Supplementary information

Preparation of a compressible and hierarchically porous polyimide sponge via sol-gel process of an aliphatic tetracarboxylic dianhydride and an aromatic triamine

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Materials. 1,3,5-Tris(4-aminophenyl)benzene (TAPB) and 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) were purchased from Tokyo Chemical Industry. All solvents such as mesitylene, isoquinoline, NMP were purchased from Sigma-Aldrich, Acros Organics, or Junsei Chemical and used as received.

Characterization. Fourier–transform Infrared (FT–IR) spectra were recorded using a Bruker TENSOR 27 using an ATR accessory. Solid state ^{13}C NMR spectra were recorded on a Bruker Avance 400WB spectrometer (100 MHz) equipped with a cross polarization magic angle spinning (CP/MAS) probe. Thermogravimetric analyses (TGA) were performed on a TA modulated TGA2050 with a heating rate of 10 °C/min under nitrogen. Scanning electron microscopy (SEM) images were obtained by a JEOL JSM-6330F microscope. Transmission electron microscope (TEM) images were obtained by a JEOL JEM-2010 microscope at 200 keV. TEM samples were dispersed in ethanol by using sonication and a drop was placed on a TEM grid. Powder X-ray diffraction (PXRD) data were collected on a Bruker New D8 Advance using a Cu Kα source (λ = 1.5418 Å). The sorption isotherm for N_2 was measured with a Belsorp–Max (BEL Japan, Inc.) apparatus with ultra-high purity nitrogen (99.999%). Pore size distribution was calculated on the basis of nonlocal density functional theory (NLDFT). UV–Vis spectra were obtained with the use of a Sinco S-3150 spectrometer.

Preparation of monolithic microporous polyimide (MMPI). CBDA (0.45 mmol) was dissolved in a mixed solution of NMP / mesitylene / isoquinoline (1.75 mL, 10 / 10 / 1 by vol.) in a 10 mL tube. To the solution was added a solution of TAPB (0.3 mmol) in a mixed solution of NMP, mesitylene, and isoquinoline (2.25 mL, 10 : 10 : 1 by vol.) at room temperature. After stirring for 2 min, the

solution turned to a yellowish opaque gel. The gel was heated at 200 ^{o}C for 2 days in nitrogen atmosphere. The resulting monolithic polyimide was taken out of the tube and washed with acetone, methanol, and THF. After Soxhlet extraction with acetone and THF, the polymer was dried *in vacuo* at 120 ^{o}C.

Compression test. The compression tests were performed by a KES-FB3 automatic compression tester. Stress–strain curves were measured at a strain rate of 50 mm/min. During the compression test, MMPI was saturated with acetone in a schale.

Solvent absorption and syringe filter test. A piece of MMPI (22.5 mg) was immersed in a solvent (50 mL) for 30 min. After removal from the solvent, MMPI was dried with paper toweling and immediately weighed. The measurement was carried out three times for each solvent. MMPI was fabricated to have a shape that fitted into a 5 mL syringe and used for syringe filtration. An aqueous methylene blue solution, methyl orange solution or a sudan I ethanol solution (0.05 mM) was poured into a syringe plugged with MMPI and filtered. The breakthrough profile was measured using a MMPI filter (80 mg) fitted into 5 mL syringe and a methylene blue aqueous solution (0.5 mM) Every 5 mL of the filtrate was collected (flow rate: 2.5 mL min^{-1}) and its concentration was measured by UV-Vis spectroscopy.

Dynamic and static adsorption test. A piece of MMPI (50 mg) was immersed in a methylene blue aqueous solution (10 mL, 5.0 x 10^{-5} M). MMPI was manually compressed and released at a rate of ~3 s per cycle. The UV-Vis absorption of the solution was measured every 20 times (1 min). For comparison, a static adsorption experiment was carried out by immersing the same mass of MMPI in the methylene blue aqueous solution without the compression and release and the UV-Vis absorption of the solution was monitored.

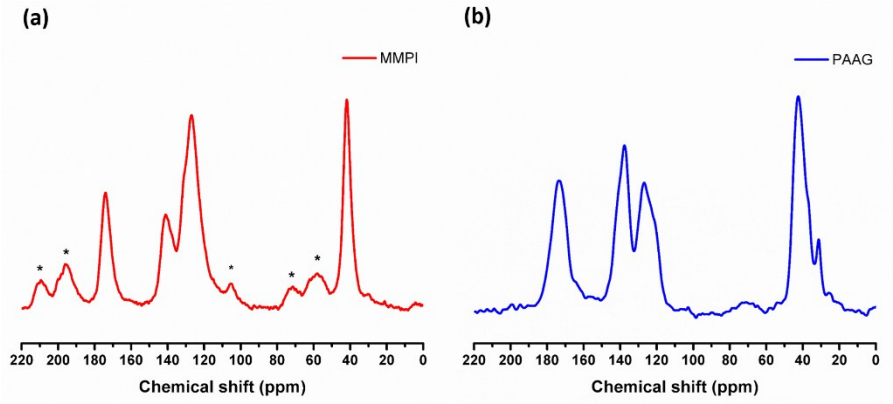

Fig S1. Solid-state ^{13}C CP/MAS NMR spectra of (a) MMPI and (b) PAAG. Asterisks indicate spinning side bands.

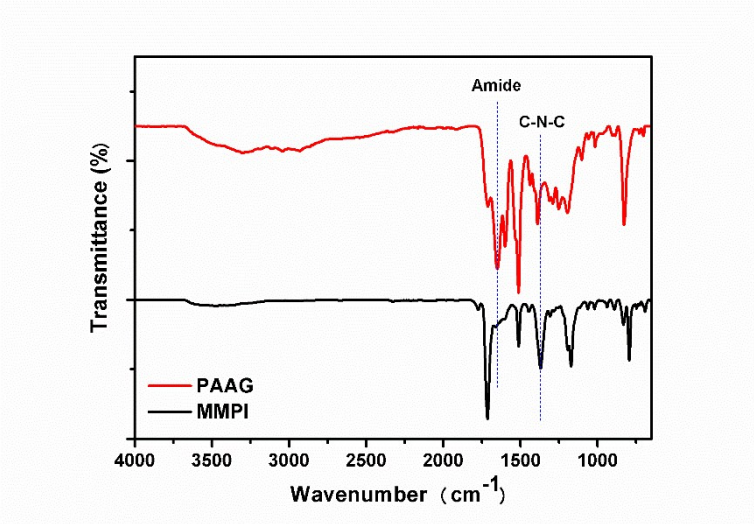

Fig. S2 FT-IR spectra of PAAG (red line) and MMPI (black line).

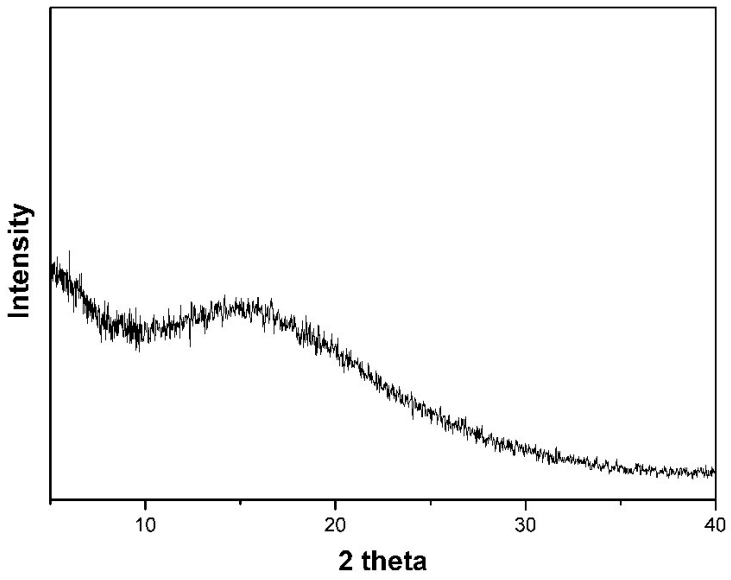

Fig. S3 XRD pattern of MMPI.

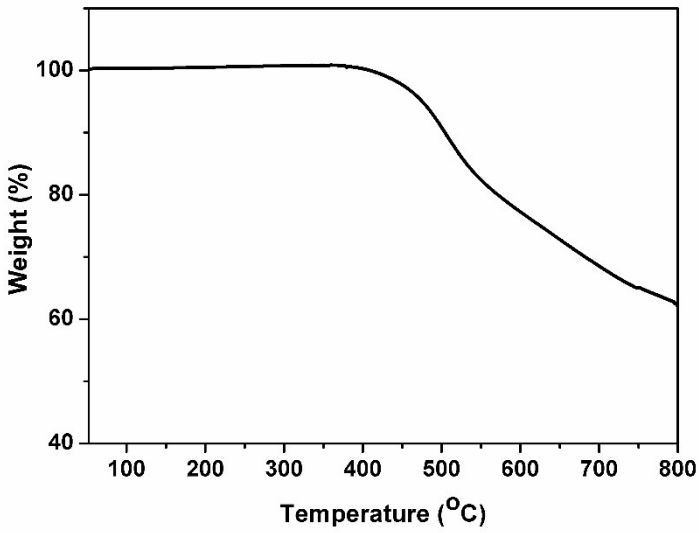

Fig. S4 Thermogravimetric analysis curve of MMPI measured under nitrogen atmosphere with a heating rate of 10 ^{o}C min^{-1}.

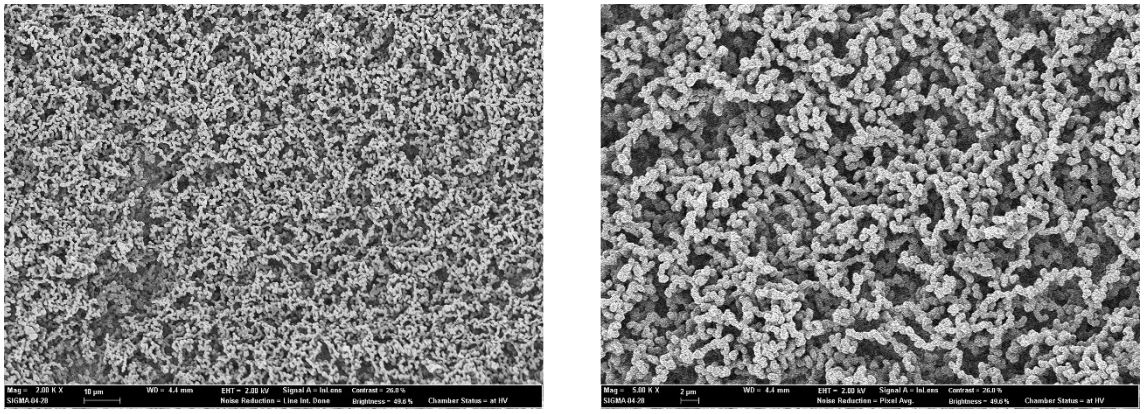

Fig. S5 Low magnification SEM images of the cut planes of MMPI.

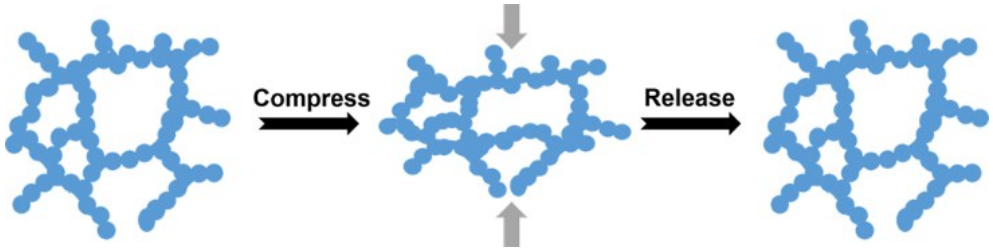

Fig. S6 Schematic drawing showing the mechanism for the compressibility of MMPI.

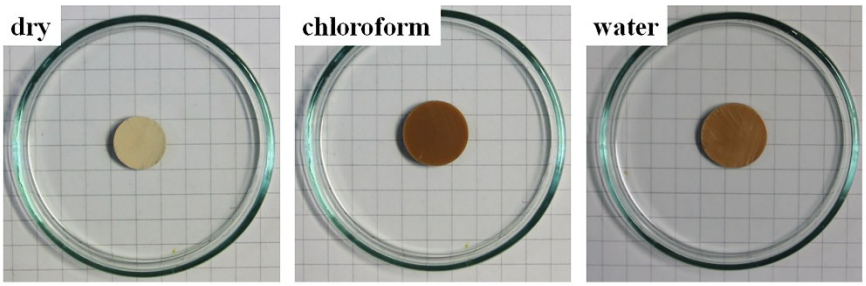

Fig. S7 Images of MMPI before and after absorption of chloroform and water.

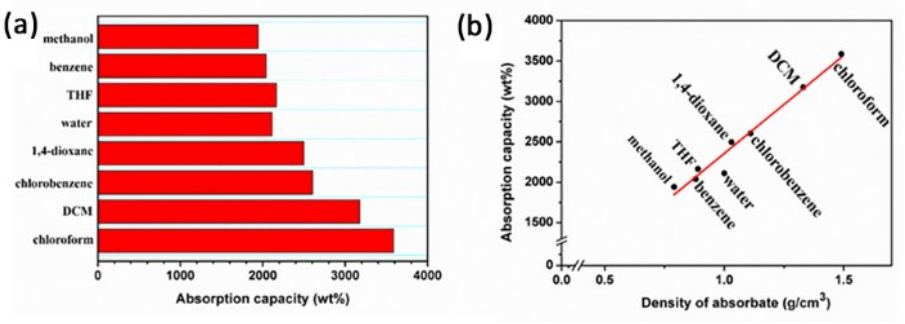

Fig. S8 (a) Absorption capacity of MMPI for various solvents. (b) Correlation between absorption capacity and absorbate density.

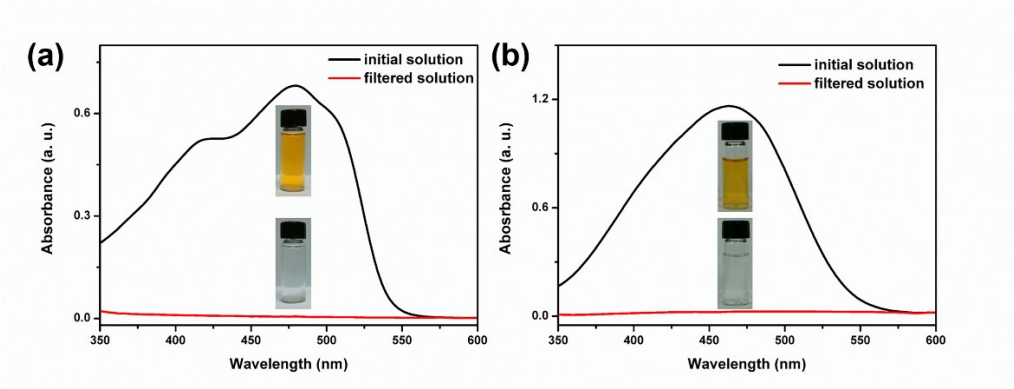

Fig. S9 UV-Vis spectra of (a) a solution of Sudan I in ethanol (5.0 X 10^{-5} M) and an aqueous solution of methylene orange (5.0 X 10^{-5} M) measured before and after the syringe filtration .