

Supporting Information

Advancing Polymers of Intrinsic Microporosity by Mechanochemistry

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General methods for PIMs

Characterization

Before adsorption measurements, the samples were degassed in flowing nitrogen at 110°C overnight. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05 to 0.20. Pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model. The total pore volume was determined from the amount of N₂ uptake at a relative pressure of $P/P_0 = \sim 0.95$. The SFM-3 Desk-Top High Speed Vibrating Ball Miller from MTI Corporation was used for the ball grinding synthesis. The molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) using Ultrastyrigel columns and DMF as the eluent at a flow rate of 1 mL/min. The values obtained were determined by comparison with a series of polystyrene standards.

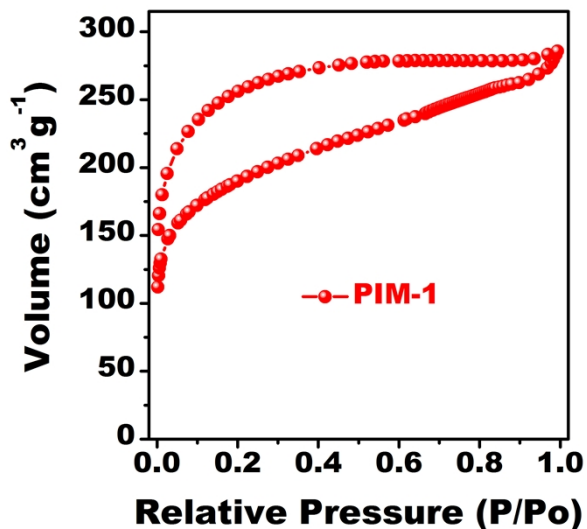
Typical procedure for PIM-1 by ball grinding

In a typical synthesis, 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethyl-1,1'-spirobisindane (680 mg, 2 mmol), tetrafluoroterephthalonitrile (400 mg, 2 mmol), inorganic base (K₂CO₃ 1200 mg) were added to a commercial-available 4.5 cm (diameter) by 5.5 cm (height) screw capped stainless steel reactor along with twelve stainless steel ball bearings (4 × diameter 1.2 cm; 4 × diameter 0.7 cm; 4 × diameter 0.5 cm). The reactor was placed in a high speed vibrating ball miller (300 W Motor Power) and the contents were ball milled for 15 minutes. The resulting mixture was throughout washed with deionized H₂O, methanol and ethanol. The final powder was dried at 60 °C in vacuum for 24 hours. ¹H NMR (d₆-CHCl₃): δH 1.1-1.5 (12 H), 2.1-2.4 (4H), 6.5 (2H), 7.1 (2H). The PIM-4-MS

sample was synthesized by a similar method except for another monomer (2,2',3,3'-tetrahydroxy-1,1'-binaphthyl): $^1\text{H NMR}$ ($d_6\text{-CHCl}_3$): δH 7.0-7.5 (3H), 7.8-8.2 (2H).

Typical procedure for PIM-1 by solution-based method

5,5,6,6-tetrahydroxy-3,3,3,3-tetramethyl-1,1'-spirobisindane (510 mg, 1.5 mmol), tetrafluoroterephthalonitrile (300 mg, 1.5 mmol) and K_2CO_3 (828 mg, 6 mmol) were added to DMF (20 mL) solvent. The glass reactor was flowed with Ar for 10 minutes and then heated to 60 °C for 2 days under Ar atmosphere. The resulting mixture was poured into 200 mL deionized H_2O and the solid product was collected by filtration. The yellow powder was throughout washed with H_2O and methanol. The yellow product was dried in vacuum for 12 hours. The N_2 sorption test of PIM-1 (77 K) showed a BET surface area of 660 m^2/g .



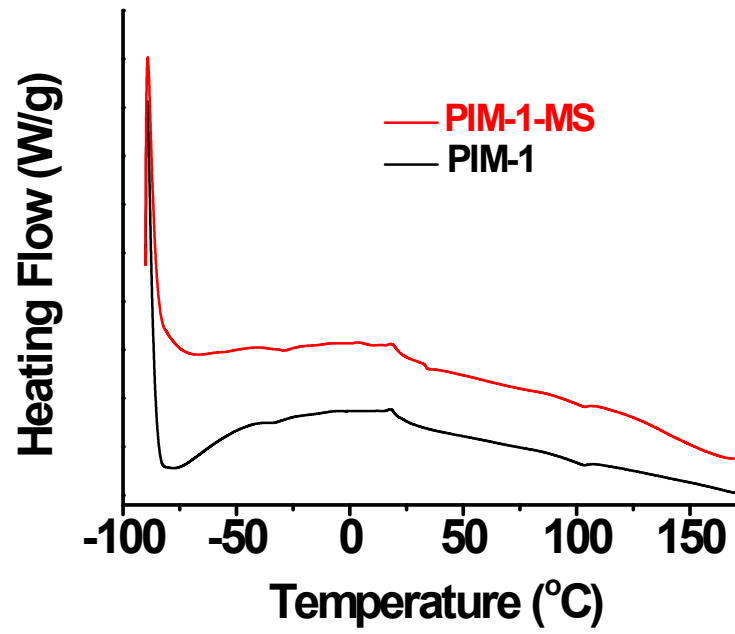


Figure S1. DSC curves of PIM-1 samples.