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Noninvasive functionalization of polymers of intrinsic microporosity for enhanced CO₂ capture†

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Modifying sorbents for the purpose of improving carbon dioxide capture often results in the loss of surface area or accessible pores, or both. We report the first noninvasive functionalization of the polymers of intrinsic microporosity (PIMs) where inclusion of the amidoxime functionality in PIM-1 increases carbon dioxide capacity up to 17% and micropore surface area by 20% without losing its film forming ability.

The generation of intrinsic microporosity, “a continuous network of interconnected intermolecular voids, which forms as a direct consequence of the shape and rigidity of the component macromolecules”, in polymers results in Polymers of Intrinsic Microporosity (PIMs), which can be utilized for gas adsorption and separation, catalysis, and membrane applications.^{1,2} Microporous polymeric materials combine high surface areas with good physicochemical stability and potential for synthetic diversification.³ They are often grouped as amorphous polymers^{4,5} or crystalline polymers⁶ and can further be tailored for versatile applications based on their pore sizes and shape, surface area and regularity in the networks.^{7–12} PIMs usually consist of a fused ring structure, obtained by a dioxane forming polymerization reaction.^{13,14} The solubility of PIMs is one of the major benefits for casting robust, self-standing films by conventional solution based polymer processing techniques. Membranes, then, offer a low cost, more energy-efficient carbon dioxide (CO₂) capture option, if highly CO₂ permeable, selective membranes existed with the ease in their manufacturing.

CO₂ capture and storage remains a key challenge for a clean environment. In addition to the current strategies for improving the energy efficiency in generation and consumption, and increasing the use of renewable energy resources, economical CO₂ capture processes may offer new options for reducing greenhouse-gas emissions.¹⁵ Conventional amine absorption technologies are energy intensive and costly, albeit there is no viable alternative

and they do result in large incremental cost, aka energy penalty.¹⁶ In order to alleviate this problem, CO₂ sorption capacities were studied for a range of high surface area porous polymers under various conditions of temperature and pressures.³ For a post-combustion CO₂ sorption at ambient pressures, however, high surface areas may not be the most desirable.¹⁷ Hence, inclusion of the CO₂-philic functionality within the microporous framework is necessary for an economically sound technology where pressure swing or temperature swing adsorption is used. Nitrogen and hydroxyl groups are known for their strong interactions with CO₂ and there exist numerous attempts to generate these kinds of functionalities within the polymeric networks, mainly, tetrazole,³ triazine,^{18,19} primary, secondary or tertiary amines,^{19–23} hydroxyls¹⁰ and imidazole.²⁴

Modifying sorbents for the purpose of improving CO₂ capture, however, often results in the loss of surface area or accessible pores, or both. Recently, functionalization of PIMs through post-modification of nitriles (–C≡N) was reported by incorporation of tetrazole,³ carboxylate,²⁵ thioamide,²⁶ azide²⁷ and hydroxyl²⁸ functionalities. Although all the modified PIMs show good processability and improved gas separation properties, their surface areas are considerably reduced, negating the very reason for developing highly microporous polymers.

Here we report the first noninvasive functionalization of PIMs by the amidoxime functionality to increase carbon dioxide capacity without adversely affecting physicochemical properties. Amidoximes are known to be CO₂-philic¹⁶ and our results challenge the common perception in which post-modifications are expected to diminish properties of the original solid. In order to introduce the amidoxime²⁹ moiety, P–(NH₂)C=N(OH) where P is the polymeric chain, PIM-1 was functionalized by a rapid reaction of nitrile groups of PIM-1 with hydroxyl amine (Fig. 1a) under reflux conditions. The formation of amidoxime–PIM-1 was confirmed by ¹H NMR, FTIR and elemental analysis.

The original PIM-1 is readily soluble in tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), and chloroform (CHCl₃), but insoluble in polar aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone (NMP).^{13,14} After functionalization, amidoxime–PIM-1 was found to be insoluble in CH₂Cl₂, CHCl₃, and THF, however, DMSO, DMF, DMAc and NMP were good solvents, indicating that the amidoxime based PIM-1 still have good processability (Scheme S1, ESI†)

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† Electronic supplementary information (ESI) available: Synthetic procedure and characterization methods for PIM-1 and amidoxime–PIM-1, tables for elemental analysis, porosity and gas uptake, BET linear plots. See DOI: 10.1039/c2cc35392j

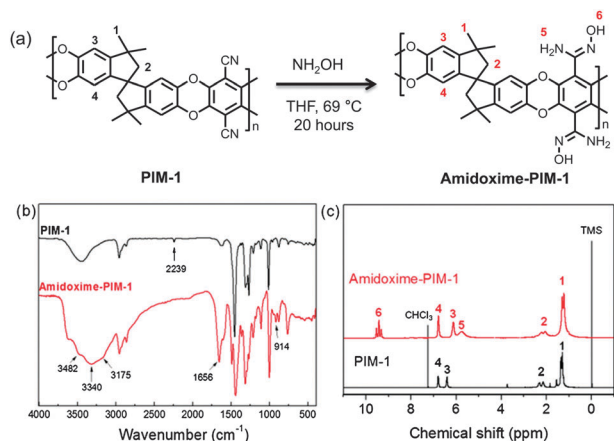


Fig. 1 (a) Molecular structures and synthetic pathway, (b) FTIR spectra and (c) ¹H NMR spectra of PIM-1 and amidoxime-PIM-1.

with an inversion of the polarity. Du *et al.*²⁵ observed similar patterns for solubility of carboxylated PIMs.

The characteristic stretching band of nitrile groups appears at 2239 cm⁻¹ in PIM-1 (Fig. 1b). A nitrile peak that is not visible in amidoxime-PIM-1 would suggest that complete conversion of nitriles to amidoxime groups was achieved. Some other important vibrations for amidoxime are the bands at 3482 and 3340 cm⁻¹, which could be assigned to an antisymmetric and a symmetric stretching mode of NH₂ groups, respectively. A band at 3175 cm⁻¹ is assigned to O–H stretching vibration. The bands at 1656 and 914 cm⁻¹ are assigned to a C=N stretching mode and a N–O stretching mode of oxime groups, respectively. The chemical shift in ¹H NMR spectra (Fig. 1c) of PIM-1 and amidoxime-PIM-1 is shown at 5.81 (–NH₂) and 9.44 (–OH) ppm assigned to the amidoxime moiety, which provides evidence for the conversion of nitrile to amidoxime groups. The structure of the polymer is not hindered upon functionalization (see full ¹H NMR in Fig. S1, ESI†). Elemental analysis of PIM-1 and amidoxime-PIM-1 reveals 6.3 and 10.1% N, respectively, which is comparable with theoretical values (Table S1, ESI†). TGA of amidoxime-PIM-1 shows two-step decomposition (Fig. S1, ESI†). The mass loss of 12.4% within 200–380 °C is caused by the loss of amidoxime functionality. The thermal decomposition of amidoxime results in hydroxyl amine and nitrile²⁹ within first mass loss and this reversible reaction leads to PIM-1. Mason *et al.*²⁶ observed a similar type of thermal behavior in the case of thioamide-PIM-1.

The architectural rigidity and consequently the permanent porosity of PIM-1 and amidoxime-PIM-1 were unambiguously proven by N₂ adsorption–desorption isotherms at 77 K (Fig. 2 and Table S2 (ESI†)). Type I nitrogen sorption isotherm behavior was observed for both samples, which reveals its microporous nature. Apparent surface areas of 889 and 577 m² g⁻¹ for PIM-1 and amidoxime-PIM-1 (Langmuir model) and 771 and 531 m² g⁻¹ for PIM-1 and amidoxime-PIM-1 (Brunauer–Emmett–Teller) (BET) models were obtained by using the data points on the adsorption branch in the range of $P/P_0 = 0.01–0.10$ (Fig. S2 and S3, ESI†). In contrast, an unprecedented increase in micropore surface areas (313 and 376 m² g⁻¹ for PIM-1 and amidoxime-PIM-1) was observed.

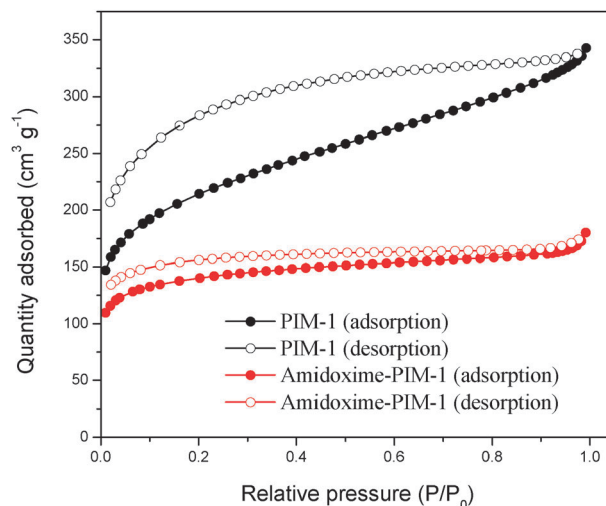


Fig. 2 Nitrogen adsorption–desorption isotherms at 77 K.

This may be because of the conversion of mesopores to micropores upon replacement of a nitrile group by a more bulky amidoxime group while the reduction in the total surface area is due to intermolecular interactions between neighboring chains of amidoxime-PIM-1 forming hydrogen bonding.^{25,26} The pore volume was also reduced: the total pore volume of PIM-1 is 0.57 cm³ g⁻¹ and of amidoxime-PIM-1 is 0.28 cm³ g⁻¹. The contorted shape and extreme rigidity restrict packing of polymeric chains which is responsible for microporosity in PIM-1.¹³ There is also mesoporosity in both samples as evident from hysteresis in nitrogen isotherms. The mesoporosity is dependent on the form of the material and is generally greater in the powder sample than the film.³⁰ The calculated average pore size according to the N₂ isotherm is 2.7 and 2.1 nm for PIM-1 and amidoxime-PIM-1, respectively, suggesting a nanoporous polymeric structure.

Featuring ample, basic nitrogen and hydroxyl groups and intrinsic microporosity, amidoxime-PIM-1 was used as an adsorbent for CO₂ capture. Fig. 3 shows CO₂ adsorption–desorption isotherms of PIM-1 and amidoxime-PIM-1 at 273 and 298 K, at pressures up to 1 bar. Strong interactions between the porous polymeric networks and CO₂ are essential for enhancing the CO₂ adsorption capacity. Functionalization of PIM-1 by amidoxime creates sites that have a strong affinity toward CO₂ through its high quadrupole moment. Indeed, amidoxime-PIM-1 displayed enhanced CO₂ uptake capacities. PIM-1 has a CO₂ adsorption capacity of 111.4 mg g⁻¹ at 273 K and 1 bar, whereas amidoxime-PIM-1 showed increases in CO₂ uptake, with values of 120.5 mg g⁻¹, an 8% enhancement. CO₂ uptake difference of amidoxime-PIM-1 (72.4 mg g⁻¹) is doubled to 17% when compared to PIM-1 (62 mg g⁻¹) at 298 K and 1 bar. Furthermore, dipole–quadrupole interactions of amidoxime groups with CO₂ can be clearly visible from the smaller hysteresis in the CO₂ adsorption–desorption isotherm unlike PIM-1. The isosteric heats of adsorption (Q_{st}) were calculated from the CO₂ isotherms measured at 273 K and 298 K.²¹ The Q_{st} for PIM-1 and amidoxime-PIM-1 is 28.4 and 30.2 kJ mol⁻¹. These values are comparable to nitrogen-rich networks^{8,20} and CO₂ selective metal–organic frameworks^{31–33} which generally feature –NH₂ or –OH functionalized pores.

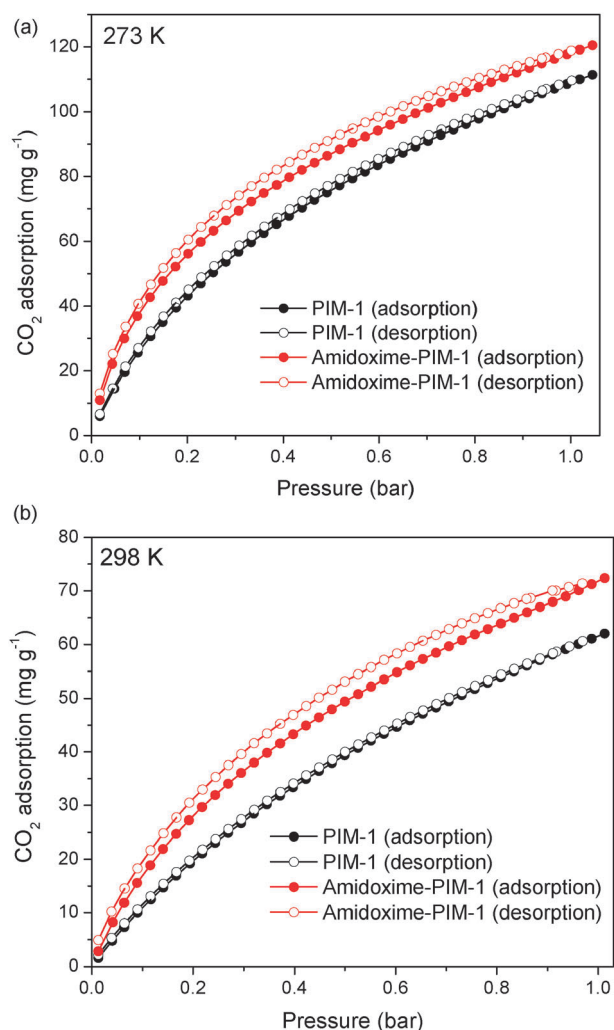


Fig. 3 CO₂ adsorption–desorption isotherms of PIM-1 and amidoxime-PIM-1 up to 1 bar at (a) 273 K and (b) 298 K.

In conclusion, amidoxime-PIM-1 was successfully synthesized through a conventional, noninvasive, chemical synthetic route. CO₂ uptake was improved 17% along with its micro-pore surface area. Processability of amidoxime-PIM-1 remained preserved with a complete inversion of solubility to polar aprotic solvents. In the light of our findings, we expect the amidoxime functionality to expand the area of post-modification of porous materials and provide better alternative for membrane based separations of carbon dioxide and other gases.

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