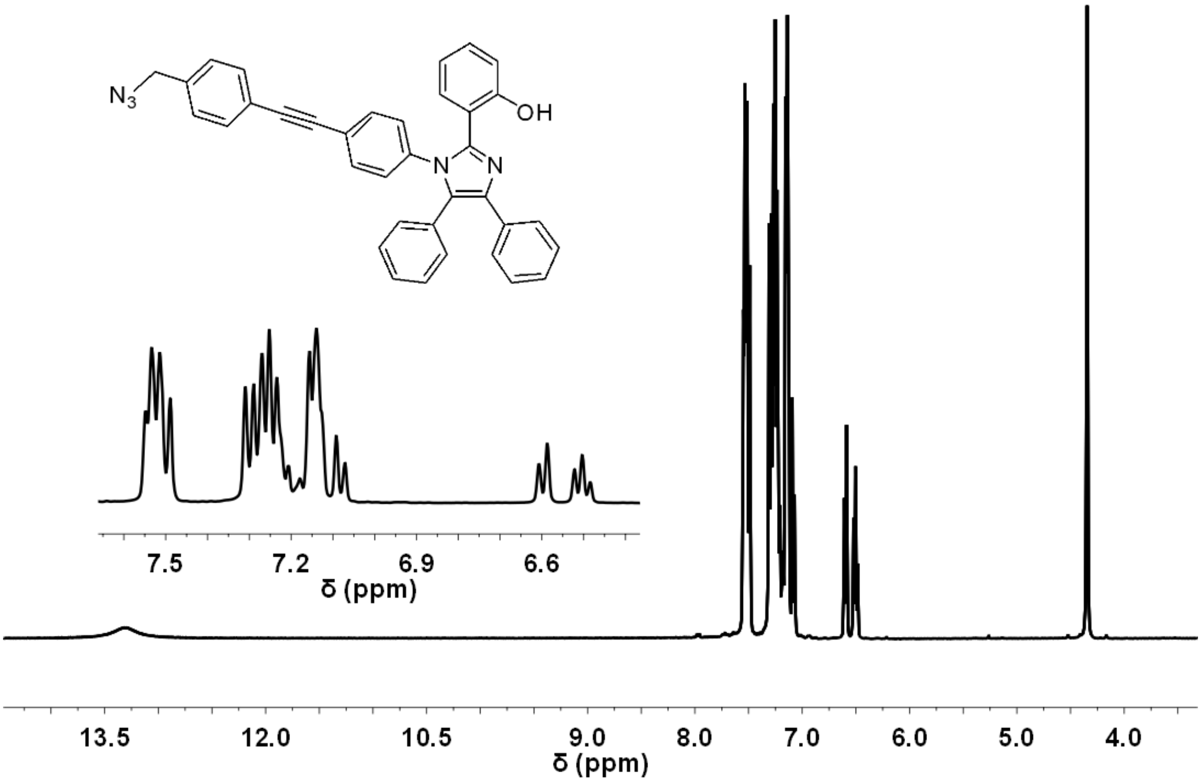
^{1}H NMR spectrum (400 MHz, 298 K, CDCl$_3$) of **S2**



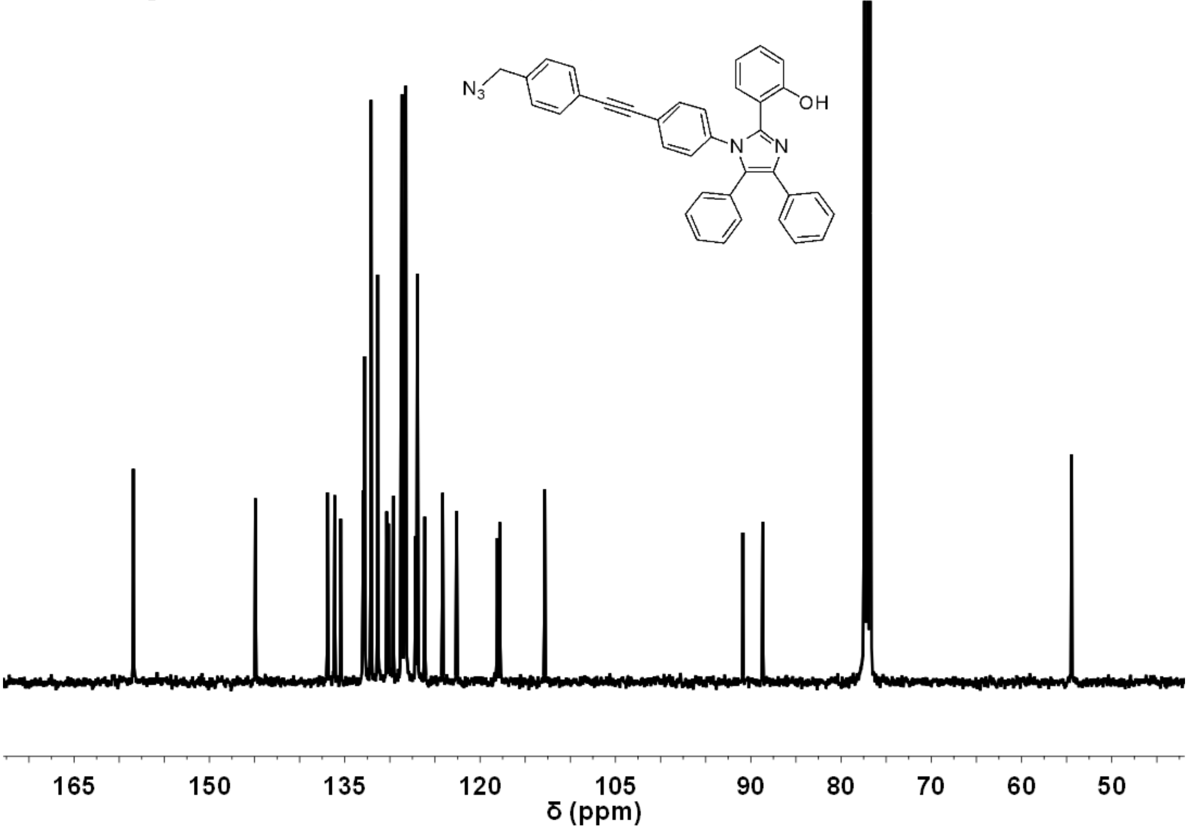
^{13}C NMR spectrum (100 MHz, 298 K, CDCl$_3$) of **S2**



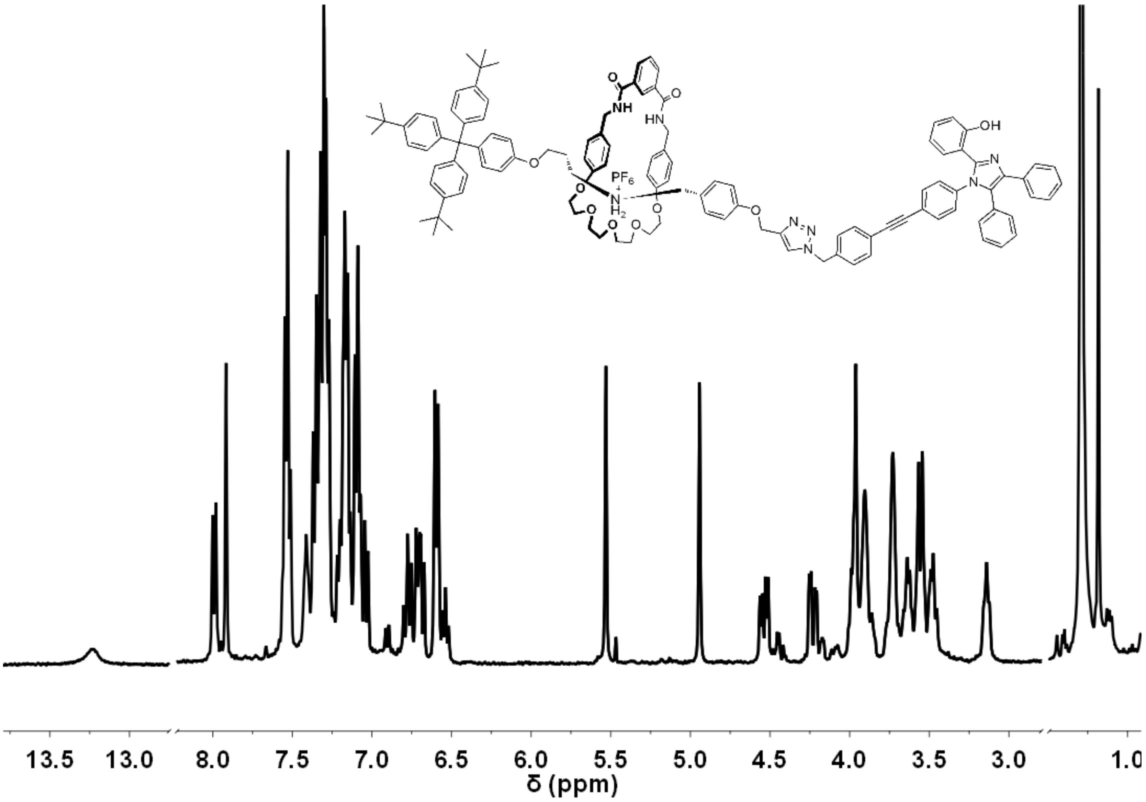
^{1}H NMR spectrum (400 MHz, 298 K, CDCl$_3$) of **2**



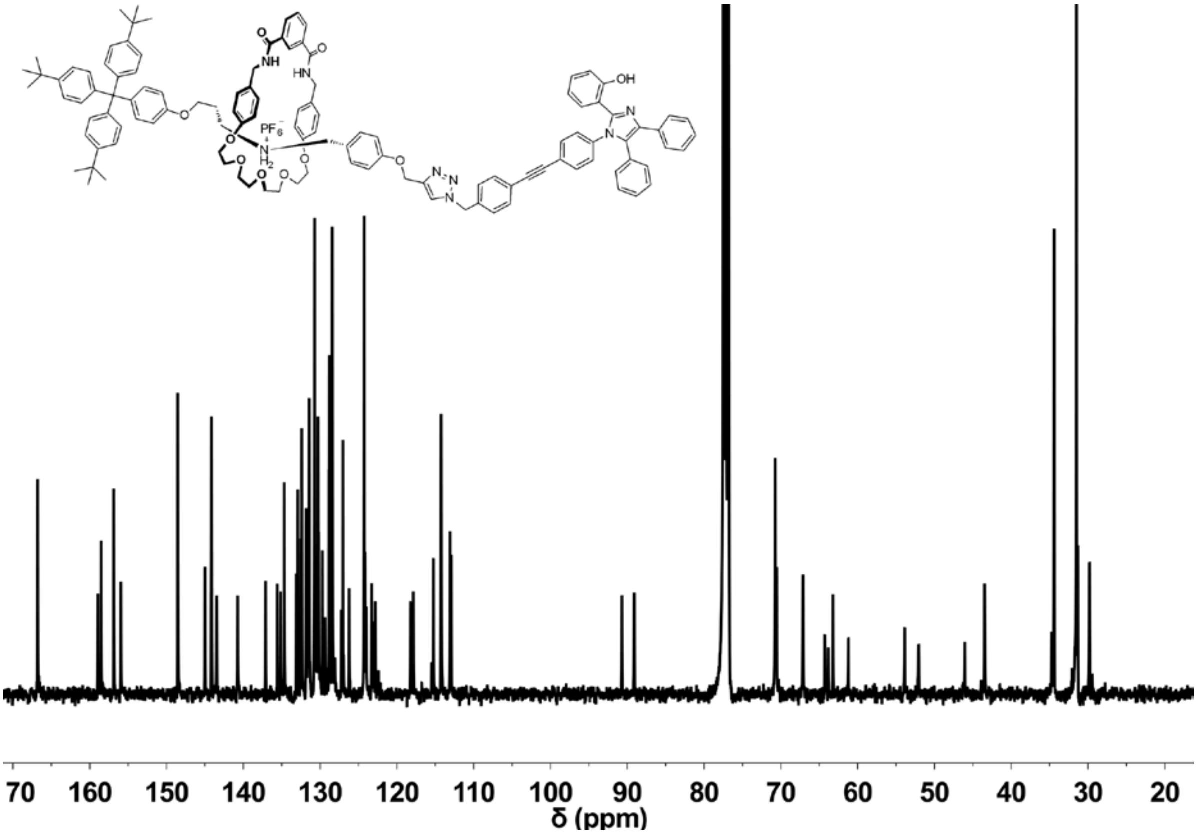
^{13}C NMR spectrum (100 MHz, 298 K, CDCl$_3$) of **2**



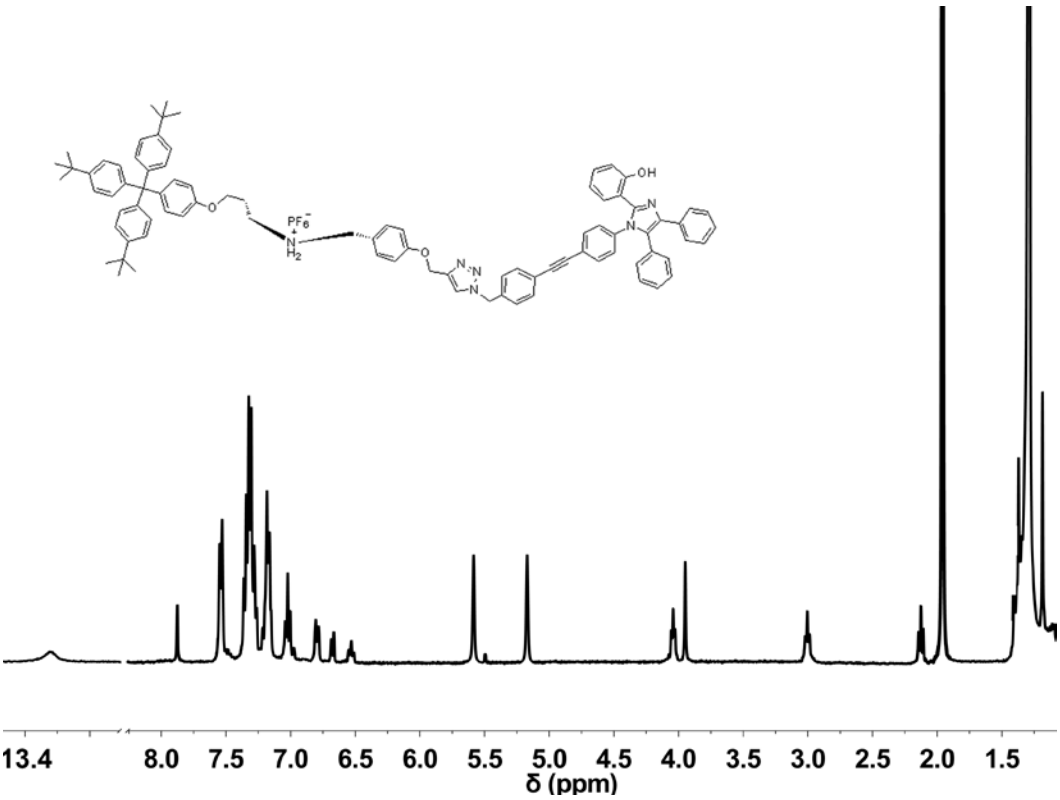
^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **4**



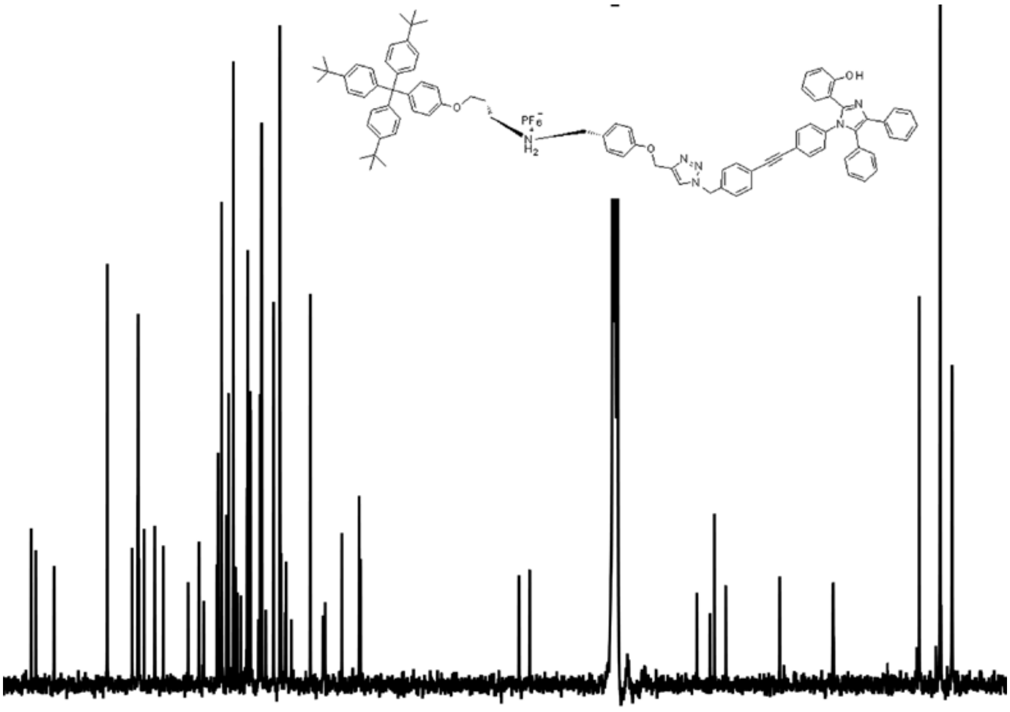
^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **4**



^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **5**



^{13}C NMR spectrum (100 MHz, 298 K, $CDCl_3$) of **5**



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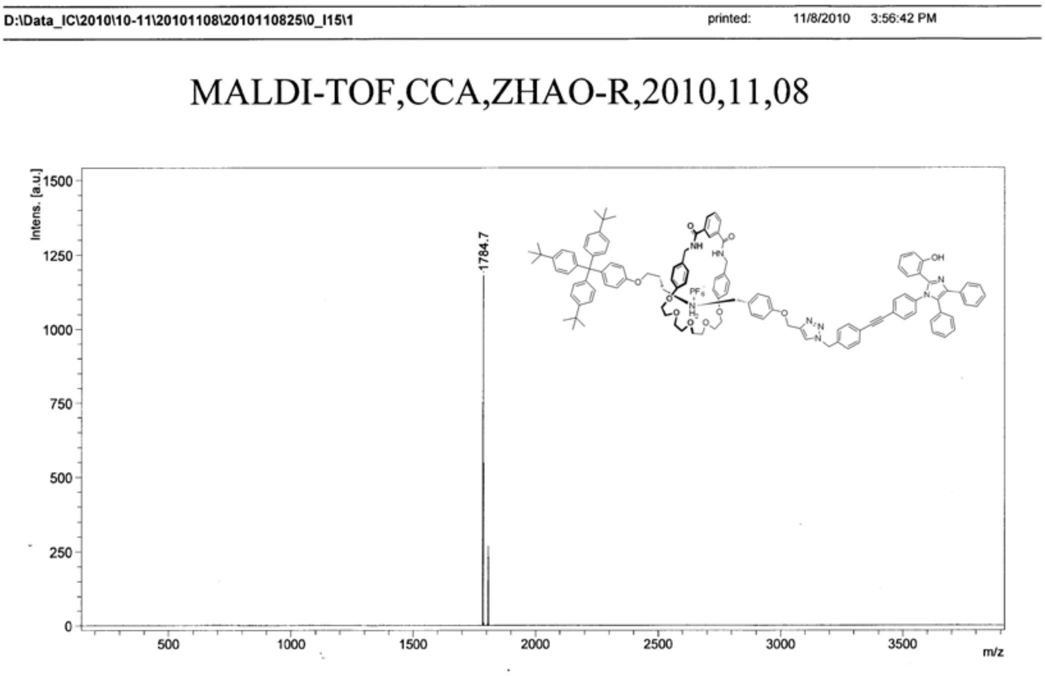
3. MALDI-TOF of 4



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MALDI-TOF,CCA,ZHAO-R,2010,11,08

4. The crystal structure and molecular packing of 2

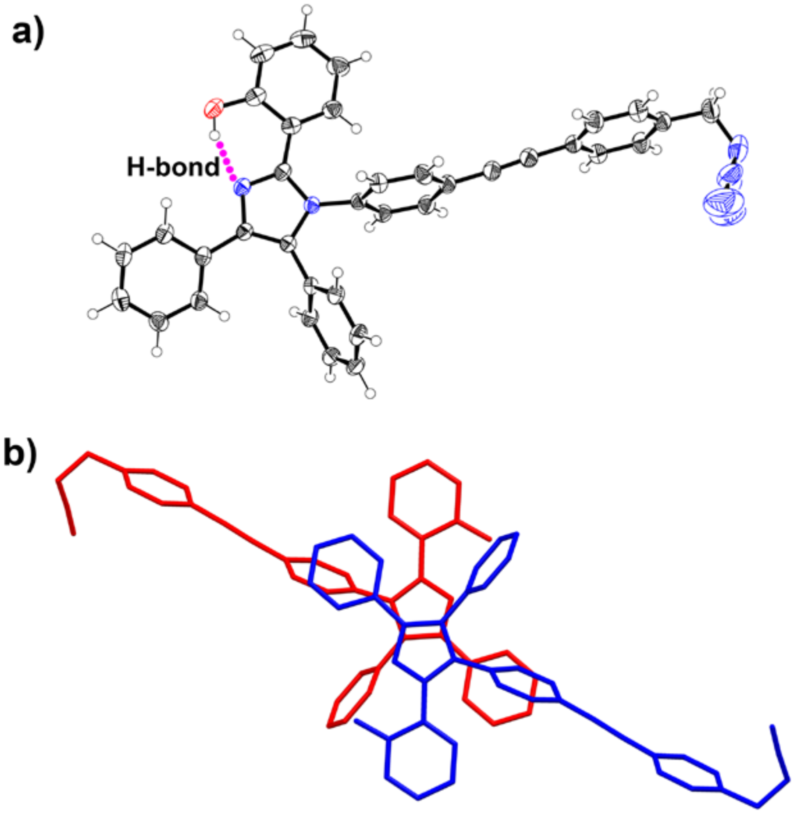
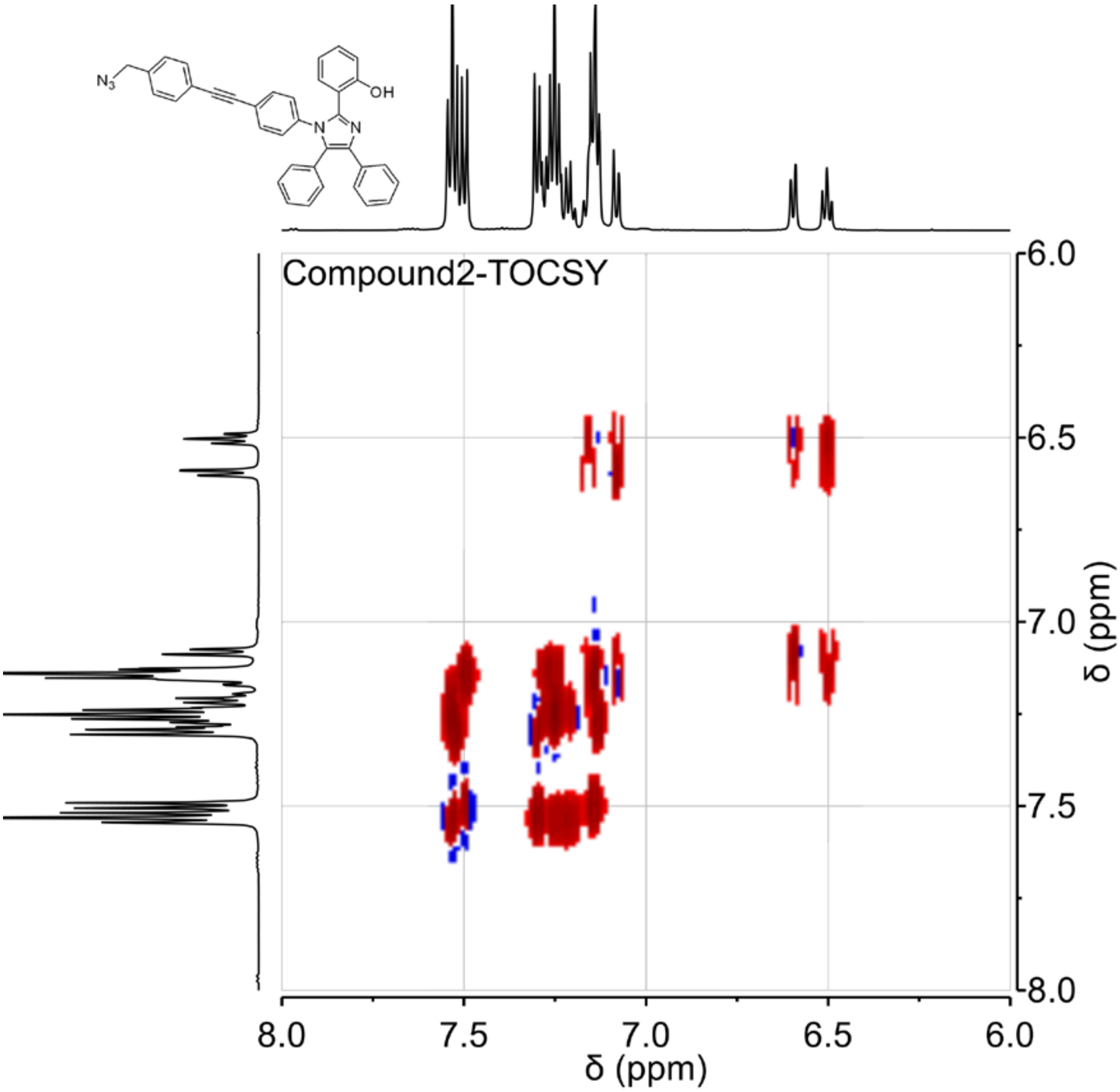


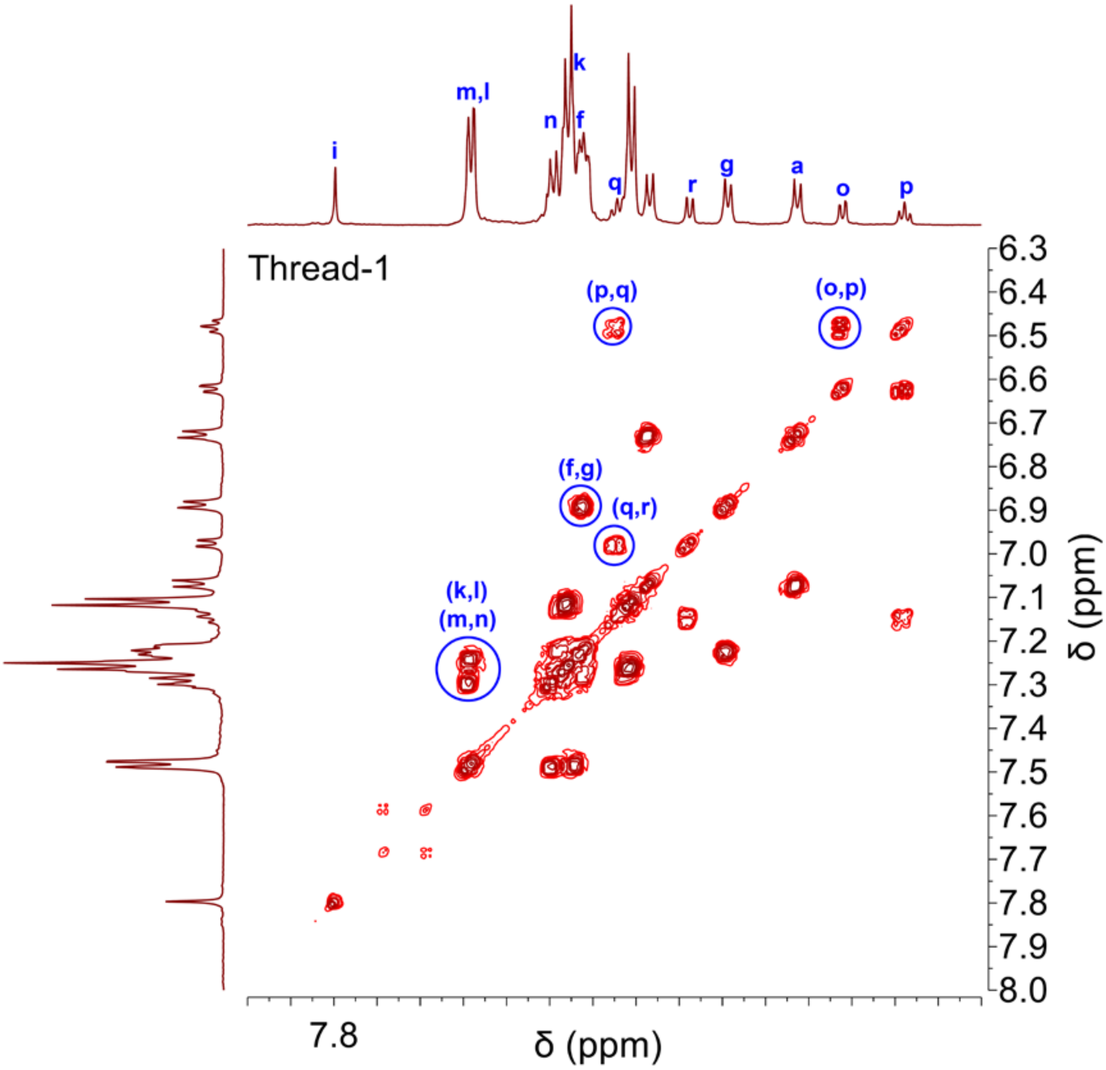
Figure S1. a) ORTEP drawing of **2**; b) Molecular packing diagram of **2** in a crystal.

The crystal structure and molecular packing of 2 are shown in Figure 2. The obvious hydrogen bonding interaction between the hydroxyl group and the tetraphenylimidazole N atom is observed which make this structure ESIPT active. The two phenyl rings at the central imidazole ring are twisted almost perpendicular to the chromophore plane. Such structure can prevent the π-π stacking of the imidazole plane and suppress the concentration quenching of fluorescence. In the molecular packing diagram, there are edge-to-face interactions in the crystal structure. The distance between the central imidazole planes is 4.1 Å.

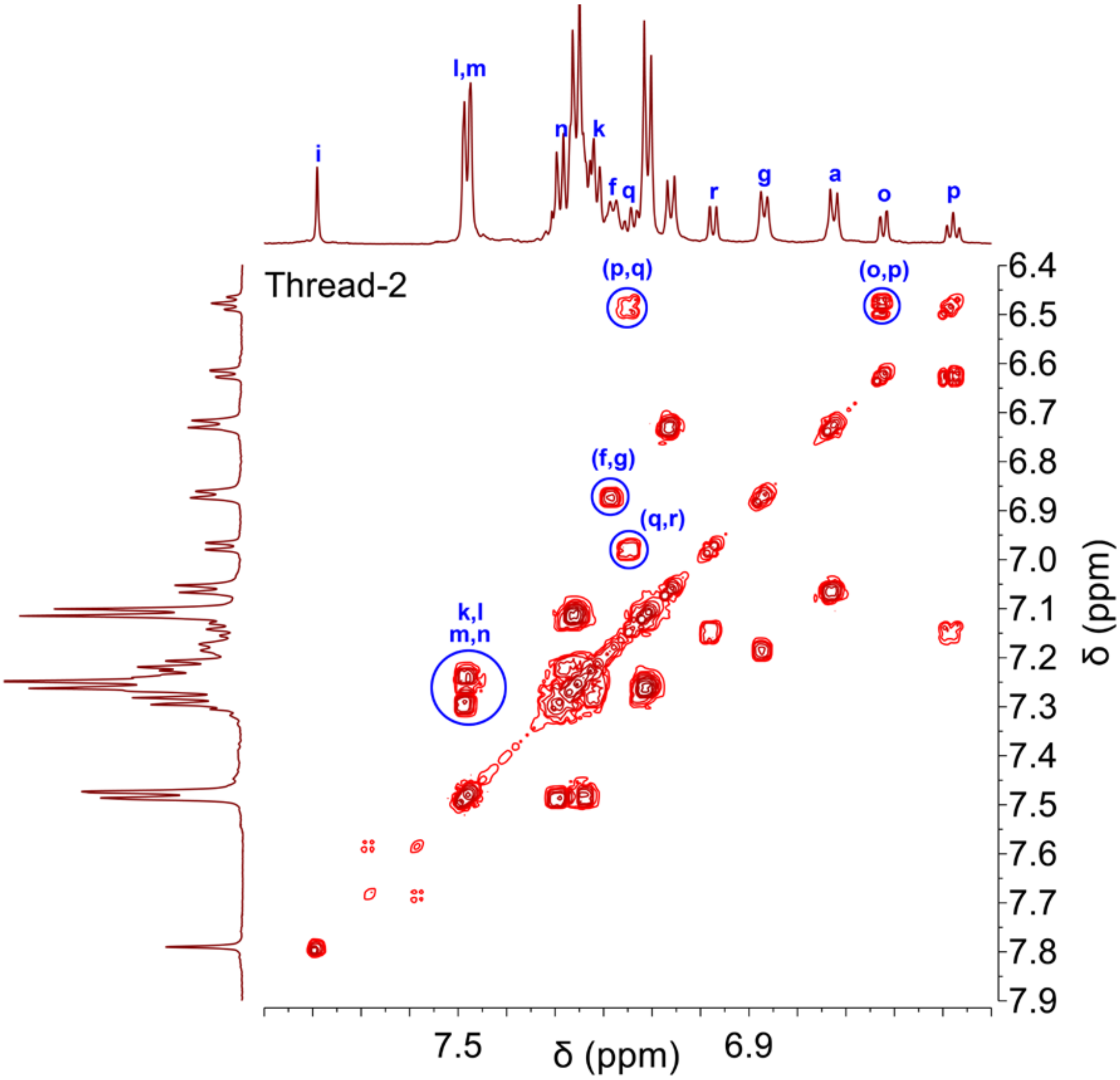
5. 2D ^{1}H NMR of 2, 4, 5.



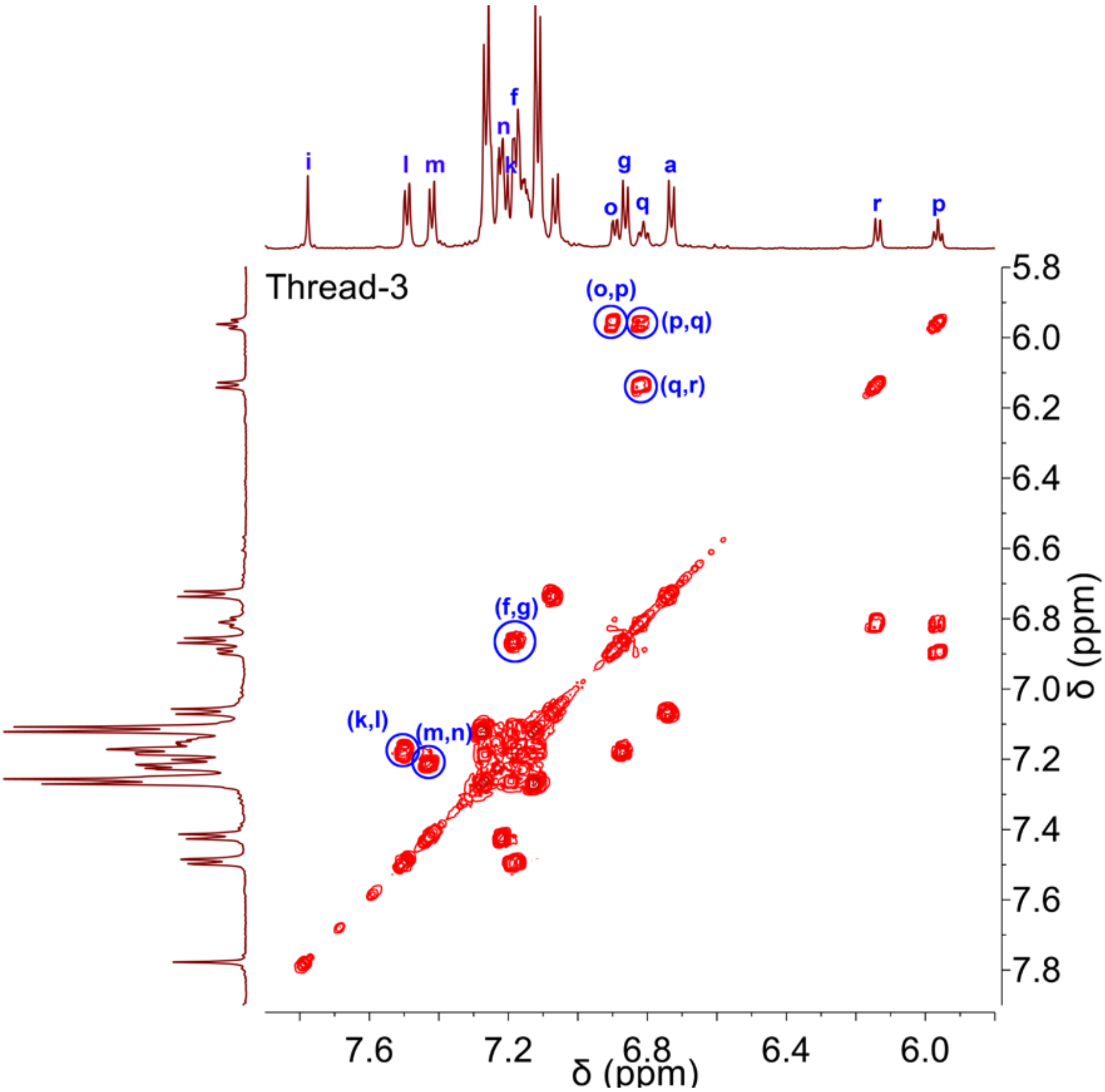
TOCSY of compound 2



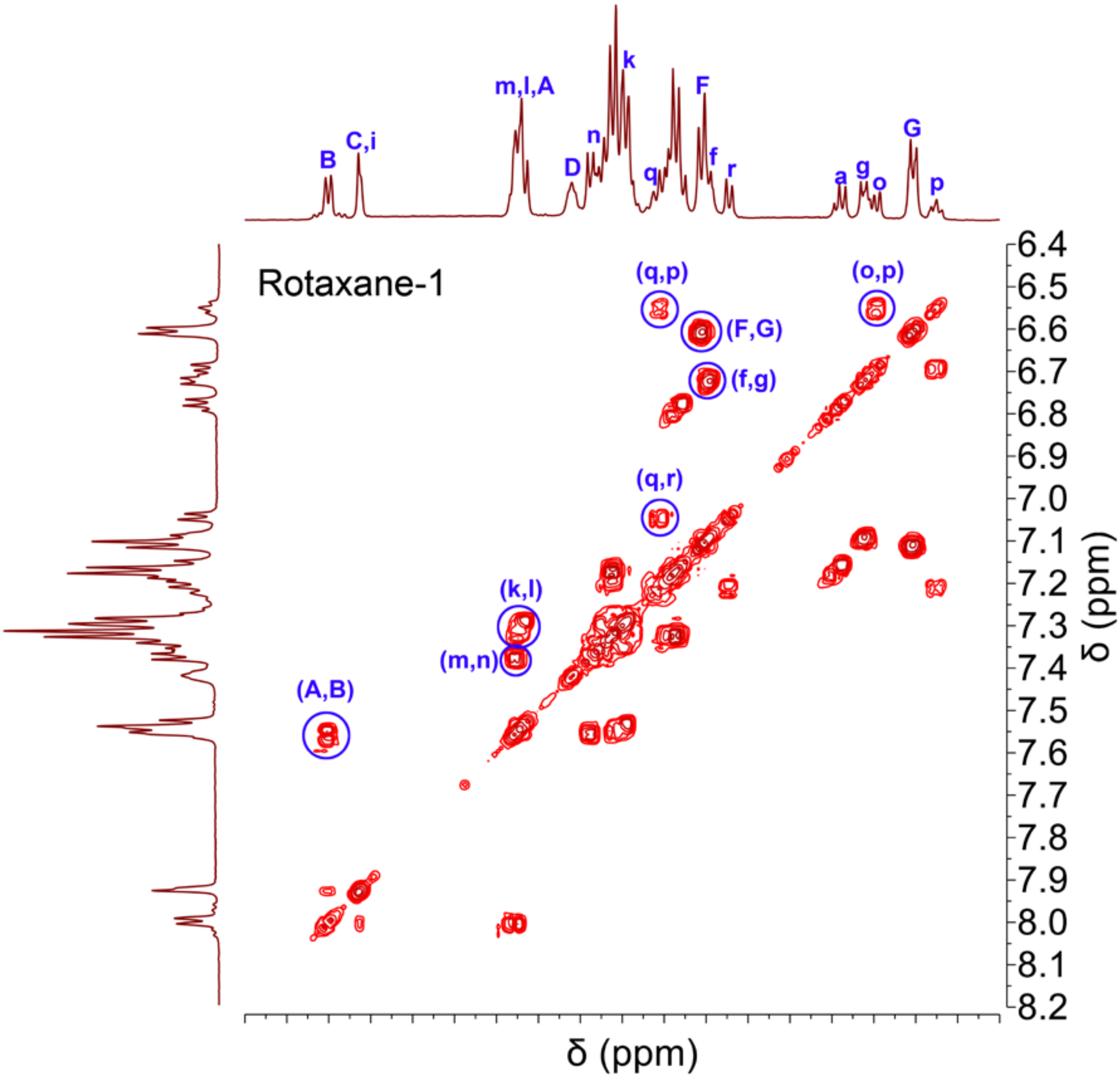
Partial H-H COSY spectra (600 MHz, 298 K, CD_3CN) of **5**.



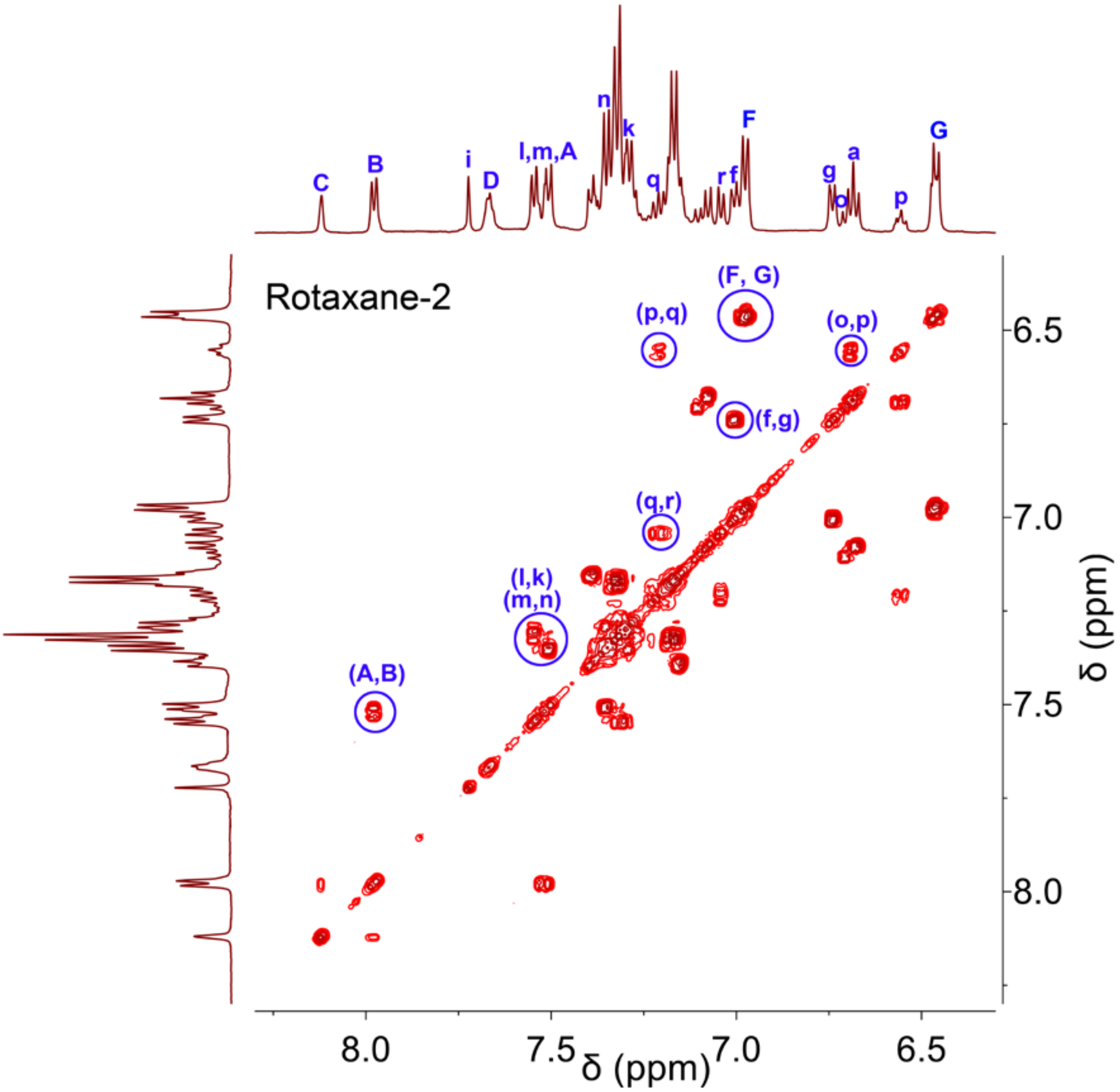
Partial H-H COSY spectra (600 MHz, 298 K, CD_3CN) of **5**+1.2 equiv Et_3N.



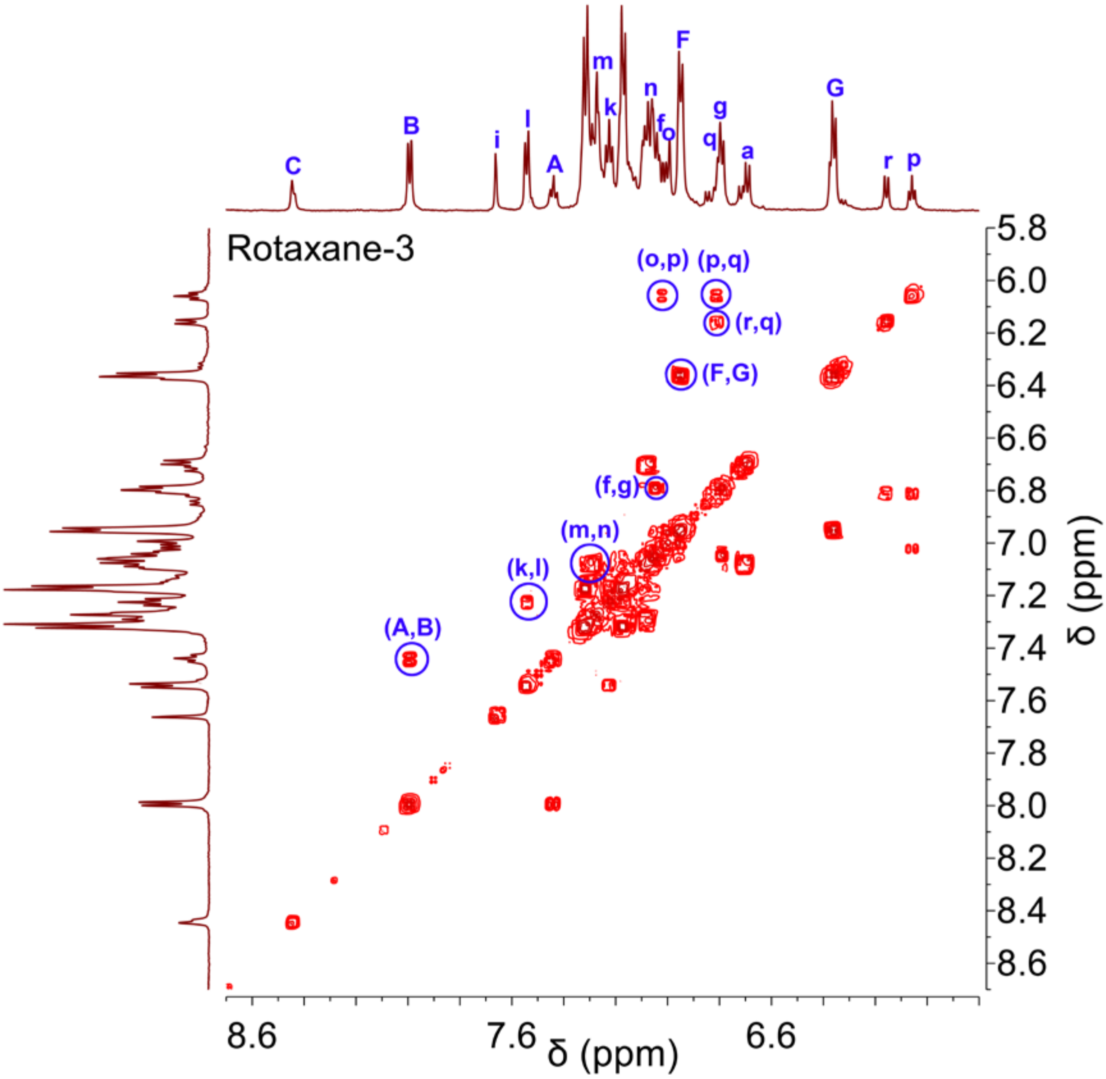
Partial H-H COSY spectra (600 MHz, 298 K, CD_3CN) of **5**+1.2 equiv Et_3N+10 equiv P_1 base



Partial H-H COSY spectra (600 MHz, 298 K, CD_3CN) of **4**.



Partial H-H COSY spectra (600 MHz, 298 K, CD$_3$CN) of **4**+1.2 equiv Et$_3$N.



Partial H-H COSY spectra (600 MHz, 298 K, CD_3CN) of **4**+1.2 equiv Et_3N+10 equiv P_1 base

6. Reversibility of the process

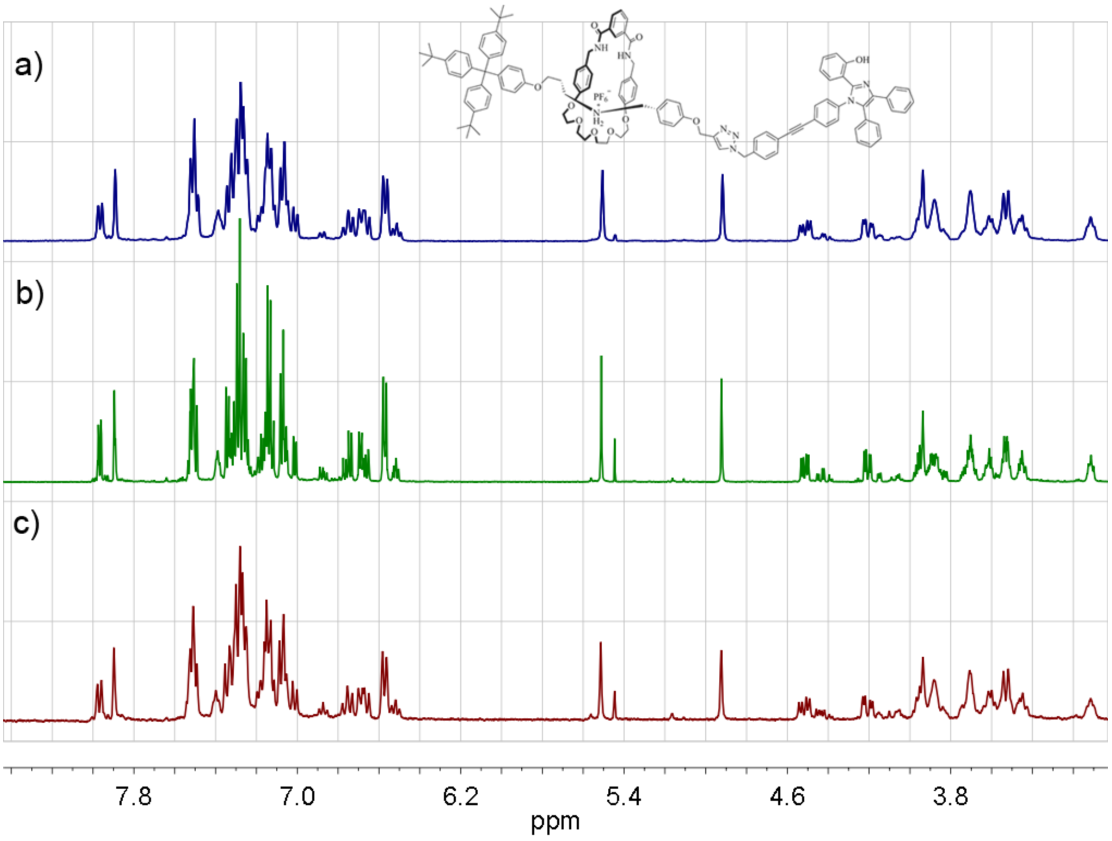


Figure S2. a) The ^{1}HNMR of the rotaxane **4**; b) **4**+Et_3N+CF_3COOH; c) **4**+Et_3N+Schwesinger's P_1 base+ CF_3COOH.

7. Absorption spectra changes of 4 and 5.

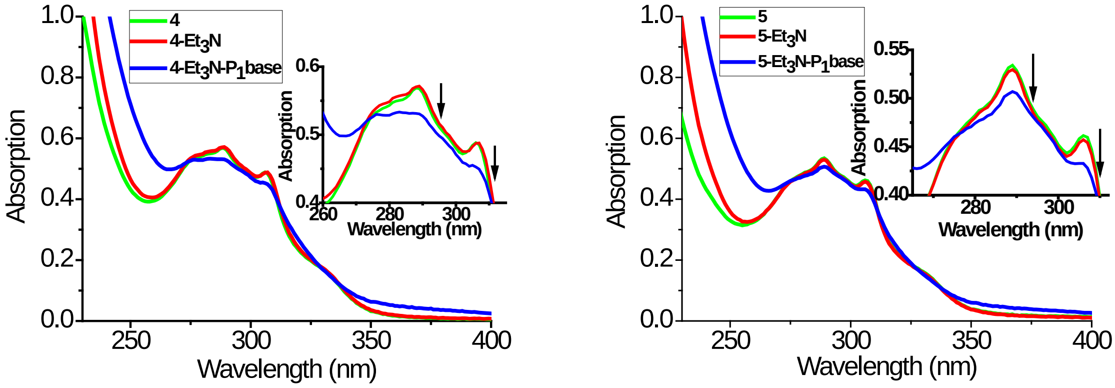


Figure S3. Absorption spectra changes of **4** and **5** upon the addition of Et_3N and Schwesinger's P_1 base in CH_3CN (2×10^{-5}M).

8. Fluorescence emission spectra of 5 from 293 to 308 K

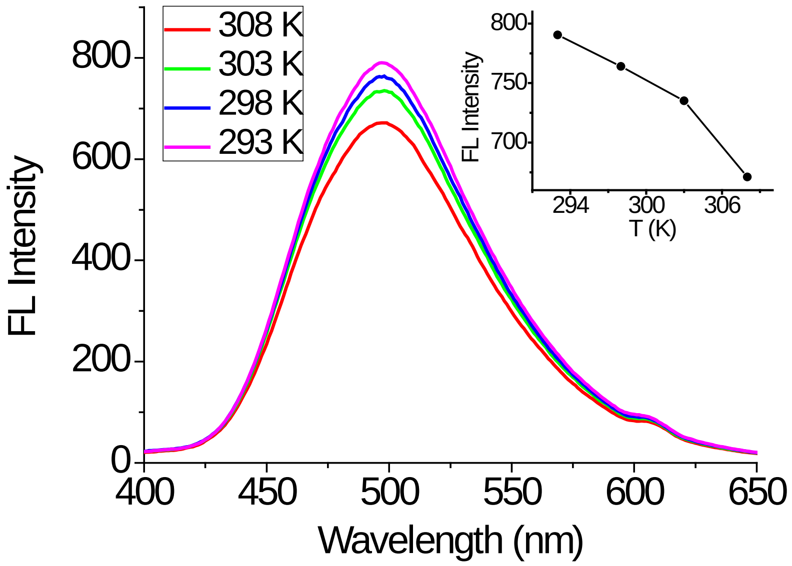


Figure S4. Fluorescence emission spectra and intensity of **5** from 293 to 308 K

10. Study of fluorescence lifetime changes

Table 1. Fluorescence lifetime changes of **4** and **5** upon the addition of Et_3N (Station 2) and Schwesinger's P_1 base (Station 3) in CH_3CN (2×10^{-5} M, λ_{ex} / λ_{em}=307 / 500 nm).

	Station 1	Station 2	Station 3
4 Lifetime1/Lifetime2 (ns)	0.91 / 0.10	0.99 / 0.16	0.95 / 0.09
5 Lifetime1/Lifetime2 (ns)	1.64 / 0.42	1.26 / 0.18	1.02 / 0.15

The changes of fluorescence lifetime of **4** and **5** upon the addition of Et_3N and Schwesinger's P_1 base in CH_3CN are shown in Table 1. The fluorescence lifetimes show tiny difference when the macrocycle located on three different states in **4**. The addition of Schwesinger's P_1 base changed the fluorescence lifetime of **5** from 1.64 / 0.42 to 1.02 / 0.15, while the changes are much smaller in the case of **4.**