Electronic Supplementary Information

Noninvasive Functionalization of Polymers of Intrinsic Microporosity for Enhanced CO_2 Capture

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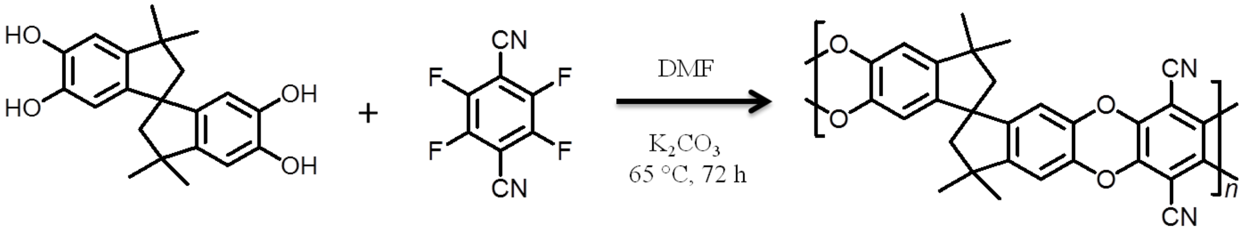
1. Materials

Tetrafluoroterephthalonitrile (> 98%) and 5,5’,6,6'-tetrahydroxy-3,3,3’,3’-tetramethyl-1,1'-spirobisindane (> 96%) were obtained from TCI, Japan. *N,N*-dimethyl formamide (99%), anhydrous potassium carbonate (99.5%), chloroform (99.5%), methanol (99.5%), tetrahydrofuran (99 %) and dimethyl sulfoxide (99.5%) from SAMCHUN, South Korea. Hydroxyl amine (50 %wt solution in water, 99.999%), $CDCl_3$ (99.8%) and DMSO-*d6* (99.96%) were purchased from Sigma-Aldrich, USA.

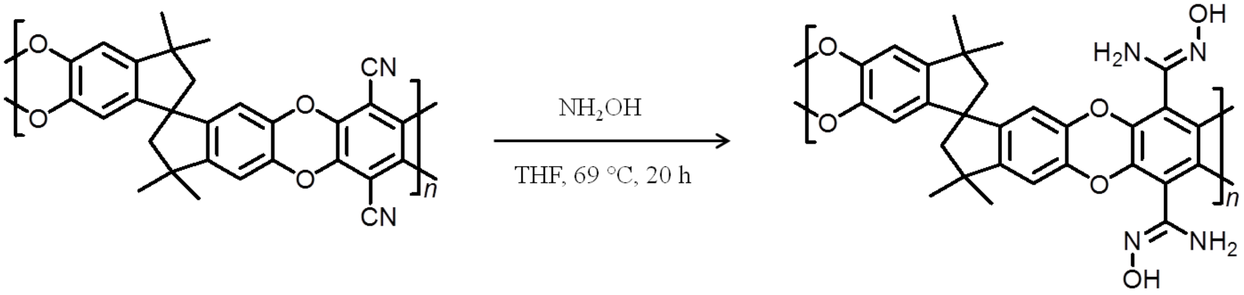
2. Synthesis of PIM-1



PIM-1

PIM-1 was synthesized according to procedure reported by Budd et al. [1]. 2 g (10 mmol) of tetrafluoroterephthalonitrile, 3.4 g (10 mmol) 5,5’,6,6'-tetrahydroxy-3,3,3’,3’-tetramethyl-1,1'-spirobisindane and 70 mL of anhydrous *N,N*-dimethyl formamide was added to a three neck round bottom flask. The reaction mixture was stirred under inert atmosphere of nitrogen at 65 °C until clear solution formed. 4.15 g of potassium carbonate was then added slowly and the reaction mixture was stirred for 72 hours. After cooling, the reaction mixture was added to 650 mL of water and the precipitate collected by filtration. The crude PIM-1 was then dissolved in chloroform (160 mL) and precipitated from methanol (500 mL). Further precipitation was performed by dissolving in tetrahydrofuran (200 mL) and adding to a mixture of acetone-tetrahydrofuran (600 mL, 2:1 v/v). The precipitated product was collected by vacuum filtration before washing with 1,4-dioxane (80 mL), acetone (80 mL), water (100 mL) and a further portion of acetone (50 mL). The product was dried in an oven at 110 °C overnight, to give PIM-1 as a luminous yellow solid (Yield: 64.8 %, 3.5 g).

3. Synthesis of Amidoxime-PIM-1



PIM-1

Amidoxime-PIM-1

In a three neck round bottom flask equipped with spiral condenser, thermocouple and magnetic stirrer, 0.6 g of PIM-1 powder was dissolved in 40 mL tetrahydrofuran and heated up to 65 °C in inert environment of nitrogen. 6.0 mL hydroxyl amine was then added drop-by-drop through syringe to the clear solution (formation of precipitates which dissolved, hazy solution, after 20 minutes). The reaction mixture was refluxed at 69 °C for 20 hour. After completion of reaction, hazy solution was cooled down to the room temperature and 150 mL ethanol was added to form off white precipitates. The precipitates were filtered and washed with 50 mL ethanol (four times). The product was dried in an oven at 110 °C for 3 hours, to give amidoxime-PIM-1 as an off-white powder (0.58 g). Yield (based on PIM-1): 96.7 %.

4. Characterizations

FTIR spectra were recorded as KBr pellet using a Perkin-Elmer FT–IR spectrometer. ^{1}H NMR spectra were recorded using $CDCl_3$ and DMSO-d_6 as solvent on a Bruker DMX400 NMR spectrometer. Elemental (CHNO) analyses were performed on elemental analyzer ThermoQuest Italia S.P.A (CE instrument). Thermogravimetric analysis (TGA) was performed on a NETZSCH-TG 209 F3 instrument by heating the samples to 800 °C at 10 °C.min^{-1} in N_2. In order to find out the porosity of powder samples, nitrogen adsorption isotherms were obtained with a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer at 77 K after the samples were degassed at 110 °C for 5 h under vacuum. The adsorption-desorption isotherms were evaluated to give the pore parameters, including *Brunauer-Emmett-Teller (BET)*, Langmuir, pore size and pore volume. The micropore surface area was determined by the *t*-plot method. The slope of the *t*-plot is directly proportional to the surface area of the sample. Any upward deviation from linearity is a result of the capillary condensation inside the pores and the initial slope is proportional to the micropore surface area.

The low pressure CO_2 adsorption-desorption isotherms for powder samples were measured at 273 and 298 K using a static volumetric system (ASAP 2020, Micromeritics Inc., USA). The temperature during adsorption and desorption was kept constant using a circulator. Prior to adsorption measurements, samples were further degassed/activated in situ by increasing the temperature at a heating rate of 1 K min^{-1} up to 383 K under vacuum (5 × 10^{-3} mmHg) and the temperature and vacuum was maintained for 5 h before the sorption measurements. All the adsorption-desorption experiments were carried out twice to ensure the reproducibility. There were no noticeable differences in the isotherm points of both experiments. Heats of adsorption were determined from CO_2 adsorption isotherms at 273 and 298 K temperature using a Micromeritics ASAP 2020 instrument and the standard calculation routines in the Datamaster offline data reduction software (Micromeritics).

TGA of PIM-1 shows thermal stability as high as 468 °C and single step decomposition pattern while amidoxime-PIM-1 starts to decompose at 200 °C with two-step decomposition. Amidoxime-PIM-1 show mass loss of 12.4 % in between 200 - 380 °C which is caused by the loss of amidoxime functionality. The thermal decomposition of amidoxime results in hydroxyl amine and nitrile[2] within first mass loss and this reversible reaction leads to PIM-1. Mason et al.[3] observed similar type of thermal behavior in the case of thioamide-PIM-1. The second stage of decomposition for amidoxime-PIM-1 is attributed to the loss of polymeric networks.

Scheme S1. Processability of PIM-1 was not hindered upon functionalization by amidoxime (amidoxime-PIM-1)

Table S1. Elemental (CHNO) analysis of PIM-1 and amidoxime-PIM-1

	% C		**% H**		**% N**		**% O**	
	Theo.	**Exp.**	**Theo.**	**Exp.**	**Theo.**	**Exp.**	**Theo.**	**Exp.**
PIM-1	75	75.1	5.2	4.4	6	6.3	13.8	14.5
Amidoxime-PIM-1	65.7	62.7	5.6	4.8	10.6	10.1	18.1	23.3

Elemental analysis reveals increase in the nitrogen and oxygen content in amidoxime-PIM-1. PIM-1 and amidoxime-PIM-1 contains 6.3 and 10.1 % nitrogen respectively which is comparable with theoretical values (6 and 10.6 % nitrogen for PIM-1 and amidoxime-PIM-1).

Table S2. Porosity and carbon dioxide uptake of PIM-1 and amidoxime-PIM-1

	BET, m^2 g^{-1}	**Langmuir, m^2 g^{-1}**	**SA_{micro}, m^2 g^{-1}**	**Pore size, nm**	**Pore Volume, cm^3 g^{-1}**	**CO_2 uptake, mg g^{-1}**		**Q_{st}, kJ/mol**
						273K	**298K**	
PIM-1	771	889	313	2.7	0.57	111.4	62	28.4
Amidoxime-PIM-1	531	577	376	2.1	0.28	120.5	72.4	30.2

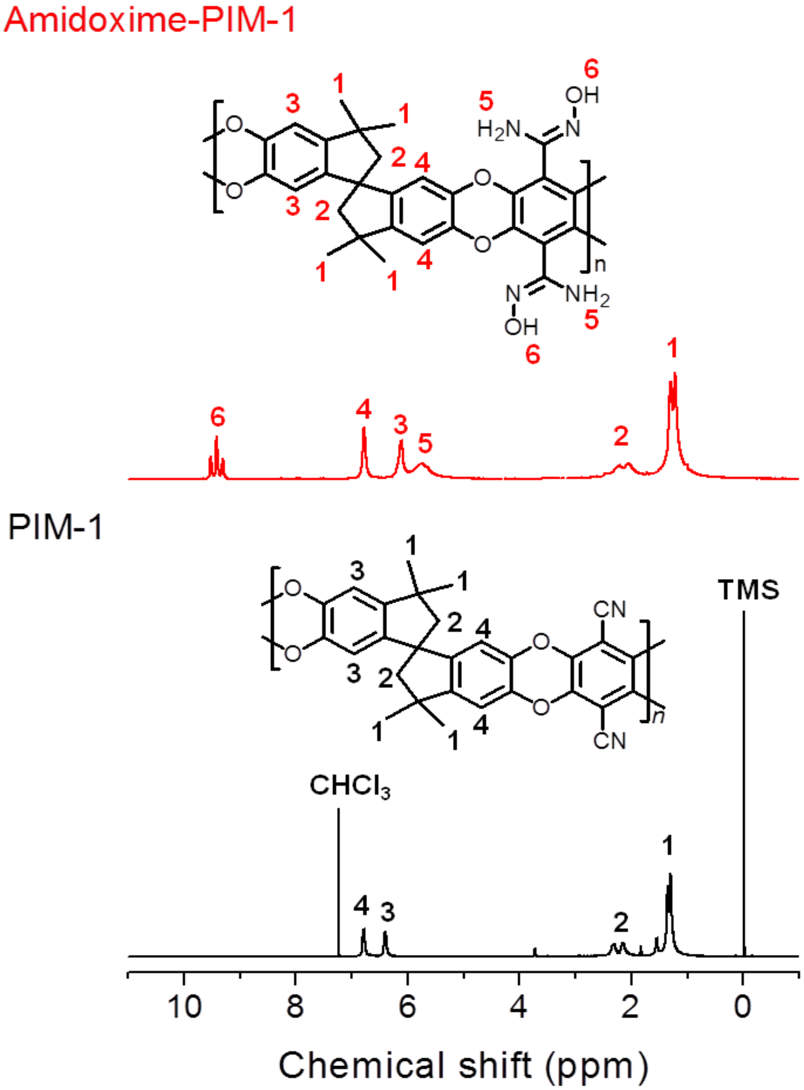


Figure S1. ^{1}H NMR spectra of PIM-1 and amidoxime-PIM-1

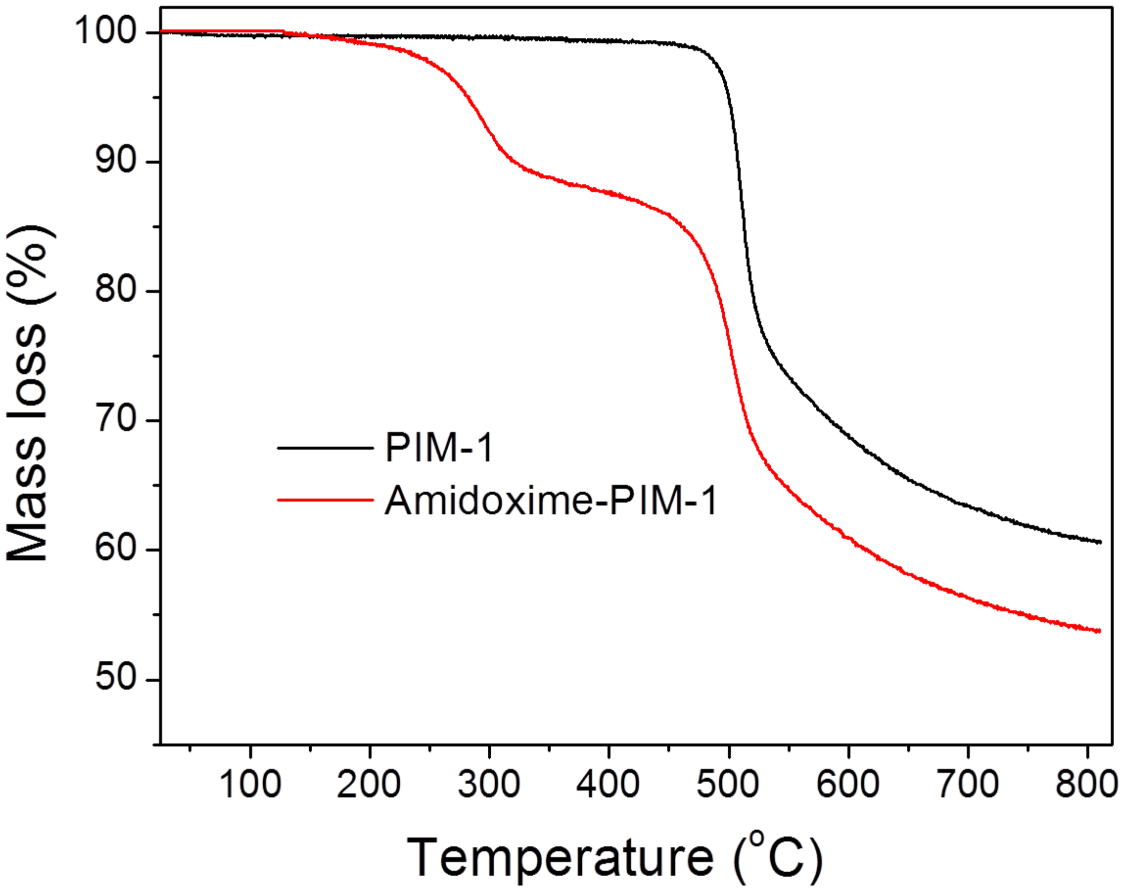


Figure S2. Thermogravimetric analysis (TGA) of PIM-1 and amidoxime-PIM-1 up to 800 °C under nitrogen environment.

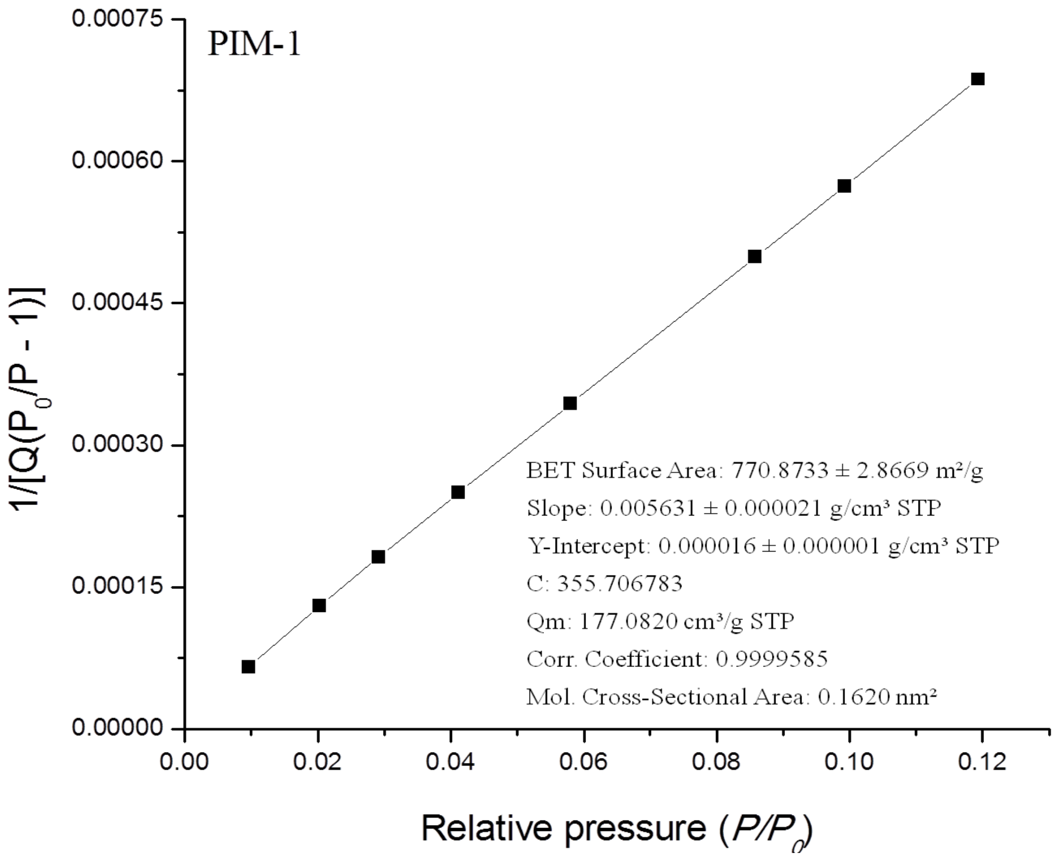


Figure S3. BET linear plot for PIM-1 (from N_2 adsorption at 77 K).

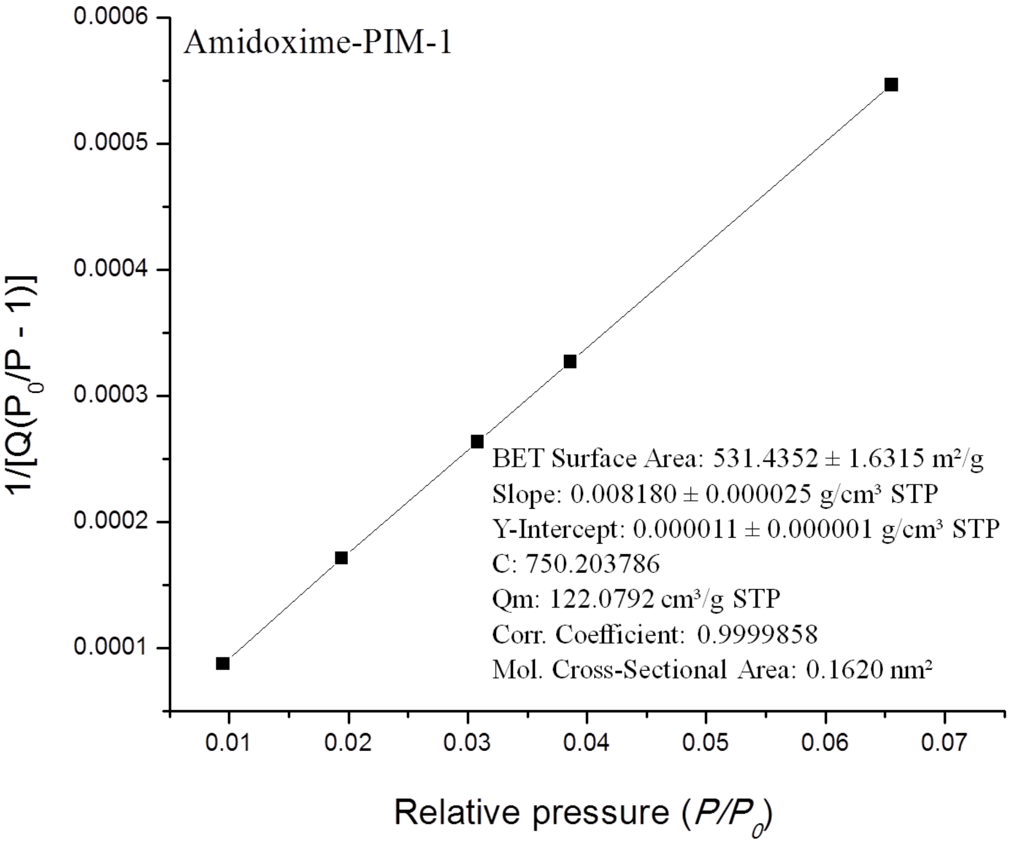


Figure S4. BET linear plot for amidoxime-PIM-1 (from N_2 adsorption at 77 K).

References

1. P. M. Budd, E. S. Elabas, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, C. E. Tattershall and D. Wang, *Adv. Mater.*, 2004, **16**, 456-459.
2. F. Eloy and R. Lenaers, *Chem. Rev.*, 1962, **62**, 155-183.
3. C. R. Mason, L. Maynard-Atem, N. M. Al-Harbi, P. M. Budd, P. Bernardo, F. Bazzarelli, G. Clarizia and J. C. Jansen, *Macromolecules*, 2011, **44**, 6471-6479.