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Invited paper

Photophysical properties of Lanthanide(III) 1,1,1-trifluoro-2,4-pentanedione complexes with 2,2′-Bipyridyl: An experimental and theoretical investigation

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ABSTRACT

Semi-empirical Sparkle/RM1 model is employed to elucidate the ground state geometry of [Ln(tfaa)$_3$bpy] complexes [Ln = Pr **(1)**, Eu **(2)**, Tb **(3)**, Dy **(4)** and Tm **(5)**; tfaa = 1,1,1-trifluoro-2,4-pentanedione and bpy = 2,2′-bipyridyl], which were synthesized in high yield by a one-step method and thoroughly characterized. The room-temperature photoluminescence study confirms the sensitization of Pr (III), Eu (III), Tb (III), Dy (III) and Tm (III) ions by the *antenna effect*, leading to characteristic red, brilliant red, green, yellow and blue emissions, respectively. Replacement of the water molecule from the coordination sphere of [Ln(tfaa)$_3$H$_2$O] by bpy results in appreciable enhancement of the quantum yields [(i.e., 3.2% vs. 35% for Eu(III); 21.0% vs 24.0% for Tb(III); 0.3% vs.1.2% for Dy(III) and 0.03% vs. 0.14% for Tm(III)) and lifetimes (330 vs. 870 μs for $^5D_0$; and 220 vs 330 μs for $^5D_4$). The Judd-Ofelt parameters (Ω_2 *and* Ω_4) were calculated for the Eu(III) complexes and theoretical values of these parameters (Ω_2 *and* Ω_4) were obtained by using Sparkle/RM1 structures. The higher value of the Ω_2 parameter (14.37×10^{-20} cm^2) shows a highly polarizable chemical environment around Eu(III) ion and suggests that the dynamic-coupling mechanism is dominant. The Judd-Ofelt parameters were used to calculate the radiative decay rate, energy transfer rate (W_{ET}) and back energy transfer rate (W_{BT}) in the case of (**2**). The energy transfer processes show that energy transfer occurs from the triplet state of the ligands (T) to the first emissive level $^5D_1$ of Eu(III) and immediate next lower energy level $^5D_0$ of Eu(III) ion i.e., T → $^5D_1$ ($W_{ET} = 5.33 \times 10^9$ s^{-1}) and T→ $^5D_0$ ($W_{ET} = 4.91 \times 10^9$ s^{-1}) levels. Furthermore, the lower value of energy transfer rate of S$_1$ → $^5D_4$ ($W_{ET} = 4.61 \times 10^3$ s^{-1}) reflects that exchange mechanism is dominant. The theoretical emission quantum yield (31%) obtained from the Sparkle/RM1 structure is in good agreement with the experimental emission quantum yield (35%), which reflects that the present theoretical approach could be a great means for the a priori design of highly luminescent lanthanide complexes.

1. Introduction

The rationale behind design and synthesis of stable strong luminescent lanthanide coordination complexes have attracted great deal of interest due to their potential application in the fields as diverse as bioassays [1], sensor systems [2] and optical materials [3]. Lanthanide at hand have special spectroscopic properties due to the shielding of the 4*f*- orbitals with forbidden intra-configuration 4f–4f electronic transitions resulting in a very low extinction coefficient (ε typically 0.1 mol^{-1} dm^3 cm^3) characteristic narrow line-like emission bands. Since most of the members of the trivalent lanthanides are paramagnetic [with exception of La(III) and Lu(III)] with short electron relaxation times (10^{-4} s)] and, therefore, their β-diketonate complexes are routinely used as shift reagents to resolve the complicated NMR spectra of organic molecules [4]. The lanthanide coordination complexes with β-diketones [5] are important since the β- diketone ligands possess a strong π- π* absorption in the UV region, which is advantageous for efficient transfer of the absorbed energy from the triplet stage of the ligand to the emitting levels of Ln(III) ions by the antenna effect [6]. The lanthanide tris-(β-diketonates) are stable enough for practical usage and are coordinatively unsaturated and, therefore, can easily bind to one or more ancillary ligands to attain higher coordination requirement of Ln(III) ions.

In the field of lanthanide coordination complexes, the semi-empirical Sparkle model [7] has been proved to be an important means to design new light conversion molecular device (LCMD) [8]. Since, it allows the treatment of large number of lanthanide

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complexes within the reasonable time and low computational demand [9] and, therefore, is used rigorously for elucidating the unknown geometry of lanthanide complexes. As a matter of fact, the information of the structure and geometry are important for further calculation to find out the singlet and triplet states and other important spectroscopic properties. With the help these parameters, it is possible to construct the rate equations that involve the energy transfer mechanism to calculate the quantum yield [8a].

A large number of lanthanide tris(β-diketonate) adducts with variegated β-diketonate are reported in the literature [3,10]. Of the various β-diketones studied, the 1,1,1-trifluoro-2,4-pentanedione (Htfaa) is much less explored. This paper deals with the syntheses of lanthanide complexes of general formula [Ln(tfaa)$_3$bpy] (where Ln stands for trivalent lanthanides and tfaa is the anion of 1,1,1-trifluoro-2,4-pentanedione and bpy is 2,2′-bipyridyl) by an efficient one step method, at room temperature, in very high yield (between 75 and 81%). The highlights of the paper are: calculation of the ground state geometry of the complexes by the Sparkle/RM1 model; impact of ancillary ligand bpy on the 4f–4f absorption spectra (oscillator strength and band shape of the transitions) and photoluminescence properties (Intensity ratio, luminescence lifetime (τ_{obs}) and overall quantum yield ($\Phi_{overall}$). The experimental and theoretical Judd-Ofelt parameters (Ω_2 *and* Ω_4), quantum yields, intrinsic quantum yield (Φ_{Ln})), energy transfer (W_{ET}) and back energy transfer (W_{BT}) rates are calculated and discussed for the Eu(III) complexes.

2. Experimental section

2.1. Materials

The lanthanide oxides (99.90%, Leico Chem., USA) were converted to the corresponding chlorides, $LnCl_3{\cdot}nH_2O$ (n = 6–7) by dissolving the oxides in minimum amount of conc. HCl. It was then diluted with water and evaporated to near dryness on a water bath. This process of adding water and then evaporating to near dryness was repeated several times until the solution attains pH between 4 and 6. The chloride solution was finally evaporated to dryness and kept in a desiccator. The 1,1,1-trifluoro-2,4-pentanedione (Htfaa) was purchased from MTM Lancaster, England and 2,2′-bipyridyl from Merck, Germany. The solvents used in this study were either AR or spectroscopic grade.

2.2. Methods

Elemental analyses were carried out at the Chemistry Department, BHU Banaras, India. The melting point of the complexes was recorded by the conventional capillary method as well as on a DSC instrument (6220 Exstar 6000, from SII Nano Technology Inc., Japan.) in aluminum pans at a heating rate of 10 °C min^{-1}. Infrared spectra were recorded on a Perkin-Elmer spectrum RX I FT-IR spectrophotometer as KBr disc in the range 4000–400 cm^{-1}. The electrospray ionization mass spectrum of the complex in positive ion mode was recorded on Waters Micromass Q-T mass spectrometer.

The electronic spectra of the complexes were recorded on a Perkin-Elmer Lambda-40 spectrophotometer equipped with deuterium lamp (ultraviolet region) and tungsten lamp (visible region), with the samples contained in 1 cm^3 stoppered quartz cell of 1 cm path length. The concentration of the complex was 6×10^{-3} and 5×10^{-3}. The slit was fixed at 2 nm. The intensity of the absorption bands are expressed in terms of a quantity called oscillator strength ($P \times 10^6$). Experimentally it is related to the integrated area of the absorption band and can be expressed in terms of absorption coefficient ε(υ) and the energy of the transition "υ" (cm^{-1}) as given in the Eq. (1) [11].

$$P = 4.31 \times 10^{-9} \left|\frac{9\eta}{(\eta^2+2)^2}\right| \int \varepsilon(\nu)\mathrm{d}\nu \quad (1)$$

where η is the refractive index of the solution, ε(υ) is the molar extinction coefficient at wavelength υ. The oscillator strength of the transitions were determined by evaluating the area under the peak (area is calculated by the software supplied by Perkin-Elmer). The electronic spectra of the complexes have been recorded in chloroform in the visible region between 400 and 1000 nm.

Steady-state luminescence and excitation spectra were recorded on Horiba–Jobin Yvon Fluorolog 3–22 spectrofluorimeter equipped with a 450 W xenon lamp as the excitation source and R-928P Hamamatsu photomultiplier tube as detector and detected at an angle of 90° for diluted solution measurements. All the spectra were corrected for the instrumental functions. In order to determine the peak center maximum, full width at half-maximum (fwhm or peak width), and peak area Origin Pro 8 was used. Luminescence lifetimes were recorded on a single photon counting spectrometer from Edinburgh Instrument (FLS920) with microsecond pulse lamp as the excitation. The data were analyzed by software supplied by Edinburgh Instruments.

The overall quantum yields (Q_r) of the sensitized Ln(III) emission of the complexes, in the visible region, were measured in chloroform at room temperature and are cited relative to a reference ([Eu(hfaa)$_3$phen] and [Tb(hfaa)$_3$phen] Q_r = 46% for Eu and Q_r = 32% for Tb) [12]. The overall quantum yield was calculated using the Eq. (2) [13].

$$\frac{Q_s}{Q_r} = \frac{A_r}{A_s} \times \frac{\eta_s^2}{\eta_r^2} \times \frac{I_s}{I_r} \quad (2)$$

where r stands for the reference and s stands for sample. A is the absorbance at the excitation wavelength, η is the index of refraction of the solvent, and I is the integrated luminescence intensity. The refractive index is assumed to be equivalent to that of the pure solvent (η = 1.45 for chloroform).

2.3. Synthesis of [Ln(tfaa)$_3$H$_2$O]

The hydrated complexes [Ln(tfaa)$_3$H$_2$O] were synthesized by the literature method [14].

2.4. Synthesis of [Ln(tfaa)$_3$bpy]

All the complexes were synthesized by a similar *one-pot* method (Scheme 1). The synthesis of [Pr(tfaa)$_3$bpy] given here is representative.

[Pr(tfaa)$_3$bpy] (1). A solution of Htfaa (1.0 g, 6.48 mmol) in ethanol (5 mL) was added to 0.48 mL (0.108 g, 6.48 mmol) 25% ammonia solution contained in 50 mL beaker covered with a watch glass. It was shaken frequently to convert Htfaa into its ammonium salt. To this ammonium salt of tfaa was added 5 mL ethanol solution of bpy (0.3378 g, 2.16 mmol) and 5 mL ethanol solution of $PrCl_3{\cdot}6H_2O$ (0.7638 g, 2.16 mmol). The reaction mixture was stirred at room temperature for 5 h. A white precipitate appeared during stirring which was filtered off repeatedly. The filtrate was covered and left for slow evaporation of the solvent. Light green powder appeared after three days, which was filtered off and washed with hexane several times. The product thus obtained was recrystallized twice from ethanol to get the pure compound and dried under *vacuum* over P_4O_{10}. Similar procedure was employed to synthesize other complexes. Colour: Light Green, Yield: 75%, melting point: