

# Supporting Information

## Defect-engineering of Anionic Porous Aromatic Frameworks for Ammonia Capture

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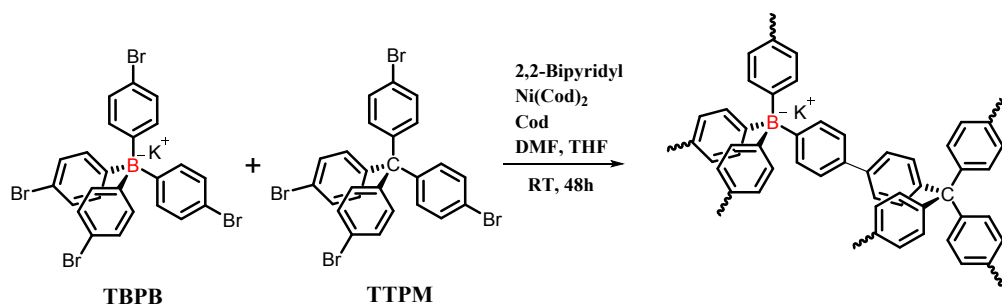
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## Section 1. Methods

$^1\text{H}$  NMR were recorded on a Bruker AV 400MHz spectrometer (Bruker). The  $^{11}\text{B}$  solid-state NMR and  $^{13}\text{C}$  solid-state NMR experiments were performed on an Agilent DD2 600 spectrometer. The  $^{11}\text{B}$  solid-state NMR experiments were operated at Larmor frequency of 192.232 MHz. A triple-resonance 3.2-mm T3 MAS probe and the 3.2 mm  $\text{ZrO}_2$  rotor were used for the experiments. The  $^{11}\text{B}$  mas-angle spinning MAS NMR spectra were acquired using a one pulse sequence, with  $90^\circ$  pulse length of 2.2  $\mu\text{s}$  (58 dB). The number of scan was set to 2048 and the recycle delay was set to 2 s. The magic angle spinning speed was 15 kHz. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker model VERTEX 70 infrared spectrometer. Thermogravimetric analysis (TGA) was performed under  $\text{N}_2$  on a NETZSCH STA449F3 with a heating rate of 10  $^\circ\text{C min}^{-1}$ . X-ray photoelectron spectroscopy (XPS) experiments were carried out on an Thermo ESCALAB 250Xi with Al  $\text{K}\alpha$  radiation as X-ray source for radiation Thermogravimetric analysis (TGA) was performed under  $\text{N}_2$  on a NETZSCH STA449F3 with a heating rate of 10  $^\circ\text{C min}^{-1}$ . The morphology of samples was characterized by scanning electron microscope (SEM, JSM-6360LV and TEM, JEOL JEM-2100). Ultraviolet-visible (UV-Vis) spectra were recorded on a SHIMADZU UV-2500 Spectrophotometer. The fluorescence emission spectra were obtained with a Horiba FluoroMax-4 spectrophotometer.

## Section 2. Materials and experimental procedures

Solvents, reagents and chemicals were purchased from Aldrich and TCI. All solvents were dried before use. All air-sensitive reactions were carried out under a nitrogen atmosphere and performed using Schlenk techniques. TBPB and TTPM were prepared by previous reports.<sup>1</sup>



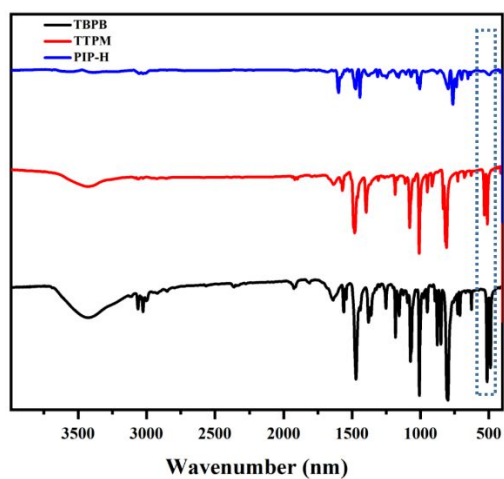
**Scheme S1.** Synthetic scheme of porous ionic polymers PIP-H.

**Synthesis of PIP-H:** The experimental procedure was performed in a glove box. To a solution of bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)<sub>2</sub>) (1g, 3.65mmol) and 2,2'-bipyridyl (565mg, 3.65 mmol) in dehydrated extra dry DMF and THF (60 mL/90mL), 1,5-cyclooctadiene(cod) (0.45 mL, 3.65 mmol) was added, and the mixture was stirred at room temperature for 0.5 h. To the resultant purple solution, TBPB (270mg, 0.4mmol) and TTPM (255 mg, 0.4 mmol) were added, and the mixture was stirred at room temperature for 48 h to obtain the deep purple suspension. After polymerization, 30 mL deionized water was added and stirred for about 6 hours. Then the suspension was vacuum filtered. The residue solid was washed with dimethylacetamide, tetrahydrofuran, acetone, methanol and water and dried in vacuo to give PIP-X as a deep black powder.

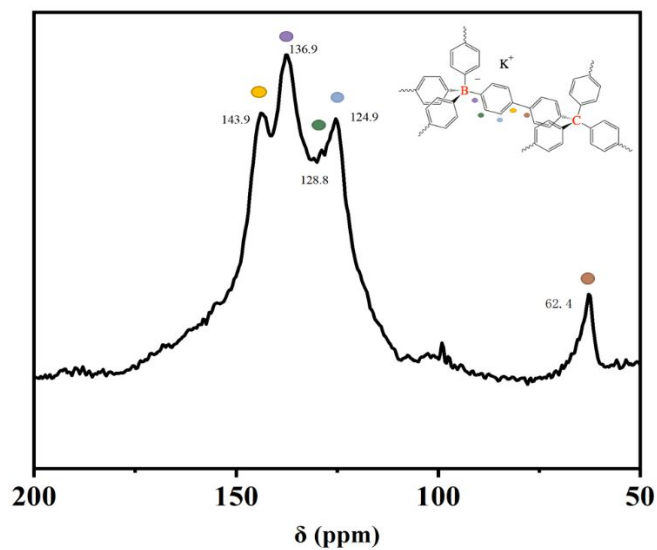
**Synthesis of PIP-X:** The experimental procedure was performed in a glove box. To a solution of bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)<sub>2</sub>) (1g, 3.65mmol, ) and 2,2'-bipyridyl (565mg, 3.65 mmol) in dehydrated extra dry DMF and THF (60 mL/90mL), 1,5-cyclooctadiene(cod) (0.45 mL, 3.65 mmol) was added, and the mixture was stirred at room temperature for 0.5 h. To the resultant purple solution, TBPB (270mg, 0.4mmol) and TTPM (255 mg, 0.4 mmol) were added, and the mixture was stirred at room temperature for 48 h to obtain the deep purple suspension. After polymerization, the reaction was quenched by adding concentrated HCl and stirred for about 3 h. Then the suspension was vacuum filtered. The residue solid was washed with dimethylacetamide, tetrahydrofuran, acetone, methanol and water and dried in vacuum to give PIP-X as a milk white powder. PIP-X (6 M HCl, 3 M HCl, 1 M HCl) were also synthesized using the same method except the different concentration of HCl were added.

**Synthesis of Cu@PIP-X:** The ion exchange was carried out by slurrying 30 mg PIP-X for 24 h in saturated copper acetate solvent mixture of H<sub>2</sub>O and methyl alcohol, filtered and washed with portions of 100 mL deionized water and methyl alcohol. Afterwards the material was dried under vacuum at 100 °C. The product was obtained as a beige powder.

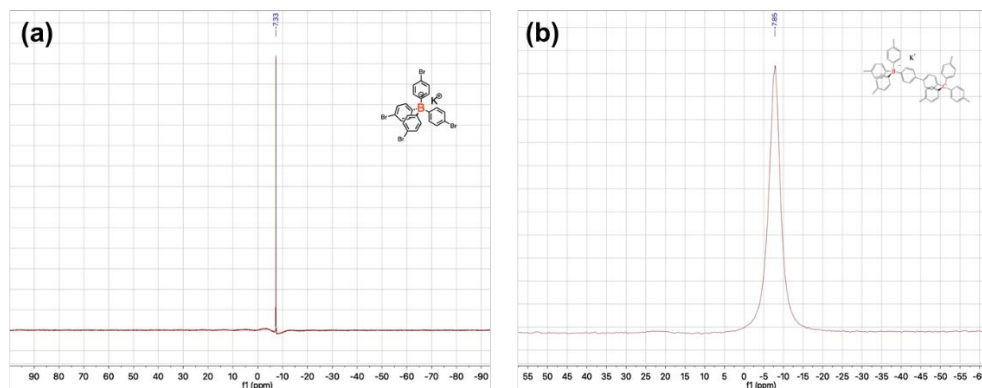
### Section 3. Supporting Figures



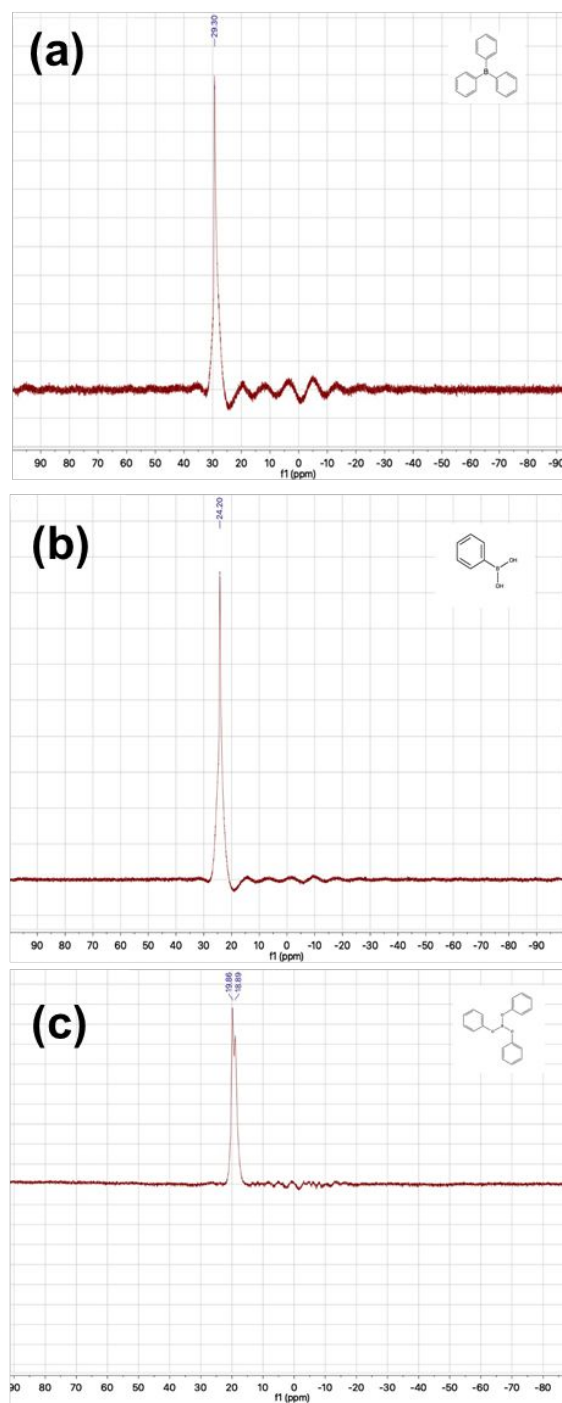
**Figure S1.** FT-IR spectrum of TBPB (black), TTPM (red) and PIP-H (blue).



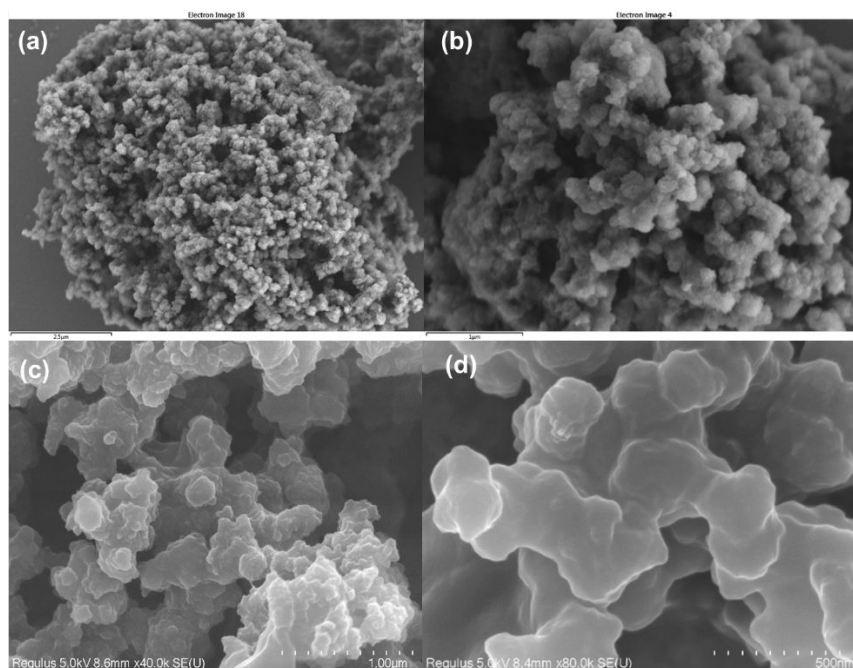
**Figure S2.**  $^{13}\text{C}$  SSNMR spectra of PIP-H.



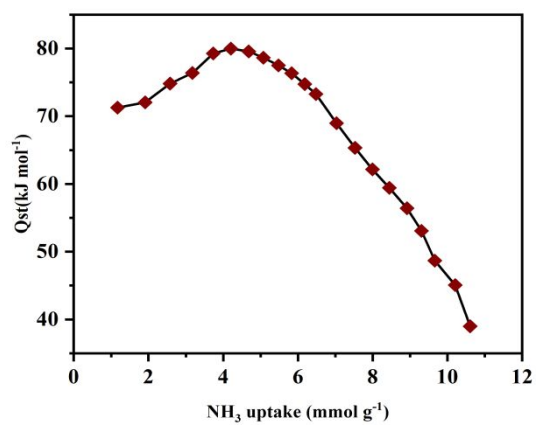
**Figure S3.**  $^{11}\text{B}$  SSNMR spectra of (a) TBPB; and (b) PIP-H.



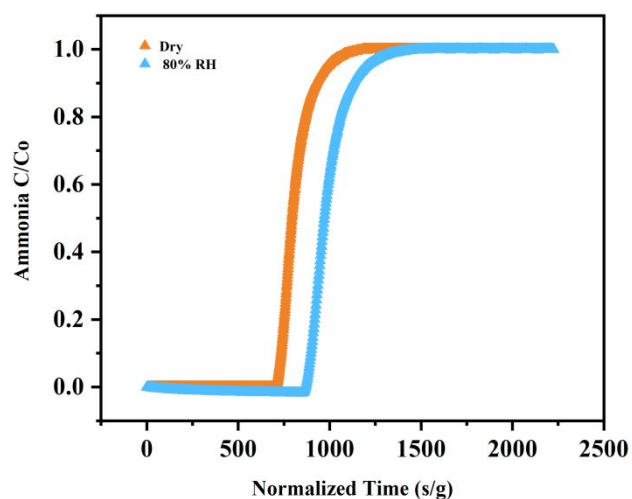
**Figure S4.**  $^{11}\text{B}$  SSNMR spectra of the possible units of tri-coordinate boron units including (a) triphenylborane; (b) phenylboronic acid; and (c) triphenyl borate.



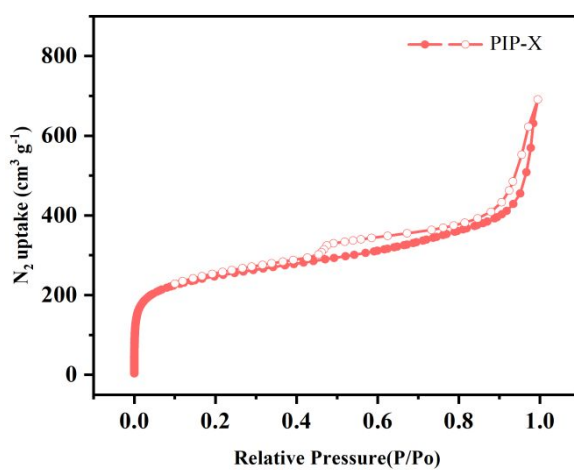
**Figure S5.** SEM images of (a), (b) PIP-H; and (c), (d) PIP-X.



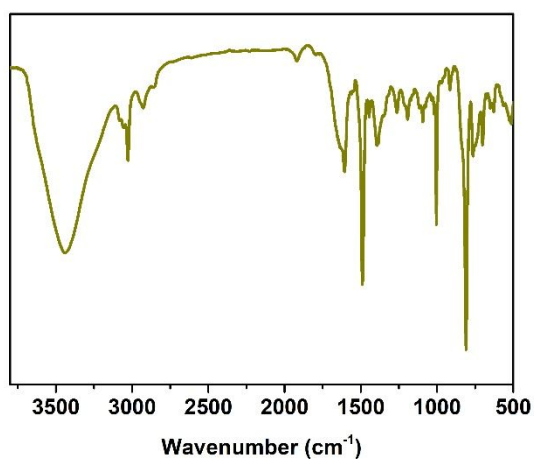
**Figure S6.** Isosteric adsorption heat ( $Q_{st}$ ) of  $NH_3$  for PIP-X fit from isotherms at 298 and 308 K.



**Figure S7.** Ammonia breakthrough curves for PIP-X under dry (0% RH) and wet (80% RH) conditions.

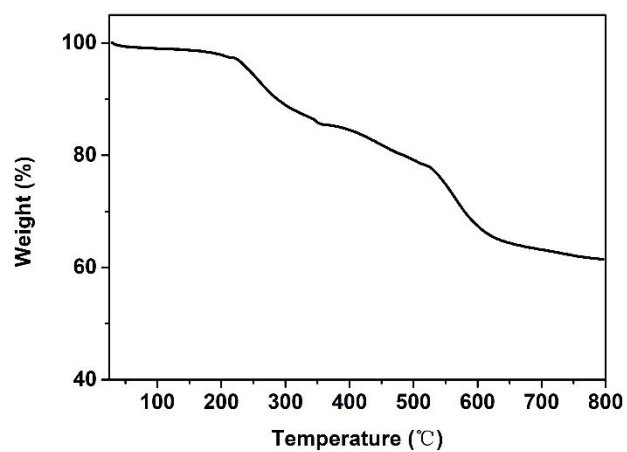


**Figure S8.** N<sub>2</sub> adsorption/desorption isotherms of PIP-X after cycling tests.

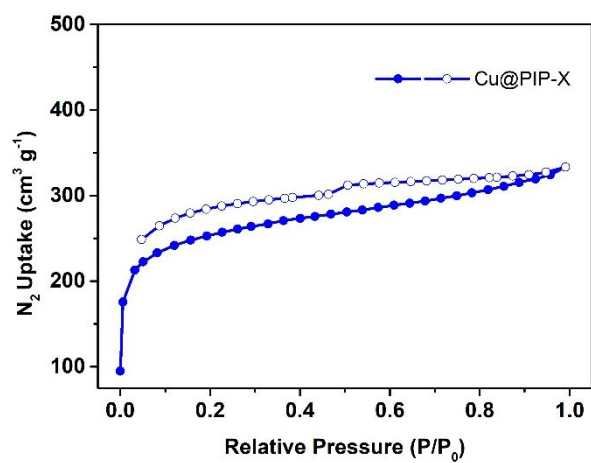


**Figure S9.** The FTIR patterns of the as-synthesized Cu@PIP-X.





**Figure S10.** TGA curve of the as-synthesized Cu@PIP-X.



**Figure S11.** N<sub>2</sub> adsorption/desorption isotherms of Cu@PIP-X after cycling tests.

## Section 4. Supporting Tables

**Table S1.** Summary of the results from ICP analysis of boron (B), nickel (Ni) and copper (Cu).

Polymer	ICP-B (wt %)	ICP-Ni (wt %)	ICP-Cu (wt %)
PIP-H	0.75	21	/
PIP-X	1.4	<0.2	/
Cu@PIP-X	0.81	/	2.3

**Table S2.** Calculated binding energies of NH<sub>3</sub> to [B(pph)<sub>4</sub>]<sup>-</sup> and the possible units of tri-coordinate boron.

Binding Energy	Triphenylborane (B(pph) <sub>3</sub> )	Tetrakis(halophenyl)borate [B(pph) <sub>4</sub> ] <sup>-</sup>
E <sub>(unit)</sub> (a.u.)	-718.1559868	-950.6621836
E <sub>(NH3+unit)</sub> (a.u.)	-775.6819382	-1007.1870975
E (KJ mol <sup>-1</sup> )	-48.5286918	-45.8047356

**Table S3.** Calculated binding energies of NH<sub>3</sub> to M[B(pph)<sub>4</sub>] (M=K<sup>+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>).

Binding Energy	K <sup>+</sup>	Mg <sup>2+</sup>	Cu <sup>2+</sup>	Co <sup>2+</sup>	Mn <sup>2+</sup>	Zn <sup>2+</sup>
E <sub>(M[B(pph)<sub>4</sub>])</sub> (a.u.)	-1550.3767198	-1150.3612474	-1172.7896743	-1117.1522031	-1072.0859974	-1204.7176842
E <sub>(NH3+M[B(pph)<sub>4</sub>])</sub> (a.u.)	-1606.9088588	-1206.9433637	-1229.3875087	-1173.732746	-1128.6730204	-1261.2914786
E (KJ mol <sup>-1</sup> )	- 64.7747607	-195.98963675	-213.6380083	-191.90855955	-208.8721776	-174.1404883

## Section 5. Supporting References

- [1] Tomaszewski, P.; Wiszniewski, M.; Serwatowski, J.; Woźniak, K.; Durka, K.; Luliński, S. Synthesis of tetraarylbates via tetralithio intermediates and the effect of polar functional groups and cations on their crystal structures. *Dalton Trans.*, **2018**, 47, 16627-16637.