

# INORGANIC SEMINAR

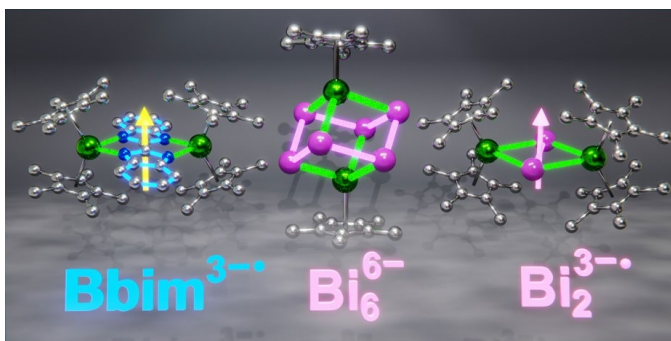
## Organometallic Single-Molecule Magnets Containing Radicals and Bismuth

Selvan Demir

Department of Chemistry  
Michigan State University



Single-molecule magnets (SMMs) are molecules that possess an energy barrier to spin inversion, giving rise to slow magnetic relaxation and magnetic hysteresis. To realize their intriguing potential applications, ranging from molecular spintronics, quantum computing, to high-density information storage, spin-reversal barriers ( $U_{\text{eff}}$ ) and magnetic blocking temperatures ( $T_B$ ) must be increased. Lanthanide ions are especially well-suited for the design of SMMs due to their large magnetic moments and magnetic anisotropy that originate from strong spin-orbit coupling of the 4f orbitals. One effective methodology to boost blocking temperatures of multinuclear compounds is to generate strong magnetic exchange between lanthanide centers using radical bridging ligands. In the event of strong magnetic exchange coupling, undesirable relaxation pathways such as quantum tunneling of the magnetization can be suppressed. Here, the first isolation of the



**Fig. 1.** Structures of the developed organometallic lanthanide complexes.

bisbenzimidazole radical anion ( $\text{Bbim}^{3-\bullet}$ ) and its use in radical-bridged SMMs will be discussed, Fig. 1.<sup>1,2</sup> Furthermore, the isolation of the first fluo flavine radicals will be presented.<sup>3</sup> A second approach to strong coupling employs heavy p-block elements since their diffuse valence orbitals facilitate better penetration of the core electron density of the lanthanide ions relative to diamagnetic ligands comprising lighter p-block elements. Here, we will present the first lanthanide bismuth cluster SMMs containing a  $[\text{Ln}_2\text{Bi}_6]$  heterometallocubane core, Fig. 1. We will also show that the  $\text{Bi}_2^{3-\bullet}$  radical anion can be tamed with rare earth ions to give the first SMMs featuring bismuth radicals, Fig. 1.<sup>4,5</sup> We also synthesized complexes with diamagnetic  $^{89}\text{Y}$  ( $I = 1/2$ ) to gain insight into the electronic

structure and spin density distribution.<sup>6-9</sup> The organometallic rare earth chemistry has been further advanced by the isolation of the first guanidinate complexes featuring a weakly coordinated tetraphenylborate anion,<sup>10</sup> which have ramifications for both magnet design and reactivity studies.<sup>11,12</sup>

**References.** (1) Benner, F.; Demir, S. *Chem. Sci.* **2022**, *13*, 5818. (2) Benner, F.; La Droitte, L.; Cador, O.; Le Guennic, B.; Demir, S.; *Chem. Sci.* **2023**, *14*, 5577. (3) Benner, F.; Demir, S. *J. Am. Chem. Soc.* **2024**, *146*, 26008. (4) Zhang, P.; Benner, F.; Chilton, N. F.; Demir, S. *Chem* **2022**, *8*, 717. (5) Zhang, P.; Nabi, R.; Staab, J. K.; Chilton, N. F.; Demir, S. *J. Am. Chem. Soc.* **2023**, *145*, 9152. (6) Pugliese, E. R.; Benner, F.; Demir, S. *Chem. Commun.* **2023**, *59*, 14791. (7) Delano IV, F.; Castellanos, E.; McCracken, J.; Demir, S. *Chem. Sci.* **2021**, *12*, 15219. (8) Benner, F.; Demir, S. *Inorg. Chem. Front.* **2023**, *10*, 4981. (9) Delano IV, F.; Benner, F.; Jang, S.; Greer, S. M.; Demir, S. *Chem. Sci.* **2024**, *15*, 13389. (10) Delano IV, F.; Demir, S. *Cryst. Growth Des.* **2023**, *23*, 3134. (11) Delano IV, F.; Deshapriya, S.; Demir, S. *Inorg. Chem.* **2024**, *63*, 9659. (12) Delano IV, F.; Demir, S. *Angew. Chem. Int. Ed.* **2025**, *64*, e202417217.



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