

Supporting Information

Design and Assembly of AIE-active Fluorescent Organic Nanoparticles for Anti-counterfeit Fluorescent Hydrogel and Ink

Xia-fen Li,^a Wei Zhou,^a Yi-chen Liu,^a Min Hou,^a Gai-li Feng,^a Yan-ming Ji,^a Yuan Zhang^{*a,b} and Guo-wen Xing^{*a}

^a College of Chemistry, Beijing Normal University, Beijing, 100875, China. E-mail: yuanzhang@bnu.edu.cn, gwxing@bnu.edu.cn

^b Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry Beijing Normal University, Beijing 100875, China.

Materials and instruments: All reagents and solvents used in the experiment were purchased from commercial suppliers and used directly unless otherwise specified. Double-distilled water was applied to throughout optical analysis. The reaction process was monitored by TLC on silica gel plate (HSGF254) and displayed under UV light (254 nm or 365 nm) or ethanol-sulfuric acid (7%). Column chromatography was conducted over silica gel (mesh 200-300) or SiliaSphere C18 (50 μm 120Å), or BioGel P-2 fine resins (Bio-Rad, Hercules, CA). High-resolution electrospray ionization mass spectra (HRMS-ESI) were performed with a Waters LCT Premier XEmass spectrometer. Nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorder at room temperature with JEOL's NMR (400 or 600 MHz) spectrometer and the chemical shifts (in ppm) were related to solvent peaks. The fluorescence spectra were recorded by an Edinburgh Instruments FS5 fluorescence spectrometer with samples contained in quartz cells. Transmission electron microscopy (TEM) photos were captured using a FEI Talos F200S instrument. Dynamic light scattering (DLS) experiment was obtained by Zata Potential Analyzer (Brookhaven).

Encapsulation of F127 surfactant: Firstly, 1 mg of solid probe **TPE-1',2',3'** were dissolved in 1 mL of THF, and 10 mg of surfactant pluronic F127 was added for encapsulation until the solution was clarified. Secondly, it was dropped into 10 mL of double-distilled water to make it evenly spread in the aqueous solution. Finally, the aqueous solution was placed in the ventilation cabinet to volatilize the THF solution to obtain the encapsulated probe **F-TPE-1',2',3'** aqueous solution, respectively.

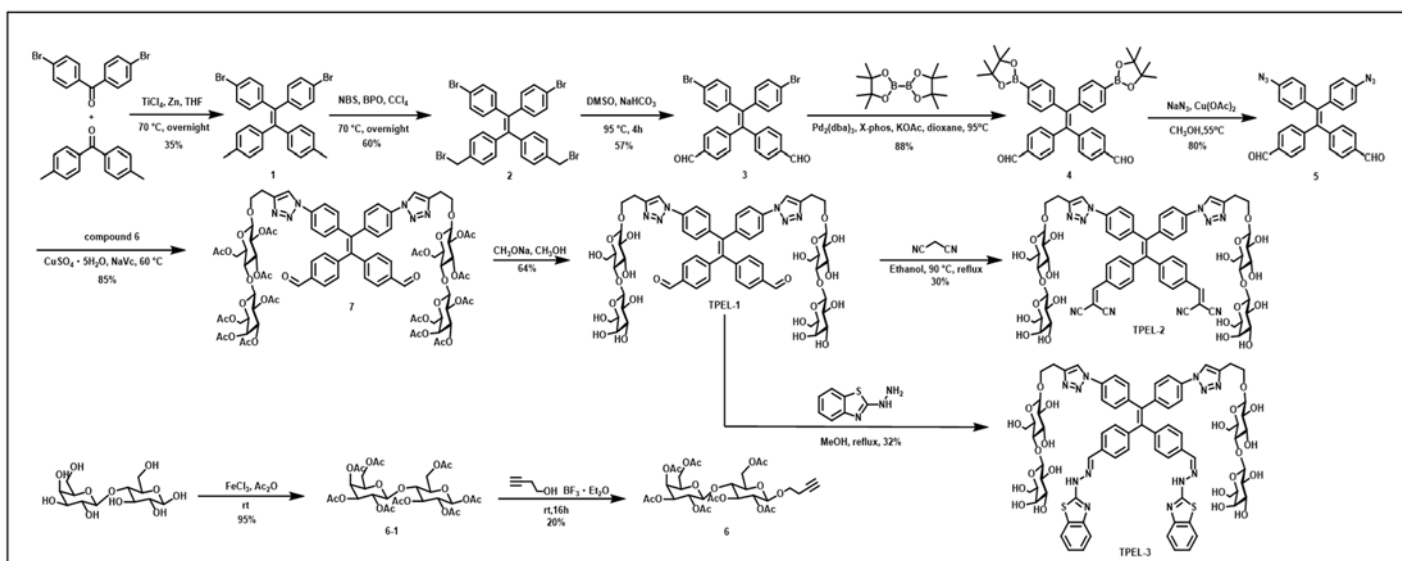
Preparation of fluorescent hydrogel: Firstly, 1 mg of TPEL-1,2,3 was dissolved in an

appropriate amount of secondary distilled water to obtain 0.2 mM aqueous solution probes, respectively. Next, take 1 mL of the above-mentioned aqueous solutions of TPEL-1, 2, 3 and F-TPE-1', 2', 3' into the ep tubes, and then put the purchased transparent colorless spherical gels into the ep tubes, respectively. After the gels were immersed in aqueous solution for 2 h, the excess aqueous solution on the surface of the gels was washed with secondary distilled water to obtain transparent fluorescent gel spheres with a diameter of 1 cm, respectively.

Preparation of fluorescent ink: Firstly, pipette 100 μ L 0.2 mM TPEL-1,2,3 aqueous solution was put into ep tubes, respectively. Secondly, transfer 2.9mL of secondary distilled water to dilute the solution to obtain 10 μ M TPEL-1,2,3 aqueous ink, respectively. Finally, the capillary tube was used as a pen to encrypt information on non-fluorescent paper.

Fluorescence / UV-vis experiment: The probes **TPEL-1,2,3** and **F-TPE-1',2',3'** were prepared to a stock solution of 0.2 mM in double-distilled water. The probes **TPE-1',2',3'** were prepared to a stock solution of 0.2 mM in tetrahydrofuran (THF). The testing solution 3 mL was firstly placed in an ep tube, which was shaken well and interacted at ambient temperature. Then it was decanted in a 3 mL quartz cuvette for optical measurements. In fluorescence test, excitation wavelengths were 340 nm, 300 nm and 380 nm, respectively and the slit width was set to 3nm. The slit width was set to 2 nm in the UV-vis test.

Synthesis of probes TPEL-1,2,3 and TPE-1',2',3'.

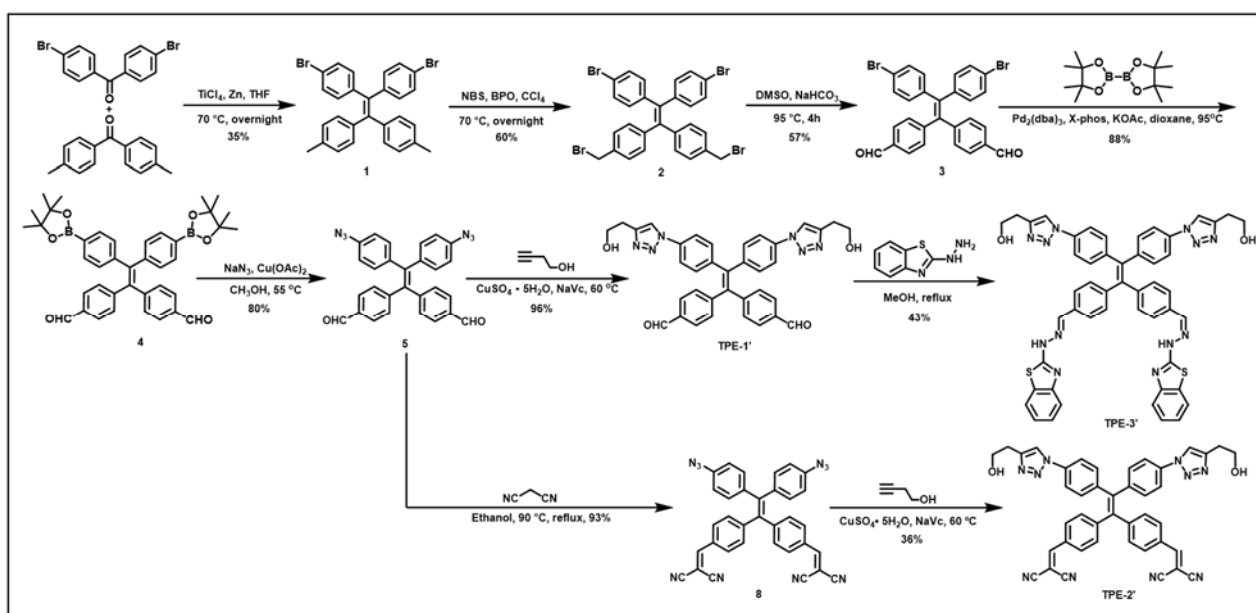


Scheme. S1 Synthetic routes of **TPEL-1,2,3**.

Compounds 1, 2, 3, 4, 5, 6, 7 and **TPEL-1,2** were synthesized according to the procedures in the literatures. ^[1]

Synthesis of Compound TPEL-3: Compound **TPEL-1** (0.050 g, 0.040 mmol) and 2-hydrazyl benzothiazole (0.015g, 0.088 mmol) were added in a 25 mL eggplant-shaped bottle under nitrogen protection, followed by the addition of anhydrous methanol (5 mL) and 1 M HCl (a few drops). The reaction mixture was stirred at 60 °C overnight. The solvent was removed under reduced pressure and the crude product was purified to obtain the target product **TPEL-3**. Yield: 0.020g (32%). ¹H NMR (600 MHz, DMSO-d₆): δ 8.68 (s, 1H), 8.64 (s, 1H), 8.06 (s, 2H), 7.73 (d, *J* = 7.1 Hz, 6H), 7.54 (d, *J* = 7.8 Hz, 4H), 7.42 (s, 2H), 7.29 (d, *J* = 7.8 Hz, 6H), 7.14 (d, *J* = 7.1 Hz, 4H), 7.09 (t, *J* = 7.4 Hz, 2H), 5.33 (s, 1H), 5.07 (s, 2H), 4.79 (s, 1H), 4.73 (s, 1H), 4.70 (s, 1H), 4.64 (s, 2H), 4.57 (d, *J* = 9.3 Hz, 2H), 4.53 (s, 1H), 4.52 (s, 2H), 4.30 (d, *J* = 7.6 Hz, 1H), 4.19 (m, 2H), 4.06 (m, 1H), 3.89 (m, 1H), 3.70 (m, 4H), 3.61 (s, 4H), 3.57 (d, *J* = 9.7 Hz, 2H), 3.50 (m, 6H), 3.45 (d, *J*

= 5.0 Hz, 4H), 3.05 (s, 1H), 2.96 (s, 4H). ¹³C NMR (150MHz, DMSO-d₆): δ 167.70, 167.49, 145.88, 144.17, 143.18, 133.65, 132.83, 132.24, 132.04, 131.90, 129.19, 126.80, 126.46, 122.10, 121.65, 121.47, 119.86, 119.81, 104.39, 103.00, 98.97, 81.23, 76.05, 75.39, 73.77, 72.22, 71.10, 70.32, 68.67, 68.19, 66.75, 65.55, 60.93, 30.54; HRMS (ESI): m/z calcd for C₇₄H₈₁N₁₂O₂₂S₂ ([M+H]⁺): 1553.5024; Found: 1553.5101.



Scheme. S2 Synthetic routes of **TPE-1',2',3'**.

Synthesis of Compound TPE-1': Compound 5 (0.040 g, 0.085 mmol) and 3-Butyn-1-ol (0.013 g, 0.19 mmol) were added to a 25 mL eggplant shaped bottle and then protected by nitrogen gas, followed by the addition of anhydrous THF (4 mL). After the reaction temperature rose to 50 °C, an aqueous solution (1 mL) of CuSO₄ (0.0042 g, 0.017 mmol) and NaVc (0.067 g, 0.034 mmol) was then injected into the reaction and the mixture was stirred at 50 °C overnight. The mixture was washed with saturated sodium chloride solution three times and dried with anhydrous sodium sulfate. After removing the solvent by a rotary evaporator, the obtained solid was purified by column chromatography. Yield: 0.050 g (96%). ¹H NMR (400 MHz, DMSO-d₆): δ 9.90 (s, 2H),

8.51 (s, 2H), 7.69 (d, $J = 8.6$ Hz, 4H), 7.20 (d, $J = 7.4$ Hz, 4H), 7.18 (d, $J = 7.8$ Hz, 4H), 7.05 (d, $J = 8.0$ Hz, 4H), 5.30 (s, 2H), 3.67 (t, $J = 6.7$ Hz, 4H), 2.83 (t, $J = 6.7$ Hz, 4H); ^{13}C NMR (150 MHz, DMSO- d_6): δ 193.06, 146.22, 143.14, 142.21, 139.22, 137.34, 135.65, 132.67, 131.98, 130.95, 129.80, 126.80, 121.04, 119.67, 102.95, 60.74, 29.70; HRMS (ESI): m/z calcd for $\text{C}_{36}\text{H}_{31}\text{N}_6\text{O}_4$ ($[\text{M}+\text{H}]^+$): 611.2401; Found: 611.2397.

Synthesis of Compound 8: Compound 5 (0.050g, 0.11 mmol) and malononitrile (0.056 g, 0.85 mmol) were added in a 25 mL eggplant-shaped bottle under nitrogen protection, followed by the addition of anhydrous ethanol (4.4 mL). The reaction mixture was stirred for 2 hours at 80 °C. The solvent was removed under reduced pressure and the crude product was purified by column chromatography. Yield: 0.056g (93%). ^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, $J = 7.7$ Hz, 4H), 7.66 (s, 2H), 7.15 (d, $J = 7.9$ Hz, 4H), 6.99 (d, $J = 8.0$ Hz, 4H), 6.83 (d, $J = 8.1$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.74, 149.43, 144.82, 140.12, 138.44, 137.90, 132.87, 132.49, 130.80, 129.70, 128.93, 119.05, 113.84, 112.74, 82.51.

Synthesis of Compound TPE-2': Compound 8 (0.045 g, 0.080 mmol) and 3-Butyn-1-ol (0.012 g, 0.17 mmol) were added to a 25 mL eggplant shaped bottle and then protected by nitrogen gas, followed by the addition of anhydrous THF (4 mL). After the reaction temperature rose to 50 °C, an aqueous solution (1 mL) of CuSO_4 (0.0040 g, 0.016 mmol) and NaVc (0.063 g, 0.031 mmol) was then injected into the reaction and the mixture was stirred at 50 °C overnight. The mixture was washed with saturated sodium chloride solution three times and dried with

anhydrous sodium sulfate. After removing the solvent by a rotary evaporator, the obtained solid was purified by column chromatography. Yield: 0.020g (36%). ¹H NMR (600 MHz, DMSO-d₆): δ 8.54 (s, 2H), 8.42 (s, 2H), 7.80 (d, *J* = 8.5 Hz, 4H), 7.77 (d, *J* = 8.6 Hz, 4H), 7.30 (d, *J* = 8.4 Hz, 4H), 7.26 (d, *J* = 8.6 Hz, 4H), 4.76 (s, 2H), 3.69 (d, *J* = 6.9 Hz, 2H), 3.67 (d, *J* = 6.8 Hz, 2H), 2.83 (t, *J* = 6.8 Hz, 4H). ¹³C NMR (100 MHz, DMSO-d₆): δ 161.01, 146.29, 140.18, 136.28, 132.79, 132.42, 131.04, 129.22, 121.13, 119.90, 81.74, 68.73, 65.54, 60.63, 49.07, 29.67; HRMS (ESI): *m/z* calcd for C₄₂H₃₁N₁₀O₂ ([M+H]⁺): 707.2625; Found: 707.2629.

Synthesis of Compound TPE-3': Compound **TPE-1'** (0.069 g, 0.11mmol) and 2-hydrazyl benzothiazole (0.041g, 0.25 mmol) were added in a 25 mL eggplant-shaped bottle under nitrogen protection, followed by the addition of anhydrous methanol (12 mL) and 1 M HCl (a few drops). The reaction mixture was stirred for 2 hours at 60 °C. The solvent was removed under reduced pressure and the crude product was purified to obtain the target product **TPE-3'**. Yield: 0.044g (43%). ¹H NMR (600 MHz, DMSO-d₆): δ 8.54 (s, 2H), 8.08 (s, 2H), 7.74 (d, *J* = 8.2 Hz, 6H), 7.52 (d, *J* = 7.9 Hz, 4H), 7.43 (s, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 4H), 7.13 (d, *J* = 7.9 Hz, 4H), 7.09 (t, *J* = 7.2 Hz, 2H), 4.76 (s, 2H), 3.67 (d, *J* = 6.4 Hz, 2H), 3.65 (d, *J* = 6.4 Hz, 2H), 2.82 (t, *J* = 6.7 Hz, 4H); ¹³C NMR (150 MHz, DMSO-d₆): δ 167.58, 146.19, 144.20, 143.09, 141.83, 139.84, 135.82, 133.62, 132.79, 132.23, 132.06, 131.90, 129.20, 126.79, 126.48, 122.14, 122.08, 121.08, 119.83, 60.71, 29.70; HRMS (ESI): *m/z* calcd for C₅₀H₄₁N₁₂O₂S₂ ([M+H]⁺): 905.2911; Found: 905.2919.

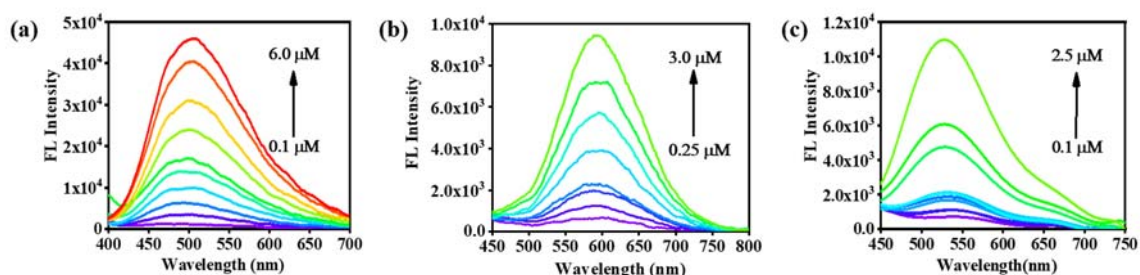


Fig. S1 Fluorescence spectra of different concentrations of TPEL-1 (a, $\lambda_{ex} = 340$ nm), TPEL-2 (b, $\lambda_{ex} = 300$ nm), TPEL-3 (c, $\lambda_{ex} = 380$ nm) in water.

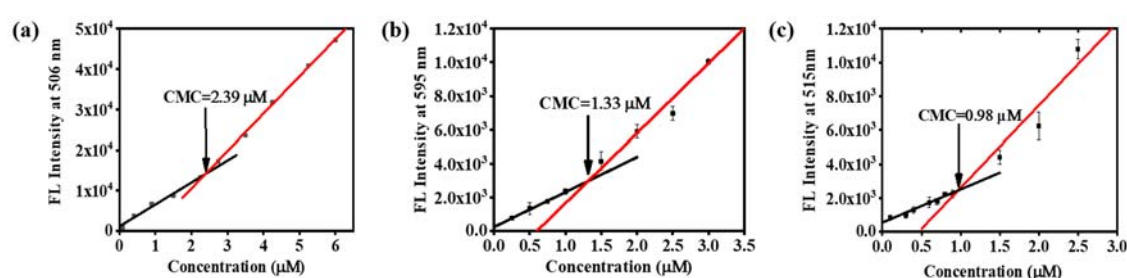


Fig. S2 The curve of fluorescence intensity of TPEL-1 (a, at 506 nm), TPEL-2(b, at 595nm), TPEL-3 (c, at 515 nm) with concentration in water. The crosspoint corresponds to the CMC of TPEL-1,2,3 respectively.

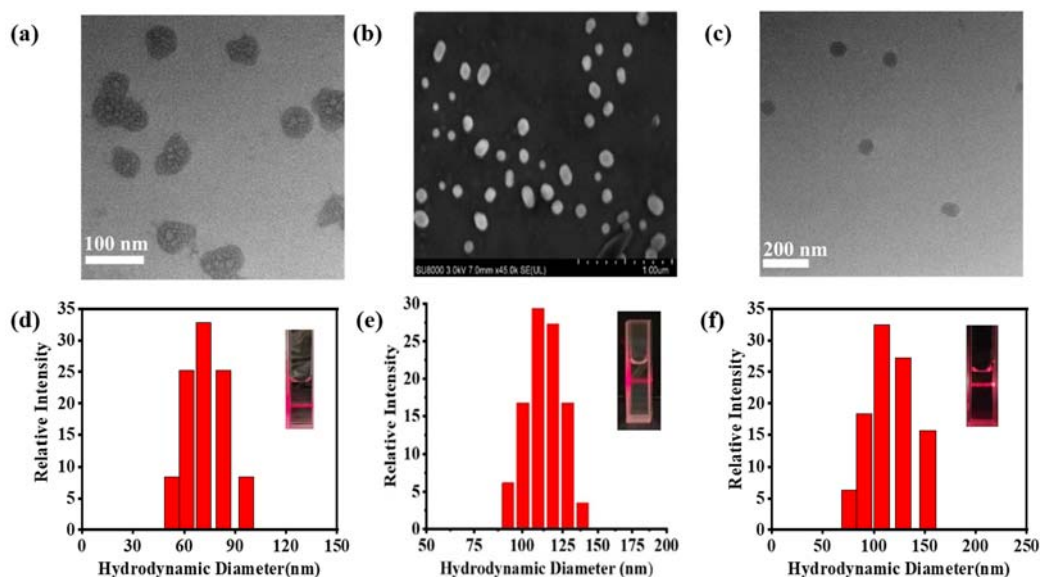


Fig. S3 TEM images of TPEL-1 (a), TPEL-3 (c) and SEM images of TPEL-2 (b)^[1]. DLS data of the TPEL-1 (d), TPEL-2 (e)^[1] and TPEL-3 (f) (10 μ M) assemblies in pure water. Inset: the Tyndall effect.

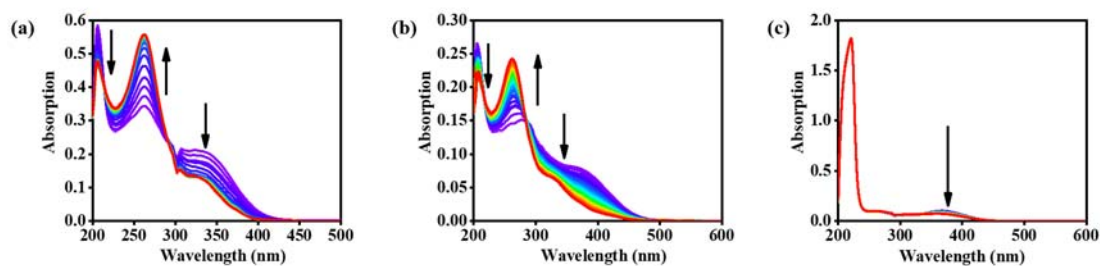


Fig. S4 Absorption spectra of **TPEL-1** (a), **TPEL-2** (b) and **TPEL-3** (c) (10 μ M) in pure water under irradiation of UV-light ($\lambda = 365$ nm)

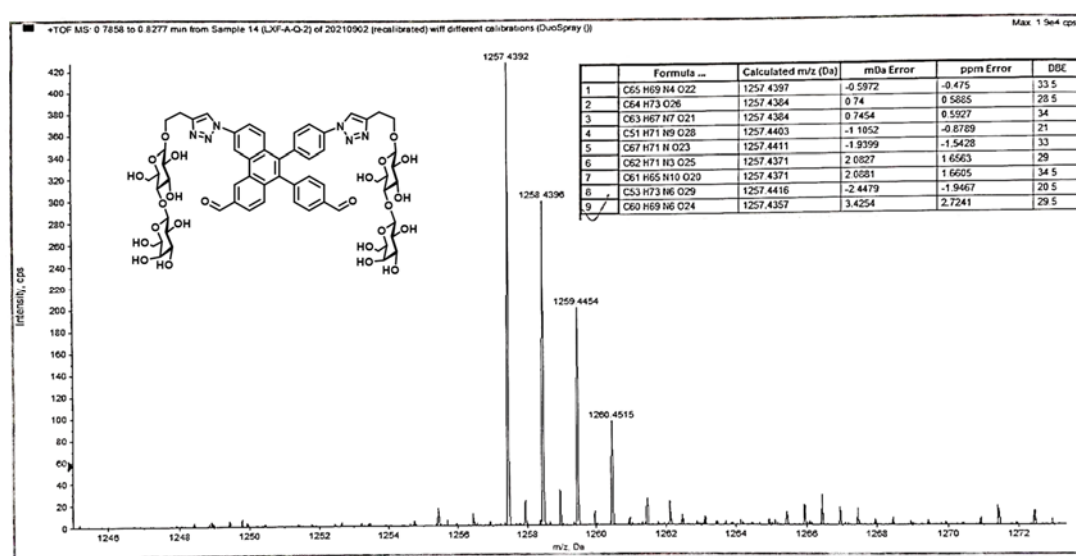


Fig. S5 ESI-MS spectra of **DPPL-1**.

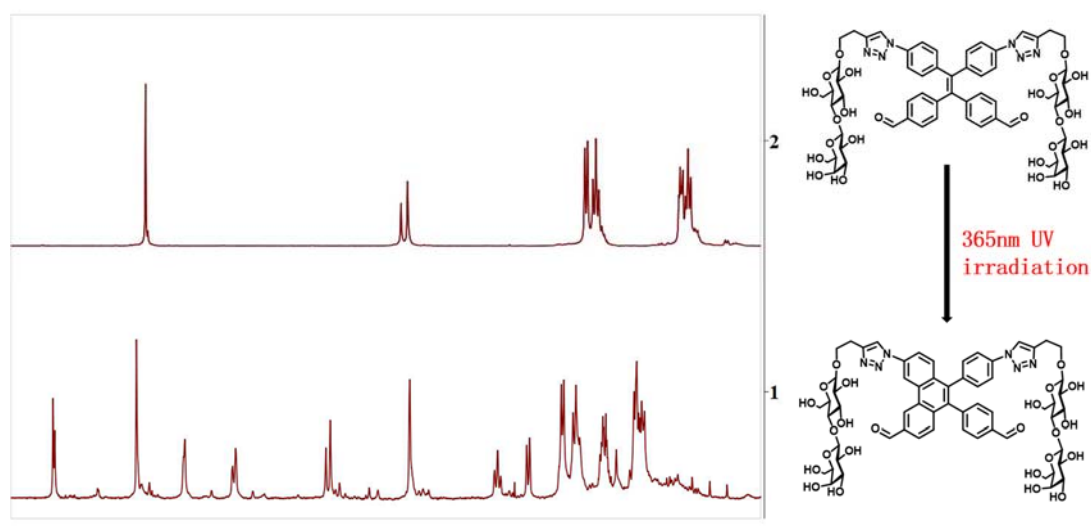


Fig. S6 The ^1H NMR spectra comparison of **TPEL-1** and **DPPL-1** (600MHz, DMSO- d_6).

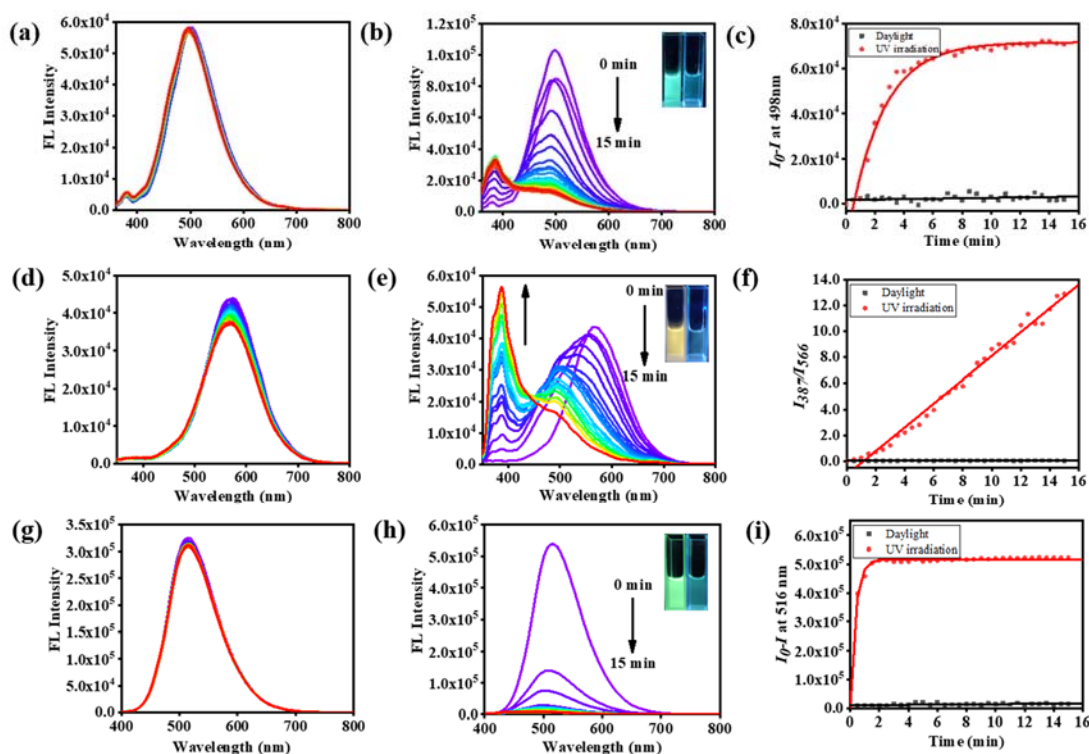


Fig. S7 Time-dependent fluorescence spectra of F-TPE-1' (a), F-TPE-2' (d), F-TPE-3' (g) (10 μ M) without irradiation and F-TPE-1' (b), F-TPE-2' (e), F-TPE-3' (h) under irradiation of UV-light ($\lambda = 365$ nm) in pure water. The curve of fluorescence intensity of F-TPE-1' (c), F-TPE-2' (f), F-TPE-3' (i) with time. Inset: the image of F-TPE-1', 2', 3' upon excitation with a UV lamp ($\lambda = 365$ nm) before and after UV irradiation, respectively.

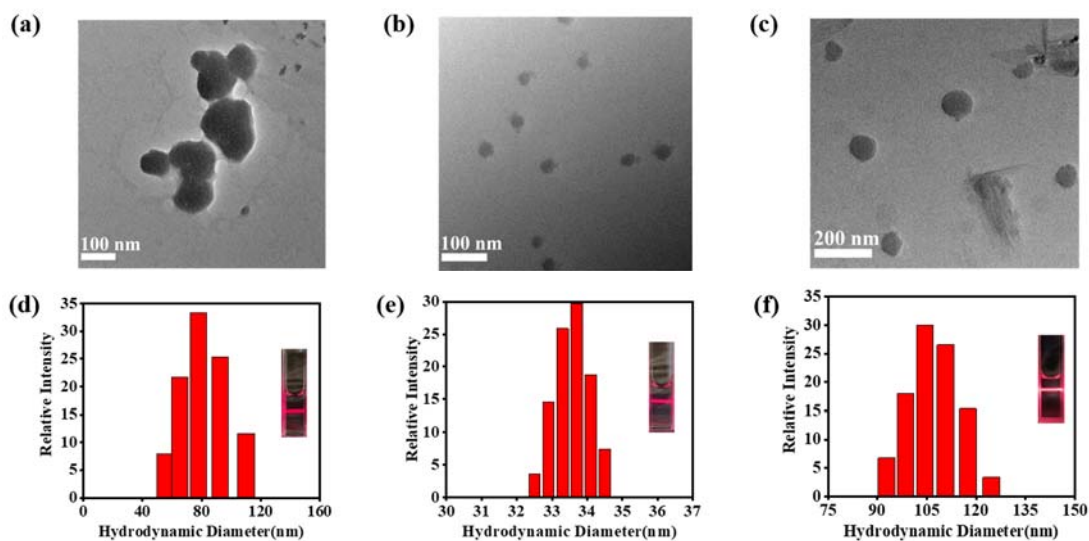


Fig. S8 TEM images of **F-TPE-1'** (a), **F-TPE-2'** (b) and **F-TPE-3'** (c) ($10\mu\text{M}$) in pure water. DLS data of the **F-TPE-1'** (d), **F-TPE-2'** (e) and **F-TPE-3'** (f) ($10\mu\text{M}$) assemblies in pure water. Inset: the Tyndall effect.

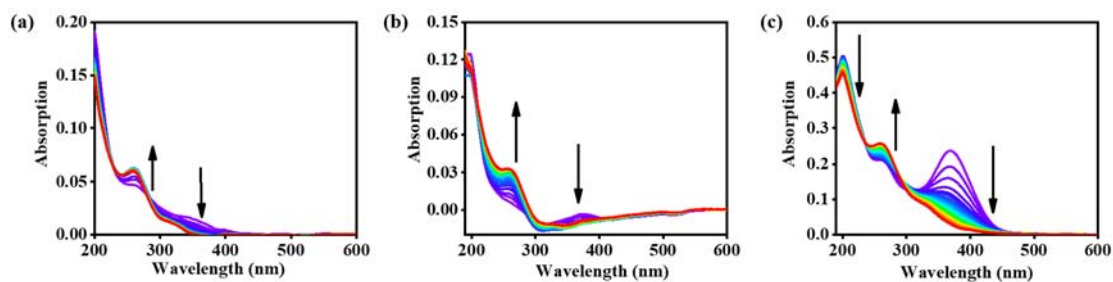


Fig. S9 Absorption spectra of **F-TPE-1'** (a), **F-TPE-2'** (b) and **F-TPE-3'** (c) ($10\mu\text{M}$) in pure water under irradiation of UV-light ($\lambda = 365\text{ nm}$)

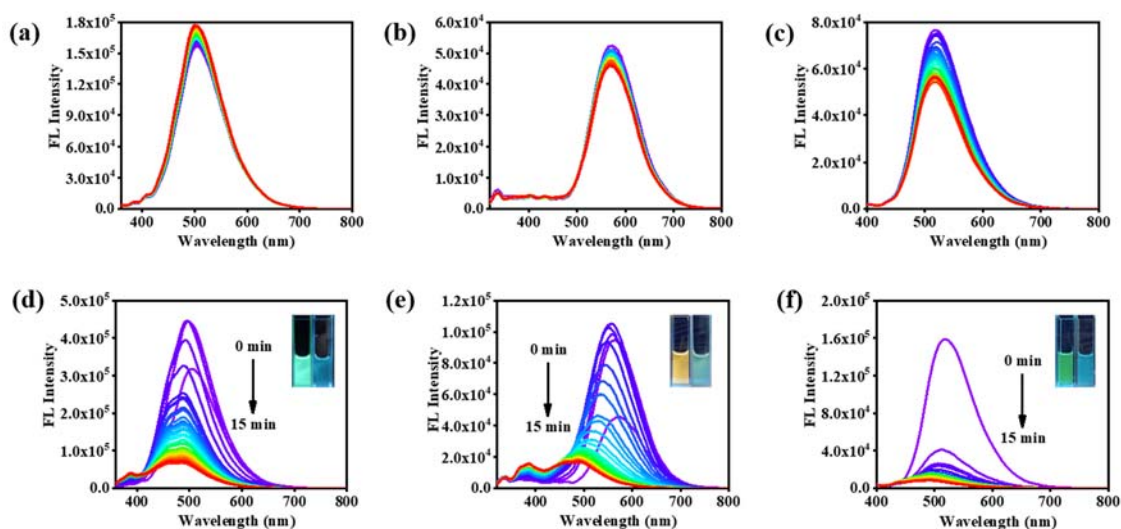


Fig. S10 Time-dependent fluorescence spectra of **TPE-1'** (a), **TPE-2'** (b), **TPE-3'** (c) (10 μ M) without irradiation and **TPE-1'** (d), **TPE-2'** (e), **TPE-3'** (f) under irradiation of UV-light ($\lambda = 365$ nm) in THF/H₂O (5:95, V/V). Inset: the image of **TPE-1',2',3'** upon excitation with a UV lamp ($\lambda = 365$ nm) before and after UV irradiation, respectively.

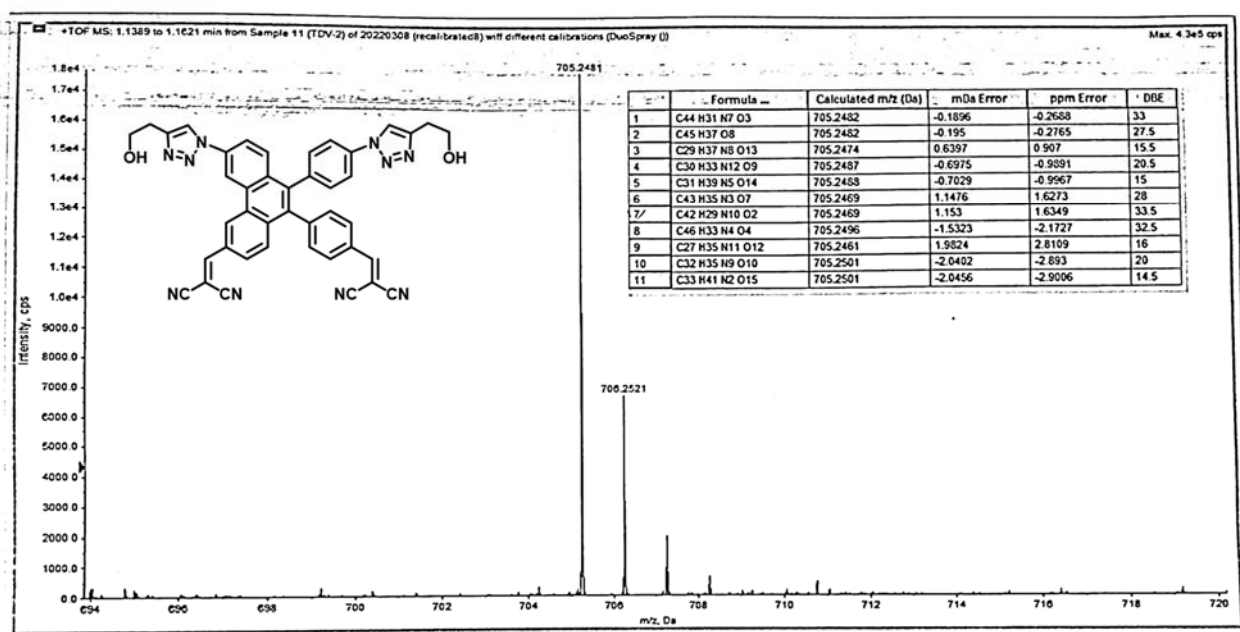


Fig. S11 ESI-MS spectra of **DPP-2'**.

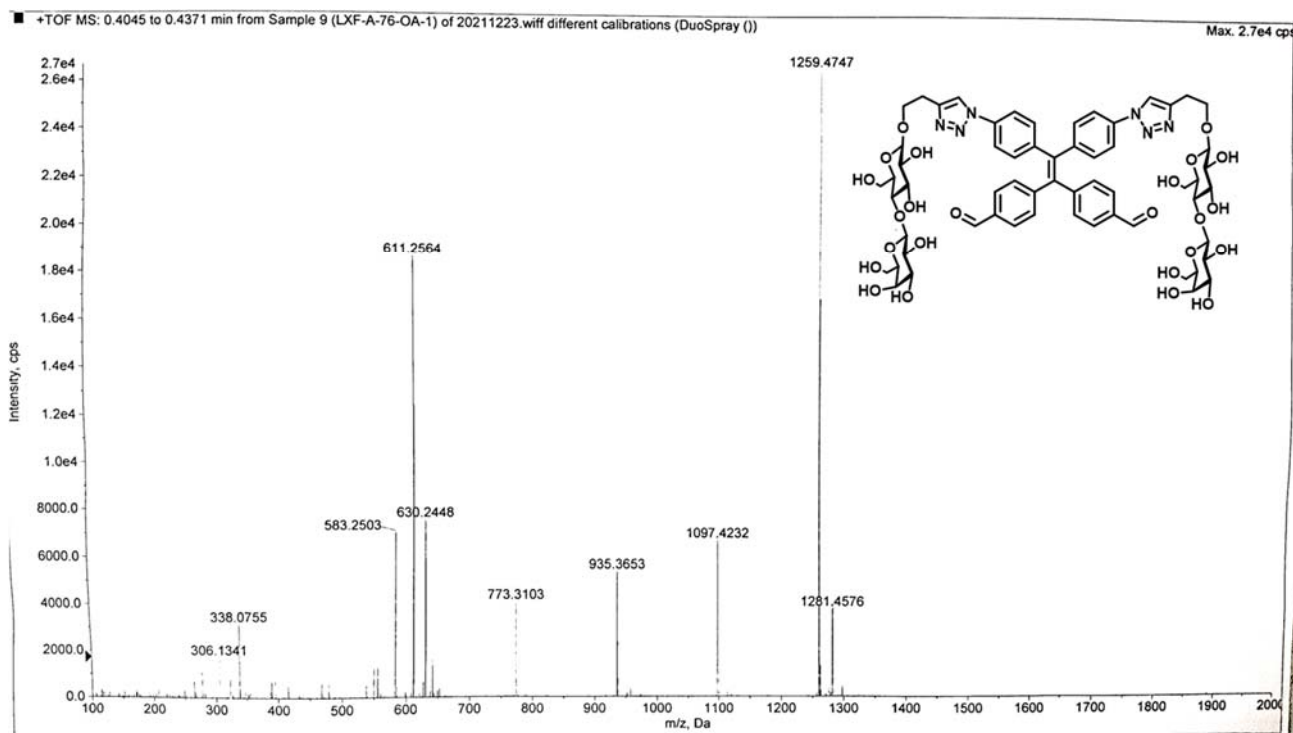


Fig. S12 ESI-MS spectra of TPEL-1.

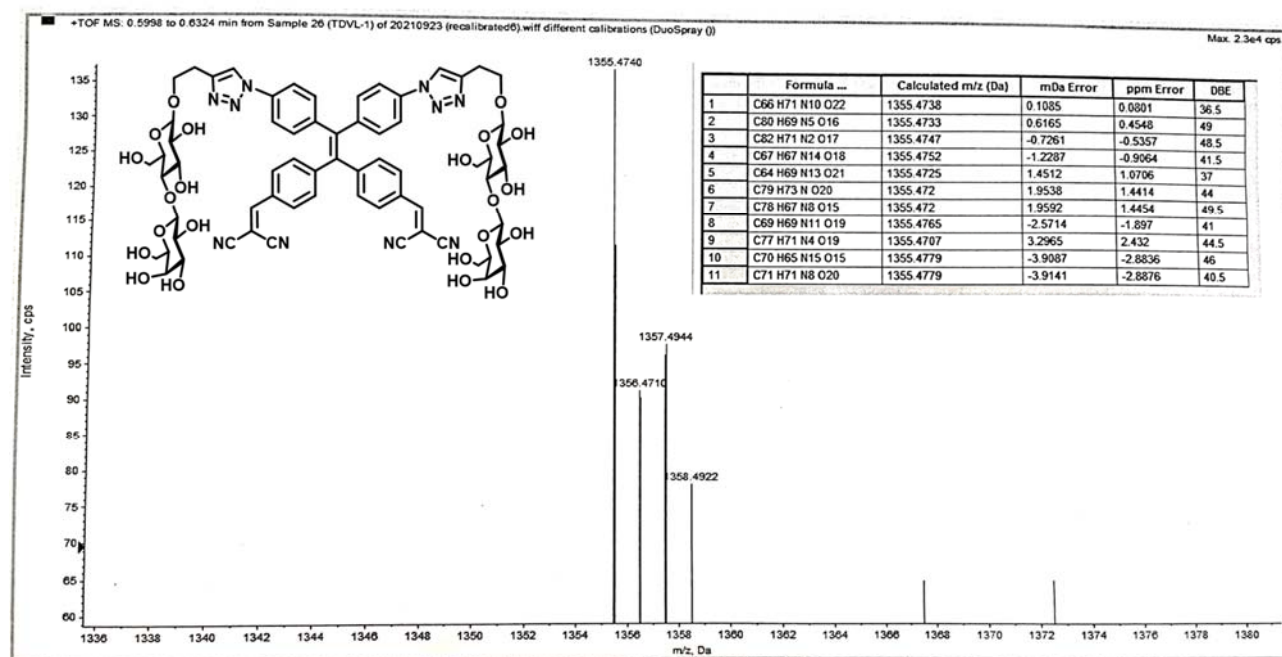


Fig. S13 ESI-MS spectra of TPEL-2.

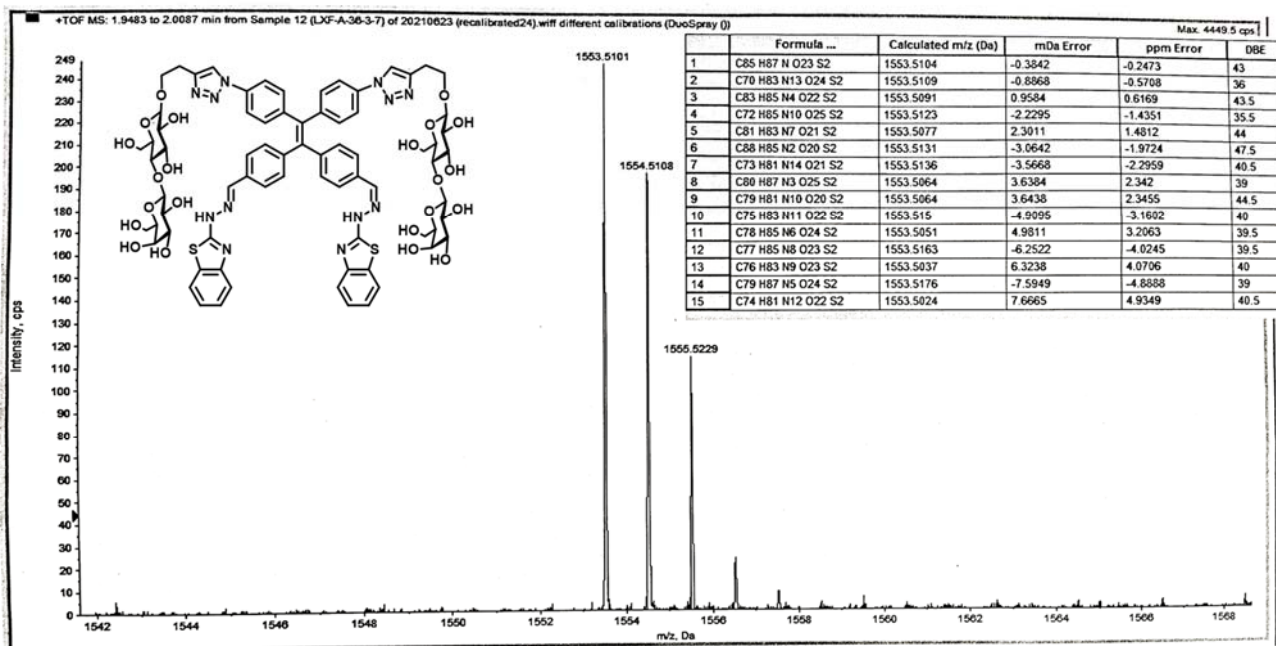


Fig. S14 ESI-MS spectra of TPEL-3.

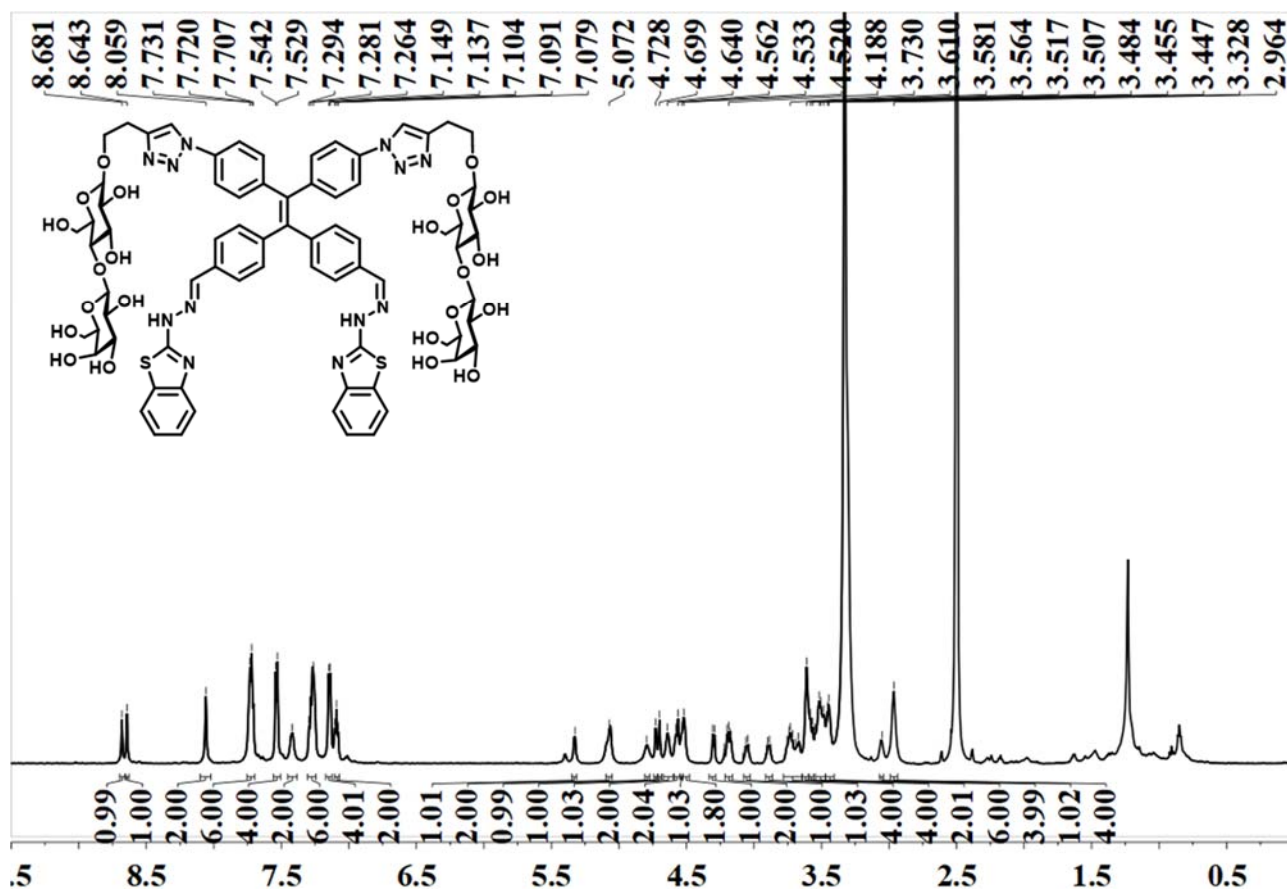


Fig. S15 ¹H NMR spectra of TPEL-3 (600MHz, DMSO-d₆).

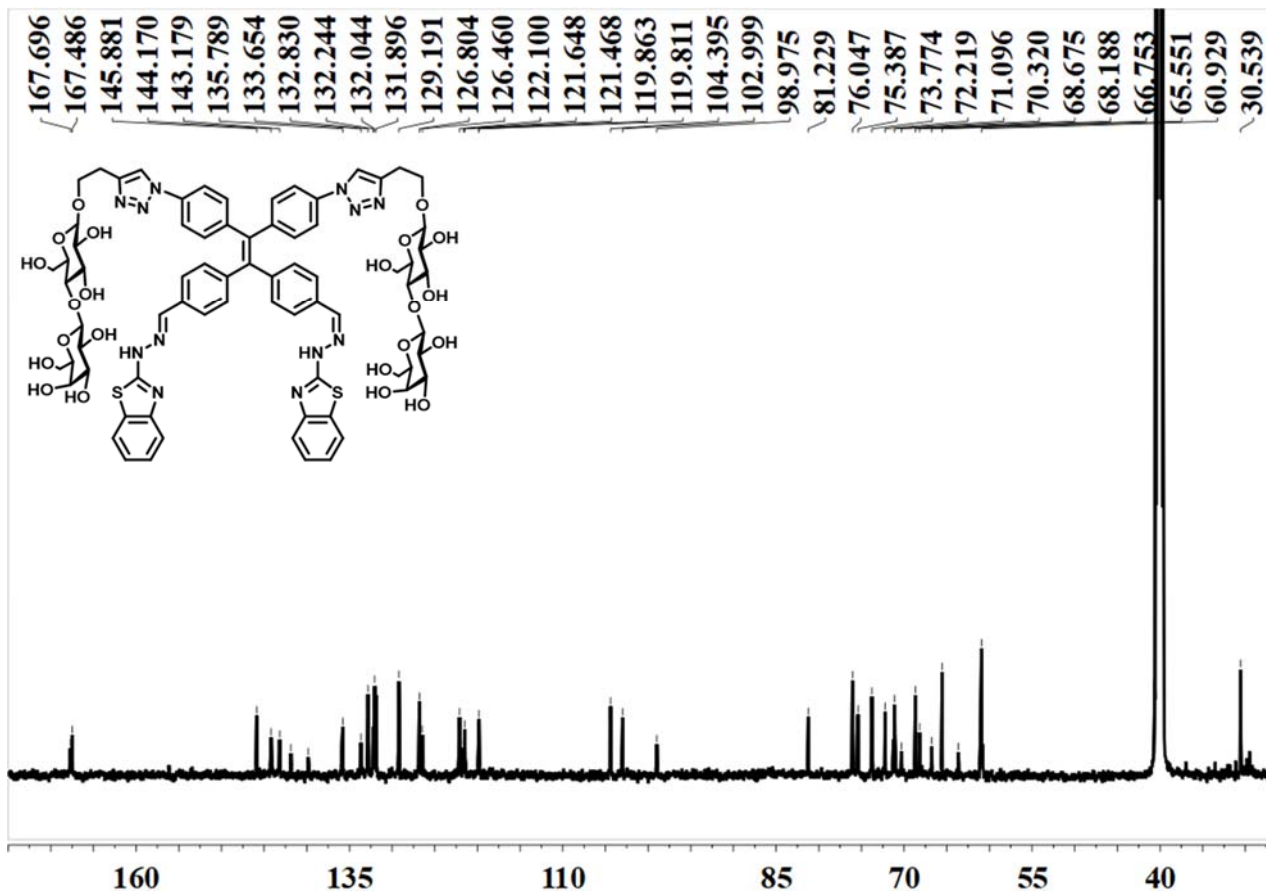


Fig. S16 ^{13}C NMR spectra of TPEL-3 (100 MHz, DMSO- d_6).

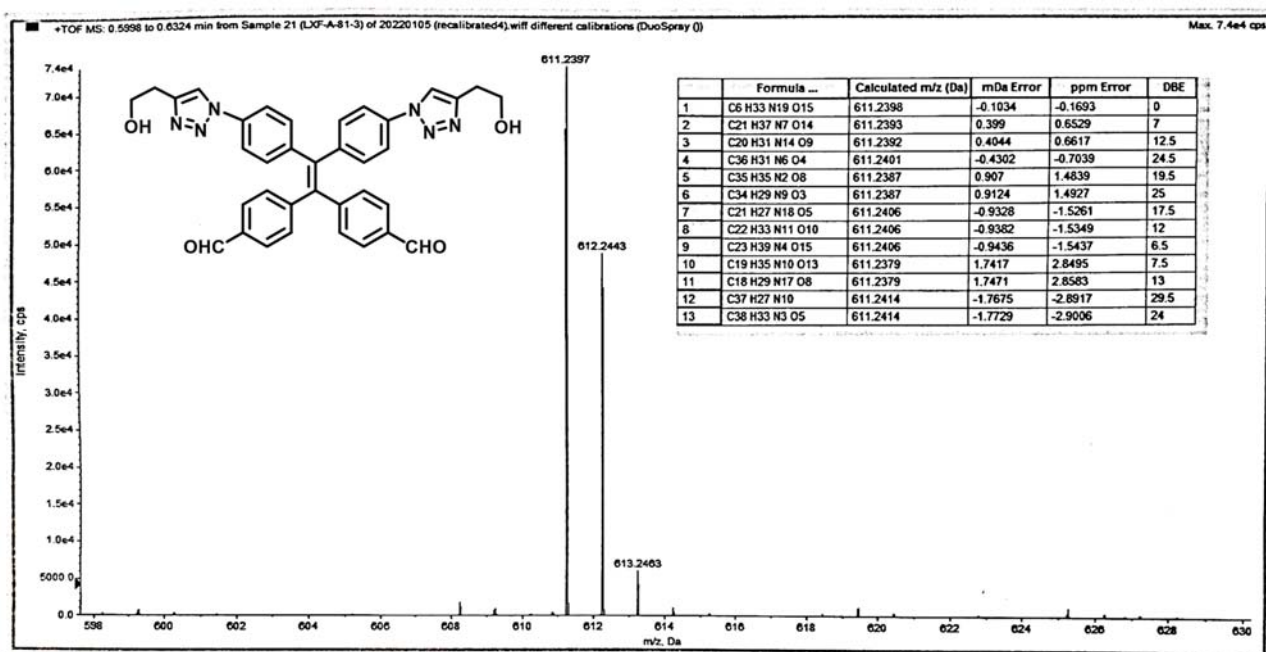


Fig. S17 ESI-MS spectra of TPE-1'.

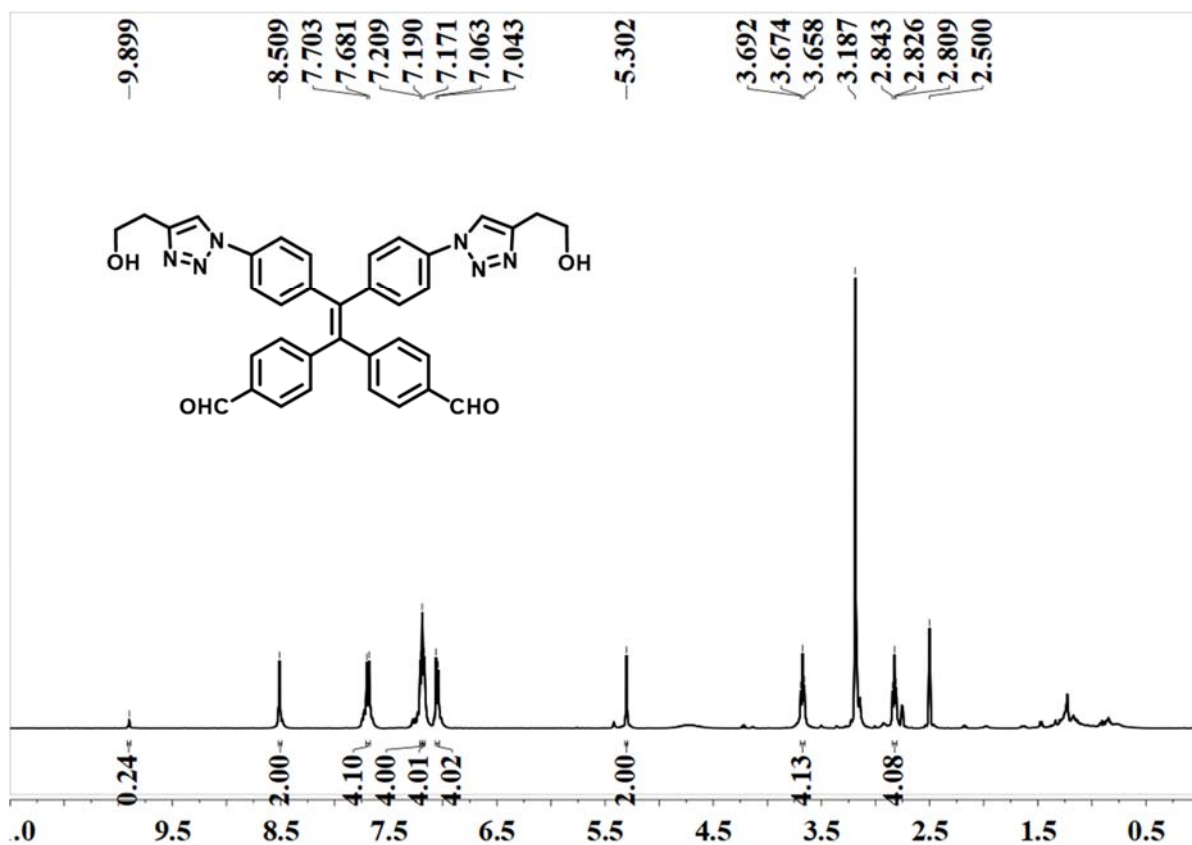


Fig. S18 ¹H NMR spectra of TPE-1' (400 MHz, DMSO-d₆).

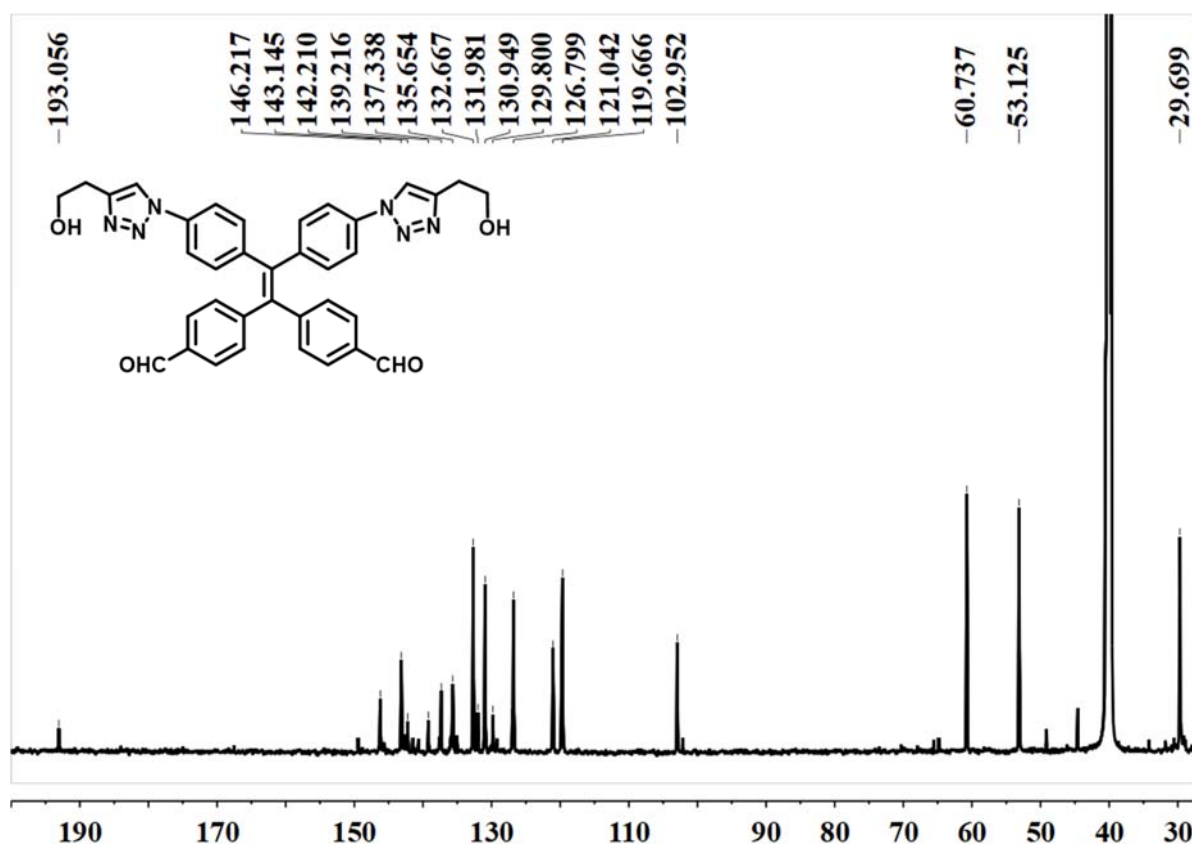


Fig. S19 ¹³C NMR spectra of TPE-1' (150 MHz, DMSO-d₆).

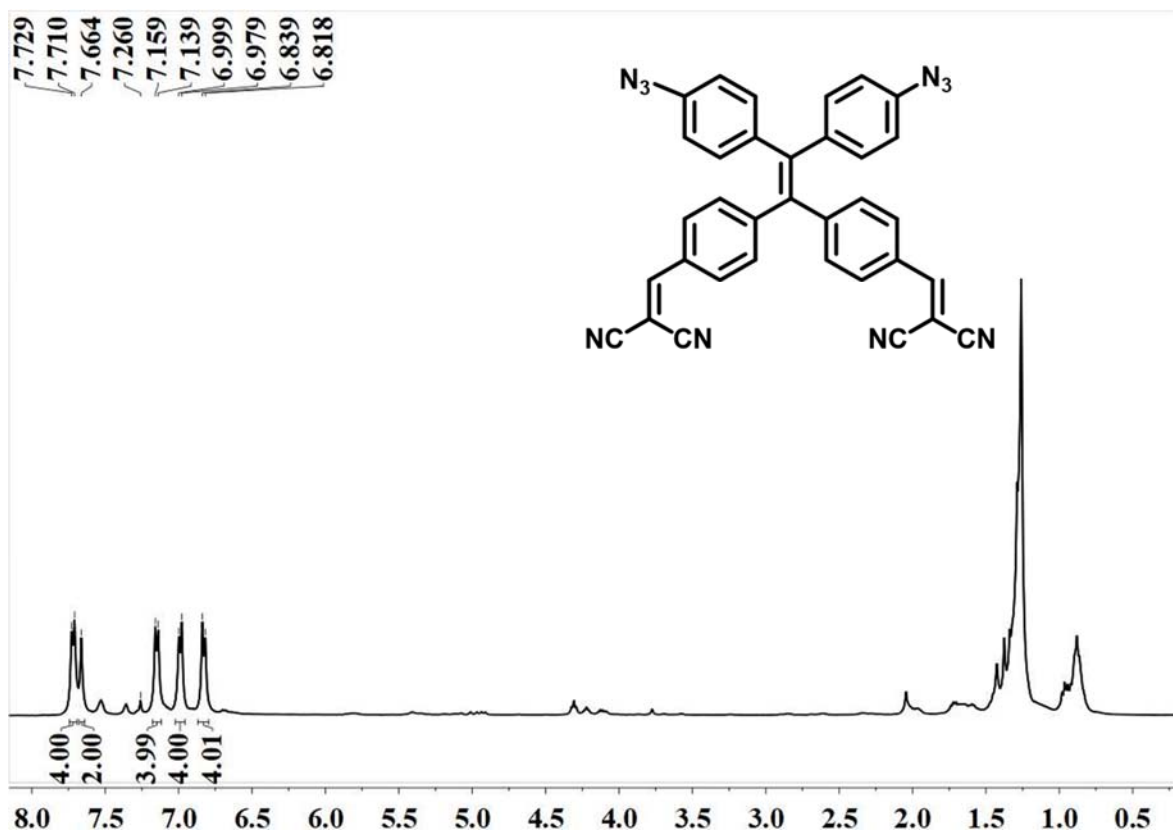


Fig. S20 ¹H NMR spectra of **Compound 8** (400 MHz, CDCl₃).

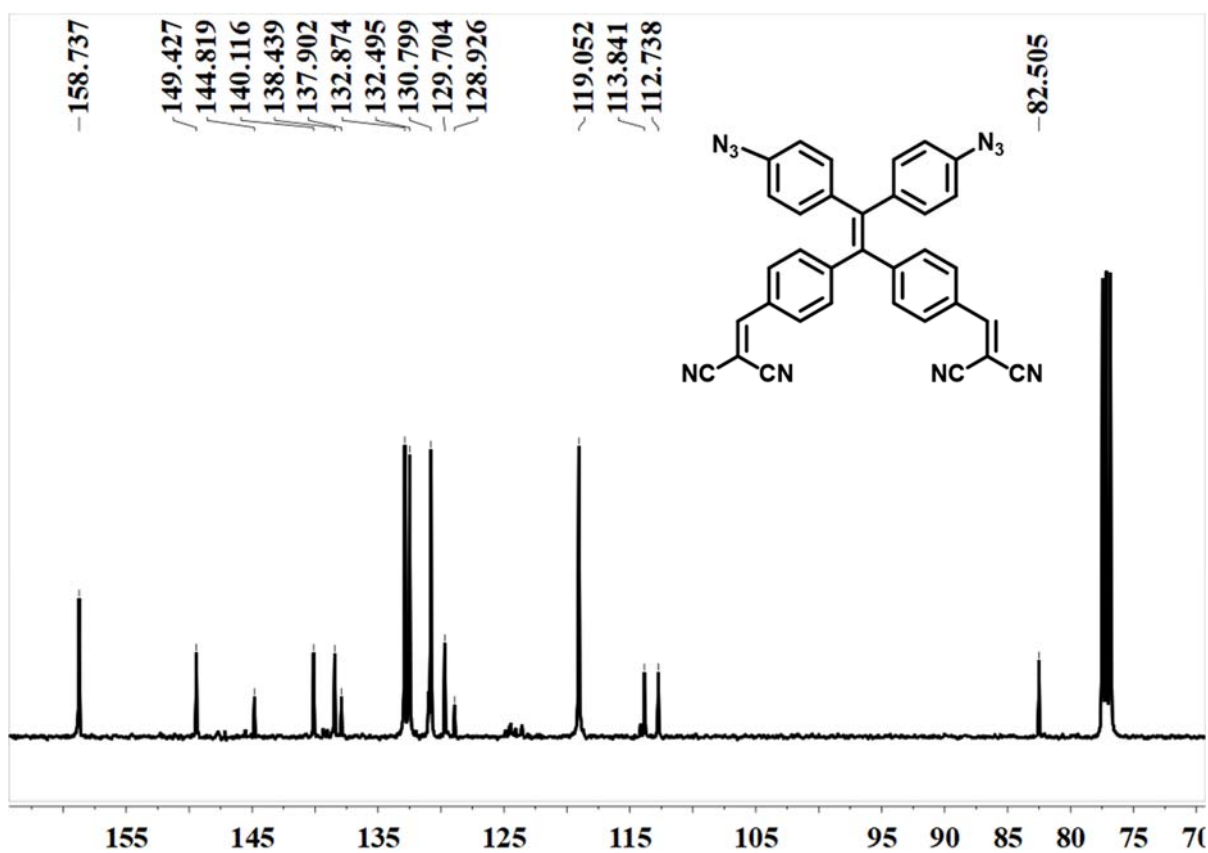


Fig. S21 ¹³C NMR spectra of **Compound 8** (100 MHz, CDCl₃).

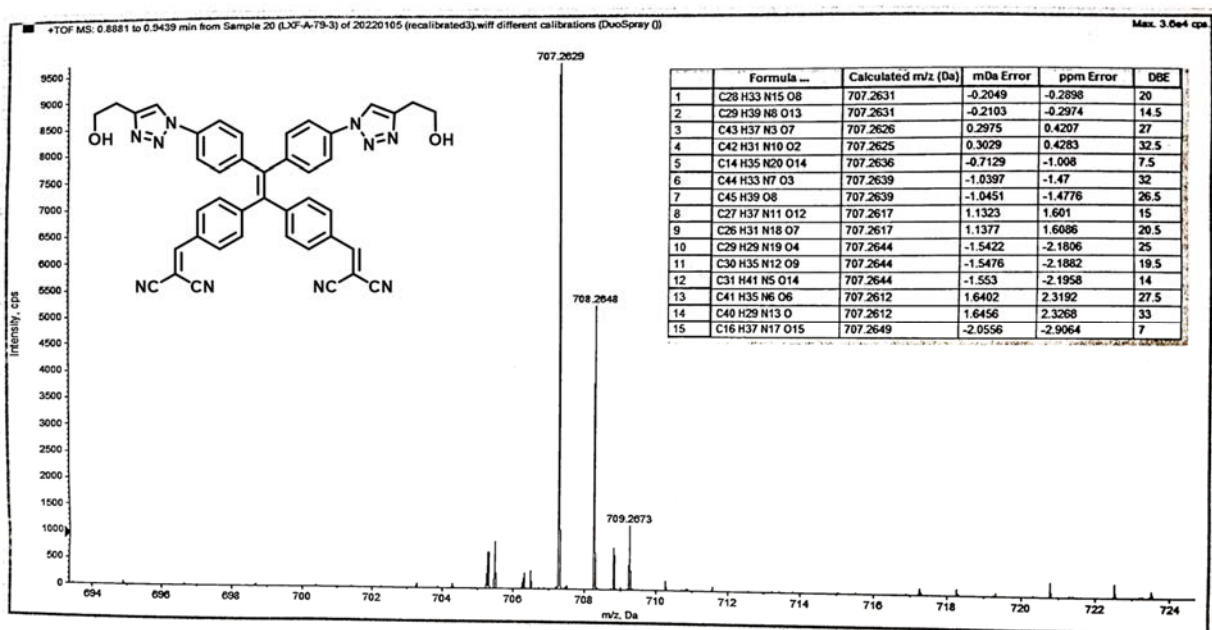


Fig. S22 ESI-MS spectra of TPE-2'.

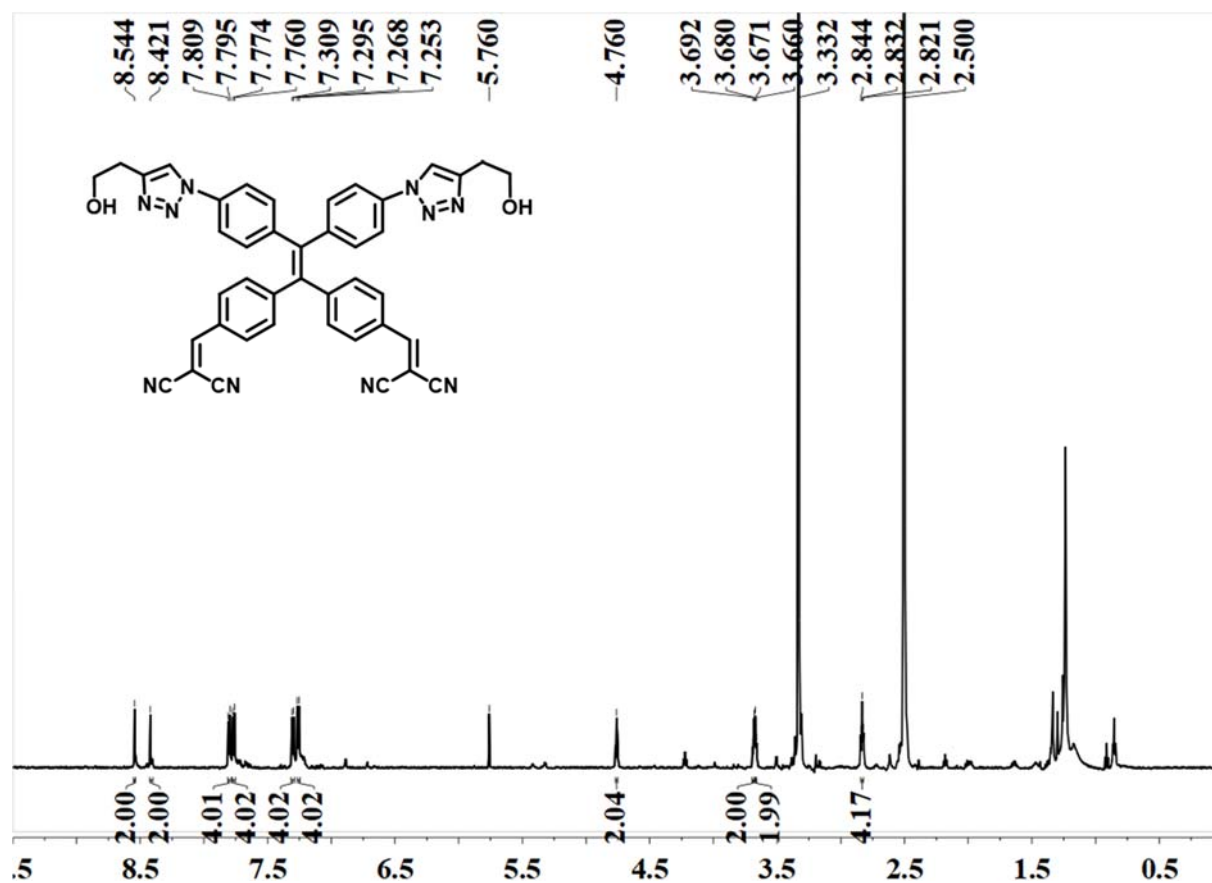


Fig. S23 ¹H NMR spectra of TPE-2' (600 MHz, DMSO-d₆).

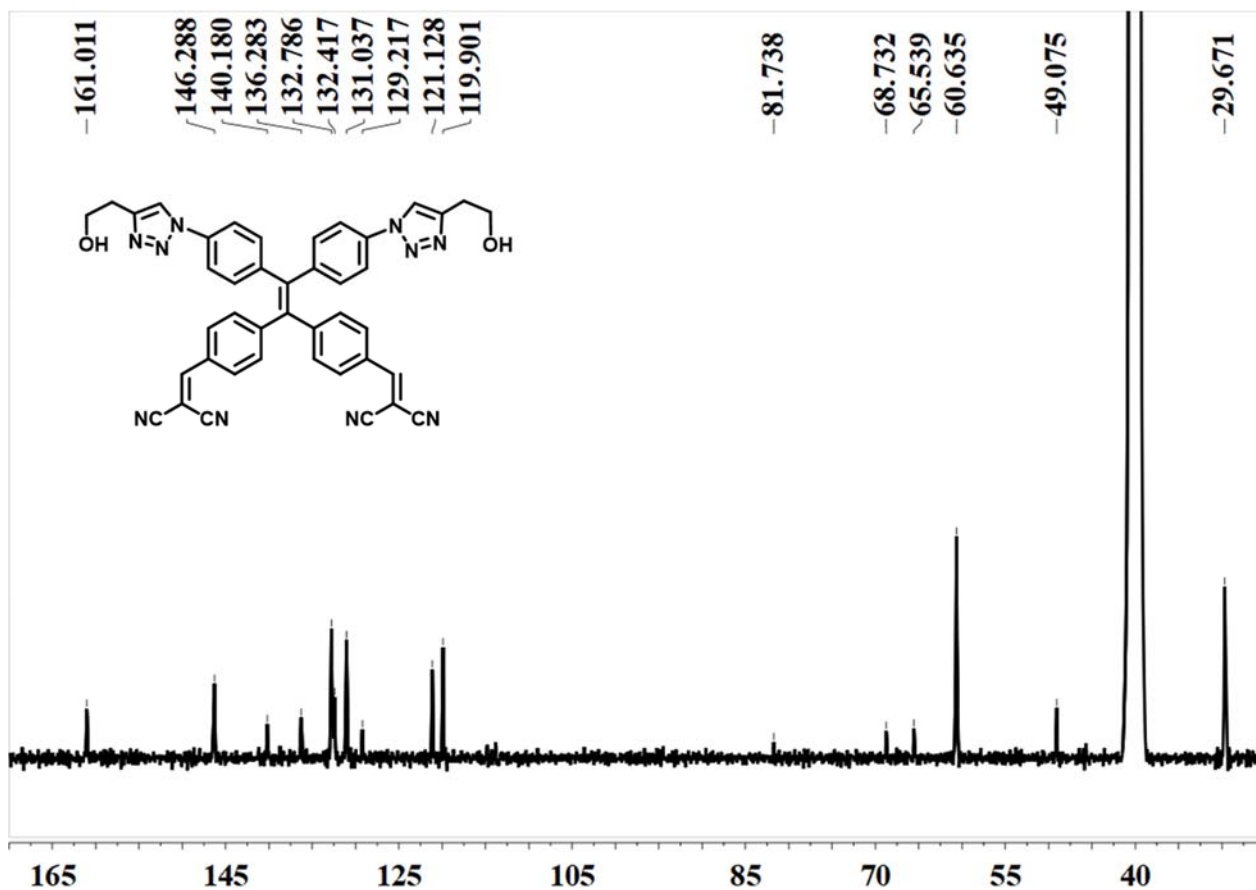


Fig. S24 ¹³C NMR spectra of TPE-2' (100 MHz, DMSO-d₆).

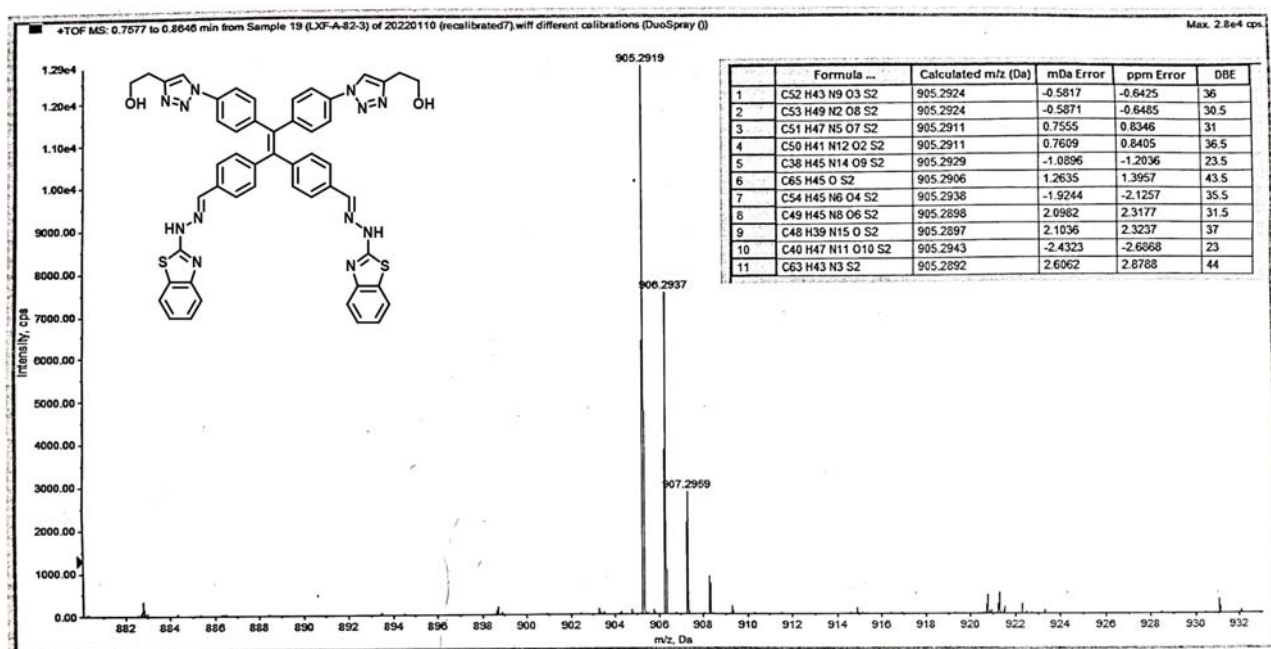


Fig. S25 ESI-MS spectra of TPE-3'.

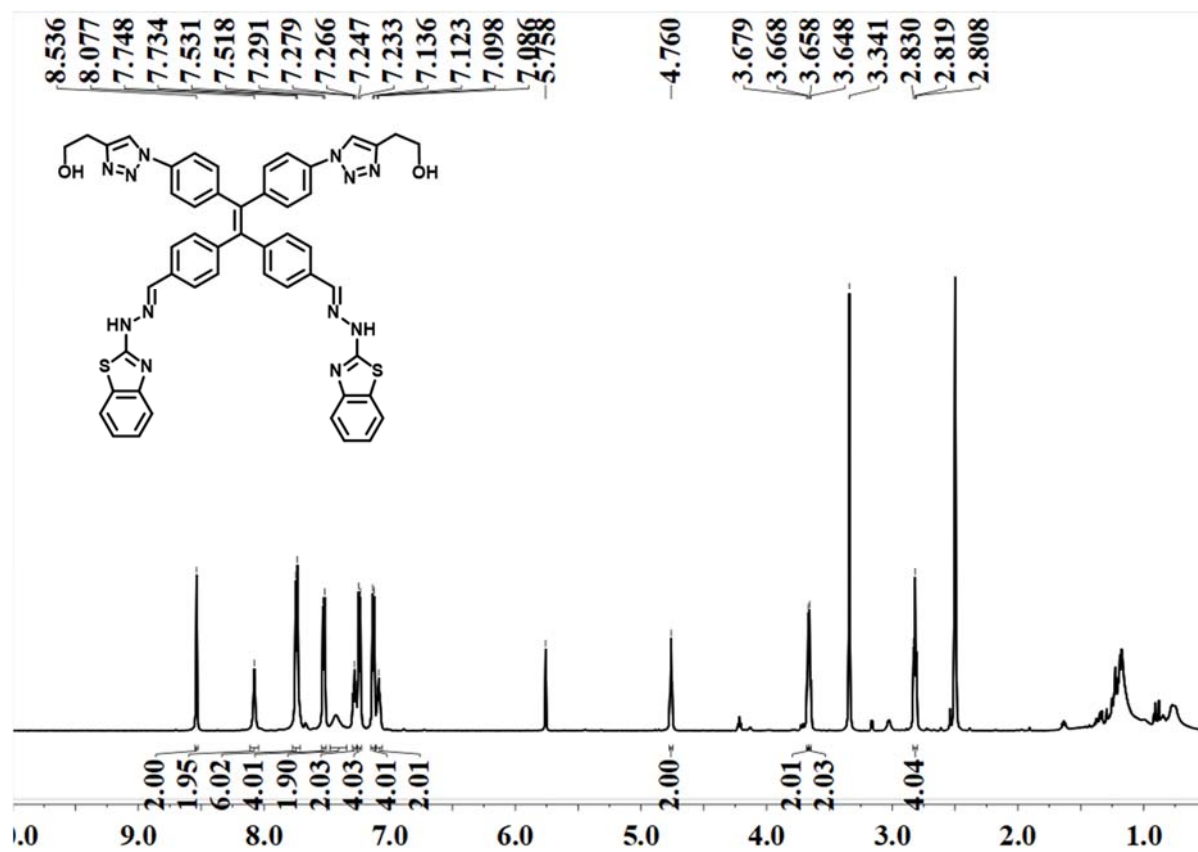


Fig. S26 ¹H NMR spectra of TPE-3' (600 MHz, DMSO-d₆).

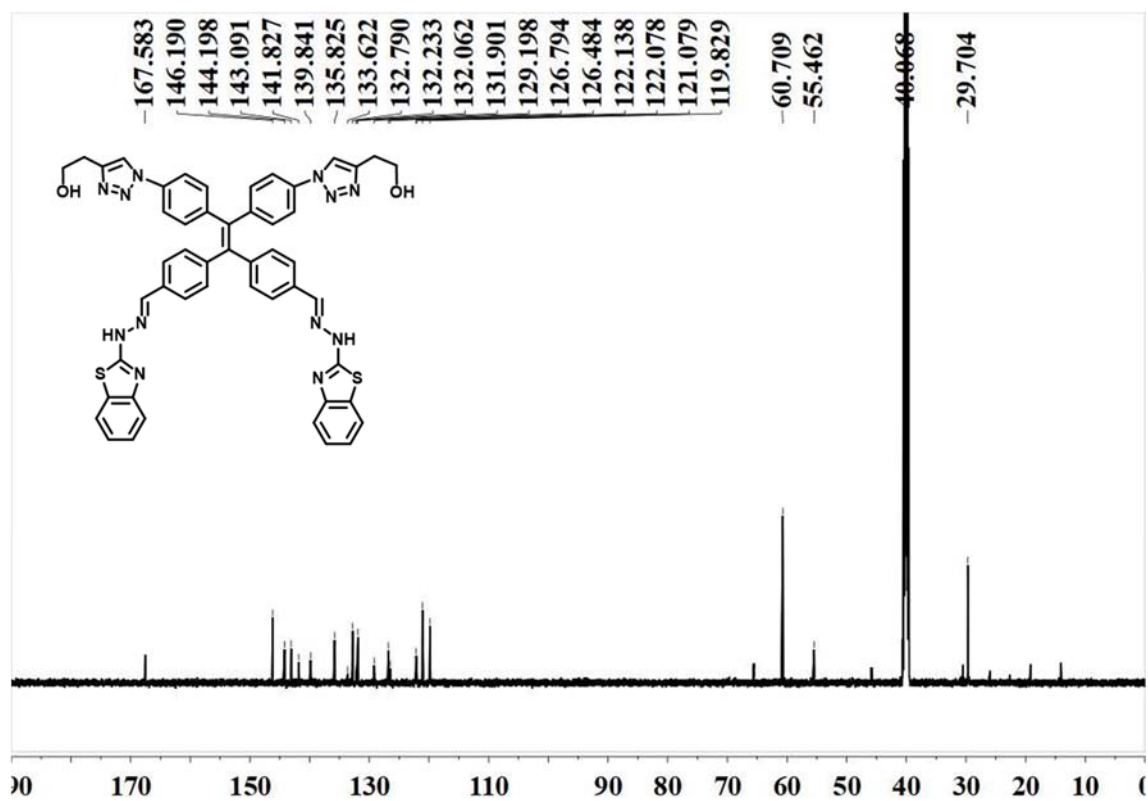


Fig. S27 ¹³C NMR spectra of TPE-3' (150 MHz, DMSO-d₆).

References

- [1] M. Hou, Y. C. Liu, W. Zhou, J. D. Zhang, F. D. Yu, Y. Zhang, G. J. Liu and G. W. Xing, *Chem Asian J.*, 2021, 16, 2014-2017.