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Coordination polymer of Ln(III)-oxamate (Ln = Dy^{3+}, Gd^{3+}, Tb^{3+}, and Eu^{3+}): structural characterization and photoluminescent properties

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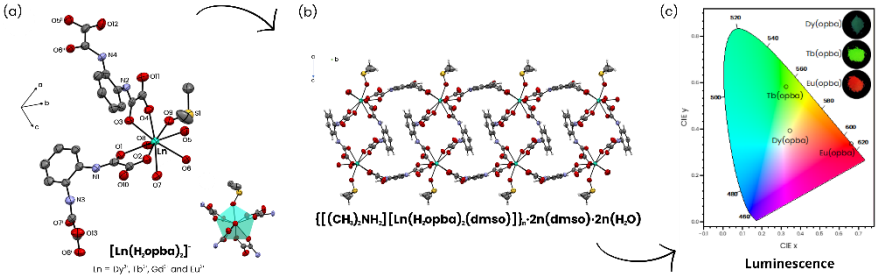
Lanthanide complexes have interesting optical properties attributed to the fact that the valence electrons of the lanthanide ions occupy innermost orbitals – 4f – which makes these ions, even when coordinated, maintain the properties of free ions.[1] In addition, these optical properties present a high rate of conversion of the absorbed energy into emitted energy when inserted in an adequate coordination environment.[2] Herein, we report a joint optical-structural study for the one novel series of lanthanide(III) complexes of general formula $\{[(CH_3)_2NH_2][Ln(H_2opba)_2(dmso)]\}n{\cdot}2n(dmso){\cdot}2n(H_2O)$ in which opba = o-phenylenebis(oxamate) and Ln = Dy^{3+}, Tb^{3+}, Gd^{3+}, and Eu^{3+}. The crystal structure determined by single-crystal X-ray diffraction shown polymeric compouds with each lanthanide(III) cation in a capped square antiprism symmetry nine-coordinate environment (LnO_9). The coordination sphere is constituted of nine oxygen, eight from two bis(bidentate) oxamate groups and one from the dmso molecule (Fig. 1a-b). Hydrogen bonds and π-π offset interactions lead to the 2D supramolecular arrangement. Solid-state photophysical measurements for the Dy^{3+}, Tb^{3+}, and Eu^{3+} reveal that oxamate ligands can sensitize the lanthanide(III) luminescence in the visible region, through an energy transfer process (“antenna effect”) (Fig. 1c). Furthermore, XEOL measurements revealed that luminescence is the main response to X-ray excitation. In other words, one can apply the complexes to detect radiation at different wavelengths without observing the degradation of the samples under the measured conditions.

Figure 1. Structure and color luminescence of $[Ln(H_2opba)_2]^-$ (Ln = Dy^{3+}, Tb^{3+}, Gd^{3+} and Eu^{3+}) complexes



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