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Significant Increase of the Barrier Energy for Magnetization Reversal of a Single-4f-Ionic Single-Molecule Magnet by a Longitudinal Contraction of the Coordination Space

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Two-electron oxidation of $[\{Pc(OEt)_8\}_2Tb^{III}]^-$ [$Pc(OEt)_8$ = dianion of 2,3,9,10,16,17,23,24-octaethoxyphthalocyanine], which leads to a longitudinal contraction of the coordination space of the single-4f-ionic single-molecule magnet (SMM), resulted in a significant increase of the magnetization-reversal barrier energy and a remarkable upward temperature shift of χ'' peaks and $\chi'T$ drops. This is the first evidence that the dynamic magnetism of 4f SMMs can be controlled by a redox reaction on the ligand side without introducing any additional magnetic site or spin system.

When a lanthanide ion is placed in a certain type of ligand field, it can acquire a very large axial magnetic anisotropy, which allows the complex to show long magnetic relaxation times and magnetization hysteresis loops at the single-molecule level. The bis(phthalocyaninato)terbium anion, $[Pc_2Tb^{III}]^-$ (Pc = dianion of phthalocyanine), is the first example of compounds showing such a phenomenon.[1,2] The terbium complex exhibits long magnetization relaxation times at considerably higher temperatures (for example, 0.16 ms at 40 K and 1.6 s at 8 K)[3] than those reported for the polynuclaear metal complexes known as single-molecule magnets (SMMs),[4–6] a rapidly growing family of compounds adding members with new structure motifs,[7,8] ligand substitutions,[9] and metal combinations.[10]

An important goal for investigating a vast variety of new SMMs would be to deepen the understanding of the relationship between structures and properties. On the other hand, the search and development of SMMs functioning at high temperatures is also another important objective. For the polynuclear-type SMMs, the possible strategies for this aim may be divided into three types. One is to construct structures with a large number of metal ions in one molecule to achieve very large spin multiplicity. The second is to modify

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structures and interactions among metal ions in an existing SMM to magnify negative axial zero-field-splitting parameter *D*. The third approach is to employ hybrid systems containing 3d metal ions and lanthanide ions, in which a 4f electronic system can afford large axial magnetic anisotropy.[10]

For the single-4f-ionic SMM, a different approach must be taken. In the $[Pc_2Tb^{III}]^-$ case, the trivalent terbium ion with $(4f)^8$ configuration is placed in an eight-coordinate square-antiprism ligand field made by two Pc ligands in a "double-decker" structure. This ligand field lifts the 13-fold degeneracy of the $J = 6$ ground multiplet and generates a situation where the lowest substrates with $J_z = \pm 6$ are separated by several hundreds of reciprocal centimeters from the rest of the substrates.[11] This splitting pattern gives a low transition rate between the lowest substrates corresponding to "spin-up" and "spin-down" states. Because the dynamic magnetism is thus governed by the ground-multiplet substructure, systematic modification of the ligand field is the key strategy to increasing the temperature range for the SMM behavior.

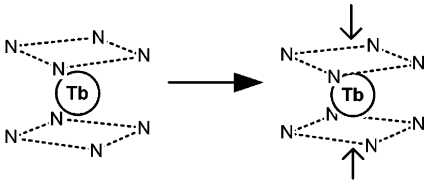
We report herein the first example of a significant increase of the barrier energy and temperature range, achieved by reducing the coordination space of the single-4f-ioninc SMM with a purely chemical procedure, namely, ligand oxidation.

In previous theoretical studies, the highest occupied molecular orbital (HOMO) and the next HOMO of $[Pc_2Ln^{III}]^-$ (Ln^{III} = trivalent lanthanide cation) were revealed to be the antibonding and bonding linear combinations, respectively, of the highest occupied π orbitals of the component Pc^{2-} ligands.[12] Because the HOMO has an antibonding character, removal of the two electrons from the orbital leads to increased bond strength and a shorter interplanar distance.

A recent geometry optimization study of $[Pc_2Y^{III}]^-$ and $[Pc_2Y^{III}]^+$ by density functional theory (DFT) calculations using the B3LYP model with a 6-311G(d) basis set for the C, N, and H atoms and LANL2DZ for the Y atom indeed showed that the cationic complex has a greatly reduced interligand distance from that of the anionic complex.[13] The closest Pc−Pc contact distance, which is between the C atoms bonding to the two N atoms, was predicted to be reduced by 0.10 Å from 3.38 Å of $[Pc_2Y^{III}]^-$ to 3.28 Å of $[Pc_2Y^{III}]^+$. Accordingly, the N_4-N_4 distance, which is the height of the square antiprism made by the eight coordinating N atoms, was reduced by 0.08 Å from 2.87 Å upon two-electron oxidation, while maintaining the size of the N_4 square (Scheme 1). This result implies that the axial component of the ligand-field potential at the lanthanide ion is greatly increased in the cationic complex.

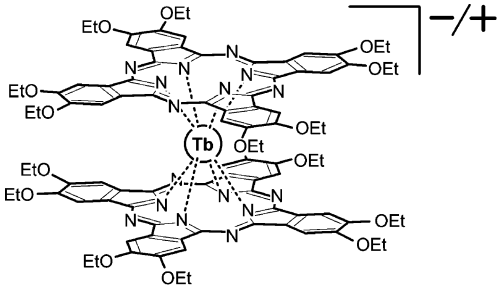
With an expectation that the longitudinally reduced coordination space would increase the ligand-field splitting of the $(4f)^8$ ground multiplet, we carried out an experimental study of two-electron oxidation of the 4f SMM as described hereinafter. Because the synthesis and purification of $[Pc_2Tb]^+$ was very difficult due to its extremely low solubility to organic solvents, we examined several ligand modifications to increase the solubility of the cationic species and found that an octaethoxyl group (Scheme 2) gives moderate solubility, leading to easier purification.

Scheme 1. Schematic Diagram of the Contraction of the Coordination Space upon Two-Electron Oxidation from $[Pc_2Tb]^-$ to $[Pc_2Tb]^+$



$[Pc_2Tb^{III}]^-$ $[Pc_2Tb^{III}]^+$

Scheme 2. Structure of $[\{Pc(OEt)_8\}_2Tb]^{-/+}$



Sample preparation was carried out as follows. We first prepared an electrically neutral complex $[\{Pc(OEt)_8\}_2Tb]^0$, where $Pc(OEt)_8$ is a dianion of 2,3,9,10,16,17,23,24-octaethoxyphthalocyanine. Anionic complex $[\{Pc(OEt)_8\}_2Tb]^-(nBu_4N)^+$ (**1**) was obtained by reducing $[\{Pc(OEt)_8\}_2Tb]^0$ with hydrazine monohydrate followed by the addition of $(nBu_4N)^+Br^-$. The cationic complex $[\{Pc(OEt)_8\}_2Tb]^+(SbCl_6)^-$ (**2**) was obtained by oxidizing $[\{Pc(OEt)_8\}_2Tb]^0$ with phenoxathiinylium hexachloroantimonate in dichloromethane. The end points of the redox reactions were determined using the characteristic spectra of the anionic and cationic Pc double-decker complexes in the UV region.[14] Purification of **2** was carried out by recrystallization from a dichloromethane/hexane solution. Magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL SQUID magnetometer.

Figures 1a and 2a show alternating current (ac) susceptibility of **1** as a function of temperature measured with varied ac-field frequencies. The anionic terbium complex exhibits a sharp drop of $\chi'T$ values and χ'' peaks at the temperature ranges dependent on the frequencies, indicating that **1** is an SMM. The figure shows essentially the same temperature and frequency dependences as those of the unsubstituted compound $[Pc_2Tb]^-TBA^+$.[1,3]

The cationic complex **2**, which corresponds to the two-electron-oxidation product of **1**, exhibited a similar temperature and frequency dependence but in significantly higher temperature ranges, as shown in Figures 1b and 2b. The $\chi'T$ drop and χ'' peak for an ac field of 10^3 Hz are observed at

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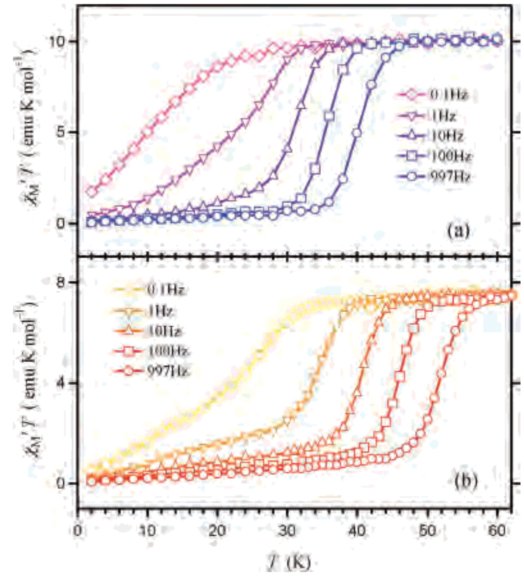

Figure 1. Plot of the product of in-phase ac susceptibility χ' and temperature T for (a) **1** and (b) **2** at the indicated oscillation frequencies. No direct current (dc) magnetic field was applied.

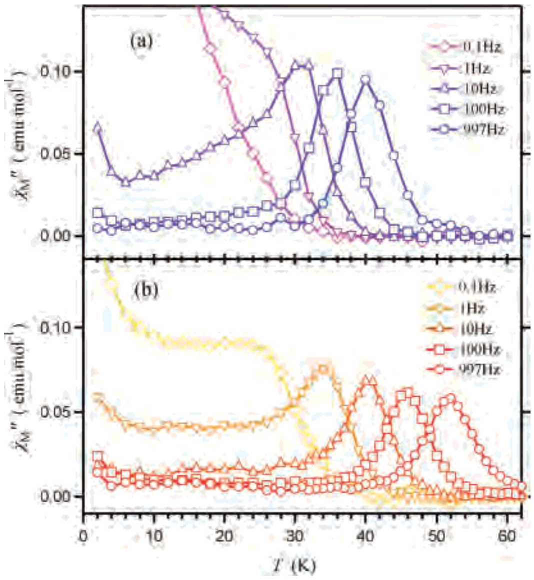

Figure 2. Plot of the out-of-phase ac susceptibility χ'' for (a) **1** and (b) **2** at the indicated oscillation frequencies. No dc magnetic field was applied.

52 K, which is 12 K higher than those of **1** in the "normal" oxidation state.

The $\chi_M''-\chi_M'$ plot (Cole−Cole diagram; Figure 3) for **2** shows a near-semicircle shape, which is reproduced by the generalized Debye model[16] with a small α value. This indicates that the magnetic relaxation is dominated by one process and excludes the possibility of the spin-glass- or bulk-magnet-type behavior.

The dominant path of the magnetic relaxation of $[Pc_2Tb]^-$ in these temperature ranges is the Orbach process,[15] in which the transition between $J_z = +6$ and -6 states occurs by the absorption of a phonon to reach an excited state followed by an emission of the second phonon.[3] The situation is essentially unchanged for the cation **2**. The effective barrier height U_{eff}, which corresponds to the energy of the excited state, is estimated by Arrhenius analysis (Figure S1 in the Supporting Information) to be 5.5×10^2 cm^{-1} for **2**, which is 8% greater than that of **1**. This is interpreted by the fact that the multiplet splitting is increased by the strengthened ligand field in the squeezed coordination space of **2**, resulting in a diminished transition rate between the "spin-up" and "spin-down" states.

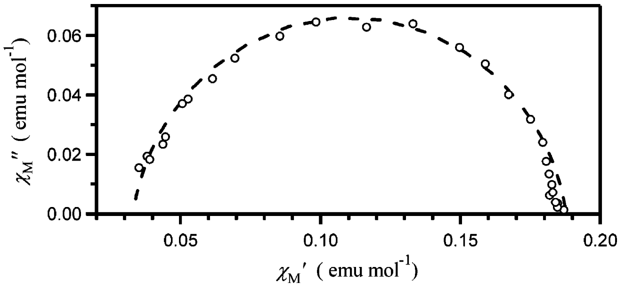

Figure 3. Cole−Cole diagram at 40 K for **2**. The broken line represents the least-squares fit obtained with a generalized Debye model[16] with α = 0.10.

In a previous study on an electrically neutral complex $[Pc_2Tb]^0$, which is generated by one-electron oxidation of $[Pc_2Tb]^-$, we observed a similar temperature shift with a smaller degree than the present case.[17] At that time, it was uncertain whether the shift was caused by the unpaired π electron or by modification of the 4f multiplet substructure. Considering the present findings, it should be concluded that the temperature shift observed for $[Pc_2Tb]^0$ is actually due to the increased ligand-field strength caused by removal of one electron from the antibonding HOMO of $[Pc_2Tb]^-$.

In conclusion, we have shown that two-electron ligand oxidation of the single-4f-ionic SMM results in a significant increase of the magnetization-reversal barrier and a remarkable upward temperature shift of the χ'' peaks and $\chi'T$ drops. Considering the theoretical prediction on the geometry change, we attribute this phenomenon to the longitudinal contraction of the coordination space of the Tb^{3+} ion induced by the ligand oxidation. The observations presented here provide the first evidence that the dynamic magnetism of the 4f SMM can be controlled by a redox reaction on the ligand side without introducing any additional magnetic site or spin system.

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Supporting Information Available: Plot of the natural logarithm of the inverse of the relaxation time τ against the inverse of the peak temperature of χ'' for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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