ELECTRONIC SUPPLEMENTARY INFORMATION

Microporous polyimide networks with large surface areas and their hydrogen storage properties

Zhonggang Wang,[a] Bufeng Zhang,[a] Hao Yu,[a] Lixian Sun,[b]*

Chengli Jiao,[b] *Wanshuang Liu[a]*

[a]Department of Polymer Science and Engineering, State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, 116012, China. [b]Materials and Thermochemistry Group, Laboratory of Catalysis and New Materials for Aerospace, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China.

zgwang@dlut.edu.cn

Contents

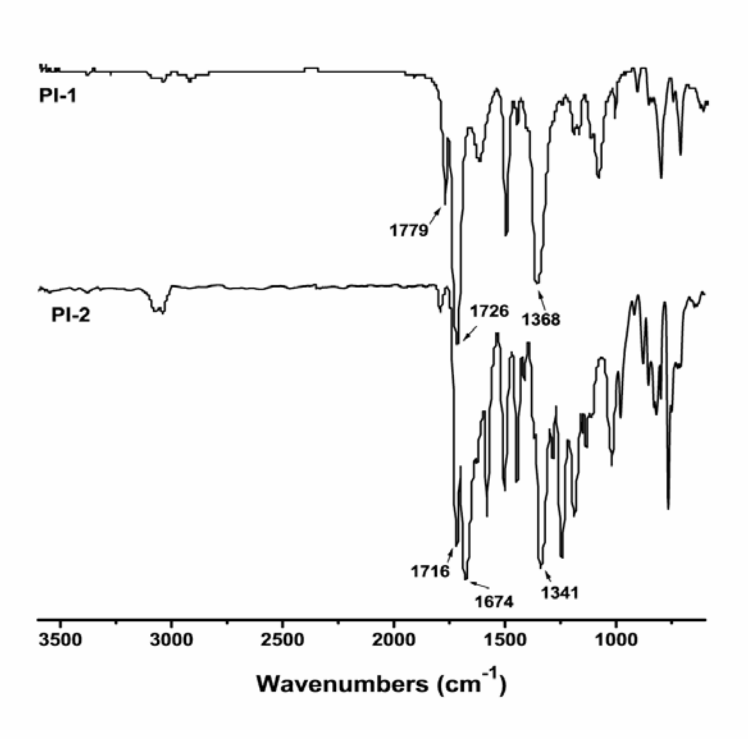

Fig. S1 FTIR spectra of two polyimide networks.

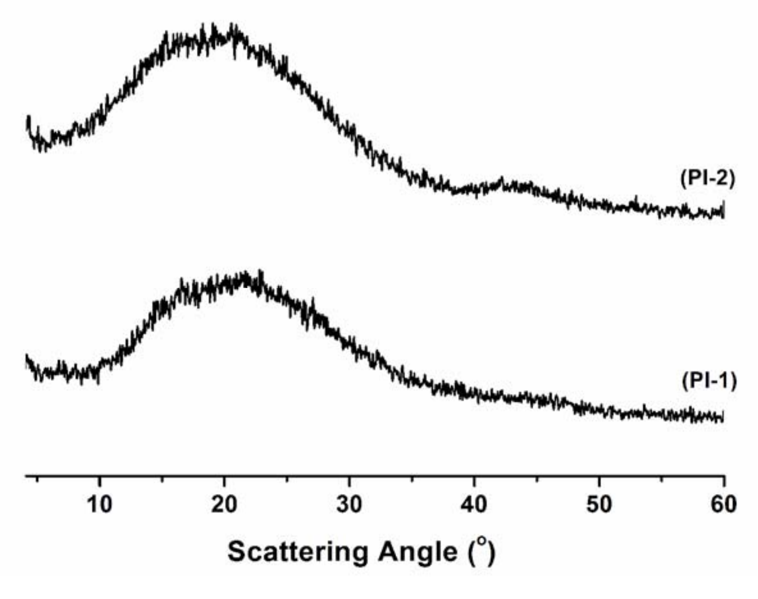

Fig. S2 WAXD patterns of two polyimide networks

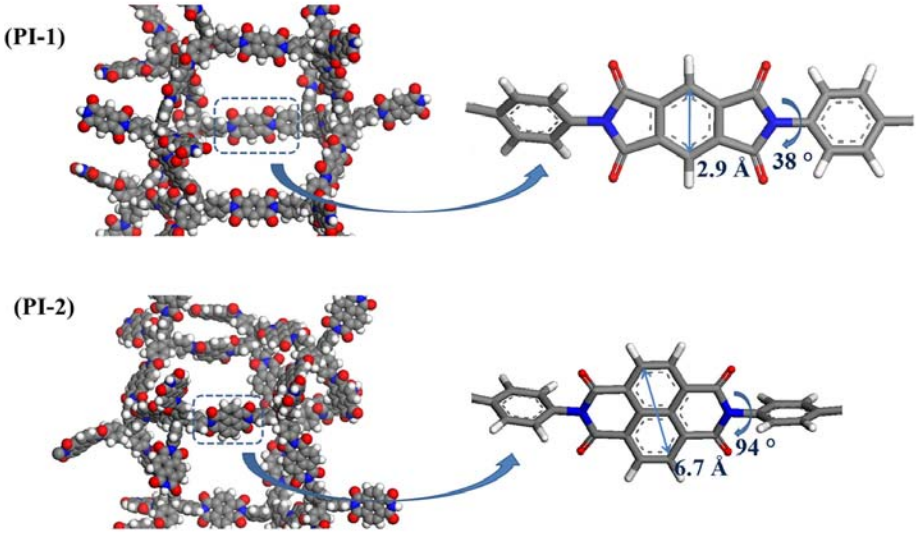

Fig. S3 Molecular models for PI-1 and PI-2 at energy-minimized state.

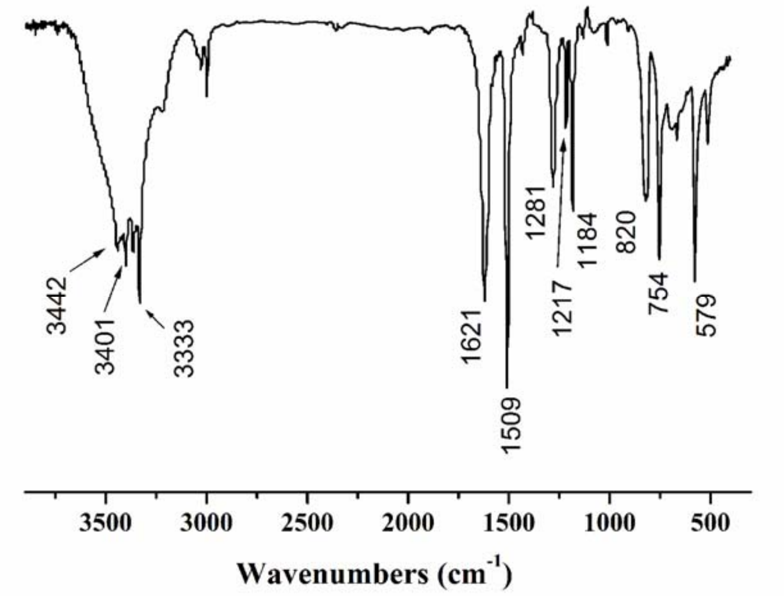

Fig. S4 FTIR spectrum of TAPM

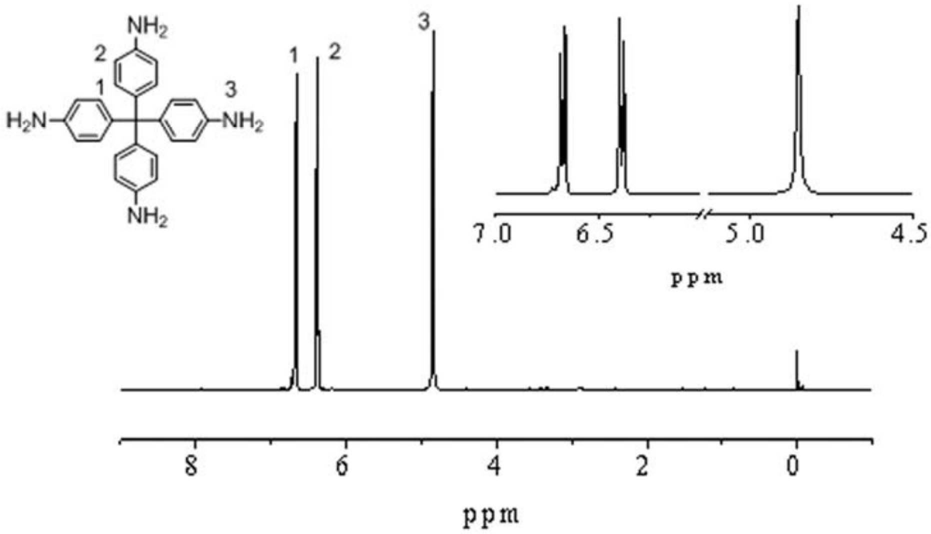

Fig. S5 ^{1}H NMR spectra of TAPM

Table S1 Pore structures of Polyimide networks

polyimide	tetraamino monomer	dianhydride monomer	S_{BET} [m^2 g^{-1}]	V_{total} [cm^3 g^{-1}]	median pore diameter[Å]
PI-1	TAPM	PMDA	1407	0.78	4-8
PI-2	TAPM	NTDA	732	0.51	4-8

Table S2 Gravimetric H_2 uptakes for polyimide networks

	density	H_2 adsorption [wt%]			Q_0
polymer	[g cm-^{3}]	1 bar	15 bar	30 bar	[kJ mol^{-1}]
PI-1	1.5449	1.33	2.84	3.30	5.3
PI-2	1.4898	0.36	2.10	2.76	7.0

Experimental Section

Instrumentation. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Model 20DXB IR spectrophotometer. Sixty four (64) scans were signal-averaged, with a resolution of 2 cm^{-1} at room temperature. Samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks. ^{1}H NMR spectra were recorded on 400-MHz Varian Model INOVA NMR spectrometer, with the tetramethylsilane (TMS) as an internal reference. Thermogravimetric analyses (TGA) was performed on a Netzsch Model TG 209 thermal analyzer both in purified nitrogen and an air atmosphere, and all samples (with masses of ~10 mg) were heated from 25 °C to 700 °C at a rate of 10 °C /min, under the gas flow rates of 60 mL/min. Wide-angle X-ray diffraction (WAXD) measurements were performed on a D/Max-2400 X-ray diffractometer with CuKa1 radiation (λ= 1.54 Å) over the 2θ range of 4 -60°. Powder samples were vacuum dried at 180 °C for at least 24 h before measurement. Nitrogen adsorption-desorption experimentation was conducted using an automated micropore gas analyzer (Autosorb-1-MP, Quantachrome Instruments). Before sorption measurement, the cured film sample was degassed at 150 °C under high vacuum overnight. Apparent surface area was calculated from N_2 adsorption data by multipoint BET analysis. The true density was measured on a Micromeritics Accupyc II 1340 Pycnometer. The isothermal dehydrogenation kinetics was measured by a Sievert-type apparatus (Advanced Materials Corporation) under a background pressure of 100 Pa H_2. The pressure-composition isotherm (*P*-*C*-*T*) measurements were carried out at temperatures of 77 K and 110 K. The test pressure was within the range of 0.01-3.0 MPa. The cured film sample was degassed at 200 °C under high vacuum overnight.

Materials. Tetraphenylmethane was were purchased from J&K-Chemical Co., Ltd. m-Phenylene diamine (MPDA), pyromellitic dianhydride (PMDA) and Naphthalene-1,4,5,8- tetracarboxylic dianhydride (NTDA) were purchased from Shanghai Chemical Reagent Corp. PMDA and NTDA were purified by sublimation prior to use. m-Cresol was purified by distillation under reduced pressure and dehydrated with 4A molecular sieves. Isoquinoline, concentrated sulfuric acid, fuming nitric acid, acetic acid, acetic anhydride and other reagents were used as received.

Tetra(*p*-nitrophenyl)methane (TNPM). Tetraphenylmethane (7.4 g, 23 mmol) was added into fuming nitric acid (40 mL) at -40 °C with vigorous stirring. Then acetic anhydride (12.5 mL) and glacial acetic acid (25 mL) were slowly added and stirred for 1 h. After filtration, the resultant yellow solid was recrystallized with tetrahydrofuran to get pale yellow crystals with 65 % yield. M.p.: 339 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.22-8.24 (d, 8H, Ar-H), 7.59-7.61 (d, 8H, Ar-H); IR (KBr, cm^{-1}): 3070, 3100, 1605, 1591, 1519, 1493, 1347 (Ar-NO_2), 840, 757, 744, 711.

Tetra(*p*-aminophenyl)methane (TAPM). Into a hydrogenator containing tetrahydrofuran (100 mL), TNPM (4.0g, 7.97 mmol) and small amount of Pd/C (10 wt%) was added. After purging with nitrogen three times, the reaction mixture was stirred under 1.2 MPa hydrogen pressure at room temperature for 3 days. After removal of the Pd/C powders and solvent, the crude product was recrystallized with methanol get white crystals with 95 % yield. M.p.: 262 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 6.31-6.40 (d, 8H, Ar-H), 6.67-6.69 (d, 8H, Ar-H), 6.77 (6H, Ar-H), 4.82 (s, 8H, -NH_2); IR (KBr, cm^{-1}): 3442, 3400, 3363, 3333, 3027, 3100, 1620, 1508, 1281, 1216, 1184, 820, 754, 577; HRMS calculated for $C_{25}H_{24}N_4$ 380.2001, found 380.2004.

Polyimides networks. The two polyimides were prepared by the similar method. The polycondensation reaction, described here for the case of PMDA-TAPM, was carried out as follows: in a dry three-necked flask fitted with a mechanical stirrer, gas inlet and condenser, at ice-bath temperature, m-cresol (10 mL), TAPM (0.400g, 1.05 mmol) and PMDA (00457g, 2.10 mmol) were added. The mixture was stirred under an argon flow until all the solids dissolved. Then, the system was slowly heated to room temperature, and stirred at this temperature overnight. Several drops of isoquinoline were added, and the temperature was increased and allowed to polymerize at 80 °C for 4 h, 180 °C for 6 h and 200 °C for 8 h. The system was cooled down and the insoluble solid was isolated from the solvent by filtration, washed with methanol several times. Then the solid was grounded into fine powder, which was treated with methanol in a Soxhlet apparatus and dried at 180 °C under vacuum for 36 h. Quantitative yield in every case.