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A water stable layered Tb(III) polycarboxylate with high proton conductivity over 10^{-2} S·cm^{-1} in a wide temperature range

Lu Feng,[1a] Hui-Sheng Wang,[1a] Hai-Long Xu,[a] Wen-Tao Huang,[a] Tian-Yu Zeng,[a] Qing-Rong Cheng,[a] Zhi-Quan Pan[a] and Hong Zhou*[a]

[a] College of Chemistry and Environmental Technology, Wuhan Institute of Technology, Wuhan 430073, Hubei, China

[1] These two authors contributed same to this article.

*Corresponding author: hzhouh@126.com

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. Thermogravimetric analyses was carried out on a NETZSCH STA 449C unit at a heating rate of 10 ^0C min^{-1} under a nitrogen atmosphere.

3. Synthesis of complex $\{[Tb_4(TTHA)_2(H_2O)_4]\cdot 7H_2O\}_n$ (1)

H_6TTHA (0.082 mmol, 0.0388 g), $Tb(NO_3)_3\cdot 6H_2O$ (0.04 mmol, 0.0178 g), 2 mL water and 1 mL acetonitrile were added in 10 mL vial. Then, 70 µL 6 mol/L HCl was added. The vial was kept in an autoclave at 140 ^0C for three days. Colorless crystals were obtained and washed with deionized water. Yield: 32.83 mg (58%, based on Tb). Anal. Calcd. For $C_{30}H_{46}N_{12}O_{35}Tb_4$: C, 20.35; H, 2.62; N, 9.49%. Found: C, 20.73; H, 2.21; N, 9.83%. Main IR data (KBr, cm^{-1}): 3447(m), 3188(m), 2935(w), 1553(s), 1491(m), 1429(w), 1309(s), 1195(s), 991(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 F^2 using the SHELXTL-2014 program.[4] Hydrogen atoms were placed in calculated positions and refined isotropically using the riding model. Details of the crystallographic data and selected bond lengths (Å) as well as angles (^{0}) for **1** are summarized in Table S1 and Table S2, respectively. In this heavy-atom structure as it was not possible to see clear electron-density peaks in difference maps which would correspond with acceptable locations for the various H atoms bonded to water oxygen atoms, the refinement was completed with no allowance for these water H atoms in the model.

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 (287 - 358 K) and relative humidity (60%, 70%, 80%, 90% and 98%). All measurements were electronically controlled by the winDETA package of programs.[5]

Table S1 Crystallographic data and refinement parameters of **1**

	1
CCDC number	1876158
Empirical formula	$C_{30}H_{46}N_{12}O_{35}Tb_4$
Formula weigh	1770.47
Temperature/K	173
Crystal system	triclinic
Space group	$P\ \bar{1}$
a/Å	10.7095(7)
b/Å	11.3590(6)
c/Å	12.0866(7)
α/°	62.703(2)
β/°	74.569(2)
γ/°	68.667(2)
V/Å^3	1208.29(13)
Z	1
D_{calc}/g cm^{-3}	2.433
μ/mm^{-1}	5.905
F(000)	850.0
h, k, l max	12, 13, 14
No. of parameters	370
S	1.011
R_1, wR_2 [I > 2σ(I)]	0.0389, 0.0634
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å	0.745, 0.605

Table S2 Selected bond lengths (Å) of **1**.

1			
Tb1-O1	2.540(6)	Tb1-O9^{i}	2.527(7)
Tb1-O2	2.397(7)	Tb1-O4^{i}	2.217(5)
Tb1-O5	2.310(6)	Tb1-O9^{ii}	2.387(6)
Tb1-O10^{i}	2.435(5)	Tb1-O12	2.365(4)
Tb2-O3	2.342(7)	Tb2-O6^{i}	2.328(5)
Tb2-O7^{i}	2.303(6)	Tb2-O7^{iii}	2.571(4)
Tb2-O8^{iii}	2.459(5)	Tb2-O11^{iii}	2.338(6)
Tb2-O13	2.318(5)	Tb2-O14^{i}	2.387(6)

Symmetry codes (^{i}: 1-x, -y, 1-z; ^{ii}: 1+x, y, z; ^{iii}: x, -1+y, 1+z)

Table S3 The resistance (R) and conductivity (σ) of **1** under different temperature and 98% relative humidity. The values of pellet dimensions including sample thickness (*l*) and diameter are 500 um and 2 mm, respectively.

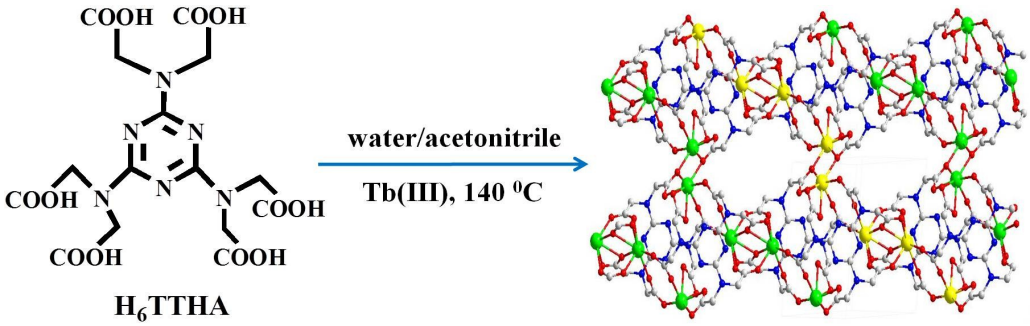
Temperature (K)	R (Ω)	σ (S/cm)
287	287.87	5.53×10^{-3}
289	250.40	6.36×10^{-3}
291	200.93	7.93×10^{-3}
293	169.53	9.39×10^{-3}
295	145.17	1.10×10^{-2}
297	119.73	1.33×10^{-2}
313	89.93	1.77×10^{-2}
333	61.96	2.57×10^{-2}
358	76.40	2.08×10^{-2}

Table S4 The resistance (R) and conductivity (σ) of **1** under different relative humidity (RH) and 297 K.

RH (%)	R (Ω)	σ (S/cm)
60	1.14×10^{5}	1.40×10^{-5}
70	3.92×10^{4}	4.07×10^{-5}
80	2.49×10^{4}	6.39×10^{-5}
90	1.10×10^{4}	1.45×10^{-4}
98	119.73	1.33×10^{-2}

Table S5 The resistance (R) and conductivity (σ) of **1** (297 K and 98% RH) under different time.

Time (h)	R (Ω)	σ (S/cm)
0	119.73	1.33×10^{-2}
2	126.38	1.26×10^{-2}
4	123.04	1.29×10^{-2}
6	121.74	1.31×10^{-2}
8	120.09	1.33×10^{-2}



Scheme S1 The synthesis route of the complex **1**.

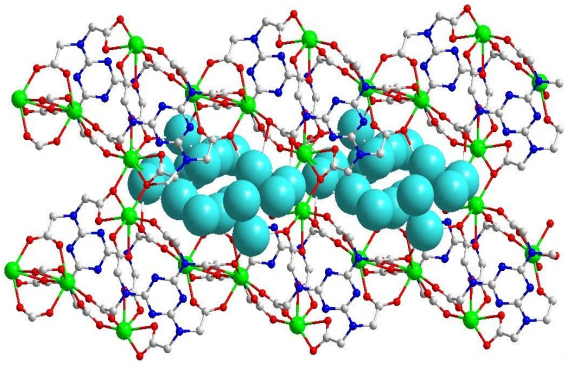


Fig. S1 The layered structure of **1** filled with protons inside the cavities, where the protons are labeled as aqua for clearly.

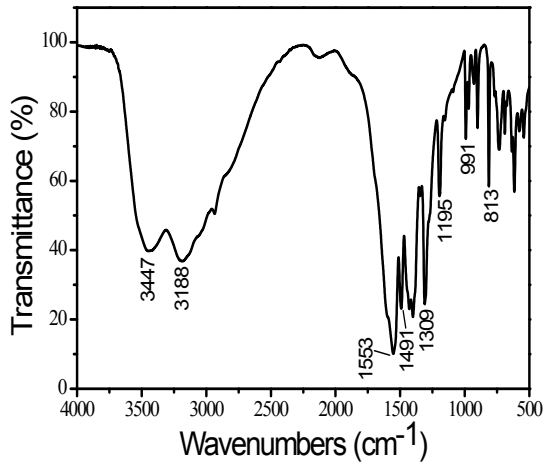


Fig. S2 The IR spectra of complex **1**.

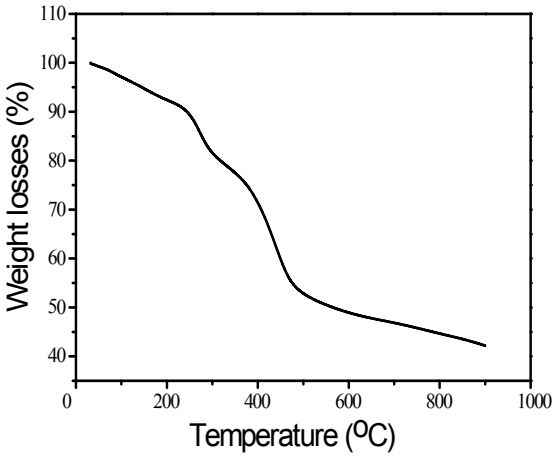


Fig. S3 The TGA curve of complex **1**.

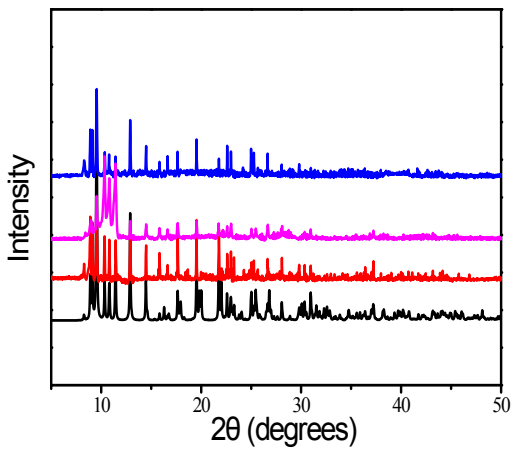


Fig. S4 Powder X-ray diffraction spectra for **1** in different conditions. Simulated (black), As-synthesized (red), Immersed in water for a week (magenta) and Post-impedance (blue).

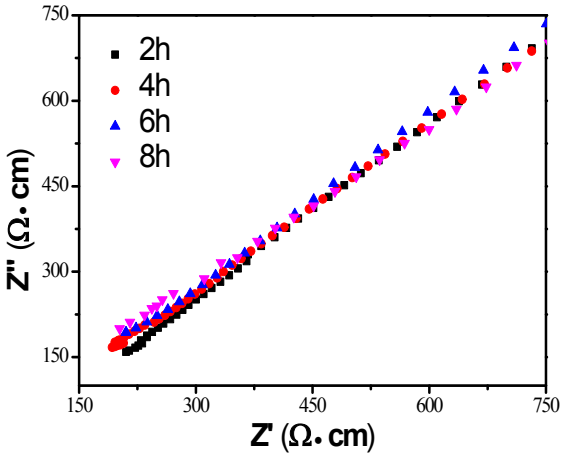


Fig. S5 The Nyquist plots for proton conductivity of **1** (297 K and 98% RH) at 2h, 4h, 6h and 8h.

References

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