Surface Self-Assembly of Trans-Substituted Porphyrin Double-Decker Complexes Exhibiting Slow Magnetic Relaxation*

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A novel single-molecule magnet (SMM) of trans-substituted Tb(III) porphyrin, $\{\text{Tb}([\text{BIPPP}]_2)[\text{DBU-H}]\}$ (BIPPP: 5,15-bis(3,5-isopentoxyphenyl)porphyrin, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene), is reported here. The alternating current magnetic susceptibility measurements showed the frequency dependence on the in-phase and out-of-phase magnetic susceptibility under both zero and 2000 Oe direct current magnetic fields. The barrier height for the reversal of the magnetic moment at the high-temperature region was estimated to be 299 cm$^{-1}$, which is the same order as that of the previously reported tetraphenylporphyrin-based Tb(III) double-decker complex. Atomic force microscopy revealed that $\{\text{Tb}([\text{BIPPP}]_2)[\text{DBU-H}]\}$ formed self-assembled monolayers on highly oriented pyrolytic graphite using the simple drop-cast technique. The result proves the high design freedom of porphyrin-based double-decker SMMs.

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I. INTRODUCTION

Single molecule magnets (SMMs) are molecules with strong easy-axis magnetic anisotropy; they exhibit slow relaxation of magnetization and stable magnetization below the blocking temperature [1–3]. SMMs have attracted wide attention in the scientific community owing to their application to molecular spintronics [4]. So far, an interesting topic of research has been the design of new SMMs exhibiting a slow magnetic relaxation process. On the other hand, another interesting topic of research in the recent years has been the design of SMMs as the active units in spintronic devices [5]. The organization of SMMs on surfaces rather than in bulk phases is regarded as the first step along this direction.

The studies of SMMs on surfaces have been mainly based on the phthalocyanine Tb(III) double-decker compounds because of their considerably high energy barrier for magnetic moment reversal and planar structure that is suitable for their organization on a surface [6–9]. Recently, we focused on Tb(III) porphyrin double-decker SMMs owing to their higher functional group tunability [10, 11]. In this paper, we report the synthesis, magnetic relaxation process, and surface self-assembly of a SMM of trans-substituted porphyrin, $\{\text{Tb}([\text{BIPPP}]_2)[\text{DBU-H}]\}$ (BIPPP: 5,15-bis(3,5-isopentoxyphenyl)porphyrin, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene).

II. EXPERIMENTAL

A. General

All chemicals and solvents were of reagent grade and used as received without further purification. The elemental analyses were performed using a Yanaco CHN CORDER MT-5. Mass spectra (MS) were recorded using a Shimadzu AXIMA-CFR matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer. Ultraviolet-visible-near-infrared (UV-vis-NIR) absorption spectra were recorded using a Shimadzu UV-3150 double-beam spectrophotometer and 1.0 cm quartz cuvettes. The alternating current (ac) magnetic susceptibility and hysteresis loop measurements were carried out using a Quantum Design MPMS-XL7AC SQUID magnetometer. The atomic force microscopy (AFM) mea-

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FIG. 1: Synthesis of porphyrin double-decker complex, \{[\text{Tb(BIPPP)}_2](\text{DBU-H})]\}.

FIG. 2: UV-vis-NIR absorption spectra of \{[\text{Tb(BIPPP)}_2](\text{DBU-H})]\} in CH$_2$Cl$_2$.

measurements were carried out using a Multimode 8 setup equipped with a NanoScope V controller (Bruker Nano Inc., Nano Surfaces Division, Santa Barbara, CA, USA). ScanAsyst-air cantilevers with $k = 0.4$ Nm$^{-1}$ were used.

B. Synthesis of \{[\text{Tb(BIPPP)}_2](\text{DBU-H})]\}

The free-base porphyrin, 5,15-bis(3,5-isopentoxyphenyl)porphyrin (H$_2$BIPPP), was prepared according to the reported procedure [12]. The protonated complex was prepared by the reaction of [\text{Tb}^{III}(\text{acac})_3] (acac = acetylacetonate) (152.4 mg), H$_2$BIPPP (80.1 mg, 0.099 mmol) in DBU (0.6 mL) at 330°C for 1.5 h under anhydrous nitrogen atmosphere. The residue obtained was purified by alumina column chromatography using dichloromethane (CH$_2$Cl$_2$) as the eluent to afford a dark purple solid of protonated Tb(III) double-decker complex (34.0 mg, 0.019 mmol, 38.7% yield). DBU (0.1 mL) was added to a solution of the protonated complex (28.1 mg, 0.016 mmol) in acetone. Then, methanol was slowly added to the solution to afford a crystalline powder of \{[\text{Tb(BIPPP)}_2](\text{DBU-H})]\} (26.5 mg, 0.014 mmol, 86.8% yield). MALDI-TOF MS (m/z): M$^+$ Calcd for C$_{104}$H$_{121}$N$_8$O$_8$Tb, 1768.86; Found, 1768.7. Anal. Calcd for \{[\text{Tb(BIPPP)}_2](\text{DBU-H})]\}; C, 70.64; H, 7.27; N, 7.22; Found C, 70.60; H, 7.29; N, 7.18.

FIG. 3: Temperature dependence of the in-phase ($\chi'$) and out-of-phase ($\chi''$) alternating current (ac) susceptibility of \{[\text{Tb(BIPPP)}_2](\text{DBU-H})]\} with a 3.9 G ac field amplitude under zero direct current (dc) magnetic field (a, b), and 2000 Oe magnetic field (c, d), respectively.

III. RESULTS AND DISCUSSION

The double-decker complex, \{[\text{Tb(BIPPP)}_2](\text{DBU-H})]\}, was synthesized by the reaction of H$_2$BIPPP, [\text{Tb}^{III}(\text{acac})_3], and DBU at 330°C for 1.5 h, and the obtained complex was recrystallized in an acetone/methanol solution of DBU (Fig. 1). The powder sample obtained was characterized by the MS and CHN elemental analyses. The elemental analysis showed that one protonated DBU molecule (DBU-H) is included as a counter cation. A UV-vis-NIR spectrum of \{[\text{Tb(BIPPP)}_2](\text{DBU-H})]\} was measured in CH$_2$Cl$_2$ (Fig. 2). The absorption spectrum exhibited a characteristic Soret band at 398 nm and broad Q bands in the 500-750-nm range, which are usually observed in the typical spectra of porphyrin double-decker complexes [10]. Notably, the spectrum does not exhibit the characteristic NIR absorption band of oxidized double-decker complexes in the 800-1200-nm range [13]. This result strongly indicates that pure anionic complexes were isolated, and no neutral $\pi$ radical complex was formed.

It is known that ac magnetic susceptibility measurements monitor the response of a magnetic moment to an applied oscillating magnetic field, and are suitable to detect the slow relaxation of magnetization of SMMs. To estimate the magnetization relaxation behavior of
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FIG. 4: Frequency dependence of the ac susceptibility for a powder sample of \([\text{Tb(BIPPP)}_2(\text{DBU-H})]\) under 2000 Oe dc magnetic field with a 3.9 G ac field amplitude. (a) in-phase \((X'_M)\) and (b) out-of-phase \((X''_M)\). (c) Argand plots for the powder sample. The solid lines were fitted using a generalized Debye model.

FIG. 5: Hysteresis loops at 1.8 K recorded on a powder sample of \([\text{Tb(BIPPP)}_2(\text{DBU-H})]\).

The ac magnetic susceptibility measurements were carried out. Figure 3 shows the temperature dependences of the ac susceptibilities of a polycrystalline powder sample of \([\text{Tb(BIPPP)}_2(\text{DBU-H})]\). The frequency dependence on the in-phase \((X'_M)\) and out-of-phase \((X''_M)\) with a 3.9 G ac field oscillating at the indicated frequencies was observed under both zero and 2000 Oe direct current (dc) magnetic fields. Because ferromagnetic transition do not show such frequency dependency, the ac susceptibilities indicate that \([\text{Tb(BIPPP)}_2(\text{DBU-H})]\) behaves as an SMM. To the best of our knowledge, this is the first report on an SMM based on a trans-substituted porphyrin. A sharp drop in \(X'_M\) and \(X''_M\) peaks was observed at 16, 19, and 22 K under 2000 Oe dc magnetic field with ac frequencies of 10, 100, and 1000 Hz, respectively. The \(X''_M\) peak temperature for an AC field of 1000 Hz under 2000 Oe magnetic field was estimated to be 299 cm\(^{-1}\) with a frequency factor \((\tau_0)\) of \(4.2 \times 10^{-13}\) s; these were estimated from the Arrhenius plot using the \(X''_M\) peak tops of 10, 100, and 1000 Hz under 2000 Oe magnetic field. The value obtained for the barrier height was of the same order as that of the previously reported \(\text{Tb(III)}\) tetraphenylporphyrin (TPP) double-decker complex (283 cm\(^{-1}\)) [10].

To investigate the SMM property in more detail, the variable-frequency ac magnetic susceptibility measurements under 2000 Oe dc magnetic fields were performed (Figs. 4(a) and (b)). In the measurement temperature range (12, 14, and 16 K), clear frequency dependency of \(X'_M\) and \(X''_M\) peaks was observed. The Argand plots (i.e., \(X''_M\) vs. \(X'_M\) plot) are shown in Fig. 4(c), which can be fitted by the generalized Debye model [14]. The \(\alpha\) parameters, which quantifies the width of the relaxation time \((\tau)\) distribution and are obtained in the fitting of the generalized Debye model, are in the 0.28-0.30 range, proving that the distribution is sufficiently small.

When the dc magnetization of \([\text{Tb(BIPPP)}_2(\text{DBU-H})]\) was measured at 1.8 K within \(\pm 20\) kOe, a butterfly shape was observed (Fig. 5). The butterfly-shaped loop can be attributed to the fast magnetization tunneling process occurring near the zero field assisted by nuclear spin \(I = 3/2\) of Tb, which was typically observed in other Tb double-decker complexes [15].

To investigate the self-assembly properties of \([\text{Tb(BIPPP)}_2(\text{DBU-H})]\) on a surface, a solution of the complex in CH\(_2\)Cl\(_2\), which has an absorbance of 0.3 for the Soret peak at 398 nm, was drop cast onto a freshly cleaved highly oriented pyrolytic graphite (HOPG) under ambient conditions. The solvent was allowed to evaporate; the films obtained were observed by AFM. Figure 6(a) shows the AFM image of the complex on the HOPG. The molecules on the HOPG were observed as thin films with porous structures. The height or thickness of the thin film layer is approximately 1.6 nm, as shown in Fig. 6(b). The surface of the films were relatively smooth, indicating that well-ordered structures were formed. To investigate the assembled...
FIG. 6: (a) Topographic image of the thin film of $\{\text{Tb(BIPP})_2\text{(DBU-H)}\}$ on HOPG. (b) Cross section of the white line in (a). (c) The molecular model for the core structure of $\{\text{Tb(BIPP})_2\text{(DBU-H)}\}$.

In conclusion, a novel porphyrin double-decker complex, $\{\text{Tb(BIPP})_2\text{(DBU-H)}\}$ was synthesized. The UV-vis-NIR absorption spectrum showed that the isolated complex exists in an anionic form. The ac magnetic susceptibility measurements showed that $\{\text{Tb(BIPP})_2\text{(DBU-H)}\}$ behaves as an SMM. This is the first report on an SMM of trans-substituted porphyrins. The results show that the low-symmetry porphyrins can also be a component of SMMs, proving that the porphyrin-based SMMs may have significantly high design freedom. Furthermore, the AFM study showed that $\{\text{Tb(BIPP})_2\text{(DBU-H)}\}$ forms self-assembled monolayers on HOPG by the simple drop-cast technique. We expect that porphyrin-based SMM systems will provide a new design strategy for SMM-based molecular devices.

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