

Multiple-decker phthalocyaninato dinuclear terbium (III) single-molecule magnets with dual-magnetic relaxation processes

In principle, a single spin can be used as a 'bit' of information to prepare high-density storage and quantum computing devices [1]. Quantum tunneling of the magnetization (QTM) between double well potentials, which is a prominent, characteristic property of single molecule magnets (SMMs), underpins this concept. SMMs behave like magnets with frozen spins, and a potential exists across two energy barriers at low temperatures, known as the blocking temperature (T_B). In the case of 3d cluster SMMs, an easy axis-type magnetic anisotropy, which is represented by a negative zero-field splitting constant (D), occurs due to magnetic interactions among high-spin 3d metal ions in the clusters. Researchers have been studying complexes with higher values of T_B than that of a well-known Mn cluster. In recent years, lanthanoid(III)-phthalocyaninato (Ln(III)-Pc) sandwich complexes have been shown to be SMMs, which originates from the ligand field (LF), and researchers have utilized their QTM and magnetic relaxation behavior [2]. Ln(III)-Pc molecules showing SMM behavior have significantly large axial magnetic anisotropies, which occur by a different mechanism than those for known 3d metal cluster SMMs. On the other hand, in the case of Ln(III) SMMs, the LF of the Ln^{3+} ion controls the anisotropy. The LF potential around a Tb^{3+} ion ($4f^8$) with a total angular momentum (J) of 6 splits the ground multiplet so that the lowest sublevel has the largest J_z value ($|J_z| = 6$, corresponding to up/down spin states) and large energy gaps to the remaining sublevels. Being able to control the QTM of Ln(III)-Pc SMMs will make it possible to design new spintronics devices.

In this study, we report the molecular structure and magnetic relaxation properties of dinuclear Ln(III)-Pc multiple-decker complexes: quadruple-decker $\{[\text{Ln}(\text{obPc})_2]\text{Cd}[\text{Ln}(\text{obPc})_2]\}$ (**1**: Ln = Tb^{3+} , **2**: Ln = Dy^{3+}), triple-decker $\text{Ln}_2(\text{obPc})_3$ (**3**: Ln = Tb^{3+} , **4**: Ln = Dy^{3+}), double-decker $\text{Ln}(\text{obPc})_2$ (**5**: Ln = Tb^{3+} , **6**: Ln = Dy^{3+}), and quintuple-decker $\{[\text{Tb}(\text{obPc})_2]\text{Cd}(\text{obPc})\text{Cd}[\text{Tb}(\text{obPc})_2]\}$ (**7**). Our work shows that the SMM/QTM properties can be fine-tuned by introducing weak intermolecular magnetic interactions in controlled spatial arrangements of lanthanides ions [3].

In order to control the spin orientation in the molecules, we designed **1–7** so that the two Ln^{3+} ions are along the anisotropy axis (Fig. 1). The SMM behavior of dinuclear Ln(III)-Pc multiple-decker complexes (Ln = Tb^{3+} and Dy^{3+}) with large energy barriers and slow-relaxation behavior were explained by using X-ray crystallography (Figs. 2(a) and 2(b): BL02B1 and BL40XU beamlines) and static and

dynamic susceptibility measurements [3]. There was a decrease in the in-phase (χ_M') and out-of-phase (χ_M'') peaks in different T ranges, which were dependent on the frequency (f), indicating that dinuclear Ln(III)-Pc multiple-decker complexes (Ln = Tb^{3+} and Dy^{3+}) are SMMs. In micro-SQUID experiments, quadruple-decker **1** and **2** clearly exhibited SMM behavior (Fig. 2(c)) [3].

Dinuclear Tb(III)-Pc multiple-decker SMMs **1**, **3**, and **7** exhibited dual magnetic relaxation processes (Fig. 3) [3]. These magnetic relaxation processes have T -independent (τ_1) and T -dependent (τ_2) regimes in the low T region. The dual magnetic relaxation behavior was observed not only for discrete dinuclear Tb(III)-Pc complexes but also for the spatially closed Tb(III)-Pc double-decker complex **5** [4]. On the other hand, mononuclear system **5a**, where the effects of intermolecular interactions in **5** have been eliminated, exhibited only a single magnetic relaxation process [4]. In the case of the dinuclear Tb(III)-Pc complexes, the value of T_B and the distance between Tb^{3+} ions follows the strength of the dipole-dipole interactions (D_{ij}), and T_B shifted to the high- T side, indicating that the Tb^{3+} – Tb^{3+} interactions affect the spin dynamics (Fig. 2(d)). Moreover, the presence of the dual magnetic relaxation processes is related to the distance between Tb^{3+} ions sites in the dinuclear complexes (Fig. 3).

In other words, the magnetic relaxation mechanism depends heavily on the dipole-dipole (f - f) interactions between the Tb^{3+} ions in the dinuclear systems [3]. The above results demonstrate that even weak exchange interactions can have a large influence on the quantum properties of Ln(III)-Pc type SMMs. Two magnetic relaxation processes occur under the

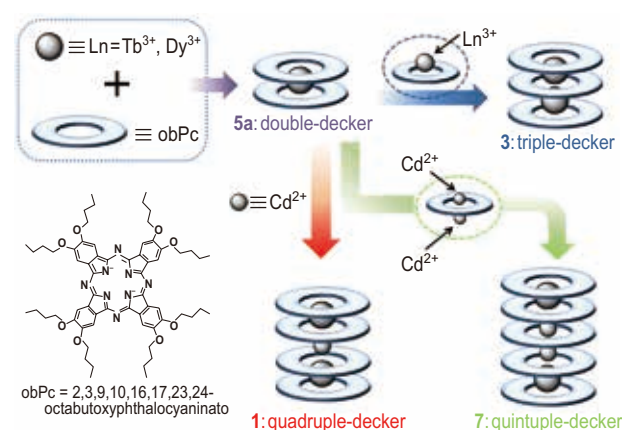


Fig. 1. Schematic illustration of sequential synthetic routes for multiple-decker phthalocyaninato dinuclear lanthanoid (III) single-molecule magnets [3].

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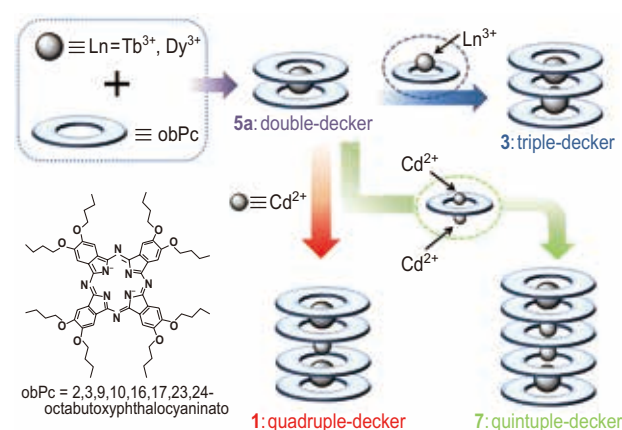


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