



Approaches for variation of luminescence characteristics of lanthanide coordination compounds

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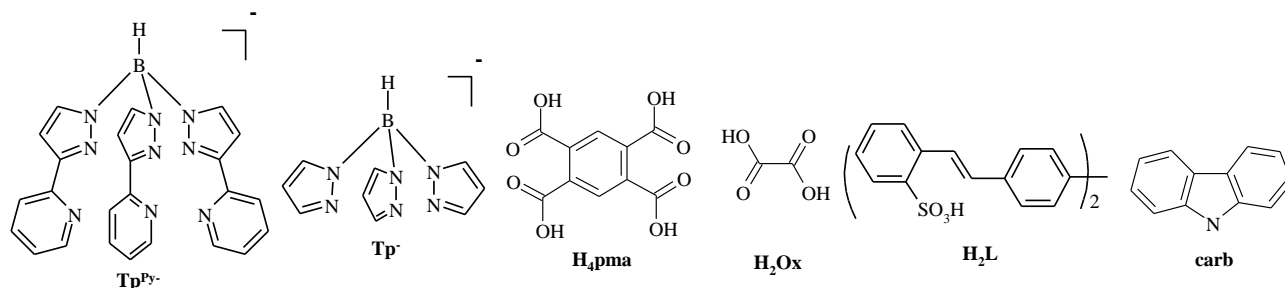
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The electronic structure of the lanthanide ions provides for high purity and reproducibility of the emitted color, so these compounds are prospective candidates as components of materials for lasers, displays, biomarkers, *etc.* At the same time, variation of luminescence color and prediction of emission characteristics is still a challenging task. The aim of this study was to search for ways to tune the luminescence properties of lanthanide coordination compounds. Two approaches were studied: (i) the variation of different lanthanide ions' ratio in their complexes and (ii) generation of molecular structures with a highly luminescent anion and inclusion of carbazole in the crystal lattices of these complexes.

For (i) two types of mixtures (**A** and **B**) with composition $x[(\text{Tp}_2\text{Eu})_2\text{Ox}] \cdot (1-x)[(\text{Tp}_2\text{Ln})_2\text{Ox}]$ and $x[(\text{Tp}^{\text{Py}}\text{Eu})_2\text{pma}] \cdot (1-x)[(\text{Tp}^{\text{Py}}\text{Eu}_x\text{Ln}_{1-x})_2\text{pma}]$ ($\text{Ln} = \text{Tb}, \text{Gd}, x = 0.0, 0.1, 0.5, 0.9, 1.0$) were obtained and the metals' ratios were confirmed by X-ray fluorescence spectroscopy. Mixtures **A** were obtained by cocrystallization of the different lanthanide ions' complexes from solution in the appropriate ratio, while mixtures **B** were obtained by mechanical grinding of appropriate quantities of the respective homodinuclear compounds. In the luminescence spectra of mixtures of Eu^{3+} and Tb^{3+} compounds, the emission from both these ions appeared with quantum yields up to 30% and 80%, respectively. This allowed us to achieve variation of the emission color in the range red-yellow-green by changing the metals' ratio. In type **A** mixtures, sensitization of Eu^{3+} emission was observed, whereas in the **B** ones, Tb^{3+} to Eu^{3+} energy transfer didn't occur. For mixtures of Eu^{3+} and Gd^{3+} complexes, Eu^{3+} -centred emission was observed in the luminescence spectra; in the type **A** mixtures, sensitization was more efficient than in the type **B** mixtures and this effect was more significant in the case of compounds with pma⁴.

To study the approach (ii), complexes with composition $(\text{Tp}_2\text{Ln})_2\text{L}$, $(\text{Tp}^{\text{Py}}\text{Ln})_2\text{L}$, $(\text{Tp}^{\text{Py}}\text{Ln})_2\text{L} \cdot 0.7\text{carb}$, Ln_2L_3 and $\text{Ln}_2\text{L}_3 \cdot 0.7\text{carb}$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Gd}, \text{Dy}$) were synthesized and characterized by single crystal X-ray diffraction and luminescence spectroscopy. It was shown that in Tb^{3+} , Gd^{3+} and Dy^{3+} complexes, the emission of L^{2-} appeared, its color was dependent on the structure of the compound and varied from violet to cyan. Carbazole inclusion showed no significant influence on the emission colors of the compounds studied.

Figure 1: Ligands used in this study.



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