Magneto-Luminescent d–f Complexes: from Tunable Emission to Non-Invasive Optical Thermometry of Single Molecule Magnets

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Single molecule magnets (SMMs) based on trivalent lanthanide ions (Ln^{III}) stand at the research forefront of molecular magnetism owing to the large magnetic anisotropy of a single molecule origin, leading to the magnetic memory effect at molecular level. Additionally, thanks to the unique electronic structure of 4f elements, Ln^{III} shows characteristic emission transitions, offering various intriguing luminescent functionalities. My research works have been focusing on the combination of these two functionalities, i.e., Ln^{III}-centered SMM behavior and Ln^{III}-centered luminescence, into a single-phase material by embedding Ln^{III} ion into cyanido-bridged bimetallic d-f coordination assemblies. Such df coordination system can be readily constructed from Ln^{III} (as bifunctional center), diamagnetic polycyanometallate $[M^{n+}(CN)_x]^{-(x-n)}$ (as bridging linker), and organic ligand (as crystal field tailor), and we have reported a plethora of luminescent SMMs, exploring their magneto-luminescent functionalties.¹⁻⁵ Furthermore, by playing with the non-innocent solvent molecules within the coordination system, the luminescent SMMs can be additionally endowed with switching character,³ or even a third dimension of functionality of proton-conductivity.² In this talk, I will present several featured luminescent SMMs based on cyanido-bridged d-f complexes (Fig 1), and discuss their interesting luminescent functionalities, including 1) yellow-white-blue color-tunable emission in Dy-Co/Dy-Rh SMMs,⁴ 2) NIR luminescence ratiometric thermometry in a Co-Yb-Co SMM,² and 3) visible luminescence thermometry adopting re-absorption effect in Ho–M SMMs (M = Co/Rh/Ir).¹

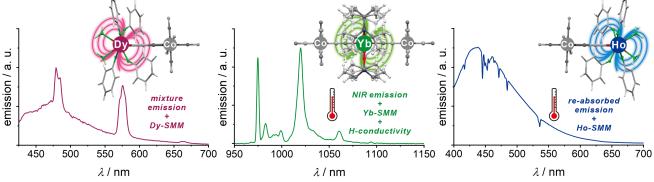


Fig. 1 Representative luminescent SMMs based on cyanido-bridged d-f complexes showing indicated functional features.

[2] J. Wang, J. J. Zakrzewski, M. Heczko, M. Zychowicz, K. Nakagawa, K. Nakabayashi, B. Sieklucka, S. Chorazy and S. Ohkoshi J. Am. Chem. Soc., 2020, 142, 3970–3979

[3] Y. Xin, J. Wang, M. Zychowicz, J. J. Zakrzewski, K. Nakabayashi, B. Sieklucka, S. Chorazy and S. Ohkoshi *J. Am. Chem. Soc.*, 2019, *141*, 18211–18220.

[4] J. Wang, S. Chorazy, K. Nakabayashi, B. Sieklucka and S. Ohkoshi J. Mater. Chem. C, 2018, 6, 473-481

[5] S. Chorazy, J. Wang and S. Ohkoshi Chem. Commun., 2016, 52, 10795–10798

J. Wang, J. J. Zakrzewski, M. Zychowicz, V. Vieru, L.F. Chibotaru, K. Nakabayashi, S. Chorazy and S. Ohkoshi *Chem. Sci.*, 2021, *12*, 730–741