Journal of Luminescence 187 (2017) 555–563

Contents lists available at ScienceDirect

Journal of Luminescence

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

Improving the quantum efficiency of the lanthanide-organic framework $[Eu_2(MELL)(H_2O)_6]$ by heating: A simple strategy to produce efficient luminescent devices

Raquel Milani[a], Leonis L. da Luz[b], Ana Cláudia V. de Araújo[c], Nailton M. Rodrigues[d], Eduardo H.L. Falcão[a,b], Walter M. de Azevedo[b], Nivan B. da Costa Jr.[d], Mateus B. Cardoso[e], Ricardo O. Freire[d,*], Severino A. Júnior[a,b,**]

[a] *Programa de Pós-Graduação em Ciências dos Materiais, Universidade Federal de Pernambuco, Recife – PE, Brazil*
[b] *Departamento de Química Fundamental, Universidade Federal de Pernambuco, Recife – PE, Brazil*
[c] *Unidade Acadêmica de Garanhuns, Universidade Federal Rural de Pernambuco, Garanhuns – PE, Brazil*
[d] *Pople Computational Chemistry Laboratory, Departamento de Química, Universidade Federal de Sergipe, São Cristóvão – SE 49100-000, Brazil*
[e] *Laboratório Nacional de Luz Síncrotron, Campinas – SP 13083-970, Brazil*

ARTICLE INFO

Keywords:
Temperature effect
Luminescence
LOF
Theoretical simulation
Quantum efficiency improvement

ABSTRACT

Luminescent materials have been widely studied due to the increasing number of applications in catalysis, biosensors and electro-optical devices. In this sense, the improvement of luminescent efficiency has been sought and several strategies have been proposed. In this work, experimental and theoretical approaches were used to achieve and understand the improvement of luminescent efficiency of lanthanide organic frameworks through a heating process. In this study, $[Eu_2(MELL)(H_2O)_6]$ (EuMELL) was synthesized and characterized by scanning electron and fluorescence microscopies, thermogravimetric analysis, powder X-ray diffraction and photoluminescence techniques. In parallel, theoretical simulations of the material in solid phase were carried out using semiempirical approaches. The comparison between experimental and theoretical results indicated that the more accurate structure was calculated using the Sparkle/PM3 model. The temperature effects on the structure as well as the photophysical properties were evaluated by measurements *in situ* heating and compared to theoretical simulations using the Sparkle/PM3 geometry. The excellent agreement between the computational and experimental results in this study opens up a series of possibilities for studying other systems, particularly when structural details are not easily available. Moreover, that the controlled heating contributes to improve its the quantum efficiency by approximately 45%, suggesting that this approach can be a valuable tool for technological applications.

1. Introduction

Lanthanide-Organic Frameworks (LOFs) have been widely studied due to applications in relevant areas such as catalysis [1], luminescent device production [2,3], identification of gunshot residues [4] and magnetic resonance imaging (MRI) [5]. Most of these applications are based on the lanthanide presence, which presents strong luminescence in their electronic spectra upon irradiation with ultraviolet light [6]. The 4f–4f intraconfigurational transition of lanthanides exhibits narrow line emissions and long lifetimes, due to chemical shielding of the 4f orbitals by the 5s and 5p sub-shells, and the forbidden nature (parity rule) of the f–f transitions, respectively [7,8]. These properties make them extremely sensitive to small and discrete perturbations in their surroundings. All of these properties, when associated with LOFs, can lead to new devices with applications in the technological and medical fields. LOF systems usually exhibit low quantum yield emissions that can be improved either by exchanging coordinating water molecules by a different organic ligand or by removing those water molecules by a heating process. Experimental studies have focused on the luminescence of these systems, but no satisfactory explanation for those improvements is given. In order to overcome this deficiency, theoretical tools and experimental studies must be associated to elucidate these phenomena and answer fundamental questions related to the luminescence improvement [9].

---

* Corresponding author.
** Corresponding author at: Departamento de Química Fundamental, Universidade Federal de Pernambuco, Recife, PE 50740-560, Brazil.
E-mail addresses: rfreire@ufs.br (R.O. Freire), salvesjr@ufpe.br (S.A. Júnior).

http://dx.doi.org/10.1016/j.jlumin.2017.04.001
Received 9 November 2016; Received in revised form 22 March 2017; Accepted 4 April 2017

Different theoretical approaches and models can be used to predict the geometric details of LOFs. The computational processing time has been the key factor for choosing the most appropriate theoretical methodology for studying the system of interest. Nowadays, many works have performed quantum chemical calculations of solid phase structures using the Density Functional Theory (DFT) approach [10,11]. During these calculations, single DFT potentials are used to study those systems with plane wave pseudopotential or considers the periodic boundary conditions with a traditional basis set. On the other hand, solid state calculations using semiempirical methods remained forgotten up to 2008, when Stewart evaluated the PM6 method for a large set of organic and inorganic crystalline structures, showing accuracy for some structures involved [12]. His calculations used (a) the Born-Von Karman periodic boundary conditions, (b) Ewald sum [13] to resolve the Madelung integral and (c) additional corrections applied to the NDDO method to treat periodic systems [14]. Such algorithm has been implemented in MOPAC2012 program [15] for all methods NDDO available.

Regarding the luminescent properties of these LOFs, theoretical models for simple lanthanide systems have been applied to simulate and understand these properties. To the best of our knowledge, only three papers were published where theoretical procedures and experimental results were compared and presented a good agreement [2,13,14].

In the present paper, we aimed to understand the temperature influence on the structure and photophysical properties of LOFs in order to elucidate the mechanism and the parameters that govern their emission yield. To accomplish this, we synthesized a LOF with europium and mellitic acid, $[Eu_2(MELL)(H_2O)_6]$ (EuMELL), which then underwent in situ thermal treatment. The material was characterized by scanning electron and fluorescence microscopies, thermogravimetry analysis, powder X-ray diffraction and photoluminescence. A complete theoretical study of the photoluminescent properties was carried out based on a theoretical ground state geometry calculated from solid state methods. The accuracy of the geometries obtained using the four different Semiempirical Models [17–21] was evaluated and the best model was used to predict the structures at 150 °C. The elucidation of both experimental structures was performed comparing the experimental and theoretical powder X-ray diffraction. Lastly, the theoretical tools implemented in the LUMPAC Program [22] were used to study the evolution of the luminescent processes.

2. Experimental section

2.1. Chemicals

Mellitic acid (H_6MELL, $C_{12}O_{12}H_6$, 99.9%) and europium oxide (Eu_2O_3, 99.99%) were purchased from Aldrich and used as received. $EuCl_3{\cdot}6H_2O$ was obtained by reaction of hydrochloric acid with Eu_2O_3.

2.2. Syntheses

The lanthanide-organic framework EuMELL (in which MELL refers to the mellitate ion) was prepared according to a procedure modified from our previous paper [16]. An equimolar mixture (0.85 mmol) of mellitic acid and $EuCl_3{\cdot}6H_2O$ and H_2O (4.0 mL) was placed inside an 8.0 mL Teflon-lined stainless steel autoclave. The reaction took place at 160 °C under autogenous pressure over a period of 72 h, after which the vessel was allowed to cool to room temperature. The filtered solid was washed with water and ethanol and dried in open air.

2.3. Sample characterization

2.3.1. SEM

Size and morphology of the samples were investigated by scanning electron microscopy (SEM). SEM images were obtained using a FEI Inspect F50 High Resolution SEM at the Brazilian Laboratory of Nanosciences (LNNano) operating at an accelerating voltage of 5 kV. The samples were coated with a thin carbon film before imaging.

2.3.2. FM

Fluorescence microscopy images (FM) were obtained using a Nikon-Eclipse E600 microscope equipped with a Y-FL epifluorescence accessory at the Brazilian Biosciences National Laboratory (LNBio). The fluorescence images were captured with a CoolSNAP-Pro CF Color (Media Cybernetics) camera.

2.3.3. TGA

Thermogravimetric analysis (TGA) was performed with a Shimadzu DTG-60H instrument, from 25 °C to 900 °C, under dynamic nitrogen atmosphere (50 mL min^{-1}) and a constant heating rate of 5 °C min^{-1}.

2.3.4. PXRD

Powder X-ray diffraction (PXRD) patterns were obtained using synchrotron radiation (Energy = 8 keV) on the D10A-XRD2 beamline at the Brazilian Synchrotron Light Laboratory (LNLS). The measurements were collected in a 2θ range of 10–35°, with a Huber diffractometer and 1D Mythen detector. A furnace was coupled to the diffractometer in order to allow PXRD measurements in different temperatures: 25, 150, 200 °C, respectively, and 25 °C* (room temperature measurement after heating the sample to 150 °C). The PXRD patterns were acquired after 10 min stabilization in each temperature. All measurements were recorded with identical instrument parameters.

2.3.5. Photoluminescence

Photoluminescence (PL) spectra were measured on powder samples and collected using a HORIBA Jobin-Yvon Fluorolog-3 ISA spectrofluorometer equipped with a Hamamatsu R928P photomultiplier, a SPEX 1934 D phosphorimeter and a 450 W Xenon pulsed-lamp. Lifetime data were obtained by monitoring the emission maxima at 615 nm for the Eu^{3+} ion.

In situ photoluminescence measurements in different temperatures were obtained using a heating plate with digital temperature control coupled to the spectrofluorometer. 50 mg of EuMELL were placed on the surface of the plate and positioned in the spectrofluorometer optimizing the maximum incidence of radiation on the sample. Photoluminescence spectra were collected at 25, 150, and 200 °C. To ensure uniform heating in the sample, the acquisition of the PL spectra were carried out 15 min after stabilization in each temperature. An additional luminescence data set was collected at room temperature after heating the sample to 150 °C for 15 min. This data set was labelled 25 °C*.

The experimental quantum efficiency (η), *i.e.*, the direct lanthanide-excitation-based efficiency, was determined by the experimental values of the lifetime of the $^5D_0$ emitting level (τ), radiative (A_{rad}) and nonradiative (A_{nrad}) rates, according to Eq. (1) [23]:

$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrad}} \tag{1}$$

The radiative decay rate (A_{rad}) was calculated based on the emission spectrum. The total decay rate is defined by $A_{tot} = (1/\tau) = A_{rad} + A_{nrad}$. Thus, based on the experimental lifetime (τ) and the A_{rad} rate, it possible to determine the nonradiative rate (A_{nrad}).

For experimental determination of emission quantum yield, q, (is defined as the ratio between the number of photons emitted by the Eu^{3+} ion and the number of photons absorbed by the ligand) was employed the method developed by Bril and Veenis at Philips Research Laboratories [24,25]. The q values for a given material can be determined by comparison with standard phosphors with known q values. The quantum yield can, thus, be calculated by using the expression as follows: