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Colour tunable emission from $\text{Eu}_{0.5}\text{Sm}_{0.5}(\text{TTA})_3$ dpphen β -diketonate hybrid organic complex in various organic solvents

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ABSTRACT

We propose the synthesis and characterization of an orange-red light emitting binuclear Samarium and Europium β -diketonate complex ($\text{Sm}_{0.5}\text{Eu}_{0.5}(\text{TTA})_3\text{dpphen}$) [Sm: Samarium, Eu: Europium, TTA: Thenoyl Trifluoro Acetone, dpphen: bathophenanthroline] by cost effective precipitation technique at pH 7.0, maintaining the stoichiometric ratio by mole percentage. The XRD spectrum reveals low crystallinity of the complex and FTIR spectra confirms the structure formation of the complex. Thermogram unveils the thermal stability of the complex as 273.76 °C, while DTA reveals a peak at 507.66 °C, corresponding to the melting point of the complex. UV-Visible absorption spectra of the solvated complex in different basic solvents registers wide band absorption spectra with two sets of peaks, one peaking in the range of 249 - 314 nm and 379-386 nm. PL spectra of the complex in solid state and in solvated state reveal tunable emission from 614 nm to 443 nm when excited at 385 nm. Various photo physical parameters such as absorbance, optical band gap, Stokes shift, radiative life time, CIE and CCT were evaluated. These results proved that the synthesized complex have potential as tunable orange-red to blue emissive material for OLED devices, flat panel displays and solid state lighting.

1. Introduction

Owing to the versatile advantages of using rare earths as emissive centers in OLEDs, a range of red emissive materials have been designed, synthesized and evaluated [1–3]. This is due to their superior characteristic features such as (i) sharp emission from electronic transitions within the 4f subshells due to the effective shielding by the overlying 5s and 5p orbitals [4], (ii) possibility of enhancing the efficiency of the OLEDs as both singlet and triplet excitons can transfer their energy to the rare earth ions [5] and (iii) highly monochromatic clear emission [6]. When organic β -diketonate ligands are added to these rare earths, they result in rare earth diketonates hybrid organic complexes and yield unique and promising fluorescence properties. These ligands have a superior feature such as (i) absorbing energy from the external environment and transferring it to the central rare earth ions such as Eu(III), Sm(III), thereby enhancing the luminescent intensity of the complex. Among many, $[\text{RE}^{3+}(\text{TTA})_3\text{phen}]$; $\text{RE}^{3+} = \text{Sm}$ and Eu) complexes have attracted a lot of attention because of their high fluorescence emission efficiency [7]. These complexes find versatile applications in lasers [8], electroluminescent (EL) materials for OLED large-area flat panel displays [9], solid state lighting and many more, due to numerous advantages like easy synthesis, elevated quantum efficiency, quick response, elevated contrast flexibility and lighter weight. In spite of these progresses, immense confront in this field is the comprehension of a competent pure red light emitting device

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with narrow emission line. The exploration of prior state of art in this field showed that rare earth metal ions, especially europium and samarium exhibit red light emission with narrow bands in the visible region with long lifetime, large Stokes shift and sharp band emission. On that account, small efforts has been taken to synthesize and characterize $\text{Eu}_{0.5}\text{Sm}_{0.5}(\text{TTA})_3\text{dpphen}$ hybrid complex by maintaining stoichiometric ratio.

2. Experimental

Chemicals of analytical reagent (AR) grade, purchased from Sigma Aldrich were employed for the synthesis of the $\text{Eu}_{0.5}\text{Sm}_{0.5}(\text{TTA})_3\text{dpphen}$ complex. Throughout the process of synthesis, each and every reaction was carried out with freshly distilled solvents and under anhydrous conditions.

2.1. Reagents and Solvents

The starting materials used for the synthesis of the complex were europium chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$), purity 99.5%, M. wt. = 366.41 g/mol, samarium Chloride hexahydrate ($\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$), purity 99.5%, M. wt. = 364.81 g/mol, 2-Thienyl trifluoro acetone (TTA) purity 99% M. wt. = 222.19 g/mol, m.p. 40-45 °C, 4,7-diphenyl 1,10-phenanthroline (dpphen) purity 99%, M. wt. = 332.396 g/mol. Ethanol Absolute ($\text{C}_2\text{H}_5\text{OH}$), purity 99.98%, M. wt. = 46.07 g/mol, chloroform(CHCl_3) [Qualigens company] purity - 99.7 %, M.wt. = 119.38, Toulene ($\text{C}_6\text{H}_5\text{CH}_3$), M.wt = 92.14 g purity - 99.9%, refractive index is 1.493-1.497, b.p (92%) = 110-111 °C, Dichloromethane (CH_2Cl_2), M.wt = 84.93 g m purity - 99.5%, refractive index at 20 °C is 1.424-1.425, Acetic acid (CH_3COOH) [sd fine chemicals] purity - 99.5%, M.wt. = 60.05, Formic acid (HCOOH) M.wt = 46.03 g purity - 99.9%, refractive index is 1.377, Potassium hydroxide (KOH), purity - 99.9% and double distilled water.

2.2. Structure

Three dimensional chemical structure of $\text{Eu}_{0.5}\text{Sm}_{0.5}(\text{TTA})_3\text{dpphen}$ is depicted in Fig. 1.

2.3. Synthesis procedure

Synthesis of $\text{Eu}_{0.5}\text{Sm}_{0.5}(\text{TTA})_3\text{dpphen}$ by simple precipitation method involves the following steps: Thienyltrifluoroacetone (TTA) and 4, 7-diphenyl 1, 10-phenanthroline (dpphen) were dissolved in 20 ml ethanol. KOH was added drop by drop to attain pH value of 7 (sol. 1). 0.4048 g m of Europium chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$) and 0.4031 g m of Samarium chloride hexahydrate ($\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$) were dissolved in 10 ml distilled water (sol. 2). Solution 1 and solution 2 were mixed and stirred for 10 minutes at room temperature so as to obtain homogeneous solution. This mixed solution was then stirred for one hour on hot plate at constant temperature of 60 °C. Pinkish precipitate was obtained with good quantitative yield (79 %). This precipitate is thoroughly washed with ethanol and then with double distilled water twice. The precipitate is then dried at 80 °C for 1 hr so as to remove the residual moisture. When exposed to an UV source, it exhibits orange-red light emission. The synthesis procedure is pictorially depicted in Fig. 2.

A combination of samarium and europium RE^{3+} ions have been selected due to the fact that they exhibits almost similar physical and chemical properties as tabulated in Table 1.

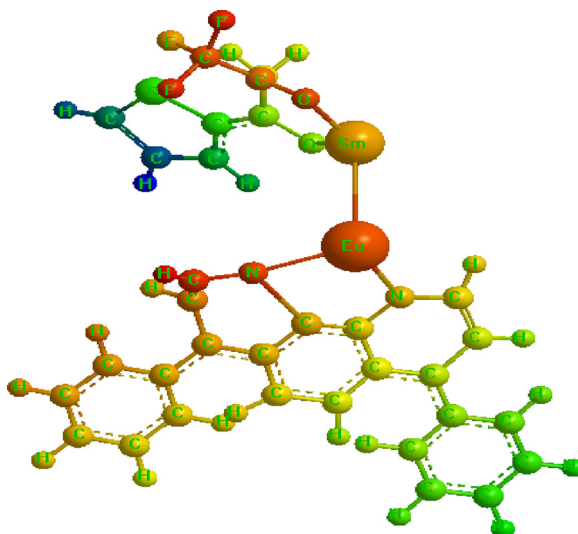


Fig. 1. Three dimensional chemical structure of $\text{Eu}_{0.5}\text{Sm}_{0.5}(\text{TTA})_3\text{dpphen}$.

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