# Fluorescent Chemosensing Properties of New Isoindoline Based-Receptors towards F<sup>-</sup> and Cu<sup>2+</sup> Ions

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## ABSTRACT

Two simple colorimetric and fluorescent anion chemosensors based on amide moieties, 4-nitro-N-[(1,3-dioxoisoin-dolin-2yl)benzamide (1), 3,5-dinitro-N-[(1,3-dioxoisoindolin-2yl)benzamide (2) have been synthesized and characterized. Comparing with other anions studied, the UV-visible absorption spectrum in DMSO shows significant response toward  $F^-$  ion with high selectivity, and meanwhile color change is observed from colorless to pink and violet for 1 and 2 respectively in the presence of tetrabutylammonium fluoride (TBAF) (5 × 10<sup>-3</sup> M). Moreover,  $F^-$ -induced color changes remain the same even in the large excess of Cl<sup>-</sup>, Br<sup>-</sup> and  $\Gamma$ . In addition, the <sup>1</sup>H NMR spectrum titration in DMSO-*d*<sub>6</sub> shows deprotonation of the receptors 1 and 2 in the presence of basic  $F^-$  ion. In particular, addition of  $F^-$  to the receptors 1 and 2 resulted in an enhancement in fluorescence intensity at 770 nm. Both receptors 1 and 2 exhibit a fluorescent emission enhancement when addition of Zn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup> and Mn<sup>2+</sup> metal ions. The fluorescent enhancement values for the receptor 1 are 2.29 (Cu<sup>2+</sup>), 1.85 (Ni<sup>2+</sup>), 1.37 (Co<sup>2+</sup>), 1.27 (Mn<sup>2+</sup>), 1.25 (Zn<sup>2+</sup>) and for 2, 2.57 (Cu<sup>2+</sup>), 1.66 (Ni<sup>2+</sup>), 1.36 (Co<sup>2+</sup>), 1.15 (Mn<sup>2+</sup>), 1.09 (Zn<sup>2+</sup>). The selectivity of Cu<sup>2+</sup> is higher for 1 and 2 than other metal ions such as Zn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Mn<sup>2+</sup>

Keywords: Chemosensors; Colorimetric; Fluoride; Napththalimide; Cations; Copper(II) Sensor; Fluorescence

## **1. Introduction**

The development of new molecular systems for the colorimetric detection of anions [1-3], and cations [4,5] or neutral molecules [6] have attained prime significance due to their biological and environmental applications. The incorporation of fluorescent chromophores into the receptors that are sensitive interactions between the host and guest molecules has recently gained considerable attention because of their highly sensitivity and low detection limit [7,8]. The appeal of fluorescent sensors originnates from the high sensitivity of fluorescent detection compared to other spectroscopic methods. When a guest species binds to the fluorescent receptor, a certain property such as fluorescent intensity, wavelength, lifetime, etc changes, and such a change serve as an indicator of guest binding.

Among the anions, the detection of fluoride ( $F^-$ ) is of particular interests [9,10] as it plays an essential role in a broad range of biological, medical and chemical processes and applications such as dental care [11], treatment of osteoporosis [12], association with hydrolysis of the nerve gas sarin [13], or even chemical and nuclear warfare agents [14]. Being small and highly electronegative,

fluoride has unique chemical properties and can form strong hydrogen bonds with hydrogen-bond donors. The majority of reported fluoride sensors are based on colorimetric changes [15] or fluorescence quenching [16], few of them experience fluorescence enhancement [17].

The development of fluorescent molecular sensors for metal ions, especially for cations with biological interest, has always been of particular interest. More specifically, fluorescent sensors for the detection and measurement of copper ions are actively investigated, as this metal ion is a significant environmental pollutant and an essential trace element in biological systems [18]. For most of the reported Cu<sup>2+</sup> fluorescent sensors, the binding of the metal ion causes a quenching of the fluorescence emission [19]. Only a few sensors in which the binding of  $Cu^{2+}$  ion causes an increase in the fluorescence have been reported [20]. A good case in point is Kumar's sensor displaying fluorescence enhancement with Cu<sup>2+</sup> [21]. Samanta and co-workers have also achieved fluorescence enhancement with Cu<sup>2+</sup> using an electron an electron-deficient fluorophore component to reduce the M-F interaction [22,23].

We have recently embarked upon designing systems that can sense both anions and metal ions [24]. Commonly, a typical chemosensor is the compound coupling of at least two units: a fluorophore and a binding unit. In



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this paper, with the conception of designing fluorescent receptors for  $F^-$  and Cu(II), two receptors were designed and synthesized by the combination of naphthalimide moiety (as the fluorophore) and amide group (as the anion binding unit) (see **Scheme 1**).



# Scheme 1.

## 2. Experimental

#### 2.1. Chemicals

The solvent DMSO was used as HPLC grade and purchased from Qualigens (Chennai, India). All anions, in the form of tetrabutylammonium salts, were purchased from Sigma-Aldrich Chemical Co. (Bangalore, India).

#### 2.2. Physical Measurements

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL 400 MHz spectrometer in DMSO- $d_6$ . The IR spectra were recorded on a Perkin-Elmer FT-IR LX-185256 spectrometer. UV-visible experiments were performed on a Perkin-Elmer FT UV-Visible  $\lambda$ -35 spectrometer. Elemental analysis of the receptors was obtained in Heraeus CHN rapid analyzer. The EI mass spectra were recorded using a JEOL DX 303 mass spectrometer. Emission spectrum was recorded using a Perkin-Elmer Fluores-cence  $\lambda$ -45 spectrometer.

#### 2.3. UV-Visible Spectroscopic Methods

The solutions of receptors **1** and **2** ( $5 \times 10^{-5}$  M) were made up with HPLC grade DMSO solvent. UV-visible and fluorescence titrations were carried out by adding 10 µl aliquots of the titrant as tetrabutylammonium salts ( $5 \times 10^{-3}$  M) and cations as its perchlorate salts ( $5 \times 10^{-3}$  M). The UV-visible and fluorescence spectra were recorded after each addition.

#### 2.4. Synthesis of 4-Nitro-N-[(1,3-dioxoisoindolin-2yl) benzamide

A solution of 4-nitrobenzoic acid (0.515 g, 3.08 mmol) in THF (20 mL) was added to N-aminopthalimide (0.5 g, 3.08 mmol) and N,N'-dicyclohexylcarbodiimide (0.636 g, 3.08 mmol) in THF (30 mL). This mixture was stirred at

room temperature for 4 hours. The insoluble N,N'-dicyclohexylurea was removed by filtration and the solution was concentrated to dryness under reduced pressure. The resulting compound was dissolved in ethyl acetate (10 mL) and addition of hexane (25 mL) to the solution afforded receptor **1** as white powder.

Yield: 0.74 g (78.7%) m.p.: 186°C. Elemental analysis: C<sub>15</sub>H<sub>9</sub>N<sub>3</sub>O<sub>5</sub> Calcd (%): C, 57.88; H, 2.91; N, 13.95. Found (%): C, 57.86; H, 2.93; N, 13.92, EI Mass: 311.1 (M)<sup>+</sup>, IR data (KBr, v/cm<sup>-1</sup>): 3298 (N-H stretching), 1701 (phthalimide stretching), 1648 (benzamide stretching), 1528 (NH bending), 1450 (NO<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm):  $\delta$  9.0 - 8.8 (d, 1H, *J* = 8 Hz),  $\delta$  8.5 (s, 1H),  $\delta$  8.0 - 7.8 (d, 1H, *J* = 8 Hz),  $\delta$  7.6 - 7.3 (m, 4H ). <sup>13</sup>C (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm):  $\delta$  120, 122, 126, 127, 141, 147, 167.

#### 2.5. Synthesis of 3,5-Dinitro-N-[(1,3-dioxoisoindolin-2yl) benzamide

The receptor **2** was synthesized by the method as described above from 3,5-dinitrobenzoic acid (0.654 g, 3.08 mmol) with N-aminopthalimide (0.5 g, 3.08 mmol) and N,N'-dicyclohexylcarbodiimide (0.636 g, 3.08 mmol) in THF (30 mL).

Yield: 0.77 g (70%) m.p.: 160°C. Elemental analysis: C<sub>15</sub>H<sub>8</sub>N<sub>4</sub>O<sub>7</sub> Calcd (%): C, 57.57; H, 2.26; N, 15.73. Found (%): C, 57.56; H, 2.28; N, 15.71. EI Mass: 356.2 (M)<sup>+</sup>. IR data (KBr, v/cm<sup>-1</sup>): 3232 (N-H stretching), 1705 (phthalimide stretching), 1627 (benzamide), 1547 (NH bending), 1480 (NO<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm):  $\delta$  9.7 (s, 1H),  $\delta$  9.0 (s, 1H),  $\delta$  8.7 - 8.5 (d, 1H, *J* = 8 Hz),  $\delta$  7.8 - 7.5 (m, 4H). <sup>13</sup>C (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm):  $\delta$  120, 124, 127, 134, 140, 148, 153, 165.

## 3. Results and Discussion

## 3.1. <sup>1</sup>H NMR Spectral Studies

<sup>1</sup>H NMR spectra of the receptors **1** and **2** were recorded using DMSO- $d_6$  in the presence and absence of fluoride ion to know the interaction between them. <sup>1</sup>H NMR spectrum of the receptor **1** showed -NH proton signal at  $\delta$ 8.5 and the receptor **2** showed NH proton signals at  $\delta$  9.7. The signals at  $\delta$  7.6 - 7.3 and  $\delta$  7.8 - 7.5 indicated the presence of aromatic group present in phthalimide ring for the receptors **1** and **2** respectively. To investigate anion-binding properties of the receptors **1** and **2**, the <sup>1</sup>H NMR spectral change caused by the addition of the fluoride as tetrabutylammonium salts were studied. The <sup>1</sup>H NMR spectrums of receptors **1** and **2** (before and after addition of F<sup>-</sup>) are shown in **Figures 1(a)** and **(b)** respectively. Before discussing the spectroscopic features in detail, two effects, which were responsible for <sup>1</sup>H NMR



Figure 1. (a) Partial <sup>1</sup>H NMR (400 MHz) spectra of receptor 1 in DMSO- $d_6$  in the (a) absence (b) presence of 1 equiv. and (c) 5 equiv. of  $[nBu_4N]F$ . The signals of NH protons are marked with black dots; (b) Partial <sup>1</sup>H NMR (400 MHz) spectra of receptor 2 in DMSO- $d_6$  in the (a) absence (b) presence of 1 equiv. and (c) 5 equiv. of  $[nBu_4N]F$ . The signals of NH protons are marked with black dots.

changes upon hydrogen-bond formation, would be considered [26]: 1) through-bond effects, which increase the electron density of the phenyl ring and promote an upfield shifts; and 2) through-space effects, which polarize C-H bond in proximity to hydrogen bond, create the partial positive charge and the proton and cause a downfield shifts. Upon addition of five equiv. of F<sup>-</sup> ions, the peaks at  $\delta$  8.5, 9.7 ppm which were assigned to NH for receptors 1 and 2 respectively, shifted downfield, broadened and finally the signal for NH disappeared which might be ascribed to the occurrence of deprotonation of NH suggests the formation of FHF<sup>-</sup> dimmer as a new signal observed at ca. 16 ppm [27]. This result indicated that there was decrease in the electron density of NH protons causing a deshielding effect, which were involved in hydrogen-bonding interactions with  $F^{-}$  [28].

The increase of electron density in the phenyl ring causes a shielding effect and should promote an upfield shift, which is expected to come from the formed hydrogen bond [29].

## 3.2. Anion Sensing

The recognition properties of the receptors 1 and 2 toward different anions were studied by the several methods such as the naked-eye experiment (**Figures 2(a)** and (b)), the <sup>1</sup>H NMR, UV-visible and fluorescence titrations. The UV-visible titrations were carried out by adding  $5 \times 10^{-3}$  M solution of tetrabutylammonium salts of anions to the DMSO solution of receptors 1 and 2 ( $5 \times 10^{-5}$  M).

#### 3.3. Absorption Titration Studies

In the naked-eye experiments, receptors **1** and **2** ( $5 \times 10^{-5}$  M in DMSO) showed color changes from colorless to pink and violet respectively in the presence of 2 equivalents of TBAF ( $5 \times 10^{-3}$  M in DMSO). Both the receptors were found to be insensitive even to the addition of large excess of Cl<sup>-</sup>, Br<sup>-</sup> and l<sup>-</sup> ions ( $5 \times 10^{-1}$  M).





Figure 2. (a) Color changes of receptor (R) 1 in DMSO (5.0  $\times$  10<sup>-5</sup> M) before and after the addition of 2 equivalents of representative anions (from the left to right: R, R + F<sup>-</sup>, R + CI<sup>-</sup>, R + Br<sup>-</sup>, R + I<sup>-</sup>); (b) Color changes of receptor (R) 2 in DMSO (5.0  $\times$  10<sup>-5</sup> M) before and after the addition of 2 equivalents of representative anions (from the left to right: R, R + F<sup>-</sup>, R + CI<sup>-</sup>, R + Br<sup>-</sup>, R + I<sup>-</sup>).

The interaction of receptors 1 and 2 with different halide (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) ions were evaluated through UV-visible titrations by adding a standard solution (5  $\times$  $10^{-3}$  M) solution of tetrabutylammonium salt of anions in DMSO solution of receptors. For the receptors 1 and 2, UV-visible titrations were carried out in DMSO at a concentration level of  $5.0 \times 10^{-5}$  M upon incremental addition of 0.01 ml (0.33 equiv.:  $5 \times 10^{-3}$  M) of tetrabutylammonium fluoride up to 4 equivalents and the resulting spectra are shown in Figures 3(a) and (b) respectively. The Figure 3(a) shows the receptor 1 was characterized by strong absorption bands at 258 and 287 nm. Peaks at 258 and 287 nm of receptor 1 decreased gradually while two new peaks formed and increased gradually at 383 and 535 nm simultaneously with increasing amounts of F<sup>-</sup> ions (0.01 ml (0.33 equiv) of  $5 \times 10^{-3}$  M). The colourless solution of the receptor 1 turned pink at the same time (Figures 2(a) and (b)). These results indicate that the strong electron-withdrawing effect of NO<sub>2</sub> substituents makes the charge delocalization more easily upon interaction with fluoride [28]. This could be explained based on the intramolecular electron-transfer interactions [30] between the electron rich amide bond anion and the electron deficient phthalimide ring. In addition there is one isobestic point at approximately 310 nm, which indicated that equilibrium between 1 and 1. F<sup>-</sup> during the

course of the titration. While for the receptor **2**, the peak around 260 nm decreased and two new peaks were observed at 405 and 534 nm with an isobestic point at 270 nm, but no detectable spectral changes were observed even in the presence of larger excess of hundred equivalents of the corresponding anions such as  $CI^-$ ,  $Br^-$  and  $I^-$ , which made it clear that **1** and **2** could sense  $F^-$  over other anions. These observation could be attributed to the small size and higher electro negativity of the  $F^-$  compared to the other halide ions [25,31]. The binding constant of the receptor **1** and **2** were calculated from the fluoride-induced absorption changes using the following Equation (1) [32].

$$A_0 / (A_0 - A) = e_L / (e_L + e_{ML}) x (1/K_S [M] + 1) - Eq \quad (1)$$

Where,  $A_0$  and A are the intensities of absorption of the receptor and complexes (receptor with guest ions) respectively,  $\varepsilon_L$  is a molar absorption co-efficient of the receptor,  $\varepsilon_{ML}$  is a molar absorption co-efficient of the receptor with guest ions and  $K_s$  is the binding constant. The binding constant can be obtained by the ratio of intercept and slope. The binding constant for F<sup>-</sup> complexation for the receptors 1 and 2 were estimated as  $(1.7 \pm 0.20) \times 10^3$  M<sup>-1</sup> (Figure 3(b) and Table 1) and  $(2.6 \pm 0.05$  and Table 1) × 10<sup>3</sup> M<sup>-1</sup> (Figure 3(d)) respectively.



Figure 3. (a) Absorption spectra of receptor 1 recorded in DMSO  $(5.0 \times 10^{-5} \text{ M})$  after addition of 0 to 4 equivalents of tetrabutylammonium fluoride; (b) Plot of  $A_0/A_0$ -A against  $1/[F^-]$  for 1; (c) Absorption spectra of receptor 2 recorded in DMSO  $(5.0 \times 10^{-5} \text{ M})$  after addition of 0 to 4 equivalents of tetrabutylammonium fluoride; (d) Plot of  $A_0/A_0$ -A against  $1/[F^-]$  for 2.

Receptor	F <sup>−</sup> Amax (nm)	Binding constants		Correlation coefficient ( <b>P</b> )
		$\mathrm{F}^-$	Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup>	Contention coefficient (K)
1	258, 287, 383, 535	$(2.7\pm 0.20)^b \times 10^3$	ND <sup>c</sup>	0.9959
2	260, 284, 405, 534	$(4.0\pm 0.05)^b \times 10^3$	ND <sup>c</sup>	0.9940

Table 1. Data obtained from the UV-visible spectra upon titration of receptors 1 and 2 with anions<sup>a</sup> in DMSO.

<sup>a</sup>Countercation was tetrabutylammonium salts for anions. All errors are ±5%; <sup>b</sup>The error value was obtained by the result of linear fitting. All errors are ±5%; <sup>c</sup>Changes in the UV-visible spectra were not enough to calculate the binding constant.

600.0

The higher binding constant was achieved for the receptor **2** which might be due to the introduction of another nitro group in **2**, which increases the acidity of amide-NH group and which enhance the hydrogen bond donating character of this receptor. [33] Restoration of the original spectrum of the sensor system from this receptor- $F^-$  adduct upon addition of a trace amount of water/methanol not only suggests that the complexation between  $F^-$  and **1** or **2** are reversible in nature but also leads further support to the proposition that hydrogen bonding exists between the receptor and  $F^-$  [34].

#### 3.4. Emission Spectral Studies

#### 3.4.1. Anion Sensing

To corroborate well with those obtained during the UVvisible titrations described above, the fluorescence titration experiment was carried out with TBAF. These observations were illustrated in Figures 4(a) and (b), which showed the fluorescence spectra in different concentration of the receptors 1 and 2 respectively. The fluorescent spectral properties of the receptors 1 and 2 (5  $\times$  10<sup>-5</sup> M) were determined in DMSO showing fluorescence intensity at 770 nm ( $\lambda_{exc}$  = 380 nm). Upon the addition of F<sup>-</sup> (0.01 ml (0.33 equiv.) of 5 × 10<sup>-3</sup> M) to DMSO solutions of 1 and 2, the fluorescence emission intensity of the receptors 1 and 2 enhanced at 770 nm and the enhancement efficiency increases along with the increases in concentration of F<sup>-</sup> up to 2 equiv. However no detectable changes were observed even in the presence of large excess of hundred equivalents of the corresponding anions such as Br<sup>-</sup>, Cl<sup>-</sup>, and I<sup>-</sup> which made it clear that 1 and 2 could sense F<sup>-</sup> over other anions. These results suggested that the receptors 1 and 2 have a higher selectivity for F compared to other halide anions. The selectivity for F<sup>-</sup> can be attributed to Brønsted basicity of the receptor. The F<sup>-</sup> anions have the strongest basicity, and also exhibit the most effective hydrogen bonding or deprotonation with the binding site, amide group. F<sup>-</sup> coordination to the binding site of the receptors 1 and 2 results in an enhancement of the phthalimide emission. The enhancement of the fluorescence intensities may due to the result of an increase of the rigidity of the receptor molecules upon receptor: F<sup>-</sup> complexation [35].



Figure 4. (a) The changes in the fluorescence emission spectra of receptor 1 ( $5.0 \times 10^{-5}$  M) and (b) for 2 upon titration with solutions of tetrabutylammonium fluoride in DMSO.

#### 3.4.2. Cation Sensing

To investigate the metal-induced fluorescence change the fluorescence spectra of receptors **1** and **2** in complexation with different transition metal ions ( $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$  and  $Mn^{2+}$ ) were recorded in DMSO to examine the selectivity.

The emission spectrum of free receptors 1 and 2 display a broad band with an emission maximum at 770 ( $\lambda_{exc} = 380$  nm). Upon addition different metal ions (0.01 ml (0.03 equiv.) of  $5 \times 10^{-3}$  M) to a solution of receptors 1 and 2 in DMSO, a significance intensity enhancement

of the emission bands a significant increase in the 770 nm emission, which was attributed to the formation of receptors: metal complex was observed (Figures 5(a)-6(b)). The dependence of the metal cations (Cu<sup>2+</sup>, Zn<sup>2+</sup>,

 $Ni^{2+}$ ,  $Co^{2+}$  and  $Mn^{2+}$ ) for the receptors 1 and 2 on the fluorescence enhancement (FE) is presented in **Figure 6(c)** respectively. The changes in the fluorescence emission observed upon metal cation addition depend on the



Figure 5. (a) The changes in the fluorescence emission spectra of receptor 1 ( $5.0 \times 10^{-5}$  M) and (b) for 2 upon titration with solutions of Cu<sup>2+</sup> ions in DMSO.



Figure 6. (a) The changes in the fluorescence emission spectra of receptor 1 ( $5.0 \times 10^{-5}$  M) upon titration with solutions of metal ions ( $Cu^{2+} Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ , and  $Mn^{2+}$ ) in DMSO; (b) The changes in the fluorescence emission spectra of receptor 2 ( $5.0 \times 10^{-5}$  M) upon titration with solutions of metal ions ( $Cu^{2+} Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ , and  $Mn^{2+}$ ) in DMSO; (c) The changes in the fluorescence emission spectra of receptor 2 ( $5.0 \times 10^{-5}$  M) upon titration spectra of receptor 2 ( $5.0 \times 10^{-5}$  M) upon titration with solutions of metal ions ( $Cu^{2+} Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ , and  $Mn^{2+}$ ) in DMSO; (c) The changes in the fluorescence emission spectra of receptor 2 ( $5.0 \times 10^{-5}$  M) upon titration with solutions of metal ions ( $Cu^{2+} Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ , and  $Mn^{2+}$ ) in DMSO.

nature of the added metal cations. The  $FE = I/I_0$  was determined from the ratio of maximum fluorescence intensity I (after addition metal cations) and minimum fluorescence intensity  $I_0$  (before metal cations addition).

The FE values for the receptor **1** are 2.29 (Cu<sup>2+</sup>), 1.85 (Ni<sup>2+</sup>), 1.37 (Co<sup>2+</sup>), 1.27 (Mn<sup>2+</sup>), 1.25 (Zn<sup>2+</sup>) and for **2**, 2.57 (Cu<sup>2+</sup>), 1.66 (Ni<sup>2+</sup>), 1.36 (Co<sup>2+</sup>), 1.15 (Mn<sup>2+</sup>), 1.09 (Zn<sup>2+</sup>). The highest effect has been observed in the presence of Cu<sup>2+</sup> cations (for **1**, FE = 2.29; for **2** FE = 2.57) and the order of FE values for all the metal ions are given as follows.

It is noticeable that only  $Cu^{2+}$  from all other metal ion tested is able to produce large change in the emission spectrum indicating that this enhancement for the fluorescence is highly specific for  $Cu^{2+}$  cations.

## 4. Conclusion

In conclusion, we have developed selective and sensitive dual chromo as well as fluorogenic receptors 1 and 2 using phthalimide moiety for the determination of  $F^-$  and  $Cu^{2+}$ . These receptors selectively recognize  $F^-$  ions even in the presence of other halide ions and shows higher selectivity towards  $Cu^{2+}$  ions than other metal ions studies.

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