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# Supporting Information

# A porous supramolecular ionic solid

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#### A. General Considerations

**Materials** Solvents were obtained as ACS reagent grade and used as received. Unless otherwise noted, all chemicals and solvents were used as received. 3,5-Pyridinedicarboxylic acid was obtained from AmBeed. Iodomethane (CH<sub>3</sub>I) was obtained from Beantown Chemical. Methanol (MeOH), hydrochloric acid (HCl, 36.5–38%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95–98%), acetone, dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), and acetonitrile (MeCN) were obtained from VWR Chemicals BDH. Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), toluene, deuterated chloroform (CDCl<sub>3</sub>), copper(II) acetate monohydrate (Cu(OAc)<sub>2</sub>·H<sub>2</sub>O), *N*,*N*-dimethylformamide (DMF) were purchased from Oakwood Chemical. EtOH (KOPTEC 200 proof) was purchased from Decon Labs. Deuterium oxide (D<sub>2</sub>O) was obtained from ACROS Organics. Tetrahydrofuran (THF) was purchased from EMD Millipore. UHP-grade N<sub>2</sub> and He, used in gas adsorption measurements, were obtained from Air gas. All reactions were carried out under ambient atmosphere unless otherwise noted.

**Characterization Details** NMR spectra were recorded on a Bruker Avance III 400 operating at 400.13 MHz for <sup>1</sup>H and 100.61 MHz for <sup>13</sup>C acquisitions. Spectra were referenced against residual proton solvent resonances: CDCl<sub>3</sub> (7.26 ppm, <sup>1</sup>H; 77.16 ppm, <sup>13</sup>C), D<sub>2</sub>O (4.79 ppm, <sup>1</sup>H), and DMSO-*d*<sub>6</sub> (39.52 ppm, <sup>13</sup>C).<sup>1</sup> <sup>1</sup>H NMR data are reported as follows: chemical shift ( $\delta$ , ppm), (multiplicity: s (singlet), d (doublet), t (triplet), quadruplet (q), m (multiplet), br (broad); integration; coupling constant *J* in Hz). IR spectra were recorded on a Thermo Nicolet Avatar 370 DTGS spectrometer with a SMART PERFORMER ATR module. Spectra were blanked against air and were determined as the average of 50 scans. IR data are reported as follows: wavenumber (cm<sup>-1</sup>), (peak intensity: s, strong; m, medium; w, weak). Thermogravimetric analysis was performed on a TA Q50 thermogravimetric analyzer.

**Gas Sorption Details** N<sub>2</sub> adsorption isotherms (0–1.0 bar pressure range) were measured volumetrically at 77 K using a Quantachrome Autosorb-1. The synthesized sample underwent solvent exchange with MeCN for 3 d (15 mL × 9). The solvent exchanged samples were transferred under N<sub>2</sub> atmosphere to pre-weighed analysis tubes. The sample was evacuated at 90 °C until the outgas rate was <10 µbar/min and further maintained for 24 h. The tube was weighed to determine the mass of the activated sample. The tube was transferred to the analysis port of the instrument. UHP-grade (99.999% purity) N<sub>2</sub> and He were used for all adsorption measurements. Brunauer-Emmett-Teller (BET) surface areas were calculated in relative pressure range 0.02 to 0.15.

**Single-crystal X-ray Diffraction (SCXRD)** Single-crystal X-ray diffraction (SCXRD) data of **2** were collected using using synchrotron radiation ( $\lambda = 0.41328$  Å) equipped with a Pilatus3 X CdTe 1M detector and an Oxford Cryojet cooling device operating at 100 K at NSF's ChemMatCARS Sector 15 of Advanced Photon Source (APS) housed at Argonne National Laboratory (ANL). Indexing was performed using Bruker Apex3-suite. Data integration and reduction were performed using SaintPlus. Absorption corrections were performed by the multi-scan method implemented in SADABS.<sup>2</sup> Space group determinations were carried out using XPREP implemented in APEX3. Structures were solved using SHELXT and refined using SHELXL-2017 (full-matrix least-squares on F<sup>2</sup>)<sup>3-4</sup> using the OLEX2 interface.<sup>5</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized

positions and refined using a riding model. Solvent masks were employed in OLEX2 to treat the disordered DMF molecules (identified by elemental analysis and TGA) in the cavities.

**Powder X-ray Diffraction (PXRD)** PXRD measurements were carried out on a Panalytical X'Pert Pro Diffractometer (Cu K $\alpha$ , 1.5418 Å; 40 kV, 25 mA). The angular range was measured from 4.00 to 50.00° (2 $\theta$ ) with steps of 0.017° and a measurement time of 0.4 second per step. Simulated PXRD patterns were calculated using Mercury 3.9.<sup>6</sup>

**Piezoelectric Characterization** The piezoelectric response ( $d_{33}$ ) was measured using the Berlincourt method with a piezometer (PM 300, Piezotest). A custom 3D printed chamber was created to in-house the powder, which was bonded onto a copper bottom electrode plate. The powder was placed in between two copper electrodes that were connected to the 3 mm diameter testing clamps. A dynamic force of 0.25 N was applied at 110 Hz along with a static force of approximately 12 N. The  $d_{33}$  value was measured across n=10 samples and averaged. The test chamber and testing method was validated using ZnO powder.

#### B. Synthesis and Characterization

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Synthesis of of 3,5-dicarboxy-1-methylpyridinium chloride (1)

This synthetic procedure was adapted from the literature.<sup>7-8</sup> A 100-mL round bottom flask was charged with 3,5-pyridinedicarboxylic acid (2.00 g, 12.0 mmol), ethanol (40.0 mL), and sulfuric acid (1.90 mL). The reaction mixture was stirred at 78 °C for 24 h. The reaction mixture was cooled to 23 °C and the solvent was removed under vacuum. The residue was neutralized by saturated Na<sub>2</sub>CO<sub>3</sub> solution until pH = 7, while the white solids were formed. Solids were collected by vacuum filtration and were dried under reduced pressure to afford **S1** (2.02 g, 76% yield) as a white powder. <sup>1</sup>H NMR ( $\delta$ , 23 °C, CDCl<sub>3</sub>, Figure S6a): 9.36 (d, 2H, *J* = 2.0 Hz), 8.86 (t, 1H, *J* = 2.0 Hz), 4.45 (q, 4H, *J* = 7.2 Hz), 1.43 (t, 6H, *J* = 7.2 Hz). The obtained spectral data is well-matched to that reported in the literature.<sup>7</sup> <sup>13</sup>C NMR ( $\delta$ , 23 °C, CDCl<sub>3</sub>, Figure S6b): 164.4, 154.0, 137.9, 126.3, 61.8, 14.2 ppm.

A 50-mL round bottom flask was charged with **S1** (1.85 g, 8.29 mmol, 1.00 equiv), iodomethane (2.16 mL, 34.7 mmol, 4.19 equiv), toluene (13.2 mL), and acetonitrile (6.6 mL). The reaction mixture was stirred at 65 °C for 24 h. The solvent was removed under vacuum to give a yellow residue without further characterization. The yellow residue was dissolved in hydrochloric acid (36.5–38%, 20 mL). The reaction mixture was stirred at 90 °C for 72 h. The solvent was removed under vacuum to afford the title compound (1.61 g, 89% yield) as an off-white powder. <sup>1</sup>H NMR ( $\delta$ , 23 °C, D<sub>2</sub>O, Figure S7a): 9.42 (s, 2H), 9.32 (s, 1H), 4.53 (s, 3H). The obtained spectral data is well-matched to that reported in the literature.<sup>8</sup> <sup>13</sup>C NMR ( $\delta$ , 23 °C, DMSO, Figure S7b): 162.5, 149.6, 143.9, 130.8, 48.4 ppm. IR (cm<sup>-1</sup>, Figure S4): 2712 (w), 2494(w), 1723 (s), 1702 (m), 1609 (w), 1387 (w), 1316 (m), 1298 (m), 1234 (s), 1203 (m), 1170 (m), 893 (w), 746 (s).

### Synthesis of [Cu<sub>12</sub>(OCH<sub>3</sub>)<sub>12</sub>(C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>N)<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>] (2)



A 1-dram scintillation vial was charged with **1** (0.010 g, 0.046 mmol, 1.0 equiv),  $Cu(OAc)_2 \cdot H_2O$  (0.016 g, 0.080 mmol, 1.7 equiv), methanol (1.0 mL), and *N*,*N*-dimethylformamide (DMF, 1.0 mL). The resulting mixture was sonicated for 3 min to obtain a homogeneous solution. Then the vial was kept in oven at 75 °C for 24 h. The blue block-

shaped crystals were isolated by removing the solvent.<sup>a</sup> The obtained product was washed with MeCN (3.0 mL × 4) and dried under vacuum to afford blue solids (0.012 g, 93% yield). Primary data is presented in the following figures: SCXRD, Table S1; PXRD data, Figure S2; N<sub>2</sub> adsorption isotherms, Figure 4b; thermogravimetric analysis (TGA) data, Figure S8. Elemental analysis (EA) for  $[Cu_{12}(OCH_3)_{12}(C_8H_6O_4N)_{12}(H_2O)_4]\cdot11(C_3H_7NO)\cdot1.5(H_2O)$ : found, C, 40.12; H, 4.70; N, 7.93; calcd. C, 40.32; H, 4.70; N, 7.67. The EA data is consistent with the observed initial continuous 21% weight loss until ~230 °C, which is assigned to the guest molecules of DMF and H<sub>2</sub>O as well as coordinated aqua ligands.<sup>b</sup> IR (cm<sup>-1</sup>, Figure S4): 1668 (m), 1655 (m), 1612 (w), 1398 (w), 1360 (s), 1273 (w), 1236 (w), 1176 (w), 929 (w), 789 (w), 765 (m), 739 (m).

<sup>&</sup>lt;sup>a</sup> Employment of pyridine-3,5-dicarboxylic acid under the same conditions does not afford any crystalline phase (Figure S1). A 1-dram scintillation vial was charged with **1** (0.008 g, 0.05 mmol, 1.0 equiv), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.017 g, 0.085 mmol, 1.7 equiv), methanol (1.1 mL), and *N*,*N*-dimethylformamide (DMF, 1.1 mL). The resulting mixture was sonicated for 3 min to obtain a homogeneous solution. Then the vial was kept in oven at 75 °C for 24 h. Light green amorphous solids were harvested and analyzed by PXRD in Figure S1.

<sup>&</sup>lt;sup>b</sup> The crystallographic solvent mask tool indicates a smaller number of DMF molecules (Table S1), which are the guest molecules in the cavities. This is caused by the bulk samples for EA and TGA containing additional DMF molecules on the surface.

## C. Supporting Data



 $2\theta$  / degrees **Figure S1**. The solvothermal reaction between Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and pyridine-3,5-dicarboxylic acid does not afford crystalline phases under the same conditions of preparing **2**.

Crystal data	
Chemical formula	C108H116Cu12N12O64·5[C3H7NO]
Fw (g/mol)	3734.08
Temperature (K)	100
Crystal system, space group	Cubic, <i>I</i> 43 <i>m</i>
a (Å)	20.746(3)
α(°)	90
V (Å <sup>3</sup> )	8928(4)
Ζ	2
Radiation type	Synchrotron radiation, $\lambda$ = 0.41328 Å
μ (mm <sup>-1</sup> )	0.31
Crystal size (mm)	$0.1 \times 0.1 \times 0.1$
Data collection	
Diffractometer	Huber 3 circles
Detector	Pilatus3 X CdTe 1M
Absorption correction	Multi-scan, SADABS
No. of measured, independent and observed [I>2σ (I)] reflections	177274, 3122, 3054
$R_{ m int}$	0.050
$\sin(\theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.769
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.029, 0.081, 1.07
No. of reflections	3122
No. of parameters	86
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
r <sub>max</sub> , r <sub>min</sub> (e Å <sup>-3</sup> )	0.59, -0.72

**Table S1**. Crystal data and structure refinement for **2** (CCDC 2085461).



**Figure S2**. The comparison between the calculated PXRD patterns (—) and the assynthesized ones (—) indicates the phase purity of the obtained material. **2** demonstrates consistent PXRD patterns upon acetonitrile exchange and desolvation at 90 °C (—).



**Figure S3**. The permanent porosity is observed from the extended packing structure (view toward (111) plane). The axial partially occupied aqua ligands were omitted for clarity.



**Figure S4**. IR spectra (4000–700 cm<sup>-1</sup>) of **1** (—) and **2** (—). The comparison of these two spectra highlights that the carbonyl stretching from free carboxylic acid groups around 1723 cm<sup>-1</sup> in **1** is no longer observed in the coordination cage, **2**, due to its participation in coordination.



**Figure S5**. An octahedron is generated by connecting the six negatively charged metal clusters in the coordination cage.



Figure S6a. <sup>1</sup>H NMR spectrum of diethyl pyridine-3,5-dicarboxylate (S1) acquired at 23 °C in CDCl<sub>3</sub>.



**Figure S6b**. <sup>13</sup>C NMR spectrum of diethyl pyridine-3,5-dicarboxylate (**S1**) acquired at 23 °C in CDCl<sub>3</sub>.



**Figure S7a**. <sup>1</sup>H NMR spectrum of 3,5-dicarboxy-1-methylpyridinium chloride (**1**) acquired at 23 °C in D<sub>2</sub>O.



**Figure S7b**. <sup>13</sup>C NMR spectrum of 3,5-dicarboxy-1-methylpyridinium chloride (**1**) acquired at 23 °C in *d*<sub>6</sub>-DMSO.



Figure S8. Plots of weight% vs. temperature obtained by thermogravimetric analysis of 2.

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