EU(III)- BASED ORGANIC/INORGANIC LAMELLAR HYBRIDS SELF-DIRECTED ASSEMBLED

Sónia Nobre [1,2*], *Rute A. Sá Ferreira* [1], *Carlos Brites* [1], *Carole Carcel* [2], *Michel W. C. Man* [2],
Joël J.E. Moreau [2], *Luís D. Carlos* [1]

[1]*University of Aveiro, Physics Department, CICECO, 3810-193 Aveiro, Portugal*
[2]*Ecole Nationale Supérieure de Chimie de Montpellier, Laboratoire Hétérochimie Moléculaire et Macromoléculaire (UMR-CNRS 5076) - 8, rue de l'école normale, 34296 Montpellier CEDEX 05, France*

snobre@ua.pt

Self-assembly of synthetic soft-matter components - such as polymers, liquid crystals, surfactants, colloids, and organic/inorganic hybrids - results in regular hierarchically organized structures. The importance of combining sol-gel methods and self-assembly routes to synthesize hierarchically structured organic/inorganic materials, has been highlighted recently.[1,2] Moreover, the recent advances in the structuring of sol-gel derived bridged silsesquioxanes represented an important breakthrough in the field of hierarchically organized hybrid materials. [3]

Since the beginning of the twentieth century, the radiative transitions of lanthanide ions have received academic and industrial attention. Moreover, the technological applications of lanthanide luminescence encompass not only fluorescent tubes and colour televisions, but also immunoassays, optical amplifiers and light-emitting diodes (LEDs).[4] The Eu^{3+} ion, in addition, is also considered the best choice to act as a probe to investigate the local structure around optically active ions in condensed matter. This is due to its relatively simple energy level diagram and the sensitivity of the energy positions and the intensity of its electronic transitions with the symmetry of the lanthanide local site.[5]

Here, we report on the structural and photoluminescence features of Eu(III)-modified bridged silsesquioxanes. The organic/inorganic precursor molecule - $(EtO)_3Si(CH_2)_3NH(C{=}O)NH-(CH_2)_{12}-NH(C{=}O)NH(CH_2)_3Si(OEt)_3$ -is formed of siliceous domains covalently bonded to an alkylene chain with 12 repeat units through urea functional groups. Sol-gel reactions using an acid catalyst, large excess of water and $EuCl_3$ gave rise to the formation of crystalline Eu(III)-based lamellar hybrids through a self-organization process. Three different Eu^{3+}-based hybrids were prepared. The hybrids were studied by X-ray diffraction (XRD), small angle diffraction (SAXS), scanning electronic (SEM) and atomic force microscopy (AFM), Fourier transform absorption mid-infrared (FT-IR), Fourier transform Raman and photoluminescence spectroscopies, ^{29}Si and ^{13}C solid state nuclear magnetic resonance,

The hybrids are the first lamellar organic/inorganic luminescent hybrids incorporating trivalent europium, figure 1 shows a SEM picture of one of the hybrids prepared. The emission spectra of these hybrids, figure 2, are composed of a broad band (380-560 nm), ascribed to electron-hole recombination's occurring within the urea cross-linkages and the siliceous nanodomains [2], and a series of straight lines, ascribed to Eu^{3+} intra-$4f^6$ transitions between the $^5D_0$ first excited state and the $^7F_{0-4}$ levels of the ground multiplet. Based on the photoluminescence features of the hybrids we were able to calculate the quantum efficiency and the number of water molecules coordinated to the Eu^{3+} ion.

References:

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Figures:

Figure 1 – SEM image of the Eu@L12-1 hybrid.

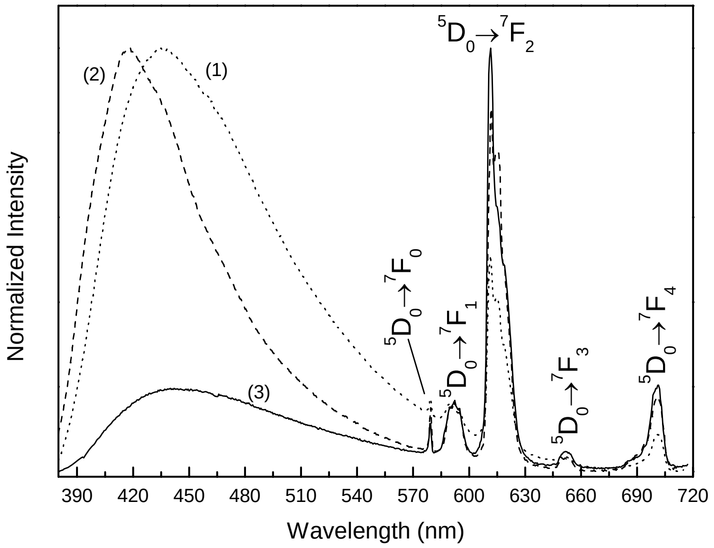

Figure 2 Emission spectra of the lamellar hybrids incorporating three different Eu3+ concentrations (1) 1.01%-Eu@L12 (2) 1.87%-Eu@L12 and (2) 15.0%-Eu@L12.