# Ferromagnetic-type Interaction between Two Angular Momenta in π-π* Excited State of Lanthanide(III)-Monoporphyrin Complex

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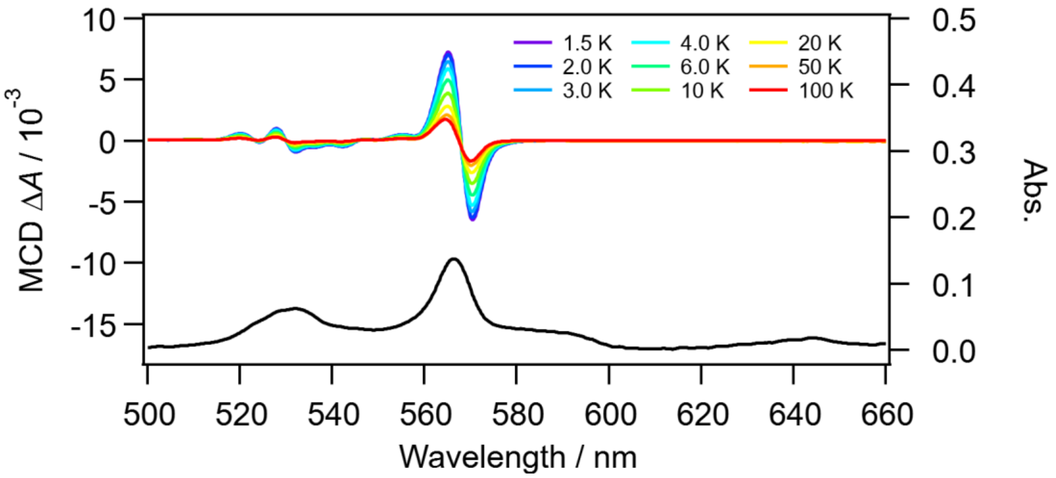
This study aims to investigate the electronic interaction in the π–π* excited state of terbium(III) octaethylporphyrinato complex, [Tb(OEP)(cyclen)]Cl (OEP = Octaethylporphyrin; cyclen = 1,4,7,10-tetraazacyclododecane), using magnetic circular dichroism (MCD) spectroscopy. The complex exhibits distinct MCD A-term patterns corresponding to the Soret and Q absorption bands. These patterns show strong temperature dependence and significant non-linearity in the magnetic field dependence, indicating the interaction between two angular momenta: the total angular momentum **J** of 4f-electronic system and the orbital angular momentum **L** of the photoexcited cyclic π–conjugated system.

The coupling between **J** and **L** is parallel, resulting in a ferromagnetic-type interaction. The magnitude of this interaction is estimated by a least-squares fitting to the experimental $\mathcal{A}_1/\mathcal{D}_0$ ratios, with $\Delta_{JL}$ and $|L_z|$ as parameters, where $\mathcal{A}_1$ represents A-term intensity and $\mathcal{D}_0$ represents the dipole strength.[1,2] At Q band, the $\Delta_{JL}$ matches that of [Tb(TPP)(cyclen)]Cl, while $|L_z|$ value is twice a large. Ab initio calculations support these findings, showing ferromagnetic-type interaction between $L_z$(f) and $L_z$(π). Although $L_z$(π) is larger in $[\mathrm{Tb(OEP)(cyclen)}]^+$, the $\Delta_{JL}$ remains comparable to that in $[\mathrm{Tb(TPP)(cyclen)}]^+$, offering new insights into the magnetic interactions of lanthanide porphyrins.



1) K. Kizaki, A. Fuyuhiro, T. Fukuda, N. Ishikawa, *Chem. Commun.*, 2017, *53*, 6168; 2) A. Santria, and N. Ishikawa, *Inorg. Chem.* **2020**, *59*, 14326