DOI: 10.1002/ange.200905007

Single-Molecule Magnets

A Liquid-Crystalline Single-Molecule Magnet with Variable Magnetic Properties**

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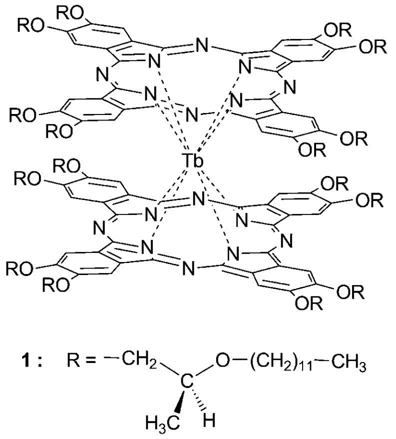
Dedicated to Jean-Pierre Sauvage on the occasion of his 65th birthday

Single-molecule magnets (SMMs) are attractive because they present magnetic bistability of each isolated molecule,[1] thus enabling the discovery of a wide variety of intriguing phenomena and the possibility of preparing multifunctional molecular nanosystems.[2] The so-called double-decker lanthanide complexes of phthalocyanines, in which a lanthanide ion with a large total angular momentum is coordinated between two parallel phthalocyanine derivatives, are particularly attractive because of their relatively high blocking temperatures.[3–5]

Our interest in these systems arose from the possibility of using organic synthesis to functionalize the SMM core. In particular, we have been engaged in a program aimed at preparing chiral SMMs which might show interesting chiroptical phenomena,[6,7] such as magnetochiral dichroism (MChD), which could be useful for data storage and processing.[8] To facilitate processing of SMMs and related materials, the incorporation of long alkyl chains is advantageous, and we were particularly attracted by liquid-crystalline phases, as previously carried out with a Mn_{12} SMM[9] and spin-crossover iron(II) compounds.[10]

For this reason, we prepared compound **1**, a chiral derivative of the double-decker terbium complex. It behaves both as a liquid crystal at room temperature and as a single-molecule magnet at low temperatures. Importantly, when the material is cooled at different rates, the magnetic properties vary because of different degrees of supramolecular order. Herein we describe the preparation and characterization of this liquid-crystalline terbium double-decker phthalocyanine complex and how its mesomorphic properties can be used as a tool to adjust its magnetic properties reversibly at will. The terbium ion is used as a direct and very sensitive probe of the structural changes occurring at low temperatures, at which magnetic relaxation is dominated by direct tunneling transitions.



1: $R = -CH_2-C(H)(CH_3)-O-(CH_2)_{11}-CH_3$

The chiral metal-free (free-base) phthalocyanine **5**, bearing eight identical stereocenters, was prepared in three steps from 4,5-dibromocatechol (Scheme 1) and the chiral bromoalkyl compound **2** derived from methyl lactate by a known procedure.[11]

Compound **3** was converted into the bis(cyano) derivative **4** using zinc(II) cyanide,[12] and the purified compound was cyclized in *n*-hexanol using lithium metal to give **5**. The corresponding terbium double-decker complex **1** was prepared by reacting **5** with anhydrous terbium chloride and lithium bis(trimethylsilyl)amide with minor changes from a published method.[13] The new compound was thoroughly purified by column chromatography, and was characterized by MALDI-TOF mass spectrometry, IR, UV/Vis absorption spectroscopy, circular dichroism spectroscopy, and elemental

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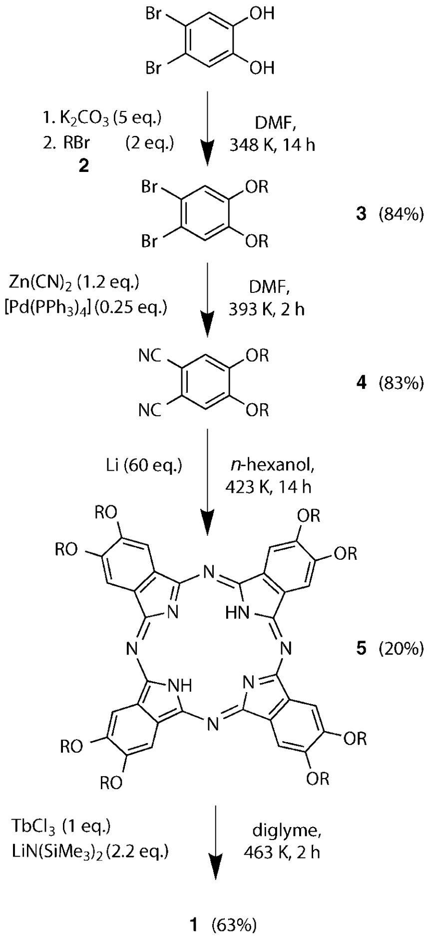
[**] We warmly thank Amable Bernabé for recording the LDI-TOF MS and IR spectra. This work was supported by the Marie Curie EST FuMaSSEC, EU NoE MAGMANet (515767-2), EMOCIONA (CTQ2006-06333/BQU), Grup de Recerca de Catalunya (2009 SGR-516) and Molecular Nanoscience (CSD2007-00010) and Molchip (MAT2009-13977-C03) projects

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905007.



Scheme 1. Synthesis of **1** from 4,5-dibromocatechol and (*S*)-1-bromo-2-dodecyloxypropane (RBr; **2**).

analysis. The absorption spectrum of **1** shows the characteristic bands of neutral double-decker complexes,[14] and the optical activity of the compound was shown by circular dichroism spectroscopy, with Cotton effects at 668, 610, 455, and 368 nm (see the Supporting Information).

Polarized optical microscopy (POM) shows that compound **1** is mesomorphic at room temperature, with a clearing point at 304 K and an optical texture that suggests a columnar (Col) mesophase (see the Supporting Information). Upon cooling from the isotropic (I) liquid, some hexagonal dendritic growth could be observed in the optical texture of **1** under uncrossed polarizing filters at 298 K. The observation of this fan-like texture suggests a homeotropic alignment on glass of a columnar hexagonal (Col$_h$) mesophase.[15–18]

Differential scanning calorimetry (DSC) shows only one endothermic peak (see the Supporting Information) at 261 K corresponding to the Cr→Col$_h$ transition with $\Delta H = 86.1\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S = 340.7\ \mathrm{J\,K^{-1}\,mol^{-1}}$, but does not show any peak near 304 K corresponding to the clearing point observed by POM, presumably because of the small enthalpy difference between the two phases.

Small-angle X-ray scattering (SAXS) was used to confirm the nature of the observed mesophase. Only three reflections (see the Supporting Information) could be observed in the small angle region (0–8°) at 298 K, with d spacing ratios of $1{:}\sqrt{3}{:}2$, thus allowing unambiguous identification of a hexagonal lattice. The observed reflections, obeying $(h^2+hk+k^2)^{1/2} = d/d_{hkl}$, were labeled (100), (110), and (200). This observation confirms the hexagonal columnar mesophase, which is qualitatively consistent with previously reported mesomorphic double-decker compounds of cerium[15–17] and various lanthanides.[18,19]

The phase behavior of the free-base phthalocyanine **5** is found to be qualitatively similar to the behavior of **1**. It also presents a hexagonal columnar mesophase, as evidenced by POM and SAXS (see the Supporting Information). Nevertheless, the clearing point is much lower in complex **1** than in **5** (304 K compared with 415 K), as occurs in analogous systems.[18–20]

The properties of single-molecule magnets can be very sensitive to the structural changes in the solid state. Differences of magnetic behavior have been seen in dodecamanganese complexes and attributed to Jahn–Teller isomerism in the coordination sphere of the manganese ion.[21] It has also been shown that the degree of dipolar interactions and also changes in the matrix arrangements around the molecular core of double-decker lanthanide complexes can influence the magnetic behavior of these compounds.[22,23] For this reason, the mesomorphism of **1** can be seen as a tool to tune the superstructure and probe the robustness of its magnetic properties in a variety of discrete structural situations. As the SMM behavior and magnetic ordering occur at low temperatures, the sample can be kinetically trapped in a given structural state, and its magnetic properties measured at low temperature. Using suitable rates of cooling, a structurally disordered sample $\mathbf{1}_{\mathrm{dis}}$, an intermediate partially ordered sample $\mathbf{1}_{\mathrm{po}}$, or an ordered crystalline state $\mathbf{1}_{\mathrm{cr}}$ can be prepared from the same specimen.

Alternating current magnetic susceptibility measurements of $\mathbf{1}_{\mathrm{dis}}$ and $\mathbf{1}_{\mathrm{cr}}$ as a function of temperature and frequency of the oscillating magnetic field were carried out with a SQUID magnetometer. The disordered sample $\mathbf{1}_{\mathrm{dis}}$ was prepared by warming up the material to the isotropic phase ex-situ at 333 K for 2 minutes and quenching at 150 K inside the susceptometer. The ordered sample $\mathbf{1}_{\mathrm{cr}}$ was prepared entirely in situ by warming up the same sample again and cooling it down slowly at a controlled rate. By doing so, any change in composition is ruled out, and the only difference from one sample to the other being the structure that is reached in the frozen state.

The temperature dependence of the in-phase (χ_M') and out-of-phase (χ_M'') susceptibilities measured at several frequencies of the two samples (see Supplementary Information) proved to be very similar to previously reported neutral double-decker complexes of terbium.[24] The $\chi_M'T$ product of the ordered and disordered samples converge above 54 K and for all the studied frequencies (0.5–1488 Hz) to approximately the same value (9.2–9.6 $\mathrm{emu\,mol^{-1}}$). Similarly, the $\chi_M''(T)$ curves of $\mathbf{1}_{\mathrm{dis}}$ and $\mathbf{1}_{\mathrm{cr}}$ show qualitatively the same behavior under the above-mentioned conditions. Having a closer look at the data however, the appearance of a second drop can be observed in the $\chi_M'(T)$ curves corresponding to the disordered sample, which becomes more evident below 15 Hz. The peak in $\chi_M''(T)$ also appears to be shifted up by about 2–3 K and the divergence at low temperature is notably higher for the disordered sample $\mathbf{1}_{dis}$ with respect to the ordered one $\mathbf{1}_{cr}$ (see the Supporting Information).

The difference between the magnetization dynamics of $\mathbf{1}_{cr}$ and $\mathbf{1}_{dis}$ samples shows up more clearly in the frequency-dependent plots of the magnetic susceptibility (Figure 1).

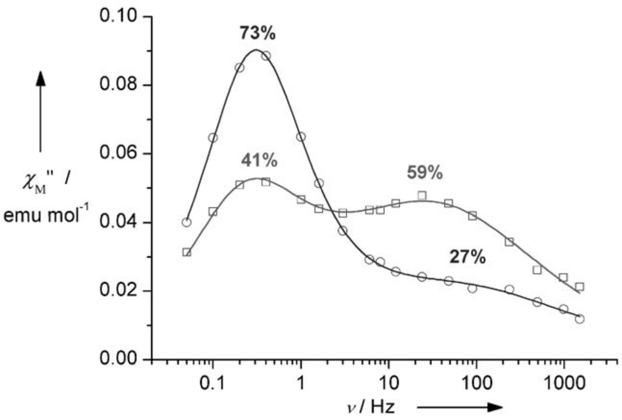


Figure 1. $\chi_M''(\nu)$ for the sample $\mathbf{1}_{dis}$ (□) and $\mathbf{1}_{cr}$ (○) at 25 °C. The solid lines are best fits to a Cole–Cole model.

Although, the former sample shows mainly one peak centered at 0.3 Hz in the χ_M'' versus ν plot at 25 K, the disordered sample clearly shows two peaks, which are centered at 0.3 and 40 Hz. This result is evidence of the coexistence of two different magnetic relaxation processes, meaning that the sample behaves magnetically as a mixture of two different entities. As changes in the chemical composition can be ruled out, the nature of these slow and fast relaxing species must be associated with different molecular conformations or supramolecular arrangements. These structural changes can modify the anisotropy parameters and the intermolecular dipolar interactions, both of which may play a role in determining the magnetic relaxation rates. Deciding which of these two effects dominates requires a more detailed and quantitative analysis, which we describe in what follows.

The $\chi_M''(\nu)$ curves were fitted as the weighted sum of two Cole–Cole functions [Eq. (1)][25]

$$\chi''(\omega) = \sum_{i=1,2} (\chi_{\tau_i} - \chi_{S_i}) x_i \frac{(\omega\tau_i)^{1-\alpha_i} \cos(\pi\alpha_i/2)}{1 + 2(\omega\tau_i)^{1-\alpha_i} \sin(\pi\alpha_i/2) + (\omega\tau_i)^{2-2\alpha_i}} \qquad (1)$$

where τ_1 and τ_2 are the relaxation times of the fast and slow magnetic species, respectively, and $x_1 = 1 - x_2$ is the fraction of the former. The results show that the percentage of slowly relaxing species was almost doubled, changing from 41 % to 73 % upon switching from $\mathbf{1}_{dis}$ to $\mathbf{1}_{cr}$, which indicates that the more slowly relaxing fraction is characteristic of the ordered or crystalline state. After letting the sample equilibrate at room temperature (i.e., in the mesophase) for several weeks, it was quenched again to 150 K using the same procedure as that used for $\mathbf{1}_{dis}$. The magnetic characterization reveals that the ratio of slowly relaxing species in this partially ordered sample $\mathbf{1}_{po}$ dropped even lower than in the disordered sample $\mathbf{1}_{dis}$ to a value of only 32 %. The reversibility of the process was checked by submitting the sample to the same thermal treatments after several months. The new data proved to be identical to the first set (see the Supporting Information).

A deeper insight into the nature of the two species, and thus also on the influence of the thermal history, is provided by the relaxation times τ_1 and τ_2, which are plotted in Figure 2 as a function of the reciprocal temperature.

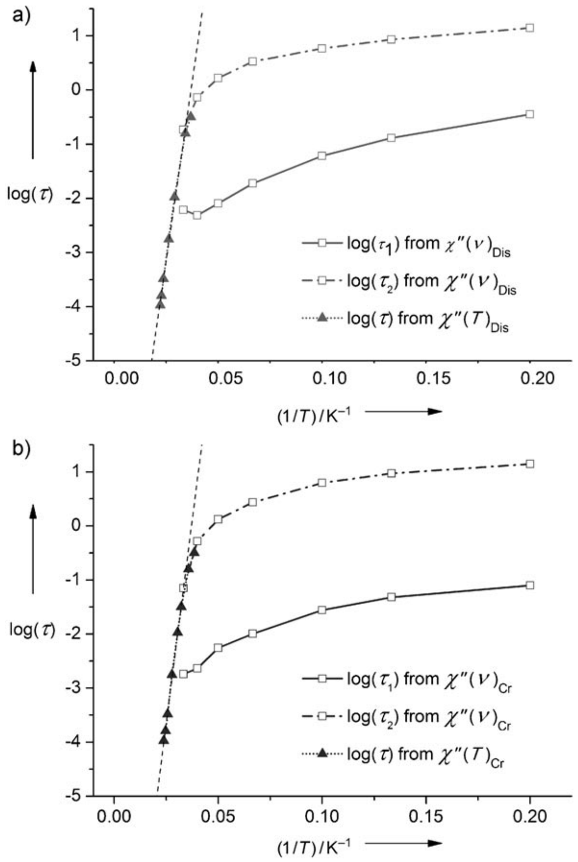


Figure 2. Log(τ) versus 1/*T* plots for a) $\mathbf{1}_{dis}$ and b) $\mathbf{1}_{cr}$. Key: —— □ log(τ_1), –•–• □ log(τ_2) obtained from $\chi_M''(\nu)$. ▲ log(τ) obtained from $\chi''(T)$. τ_1 and τ_2 are the relaxation times of the fast and slow species, respectively.

We find that for the two samples, log(τ_2) is proportional to $1/T$ for $T > 30$ K, and becomes weakly dependent on T (more specifically $\tau_2 \propto T^{-1}$; see the Supporting Information) at lower temperatures. This behavior shows a crossover from a thermally activated Orbach mechanism that is predominant at high temperature to a direct or phonon-induced tunneling process taking over at $T < 30$ K. The Arrhenius analysis gives $\Delta_{obs} = 4.80 \times 10^2$ cm^{-1} for sample $\mathbf{1}_{cr}$ and $\Delta_{obs} = 4.22 \times 10^2$ cm^{-1} for sample $\mathbf{1}_{dis}$, which is in agreement with previously reported barrier height in neutral terbium double-deckers.[3] A crucial observation is that the relaxation times of the two species diverge dramatically in the low-temperature or tunneling regime, where τ_1 becomes two orders of magnitude shorter than τ_2. The same applies under magnetic fields (see the

Supporting Information), which should tend to suppress the influence of dipolar interactions. The strong difference between τ_1 and τ_2 must then be associated with changes in the molecular conformation. Tunneling rates are determined by the intensity and symmetry of the off-diagonal anisotropy terms present in the spin Hamiltonian which, in its turn, reflect the local molecular symmetry and are, for this reason, extremely sensitive to even very weak distortions in the plane perpendicular to the easy magnetic axis.[26,27] Based on these observations, we assign the origin of the fast relaxing species, characteristic of the disordered $\mathbf{1}_{\mathrm{dis}}$ sample, to intramolecular distortions.

Although the coexistence of two different relaxation processes is a common feature in some SMMs,[9,21] it is the first time that it is observed in lanthanide double-decker complexes, and it is the only system in which the ratio between these responses has been shown to be reversibly modified by simple thermal treatments.

In conclusion, we have shown the important influence that the structural environment of a single-molecule magnet has on its magnetic behavior, taking advantage of the phase behavior of the complex. A reversible change of the magnetic properties was achieved by simple heating and cooling cycles. The absence of compositional change was demonstrated by the reversibility of the process, thus providing evidence for the structural origin of the modification of the magnetic behavior, because of variations in the arrangement of the molecules. This discovery was made possible by the synthesis of a room-temperature liquid-crystalline molecular material whose phase behavior depends critically on the chiral substituents.

Received: September 7, 2009
Revised: December 3, 2009

Keywords: lanthanides · liquid crystals · magnetic properties · metallomesogens · single-molecule studies

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