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Direct Visualization of Energy-transferred Excited State in Eu Complex

K. Sugimoto¹, A. Fujiwara¹, M. Takata², H. Tanaka³, M. Hasegawa⁴

¹JASRI/SPring-8, Reserach & Utilization Division, Hyogo, Japan, ²RIKEN SPring-8 Center, Hyogo, Japan, ³Shimane University, Department of Material Science, Matsue, Japan, ⁴Aoyama Gakuin University, Department of Chemistry and Biological Science, Sagamihara, Japan

Highly luminescent lanthanide (Ln) complexes have attracted much attention because Ln³⁺ ions show long-lived ff-emissions with narrow band shape. Their unique photo-optical properties are promising for the design of light-emitting materials and sensing devices. Although the ff-emissions are essentially weak because of Laporte forbidden, chelate ligands is effective to strengthen the intramolecular energy transfer from photo-excited organic ligands to Ln³⁺ ions. The direct evidence of energy transfer from ligands to Ln³⁺ and details of excited state, however, are still veiled. Here, we report direct visualization of energy-transferred excited state in Eu complex with a hexadentate ligand (L) consisting of two bipyridine moieties bridged by an ethylenediamine unit, [Eu³⁺(L)(NO₃)₂](PF₆) (Eu(L))[1] by Maximum Entropy Method (MEM) charge density[2] and electrostatic potential analysis[3] based on SR X-ray diffraction. First, we confirmed that the electron numbers of Eu and ligand L in the excited state are the same as those in the ground state, which is a direct evidence of energy transfer instead of charge transfer. Next, we observed charge re-distribution in the Eu ion and the ligand L. The electrostatic potential distributions calculated using MEM charge density give an experimental evidence for the existence of polarization of ligand L both in the ground and photo-excited states. The orientation polarization in the ground state changed during pumping at 315 nm, and the charge re-distribution are qualitatively consistent with a theoretical prediction. This characteristic luminescence behavior based on the energy relaxation process have not been detected by fundamental crystal structural analysis. We have succeeded in visualization of subtle but important change due to energy transfer in the mononuclear Europium complex with hexadentate ligand at the first time.

[1] M. Hasegawa, H. Ohtsu, D. Kodama, T. Kasai, S. Sakurai, A. Ishij, K. Suzuki, *New J. Chem.*, 2014, *in press*, [2] M. Takata, *Acta Cryst.* 2008, A64, 232-245, [3] H. Tanaka, Y. Kuroiwa, M. Takata, *Phys. Rev. B*, 2006, 74, 172105

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