

**Two histidine-templated metal phosphate-oxalates: solvent-free  
synthesis, luminescence, and proton-conducting properties**

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## Synthesis

Ga<sub>2</sub>O<sub>3</sub> (99.99%, ALADDIN), In(OH)<sub>3</sub> (99.8%, ALADDIN), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (AR, ALADDIN), L-histidine (99%, MACKLIN), H<sub>3</sub>PO<sub>4</sub> (85%, ALADDIN), were used without further treatment.

In<sub>2</sub>(C<sub>6</sub>H<sub>10</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> (**1**) was prepared by heating a mixture of In(OH)<sub>3</sub> (0.166 g, 1 mmol), H<sub>3</sub>PO<sub>4</sub> (68 μL, 1 mmol), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.378 g, 3 mmol), and L-histidine (0.155 g, 1 mmol) in a 25 mL Teflon-lined stainless steel autoclave at 120 °C for 7 days. After cooling to room temperature, dull yellow crystals of compound **1** were separated from the resulting product by filtration, washed with distilled water, and dried in air (58% yield based on In).

[(C<sub>6</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)] [Ga<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] (**2**) was prepared by heating a mixture of Ga<sub>2</sub>O<sub>3</sub> (0.094 g, 0.5 mmol), H<sub>3</sub>PO<sub>4</sub> (135 μL, 2 mmol), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (0.378 g, 3 mmol), and L-histidine (0.208 g, 1.25 mmol) in a 25 mL Teflon autoclave at 120 °C for 5 days. After cooling to room temperature, colourless crystals of compound **2** were separated from the resulting product by filtration, washed with distilled water, and dried in air (64% yield based on Ga).

## Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected on an Agilent Gemini E diffractometer at room temperature. The structures were refined on  $F^2$  by full-matrix least-squares methods using the *SHELXTL* program package.<sup>1,2</sup>

## Powder X-ray diffraction

Powder X-ray diffraction data were obtained using a Shimadzu XRD-6100 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), in the angular range of  $2\theta = 5\text{-}50^\circ$  (step width:  $0.02^\circ$ ).

## Elemental analysis

The elemental analysis was carried out on a Vario EL Cube analyzer.

## Thermogravimetric analysis

The thermogravimetric analysis was performed on a Netzsch STA 409 PC thermal analyzer, with a heating rate of 10 °C /min in the range of RT-800 °C at N<sub>2</sub> atmosphere.

## UV-vis diffuse reflectance spectroscopy

UV-vis diffuse reflectance spectra of compounds **1** and **2** were recorded by using Shimadzu UV-2600 UV-vis spectrophotometer at room temperature. The Kubelka-Munk function is used to calculate the absorption spectrum from the reflection spectrum:  $F(R) = \alpha/S = (1-R)^2/2R$ , where R is the reflectance,  $\alpha$  is the absorption coefficient, and S is the scattering coefficient.<sup>3, 4</sup>

### **Photoluminescent spectroscopy**

The excitation spectra, emission spectra and photoluminescence quantum yield (PLQY) were measured using an Edinburgh FS-5 fluorescence spectrometer with a calibrated integrating sphere system. Time-resolved PL decay curves were measured using a Fluoromax-3 fluorescence spectrometer.

### **Alternating current impedance spectroscopy**

Alternating current impedance measurements were carried out with a Solartron SI 1260 impedance/gain-phase analyzer over the frequency range from 0.1 Hz to 10MHz with an applied voltage of 10 mV. The relative humidity was controlled by a STIK Corp. CIHI-150B incubator. The sample was pressed to form a cylindrical pellet of crystalline powder sample (~2 mm thickness  $\times$  5 mm  $\phi$ ) coated with C-pressed electrodes. Two silver electrodes were attached to both sides of pellet to form four end terminals (quasi-four-probe method).

### **Computational descriptions**

The first-principles calculations were carried out on compounds **1** and **2** by using the CASTEP software package.<sup>5</sup> The band structures and density of states (DOSs) / partial density of states (PDOSs) of compounds **1** and **2** were calculated. The gradient-corrected functional (GGA) with Perdew-Burke-Ernzer (PBE) was used for all the calculations.<sup>6</sup> All the atoms were performed by Norm-conserving pseudopotentials (NCP), with H 1s<sup>1</sup>, C 2s<sup>2</sup>2p<sup>2</sup>, N 2s<sup>2</sup>2p<sup>3</sup>, O 2s<sup>2</sup>2p<sup>4</sup>, P 3s<sup>2</sup>3p<sup>3</sup>, Ga 3d<sup>10</sup>4s<sup>2</sup>4p<sup>1</sup>, In 5s<sup>2</sup>5p<sup>1</sup> treated as valence electrons.<sup>7</sup> The kinetic energy cutoff of 750eV and the k-point sampling of  $3 \times 2 \times 1$  were chosen for the compound **1**. The kinetic energy cutoff of 800eV and the k-point sampling of  $4 \times 3 \times 3$  were chosen for the compound **2**.<sup>8</sup> All other parameter settings are CASTEP default values.

**Table S1.** Proton conductivity of compounds **1**, **2**, and some representative metal phosphate-oxalates

Compound	RH (%)	T (°C)	$\sigma$ (S cm <sup>-1</sup> )	Reference
In <sub>2</sub> (C <sub>6</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ( <b>1</b> )	95	85	3.41×10 <sup>-5</sup>	this work
[(C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> )] [Ga <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] ( <b>2</b> )	40/70	85	3.71×10 <sup>-6</sup> /2.43×10 <sup>-4</sup>	this work
SCU-26	95	85	5.83×10 <sup>-5</sup>	9
SCU-27	95	85	9.03×10 <sup>-4</sup>	9
SCU-40	95	85	3.6×10 <sup>-4</sup>	10
SCU-42	95	85	4.2×10 <sup>-3</sup>	11
H <sub>2</sub> mpip·Sc(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )·0.5C <sub>2</sub> O <sub>4</sub> ·1.5H <sub>2</sub> O	95	85	2.1×10 <sup>-5</sup>	12
SCU-50	95	75	1.9×10 <sup>-5</sup>	13
SCU-65	80	85	3.0×10 <sup>-6</sup>	14
SCU-25	75	85	8.1×10 <sup>-6</sup>	15
[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ] <sub>2</sub> [Al <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )	98	85	9.09×10 <sup>-3</sup>	16
[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ] <sub>2</sub> [Ga <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )	98	85	6.43×10 <sup>-3</sup>	16
C <sub>4</sub> N <sub>2</sub> H <sub>14</sub> ·Sc <sub>2</sub> (HPO <sub>4</sub> )(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	95	85	5.4×10 <sup>-4</sup>	17
V <sub>2</sub> O <sub>2</sub> (HPO <sub>4</sub> )(HPO <sub>3</sub> )(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>4</sub> N <sub>2</sub> H <sub>12</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	98	75	4.35×10 <sup>-4</sup>	18

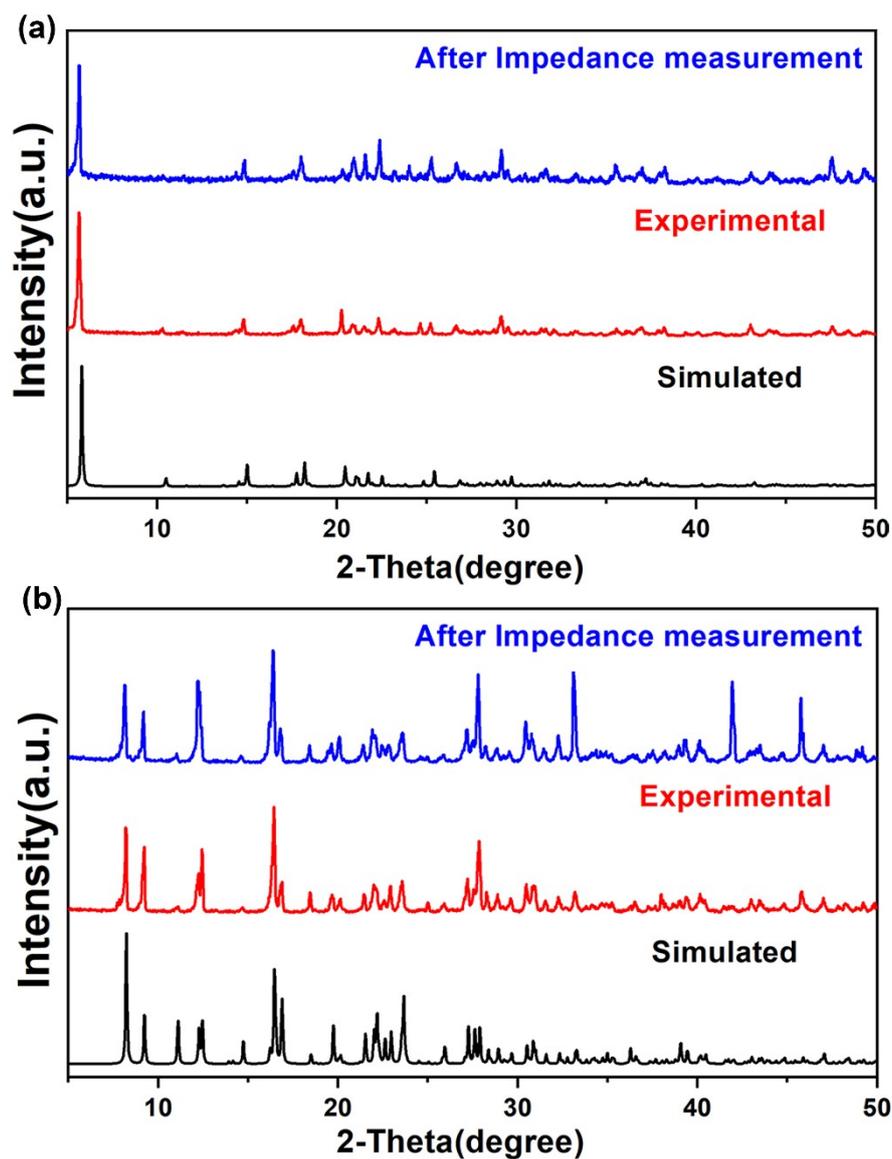


Fig. S1 Powder X-ray diffraction patterns of compound 1 (a) and compound 2 (b).

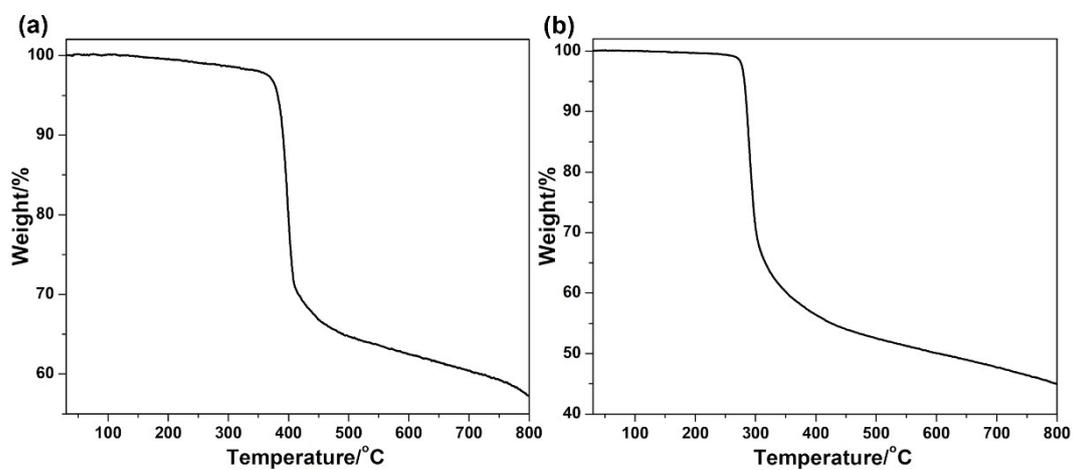
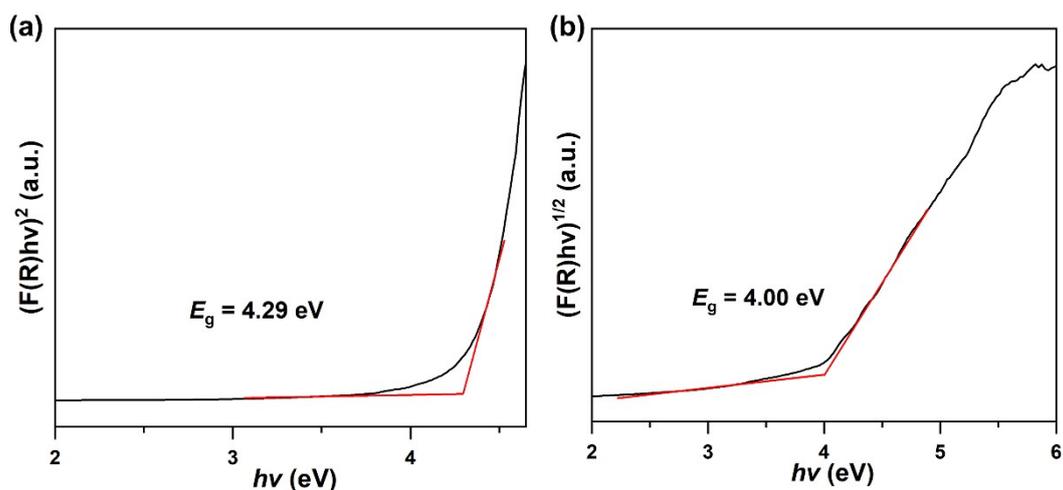
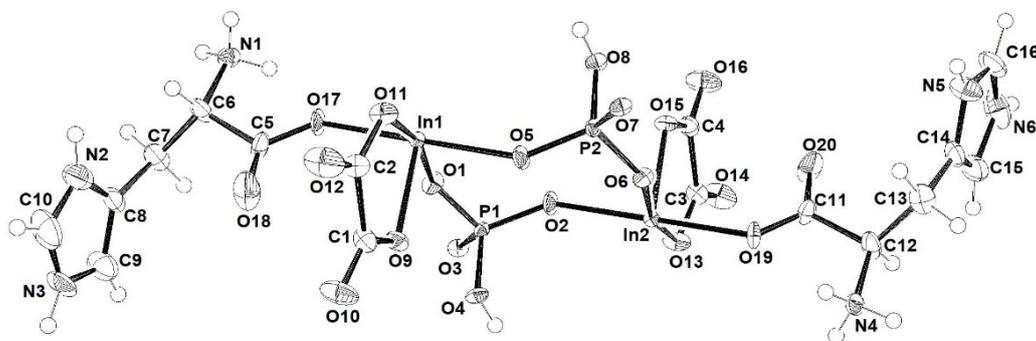


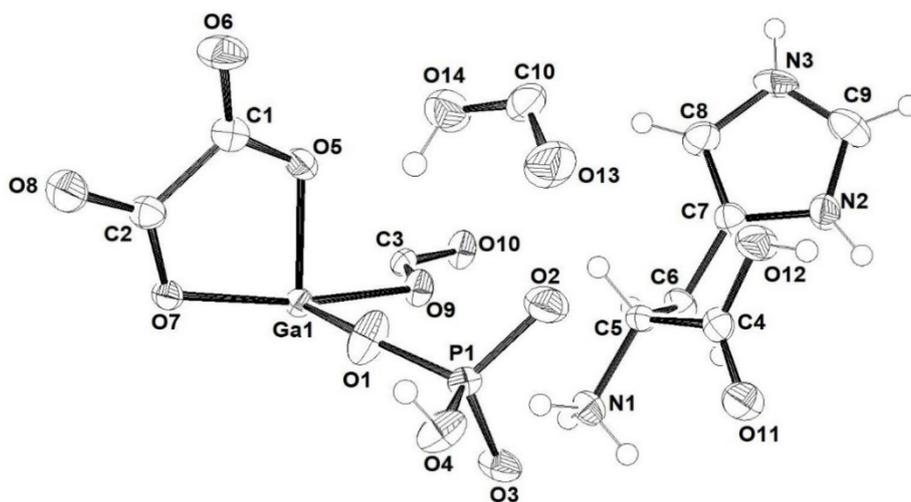
Fig. S2 TGA curves of compound 1 (a) and compound 2 (b) under N<sub>2</sub> atmosphere.



**Fig. S3** (a) The Tauc plots of compound **1** showing the optical band gap. (b) The Tauc plots of compound **2** showing the optical band gap.



**Fig. S4** ORTEP plot of the asymmetric unit of compound **1**, showing the labeling scheme and the 50% probability displacement ellipsoids.



**Fig. S5** ORTEP plot of the asymmetric unit of compound **2**, showing the labeling scheme and the 50% probability displacement ellipsoids.

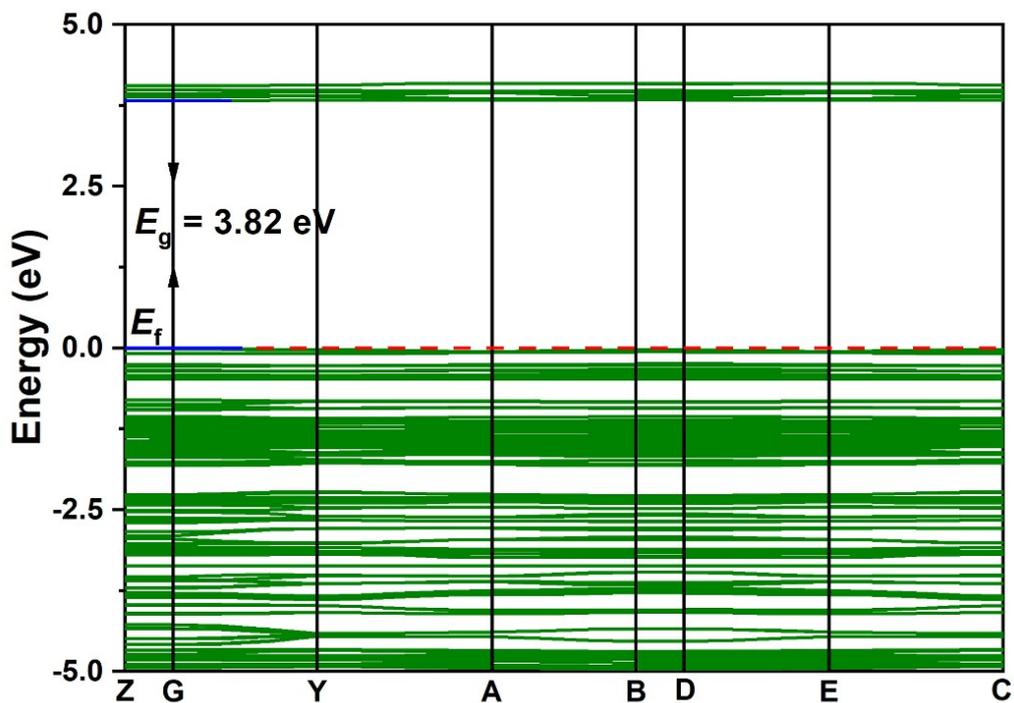


Fig. S6 Calculated band structure of compound 1 (the Fermi level is set at 0 eV).

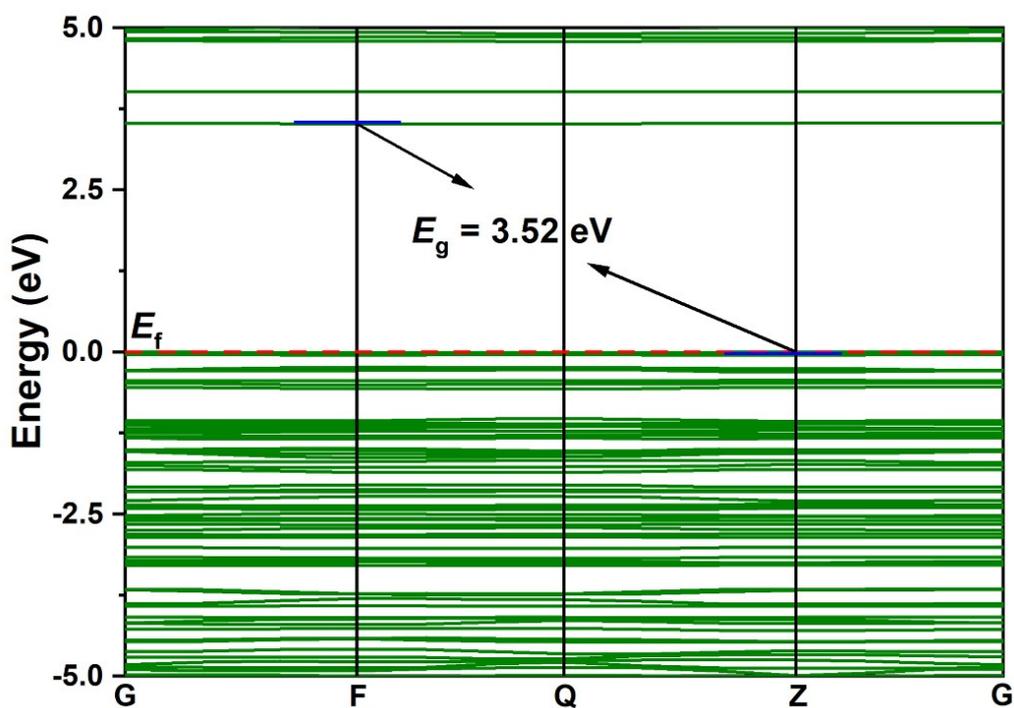


Fig. S7 Calculated band structure of compound 2 (the Fermi level is set at 0 eV).

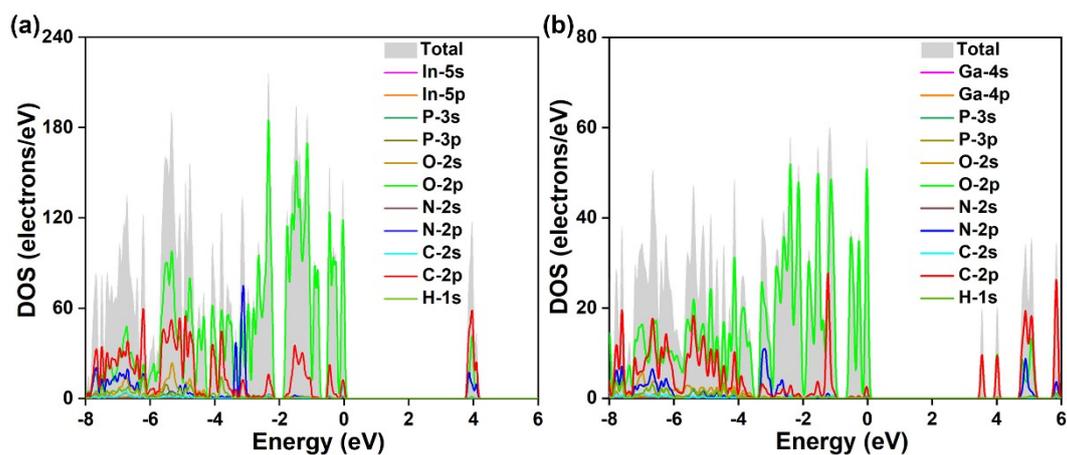


Fig. S8 Total and partial DOS of compound 1 (a) and compound 2 (b).

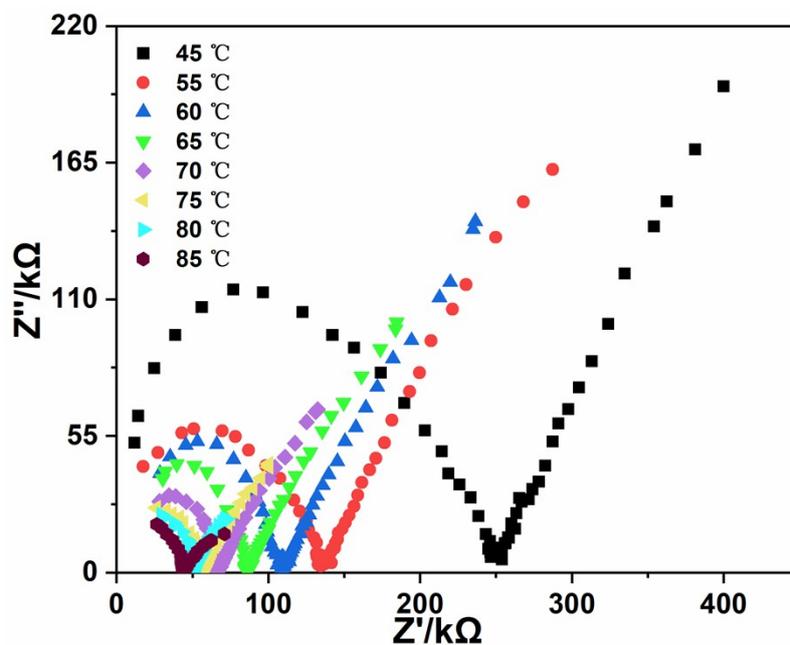
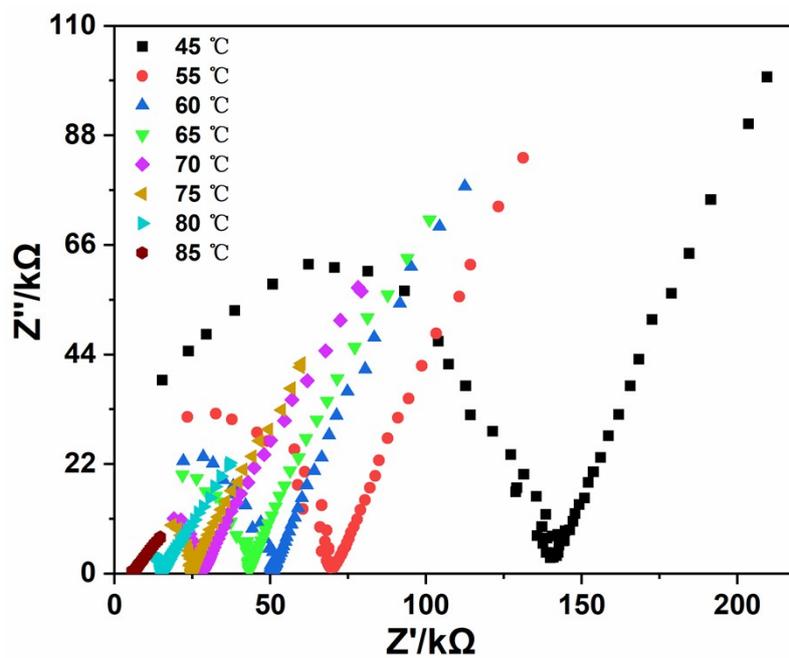


Fig. S9 Nyquist plots of compound 1 at different temperature under 95% relative humidity.



**Fig. S10** Nyquist plots of compound **2** at different temperature under 75% relative humidity.

## References

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