

Designer Magnetic Anisotropy: Engineering better Single Molecule Magnets

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The synthetic technique of serendipitous self-assembly has been responsible for the generation of a large number of fascinating and beautiful molecular species. While this approach has been quite fruitful for the discovery new Single Molecule Magnets (SMMs), from both the d- and f-block, the time for its usefulness is coming to an end. Specifically for complexes of the 4f elements, coordination geometries are much more flexible and thus untargeted self-assembly processes invariably result in saturated coordination environments. Our recent work has focussed on understanding the origin of favourable magnetic anisotropy in dysprosium(III) complexes, to which end we showed that a simple electrostatic model was capable of reproducing both experimental and high-level theoretical results.¹ This implies a deep connection between the electrostatic potential of the coordination environment and the resulting character of the electronic states, and immediately suggests a design strategy for optimal magnetic anisotropy. Subsequent work involved isolation of the first pseudo-linear two-coordinate 4f complex, providing the blue-print for the next generation of SMMs.² Theoretical investigations then showed that near-linearity is not a requirement for excellent SMM performance and that any two-coordinate complex of dysprosium(III) is desirable.³ Now, we present a combined experimental and theoretical proof-of-principle study, where a strong axial ligand field generated by a *trans*-bis-methandiide motif in a monometallic dysprosium(III) complex results in large energy barriers to magnetic relaxation of 721 and 813 K and a blocking temperature of 16 K.⁴

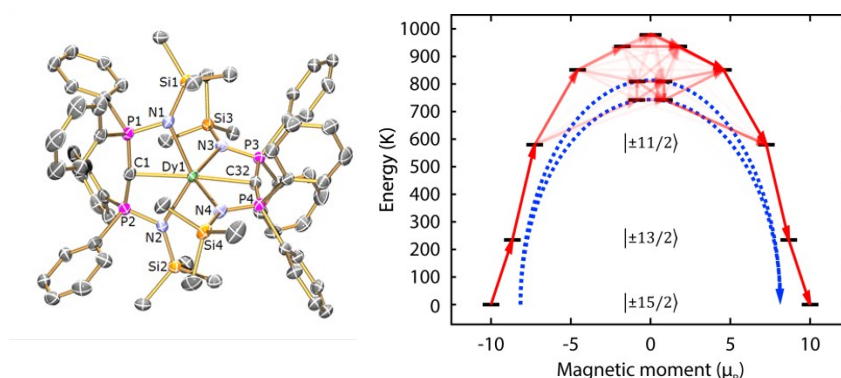


Figure 1. Molecular structure of [DyL₂]⁻ (left); magnetic states and relaxation pathways calculated with *ab initio* CASSCF methodology (right).

References

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