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$^6$) 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 \{[Ln(obPc)$_2$]Cd[Ln(obPc)$_2$]$_2$\} (1: Ln = Tb$^{3+}$, 2: Ln = Dy$^{3+}$), triple-decker Ln$_2$(obPc)$_3$ (3: Ln = Tb$^{3+}$, 4: Ln = Dy$^{3+}$), double-decker Ln(obPc)$_2$ (5: Ln = Tb$^{3+}$, 6: Ln = Dy$^{3+}$), and quintuple-decker \{[Tb(obPc)$_2$]Cd(obPc) Cd[Tb(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 ($\chi'\chi''$) and out-of-phase ($\chi'\chi''$) 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 ($\tau_1$) and $T$-dependent ($\tau_2$) regimes in the low $T$ region. The dual magnetic relaxation behavior was observed not only for discreet 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 ($I-f$) 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
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**Fig. 1.** Schematic illustration of sequential synthetic routes for multiple-decker phthalocyaninato dinuclear lanthanoid (III) single-molecule magnets [5].