Structural and luminescent properties of two lanthanide-based coordination polymers with isonicotinate ligand

Yuri Dezotti[1*], Marcos A. Ribeiro[1], Frederico A. Lima[2], Wdeson P. Barros[1]

[1]*University of Campinas, Campinas, Brazil,*

[2]*Brazilian Synchrotron Light Laboratory, Campinas, Brazil*

*yuri.dezotti@gmail.com

The study of lanthanide (III) compounds has great interest due to properties such as luminescence and magnetism[1]. This work lies on the preparation, structural and luminescent characterization of the lanthanide coordination polymers with general formula $\{[Ln(ina)_2(H_2O)_4]Cl\}_n$ (Ln = Sm, Dy, and H*ina* stands to isonicotinic acid)[2]. The complexes were synthesized at room temperature in DMF by the mixture of H*ina* and $LnCl_3 \cdot 6H_2O$. The resulting solution was left for crystallization by slow evaporation. After 5 days pale yellow (compound **1**, Ln = Sm) or colorless (compound **2**, Ln = Dy) crystals with needle shape were formed. Both compounds **1** and **2** present very similar structures, crystallizing in the orthorhombic Pbcn and Pnc2 space group respectively. Their structures are made of a cationic infinite chain with chloride anions next to the metal centers. Each lanthanide ion is coordinated by eight oxygen atoms, of which four are from water molecules, and four are from isonicotinate ligands. Lanthanide ions are linked by two isonicotinate ligands in a bidentate bridging mode by the carboxylate groups. The coordination of the double-bridged carboxylate groups occurs in a distorted manner, resulting in the formation of complexes of low symmetry, being the lanthanide ions in a distorted trigonal dodecahedral geometry. The pyridine rings are positioned parallel to each other with the presence of hydrogen bonds between the nitrogen atoms of the pyridine and the hydrogen atoms of the water molecules coordinated to the lanthanide ions of adjacent chains. The solid-state luminescent spectra show characteristic emission bands of the Sm(III) and Dy(III) ions. The emission spectrum of **1**, performed with excitation wavelength at 270 nm present emission bands at 562 nm, 600 nm, 643 nm and 699 nm due to the transition $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2 and 11/2)[3]. The emission spectrum of **2**, performed with excitation wavelength at 270 nm, present emission bands at 482 nm, 574 nm, 662 nm, and 750 nm, due to the transition $^4F_{9/2} \rightarrow {}^6H_J$ (J = 15/2, 13/2, 11/2 and 9/2 respectively)[3]. In summary, two lanthanide-based coordination polymers with photoluminescent emission bands were studied, showing potential to the development of luminescent materials. Further work is being directed towards the synthesis of lanthanide coordination networks with both luminescent and magnetic properties.

References:

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