

Electronic Supplementary Information (ESI†)

A Cu(II)-based chemosensing ensemble bearing rhodamine B fluorophore for fluorescence turn-on detection of cyanide

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1. General information and methods. All reagents and solvents were purchased from commercial sources and were of the highest grade. Solvents were dried according to standard procedures. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC). Flash chromatography (FC) was performed using silica gel 60 (200–300 mesh). Absorption spectra were taken on an Agilent 8453 spectrophotometer. Fluorescence spectra were taken on HITACHI F-2500 fluorescence spectrometer. The ^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75MHz, respectively. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High resolution mass spectra were obtained on a Varian QFT-ESI mass spectrometer.

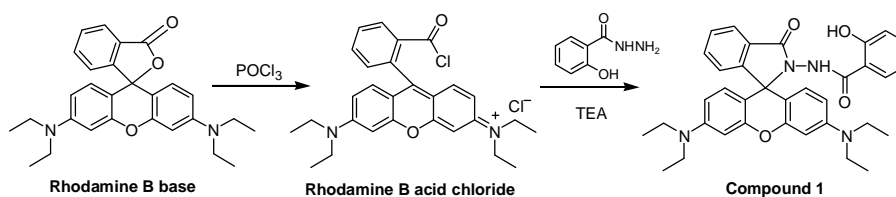
2. Procedures of ions sensing: Deionized water was used throughout all experiments. Solutions of Fe^{2+} and Ca^{2+} were prepared from their chloride salts; solutions of Na^+ , K^+ , Ag^+ , Mg^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , Hg^{2+} , Pb^{2+} , Cr^{3+} , and Fe^{3+} were prepared from their nitrate salts; all anions were prepared from their sodium salts. A stock solution of **1** (25 mM) was prepared in DMF. The stock solution of **1** was then diluted to the corresponding concentration (10 μM , 5 μM and 1 μM) with the corresponding buffer solution [MeCN/water (9:1, v/v) buffer solution (10 mM Tris-HCl, pH 7.0)]. The Cu^{2+} stock solution of 1.0×10^{-1} M was diluted to 2.5×10^{-2} M with deionized water for spectra titration studies. The sodium cyanide stock solution of 1.0×10^{-1} M was diluted to 1.0×10^{-2} M and 1.0×10^{-3} M with deionized water for spectra titration studies. In the titration experiments, a 2.5 mL solution of **1** (10 μM , 5 μM and 1 μM) was poured into a quartz optical cell of 1 cm optical path length each time, and Cu^{2+} solution or CN^- was added into the quartz optical cell gradually by using a micro-pipette. Spectra data were recorded in an indicated time after the addition.

3. Crystallography: Crystal data for **1**, $\text{C}_{35}\text{H}_{35}\text{N}_4\text{O}_4$, $M = 575.67$, Triclinic, space group P-1, $a = 8.9420$ (18) Å, $b = 13.149$ (3) Å, $c = 14.670$ (3) Å, $\alpha = 68.23$ (3) $^\circ$, $\beta =$

84.59 (3) $^\circ$, $\gamma = 75.23$ (3) $^\circ$, $V = 1548.9$ (5) \AA^3 , $\mu = 0.082$ mm^{-1} , $Z = 2$, $T = 293$ (2) K, crystal dimensions $0.20 \times 0.18 \times 0.12$ mm^3 , θ range $1.49\text{--}25.02^\circ$. 15814 reflections were collected of which 5421 reflections were unique ($R_{\text{int}} = 0.0655$). Final R indices [$I \geq 2\sigma(I)$]: $R_1 = 0.0666$, $wR_2 = 0.1276$, R indices (all data): $R_1 = 0.1226$, $wR_2 = 0.1534$, goodness of fit on $F^2 = 1.024$. CCDC 798181.

Crystal data for **1**- Cu^{2+} complex, $\text{C}_{74}\text{H}_{74}\text{Cl}_4\text{Cu}_4\text{N}_{10}\text{O}_8 \cdot 2\text{CH}_3\text{CN}$, $M = 1709.50$, Monoclinic, space group $\text{P}2(1)/n$, $a = 12.2737(19)$ \AA , $b = 24.368(4)$ \AA , $c = 12.7780(19)$ \AA , $\alpha = 90.00^\circ$, $\beta = 99.816(2)^\circ$, $\gamma = 90.00^\circ$, $V = 3765.7(10)$ \AA^3 , $\mu = 1.321$ mm^{-1} , $Z = 2$, $T = 296(2)$ K, crystal dimensions $0.30 \times 0.20 \times 0.20$ mm^3 , θ range $1.67\text{--}25.05^\circ$. 39971 reflections were collected of which 6666 reflections were unique ($R_{\text{int}} = 0.0565$). Final R indices [$I \geq 2\sigma(I)$]: $R_1 = 0.0583$, $wR_2 = 0.1480$, R indices (all data): $R_1 = 0.0810$, $wR_2 = 0.1613$, goodness of fit on $F^2 = 1.296$. CCDC 845820.

4. Synthesis of compound 1:



A solution of rhodamine B base (0.44 g, 1 mmol) in 1,2-dichloromethane (15 mL) was stirred, and phosphorus oxychloride (0.4 mL) was added dropwise over 10 minutes. The solution was refluxed for 4 h. The reaction mixture was cooled and the solvent was evaporated in vacuo to give rhodamine B acid chloride, which was directly used for next step without further purification.

The crude acid chloride was dissolved in dry acetonitrile (30 mL) and added dropwise over 2 h to a solution of salicylic hydrazide (0.15 g, 1 mmol) containing TEA (0.8 mL) in acetonitrile (20 mL) at room temperature. The reaction mixture was then stirred at room temperature for 4 h. The solvent was evaporated in vacuo to give crude product, which was purified by column chromatography (PE : EtOAc, 10 : 1, v/v) to provide pure **1**. Yield: 0.41 g, 71 %. $^1\text{H NMR}$ (300MHz, $\text{DMSO-}d_6$): δ 11.41

(b, 1H), 9.99 (b, 1H), 7.85 (d, $J = 6.6$, 1H), 7.68 (d, $J = 7.5$, 1H), 7.55 (m, 2H), 7.34 (t, $J = 7.5$, 1H), 7.05 (d, $J = 6.9$, 1H), 6.84 (m, 2H), 6.57 (d, $J = 8.7$, 2H), 6.35 (d, $J = 9.3$, 2H), 6.29 (s, 2H), 3.29 (q, $J = 6.6$, 8H), 1.04 (t, $J = 6.6$, 12H). ^{13}C NMR (75MHz, DMSO- d_6): 165.6, 159.9, 155.0, 150.2, 135.6, 134.9, 131.0, 130.1, 125.7, 124.5, 120.7, 118.8, 109.3, 106.0, 98.9, 67.0, 45.6 14.27. HRMS (ESI) calcd. for $(\text{M} + \text{H})^+$ 577.2814, found 577.2814.

5. Supplemental spectra data

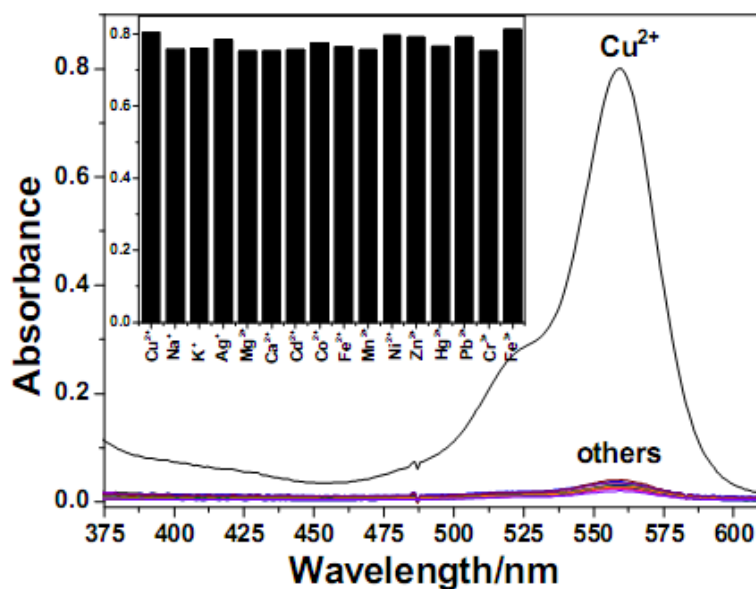


Fig. S1 The absorption spectra of **1** (10 μM) upon addition of 1 equiv. of Cu²⁺ and various other metal ions, including of Ag⁺, Cd²⁺, Co²⁺, Cr³⁺, Fe³⁺, Fe²⁺, Hg²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Mn²⁺ (3 equiv.); Ca²⁺, K⁺, Mg²⁺, and Na⁺ (30 equiv.), in 9:1 (v/v) MeCN/water solution (10 mM Tris-HCl, pH 7.0). Inset: spectra response of **1** to Cu²⁺ containing various metal ions.

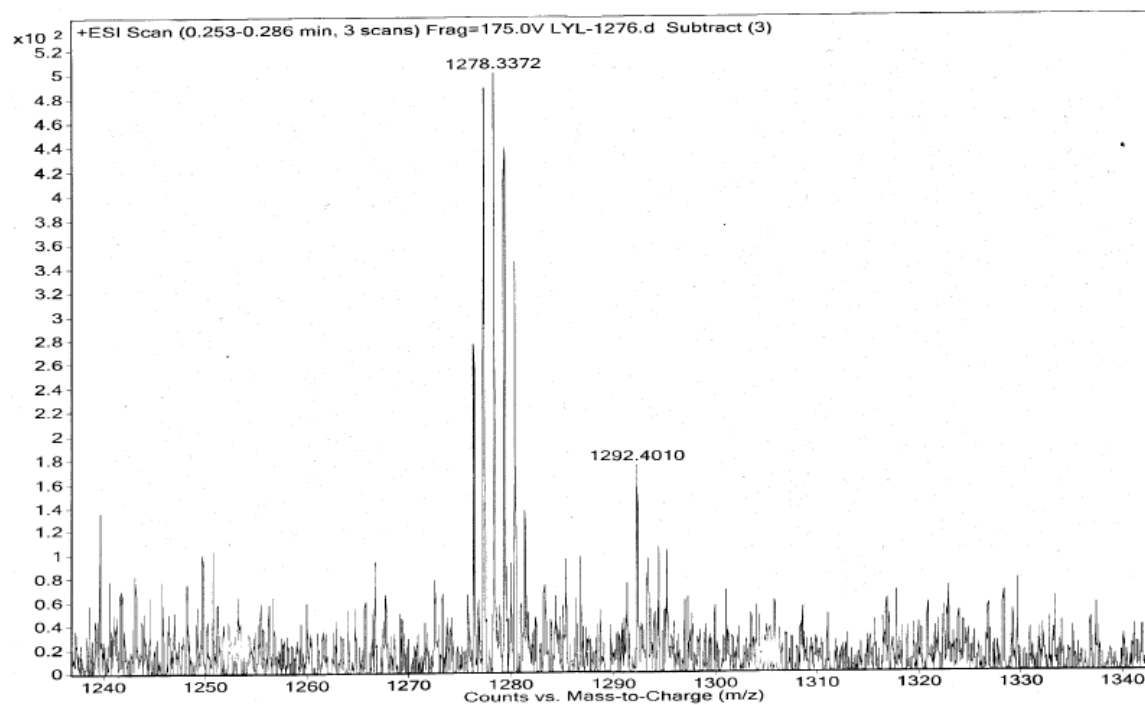


Fig. S2 ESI-MS chart of **1·Cu**.

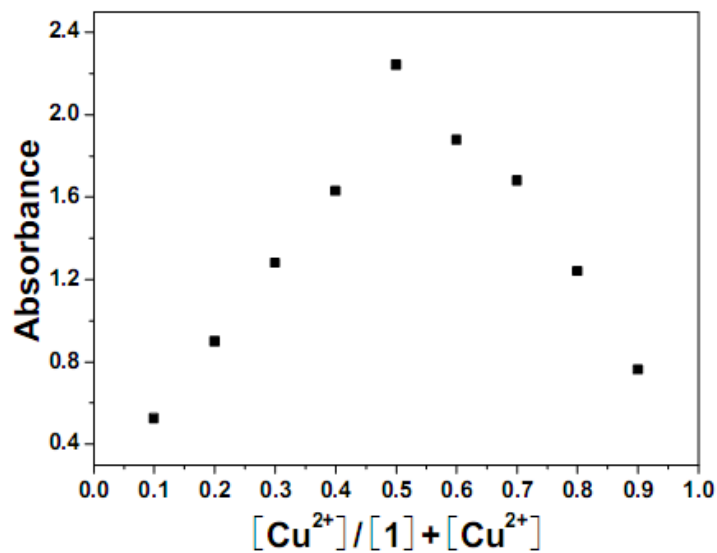
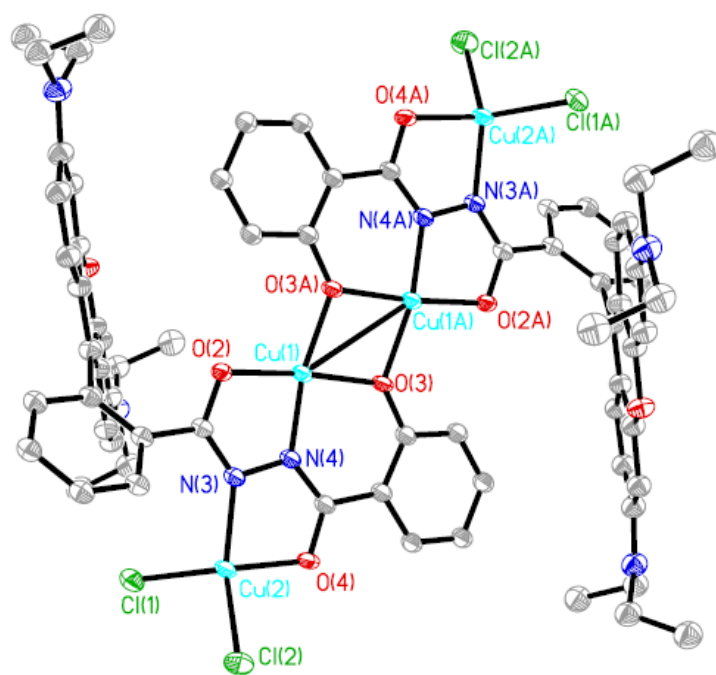
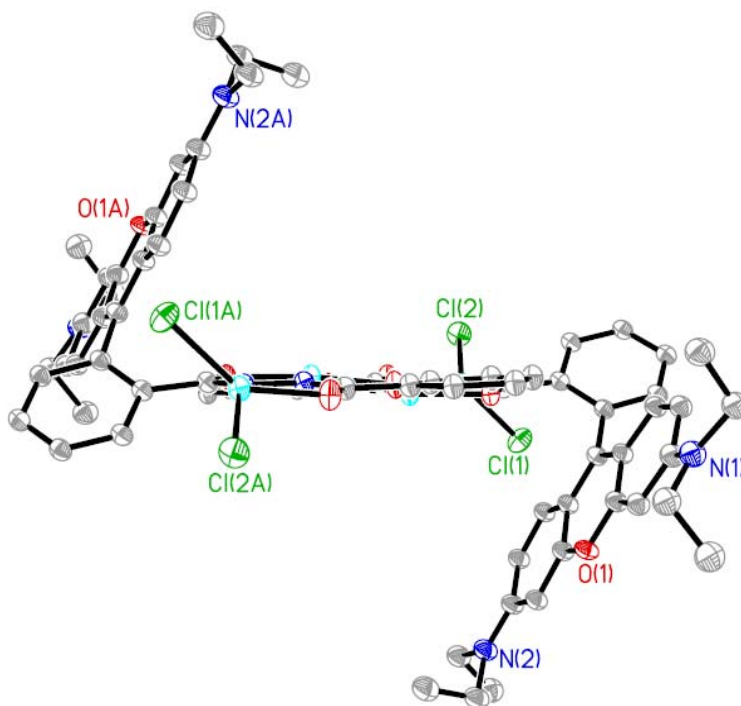


Fig. S3 Job's plots of the complexation between **1** and Cu²⁺. Total concentration of **1** + Cu²⁺ was kept constant at 100 μM.



(a)



(b)

Fig. S4 (a) Crystal structure of the **1**-Cu²⁺ complex, face-on view, with displacement atomic ellipsoids drawn at the 30% probability level. (b) Side view of the structure in (a) showing nearly planar molecular conformation of central moiety of **1**-Cu²⁺ complex.

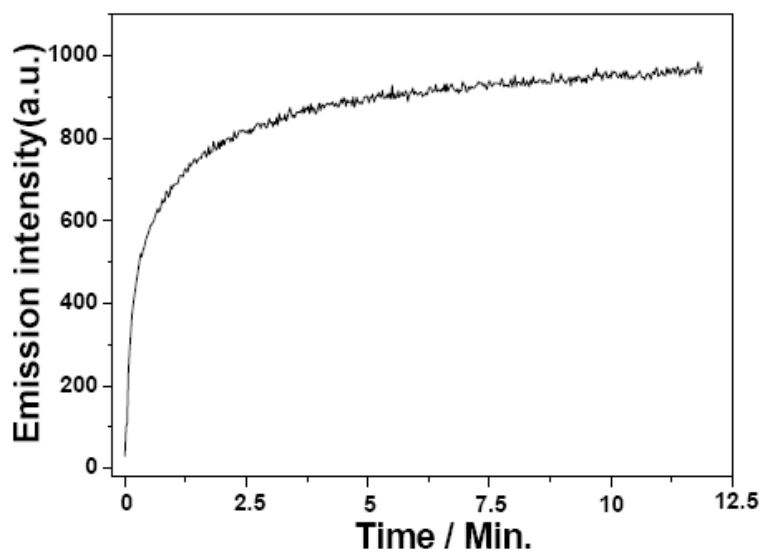


Fig. S5 Time course of the response of **1•Cu** (2.5 μM) in 9:1 (v/v) MeCN/water solution (10 mM Tris-HCl, pH 7.0) upon addition of 40 equiv. of CN^- .

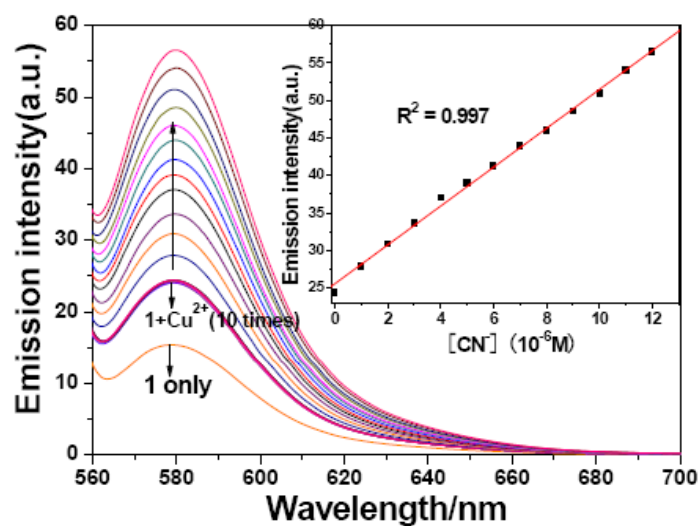


Fig. S6 Fluorescence response of **1•Cu** (0.5 μM) to CN^- . $\lambda_{\text{ex}}/\lambda_{\text{em}} = 535 / 580 \text{ nm}$. Slit: 20 nm/20 nm.

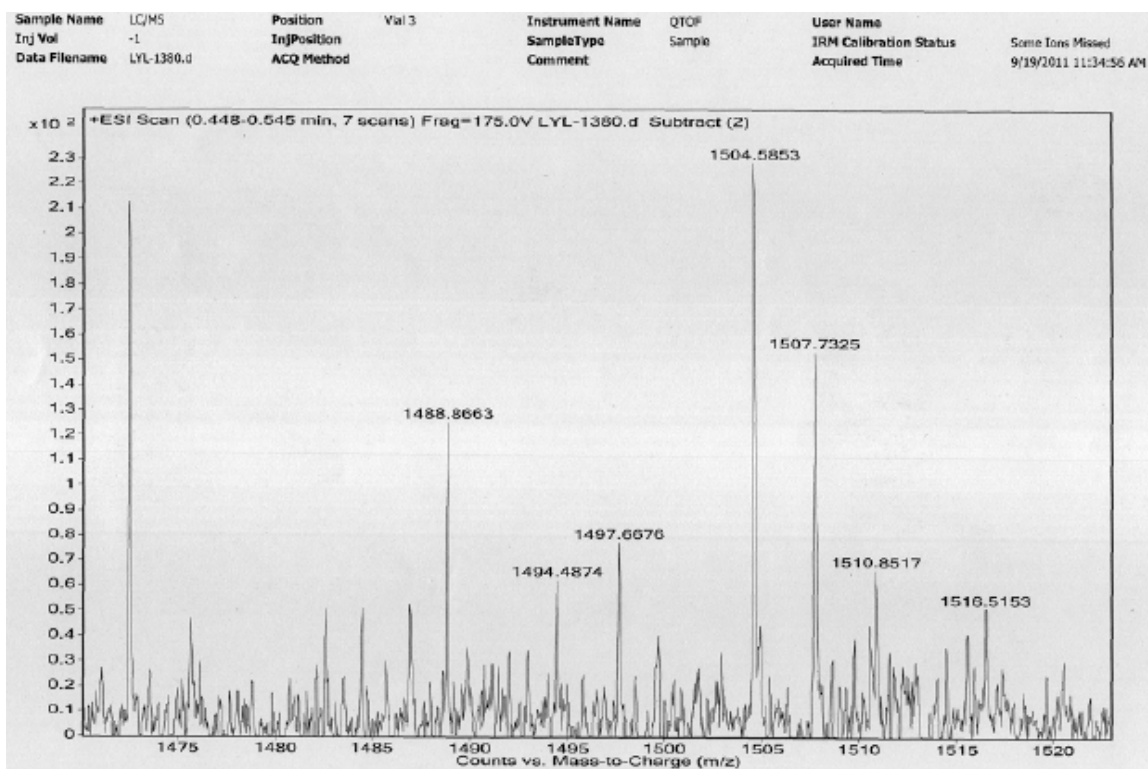


Fig. S7 ESI-MS chart of **1**·Cu upon addition of CN⁻.

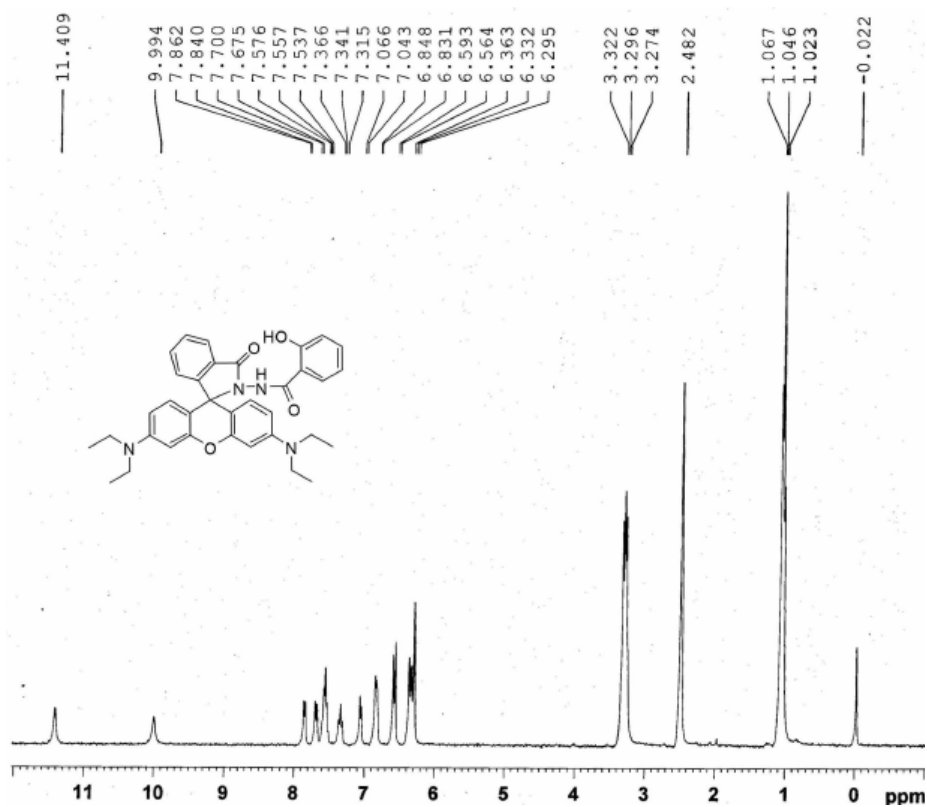


Fig. S8 ¹H NMR chart of **1** (DMSO-*d*₆).

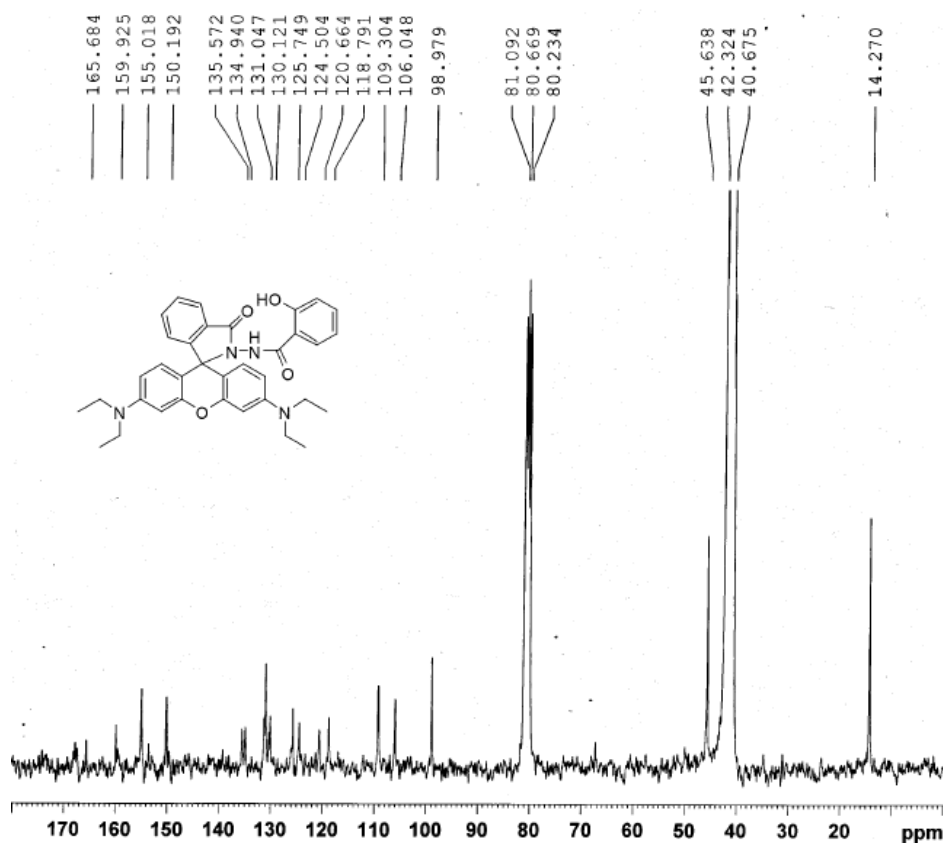


Fig. S9 ^{13}C NMR chart of 1 (DMSO- d_6).

Sample Name	LQMS	Position	Val 3	Instrument Name	QTOF	User Name	
Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	YU-A.d	ACQ Method		Comment		Acquired Time	6/29/2011 11:24:00 AM

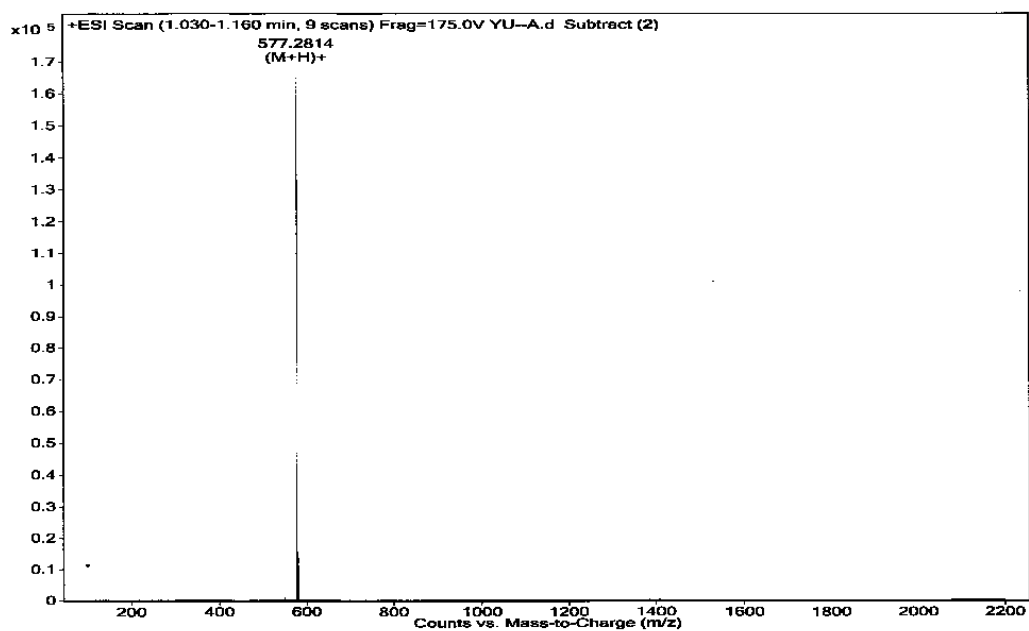


Fig. S10 ESI-MS chart of 1.