Electronic Supplementary Material (ESI) for Dalton Transactions.

Water-mediated proton conduction in Ni(II) and Co(II) benzenetriphosphonates

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Supporting Information

Experimental

1. Materials

Chemical reagents were purchased commercially and used as received without further purification. benzene-1,3,5-tris(methylenephosphonic acid) (H_6bmt) 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 measurements were conducted on a Bruker D8 ADVANCE X-ray diffractometer. Infrared (IR) spectra were recorded in the range of 4000 - 400 cm^{-1} on a FT-IR analyzer (1601, shimadzu Co., Japan) by using KBr-pellet method. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 10 ^{0}C min^{-1} under a nitrogen atmosphere.

3. Synthesis of [Ni(4,4′-bipyH)$_2$(H_2O)$_4$]·2(H_4bmt)·9H_2O (1)

H_6bmt (0.1 mmol, 0.0358 g), 4, 4′-bipy (0.1 mmol, 0.0156 g), Ni(OAc)$_2$·4H_2O (0.1 mmol, 0.0247 g) and 3 mL water were added in 10 mL vial. The vial was kept in an autoclave at 140 ^{0}C for three days. Green crystals were obtained and washed with deionized water. Yield: 49.47 mg (65%, based on Ni). Anal. Calcd. For $C_{38}H_{70}N_4NiO_{31}P_6$: C, 34.48; H, 5.33; N, 4.23 %. Found: C, 34.07; H, 5.76; N, 3.89 %. Main IR data (KBr, cm^{-1}): 3345 (s), 3097 (w), 3057 (w), 2911 (w), 1611 (m), 1493 (m), 1453 (w), 1304 (w), 1151 (m), 1021 (m), 951 (m).

4. Synthesis of [Co(4,4′-bipy)(H_2O)$_4$][Co(4,4′-bipyH)$_2$(H_2O)$_4$]·2(H_3bmt)·6H_2O (2)

The preparation of **2** was similar to that of **1** except the displacement of Ni(OAc)$_2$·4H_2O by Co(OAc)$_2$·4H_2O under the same mole ratio. Pink crystals were obtained and washed with deionized water. Yield: 36.72 mg (48%, based on Co). Anal. Calcd. For $C_{48}H_{78}Co_2N_6O_{32}P_6$: C, 37.08; H, 5.06; N, 5.41 %. Found: C, 37.46; H, 5.42; N, 5.04 %. Main IR data (KBr, cm^{-1}): 3379 (s), 3098 (w), 3056 (w), 2911 (w), 1611 (m), 1521 (m), 1453 (m), 1237 (w), 1151 (m), 1020 (s), 934 (m).

5. X-ray crystallography

Single-crystal X-ray diffraction data for **1** and **2** were 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 structures of **1** and **2** were 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** and **2** are summarized in Table S1 and Table S2, respectively.

6. 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 - 373 K) and relative humidity (60%, 70%, 80%, 90% and 98%). All measurements were electronically controlled by the winDETA package of programs.[5]

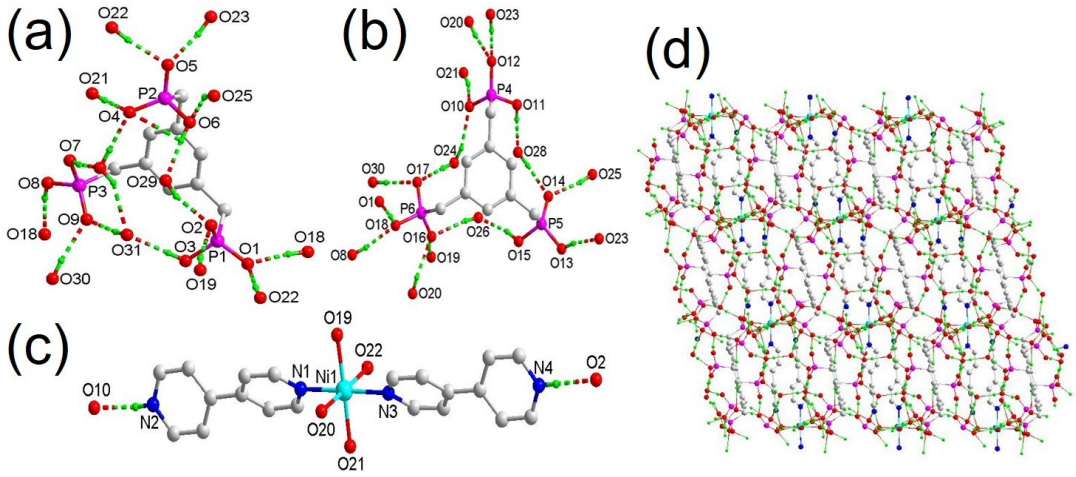

Fig. S1 (a) The hydrogen bonding of oxygen atoms derived from P1, P2 and P3 in **1**. (b) The hydrogen bonding of oxygen atoms derived from P4, P5 and P6 in **1**. (c) The coordination environment of Ni^{2+} ion. (d) The 3D network structure formed by the coordination and H-bond interactions of Ni^{2+} ions and ligands as well as water molecules.

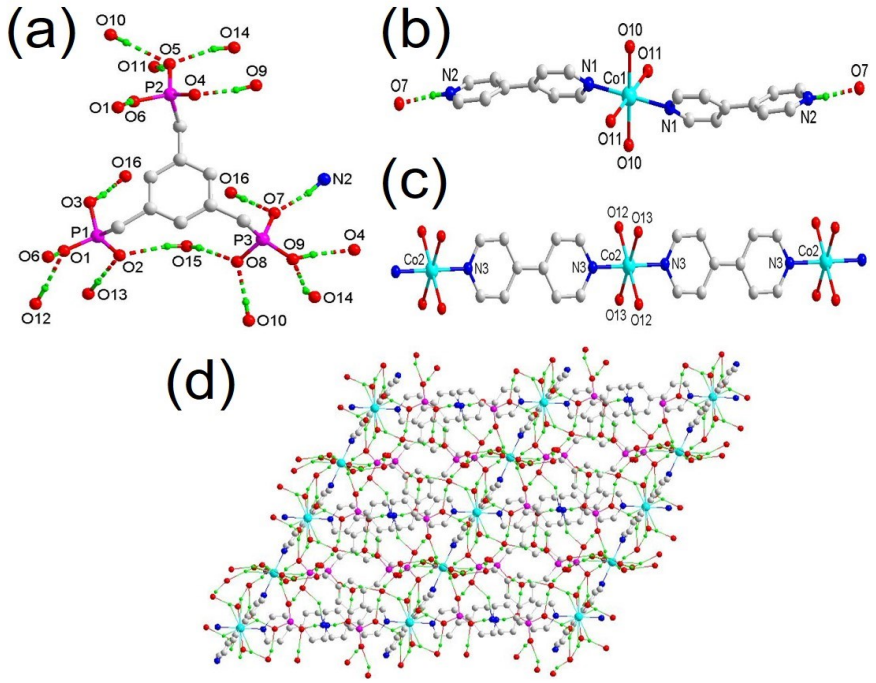

Fig. S2 (a) The hydrogen bonding of oxygen atoms derived from P1, P2 and P3 in **2**. (b) The mononuclear structure formed by Co1(II), 4, 4′-bipy and water molecules. (c) The 1D chain structure formed by Co2(II), 4, 4′-bipy and water molecules. (d) The 3D network structure formed by the coordination and H-bond interactions of Co^{2+} ions and ligands as well as water molecules.

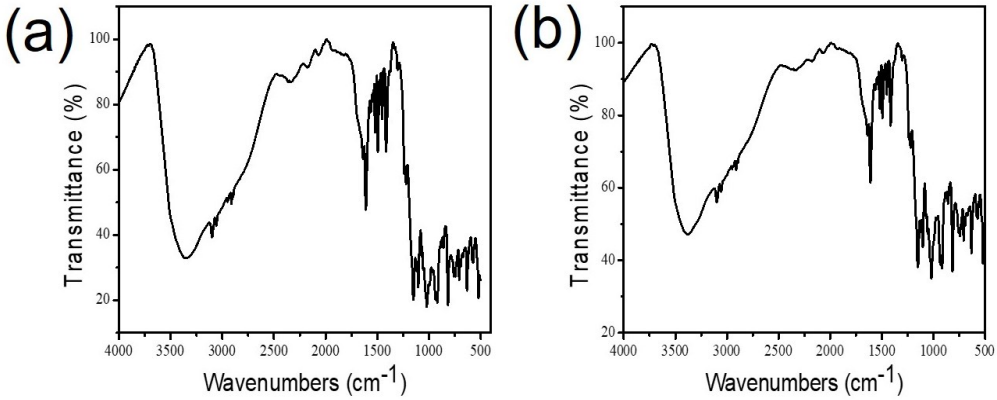

Fig. S3 The IR spectra of complexes **1**(a) and **2**(b).

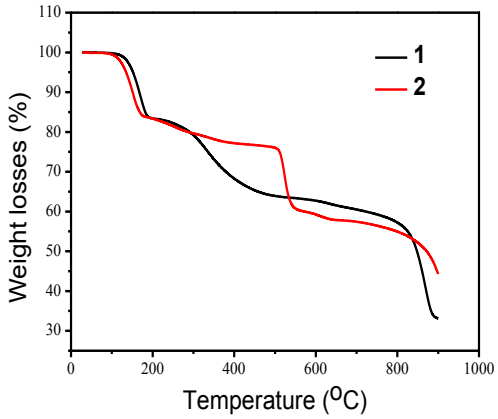

Fig. S4 The TGA curves of complexes **1** and **2**.

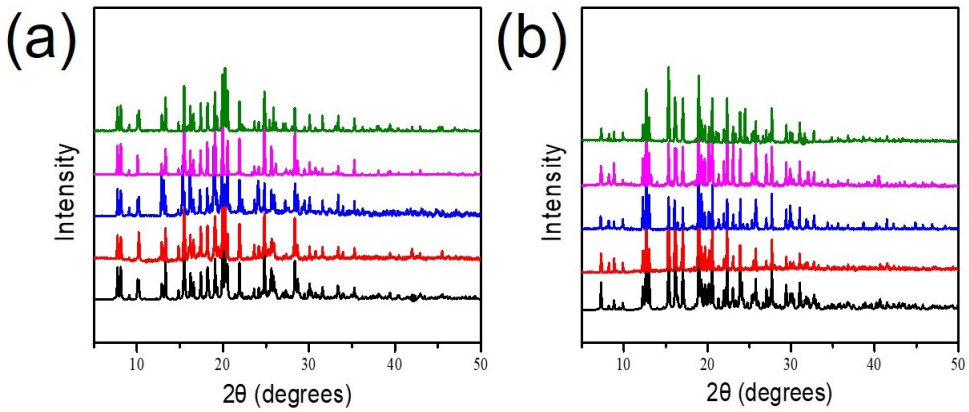

Fig. S5 Powder X-ray diffraction spectra for **1**(a) and **2**(b) in different conditions. Simulated (black), As-synthesized (red), Immersed in water for two weeks (blue), Reflux for one day (magenta) and Post-impedance (olive).

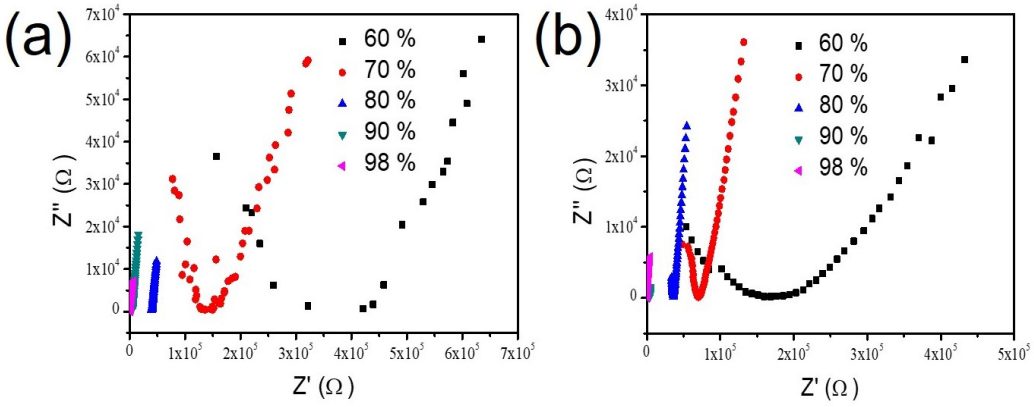

Fig. S6 Plots of the impedance plane for **1** (a) and **2** (b) at different relative humidity and 297 K.

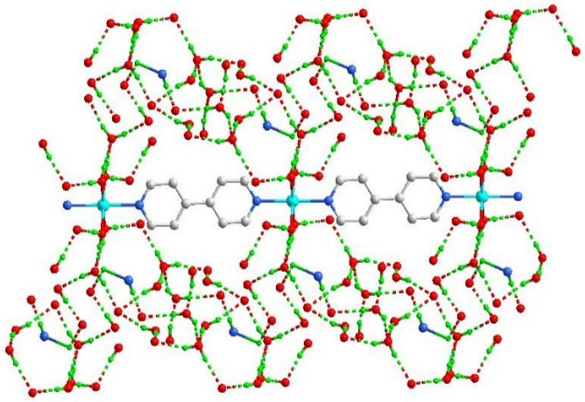

Fig. S7 The interchains hydrogen bonding network in the structure of **2**.

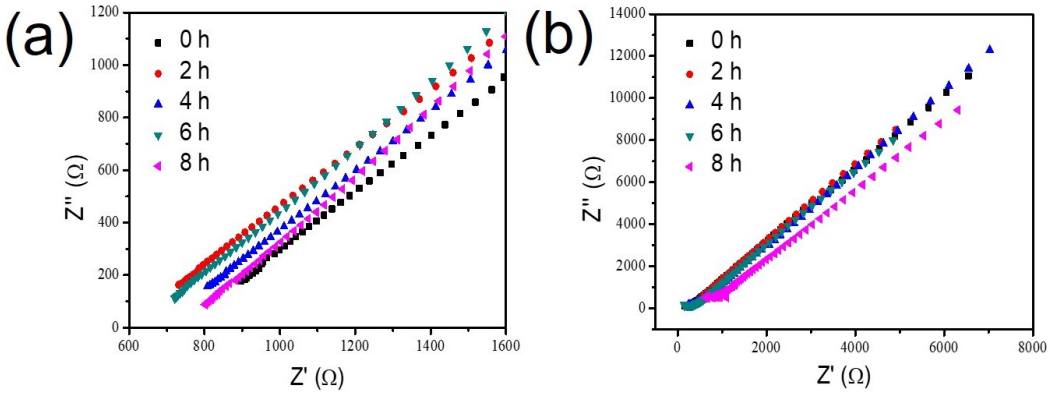

Fig. S8 Nyquist plots for proton conductivity of **1** (a) and **2** (b) (373 K and 98% RH) at 0h, 2h, 4h, 6h and 8h.

Table S1 Crystallographic data and refinement parameters for **1** and **2**.

	1	**2**
CCDC number	1922400	1922402
Empirical formula	$C_{38}H_{70}N_4NiO_{31}P_6$	$C_{48}H_{78}Co_2N_6O_{32}P_6$
Formula weigh	1323.51	1554.84
Temperature/K	173	173
Crystal system	triclinic	triclinic
Space group	$P\ \bar{1}$	$P\ \bar{1}$
a/Å	10.5385(5)	11.3714(7)
b/Å	12.3978(6)	11.8312(7)
c/Å	22.3593(12)	13.1735(7)
α/°	99.057(2)	107.348(2)
β/°	98.106(2)	100.689(2)
γ/°	101.379(2)	101.407(2)
V/Å^3	2783.2(2)	1600.69(16)
Z	2	1
D_{calc}/g cm^{-3}	1.579	1.613
μ/mm^{-1}	0.618	0.765
F(000)	1384.0	808.0
h, k, l max	12, 14, 26	13, 14, 15
No. of parameters	829	481
S	1.018	1.021
R_1, wR_2 [I >2σ(I)]	0.0465, 0.0985	0.0404, 0.0878
$\Delta\rho_{max}$/e Å	0.745	0.745
$\Delta\rho_{min}$/e Å	0.707	0.699

Table S2 Selected bond lengths (Å) of **1** and **2**.

1	Ni1-N1	2.106(2)	Ni1-N3	2.110(3)
	Ni1-O21	2.045(2)	Ni1-O22	2.063(2)
	Ni1-O19	2.067(2)	Ni1-O20	2.068(2)
2	Co1-O10	2.091(3)	Co1-O11	2.109(3)
	Co2-O12	2.105(3)	Co2-O13	2.116(2)
	Co1-N1	2.147(2)	Co2-N3	2.151(2)

Table S3 Hydrogen-bond geometry (Å, °) for **1**.

D-H···A	D-H	H···A	D···A	D-H···A
O23^{i}-H23C^{i} ···O5^{ii}	0.863(2)	1.748(2)	2.595(3)	166.6(2)
O23^{i}-H23D^{i}···O12^{ii}	0.855(3)	1.768(2)	2.618(3)	172.0(2)
O13^{iii}-H13C^{iii}···O23^{i}	0.794(3)	1.675(3)	2.459(4)	169.2(3)
O20^{iv}-H20D^{iv}···O12^{ii}	0.826(3)	1.839(3)	2.660(4)	172.7(3)
O20^{iv}-H20C^{iv}···O16^{i}	0.814(3)	1.973(2)	2.738(3)	156.4(2)
O26^{iv}-H26D^{iv}···O16^{i}	0.822(3)	2.127(2)	2.936(3)	167.8(3)
O26^{iv}-H26C^{iv}···O24^{iv}	0.827(2)	2.127(4)	2.734(4)	130.0(2)
O15^{i}-H15C^{i}···O26^{iv}	0.824(3)	1.724(3)	2.527(4)	164.2(3)
O21^{v}-H21D^{v}···O4^{iv}	0.825(3)	1.820(3)	2.641(3)	173.9(3)
O21^{v}-H21C^{v}···O10^{i}	0.810(3)	1.980(3)	2.764(3)	162.7(3)
O27^{iv}-H27D^{iv}···O4^{iv}	0.833(2)	1.785(2)	2.619(3)	179.1(2)
O27^{iv}-H27C^{iv}···O29^{iv}	0.797(2)	2.548(3)	3.042(4)	121.6(2)
O27^{iv}-H27C^{iv}···O31^{iv}	0.797(2)	2.278(2)	2.980(4)	147.4(2)
O7^{iv}-H7C^{iv}···O27^{iv}	0.802(3)	1.671(2)	2.468(3)	172.4(2)
O22^{i}-H22D^{i}···O1^{i}	0.812(3)	1.902(3)	2.712(3)	176.1(2)
O22^{i}-H22C^{i}···O5^{ii}	0.807(3)	1.884(3)	2.686(4)	172.6(3)

$O18^{i}$-$H18C^{i}$···$O1^{i}$	0.826(2)	1.757(2)	2.578(3)	172.7(2)
$O8^{vi}$-$H8C^{vi}$···$O18^{i}$	0.805(2)	1.874(2)	2.674(3)	171.6(3)
$O29^{iv}$-$H29C^{iv}$···$O2^{iv}$	0.815(3)	1.929(3)	2.723(4)	164.3(3)
$O29^{iv}$-$H29D^{iv}$···$O24^{iv}$	0.816(4)	1.907(4)	2.712(4)	168.5(3)
$O6^{iv}$-$H6C^{iv}$···$O29^{iv}$	0.818(2)	1.720(2)	2.537(3)	176.5(3)
$O25^{vii}$-$H25D^{vii}$···$O6^{iv}$	0.812(2)	2.226(2)	2.978(4)	154.1(2)
$O25^{vii}$-$H25C^{vii}$···$O14^{viii}$	0.826(2)	1.957(2)	2.773(3)	169.6(3)
$O28^{viii}$-$H28D^{viii}$···$O14^{viii}$	0.833(4)	1.894(4)	2.726(4)	176.6(3)
$O28^{viii}$-$H28C^{viii}$···$O25^{iv}$	0.835(2)	1.942(2)	2.774(4)	174.6(2)
$O11^{viii}$-$H11C^{viii}$···$O28^{viii}$	0.796(4)	1.784(4)	2.578(5)	177.0(4)
$O24^{iv}$-$H24C^{iv}$···$O10^{i}$	0.825(3)	1.982(3)	2.780(4)	162.6(2)
$O24^{iv}$-$H24D^{iv}$···$O17^{i}$	0.846(3)	1.872(2)	2.714(3)	173.8(3)
$O30^{i}$-$H30C^{i}$···$O17^{i}$	0.806(2)	1.979(3)	2.783(4)	174.8(2)
$O30^{i}$-$H30D^{i}$···$O9^{vi}$	0.812(2)	1.941(2)	2.749(3)	173.6(3)
$O31^{iv}$-$H31C^{iv}$···$O9^{iv}$	0.820(3)	1.929(3)	2.743(3)	171.8(2)
$O31^{iv}$-$H31D^{iv}$···$O30^{i}$	0.829(2)	1.853(2)	2.682(4)	179.4(2)
$O3^{iv}$-$H3C^{iv}$···$O31^{iv}$	0.796(4)	1.811(4)	2.603(4)	173.1(4)
$O19^{iv}$-$H19C^{iv}$···$O2^{iv}$	0.822(3)	1.979(3)	2.784(3)	166.0(2)
$O19^{iv}$-$H19D^{iv}$···$O16^{i}$	0.827(3)	1.929(2)	2.695(3)	153.7(2)
$N2^{vi}$-$H2E^{vi}$···$O10^{i}$	0.854(3)	1.853(3)	2.698(3)	170.2(3)

Symmetry codes (^{i}: 1-x, 2-y, 1-z; ^{ii}: 1-x, 3-y, 1-z; ^{iii}: -1+x, 1+y, z; ^{iv}: -x, 2-y, 1-z; ^{v}: -x, 1-y, 1-z; ^{vi}: x, 1+y, 1+z; ^{vii}:-1+x, y, z; ^{viii}: -2+x, y, z)

Table S4 Hydrogen-bond geometry (Å, °) for **2**.

D-H···A	D-H	H···A	D···A	D-H···A
$O3^{i}$-$H3C^{i}$···$O16^{ii}$	0.812(2)	1.792(2)	2.594(4)	169.4(3)
$O16^{ii}$-$H16C^{ii}$···$O7^{iii}$	0.807(4)	1.980(4)	2.786(5)	178.8(4)
$O16^{ii}$-$H16D^{ii}$···$O15^{iv}$	0.803(2)	2.210(3)	2.913(3)	146.4(3)
$O15^{iv}$-$H15C^{iv}$···$O2^{iii}$	0.817(3)	1.977(2)	2.782(3)	168.3(3)
$O15^{iv}$-$H15D^{iv}$···$O8^{iii}$	0.832(3)	1.933(3)	2.720(3)	157.2(2)
$O13^{i}$-$H13C^{i}$···$O2^{iii}$	0.827(2)	1.873(2)	2.700(3)	179.0(2)
$O13^{i}$-$H13D^{i}$···$O14^{i}$	0.809(3)	2.038(4)	2.785(4)	153.2(3)
$O12^{v}$-$H12D^{v}$···$O1^{vi}$	0.804(2)	1.876(2)	2.679(3)	176.2(2)
$O12^{v}$-$H12C^{v}$···$O14^{i}$	0.813(2)	1.977(2)	2.766(3)	163.3(2)
$O14^{i}$-$H14C^{i}$···$O5^{i}$	0.826(3)	1.924(3)	2.721(3)	161.7(3)
$O14^{i}$-$H14D^{i}$···$O9^{iv}$	0.825(3)	2.077(3)	2.853(4)	156.6(3)
$O9^{iv}$-$H9C^{iv}$···$O4^{i}$	0.829(3)	1.682(3)	2.507(3)	173.2(3)
$O6^{viii}$-$H6C^{viii}$···$O1^{vi}$	0.819(3)	1.775(3)	2.586(3)	170.7(3)
$O10^{ii}$-$H10C^{ii}$···$O5^{i}$	0.799(3)	2.011(3)	2.786(3)	163.3(3)
$O10^{ii}$-$H10D^{ii}$···$O8^{vii}$	0.794(2)	1.780(2)	2.570(3)	173.3(2)
$O11^{ii}$-$H11D^{ii}$···$O5^{i}$	0.828(3)	1.944(3)	2.754(4)	165.7(3)
$O11^{ii}$-$H11C^{ii}$···$O15^{iv}$	0.814(3)	1.873(3)	2.680(4)	170.9(3)
$N2^{ix}$-$H2E^{ix}$···$O7^{iii}$	0.889(3)	1.693(3)	2.573(3)	170.0(4)

Symmetry codes (^{i}: -2+x, -1+y, -1+z; ^{ii}: -1+x, -1+y, -1+z; ^{iii}: -x, -y, -z; ^{iv}: -1-x, -y, -z; ^{v}: -1-x, -1-y, -1-z; ^{vi}: -3+x, -2+y, -2+z; ^{vii}:-2+x,-1+y, -2+z; ^{viii}: -1-x, -y, -1-z; ^{ix}: -x, 1-y, -z)

Table S5 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	2.23×10^3	7.15×10^{-4}
289	2.08×10^3	7.66×10^{-4}
291	1.97×10^3	8.07×10^{-4}
293	1.85×10^3	8.61×10^{-4}
295	1.76×10^3	9.07×10^{-4}
297	1.64×10^3	9.74×10^{-4}
313	1.32×10^3	1.20×10^{-3}
333	1.18×10^3	1.35×10^{-3}
358	8.96×10^2	1.78×10^{-3}
373	5.67×10^2	2.81×10^{-3}

Table S6 The resistance (R) and conductivity (σ) of **2** 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	1.12×10^3	1.42×10^{-3}
289	1.02×10^3	1.55×10^{-3}
291	9.65×10^2	1.65×10^{-3}
293	8.97×10^2	1.78×10^{-3}
295	8.30×10^2	1.92×10^{-3}
297	7.88×10^2	2.02×10^{-3}
313	5.16×10^2	3.09×10^{-3}
333	2.70×10^2	5.89×10^{-3}
358	1.61×10^2	9.87×10^{-3}
373	2.36×10^2	6.75×10^{-3}

Table S7 The resistance (R) and conductivity (σ) of **1** under different relative humidity (RH) and 297 K.

RH (%)	R (Ω)	σ (S/cm)
60	4.24×10^5	3.76×10^{-6}
70	1.46×10^5	1.09×10^{-5}
80	3.99×10^4	3.99×10^{-5}
90	4.18×10^3	3.81×10^{-4}
98	1.64×10^3	9.74×10^{-4}

Table S8 The resistance (R) and conductivity (σ) of **2** under different relative humidity (RH) and 297 K.

RH (%)	R (Ω)	σ (S/cm)
60	2.10×10^5	7.60×10^{-6}
70	5.48×10^4	2.91×10^{-5}
80	3.54×10^4	4.51×10^{-5}
90	1.07×10^3	1.49×10^{-3}
98	7.88×10^2	2.02×10^{-3}

Table S9 The resistance (R) and conductivity (σ) of **1** (373 K and 98% RH) under different time.

Time (h)	R (Ω)	σ (S/cm)
0	5.67×10^2	2.81×10^{-3}
2	6.01×10^2	2.65×10^{-3}
4	6.42×10^2	2.48×10^{-3}
6	7.06×10^2	2.25×10^{-3}
8	7.54×10^2	2.11×10^{-3}

Table S10 The resistance (R) and conductivity (σ) of **2** (373 K and 98% RH) under different time.

Time (h)	R (Ω)	σ (S/cm)
0	2.36×10^2	6.75×10^{-3}
2	2.36×10^2	6.75×10^{-3}
4	2.35×10^2	6.78×10^{-3}
6	3.29×10^2	4.84×10^{-3}
8	5.21×10^2	3.06×10^{-3}

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