

# Bifunctional optical and magnetic nanocomposites containing Fe<sub>3</sub>O<sub>4</sub> grafted inorganic matrices and functionalize with RE<sup>3+</sup> complexes

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The design of bifunctional magnetic luminescent nanomaterials containing Fe<sub>3</sub>O<sub>4</sub> functionalized with rare earth ion complexes of calixarene and  $\beta$ -diketonate ligands is reported. Their preparation is accessible through a facile onepot method. These novel Fe<sub>3</sub>O<sub>4</sub>@calix-Eu(TTA) (TTA = thenoyltrifluoroacetate) and Fe<sub>3</sub>O<sub>4</sub>@calix-Tb(ACAC) (ACAC = acetylacetonate) magnetic luminescent nanomaterials show interesting superparamagnetic and photonic properties. Besides, the preparation of bifunctional nanocomposites, co-assembling photonic (RE<sup>3+</sup>) and magnetic (Fe<sub>3</sub>O<sub>4</sub>) features into single entity nanostructures is reported through a facile method, using Fe<sub>3</sub>O<sub>4</sub> as core nanoparticles, which were coated with SiO<sub>2</sub> shell and further grafted with Eu<sup>3+</sup> and Tb<sup>3+</sup> complexes. The sophisticated structural features and morphologies of the core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-(TTA-RE-L) nanomaterials were studied by SAXS analysis.

The core mean size ( $D_{\text{SAXS}}$ ), shell thickness  $\Delta R$ , cluster size  $\xi$  and fractal dimension  $D_F$  were determined by fitting the experimental SAXS data, corroborating through Transmission Electron Microscopy images. The DC magnetic properties at temperatures of 2 and 300 K were explored in support to the structural conclusions from SAXS and TEM analyses. The magnetic contributions of the RE<sup>3+</sup> ions to the magnetizations of the Eu<sup>3+</sup> and Tb<sup>3+</sup> nanocomposites were discussed. The photoluminescence properties of the Eu<sup>3+</sup> and Tb<sup>3+</sup> nanocomposites based on the emission spectral data and luminescence decay curves were studied (Fig.1). The experimental intensity parameters ( $\Omega_\lambda$ ), lifetimes ( $\tau$ ),

emission quantum efficiencies ( $\eta$ ) as well as radiative ( $A_{\text{rad}}$ ) and non-radiative ( $A_{\text{nrad}}$ ) decay rates were calculated and discussed, in addition, the structural conclusions from the values of the 4f-4f intensity parameters in the case of the Eu<sup>3+</sup> ion. These novel Eu<sup>3+</sup> and Tb<sup>3+</sup> nanocomposites may act as red and green emitting layers for magnetic and light converting molecular devices.

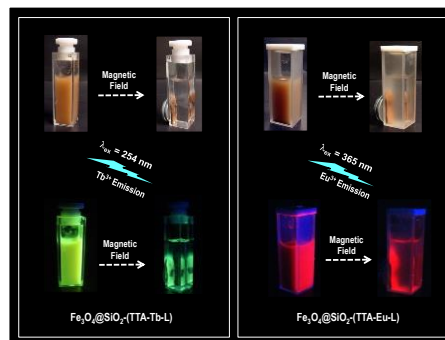


Fig. 1. Photographs of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-(TTA-RE-L), (RE: Eu and Tb) nanocomposites.

[1] Khan, L.U.; Brito, H.F.; Hölsä, J.; Pirota, K.R.; Muraca, D.; Felinto, M.C.F.C.; Teotonio, E.E.S.; Malta, O.L. *Inorg. Chem.*, **53** (2014) 2902.

[2] Khan, L.U.; Muraca, D.; Brito, H.F.; Moscoso-Londoño, O.; Felinto, M.C.F.C.; Pirota, K.R.; Teotonio, E.E.S.; Malta, O.L. *J Alloys and Compd.*, **686**, 453–466 (2016).

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