

Supporting Information

Diphenylacrylonitrile-bridging triphenylene dimers: The Columnar liquid crystals with high fluorescence in both solid state and solution

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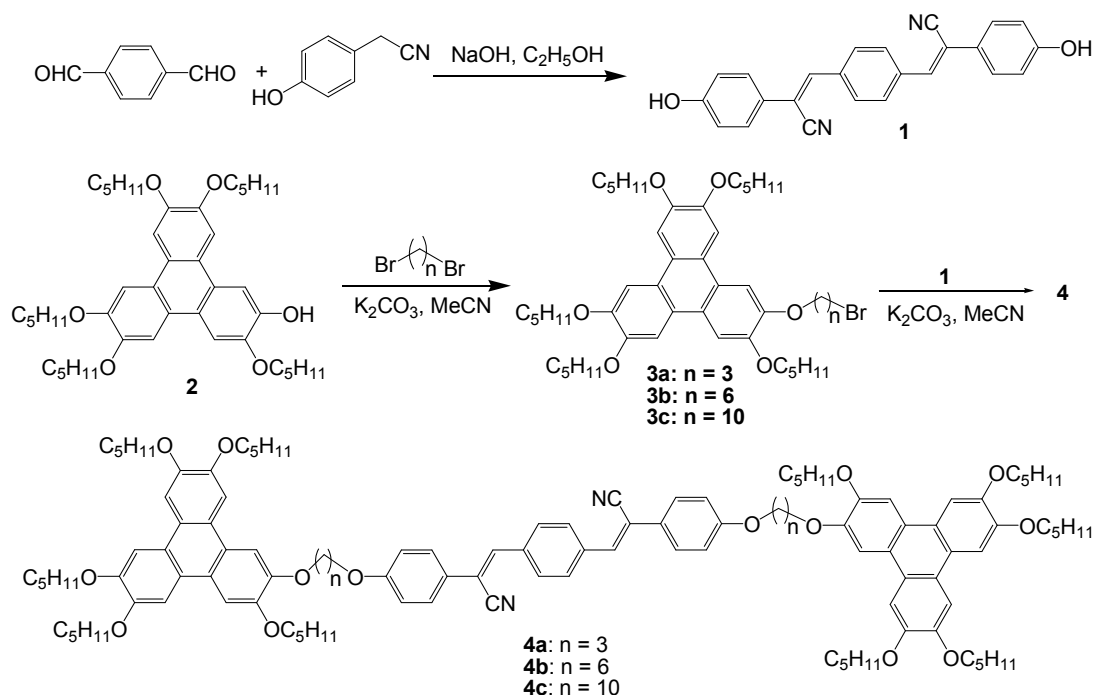
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1. General

All chemical reagents, organic solvents and inorganic reagents were purchased from Aladdin Reagent Co. Ltd. They were purified by the standard anhydrous methods before use. TLC analysis was done on pre-coated glass plates. Column chromatography was carried out by using silica gel (200-300 mesh). NMR spectra were performed in CDCl₃ at 26°C on a Bruker-ARX 400 instrument. Chemical shifts were recorded in ppm with tetramethylsilane (TMS) as internal standard. MS spectra were obtained on Bruker mass spectrometer. Compounds **3a** and **3b** were synthesized according to the published literature (Tetrahedron Letters, 2016, 57, 4939-4943). Compound **3c** was prepared by the literature method (Tetrahedron Letters, 2014, 55, 252-255).

UV-Vis spectra were done on Varian UV-Vis spectrometer. Fluorescence spectra were recorded in a conventional quartz cell (10×10×45 mm) at 26 °C on a Hitachi F-4500 spectrometer, which was equipped with a constant-temperature water bath. The excitation and emission slits were 5 nm wide. The fluorescence absolute Φ_F values were obtained on an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 6-inch integrating sphere. A polarized optical microscopy (Leica DMRX) was measured on a hot stage (Linkam THMSE 600) to investigate phase transitions. Thermal analysis of the materials was measured on a differential scanning calorimeter (DSC) (Thermal Analysis Q100) under N₂ atmosphere at a scanning rate of 10°C/min. XRD experiments were studied by SEIFERT-FPM (XRD7), using Cu K α 1.5406Å as the radiation source with 40 kV, 30 mA power.

2. The synthetic process of target compounds and their characteristic spectra.



Scheme S1. Synthetic routes for target compounds **4a**, **4b** and **4c**

2.1 Synthesis of compound **1**.

A mixture of 4-hydroxyphenylacetonitrile (0.51 g, 3.8 mmol), terephthalaldehyde (0.25 g, 1.9 mmol) and NaOH (0.30g, 7.5mmol) in 30 mL of EtOH solution was stirred for 12 h at room temperature. The reaction was monitored by TLC technique, indicating the disappearance of the starting materials. Then, 20 mL of HCl solution (1M) was added into the reaction system. The precipitate was formed and collected. The obtained precipitate was further purified by recrystallization in MeOH / water (1:1, *V/V*). After dryness over vacuum, compound **1** was obtained as a pale yellow solid in yield of 78%. ¹H NMR (400 MHz, CHCl₃) δ : 7.01 (d, *J* = 8.0 Hz, 4H, ArH), 7.46 (s, 2H, CH=C), 7.66(d, *J* = 8.0 Hz, 4H, ArH), 7.95(s, 4H, ArH), 8.22 (s, 2H, OH). MALDI-TOF-MS Calcd. (C₂₄H₁₆N₂O₂) for *m/z* = 364.2, found: *m/z* = 387.2 (MNa⁺), 403.2 (MK⁺).

2.2 Synthesis of compound **3a**, **3b** and **3c**.

According to the published method (Tetrahedron Letters, 2016, 57, 4939-4943), Monohydroxytriphenylene **2** (1.35 g, 2 mmol) and corresponding dibromoalkane (5 mmol) with K₂CO₃ (0.97g, 7 mmol) were stirred and refluxed in 60 mL of dry acetonitrile for 24 h under N₂.

After reaction, the solution was cooled, filtered and evaporated to dryness under reduced pressure. Then the residue was further purified by rapid column chromatography (SiO₂ 200-300 mesh, petroleum ether / CH₂Cl₂ (10:1, *V/V*) as eluant). The compounds **3a**, **3b** and **3c** was obtained as soft gray solid in yield of 80%, 72% and 66%, respectively. Compound **3a**: ¹H NMR (400 MHz, CDCl₃) δppm: 0.97 (t, 15H, *J* = 8.0 Hz, CH₃), 1.41~1.99 (m, 32H, CH₂), 3.49 (t, 2H, *J* = 6.0Hz, BrCH₂) , 4.23=4.26 (m, 12 H, OCH₂), 7.85 (bs, 6H, ArH); Compound **3b**: ¹H NMR (400 MHz, CDCl₃) δppm: 0.98 (t, 15H, *J* = 8.0 Hz, CH₃), 1.42~1.98 (m, 38 H, CH₂), 3.46 (t, 2 H, *J* = 6.0 Hz, BrCH₂) , 4.23 (t, 12 H, *J* = 8.0 Hz, OCH₂), 7.84 (s, 6 H, ArH); Compound **3c**: ¹H NMR (400 MHz, CDCl₃) δppm: 0.98 (t, 15H, *J* = 6.9 Hz, CH₃), 1.22~1.98 (m, 46 H, CH₂), 3.41 (t, 2 H, *J* = 8.0 Hz, BrCH₂) , 4.24 (t, 12 H, *J* = 8.0 Hz, OCH₂), 7.85 (s, 6H, ArH).

2.3 Synthesis of compounds **4a**, **4b** and **4c**.

Under the protection of N₂ atmosphere, a mixture of compound **3a** (**3b** or **3c**, 0.5 mmol), compound **1** (0.091g, 0.25 mmol), K₂CO₃ (0.28g, 2.0 mmol) and KI (0.1g, 0.6 mmol) was stirred and refluxed in dry MeCN (30 mL) for 48 h at 85 °C. The monitor of TLC technique implied the disappearance of reactants. After reaction, the mixture was cooled, treated with 50 mL of HCl (1 M) and extracted with 50 mL CHCl₃. The CHCl₃ layer was separated and concentrated under reduced pressure. The obtained residue was further purified by rapid column chromatography by using ethyl acetate/hexane (1:5, *V/V*) as eluant. After dryness, compounds **4a**, **4b** and **4c** were obtained as pale yellow solid in yields of 72%, 78% and 84%, respectively.

Compound **4a**: ¹H NMR (400 MHz, CDCl₃) δ: 7.93 (s, 4H, ArH), 7.87 (s, 2H, TpH), 7.83 (bs, 10H, TpH), 7.61 (d, *J* = 8.0 Hz, 4H, ArH), 7.39 (s, 2H, CH=CCN), 7.02 (d, *J* = 8.0 Hz, 4H, ArH), 4.45 (t, *J* = 8.0 Hz, 4H, OCH₂), 4.35 (t, *J* = 8.0 Hz, 4H, OCH₂), 4.23(t, *J* = 8.0 Hz, 20H, OCH₂), 1.40-2.47(m, 64H, CH₂), 0.97(t, 30H, *J* = 8.0 Hz, 30H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δppm: 160.17, 148.86, 148.37, 138.40, 135.30, 129.26, 127.27, 126.85, 123.71, 123.29, 117.96, 115.04, 111.92, 107.67, 107.24, 107.03, 69.47, 66.06, 64.79, 53.45, 31.85, 29.79, 29.14, 18.38, 22.48, 13.86. MALDI-TOF-MS Calcd.for *m/z* = 1794.1, found: *m/z* = 1795.5 (MH⁺).

HR-MS(ESI) (C₁₁₆H₁₄₈N₂O₁₄) [M]⁺: Calcd.: 1794.0958. found:1794.0949.

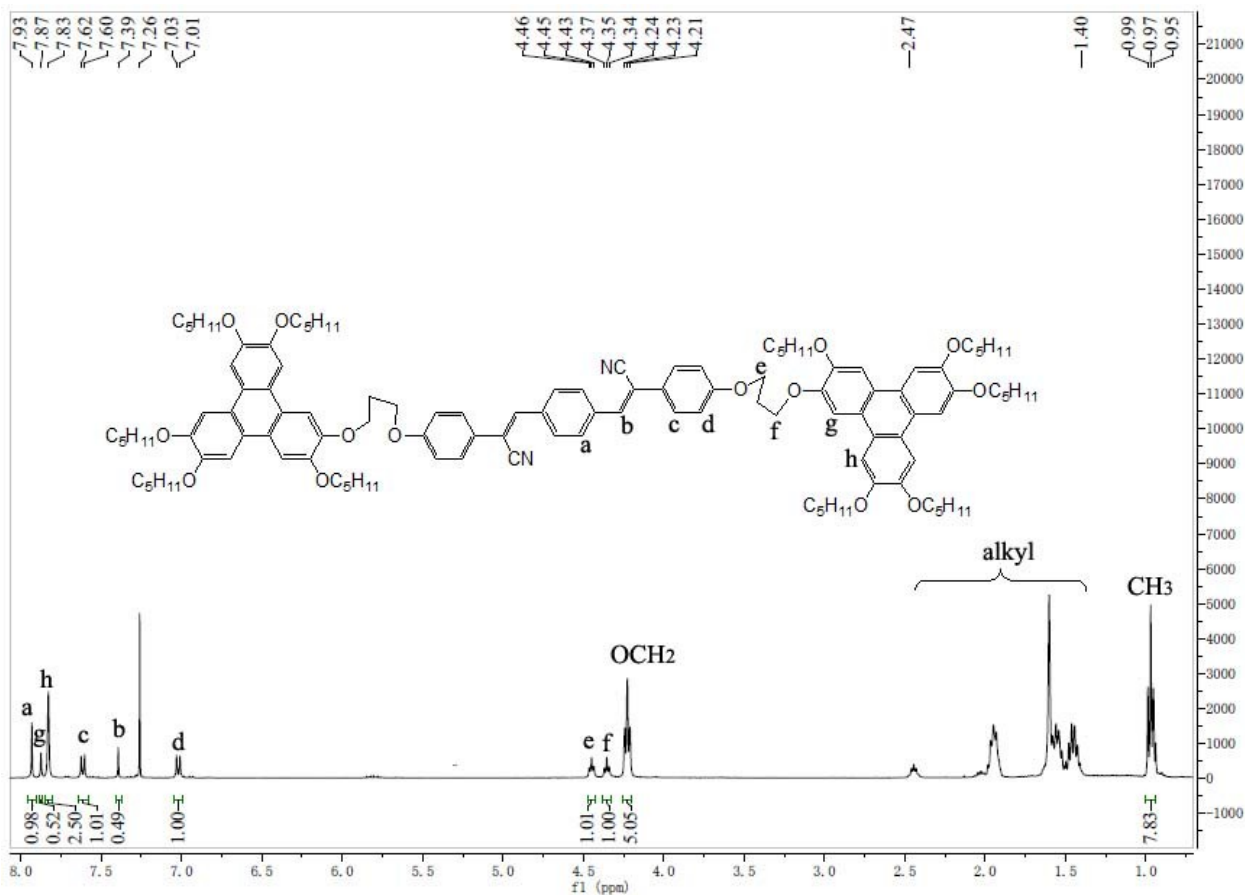


Figure S1. The ^1H NMR of compound 4a

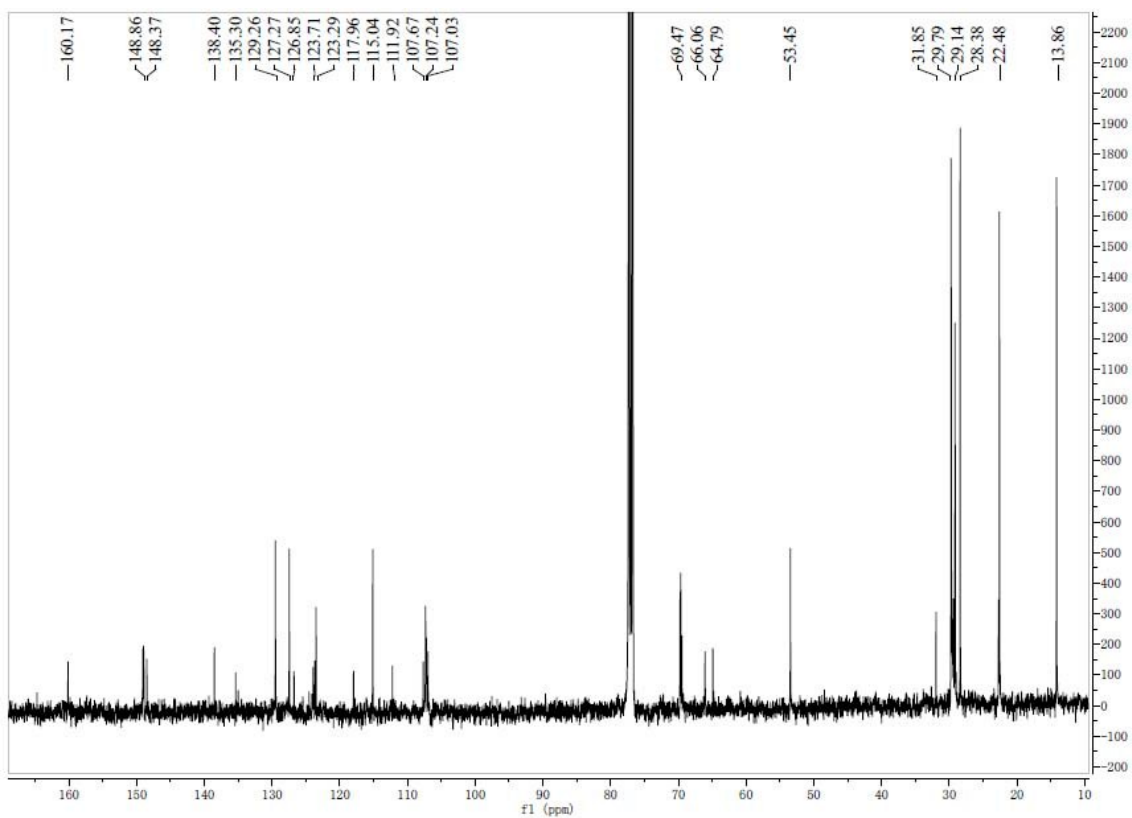


Figure S2. The ^{13}C NMR of compound 4a

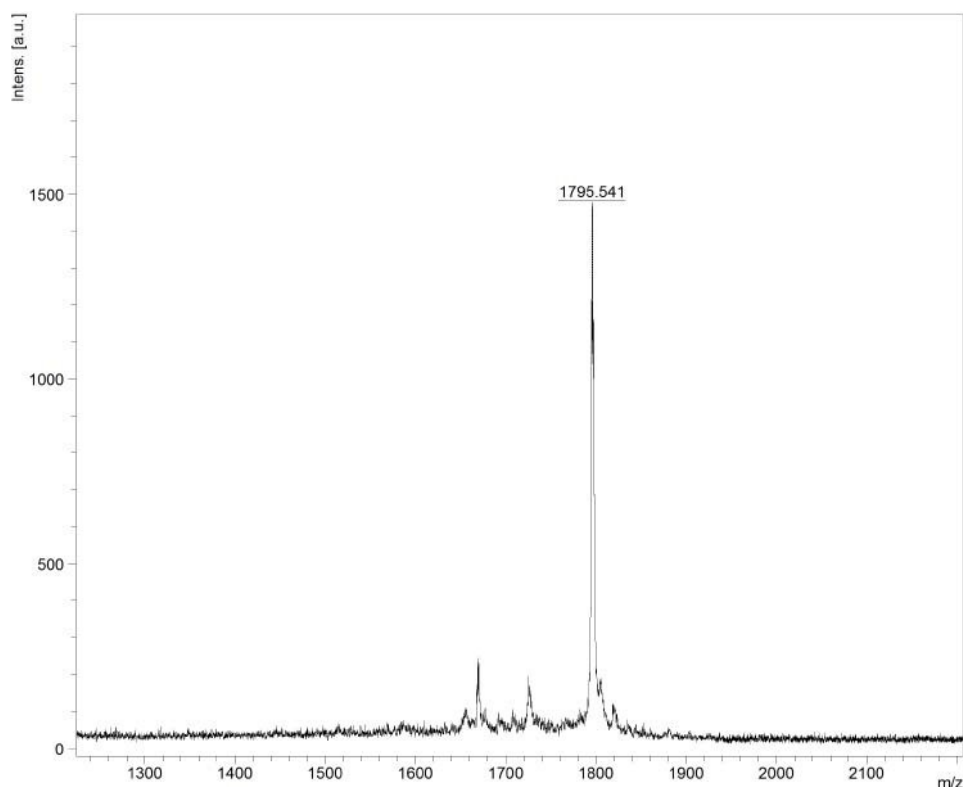


Figure S3. The MALDI-TOF-MS spectrum of compound **4a**

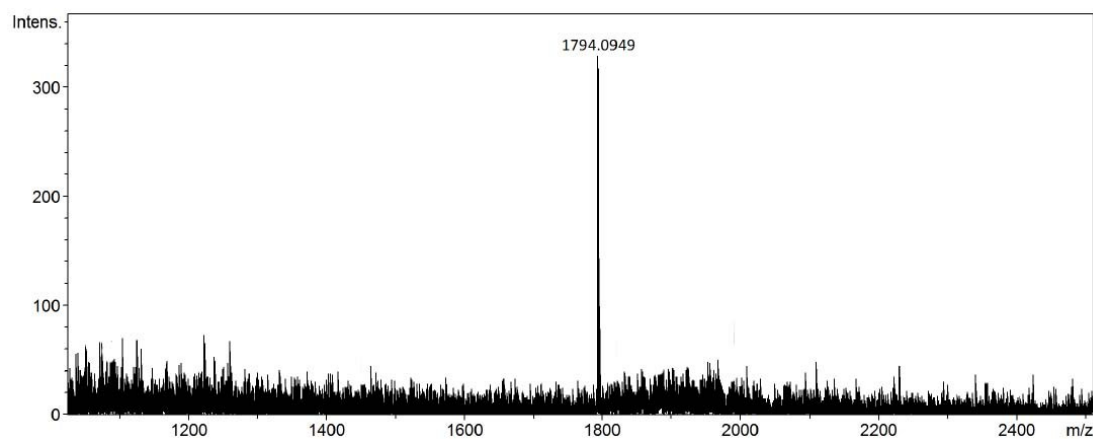


Figure S4. The HR-MS spectrum of compound **4a**

Compound **4b**: ^1H NMR (400 MHz, CDCl_3) δ : 7.91 (s, 4H, ArH), 7.84 (bs, 12H, TpH), 7.61 (d, $J = 8.0$ Hz, 4H, ArH), 7.37 (s, 2H, CH=CCN), 6.95 (d, $J = 8.0$ Hz, 4H, ArH), 4.23 (t, $J = 8.0$ Hz, 24H, OCH_2), 4.04 (t, $J = 8.0$ Hz, 4H, OCH_2), 1.39-2.05(m, 76H, CH_2), 0.98(t, 30H, $J = 8.0$ Hz, 30H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 160.26, 148.99, 138.18, 135.40, 130.10, 129.45, 129.07, 127.36, 126.53, 123.60, 117.79, 115.01, 112.24, 107.34.

MALDI-TOF-MS Calcd. for $m/z = 1878.2$, found: $m/z = 1880.6$ (MH^+).

HR-MS(ESI) ($\text{C}_{122}\text{H}_{160}\text{N}_2\text{O}_{14}$) $[\text{M}]^+$: Calcd.: 1878.1897. found: 1878.1868.

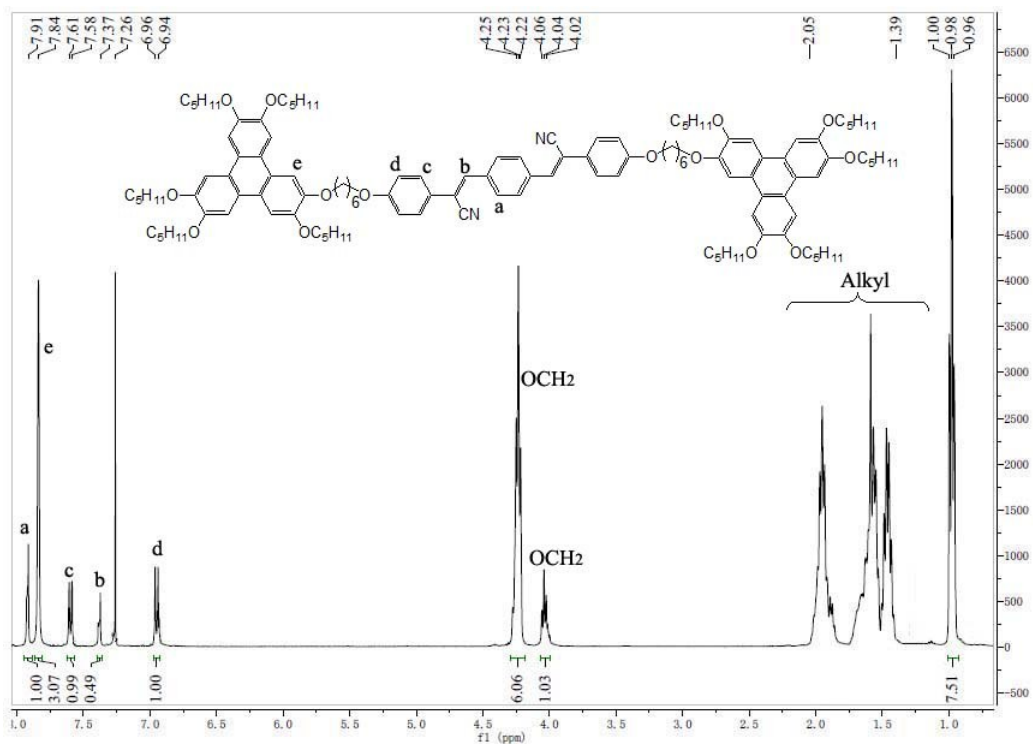


Figure S5. The 1H NMR of compound **4b**

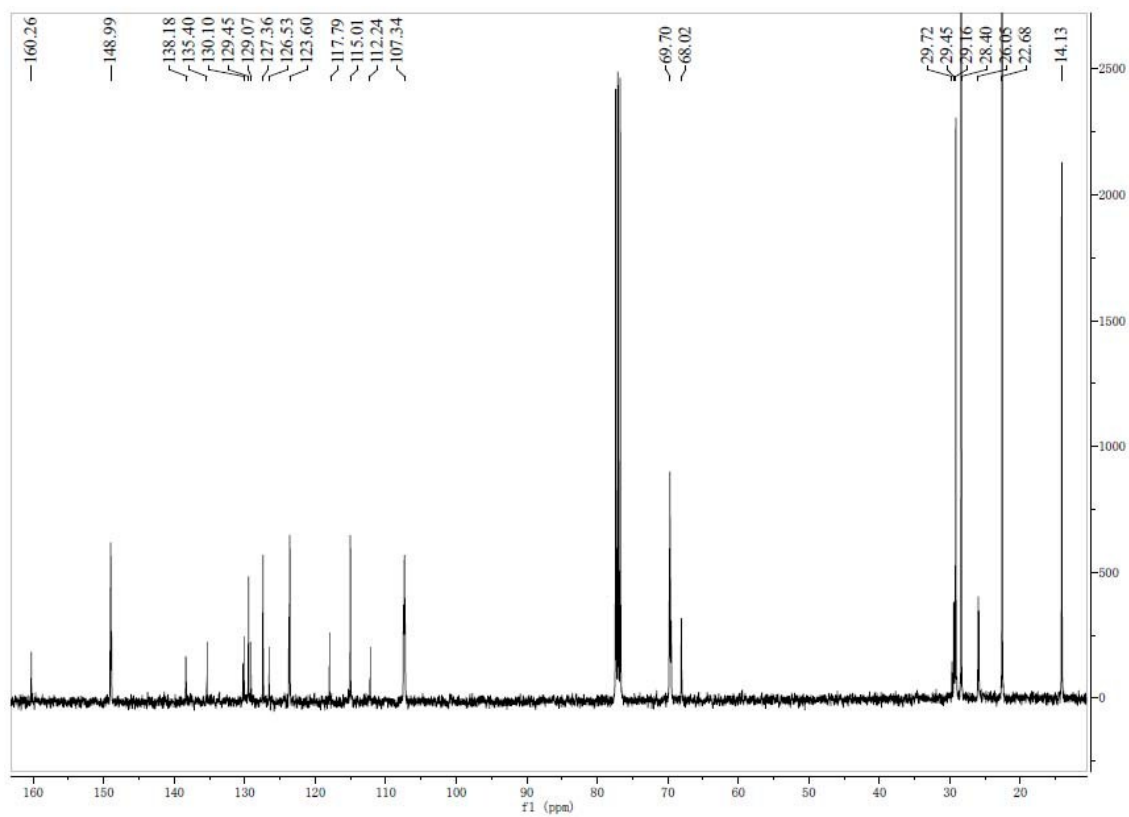


Figure S6. The ^{13}C NMR of compound **4b**

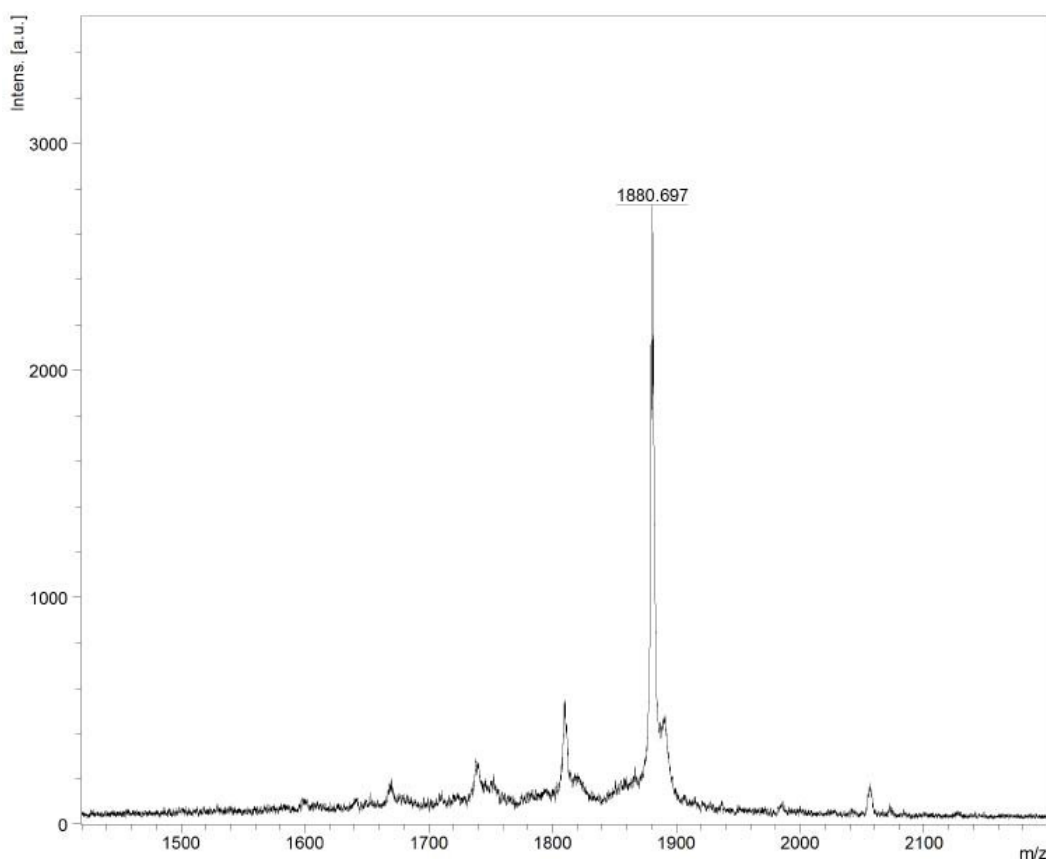


Figure S7. The MALDI-TOF-MS spectrum of compound **4b**

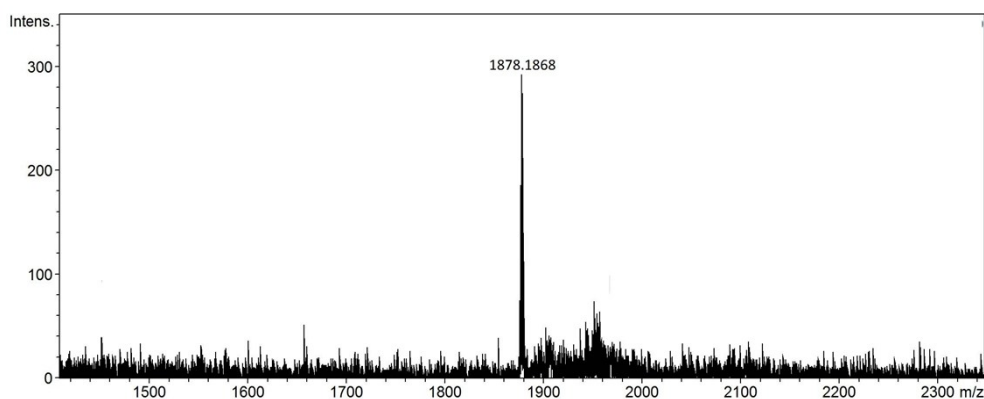


Figure S8. The HR-MS spectrum of compound **4b**

Compound **4c**: ^1H NMR (400 MHz, CDCl_3) δ : 7.83 (bs, 12H, TpH), 7.81 (s, 4H, ArH), 7.56 (d, $J = 8.0$ Hz, 4H, ArH), 7.27 (s, 2H, CH=CCN), 6.90 (d, $J = 8.0$ Hz, 4H, ArH), 4.24 (t, $J = 8.0$ Hz, 24H, OCH_2), 3.96 (t, $J = 8.0$ Hz, 4H, OCH_2), 1.33-2.03 (m, 92H, CH_2), 0.98 (t, 30H, $J = 8.0$ Hz, 30H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 160.23, 148.92, 138.19, 135.18, 132.30, 132.00, 130.19, 128.92, 127.29, 126.23, 123.60, 117.73, 116.08, 114.93, 114.70, 107.21, 69.64, 68.37, 31.88, 29.76, 29.09, 28.44, 26.24, 25.80, 22.64, 14.18.

MALDI-TOF-MS Calcd. for $m/z = 1990.3$, found: $m/z = 1992.9$ (MH^+).

HR-MS(ESI) (C₁₃₀H₁₇₆N₂O₁₄) [MNH₄]⁺: Calcd.: 2008.3493. found:2008.3415.

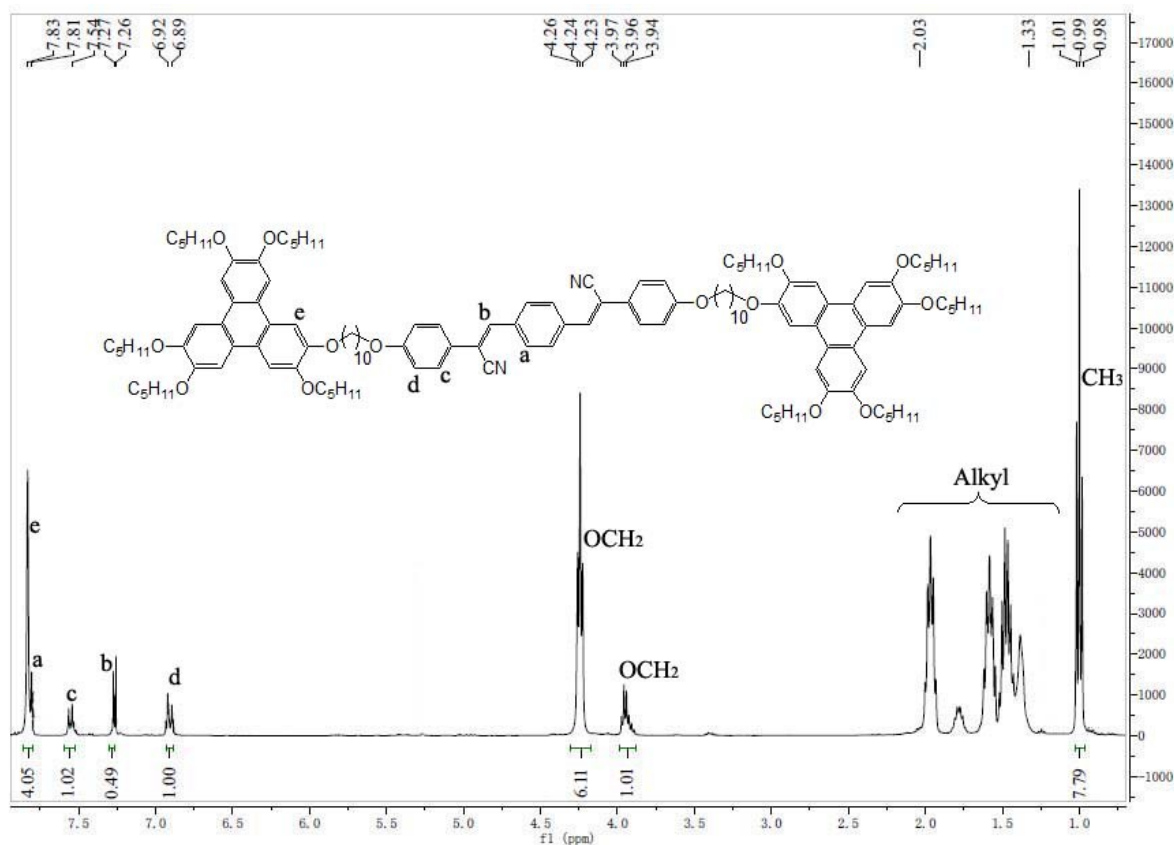


Figure S9. The ¹H NMR of compound 4c

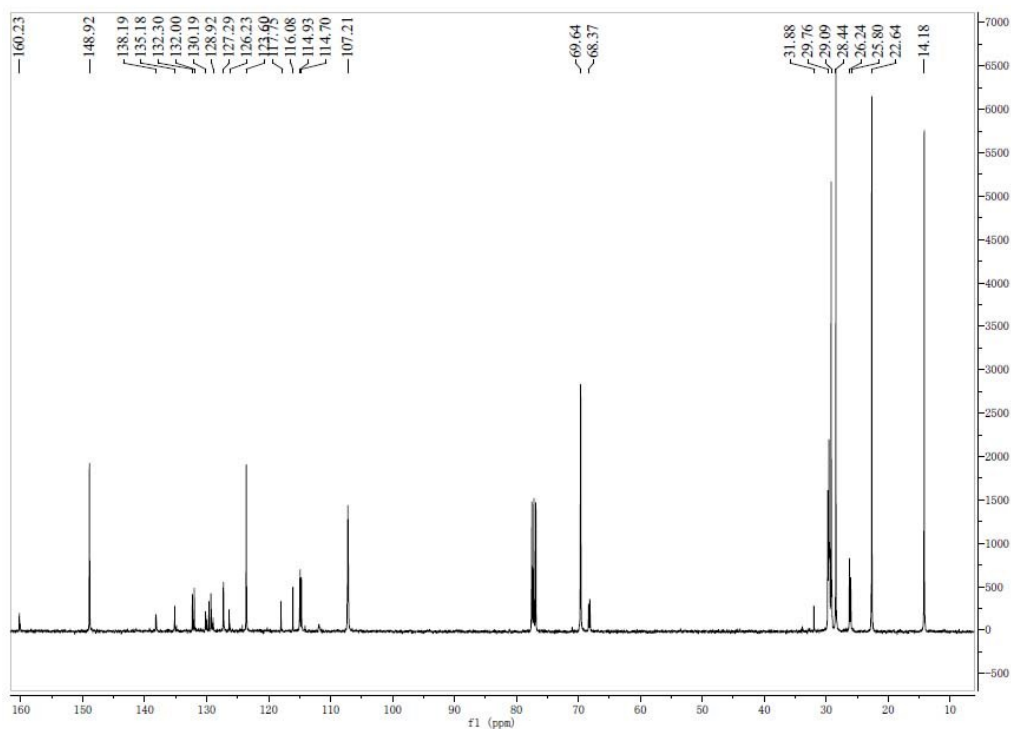


Figure S10. The ¹³C NMR of compound 4c

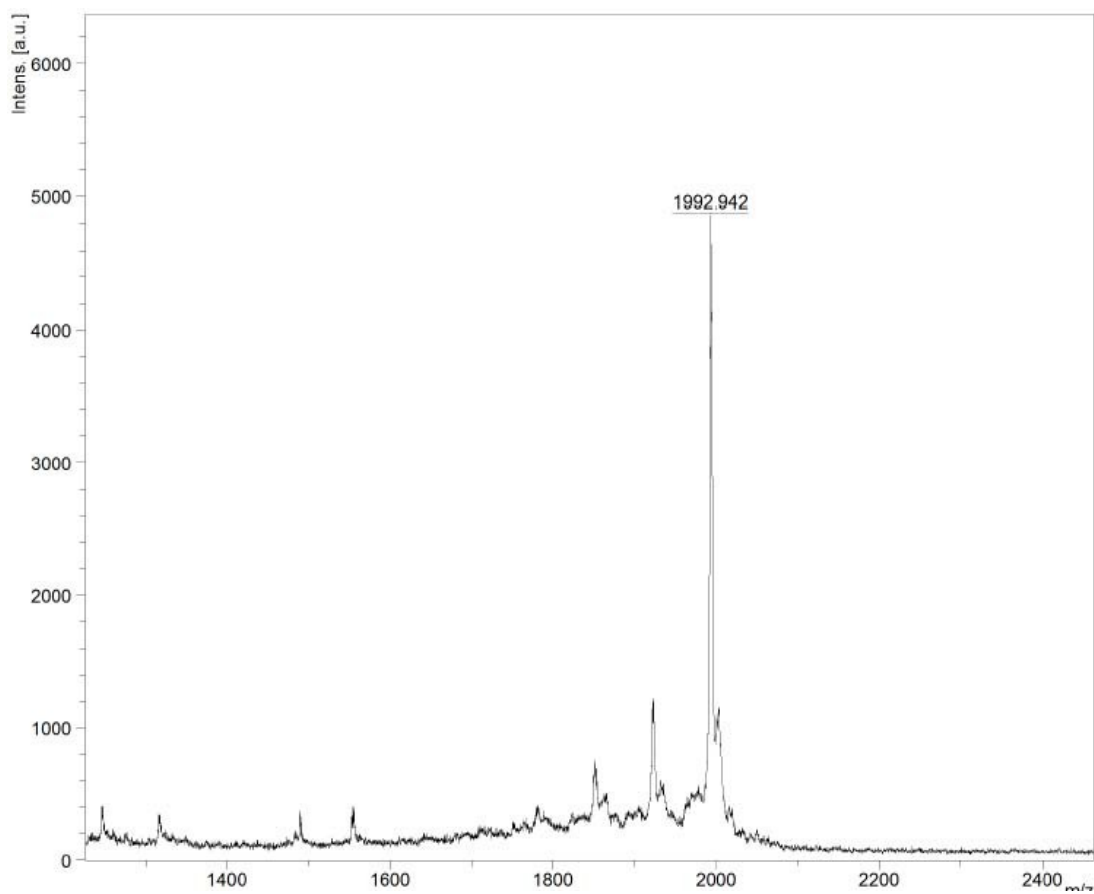


Figure S11. The MALDI-TOF-MS spectrum of compound **4c**

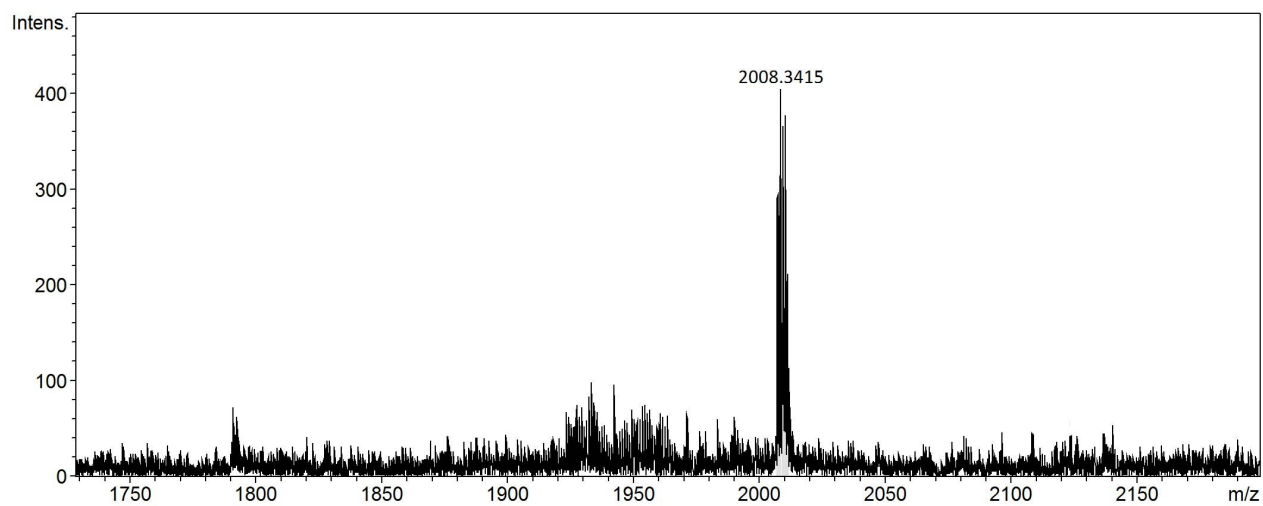


Figure S12. The HR-MS spectrum of compound **4c**

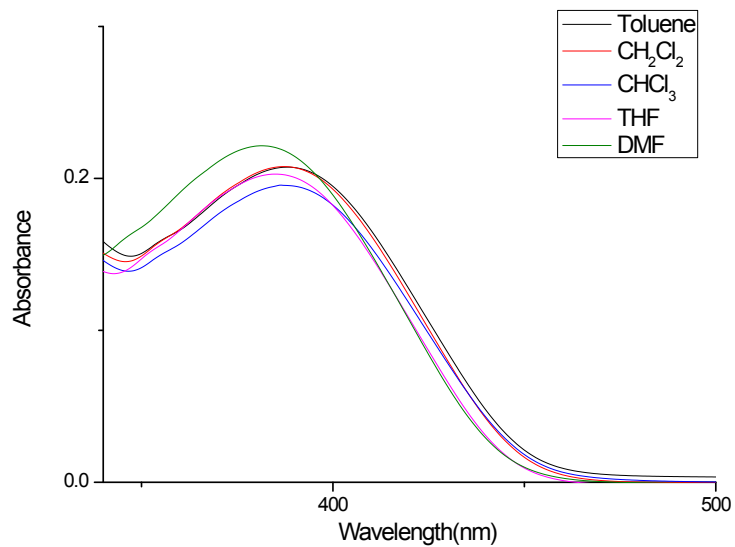


Figure S13. The UV-Vis absorption spectra of compound **4a** in different solvents ($1.0 \times 10^{-6} \text{M}$)

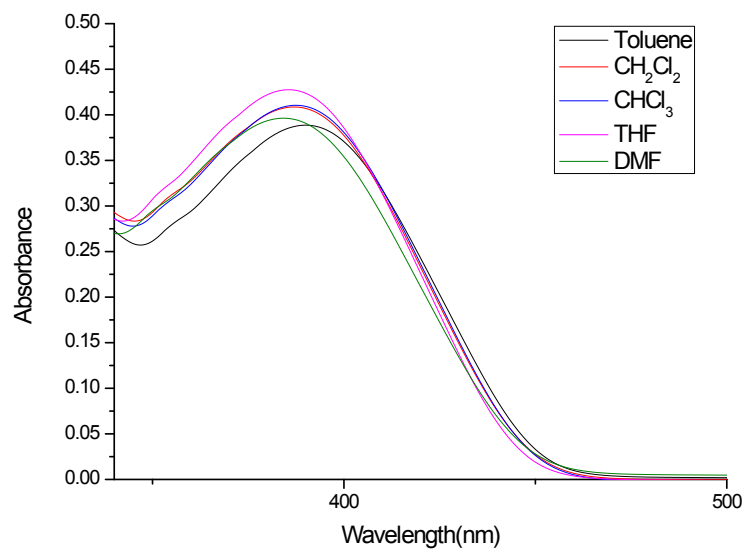


Figure S14. The UV-Vis absorption spectra of compound **4b** in different solvents ($1.0 \times 10^{-6} \text{M}$)

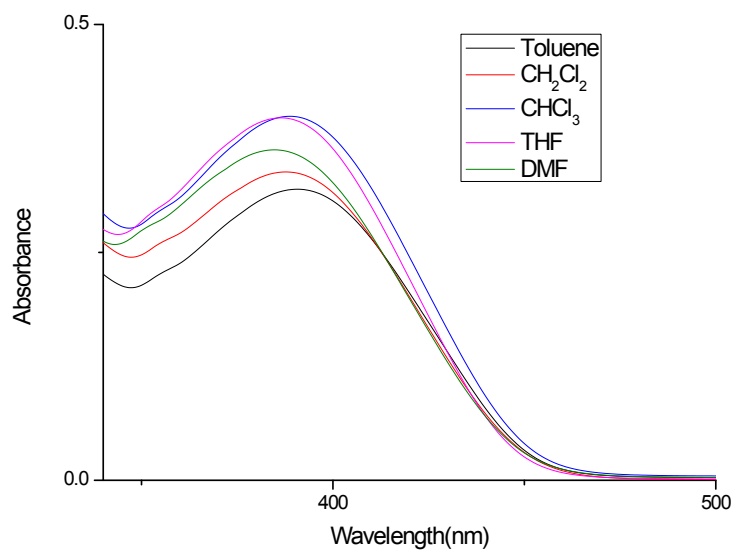


Figure S15. The UV-Vis absorption spectra of compound **4c** in different solvents ($1.0 \times 10^{-6} \text{M}$)

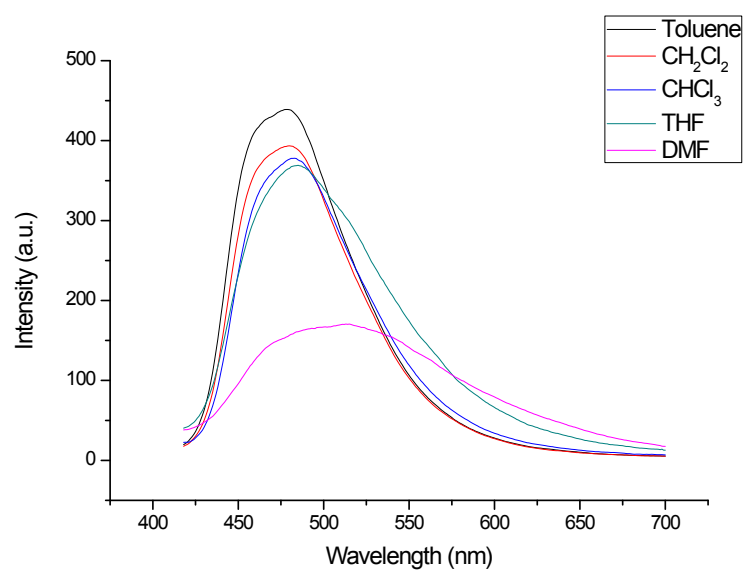


Figure S16. The emission spectra of compound **4a** in different solvents ($1.0 \times 10^{-5} \text{M}$) with the excitation wavelength of 390 nm.

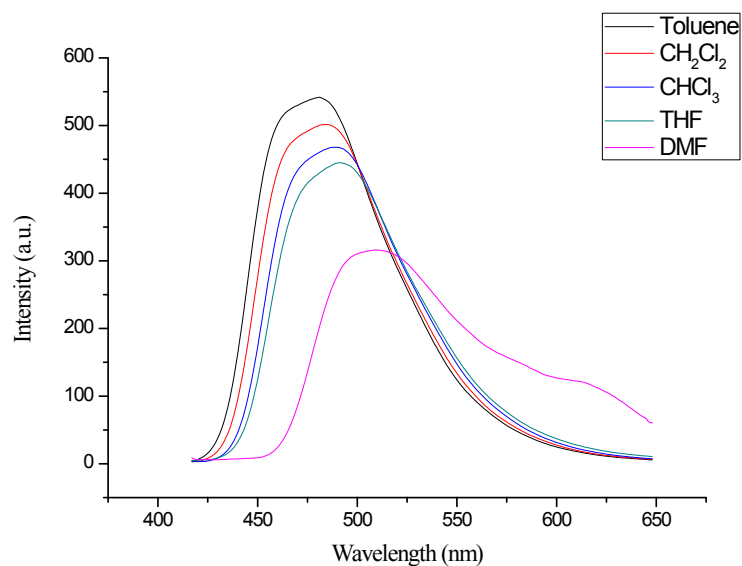


Figure S17. The emission spectra of compound **4b** in different solvents ($1.0 \times 10^{-5} \text{M}$) with the excitation wavelength of 390 nm.

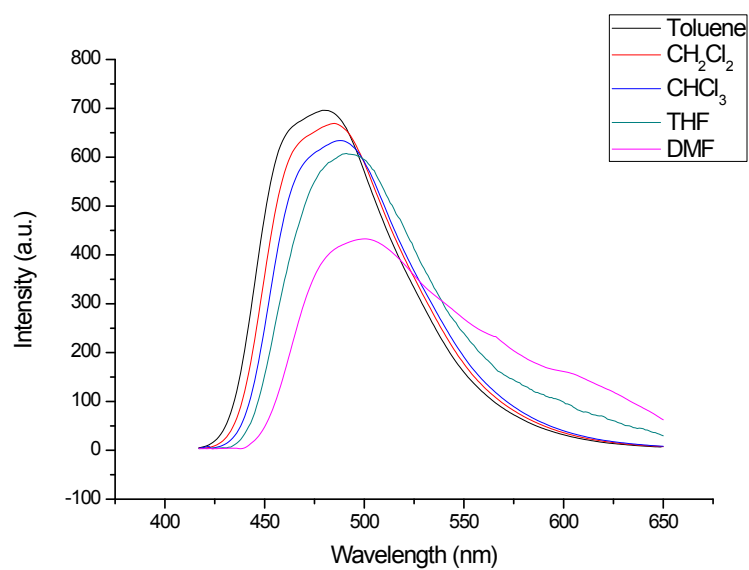


Figure S18. The emission spectra of compound **4c** in different solvents ($1.0 \times 10^{-5} \text{M}$) with the excitation wavelength of 390 nm.

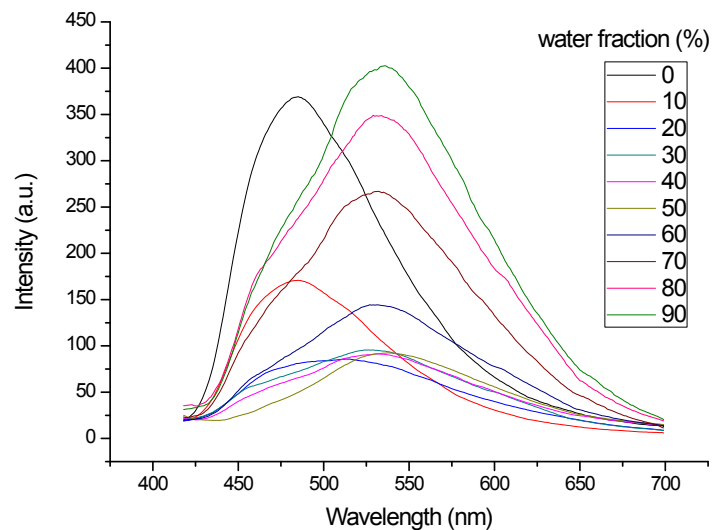


Figure S19. The emission spectra of compound **4a** in H₂O/THF mixtures with different water fractions ($1.0 \times 10^{-5} \text{M}$) and the excitation wavelength of 390 nm.

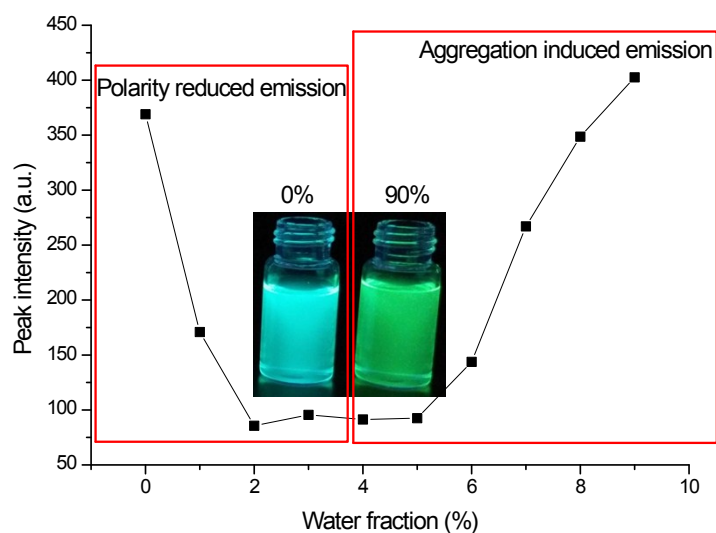


Figure S20. The changes in peak intensity and emission images of compound **4a** in H₂O/THF mixtures with different water fractions ($1.0 \times 10^{-5} \text{M}$) and the excitation wavelength of 390 nm.

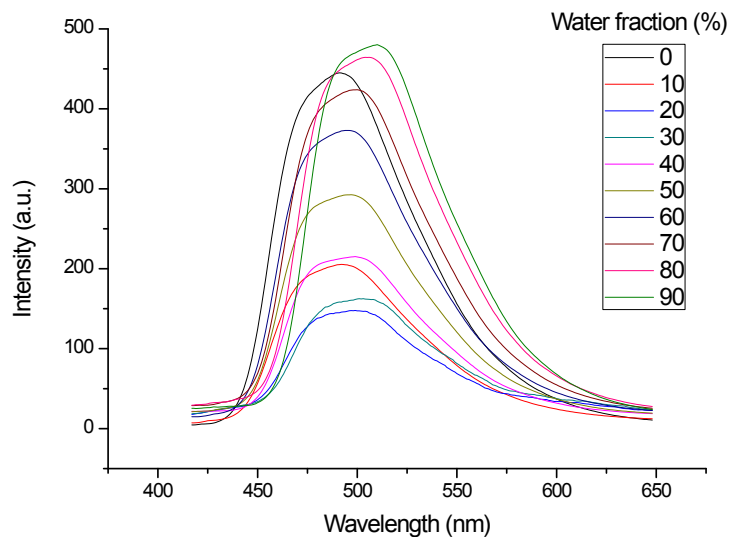


Figure S21. The emission spectra of compound **4b** in H₂O/THF mixtures with different water fractions (1.0×10^{-5} M) and the excitation wavelength of 390 nm.

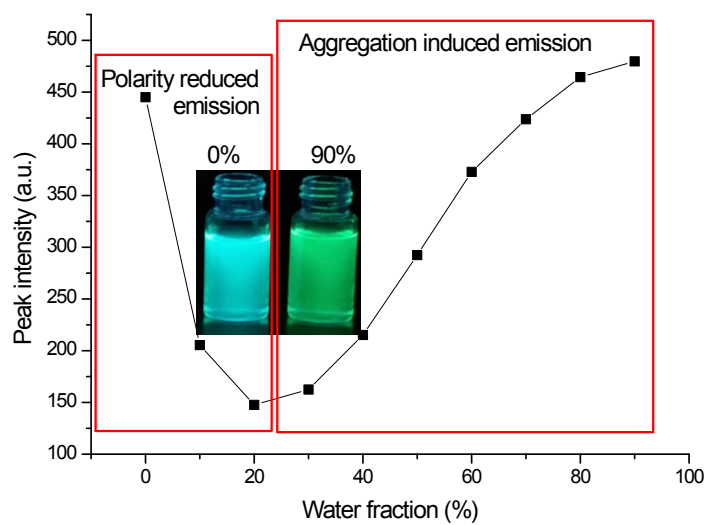


Figure S22. The changes in peak intensity and emission images of compound **4b** in H₂O/THF mixtures with different water fractions (1.0×10^{-5} M) and the excitation wavelength of 390 nm.

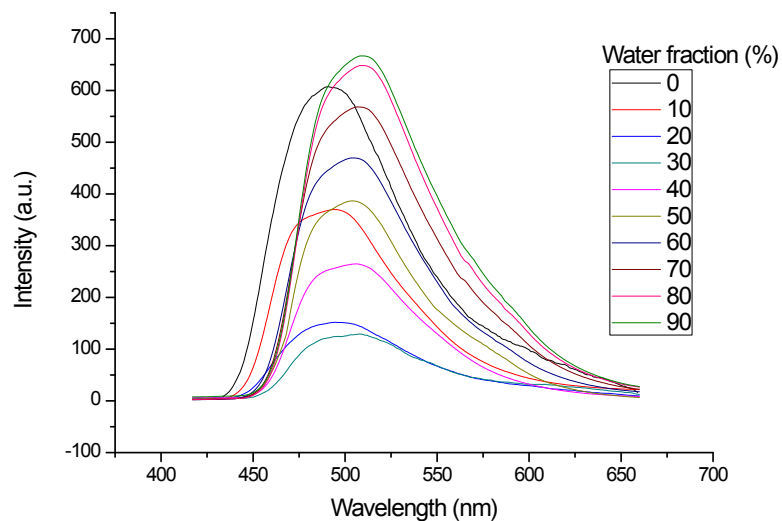


Figure S23. The emission spectra of compound **4c** in H₂O/THF mixtures with different water fractions (1.0×10^{-5} M) and the excitation wavelength of 390 nm.

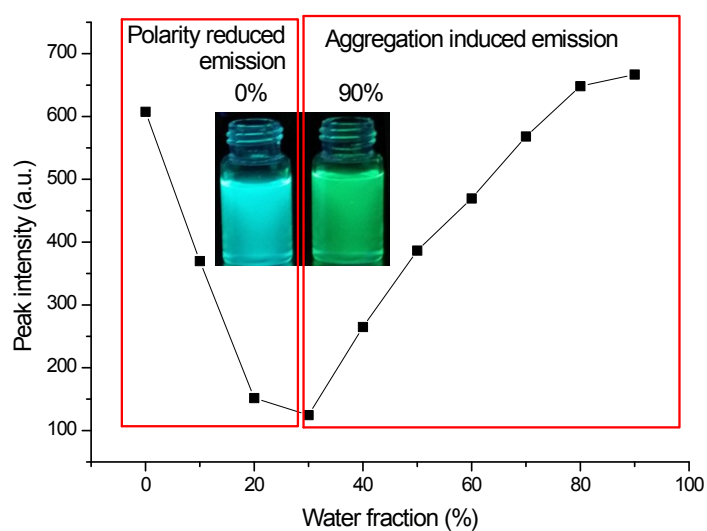


Figure S24. The changes in peak intensity and emission images of compound **4c** in H₂O/THF mixtures with different water fractions (1.0×10^{-5} M) and the excitation wavelength of 390 nm.

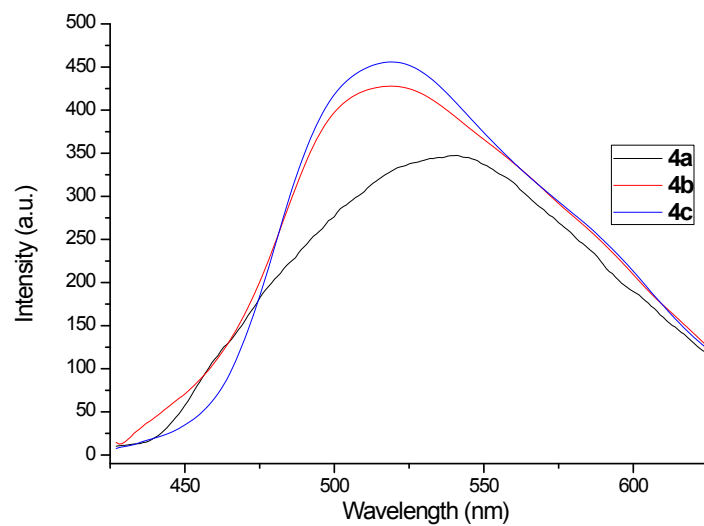


Figure S25. The emission spectra of the powders of compounds **4a**, **4b** and **4c** ($\lambda_{\text{ex}}=390$ nm)

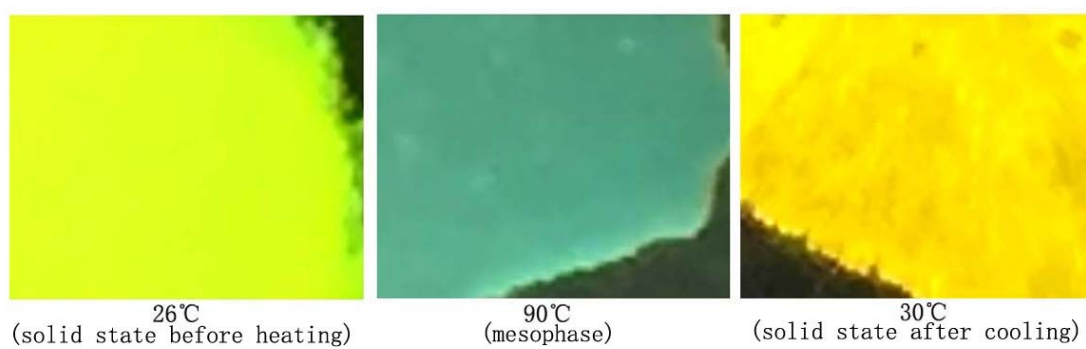


Figure S26. The fluorescent emission pictures at different temperature of compound **4a** ($\lambda_{\text{ex}}=365$ nm)