Sulfonate-Grafted Porous Polymer Networks for Preferential CO$_2$ Adsorption at Low Pressure

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ABSTRACT: A porous polymer network (PPN) grafted with sulfonic acid (PPN-6-SO$_3$H) and its lithium salt (PPN-6-SO$_3$Li) exhibit significant increases in isosteric heats of CO$_2$ adsorption and CO$_2$-uptake capacities. IAST calculations using single-component-isotherm data and a 15/85 CO$_2$/$N_2$ ratio at 295 K and 1 bar revealed that the sulfonate-grafted PPN-6 networks show exceptionally high adsorption selectivity for CO$_2$ over $N_2$ (155 and 414 for PPN-6-SO$_3$H and PPN-6-SO$_3$Li, respectively). Since these PPNs also possess ultrahigh physicochemical stability, practical applications in postcombustion capture of CO$_2$ lie within the realm of possibility.

One of the primary scientific discussions currently ongoing is that of global climate change, which is at least in part attributed to the increasing CO$_2$ concentration in the air. Carbon capture and sequestration (CCS), a process to separate CO$_2$ from flue gas, has been proposed as a feasible way to mediate the atmospheric CO$_2$ concentration. Conventional CO$_2$ capture processes employed in power plants worldwide are postcombustion "wet scrubbing" methods involving chemical adsorption of CO$_2$ by amine solutions such as monoethanolamine (MEA). There are several disadvantages with wet scrubbing, including the considerable parasitic power consumption involved in the regeneration of the solutions and the measures that must be taken to control the corrosive solutions, both of which lead to reduced efficiencies and increased costs for electricity generation.$^3$

An alternative, energy-conserving approach involves the use of porous materials, which can easily take up and release CO$_2$ through a physisorption mechanism. Recently, metal–organic frameworks (MOFs), adsorbents made of metal ions and organic linkers with high surface areas and tunable pore sizes, have emerged to show remarkable CO$_2$-uptake capacities and CO$_2$/N$_2$ selectivities at room temperature.$^5$ However, the majority of MOFs have difficulty in meeting the stringent industrial requirements.$^3$ On the other hand, purely organic porous polymers, another class of adsorbents with comparable surface areas and pore sizes, exhibit much higher physicochemical stability as a result of the covalent bonding nature of the network construction.$^4$ Despite the fact that most of them are amorphous, their stability is desirable in practical applications.

Besides physicochemical stability, high CO$_2$-uptake capacity and CO$_2$/N$_2$ selectivity under ambient conditions are equally essential for porous materials to be industrially applicable. Presumably, increasing the isosteric heat of CO$_2$ adsorption through the introduction of CO$_2$-philic moieties should have a great influence on both. Indeed, significant increases of isosteric heats and CO$_2$/N$_2$ adsorption selectivity have been observed upon pre- or postsynthetic introduction of polar functionalities;$^7$ however, this approach usually has a negative impact on the surface area that can lead to very low CO$_2$-uptake capacity if the surface area is severely compromised. One possible strategy to tackle this issue is to judiciously select porous polymers with ultrahigh surface areas and physicochemical stability as starting materials. Therefore, sufficient surface area can be retained after the introduction of CO$_2$-philic moieties.

Herein we report the synthesis of PPN-6, a porous polymer network (PPN) with permanent porosity, and grafting of PPN-6 with sulfonic acid and lithium sulfonate. The resulting PPN-6-SO$_3$H and PPN-6-SO$_3$Li materials showed significant increases in CO$_2$-uptake capacities and exceptionally large CO$_2$/N$_2$ adsorption selectivities under ambient conditions.

PPN-6 (also known as PAF-1$^{4a}$) was synthesized by an optimized Yamamoto homocoupling reaction$^8$ using tetrasik(4-bromophenyl)methane. The default diamondoid framework topology imposed by the tetrahedral monomers provides widely open and interconnected pores that efficiently prevent the formation of “dead space”;$^{4b}$ more importantly, the extremely robust all-carbon scaffold of the network makes it ideal for attachment of polar functionalities on biphenyl species under harsh reaction conditions. By reaction with chlorosulfonic acid, PPN-6 was modified to give PPN-6-SO$_3$H, which was further neutralized to produce PPN-6-SO$_3$Li (Scheme 1).

Nitrogen gas adsorption/desorption isotherms of the three networks were collected at 77 K [Figure S1a in the Supporting Information (SI)]. Notably, the large desorption hysteresis in PPN-6 disappeared and almost ideal type-I isotherms were obtained for sulfonate-grafted PPN-6. The Brunauer–Emmett–Teller (BET) surface areas obtained from the experimental data were 4023, 1254, and 1186 m$^2$ g$^{-1}$ for PPN-6, PPN-6-SO$_3$H, and PPN-6-SO$_3$Li, respectively (Figures S2–S4). As expected, the surface area decreased upon functionalization. The pore size distributions of the three networks were derived using the entire range of the N$_2$ adsorption isotherms measured at 77 K. Along with the decrease in surface area, the pore size became progressively smaller with aromatic sulfonation and ensuing lithiation (Figure S1b).
Recent studies have revealed that one of the desirable features for enhancing the CO2-uptake capacity at ambient temperature is a suitable pore size commensurate with the kinetic diameter of a CO2 molecule.7 The relatively small pore sizes of both sulfonate-grafted PPN-6 networks fall into the 5.0–10.0 Å range, which is believed to be suitable for CO2 uptake and thus for CO2 separation from other gases with relatively larger kinetic diameters, such as N2 and CH4.

Strong interactions between the network and CO2 are another desirable feature for enhancing the CO2-uptake capacity. Functionalization of all-carbon-scaffold networks can be expected to create electric fields on the surface that impart to the networks a strong affinity toward CO2 through its high quadrupole moment. Indeed, the sulfonate-grafted PPN-6 materials displayed significantly enhanced CO2-uptake capacities. As shown in Figure 1, nongrafted PPN-6 has a gravimetric CO2 uptake of 5.1 wt % at 295 K and 1 bar, whereas sulfonate-grafted PPN-6 showed remarkable increases in gravimetric CO2 uptake, with values of 13.1 and 13.5 wt % (equivalent to 3.6 and 3.7 mmol g−1, respectively) for PPN-6-SO3H and PPN-6-SO3Li, respectively. To the best of our knowledge, the values are the highest among all microporous organic polymers reported to date.8 The surge in volumetric uptake with sulfonate grafting is even more significant, from 8.1 g L−1 for PPN-6 to 52.5 g L−1 for PPN-6-SO3H and 79.9 g L−1 for PPN-6-SO3Li (Figure S5; the tap densities of the three networks used to calculate the volumetric capacities were measured to be 0.15, 0.35, and 0.51 g cm−3, respectively). Relative to PPN-6-SO3H, the initial CO2 uptake for PPN-6-SO3Li is more pronounced; the Li+ cation in −SO3Li has up to three open coordination sites after full activation, which results in stronger interactions with CO2 molecules.9

These two sulfonate-grafted PPNs showed no obvious loss of surface area or decrease in CO2-uptake capacity even after being boiled in water for 6 h (Figure 2 and Figure S8). Since they were synthesized in highly corrosive acid (CISO3H) and/or base (LiOH) solution, we can be confident of their ultrahigh physicochemical stability.

Aside from high CO2-uptake capacity and physicochemical stability, high selectivity for CO2 over N2 under ambient conditions is another prerequisite for industrial CO2 capture applications. The ideal adsorption solution theory (IAST) of Myers and Prausnitz10 has been reported to predict binary gas mixture adsorption in many porous materials accurately.11 To judge the merit of the sulfonate groups for CO2/N2 separation, the adsorption selectivities [defined as Sads = (q1/q2)/(p1/p2), where qi is the amount of i adsorbed and pi is the partial pressure of i in the mixture] of the three networks for CO2 over N2 in flue-gas streams (typically 15% CO2 and 85% N2) were estimated from the experimental single-component isotherms. Sulfonate-grafted PPN-6 exhibited exceptionally high adsorption selectivity for CO2 over N2 at 295 K and 1 bar (Sads = 150 for PPN-6-SO3H and 414 for PPN-6-SO3Li). As shown in Figure 3, the selectivities of sulfonate-grafted PPN-6 are comparable to that of NaX zeolite, which was calculated with the same parameters using the experimental isotherm data of Belmabkhout et al.12 and Cavenati et al.13 Thus, these materials hold considerable promise for postcombustion carbon capture applications. To understand the hierarchy of adsorption selectivity, we note that the calculated pore volumes for PPN-6, PPN-6-SO3H, and PPN-6-SO3Li are

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**Scheme 1. Synthesis and Grafting of PPN-6**

![Scheme 1](image)

**Figure 1.** Gravimetric CO2 and N2 adsorption (●)/desorption (○) isotherms at 295 K (see the SI for magnified N2 isotherm curves).

**Figure 2.** (a) N2 adsorption (●)/desorption (○) isotherms of PPN-6-SO3Li at 77 K. (b) Gravimetric CO2 adsorption curves for PPN-6-SO3Li at 273 K. Run 2 employed material regenerated after run 1 by boiling in water for 6 h.

**Figure 3.** IAST-predicted adsorption selectivities for PPN-6 (red), PPN-6-SO3H (green), PPN-6-SO3Li (blue), and NaX zeolite (black).
The general understanding is that the CO₂-uptake capacity is dictated by many factors, such as surface area, pore functionality, pore size, etc., with each factor carrying different weights at various pressures and temperatures. At very low pressures, the interactions between CO₂ and the pore surface play the dominant role for CO₂ uptake. This appears to be the case for both sulfonate-grafted PPNs, as is most evident in the high heats of adsorption. However, as the pressure is increased to 1 bar, the effect of functionality gradually weakens, and the influence of surface area progressively weighs in, consistent with the decrease of the heat of adsorption.

The foregoing results demonstrate that aromatic sulfonation and ensuing lithiation result in significant enhancements of the CO₂-uptake capacity and CO₂/N₂ adsorption selectivity under ambient conditions. Given the outstanding physicochemical stability, these materials might find practical applications in postcombustion CO₂ capture. To improve the CO₂-uptake capacity and CO₂/N₂ selectivity further with this strategy, using porous materials with even higher surface areas as starting materials should have great potential. In addition, uniformly large pores would be ideal for shuttling the reactants and improving the diffusion rates. Moreover, much stronger CO₂-phobic moieties, such as alkylamine groups, would be more effective in increasing the heat of adsorption. Work on further expansion of this series of materials along these lines is currently underway in our lab.

**ASSOCIATED CONTENT**

Supporting Information. Detailed experimental procedures, elemental analysis results, FT-IR and solid-state NMR spectra, additional gas sorption isotherms, and details of the IAST calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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