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Simulation of the chemical interactions of luminescent lanthanide complexes series $[Ln(cin)_3(H_2O)_3]\cdot Hcin$ and $[Ln_2(cin)_6(bpy)_2]$ using DFT calculations

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ABSTRACT

In this work, DFT calculations were conducted to understand the interactions of two luminescent complexes series, named $[Ln(cin)_3(H_2O)_3]\cdot Hcin$ and the $[Ln_2(cin)_6(bpy)_2]$ (where cin = hydrocinnamate anion and bpy = 2,2′-bipyridine). For the reduction of the computational cost in the geometry optimization calculations, the PBE-D2 and the GGA + U methodologies were tested, even as the 4f electrons treatment, in the core and in the valence shell of the lanthanide metals.

As a result of the electronic structure calculations, the lattice parameters of these complexes was obtained and corroborated by a comparison between the simulated and experimental diffractograms. The projected density of states and the charge density analysis were made for a better understanding of the electronic structure and the stabilization of these complexes, like the importance of some ligands and the difference of the interaction between the rare-earth metals and the ligands.

It could be concluded that there is no need to compute the spin polarization and to include the hubbard correction in order to conduct a structural analysis of these rare-earth metal complexes. The electronic density maps show that the structures are mainly stabilized by charge transfer between the ligands and the rare-earth cations. This result also corroborates the geometry optimizations performed with the DFT-D2 method, which indicate that the computation of the Van der Waals forces are negligible.

1. Introduction

The electronics industry is, certainly, one of the most important segments of the global trade, responsible for moving trillions of dollars annually around the world with products such as laptops, smartphones, cameras, and TVs. All these devices are based on integrated circuits, better known as chips or microchips. These components are manufactured primarily of inorganic semiconductor materials, where the most important chemical element is the silicon. However, a new research segment, known as Organic Electronic, was established in recent years. The difference between these technologies is that the inorganic materials are replaced by organic compounds in the manufacture of some components such as Organic Diodes, Transistors, and Sensors. The main advantage of these substitutions is the possibility to create microchips, or even microprocessors with great flexibility, since this is a common feature of organic compounds, such as plastic for example. Another important advantage of this development is the ability to create devices able to emit light, which are used today for the manufacture of Organic Light Emitting Diodes (OLED) displays. However, many of these electroluminescent organic compounds have broad emission bands, hindering its application in the fabrication of the displays. This problem can be circumvented with the use of compounds containing trivalent rare earth ions [1,2]. The use of the trivalent lanthanide complexes is a viable and promising route for photon emissions converted from singlet and triplet excitons since, theoretically, these complexes can reach the internal quantum efficiency, η, to about 100% due to the antenna effect. This is not possible for organic compounds, in which the emission is given by the transition between singlet states, and the theoretical upper limit for the quantum efficiency of the emission is approximately 25% [3,4]. In addition to the much higher quantum efficiency of lanthanide complexes, another characteristic of these compounds

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is their wide range of properties since small structural changes can significantly increase the photoluminescence or electroluminescent properties of these materials. Because of these advantages, the development of new classes of complexes with mixed ligands is a current research activity [5–7].

Although promising, the use of lanthanide complexes, in OLED manufacturing is very difficult. This difficulty is due to the fact that these compounds, when used in OLED, have their quantum efficiency decreased drastically [8], because in these conditions the X–X annihilation occurs [9]. Therefore, to avoid this phenomenon, it is very important to understand the electronic structure of this type of compounds. In this sense, electronic structure calculations can be a powerful tool to develop OLEDs based on Rare-Earth complexes.

Density Functional Theory (DFT) was used to study lanthanide complexes treating the molecules of the crystal as isolated molecules [10–12]. However, with the increase of the computational power, it is now possible to simulate the atomic scale behavior of materials using *ab initio* methods with solid state theory. For instance, boundary periodic conditions were used for the calculations of Monazite-Type crystals, species containing lanthanide metals in their structure [13] and for rare earth aluminum hydrides [14]. These compounds are so important that specific softwares were developed to calculate the properties of these systems, as the Sparkle [15,16], which is part of the Lanthanide Luminescence Software Package (LUMPAC) [17,18].

Recently, two new series of these compounds were synthesized, $[Ln(cin)_3(H_2O)_3]{\cdot}Hcin$ (where Ln = Dy, Er, Eu, Gd or Tb, cin = hydrocinnamate ligand and Hcin = hydrocinnamic acid) [19], and $[Ln_2(cin)_6(bpy)_2]$ (where Ln = Eu, Gd or Tb and bpy = 2, 2′-bipyridine) [20]. The measured quantum efficiency for the $[Eu(cin)_3(H_2O)_3]{\cdot}Hcin$ complex was about 11% and for the $[Eu_2(cin)_6(bpy)_2]$ was approximately 67%. This significant difference between the η values occurs when the water molecules are replaced by bpy ligand [20].

In this work, these two luminescent complexes series were studied in order to unravel the supramolecular chemistry behind their structure stabilization. Hence DFT and DFT-D2 calculations with periodic boundary conditions were performed. The geometry of the studied systems was fully optimized and the resulting electronic densities were used for obtaining the charge density difference maps. The pDOS (projected density of states) of the different lanthanide ions was also computed for the sake of a qualitative comparison of their energy gaps.

2. Methodology

All calculations in this work were performed by means of the Quantum-ESPRESSO package [21], with periodic boundary conditions and plane wave basis set [22]. The calculations were carried out using Density Functional Theory with the Generalized Gradient Approximation with the exchange–correlation potential from the Perdew, Burke and Ernzerhof (PBE) approach [23] and the pseudopotentials used in this work were of ultrasoft Vanderbilt-type [24]. The performed tests for the energy cutoff showed that the basis set of plane waves with kinetic energy of 65 Ry is appropriate for our calculations. A sampling in the $\vec{k}$-points of $1 \times 1 \times 2$ for the $[Ln(cin)_3(H_2O)_3]{\cdot}Hcin$ series and of $1 \times 1 \times 1$ for the $[Ln_2(cin)_6(bpy)_2]$ were used, following Monkhorst–Pack method [25]. Dispersion interactions were estimated by an instantaneous dipole-induced-dipole term damped at short-range distances, as described by the PBE-D2 methodology [26,27]. The figures were made with the softwares XCrysDen [28] and Grace [29].

For the optimization calculations of $[Ln_2(cin)_6(bpy)_2]$ systems the crystallographic cells were used, because the space group of these complexes is the irreductible *P*-1 [20]. For the $[Ln(cin)_3(H_2O)_3]{\cdot}Hcin$ series the crystallographic cell (space group *R*3) [19] was reduced to a cell containing only one-third of the number of atoms from the original cell (133 and 399, respectively), Fig. 1 illustrates the procedure described previously [30].

The electronic density difference maps were made with a isosurface value of 0.003 electron/angstrom^3 isosurface value. In this analysis, the red clouds represent the positive values (established electronic cloud) and the blue surfaces represent the negative values (shifted electronic cloud) of charge difference. The maps were calculated following the equations:

$$\rho_{diff} = \rho_{system} - \rho_{ln} - \rho_{molecules} \tag{1}$$

where ρ_{diff} is the electronic density difference, ρ_{system} is the electronic density for the whole system, ρ_{ln} is the electronic density of the lanthanide metals and $\rho_{molecules}$ is the electronic density of all organic molecules.

$$\rho_{diff} = \rho_{system} - \rho_{ln+cin+water} - \rho_{hcin} \tag{2}$$

where ρ_{diff} is the electronic density difference, ρ_{system} is the electronic density for the whole system, $\rho_{ln+cin+water}$ is the electronic density of the lanthanide metals plus cin ligands plus water molecules in the system and ρ_{hcin} is the electronic density of all hcin ligands molecules.

$$\rho_{diff} = \rho_{system} - \rho_{ln+cin} - \rho_{bpy} \tag{3}$$

where ρ_{diff} is the electronic density difference, ρ_{system} is the electronic density for the whole system, ρ_{ln+cin} is the electronic density of the lanthanide metals with the cin ligands and ρ_{bpy} is the electronic density of all bpy ligands.

3. Results and discussion

3.1. Computational parameters

In order to reduce the processing time for the structure optimization calculations, the dispersion interactions, calculated by

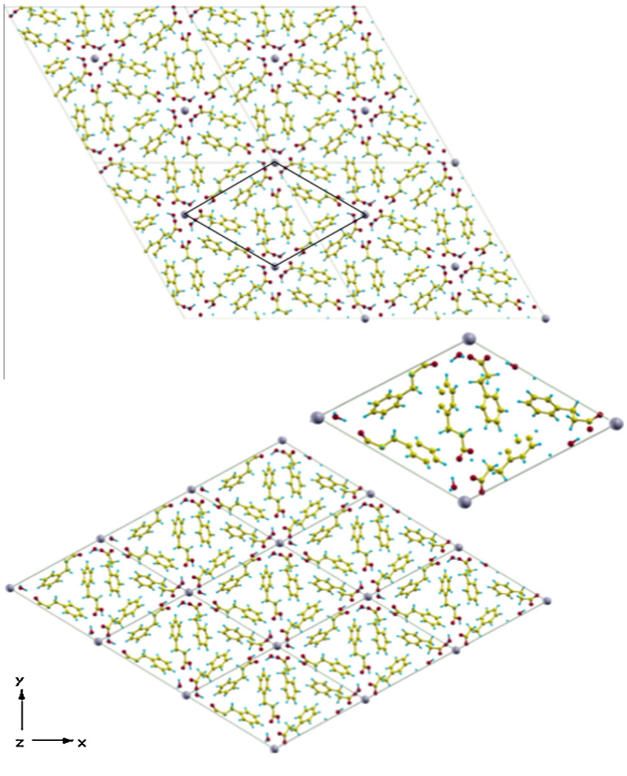

Fig. 1. Construction, step-by-step, of the reduced cell from crystallographic cell.