Electronic supplementary information

Oxalate-assisted assembly of two polyoxotantalate supramolecular frameworks with proton conduction property

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Section S1： Syntheses and Methods

1. Characterization Methods

Materials and General methods: All the other reactants and solvents were obtained from commercial sources and used for reactions without further purification. Powder X-ray diffraction (PXRD) patterns were measured using a Rigaku Ultima IV diffractometer with Cu-Kα radiation (λ = 1.5418 Å) in the range 5-50° IR spectra were recorded on PerkinElmer Spectrum One FT-IR infrared spectrophotometer with pressed KBr pellets in the range of 4000-500 cm^{-1}. The UV-vis spectra were collected on a SHIMADZU UV-2600 UV-visible spectrophotometer by using the BaSO4 as the blank. Simulated XRD data were simulated by the Mercury Software with the step of 0.02° from 5° to 50° (λ=1.54056Å). Thermal analyses were performed from 30 °C to 800 °C in a dynamic air atmosphere with a heating rate of 10 ^{o}C/min, using a NETZSCH STA 449C thermal analyzer. N2 and water vapor adsorption capacities were tested by using Micromeritics ASAP (Accelerated Surface Area and Porosimetry) 2020 system. Energy dispersive spectrometry (EDS) analyses were performed using a Hirox SH-4000 M type desktop scanning electron microscope.

Single-crystal structure analysis: Crystals data of **1** and **2** were collected on Bruker Apex Duo CCD diffractometer equipped with a fine focus, 2.0 kW sealed tube X-ray source (MoKα radiation, λ = 0.71073 Å) operating at 175 K. Structures were solved by direct methods followed by successive difference Fourier methods. The structures of **1** and **2** were solved through direct methods and refined by full-matrix least-squares refinements based on F^2 adopting the SHELXTL program package. All non-H atoms were located with successive difference Fourier syntheses and refined anisotropically. The contribution of disordered solvent molecules to the overall intensity data of structures was treated using the SQUEEZE method in PLATON. The cobalt complex (Co5) in **1** is disordered over two positions. The crystallographic data of **1** and **2** was summarized in Table S6. CCDC 2231766 and 2231765 contain supplementary structural information for **1** and **2**.

Proton Conduction measurement: Ac impedance measurements were carried out with a SI 1260 IMPEDANCE/GAINPHASE analyzer over the frequency range from 0.1 Hz to 10 MHz with an applied voltage of 50 mV. The relative humidity was controlled by a STIKCorp CIHI-150BS3

incubator. The test sample was pressed to form a cylindrical pellet of crystalline powder sample (~1mm thickness × 5mm diameter) coated with C-pressed electrodes, and both sides of the sample pellet were attached to two silver electrodes. The self-made device containing a cylindrical pellet was placed in a constant temperature & humidity incubator before testing in a temperature range from 25 °C to 85 °C and relative humidity between 55% -98%.

2. Syntheses

Synthesis of $H[Co^{III}(en)_3]_3[Co^{III}(en)_2O](C_2O_4)\{(Ta_6O_{19})_2[Co^{II}(C_2O_4)(H_2O)_2]_2[Co^{III}(en)(H_2O)]_2\}\cdot 41H_2O$ (1): A mixture of $Na_8[Ta_6O_{19}]\cdot 24.5H_2O$ (**Ta_6**) (0.12 g), $K_2C_2O_4$ (0.09 g), CoC_2O_4 (0.08 g), 0.05 mL en (en=ethylenediamine), and 6 mL of C_2H_3N /H_2O (1:5) (C_2H_3N = Acetonitrile) (pH = 10.4) was stirred in a 20 mL vial, and then heated at 80 °C for 3 days, finally cooled to room temperature. After washing with ethanol, brown strip crystals were obtained. Yield: 19 mg (11.8% based on **Ta_6**). IR (KBr pellet, *v*/cm^{-1}, Fig. S10): 3210(s), 1631(m), 1384(w), 1309(s), 1159(s), 1054(w), 865(s), 730(s), 547(m).

Synthesis of $[Co^{III}(en)_3]_4C_2O_4\{Ta_6O_{19}[Co^{III}(en)]\}_2\cdot 66H_2O$ (**2**): A mixture of $Na_8[Ta_6O_{19}]\cdot 24.5H_2O$ (**Ta_6**) (0.12 g), $K_2C_2O_4$ (0.09 g), CoC_2O_4 (0.08 g), 0.05 mL en (en=ethylenediamine), and 6 mL Na_2CO_3/$NaHCO_3$ buffer solution (pH = 10.0) was stirred in a 20 mL vial, and then heated at 80 °C for 3 days, finally cooled to room temperature. After being washed with ethanol, green bar crystals were obtained. Yield: 30 mg (19.9% based on **Ta_6**). IR (KBr pellet, *v*/cm^{-1}, Fig. S10): 3280(s), 1644(m), 1386(w), 1322(s), 1159(s), 1058(w), 856(s), 730(s), 547(m).

Section S2 Additional Tables

Table S1 Bond lengths and valence band summations of cobalt atoms in **1**.

Atom 1	Atom 2	Rjj	R0	B	Sjj	SUM
Co1	N9	1.977(12	1.62	0.4	0.43241004	
	N10	1.947(12	1.62	0.4	0.46442630	
	O2	1.961(8)	1.65	0.4	0.48167956	
	O3	1.954(8)	1.65	0.4	0.48977483	
	O17	1.997(8)	1.65	0.4	0.44211268	
	O3W	1.955(11	1.65	0.4	0.48941346	2.79981
Co2	N2	1.941(9)	1.62	0.4	0.47023448	
	N3	1.972(9)	1.62	0.4	0.43677664	
	N4	1.962(9)	1.62	0.4	0.44730087	
	N5	1.962(10	1.62	0.4	0.44815369	
	N6	1.980(9)	1.62	0.4	0.42853581	
	N7	1.975(10	1.62	0.4	0.43449474	2.66549
Co3	O6	2.020(7)	1.65	0.4	0.41865240	
	O9	2.089(8)	1.65	0.4	0.35514181	
	O13	2.080(8)	1.65	0.4	0.36283411	
	O21	2.014(8)	1.65	0.4	0.42457497	
	O1W	2.149(9)	1.65	0.4	0.30779129	
	O2W	2.158(10	1.65	0.4	0.30184032	2.17083
Co4	N1	1.952(10	1.62	0.4	0.45895205	
	N1	1.952(10	1.62	0.4	0.45895205	
	N8	1.966(9)	1.62	0.4	0.44306108	
	N8	1.966(9)	1.62	0.4	0.44306108	
	N11	1.961(9)	1.62	0.4	0.44836714	
	N11	1.961(9)	1.62	0.4	0.44836714	2.70076
Co5	N13	1.91(2)	1.62	0.4	0.50734124	
	N14	2.11(2)	1.62	0.4	0.31513256	
	N12	1.87(2)	1.62	0.4	0.55803514	
	N15	1.81(2)	1.62	0.4	0.64372981	
	O11	1.964(18	1.65	0.4	0.47916307	
	O11	2.066(18	1.65	0.4	0.37584764	2.87924

Table S2 Hydrogen Bond Lengths (Å) and Bond Angles (°) in **1**

No	D-H	H···O	D···O	<(DHO)	Hydrogen bonds

1	0.91	2.29	3.019(13)	137.3	N1-H1A···O5
2	0.91	2.21	3.016(12)	146.7	N1-H1A···O7
3	0.91	2.56	2.990(13)	109.8	N1-H1A···O15
4	0.91	2.06	2.955(13)	165.6	N2-H2A···O9
5	0.91	1.92	2.800(11)	162.7	N2-H2B···O4#1
6	0.91	2.1	3.004(13)	175.7	N3-H3A···O24#5
7	0.91	2.19	3.013(11)	149.4	N3-H3B···O16#1
8	0.91	2.65	3.331(13)	132.6	N4-H4A···O24#5
9	0.91	2.17	3.060(13)	166.9	N4-H4A···O25#5
10	0.91	2.07	2.944(11)	160	N4-H4B···O16#6
11	0.91	2.66	3.307(13)	128.7	N5-H5A···O9
12	0.91	2.08	2.955(13)	161.8	N5-H5A···O20
13	0.91	1.94	2.841(13)	170.7	N5-H5B···O10#6
14	0.91	2.24	3.062(13)	149.9	N6-H6A···O18#7
15	0.91	2.31	3.132(12)	150.2	N6-H6B···O5#6
16	0.91	2.52	3.283(11)	141.1	N6-H6B···O10#6
17	0.91	2.35	3.069(14)	135.8	N7-H7A···O18#7
18	0.91	2.16	2.960(13)	146.3	N7-H7A···O20#7
19	0.91	1.96	2.839(12)	163.1	N8-H8C···O7
20	0.91	1.97	2.854(13)	162	N8-H8D···O24#3
21	0.91	2.19	2.974(15)	143.6	N9-H9A···O6
22	0.91	2.13	3.036(14)	173.2	N9-H9B···O8#1
23	0.91	2.2	3.038(15)	152.9	N10-H10B···O26
24	0.91	2.07	2.948(12)	161.1	N11-H11A···O16#2
25	0.91	1.97	2.871(12)	171.7	N11-H11B···O25
26	0.99411	2.6839	3.337(15)	123.67	C2-H2D···O24#5
27	0.99	2.59	3.310(15)	129.9	C3-H3D···O9
28	0.99	2.6	3.491(14)	149.7	C4-H4C···O25#5
29	0.99	2.56	3.36(2)	138.6	C6-H6C···O7W#6
30	0.99	2.64	3.549(15)	153.1	C6-H6D···O20
31	0.99	2.5	3.404(14)	151.7	C7-H7C···O20#7
32	0.99	2.61	3.198(16)	118	C8-H8B···O18#7
33	0.99	2.42	3.405(16)	171.9	C9-H9D···O22
34	0.99	2.35	3.262(16)	152.1	C11-H11D···O24#8
35	0.99	2.57	3.33(2)	133.6	C14-H14C···O25#2
36	0.91	2.14	2.99(2)	155.5	N12-H12C···O17#4
37	0.91	2.25	3.07(3)	149.7	N13-H13C···O12
38	0.91	2.35	3.02(2)	130.5	N13-H13C···O23

39	0.91	2	2.89(2)	165.3	N14-H14A···O26#4
40	0.91	1.92	2.78(2)	157.5	N14-H14B···O18
41	0.99	2.3	3.07(3)	134.3	C16-H16B···O13#4
42	0.99	2.73	3.26(3)	113.5	C17-H17A···O13#4
43	0.99	2.44	3.32(3)	147.2	C17-H17A···O18#4
44	0.99	2.58	3.39(3)	138.7	C19-H19B···O13
45	0.85	2.65	3.15(3)	119.3	O11-H11···O13
46	0.9589	2.80911	2.997(14)	91.96	O1W-H1WA···O3W
47	0.9589	2.21414	2.725(15)	112.38	O1W-H1WA···O4W
48	0.95	1.93	2.873(16)	172.3	O2W-H2WA···O8W
49	0.95	2.32	3.013(13)	129.3	O3W-H3WB···O1#1
50	0.95	2.58	3.073(15)	112.3	O3W-H3WB···O21
Symmetric codes:					
#1 -x+1/2,-y+1/2,-z,		#2 -x+1,y,-z+1/2,		#3 -x+1,-y+1,-z,	
#4 -x+1/2,-y+1/2,-z+1,		#5 x-1/2,y-1/2,z		#6 -x+1/2,y-1/2,-z+1/2,	
#7 x,-y,z-1/,		#8 x,-y+1,z+1/2			

Table S3 Bond lengths and valence band summations of cobalt atoms in **2**.

Atom 1	Atom 2	Rjj	R0	B	Sjj	SUM
Co1	O9	1.884(8)	1.655	0.42	0.576401	□
□	N13	1.938(12)	1.625	0.42	0.48168	□
□	N14	1.949(9)	1.625	0.42	0.468001	□
□	O8	1.957(12)	1.655	0.42	0.500026	□
□	O2	1.959(8)	1.655	0.42	0.482828	□
□	O3	1.976(8)	1.655	0.42	0.459718	2.968652
Co2	N12	1.937(14)	1.625	0.42	0.48444	□
□	N2	1.936(13)	1.625	0.42	0.478024	□
□	N8	1.941(11)	1.625	0.42	0.474734	□
□	N10	1.950(12)	1.625	0.42	0.46467	□
□	N6	1.986(11)	1.625	0.42	0.450615	□
□	N11	1.980(14)	1.625	0.42	0.427313	2.779795
Co3	N3	1.949(14)	1.625	0.42	0.467221	□
□	N4	1.955(13)	1.625	0.42	0.449008	□
□	N7	1.957(12)	1.625	0.42	0.447514	□
□	N9	1.961(13)	1.625	0.42	0.432843	□
□	N5	1.973(14)	1.625	0.42	0.430376	□
□	N1	1.976(13)	1.625	0.42	0.418952	2.645914

Table S4 Hydrogen Bond Lengths (Å) and Bond Angles (°) in **2**

No.	D-H	H···O	D···O	<(DHO)	Hydrogen bonds
1	0.89	2	2.839(18)	157.1	N1-H1D···O13
2	0.89	2.3	3.103(15)	149.5	N2-H2A···O4
3	0.89	2.66	3.154(15)	116.4	N2-H2A···O14
4	0.89	2.51	3.255(16)	141.2	N2-H2A···O15
5	0.89	2.6	3.35(3)	142	N3-H3C···O5W
6	0.89	1.91	2.796(15)	176	N3-H3D···O16#3
7	0.89	2.43	3.22(2)	148.3	N4-H4A···O5W
8	0.89	2.12	2.934(16)	151.6	N4-H4B···O13
9	0.89	1.93	2.800(19)	167.3	N5-H5C···O20#4
10	0.89	2.21	3.016(16)	150.2	N5-H5D···O11
11	0.89	2.01	2.837(16)	153.7	N6-H6A···O11#5
12	0.89	2.11	2.976(18)	164.9	N6-H6B···O2W#6
13	0.89	2.02	2.881(17)	161.9	N7-H7C···O21#3
14	0.89	2.21	3.090(15)	169.1	N7-H7D···O10#3
15	0.89	2.14	2.940(17)	149.8	N8-H8A···O10
16	0.89	2.01	2.889(18)	170.9	N8-H8B···O21
17	0.89	2.65	3.085(17)	110.9	N9-H9A···O18#3
18	0.89	2.16	2.948(16)	147.9	N9-H9B···O15#3
19	0.89	2.5	3.184(15)	133.9	N9-H9B···O16#3
20	0.89	2.49	3.223(14)	140.7	N10-H10A···O3#5
21	0.89	2.48	3.279(15)	150.3	N10-H10A···O12#5
22	0.89	2.11	2.991(14)	169.6	N11-H11A···O4
23	0.89	2.01	2.871(15)	163.6	N12-H12A···O12#5
24	0.89	2	2.861(18)	162.8	N12-H12B···O20
25	0.89	2.18	3.009(16)	155.4	N13-H13B···O7
26	0.89	2.35	3.069(16)	137.4	N14-H14A···O11
27	0.89	2.2	3.079(18)	167.7	N14-H14B···O2W#1
28	0.97	2.56	3.051(14)	111.4	C2-H2C···O2#6
29	0.97	2.5	3.40(2)	153.7	C4-H4C···O21#3
30	0.97	2.5	3.36(2)	147.1	C6-H6C···O20#4
31	0.97	2.64	3.45(2)	141.5	C8-H8C···O17#3
32	0.97	2.57	3.41(2)	145.1	C9-H9C···O19

Symmetric codes:

#1 -x,-y+2,-z, #2 -x+1/2,-y+3/2,-z+1, #3 -x+1/2,y+1/2,-z+1/2, #4 x,-y+2,z-1/2,

#5 x,-y+2,z+1/2, #6 -x,y,-z+1/2

Table S5 The proton conductivity of known high-dimensional porous POM-based proton conducting materials

Compounds	*Conductivity [S cm^{-1}]*	*Condition (Temp., RH)*	*Ref*
$H_{14}[Na_6(H_2O)_{12}]_4[K_{42}Ge_8W_{72}O_{272}(H_2O)_{60}]$·solvent	6.80×10^{-2} S cm^{-1}	85 °C, 98% RH	S1
$[Co(en)_3]_2C_2O_4\{Ta_6O_{19}[Co(en)(H_2O)]\}_2 \cdot 17H_2O$	5.76×10^{-2} S cm^{-1}	85 °C, 98% RH	This work
$(HIm)_{24}(NH_4)_{20}[Mo_{72}{}^{VI}Mo_{60}{}^{V}O_{372}(CH_3COO)_{30}(H_2O)_{72}] \cdot 190H_2O$	5.00×10^{-2} S cm^{-1}	60 °C 98% RH	S2
$K_8Na_3Li_5\{[Na(NO_3)(H_2O)]_4[Al_{16}(OH)_{24}(H_2O)_8(P_8W_{48}O_{184})]\} \cdot 66H_2O$	4.50×10^{-2} S cm^{-1}	85 °C, 70% RH	S3
$Na_5[H_7\{N(CH_2PO_3)_3\}Mo_6O_{16}(OH)(H_2O)_4]_4 \cdot 18H_2O$	2.55×10^{-2} S cm^{-1}	100 °C, 98% RH	S4
$[P_2Mo_5O_{23}][C_7H_7N_2]_6 \cdot H_2O$	1.91×10^{-2} S cm^{-1}	50 °C, 98% RH	S5
$(TEAH)_{14}Na_{10}K_8H_8\{P_5W3_0\}_2\{Mo_{22}Fe_8\} \cdot 50H_2O$	1.70×10^{-2} S cm^{-1}	95 °C 90% RH	S6
$[La_3(H_2O)_{22}][P_2W_{15}Ta_3O_{62}] \cdot 16H_2O$	1.26×10^{-2} S cm^{-1}	95 °C, 98% RH	S7
$H_2[Cu(en)_2(H_2O)_2]\{[Cu(en)_2]_4[Cu(en)(Ta_6O_{19})]_2\} \cdot 14H_2O$	1.04×10^{-2} S cm^{-1}	75 °C, 98% RH	S8
$[Sm(H_2O)_5(CO_2CH_2NH_3)_2][Al(OH)_6Mo_6O_{18}] \cdot 10H_2O$	4.53×10^{-3} S cm^{-1}	80 °C, 95% RH	S9
$[H_3(3\text{-}PyBim)_2][PMo_{12}O_{40}] \cdot 3.5H_2O \cdot CH_3CN \cdot CH_3OH$	3.34×10^{-3} S cm^{-1}	100 °C, 98% RH	S10
$Na_{16}(NH_4)_{10}H_8\{[W_{14}Ce^{IV}{}_6O_{61}]([W_3Bi_6Ce^{III}{}_3(H_2O)_3O_{14}][BiW_9O_{33}]_3)_2\} \cdot ca38H_2O$	2.40×10^{-3} S cm^{-1}	25 °C, 98% RH	S11
$[Co(bpz)(Hbpz)][Co(SO_4)_{0.5}(H_2O)_2(bpz)]_4[PMo^{VI}{}_8Mo^{V}{}_4V^{IV}{}_4O_{42}] \cdot 13H_2O$	1.50×10^{-3} S cm^{-1}	75 °C, 98% RH	S12
$[M(H_2O)_8][H(H_2O)_{23}](HINO)_4[PXO_{40}]$ (M=Zn, Mn, Cu; X=W, Mo)	1.30×10^{-3} S cm^{-1}	100 °C, 98% RH	S13
$H[Co(en)_3]_3[Co(en)_2O]C_2O_4\{Ta_6O_{19}[Co(C_2O_4)(H_2O)_2][Co(en)(H_2O)]\}_2$	1.00×10^{-3} S cm^{-1}	85 °C, 98% RH	This work
$A_2[Cr_3O(OOCH)_6(etpy)_3]_2[aSiW_{12}O_{40}] \cdot nH_2O$	4.40×10^{-4} S cm^{-1}	50 °C 95% RH	S14
$(H_2en)_4H_2[V_{12}B_{18}O_{54}(OH)_6(H_2O)] \cdot 11H_2O$	1.90×10^{-4} S cm^{-1}	60 °C 98% RH	S15

Table S6 Crystallographic data of **1** and **2**

Compounds	***1***	***2***
Empirical formula	$H_{177}C_{32}Co_8N_{26}O_{98}Ta_{12}$	$H_{218}C_{30}Co_6N_{28}O_{111}Ta_{12}$
formula weight	5137.83	5273.29
crystal system	monoclinic	Monoclinic
space group	*C*2/*c*	*C*2/*c*
a (Å)	31.6228(8)	37.181(13)
b (Å)	31.5888(7)	18.194(6)
c (Å)	15.5673(3)	24.574(9)
α (°)	90	90
β (°)	99.348(2)	118.206(4)
γ (°)	90	90
volume (Å^3), Z	15344.1(6)	14649(9)
D_{calc} (g/cm^3)	2.224	2.391
F(000)	9708	10080
Temperature (K)	175	175
μ (mm^{-1})	9.454	9.696
θ range (°)	4.082 - 61.508	3.762 - 51.764
reflns collected / unique	55766 / 19080	31805 / 13196
restraints / parameters	352 / 703	312 / 577
completeness / %	99.3%	97.5%
GOF on F^2	1.011	1.009
R_{int}	0.0569	0.0474
R_1, wR_2 *[I >2σ(I)]*	R_1 = 0.0633, wR_2 = 0.1447	R_1 = 0.0549, wR_2 = 0.1512
R_1, wR_2 *(all data)*	R_1 = 0.0887, wR_2 = 0.1542	R_1 = 0.0760, wR_2 = 0.1610

$R_1{}^a = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(xP)^2 + yP]$, $P = (F_o^2 + 2Fc^2)/3$, where x = 0.0773, y = 309.1895 for **1**; x = 0.0403, y = 822.5073 for **2** .

Section S3 Additional Figures

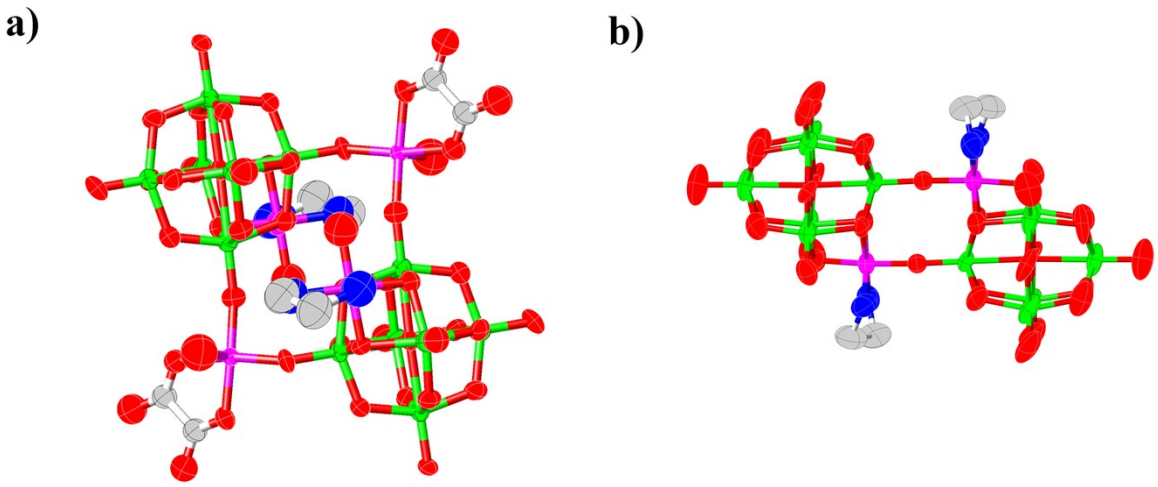

Fig. S1 a) Ball-stick and ellipsoid diagrams of the SBU in compound **1**; b) Ball-stick and ellipsoid diagrams of the SBU in compound **2**.

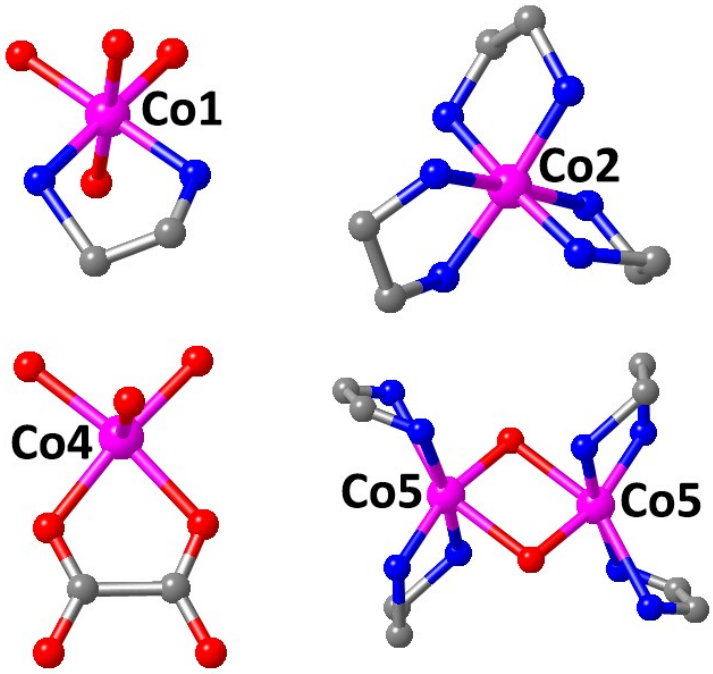

Fig. S2 View of the coordination environments of the cobalt ions in **1**.

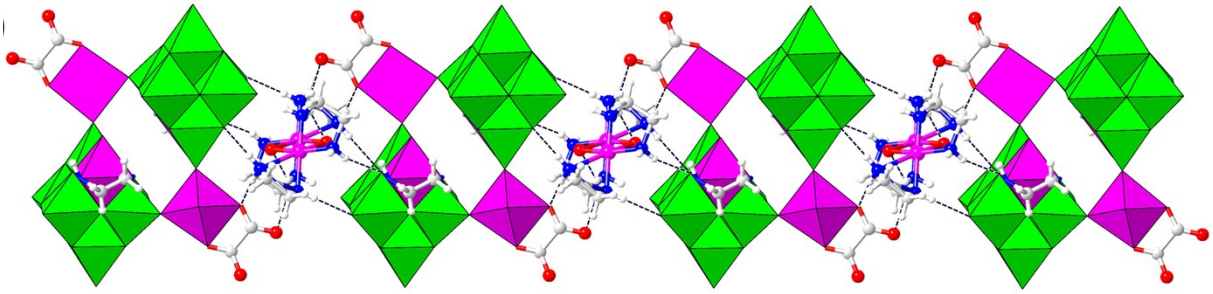

Fig. S3 View of 1D chain built by the dimers $\{Co_2Ta_6\}_2$ and $[Co_2^{III}(\mu\text{-}O)_2(en)_4]$ complexes in **1**.

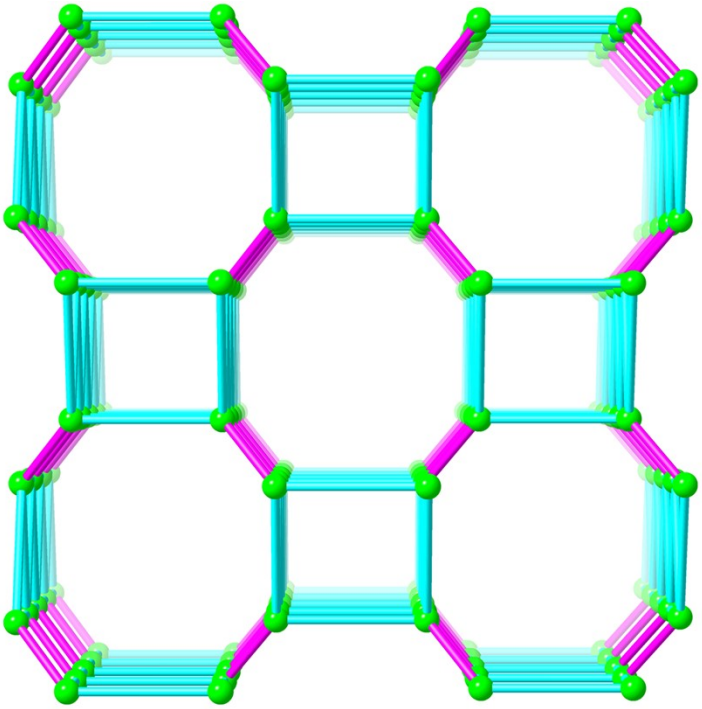

Fig. S4 The topology of **1**. The $\{Co_2Ta_6\}_2$ SBU (green) was simplified as a 5-connected node.

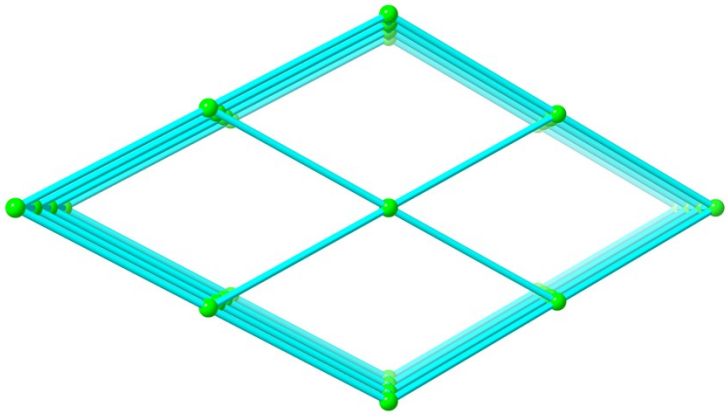

Fig. S5 The topological graph of **2**. $\{Co_2Ta_6\}_2$ SBU (green) as 6-connected nodes.

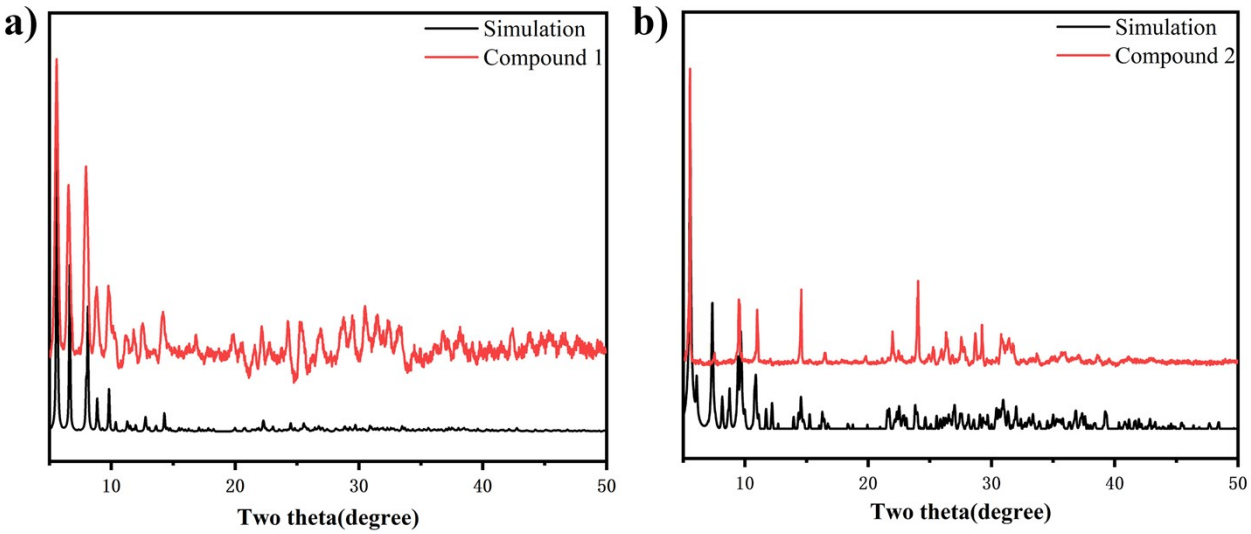

Fig. S6 PXRD patterns of compounds **1** and **2.**

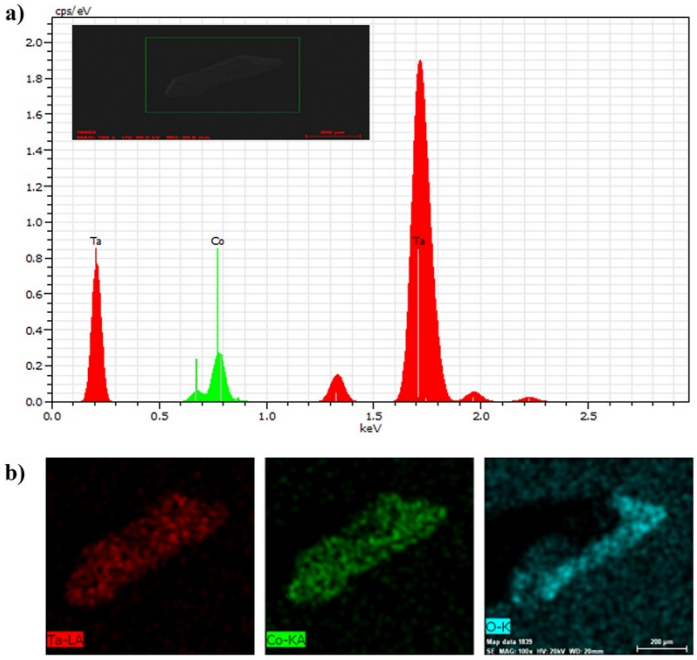

Fig. S7 a) EDS spectra for **1**; b) EDS-mapping for **1**.

EDS analyses of **1**

	Calc	Exp
Ta/Co	1.62	1.5

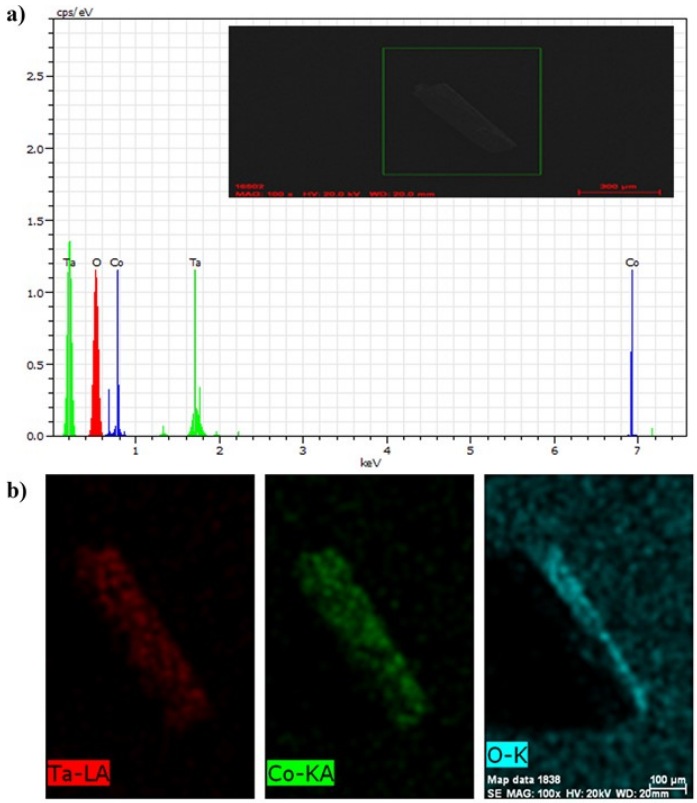

Fig. S8 a) EDS spectra for **2**; b) EDS-mapping for **2**.

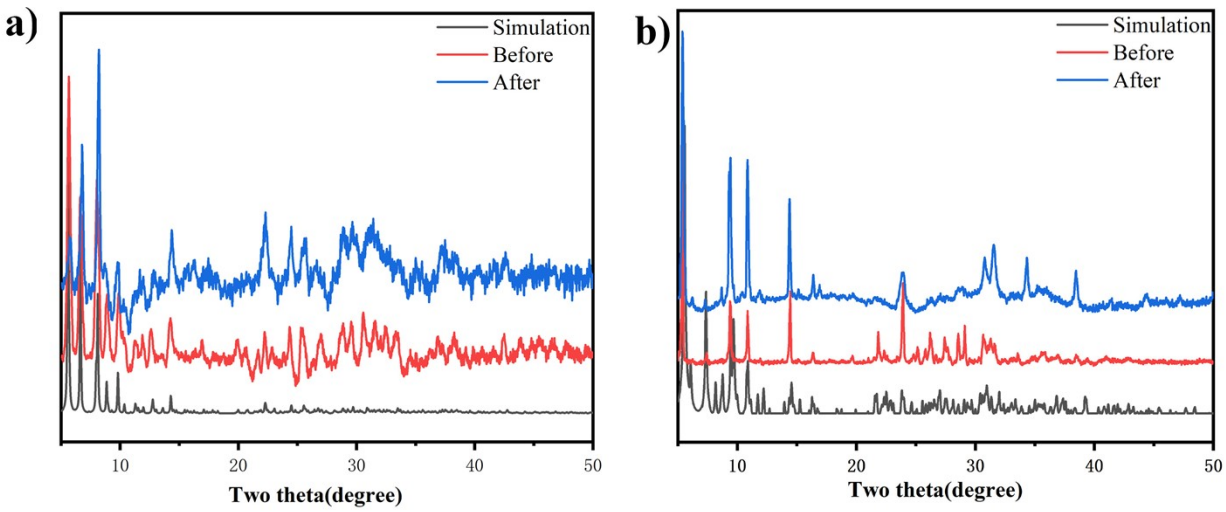

Fig. S9 PXRD patterns of **1** and **2** after the proton conduction test.

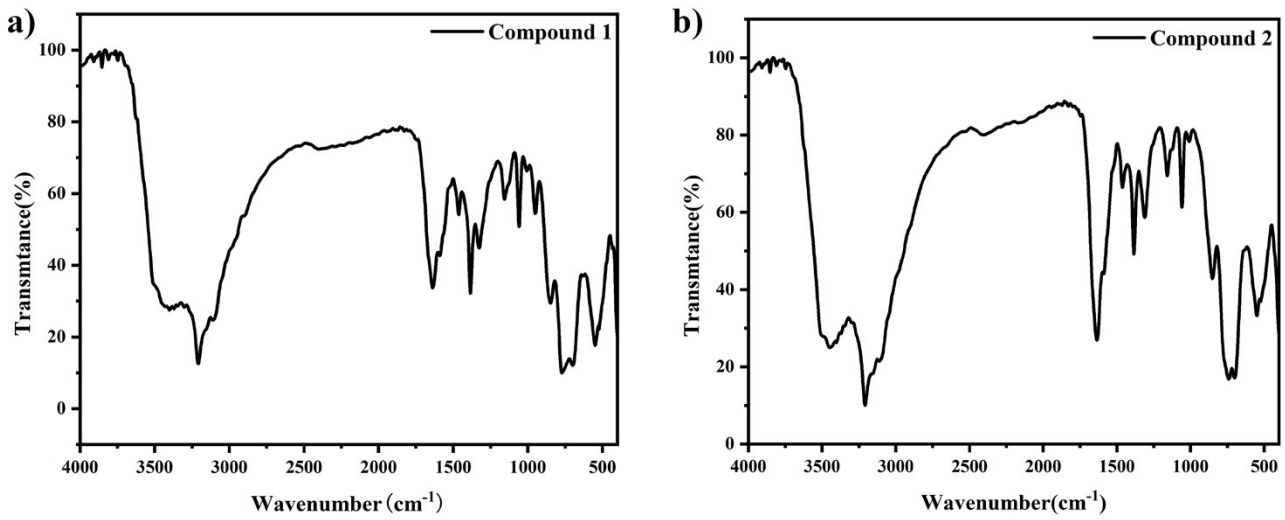

Fig. S10 IR spectra of as-synthesized samples.

The broad absorption peak at 3400cm^{-1} to 3210cm^{-1} is attributed to the ν (O-H) stretching vibration in the IR spectrum. *ν* (C-H) and *ν* (N-H) stretching vibrations occur at about 3140 cm^{-1} and 2930 cm^{-1}. These signals confirmed the presence of organic amine species in the product. The bands between 1465-1324 cm^{-1} and around 820 cm^{-1} are attributed to *ν*C–O and *ν*C–C oxalate symmetric stretching vibrations, respectively. The peaks at $\tilde{\nu}$ = 1060-450 cm^{-1} are assigned to the *ν*(Ta–O_t) and *ν*(Ta–O_b–M) stretching vibrations.

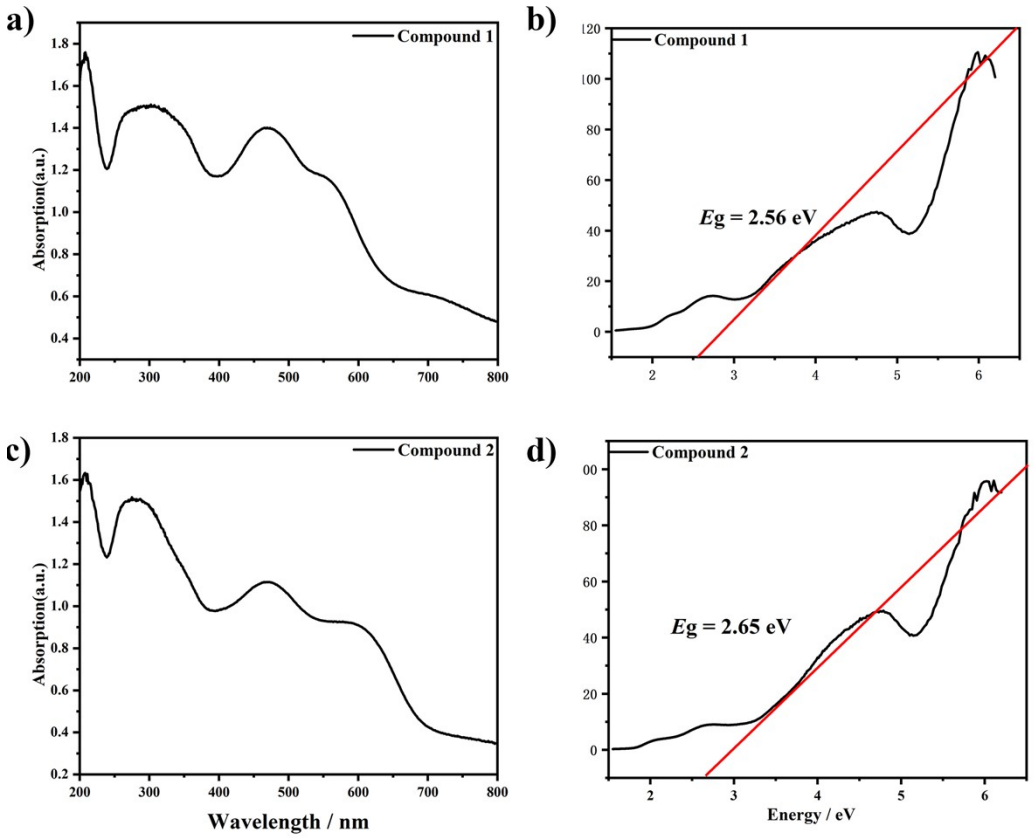

Fig. S11 a-b) The UV-Vis absorption spectra and Kubelka-Munk Function vs. energy curves of **1** (a-b) and **2** (c-d).

The UV diffuse spectra of **1** and **2** are determined in the range of 240 to 800 nm. The absorption peak at around 270 nm can be ascribed to the charge transfer of O→Ta. The two characteristic absorption peaks in the range of 400 and 700 nm can be attributed to organic amine ligands and oxalate to metal charge transfer and *d–d* transitions of cobalt complexes. The E_g values of **1** and **2** are 2.56 eV and 2.65 eV.

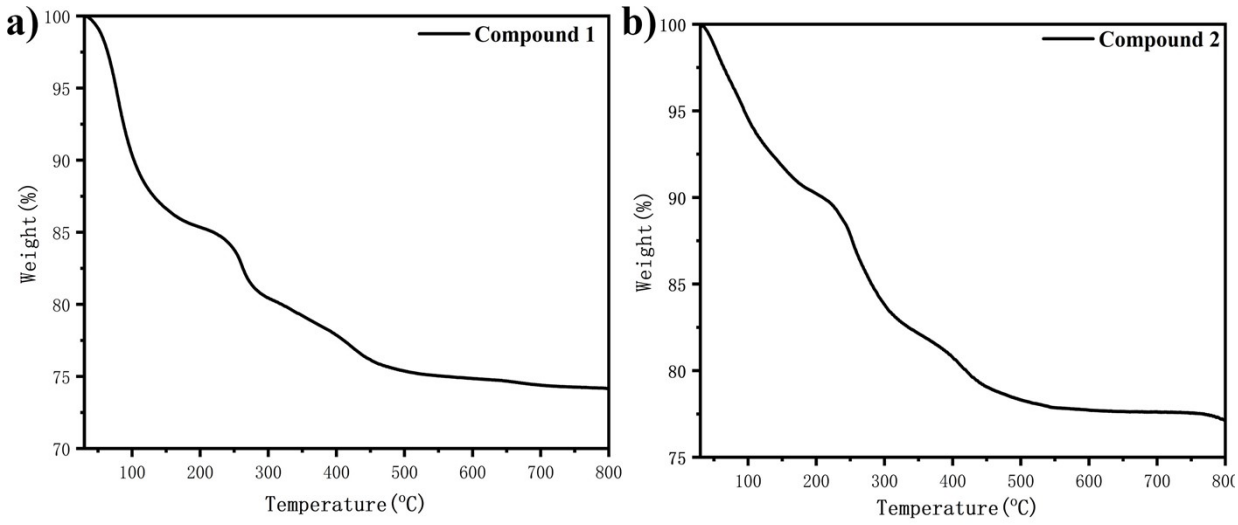

Fig. S12 TG curves of **1** and **2**.

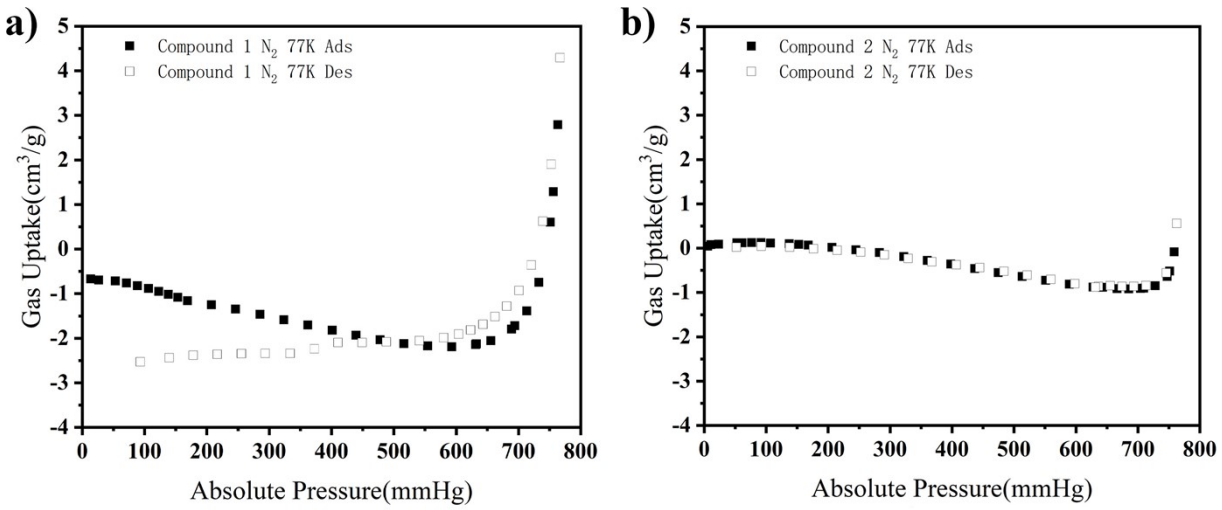

Fig. S13 N_2 adsorption isotherms of **1** and **2**.

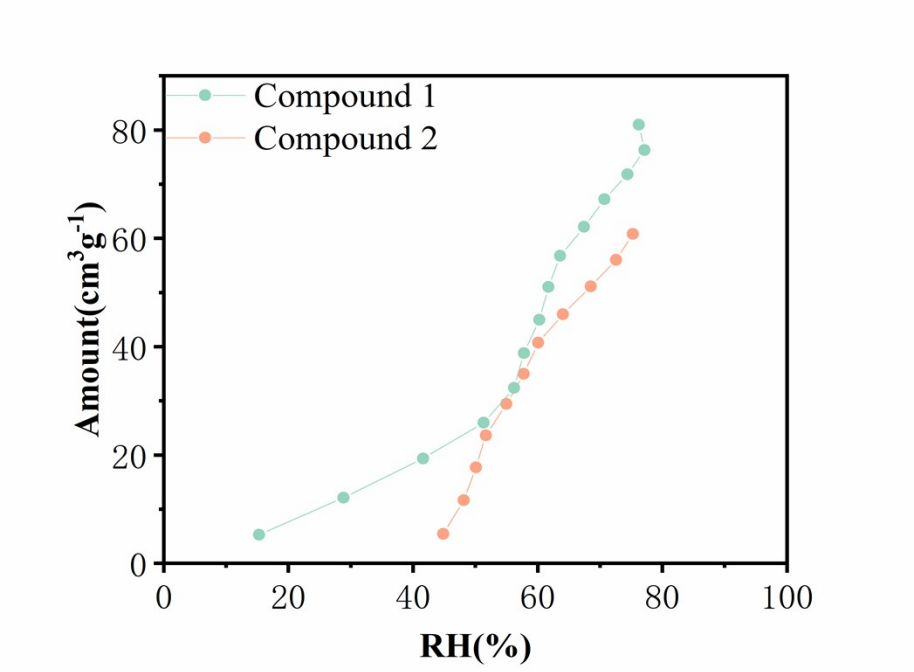

Fig. S14 Water vapor adsorption curve of samples **1** and **2** as a function of *p/p0*.

The weight losses in the TGA curves indicate that the extra-framework species in compounds **1** and **2** were removed as the temperatures increased (Fig. S12). Furthermore, no N_2 uptakes were observed at 77 K for compounds **1** and **2** (Fig. S13), but they show moderate water vapor adsorption capacities (Fig. S14). Actually, POM cluster-based porous materials show no N_2 uptake capacities but have water vapor adsorption capacities that have been reported.[S16] Therefore, combining the single-crystal data, the TGA, the gas adsorption, and water vapor adsorption results, compounds **1** and **2** can be considered as potential porous materials.

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