

Intramolecular energy transfer process on bis- and tris-diketonate trivalent europium complexes with phosphine and arsine oxide ancillary ligands

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The present work reports about the investigation of the intramolecular energy transfer in the $[\text{Eu}(\beta\text{-diketonate})_2(\text{NO}_3)(\text{L})_2]$ and $[\text{Eu}(\beta\text{-diketonate})_3(\text{L})_2]$ compounds, where $\beta\text{-diketonate}$ = 2-thienoyltrifluoroacetone (TTA) and dibenzoylmethane (DBM), L = triphenylarsine oxide (TPAsO), tricyclohexylphosphine oxide (TCHPO) and tributylphosphine oxide (TBPO). The synthesized complexes were characterized by complexometric titrations, CHN elemental analysis, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis. Then spectroscopic properties of these systems were investigated based on the diffuse reflectance, excitation and emission spectra as well as decay times of $^5\text{D}_0$ emitting state. Experimental data of CHN analysis and complexometric titrations of the synthesized complexes are in agreement with theoretical data for their respective formulas. FTIR spectra in the infrared region show that the coordination of $\beta\text{-diketonate}$ and phosphine oxide ligands to the Eu^{3+} ions occurs by the oxygen atoms of C=O, As=O and P=O groups, respectively. The excitation spectra of the samples exhibited broad bands associated to $\text{S}_0\text{-S}_1$ transitions on coordinated organic ligands indicating an operative intramolecular energy transfer to the Eu^{3+} ion levels. Photoluminescent properties were investigated through intensity parameters Ω_2 and Ω_4 , spontaneous emission rates (A_{rad}), luminescence lifetime (τ), emission quantum efficiency (η). The highest values of η were found for $[\text{Eu}(\beta\text{-diketonate})_2(\text{NO}_3)(\text{L})_2]$ complexes in the range of 56-89%, due to the more efficient energy transfer between the Triplet state of the organic ligand and $^5\text{D}_0$ level of Eu^{3+} ion. It was observed that $[\text{Eu}(\beta\text{-diketonate})_3(\text{L})_2]$ compounds displayed the shortest luminescence lifetime probably owing to the back energy transfer process, which results in higher values of A_{nrad} . The intensity parameters Ω_2 and Ω_4 changed only slightly when auxiliary ligands were changed in the first coordination sphere of the $[\text{Eu}(\beta\text{-diketonate})_2(\text{NO}_3)(\text{L})_2]$ and $[\text{Eu}(\beta\text{-diketonate})_3(\text{L})_2]$ compounds. The high values of emission quantum efficiency suggest that the novel compound can be applied as Light Conversion Molecular Devices (LCMDs).

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