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Full Length Article

Elucidating the energy transfer process in mononuclear and binuclear lanthanide complexes of the anti-inflammatory drug ibuprofen: From synthesis to high luminescence emission

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ABSTRACT

This work presents the synthesis, solid state characterization and complete photoluminescence study of three new important classes of lanthanide complexes containing the non-steroidal anti-inflammatory drug (NSAID) Ibuprofen. The analytical and spectroscopic data reveals the formation of nine complexes with the general formula $[Ln(Ibf)_3(H_2O)_2]$, $[Ln_2(Ibf)_6(bpy)_2]$ and $[Ln_2(Ibf)_6(phen)_2]$ (Ln=Eu^{III}, Gd^{III} and Tb^{III}, Ibf=Ibuprofen ligand, bpy=2,2′- bipyridine and phen=1,10-phenanthroline). The molecular structures of the Eu^{III} complexes were calculated using the RM1 model, and your optimized ground state geometries were used to calculated all details involved in the energy transfer process and compared with experimental data. The phosphorescence measurements of the Gd^{III} complexes, allowed the identification of the lowest ligand triplet state, proving that the photoluminescence in the Eu^{III} and Tb^{III} Ibuprofen complexes is proposed to be a ligand sensitized luminescence process. The presence of N,N-donors (bpy or phen) in the structure of the Eu^{III} Ibuprofen complexes results in an 3 to 4-fold increase in the quantum efficiency when compared with the Eu^{III} complex without N,N-donors ligands. The high emission quantum efficiency (η=69–80%) for Eu^{III} complexes showed that they can be potential candidates as emitters in biologic assays.

1. Introduction

In recent years, the lanthanides elements (Ln) have become to a wealth of advanced materials and technologies, including catalysts, magnets, optics and lasers, alloys, rechargeable batteries, electronics, imaging and bio analysis [1–8]. However, the usual impediment to the use of such lanthanide ions (Ln^{III}) systems is that the direct absorption of the 4f–4f excited states is very inefficient, with such transitions being parity forbidden and consequently resulting in very low absorption coefficients. In order to overcome this drawback, suitable chromophores have been employed as antennas or sensitizers that have the capability of transferring energy indirectly to the lanthanide ions [9]. This sensitization process consists of the absorption of the light by the ligand in the ultraviolet (UV) region, followed by an intramolecular energy transference from the triplet state (T_1) of the ligand to an excited level of the Ln^{III} ion. Ultimately, the excited Ln^{III} ion decays to the ground state via photon emission in the visible or near infrared regions (Antenna Effect) [10]. In this context, the lanthanide complexes containing carboxylate ligands are the most largely investigated kinds of coordination compounds due the luminescent and higher thermal stabilities, which make them potential candidates for Light Conversion Molecular Devices (LCMDs) [11,12]. In particular, the Ibuprofen (Ibf), represented in Chart 1, is an optically active compound with both *S* and *R*-isomers, belonging to non-steroidal anti-inflammatory drug (NSAID) class. This drug is used to treat rheumatoid arthritis, headaches, fever and pains related with the inflammatory process. The Ibuprofen molecule contains a aromatic group able to absorption in the UV region, acting like a good

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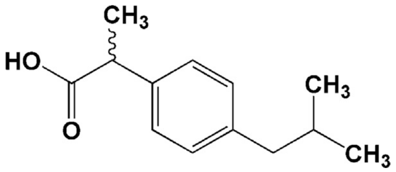

Chart 1. Chemical structure of the Ibuprofen (Ibf).

antenna. Despite its structural simplicity, there are very few studies focused on solid state chemistry and optical properties of lanthanide complexes with Ibuprofen [13], being the majority of these studies associated to d block metal complexes [14–17]. Still, to the best of our knowledge, do not exist a detailed scrutiny of important energy transfer process in these luminescent compounds once that such are employed in molecular recognition of NSAID, as Ibuprofen [18,19]. In addition, previous studies show that the emission intensities and fluorescence lifetimes of lanthanide complexes are enhanced after introducing the second organic ligand as 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) [20,21]. These ligands act as energy donors and enhance the fluorescence intensities of lanthanide complexes in a so-called "*synergistic effect*". The introduction of these ligands not only reinforces the fluorescence emission, but also increases the thermal stability and fulfills the coordination numbers of the lanthanide complexes. In the field of the lanthanide coordination compounds, theoretical tools can be helpful in the investigation of these systems [22–24]. The development of the accurate semiempirical RM1 model [25] for trivalent lanthanide ions has allowed the prediction of the ground states geometries of large lanthanide coordination compounds. Based on the knowledge of this geometry and using different approaches, several spectroscopic properties can be predicted and shed light on numerous details of the energy transfer mechanism in these compounds. We describe herein the synthesis, structural characterization and full photoluminescence properties of three mononuclear *[Ln(Ibf)$_3$(H$_2$O)$_2$]* (Ln=Eu **1**; Gd **2**; Tb **3**; where Ibf=ibuprofenate anion) and six binuclear complexes: *[Ln$_2$(Ibf)$_6$(bpy)$_2$]* (Ln=Eu **4**; Gd **5** and Tb **6**, where bpy=2,2′bipyridine) and *[Ln$_2$(Ibf)$_6$(phen)$_2$]* (Ln=Eu **7**; Gd **8** and Tb **9**, where phen=1,10-phenanthroline). Spectroscopic properties as Ω_λ intensity parameters (λ=2, 4 and 6), energy transfer (W$_{ET}$) and back-transfer (W$_{BT}$) rates, radiative (A$_{rad}$) and nonradiative (A$_{nrad}$) decay rates, quantum efficiency (η) and quantum yield (q) of Eu^{III} compounds were theoretically modeled using the electronic and spectroscopic semiempirical models and compared with those experimental values.

2. Experimental

2.1. Materials and measurements

All synthetic procedures were performed in air and $TbCl_3 \cdot 6H_2O$, (R,S)-Ibuprofen (Ibf), 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) were obtained either from Aldrich® or Fluka® and used as received. $EuCl_3 \cdot 6H_2O$ and $GdCl_3.6H_2O$ were prepared by dissolving europium and gadolinium oxide in hydrochloric acid solution and then dried. Elemental analyses for C, H and N were carried out using a *Perkin Elmer 2400CHN analyzer*. The metal contents were determined by complexometric titrations with standard EDTA solution and using xilenol orange as indicator [26]. FTIR spectra were recorded with a *Perkin Elmer Spectrum One model* using the ATR mode in the wavenumber range of 4000–400 cm^{-1} with an average of 128 scans and 4 cm^{-1} of spectral resolution. Powder diffraction analysis (PXRD) was performed using a *Bruker AXS D8 da Vinci* diffractometer (the generator was set at 40 kV and 40 mA), equipped with Ni-filtered CuKα radiation (λ=1.5418 Å), a Lynxeye linear position-sensitive detector and the following optics: primary beam Soller slits (2.94°), fixed divergence slit (0.3°) and receiving slit (9.0 mm), where the polycrystalline compounds were previously grounded in an agate mortar and they were deposited in hollow of thin glass sample-holder plate, with nearly zero-background. The diffraction data of all compounds were collected by overnight scans in the 2θ range of 6–105° with steps of 0.02° degree. Diffuse reflectance (DR) spectra were acquired with a *Cary 500 spectrophotometer* from 200 to 500 nm with spectral resolution of 1 nm. Thermal analysis (TG curves) were obtained on a *Shimadzu TG – 60* equipment where about 6 to 10 mg of samples were heated at 10 °C/min from room temperature to 800 °C in a dynamic nitrogen atmosphere (flow rate=100 mL/min). The luminescence excitation and emission spectra were recorded using a *Jobin – Yvon Model Fluorolog FL3 – 22 spectrophotometer* equipped with a *R928 Hamamatsu* photomultiplier and 450 W xenon lamp as excitation source and the spectra were corrected with respect to the Xe lamp intensity and spectrometer response. Measurements of emission decay were performed with the same equipment by using a pulsed Xe (3 μs bandwidth) source. Experimental intensity parameters, Ω_λ, for the *[Eu(Ibf)$_3$(H$_2$O)$_2$]* **1**, *[Eu$_2$(Ibf)$_6$(bpy)$_2$]* **4** and *[Eu$_2$(Ibf)$_6$(phen)$_2$]* **7** were determined from the emission spectra using the following equation [27,28]:

$$\Omega_\lambda = \frac{3\hbar c^3 A_{0\to J}}{4e^2\omega^3\chi\left\langle {}^7F_J\|U^{(\lambda)}\|{}^5D_0\right\rangle^2} \tag{1}$$

where χ is the Lorentz local field correction term, given by $\chi=n(n+2)^2/9\chi=\frac{n(n+2)^2}{9}$ and is $\left\langle {}^7F_J\|U^{(\lambda)}\|{}^5D_0\right\rangle^2$ a squared reduced matrix element with value of 0.0032 for the $^5D_0\to{}^7F_2$ transition and 0.0023 for the $^5D_0\to{}^7F_4$ one. The refractive index (n) has been assumed equal to 1.5. In this work, the $^5D_0\to{}^7F_6$ transition was not observed experimentally; consequently, the experimental Ω_6 parameter could not be estimated. The spontaneous emission coefficient, $A_{01}=0.31\times10^{-11}(n)^3(\nu_{01})^3$, leading to an estimated value around 50 s^{-1} for the refractive index (n) defined above. In Eq. (1), the $A_{0\lambda}$ term, where λ=2 and 4, represents the spontaneous emission coefficients of the $^5D_0\to{}^7F_2$ and $^5D_0\to{}^7F_4$ transitions, which can be calculated from $^5D_0\to{}^7F_1$ reference transition (magnetic dipole mechanism), therefore this transition is practically insensitive to chemical environment changing, Eq. (2).

$$A_{0\lambda} = \frac{\nu_{01}}{\nu_{0\lambda}}\frac{S_{0\lambda}}{S_{01}}(A_{01}) \tag{2}$$

where S_{01} and $S_{0\lambda}$ are the areas under the curves of the $^5D_0\to{}^7F_1$ and $^5D_0\to{}^7F_\lambda$ transitions, with ν_{01} and $\nu_{0\lambda}$ being their energy barycenters respectively.

2.2. Synthesis of the [Ln(Ibf)$_3$(H$_2$O)$_2$]complexes

A solution of sodium ibuprofenate (NaIbf) was prepared by the addition of NaOH aqueous solution (0.40 mL, 1 mol L^{-1}) to an aqueous suspension (30 mL) containing 84 mg (0.40 mmol) of Ibuprofen. To this solution was added the respective lanthanide chloride aqueous solutions (10 mL, 0.13 mmol) until total precipitation of the complexes. The precipitates were washed three times with hot distilled water, filtered and dried in a desiccator over anhydrous calcium chloride.

[Eu(Ibf)$_3$(H$_2$O)$_2$] ***1***: Yield: 73%. Anal. Calc. for $C_{39}H_{55}O_8Eu$: C: 58.2, H: 6.9 % Eu:18.9 %; Found: C: 58.5 , H: 6.7, Eu: 18.9 %.
[Gd(Ibf)$_3$(H$_2$O)$_2$] ***2***: Yield: 74%. Anal. Calc. for $C_{39}H_{55}O_8Gd$: C: 57.8, H: 6.8, Gd: 19.4 %; Found: C: 58.1, H: 6.5, Tb: 19.3 %.