Spectroscopic aspects for the Yb^{3+} coordination compound with a large energy gap between the ligand and Yb^{3+} excited states

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We present the experimental and theoretical results that made it possible to propose the energy transfer mechanism for a Yb complex with a large energy gap between the ligand and Yb excited states using a theoretical model and experimental data. Absorption and emission spectroscopy in the 300–4 K range is used for the study of the Yb^{3+} compound with N-phosphorylated sulfonamide (**Na[YbL$_4$]**), which, despite the large energy gap, is characterized by high emission sensitization efficiency (η_{sens} = 40%) and relatively long Yb^{3+} emission lifetime (27 μs). The crystal structure of **Na[YbL$_4$]**, radiative lifetime (930 μs), refractive index (1.46), intrinsic (3.0%), and overall (1.3%) emission quantum yield were determined. To obtain the electronic properties of the **Na[YbL$_4$]**, a time-dependent density functional theory (TD-DFT) was performed. The intramolecular energy transfer (IET) rates from the excited states S_1 and T_1 to the Yb^{3+} ion as well as between the ligand and the ligand-to-metal charge transfer (LMCT) states were calculated. Once the intersystem crossing $S_1 \rightarrow T_1$ is not so effective due to a large energy gap between S_1 and T_1 (≈10000 cm^{-1}), it has been shown that the LMCT state acts as an additional channel to feed the T_1 state. Then, the T_1 can transfer energy to the Yb^{3+} $^2F_{5/2}$ energy level (), where is dominated by the exchange mechanism. Based on IET and a rate equation model, the overall emission quantum yield Q^L_{Ln} was simulated with and without the LMCT, this also confirmed that the pathway $S_1 \rightarrow$ LMCT $\rightarrow T_1 \rightarrow Yb^{3+}$ is more likely than the $S_1 \rightarrow T_1 \rightarrow Yb^{3+}$ one.

Słowa kluczowe

Ytterbium, Absorption spectroscopy, Luminescence, N-phosphorylated sulfonamide, Energy transfer, Theoretical calculations