Optical emission studies of new europium and terbium dinuclear complexes with trifluoroacetylacetone and bridging bipyrimidine. Fast radiation and high emission quantum yield

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ABSTRACT

New homodinuclear lanthanide complexes of the type $[Ln(tfaa)_3]_2bpm$ (Ln = La, Eu and Tb; tfaa = 1,1,1-trifluoro-2,4-pentanedione) were synthesized by a one pot-one step method and characterized by elemental analysis, FT-IR, thermogarvimetry and ^1H NMR spectroscopy. In these complexes the planar 2,2′-bipyrimidine (bpm) ligand affords a tetradentate coordination mode. The crystal structure of $[Tb(tfaa)_3]_2bpm$ was determined by single-crystal X-ray diffraction. The intramolecular Tb–Tb distance across the bpm bridging ligand is 6.760(1) Å. The dinuclear complexes are thermally stable up to 180 °C, as shown by thermal analysis. The Eu(III) and Tb(III) dinuclear complexes exhibit intense red and green emissions with luminescence lifetimes of 810 and 490 μs, respectively. The quantum yields, $\Phi_{overall}$, for the two complexes $[Eu(tfaa)_3]_2bpm$ and $[Tb(tfaa)_3]_2bpm$ are 34% and 48%, respectively. Substitution of a water molecule from the coordination sphere of $[Ln(tfaa)_3H_2O]$ by bpm and the joining of two $[Ln(tfaa)_3]$ units through bpm leads to 10- and 2-fold increases, respectively, in the overall quantum yield for the dinuclear Eu and Tb complexes. This enhanced improvement originates mainly due to the (i) better sensitization efficiency of the ancillary ligand (bpm) and (ii) elimination of non-radiative deactivation pathways through harmonics of O–H vibrations.

1. Introduction

The pursuit to design stable luminescent lanthanide complexes with conjugated organic ligands continues to stimulate ever increasing technological applications, such as light emitting diodes and display devices [1], optoelectronic devices [2], lasers [3], biological imaging applications [4], light-emitting sensors for hetero- and homogeneous fluoroimmunoassays [5], which are based on the exploitation of their magnetic or optical properties. In the case of trivalent lanthanides, the emission is due to transitions inside the 4f shell, thus intraconfigurational f–f transitions. Because the partially filled 4f shell is well shielded from its environment by the closed $5s^2$ and $5p^6$ shells, ligands in the first and second coordination spheres perturb the electronic configurations of the trivalent lanthanide ions (Ln^{3+}) only to a very limited extent. This shielding is responsible for the specific properties of lanthanide luminescence, more particularly for the narrow band emission and the long lifetimes of the excited states. Although photoluminescence of lanthanide ions can be an efficient process, all

lanthanide ions suffer from weak light absorption. Because the molar absorption coefficient ε of most of the transitions in the absorption spectra of trivalent lanthanide ions is smaller than $10\,L\,mol^{-1}\,cm^{-1}$, only a very limited amount of radiation is absorbed by direct excitation in the 4f levels. Since the luminescence intensity is not only proportional to the luminescence quantum yield but also to the amount of light absorbed, weak light absorption results in weak luminescence. However, the problem of weak light absorption can be circumvented by the so-called antenna effect [6] (or sensitization), appearing as a magic potion.

The coordination chemistry of the lanthanides is driven by electrostatic interactions between the ligands and generally trivalent lanthanide ions. The lanthanides typically adopt high coordination numbers and the coordination geometries are heavily influenced by steric effects [7]. The use of chelating ligands and hard donor atoms is important for generating stable complexes of the trivalent lanthanide ions. 2,2′-Bipyrimidine (bpm) is a planar and electronically delocalized heterocyclic ligand that has been shown to be a suitable ligand for generating dinuclear complexes by offering the two equivalent NN binding sites for the lanthanide ion [8]. Apart from acting as a neutral subordinate ligand, it can also link two Ln(β-diketone)₃ units to form a facile lanthanide(III) dinuclear

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complex. This laboratory has recently become interested in the synthesis, NMR, 4f–4f absorption and luminescent properties of homo as well as hetero-dinuclear lanthanide(III) complexes bridged by 2,2′-bipyrimidine (bpm) using different β-diketones [8a–e]. There are recent reports of structurally characterized dinuclear lanthanide complexes of bpm in which bpm acts as bridging unit to connect two lanthanide β-diketonate units [8f–k,8m]. Other homo- and hetero-dinuclear lanthanide complexes are also known in which ligands other than bpm are used to connect two lanthanide units [8n]. However, there are only few reports on structurally characterized Tb(III) dinuclear complexes of β-diketone bridged by bpm [8i,8m]. Recently, we have reported the synthesis and 4f–4f absorption and luminescence properties of nine-coordinated mononuclear and seven-coordinated dinuclear lanthanide complexes of 1,1,1-trifluoro-2,4-pentanedione with tptz and pyz (where tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine and pyz = pyrazine) [9a,b]. Two most interesting things that require attention are: (i) as far as we know, most of the studies on 1,1,1-trifluoro-2,4-pentanedione are devoted to hybrid materials, i.e. incorporated into polymer matrices [10], and report their photoluminescence properties and (ii) the majority of the complexes of this particular 1,1,1-trifluoro-2,4-pentanedione ligand are mononuclear [9b,c,11] and reports on polynuclear or dinuclear complexes are very limited for 1,1,1-trifluoro-2,4-pentanedione. As far as we know there is only one report on dinuclear complexes of the type [Ln(tfaa)$_3$]$_2$pyz [9a] (where Ln = La, Nd, Eu and Tb) by us and a one-dimensional polynuclear species reported by Zhu et al. of the general type [La(tfaa)$_3$(bpyN$_2$O$_2$)]$_n$ [12] (where bpyN$_2$O$_2$ = 4,4′-bipyrdyl-N,N′-oxide). Therefore, it is very motivating to study the synthesis of dilanthanide complexes of the 1,1,1-trifluoro-2,4-pentanedione ligand with the bridging bpm ligand and subsequent to investigate the effect of this bridging ligand on the resulting properties of the complexes. In this paper, we report on a deliberate facile one step-one pot synthesis for complexes of the type [Ln(tfaa)$_3$]$_2$bpm (Ln stands for La, Eu and Tb).

2. Experimental

2.1. Chemical and general procedures

The commercially available chemicals that were used without further purification are: Ln$_2$O$_3$ (Ln = La, Eu and Tb; 99.9%) from Aldrich, 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone) from Lancaster and 2,2′-bipyrimidine (bpm) from Merck. The solvents used in this study were either AR or spectroscopic grade. Oxides were converted to the corresponding chlorides, LnCl$_3$·nH$_2$O (n = 6–7), by dissolving the oxides in minimum conc. HCl, then diluting with water and evaporating to near dryness on a water bath. This process of adding water and then evaporating to near dryness was repeated several times until the pH of the solution was between 4 and 6. The chloride solution was finally evaporated to dryness and kept in a desiccator [13]. Infrared spectra were recorded on a Perkin–Elmer spectrum RX 1 FT-IR spectrophotometer as KBr discs operating between 4000 and 400 cm^{-1}. Elemental analyses were carried out at the University of Delhi. A Bruker Avance III 500 MHz NMR spectrometer was used to record the ^{1}H NMR spectra of the new compounds in a chloroform-d solution at 300 K, equipped with 5 mm PABBO probe. The chemical shifts are reported in parts per million relative to tetramethylsilane (SiMe$_4$). The melting points of the complexes were recorded by the conventional capillary method as well as on a DSC instrument (6220 Exstar 6000) in aluminum pans at a heating rate of 10 °C min^{-1}. Thermal analyses of the complexes were carried out under a dinitrogen atmosphere at a heating rate of

10 °C min^{-1} on Exstar 6000 TGA/DTA and DSC 6220 instruments from SII Nano Technology Inc., Japan.

The electronic spectra of the complexes were recorded on a Perkin–Elmer Lambda-40 spectrophotometer equipped with a deuterium lamp (ultraviolet region) and a tungsten lamp (visible region), with the samples contained in a 1 cm^3 stoppered quartz cell of 1 cm path length, in the range 200–1100 nm. The slit width was 2 nm.

Steady state luminescence and excitation spectra were recorded on an Horiba − Jobin Vyon Fluorolog 3–22 spectrofluorimeter with a 450 W xenon lamp as the excitation source and an R-928P Himamatsu photomultiplier tube as the detector and they were detected at an angle of 90° for diluted solution measurements. All the spectra were corrected for instrumental functions. The excitation and emission slit width was 2 nm. 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. The luminescence lifetimes were recorded on a single photon counting spectrometer from Edinburgh Instruments (FLS920), with a microsecond pulse lamp as the excitation source. The data were analyzed by software supplied by Edinburgh Instruments.

Relative quantum yields ($\Phi_{overall}$) of the sensitized Eu(III) and Tb(III) emissions of the complexes were measured in chloroform at room temperature and are cited relative to a reference solution of [Eu(hfaa)$_3$phen] (Φ_r = 46%) [14] and [Tb(hfaa)$_3$phen] (Φ_r = 32%) [14], with an experimental error of 10%. The relative quantum yields were calculated using Eq. (1) [15]:

$$\Phi_S = \frac{(A_r)(\eta_S^2)I_S}{(A_S)(\eta_r^2)I_r}\Phi_r \tag{1}$$

where r stands for the reference and s for the 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). The concentration of the samples was measured as 6×10^{-4} M, to avoid complex dissociation. For the determination of the quantum yield, the excitation wavelength was chosen so that $A < 0.05$.

2.2. X-ray structure determination

A single crystal suitable for X-ray analysis was obtained by slow evaporation of an ethanolic solution of the [Tb(tfaa)$_3$]$_2$bpm complex. A single crystal X-ray diffraction study of a crystal mounted on a capillary was carried out on a BRUKER AXS SMART APEX diffractometer with a CCD area detector (KR, 0.71073 Å, monochromator: graphite) [16]. Frames were collected at T = 293 K by ω, φ and 2θ-rotation at 10 s per frame with SAINT software [17]. The measured intensities were reduced to F^2 and corrected for absorption with SADABS [16]. The structure solution, refinement and data output were carried out with the SHELXTL program [18]. Non-hydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions using a riding model. Images were created with the Diamond program [19].

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

The synthesis of the [Eu(tfaa)$_3$H$_2$O] and [Tb(tfaa)$_3$H$_2$O] complexes is reported elsewhere [9a].

2.4. Synthesis of complexes of the type [Ln(tfaa)$_3$]$_2$bpm

All the complexes of the type [Ln(tfaa)$_3$]$_2$bpm (where Ln = La, Eu and Tb) have been synthesized by a similar one step-one pot