Supporting Information

High proton conduction behavior in 12-connected 3D porous Lanthanide-organic frameworks and their polymer composite

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Table S1. Crystal Data and Structure Refinements for **1-2.**

complex	1	2
Formula	$C_{85}H_{77}N_{10}O_{22}Eu_3$	$C_{85}H_{75}N_{10}O_{21}Tb_3$
Mr	2046.44	2049.31
T/K	120.00(10)	119.8(9)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
***a*/ Å**	14.5999(5)	14.5486(4)
***b* / Å**	17.7683(6)	17.7273(4)
***c*/ Å**	31.8703(13)	31.9630(7)
***α* /°**	90	90.01
***β* /°**	90.663(4)	90
***γ*/°**	90	90
Z	4	4
Volume /Å^3	8267.1(5)	8243.5(3)
***ρ* /g cm^{-3}**	1.644	1.651
***μ* /mm^{-1}**	2.329	2.625
***F*(000)**	4088.0	4072.0
Crystal size /mm^3	0.20×0.18×0.12	0.20×0.18×0.12
***2θ* /°**	5.978 to 50.02	5.954 to 50.02
Reflections/ unique	35964/14569	58815/14514
$R_{(int)}$	0.0345	0.0398
Data / restraints / parameters	14569/155/1100	14514/1/1090
GOF on F^2	1.04	1.097
R_1 **[I>2δ(I)]**	0.0381	0.0316
wR_2 **[I>2δ(I)]**	0.0957	0.0723
R_1 **(all data)**	0.0480	0.0374
wR_2 **(all data)**	0.1038	0.0758

Table S2. Selected Bond Lengths (Å) and angles(°) of **1** and **2**.

1			
Eu(1)-O(1)	2.380(3)	Eu(2)-(O15)#3	2.388(3)
Eu(1)-O(5)	2.450(3)	Eu(2)-O(15)#3	2.563(3)
Eu(1)-O(7)#2	2.380(3)	Eu(2)-O(16)#3	2.597(4)
Eu(1)-O(10)	2.747(3)	Eu(3)-O(3)#4	2.452(4)
Eu(1)-O(13)	2.429(3)	Eu(3)-O(4)#4	2.558(3)
Eu(1)-O(14)	2.391(3)	Eu(3)-O(5)#1	2.528(3)
Eu(1)-O(14)#1	2.420(3)	Eu(3)-O(6)#1	2.489(4)
Eu(1)-O(17)	2.383(4)	Eu(3)-O(9)	2.403(4)
Eu(2)-O(2)	2.314(4)	Eu(3)-O(10)	2.687(4)
Eu(2)-O(4)#2	2.460(3)	Eu(3)-O(11)#5	2.316(4)
Eu(2)-O(8)#2	2.374(4)	Eu(3)-O(13)	2.384(3)
Eu(2)-O(12)#5	2.348(2)	Eu(3)-O(14)	2.343(3)
Eu(2)-(O13)	2.350(2)	Eu(3)#6-O(3)	2.452(4)
O(13)-Eu(1)-O(5)	155.29(11)	O(17)-Eu(1)-O(13)	115.04(13)
Eu(3)-O(13)-Eu(1)	98.99(12)	O(17)-Eu(1)-O(14)	140.68(12)
Eu(1)-O(5)-Eu(3)#1	106.39(12)	O(14)-Eu(1)-O(13)	73.15(11)
Eu(2)-O(15)-Eu(2)#3	113.68(14)	Eu(1)-O(14)-Eu(1)#1	109.28(13)
Eu(2)#6-O(4)-Eu(3)#6	102.61(12)	Eu(3)-O(14)-Eu(1)#1	113.60(13)
Eu(1)-O(10)-Eu(3)	90.20(11)	O(13)-Eu(2)-O(8)#2	107.94(12)

O(1)-Eu(1)-O(13)	75.93(12)	O(13)-Eu(2)-O(15)	167.21(12)
O(1)-Eu(1)-O(5)	91.40(12)	O(8)#2-Eu(2)-O(16)#3	151.17(14)
O(1)-Eu(1)-O(17)	72.39(12)	O(3)#4-Eu(3)-O(13)	85.04(12)
O(1)-Eu(1)-O(14)	142.68(11)	O(11)#5-Eu(3)-O(14)	148.53(12)
		2	
Tb(1)-O(1)	2.470(3)	Tb(2)-O(15)	2.396(3)
Tb(1)-O(2)	2.504(3)	Tb(2)-O(15)#1	2.369(3)
Tb(1)-O(5)	2.371(3)	Tb(2)-O(16)#1	2.404(3)
Tb(1)-O(6)	2.681(3)	Tb(2)-O(17)	2.368(3)
Tb(1)-O(7)#7	2.288(3)	Tb(3)-O(3)#2	2.366(3)
Tb(1)-O(11)#6	2.418(3)	Tb(3)-O(8)#5	2.307(3)
Tb(1)-O(12)#6	2.531(3)	Tb(3)-O(10)	2.284(3)
Tb(1)-O(15)	2.304(3)	Tb(3)-O(12)#4	2.437(3)
Tb(1)-O(16)	2.359(3)	Tb(3)-O(13)	2.353(3)
Tb(2)-O(2)	2.425(3)	Tb(3)-O(14)	2.553(3)
Tb(2)-O(4)#2	2.348(3)	Tb(3)-O(14)#3	2.353(3)
Tb(2)-O(6)#1	2.452(3)	Tb(3)-O(16)#1	2.340(3)
Tb(2)-O(9)	2.358(3)	Tb(3)#3-O(14)	2.353(3)
O(11)#6-Tb(1)-O(12)#6	52.81(10)	O(9)-Tb(2)-O(15)#1	143.03(10)
O(11)#6-Tb(1)-O(6)	50.31(10)	O(4)#2-Tb(2)-O(15)	120.22(10)
O(16)-Tb(1)-O(2)	134.17(10)	O(4)#2-Tb(2)-O(17)	144.10(10)
O(16)-Tb(1)-O(5)	81.12(10)	O(14)#3-Tb(3)-O(14)	66.62(11)
O(16)-Tb(1)-O(12)#6	67.50(9)	O(14)-Tb(3)-O(13)	50.82(10)
O(15)-Tb(1)-O(16)	75.01(9)	O(14)#3-Tb(3)-O(13)	115.72(11)
O(2)-Tb(2)-O(6)#1	136.20(10)	O(16)#1-Tb(3)-O(14)	118.51(19)
O(9)-Tb(2)-O(2)	91.38(10)	O(16)#1-Tb(3)-O(12)#4	69.40(10)
O(9)-Tb(2)-O(16)#1	75.96(10)	O(10)-Tb(3)-O(14)	78.30(10)

Symmetry Codes: #1=1-x, 1-y, 1-z, #2=3/2-x, -1/2+y, 3/2-z, #3=2-x, 1-y, 1-z, #4=+x, -1+y, +z, #5=3/2-x, -1/2+y, 1/2-z, #6=+x, 1+y, +z, #7=5/2-x, 1/2+y, 1/2-z.

Table S3. Hydrogen bond Lengths (Å) and Angles (°) for **1-2**

		1		
D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
O(13)-H(13)…O(16)	0.826	2.224	2.782	124.9
O(13)-H(13)…O(21)	0.826	2.204	2.958	151.9
O(22)-H(22A)…O(3)	0.851	2.130	2.970	169.2
O(14)-H(14)…O(7)	0.846	2.471	2.847	107.9
		2		
D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
C(5)-H(5)…O(9)	0.930	2.580	3.162	121.1
C(5)-H(5)…O(4)	0.930	2.572	3.475	163.9
O(15)-H(15)…O(4)	0.836	2.517	2.855	105.3
O(16)-H(16)…O(13)	0.840	2.295	2.740	113.4

Table S4. Proton conduction performances at high RH of some selected Ln-MOF

Selected MOFs	Conductivity ($S \cdot cm^{-1}$)	Measurement condition	Ea (ev)	Ref
$\{[Eu_3(bpydb)_3(HCOO)(OH)_2(DMF)]\cdot 3DMF\cdot 2H_2O\}_n$	1.7×10^{-4}	52℃, 98%RH	0.64	This work
$\{[Tb_3(bpydb)_3(HCOO)(OH)_2(DMF)]\cdot 3DMF\cdot H_2O\}_n$	1.1×10^{-4}	61℃, 98%RH	0.48	This work
$\{[Gd(L)(OX)(H_2O)]n\cdot 3H_2O\}$	4.7×10^{-4}	80℃, 95%RH	0.88	1
$\{[Dy(L)(OX)(H_2O)]n\cdot 1.5H_2O\}$	9.06×10^{-5}	80℃, 95%RH	0.70	1
$\{[Gd_4(R\text{-}ttpc)_2(R\text{-}Httpc)_2(HCOO)_2(H_2O)_8]\cdot 4H_2O\}_n$	1.5×10^{-4}	50℃, 97%RH	0.32	2
$\{[Eu_2(L)_2]\cdot(H_2O)_3\cdot(Me_2NH_2)_2\}_n$	1.1×10^{-3}	100℃, 68%RH	0.97	3
$[EuL(H_2O)_3]\cdot 2H_2O$	1.6×10^{-5}	75℃, 97%RH	0.91	4
$[DyL(H_2O)_3]\cdot 2H_2O$	1.33×10^{-5}	75℃, 97%RH	0.87	4

H_2L=mucic acid oxH_2=oxalic acid (1)

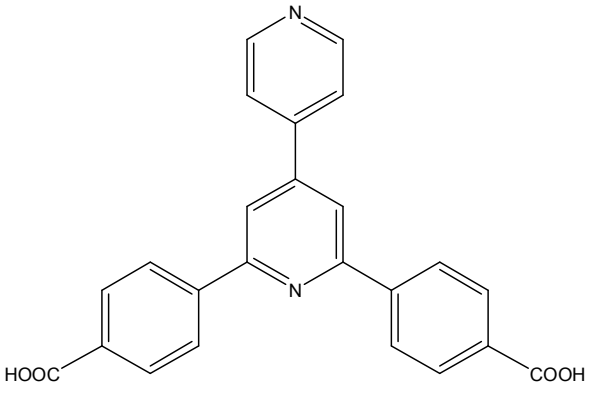
R-H_3ttpc=(3R,3'R,3"R)-1,1',1"-(1,3,5-triazine-2,4,6-triyl)-tripiperidine-3-carboxylic acid (2)

H_4L=5-(3,5-dicarboxybenzyloxy)-isophthalic acid (3)

L=N-phenyl-N'-phenyl bicycle[2,2,2]oct-7-ene-2,3,5,6-tetracarboxdimide tetracarboxylic acid (4)

Table S5. Proton conduction properties of some selected MOF composite membranes

Selected MOF composite membranes	Conductivity ($S \cdot cm^{-1}$)	Measurement condition	Ea (ev)	Ref
1@PVA-10	2.1×10^{-4}	65℃, 98% RH	0.21	This work
2@PVA-10	2.9×10^{-4}	65℃, 98% RH	0.29	This work
MOF-508@PVDF-55	1.56×10^{-4}	65℃, 100% RH	0.17	5
JUC-200@PVA-10	1.25×10^{-3}	50℃, 100% RH	0.46	6
Ca-MOF@PVP-50	5.7×10^{-5}	25℃, 65% RH	0.54	7
S-MIL-101@CS-4	6.4×10^{-2}	100℃,100% RH	0.17	8
S-UiO-66@GO@SPEEK-10	2.68×10^{-1}	70℃, 95% RH	0.10	9



Scheme. 1 Structure of $bpydbH_2$ ligand.

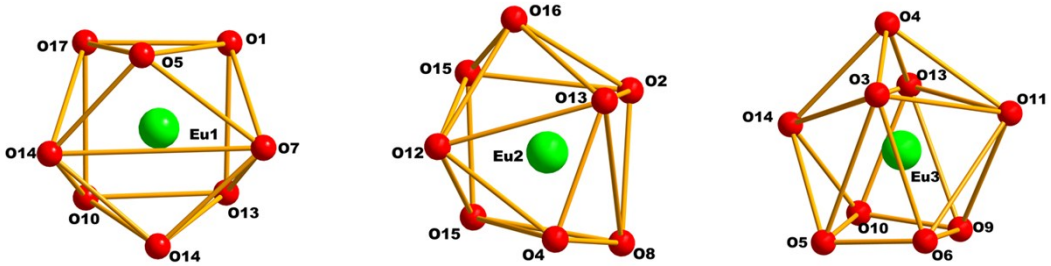
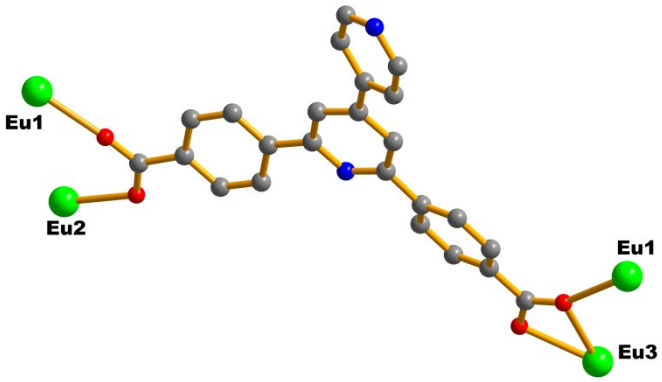


Fig. S1 The coordination polyhedron of Eu center of **1**.



μ_4-η^2:η^1:η^1:η^1

Fig. S2 Coordination mode of the bpydb^{2-} ligand in **1** (Gray, C; Red, O; Green, Eu; Blue, N).

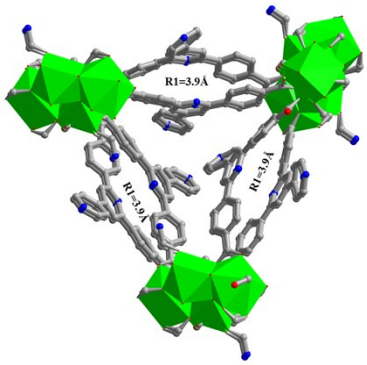


Fig. S3 The 3D framework of **1** contains two types irregular 1D channel along a direction and Eu^{3+} is represent as polyhedral.

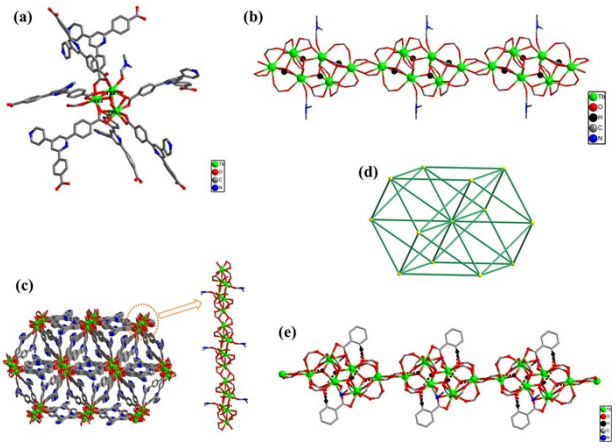


Fig. S4 (a) The asymmetric unit of **2**. All hydrogen atoms are omitted. (b) 1D rod-shaped secondary building units of **2** running alone the a axis. (c) 3D framework of **2**. (d) Schematic representation of 12-connected *fcu* topology for **2**(yellow atoms represent {Tb_6} clusters). (e) Three types of hydrogen-bonding interactions in the cavity.

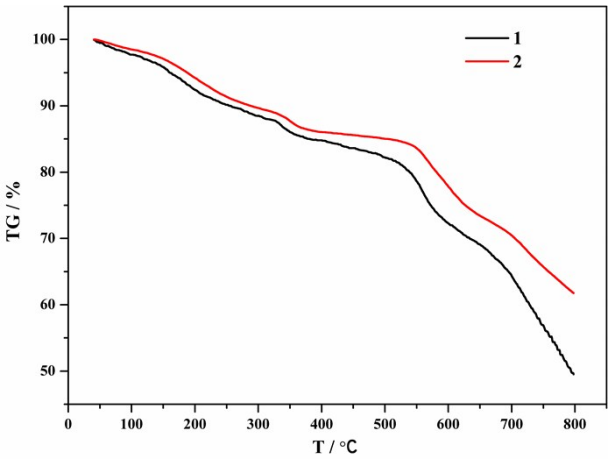


Fig. S5 TG curves for **1-2**.

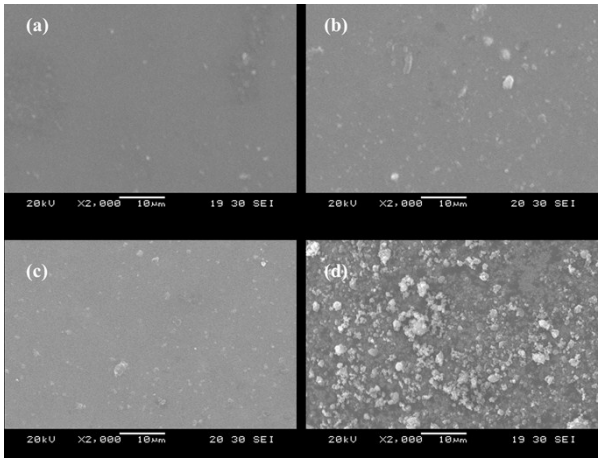


Fig. S6 SEM images of the **2**@PVA composite membranes with different contents of

the crystal. (a) 0 wt%, (b) 5 wt%, (c) 10 wt%, (d) the pure crystals after grinding.

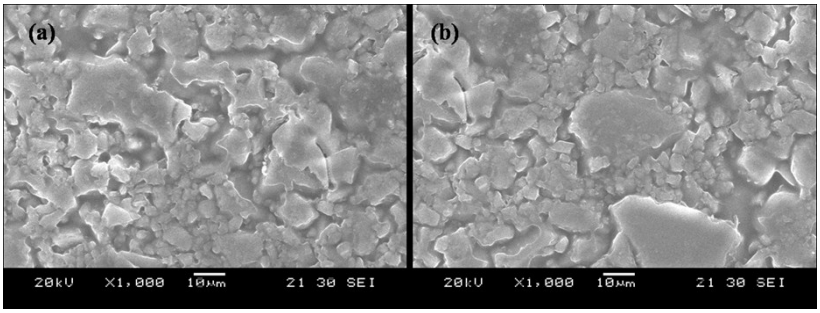


Fig. S7 The SEM image shows the surfaces of the **1**@PVA-15 (a) and **2**@ PVA-15 (b) composite membrane.

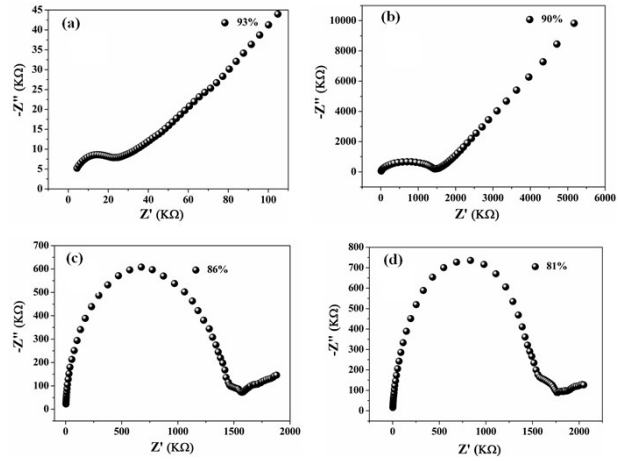


Fig. S8 Nyquist plats of **1** under different relative humidity and 298K, (a): 93% RH, (b): 90% RH, (c): 86% RH, and (d): 81% RH.

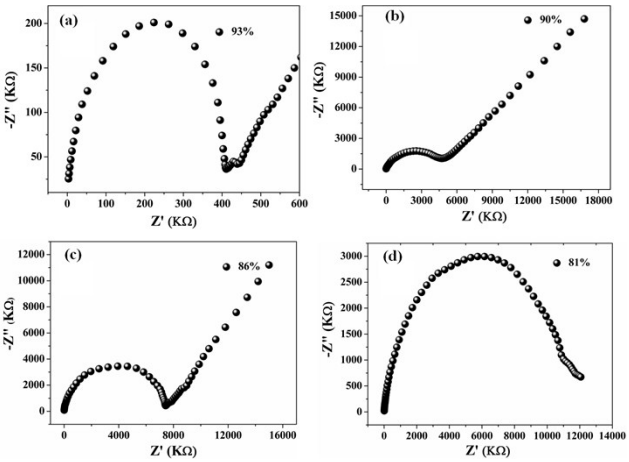


Fig. S9 Nyquist plats of **2** under different relative humidity and 298 K, (a): 93% RH, (b): 90% RH, (c):86% RH, and (d): 81% RH.

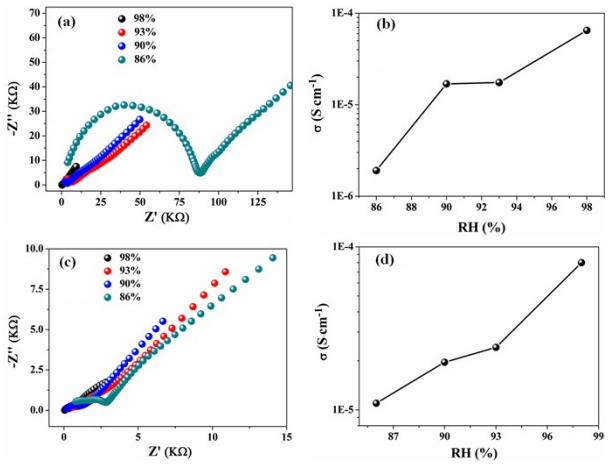


Fig. S10 (a) Nyquist plats of **1**@PVA-10 composite membranes under different relative humidity at 298 K. (b) RH-dependent proton conductivity (σ) of **1**@PVA-10 composite membranes at 298 K. (c) Nyquist plats of **2**@PVA-10 composite membranes under different relative humidity at 298 K. (d) RH-dependent proton conductivity (σ) of **2**@PVA-10 composite membranes at 298 K.

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