Energy transfer and photoluminescence properties of lanthanide-containing polyoxotitanate cages coordinated by salicylate ligands

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Fig. S1. UV-Vis absorbance spectra of the Ln-1 compounds in anhydrous chloroform. The peak position and extinction coefficients for the ca. 350 nm band differ slightly, depending on the choice of Ln³⁺ ion.

Fig. S2. Digital pictures of the photoluminescence of (a) Pr-1, (b) Sm-1 and (c) Eu-1 in anhydrous n-pentane.
solution upon excitation by a 405 nm laser beam.

**Fig. S3.** The excitation spectra upon monitoring emission signals across the 700 - 550 nm range in 50 nm steps for (a) La-1, (b) Gd-1, (c) Tb-1 and (d) Dy-1 in anhydrous n-pentane solution.

**Fig. S4.** The excitation spectra upon monitoring emission signals across the 700 - 550 nm range in 50 nm steps for (a) Ce-1 and (b) Eu-1 in anhydrous n-pentane. The peaks labeled with ‘*’ in (b) is not from Eu-1, as their positions are exactly half of the monitored emission wavelengths. The difference between the excitation spectra of Ce-1 and those shown in Fig. S3 could be due to the relatively lower energy required for the d-f transitions of Ce$^{3+}$ ions, although further investigations are required to reveal the detailed mechanisms behind this. In contrast, the unique shape of the Eu-1 excitation spectra is due to the fact that emission signals from the Eu$^{3+}$ ion can be clearly observed. Therefore, the excitation spectra are dominated by the Eu$^{3+}$-centered emission signals, instead of the shifting of the monitored emission wavelengths.
Fig. S5. (a) Decaying profile of the emission signal at 525 nm for respective Ln-1 cage; calculated lifetimes using single exponential curve fitting are also shown; (b) decaying profile representing the response of the equipment employed.
Fig. S6. $^1$H NMR spectra of La-1 at room temperature with the sample prepared by: (a) dissolving 5.2 mg La-1 in 0.7 mL anhydrous CD$_2$Cl$_2$; (b) dissolving one crystal block of La-1 (around 0.5 mg) in 0.7 mL anhydrous CD$_2$Cl$_2$. The resultant solution is of similar colour with that used for photoluminescence study; (c) further diluted by 5 times from the sample in (b); (d) in vacuo removing the $n$-pentane solvent from the prepared La-1 sample for photoluminescence study, and re-dissolving the solid residue in 0.7 mL anhydrous CD$_2$Cl$_2$. It is clearly seen that both the $^1$H signals from the salicylate aromatic ring (denoted by ‘*’) and that from the isopropoxide groups (denoted by ‘¤’; the signal at around 5.3 ppm overlaps with the residual signal from CD$_2$Cl$_2$) are all well resolved, indicating that majority of the La-1 cages retain their molecular structure in dilute solution.
Fig. S7. Emission spectra of solid-state Eu-1 sample with excitation at 400 nm (red trace) and 420 nm (blue trace).

Fig. S8. Comparison of the normalized steady-state emission spectra for La-1, Ce-1, Gd-1, Tb-1 and Dy-1. The normalization was based on the main emission band at ca. 450 nm.

Fig. S9. Energy diagram of the proposed LMCT state and the emissive state of respective Ln$^{3+}$ ions.