XXI Brazilian Meeting on Inorganic Chemistry
X Brazilian Meeting on Rare Earths
III Workshop on Theoretical Bioinorganic Chemistry

Belo Horizonte, September 12 - 15th 2024

Exploiting structural and electronic parameters to boost the slow magnetic relaxation and luminescence thermometry of Dy^{III} single-molecule magnets

Airton G. Bispo-Jr,[1,2] Diogo A. Gálico,[2] Muralee Murugesu[2], Fernando A. Sigoli,[1]

[1] Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Canada.
[2] Department of Inorganic Chemistry, Institute of Chemistry, University of Campinas, Campinas, Brazil.
E-mail: airton.germano.junior@gmail.com

Thematic Area: Rare-Earths

Keywords: Lanthanides, magnetism, luminescence.

Single-molecule magnets (SMMs) have been anticipated as promising candidates for ultra-compact information storage in the next generation molecular devices.[1] Nowadays, Dy^{III} complexes are amongst the state-of-the-art SMMs. In these SMMS, the magnetic dynamic is influenced by the local temperature, which can be self-probed by luminescence thermometry.[1] In the multifunctional SMMs, luminescence thermometry is mainly achieved by taking advantage of the thermal population of Kramers duplets (KDs) arising from the Dy^{III} $^4F_{9/2}$ emitting level. Yet, Dy^{III} SMMs with luminescence thermometry capabilities are far away in magnetic performance than the highest-development Dy^{III} SMMs. That is because short energetic gaps between the *KDs* lead to superior relative thermal sensitivity, but this condition is favoured by distorted Dy^{III} pseudo-symmetries. Such condition contrasts the high-symmetry of the Dy^{III} polyhedron envisaged to enhance the magnetic performance.[2] To tackle this exciting challenge, herein, it is investigated the compromise between Dy^{III} polyhedron pseudo-symmetry, slow relaxation of magnetization, fine electronic structure, and luminescence to shed light on the synergistic improvement of the magnetic and luminescent features of SMMs. For that, the electronic features and the distortion of the Dy^{III} coordination polyhedron were tuned by employing different terminal ligands in the $[Dy_2(\mu\text{-bpm})(hexd)_6]$ (**1**) and $[Dy_2(\mu\text{-bpm})(hpd)_6]$ (**2**) dinuclear complexes (bpm = 2,20-bipyrimidine, hexd = 2,4-hexanedione, hpd = 3,5-Heptanedione). In these complexes, the DyO_6N_2 polyhedron is described by a distorted square antiprismatic (SAP) configuration (D_{4d} pseudo-symmetry). Yet, **2** displays a slightly larger distortion degree than **1**. The different terminal ligand scaffold also changes the skew angle of the SAP symmetry, which induces different axial and equatorial crystal field components acting on Dy^{III}. Upon a static external magnetic field, the less distorted Dy^{III} coordination polyhedra in **1** lead to a larger effective barrier (U_{eff}) to the reversal of magnetization (335 K) than in **2** (288 K). Moreover, at zero static field, the U_{eff} of both complexes is quite similar (280 – 290 K). From the luminescence perspective, the two complexes display the typical Dy^{III} emission at 10 K. However, **2** presents a poor ligand-to-Dy^{III} energy transfer due to a larger triplet state energy, which limits its use for luminescence thermometry. This is not an issue for **1**, which presents relative thermal sensitivity of 0.1 - 0.7% K^{-1} within the SMM operation range (up to 30 K). Therefore, the $hexd^-$ ligand with a larger electronic donating capability than hpd^- leads to a lower polyhedron distortion degree and slightly larger U_{eff}. The luminescence performance, in its turn, is controlled by the terminal ligand triplet state energy and its impact on the energy transfer. The lessons learned from this study help to draw a picture on how structural changes and the electronic structure can play synergistically to enhance the magnetic and luminescent performance of SMMs.

Acknowledgments: INCT/INOMAT (CNPq 465452/2014-0 and FAPESP 50906-9/2014), FAPESP (2021/06326-1, 2021/09755-0, 2019/23763-6, and 2020/02614-0), the Canadian Foundation for Innovation (CFI), and the Natural Sciences and Engineering Research Council of Canada (NSERC).

References

[1] K. L. M. Harriman et al,. Trends Chem., **1**, 425 (2019).
[2] A. G. Bispo-Jr et al., Chem. Commun., **59**, 8723 (2023).