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# Polyamines with reactive CO<sub>2</sub> diffusion for carbon capture: the obvious and the unexpected

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Polyamines have emerged as a leading materials platform for sorbents in direct air capture (DAC) of CO<sub>2</sub> and membranes for post-combustion capture (PCC) due to their reactions with CO<sub>2</sub>. Such reactions compete with hydrogen bonding among amine groups, are sensitive to temperature and water content, and can self-limit the further diffusion and sorption of CO<sub>2</sub> in polyamines. These unique characteristics give rise to interesting, often conflicting phenomena in DAC sorbents and PCC membranes, which have not been resolved at the molecular level. Herein, we highlight the imbalanced effects of substrates on amine efficiency for CO<sub>2</sub> sorption, the complex interplay of temperature and time on pseudo-equilibrium CO<sub>2</sub> sorption, and the intricate effects of water vapor on CO<sub>2</sub> sorption and desorption in DAC. For PCC membranes, both facilitated and hindered CO<sub>2</sub> transport are critically reviewed with an integrated experimental and simulation approach. We elucidate the role of CO<sub>2</sub>-reactive diffusion in both sorbent and membrane applications, providing cohesive guidance for designing polyamine-based systems to enhance CO<sub>2</sub> capture performance.

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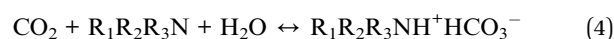
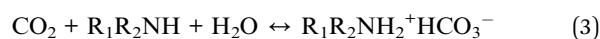
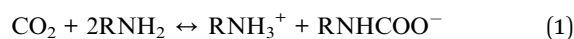
## 1 Introduction

The use of abundant carbon-based energy sources (such as coal, natural gas, oil, and traditional biomass) has dramatically improved living conditions for our society, but it inevitably increases atmospheric CO<sub>2</sub> concentrations, influencing the global climate. These carbon-based energy sources are inexpensive, account for 80–90% of global energy consumption, and are expected to continue playing a significant role in the energy landscape due to their well-established infrastructure and reliability. Therefore, mitigating CO<sub>2</sub> emissions into the atmosphere has emerged as a grand challenge for our society.

Various approaches to carbon capture have been explored, and two have attracted significant attention for their potential impacts.<sup>1</sup> First, CO<sub>2</sub> can be captured from the air (*i.e.*, direct air capture, or DAC), thereby directly reducing atmospheric CO<sub>2</sub> concentration.<sup>2–4</sup> Such technologies can be used at any location and may be carbon-negative. To this end, solid sorbents are widely used for DAC, as they offer low energy input, low operating costs, and good scalability. Second, CO<sub>2</sub> can be captured from flue gas at various point sources after combustion of carbon sources (*i.e.*, post-combustion carbon capture, or PCC).<sup>5–7</sup> For instance, flue gas streams from coal-fired power plants contain 10–13% CO<sub>2</sub>, 82% N<sub>2</sub>, and other components such as O<sub>2</sub> and H<sub>2</sub>O. As an add-on approach, it does not disrupt existing industrial or power plants

and may significantly reduce CO<sub>2</sub> emissions, as these point sources account for ~40% of CO<sub>2</sub> emissions. To this end, membrane technology has emerged as one of the leading technologies due to its high energy efficiency, small footprint, and avoidance of chemical use and emission.<sup>5,8–10</sup>

Interestingly, polyamines have emerged as a leading materials platform for both DAC sorbents<sup>11–14</sup> and PCC membranes.<sup>7,8,15,16</sup> Amine groups are key to achieving high CO<sub>2</sub> sorption capacity and selectivity over the major components of air (N<sub>2</sub> and O<sub>2</sub>).<sup>17,18</sup> Eqn (1) and (2) elucidate the reaction mechanisms for the reaction between primary and secondary amines and CO<sub>2</sub>. Under dry conditions, these amines react with CO<sub>2</sub> to form ammonium carbamate.<sup>19,20</sup> The maximum molar ratio of CO<sub>2</sub>/N can reach 0.5 and increase to 1.0 in the presence of moisture (forming bicarbonates), as shown in eqn (3). Eqn (4) also shows that tertiary amines can react with CO<sub>2</sub> at a 1:1 molar ratio in the presence of water vapor:



Separated review articles have been published on polyamines for DAC sorbents<sup>12,21,22</sup> and PCC membranes.<sup>23</sup> The effect of amine type and its structure (*e.g.*, tetraethylenepentamine (TEPA), polyethylenimine (PEI), and diethylenetriamine (DETA)) on CO<sub>2</sub> sorption performance has

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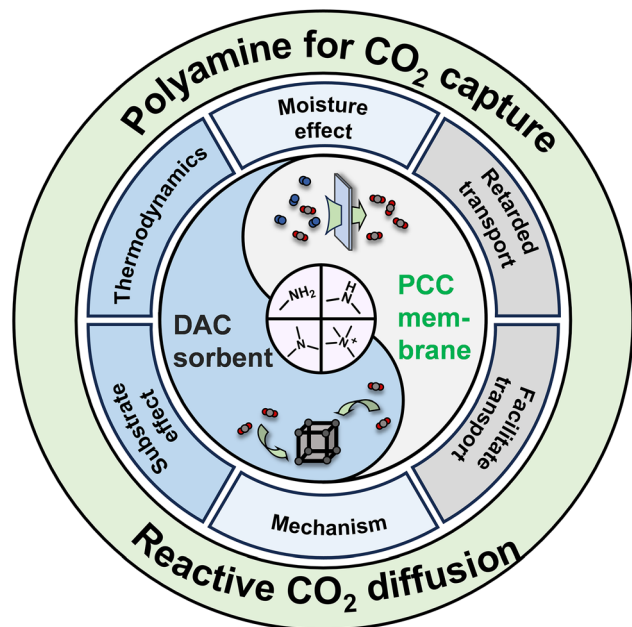


Fig. 1 Overview of polyamine-based sorbents for direct air capture (DAC) and membranes for post-combustion carbon capture (PCC: CO<sub>2</sub>/N<sub>2</sub> separation).

also been reviewed in the literature.<sup>21,22</sup> In most cases, the affinity of amines for CO<sub>2</sub> was exploited to enhance CO<sub>2</sub> sorption and permeation, resulting in superior CO<sub>2</sub> separation performance. However, unusual phenomena have been reported in the literature: CO<sub>2</sub> sorption in polyamines increased with increasing temperature;<sup>13,24,25</sup> their affinity hindered CO<sub>2</sub> diffusion and reduced CO<sub>2</sub> permeability, resulting in unexpectedly high N<sub>2</sub>/CO<sub>2</sub> and H<sub>2</sub>/CO<sub>2</sub> selectivity.<sup>26,27</sup> These apparent contradictions in these two processes have not been resolved at the mechanistic level.

This paper highlights the unusual behaviors of polyamines for DAC sorbent and PCC membrane applications, underlying reactive CO<sub>2</sub> diffusion and its impact on CO<sub>2</sub> capture performance, and provides a cohesive framework for CO<sub>2</sub> transport in both sorbents and membranes (Fig. 1). First, we critically review polyamines on a broad spectrum of substrates for DAC and underline how substrates affect reactive CO<sub>2</sub> diffusion and sorption in these sorbents. The effect of water vapor, temperature, and time on CO<sub>2</sub> capture capability is revealed. Second, polyamine-based membranes for PCC are discussed, and the facilitated and hindered transport mechanisms are elucidated and contrasted through modeling and experiments. Finally, the contradictory results are analyzed to emphasize CO<sub>2</sub> reactive diffusion in polyamines, shedding light on the design of next-generation sorbents and membranes with enhanced carbon capture performance.

## 2 Polyamine-based sorbents for direct air capture

The key to DAC is high-performance sorbents with high CO<sub>2</sub> sorption capacity, long-term durability, and low costs.<sup>12,28,29</sup>

Polyamines, such as polyethylenimine (PEI), have been widely used due to their strong interactions with CO<sub>2</sub>, and they are often incorporated into porous supports to enhance the accessibility of amines to dilute CO<sub>2</sub> in air and to reduce pressure drops through the sorbents.<sup>22,30–32</sup>

The morphology of the support materials used to incorporate or append polyamines for DAC applications plays a significant role in determining carbon capture performance.<sup>11,13</sup> Support materials are selected based on key properties, including high surface area, appropriate pore size and pore structure, and good thermal and mechanical stability, as well as their interactions with polyamines. All these factors determine the distribution of polyamines (such as their layer thickness on the inner wall) and the structural characteristics of the resulting sorbents (such as pore size and porosity), thereby impacting CO<sub>2</sub> diffusion to amine sites and CO<sub>2</sub> sorption kinetics, including effects of diffusion resistance.<sup>19,33</sup> Notably, various approaches have been adopted to reduce diffusion limitations in these sorbents and enhance CO<sub>2</sub> accessibility to active amine sites, such as incorporating surfactants<sup>34</sup> and low viscosity diluents like polyethylene glycol (PEG)<sup>35</sup> and ionic liquids.<sup>36</sup> Additionally, supports with bimodal porous structures have been shown to facilitate rapid CO<sub>2</sub> diffusion while maintaining high amine loading.<sup>37</sup>

A variety of porous materials suitable for amine impregnation have been explored for DAC applications, including silica, zeolites, polymeric porous substrates, and newly emerging microporous materials such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs). Table 1 lists representative polyamine sorbents, based on various substrates and amine structures (primary, secondary, and tertiary amines), along with their DAC properties. In general, it is difficult to directly compare the capture performance of the sorbents due to the complex interplay between the supports' pore morphologies and interactions with polyamines, and there is no quantitative analysis or prediction of the effect of the porous support on DAC properties, in addition to CO<sub>2</sub> binding strength and diffusion resistance. Therefore, instead of conducting a comprehensive review, we highlight representative sorbents with high CO<sub>2</sub> sorption capacities, particularly their unusual behaviors, including the effects of temperature and water vapor on DAC performance. Detailed mechanisms are also provided in Section 4. Discussion and conclusion.

### 2.1 Sorbents based on inorganic porous substrates

Porous silica supports, such as SBA-15, have been widely used to incorporate PEI for DAC applications. SBA-15 was further modified with hydrophobic vinyltrimethoxysilane (VTMS), as shown in Fig. 2a.<sup>48</sup> The modified support was then acid-etched to remove boron and hydrolyze the remaining methoxy groups, followed by impregnation with 20 wt% PEI. The generated hydroxyl groups had a good affinity towards PEI. Additionally, a hydrophobic agent, HMDS (hexamethyldisilazane), was also used to modify SBA-15, enhancing the surface morphology.

Fig. 2b illustrates how surface hydrophobicity affects PEI distribution on the support and amine efficiency of the



Table 1 Physical properties and DAC performance of representative sorbents based on polyamines. Gas mixtures contain 400 ppm CO<sub>2</sub> in air

Substrates		Polyamines							
Types	Names	Types <sup>a</sup>	Content (%)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Temp. (°C)	RH (%)	CO <sub>2</sub> sorption (mmol g <sup>-1</sup> )	Ref.	
Silica	Silica	PEI	47	—	25	0	2.4	38	
	HS	TEPA	70	—	30	0	5.2	39	
	H-SiO <sub>2</sub>	PEI	~70	—	30	19	3.4	40	
	γ-Alumina	PEI	48.1	—	25	0	1.7	41	
	γ-Al <sub>2</sub> O <sub>3</sub>	TEPA	20	—	-20	0	0.81	42	
	SBA-15	PEI	40	—	25	70	2		
			TEPA	—	500–800	25	0	1.5–2.5	43
		LPII	50	80	25	0	1.2	44	
		PPI	40	—	35	0	1.4	45	
		PEI	39.9	—	25	0	1.1	41	
		Ph-3-ED	60	—	35	0	1.9	46	
		Ph-3-PD	35	30	2.9				
			AEAPTMS	—	45	25	0	1.7	47
		V-B-SBA-15	PEI	20	600–900	25	40	2.5–3	48
		Ti-SBA-15	PEI	31.8	209	25	0	0.64	49
	Zr-SBA-15	PEI	34.7	230	25	0	0.85	49	
	Mg/Al-MMO	PEI	67	—	25	0	2.3	50	
		TEPA	67	—	25	0	3.0	51	
	Titania-silsesquioxane aerogel	APTES	—	—	30	0	1.6	52	
	Porous polymers	Solupor	PEI	48	—	25	0	0.53	13
PEI			48	—	25	30	1.3		
PIM-1 (powder)		PEI	21	220	35	—	0.23	53	
PIM-1 (fibers)		PEI	25	30	35	—	0.25		
PF-15		TAEA	21	8	25	50	1.0	54	
NFC		AEAPDMS	50	7.1	25	40	1.4	55 and 56	
Ion exchange resin		Quaternary ammonium	—	800	23	0.5	0.98	57	
MOFs	Mg <sub>2</sub> (dobpdc)	MMEN	12	70	25	0	2.1	58	
		EN	—	1253	25	0	2.8	59	
	MIL-101(Cr)	TREN	45	—	25	0	2.8	60	
		PEI	45	—	25	0	1.1		
	MIL101(Cr)/CA	TEPA	10	1247	-20	70	0.46	61	
		PEI	10	1200	-20	70	0.66		
COFs	MOF-808	PA	—	—	25	50	0.7	62	
	COF-999	PEI	—	—	25	75	2.1	63	
	COF-609	TAPA	—	—	25	50	0.39	64	
	COF-709	SH-bPEI	—	—	25	75	1.2	65	
	PE-MCM-41	Triamine	—	367	25	0	0.98	66	
Hybrid materials	SIPs	PEI	49	—	25	0	3.7	67	
		NPEI	49	—	25	0	2.8	67	
	PAN/OPZN	NPEI	—	—	25	0	1.7	68	
Li-SX zeolite	—	—	>600	25	0	1.3	69		

<sup>a</sup> Ph-3-ED: phenyl-3-ethylene diamine; Ph-3-PD: phenyl-3-propylenediamine; PPI: branched poly(propylenimine); AEAPTMS: *N*-(3-(trimethoxysilyl)propyl)ethane-1,2-diamine; APTES: 3-aminopropyltriethoxysilane; NFC: nanofibrillated cellulose; TREN: tris(2-aminoethyl)amine; TEPA: tetraethylenepentamine; TAPA: tris(3-aminopropyl)amine; TAEA: tris(2-aminoethyl)amine; SH-bPEI: sulfhydryl-grafted PEI; AEAPDMS: *N*-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane; PIM-1: polymer of intrinsic microporosity; PF-15: fibers of amidoxime functionalized PIM-1.

sorbents. On untreated substrates, PEI showed strong affinity for the surface due to its strong hydrogen bonding with surface silanol groups; HMDS treatment reduced amine-silanol interactions, and the high PEI loading resulted in plug-like domains. By contrast, for VTMS-treated support (V-SBA-15), the vinyl groups exerted a caging effect, limiting PEI mobility and its interactions with silanol groups, thereby improving amine accessibility.

Fig. 2c shows water isotherms for the substrates alone to compare their hydrophobicity and better understand the distribution and interactions of PEI after impregnation. H-SBA-15 and V-SBA-15 exhibited low water uptake due to their hydrophobic surface, whereas the pristine SBA-15 and V-B-SBA-15 showed higher water uptake. Particularly, V-B-SBA-15 had silanol nests that promoted water condensation. When incorporating 20 wt% PEI, SBA-15, H-SBA-15, and V-SBA-15 showed



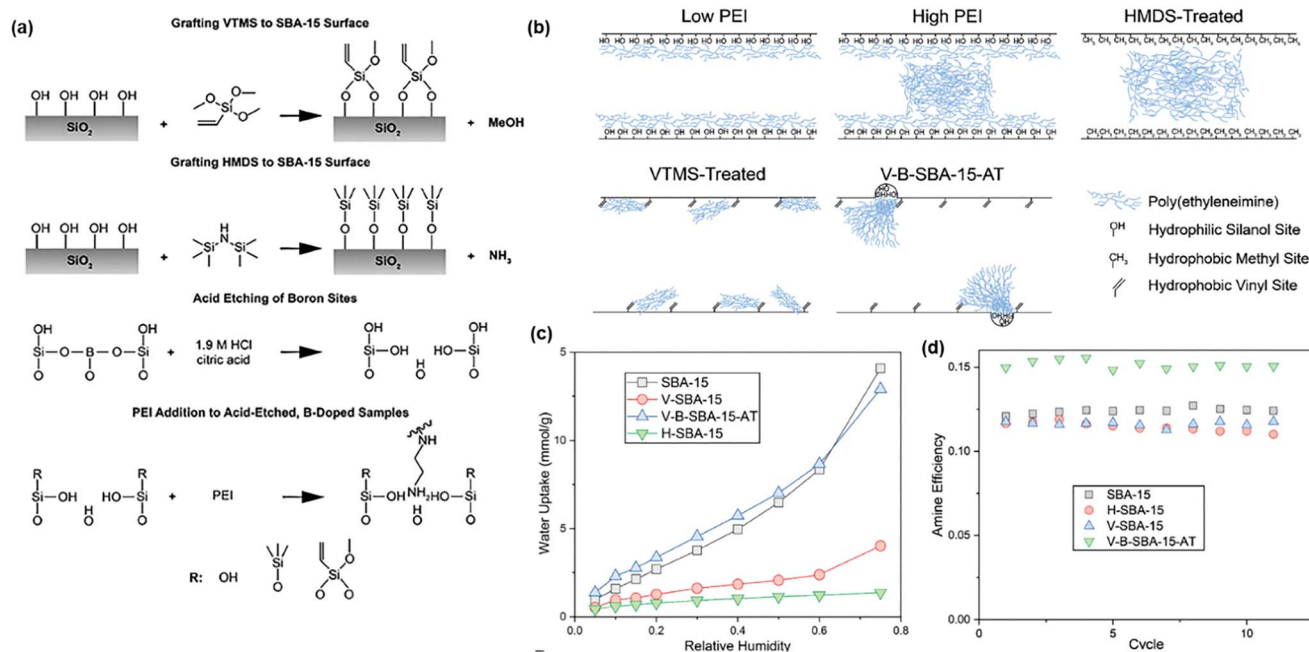


Fig. 2 PEI incorporated into SBA-15 modified using VTMS and HMDS. (a) Reaction scheme showing surface functionalization, acid etching of boron sites, and subsequent PEI incorporation. (b) Schematic illustration of porous supports with different PEI loadings and surface treatments. (c) Water sorption isotherms at 30 °C. (d) Amine efficiency at 40% RH and 400 ppm CO<sub>2</sub>. Copyright 2024 Wiley.<sup>48</sup>

similar amine efficiency with 400 ppm CO<sub>2</sub> and 40% RH (Fig. 2d). By contrast, the V-B-SBA-15 showed 25% higher amine efficiency and good stability over 11 cycles. Additionally, H-SBA-15 showed degraded performance after 10 cycles due to its high hydrophobicity and the loss of PEI during thermal desorption.

## 2.2 Sorbents based on polymeric porous supports

Polymeric substrates have been used to prepare DAC sorbents due to their excellent processability, good handleability, and low costs, such as PIM-1 with microporosity and high surface area (>700 m<sup>2</sup> g<sup>-1</sup>).<sup>54,70</sup> Fig. 3a displays cellulose acetate hollow fibers containing MIL-101(Cr) (MIL-101(Cr)/CA), which were first spun *via* “dry-jet wet quench” process and then functionalized with polyamines such as tetraethylenepentamine (TEPA) and PEI *via* the wet impregnation method.<sup>61</sup> The fibers were porous, resulting in low pressure drops. Fig. 3b displays that the obtained sorbent exhibited a working capacity of 0.9 mmol g<sup>-1</sup> during a temperature swing operation between -20 and 60 °C. The samples did not degrade throughout the 10 sorption/desorption cycles.

A commercial support, Solupor, made of high-density polyethylene (HDPE), was impregnated with branched PEI by wet impregnation (Fig. 3c).<sup>13,71</sup> Fig. 3d displays the effect of temperature and testing time on the sorption performance of a sorbent containing 48% PEI. Interestingly, increasing the temperature from 25 to 50 °C increased CO<sub>2</sub> pseudo-equilibrium sorption capacity by 36% from 0.53 to 0.72 mmol g<sup>-1</sup> due to greater CO<sub>2</sub> diffusivity, which can be attributed to non-equilibrium CO<sub>2</sub> sorption caused by its self-restricted diffusion and pore blocking by PEI. As CO<sub>2</sub> reacts with PEI, it

cross-links the PEI surface and lowers CO<sub>2</sub> diffusion (Fig. 3e). Increasing the temperature from 25 to 50 °C reduced the CO<sub>2</sub> content on the PEI surface and accelerated CO<sub>2</sub> diffusion into the films, enhancing CO<sub>2</sub> sorption. On the other hand, further increasing the temperature to 65 °C reduced CO<sub>2</sub> sorption capacity due to the dominant thermodynamic effect. The effect of diffusion-limited sorption has also been reported elsewhere.<sup>24,25,72</sup> For instance, increasing the temperature from -20 to 25 °C increased the sorption capacity by 70% from 1.26 to 2.14 mmol g<sup>-1</sup> in 50 mass% TEPA-modified MIL-101(Cr).<sup>73</sup>

## 2.3 Sorbents based on MOFs

MOFs have emerged as a highly attractive platform for CO<sub>2</sub> capture due to their tunable pore structures, high surface areas, and thus high CO<sub>2</sub> sorption capacity.<sup>74,75</sup> Many MOFs containing open metal sites, such as MOF-74,<sup>76</sup> exhibit remarkable CO<sub>2</sub> uptake once guest molecules are removed from the framework. However, these materials often exhibit structural instability in the presence of water vapor, thereby reducing CO<sub>2</sub> sorption. Amine functionalization has been employed not only to enhance structural robustness but also to substantially improve CO<sub>2</sub> adsorption capacity through a moisture-assisted mechanism.

Fig. 4 compares the DAC performance of sorbents based on MIL-101(Cr) and a conventional  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> impregnated with TEPA.<sup>11</sup> Interestingly, MIL-101(Cr)-TEPA(30) showed weak chemisorption dominance (*i.e.*, CO<sub>2</sub> desorption occurred below 25 °C), while Al<sub>2</sub>O<sub>3</sub>-TEPA(20) showed strong chemisorption dominance (*i.e.*, CO<sub>2</sub> desorption occurred above 25 °C). Fig. 4a displays that MIL-101(Cr)-TEPA(30) mostly formed carbamic



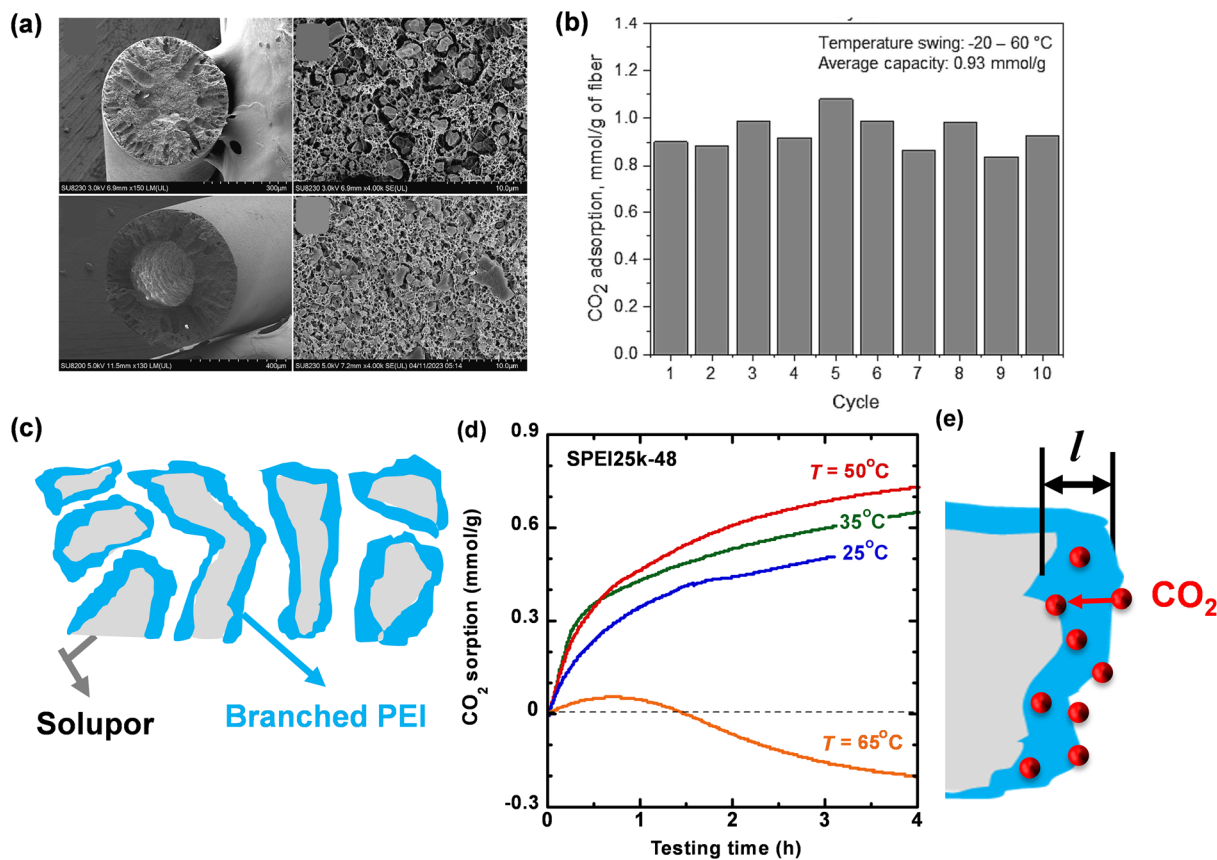


Fig. 3 Sorbents based on polymeric porous supports. (a) SEM images of dense and hollow MIL-101(Cr)/CA fibers; (b) PEI10 MIL-101(Cr)/CA fibers for TPD cycles under dry 400 ppm CO<sub>2</sub>.<sup>61</sup> Copyright 2023 Elsevier. (c) PEI-incorporated Solupor (SPEI). (d) Effect of testing time and temperature on CO<sub>2</sub> sorption in the SPEI containing 48 mass% PEI (25k).<sup>13</sup> (e) Schematic of CO<sub>2</sub>-reactive diffusion in PEI films. Copyright 2024 American Chemical Society.

acid with weak binding energy due to the strong amine-support interaction, along with a small amount of ammonium carbamate ion pairs, while Al<sub>2</sub>O<sub>3</sub>-TEPA(20) only formed ammonium carbamate with strong binding energy (Fig. 4b), which can be ascribed to the weak amine-support interactions and amine clustering. Nevertheless, there are no quantitative models in the literature for how support properties affect CO<sub>2</sub> binding strength under DAC conditions.<sup>11,42,77</sup>

Fig. 4c and d compares the effect of temperature and humidity on the sorption performance of MIL-101(Cr)-TEPA(30) and Al<sub>2</sub>O<sub>3</sub>-TEPA(20). Decreasing temperature increased the sorption capacity of MIL-101(Cr)-TEPA but decreased the capacity of Al<sub>2</sub>O<sub>3</sub>-TEPA, suggesting that the sorption in MIL-101(Cr)-TEPA was dominated by thermodynamic equilibrium, and the sorption in Al<sub>2</sub>O<sub>3</sub>-TEPA was limited by CO<sub>2</sub> diffusion into the bulk TEPA.

Fig. 5 demonstrates superior DAC performance by pip2-Mg<sub>2</sub>(dobpdc) (pip2 = 1-(2-aminoethyl)piperidine).<sup>78</sup> Mg<sub>2</sub>(dobpdc) containing diamines exhibited a maximum CO<sub>2</sub> uptake at a molar ratio of 1 for CO<sub>2</sub>:diamine; by contrast, pip2-Mg(dobpdc) exhibited a CO<sub>2</sub>:diamine ratio of 1.5 due to the cooperative chemisorption and physisorption steps.

Fig. 5b shows pure CO<sub>2</sub> adsorption isotherms with a two-step adsorption profile at 25, 40, and 50 °C, implying cooperative

chemisorption and physisorption. At 25 and 40 °C, the first step of adsorption occurred at 50 and 150 mbar, yielding uptakes of 1.3 and 1.5 mmol g<sup>-1</sup>, respectively. The second step showed a doubling of sorption capacity compared to the first step, yielding total capacities of 4.9 and 4.6 mmol g<sup>-1</sup>, respectively. A similar increase in CO<sub>2</sub> uptake was observed at 50 °C; however, the uptake value was lower than that at lower temperatures. Fig. 5c shows the stability of pip2-Mg<sub>2</sub>(dobpdc) over 500 cycles of adsorption-desorption, where the adsorption was conducted for 15 min with a dry CO<sub>2</sub>/N<sub>2</sub> (60/40) mixture at 30 °C, and the desorption took place for 1 min under dry CO<sub>2</sub> at 80 °C. The sorbent demonstrated a consistent sorption capacity of 3.8 mmol g<sup>-1</sup>.

#### 2.4 Sorbents based on COFs

COFs have also been explored for CO<sub>2</sub> capture due to their pore structure and tunability, combining the structural advantages of MOFs with enhanced chemical and thermal stability enabled by covalent bonding.<sup>79,80</sup> Fig. 6a displays the synthesis of an amine-functionalized COF (COF-999), achieving high CO<sub>2</sub> sorption capacity, fast kinetics, and low regeneration energy.<sup>63</sup> Crystalline olefin-linked COF precursor (COF-999-N<sub>3</sub>) was first synthesized, and then the azide group was converted to an amine group *via* the Staudinger reaction. The obtained COF-



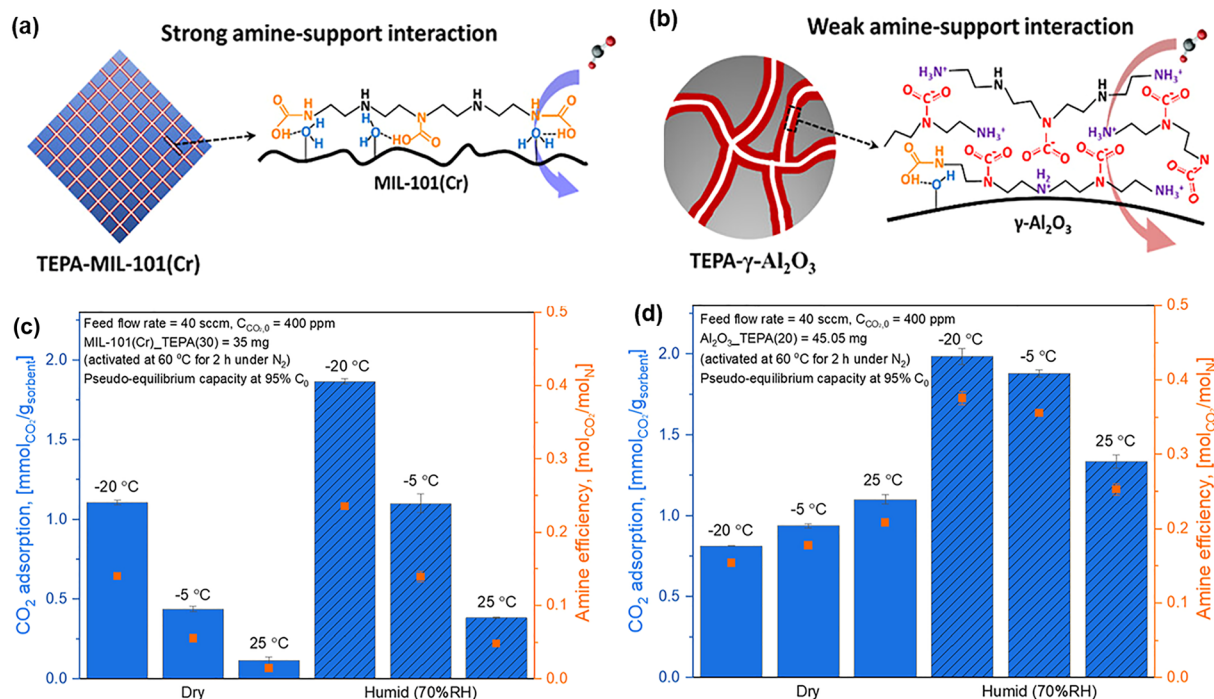


Fig. 4 Comparison of TEPA-containing sorbents based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MIL-101(Cr). Reaction mechanism of CO<sub>2</sub> with (a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-TEPA (with weak amine-support interaction) and (b) MIL-101(Cr)-TEPA (with strong amine-support interaction). Pseudo-equilibrium adsorption and amine efficiency of (c) MIL-101(Cr)-TEPA(30) and (d)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-TEPA(20) at various temperatures under dry and humid (70% RH) conditions. Copyright 2023 American Chemical Society.<sup>11</sup>

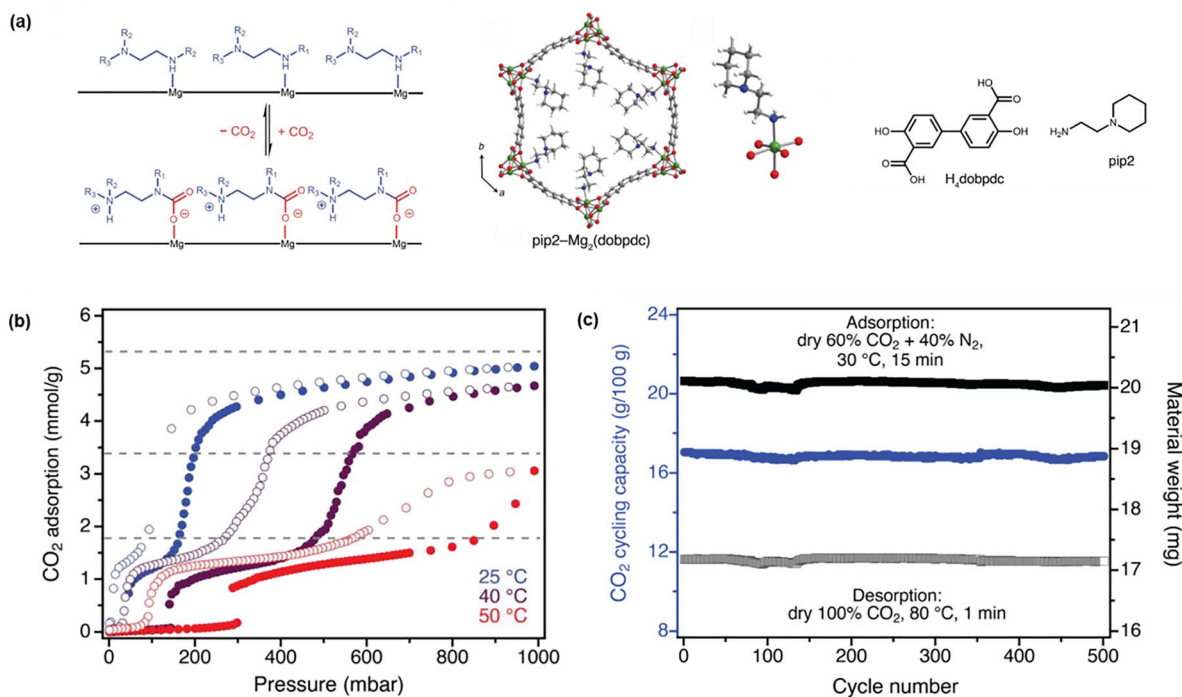


Fig. 5 Superior DAC performance by pip2-Mg<sub>2</sub>(dobpdc). (a) (Left) CO<sub>2</sub> adsorption mechanism, (mid) simulated structure, and (right) H<sub>4</sub>dobpdc and pip2 structures; (b) CO<sub>2</sub> sorption isotherms at 25, 40, and 50 °C. (c) Temperature-swing adsorption-desorption cycle at atmospheric pressure. Copyright (2024) American Chemical Society.<sup>78</sup>



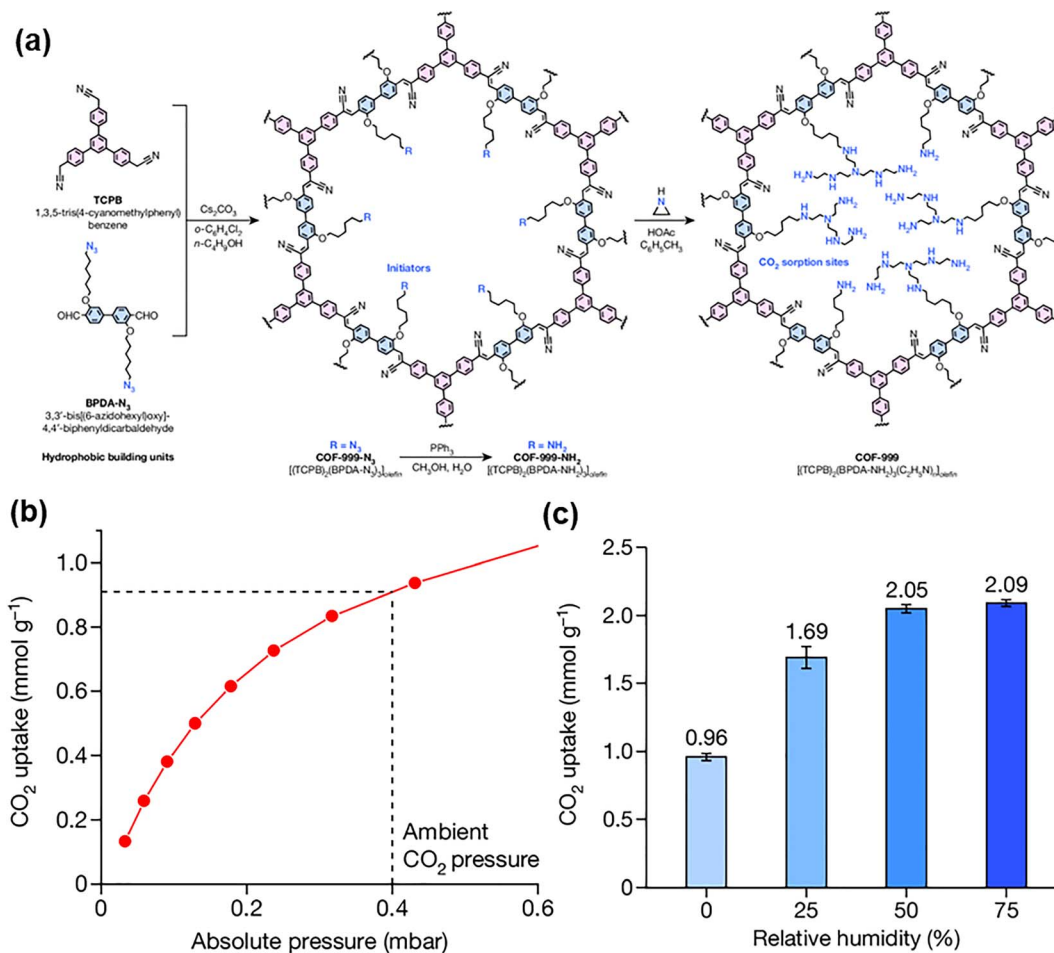


Fig. 6 DAC sorbent based on COF-999. (a) Schematic diagram of the material synthesis; (b) CO<sub>2</sub> sorption isotherm with 400 ppm CO<sub>2</sub>; (c) CO<sub>2</sub> sorption uptake with RH values of 0%, 25%, 50% and 75% at 400 ppm CO<sub>2</sub>. Copyright 2024 Springer Nature.<sup>65</sup>

999-NH<sub>2</sub> was further treated with aziridine to produce polyamines in the pores, ultimately yielding COF-999. Fig. 6b shows that COF-999 exhibited CO<sub>2</sub> uptake of 0.91 mmol g<sup>-1</sup> with 400 ppm CO<sub>2</sub>. The CO<sub>2</sub> sorption capacity increased with increasing RHs (Fig. 6c). The sorbent achieved a CO<sub>2</sub> sorption capacity of 2.09 mmol g<sup>-1</sup> under 75% RH at 25 °C.

## 2.5 Sorbents based on hybrid liquid-nanoparticles

Hybrid materials have been developed for DAC sorbents using waterless CO<sub>2</sub> solvents, such as ionic liquids (ILs), CO<sub>2</sub>-binding organic ligands, and liquid-like nanoparticle organic hybrid materials (NOHMs).<sup>67</sup> Fig. 7a shows that PEI-functionalized NOHMs (NOHM-I-PEI) can be encapsulated in a polymer shell by UV curing and formed into thin films. The solvent impregnated polymers (SIP) particles were synthesized by grinding these films, and the CO<sub>2</sub> capture mechanism of the NOHM-I-PEI-incorporated SIPs (NPEI-SIPs) is shown in Fig. 7a.

Fig. 7b compares the CO<sub>2</sub> capture kinetics of the hybrid material (NPEI-SIPs) containing 49% NOHM-I-PEI with that of the pristine NOHM-I-PEI. The NPEI-SIPs exhibited CO<sub>2</sub> sorption capacity of 5.55 mmol CO<sub>2</sub> per g NOHM-I-PEI, much higher than that for NOHM-I-PEI (0.09 mmol CO<sub>2</sub> per g). The base liquid exhibited high viscosity, resulting in very slow sorption kinetics; by

contrast, the polymer matrix in the SIPs showed high CO<sub>2</sub> diffusivity, leading to fast kinetics. Fig. 7c shows that introducing water vapor (80% RH) increased CO<sub>2</sub> sorption capacity.

## 2.6 Moisture-driven DAC based on polyamine derivatives

Most polyamines are thermally regenerated after CO<sub>2</sub> sorption, leading to high energy consumption, and they are susceptible to oxidative degradation at high temperatures.<sup>81,82</sup> Recently, a novel approach of moisture-swing-based DAC has been developed with the sorbents regenerated at high RH and ambient temperature,<sup>83–86</sup> as shown in Fig. 8. These processes are often based on polyamine derivatives, such as quaternary ammonium-containing polymers. Specifically, CO<sub>2</sub> is captured under dry conditions and released upon exposure to higher RH levels, as shown in the equations in Fig. 8a. The hydroxide-functionalized quaternary ammonium groups react with CO<sub>2</sub> under dry conditions to form bicarbonate (eqn (i)). When exposed to high RH levels, water drives the reverse reaction, thereby converting bicarbonate to carbonate and releasing CO<sub>2</sub> (eqn (ii) and (iii)), enabling sorbent regeneration.

Fig. 8b displays the effect of RHs on CO<sub>2</sub> sorption in an example moisture-swing sorbent (fGO), prepared by functionalizing graphene oxide (GO) with glycidyltrimethylammonium



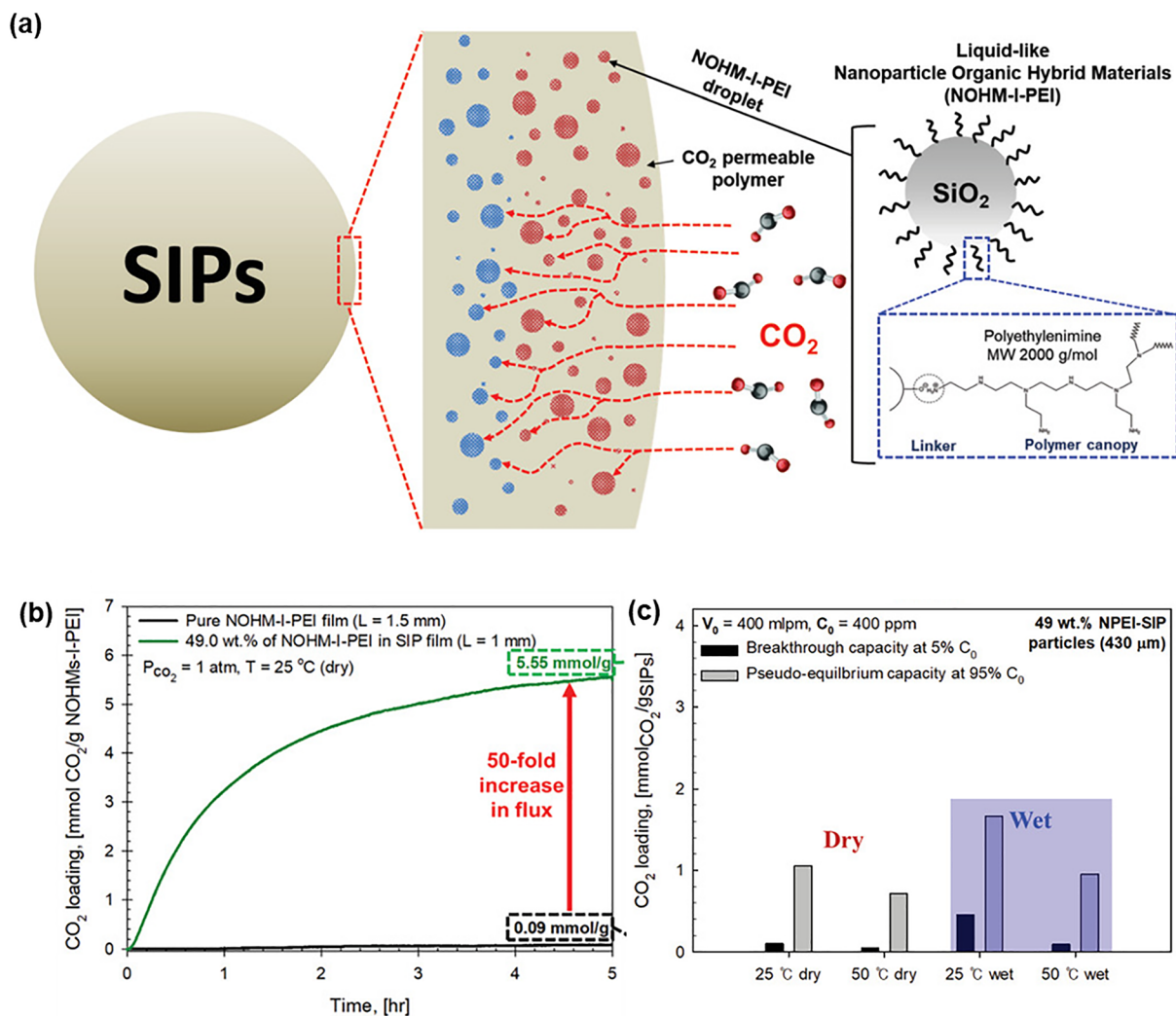


Fig. 7 CO<sub>2</sub> capture in NPEI-SIPs containing 49 mass% NOHM-1-PEI. (a) Structure and sorption mechanism. (b) Comparison with pristine NOHM-I-PEI. (c) Effect of humidity on CO<sub>2</sub> capture for 400 ppm CO<sub>2</sub>.<sup>67</sup> Copyright 2021 Wiley.

chloride.<sup>83</sup> The fGO displayed the highest CO<sub>2</sub> uptake at 20% RH, followed by a decline in capacity as RH increased to 100%, giving a moisture-swing working capacity of 2.3 mmol g<sup>-1</sup>.

Moreover, the fGO sorbent exhibited excellent cycling stability, retaining performance for over 40 adsorption-desorption cycles, with only a 7.5% loss after 50 cycles.

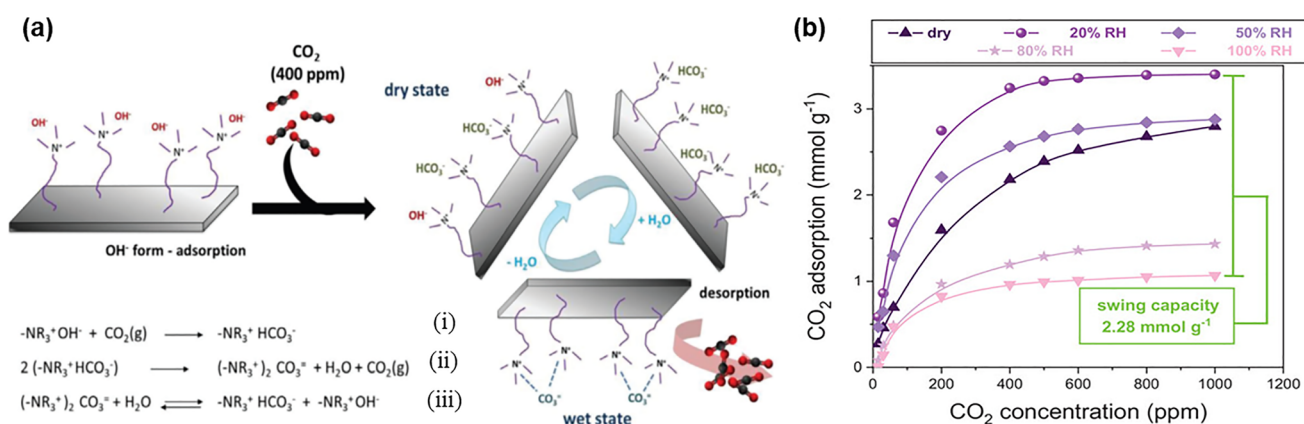


Fig. 8 Moisture-swing sorbents based on quaternary ammonium-functionalized graphene oxide (fGO). (a) Sorption and desorption mechanism, including three reactions, and (b) effect of humidity on CO<sub>2</sub> sorption.<sup>83</sup> Copyright 2024 Wiley.



### 3 Polyamines for membrane CO<sub>2</sub> separation

#### 3.1 Modeling of facilitated CO<sub>2</sub> transport in polyamines

Gas transport in non-facilitated polymers is usually described using the solution-diffusion model, and gas permeability

( $P_A$ , Barrer,  $10^{-10} \frac{\text{cm}^3(\text{STP})\text{cm}^{-1}}{\text{cm}^2 \text{s}^{-1} \text{cm Hg}}$ ) is expressed as:

$$P_A = S_A \times D_A \quad (5)$$

where  $S_A$  is the gas solubility, and  $D_A$  is the gas diffusivity. Gas permeance of a membrane ( $Q_A$ , GPU,  $10^{-6} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \text{s}^{-1} \text{cm Hg}}$ ) with a thickness ( $l$ , cm) is given by:

$$Q_A = P_A/l \quad (6)$$

Polyamines have been widely reported to facilitate CO<sub>2</sub> transport in the presence of water through reversible reactions with amines.<sup>87,88</sup> For example, in eqn (3), reagents and products can be simplified using the following abbreviations: A = CO<sub>2</sub>, B = R-NH<sub>2</sub>, C = HCO<sub>3</sub><sup>-</sup>, and D = R-NH<sub>3</sub><sup>+</sup>. Water solubility in polyamines is significantly larger than CO<sub>2</sub> solubility, and therefore, it is considered a constant.<sup>89</sup> The total amine concentration in polyamines ( $C_T$ ) can be defined as follows:

$$C_T = C_B + C_D \quad (7)$$

The reaction equilibrium constant ( $K_{\text{eq}}$ ) can be defined as:

$$K_{\text{eq}} = \frac{C_C C_D}{C_A C_B} \quad (8)$$

Assuming that the CO<sub>2</sub> partial pressure in the permeate is negligible, CO<sub>2</sub> flux ( $J_{\text{CO}_2}$ ) can be calculated as follows:<sup>90</sup>

$$J_{\text{CO}_2} = \frac{D_A}{l} C_A^F + \frac{D_C}{l} C_C^F \quad (9)$$

where the superscript F indicates the properties in the feed. CO<sub>2</sub> concentration at the feed side ( $C_A^F$ ) can be calculated using Henry's law:  $C_A^F = H_A p_A^F$ , where  $H_A$  is the Henry constant for CO<sub>2</sub>.

HCO<sub>3</sub><sup>-</sup> concentration can be correlated to the CO<sub>2</sub> concentration using eqn (7) and (8).

$$C_C^F = \frac{K_{\text{eq}} C_A}{2} \left( \sqrt{1 + \frac{4C_T}{K_{\text{eq}} C_A^F}} - 1 \right) \quad (10)$$

By using eqn (9) and (10), CO<sub>2</sub> permeance ( $Q_{\text{CO}_2}$ ) can be written as:<sup>90</sup>

$$Q_{\text{CO}_2} = \frac{J_{\text{CO}_2}}{p_A^F} = \frac{D_A H_A}{l} + \frac{D_C K_{\text{eq}} H_A}{2l} \left( \sqrt{1 + \frac{4C_T}{K_{\text{eq}} H_A p_A^F}} - 1 \right) \quad (11)$$

where the 1st term on the right side of the equation describes Fickian diffusion, and the 2nd term accounts for the carrier-mediated diffusion for facilitated transport.

The physical properties parameters used in eqn (11) can be determined from CO<sub>2</sub> sorption isotherms. Additionally, a lumped form of eqn (7) was used to investigate the effect of CO<sub>2</sub> partial pressure on permeance, as follows.

$$\frac{Q_{\text{CO}_2}}{Q'_{\text{CO}_2}} = 1 + \eta \left( \sqrt{1 + \frac{4C_T}{K_{\text{eq}} H_A p_A^F}} - 1 \right) \quad (12)$$

where  $Q'_{\text{CO}_2}$  is the permeance due to the solution-diffusion mechanism, and  $\eta$  represents the contribution of the facilitated transport. This facilitated transport model was validated using experimental data. As an example, eqn (12) agrees well with experimental CO<sub>2</sub> permeances as a function of CO<sub>2</sub> partial pressure (0.1–100 kPa) and operating temperatures (57–77 °C).<sup>90</sup>

To better understand the complex mechanism of facilitated transport, the role of amine carriers in these membranes was examined at the molecular level using computational approaches, including density functional theory (DFT) calculations and molecular simulations.<sup>91–93</sup> For example, DFT methods were utilized to investigate the amine-CO<sub>2</sub> chemistry of poly(*N*-vinylformamide-*co*-vinylamine) (PNVF-*co*-VAM) with fixed carriers and two mobile carriers, piperazine glycinate (PZ-Gly) and 2-(1-piperazinyl)ethylamine sarcosinate (PZEA-Sar) (Fig. 9a).<sup>92</sup> CO<sub>2</sub> interacts with amino groups *via* two primary reaction pathways: carbamate pathway (eqn (1) and (2)) and bicarbonate pathway (eqn (3) and (4)), in which the bicarbonate pathway with equimolar stoichiometry provides a higher CO<sub>2</sub> sorption capacity.

Fig. 9b displays that PZEA-Sar and PZ-Gly exhibited lower relative electronic energy ( $\Delta E_{\text{carbamate}}$ ) values (−18.1 and −17.5 kcal mol<sup>-1</sup>, respectively), compared to VAM (−13.8 kcal mol<sup>-1</sup>) following the carbamate pathway, suggesting that CO<sub>2</sub> has a higher reactivity towards the primary amino group on the mobile carrier than the fixed carrier. The simulation results confirmed that adding PZEA-Sar to PNVF-*co*-VAM increased CO<sub>2</sub> permeance, with an increase greater than that observed with PZ-Gly. Furthermore, an MD simulation suggested that CO<sub>2</sub> diffused faster through the bicarbonate state than through the carbamate state, since bicarbonate species can not only associate with protonated carriers but also hop between them.<sup>93</sup> CO<sub>2</sub> reaction intermediates (carbamate and bicarbonate species) were also confirmed using *operando* surface-enhanced Raman spectroscopy (SERS) in combination with *in situ* transmission FTIR spectroscopy.<sup>94</sup>

#### 3.2 Polyamine-based membranes with facilitated CO<sub>2</sub> transport

Amines can act as either fixed or mobile carriers within the polymer matrix. For fixed-carrier polyamines, the reactive amino groups are covalently bonded to the polymer backbone, in which CO<sub>2</sub> molecules can hop across amine reactive sites down the concentration gradient.<sup>93,95,96</sup> Alternatively, amine groups can be dispersed as small molecules within the polymer



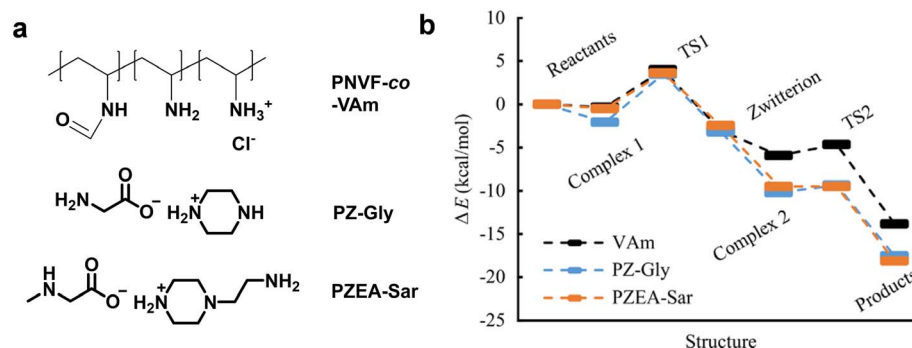


Fig. 9 DFT and MD calculation of facilitated CO<sub>2</sub> diffusion in PZ-Gly and PZEA-Sar. (a) Chemical structures. (b) Relative electronic energy ( $\Delta E_{\text{carbamate}}$ ) of structures in the amine-CO<sub>2</sub> reactions of carriers. Copyright 2020 American Chemical Society.<sup>92</sup>

matrix, where they reversibly react with CO<sub>2</sub> and diffuse through the membrane, thereby enhancing CO<sub>2</sub> transport efficiency. Table 2 lists the representative polyamines and their CO<sub>2</sub>/N<sub>2</sub> separation properties in water-saturated gas mixtures. In general, there is no correlation between the amine content and CO<sub>2</sub>/gas separation properties,<sup>97</sup> while increasing water content typically increases CO<sub>2</sub> permeance and CO<sub>2</sub>/gas selectivity.<sup>98,99</sup>

Fig. 10 illustrates the structure, composition, and CO<sub>2</sub>/N<sub>2</sub> separation performance of polyamine-based TFC membranes.<sup>8</sup> Fig. 10a displays the configuration of membranes comprising a dense selective layer (~170 nm) supported on a porous support (30 μm). The selective layer contained both PNVF-co-VAm and PEGu as the fixed layer and PZEA-Sar as the mobile layer, which together provided a balance between CO<sub>2</sub> reactivity and structural integrity. Increasing the temperature from 67 to 77 °C increased CO<sub>2</sub> permeance from 2500 to 4200 GPU, accompanied by a slight decline in CO<sub>2</sub>/N<sub>2</sub> selectivity. Additionally, PEI-decorated multilayered montmorillonite (MMT)

was incorporated into PVAm membranes, resulting in CO<sub>2</sub> permeance of 217 GPU and CO<sub>2</sub>/N<sub>2</sub> selectivity of 112.<sup>111</sup>

Fig. 11a shows a hybrid-integrated (HI) membrane comprising a modified amine-rich surface layer and a polymeric support layer with superior CO<sub>2</sub>/N<sub>2</sub> separation properties.<sup>7</sup> Two commercial membranes, polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE AF), were selected as the support layer. The amine-functionalized PDMS and PTFE AF (am-PDMS and am-PTFE) exhibited lower CO<sub>2</sub> permeability than their pristine membranes, and CO<sub>2</sub> permeability decreased slightly with increasing pressure, consistent with the facilitated transport mechanism (Fig. 11b). By contrast, these membranes exhibited much higher mixed-gas CO<sub>2</sub>/N<sub>2</sub> selectivity than their unmodified membranes (Fig. 11c). These membranes exhibited CO<sub>2</sub> permeability >1000 Barrer and CO<sub>2</sub>/N<sub>2</sub> selectivity >100, surpassing the 2019 upper bound.<sup>112</sup>

Polyamines can also be used to fabricate porous materials (metal-induced ordered microporous polymers, or MMPs) for

Table 2 Representative polyamine-based facilitated transport membranes with CO<sub>2</sub> permeability ( $P_{\text{CO}_2}$ , Barrer) or permeance ( $Q_{\text{CO}_2}$ , GPU) and CO<sub>2</sub>/N<sub>2</sub> selectivity with gas mixtures saturated by water

Polyamines <sup>a</sup>	Amine loading (wt%)	Thickness (μm)	Temp. (°C)	Pressure (bar)	CO <sub>2</sub> : N <sub>2</sub> mixture	$Q_{\text{CO}_2}$	$P_{\text{CO}_2}$	CO <sub>2</sub> /N <sub>2</sub> selectivity	Ref.
PVAm		1.2	25	2	10 : 90	104		197	100
PG <sup>b</sup> (PVAm)	65	0.25	57	0.1	20 : 80	945		87	101
HMMP-1 (PVAm)	0.1	0.18	45	2	15 : 85	1544		252	102
PZEA-Sar/PEGu (PNVF-co-VAm)		0.17	67	4	20 : 80	2397		186	8
ProK (PVA)	40	0.5	≈ 23	2	10 : 90	791		40	103
UiO-66-NH <sub>2</sub> (aPEO)	10	0.328	23	2.36	15 : 85	1400		76	6
MMP-3		0.05	25	2	15 : 85	3000		78	104
am-PTFE AF		0.01	25	1.2	10 : 90		~1000	~1000	7
TMC/DNMDAm/DGBAmE		0.5	22	1.1	10 : 90	1613		138	105
PMVAm		12	102	1	20 : 80	6804		350	20
Lupamin® 9095/AIBA-K/AF-MWNT (PVA)	40	21	107	15	20 : 40	886		428	106
PAA-C <sub>3</sub> H <sub>7</sub> (PVA)	70	25	110	2	20 : 40	295		335	88
NH <sub>2</sub> -Co/ZIF-8 (PEO)	5	300	25	~0.1	10 : 90	2916		47	107
Porphyrin (PSF)	20		≈ 23	2–10	50 : 50	134		115	108
NUS-8-NH <sub>2</sub> (PIM-1)	10	54	25	2	20 : 80	14 638		29	109
UiO-66-NH <sub>2</sub> @IL (PIM-1)	10	~70	20	1		8283		23	110

<sup>a</sup> The matrix is displayed in brackets. <sup>b</sup> PG: piperazine glycinate. PNVF-co-VAm: poly(*N*-vinylformamide-co-vinylamine); PEGu: poly(ethylene guanidine); PZEA-Sar: 2-(1-piperazinyl)ethylamine sarcosinate; ProK: potassium proline; PMVAM: poly(*N*-methyl-*N*-vinylamine); HMMP: high-valence MMP; MMP: metal-induced ordered microporous polymers; AIBA-K: 2-aminoisobutyric acid potassium salt.



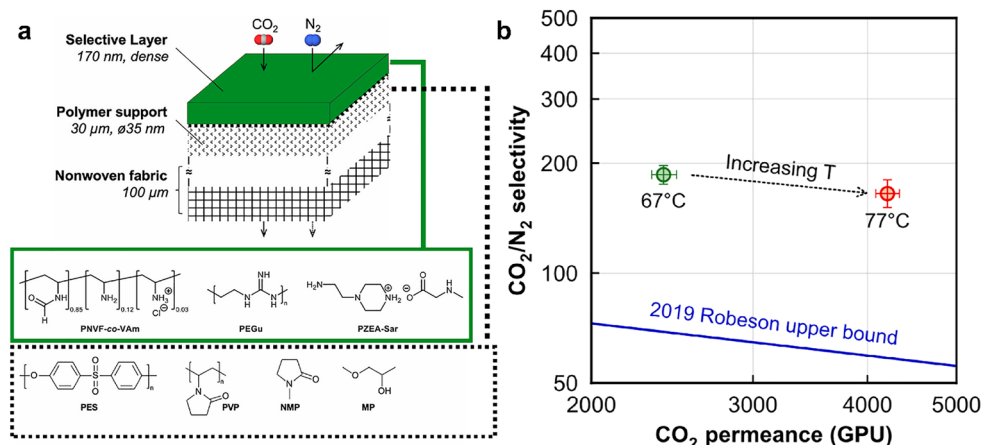


Fig. 10 Superior CO<sub>2</sub>/N<sub>2</sub> separation performance in FTMs based on PNVF-co-VAm. (a) Schematic illustration and chemical composition, and (b) CO<sub>2</sub>/N<sub>2</sub> separation performance of the scale-up membrane at 67 and 77 °C.<sup>8</sup> Copyright 2024 Elsevier.

CO<sub>2</sub>/N<sub>2</sub> separation.<sup>104</sup> PVAm or PEI were selected as the amine-rich polymer, while aceclofenac or 4-chloroisophthalic acid served as small organic linkers, and Cu(CH<sub>3</sub>COO)<sub>2</sub> or Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as divalent metal ions (Fig. 12a). The Cl and carboxylate groups interacted with the polymer chains through dipolar interactions, forming the MMP structure (Fig. 12b). TFC membranes with a selective layer as thin as 50 nm on an mPSP support were fabricated over large areas (>100 cm<sup>2</sup>) (Fig. 12c

and d). The membrane exhibited a CO<sub>2</sub> permeance of 3000 GPU and CO<sub>2</sub>/N<sub>2</sub> selectivity of 78 in the presence of saturated water vapor at 25 °C (Fig. 12e).

### 3.3 Polyamine-based membranes with hindered CO<sub>2</sub> transport

Although a variety of amine-modified polymers exhibit improved CO<sub>2</sub>/N<sub>2</sub> selectivity under humidified conditions,

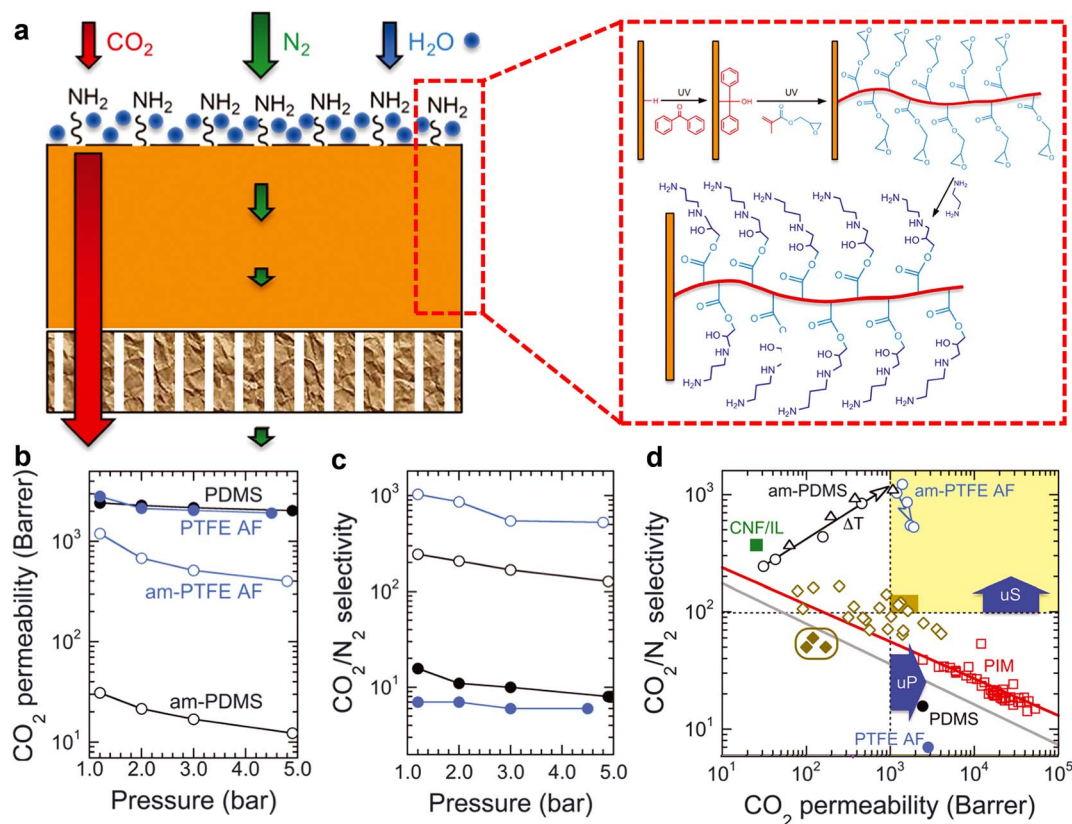
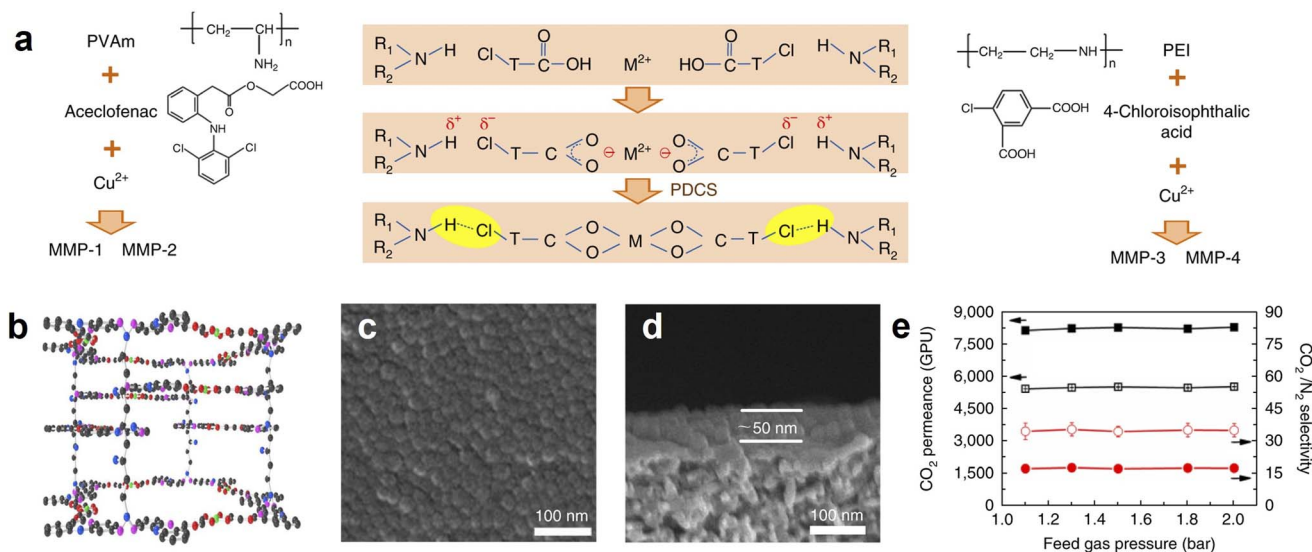


Fig. 11 Superior CO<sub>2</sub>/N<sub>2</sub> separation properties in hybrid-integrated membranes of polymeric supports with amine-enriched surface. (a) Schematic. (b) CO<sub>2</sub> permeability and (c) CO<sub>2</sub>/N<sub>2</sub> selectivity as a function of pressure. (d) Comparison with other polymers. The solid gray and red lines represent the 2008 (ref. 113) and 2019 upper bound,<sup>112</sup> respectively. Copyright 2022 AAAS.<sup>7</sup>

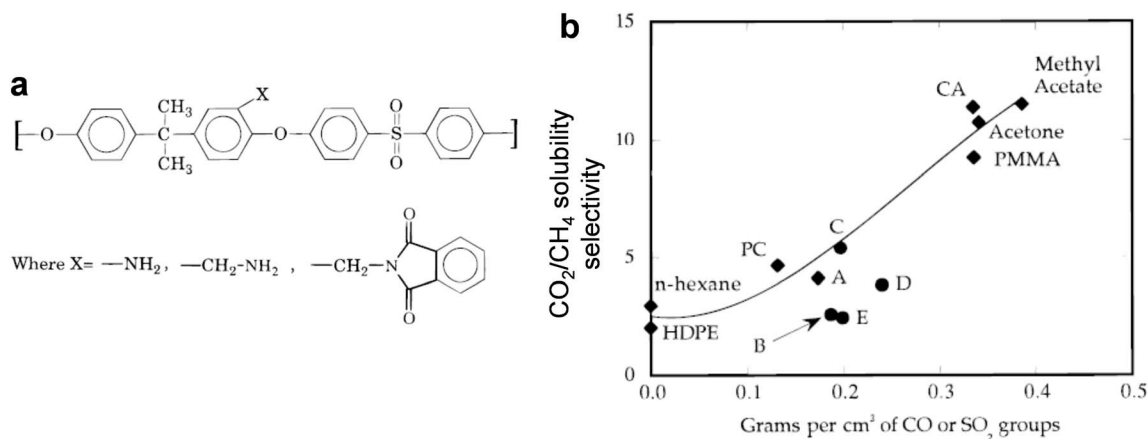




**Fig. 12** Polyamine-derived MMP by the polymer-directed chemical synthesis (PDCS) strategy. (a) Schematic. (b) Independent frameworks of MMP-1. (c) Surface, (d) cross-section image, and (e)  $\text{CO}_2/\text{N}_2$  separation performance of MMP-1/mPSf membrane. Filled and open points represent the mPSf and MMP/mPSf membrane, respectively. The feed gas was humid  $\text{CO}_2/\text{N}_2$  mixed gas (v/v: 15/85) at 25 °C and 1–2 bar.<sup>104</sup> Copyright 2019 Springer Nature.

contradictory results have also been reported. For example, amine-functionalized polysulfone (PSF) was synthesized by introducing three basic substituents, namely arylamine, benzylamine, and phthalimide, leading to PSF- $\text{NH}_2$ , PSF- $\text{CH}_2\text{-NH}_2$ , and PSF- $\text{CH}_2$ -imide, respectively (Fig. 13a).<sup>114</sup> Only PSF- $\text{CH}_2$ -

$\text{NH}_2$  showed enhancement in  $\text{CO}_2$  solubility and  $\text{CO}_2/\text{CH}_4$  solubility selectivity, and introducing arylamine and phthalimide diminished  $\text{CO}_2/\text{CH}_4$  solubility selectivity (Fig. 13b and Table 3). For instance, PSF- $\text{NH}_2$  (38%) showed  $\text{CO}_2$  solubility of  $2.2 \text{ cm}^3 \text{ (STP) (cm}^{-3} \text{ atm}^{-1})$  and  $\text{CO}_2/\text{CH}_4$  solubility selectivity of



**Fig. 13** Ineffective amine groups in amine-functionalized PSF. (a) Chemical structures. (b) Effect of polar group concentration on  $\text{CO}_2/\text{CH}_4$  solubility selectivity. A = PSF, B = PSF- $\text{NH}_2$  (16%), C = PSF- $\text{NH}_2$  (51%), D = PSF- $\text{CH}_2$ -imide (51%), and E = PSF- $\text{NH}_2$  (38%). Copyright 1996 American Chemical Society.<sup>115</sup>

**Table 3** FFV and  $\text{CO}_2/\text{CH}_4$  separation properties of the modified and unmodified PSF at 35 °C.<sup>114,116</sup>  $S_{\text{CO}_2}$  has a unit of  $\text{cm}^3 \text{ (STP) cm}^{-3} \text{ atm}^{-1}$ , and  $D_{\text{CO}_2}$  has a unit of  $10^{-8} \text{ cm}^2 \text{ s}^{-1}$

Polymers	FFV	$S_{\text{CO}_2}$	$S_{\text{CO}_2}/S_{\text{CH}_4}$	$D_{\text{CO}_2}$	$D_{\text{CO}_2}/D_{\text{CH}_4}$	$P_{\text{CO}_2}$ (Barrer)	$P_{\text{CO}_2}/P_{\text{CH}_4}$
PSF	0.147	2.08	3.1	2.0	7.4	5.5	23
PSF- $\text{NH}_2$ (16%)	0.134	1.90	3.2	1.1	7.9	2.7	24
PSF- $\text{NH}_2$ (38%)	0.118	2.20	2.8	1.1	8.5	3.2	25
PSF- $\text{CH}_2\text{-NH}_2$ (51%)	0.125	3.04	4.7	0.5	3.5	1.95	18
PSF- $\text{CH}_2$ imide (51%)	0.122	1.76	3.4	0.9	7.6	2.12	26



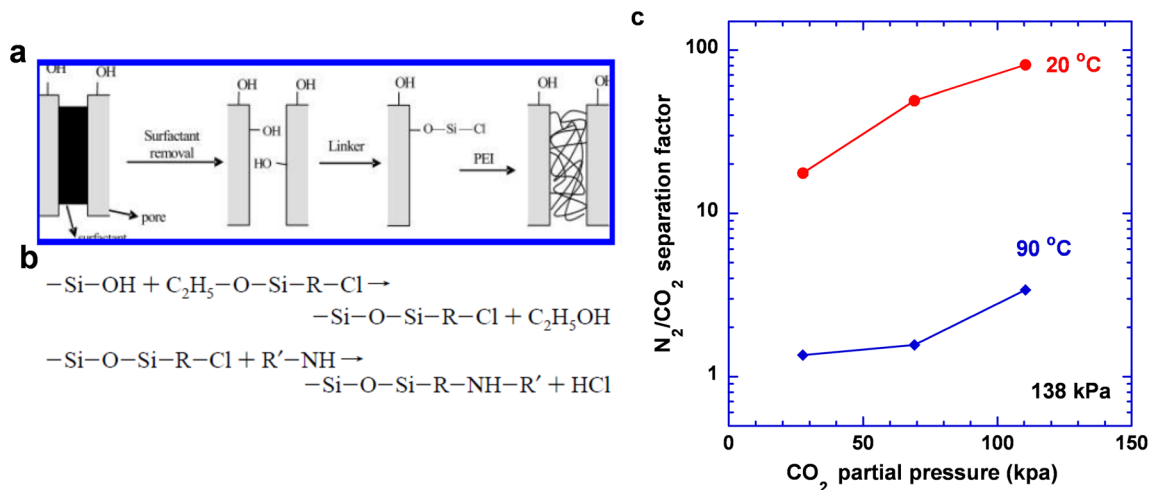


Fig. 14 Unexpectedly high  $\text{N}_2/\text{CO}_2$  separation factor in HTMs based on PEI-modified MCM-48. (a) Membrane structure. (b) Reaction. (c) Effect of  $\text{CO}_2$  partial pressure on  $\text{N}_2/\text{CO}_2$  separation factor at 20 and 90 °C with 2.6% water vapor.<sup>26</sup> Copyright 2007 American Chemical Society.

2.8 at 35 °C, which were comparable to those of PSF (2.08  $\text{cm}^3$  (STP) ( $\text{cm}^{-3} \text{atm}^{-1}$ ) and  $\text{CO}_2/\text{CH}_4$  solubility selectivity of 3.1, respectively).

The amine functionalization decreased  $\text{CO}_2$  diffusivity and thus permeability, which can be attributed to reduced fractional free volume (FFV). All amine-functionalized PSFs showed

similar  $\text{CO}_2/\text{CH}_4$  selectivity (Table 3), suggesting that amines interact with  $\text{CO}_2$  with extremely low efficiency. Similarly, functionalization of PSF with tertiary amine groups (benzyl-dimethylamine or DMA) or quaternary ammonium groups did not enhance  $\text{CO}_2$  solubility or  $\text{CO}_2/\text{CH}_4$  solubility selectivity.<sup>116</sup>

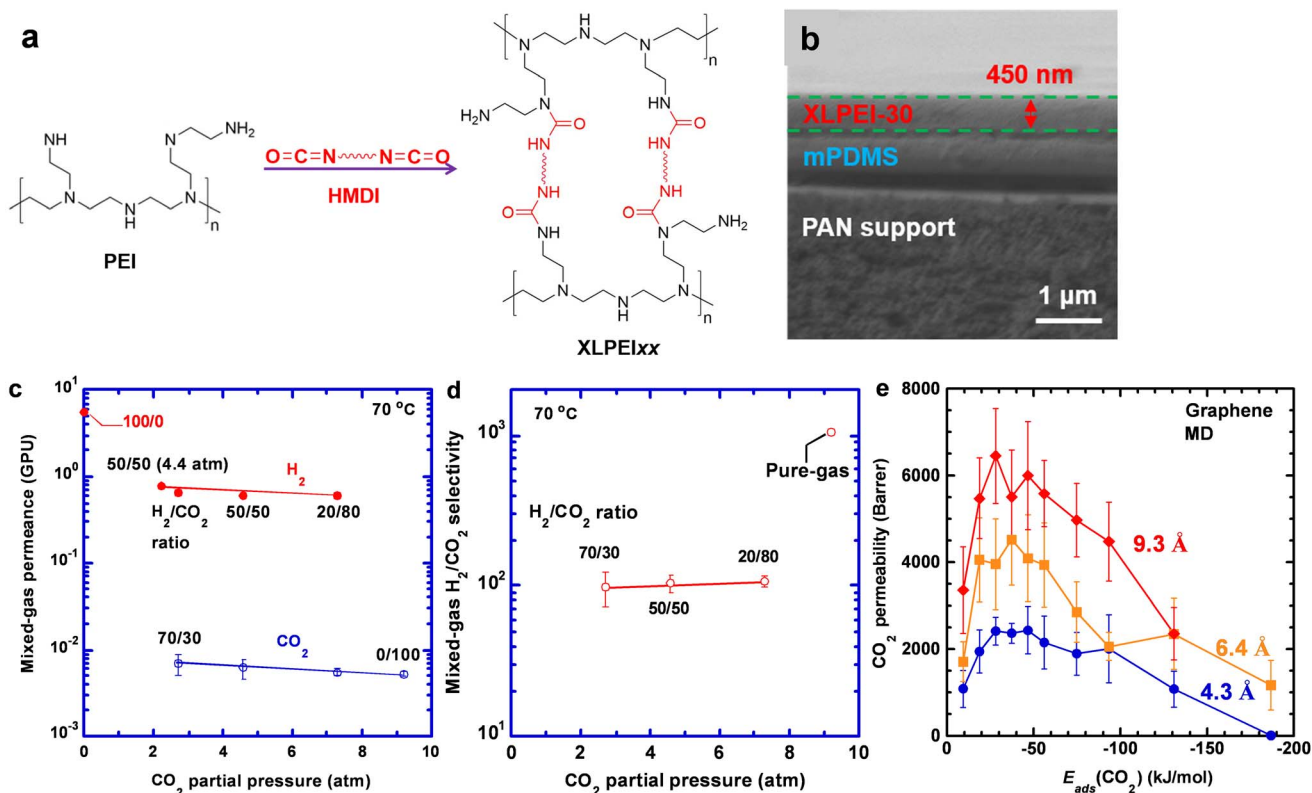


Fig. 15 Superior  $\text{H}_2/\text{CO}_2$  separation performance of HTMs of XLPEI30.<sup>27</sup> (a) Synthesis of XLPEIs from PEI and HMDI. (b) Cross-sectional SEM image. (c) Mixed-gas permeance and (d)  $\text{H}_2/\text{CO}_2$  selectivity as a function of the feed  $\text{CO}_2$  partial pressure at 70 °C and 9 atm. (e) Mixed-gas  $\text{CO}_2$  permeability as a function of  $\text{CO}_2$  adsorption energy ( $E_{\text{ads}}(\text{CO}_2)$ ) in simulated nanoporous graphene membranes with pore diameter from 4.3 to 9.3 Å. The error bars were calculated from ten replicate runs.



Fig. 14 presents another example of PEI-based hindered transport membranes (HTMs) with an unusual  $N_2/CO_2$  separation factor.<sup>26</sup> A mesoporous MCM-48 membrane was impregnated with PEI, and the obtained membrane exhibited unexpectedly high  $N_2/CO_2$  selectivity (18–81) at 20 °C, even in the presence of 2.6% water vapor, and the selectivity increased with increasing  $CO_2$  concentration (or partial pressure) in the feed. By contrast, the membrane exhibited  $N_2/CO_2$  separation factor of  $\sim 1$  at 90 °C (Fig. 14c), which is still unexpected, considering the high content of amine groups in the membranes.

PEI can be cross-linked with hexamethylene diisocyanate (HMDI) at a 7 : 3 mass ratio (Fig. 15a) and used to form TFC membranes with a 450 nm-selective layer (XLPEI30, Fig. 15b).<sup>27</sup> Despite the high content of amine groups, the membrane exhibited  $H_2$  permeance of 5.5 GPU and  $H_2/CO_2$  selectivity of 1100, the highest reported for known polymeric membranes. The membrane was further evaluated with various  $H_2/CO_2$  mixtures at 9.0 atm and 70 °C (Fig. 15c and d). The mixed-gas  $H_2$  permeance was much lower than the pure-gas value (where  $CO_2$  partial pressure is 0 atm) because of the ionic cross-linking of the XLPEI30 by the sorbed  $CO_2$  during the mixed-gas permeation. Higher  $CO_2$  partial pressure increased  $CO_2$  sorption and cross-linking degree, decreased free volume, and decreased gas permeance, but retained mixed-gas  $H_2/CO_2$  selectivity at 100.

Water vapor content plays an important role in determining  $H_2/CO_2$  selectivity. Increasing relative humidity at 70 °C from 25% to 100% decreased  $H_2/CO_2$  selectivity from 10 to 0.14.<sup>27</sup> To elucidate the hindered transport at the molecular level,  $CO_2$  transport through a nanoporous graphene membrane was simulated using MD simulations (Fig. 15e), with adjustable  $CO_2$  adsorption energies ( $E_{ads}(CO_2)$ ) from  $-9.3$  to  $-190$  kJ mol<sup>-1</sup> and pore diameters from 4.3 to 9.3 Å.  $CO_2$  permeability initially increased with increasing  $E_{ads}(CO_2)$  due to the enhanced affinity, but then decreased as the affinity became too strong for the sorbed  $CO_2$  to desorb and diffuse through the membrane. Consequently,  $CO_2$  permeability exhibited a volcano-shaped trend across all three pore sizes, with peaks at about  $-37$  kJ mol<sup>-1</sup>, indicating the boundary between  $CO_2$ -facilitated and hindered transport. Notably, this was only for dry conditions; when water vapor was introduced, it participated in the reaction between  $CO_2$  and amines, facilitating  $CO_2$  transport, decreasing  $H_2/CO_2$  selectivity with increasing RH levels.

## 4 Discussion and conclusion

Polyamines with a strong affinity towards  $CO_2$  have emerged as one of the most promising classes of materials for  $CO_2$  capture, and their highly tunable molecular architecture has greatly expanded the design space for DAC sorbents and PCC membranes. As expected, polyamines react with  $CO_2$ , resulting in high  $CO_2$  sorption capacity even at  $CO_2$  levels as low as 400 ppm, and introducing water vapor further enhances  $CO_2$  sorption capacity. However, several unusual, sometimes counterintuitive phenomena have been reported and are summarized below.

1. The amine efficiency towards  $CO_2$  sorption depends sensitively on the substrates, and the measured pseudo-equilibrium  $CO_2$  sorption may unconventionally increase with increasing temperature, reflecting the importance of the  $CO_2$  diffusion and access of amine sites.

2. Polyamines can exhibit hindered  $CO_2$  diffusion, leading to much lower  $CO_2$  diffusivity than expected and unexpectedly high  $N_2/CO_2$  or  $H_2/CO_2$  selectivity. These results differ dramatically from those of FTMs, showing that  $CO_2$  transport can be governed by reactive diffusion rather than a solution-diffusion mechanism.

3. The presence of water vapor influences  $CO_2$  sorption and desorption, which has been harnessed to design moisture-swing sorbents and membranes for uphill  $CO_2$  permeation based on polyamine derivatives.<sup>84,85</sup>

The key to understanding these discrepancies lies in the role of reactive  $CO_2$  diffusion in polyamines.<sup>93,117</sup> As  $CO_2$  diffuses through polyamines, it reacts with amines, forming ionic cross-links among polymer chains, increasing chain rigidity, reducing  $CO_2$  diffusivity, and shielding the remaining polyamines from  $CO_2$  access. However, no quantitative models are available to describe this behavior.<sup>13,27</sup> Furthermore, the strong interaction between  $CO_2$  and amines may prevent the  $CO_2$  dissociation and dramatically reduce its overall diffusivity. Consequently, the reported  $CO_2$  sorption data are mostly at pseudo-equilibrium, and sorption is influenced by temperature thermodynamically and kinetically.

We expect that polyamines will remain a dominant materials platform for DAC sorbents and PCC membranes, and they may be optimized through integrated experimental and modeling studies. A key priority will be the creation of robust predictive frameworks that couple  $CO_2$  sorption thermodynamics with mass-transfer kinetics, providing fundamental understanding of  $CO_2$  reactive diffusion and facilitating scale-up from bench-top demonstration to commercial deployment.

## Conflicts of interest

The authors declare no competing financial interests.

## Data availability

Data are available upon request to the corresponding author.

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