

Single Molecule Magnets

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As technological advancement pushes the size of ferromagnetic domains of digital media storage devices to their limit, alternative methods of data storage are required. Potentially, data may be encoded into the magnetic states of single molecule magnets (SMMs), effectively reducing the size of one bit to a single molecule.¹ Other potential uses of SMMs are in quantum computing² and magnetic refrigeration. Unlike ferromagnets and ferrimagnets which are composed of individual magnetic domains possessing long range magnetic order, SMMs are superparamagnets frozen into a single spin state in the absence of long range magnetic order.³ To produce a single molecule magnet, three criteria must be met: the molecule must have a large axial magnetic anisotropy induced by ligand geometry and coupling of orbital and spin angular momentum, there must be a high spin ground state, and the magnetic interaction with neighboring molecules must be low.⁴

The first SMM was the $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4$ cluster whose SMM properties were discovered by Sessoli *et al.*⁵ Since then, various other SMMs have been described; one of the largest is the 26 metal cluster $[\text{Mn}_{26}\text{O}_{16}(\text{OMe})_{12}(\text{dpkd})_{12}(\text{MeOH})_6](\text{OH})_6$.⁶ Remarkably, the bis(phthalocyaninato)lanthanide compounds, $\text{N}(\text{C}_4\text{H}_9)_4^+ [\text{Pc}_2\text{Ln}]^-$ Ln = Tb (**1**), Dy (**2**) Pc = dianion of phthalocyanine (Figure 1) have been shown to exhibit the slow magnetic relaxation characteristic of SMMs. These compounds not only are the first lanthanide containing SMMs but are also the first mononuclear SMMs.¹ The slow magnetic relaxation observed in these two compounds is a result of the large energy barrier between the two lowest substates in the ground state multiplet and a large magnetic anisotropy.⁷

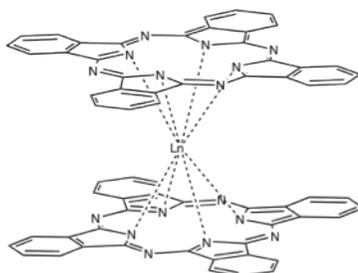


Figure 1: $\text{N}(\text{C}_4\text{H}_9)_4^+ [\text{Pc}_2\text{Ln}]^-$

To determine the magnetic relaxation characteristics of **1** and **2**, both pure and diluted ($1/50 = [\text{Pc}_2\text{Ln}^-]/[\text{Pc}_2\text{Y}^-]$) samples were measured using dc magnetic susceptibility (χ_M) and in-phase and out-of-phase ac magnetic susceptibility (χ_M' and χ_M'') as a function of temperature at various frequencies. Figures 2 and 3 illustrate that both compounds show a slowed response to an external ac magnetic field. The maximum χ_M'' for **1** and **2** in a 1 kHz ac magnetic field occurs at temperatures of 40 K and 10 K and the energy barriers for magnetic relaxation are 260 cm^{-1} and 31 cm^{-1} , respectively.¹

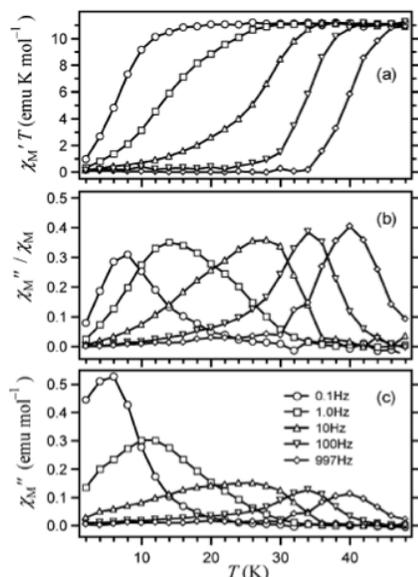


Figure 2: $N(C_4H_9)_4^+ [Pc_2Tb]^-$ diluted to a molar concentration of $1/50 = [Pc_2Ln]^-/[Pc_2Y]^-$, measured in a 3.5 G ac field.

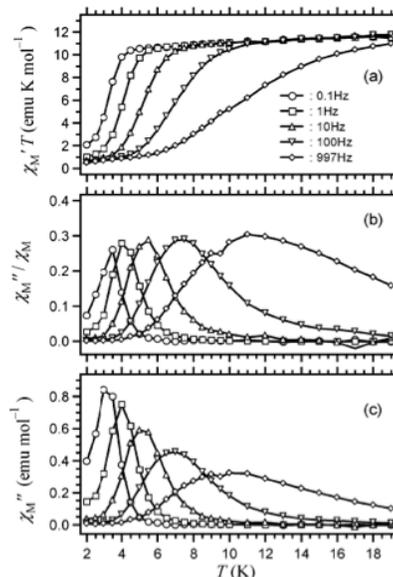


Figure 3: $N(C_4H_9)_4^+ [Pc_2Dy]^-$ diluted to a molar concentration of $1/50 = [Pc_2Ln]^-/[Pc_2Y]^-$, measured in a 3.5 G ac field.

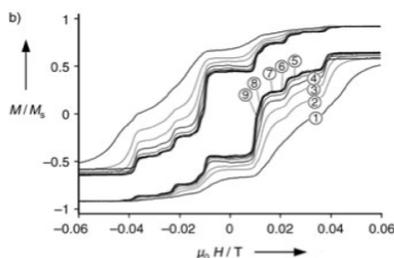


Figure 4: Hysteresis loops for $N(C_4H_9)_4^+ [Pc_2Tb]^-$

The magnetic susceptibility data shown above suggest that **1** and **2** should exhibit magnetization hysteresis as seen for transition metal SMM clusters. Both compounds do display the expected open hysteresis loops at 1.7 K.¹ At 0.04 K, quantum tunneling of magnetization is indicated by the staircase like loops seen in Figure 4.^{8,9}

To increase the barrier energy of **1**, $[Pc_2Tb]^-$ was oxidized to $[Pc_2Tb]^0$ which produces two spin systems, the ligand open shell π system and the Tb $4f^8$ system. The maximum χ_M'' increased to 50 K at 1 kHz and the energy barrier for magnetic relaxation increased to $\sim 410 \text{ cm}^{-1}$.¹⁰ When $[\{Pc(OEt)_8\}_2Tb]^-$ is oxidized to $[\{Pc(OEt)_8\}_2Tb]^+$ there is an increase in the ligand field splitting of the ground multiplet. This increased splitting increases the temperature of the maximum χ_M'' from approximately 40 K for $[\{Pc(OEt)_8\}_2Tb]^0$ to 52 K for $[\{Pc(OEt)_8\}_2Tb]^+$ ($SbCl_6$)⁻ and increases the energy barrier for magnetic relaxation to $\sim 550 \text{ cm}^{-1}$.¹¹ Similarly, $[\{Pc(OEt)_8\}_2Dy]^0$ was oxidized to $[\{Pc(OEt)_8\}_2Dy]^+$ ($SbCl_6$)⁻, resulting in an increase of the maximum χ_M'' from 10 K to 25 K at 1 kHz and an increase in the energy barrier for magnetic relaxation from $\sim 27 \text{ cm}^{-1}$ to $\sim 55 \text{ cm}^{-1}$.¹²

To further improve lanthanide mononuclear SMMs and make them useful technologically, alternative ligands and oxidation states which will increase the barrier

for magnetic relaxation need to be explored. The ultimate goal is to increase the energy barrier sufficiently to produce a SMM with a blocking temperature at or above room temperature.

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