Classification of Crystallization Behavior and Chirality Control of M^{II}-Ln^{III}-M^{II} Trinuclear Complexes exhibiting Absolute Spontaneous Resolution

([1]*Graduate School of Natural Science and Technology, Okayama University*, [2]*Research Institute for Interdisciplinary Science, Okayama University*) ○Kazuma Takahara,[1] Yuuki Horino,[1] Yukinari Sunatsuki,[1] Takayoshi Suzuki[1,2]

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A series of trinuclear complexes, $[(M^{II}L)_2Ln^{III}]NO_3$ (M-Ln-M), which were synthesized from achiral tripodal Schiff base ligand H_3L (Fig. 1), 3d-metal acetate $M(OAc)_2$, and lanthanoid nitrate $Ln(NO_3)_3$ in a 2:2:1 molar ratio, have two asymmetric centers at M^{II} sites derived from twist of the tripodal arms of the ligand. In the most cases, the absolute configuration of the resulting molecule was homochiral, i.e., *Λ,Λ* and *Δ,Δ* enantiomers.

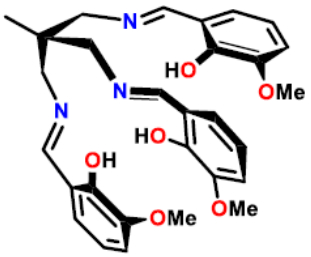

Fig. 1 The structure of H_3L

Among these complexes, a specific combination of the metal ions, such as Zn-Tb-Zn (Fig. 2), resulted exclusively in a particular enantiomorphic crystals (*Λ,Λ* conglomerates). This novel phenomenon is named as "Absolute Spontaneous Resolution."

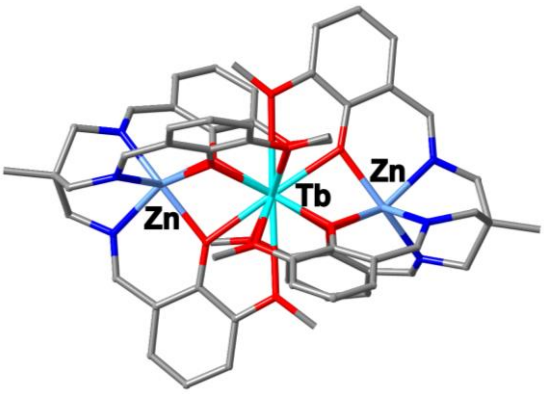

Fig. 2 Crystal structure of *Λ,Λ*-Zn-Tb-Zn

In this study, we have classified the crystallization behaviors of these complexes dependent on the kind of lanthanoid ion. In the case of the Mn^{II} complexes, it was revealed that all lanthanoids exhibited at least total spontaneous resolution (i.e., only left-handed *Λ,Λ* enantiomorphic crystals were deposited in a crystallization experiment). On the other hand, crystallization behaviors of the Zn^{II} complexes were obviously affected by the lanthanoids. For instance, Zn-Y-Zn provided both *Λ,Λ* and *Δ,Δ* conglomerates in an experiment (i.e., a normal spontaneous resolution) and Zn-La-Zn was crystallized as a racemic compound which contains both enantiomers in a crystal.

Also, the control of chiral crystallization by addition of seed crystals was attempted. For instance, when *Δ,Δ*-crystals of Zn-Y-Zn were crushed and seeded into a saturated Zn-Tb-Zn solution, all of the resulting crystals were *Δ,Δ*-conglomerates of Zn-Tb-Zn, which have never been obtained by synthesis and recrystallization in a normal condition.