Supplementary Information:

Synthesis of cost-effective porous polyimides and their gas storage properties

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Contents

Experimental Section

Instrumentation. The infrared spectra were recorded by a Fourier transform infrared (FTIR) spectrometer Bruker Vertex 70 equipped with an attenuated total reflection (ATR) accessory. The ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectra were obtained on a WB 400 MHz Bruker Avance Ⅱ spectrometer. The elemental analysis was carried out on a Vario Micro cube Elemental Analyzer (Elementar, Germany). Thermogravimetric analysis (TGA) measurement was made using a TGA Q500 instrument at a heating rate of 10°C/min from room temperature to 800 °C. Field emission scanning electron microscope (FE-SEM) micrographs were measured using a Sirion 200 microscope (FEI Corp., NL) operated at 10 kV. Samples adhering to clean glass slides were mounted on aluminium studs using adhesive graphite tape and sputter-coated with gold before analysis. X-ray diffraction (XRD) was carried out on X'Pert PRO XRD spectrometer (PANalytical B.V., Holand) using Cu Kα (λ = 1.54056 Å) radiation in the 2θ range of 10-80°. Polymer surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using a Micrometics ASAP 2020 M surface areas and porosity analyzer. Before analysis, the samples were degassed at 150 °C for 12 h under vacuum (10^{-5} bar). H_2 adsorption isotherms were measured at 77 K (liquid N_2 bath) up to 1.13 bar. CO_2 isotherms were measured at 273 K in a temperature-controlled ethanol bath.

Materials. Melamine (99.0%) and pyromellitic dianhydride (PMDA, 98.5%) were obtained from China National Pharmaceutical Group Chemical reagent Co., Ltd. Naphthalene-1, 4, 5, 8-tetracarboxylic dianhydride (NTCD, 98%) was supplied by Funan Chemical Industrial Co. Ltd (Hebei, China). All the chemicals were vacuum dried at 100°C for 4h before use. 3, 3′, 4, 4′-Biphenyltetracarboxylic dianhydride (BPDA, 97%) were purchased from Aladdin Reagent Corp. and used without further purification. Dimethyl sulfoxide (DMSO) was purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieves. Other chemicals were of analytical grade and used without further purification.

Synthesis of PI1

A dried 50 mL round-bottomed flask equipped with mechanical stirring, nintroge inlet, Dean-Stark trap and reflux condenser was charged with melamine (1.27 g, 10 mmol) and freshly distilled DMSO (30 mL). After 5 min of stirring, pyromellitic dianhydride (3.32 g, 15 mmol) was added as a solid. The mixture was stirred at room temperature for 30 min under nitrogen atmosphere. Then toluene (2 mL) was added into the flask. After that the temperature was raised gradually to 180 °C and held at that temperature for 72 h. During this time water was removed from the reaction mixture by azeotropic distillation. After cooling to room temperature, the resulting solid precipitate was collected by filtration, washed with excess acetone, tetrahydrofurane and dichloromethane. The solvent was removed under vacuum at 50°C to afford the materials in 65% yield. Elemental analysis calculated for $C_{18}H_3N_6O_6$: C, 54.15; H, 0.76; N, 21.05; O, 24.04%. Found: C, 42.00; H, 5.15; N, 40.58%.

Synthesis of PI2

In a fashion similar to the preparation of PI1 melamine (0.25 g, 2 mmol) and 3, 3′, 4, 4′-Biphenyltetracarboxylic dianhydride (0.91 g, 3 mmol) were reacted in DMSO (30 mL) at

180 °C for 72 h to afford PI2 in 37% yield. Elemental analysis: for $C_{27}H_9N_6O_6$, calculated: C, 63.17; H, 1.77; N, 16.37; O, 18.7%. Found: C, 44.16; H, 5.21; N, 36.45%.

Synthesis of PI3

In a fashion similar to the preparation of PI1 melamine (1.27 g, 10 mmol) and Naphthalene-1,4,5,8-tetracarboxylic dianhydride (4.10 g, 15 mmol) were reacted in DMSO (30 mL) at 180 °C for 72 h to afford PI3 in 41% yield. Elemental analysis: for $C_{24}H_6N_6O_6$, calculated for $C_{24}H_6N_6O_6$: C, 60.77; H, 1.27; N, 17.72; O, 20.24%. Found: C, 47.02; H, 4.73; N, 28.29%.

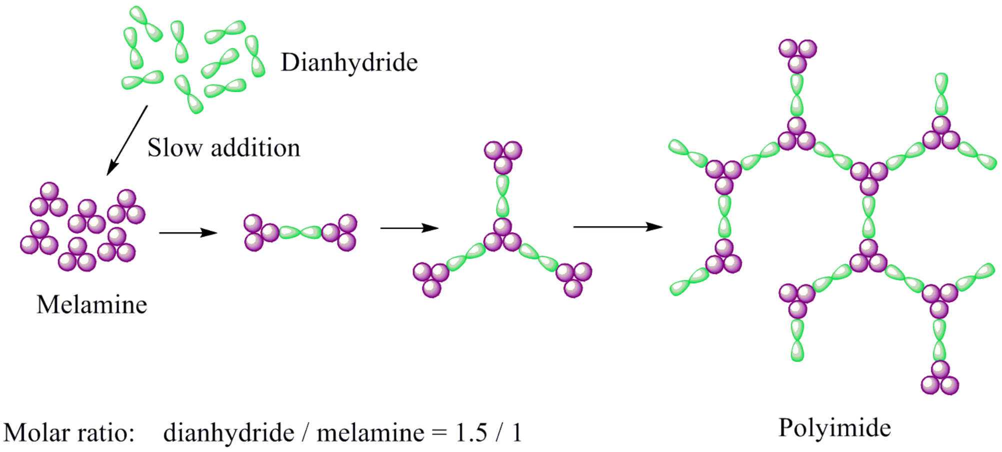


Fig. S1 The schematic representation of the porous polyimide.

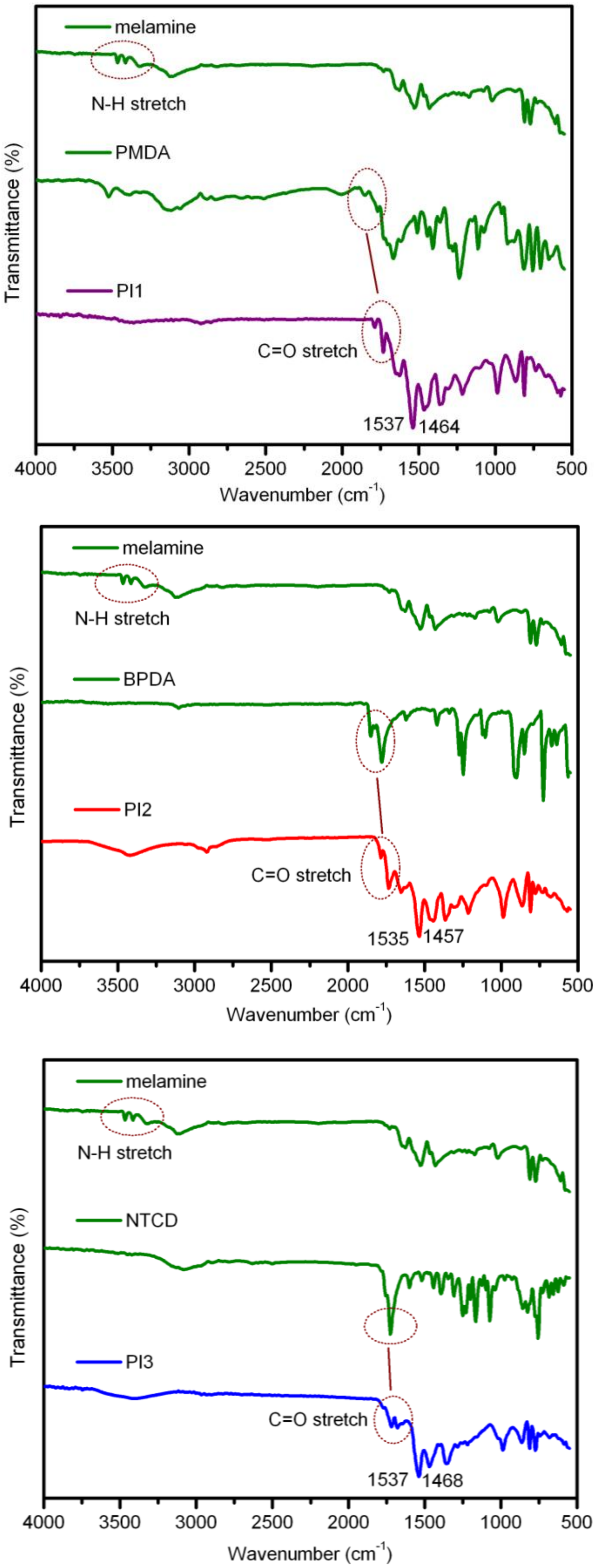


Fig. S2 FTIR spectra of monomers and the polyimide networks.

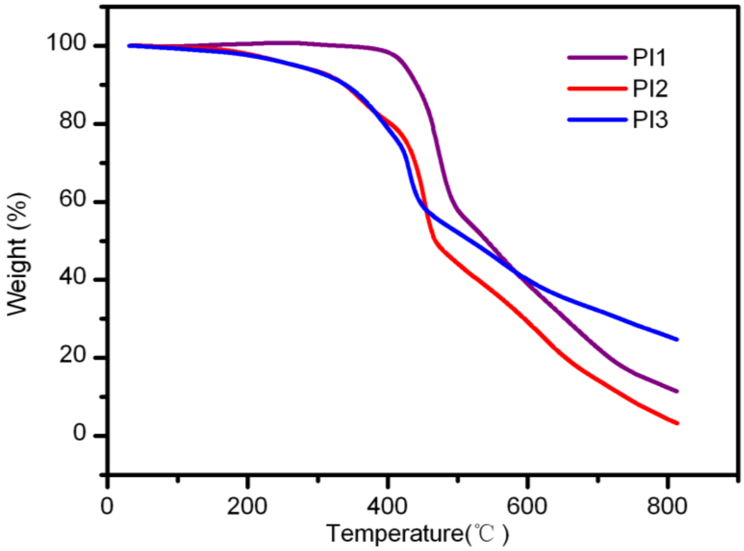


Fig. S3 TGA curves of the polyimides under a nitrogen atmosphere and heating rate of 10 °C min^{-1}.

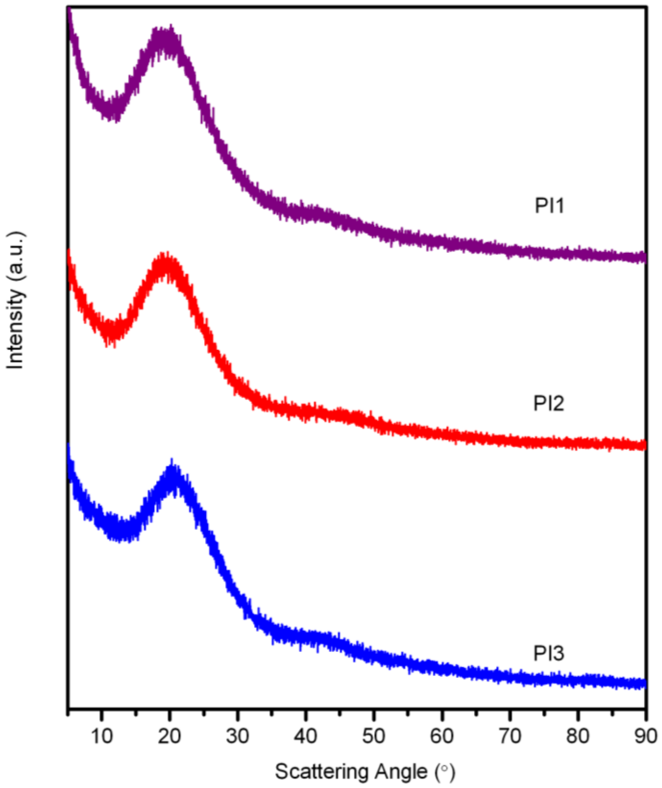
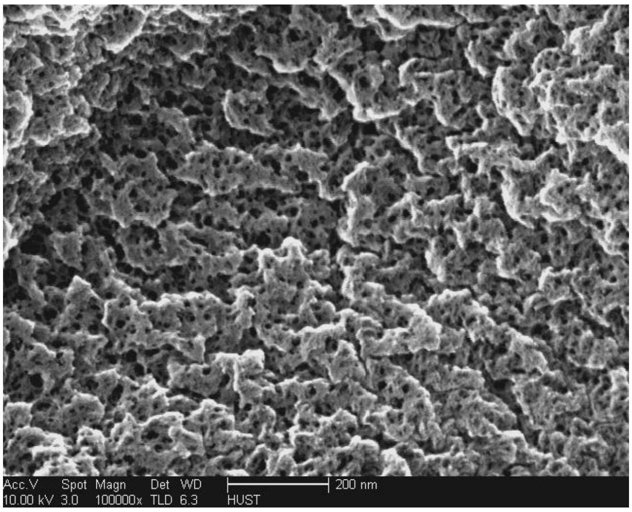
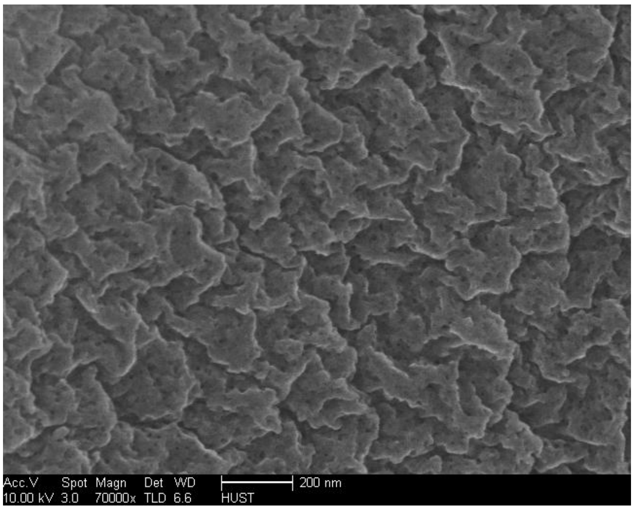


Fig. S4 XRD patterns of the polyimide networks.

PI1



PI2



PI3

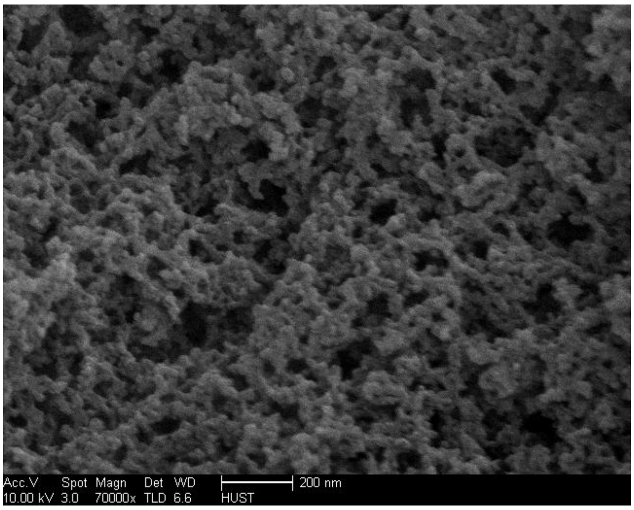


Fig. S5 FE-SEM images for the polyimides networks.

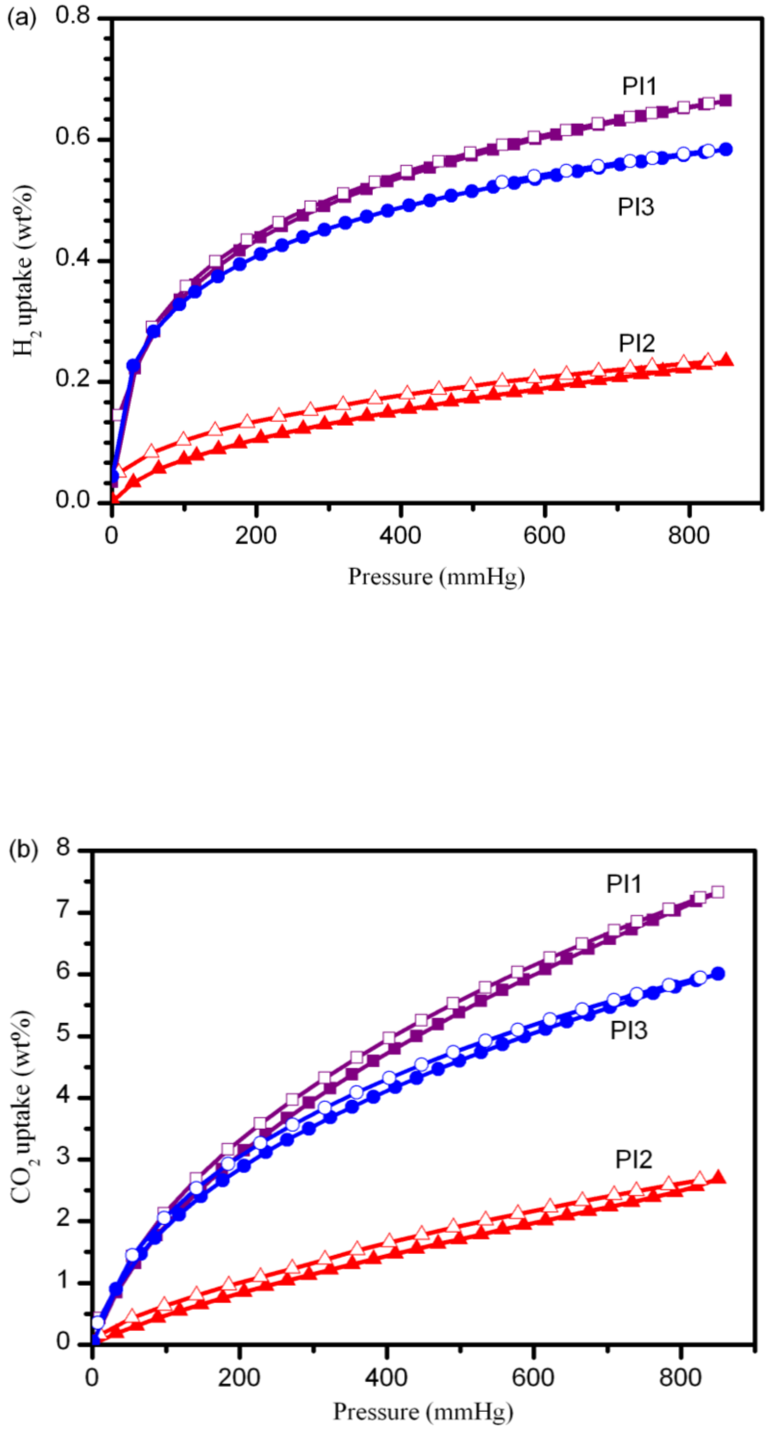


Fig. S6 Gas uptake data for polyimides networks: (a) H_2 isotherms measured at 77 K and (b) CO_2 isotherms measured at 273 K.