Novel lithium-laded porous aromatic framework for efficient CO$_2$ and H$_2$ uptake

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Novel porous aromatic frameworks, PAF-18-OH and its lithiated derivative PAF-18-OLi, have been successfully synthesized. In particular, PAF-18-OLi displays significant enhancements of H$_2$ and CO$_2$ adsorption capacity, especially for the CO$_2$ uptake (14.4 wt%). More valuably, the stable PAF-18-OLi material exhibits high CO$_2$/N$_2$ selectivity, as high as 129 in the case of CO$_2$ capture from simulated post-combustion flue gas mixtures (85% N$_2$ and 15% CO$_2$). Furthermore, the PAF-18-OLi has shown an improved H$_2$ storage capacity after lithiation.

Introduction

The environmental degeneration and adverse climate change are currently two of the challenges mostly affecting our daily life.$^{[1]}$ The increasing utilization of world’s fast diminishing fossil fuels is the major source of environmental pollution.$^{[2]}$ The emission of CO$_2$ is considered as the most significant contribution to the global warming among all of the Earth’s radiative-forcing components.$^{[3]}$ To solve these two pressing environmental issues, it requires the development of new technologies for capture and sequestration of CO$_2$ and efficiently harness a range of renewable energy sources and carriers such as H$_2$. Porous materials, such as activated carbon,$^{[3]}$ zeolites,$^{[6]}$ and metal–organic frameworks (MOFs),$^{[7]}$ have demonstrated a promising prospect in applications for H$_2$ storage and CO$_2$ capture owing to their high specific surface areas and low energy consumption for regeneration. Recently, a new family of porous materials, porous organic frameworks (POFs), composed of light elements (C, H, O, N, B, etc) via covalent bonds, have attracted a great deal of attention thanks to their high surface areas, high stability and controllable skeletons.$^{[8-13]}$ Current investigations have demonstrated that POFs are promising materials for H$_2$ storage and CO$_2$ capture.$^{[14]}$

Up to date, H$_2$ storage in porous materials are usually implemented under either high pressure or very low temperature conditions, which are not easily adapted in commercial and realistic applications.$^{[2a]}$ Traditional CO$_2$ capture is based on the chemical absorption of CO$_2$ using the aqueous solutions of amines.$^{[15]}$ and a substantially large amount of energy are required for the activity regeneration of the amines. Although the use of porous materials for physical adsorption of CO$_2$ is fairly energy-effective, the considerable amount of N$_2$ are co-adsorbed in the porous materials, resulting in low CO$_2$/N$_2$ selectivity.$^{[16]}$ To enhance H$_2$ or CO$_2$ uptake and especially improve the CO$_2$/N$_2$ adsorption selectivity, porous materials should possess strong interaction with H$_2$ or CO$_2$. Several strategies in literatures have been developed to enhance the interactions between porous materials and gas molecules via the control of the pore size, incorporation of polar functional groups or introduction of open metal sites into the porous networks.$^{[17]}$ For instance, doping atomically dispersed alkali metal cations, for example Li$^+$ ions into MOFs and POFs is expected to increase H$_2$ and CO$_2$ storage capacities.$^{[18,19]}$ However, Li$^+$-doped MOFs or POFs have limited success in H$_2$ storage and CO$_2$ capture due to the instability of Li$^+$ ions or the modified porous structures.$^{[19]}$ Herein we synthesized new porous aromatic frameworks (PAFs) with permanent porosity and functionalized OH groups, referred as PAF-18-OH. The OH groups of PAF-18-OH have been further transformed into the lithium alkoxo groups, resulted in lithium-laded PAF, referred as PAF-18-OLi (Scheme 1).

![Scheme 1 Schematic depict for the synthesis of PAF-18-OH and PAF-18-OLi.](image-url)
PAF-18-OLi has exhibited a significantly increased uptake of CO₂ with high CO₂/N₂ selectivity as large as 129 at 273 K. Furthermore, the PAF-18-OLi has shown an enhanced H₂ storage capacity.

**Experimental section**

**Chemicals:**
All chemicals were purchased from Aldrich, Alfa-Aesar, and Aladdin-reagent, and were used as purchased unless it was noted. N,N-Dimethylformamide (DMF) and triethylamine (Et₃N) were dehydrated with CaH₂. Tetrahydrofuran (THF) was distilled in the presence of sodium benzophenone ketyl under N₂ condition. Tetraakis(4-ethynylphenyl)methane[20a] and 2,4,6-Tribromo-benzene-1,3,5-triol[20b] were prepared according to the previously reported method.

**Synthesis of PAF-18-OH:**
Tetrakis(4-ethynylphenyl)methane (125 mg, 1.5 mmol), 2,4,6-tribromo-benzene-1,3,5-triol (116 mg, 1.5 mmol), tetrakis(triphenylphosphine)palladium (30 mg), and copper iodide (8 mg) were dissolved in the mixture of DMF (5 mL) and Et₃N (5 mL) in a 50 mL two-necked flask. After degassing via three freeze-pump-thaw cycles, the mixture was stirred at 85 °C for 36 h under N₂. After cooling down to room temperature, the resulting PAF-18-OH was collected by filtration, followed by consecutive washing by Soxhlet extraction for 48 h with THF, methanol to remove the unreacted monomers or catalysts. After drying at 90 °C in vacuum overnight, PAF-18-OH was obtained in the form of brown powder (150 mg, 90% yield).

**Synthesis of PAF-18-OLi:**
Synthesis of PAF-18-OLi was performed in an argon atmosphere glove box. Lithium-naphthalenide (Li⁺C₆H₅⁻N) was synthesized by adding small pieces of clean lithium (3 mg, stored in glove box) into 100 mL naphthalene solution in THF (0.1 M), followed by 4 h vigorous stirring. After reaction, the solution became dark green; a given volume of this solution was taken out by a volumetric syringe and mixed with the dried powders of PAF-18-OLi with a given mass (see supporting information). After stirring overnight to ensure the complete reaction of Li⁺C₆H₅⁻ with PAF-18-OH, the powder of PAF-18-OLi was filtrated and washed with THF for several times to remove naphthalene and then dried under vacuum at 120 °C for 12 h.

**Characterizations:**
FTIR spectra were obtained using an IFS 66/S Fourier transform infrared spectrometer. Thermogravimetric analysis (TG) was implemented using a Netzsch Sta 449c thermal analyzer system at a heat rate of 10 °C/min under air. Scanning electron microscopy (SEM) imaging was performed on JEOL JSM 6700. Transmission electron microscopy (TEM) imaging was carried out on JEOL JEM 3010 with an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific) was performed by using a monochromatized Al Kα (1486.6 eV) X-ray source. ²⁹Li MAS NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer. Powder X-ray diffraction (PXRD) was carried out by a Rigaku D/MAX2550 diffractometer using CuKα radiation, 40 kV, 200 mA with scanning rate of 3 °/min (2θ). The lithium content in PAF-18-OLi was determined by inductively coupled plasma (ICP) spectroscopy (Perkin-Elmer ICP-OES Optima 3300DV). Before analysis, ~15 mg sample was digested in 3:1 HCl/HNO₃ (10 mL) and transferred to 50 mL volumetric flask with distilled water.

**Low-pressure gas adsorption measurements:**
The gas adsorption/desorption isotherms were measured on a Quantachrome Autosorb iQ2 analyzer. N₂ adsorption/desorption measurements were carried out at 77 K, 273 K, and 298 K; H₂ adsorption/desorption isotherms recorded at 77 K and 87 K; and CO₂ adsorption/desorption isotherms collected at 273 K and 298 K, respectively. Ultra-high-purity grade (99.999%) N₂, H₂, and CO₂ gases were used for all adsorption measurements. Liquid nitrogen and liquid argon baths were utilized to control the temperature at 77 K and 87 K, respectively. Ice-water bath and water baths equipped with a temperature sensor were used to control the temperature at 273 K and 298 K.

**Results and discussion**

**Description of PAF-18-OH and PAF-18-OLi:**
PAF-18-OH was synthesized via palladium-catalyzed Sonogashira-Hagihara cross-coupling reaction of tetrahydrofuran (THF) with a temperature sensor were used to control the temperature at 77 K and 87 K, respectively. Ice-water bath and water baths equipped with a temperature sensor were used to control the temperature at 273 K and 298 K.

Further, the morphologies of PAF-18-OH and its derivative PAF-18-OLi are monitored by scanning electron microscopy (SEM). SEM images show both PAF-18-OH and PAF-18-OLi are aggregates of microgel particles with a size of 100 nm (Fig. 1a and 1b). The appearance of PAF-18-OLi is similar to PAF-18-OH, indicating the structure of PAF-18-OLi is preserved after lithiation. In addition, the microstructure is studied by transmission electron microscopy (TEM). The TEM images of PAF-18-OH and PAF-18-OLi are displayed in Fig. 1c and d. As can be seen, the worm-like porous texture is observed in both materials.
Fig. 1 SEM images of PAF-18-OH (a) PAF-18-OLi (b), scale bars: 300 nm. TEM images of PAF-18-OH (c) PAF-18-OLi (d), scale bars: 20 nm.

Porosity of PAF-18-OH and PAF-18-OLi:

The porosity of PAF-18-OH and PAF-18-OLi is probed with physical nitrogen sorption at 77 K. A sharp increase in gas uptake is observed at low pressure in the nitrogen adsorption-desorption isotherms of PAF-18-OH and PAF-18-OLi, which further confirms an existence of the micropores in both PAFs; a distinct adsorption–desorption hysteresis at high relative pressure sheds light on the presence of some mesopores, which is a common character for many porous organic frameworks (Fig. 2a). [24,18c]

The Brunauer-Emmett-Teller (BET) surface area of PAF-18-OH is measured as 1121 m² g⁻¹. As shown in Fig. 2a, the lithiation of PAF-18-OH causes a small reduction in the BET surface area. The BET surface areas of PAF-18-OLi are decreasing with an increase of the lithium content. Typically, the surface area of 981 m² g⁻¹ is obtained after the complete lithiation (Li content is 4.2 wt%) (Table S1). The pore size distributions of PAF-18-OH and PAF-18-OLi have been calculated based on nonlocal density functional theory. As shown in Fig. 2b, the transformation of the OH groups into the lithium alkoxy groups gives negligible change of the pore size distribution within the PAF-18 materials (Table 1). The little change in pore width is interpreted by the very close radius of ionic lithium and the hydrogen atom. But an increase of the density after lithiation causes noticeable decrease in the pore volume (Fig. 2c), which is the same phenomenon observed in the small reduction of the surface areas of the PAFs. The calculated pore volumes for PAF-18-OH and PAF-18-OLi are 0.82 and 0.57 cm³ g⁻¹, respectively. Also, PAF-18-OLi exhibits a micropore volume of 0.34 cm³ g⁻¹, which is a bit less than that of PAF-18-OH (0.4 cm³ g⁻¹).

The CO₂ adsorption for PAF-18-OH and PAF-18-OLi:

Given the particular polarity of PAF-18-OH and PAF-18-OLi for effective adsorption of CO₂[17] the -OLi in PAFs may provide strong polar open coordination sites, which could result in stronger interactions with CO₂ molecules. The CO₂ adsorption is studied on both PAF-18-OH and PAF-18-OLi samples (Fig. 3).
Table 1 The properties of porosity, gas uptake and isosteric heat of adsorption of PAF-18-OH and PAF-18-OLi.

<table>
<thead>
<tr>
<th>Materials</th>
<th>BET (m² g⁻¹)</th>
<th>DFT pore diameter (nm)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Micropore volume (cm³ g⁻¹)</th>
<th>CO₂ uptake at 273K (wt%)</th>
<th>Qₑ for CO₂ (kJ mol⁻¹)</th>
<th>H₂ uptake 77K (wt%)</th>
<th>Qₑ for H₂ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAF-18-OH</td>
<td>1121</td>
<td>1.33</td>
<td>0.82</td>
<td>0.4</td>
<td>11</td>
<td>28</td>
<td>2.15</td>
<td>7.4</td>
</tr>
<tr>
<td>PAF-18-OLi</td>
<td>981</td>
<td>1.32</td>
<td>0.57</td>
<td>0.34</td>
<td>14.4</td>
<td>29.5</td>
<td>1.65</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Fig. 3a shows that the CO₂ uptake of PAF-18-OH is about 110 mg g⁻¹ at 273 K and 66 mg g⁻¹ at 298 K at 1 bar, respectively. The PAF-18-OLi with 4.2 wt % Li shows a maximum CO₂ uptake; 144 mg g⁻¹ at 273 K and 89 mg g⁻¹ at 298 K at 1 bar, respectively, which are comparable to the best CO₂ adsorption performances of lithiated MOFs and POFs reported in the open literature.⁴,²⁵ Additionally, in the case of PAF-18-OLi, the CO₂ uptake is increasing with more Li contents introduced into the PAF structure (Fig. S7a). When the Li content is larger than 4.2 wt%, the CO₂ uptake decreases distinctly. Excess lithium would aggregate on the skeleton surface, which poses a negative contribution to CO₂ uptake.

The affinity of guest molecules to host materials is usually evaluated by the isosteric heat of adsorption (Qₑ). Fig. 3b shows that PAF-18-OLi has a larger Qₑ than that of PAF-18-OH; the Qₑ value of PAF-18-OLi is slowly reduced from 29.5 kJ mol⁻¹ to 23.5 kJ mol⁻¹ as the CO₂ uptake reaches the maximum while the Qₑ of PAF-18-OH from 28 kJ mol⁻¹ to 23 kJ mol⁻¹ (details of Qₑ calculation in supporting information). Since the lithiation causes reduction in the surface area and pore volume, the enhanced CO₂ uptake (Fig. 3a) could be assigned to the presence of the Li ions in the PAF-18-OLi framework. It is usually envisioned that the Li ions in PAF-18-OLi create a high electric field on the framework surface, which leads to a high binding force with quadrupolar CO₂ molecules.²⁷ Due to the high activity of Li ions, Li doped MOFs and POFs are usually unstable under the wet condition.¹⁹-b, c, e To verify their stability under wet condition, PAF-18-OLi samples were exposed to wet air (the average relative humidity is about 65%) for 10 days. This treatment causes little reduction in the CO₂ uptake of the PAF-18-OLi, as shown in Fig. 3a. This promises a great potential for future application of PAF-18-OLi in rigorous conditions, such as wet and oxygen.

The CO₂/N₂ selectivities of PAF-18-OH and PAF-18-OLi:

Carbon dioxide capture or storage from the flue gas (> 70% N₂ content) is critical to reduce global greenhouse effects.⁴ On the other hand, CO₂ is a useful chemical raw resource in industry. From the environment and energy perspective views, it requires adsorbents with large CO₂ adsorption capacity but with low N₂ adsorption ability in the range of low pressure and at ambient temperature. The adsorption isotherms of PAF-18-OH and PAF-18-OLi for CO₂ are investigated at different temperature of 273 K and 298 K, the results are shown in Fig. 4. It is found that both PAF-18-OH and PAF-18-OLi exhibit a pronounced CO₂ uptake and a fairly low N₂ adsorption at pressure of < 1 bar. The different adsorption ability towards CO₂ and N₂ provides a basis on the selective capture of CO₂ from gas mixture streams. We have employed the ideal adsorption solution theory (IAST) to assess the merit of lithiation for CO₂/N₂ separation, the method of which has been documented to accurately predict binary gas mixture adsorption in many porous materials.²⁸

![Fig. 4 The adsorption isotherms of CO₂ and N₂ at 273K and at 298K for PAF-18-OH (a) and PAF-18-OLi (b).](image)

Dual-site Langmuir-Freundlich equation is used to fit the experimental single component adsorption isotherm. The selectivities of PAF-18-OH and PAF-18-OLi for CO₂ over N₂ in post-combustion flue gas stream (typically 15% CO₂ and 85% N₂) are shown in Fig. 5. The CO₂/N₂ selectivity is 34 for PAF-18-OH and 129 for PAF-18-OLi at 273 K, respectively. After temperature is elevated from 273 K to 298 K, the selectivities are correspondingly reduced to 16 for PAF-18-OH and 45 for PAF-18-OLi, respectively. The selectivity of PAF-18-OLi at 273 K is nearly four times higher than that of PAF-18-OH at the same conditions. The exceedingly high CO₂/N₂ selectivity of PAF-18-OLi could be attributed to the presence of the Li ions in the framework which drastically enhances the adsorption of polar CO₂ molecules, and the decrease in the BET surface area and pore volume limits N₂ uptakes.

Further, we have also studied the capture of CO₂ from low-pressure post-combustion flue gas mixtures with the CO₂ content of ~15%. The CO₂ uptake is carried out at 0.15 bar and the N₂ adsorption at 0.85 bar, which is more relevant to practical application.
In this respect, the CO$_2$/N$_2$ selectivity in the flue gas is evaluated by the mass of CO$_2$ taken up at 0.15 bar divided by the mass of N$_2$ taken up at 0.85 bar. For example at 298 K (ambient temperature), the CO$_2$/N$_2$ selectivity of PAF-18-OH is estimated to be 4.3 whereas the value of 15.6 is calculated for PAF-18-OLi (Table 2). The tremendous increase in CO$_2$/N$_2$ selectivity for PAF-18-OLi can be due to high adsorption affinity of CO$_2$ onto available Li ions sites, simultaneously with the effect of a decline in the pore volume of PAF-18-OH, which would greatly limit the nitrogen uptake in gas mixture if CO$_2$ is pre-adsorbed at ambient temperature and pressure (Fig. S8). To be mentioned, the selectivity of CO$_2$ over N$_2$ is increased in low temperature (273 K, see Table 2), which is in good agreement with the IAST predicted result. The enhanced CO$_2$/N$_2$ selectivity after lithiation provides a new approach to develop new type solid adsorbents for CO$_2$ capture and sequestration.

The H$_2$ adsorption for PAF-18-OH and PAF-18-OLi:

In the current work, we have also studied the possibility of PAF-18-OH and PAF-18-OLi for H$_2$ storage. Fig. 6a shows hydrogen adsorption isotherms for both PAF materials at 77 K and 87 K. Based on the isotherms, the H$_2$ uptake of PAF-18-OH is calculated to be 1.35 wt% at 77 K and 0.95 wt% at 87 K at 1 bar, respectively. After lithiation, the H$_2$ uptake has been significantly increased. The H$_2$ uptake of PAF-18-OLi increases with the Li content in PAF-18-OLi (Fig. S7b), while the Li content is exceeding 4.2 wt%, the H$_2$ uptake decreases (Fig. S7b).

Table 2 Summary of the CO$_2$/N$_2$ selectivity for PAF-18-OH and PAF-18-OLi

<table>
<thead>
<tr>
<th>Materials</th>
<th>273K</th>
<th>298K</th>
<th>273K</th>
<th>298K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAF-18-OH</td>
<td>34</td>
<td>16</td>
<td>8.4</td>
<td>4.3</td>
</tr>
<tr>
<td>PAF-18-OLi</td>
<td>129</td>
<td>45</td>
<td>25</td>
<td>15.6</td>
</tr>
</tbody>
</table>

$^1$ $S^i_{(CO2)}$ is calculated by IAST model from 85% N$_2$ and 15% CO$_2$, 1 atm.
$^2$ $S^h_{(CO2)}$ is calculated by dividing the mass of CO$_2$ taken up at 0.15 bar by that of N$_2$ taken up at 0.85 bar.

PAF-18-OLi with the complete lithiation Li content of 4.2 wt% shows a maximum uptake of 1.65 wt% at 77 K and 1.17 wt% at 87 K at 1 bar, respectively. Additionally, the $Q_a$ is calculated from the H$_2$ adsorption data at 77 K and 87 K using the virial method (details in supporting information). Fig. 6b shows that the $Q_a$ of PAF-18-OLi is higher than that of PAF-18-OH. This suggests that the Li ions in PAF-18-OLi promotes strong mutual interactions between hydrogen molecules and the PAF framework.

Conclusions

In conclusion, we have synthesized novel porous aromatic frameworks, PAF-18-OH and its lithiated derivative, PAF-18-OLi via Sonogashira-Hagihara cross-coupling reaction. The tunability of Li contents in PAF-18-OLi shows different capacities for CO$_2$ and H$_2$ adsorption. The complete lithiated PAF-18-OLi exhibits the highest CO$_2$ and H$_2$ adsorption ability, which is due to stronger interaction of gas molecules with lithium derivative PAF framework. CO$_2$ capture from simulated flue gas is exemplified by PAF-18-OH and PAF-18-OLi. In the case of PAF-18-OLi, high CO$_2$/N$_2$ selectivity, up to 129 under ambient temperature and pressure is obtained, the value of which is almost four times higher than that of PAF-18-OH at the same condition. Notably, PAF-18-OLi material also exhibits high stability. The development of high-performance porous organic frameworks with remarkably high CO$_2$/N$_2$ selectivity, excellent sorption
capacity of CO$_2$ and H$_2$, and high stability would pave its significant way in carbon dioxide capture and sequestration, and hydrogen storage.

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Notes and references

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† Electronic Supplementary Information (ESI) available: This material includes: XRD, SEM, IR, TG, XPS figures; CO$_2$ and H$_2$ adsorption isotherms of PAF-18-OLi with different Li contents as well as details on the calculations of $Q_e$ and selectivity from ideal adsorption solution theory (IAST). See DOI: 10.1039/b000000x/


