High-Performance Lanthanide Single-Molecule Magnets with D_{5h} and D_{6h} Symmetries

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The search for new molecules exhibiting slow relaxation of magnetization under a plausible blocking temperature is currently one of the most appealing research topics in the interdisciplinary fields of inorganic and coordination chemistry, materials science, physics, and theoretical chemistry. Lanthanide(III) ions (Ln^{III}) play a pivotal role in the quest for efficient single-molecule magnets with potential applications in memory storage, molecular spintronics, and quantum computation. This is mainly due to the large magnetic anisotropy that most 4f-metal ions possess, which arises from the strong spin-orbit coupling and the crystal-field effects from the coordinated ligands.[1]

Seeking for new synthetic strategies towards the preparation of air-stable, single-molecule magnets (SMMs) with large energy barriers for the thermally-assisted relaxation of magnetization, the focus of our research is placed around mononuclear Dy^{III} (or Ho^{III}) complexes with designed ligands suitable to yield the targeted D_{5h} or D_{6h} coordination geometry and subsequently reducing the efficiency of the through-barrier relaxation pathways.[2] In this seminar, we will discuss our results associated with the synthesis, structural and magnetic characterization of various new families of mononuclear, air-stable lanthanide(III) SMMs. These were derived by the employment of the macrocyclic effect, which has yielded N_5, N_6, N_3O_3, and N_4O_2 equatorial ligation around a single Ln^{III} ion resulting from rare (in pentagonal or hexagonal equatorial ligation) [1+1] metal-assisted condensation reactions (**Figure 1**). As a result, we have been able to chemically engineer new coordination compounds with D_{5h} or D_{6h} geometries, bearing strongly bound axial ligands and exhibiting SMM behaviors with large U_{eff} values, among the highest yet reported in the field of SMMs.

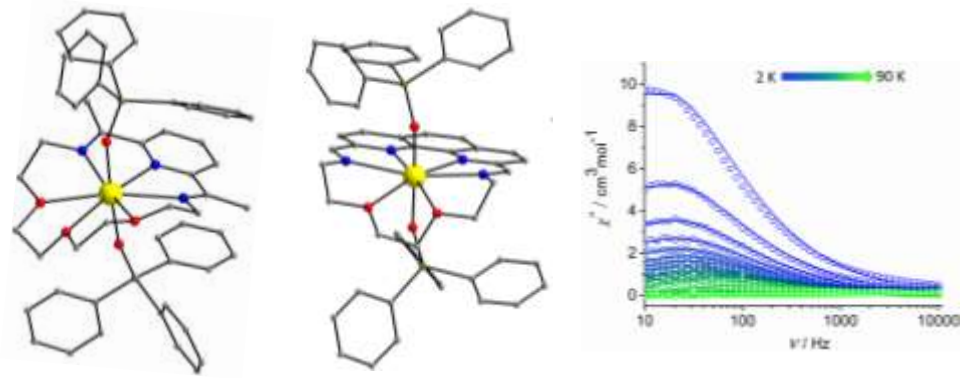

Figure 1: Molecular structures and ac magnetic dynamics of representative D_{6h} complexes discussed in this work. Color scheme: Dy=yellow; O=red; N=blue; C=grey. Hydrogen atoms are omitted for clarity.

References:

[1] Rinehart, J. D.; Long, J. R. *Chem. Sci.* **2011**, *2*, 2078.

[2] Zhu, Z.; Tang, J. *Natl. Sci. Rev.* **2022**, *9*, nwac194.