



## Research paper

# Solvent dependent colorimetric, ratiometric dual sensor for copper and fluoride ions: Real sample analysis, cytotoxicity and computational studies



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## ABSTRACT

A novel colorimetric chemosensor based on terephthalic acid and pyridine aldehyde moiety was designed to detect  $\text{Cu}^{2+}/\text{F}^-$  ions in aqueous and DMSO solutions at physiological pH conditions with the detection limit of 0.25  $\mu\text{M}$  and 3  $\mu\text{M}$  for  $\text{Cu}^{2+}/\text{F}^-$  ions respectively. The probe was found to be highly selective to sense  $\text{F}^-$  ion rather than  $\text{CH}_3\text{COO}^-$  and  $\text{H}_2\text{PO}_4^-$  ions. Interestingly, the probe behaved as a promising receptor by detecting  $\text{F}^-$  ions even in ordinary tap water through distinct colour change. Moreover, the chemosensor showed lower cytotoxicity against AGS cancer cells and thus found to be biologically friendly. The reversibility of probe- $\text{F}^-$  binding was investigated using HCl in UV-vis experiment. The binding mechanism of chemosensor to  $\text{Cu}^{2+}/\text{F}^-$  ions was elucidated based on the UV-vis spectroscopy, NMR, ESI-Mass spectroscopy and cyclic voltammogram techniques. Furthermore, theoretical investigation was carried out using Gaussian 09 program.

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## 1. Introduction

For the past few decades researchers were mainly interested on design and synthesis of fluorescence probes to recognize diverse of single guest species such as anions, cations and neutral molecules [1–3]. Recently, bifunctional probes, which refer to those based on a single host that can independently recognize two guest species with distinct spectral responses is becoming a novel research focus [4]. Among them, anions and cations sensing probes hold the utmost importance due to their biological and environmental significance. As per our knowledge, only very few reports are available on simultaneous recognition of cations and anions. Among them, a very few accounts for probes which can detect  $\text{F}^-/\text{Cu}^{2+}$  ions through ratiometric and colorimetric techniques [5]. Generally, the interaction of anions/cations with the host molecules can be analysed by fluorometric [6–9] (or) visible colorimetric techniques [10–14]. Among the above mentioned analytical methods, the latter is commendable in view of its application [15]. Anions are omnipresent and play a vital role in the biological system such as co-factors and enzyme substrates [16–19]. Among all other biologically functional anions,  $\text{F}^-$  ion is the smallest and highly electro negative atom and it can form strong hydrogen bond with various

donor atoms [20].  $\text{F}^-$  ions plays a vital role in medicinal department such as dental health and has the potential for the treatment of osteoporosis [21–23] also, it's recognition and detection is allied with nerve gases, drinking water analysis, and the refinement of uranium used in nuclear weapons manufacture [24]. In general,  $\text{F}^-$  ions are identified by Lewis acid-base interaction [25] or hydrogen bonding [26]. As anions such as  $\text{CH}_3\text{COO}^-$  and  $\text{H}_2\text{PO}_4^-$  have same basicity as that of  $\text{F}^-$ , they can interfere with the detection of  $\text{F}^-$  ions. Hence only a very few probes which are free from cross sensitivities towards these ions are reported in the literature [27–30].

Besides, transition metal ions are very paramount for the living organisms [31]. Copper is the third most essential trace element after  $\text{Fe}^{\text{III}}$  and  $\text{Zn}^{\text{II}}$  in biological system [32] and it plays an important role in various biological processes such as electron transfer, catalytic activities, neurotransmitter biosynthesis and denaturation, as well as the functioning and maintenance of the structural stability of proteins. However overdose of copper ion can be highly toxic [33–35], as it causes serious cellular or organ damage and neuro degenerative diseases like Wilson disease and Alzheimer's disease [36–39]. Therefore, it is highly desirable to design and synthesize novel sensors for its measurement and detection. Consequently, we have designed and synthesized a probe based on terephthalic acid, which can colorimetrically and ratiometrically detect  $\text{F}^-/\text{Cu}^{2+}$  ions in DMSO and water: DMSO mixture (9:1) system.

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## 2. Materials and methods

Terephthalic acid, methanol, dimethylsulfoxide (DMSO), potassium bromide (KBr) (for IR spectroscopy) and all metal salts such as Cd, Zn, Hg, Cu, Ni, Co, Mn (as perchlorate salts), Fe, Al, Ba, Ca, Mg, Pb, K, Na (as chloride salt) and Ag, Cr (as nitrate) were purchased from Merck. Hydrazine monohydrate (CDH), pyridine aldehyde (Alfa Acer) and double distilled water were purchased and used without further purification. All anions as tetra-n-butyl ammonium salts were purchased from the Sigma-Aldrich.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded using Bruker 300 MHz spectrometer. The chemical shifts were shown in parts per million (ppm) downfield from tetramethylsilane (reference chemical shift is zero ppm) using residual DMSO (internal standard). Multiplicities were reported as follows: s (singlet), d (doublet), t (triplet), m (multiplet) and br (broadened). UV–vis absorbance spectrum measurements were recorded using UV-8453 Agilent spectrometer in the range of 190–1100 nm at room temperature. ESI-Mass spectrum was performed in the positive ion mode on liquid chromatography-ion trap mass spectrometer at room temperature (LCQ Fleet, Thermo Fisher instruments limited, USA). FT-IR spectrum was recorded in Shimadzu instrument in solid state at room temperature by embedding them in KBr discs. The broad and sharp bands are represented as 'br' and 's' respectively.

### 2.1. Synthesis of the probe (BPTH)

The synthetic procedure of the probe is illustrated in the Scheme 1. Methanolic solution (10 ml) of terephthalic acid in the presence of con. $\text{H}_2\text{SO}_4$  (10:1) was refluxed for 6 h. The reaction mixture was cooled to room temperature and evaporated under pressure, provided a dirty white colour solid. The solid formed was extracted with DCM for at least 3 times in order to completely remove the impurities and dried using  $\text{MgSO}_4$ . The solution was then filtered and evaporated to give milky white solid (1 mmol). Subsequently, it was re-dissolved in methanol followed by slow addition of hydrazine monohydrate (2 mmol) and allowed to reflux for 3 h. The obtained white solid (bis-hydrazine derivative) was filtered, washed with water and dried under vacuum. A hot-aqueous solution of bis-hydrazine derivative (1 mmol) was mixed dropwise with pyridine-2-aldehyde (2 mmol) and again refluxed at  $80^\circ\text{C}$  for 2 h. The probe (BPTH) was obtained as a white puffy solid which was filtered and dried in vacuum.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ )  $\delta$  12.2 (s, 1H), 8.6 (d,  $J = 4.5$  Hz, 1H), 8.5 (s, 1H), 8.1 (s, 1H), 8.0 (d,  $J = 8.0$  Hz, 1H), 7.9 (t,  $J = 7.1$  Hz, 1H), 7.5–7.4 (m, 1H) (ESI Fig. S1).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-d}_6$ )  $\delta$  163.15, 153.62, 150.00, 149.07,

137.35, 136.50, 128.37, 124.94, 120.50. (ESI Fig. S2). Mass: 373.10(M+1), 395.11(M+Na). (ESI Fig. S3). IR-Spectrum 3412, 3202, 3053, 2926, 2555, 1647, 1562, 1470, 1435, 1360, 1284, 1148, 1068, 1018, 955, 918, 868, 779, 714, 673, 621, 522,  $465\text{ cm}^{-1}$  (Fig. S4).

### 2.2. UV–vis titration of probe with $\text{Cu}^{2+}$ ions

The probe was dissolved in minimum amount of DMSO and diluted to make  $10^{-3}$  M solution using buffer (the ratio of DMSO and buffer is 1:9).  $40\ \mu\text{L}$  of this solution was diluted with  $1960\ \mu\text{L}$  buffer containing 10% DMSO to make the final concentration ( $2 \times 10^{-5}$  M) of probe and it was used to monitor the absorption changes in the presence of anions and cations respectively. An aqueous solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $10^{-3}$  M, 0–50  $\mu\text{L}$ ) was slowly added to the BPTH (20  $\mu\text{M}$ , 2 mL). The final concentration of the copper ions in 2 mL solution was up to 30  $\mu\text{M}$ . Solution of copper was added in portions to probe and UV–vis spectral changes were monitored at room temperature after each addition.

### 2.3. UV–vis titration of probe with $\text{F}^-$ ions

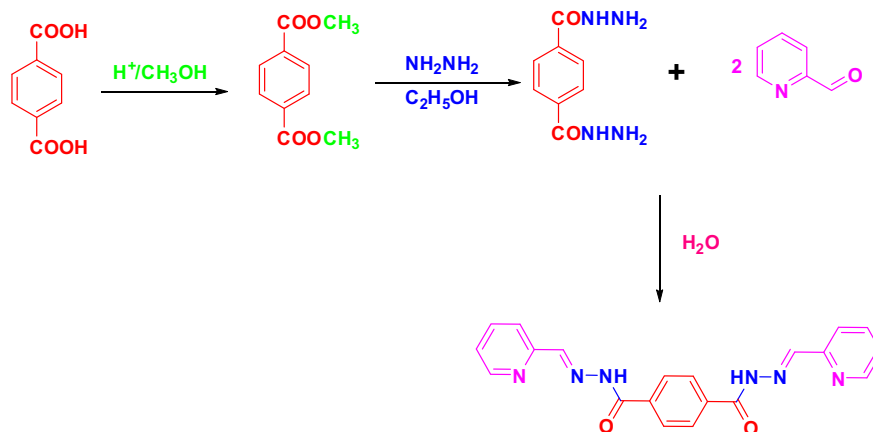
The probe ( $10^{-3}$  M, 40  $\mu\text{L}$ ) in DMSO was diluted with  $1960\ \mu\text{L}$  of DMSO to prepare 20  $\mu\text{M}$  concentrated solution.  $10^{-2}$  M of tetra-n-butylammonium fluoride in DMSO (0–30  $\mu\text{L}$ ) was added to the probe (20  $\mu\text{M}$ , 2 mL) and the final concentration of the  $\text{F}^-$  ion was 300  $\mu\text{M}$  in 2 mL of probe in a typical experiment. The observed colour changes due to the addition of anion ( $\text{F}^-$ ) with probe were monitored in the electronic absorption spectra after a few seconds at RT.

### 2.4. Job's plot analysis for probe with $\text{F}^-$ ions

The equimolar ( $10^{-4}$  M) concentration of probe and  $\text{F}^-$  ion were prepared in DMSO as two separate solutions. The probe to  $\text{F}^-$  ion ratio of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1 in DMSO were prepared in an appropriate manner and the colour changes were monitored using UV–vis spectra at RT.

### 2.5. Job's plot analysis for probe with $\text{Cu}^{2+}$ ions

An equimolar concentration of ( $10^{-4}$  M) probe and  $\text{Cu}^{2+}$  ion were made in buffer:DMSO (9:1) mixture. The probe to  $\text{Cu}^{2+}$  ion ratio of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1 were prepared in an appropriate manner and the colour changes were monitored using UV–vis spectra at RT.



**Scheme 1.** Chemical synthesis of the probe (BPTH).

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