Luminescence–absorption hybrid thermometry towards self temperature sensing of molecule-based magnetic materials

([1]*Institute of Pure and Applied Sciences, University of Tsukuba*, [2]*Faculty of Chemistry, Jagiellonian University*, [3]*Graduate School of Science, The University of Tokyo*)
○Junhao Wang,[1] Jakub J. Zakrzewski,[2] Mikolaj Zychowicz,[2] Hiroko Tokoro,[1] Szymon Chorazy,[2] Shin-ichi Ohkoshi[3]

Keywords: Luminescence; Absorption; Thermometry; Single-molecule magnet; Lanthanide

Accurate temperature sensing at the molecular level is a critical prerequisite for achieving precise control over advanced functional materials and devices, such as molecular magnets, miniaturized electronic systems, and quantum technologies. To develop non-invasive, self-referenced temperature sensing methods for nanoscale objects, we focused on single-molecule magnets (SMMs), which exhibit magnetic memory effects at the sub-nanometer scale, and designed functional SMMs capable of self-thermometry using lanthanide-centered luminescence.[1–3]

By utilizing the near-infrared (NIR) emission of Yb^{3+} ions, we developed an SMM, $[Yb^{III}(hmpa)_4][Co^{III}(CN)_6]_2$ (hmpa = hexamethylphosphoramide), which demonstrates luminescence thermometry functionality with reliable performance in the temperature range of 50–175 K.[1] To enable thermometry using visible emission, we designed green-emissive SMMs by incorporating Tb^{3+} ions within a highly symmetrical coordination framework, $Tb^{III}[Co^{III}(CN)_6]\}_n$.[3] This system exhibits wide overlap between the dual functionalities of luminescence thermometry and SMM behavior at lower temperatures (7–42 K).

However, such an approach faces the challenge that some lanthanide ions are inherently non-emissive. To address this limitation, we have recently been developing versatile optical thermometers that mimic the thermometry features of the above SMMs by utilizing the optical absorption properties of lanthanide ions in conjunction with adjacent luminophores. This approach has been attempted using lanthanide ions such as Ho^{3+}, Er^{3+}, and Nd^{3+}. Our goal is to push the boundaries of this field by expanding its applications through innovative emission–absorption hybrid molecular temperature probes.

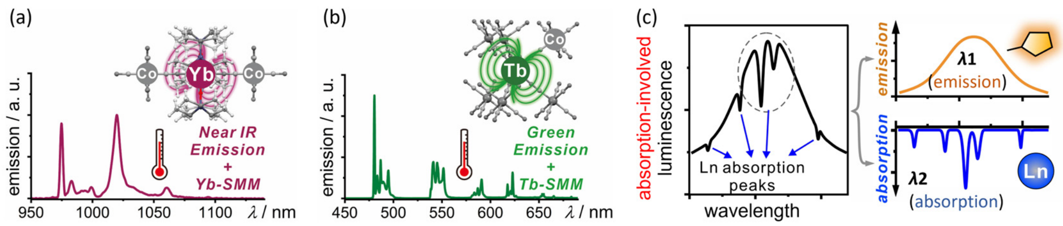

Figure 1. SMM-based luminescence thermometers using Yb^{3+}-centered NIR emission (a) and Tb^{3+}-centered green emission (b), and concept absorption–emission hybrid thermometer (c).

1) J. Wang et al., *J. Am. Chem. Soc.*, **2020**, *142*, 3970–3979. 2) J. Wang et al., *Chem. Sci.*, **2021**, *12*, 730–741. 3) J. Wang et al., *Angew. Chem. Int. Ed.*, **2023**, *62*, e2023063.