Electronic Supplementary Material (ESI) for RSC Advances.

Theoretical hydrogen bonding calculations and proton conduction for Eu(III)-based metal-organic framework

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Supporting Information

Experimental

1. Materials

Chemical reagents were purchased commercially and used as received without further purification. The ligand of 1,3,5-triazine-2,4,6-triamine hexaacetic acid (H_6TTHA) was prepared according to the method reported in literature. [1]

2. Physical measurements

Elemental analysis (C, H and N) was performed by using a Perkin-Elmer 2400 series II CHN analyzer. The powder X-ray diffraction measurement was conducted on a Bruker D8 ADVANCE X-ray diffractometer. Infrared (IR) spectrum was recorded in the range 4000 - 400 cm^{-1} on a FT-IR analyzer (1601, shimadzu Co., Japan) by using KBr-pellet method. The water adsorption property of **1** was investigated at 25 ^{0}C and in the RH range of 0%-95% by DVS Intrinsic Plus (Surface Measurement Systems, English). Before the measurement, the sample was treated under 0% RH for 6 h until the water molecules in the samples were completely removed.

3. Synthesis of the complex $\{[Eu_2(TTHA)(H_2O)_4]\cdot 9H_2O\}_n$ (1)

H_6TTHA (0.04 mmol, 0.0191 g), 4, 4′-bipy (0.12 mmol, 0.019 g), $Eu(NO_3)_3\cdot 6H_2O$ (0.04 mmol, 0.0181 g), 2 mL water and 1 mL acetonitrile were added in 10 mL vial. Then, 90 μL 6 mol/L HCl was added. The vial was kept in an autoclave at 140 ^{0}C for three days. Colorless crystals were obtained and washed with deionized water. Yield: 63 % (35.41 mg, based on Eu). Anal. Calcd. For $C_{15}H_{38}Eu_2N_6O_{25}$: C, 17.9; H, 3.81; N, 8.35 %. Found: C, 17.54; H, 3.49; N, 8.76 %. Main IR data (KBr, cm^{-1}): 3422(m), 3267(m), 2941(w), 1551(s), 1492(m), 1432(w), 1400(m), 1306(s), 1192(m).

4. X-ray crystallography

Single-crystal X-ray diffraction data for **1** was collected at 173 K on a Bruker Smart CCD area-detector diffractometer with graphite-monochromatic Mo/Kα radiation (λ = 0.71073 Å) in ω-scan mode. The collected data were reduced using the software package SAINT [2] and semi-empirical absorption correction was applied to the intensity data using SADABS program. [3] The structure of **1** was solved using direct methods, and all nonhydrogen atoms were refined anisotropically by least squares on F2 using the SHELXTL-2014 program.4 Hydrogen atoms were placed in calculated positions and refined isotropically using the riding model. Details of the hydrogen-bond geometry, crystallographic data and selected bond lengths (Å) for **1** are summarized in Table S1, Table S2 and Table S3, respectively.

5. Proton conductivity studies

Electrical characterization was carried out on a cylindrical pellet (10 mm of diameter and 0.5 mm of thickness) obtained by pressing 50 mg of sample at 500 MPa for 5 min. The pellet was pressed between porous C electrodes (Sigracet, GDL 10 BB, no Pt). Impedance spectroscopy data were collected using a HP4284A impedance analyzer over the frequency range from 20 Hz to 1 MHz with an applied voltage of 0.2 V. Electrical measurements were taken at different temperature (293 - 353 K) and relative humidity (60%, 70%, 80%, 90% and 98%) as well as different times (0h, 4h, 8h and 12h). All measurements were electronically controlled by the winDETA package of programs. [5]

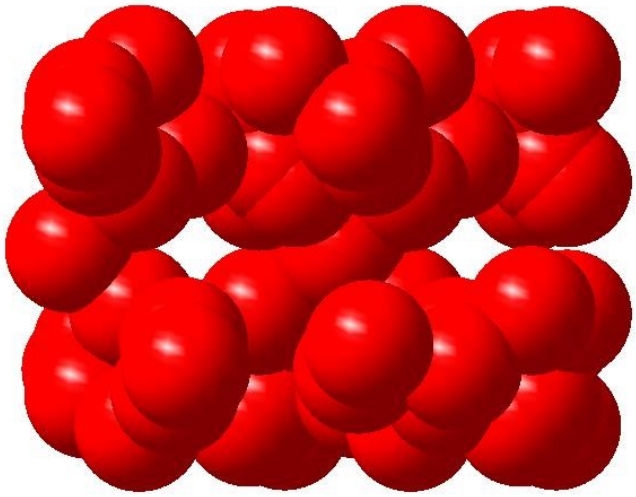

Fig. S1 The space-filling model of water cluster ($(H_2O)_n$).

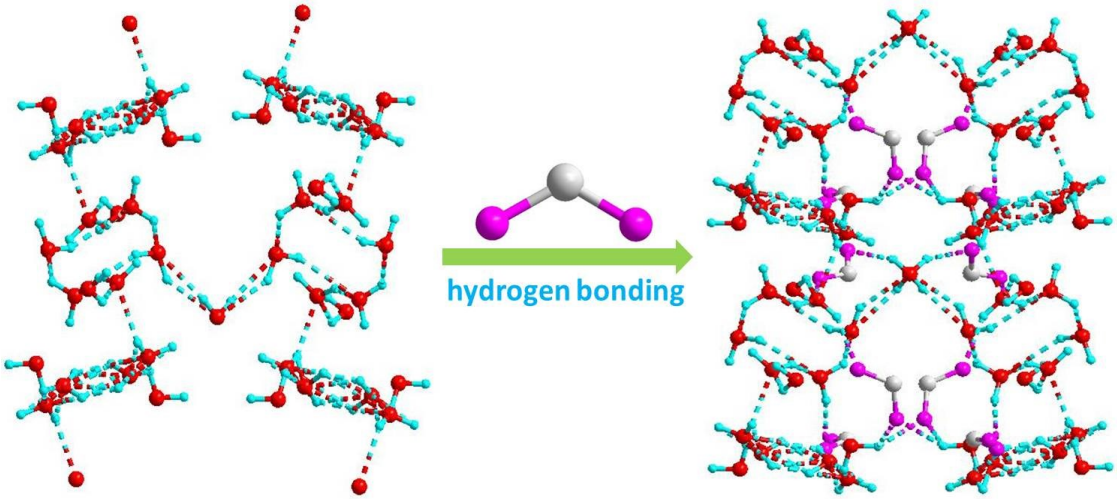

Fig. S2 The infinite water cluster of $(H_2O)_n$ (left) and abundant hydrogen bond network formed by $(H_2O)_n$ and $-COO^-$ groups (right), where the carboxylic acid oxygen atoms are labeled as pink for clearly.

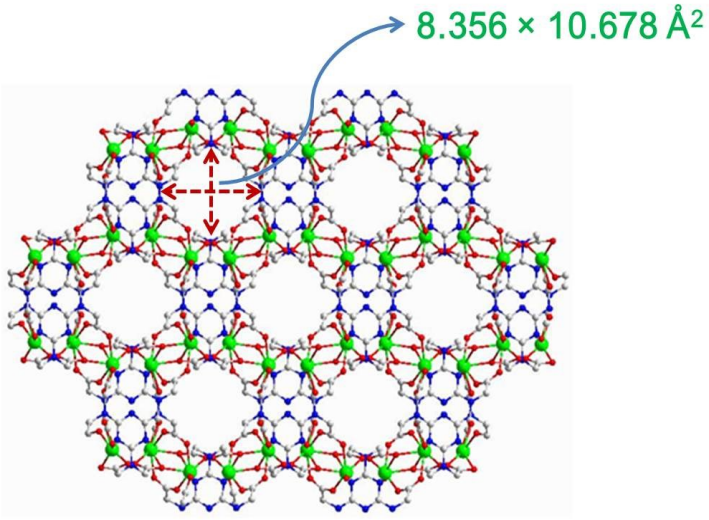

Fig. S3 The cavities with regular size of 8.356 × 10.678 Å^2 are left in the three-dimensional network structure of **1**.

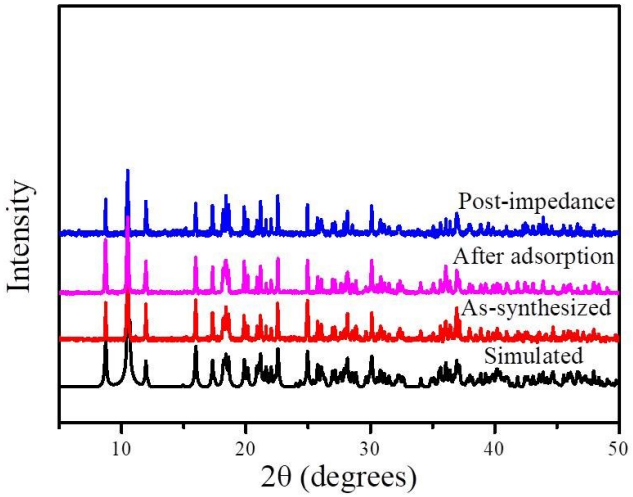

Fig. S4 The XRD patterns of **1** under different experimental conditions.

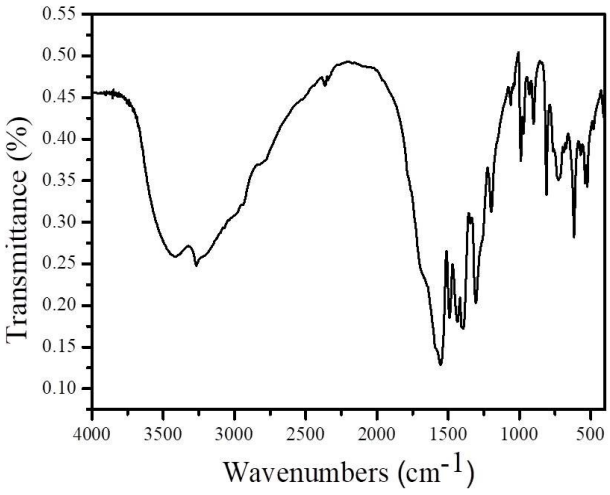

Fig. S5 The IR spectrum of **1**.

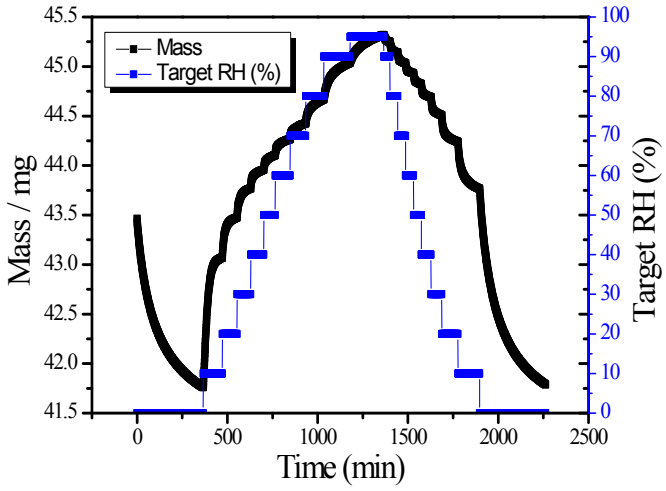

Fig. S6 The change curves of mass and RH with time for the complex **1**.

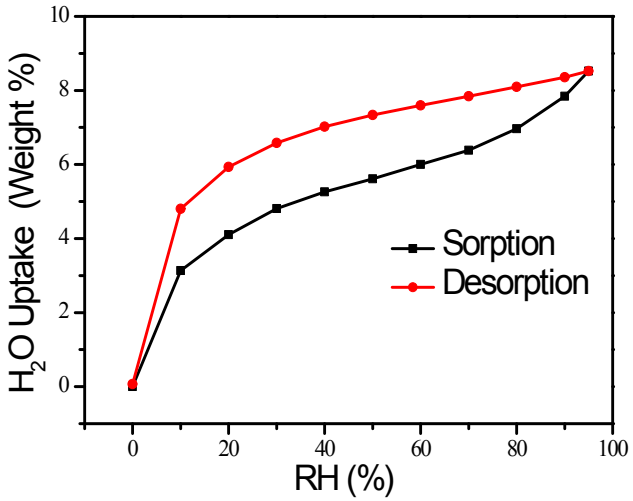

Fig. S7 Water adsorption–desorption isotherms (25 ^{0}C) of **1** measured by DVS Intrinsic Plus.

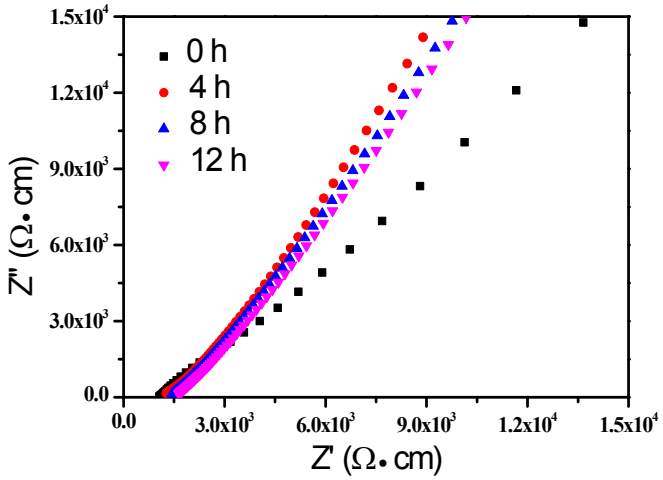

Fig. S8 The Nyquist plots for proton conductivity of **1** (343 K and 98% RH) at 0h, 4h, 8h and 12h.

Table S1 Hydrogen-bond geometry (Å, °) for **1**.

D-H···A	D-H	H···A	D···A	D-H···A

O1-H1A···O7^{i}	0.876(6)	2.320(5)	2.713(7)	107.4(4)
O1-H1B···O9^{ii}	0.876(5)	2.044(6)	2.701(8)	131.1(4)
O9^{ii}-H9A^{ii}···O5^{ii}	0.871(6)	1.941(5)	2.737(8)	151.3(4)
O9^{ii}-H9B^{ii}···O10^{iii}	0.871(7)	2.084(7)	2.863(9)	148.5(5)
O13^{i}-H13A^{i}···O13A^{i}	0.870(2)	1.642(2)	0.818(3)	13.0(2)
O13^{i}-H13B^{i}···O9^{ii}	0.871(2)	1.990(5)	2.554(2)	121.4(1)
O13A^{i}-H13C^{i}···O13^{i}	0.870(2)	1.522(2)	0.818(3)	24.8(1)
O13A^{i}-H13D^{i}···O13^{i}	0.869(2)	1.306(2)	0.818(3)	37.9(2)
O13A^{i}-H13D^{i}···O13^{iV}	0.869(2)	2.507(2)	2.888(3)	107.3(1)
O13A^{i}-H13D^{i}···O13A^{iV}	0.869(2)	1.742(2)	2.193(3)	109.6(1)
O10^{iii}-H10A^{iii}···O4^{iii}	0.870(7)	2.219(5)	3.031(8)	155.4(5)
O10^{iii}-H10B^{iii}···O12^{v}	0.870(7)	2.244(7)	2.726(9)	114.9(5)
O12^{v}-H12A^{v}···O11^{vi}	0.868(7)	2.033(6)	2.786(1)	144.4(5)
O12^{v}-H12B^{v}···O10^{vii}	0.869(8)	2.363(7)	3.106(1)	143.7(5)
O11^{vi}-H11A^{vi}···O12^{vi}	0.870(6)	2.075(7)	2.786(1)	138.3(2)
O11^{vi}-H11B^{v}···O8^{viii}	0.869(6)	1.999(5)	2.804(6)	153.7(1)
O2^{ix}-H2A^{ix}···O13^{vii}	0.877(5)	2.353(2)	2.813(2)	112.9(6)
O2^{ix}-H2A^{ix}···O13A^{vii}	0.877(5)	2.399(2)	2.730(2)	102.7(6)
O2^{ix}-H2B^{ix}···O6^{ii}	0.876(6)	2.000(5)	2.684(7)	134.1(4)
O2^{ix}-H2B^{ix}···O6^{i}	0.876(6)	2.418(5)	2.810(7)	107.6(4)

Symmetry codes (i: 0.5+x, 1.5-y, -0.5+z; ii: 1.5-x, 1.5-y, 1-z; iii: 1+x, y, z; iv: 2-x, y, 1.5-z; v: 2.5-x, 0.5+y, 1.5-z; vi: 0.5+x, 0.5+y, z; vii: 2-x, 2-y, 1-z; viii: 1.5+x, 0.5+y, z; ix: x, 2-y, -0.5+z).

Table S2 Crystallographic data and refinement parameters of **1**

	1
CCDC	2036641
Empirical formula	$C_{15}H_{38}Eu_2N_6O_{25}$
Formula weigh	1006.43
Temperature/K	173
Crystal system	monoclinic
Space group	*C* 2/*c*
a/Å	12.7130(11)
b/Å	16.7745(15)
c/Å	14.7977(13)
α/°	90
β/°	91.265(4)
γ/°	90
V/Å^3	3154.9(5)
Z	4

D_{calc}/g cm^{-3}	2.119
μ/mm^{-1}	4.048
F(000)	1984.0
h, k, l max	15, 20, 17
No. of parameters	243
S	0.998
R_1, wR_2 [I > 2σ(I)]	0.0392, 0.07
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å	0.745, 0.566

Table S3 Selected bond lengths (Å) of **1**.

1			
Eu1-O1	2.472(5)	Eu1-O2	2.424(5)
Eu1-O3^{i}	2.606(5)	Eu1-O4^{i}	2.478(6)
Eu1-O3	2.374(5)	Eu1-O5^{ii}	2.524(5)
Eu1-O6^{ii}	2.461(5)	Eu1-O7^{iii}	2.401(5)
Eu1-O8^{iv}	2.379(5)		

Symmetry codes (i: 1.5-x, 1.5-y, 1-z; ii: 0.5+x, 0.5+y, z; iii: 0.5+x, 1.5-y, -0.5+z; iv: 1-x, y, 1.5-z)

Table S4 The resistance (R) and conductivity (σ) of **1** under different temperature and 98% RH. The values of pellet dimensions including sample thickness (*l*) and diameter are 500 um and 2 mm, respectively.

Temperature (K)	R (Ω)	σ (S/cm)
293	11892.8	1.34×10^{-4}
298	9785.52	1.63×10^{-4}
303	8025.75	1.98×10^{-4}
308	6321.61	2.52×10^{-4}
313	5016.63	3.17×10^{-4}
318	3914.39	4.07×10^{-4}
323	3013.24	5.28×10^{-4}
333	1980.25	8.04×10^{-4}
343	1074.69	1.48×10^{-3}
353	455.31	3.50×10^{-3}

Table S5 The resistance (R) and conductivity (σ) of **1** under different relative humidity and 298 K.

RH (%)	R (Ω)	σ (S/cm)
60	112098.428	1.42×10^{-5}
70	66985.6459	2.38×10^{-5}
80	32516.53	4.9×10^{-5}
90	21360.46	7.45×10^{-5}
98	9785.52	1.63×10^{-4}

Table S6 The resistance (R) and conductivity (σ) of **1** (343 K and 98% RH) under different time.

Time (h)	R (Ω)	σ (S/cm)
0	1.07×10^3	1.48×10^{-3}
4	1.12×10^3	1.43×10^{-3}
8	1.38×10^3	1.16×10^{-3}
12	1.52×10^3	1.05×10^{-3}

References

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