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Benzthiazole-based multifunctional chemosensor: fluorescent recognition of Fe^{3+} and chromogenic recognition of HSO_4^-

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1. Introduction

Recently, there has been significant interest in the design and development of artificial optical chemosensors that recognize biologically and environmentally important analytes.¹ Considerable efforts have been made to develop multifunctional sensors that simultaneously recognize multiple analytes.² Due to their high sensitivity and prompt analyte detection, UV–vis absorption spectroscopy and fluorescent spectroscopy-based analytical techniques are immensely preferred. A large number of chemosensors have been proposed to selectively detect cations and anions by a simple turn-on or turn-off response.³ Most of these chemosensors are selective for only one particular analyte.⁴ In various complex molecular events, the simultaneous recognition of different analytes is required to screen for many target molecules at the same time.

Iron plays an important role in several biological activities.⁵ Iron deficiency is toxic and can lead to a number of severe neurological disorders, developmental defects, and malfunctions.⁶ A lack of adequate iron levels in the blood leads to anemia.⁷ To supplement iron levels in the body, pharmacological forms that use the oral route are recommended, such as iron sulfate and ferroglycine

ABSTRACT

A benzthiazole-based multifunctional chemosensor was designed with siderophores like binding sites for recognition of Fe^{3+} and both hydrogen bond donor and acceptor binding sites for oxyanion HSO_4^- . The sensor recognizes Fe^{3+} selectively through enhancement of fluorescence emission intensity at 440 nm and recognizes HSO_4^- through a bathochromic shift in UV–vis spectra from 315 nm to 365 nm with clear isosbestic points at 345 nm and 395 nm. The recognition of both Fe^{3+} and HSO_4^- is free from the interference from the other cations and anions, respectively.

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sulfate. However, iron supplementation leads to accumulation of externally administered iron in the body, which has deleterious effects. For instance, a high level of iron in serum increases the risk of several types of tumors.⁸ Iron excess also leads to Alzheimer's disease, which is responsible for some neural disorders.⁹ With excess iron content, counter anion content (sulfate/hydrogen sulfate) also increases, which can also have harmful effects on the body. High doses of sulfate may cause laxative effects that lead to diarrhea.¹⁰ Iron and sulfate/hydrogen sulfate content should be simultaneously monitored. Although there are number of sensors that separately detect iron¹¹ and sulfate/hydrogen sulfate ions,¹² to best of our knowledge, there is no sensor for simultaneous estimation of Fe³⁺ and HSO₄⁻. Therefore, developing multiple analyte sensors can be quite challenging.

The current work focuses on recognizing Fe^{3+} and HSO_4^- simultaneously. A coordination sphere that consists of an array of hydrogen bond donors and acceptors is required. For this purpose, we designed and synthesized sensors **1** and **2** as shown in Scheme 1.

The design of the sensors is based upon the reports available in literature on iron chelating agents, such as siderophores and other synthetic designs.¹³ The coordination sphere of these agents makes use of the binding units containing phenol substituent along with sp^2 -nitrogen donor. Thus, the insertions of these binding sites in our designs might be beneficial for iron recognition. On the other hand, these binding sites show both a hydrogen bond donor and acceptor, making an interesting combination for the coordination of oxy-anions, such as HSO₄⁻.





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2. Results and discussion

Benzthiazole-based sensors 1 and 2 were synthesized by condensation of 2-(2-aminophenyl)-benzthiazole with 2-hydroxynaphthaldehyde or salicylaldehyde, respectively. The compounds were characterized by spectroscopic methods. The presence of imine linkages was confirmed by observing signals at 9.58 and 8.98 ppm in ¹H NMR spectra and bands at 1610 and 1635 cm⁻¹ in IR spectra. The structure of sensor **1** was also confirmed with a single crystal X-ray crystallography image, as shown in Fig. 1. The crystal structure of sensor **1** shows that all bond parameters are normal. The benzthiazole ring and naphthyl ring were rotated by 15.10(5)° and 47.29(4)° with respect to the central phenyl rings. The –OH group formed intramolecular H-bonds with imine N and S, with 01–H1A…N2 (2.567(2) Å, 1.84 Å, 147°), and with O1–H1A…S1 (3.441(2) Å, 2.94 Å, 121°). Downfield chemical shift of hydroxyl proton in sensor 1 and 2 is verifying intramolecular hydrogen bonding in both. The chemical shift value for hydroxyl proton in the case of sensor 1 is 14.67 ppm and in the case of sensor 2 is 11.59 ppm, indicating extensive hydrogen bonding in sensor 1.



Fig. 1. ORTEP diagram of sensor 1 labeling scheme.

UV-vis absorption and fluorescence spectroscopy were used to examine the binding behaviors of sensors **1** and **2** with different cations and anions. UV-vis absorption spectra of sensors **1** and **2** showed absorption bands at 310 and 370 nm, respectively, due to imine linkages (Fig. S1). By recording UV-vis absorption and fluorescence spectra of sensors **1** and **2** in the presence of various metal ions in TRIS buffered CH₃CN/H₂O (8/2, v/v, pH=7.6), the ability of sensors **1** and **2** to detect cations was investigated. There was no unique and selective change in UV-vis absorption spectra of sensors **1** and **2** in the presence of any cation as shown in Fig. S1. The fluorescence spectra of sensor **1** showed enhanced fluorescence intensity at 440 nm with Fe³⁺ when excited at 310 nm (Fig. 2A), while there were no changes with any other tested metal ions. The enhanced fluorescence intensity is attributed to



Fig. 2. (A) Fluorescence spectra of sensor **1** (1.3 μ M) upon adding nitrate salt of various metal ions (20 μ M) in TRIS buffered CH₃CN/H₂O (8/2, v/v, pH=7.6) when excited at 310 nm. (B) Fluorescence spectra of sensor **1** upon adding Fe³⁺ (0–20 μ M).

molecular rigidification and restricted PET binding with Fe³⁺. In addition, sensor **2** showed fluorescence intensity quenching at 440 nm with Fe³⁺ when excited at 370 nm (Fig. S2). Even the sensor is selective for Fe³⁺ over Fe²⁺, showing the incompatible coordination sphere of sensor for Fe²⁺ in terms of size, shape and steric factors. The selectivity of coordination sphere for one oxidation state of iron over the other is the basis of redox-driven translocations in molecular machines. The concept is well documented in literature, where the transition metal ions can be moved reversibly between the two different co-ordination spheres using some inputs.¹⁴ In addition, sensor **2** showed fluorescence intensity quenching at 440 nm with Fe³⁺ when excited at 370 nm (Fig. S2).

To further confirm the sensing properties of sensor **1** with Fe^{3+} , fluorescence titration was performed. As the concentration of Fe^{3+} increased from 0 to 20 μ M, fluorescence intensity at 440 nm increased (Fig. 2B). The effect of pH on sensor **1** was visualized by recording UV–vis absorption and fluorescence spectra of sensor **1** in CH₃CN/H₂O (8/2, v/v) at variable pH (Fig. S3). Variation in pH caused drastic changes in the spectra of sensor **1**. Thus, recognition studies were carried out in TRIS buffered solution to exclude the

effect of pH. The application of sensor **1** as a selective sensor for Fe³⁺ was established by recording the spectra of sensor **1** with Fe³⁺ in TRIS buffered CH₃CN/H₂O (8/2, v/v, pH=7.6) in the presence of the same equivalents of other tested metal ions. There was no significant effect on the fluorescence emission profile of **1**.Fe³⁺ in the presence of any tested metal ion, as shown in Fig. S4. This result clearly indicates that sensor **1** recognized Fe³⁺ selectively over other metal ions. Mass spectrum of **1**.Fe³⁺ showing a peak at m/z=560, which corresponds to **1**+Fe³⁺+2NO₃⁻, shows 1:1 binding of sensor **1** with Fe³⁺ (Fig. S5). The association constant for **1**.Fe³⁺ was calculated as (2.9±0.13)×10⁵ M⁻¹ using Benesi–Hildebrand plot (Fig. S6).¹⁵ The detection limit was calculated from titration data as 8.5 μ M (Fig. S7).¹⁶

Sensors **1** and **2** were checked for anion sensing by monitoring UV-vis absorption and fluorescent spectra in the presence of different anions. The absorption maxima of the UV-vis absorption spectra of sensor **1** in TRIS buffered CH₃CN/H₂O (8/2, v/v, pH=7.6) shifted to 365 nm with clear isosbestic points at 345 and 395 nm upon treatment with HSO_4^- (Fig. 3A). However, there were no changes in the UV-vis absorption spectra of sensor 1 with any other anions. There were no changes in the UV-vis absorption spectra of sensor 2 in the presence of any anions (Fig. S8). The binding of sensor **1** with HSO_4^- was further verified by titration with UV-vis spectroscopy. Stepwise addition of HSO_4^- (0-20 μ M) to sensor 1 (1.3 µM) in TRIS buffered CH₃CN/H₂O (8/2, v/v, pH=7.6) caused a decrease in absorbance at 310 and 450 nm and an increase in absorbance at 365 nm. It also gave rise to a new absorption maximum at 365 nm (Fig. 3B). The association constant of 1.HSO₄was calculated from UV-vis absorption titration data as $(1.8\pm0.05)\times10^2$ M⁻¹ (Fig. S9).¹⁵ From UV-vis absorption titration data, the detection limit of HSO_4^- was calculated to be 5.4 μM (Fig. S10).¹⁶ Selective binding of sensor **1** with HSO_4^- was determined by executing competitive experiments in the presence of other tested anions. The UV-vis absorption profile of 1.HSO₄remained undisturbed (Fig. S11) in the presence of the same equivalents of all other anions in TRIS buffered CH₃CN/H₂O (8/2, v/v, pH=7.6), verifying its selective binding. In ¹H NMR titration, upon interaction of HSO_4^- with sensor **1**, major shifts were observed for the signal -OH and -N=CH, both the signals shifted downfield by $\Delta\delta$ 0.05 ppm (Fig. S12). The shift in –OH signal shows that the complex has intense hydrogen-bonding than one prevailed in the pure receptor. The shifts of aromatic protons were also observed by $\Delta \delta$ 0.02–0.07 ppm. These show that HSO₄⁻ binds in the receptor pseudocavity by using both hydrogen bond donor and hydrogen bond acceptor sites. The overall picture of ¹H NMR spectra of pure host and spectra recorded upon addition of HSO₄prevails the authentic bonding between sensor $\mathbf{1}$ and HSO_4^{-} .

Although there are no substantial differences between the structures of sensors 1 and 2, the binding affinity for anions are quite different. The structural features of the sensors might explain this difference. All of our attempts failed to grow a single crystal on sensor 2. We compared the optimized structure of sensors 1 and 2 using DFT calculations (Figs. 4 and 5). A comparison between the crystal structures of sensor 1 with the optimized structure of sensor **2** may give some misleading information. The optimized structures of sensors 1 and 2 lead to the conclusion that both the structures have the same donor atoms in the pseudocavity of the sensors. However, the difference lies in the relative distances and dihedral angles of both the sensors. The donor sites of sensor 1 are planar compared to sensor 2. The dihedral angle corresponding to an angle between the planes of naphthalene rings or benzene rings and the plane of the amine group plays an important role in defining pseudocavities of both sensors. The dihedral angle $(C_{39}-C_{25}-C_{26}-O_{44})$ in sensor **1** is 3.114, which leads to a regular size and shape of cavity for metal ion coordination. On the other hand, the same type of angle $(C_{33}-C_{25}-C_{26}-O_{36})$ in sensor **2** is in the reverse direction, (i.e., -1.697), which may influence the binding capacity of sensor 2. The other dihedral angles and bond angles also support the poor binding cavity of sensor **2** (Table S6). Furthermore, it was noticed that sensor **1** has smaller HOMO–LUMO energy gap compared to sensor 2, resulting in effective overlapping (Table S7). The smaller HOMO-LUMO energy gap has been reported to be beneficial for metal binding.¹⁷



Fig. 4. Optimized structure of sensor 1 (6,31G*d,p).

With fluorescence spectroscopy, sensor **1** selectively recognizes Fe^{3+} over all tested cations while it recognizes HSO_4^- over all tested anions using UV–vis absorption spectroscopy. We evaluated the interference between Fe^{3+} and HSO_4^- by recording spectra of sensor **1** with Fe^{3+} in the presence of HSO_4^- and vice versa. Fig. 6A



Fig. 3. (A) Changes in UV–vis absorption spectra of sensor 1 (1.3 μ M) upon adding tetrabutyl ammonium salt of various anions (20 μ M) in TRIS buffered CH₃CN/H₂O (8/2, v/v, CH₃CN/H₂O, pH=7.6). (B) Changes in UV–vis absorption spectra of sensor 1 (1.3 μ M) upon successive addition of HSO₄⁻ (0–20 μ M) in TRIS buffered CH₃CN/H₂O (8/2, v/v, pH=7.6).



Fig. 5. Optimized structure of sensor 2 (6,31G*d,p).



Fig. 6. (A) Fluorescence intensity of sensor **1** at 440 nm in the presence of (a) Fe^{3+} (blue diamonds) or (b) Fe^{3+} with equimolar HSO_4^- (red squares). (B) Absorbance of sensor **1** at 365 nm in the presence of (a) HSO_4^- (blue diamonds) or (b) HSO_4^- with equimolar Fe^{3+} (red squares).

shows the overlay plots of fluorescence intensity at 440 nm for solutions containing sensor **1** and Fe³⁺ with solutions containing sensor **1**, Fe³⁺, and equimolar HSO₄⁻. Likewise, Fig. 6B shows overlay plots of absorbance at 365 nm for solutions containing sensor **1** and HSO₄⁻ with solutions containing sensor **1** and HSO₄⁻, and equimolar Fe³⁺. Fluorescence emission intensity at 440 nm of sensor **1** with Fe³⁺ only remains approximately the same even on addition of equimolar amount of HSO₄⁻ (Fig. 6A). Absorbance of sensor **1** at 365 nm with HSO₄⁻ remains approximately the same on addition of equimolar amount of Fe³⁺ as well (Fig. 6B). These facts remain true over a wide range of concentration of Fe³⁺ and HSO₄⁻. Thus, these plots signify that Fe³⁺ and HSO₄⁻ do not cause any interference in recognition of each other.

3. Conclusion

In summary, we have synthesized a sensor that simultaneously recognizes multiple analytes using two different spectroscopic techniques. Sensor **1** selectively showed enhanced fluorescence intensity at 440 nm with Fe^{3+} . It also demonstrated selectively for HSO_4^- by a shift in absorption maxima to 365 nm with clear isosbestic points at 345 and 395 nm.

4. Experimental section

4.1. Materials and methods

Chemicals were purchased from Sigma Aldrich and used without further purification. The NMR spectra were recorded on an Avance-II (Bruker) instrument, which operated at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR. IR spectra were recorded on a Perkin Elmer Spectrum One for compounds in the solid state prepared as KBr discs. Absorption spectra were recorded on a Perkin Elmer Lambda 25. Fluorescence measurements were performed on a Perkin Elmer LS55 fluorescence spectrophotometer.

4.1.1. Synthesis of compound 1. A solution of 2-(2-aminophenyl)benzthiazole (226 mg, 1 mmol) and 2-hydroxy-1-naphthaldehyde (258 mg, 1.5 mmol) in dry methanol (50 mL) was heated at reflux for 14 h. After the reaction was completed, the solvent was evaporated to 25 mL and kept at 5 °C for slow evaporation. A brown crystalline material was separated out. The solid was filtered and washed with cold methanol three times and compound **1** was obtained in 85% yield (323 mg). Mp 214–215 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 14.67 (br s, 1H, OH), 9.58 (s, 1H, CH=N), 8.59 (d, J=8.4 Hz, 1H, Ar), 8.30-8.10 (m, 3H), 7.97 (d, J=7.2 Hz, 1H, Ar), 7.83 (t, J=6.8 Hz, 1H, Ar), 7.70 (t, J=8.4 Hz, 1H, Ar), 7.61-7.45 (m, 5H, Ar), 7.38 (t, J=7.2 Hz, 1H, Ar), 7.06 (d, J=9.2 Hz, 1H, Ar); ¹³C NMR $(100 \text{ MHz}, \text{DMSO-}d_6) \delta$ 109.7, 116.8, 118.6, 119.8, 121.4, 121.7, 122.4, 123.7, 123.9, 124.5, 124.9, 125.3, 126.0, 128.4, 129.1, 130.3, 131.6, 139.2, 146.7, 153.1, 153.7, 156.1, 164.5, 169.2; IR (KBr) 1610 cm⁻¹; Anal. Calcd for C₂₄H₁₆N₂OS: C, 75.77; H, 4.24; N, 7.36. Found: C, 75.91; H, 4.31; N, 7.26.

4.1.2. Synthesis of compound 2. A solution of 2-(2-aminophenyl)benzthiazole (226 mg, 1 mmol) and salicylaldehyde (183 mg, 1.5 mmol) in dry methanol (50 mL) was heated to reflux for 16 h. After the reaction was completed, the solvent was evaporated to 25 mL and kept at 5 °C for slow evaporation. An off-white solid material was separated out. The solid was filtered and washed with cold methanol three times. White solid compound 2 was obtained in 82% yield (271 mg). Mp 139-140 °C; ¹H NMR (400 MHz, DMSO- d_6) δ 11.59 (br s, 1H, OH), 8.98 (s, 1H, CH=N). 8.40-8.45 (m, 1H, Ar), 8.12 (d, J=7.6 Hz, 1H, Ar), 8.08 (d, J=6.8 Hz, 1H, Ar), 7.99-7.97 (m, 1H, Ar), 7.62-7.65 (m, 1H, Ar), 7.60-7.35 (m, 5H, Ar), 7.05 (d, *J*=7.2 Hz, 1H, Ar), 7.02 (d, *J*=8.0 Hz, 1H, Ar); ¹³C NMR (100 MHz, DMSO- d_6) δ 116.8, 119.5, 120.1, 120.8, 121.9, 122.8, 125.2, 126.4, 126.6, 128.8, 130.9, 132.2, 134.0, 136.3, 148.9, 152.0, 159.7, 162.1, 163.6; IR (KBr) 1635 cm⁻¹. Anal. Calcd for C₂₀H₁₄N₂OS: C, 72.70; H, 4.27; N, 8.48. Found: C, 72.46; H, 4.61; N, 8.53.

4.1.3. Metal recognition studies of sensors **1** and **2**. All recognition studies were performed at 25 ± 1 °C. Before recording any spectrum, the sample was shaken to ensure solution uniformity. The effect of pH on the UV–vis absorption and fluorescence spectra of sensor **1** was investigated with a solution of sensor **1** prepared in a CH₃CN/H₂O (8:2, v/v, pH=7.6) solvent system. The cation binding ability of sensors **1** and **2** in a TRIS buffered CH₃CN/H₂O (8:2, v/v, pH=7.6) solvent system was determined by preparing standard solutions of

sensor **1** along with fixed amounts of a particular metal nitrate salt in TRIS buffered CH₃CN/H₂O (8:2, v/v, pH=7.6). The cation recognition behavior of sensors **1** and **2** was evaluated by changes in the photophysical properties of sensors upon adding metal salt. The fluorescence spectra of sensors **1** and **2** were recorded with excitation wavelengths as shown in the respective figures. Titrations used volumetric flasks containing standard solutions of sensors **1** and **2** along with varied amounts of a particular metal nitrate salt in TRIS buffered CH₃CN/H₂O (8:2, v/v, pH=7.6). To evaluate possible interference due to other metal ions, the solutions were prepared to contain sensor **1** (1.3 μ M) along with a fixed concentration of Fe³⁺, both with and without other background cations in TRIS buffered CH₃CN/H₂O (8:2, v/v, pH=7.6). The fluorescence intensity of each solution was recorded.

4.1.4. Anion recognition studies of sensors **1** and **2**. These studies were performed in a manner similar to those investigating the cation recognition properties of sensor **1**. Tetrabutylammonium salts of anions were used and detailed concentrations are mentioned in the manuscript text.

4.1.5. X-ray structure data. Crystals of compound **1** were grown by slow solvent evaporation from methanol solution. X-ray data were collected on a Bruker's Apex-II CCD diffractometer using Mo K α (λ =0.71069 Å). The data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied using SADABS from Bruker. A total of 32,150 reflections were measured. Of these, 5973 were independent and 4288 were observed [I>2 σ (I)] for θ 32°. The structure was deduced by direct methods using SIR-92¹⁸ and refined by full-matrix least squares refinement methods based on F² and using SHELX-97.¹⁹ All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U_{iso} values at 1.2 times the values of the phenylene carbons. All calculations were performed using the Wingx package.²⁰ Important crystal and refinement parameters are given in Table S1.

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Supplementary data

Additional spectroscopic data, graphs, and crystallographic data are available as supplementary data. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, deposition number CCDC 892804. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/ j.tet.2012.11.090.

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