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Structure elucidation by sparkle/RM1, effect of lanthanide contraction and photophysical properties of lanthanide(III) trifluoroacetylacetonate complexes with 1,10-phenanthroline

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ABSTRACT

A series of luminescent anhydrous eight-coordinated anhydrous complexes of the general formula [Ln(tfaa)$_3$phen] [Ln = La(**1**), Pr(**2**), Nd(**3**), Eu(**4**), Tb(**5**), Dy(**6**), Ho(**7**), Er(**8**), Tm(**9**), Yb(**10**) and Lu(**11**); tfaa = 1,1,1-trifluoro-2,4-pentanedione and phen = 1,10-phenanthroline] have been synthesized and fully characterized by elemental analysis, ESI–MS, thermogarvimetric analysis (TGA), FT-IR and ^{1}H NMR spectroscopy. The complexes retain their identity in solution, phen and β-diketonate (methine and methyl) protons resonances are shifted in opposite directions and lanthanide induced shifts (LISs) is dipolar in nature. The unknown geometry of the complexes was determined from semi-empirical Sparkle/RM1 method. A distorted square antiprism geometry is proposed for [Eu(tfaa)$_3$phen] which is further attested by NMR spectroscopy. The hypersensitive transitions of Nd(III), Ho(III) and Er(III) complexes are sensitive to the environment (solvent), which is reflected by the oscillator strength and band shape of the transitions. The room-temperature PL spectra of Pr(III), Eu(III), Tb(III), Dy(III) and Tm (III) complexes in solution produce their characteristic red, brilliant red, green, yellow and blue emissions, respectively. The replacement of water molecule from the inner-coordination sphere by phen ligand and forming highly protective coordination environment (LnO$_6$N$_2$) by the tfaa$^-$ and phen around the Ln(III) ion, leads to increase in the photoluminescence quantum yield (PLQy) and the luminescence lifetime. Theoretical Judd-ofelt and PL parameters of [Eu(tfaa)$_3$phen] complex including PLQy predicted by the Sparkle/RM1 method are in excellent agreement with the experimental values, reflecting the efficacy of this method. The energy transfer processes show that energy transfer occurs via both T → $^5D_1$ (6.98 × 10^6) and T → $^5D_0$ (7.39 × 10^6) levels. Furthermore, Eu and Tb complex display bright red and green luminescence and therefore interesting photonics applications could be foreseen.

1. Introduction

Encouraged by the potential applications such as optical materials [1–4] and medical imaging [5,6] there is growing interest to design and synthesize stable luminescent lanthanide complexes with conjugated organic ligands [7–11]. However, the 4f- 4f electronic transitions of trivalent lanthanide ions are forbidden by parity and selection rules, which results in low molar absorption coefficients ε (smaller than 10 Lmol^{-1}cm^{-1}). In view of the fact that the luminescence intensity is not only proportional to the luminescence quantum yield but also to the amount of light absorbed, therefore, weak light absorption results in weak luminescence. Nevertheless, the problem of very weak light absorption can be prevented by the use of suitable organic chromophores which can sensitize the lanthanide ion via the so-called antenna effect [12]. The β-diketone is an important antenna molecules in terms of high harvest emissions because of the effectiveness of the energy transfer from this ligand to Ln(III) ion [1,2,13–25]. However, the lanthanide tris-β-diketonates always have high energy oscillators (O—H ~3300–3500 cm^{-1}, N—H ~ 3100–3300 cm^{-1} and C—H ~ 2950 cm^{-1}) in the inner-coordination sphere from the coordinated water molecules or other solvent molecules, which has hampering effect on the luminescence. Therefore, removing these deleterious high energy oscillators is the prime concern to improve the luminescence properties i.e., overall quantum yield. These can be achieved by (i)

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choosing the fluorinated β-diketone and (ii) coordination of ancillary ligands.

The expulsion of solvent molecules from the inner-coordination sphere can be efficiently achieved by the use of neutral NN donor ligands, which act as Lewis bases and readily form adducts with tris-β-diketonate complexes because of the thrust of lanthanide ion to fulfill their high coordination number requirement. These ligands improve overall properties by improving their thermal stability, volatility and most importantly enhancing the luminescence of these complexes in the solution by shielding the inner coordination sphere of Ln(III) ion from the high energy oscillators such as O—H, N—H, and C—H [26–30].

In an effort to fulfill the above mentioned requirements, we have used 1,1,1-trifluoro-2,4-pentanedione (Htfaa) and 1,10-phenanthroline (phen) ligand. 1,10-phenanthroline is one of the most studied ancillary ligand for designing the highly luminescent and stable lanthanide complexes because (i) rigid structure imposed by the central ring and (ii) intense absorption band in the near UV-region. The introduction of phen eliminates the undesirable outcome of O—H oscillators by removing the solvent molecules from the inner coordination sphere while the fluorinated ligand excludes the deleterious C—H oscillators. This paper deals with the syntheses of series of [Ln(tfaa)$_3$phen] complexes (where Ln stands for trivalent lanthanides and tfaa is the anion of 1,1,1-trifluoro-2,4-pentanedione) by an efficient one step method, at room temperature, in very high yield (70 and 81%). The important highlights of the paper are (i) elucidation of the structures by semi-empirical Sparkle/RM1 method (ii) the results of ^{1}H NMR of diamagnetic as well as paramagnetic complexes (iii) the role of phen ligand on the 4f – 4f absorption (oscillator strength and band shape of the hypersensitive transitions) and photoluminescence properties [luminescence lifetime (τ_{obs}) and overall quantum yield ($\Phi_{overall}$)] and (v) experimental and theoretical intensity parameters (Ω_2 and Ω_4), quantum yields, intrinsic quantum yield (η) and energy transfer rates is calculated and discussed for the Eu(III) complexes.

2. Experimental

2.1. Materials

The lanthanide oxides from Leico Chem., USA (99.90%) were converted to the corresponding $LnCl_3 \cdot nH_2O$ (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 1,10-phenanthroline (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 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 analysis of the complexes were carried out under 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. 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 spectra of the complexes in positive ion mode were recorded on Waters Micromass Q-T mass spectrometer. A BRUKER AVANCE II 400 NMR spectrometer was used to record the ^{1}H NMR spectra of the complexes in a chloroform-d ($CDCl_3$) 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 electronic spectra of the complexes were recorded on UV–vis spectrophotometer (Perkin-Elmer Lambda-40), with the samples contained in 1 cm^3 stoppered quartz cell of 1 cm path length and the concentration range between 6×10^{-3} and 5×10^{-3}. The slit width was 2 nm. The intensity of the absorption bands have been 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(ν) and the energy of the transition "ν" (cm^{-1}) as given in the Eq. (1) [31],

$$P = 4.31 \times 10^{-9} \left| \frac{9\eta}{(\eta^2+2)^2} \right| \int \varepsilon(v)dv \qquad (1)$$

where η is the refractive index of the solution, ε(ν) is the molar extinction coefficient at wavelength ν. The oscillator strength of the transitions was 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 solution in the region between 200 and 1000 nm.

The photoluminescence (PL) spectra were recorded on Horiba–Jobin Vyon Fluorolog 3–22 spectrofluorimeter with a 450 W xenon lamp as the excitation source and R–928 P Hamamatsu photomultiplier tube as detector and detected at an angle of 90° for diluted solution measurements. Excitation and emission slit width was 2 nm. All the spectra were corrected for the instrumental functions. In order to determine the peak centre maximum, full width at half-maximum (fwhm or peak width), and peak area Origin Pro 8 was used. The lifetime measurements were carried out on a single photon counting spectrometer from Edinburgh Instrument (FLS 920). A microsecond pulse lamp having pulse width ~0.2 μs and repetition frequency 10 Hz was used as excitation source for the decay curves. All measurements were done at room temperature. The data were analyzed by software supplied by Edinburgh Instruments.

The overall quantum yields (Q_s) 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) [17]. The overall quantum yield was calculated using the Eq. (2) [32].

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

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). Several measurements were carried out for each sample, so that the presented value corresponds to the arithmetic mean value. The estimated error for the quantum yields is (±10%).

2.3. Synthesis of [Ln(tfaa)$_3$phen]

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

[La(tfaa)3phen](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. This mixture, contained in 50 mL beaker was