

## ***Electronic Supplementary Information (ESI)***

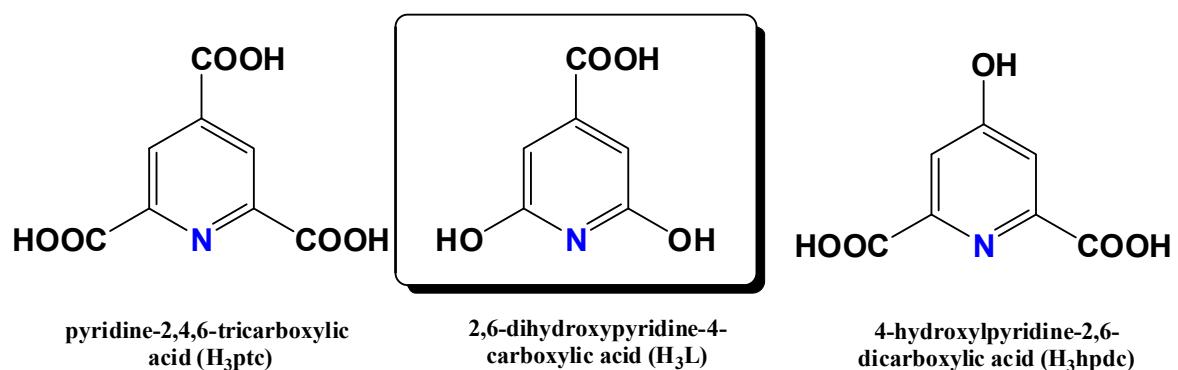
### **Highly-thermostable lanthanide–organic coordination frameworks with N-protonated 2,6-dihydroxypyridine-4-carboxylate exhibiting unusual 3-D mixed-connected network topology**

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Miao Du<sup>\*,b</sup> and Chun-Sen Liu<sup>\*,a</sup>**

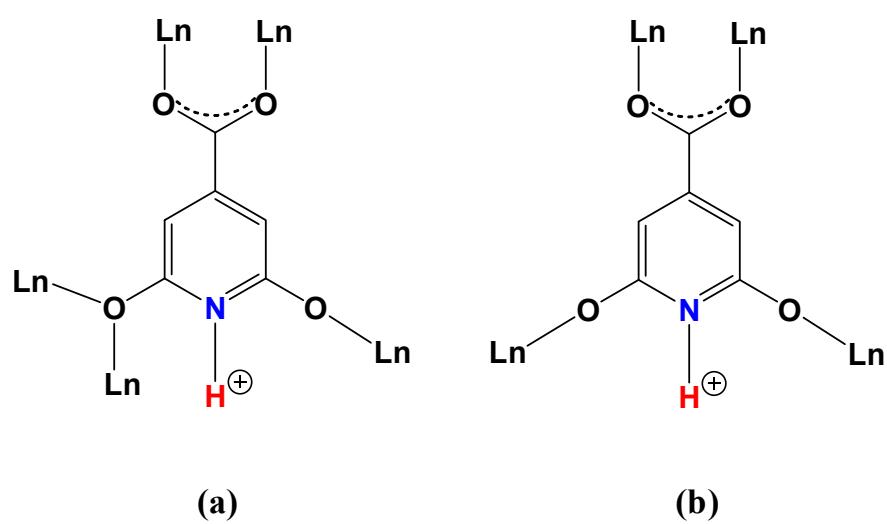
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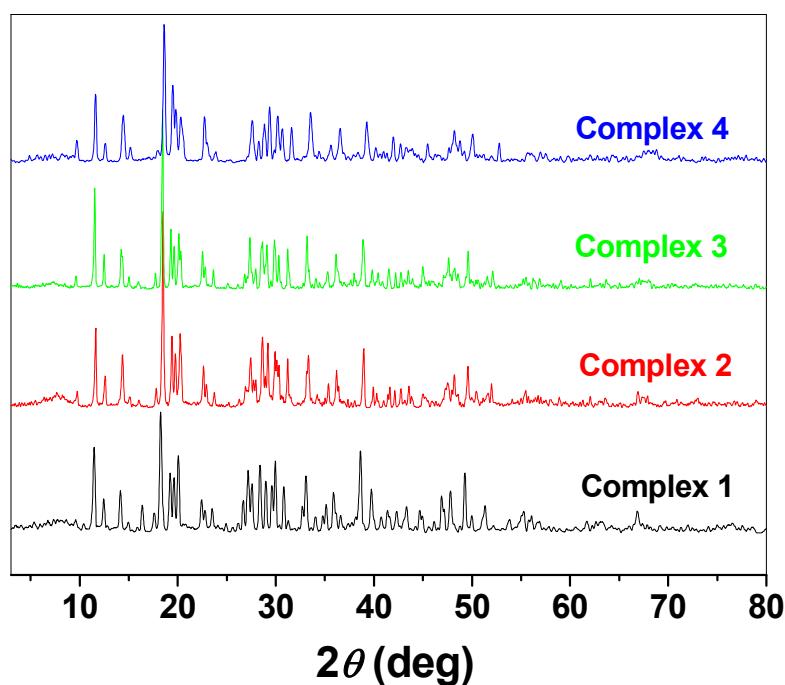
***CrystEngComm***



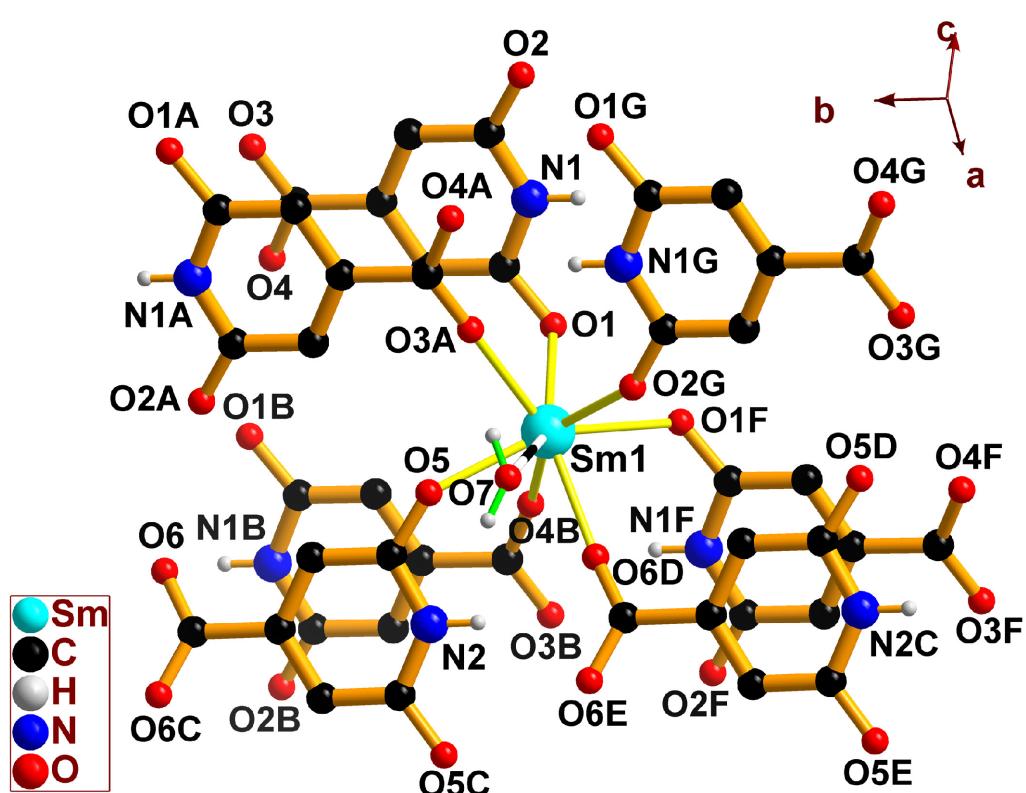
**Scheme S1** Chemical structures of  $\text{H}_3\text{L}$  and the related ligands  $\text{H}_3\text{ptc}$  and  $\text{H}_3\text{hpdc}$ .



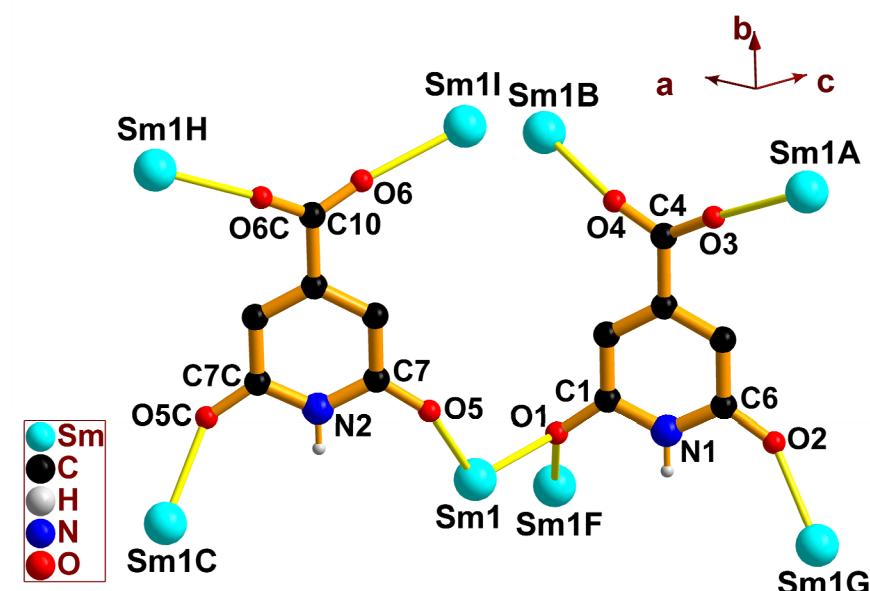
**Scheme S2** Coordination modes of the H-L ligands in **1–4**: (a)  $\mu_5$ -bridging carboxyl/hydroxyl mode comprised of  $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}syn\text{-}syn$  bridging carboxylate as well as  $\mu_1$ -monodentate and  $\mu_2$ -bidentate hydroxyl; (b)  $\mu_4$ -bridging carboxyl/hydroxyl mode containing  $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}syn\text{-}syn$  bridging carboxylate and  $\mu_1$ -monodentate hydroxyl.



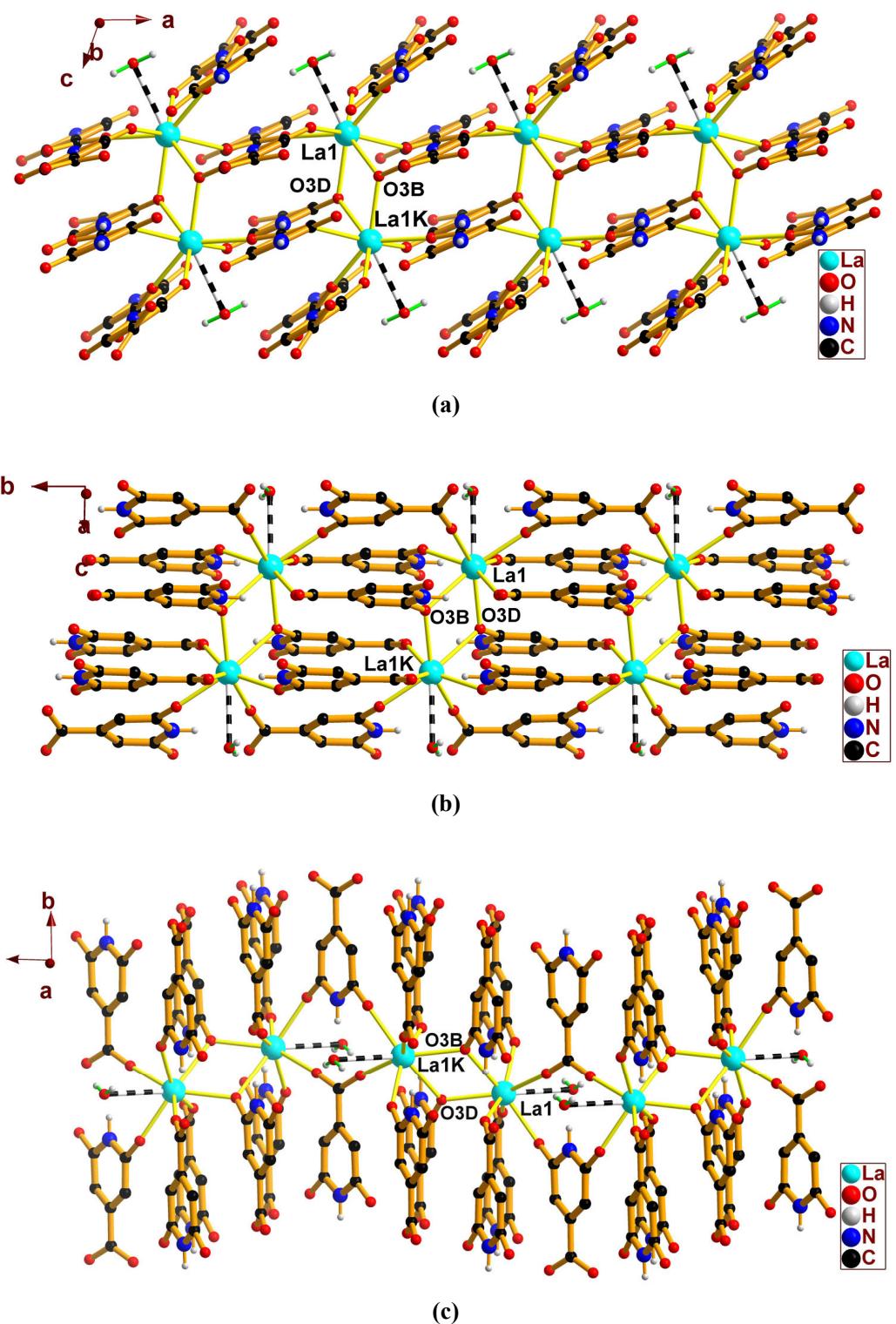
**Fig. S1** Comparison of PXRD patterns of **1–4**.



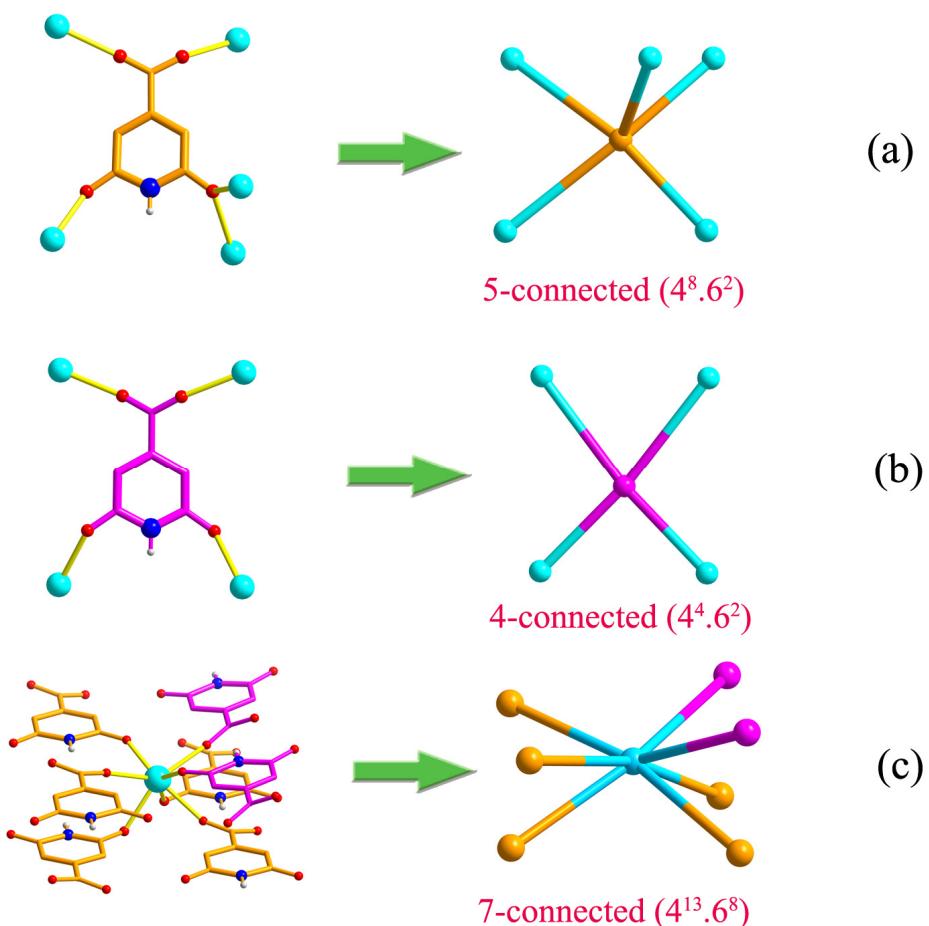
**Fig. S2** Local coordination environment of Sm<sup>III</sup> in **4**, in which the Sm–O<sub>water</sub> bond is shown as striped bond. Symmetry codes: A =  $-x, -y + 1, -z + 2$ ; B =  $-x + 1, -y + 1, -z + 2$ ; C =  $-x + 1, y, -z + 3/2$ ; D =  $x, y - 1, z$ ; E =  $-x + 1, y - 1, -z + 3/2$ ; F =  $-x + 1, -y, -z + 2$ ; G =  $-x, -y, -z + 2$ ).



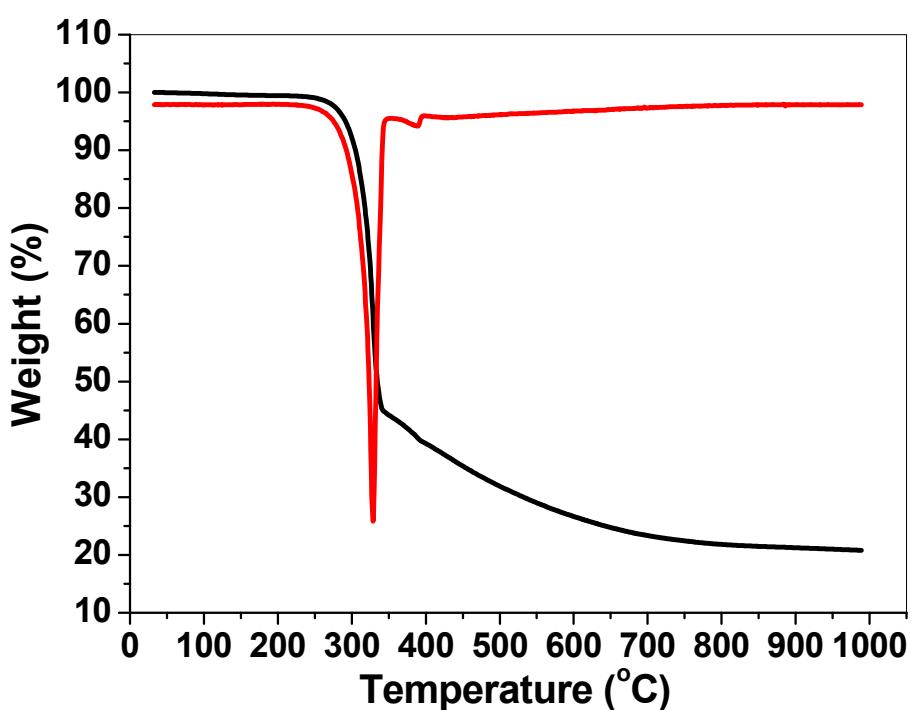
**Fig. S3** Coordination modes of H-L in 4:  $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}syn\text{-}syn$  bridging mode for carboxylate groups of O6–C10–O6C and O3–C4–O4,  $\mu_1$ -monodentate mode for ionized hydroxyl groups of O2, O5, and O5G, and  $\mu_2$ -bridging mode for ionized hydroxyl group of O1. Symmetry codes: A =  $-x, -y + 1, -z + 2$ ; B =  $-x + 1, -y + 1, -z + 2$ ; C =  $-x + 1, y, -z + 3/2$ ; F =  $-x + 1, -y, -z + 2$ ; G =  $-x, -y, -z + 2$ ; H =  $-x + 1, y + 1, -z + 3/2$ ; I =  $x, y + 1, z$ .



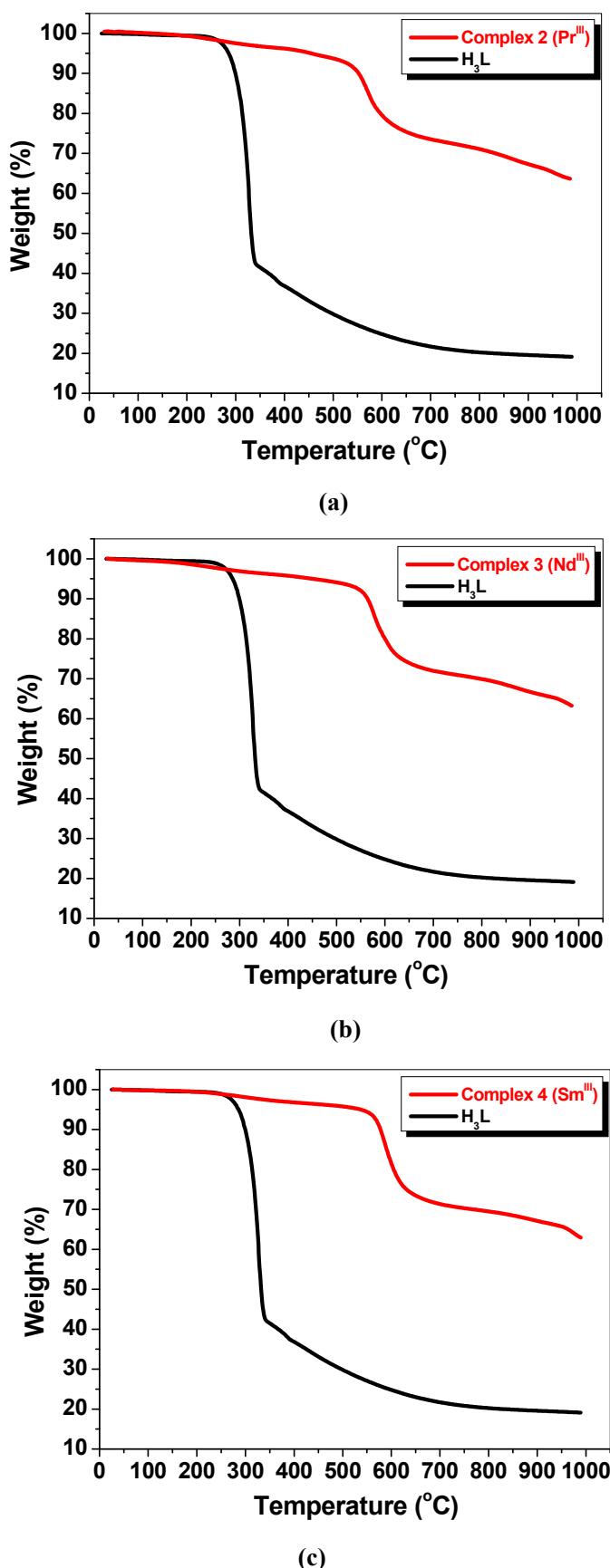
**Fig. S4** 1-D chain motifs via the linkage of dinuclear  $\text{La}^{\text{III}}$  units by H-L ligands, viewed along the (a) [100], (b) [010], and (c) [001] direction, respectively. Symmetry codes: B =  $x, y + 1, z$ ; D =  $-x + 1, -y - 1, -z$ ; K =  $-x + 1, -y, -z$ .



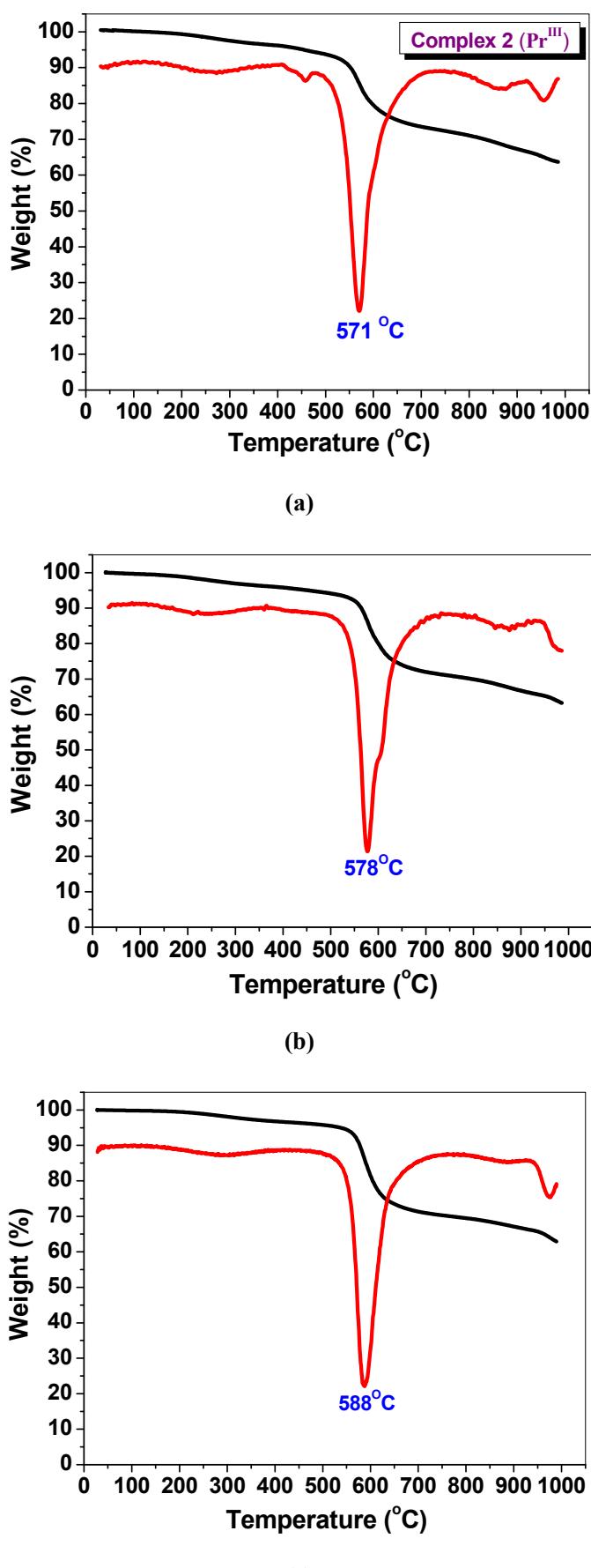
**Fig. S5** Illustration of the connectivity between  $\text{La}^{\text{III}}$  ions and  $\text{H-L}$  ligands: (a)  $\mu_5\text{-H-L}$  ligand (orange sphere), (b)  $\mu_4\text{-H-L}$  ligand (pink sphere), and (c) 7-connected  $\text{La}^{\text{III}}$  center.



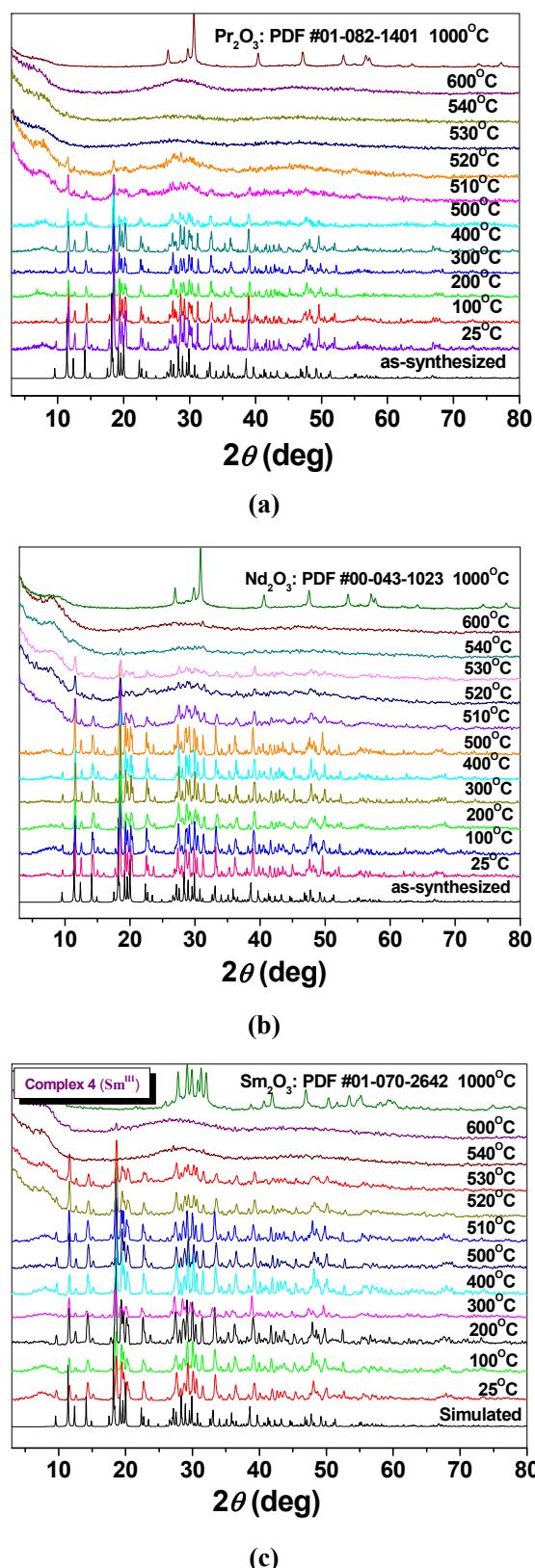
**Fig. S6** TG-DTA curve for the free ligand 2,6-dihydroxypyridine-4-carboxylic acid ( $\text{H}_3\text{L}$ ).



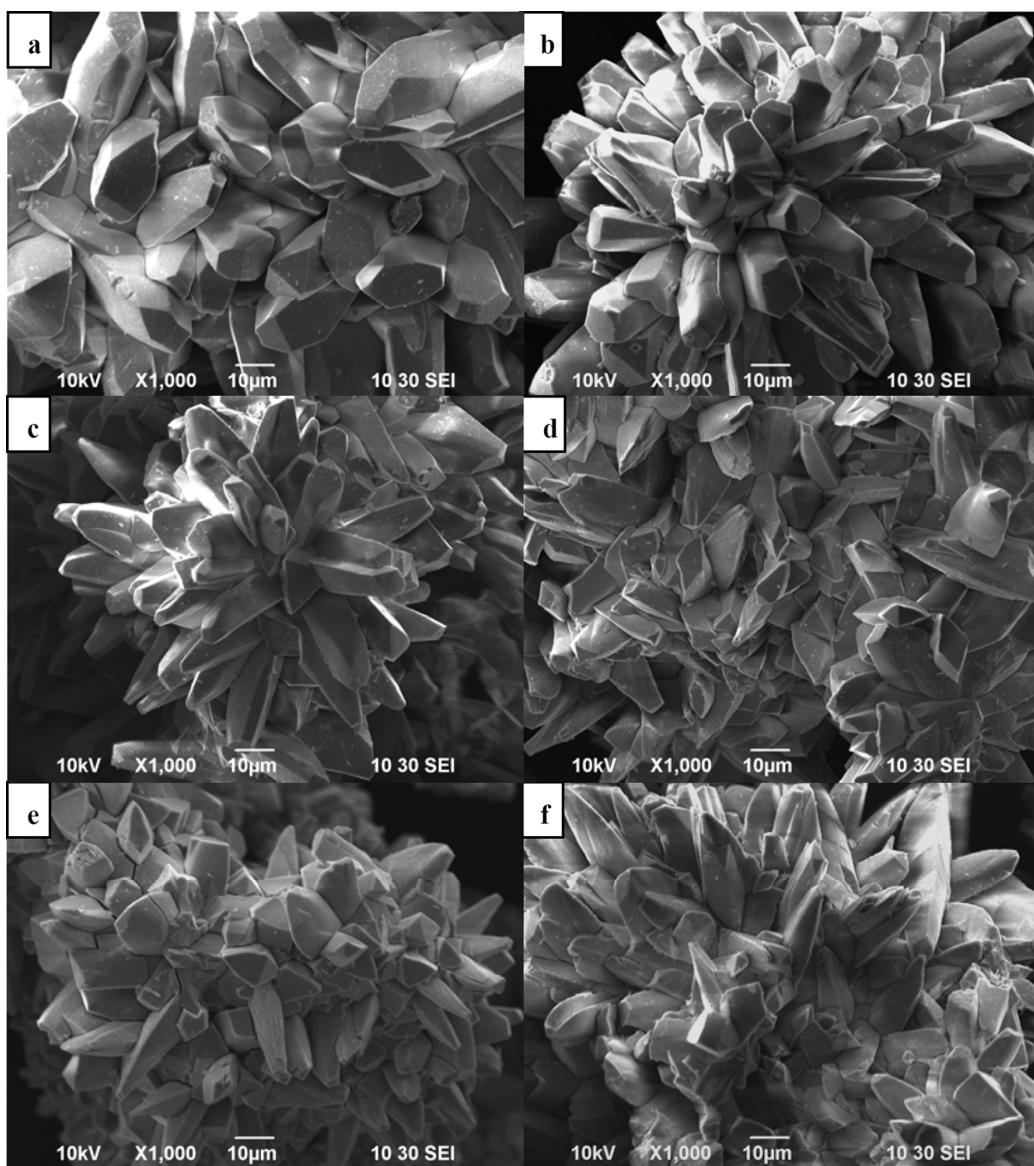
**Fig. S7** Comparison of the TG curves of (a)  $\text{H}_3\text{L}$  and **2**, (b)  $\text{H}_3\text{L}$  and **3**, and (c)  $\text{H}_3\text{L}$  and **4**.



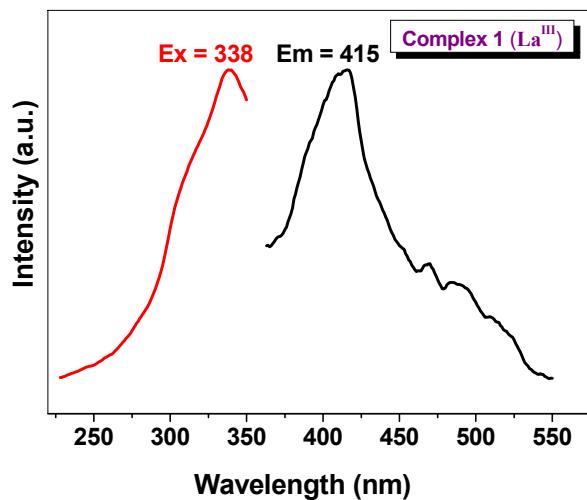
**Fig. S8** TG-DTA curves for (a) 2, (b) 3, and (c) 4.



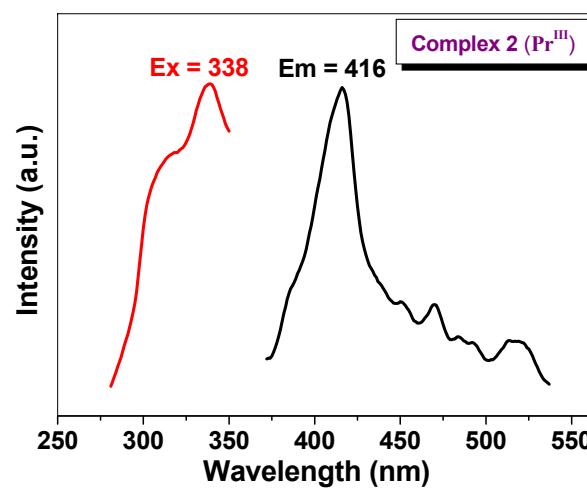
**Fig. S9** PXRD patterns of (a) 2, (b) 3, and (c) 4. The bottom simulated pattern for 4 was obtained from single-crystal data. The others from the bottom were taken from the as-synthesized samples that were treated by heating at different temperatures.



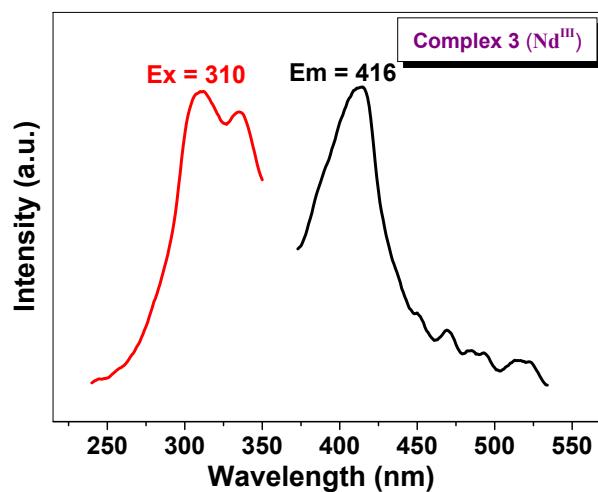
**Fig. S10** SEM images of complex **1** based on the samples treated at different temperatures: (a) as-synthesized products; (b)–(f): the products after a prolonged heating in a crucible of thermogravimetric analyzer at 100, 200, 300, 400, and 500 °C, respectively.



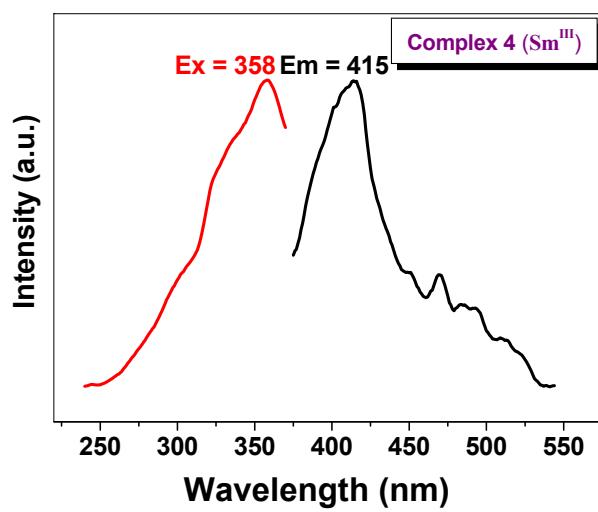
(a)



(b)

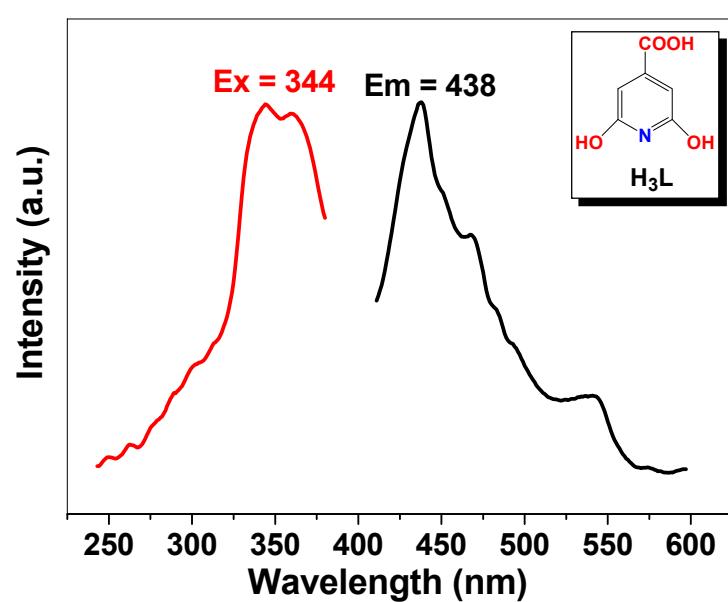


(c)



(d)

**Fig. S11** The emission and excitation fluorescent spectra of (a) **1**, (b) **2**, (c) **3**, and (d) **4**.



**Fig. S12** The emission and excitation fluorescent spectra of the  $\text{H}_3\text{L}$  ligand.