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

Hasmukh A. Patel and Cafer T. Yavuz*

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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 polymers4,5 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-phlic 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, triazine, primary, secondary or tertiary amines, hydroxyl 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,2 carbamate,22 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-phlic16 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 amidoxime 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†).

† 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
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 NH\(_2\) 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 \(^1\)H NMR spectra (Fig. 1c) of PIM-1 and amidoxime–PIM-1 is shown at 5.81 (–NH\(_2\)) 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 \(^1\)H 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 nitrile\(^29\) 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 N\(_2\) 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 m\(^2\) g\(^{-1}\) for PIM-1 and amidoxime–PIM-1 (Langmuir model) and 771 and 531 m\(^2\) 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 m\(^2\) g\(^{-1}\) for PIM-1 and amidoxime–PIM-1) was observed.

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 cm\(^3\) g\(^{-1}\) and of amidoxime–PIM-1 is 0.28 cm\(^3\) 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 N\(_2\) 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 CO\(_2\) capture. Fig. 3 shows CO\(_2\) 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 CO\(_2\) are essential for enhancing the CO\(_2\) adsorption capacity. Functionalization of PIM-1 by amidoxime creates sites that have a strong affinity toward CO\(_2\) through its high quadruple moment. Indeed, amidoxime–PIM-1 displayed enhanced CO\(_2\) uptake capacities. PIM-1 has a CO\(_2\) adsorption capacity of 111.4 mg g\(^{-1}\) at 273 K and 1 bar, whereas amidoxime–PIM-1 showed increases in CO\(_2\) uptake, with values of 120.5 mg g\(^{-1}\), an 8\% enhancement. CO\(_2\) 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 CO\(_2\) can be clearly visible from the smaller hysteresis in the CO\(_2\) adsorption–desorption isotherm unlike PIM-1. The isosteric heats of adsorption (\(Q_{st}\)) were calculated from the CO\(_2\) 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 CO\(_2\) selective metal–organic frameworks\(^31–33\) which generally feature –NH\(_2\) or –OH functionalized pores.

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

Fig. 2 Nitrogen adsorption–desorption isotherms at 77 K.
In conclusion, amidoxime–PIM-1 was successfully synthesized through a conventional, noninvasive, chemical synthetic route. CO₂ uptake was improved 17% along with its micropore 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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![Fig. 3](image)

**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.

Notes and references