

## VT-VH-MCD Spectroscopic Study of the Magnetic Interaction in the Excited States of Lanthanide-Porphyrin Complexes with Different Hetero-Cyclododecane Ligands

(<sup>1</sup>Department of Chemistry, School of Science, Osaka University) ○Langit Cahya Adi,<sup>1</sup>  
Anas Santria,<sup>1</sup> Naoto Ishikawa,<sup>1</sup>

**Keywords:** Magnetic circular dichroism, lanthanides, porphyrin

The electronic interactions between orbital angular momentum of porphyrin denoted as **L** and the total angular momentum of lanthanides (III) **J** in lanthanide (Ln)-porphyrinoid molecular systems were investigated with variable-temperature and variable-magnetic field magnetic circular dichroism (VT-VH-MCD) spectroscopy where lanthanide(III) are Tb(III) and Dy(III). Here, investigations were carried out on [Ln(TPP)Crown]Cl and [Ln(TPP)Azacrown]Cl (TPP: 5,10,15,20-tetraphenylporphyrinato; Crown: 12-crown-4 ether or 1,4,7,10-tetraoxacyclododecane; Azacrown: 1-aza-12-crown-4 ether or 1,4,7-Trioxa-10-azacyclododecane). The aim of this research was to investigate how **J–L** interaction ( $\Delta_{JL}$ ) is tuned by symmetric non-aromatic ligand (12-crown-4 ether) and asymmetric ligand (1-aza-12-crown-4 ether). Furthermore, *ab-initio* RASSCF calculation was performed to investigate the electronic energy states at ground state, the angular momentum at excited states, and magnitude of **J–L** interaction.

The interaction was determined by simulation-based fitting to experimental  $A_1/D_0$  ratios ( $A_1$ : the A-term intensity,  $D_0$ : the oscillator strength of the band) for Q(0,0) and Q(1,0) bands, detected in visible wavelength region, and B(0,0) band, appearing near UV region, all of which correspond to the  $\pi-\pi^*$  transition within porphyrin. By treating **J** to be constant and **L** as a variable, it was found that different symmetries of the non-aromatic ligands did not alter orbital angular momentum of the complexes. However, the interaction was observed to increase in all bands when the symmetric ligand was replaced with the asymmetric one.

