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Theoretical study of antenna-chromophore mechanism in luminescent lanthanide complexes

Rare-earth complexes are attracting attention as clean energy conversion materials utilizing chromophores for efficient photo-excited energy conversion that emit light having well defined narrow bands in different spectral ranges with long lifetimes and high quantum yields. The dithiocarbamate ligands (*dtc*, S2CR) are a special class of chromophores that have been poorly studied in relation to their sensitization ability of the lanthanide luminescence. The presence of dtc ligand in Ln(III)-phen complexes leads to alteration of the Ln luminescence. Moreover, the europium complex possesses unusual orange color, which changes to yellow under temperature decrease. Ln(S2CR)3(phen) complexes are suitable materials for novel electronic devices and precursors for preparation of lanthanide sulphide nanoparticles for photocatalytic applications. Various ambiguous mechanisms and interpretations of the observed optical features have been proposed in the previous reports. For detailed explanation of the photophysical properties of Ln(S2CR)3(phen) complexes (Ln = Eu, Sm; R = N(C2H5)2, N(C4H8)) we examined them by theoretical modelling in solution and solid phase at various temperatures.1 DFT/TDDFT/ωB97xD and multireference SA-CASSCF/NEVPT2 calculations with perturbative spin–orbit coupling corrections and semiempirical methods are applied to construct the Jablonski energy diagrams. The excited-state energy transfer mechanism is discussed regarding the competing excited state processes and possible sensitized mechanism of the metal-centered emissions. The theoretical estimations are supported by experimental data (single crystal X-ray diffraction analysis, powder XRD, TG-DTA, EPR, IR, UV-Vis, photoluminescence spectra). The combined theoretical and experimental research gives a new insight concerning: 1) ground state electron density distribution in the studied complexes, which produces a partial reduction of Eu(III); 2) interligand n(dtc)-⊠*(phen) charge transfer character of the first excited state (dark state), which favors the S1-T1 intersystem crossing or S1(phen)-Ln energy transfer over the S1-S0 (fluorescence); 3) appropriate T1-Ln(acceptor) energy resonance for effective excited state energy transfer. The established energy transfer mechanism and the key factors controlling the effective luminescence may help to carry out the targeted synthesis of new lanthanide materials with selected chromophore ligands with desired optical or magnetic (Eu2+) properties.

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