

Supporting Information

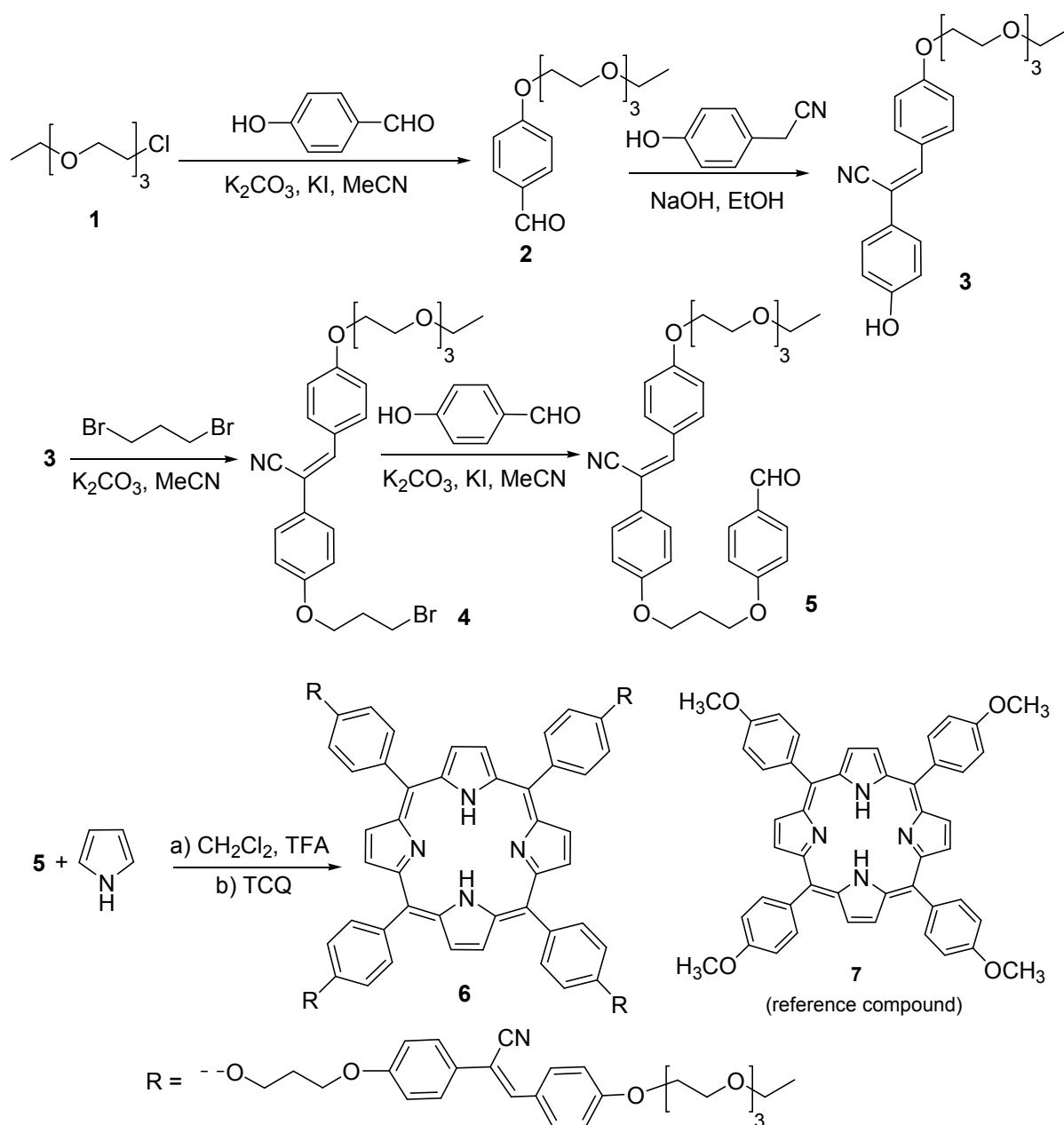
First porphyrin liquid crystal with strong fluorescence in both solution and solid state based on AIE-FRET effect

Hongyu Guo,^a Sining Zheng,^a Shibing Chen,^a Chenyang Han,^{a,b} and Fafu Yang^{*a,c}

a. College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 350007, P. R. China; Email: yangfafu@fjnu.edu.cn. b. Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, P. R. China. c. Fujian provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering, Fuzhou 350007, P. R. China. c. Fujian provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering, Fuzhou 350007, P. R. China

1. General

All chemical reagents were supplied by Aladdin Reagent Co., Ltd. and used without further purification. The other organic solvents and inorganic reagents were purified by standard anhydrous methods before use. TLC analysis was carried out by using pre-coated glass plates. Column chromatography was done by using silica gel (200-300 mesh). NMR spectra were measured on a Bruker-ARX 400 instrument at 26 °C. Chemical shifts are reported in ppm with tetramethylsilane (TMS) as internal standard. MS spectra were recorded on Bruker mass spectrometer. UV-Vis spectra were examined on Varian UV-Vis spectrometer. Fluorescence spectra were recorded in a conventional quartz cell (10×10×45 mm) at 25 °C on an Edinburgh Instruments FS5 spectrometer. The fluorescence absolute Φ_F values were studied on an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 6-inch integrating sphere.



2. The synthetic process and characteristic spectra.

2.1 Synthesis of compound 2

A mixture of 4-hydroxybenzaldehyde (0.4 g, 2.0 mmol), compound **1** (0.25 g, 2.0 mmol), K_2CO_3 (0.5 g, 3.7 mmol) and KI (0.1 g, 0.6 mmol) in 40 mL of dry MeCN was stirred refluxed for 12 h. After reaction and cooling, 20 mL of HCl solution (1 M) and 40 mL of CHCl_3 added in. Then the CHCl_3 layer was partitioned, washed by 20 mL of distilled water, dried over anhydrous MgSO_4 , and concentrated. The residue was further purified by rapid column chromatography using CH_2Cl_2 /hexane (1:1, *V/V*) as eluant. Compound **2** was collected as a sticky solid in yield of 82%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 9.88 (s, 1H, CHO), 7.83 (d, $J = 8.0$ Hz, 2H, ArH), 7.03 (d, $J = 8.0$ Hz, 2H, ArH), 4.22 (t, $J = 4.0$ Hz, 2H, OCH_2),

3.90 (t, $J = 4.0$ Hz, 2H, OCH₂), 3.64-3.78 (m, 10H, OCH₂), 1.23 (t, $J = 4.0$ Hz, 3H, CH₃).

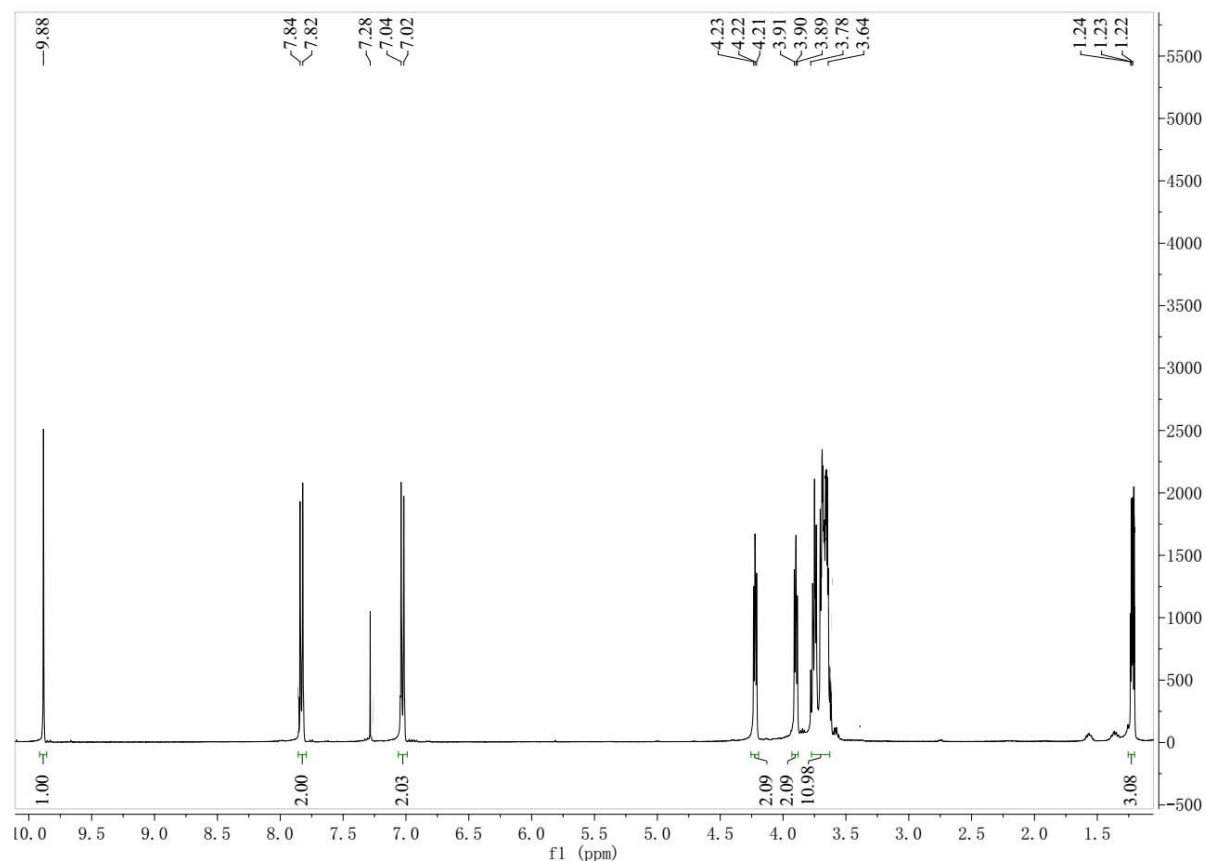


Figure S1. The ¹H NMR spectrum of compound **2**

2.2 Synthesis of compound **3**

A mixture of 4-hydroxyphenylacetonitrile (0.14 g, 1.0 mmol), compound **2** (0.28 g, 1.0 mmol) and NaOH (0.10g, 2.5 mmol) in 30 mL of EtOH solution was stirred for 10 h at room temperature. The reaction was detected by TLC technique, suggesting the disappearance of the materials. After reaction, 10 mL of HCl solution (1M) was poured into the reaction mixture. The precipitate was formed and filtered. The obtained precipitate was purified by recrystallization in MeOH/CH₂Cl₂ (1:1, V/V). After dryness, compound **3** was collected as a pale yellow solid in yield of 78%. ¹H NMR (400 MHz, DMSO) δ : 9.91 (s, 1H, OH), 7.91 (d, $J = 12.0$ Hz, 2H, ArH), 7.78 (s, 1H, C=CH), 7.57 (d, $J = 8.0$ Hz, 2H, ArH), 7.26 (d, $J = 8.0$ Hz, 2H, ArH), 6.88 (d, $J = 8.0$ Hz, 2H, ArH), 4.18 (t, $J = 4.0$ Hz, 2H, OCH₂), 3.78 (t, $J = 4.0$ Hz, 2H, OCH₂), 3.40-3.61 (m, 10H, OCH₂), 1.10 (t, $J = 8.0$ Hz, 3H, CH₃); MALDI-TOF-MS (C₂₃H₂₇NO₅) Calcd. for $m/z = 397.19$, found: $m/z = 399.04$ (MH⁺), 421.20 (MNa⁺), 437.63 (MK⁺).

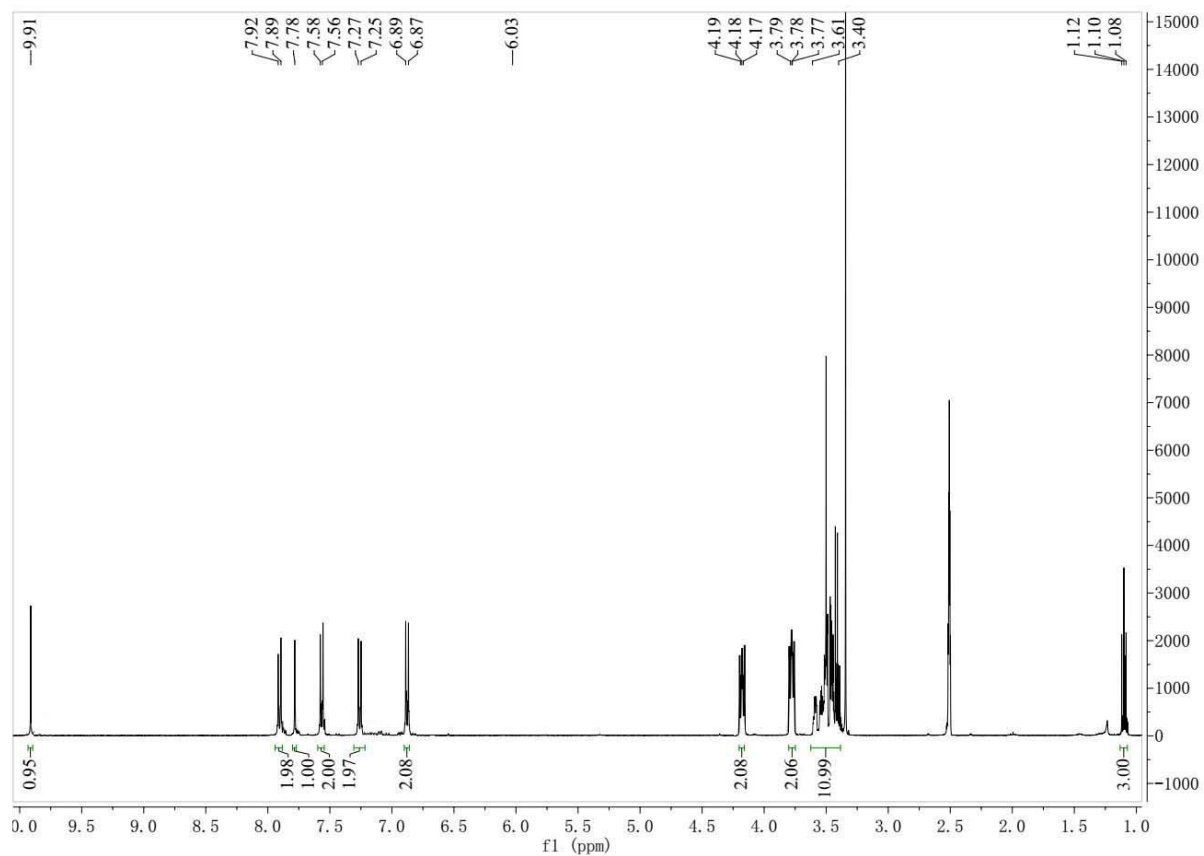


Figure S2. The ^1H NMR spectrum of compound **3**

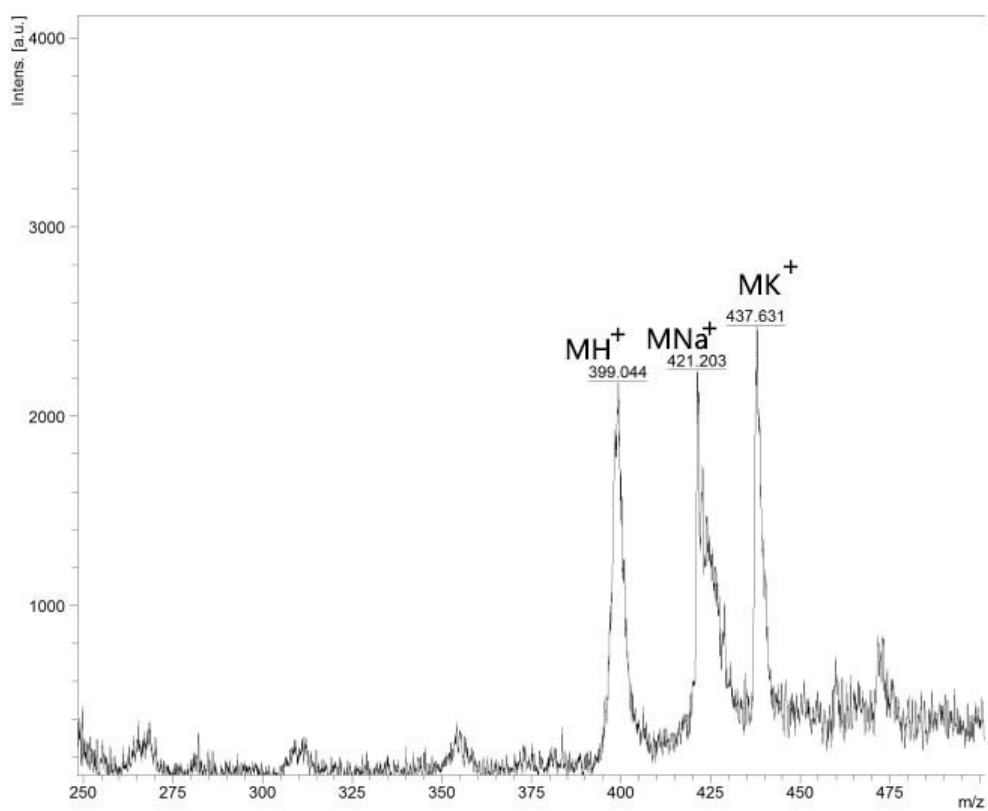


Figure S3. The MALDI-TOF-MS spectrum of compound **3**

2.3 Synthesis of compound 4

Under N₂ atmosphere, a mixture of compound **3** (0.40 g, 1.0 mmol), 1,3-dibromopropane (0.4 g, 2 mmol), and K₂CO₃ (0.36 g, 2.6 mmol) was stirred and refluxed in 30 mL of dry MeCN for 20 h. The reaction was monitored by TLC technique implying the disappearance of reactants. After reaction, the mixture was treated with 50 mL of HCl (1 M) and extracted with 30 mL of CHCl₃. The CHCl₃ layer was partitioned, washed by 20 mL of distilled water, dried over anhydrous MgSO₄, and then concentrated. The residue was treated by 15 mL of MeOH and the precipitate was obtained. The crude product was further purified by recrystallization in MeOH/CH₂Cl₂ (2:1, *V/V*). After dryness, compound **4** was collected as a pale yellow solid in yield of 69%. ¹H NMR (400 MHz, CDCl₃) δ: 7.83 (d, *J* = 8.0 Hz, 2H, ArH), 7.57 (d, *J* = 8.0 Hz, 2H, ArH), 7.34 (s, 1H, C=CH), 6.97 (d, *J* = 8.0 Hz, 2H, ArH), 6.94 (d, *J* = 8.0 Hz, 2H, ArH), 3.50-4.19 (m, 18H, OCH₂), 2.30-2.36 (m, 2H, CH₂), 1.20 (t, *J* = 8.0 Hz, 3H, CH₃); MALDI-TOF-MS (C₂₆H₃₂NO₅) Calcd. for *m/z* = 519.14, found: *m/z* = 520.01 (MH⁺).

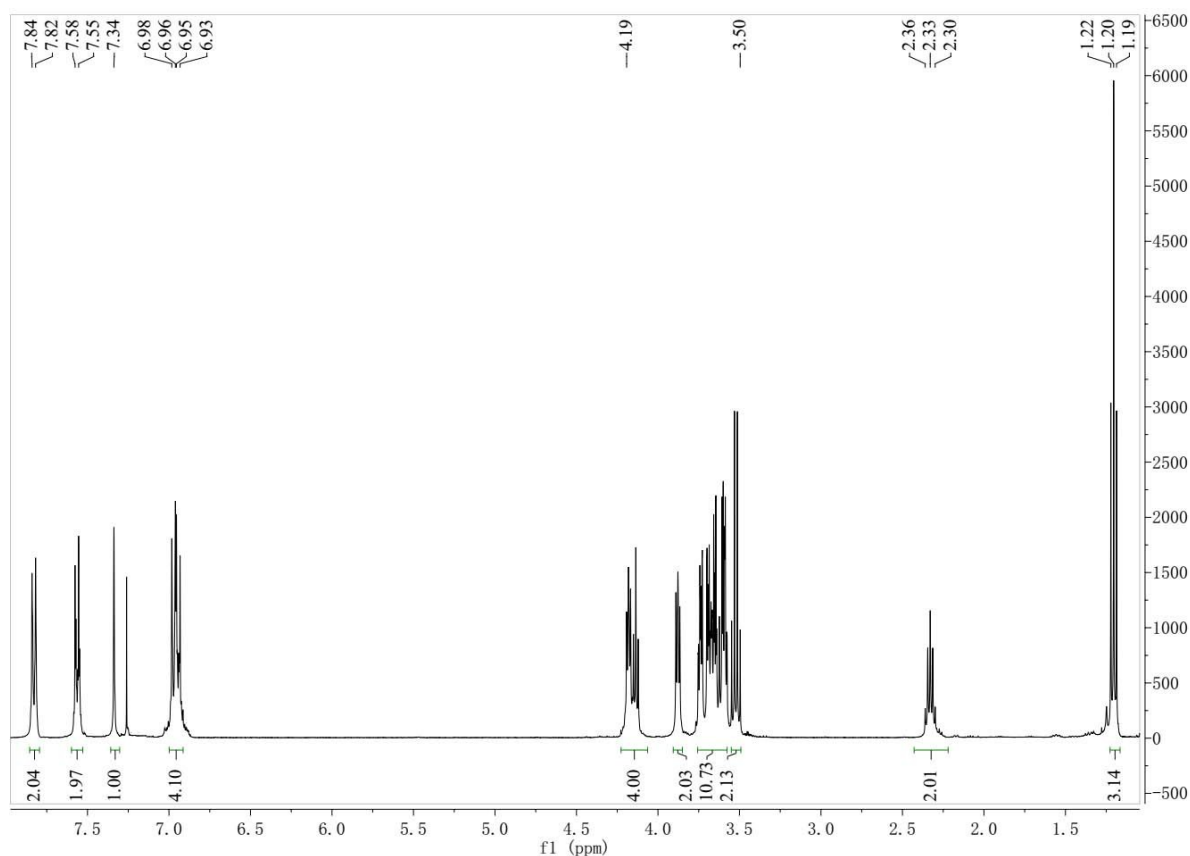


Figure S4. The ¹H NMR spectrum of compound **4**

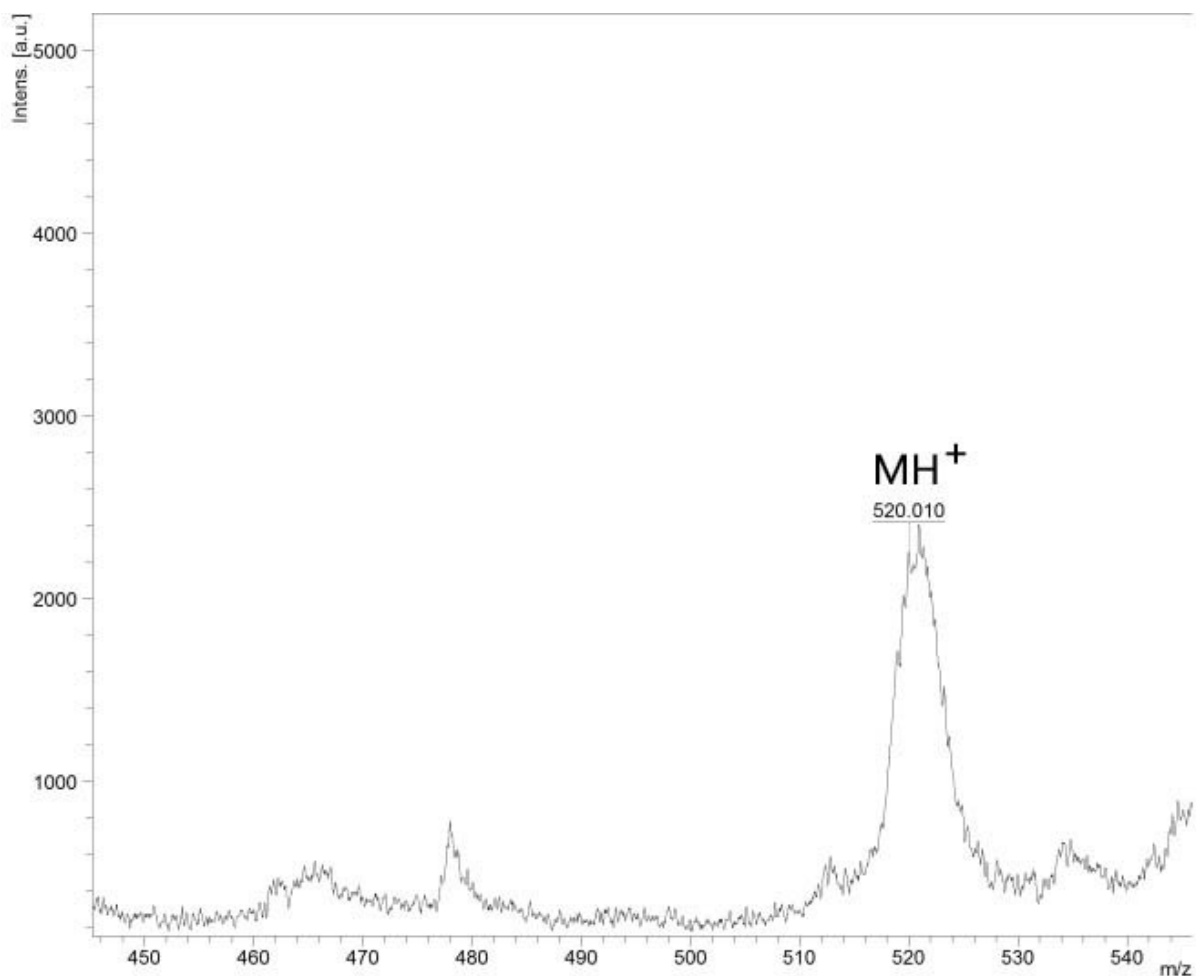


Figure S5. The MALDI-TOF-MS spectrum of compound **4**

2.4 Synthesis of compound **5**

Under N₂ atmosphere, a mixture of compound **4** (0.52 g, 1.0 mmol), 4-hydroxybenzaldehyde (0.20 g, 1.6 mmol) and K₂CO₃ (0.28 g, 2.0 mmol) was stirred and refluxed in 25 mL of dry MeCN for 24 h. The reaction was monitored by TLC technique implying the disappearance of reactants. After reaction, the mixture was treated with 30 mL HCl (1 M) and extracted with 30 mL of CHCl₃. The CHCl₃ layer was partitioned, washed by 15 mL of distilled water, dried over anhydrous MgSO₄, and then concentrated. The residue was treated by 15 mL of MeOH and the precipitate was obtained. The crude product was further purified by column chromatography using CH₂Cl₂/hexane (1:1, *V/V*) as eluant. After dryness, compound **5** was collected as a pale yellow solid in yield of 82%. ¹H NMR (400 MHz, CDCl₃) δ: 9.87 (s, 1H, CHO), 7.83 (d, *J* = 8.0 Hz, 4H, ArH), 7.56 (d, *J* = 8.0 Hz, 2H, ArH), 7.33 (s, 1H, C=CH),

6.93-7.03 (m, 6H, ArH), 3.48-4.27 (m, 18H, OCH₂), 2.28-2.34 (m, 2H, CH₂), 1.20 (t, *J* = 8.0 Hz, 3H, CH₃). MALDI-TOF-MS (C₃₃H₃₇NO₇) Calcd. for *m/z* = 559.65, found: *m/z* = 561.47 (MH⁺).

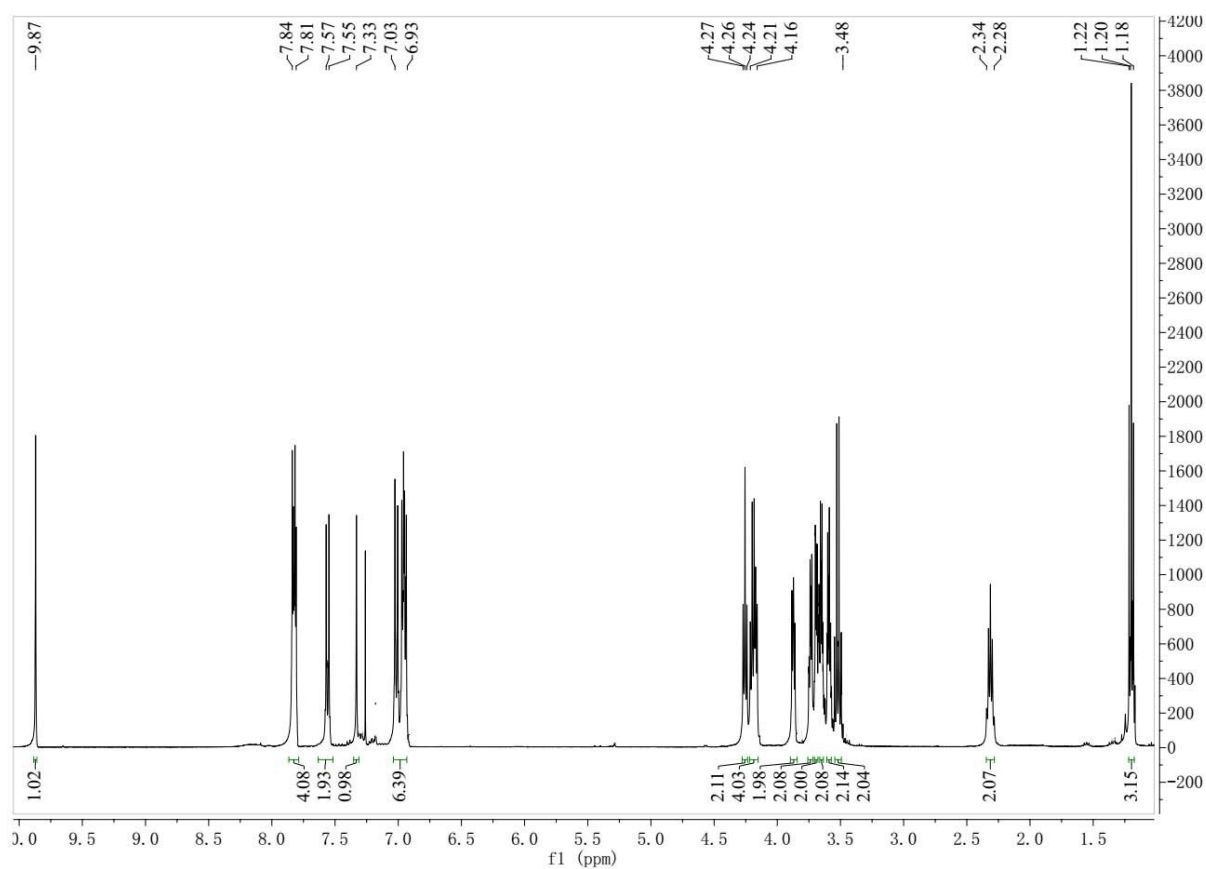


Figure S6. The ¹H NMR spectrum of compound 5

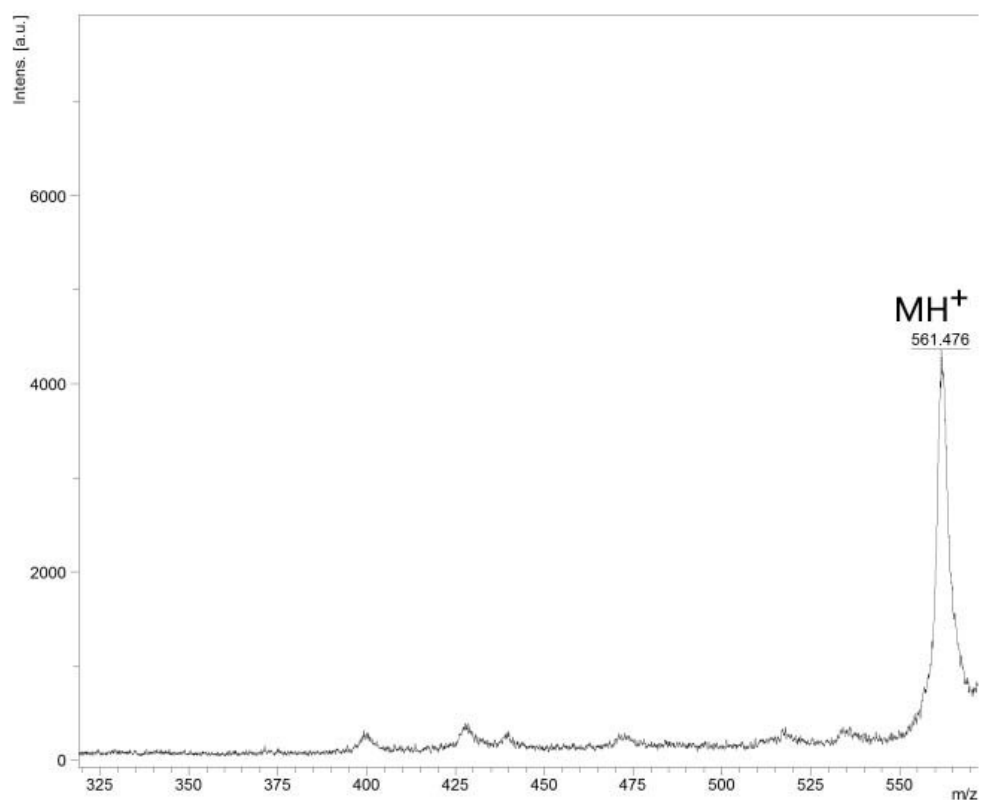


Figure S7. The MALDI-TOF-MS spectrum of compound **5**

2.5 Synthesis of compound **6**.

A mixture of compound **5** (0.56 g, 1 mmol) and pyrrole (67 mg, 1 mmol) were stirred for 60 min at room temperature in 100 mL of CH_2Cl_2 with 0.3 mL of trifluoroacetic acid (TFA), followed by oxidation with tetrachlorobenzoquinone (TCQ) (197mg, 0.8 mmol). After reaction, the solvent was removed by rotary evaporator. The crude product was further purified by silica chromatography on silica gel (eluent : CHCl_3 : ethyl acetate = 85:15), affording compound **6** in 8.8% yield as purple solid. ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.85 (s, 8H, pyrrole CH), 8.11 (d, $J = 8.0$ Hz, 8H, ArH), 7.33 (d, $J = 8.0$ Hz, 8H ArH), 7.63 (d, $J = 8.0$ Hz, 8H, ArH), 7.36 (s, 4H, C=CH), 7.29 (d, $J = 8.0$ Hz, 8H, ArH), 7.06 (d, $J = 8.0$ Hz, 8H, ArH), 6.96 (d, $J = 8.0$ Hz, 8H, ArH), 3.50-4.47 (m, 72H, OCH_2), 2.49 (t, $J = 4.8$ Hz, 8H, CH_2), 1.21 (t, $J = 8.0$ Hz, 12H, CH_3), -2.76 (s, 2H, pyrrole NH); ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 15.18, 29.56, 64.63, 64.81, 66.66, 67.58, 69.60, 69.84, 70.67, 70.76, 70.91, 108.39, 112.68, 114.60, 114.85, 118.69, 119.74, 126.76, 127.18, 127.55, 130.30, 130.87, 131.40, 134.79, 135.64, 139.98, 158.15, 158.62, 160.35; MALDI-TOF-MS ($\text{C}_{148}\text{H}_{154}\text{N}_8\text{O}_{24}$) Calcd. for $m/z = 2428.11$, found: $m/z = 2429.67$ (MH^+). Anal. Calcd for $\text{C}_{148}\text{H}_{154}\text{N}_8\text{O}_{24}$: C, 73.19; H, 6.39; N, 4.61. Found: C, 73.15; H, 6.44; N, 4.52.

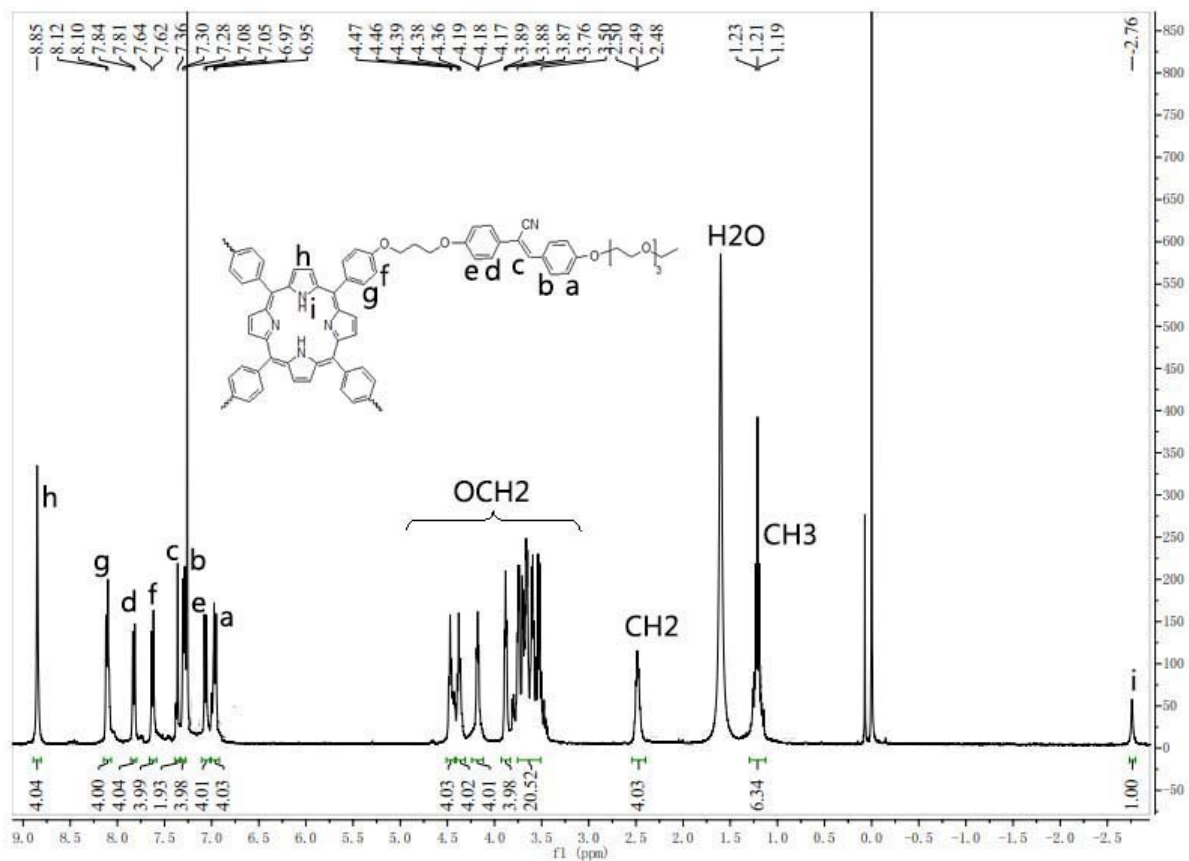


Figure S8. The ¹H NMR spectrum of compound 6

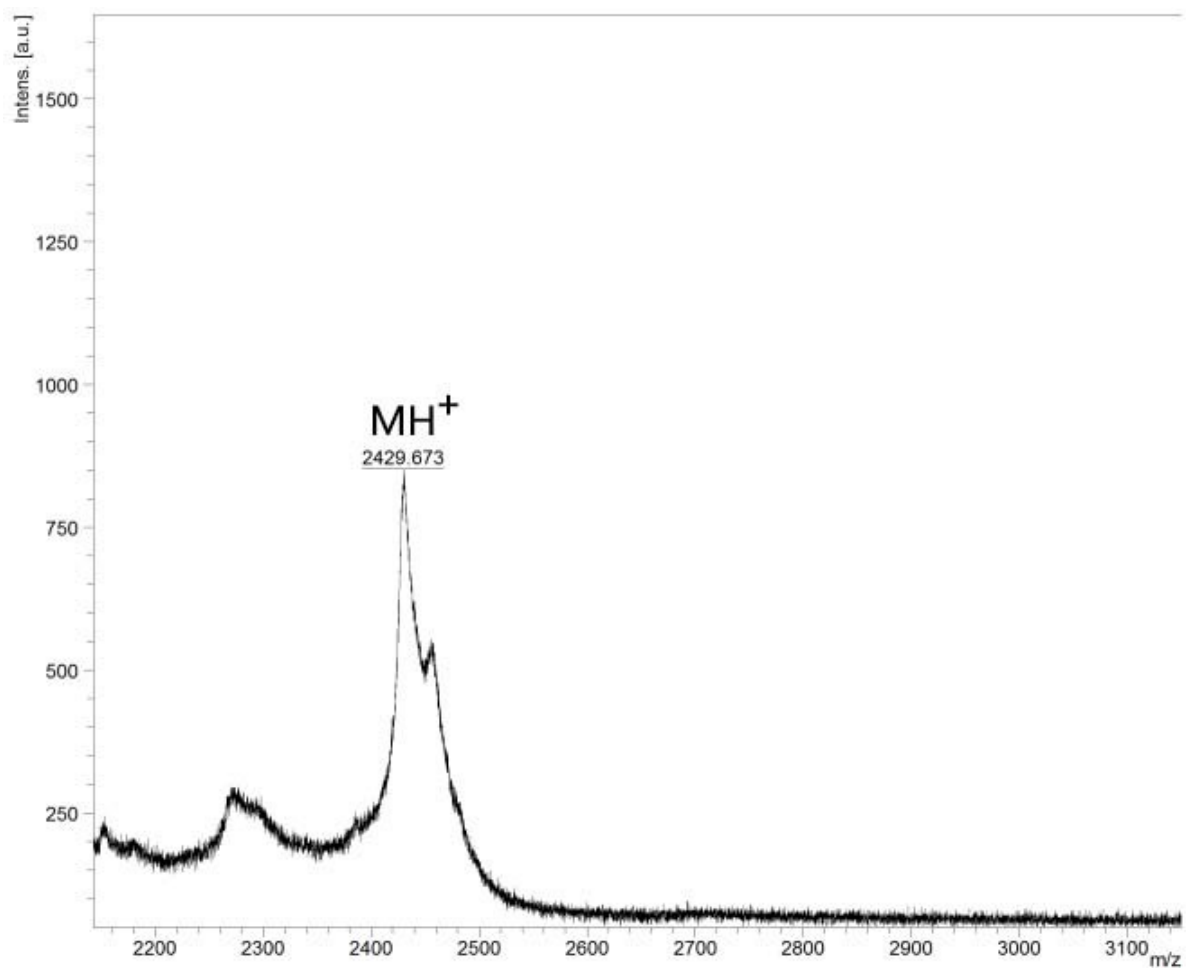


Figure S9. The MALDI-TOF-MS spectrum of compound **6**

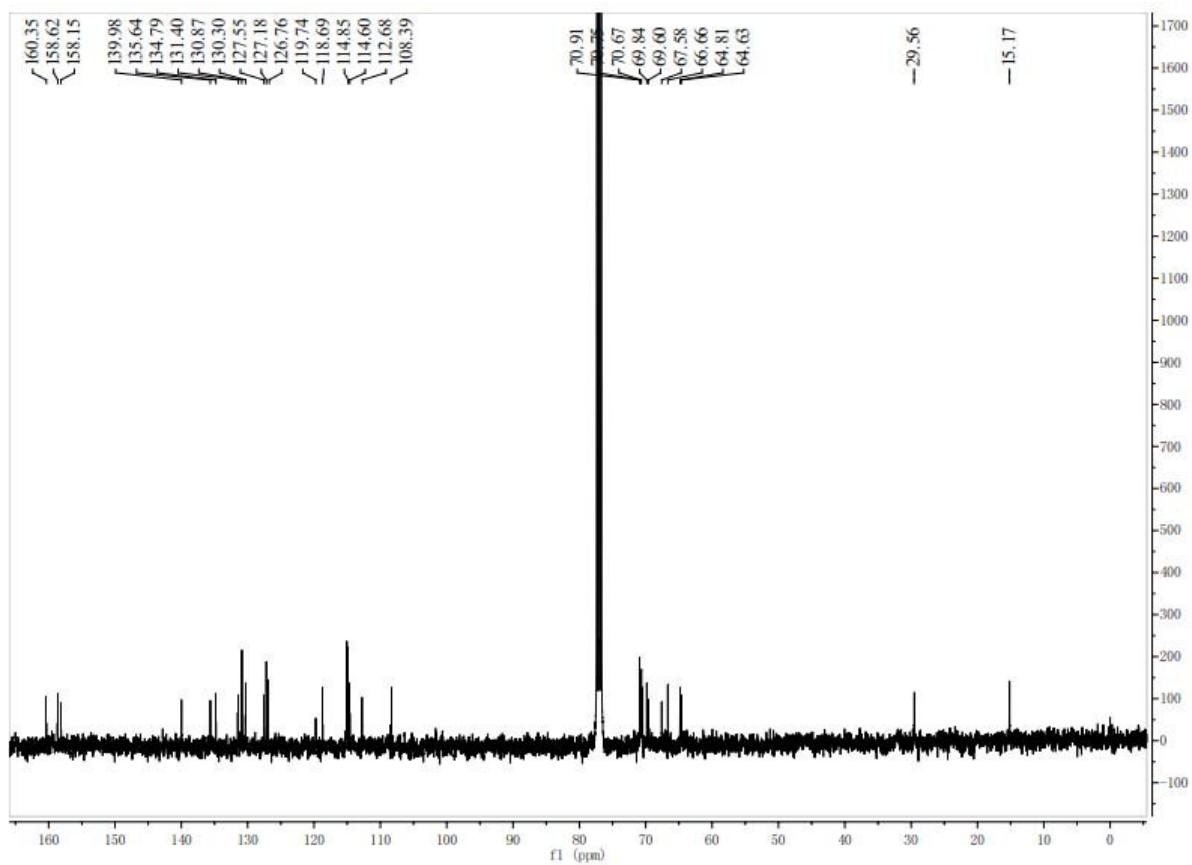


Figure S10. The ^{13}C NMR spectrum of compound **6**

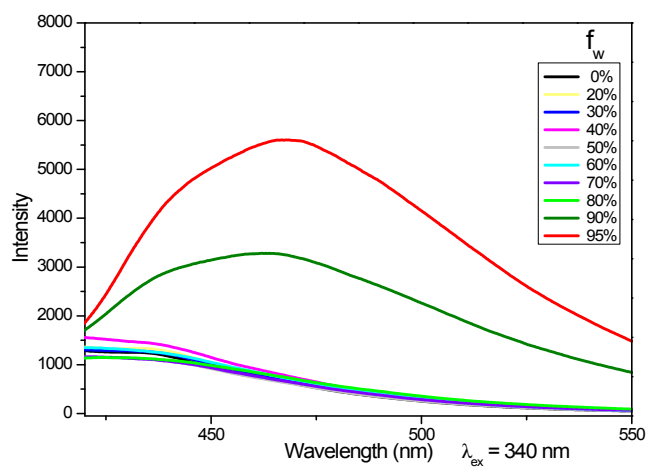


Figure S11 The fluorescence spectra of precursor **4** with different fractions of H_2O in $\text{THF}/\text{H}_2\text{O}$ mixtures (1×10^{-6} M, $\lambda_{\text{ex}} = 340$ nm).

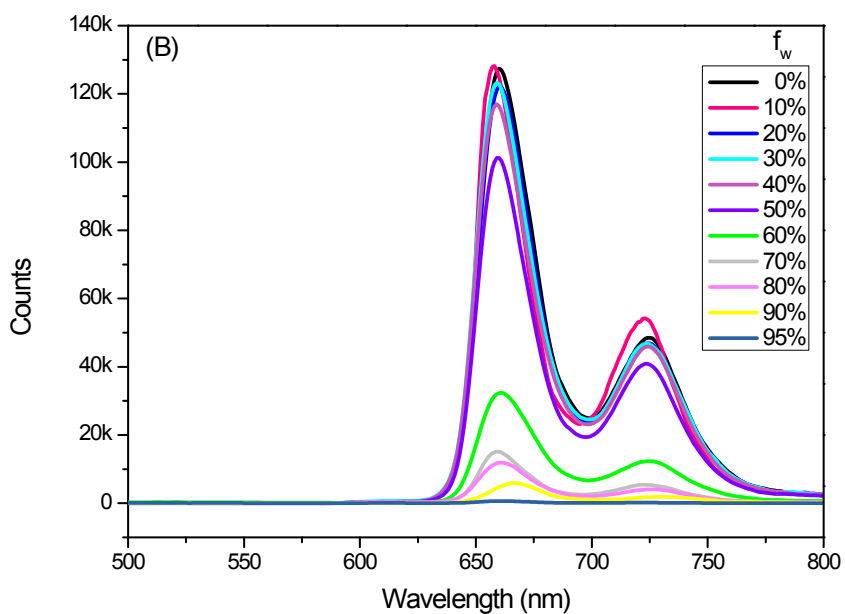


Figure S12 The fluorescence spectra of reference compound **7** with different fractions of H₂O in THF/H₂O mixtures (1×10^{-5} M, $\lambda_{\text{ex}} = 420$ nm).

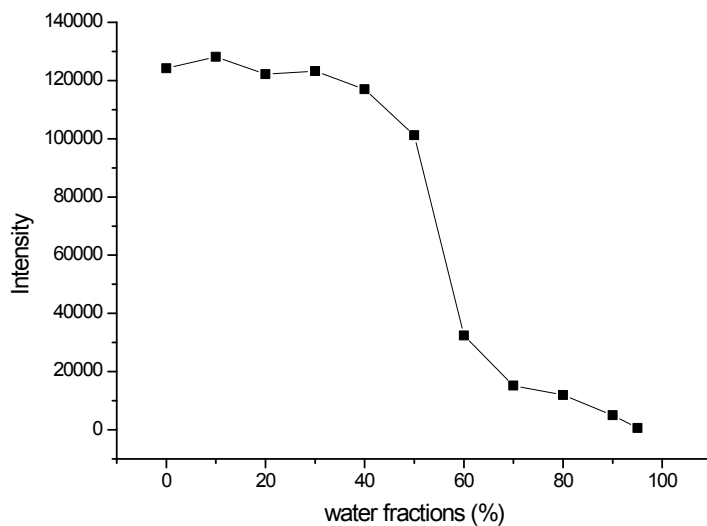


Figure S13 The line plot of fluorescence intensity change from 0-95% water fractions of sample **7**