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Benzimidazole-based fluorescent sensors for Cr^{3+} and their resultant complexes for sensing HSO_4^- and F^-

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ABSTRACT

A benzimidazole-based receptor that selectively recognized Cr^{3+} without interference from other metal ions was synthesized in this study. The resultant Cr-complex recognized HSO_4^- and F^- via two approaches. HSO_4^- ions bound to the metal center, causing changes in the fluorescent spectra at different wavelengths, whereas F^- ions displaced Cr^{3+}, thereby switching ON the fluorescent spectra at the same wavelength.

1. Introduction

Anions play an important role in biochemistry, medicine, and in clinical and environmental analysis.[1] Fluoride has a role in preventing dental caries, in the treatment for osteoporosis, and in the refinement of uranium used in the manufacture of nuclear weapons.[2] Hydrogen sulfate is usually required to maintain the level of dissolved calcium in boiling water as it helps to prevent the loss of calcium due to precipitation.[3] However, excess of these anions can have adverse effects. (a) Fluoride leads to fluorosis, which is a type of fluoride toxicity,[2] and (b) hydrogen sulfate released in industrial processes has deleterious effects on the environment.[4] Thus, monitoring these anions in biological or environmental samples is of great importance because of their diverse effects, both beneficial and otherwise.

Few reports of a single sensor behaving differently for these two anions exist,[6] although several selective and sensitive sensors are available for individual recognition of these anions.[2,5] The recognition of any anion in water is difficult because of the high hydration energy of anions. Anions usually experience competition from the solvent for sensor binding sites.[7] Nevertheless, a metal complex may resolve this problem through either a cation displacement assay,[8] in which an anionic guest displaces the metal ion causing the revival of the original UV–vis or fluorescence spectrum, or via simple electrostatic interaction of an anion with a metal center, causing a change in the UV–vis or fluorescence spectrum.[9] Thus, a single metal sensor complex can recognize two anions via two different approaches, i.e., the cation displacement approach, which causes an ON–OFF switch of fluorescence intensity at the same wavelength, and electrostatic interaction of anions with a metal center, which may cause a shift in wavelength.

In this context, we have designed a set of sensors in such a way that receptors have both hydrogen bond donor and hydrogen bond acceptor sites (Scheme 1). The receptors bind with metal ions. The resulting complexes recognize oxyanions such as hydrogen sulfate and undergo decomplexation with anions such as halides.

2. Results and discussion

Receptors **1**–**3** were synthesized by a condensation reaction of 2-(2-aminophenyl)-1*H*-benzimidazole with pyridine-2-carbaldehyde, pyridine-3-carbaldehyde or pyridine-4-carbaldehyde, respectively. The photophysical properties of receptors **1**–**3** were examined using UV–vis absorption and fluorescence spectroscopy. UV–vis absorption spectroscopic studies of receptors **1**–**3** were performed with 20 μM solutions of receptors **1**–**3** in a HEPES-buffered CH_3CN/H_2O (8/2, v/v) solvent system to understand their ground state behaviors. The solutions of receptors **1**–**3** exhibited absorption bands at 352,

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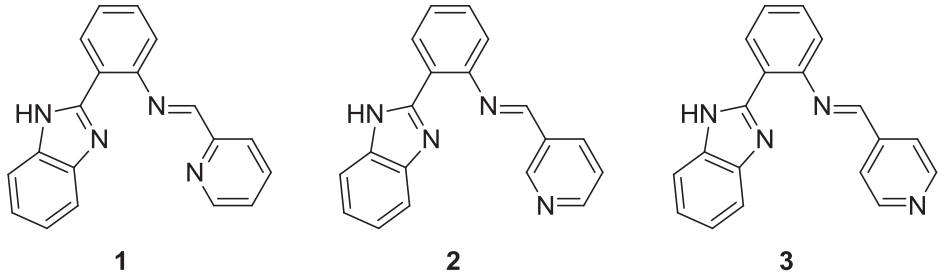

Scheme 1. Structure of receptors **1**–**3**.

340, and 334 nm, respectively. These bands are the result of intramolecular charge transfer transitions due to imine linkages.[10] UV–vis absorption spectra of receptors **1**–**3** were recorded immediately after preparing a solution and then after 24 h (Fig. S1). If there would be any hydrolysis of imine linkages, then the intensity of band around 350 nm is expected to fall. In the present case, no such changes in absorption spectra were observed. This indicates that receptors **1**–**3** are stable in a HEPES-buffered CH_3CN/H_2O solvent system.

The absorption profiles of receptors **1**–**3** were examined in the absence or presence of various metal species. The absorption profiles on addition of different metal ions to solutions of receptors **1**–**3** showed no selectivity (Fig. S2). A 1.0 μM concentration of receptors **1**–**3** in a HEPES-buffered CH_3CN/H_2O (8/2, v/v) solvent system was excited at 352, 340, and 334 nm, respectively, to determine the fluorescence behavior of these sensors. Receptors **1** and **2** showed emission at 420 nm (Fig. 1), whereas receptor **3** had dual emission at 420 and 510 nm (Fig. S3). The addition of some selected metal ions caused fluorescence quenching of receptors **1** and **2** to different extents. However, the binding event of Cr^{3+} led to unique modulation. Receptor **3** showed no specific binding with any of the tested metal ions.

fluorescence intensity at 470 nm (Fig. 2). This gave rise to a new emission band at 470 nm with an isosbestic point. The selective recognition of Cr^{3+} with receptors **1** and **2** seems to be due to the compatible binding sites and the optimum size of the pseudocavity of receptors. On the basis of the fluorescence titration data, binding constants for the Cr^{3+} complexes were calculated using a Benesi–Hildebrand plot[12] and were found to be $(7.67\pm0.30)\times10^4$ and $(7.09\pm0.35)\times10^4$ M^{-1} for **1** and **2**, respectively (Fig. S4). Job's plots were constructed for **1**·Cr^{3+} and **2**·Cr^{3+}, showing a 1:1 stoichiometry (Figs. S5 and S6). The mass spectrum showed m/z=151.8, which corresponds to $[M+H]^{3+}$, where M is [**1**+Cr^{3+}+NO_3+CH_3CN], indicating 1:1 binding of receptor **1** to Cr^{3+} (Fig. S7). Similarly, m/z=254.9 was detected, which corresponds to $[M+1]^{2+}$, where M is [**2**+Cr^{3+}+2NO_3^-+CH_3OH] (Fig. S8). The detection limits for the estimation of Cr^{3+} by receptors **1** and **2** turned out to be 1.25 and 0.63 μM, respectively (Fig. S9).[13] The detection limits for receptors **1** and **2** are sufficiently low for use in any biological or industrial samples containing low concentrations of Cr^{3+}.[11e,14]

The specific responses of receptors **1** and **2** for Cr^{3+} were assessed by performing competitive binding experiments in the

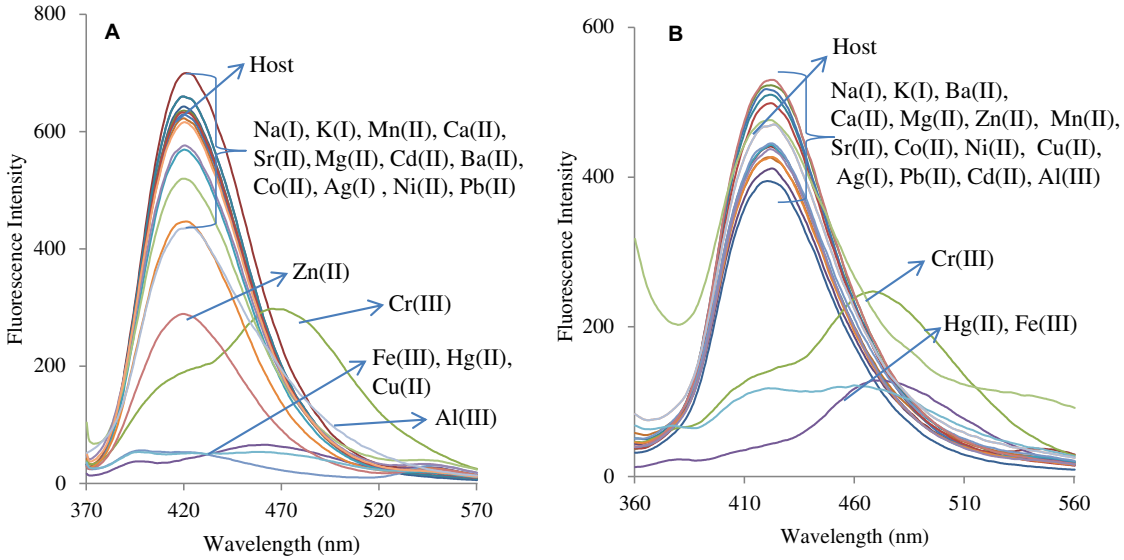

Fig. 1. (A) Changes in the fluorescence spectra of receptor **1** (1 μM) upon addition of a particular metal nitrate salt (10 μM) in HEPES-buffered CH_3CN/H_2O (8:2, v/v) with excitation at 352 nm. (B) Changes in the fluorescence spectra of receptor **2** (1 μM) upon the addition of a particular metal nitrate salt (10 μM) in HEPES-buffered CH_3CN/H_2O (8:2, v/v) with excitation at 340 nm.

A 1.0 μM solution of receptors **1** and **2** was titrated against Cr^{3+} (0–10 μM) with a fluorospectrometer. A gradual increase in the concentration of Cr^{3+} quenched the intensity of the emission band of receptors **1** and **2** at 420 nm, and there was a small increase in the

presence of all tested metal ions, i.e., Na^+, K^+, Mn^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, Hg^{2+}, and Cd^{2+}. The emission profile of receptor **1** with Cr^{3+} was unperturbed in the presence of these metal ions (Fig. 3), confirming its selective

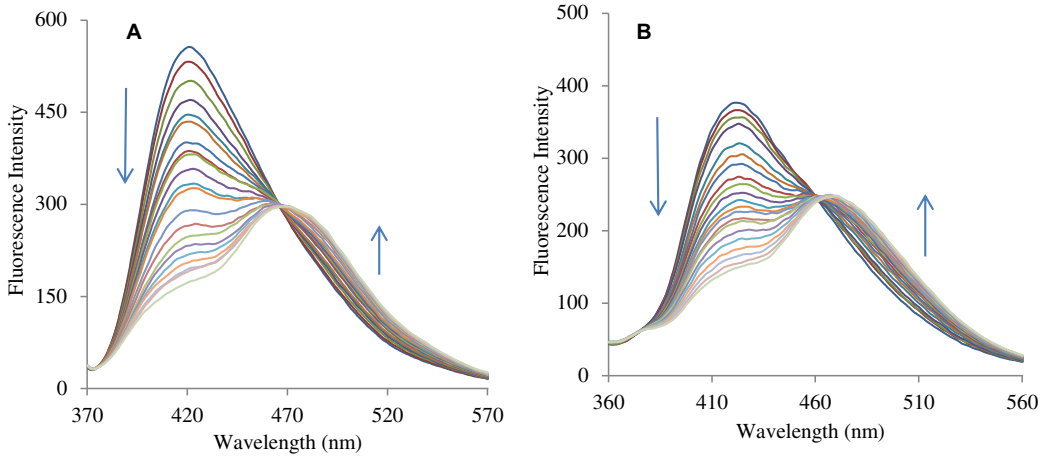

Fig. 2. (A) Fluorescence emission spectra of receptor **1** (1 μM) showing changes upon successive addition of Cr^{3+} (0–10 μM) in HEPES-buffered CH_3CN/H_2O (8:2, v/v) with excitation at 352 nm. (B) Fluorescence emission spectra of receptor **2** (1 μM), showing changes upon successive addition of Cr^{3+} (0–10 μM) in HEPES-buffered CH_3CN/H_2O (8:2, v/v) with excitation at 340 nm.

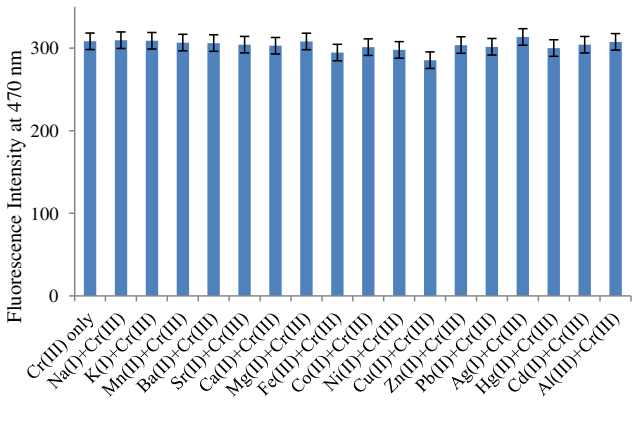

Fig. 3. Fluorescent response of receptor **1** (1 μM) to Cr^{3+} (10 μM) over other selected metal ions (10 μM). The intensity at 470 nm was used for the bar diagram.

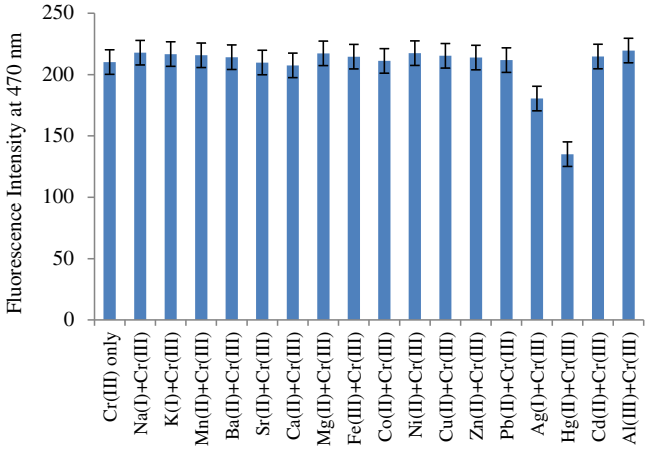

Fig. 4. Fluorescent response of receptor **2** (1 μM) to Cr^{3+} (10 μM) over other selected metal ions (10 μM). The intensity at 470 nm was used for the bar diagram.

binding with Cr^{3+}. In contrast, the binding of receptor **2** with Cr^{3+} was interfered with by many of the tested metal ions, as indicated by the changes in its emission profile (Fig. 4).

The ground state behavior of receptors **1** and **2** was examined by titrating 20 μM solutions of receptors **1** and **2** with Cr^{3+} using UV–vis absorption spectroscopy. When the concentration of Cr^{3+} was increased steadily, the absorption band shifted to 380 nm with an isosbestic point at 370 nm (Fig. S10). The shifts in absorption and emission spectra imply that the addition of Cr^{3+} modulates internal charge transfer.[11] UV–vis absorption spectra and fluorescence spectra were recorded while varying the pH of the solution of receptor **1** in order to examine the effect of pH on the photophysical properties of the receptor (Figs. S11 and S12). Changes in pH values resulted in changes in both the UV–vis absorption and fluorescence spectra of receptor **1**. Thus, we conducted all studies in HEPES-buffered solutions. Our findings indicate that the photophysical properties are not prone to change with pH under buffered conditions.

To examine the applicability of complexes $\mathbf{1}\cdot Cr^{3+}$ and $\mathbf{2}\cdot Cr^{3+}$ as anion sensors,[8,9] we have examined the fluorescence behavior of complexes $\mathbf{1}\cdot Cr^{3+}$ and $\mathbf{2}\cdot Cr^{3+}$ in the presence of different anions. Fluorescence spectra were recorded by mixing a 5.0 μM solution of $\mathbf{1}\cdot Cr^{3+}$ and $\mathbf{2}\cdot Cr^{3+}$ in a HEPES-buffered CH_3CN/H_2O (8/2, v/v) solvent system along with 20 μM of tetrabutylammonium salt of anions such as F^-, Cl^-, Br^-, I^-, NO_3^-, CN^-, HSO_4^-, PO_4^{3-}, ClO_4^-, and AcO^- (Fig. 5). Complex $\mathbf{1}\cdot Cr^{3+}$ showed two different profiles in the presence of F^- and HSO_4^-. In the presence of F^-, the fluorescence intensity at 420 nm was enhanced, while in the presence of HSO_4^- there was a decrease in fluorescence intensity at 420 nm and an increase in fluorescence intensity at 475 nm. These phenomena suggest that complex $\mathbf{1}\cdot Cr^{3+}$ behaves differently with these two anions and can recognize both. However, complex $\mathbf{2}\cdot Cr^{3+}$ was not selective for any of the anions (Fig. S13).

The fluorescence behavior of $\mathbf{1}\cdot Cr^{3+}$ in the presence of different anions shows that fluoride causes decomplexation of the $\mathbf{1}\cdot Cr^{3+}$ complex, thereby restoring the original emission band of receptor **1**. Interestingly, hydrogen sulfate coordinated with the metal complex and further modulated the internal charge transfer. The effect of pH on the $\mathbf{1}\cdot Cr^{3+}$ was examined by recording fluorescence spectra of $\mathbf{1}\cdot Cr^{3+}$ (5 μM) in CH_3CN/H_2O (8/2, v/v) under variable pH (Fig. S14). The pH values influenced the profile of the fluorescence spectra of $\mathbf{1}\cdot Cr^{3+}$. Thus, a buffered solvent system was used. The effect of F^- and HSO_4^- on $\mathbf{1}\cdot Cr^{3+}$ in its ground state was investigated by recording UV–vis spectra of 20 μM $\mathbf{1}\cdot Cr^{3+}$ in a HEPES-buffered CH_3CN/H_2O (8/2, v/v) solvent system with 100 μM

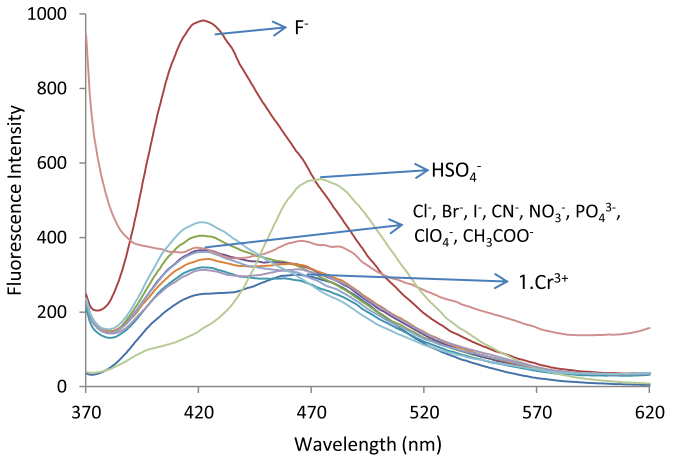

Fig. 5. Changes in the fluorescence spectra of $\mathbf{1}\cdot Cr^{3+}$ (5 μM) upon addition of a particular tetrabutylammonium anion salt (20 μM) in HEPES-buffered CH_3CN/H_2O (8:2, v/v) with excitation at 352 nm.

tetrabutylammonium salt of fluoride and hydrogen sulfate (Fig. S15). The interactions of F^- and HSO_4^- with $\mathbf{1}\cdot Cr^{3+}$ were further confirmed by stepwise addition of these anions to 5 μM $\mathbf{1}\cdot Cr^{3+}$ in a HEPES-buffered CH_3CN/H_2O (8/2, v/v) solvent system (Fig. 6).

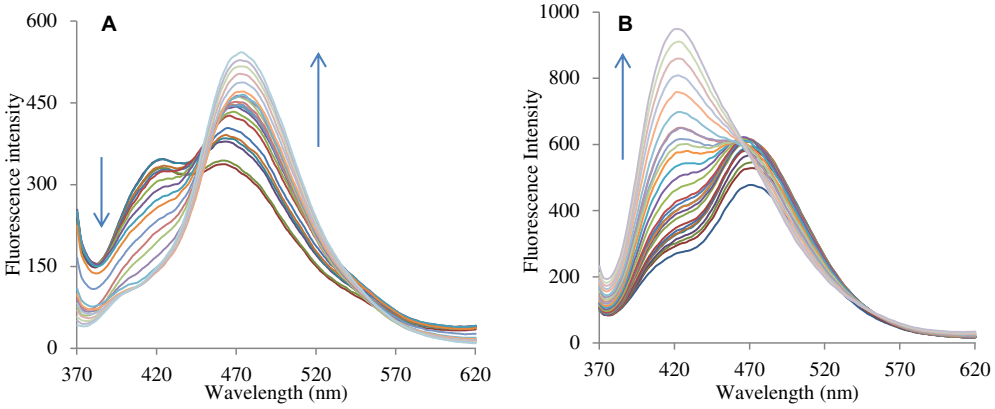

Fig. 6. (A) Fluorescence emission spectra of $\mathbf{1}\cdot Cr^{3+}$ (5 μM) showing changes upon successive addition of tetrabutylammonium hydrogen sulfate (0–20 μM) in HEPES-buffered CH_3CN/H_2O (8:2, v/v) with excitation at 352 nm. (B) Fluorescence emission spectra of $\mathbf{1}\cdot Cr^{3+}$ (5 μM) showing changes upon successive addition of tetrabutylammonium fluoride (0–20 μM) in HEPES-buffered CH_3CN/H_2O (8:2, v/v) with excitation at 352 nm.

To exclude the possibility of receptor **1** binding to other anions, we have assessed the effect of additional anions on the fluorescence profile of receptor **1**. The fluorescence signal of receptor **1** (1 μM) was unaffected in the presence of all tested anions (10 μM) in HEPES-buffered CH_3CN/H_2O (8:2, v/v) with excitation at 352 nm (Fig. S16). Binding constants of $\mathbf{1}\cdot Cr^{3+}$ for hydrogen sulfate and fluoride ions were calculated using a Bensei–Hildebrand plot (Fig. S17) and were found to be $(2.89\pm0.25)\times10^5$ and $(2.30\pm0.20)\times10^6$ M^{-1}, respectively. Interference of other oxyanions and halides in the binding of hydrogen sulfate and fluoride ion, respectively, with receptor **1** was examined. Fluorescence spectra of 5 μM $\mathbf{1}\cdot Cr^{3+}$ in a HEPES-buffered CH_3CN/H_2O (8/2, v/v) solvent system with 20 μM tetrabutylammonium salt of hydrogen sulfate in the presence of 20 μM of a tetrabutylammonium salt of oxyanions including NO_3^-, PO_4^{3-}, ClO_4^-, and AcO^- were recorded. Similarly, spectra for a 5.0 μM concentration of $\mathbf{1}\cdot Cr^{3+}$ in a HEPES-buffered CH_3CN/H_2O (8/2, v/v) solvent system with 20 μM tetrabutylammonium salt of fluoride anion in the presence of 20 μM of a tetrabutylammonium salt of halides including Cl^-, Br^- and I^- were also recorded. No interference from any of the competitive anions was detected (Fig. 7). From the titration plot, the detection limits for HSO_4^- and F^- were calculated to be 1.58 and 0.125 μM, respectively (Fig. S18). The differential sensing of F^- and HSO_4^- with $\mathbf{1}\cdot Cr^{3+}$ is explained by a hard–hard interaction between hard Lewis acid (Cr^{3+}) and hard Lewis base (F^-). Secondly, the high charge density of F^- leads to equip F^- as proficient anion to displace Cr^{3+} from the coordination sphere of $\mathbf{1}\cdot Cr^{3+}$.[15] On the other hand, the charge is not localized in HSO_4^-. Hence, relatively lower charge density of HSO_4^- restricts the cation displacement, although HSO_4^- has a good a binding affinity for Cr^{3+} through hydroxo groups.[16]

3. Conclusion

In summary, we synthesized receptor **1**, which recognizes Cr^{3+} selectively without interference from other metal ions. The resultant $\mathbf{1}\cdot Cr^{3+}$ complex behaves differently with HSO_4^- and F^-. Specifically, $\mathbf{1}\cdot Cr^{3+}$ in the presence of HSO_4^- results in a decrease in fluorescence intensity at 420 nm and enhanced fluorescence intensity at 475 nm. In the presence of F^-, cation displacement occurs, i.e., Cr^{3+} is displaced and the fluorescence spectrum is switched ON at the same wavelength (420 nm). None of the competitive anions tested interfered with either interaction.

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 was operated at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR. IR spectra were recorded on a Perkin Elmer Spectrum One for the compounds in the solid state, which were prepared as KBr discs. The absorption spectra were recorded on a Perkin Elmer Lambda 25. Fluorescence measurements were performed on a Perkin Elmer LS55 fluorescence spectrophotometer.

4.2. General procedure for the synthesis of receptors 1–3

A solution of 2-(2-aminophenyl)-1*H*-benzimidazole (209 mg, 1 mmol) and the corresponding pyridine carboxaldehyde (1.5 mmol) in dry methanol (50 mL) was heated to reflux for 12 h.

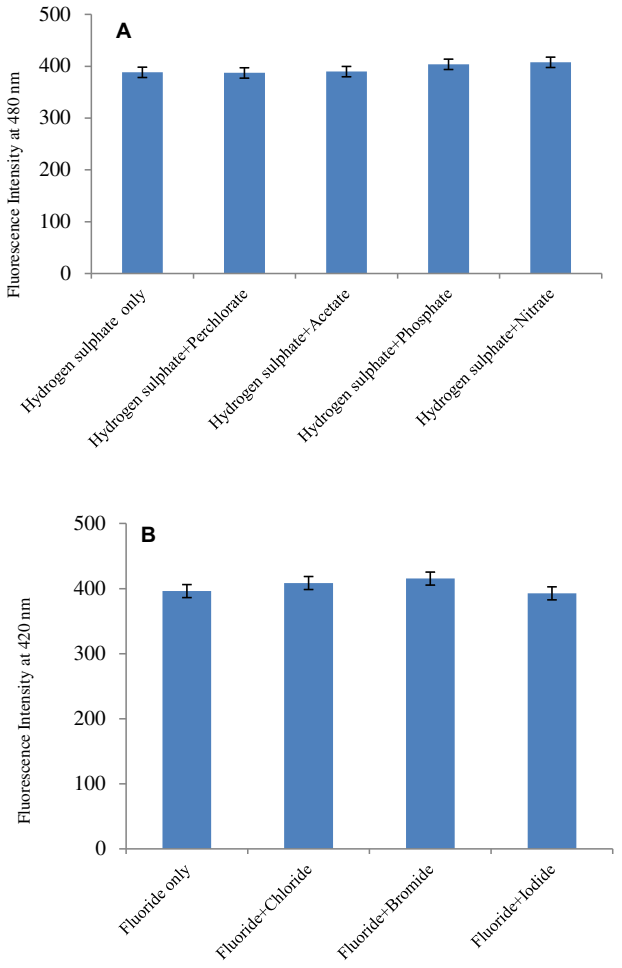

Fig. 7. (A) Bar diagram showing the fluorescence response of $\mathbf{1}\cdot Cr^{3+}$ (5 μM) to HSO_4^- (20 μM) in the presence of other oxyanions (20 μM). (B) Bar diagram showing the fluorescence response of $\mathbf{1}\cdot Cr^{3+}$ (5 μM) to F^- (20 μM) in the presence of other halides (20 μM).

After the reaction was completed, the solvent was evaporated to 25 mL and was kept at 5 °C to facilitate slow evaporation. A white solid material separated out. This solid was filtered and washed with cold methanol three times.

4.3. Synthesis of receptor 1

Following the general procedure described above, **1** was obtained as a white solid in 80% yield. Mp 228–230 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (d, J=4.4 Hz, 1H), 7.93 (d, J=7.6 Hz, 1H), 7.75 (t, J=7.6 Hz, 1H), 7.70 (s, 1H), 7.64 (d, J=8.0 Hz, 1H), 7.34 (d, J=8.0 Hz, 1H), 7.31–7.10 (m, 6H), 6.85 (d, J=8.0 Hz, 1H), 6.80 (t, J=7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 110.3, 112.0, 115.7, 118.0, 118.6, 120.2, 122.0, 122.2, 123.9, 124.6, 131.5, 133.0, 137.4, 142.9, 143.8, 146.8, 149.5, 158.4; IR (KBr pellet) ν 1645 cm^{-1}; Anal. Calcd for $C_{19}H_{14}N_4$: C, 76.49; H, 4.73; N, 18.78. Found: C, 76.03; H, 4.94; N, 19.03.

4.4. Synthesis of receptor 2

Following the general procedure above, **2** was obtained as a white solid in 81% yield. Mp 178–180 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.53–8.51 (m, 2H), 7.98–7.96 (m, 1H), 7.70–7.65 (m, 2H), 7.52–7.49 (m, 1H), 7.35–7.13 (m, 6H), 6.88–6.84 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 110.3, 112.0, 115.0, 118.6, 118.8, 119.6, 122.3, 123.9, 124.7, 131.8, 132.6, 133.3, 135.8, 142.7, 143.8, 146.7, 147.1, 150.1; FTIR (ν_{max} KBr pellet) 1620 cm^{-1}. Anal. Calcd for $C_{19}H_{14}N_4$: C, 76.49; H, 4.73; N, 18.78. Found: C, 76.17; H, 4.90; N, 18.93.

4.5. Synthesis of receptor 3

Following the general procedure above, **3** was obtained as a white solid in 78% yield. Mp 239–240 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.96 (d, J=6.0 Hz, 2H), 8.67 (d, J=9.2 Hz, 1H), 8.00–7.81 (m, 6H), 7.51 (t, J=6.4 Hz, 1H), 7.22 (t, J=9.2 Hz, 1H), 6.55 (d, J=8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) 113.7, 118.3, 119.7, 122.7, 122.9, 123.8, 125.4, 127.9, 128.7, 132.0, 141.5, 141.8, 143.9, 146.1, 147.2, 150.6; FTIR (ν_{max} KBr pellet) 1630 cm^{-1}; Anal. Calcd for $C_{19}H_{14}N_4$: C, 76.49; H, 4.73; N, 18.78. Found: C, 76.23; H, 4.83; N, 18.94.

4.6. Synthesis of $\mathbf{1}\cdot Cr^{3+}$ complex

Compound **1** (298 mg, 1.0 mmol) was dissolved along with $Cr(NO_3)_3$ (400 mg, 1.0 mmol) in a CH_3CN/CH_3OH solvent system. The solution was heated to reflux for 8 h. Upon completion of the reaction, the product was separated via slow diffusion of diethyl ether into the reaction mixture. The solid metal complex ($\mathbf{1}\cdot Cr^{3+}$) was washed with cold methanol and a dark green solid was obtained in 87% yield (305 mg). Mp >300 °C; IR (KBr pellet) ν 1620 cm^{-1}; Anal. Calcd for $C_{21}H_{17}CrN_8O_9$: C, 43.68; H, 2.97; Cr, 9.01; N, 19.41; O, 24.94. Found: C, 43.93; H, 2.88; N, 19.36.

4.7. Synthesis of $\mathbf{2}\cdot Cr^{3+}$ complex

Following the procedure for the synthesis of the $\mathbf{1}\cdot Cr^{3+}$ complex described above, the $\mathbf{2}\cdot Cr^{3+}$ complex was obtained as a dark green solid in 86% yield (300 mg). Mp >300 °C; IR (KBr pellet) ν 1620 cm^{-1}; Anal. Calcd for $C_{20}H_{18}CrN_7O_{10}$: C, 42.26; H, 3.19; Cr, 9.15; N, 17.25; O, 28.15. Found: C, 42.33; H, 3.07; N, 17.16.

4.8. Metal recognition studies of receptors 1–3

All of the recognition studies were performed at 25±1 °C, and, before recording any spectrum, sufficient time was allowed for shaking to ensure the uniformity of the solution. The effect of pH on the UV–vis absorption and fluorescence spectrum of receptor **1** was investigated with a solution of receptor **1** prepared in a CH_3CN/H_2O (8:2, v/v) solvent system. The cation binding ability of receptors **1**–**3** in a HEPES-buffered CH_3CN/H_2O (8:2, v/v) solvent system was determined by preparing standard solutions of receptor **1** along with fixed amounts of particular metal nitrate salts in HEPES-buffered CH_3CN/H_2O (8:2, v/v). The cation recognition behavior of receptors **1**–**3** was evaluated according to changes in the fluorescence spectrum of the receptor upon addition of the metal salt. The fluorescence spectra of receptors **1**–**3** were recorded with the excitation wavelengths shown in Fig. 1 and Fig. S3. Volumetric flasks containing standard solutions of receptors **1** and **2** and varied amounts of a particular metal nitrate salt in HEPES-buffered CH_3CN/H_2O (8:2, v/v) were used for titrations. To evaluate any possible interference in the estimation of Cr^{3+} due to the presence of other metal ions, solutions containing receptor **1** (1 μM) along with a fixed concentration of Cr^{3+} both with and without other background cations were prepared in HEPES-buffered CH_3CN/H_2O (8:2, v/v). The fluorescence intensity of each solution was recorded.

4.9. Anion recognition properties of $\mathbf{1}\cdot Cr^{3+}$ and $\mathbf{2}\cdot Cr^{3+}$

The studies were performed in a fashion similar to the cation recognition experiments, except for the fact that

tetrabutylammonium salts of anions were used. Detailed concentrations are given in the main text.

Acknowledgements

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Supplementary data

Additional spectroscopic data are available as supplementary data. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2012.08.022.

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