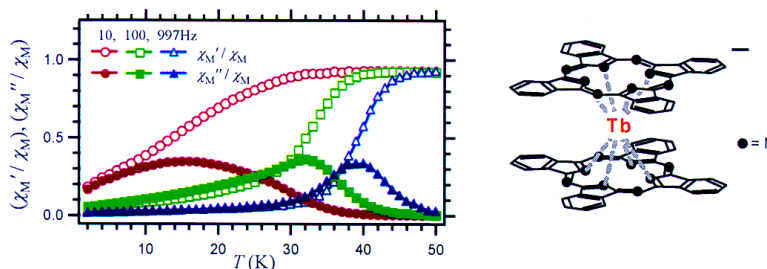Communication

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Lanthanide Double-Decker Complexes Functioning as Magnets at the Single-Molecular Level

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Considerable effort has been focused on the realization of nanometer-scale magnets functioning at temperatures higher than the cryogenic range. The approach that has been undertaken extensively is employing transition-metal clusters with a high spin multiplicity.[1] Behaviors as magnets have been observed at low temperature in several classes of transition-metal clusters, including the most well-studied Mn_{12} clusters $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]^{n-}$ ($n = 0, 1, 2; x = 3, 4$),[1-6] distorted cubane complexes with $[M^{IV}M^{III}_4O_3X]$ cores,[7-9] tetranuclear vanadium complexes $[V_4O_2(O_2CR)_7(L)_2]^n$,[10] and iron complexes formulated as $[Fe_8O_2(OH)_{12}(L)_6]^{8+}$.[11] These polynuclear metal complexes are called "single-molecule magnets" (SMM).[1] The origin of magnetism in the SMMs is the spins on individual metal ions which couple to give rise to a high-spin ground state. The SMMs have an axial zero-field splitting, which leads to a double-well potential with an energy barrier between "spin-up" ($S_z = S$) and "spin-down" ($S_z = -S$) states. The height of the barrier U_{eff} is determined by the equation $U_{eff} = |D|S^2$, where D is the zero-field splitting parameter. At low temperatures, the magnetic moment responds sluggishly to the AC external magnetic field, and therefore slow relaxation of magnetization is observed.

In this Communication, we report a new class of compounds functioning as magnets at the single-molecular level by a mechanism different from that of the transition-metal-cluster SMMs.

Recently, Ishikawa et al. reported a new method to determine sublevel structures of ground-state multiplets of a set of isostructural lanthanide complexes by multidimensional minimization analysis of the magnetic susceptibility and ^1H NMR data.[12] As the first application of the method, the ligand-field parameters were determined for dinuclear lanthanide complexes with phthalocyanine in a study of the interaction between f-electronic systems.[12,13] The studies showed that suitable choices of ligand field can yield a situation where the lowest substates have a large $|J_z|$ value and the energy gap between the lowest and second-lowest substates is more than a few hundred wavenumbers. This can be regarded as a situation similar to that of the transition-metal-cluster SMMs but with a much higher thermal barrier between $+J_z$ and $-J_z$ substates.

We measured the AC magnetic susceptibilities on a series of phthalocyanine double-decker complexes, $[Pc_2Ln]^-·TBA^+$ (Scheme 1; Ln = Tb, Dy, Ho, Er, Tm, or Yb; Pc = dianion of phthalocyanine; $TBA^+ = N(C_4H_9)_4^+$). A comprehensive X-ray study of $[Pc_2Ln]^-·TBA^+$ has been reported by Koike, et al.[14] Of the six compounds, $[Pc_2Tb]^-·TBA^+$ (**1**) and $[Pc_2Dy]^-·TBA^+$ (**2**) showed slow magnetization relaxation, while the rest did not.

The samples were prepared by a literature method.[15,16] Purifications were carried out by column chromatography with careful attention given to the potential contaminant of noncharged $[Pc_2$
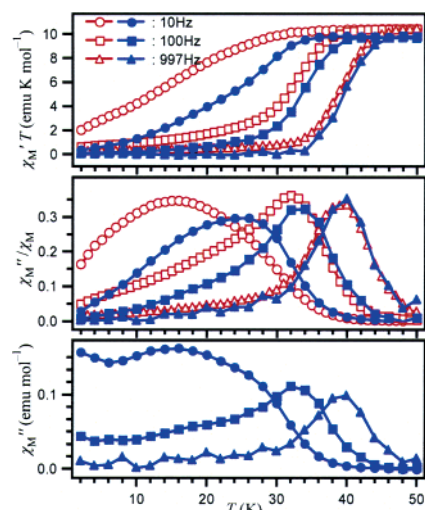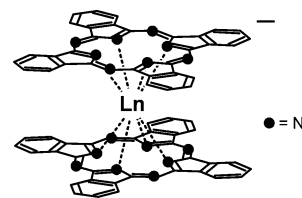

Figure 1. Plots of (top) $\chi_M'T$ and (bottom) χ_M''/χ_M against temperature T, where χ_M', χ_M'', and χ_M are in-phase-AC, out-of-phase-AC, and DC molar magnetic susceptibilities, respectively, for a powder sample of **1** (open marks) and that diluted in $[Pc_2Y]^-·TBA^+$ (filled marks) measured in a 3.5 G AC magnetic field oscillating at indicated frequencies.

Scheme 1. $[Pc_2Ln]^-$ (Ln = Tb, Dy, Ho, Er, Tm, or Yb)

$Ln]^0$. The AC magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL magnetometer.

Figure 1 shows temperature dependences of AC susceptibilities of a polycrystalline powder sample of **1** fixed in Apiezon N grease. The relative intensity of the out-of-phase AC susceptibility χ_M'' to the DC molar susceptibility χ_M shows a maximum at 15, 32, and 40 K with an AC frequency of 10, 100, and 997 Hz, respectively. At these temperatures, each corresponding $\chi_M'T$ versus T plot, where χ_M' is the in-phase AC susceptibility, exhibits a dispersion curve.

To ensure that the slow magnetization relaxation behavior is an intrinsic molecular property, the measurement was carried out for **1** doped in diamagnetic $[Pc_2Y]·TBA^+$ with the molar ratio $[Pc_2Tb]^-/[Pc_2Y]^- = ^1/_4$ (Figure 1, filled marks). The peaks of the χ_M''/χ_M curves and dispersion in $\chi_M'T$ shifted to higher temperature in the diluted sample. This indicates that the removal of intermolecular interaction from neighbor $[Pc_2Tb]^-$ complexes slows down the flip of the magnetic dipole. The experiments clearly show that the slow

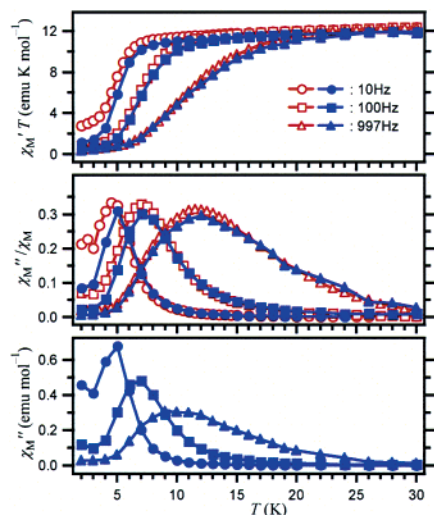† Department of Chemistry.
‡ Department of Materials Science.

Figure 2. Plots of (top) $\chi_M'T$ and (bottom) χ_M''/χ_M against temperature T, for **2** (open marks) and that diluted in $[Pc_2Y]^-\cdot TBA^+$ (filled marks) measured in a 3.5 G AC magnetic field oscillating at indicated frequencies.

magnetization relaxation is the single-molecular property of $[Pc_2Tb]^-$, rather than resulting from intermolecular interactions and long-range order.

Figure 2 shows the AC susceptibility measurements on **2**. Temperature dependences of $\chi_M'T$ and χ_M''/χ_M similar to those of **1** are seen. The peaks of χ_M''/χ_M plot are observed at 4.5, 7, and 11.5 K with an AC frequency of 10, 100, and 997 Hz, respectively. Diluted sample of **2** in $[Pc_2Y]^-\cdot TBA^+$ (molar ratio $[Pc_2Dy]^-/$ $[Pc_2Y]^- = 1/4$) also exhibited frequency-dependent out-of-phase AC signals. The peaks of the χ_M''/χ_M versus T plots shift to higher temperature in the diluted sample but to a smaller degree than in the Tb case. The amplitudes of the molar susceptibilities are unchanged in the diluted sample. These results show that the slow relaxation in $[Pc_2Dy]^-$ is of single-molecular property.

The temperature ranges in which the magnetization relaxations are observed in **1** and **2** are significantly higher than those of the transition-metal-cluster SMMs. There has been no report of SMMs with the peak temperature of χ_M'' higher than 8 K.

The significant rise of the temperature is strongly related to the sublevel structures of the ground-state multiplets of the complexes. We determined the sublevel structures of $[Pc_2Ln]^-$ by the method reported in ref 12 using DC susceptibility and ^1H NMR data of $[Pc_2Ln]^-\cdot TBA^+$.[17] Figure 3 shows obtained substate energy levels of **1** and **2**. In the Tb complex, the lowest substates are assigned to $J_z = \pm 6$, which are the maximum and minimum values in the $J = 6$ ground state. The energy separation from the rest of the substates is more than 400 cm^{-1}. If the relaxation occurs through a path consisting of stepwise transitions from J_z to $J_z \pm 1$ states, the "rate-determining step" is the first transition from $J_z = 6$ to $J_z = 5$ (or from -6 to -5) because of the large energy gap. In the Dy complex, the lowest substates are characterized as $J_z = 13/2$ and $-13/2$, which are the second largest in the $J = 15/2$ ground state. The sublevels are distributed more evenly than in the Tb case. This implies a possibility that there is no step requiring extremely high energy in the relaxation path.

The data of the diluted samples were fit to the Arrhenius low to give the barrier heights for reversal of the magnetic moment of
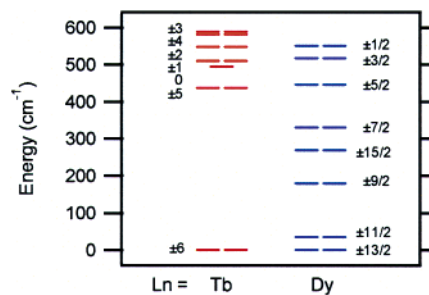

Figure 3. Energy and J_z values of the sublevels of the ground multiplets of $[Pc_2Ln]^-TBA^+$ (Ln = Tb or Dy).

230 and 28 cm^{-1} with preexponential factors ($1/\tau_0$) of 1.6×10^7 and 1.6×10^5 s^{-1} for **1** and **2**, respectively. The barrier height of **1** is of the same order of magnitude as the separation between the first- and second-lowest sublevels. This suggests the strong correlation between the relaxation rate and the substate distribution.

In conclusion, the slow magnetization relaxation as a single-molecular property in **1** and **2** results from a mechanism different from that of the transition-metal-cluster SMMs. In the new class of magnets at the molecular level, the origin of the magnetism is from both orbital and spin angular momentums of a single lanthanide ion, which is placed in a ligand field, giving the lowest sublevels a large $|J_z|$ value and energy gaps from the rest of the sublevels.

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