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A single molecular probe for multi-analyte (Cr^{3+}, Al^{3+} and Fe^{3+}) detection in aqueous medium and its biological application†

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An ESIPT based fluorescent sensor 1 was developed, which could selectively detect and differentiate trivalent metal ions Cr^{3+}, Al^{3+} and Fe^{3+} in aqueous medium. The cell imaging experiments confirmed that 1 can be used for monitoring intracellular Cr^{3+} and Al^{3+} levels in living cells.

Trivalent cations have important biological properties and are directly involved in the cell function where there is a critical control of M^{3+} levels.[1] For example, Cr^{3+} has direct impacts on the metabolism of carbohydrates, fats, proteins and nucleic acids by either activating certain enzymes or stabilizing proteins and nucleic acids.[2] Chromium deficiency can increase the risk factors associated with diabetes and cardiovascular diseases.[3] Al^{3+} could also have adverse effects on human health, as an excessive amount of Al^{3+} in the brain is believed to cause neurodementia, including neurological disorders such as Parkinson's disease, Alzheimer's disease and dialysis encephalopathy.[4] Fe^{3+} plays an indispensable role in many biochemical processes at the cellular level,[5] and in the oxygen transport processes in all tissues in the form of hemoglobin.[6] The deficiencies or excesses of Fe^{3+} can lead to a variety of diseases, such as Alzheimer's, Huntington's, and Parkinson's diseases.[7] Thus, there is an urgent need to develop chemical sensors that are capable of detecting the presence of Cr^{3+}, Al^{3+} and Fe^{3+} ions in biological samples.

Due to their paramagnetic nature, trivalent chromium (Cr^{3+}) and iron (Fe^{3+}) are among the most effective fluorescent quenchers,[8] which makes it difficult to develop a fluorescence turn-on sensor. For this reason, very few sensors for Cr(III)[3c,8,9] and Fe(III)[10] have been reported, and far fewer find application in cell imaging.[3c,9d,10h] In contrast, Al^{3+} is diamagnetic, whose binding to sensors often enhances the fluorescence.[11] Due to strong hydration of Al^{3+} in water, however, most reported dyes for Al^{3+} are required to be used in organic solvents or mixed solvents, with very few being suitable for Al^{3+} imaging applications.[11a,e] Recently, the study by Costero *et al.*[9a] reported a fluorescein derivative, whose fluorescence at 475 nm could be turned on by Cr^{3+}, Fe^{3+} and Al^{3+} in dry CH_3CN. The presence of 4% of water in CH_3CN, however, will quench the fluorescence of the fluorescein complex with Cr^{3+} and Fe^{3+} ions. It remains a challenge to design a fluorescent sensor that *not only* can recognize *but also* differentiate the trivalent cations (Al^{3+}, Cr^{3+} and Fe^{3+}), especially in aqueous solution. Herein, we disclose a sensor that can simultaneously detect Cr^{3+}, Al^{3+} and Fe^{3+} ions by the naked eye in an aqueous medium.

The sensor design incorporates the 2-(2′-hydroxyphenyl) benzoxazole (HBO) unit as an emitting fluorophore, whose emission has a large Stokes shift (>150 nm) arising from the excited-state intramolecular proton transfer (ESIPT). As shown in Fig. 1, the cation binding is expected to occur by using two stronger ligands 2-(pyridin-2′-yl)hydrozono groups (**2**). Due to steric hindrance by the H_a atom, the C=N will be twisted away from the coplanarity (with HBO) upon binding metal cations, resulting in a decrease of the conjugation length (absorbance hypsochromic shift). It is assumed that only those metal cations that can bind strongly to the imine bonds will be able to compete, thus separating the trivalent cations from the divalent and monovalent ones. In addition, the cation binding removes the adverse effect of Schiff base on fluorescence, thereby turning on the emission. The proposed metal complex **2** has four-coordination, which should be more stable than **3** (three coordination). The two different binding modes could be easily identified by their ESIPT ON–OFF properties (large or smaller Stokes shift). The design also includes a phenol group, whose participation in the cation binding event could act as a switch to manipulate the ESIPT properties. By using the dual channel control (*i.e.*, fluorescence intensity and ESIPT), the study aims to differentiate the trivalent cations, since the ESIPT of the HBO unit is quite sensitive to electronic perturbation from the cation binding.[12]

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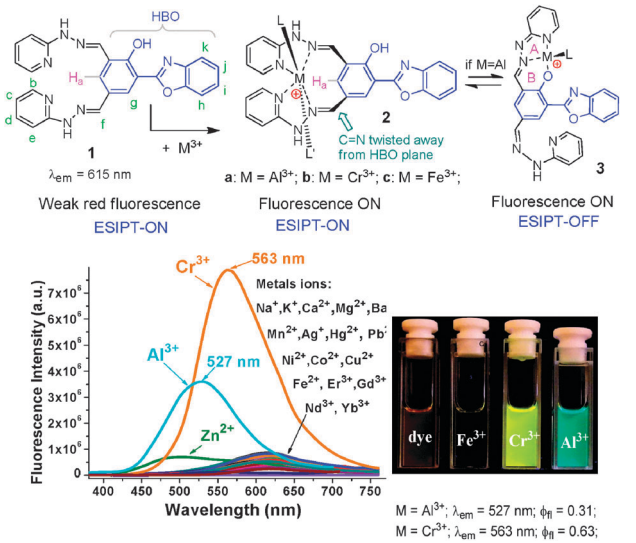


Fig. 1 Top: dye **1** and its Cr^{3+} complex **2** (**3** is possible but not preferred). The cation in **2** is likely to adopt six-coordination geometry with two additional ligands (L & L′). Bottom: fluorescence response of **1** upon addition of 10 equiv. of different metal ions in aqueous solution (8 : 2 = water : EtOH).

The absorption of **1** revealed a major peak (at 315 nm, attributed to π–π*) and a minor peak (at 432 nm, attributed to n–π*) (ESI,† Fig. S1b). The fluorescence response of **1** was examined in aqueous medium (H_2O : EtOH = 8 : 2) by addition of various metal ions (Fig. 1). Sensor **1** showed weak red fluorescence ($\Phi_F = 0.1$) with a large Stokes shift (180 nm), attributed to emission from its *keto* tautomer associated with its ESIPT properties. Sensor **1** was silent toward monovalent and divalent metal ions. Surprisingly, the fluorescence of **1** showed immediate turn-on upon addition of trivalent ions Cr^{3+}, Al^{3+} and Fe^{3+}, although Cr^{3+} and Fe^{3+} are widely known to be fluorescence quenchers. The sample with Fe^{3+} showed the initial fluorescence turn-on but quickly decays within 5 minutes (ESI,† Fig. S5b), while the yellow fluorescence of Cr^{3+} complexes was quite stable (ESI,† Fig. S3). The fluorescence of Al^{3+} complexes changed to blue-green (527 nm). The distinctive feature in optical response thus allowed us to distinguish Fe^{3+} (which gives pulse-like fluorescence) from Cr^{3+} (emission $\lambda_{em} \sim 556$ nm, yellow green) and Al^{3+} ($\lambda_{em} \sim 527$ nm, blue-green). In summary, different response to trivalent ions enabled the naked eye detection of Cr^{3+}, Fe^{3+} and Al^{3+} cations (Cr: $\Phi_F = 0.63$; Al: $\Phi_F = 0.31$). It was noted that the sensor also showed different responses for Fe^{2+} and Fe^{3+}, as Fe^{2+} only slightly quenched the fluorescence without showing initial turn-on.

To elucidate the metal binding mode, the UV-vis spectra of **1** were recorded upon addition of different equiv. of Cr^{3+} (ESI,† Fig. S2). As is known, the deprotonation of the phenol upon metal binding will lead to large spectral bathochromic shift together with fluorescence blue shift, resulting in a smaller Stokes shift.[12a,d] Upon addition of Cr^{3+}, the absorption band at 432 nm (n–π*) progressively decreased, indicating that the cation binds to the Schiff base. The new π–π* absorption band was observed at about 358 nm. It should be noted that the emission of the metal complex exhibited a large Stokes shift (at 195 nm for Cr^{3+} and at 170 nm for Al^{3+} respectively), which indicates the existence of the free phenol group and ruled out the binding mode **3**. All these facts point to the formation of the metal complex **2**, where Al^{3+} and Fe^{3+} showed a similar binding mode.

Mass spectral studies revealed that ligand **1** disappeared (TOF-MS-ES$^+$ at peaks 472.1815 and 494.1637) upon addition of Cr^{3+} (ESI,† Fig. 8d). The newly formed positively charged peak of TOF-MS-ES$^+$ at 577.1374 matched $[\mathbf{1} + Cr^{3+} + MeO^- + EtO^-]^+$ = 577.1507, indicating the formation of **2** (ESI,† Fig. S8) with a 1 : 1 ratio of the ligand to trivalent metal ions. In aqueous solution, TOF-MS-ES$^+$ also detected the formation of **2** where L═L′═OH (ESI,† Fig. S8a) with six-coordination geometry. ^{1}H NMR spectra revealed consistent evidence to support the formation of **2**. Upon addition of 1.0 equiv. of $Cr(NO_3)_3$, the turbid solution of **1** in CD_3OD/DMSO-d_6 became transparent, indicating the Cr^{3+} complex formation. The characteristic pyridine signal H_b and imine H_f (at ~8.5 ppm) were shifted downfield to about ~8.7 ppm, supporting the assumption that both pyridine units and imine groups were bound to the Cr^{3+} ion, as shown in complex **2** (ESI,† Fig. S19).

To gain a better understanding of M^{3+} binding mode, compounds **4** and **5** were prepared (Fig. 2). UV-vis absorption of **4** exhibited nearly no change (at ~417 nm, Fig. 2a) upon addition of the M^{3+} cations, in comparison with **1**. In sharp contrast, UV-vis absorption of **5** showed a clear blue shift upon addition of M^{3+} (Fig. 2b). This observation supported the proposed binding mode that the cation binds to both Schiff base groups as shown in **2**, whose formation caused the twisting of imine bonds. This was also consistent with the hypsochromic shift in UV-vis absorption. Fluorescence of **5** also exhibited a similar blue shift as **1** upon interaction with the M^{3+} cation (ESI,† Fig. S20). The fluorescence of metal complex **5**-M^{3+} exhibited a small Stokes shift (~60 nm), which is far smaller than that of **1** + M^{3+} (~190 nm). The results thus indicate the formation of complex **2**, whose ESIPT remains on.

In an effort to seek additional evidence for the binding mode, **4** was further examined with addition of Zn^{2+} cations, as its complex can involve the adjacent phenol as observed.[12d] While ligand **4** exhibited weaker interaction with Zn^{2+} in an aqueous medium (ESI,† Fig. S16 and S17b), it reacted readily with Zn^{2+} in ethanol to form stable **4**-Zn complexes (ESI,† Fig. S9e and S18). As a consequence of the removal of the phenolic proton, the UV-vis absorption of **4** ($\lambda_{max} \approx 375$ nm) was notably shifted to $\lambda_{max} \approx 417$ nm *via* forming **4**-Zn (Scheme 1, and ESI,† Fig. S18a). In addition, the weak emission of **4** at ~582 nm (assigned to ESIPT from the *keto* tautomer) disappeared, which was accompanied

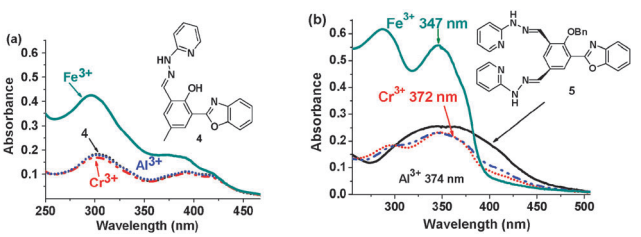
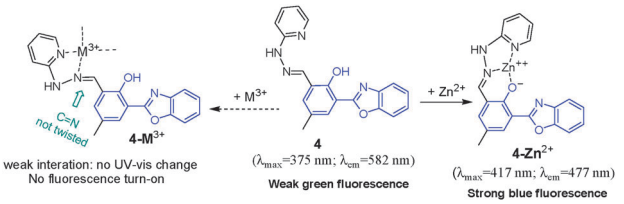


Fig. 2 UV-vis response of **4** (a) and **5** (b) upon addition of 10 equiv. of different metal ions in aqueous solution (8 : 2 = water : EtOH).



Scheme 1 Structures of **4** and its metal complexes.

by a stronger new emission at ~477 nm upon formation of the zinc complex. It was clear that participation of phenol in cation binding would result in a large spectral shift with a small Stokes shift (60 nm). Since no large spectral shift was observed when ligand **1** binds to the trivalent Cr^{3+} cation, it is not likely that the phenol participated in binding. Therefore, the proposed binding mode **2** was predominant for the Cr^{3+} complex of **1**. For the Al^{3+} cation, the resulting complex with **1** initially formed *via* binding mode **2**, while some of the Al^{3+} complex might adopt binding mode **3** to give blue-green emission as suggested from its fluorescence in EtOH (ESI,† Fig. S15). In the sensing of Fe^{3+} ions, the formation of complex **2** initially turned on the fluorescence. However, the tautomerization of **2** took place quickly within 5 min leading to the formation of **2′** (ESI,† Scheme S1), which was captured by TOF-MS-ES$^+$: the positively charged peak of TOF-MS-ES$^+$ at 503.0999 matched $[1 + Fe^{3+} - 2H^+]^+ = 503.0762$ (see ESI,† Fig. S21). The formation of **2′** could be responsible for the observed fluorescence quenching.

In order to examine the selectivity of **1**, some other cations were added to a solution of **1** under the same conditions. Addition of M^+ and M^{2+} cations (10 equiv.) induced almost no change in the UV-vis spectra of **1** (except Cu^{2+}, see ESI,† Fig. S1). The results indicated weak binding between dye **1** and the mono- and divalent metal ions. Physiologically important metal ions, which exist in living cells, such as Ca^{2+}, Mg^{2+}, Na^+ and K^+, gave negligible fluorescence response. Upon addition of one of the metal ions with the subsequent addition of Cr^{3+}/Al^{3+}, the green-yellow fluorescence was turned on (see ESI,† Fig. S10). Therefore, **1** is a highly selective chemosensor for Cr^{3+}/Al^{3+} with the detection limits of 0.2 μM and 0.5 μM for Cr^{3+} and Al^{3+}, respectively.

The potential application of **1** for both Cr^{3+} and Al^{3+} in biological samples was examined by using confocal fluorescence microscopy. In the control experiment, staining human mesenchymal stem cells (hMSCs) with 10 μM dye **1** for 30 min led to a negligible intracellular fluorescence (Fig. 3d). When the cells were first incubated with 30 μM of metal ions (Cr^{3+} or Al^{3+}) for 30 min, and then further treated with 10 μM sensor **1** for another 30 minutes, a significant increase in the fluorescence from the intracellular area was observed (Fig. 3e and f). Bright-field measurements confirmed that the cells, after being treated with Cr^{3+}/Al^{3+} and **1**, were viable throughout the imaging experiments. These results demonstrate that the probe is permeable to cells, binds to intracellular Cr^{3+} and Al^{3+}, and emits strong fluorescent light, thus it is highly suitable for determining intracellular Cr^{3+} and Al^{3+} ions. Response to Cr^{3+} and Al^{3+} ions with distinctly different colors (yellow-green and cyan, respectively) from the cell samples raised the prospect that the Cr^{3+} and Al^{3+} ions could be simultaneously determined.

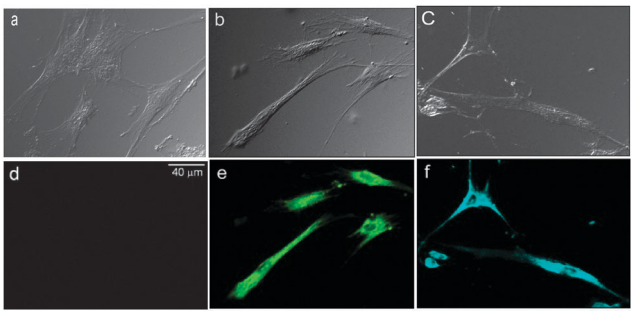


Fig. 3 Confocal fluorescence images of Human mesenchymal stem cells (hMSCs) excited with a Diode laser (405 nm) on an Olympus FV-1000 laser scanning microscope. The images were collected at bright field (a–c) and fluorescent channels (d–f). (a–d): the cells were incubated with dye **1** in PBS for 60 min; (b–e) the cells were first treated with Cr^{3+} (30 μM) for 30 min and further exposed to dye **1** (10 μM) in PBS for another 60 min, and image e was collected from 535 to 565 nm; (c–f) the cells were first treated with Al^{3+} (30 μM) for 30 min and further exposed to dye **1** (10 μM) in PBS for another 60 min, and image (f) was collected from 505 to 525 nm.

In conclusion, we have demonstrated a single fluorescent molecular probe that can *specifically* detect trivalent ions (Cr^{3+}, Al^{3+} and Fe^{3+}) in aqueous medium. In the molecular design, the sensor cleverly utilized two "hydrazone Schiff bases" (binding mode **2**) to bind trivalent cations Al^{3+}, Cr^{3+} and Fe^{3+} (M^{3+} cations), while being silent to mono- and divalent metal ions. Simultaneous binding to two "hydrazone Schiff bases" by M^{3+} cations removed the fluorescence "quenching effect" associated with Schiff base, thereby leading to great fluorescence turn-on. Large response from both fluorescence intensity and spectral shift provided distinctly different profiles for each of the three trivalent metal ions, thereby allowing their naked eye detection. By using the different cation binding modes to switch the ESIPT ON and OFF, the study further illustrates an effective and novel strategy to differentiate Al^{3+}, Cr^{3+} and Fe^{3+}. Cell imaging of confocal fluorescence microscopy further demonstrated that **1** can be used for monitoring intracellular Cr^{3+} and Al^{3+} levels in living cells.

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