

Polymer Ligands as Energy Donors for Lanthanide Luminescence

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The design of complexes of lanthanide ions with encapsulating ligands is an important theme in the field of supramolecular chemistry because it offers the possibility to obtain stable luminescent compounds, which can be used as emitters in organic electroluminescent devices (OLED) or for plastic fiber lasers and amplifiers. The luminescent properties of the metal ion can be optimized by a suitable choice of the ligand. There are two principal ways of increasing the weak luminescence of lanthanide metal ions. First of all, it is necessary to suppress the environmental vibronic quenching by a suitable encapsulating ligand. Second, we have to overcome the low molar absorption coefficients of lanthanide metal ions. In complexes of lanthanide ions with some strongly absorbing ligands, an intense luminescence of the ion may be obtained by the antenna effect, which is a light conversion process via absorption – energy transfer – emission involving distinct absorbing (ligand) and emitting (metal ion) components. In such a process, the quantities contributing to the luminescence intensity are: (1) the intensity of the ligand absorption, (2) the efficiency of the ligand-to-metal energy transfer and (3) the efficiency of the lanthanide metal luminescence. The synthesis of strongly fluorescent lanthanide complexes with encapsulating ligands is based, for example, on 2,2'-bipyridine, 2,2'-biquinoline cryptands, or on their *N*-oxide derivatives. The 2,2'-bipyridine group has also been used as a building block in the synthesis of branched macrocyclic, tripode and tetrapode ligands.

Recently^{1,2}, we replaced the low-molecular-weight pyridine cryptands with poly(2- and 4-vinylpyridine)s or poly(2- and 4-vinylpyridine *N*-oxide)s. The fluorescence of the polymer ligand (donor) was overlapped with the absorption of the lanthanide metal (acceptor) and a ligand-to-metal energy transfer was observed. The increase in Tb³⁺ luminescence intensity was due to both the replacement of the inner-coordinated solvent (water or methanol) molecules and ligand-to-metal energy transfer.

Alternating and statistical copolymers of 9-vinylcarbazole with diethyl fumarate (**1**), diethyl maleate (**2**), methacrylic acid (**3**), maleic anhydride (**4**), or maleic acid (**5**) were synthesized and characterized³. These copolymers were tested as polymer ligands, which would have the ability to suppress the environmental vibronic quenching of lanthanide metal ion and, simultaneously, to function as energy donors in the ligand-to-metal energy transfer processes. Time-resolved luminescence of the [Tb(III)-ligand] complexes in common and deuterated solvents (Fig. 1) revealed that the complexing properties of copolymers **3** or **5** are stronger than those of **1** or **2**. Consequently, the strong binding affinity decreases the ligand-to-metal (donor-acceptor) distance and gives rise to an efficient ligand-to-metal energy transfer. Thus, the long-lived emission intensities (³D₄→⁷F₆, ⁵D₄→⁷F₅, ⁵D₄→⁷F₄, ⁵D₄→⁷F₃) of the [Tb(III)-**3**], [Tb(III)-**5**], and [Tb(III)-**1** or **2**] complexes were found to be eight times, five times, and less than twice that of Tb³⁺, respectively (Fig. 2).

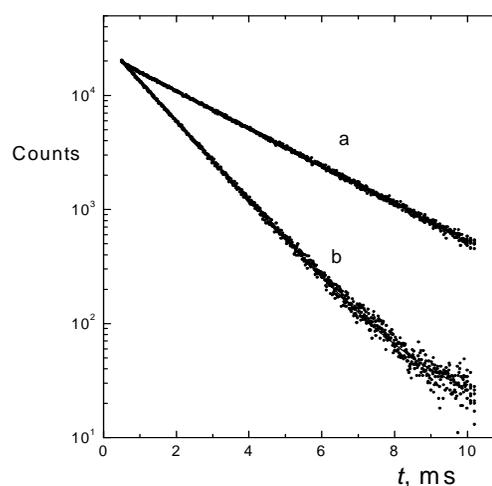


Fig. 1: Time-resolved luminescence ($\lambda_{\text{exc}} = 340 \text{ nm}$, $\lambda_{\text{em}} = 545 \text{ nm}$) of the [Tb(III)-**5**] complex measured in 1,4-dioxane/MeOD (a) or 1,4-dioxane/MeOH (b); $\tau_{\text{OD}} = 2.62 \text{ ms}$, $\tau_{\text{OH}} = 1.245 \text{ ms}$, $[\text{Tb}^{3+}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[\mathbf{5}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$.

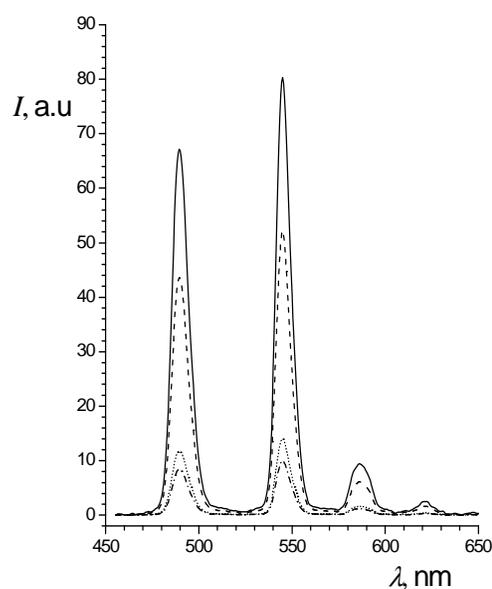


Fig. 2: Luminescence emission spectra ($\lambda_{\text{exc}} = 340 \text{ nm}$) of Tb³⁺ in the absence (dash-and-dot line) and presence of the ligands; **1** or **2** (dotted line for both), **3** (solid line), and **5** (dashed line) taken with the 0.05 ms delay. $[\text{Tb}^{3+}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{ligand}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$.

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