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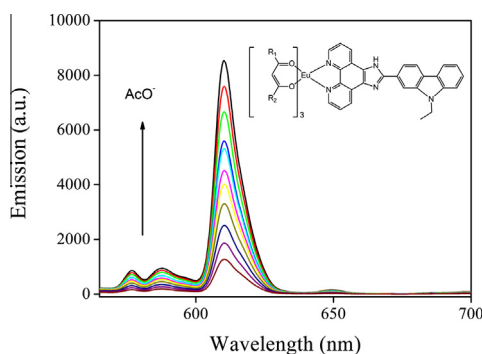
Emission “Off–On” effect from europium complexes triggered by AcO anion: Synthesis, characterization and sensing performance

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HIGHLIGHTS

- The correlation between emissive performance and ligand structure was studied.
- Conjugation chain might trigger energy transfer roll-back and compromise emission.
- The presence of AcO anion could stop the energy transfer roll-back.
- A sensing system was developed with high sensitivity and selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a series of Eu(III) complexes based on four diamine ligands and two diketone ligands were synthesized. Their single crystal structures were studied, where intermolecular π – π stacking was found. The photophysical parameters of these Eu(III) complexes were measured, along with their ligand triplet levels. The energy transfer mechanism between ligand and metal center was discussed in detail. Energy transfer roll-back was found in Eu(III) complexes owing large-conjugated diamine ligands, compromising emissive performance. This energy transfer roll-back, however, could be stopped by the presence of AcO anion, leading to Eu(III) complex emission enhancement. The sensing performance of such Eu(III) complexes was thus investigated in detail. High sensitivity and selectivity were observed.

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Introduction

Owing to their participation in biological reaction of many animal species, including human beings, more and more research interests have been focused on the detection of anions [1]. Particularly, AcO anion has been recently reported as an important molecular switcher for proteins and enzymes in vital biological

activities such as cell division, DNA genetics and cell senescence [2]. The switch missing or malfunction leads to a series of diseases, including Alzheimer disease, Parkinson's disease and even cancer. Thus, the exploration for AcO anion detection and sensing has been sparked.

Traditionally, AcO anion can be precisely detected using high performance liquid chromatography (HPLC) [3]. Then optical sensors have shown their promising aspects with simple, fast and non-destructive characters, along with the fact that the detection operation has a low need for instrumentation and sample

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pretreatment [4]. Literatures have reported some optical sensing systems for AcO anion which are, however, generally emission “On–Off” ones [5–7]. In other words, the detection is based on probe emission quenching triggered by AcO anion. Considering that some competing species and energy acceptors may quench probe emission as well, those emission “On–Off” sensors suffer from limited selectivity. In addition, the interaction between AcO anion and probe usually causes probe emission spectral shift, leading to emission intensity variations and thus compromising accuracy.

Due to the unique $f-f$ radiative transitions, rare earth based emitters can give sharp and narrow emissions which are immune to surrounding environment or reagents, offering high stability towards environmental variations [8]. The antenna ligand excitation mechanism makes the modification on ligands feasible to be carried out, without compromising metal-centered $f-f$ emissions. By modulating ligand energy level, the energy transfer between ligand, metal center and analyte can be finely controlled, which means that emission “Off–On” effect towards analyte may be realized by choosing ligands with suitable energy level [9]. In addition, rare earth based emitters own good solubility in common solvents, allowing themselves to be easily loaded into various supporting matrixes. All these excellent characters make rare earth based emitters a promising candidate for anion detection.

Enlightened by above considerations, in this paper, we design a series of Eu(III) complexes with similar diamine ligands. Their emission parameters, as well as the energy transfer between ligand, metal center and AcO anion, are carefully measured and discussed. The correlation between ligand structure and emission “Off–On” is tentatively explained.

Experimental details

General chemicals and methods

Scheme 1 shows the molecular structures of those Eu(III) complexes studied in this paper. The starting chemicals, including 1,10-phenanthroline (Phen), 2-thenoyltrifluoroacetate (TTA), 1,3-diphenyl-propane-1,3-dione (DBM), indoline-2,3-dione, 9H-carbazole and triphenylamine were bought from Shanghai Chemical Company (Shanghai, China) and used for synthesis directly. The inorganic salts and reagents were bought from Tianjin Chemical Company (Tianjin, China) and used as received. The organic solvents were redistilled prior to use.

The equipments and measuring methods used in this paper are listed as follows. ^1H NMR spectra were taken from a Varian INOVA 300 spectrometer. Single crystal data were detected by a Siemens P4 single-crystal X-ray diffractometer equipped with a Smart

CCD-1000 detector using graphite-monochromated Mo $K\alpha$ radiation at 298 K. Elemental analysis data were collected on a Carlo Erba 1106 elemental analyzer. UV–Visible absorption spectra were recorded using a HP 8453 UV–Vis–NIR diode array spectrophotometer. Photoluminescence (PL) spectra were measured with a F-4500 fluorescence spectrophotometer. Excited state lifetimes were measured using 355 nm light excited by a pulsed Nd:yttrium aluminum garnet (YAG) laser, with line width of 1.0 cm^{-1} , pulse duration of 10 ns and repetition frequency of 10 Hz, respectively. PL quantum yields were determined using a literature method [10]. All operations were finished at room temperature and ambient condition without being specified.

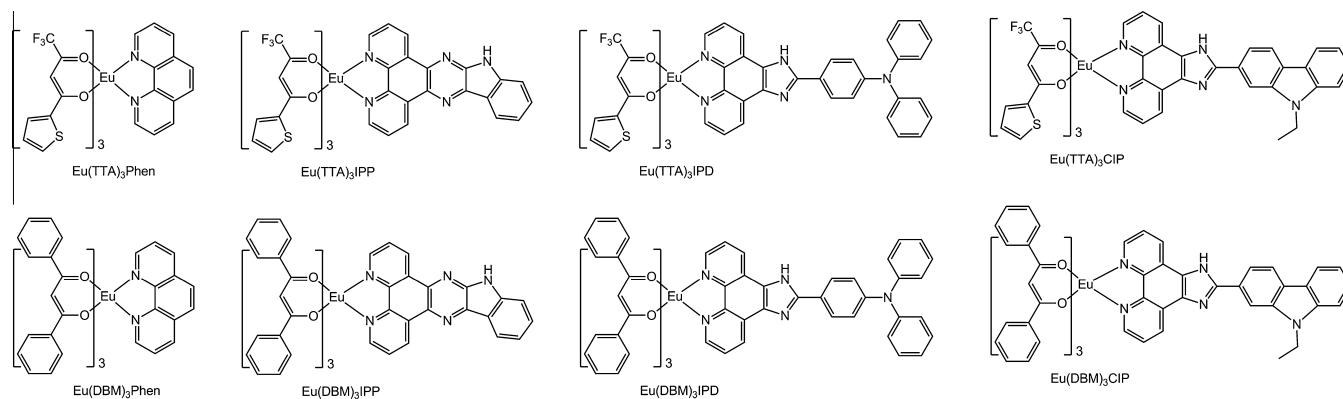
Synthesis of diamine ligands

The starting reagents of 4-(diphenylamino)benzaldehyde (TPA-CHO), 9-ethyl-9H-carbazole-2-carbaldehyde (Cab-CHO), 1,10-phenanthroline-5,6-dione (Phen-O), 1,10-phenanthroline-5,6-dione-dioxime (Phen-NOH) and 1,10-phenanthroline-5,6-diamine (Phen-NH₂) were prepared following literature procedures [11–15].

10H-indolo[2',3':5,6]pyrazino[2,3-f][1,10]phenanthroline (IPP). 5 mmol of Phen-NH₂, 5.5 mmol of indoline-2,3-dione and 0.1 mmol of 4-methylbenzenesulfonic acid were added into 25 mL of ethanol and heated to reflux overnight. After cooling, the solution was poured into 300 mL of cold water. The crude product was collected and recrystallized in ethanol to yield IPP as gray powder. ^1H NMR (300 Hz, CDCl₃, 25 °C): δ 10.13 (d, 1H, $J = 8.5$ Hz), 9.24 (d, 1H, $J = 2.5$ Hz), 9.17 (d, 1H, $J = 2.0$ Hz), 9.09 (d, 1H, $J = 5.5$ Hz), 8.55 (d, 1H, $J = 5.5$ Hz), 7.60–7.64 (m, 2H), 7.55 (d, 1H, $J = 8.5$ Hz), 7.34 (m, 2H). Anal. Calcd for C₂₀H₁₁N₅: C, 74.76; H, 3.45; N, 21.79. Found: C, 74.67; H, 3.60; N, 21.68.

4-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)-N,N-diphenylaniline (IPD). 5 mmol of Phen-O, 5 mmol of TPA-CHO and 20 g of NH₄Ac were added into 30 mL of HAc and heated to reflux overnight. After cooling, the solution was poured into 500 mL of cold water and extracted with CH₂Cl₂. After the evaporation of solvent, the crude product was recrystallized in ethanol to give IPD as pale yellow powder. ^1H NMR (300 Hz, CDCl₃): δ 9.18 (t, 2 H), 7.74 (m, 2 H), 7.67 (m, 2 H), 7.31–7.17 (m, 14 H). Anal. Calcd for C₃₁H₂₁N₅: C, 80.32; H, 4.57; N, 15.11. Found: C, 80.27; H, 4.67; N, 15.02.

2-(9H-carbazol-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (CIP). The synthetic route for CIP was similar to that for IPD, except that Cab-CHO was replaced by TPA-CHO. ^1H (300 MHz, CDCl₃): δ : 9.14 (2H), 8.99 (1H), 8.93 (1H), 8.67 (1H), 8.35 (1H), 7.92 (3H), 7.86 (1H), 7.85 (1H), 7.58 (1H), 7.31 (1H), 4.70 (2H), 1.48 (3H). Anal. Calcd for C₂₇H₁₉N₅: C, 78.43; H, 4.63; N, 16.94. Found: C, 78.25; H, 4.67; N, 17.02.



Scheme 1. The molecular structures of Eu(III) complexes studied in this paper.

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