Supporting Information

Pyrophosphate selective fluorescent probe and molecular flip flop

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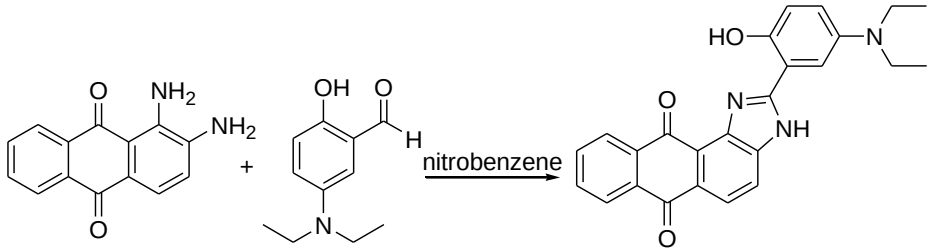
1. General Experiment Conditions: ^{1}H NMR Spectra and titrations were carried at temperaute 25 ^{o}C using Bruker spectrometer operating at 400 MHz. ^{13}C NMR sepctra were recorded at 100 MHz. All chemical shifts are reported in ppm relative to the TMS as an internal reference. UV-Vis studies were carried out on Shimadzu UV-2400 machines using slit width of 1.0 nm and matched quartz cells. The fluorescence experiments were performed on Perkin Elmer LS-54 fluorescence spectrophotometer. Elemental analysis were performed on Flash EA-1112 series CHNS-O analyser instrument.

2. Synthesis of Probe 1



2 **3** **1**

A solution of 4-diethylamino-2-hydroxybenzaldehyde (193 mg, 1 mmol) and 1,2-diaminoanthracene-9,10-dione (238 mg, 1 mmol) in nitrobenzene (5 mL) was heated at 120 ^{o}C. The reaction was monitored through TLC and after completion of the reaction (18 h), the reaction mixture was cooled to room temperature and yellow solid separated was filtered which on column chromatography and re-crystallisation from chloroform - methanol (1:1) mixture gave pure **1**. Yield 87 %; mp. 180 ^{o}C, FAB mass M^{+} m/z 411.2 (M^{+}). ^{1}H NMR (400 MHz, $CDCl_3$): **δ** 2.502 (t, *J* = 8.4 Hz, CH_3), 3.260 (q, *J* = 8.4 Hz, CH_2), 7.056 (t, *J* = 9 Hz, 1H, ArH), 7.11 (d, *J* = 9 Hz, 1H, ArH), 7.45 (t, *J* = 9 Hz, 1H, ArH), 7.90-7.94 (m, 2H, ArH), 8.07- 8.13 (m, 2H, ArH), 8.19-8.28 (m, 2H, ArH), 8.39 (d, *J* = 7.5 Hz, 1H, ArH), 12.01 (bs, 1H, NH), 12.78 (bs, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): **δ** 13.3, 45.0, 98.3, 106.0, 108.6, 117.6, 118.9, 119.3, 123.5, 124.5, 128.7, 129.5, 131.8, 132.7, 133.1, 149.4, 153.9, 154.2. Anal. Calcd for $C_{25}H_{21}N_3O_3$: C, 72.98; H 5.14; N 10.21; Found: C, 72.89; H, 5.08; N 10.25.

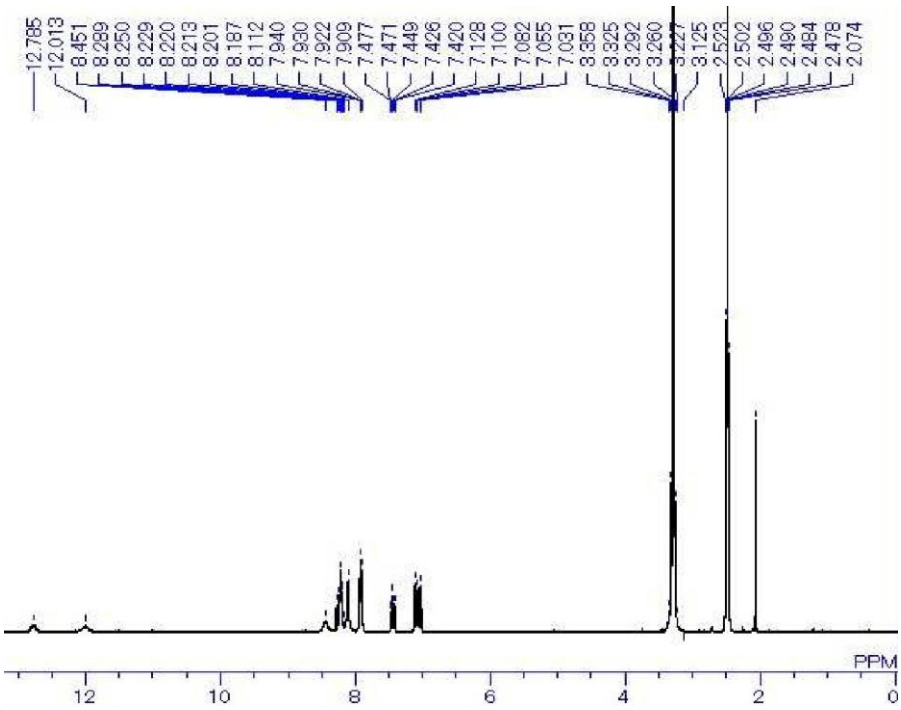


Figure S1: ^{1}H NMR spectrum of Probe **1**

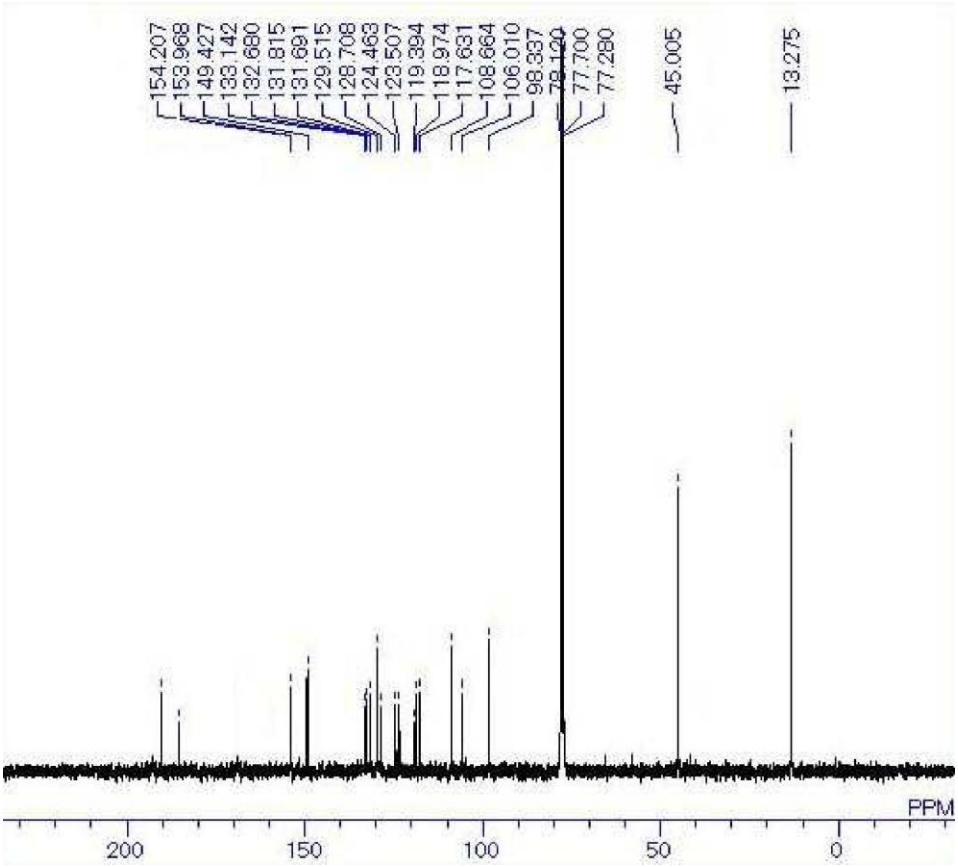


Figure S2: ^{13}C NMR spectrum of Probe **1**

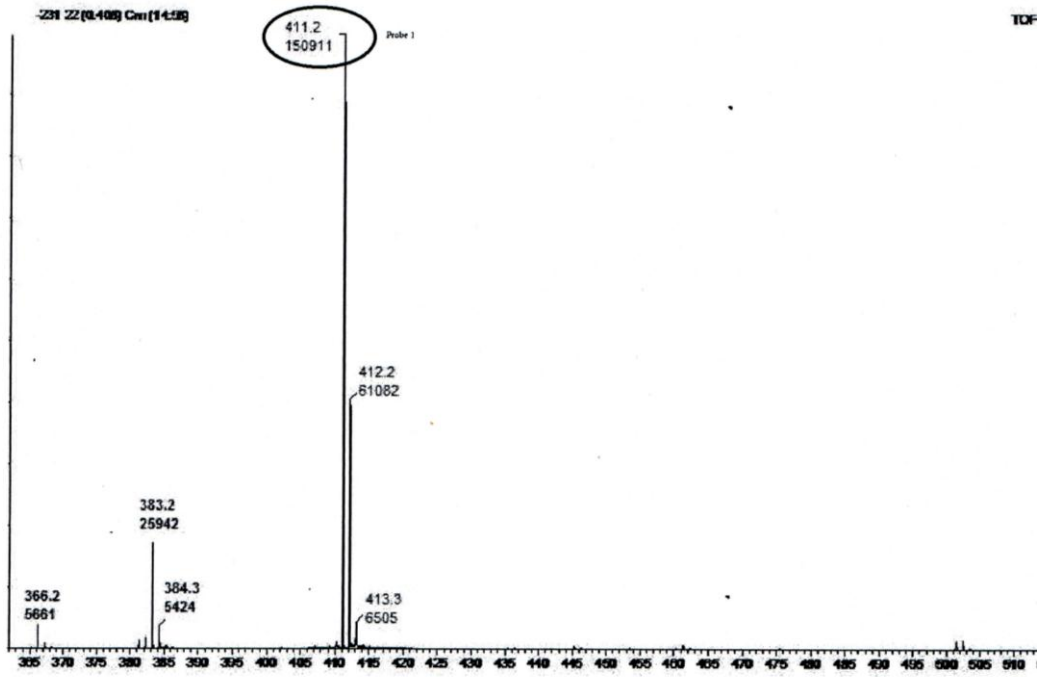


Figure S3: Mass spectrum of Probe **1**

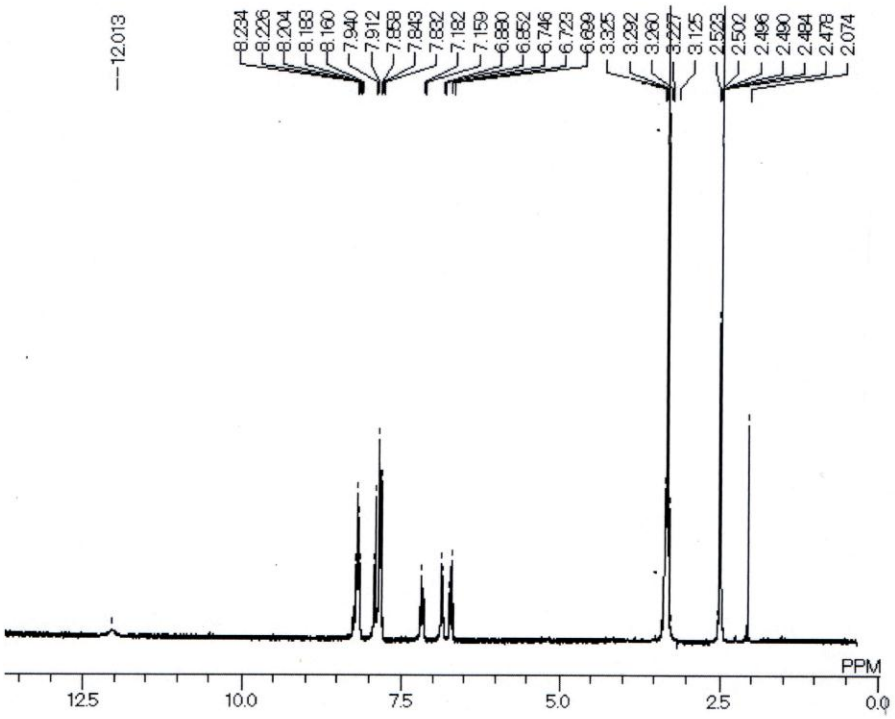


Figure S4: ^{1}H NMR spectrum of Probe **1.Zn^{2+}**

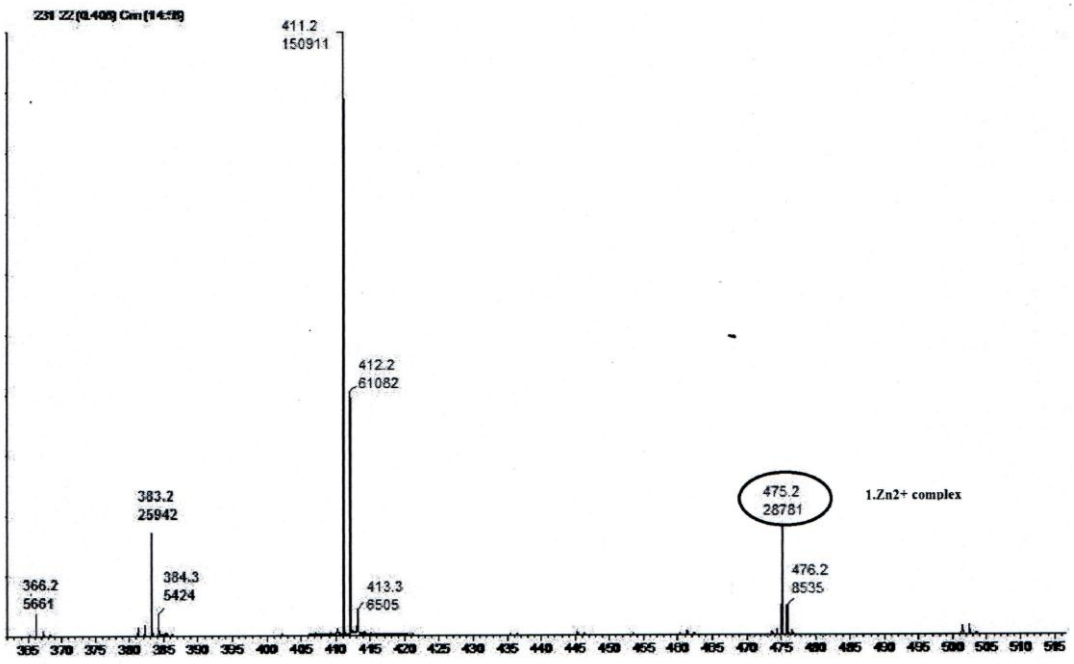


Figure S5: Mass spectrum of Probe **1.Zn**$^{2+}$

3. Photophysical studies – Parameters and Conditions

All absorption scans and fluorescence spectra were saved as ACS II files and further processed in Excel™ to produce all graphs shown. Solutions of **1** were typically 20 μM for UV-Vis studies and 1-2 μM for fluorescence studies.

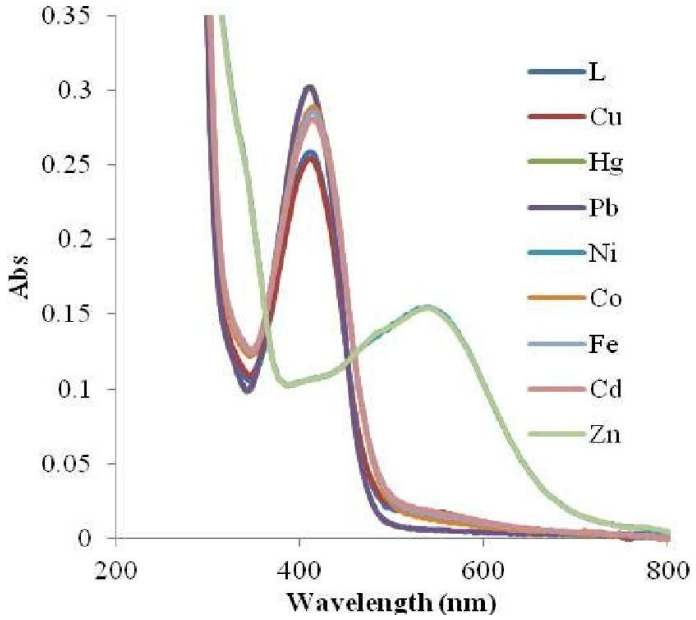


Figure S6: Effect of addition of different metal ions on absorption spectrum of probe **1**.

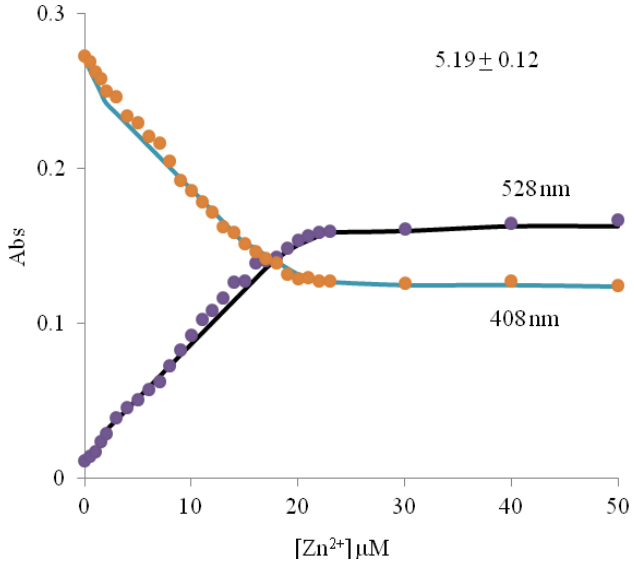


Figure S7: Spectral curve fitting[1] of data of probe **1** showing absorbance vs [Zn^{2+}] (points show the experimental data and line is curve fit.

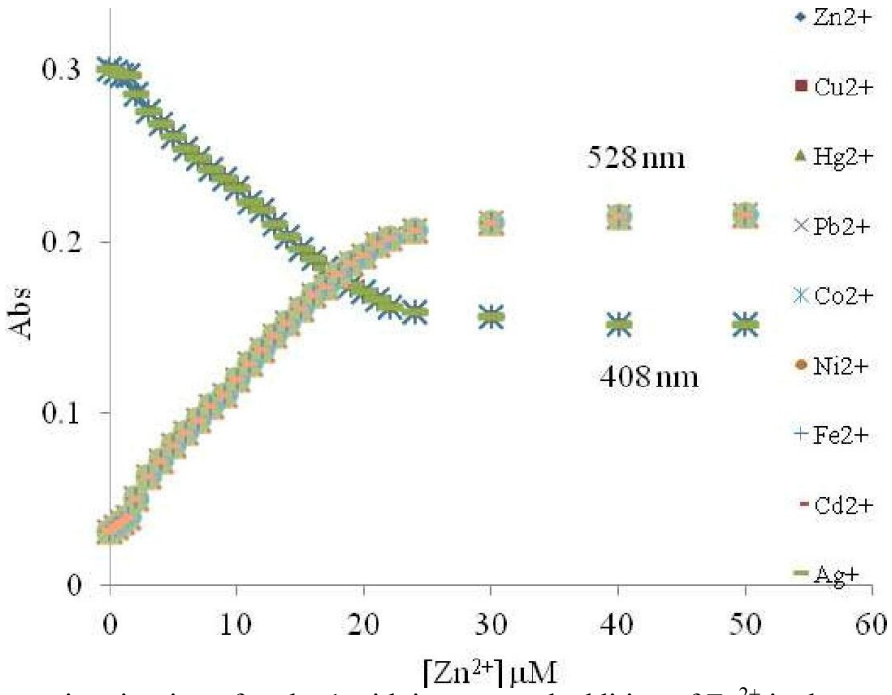


Figure S8: Absorption titration of probe **1** with incremental addition of Zn^{2+} in the presence of other metal ions (1000 equiv.) to show the interference.

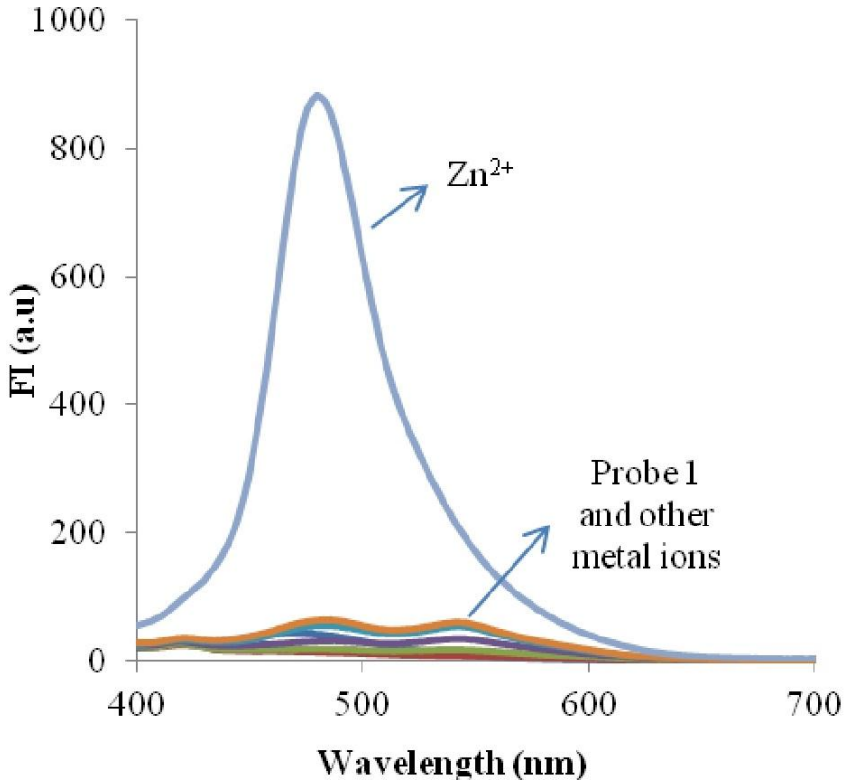


Figure S9: Effect of different metal ions on fluorescence spectrum of Probe **1.**

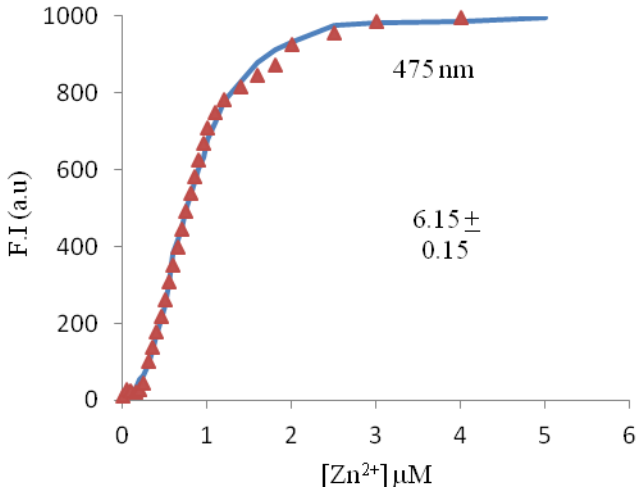


Figure S10: Spectral curve fitting of the fluorescence data showing fluorescence vs [Zn^{2+}] (points show the experimental data and line is curve fit.

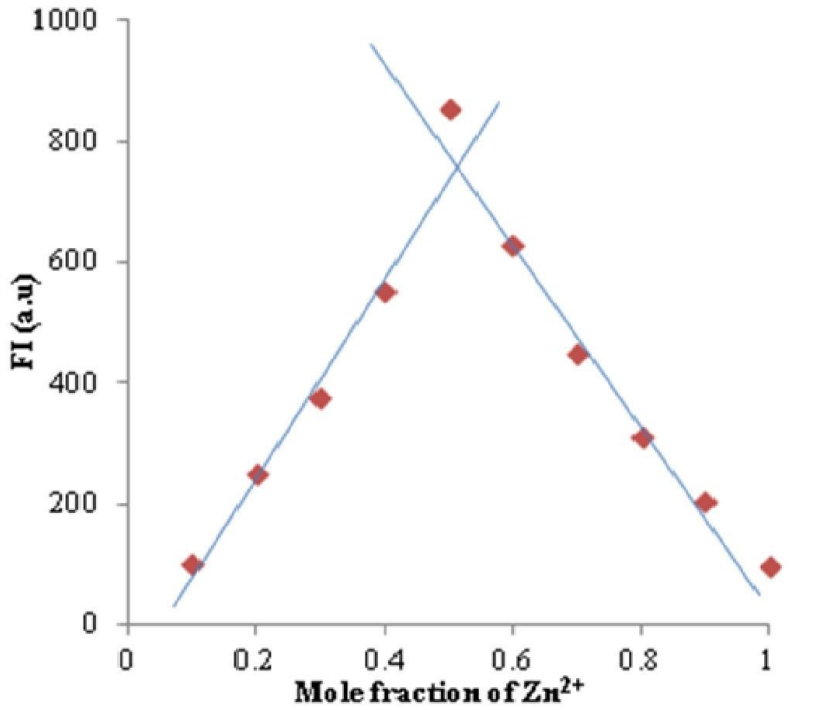


Figure S11: Job`s plot showing the 1:1 stoichiometry between Probe **1** and Zn^{2+}.

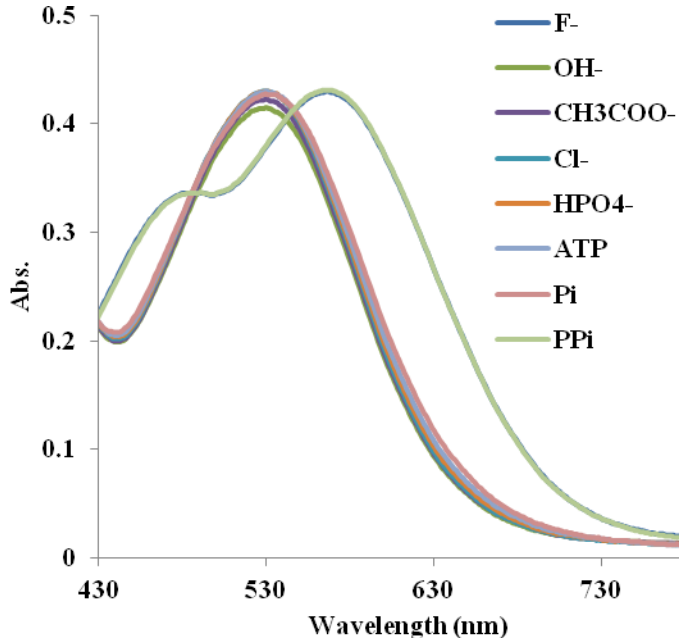


Figure S12: Effect of other anions on UV-Vis spectra of **1.Zn**$^{2+}$ complex.

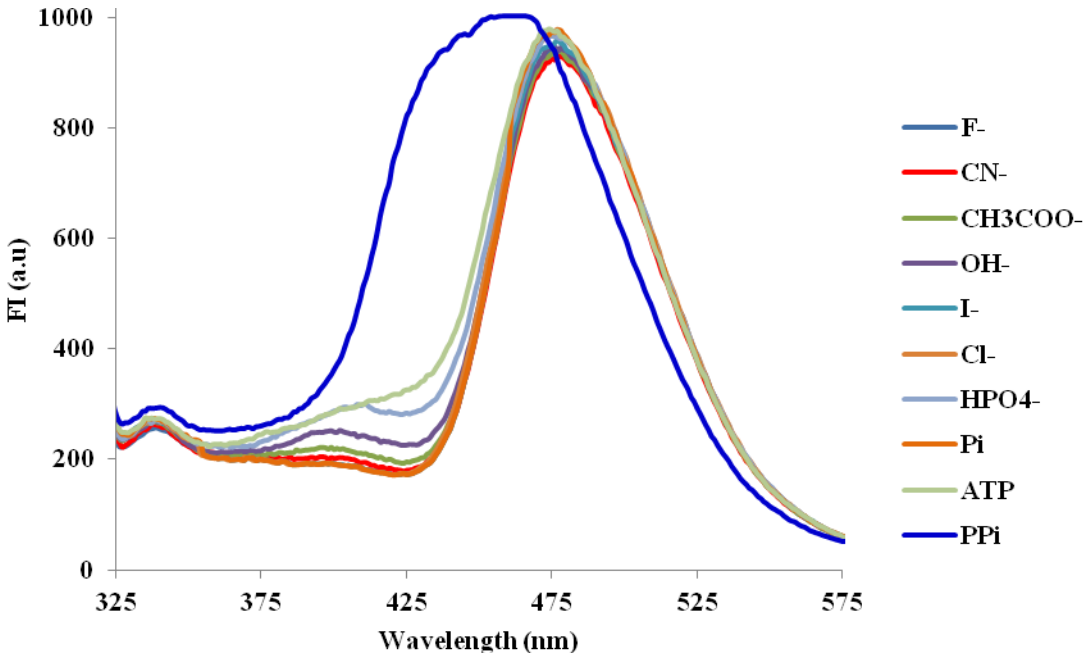


Figure S13: Effect of other anions on fluorescence spectra of **1.Zn**$^{2+}$ complex.

Fluorescence Quantum Yield: The fluorescence quantum yield Φ_f for **1** was determined at room temperature in analytical grade CH_3CN using optically matching solutions of resublimed anthracene ($\Phi_f = 0.65$) in ethanol as the standard at an excitation wavelength of

343 nm from a xenon lamp of the spectrofluorophotometer and the quantum yield was calculated by using Equation (1), in which **Φ**fs is the radiative quantum yield of the sample, **Φ**fr the radiative quantum yield of reference, *A*s and *A*r are the absorbances of the sample and the reference, respectively, *D*s and *D*r the areas of emission for the sample and reference, Ls and Lr are the lengths of the absorption cells, and *N*s and *N*r are the refractive indices of the sample and reference solutions (pure solvents were assumed).

$$\phi_{fs} = \phi_{fr} \times \frac{1-10^{-ArLr}}{1-10^{-AsLs}} \times \frac{N_s^{\,2}}{N_r^2} \times \frac{D_s}{D_r}$$

References

1. Specfit-32 global analysis programme: http://www.hi-techsci.com/products/specfit32.