Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Multifunctional AIE-ESIPT dual mechanism tetraphenylethene-based Schiff base for inkless rewritable paper and colorimetric/fluorescent dual-channel Zn^{2+} sensor

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1 Experimental section

1.1. Materials and instrumentation

All the reagents and solvents were purchased commercially (AR grade) and used without further purification unless otherwise noted. 2-Hhydroxy-5-(1,2,2-triphenylvinyl)benzaldehyde was obtained from Xuzhou Da Yang Biochemical Technology Co., Ltd. The THF/water mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of samples at room temperature. ^{1}H-NMR spectra were collected on a Bruker-600 MHz spectrometer in acetone solutions with TMS as an internal standard. Mass spectra were obtained on a Bruker UltrafleXtreme MALDI-TOF/TOF mass spectrometer. UV-vis spectra were recorded on Shimadzu UV-3600 with a UV-VIS-NIR spectrophotometer. Emission spectra were performed by a HITACHI fluorescence spectrometer (F-4600). The fluorescence life time was obtained from a FS5 spectrofluorometer. SEM images were obtained from Gemini SEM 500. The IR spectra has been recorded with FT-IR Spectrophotometer Model NICOLET iS5 (Thermo fisher, America). Images were taken using an Apple 8plus phone. The theoretical calculation is finished in the Gaussian 09 package using the method b3lyp and the base group 6-31G. The printer used in this work was commercially available HP Desk Jet 2621.

1.2. Cytotoxicity assay

SiHa cells were cultured in Dulbecco's modified eagle medium (DMEM) supplemented with 10% FBS in an atmosphere of 5% CO_2 and 95% air at 37 ℃. **TPESB** was dissolved in DMSO to get the stock solution (10 mM). The cells were placed in a 96-well plate for 24 h, followed by addition of **TPESB** with final concentrations of 0, 5, 10, 20, 30, 40 and 50 μM, respectively. The cells were then

incubated for 24 h, followed by SRB assays.

1.3. Image of Zn^{2+} in living cells

Cells were adherent-cultured in 96-well culture plates for 24 h. Subsequently, the first group were incubated with probe **TPESB** (30.0 μM) solution at 37 °C for 40 min, then washed with phosphate-buffered saline solution (PBS, pH = 7.20). The initial image was acquired using a confocal laser scanning microscope (LSM700) without disturbing the cell positions. The second group were pre-incubated with probe **TPESB** (30.0 μM) solution at 37 °C for 40 min, then with zinc acetate (30 μM) for another 40 min and then washed with PBS for 2 times. These cells were underwent imaging measurement by a confocal microscope (LSM700). The exciting light was 488 nm. The emission range of the green channel was 500-550 nm.

1.4. Preparation of rewritable paper

The rewritable paper integrated with **TPENOCN** was prepared in a layer-by-layer manner. The filter paper substrate was coated with a layer of 10 wt% PEG (PEG 20000) aqueous solution and dried at 70 °C. Then THF/H_2O (9/1 by volume) solution of **TPENOCN** (3mg/ml) containing 6 wt% PEG is coated over the initial PEG layer and dried at 70 °C.

1.5. Synthesis of 2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(4-(1,2,2-triphenylvinyl)phenol) (TPESB)

2-hydroxy-5-(1,2,2-triphenylvinyl)benzaldehyde (0.414 g, 1.1 mmol) and *o*-phenylenediamine (0.058g, 0.5 mmol) were added to 30 ml EtOH and the mixture was refluxed for 10 hours. The yellow precipitation was filtered and washed with EtOH for several times. Then, the obtained solids were recrystallized from mixture of dichloromethane and ethyl acetate (v/v = 1/2). Yield: 53%. ^{1}H NMR (600 MHz, Acetone) δ 13.04 (d, J = 11.9 Hz, 2H), 8.65 (d, J = 6.7 Hz, 2H), 7.36 (s, 4H), 7.24 (s, 2H),

7.19 (s, 1H), 7.17 (s, 3H), 7.16 (s, 3H), 7.15 (s, 2H), 7.14 (s, 2H), 7.13 (s, 4H), 7.11 (d, J = 4.5 Hz, 9H), 7.09 (s, 4H), 7.05 (d, J = 0.9 Hz, 2H), 7.04 (s, 2H), 6.74 (d, J = 1.6 Hz, 1H), 6.73 (d, J = 1.5 Hz, 1H). Calculated exact mass: m/z 824.3403, MALDI TOF-MS: m/z 825.3441$[M+H]^+$.

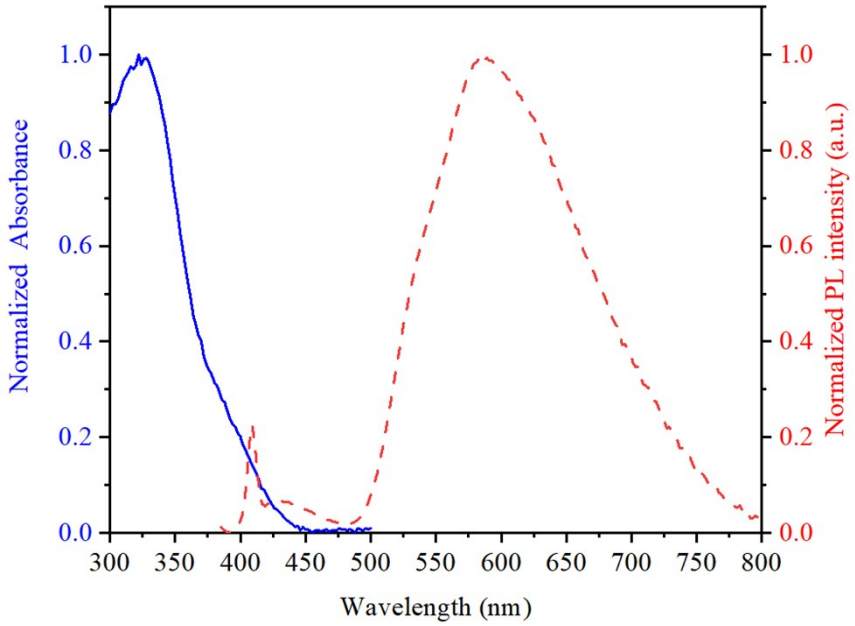

Figure S1 The normalized PL and UV-vis absorption spectra of **TPESB** in THF. For PL and absorption spectra measurement, **TPESB** concentration: 10^{-5} M, excitation wavelength: 365 nm.

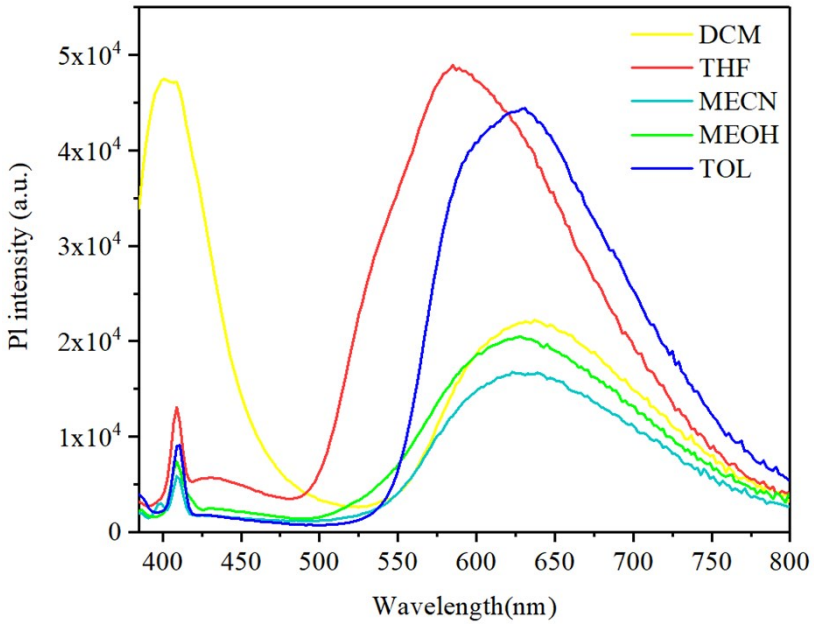

Figure S2 The PL spectra of **TPESB** in different solvents. For PL measurement, **TPESB**

concentration: 10^{-5} M, excitation wavelength: 365 nm.

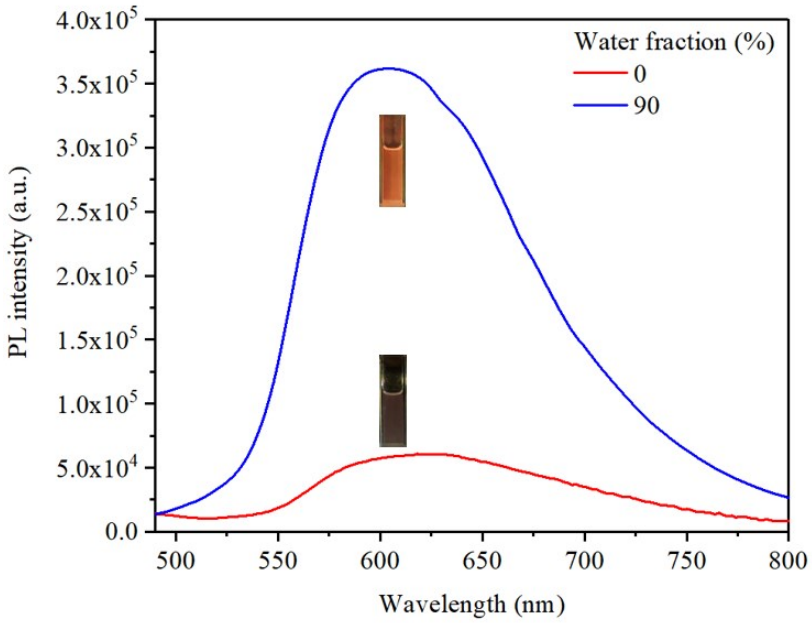

Figure S3 The PL spectra of **TPESB** in THF and THF/water mixture with 90% water fraction. Insets: the emission images of **TPESB** in THF and THF/water mixture with 90% water fraction taken under 365 UV. For PL measurement, **TPESB** concentration: 10^{-5} M, excitation wavelength: 365 nm.

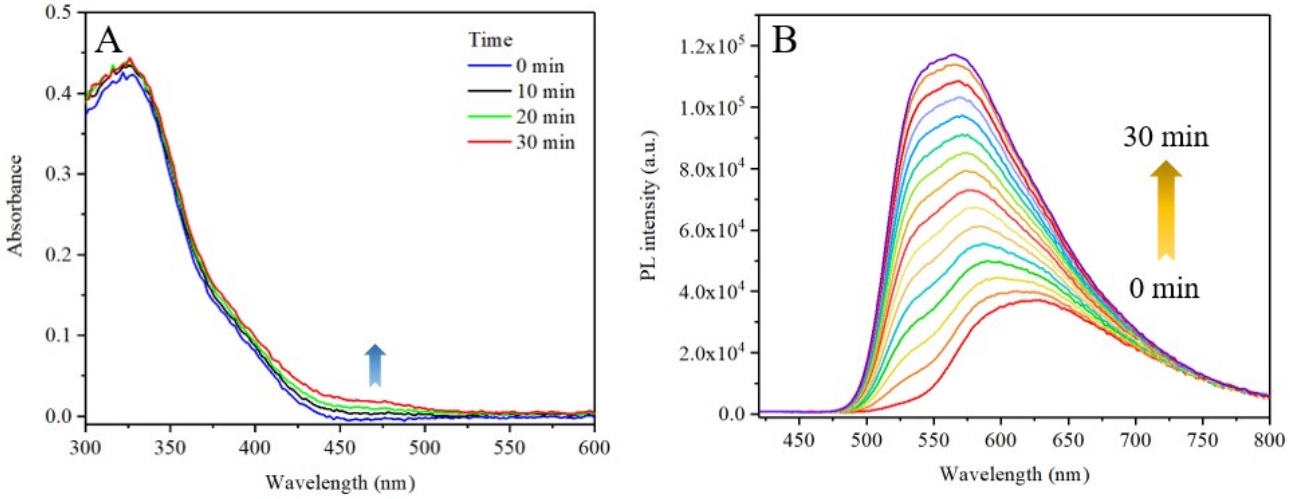

Figure S4 The absorbance (A) and PL spectra (B) changes before and after addition of 1% water fraction. For PL measurement, **TPESB** concentration: 10^{-5} M, excitation wavelength: 365 nm.

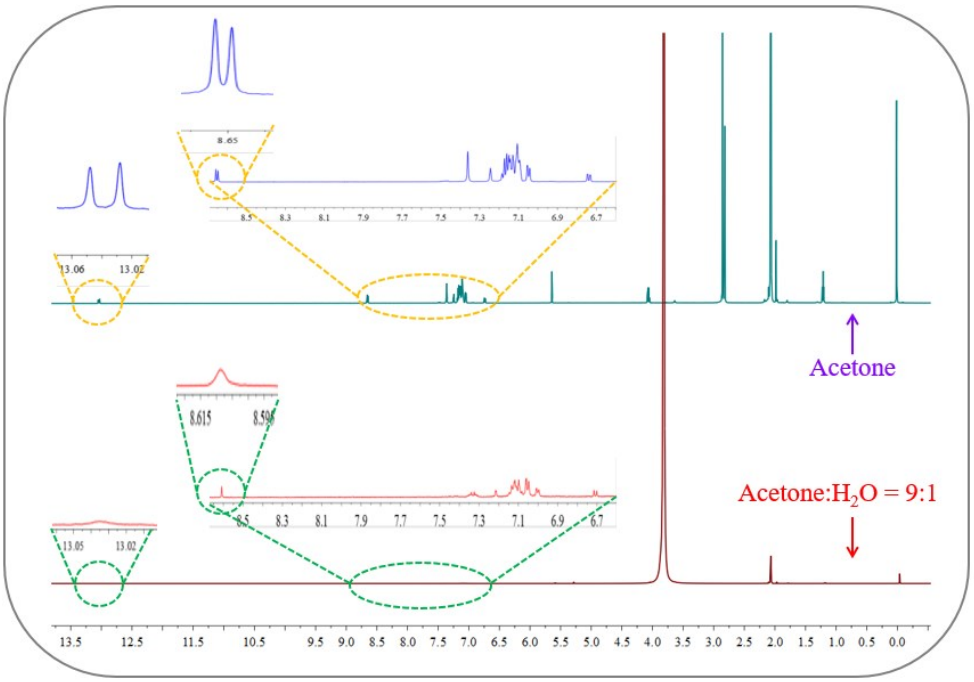

Figure S5 The NMR spectroscopy of **TPESB** in acetone and acetone/water mixture with 10% water fraction.

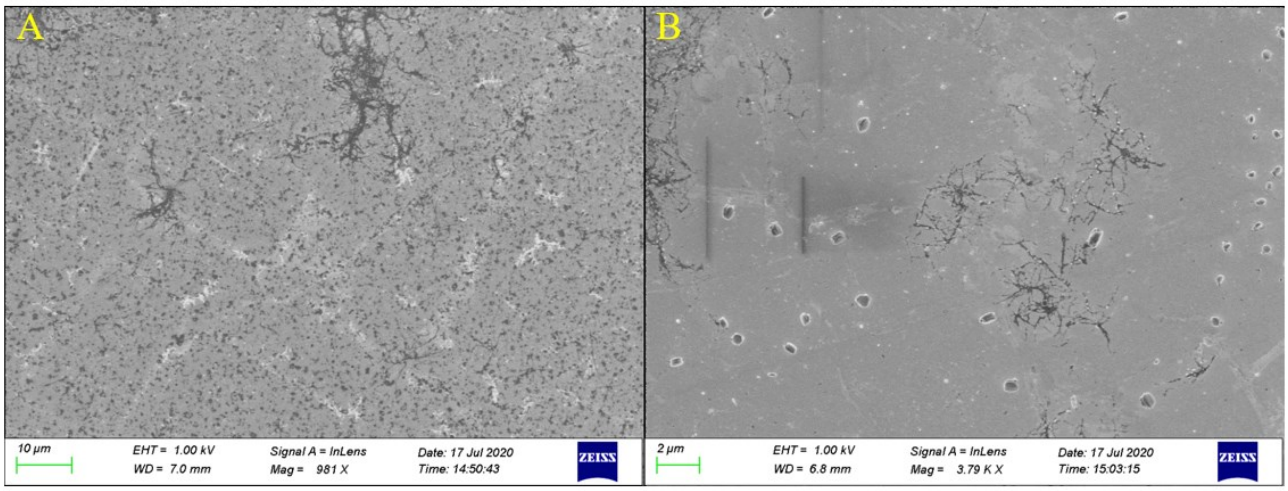

Figure S6 The SEM images of **TPESB** prepared in the 9:1 mixed THF/water solvents in the time course of 0 min (A), 5 min (B).

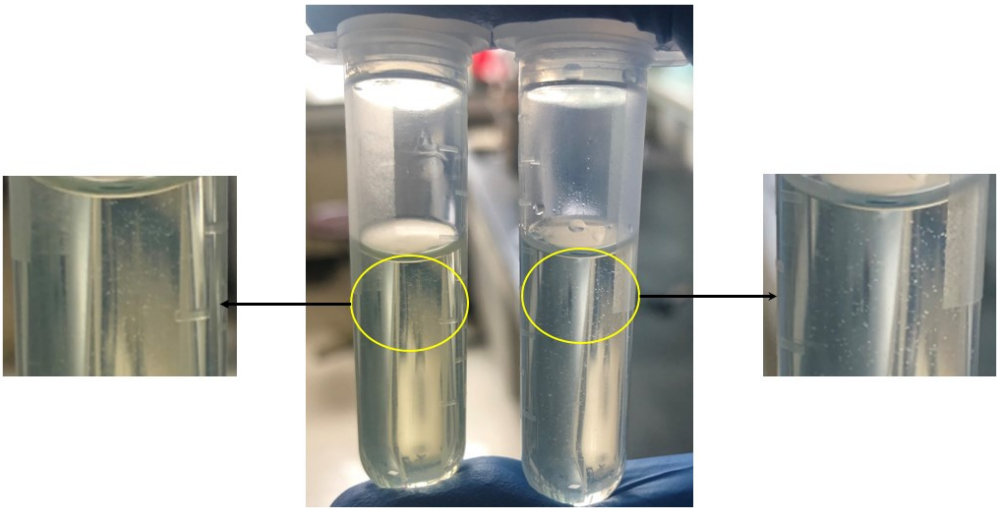

Figure S7 The images of **TPESB** in mixed THF/water solvents with 10% (left) and 20% (right) water fraction after standing for several hours.

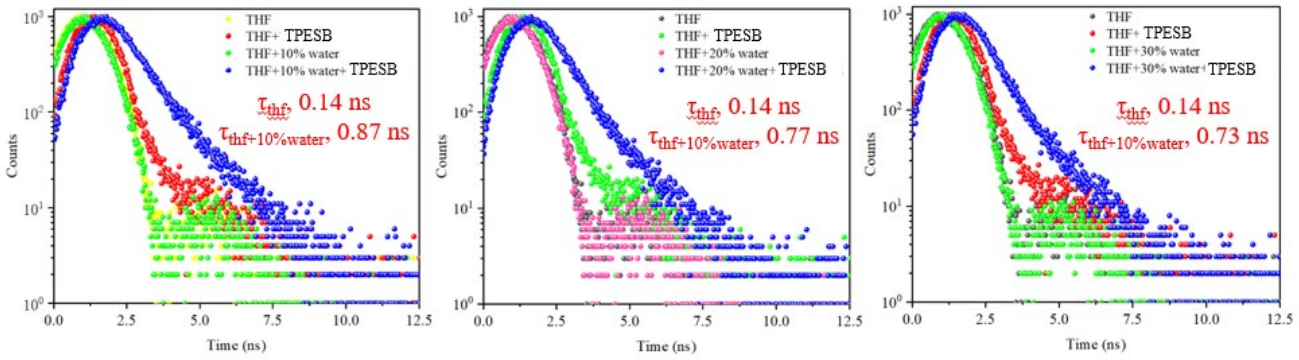

Figure S8 Time resolved fluorescence spectra of compound **TPESB** in THF and THF/H_2O mixture with 10%, 20% and 30% water fraction, respectively. **TPESB** concentration: 10^{-5} M.

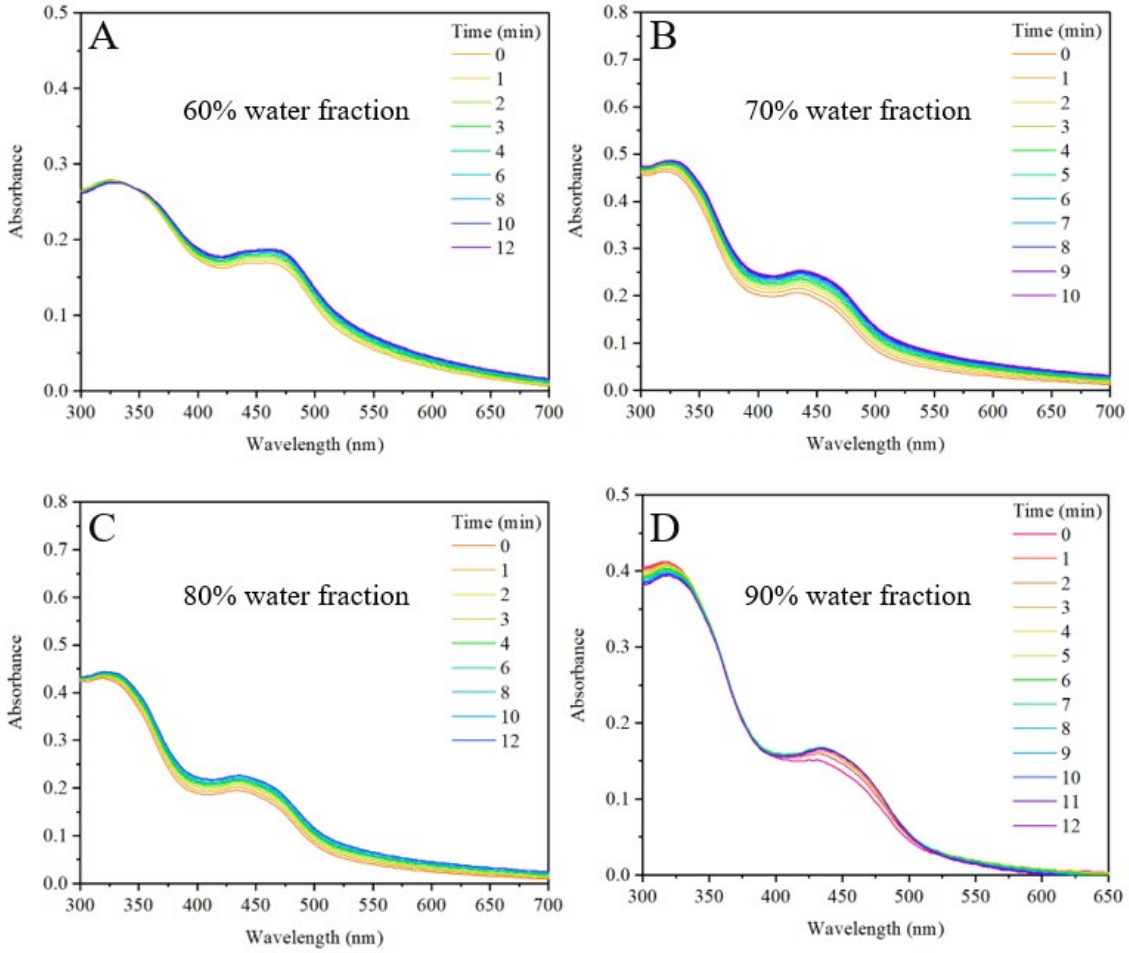

Figure S9 The absorbance spectra changes of **TPESB** in THF/H_2O mixture with 60% 70%, 80% and 90% water fraction, respectively. **TPESB** concentration: 10^{-5} M.

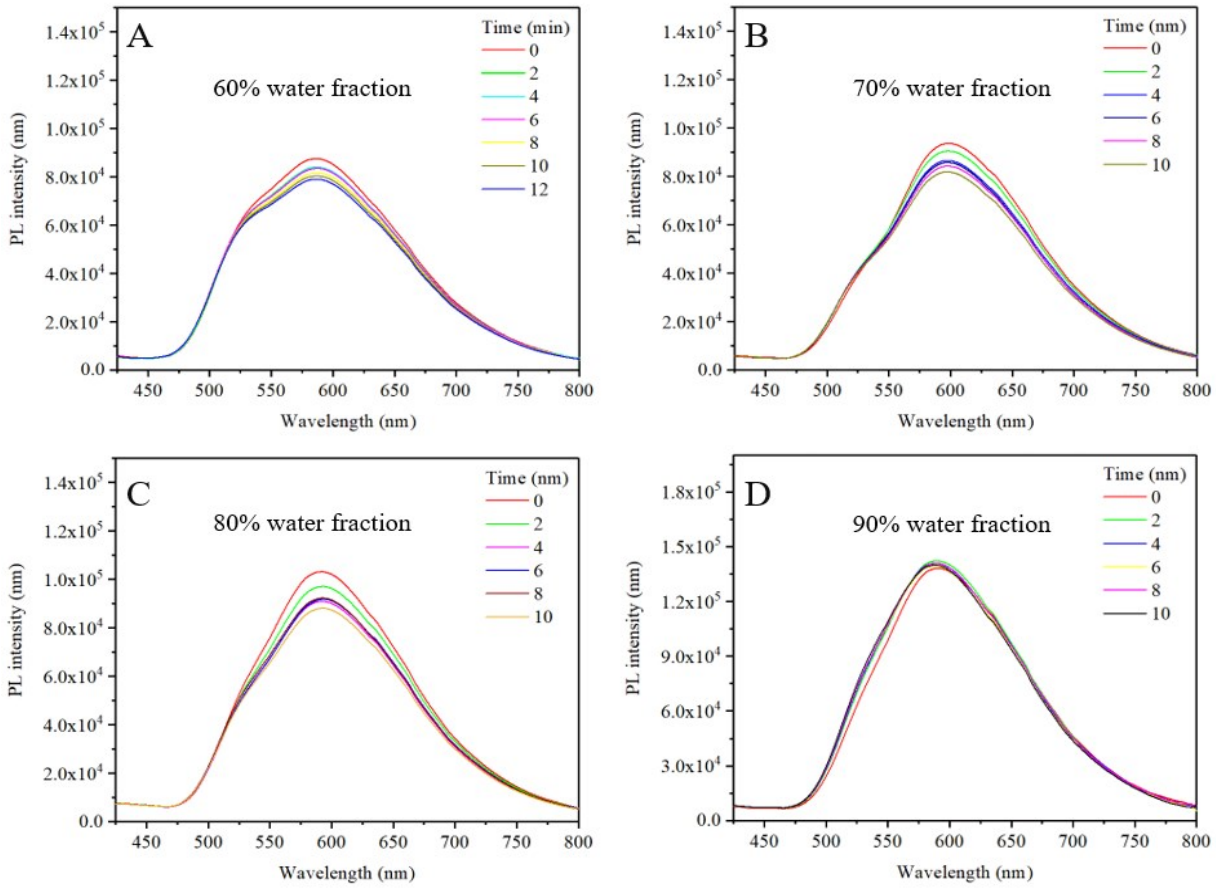

Figure S10 The PL spectra changes of **TPESB** in THF/H_2O mixture with 60% 70%, 80% and 90% water fraction, respectively. **TPESB** concentration: 10^{-5} M.

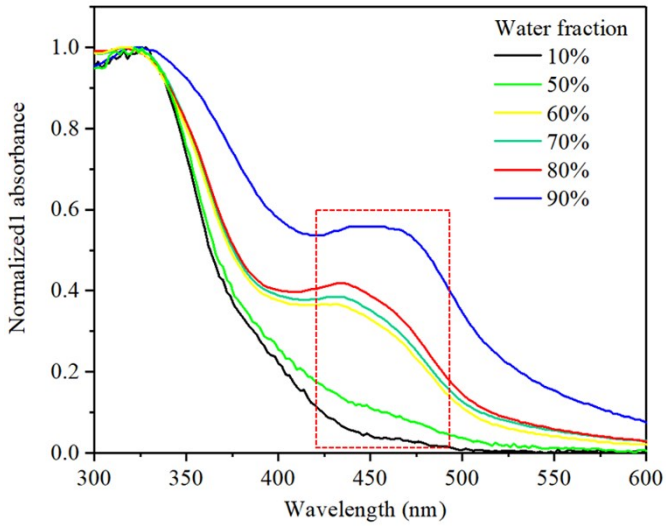

Figure S11 The absorbance spectra of **TPESB** in THF/H_2O mixture with 10%, 50%, 60% 70%, 80% and 90% water fraction, respectively. **TPESB** concentration: 10^{-5} M.

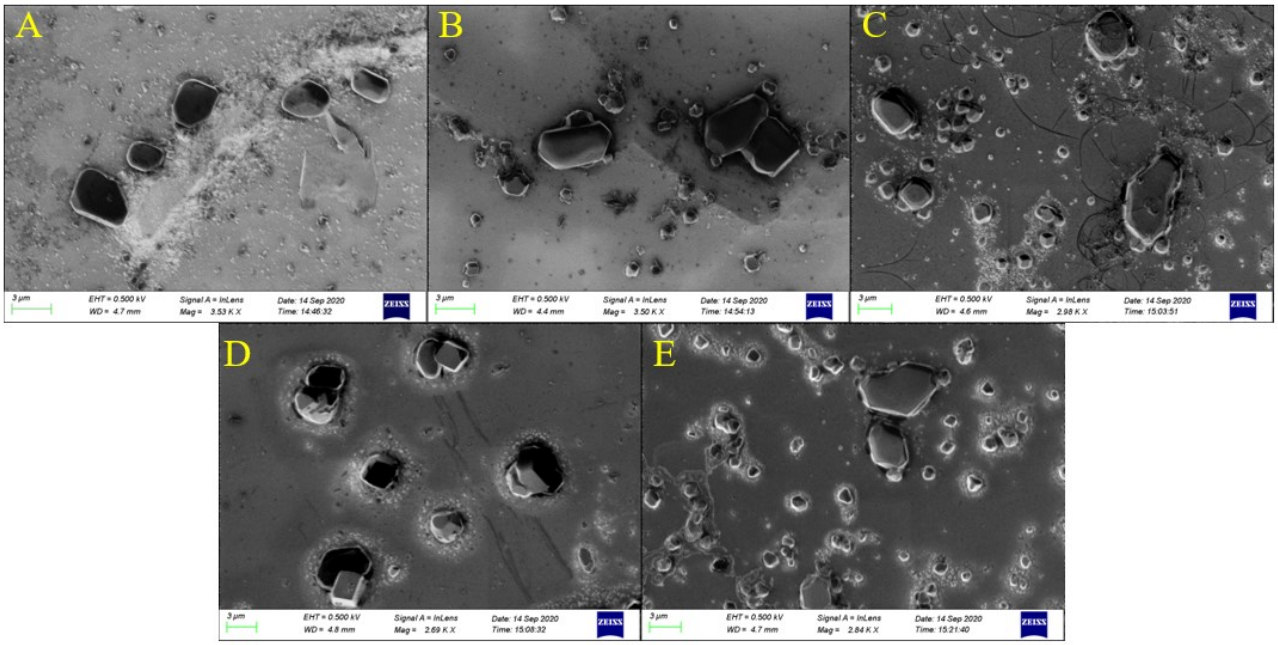

Figure S12 The SEM images of **TPESB** prepared in THF/water solvents with 50% (A), 60% (B), 70% (C), 80% (D) and 90% (E) water fraction.

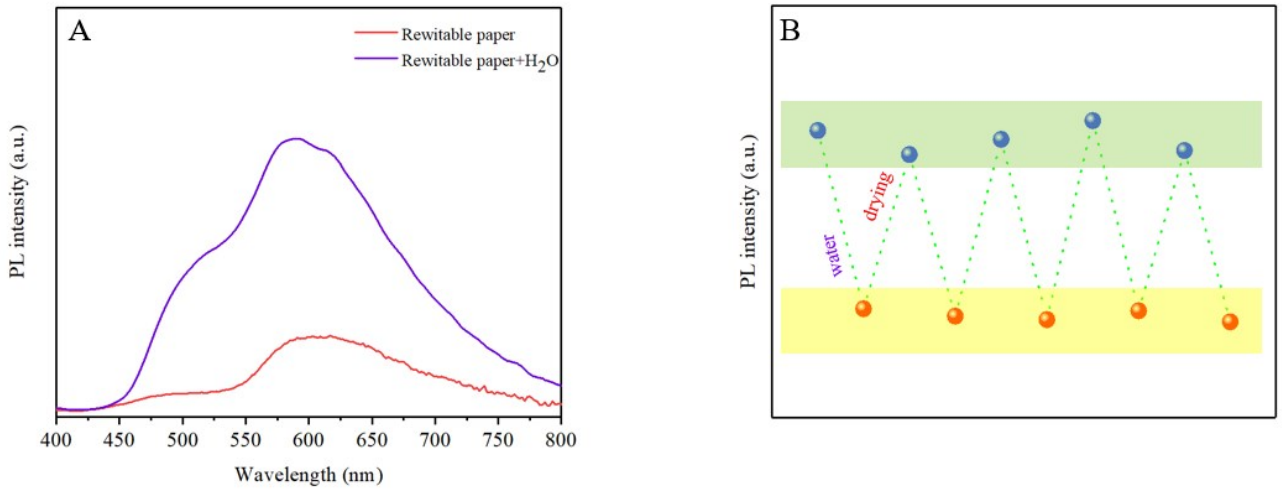

Figure S13 (A) The PL spectra of the fabricated rewritable paper before and after explored to water. (B) A plot of the PL intensity at 600 nm versus the number of cycles as the produced paper is cycled through water printing and heat erasing.

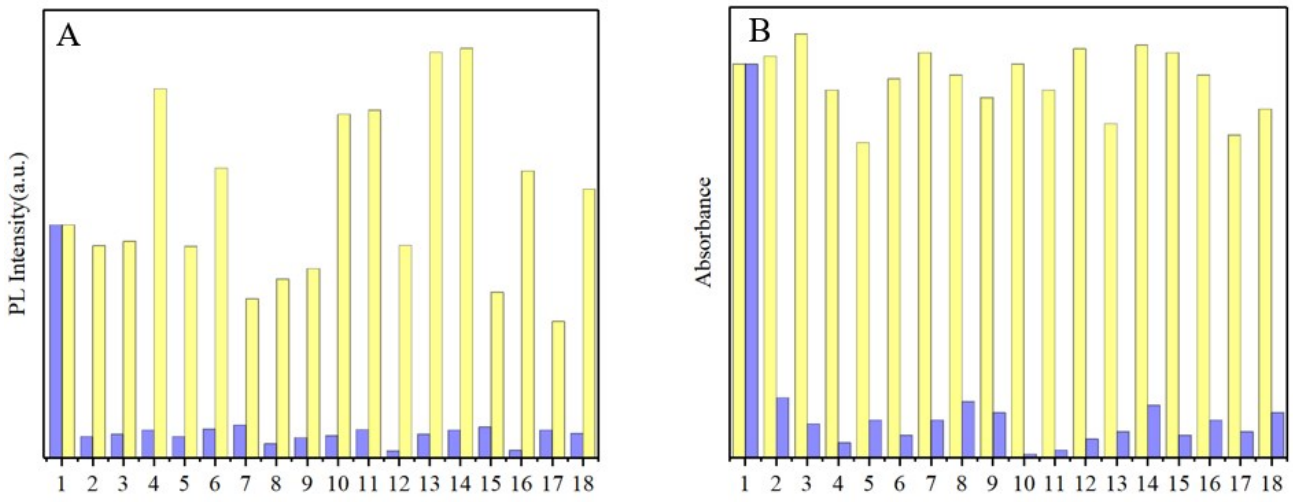

Figure S14 Fluorescence (A) and absorbance (B) responses of **TPESB** in the presence of various anions (1 equiv) in THF/H_2O mixture with 50% water fraction. The yellow bars represent emission and absorbance upon the addition of 1 equiv of Zn^{2+} to compound **TPESB** (10^{-5} M). The blue bars represent the change in emission and absorbance that occurs upon the subsequent addition of 1 equiv of various anions to a 10^{-5} M solution of **TPESB**. 1-18 represents Zn^{2+}, Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, Ag^{+}, Pb^{2+}, Ba^{2+}, Cs^{+}, NH^{+}, Bi^{3+} and Sn^{4+}, respectively.

Table S1 Comparison of detection limit (LOD) of **TPESB** with recently reported probes

Reference	LOD
45	4.85×10^{-7}
46	1.44×10^{-7}
47	2.0×10^{-7}
48	1.0×10^{-5}
49	6.0×10^{-7}
50	1.29×10^{-6}
51	3.2×10^{-7}
52	6.3×10^{-8}
53	5.26×10^{-7}
54	7.02×10^{-8}
55	5.76×10^{-8}
This work	3.89×10^{-8}

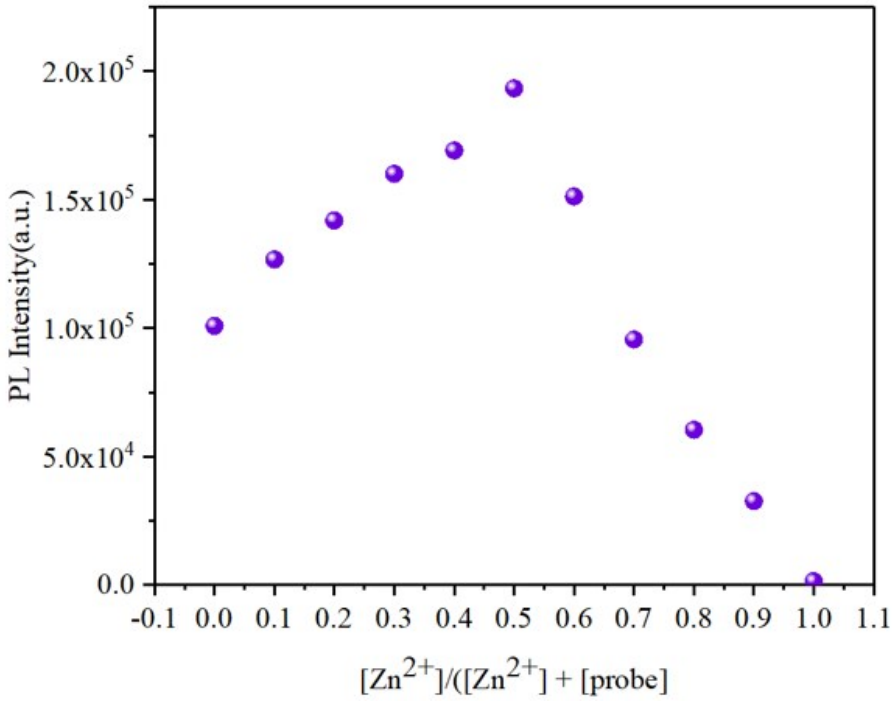

Figure S15 Job's plot of **TPESB** and Zn^{2+} in THF/water (v/v = 1/1) solution. The total concentration of **TPESB** and Zn^{2+} was 10 μM. The absorbance was measured at 366 nm.

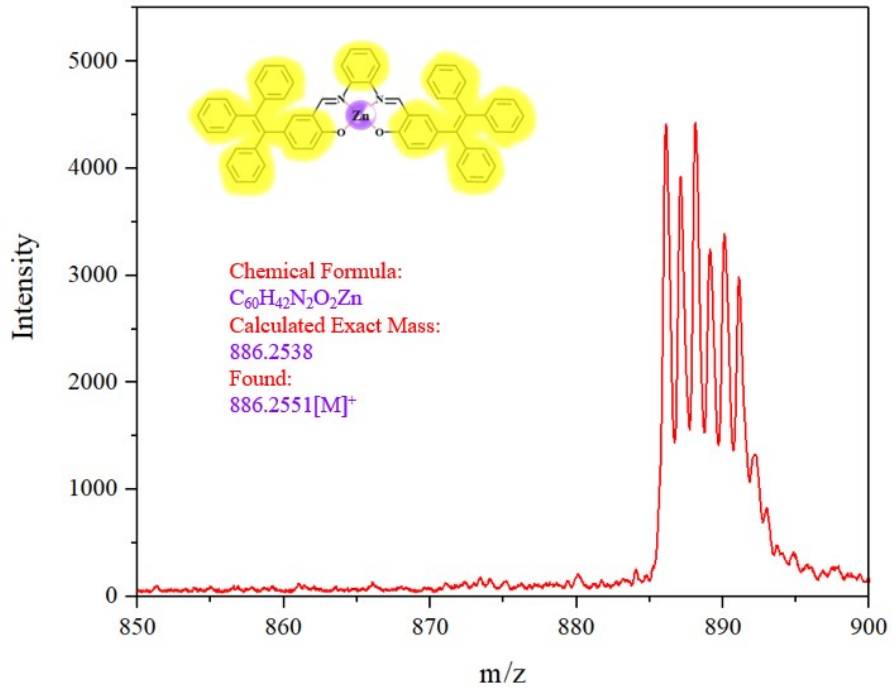

Figure S16 Mass spectra of **TPESB** and Zn^{2+}.

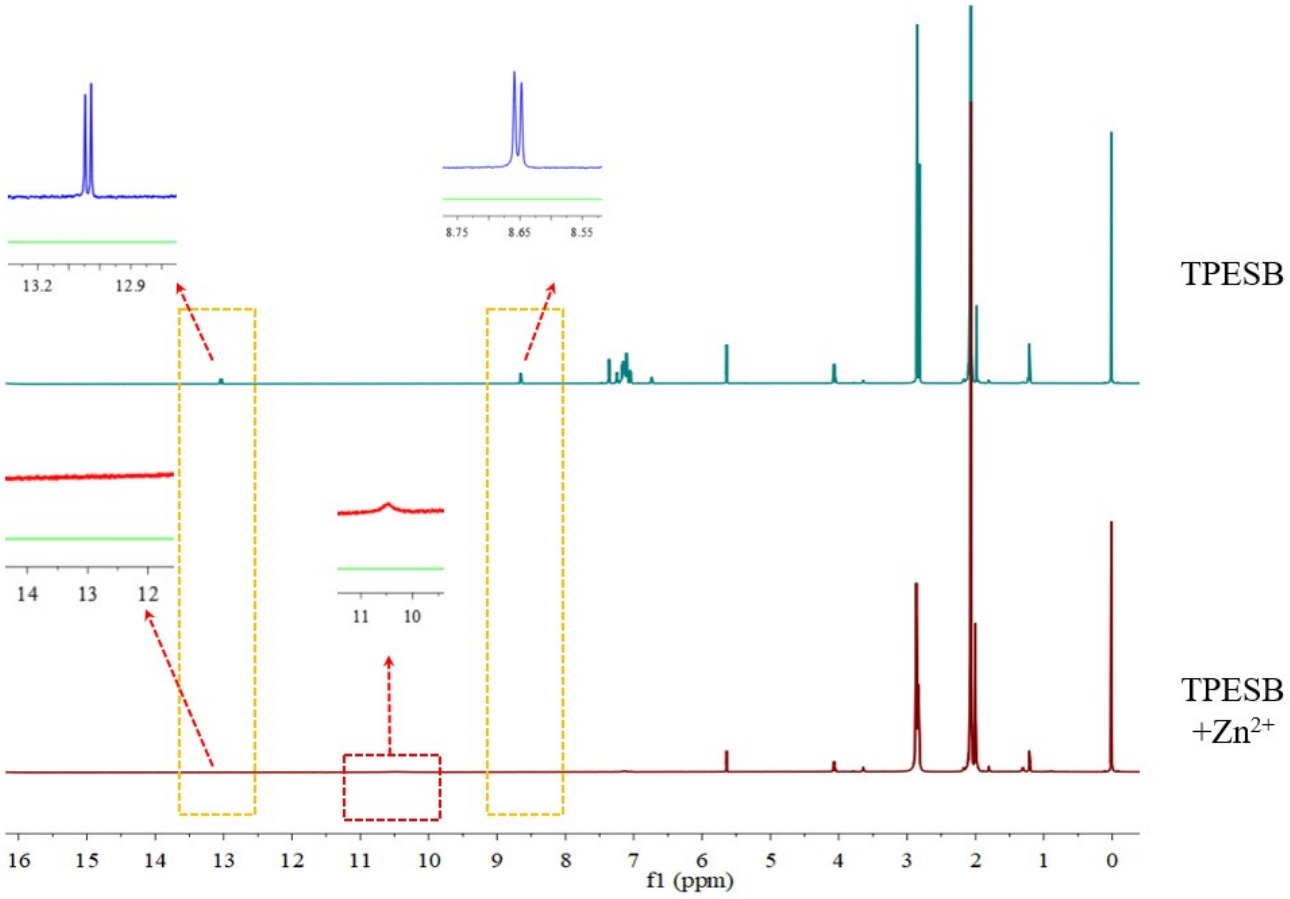

Figure S17 The NMR spectra of **TPESB** in acetone before and after addition of 1 eq Zn^{2+}.

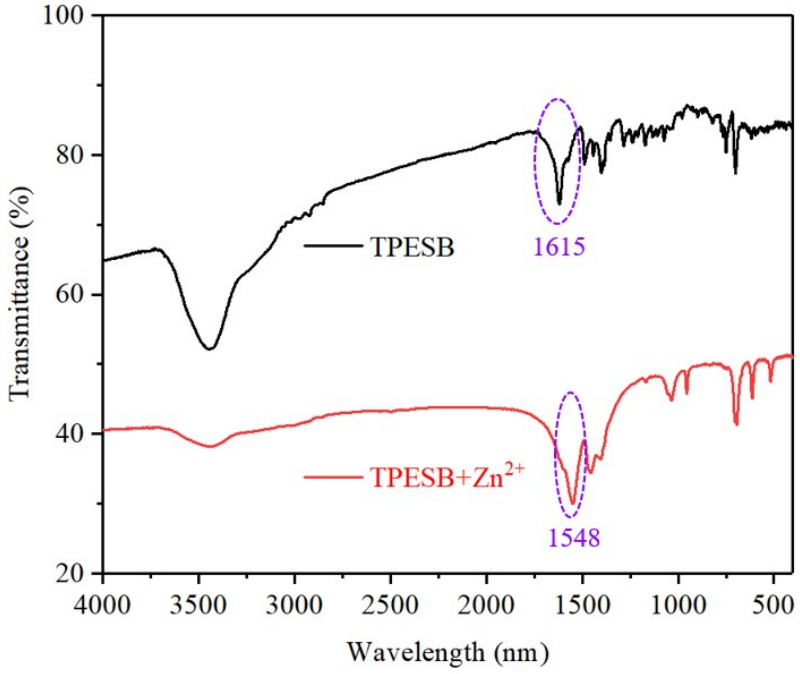

Figure S18 The IR spectra of TPESB and TPESB-Zn^{2+}.

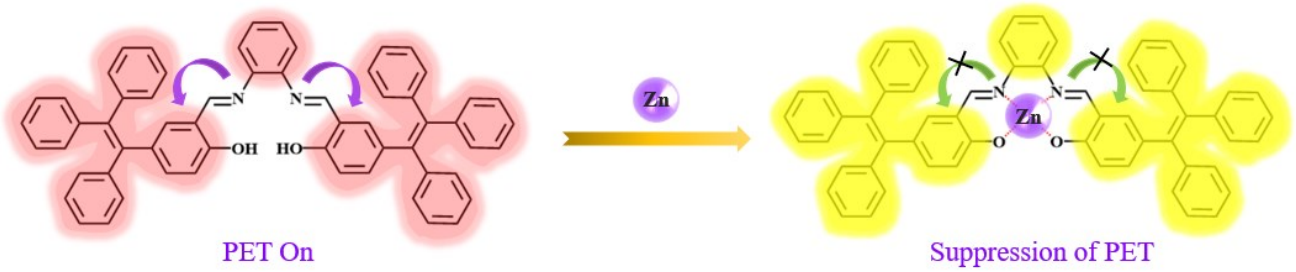

Figure S19 The proposed binding mechanism of **TPESB** with Zn^{2+}.

Table S2 Detection results of Zn^{2+} in water samples by probe **TPESB**.

Sample	Colorimetry			Fluorescence		
	Added (μmol/L)	Found (μmol/L)	Recovery	Added (μmol/L)	Found (μmol/L)	Recovery
Tap	0	–	–	0	–	–
water	12.5	11.88	95.04	0.4	0.379	94.75
Lake	0	–	–	0	–	–
water	24.5	23.24	94.86	4	4.17	104.25

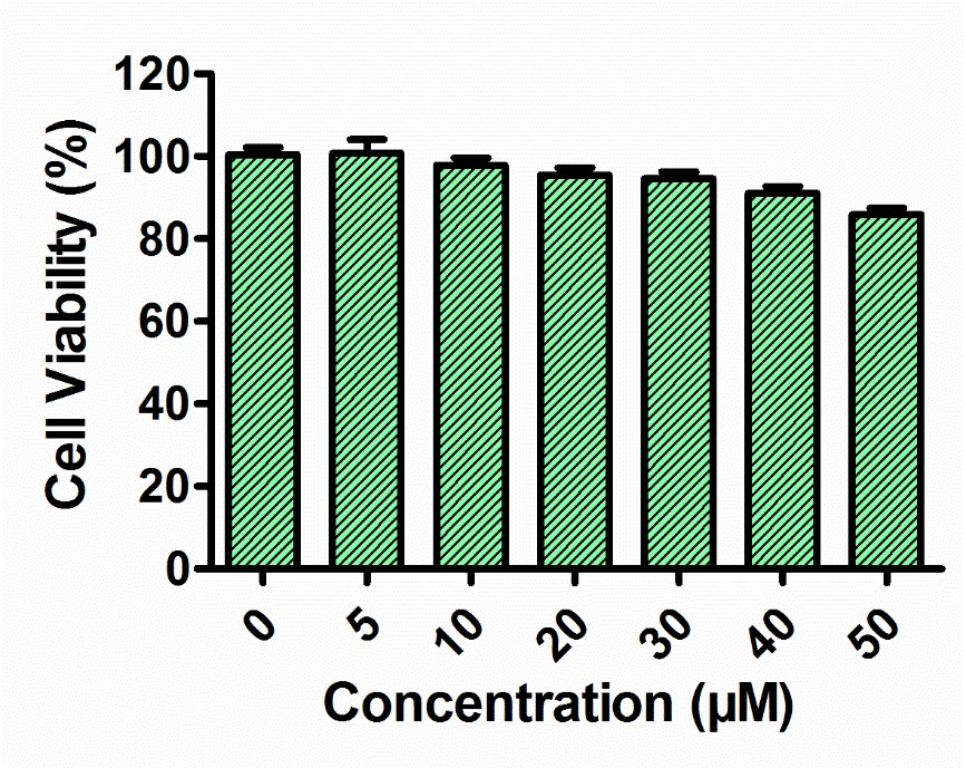

Figure S20 Viability of HeLa cells incubated with different concentration of **TPESB** (0, 5 μM, 10 μM, 20 μM, 30 μM, 40 μM and 50 μM) for 24 h. Data are mean±SD (bars) (n = 3).

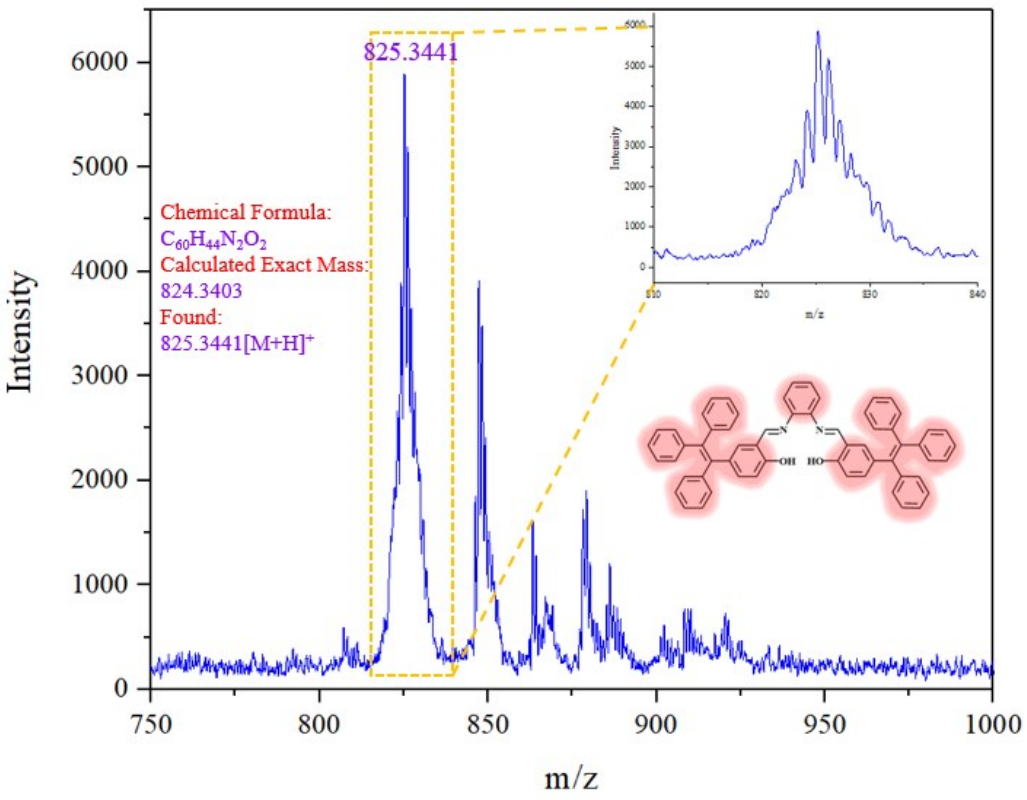

Figure S21 Mass spectra of **TPESB**.

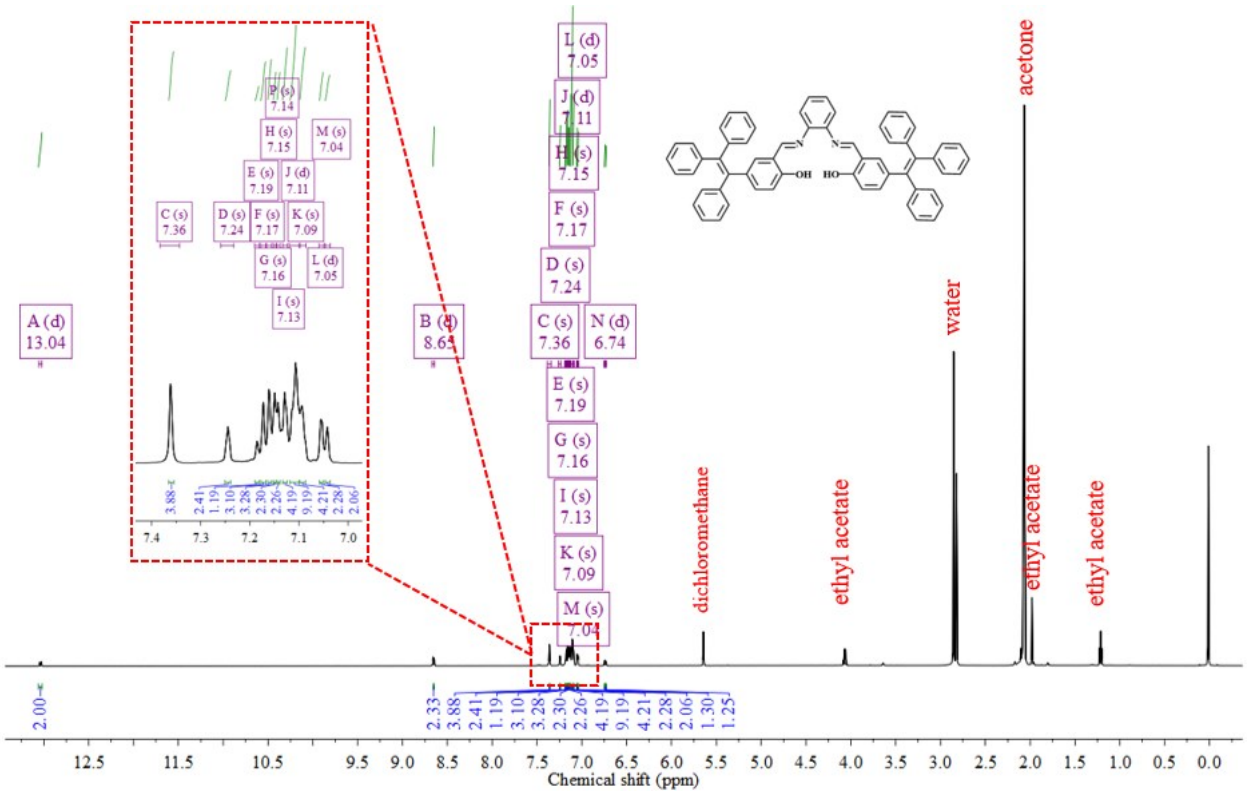

Figure S22 ^{1}H NMR spectrum of **TPESB**.

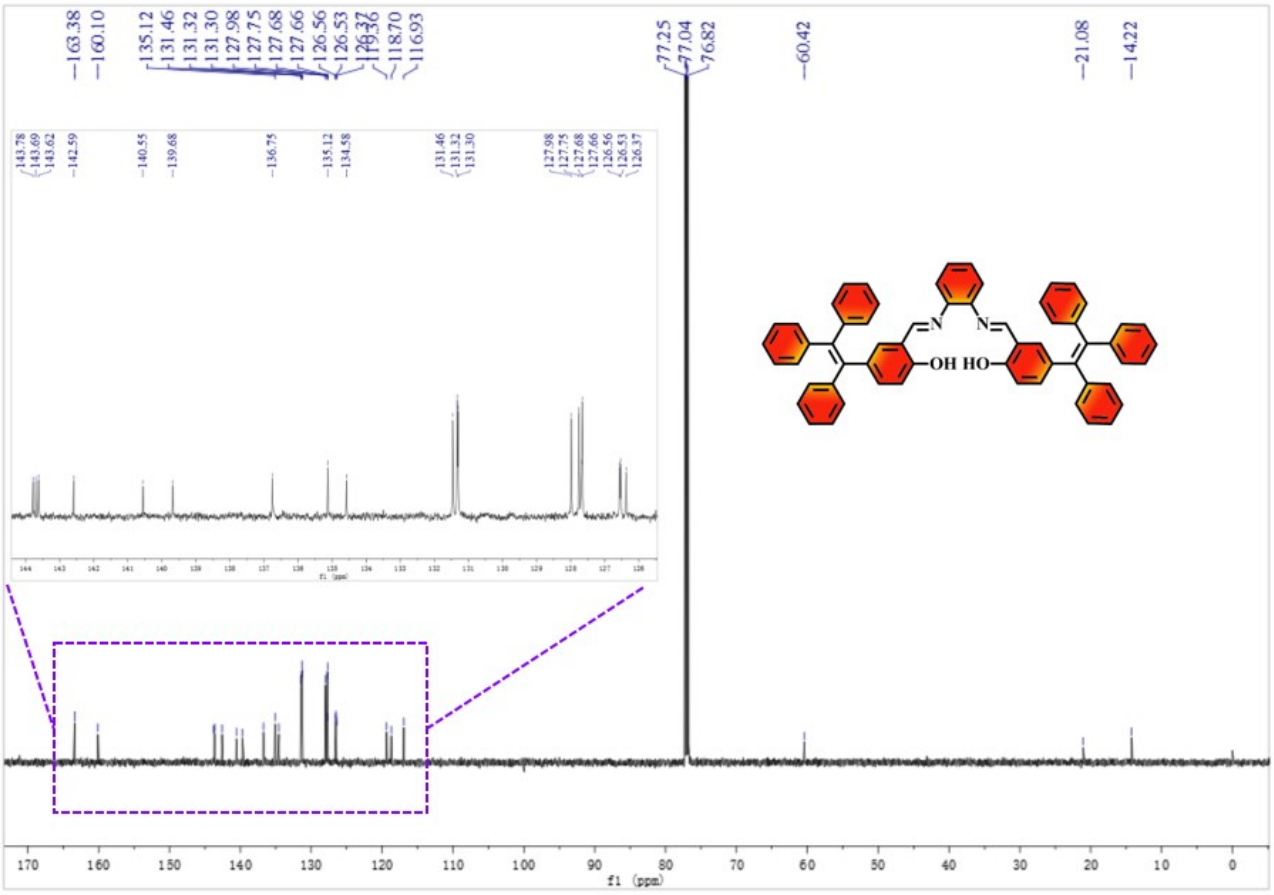

Figure S23 ^{1}C NMR spectrum of **TPESB**.