Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

A novel quinolinyl-tetraphenylethene based fluorescence "turn-on" sensor for Zn^{2+} with a large Stokes shift and its applications for portable test strips and biological imaging

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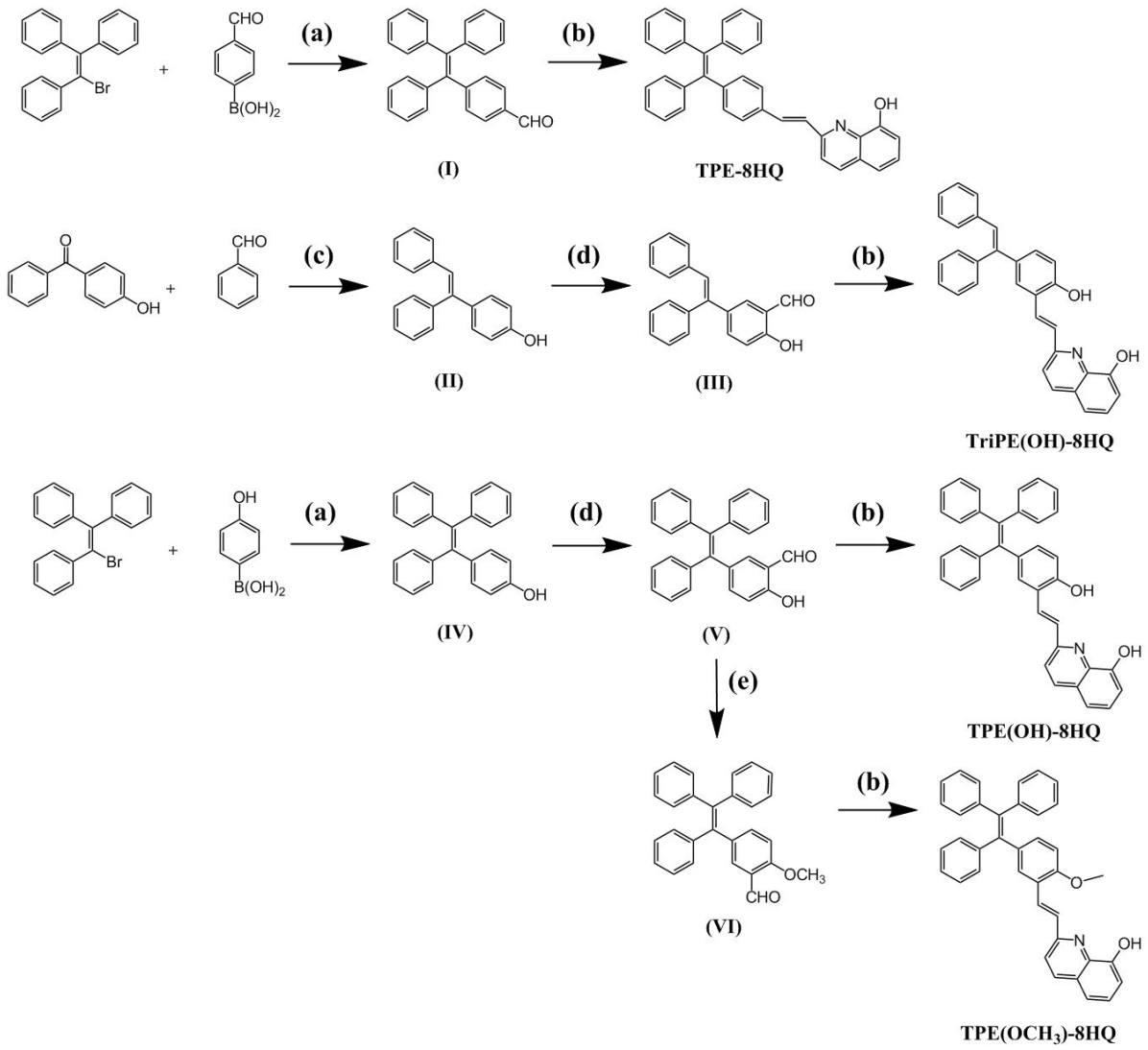
1. Experimental section

Materials and instruments

Ethanol was purified prior to use. Other reagents and chemicals were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE III 400 MHz Superconducting Fourier in DMSO-d6 or $CDCl_3$ solution with TMS as an internal standard. Mass spectra (ES-MS) were obtained on Ultra High Performance Liquid Chromatography Tandem Triple Quadrupole Mass Spectrometer (*/TSQ Endura). The IR (KBr pellet) spectrum was recorded (400–4000 cm^{-1}region) on a Nicolet Magna 750 FT-IR spectrometer. Emission Spectra were performed by steady-state fluorescence spectrometer (Edinburgh Instruments). UV-vis spectra were recorded on Lambda 20 UV–vis Spectrometer (PerkinElmer, Inc, USA). Stock solutions of various metal ions (1×10^{-3}M) were prepared using chloride salts, except Ag^{+} ($AgNO_3$). A stock solution of probes (1×10^{-3}M) was prepared and then the stock solution was diluted 100 times.

2. Synthesis routes and Characterization



Scheme S1. The synthesis ways of these probes were according to previous reports.

Synthetic procedures:

(a) $Pd(PPh_3)_4$, K_2CO_3, toluene / MeOH, 75°C,reflux over night under N_2 atmosphere;

(b) 1) 2-Methyl-8-hydroxyquinoline, Ac_2O, 140 °C, reflux over night under air atmosphere;

2) pyridine, H_2O,140 °C, reflux over 3h under air atmosphere;

(c) Zn powder,titanium tetrachloride, degassed THF,80°C, reflux for 5.5 hours under N_2 atmosphere;

(d) 1,3,5,7 -tetraazaadamantane,CH_3COOH, 90 °C, reflux for 3 hours under air atmosphere;

(e) CH_3I, K_2CO_3,acetone, 65°C, reflux over night under N_2 atmosphere.

2.1 Synthesis of 4-(1,2,2-triphenylvinyl)benzaldehyde (I) [1]:

2-bromo-1,1,2-tristyrene (3.36 g, 10 mmol), 4-formylphenylboronic acid (1.94 g, 13 mmol), K_2CO_3 (4.14 g, 30 mmol), $Pd(PPh_3)_4$ (0.064 g, 0.08 mmol) and 120 mL methanol-toluene (1:1, v/v) mixed solution was added to a 250 mL round bottom flask, stirred under N_2 at 75 °C for 16 hours. After completion of the reaction, it was cooled to room temperature and removal of solvent from the reaction mixture followed by purification through column chromatography using petroleum ether / ethyl acetate (8:1, v/v) as eluent after extraction , dried in vacuo to give a white solid, Yield: 3.24 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.16–7.07 (m, 9H), 7.07–6.96 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 150.5, 143.0, 142.9, 139.8, 134.3, 131.9, 131.3, 131.2, 129.1, 127.9, 127.9, 127.7, 127.0, 126.9, 126.9.

Synthesis of 4-(1,2,2-triphenylvinyl)phenol (IV): dried in vacuo to give a white solid, Yield: 71.7%. ^{1}H NMR (400 MHz, DMSO) δ 9.39 (d, *J* = 10.4 Hz, 1H), 7.17 (m, 9H), 7.00 (m, 5H), 6.80 (m, 3H), 6.55 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 157.8, 156.4, 144.2, 144.1, 141.1, 139.6, 134.2, 132.4, 131.2, 131.2, 131.1, 129.8, 128.3, 128.2, 128.2, 126.9, 126.7, 119.3, 115.7, 115.1.

2.2 Synthesis of (E)-4-(1,2-diphenylvinyl)phenol (II) [2]:

benzaldehyde (1.06 g, 10 mmol), 4-hydroxybenzophenone (1.98 g, 10 mmol), Zn powder (6.5 g, 20 mmol) dissolved in degassed THF and then stir at room temperature for 1 hour under vacuum. After adding titanium tetrachloride (5.2 mL, 50 mmol) and then stirred at room temperature for 1hour.Finally, stirred under N_2 at 80 °C for 5.5 hours. It was cooled to room temperature and removal of solvent from the reaction mixture followed by purification through column chromatography using petroleum ether / ethyl acetate (10:1, v/v) as eluent after extraction, dried in vacuo to give a white solid, Yield: 0.88 g (32.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 1H), 7.16 (m, 15H). ^{13}C NMR (101 MHz, DMSO) δ 156.4, 144.2, 144.1, 141.1, 139.6, 134.2, 132.4, 131.2, 131.2, 131.1, 128.3, 128.2, 128.1, 126.9, 126.7, 115.1.

2.3 Synthesis of 2-hydroxy-5-(1,2,2-triphenylvinyl)benzaldehyde (V) [3]**:**

TPE-OH (1.0 g, 3 mmol)(II) was added to 50 ml of acetic acid at room temperature and stirred slightly, hexamethylenetetramine (2.1 g, 15 mmol) was added to the reaction system after dissolving. The reaction was refluxed for 3 hours under air atmosphere. After the reaction was stopped, removal of solvent from the reaction mixture followed by purification through column chromatography using petroleum ether / ethyl acetate (5:1, v/v) as eluent after extraction, dried in vacuo to give a yellow solid.Yield: 0.55g (48.8%). ^{1}H NMR (400 MHz, DMSO) δ 10.68 (s, 1H), 10.11 (s, 1H), 7.44 (t, *J* = 5.9 Hz, 1H), 7.23 (s, 1H), 7.11 (m, 9H), 6.98 (dd, *J* = 12.8, 8.0 Hz, 6H), 6.74(m,1H). ^{13}C NMR(101

MHz, DMSO) δ 191.3, 159.9, 143.6, 143.6, 143.3, 140.9, 139.8, 139.1, 134.9, 131.3 , 131.2 , 131.1, 131.1, 128.4 , 128.4 , 128.3, 127.2, 127.1 , 126.9, 122.3, 117.2.

(E)-5-(1,2-diphenylvinyl)-2-hydroxybenzaldehyde (III): dried in vacuo to give a yellow solid, Yield: 40.7%. ^{1}H NMR (400 MHz, DMSO) δ 10.89 (s, 1H), 10.24 (d, *J* = 2.3 Hz, 1H), 7.54 (m, 1H), 7.35 (m, 5H), 7.08 (m, 8H).

2.4 Synthesis of 2-methoxy-5-(1,2,2-triphenylvinyl)benzaldehyde (VI) [4]:

The K_2CO_3 (0.27 g, 2 mmol) was added to a solution of compound (V) (0.37 g, 1 mmol) in acetone (20 mL) and the mixture was stirred for 0.5 h. Then the methyl iodide (0.28 g, 2 mmol) was added dropwise and stirred overnight at 65 °C . Removal of solvent from the reaction mixture followed by purification through column chromatography using petroleum ether / ethyl acetate (8:1, v/v) as eluent, dried in vacuo to give a light yellow solid.Yield: 0.56g (81.4%). ^{1}H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.23 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.13 (m, 9H), 6.99 (m, 7H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 189.2, 160.6, 143.5, 143.4, 143.3, 141.3, 139.5, 139.0, 135.9, 131.2, 131.1, 131.1, 130.3, 128.5, 128.4, 128.3, 127.2, 127.2, 127.0, 123.9, 112.7, 56.4.

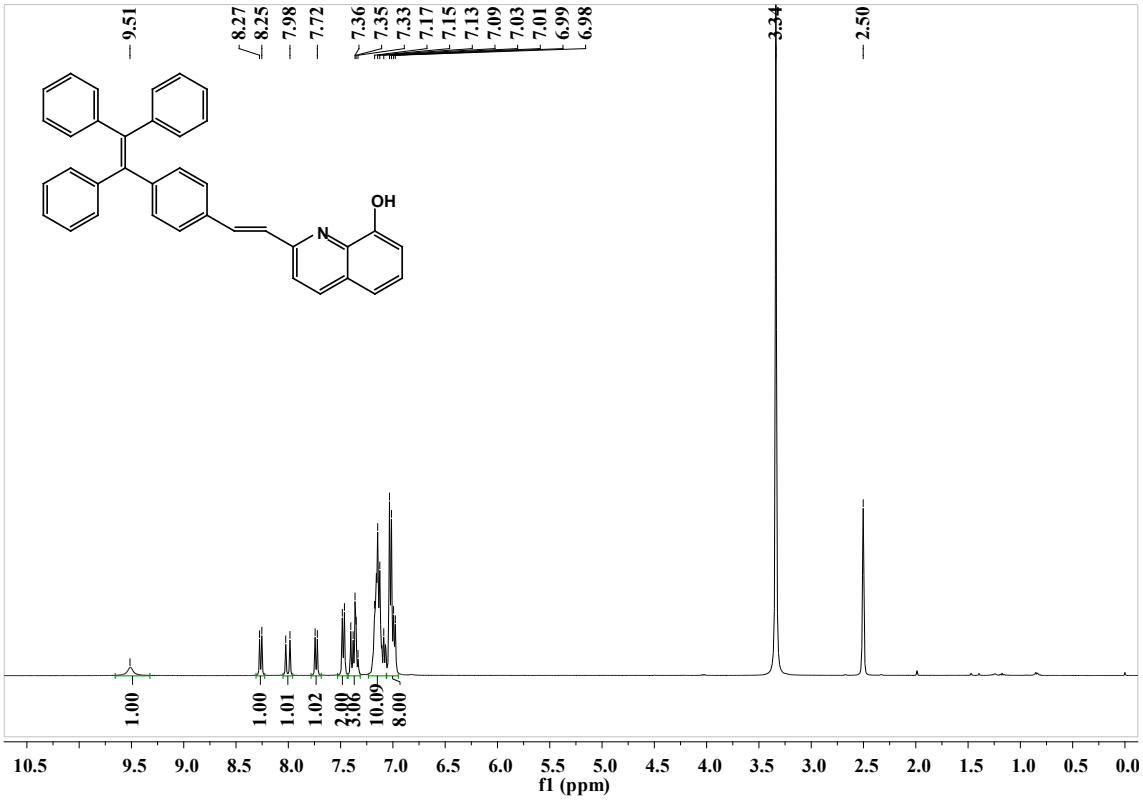


Fig. S1. ^{1}H NMR spectrum of TPE-8HQ

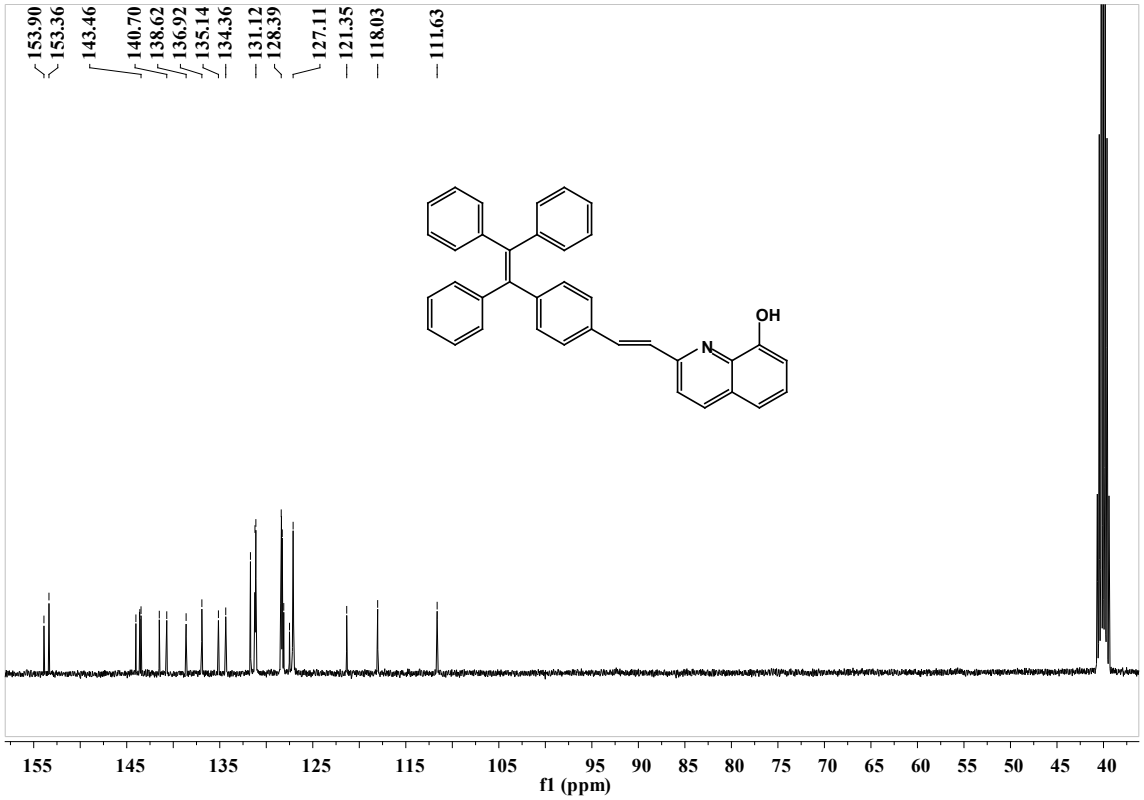


Fig. S2. ^{13}C NMR spectrum of TPE-8HQ

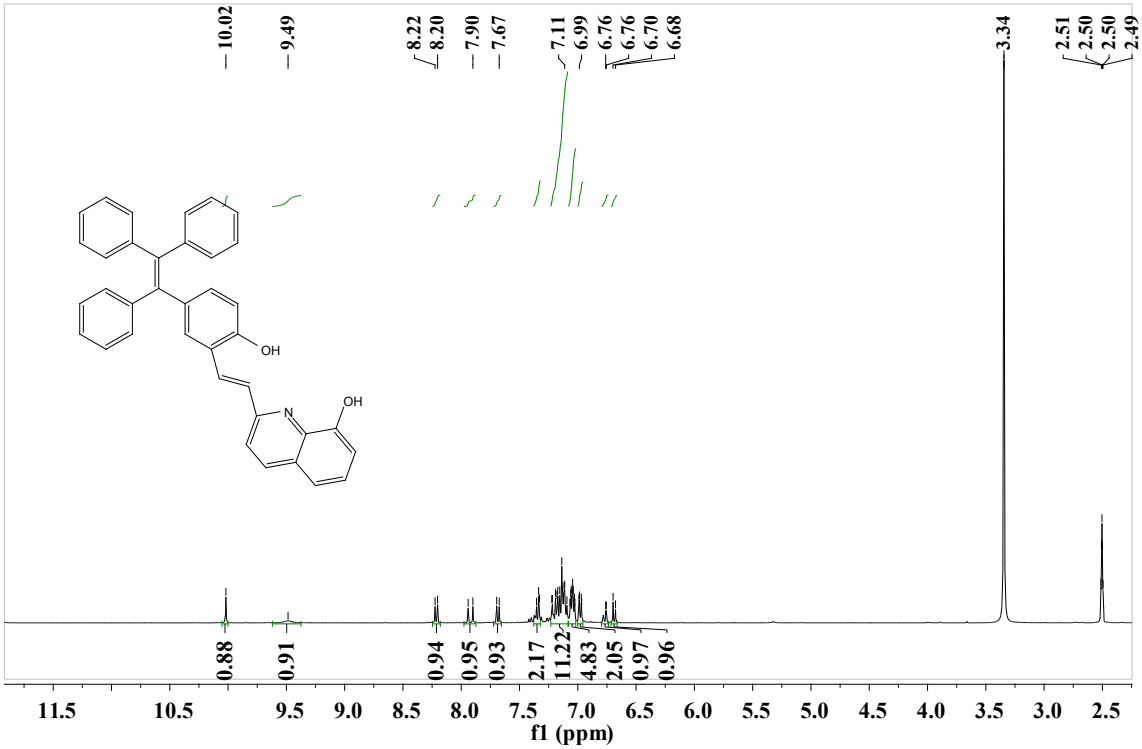


Fig. S3. ^{1}H NMR spectrum of TPE(OH)-8HQ.

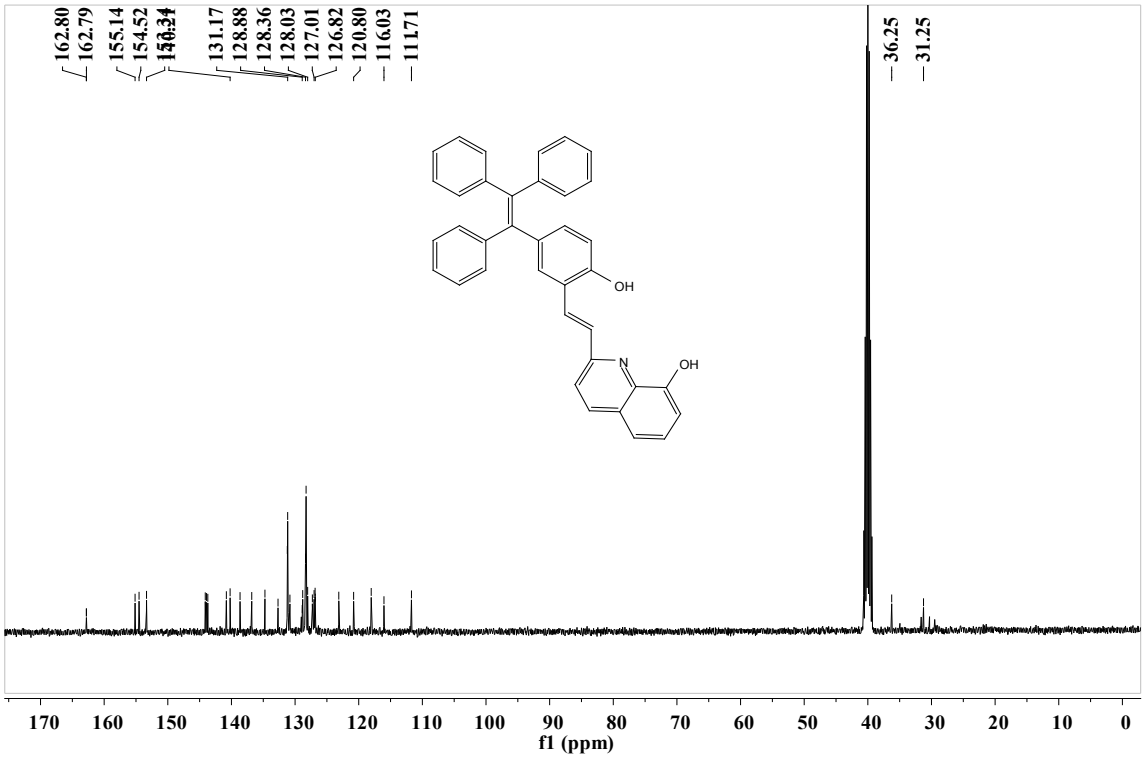


Fig. S4. ^{13}C NMR spectrum of TPE(OH)-8HQ.

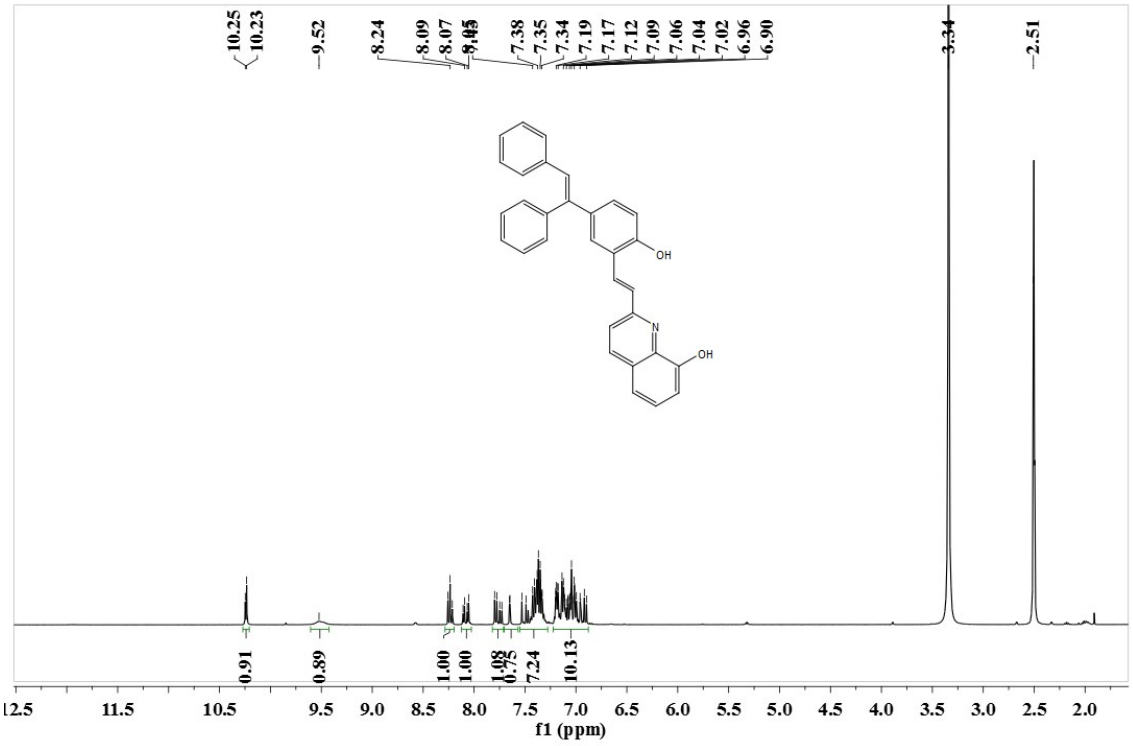


Fig. S5. ^{1}H NMR spectrum of TriPE(OH)-8HQ.

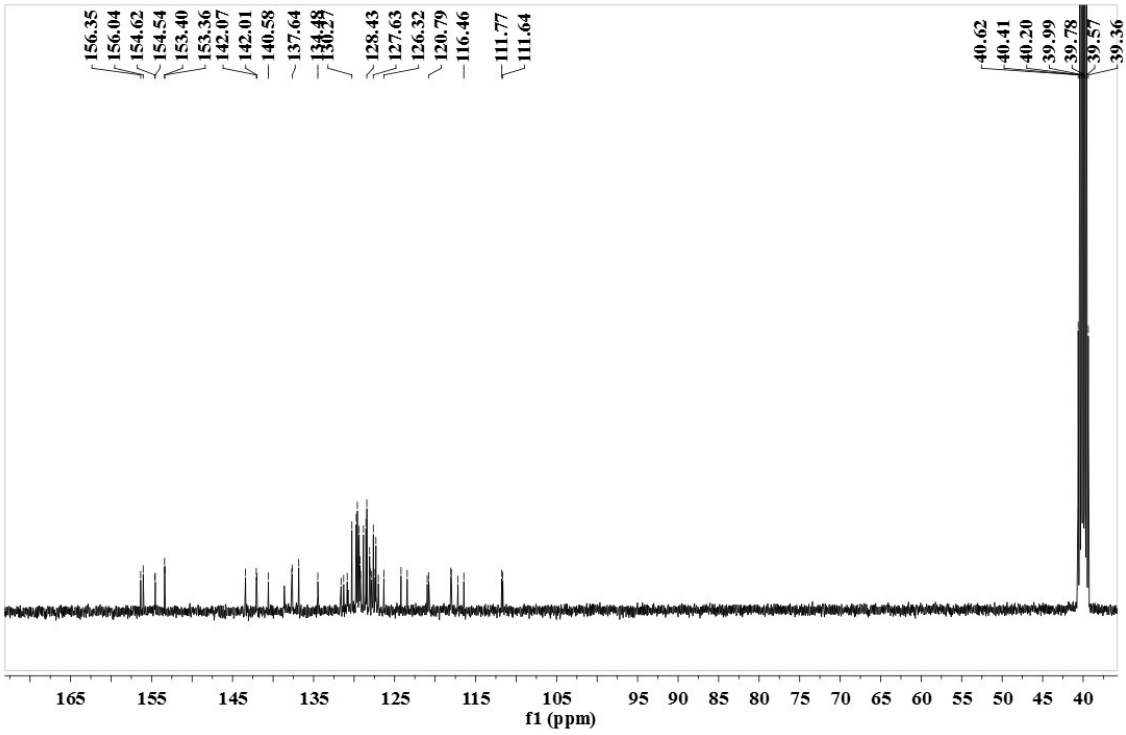


Fig. S6. ^{13}C NMR spectrum of TriPE(OH)-8HQ.

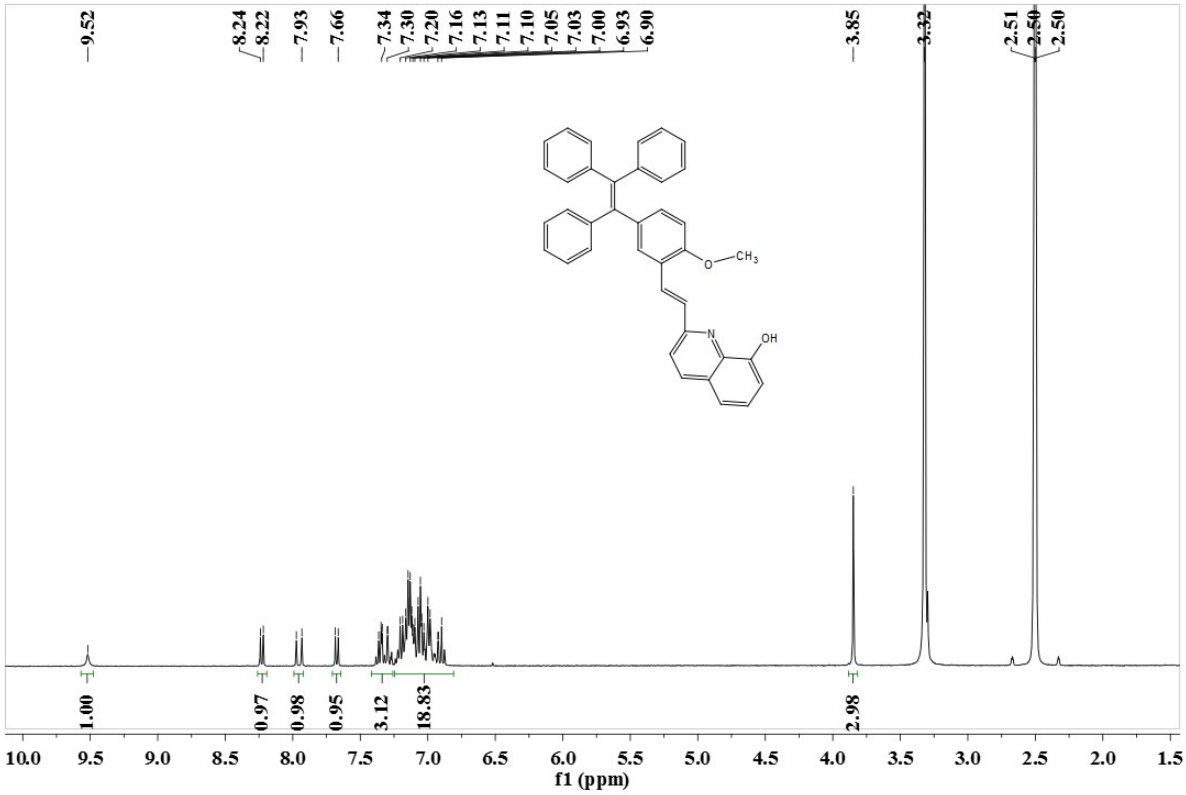


Fig. S7. ^{1}H NMR spectrum of TPE(OCH_3)-8HQ.

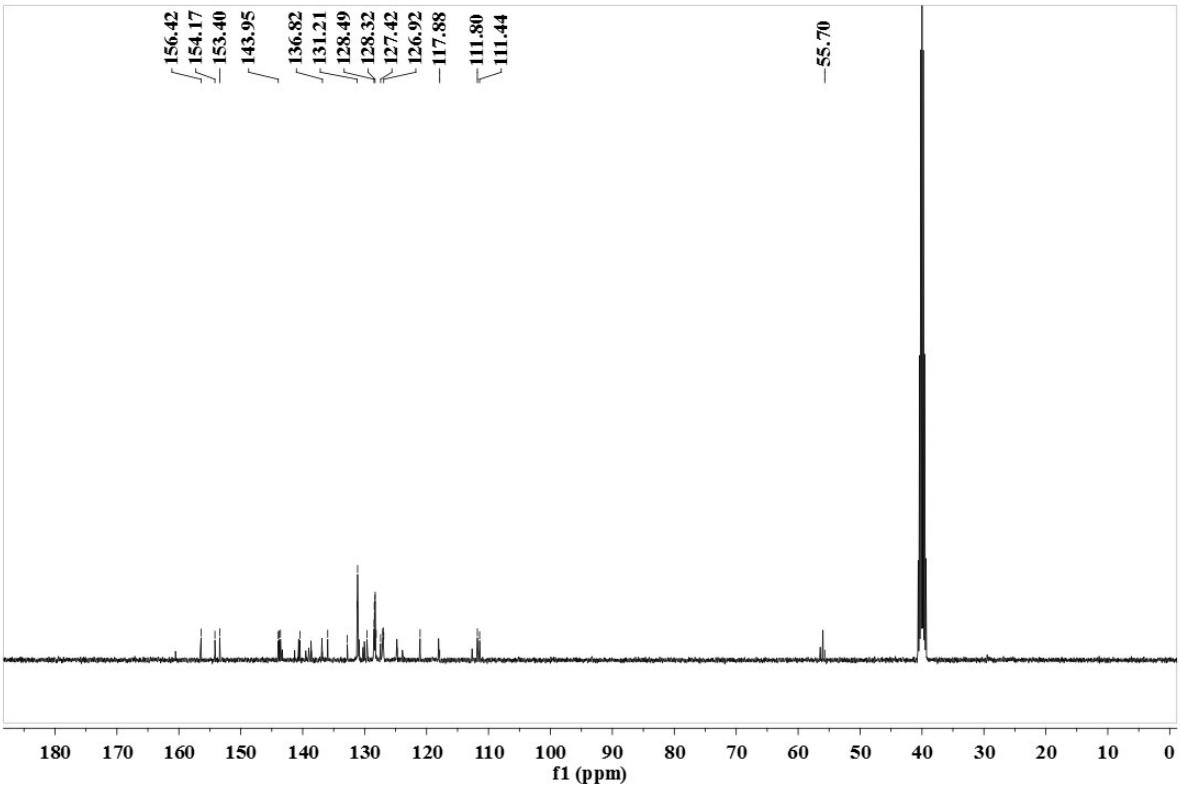


Fig. S8. ^{13}C NMR spectrum of TPE(OCH_3)-8HQ.

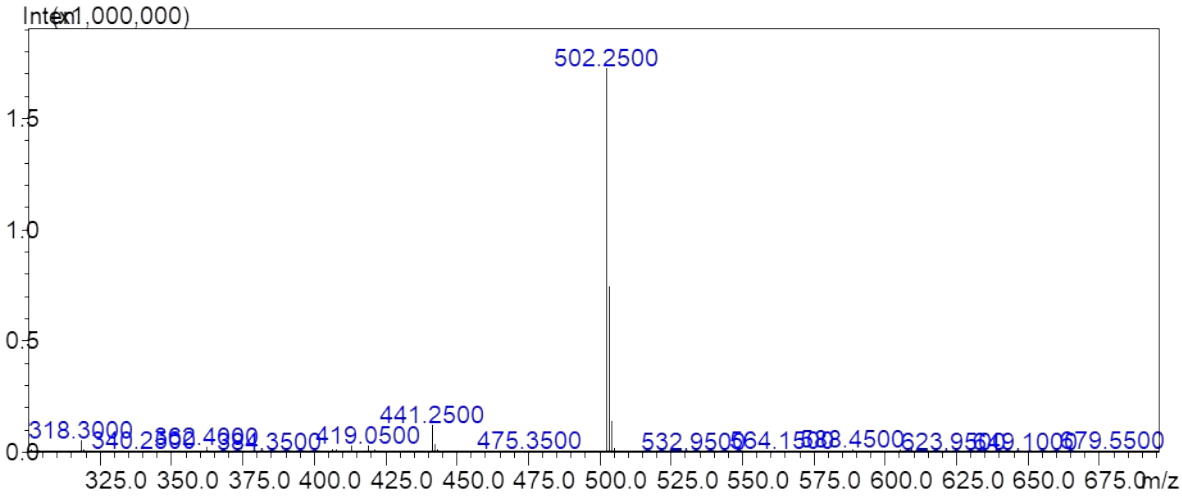


Fig. S9. Mass spectrum of TPE-8HQ

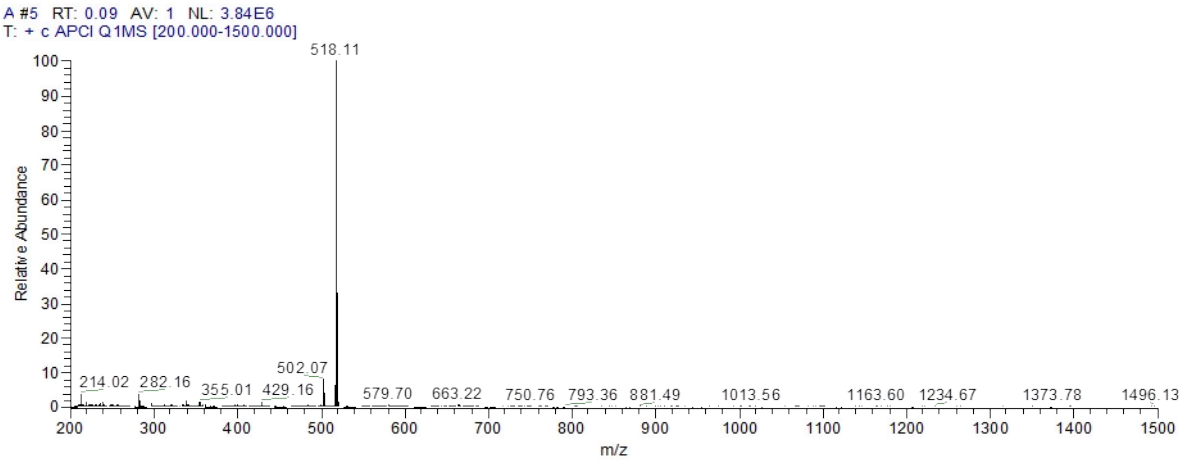


Fig. S10. Mass spectrum of TPE(OH)-8HQ

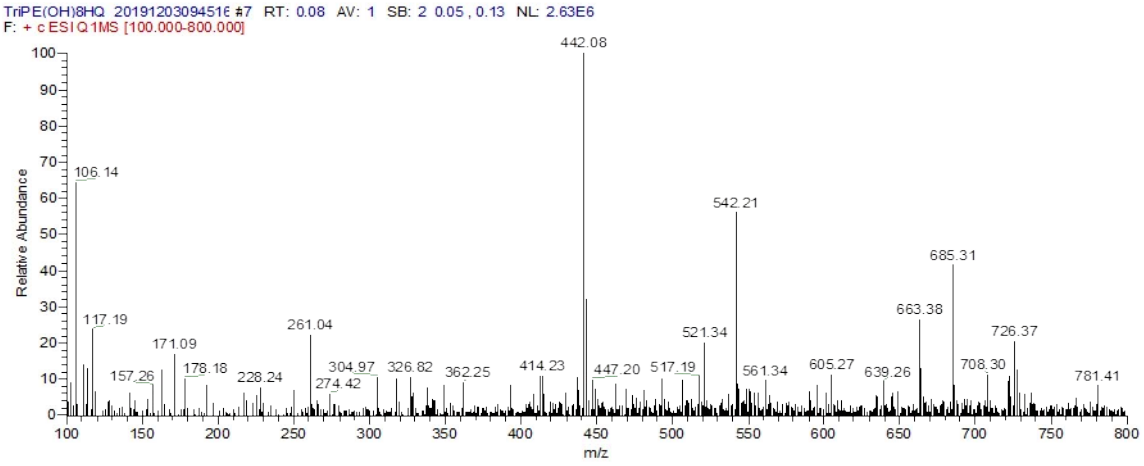


Fig. S11. Mass spectrum of TriPE(OH)-8HQ

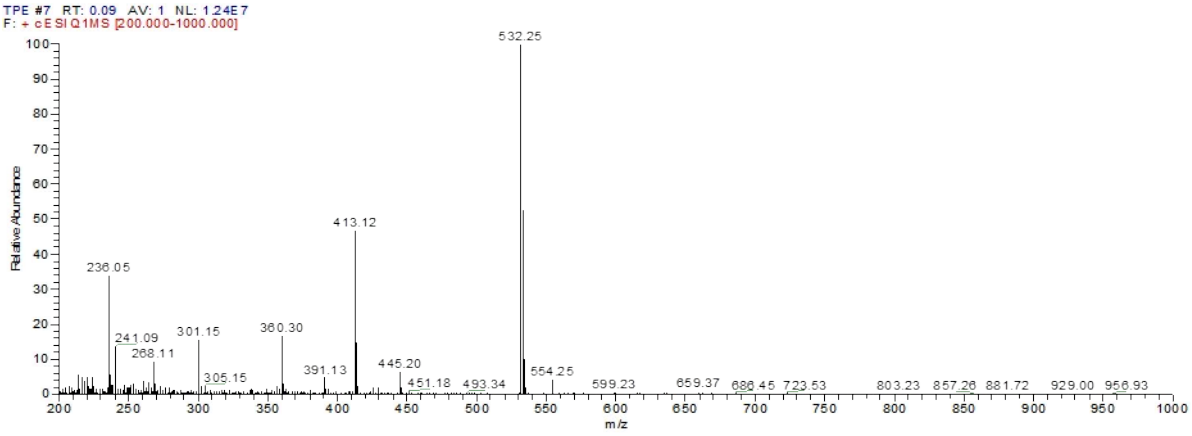


Fig. S12. Mass spectrum of TPE(OCH_3)-8HQ

3. IR spectrum of probe TPE(OH)-8HQ

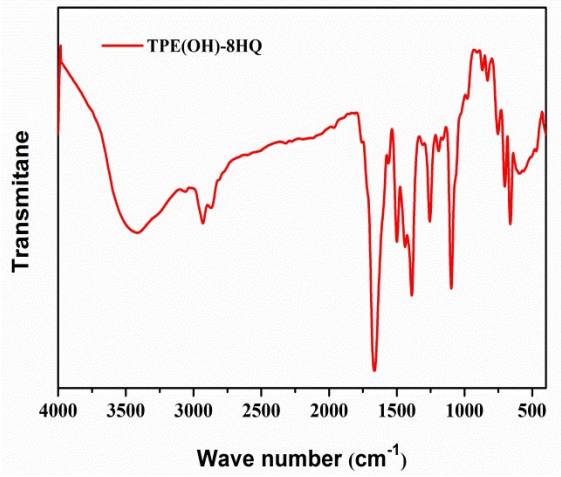


Fig. S13. IR spectrum of probe TPE(OH)-8HQ.

4. DLS characterization of the TPE-8HQ in ethanol and mixed solvent

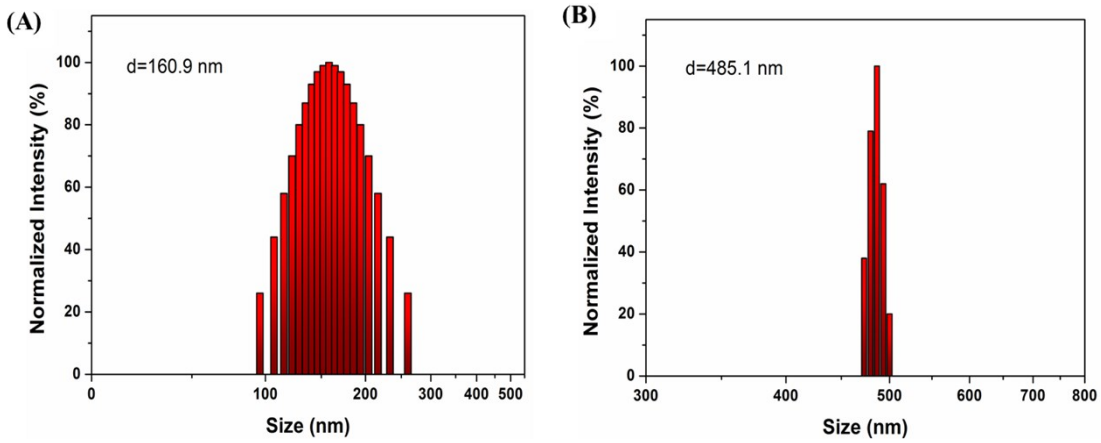


Fig.S14. DLS characterization of the **TPE-8HQ** in ethanol and mixed solvent (ethanol /H_2O = 9:1, v/v, 10 μM).

5. DLS characterization of the TPE(OH)-8HQ in ethanol and mixed solvent

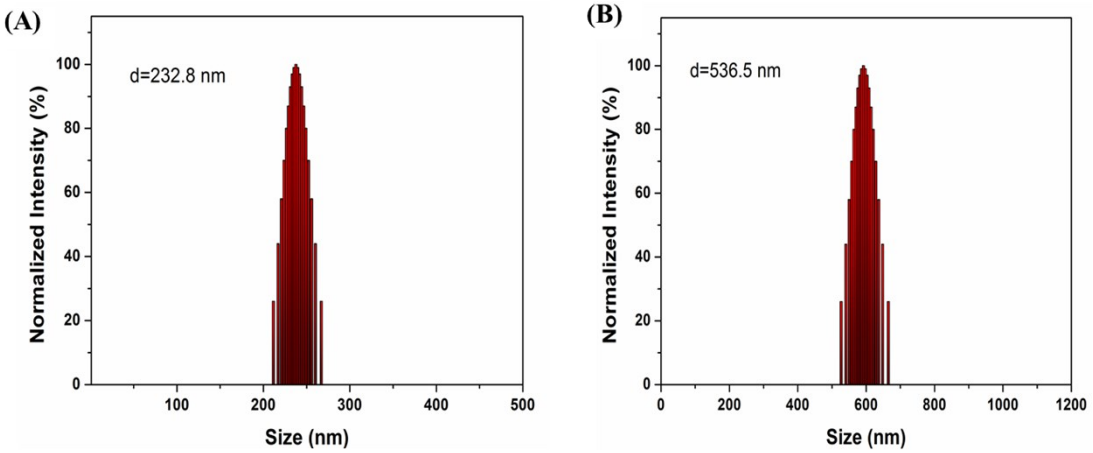


Fig.S15. DLS characterization of the **TPE(OH)-8HQ** in ethanol and mixed solvent (ethanol /H_2O = 9:1, v/v, 10 μM).

6. DLS characterization of the TriPE(OH)-8HQ in ethanol and mixed solvent

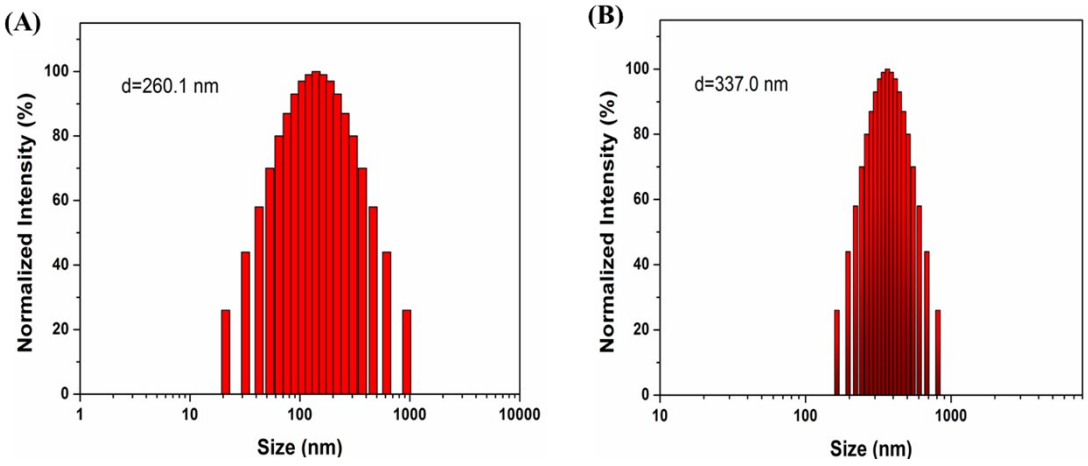
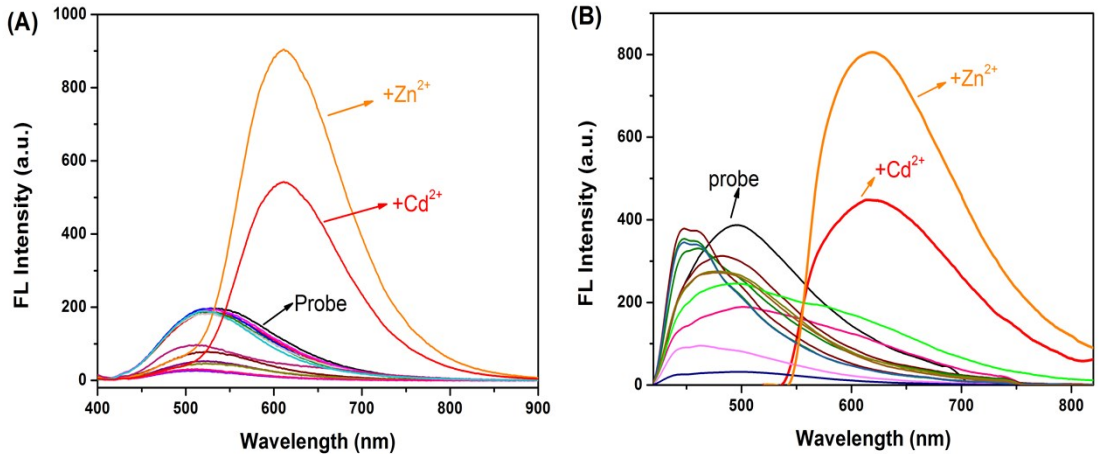


Fig.S16. DLS characterization of the **TriPE(OH)-8HQ** in ethanol and mixed solvent (ethanol /H_2O = 9:1, v/v, 10 μM).

7. Selectivity of probes toward Zn^{2+}



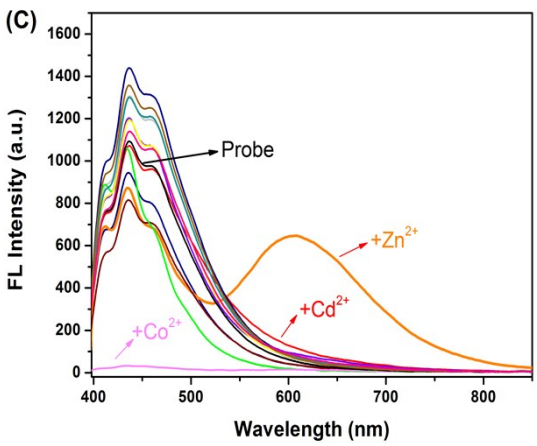


Fig.S17. Fluorescence emission spectra for (A) **TPE-8HQ**, (B) **TPE(OCH$_3$)-8HQ** and (C) **TriPE(OH)-8HQ** in C_2H_5OH /H_2O (9:1, v/v, 10 μM) after the addition of 10.0 eq of various metal ion (λ_{ex} = 380 nm).

8. Competitive experiment results of TriPE(OH)-8HQ

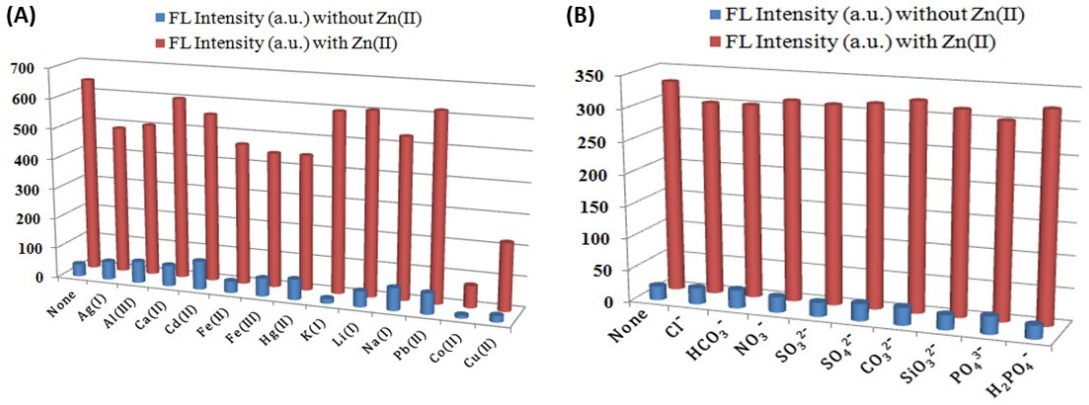


Fig. S18. (A) The fluorescent intensity at 605 nm of TriPE(OH)-8HQ (10 μM) with 50 μM of various metal ions, and then added 10 μM of Zn^{2+} in C_2H_5OH /H_2O (9:1, v/v) solution. (B)The fluorescent intensity of TriPE(OH)-8HQ (10 μM) with 50 μM of various anions, and then added 10 μM of Zn^{2+} in C_2H_5OH /H_2O (9:1, v/v) solution. (λ_{ex}=380nm).

9. The process of protonation and deprotonation of TPE(OH)-8HQ

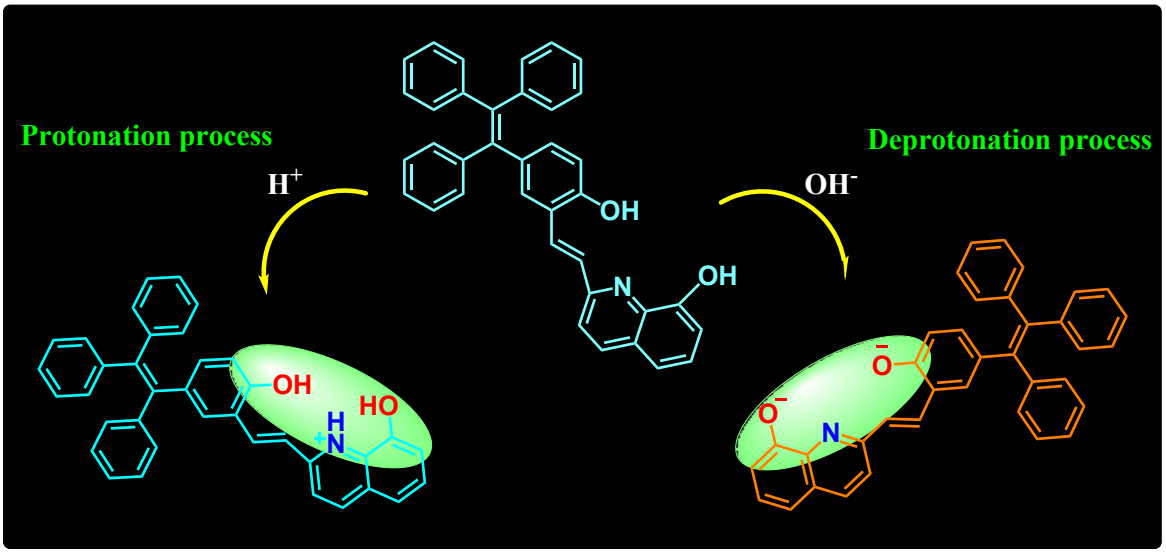
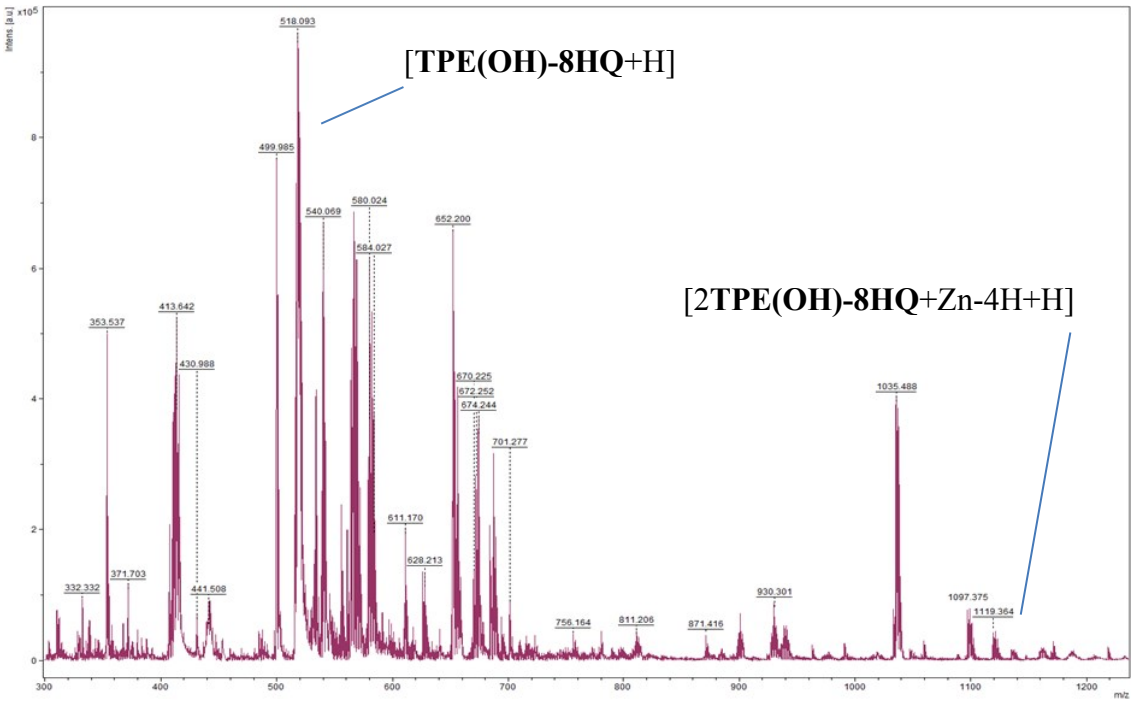


Fig. S19. The process of protonation and deprotonation of TPE(OH)-8HQ

10. Mass spectra analysis for probes-Zn^{2+} complex



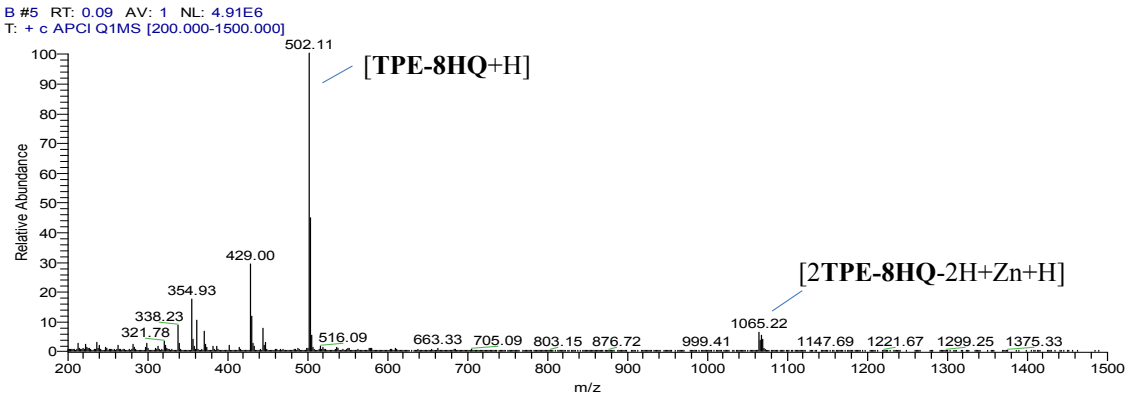


Fig. S20. Mass spectrum of **TPE(OH)-8HQ**(top) and **TPE-8HQ**(bottom) after added Zn^{2+} (5 equiv.) in the THF solution, indicating that the formation of a 2:1 probes-Zn^{2+} complex.

11. Calculation of the binding constant

Where K is the binding constant[5], ΔI is the difference between the intermediate coordination emission intensity and the probe emission intensity without the Zn^{2+} ion; ΔI_{max} is the fully coordinated emission intensity and the probe emission intensity without the Zn^{2+} ion; K is the binding constant; [M] is the Zn^{2+} ion concentration. The calculated binding constant K between TPE(OH)-8HQ and Zn^{2+} ion was 2.17×10^5 M^{-1}, and the binding constant indicates that the probe has strong binding ability to Zn^{2+} ions.

$$\frac{1}{\Delta I} = \frac{1}{\Delta I_{max}} + (1/K[M])(1/\Delta I_{max}) \quad \text{Eq. S1}$$

12. Calculation of the limit of detection

LOD is the limit of detection which was calculated based on equation (Eq.S2) [6], where σ is the standard deviation of the blank probe solution, S is the slope of the calibration plot in Fig.7(B).

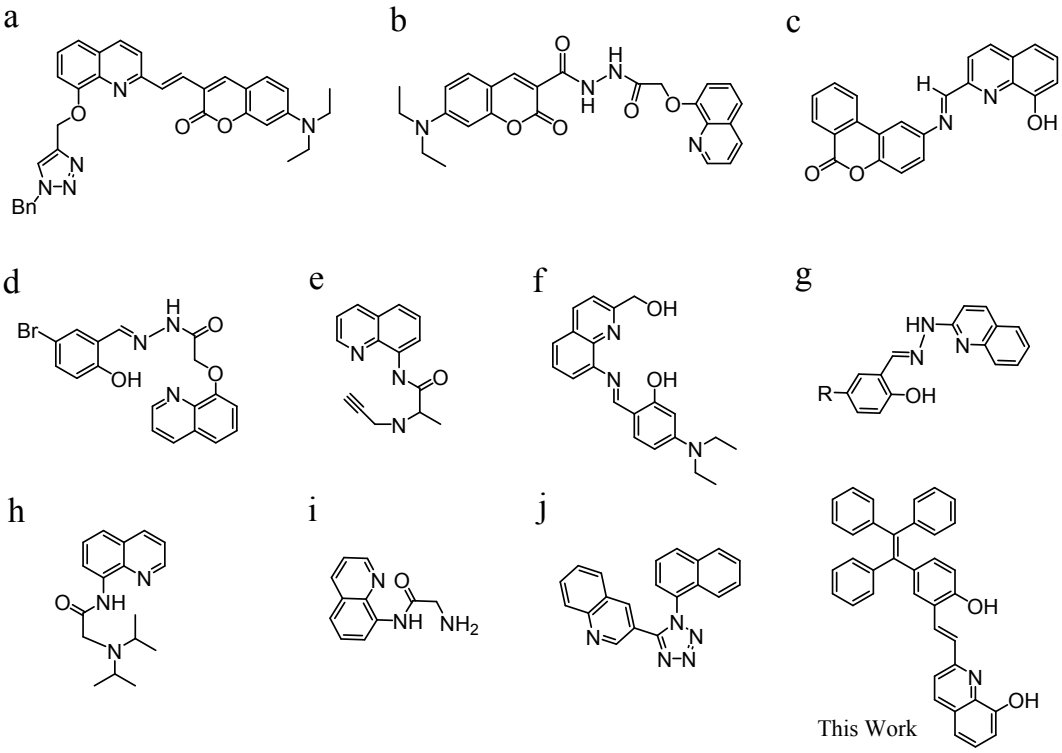
$$LOD = \frac{3\sigma}{s} \quad \text{Eq. S2}$$

13. Comparison of Zn^{2+} probes

Table S1

The structures of some quinoline contained fluorescent probes for Zn^{2+} in the previous literatures.

Comparison of some quinoline contained fluorescent probes for Zn^{2+} in the literatures.



Probe	λ_{em} /nm	LOD/10^{-6}M	Stokes Shift /nm	Reference
a	516	0.98	25	Ref. [7]
b	469	0.6	59	Ref. [8]
c	425	10	75	Ref. [9]
d	*	0.02	80	Ref. [10]
e	416	0.063	82	Ref. [11]
f	458	0.027	96	Ref. [12]
g	502	0.22	105	Ref. [13]
h	*	0.041	151	Ref. [14]
i	420	1.6	160	Ref. [15]
j	460	0.02	170	Ref. [16]
This Work	**470**	**0.164**	**289**	

"*"—The data is not given in the literature.

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