



Synthesis and photoluminescence study of two new complexes [Sm(hfaa)₃(impy)₂] and [Eu(hfaa)₃(impy)₂] and their PMMA based hybrid films

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ABSTRACT

The synthesis, characterization and photoluminescence studies of two new highly photoluminescent complexes, [Sm(hfaa)₃(impy)₂] and [Eu(hfaa)₃(impy)₂] (impy is 2-(1H-imidazol-2-yl)pyridine and hfaa is the anion of hexafluoroacetylacetonate) are reported. The photoluminescence of these complexes were studied in solid, solution and PMMA thin films. These complexes were incorporated independently into polymer matrix of PMMA with varying amounts. The calculated quantum yield (ϕ) and experimental life time (τ) in solution for (i) Sm complex are $\phi = 0.013$, $\tau = 0.036$ ms and (ii) Eu complex are $\phi = 0.36$, $\tau = 0.98$ ms. The Judd–Ofelt intensity parameters, radiative parameters, intramolecular energy transfer rates and theoretical quantum efficiency are calculated and discussed. The intramolecular energy transfer rates, in the case of europium complex, suggest that the major energy transfer channels are $T_1 \rightarrow {}^5D_1$ and $T_1 \rightarrow {}^5D_0$ and these contribute 55.33% and 44.65%, respectively, to the overall energy transfer process. The emission colour changes with a change in concentration of the complexes in PMMA substrate. This feature may be employed in fabricating 'colour indicator diodes'. The thin hybrid films of these structurally ten-coordinate complexes in PMMA matrix exhibit outstanding photostability upon UV irradiation that defines their robust nature. The efficient photophysical properties of PMMA hybrids of these complexes, may possibly find their applications in optoelectronic devices.

1. Introduction

The luminescent lanthanide materials are attracting huge interest in recent days. The lanthanide materials are acquiring promising applications extending from optical devices [1–4] to biological labelling [5,6]. The luminescence from lanthanide complexes are typically characterised by narrow line-like emission peaks [2], Richardson's shift [7] and relatively longer lifetimes (*microseconds to milliseconds*) [8]. However, the 4f–4f transitions of trivalent lanthanide ions are parity forbidden with low molar absorption coefficient ($\epsilon < 10 \text{ LM}^{-1} \text{ cm}^{-1}$) due to which the direct excitation is not fruitful [9,10]. The 4f–4f transitions are magnetic-dipole (MD) and induced electric-dipole (ED) transitions in nature. The ED transitions are highly sensitive to the chemical environment [11]. The intensity of the emission peaks of the luminescent lanthanide ions can be increased by several orders of magnitude by coordinating them with the organic chromophores of high absorption coefficient [12,13]. The chromophores are excellent light harvesting and sufficiently populate the emitting levels of the lanthanide ions by efficiently transferring absorbed energy to the lanthanides via a well-known 'antenna effect' [14]. These chromophores also shield the lanthanide ions and protect the emission from

detrimental effect of non-radiative deactivation. The choice of a good sensitizer which can efficiently transfer the energy to the lanthanide ions is a challenging task. Among the organic chromophores studied, the β -diketonates constitute an important class which acts as good antenna ligand [13]. The tris(β -diketonate) lanthanide complexes have been extensively investigated because of their significant thermodynamic stability, higher volatility and intense luminescence [2]. However, Ln(β -diketonate)₃ complexes are coordinatively unsaturated and are usually solvated. The solvent molecules contain high energy O—H/C—H oscillators which are detrimental for the lanthanide luminescence since these lead to the non-radiative energy loss [15,16]. This can be taken care of by coordinating tris(β -diketonate) lanthanide complexes with neutral ancillary ligands containing oxygen/nitrogen donor atoms to achieve coordinative saturation [2,17–19]. These coordinatively saturated lanthanide β -diketonate complexes are associated with high quantum efficiency due to an effective decrease in oscillator-induced luminescent quenching [2]. Due to the efficient quantum efficiency, these are suitable materials for luminescent devices [20,21]. The samarium and europium complexes which are visible light emitters have found applications in display devices [22], fluoro-immunoassays [23,24], sensors [25], etc. The luminescent materials based on

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samarium and europium which display, respectively pink and red colours can easily be modulated for fabrication of white light emitting diodes (WLEDs) or full-colour RGB (red green blue) display devices [2,26–31]. The samarium- and europium-organic frame works embedded in the suitable substrate are proving excellent luminescent materials in achieving white light emission, either by varying excitation wavelength or temperature [32–36]. The white light emitting diodes (WLED) are nowadays being regarded as next-generation solid state lighting devices since these can play significant role in energy conservation by replacing the conventional light sources [37]. Photostability of luminescent lanthanide complexes is a pre-requisite for the fabrication of stable and long-lived high-performance optoelectronic devices. The photostability of luminescent lanthanide complexes can be enhanced by incorporating them into polymethylmethacrylate (PMMA) [38,39], poly(vinyl alcohol) (PVA) [40,41], or organic-inorganic hybrid (di-ureasils) [42] substrates. The incorporation of the luminescent Sm(III) and Eu(III) complexes in polymer matrices provides efficient thermal and chemical stability, bio-compatibility and importantly these hybrids retain the basic characteristics of lanthanide luminescence of the complex [43].

The photophysical properties and structure of several tris- β -diketonate lanthanide (III) with N-heterocyclic amines such as pyrazole [44], 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) [45–47], 1,10-phenanthroline (phen) [48,49] and 2,2'-bipyridyl (bpy) [50,51] are reported in the literature [1,2,18,40]. Selection of the hetero-aromatic ligands were based since they interact strongly with the Ln(III) ion and the fact that the delocalized π -electron system of the aromatic moiety offers a strongly absorbing chromophore. The Ln(III) complexes of hexafluoroacetylacetone and hetero-aromatic ligands had a favourable effect in terms of tuning the triplet state of the antenna which is significant for higher quantum efficiency initiated from a good overlap of the ligand orbitals and lanthanide ion excited states [52]. In this paper, we report the photophysical properties of two new ternary β -diketonate complex of samarium and europium; [Sm(hfaa)₃(impy)₂] and [Eu(hfaa)₃(impy)₂] (impy is 2-(1H-imidazol-2-yl)pyridine and hfaa is the anion of hexafluoroacetylacetone). The N, N donor 2-(1H-imidazol-2-yl)pyridine forms complexes with lanthanides by coordination through both imidazolyl and pyridyl nitrogen. Several reports in the literature [42,53–56] and our own experience [1,2,18,40] prompted us to choose impy as ancillary ligand with the expectation that it would be able to enhance the photophysical properties of the resulting complexes which is very critical for high performance luminescent materials. To our knowledge, 2-(1H-imidazol-2-yl)pyridine has never been tested to coordinate lanthanides (unlike d-metals) and the complexes being reported are new, and their luminescence efficiency are reasonably higher, which makes these complexes worthy. The emission colour change with the change in concentration of the complexes in PMMA substrate is demonstrated that is worth exploring for their use as 'colour indicator diodes'. The energy transfer mechanism for the Eu(III) complex is also studied and presented.

2. Experimental

2.1. Materials

The commercially available chemicals that were used without further purification are oxides of Sm and Eu (99.9%, Aldrich), hexafluoroacetylacetone, Hhfaa (98%, Aldrich) and 2-(1H-imidazol-2-yl)pyridine (97%, Aldrich). The oxides were converted to the corresponding chlorides. The solvents used in this study were either AR or spectroscopic grade.

2.2. Methods

Elemental analyses of the complexes were carried out on "Elementar Modern Analyzer, vario EL cube". Melting Points were obtained by

conventional capillary method. The thermo-grams (TGA and DTA) were recorded in the dinitrogen with a heating rate of 10 °C/min on Exstar 6000 TGA /DTA from SIINT, Japan. The ESI-MS⁺ mass spectra of the complexes in positive ion mode were recorded on a Waters Micromass Q-Tmass spectrometer. Steady state luminescence and excitation spectra were recorded on Horiba Jobin Yvon Fluorolog 3 – 2 2 Spectrofluorometer with a 450 W Xenon lamp as the excitation source and a R928P Hamamatsu photomultiplier tube as detector. The slit width was 2 nm for recording both excitation and emission spectra. The luminescence lifetimes were recorded on a single photon counting spectrometer from Edinburgh FLS920 fluorescence spectrometer equipped with a Hamamatsu R5509-72 supercooled photomultiplier tube at 193 K and a TM300 emission monochromator instrument (FLS920). The decay curves were investigated by studying the normalized intensity of the hypersensitive ⁵D₀ → ⁷F₂ transition (612 nm) of europium complex and ⁴G_{5/2} → ⁶H_{9/2} transition (646 nm) of samarium complex at an excitation wavelength of 375 nm. The electronic spectra (200–1100 nm) were recorded on a PerkinElmer Lambda-40 spectrophotometer in stoppered 1 cm³ quartz cuvette. The experimental quantum yields (Φ_s or Q_L^{Eu}) of the complexes, in the visible region, were calculated in ethanol at room temperature using Eq. (1) against the reference solution of quinine bisulfate in 1 N H₂SO₄ ($\eta = 1.338$, $\Phi_r = 54.6\%$) [57].

$$\frac{\Phi_s}{\Phi_r} = \frac{A_r \eta_s^2 I_s}{A_s \eta_r^2 I_r} \quad (1)$$

Where r and s imply the reference and sample, respectively. A is the absorbance at the excitation wavelength, η is the refractive index of the solution and I is the integrated luminescence intensity. The refractive index is presumed to be equivalent to that of the pure solvent ($\eta = 1.36$ for ethanol). The PMMA based hybrid films were obtained by drop-casting technique on glass slides.

2.3. Synthesis

The complexes were synthesized by a similar method. The synthesis of [Eu(hfaa)₃(impy)₂] given here is representative:

To an ethanol (5 ml) solution of Hhfaa (0.74 g, 3.6 mmol) was added potassium t-butoxide, KOB^{ut} (0.40 g, 3.6 mmol) in small portions over a period of half an hour with continuous stirring and was kept covered. Then after ethanol (5 ml) solution each of impy (0.35 g, 2.4 mmol) and EuCl₃·6H₂O (0.44 g, 1.2 mmol), were added to the potassium salt of hfaa solution with constant stirring for 6 h. With the passage of time white precipitate of KCl appeared. The precipitate was filtered off repeatedly. The filtrate, thus obtained, was covered and left for slow evaporation at room temperature. Pale yellow crystalline product appeared after 48 h and it was washed with CHCl₃ and cold ethanol. The compound was recrystallized repeatedly from ethanol and dried in vacuum over P₄O₁₀.

[Sm(hfaa)₃(impy)₂] (1). Colour: white; Yield: 63%; Elemental analysis, Found (calculated): C, 34.82 (35.06); H, 1.67 (1.61); N, 7.84 (7.91). TOF ESI-MS⁺ m/z: 1063.8, [Sm(hfaa)₃(impy)₂+H]⁺ (76%); melting point is 200 °C

[Eu(hfaa)₃(impy)₂] (2). Colour: pale yellow; Yield: 64%; Elemental analysis, Found (calculated): C, 34.95 (35.01); H, 1.64 (1.61); N, 7.82 (7.90). TOF ESI-MS⁺ m/z: 1064.6, [Eu(hfaa)₃(impy)₂+H]⁺ (78%); melting point is 202 °C

2.4. Ground state geometry optimization

In the absence of crystal structure, the semi-empirical method, Sparkle/RM1 [58a] model implemented in MOPAC2009 programme [58b], was employed to calculate the ground-state geometry of the [Eu(hfaa)₃(impy)₂]. The keywords used in MOPAC programme were: RM1; SPARKLE; PRECISE, GNORM = 0.25; T = 1.D-10; GEO-OK and XYZ

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