Magnetic properties of lanthanoid(III) phthalocyaninato triple-decker complexes in an external magnetic field and electronic transport properties for molecular spintronics

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Abstract. Lanthanoid phthalocyaninato complexes of Dy₂(obPc)₃ (1) and Tb₂(obPc)₃ (2) are shown to be a single-molecule magnet. The relationships among the magnetic relaxation properties of 1 in a direct current (dc) magnetic field in comparison to 2 and the electronic properties of a cast film are discussed.

1. Introduction

Scientists have envisioned using a single spin as a ‘bit’ of information to prepare high-density storage and quantum-computing devices[1]. Quantum tunneling of the magnetization (QTM) in systems with double-well potentials[2], which is a characteristic property of single-molecule magnets (SMMs), underpins this idea[3]. On the basis of the properties of lanthanoid-phthalocyaninato (LnPc₂) SMMs[4], we believe that TbPc₂ can be used as a ‘bit’ of information in high-density storage technology by taking advantage of the single up-spin/down-spin property, which is equivalent to 2¹. For triple- and quadruple-decker type SMMs, this is equivalent to 2² and 2³, respectively, in relation to the number of spins.

We have recently reported the characteristics of LnPc₂ and LnPc (Ln = Tb and Dy) deposited on an Au(111) surface in an ultrahigh vacuum (UHV) using a dry process technique[5]. Both LnPc₂ and LnPc are present on the Au(111) surface on the basis of height profiles and dI/dV mapping obtained by using scanning tunneling microscopy (STM) and spectroscopy (STS). A Kondo peak, which is due to coupling between magnetic impurities, including Tb³⁺ ions, and conduction electrons from the STS, is only observed at the center of TbPc at a Kondo temperature (T_K) of ~250 K. More recently, we have observed a Kondo peak for TbPc₂ on an Au(111) surface[6]. We believe that the relation between T_K and the blocking temperature (T_B) must be studied further. In addition, the properties of SMMs and the Kondo effect can be modulated with an external magnetic field[7].

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Although Ln-Pc double-decker complexes have been studied in detail, little is known about Ln(III)-Pc triple-decker complexes Ln3Pc3. The first lanthanoid phthalocyaninato triple-decker, Ln3Pc3 (Ln3+ = Y, Nd, Gd, Er, and Lu) was reported in 1986[8]. However it is not well characterized. Ishikawa et al. have reported a series of studies on the magnetic properties of the Ln(III)-Pc triple-decker complex [(Pc)Ln(Pc)Ln(obPc)] (obPc = dianion of 2,3,9,10,16,17,23,24-octabutoxy-phthalocyanine), which were the first reports on the dynamic magnetism of a coupled 4f system[9]. The effects of the Jf interactions on the temperature and frequency dependence of the ac magnetic susceptibility were discussed by comparing experimental data for isostructural bis-Tb and mono-Tb complexes. In addition, they have reported that Tb(III)-Pc triple-decker SMMs with asymmetric Tb3+ sites exhibit two \( \chi_{m}^*T \) peaks at 20 and 27 K. However, they have not reported its crystal structure. Therefore, the relationship between the molecular structure and the magnetic relaxation mechanisms in the Tb(III)-Pc triple-decker SMMs is not clear. Very recently, we have reported a new magnetic relaxation relationship between the molecular structure and the magnetic relaxation mechanisms in the Tb(III)-Pc phenomon for an Ising dimer of the Tb-phthalocyaninato triple-decker SMMs Tb2(obPc)3 (a loop rod coated with Paratone-N (HAMPTON RESEARCH). The crystal dimensions were 0.31 × 0.14 × 0.09 mm3 for addition, they have reported that Tb(III)-Pc triple-decker SMMs with asymmetric Tb3+ sites exhibit discussion by comparing experimental data for isos tructural bis-Tb and mono-Tb complexes. In interactions on the temperature and frequency dependence of the ac magnetic susceptibility were published procedure[8]. Dy(acac)3·4H2O (57 mg, 0.13 mmol) was added to a refluxing 1-octanol suspension (2.5 mL) of H2obPc (55 mg, 0.05 mmol). After 4 h of refluxing, the reaction mixture was added to methanol (100 mL). The crude product was purified by using column chromatography on silica gel with CHCl3 as the eluent. The collected deep blue fraction was evaporated to dryness to obtain a dark blue solid. Column chromatography (C-200 silica gel, Wako and Sephadex G-10, Pharmacia Biotech) was used to remove the remaining impurities. Dark blue fine needle crystals were obtained from chloroform/ethanol (30 mg, 8.15 × 10−6 mol, 16%). ESI-MS: elemental analysis calcd (%) for C192H240N24O24Dy2: C 64.18, H 6.71, N 9.36; found: C 64.0, H 6.56, N 9.20.

Single crystals of 1 were prepared by the method described above. A single crystal was mounted on a loop rod coated with Paratone-N (HAMPTON RESEARCH). The crystal dimensions were 0.31 × 0.14 × 0.09 mm3 for 1. Data collection was performed on a Rigaku CCD diffractometer (Saturn70) with graphite monochromated Mo Kα radiation (\( \lambda = 0.71069 \) Å) at a temperature of –180 ± 1 °C. An empirical absorption correction based on azimutal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. All non-hydrogen atoms were refined anisotropically using a least-squares method, and hydrogen atoms were fixed at calculated positions and refined using a riding model. SHELXTL[12] was used for structure refinement, and the structure was expanded using Fourier techniques[13]. The weighting scheme was based on counting statistics. Full-matrix least-squares refinements on \( F_2 \) based on unique reflections were employed, where the unweighted and weighted agreement factors of \( R = \Sigma |F_o| - |F_c| / \Sigma |F_o| \) (I > 2.00σ(I)), and \( wR = \Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2 \)1/2 were used. Crystal data for 1·2EtOH (CCDC-807110): C196H250N24O26Dy2, Mr = 3683.20, triclinic, \( P\bar{1} \), a = 1.32329(15), b = 1.7835(2), c = 2.0575(3) nm, \( \alpha = 107.421(2), \beta = 90.530(2), \gamma = 100.852(2)^\circ, V = 4.5391(10) \) nm3, \( T = 93(1) \) K, \( Z = 1, \rho_{calc} = 1.347 \) Mg m−3, \( F_{000} = 1934, \lambda = 0.7107 \) Å, \( \mu(MoKα) = 0.893 \) mm−1, 28306 measured reflections, 19941 unique which were included in

2. Sample and technique

Ln2(obPc)3 was synthesized in one step starting from Ln(acac)3·4H2O and H2obPc by using a published procedure[8]. Dy(acac)3·4H2O (57 mg, 0.13 mmol) was added to a refluxing 1-octanol suspension (2.5 mL) of H2obPc (55 mg, 0.05 mmol). After 4 h of refluxing, the reaction mixture was added to methanol (100 mL). The crude product was purified by using column chromatography on silica gel with CHCl3 as the eluent. The collected deep blue fraction was evaporated to dryness to obtain a dark blue solid. Column chromatography (C-200 silica gel, Wako and Sephadex G-10, Pharmacia Biotech) was used to remove the remaining impurities. Dark blue fine needle crystals were obtained from chloroform/ethanol (30 mg, 8.15 × 10−6 mol, 16%). ESI-MS: elemental analysis calcd (%) for C192H240N24O24Dy2: C 64.18, H 6.71, N 9.36; found: C 64.0, H 6.56, N 9.20.
all calculations. $R_1 = 0.0506 (I > 2\sigma(I))$ and $wR_2 = 0.1396$ (all data) with GOF = 1.087. Powder X-ray diffraction (XRD) patterns of 1 and 2 were collected at room temperature using a Rigaku X-ray diffractometer (AFC-7R/LW) operated at 50 kV and 300 mA. Powder samples in a capillary tube were scanned in the diffraction angle range of $2\theta$ in steps of $0.02^\circ$ at 2s/step.

UV-Vis-NIR spectra for CHCl$_3$ solutions in a quartz cell with a pathlength of 1 cm and for cast films on a quartz plate were acquired on a SHIMADZU UV-3100PC spectrometer at 298 K.

Magnetic susceptibility measurements were performed on Quantum Design SQUID magnetometers MPMS-5S and MPMS-XL. The dc measurements were performed in the temperature range of 1.8–300 K and dc fields of–7–7 T. Ac measurements were performed in the frequency range of 1–1500 Hz with an ac field amplitude of 3 Oe in the presence of a dc field (zero, 0.1, 0.2, 0.3, 0.5, and 1.0 T). Measurements were performed on a randomly oriented powder sample of 1, which was suspended in $n$-eicosane, heated to 330 K, and then cooled to 300 K for solidification. All data were corrected for sample holder, $n$-eicosane, and diamagnetic contributions from the molecules by using Pascal’s constants.

Cyclic voltammetry (CV) was carried out on a Bioanalytical Systems CV-50W. Solutions of 1 $(10^{-4}$ mol dm–3) in dry CH$_2$Cl$_2$ with n-Bu$_4$PF$_6$ (0.1 mol dm–3) as the supporting electrolyte were used with glassy-carbon working, Pt wire counter, and Ag/AgCl reference electrodes. A scan rate of 100 mV s–1 was used. In the case of the cast film of 1, films were deposited on a glassy-carbon working electrode. The CVs were acquired in an aqueous solution of KClO$_4$ (0.1 mol dm–3), which was used as the supporting electrolyte. A Pt wire was used as the counter electrode, and an SCE was used as the reference electrode. A scan rate of 100 mV s–1 was used.

Field-effect transistors (FETs) were fabricated from 2 to determine the charge transport properties the assembly. Drop-casting from heptane solutions on doped-Si/SiO$_2$ substrates was used to prepare the FET, which was used a doped-Si layer as a gate-electrode. Source and drain electrodes were formed from the top of the semiconductor layer affording a top-contact geometry is adopted. The effective width and length of the channel were 150 µm and 20 µm, respectively. The FET characteristics were measured using a Keithley 4200 semiconductor parameter analyzer.

**3. Result and discussion**

Although Takahashi et al. have reported the Dy-Pc triple-decker complex 1, they have not reported its crystal structure and magnetic properties[8]. We used a Pc ligand with 2,3,9,10,16,17,23,24-octabutoxy substituents because it should have a higher solubility, thus making crystallization easier.

Complex 1, shown in Fig. 1, crystallized with ethanol in the crystal lattice in the triclinic space group $P–1$ and was isomorphous with 2. Crystal-packing diagrams of 1 are shown in Fig. 2.

![Figure 1. View of the molecular structure of Dy$_2$(obPc)$_3$ (1) with ellipsoids at 50% probability.](image-url)
Complex 1 has two Dy$^{3+}$ ions sandwiched between three Pc ligands with eight isoindole-nitrogen donor atoms ($N_{iso}$) and a center of symmetry. The center of the square formed by the four pyrrolic nitrogens of Pc form a crystallographically imposed inversion center, making the two Ln$^{3+}$ ions and outer-Pcs equivalent. The crystal structure of 1 is similar to that of 2, and both outer Pc ligands of 1 are equally distorted from planarity, adopting a biconcave shape[10]. The Dy$^{3+}$ ions are unevenly spaced between the two Pc ligands, being displaced 0.258–0.262 nm (2: 0.258–0.263 nm) from the mean plane of the four $N_{iso}$ of the inner Pc ligands and 0.234–0.237 nm (2: 0.235–0.237 nm) from the mean plane of the four $N_{iso}$ of the outer ones. These bond lengths are different from those in DyPc$_2$ (0.239–0.242 nm)[5]. The intramolecular Dy–Dy distance is 0.350 nm (Tb-Tb distance is 0.352 nm in 2). The twist angle between the outer rings and the center one was determined to be 32°, causing a pseudo 4-fold axis. The intermolecular Dy–Dy distance along the $a$, $b$, and $c$ axes were determined to be 1.104, 1.588, and 1.861 nm, respectively. Each molecule of 1 is rather well separated from neighboring molecules due to the $n$-butoxy chains. The size and height of 1 were estimated to be ~2.4 and ~0.7 nm same as 2 (DyPc$_2$: ~1.6 and ~0.4 nm[5]) on the basis of the distance between two hydrogen atoms of the $n$-butoxy chains at both ends of the molecules and between the oxygen atoms of the line splitting the two Pc rings, respectively. Powder XRD of 1 and 2 (Fig. 3) are similar to simulated patterns based on X-ray single crystallographic data of 1 at room temperature[10].

Figure 2. Packing diagrams of 1. Solvent molecules located between the $n$-butoxy chains and the $n$-butoxy chains have been omitted for clarity. Each column of 1 is rather well separated from neighboring columns by the $n$-butoxy chains.

$\chi_M^T$ versus $T$ plots for 1 increased with a decrease in $T$ and reached a maximum of ~37 cm$^3$ K mol$^{-1}$ at 1.8 K, which suggests the existence of a ferromagnetic interaction between the Dy$^{3+}$ ions (Fig. 4a). The magnetic dipolar term, not the exchange term, is dominant. 2 exhibits the same behavior[10].

The M-H curve for 1 as well as 2 at 1.8 K showed no magnetic hysteresis (Fig. 4b). At this temperature the spins are not frozen. In the case of 2, below 1.5 K, hysteresis loops were observed by using a micro-SQUID. However, there was a sharp drop at near zero-field leaving practically no remanent magnetization because the relaxation time, which was strongly temperature dependent down to ~0.4 K and field sweep-rate dependent even at 0.04 K, was not sufficiently long[10]. This behavior is typical for an SMMs with a crossover temperature of ~0.4 K.

Fig. 5 shows ac susceptibility measurements on a powder sample of 1. A maximum $\chi_M^T$, which was dependent on the applied ac field, indicating that 1 is an SMMs, appeared at 4.5 K at an ac frequency ($f$) of 1488 Hz, whereas that for 2 was observed at 24 K[10]. It is clear that the magnetic relaxation process is related to the sublevel structures of the ground-state multiplets of the Ln$^{3+}$.
complexes[4]. In addition, $\chi_M^T$ did not disappear below 3 K in a zero field, indicating that the magnetic moment is not frozen (Fig. 5). In other words, as in the case of 2, a different relaxation process becomes dominant in the low-temperature region.

![Figure 3. Powder XRD patterns of 1 and 2 at 298 K.](image)

Dependence of $\chi_M^T$ on the ac field frequency was clearly observed in the low-temperature region in several dc magnetic fields. At $f = 1$ Hz, in a 0.2 T dc field, only one peak at 2.5 K was observed, whereas, at $f = 1488$ Hz, two $\chi_M^T$ peaks were observed at 4.5 and ~2.5 K, which correspond to two different magnetic relaxation processes. The $\chi_M^T$ peak for 1 at 4.5 K ($f = 1488$ Hz) was independent of the dc field.

On the other hand, the shape of the peak at ~2.5 K ($f = 1, 100,$ and 1488 Hz) drastically changed, and the peak shifted to a higher temperature with an increase in the strength of the dc magnetic field. In Dy$^{3+}$ SMMs, the lowest substates are $J_z = \pm 13/2$[14], and in Dy-Pc as well as Tb-Pc triple-decker complexes, a Zeeman effect involving the ground-state energy levels plays a role in the observed changes[10]. Investigations to clarify the mechanism of these observations, including determination of the multiplet substructures of 1, are in progress.

Since 1 and 2 are soluble in most organic solvents, except for alcohols, we could prepare cast films for potential application in devices. They were prepared on quartz plates directly by using a hand-casting method. UV-vis-NIR spectra of a solution and cast films of 1 are shown in Fig. 6. The electronic spectrum of 1 is similar to that of 2[10]. The spectra of the cast films are similar to that of the solution; however, the bands are broader. In addition, the Q band region is red-shifted. In the solution (cast film) spectra, two intense Q bands were observed at 643 nm (666 nm) with a shoulder peak at 547 nm (561 nm) and 760 nm (824 nm). These bands drastically changed, and a broad band in the near-IR region (600–1200 nm) appeared in the spectra of the cast film. On the basis of Kasha’s
theory and previously published results, the red shift suggests that 1 forms J-aggregates in the cast films[15].

Figure 4. dc magnetic measurements on a powder sample of 1. (a) $\chi_M T$ versus $T$ plots. In the room temperature region, the $\chi_M T$ value as asymptotically approached that of two free Dy$^{3+}$ ions (14.18 cm$^3$ K mol$^{-1}$ × 2). (b) Field dependence of the magnetization at 1.8 K.

Figure 5. $\chi_M' T$ and $\chi_M'' T$ versus temperature ($T$) for 1 in dc fields of 0, 0.1, 0.2, 0.3, 0.7, and 1.0 T measured in a 3 Oe ac magnetic field with frequencies ($f$) of (a) 1, (b) 100, and (c) 1488 Hz.
The spectra clearly show that there is intermolecular $\pi-\pi$ stacking (edge-to-edge interaction) in the cast films, and the results agree with those from X-ray crystal analysis, in which 1 is arranged in columns along the a axis with $\pi-\pi$ stacking (0.343 nm, Fig. 2).

![Figure 6](image)

**Figure 6.** Electronic absorption spectra of 1 in chloroform ($10^{-5}$ mol dm$^{-3}$) and cast film at 298 K. The cast film of 1 was prepared on a quartz plate from a dichloromethane solution ($10^{-4}$ mol dm$^{-3}$) by evaporation of the solvent.

Fig. 7a shows a cyclic voltammogram (CV) of a cast film of 1 in a 0.1 mol dm$^{-3}$ aqueous solution of KClO$_4$. The cast film was prepared on a glassy-carbon working electrode (geometric area 0.07 cm$^2$) directly by using a hand-casting method. The CVs of 1 and 2 film showed only two irreversible oxidation waves Ox1 ($E_{1/2}^1 = 294$ mV) and Ox2 ($E_{1/2}^2 = 476$ mV). This is clear evidence that only the Pc ligands in the triple-decker structure undergo redox reactions. The CVs did not change even after more than 10 cycles. On the other hand, the CVs of 1 in dichloromethane showed four reversible waves (Ox1[$E_{1/2}^1 = 111$ mV], Ox2[$E_{1/2}^2 = 369$ mV], Ox3[$E_{1/2}^3 = 855$ mV], Ox4[$E_{1/2}^4 = 1217$ mV]), as shown in Fig. 7b. The oxidation processes in solution are similar to those previously reported[8]. The differences between the CVs of the cast film and the solution of 1 show that J-aggregates are present. In order to obtain stabler films, we are investigating other CV conditions. However, the electrochemical stability of the cast films of 1 and 2 in these studies are satisfactory for preliminary studies on their use in field-effect transistor (FET) devices.

Fig. 8 shows an optical image of the device. Fiber-like 2 was coated on the SiO$_2$ gate dielectric layer. A plot of the transfer characteristics, i.e., drain current ($I_D$) vs. gate voltage ($V_G$), of the device is shown in Fig. 9. The drain voltage $V_D$ was fixed at $-150$ V. $I_D$ increased when $V_G$ was increased in the negative direction, indicating that the device shows p-type FET behavior. In other words, $p$-type charges (holes) accumulate in the semiconductor layer, and the charges are mobile in the fiber-like assembly of 2. The mobility ($\mu$) of the semiconductor was estimated using the standard formula for
FETs to be $2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when $V_G > 100 \text{ V}$ and $V_G < 100 \text{ V}$, respectively. The gate leakage current, which was measured simultaneously, was negligibly small. We note that the current is induced only at the bottom surface of the semiconductor film by the electric field. Since the rest of the semiconductor layer has pronounced conductivity, only 10% of the total current is modulated.

Figure 7. Cyclic voltammogram of (a) a cast film of 1 on a glassy-carbon working electrode versus SCE in 0.1 mol dm$^{-3}$ aqueous solution of KClO$_4$. Start at –200 mV, $v = 100 \text{ mV s}^{-1}$, 298 K. (b) 10$^{-4}$ mol dm$^{-3}$ dichloromethane solution of 1 using glassy-carbon working electrode versus Ag/AgCl in 0.1 mol dm$^{-3}$ of TBAPF$_6$. Start at –200 mV, $v = 100 \text{ mV s}^{-1}$, 298 K.

Figure 8. Optical image of field-effect transistors of 2.
4. Conclusions
Complexes 1 and 2 showed two magnetic relaxation processes in the low temperature region in the presence of a dc magnetic field. Our results suggest that the SMMs/magnetic properties of 1 and 2 significantly change in a dc magnetic field. These relaxation mechanisms are related to the energy gap of the ground-state and QTM[10]. In order to elucidate fully the magnetic relaxation mechanism, further experimental and theoretical studies are required.

Furthermore, our work clearly shows that the cast films of 1 and 2 can be studied for use in devices, such as molecular electronic sensors, electrochromic displays, field-effect transistor devices etc. For preparing devices, the relationship between the SMMs and electron transport properties of Ln₂Pc₃ as well as LnPc₂ must be clarified. The carrier mobility increased by reducing the lattice thermal vibrations of the atoms at low temperature. It might be possible to switch the magnetism of OFETs containing Ln(III)-Pc multiple-decker SMMs between SMMs ↔ paramagnetic by changing the gate voltage[16] and the magnetoresistance between the SMMs as a localized spins and the conduction electrons at low temperature[17]. We believe that these studies will lead to an understanding of the effect of the magnetic field on the magnetic relaxation mechanism and electronic properties. Further studies involving molecular spintronics are now in progress.

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