Applications of Coordination Chemistry in the Synthesis of Single-Molecule Magnets

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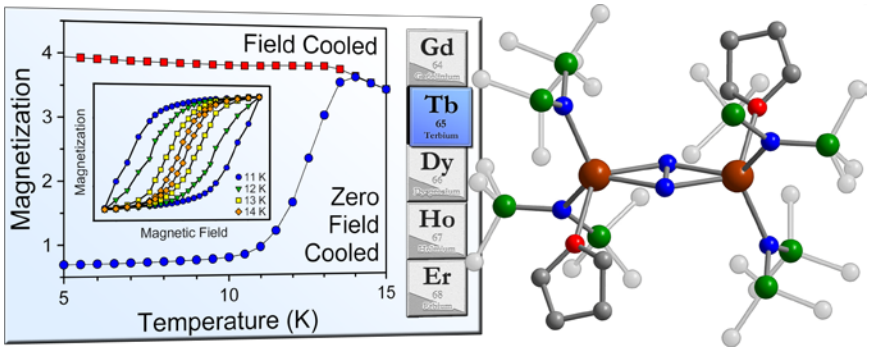
In an effort to produce new examples of single-molecule magnets, we are exploring routes to mononuclear complexes with a large magnetic anisotropy and their incorporation into high-nuclearity metal-cyanide clusters. The use of multidentate capping ligands has led to the synthesis of a range of new cyano-bridged cluster geometries, wherein variation of the transition metal ions permits adjustment of the ground state spin and magnetic anisotropy. In particular, the incorporation of transition metal ions with unquenched orbital angular momentum has been found to enhance magnetic relaxation barriers. Additional focus will be on recent work involving: (i) attempts to generate well-isolated high-spin ground states via electron delocalization in imidazolate-bridged clusters,[1] (ii) the observation of slow magnetic relaxation in mononuclear iron(II),[2] cobalt(II),[3] and uranium(III)[4] complexes, and (iii) the characterization of N_2^{3-} radical-bridged dilanthanide complexes exhibiting strong magnetic exchange and record high blocking temperatures.[5]



[1] Bechlars, B.; D'Alessandro, D. M.; Jenkins, D. M.; Iavarone, A. T.; Glover, S. D.; Kubiak, C. P.; Long, J. R. *Nat. Chem.* **2010**, *2*, 362.
[2] (a) Freedman, D. E.; Harman, W. H.; Harris, T. D.; Long, G. J.; Chang, C. J.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 1224. (b) Harman, W. H.; Harris, T. D.; Freedman, D. E.; Fong, H.; Chang, A.; Rinehart, J. D.; Ozarowski, A.; Sougrati, M. T.; Grandjean, F.; Long, G. J.; Long, J. R.; Chang, C. J. *J. Am. Chem. Soc.* **2010**, *132*, 18115.
[3] (a) Zadrozny, J. M.; Long, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 20732. (b) Zadrozny, J. M.; Liu, J.; Piro, N. A.; Chang, C. J.; Hill, S.; Long, J. R. *Chem. Commun.* **2012**, *48*, 3927.
[4] (a) Rinehart, J. D.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 12558. (b) Rinehart, J. D.; Meihaus, K. R.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 7572. (c) Meihaus, K. R.; Rinehart, J. D.; Long, J. R. *Inorg. Chem.* **2011**, *50*, 8484.
[5] (a) Rinehart, J. D.; Fang, M.; Evans, W.; Long, J. R. *Nat. Chem.* **2011**, *3*, 538. (b) Rinehart, J. D.; Fang, M.; Evans, W.; Long, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 14236.