Supplementary Information for

Highly proton conductive nanoporous coordination polymers with sulfonic acid groups on the pore surface

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Materials:

All the reagents and solvents employed were commercially available and used as supplied without further purification.

X-ray Crystal Analysis:

Single crystal X-ray diffraction data collection was carried out on a Rigaku mercury diffractometer with a MoK α radiation ($\gamma = 0.71069$ Å) and a CCD detector. The crystal structure was solved and refined by direct methods with the use of SHELXL-97 present in the WinGx suite of programs. The positions of non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically and refined using a riding model.

Crystallographic data for 1: C₂₁H₁₂N₃O₁₀SZn, M = 563.38, Monoclinic, $P2_1/c$ (No .14), a = 9.642(4), b = 16.575(8), c = 19.660 (9), $\beta = 90.784(6)^\circ$, $V = 3142(2)\text{Å}^3$, Z = 4, T = 123K, $D_c = 1.192 \text{ gcm}^{-3}$, $R_1 = 0.0846$, w $R_2 = 0.2229$, GoF=1.054;

Crystallographic data for **2**: C₁₇H₁₁N₂O₉SZn, M = 484.38, Monoclinic, $P2_1/c$ (No .14), a = 13.818(3), b = 9.544(2), c = 15.309 (3), $\beta = 116.08(3)^\circ$, $V = 1813.2(6)\text{Å}^3$, Z = 4, T = 123K, $D_c = 1.776 \text{ gcm}^{-3}$, $R_1 = 0.0582$, w $R_2 = 0.1057$, GoF=0.901;

Crystallographic data for **3**: C₄₁H₄₀N₅O₂₂S₃Zn₃, M = 1246.14, $P2_1/c$ (No .14), a = 17.614(4), b = 21.916(4), c = 18.046 (4), $\beta = 105.64(3)^\circ$, V = 6709.0(2)Å³, Z = 4, T = 123K, $D_c = 1.235$ gcm⁻³, $R_1 = 0.0866$, w $R_2 = 0.1865$, GoF=0.951.

Comments on checkcif:

Checkcif highlighted A level alerts which have been commented on here

Compound I

<u>PLAT601 ALERT 2 A</u> Structure Contains Solvent accessible VOIDS of .375 A**3 Author response: The highest peak in the final difference map is just 1.039 e/A^3 and no model for any solvent could be found.

Compound II

<u>PLAT221 ALERT 2 A</u> Large Solvent/Anion CUeq(max)/Ueq(min) ... 10.0 Ratio **Author Response:** This high ratio of Ueq(max)/Ueq(min) involves C atoms within the partially disordered solvent moiety of DMF.

Compound III

<u>PLAT602_ALERT_2_A</u> VERY LARGE Solvent Accessible VOID(S) in Structure ! **Author Response:** During the structure analysis, it was observed that the unit cell contains large accessible voids in the crystal structure, even after assigning electron density peaks to solvent molecules. This affects the diffraction pattern, mostly at low scattering angles; this was corrected with the SQUEEZE program.

Proton conductivity measurement (general):

Proton Conductivity of compounds 1-3 were measured using an impedance and gain-phase analyzer (Solartron SI 1260) over frequency range 100 Hz – 10 MHz with an input voltage amplitude of 500 mV. 44, 20 and 25 mg of as-synthesized sample 1-3, respectively, was pressed in a pellet maker to obtain a uniform pellet of 0.33, 0.20, and 0.27 mm thickness, respectively, and 10 mm diameter, and sandwiched between two brass electrodes. The resistance values were measured from the semicircle of the Nyquist plot using ZView software. Proton conductivity was calculated by the following equation; $\sigma = L/(R.A)$ where σ = proton conductivity, L = thickness of the pellet, R = resistance of the pellet and A = area of the pellet = πr^2 where r = radius of the pellet.

Proton conductivity measurement (at high humidity):

Proton conductivity studies on the three compounds at high humidity condition were carried out. In compound **I**, the increase in conductivity was minimal, from $3.9 \times 10^{-4} \text{ Scm}^{-1}$ at 60%RH to 8.4 x 10^{-4} Scm^{-1} at 95%RH. We observed a significant increase in conductivity in compound **II**, from $3.4 \times 10^{-8} \text{ Scm}^{-1}$ at 60%RH to 5.6 x 10^{-4} Scm^{-1} at 95%RH, indicating that water molecules, which are absent in the structure originally, have a significant role to play in the conductivity. In compound **III**, although DMA cations are present which contribute towards conductivity, the introduction of water improves the conductivity from 8.7 x 10^{-5} Scm^{-1} at 60%RH to $1.0 \times 10^{-3} \text{ Scm}^{-1}$ at 95%RH.

Elemental Analysis:

 $[Zn(C_8H_4O_7S)(C_{10}N_2H_8)]$ ·DMF·2H₂O, 1

Found: C 43.12%, H 3.98%, N 7.03%; calculated: C 43.87% H 4.004% N 7.31%

 $[Zn(H_2O)(C_8H_4O_7S)(C_{12}N_2H_{10})_{0.5}]$ ·DMF, 2

Found: C 41.02%, H 3.61%, N 5.25%; calculated: C 41.52%, H 3.66% N 5.69%

 $[Zn_3(C_8H_3O_7S)_2(C_8H_4O_7S)(C_{10}H_8N_2)] \cdot (DMF) \cdot 2(DMA), 3$

Found: C 39.09%, H 2.13%, N5.59%; calculated: C 39.45%, H 3.29% N 5.61%

Additional structural details

Compound 1:

The distance between the aryl ring of 5-sip and one of the pyridyl rings of bpy is around 4.12

Å, indicating weak π - π interactions.

Compound 3:

In the trinuclear cluster, Zn1 is connected to two μ_2 and four single coordination carboxylate oxygen atoms, while both Zn2 and Zn3 are each connected to one μ_2 , three single coordination carboxylate oxygen atoms, one sulfonate oxygen and a nitrogen atom from the bipyridyl group. The clusters are connected to neighbouring clusters through 5-sip ligands to form a three-dimensional structure.



Fig. S1. Synthetic scheme of the compound 1, 2 and 3.



Fig. S2. TG analysis of **1.** 26.3 wt% loss observed below 125 °C is due to the loss of the lattice DMF and water molecules. Calcd. for **1**: 26.45%



Fig. S3. TG analysis of **2**. 17.8wt% loss observed below 220 °C is due to the loss of the lattice DMF and coordinated water molecules. Calcd. for **2**: 18.7%.



Fig. S4. TG analysis of **3**. 14.6wt% loss observed below 220 °C is due to the loss of the lattice DMF and dimethyl ammonium cations. Calcd. for **3**: 13.5%



Fig. S5. Simulated (blue) and experimental (black) PXRD patterns of **1-3** using $CuK\alpha$ radiation.

Compound	σ / S cm $^{-1}$	RH (%)	Т/К	reference
$[Ca(C_4O_4)Cl_{0.5}(H_2O)_{0.5}]\cdot Li_{0.5}\cdot (H_2O)_{3.5}$	1.8×10^{-2}	40	298	i
1	3.9×10^{-4}	60	298	This work
{NMe ₃ (CH ₂ CO ₂ H)}[FeCr(ox) ₃] $\cdot n$ H ₂ O	0.8×10^{-4}	65	298	ii
3	4.2×10^{-5}	60	298	This work
$(NH_4)_4[MnCr_2(ox)_3] \cdot nH_2O$	3.0×10^{-5}	69	295	iii
$Co[Cr(CN)_6]_{2/3}$ ·zH ₂ O	2.9×10^{-5}	69	293	iv
$\{NH(C_3H_7OH)_3\}[MnCr(ox)_3]\cdot 2H_2O$	2.0×10^{-6}	65	298	v
$(NH_4)_2(adp)[Zn_2(ox)_3]\cdot 2H_2O$	6.0×10^{-6}	70	298	vi
$[Sr_5(SBBA)_4(HCOO)_2(DMF)_8]\cdot 2DMF$	3.5×10^{-6}	60	298	vii
$Zn_3(L)(H_2O)_2 \cdot 2H_2O$	1.4×10^{-6}	75	298	viii
(HOC ₂ H ₄) ₂ dtoaCu	5.9×10^{-8}	70	300	ix
2	3.4×10^{-8}	60	298	This work
$Mn(dhbq)(H_2O)_2$	3.5×10^{-9}	60	298	х

Table S1. Proton conductivity of the MOFs under ambient conditions

adp = adipic acid. SBBA = 4,4'-sulfobisbenzoate. L = 1,3,5-benzenetriphosphonate. dtoa = dithiooxamide.

 H_2 dhbq = 2,5-dihydroxy-1,4-benzoquinone.

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