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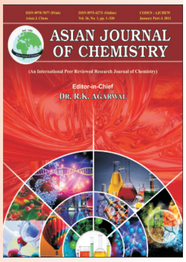

Synthesis and Fluorescence Properties of Europium and 2-Acryloyl isoindoline-1,3-dione Complexes†

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This paper studies the process conditions on the fluorescence properties of ternary complex compound of Eu(AID)$_2$Phen. The conditions are feeding method, feeding order, feeding ratio and synthesis temperature. It reveals that the feeding method, feeding order and feeding ratio have greater impact on the fluorescence properties. Within a synthesis temperature range of 30-70 °C, the fluorescence of Eu(AID)$_2$Phen is enhanced. When the temperature exceeds 70 °C, the fluorescence of Eu(AID)$_2$Phen reduces. The results come to a conclusion of the best synthesis condition, that is, when synthesis temperature is 50 °C, feeding ratio of $EuCl_3$, 2-acryloyl isoindoline-1,3-dione and 1,10-phenanthroline is 1:2:1 and the feeding order is adding N-acryloyl phthalimide (AID) first, then 1,10-phenanthroline, the product Eu(AID)$_2$Phen has a best fluorescent effect.

Keywords: 2-Acryloyl isoindoline-1,3-dione, Rare earth complex, Fluorescence property.

INTRODUCTION

Organic complexes of rare earth luminescent materials are interdiscipline of inorganic luminescent, organic light-emitting and bioluminescence. It has important theoretical significance and practical application value[1,2]. The luminescence properties of rare earth metal complexes are based on their transition between the 4*f* energy levels, which become a huge luminous treasure. These complexes provide a great number of high-tech light-emitting materials and laser materials of superior performance[3-5].

Rare earth organic complexes attract more and more attention due to their high luminescene intensity, high colour purity, high stability and other unique advantages, which widely used in industry, agriculture, medicine and other high-tech industries.These applied researches promote the development of basic subjects and also have great significance on national economy development and high-tech industries[6,7].

Aromatic imide, especially phthalimide and its derivatives are important organic intermediates, which have been widely applied in pesticide, medicine, dyestuff, brightener, photocatalysis and other industries[8].

EXPERIMENTAL

Material preparation: Phthalimide ($C_8H_5NO_2$), europium oxide (Eu_2O_3) and phenanthroline (abbreviated Phen)were bought from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Acrylic acid (99 %) was bought from Tianjin Damao Chemical Reagent (Tianjin, China). Thionyl chloride (99 %) was bought from Tianjin Bodi Chemical Co., Ltd (Tianjin, China).

Firstly, mix some acryloyl chloride and potassium phthalimide, acetone as solvent, at 28 °C, then keep stirring for 8 h. Secondly, cool the mixture to room temperature after the reaction, wash it with ethanol and 12 % acetic acid solution while boiling, filter it, dry it and finally obtain white powders of 2-acryloyl isoindoline-1,3-dione (abbreviated AID).

To prepare $EuCl_3$, dissolve some Eu_2O_3 in hot hydrochloric aqueous solution (10 mL H_2O:10 mL HCl), then concentrate, filter, wash and dry.

Synthesis process of Eu(AID)$_2$Phen: The $EuCl_3$, N-acryloyl phthalimide and 1,10-phenanthroline were mixed in a molar ratio of 1:2:1 in different conditions (feeding methods, feeding order, feeding ratio and synthesis temperature). After reaction, add some aqueous ammonia solution (the volume ratio of H_2O to $NH_3{\cdot}H_2O$ is 1:1.5) so as to adjust pH to 7, separate out light red solid, filter, wash and dry to obtain rare earth complex of Eu(AID)$_2$Phen.

RESULTS AND DISCUSSION

UV-visible spectral properties of Eu(AID)$_2$ and Eu(AID)$_2$Phen: The UV-visible spectra for each rare earth

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metal complexes are shown in Figs. 1 and 2. The UV-visible characteristic absorption peaks are generally red-shifted with the introduction of donating electron.

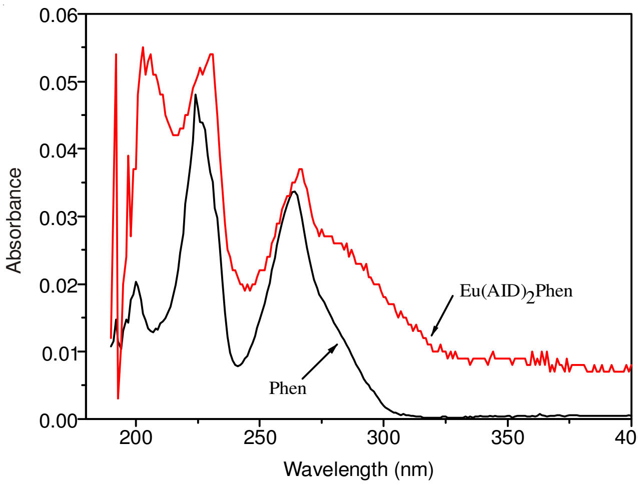

Fig. 1. UV-spectrum of Eu(AID)$_2$Phen and Phen

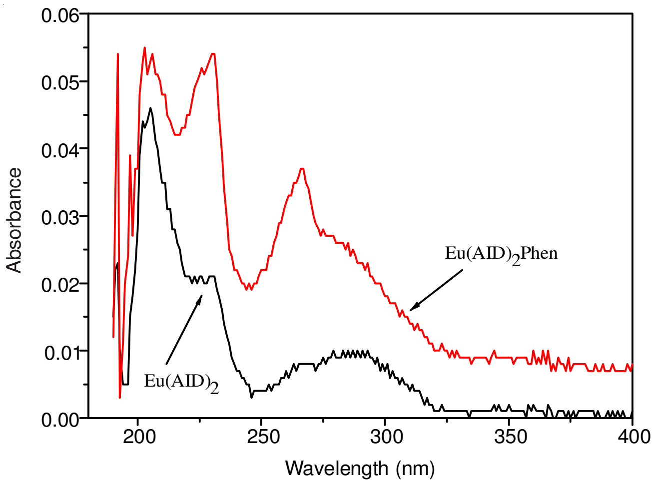

Fig. 2. UV-spectrum of Eu(AID)$_2$ and Eu(AID)$_2$Phen

There are three strong absorption peaks at 203, 231 and 264 nm and several weak peaks in the range of 300-400 nm. The absorption peaks of Eu(AID)$_2$Phen apparently produce red-shift compared with peaks of pure phen which are at 223 and 264 nm. In addition, the absorption peak of 2-acryloyl isoindoline-1,3-dione disappears at 218 nm. It declares that 2-acryloyl isoindoline-1,3-dione has coordinated well with Eu^{3+}, which can be considered that UV absorption of the complex is mainly due to the UV absorption of its ligands.

Fluorescence properties of Eu(AID)$_2$Phen on different feeding methods: The excitation and emission spectra of Eu(AID)$_2$Phen are shown in Figs. 3-5, respectively.

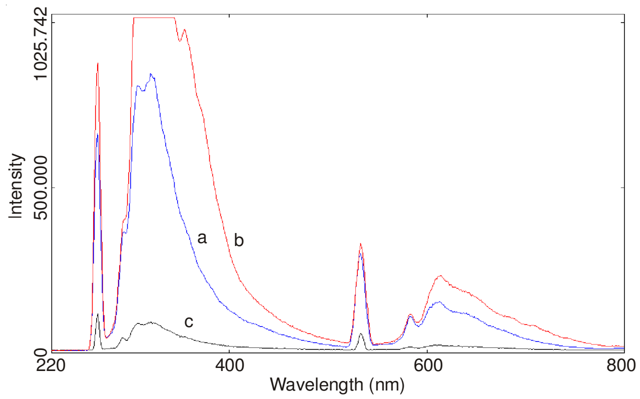

Fig. 3. Emission spectrum of Eu(AID)$_2$Phen prepared at different sequences of adding reagents a. adding AID and Phen at the same time; b. adding AID first, then Phen; c. adding Phen first, then AID

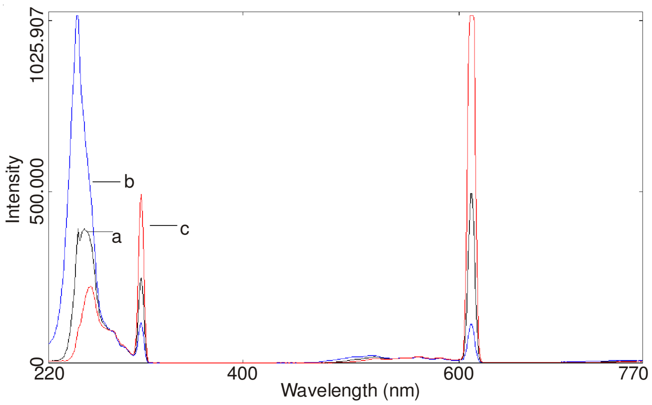

Fig. 4. Excitation spectrum of Eu(AID)$_2$Phen prepared at different sequences of adding reagents a. adding AID and Phen at the same time; b. adding AID first, then Phen; c. adding Phen first, then AID

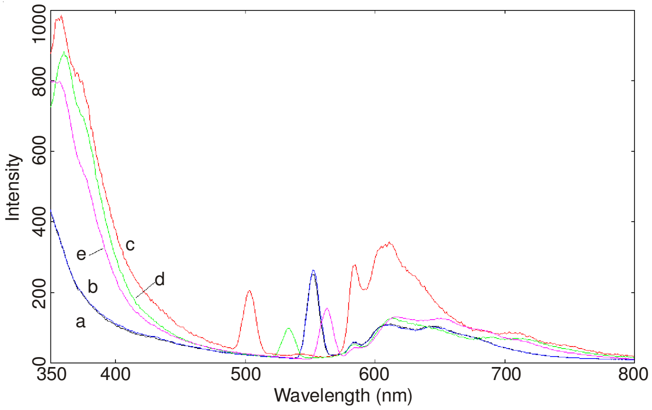

Fig. 5. Emission spectrum of Eu(AID)$_2$Phen prepared at the different reaction temperature a. the reaction temperature of 30 ºC; b. the reaction temperature of 40 ºC; c. the reaction temperature of 50 ºC; d. the reaction temperature of 60 ºC; e. the reaction temperature of 70 ºC

Figs. 3 and 4 show that regardless of the kind of feeding method, the shape and position of excitation and emission spectra are similar, only the intensity of peaks are different. In Fig. 4, the excitation spectrum of the complex contains several absorption peaks in a range between 220 and 400 nm. Besides, a strong absorption peak emerges in the range of 500-620 nm. In Fig. 3, the emission spectra of the complex shows a characteristic emission of Eu^{3+} between 613 and 615 nm, which is assigned to the electric dipole transition of $^5D_0 \rightarrow {}^7F_2$. Similar absorption at 533 and 583 nm are ascribed to the magnetic dipole transition of $^5D_0 \rightarrow {}^7F_1$[9]. It can be speculated that the chemical structure is similar in spite of different feeding methods. From Fig. 3, the best process condition is "adding AID first, then Phen", in which fluorescence of the complex is strongest; followed by "adding AID and Phen at the same time"; last one is "adding Phen first, then AID", in which the complex has worst fluorescent. In Fig. 3, in the vicinity of 613-615 nm, europium complexes emit the characteristic luminescence of Eu^{3+}. Fluorescence intensity of process b is promoted by 49.9 and 87.0 % compared with process a and c, respectively. It can be seen that feeding mode and feeding order have a certain influence on fluorescence intensity.

Fluorescence properties of $Eu(AID)_2Phen$ on different synthesis temperature: As can be seen from Fig. 5, within the synthesis temperature range, when temperature increases, fluorescence intensity increases in 30-50 ºC. When continuing raising temperature from 50-70 ºC, on the contrary, fluorescence intensity decreases. When temperature is below 40 ºC, fluorescence peak of the complex can be observed at 550 nm, which is due to the $^5D_0 \rightarrow {}^7F_1$ transition centered onto the ligand. When temperature is 50 ºC, the complex emission bands at 503 nm are corresponding to $^7F_0 \rightarrow {}^5D_2$[10] and when temperature is 60 ºC, around 534 nm appears the $^5D_0 \rightarrow {}^7F_1$ transition. Thus, the optimum synthesis temperature is 50 ºC and fluorescence intensity of the complex synthesized under 50 ºC is 2.6 times of that of the complex synthesized under 70 ºC.

Conclusion

A new rare earth complex synthesis condition is that a temperature is 50 ºC, feeding order is adding N-acryloyl phthalimide at first, then 1,10-phenanthroline. In this process, the complex has a best fluorescence effect and the maximum emission wavelength belongs to 613 nm.

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