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Ratiometric fluorescent chemosensor for fluoride ion based on inhibition of excited state intramolecular proton transfer



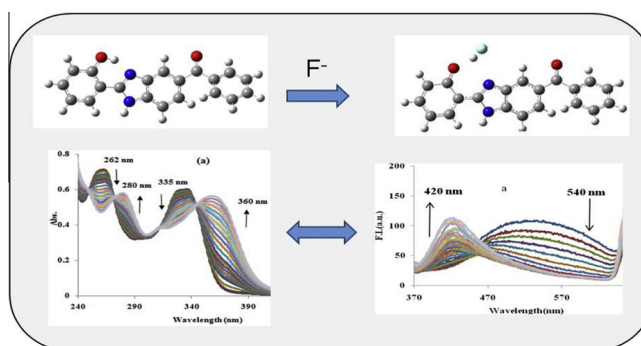
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HIGHLIGHTS

- Synthesis of hydroxyaryl-benzimidazole based ESIPT sensor.
- Ratiometric chromofluorescent sensor for fluoride ions.
- Broad range of fluoride ion detection limit.
- Practical usability of probe **2** by dip coating method.

GRAPHICAL ABSTRACT



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ABSTRACT

ESIPT based benzimidazole derivative has been synthesized and investigated their photophysical behavior towards various anions. The probe **2** has been used for selective estimation of F^- ions as compared to other anions and signaled the binding event through formation of new absorption band at 360 nm and emission band at 420 nm. The probe **2** showed fluorescence behavior towards fluoride ions through hydrogen bonding interactions and restricted the ESIPT emission at 540 nm from OH to nitrogen of benzimidazole moiety to release its enol emission at 420 nm.

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Introduction

Fluoride ion, being the smallest and most electronegative anion has received much attention due to its profound effects on human

health, thus intake of acute amount of it is beneficial to the treatment of osteoporosis and dental health [1–3]. But an overdose of fluoride ion can cause many problems such as bone disorder, collagen breakdown, thyroid activity and depression [4]. Thus, to determine the level of fluoride ions, various detection methods have been reported including highly accurate but expensive analytical instruments that use ion selective electrodes and chromogenic and fluorescent probes [5–7]. Fluoride ions can contaminate the human body and other materials in the surroundings during the manufacture of rocket fuel and fireworks [8]. Detection of these traces is a major concern in the field of analytical and forensic

Abbreviations: ESIPT, excited state intramolecular proton transfer; TMS, tetra methyl silane; ASC II, American Standard Code for Information Interchange; B3LYP, Becke, 3-Parameter, Lee–Yang–Parr; TD-DFT, Time Dependent-Density Functional Theory; Mpt., melting point; Excel TM, Microsoft Excel Trade Mark; 6-31G(d,p), basis set method-double diffuse function.

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sciences. Colorimetric sensors do not need any spectroscopic instrument since colorimetric changes can be detected by the naked eye. But use of such sensors is limited because of their low absorption. Fluorescent sensors based on excited-state intramolecular proton transfer (ESIPT), as seen from 2-(2-hydroxyphenyl)benzimidazole/thiazole/oxazole have been attracted more attention [9]. ESIPT sensors exhibit dual emissions from both the excited enol and keto tautomers [10]. Fluorescent sensing of fluoride ion could realize by prohibiting ESIPT through coordination or deprotonation induced by fluoride with ESIPT centers, resulting in detectable spectral change. Compared with widely used photoinduced electron transfer (PET) mechanism for sensing [11], the fluorescent sensors based on ESIPT can afford many advantages including dual fluorescence intensity changes and large Stokes shift, thus the excited state intramolecular proton transfer (ESIPT) has attained a special importance due to vast applications as laser dyes, UV-photostabilizer, scintillators, membrane and protein probes and as a potential component for photo switches and organic LEDs. ESIPT usually occur in the molecules bearing an H-bond donor group usually a phenolic/amino moiety associated with basic site (O, N, S) in the ground state through H-bond interactions. This proton which is covalently attached in the electronically excited state migrates to a neighboring hydrogen-bonded atom which is less than 2 Å. The significant amount of excited state energy is dissipated in this process. The formed phototautomer emits light at a lower energy with an unusually large Stokes shift (range from 100 to 500 nm) and thermally equilibrates back to the ground state with the proton bound to its original atom. This large Stokes shift is an important property for fluorophores because the self-absorption, or the inner filter effect, can be avoided and the fluorescent analysis can also be improved. They can detect metal ions with ratiometric fluorescence response, providing self calibration function and avoiding photodamage, scattering light and strong interference derived from short wavelength emission in biological media.

We have recently reported some ESIPT based cation and anion sensors based on hydroxyarylbenzimidazole moiety [12]. In the present manuscript ESIPT fluorescent probe **2** has been synthesized with different strategy other than reported scheme [13] which showed sensitivity changes towards fluoride ions. The presence of fluoride ions caused decrease in absorption intensity at 335 nm and emergence of new absorption band at 360 nm. However, in case of emission presence of fluoride ion caused quenching of keto tautomer at 540 nm and enol tautomer band is released at 420 nm.

Experimental section

Materials and equipments

All chemicals were purchased from Loba and Sigma Aldrich Chemical Co and used without further purification. Column chromatography was performed using silica gel (60–120 mesh). All reactions were monitored by thin layer chromatography. Chloroform: Methanol was the adopted solvent system. Melting points were carried out by the open capillary tube method [14] and uncorrected. ^1H NMR and ^{13}C NMR spectra were carried out using a JEOL ECS-400 MHz spectrometer in SAI Labs, Thapar University, Patiala with TMS as an internal reference. Mass Spectra of the synthesized compounds were recorded at MAT 120 in SAIF, Punjab University. All chemical shifts are reported in ppm relative to the TMS as an internal reference. UV–Vis studies were carried out on a Specord PC machines using slit width of 1.0 nm and matched quartz cells. Fluorescence spectra were determined on a Varian Cary Eclipse fluorescence spectrometer. Stock solution of probes

1 and **2** was prepared at 10^{-3} M in distilled CH_3CN . Tetrabutylammonium salts were used for the anions. All absorption and fluorescence scans were saved as ASC II files and further processed in Excel™ to produce all graphs shown. Solutions of **1** and **2** were typically 20 μM for UV–Vis studies. Stability constants were determined using Benesi–Hildebrand Equation [15] (Eq. (1))

$$\frac{1}{(A - A_0)} = \frac{1}{(A_{\max} - A_0)} + \frac{1}{K[F^-]^n(A_{\max} - A_0)} \quad (1)$$

where A_0 , A , A_{\max} are the absorption considered in the absence of ion, at an intermediate, and at a concentration of saturation. K is binding constant, $[F^-]$ is concentration of ion. n is the stoichiometric ratio.

Computational methods

The ground state (S_0) geometry of probe **2** was optimized using Density Functional Theory (DFT) [16]. The functional used was B3LYP and basis set used for all atoms were 6-31G(d,p). The vertical excitation energy and oscillator strengths at the ground state equilibrium geometries were calculated using with the same hybrid functional and basis set. The low-lying first singlet excited state (S_1) of the probe **2** was relaxed using to obtain its minimum energy geometry. Frequency computations were also carried out on the optimized geometry of the low-lying vibrationally relaxed first excited state of the probe **2** and probe **2.F**⁻.

Synthesis of probes **1** and **2**

Probe **1** – 3,4 Diaminobenzophenone (500 mg, 2.3 mmol) and benzaldehyde (374 mg, 3.5 mmol) were dissolved in 10 mL nitrobenzene. The reaction mixture was refluxed for about 24 h, and then cooled to room temperature. The solid separated was filtered by using sintered crucible with the help of vacuum filtration method and washed with diethyl ether to obtain colorless solid of probe **1** (225 mg, 89% yield); Mpt. 220–221 °C; ^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 400 MHz): δ 8.26–8.25 (m, 2H, Ar), 8.17 (s, 1H, Ar), 7.85–7.76 (m, 4H, Ar), 7.66–7.48 (m, 7H, Ar), 4.97 (bs, NH); ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 100 MHz): δ 195.52 (C=O), 137.50, 130.94, 128.72, 127.90, 127.17, 123.08, 120.82, 117.33, 113.28, 110.96 (Ar H); (Figs. S1 and S2). MS (ESI) m/z 299 (M^+H) (Fig. S3).

Probe **2** – 3,4 Diaminobenzophenone (1 g, 4.7 mmol) and salicylaldehyde (630 mg, 5.1 mmol) were dissolved in 30 mL nitrobenzene. The reaction mixture was refluxed for about 24 h, and then cooled to room temperature. The solid separated was filtered and washed with diethyl ether to obtain yellow colored solid which was further purified by column chromatography to get pure probe **2** (528 mg, 92% yield); Mpt. 240–241 °C; ^1H NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 400 MHz): δ 12.57 (bs, 1H, NH), 9.63 (bs, 1H, OH), 8.35 (s, 1H, ArH), 7.96 (s, 1H, ArH), 7.88 (d, 1H, $J = 8.28$ Hz, ArH), 7.61–7.57 (m, 4H, ArH), 7.29–7.24 (t, 1H, $J = 9.16$ Hz, ArH), 7.14–7.10 (t, 1H, $J = 11.0$ Hz, ArH), 7.00–6.96 (t, 1H, $J = 7.36$ Hz, ArH), 6.86–6.79 (m, 1H, ArH), 5.77 (s, 1H, ArH); ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO-d}_6$, 100 MHz): δ 195.56 (C=O), 158.29, 137.86, 131.68, 129.31, 127.90, 126.06, 124.82, 124.29, 120.72, 118.71, 117.09, 113.75, 112.06, 110.97 (ArH); (Figs. S4 and S5). MS (ESI) m/z 314.11 (M^+H) (Fig. S6) (see Scheme 1).

Results and discussion

Photophysical properties of probes **1** and **2**

The UV–Vis spectroscopic properties of probe **1–2** were investigated in CH_3CN at 20 μM . Probe **1** and **2** displayed an absorption band centered at 320 nm and 335 nm respectively. Addition of

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