

A New Fluorimetric Reagent for Determination of Trace Amounts of Europium

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In this paper, a new ligand, 2,9-bis[*N,N*-bis(carboxymethyl)-aminomethyl]-1,10-phenanthroline, was synthesized and used to establish a novel fluorimetric method for the determination of trace amounts of europium. The fluorescence intensity was a linear function of the concentration of europium in the range of 4.0×10^{-9} — 1.0×10^{-6} mol/L. The detection limit was 1.0×10^{-9} mol/L. The standard addition method was used to determine the europium in a synthetic rare-earth sample and high purity Y_2O_3 matrix with satisfactory results.

Keywords europium, fluorescence, 2,9-bis[*N,N*-bis(carboxymethyl)-aminomethyl]-1,10-phenanthroline

Introduction

The chemical properties of rare-earth elements are very similar, consequently, it is difficult to detect an individual ion in their mixtures owing to the interference of other rare-earth elements. Due to a higher sensitivity and selectivity, fluorimetric methods of rare-earth elements have attracted much attention. β -Diketone chelating agents were often employed to establish a highly sensitive, well selective ternary fluorescent system for the determination of trivalent europium in the presence of synergic agents and surfactants.¹⁻⁵ However, selectivity was not really resolved. Tolerance limit of other ions was: Ce 5, Pr 5, Nd 5, Sm 3, Gd 3, Dy 4, Ho 4, Er 4, Tm 4, Yb 5, Y 2 during a study of europium-2-benzoyl-1,3-dione-tri-octyl-phosphine oxide-Triton X-100 system. 10-Fold amounts of Ce, Sm, Gd and Tb interfered with the deter-

mination of europium in the system of europium with thenoyltrifluoroacetone and trisalicylicamido triethylamine. Enhanced luminescence was observed during a study of the Eu-TTA-1,10-phenanthroline-surfactant system in the presence of terbium and allowed a determination range of 10^{-11} — 10^{-8} mol/L europium with a detection limit of 10^{-13} mol/L.⁶ Unfortunately, 10-fold amounts of La, Ce, Pr, Nd, Ho, Er, Yb, Y and Lu interfered with the determination of 10^{-9} mol/L europium. It is significant to establish a well selective method for the detection of europium in rare-earth mixture, for instance in ores.

In this paper, the fluorescence characteristics of the complex of europium with a new fluorimetric reagent, 2,9-bis[*N,N*-bis(carboxymethyl)-aminomethyl]-1,10-phenanthroline (BBCAP), were reported and a novel fluorimetric method for the determination of europium was developed. This method showed a good selectivity. The effects of all rare-earth (excluding Pm) metal ions on the determination of europium were tested and the results showed that a large amounts of coexisting ions except for terbium caused no interference. In comparison with β -diketone, BBCAP was more easily soluble in water, the method was easier to operate, and synergic agents and surfactants were not needed. The method using a binary complex system for the determination of europium was not reported previously. The sensitivity for the determination of europium in this method was similar to that in the

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ternary system. Based on its chemical properties and the fact above-mentioned, this reagent was considered to have potential application prospects serving as a luminescent labeling reagent.

Experimental

Apparatus

All measurements of fluorescence intensity were made on a Hitachi 650-10S fluorescence spectrophotometer (Japan) with the use of 1.0-cm quartz cells.

Reagents

Chemicals used were of analytical grade and solutions were prepared in redistilled deionized water. Stock solution of europium (1.0×10^{-3} mol/L) was prepared by dissolving a desired amount of Eu_2O_3 (99.99% in purity) in concentrated hydrochloric acid, evaporating to near dryness and diluting with water. BBCAP was synthesized by the method described in this paper and the recrystallized product was directly dissolved in water to prepare a working solution (1.0×10^{-4} mol/L). Na_2CO_3 - NaHCO_3 solution (1.0 mol/L) was used as the buffer solution.

General procedure

The fluorimetric reagent, BBCAP, was synthesized according to the following steps described in Scheme 1.

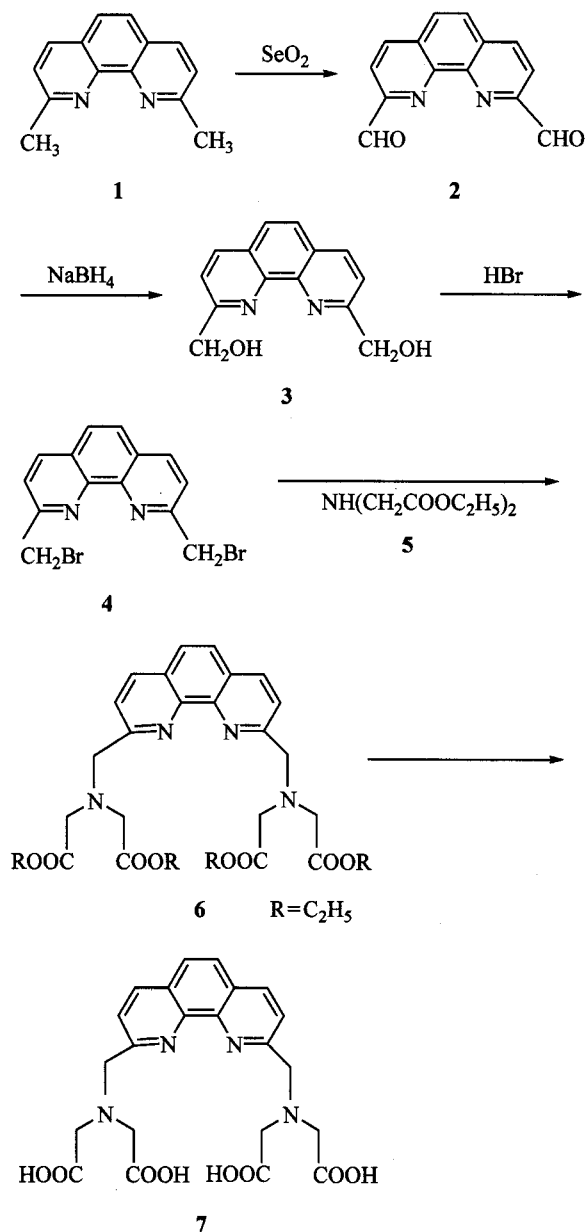
Preparation of 2,9-dicarboxaldehyde-1,10-phenanthroline (2)⁷

A mixture of **1** (2,9-dimethyl-1,10-phenanthroline, 2.0 g) and selenium dioxide (5.0 g) in dioxan containing 4% water (200 mL) was heated under reflux for 2 h and then filtered through celite while hot. The product was separated from the cold filtrate as yellow crystals (2.01 g, yield 92%).

Preparation of 2,9-bis(hydroxymethyl)-1,10-phenanthroline (3)⁷

A solution of compound **2** (2.0 g) and sodium borohydride (0.4 g) in ethanol (200 mL) was heated under

Scheme 1 Synthesis of BBCAP



reflux for 2 h. The mixture was then concentrated, and the residue recrystallized from water to give compound **3** as yellow needles (1.27 g, yield 62%).

Preparation of 2,9-bis(bromomethyl)-1,10-phenanthroline (4)⁷

A solution of compound **3** (1.2 g) and hydrobromic acid (50 mL, 48%) was heated under reflux for 2 h and then cooled on ice-water bath and treated with solid sodium carbonate until precipitation was complete. Recrystal-

lization from aqueous ethanol gave the bromo compound **4** as red plates (0.90 g, yield 49%).

Preparation of diethyl iminobis (acetate) (**5**)

A solution of iminodiacetic acid (10.0 g) and sulfuric acid (5 mL, 98%) in ethanol (100 mL) was heated under reflux for 6 h. The mixture was then concentrated. The residue was poured into water (20 mL), and neutralized with solid potassium carbonate. After filtration, the mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic phase was washed with water and dried with solid sodium sulfate. Evaporation *in vacuo* left a yellow oil (5.6 g, yield 39%).

Preparation of 2,9-bis [*N,N*-bis (ethoxycarbonylmethyl)-aminomethyl]-1,10-phenanthroline (**6**)

A solution of compound **4** (0.90 g), compound **5** (0.93 g) and sodium carbonate (1.85 g) in dry acetonitrile (60 mL) was stirred under a nitrogen atmosphere for 24 h at room temperature. The mixture was filtered and the filtrate was evaporated *in vacuo*. A yellow solid product was obtained (1.40 g, yield 98%).

Preparation of BBCAP (**7**)

To a solution of compound **6** (1.4 g) in acetone (30 mL), 15 mL of NaOH (1 mol/L) was added. The mixture was stirred for 2 h at room temperature. After neutralization with HCl, the solution was evaporated and the product precipitated by adding more acetone. The product was washed with acetone and dried. The dried product was re-crystallized three times by resolving in water and precipitating in acetone (0.40 g, yield 35%). UV-vis (H₂O) λ : 232, 277 nm; ¹H NMR (500 MHz, D₂O) δ : 3.29 (s, 8H), 4.11 (s, 4H), 7.56 (s, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 8.13 (d, *J* = 7.5 Hz, 2H); IR (KBr): 3420, 3009, 1716, 1635, 1411, 1220 cm⁻¹.

Procedures for fluorescence measurements

To each of a series of 10 mL test tubes, different quantities of europium solution (4.0×10^{-9} – 1.0×10^{-6} mol/L) and 0.2 mL of BBCAP (1.0×10^{-4} mol/L) were added. After fully mixing, 1.0 mL of Na₂CO₃-NaHCO₃ (1.0 mol/L) buffer was added. The mixture solution was

diluted to the volume with water and mixed thoroughly by shaking. Band-pass widths of excitation and emission were adjusted to 5 nm and 20 nm, respectively. Fluorescence measurements were carried out at 615 nm with the excitation wavelength at 284 nm.

Results and discussion

Fluorescence spectra

Fig. 1 shows the excitation and emission spectra of Eu-BBCAP system. In the system, the excitation and emission peaks were at 284 and 615 nm, respectively. For hydrated trivalent europium ion, very weak emission was observed at 615 nm with the excitation wavelength at 284 nm. Under uniform conditions, no appreciable emission at 615 nm was observed for BBCAP.

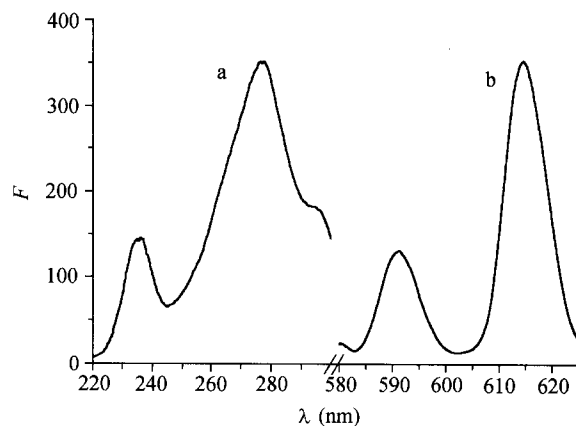


Fig. 1 Excitation (a) and emission (b) spectra (conditions: Eu 5.0×10^{-7} mol/L; BBCAP 2.0×10^{-6} mol/L; Na₂CO₃-NaHCO₃ 0.1 mol/L).

Factors affecting the fluorescence intensity of the system

Effects of pH and buffers

The effect of pH on the fluorescence intensity was tested in the range of pH 2.0–12 by adjusting the pH value with 0.04 mol/L Britton-Robinson buffer solution. It was found that the fluorescence intensity was lower in acidic condition than that in basic condition. The optimum pH range was 8.0–12.0. Fixing pH to 10.5, the effect of different types of buffers on the fluorescence intensity is shown in Table 1, where it can be seen that Na₂CO₃-NaHCO₃ is the most suitable. When the concen-

Table 1 Effects of different types of buffers on fluorescence intensity

Buffer	NH ₃ -NH ₄ Cl	Glycin-NaOH	Na ₂ CO ₃ -NaHCO ₃	Britton-Robinson
Relative intensity	58.8	64.0	100	62.6

Table 2 Effects of surfactants and synergic agents

Surfactant or synergic agent	Concentration (10 ⁻³ mol/L)	Relative fluorescence intensity
No	0.0	100
CTMAB	1.0	97.7
SDS	9.0	94.7
Triton X-100	2.0	28.0
TOPO	10	99.3
EDTA	4	73.3

tration of buffer was less than 0.1 mol/L, the fluorescence intensity increased with the increase of buffer concentration. When the concentration of buffer reached 0.1 mol/L, the fluorescence intensity reached constant. In further experiments a Na₂CO₃-NaHCO₃ (0.1 mol/L) buffer was employed. The value of pH and buffer concentration were important for the analytical sensitivity of the method.

Effect of adding sequence of reagents

It was found that the adding sequence was an important factor for the sensitivity and accuracy of the method, and the adding sequence of europium, BBCAP and buffer was proved to be suitable. Fluorescence intensity was low and unstable if the adding sequence was europium, buffer and BBCAP. The reason probably is that europium ion is firstly hydrolyzed in basic buffer, which retards the formation of BBCAP-Eu complex.

Effects of surfactants and synergic agents

As shown in Table 2. It can be seen that cationic, anionic and nonionic surfactants all have hardly enhancing effects. It was reported^{2,8,9} that synergic agents, tri-*n*-octylphosphine oxide (TOPO), EDTA had enhancing effect on the fluorescence intensity of rare-earth ion. In our experiments, however, the agents had no enhancing effects in the presented system.

Effect of BBCAP concentration

For 5 × 10⁻⁷ mol/L europium, the fluorescence in-

tensity reached a maximum at 2 × 10⁻⁶ mol/L BBCAP and remained constant up to 5 × 10⁻⁶ mol/L. Therefore, 2 × 10⁻⁶ mol/L BBCAP was chosen for future use.

Effect of temperature

The effect of experimental temperature on the fluorescence intensity was studied and the results are shown in Fig. 2, where it is found that the reaction temperature should be controlled at about 20—30 °C. Thus, experiments were carried out at room temperature.

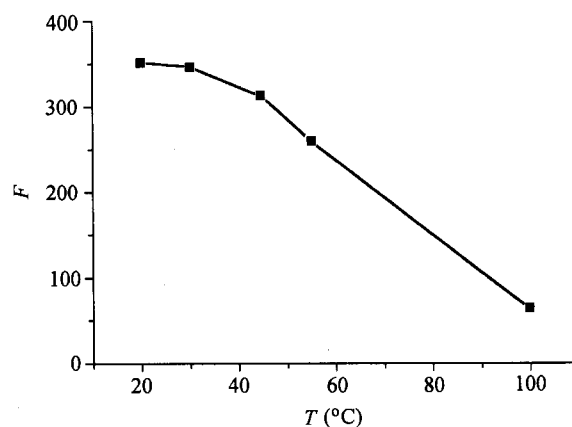


Fig. 2 Effect of temperature (the conditions were the same as those in Fig. 1).

Effect of reaction time

The effect of the reaction time on the fluorescence intensity was investigated. The results showed that the solutions were allowed to stand under normal laboratory conditions. The maximum fluorescence intensity could keep at least 1 h. Continuous irradiation of the solution for 6 h

under laboratory conditions caused reduction of 5% in the fluorescence intensity.

Effect of dissolved oxygen

The effect was investigated by measuring the fluorescence intensity of 5×10^{-7} mol/L europium solution before and after de-gassing with nitrogen for 20 min. Oxygen was then bubbled through the solution for 5 min and the fluorescence intensity measured again. Three identical readings were obtained, showing that no quenching of fluorescence by dissolved oxygen occurred.

Effects of other trivalent rare-earth ions

The effects of various rare-earth ions on the determination of 1.0×10^{-8} mol/L europium ion were investigated and an error within $\pm 5\%$ was considered as tolerated. The results are given in Table 3. Yttrium and ytterbium of 1000-fold amounts did not interfere with the determination of europium. This implies that the proposed method can probably be used to the determination of trace amounts of europium in high purity yttrium and ytterbium. However, the co-existence of Tb enhanced the fluorescence intensity. The effect of Tb could be removed if the standard addition method was used or calibration curve was obtained in the same matrix. Moreover, it was likely that the sensitivity could be improved on addition of terbium.^{1,6}

Analytical application

Calibration curve and detection limit

The calibration curve for determining europium was obtained under optimum conditions. The results showed that there was a linear relationship between the fluorescence intensity and the concentration of europium in the range of 4.0×10^{-9} — 1.0×10^{-6} mol/L. The regression equation of calibration curve was $F = 2.8775 + 7.0058 \times 10^8 c$, with a correlation coefficient of 0.9994, where c was the concentration of europium (in mol/L). The limit of detection (3σ) was 1.0×10^{-9} mol/L calculated from the standard deviation of the blank measurements ($n = 9$).

Composition of complex

The composition of the Eu-BBCAP complex was ex-

amined using the molar ratio method. Experiments showed that the molar ratio of Eu to BBCAP was 1:1.

Determination and recovery test

The standard addition method was used for the determination of europium in sample in order to eliminate the effects of other rare-earth ions on the fluorescence intensity of the system. The new system was applied to the determination of trace amounts of europium in a synthetic rare-earth sample. The synthetic mixture was prepared according to the content of rare-earth metals in lithosphere.¹⁰ The sample contained rare-earth ions (μg) as follows: La (190), Ce (440), Pr (56), Nd (240), Sm (105), Eu (11), Gd (63), Tb (10), Dy (43), Ho (12), Er (24), Tm (2.1), Yb (26), Lu (7), Y (310) in 100 mL of solution. The results (Table 4) showed that the proposed method was suitable for the determination of trace amounts of europium. The procedure was also used to the determination of trace europium in a high purity Y_2O_3 matrix. Owing to the purity of Y_2O_3 sample used more than 99.999%, the europium in the sample could not be directly detected, here a recovery test was, therefore, used and the results are shown in Table 5.

Luminescence mechanism

The absorption spectrum of BBCAP displayed the absorption peaks at 232 and 277 nm. When a solution of BBCAP was added to the system containing europium ion, the fluorescence intensity of the system increased remarkably but the absorption peaks of BBCAP ligand in Eu-BBCAP system did not change. Thus the absorption spectra of Eu-BBCAP were attributed to the $L \rightarrow L^*$ transition of BBCAP. As shown in Fig. 1, The excitation peaks of the Eu-BBCAP system approached the absorption peaks of BBCAP. However, the emission spectrum obtained was characteristic emission of europium. This implies that an energy transfer exists in the process. The process is considered as follows: when BBCAP ligand is excited, the excitation energy is transferred from BBCAP ligand to europium ion, via intramolecular energy transfer, to excite the latter to the 5D_0 level. Then the transition from the 5D_0 level of europium ion to the 7F_1 and 7F_2 levels occurs, corresponding to the emission peaks at 593 and 615 nm, respectively. Moreover, a weak emission peak of

Table 3 Effects of other rare-earth ions^a

Ion	La	Ce	Pr	Nd	Sm	Gd	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc
TF ^b	10 ²	10 ²	10 ²	10 ²	10 ²	10 ²	10 ²	10 ²	10 ²	10 ²	10 ³	10 ²	10 ³	10 ²

^a For the determination of 1.0×10^{-8} mol/L europium ion. ^b Tolerated molar ratio.

Table 4 Determination and recovery of europium in synthetic rare-earth sample

Known europium (μg)	Found europium (μg)	Mean (μg)	Added europium (μg)	Found europium (μg)	Mean (μg)	Recovery (%)	RSD ^a (%)
11.00	11.00, 10.51, 11.00, 10.90, 10.70	10.82	5.00	4.98, 4.90, 4.81, 4.82, 4.81	4.86	99.67, 98.09, 96.14, 96.14, 96.45	1.54

^a Relative standard deviation.

Table 5 Determination of europium in high purity of Y₂O₃ matrix

Y ₂ O ₃ sample ^a	Added (10^{-7} mol/L)	Found (10^{-7} mol/L)	Mean (10^{-7} mol/L)	Recovery (%)	RSD (%)
1	0	0	—	—	—
2	1.0	0.9987, 0.9987, 0.9923, 0.9923, 0.9987	0.9961	99.61	0.35
3	2.0	2.0476, 2.0541, 2.0476, 2.0541, 2.0412	2.0489	102.44	0.26

^a Concentration, 1.0×10^{-5} mol/L.

BBCAP at 372 nm was obtained while the concentration of BBCAP increased, but the emission peak disappeared absolutely in Eu-BBCAP complex. Based on the above facts, the luminescence of the complex is considered to belong to the $M^* \rightarrow M$ luminescence mechanism.

Since BBCAP is composed of eight dentates, therefore, the ligand itself can prevent from the coordination of europium ion with water molecules. Based on the same

reason, the synergic agent TOPO has no enhancing effect on the fluorescence intensity in the system. Surfactants play an important role in the dissolution of complexes and prevent the europium ion from collision with solvent molecules. But the effect of surfactants is not obvious in this system since BBCAP itself has eight dentates and the complex with europium ion is easily dissolved in water.

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