## A proton-conductive lanthanide oxalatophosphonate framework

## featuring unique chemical stability: stabilities of bulk phase and

## surface structure

Xiaoqiang Liang, <sup>b‡</sup> Kun Cai, <sup>c‡</sup> Feng Zhang, <sup>d‡</sup> Jia Liu, <sup>c</sup> and Guangshan Zhu <sup>a,e</sup>\*

<sup>a</sup> Key Laboratory of Polyoxometalate Science of the Ministry of Education, Faculty of Chemistry,

Northeast Normal University, Changchun, 130024, P. R. China; E-mail: zhugs100@nenu.edu.cn

<sup>b</sup> College of Environmental and Chemical Engineering, Xi'an Polytechnic University, Xi'an 710048, PR China

<sup>c</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

<sup>d</sup> College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin, Heilongjiang 150025, PR China

<sup>e</sup> College of Chemistry and Chemical Engineering, Xuchang University, Xuchang, Henan 461000, PR China

<sup>‡</sup> These authors contributed equally to this work.

## SUPPLEMENTARY INFORMATION

	Ţ	OF 1	
$\mathbf{E}_{r}(1) = O(16_{0})$	1 2 256(7)	$\Delta \Gamma I$ $F_r(1) = O(4h)$	2 222(6)
$E_{1}(1) = O(16a)$	2.230(7)	EI(1) = O(4b)	2.332(0)
$E_{1}(1) = O(3)$	2.303(7)	EI(1) = O(10) $E_{r}(1) = O(2W)$	2.379(6) 2.404(5)
Er(1) = O(1W)	2.390(7)	EI(1) = O(3W)	2.404(3)
Er(1) = O(6)	2.410(6)	Er(1) = O(2W)	2.410(6)
Er(2) = O(14)	2.24/(6)	Er(2) = O(15c)	2.261(7)
Er(2) = O(4W)	2.329(6)	Er(2) = O(10)	2.330(7)
Er(2) = O(7)	2.339(7)	Er(2) = O(8)	2.360(6)
Er(2) = O(5W)	2.401(6)	Er(2) = O(9)	2.455(6)
Er(3) = O(1/a)	2.259(6)	Ef(3) = O(18d)	2.312(7)
Er(3) = O(11)	2.326(6)	Er(3) = O(7W)	2.400(6)
Er(3) = O(2)	2.400(6)	Er(3) = O(6W)	2.418(6)
Er(3) = O(12)	2.419(7)	Er(3) = O(3)	2.583(6)
O(16a) - Er(1) - O(4b)	11/.1(2)	O(16a) - Er(1) - O(5)	134.8(2)
O(4b) - Er(1) - O(5)	//.8(2)	O(16a) - Er(1) - O(1b)	/4.5(2)
O(4b) - Er(1) - O(1b)	66.8(2)	O(5) = Er(1) = O(1b)	142.9(2)
O(16a) - Er(1) - O(1W)	156.7(3)	O(4b) - Er(1) - O(1W)	/4.9(3)
O(5) - Er(1) - O(1W)	65.1(2)	O(1b) - Er(1) - O(1W)	94.3(2)
O(16a) - Er(1) - O(3W)	81.2(2)	O(4b) - Er(1) - O(3W)	149.0(2)
O(5) - Er(1) - O(3W)	72.0(2)	O(1b) - Er(1) - O(3W)	144.2(2)
O(1W) - Er(1) - O(3W)	98.0(2)	O(16a) - Er(1) - O(6)	/5.2(2)
O(4b) - Er(1) - O(6)	/6.2(2)	O(5) - Er(1) - O(6)	67.3(2)
O(1b) - Er(1) - O(6)	112.3(2)	O(1W) - Er(1) - O(6)	128.1(2)
O(3W) - Er(1) - O(6)	85.8(2)	O(16b) - Er(1) - O(2W)	/8./(2)
O(4b) - Er(1) - O(2W)	129.4(2)	O(5) - Er(1) - O(2W)	126.7(2)
O(1b) - Er(1) - O(2W)	73.3(2)	O(1W) - Er(1) - O(2W)	/8.5(2)
O(3W) = Er(1) = O(2W)	/6.4(2)	O(6) - Er(1) - O(2W)	150.3(2)
O(14) - Er(2) - O(15c)	99.7(2) 97.8(2)	O(14) - Er(2) - O(4W)	148.2(2)
O(15c) - Er(2) - O(4W)	87.8(2)	O(14) - Er(2) - O(10)	/2.0(2)
O(13c) - Ef(2) - O(10)	/4.8(2)	O(4W) - Ef(2) - O(10)	139.4(2)
O(14) - Er(2) - O(7)	89.5(2)	O(15c) - Er(2) - O(7)	144.3(2)
O(4W) = EF(2) = O(7)	102.4(2)	O(10) - Er(2) - O(7)	/5.4(2)
O(14) - Ef(2) - O(8)	81.0(2)	O(15c) - Ef(2) - O(8)	147.8(2)
O(4W) = Ef(2) = O(8)	/6./(2)	O(10) - Ef(2) - O(8)	133.9(2)
O(1) = EI(2) = O(8)	07.3(2)	O(14) - EI(2) - O(5W)	77.0(2)
O(13C) - EI(2) - O(3W)	77.0(2)	O(4W) = EI(2) = O(5W)	128 7(2)
O(10) - Er(2) - O(5W)	133.7(2)	O(7) - Er(2) - O(3W)	138.7(2)
O(8) = Ef(2) = O(5W)	71.8(2)	O(14) - Er(2) - O(9)	138.9(2)
O(13C) - EI(2) - O(9)	(7.7(2))	O(4W) = EI(2) = O(9)	72.9(2)
O(10) - Er(2) - O(9)	67.7(2)	O(7) - Er(2) - O(9)	/3.5(2)
O(8) = Er(2) = O(9)	122.9(2)	O(5W) - Er(2) - O(9)	138.4(2)
O(1/a) - Ef(3) - O(18d)	104.4(3)	O(17a) - Er(3) - O(11)	//.0(2)
O(180) = EI(3) = O(11) O(180) = Er(3) = O(7W)	143.3(2)	O(1/a) = EI(3) = O(7W) O(11) = Er(2) = O(7W)	142.4(2)
O(180) - EI(3) - O(7W) O(17a) = Er(3) - O(7W)	95.2(3) 80.4(2)	O(11) = EI(3) = O(7W) O(18d) = Er(3) = O(2)	105.5(3)
O(1/a) = EI(3) = O(2)	80.4( <i>2</i> )	O(180) = EI(3) = O(2) $O(7W) = E_{2}(3) = O(2)$	$(1.\delta(2))$
O(11) = EI(3) = O(2)	72.5(2)	O(7W) = EI(3) = O(2)	130.8(2)
O(1/a) - Er(3) - O(6W)	/4.0(2)	O(18a) - Er(3) - O(6W)	/6.8(2)

Table S1 Selected bond lengths (Å) and angles (°) for LOF 1  $\,$ 

O(11)-Er(3)-O(6W)	135.7(2)	O(7W)-Er(3)-O(6W)	79.9(2)
O(2)-Er(3)-O(6W)	132.5(2)	O(17a)-Er(3)-O(12)	78.4(2)
O(18d)-Er(3)-O(12)	149.1(2)	O(11)-Er(3)-O(12)	67.4(2)
O(7W)-Er(3)-O(12)	68.8(2)	O(2)-Er(3)-O(12)	137.8(2)
O(6W)-Er(3)-O(12)	74.5(2)	O(17a)-Er(3)-O(3)	144.3(2)
O(18d)-Er(3)-O(3)	85.3(2)	O(11)-Er(3)-O(3)	75.4(2)
O(7W)-Er(3)-O(3)	67.9(2)	O(2)-Er(3)-O(3)	70.1(2)
O(6W)-Er(3)-O(3)	141.4(2)	O(12)-Er(3)-O(3)	110.7(2)

Symmetry codes: a) -x+2, -y, -z+2; b) x+1, y+1, z; c) -x+1, -y, -z+2; d) x-1, y-1, z-1 for LOF 1.

Table S2 Hydrogen-bonding geometry parameters (A, <sup>-</sup> ) for LOF 1				
	LOF	1		
D–H…A	d(D-H)	d(H···A)	$d(D \cdots A)$	<(DHA)
O1W-H1X···O5	0.960	1.971	2.560	117.48
O1W-H1X…O11We	0.960	2.532	3.404	151.09
O2W-H2Y…O1b	0.959	2.382	2.858	110.15
O2W-H2Y…O4Wf	0.959	2.651	3.600	170.47
O3W-H3Y…O14a	0.850	2.014	2.843	164.72
O3W-H3Y···O10a	0.850	2.538	3.027	117.58
O4W-H4X···O8Wg	0.850	2.495	3.149	134.44
O4W-H4Y…O1h	0.850	2.233	2.896	134.86
O4W-H4Y…O16i	0.850	2.422	3.191	150.69
O5W-H5YO15	0.850	2.255	2.890	131.56
O5W-H5Y…O14j	0.850	2.559	3.194	132.32
O5W-H5Y…O10j	0.850	2.577	3.286	141.62
O6W-H6X···O2k	0.850	2.216	2.996	152.68
O6W-H6Y…O10Wl	0.851	2.317	3.121	157.88
O6W-H6Y…O7W	0.851	2.620	3.094	116.46
O7W-H7X···O10Wl	0.849	1.904	2.708	157.58
O8W-H8Y…O6Wh	0.850	1.956	2.663	139.79
O9W-H9X…O12h	0.850	2.075	2.923	175.18
O9W-H9Y…O9g	0.850	2.197	2.929	144.34
O10W-H10Y… O4	0.850	2.212	2.868	133.92

Table S2 Hydrogen-bonding geometry parameters (Å, °) for LOF 1

Symmetry codes: a) -x+2, -y, -z+2; b) x+1, y+1, z; e) x+1, y, z+1; f) x+1, y, z; g) -x+1, -y+1, -z+1; h) x, y+1, z; i) -x+1, -y, -z+2; j) -x+1, -y, -z+2; k) -x+1, -y-1, -z+1; l) x, y-1, z for LOF 1.



**Fig. S1** Local coordination geometries of Er(III) ions in LOF 1. The other atoms have been omitted for clarity (Symmetry codes: a) -x+2, -y, -z+2; b) x+1, y+1, z; c) -x+1, -y, -z+2; d) x-1, y-1, z-1) (Red, O; Green, Er).



**Fig. S2** Two dimensional layer of LOF 1 (Black, C; blue, N; Red, O; Magenta, P; Green, Er).



**Fig. S3** Schematic description of the (3, 6)-c network with a Schläfli symbol of  $(46^2)_2$   $(4^26^88^410)$ .



**Fig. S4** The hydrophilic channel formed by oxalate anions, and carboxylate and phosphonate oxygen atoms from ligands in LOF 1 (Black, C; blue, N; Red, O; Magenta, P; Green, Er).



**Fig. S5** The H-shape channel with dimensions of ca.  $4.3 \times 2.9$  Å<sup>2</sup> and the irregularly rectangular channel with dimensions of ca.  $6.4 \times 4.3$  Å<sup>2</sup> in LOF 1 (Black, C; blue, N; Red, O; Magenta, P; Green, Er).



**Fig. S6** The residual O–H…O hydrogen-bonding interactions formed by coordinated aqua molecules, oxygen atoms from oxalate anions, and phosphonate oxygen atoms in LOF 1' (Black, C; blue, N; Red, O; Magenta, P; Green, Er; Gray, H).



Fig. S7 Thermogravimetric curve for LOF 1.



Fig. S8 The PXRD patterns for LOF 1 of a simulation based on single-crystal analysis, as-synthesized bulk crystals, the sample placed in  $\sim$ 97% RH (relative humidity) for 1d, and after impedance measurement. The patterns of samples in  $\sim$ 97% RH and after impedance measurement are similar to that of the simulated one, showing that the sample is stable in moisture and tested environment.



Fig. S9 The PXRD patterns for LOF 1 of a simulation based on single-crystal analysis, as-synthesized bulk crystals, and soaked in aqueous HCl solution at pH=2 for 1 day. The PXRD result shows that there are some notable new peaks in the sample soaked in aqueous HCl solution at pH=2 for 1 day, suggesting that LOF 1 occurs phase transitions to give a new phase.



**Fig. S10** The PXRD patterns for LOF 1 soaked in aqueous HCl solution at pH=3 for up to 4 days.



**Fig. S11** The PXRD patterns for LOF 1 soaked in aqueous HCl solution at pH=4 for the different days.



**Fig. S12** The PXRD patterns for LOF 1 soaked in aqueous HCl solution at pH=5 for the different days.



**Fig. S13** The PXRD patterns for LOF 1 soaked in aqueous HCl solution at pH=10 for the different days.



**Fig. S14** The PXRD patterns for LOF 1 soaked in aqueous HCl solution at pH=11 for the different days.



**Fig. S15** The PXRD patterns for LOF 1 soaked in aqueous NaOH solution at pH=12 for up to 7 days.



**Fig. S16** The PXRD patterns for LOF 1 soaked in aqueous NaOH solution at pH=13 for 3 days. According to the PXRD pattern, all peaks disappear after being soaked in aqueous NaOH solution at pH=13 for 3 days, implying that the sample becomes an amorphous solid.

Sample	C%	Н%	N%
LOF 1	14.01	2.25	1.50
LOF 1a	14.40	3.07	1.36
LOF 1b	14.56	3.04	1.41
LOF 1c	14.50	2.65	1.61
LOF 1d	14.12	2.37	1.51
LOF 1e	12.13	2.83	1.12
LOF 1f	15.00	3.02	1.41
LOF 1g	15.64	2.21	1.93
LOF 1h	15.80	2.72	1.27
LOF 1i	15.54	2.51	1.87

Table S3 EA results of original and treated LOF 1 samples under different conditions

As shown in Table S3, the elemental contents for C of treated samples LOF 1a-1d are similar to the original LOF 1. However, the obvious differences are found in the C contents of LOF 1e-1i and LOF 1. The C contents of LOF 1e is lower than that of LOF 1, which may be associated with the decrease of the effective C content caused by a small number of NaOH captured in channel. On the contrary, the C contents of LOF 1f-1i higher than that of LOF 1, which is related to a very small amount of organic solvents with high C content exchanged in channels. The larger differences of H and N contents between untreated and treated samples may be assigned to a few defects and hygroscopic water and exchanged solvent molecules with the different extent caused by various treating conditions.



**Fig. S17** Thermogravimetric curves for the original LOF 1 and the different treated LOF 1a- LOF li. Samples after being soaked in water for 2 weeks at room temperature (LOF 1a), refluxed in water for 3 days (LOF 1b), treated by the hydrothermal method at 150 °C for 1 day (LOF 1c), immersed in aqueous solutions with pH=3 for 4 days (LOF 1d) and pH=12 for 7 days (LOF 1e), and boiled in CH<sub>3</sub>OH (LOF 1f), C<sub>2</sub>H<sub>5</sub>OH (LOF 1g), CH<sub>3</sub>CN (LOF 1h), and petroleum ether (LOF 1i) for 2 days.



**Fig. S18** XPS spectra of Er 4d. (a) Sample before the treatment (LOF 1). (b) Samples after being soaked in water for 2 weeks at room temperature (LOF 1a), refluxed in water for 3 days (LOF 1b), and treated by the hydrothermal method at 150 °C for 1 day (LOF 1c). (c) Samples after being immersed in aqueous solutions with pH=3 for 4 days (LOF 1d) and pH=12 for 7 days (LOF 1e). (d) Samples after being boiled in CH<sub>3</sub>OH (LOF 1f), C<sub>2</sub>H<sub>5</sub>OH (LOF 1g), CH<sub>3</sub>CN (LOF 1h), and petroleum ether (LOF 1i) for 2 days.



**Fig. S19.** O 1s XPS spectra of samples after being (a) soaked in water for 2 weeks at room temperature (LOF 1a), (b) refluxed in water for 3 days (LOF 1b), (c) treated by the hydrothermal method at 150 °C for 1 day (LOF 1c), (d) immersed in aqueous solutions with pH=3 for 4 days (LOF 1d), (e) submerged in aqueous solutions with pH=12 for 7 days (LOF 1e), boiled in (f) CH<sub>3</sub>OH (LOF 1f), (g) C<sub>2</sub>H<sub>5</sub>OH (LOF 1g), (h) CH<sub>3</sub>CN (LOF 1h), and (i) petroleum ether (LOF 1i) for 2 days.



Fig. S20 Water adsorption capacity of LOF 1 as a function of humidity.



Fig. S21 N<sub>2</sub> sorption isotherm of LOF 1 at 77 K.



**Fig. S22** Nyquist plots of LOF 1 at ~97% RH (a), ~84% RH(b), ~75% RH (c), ~65% RH (d) and ~53% RH (e) and 298 K.



**Fig. S23** Nyquist plots of LOF 1 at 303K (a), 293K (b), 291K (c), 288K (d) and 284K (e) and ~97% RH.



Fig. S24 Temperature dependence of the conductivity ( $\sigma$ ) for LOF 1 at ~97% RH.



Fig. S25 Nyquist plot of the dehydrated LOF 1 at ~97% RH and 298 K.



Fig. S26 Nyquist plots of LOF 1d (a) and LOF 1e (b) at ~97% RH and 298 K.



Fig. S27 Infrared spectrometers of LOF 1, LOF 1d and LOF1e in the range of 3150–4000 cm<sup>-1</sup>.



**Fig. S28** Nyquist plots of LOF 1f (a), LOF 1g (b), LOF 1h (c) and LOF 1i (d) at ~97% RH and 298 K.