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Probing the Magnetic Properties of Three Interconvertible Redox States of a Single-Molecule Magnet with Magnetic Circular Dichroism Spectroscopy

Mathieu Gonidec,[†,§] E. Stephen Davies,[‡] Jonathan McMaster,*[,‡] David B. Amabilino,*[,†] and Jaume Veciana*[,†,§]

Institut de Ciència de Materials de Barcelona (CSIC) and Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Campus Universitari de Bellaterra, E-08193 Bellaterra, Barcelona, Spain, and School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

Received November 11, 2009; E-mail: vecianaj@icmab.es; amabilino@icmab.es; j.mcmaster@nottingham.ac.uk

Single-molecule magnets (SMMs), which are capable of exhibiting magnetic bistability[1] and present unique quantum properties,[2,3] have a range of potential applications in nanoscience including information storage[4] and molecular spintronics.[5] The anionic double-decker phthalocyanine complexes of Tb, Dy, and Ho behave as single-molecule magnets.[6,7] While efforts have been made to study the magnetic behavior of their one- and two-electron oxidized forms,[8,9] no magnetic hysteresis data have been reported. Herein, we present the spectroelectrochemical characterization of the anionic, neutral, and cationic equivalents of a terbium double-decker complex (**1**, Figure 1) and report a study of the corresponding hysteresis of magnetization using magnetic circular dichroism (MCD) spectroscopy in frozen dilute solutions at low temperature (1.5 K). Our results show that low temperature MCD spectroscopy is a viable and powerful technique to study the magnetization properties of this interesting family of compounds.

MCD spectroscopy has been shown to be a powerful tool for the optical detection of the magnetic behavior of Mn_{12} cluster SMMs.[10−13] An advantage that MCD spectroscopy offers, when compared to standard magnetometric measurements, is high sensitivity; this allows measurements of the magnetization of a collection of isolated molecules in dilute frozen solutions with diamagnetic solvents, thus minimizing the effect of intermolecular magnetic interactions and facilitating measurements at the single-molecule level.

We synthesized the neutral complex **1** following a previously reported procedure.[14] The redox properties of **1** were determined by cyclic voltammetry (Figure S1), and the oxidation and reduction processes at $E_{1/2} = 0.45$ and 0.09 V vs SCE, respectively, were studied further by UV/vis spectroelectrochemistry at 273 K. The spectroscopic changes in the absorption spectra associated with the one-electron electrochemical interconversions of $[Pc_2Tb]^{+/0/-}$ are shown in Figure S2. These demonstrate that $[Pc_2Tb]^{+/0/-}$ species may be electrogenerated reversibly and are stable on the time scale of the experiment. The UV/vis spectra of $[Pc_2Tb]^{+/0/-}$ (Figure 1) show the characteristic absorption bands of double-decker phthalocyanine complexes, including Soret bands at 387, 371, and 358 nm and Q bands at 705, 663, 624 nm, respectively.[15] In the case of $[Pc_2Tb]^{+/0}$, the characteristic π-radical band is observed at 495 and 475 nm, respectively.[15]

The samples for MCD spectroscopy, as solutions in CH_2Cl_2 with 0.8 M $[NBu_4][BF_4]$, were frozen in liquid nitrogen, which afforded glasses of suitable quality for optical measurements. In situ absorption spectra support the absence of aggregation of $[Pc_2Tb]^{+/0/-}$ under the conditions used (Figure S3−S5), an important feature of these experiments in which we probe the magnetic properties of a collection of molecules for which intermolecular magnetic interactions are minimized.

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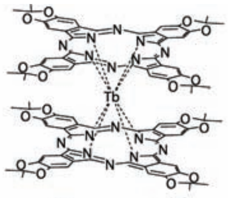

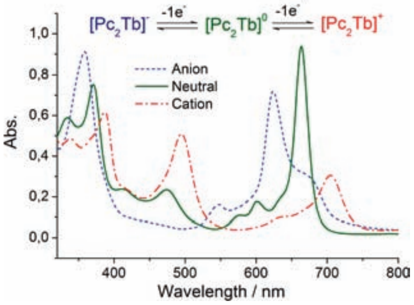

Figure 1. UV/vis absorption spectrum of solution of $[Pc_2Tb]^0$, in CH_2Cl_2 with 0.4 M $[NBu_4][BF_4]$, and of solutions of $[Pc_2Tb]^{+/-}$ generated electrochemically from $[Pc_2Tb]^0$. All spectra recorded at 273 K.

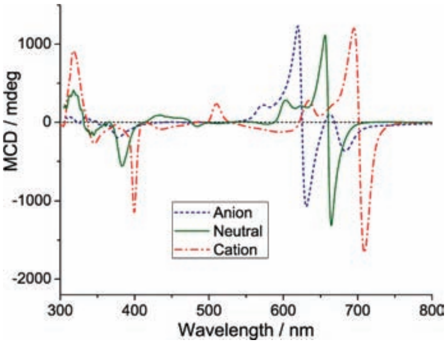

Figure 2. MCD spectra of solutions of $[Pc_2Tb]^{+/0/-}$ at 1.5 K and 7 T in CH_2Cl_2 with 0.8 M $[NBu_4][BF_4]$.

The rich MCD spectra of solutions of $[Pc_2Tb]^{+/0/-}$ (Figure 2) contain prominent temperature and field dependent pseudo-A terms at 701, 660, and 624 nm, respectively, that correspond to the intense Q-band features in the UV/vis absorption spectra (Figure 1). In addition, the fingerprint π-radical band of $[Pc_2Tb]^0$ and $[Pc_2Tb]^+$ show temperature-dependent MCD bands of opposite sign at 484 and 510 nm, respectively.

[†] Institut de Ciència de Materials de Barcelona (CSIC).
[§] CIBER-BBN.
[‡] University of Nottingham.

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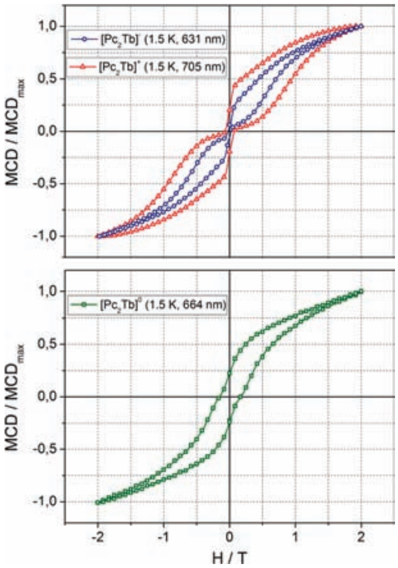

Figure 3. Hysteresis curves of the normalized MCD intensity vs *B* recorded at 1.5 K and a sweep rate of 1 T·min^{-1} for the Q-band of [*Pc*$_2$Tb]$^{+/-}$ (top) and [*Pc*$_2$Tb]^0 (bottom). The symbols represent 1 of every 5 data points.

The MCD intensity was monitored at 705, 664, and 631 nm for [*Pc*$_2$Tb]$^{+/0/-}$, respectively, over a $B = \pm 2$ T field range at a sweep rate of 1 T·min^{-1} and plotted as magnetization hysteresis curves (Figure 3). The field dependent MCD intensity of solutions of [*Pc*$_2$Tb]$^{+/-}$ recorded at 705 and 631 nm, respectively, (Figure 3, top) both present butterfly shaped hysteresis curves that are almost saturated at $B = \pm 2$ T, with an abrupt drop at $B < 0.09$ T. These data are similar to the hysteresis curves obtained by magnetometry on dilute solid solutions of [NBu$_4$][*Pc*$_2$Tb] in the isostructural diamagnetic [NBu$_4$][*Pc*$_2$Y] host,[16] suggesting that MCD of frozen solutions of [*Pc*$_2$Tb]$^{+/0/-}$ is a viable probe of the magnetic properties of isolated [*Pc*$_2$Tb]$^{+/0/-}$ complexes. The principal differences between the responses for [*Pc*$_2$Tb]$^+$ and [*Pc*$_2$Tb]$^-$ include a larger coercive field (0.071 T compared to 0.023 T) and a stronger remnant signal (0.198 as compared to 0.065 of the saturated signal intensity) for [*Pc*$_2$Tb]$^+$.

The sharp drop in magnetization at $B < 0.09$ T for the dilute solid solution of [*Pc*$_2$Tb]$^-$ arises from eight |Jz> ||Iz> states which are brought to resonance by the Zeeman splitting.[17] This resonance only occurs at low field because of the small energy differences between these states. The very similar behaviors observed in the MCD of frozen solutions of [*Pc*$_2$Tb]$^{+/-}$, especially the coincidence of the change in magnetization around $B = \pm 0.09$ T, suggest that the source of their magnetic behavior is closely related. The difference in the width of their hysteresis curves above approximately 0.2 T suggests that the |Jz> multiplet splitting is larger for [*Pc*$_2$Tb]$^+$ than for [*Pc*$_2$Tb]$^-$. This is consistent with the temperature dependence of the maximum in the imaginary component of the ac-susceptibility measurements previously reported for these oxidation states.[9] The field dependent MCD of [*Pc*$_2$Tb]^0 recorded as a frozen solution at 664 nm exhibits different hysteresis behavior as compared to those recorded for [*Pc*$_2$Tb]$^{+/-}$. Notably, the hysteresis is maintained over the whole range of magnetic field, between ±1.5 T, and does not narrow around $B = 0$ T. Consequently, the coercive field is larger for [*Pc*$_2$Tb]^0 (0.16 T) than for [*Pc*$_2$Tb]$^{+/-}$ in these frozen solutions. The derivatives of the hysteresis cycles of [*Pc*$_2$Tb]$^{+/0/-}$ show features at *ca.* ±0.4−0.5 T that may arise from quantum tunneling effects (Figures S6−S8), although the sharp decrease in the gradient at 0 T strongly indicates that in all three systems there is relatively little tunneling at zero field. The relatively smooth profile of the hysteresis of [*Pc*$_2$Tb]^0 suggests that tunneling is not dominant in this complex when compared to [*Pc*$_2$Tb]$^{+/-}$.

To conclude, the optical MCD technique used here for the characterization of bis(phthalocyaninato)lanthanide-based SMMs does not rely on the preparation of solid solutions and on the identification of suitable isostructural diamagnetic hosts to minimize intermolecular magnetic interactions. Furthermore, the MCD method can be used to probe the magnetic properties of a range of different redox states of the same complex under essentially the same frozen solution conditions. While data from magnetic susceptibility studies suggest that the cationic form, [*Pc*$_2$Tb]$^+$, is more attractive for SMM applications,[8,9] we show that, under the conditions of our experiment, the neutral complex, [*Pc*$_2$Tb]^0, has a greater coercive field than the oxidized or reduced states.

Acknowledgment. This work was supported by the Marie Curie EST FuMaSSEC, EU NoE MAGMANet (515767-2), EMOCIONA (CTQ2006-06333/BQU) projects and by CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN, promoted by ISCIII), Spain.

Supporting Information Available: Cyclic voltammetry, spectroelectrochemistry, *in situ* absorption data of the frozen samples, derivatives of the hysteresis cycles. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA9095895