Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Polyoxometalate-Functionalized Metal-Organic Frameworks with Improved Water Retention and Uniform Proton-Conducting Pathways in Three Orthogonal Directions

Yiwei Liu,[a] Xiao Yang,[b] Qun Tang,[a] Jun Miao,[a] Shumei Liu,[a] Zhan Shi,[c] Shuxia Liu*[a]

[a] *Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, PR China. E-mail: liusx@nenu.edu.cn; Fax: +86-431-85099328; Tel: +86-431-85098260*

[b] *College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China*

[c] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, Jilin 130012, P. R. China*

Materials.

All the raw chemicals were obtained commercially and used without additional purification. $H_3PW_{12}O_{40}$ is synthesized according to the procedure described in the literature.[1]

Characterization.

FTIR spectra were recorded in the range 400-4000 cm^{-1} on an Alpha Centaurt FTIR spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku D/MAX-3 instrument with Cu Kα radiation in the angular range 2θ 3°-60° at 293 K. Hiden isochema IGA 100B instrument was used to measure N_2 sorption and water vapor adsorption measurement. AC impedance measurements of the samples were performed on a PARSTAT 2273 (AMETEK Instruments, USA) electrochemical workstation, the temperature and relative humidity are controlled by using an HDHWHS-50 incubator.

Preparation of HKUST-1

HKUST-1 was prepared according to the reported method.[2] $Cu(NO_3)_2 \cdot 3H_2O$ (2.6 g, 10.7 mmol) was dissolved in 30 mL of H_2O. BTC (0.68 g, 3.2 mmol) was dissolved in 30 mL of EtOH. The $Cu(NO_3)_2 \cdot 3H_2O$ solution was slowly added to the BTC solution with stirring at room temperature. The solution became turbid, with a precipitate forming. Then the combination was transferred to Teflon-lined autoclave and allowed to be reacted at 120 °C for 24 h. After allowing the autoclave and its contents to cool to room temperature, a crystalline solid, was collected and rinsed with H_2O and EtOH. Then the powder was dried in an oven at 150 °C for 24 hours to remove all the solvent molecules.

Preparation of NENU-3

NENU-3 was prepared according to the reported method.[3] The solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.24 g, 1mmol) and $H_3PW_{12}O_{40} \cdot nH_2O$ (0.22g, 0.092mmol) in distilled water (10 ml) was stirred for 20 min (solution A). The pH was adjusted to 2.5 by dropwise addition of 1M NaOH solution. H_3BTC (0.14 g, 0.67mmol) was dissolved in alcohol (10 ml) . Drop H_3BTC solution into solution A under continuous stirring at room temperature. Blue precipitates appeared gradually. The precipitates were collected by centrifugation and washed through centrifugation and redispersion in alcohol and distilled water. After dried in an oven at 150 °C for 24 h, NENU-3 can be obtained.

Preparation of NENU-3-Ina and NENU-3-ImHCl

NENU-3-Ina was prepared by an immersion method. Ina (0.123g, 1.2 mmol) was dissolved in 50 mL alcohol. The solution was heated to 50 °C. Then thermal activated NENU-3 powder (0.552g, 0.1 mmol) was added to the solution. The suspension was kept at 50 °C for 10 hours under continuous stirring. Then the solvent was evaporated. The powder was collected.

The prepare process of NENU-3-ImHCl is similar to NENU-3-Ina. Only Ina was replaced by imidazole hydrochlorid.

Water adsorption isotherms measurements

Water adsorption isotherms were measured at 1 bar and different temperatures. All samples were activated to remove residual guest molecules. Dry N_2 was used as the carrier gas, with a portion of

the carrier gas being bubbled through a vessel of deionized water. The relative humidity (RH) was controlled by varying the ratio of saturated N_2 and dry N_2 via two mass flow controllers from 0% to 90% RH. The total gas flow rate was 100 ml/min for the entire experiment. Variable timeouts were used with a maximum limit of 4 h per isotherm point.

AC impedance measurements

Impedance analyses were performed on powders of samples. The powders were pressed to discs under a pressure of 30 MPa for 1 minute. The samples used for measurement have a diameter of 12 mm and thickness of 1.6±0.2mm. The samples are sandwiched between two copper electrodes. Measurements were performed over frequency range 1 Hz - 1 MHz with an input voltage amplitude of 150 mV. Each conductivity measurement was conducted after waiting for 4 hours at the target condition (temperature and relative humidity). ZView software was used to fit impedance data sets by means of an equivalent circuit simulation to obtain the resistance values.

References.

(1) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R., *Inorg. Chem.* **1983,** *22*, 207.

(2) Schlesinger, M.; Schulze, S.; Hietschold, M.; Mehring, M., *Micropor. Mesopor. Mater.* **2010,** *132*, 121.

(3) Liu, Y.; Liu, S.; Liu, S.; Liang, D.; Li, S.; Tang, Q.; Wang, X.; Miao, J.; Shi, Z.; Zheng, Z., *ChemCatChem* **2013,** *5*, 3086.

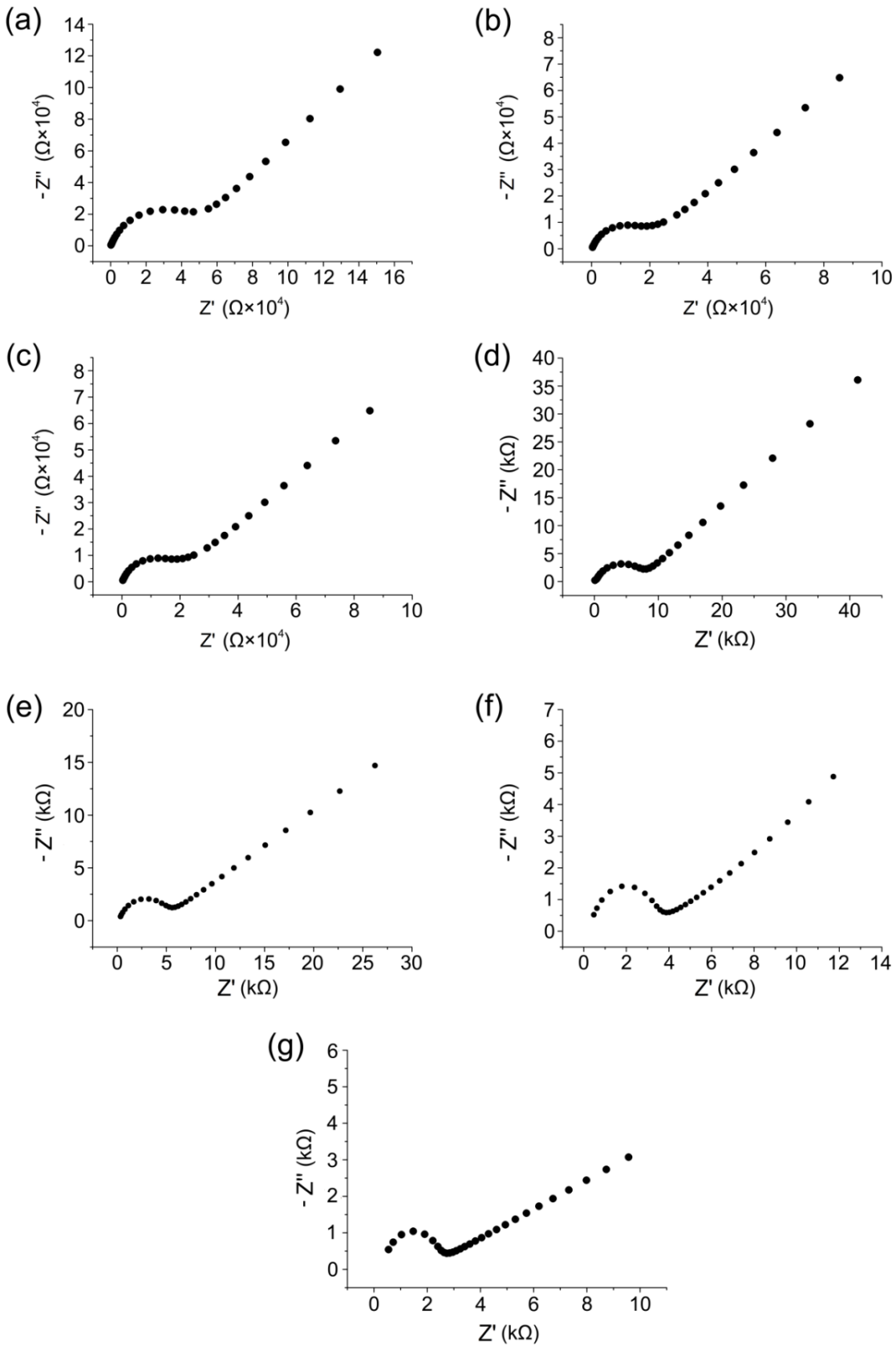

Figure S1. Nyquist plots of NENU-3 at at 70% RH and various temperatures (a) 25 ℃, (b) 40 ℃, (c) 50 ℃, (d) 60 ℃, (e) 70 ℃, (f) 80 ℃, (g) 90 ℃.

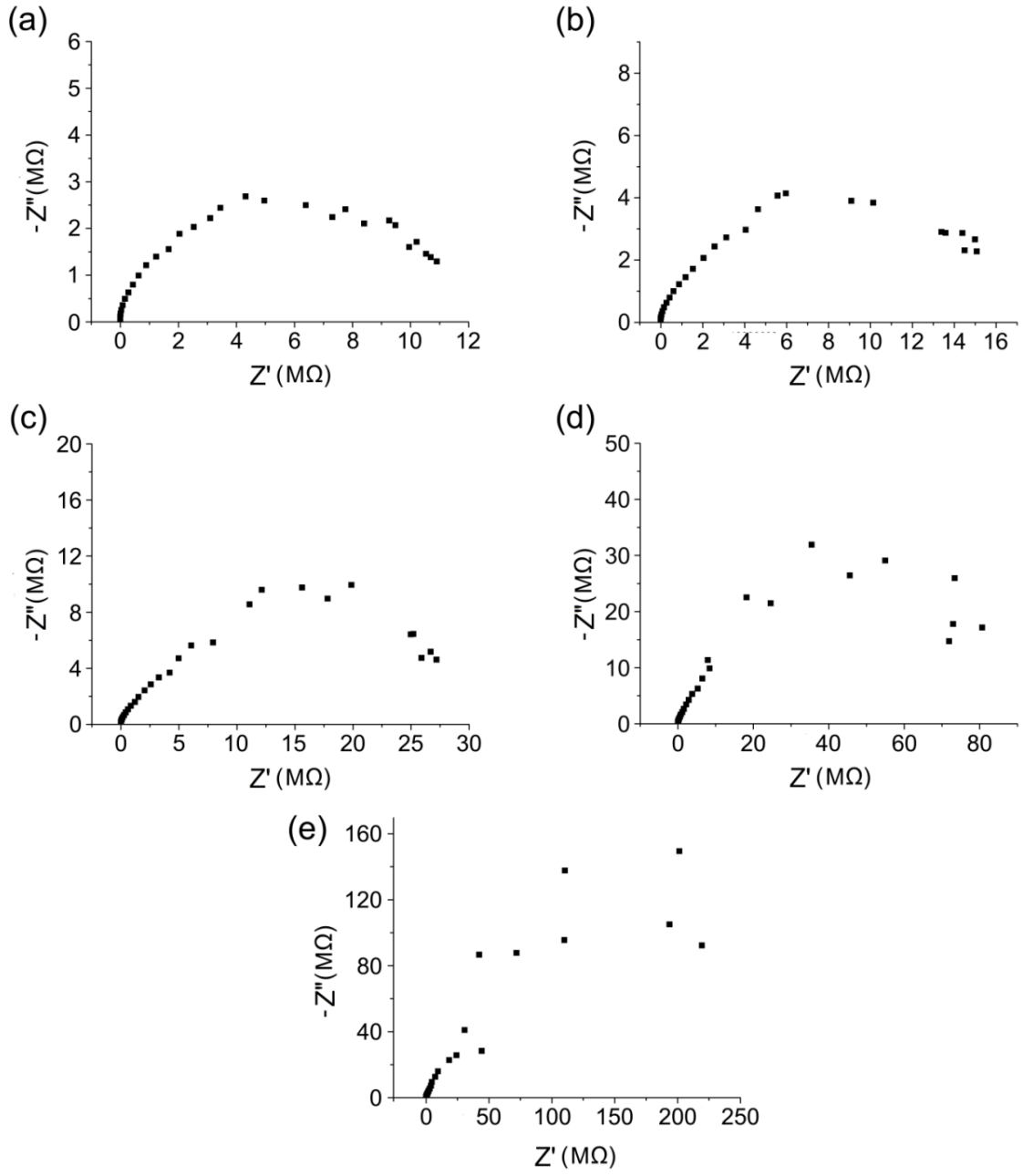

Figure S2. Nyquist plots of HKUST-1 at 70% RH and various temperatures (a) 90 ℃, (b) 80 ℃, (c) 70 ℃, (d) 60 ℃, (e) 50 ℃.

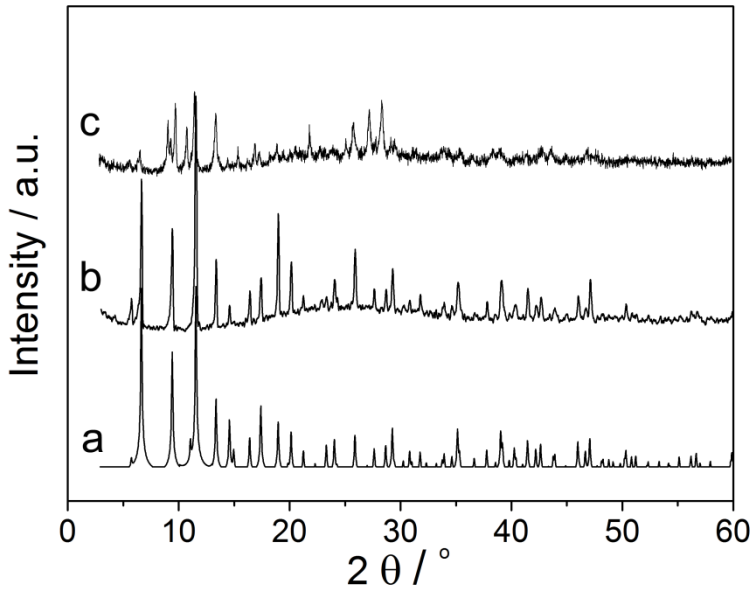

Figure S3. PXRD patterns of HKUST-1 (a) simulated, (b) as-synthesized, and (c) the sample after be exposed in water vapor for ~2 hours.

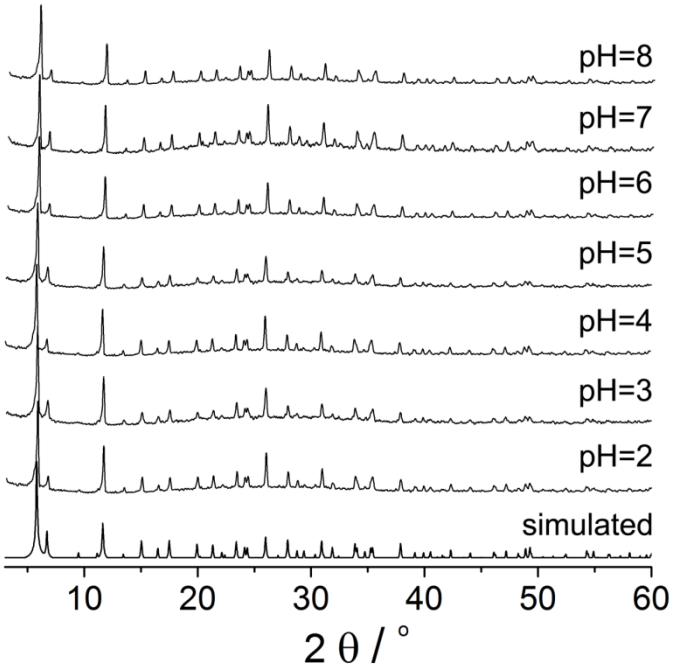

Figure S4. PXRD patterns of NENU-3 after having been soaked in aqueous solution with different pH value for 1 week, the pH value is adjusted by HCl or NaOH.

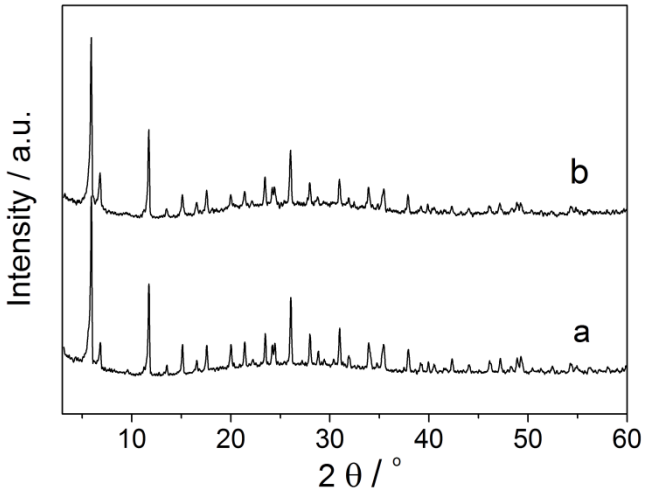

Figure S5. PXRD patterns of NENU-3 before (a) and after (b) the impedance measurement.

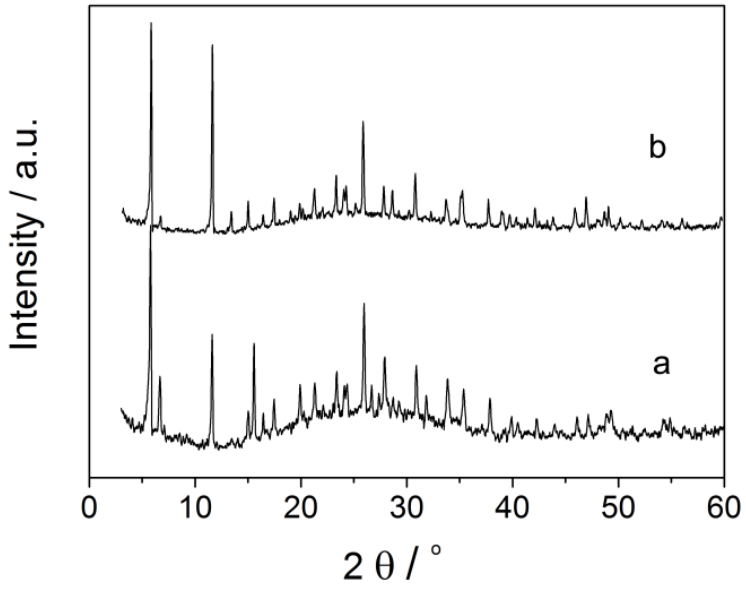

Figure S6. PXRD patterns of (a) NENU-3-Ina, (b) NENU-3

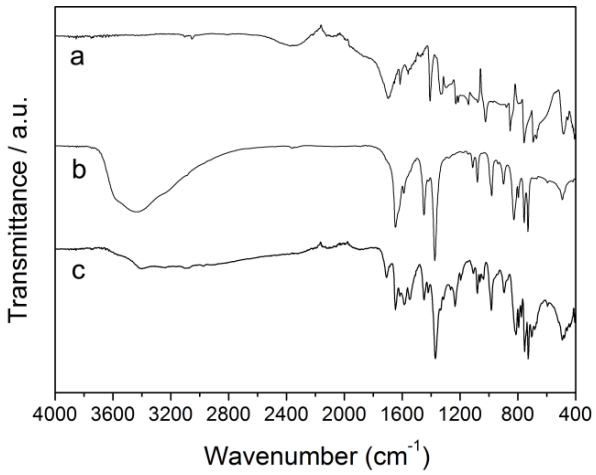

Figure S7. FTIR spectrum of (a) Isonicotinic acid, (b) NENU-3, and (c) NENU-3-Ina.

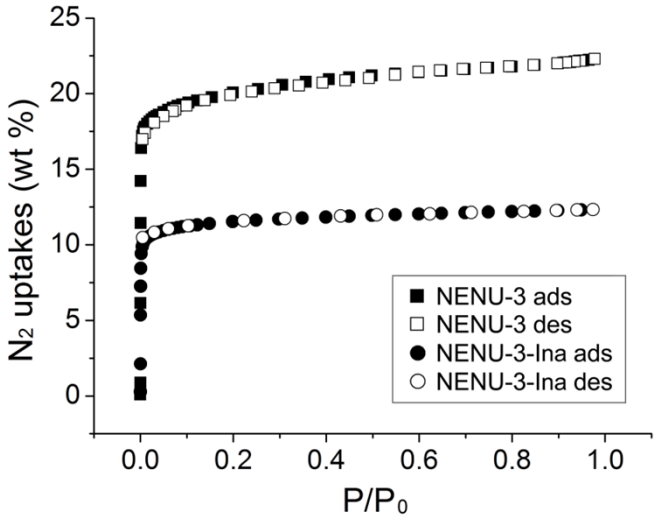

Figure S8. N_2 adsorption and desorption isotherms of NENU-3 and NENU-3-Ina

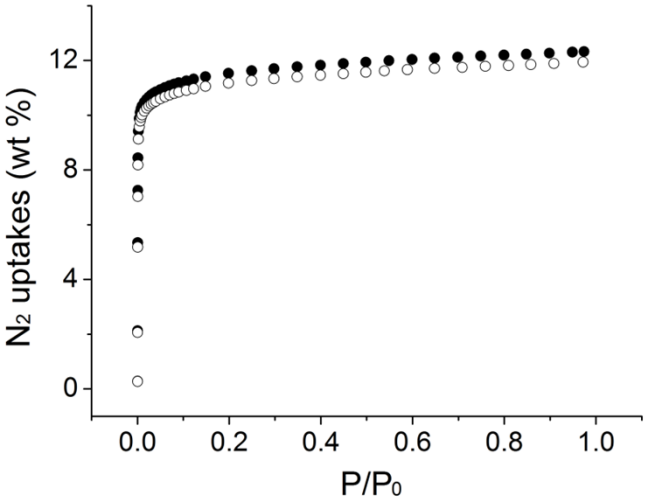

Figure S9. N_2 adsorption and desorption isotherms of NENU-3-Ina before (solid disc) and after (hollow circle) be rinsed with hot water and ethanol.

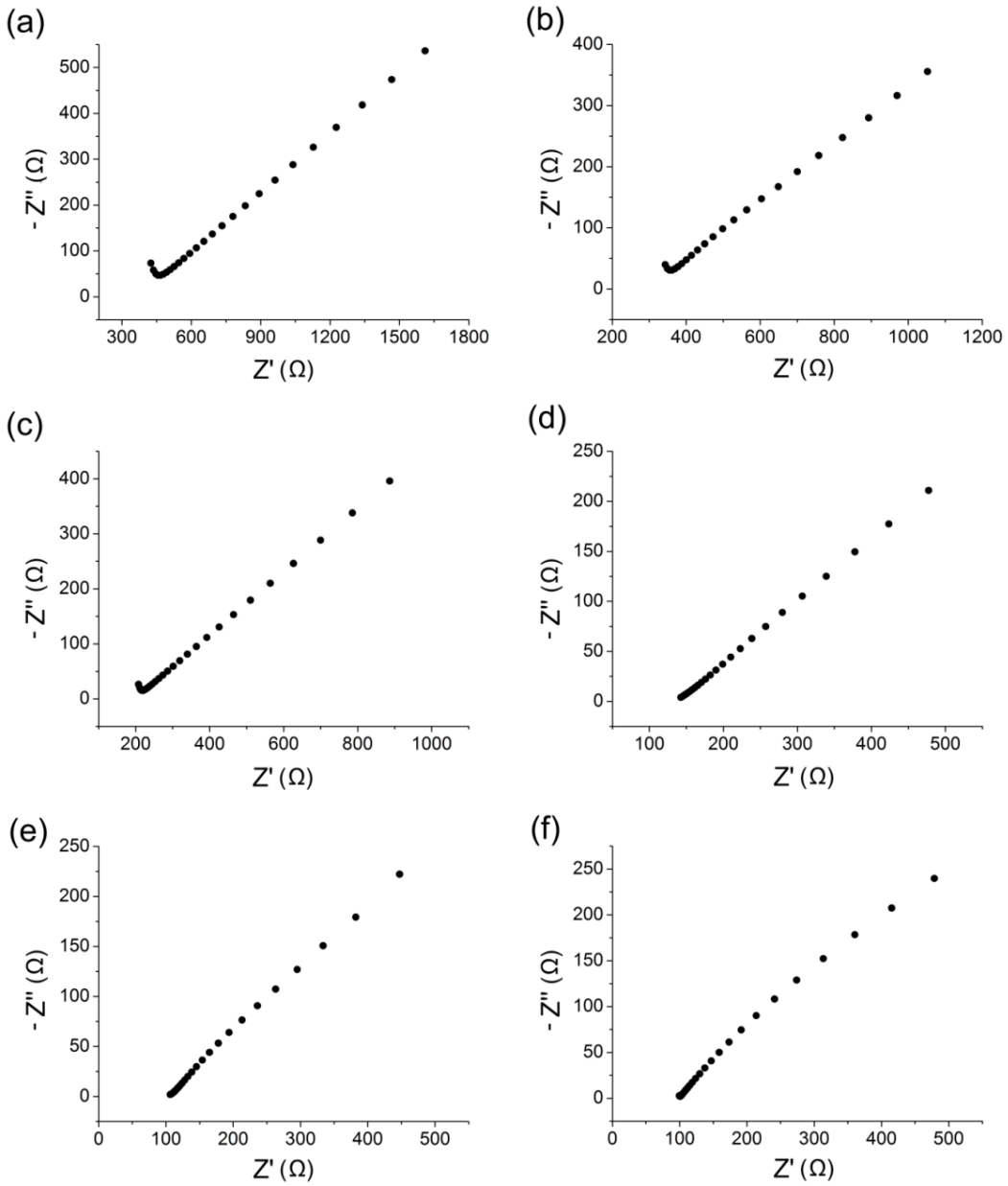

Figure S10. Nyquist plots of NENU-3-Ina at at 70% RH and various temperatures (a) 40 ℃, (b) 50 ℃, (c) 60 ℃, (d) 70 ℃, (e) 80 ℃, (f) 90 ℃.

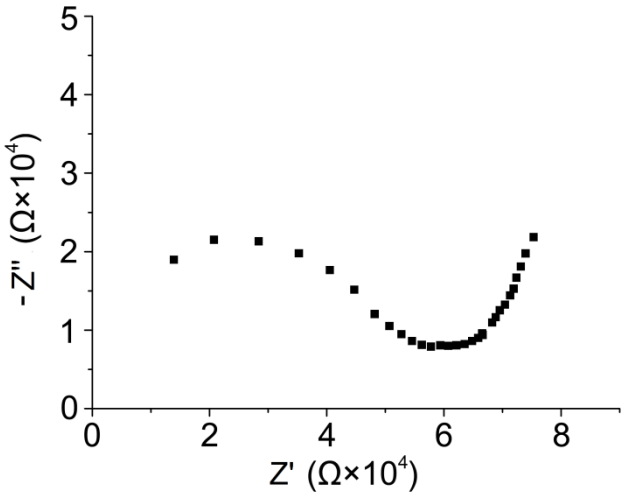

Figure S11. Nyquist plots of isonicotinic acid at 90 ℃ and 70% RH.

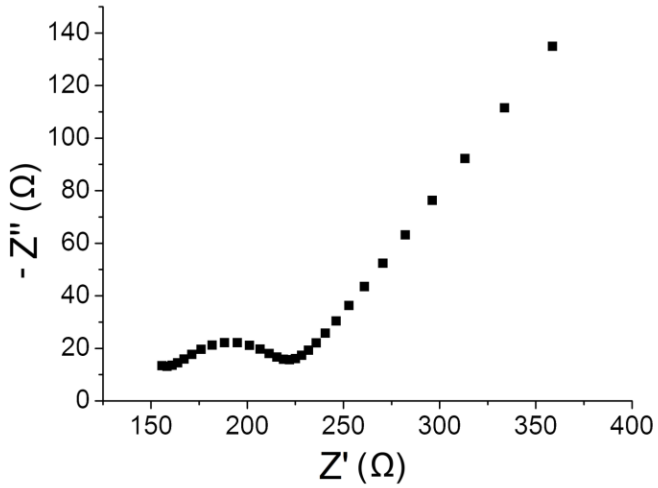

Figure S12. Nyquist plots of NENU-3-ImHCl at 90 ℃ and 70% RH.