

MULTIPHOTONIC EMISSION IN THE COMPLEXES OF LANTHANIDS

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Lanthanide coordination compounds (Ln CCs) attract much attention due to their luminescent properties. The use of an auxiliary ion that partially replaces the luminescent ion in its crystallographic positions allows one to further influence the luminescent properties. In the present work to study the influence of the auxiliary ion we selected bimetallic lanthanide terephthalates $(\text{Ln}_x\text{M}_{1-x})_2(\text{tph})_3(\text{H}_2\text{O})_4$ and dehydrated $(\text{Ln}_x\text{M}_{1-x})_2(\text{tph})_3$ (Ln = Tb, Eu; M = Y, Gd) since monometallic $\text{Ln}_2(\text{tph})_3(\text{H}_2\text{O})_4$ are isostructural in the whole row, and complexes of Ln = Tb or Eu possess high quantum yields.

Starting the investigation on $(\text{Eu}_x\text{Y}_{1-x})_2(\text{tph})_3(\text{H}_2\text{O})_4$ luminescence we found that when luminescent Ln = Eu was substituted with non-luminescent Ln = Y, an amazing feature called multiphotonic emission was discovered: the quantum yield of luminescence remained unchanged over a wide range of luminescent ion concentrations of $0.005 < x < 1$. This effect consists in multiple photon emission by a single Eu ion after a single excitation, and is witnessed by biexponential character of luminescence decay curve [1]. We suggested that multiphotonic emission can be caused by (1) a large ratio of the observed lifetimes of the ligand and lanthanide ($\tau_{\text{obs}}(\text{L})/\tau_{\text{obs}}(\text{Ln})$) or (2) high efficiency energy transfer across the crystal, which is characterized by a large exciton free path length. We increased the ratio $\tau_{\text{obs}}(\text{L})/\tau_{\text{obs}}(\text{Ln})$ by replacing Eu with Tb, known for a longer lifetime, or by dehydrating the compounds. It turned out that for $(\text{Tb}_x\text{Y}_{1-x})_2(\text{tph})_3(\text{H}_2\text{O})_4$ the range of constant quantum yield and lifetime decreased down to $0.1 < x < 1$ due to smaller $\tau_{\text{obs}}(\text{L})/\tau_{\text{obs}}(\text{Ln})$ ratio, and the character of luminescence decay became monoexponential, witnessing no multiphotonic emission.

Dehydration did not lead to a change in the range of effect manifestation, but allowed to detect the luminescence concentration quenching, which was expressed in a decrease in the observed lifetime with an increase in the fraction of the luminescent ion. The analysis of these data allowed determining the criteria of concentration quenching in the Ln CC, which are associated with the values of the lifetimes and volume concentrations of the luminescent ion. The use of paramagnetic M = Gd instead of diamagnetic M = Y did not lead to a change in the range of manifestation of the multiphotonic emission, however, the intensity of ligand luminescence decreases due to the increase in the efficiency of intersystem crossing (ISC).

To study the influence of the free path length of an exciton, which for $(\text{Eu}_x\text{Y}_{1-x})_2(\text{tph})_3(\text{H}_2\text{O})_4$ was estimated as $\lambda = 40$ Å, bimetallic $\text{Eu}_x\text{Y}_{1-x}(\text{dbm})_3(\text{Phen})$ ($\lambda = 250$ Å) were chosen. It turned out that the multiphotonic emission is actually observed in $(\text{Eu}_x\text{Gd}_{1-x})(\text{dbm})_3(\text{Phen})$ in the range of $0.1 < x < 1$, which confirms the role of the exciton free path length as one of the reasons for the appearance of the effect. In addition, the use of paramagnetic gadolinium in place of diamagnetic yttrium in $(\text{Eu}_x\text{M}_{1-x})(\text{dbm})_3(\text{Phen})$ leads to an increase in the quantum yield due to the increase in the efficiency of ISC [2].

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