Iodeosin-based Fluorescence and Colorimetric Sensing for Ag⁺, Hg²⁺, Fe³⁺, and Further for Halide Ions in Aqueous Solution

Meiling Wang,[†] *Guowen Meng*, $*^{\dagger,\#}$ *Qing Huang*[‡]

[†]Key Laboratory of Materials Physics, and Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031, China; [#] University of Science and Technology of China, Hefei,
230026, China; and [‡]Institute of Biotechnology & Agriculture Engineering, Chinese Academy of Sciences, Hefei, 230031, China

*To whom correspondence should be addressed. E-mail: <u>gwmeng@issp.ac.cn</u>

Part S1 Evaluation of the bonding constants between erythrosin B and Ag^+ , Hg^{2+} and Fe^{3+}

Part S2 Confirmation of the involvement of iodine atoms in the complex formation between erythrosin B and Ag⁺, Hg²⁺ and Fe³⁺

Fig. S1-Fig. S14

Part S1 Evaluation of the bonding constants between erythrosin B and Ag^+ , Hg^{2+} and Fe^{3+}

We evaluated the binding constants *K* between erythrosin B and Ag⁺, Hg²⁺and Fe³⁺ from the plot of $Log(I_0-I)/I$ versus $Log[M^{n-}]$ according to our previous approach [1]. where I_0 , *I*, *K*, *n* and $[M^{n-}]$ are fluorescence intensity of the erythrosin B solution in the absence and presence of the quenchers, binding constant, the number of the bonding sites per fluorescent molecule and the concentration of the quenchers respectively. Thus *K* and *n* can be calculated from the plot of $Log(I_0-I)/I$ versus $Log[M^{n-}]$ shown in Fig. S9.

Part S2 Confirmation of the involvement of iodine atoms in the complex formation between erythrosin B and Ag^+ , Hg^{2+} and Fe^{3+}

In order to further confirm the involvement of iodine atoms in the complex formation between erythrosin B and Ag^+ , Hg^{2+} and Fe^{3+} , fluorescein (as molecular structure shown in Fig. S14a), was used for the fluorescence and absorption titration experiments. As shown in Fig. S14c, almost no fluorescence quenching was observed with the addition of Ag^+ , Hg^{2+} and Fe^{3+} . Moreover, no absorption decreases appeared for the fluorescein with addition of whichever of Ag^+ , Hg^{2+} and Fe^{3+} (Fig. S14d), which indicated the number of free dye molecules did not decrease after the addition of Ag^+ , Hg^{2+} and Fe^{3+} , proving that there did not exist complexation between fluorescein and the metal ions. Thus the involvement of the iodine atoms in the complex formation between erythrosin B and Ag^+ , Hg^{2+} and Fe^{3+} was confirmed.



pH Fig. S1. Relative fluorescence intensity of 10^{-5} M erythrosin B solution with different pH.



Fig. S2. Fluorescence responses of 10^{-5} M erythrosin B in water solution to Co^{2+} and

Ni²⁺ (3×10⁻⁶ M). (λ_{ex} =510 nm)



Fig. S3. Fluorescence spectrum of Fe^{3+} contained erythrosin B solution excited with 365 nm.



Fig. S4. Fluorescence intensity decay curves of erythrosin B, and erythrosin B with addition of Ag^+ , Hg^{2+} and Fe^{3+} . (black lines: fluorescence decay curves; red lines: exponential simulation curves, λ_{ex} =460 nm, λ_{em} =565 nm)



Fig. S5. Job's plot curves of erythrosin B for Ag^+ (a), Hg^{2+} (b) and Fe^{3+} (c) determined by fluorescence method.



Fig. S6. Relative fluorescence intensity of the silver complex solution with different anions.



Fig. S7. Relative fluorescence intensity of the a) mercury and b) ferric complex with

different anions.



Fig. S8. Fluorescence spectra and corresponding titration curves of 10^{-5} M erythrosin B+4 equiv. Ag⁺ in water solution to F⁻ (a, b), Cl⁻ (c, d), Br⁻ (e, f) and I⁻ (g, h). (λ_{ex} =510 nm)



Fig. S9. UV-vis absorption spectra and corresponding titration curves (absorption at 565 nm) of 10^{-5} M erythrosin B+4 equiv. Ag⁺ in water solution to F⁻ (a, b), Cl⁻ (c, d), Br⁻ (e, f) and I⁻ (g, h).



Fig. S10. Bonding equilibration between erythrosin B and metal ions. $(M^{n+}=Ag^+, M^{n+}=Ag^+)$

Hg²⁺, Fe³⁺)



Fig. S11. Relative fluorescence intensity histograms of 10^{-5} M erythrosin B (brown), upon addition of 4 equiv. Ag⁺ (red), and successive addition of 4 equiv. I⁻ (green), 4 equiv. Ag⁺ (blue), 4 equiv. I⁻ (light blue), 4 equiv. Ag⁺ (hot pink), respectively.



Fig. S12. X-ray Photoelectron Spectra of erythrosin B and its complexes with Ag^+ , Hg^{2+} and Fe^{3+} , respectively (from left to right). (a-d: I3d spectra; e-h: O1s spectra)



Fig. S13. X-ray Photoelectron C1s Spectra of (a) erythrosin B, and its complexes with

(b) Ag^+ , (c) Hg^{2+} and (d) Fe^{3+} , respectively.



Fig. S14. Molecular structures of (a) fluorescein and (b) erythrosin B, (c) and (d) fluorescence and absorption spectra of 10^{-5} M fluorescein solution with addition of 1 equ. Ag⁺, Hg²⁺ and Fe³⁺, respectively.

REFERENCE

[1] Meiling Wang, Guowen Meng, Qing Huang, Qiaoling Xu and Guodong Liu. A GBI@PPyNWs-based prototype of reusable fluorescence sensor for the detection of Fe³⁺ in aqueous solution. *Anal. Methods*, **2012**, 4, 2653.