Supplementary Material (ESI) for CrystEngComm

Supporting Information

Unique $(H_2O)_{14}$ water clusters with cyclic $(H_2O)_4$ tetramer unit trapped in 3D porous lanthanoid-cyclohexanetetracarboxylate frameworks †

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Experimental Section:

Improved synthesis of $[Tb_4(chtc)_3(H_2O)_{10}]\cdot 9H_2O$ (1): a mixture of $Tb(NO_3)_3\cdot 6H_2O$ (0.2 mmol, 0.090 g), $CuCl_2\cdot 4H_2O$ (0.1 mmol, 0.018 g), H_4chtc (0.2 mmol, 0.051 g), triethylamine (0.6 mmol, 0.061 g) and distilled H_2O (10 mL) was sealed in a 23-mL Teflon-liner autoclave. Heated in an oven to 140 ^oC for 5 days, and then cooled to room temperature in the rate of 5 ^oC/h, yielded colorless crystals of **1** (yield: 23 mg, 26 % based on Tb).

Materials and Physical Measurements. The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRPD) intensities for polycrystalline samples of **1-3** were measured at 293 K on Bruker D8 Advance Diffratometer (Cu-K_α, λ= 1.54056 Å) by scanning over the range of 5-60^o with step of 0.2^o/s. Calculated patterns of **1-3** were generated with Mercury. TG data were obtained on a TG209F3 Tarsus thermogravimetry, with a heating rate of 10 °C min^{-1} in an nitrogen atmosphere. The emission/excitation spectra in the visible and near-infrared region were measured on an Edinburgh FLS-920 spectrophotometer.

X-Ray Crystallography. Single crystal diffraction intensities of **1** and **2** was collected on a Rigaku R-AXIS SPIDER Image Plate diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Diffraction data for compound **3** were recorded on a Bruker Apex CCD area detector diffractometer with Mo KR radiation (λ = 0.71073 Å) at 123 K. Absorption corrections were applied by using multiscan program SADABS.[1] The structure was solved with direct method and refined with full-matrix least-squares technique with the SHELXTL program package.[2] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C-H 0.96 Å).

Reference:

1 G. M. Sheldrick, *SADABS 2.05*, University of Göttingen.

2 *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison, Wisconsin, USA, 2000.

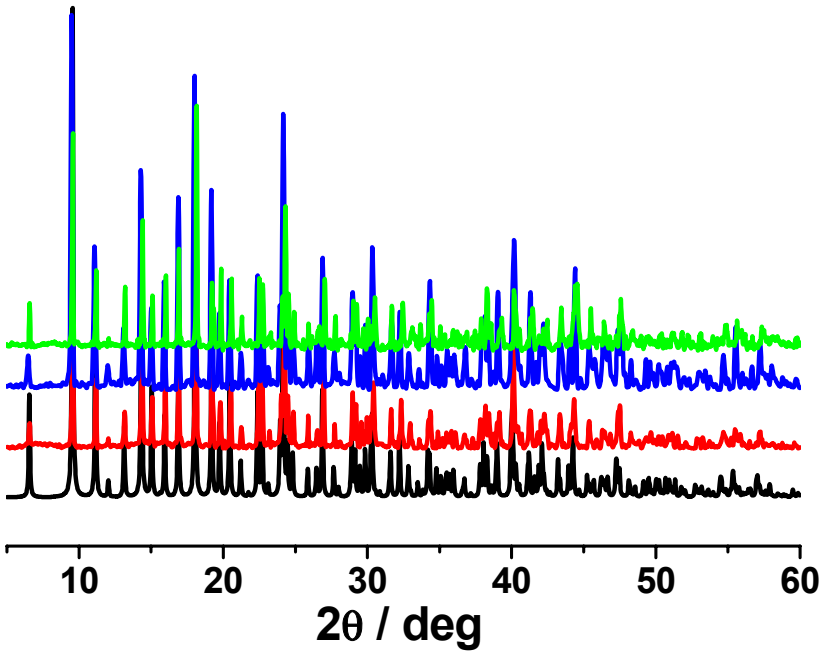

Fig. S1 XRD patterns of **1** (red), **2** (blue) and **3** (green).

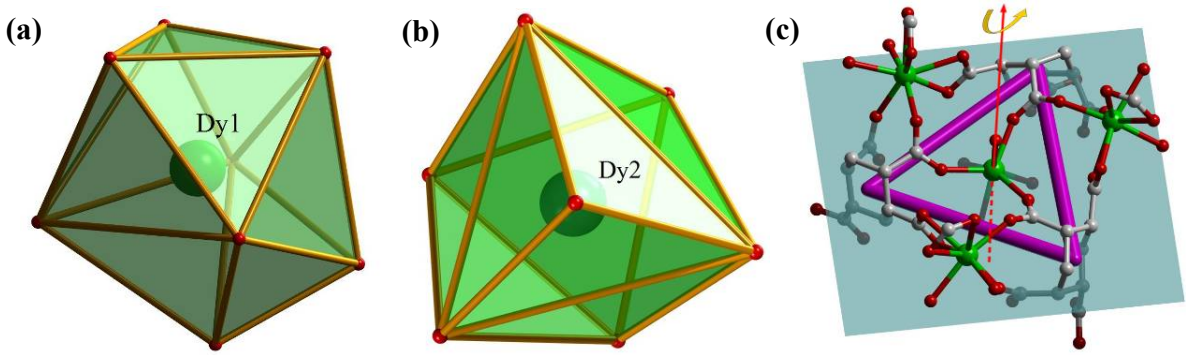

Fig. S2. Coordinated modes of Dy1 (a) and Dy2 (b) atoms, and the view of the 3-fold axis on Dy2 atom (c).

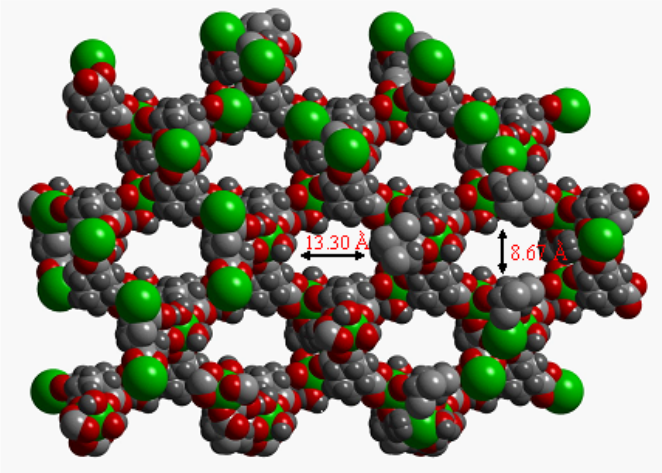

Fig. S3. Space-filling graph of porous sizes in one-fold 3D network structure.

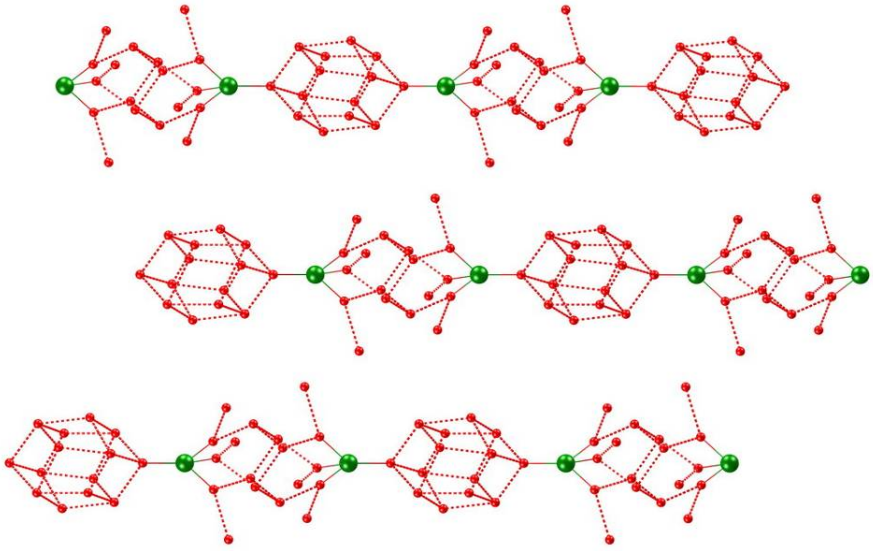

Fig. S4 The space arrangement of two kinds of water clusters along *c*-axis.

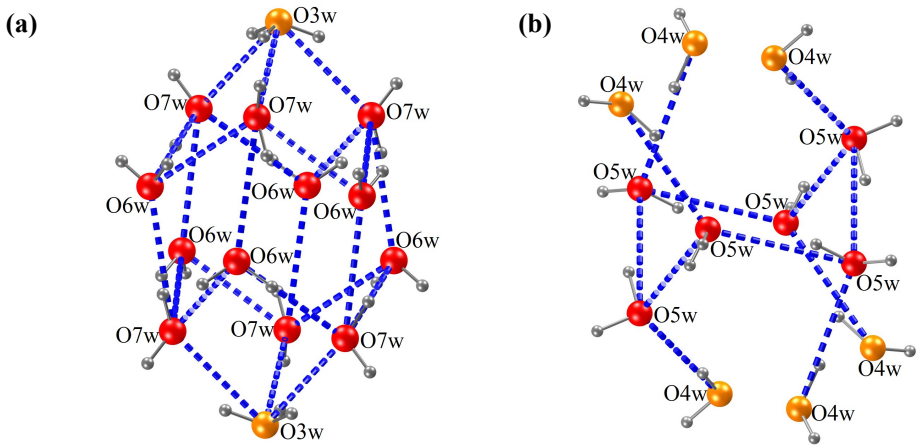

Fig. S5 The binding modes of $(H_2O)_{14}$ (a) and $(H_2O)_{12}$ (b) clusters. Colours: red and orange atoms, guest and coordinated water molecules, respectively; grey atoms, hydrogen molecules; green and light purple.

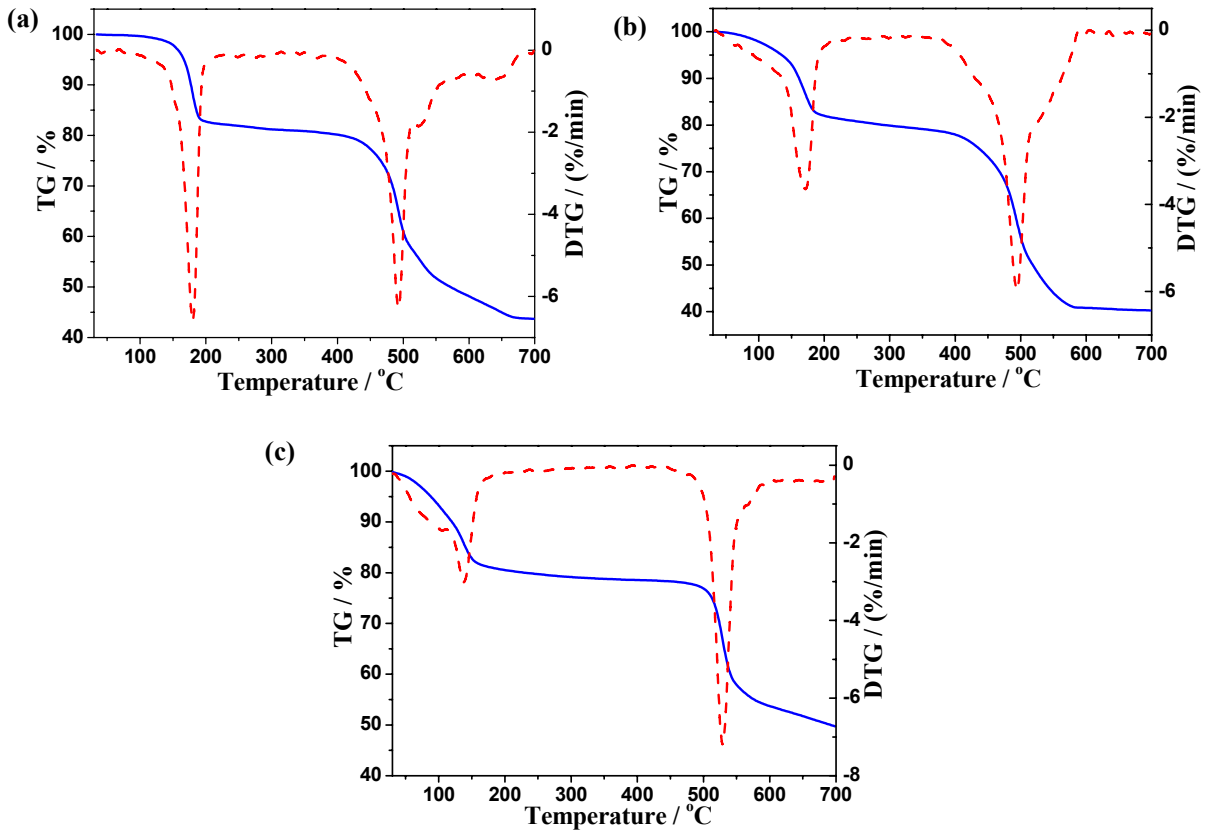

Fig. S6. TGA curve of **1** (a), **2** (b) and **3** (c) under nitrogen gas.

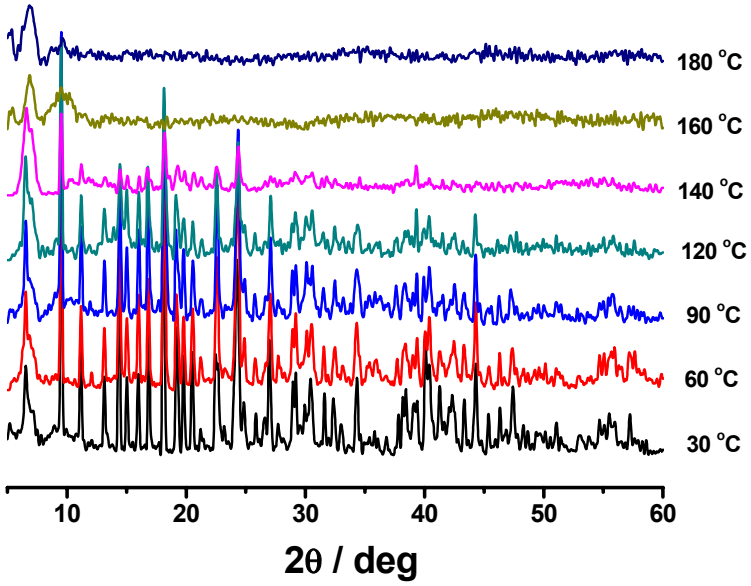

Fig. S7 Variable-temperature X-ray powder diffraction (VTXRPD) of **1** under N_2 blowing at standard atmospheric pressure from 30 °C to 180 °C

Table S1. Selected bond lengths (Å) and angles (°) for **3**.

Dy(1)-O(1)	2.244(7)	Dy(2)-O(2*b*)	2.229(8)
Dy(1)-O(8)	2.316(7)	Dy(2)-O(2)	2.229(8)
Dy(1)-O(2w)	2.324(7)	Dy(2)-O(2*c*)	2.229(8)
Dy(1)-O(6*a*)	2.363(7)	Dy(2)-O(4w*b*)	2.347(8)
Dy(1)-O(1w)	2.379(7)	Dy(2)-O(4w)	2.347(8)
Dy(1)-O(3*b*)	2.389(7)	Dy(2)-O(4w*c*)	2.347(8)
Dy(1)-O(4*b*)	2.488(7)	Dy(2)-O(3w)	2.386(17)
Dy(1)-O(5*a*)	2.515(7)		
O(1)-Dy(1)-O(8)	77.5(3)	O(6*a*)-Dy(1)-O(5*a*)	53.4(2)
O(1)-Dy(1)-O(2W)	156.2(3)	O(3*b*)-Dy(1)-O(5*a*)	71.6(2)
O(8)-Dy(1)-O(2W)	79.9(2)	O(4*b*)-Dy(1)-O(5*a*)	115.2(2)
O(1)-Dy(1)-O(1W)	99.1(3)	O(2)-Dy(2)-O(2*c*)	114.17(19)
O(8)-Dy(1)-O(1W)	80.8(2)	O(2)-Dy(2)-O(2*b*)	114.17(18)
O(2W)-Dy(1)-O(1W)	84.7(2)	O(2*c*)-Dy(2)-O(2*b*)	114.17(19)
O(1)-Dy(1)-O(6*a*)	75.3(3)	O(2)-Dy(2)-O(4W*b*)	147.3(3)
O(8)-Dy(1)-O(6*a*)	139.2(2)	O(2*c*)-Dy(2)-O(4W*b*)	83.9(3)
O(2W)-Dy(1)-O(6*a*)	127.9(2)	O(2*b*)-Dy(2)-O(4W*b*)	78.5(3)
O(1W)-Dy(1)-O(6*a*)	74.1(2)	O(2)-Dy(2)-O(4W)	78.5(3)
O(1)-Dy(1)-O(3*b*)	96.8(3)	O(2*c*)-Dy(2)-O(4W)	147.3(3)
O(8)-Dy(1)-O(3*b*)	130.7(2)	O(2*b*)-Dy(2)-O(4W)	83.9(3)
O(2W)-Dy(1)-O(3*b*)	92.1(2)	O(4W*b*)-Dy(2)-O(4W)	72.9(3)
O(1W)-Dy(1)-O(3*b*)	147.3(2)	O(2)-Dy(2)-O(4W*c*)	83.9(3)
O(6*a*)-Dy(1)-O(3*b*)	82.6(2)	O(2*c*)-Dy(2)-O(4W*c*)	78.5(3)
O(1)-Dy(1)-O(4*b*)	91.9(3)	O(2*b*)-Dy(2)-O(4W*c*)	147.3(3)
O(8)-Dy(1)-O(4*b*)	78.4(2)	O(4W*b*)-Dy(2)-O(4W*c*)	72.9(3)
O(2W)-Dy(1)-O(4*b*)	76.0(2)	O(4W)-Dy(2)-O(4W*c*)	72.9(3)
O(1W)-Dy(1)-O(4*b*)	153.7(2)	O(2)-Dy(2)-O(3W)	75.8(2)
O(6*a*)-Dy(1)-O(4*b*)	132.0(2)	O(2*c*)-Dy(2)-O(3W)	75.8(2)
O(3*b*)-Dy(1)-O(4*b*)	52.6(2)	O(2*b*)-Dy(2)-O(3W)	75.8(2)
O(1)-Dy(1)-O(5*a*)	128.2(3)	O(4W*b*)-Dy(2)-O(3W)	136.67(19)
O(8)-Dy(1)-O(5*a*)	147.6(2)	O(4W)-Dy(2)-O(3W)	136.67(19)
O(2W)-Dy(1)-O(5*a*)	75.6(2)	O(4W*c*)-Dy(2)-O(3W)	136.67(19)
O(1W)-Dy(1)-O(5*a*)	76.0(2)		

Symmetry code: *a*) -x+y+7/3, -x+2/3, z-1/3; *b*) -y+1, x-y-1, z; *c*) -x+y+2,-x+1,z.

Table S2. Selected hydrogen bond lengths (Å) and angles (°) for **3**.

D-H···A	d(D-H)	D(H···A)	d(D···A)	<(D-H···A)
O(1W)-H(1WA)...O(7*a*)	0.85	1.92	2.761(10)	171.7
O(1W)-H(1WB)...O(5*e*)	0.84	2.16	2.846(9)	138.4
O(2W)-H(2WA)...O(4*e*)	0.85	1.86	2.651(10)	155.1
O(2W)-H(2WB)...O(7*f*)	0.84	1.83	2.653(9)	164.6
O(3W)-H(3W)...O(7W)	0.84	1.94	2.67(3)	144.2
O(4W)-H(4WA)...O(5W)	0.85	1.97	2.786(12)	163.0
O(4W)-H(4WB)...O(4*b*)	0.84	2.24	2.908(11)	136.0
O(5W)-H(5WA)...O(5)	0.84	2.08	2.874(10)	157.1
O(5W)-H(5WB)...O(5W*g*)	0.84	1.97	2.767(11)	157.5
O(6W)-H(6WA)...O(6)	0.84	2.07	2.906(19)	173.2
O(6W)-H(6WB)...O(7W*d*)	0.84	2.10	2.83(4)	144.9
O(7W)-H(7WA)...O(3)	0.85	2.35	3.18(3)	168.0
O(7W)-H(7WB)...O(6W*h*)	0.85	2.14	2.86(4)	142.0

Symmetry codes: *a*) -x+y+7/3,-x+2/3,z-1/3; *b*) -y+1,x-y-1,z; *c*) -x+y+2,-x+1,z; *d*) -y+2/3,x-y-5/3,z+1/3; *e*) y+4/3,-x+y+2/3,-z-1/3; *f*) -x+7/3,-y-1/3,-z-1/3; *g*) x-y,x-1,-z; *h*) -x+5/3,-y-2/3,-z-2/3.