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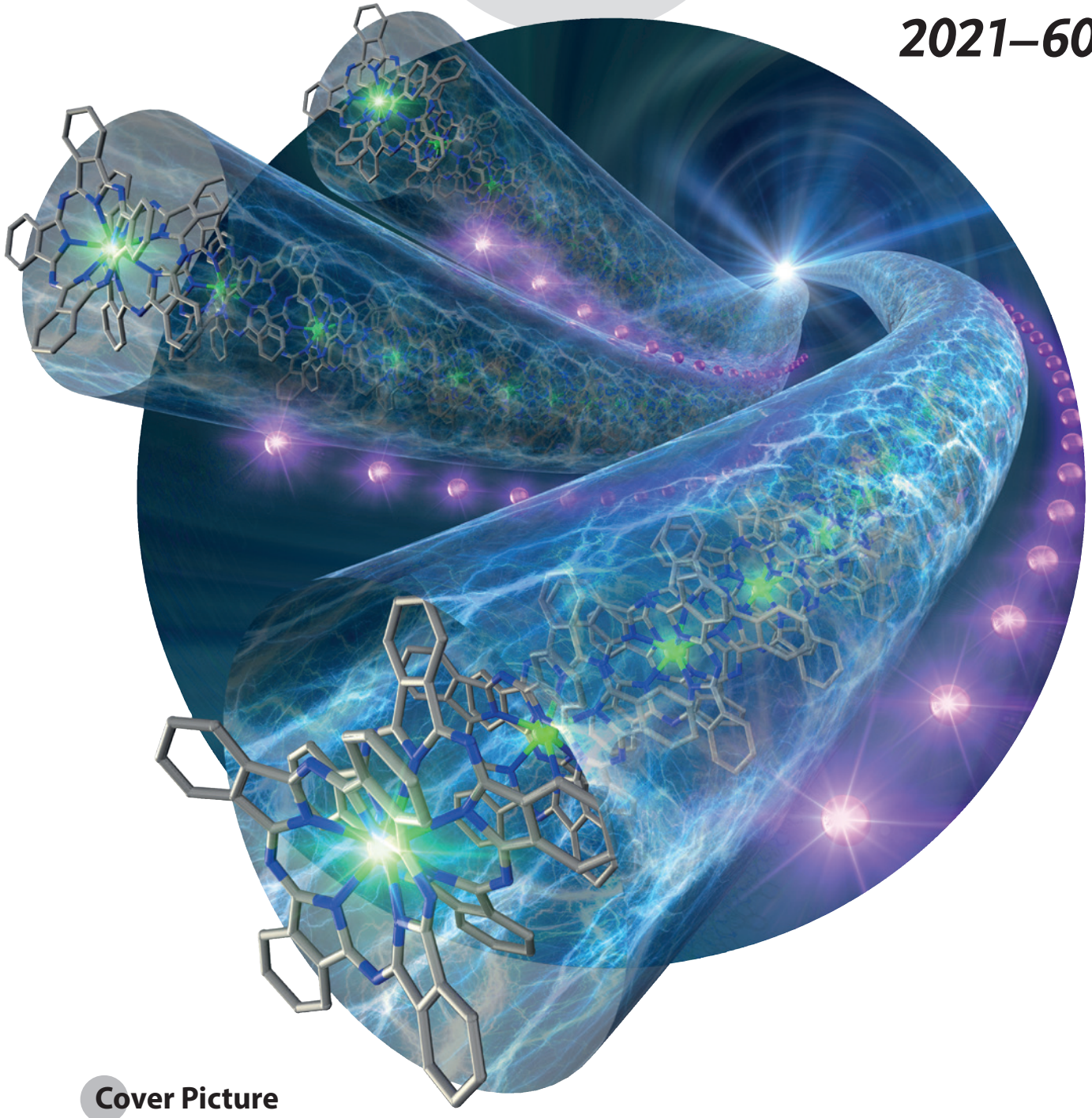

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Magnetic Properties | Hot Paper

Electro-Conductive Single-Molecule Magnet Composed of a Dysprosium(III)-Phthalocyaninato Double-Decker Complex with Magnetoresistance

Tetsu Sato, Brian K. Breedlove, Masahiro Yamashita, and Keiichi Katoh**

Abstract: *A one-dimensional (1D) arrangement of an unsubstituted partially oxidized Dy^{3+} double-decker complex, $[DyPc_2]I_x$ (Pc = phthalocyaninato, I = iodide; 1.93 < x < 2.26) (**1**), was obtained by using electro-oxidation and chemical oxidation. In **1**, the Pc ligands were partially oxidized, and I_3^- ion was present as a counter ion. From the results of spectrophotometric analysis on **1**, the π radicals were delocalized in a 1D column and behaved as a conductor even at low-temperatures. Since conductivity was observed at temperatures lower than the blocking temperature (T_B), magnetoresistance (MR) effects corresponding to a magnetic hysteresis of single-molecule magnet (SMM) were observed when the galvanomagnetic characteristics were investigated at 2.2 K.*

In the 21st century, the development of an information society has been remarkable. In order to support this society, fast processing capabilities for huge amounts of data and molecule-sized information elements are necessary. To achieve fast processing, a mechanism by which two states or any quantum superposition state can be controlled by applying an external magnetic field is desirable.[1] Magnetic recording devices are examples of this technology, which have been widely used so far. However, if they are reduced to few nanoscale domains, where the three-dimensional magnetic interactions between spins are lost, superparamagnetism appears, and the registration phenomenon is lost. Single-molecule magnets (SMMs) have the potential to overcome this problem.[2]

Since an Mn_{12} cluster complex was shown to exhibit SMM phenomena in 1993, 3d and/or 4f metal complexes have been studied as SMMs.[1] In the last 20 years, SMMs with high blocking temperature (T_B) have been synthesized by controlling the ligand field around the metal ion even in single-ion magnets (SIMs).[3] In recent research, we have improved the properties of SMMs by adding functionality to SMMs through careful design of organic ligands and developed multi-functional SMMs in which magnetism and other physical properties, such as luminescent properties and chirality, are correlated.[4–8] Among them, electrically conductive SMMs are attractive systems because they can convert a minute change in the local magnetic field of one molecule into a drastic change in current. The first example of conducting SMMs, where an Mn_4 cluster was combined with a platinum-based molecular conductor, was reported in 2007.[9] This complex, which is arranged in a segregated stack structure, is synthesized by electrochemically combining an anionic conductive complex site $[Pt(mnt)_2]^{n-}$ and a cationic site $[Mn_4]^{4+}$ with SMM properties. This complex has a high conductivity of 0.22 S cm^{-1} at room temperature due to a conduction path based on the platinum $5d_{z^2}$ orbital and undergoes slow magnetic relaxation below 10 K. However, it exhibits insulator properties at 110 K, which is higher than T_B of the $[Mn_4]^{4+}$ SMM unit. In other words, although this complex is bifunctional, the conduction properties and the SMM properties are not observed at the same time. There are only a few recent examples exhibiting bifunctionality in the same temperature range.[10] In order to solve this problem, there has been a demand for conductive SMMs that have high conductivities even at low-temperature and high T_B.[10] In order to overcome this, supramolecular materials where SMMs have been attached to the outside of carbon nanotubes (CNTs) have been synthesized.[11] However, the orientation of the guest SMM on the CNT surface has not been determined, and a correlation occurs only at an extremely low-temperature of 40 mK. Thus, innovative design in which the conduction π electrons and localized f electrons are correlated in a single molecule, rather than the previous combination of a conductive unit and an SMM, is desired.

In this work, we focused on bis-phthalocyaninato (Pc^{2-}) lanthanoid (Ln^{3+}) double-decker SMMs ($LnPc_2$) with electrical conduction properties. In the structure of $LnPc_2$, an Ln^{3+} ion is sandwiched between two Pc^{2-} ligands. The axial ligand field strongly stabilizes the crystal field sublevels with oblate type electron configurations, and some $LnPc_2$ SMMs have high energy barriers (U_{eff}) to the inversion of their magnetic moment.[12,13] In addition, since these $LnPc_2$ SMMs have high heat resistances of several hundred degrees, one molecule can be detected after vacuum deposition onto the substrate,[14] and it has been confirmed that SMM performance is maintained after undergoing a redox reaction.[15,16] Our group has focused on $LnPc_2$ with Tb^{3+} and Dy^{3+} ions and has continued to investigate the effects of the twist angle (φ) between the ligands and the intermolecular distance between the central Ln^{3+} ions on the magnetic relaxation behavior. In particular, it

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has been reported that the magnetic relaxation time (τ) is elongated more than 100 times by changing the packing of the neutral $TbPc_2$[17] and that the linear packing of heteroleptic complex $[TbNcPc]^{0/+}$ (Nc^{2-} = naphthalocyaninato) can effectively suppress the quantum tunneling of the magnetization (QTM).[18] These reports mean that the magnetic interactions between SMMs increase the performance of the SMM components.

The Dy^{3+} ion has a large spin multiplicity ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $J = 15/2$) and is a Kramers ion. In other words, the degenerate magnetic ground state is preserved regardless of the symmetry of the crystal field. So, it should be easy to obtain bistability, and QTM between degenerate orbitals can be suppressed by applying a magnetic field.[19] For this reason, there are a large number of reports on SMMs using Dy^{3+} ions.[20] This time, we focused on the partially oxidized $[DyPc_2]I_x$ (**1**) (I = iodide), in which the unsubstituted $DyPc_2$ molecules are arranged in one dimensional (1D) stacks. 1D MPc complexes (M = H_2, Cu, Ni) are known as organic conductors[21,22] and show conduction properties down to the low-temperature region with holes as carriers on the Pc ligands in partially oxidized states. Moreover, in these complexes, the vacancies are parallelly arranged beside the 1D columns composed of Pc ligands, and counter anions are present to compensate for the charge of the partially oxidized Pc skeleton. Pc complexes with various valences, depending on the metal ion and so on, have been reported.[21] Thus, the valences of the Pc complexes are determined by the number of counter ions, for which polyhalides are sometimes used.[23] The attractive point of using 1D stacked Pc ligands is that the electrical conductivity can be changed drastically by tuning the valence of the ligand continuously by doping with counter ions.[24] There are many reports of porous coordination polymers whose conductivities and magnetism change discretely by introducing guests,[25] but there are only a few systems of which the electronic and physical properties can be adjusted continuously.

Even for MPc_2 systems, semiconductor-like behavior has been reported from room to low-temperature regions when the metal (M) ions are In^{3+}, Zr^{4+}, and U^{3+},[26] and low-temperature conduction properties are expected for 1D stacked $DyPc_2$ complex. There have been several reports on partially oxidized 1D $[LnPc_2]I_x$ complexes (Ln = Ce, Pr, Sm, Ho and Yb).[27–31] In these reports, $[LnPc_2]I_x$ is synthesized using harsh oxidation conditions in ampules containing phthalonitrile, Ln powder and iodine above 200 °C. In recent years, we have developed method A for synthesizing 1D partially oxidized forms by electro-oxidation of neutral $LnPc_2$.[32] In method A, the neutral product was electrolytically oxidized while adding tetrabutylammonium iodide (TBAI) in dichloromethane to obtain **1** over 4 weeks. In addition to obtaining a sample with high purity, this method has the advantage that a large single crystal, which is indispensable for measuring physical properties, can be obtained. In this paper, we report synthetic method B, which involves chemical oxidation. Method B requires shorter sample preparation times, and magnetic dilution using isostructural diamagnetic YPc_2 molecules can be performed without spontaneous separation. For method B, tetrabutylammonium triiodide ($TBAI_3$) was used as the oxidizing agent, and a suitable sample was obtained overnight. A structure of **1**[46] is shown in Figure 1. Since the Y^{3+} complex $[YPc_2]I_x$ (**2**) is isostructural, its structure[46] is described in the supporting information (Figures S1, S2 and Table S1).

Structure determination was performed using a single crystal of **1** prepared by using method A. The zenithal angle (θ) and φ between intramolecular Pc ligands, which determine the ligand field of double-decker type SMMs,[33] were 53.9° and 40.3°, respectively. The coordination geometry of **1** is quite similar to that of neutral $DyPc_2$ ($\theta = 54.8°$, $\varphi = 41.0°$).[34] Dy^{3+} ions are precisely aligned on a magnetic easy axis (C_4 rotation axis). Therefore, $|J_Z| = 13/2$ was estimated to be the lowest ground state for **1**.[12,33,35,36] In addition, the first proximity distance between the Dy^{3+} ions in **1** was determined to be 6.34 Å along the *c*-axis, and the second proximity distance was 14.3 Å. There are strong 1D magnetic dipole-dipole interactions between the Dy^{3+} ions in **1**.

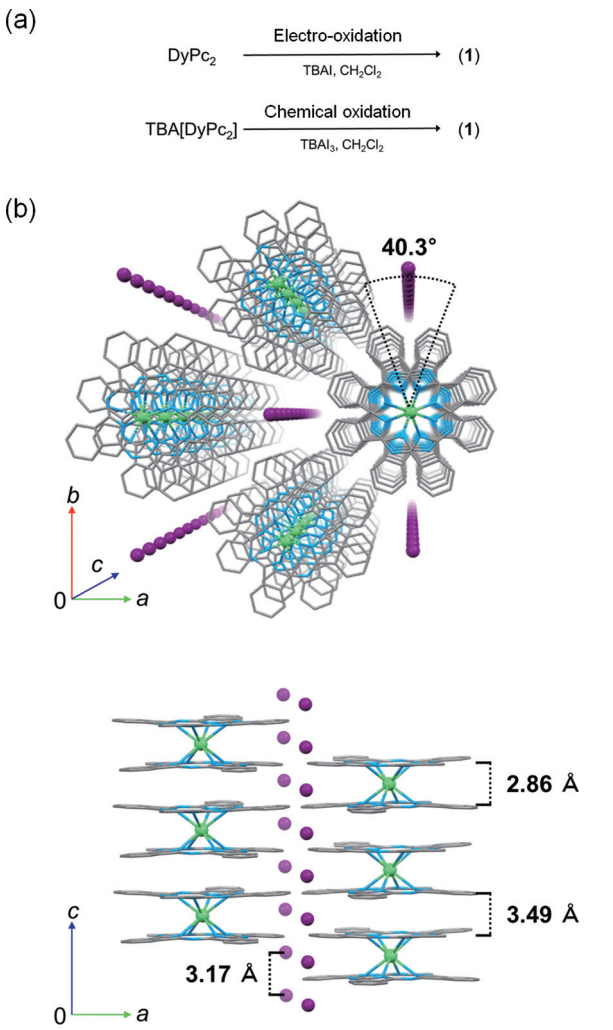

Figure 1. a) Method (A: electro-oxidation) and (B: chemical oxidation) for the synthesis of **1**. b) Top and side views of **1**,[46] high-lighting the intermolecular twist angle of Pc ligands and the distance along the *c*-axis. H atoms are omitted for clarity. Dy^{3+}: light green, C: gray, N: light blue, and I: purple.

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The optimized occupancy of the I counter ions from X-ray diffraction indicates that there are two I atoms to one molecule of $DyPc_2$. The occupancy of the I atoms had a range of $1.93 < x < 2.26$, and the results of elemental analysis and thermogravimetry support the ratio for this element (Table S2 and Figure S3). From solid-state Raman microspectroscopy, the I atoms are present as triiodide ions (I_3^-), and this is consistent with several reports of 1D MPc complexes with 3d metal ions.[21] From the above results, the valence of the Pc ligands was calculated to be −1.2. Since the ligand is in a partially oxidized state, the delocalized electrons should exhibit low-dimensional conduction behavior through the π orbitals between molecules, as shown in previous reports.[28] In order to investigate this delocalization, microspectroscopic measurements were performed on a single crystal at 298 K, and a broad absorption band due to a conduction electron was observed from the near-infrared (NIR) to the infrared (IR) regions (Figure S4). For further details, the angular dependence of the reflection spectra was investigated (Figure 2). When a crystal was irradiated parallel to the $DyPc_2$ stacking direction (//*c*), a sharp decrease in the IR region was observed. This reflection edge means that electrons behave like free electrons along the *c*-axis, which is consistent with the Drude model, which theoretically explains the optical response of metal.[37] This indicates that **1** has anisotropic metal conduction along the *c*-axis.

The magnetic susceptibilities of polycrystalline and single crystal samples of **1** synthesized by using both methods (A and B) were measured using a superconducting quantum interference device (SQUID) magnetometer. Moreover, we measured the magnetic anisotropy of a single crystal and directly observed the magnetic easy axis (Figure 3 a). Splitting in M vs. HT^{-1} plots for a bulk sample was observed due to the magnetic anisotropy of **1** (Figure S5).[38] The value of $\chi_M T$ vs. T increased rapidly when $T < 10$ K, suggesting that there are ferromagnetic dipole-dipole interactions between the Dy^{3+} ions in **1**, which is called a "dipolar bias" (Figure S6).[39–41] This result is consistent with that for a previous 1D array of Tb^{3+} double-decker complexes.[18] A 1D array of Ln^{3+} double-decker type complexes can induce strong ferromagnetic interactions between Ln^{3+} ions in comparison with those in slip-stacking arrays.[17,42] When MH of **1** at 2.2 K was measured using a vibrating sample magnetometer (VSM) unit for Physical Property Measuring System (PPMS), magnetic hysteresis indicated the presence of a coercive force (H_c), and it was dependent on the sweep rate of magnetic field (Table S3, S4 and Figure S7). From alternating current (ac) susceptibility measurements in a zero-field, **1** underwent slow magnetic relaxation behavior when $T <$ 20 K (Figure S8). τ was calculated by fitting the ac susceptibilities with an extended Debye model [Eq. (S1)–(S3)]. From the fitting of the Arrhenius plot, the mechanism of the magnetic relaxation was thought to be a combination of Orbach, Raman, and QTM processes (Table S5, S6). It is dominated by the Orbach process in the high-temperature region and QTM in the low-temperature region. The Raman process, which has a low exponent, is estimated from the two phonon Raman process of the spin-lattice relaxation.[43] From the results of fitting using the Orbach process, U_{eff} and the pre-exponential factor (τ_0) were determined to be 57.8 cm^{-1} and 3.62×10^{-7} sec, respectively. The values are relatively high in comparison with those for other Dy^{3+} double-decker complexes,[44] which is thought to be due to φ approaching 45° and a narrower intramolecular Pc distance. Comparing the Arrhenius plots with those for a magnetically diluted sample $[Dy_{0.02}Y_{0.98}Pc_2]I_x$ (**3**), τ for **1** is four times longer at 1.8 K (**1**: 0.0050 s, **3**: 0.0013 s) (Figures S9, S10), and QTM at low-temperature was suppressed by the dipolar bias in the 1D array (Figure S5). This indicates that the dipolar bias can be controlled by careful arrangement of the Ln^{3+} double-decker complexes.

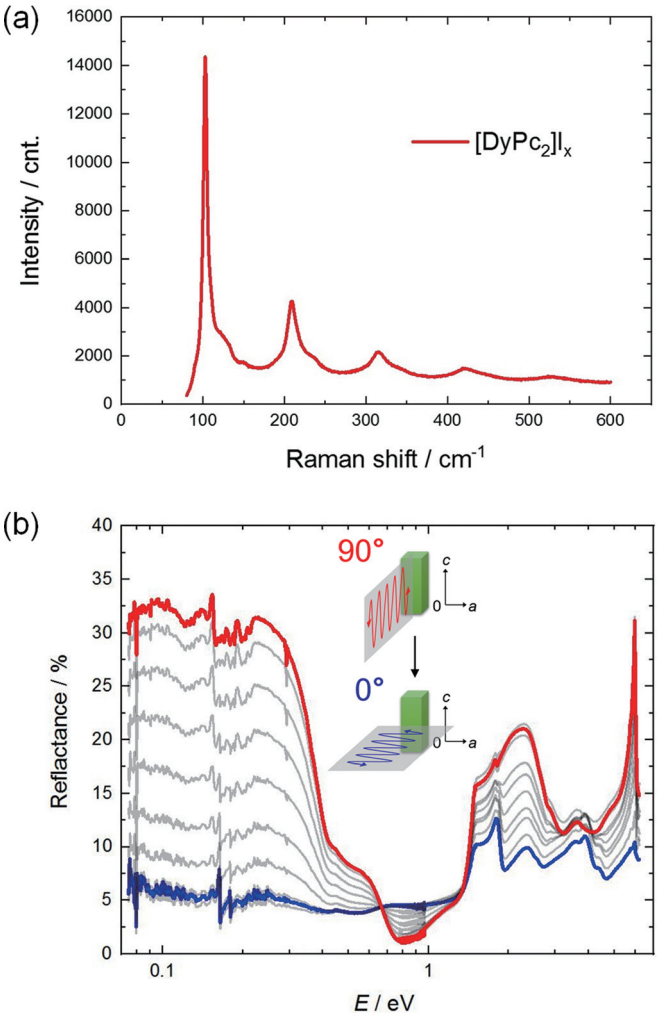

Figure 2. a) Raman spectrum of a single crystal of **1** at 298 K without polarization. b) Polarized reflection spectra for **1** from IR to UV regions obtained using a single crystal at 298 K. Polarization parallel to *c*-axis (red solid line) and perpendicular to *c*-axis (blue solid line). The spectral transition is shown as the gray line. Green cuboids represent single crystal as schematic illustration.

Since the results from polarized reflection spectroscopy indicated 1D metallic conductivity, the temperature dependence of the ac electrical conductivity of **1** was investigated using a PPMS. An alternating current four-terminal (ACT) method was used on a single crystal of **1** (Figure S11). In the range of 300–150 K, the conductivity increased, and metallic

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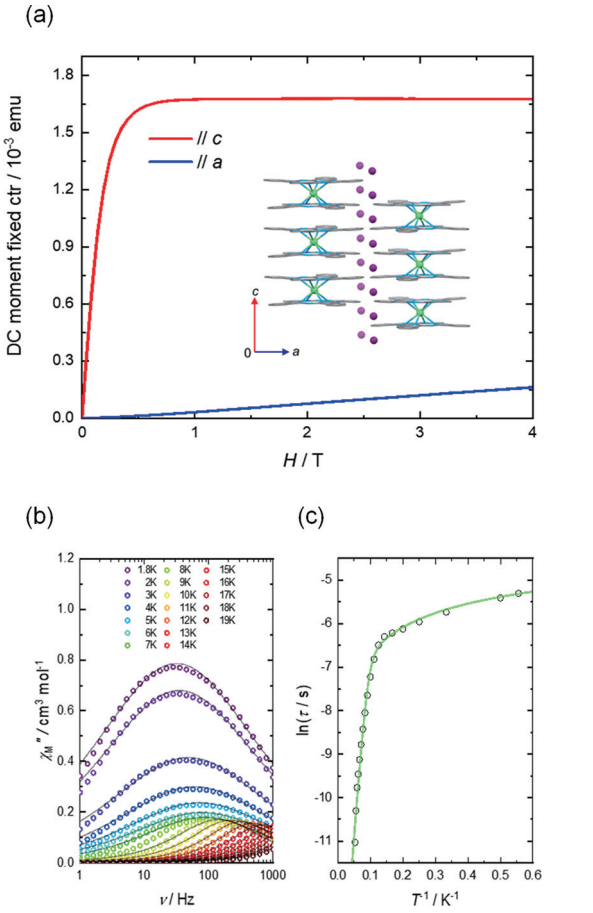

Figure 3. a) *MH* at 1.8 K for a single crystal of **1** with a magnetic field parallel (red line) and perpendicular to the *c*-axis (blue line). b) Frequency dependence of χ_M'' for **1** at zero field as a function of temperature. c) Temperature dependence of the magnetic relaxation times (τ) for **1**. Green solid line represents the best fit of the temperature dependence of τ at zero field to a combination of Orbach, Raman, and QTM relaxation processes.

behavior ($\approx 30\ S\,cm^{-1}$) was observed (Table S7). On the other hand, in the range of 150–2.2 K, the conductivity decreased rapidly. The fully oxidized form, $[TbPc_2]BF_4$, reported in 2017, has a crystal structure similar to **1**.[45] However, since this complex was a simple ionic compound, it exhibits a certain degree of electrical conductivity via hopping, and it acts as an insulator at 40 K. This transition temperature is higher than the T_B of $[TbPc_2]BF_4$. This is why no interactions have been observed between delocalized conduction π electrons and localized f electrons. Due to the sample batch dependence of **1**, galvanomagnetic properties are currently under investigation, but since it has a conductivity of about $2.4 \times 10^{-3}\ S\,cm^{-1}$ even near the T_B of **1**, the magnetic field dependence of the resistance value was measured using the same single crystal above 2 K. As a result, the resistance showed hysteresis (Figures 4 and S12), and a negative magnetoresistance was observed ($\Delta MR = -0.5\,\%$). Since the hysteresis opening corresponds to the *MH* curve, we concluded that the galvanomagnetic properties between the SMMs and the electrical conduction characteristics due to the π-f interactions could be observed.

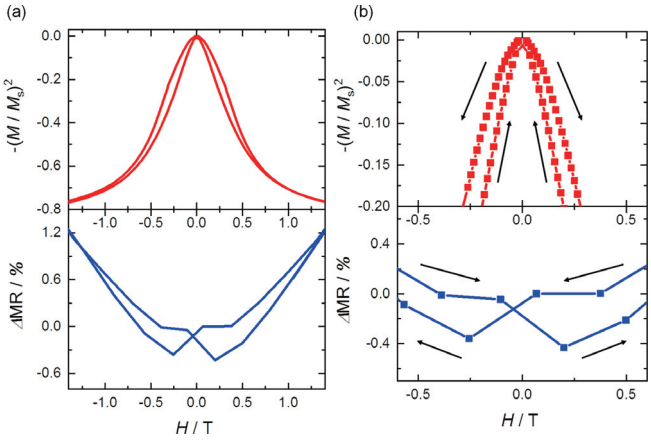

Figure 4. a) *MH* curve at 2.2 K for polycrystalline sample (top) and magnetoresistance (MR) measurement of single crystal at 2.2 K (bottom). b) A magnified plot in the range of ±0.5 T. Four-probe conductivity measurements in a magnetic field were performed with an ac transport measurement system: amplitude, 0.1 mA; frequency, 10 Hz; duration, 1 s, sweep rate, 0.0150 T sec^{-1}.

In conclusion, we obtained the partially oxidized 1D complex $[DyPc_2]I_x$ (**1**) by using both electrical and chemical oxidation methods. Magnetic dipole interactions occur between the Dy^{3+} ions in **1**. In addition, QTM was suppressed by applying a dipolar bias like it was for Tb^{3+} analogues. From conductivity measurements on single crystals, electrical conductivity through the partially oxidized Pc ligands was observed. A negative magnetoresistance effect for SMMs near the T_B of **1** was observed. We are continuing to investigate the galvanomagnetism due to π-f interactions in partially oxidized $[LnPc_2]I_x$ 1D complexes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: dipolar bias · dysprosium · magnetoresistance · metallic conductivity · single-molecule magnets

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