

Tunable White-Light-Emitting Molecules Based on Europium(III) Complexes

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Abstract—New Europium(III) complexes were designed and synthesized as new white light emitting molecules. Eu(III) complexes comprised a blue light emitting Courmarin 6G fluorophore and a Eu^{III} moiety as the origin of red light and thus exhibited red, blue or white light in different excitation wavelength and concentration.

Keywords—white light; courmarin; europium complexes

I. INTRODUCTION

White-light-emitting single molecules are promising materials for use in a new generation of display and light sources, because they offer possibility of simple fabrication with perfect color reproducibility and stability.[1-2] They are composed of covalently linked emitter components and utilize partial energy transfer to generate white light covering the visible range for 400 to 700 nm.[3-4]

Lanthanide are elements of growing importance due to their unique optical properties arising from the f-orbital filling, such as sharp transitions in the visible or in the near-infrared range with large Stokes shifts, long excited-state lifetimes up to milliseconds, and sensitivity to the local environment.[4-6] So emissive lanthanide complexes have been applied widely in materials chemistry, especially as organic light-emitting devices (OLEDs).[7] On the other hand, because of the extremely weak absorption from *f-f* transitions for the Ln^{III} ions, luminescence from lanthanide is usually sensitized by energy transfer from ligand singlet to ⁵D₀ (Eu). As we know, the combination of bluish-green and red light can generate the white light. So, it is feasible to design the white-emitting single component, fabricated from the ligand with bluish-green emission and Eu(III) with red f-f emission by partly energy transfer.[8-12]

Herein we report the white light-emitting compound that comprises a bluish-green light emitting Coumarin fluorophore and a Eu^{III} moiety as the origin of red light within one molecule. Since the little luminescence change of the white-light-emitting molecule, either fluorescence quenching or enhancement, could lead to the significant colour variation of the visible emitting, the compounds exhibits tunable emissive properties with the change of excitation wavelength and concentration of compounds.

The Schiff base was synthesized from a reaction of Coumarin derivatives and the corresponding aldehyde directly and recrystallized from ethanol as a yellow powder. The corresponding Eu(III) complex was prepared by refluxing the resulted ligand and Eu(TTA)₃ in ethanol (TTA = thiophenetrifluoroacetone), which was purified by recrystallization as an amorphous yellow powder. ESI-MS spectra confirm the formation of the complexation species and revealing its stability in solution.

II. RESULT AND DISCUSSION

Synthesis and Spectral Properties of complexes

CR-Py was synthesized from a reaction of Coumarin hydrazine hydrate and 2-pyridine carboxaldehyde directly and recrystallized from ethanol as a white powder. CRPy-Eu was prepared by refluxing the resulted ligand and Eu(TTA)₃ in ethanol (TTA = thiophenetrifluoroacetone), which was purified by recrystallization as an amorphous yellow powder. ESI-MS spectrum of CRPy-Eu exhibited the intense peak at *m/z* = 959.2750, 1037.3177 and 1323.5320 (Figure 1), which was assigned to the [Eu(TTA)₂(CRPy)]⁺, [Eu(TTA)₂(CRPy) + CH₃OH + C₂H₅OH]⁺ and [Eu(TTA)₂(CRPy)₂]⁺ cation according to the exact comparison of the peak with the simulation based on natural isotopic abundances, confirming the formation of the complexation species and revealing its stability in solution.

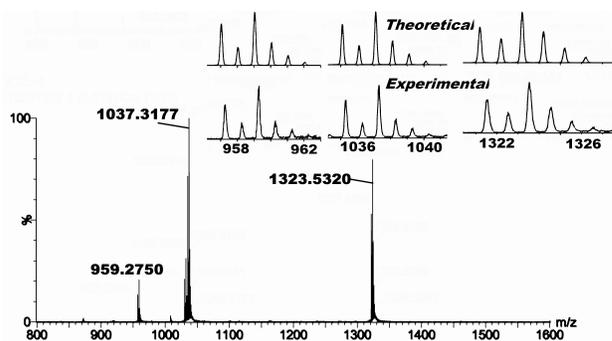


Figure 1. ESI-MS spectrum of CRPy-Eu in acetonitrile solution. Insets showing the calculated and measured isotopic distributions of the intense interested peak at *m/z* = 959.2750, 1037.3177 and 1323.5320.

The photophysical properties of a solution of complex CRPy-Eu in acetonitrile were investigated. From the Figure 1, Upon the coordination of CRPy to Eu(III), the ligand absorption band is shifted from 432 nm to 438 nm owing to the stabilization of the very polar excited states (Figure 2). When exciting the CRPy-Eu selectively at room temperature, the emission spectrum of complex CRPy-Eu displays a broad band centered at 480 nm, derived from the coordinated ligand, and the characteristic sharp peaks associated with the $^5D_0 - ^7F_1$ transitions of the Eu(III) ion. The five expected components of the $^5D_0 - ^7F_{0-4}$ transition are well resolved and the hypersensitive $^5D_0 - ^7F_2$ transition is very intense, which reflects a low symmetry of the Eu(III) site.

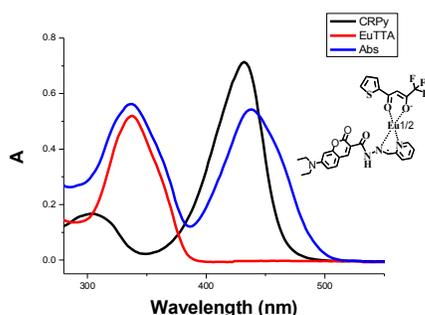


Figure 2. Absorption spectra of compounds CRPy (black), Eu(TTA)₃ (red) and CRPy-Eu(blue) in acetonitrile.

The actual emission colour of compound CRPy-Eu is quite sensitive to and precisely controllable by the excitation wavelength, because the extinction coefficients of bluish-green fluorophore and Eu(TTA)₃ moiety are not identical within their entire absorption ranges. The increase of excitation wavelength from 360 nm to 450 nm lowers the intensity of the red emission from the Eu(TTA)₃ moiety, because of the deviation of excitation from the ligand sensitizing Eu moiety, but enhances that of bluish-green emission and at last only generates bluish-green light from coumarin moiety.

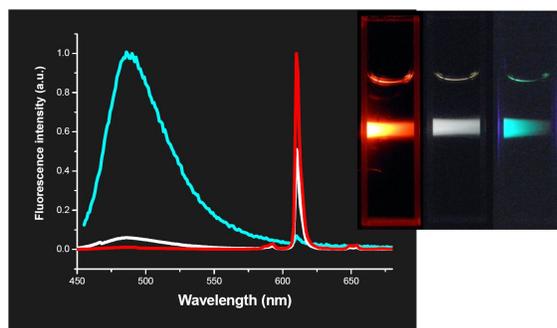


Figure 3. Fluorescence spectrum of CRPy-Eu in acetonitrile solution. Insets showing the fluorescence photos of CRPy-Eu in different excitation wavelength.

For a better understanding of the relationship among change of colour, excitation wavelength and the

concentration of compound, the emission spectra resulting from each excitation wavelength at different concentration of the complex was converted into the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates system.[13] As depicted in the Figure 4, when the concentration of CRPy-Eu is 1 μ M, the CIE coordination of compound CRPy-Eu transfers from the red light district to blue-green light district passing through the white light district with the increase of excitation wavelength from 360 to 450 nm. Furthermore, this curve can gradually close to green light district with the increase of concentration. When the concentration is 30 μ M, the corresponding color change can be clearly observed from the Figure with the change of excitation wavelength. It can emit white light at the excitation of 385 nm

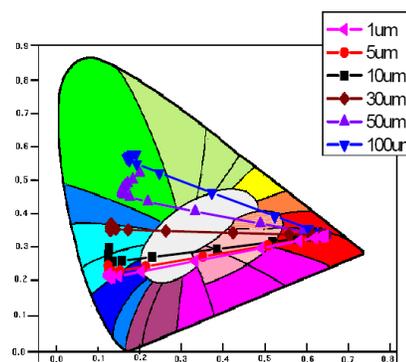
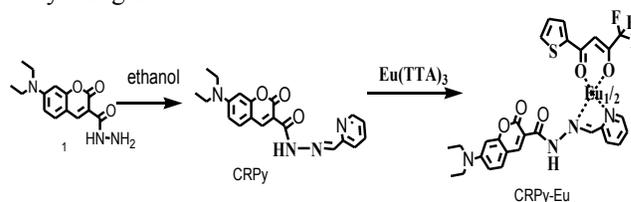


Figure 4. Luminescence spectra of CRPy-Eu plotted on a CIE diagram showing tunability of chromaticity of visual emission image, following the excitation wavelength at fixed concentration.

III. EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were measured on a Varian INOVA 400M spectrometer. API mass spectra were recorded on a HP1100LC/MSD spectrometer. ESI mass spectra were carried out on a HPLC-Q-ToF MS spectrometer by using methanol as mobile phase. Uv-vis spectra were measured on a HP 8453 spectrometer. The solution fluorescent spectra were measured on Edinburgh F920. For all fluorescent measurements, both excitation and emission slit widths were set as 2 nm. Acetonitrile for spectrometric detection was HPLC reagent without fluorescent impurity in the experiment. All the other solvents and reagents were of analytical grade.



Scheme 1. synthetic route of compounds

7-(diethylamino)-2-oxo-2H-chromene-3-carbohydrazide (1): ethyl 7-(diethylamino)-2-oxo-2H-

chromene-3-carboxylate (2g, 0.70 mmol) and hydrazine hydrate (2 mL) were dissolved in 30 mL ethanol. The reaction mixture was stirred for 30 min and the formed precipitate was collected as yellow powder (1.71g, 0.62 mmol). Crude product was used without further purification.

CRPy: Compound 1 (500 mg, 1.82 mmol) and picolinaldehyde (292mg, 2.73mmol) was dissolved in the ethanol. The reaction mixture was refluxed for about 2 hours. The reaction was cooled to room temperature, and the formed precipitate was collected and obtained as yellow powder (529 mg, 1.45 mmol). Yield: 80%. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 12.05 (s, 1H, -NH-), 8.85 (s, 1H, -N=CH-), 8.62 (d, 1H, *J* = 8.0 Hz, *ArH*), 8.29 (s, 1H, *ArH*), 8.23 (d, 1H, *J* = 8.0 Hz, *ArH*), 7.74 (d, 1H, *J* = 8.8 Hz, *ArH*), 7.48 (d, 1H, *J* = 8.8 Hz, *ArH*), 7.29 (m, 1H, *ArH*), 6.69 (d, 1H, *J* = 8.8 Hz, *ArH*), 6.53 (s, 1H, *ArH*), 3.47 (q, 4H, *J* = 6.4 Hz, -CH₂CH₃), 1.25 (t, 4H, *J* = 6.4 Hz, -CH₂CH₃). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.7, 160.2, 157.9, 153.2, 153.1, 149.4, 149.3, 148.7, 136.3, 131.4, 124.2, 121.3, 110.3, 108.8, 108.6, 96.6, 45.2, 12.4. TOF MS calcd for C₃₃H₃₀N₄O₃ 364.1535, found 364.1532.

CRPy-Eu: Compound Cpy (80 mg, 0.22 mmol) was dissolved in 30 mL ethanol followed by addition of Eu(TTA)₃(H₂O)₂ (94 mg, 0.11 mmol). The reaction mixture was stirred for 6 hours. The reaction was cooled to room temperature, and the formed precipitate by diffusing hexane into the solution was collected. Crude product was purified by recrystallization in ethanol and obtained as an amorphous yellow powder to give compound CRPy-Eu. Yield 81%. HRMS (ESI) calculated for [Eu(TTA)₂(CRPy)]⁺ 959.1, found 959.3. HRMS (ESI) calculated for [Eu(TTA)₂(CRPy)₂]⁺ 1323.2, found 1323.5.

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