Journal of Luminescence 162 (2015) 41–49

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Synthesis, structure, theoretical studies and luminescent properties of a ternary erbium(III) complex with acetylacetone and bathophenanthroline ligands

Pablo Martín-Ramos [a,b], Pedro S. Pereira Silva [a,*], Pedro Chamorro-Posada [c], Manuela Ramos Silva [a], Bruce F. Milne [d,e], Fernando Nogueira [d], Jesús Martín-Gil [b]

[a] CEMDRX, Department of Physics, Universidade de Coimbra, Rua Larga, P-3004-516 Coimbra, Portugal
[b] Advanced Materials Laboratory, ETSIIAA, Universidad de Valladolid, Avenida de Madrid 44, 34004 Palencia, Spain
[c] Higher Technical School of Telecommunications Engineering, Universidad de Valladolid, Campus Miguel Delibes, Paseo Belén 15, 47011 Valladolid, Spain
[d] Centre for Computational Physics, Department of Physics, Universidade de Coimbra, P-3004-516 Coimbra, Portugal
[e] Donostia International Physics Centre, Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastián, Spain

ARTICLE INFO

Article history:
Received 11 December 2014
Received in revised form
29 January 2015
Accepted 16 February 2015
Available online 21 February 2015

Keywords:
β-diketonate
Erbium(III)
MOPAC
Sparkle
TDDFT

ABSTRACT

A novel erbium(III) complex with acetylacetone (Hacac) and bathophenanthroline (4,7-diphenyl-1,10-phenanthroline, bath) ligands, formulated as [Er(acac)$_3$(bath)], has been characterized by elemental analysis, X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy, Raman spectroscopy, absorption and emission spectroscopies. In the theoretical part of this study, semi-empirical quantum chemistry methods using AM1, PM3, PM6 and PM7 models have been employed to predict the structure of the complex, calculate the geometric and crystallographic parameters, and make comparisons with spectroscopic data using INDO/S-CI calculations. Real-time time-dependent density-functional theory (TDDFT) has also been used to calculate the optical absorption spectrum of the complex in the gas phase.

1. Introduction

Different approaches for the design of lanthanide coordination compounds as potential precursors for electroluminescent device thin films have been proposed [1]. In fact, formation of mixed ligand complexes is a well-known methodology so as to modify the different properties of lanthanide compounds. The composition and the structure of such compounds strongly depend on the electronic features of the ligands. In this respect, it is very important to analyze the changes in structural parameters, bond energies and other properties of lanthanide complexes as a function of ligand types. A solution to these tasks lies in combining experimental and theoretical characterization resources. In theoretical chemistry, the ability to predict geometries of lanthanide complexes is fundamental in the design of luminescent complexes, for which theoretical models such as Sparkle [2], the combined quantum mechanical/molecular mechanical (QM/MM) technique [1,3] and the universal force field for the MM part have been successfully used so as to model the structures and properties of β-diketonate-based lanthanide complexes. As a counterpart to this theoretical approach, our research team has set the goal of conducting an experimental study on the structure and properties of erbium β-diketonate-based mixed ligand complexes with N,N-donor molecules [4–11].

The choice of β-diketonates amongst the various strategies aimed at improving lanthanide luminescent quantum efficiencies discussed in the literature [12] is supported by their wide commercial availability and by their remarkable synthetic versatility. In this study the simplest β-diketonate (acetylacetonate, acac), where the substituents on both carbonyl groups are methyl groups, has been chosen to exemplify the numerical techniques. Nevertheless, the substitution of these CH_3 groups by other groups would allow to control and enhance the properties of the corresponding rare-earth complexes (for instance, branched alkyl chains are known to increase the solubility in organic solvents and the volatility, perfluorinated alkyl groups increase the Lewis acidity, aromatic substituents increase the light absorption in comparison to aliphatic substituents, etc.). Such flexibility has allowed the successful application of analogous erbium(III) complexes as, for example, active layers in organic light-emitting diodes [13], as dopants in liquid-crystals aimed at LCDs [14] or in other matrices with a view to optical amplification [15–20].

With regard to the role of the N,N-donor ligands, they act as Lewis bases and complete the rare-earth ion's first coordination

---

[*] Corresponding author.
E-mail address: psidonio@pollux.fis.uc.pt (P.S.P. Silva).

http://dx.doi.org/10.1016/j.jlumin.2015.02.024
0022-2313/© 2015 Elsevier B.V. All rights reserved.

sphere. Two very popular diimides are 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy). In the novel complex reported herein, bathophenanthroline (bath) has been chosen instead. Being more basic than phen (pKa=4.27) or bipy (pKa=4.38), bath (pKa=4.67) would be expected to contribute more electron density through Er–N bond making the Er^{3+} ion more electron rich. As a result, the Er^{3+} will show less attraction for electron donor solvents. The rigidly planar structure of bath would also be helpful in obstructing the coordination of solvent molecules to inner coordination sphere of Er^{3+} and restricting the complex–solvent interaction [21]. This should help to decrease non-radiative losses. Secondly, the bulkier and more rigid planar structure of bathophenanthroline should cause a higher intensity of the sensitized luminescence, because such structure allows a better energy transfer [21–24].

In this paper, the erbium(III) complex formulated as $[Er(acac)_3(bath)]$ has been thoroughly characterized by elemental analysis, X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy, Raman spectroscopy, absorption spectroscopy and luminescence in solid state. Part of this data has then been used as a reference in order to evaluate the suitability of several semi-empirical calculation methods for predicting the equilibrium energy configuration and – in combination with INDO/S method and CIS – the electronic properties of the complex. Finally, a comparison with more computationally-intensive TDDFT calculations for the optical absorption spectrum has been conducted.

2. Experimental and computational methods

2.1. Materials, synthesis and analytical data

All reagents and solvents employed were commercially available and used as supplied without further purification. All the procedures for complex preparation were carried out under nitrogen environment and using dry reagents to avoid the presence of water and oxygen, which can quench metal photoluminescence (PL).

Tris(acetylacetonate)mono(bathophenanthroline)erbium(III), $[Er(acac)_3(bath)]$, was obtained by mixing equimolar quantities of methanol solutions of erbium(III) 2,4-pentanedionate [erbium(III) acetylacetonate hydrate 97%, CAS no. 70949-24-5, Sigma Aldrich] (0.464 g, 1 mmol) and bathophenanthroline [4,7-diphenyl-1,10-phenanthroline 97%, CAS no. 1662-01-7, Sigma Aldrich] (0.332 g, 1 mmol). The mixture was heated to 75 °C and stirred overnight, then washed with dioxane, and finally dried in vacuum to give the product in 86.2% yield (based in Er). Crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol-dioxane solution at room temperature (RT).

Chemical formula: $C_{39}H_{37}ErN_2O_6$. M_W: 796.98. Anal. Calcd. For $C_{39}H_{37}ErN_2O_6$: C, 58.77; H, 4.68; Er, 20.99; N, 3.51; O, 12.05. Found: C, 58.81; H, 4.66; N, 3.45%.

2.2. Physical and spectroscopic measurements

C, H, N elemental analyses were conducted using a PerkinElmer CHN 2400 apparatus.

Differential scanning calorimetry (DSC) data were obtained on a DSC TA instrument mod Q100 v.9.0 with a heating rate of 10 °C/min under a N_2 atmosphere. Thermogravimetric and differential thermal analyses were carried out in an inert atmosphere with a PerkinElmer STA 6000 Simultaneous Thermal Analyzer, by heating 7 mg of sample in a slow stream of N_2 (20 mL/min) from room temperature up to 800 °C, with a heating rate of 20 °C/min.

Infrared spectrum was recorded with a Thermo Nicolet 380 FT-IR spectrometer in KBr pellets.

Raman spectrum was recorded with a FT-Raman Bruker FRA106 by using a near-IR (Nd:YAG, 1064.1 nm) laser to excite the sample.

The crystal structure was elucidated by X-ray diffraction analysis. Prior to structural characterization, the powder diffractogram of the erbium complex was obtained using an ENRAF-NONIUS powder diffractometer (Debye–Scherrer geometry) equipped with an INEL CPS120 detector and a quartz monochromator selecting the Cu Kα1 wavelength (transmission geometry, capillary of 0.3 mm diameter).

For the determination of crystal structure by X-ray diffraction, a crystal of $[Er(acac)_3(bath)]$ was glued to a glass fiber and mounted on a Bruker APEX II diffractometer. Diffraction data was collected at room temperature 293(2) K using graphite monochromated MoKα (λ=0.71073 Å). Absorption corrections were made using SADABS [25]. The structure was solved by direct methods using SHELXS-97 [26] and refined anisotropically (non-H atoms) by full-matrix least-squares on F^2 using the SHELXL-97 program [26]. PLATON [27] was used to analyze the structure. Mercury version 3.1 [28] was used for figure plotting. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC 966774.

The optical absorption spectrum of the product in the UV–vis region was recorded with a Hitachi U-2010 spectrophotometer in methanol diluted solutions (10^{-5} and 10^{-3} M). The absorbance in the NIR range was recorded using a Varian 660-IR FT-IR spectrometer in 10 wt% KBr pellet.

Steady state luminescence and excitation spectra for the samples in powder form were collected with a Jobin Yvon Fluorolog 3 spectrofluorometer equipped with a liquid nitrogen cooled InGaAs detector. The PL spectrum was recorded upon excitation at 350 nm and at $^2H_{11/2}$ (λ_{exc}=532 nm) Er^{3+} absorption with a 450 W Xenon lamp and a 500 mW continuous laser, respectively. The spectrum was acquired in the 850–1600 nm range with 1 s integration time at 1 nm steps. The NIR luminescence decay curve was measured upon excitation of the Er^{3+} ions at 980 nm with a Spectra Physics Quanta-Ray MOPO-730 laser system. The emitted light was dispersed using a single-grating 0.34 m focal length spectrometer (Spex 340E) and detected with a Peltier-cooled, NIR-extended photomultiplier (Hamamatsu H9170-75) and a lock-in amplifier. The lifetime was measured by using a digital oscilloscope (Tektronix TDS520). The optical absorption and photoluminescence spectra have been measured at room temperature and have been corrected by the spectral response of the experimental setups.

2.3. Computational methods

2.3.1. Semi-empirical calculations

Using the experimental crystallographic data as an initial guess, the ground state geometries and the corresponding vibrational frequencies were obtained using the Sparkle/AM1 [29,30], Sparkle/PM3 [31], Sparkle/PM6 [32,33] and Sparkle/PM7 [34,35] models implemented in the MOPAC2012 software [36]. The computations were performed on a server with four AMD Opteron 16 Core processors and 128 GB of memory and a Linux operating system. No imaginary vibrational frequencies were found for any of the optimized geometries.

The electronic spectra for each of the optimized structures were calculated using the ORCA electronic structure package version 2.9.1 [37,38] via the intermediate neglect of differential overlap/spectroscopic (INDO/S) method and configuration interaction with singles (CIS) [39,40] replacing the Er^{3+} ion with a point charge as described by Andrade et al. [41]. Triplet excited states have also been calculated for the PM7 optimized geometry using the CIS module in ORCA software package.

Semi-empirical calculations were also performed in order to optimize the solid crystalline structures using a treatment of periodic boundary conditions [39] in the MOPAC2012 software [36]. In