

LARGE COERCIVITY AND HIGH MAGNETIC BLOCKING TEMPERATURES FOR LANTHANIDE-BASED SINGLE-MOLECULE MAGNETS

Selvan Demir

Michigan State University, Department of Chemistry, East Lansing, MI 48824

sdemir@chemistry.msu.edu

Molecules that possess an energy barrier to spin inversion have intriguing potential applications in areas such as magnetic refrigeration, molecular spintronics and high-density information storage. For these applications, however, key performance characteristics such as large spin-relaxation barriers and high magnetic blocking temperatures are required. Lanthanides have been proven to be particularly well-suited for the design of single-molecule magnets owing to their large magnetic moments and magnetic anisotropy that stem from strong spin-orbit coupling of the 4f orbitals. By using lanthanide ions such as Tb³⁺, Dy³⁺, and Er³⁺ which possess intrinsically large orbital angular momentum, significantly higher barriers and blocking temperatures can be achieved. A general methodology to enhance single-molecule magnet properties in mononuclear lanthanide complexes comprises matching the ligand field symmetry with the anisotropic electron density distribution of the maximal M_J state. Employing this methodology, we will present the synthesis of mononuclear rare-earth metallocene complexes that function as new f-metal-based single-molecule magnets [1-3]. Another particularly successful approach to improve blocking temperatures is to generate strong magnetic exchange between lanthanide centers through the employment of radical bridging ligands. If the magnetic exchange coupling is large enough then quantum tunneling of the magnetization can be attenuated. Here, we will further present the synthesis of multiple bimetallic radical-bridged lanthanide-based single-molecule magnets and describe effective suppression of quantum tunneling pathways using various organic bridging radical ligands [4-7]. In addition, we combine both methodologies and demonstrate with the first series of N₂³⁻ radical-bridged metallocene complexes that the combination of axial magnetic anisotropy provided by the cyclopentadienyl ligands with the strong magnetic exchange coupling enabled by the inorganic N₂³⁻ radical results in exceptionally large magnetic hysteresis loops which remain open up to high temperatures, Figure 1.[8]

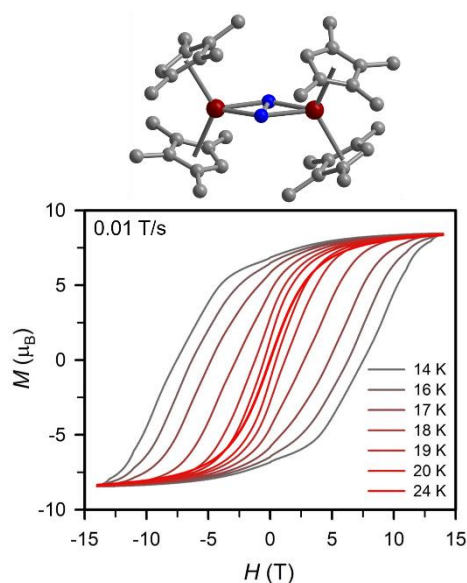


Figure 1. Magnetic hysteresis data and structure for [(Cp^{Me}₄H₂Tb)₂(μ-N₂³⁻)]⁻.⁸

References

- [1] S. Demir, J. M. Zadrozny, J. R. Long, *Chem. Eur. J.*, **2014**, *31*, 9524–9529.
- [2] S. Demir, M. D. Boshart, J. F. Corbey, D. H. Woen, M. I. Gonzalez, J. W. Ziller, K. R. Meihaus, J. R. Long, W. J. Evans, *Inorg. Chem.*, **2017**, *56*, 15049–15056.
- [3] S. Demir, K. R. Meihaus, J. R. Long, *J. Organomet. Chem.*, **2018**, *857*, 164–169.
- [4] S. Demir, J. M. Zadrozny, M. Nippe, J. R. Long, *J. Am. Chem. Soc.*, **2012**, *134*, 18546–18549.
- [5] S. Demir, M. Nippe, M. I. Gonzalez, J. R. Long, *Chem. Sci.*, **2014**, *5*, 4701–4711.
- [6] S. Demir, I.-R. Jeon, J. R. Long, T. D. Harris, *Coord. Chem. Rev.*, **2015**, *289–290*, 149–176.
- [7] S. Demir, *manuscripts in preparation*.
- [8] S. Demir, M. I. Gonzalez, L. E. Darago, W. J. Evans, J. R. Long, *Nat. Commun.*, **2017**, *8*, 2144.