LANTHANIDE-BASED OPTICAL THERMOMETERS SHOWING THERMAL VARIATION OF EMISSION SWITCHED BY EXCITATION WAVELENGTH

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The use of lanthanides in optical sensors and optoelectronic devices is an active area of research.[1] Recently, lanthanide(3+) ions, e.g., Eu^{3+} and Tb^{3+}, embedded in coordination polymers and metal-organic frameworks, including heterometallic d-f cyanido-bridged assemblies, have been explored for high-performance ratiometric optical thermometry.[2],[3],[4] Here, we report the application of the rarely explored hexacyanidoplatinate(IV) ions as linkers for luminescent lanthanide-based molecular materials. We synthesized four novel isostructural compounds composed of trinuclear cyanido-bridged $\{Ln^{III}_2Pt^{IV}\}$ (Ln = Eu, Tb and Y) molecular ions, coordinating 4-pyridone ligands, and crystallizing with chloride counter-ions and solvent molecules. Among them, the mixed-lanthanide compound, $\{[Eu^{III}_{0.5}Tb^{III}_{0.5}(4\text{-pirydone})_5(MeOH)]_2[Pt^{IV}(CN)_6]\}Cl_4 \cdot 2MeOH$, **{EuTbPt}** serves as a unique luminescent thermometer that exhibits the shift from red to green emissions with the decreasing temperature for the 340 nm excitation, and the opposite trend for the 280 nm excitation. This effect was utilized for the extraordinary tunable ratiometric optical thermometry exploring the ratios between the intensities of the Eu- and Tb-based emissions (Figure 1). The role of the molecular components, including cyanido complex and 4-pyridone ligands, in achieving this unusual phenomenon is discussed.

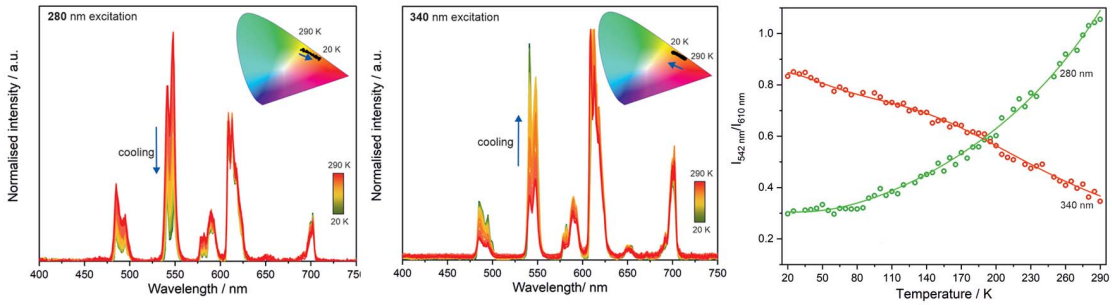

Figure 1. Temperature-dependent emission spectra of **{EuTbPt}** under the 280 (left) and 340 nm (middle) excitations, shown with the resulting emission colors depicted on the CIE 1931 chromaticity diagram. The right image shows the temperature dependence of the ratio between the Eu- and Tb-based emission components under the indicated excitation wavelengths.

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[2] J. Rocha, C. D. S. Brites, L. D. Carlos, *Chem. Eur. J.*, **2016**, *22*, 14782–14795.

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