

## Single-Molecule Magnets

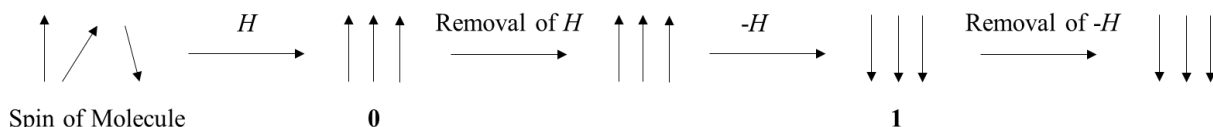
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In 1993, the first single molecule magnet (SMM) was reported by Christou and Hendrickson: this molecule,  $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]$ , exhibited an unexpected property, magnetic slow relaxation of magnetization.<sup>1</sup> Slow magnetic relaxation results in an out-of-phase magnetic susceptibility response ( $\chi''$ ) when the sample is exposed to an oscillating (AC) external magnetic field. Later that year, this same molecule was shown to display the phenomenon of magnetic hysteresis: just as for classical magnet materials such as iron metal, the sample remained magnetized for some time even after the external magnetic field is removed.<sup>2</sup> For  $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4]$ , however, the hysteresis effect is seen only at temperatures below 10 K.

This discovery led to hopes that someday SMMs could be used in high-density data processing and storage devices.<sup>3,4</sup> The general concept is that, when an SMM is exposed to an external magnetic field, the sample will be magnetized in alignment with the field direction (+z-axis). If the orientation of the external field is reversed to lie along the -z axis, the magnetization will also reverse. Up to a certain temperature called the blocking temperature,  $T_b$ , the magnetization obtained in either field would be maintained after the removal of the field. The magnetization along the z-axis and -z-axis could be assigned the “0” and “1” in binary code respectively (**Figure 1**).<sup>3</sup> However, before these molecules can be incorporated into these technologies, a major issue must be addressed:  $T_b$  must be drastically increased. The SMM discovered in 1993 featured a  $T_b$  of 4 K,<sup>2</sup> and therefore was only operational at liquid helium temperatures – not ideal for incorporation into practical data storage devices.



**Figure 1.** How an ideal SMM reacts in presence of a magnetic field ( $H$ ) and its application to data storage.

The desire to synthesize SMMs with higher blocking temperatures led to the discovery and characterization of many new coordination complexes. The class of manganese carboxylate clusters has expanded to include mono- and polynuclear 4f complexes,<sup>5,6,7</sup> mono- and polynuclear 3d complexes,<sup>3,8</sup> and heterometallic 3d/4f<sup>4,9</sup> and 4d/4f<sup>8</sup> complexes. Due to the wide range of SMMs, the current review will provide an overview of the design principles employed to increase  $T_b$  in some representative heterometallic 3d/4f complexes, and the challenges still to be overcome.<sup>10–13</sup>

Unlike bulk magnets, single molecule magnets eventually lose the ability to remain magnetized after removal of a magnetic field, due to their small magnetic domains (regions in which spins are aligned in same direction). The length of time required for the magnet to lose magnetization is referred to as the relaxation time ( $\tau_0$ ). At low temperatures, this relaxation time lengthens, and the magnetization of the SMM becomes more persistent. One way to increase  $\tau_0$  and  $T_b$  is to increase the energy barrier,  $U_{\text{eff}}$ , for reversal of the magnetization of the molecule. The main strategies employed to increase  $U_{\text{eff}}$  of SMMs are to increase the spin of the molecule,  $S$ , and to make the zero-field splitting parameter,  $D$ , more negative (**Equations 1 and 2**).<sup>3,4</sup> The value of  $D$  characterizes the magnitude of the axial distortion (i.e., anisotropy) in a molecule.

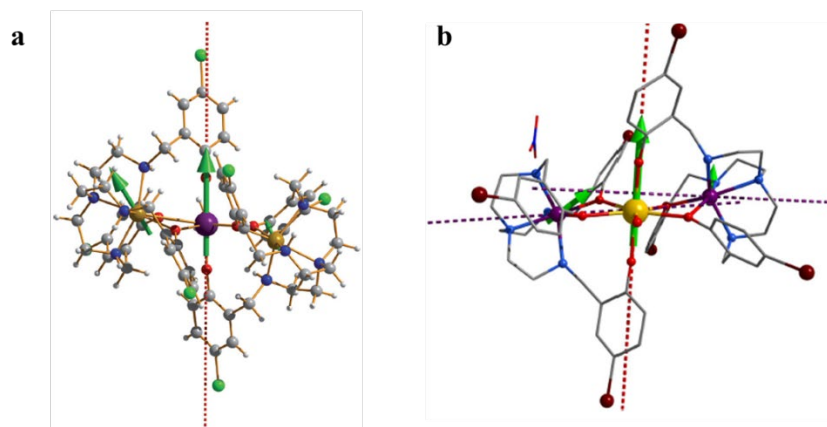
$$\text{for integer spin systems: } U_{\text{eff}} = |D| \cdot S^2 \quad (1)$$

$$\text{for half - integer spin systems: } U_{\text{eff}} = |D| \cdot \left(S^2 - \frac{1}{4}\right) \quad (2)$$

In the early 2000s, 3d SMMs with very high  $S$  values (mostly manganese clusters) were reported, but the complexes had small values for  $D$ .<sup>4</sup> Concurrently, mononuclear 4f SMMs were reported that relatively small values of  $S$  but large values for  $D$ . This led to the idea to incorporate 3d and 4f elements into the same molecule to increase the anisotropy and consequently  $U_{\text{eff}}$ .<sup>8</sup>

In 2004, multiple researchers reported the first sets of 3d-4f SMMs, which unfortunately displayed lower values of  $U_{\text{eff}}$  (less than 2 K) than did the separate 3d and 4f SMMs.<sup>4</sup> However, in 2009, Powell and coworkers investigated replacing a central  $\text{Mn}^{\text{II}}$  ion with  $\text{Dy}^{\text{III}}$  in  $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7(\mu^4\text{-O})_8(\mu^3, \eta^1\text{-N}_3)_8(\text{HL}_1)_{12}(\text{MeCN})_6]\text{Cl}_2$ . Before the replacement, the  $\text{Mn}_{19}$  complex had a record spin of  $S = 83/2$  but did not display magnetic behavior due to lack of anisotropy. The new  $[\text{Mn}_{18}\text{Dy}]$  complex displayed slow relaxation of magnetization in the susceptibility measurements, which is characteristic of SMM behavior, but it should be noted that magnetization of hysteresis was only observed below 0.5 K.<sup>14</sup>

Since then, a structurally diverse array of 3d-4f SMMs have been reported, with the most commonly used elements being  $\text{Mn}^{\text{III/IV}}$ ,  $\text{Fe}^{\text{II/III}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Dy}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$ ,  $\text{Er}^{\text{III}}$ , and  $\text{La}^{\text{III}}$ .<sup>4,8,9</sup> There has been steady progress in increasing the  $U_{\text{eff}}$ s of 3d/4f SMMs, with the most notable examples being  $[\text{Co}^{\text{II}}_2\text{Dy}^{\text{III}}(2,2',2''\text{-}(((\text{nitrilotris}(\text{ethane-2,1-diyl}))\text{tris}(\text{azanediyl}))\text{tris}(\text{methylene}))\text{tris}(4\text{-bromophenol})))_2(\text{H}_2\text{O})]\text{NO}_3$ <sup>15</sup> with a  $U_{\text{eff}}$  of 600 K and  $[\text{Fe}^{\text{II}}_2\text{Dy}^{\text{III}}(2,2',2''\text{-}(((\text{nitrilotris}(\text{ethane-2,1-diyl}))\text{tris}(\text{azanediyl}))\text{tris}(\text{methylene}))\text{tris}(4\text{-chlorophenol})))_2(\text{H}_2\text{O})](\text{ClO}_4)$ <sup>16</sup> with a  $U_{\text{eff}}$  of 459 K (**Figure 2**).  $T_b$  was not reported for either complex.



**Figure 2.** a)  $[\text{Fe}^{\text{II}}_2\text{Dy}^{\text{III}}(2,2',2''\text{-}(((\text{nitrilotris}(\text{ethane-2,1-diyl}))\text{tris}(\text{azanediyl}))\text{tris}(\text{methylene}))\text{tris}(4\text{-chlorophenol})))_2(\text{H}_2\text{O})](\text{ClO}_4)$ <sup>16</sup> b)  $[\text{Co}^{\text{II}}_2\text{Dy}^{\text{III}}(2,2',2''\text{-}(((\text{nitrilotris}(\text{ethane-2,1-diyl}))\text{tris}(\text{azanediyl}))\text{tris}(\text{methylene}))\text{tris}(4\text{-bromophenol})))_2(\text{H}_2\text{O})]\text{NO}_3$ <sup>15</sup>

The main obstacle faced by researchers with increasing the  $U_{\text{eff}}$  of 3d/4f SMMs is mitigating quantum tunneling of magnetization (QTM), which causes the experimental blocking temperature,  $T_b$ , to be less than the theoretical value given by  $U_{\text{eff}}$ . Tunneling can be minimized by achieving strong ferromagnetic coupling between the 3d and 4f centers with bridging oxo- or cyano ligands that facilitate magnetic exchange, and by utilizing ligands with high symmetries ( $\text{C}_{\text{ov}}$ ,  $\text{D}_{6h}$ , etc).<sup>8</sup> The most recent work is shifting towards mononuclear 4f complexes:  $[(\eta^5\text{-}$

Cp\*)Dy<sup>III</sup>( $\eta^5$ -Cp<sup>iPr5</sup>)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] currently has the highest reported  $U_{\text{eff}}$  of 2,217.2 K and a  $T_b$  of 80 K, which is almost to the working temperature of liquid nitrogen.<sup>17</sup>

Twenty-seven years after the first report of SMMs, the phenomenon is still one that is seen at very low temperatures. A general aspect of the field of 3d/4f SMMs (but which can also be applied to all SMMs) is that much of the research focuses on synthesizing complexes that are only slightly different from those previously studied. More should be done to learn from the SMMs already synthesized and to apply those lessons to the development of new molecular designs.

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