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Communication

Upward Temperature Shift of the Intrinsic Phase Lag of the Magnetization of Bis(phthalocyaninato)terbium by Ligand Oxidation Creating an $S = {}^1/_2$ Spin

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An alternating-current (ac) magnetic susceptibility measurement for the $[(Pc)_2Tb^{III}]^0$ complex (Pc = phthalocyaninato) has shown that ligand oxidation of the anionic $[(Pc)_2Tb^{III}]^-$ complex gives rise to a significant upward shift of the temperature range where the magnetization response shows a phase lag behind the time-varying external magnetic field. The peaks of the out-of-phase component of the ac susceptibility of the π-radical $[(Pc)_2Tb^{III}]^0$ were observed at 50, 43, and 36 K with ac magnetic fields of 10^3, 10^2, and 10 Hz, respectively, which were more than 10 K higher than the corresponding values of the anionic complex with a closed-shell π-system. The ac susceptibility measurements on the complex with octa(dodecoxy)-substituted Pc ligand, which is readily dilutable in diamagnetic media, proved that the significant rise of the temperatures occurs as an intrinsic single-molecular property of the complex possessing both $J = 6$ and $S = {}^1/_2$ systems, and is not due to long-range magnetic order or interactions between adjacent unpaired π-electrons.

Extensive research has been undertaken to develop nanometer-scale magnets functioning above cryogenic temperatures. Recently, Ishikawa et al. reported that double-decker phthalocyaninato lanthanide complexes $[Pc_2Tb]^-$ (Pc = dianion of phthalocyanine) have a long magnetization relaxation time as an intrinsic molecular property, and can function as a magnet at single-molecular level.[1] In the complex, a Tb^{3+} ion with a total angular momentum $J = 6$ is placed in a ligand field potential that splits the ground multiplet so that the lowest sublevel has the largest J_z value ($|J_z| = 6$) and large energy gaps from the rest of the sublevels

(ca. 400 cm^{-1}).[2] This unusual condition leads to a small probability of the transition between $J_z = 6$ and -6 substates, and hence a slow magnetization response to an applied magnetic field. More importantly, the slow magnetization relaxation phenomenon is observed at significantly higher temperatures than the single molecule magnets (SMMs)[3] consisting of a cluster of transition-metal ions, such as $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]^{n-}$ ($n = 0, 1, 2; x = 3, 4$),[3–8] $[Mn^{IV}Mn^{III}_4O_3X]$,[9,10] $[V_4O_2(O_2CR)_7(L)_2]^n$,[11] and $[Fe_8O_2(OH)_{12}(L)_6]^{8+}$.[12] In alternating current (ac) magnetic susceptibility measurements, $[Pc_2Tb]^-$ exhibits a characteristic peak in the χ_M'' versus T plot (χ_M'' refers to the out-of-phase component of ac molar susceptibility) at 40 K under 10^3 Hz ac magnetic field,[1] while there has been no report of transition-metal-cluster SMMs showing χ_M'' peak at higher than 7 K.

The anionic form of bis(phthalocyaninato)lutetium, $[Pc_2Ln^{III}]^-$, consists of a trivalent lanthanide ion and the two

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Scheme 1. [Pc$_2$Tb]^0

[Pc$_2$Tb^{III}]^0
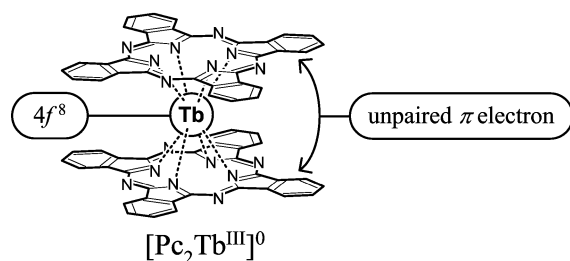
Pc ligands, each having a formal charge of -2 with a closed shell π electronic system. It has been known that one-electron oxidation of [Pc$_2$Ln^{III}]$^-$ occurs on the ligand side, resulting in a neutral [Pc$_2$Ln^{III}]^0 having an open shell π electronic system. The [Pc$_2$Tb]^0 complex therefore has two spin systems, i.e., an unpaired π electron on the ligands and the 4f^8 system on the Tb ion (Scheme 1).

The purpose of this Communication is to report the remarkable consequence of the ligand oxidation creating an $S = \frac{1}{2}$ spin on the intrinsic dynamic magnetism of the bis-(phthalocyaninato) complex of Tb^{3+} ion with a $J = 6$ system.

An experimental demonstration of the delocalized nature of the unpaired π electron over two Pc ligands[13] and a theoretical study of the π electronic structure have been reported by Ishikawa et al.[14,15] The behaviors as intrinsic semiconductors due to the unpaired π electron of the neutral complexes in the solid states have been extensively studied by Simon and André et al.[16−19]

The unsolvated sample of [Pc$_2$Tb]^0 was prepared by a literature method,[20] followed by a purification using column chromatography with careful attention given to potential contamination of the anionic complex. The ac magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL magnetometer.

Figure 1 shows the temperature and frequency dependence of the ac susceptibilities of a powder sample of [Pc$_2$Tb]^0. An abrupt drop in the $\chi_M'T$ plot with lowering T is observed at a temperature range depending on the frequency of the ac magnetic field, indicating a phase lag of the magnetization response behind the ac field is taking place. The corresponding χ_M'' plots show peaks at 36, 43, and 50 K with frequencies of 10, 100, and 997 Hz, respectively. The $\chi_M'T$ drop and the χ_M'' peaks are shifted to significantly higher temperatures with respect to those of the anionic [Pc$_2$Tb]$^-$ complex.

The phenomenological barrier height for reversal of the magnetic moment is estimated at 410 cm^{-1} with a pre-
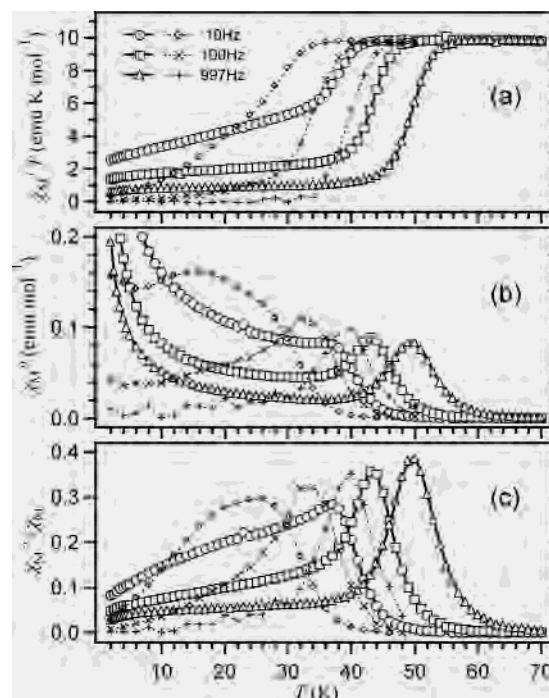

Figure 1. Plots of (a) $\chi_M'T$, (b) χ_M'', and (c) χ_M''/χ_M against temperature T, where χ_M', χ_M'', and χ_M are in-phase-ac, out-of-phase-ac, and dc molar magnetic susceptibilities, respectively, for a powder sample of [Pc$_2$Tb]^0 fixed in eicosane (open markers with solid lines). The ac susceptibility measurements were performed in 7 G ac magnetic field oscillating at indicated frequencies with absence of dc component. The corresponding data for the anionic complex [Pc$_2$Tb]$^-\cdot$(C$_4$H$_9$)$_4$N$^+$ are shown with dotted lines.[1]

exponential factor ($1/\tau_0$) of 6.8 × 10^8 s^{-1} by the fit to the Arrhenius low.[21] This is a significant increase from 230 cm^{-1} ($1/\tau_0$ = 5.0 × 10^7 s^{-1}) observed for [Pc$_2$Tb]$^-\cdot$(C$_4$H$_9$)$_4$N$^+$.[1] These numbers, however, must be interpreted cautiously. As seen in the figure, the $\chi_M'T$ and χ_M'' values do not vanish in the low temperature region below 30 K, indicating that the magnetic moment is not completely frozen. This can be ascribed to the presence of a different relaxation process that becomes dominant in the lower temperature region.

To clarify whether the upward temperature shift is attributed to an intrinsic molecular property or to long-range magnetic order by intermolecular interactions, we have carried out the ac susceptibility measurements of the π radical Tb complex under two different dilute conditions, namely dilution in a diamagnetic media and dilution in [Pc$_2$Y]^0 having $S = \frac{1}{2}$ spin on the ligand but no f electron in the metal ion.

To dilute the complex in a diamagnetic media, we have prepared bis[2,3,9,10,16,17,23,24-octakis(dodecoxy)-phthalocyaninato]terbium(III) (Scheme 2, denoted as [(C$_{12}$H$_{25}$O)$_8$Pc]$_2$Tb hereafter), which is composed of the Pc

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(21) The Bloch equation for the longitudinal magnetization, d$M(t)$/dt = $(1/\tau)(\chi_M H(t) - M(t))$, gives $\chi_M'' = \omega\tau\chi_M/(1 + \omega^2\tau^2)$, where τ is the magnetization relaxation time and ω is the angular frequency of the applied ac magnetic field $H(t)$. Strictly speaking, when χ_M is a function of T, τ coincides to $1/\omega$ at a χ_M''/χ_M peak temperature which corresponds to the condition d(χ_M''/χ_M)/d$T = 0$, but not at a χ_M'' peak temperature where dχ_M''/d$T = 0$. We used in the present paper the χ_M''/χ_M peaks (37, 43, and 50 K with 10, 100, and 997 Hz field, respectively) for the Arrhenius analysis.
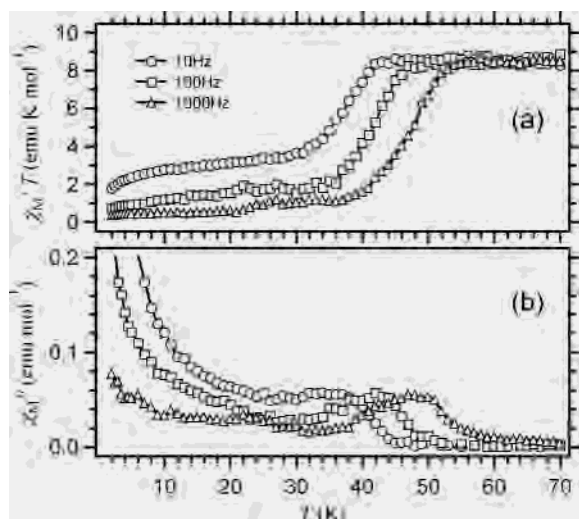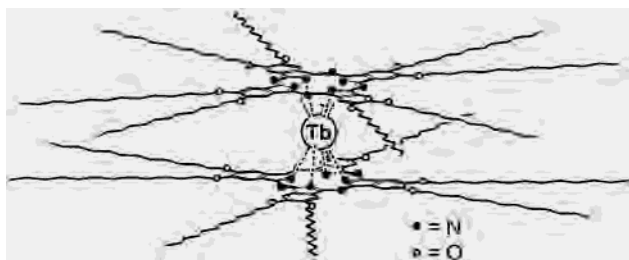
Figure 2. Plots of (a) $\chi_M'T$ and (b) χ_M'' against temperature T for a frozen solution of $[(C_{12}H_{25}O)_8Pc]_2Tb$ in eicosane. The molar ratio of the Tb complex and eicosane is 1:370. The ac susceptibility measurements were performed in 5 G ac magnetic field oscillating at indicated frequencies with absence of dc component.

Scheme 2. $[(C_{12}H_{25}O)_8Pc]_2Tb$

ligands whose periphery is substituted by long-chain alkoxy substituents, using a literature method for an isostructural Lu complex.[22] The lanthanide complexes with long-chain-substituted Pc ligands are well-known to form discotic mesophases in undiluted condition.[22,23] We have confirmed that the complex has a remarkably high solubility in eicosane above its melting point, and that the complex shows UV−vis spectra with no indication of aggregation up to the concentration at which the susceptibility measurements were carried out.

The temperature and frequency dependence of the ac susceptibility of $[(C_{12}H_{25}O)_8Pc]_2Tb$ in a frozen solution of eicosane is shown in Figure 2. The characteristic drop in the $\chi_M'T$ plot and the peaks in the χ_M'' plot are observed at almost the same temperatures as those of $[Pc_2Tb]^0$. This result clearly shows that the upward temperature shift of the magnetic relaxation phenomena is of an intrinsic molecular property of $[Pc_2Tb]^0$, rather than resulting from intermolecular interactions and long-range magnetic order.

In contrast to the above case, dilution of $[Pc_2Tb]^0$ in $[Pc_2Y]^0$ having an $S = {}^1\!/_2$ ligand system with no f electron led to a suppression of the magnetic relaxation phenomena.
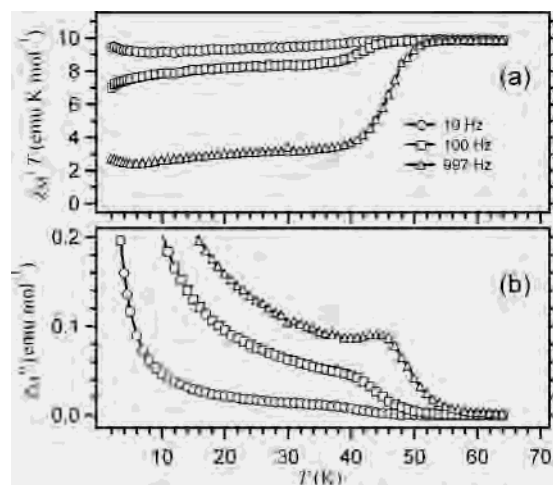
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Figure 3. Plots of (a) $\chi_M'T$ and (b) χ_M'' against temperature T, of $[Pc_2Tb]^0$ diluted in $[Pc_2Y]^0$ with the molar ratio $[Tb]/[Y] = 1:10$ measured in 7 G ac magnetic field oscillating at indicated frequencies. The χ_M' values were obtained by subtracting the contribution from $[Pc_2Y]^0$. It was confirmed that the $[Pc_2Y]^0$ matrix itself showed neither nonzero χ_M'' value nor deviation of $\chi_M'T$ from the dc $\chi_M T$ values[21] with ac field frequency of $10-10^3$ Hz, reflecting its short relaxation time.

As seen in Figure 3, the drops in the $\chi_M'T$ plots are greatly decreased from the undiluted sample. The degree of the decrease is larger for the lower ac frequency. In particular, the flatness of the $\chi_M'T$ plot with 10 Hz field indicates that the reversal of the magnetic moment almost completely follows the oscillation of the ac field of this frequency. Although the peak in the χ_M'' plot is observed with 997 Hz field, its position is 5 K lower than that of the undiluted sample. No clear peak in the χ_M'' plot is seen for the 10 and 100 Hz cases. These observations show that the presence of unpaired π electronic systems in neighbor molecules does not cause upward temperature shift of $[Pc_2Tb]^0$, but rather reduces the relaxation time of the Tb complex.

In conclusion, we have found that the $[Pc_2Tb]^0$ complex possessing both $J = 6$ and $S = {}^1\!/_2$ systems shows the characteristic magnetization lag to ac magnetic field at significantly higher temperature range than the anionic $[Pc_2Tb]^-$ complex with only a $J = 6$ system. It was proved experimentally that this phenomenon is due to an intrinsic single-molecular property of the $[Pc_2Tb]^0$ complex. At the present stage, the actual mechanism of the phenomenon is not yet known, and further study, both experimentally and theoretically, on the f−π interaction will be definitely required, although it is highly challenging. Possible modification of the ligand filled by the oxidation and its effect should also be investigated. Nonetheless, the phenomenon presented here is, we believe, potentially very important in terms of developing molecular or nanometer-scale magnets functioning at high temperatures.