

## Exploiting Structural and Electronic Parameters to Tune the Performance of Lanthanide(III) Coordination Polymers as Luminescent Temperature Probes

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### Highlights

Fine control of the structure for tuning the luminescence thermometry of Eu<sup>III</sup> and Tb<sup>III</sup> coordination polymers. Unraveling the ligand-to-Ln<sup>III</sup> and Ln<sup>III</sup>-to-Ln<sup>III</sup> energy transfer through experimental and theoretical approaches. Toward superior thermal sensitivity of luminescence by controlling structural and electronic parameters.

### Abstract

Temperature is a crucial thermodynamic parameter studied in several fields to monitor chemical, physical, or biological processes.<sup>[1]</sup> As the demand for temperature probes escalates, a wealth of research is being conducted on the development of luminescent thermometers with enhanced performance.<sup>[2]</sup> Among such probes, lanthanide(III) (Ln<sup>III</sup>)-based coordination polymers have been investigated owing to their bright luminescence and fine control of structure.<sup>[1,2]</sup> The molecular structure of Ln(III) coordination polymers is a key parameter for controlling the thermal response of luminescence. However, fine control of structure and composition is a challenging task considering the typically employed trial-and-error methods, especially when integrating multiple lanthanide ions such as Eu<sup>III</sup> and Tb<sup>III</sup>. Motivated by this exciting task, herein, we endeavor to offer additional guidance to optimize luminescence thermometry using the dual-center approach (Ln = Eu<sup>III</sup>/Tb<sup>III</sup>) with two 1D coordination polymers, namely: [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub> (**1**) and [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (**2**) (tfa<sup>-</sup> = trifluoroacetylacetate, and the bridge ligands are [(diphenylphosphoryl)R](diphenyl)phosphine oxide, R = ethyl – dppeo – or butyl – dppbo).<sup>[1,2]</sup> The short μ-dppeo bridge ligand leads to a more linear 1D polymeric chain, while the longer μ-dppbo bridge leads to tighter packed chains. The temperature-dependent emission of the systems enables the development of ratiometric luminescent temperature probes featuring maximum relative thermal sensitivity of up to 4.3% K<sup>-1</sup> for **1** (at 377 K, upon direct Tb<sup>III</sup> excitation at 484 nm) and 3.18% K<sup>-1</sup> (at 293 K, upon ligand excitation at 340 nm) for **2**. By combining experimental and theoretical methods, the mechanisms governing intramolecular and intermolecular energy transfer and their interplay with the molecular structure were investigated. Under ligand excitation at 340 nm, the thermal behavior of Eu<sup>III</sup> is primarily controlled by ligand-to-Eu<sup>III</sup> ET, whereas the <sup>5</sup>D<sub>4</sub> level decay of Tb<sup>III</sup> dictates the thermometric response of Tb<sup>III</sup>. In contrast, when the excitation channel is switched to Tb<sup>III</sup>, the primary pathway for the <sup>5</sup>D<sub>4</sub> decay shifts to Tb<sup>III</sup>-Eu<sup>III</sup> ET. In this context, besides the Tb<sup>III</sup>-Eu<sup>III</sup> distance, the <sup>7</sup>F<sub>1</sub> manifold of Eu<sup>III</sup> plays a critical role. Specifically, increasing the population of the Eu<sup>III</sup> <sup>7</sup>F<sub>1</sub> level enhances the Tb<sup>III</sup>-Eu<sup>III</sup> ET, enabling us to strategically tailor the ligand scaffold toward minimizing the <sup>7</sup>F<sub>0</sub>-<sup>7</sup>F<sub>1</sub> energy gap. Thus, our investigation helps to provide further understanding of the thermal response of luminescence, offering a guideline for harvesting enhanced performance by tuning the molecular structure of Ln(III)-based coordination polymers.

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