

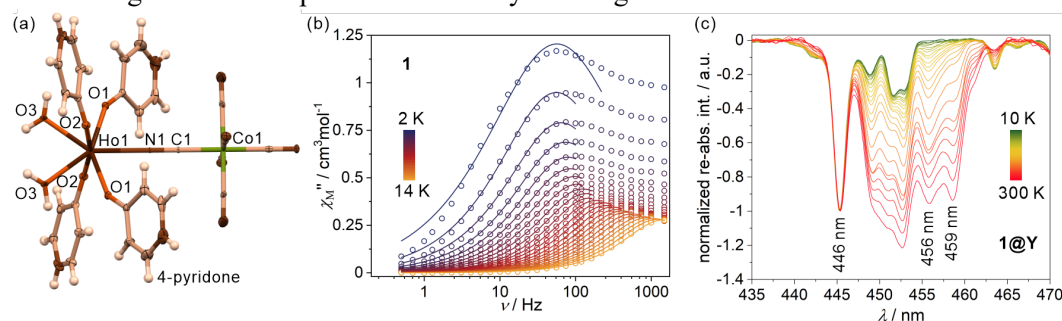
## Cyano-Bridged Ho<sup>III</sup>-M<sup>III</sup> (M = Co, Rh, and Ir) Dinuclear Molecules Showing Slow Magnetic Relaxation and Luminescence Thermometry Based on Re-Absorption Effect

(<sup>1</sup>the University of Tokyo, <sup>2</sup>Jagiellonian University, <sup>3</sup>Katholieke Universiteit Leuven, <sup>4</sup>Maastricht University) ○ Junhao Wang,<sup>1</sup> Jakub Zakrzewski,<sup>2</sup> Mikolaj Zychowicz,<sup>2,3</sup> Veacheslav Vieru,<sup>3,4</sup> Liviu Chibotaru,<sup>3</sup> Koji Nakabayashi,<sup>1</sup> Szymon Chorazy,<sup>2</sup> Shin-ichi Ohkoshi<sup>1</sup>

**Keywords:** Single Molecule Magnet, Luminescence Thermometry, Re-Absorption Effect

Trivalent lanthanide ions (Ln<sup>III</sup>), due to their large magnetic anisotropies, have been regarded as one of the most promising candidates in designing single molecule magnets (SMMs), which exhibit slow magnetic relaxation in the single-molecule domain. Since the behavior of such nanomagnets strongly depends on temperature, a contactless and accurate temperature measurement is of great importance for the future practical SMM operations. Thanks to the emissive properties of Ln<sup>III</sup>, numerous research interest has been focused on the combination of SMMs with luminescent thermometry based on Ln<sup>III</sup> complexes.<sup>1</sup>

In these regards, we reported a series of cyano-bridged dinuclear molecules, {[Ho<sup>III</sup>(4-pyridone)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>][M<sup>III</sup>(CN)<sub>6</sub>]} · nH<sub>2</sub>O (M = Co, **1**; Rh, **2**; Ir, **3**) and their respective magnetically diluted samples by yttrium(III), **1@Y-3@Y**.<sup>2</sup> These compounds exhibit rare slow magnetic relaxation centered at the non-Kramer Ho<sup>III</sup> ion, and their SMM behaviors were elucidated by *ab initio* calculations. Photoluminescence study on **1@Y-3@Y** revealed an intense blue emission band from the 4-pyridone ligand, together with a series of re-absorption lines ascribed to the f-f transitions of Ho<sup>III</sup> ion. Additionally, the re-absorption peaks show variable temperature dependences, giving rise to an innovative approach in constructing ratiometric optical thermometry with high sensitivities.



**Fig. 1.** Structure of dinuclear molecule of **1** (a), SMM characterization of **1** under zero *dc* field (b), and normalized 7-dependent luminescent re-absorption f-f transitions of **1@Y** used for constructing optical thermometry (c).

1) J. Wang, J. J. Zakrzewski, M. Heczko, M. Zychowicz, K. Nakagawa, K. Nakabayashi, B. Sieklucka, S. Chorazy, S. Ohkoshi, *J. Am. Chem. Soc.* 2020, *142*, 3970-3979. 2) J. Wang, J. J. Zakrzewski, M. Zychowicz, V. Vieru, L. F. Chibotaru, K. Nakabayashi, S. Chorazy, S. Ohkoshi, *Chem. Sci.*, 2021, DOI: 10.1039/D0SC04871B.