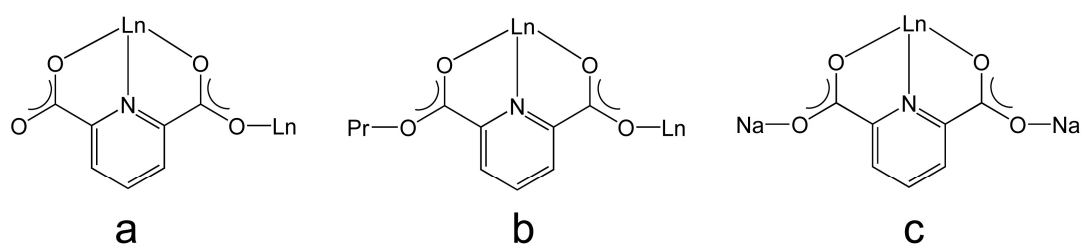


Supplementary Information

Title: New class of Preyssler-lanthanide complexes with modified and extended structures tuned by the lanthanide contraction effect

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Scheme S1 Schematic presentation of the coordination modes of pydc ligand in compounds **1–5**. (a) chelate-monodentate coordination mode. (b) chelate-bidentate coordination mode. (c) monodentate coordination mode.

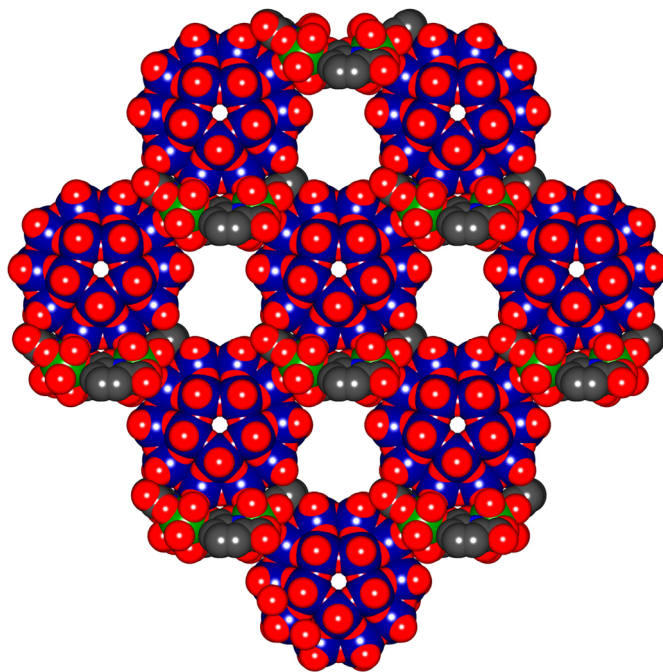


Fig. S1 View of the stacking arrangement of the layers in **1** perpendicular to the crystallographic *c* axis, showing the 1D channels.

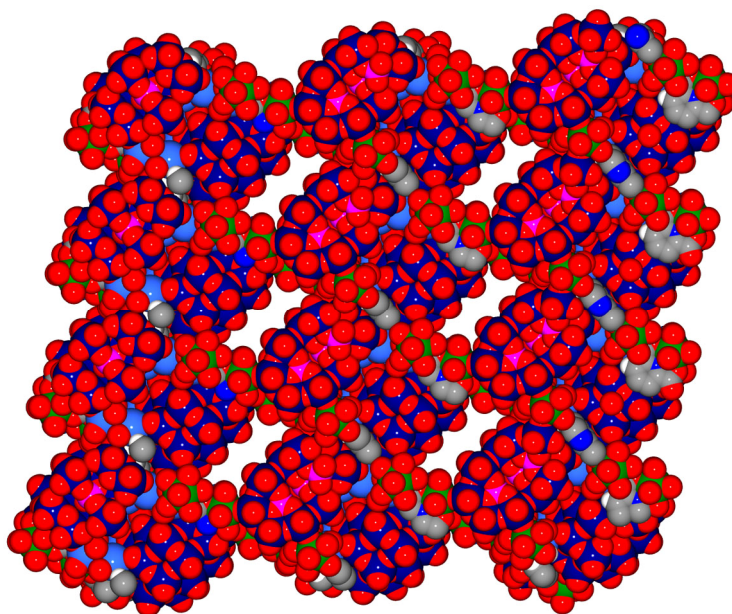


Fig. S2 View of the stacking arrangement of the layers in **2** perpendicular to the crystallographic *b* axis, showing the rectangular channels.

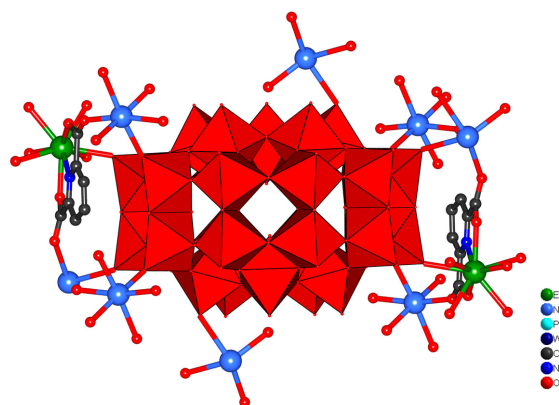


Fig. S3 View of the linkages of a Preyssler anion with two Sm^{3+} ions and eight Na^+ ions in **3**.

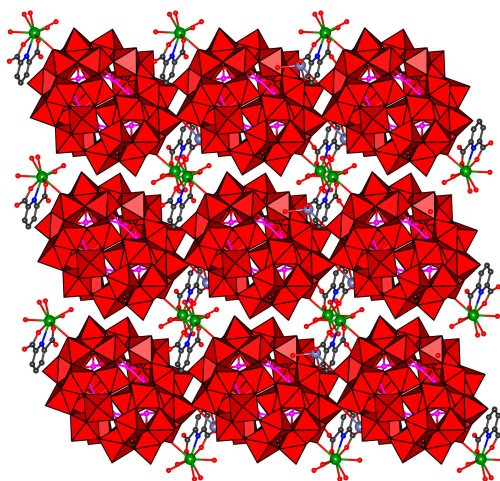


Fig. S4 The 3D supramolecular network of **3**.

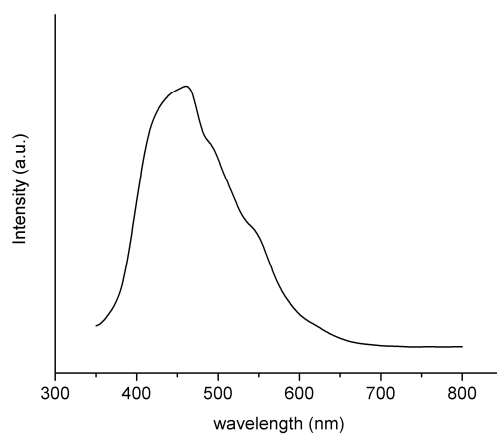


Fig. S5 Solid-state emission spectrum for **3** at room temperature (excited at 254 nm)

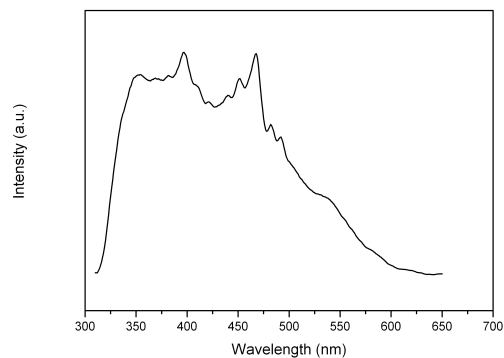


Fig. S6 Solid-state emission spectrum for H₂pydc at room temperature (excited at 288 nm).

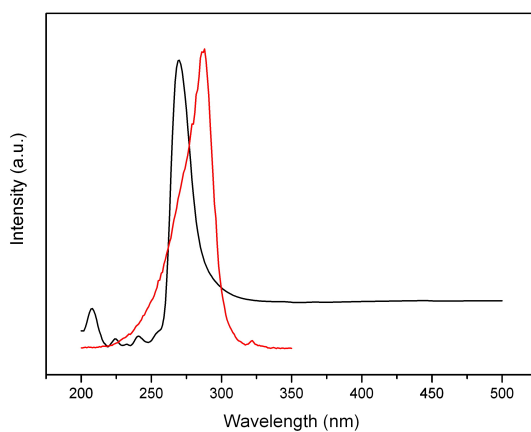


Fig. S7 UV-vis absorption spectrum (black line) at room temperature for the free organic ligand and the excitation spectrum (red line) for compound **4** (excited at 612 nm).