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Electronic Supplementary Information

New type composite MOFs based on high-valent Sb(V)-based units and cuprous-halide clusters

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This file includes:

Section S1 Experimental Section

Section S2 Additional Tables

Section S3 Additional Structural Figures and Characterizations.

Section S3 References

Section S1 Experimental Section

Materials: All chemicals were commercially purchased and used without further purification. The ligand H_3L[1] was synthesized according literatures procedure.

Instruments: Elemental analyses of C, H and N were carried out with a Vario EL III elemental analyzer. IR spectra were recorded on an Opus Vertex 70 FT-IR infrared spectrophotometer in the range of 450-4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 spectrometer with an Al-Ka (1486.6 eV) achromatic X-ray source. Thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851e analyzer under an air-flow atmosphere with a heating rate of 10 ºC/min in the temperature of 30-800 ºC. Powder XRD patterns were obtained using a Philips X'Pert-MPD diffractometer with CuKα radiation (λ = 1.54056 Å). Fluorescence spectra were measured with an Edinburgh FLS980 fluorescence spectrophotometer equipped with an Oxford Instruments liquid nitrogen flow cryostat.

Proton-conducting measurement: Ac impedance measurements were carried out with a zennium/IM6 IMPEDANCE/GAINPHASE analyzer over the frequency range from 0.1 Hz to 5 MHz with an applied voltage of 50 mV. The relative humidity was controlled by a STIK Corp CIHI-150B incubator. The samples were pressed to form a cylindrical pellet of crystalline powder sample (~1.2 mm thickness ×5 mm ϕ) coated with C-pressed electrodes. Two silver electrodes were attached to both sides of pellet to form four end terminals (quasi-four-probe method). The bulk conductivity was estimated by semicircle fittings of Nyquist plots.

Synthesis of $Sb_2L_4Cu_6I_4Cl_2$·solvent (1) A mixture containing 33.5 mg $SbCl_3$, 18.0

mg H_3L, 19.0 mg CuI and 62.0 mg $Cu(NO_3)_2 \cdot 5H_2O$ and 5.0 g N-Methylformamide (NMF) solution was sealed and heated in an oven at 100 ^oC for 72 h, then cooled to room temperature. Colorless hexagonal crystals were obtained after washed with fresh NMF solvent. Due to the low yield and too many impurities in the final product, we could not collect enough pure crystals for further characterization.

Synthesis of $[NH_2(CH_3)_2]_2Sb_2(Cu_2I_2)(L)_4 \cdot 3NMF \cdot 5H_2O$ (2) A mixture containing 33.4 mg $SbCl_3$, 18.0 mg H_3L, 18.0 mg CuI and 79.2 mg Tetrabutylammonium iodide and 5.0 g N-Methylformamide (NMF) solution was sealed and heated in an oven at 100 ^oC for 72 h, then cooled to room temperature. Pale yellow needle-like crystals were obtained after washed with fresh NMF solvent. The yield was about 68 % based on CuI. Elemental analysis calcd (%) for $H_{81}C_{46}N_9O_{20}Cu_2I_2Sb_2$ (M_r = 1704.60): C, 32.41; H, 4.80; N, 7.40. Found: C, 32.36; H, 4.91; N, 7.37. IR (KBr, cm^{-1}): 3374 (w), 3053(w), 2854 (w), 1608 (m), 1498 (w), 1408 (w), 1229 (w), 1083 (s), 959 (m), 818 (w), 677 (w), 569 (s).

Synthesis of $[NH_2(CH_3)_2][SbL_2Cu_4I_4] \cdot 5NMF \cdot 2H_2O$ (3) A mixture containing 33.0 mg $SbCl_3$, 18.0 mg H_3L, 18.0 mg CuI and 79.2 mg Tetrabutylammonium iodide and 5.0 g N-Methylformamide (NMF) solution was sealed and heated in an oven at 100 ^oC for 72 h, then cooled to room temperature. Pale yellow needle-like crystals were obtained after washed with fresh NMF solvent. The yield was about 68 % based on CuI. Elemental analysis calcd (%) for $H_{57}C_{30}N_8O_{13}Cu_4I_4Sb$ (M_r = 1621.38): C, 22.22; H, 3.54; N, 6.91. Found: C, 22.15; H, 3.70; N, 6.84. IR (KBr, cm^{-1}): 3275 (w), 3066 (w), 2865 (w), 1652 (m), 1609 (w), 1543 (w), 1419 (w), 1382 (m), 1230 (w),

1083 (s), 1013 (m), 954 (m), 889 (w), 677 (w), 568 (s).

Synthesis of $Sb(L)_2CuCl(NMF)_3 \cdot NMF \cdot 2H_2O$ (4): A mixture containing 33.4 mg $SbCl_3$, 18.0 mg H_3L, 10.0 mg CuCl and 30 mg KCl and 5.0 g N-Methylformamide (NMF) solution was sealed and heated in an oven at 100 ^oC for 72 h, then cooled to room temperature. Green flake crystals were obtained after cooling to room temperature. The yield was about 48 % based on CuCl. Elemental analysis calcd (%) for $H_{44}C_{26}N_6O_{12}ClCuSb$ (M_r = 853.42): C, 36.59; H, 5.20; N, 9.85. Found: C, 36.79; H, 5.13; N, 9.87. IR (KBr, cm^{-1}): 3251 (w), 3054 (w), 2862 (w), 1648 (m), 1542 (w), 1369 (w), 1233 (m), 1152 (w), 1078 (s), 960 (m), 893 (w), 836 (w), 681 (m), 570 (s).

Single-crystal structure analyses: Single-crystal X-ray diffraction data for **1-4** were collected on a Bruker APEX II diffractometer at 296 K or 175 K equipped with a fine focus, 2.0 kW sealed tube X-ray source (MoK radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. The program SADABS was used for the absorption correction. The structures were solved by the direct method and refined on F^2 by full-matrix least-squares methods using the SHELX-2013 program package. All hydrogen atoms attached to carbon atoms were generated geometrically. Due to the highly porous characteristic of structures, the charge compensation anions and guest solvent molecules cannot be definitely mapped by single-crystal X-ray diffractions. The residual electron density that could not sensibly be modeled as solvents or cations were removed via application of the SQUEEZE[2] function in PLATON. The final formula of **1-4** were determined by the combination of single-crystal X-ray diffractions with the elemental analysis, thermogravimetric analysis and charge

balance. Crystallographic data and structure refinements for **1**-**4** are summarized in Table S1. X-ray crystallographic data for **1**-**4** (CCDC1960359−1960362). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Section S2 Additional Structural Tables

Table S1 X-ray crystallographic data for **1-4**

	1	**2**	**3**	**4**
Empirical formula	$C_{19}H_{20}O_6N_3ClCu_3I_2Sb$	$C_{46}H_{81}N_9O_{20}Cu_2I_2Sb_2$	$C_{30}H_{57}N_8O_{13}Cu_4I_4Sb$	$C_{26}H_{44}N_6O_{12}ClCuSb$
Formula weight	988.00	1704.60	1621.38	853.42
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	*Pbcn*	*C2/m*	*Fddd*	*Cc*
a (Å)	12.5861(12)	17.557(3)	16.995(2)	7.582(5)
b (Å)	13.0814(12)	26.674(4)	44.439(6)	29.72(2)
c (Å)	32.104(3)	8.0497(12)	54.864(8)	15.255(11)
α (°)	90	90	90	90
β (°)	90	109.822(3)	90	100.104(10)
γ (°)	90	90	90	90
V (Å^3)	5285.7(8)	3546.5(9)	41436(10)	3378(4)
Z	8	2	32	4
F(000)	3712	1292	12960	1660
ρ_{calcd} (g cm^{-3})	2.483	1.260	1.107	1.607
Temperature (K)	296(2)	296(2)	175(2)	296(2)
μ(mm^{-1})	5.870	2.254	2.540	1.569
Refl. Collected	20123	5956	28486	5669
Independent relf.	4626	3146	5517	3634
Parameters	311	136	154	411
GOF on F^2	1.009	1.050	0.995	1.009
Final *R* indices (I= 2σ(I))	R_1=0.0342 wR_2=0.0791	R_1=0.0607 wR_2=0.1586	R_1=0.0983 wR_2=0.2788	R_1=0.0409 wR_2=0.1043
R indices (all data)	R_1=0.0439 wR_2=0.0842	R_1=0.0777 wR_2=0.1689	R_1=0.01193 wR_2=0.2976	R_1=0.0458 wR_2=0.1069

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, where x = 0.036900, y =45.711197 for **1**; x = 0.091600, y = 8.435596 for **2**; x = 0.220000, y = 0 for **3**; x = 0.076400, y = 0.472100 for **4**.

Table S2 The bond valence sum calculations for **1-4**

Compound	*Atoms*	*Calcd for Sb^{III}*	*Calcd for Sb^{V}*	*Oxidation state*
1	**Sb1**	**5.12**	**5.13**	***Sb^{V}***
2	**Sb1**	**5.09**	**5.10**	***Sb^{V}***
3	**Sb1**	**4.82**	**4.83**	***Sb^{V}***
4	**Sb1**	**5.21**	**5.23**	***Sb^{V}***

Compound	*Atoms*	*Calcd for Cu^{II}*	*Calcd for Cu^{I}*	*Oxidation state*
4	**Cu1 (4)**	**1.87**	**1.81**	***Cu^{II}***

Section S3 Additional Structural Figures and Characterizations

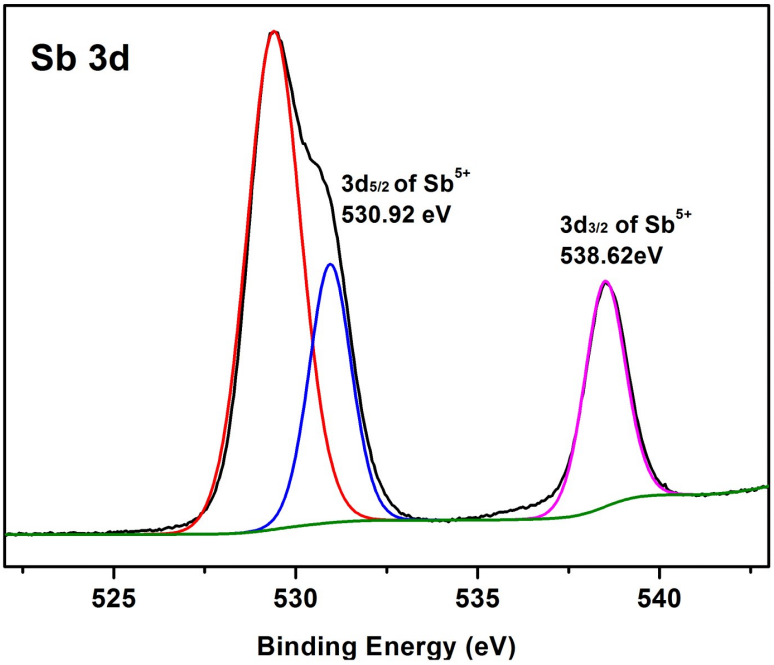

Fig. S1 Sb 3d XPS spectrum of **2**.

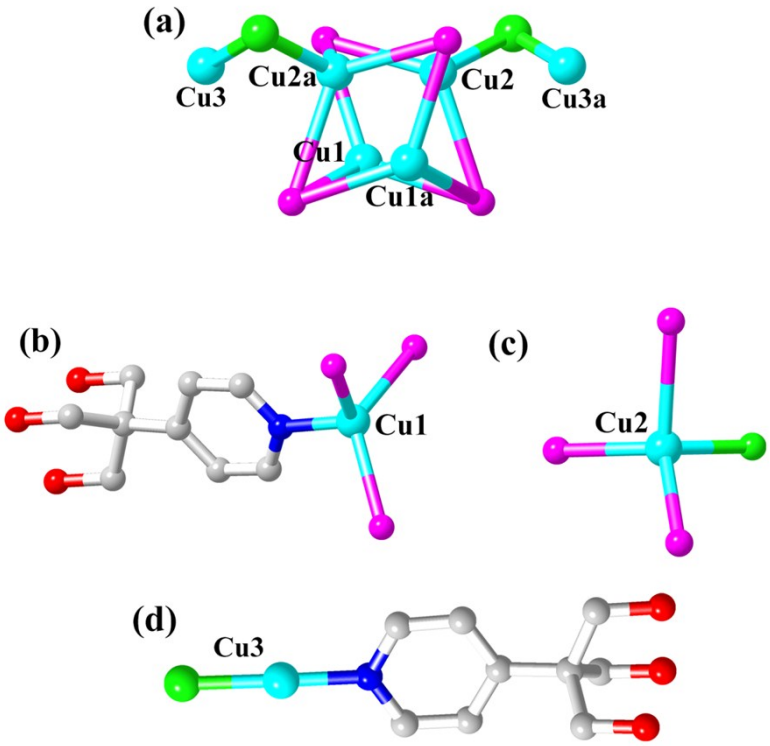

Fig. S2 (a) the $Cu_6I_4Cl_2$ cluster in **1**; (b) the coordination environment of Cu1 ions in **1**; (c) the coordination environment of Cu2 ions in **1**; (d) the coordination environment of Cu3, all hydrogen atoms are omitted for clarity.

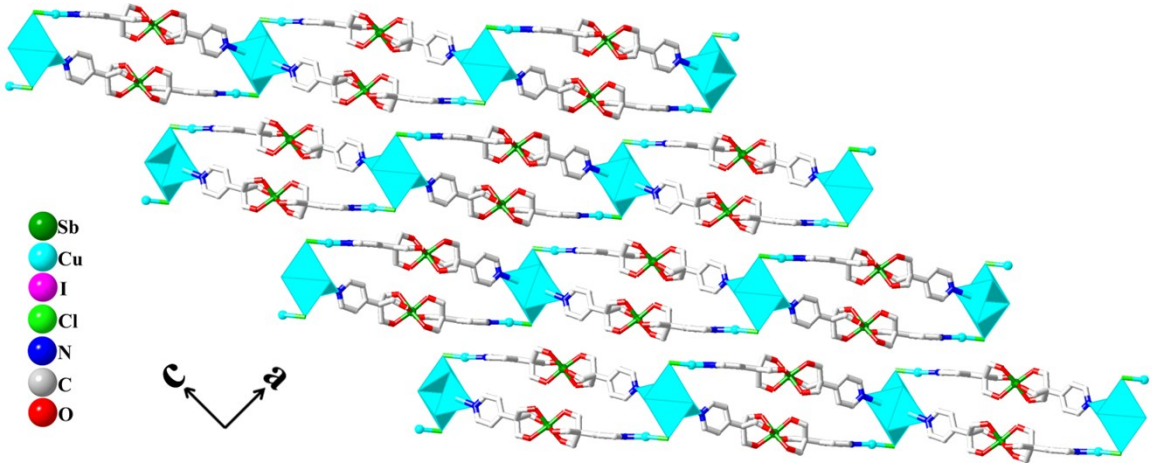

Fig. S3 Two-dimensional (2-D) layered structure in **1** along *b* axis in the *ac* plane, all hydrogen atoms are omitted for clarity.

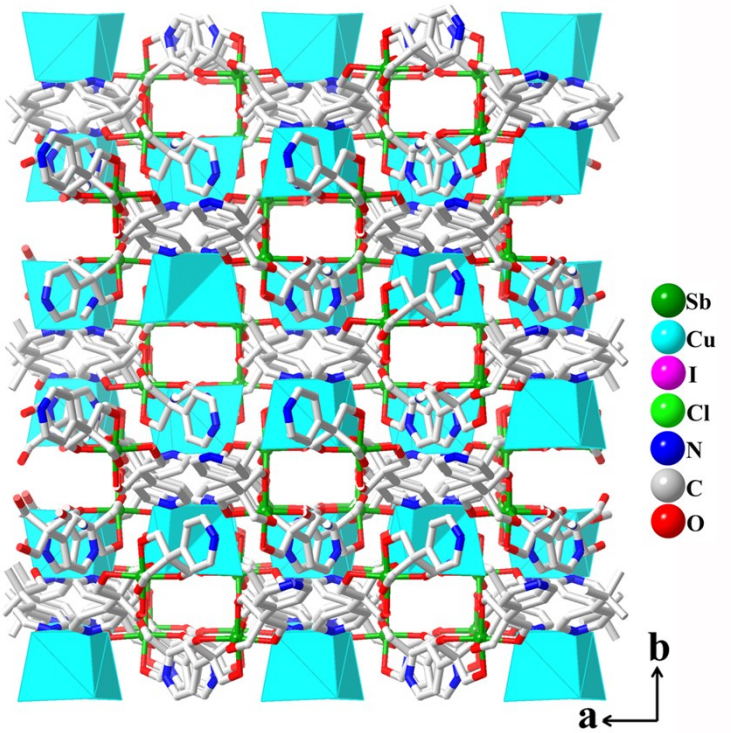

Fig. S4 Three-dimensional (3-D) supramolecular framework in **1** along *c* axis in the *ab* plane, all hydrogen atoms are omitted for clarity.

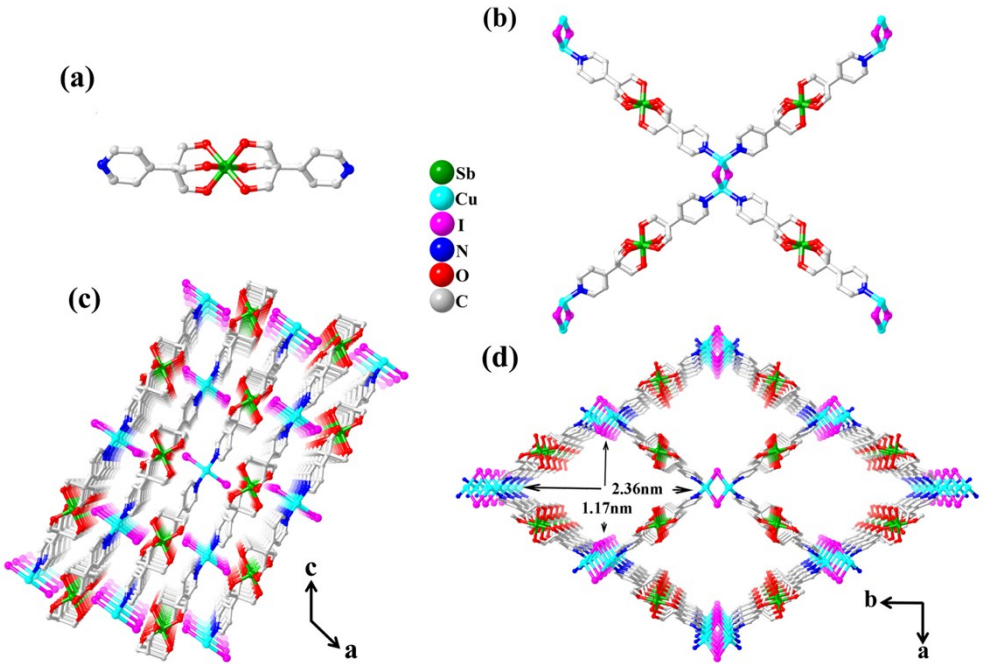

Fig. S5 (a) the $[SbL_2]^-$ unit in **2**; (b) each Cu_2I_2 cluster connects four Cu_2I_2 clusters as four-connected planar nodes in **2**; (c) the 2-D layers stack in parallel in *ac* plane; (d) the 3-D supramolecular framework with 1-D channels with reduced size of 1.17 × 2.36 nm^2 along *c* axis.

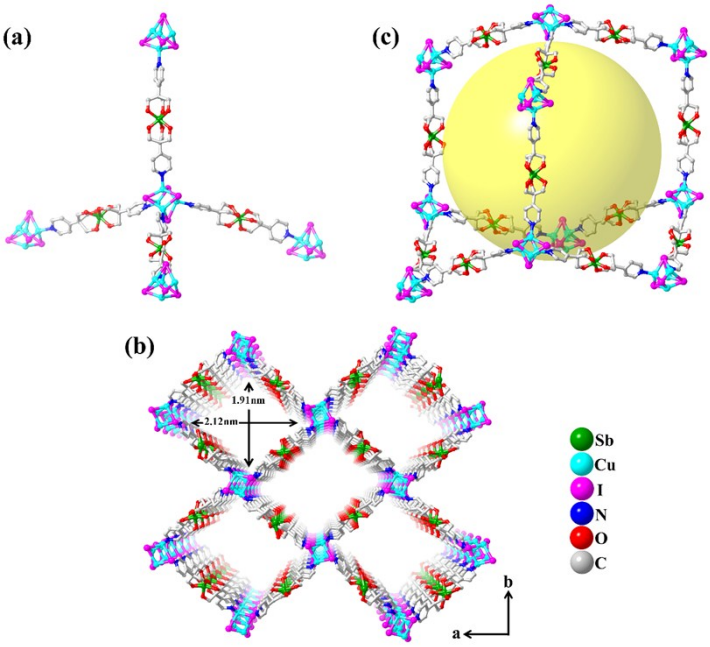

Fig. S6 (a) Cu_4I_4 cluster as a four-connected node, connecting four identical Cu_4I_4 cluster through four $[SbL_2]^-$ unit in **3**; (b) the 3-D framework with dia-type topology in **3**; (c) the diamondoid cage based on eight Cu_4I_4 clusters and twelve $[SbL_2]^-$ units in **3**.

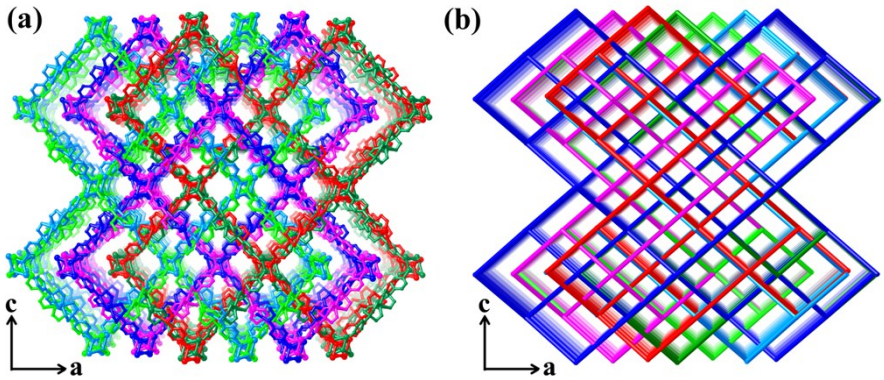

Fig. S7 The six-fold interpenetration 3-D framework in **3**.

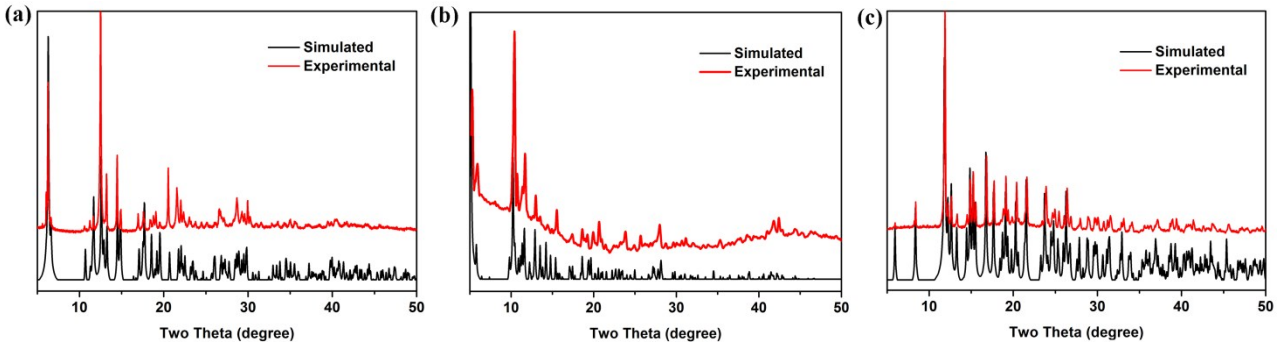

Fig. S8 The simulated and experimental PXRD patterns of **2** (a), **3** (b) and **4** (c).

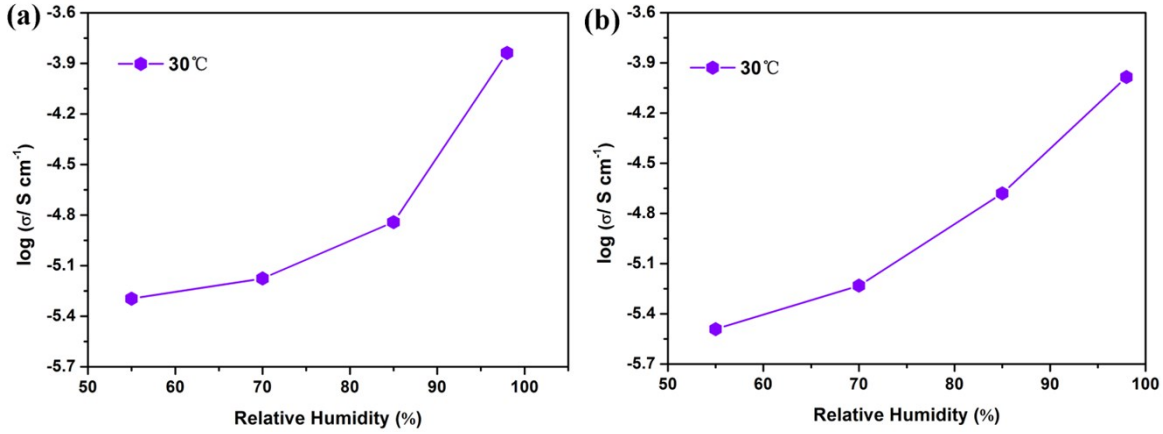

Fig. S9 Dependence of proton conductivity in **2** (a) and **3** (b) as a function of relative humidity at 30 °C.

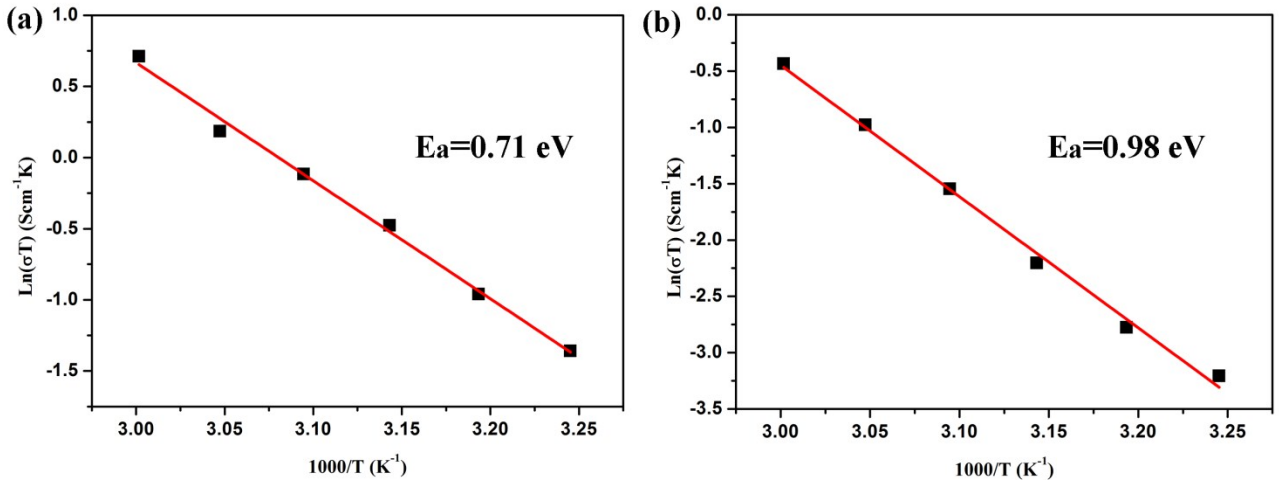

Fig. S10 Arrhenius plots of **2** (a) and **3** (b).

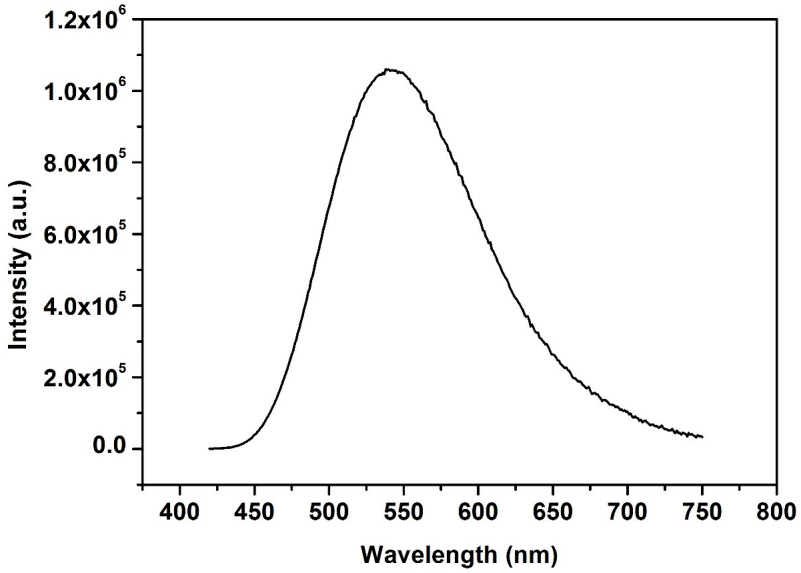

Fig. S11 The solid-state luminescent property of **2** at room temperature.

Section S4 References

[1] D. Menozzi, E. Biavardi, C. Massera, F. P. Schmidtchen, A. Cornia and E. Dalcanale, *Supramol. Chem.*, 2010, **22**, 768.

[2] A. L. Spek, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 9.