Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Supporting information

## BINOL-based differential chromo-fluorescent sensor and its application for miniaturization of 1-2/4-2 bit encoders and decoders

Akul Sen Gupta, Gulshan Kumar, Kamaldeep Paul and Vijay Luxami*

School of Chemistry and Biochemistry, Thapar University, Patiala-147004, INDIA

Email: vluxami@thapar.edu

## Table of Contents

**Figure S15:** Benesi-Hildebrand plot from emission titration data of receptor (20 μM) with $Cu^{2+}$ in $CH_3OH$.

**Figure S16.** Plot of emission intensity at 590 nm ($F_{590}$) vs [$Cu^{2+}$] ions of probe **1** (20 μM, $CH_3OH$, 20 slit)

**Figure S17:** Benesi-Hildebrand plot from emission titration data of receptor (20 μM) with $Zn^{2+}$ in $CH_3OH$.

**Figure S18.** Plot of emission intensity at 485 nm ($F_{485}$) vs [$Zn^{2+}$] ions of probe **1** (20 μM, $CH_3OH$, 20 slit)

**Figure S19.** Yellow and green bars represent selectivity of probe **1** (20 μM) upon addition of different metal ions in $CH_3OH$ at 430 nm and 415 nm, respectively, red and blue bars show the competitive selectivity of probe **1** for $Cu^{2+}$ at 430 and $Al^{3+}$ at 415 nm, respectively in case absorption spectroscopy.

**Figure S20.** Yellow and green bars represent selectivity of probe **1** (10 μM) upon addition of different metal ions in $CH_3OH$ at 590 nm and 515 nm, respectively, red and blue bars show the competitive selectivity of probe **1** for $Cu^{2+}$ at 590 and $Al^{3+}$ at 515 nm, respectively in case emission spectroscopy.

**Figure S21**: Effect of addition of anions on absorption spectrum of probe **1** (20 μM, $CH_3OH$).

**Figure S22**: Effect of addition of anions on emission spectrum of probe **1** (20 μM, $CH_3OH$).

**Figure S23**. **Figure S20**. Visual color changes under UV light color changes upon different addition of anions with probe **1** in $CH_3OH$.

**Figure S24.** Plot of absorption intensity ratio between 395 and 370 nm ($A_{395}$ / $A_{370}$) vs [$CN^-$] ions of probe **1** (20 μM, $CH_3OH$)

**Figure S25:** Benesi-Hildebrand plot from emission titration data of receptor (20 μM, $CH_3OH$) with $CN^-$ ion

**Figure S26.** Plot of emission intensity at 495 nm ($F_{495}$) vs [$CN^-$] ions of probe **1** (20 μM, $CH_3OH$)

**Figure S27.** Blue bars represent selectivity of probe **1** (20 μM) upon addition of different metal ions in $CH_3OH$ and red bars show the competitive selectivity of probe **1** in UV-Vis spectroscopy for $CN^-$ ion.

**Figure S28.** Blue bars represent selectivity of probe **1** (20 μM) upon addition of different metal ions in $CH_3OH$ and red bars show the competitive selectivity of probe **1** in fluorescence spectroscopy for $CN^-$.

**General Experimental Conditions**

- **Synthesis of compound 2:** To the stirred solution of 3-hydroxy-2-naphthoic acid (200 mg, 1 mmol) and 4-aminoantipyrine (259 mg, 1.2 mmol) in tetrahydrofuran (30 ml), *o*-(1*H*-benzotriazol-1-yl)-*N,N,N′,N′*-tetramethyluroniumtetrafluoroborate (409 mg, 1.2 mmol), *N,N*-diisopropylethylamine (206 mL, 1.2 mmol) and hydroxybenzotriazole (172 mg, 1.2 mmol) were added and refluxed for 24 h (checked by TLC). The reaction mixture was washed with water and extracted with $CHCl_3$ (3 times), the solvent was removed under vacuum and dried over sodium sulphate. The residue was column chromatographed on silica gel by using $CHCl_3$: MeOH (99:1) to get pure amide as probe **1** in 70% yield (280 mg). Mpt: 202-204 $^oC$; $^1H$ NMR ($CDCl_3$, 400 MHz): δ 2.27 (s, 3H, $CH_3$), 3.19 (s, 3H, N-$CH_3$), 7.11 (s, 1H, ArH), 7.15-7.19 (m, 1H, ArH), 7.33 (d, *J* = 7.64 Hz, 1H, ArH), 7.37-7.40 (m, 2H, ArH), 7.46-7.55 (m, 5H, ArH), 7.90 (s, 1H, ArH), 9.78 (bs, 1H, NH), 11.85 (bs, 1H, OH); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 11.8 ($CH_3$), 35.4 (N-$CH_3$), 107.1, 111.3, 118.1, 123.1, 125.3, 125.7, 127.0, 127.8, 127.9, 129.0, 129.5, 130.8, 134.0, 136.5, 150.8, 154.4 (ArC), 162.4, 167.2 (C=O); MS (ESI) m/z 396.3 ($M^+$ + Na).
- **Detection limit calculation:** The detection limit was calculated based on the titration. To determine the S/N ratio, the emission intensity of the probes was measured 5 times and the standard deviation of blank measurements was determined. The detection limit was then calculated using the equation.

  - Detection limit = $3\sigma_{bi}/m$

  where $\sigma_{bi}$ is the standard deviation of blank measurements; m is the slope of intensity versus sample concentration. The detection limit was measured at S/N = 3.

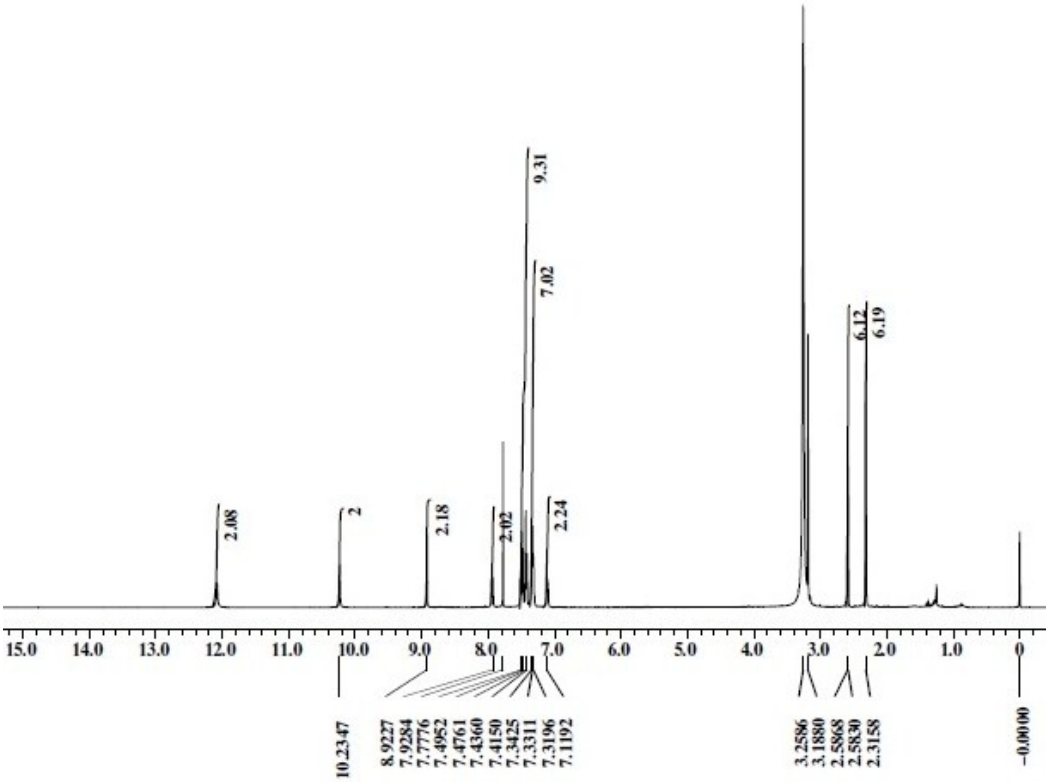


**Figure S1:** $^{1}$H NMR spectrum of probe **1**

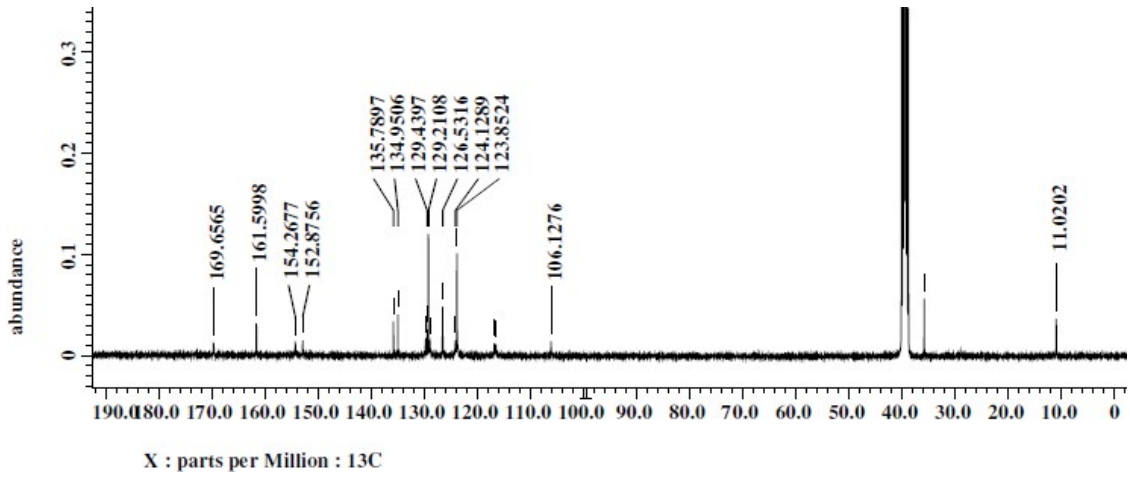


**Figure S2:** $^{13}$C NMR spectrum of probe **1**

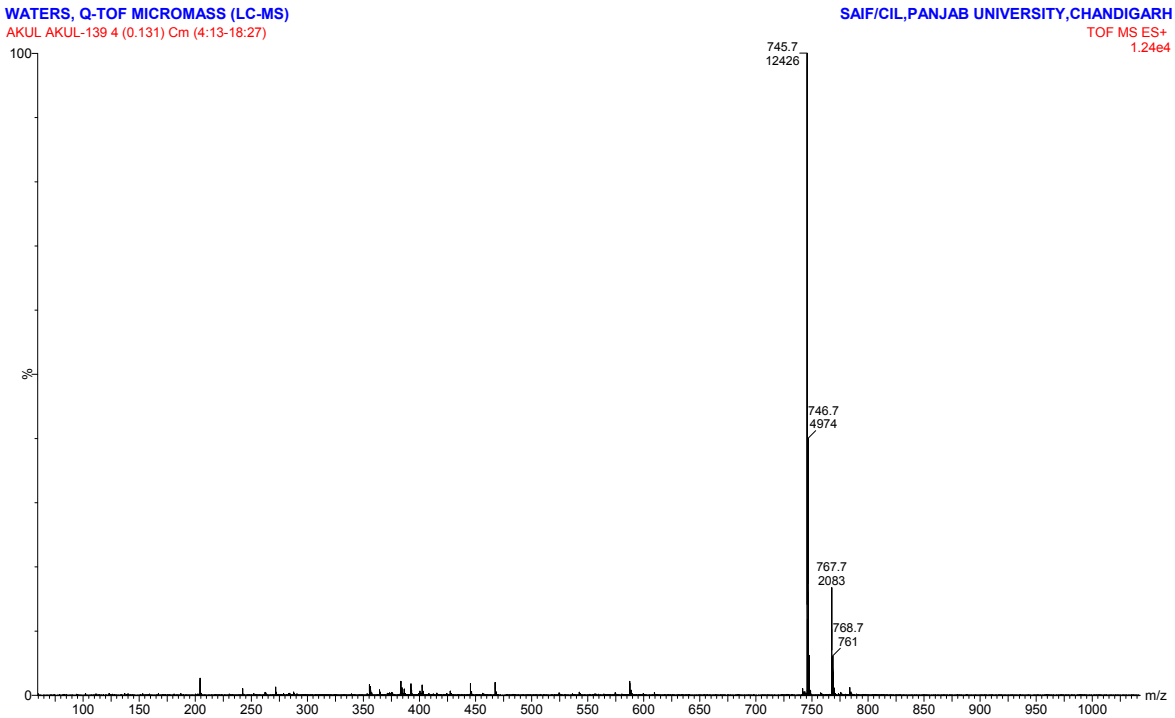


**Figure S3:** Mass spectrum of probe **1**

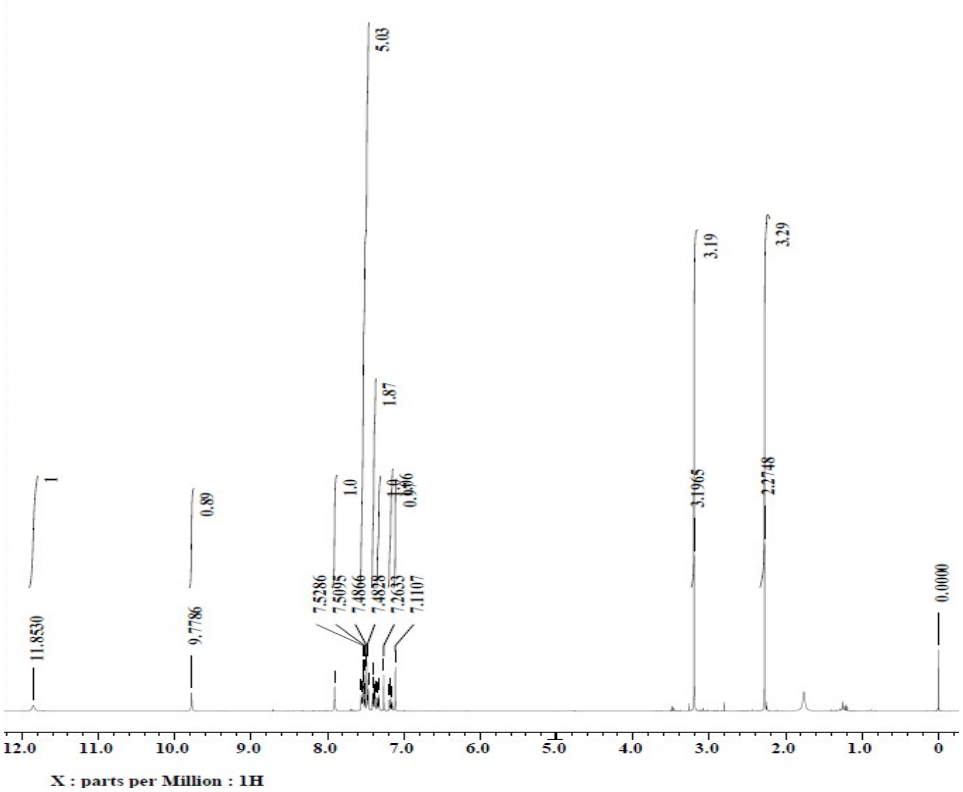


**Figure S4:** $^{1}$H NMR spectrum of Compound **2**

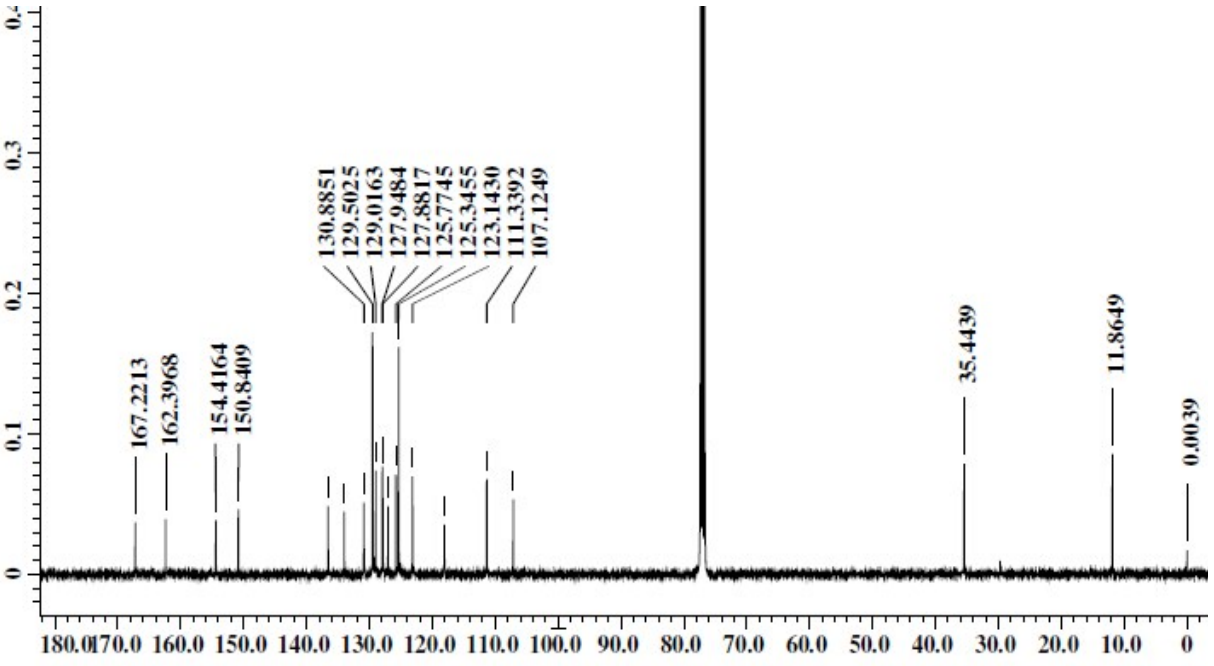


**Figure S5:** $^{13}$C NMR spectrum of compound **2.**

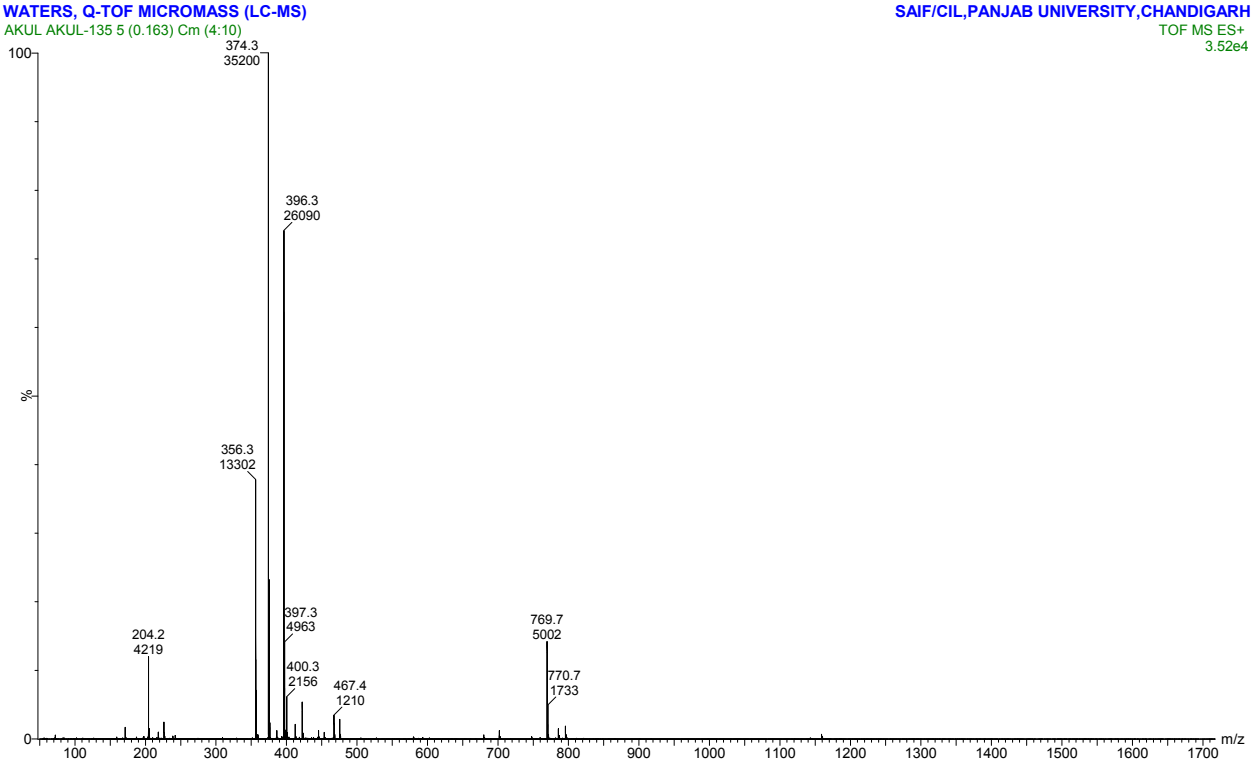

**Figure S6: Mass spectrum of compound 2.**

**Calculation of binding constant**

Binding constants were calculated according to the Benesi-Hildebrand equation. $K_a$ was calculated following the equation stated below.

$$1/(A\text{-}A_o) = 1/\{K(A_{max} – A_o)\,[M^{x+}]^n\} + 1/[A_{max}\text{-}A_o]$$

Here $A_o$ is the absorbance of receptor in the absence of guest, A is the absorbance recorded in the presence of added guest, $A_{max}$ is absorbance in presence of added $[M^{x+}]_{max}$ and K is the association constant. The association constant (K) could be determined from the slope of the straight line of the plot of 1/(A-Ao) against $1/[M^{x+}]$ and is found to be $0.9 \times 10^4\ M^{-1}$ in case of case $Al^{3+}$ ions in methanol.

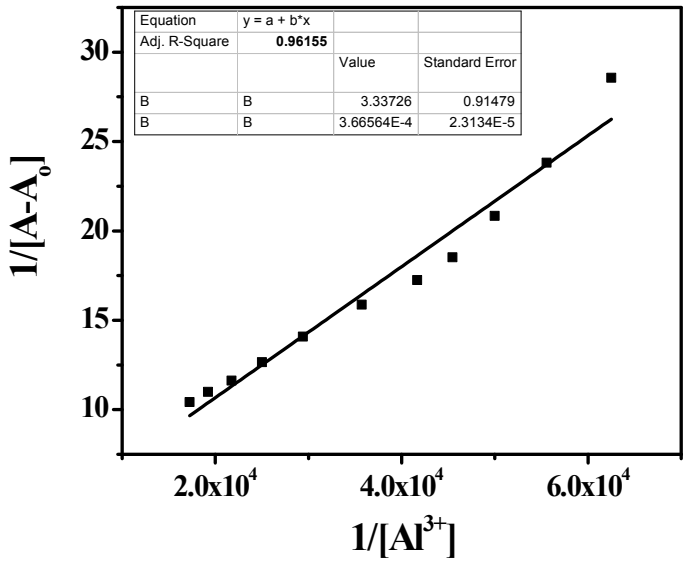


**Figure S7:** Benesi-Hildebrand plot from absorption titration data of receptor (20 μM) with $Al^{3+}$ ions.

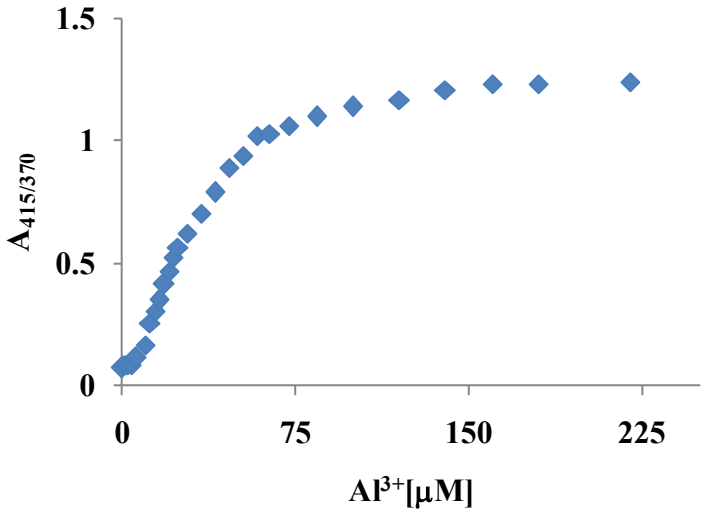


**Figure S8.** Plot of absorption intensity ratio between 415 and 370 nm ($A_{415}$ / $A_{370}$) vs [$Al^{3+}$] ions of probe **1** (20 μM, $CH_3OH$)

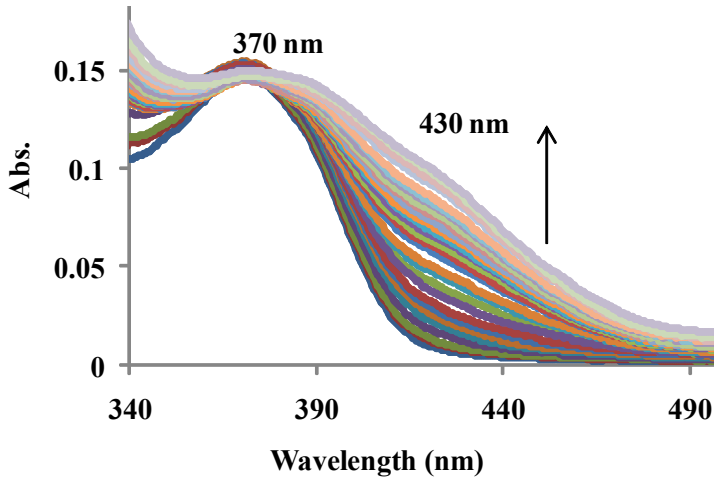


**Figure S9**. Effect of addition of $Cu^{2+}$ on absorption spectrum of probe **1** (20 μM, $CH_3OH$)

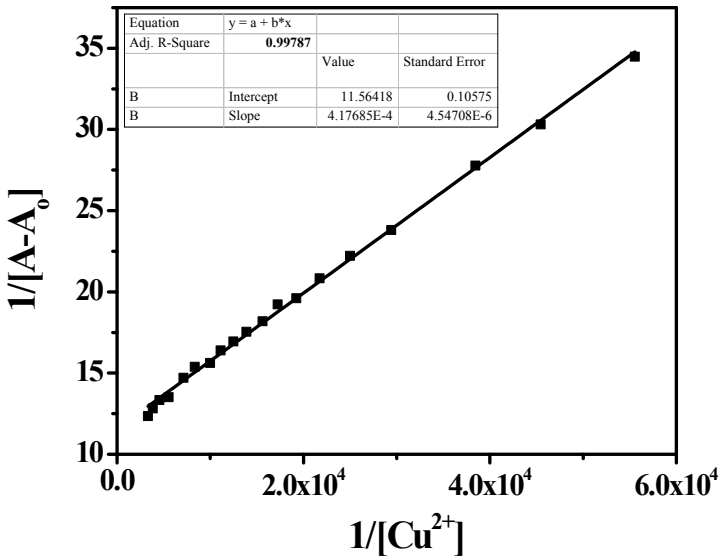


**Figure S10:** Benesi-Hildebrand plot from absorption titration data of receptor (20 μM, $CH_3OH$) with $Cu^{2+}$ ions.

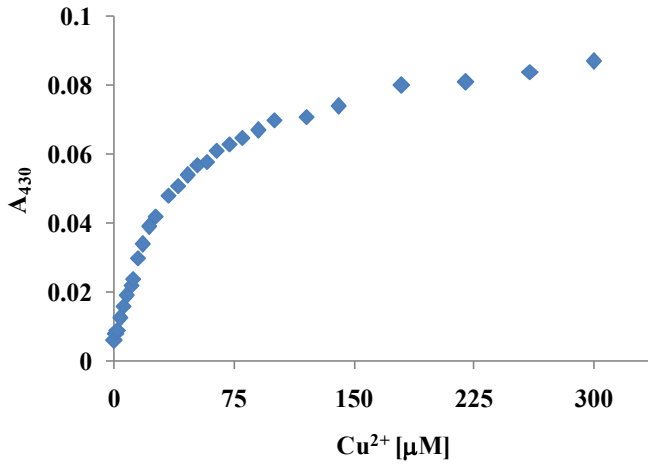


**Figure S11.** Plot of absorption intensity at 430 ($A_{430}$) vs [$Cu^{2+}$] ions of probe **1** (20 µM, $CH_3OH$)

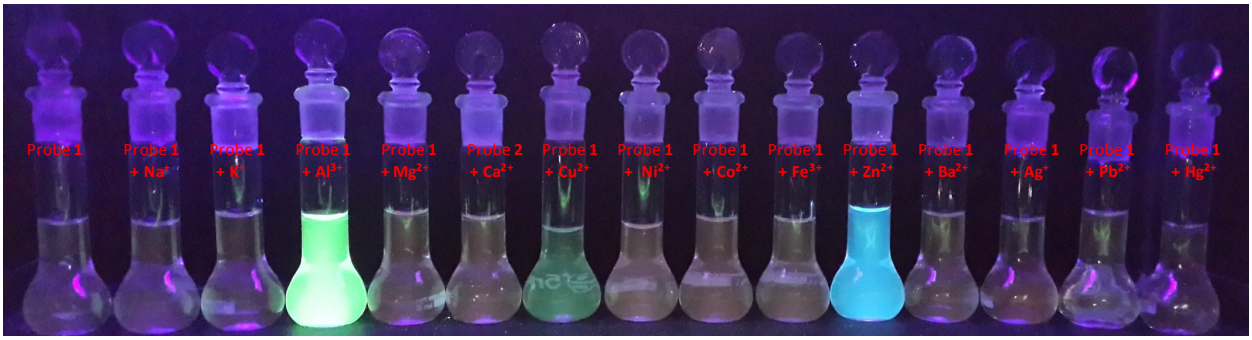


**Figure S12**. Visual color changes under UV light upon addition of different cations with probe **1** in $CH_3OH$.

**By fluorescence method:**

The binding constant value of anions with receptor has been determined from the emission intensity data following the modified Benesi–Hildebrand equation,

$1//\Delta I = 1//\Delta I_{max} + (1/K[C])\ (1//\Delta I_{max})$

Here $\Delta I = I\text{-}I_{min}$ and $\Delta I$ max = $I_{max}\text{-}I_{min}$, where $I_{min}$, I, and $I_{max}$ are the emission intensities of receptor observed in the absence of anions, at an intermediate anion concentration, and at a concentration of complete saturation where K is the binding constant and [C] is the anion concentration respectively. From the plot of [1 / ($I_{min}$ –I)] against [C]-1 for receptor, the value of

K has been determined from the slope. The association constant (*K*) as determined by fluorescence titration method for the receptor with aluminium ions in methanol is found to be 5.2 × $10^3$ $M^{-1}$ (error < 10%).

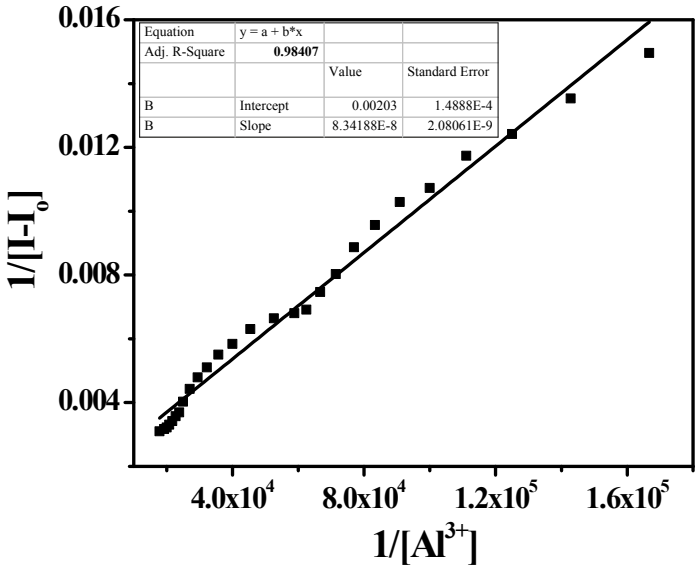


**Figure S13:** Benesi-Hildebrand plot from emission titration data of receptor (20 μM) with $Al^{3+}$ in $CH_3OH$.

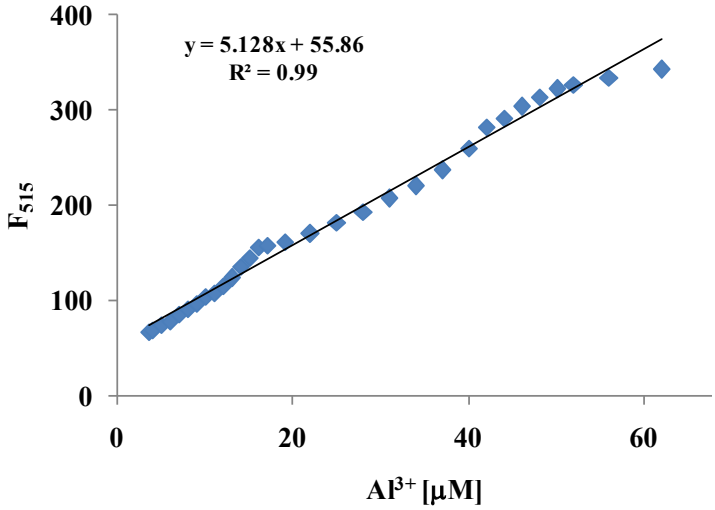


**Figure S14.** Plot of emission intensity at 515 nm ($F_{515}$) vs [$Al^{3+}$] ions of probe **1** (20 μM, $CH_3OH$, 10 slit)

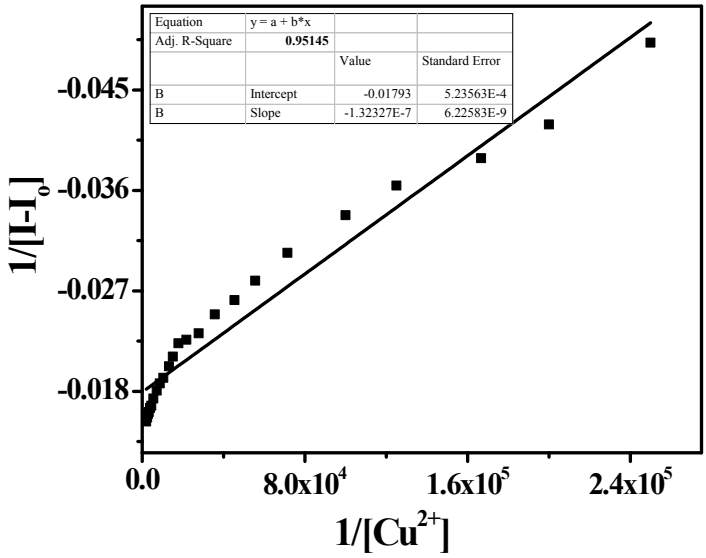


**Figure S15:** Benesi-Hildebrand plot from emission titration data of receptor (20 μM) with $Cu^{2+}$ in $CH_3OH$.

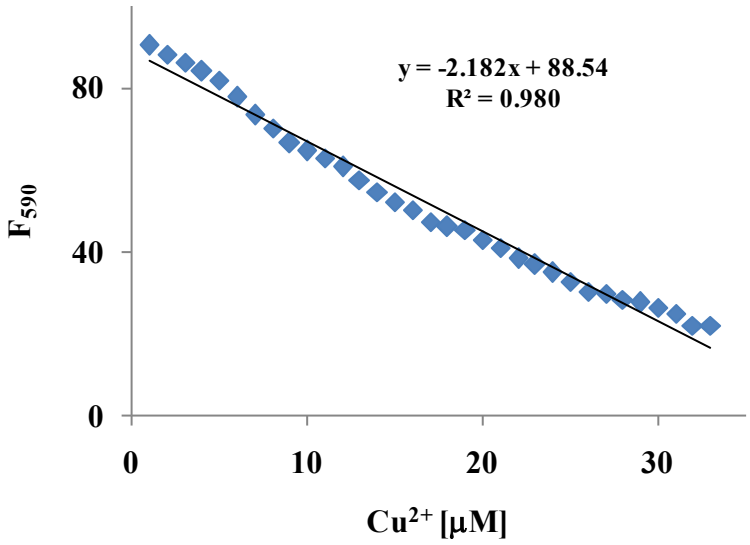


**Figure S16.** Plot of emission intensity at 590 nm ($F_{590}$) vs [$Cu^{2+}$] ions of probe **1** (20 μM, $CH_3OH$, 20 slit)

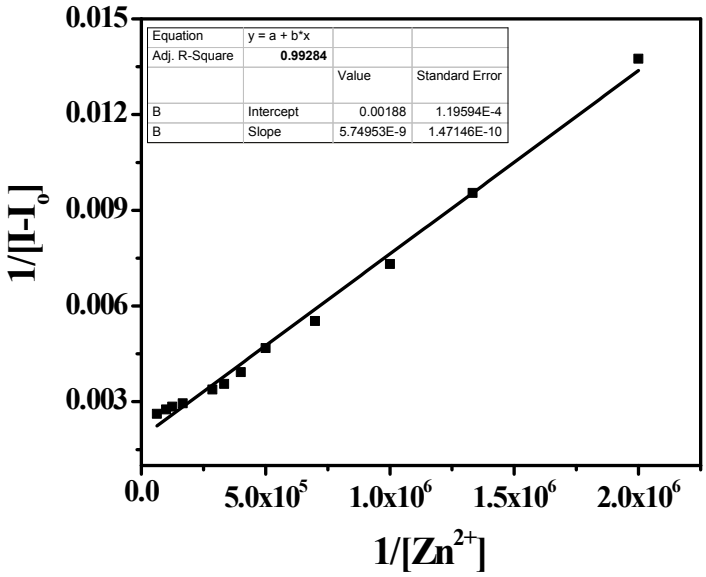


**Figure S17:** Benesi-Hildebrand plot from emission titration data of receptor (20 μM) with $Zn^{2+}$ in $CH_3OH$.

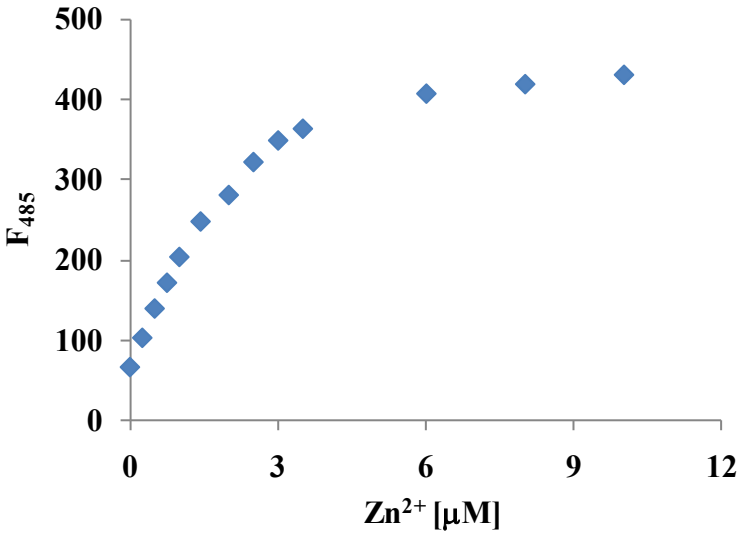


**Figure S18.** Plot of emission intensity at 485 nm ($F_{485}$) vs [$Zn^{2+}$] ions of probe **1** (20 μM, $CH_3OH$, 20 slit)

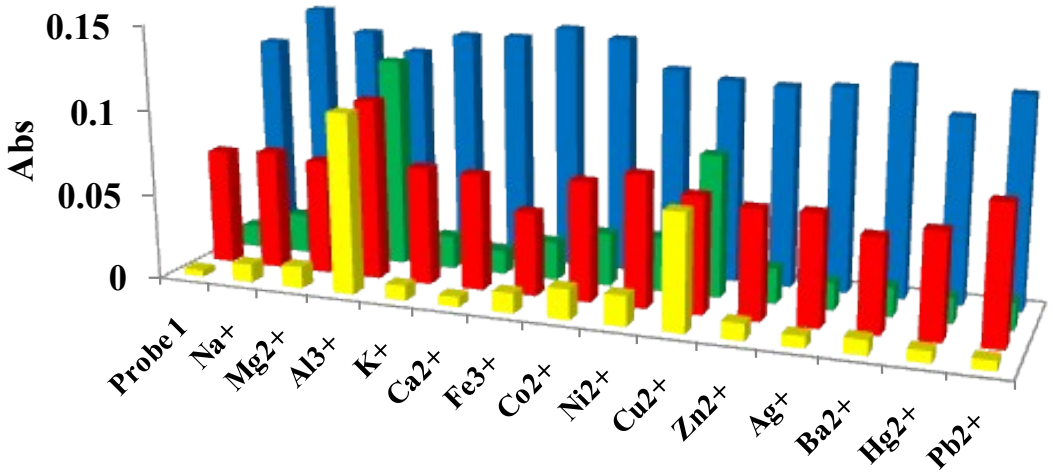


**Figure S19.** Yellow and green bars represent selectivity of probe **1** (20 μM) upon addition of different metal ions in $CH_3OH$ at 430 nm and 415 nm, respectively, red and blue bars show the competitive selectivity of probe **1** for $Cu^{2+}$ at 430 and $Al^{3+}$ at 415 nm, respectively in case absorption spectroscopy.

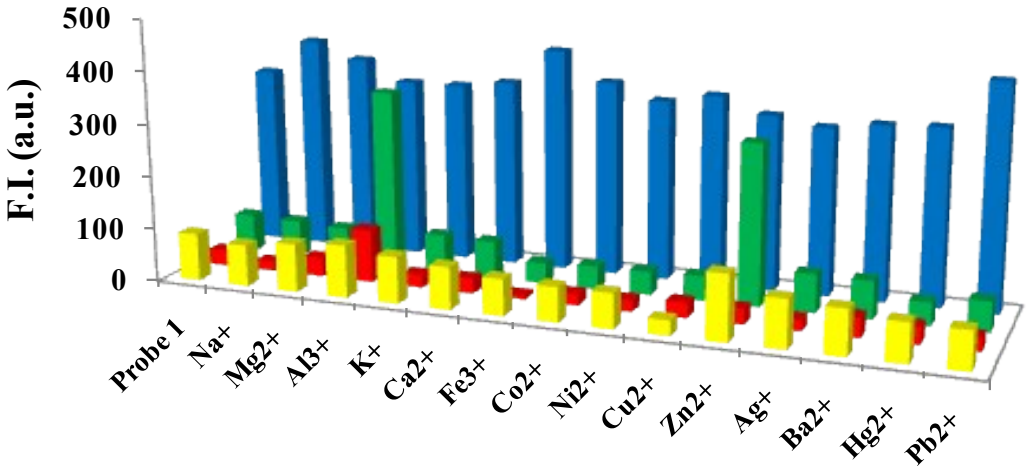


**Figure S20.** Yellow and green bars represent selectivity of probe **1** (10 μM) upon addition of different metal ions in $CH_3OH$ at 590 nm and 515 nm, respectively, red and blue bars show the competitive selectivity of probe **1** for $Cu^{2+}$ at 590 and $Al^{3+}$ at 515 nm, respectively in case emission spectroscopy.

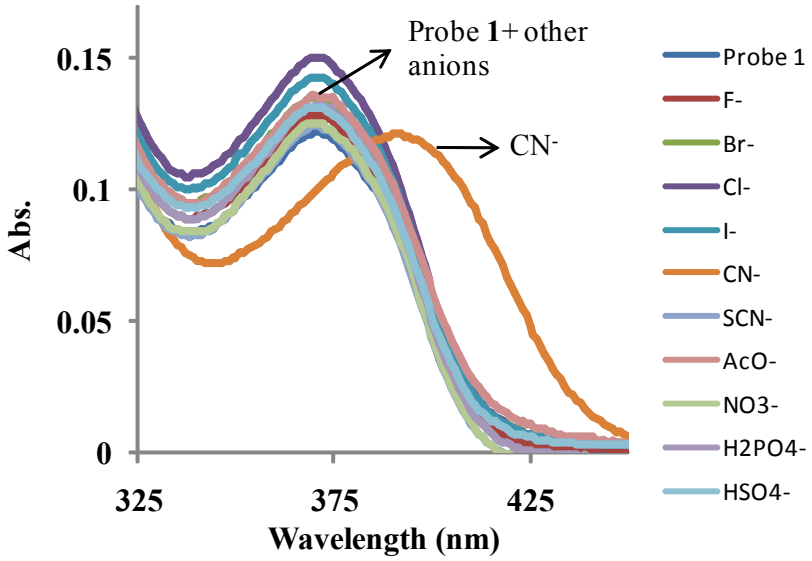


**Figure S21**: Effect of addition of anions on absorption spectrum of probe **1** (20 μM, $CH_3OH$).

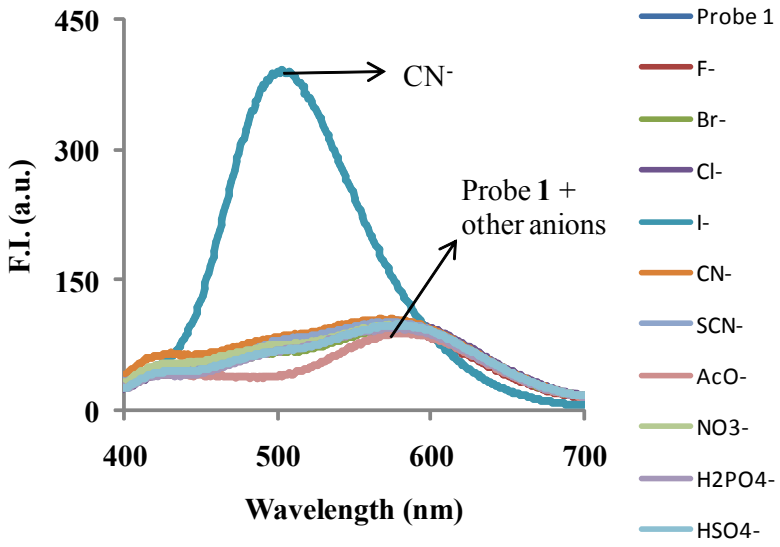


**Figure S22**: Effect of addition of anions on emission spectrum of probe **1** (20 μM, $CH_3OH$).

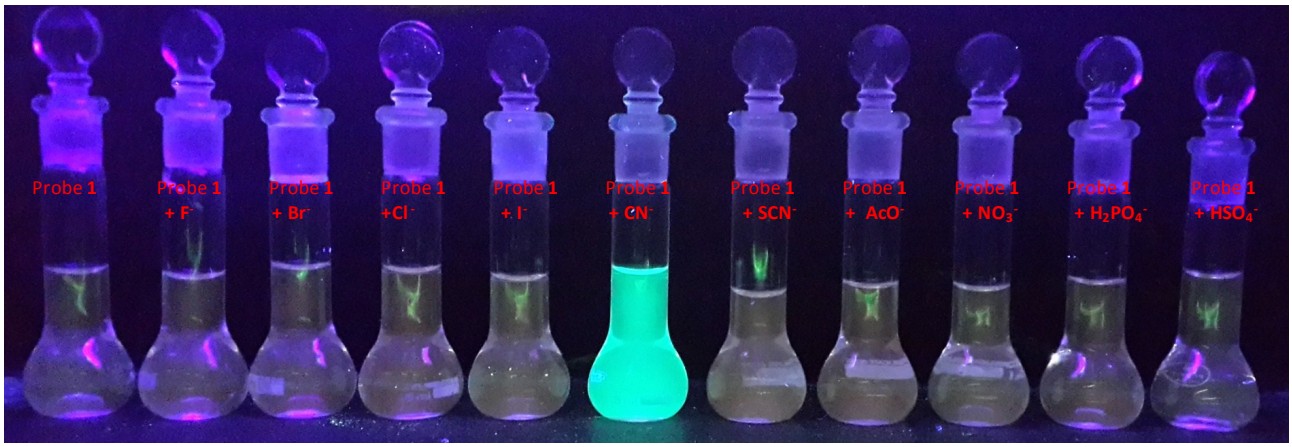


**Figure S23**. Visual color changes under UV light color changes upon different addition of anions with probe **1** in $CH_3OH$.

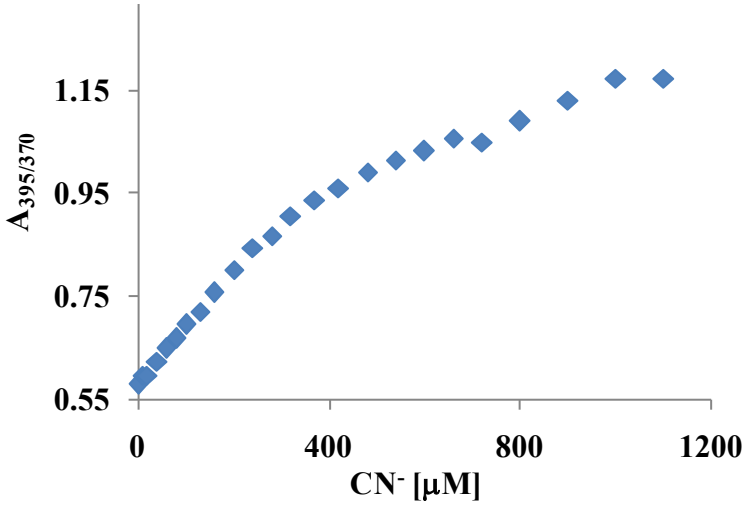


**Figure S24.** Plot of absorption intensity ratio between 395 and 370 nm ($A_{395}$ / $A_{370}$) vs [$CN^-$] ions of probe **1** (20 μM, $CH_3OH$)

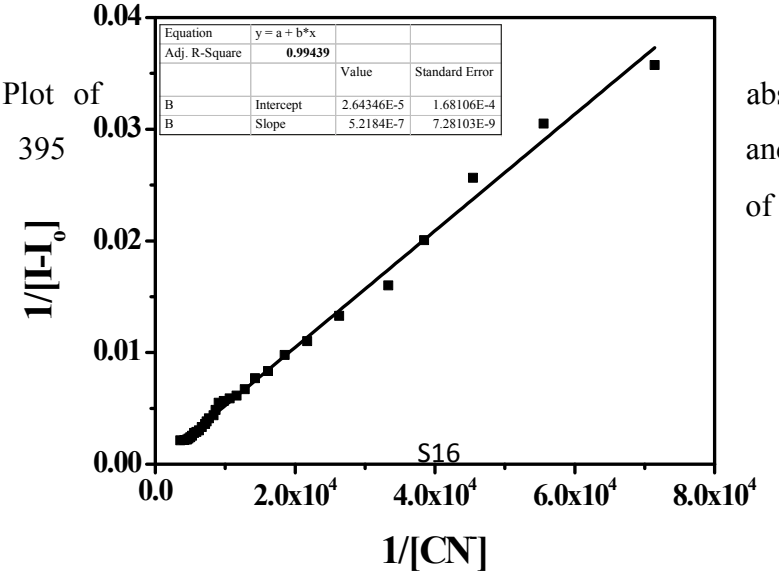

**Figure S25:** Benesi-Hildebrand plot from emission titration data of receptor (20 μM, $CH_3OH$) with $CN^-$ ion.

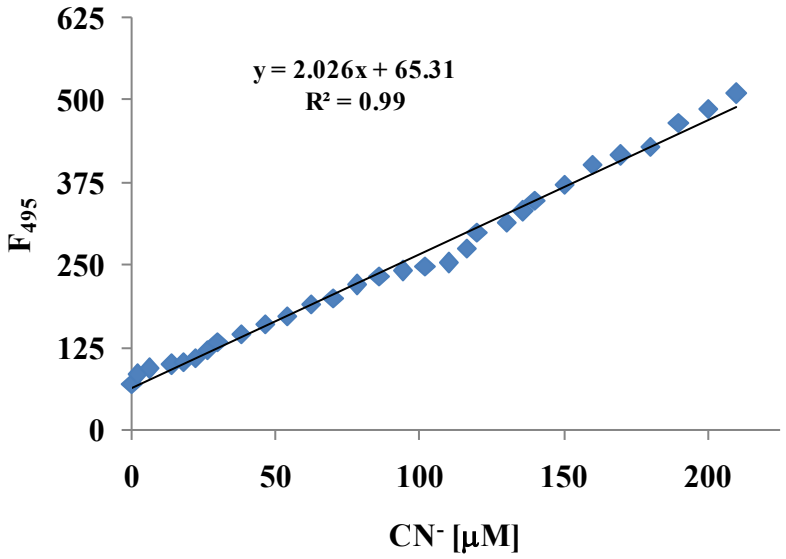


**Figure S26.** Plot of emission intensity at 495 nm ($F_{495}$) vs [$CN^-$] ions of probe **1** (20 μM, $CH_3OH$)

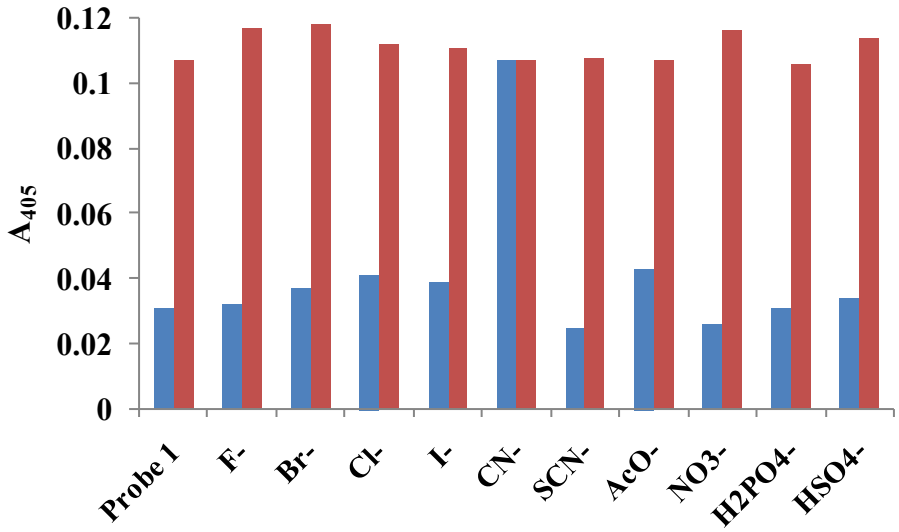


**Figure S27.** Blue bars represent selectivity of probe **1** (20 μM) upon addition of different metal ions in $CH_3OH$ and red bars show the competitive selectivity of probe **1** in UV-Vis spectroscopy for $CN^-$ ion.

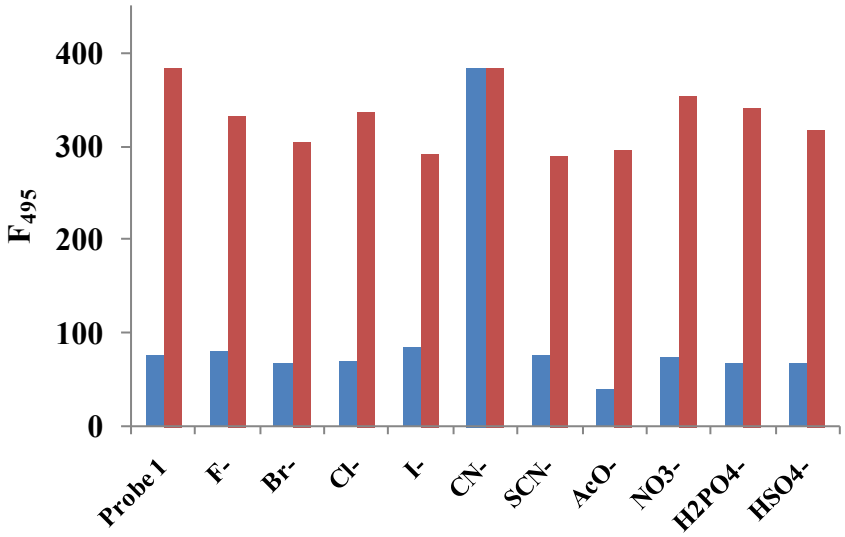


**Figure S28.** Blue bars represent selectivity of probe **1** (20 μM) upon addition of different metal ions in $CH_3OH$ and red bars show the competitive selectivity of probe **1** in fluorescence spectroscopy for $CN^-$.