Electronic Supplementary Material (ESI) for Dalton Transactions.

Mixed-valence compounds based on heterometal-oxo-clusters containing Sb(III, V): Crystal structures and proton conduction

Wei-Yang Wen,[b,c] Wen Ma,*[a,b] Bing Hu,*[b,d] Hui-Ping Xiao,[c] Tian-Yu Pan,[b,c] Jia-Ting Liu,[b,c] Hao-Wei Lin,[b,c] Xin-Xiong Li[c] and Xiao-Ying Huang*[b,d]

[a] *School of Materials and Chemical Engineering, Xuzhou University of Technology, Xuzhou, Jiangsu, China. mawen@xzit.edu.cn*

[b] *State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China. E-mail: xyhuang@fjirsm.ac.cn, hubing@fjirsm.ac.cn*

[c] *College of Chemistry, Fuzhou University, Fuzhou 350116, Fujian, China.*

[d] *University of Chinese Academy of Sciences, Beijing 100049, China.*

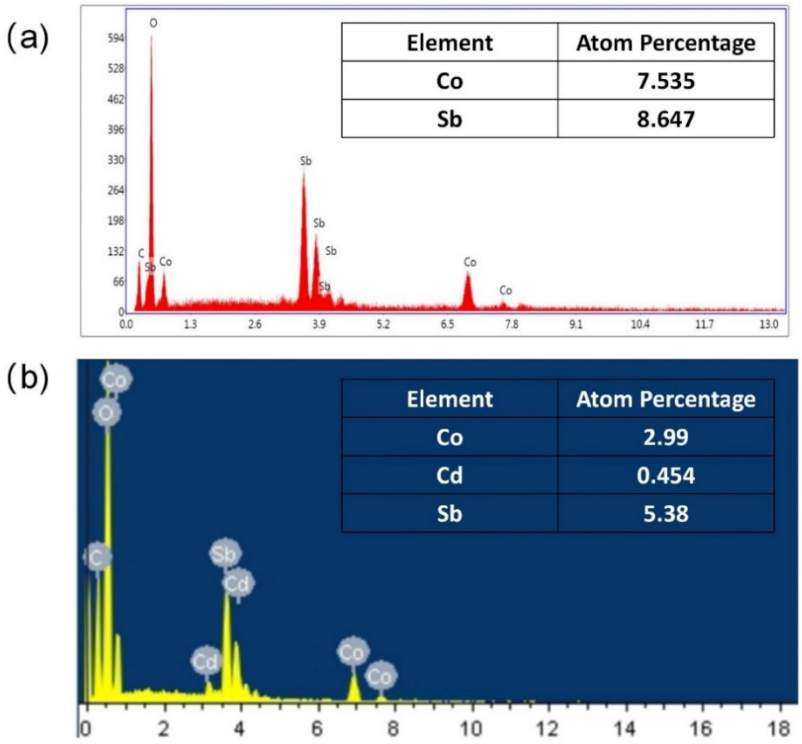

Fig. S1 Energy dispersive spectroscopy (EDS) results of compounds **1** (a) and **2** (b).

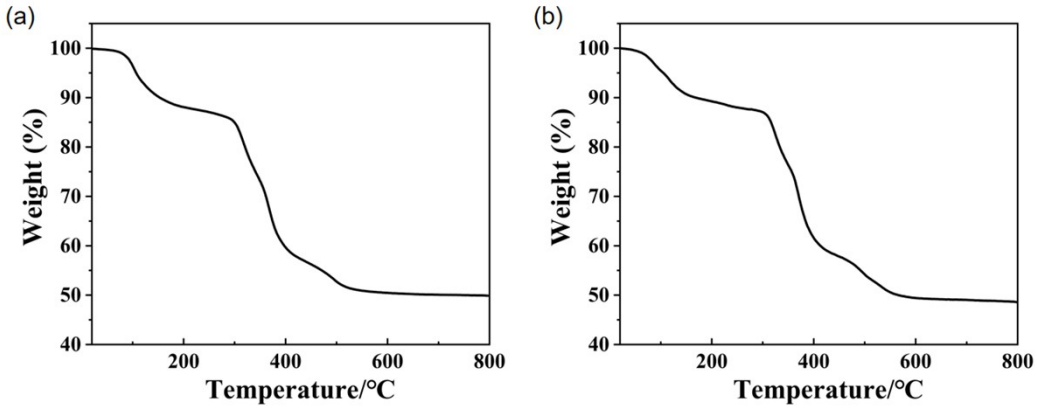

Fig. S2 Thermogravimetric curves for compounds **1** (a) and **2** (b).

Table S1 Selected bond lengths (Å) and angles (°) for **1** and **2**.

compound **1**			
Sb(1)-O(37)	1.983(4)	Sb(4)-O(23)	2.271(5)
Sb(1)-O(38)	1.980(4)	Sb(4)-O(42)	1.978(4)
Sb(1)-O(39)	1.985(4)	Sb(4)-O(43)	2.106(4)
Sb(1)-O(40)	1.993(4)	Sb(5)-O(4)	2.001(4)
Sb(1)-O(41)	1.981(4)	Sb(5)-O(5)	2.262(5)
Sb(1)-O(42)	1.981(4)	Sb(5)-O(41)	1.977(4)
Sb(2)-O(10)	2.020(4)	Sb(5)-O(44)	2.137(4)
Sb(2)-O(11)	2.331(4)	Sb(6)-O(34)	2.016(4)
Sb(2)-O(39)	1.972(4)	Sb(6)-O(35)	2.339(4)
Sb(2)-O(43)	2.094(4)	Sb(6)-O(40)	1.969(4)
Sb(3)-O(28)	2.002(4)	Sb(6)-O(44)	2.086(4)
Sb(3)-O(29)	2.297(4)	Sb(7)-O(13)	2.326(5)
Sb(3)-O(37)	1.988(4)	Sb(7)-O(15)	2.002(5)
Sb(3)-O(43)	2.123(4)	Sb(7)-O(38)	1.969(4)
Sb(4)-O(22)	2.021(5)	Sb(7)-O(44)	2.086(4)
O(37)-Sb(1)-O(40)	169.90(17)	O(43)-Sb(3)-O(29)	151.55(16)
O(38)-Sb(1)-O(37)	80.11(17)	O(22)-Sb(4)-O(23)	75.29(18)
O(38)-Sb(1)-O(39)	93.52(17)	O(22)-Sb(4)-O(43)	79.81(18)
O(38)-Sb(1)-O(40)	93.31(17)	O(42)-Sb(4)-O(22)	97.45(18)
O(38)-Sb(1)-O(41)	93.50(17)	O(42)-Sb(4)-O(23)	82.86(17)
O(38)-Sb(1)-O(42)	170.82(17)	O(42)-Sb(4)-O(43)	86.19(16)
O(39)-Sb(1)-O(37)	93.51(17)	O(43)-Sb(4)-O(23)	151.15(17)
O(39)-Sb(1)-O(40)	79.15(16)	O(4)-Sb(5)-O(5)	75.49(17)
O(41)-Sb(1)-O(37)	95.49(17)	O(4)-Sb(5)-O(44)	77.66(16)
O(41)-Sb(1)-O(39)	169.41(18)	O(41)-Sb(5)-O(4)	97.07(17)
O(41)-Sb(1)-O(40)	92.54(17)	O(41)-Sb(5)-O(5)	85.34(17)
O(41)-Sb(1)-O(42)	80.07(17)	O(41)-Sb(5)-O(44)	85.01(16)
O(42)-Sb(1)-O(37)	93.90(17)	O(44)-Sb(5)-O(5)	150.05(17)
O(42)-Sb(1)-O(39)	93.78(17)	O(34)-Sb(5)-O(35)	74.54(17)

O(42)-Sb(1)-O(40)	93.51(17)	O(34)-Sb(5)-O(44)	79.76(17)
O(10)-Sb(2)-O(11)	74.80(16)	O(40)-Sb(5)-O(34)	97.93(17)
O(10)-Sb(2)-O(43)	79.34(17)	O(40)-Sb(5)-O(35)	83.47(17)
O(39)-Sb(2)-O(10)	97.92(17)	O(40)-Sb(5)-O(44)	86.33(16)
O(39)-Sb(2)-O(11)	84.37(17)	O(44)-Sb(5)-O(35)	150.66(16)
O(39)-Sb(2)-O(43)	85.98(16)	O(15)-Sb(7)-O(13)	74.58(17)
O(43)-Sb(2)-O(11)	150.79(17)	O(15)-Sb(7)-O(44)	80.37(17)
O(28)-Sb(3)-O(29)	75.78(17)	O(38)-Sb(7)-O(13)	82.56(17)
O(28)-Sb(3)-O(43)	78.88(17)	O(38)-Sb(7)-O(15)	96.88(17)
O(37)-Sb(3)-O(28)	95.85(17)	O(38)-Sb(7)-O(44)	86.74(16)
O(37)-Sb(3)-O(29)	85.10(16)	O(44)-Sb(7)-O(13)	151.27(17)
O(37)-Sb(3)-O(43)	84.82(16)		

Compound **2**

Sb(1)-O(37)	1.990(5)	Sb(4)-O(23)	2.288(6)
Sb(1)-O(38)	1.978(5)	Sb(4)-O(42)	1.991(5)
Sb(1)-O(39)	1.983(5)	Sb(4)-O(43)	2.096(5)
Sb(1)-O(40)	1.994(5)	Sb(5)-O(4)	2.009(6)
Sb(1)-O(41)	1.982(5)	Sb(5)-O(5)	2.265(7)
Sb(1)-O(42)	1.983(5)	Sb(5)-O(41)	1.984(5)
Sb(2)-O(10)	2.020(5)	Sb(5)-O(44)	2.130(5)
Sb(2)-O(11)	2.335(6)	Sb(6)-O(34)	2.017(6)
Sb(2)-O(39)	1.979(5)	Sb(6)-O(35)	2.335(6)
Sb(2)-O(43)	2.108(5)	Sb(6)-O(40)	1.979(5)
Sb(3)-O(28)	2.014(6)	Sb(6)-O(44)	2.090(5)
Sb(3)-O(29)	2.297(6)	Sb(7)-O(13)	2.319(6)
Sb(3)-O(37)	1.986(5)	Sb(7)-O(15)	1.998(5)
Sb(3)-O(43)	2.129(5)	Sb(7)-O(38)	1.976(5)
Sb(4)-O(22)	2.006(6)	Sb(7)-O(44)	2.090(6)

O(37)-Sb(1)-O(40)	169.8(2)	O(43)-Sb(3)-O(29)	150.9(2)
O(38)-Sb(1)-O(37)	80.1(2)	O(22)-Sb(4)-O(23)	75.4(2)
O(38)-Sb(1)-O(39)	93.5(2)	O(22)-Sb(4)-O(43)	79.9(2)
O(38)-Sb(1)-O(40)	93.5(2)	O(42)-Sb(4)-O(22)	97.2(2)
O(38)-Sb(1)-O(41)	93.7(2)	O(42)-Sb(4)-O(23)	82.7(2)
O(38)-Sb(1)-O(42)	171.0(2)	O(42)-Sb(4)-O(43)	87.1(2)
O(39)-Sb(1)-O(37)	93.1(2)	O(43)-Sb(4)-O(23)	151.7(2)
O(39)-Sb(1)-O(40)	79.2(2)	O(4)-Sb(5)-O(5)	75.2(2)
O(41)-Sb(1)-O(37)	95.3(2)	O(4)-Sb(5)-O(44)	78.0(2)
O(41)-Sb(1)-O(39)	169.8(2)	O(41)-Sb(5)-O(4)	96.4(2)
O(41)-Sb(1)-O(40)	93.0(2)	O(41)-Sb(5)-O(5)	84.6(2)
O(41)-Sb(1)-O(42)	79.9(2)	O(41)-Sb(5)-O(44)	85.6(2)
O(42)-Sb(1)-O(37)	94.2(2)	O(44)-Sb(5)-O(5)	150.2(2)
O(42)-Sb(1)-O(39)	93.8(2)	O(34)-Sb(5)-O(35)	74.4(2)
O(42)-Sb(1)-O(40)	93.1(2)	O(34)-Sb(5)-O(44)	80.1(2)

O(10)-Sb(2)-O(11)	74.5(2)	O(40)-Sb(5)-O(34)	97.9(2)
O(10)-Sb(2)-O(43)	80.2(2)	O(40)-Sb(5)-O(35)	83.8(2)
O(39)-Sb(2)-O(10)	98.2(2)	O(40)-Sb(5)-O(44)	86.7(2)
O(39)-Sb(2)-O(11)	84.6(2)	O(44)-Sb(5)-O(35)	151.2(2)
O(39)-Sb(2)-O(43)	86.6(2)	O(15)-Sb(7)-O(13)	75.3(2)
O(43)-Sb(2)-O(11)	151.6(2)	O(15)-Sb(7)-O(44)	80.0(2)
O(28)-Sb(3)-O(29)	75.2(2)	O(38)-Sb(7)-O(13)	82.7(2)
O(28)-Sb(3)-O(43)	78.9(2)	O(38)-Sb(7)-O(15)	97.2(2)
O(37)-Sb(3)-O(28)	96.1(2)	O(38)-Sb(7)-O(44)	86.7(2)
O(37)-Sb(3)-O(29)	84.6(2)	O(44)-Sb(7)-O(13)	151.6(2)
O(37)-Sb(3)-O(43)	85.27(19)		

Table S2 The bond valence sum calculations for compounds **1** and **2**.

Atom	BVS of **1**	BVS of **2**	Valence
Sb(1)	4.942	4.926	+5
Sb(2)	2.835	2.788	+3
Sb(3)	2.820	2.786	+3
Sb(4)	2.959	2.860	+3
Sb(5)	2.865	2.837	+3
Sb(6)	2.859	2.828	+3
Sb(7)	2.904	2.896	+3

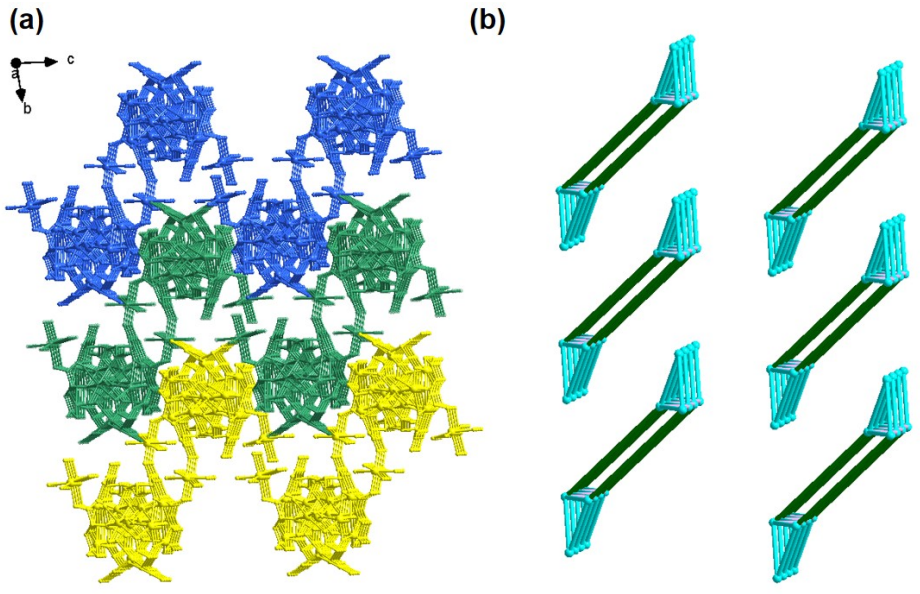

Fig. S3 (a) Packing of the anionic 1-D belts in compound **2** viewed along the *a*-axis. The neighbouring 1D belts are represented in different colors for clarity. (b) Schematic 1-D belt structure viewed along the *a*-axis.

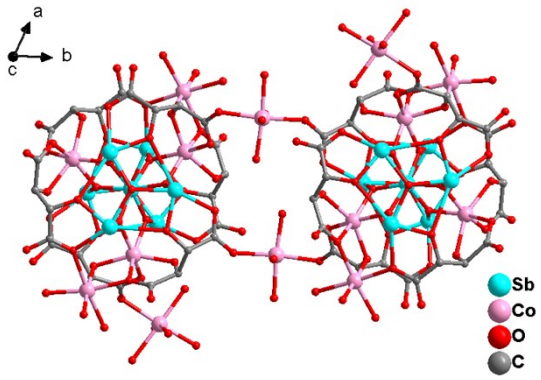

Fig. S4 Structure of the dimerization unit in compound **1**. For clarity, the hydrogen atoms are omitted.

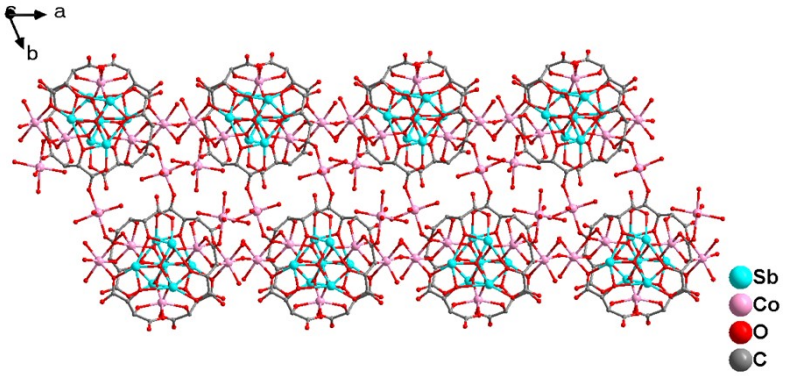

Fig. S5 Structure of the 1-D belt in compound **1**. For clarity, the hydrogen atoms and cation groups are omitted.

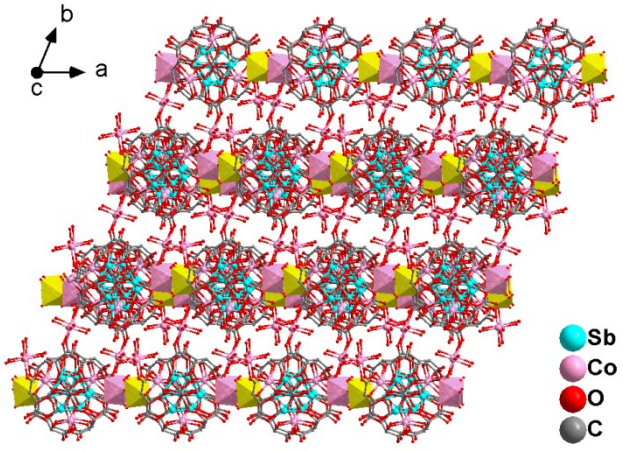

Fig. S6 Packing of the anionic 1-D belts in compound **1** viewed along the *c*-axis. For clarity, the cationic groups as well as lattice water molecules are omitted. Pink polyhedra represent the bridging {Co(4)O_6} structural motifs; yellow polyhedra represent the bridging {$Co_{0.2}$(7)O_6} structural motifs.

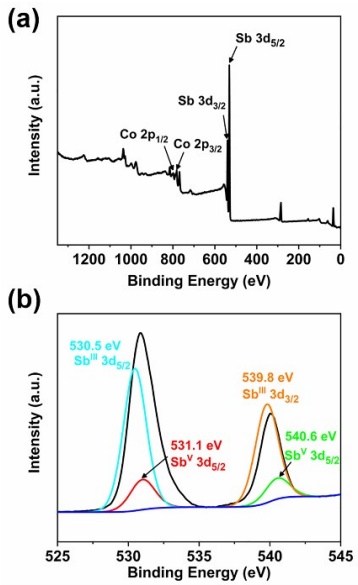

Fig. S7 (a) The survey spectrum of compound **1**. (b) X-ray photoelectron spectra of Sb3d of **1**.

We also carried out the X-ray photoelectron spectroscopy analysis of compound **1**. The characteristic peaks of elements Co and Sb can be found in the total spectrum (Fig. S7a); the characteristic peaks of Sb(III)3d5/2 and Sb(III)3d3/2 are shown at 530.5 eV and 539.8 eV, respectively, and the characteristic peaks of Sb(V)3d5/2 and Sb(V)3d3/2 are shown at 531.1 eV and 540.6 eV, respectively, Fig. S7b.

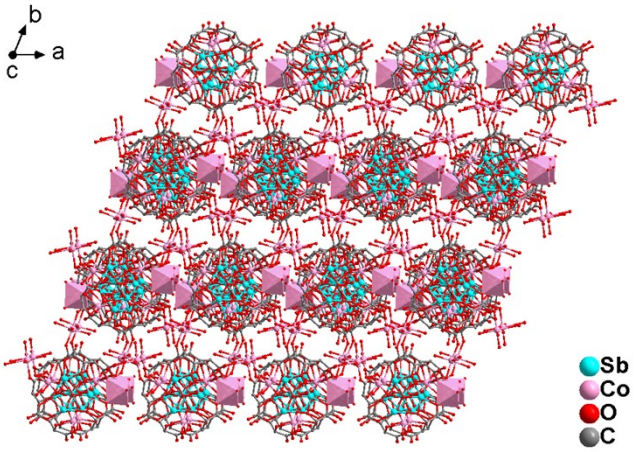

Fig. S8 Packing of the anionic 0-D cluster-dimers in compound **1** viewed along the *c*-axis, when Co(7) atoms are not considered. Pink polyhedra represent the bridging {Co(4)O_6} structural motifs. For clarity, the cationic part as well as the lattice water molecules are omitted.

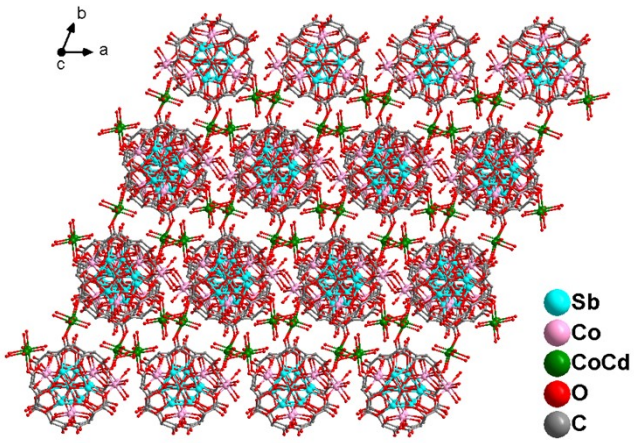

Fig. S9 Packing of the anionic 0-D cluster-dimers in compound **2** viewed along the *c*-axis, when Co(7) atoms are not considered. For clarity, the cationic part as well as the lattice water molecules are omitted.

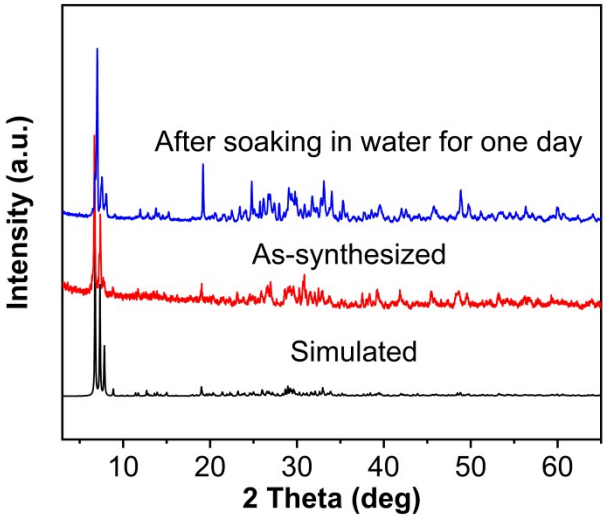

Fig. S10 Experimental PXRD patterns for **1** compared with the simulated one from single-crystal X-ray data.

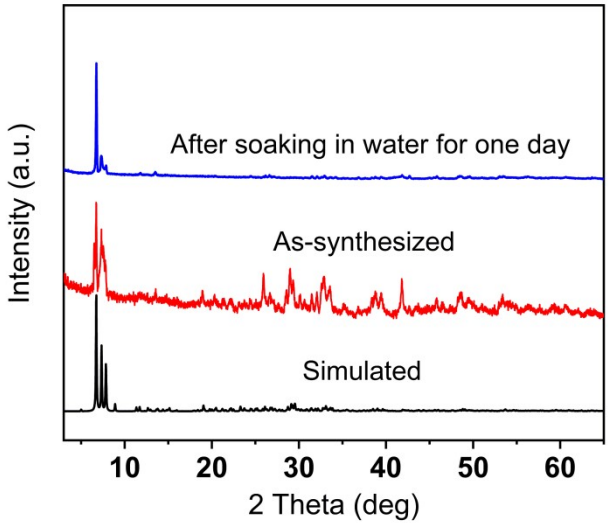

Fig. S11 Experimental PXRD patterns for **2** compared with the simulated one from single-crystal X-ray data.

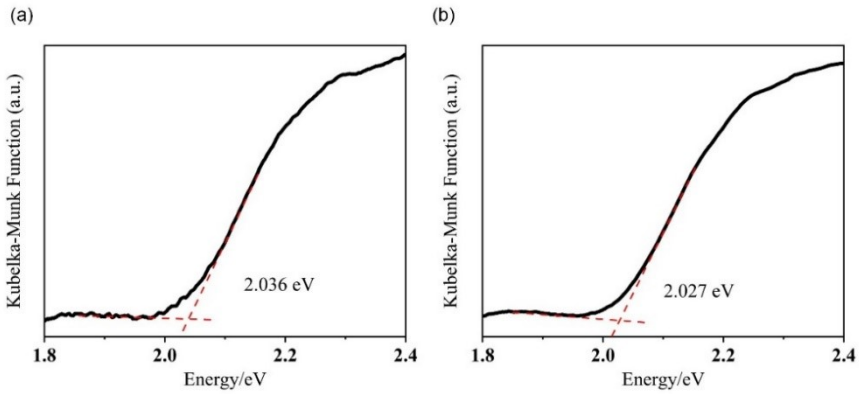

Fig. S12 Solid-state UV-vis absorption spectra of compounds **1** (a) and **2** (b).

Table S3 Proton conductivity (σ) values of **2** under 25 °C at different relative humidity.

RH %	55	70	85	98
σ (S·cm^{-1})	2.84×10^{-8}	6.19×10^{-8}	2.98×10^{-7}	3.92×10^{-6}

Table S4 Proton conductivity (σ) values of **2** under 98% RH at different temperature.

T/°C	25	35	40	50	55	65	70	85
σ (S·cm^{-1})	3.92×10^{-6}	3.92×10^{-5}	8.72×10^{-5}	1.76×10^{-4}	2.42×10^{-4}	3.79×10^{-4}	5.03×10^{-4}	1.42×10^{-3}

Table S5 The proton conductivity of selected metal-oxo-cluster based proton conducting materials.

Compounds	Conductivity (S cm^{-1})	Test Conditions	ref
$H_{14}[Na_6(H_2O)_{12}]_4[K_{42}Ge_8W_{72}O_{272}(H_2O)_{60}]$·solvent	6.80×10^{-2}	85 °C, 98% RH	9
$Na_{70}K_4H_{12}[La_{10}Ni_{48}W_{140}Sb_{16}P_{12}O_{568}(OH)_{24}(H_2O)_{20}]\cdot252H_2O$	2.05×10^{-2}	22 °C, 100% RH	10
$H_{13}(HIm)_4K_2Na_4(H_2O)_9[Sb^{III}_9Sb^{V}Sm_3O_{14}(H_2O)_3][(SbW_9O_{33})_3(PW_9O_{34})]\cdot26H_2O$	1.64×10^{-2}	85 °C, 98% RH	8
$[pyH]_8Ba_{13}Sb_{36}Cl_{34}O_{54}$ 2py $24H_2O$	1.55×10^{-2}	80 °C, 95% RH	48
$Sm(H_2O)_5(CO_2CH_2NH_3)_2][Al(OH)_6Mo_6O_{18}]\cdot10H_2O$	4.53×10^{-3}	80 °C, 95% RH	42
$[3\text{-}MepyH]_8Ba_{13}Sb_{36}Cl_{34}O_{54}$ 2(3-Mepy) $16H_2O$	3.1×10^{-3}	80 °C, 95% RH	48
$H_3K_5(H_2O)_{11}\{Cd(H_2O)_4[Cd(H_2O)Fe_4Cd_2Sb_6(\mu_4\text{-}O)_5(\mu_3\text{-}O)_3$ (L-tta)$_6$][Cd(H$_2$O)$_2$Fe$_4$Cd$_2$Sb$_6$(μ_4-O)$_4$(μ_3-O)$_4$(L-tta)$_6$] [Cd(H$_2$O)$_2$Fe$_4$Cd$_2$Sb$_6$(μ_4-O)$_4$(μ_3-O)$_4$(L-tta)$_6$Cd(H$_2$O)$_5$]}·17H$_2$O	2.95×10^{-3}	85 °C, 98% RH	29
$H_2[Co(en)_3]_3Ta_6O_{19}$	2.67×10^{-3}	85 °C, 98% RH	46
$H_5\{M Cd(H_2O)_6[M(H_2O)_3Co_3Sb^{V}Sb^{III}_6(\mu_3\text{-}O)_8(L\text{-}tta)_6]\}\cdot7H_2O$ (M = $Cd_{0.5}$ + $Co_{0.5}$)	2.43×10^{-3}	85 °C, 98% RH	29
$Na_{16}(NH_4)_{10}H_8\{[W_{14}Ce^{IV}_6O_{61}](W_3Bi_6Ce^{III}_3(H_2O)_3O_{14}]$ [α-BiW$_9$O$_{33}$]$_3$)$_2$}·ca.38H$_2$O	2.4×10^{-3}	25 °C, 98% RH	40

$Li_2[Cr_3O(OOCH)_6(etpy)_3]_2[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$	1.9×10^{-3}	50 °C, 95% RH	44
$(H_3O)_7[Cd_7Sb_{24}O_{24}(L\text{-}tta)_9(L\text{-}Htta)_3(H_2O)_6]\cdot 29H_2O$	1.88×10^{-3}	85 °C, 98% RH	30
$(H_3O)(UO_2)_3[Cd_7Sb_{24}O_{24}(L\text{-}tta)_9(L\text{-}Htta)_3(H_2O)_6]\cdot 48H_2O$	1.87×10^{-3}	85 °C, 98% RH	30
$(H_3O)_4Sr_{1.5}[Cd_7Sb_{24}O_{24}(L\text{-}tta)_9(L\text{-}Htta)_3(H_2O)_6]\cdot 34H_2O$	1.45×10^{-3}	85 °C, 98% RH	30
$La_{0.67}(H_2O)La(H_2O)_6$ $[\{La(H_2O)_3(SiW_{11}O_{39})\}]\cdot 7H_2O$	1.26×10^{-3}	90 °C, 98% RH	45
$[Co^{III}(en)_3]_4C_2O_4\{Ta_6O_{19}[Co^{III}(en)]\}_2\cdot 66H_2O$	1.1×10^{-3}	85 °C, 98% RH	47
$(H_3O)_3Ba_2[Cd_7Sb_{24}O_{24}(L\text{-}tta)_9(L\text{-}Htta)_3(H_2O)_6]\cdot 36H_2O$	1.03×10^{-3}	85 °C, 98% RH	30
$Na_2(H_2O)_6H_2[Co(en)_3]_2Ta_6O_{19}$	6.18×10^{-4}	85 °C, 98% RH	46
$Na_2[Cr_3O(OOCH)_6(etpy)_3]_2[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$	4.4×10^{-4}	50 °C, 95% RH	44
$[H_2en]_4[Ni_5(OH)_3(trzS)_3(en)(H_2O)(B\text{-}\alpha\text{-}PW_9O_{34})]\cdot 6H_2O$	2.4×10^{-4}	85 °C, 98% RH	43
$(H_2en)_4H_2[V_{12}B_{18}O_{54}(OH)_6(H_2O)]\cdot 11H_2O$	1.87×10^{-4}	60 °C, 98% RH	41
$K_2[Cr_3O(OOCH)_6(etpy)_3]_2[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$	1.6×10^{-4}	50 °C, 95% RH	44
$Cs_2[Cr_3O(OOCH)_6(etpy)_3]_2[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$	1.2×10^{-7}	50 °C, 95% RH	44