

CIRCULARLY POLARIZED LUMINESCENCE OF TETRA-NUCLEAR EUROPIUM (III) COMPLEXES

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Circularly Polarized Luminescence (CPL) is the spontaneous emission of left or right circularly polarized radiation by chiral-luminescent molecular systems. Among various CPL-active substances, optically active trivalent lanthanide coordination compound is one of the susceptible materials that exhibit intense CPL property from their f-f transition. In the present study, tetra-nuclear europium complexes with achiral bis- β -diketonates (BTP) and chiral bis(((4)-4-phenyl-2-oxazoliny]pyridine (Ph-Pybox) ligands, $\text{Eu}_4(\text{BTP})_6(\text{Ph-Pybox})_4$ were synthesized. The trivalent Europium (III) ions are nona-coordinated with six oxygen atoms from the BTP ligands and three nitrogen atoms from the Ph-Pybox ligands. They crystallize in monoclinic system with a space group of $C2$. X-ray analysis reveals the presence of π - π stacking ligand-ligand interactions between the side phenyl group of Ph-Pybox ligands and the β -diketonates moiety of BTP ligands. It is believed that these interactions are responsible for the formation of the square-like, tetra-nuclear complexes.

NMR comparison study was performed between the Yttrium and Europium tetra-nuclear complexes, due to the paramagnetic effect of the Europium ions which causes a broadening of the NMR peaks and spreading of the chemical shift. Both give 24 NMR resonance peaks. From the NMR analysis, there are two different BTP ligand chemical environments, out of the six BTP ligands. Thus, the complexes exhibit D_2 symmetry in solution. Besides, the NMR analysis also indicates the presence of the ligand-ligand interactions as mentioned above.

The tetra-nuclear europium complexes, $\text{Eu}_4(\text{BTP})_6(\text{Ph-Pybox})_4$ are CPL active, CPL signature of $\text{Eu}_4\text{BTP}_6[(R)\text{-Ph-pybox}]_4$ and $\text{Eu}_4\text{BTP}_6[(S)\text{-Ph-Pybox}]_4$ show a nearly complete mirror signals with each other. They show g_{lum} value of ca. |0.2|, which are about double if compare with the analogue mononuclear complexes. In addition, the other photo-physical characterizations suggest that tetra-nuclear assembly is identical in both solution and solid state.

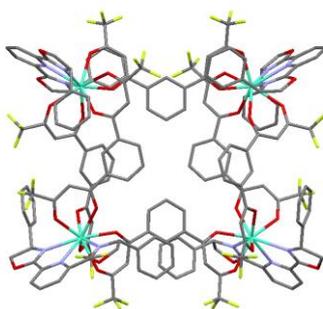


Figure 1. Molecular structure of $\text{Eu}_4(\text{BTP})_6[(R)\text{-ph-pybox}]_4$ (without hydrogen atoms).

[1] J. Yuasa, T. Ohno, K. Tsumatori, Y. Hasegawa, T. Kawai *J. Am. Chem. Soc.*, 133 (2011) 9892-9902.

[2] *Handbook on the Physics and Chemistry of Rare Earths Volume 34*. Elsevier B.V. 2005, pp 289-357.