

# **Lanthanide Metal-Organic Frameworks with Hexa-carboxylate Ligands Derived From Cyclotriphosphazene as Bridging Linkers: Synthesis, Thermal and Luminescent Properties**

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## Experimental sections:

**Materials and General Methods.** All reagents were purchased from commercial sources and were used without further purification. FT–IR spectra were recorded as KBr pellets with an Equinox 55 FT–IR spectrophotometer (4000–400  $\text{cm}^{-1}$ ). Thermal gravimetric analyses (TGA) were performed under  $\text{N}_2$  atmosphere (100 ml/min) with a heating rate of  $4^\circ\text{C}/\text{min}$  between ambient temperature and  $500^\circ\text{C}$  using a Pyris1 thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected over the  $2\theta$  range  $5\sim 60^\circ$  using a X'Pert PRO automated diffractometer at room temperature, with a step size of  $0.02^\circ$  in  $2\theta$  angle. The hexa-carboxylate ligand was synthesized according to the literature.<sup>1</sup>

**Synthesis of  $\{[\text{Eu}_2(\text{C}_{42}\text{H}_{24}\text{O}_{18}\text{P}_3\text{N}_3)(\text{H}_2\text{O})_4]\cdot(\text{H}_2\text{O})_4\cdot(\text{C}_2\text{H}_7\text{N})_2\}_n$  (1).** A mixture of  $\text{Eu}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  ( 23 mg ), H6L1 ( 12 mg ) was dissolved in 15 mL of DMF/ $\text{H}_2\text{O}$  (1:2, v/v), and then pH value was adjusted to 2-3. The final mixture was heated at  $130^\circ\text{C}$  under autogenous pressure for 120 hours in 10 Parr Teflon-lined stainless steel vessels, and then cooled to room temperature. The resulting solution was standed undisturbedly from which square-like crystals were obtained. The crystals were collected together, washed with mother liquid, and dried under ambient conditions. Yield of the reaction was ca. 43% based on H<sub>6</sub>L1. Anal. Calcd for dyhydrated  $\text{C}_{46}\text{H}_{54}\text{Eu}_2\text{N}_5\text{O}_{26}\text{P}_3$ : C, 37.09%, H, 3.65%, N, 4.70%; found C, 36.79%, H, 4.02%, N, 4.67%. IR (KBr,  $\text{cm}^{-1}$ ): 3481, 1603, 1543, 1420, 1384, 1210, 1159, 966, 790.

**Synthesis of  $\{[\text{Eu}_2(\text{C}_{42}\text{H}_{24}\text{O}_{18}\text{P}_3\text{N}_3)(\text{H}_2\text{O})_8]\cdot(\text{H}_2\text{O})_2\cdot\text{C}_2\text{H}_7\text{N}\}_n$  (2).** The synthesis process was very similar to **1** except adding 4,4-bipyridine 14mg in the reaction system, adjusting the pH range located in 4~5 and for 96 hours. Square-like crystals were directly obtained, and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield of the reaction was ca. 40% based on H6L1. Calcd for dyhydrated  $\text{C}_{44}\text{H}_{51}\text{Eu}_2\text{N}_4\text{O}_{28}\text{P}_3$ : C, 35.69%, H, 3.47%, N, 3.78%; found C, 35.92%, H, 3.03%, N, 3.98%. IR (KBr,  $\text{cm}^{-1}$ ): 3418, 1604, 1540, 1420, 1384, 1211, 1159, 967, 790.

**Synthesis of  $\{[\text{Eu}_2(\text{C}_{42}\text{H}_{24}\text{O}_{18}\text{P}_3\text{N}_3)(\text{H}_2\text{O})_3(\text{DMF})]\cdot(\text{H}_2\text{O})_2\cdot(\text{C}_2\text{H}_7\text{N})\}_n$  (**3**).** The synthesis process was very similar to **1** except adding  $\text{H}_6\text{L2}$  12mg in the reaction system and adjusting the pH range located in 3~4. Square-like crystals were directly obtained, and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield of the reaction was ca. 34% based on  $\text{H}_6\text{L2}$ . Calcd for dyhydrated  $\text{C}_{47}\text{H}_{48}\text{Eu}_2\text{N}_5\text{O}_{24}\text{P}_3$  : C, 38.57%, H, 3.31%, N, 4.78%; found C, 39.02%, H, 3.81%, N, 5.02%. IR (KBr,  $\text{cm}^{-1}$ ): 3418, 1604, 1540, 1420, 1384, 1211, 1159, 966, 789.

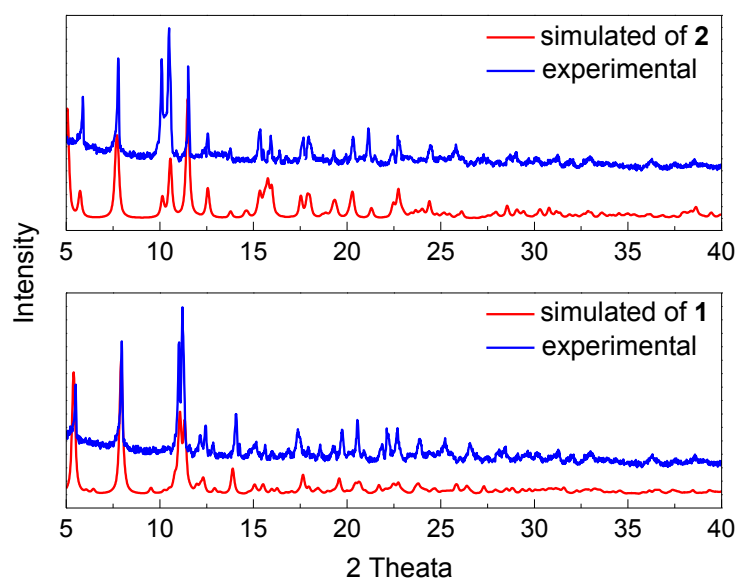
**X-Ray Structural Determination.** Suitable single crystals were selected and mounted onto the end of a thin glass fiber. X-ray intensity data were measured on a Bruker SMART APEX CCD for **1** - **3** based diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation.<sup>2</sup> The structure was solved by direct methods and refined by full-matrix least squares using the *SHELXTL* crystallographic software package.<sup>3</sup> All the non-hydrogen atoms were refined anisotropically, except for O6w and O7w for **1**. The hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The hydrogen atoms of the coordinated water molecules were not located for compounds **1-3**. In compound **1-3**, because of disorder, thermal parameters of disordered atoms and Ow atoms were restrained. In addition, due to the highly disordered solvent molecules in compounds **1-3**, the PLATON/SQUEEZE routine<sup>4</sup> was employed to calculate the diffraction contribution from the solvent molecules, and thereby to produce a set of solvent-free diffraction intensities. Not unusual for large flexible complexes might be responsible for the CheckCIF B alert PLAT094 of **1** and **2**. The final formula were derived from crystallographic data combined with elemental and thermogravimetric analyses data. Details of the crystal parameters, data collection and refinements for complexes **1-3** are summarized in Table 1. Selected bond lengths and angles are shown in Table S1. CCDC 926681 (**1**), CCDC 926682 (**2**) and CCDC 926683 (**3**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).

Reference:

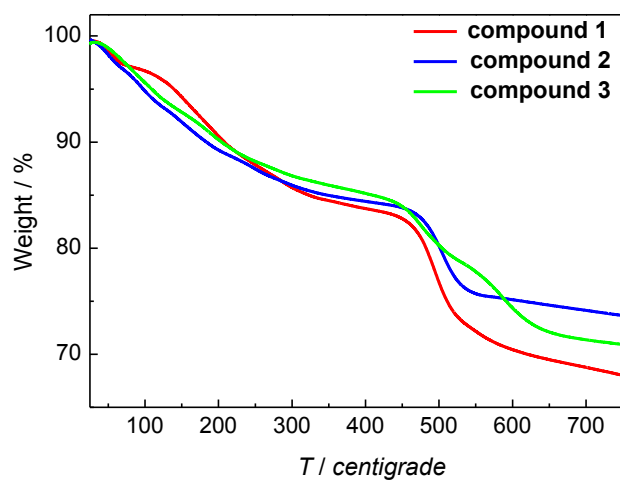
- 1 Chandrasekhar, V.; Krishnan, V.; Steiner, A.; Bickley, J. F. *Inorg. Chem.*, **2004**, *43*, 166.
- 2 SMART and SAINT, *Area Detector Software Package and SAX Area Detector Integration Program*; Bruker Analytical X-Ray; Madison, WI, USA, **1997**.
- 3 G. M. Sheldrick, *SHELXTL-PLUS, Crystal Structure Analysis Package*; Bruker Analytical X-Ray; Madison, WI, USA, **1997**.
4. PLATON program: A. L. Spek, *Acta Crystallogr. Sect. A*, **1990**, *46*, 194.

**Table S1** the selected bond length of 1-3

Compound 1		Compound 2		Compound 3	
Eu1 O13	2.397(8)	Eu1 O6	2.367(7)	Eu1 O3	2.353(5)
Eu1 O2W	2.401(7)	Eu1 O3	2.393(7)	Eu1 O8	2.356(4)
Eu1 O14	2.419(8)	Eu1 O11	2.411(7)	Eu1 O19	2.392(5)
Eu1 O10	2.427(7)	Eu1 O10	2.428(7)	Eu1 O2	2.406(5)
Eu1 O11	2.436(7)	Eu1 O8	2.437(7)	Eu1 O15	2.458(5)
Eu1 O1W.	2.449(8)	Eu1 O14	2.439(8)	Eu1 O9	2.469(4)
Eu1 O2	2.508(7)	Eu1 O13	2.441(8)	Eu1 O1W	2.483(5)
Eu1 O1	2.525(8)	Eu1 O9	2.611(7)	Eu1 O14	2.549(5)
Eu1 O13	2.828(8)	Eu1 O2	2.838(7)	Eu1 O8	2.678(4)
Eu1 Eu1	4.1356(12)	Eu1 C21	2.908(10)	Eu1 Eu1	3.9646(6)
Eu2 O17	2.392(7)			Eu2 O2W	2.379(8)
Eu2 O16	2.399(7)			Eu2 O18	2.375(8)
Eu2 O4	2.399(7)			Eu2 O11	2.386(7)
Eu2 O4W	2.414(9)			Eu2 O12	2.422(7)
Eu2 O7	2.464(7)			Eu2 O6	2.427(5)
Eu2 O5	2.474(8)			Eu2 O3W	2.464(8)
Eu2 O3W	2.497(10)			Eu2 O17	2.477(7)
Eu2 O8	2.509(9)			Eu2 O5	2.593(7)
Eu2 O4	2.747(7)			Eu2 O18	2.679(6)
Eu2 Eu2	4.0678(11)			Eu2 Eu2	4.0940(9)



**Fig. S1** XRD spectrum of **2**



**Fig. S2** TGA curve of **1 - 3**.