How minor structural changes generate major consequences in photophysical properties of RE coordination compounds : resonance effect, LMCT state.

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Streszczenie

Lanthanide coordination compounds of the formula $Na[Ln(L)_4]$ (**1Ln**), where Ln = La^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, L = $[L]^-$ and HL = dimethyl(4-methylphenylsulfonyl)amidophosphate, were synthesized. Their structural and spectroscopic properties were discussed in detail based on X-ray diffraction measurements, IR spectroscopy, absorption and emission spectroscopy at 293 and 77 K and theoretical calculations of the intramolecular energy transfer (IET) rates. DFT calculations were used to investigate the **1Ln** electronic properties required to calculate the transition rates. 30 and 22 pathways of intramolecular nonradiative energy transfer were examined in the case of **1Eu** and **1Tb**, respectively. It is shown that the main pathway for sensitization of the lanthanide emission is either the triplet (**1Eu**) or singlet (**1Tb**) transfer, occurring mainly through the exchange mechanism. The energy rates for energy transfer from S_1 and T_1 equal (**1Eu**), (**1Eu**) and (**1Tb**), (**1Tb**). The crucial role of the $^7F_5$ level in the energy transfer process of **1Tb** and the participation of the LMCT state in the depopulation of the ligand singlet state of **1Eu** were demonstrated. The influence of the resonance effect on the splitting of the $^7F_1$ level in **1Eu** was analyzed. By comparing the properties of**1Ln** with the properties of **2Ln** coordination compounds, sharing the same ligand and crystallizing in the same crystallographic system (monoclinic), but with a different space group, it is demonstrated how slight structural changes can affect the photophysical properties of Ln compounds.

Słowa kluczowe

Lanthanide, Phosphorylated sulfonamides, energy transfer, Antenna effect, crystal structure, Resonance effect

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