

Supporting Information for

A novel triple-mode fluorescent pH probe from monomer emission to aggregation-induced emission

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1 General Experimental Section

1.1 General Methods.

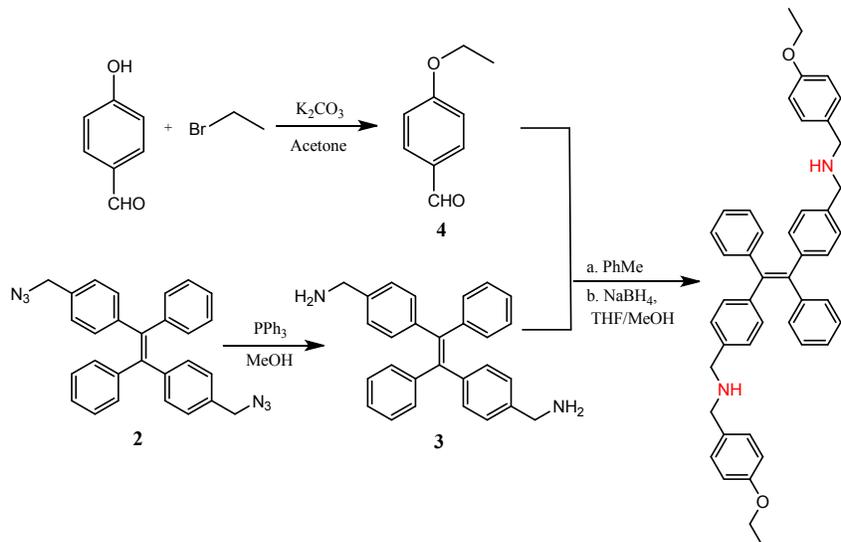
All of the chemicals were purchased from the commercial source and used as analytic grade without further purification except especially noted. The stock solutions of metal ions were prepared from LiCl, NaCl, KCl, MgSO₄, CaCl₂, Ba(NO₃)₂, Al(NO₃)₂•9H₂O, Pb(NO₃)₂, Cr₂(SO₄)₃, MnCl₂•4H₂O, FeCl₃•6H₂O, Cd(NO₃)₂•6H₂O, Ni(NO₃)₂•6H₂O, CuCl₂, AgNO₃, Zn(OAc)₂•2H₂O, CdCl₂•H₂O and HgCl₂ with doubly distilled water. NMR spectra were recorded at 25 °C on a Bruker AVANCE III 500 MHz (500 MHz and 125.72 MHz for ¹H and ¹³C nuclei, respectively) with chemical shifts reported in ppm (in CDCl₃, TMS as internal standard, and the multiplicities were expressed as follows: s = single, d = double, t = triplet, m = multiples). TLC analysis was performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300). ESI-MS spectral data were recorded on a TSQ Quantum-HPLC/MS/MS (Thermo, USA). Fluorescence spectrums were determined on a Perkin Elmer LS 55. The pH values of sample solution were monitored by a PHS-3 system. Spectroscopic and colorimetric measurements were carried out in THF (HPLC) and deionized water. Solution samples were measured in 1.00 cm quartz cell. All emission spectra were recorded at 25 °C and under atmospheric pressure. UV-vis spectra were measured on a Shimadzu UV3600. FT-IR spectrum was performed on an ATR accessory with a Nicolet IS-10 FT-IR spectrometer, in the wave number range 500–4000 cm⁻¹. Transmission electron microscope (TEM) images were recorded on a JEM-2100 instrument. Samples were prepared by dropping the solution onto a carboncoated copper grid.

1.2 General procedure for UV-vis and fluorescence studies

Stock solution of metal ions were prepared (1.0×10^{-2} M) in buffer solution pH = 6.86. A stock solution of probe **1** (1.0×10^{-5} M) was prepared in THF/H₂O (2:8, v/v) immediately before the experiments. Stock solution of base and acid solution were obtained from NaOH and HCl and diluted into different concentrations. In experiments, a 3 mL solution of probe **1** was filled in a quartz optical cell of 1 cm optical path length and the base and acid were added, pH value were collected before fluorescence test. For fluorescence measurements, excitation was provided at 305 nm and emission was collected from 325 nm to 590 nm. The excitation and emission slits were set to 3 and 3 nm, respectively.

2 Synthesis Section

2.1 Synthesis of probe 1^{S1,S2}



Scheme S1: Synthesis of probe 1.

A mixture of p-Hydroxybenzaldehyde (1.22 g, 10 mmol), bromoethane (1.39 g, 12 mmol) and Potassium carbonate (4.14 g, 30 mmol) in acetone (50 ml) was refluxed for 24 h in a 100 ml flask. Afterwards filtered and the solvent was removed under reduced pressure. Residue was resolved with ethyl acetate and washed with brine, dried with anhydrous $MgSO_4$, filtered, and concentrated. The residual compound was purified by chromatography on silica gel (EtOAc/PE = 6:1) to give compound 4 as a colorless oily liquid (1.08 g, 73% yield). 1H NMR (500 MHz, $CDCl_3$) δ (TMS ppm): 9.77 (s, 1H), 7.72 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 4.01 (d, $J = 7.0$ Hz, 2H), 1.34 (t, $J = 7.0$ Hz, 3H).

In a 100 ml three-necked flask, compound 2 (884 mg, 2 mmol) and PPh_3 (1.572 g, 6 mmol) was dissolved in 40 ml methanol and then heated under $70^\circ C$ for 2 h. Then, the mixture was cooled down to room temperature and the solvent was removed to get a yellow oil. HCl was added and a yellow solid was obtained. Filtered and the solid was washed with Et_2O , water was added to the filtrate and washed with Et_2O . The water layer was combined and aqueous ammonia was added to it. The solid was dissolved, extracted with dichloromethane. The organic layer was combined and dried over anhydrous $MgSO_4$, filtered, and concentrated. The residual compound was purified by flash chromatography on silica gel (EtOAc/ Et_3N = 100:5) to yield 3 as a yellow solid (0.41 g, 52.6% yield).

A mixture of **3** (405 mg, 1 mmol, 1 equiv.) and **4** (300 mg, 2 mmol, 2 equiv.) in toluene (50 mL), in a flask equipped with a Dean-Stark trap, was refluxed for 24 h. Afterward, solvents were evaporated under reduced pressure, and the residual oil obtained was directly dissolved in ethanol/tetrahydrofuran (v:v = 1:1) 40 ml. Sodium borohydride (NaBH₄; 0.15 g, 4 mmol, 4 equiv.) was added under ice bath, and the reaction mixture was stirred at 0 °C for 30 min and then refluxed for about 7 h. Afterward, water was added to quenching the reaction, extracted with dichloromethane. The organic layer was combined and washed with water, dried over anhydrous MgSO₄, filtered, and concentrated. The residual compound was purified by flash chromatography on silica gel (EtOAc/PE=3:1) to give compound **1** as yellow solid (285 mg, 43.3% yield). ¹H NMR (500 MHz, CDCl₃) δ (TMS ppm): 7.20 (d, J = 8.5 Hz, 4H), 7.13–6.99 (m, 14H), 6.97 (d, J = 8.1 Hz, 4H), 6.84 (d, J = 8.5 Hz, 4H), 4.02 (q, J = 7.0 Hz, 4H), 3.68–3.69 (m, 8H), 1.41 (t, J = 7.0 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 158.04, 143.86, 142.47, 140.70, 132.16, 131.39, 131.37, 129.44, 127.66, 127.51, 126.39, 114.41, 63.46, 52.74, 52.52, 14.91. ESI-MS m/z: 659.28 [M+H⁺]

3 Photophysical properties detail

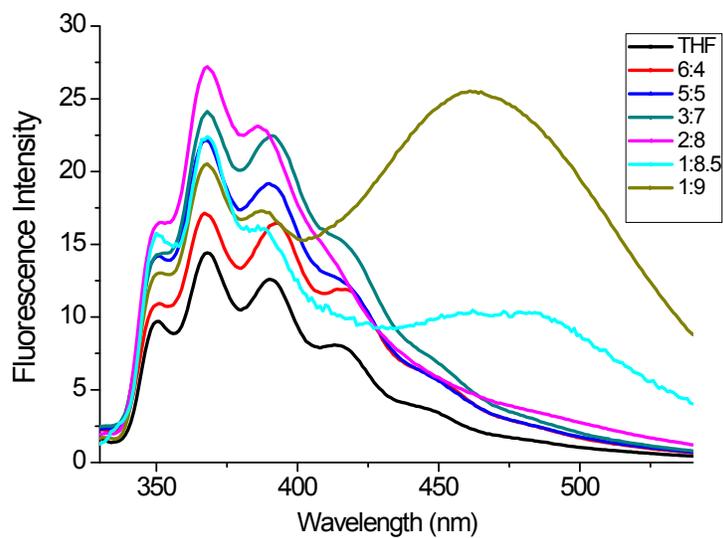


Fig. S1: Fluorescence spectra ($\lambda_{\text{ex}} = 305 \text{ nm}$) of probe **1** ($10 \mu\text{M}$) in a THF/H₂O binary solvent mixture.

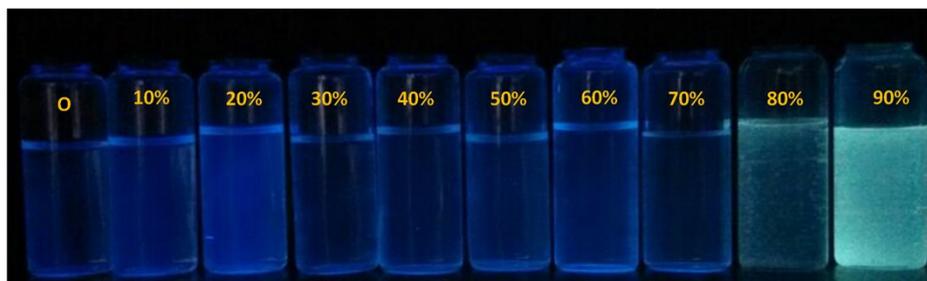


Fig. S2: Observed fluorescence changes of probe **1** ($10 \mu\text{M}$) under UV light (365 nm lamp) in a THF/H₂O binary solvent mixture (water fraction increased from left to right)

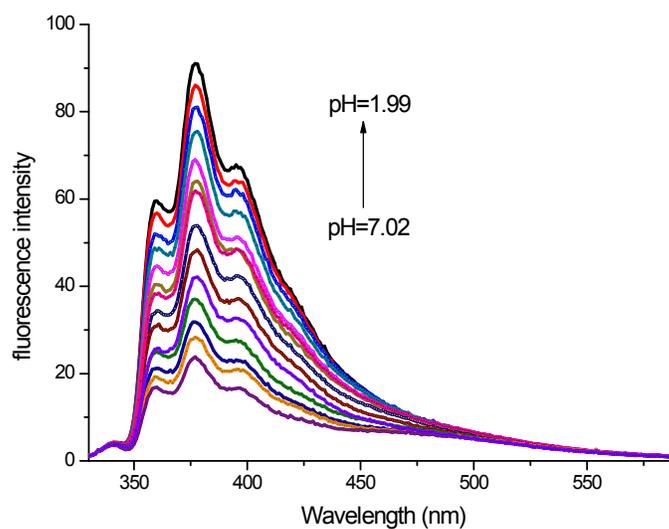


Fig. S3: Fluorescence responses to the probe **1** (10 μM) to different pH: 1.99, 2.01, 2.55, 2.98, 3.60, 4.00, 4.77, 5.08, 5.62, 6.58 and 7.02 in THF/H₂O (2:8, v/v)

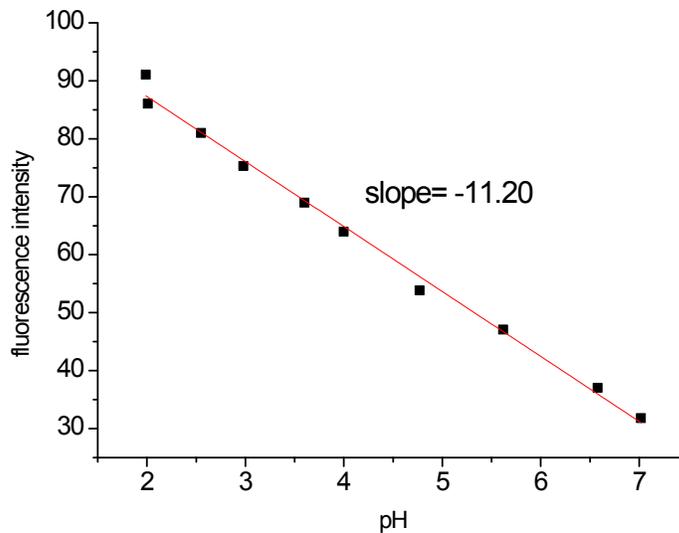


Fig. S4: The fluorescence emission changes at 377 nm with the pH titration curve of probe **1** (10 μM) in THF/H₂O (2:8, v/v), pH = 1.99~7.02

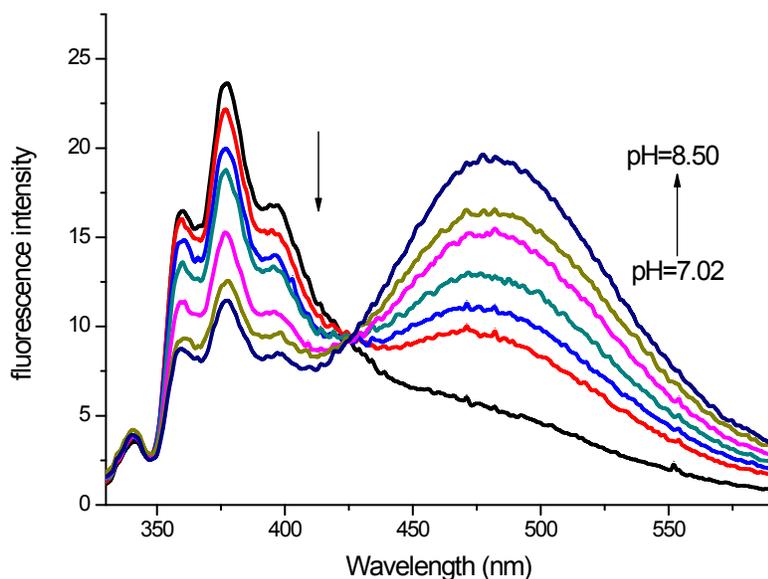


Fig. S5: Fluorescence responses to the probe **1** (10 μM) to different pH: 7.02, 7.24, 7.59, 7.85, 8.03, 8.43 and 8.50

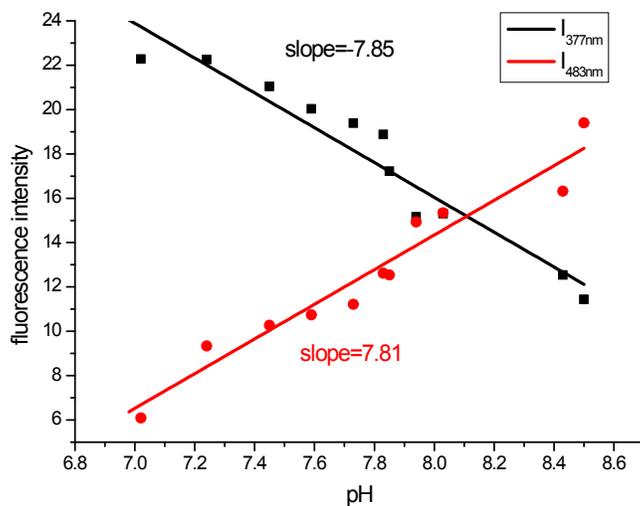


Fig. S6: The fluorescence emission changes at 377 nm with the pH titration curve of probe **1** (10 μM), pH = 7.02~8.50

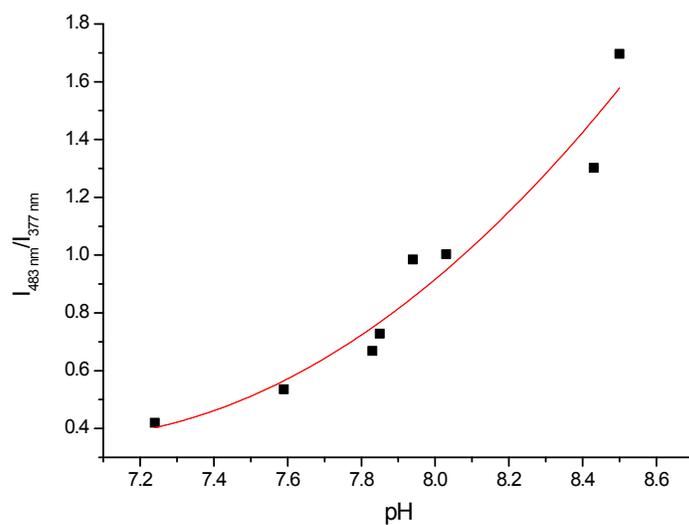


Fig. S7: Ration metric calibration curve $I_{483\text{ nm}}/I_{377\text{ nm}}$ (intensity at 483 nm vs intensity at 377 nm) of probe **1** (10 μM) to different pH from 7.02 to 8.50 in THF/ H_2O (2:8, v/v).

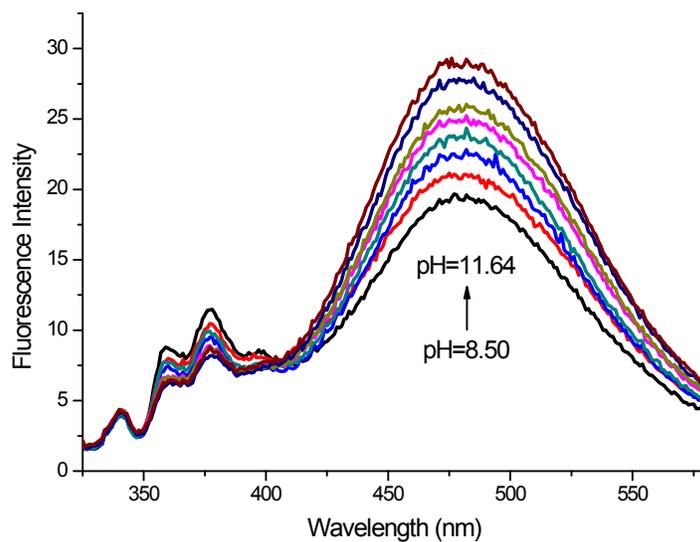


Fig. S8: Fluorescence responses to the probe **1** (10 μM) to different pH: 8.50, 8.94, 9.57, 10.11, 10.51, 10.74, 11.13 and 11.64 in THF/ H_2O (2:8, v/v)

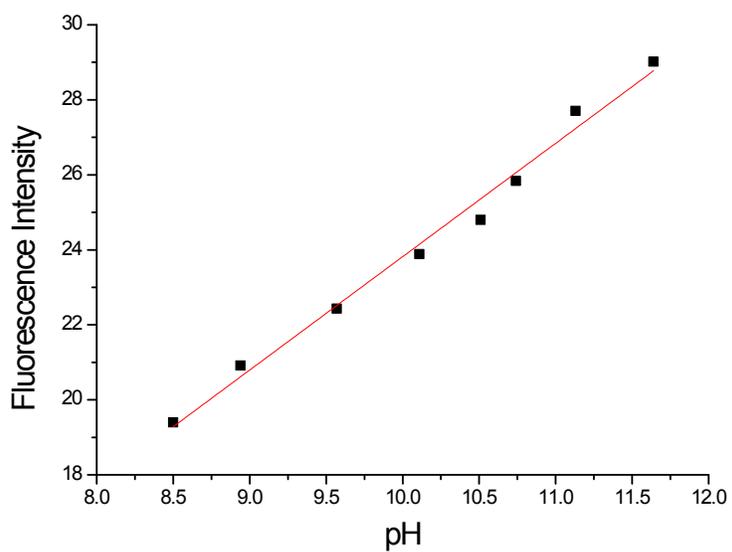


Fig. S9: The fluorescence emission changes at 483 nm with the pH titration curve of probe **1** (10 μM), pH = 8.50~11.64

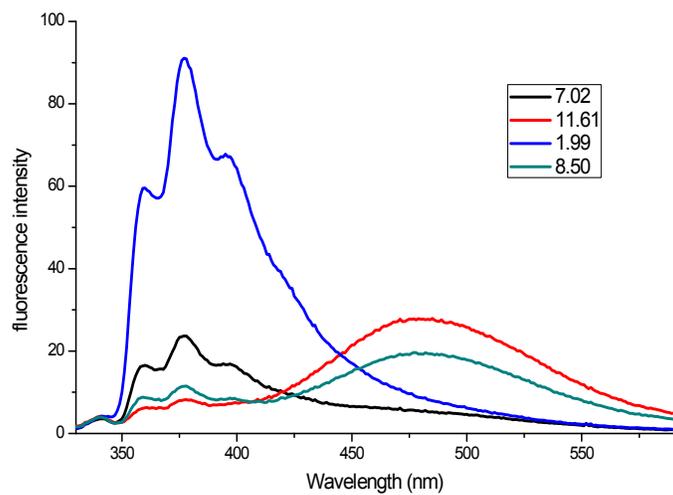


Fig. S10: Fluorescence intensity of probe **1** (10 μM) at different pH value in a solution of THF/ H_2O =(2:8, v/v) media

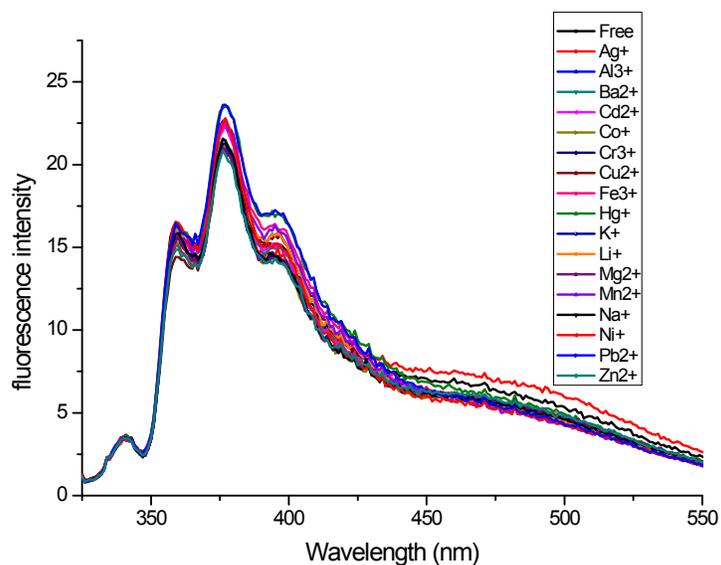


Fig. S11: Fluorescence response of probe **1** (10 μM) to various metal cations (4 equiv.) in THF/H₂O (2:8, v/v) medium.

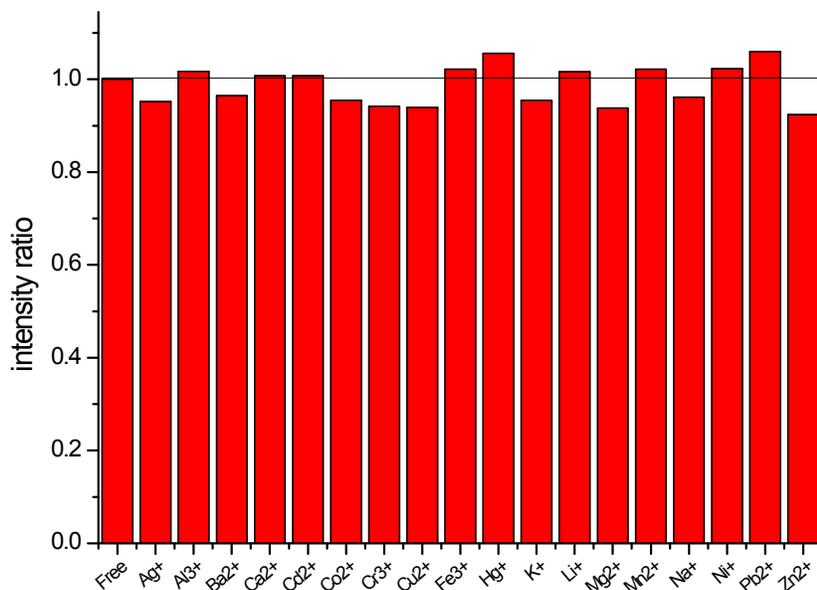
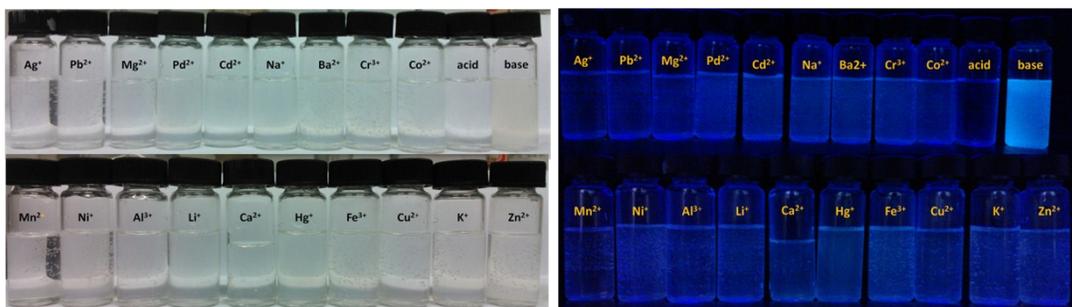


Fig. S12: Ratios of fluorescence intensity at 377 nm of probe **1** (10 μM) in the presence of various metal cations (4 equiv.) in aqueous solution of THF/H₂O (2:8, v/v)



(a) Visible light

(b) UV light (365 nm)

Fig. S13: Observed visual color and fluorescence change of probe **1** (10 μM) in a solution of THF/ H_2O (2:8, v/v) upon addition of various metal ions (4 equiv.), acid and base.

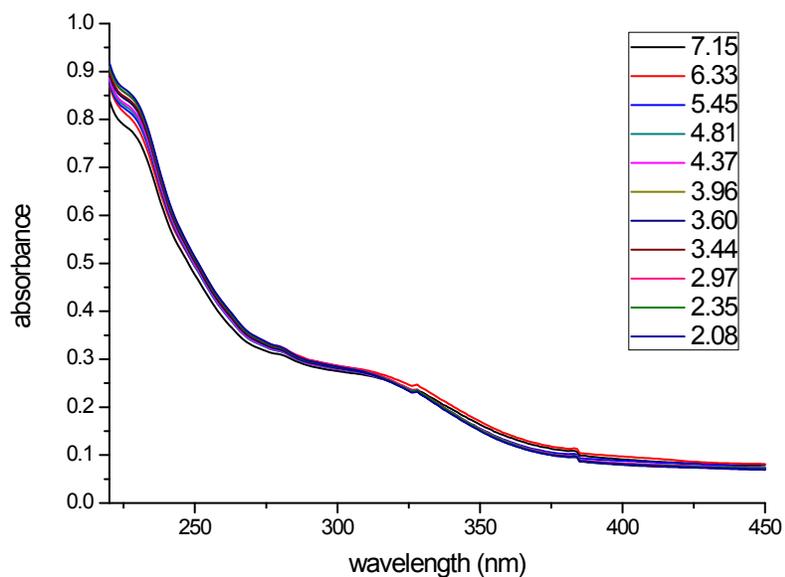


Fig. S14: Absorbance spectra of probe **1** (10 μM) in a solution of THF/ H_2O (2:8, v/v) to different pH from 2.08 to 7.15.

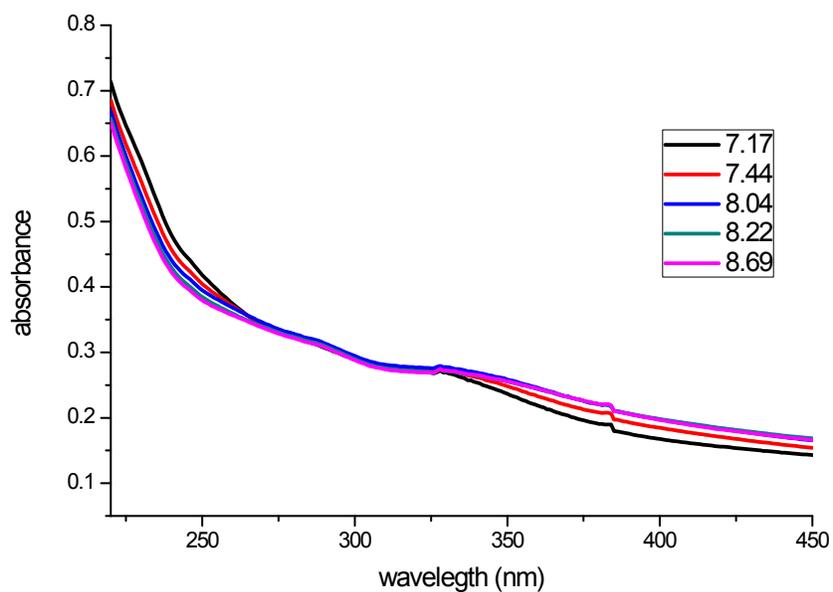


Fig. S15: Absorbance spectra of probe **1** (10 μM) in a solution of THF/H₂O (2:8, v/v) to different pH from 7.17 to 8.69.

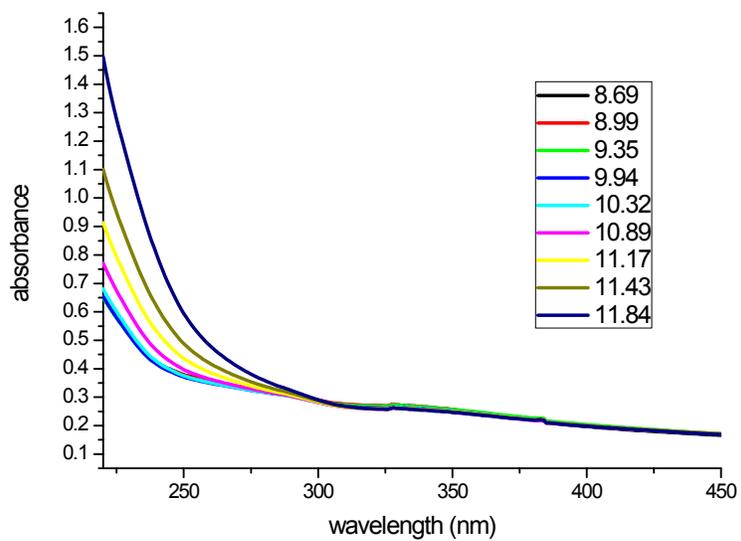


Fig. S16: Absorbance spectra of probe **1** (10 μM) in a solution of THF/H₂O (2:8, v/v) to different pH from 8.69 to 11.84.

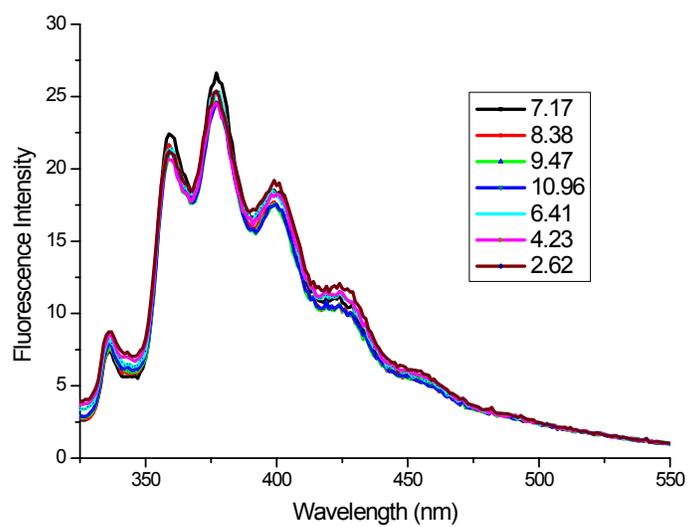


Fig. S17: Fluorescence intensity of probe **1** responses to different pH in a solution of THF (10 μM)

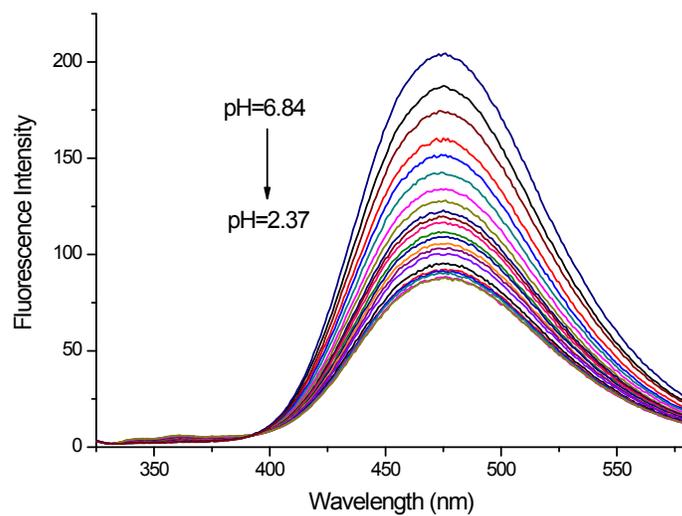


Fig. S18: Fluorescence intensity of probe **1** response under acidic condition (pH changed from 6.84 to 2.37) in a solution of water (10 μM)

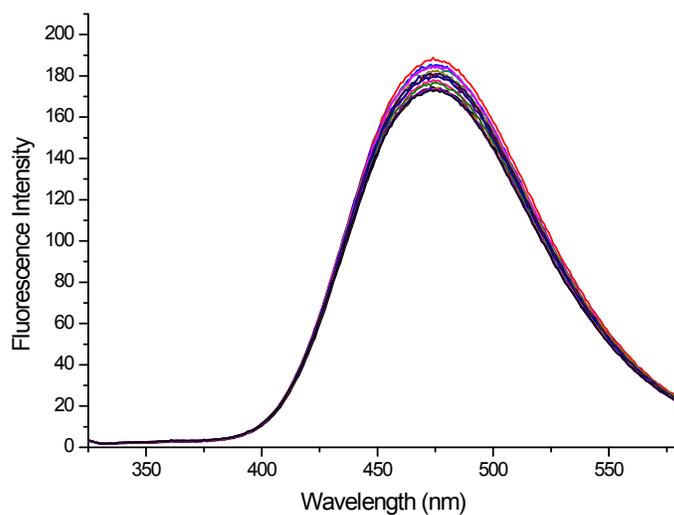


Fig. S19: Fluorescence intensity of probe **1** response with the addition of base (pH changed from 6.84 to 10.73) in a solution of water (10 μ M)

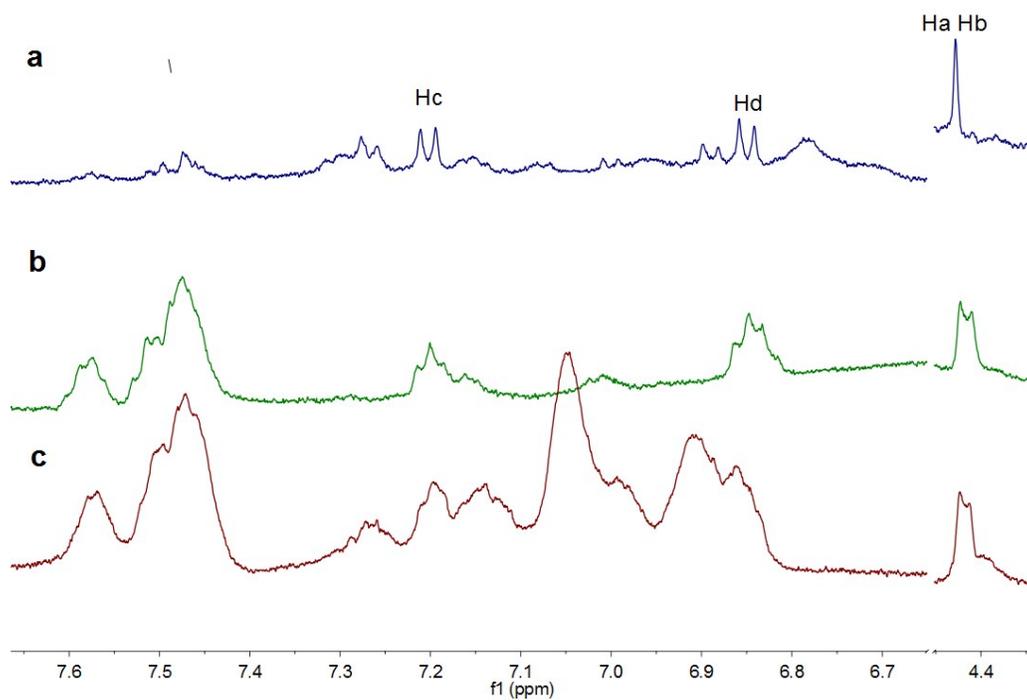


Fig. S20: Change of ^1H NMR spectra of probe **1** in d_8 -THF / D_2O . (a) with the addition of 4 equiv. CF_3COOH ; (b) with the addition of 4 equiv. NaOH ; (c) without any addition

4 ¹H NMR, ¹³C NMR mass spectra and FT-IR spectra



Fig. S21: ¹H NMR of compound 1 in CDCl₃

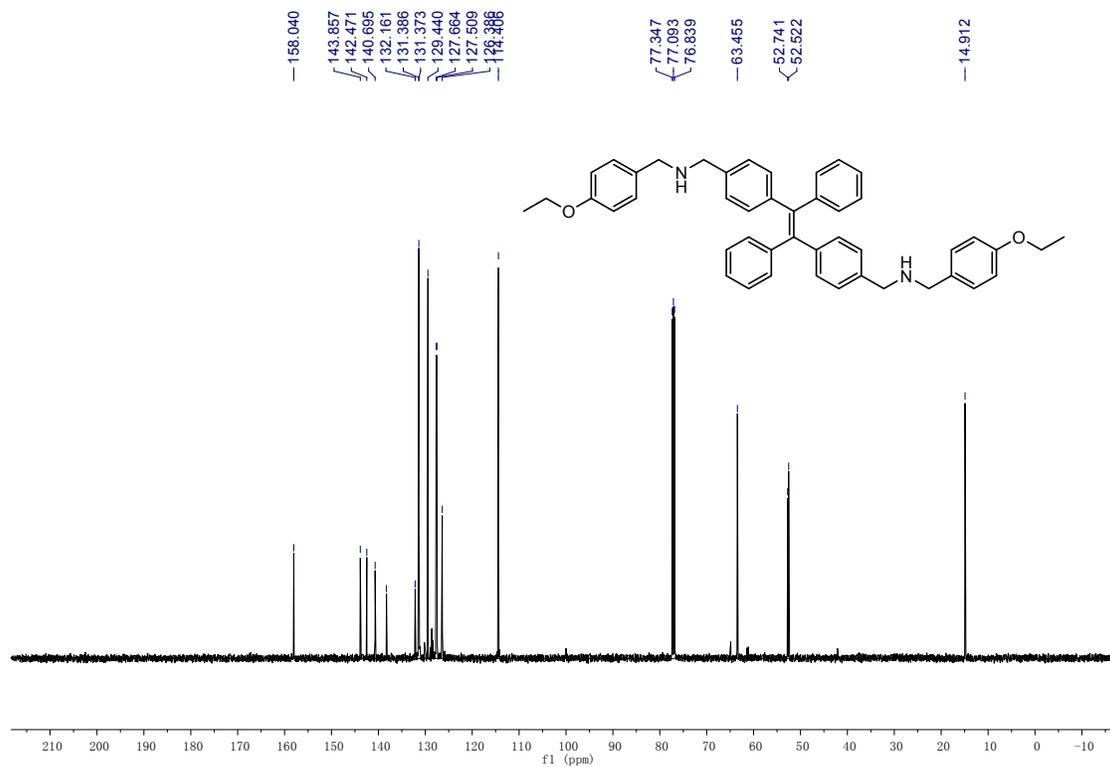


Fig. S22: ¹³C NMR of compound 1 in CDCl₃

20140509-WZH #20 RT: 0.25 AV: 1 NL: 7.04E7
T: + e sid=-20.00 Q1MS [570.90-800.00]

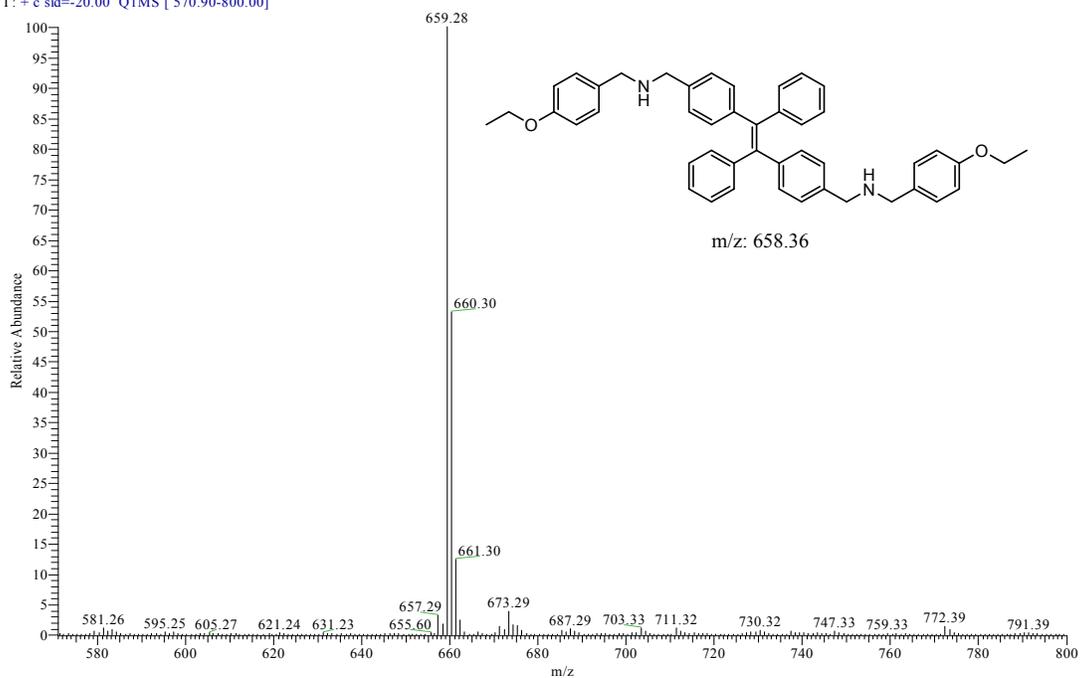


Fig. S23: MS (ESI) spectrum of compound 1

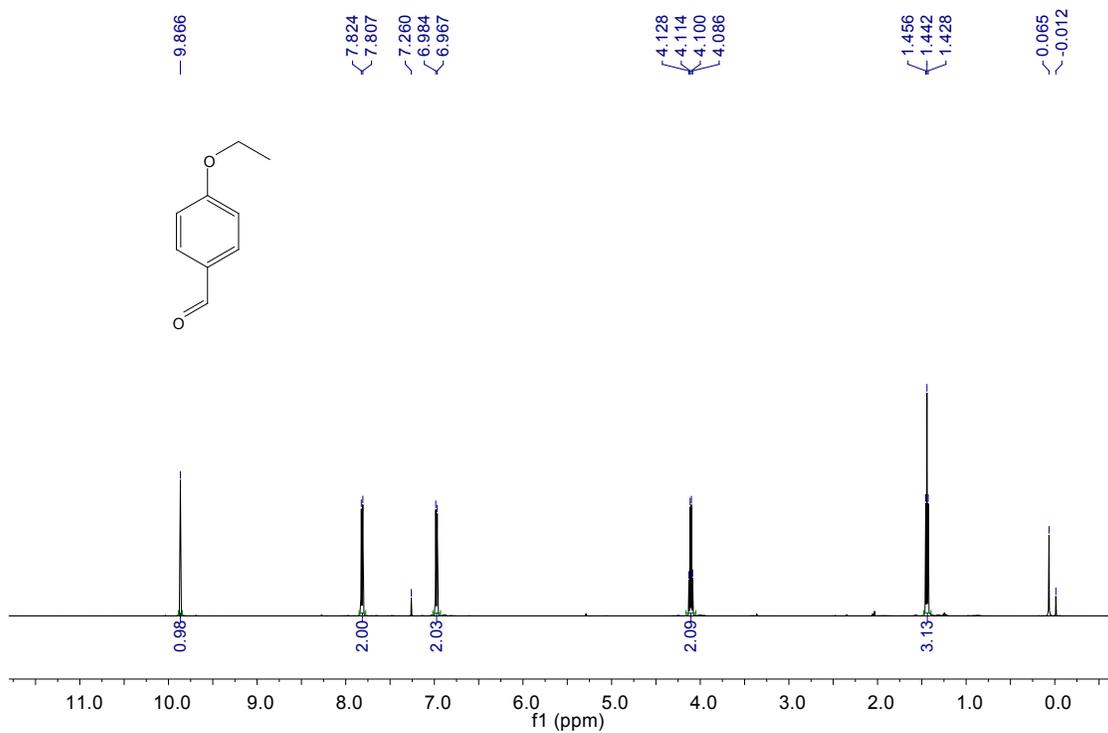


Fig. S24: ^1H NMR of compound 4 in CDCl_3

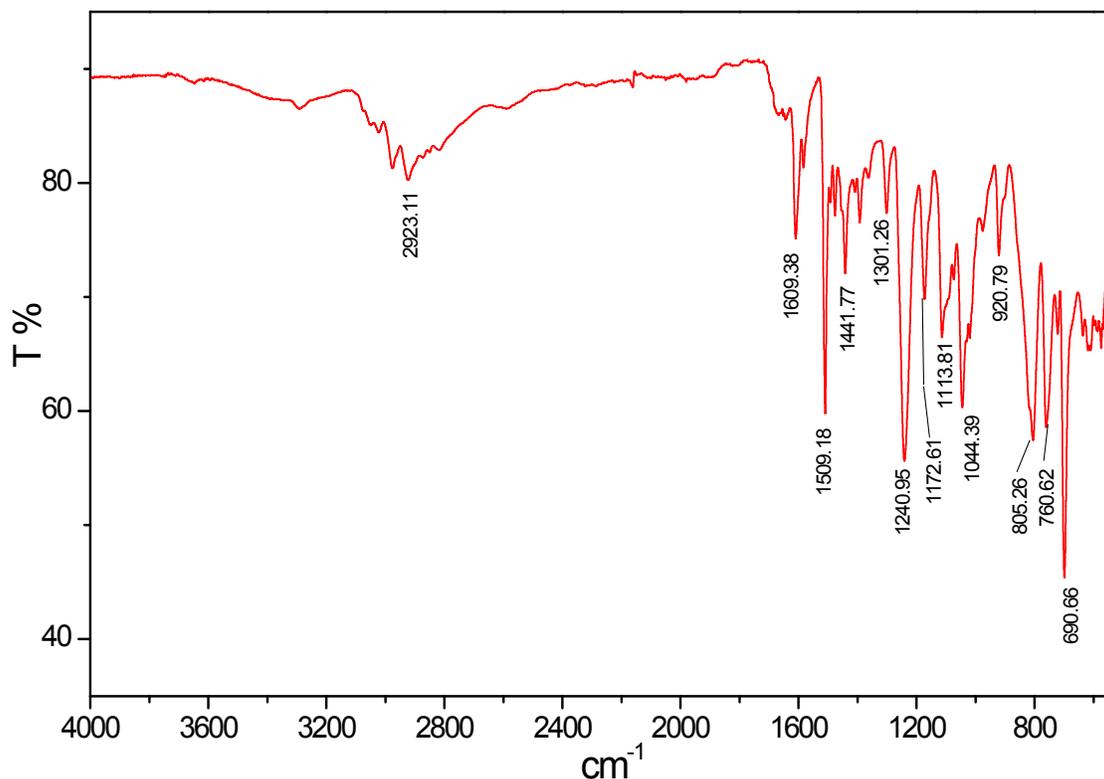


Fig. S25: FT-IR of compound **1**

The FT-IR analysis was carried out, as displayed in Fig. S25. The compound **1** shows characteristic absorption at 2923 cm⁻¹ corresponding to the asymmetric and symmetrical stretch vibration of N-H, at 1609 cm⁻¹ assigned to the stretching vibration of C=C of TPE core, at 1509 and 1441 cm⁻¹ due to the phenyl rings backbone (skeletal vibration), at 1240 cm⁻¹ caused by the vibration of C-O, at 1113 and 1044 cm⁻¹ belong to C-C backbone (skeletal vibration), at 805, 760 and 690 cm⁻¹ related to Ar-H out-of-plane bending vibration.

5 Calculation of fluorescence quantum yields

The absolute quantum yields were measured, referring to the procedure in the literature.^{S3} They were calculated by using following equation:

$$\Phi_u = (\Phi_s \cdot F_u \cdot A_s \cdot \eta_u^2) / (F_s \cdot A_u \cdot \eta_s^2)$$

Where the subscripts s and u denote standard and test respectively, Φ is the fluorescence quantum yield, F is the integrated fluorescence intensity (area) spectra, A is the integrated absorbance area spectra, and η the refractive index of the solvent.

6 TEM images

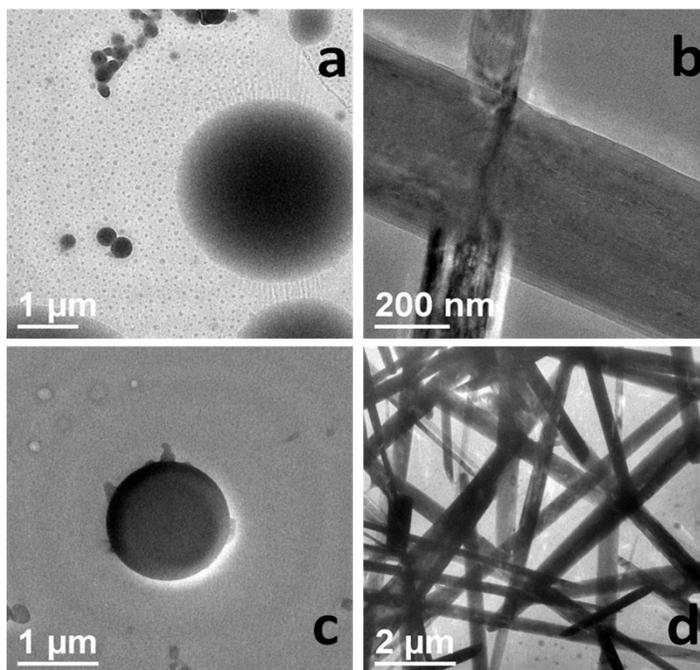


Fig. S26: TEM images of compound **1** with the addition of (a and c): acid; (b and d) base in THF/H₂O mixture.

7 References

- S1. J.-H. Ye, L. Duan, C. Yan, *et al.*, *Tetrahedron Letters*, 2012, **53**, 593.
- S2. C. Anastasi, O. Hantz, E. De Clercq, *et al.*, *Journal of Medicinal Chemistry*, 2004, **47**, 1183.
- S3. Albert M. B., *Pure Appl. Chem.*, 2011, **83**, 2213.