



A molecular-templating strategy to polyamine-incorporated porous organic polymers for unprecedented CO₂ capture and separation

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Carbon capture and storage (CCS) is a feasible strategy to mitigate the increasing carbon dioxide (CO₂) emission, which is believed to be responsible for ocean acidification and global warming. Simultaneously, the separation of CO₂ from natural gas is also of critical importance in industry, because CO₂ as the major impurity significantly reduces the conversion rate and energy content of natural gas [1]. Currently, the main-stream technology for large-scale capture and sorption of CO₂ from industrial streams is amine-based wet scrubbing because the amine-based solutions have large CO₂ capacity and high selectivity for acidic gases. However, a major drawback of their high heat capacity makes the regeneration very energy intensive and costly. To address the issue, solid porous adsorbents have emerged as the promising alternative owing to their much lower heat capacity [2]. Moreover, the corrosion and volatility issues, which are intrinsic to the amine solutions, can also be greatly suppressed in solid adsorbents [3]. To capture CO₂ in an energy-efficient and economical manner, the solid porous materials should have highly-selective CO₂ adsorption ability at low CO₂ partial pressure and elevated temperatures, as well as high water stability and regenerability because the typical post-combustion flue gas contains ~15% CO₂, ~75% N₂ and ~6% water with the emission temperature of ~323 K. To date, numerous solid adsorbents such as silica [4], activated carbon [5], zeolites [6–8], metal organic frameworks (MOFs) [9–14], and porous organic materials [15–22] have been developed. While each of these solid materials has its unique drawbacks, a practically useful

solid adsorbent for large-scale and highly efficient CO₂ capture and separation has not been realized yet. Although porous organic polymers (POPs) have attracted great attention due to their high surface areas, excellent thermal, chemical and water stabilities, their selective CO₂ adsorption capacities are unsatisfying at low pressures due to weak interactions with CO₂ molecules [23]. One common issue for many solid adsorbents is insufficient affinity for CO₂. To this end, ammonium sulfonate and diamines were incorporated into POPs [24] and MOFs [25], respectively, which greatly improved their CO₂ capture capacity.

Polyethyleneimine (PEI), a polymer with the repeating unit composed of the amine group and the two-carbon spacer, has been widely impregnated into silica, zeolite, MOFs, and POPs for enhanced CO₂ capture [26–29]. PEI has been demonstrated as an effective CO₂ adsorption enhancer, but there are still two largely unresolved challenges preventing its general application. The first challenge is the even dispersion of PEI into the solid adsorbents. PEI can be readily dispersed into MOFs with open metal sites due to strong interactions between Lewis basic amine groups of PEI and the open metal sites acting as Lewis acids [29,30]. Most other classes of porous materials often lack this kind of site and thus cannot provide handle for the dispersion of PEI. The second challenge is the pore blocking effect of PEI. Introduction of any amount of PEI into a porous material inevitably reduces porosity which must be compensated by the increased CO₂ affinity, and as such an optimal amount of PEI needs

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to be identified. Thus PEI/MIL-101 showed high adsorption capacity and high selectivity for CO₂, but at 125 wt% PEI loading significant pore blocking occurred and resulted in decreased efficiency [29]. Here it should be noted that most of MOFs are unstable under moisture atmosphere, which greatly limits their practical applications [31].

Herein we report a novel, simple and general molecular-templating (MT) strategy to the rational design and synthesis of PEI-incorporated porous solid adsorbents with remarkable CO₂ capture and separation performance, in which PEI dispersion and pore size can be well tuned (Fig. 1). Different from the traditional method of simply mixing PEI and porous material [29], our MT strategy utilizes molecular carbon dioxide as a template to facilitate the even dispersion of PEI in the pores of parent solid material. Effective pores can be created by easy removal of CO₂ molecular template. Most importantly, the pore is greatly dominated by and matches kinetic diameter of the molecular template CO₂, resulting in superior selectivity for CO₂ against other larger gas molecules in flue gas. In addition to the detailed investigations on the PEI incorporated POPs, different PEI-incorporated solid adsorbents of UiO-66/PEI and NH₂-MIL-101/PEI have also been prepared, indicating the generality of this strategy. Compared to the parent materials and adsorbents prepared by the traditional method, the resultant adsorbents prepared by the MT method display much higher CO₂-selective adsorption ability. In addition, the adsorbent shows exceptional regenerability and recyclability with low energy cost as well as high stability against moisture, favorable to industrial application.

We chose to begin with POPs because they possess some of the highest reported porosity, yet they are very challenging for PEI incorporation due to the lack of anchored sites. A representative POP, porous polymer network (PPN-6) [23] (also called porous aromatic framework (PAF-1) [22]), was selected as the model material, given its high porosity and stability. PPN-6 with different PEI loadings, corresponding to 75, 100, 125, 140 and 165 wt% (denoted as PPN-6/PEI-75, PPN-6/PEI-100, PPN-6/PEI-125, PPN-6/PEI-140 and PPN-6/PEI-165), respectively, were prepared by the MT method. In comparison, PEI incorporated PPN-6 adsorbents were also prepared by the traditional method in the absence of CO₂ template. As shown in the scanning electron microscopy (SEM) images (Fig. S1), the morphology of PPN-6 after PEI loading remained intact and no particle stacking was observed, suggesting that PEI was indeed loaded into

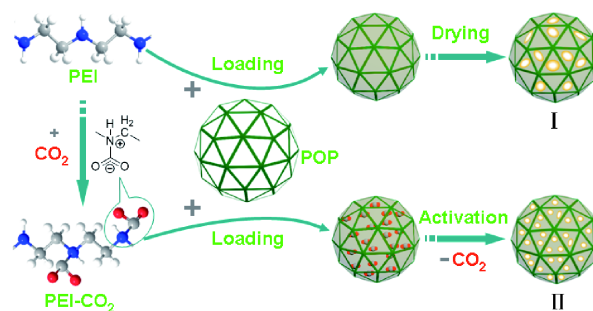


Figure 1 Schematic description for the fabrication of POP/PEI adsorbents by the traditional (I) and MT (II) methods, respectively.

PPN-6 pores without destroying its structure. The infrared (IR) spectra of activated PPN-6/PEI samples only showed characteristic peaks of PPN-6 and PEI (Fig. S2). The lack of CO₂ and NCOO peaks (Fig. S3) in the activated samples suggested that the CO₂ molecular template was completely removed, generating abundant pores for CO₂-selective adsorption. Thermogravimetric (TG) analysis of PPN-6/PEI samples showed sharp weight losses at about 493 and 773 K (Fig. S4), corresponding to the decomposition of PEI and PPN-6, respectively. N₂ sorption isotherms of PPN-6 at 77 K before and after PEI loading clearly indicated that porosity of PPN-6 dramatically decreased with increasing PEI loadings (Fig. S5), which was expected with the occupation of PEI inside PPN-6 pores. The pore volume and surface area of PPN-6/PEI samples are summarized in Table S1. The desorption hysteresis can be explained by the elastic deformations or the swelling effect of polymeric networks (Fig. S5) [32].

As shown in Fig. 1, CO₂ molecular template is critical for tuning the dispersion of PEI in PPN-6 framework, and creating effective pores for selective-CO₂ adsorption. Therefore, we first investigated the influence of CO₂ pressure on the resulting adsorbent's performance. The reaction to generate the adsorbent was performed in a reaction vessel with a gas regulator that can control and measure the system pressure. Fig. 2 shows that the CO₂ uptake of PPN-6/PEI adsorbents significantly increased with CO₂ pressure up to about 0.5 bar, but further increase of CO₂ pressure to 1.0 bar resulted in no more significant CO₂ uptake. We considered that CO₂ adsorption by PEI reached a saturation pressure at 0.5 bar, so all PEI-incorporated samples were prepared under a CO₂ pressure of 0.5 bar thereafter.

To determine the gas sorption property of activated PPN-6/PEI adsorbents, CO₂, N₂ and CH₄ single gas adsorption isotherms were tested at 323 K. As expected, all PPN-6/PEI adsorbents displayed drastically enhanced

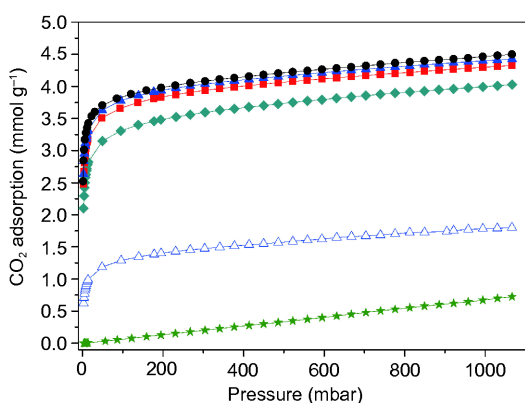


Figure 2 CO₂ adsorption isotherms of PPN-6 (★), PPN-6/PEI-125 prepared by the traditional method (hollow △), and PPN-6/PEI-125 prepared by the MT method (solid) with a CO₂ pressure of 0.05 bar (◆), 0.3 bar (■), 0.5 bar (▲) and 1.0 bar (●), respectively, at 323 K.

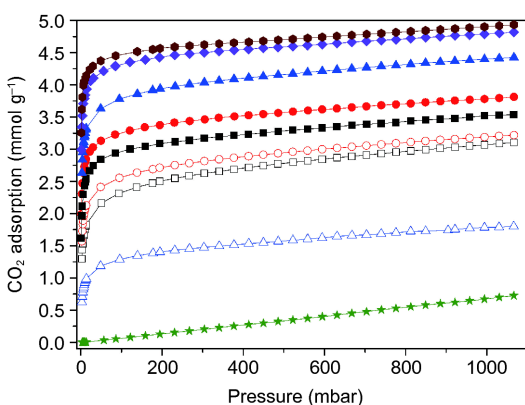


Figure 3 CO₂ adsorption isotherms of PPN-6 (★), PPN-6/PEI-75 (□/■), PPN-6/PEI-100 (○/●), PPN-6/PEI-125 (△/▲), PPN-6/PEI-140 (◇/◆), PPN-6/PEI-165 (●/◆) samples prepared by the traditional (hollow) and MT (solid) methods, respectively, at 323 K.

CO₂ adsorption capacity, compared to the pristine PPN-6, as shown in Fig. 3. On the contrary, the N₂ and CH₄ uptakes of PPN-6/PEI adsorbents decreased dramatically compared to the pristine PPN-6 (Figs S6 and S7), due to pore occupation and weak interaction of these gases with PEI as well as PPN-6. The different performance of PPN-6/PEI toward different gases is desirable for selective capture and separation of CO₂ from gas mixtures, such as CO₂/N₂ and CO₂/CH₄. Another trend we observed was enhanced performance of PPN-6/PEI samples generated from the MT strategy as compared to corresponding samples prepared by the traditional methods in the absence of CO₂ template. We systematically increased the PEI loading in PPN-6 from 75 to 165 wt% using the MT strategy, and increasing CO₂ uptake was observed (Fig. 3, solid markers). The enhancing effect reached a plateau at

140% to 165% PEI loading, and at 165% PEI loading a maximum CO₂ uptake of 4.52 mmol g⁻¹ was observed at 0.15 bar and 323 K. When PPN-6/PEI samples were prepared by the traditional method, i.e., mixing of PPN-6 and PEI in the absence of CO₂, a different trend was observed, in which the CO₂ uptake increased moderately from 75% to 100% PEI loading, then it decreased sharply upon increase of PEI loading to 125% (Fig. 3, hollow markers and Fig. S8). It is noteworthy that the highest CO₂ uptake capacity of the adsorbent prepared from the traditional method (PPN-6/PEI-100, red hollow circles, Fig. 3) is still lower than the lowest CO₂ uptake capacity of the adsorbent prepared by our MT method (PPN-6/PEI-75, black solid squares, Fig. 3). We consider the different CO₂ uptake profiles observed as a direct proof for the beneficial effect of CO₂ template. In the absence of CO₂, PEI forms random aggregates in the pores of PPN-6 and pore size distribution is uneven. While PEI first exhibits enhancing effect for CO₂ uptake with its amine groups from 75 to 100 wt% loading, with further increase in loading the pore-blocking effect [29] outweighs the CO₂ affinity to result in performance drop.

Another indication of the effective pores of MT method comes from study with different gases. The Ar adsorption isotherm of PPN-6/PEI-125 prepared by the MT method shows that a great number of small pores are created, as the calculated BET surface area from Ar adsorption isotherms is much larger than that from N₂ adsorption (Fig. S9). In contrast, the calculated BET surface area of the related sample prepared by the traditional method remained largely constant based on Ar and N₂ adsorptions (Fig. S10). This can be explained by the kinetic diameter difference of CO₂ (~0.33 nm), Ar (~0.34 nm), and N₂ (~0.36 nm). The pores generated by the MT method are ideal for CO₂ but can still accommodate the slightly larger Ar. The pores are however too small for the significantly larger N₂ molecules and adsorption becomes poor (Fig. S11). It should be noted that the template-generated pores can be further tuned to expel Ar, which is only slightly larger than CO₂. When PEI loading was further increased to 140 wt% or higher, adsorptions of Ar and N₂ became significantly close to each other (Figs S12 and S13). These results indicate that the MT method is very effective at creating pores that are perfect match for CO₂ but mismatch for N₂ and other larger molecules.

A summary of CO₂ adsorption capacities and selectivities of the reported high-performing solid porous adsorbents with PPN-6/PEI-165 from this work is presented in Table S2 (CO₂/N₂) and Table S3 (CO₂/N₂ and CO₂/CH₄). Our PPN-6/PEI-165 adsorbent prepared by

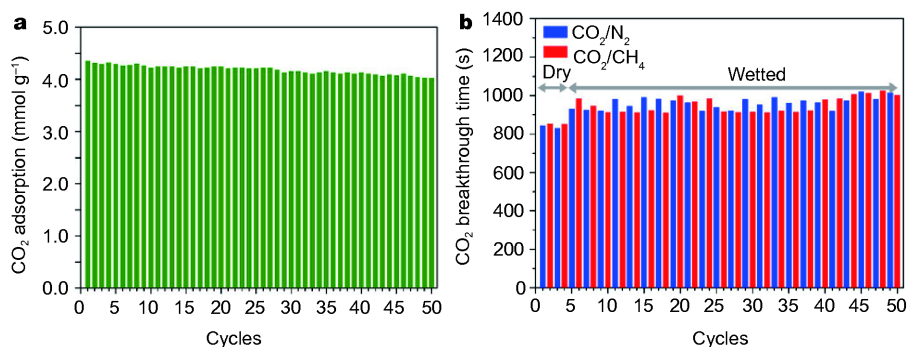


Figure 4 Cycles of adsorption and breakthrough curves. Cycles of CO_2 adsorption isotherms (a) and breakthrough curves with an equimolar CO_2/N_2 and CO_2/CH_4 mixtures (b) of PPN-6/PEI-140 at 323 K.

the MT method displays a superior CO_2 uptake capacity of 4.52 mmol g^{-1} at 0.15 bar and 323 K, a condition pertinent to flue gas, which is surpassed only by Mg-MOF-74 ($\sim 4.85 \text{ mmol g}^{-1}$, 0.15 bar), the best-performing MOF among all porous adsorbents in CO_2 capture (Table S2). It should be noted that the presence of coordinatively unsaturated Mg^{2+} of Mg-MOF-74 is responsible for its ultrahigh CO_2 adsorption capacity at 0.15 bar (low pressure), which would be greatly weakened at the presence of moisture, unfortunately, that is inevitable at practical application. In addition to an adsorbent's CO_2 uptake capacity, the high selectivity for CO_2 over N_2 and CH_4 are essential for practical applications like flue gas adsorption and natural gas purification. In this regard, our PPN-6/PEI-165 is far superior to literature, as we were unable to detect N_2 or CH_4 adsorption (Figs S6 and S7). While some CO_2 adsorbents exhibit high capacity but low to moderate selectivity (e.g., Mg-MOF-74 and UTSA-16), some exhibit moderate capacity but high selectivity (e.g., Qc-5-Cu-sql and SIFSIX-3-Zn), we consider our PPN-6/PEI-165 to be the top adsorbent to this date based on overall performance.

To examine the stability and regenerability of PPN-6/PEI adsorbents, cyclic CO_2 adsorption measurements were conducted. As an example, PPN-6/PEI-140 was degassed at 383 K under vacuum for 1 h between each cycle of measurement. The CO_2 capture capacity of PPN-6/PEI-140 decreased only slightly at 0.15 bar and 323 K after fifty cycles, as shown in Fig. 4a. Furthermore, the high separation performance of PPN-6/PEI-140 is further corroborated by the breakthrough experiment with equimolar CO_2/N_2 and CO_2/CH_4 mixtures at 323 K (Fig. 4b). Between every two cycles, PPN-6/PEI-140 is degassed at 383 K under Ar sweeping for 1 h. The distinct breakthrough data of the two components revealed the

strong interaction between CO_2 and PPN-6/PEI and corroborated the ultrahigh CO_2/N_2 (Fig. S14) and CO_2/CH_4 (Fig. S15) selectivities calculated from single component gas adsorption. N_2 and CH_4 were eluted rapidly through the column, whereas CO_2 started to elute only after a relatively constant time period. The breakthrough time for CO_2 was well retained after fifty cycles. It is worth mentioning that gas with 100% relative humidity was utilized after four cycles in the breakthrough experiments. The experiment indicates that PPN-6/PEI-140 displays remarkable stability against moisture, which is very important for CO_2 capture [33–36]. Although water molecules can be adsorbed into PEI, no noticeable change of CO_2 selectivity was observed after fifty cycles (Figs S16 and S17). We attributed the remarkable performance of PPN-6/PEI-140 to the high stability and hydrophobicity of the parent PPN-6.

After demonstrating the effectiveness of CO_2 -based MT strategy to incorporate PEI into POPs, we attempted to extend it to other classes of porous materials including MOFs. Since many MOFs only have moderate stability toward moisture [31], we deliberately chose the stable MOFs UiO-66 [37] and MIL-101- NH_2 [38]. Similar enhancement of CO_2 uptake capacity by PEI incorporation was observed in both systems, and our MT method consistently turned out to be superior to the traditional method of simple mixing without CO_2 (Figs S18 and S19). We believe that the strategy can be readily applicable to other types of additive and porous materials such as zeolite and silica. Such effort is ongoing in our lab. An optimization of the interplay of polyamine and porous solid materials can lead to an optimal polyamine-incorporated solid adsorbent for highly efficient CO_2 capture. It should be pointed out that, polyamine incorporated solid porous adsorbents are economically

very promising because they have much lower energy cost for regeneration than amine-based solutions. There has been some promising progress. As for the PPN-6/PEI adsorbents, we propose a temperature and vacuum swing adsorption process to achieve an exceptional working capacity. Upon heating to 343 K, almost all adsorbed CO₂ in PPN-6/PEI-140 (Fig. S20) and PPN-6/PEI-165 (Fig. S21) can be released under vacuum, thus yielding a remarkable working capacity of above 18.4 wt% (4.2 mmol g⁻¹) and 19.3 wt% (4.4 mmol g⁻¹), respectively.

In summary, we have utilized CO₂ molecules as the template to fabricate polyamine incorporated solid porous adsorbents. We demonstrate that the CO₂ template plays a crucial role in the formation of evenly distributed pores with controlled porosity that perfectly matches the kinetic diameter of CO₂ molecules. Our representative PPN-6/PEI adsorbents prepared by the MT strategy not only display exceptional adsorption capacity and ultra-high selectivity for CO₂, but also possess remarkable water stability and retain their efficiency even after 50 cycles of usage. This strategy opens an avenue to the design of highly efficient and selective adsorbents for the CO₂ capture and the separation of gas mixtures such as CO₂/N₂ and CO₂/CH₄ even under humid conditions.

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Author contributions Kong C and Chen L conceived the idea and supervised the project; Zhao D and Du H designed and performed the experiments and collected the data; Zhao D and Kong C analyzed the data and co-wrote the paper; Chen L, Jiang HL, Yan Y and Wang Z discussed the results and commented the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental section; characterization of PPN-6/PEI solid adsorbents; gas adsorption properties of PPN-6/PEI adsorbents; stability and regenerability of PPN-6/PEI adsorbents; gas adsorption properties of MOF/PEI solid adsorbents; regeneration of PPN-6/PEI adsorbents; Table S1; Table S2; Table S3. These materials are available in the online version of the paper.



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分子模板法策略制备多胺注入的多孔有机聚合物实现高效CO₂捕获与分离

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摘要 本论文用简单、通用的分子模板策略制备了具有极高CO₂吸附与分离效率的多胺注入多孔有机聚合物(POPs)。在该策略中, CO₂分子存在下, 多胺能均匀分散在母体多孔材料中。CO₂模板分子能够产生有效的均匀分布孔, 能允许CO₂分子进入但不允许其他较大分子如N₂和CH₄进入。在0.15 bar和323 K下, 制备的PPN-6/PEI-165展现出超高的4.52 mmol g⁻¹ CO₂吸附量且没有检测到N₂和CH₄吸附。此外, 该材料对水汽稳定且温和条件(343K下真空)下易再生。据我们所知, 该结果在迄今为止所报道的固体多孔吸附剂中有最好的CO₂选择性捕获性能。