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Communication

Eu^{3+} chelate with phenanthroline derivative gives selective emission responses to $\mathrm{Cu}(\mathrm{II})$ ions

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1. Introduction

Cation complexation, in particular copper cation recognition behavior through metal—ligand bonds or hydrogen bond formation, has attracted great interests in last decade because of its essential role in biological or environmental system [1,2]. Among various chemical or physical properties, the purpose of using luminescence to investigate the non-covalent interactions is that emission could be considered as straightforward approach and sensitive to human eyes [3].

In recent years, the application of f elements such as Eu³⁺, Tb³⁺ and Sm³⁺ ions in signaling system has provided the possibility of sensitizing the lanthanide luminescence via other cation or anions [4]. The promising feature of lanthanide compounds is presently the subject of a growing interest. In detail, their narrow line emissions caused by forbidden transitions, which lead to high color purity of resulted light, can extend from short wavelength like UV to visible until near infrared region. In addition, their long-lived emission excited states cover a wide range from micro to millisecond scale. This area has been extensively studied by Parker, Tsukube, Bunzli, Faulkner, Gunnlaugsson and several related researchers [4–9].

Lately, Gunnlaugsson et al. [10] reported a supramolecular phenanthroline complex as a receptor for Cu(II) especially by nitrogen atom coordination in heterocyclic ring. However, the neutral ligand is much less effective in selectively binding copper cation than

ABSTRACT

Two novel ternary europium(III) complexes (Eu-1 and 2) based on modified phenanthroline ring have been successfully synthesized and give characteristic purple–red emissions. The complex with 4-substituted carboxyl group has been proved to act as a selective luminescence quencher for copper(II) ions, as shown by the "on/off" switch phenomenon and the smart responsive changes in the UV–vis region (detection limit up to $0.5 \,\mu$ M). The preliminary data imply that Eu-1 could be applicable as a potential fluorescent sensor for detection of copper(II) ions.

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electronegative group such as carboxyl moiety. Therefore, we constructed a ternary europium(III) complex with benzoyl trifluoroacetonate-phenanthroline (Eu-1) for the first step, then performed corresponding sensing experiments towards a class of cations through the remaining COOH group. Facts substantiate that the resulting complex gives rise to sharp luminescence changes unique to copper ions in the presence of other tested cations (Fig. 1). To the best of our knowledge, here is the first report which concentrates on the lanthanide emission change in terms of mixed heterometallic (copper—ligand—europium) complex through functional carboxyl group interactions.

2. Experimental

All the starting materials were obtained from commercial suppliers and used as received.

2.1. Synthesis and characterization of europium(III) complex of 2-(4-carboxyphenyl)imidazo [4,5-f]-1,10-phenanthroline (Eu-1, see Fig. 1)

Phen-a = 2-(4-carboxyphenyl)imidazo [4,5-f]-1,10-phenanthroline

 $\label{eq:phen-b} Phen-b=2-(3,5-difluorophenyl) imidazo [4,5-f]-1,10-phenanthroline$

The preparation of *phen-a* and *b* used the same method as reported in Ref. [11]. Eu(benzoyl trifluoroacetonate)₃· $2H_2O$

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Fig. 1. Chemical structures of europium(III) complex of 2-(4-carboxyphenyl)imidazo [4,5-f]- 1,10-phenanthroline (Eu-1).

(Eu(BTA)₃·2H₂O) was prepared according to Ref. [12]. In brief, Eu-1 was prepared by the coordination of Eu(BTA)₃·2H₂O (20 mg, 25 μ mol) and **1** (8.5 mg, 25 μ mol) in methanol (8 mL). The whole mixture was refluxed for 4 h and cooled to room temperature. The resulting precipitate was collected and washed twice with water and ethanol to give the titled complex (27 mg, 95%) as yellow powder. EA found: C, 52.71; H, 2.43; N, 4.99%, Anal. Calcd for C₅₀H₃₀EuF₉N₄O₈ [=Eu(BTA)₃(1)]: C, 52.78; H, 2.66; N, 4.92%.

The preparation of Eu-**2** was very similar to Eu-**1** except that 2-(3,5-difluorophenyl)imidazo[4,5-f]-1,10-phenanthroline (2) takes place of **1**. EA found: C, 52.15; H, 2.41; N, 4.91%, Anal. Calcd for $C_{49}H_{28}EuF_{11}N_4O_6 = EuBTA_3$ -**2**: C, 52.09; H, 2.50; N, 4.96%.

2.2. Fluorescence titration experiments

Fluorescence emission spectra were recorded on a computer controlled HITACHI F-2500 fluorescence spectrophotometer. A fixed excitation wavelength at 350 nm was used in the emission spectra. Fluorescence titration experiments were performed in DMSO by using chloride of metal ions respectively. The concentration of Eu-**1** in all the fluorescent experiments is 5.0×10^{-6} mol L⁻¹ in DMSO.

2.3. UV-vis absorption experiments

The measurements of UV–vis absorption spectra were carried out with a SHIMADZU UV-1700 Spectrophotometer. The concentration of Eu-1 in all the UV–vis experiments is 5.0×10^{-6} mol L⁻¹ in DMSO.

2.4. NMR experiments

¹H NMR spectra of **1** (40.0 mmol L^{-1}) in the absence and presence of CuCl₂ (0.8 mmol L^{-1}) were measured in DMSO-d₆ by using Varian NMR Systems 400 MHz spectrometer at room temperature.

3. Results and discussion

The total emission spectrum reveals the typical europium spectral bands (${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ transitions J = 0,1,2 for peaks at 585, 591 and 617 nm respectively) and also exhibits the phenanthroline fluorescence centered at around 420 nm (Fig. 2A) [12]. This ligand emission, although limiting europium-based quantum efficiency, shows a striking purple luminescence due to overlapping with lanthanide red bands. Upon addition of Cu^{2+} , a rapid decrease of the emission band at 420 nm occurred (saturated at 10.0 μ M Cu²⁺ with a 119-fold decrease), going with a large reductions of emission band at 593 and 617 nm, and the fluorescent color of the solution turned from purple to colorless (fluorescent intensity of $\lambda_{em} = 617$ nm showed *ca.* 80% quenching at 25.0 μ M Cu²⁺, inset in Fig. 2A). The fluorescent quenching effect can be compared to the results previously obtained with Eu (III)-containing probes [13]. Due to complexation, consequent electron transfer quenching of the *phen-a* S1 excited state by paramagnetic Cu^{2+} , and Eu-1 exhibits a luminescent switch for Cu^{2+} . The effective stability constant (K_a) can be obtained based on the Hildebrand-Bebesi equation [14]. The linear least-squares curve fitting of the plot with $I_0/(I - I_0)$ versus $[H]^{-1}$ indicates a 1:1 binding model between the host and the guest molecules. The binding constant of $Eu-1/Cu^{2+}$ is $5.70 \times 10^3 \, L \, mol^{-1}$ (Fig. 2B), revealing a medium complexation of Eu-1 with Cu²⁺. We also examined the fluorescence response of Cd^{2+} , Co^{2+} , Cr^{3+} , Hg^{2+} and Pb^{2+} under the same conditions used to test Cu²⁺ (Figs. S1A and S2A). The fluorescent intensity of Eu-1 resulted in less quenching, especially for the emission peak at 617 nm.

Obvious changes in the absorption spectrum of Eu-**1** occurred with the addition of Cu^{2+} (Fig. 3A). As the concentration of Cu^{2+} varied from 0.0 to 20.0 μ M, a new absorption peak at 305 nm appeared and the absorption bands at 333 nm red shifted. The changes of the absorption spectrum of Eu-**1** signify the coordination of Cu(II) by the *phen-a* moiety [14]. However, the absorption spectra of Eu-**1** give no response for the addition of Cd²⁺, Co²⁺, Cr³⁺, Hg²⁺ and Pb²⁺, respectively (Figs. S1B and S2B). The significant difference of Cu²⁺ from these metal ions in absorption spectrum of Eu-**1**/metal ions possibly attributed to the inherent to paramagnetic species of Cu²⁺ (it produces energy or electron transfer) [15,16]. The shifts of absorption peak changed with addition of various metal ions (Fig. 3B). Therefore, such a dual response,



Fig. 2. (A) Fluorescence emission spectra of Eu-1 (5.0μ M) with different concentrations of Cu²⁺ ($0, 0.66, 1.3, 2.0, 3.0, 4.0, 5.0, 7.5, 10.0, 12.5, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 50.0, 60.0, 80.0, 100.0 and 120.0 <math>\mu$ M) in DMSO. Inset shows fluorescence photographs of Eu-1 and Eu-1/Cu²⁺ (5.0μ M:25.0 μ M) under illumination with 365 nm light. (B) Estimation of binding constant for Eu-1 with Cu²⁺ in DMSO at room temperature. The plot based on the intensity changes at 617 nm with a 1:1 binding model: $I_0[(I - I_0) \text{ versus } [Cu^{2+}]^{-1}$ ($R^2 = 0.9994$).



Fig. 3. (A) UV-vis spectra of europium complex (5.0 μ M) with different concentrations of Cu²⁺ 0.0, 1.0, 2.0, 4.0, 5.0, 7.5, 10.0, 15.0 and 20.0 μ M (from 1 to 9). (B) Dependence of peak shift on the concentration of Cu^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Hg^{2+} and Pb^{2+} .

distinguished by both the appearance of the new peak of 305 nm and the red shift of peak in absorption spectra, illustrated the high selectivity of Eu-1 to Cu²⁺ over the other examined metal ions. In addition, it should be noted that high sensitivity for Cu^{2+} (detection limit up to 0.5μ M) is achieved by the absorption spectra of Eu-1 in the present study. The red shift of the maxima absorption peak can be ascribed to be the formation of a J-pattern aggregate and copper (II) coordination leads to the close interactions of adjacent phenanthroline planes [17].

In order to further confirm the function of -COOH group, we prepared another europium(III) complex, 2-(3,5-fluorophenyl) imidazo [4,5-f]-1,10-phenanthroline (Eu-2, Fig. S3), which possesses a structure analogous to Eu-1 and only a 4-substituted carboxyl group replaced by 3,5 substituted fluorine at phenanthroline. The fluorescent emission bands of Eu (III) at 617 nm present no obvious change with the addition of Cu²⁺ in the fluorescent spectra of Eu-2 (Fig. S4A). Simultaneously, the absorption bands exhibit no obvious shifts in UV-vis absorption spectra of Eu-2 (Fig. S4B). Therefore, it can be concluded that the 4-substituted carboxyl group in phenanthroline plays a crucial role for the response of Eu-1 for Cu²⁺. In terms of the paramagnetism of Eu (III), we attempted to explore the coordination mechanism of $Eu-1/Cu^{2+}$ using ¹H NMR experiment of phenanthroline/Cu²⁺ (see Supporting Information). The addition of Cu^{2+} led to the large chemical shift of 4-substituted carboxyl group in phenanthroline (from 13.694 to 12.799 ppm). The proton signals of phenanthroline ring (a and c) were more adjacent to each other, showing that copper recognition might induce the phenanthroline plane stacking together. Particularly, H_e which is in proximity to carboxyl moiety, has relative large downfield shift (8.414–8.431, see Table 1) compared with H_d and H_b. The fact suggests that the coordination through carboxylate group will make the nearer aromatic protons locate in a decreasing π -electron density environment. All the experiment results displayed the strong interaction of carboxyl group and Cu²⁺.

4. Conclusions

We have reported a lanthanide luminescent switch and UV-vis sensor for Cu^{2+} , which shows a fluorescent quenching of Eu (III) by Cu^{2+} in fluorescent spectra and a high selectivity to Cu^{2+} over others examined metal ions in absorption spectra. The sensor exhibited a dual response, distinguished by both the appearance of new peak and red shift of peak in absorption spectra. These studies will provide a foundation for future developments of the fluorescent, spectrophotometric switches and sensors by lanthanide ions. Our effort is aimed to exploit the luminescence sensitivity and expand its application as fluorescent label devices used in biological or industrial fields.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.10.023.

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