

Electronic Supporting Information for

Li-ion Storage and Gas Adsorption Properties of Porous Polyimides (PIs)

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Experimental procedures

Chemicals and Physical measurements. All the chemicals used for synthesis were commercially available and used as received. Solid-state NMR experiment was carried on a Varian Infinityplus-400 wide-bore (89 mm) NMR spectrometer at a proton frequency of 399.7 MHz using a 4 mm double-resonance HX CP/MAS NMR probe. IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Thermogravimetric analyses (TGA) was carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C min⁻¹ from room temperature to 700 °C. The X-ray powder diffraction spectra (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100mA for a Cu-target tube and a graphite. Scanning electron microscope (SEM) images were recorded using a Nova Nano 230 (FEI company) scanning electron microscope. Gas adsorption measurements were performed using an ASAP 2020 M gas adsorption analyzer.

Synthesis of the TAPB. 1,3,5-Tris(4-aminophenyl)benzene was prepared according to the literature.^{S1}

Syntheses of polyimides.^{S2} For PI-1, to a dried round-bottom three-necked flask equipped with a magnetic stirrer were charged 1,2,4,5-benzenete-tricarboxylic anhydride (82 mg, 0.375 mmol) and 10 mL DMF. Then the system was heated with stirring in a 170 °C oil bath. Once refluxing, a solution of TAPB (88 mg, 0.25 mmol) in 5 mL propionic acid was added dropwise over a period of 30 min. When the brown mixture became cloudy, 5 mL DMF were added and a brown yellow precipitate soon formed. The solution was stirred at 170 °C for 20 hours, then filtered and washed with DMF to yield a yellow, fluffy powder. The powder was collected after Soxhlet extracted over night with tetrahydrofuran, methanol, acetone, dichloromethane (yield: 60% ~ 70%).

The PI-2 was obtained by similar procedures, with 1,2,4,5-benzenete-tricarboxylic anhydride replaced by 1,4,5,8-naphthalenete-tricarboxylic dianhydride (100 mg, 0.375 mmol).

PI-3 was obtained according to literature procedure.^{S3} Perylene dianhydride (0.375 mmol) was taken in 40 g imidazole and stirred at 150 °C under nitrogen atmosphere until it dissolves. TAPB (0.125 mmol) in 5 mL N,N-dimethylformamide (DMF) was added drop by drop to the above mixture, and the mixture was stirred at 180 °C for 24 h. After this the reaction mixture was cooled to 100 °C and methanol was added. The precipitate was collected by filtration followed washing with DMF and ethanol. The black powder was collected after Soxhlet

extracted over night with tetrahydrofuran, methanol, dichloromethane. Among three PIs, PI-3 possesses high density, while PI-1 is most fluffy.

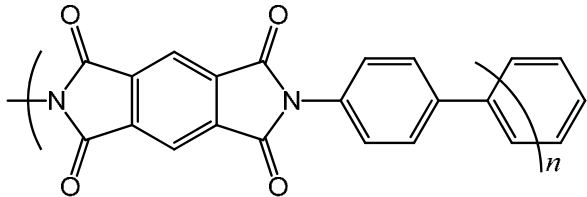
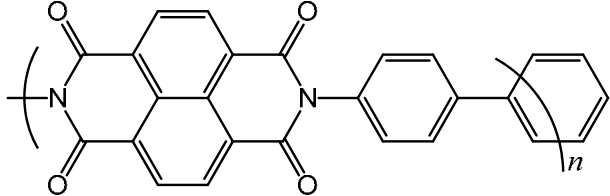
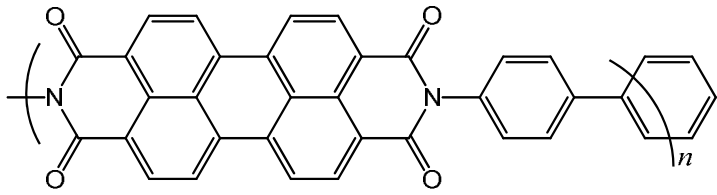
Electrochemical Studies. The PIs sample, acetylene black, and polytetrafluoroethylene (PTFE, as binder) were mixed at a weight ratio of 80:15:5, and compressed to prepare the working electrode. A metallic lithium foil was used as the counter electrodes. The electrolyte was LiPF₆ (1 M) dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) with a volume ratio of 1:1:1. The galvanostatic charge and discharge tests were performed between 1.5 and 4.2 V (vs Li/Li⁺) with LAND CT-2001A instrument. The cyclic voltammetry (CV) measurement was conducted with a CHI 600 A electrochemical workstation at a scan rate of 0.1 mV/s. All electrochemical measurements were carried out at room temperature.

Sorption measurements. The samples were loaded in sample tubes and activated under high vacuum (less than 10⁻⁵ Torr) at 150 °C for three materials. Degassed samples (98 mg for PI-1, 94 mg for PI-2 and 97 mg for PI-3) were used for gas sorption measurements. Gas adsorption measurements were performed using an ASAP 2020 M gas adsorption analyzer.

The N₂ sorption isotherms were collected at 77 K in a liquid nitrogen bath, at 273 K in an ice water mixture bath and at 298 K in an electric heating jacket. The H₂ sorption isotherms were collected at 77 K in a liquid nitrogen bath and at 87 K in a liquid argon bath. The CO₂ sorption isotherms were collected at 273 K in an ice water mixture bath, at 298 K in an electric heating jacket. The CH₄ sorption isotherms were collected at 273 K in an ice water mixture bath and at 298 K in an electric heating jacket.

- S1. C. Y. Bao, R. Lu, M. Jin, P. C. Xue, C. H. Tan, T. H. Xu, G. F. Liu and Y. Y Zhao, *Chem.-Eur. J.*, 2006, **12**, 3287.
- S2. O. K. Farha, A. M. Spokoyny, B. G. Hauser, Y. Bae, S. E. Brown, R. Q. Snurr, C. A. Mirhin and J. T. Hupp, *Chem. Mater.*, 2009, **21**, 3033.
- S3 K. V. Rao, R. Haldar, C. Kulkarni, T. K. Maji and S. J. George, *Chem. Mater.*, 2012, **24**, 969.

Table S1: General description of the three polyimide samples.^[a]

Name	Structure	Color	Theoretical capacity [mA h g ⁻¹]
PI-1		pale yellow	338.2
PI-2		deep yellow	292.1
PI-3		black	218.3

[a] The theoretical capacity is calculated based on a four-electron transfer redox process for each formula unit.

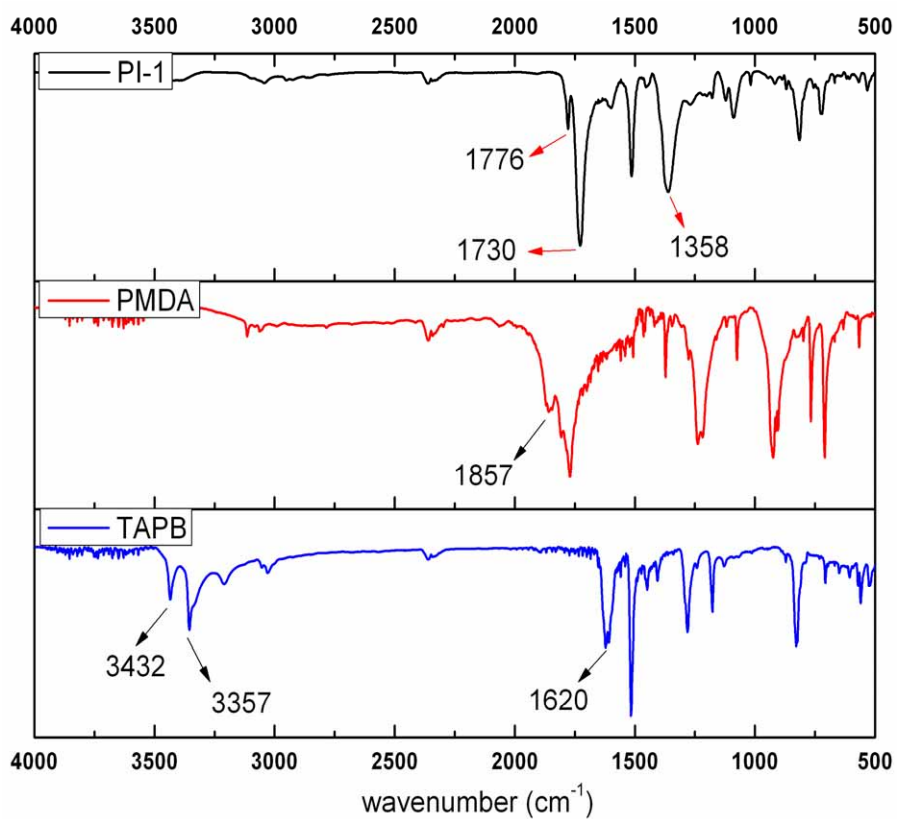


Fig. S1 FT-IR spectra of PI-1, the reactant TAPB and PMDA.

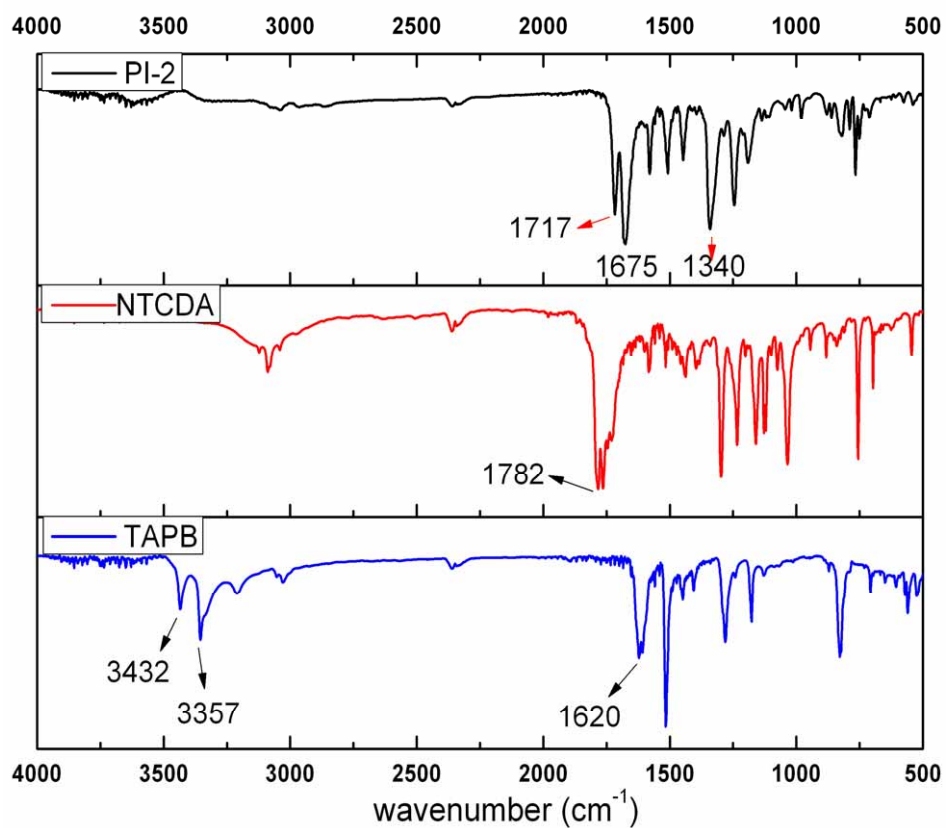


Fig. S2 FT-IR spectra of PI-2, the reactant TAPB and NTCDA.

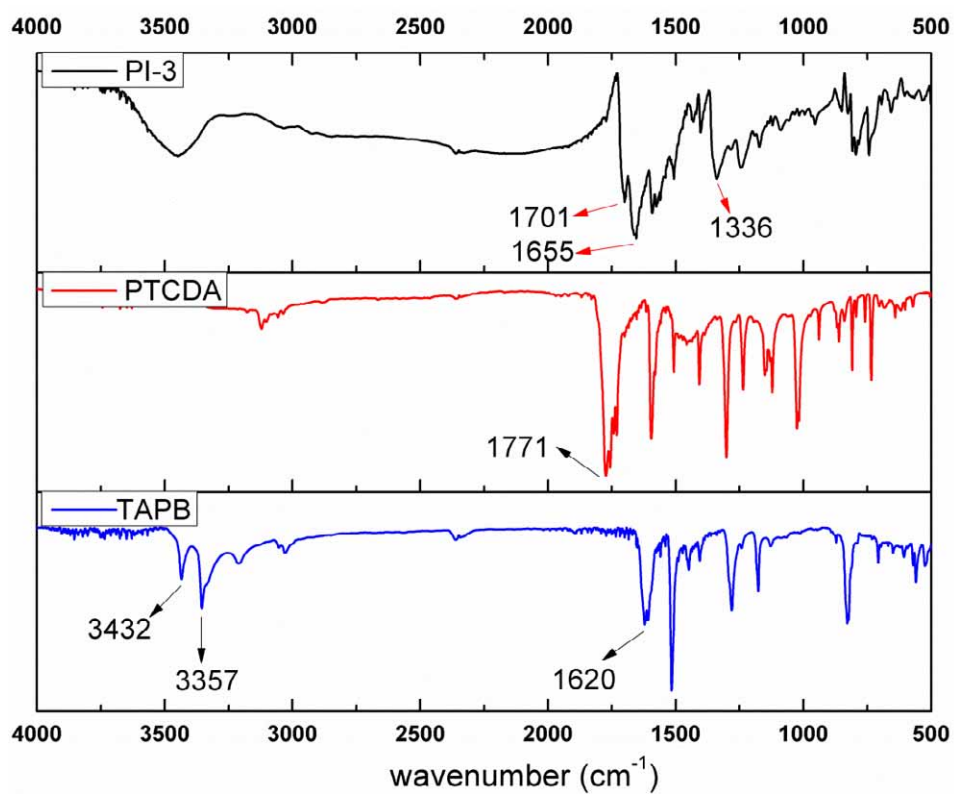


Fig. S3 FT-IR spectra of PI-3, the reactant TAPB and PTCDA.

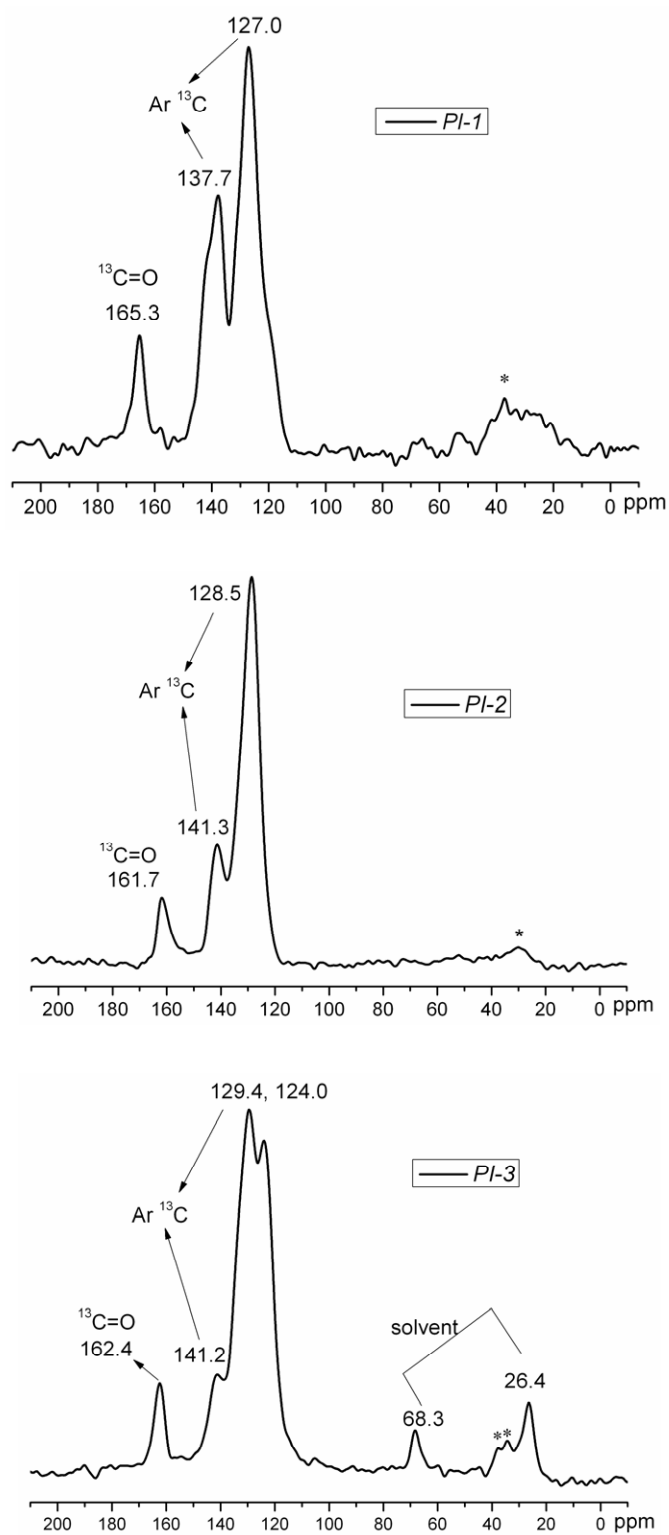


Fig. S4 Solid ^{13}C NMR spectra of PI-1, PI-2 and PI-3. Asterisks denote spinning sidebands.

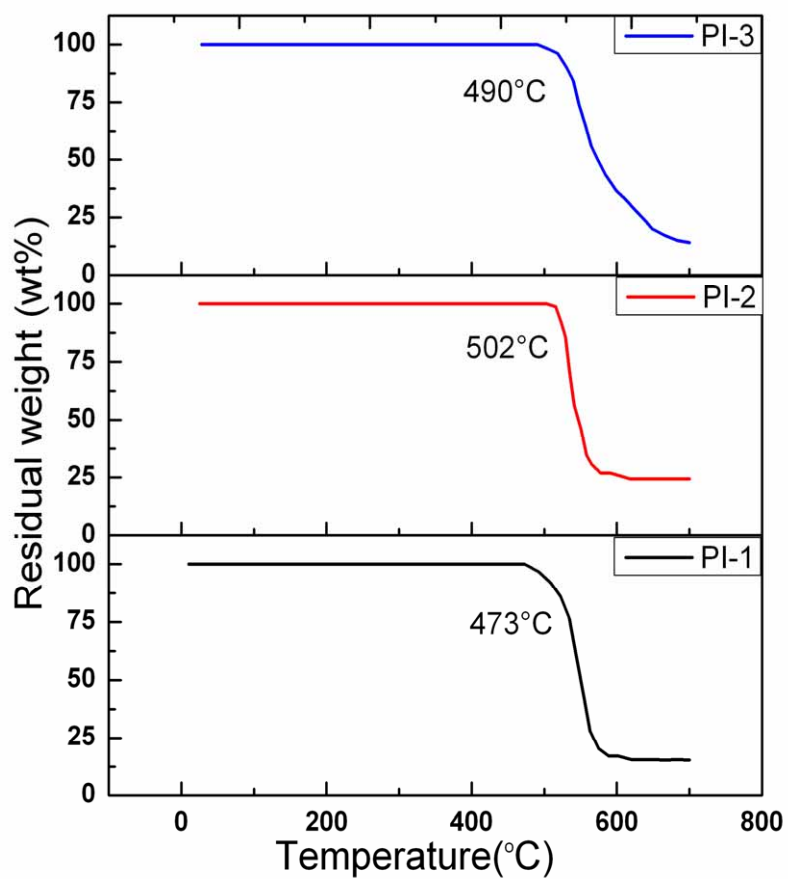


Fig. S5 TGA curves of PI-1, PI-2 and PI-3 under air atmosphere and heating rate of 10 °C min⁻¹.

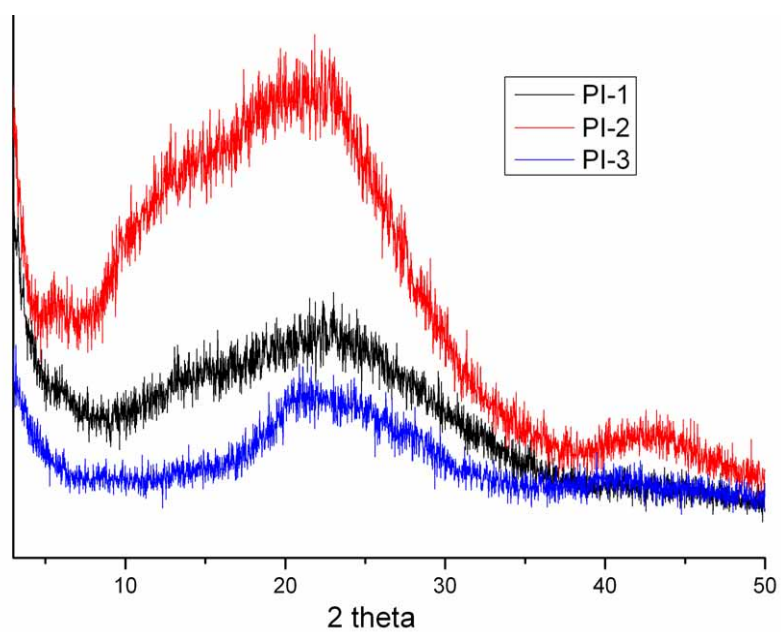


Fig. S6 X-ray powder diffraction patterns of PI-1 (black), PI-2 (red), and PI-3 (blue).

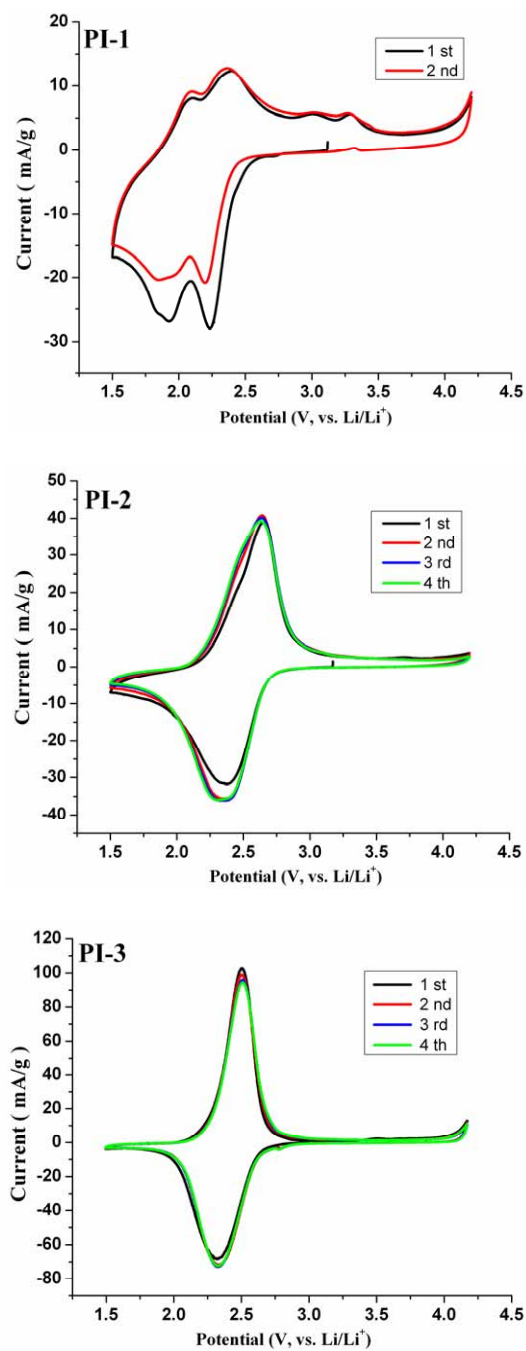


Fig. S7 The CV curves of the PIs film cathode (scan rate = 0.1 mV/s).

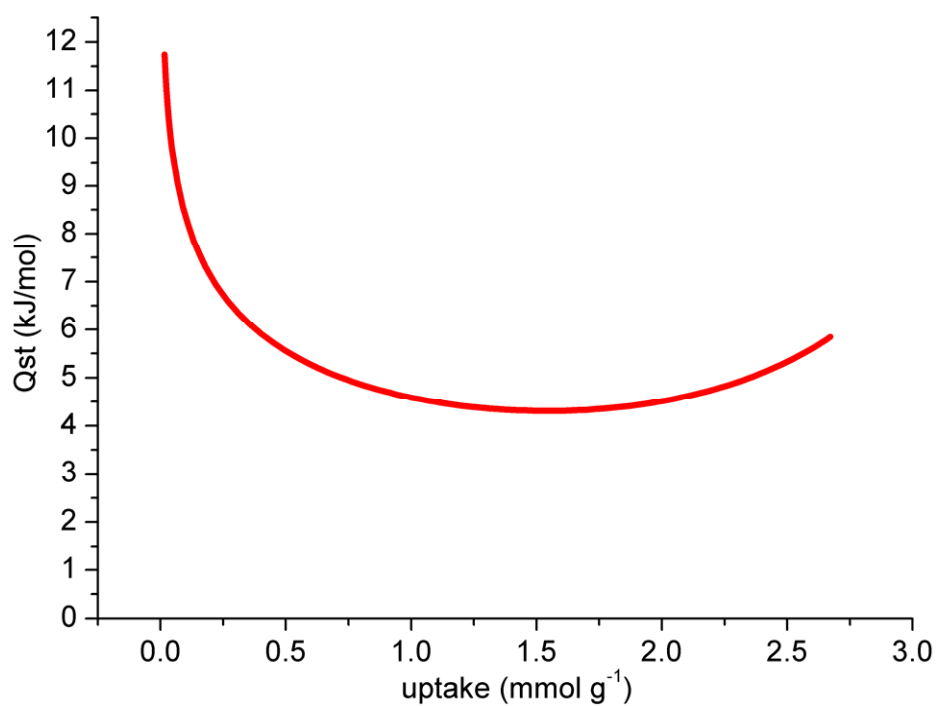


Fig. S8 H₂ adsorption enthalpy calculated using Clausius-Clapeyron equation from the H₂ adsorption isotherms at 77 K and 87 K.

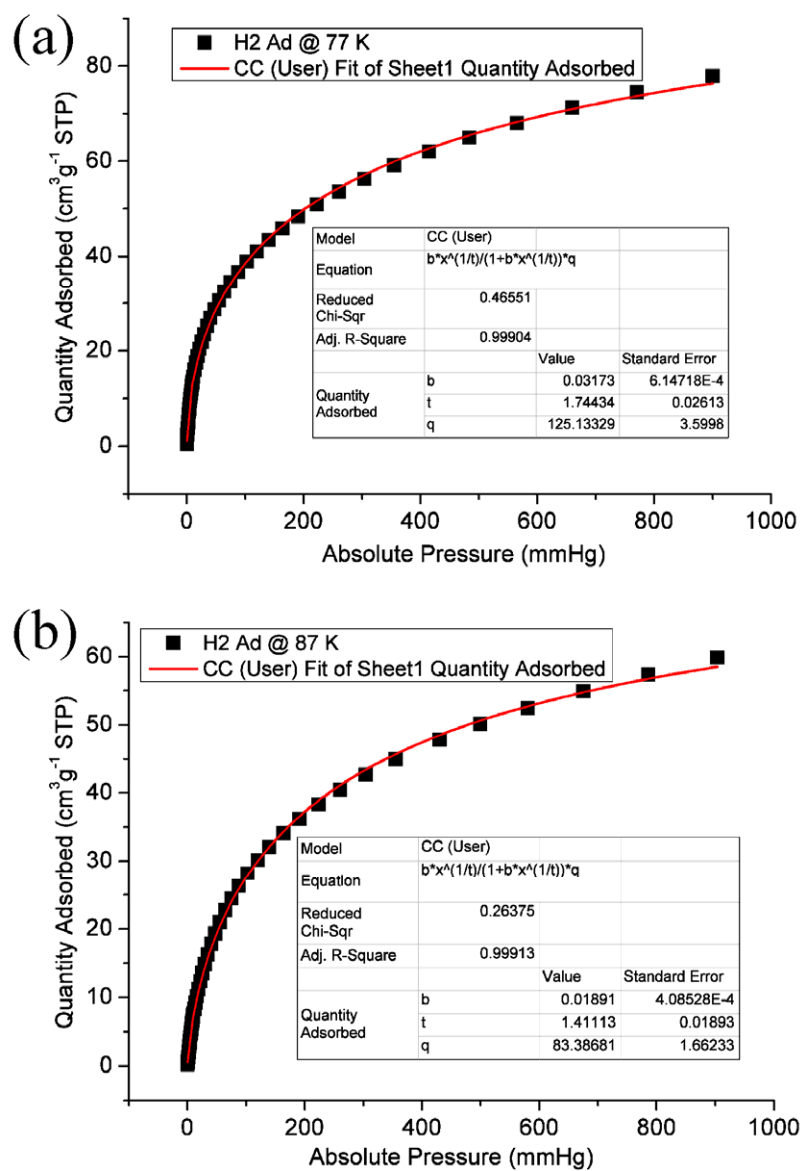


Fig. S9 Langmuir-Freundlich fitting of H₂ adsorption isotherms at 77K and 87K.