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ARTICLE TYPE

Iodeosin-based Fluorescent and Colorimetric Sensing for Ag^+, Hg^{2+}, Fe^{3+}, and Further for Halide Ions in Aqueous Solution

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We report that common erythrosin B can be used as dual-mode fluorescent and colorimetric sensor to Ag^+, Hg^{2+} and Fe^{3+}, and further for halide ions in aqueous solution based on erythrosin B complexation with the three metal ions.

The demand for multifunctional sensors for toxic heavy metal ions, such as Ag^+, Hg^{2+} and Fe^{3+}, is increasing over time. Ag^+ does great harm to human health by inactivating sulfhydryl and combining itself with various metabolites.[1] Hg^{2+}, usually exists in inorganic form or organic form as methylmercury, and harms aquatic life and bio-accumulates through food chain.[2] Fe^{3+}, although plays important roles in metabolic processes, either Fe^{3+} deficiency or overloading could induce various biological disorders.[3] Thus it is of great importance to monitor these three heavy metal ions in aqueous solutions. Fluorescence-based sensing offers significant advantages of simplicity, high sensitivity, high selectivity and instantaneous response, while alternate colorimetric sensing is a much less labor-intensive method.[4]

For this purpose, xanthene dye becomes a good candidate as the sensing material due to its visible absorption range and high fluorescence quantum efficiency, and actually it has been widely used as biological stain, sensitizer, laser dye, quantum yield standard dyes and sensors in many different fields.[5] Erythrosin B, a representative xanthene dye, well known for its high quantum yields of triplet formation,[6] has been used as phosphorescence sensor for gaseous oxygen.[7] The fluorescence quantum efficiency of erythrosin B is about 6% under normal ambient experimental conditions, which is also high enough for fluorescence applications. For example, the erythrosin B based fluorescence sensor for periodate has been reported.[6b] However, fluorescence sensors based on erythrosin B for heavy metal ions have not been reported so far. As erythrosin B has carboxyl groups, oxygen heterocyclic ring and the iodinations, which may provide coordination sites with metal ions, also, there may exist electrostatic interaction between the anionic erythrosin B and cationic metal ions, so we expect that multiple-mode sensing for metal ions based on erythrosin B is possible. This kind of multiple-mode sensing will fill the gaps of intensity-based single-mode fluorescence sensor, and may provide more reliable measurement results.

With such anticipation, we investigated how erythrosin B responds to different metal ions. Strikingly, both fluorescence and absorption spectra of erythrosin B show dramatically

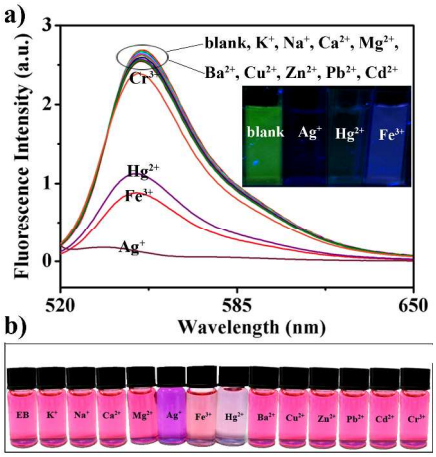

Fig. 1 a) Relative fluorescence intensity of 10^{-5} M erythrosin B in water solution to different metal ions (3×10^{-6} M). (λ_{ex}=510 nm) Inset: Fluorescence images of erythrosin B with addition of Ag^+, Hg^{2+} and Fe^{3+} with excitation of 365 nm. b) Colorimetric response of tested metal ions to erythrosin B in water solution.

different characteristic responses to Ag^+, Hg^{2+} and Fe^{3+}, which endows it with the dual-mode sensing ability to the three heavy metal ions. The sensing mechanism based on coordination complexation was confirmed by X-ray photoelectron spectra (XPS). Moreover, the '*in situ*' prepared silver complex with erythrosin B showed remarkable selectivity to halogen ions by giving reversed spectral signals compared to erythrosin B with addition of Ag^+, rendering the '*in situ*' prepared silver complex dual-mode chemosensor for F^-, Cl^-, Br^- and I^- as well. Furthermore, the addition of I^- resulted in a complete recovery of erythrosin B fluorescence and absorption, which makes the erythrosin B based sensor reversible for the dual-mode sensing of Ag^+.

Another reason for the choice of erythrosin B is its long emission wavelength and emission insensitivity to pH over a wide range of pH (pH=5～9, Fig. S1), which may enhance its pH anti-interference ability in practical applications. Erythrosin B gave strong emission at 549 nm with excitation of 510 nm, as shown in Fig. 1a. Fluorescence responses of erythrosin B to various metal ions indicate that Ag^+ obviously quenches the fluorescence of erythrosin B at 549 nm, and Hg^{2+} and Fe^{3+} also quench erythrosin B emission although not as sharp as that for Ag^+. However, other common metal ions

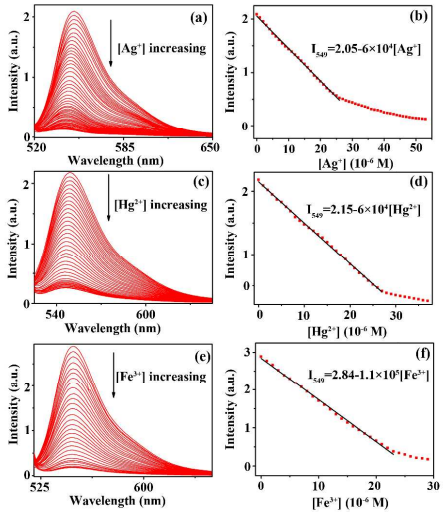

Fig. 2 Fluorescence spectra and corresponding titration curves of 10^{-5} M erythrosin B in water solution to Ag^+ (a, b), Hg^{2+} (c, d) and Fe^{3+} (e, f).

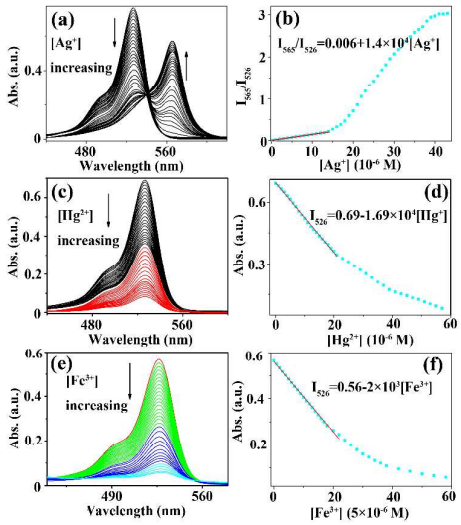

Fig. 3 UV-vis absorption spectra and corresponding titration curves of 10^{-5} M erythrosin B in water solution upon addition of Ag^+ (a, b), Hg^{2+} (c, d) and Fe^{3+} (e, f), respectively.

including Co^{2+} and Ni^{2+} have little or no impact on erythrosin B emission (Fig. 1a and Fig. S2). Thus erythrosin B in aqueous solution can be used to selectively identify Ag^+, Hg^{2+} and Fe^{3+} by simply measuring its fluorescence. Moreover, it should be noted that there exists weak blue fluorescence for erythrosin B with addition of Fe^{3+} (with excitation of 365 nm, as the fluorescence images shown in the inset of Fig. 1a and the fluorescence spectrum shown in Fig. S3), which may come from some erythrosin B aggregates induced by high charged Fe^{3+}, and this can be used to distinguish Fe^{3+} from Ag^+ and Hg^{2+}. Moreover, with the addition of various common metal ions (including K^+, Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, Ag^+, Hg^{2+} and Fe^{3+}), there exists naked eyes perceived solution color change from rose to purple for Ag^+ (Fig. 1b), and this is beneficial for instantaneous visual identification of Ag^+ from Hg^{2+}. Thus there exist characteristic responses of erythrosin B to Ag^+, Fe^{3+} and Hg^{2+}, which further ensures the good selectivity of the sensor. In addition, as shown in Fig. 2, there exist linear relationships between the fluorescence intensity of erythrosin B and $[Ag^+]/[Hg^{2+}]/[Fe^{3+}]$ in given concentration ranges ($0-27\times10^{-6}$ M for Ag^+, $0-27\times10^{-6}$ M for Hg^{2+} and $0-24\times10^{-6}$ M for Fe^{3+}, as Eqs. shown in Fig. 2b, d and f), rendering erythrosin B quantitative fluorescence detection of the three heavy metal ions. On the basis of the 10% fluorescence quenching method, fluorescence detection lower limit of 5×10^{-7} M was achieved for all Ag^+, Hg^{2+} and Fe^{3+}. Coupled with the above-mentioned linear relationships between erythrosin B fluorescence intensity and $[Ag^+]$, $[Hg^{2+}]$ and $[Fe^{3+}]$, sensitive and selective fluorescence sensing of Ag^+, Hg^{2+} and Fe^{3+} can be realized. Furthermore, the strong visible absorption peak of erythrosin B (at 526 nm) shows characteristic colorimetric responses to Ag^+, Hg^{2+} and Fe^{3+}, respectively (Fig. 3a, c and e), and the details can be stated as follow. With the addition of Ag^+, the absorption peak at 526 nm decreases with $[Ag^+]$ (Fig. 3a), however, a new absorption peak at 565 nm appears and increases with $[Ag^+]$. The ratio of the relative absorption intensities, i.e., I_{565}/I_{526}, increased by 54-fold with addition of Ag^+, which is attributed to the formation of silver complex. In addition, as I_{565}/I_{526} linearly increases with $[Ag^+]$ in a certain concentration range, i.e., $0-15\times10^{-6}$ M, it can be used for ratiometric quantitative analysis of $[Ag^+]$ in solution for a given concentration range (Fig. 3b). In contrast, with the addition of Hg^{2+} and Fe^{3+}, only decreased erythrosin B absorption at 526 nm was observed (Fig. 3c-f), therefore, I_{526} can be directly used to quantify $[Hg^{2+}]$ and $[Fe^{3+}]$ in given concentration ranges ($0-22\times10^{-6}$ M for Hg^{2+} and $0-21\times10^{-6}$ M for Fe^{3+}, see Fig. 3e and g). By combining these results with the characteristic fluorescence and colorimetric responses of erythrosin B solution to Ag^+, Hg^{2+} and Fe^{3+}, both qualitative and quantitative colorimetric sensing of Ag^+, Hg^{2+} and Fe^{3+} can be realized. Therefore, erythrosin B gives dual-mode sensing (fluorescence and colorimetric) to Ag^+, Hg^{2+} and Fe^{3+}.

In order to elucidate the sensing mechanism, fluorescence lifetimes of erythrosin B both in the absence and presence of Ag^+, Hg^{2+} and Fe^{3+} were obtained by exponential simulation of the fluorescence decay curves recorded (Fig. S4). And the results indicate that erythrosin B fluorescence lifetime (0.098±2 ns) almost keeps constant within experimental error (10%), indicating the presence of static quenching [7b]. And the stoichiometry of the erythrosin B complex with silver, mercury and ferric was proved to be 1:4 (erythrosin B: quencher), determined by Job's plot curves based on fluorescence (Fig. S5). It should be noted that the averages of three measurements are used in the experiments to obtain reliable data.

Moreover, we studied the behavior of the '*in situ*' prepared silver, mercury and ferric complexes toward common anions (including $C_2H_3O_2^-$, OH^-, NO_3^-, CO_3^{2-}, PO_3^{3-}, SO_4^{2-}, F^-, Cl^-, Br^-, I^-, see Fig. S6 and S7), and have found that the silver complex shows profound selectivity toward halogen ions by giving enhanced fluorescence (Fig. S6), while all the anions tested have little or no impact on the fluorescence of the mercury and ferric complexes (Fig. S7). The addition of increasing amounts of halogen ions, no matter of F^-, Cl^-, Br^- or I^-, to the silver complex resulted in a recovering of the

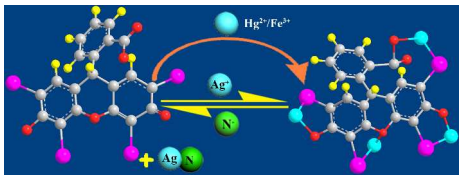

Fig. 4 Ball and stick model of the mechanism for selective recognition of Ag^+, Hg^{2+}, Fe^{3+}, and further for F^-, Cl^-, Br^- and I^-. (N-= F^-, Cl^-, Br^- and I^-) Color code: red, O; gray, C; yellow, H; bright pink, I; light blue, heavy metal ions.

erythrosin B emission, together with the solution color changes from colorless to rose. The fluorescence spectra and corresponding titration curves of the erythrosin B with 4 equiv. Ag^+ (erythrosin B+4 equiv. Ag^+) solution titrated with F^-, Cl^-, Br^- and I^- are shown in Fig. S8, revealing that there exist good linear relationships between fluorescence intensity and concentrations of halogen ions. Therefore, the '*in situ*' prepared silver complex can be used for selective fluorescence detection of halogen ions. Further, absorption spectra and the corresponding titration curves (absorption intensity at 565 nm versus concentrations of halogen ions) of the silver complex with successive addition of F^-, Cl^-, Br^- and I^- were recorded, which proves a revival of the erythrosin B absorption as expected (Fig. S9). Especially, I^- resulted in a complete revival of the erythrosin B absorption (Fig. S9g), indicating that Ag^+ can be completely removed from the silver complex by I^-. Based on these results, colorimetric detection of halogen ions can be realized.

To evaluate the bonding ability of erythrosin B with Ag^+, Hg^{2+} and Fe^{3+}, their bonding constants were determined based on our previous report (Part S1). And the large K values (~10^5 M^{-1}, Fig. S10) ensured the high sensitivity of erythrosin B as a fluorescence sensor for Ag^+, Hg^{2+} and Fe^{3+}. Furthermore, as mentioned above, the addition of I- can make a complete recovery of erythrosin B fluorescence and a complete revival of erythrosin B absorption, and fluorescence can be quenched again by successive addition of Ag^+. Thus as a fluorescence and colorimetric sensor of Ag^+, erythrosin B is expected to be reusable within experimental error, which has been proved experimentally (Fig. S11, experimental error＜5%).

In order to get more information about the interactions between erythrosin B and Ag^+, Hg^{2+} and Fe^{3+}, XPS spectra of erythrosin B and its complexes with Ag^+, Hg^{2+} and Fe^{3+} are measured (Fig. S12 and Fig. S13). The I3d peaks of erythrosin B, i.e., 620.6 and 632.1 eV, are shifted to lower energy sides (Fig. S12a-d), while the O1s peaks (530.8 eV and 533.7 eV) corresponding to C=O and C-O, are shifted to higher and lower energy respectively (Fig. S12e-h), and the peak at 288 eV corresponding to C=O in the C1s spectra, is shifted to 288.7, 288.9 and 288.7 eV respectively after interaction with Ag^+, Hg^{2+} and Fe^{3+} (Fig. S13). All these results indicate the interactions between metal ions and atomic I, single-bonded oxygen and double-bonded oxygen. Furthermore, the involvement of the iodine atoms in the complex formation between erythrosin B and Ag^+, Hg^{2+} and Fe^{3+} was determined by testing non--iodinated erythrosin B analogue (fluorescein, see Part S2). Thus a feasible sensing mechanism of erythrosin B for Ag^+, Hg^{2+}, Fe^{3+} and further for halogen ions is shown in Fig. 4. As a result of the complexation between erythrosin B and Ag^+, Hg^{2+} and Fe^{3+}, the number of the free erythrosin B molecules decreases, as indicated by the decrease of the characteristic absorption of erythrosin B. And the number of the photoexcited molecules also decreases, causing the decrease of fluorescence. So the colorimetric and fluorescence sensing of erythrosin B to Ag^+, Hg^{2+}, Fe^{3+} is ensured. Furthermore, for the '*in situ*' prepared silver complex, with the addition of halogen ions, 'free' erythrosin B molecules are released, which results in recovered fluorescence and characteristic absorption of erythrosin B. Thus the '*in situ*' prepared silver complex gives dual-mode sensing for halogen ions.

In summary, erythrosin B based fluorescent and colorimetric sensing for Ag^+, Hg^{2+} and Fe^{3+}, and further for halogen ions has been studied. The sensing mechanism based on coordination complexation between erythrosin B and metal ions has been confirmed by fluorescence lifetime, stoichiometry and XPS measurements. This work demonstrates a new method for spectroscopic detection of Ag^+, Hg^{2+} and Fe^{3+}, and further for halogen ions; and also extends the application of xanthene dyes as fluorescent and colorimetric sensors for heavy metal ions.

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