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Supporting information

Chiral Transposing from Diphosphonate Metal-Organic Framework Precursors to Porous Lanthanide Pyrophosphates

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Experimental details

General: All reagents were readily available from commercial sources and used as received without further purification. 1-hydroxyethylidenediphosphonic acid (H_5hedp, $C_2H_8O_7P_2$, ≥97%, Fluka) and lanthanide(III) chloride hexahydrate ($LnCl_3 \cdot 6H_2O$, ≥99.9% Aldrich, Ln = Tb, Dy, Ho, Er, and Y). The final products were air- and light-stable, and insoluble in water and common organic solvents such as methanol, ethanol, acetone, dichloromethane, toluene, DMSO and chloroform.

Synthesis of $[Er_8(H_2O)_4(Hhedp)_6]_n$: The typical hydrothermal synthesis of single crystals of Er-Hedp is as follows: A mixture of 0.160g of H_5hedp (~0.77mmol) and 0.290g of $ErCl_3 \cdot 6H_2O$ (~0.76mmol) in ca. 18g of distilled water was stirred thoroughly for 30 minutes at ambient temperature yielding homogeneous solution ($1 \leq pH \leq 2$) with a molar composition of 1 : 1 : 1000. The homogeneous solution was moved to one PTFE-lined stainless steel reaction vessel (40 ml), under autogeneous pressure and static conditions and heated at temperatures in the range 150 – 230 ºC in a preheated oven. The reaction took place over a period of 3 days, then the vessel was removed from the oven and left to cool naturally to ambient temperature before opening. Well-formed single crystals were harvested (after dried, 0.230g, about 92% based on $ErCl_3 \cdot 6H_2O$) as a pure phase, and were washed by copious amounts of distilled water (3×50ml), then air-dried at ambient temperature.

Synthesis of $[Y_8(H_2O)_4(Hhedp)_6]_n$: A mixture of 0.160g of H_5hedp and 0.330g of $YCl_3 \cdot 6H_2O$ in 18g of distilled water was stirred to get a homogeneous solution with a molar ratio of 3:4:3000. The homogeneous solution was moved in one PTFE-lined stainless steel reaction vessels (40 ml), under autogeneous pressure and static conditions at 230ºC in a preheated oven. The reaction took place over a period of 3 days, then the final product of white single crystals (0.100g) and small amount of white powder (0.050g), which was also confirmed to be the cubic phase by powder XRD data, was obtained by washed with distilled water (3×50ml), then air-dried at ambient temperature.

Synthesis of $[Dy_8(H_2O)_4(Hhedp)_6]_n$, $[Tb_8(H_2O)_4(Hhedp)_6]_n$ and $[Ho_8(H_2O)_4(Hhedp)_6]_n$: A mixture of 0.160g of H_5hedp and 0.300g of $DyCl_3 \cdot 6H_2O$ (0.300g of $TbCl_3 \cdot 6H_2O$ or 0.300g of

$HoCl_3 \cdot 6H_2O$) in ca. 8g of distilled water was stirred to get a homogeneous solution. The reaction was carried out at 230ºC for 3 days. The treatment of the products was the same as above with **$[Y_8(H_2O)_4(Hhedp)_6]_n$**.

SC-SC Transition. All thermal treatments were performed in a programmed furnace under air. The samples were put inside a clean porcelain crucible since the temperature was below 750 ºC. To effectively compare the physical and structural properties (**Er**) of the as-synthesized, dehydrated form, intermediate phase and pyrophosphate were calcined at different temperature and kept under conditions that avoid partial or total rehydration.

The dehydrated form was obtained by calcination of the as-synthesized samples at 300ºC in air for 4 hours, and then cooled to 200ºC before removal from furnace. The calcined sample was immediately immersed in organic oil in order to protect it from the air moisture.

The intermediate phase was prepared by calcination of the as-synthesized samples at 400-500 ºC in air for 4 hours, and then cooled to 200 ºC before removal from furnace. The dry sample was immediately immersed in organic oil.

The inorganic pyrophosphate was produced by calcination of the as-synthesized samples between 600 and 700 ºC in air for 4 hours, and then cooled to 200 ºC before removal from furnace. The dry sample was immediately immersed organic oil to protect the single crystal particles from air and humidity.

All the water-free phases were then transferred to a clean glass vial and placed inside a humid environment where they stayed for 5 days to ensure full rehydration. The obtained rehydrated samples were then used for further single crystal structure determination.

The yttrium sample was calcined at 330 ºC in air for 12 hours and then cooled naturally to room temperature to get the intermediate phase and pyrophosphate was obtained via calcination around 380-480 ºC for 4 hours. After the calcination, the single crystal particles were directly exposed in the open air and did the X-ray data collection without protection with the organic oil.

Experiments for the guest exchange. The exchange of guest water with methanol for the as-synthesized sample was performed as follows: a small amount of particles was immersed in 100 ml of dehydrated methanol on the bottom of a well sealed flask with steady mechanical stirring over 24 hours at the ambient environment. The stirring was slow enough to ensure that the single crystals of **1** were not damaged. Then the single crystals were recovered and immediately immersed in organic oil. The guest exchange in the pore of the as-synthesized MOF was confirmed by single-crystal X-ray diffraction.

Elemental analysis: Calcd (%) for $[Er_8(H_2O)_4(Hhedp)_6]_n$ (**1** As-synthesized, MW = 2622.10): C 5.49, H 1.22; found: C 5.64, H 1.26. Calcd (%) for $[Er_8C_6H_6O_{36}P_{12}]_n$ (**2** Intermediate phase. If hydrated, based on the TGA data, the molecular formula need to be added with ca. 10% of water corresponding to ca. 14 water molecules, MW = 2363.83 + 252 = 2615.83): C 2.75, H 1.07; Found: C 1.58, H 1.35. The deviation from the calculated C value is due to a mixture of phases of the intermediate and inorganic phase during the 4 hours calcination at between 400ºC to 500ºC. Calcd (%) for $[Er_8O_{42}P_{12}]_n$ (Inorganic phase. If hydrated, adding ca 10% of guest water corresponding to 14 water molecules in each formula, MW = 2381.72 + 252 = 2633.72): C 0, H 1.06; Found: C 0.00, H 1.16. EDS analysis: for the Er-as synthesized sample, P : Er = 61.47 : 35.96 ≈ 1.70 : 1, is very close to the molecular formula: $[Er_4(Hhedp)_3(H_2O)_2]_n$ (where the calculated P : Er = 1.5 : 1); For the intermediate phase, P : Er = 60.83 : 39.17 = 1.55:1; For the pyrophosphate phase, P : Er =: 62.48 : 37 : 52 ≈ 1.66 : 1, is very close to the molecular formula: $[Er_4(PO_3–O–PO_3)_3]_n$ (where the calculated P : Er = 1.5 : 1). The EDS spectra of the three phases are exhibited in Figure S6.

General Characterization. FT-IR spectra were collected from KBr pellets (Aldrich 99%+, FT-IR grade) on a Mattson 7000 FT-IR spectrometer. FT-Raman spectra were measured on a Bruker RFS 100 with a Nd:YAG coherent laser (λ) 1064 nm). C, H elemental analyses were performed with a CHNS-932 Elemental analyzer in the Microanalysis Laboratory of the University of Aveiro, Department of Chemistry. TGAs were carried out using a Shimadzu TGA 50 with a heating rate of 5

°C/min in air. Scanning electron microscopy (SEM) and energy dispersive analysis of X-rays spectroscopy (EDS) were performed using a Hitachi S-4100 field emission gun tungsten filament instrument working at 25 kV. Powder X-ray diffraction patterns (PXRD) were recorded at room temperature using a Philips X'Pert instrument, operating with a monochromated Cu-K_α radiation source at 40 kV and 50 mA. Simulated powder patterns were based on single-crystal data. The variable temperature experiments performed on compound **1** were conducted on the same instrument using a high-temperature Antoon Parr HKL 16 chamber, controlled by an Antoon Parr 100 TCU unit. Intensity data were collected in the step mode (0.02°, 5 s per step) in the range ca. $6 \leq 2\theta° \leq 35$.

N_2 adsorption measurements: The adsorption of nitrogen (77 K) was monitored using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. The solid was outgassed at 473 K to a residual pressure of *ca.* 10^{-3} mbar. Dissolved air was removed from distilled-deionized water using freeze-pump-thaw cycles before use.

Single-Crystal X-ray Diffraction:

Data collection (except those of Dy compound (at 100 K) and Ho compound (at ambient condition)) was performed at 150 K. Suitable single-crystals were mounted on a glass fiber using FOMBLIN Y perfluoropolyether vacuum oil (LVAC 25/6) purchased from Aldrich. Data for compounds **1**-as synthesized, **1**-dehydrated, **1**-rehydrated, **2**-intermediate, **3**-pyrophosphate, **4**-methanol, **Tb**, **Dy**, **Ho**, **Y-as synthesized**, **Y-intermediate** and **Y-pyrophosphate** were collected on a Bruker X8 APEX-II diffractometer (Mo Kα graphite-monochromated radiation, λ = 0.7107 Å) and controlled by the APEX-II software package.[1] The device is equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely by using the software interface Cryopad.[2] Images were processed using the SAINT Plus software package.[3] Integrated data sets for all materials were corrected for absorption using the multi-scan method implemented in SADABS.[4] All structures were solved by the direct methods of SHELXS-97,[5] which allowed the location of the majority of the heaviest atoms, with the remaining non-hydrogen atoms being located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on F^2 using SHELXL-97.[6] Non-hydrogen atoms of all materials were successfully refined using anisotropic displacement

parameters. The crystal data collection and structure refinement parameters are listed in Table S1-S4, and selected bond lengths and angles are given in Table S5-S8.

Table S1: Details on Crystal Data Collection and Structure Refinement

	1-as synthesized	**1**-dehydrated (300ºC)	**1**-rehydrated
formula	$C_3H_8Er_2O_{11.5}P_3$	$C_3H_6Er_2O_{10.5}P_3$	$C_3H_8Er_2O_{11.5}P_3$
formula weight	655.52	637.51	655.52
temperature/K	150	150	150
crystal type	Colorless, prisms	Pink, prisms	Pink, prisms
crystal size/mm	0.04 x 0.04 x 0.02	0.18 x 0.15 x 0.12	0.18 x 0.18 x 0.16
crystal system	cubic	cubic	cubic
space group	$I2_13$	$I2_13$	$I2_13$
a/Å	13.4618(2)	13.4484(2)	13.52000(10)
b/Å	13.4618(2)	13.4484(2)	13.52000(10)
c/Å	13.4618(2)	13.4484(2)	13.52000(10)
α/deg	90	90	90
β/deg	90	90	90
γ/deg	90	90	90
volume/Å^3	2439.55(6)	2432.27(6)	2471.33(3)
Z	8	8	8
$\rho_{calculated}$/g cm^{-3}	3.570	3.482	3.524
μ/mm^{-1}	14.115	14.146	13.934
ϑ range/deg	3.71 to 28.75	3.71 to 40.17	3.69 to 40.16
index ranges	-18<=h<=16, -17<=k<=18, -18<=l<=18	-15<=h<=21, -22<=k<=24, -21<=l<=24	-20<=h<=24, -19<=k<=14, -22<=l<=24
collec. reflections	21211	20021	19790
indep. reflections	1056 [R(int) = 0.0537]	2564 [R(int) = 0.0251]	2476 [R(int) = 0.0307]
Data / restraints / parameters	1056 / 24 / 71	2564 / 0 / 68	2476 / 0 / 70
Goodness-of-fit on F^2	1.143	1.200	1.159
final R indices	R1 = 0.0278,	R1 = 0.0351,	R1 = 0.0318,
[$I > 2\sigma(I)$]	wR2 = 0.0677	wR2 = 0.0834	wR2 = 0.0808
final R indices	R1 = 0.0298,	R1 = 0.0374,	R1 = 0.0349,
(all data)	wR2 = 0.0683	wR2 = 0.0844	wR2 = 0.0821
largest diff. peak and hole /eÅ^3	1.228 and -2.118	1.767 and -4.054	1.966 and -3.742
Absolute structure parameter	0.02(3)	0.03(2)	0.05(2)
CCDC No.	927688	927686	948279

Table S2: Details on Crystal Data Collection and Structure Refinement

	2-intermediate	**3**-pyrophosphate(700ºC)	**4**-methanol
formula	$C_{1.5}H_{1.5}Er_2O_9P_3$	$Er_2O_{10.5}P_3$	$CH_3Er_2O_{11.5}P_3$
formula weight	590.96	595.43	626.46
temperature/K	150	150	150
crystal type	Pink, prisms	Pink, prisms	Pink, prisms
crystal size/mm	0.18 x 0.18 x 0.16	0.12 x 0.12 x 0.10	0.10 x 0.09 x 0.08
crystal system	cubic	cubic	cubic
space group	$I2_13$	$I2_13$	$I2_13$
a/Å	13.43150(10)	13.4291(3)	13.4154(2)
b/Å	13.43150(10)	13.4291(3)	13.4154(2)
c/Å	13.43150(10)	13.4291(3)	13.4154(2)
α/deg	90	90	90
β/deg	90	90	90
γ/deg	90	90	90
volume/Å^3	2423.11(3)	2421.81(9)	2414.41(6)
Z	8	8	8
$\rho_{calculated}$/g cm^{-3}	3.240	3.266	3.447
μ/mm^{-1}	14.177	14.195	14.253
ϑ range/deg	3.72 to 32.57	3.72 to 39.35	3.72 to 30.45
index ranges	-20<=h<=19, -17<=k<=20, -20<=l<=19	-22<=h<=23, -22<=k<=22, -23<=l<=23	-17<=h<=18, -15<=k<=17, -19<=l<=16
collec. reflections	17144	21818	14034
indep. reflections	1488 [R(int) = 0.0268]	2413 [R(int) = 0.0489]	1232 [R(int) = 0.0762]
Data / restraints / parameters	1488 / 6 / 48	2413 / 0 / 48	1232 / 7 / 61
Goodness-of-fit on F^2	1.215	1.071	1.143
final *R* indices	R1 = 0.0252,	R1 = 0.0242,	R1 = 0.0402,
[$I > 2\sigma(I)$]	wR2 = 0.0777	wR2 = 0.0597	wR2 = 0.0838
final *R* indices	R1 = 0.0257,	R1 = 0.0263,	R1 = 0.0828,
(all data)	wR2 = 0.0779	wR2 = 0.0605	wR2 = 0.1034
largest diff. peak and hole /eÅ^3	2.388 and -4.052	2.464 and -3.644	1.920 and -2.259
Absolute structure parameter	0.02(2)	0.013(15)	0.00(5)
CCDC No.	927690	927689	927691

Table S3: Details on Crystal Data Collection and Structure Refinement

	Tb	**Dy**	**Y**
formula	$C_3H_8O_{11.5}P_3Tb_2$	$C_3H_8Dy_2O_{11.5}P_3$	$C_3H_8O_{11.5}P_3Y_2$
formula weight	638.84	646.00	498.82
temperature/K	150	100	150
crystal type	Colorless, prisms	Colorless, prisms	Colorless, prisms
crystal size/mm	0.08 x 0.08 x 0.06	0.20 x 0.18 x 0.14	0.18 x 0.16 x 0.14
crystal system	cubic	cubic	cubic
space group	*I* 21 3	*I* 21 3	*I* 21 3
a/Å	13.61780(10)	13.5416(2)	13.4853(2)
b/Å	13.61780(10)	13.5416(2)	13.4853(2)
c/Å	13.61780(10)	13.5416(2)	13.4853(2)
α/deg	90	90	90
β/deg	90	90	90
γ/deg	90	90	90
volume/Å^3	2525.35(3)	2483.19(6)	2452.35(6)
Z	8	8	8
$\rho_{calculated}$/g cm^{-3}	3.361	3.456	2.702
μ/mm^{-1}	11.545	12.385	9.866
θ range/deg	3.66 to 36.27	2.13 to 40.08	3.02 to 27.16
index ranges	-22<=h<=19, -22<=k<=22, -21<=l<=21	-22<=h<=24, -22<=k<=23, -24<=l<=24	-17<=h<=16, -17<=k<=15, -17<=l<=15
collec. reflections	14555	34956	7856
indep. reflections	2041 [R(int) = 0.0377]	2605 [R(int) = 0.0546]	912 [R(int) = 0.0421]
Data / restraints / parameters	2041 / 0 / 70	2605 / 0 / 71	912 / 0 / 70
Goodness-of-fit on F^2	1.128	1.112	1.067
final *R* indices	R1 = 0.0244,	R1 = 0.0273,	R1 = 0.0264,
[$I > 2\sigma(I)$]	wR2 = 0.0531	wR2 = 0.0640	wR2 = 0.0620
final *R* indices	R1 = 0.0319,	R1 = 0.0298,	R1 = 0.0306,
(all data)	wR2 = 0.0555	wR2 = 0.0649	wR2 = 0.0628
largest diff. peak and hole /eÅ^3	1.097 and -1.717	1.871 and -2.219	0.468 and -0.394
Absolute structure parameter	0.010(18)	0.019(15)	0.035(11)
CCDC No.	934837	934836	934838

Table S4: Details on Crystal Data Collection and Structure Refinement

	Y-intermediate	**Y-pyrophosphate**	**Ho**
formula	$CH_{2.33}\square_{6.67}P_2Y_{1.33}$	$H_2O_{11.5}P_3Y_2$	$C_3H_8Ho_2O_{11.5}P_3$
formula weight	301.52	456.75	650.86
temperature/K	180	180	296
crystal type	Brown, blocks	Colorless, blocks	Pink, blocks
crystal size/mm	0.10 x 0.10 x 0.12	0.12 x 0.14 x 0.18	0.04 x 0.04 x 0.05
crystal system	cubic	cubic	cubic
space group	*I* 21 3	*I* 21 3	*I* 21 3
a/Å	13.5171(2)	13.3727(4)	13.5330(4)
b/Å	13.5171(2)	13.3727(4)	13.5330(4)
c/Å	13.5171(2)	13.3727(4)	13.5330(4)
α/deg	90	90	90
β/deg	90	90	90
γ/deg	90	90	90
volume/Å^3	2469.74(6)	2391.43(12)	2478.46(13)
Z	12	8	8
$\rho_{calculated}$/g cm^{-3}	2.433	2.537	3.489
μ/mm^{-1}	9.774	10.104	13.119
θ range/deg	3.69 to 32.43	3.73 to 25.27	2.13 to 30.43
index ranges	-20<=h<=20, -20<=k<=20, -17<=l<=20	-12<=h<=13, -16<=k<=8, -16<=l<=8	-9<=h<=19, -18<=k<=9, -17<=l<=16
collec. reflections	11402	2755	4801
indep. reflections	1479 [R(int) = 0.0391]	722 [R(int) = 0.0444]	1251 [R(int) = 0.0834]
Data / restraints / parameters	1479 / 0 / 52	722 / 6 / 52	1251 / 18 / 71
Goodness-of-fit on F^2	1.101	1.119	1.067
final *R* indices	R1 = 0.0462,	R1 = 0.0792,	R1 = 0.0513,
[$I > 2\sigma(I)$]	wR2 = 0.1214	wR2 = 0.1941	wR2 = 0.1022
final *R* indices	R1 = 0.0555,	R1 = 0.1021,	R1 = 0.0730,
(all data)	wR2 = 0.1264	wR2 = 0.2129	wR2 = 0.1148
largest diff. peak and hole /eÅ^3	1.141 and -1.372	1.027 and -1.504	1.689 and -1.993
Absolute structure parameter	0.007(14)	-0.04(4)	0.00(5)
CCDC No.	927687	948280	948281

Table S5. Selected bond lengths [Å] and angles [°] for the compounds **1**-as synthesized, **1**-dehydrated and **1**-rehydrated.

1-as synthesized		**1**-dehydrated(300ºC)		**1**-rehydrated	
Er(1)-O(3)#1	2.156(6)	Er(1)-O(3)#1	2.152(4)	Er(1)-O(3)#1	2.172(4)
Er(1)-O(3)#2	2.156(6)	Er(1)-O(3)#2	2.152(4)	Er(1)-O(3)#2	2.172(4)
Er(1)-O(3)#3	2.156(6)	Er(1)-O(3)	2.152(4)	Er(1)-O(3)	2.172(4)
Er(1)-O(1)	2.303(6)	Er(1)-O(1)#1	2.301(4)	Er(1)-O(1)#2	2.310(4)
Er(1)-O(1)#4	2.303(6)	Er(1)-O(1)	2.301(4)	Er(1)-O(1)#1	2.310(4)
Er(1)-O(1)#5	2.303(6)	Er(1)-O(1)#2	2.301(4)	Er(1)-O(1)	2.310(4)
Er(1)-Er(2)	3.4786(9)	Er(1)-Er(2)	3.4265(6)	Er(1)-Er(2)	3.4981(5)
Er(2)-O(2)#4	2.202(7)	Er(2)-O(2)#1	2.171(5)	Er(2)-O(2)	2.218(5)
Er(2)-O(2)#5	2.202(7)	Er(2)-O(2)#2	2.171(5)	Er(2)-O(2)#1	2.218(5)
Er(2)-O(2)	2.202(7)	Er(2)-O(2)	2.171(5)	Er(2)-O(2)#2	2.218(5)
Er(2)-O(5)	2.397(15)	Er(2)-O(1)	2.371(4)	Er(2)-O(5)	2.385(10)
Er(2)-O(1)#4	2.414(6)	Er(2)-O(1)#1	2.371(4)	Er(2)-O(1)#2	2.407(4)
Er(2)-O(1)#5	2.414(6)	Er(2)-O(1)#2	2.371(4)	Er(2)-O(1)#1	2.407(4)
Er(2)-O(1)	2.414(6)	P(1)-O(3)#6	1.498(4)	Er(2)-O(1)	2.407(4)
P(1)-O(3)	1.511(6)	P(1)-O(2)#5	1.511(6)	P(1)-O(3)#3	1.503(4)
P(1)-O(1)#6	1.521(6)	P(1)-O(1)	1.545(4)	P(1)-O(1)	1.527(4)
P(1)-O(2)	1.520(7)	P(1)-C(1)	1.805(6)	P(1)-O(2)#4	1.528(5)
P(1)-C(1)	1.826(8)	O(3)#2-Er(1)-O(1)	86.54(16)	P(1)-C(1)	1.793(5)
O(3)#1-Er(1)-O(1)	88.2(2)	O(3)#1-Er(1)-O(1)	105.35(17)	O(3)#2-Er(1)-O(1)	106.35(16)
O(3)#2-Er(1)-O(1)	160.9(2)	O(3)-Er(1)-O(1)	159.50(18)	O(3)-Er(1)-O(1)	159.40(17)
O(3)#3-Er(1)-O(1)	107.1(2)	O(1)#1-Er(1)-O(1)	73.40(16)	O(3)#1-Er(1)-O(1)	87.23(15)
O(1)-Er(1)-O(1)#4	73.6(2)	O(3)-Er(1)-Er(2)	121.71(12)	O(1)#1-Er(1)-O(1)	72.73(15)
O(3)#1-Er(1)-Er(2)	123.88(17)	O(1)-Er(1)-Er(2)	43.64(10)	O(3)-Er(1)-Er(2)	122.32(11)
O(1)-Er(1)-Er(2)	43.74(15)	O(2)#1-Er(2)-O(1)	90.4(3)	O(1)-Er(1)-Er(2)	43.21(9)
O(2)#4-Er(2)-O(1)	143.9(2)	O(2)-Er(2)-O(1)	80.26(16)	O(2)#2-Er(2)-O(1)	85.0(2)
O(2)#5-Er(2)-O(1)	85.3(3)	O(2)#2-Er(2)-O(1)	149.35(17)	O(2)-Er(2)-O(1)	78.97(15)
O(2)-Er(2)-O(1)	77.5(2)	O(1)-Er(2)-O(1)#1	70.88(15)	O(2)#1-Er(2)-O(1)	144.52(17)
O(5)-Er(2)-O(1)	138.73(14)	O(1)-Er(2)-O(4B)#3	128.6(3)	O(5)-Er(2)-O(1)	138.92(9)
P(1)#6-O(1)-Er(1)	132.0(4)	P(1)-O(1)-Er(1)	133.8(3)	P(1)-O(1)-Er(1)	131.9(2)
P(1)#6-O(1)-Er(2)	133.0(3)	P(1)-O(1)-Er(2)	131.9(2)	P(1)-O(1)-Er(2)	132.3(2)
Er(1)-O(1)-Er(2)	95.0(2)	Er(1)-O(1)-Er(2)	94.33(14)	Er(1)-O(1)-Er(2)	95.71(13)

Symmetry transformations used to generate equivalent atoms:

1-as synthesized: #1 -x+1,y-1/2,-z+3/2; #2 -y+3/2,-z+1,x+1/2; #3 z,x,y; #4 -z+3/2,-x+1,y+1/2; #5 -y+1,z-1/2,-x+3/2; #6 x+0,-y+1,-z+3/2.

1-dehydrated: #1 -z+3/2,-x+1,y+1/2; #2 -y+1,z-1/2,-x+3/2; #3 z-1/2,x-1/2,y+1/2; #4 -y+1,-z+3/2,x+0; #5 -x+3/2,y+0,-z+2; #6 y+0,-z+1,-x+3/2.

1-rehydrated: #1 -z+1/2,-x+1,y-1/2; #2 -y+1,z+1/2,-x+1/2; #3 z+1/2,x+1/2,y-1/2; #4 x+0,-y+1,-z+1/2.

Table S6. Selected bond lengths [Å] and angles [°] for the compounds **2**-intermediate, **3**-pyrophosphate and **4**-methanol.

2-intermediate		**3**-pyrophosphate		**4**-methanol	
Er(1)-O(3)#1	2.161(5)	Er(1)-O(3)#1	2.170(3)	Er(1)-O(4)#1	2.195(10)
Er(1)-O(3)#2	2.161(5)	Er(1)-O(3)#2	2.170(3)	Er(1)-O(4)#2	2.195(10)
Er(1)-O(3)	2.161(5)	Er(1)-O(3)	2.170(3)	Er(1)-O(4)#3	2.195(10)
Er(1)-O(1)	2.318(5)	Er(1)-O(1)	2.339(3)	Er(1)-O(1)	2.314(9)
Er(1)-O(1)#1	2.318(5)	Er(1)-O(1)#1	2.339(3)	Er(1)-O(1)#4	2.314(9)
Er(1)-O(1)#2	2.318(5)	Er(1)-O(1)#2	2.339(3)	Er(1)-O(1)#5	2.314(9)
Er(1)-Er(2)	3.4499(6)	Er(1)-Er(2)	3.4775(4)	Er(1)-Er(2)	3.5666(14)
Er(2)-O(2)	2.178(4)	Er(2)-O(2)	2.155(3)	Er(2)-O(2)#6	2.197(10)
Er(2)-O(2)#1	2.178(4)	Er(2)-O(2)#1	2.155(3)	Er(2)-O(2)#7	2.197(10)
Er(2)-O(2)#2	2.178(4)	Er(2)-O(2)#2	2.155(3)	Er(2)-O(2)#8	2.197(10)
Er(2)-O(1)	2.340(4)	Er(2)-O(1)	2.332(3)	Er(2)-O(1M)	2.356(19)
Er(2)-O(1)#1	2.340(4)	Er(2)-O(1)#1	2.332(3)	Er(2)-O(1)	2.414(9)
Er(2)-O(1)#2	2.340(4)	Er(2)-O(1)#2	2.332(3)	Er(2)-O(1)#5	2.414(9)
P(1)-O(3)#3	1.492(5)	P(1)-O(3)#3	1.498(3)	Er(2)-O(1)#4	2.414(9)
P(1)-O(2)#4	1.513(5)	P(1)-O(2)#4	1.507(3)	P(1)-O(4)	1.477(10)
P(1)-O(1)	1.552(4)	P(1)-O(1)	1.545(3)	P(1)-O(2)	1.513(10)
P(1)-C(1)	1.661(4)	P(1)-O(4)	1.615(2)	P(1)-O(1)	1.522(9)
O(3)#1-Er(1)-O(1)	159.03(18)	O(3)#2-Er(1)-O(1)	152.73(10)	P(1)-O(3)	1.609(7)
O(3)#2-Er(1)-O(1)	102.91(16)	O(3)-Er(1)-O(1)	83.55(10)	O(4)#1-Er(1)-O(1)	105.0(3)
O(3)-Er(1)-O(1)	87.50(18)	O(3)#1-Er(1)-O(1)	93.33(11)	O(4)#2-Er(1)-O(1)	90.8(3)
O(1)-Er(1)-O(1)#1	71.54(17)	O(1)-Er(1)-O(1)#1	70.52(11)	O(4)#3-Er(1)-O(1)	161.7(3)
O(3)-Er(1)-Er(2)	120.20(12)	O(3)-Er(1)-Er(2)	111.92(8)	O(4)#1-Er(1)-Er(2)	123.3(2)
O(1)-Er(1)-Er(2)	42.45(11)	O(1)-Er(1)-Er(2)	41.81(7)	O(1)-Er(1)-Er(2)	42.1(2)
O(2)#2-Er(2)-O(1)	83.27(16)	O(2)#1-Er(2)-O(1)	88.18(11)	O(2)#6-Er(2)-O(1M)	75.2(2)
O(2)#1-Er(2)-O(1)	152.38(16)	O(2)-Er(2)-O(1)	100.87(10)	O(2)#6-Er(2)-O(1)	86.1(3)
O(2)-Er(2)-O(1)	92.27(17)	O(2)#2-Er(2)-O(1)	158.84(11)	O(2)#7-Er(2)-O(1)	80.9(3)
O(1)-Er(2)-O(1)#1	70.77(18)	O(1)-Er(2)-O(1)#1	70.77(11)	O(2)#8-Er(2)-O(1)	144.6(3)
P(1)-O(1)-Er(1)	136.1(3)	P(1)-O(1)-Er(1)	126.91(17)	O(1M)-Er(2)-O(1)	140.0(2)
P(1)-O(1)-Er(2)	128.3(3)	P(1)-O(1)-Er(2)	136.86(17)	O(1)-Er(2)-Er(1)	40.0(2)
Er(1)-O(1)-Er(2)	95.59(15)	Er(1)-O(1)-Er(2)	96.23(10)	Er(1)-O(1)-Er(2)	97.9(3)

Symmetry transformations used to generate equivalent atoms:
2-intermediate: #1 -z+1/2,-x+1,y-1/2; #2 -y+1,z+1/2,-x+1/2; #3 -x+1/2,y+0,-z+0; #4 -y+1,-z+1/2,x+0.
3-pyrophosphate: #1 y+1/2,-z+1/2,-x+1; #2 -z+1,x-1/2,-y+1/2; #3 y+1/2,z+1/2,x-1/2; #4 -x+3/2,y+0,-z+0.
4-methanol: #1 z-1/2,x+1/2,y+1/2, #2 x+0,-y+1,-z+3/2, #3 -y+1/2,z+0,-x+1, #4 y-1/2,-z+3/2,-x+1, #5 -z+1,x+1/2,-y+3/2, #6 y-1/2,z-1/2,x+1/2, #7 -x+1/2,y+0,-z+2, #8 z-1,-x+1,-y+3/2.

Table S7. Selected bond lengths [Å] and angles [°] for the **Tb**, **Dy** and **Y** cubic diphosphonates.

Tb		**Dy**		**Y**	
Tb(1)-O(3)#1	2.196(3)	Dy(1)-O(3)#1	2.178(3)	Y(1)-O(3)#1	2.173(3)
Tb(1)-O(3)#2	2.196(3)	Dy(1)-O(3)#2	2.178(3)	Y(1)-O(3)#2	2.173(3)
Tb(1)-O(3)	2.196(3)	Dy(1)-O(3)	2.178(3)	Y(1)-O(3)	2.173(3)
Tb(1)-O(1)	2.343(3)	Dy(1)-O(1)#1	2.324(3)	Y(1)-O(1)#1	2.299(3)
Tb(1)-O(1)#1	2.343(3)	Dy(1)-O(1)	2.324(3)	Y(1)-O(1)	2.299(3)
Tb(1)-O(1)#2	2.343(3)	Dy(1)-O(1)#2	2.324(3)	Y(1)-O(1)#2	2.299(3)
Tb(1)-Tb(2)	3.5463(4)	Dy(1)-Dy(2)	3.5199(4)	Y(1)-Y(2)	3.4919(10)
Tb(2)-O(2)#2	2.252(4)	Dy(2)-O(2)	2.227(3)	Y(2)-O(2)#3	2.227(4)
Tb(2)-O(2)#1	2.251(4)	Dy(2)-O(2)#1	2.227(3)	Y(2)-O(2)#4	2.227(4)
Tb(2)-O(2)	2.252(4)	Dy(2)-O(2)#2	2.227(3)	Y(2)-O(2)#5	2.227(4)
Tb(2)-O(5)	2.439(8)	Dy(2)-O(5)	2.416(8)	Y(2)-O(5)	2.401(7)
Tb(2)-O(1)#1	2.449(3)	Dy(2)-O(1)#2	2.428(3)	Y(2)-O(1)	2.411(3)
Tb(2)-O(1)	2.449(3)	Dy(2)-O(1)#1	2.428(3)	Y(2)-O(1)#1	2.411(3)
Tb(2)-O(1)#2	2.449(3)	Dy(2)-O(1)	2.428(3)	Y(2)-O(1)#2	2.411(3)
P(1)-O(3)#3	1.510(3)	P(1)-O(3)#3	1.509(3)	P(1)-O(2)	1.492(4)
P(1)-O(2)#4	1.516(4)	P(1)-O(2)#4	1.519(4)	P(1)-O(3)#6	1.494(3)
P(1)-O(1)	1.525(3)	P(1)-O(1)	1.524(3)	P(1)-O(1)	1.530(3)
P(1)-C(1)	1.818(4)	P(1)-C(1)	1.804(4)	P(1)-C(1)	1.815(5)
O(3)#2-Tb(1)-O(1)	159.80(13)	O(3)#1-Dy(1)-O(1)	87.66(10)	O(3)#1-Y(1)-O(1)	87.79(12)
O(3)#1-Tb(1)-O(1)	87.43(11)	O(3)#2-Dy(1)-O(1)	106.77(11)	O(3)#2-Y(1)-O(1)	106.54(12)
O(3)-Tb(1)-O(1)	106.72(12)	O(3)-Dy(1)-O(1)	159.94(12)	O(3)-Y(1)-O(1)	160.20(12)
O(1)-Tb(1)-O(1)#1	73.07(11)	O(1)-Dy(1)-O(1)#1	72.96(10)	O(1)#1-Y(1)-O(1)	73.04(13)
O(3)-Tb(1)-Tb(2)	122.83(8)	O(3)-Dy(1)-Dy(2)	122.97(7)	O(3)-Y(1)-Y(2)	122.99(8)
O(1)-Tb(1)-Tb(2)	43.42(7)	O(1)-Dy(1)-Dy(2)	43.36(7)	O(1)-Y(1)-Y(2)	43.40(8)
O(2)#1-Tb(2)-O(1)	77.84(12)	O(2)#2-Dy(2)-O(1)	84.54(16)	O(2)#3-Y(2)-O(1)	143.55(12)
O(2)#2-Tb(2)-O(1)	84.19(16)	O(2)-Dy(2)-O(1)	78.09(11)	O(2)#4-Y(2)-O(1)	85.42(13)
O(2)-Tb(2)-O(1)	143.35(13)	O(2)#1-Dy(2)-O(1)	143.64(12)	O(2)#5-Y(2)-O(1)	77.75(12)
P(1)-O(1)-Tb(1)	132.11(18)	P(1)-O(1)-Dy(1)	131.85(16)	P(1)-O(1)-Y(1)	131.89(18)
P(1)-O(1)-Tb(2)	132.34(18)	P(1)-O(1)-Dy(2)	132.53(16)	P(1)-O(1)-Y(2)	132.41(18)
Tb(1)-O(1)-Tb(2)	95.46(10)	Dy(1)-O(1)-Dy(2)	95.56(9)	Y(1)-O(1)-Y(2)	95.67(12)

Symmetry transformations used to generate equivalent atoms:

Tb: #1 y+1/2,-z+1/2,-x+1; #2 -z+1,x-1/2,-y+1/2; #3 -y+1,-z+1/2,x-1; #4 -y+3/2,z+0,-x+1.

Dy: #1 -z+3/2,-x+1,y+1/2; #2 -y+1,z-1/2,-x+3/2; #3 z-1/2,x-1/2,y+1/2; #4 x+0,-y+1,-z+3/2.

Y: #1 y+1/2,-z+1/2,-x+1; #2 -z+1,x-1/2,-y+1/2; #3 -y+1,-z+1/2,x-1; #4 -z+1,-x+3/2,y+0; #5 -x+2,-y+1/2,z+0; #6 y+1/2,z+1/2,x-1/2.

Table S8. Selected bond lengths [Å] and angles [°] for the **Y-intermediate**, **Y-pyrophosphate** and **Ho** cubic compounds.

Y-intermediate		**Y-pyrophosphate**		**Ho**	
Y(1)-O(3)#1	2.186(5)	Y(1)-O(3)#1	2.128(15)	Ho(1)-O(3)#1	2.182(10)
Y(1)-O(3)#2	2.186(5)	Y(1)-O(3)#2	2.128(15)	Ho(1)-O(3)#2	2.182(10)
Y(1)-O(3)	2.186(5)	Y(1)-O(3)	2.128(15)	Ho(1)-O(3)	2.182(10)
Y(1)-O(1)	2.308(4)	Y(1)-O(1)	2.296(12)	Ho(1)-O(1)	2.306(10)
Y(1)-O(1)#1	2.308(4)	Y(1)-O(1)#1	2.296(12)	Ho(1)-O(1)#4	2.306(10)
Y(1)-O(1)#2	2.308(4)	Y(1)-O(1)#2	2.296(12)	Ho(1)-O(1)#5	2.306(10)
Y(1)-Y(2)	3.5351(13)	Y(1)-Y(2)	3.597(5)	Ho(1)-Ho(2)	3.5000(16)
Y(2)-O(2)	2.224(5)	Y(2)-O(5)	2.267(16)	Ho(2)-O(2)	2.220(12)
Y(2)-O(2)#1	2.224(5)	Y(2)-O(2)#5	2.35(2)	Ho(2)-O(2)#1	2.220(12)
Y(2)-O(2)#2	2.224(5)	Y(2)-O(2)#3	2.35(2)	Ho(2)-O(2)#2	2.220(12)
Y(2)-O(4)	2.386(12)	Y(2)-O(2)#4	2.35(2)	Ho(2)-O(5)	2.34(2)
Y(2)-O(1)	2.415(4)	Y(2)-O(1)	2.492(16)	Ho(2)-O(1)#1	2.431(10)
Y(2)-O(1)#1	2.415(4)	Y(2)-O(1)#1	2.492(16)	Ho(2)-O(1)#2	2.431(10)
Y(2)-O(1)#2	2.415(4)	Y(2)-O(1)#2	2.492(16)	Ho(2)-O(1)	2.431(10)
P(1)-O(3)#3	1.486(4)	P(1)-O(2)	1.444(18)	P(1)-O(3)#3	1.485(10)
P(1)-O(2)#4	1.500(5)	P(1)-O(3)#4	1.477(14)	P(1)-O(1)	1.527(10)
P(1)-O(1)	1.537(4)	P(1)-O(1)	1.508(13)	P(1)-O(2)#4	1.567(12)
P(1)-C(1)	1.694(5)	P(1)-O(4)	1.615(9)	P(1)-C(1)#4	1.834(12)
O(3)#1-Y(1)-O(1)	88.25(17)	O(3)#2-Y(1)-O(1)	89.4(6)	O(3)-Ho(1)-O(1)	160.7(4)
O(3)#2-Y(1)-O(1)	159.91(18)	O(3)-Y(1)-O(1)	101.8(6)	O(3)#1-Ho(1)-O(1)	106.6(4)
O(3)-Y(1)-O(1)	105.66(16)	O(3)#1-Y(1)-O(1)	162.4(6)	O(3)#2-Ho(1)-O(1)	87.8(4)
O(1)-Y(1)-O(1)#1	71.95(17)	O(1)#1-Y(1)-O(1)	73.0(6)	O(1)-Ho(1)-O(1)#1	73.6(4)
O(3)-Y(1)-Y(2)	122.32(12)	O(3)-Y(1)-Y(2)	121.8(4)	O(3)-Ho(1)-Ho(2)	123.4(3)
O(1)-Y(1)-Y(2)	42.71(11)	O(1)-Y(1)-Y(2)	43.4(4)	O(1)-Ho(1)-Ho(2)	43.8(2)
O(2)#2-Y(2)-O(1)	144.39(16)	O(2)#3-Y(2)-O(1)	146.1(5)	O(2)#2-Ho(2)-O(1)	78.8(4)
O(2)#1-Y(2)-O(1)	85.52(18)	O(2)#4-Y(2)-O(1)	88.7(6)	O(2)#1-Ho(2)-O(1)	144.1(4)
O(2)-Y(2)-O(1)	80.01(15)	O(2)#5-Y(2)-O(1)	82.8(5)	O(2)-Ho(2)-O(1)	84.8(4)
P(1)-O(1)-Y(1)	133.9(3)	P(1)-O(1)-Y(1)	137.7(10)	P(1)-O(1)-Ho(1)	133.0(6)
P(1)-O(1)-Y(2)	129.0(2)	P(1)-O(1)-Y(2)	124.9(8)	P(1)-O(1)-Ho(2)	131.7(6)
Y(1)-O(1)-Y(2)	96.89(14)	Y(1)-O(3)-Y(2)	97.3(5)	Ho(1)-O(1)-Ho(2)	95.2(3)

Symmetry transformations used to generate equivalent atoms:

***Y-intermediate**:* #1 y-1/2,-z+3/2,-x+1; #2 -z+1,x+1/2,-y+3/2; #3 -y+1,-z+3/2,x+1; #4 -x+0,-y+3/2,z+0.

***Y-pyrophosphate**:* #1 y-1/2,-z+3/2,-x+1; #2 -z+1,x+1/2,-y+3/2; #3 y-1/2,z-1/2,x+1/2; #4 z-1,-x+1,-y+3/2; #5 -x+1/2,y+0,-z+2.

***Ho**:* #1 -y+1,z-1/2,-x+3/2; #2 -z+3/2,-x+1,y+1/2; #3 -z+3/2,x+0,-y+1; #4 z+0,-x+1,-y+3/2.

General characterization

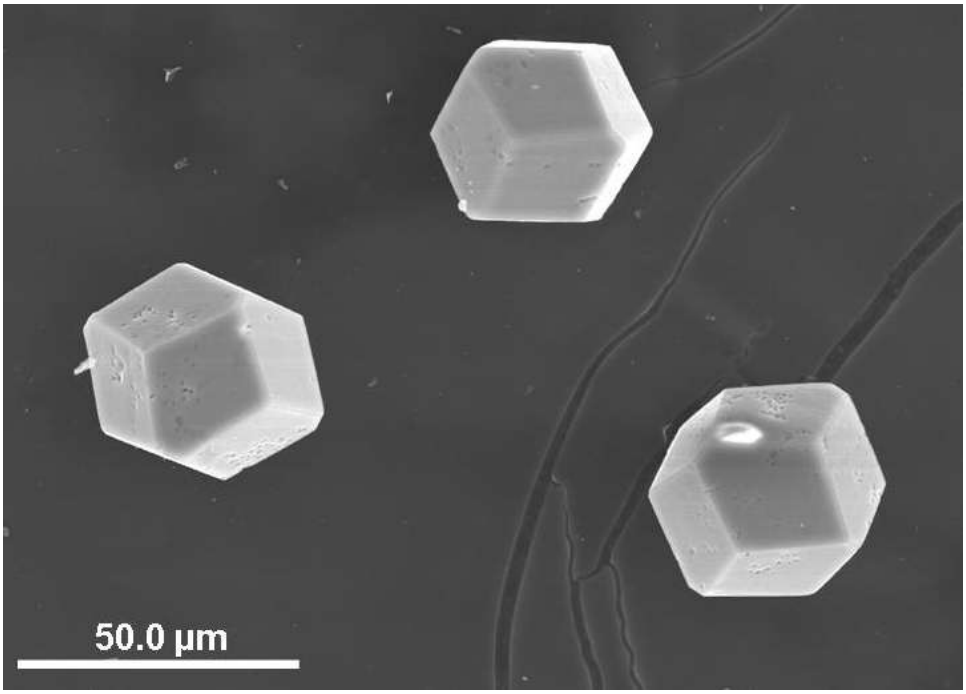


Fig. S1 SEM image of the typical crystals of MOF **1** (Er-as synthesized).

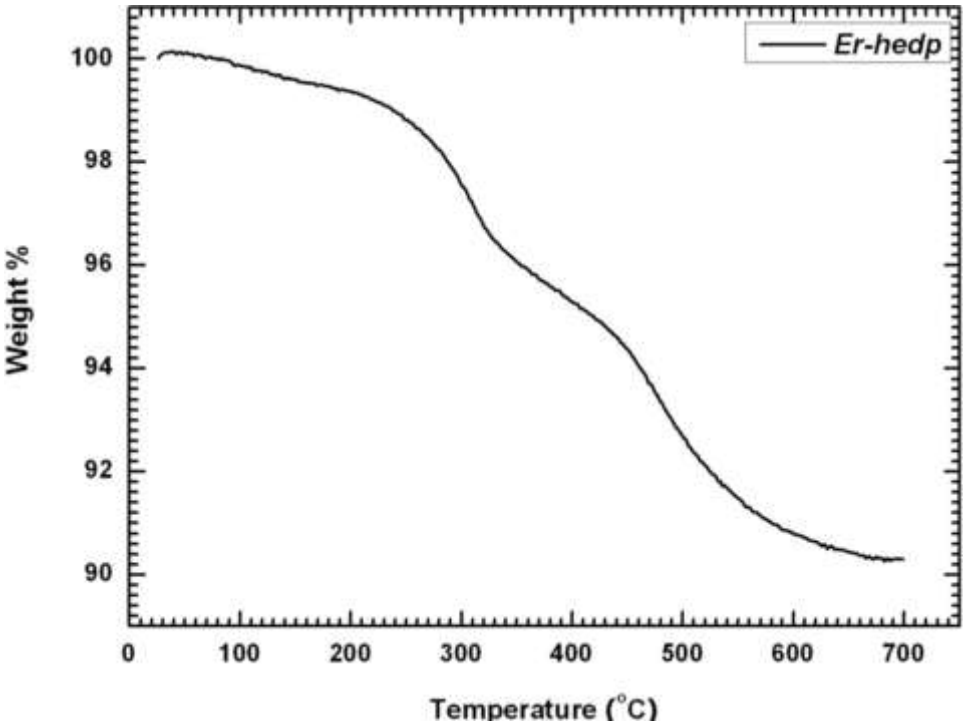


Fig. S2 TGA plot of the as synthesized MOF **1** in air.

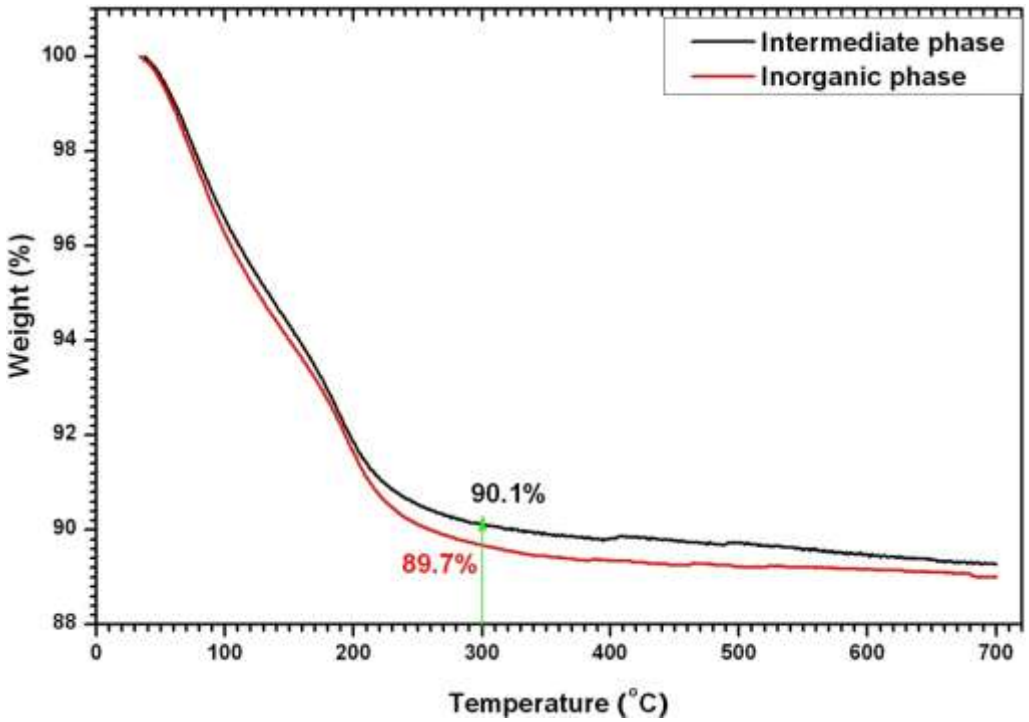


Fig. S3 TG plots of the intermediate phase **2** and the inorganic phase **3** which were calcined at 400 ºC (black curve) and 700 ºC (red curve) and then rehydrated at room temperature in wet environment, respectively. Both materials re-absorb up to 10% of water. The de-sorption and re-sorption processes are reversible.

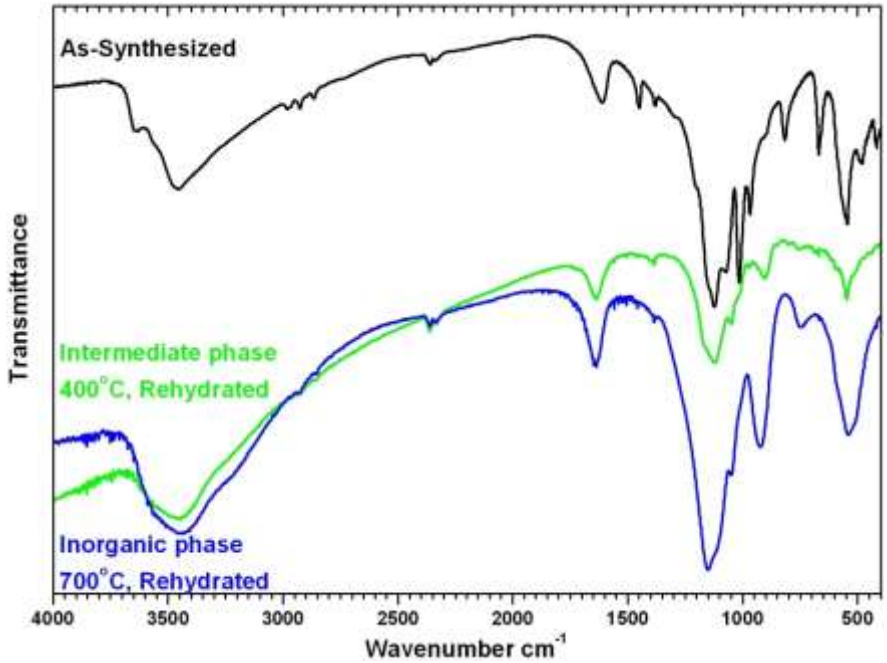


Fig. S4 FT-IR spectra of the as-synthesized **1**, intermediate phase **2** (400 ºC calcined) and inorganic phase **3** (700 ºC calcined), rehydrated at room temperature in wet environment, respectively.

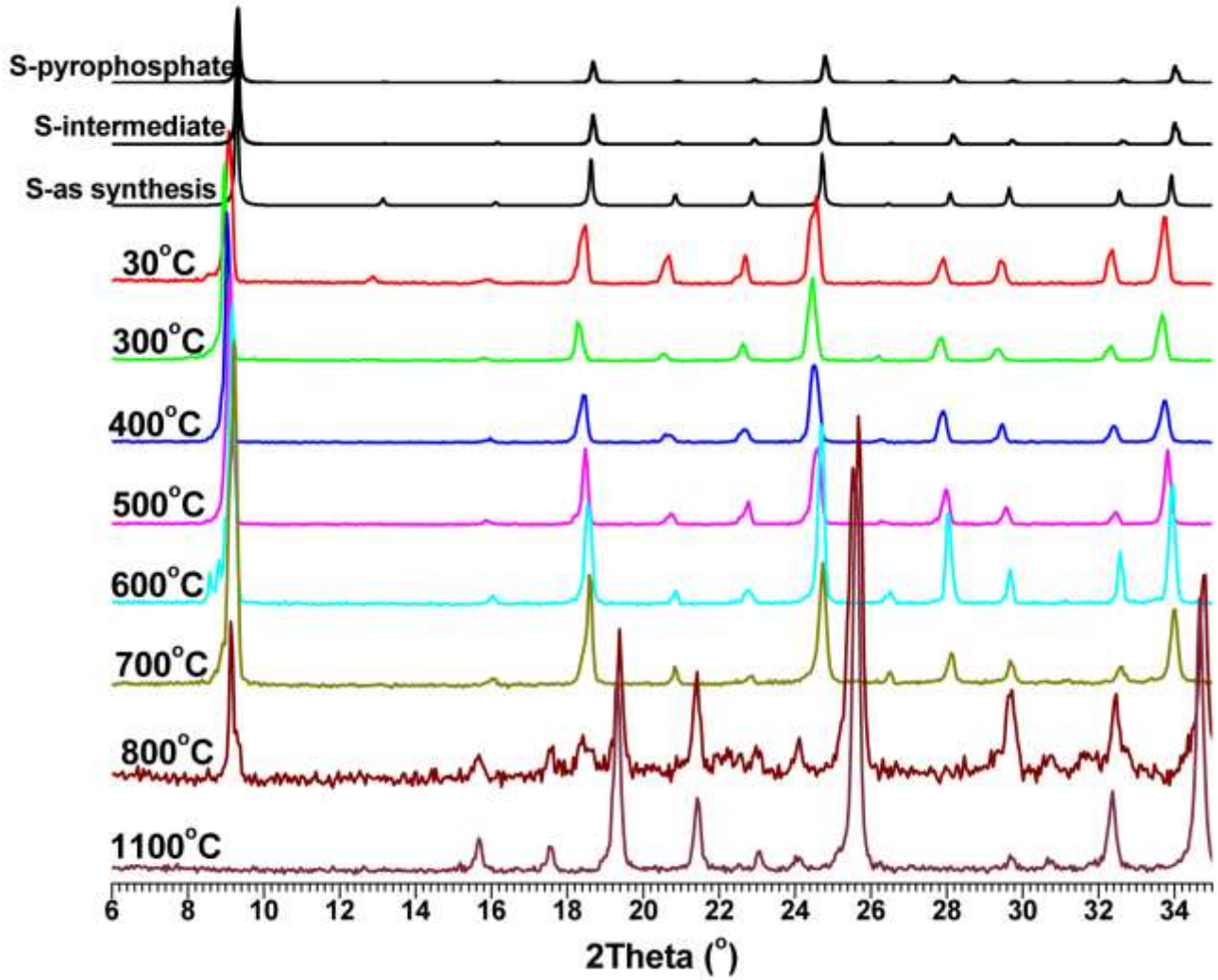
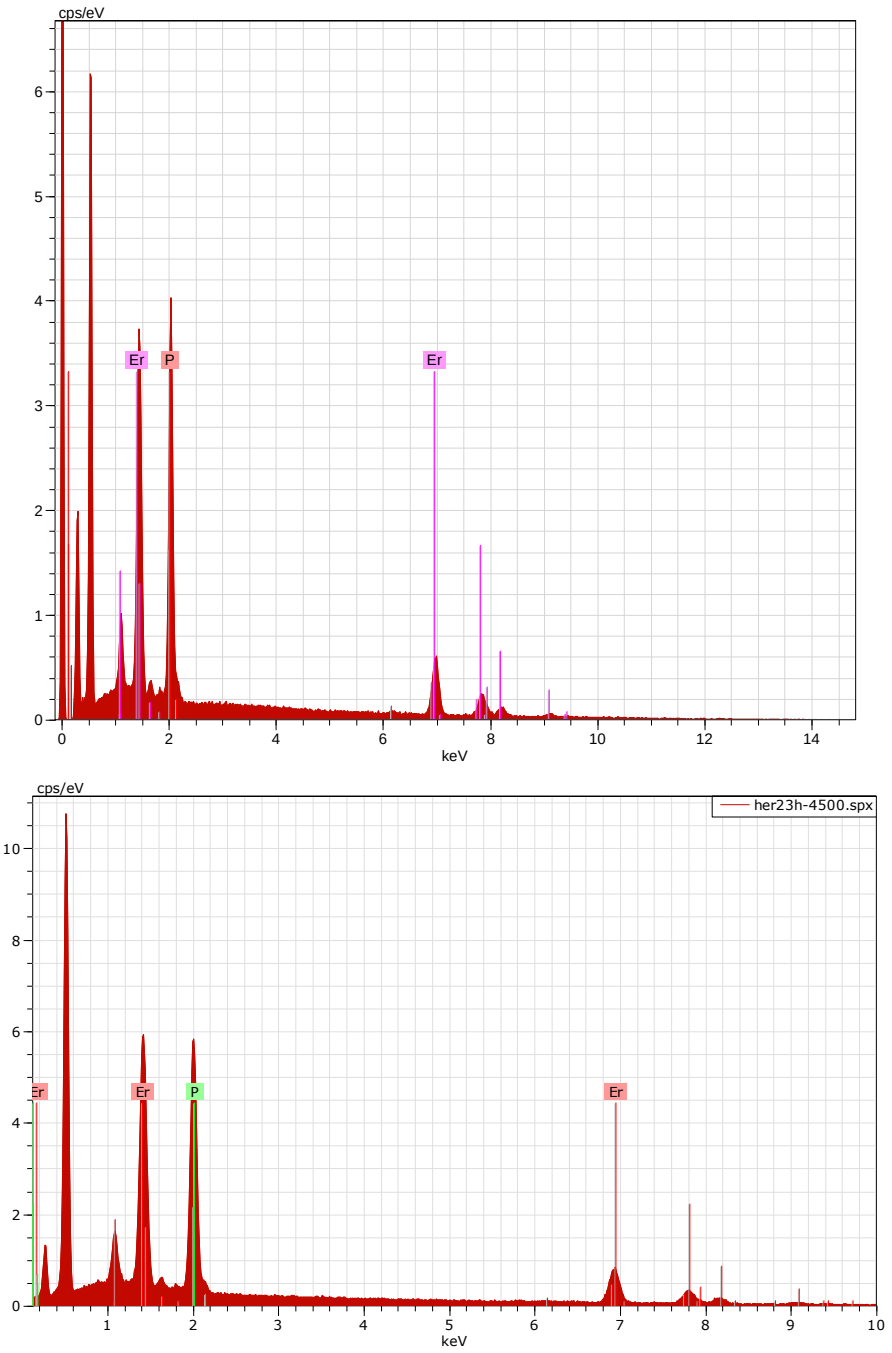


Fig. S5 In situ Powder X-ray patterns of **1** (as synthesized) and the simulated ones (S-as synthesis, S-intermediate and S-pyrophosphate) from the single crystal data of **1** confirm the bulk phase purity and show the cubic phase destroyed at 800ºC.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Er
P
Er
keV
cps/eV
her23h-4500.spx
Er
Er
P
Er
keV

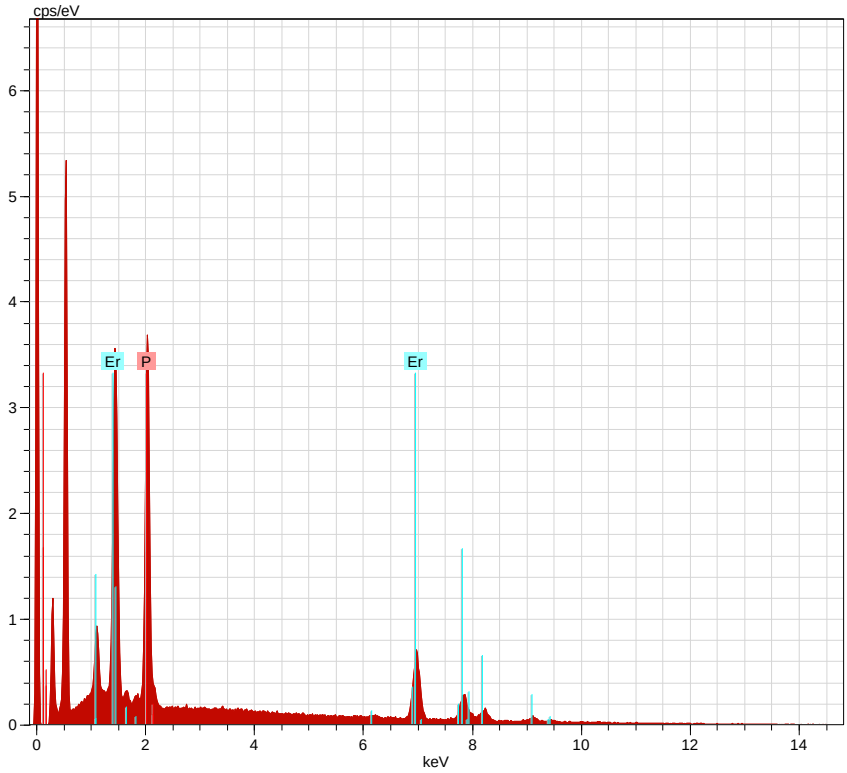


Fig. S6 EDS spectra of **(*Top*)** the as-synthesized sample **1**, **(*Middle*)** the intermediate **2** and **(*Bottom*)** erbium pyrophosphate **3**.

Adsorption results on Pyrophosphates

a) Nitrogen adsorption at 77K

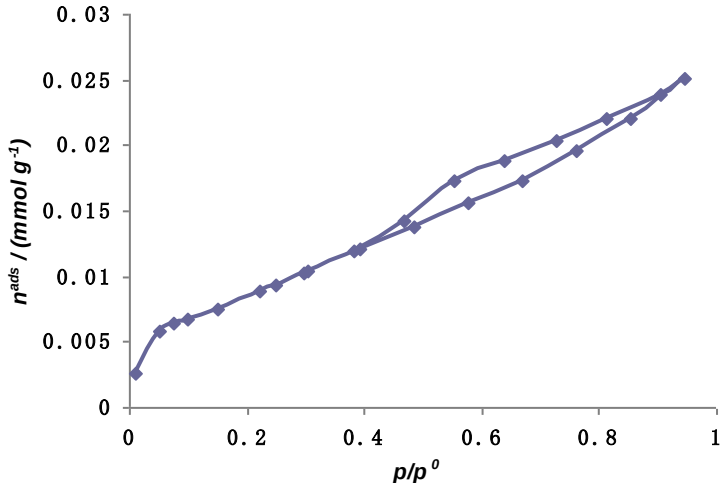


Fig. S7 N_2 adsorption at 77K on the inorganic phase **3**

The adsorbed amounts are small. The surface area calculated using the BET equation is *ca.* 22 $m^2 g^{-1}$. The external surface, estimated by the t-plot method, is about the same value. This means that the adsorption of N_2 is mainly due to the external surface of the sample, which also agrees with the

shape of the isotherm (Type II isotherm). We may then conclude that the sample does not have a significant amount of pores accessible to the N_2 molecule.

b) Water adsorption

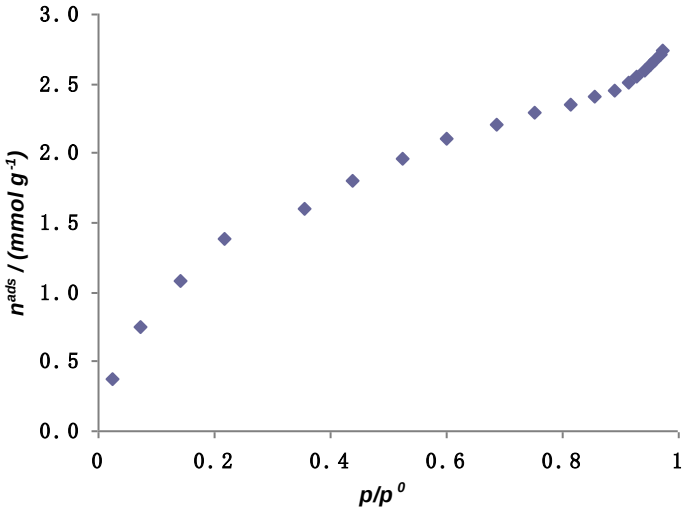
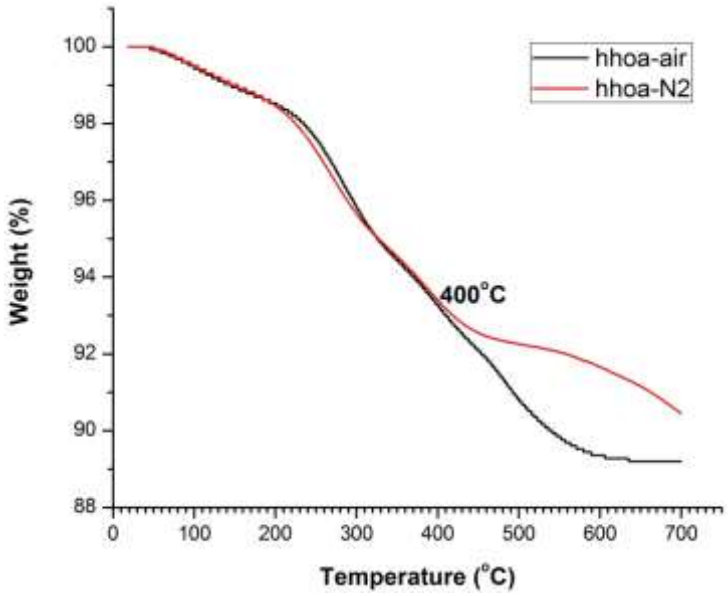


Fig. S8 water adsorption at room temperature on the inorganic phase **3**

The sample adsorbs a considerable amount of water, especially taking into account the results obtained for N_2, CO_2 and CH_4. We estimate a porous volume between 0.04 and 0.05 $cm^3\ g^{-1}$ based on the value of the inflection at 0.8 *p/p0* and assuming the density of liquid water. This is clearly higher than obtained from N_2 adsorption (about 0.025 $cm^3\ g^{-1}$ at 0.95 *p/p0*). This means that there are permanent pores on the material and they must be smaller than N_2 size but still accessible to H_2O.



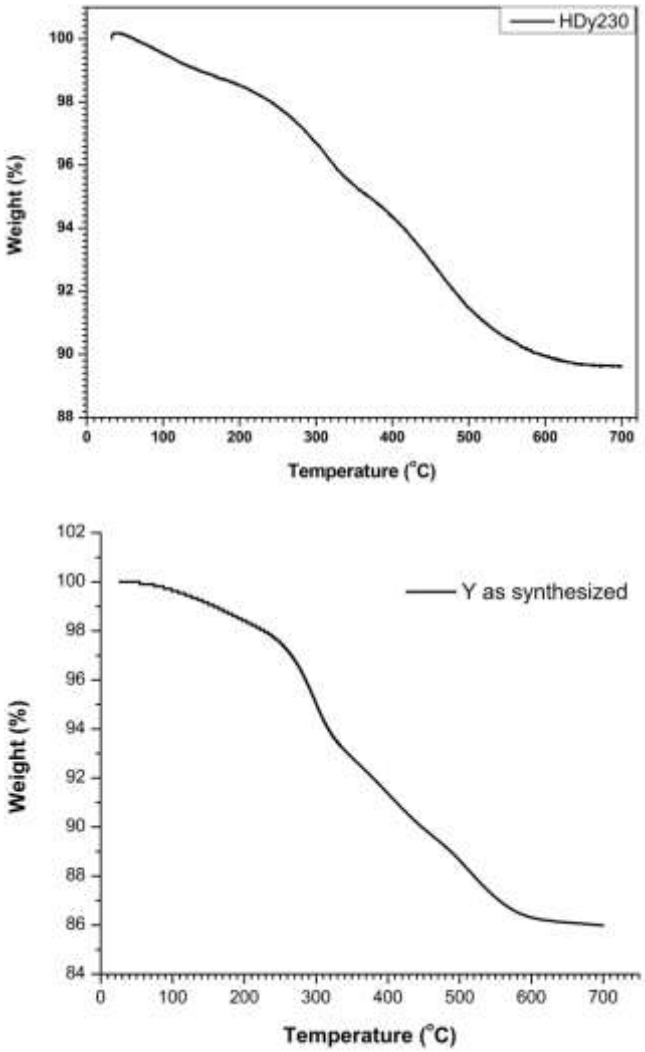


Figure S9. TGA curves of the Y (in air, Bottom), Dy (in air, Middle) and Ho (both in air and nitrogen inert atmosphere, Top) show the similar thermal behaviours as that of the Er MOF.

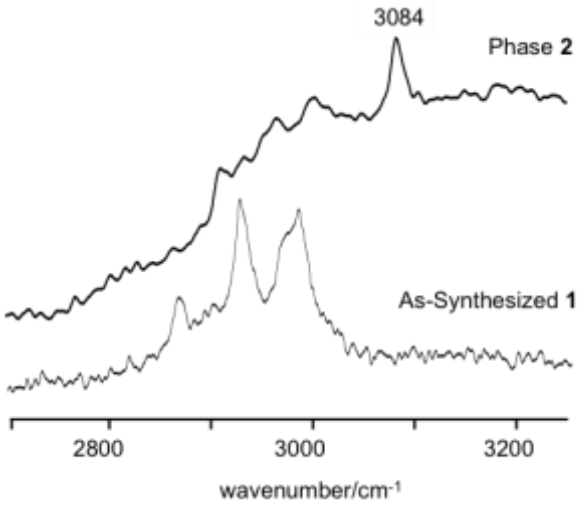


Figure S10. Selected region of FT-Raman spectra of as-synthesized **1** and intermediate phase **2**.

Additional References

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(4) Sheldrick, G. M. SADABS v. 2.01, Bruker/Siemens Area Detector Absorption Correction Program **1998**, Bruker AXS, Madison, Wisconsin, USA.
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(6) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Solution, University of Göttingen **1997**.