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Highly Fe^{3+} selective ratiometric fluorescent probe based on imine-linked benzimidazole

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Abstract

We synthesized a novel benzimidazole-based fluorescent receptor bearing imine linkages with two sets of sp^2 nitrogens, and investigated its binding properties toward various metal ions. The receptor exhibited a shift in emission band upon binding with Fe^{3+} ions, and no such significant response was noticed in other metal ions. The receptor shows a property of selective ratiometric fluorescent probe of Fe^{3+} ions without interferences of the background metal ions.

Keywords: Ratiometric; Fluorescence; Imine linkage; Benzimidazole; Iron(III)

Development of chemosensors for selective recognition and detection of important metal ions is an inspiring research area of modern supramolecular chemistry.[1] Chemosensors are fabricated to monitor host–guest interactions through the changes of their physical properties in response to the presence of a guest. The rationale behind the design of chemosensor should meet some basic requirements such as exhibiting a qualitative response to a particular analyte, displaying a different type of response to other analytes, and affording a quantitative determination for a wide concentration range of analyte.[2,3]

Among the chemosensors, fluorescent receptors have been actively investigated because of the high sensitivity of the system.[4] Especially, fluorescent chemosensors that show the shift of emission bands upon binding with analytes are particularly attractive since they are capable of the ratiometric sensing of analytes.[5] For precise analyses, ratiometric chemosensors have offered advantages over the conventional monitoring of fluorescence intensity at a single wavelength. A dual emission system can minimize the measurement errors because of the factors such as phototransformation, receptor concentrations, and environmental effects.[6,7] In recent years, a number of fluorescent receptors have been reported to have a pronounced selectivity for a particular metal ion; however, only a few have reported on fluorescent chemosensors for Fe^{3+} ions.[8–14] Furthermore, to the best of our knowledge, no ratiometric fluorescent receptor for Fe^{3+} ions has been reported while ratiometric fluorescence receptors have been available for other metal ions.[15–24]

Iron is one of the most important microelements for human health, and is known to endow a great deal of physiological functions.[25] Many structural units in the form of iron complex take part in the process of transporting and exchanging the oxygen, and several enzymes contain ferric ions as part of a catalytic site.[26] As part of our ongoing studies on benzimidazole-based receptors, here we present a receptor bearing benzimidazole moiety that can function as a highly selective ratiometric fluorescent probe for Fe^{3+} ions.[27–31]

The design of receptor is based upon the fact that iron has a strong binding affinity with receptors having sp^2 nitrogen of imidazole.[32–34] Moreover, imidazole is a ubiquitous ligand present at the active site of many metalloproteins.[35] The receptor is employed with two sets of sp^2

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nitrogens: one set from imine-linkages and the other from benzimidazole.

Receptor **1** was prepared by the condensation reaction of isophthalaldehyde with 2-(2-aminophenyl)-benzimidazole.[36] And receptor **3** was prepared by the condensation reaction of isophthalaldehyde with 2-(2-aminophenyl)-benzothiazole.[37] The corresponding reaction of benzaldehyde with 2-(2-aminophenyl)-benzimidazole afforded receptor **4**.[38] Receptor **2** was obtained with the reduction of imine linkages of receptor **1** with $NaBH_4$ (Scheme 1).[39]

The fluorescence spectrum of receptor **1** displayed an emission band at $\lambda = 412$ nm, when recorded with a 10 μM concentration of receptor **1** in CH_3CN/H_2O (95:5, v/v) upon excitation at $\lambda = 288$ nm. We evaluated the binding properties of receptor **1** toward various metal ions (Fig. 1). Upon addition of a 100 μM solution of Fe^{3+} ions to the 10 μM solution of receptor **1**, the intensity of emission band at 412 nm decreased along with the appearance of a new red-shifted emission band at 475 nm. Other metal ions (as nitrate salts) including alkali (Na^+ and K^+), alkaline earth (Ca^{2+}, Mg^{2+}, and Ba^{2+}) and transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, and Hg^{2+}) revealed no such shift in the emission band under the same conditions. Cu^{2+} ions showed some binding affinity with receptor **1**, as can be interpreted from the quenching of fluorescence intensity at $\lambda = 412$ nm, but Cu^{2+} binding did not cause any shift in the emission band. The structural rigidity of metal complex and metal binding close to the fluorophore might be the factors that cooperate to induce the emission band shift. Fluorescence ratiometric response of receptor **1** toward the surveyed metal ions is displayed in Figure 2. The results show a highly selective response of receptor **1** to Fe^{3+} ions as compared to the other metal ions.

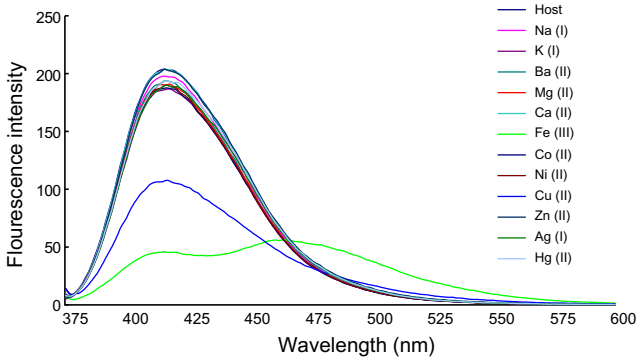


Fig. 1. Changes in fluorescent intensity of receptor **1** (10 μM) upon the addition of a particular metal salt (100 μM) in CH_3CN/H_2O (95:5, v/v).

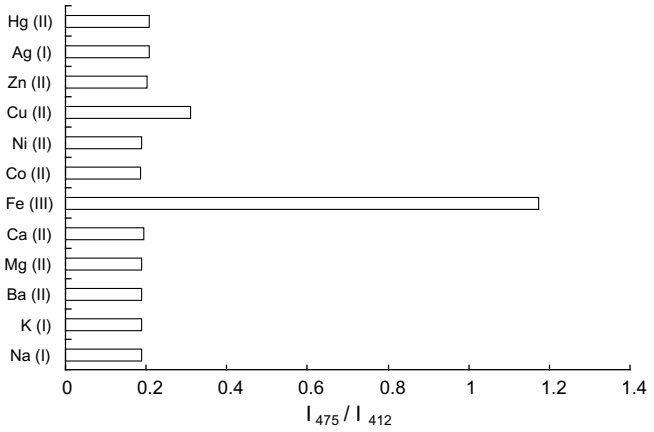
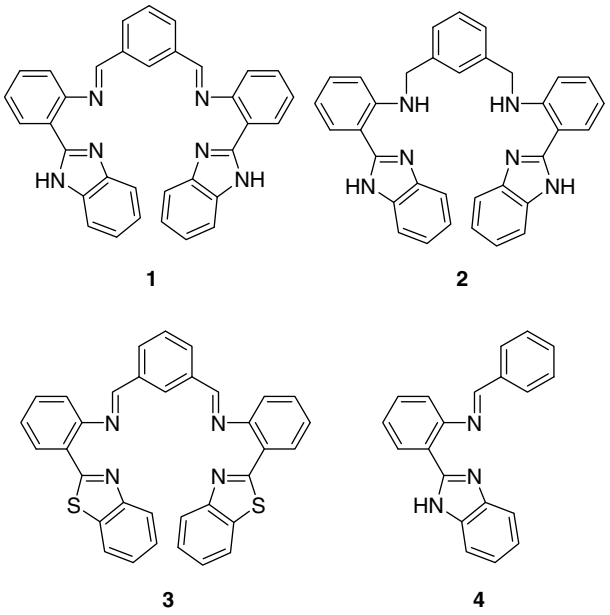


Fig. 2. Fluorescence ratiometric response (I_{475}/I_{412}) of receptor **1** (10 μM) upon the addition of a particular metal salt (100 μM) in CH_3CN/H_2O (95:5, v/v).



Scheme 1.

Our hypothesis that emphasizes two types of sp^2 nitrogens as a better combination for Fe^{3+} ion complexation was testified by the recognition behavior of compounds **2-4** (Fig. S1–3). Both receptors **2** and **3** have a dipodal skeleton similar to that of receptor **1**, except that receptor **2** lacks imine linkages while receptor **3** has two sulfurs as potential donor groups. The sulfur donors of receptor **3** can undergo complexation with a metal ion as an alternate of sp^2 nitrogens of benzimidazole. The design of receptor **4** resembles one half part of receptor **1**. To evaluate the metal ion recognition behavior of receptors **2**–**4**, we selected a 10 μM concentration of compounds **2** and **3**, and a 20 μM concentration of compound **4**, respectively. These concentration ranges have approximately the same number of binding sites as that of a 10 μM concentration of **1**. The binding affinity of receptor **2** was very poor with respect to all metal ions, implying that the reduction of imine linkages provides a receptor with a structure too much flexible to bind with any metal ions. The result supports the fact that the imine linkages of receptor **1** provide not only appropriate binding sites but also some structural rigidity required to organize the pseudocavity of receptor **1**.

To confirm our point of structural rigidity of receptor **1** compared to receptor **2**, the MacroModel calculations were performed (Fig. 3).[40] The calculated structures clearly support our hypothesis underlining pre-organization in the pseudocavity of receptor **1**, while such type of pre-organization of binding sites is not observed in the structure of receptor **2**.

Receptor **3** has high binding affinity toward a wide range of metal ions, exhibiting metal ion complexation by using alternative binding sites with a variety of metal ions. Similarly, receptor **4** was found to be non-selective for any metal ions. The metal ion recognition investigations with receptors **2**–**4** disclosed a fact that proper selections of binding sites as well as the steric features of the pseudocavity of receptor **1** are mandatory for effective complexation of Fe^{3+} ions.

Figure 4 showed the changes in fluorescence spectra pattern of **1** upon titration of Fe^{3+} ions. The titration results show that with the continuous addition of Fe^{3+} ions to the 10 μM solution of receptor **1**, the intensity of the emission band decreased at $\lambda = 412$ nm, and the intensity of a newly emerged band started increasing at $\lambda = 475$ nm gradually. A careful analysis of the changes in fluorescence intensities of receptor **1** with continuous addition of Fe^{3+} ions revealed that the addition of first two equivalent of Fe^{3+} exhibited a small enhancement in the fluorescence intensity at $\lambda = 475$ nm. However, upon addition of the next several equivalents of Fe^{3+}, a marked fluorescence intensity enhancement was observed at this wavelength. Thus, receptor **1** can be used for selective recognition of Fe^{3+} ions in quite a wide range of iron concentrations, and it can detect as little as 2.83 μM concentration of Fe^{3+} ions.[41] On the basis of Benesi–Hildebrand plot,[42] the association constant K_a of receptor **1** for Fe^{3+} ions was calculated to be $(2.9 \pm 0.2) \times 10^3\ M^{-1}$. The stoichiometry of the complex formed was found to be 1:1 as determined by Job's plot.[43]

To evaluate the effect of other background metal ions upon the signal response induced with iron complexation of receptor **1**, the cation interference experiments were carried out (Fig. 5). The experiments were performed to measure the fluorescence intensity in a series of solutions containing receptor **1**, different amounts of Fe^{3+} ions, and another metal ion. The fluorescence intensity was

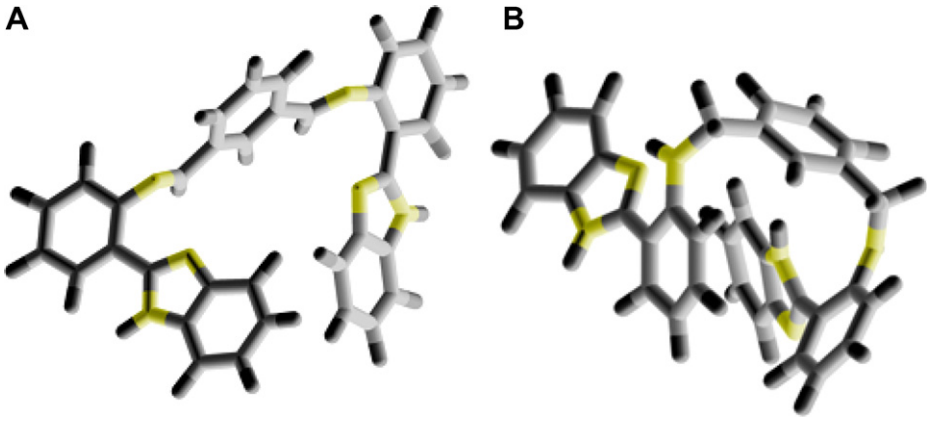


Fig. 3. Energy minimized structure of (**A**) receptor **1** and (**B**) receptor **2** as obtained by MacroModel calculation.

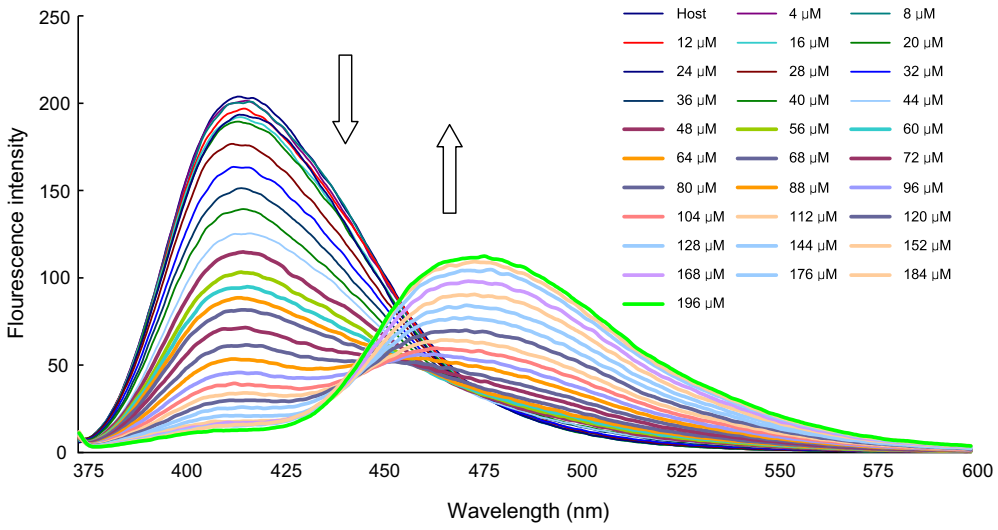


Fig. 4. Changes in fluorescence spectrum of receptor **1** (10 μM) upon the addition of $Fe(NO_3)_3$ (0–196 μM) in CH_3CN/H_2O (95:5, v/v).

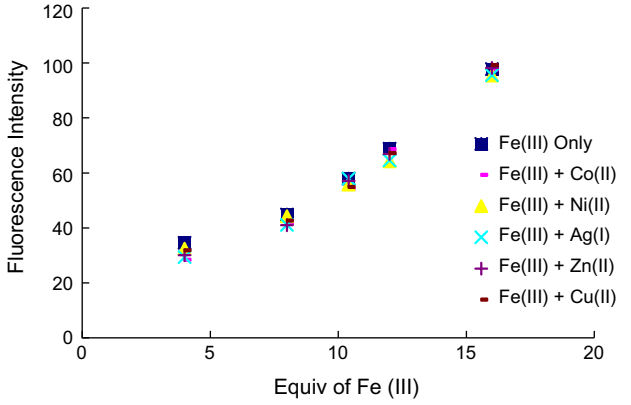


Fig. 5. Estimation of Fe^{3+} ions in the presence of other metal ions in CH_3CN/H_2O (95:5, v/v) at $\lambda = 475$ nm.

almost identical to that obtained in the absence of any interfering metal ion. The result confirmed that no metal ions show much disturbance with the signal response induced by iron complexation with receptor **1**.

To study the plausible coordination environment of Fe^{3+} in the iron complex of receptor **1**, the iron complex of receptor **1** was synthesized and characterized independently.[44] The Fe^{3+} ion are assumed to have a octahedral geometry in the complex, in which receptor **1** acts as a tetradentate ligand and other two coordination sites are occupied by nitrates. The formula of complex, Fe(receptor **1**)$(NO_3)_2$, is supported by FAB mass spectrum having $m/z = 697.1237$, which corresponds to $M+H^+$ of the proposed structure of the complex (the theoretical calculated value is $m/z = 697.1241$). Nitrate exhibits variable coordination modes in different metal complexes such as a monodentate (η^1-ONO_2) ligand and a bidentate ligand (η^2-O_2NO). The high-frequency band at 1522 cm^{-1} is assigned to $\nu_a(NO_2)$ and that near 1384 cm^{-1} to $\nu_s(NO_2)$. The smaller separation of the high-frequency bands is characteristic of monodentate nitrate coordination. The bidentate nitrate coordination is expected to have three IR-active stretching modes: ν(N=O) for the uncoordinated oxygen and two (symmetric and asymmetric) modes for the coordinated NO_2 fragment. The absence of three IR-active stretching modes implies only monodentate coordination of the nitrate.[45,46]

In conclusion, we synthesized a novel benzimidazole-based fluorescent receptor bearing imine linkages with two sets of sp^2 nitrogens, investigating its binding properties toward various metal ions. The receptor shows a selective recognition behavior for Fe^{3+} ions along with a shift in emission band. Receptor **1** exhibits ratiometric fluorescent probe along a wide concentration range of Fe^{3+} with no interferences of background metal ions.

Acknowledgment

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.03.002.

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36. *Synthesis of receptor* **1**: A solution of isophthalaldehyde (100 mg, 0.75 mmol), 2-(2-aminophenyl)-benzimidazole (390 mg, 1.87 mmol) and catalytic amount of zinc perchlorate in MeOH was stirred at room temperature for 12 h. Upon completion of reaction, the solid separated out. The solid material was washed with CH_2Cl_2 (50 mL) affording a light yellow colored solid (372 mg, 96%); mp 216–218 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.80 (d, 2H, Ar, $J = 8.4$ Hz), 6.83 (t, 2H, Ar, $J = 4.4$ Hz), 6.96–7.00 (m, 4H, Ar), 7.14–7.21 (m, 4H, Ar), 7.24–7.29 (m, 3H, Ar), 7.37 (d, 1H, Ar, $J = 11.6$ Hz), 7.51 (s, 1H, CH=N), 7.56 (s, 1H, CH=N), 7.62 (t, 2H, Ar, $J = 6.4$ Hz), 7.93 (t, 2H, Ar, $J = 8.8$ Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 102.6, 103.9, 106.8, 110.4, 110.8, 114.2, 114.3, 116.9, 118.8, 119.9, 123.8, 124.9, 133.2, 133.3, 135.2, 136.1. Anal. Calcd for $C_{34}H_{24}N_6$: C, 79.05; H, 4.68; N, 16.27. Found: C, 79.33; H, 4.30; N, 16.23.
37. *Synthesis of receptor* **2**: $NaBH_4$ (36 mg, 0.95 mmol) was added to a solution of receptor **1** (100 mg, 0.2 mmol) in 30 mL of MeOH/THF (8:2, v/v) solvent mixture. The mixture was stirred for 3 h at room temperature. Upon completion of reaction, the solvent was evaporated, and water was poured into the content of the reaction mixture. The organic material was extracted with dichloromethane (3×50 mL). The organic layer was dried over anhydrous $MgSO_4$. After filtration and evaporation, receptor **2** was obtained as a yellow solid material (89.7 mg, 89%); mp 241–243 °C; ^{1}H NMR (CD_3CN, 400 MHz) δ 2.46 (s, 4H, CH_2), 5.97 (br, 2H, NH), 6.66–6.76 (m, 6H, Ar), 6.85 (t, 2H, Ar, $J = 6.8$ Hz), 6.98 (t, 2H, Ar, $J = 6.8$ Hz), 7.16–7.28 (m, 6H, Ar), 7.62–7.67 (m, 2H, Ar), 8.02 (t, 2H, Ar, $J = 6.0$ Hz); ^{13}C NMR (DMSO-d_6, 400 MHz) δ 68.3, 110.9, 112.1, 115.1, 118.6, 119.1, 122.4, 122.6, 125.1, 127.2, 132.1, 133.2, 141.5, 143.4, 144.3, 147.1. Anal. Calcd for $C_{34}H_{28}N_6$: C, 78.44; H, 5.42; N, 16.14. Found: C, 78.43; H, 5.26; N, 16.34.
38. *Synthesis of receptor* **3**: This compound was synthesized by the same method as adopted for the synthesis of receptor **1** except that 2-(2-aminophenyl)-benzothiazole (422 mg, 1.86 mmol) was used instead of 2-(2-aminophenyl)-benzimidazole. The final product is a lemon yellow colored solid (335 mg, 81%); mp 228–230 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.47 (t, 2H, Ar, $J = 5.2$ Hz), 7.62–7.67 (m, 6H, Ar), 7.82 (t, 2H, Ar, $J = 8.0$ Hz), 8.05–8.08 (m, 3H, Ar), 8.22 (d, 2H, Ar, $J = 8.0$ Hz), 8.59 (d, 2H, Ar, $J = 8.0$ Hz), 8.76 (d, 2H, Ar, $J = 8.0$ Hz), 9.09 (s, 1H, Ar), 9.14 (s, 2H, CH=N); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 119.4, 121.6, 122.6, 124.9, 126.2, 126.7, 128.2, 130.5, 132.0, 133.1, 136.5, 136.8, 149.1, 151.6, 162.0, 163.3. Anal. Calcd for $C_{34}H_{22}N_4S_2$: C, 74.15; H, 4.03; N, 10.17. Found: C, 74.16; H, 4.02; N, 10.10.
39. *Synthesis of receptor* **4**: A solution of benzaldehyde (100 mg, 0.94 mmol), 2-(2-aminophenyl)-benzimidazole (296 mg, 1.4 mmol) and catalytic amount of zinc perchlorate in MeOH was stirred at room temperature for 12 h. The progress of the reaction was monitored by TLC. Upon completion of the reaction, half of the solvent was evaporated and diethyl ether was added to it dropwise till solid material separated out. The solid material was filtered and washed with diethylether (50 mL) affording a yellow colored solid (186 mg, 67%); mp 228–230 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.83 (t, 1H, Ar, $J = 7.4$ Hz), 7.05–7.09 (m, 2H, Ar), 7.12–7.18 (m, 2H, Ar), 7.22–7.26 (m, 3H, Ar), 7.30–7.31 (m, 3H, Ar), 7.58 (s, 1H, CH=N), 7.63 (d, 1H, Ar, $J = 7.3$ Hz), 7.94 (d, 1H, Ar, $J = 7.3$ Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 110.6, 114.81, 118.2, 118.4, 122.2, 122.3, 124.7, 126.0, 128.8, 131.8, 132.7, 140.2, 143.2, 146.8. Anal. Calcd for $C_{20}H_{15}N_3$: C, 80.78; H, 5.08; N, 14.13. Found: C, 80.49; H, 4.70; N, 13.88.
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44. *Synthesis of Fe(receptor* **1***)(NO$_3$)$_2$*: A solution of receptor **1** (260 mg, 0.50 mmol) and iron nitrate (305 mg, 0.75 mmol) was taken in acetonitrile. The reaction mixture was stirred with reflux for 2 h. Upon completion of the reaction the solid material was separated out. The solid material was filtered and washed with acetonitrile (20 mL) affording a brown-yellow colored solid (302 mg, 86%); mp above 300 °C; IR 1522 cm^{-1} $\nu_a(NO_2)$, 1384 cm^{-1} $\nu_s(NO_2)$; HRMS (FAB) calcd for $C_{34}H_{25}FeN_8O_6$ ($M+H^+$): 697.1241, found 697.1237.
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