

Frontiers of Ionic Liquids in Carbon Dioxide Separation and Valorization

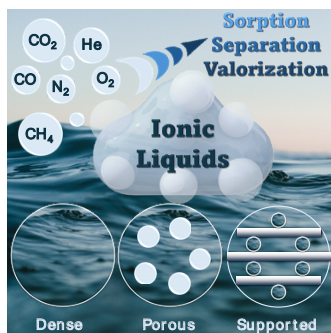
Liqi Qiu,^{1, 2} Errui Li,¹ Tian Ke,¹ Qingju Wang,¹ Yujing Tong,³ Bo Li,³ Hongjun Liu,³ De-en Jiang,^{3, *} Shannon M. Mahurin,² Zhenzhen Yang,^{2, *} and Sheng Dai^{1, 2, *}

¹ Department of Chemistry, Institute for Advanced Materials and Manufacturing, University of Tennessee, Knoxville, TN 37996, United States

² Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States.

³ Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37235, United States

E-mail: de-en.jiang@vanderbilt.edu; yangz3@ornl.gov; dais@ornl.gov



ABSTRACT

Ionic liquids (ILs) have emerged as highly tunable sorbents and membranes for gas separation, especially in the purification of CO₂-containing gas streams such as air, natural gas, biogas, and syngas. Their negligible volatility, high thermal stability, and chemical versatility position them as promising alternatives to conventional amine- and alkaline metal derivative-based systems, effectively addressing key challenges such as volatility, stability, and high regeneration energy. This review explores IL-derived systems for CO₂-related gas separation across dense, porous, and supported categories. At dense liquid level, we discuss strategies for tailoring IL properties to optimize CO₂ sorption, focusing on the correlation between IL-CO₂ interaction strength, uptake capacity, and regeneration energy. Key advancements in carbon capture, including amino-functionalized (AILs) and superbase-derived ILs (SILs), are highlighted, along with strategies such as chemical structure engineering, multiple binding sites integration, alternative driving force exploration, and stability enhancement. Then the porous liquids (PLs) scale focuses on the emerging field integrating IL properties with permanent porosity engineering, spanning ultramicropores (< 5 Å) to macropores (around 100 nm). These innovations improve gas uptake capacity, accelerate transport kinetics, introduce gating effect, and enable the coexistence of active sites with antagonistic properties within a single IL media. At the supported IL scale, the discussion shifts to IL- and ionic pair-modified sorbents and membranes, emphasizing the modulation of cations and anions, confinement effects from porous supports, and the IL-interface interaction to enhance CO₂ separation performance, particularly in diluted gas streams. Beyond separation, this review highlights IL-based integrated processes for CO₂ capture and conversion into value-added chemicals via thermocatalytic, electrocatalytic, and photocatalytic pathways. In each scale, advanced computational and experimental tools for IL design are also discussed, providing insights into stability enhancement, sorption efficiency, and process integration. The review concludes by addressing existing challenges and outlining future directions for IL-driven innovations in gas separation technologies.

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1. Introduction

Ionic liquids (ILs) are reaction media composed entirely of cation-anion pairs that remain in a liquid state below 373 K.^{1,2} Since Paul Walden's discovery of ethylammonium nitrate ([EtNH₃][NO₃]) in 1914, ILs with varying structures and features have been developed and utilized across diverse fields, including separation, energy storage, catalysis, material synthesis and beyond, spanning both academic research and industrial applications.²⁻⁶ A key distinguishing feature of ILs is their negligible volatility, coupled with high thermal, chemical, and electrochemical stability. Additionally, they exhibit solvation versatility for a wide range of organic, inorganic, and polymeric compounds and materials, a broad liquid temperature window, and significant tunability through structure engineering to meet diverse application demands.¹ These properties have enabled the use of customized ILs in numerous research areas, such as critical element enrichment and separation,⁷⁻¹² energy storage in lithium and sodium batteries,¹³⁻¹⁷ reaction media/resources for fabricating porous inorganic/carbon materials fabrication,¹⁸⁻²² organic vapor sensing,²³ spectrometer coating for separation processes,²⁴ and biomass extraction and valorization.²⁵ In recent decades, both academia and industry have explored ILs for gas sorption and separation, particularly for CO₂ capture/purification. IL-based sorbents offer promising alternatives to conventional aqueous amine and alkaline metal oxide/hydroxide systems, which suffer from drawbacks such as volatility, poor thermal stability, performance degradation over prolonged use, high energy requirements for solvent heating, and limited tunability in CO₂ interaction strength.^{26, 27} Notably, the nonvolatility of ILs allows them to function as liquid sorbents without the need for additional solvents, outperforming the traditional amine scrubbing sorbents by reducing energy consumption and yielding higher-purity CO₂ streams, which is an advantage crucial to integrated CO₂ capture and utilization processes.^{4, 28}

Early studies on ILs for carbon capture have primarily focused on physisorption, where CO₂ solubility in ILs is significantly higher than in conventional organic solvent. Functionalizing ILs with CO₂-philic groups, such as poly(ethylene glycol) (PEG)^{29, 30} and fluorinated moieties,³¹ further enhanced solubility and optimized their physiochemical properties and stability.³²⁻³⁴ Similarly, deep eutectic solvents (DES), formed via on hydrogen bonding donor/acceptor interactions, exhibited comparable behavior in carbon capture applications with tunable physisorption behavior.³⁵ Beyond CO₂ solubility, the tunable CO₂ transport behavior of ILs have been leveraged to improve its separation from other gas components (e.g., N₂, O₂, He, and CH₄) in IL-derived membrane separation procedures. The vast library of cations/anions enables the introduction of large free volumes and CO₂-philic sites, enhancing separation kinetics and selectivity.³⁶ Notably, recent advancements in the design, discovery, and synthesis of porous liquids (PLs) have established a new platform that integrates the benefits of IL phase and porous materials.³⁷⁻⁴⁰ Through the as-developed structure modification, surface engineering, and mechanochemistry-assisted approaches, permanent porous channels ranging from ultra-micropores (< 5 Å) to macropores (around 100 nm) can be incorporated into IL phase while maintaining their liquid nature.^{38, 41-43} This significantly increases free volume in ILs and further fine-tunes gas transport behavior. Inspired by the CO₂ chemistry of amine-based sorbents, chemisorption IL sorbents, such as amine-functionalized ILs (AILs), were developed by integrating amine moieties into IL cations or anions, enabling CO₂ absorption via carbamate/carbamic acid formation.^{44, 45} However, the stability and viscosity issues of AILs, resulting from degradation of amino-moieties and extensive hydrogen bonding networks formation, inspired and led to the development of superbase-derived ILs, which exhibit lower viscosity and accelerated the CO₂ capture/releasing kinetics.⁴⁶⁻⁴⁸ Furthermore, the interaction strength of superbase-derived ILs (SILs) with CO₂ can be finely tuned

from weak physisorption to strong chemisorption, with the reaction enthalpy (ΔH) varying from -19 to -120 kJ mol⁻¹. This tunability accommodates diverse application status, maximizing CO₂ capture capacity while minimizing energy input for sorbent regeneration, with the gas stream supply ranging from pure CO₂ to atmosphere air (CO₂ concentration of 400 ppm).⁴⁹⁻⁵¹ These advancements have driven the development of ILs-functionalized porous scaffolds for direct air capture (DAC) of CO₂, accelerating progress in negative emission technologies (NETs). The CO₂ molecules can be integrated into these systems via O-C, N-C, and C-C bond formation, leveraging carbonate, carbamate, carboxylate formation chemistry, structure rearrangement, and entropy change as the driving force.^{22, 52-54} The captured CO₂, particularly in chemically bonded forms, exists in an activated state, transitioning from its inert linear and nonpolar geometry to a pre-activated structure with an O-C-O bond angle of < 180 ° and increased polarity. Functionalized ILs provide a versatile platform for integrating CO₂ capture with valorization via thermocatalytic, electrocatalytic, or photocatalytic processes, offering tunable activity and selectivity.^{4, 55, 56} Fundamental studies in IL-facilitated carbon capture and utilization have been extensively explored through combined computational simulations and spectroscopy techniques.^{57, 58}

This review explores the frontiers of ILs in gas separation, with a particular focus on purification of CO₂-containing gas streams such as air, natural gas, biogas, and syngas. It highlights the unique features of ILs that offer alternative solutions covering the issues to the challenges faced by traditional amine- and alkaline metal derivative-based sorbent systems. The discussion is structured around the tunability of IL-derived systems across dense, porous, and supported categories for diverse gas separation applications (**Figure 1**). The review begins with molecular-scale studies in dense IL phase (Section 2), summarizing insights from theoretical simulations that guide the optimization of CO₂ uptake capacity while minimizing energy input for sorbent regeneration. This section covers strategies for tuning IL-CO₂ interactions through chemical structure engineering, enhancing CO₂ uptake via multiple binding sites integration, reducing energy consumption in sorbent regeneration through alternative driving force, and improving long-term stability through sophisticated structure modifications. Next, for the porous ILs media (Section 3), various categories of PLs are summarized and compared. This section highlights the benefits of engineering permanent pores in ILs to improve gas uptake capacity, accelerate the transport kinetics, introduce gating effect, and accommodate species with antagonistic properties within ILs media. Then, beyond their role as liquid sorbents for carbon capture, the CO₂ separation and transport behavior of IL-based membranes is explored (Section 4). This includes modulating cations/anions and leveraging confinement effects from selected support to enhance and stabilize gas separation performance. This section will further emphasize the influence of the ILs-interphase interaction and confinement effect from the porous channels in gas separation related to diluted CO₂-containing gas flows (Section 5). Building on these insights, Section 6 discusses integrated processes that convert captured CO₂ into value-added chemicals via thermocatalytic, electrocatalytic, and photocatalytic pathways. This section emphasizes the role of ILs in accelerating reaction kinetics, tuning thermodynamics and reaction pathways, and stabilizing catalytic sites. Across all sections, the unique design principles and computational tools used in various IL-derived systems will be discussed. The review concludes with perspectives on the existing challenges in gas separation and promising opportunities for ILs design in this field.

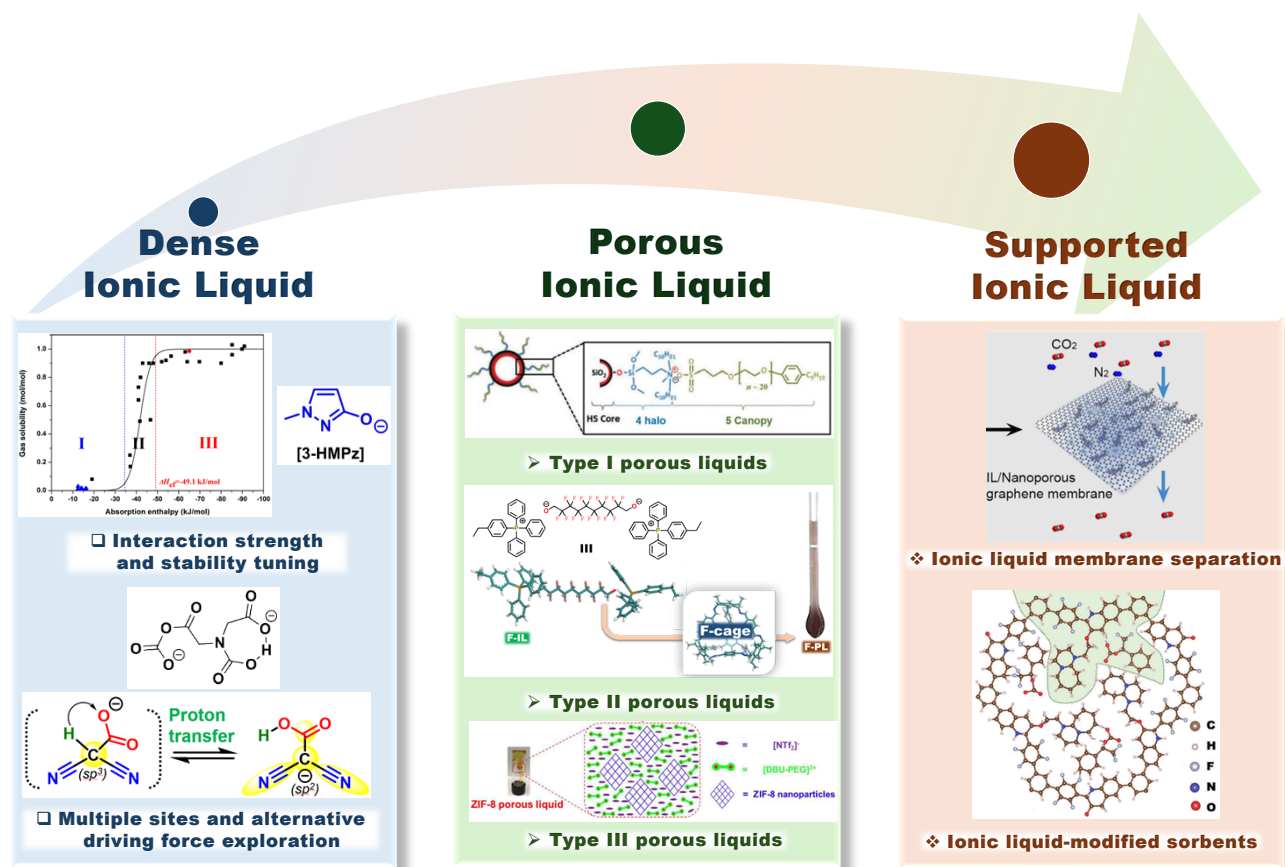


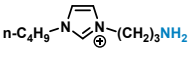
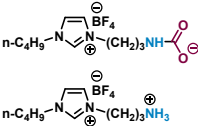
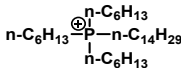
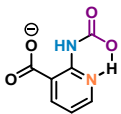
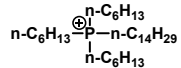
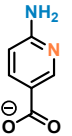
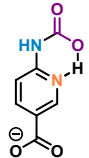
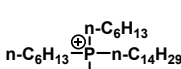
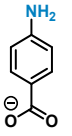
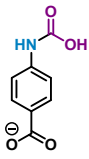
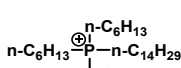
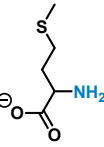
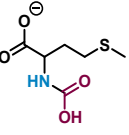
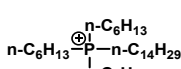
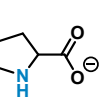
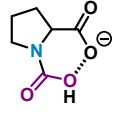
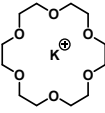
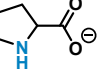
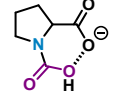
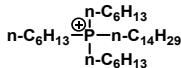
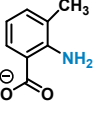
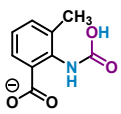
Figure 1. An illustration of the scope of this review, highlighting the application of IL systems in gas separation across dense, porous, and supported categories.

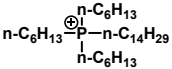
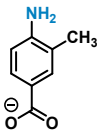
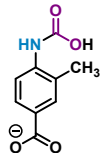
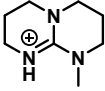
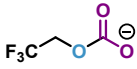
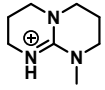
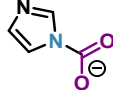
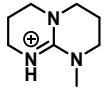
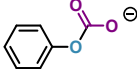
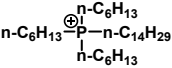
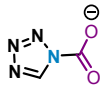
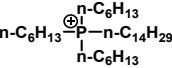
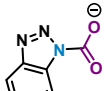
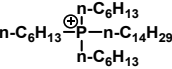
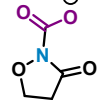
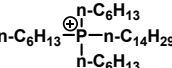
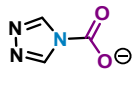
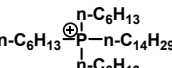
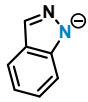
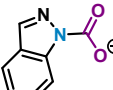
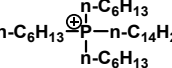
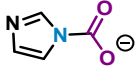
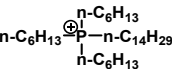
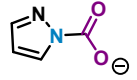
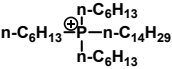
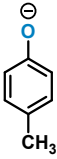
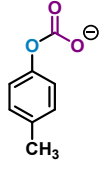
2. Tailoring the behavior of ionic liquids in CO₂ sorption

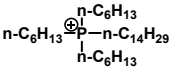
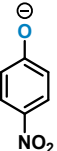
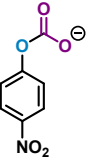
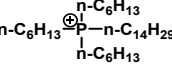
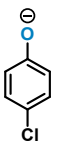
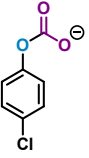
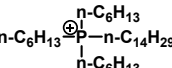
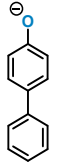
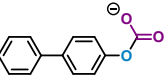
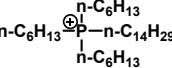
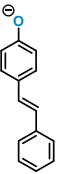
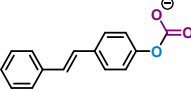
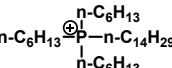
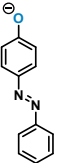
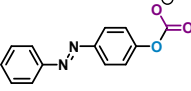
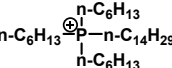
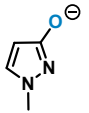
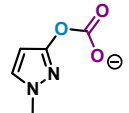
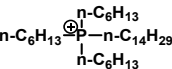
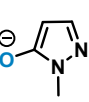
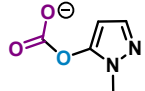
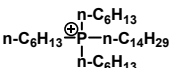
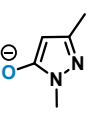
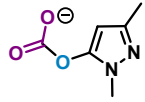
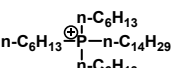
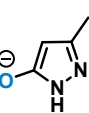
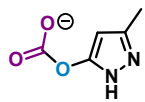
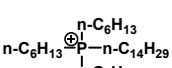
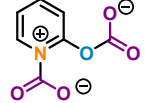
The extensive structure diversity of ILs offers versatile tools for gas separation and storage, accommodating a wide range of targeted gas pressure, sorption temperature, and gas impurities.⁴⁴ By leveraging variations in cation and anion structures, IL sorbents could be tailored to facilitate gas transport, enhance gas uptake capacity, reduce energy consumption during sorbent regeneration, and ensure long-term durability.⁵⁹ In CO₂ capture, IL sorbents present distinct advantages over traditional aqueous amine solutions and solvent-lean amine systems.^{26, 60, 61} Their key strengths lie in their non-volatility, broad tunability in interaction strength to accommodate varying CO₂ concentrations (as low as 400 ppm in ambient air), minimize the energy input for CO₂ releasing, and enhance stability under oxidative conditions (e.g., in the presence of H₂O and O₂) for practical application. This section summarizes research efforts in tailoring IL behavior for CO₂ sorption through structure engineering. First, the correlation between the IL-CO₂ interaction strength, CO₂ uptake capacity, and energy consumption for CO₂ releasing is examined (Section 2.1). This is followed by an overview of CO₂ physisorption in ILs (Section 2.2). The primary focus then shifts to advancements in CO₂ chemisorption (Table 1), including amino-functionalized ILs (AILs) (Section 2.3), stabilization of carbamic acid intermediates in AILs (Section 2.4), modulation of CO₂ binding strength in superbase-derived ILs (SILs) via basicity control (Section 2.5), improvement of IL stability in the presence of gas impurities (Section 2.6), enhancement of CO₂ uptake capacity through ILs with multiple interaction sites (Section 2.7), and exploration of alternative driving forces in CO₂ chemisorption

beyond conventional chemical bonding strength (Section 2.8).

Table 1. The summary of CO₂ chemisorption performance of ILs.

ILs	Cation	Anion	CO ₂ -integrated product	CO ₂ uptake capacity (mmol mmol ⁻¹)	Reaction enthalpy (kJ mol ⁻¹)	Ref
[ImNH ₂][BF ₄]		[BF ₄] ⁻		0.5	-	62
[P ₆₆₆₁₄][2NH ₂ -NC]				0.8	-	63
[P ₆₆₆₁₄][6NH ₂ -NC]				0.78	-	63
[P ₆₆₆₁₄][4NH ₂ -NC]				0.56	-	63
[P ₆₆₆₁₄][Met]				0.8	-64	64
[P ₆₆₆₁₄][Pro]				0.8	-80	64
[18C6-K][Pro]				0.99	-39	65
[P ₆₆₆₁₄][<i>o</i> -AA]				0.6	-56	66

[P ₆₆₆₁₄][<i>ρ</i> -AA]				0.94	-41	66
[MTBD][TFE]				1.13	-116.8	49
[MTBD][Im]				1.03	-85.2	49
[MTBD][OPh]				0.49	-41.7	49
[P ₆₆₆₁₄][Tetz]				0.08	-19.1	67
[P ₆₆₆₁₄][Bentriz]				0.17	-37.2	67
[P ₆₆₆₁₄][Oxa]				0.91	-69.8	67
[P ₆₆₆₁₄][Triz]				0.95	-56.4	67
[P ₆₆₆₁₄][Ind]				0.98	-52	67
[P ₆₆₆₁₄][Im]				1.0	-49	67
[P ₆₆₆₁₄][Pyr]				1.02	-91	67
[P ₆₆₆₁₄][4-Me-PhO]				0.91	-	68

[P ₆₆₆₁₄][4-NO ₂ -PhO]				0.3	-	68
[P ₆₆₆₁₄][4-Cl-PhO]				0.82	-	68
[P ₆₆₆₁₄][PPhO]				0.93	-51	69
[P ₆₆₆₁₄][PCCPhO]				0.96	-48	69
[P ₆₆₆₁₄][PNNPhO]				0.90	-40	69
[P ₆₆₆₁₄][3-HMPz]				0.96	-64.5	70
[P ₆₆₆₁₄][5-HMPz]				0.43	-	70
[P ₆₆₆₁₄][1-HDMPz]				0.69	-	70
[P ₆₆₆₁₄][1-HMPz]				0.83	-	70
[P ₆₆₆₁₄][2-Op]				1.58	-	71

[P ₆₆₆₁₄][4-ABI]				1.60	-	71
[P ₄₄₄₂][IDA]				1.69	-89, -52.8	72
[P ₄₄₄₂][DAA]				1.12	-	73
[P ₄₄₄₂][IDA]				1.65	-	73
[P ₄₄₄₂][MN]				0.86	-35.3	22
[P ₄₄₄₂][MMN]				0.35	-17.4	22
[P ₄₄₄₂][MSA]				1.06	-	53

2.1 Correlation between CO₂-ionic liquid interaction with separation performance

In gas separation applications, a key advantage of IL systems is their highly tunable interaction strength with targeted gas molecules, ranging from weak physisorption to strong chemisorption. This adaptability enables diverse utilization scenarios, with reaction enthalpy values varying from -19.0 to -91.0 kJ mol⁻¹.⁷⁴ For sorbents in CO₂ capture/separation, sorbent performance is evaluated based on two thermodynamic parameters: solubility and reaction enthalpy. Solubility reflects the amount of CO₂ accommodated, while reaction enthalpy indicates the CO₂-IL active sites interaction strength. By integrating the van't Hoff equation through reaction equilibrium thermodynamic model (RETM), researchers identified a sigmoidal relationship between the gas uptake capacity (r) and reaction enthalpy,⁷⁵ which was presented by the following equation: $r = \frac{P_{\text{CO}_2}^G}{e^{\Delta H^0/8.314T+140/8.314} + P_{\text{CO}_2}^G}$, where $P_{\text{CO}_2}^G$

is CO₂ partial pressure in gas, ΔH^0 is absorption enthalpy change, and T is temperature. Accordingly, the variation of r and ΔH^0 was related to T and P_{CO_2} under the determined conditions. With the input of T = 298.15 K and $P_{\text{CO}_2} = 1$ bar for ILs exhibiting a 1:1 reaction with CO₂, the absorption

behavior can be categorized into three distinct phases (Figure 2A). Phase I (physisorption region): CO₂ solubility remains below 0.05 mol mol⁻¹ in ILs with reaction enthalpy less negative than -34.5 kJ mol⁻¹. Phase II: A rapid increase in CO₂ uptake capacity up to 0.95 mmol mol⁻¹, with the reaction enthalpy reaching to -49.1 kJ mol⁻¹. Within this range, CO₂ uptake capacity exhibits an almost linear correlation with reaction enthalpy. Phase III: For ILs with more negative reaction enthalpy values, increased interaction strength provides minimal additional uptake capacity while significantly raising energy demands for CO₂ release and sorbent regeneration. This analysis offers a fundamental guideline for optimizing reaction enthalpy in carbon capture to maximize uptake while minimizing energy consumption for CO₂ release. Notably, the position of the sigmoid curve is strongly influenced by temperature and CO₂ partial pressure (Figure 2B). At a CO₂ partial pressure of 0.15 bar, more negative reaction enthalpy values are needed to achieve uptake capacities of 0.05 mol mol⁻¹ ($\Delta H_{r=0.05}^0 = -39.5$ kJ mol⁻¹) and 0.95 mol mol⁻¹ ($\Delta H_{r=0.95}^0 = -53.8$ kJ mol⁻¹) at 298.15 K. Additionally, at the same CO₂ partial pressure, the onset enthalpy shifts further negative when comparing sigmoid curves at 298.15 and 348.15 K (Figure 2B, inset). Under direct air capture (DAC) conditions (CO₂ concentration = 400 ppm, T = 298.15 K), the sigmoid curve provides a guiding principle for IL sorbents design (Figure 2C).⁷⁴ To effectively capture CO₂ from air, assuming no interference from other gas impurities, a reaction enthalpy around -68.5 kJ mol⁻¹ is optimal. At this enthalpy, 95% of the maximum uptake capacity can be achieved at 298.15 K, while over 90% of the chemisorbed CO₂ can be released by increasing the temperature to 373.15 K.

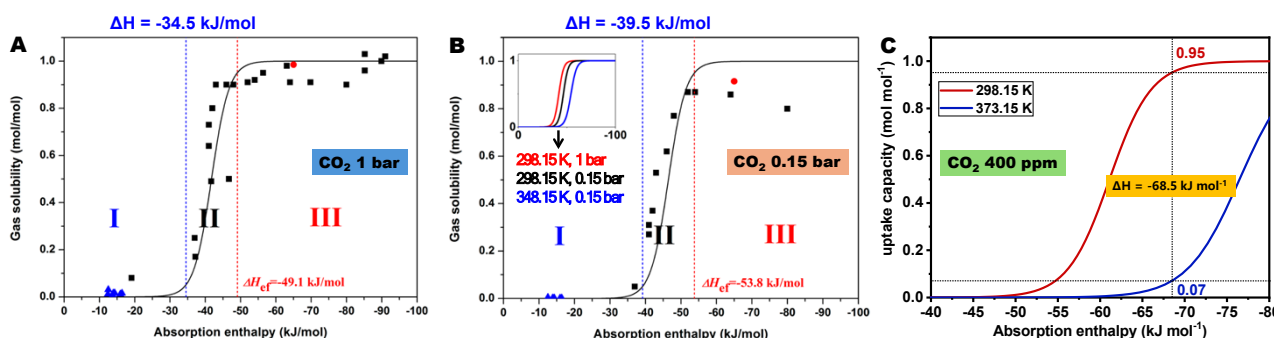


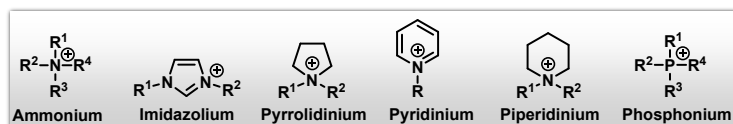
Figure 2. The sigmoid correlation between gas solubility and the reaction enthalpy of CO₂ with ILs exhibiting a 1:1 reaction mechanism.⁷⁵ Reproduced with permission from Ref 75. Copyright 2015 American Chemical Society. The input conditions are T = 298.15 K and P_{CO₂} = 1 bar (A), P_{CO₂} = 0.15 bar for (B), and CO₂ concentration of 400 ppm for (C). The inset in (B) compares sigmoid curves being obtained under varying temperatures and CO₂ pressures. The solid symbols in (A) and (B) represent experimental data points from literature.

2.2 Ionic liquids in CO₂ physisorption

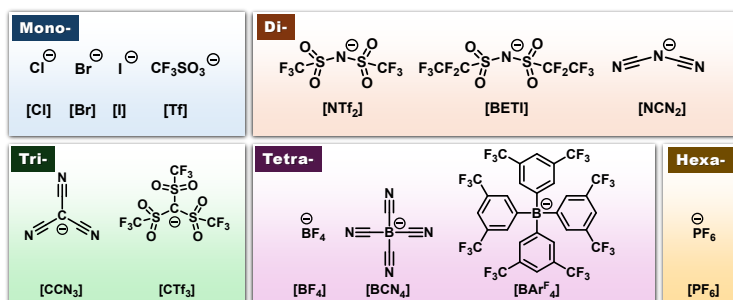
The exceptional solubility of CO₂ in ILs, surpassing that of traditional solvents, was first demonstrated by 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]), achieving 0.75 mol mol⁻¹ at 8.30 MPa CO₂ pressure and 298 K.⁷⁶ Since then, extensive research has been conducted to enhance CO₂ sorption kinetics, maximize equilibrium uptake capacity, and elucidate the structure-property-performance relationship. These studies primarily focused on the phase I region of the sigmoidal curve, characterized by relatively low reaction enthalpies (ΔH less negative than -30 kJ mol⁻¹) (Figure 3A). Cations structures employed in ILs for CO₂ physisorption include tetra-substituted

ammonium and phosphonium species, aza-fused aromatic rings (imidazolium and pyridinium), and cyclic non-conjugated structures (ammonium, pyrrolidinium, and piperidinium) (Figure 3B). Anionic structures, on the other hand, vary based on the localization of the negative charge, which may reside on halogen, oxygen, nitrogen, carbon, boron, or phosphorus atoms. Depending on the number of substitutes attached to the negatively charged center, anions can be classified as mono-, di-, tri-, tetra-, and hexa-substituted species. In most of the IL systems, CO₂ solubility is primarily governed by the structure of anions, while the cation plays a role in tuning physical properties (e.g., melting point and viscosity) and influencing the CO₂ uptake kinetics.⁴⁵ For instance, both experimental and simulation studies have shown that, for ILs with the same cation ([Bmim]), CO₂ solubility increases in the order of [NCN₂] < [BF₄] < [PF₆] < [Tf] < [NTf₂].⁷⁷⁻⁸⁰ Particularly, fluorine-containing anions generally enhance CO₂ solubility, with a preference for higher fluorine content. The solubility trend among fluorinated anions follows: [BF₄] < [PF₆] < [NTf₂] < [CTf₃].^{77, 78, 81} Beyond anionic influence, cationic structure and properties can further modulate CO₂ solubility and sorption kinetics. ILs with longer alkyl chains typically exhibit higher CO₂ solubility.^{77, 82} Additionally, introducing CO₂-phillic functionalities, such as polyethylene glycol (PEG) units or fluorinated carbon chains, enhances both solubility and sorption kinetics.^{31, 83-86} For example, CO₂ solubility in [C₈H₄F₁₃mim][NTf₂] exceeds that of its non-fluorinated counterpart, [C₈mim][NTf₂], across a wide temperature range (Figure 3B).⁸³ Other factors, including cation steric hindrance and the assembly/packing mode of cations and anions in ILs, also influence CO₂ solubility and transport behavior.^{87, 88} These properties further impact CO₂ separation performance when ILs are incorporated into membranes (see Section 3). Several comprehensive reviews have systematically analyzed and compared CO₂ solubility across various ILs, offering fundamental insights into the structure-performance relationship.⁸⁹⁻⁹¹

A Structure of cations



Structure of anions



B

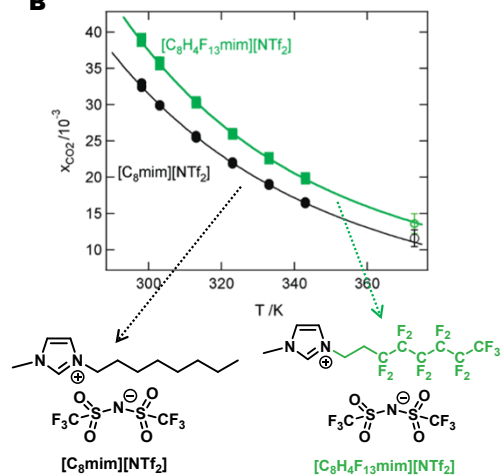


Figure 3. (A) Selected structures of IL cations and anions used in CO₂ physisorption. (B) Comparison of CO₂ solubility in [C₈mim][NTf₂] and [C₈H₄F₁₃mim][NTf₂] at different temperatures under the CO₂ pressure of 1 bar.⁸³ Reproduced with permission from Ref 83. Copyright 2010 American Chemical Society.

2.3 Amino-functionalized ionic liquids in CO₂ chemisorption

For ILs lacking the ability to chemically bond with CO₂, although CO₂ solubility can be tuned by

modifying cation and anion structures, the uptake capacity in most physisorption-based ILs remains below 0.1 mol mol^{-1} at 1 bar CO_2 pressure and 298 K.⁸⁹⁻⁹¹ This is significantly lower than that of aqueous amine solutions, which are widely used in industrial flue gas decarbonization.²⁶ The addition of water or organic solvent, or the use of ILs-amine mixed sorbents, can enhance CO_2 sorption performance to some extent. However, the carbon capture efficiency and stability of IL-derived systems still require substantial improvement for practical carbon removal applications.⁴⁴ Early studies explored liquid sorbents composed of ILs and amines, demonstrating enhanced thermal stability and lower energy compensation during sorbent regeneration compared to traditional aqueous amine solutions, as no water vaporization was required.⁹² However, valorization remained an issue, and ILs contributed little to CO_2 uptake capacity. For CO_2 removal from diluted gas sources covering flue gas stream from combustion of coal, oil, biomass ($\sim 15 \text{ vol\%}$), natural gas ($\sim 8 \text{ vol\%}$), or ambient air ($\sim 415 \text{ ppm}$), IL sorbents with stronger CO_2 interaction via chemisorption are preferred. These systems should exhibit performance comparable to or exceeding amine-based sorbents while leveraging the unique non-volatility and stability of ILs.

Inspired by the amine-based CO_2 capture mechanism, where two amino groups integrate with one CO_2 molecule, forming a carbamate anion coupled with an ammonium cation and achieving an uptake capacity of 0.5 mol mol^{-1} (0.5 molar CO_2 being absorbed per molar of amine). Davis et al. introduced amino-functionalized ILs (AILs) in 2002 (Figure 4A).⁶² This approach involved integrating an amino ($-\text{NH}_2$) group into the alkyl chain of an imidazolium cation and pairing it with a $[\text{BF}_4]^-$ anion, yielding the IL ($[\text{BpNH}_2\text{im}][\text{BF}_4]$). Using pure CO_2 as the feeding gas, a weight increase of $7.4 \text{ wt\%}$ (close to 0.5 mol mol^{-1}) was observed at 1 bar and 295 K within 180 min. The formation of carbamate product was confirmed by FT-IR (a newly appeared absorption peak at 1666 cm^{-1}) and ^{13}C NMR spectroscopy (an additional signal at 158.11 ppm). To enhance CO_2 uptake capacity, dual functionalized ILs containing $-\text{NH}_2$ groups on both the cation and anion were developed (Figure 4B).⁹³ A series of ILs featuring amino-substituted phosphonium cations paired with amino acid anions were synthesized and characterized. Selected ILs with relatively low viscosity ($[\text{Gly}]$, $[\text{Ala}]$, $[\text{Val}]$, and $[\text{Leu}]$ anions) reached equilibrium uptake within 60 min, achieving capacities of $1.0 - 1.1 \text{ mol mol}^{-1}$. The carbamate formation pathway remained dominant due to the presence of two $-\text{NH}_2$ groups per IL molecule. An aqueous AIL solution containing a doubly functionalized imidazolium cation coupled with a Br^- anion achieved an uptake capacity of $18.5 \text{ wt\%}$ (close to 1.0 mol mol^{-1}) under ambient CO_2 pressure at 303.15 K .⁹⁴

AILs formed via multidentate coordination exhibited improved thermal stability compared to alkanolamine precursors, with decomposition onset temperatures reaching 319°C under N_2 atmosphere (Figure 4C).⁹⁵ These ILs featured Li^+ cation coordinated with the O and N atoms of alkanolamines and coupled with $[\text{NTf}_2]^-$ anion. Greater coordination number correlated with higher thermal stability. The coordination was confirmed by ^1H NMR spectroscopy, where downfield shifts in $-\text{CH}_2-$ and $-\text{NH}_2$ proton signals were observed. CO_2 uptake capacity of 0.52 and $0.90 \text{ mol mol}^{-1}$ were achieved for $[\text{Li}(\text{DEA})][\text{NTf}_2]$ and $[\text{Li}(\text{DOBA})][\text{NTf}_2]$, respectively. The formation of carbamate salt pathway was further supported by FT-IR (asymmetric carbonyl stretching at 1511 cm^{-1}), as well as ^{13}C NMR (an additional peak at 164.5 ppm).

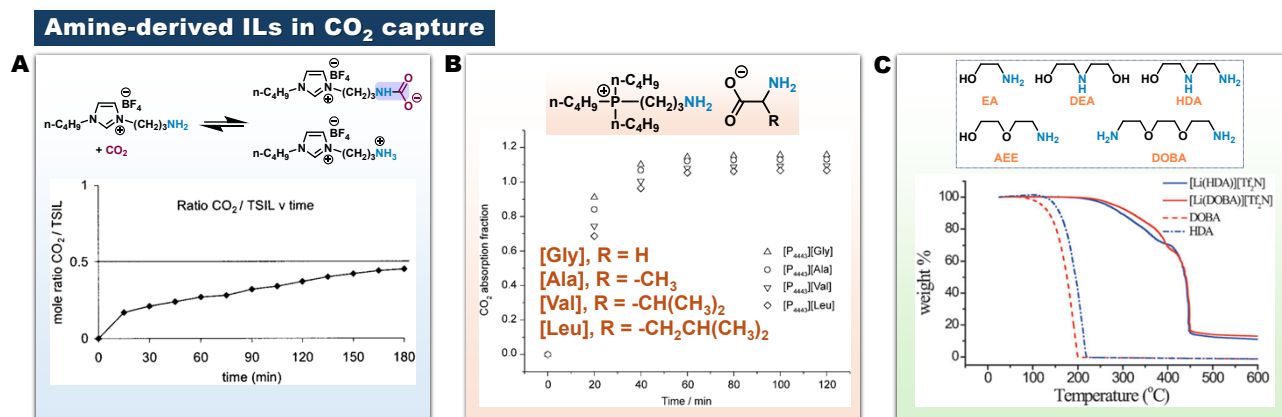


Figure 4. (A) CO₂ chemisorption by amine-derived ILs (AILs) through the integration of -NH₂ into the imidazolium cation,⁶² Reproduced with permission from Ref 62. Copyright 2002 American Chemical Society. (B) dual amino-functionalized ILs with amino acid anions,⁹³ Reproduced with permission from Ref 93. Copyright 2009 John Wiley & Sons and (C) alkanolamine-based ILs formed via multidentate cation coordination.⁹⁵ Reproduced with permission from Ref 95. Copyright 2012 Royal Society of Chemistry.

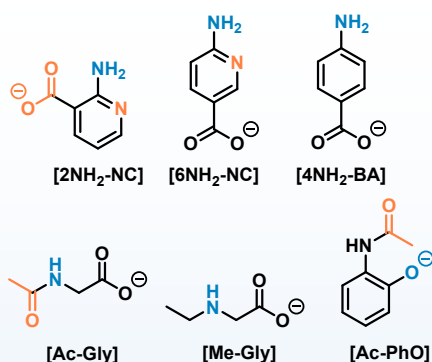
The viscosity of AILs upon CO₂ absorption can be influenced and reduced through controlled hydrogen bonding (Figure 5A).⁶³ Enhancing intramolecular hydrogen bonding, by incorporating hydrogen bond acceptors into anions, can mitigate excessive viscosity increases in CO₂-saturated systems. For instance, in [P₆₆₆₁₄][6NH₂-NC], hydrogen bonding between the pyridine N-sites and the carbamic acid (H-N bond distance: 1.62 Å) limited intermolecular hydrogen bonding, resulting in only a 3.9 fold viscosity increase after CO₂ absorption. Conversely, in [P₆₆₆₁₄][4NH₂-BA], where the pyridine ring was replaced by a benzene ring (lacking a hydrogen bond acceptor), viscosity increased 53.7 fold after CO₂ uptake. Introducing a carboxylate group at the ortho-position of -NH₂ (as in [P₆₆₆₁₄][2NH₂-NC]) further minimized viscosity changes (1.1 fold). Similar trends were observed in another IL set, where replacing an acetyl group (a hydrogen bond acceptor) in [P₆₆₆₁₄][Ac-Gly] with a methyl group in [P₆₆₆₁₄][Me-Gly] resulted in a significant viscosity increase only when CO₂ uptake exceeded 0.4 mol mol⁻¹.

Another challenge in AIL-based carbon capture is the high energy demand for CO₂ desorption. This energy requirement can be reduced by modulating the interaction strength between amino sites and CO₂. A promising approach involves coordinating metal cations with amine groups to integrate CO₂ capture and metal purification.⁹⁶ To this end, AILs were synthesized via coordination of amines with MNTf₂ salts (M = Ni, Mg, Cu, Zn, and Co) (Figure 5B).⁹⁷ Prior studies on metal organic frameworks (MOFs) demonstrated that different metal nodes influence CO₂ insertion in metal-amine bonds, resulting in stepped CO₂ uptake isotherms with varied site-specific CO₂ binding pressures.⁹⁸⁻¹⁰⁰ In the developed AILs, CO₂ uptake capacity was significantly affected by the coordinated metal cations. AILs containing Cu²⁺ exhibited low CO₂ uptake (0.07 mol mol⁻¹), whereas Mg²⁺ had negligible effects, maintaining a capacity of 0.50 mol mol⁻¹, similar to Li⁺. The CO₂ absorption trend correlated with M-N bond stability, following the order: Cu-N bond > Zn-N bond ~ Co-N bond > Ni-N bond > Mg-N bond > Li-N bond. The thermal stability of metal-containing AILs followed the same trend, as confirmed by TGA under N₂ atmosphere. CO₂ desorption behavior was investigated at 40-80 °C. Under identical desorption conditions (80 °C), n-octylamine released only 23% of absorbed CO₂

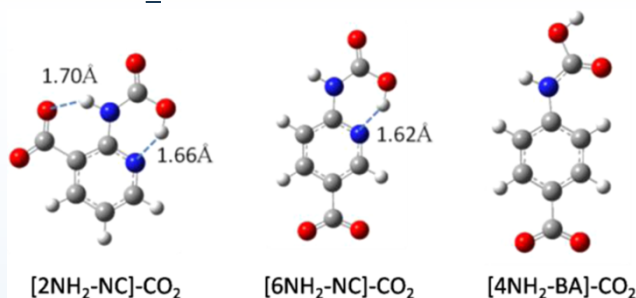
within 30 min, whereas Cu^{2+} - and Zn^{2+} -containing AILs released 100% and 91%, respectively. Although Mg-containing AILs exhibited similar uptake capacities to pure amine sorbents, their CO_2 desorption efficiency was higher (39%). The desorption process was further tunable by adjusting the metal-to-amine ratio, with higher metal loading reducing energy input for regeneration. The pressure-swing desorption study at 298 K confirmed that Cu^{2+} -containing AILs released more CO_2 than Zn^{2+} -containing AIL under low-pressure conditions. The tunability of metal cations in CO_2 chemisorption extends beyond ILs to primary amine sorbents and strong organic bases.^{97, 101}

A

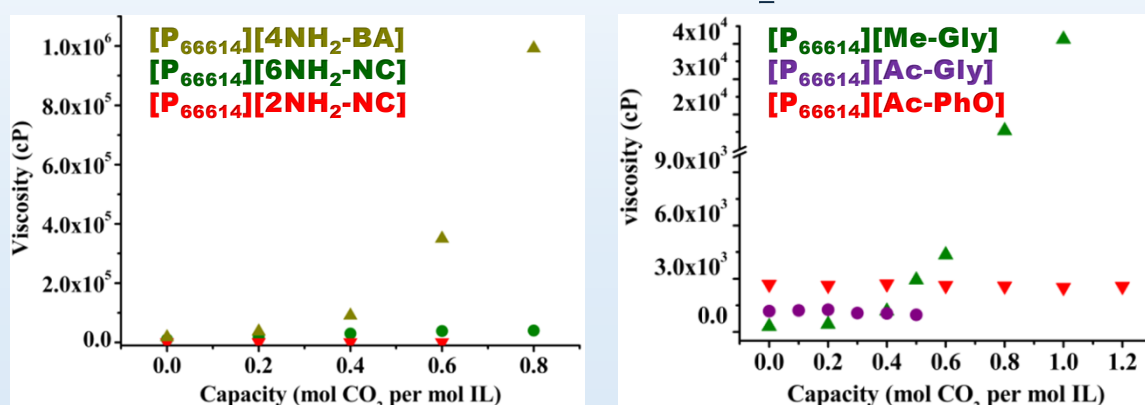
□ Anion structures



□ Optimized structures after reacting with CO₂



□ Viscosity change after reacting with CO₂

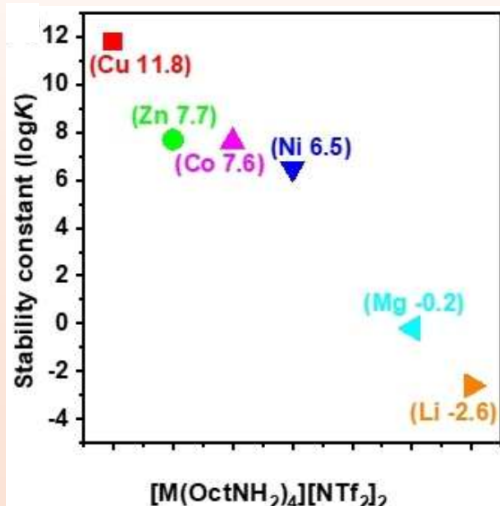


B

□ Structure of AILs via metal ion coordination and its reaction with CO₂



□ Stability constants of AILs with different metal cations



□ CO₂ desorption behavior of AILs affected by metal cations

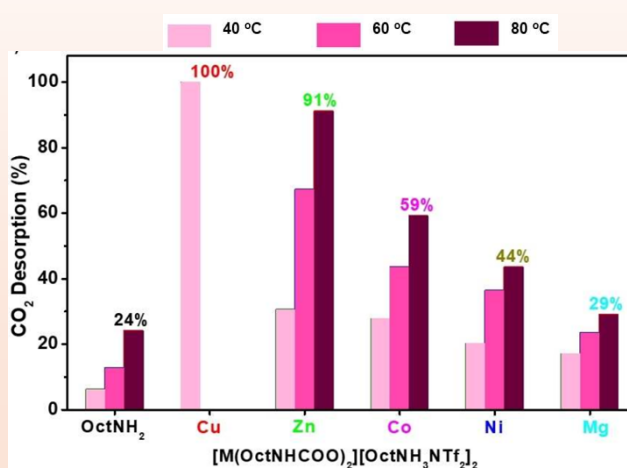


Figure 5. (A) Structures of AILs with enhanced intramolecular hydrogen bonding formation, together with the optimized structure after CO₂ integration and viscosity variation upon CO₂ absorption.⁶³ Reproduced with permission from Ref 63. Copyright 2016 American Chemical Society. (B) Structures of AILs synthesized via coordination with different metal cations and their reaction with CO₂; The stability constant of the as-synthesized AILs; Influence of metal cation-coordination on CO₂ desorption behavior.⁹⁷ Reproduced with permission from Ref 97. Copyright 2021 John Wiley & Sons.

Compared to ILs used for CO₂ physisorption, AILs significantly enhance CO₂ uptake via ammonium carbamate formation pathway.^{62, 93, 95} However, key limitations remain. Strong hydrogen bonding networks in pristine AILs and CO₂-loaded systems result in high viscosity and slow sorption kinetics.¹⁰² The strong C-N bond formation during CO₂ chemisorption leads to high reaction enthalpies (-90 kJ mol⁻¹ or lower), facilitating CO₂ capture but increasing energy consumption during desorption.¹⁰³ Two amine groups are required per CO₂ molecule integration, limiting uptake capacity.¹⁰⁴ Future research should focus on optimizing AIL structures and exploring alternative reaction pathways to enhance the CO₂ capture efficiency while reducing regeneration energy requirements.

2.4 Stabilization of carbamic acid products in amine-derived liquid sorbents

For amino-functionalized sorbents, including AILs, CO₂ capture follows an ammonium carbamate formation pathway, requiring a 2:1 molar ratio of amino groups to integrated CO₂ molecules.¹⁰⁵ Generally, carbamic acid forms as an intermediate before being deprotonated by another amino group. Therefore, strategies that stabilize carbamic acid could enable equimolar CO₂ uptake per amino site. AILs composed of a sterically hindered phosphonium cation ([P₆₆₆₁₄]) and either a proline ([Pro]) or methionine ([Met]) anion have been shown to achieve equimolar CO₂ absorption, stabilizing the carbamic acid product in the anion (**Figure 6A**).⁶⁴ Thermodynamic calculations indicate CO₂ reaction enthalpies of -71 kJ mol⁻¹ by [P₆₆₆₁₄][Pro] and -55 kJ mol⁻¹ by [P₆₆₆₁₄][Met]. The formation of the COOH moiety is evidenced by new peaks in the FT-IR spectra of CO₂-saturated [P₆₆₆₁₄][Pro] at 1689 cm⁻¹ and [P₆₆₆₁₄][Met] at 1718 cm⁻¹.

To further improve CO₂ uptake capacity, it is crucial to prevent the nucleophilic attack of a second amino group on the carbamic acid intermediate. This was accomplished by utilizing the coordination effect of crown ether with alkaline metal cations, resulting in highly sterically hindered cations (**Figure 6B**).⁶⁵ For instance, the ionic pair formed by 18-crown-6 (18C6)-coordinated K⁺ and the [Pro] anion exhibited a CO₂ uptake capacity of 0.99 mol mol⁻¹ at 298 K and 1 bar CO₂ pressure. Notably, CO₂ desorption was achieved at a low temperature (50 °C) with N₂ bubbling, and the sorbent demonstrated good stability over six cycles. The formation of carbamic acid was verified by a new peak at 157.7 ppm in the NMR spectra and at 1667 cm⁻¹ in the FT-IR spectra of [18C6-K][Pro] following CO₂ absorption. Theoretical simulations revealed that carbamic acid was stabilized via intramolecular hydrogen bonding within the anion, with a reaction enthalpy of -39.0 kJ mol⁻¹, indicative of moderate chemisorption and low energy input for desorption. Beyond ionic pairs, adding crown ether to primary amine sorbents also improved CO₂ uptake capacity to 0.69 mol mol⁻¹_{NH2}.¹⁰⁶ Spectroscopy and theoretical studies confirmed that carbamic acid was stabilized via complexation with crown ether (a strong hydrogen bond acceptor), resulting in a mixture of carbamic acid and ammonium carbamate in the CO₂-saturated product. The crown ether acted as a proton shuttle, transferring protons from ammonium cations to carbamate anions, thus promoting carbamic acid formation and freeing an -NH₂

site for further CO₂ uptake (Figure 6C).

The impact of steric hindrance on CO₂ chemisorption was further explored using amino acid salts containing bulky alkyl groups attached to amino sites.¹⁰⁷ Liquid sorbents composed of sodium N-alkylglycinates solubilized in poly(ethylene glycol) (PEG) were developed for CO₂ capture (Figure 6D). CO₂ uptake capacity at equilibrium (298 K and 1 bar CO₂ pressure) correlated directly with the steric hindrance of the alkyl chains, with *i*PrNH-GlyNa/PEG achieving 0.91 mol mol⁻¹. Furthermore, CO₂ desorption from the *i*PrNH-GlyNa/PEG mixture was facilitated at a low temperature (40 °C) with N₂ bubbling, and the sorbent remained stable over five cycles. The formation of carbamic acid was confirmed by new peaks at 1663 cm⁻¹ (FT-IR spectrum) and 161.4 ppm (¹³C NMR spectrum) of CO₂-saturated *i*PrNH-GlyNa/PEG. Theoretical simulations revealed that Na⁺ was complexed with PEG in the sorbent mixture (structure A), allowing CO₂ integration via carbamic acid formation (structure B) with a reaction enthalpy of -43.5 kJ mol⁻¹ or -10.4 kcal mol⁻¹. In contrast, further conversion to carbamate (structure C) via deprotonation of carbamic acid by another PEG-complexed *i*PrNH-GlyNa was endothermic (reaction enthalpy: 57.3 kJ mol⁻¹ or 13.7 kcal mol⁻¹), meaning it was not a spontaneous reaction. These findings highlight a promising approach to stabilize carbamic acid products through a combination of steric hindrance and solvent complexation.

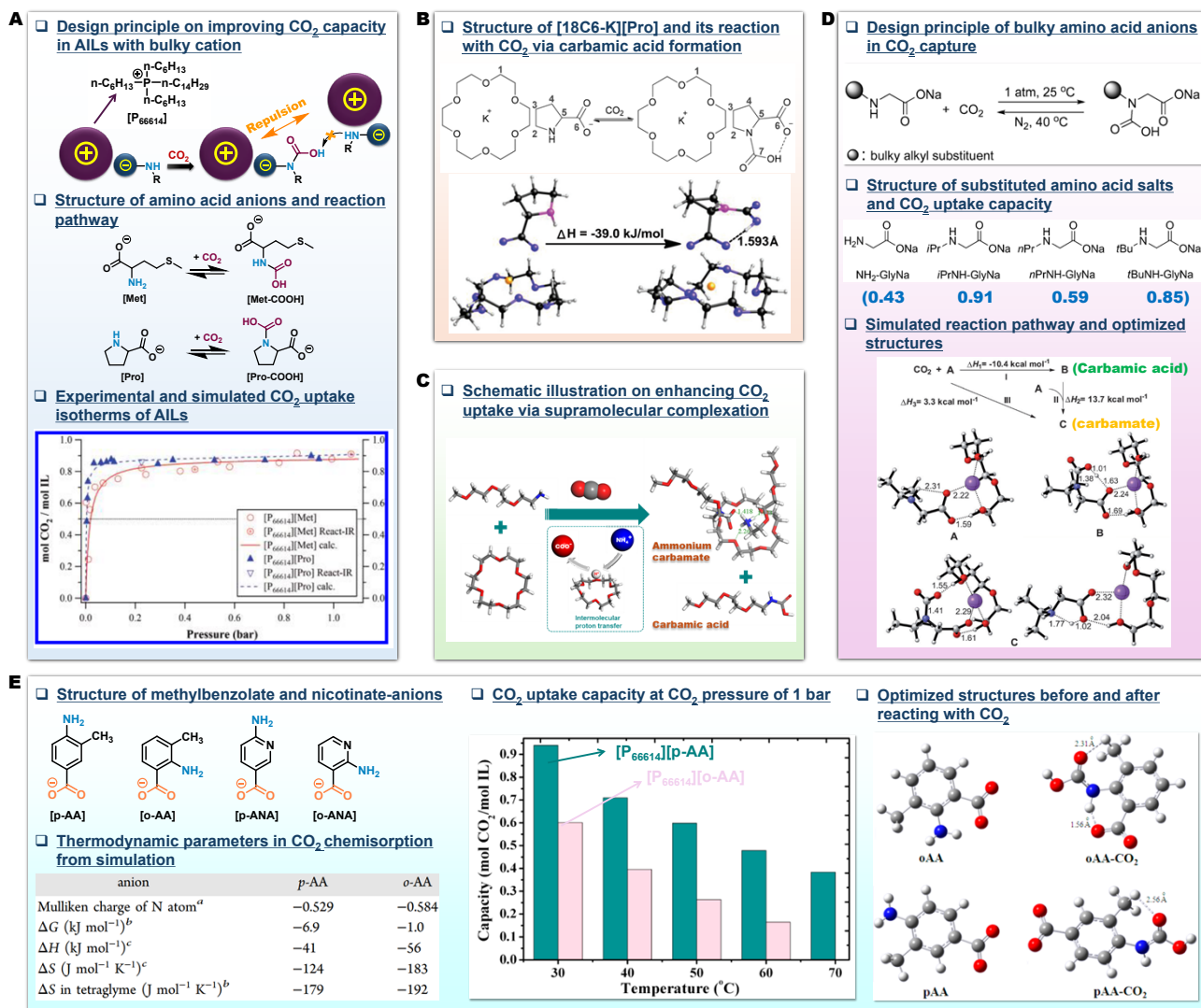


Figure 6. (A) Design principle of AILs with bulky cations to prevent carbamic acid deprotonation,

reaction pathway of amino acid anions with CO₂ via carbamic acid formation, and experimental vs. simulated CO₂ uptake isotherms of AILs.⁶⁴ Reproduced with permission from Ref 64. Copyright 2010 American Chemical Society. (B) Optimized structure of potassium proline ([Pro]) complexed with crown ether, along with its reaction pathway and enthalpy for CO₂ uptake via carbamic acid formation.⁶⁵ Reproduced with permission from Ref 65. Copyright 2014 Royal Society of Chemistry. (C) Schematic illustration of the formation of a carbamic acid and carbamate product mixture from a primary amine/crown ether mixture.¹⁰⁶ Reproduced with permission from Ref 106. Copyright 2024 John Wiley & Sons. (D) Reaction pathway of sodium amino acid salts with CO₂ via carbamic acid formation, influence of substituted alkyl groups at amino sites on CO₂ chemisorption (values in brackets indicate CO₂ capacity at 1 bar CO₂ pressure and 298 K), and theoretical energy profile comparing carbamic acid and carbamate formation.¹⁰⁷ Reproduced with permission from Ref 107. Copyright 2012 John Wiley & Sons. (E) Structure of methylbenzolate- and nicotinate-derived anions, thermodynamic parameters for CO₂ reactions with [o-AA] and [p-AA] anions from theoretical simulation, CO₂ uptake capacities of [P₆₆₆₁₄][o-AA] and [P₆₆₆₁₄][p-AA] at 1 bar CO₂ pressure across different temperatures, and optimized structures of [o-AA] and [p-AA] anions before and after CO₂ integration, highlighting hydrogen bonding formation.⁶⁶ Reproduced with permission from Ref 66. Copyright 2014 American Chemical Society.

A quantitative approach was developed to distinguish the captured CO₂ by several amino acid ILs composed of phosphonium cations ([P₆₆₆₁₄] and tetrabutylphosphonium ([P₄₄₄₄])) and deprotonated amino acid anions via different reaction pathway.¹⁰⁸ Three types of CO₂-integrated products were identified: ammonium carbamate (N_{1:2}), carbamic acid (N_{1:1}), and carbonate (N_{other}, referring to CO₂ bonded to the carboxylate group in the anion). The carbamic acid product (N_{1:1} pathway) could be precipitated and isolated by adding acetonitrile to the CO₂-saturated reaction mixture, while the other two products were classified via spectroscopic analysis. The results demonstrated that minor structural modifications to the anion led to significant differences in product distribution. For instance, the majority of CO₂ captured by [P₄₄₄₄][Pro] (0.88±0.11 mol mol⁻¹) was in the form of carbamic acid (0.81 mol mol⁻¹ from N_{1:1} pathway). In contrast, [P₄₄₄₄][Met] (capacity: 0.93±0.08 mol mol⁻¹) exhibited a mixed CO₂ integration pathway, with contributions of 0.26 mol mol⁻¹ from N_{1:2}, 0.48 mol mol⁻¹ from N_{1:1}, and 0.19 mol mol⁻¹ from N_{other}. Substituting [P₄₄₄₄] with the more sterically hindered [P₆₆₆₁₄] slightly improved CO₂ absorption capacity due to the increased cation-anion separation, which also enhanced the contribution of the N_{1:1} pathway.

Beyond steric hindrance effects from substitutes near amino functionalities, hydrogen bonding network formation in carbamic acid intermediates/products can be leveraged to tune CO₂ chemisorption performance. In methylbenzolate-derived AILs, the position of the -NH₂ group on the benzene ring significantly influenced CO₂ integration (Figure 6E).⁶⁶ Although the Mulliken charge on the nitrogen atom in the [o-AA] anion (-0.584) was more negative than in the [p-AA] anion (-0.529), and [o-AA] exhibited a more negative reaction enthalpy with CO₂ (-56 kJ mol⁻¹) compared to [p-AA] (-41 kJ mol⁻¹), the CO₂ uptake capacity of [P₆₆₆₁₄][o-AA] was lower than that of [P₆₆₆₁₄][p-AA] across different temperatures (Figure 6E). Spectroscopic analysis and theoretical simulations revealed that entropy-driven hydrogen bonding network formation governed the CO₂ insertion process. In the [o-AA] anion, CO₂ insertion and subsequent carbamic acid formation favored intramolecular hydrogen bonding, between C=O (from CO₂) and the methyl group, as well as between N-H and C=O (from the [o-AA] anion). In contrast, in the CO₂-bound [p-AA] anion, the greater spatial separation led to a

preference for intermolecular hydrogen bonding network formation, which resulted in a more favorable entropy change for CO₂ insertion. This was consistent with the higher viscosity observed in the [p-AA]-based system compared to the [o-AA]-based system, both before and after CO₂ absorption. A similar trend was observed in nicotinate-based AILs containing [p-ANA] and [o-ANA] anions, where the former exhibited higher CO₂ absorption capacity due to extensive intermolecular hydrogen bonding network formation (Figure 6E).

2.5 Superbase-derived ionic liquids in CO₂ chemisorption

Beyond amine-based systems, CO₂ can react with a mixture of an organic base and proton donors (e.g., alcohol), forming ionic pairs composed of a protonated base as the cation and carbonate as the anion.¹⁰⁹ The transformation from a neutral system to a highly polar reaction medium upon CO₂ absorption has been leveraged for the reversible phase transfer of noble metal complexes in homogeneous catalysis.¹¹⁰⁻¹¹² Building upon these preliminary studies, superbase-derived protic ILs (denoted as PILs) were developed in 2010 to provide IL sorbents with low viscosity, enhanced CO₂ capacity, and tunable interaction strength.⁴⁹ The PILs were synthesized via the deprotonation of weak proton donors by superbases (Figure 7A). Using MTBD and EtP₂ as superbases, a series of PILs incorporating anions such as fluorinated alcoholates (TFE, HFPD, and TFPA), imidazolate (Im), pyrrolidinide (Pyrr), and phenolate (PhO) were synthesized and applied in CO₂ chemisorption. At 298 K and 1 bar CO₂ pressure, [MTBDH][TFE] achieved a CO₂ uptake capacity of 1.13 mol mol⁻¹ within 10 min, while [MTBDH][HFPD] captured over 2.0 mol mol⁻¹ within 60 min, corresponding to a gravimetric increase of up to 16 wt% due to CO₂ absorption. The uptake kinetics were significantly faster than those of AIL sorbents, benefiting from PILs' low viscosity (as low as 8.63 cP). CO₂ capture in these PILs occurred via N-C or O-C bond formation, generating carbamate and carbonate products. Gas-phase energetic simulations revealed that reaction enthalpy correlated with anion basicity, following the trend: [TFE] (-116.8 kJ mol⁻¹) < [Im] (-85.2 kJ mol⁻¹) < [PhO] (-41.7 kJ mol⁻¹).¹¹³⁻¹¹⁶ The regeneration of [MTBD][Im] was achieved by bubbling N₂ through the CO₂-saturated mixture at 80 °C within 10 min. Nitroalkanes have emerged as promising proton donors for carbon capture, with their deprotonation behavior in the presence of organic superbase being extensively studied.¹¹⁵ PILs with [NTf₂] anion, synthesized via a neutralization-anion exchange approach, exhibited thermal stability comparable to conventional ILs used in CO₂ physisorption.¹¹⁷ Notably, PILs' ability to absorb and activate CO₂ made them highly effective in catalyzing the cycloaddition of 2-aminobenzonitriles with CO₂, yielding quinazoline-2,4(1H,3H)-diones in high yields with good recyclability.¹¹⁸

Hydroxyl-functionalized ILs ([Im₂₁OH][NTf₂] and [N_{ip,211}OH][NTf₂]) (Figure 7A) have been deployed as proton donors to mitigate the volatilization issues associated with alcohols.¹¹⁹ When combined with organic superbases of varying basicity, efficient CO₂ chemisorption was achieved, with CO₂ uptake capacity of 0.98-1.04 mol mol⁻¹_(superbase) obtained within 30 min using DBU and MTBD. The formation of liquid amidinium alkylcarbonate salts via O-C bond formation upon CO₂ absorption was identified by IR and NMR spectroscopy. The CO₂ absorption isotherm of [Im₂₁OH][NTf₂]-DBU at 293 K showed that the equilibrium was reached within 10 min, with 80% CO₂ uptake occurring within the first 5 min. Captured CO₂ could be released at 120 °C within 15 min, allowing efficient sorbent regeneration.

ILs with imidazolium cations paired with various anions can serve as proton donors for CO₂ capture in the presence of an organic base by utilizing the weak acidity of the proton on C-2 in imidazolium (pK_a ~24.0 in DMSO), resulting in carboxylate formation through C-C bond formation.

(Figure 7A).¹²⁰ Equimolar CO₂ uptake was observed when DBU was combined with [Bmim][NTf₂], whereas uptake decreased to 0.80 and 0.75 when using [Bmim][BF₄] and [Bmim][PF₆], respectively, due to increased viscosity in these mixtures upon CO₂ absorption. Strong bases (e.g., DBU and MTBD) were necessary for equimolar CO₂ capture, whereas using a weaker base such as TMG with [Bmim][NTf₂] resulted in reduced uptake (0.49 mol mol⁻¹) due to strong hydrogen bonding between the carboxylate product and guanidinium cation. Water had minimal impact on uptake capacity, though bicarbonate formation was observed via NMR. In the [Bmim][NTf₂]/DBU system, CO₂ could be released at 80 °C under N₂ flow within 20 min, with sorbents being recyclable for at least four cycles without significant capacity loss.

The CO₂ chemisorption behavior of PILs and superbase/proton donor systems highlights their strong potential for carbon capture via O-C, N-C, and C-C bond formation, offering improved capacity, stability, and rapid kinetics. Theoretical simulations indicated that CO₂ uptake performance closely correlated with charge distribution on oxygen sites in alcoholate or phenolate anions.¹²¹ Additionally, anions with conjugated aza-fused ring structures played a critical role in CO₂ integration.¹²² A series of superbase ILs (SILs) featuring nitrogen-containing anions coupled with trihexyltetradecylphosphonium ([P₆₆₆₁₄]) were synthesized to optimize CO₂ absorption/desorption behavior while minimizing energy consumption for sorbent regeneration (Figure 7B).⁶⁷ These SILs exhibited high thermal stability, with decomposition temperature exceeding 340 °C under an inert atmosphere. CO₂ absorption capacities ranged from 0.08 mol mol⁻¹ ([P₆₆₆₁₄][Tetz]) to 1.02 mol mol⁻¹ ([P₆₆₆₁₄][Pyr]), increasing with anion pK_a from 8.2 to 13.9 and plateauing near equimolar uptake at pK_a values above 19.8. Fast CO₂ absorption kinetics were observed, with equilibrium reached within 10 min (Figure 7B). This was attributed to the low viscosity of SILs upon CO₂ absorption, as no hydrogen bonding was involved, contrasting with AILs. For instance, [P₆₆₆₁₄][Im] exhibited decreased viscosity after CO₂ uptake. Carbamate formation in SILs was confirmed by NMR and IR spectroscopy, with new peaks at 1711 cm⁻¹ (IR) and 163.0 ppm (¹³C NMR) appearing upon CO₂ absorption by [P₆₆₆₁₄][Im]. Theoretical simulations demonstrated a direct correlation between reaction enthalpy and anion basicity, yielding values of -19.1, -56.4, and -89.9 kJ mol⁻¹ for [Tetz] (pK_a = 8.2), [Triz] (pK_a = 13.9), and [Im] (pK_a = 18.6) respectively. A rough linear relationship was elucidated between anion pK_a and absorption enthalpy (Figure 7B). TGA analysis of CO₂-saturated SILs indicated that higher anion basicity required higher regeneration temperatures. Considering performance in capacity (0.95 mol mol⁻¹), kinetics, and regeneration temperature (80 °C under N₂ within 20 min), [P₆₆₆₁₄][Triz] was selected for cycling studies, demonstrating stable CO₂ capture over 25 cycles. A two-stage CO₂ sorption process was elucidated via ¹³C-labeled CO₂ experiments, revealing an initial physical adsorption phase followed by chemisorption-dominated uptake.¹²³

In SILs synthesis, traditional neutralization reactions involving phosphonium hydroxide and N-heterocyclic precursors in aqueous or alcoholic solutions required tedious solvent removal and purification step. Residual solvents also impacted CO₂ absorption and SIL stability. An optimized approach was developed, where high-purity SILs were synthesized via anion exchange between phosphonium halides and deprotonated N-heterocycles (prepared using NaH), precipitating sodium halide salts.¹²⁴ This solvent-free method employed nonpolar solvents such as tetrahydrofuran (THF) and acetonitrile (CH₃CN) for improved product quality.

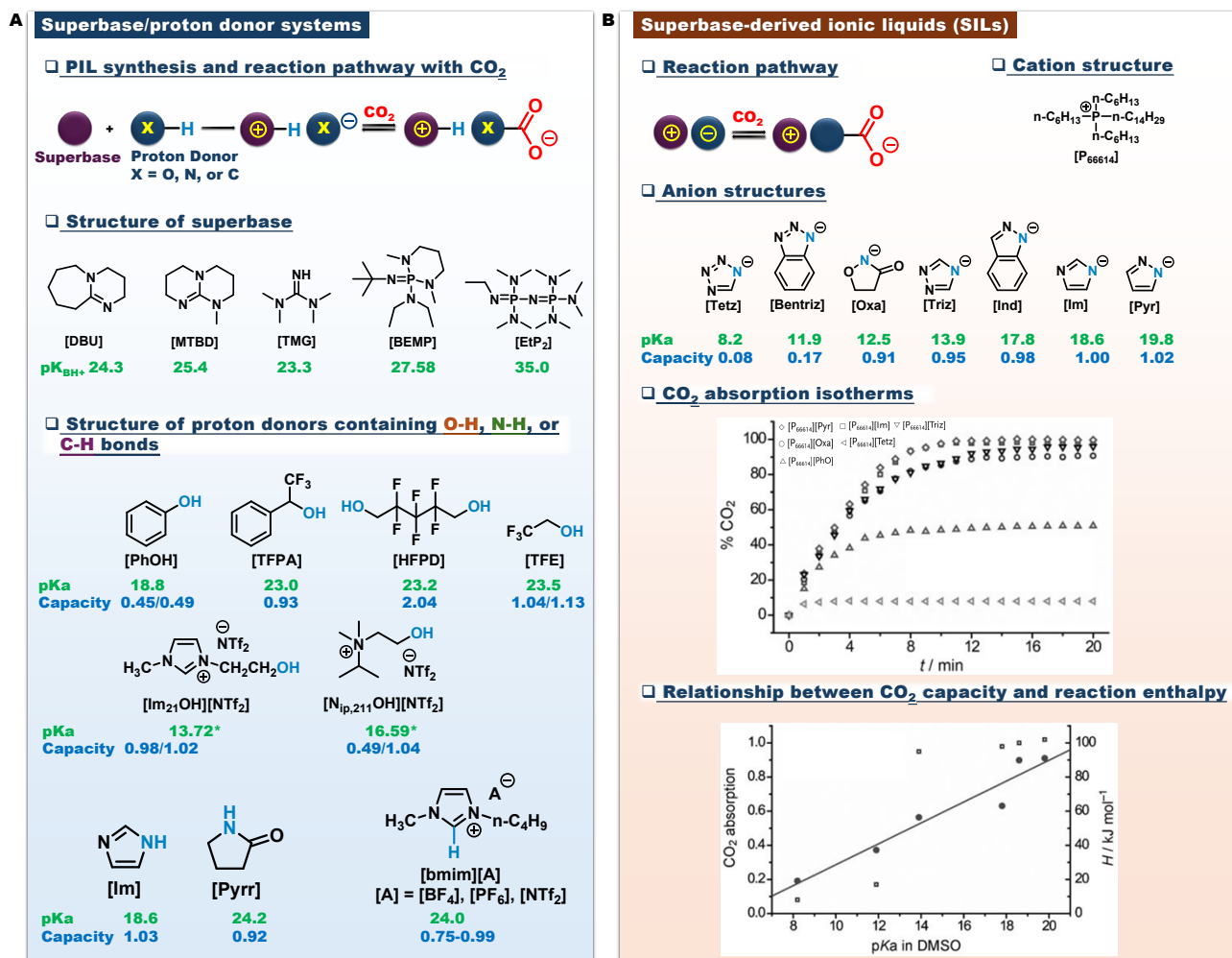


Figure 7. (A) CO₂ chemisorption achieved by superbase/proton donor systems, illustrating the CO₂ insertion mechanism, the structure and basicity of the superbases (pK_a of the conjugated acid) and proton donors containing N-H, O-H, or C-H bonds. Additionally, CO₂ uptake capacity (mol mol⁻¹) is presented.^{49, 119} *The pK_a values are predicted using a reported computational program.¹²⁵ (B) Structures of SILs with varying pK_a values and their CO₂ uptake capacities at 1 bar and 298 K, along with CO₂ absorption isotherms. The relationship between the pK_a values of anions, CO₂ uptake capacity, and reaction enthalpy from theoretical simulations for selected SILs is also shown.⁶⁷ Reproduced with permission from Ref 67. Copyright 2011 John Wiley & Sons.

A series of SILs composed of phenolate anions coupled with the [P₆₆₆₁₄] cation were developed, leveraging the position and electronic properties of substitutes on the benzene ring to tune CO₂ chemisorption behavior. Both electron-donating groups (-OCH₃ and -CH₃) and electron-withdrawing groups (e.g., -Cl, -NO₂, and -CF₃) were explored (Figure 8A).⁶⁸ The viscosity of the SILs varied depending on both the electronic property and the position of the substitutes, with [P₆₆₆₁₄][3-Cl-PhO] exhibiting the lowest viscosity (223.2 cP at 295 K). Regarding density, SILs containing phenolate anions with -Cl or -OMe groups showed relatively higher densities than others. These SILs exhibited exceptional thermal stability, with onset decomposition temperatures between 180-360 °C under N₂. However, SILs with anions of higher pK_a values exhibited lower thermal stability. In general, electron-donating groups enhanced CO₂ uptake capacity compared to electron-withdrawing groups. For

instance, $[P_{66614}][4\text{-Me-PhO}]$ achieved a CO_2 uptake of $0.91 \text{ mol mol}^{-1}$, while $[P_{66614}][4\text{-NO}_2\text{-PhO}]$ only reached $0.30 \text{ mol mol}^{-1}$, with equilibrium attained within $\sim 10 \text{ min}$ (Figure 8A). Among Cl-substituted phenolate anions, $[P_{66614}][4\text{-Cl-PhO}]$ exhibited the highest CO_2 uptake capacity ($0.82 \text{ mol mol}^{-1}$), followed by $[P_{66614}][3\text{-Cl-PhO}]$ ($0.72 \text{ mol mol}^{-1}$) and $[P_{66614}][3\text{-Cl-PhO}]$ ($0.67 \text{ mol mol}^{-1}$). The presence of more electron-withdrawing groups correlated with lower CO_2 uptake due to decreased basicity. Theoretical simulations revealed an almost linear relationship between Mulliken charge on the oxygen sites and CO_2 binding strength of phenolate anions with different substitutes (Figure 8A). $[P_{66614}][4\text{-Cl-PhO}]$ also exhibited excellent recyclability with additional 3.2% water, with regeneration occurring at 80°C within 60 min under N_2 flow. Beyond CO_2 uptake capacity, substitutes on phenolate anions significantly influenced physical properties and CO_2 sorption kinetics.¹²⁶ In fluorine-substituted phenolic ILs coupled with $[P_{4444}]$ cation, viscosities reached as low as 64.8 cP at 303.2 K, enabling rapid CO_2 uptake and equilibrium within 4 min (uptake capacity: $0.84 \text{ mol mol}^{-1}$ at 1 bar and 313.2 K).

The effect of π -conjugation in phenolate-type anions on CO_2 chemisorption was investigated by comparing $[\text{PhO}]$ -derived SILs with conjugated counterparts including $[\text{PCCPhO}]$, $[\text{PPhO}]$, and $[\text{PNNPhO}]$ (Figure 8B).⁶⁹ CO_2 uptake capacities for $[P_{66614}][\text{PPhO}]$ and $[P_{66614}][\text{PCCPhO}]$ were 0.93 and $0.96 \text{ mol mol}^{-1}$ respectively, significantly higher than $[P_{66614}][\text{PhO}]$ ($0.73 \text{ mol mol}^{-1}$). Interestingly, despite lower pK_a values of $[\text{PPhO}]$ (9.55) and $[\text{PCCPhO}]$ (9.3) compared to $[\text{PhO}]$ (10), and the Mulliken charges of oxygen atoms in the former anions was less negative compared with $[\text{PhO}]$, CO_2 uptake capacity followed the opposite trend. For CO_2 desorption, phenolate anions with conjugated structures facilitated easier CO_2 release. For example, CO_2 absorbed by $[P_{66614}][\text{PNNPhO}]$ completely desorbed at 120°C . Further NMR studies confirmed that the enhanced CO_2 uptake resulted from strengthened C-O interactions due to the aggregation of planar π -conjugated anions. Additionally, electron delocalization in these anions improved CO_2 desorption efficiency and reduced energy consumption.

Sulfur dioxide (SO_2) is another acidic gas present in flue gas ($\sim 0.2 \text{ vol}\%$) and gas streams from catalytic processes, requiring efficient absorption techniques to mitigate environmental and industrial impacts.¹²⁷ SILs composed of $[\text{Tetz}]$ or $[\text{Im}]$ anions coupled with phosphonium cation demonstrated exceptional SO_2 capture capacity, reaching 3.72 and $4.80 \text{ mol mol}^{-1}$, respectively, at 1 bar SO_2 pressure and 298 K (Figure 8C).¹²⁸ Notably, SO_2 captured by $[P_{66614}][\text{Tetz}]$ could be fully desorbed at 80°C under N_2 flow, whereas $[P_{66614}][\text{Im}]$ retained $\sim 0.7 \text{ mol mol}^{-1}$ of SO_2 under the same conditions. Due to stronger acidity of SO_2 compared to CO_2 , optimizing the balance between uptake capacity and desorption energy is crucial when selecting SILs for SO_2 chemisorption. $[P_{66614}][\text{Tetz}]$ emerged as an effective sorbent, exhibiting stable recyclability over 28 cycles. Theoretical simulations indicated that the four nitrogen sites in $[\text{Tetz}]$ interacted with SO_2 at varying strengths (-34.4 to $-89.3 \text{ kJ mol}^{-1}$), where two sites underwent chemisorption, and two sites facilitated physisorption. In contrast, the $[\text{Im}]$ anion exhibited a more negative reaction enthalpy with SO_2 (-30.3 to $-124.6 \text{ kJ mol}^{-1}$). Structure evolution during SO_2 absorption was characterized using FT-IR spectroscopy and ^1H , ^{13}C , and ^{15}N NMR spectra. A Lewis-basic IL composed of 1,4-diazobicyclo[2.2.2]octane (DABCO) cation with a PEG chain ($[\text{PEG-DABCO}]$) and $[\text{NTf}_2]$ anion achieved a SO_2 capacity of 4.4 mol mol^{-1} at 1 bar SO_2 pressure and 298 K.¹²⁹ Even at a diluted SO_2 partial pressure (0.1 bar), a substantial $1.01 \text{ mol mol}^{-1}$ uptake was retained, with desorption at 298 K via N_2 bubbling, ensuring recyclability over five cycles. Beyond direct capture, SO_2 absorbed in these ILs could be converted into cyclic sulfites via reaction with epoxides. Similar to CO_2 chemisorption, SO_2 capture and release performance could be fine-tuned by

adjusting basicity of liquid sorbents. For example, in a binary mixture of PEG and an organic base, a SO_2 uptake capacity of $1.79 \text{ mol mol}^{-1}$ at 298 K and low SO_2 partial pressure (0.1 bar diluted in N_2) was obtained using PEG-functionalized imidazole, leading to imidazolium sulfonate formation. Notably, this captured SO_2 could be released via N_2 bubbling without heating. This binary system functioned as both a sorbent to concentrate and active SO_2 from diluted sources and a catalyst to promote cyclic sulfite formation via epoxides cycloaddition.¹³⁰

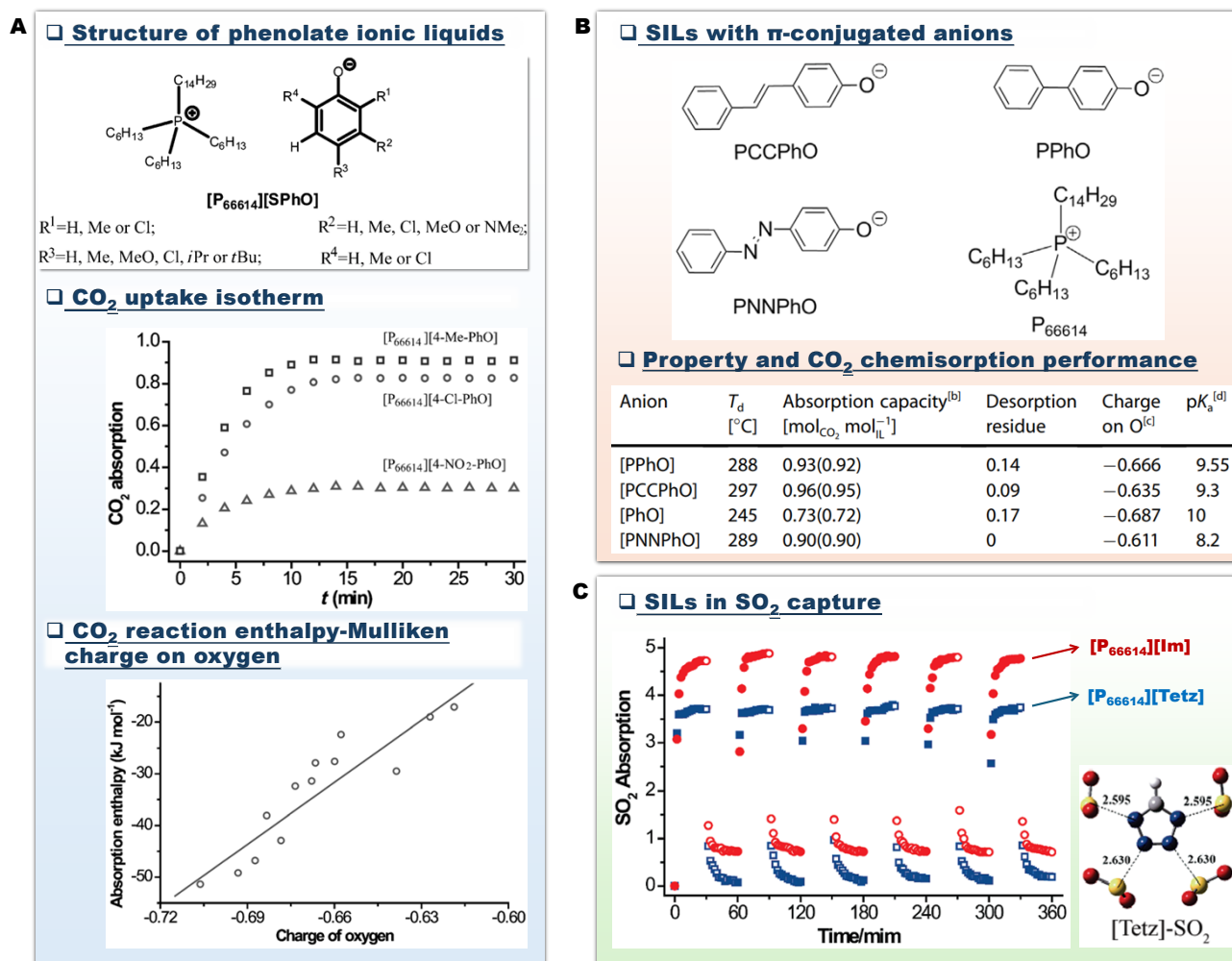


Figure 8. (A) Structure of SILs with phenolate anions, CO_2 uptake isotherms, and the relationship between the Mulliken charge on oxygen sites and the CO_2 absorption enthalpy from simulations.⁶⁸ Reproduced with permission from Ref 68. Copyright 2012 John Wiley & Sons. (B) Structure of SILs with π -conjugated anions, along with their properties and CO_2 chemisorption performance.⁶⁹ Reproduced with permission from Ref 69. Copyright 2016 John Wiley & Sons. (C) SO_2 absorption/desorption cycles of $[\text{P}_{66614}][\text{Tetz}]$ and $[\text{P}_{66614}][\text{Im}]$, along with the optimized structure of four SO_2 -integrated $[\text{Tetz}]$ anion.¹²⁸ Reproduced with permission from Ref 128. Copyright 2011 American Chemical Society.

2.6 Structure engineering of ionic liquids for enhanced stability

For IL sorbents used in CO_2 capture, beyond uptake capacity and energy input for regeneration,

thermal and chemical stability, as well as long-term durability, are crucial for practical application, especially in the presence of competing gas impurities such as O₂, SO₂, NO_x, and water.¹³¹ A key challenge in amine-based sorbents is oxidative degradation caused by O₂ or O₃ in ambient air. Structure modifications, such as alkylation or chelator functionalization, can tune the electronic properties of amine sites or neutralize redox-active metal impurities, thereby improving oxidation resistance.¹³² IL sorbents for carbon capture, particularly those relying on chemisorption, often contain anions with high basicity, making them susceptible to side reactions involving electron-withdrawing cations or acidic C-H sites. Ylide formation involving phosphonium cations ([P₆₆₆₁₄] or [P₄₄₄₂]) has been observed in SILs with azolide anions.¹³³ At 298 K, CO₂ reacts with the 2-cyanopyrrolide ([2-CNpyr]) anion via carbamate formation (N-C bonding). However, at 60 °C, additional spectral features (e.g., a newly appeared FT-IR peak at 1730 cm⁻¹, as well as a doublet at 32-33 ppm in ³¹P NMR) indicate cation involvement in CO₂ integration. Experimental and theoretical studies confirm ylide formation and carboxylate product generation at elevated temperatures. Control experiments reveal that the ammonium-based ILs, with lower acidity, are more stable and less prone to ylide formation. The proportion of ylide-derived carboxylate and carbamate products is influenced by anion basicity, steric hindrance, and reaction temperature.¹³⁴ Generally, anions stronger basicity and less steric hindrance led to more carboxylate product formation and CO₂ chemisorption at higher temperatures afforded more cation-involved carboxylate product.^{135, 136}

In phenolate-derived SILs, both carbonate (O-C bond formation) and carboxylate (C-C bond formation) products are detected, corresponding to FT-IR peaks at 1730 and 1635 cm⁻¹ respectively.¹³⁷ For SILs with stronger basicity, such as [P₆₆₆₁₄][4-MeOPhO], C-C bond formation dominates at CO₂ pressures of 0.1-1.3 bar, while increased pressure promotes O-C bond formation. Reduced steric hindrance in [P₆₆₆₁₄][PhO] favors ylide intermediates, whereas electron-withdrawing groups (e.g., -NO₂ in [P₆₆₆₁₄][4-NO₂PhO]) suppress chemisorption, allowing only physisorption. NMR and theoretical analyses further elucidate the reactivity and stability trends of phosphonium cations in different phenolate SILs. Although initial CO₂ uptake remains unaffected by ylide formation, irreversible volatilization of neutral azole or phenol products can lead to sorbent degradation over time.

Theoretical studies suggest that sorbents with a reaction enthalpy of around -68.5 kJ mol⁻¹ are ideal for DAC applications (CO₂ concentration: 400 ppm), ensuring near equimolar uptake at equilibrium and >90% CO₂ release at 100 °C (Figure 2C).^{74, 138} The reaction enthalpy of phenolate anions with CO₂ is approximately -56.56 kJ mol⁻¹ and can be tuned via benzene ring substitutes, making them promising for carbon capture from diluted sources.^{70, 139} However, their long-term stability is compromised by oxidative degradation via radical induced phenolate-to-benzoquinone transformation.¹⁴⁰⁻¹⁴² To enhance chemical stability and oxidation resistance, phosphonium-based SILs incorporating pyrazolonate anions have been developed (Figure 9).⁷⁰ At 1 bar CO₂ pressure and 298 K, uptake capacity follows anion basicity trend, influenced by oxygen site positioning and alkyl substitute effects. [P₆₆₆₁₄][3-HMPz], with a pK_a of 8.57, exhibits a CO₂ uptake of 0.96 mol mol⁻¹, surpassing [P₆₆₆₁₄][PhO] (pK_a = 10.0) despite lower basicity. Theoretical simulations attribute this to reduced steric hindrance, minimizing repulsion between the carbonate unit and the five-membered ring. FT-IR (1620 cm⁻¹) and ¹³C NMR spectra (159.4 ppm) confirmed O-C bond formation upon CO₂ uptake. To prevent ylide formation, previously observed in phenolate-derived SILs, a crown ether-complexed Na⁺ cation was introduced, eliminating active protons. This modification maintains equimolar CO₂ uptake while confirming O-C bond formation via NMR analysis. Comparative stability tests under oxidative conditions reveal that Na[PhO] undergoes quinone byproduct formation, whereas Na[3-

HMPz] remains stable. ^{31}P NMR analysis indicates that after air exposure, 32% of $[\text{P}_{66614}][\text{PhO}]$ cations are oxidized to phosphine oxide via ylide formation, compared to only 4% in $[\text{P}_{66614}][3\text{-HMPz}]$. Beyond enhanced CO_2 capture and stability, pyrazolonate-based SILs also exhibited catalytic activity in propargylic-to- α -hydroxy ketone transformations, where CO_2 -assisted α -alkylidene cyclic carbonate intermediates are formed.

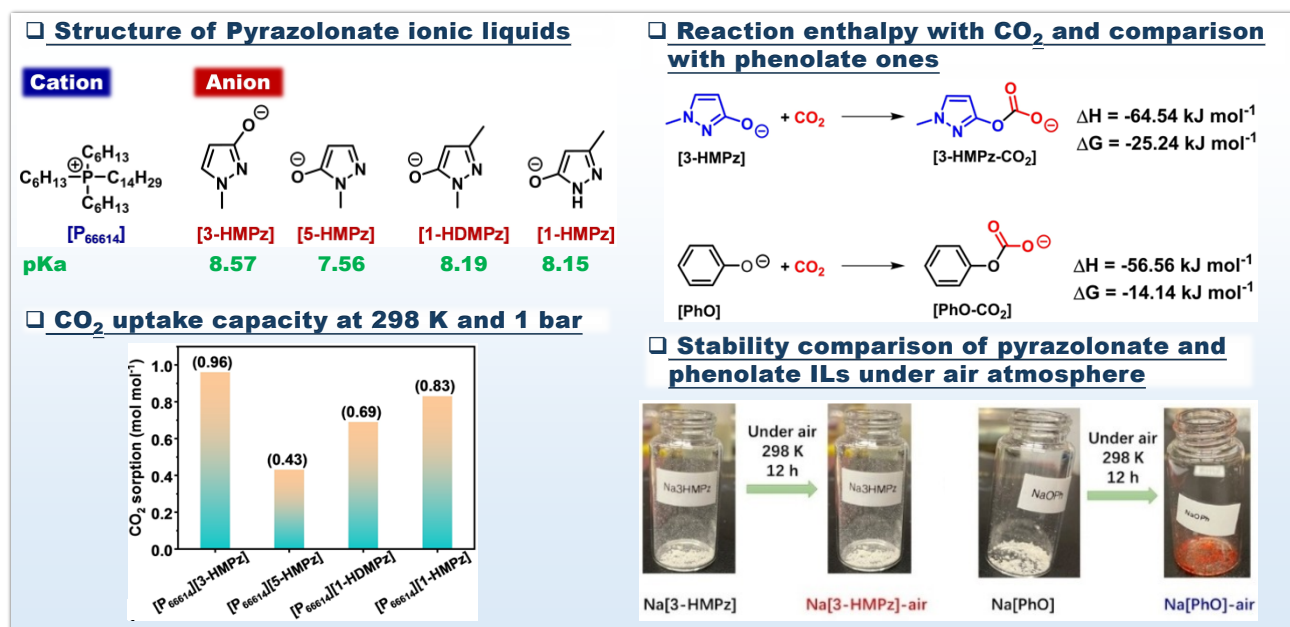


Figure 9. Structures of pyrazolonate SILs, their CO_2 uptake capacity at 298 K and 1 bar, and a comparison of reaction enthalpy in CO_2 chemisorption and air stability between pyrazolonate and phenolate SILs.⁷⁰ Reproduced with permission from Ref 70. Copyright 2023 John Wiley & Sons.

2.7 Multiple sites ionic liquids for enhanced CO_2 uptake capacity

For SILs containing a single active site in the anion, the maximum CO_2 uptake capacity is typically limited to equimolar absorption. To overcome this limitation, multiple-site SILs have been developed to enhance CO_2 uptake through cooperative interactions. Replacing the phenyl ring in phenolate-derived SILs with a pyridine ring resulted in SILs with two active sites for CO_2 integration (Figure 10A).⁷¹ The CO_2 uptake capacity exceeded equimolar levels ($1.38\text{--}1.65 \text{ mol mol}^{-1}$) and was influenced by the nitrogen site location and the presence of electron-donating groups on the pyridine ring. Temperature and pressure studies revealed that most CO_2 uptake occurred at low pressure, with $[\text{P}_{66614}][2\text{-Op}]$ achieving $1.28 \text{ mol mol}^{-1}$ at 0.1 bar and 293 K, increasing to $1.58 \text{ mol mol}^{-1}$ at 1 bar. Theoretical simulations of Mulliken atomic charges indicated that, compared to pure pyridine (-0.161 of N), the nitrogen charge in $[2\text{-Op}]$ was more negative (-0.323) due to the π -conjugated structure of the anion and charge delocalization from the oxygenate site to the pyridine ring. Consequently, the nitrogen sites became basic enough to react with CO_2 . Two distinct CO_2 integration pathways were observed in $[2\text{-Op}]$, O-C and N-C bond formation, corresponding to new peaks at 1650 and 1670 cm^{-1} (FT-IR spectra) and 159.5 for carbonate and 166.6 ppm for carbamate (^{13}C NMR spectra). In situ IR and NMR studies confirmed that O-C bond formation occurred first, followed by N-C bond formation as CO_2 loading increased. A similar activation effect was observed in imidazolate-derived SILs when an additional $-\text{CHO}$ group was introduced on the five-membered ring, enhancing CO_2 interaction with

the C=O group and increasing uptake from 0.98 mol mol⁻¹ in [P₆₆₆₁₄][Im] to 1.24 mol mol⁻¹ in [P₆₆₆₁₄][4-CHO-Im].¹⁴³

Aminopolycarboxylate-based ILs (APC-ILs) were designed to capture multiple CO₂ molecules per mole of SIL by utilizing both amino and carboxylate sites (Figure 10B).⁷² For instance, [P₄₄₄₂]₂[IDA] achieved a CO₂ capacity of 1.69 mol mol⁻¹ (13 wt%) at 1 bar and 40 °C. CO₂ can be released at 80 °C under vacuum, demonstrating good reversibility over five cycles. Thermodynamic simulations indicated that the amino group in [IDA] initially reacted with CO₂ with a reaction enthalpy -89.0 kJ mol⁻¹ (ΔH₁), followed by activation of the carboxylate group with ΔH₂ = -52.8 kJ mol⁻¹, within the chemisorption range and more negative than acetate-CO₂ interaction (-34.2 kJ mol⁻¹). The two carboxylate groups in [IDA] played a crucial role, as [H-IDA], with one carboxylate protonated to form carboxylic acid, showed reduced uptake (0.70 mol mol⁻¹), similar to glycinate-based SILs. Conversely, removing the amino proton, as in [NTA], resulted in lower CO₂ capacity (0.44 mol mol⁻¹), due to the inability to form a carbamic acid intermediate.

Preorganization was also demonstrated as an efficient strategy to improve CO₂ uptake. Converting the diacetamide anion ([DAA]) to a cyclic succinimide anion ([Suc]) enhanced uptake from 1.25 to 1.87 mol mol⁻¹ at 1 bar and 293 K (Figure 10C).^{73, 144, 145} Theoretical simulations showed that [DAA] adopted an asymmetric *cis-trans* conformation, allowing only one CO₂ to bind, while [Suc] existed in a symmetric form, enabling two CO₂ molecules to integrate with identical bonding distances. At a CO₂ concentration of 10 vol%, [P₄₄₄₂][Suc] achieved 1.65 mol mol⁻¹ uptake, which was released at 60 °C with N₂ bubbling, demonstrating recyclability and durability over 16 cycles. In situ FT-IR studies revealed a new peak at 1628 cm⁻¹ with CO₂ loadings below 0.8 mol mol⁻¹, which shifted to 1610 cm⁻¹ at higher loadings (> 1 mol mol⁻¹), indicating an initial N-C bond formation, followed by O-C-N bond formation as CO₂ dosage increased. Correspondingly, ¹³C NMR peaks shifted from 158.9 to 159.2 ppm. Further studies showed that adding water to [Suc]-derived SILs altered the reaction pathway from N-C-O bond formation to bicarbonate formation, affecting both uptake capacity and sorbent stability.^{144, 145}

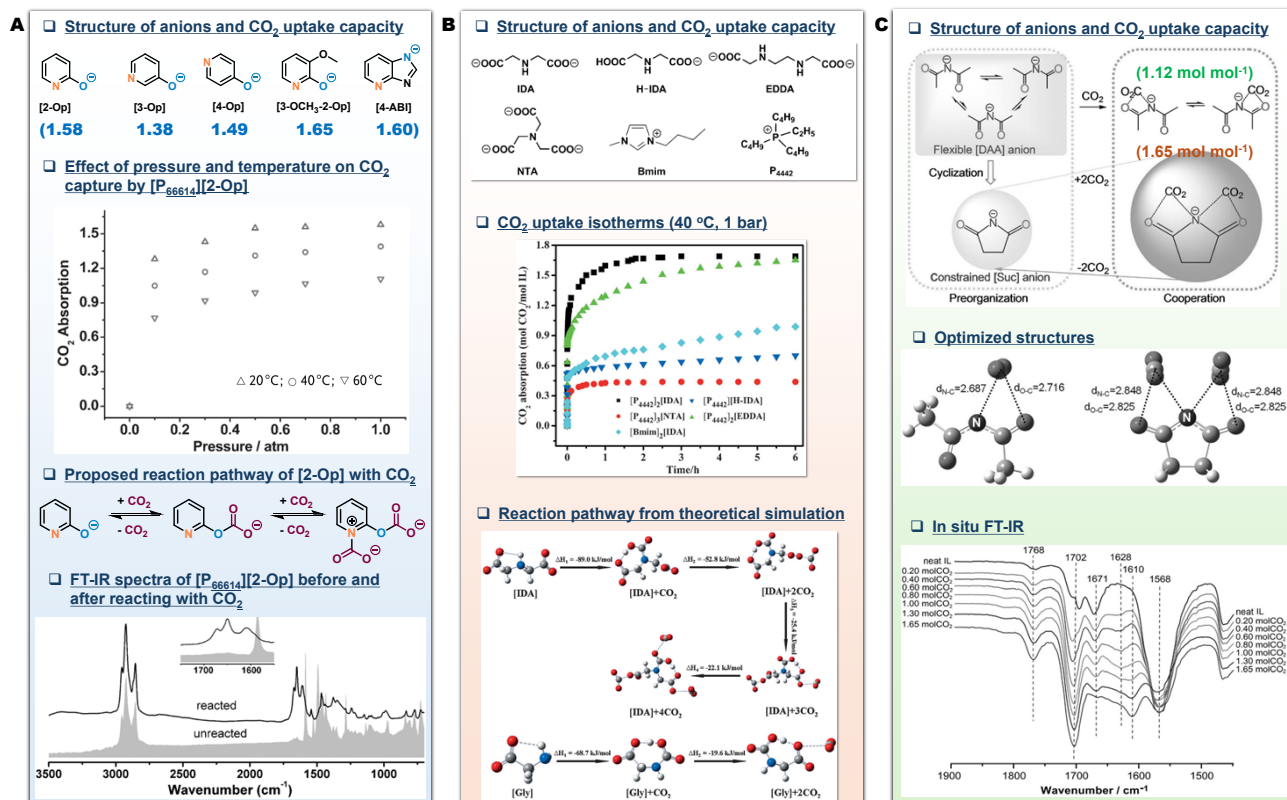


Figure 10. (A) Structure of pyridine- and oxygenate-containing SILs (numbers in brackets indicate the CO₂ uptake capacity of these anions paired with the [P₆₆₆₁₄] cation); effect of CO₂ pressure and temperature on the uptake capacity of [P₆₆₆₁₄][2-Op]; proposed reaction pathway for CO₂ integration in [2-Op]; and FT-IR spectra of [P₆₆₆₁₄][2-Op] before and after CO₂ reaction.⁷¹ Reproduced with permission from Ref 71. Copyright 2014 John Wiley & Sons. (B) Structure of aminopolycarboxylate-based ILs; CO₂ uptake isotherms at 40 °C and 1 bar CO₂ pressure; proposed reaction pathway and thermodynamic parameters for each step, compared with the glycinate anion.⁷² Reproduced with permission from Ref 72. Copyright 2016 John Wiley & Sons. (C) Structures of [DAA]- and [Suc]-derived SILs and their bonding interactions with CO₂ molecules; optimized structures of [Suc]+2CO₂ and [DAA]+CO₂; characterization of [P₄₄₄₂][Suc] by FT-IR spectra after integrating different amounts of CO₂.⁷³ Reproduced with permission from Ref 73. Copyright 2017 John Wiley & Sons.

2.8 Exploration of alternative driving forces for enhanced CO₂ capture

As demonstrated above, SILs based on oxygen- and nitrogen-derived anions exhibit promising and tunable CO₂ capture properties, with anion basicity playing a crucial role in efficient CO₂ integration through strong chemical bond formation (O-C and N-C). However, this CO₂ capture driven by strong chemical bonding formation often results in high energy consumption during sorbent regeneration. Therefore, developing SILs that integrate CO₂ via alternative driving forces beyond chemical bond strength is highly desirable. Carbanion-based SILs, known for their high carbon monoxide solubility,¹⁴⁶ are promising candidates for exploring alternative reaction pathways for CO₂ capture. The interaction of carbanions with CO₂ can be tuned by adjusting their basicity and steric hindrance.¹⁴⁷ Two carbanion-derived SILs, composed of [MN] and [MMN] anions paired with phosphonium cations, were synthesized and evaluated for CO₂ capture (Figure 11A).²² At 298 K and 1 bar CO₂ pressure [P₆₆₆₁₄][MN] and [P₆₆₆₁₄][MMN] achieved CO₂ uptake capacities of 0.84 and 0.35

mol mol⁻¹ respectively (Figure 11A). Interestingly, this trend is opposite to their basicity, as [MN] has a lower pKa (11.1) than [MMN] (12.4), which contains an electron-donating methyl group. Moreover, despite its lower basicity compared to [Im] (pKa = 18.6) and [Triz] (pKa = 13.9), [MN] achieved similar CO₂ uptake capacity.⁶⁷ The captured CO₂ in [P₆₆₆₁₄][MN] was completely released at 60 °C with N₂ bubbling, and maintaining stable performance over five cycles. Structure evolution analysis via FT-IR and NMR revealed that the ¹³C NMR signal of the C-C bonded carboxylate product did not match the simulated spectrum, but closely resembled the carboxylic acid product (new carbon signal at 177.63 ppm), suggesting an additional proton transfer step. Furthermore, ¹H NMR spectra showed the disappearance of the proton at the central carbon after CO₂ reaction, indicating potential activation. FT-IR spectra exhibited a newly formed peak at 1607 cm⁻¹, consistent with simulated carboxylic acid structure. DFT calculations confirmed that carboxylic acid formation ($\Delta H = -35.33$ kJ mol⁻¹) was thermodynamically more favorable than carboxylate formation ($\Delta H = -6.82$ kJ mol⁻¹) (Figure 11A). Proton transfer was driven by the geometric constraints of the central carbon: in the carboxylate product, hybridization changed from *sp*² (in [MN]) to *sp*³ (Figure 11A), while an additional proton transfer restored *sp*² hybridization, expanding conjugation across the two -CN groups and enhanced stability.^{148, 149} Additionally, due to the relatively weak basicity of [MN], ylide formation-induced cation decomposition was avoided, and proton transfer from the α -carbon of the phosphonium cation was highly unfavorable ($\Delta H = 79.56$ kJ mol⁻¹). Further theoretical simulations indicated that intermolecular proton transfer between two carboxylate intermediates was more feasible (activation energy = 50 kJ mol⁻¹) than an intramolecular pathway (activation energy = 152 kJ mol⁻¹), leading to a hydrogen bond-stabilized dimer with a π -conjugated planar geometry.¹⁵⁰

Building on the proton transfer-driven CO₂ integration in carbanions²² and previous findings that oxygen sites in carboxylate can act as active sites for CO₂ capture when possessing high electron density,⁷² a novel carbanion-derived SIL was designed by introducing a bulky hydrogen-bond acceptor (HBA) adjacent to the central carbon.⁵³ The proposed reaction mechanism suggests that during intermolecular proton transfer, steric hindrance prevents the second proton transfer, creating an additional oxygen site for multiple CO₂ insertions (Figure 11B). (Methylsulfonyl)acetonitrile (MSA), with a pKa of 11.52, was selected as the precursor due to its conjugated structure and bulky -SO₂CH₃ group (Figure 11B). Upon reacting with CO₂ or ¹³C-labeled CO₂, two new peaks appeared in the [P₄₄₄₂][MSA] system at 158.5 and 170.4 ppm (Figure 11B), corresponding to CO₂ integration via C-C and O-C bond formation, respectively, as confirmed by simulated NMR spectra. Two-dimensional (2D) ¹³C NMR analysis revealed spatial proximity between the two new peaks (Figure 11B), both of which disappeared completely upon heating to 60 °C. Operando ¹³C NMR confirmed that the O-C bonded product (170.4 ppm) was more stable than the C-C bonded product (158.5 ppm). Correspondingly, new peaks at 1608, 1641, and 1664, 1641, and 1608 cm⁻¹ in FT-IR spectra were displayed upon CO₂ reaction with [P₄₄₄₂][MSA]. The reversible multiple CO₂ insertion in [MSA] was further confirmed by electrospray ionization mass spectrum (ESI-MS) at different temperatures. CO₂ capacity of [P₄₄₄₂][MSA] was 1.20 mol mol⁻¹ at 1 bar CO₂ pressure and 298 K. Absorbed CO₂ was fully released within 5 min at 60 °C with N₂ bubbling, demonstrating excellent recyclability over five cycles. The multiple CO₂ insertion behavior in the [MSA] anion was further illustrated using a liquid sorbent system in which Na[MSA] was dissolved in 15-crown-5 (15c5). NMR and in situ FT-IR studies confirmed CO₂ insertion via two distinct bonding pathways. Notably, after CO₂ insertion, the resulting Na[MSA+2CO₂] rapidly precipitated from the liquid phase, allowing isolation via filtration or centrifugation. This eliminates the need for bulk solvent heating, further reducing energy consumption.

Based on the proposed reaction mechanism and CO₂ uptake capacity, theoretical simulations explored the possibility of integrating three CO₂ molecules per two [MSA] anions, highlighting the critical role of proton transfer, structure rearrangement, and hydrogen bonding stabilization in the overall pathway. Similar cascade CO₂ insertion behavior was observed in amine-derived sorbents, where tetrameric self-assembly of amine species facilitated the formation and stabilization of carbamate anhydride, as confirmed by spectroscopy, NMR, and theoretical studies.⁶¹

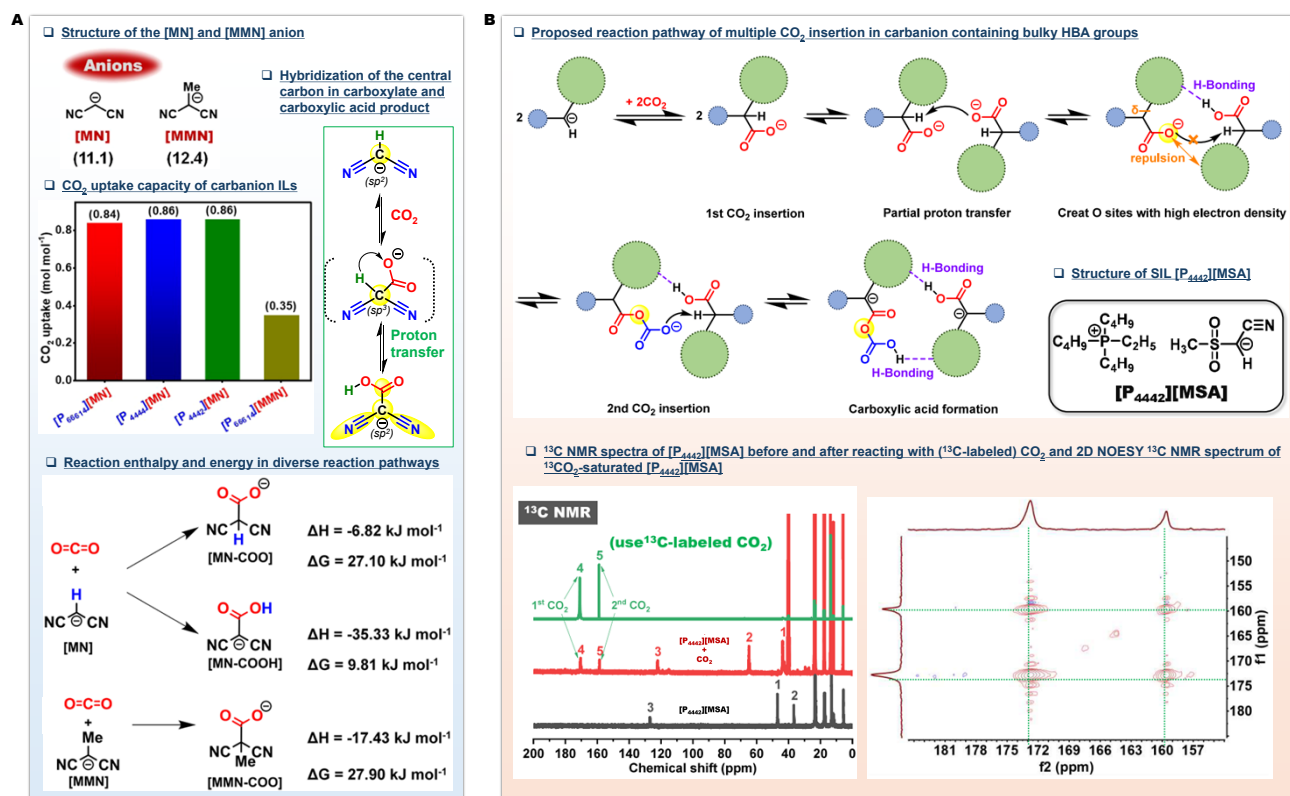


Figure 11. (A) Structure of [MN] and [MMN] anion (pKa values in brackets); CO₂ uptake capacities of different SILs at 298 K and 1 bar CO₂ pressure; hybridization of the central carbon in [MN], carboxylate intermediates, and carboxylic acid products via proton transfer; and reaction enthalpy and energy profiles of proposed reaction pathways.²² Reproduced with permission from Ref 22. Copyright 2022 American Chemical Society. (B) Proposed pathway for multiple CO₂ insertions in carbanion-derived anions containing bulky hydrogen bond acceptors; structure of [P₄₄₄₂][MSA]; and two dimensional ¹³C NMR spectra of [P₄₄₄₂][MSA] before and after reacting with CO₂ or ¹³C-labeled CO₂.⁵³ Reproduced with permission from Ref 53. Copyright 2024 American Chemical Society.

2.9 Modeling and simulations of ionic liquids in CO₂ chemisorption

Both molecular mechanical and quantum mechanical simulations are extensively used to investigate the properties of ILs and their interactions with gas molecules for separation and catalysis. Several recent reviews have explored different aspects of this topic, including ILs for carbon capture,¹⁴⁸ IL-based interfaces and composites with 2D materials for gas separation,¹⁵¹ and machine learning-assisted IL design for carbon capture.¹⁵²

Recent advancements have led to the development of ILs with novel anions that can reversibly react with CO₂. A key challenge is understanding the reaction mechanisms using quantum chemical

calculations, particularly the role proton-transfer, as proton management critically influences the final reaction products and energetics. Additionally, reactive CO₂ separation and catalytic CO₂ conversion, such as electrochemical reduction, share mechanistic similarities, particularly in proton management. Thus, both topics are reviewed together.

Computations based on density functional theory (DFT) offer important insights into CO₂ chemisorption in ILs, revealing structural details and thermodynamics of the reactions. For example, DFT methods were used to calculate reaction enthalpies for CO₂ interactions with a series of phenolate-based systems featuring varying alkali metal, alkyl substitution on the benzene ring, and coordination with crown ethers.¹³⁸ Among these, PhONa+15-crown-5 exhibited the strongest binding affinity (Figure 12A), aligning with its highest experimentally observed CO₂ uptake capacity. Theoretical calculations have also been applied to study CO₂ chemisorption in SILs such as deprotonated malononitrile ([MN]) and 2-methylmalonnointrile ([MMN]).²² The reaction enthalpy of [MN] with CO₂ to form carboxylic acid product was found to be twice that of [MMN], which forms a carboxylate product (Figure 12B). Structural comparisons revealed that in [MN], proton transfer at the α -H maintains the π -conjugation of the anion, providing a stronger thermodynamic driving force than carboxylate formation. Similarly, the newly developed pyrazolonate-derived IL [3-HMPz] exhibited a reaction enthalpy 8 kJ/mol stronger than that of phenolate-containing SILs like [PhO] (Figure 12C), correlating with its higher CO₂ uptake.⁷⁰ In another study, SIL [MeTBDH]₂[HFPDO], when confined within a Ni-MOF scaffold (Figure 12D), exhibited a calculated CO₂ reaction enthalpy of -113 kJ mol⁻¹, compared to -87.8 kJ mol⁻¹ in the liquid phase SIL.¹⁵³ These calculations suggest that confinement within the Ni-MOF scaffold enhances SIL-CO₂ interactions, improving its carbon capture performance.

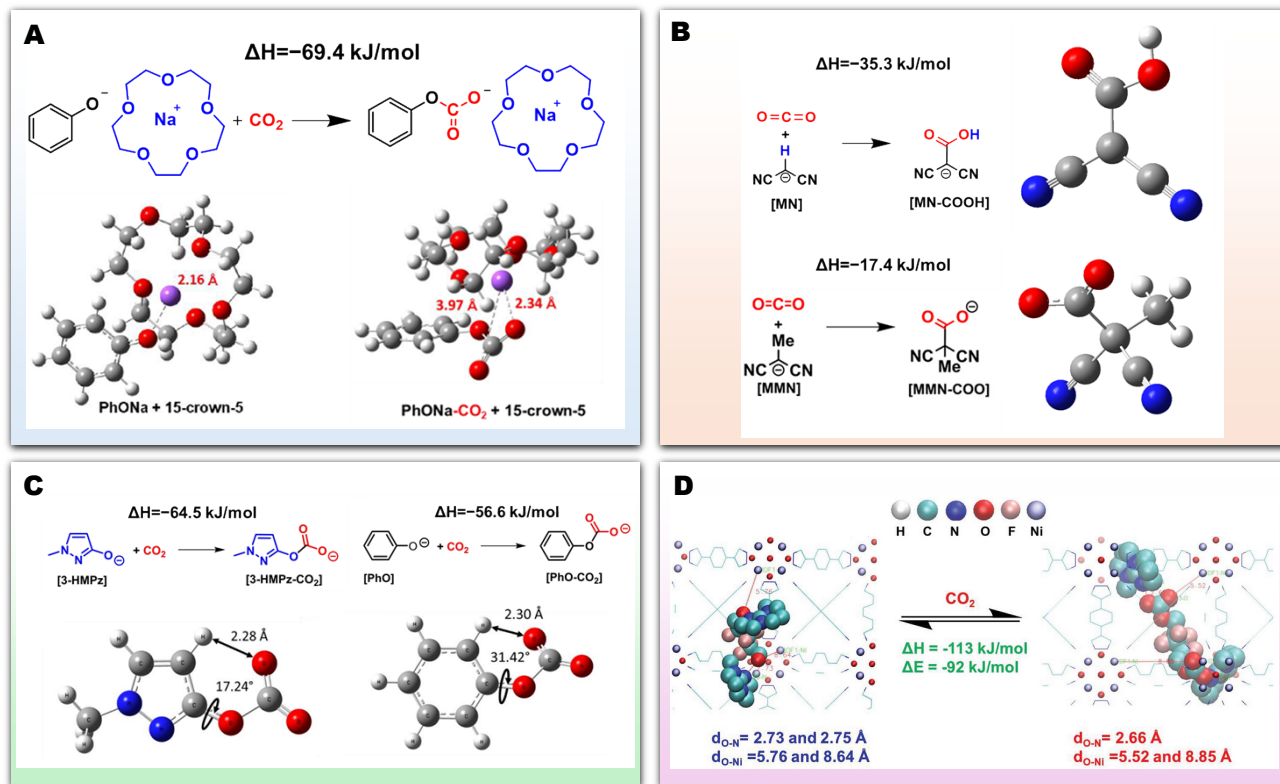


Figure 12. Calculated reaction enthalpy for CO₂ chemisorption in various SIL systems: (A) PhONa + 15-Crown-5.¹³⁸ Reproduced with permission from Ref 138. Copyright 2021 John Wiley & Sons. (B)

[MN] (top) and [MMN] (bottom).²² Reproduced with permission from Ref 22. Copyright 2022 American Chemical Society. (C) [3-HMPz] (left) and [PhO] (right).⁷⁰ Reproduced with permission from Ref 70. Copyright 2023 John Wiley & Sons. (D) SIL [MeTBDH]₂[HFPDO] confined in Ni-MOF.¹⁵³ Reproduced with permission from Ref 153. Copyright 2023 John Wiley & Sons.

The reaction mechanisms of carbanion-derived SILs have been thoroughly investigated from a theoretical perspective^{53, 149, 150} using molecular dynamics (MD), quantum mechanics/molecular mechanics (QM/MM) and density functional theory (DFT) simulations. It was revealed that CO₂ chemisorption in the malononitrile carbanion ([CH(CN)₂]⁻) begins with a nucleophilic attack by ([CH(CN)₂]⁻) on the CO₂ carbon atom, forming a carboxylate compound, [CH(CN)₂COO]⁻, with a low activation free energy (~47 kJ mol⁻¹).¹⁴⁹ This mechanism was further explored using DFT calculations with the solvation model based on density (SMD) approach, investigating the formation of the carboxylic acid derivative [C(CN)₂COOH]⁻.¹⁵⁰ The results indicated that intermolecular proton transfer between two [CH(CN)₂COO]⁻ anions occurs with low activation energy barrier of 45 kJ mol⁻¹, a process facilitated by hydrogen bonding involving the two α-H atoms and the COO⁻ groups. Additionally, hydrogen bonding between the two -COOH groups provides additional stabilization for the [C(CN)₂COOH]⁻ dimer in the Z-configuration (Figure 13A). The cascade CO₂ insertion mechanism in a carbanion IL containing deprotonated (methylsulfonyl)acetonitrile ([MSA]) is investigated using DFT+SMD calculations.⁵³ The findings indicate that the first step involves intermolecular proton transfer between two [MSA-COO] anions, generating a dianion intermediate (Figure 13B). This intermediate facilitates the third CO₂ molecule's nucleophilic attack, resulting in the formation of a carbonic anhydride product, which is stabilized by intermolecular hydrogen bonding.

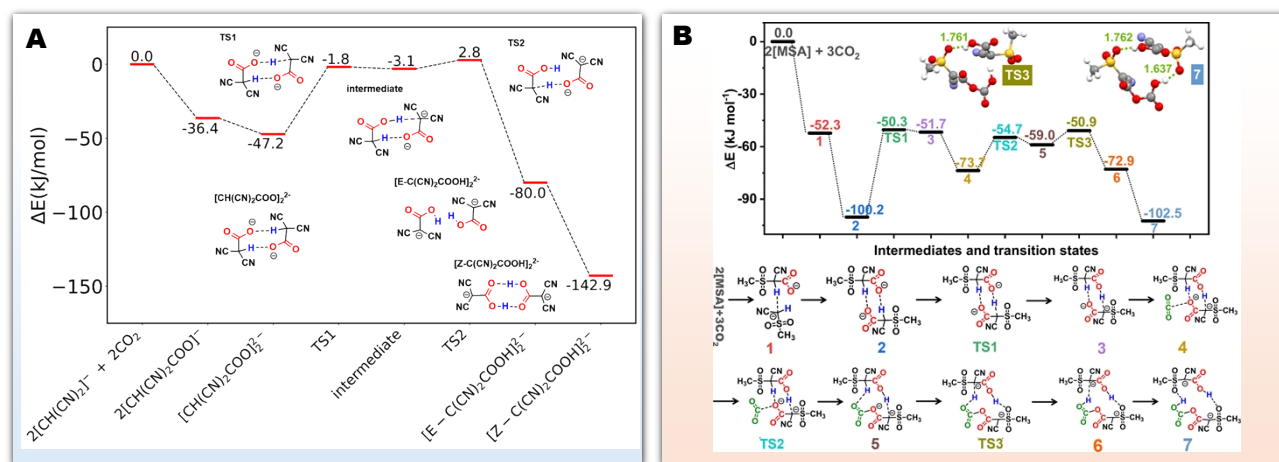


Figure 13. (A) DFT calculated reaction mechanisms of intermolecular proton transfer between carboxylate products forming carboxylic acid.¹⁵⁰ Reproduced with permission from Ref 150. Copyright 2024 American Chemical Society. (B) two [MSA] carbanions with three CO₂ to form carboxylic acid and anhydride anion.⁵³ Reproduced with permission from Ref 53. Copyright 2024 American Chemical Society.

Explicit solvation simulations was used to investigate CO₂ chemisorption mechanisms in condensed-phase amino acid ILs (AAILs) using *ab initio* molecular dynamics (AIMD) with well-tempered metadynamics.^{154, 155} The free energy calculations revealed that the intermolecular proton

transfer mechanism to carbamate formation in serine anion is the most kinetically favorable, with an activation energy barrier of approximately 51 kJ/mol (Figure 14A).¹⁵⁴ Furthermore, examining AAIL anions with different steric hindrance revealed that anions with weaker steric effects (valine > alanine > glycine) exhibit greater structural flexibility. The increased flexibility strengthens zwitterion-anion interactions, thereby reducing the energy barrier for intermolecular proton transfer (Figure 14B).¹⁵⁵

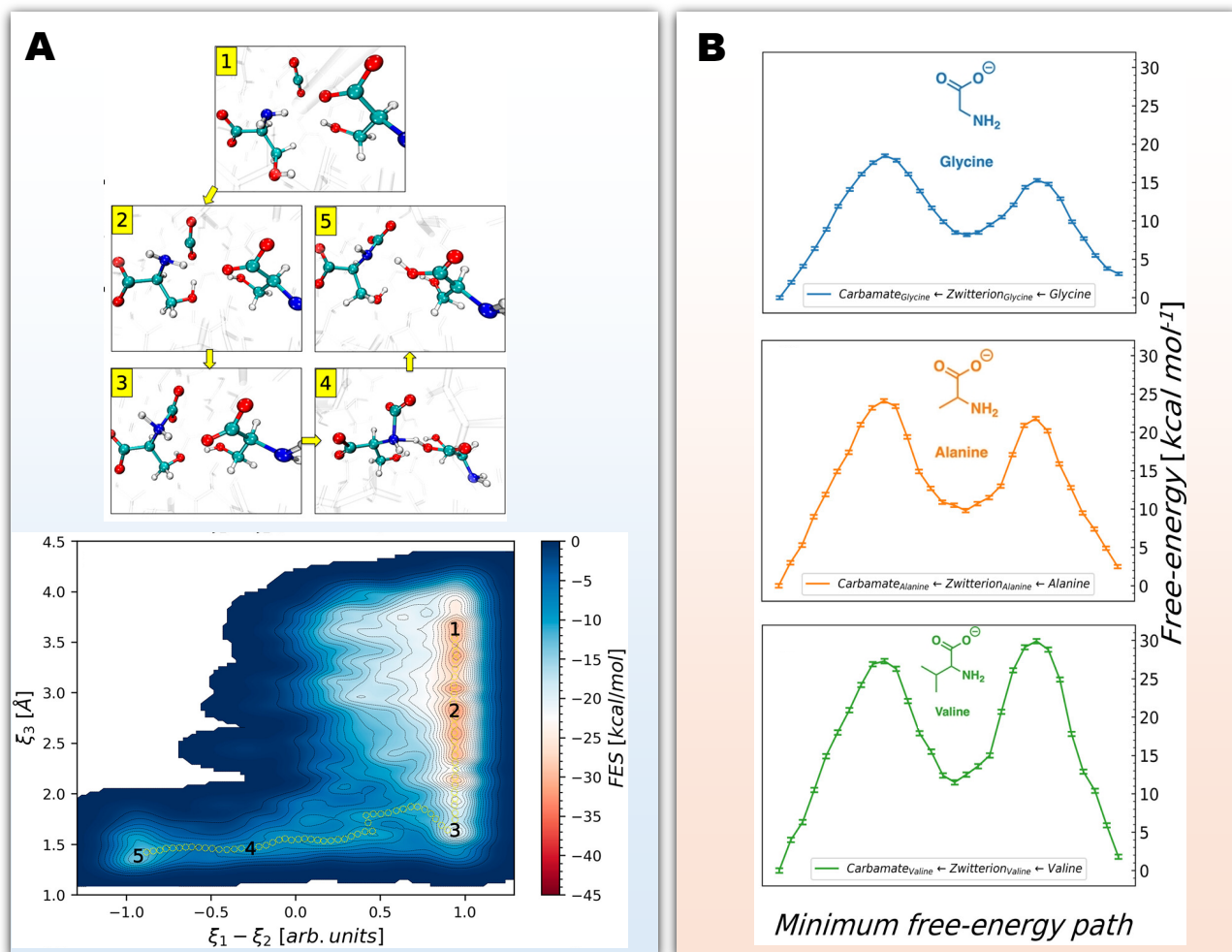


Figure 14. (A) Free energy landscape depicting carbamate formation through CO₂ interaction with serine, highlighting zwitterion generation and proton transfer between the nitrogen of the zwitterion and the adjacent carboxylate oxygen.¹⁵⁴ Reproduced with permission from Ref 154. Copyright 2023 American Chemical Society. (B) One dimensional free energy profile illustrating the minimum free-energy path for the formation of carbamate from the reaction of CO₂ with the AAIL anion of glycine (blue line), alanine (orange line), and valine (green line).¹⁵⁵ Reproduced with permission from Ref 155. Copyright 2024 American Chemical Society.

3. Engineering porosity into ionic liquids

The intrinsic characteristics of free volume in ILs, i.e., size and density, are critical physiochemical properties that govern the gas storage capacity and transport behavior within liquid media. Traditional approaches to improve and tune the free volume properties in ILs rely on the steric hindrance effects of substitutes in cations/anions, which possessed limitations in terms of cavity size and density improvement.¹⁵⁶⁻¹⁶⁰ Porous liquid (PL) represents a new frontier and advanced platform for

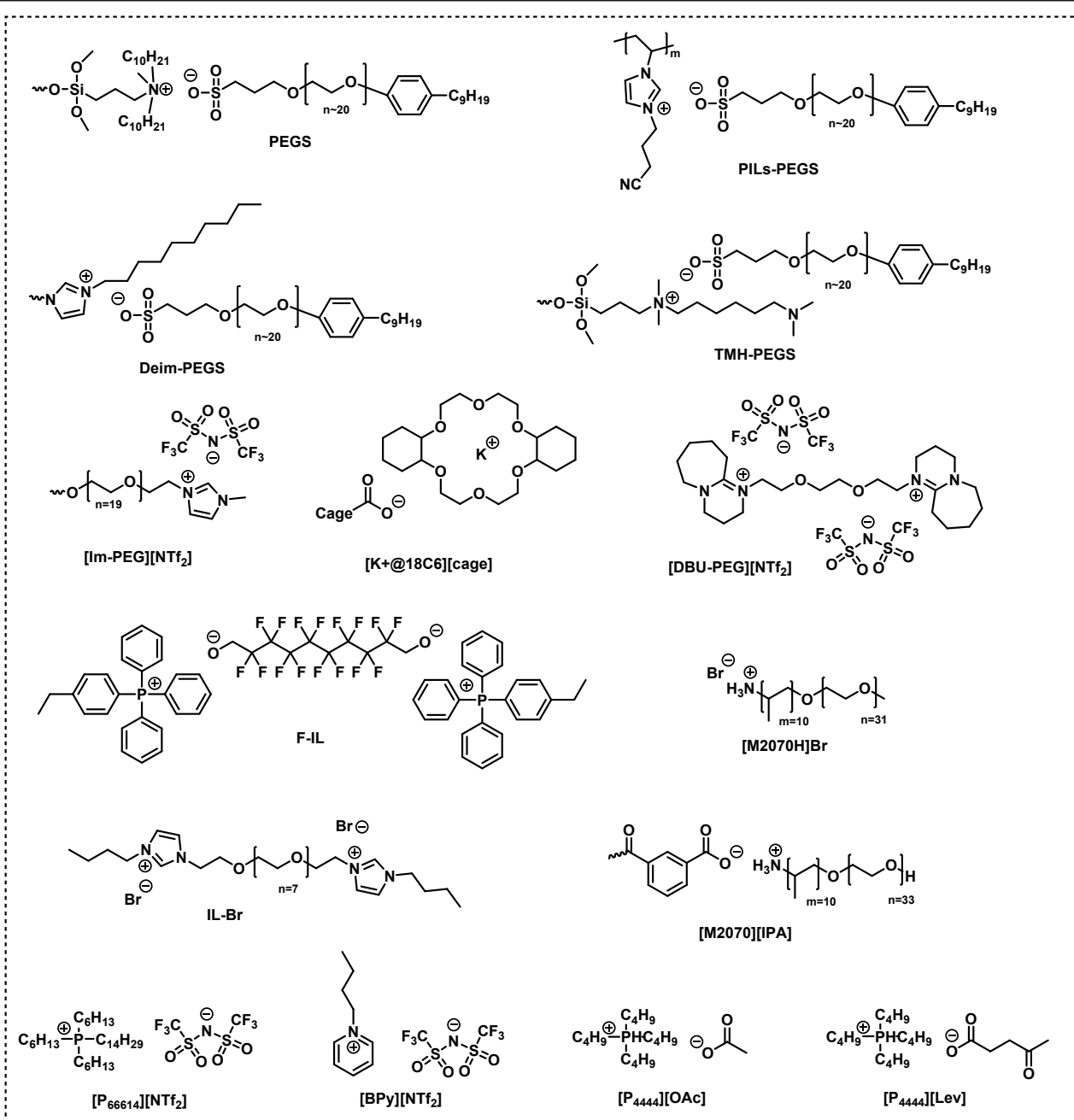
engineering permanent porosity into liquid media. The concept was raised up in 2007³⁸ and experimentally achieved in 2015 through modifications such as cationic coronas and anionic canopies on the surface of hollow silica spheres (HSS)⁴¹ or dissolving crown ether-functionalized organic cage in bulky solvents (e.g., crown ether).⁴² By incorporating additional cavities and permanent porosities into the dense liquid phase, PLs merge the advantages of porous solids and flowing liquids.^{38, 39, 161-167} The distinctive properties of PLs have been showcased in various applications, particularly in the area of separation and catalysis,¹⁶⁸⁻¹⁷² in which enhanced gas solubility,¹⁷³⁻¹⁷⁵ accelerated gas transport,⁴¹ and improved gas separation selectivity were achieved benefiting from the significantly improved free volumes/cavities and tunable liquid/solid interface properties. Currently, four categories of PLs have been developed, covering liquid molecules with rigid and intrinsic porosity (Type I),^{176, 177} dissolving (Type II)^{42, 178, 179} and dispersing (Type III)^{180, 181} solid porous hosts in liquids, and meltable microporous expanded frameworks (Type IV).¹⁸² Besides bulky organic solvents, water, and deep eutectic solvents, ILs have been widely deployed as fluids in PL formation due to their non-volatility, high thermal stability, high gas solubility, feasible structure tunability, and facile involvement of task-specific functionalities.^{183, 184} Correspondingly, a variety of porous hosts with different structures—ranging from organic to inorganic, and microporous to macroporous—have been explored, including hollow carbon/silica spheres,^{41, 185} zeolites,¹⁸⁶ porous cages,^{187, 188} metal-organic frameworks (MOFs),¹⁸⁹⁻¹⁹² covalent organic frameworks (COFs),¹⁹³ and macromolecules.¹⁷⁷ In this section, PLs formed by engineering permanent porosity in ILs will be summarized and compared (Table 2). The contents will be organized into categories of PLs, starting with Type I PL formed by modifying the surface of HSS and hollow carbon sphere (HCS) (Section 3.1), followed by type II PLs formed by dissolving porous organic cages (POCs) or coordination cages in selected ILs (Section 3.2), and then the type III PLs composed of diverse porous host (e.g., zeolite and MOFs), along with their application in separation and catalysis, particularly compared to the dense IL phase (Section 3.3). For Type IV PLs, the existing systems are still limited to meltable expanded frameworks (e.g., MOFs) through linker functionalization¹⁹⁴ or mixed linker approach, which was not covered herein as no IL components have been involved.¹⁹⁵⁻¹⁹⁷ However, in current Type IV PLs, above 300 °C is generally required to achieve the melting status and liquid nature, which leads to severe reticular structure variation and porosity reduction. This provides the opportunity to leverage the structure tunability and property control of ILs to construct Type IV PLs with deduced solid-to-liquid transition temperatures.

Table 2. Summary of porous ILs media.

ILs ^a	Porous host	Type	Application	Ref
PEGS	hollow silica	Type I	CO ₂ /N ₂ selective adsorption	41
PILs-PEGS	hollow carbon sphere	Type I	CO ₂ adsorption	185
Deim-PEGS	MOF	Type I	Catalytic CO ₂ cycloaddition	192
[K ⁺ @crown ether][cage]	anionic cage	Type I and II	CO ₂ adsorption	188
[Im-PEG][NTf ₂]	coordination cage	Type I	Chlorofluorocarbon vapor separation	176

F-IL	POC	Type II	N ₂ /CH ₄ /CO ₂ /Xe selective adsorption	198
IL-Br	coordination cage	Type II and III	CO ₂ cycloaddition	199
[BPy][NTf ₂], [BMIM][NTf ₂]	POC	Type III	CO ₂ adsorption	200
[M2070H]Br	MCM-22	Type III	CO ₂ adsorption, ethylene/ethane selective adsorption	201
[M2070][IPA]	MOF	Type III	photocatalytic CO ₂ -to-CO conversion	202
[P ₆₆₆₁₄][NTf ₂]	MOF	Type III	N ₂ /CH ₄ /CO ₂ selective adsorption	191
[P ₄₄₄₄][OAc], [P ₄₄₄₄][Lev]	MOF	Type III	CO ₂ adsorption	40
TMH-PEGS	MOF	Type I	Capture and conversion of H ₂ S	172
[DBU-PEG][NTf ₂]	ZIF-8	Type III	CO ₂ adsorption	203

^aStructures of ILs:



3.1 Type I porous liquids

Type I PLs represent a unique class of materials where the liquid itself exhibits intrinsic porosity, meaning the liquid itself forms a dynamic, porous structure capable of trapping small molecules or gases. In these systems, the liquid phase often consists of bulky ILs, organic solvents, or specially designed liquids that can maintain a porous structure. The porous host component in Type I PLs is not a solid material but rather a liquid matrix that forms physical voids. The synthesis method typically involves designing ILs with tunable properties and modifying the surface of porous hosts. Type I PLs are highly promising for gas storage, separation, and catalysis due to their homogeneous nature and tunable porosity.

Two-step synthetic strategy was pioneered for transforming porous hollow silica (HS) spheres

with 14 nm inner diameter and microporous shells into a Type I PL (Figure 15A).⁴¹ The specific liquification process involved that in the first step, positively charged organosilane (OS) moieties were covalently attached on the surface of the silica through reaction with its surface hydroxyl groups, resulting in the permanent hollow particles (OS@HS). Subsequently, a long-chain poly(ethylene glycol) canopy ended with a sulfonate group (PEGS) conducted ion-exchange with chloride anions on OS@HS, resulting in the generation of a transparent liquid (HS-liquid). Incorporating ILs into the porous matrix further enhanced the gas permeability and selectivity by providing a fluid environment and high fractional free volume, which was demonstrated by the HS-liquid supported polymeric membrane test (Figure 15B). It turned out that HS-liquid embedded membrane showed perfect CO₂ permeability and high selectivity of CO₂/N₂ compared to the membranes embedded with pure IL (PEGS) or the liquid derived from silica spheres with solid cores (Figure 15C). Moreover, silica spheres (SS) featured with a core-shell structure, both containing and lacking nickel-hydrazine cores, were employed as scaffolds for fabricating nanofluids to eliminate the impact of the particle size of porous host and the surface properties. Both exhibited quite low CO₂ permeability and CO₂/N₂ selectivity (~10), which confirmed the superiority of free cavities in gas separation.

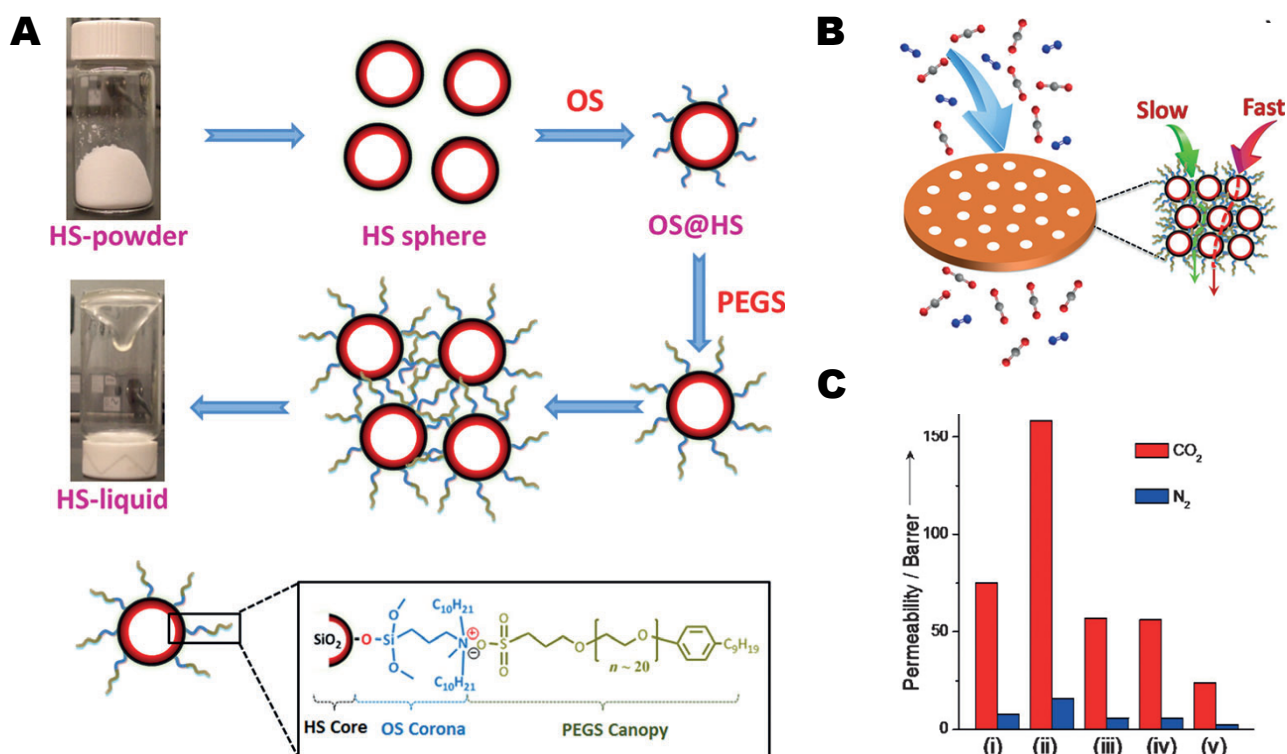


Figure 15. (A) Synthetic strategy for transforming HSS into a Type I PL. (B) Schematic representation of CO₂/N₂ separation using PL-supported membrane. (C) Gas permeability comparison of: (i) IL (PEGS), (ii) PL (HS-liquid), (iii) liquid derived from silica spheres with solid cores, and liquids including core-shell SS containing (iv) and lacking (v) nickel-hydrazine cores.⁴¹ Reproduced with permission from Ref 41. Copyright 2014 John Wiley & Sons.

Hollow carbon spheres (HCS) were another porous hosts that could be liquified into a Type I PL by utilizing electrostatic interactions (Figure 16).¹⁸⁵ First, one kind of poly(ILs) containing

imidazolium cations was attached on to the surface of HCS (PILs@HCS) to address the chemical inertness of carbon surfaces. The strong affinity between imidazolium cation species in IL and carbon networks, including π -cation/ π -electronic/ π -CH interactions, assists PIL and HCS to form a stable self-assembled structure, enabling the uniform dispersion of HCS in water. The realization of liquefaction was subsequently achieved through an ion exchange method with PEGS. The tunable ionic nature and high polarity enable strong interactions with porous carbons, improving their liquefaction efficiency. The afforded HSC-liquid exhibits enhanced CO₂ adsorption capacity, confirming the existence of well-preserved cavities inside of this system.

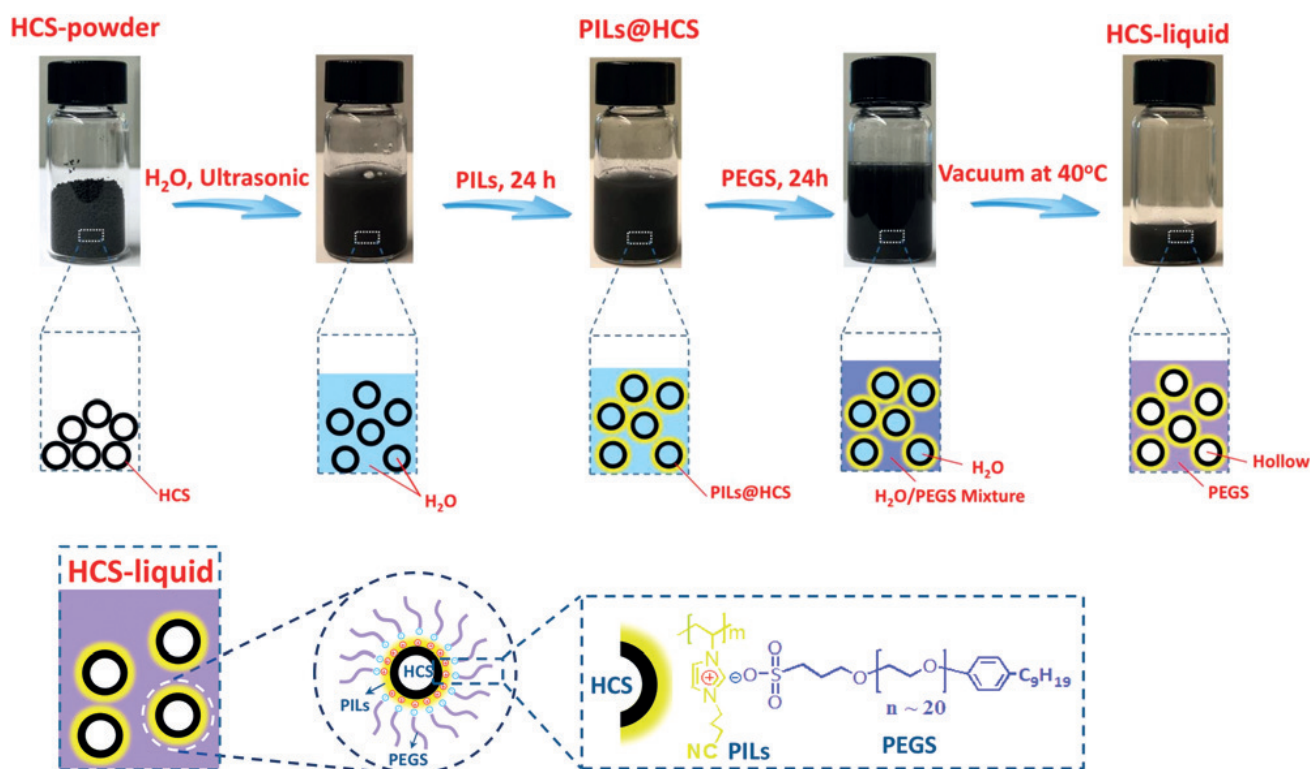


Figure 16. Synthetic strategy for transforming porous HCS into a Type I PL.¹⁸⁵ Reproduced with permission from Ref 185. Copyright 2017 John Wiley & Sons.

The first MOF-engineered PL was constructed via a surface ionization method. First, ligands bearing imidazolium cations, Cl[−] anions and long alkyl chains were employed to construct the cationic MOF (Deim-UiO-66).¹⁹² Following this, an anionic PEGS canopy was attached on Deim-UiO-66 via ion exchange with Cl[−], resulting in the liquefaction of the cationic MOF (Im-UiO-PL) (**Figure 17A**). These MOF-based liquids can efficiently capture CO₂ due to their tunable pore sizes and chemical functionalities. It's demonstrated in CO₂ uptake isotherms that PL achieved an enhanced CO₂ adsorption capacity of 5.93 mmol g^{−1} at the pressure of 9 bar, 14 times greater than that of pure IL with adsorption capacity of 0.43 mmol g^{−1} (**Figure 17B**). This enhanced gas adsorption capacity was due to the permanent pores existing inside the Im-UiO-PL. Additionally, Im-UiO-PL significantly promoted catalytic the cycloaddition reaction between epoxide and CO₂ released from the MOF liquids, comparing to PEGS (IL), Deim-UiO-66, and their physical mixture (**Figure 17C**).

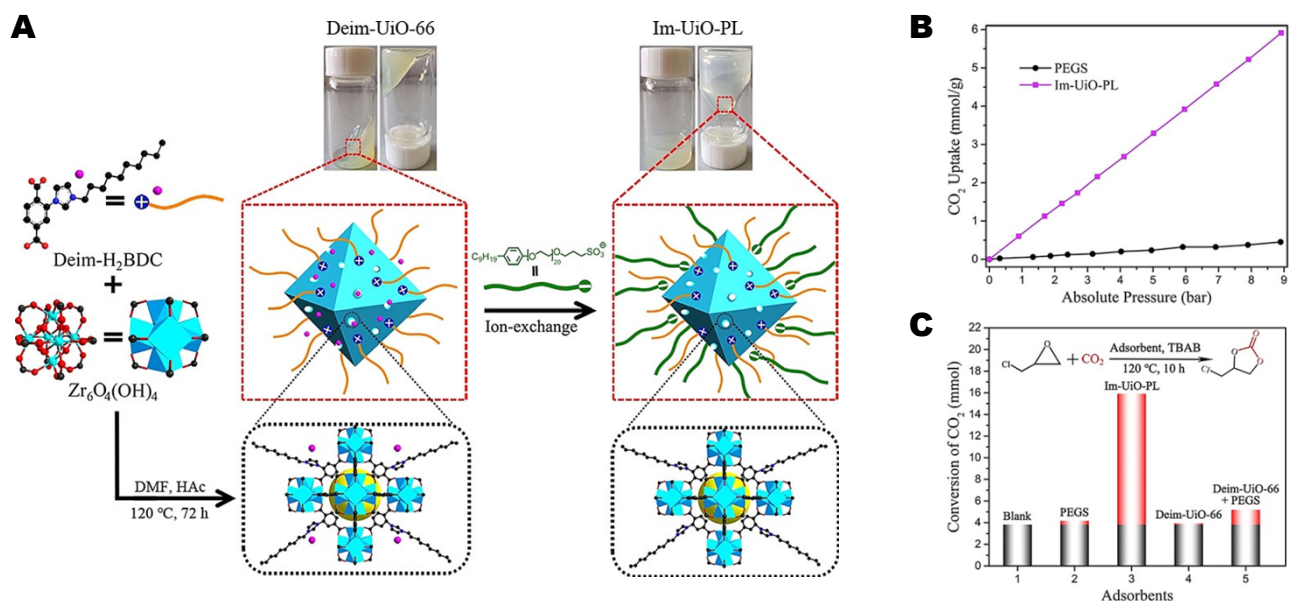


Figure 17. (A) The synthesis strategy for transforming MOF into a Type I PL. (B) CO₂ uptake isotherms of PL (Im-UiO-PL) and IL (PEGS) at 298 K. (C) Catalytic performance of cycloaddition reaction between epichlorohydrin and CO₂ stored in different counterparts.¹⁹² Reproduced with permission from Ref 192. Copyright 2021 John Wiley & Sons.

A supramolecular complexation strategy was employed to achieve the transformation of anionic imine-based cage into PLs (Figure 18A).¹⁸⁸ An anionic covalent cage modified with K⁺ was first synthesized. By mixing the liquid-phase dicyclohexano-18-crown-6 with an equimolar amount of the cage, the solid cage can be successfully liquefied to form Type I PL (18-C-6-PL) through the strong host-guest complexation between the crown ether and K⁺. However, only the addition of an excess amount of 15-crown-5 can liquefy the cage, resulting in the formation of Type II PL (15-C-5-PL). The enhanced CO₂ adsorption performance was observed in the gas uptake isotherms (Figure 18B). The permanent cavities existing in PLs was further confirmed by molecular simulations (Figure 18C and Figure 18D), which revealed that the cage cavity remained unoccupied in the liquid state, as the supramolecular complex and the free crown ether are too large to fit inside. This approach preserves the inherent porosity of organic cages, thus expanding their potential applications in gas storage.

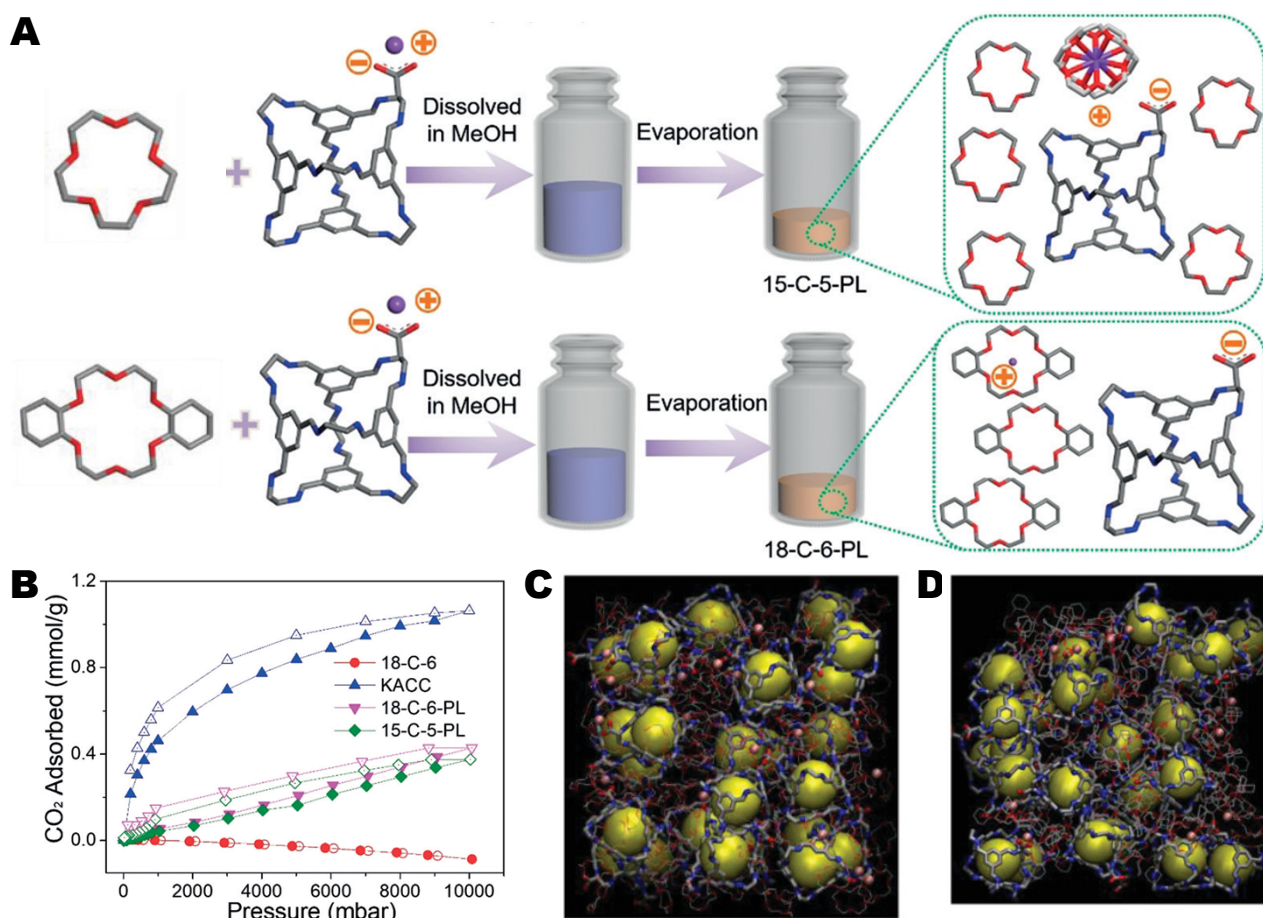


Figure 18. (A) Synthetic strategy for transforming anionic covalent cage into PLs. (B) CO₂ uptake isotherms of dicyclohexano-18-crown-6, anionic covalent cage, and PLs at 298 K. MD simulation snapshots representing accessible cavities with yellow spheres of 15-C-5-PL (C) and 18-C-6-PL (D).¹⁸⁸ Reproduced with permission from Ref 188. Copyright 2020 John Wiley & Sons.

The incorporation of PEG chains ended with imidazolium groups onto the coordination cage could also afford Type I PL (Figure 19A).¹⁷⁶ Notably, due to Coulombic repulsion, the terminal imidazolium group with a positive charge on the PEG chain are unable to penetrate the positively charged cage cavity. Besides, $-\text{NTf}_2$ was intentionally selected as the counter anion because its large size prevents it from entering the cage cavity. This approach enables the creation of permanent PLs with enhanced structural integrity and unique properties, such as vapor molecule separation capability. It's demonstrated that the coordination cage-derived PL was able to selectively bind larger guests, such as *t*-butanol over *n*-butanol (Figure 19B), and effectively sequester chlorofluorocarbons, including CFC_3 , CF_2Cl_2 and CF_3Cl (Figure 19C).

hindrance and abundant fluorinated moieties was designed to build high-quality PLs (Figure 20A). The successful construction of type II fluorinated PL (F-PL) was confirmed using multiple operando characterization techniques, such as X-ray- and neutron-based scattering, which revealed that the solubility of F-cage in F-IL could reach up to 10 wt%. Molecular dynamics (MD) simulations further validated the structural integrity of F-PL and the precision of F-IL design. The bulky cations, as end groups, occupied the window positions of the F-cage without penetrating the cavities, while the fluorinated dual-oxygenate anion chains were well-dispersed outside the F-cage. The existence of permanent voids in F-PL was demonstrated by positron annihilation lifetime spectroscopy (PALS), which also confirmed an improved gas uptake capacity in contrast with F-IL. Specifically, compared to F-IL, the significantly enhanced CO₂ absorption capacity of F-PL was observed in the pressure-swung CO₂ uptake isotherms, with increases of 48%, 55%, 65%, and 68% at 10, 20, 30, and 39 bar, respectively (Figure 20B). Interestingly, a gating effect was observed in F-PL within the low-pressure range of 1-10 bar (Figure 20C). After a gradual increase in CO₂ uptake at 298K, a plateau between 2-4 bar, followed by a steeper uptake isotherm. At high temperature (313K), the plateau shifted to the 1-2 bar range, while no plateau was observed at the low temperature (273K). Moreover, the pressure-dependent in situ FTIR was performed to prove the gating effect (Figure 20D). After dosing CO₂ with increased pressure, two characteristic peaks located at 2337 and 2362 cm⁻¹ (representing physisorbed CO₂ and gaseous CO₂ in the free space, respectively) in F-PL became broader, with a more rapid increase in peak intensity compared to F-IL. This is due to the additional free volume in F-PL, which accommodates more gaseous CO₂. Combined with structural simulation, it's indicated that F-IL occupied the windows of the F-cage through weak interactions, while still providing free space to accommodate CO₂. Under high pressure, F-IL will be squeezed away from the cage windows, creating more accessible space and enhancing CO₂ adsorption. However, for other gases including N₂ and CH₄, negligible uptake was observed in F-PL system, as confirmed by simulated gas adsorption (Figure 20E). The high adsorption selectivity for CO₂ in F-PL, compared to F-cage, illustrates the unique superiority of the PL construction approach in gas separation.

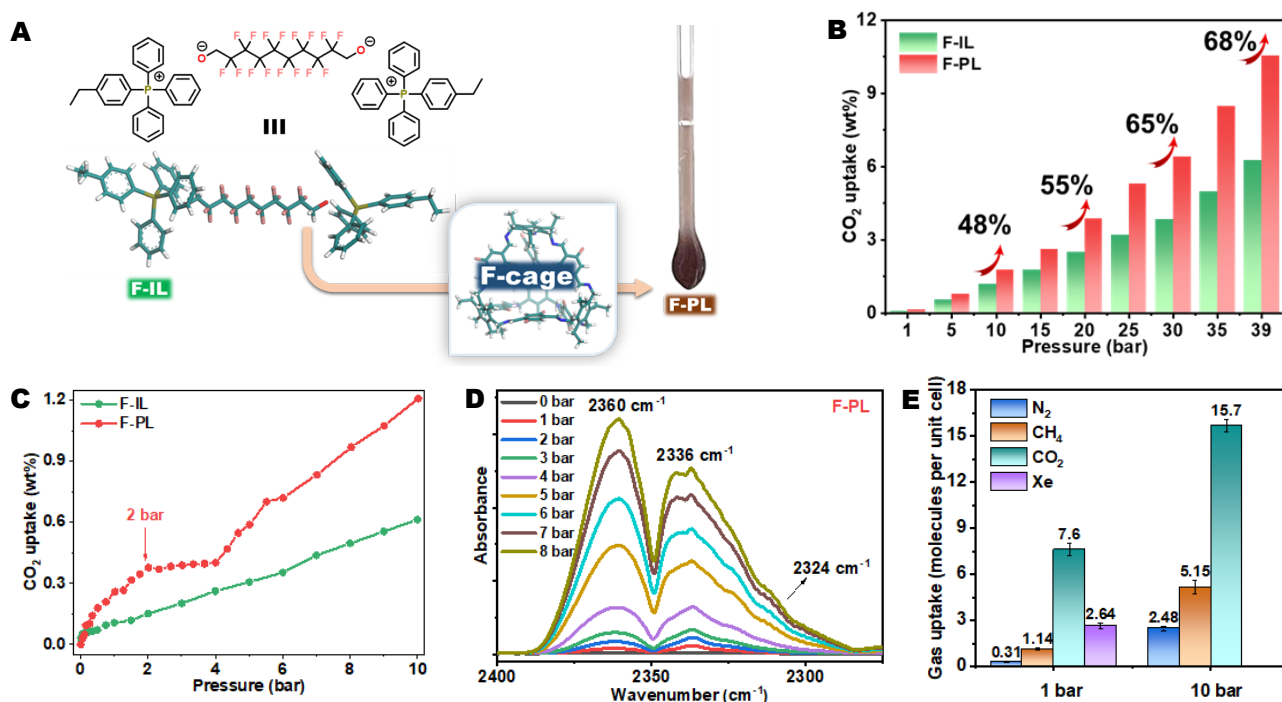


Figure 20. (A) Structure of F-IL and the optical images of F-PL. (B) CO₂ uptake capacities of F-IL and F-PL at 298 K under varying pressures. (C) CO₂ uptake isotherms of bulky IL (F-IL) and PL (F-PL) at 298 K. (D) In situ FTIR of F-PL at 298 K by dosing CO₂. (E) Simulated different gases uptake in the unit cell of the F-PL at 1 bar and 10 bar.¹⁹⁸ Reproduced with permission from Ref 198. Copyright 2024 John Wiley & Sons.

Metal-organic polyhedra (MOPs), characterized by their discrete molecular structures and intrinsic permanent cavities, have emerged as promising porous hosts for constructing PLs.²⁰⁷ Similarly, the design and selection of ILs are critical in this context. For example, an anionic organic–inorganic hybrid doughnut-like cage, which have been utilized in the synthesis of PLs, is scarcely soluble in organic solvents, such as 15-crown-5 and hexachloropropene. The use of IL (trihexyltetradecylphosphonium chloride) not only resolves this solubility issue but also enables the creation of a Type II PL that facilitates L-tryptophan identification.²⁰⁸ Another type II PL was developed using the typical MOP, Pd₁₂L₂₄, as the porous host and a PEG-linked bisimidazolium-based bulky IL as the solvent.²⁰⁹ The obtained PLs demonstrated enhanced CO₂ adsorption, achieving a high capacity of 0.892 mmol g⁻¹ at 10 bar pressure, while exhibiting negligible uptake of N₂ and CH₄. The fabrication of PL-supported membrane further confirmed its ability to reduce the gas diffusion barrier, showing high selectivity and permeability for CO₂ in CO₂–N₂ and CO₂–CH₄ gas pairs. To address the poor solubility of MOP, surface structural engineering proves to be an effective solution.¹⁹⁹ In general, rhodium(II)-based MOP (RhMOP) is difficult to dissolve in imidazolium IL (IL-Br) (**Figure 21A**). However, by introducing additional coordinating agents, such as 1-dodecylimidazole (diz) or 4-(trifluoromethyl)pyridine (CF₃-Py), into MOP, the surface rigidity of RhMOP is significantly enhanced, allowing it to dissolve more readily in IL-Br and form a type II PL. The integrity of the structure and the presence of permanent porosity were confirmed through CO₂ uptake evaluation (**Figure 21B**). At 273 K and 1 bar CO₂ pressure, type II PLs exhibited higher CO₂ sorption capacities (PIL-*diz*-RhMOP, PIL-*CF₃-Py*-RhMOP), compared to the type III PL (PIL-RhMOP) and pure IL (IL-Br). Furthermore, the catalytic cycloaddition reaction of epichlorohydrin with CO₂ was conducted to evaluate the advantages of PLs in gas-liquid phase reactions. Under the same reaction conditions, the catalytic performance and CO₂ sorption capacities followed the same trend: Type II PLs outperformed Type III PLs, and both types of PLs were superior to pure IL (**Figure 21C**). Among the Type II PLs, the *diz*-modified PL exhibited better performance than the CF₃-Py-modified PL. ILs played an irreplaceable role in cycloaddition process, and the proposed catalytic mechanism is illustrated in **Figure 21D**. Specifically, the epoxides could be activated by the imidazolium cation moiety in the IL through hydrogen bonding, while the ring-opening of the epoxide is facilitated by Br⁻ anions via nucleophilic attack, preparing the system for the subsequent addition of CO₂.

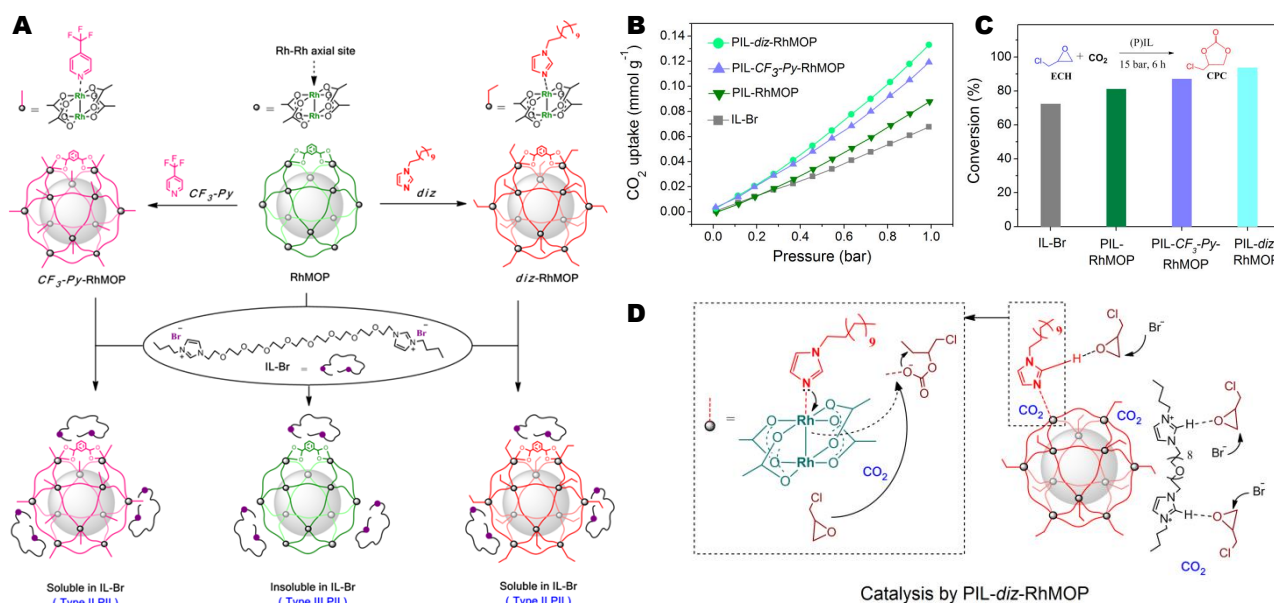


Figure 21. (A) Synthetic strategy for transforming MOP into type II PL and type III PL. (B) CO_2 uptake isotherms of PLs and IL (IL-Br) at 273 K. (C) Catalytic performance of different substrates in cycloaddition reaction of epichlorohydrin with CO_2 . (D) The plausible catalytic mechanism of CO_2 cycloaddition by PIL-diz-RhMOP.¹⁹⁹ Reproduced with permission from Ref 199. Copyright 2023 John Wiley & Sons.

3.3 Type III porous liquids

The most prevalent systems among PLs are Type III PLs where a porous solid host is dispersed in a liquid phase that can partially enter the pores but does not fully block them, preserving some degree of porosity. In these systems, the porous host is typically a microporous or mesoporous material with high surface area and tunable pore sizes such as MOFs, COFs and zeolite. The liquid phase is chosen based on its compatibility with the host material and often includes bulky ILs or organic solvents that are small enough to partially infiltrate the pores but do not completely fill them, often achieved by balancing solvent size and pore dimensions. Synthesis methods include dispersing the porous solid into the liquid phase through sonication, mechanical mixing, or surface modification to enhance compatibility and prevent aggregation.

To gain stable Type III PLs using ILs as the liquid phase, the first accomplishment of POC-based PLs was the use of imine-derived POCs.²⁰⁰ Three POC microparticles with varying compositions and cavity sizes were dispersed in different liquids, including various oils and ILs (Figure 22A). By comparing the CO_2 absorption performance at 1 bar pressure across various pure liquids and their mixtures containing 12.5 wt% CC3-*R*/CC3-*S*, the size-exclusivity and porosity of POCs were rapidly screened (Figure 22B). Among them, [BPy][NTf₂] enhanced the CO_2 solubility from 172.1 $\mu\text{mol g}_L^{-1}$ to 78.3 $\mu\text{mol g}_L^{-1}$ compared to the neat liquid, whereas [BMIM][NTf₂] did not perform the improved gas adsorption. The study indicated that the functionality of the IL cation's ring, rather than its size, primarily determines whether the intrinsic porosity inside the POC microparticles is blocked. To verify the significance of internal porosity inside the POCs in CO_2 absorption improvement, a control molecule, the CC3 cage fragment without void, was investigated (Figure 22C). It turned out that no

increase in gas adsorption was observed in the CO₂ adsorption isotherm, determining that surface adsorption makes no contribution to the notable gas solubility increase. It is also worth mentioning that IL dispersions have better thermal stability than silicone oil, particularly [BPy][NTf₂], which demonstrated high thermal stability up to 325 °C in TGA analysis (Figure 22D). Furthermore, ILs exhibited unique advantages in terms of recyclability. For [BPy][NTf₂], even after reactivation and re-adsorption over 10 cycles, no obvious decrease in CO₂ adsorption performance was observed (Figure 22E), whereas for silicone oil, the repeated adsorption lasted only two cycles due to its slight volatility.

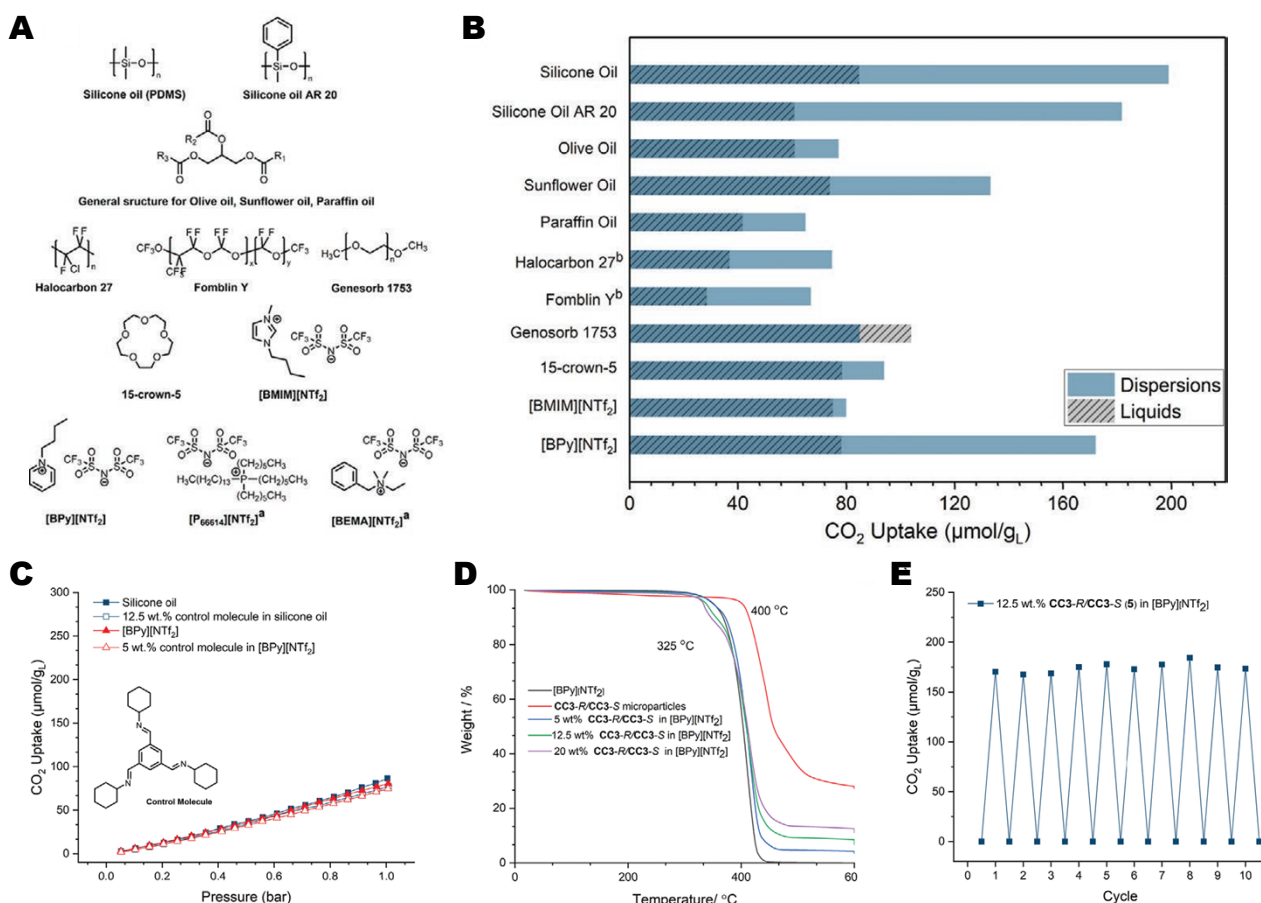


Figure 22. (A) Structure of bulky liquids screened for transforming POCs into Type III PLs. (B) CO₂ adsorption capacities comparison of the neat liquids and their mixtures with CC3-R/CC3-S. (C) CO₂ uptake isotherms of the mixtures between control molecule and silicone oil or [BPy][NTf₂]. (D) TGA analysis of [BPy][NTf₂] and the PLs derived from CC3-R/CC3-S. (E) Recycling study for POC-based PL at 1 bar.²⁰⁰ Reproduced with permission from Ref 200. Copyright 2021 John Wiley & Sons.

The most common method for constructing PLs is to disperse the porous host in ILs through physical mixing, enabling the adsorption of various gases such as CO₂,^{203, 210-216} CH₄,^{190, 217} C₂H₄,²¹⁸ and SO₂,^{219, 220}, as well as facilitating a range of applications.^{186, 193, 221-225} However, if enhanced gas-related functionality is desired in PLs, more advanced structural designs are necessary. In situ surface deposition is an effective method to uniformly coat catalytic active sites onto porous hosts, which can then be incorporated into PLs.²⁰¹ For instance, the MWW-type zeolite MCM-22 containing Na⁺ cations was initially cation-exchanged to produce MCM22 with Ag⁺ cations, which was then mixed with an

IL with good fluidity ([M2070H]Br), generating a stable type III PL coated ultra-small AgBr species (Figure 23A). The as-synthesized PLs, 20 wt% MCM22-Ag in [M2070H]Br, maintained good fluidity (Figure 23B). Compared with pure IL at 298 K, the CO₂ absorption capacity of PL containing 40% zeolite increased from 1.94 wt% to 3.48 wt%, due to the existence of internal porosity inside the PL system (Figure 23C). With the help of the abundant Ag species in the PL system, significantly enhanced ethylene uptake and selectivity of ethylene over ethane were achieved. As shown in Figure 23D, the PL of 20 wt% MCM22-Ag in [M2070H]Br showed an ethane uptake of 0.28 wt.% at 4 bar and an ethylene uptake of 0.53 wt.% at 4 bar, whereas less than 0.1 wt.% of ethylene uptake was observed in pure IL. Compared with the dispersion of 20% MCM22 without Ag species in the same IL ([M2070H]Br), there was no obvious difference in the ethylene and ethane adsorption isotherms over the entire pressure range at 298K.

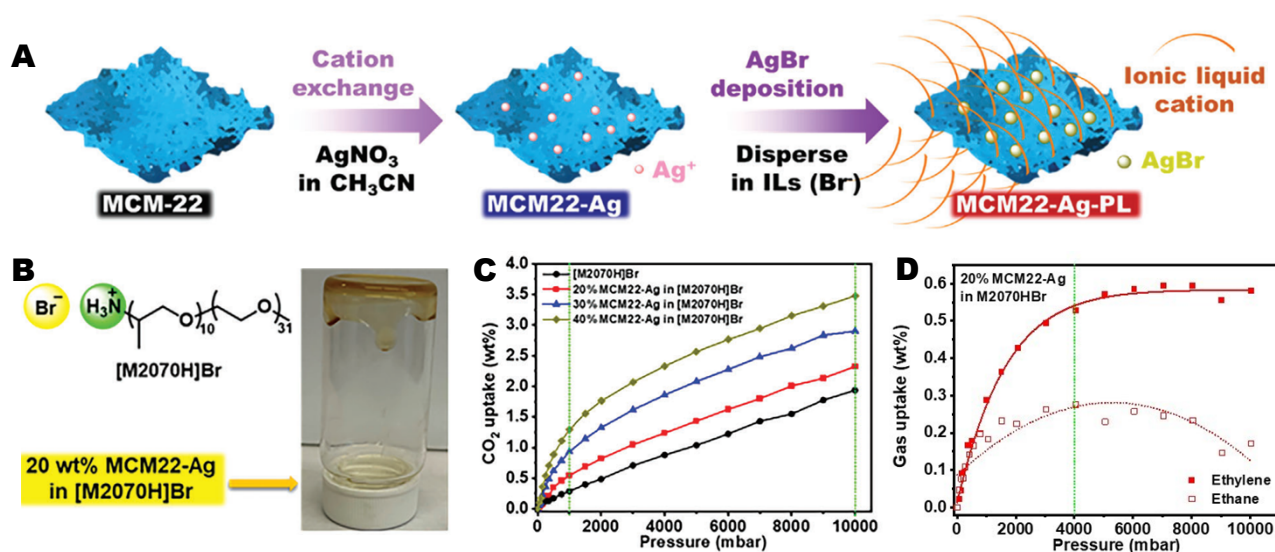


Figure 23. (A) Synthetic strategy for transforming Ag⁺ containing zeolite nanosheet into Type III PLs. (B) Chemical structure of IL ([M2070H]Br) and the optical image of PL. (C) CO₂ uptake isotherms of IL and PLs with different loading amount of MCM22-Ag at 298 K. (D) The ethylene and ethane uptake isotherms of PL at 298 K.²⁰¹ Reproduced with permission from Ref 201. Copyright 2023 John Wiley & Sons.

The surface modification of UIO-66, which possesses dangling-NH₂ groups (UIO66-NH₂), was achieved via an amide bond formation procedure. In this process, the isophthalate anion was attached to the surface and coupled with the polyether ammonium cation (protonated M2070), leading to the PL formation (Figure 24A).²⁰² The internal porosity of the CdS/NH₂-UIO-66 PL was further demonstrated by its enhanced N₂ and CO₂ uptake capacities compared to the pure IL ([M2070][IPA]) (Figure 24B and 24C). By integrating CdS NPs, the as-formed PL-composite system displayed good performance in photocatalytic CO₂-to-CO conversion, achieving 100% CO selectivity (Figure 24E), which is higher than that of the pure IL (89.74%), the porous host (80.4%) and their physical mixture (77.35%) (Figure 24D and 24E).

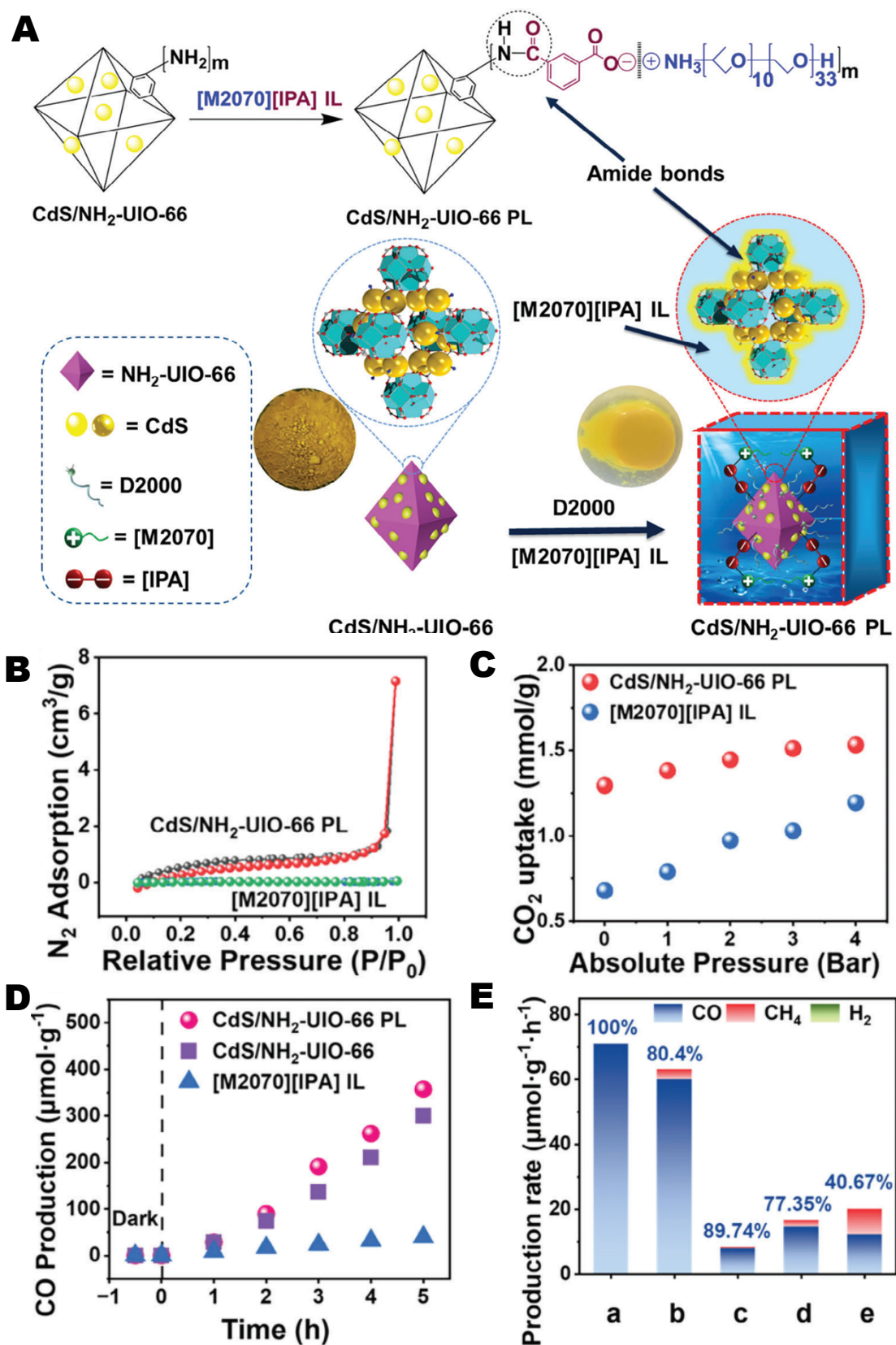


Figure 24. (A) Synthetic strategy for transforming CdS/NH₂-UIO-66 into a Type III PL. (B) N₂ adsorption isotherms of IL and PL at 77 K. (C) Comparison of CO₂ adsorption capacities for IL and PL. (D) CO₂ photoreduction performance for IL, CdS/NH₂-UIO-66 and PL. (E) Comparison of CO

evolution rate: (a) PL, (b) porous host, (c) IL, (d) physical mixture of CdS/NH₂-UIO-66 and IL, (e) PL derived from CdS/UIO-66 and IL.²⁰² Reproduced with permission from Ref 202. Copyright 2024 John Wiley & Sons.

ZIF-8 is a good candidate for PL synthesis, benefiting from its crystalline feature with particle size less than 11 μm and narrow pore apertures of 3.4 Å. [P₆₆₆₁₄][NTf₂], a stable and bulky IL with good flowable property, was selected as the dispersant.¹⁹¹ PLs were constructed by physically mixing different amount of ZIF-8 (2% and 5% w/w) with [P₆₆₆₁₄][NTf₂]. The free volume of these PLs was investigated through gravimetric gas solubility measurements of different gases. Under the conditions of 303 K and 5 bar, the CO₂ uptake capacity increased by 63% for the dispersion of 5% ZIF-8, while the uptake of N₂ and CH₄ were enhanced by over 100% (Figure 25A-25C). However, for another MOF (Mg-MOF-74) with hexagonal channels of a single-type measuring 11 Å, its 2% dispersion in [P₆₆₆₁₄][NTf₂] maintained the same uptake with pure IL (Figure 25D). Structural MD simulations vividly illustrated the distribution of ILs within MOFs. For ZIF-8, the phosphonium cations tend to accumulate on the surface of the host, with some of their alkyl chains occupying the surface-accessible pores, while most of the internal cavities remain accessible (Figure 25E and 25F). In contrast, for Mg-MOF-74, ILs freely enter the channels, since the pore size of the host is too large to exclude the ILs (Figure 25G and 25H).

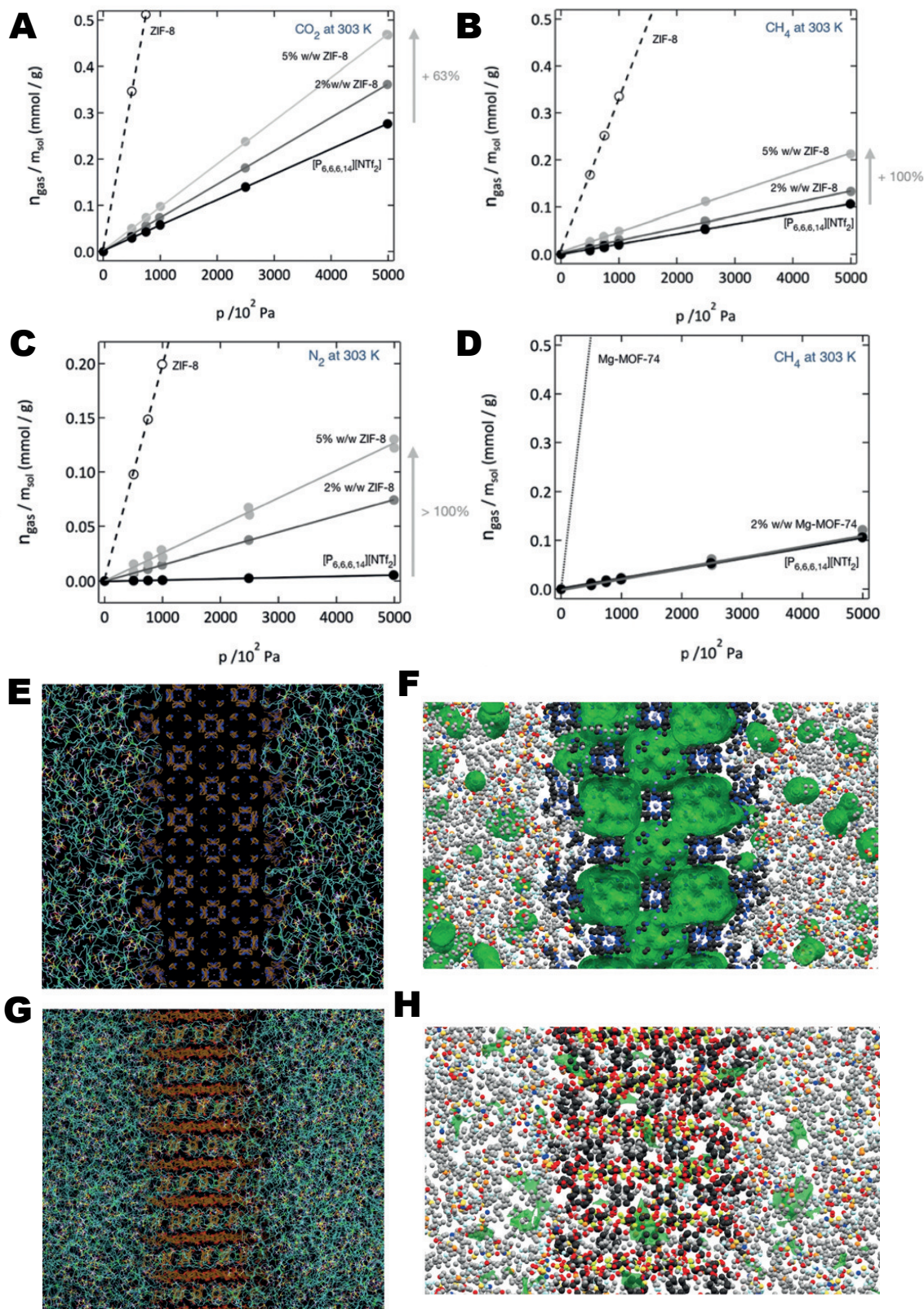


Figure 25. Solubility comparison of CO_2 (A), CH_4 (B), and N_2 (C) in IL ($[\text{P}_{66614}][\text{NTf}_2]$), ZIF-8 and their mixtures at 303 K. (D) Solubility comparison of CH_4 in $[\text{P}_{66614}][\text{NTf}_2]$ and its dispersion containing 2% Mg-MOF-74 at 303 K. MD simulation snapshots of PLs (E and F, ZIF-8 in $[\text{P}_{66614}][\text{NTf}_2]$; G and H, Mg-MOF-74 in $[\text{P}_{66614}][\text{NTf}_2]$) with accessible volume represented as green regions.¹⁹¹ Reproduced with permission from Ref 191. Copyright 2018 John Wiley & Sons.

By introducing ILs that facilitate chemisorption of gases into PL system, new liquid adsorbents can achieve CO₂ adsorption even at low pressures.⁴⁰ The IL containing phosphonium cations and carboxylate anions ([P₄₄₄₄][OAc]) was synthesized for this purpose. The chemisorption behavior of CO₂ was reflected in the nonlinear adsorption isotherm at 343 K (Figure 26A). The adsorption mechanism has been confirmed to involve the generation of ylide intermediates and the protonation of acetate anions (Figure 26E). Since [P₄₄₄₄][OAc] possesses the melting point around 343 K, making it solid at room temperature. By mixing with the other IL ([P₆₆₆₁₄][NTf₂]) with good fluidity, it is operatable over a broader temperature range. In contrast with pure [P₆₆₆₁₄][NTf₂], the IL mixtures demonstrated significantly enhanced CO₂ adsorption as shown in the corresponding adsorption isotherms (Figure 26B). Moreover, the absorption capacity increased as the concentration of [P₄₄₄₄][OAc] rose, with the chemisorption performance becoming more pronounced. When ZIF-8 was dispersed in the IL mixtures to construct a PL, no significant improvement in CO₂ adsorption was observed (Figure 26C). This is because acetic acid, the CO₂ chemisorption product of [P₄₄₄₄][OAc], can freely enter the internal pores of ZIF-8 due to its small size. To address this, ILs ([P₄₄₄₄][Lev]) with larger anions (levulinate) were then prepared. The CO₂ chemisorption of [P₄₄₄₄][Lev] and its dispersion of 5% ZIF-8 was evaluated through the isotherms at 303K (Figure 26D). In contrast, the PL demonstrated a higher adsorption capacity. It is worth mentioning that in the low-pressure range, both IL and PL showed remarkable adsorption capacities, exceeding that of pure MOF by 100%. A plausible reaction mechanism was proposed in Figure 26F. In addition to the carboxylation product at one α -carbon of the phosphonium cation, carboxylation products at positions 3 and 5 of the anions are also observed. The resulting Lev-3-CO₂-keto arises from C-3 position CO₂ addition at the. But for Lev-5-CO₂-enol, it's the consequence of CO₂ addition at the C-5 position and carbonyl enolization.

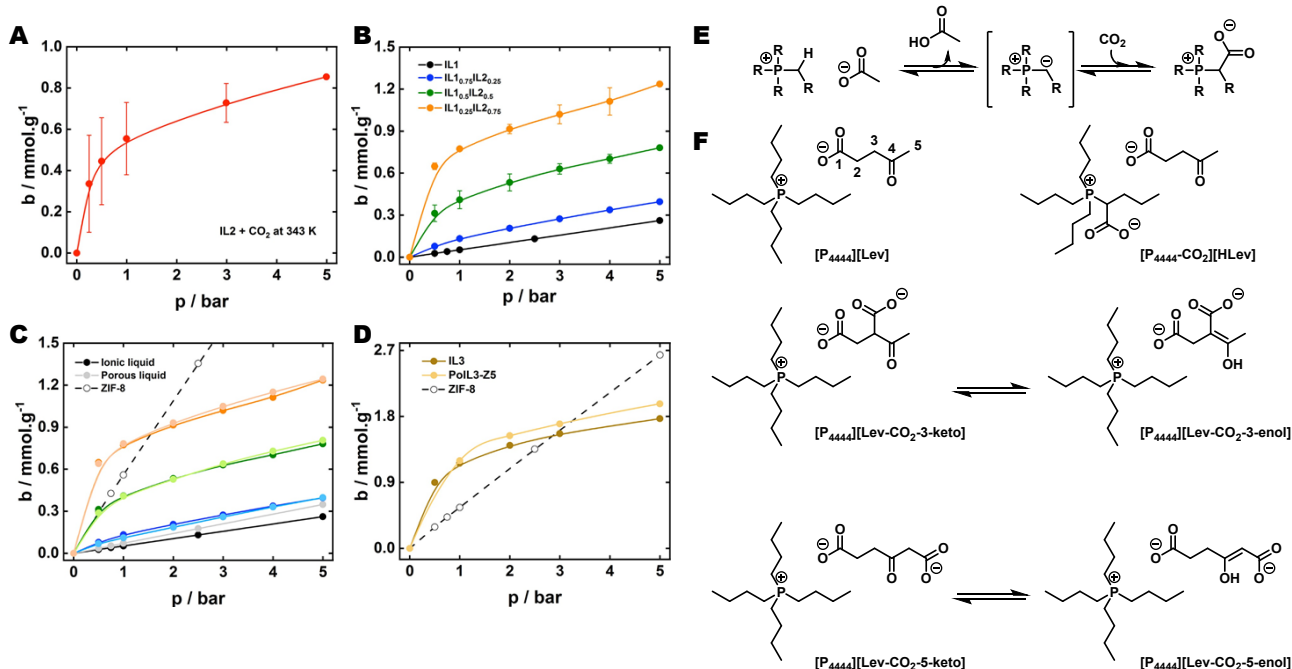


Figure 26. (A) CO₂ uptake isotherm of [P₄₄₄₄][OAc] at 343 K. (B) CO₂ uptake isotherms of IL mixtures with different ratios between [P₄₄₄₄][OAc] and [P₆₆₆₁₄][NTf₂] at 303 K. (C) CO₂ uptake isotherms of ILs and their corresponding PLs at 303 K. (D) CO₂ uptake isotherms of IL3 ([P₄₄₄₄][Lev]), ZIF-8 and corresponding PL at 303 K. (E) CO₂ chemisorption mechanism of tetraalkylphosphonium acetate. (F) Chemical structure of [P₄₄₄₄][Lev] and its CO₂ chemisorption products.⁴⁰ Reproduced with permission

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Among the Type III PLs, “porous water” is an emerging and fascinating concept primarily explored in materials chemistry.^{175, 226} It refers to water that interacts with or is contained within porous materials, rather than being a distinct type of water itself. To achieve this, the key lies in engineering porous material with a hydrophilic outer surface and a hydrophobic inner surface. Hydrophilic surfaces can attract and hold water molecules, while hydrophobic surfaces confine the water and concentrate gas molecules. For example, microporous water has been successfully constructed utilizing silicalite with abundant surface hydroxyl groups, and ZIF-8 anchored with hydrophilic PEG chains. This construction not only allows stable dispersion in water but also significantly enhances gas adsorption and diffusion. Such microporous water can be further utilized in oxygen reduction reaction (ORR) electrocatalysis, owing to its record-high oxygen solubility in aqueous solutions, overcoming the limitation of low gas solubility in water.¹⁷³ Furthermore, functionalizing PIL with imidazolium cations on the outer surface of HCS can effectively transform its hydrophobic surface into a hydrophilic one, facilitating the creation of macroporous water.¹⁷⁴ The additional free volume results in increased gas capacity and improved transport kinetics. These structural advantages are reflected in significantly enhanced electrocatalytic performance for ORR.

3.4 Simulations and modeling of porous liquids

Simulations and modeling play a crucial role in understanding the structure–property relationships of porous liquids at the molecular level. They enable the prediction of guest–host interactions, diffusion behavior, and thermodynamic stability, which are often difficult to probe experimentally. These computational insights guide the rational design and optimization of new porous liquid systems for targeted applications such as gas separation and storage. Here, we highlight key modeling and simulation studies addressing three different types of porous ILs.

The first room-temperature, optically transparent type I porous IL was developed in 2015,⁴¹ composed of functionalized hollow silica shells with ionic PEG chains on the surface. DFT studies were performed to investigate CO₂ interactions with HS-liquids,²²⁷ identifying the strongest adsorption site near the PEG unit (Figure 27A), with hydrogen bonding playing a key role. The findings also indicated that increasing the polymerization degree of the canopy enhanced gas adsorption capacity. Similarly, first-principle studies explored SO₂ adsorption on HS-liquids,²²⁸ revealing similar mechanisms. Electrostatic potential and structural analysis (Figure 27B) revealed that carbon chains in HS-liquids feature multiple C-H $\cdots\pi$ interaction sites with dibenzothiophene (DBT),²²⁹ which enhanced the desulfurization process.

Molecular dynamics simulations were used to study HS-liquids with varying canopy densities and structures,^{230, 231} concluding that steric hindrance and reduced interfacial interactions, rather than electrostatic repulsion, governed the separation behavior. It was also found that linear and long canopy structures improved dispersibility and fluidity in porous ILs.

demonstrating high adsorption capacity and selectivity for gases like H₂S. MD simulations revealed that PEGS molecules, due to their large size, could not diffuse into UiO-66-OH cavities, whereas H₂S molecules can easily penetrate. Adsorption density field analysis revealed that H₂S primarily adsorbs onto the tertiary amine and -OH groups within UiO-66-OH pore channels (Figure 27C), exhibiting greater filling and adsorption capacities than CO₂ and CH₄. DFT calculations revealed that H₂S forms the strongest adsorption configuration, as evidenced by the shortest hydrogen bonding distance with the tertiary amine and the highest enthalpy change (Figure 27D). Further transition state studies (Figure 27F) elucidated the H₂S catalytic mechanism (Figure 27E). The process begins with rapid deprotonation of H₂S at the nitrogen site of a tertiary amine. Subsequently, the electron-withdrawing carboxyl group of α -methylacrylic acid attacks the β -carbon, followed by the transfer of an active hydrogen originating from the intermediate quaternary ammonium, ultimately leading to the generation of thermodynamically stable 3-mercaptopisobutyric acid. In the CdS/NH₂-UiO-66 porous IL system,²⁰² DFT studies revealed that amide bonds between the MOF (NH₂-UiO-66) and ILs facilitated CO₂ adsorption and enhanced photocatalytic CO₂ reduction.

A supramolecular complexation strategy was developed to synthesize porous ILs.¹⁸⁸ This method involved complexing crown ethers with potassium ions (K⁺) and combining them with an anionic imine cage to form porous ILs. Specifically, dicyclohexyl-18-crown-6 formed Type I porous ILs when directly mixed with the imine cage anion. Meanwhile, a solid mixture of 15-crown-5 and the imine cage, dissolved in excess 15-crown-5, resulted in Type II porous ILs. MD simulations (Figure 18C and 18D) confirmed that both types of porous ILs contained cavities suitable for gas adsorption. Because 15-crown-5 is smaller than 18-crown-6, it partially enters the cage, leading to slightly larger cavities in 18-crown-6-based PLs compared to those formed with 15-crown-5.

CO₂ adsorption at various sites on 15-C-5-PL and 18-C-6-PL was studied via a combination of DFT and MD simulations (Figure 28A).²³² The finding revealed that, compared to N₂, the porous ILs exhibited a stronger tendency to adsorb CO₂ (Figure 28B), primarily due to hydrogen bonding with the crown ether and electrostatic interactions. The maximum molar adsorption was below four, and CO₂ uptake was weakest when positioned at the window, surface, or vertex sites. In addition, CO₂ adsorption of 11 different PL systems was analyzed by MD simulations.²³³ It was determined that the KACC/18-crown-5 with 1:3 ratio had the largest CO₂ adsorption capacity (Figure 28C). By comparing the density distribution and diffusion coefficients of CO₂ in various 18-crown-5 systems (Figure 28D), it was found that increasing the crown ether content improved fluidity and enhanced porous IL formation. However, excessive crown ether reduced pore connectivity, ultimately limiting CO₂ diffusion and adsorption. Beyond modifying ILs with anionic cage, Type I PLs was successfully synthesized by replacing the cation in ILs with a cationic coordination cage.¹⁷⁶

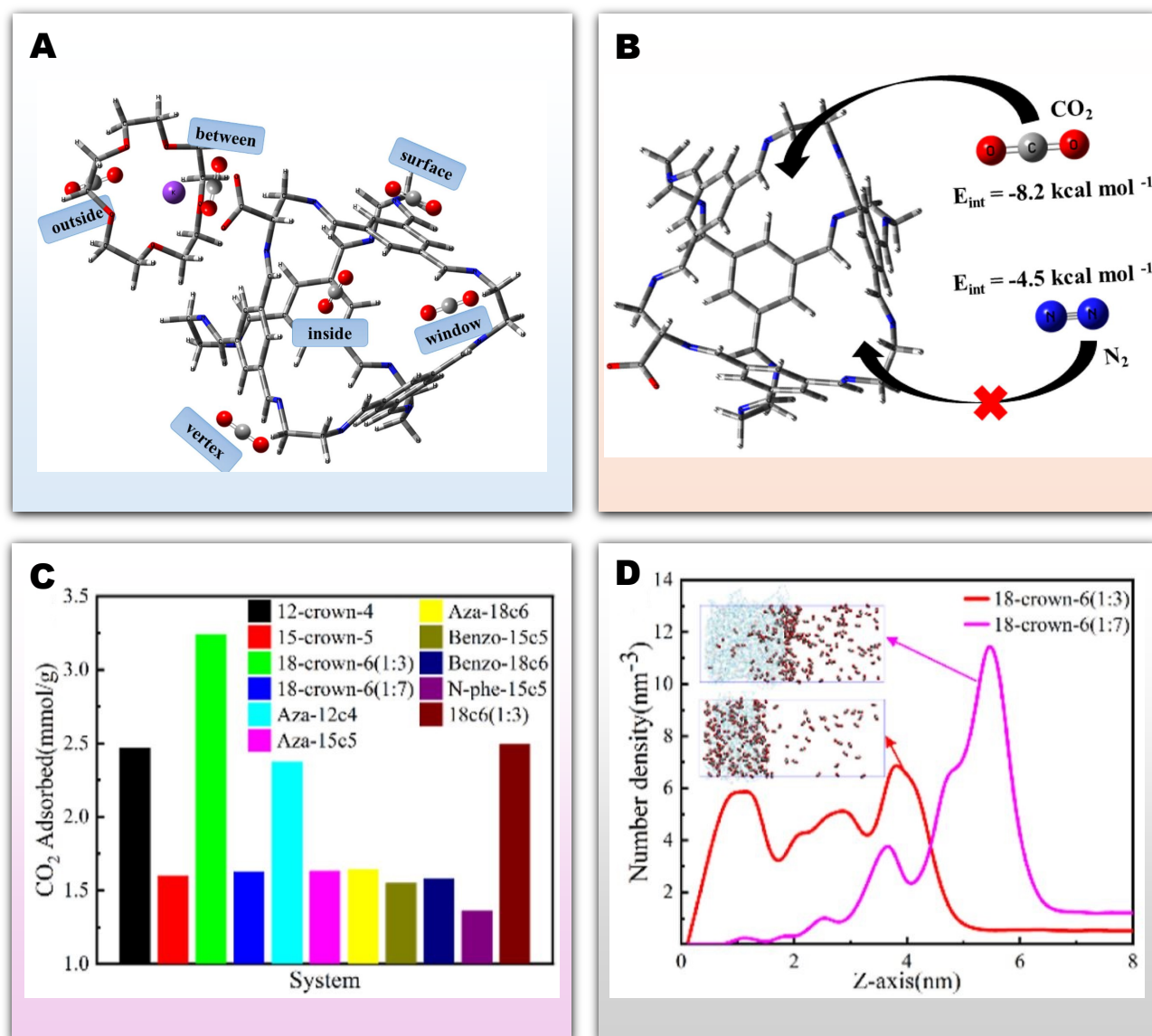


Figure 28. (A) Various adsorption sites in 15-C-5-PL.²³² (B) Interaction energy of CO₂/N₂ in 18-C-6-PL.²³² Reproduced with permission from Ref 232. Copyright 2021 Elsevier. (C) CO₂ adsorption capacities in various crown ether-based porous ILs. (D) The profile of CO₂ along the Z-axis in 18-crown-6 (1:3) and 18-crown-6 (1:7).²³³ Reproduced with permission from Ref 233. Copyright 2022 American Chemical Society.

A novel Type II porous IL was developed by dissolving a fluorinated imine cage (F-cage) as the porous host in a fluorinated IL (F-IL).¹⁹⁸ Gas absorption experiments revealed that F-PL exhibited significantly enhanced CO₂ uptake capacity compared to F-IL, with an even greater increase as pressure rose. To explore the structural arrangement of F-IL and the F-cage in F-PL, as well as their gas absorption behavior, MD simulations were conducted. The results revealed that the F-cage was well dispersed in F-IL, with bulky cations partially occupying the windows of the F-cage, while fluorinated dianions remained outside the cage (Figure 29A). Pore size distribution analysis revealed that F-PL exhibited a smaller average pore size (3.37 Å) compared to the F-cage alone (5.12 Å) due to

the partial occupation by F-IL, which modified the cavity dimensions. Further CO₂ adsorption simulations provided additional insights into this behavior (Figure 29B). At 1 bar, CO₂ molecules preferentially adsorbed onto F-IL. However, as pressure increased, some CO₂ molecules were pushed into the F-cage cavities, maximizing pore utilization. GCMC simulations confirmed that F-PL exhibited good gas uptake capacity (Figure 20E) and demonstrated CO₂ selectivity approximately three times higher than the F-cage alone. These findings highlight how the construction of PLs can enhance gas uptake selectivity by modulating pore accessibility and reducing window size.

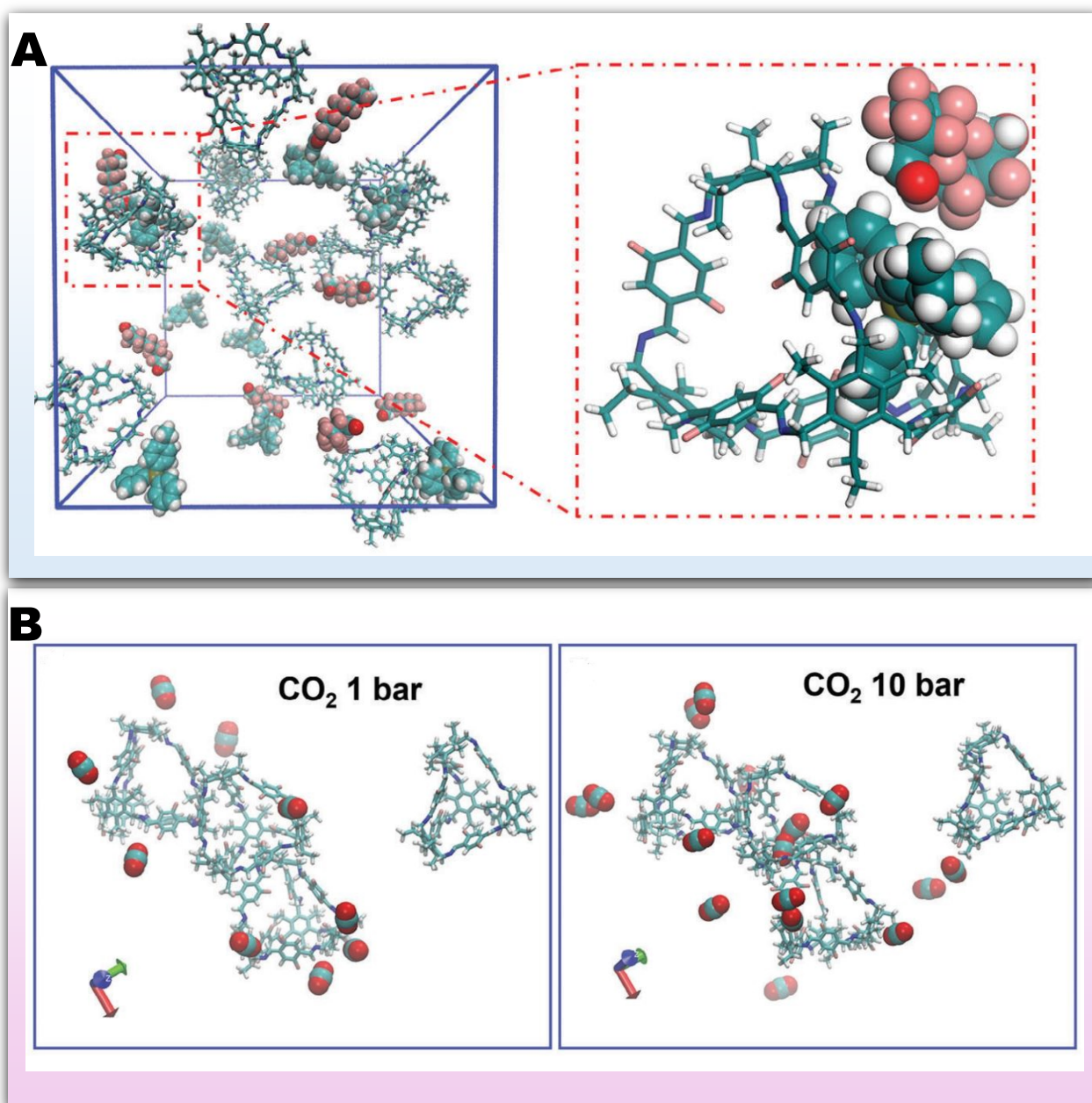


Figure 29. (A) Partial view of the MD-simulated structure of the F-PL (partial F-IL structures omitted for clarity). (B) MD snapshots of CO₂ uptake in F-PL at 1 bar (left) and 10 bar (right).¹⁹⁸ Reproduced with permission from Ref 198. Copyright 2024 John Wiley & Sons.

By 2018,²⁰³ Type III PLs were successfully developed using the IL [DBU-PEG][NTf₂] as a bulky solvent and ZIF-8 as the porous host (Figure 30A). The Gaussian-optimized [DBU-PEG] cation, measuring 1.9 nm × 0.77 nm × 0.40 nm, is significantly larger than the 0.33 nm pores of the ZIF-8 framework, effectively preventing the IL from infiltrating the pores. This concept was further explored by dispersing MOF particles, including ZIF-8 and Mg₂(DOBDC), in the IL [P₆₆₆₁₄][NTf₂].¹⁹¹ MD simulations (Figure 25E-H) confirmed that not all MOFs form porous ILs in [P₆₆₆₁₄][NTf₂]. The simulations revealed that the ILs selectively engage with the external pores of the ZIF-8, leaving a large internal free volume, whereas the cylindrical pores of Mg-MOF-74 were fully occupied by the liquid.

Additionally, machine learning was used to accelerate the screening of 4,530 CoRE MOFs employing [DBU-PEG][NTf₂] as a solvent (Figure 30B).²³⁴ The top five descriptors influencing CO₂/N₂ selectivity and CO₂ sorption were identified as pore size distribution < metal fraction < density < porosity < gravimetric surface area (GSA), leading to the prediction of five MOFs with superior gas separation performance (Figure 30C). Kinetic studies examined PLs based on solid Al(OH)(fumarate) with different particle sizes, 60 nm (PL1), 200–600 nm (PL2), and 800–1000 nm (PL3),²³⁵ revealing that the gas uptake followed the Elovich model, whereas pure polydimethylsiloxane (PDMS) exhibited first-order kinetics. The gas absorption in PLs occurs in three steps (Figure 30D): at the initial step, layer diffusion acts as the controlling step, during the second and third steps, layer diffusion, along with intraparticle diffusion, influences the process. The gas absorption rate followed the order: PL3 > PL2 > PL1 > PDMS. Furthermore, larger particle sizes resulted in faster absorption rates, suggesting that larger particles may be more effective for achieving higher gas uptake and improved absorption kinetics.

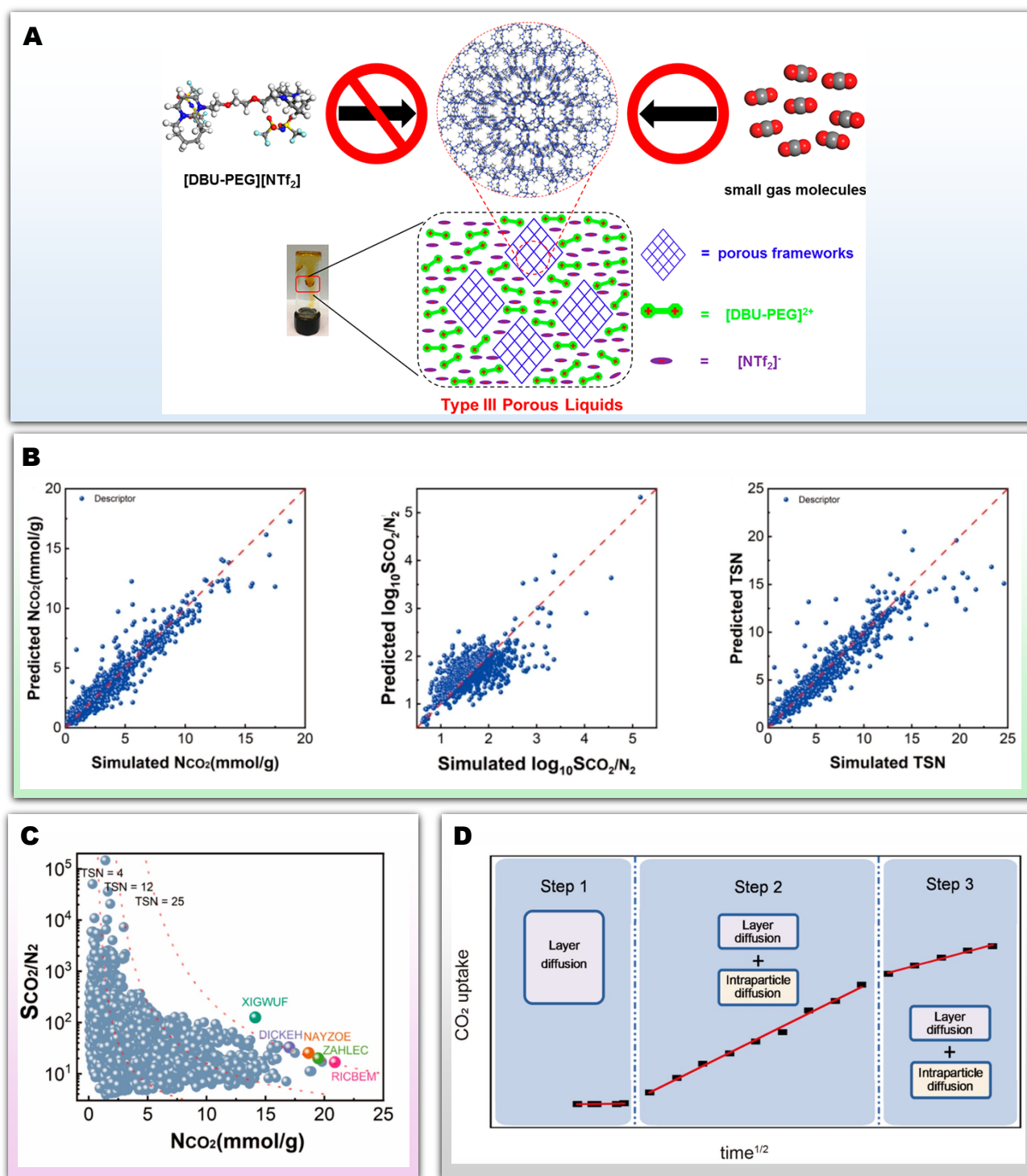


Figure 30. (A) Synthetic strategy for transforming [DBU-PEG][NTf₂] (IL) and ZIF-8 into a Type III PL.²⁰³ Reproduced with permission from Ref 203. Copyright 2018 American Chemical Society. (B) Comparison of predicted results for (left) N_{CO_2} , (middle) $\log_{10} S_{\text{CO}_2/\text{N}_2}$, and (right) sorption/selectivity trade-off (TSN) from random forest (RF) algorithm versus simulated test set results. (C) $S_{\text{CO}_2/\text{N}_2}$ versus N_{CO_2} . (D) Rate-limiting steps of CO₂ uptake into PL1–3.²³⁴ Reproduced with permission from Ref 234. Copyright 2023 American Chemical Society.

4. Ionic liquid membrane-based CO₂ separation

Membrane separation has emerged as a green, continuous and non-phase change process,²³⁶⁻²⁴² offering a promising alternative to the energy-intensive and environmentally harmful amine scrubbing method for CO₂ separation.^{243, 244} The effectiveness of this approach relies on the performance of the membrane material. Due to their remarkable structural versatility and tunability, IL-based membranes including the supported IL membranes (SILM),²⁴⁵⁻²⁵⁰ PIL (poly(IL)) membranes,²⁵¹⁻²⁵³ IL/porous scaffold composite membranes,²⁵⁴⁻²⁵⁸ have shown significant potential in various separation applications, such as gas separation,^{240, 259} light hydrocarbon separations²⁶⁰, and desalination.^{261, 262} As demand for these separations grows, a key scientific challenge is to enhance IL-based membrane performance to meet increasing requirements while gaining fundamental insights into the governing factors. In CO₂ separation, the nonvolatile nature of ILs, coupled with their tunable physical properties and interactions with CO₂, makes them attractive membrane materials. Unlike sorbent-based carbon capture, which relies on active sites with strong interactions for low-concentration CO₂ capture, membrane-based CO₂ separation depends on both CO₂ solubility and transport kinetics, specifically, solubility and diffusivity in ILs. This section summarizes recent advances in CO₂ separation using IL-derived membranes, focusing on strategies to enhance performance by modulating IL cation structures (Section 4.1) and anion structures (Section 4.2), as well as leveraging the gating behavior of ILs in IL/porous scaffold composite membranes (Section 4.3).

4.1 Influence of cations in ionic liquid-derived membrane separation

The mass transfer of solubilized molecules (e.g. CO₂) across the membrane follows the solution-diffusion model, where the transport is driven by the concentration gradient and molecular diffusion within the membrane matrix.²⁴⁰ Achieving high permeability requires a strong affinity and high solubility for CO₂ molecules. However, unlike functionalized ILs used as absorbents in carbon capture (discussed in Section 2), transmembrane mass transfer is another critical factor influencing permeability. This transfer is primarily affected by the viscosity and free volume of the ILs. Numerous studies have explored how the physicochemical properties of both cations and anions in ILs influence membrane separation performance by affecting CO₂ solubility and diffusion. Imidazolium-based ILs were among the first used in membrane separation due to their ease of synthesis and favorable CO₂ solubility via physisorption. Systematic studies on CO₂ separation with imidazolium IL-derived membranes have highlighted the critical role of cation structures.²⁶³ In membrane-based CO₂ separation, ILs are typically confined within a porous support (e.g., poly(ether sulfone) or anodisc) to form SILMs. Increasing the cation size from C₄ to C₈ significantly enhances CO₂ solubility, an effect of increased significantly further amplified by fluorination, due to stronger CO₂-cation interactions. However, this increase in cation size has an inverse effect on permeability. For instance, CO₂ permeability decreases by more than 50% when transitioning from [C₄mim][Tf₂N] to [C₈F₁₃mim][Tf₂N] (Table 3). This decline is attributed to the larger cation size of [C₈F₁₃mim], which increases IL viscosity and consequently reduces the CO₂ diffusion rate across the membrane.

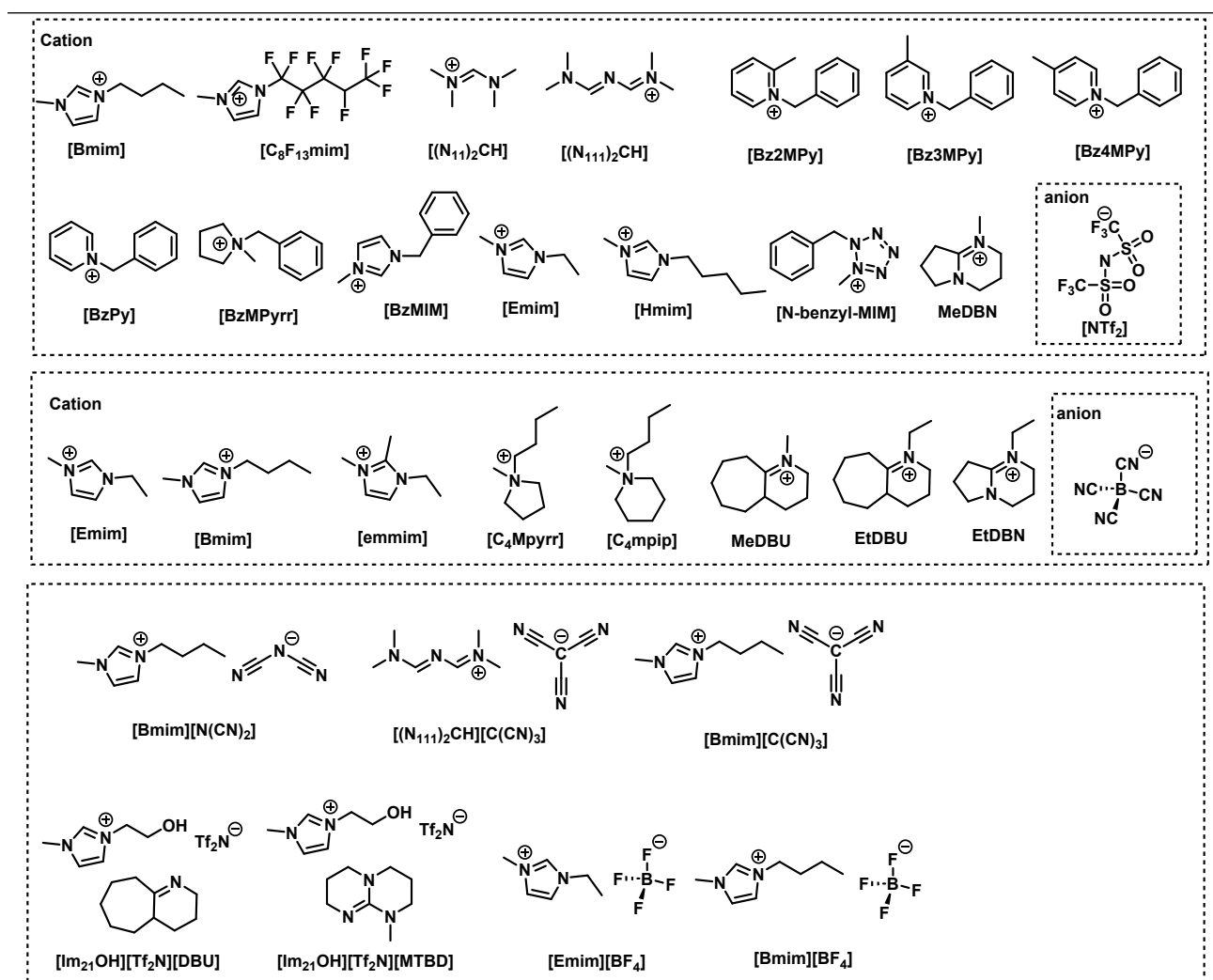
Table 3. Summary of IL-derived membranes in CO₂ separation.

ILs ^a	CO ₂ Henry's constants	CO ₂ permeability/ permeance ^b	CO ₂ /N ₂ selectivity	Pressure (KPa)	Tempera ture (K)	Thickn ess (μm)	Ref
[Bmim][NTf ₂]	37 ± 3	4 × 10 ⁻⁹ mol bar ⁻¹ cm ⁻² s ⁻¹	127	96.53- 117.21	298	60	263
[C ₈ F ₁₃ mim][NTf ₂]	31 ± 6	1.5 × 10 ⁻⁹ mol bar ⁻¹ cm ⁻² s ⁻¹	72	96.53- 117.21	298	60	263
[(N ₁₁) ₂ CH][NTf ₂]	40.7	1882 ± 65 barrer	28 ± 4	-	298	65	264
[(N ₁₁₁) ₂ N][NTf ₂]	33.7	1777 ± 46 barrer	29 ± 4	-	298	65	264
[(N ₁₁₁) ₂ N][C(CN) ₃]	52.5	1760 ± 31 barrer	45 ± 8	-	298	65	264
[Bz2MPy][NTf ₂]	41.7	358 ± 20 barrer	33.1 ± 5	30-100	298	135	265
[Bz3MPy][NTf ₂]	39.8	446 ± 12 barrer	22.0 ± 2	30-100	298	135	265
[Bz4MPy][NTf ₂]	39.3	496 ± 38 barrer	22.6 ± 3	30-100	298	135	265
[BzPy][NTf ₂]	46.1	518 ± 16 barrer	27.9 ± 3	30-100	298	135	265
[BzMPyrr][NTf ₂]	40.0	280 ± 17 barrer	25.5 ± 5	30-100	298	135	265
[BzMIM][NTf ₂]	39.9	528 ± 16 barrer	31.4 ± 7	30-100	298	135	265
[Emim][NTf ₂]	39.0	1702.4 barrer	23.1	30-100	298	135	265
[Hmim][NTf ₂]	44.0	1135.8 barrer	15.4	30-100	298	135	265
[N-benzyl- MIM][NTf ₂]	34.1	304 ± 10 barrer	21 ± 3	35	298	130	266

[Bmim][N(CN) ₂]	-	0.54×10^{-9} mol m ⁻² Pa ⁻¹ s ⁻¹	51	35	298 ± 1	130	267
[Bmim][C(CN) ₃]	-	$1.88 \pm 0.7 \times$ 10^{-9} mol m ⁻² Pa ⁻¹ s ⁻¹	45	35	298 ± 1	130	267
[Emim][B(CN) ₄]	38.9	$2.71 \pm 0.05 \times$ 10^{-9} mol m ⁻² Pa ⁻¹ s ⁻¹	53	35	298 ± 1	130	267 268
[Bmim][B(CN) ₄]	32.3	1755 ± 50 barrer	40 ± 2	35-125	298	135	268
[emim][B(CN) ₄]	31.9	1721 ± 80 barrer	46 ± 5	35-100	298	135	268
[C ₄ Mpyrr][B(CN) ₄]	30.4	1633 ± 60 barrer	38 ± 2	35-115	298	135	268
[C ₄ mpip][B(CN) ₄]	30.2	961 ± 25 barrer	37 ± 5	35-100	298	135	268
[MeDBU][B(CN) ₄]	34.6	834 barrer	49	-	298	135	269
[EtDBU][Tf ₂ N]	41.2	432 barrer	26	-	298	135	269
[EtDBU][B(CN) ₄]	28.6	672 barrer	48	-	298	135	269
[MeDBN][Tf ₂ N]	39.6	787 barrer	29	-	298	135	269
[EtDBN][B(CN) ₄]	30.0	1583 barrer	48	-	298	135	269
[Im ₂₁ OH][Tf ₂ N][DBU]	-	1.43×10^{-9} mol m ⁻² Pa ⁻¹ s ⁻¹	7.1	35	363	135	119
[Im ₂₁ OH][Tf ₂ N][MTBD]	-	1.89×10^{-9} mol m ⁻² Pa ⁻¹ s ⁻¹	8.0	35	358	135	119
SiO ₂ -g-PIL	-	53.5 ± 5.2 barrer	19.1	35	298	100- 200 / 300- 600	270

hollow SiO ₂ -g-PIL	-	129.1 ± 11.6 barrer	22.2	35	298	100- 200 / 300- 600	270
COF(CTF- 1)/[Bmim][PF ₆]	-	8.26 × 10 ⁴ GPU	-	-	298	-	271
MC-CB-supported [Emim][Tf ₂ N]	-	188-219 barrer	35.0-40.2	35-1000	295	75	272
P(VDF-co- HFP)/[Emim][Tf ₂ N]	-	131.7 barrer	90.4	35	298	-	273
porous graphene/[Emim][B F ₄]	-	1.39 × 10 ⁵ GPU	5.2	1000	300	-	274
NPG/[Bmim][BF ₄]	-	1200-4000 GPU	18-32	-	300	-	59
CMS/[Bmim][BF ₄]	-	537 barrer	48	-	300	-	60

^aStructures of ILs:



$$^b \text{1 GPU} = 3.35 \times 10^{-10} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$$

Compared to ILs with imidazolium cations, those incorporating ring-opened heterocycle cations ($[(\text{N}_{11})_2\text{CH}]^+$ and $[(\text{N}_{111})_2\text{N}]^+$) paired with the $[\text{NTf}_2]$ anion maintain excellent CO_2 permeability as SILMs,²⁶⁴ while also exhibiting enhanced CO_2/N_2 selectivity (Figure 31A and Table 3). To investigate the impact of steric hindrance on membrane-based CO_2 separation performance, ILs containing planar benzyl groups on pyridium or imidazolium cations were synthesized using $[\text{NTf}_2]$ as the anion (Figure 31B).²⁶⁵ Although introduction of bulky groups into the cation improved CO_2 uptake,²⁶⁶ the increased viscosity outweighed this benefit, leading to reduced CO_2 permeability compared to imidazolium-based SILM systems (Table 3). However, the larger cation size also restricted N_2 permeability, resulting in selectivity values between 22.0 and 33.1, higher than that of $[\text{Bmim}][\text{Tf}_2\text{N}]$ (19.7).

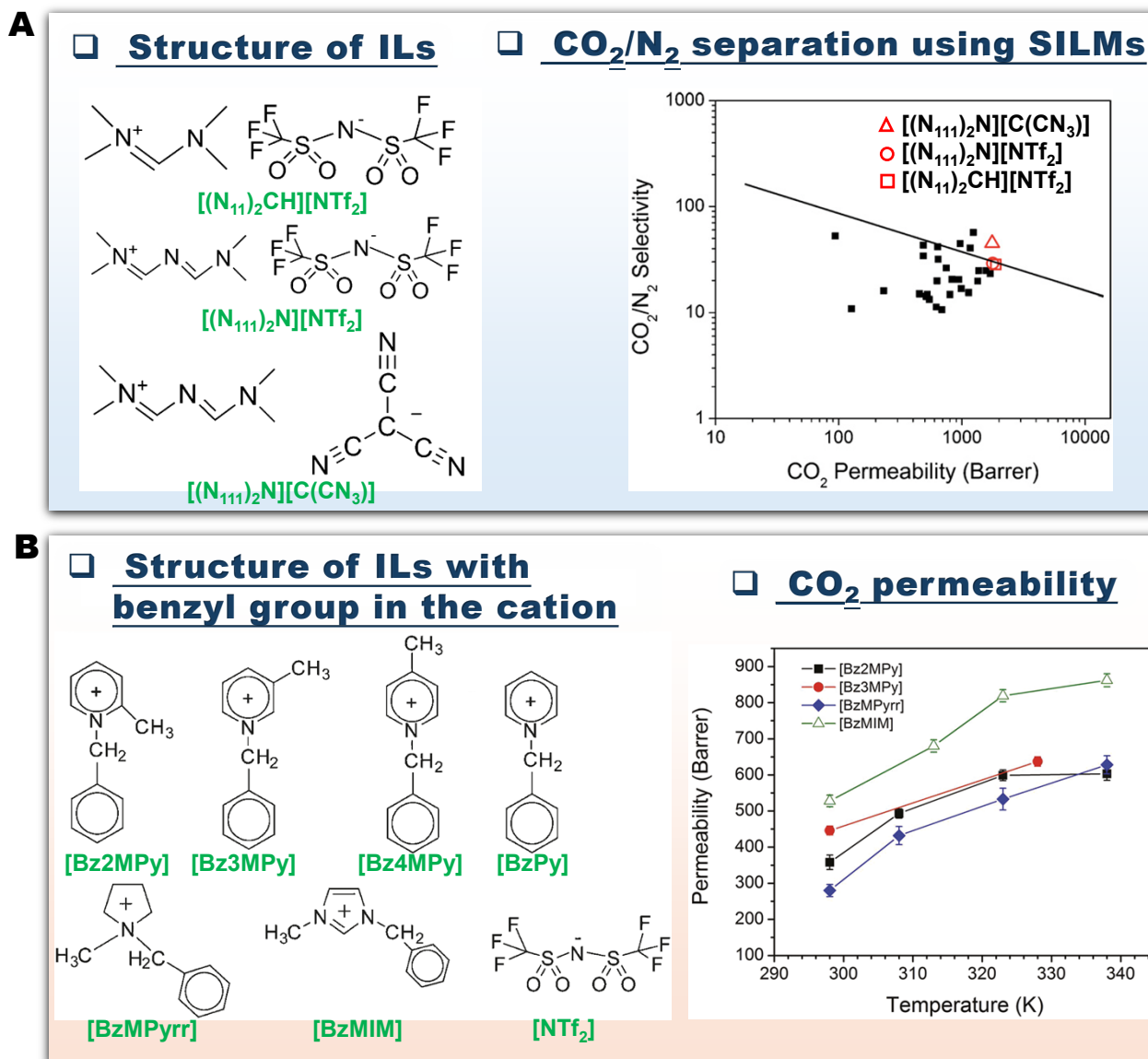


Figure 31. (A) Structures of ILs with ring-opened heterocycle cations and their membrane-based CO₂/N₂ separation performance.²⁶⁴ Reproduced with permission from Ref 264. Copyright 2012 Elsevier. The solid line represents the upper bound of Robeson plot. (C) Structures of IL cations containing benzyl group, paired with [Tf₂N] anion, and their temperature-dependent permeability.²⁶⁵ Reproduced with permission from Ref 265. Copyright 2011 American Chemical Society.

4.2 Influence of anions in ionic liquid-derived membrane separation

Compared to cation-CO₂ interactions, anions exhibit a stronger affinity for electrophilic C atom from CO₂, significantly increasing CO₂ solubility. Strengthening anion-CO₂ interaction presents a promising strategy to improve CO₂ affinity without substantially increasing the molecular size of ILs. The membrane separation performance of ILs incorporating small, nitrile-functionalized anions and imidazolium-based cations with short branched chains (up to C₄) was investigated (Figure 32A, Table 3).²⁶⁷ These nitrile-based anions offer superior environmental compatibility compared to the commonly used [NTf₂] anion as they contain no fluorine moieties. CO₂ uptake studies revealed that

increasing the nitrile group number in anion section significantly enhanced CO₂ solubility by providing additional binding sites. For instance, ILs containing [B(CN)₄]⁻ anion exhibited higher CO₂ solubility than those with [NTf₂]. Moreover, these nitrile-based anions had a minimal impact on the overall IL size, leading to CO₂ permeability trends that closely followed solubility patterns. The imidazolium-based IL with shortest ligand ([Emim][B(CN)₄]) among these ILs achieved high CO₂ permeability (2.55×10^{-9} mol m⁻² Pa⁻¹ s⁻¹), representing a 30% improvement over [Bmim][NTf₂]. To further enhance CO₂/N₂ separation performance, diverse ILs that contains the tetracyanoborate anion ([B(CN)₄]⁻) were synthesized.²⁶⁸ Instead of increasing cation size by extending branched chains, CO₂ affinity was improved by strategically positioning substituents and introducing multiple short-chain groups, thereby preventing a significant rise in viscosity (Figure 32B).²⁶⁹ This strategy proved effective, as the viscosities of these modified ILs remained relatively stable while maintaining excellent CO₂ permeability. Additionally, reducing anion-cation interaction strength within the ILs was found to enhance ion-CO₂ affinity, further improving separation performance.

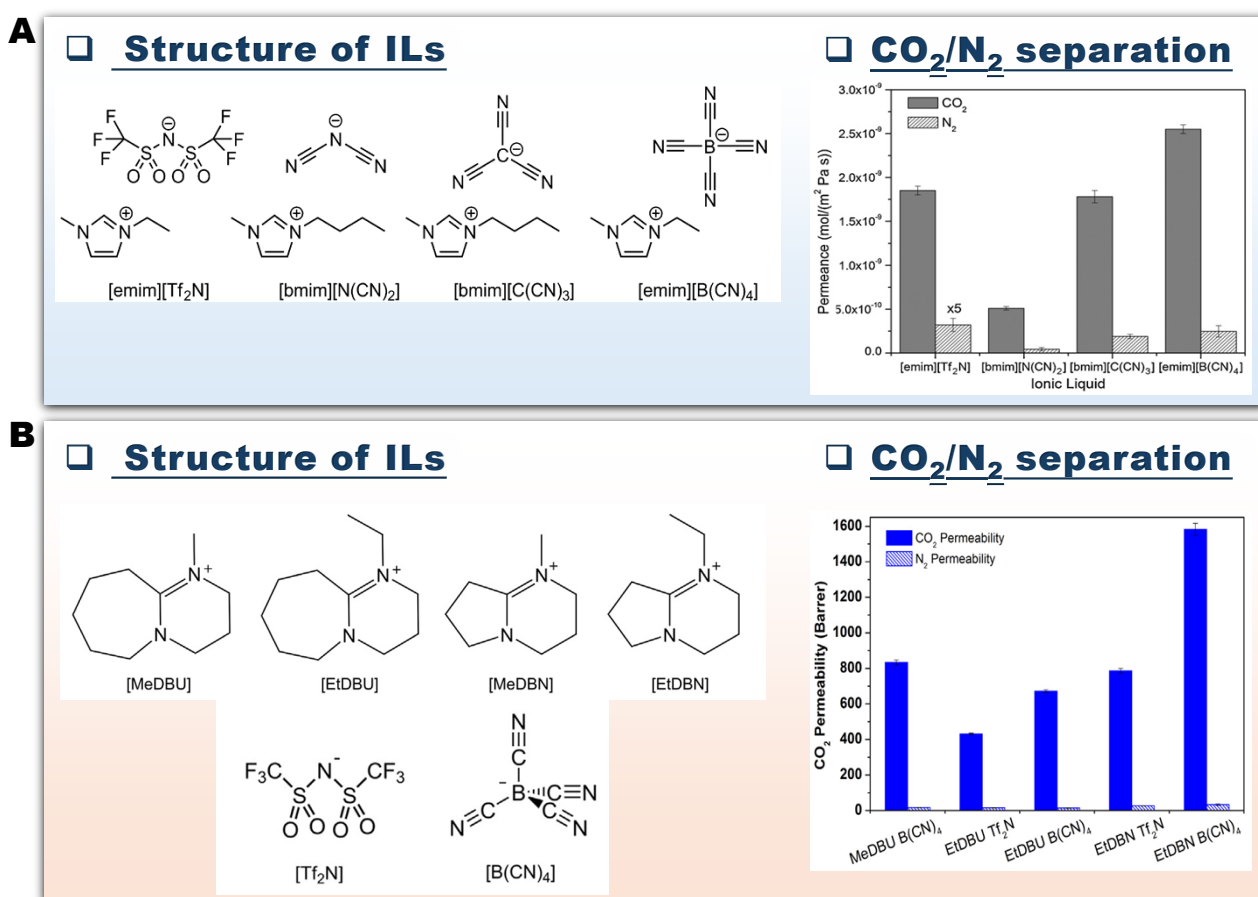


Figure 32. (A) The anion and cation structure of four imidazolium-based RTILs formed from anions containing NTf₂ and different nitrile group, respectively, and their CO₂ and N₂ permeance values.²⁶⁷ Reproduced with permission from Ref 267. Copyright 2010 Elsevier. (B) Structures of the ILs containing the bicyclic N-hybrid cations and the NTf₂ and B(CN)₄ anions, and their CO₂ and N₂ permeability.²⁶⁹ Reproduced with permission from Ref 269. Copyright 2018 Elsevier.

To investigate the impact of anions on gas permeability, molecular dynamics simulations were

employed to examine the CO₂ diffusion properties in three ILs sharing the common cation structure was studied by.^{275, 276} Consistent to previous observation, the simulated results align well with the experimental data, revealing the best performance of [B(CN)₄]⁻ compared to the other two anions of [Tf₂N]⁻ and [BF₄]⁻, with the same [Emim]⁺ cation structure; meanwhile the superior CO₂ solubility of the [Emim][B(CN)₄] is attributed to the moderate interactions between cation and anion, a greater proportion of larger cavities, increased molecular free volume, with more favorable CO₂ binding affinity. This work provided a view of the superiority of [B(CN)₄]-based ILs for an efficient CO₂/N₂ membrane separation. Building on these, a series of SILMs were synthesized by pairing superbase-derived cations with [B(CN)₄]⁻ anions (Figure 32B and Table 3).²⁶⁹ The study revealed that these cations provided comparable or even higher CO₂ solubility than their imidazolium-based counterparts due to the increased free volume within the IL matrix. However, despite the increase in free volume, the rate of CO₂ diffusion was inversely reduced, resulting in a lower overall CO₂ permeability compared to [Emim][B(CN)₄].

Using ILs containing hydroxyl groups into the imidazolium cation side chains and [NTf₂]⁻ anion as the proton donor, highly efficient CO₂ chemisorption was demonstrated by adding superbase, which, after reacting with CO₂, leading to carbonate and protonated superbase cation formation.¹¹⁹ This approach indeed significantly increased CO₂ solubility benefiting from the superbase incorporation. However, the overall CO₂ permeability at near-room temperature remained constrained by the large size of the resulting composite system and strong O-C bond formation between IL and CO₂ (Table 3). As the viscosity decreased with increasing temperature, the permeability increased significantly, e.g. more than 100-fold when the temperature increased to 90 °C due to accelerated diffusion. In addition to these SILMs, other anions and cations, such as amino-functionalized²⁷⁷ or carboxylate anions²⁷⁸ and quaternary amine/phosphine cations²⁷⁹, have also been investigated by researchers (Table 3). The results of the ion regulation have enriched the variety of IL-based membranes and offered additional methods of regulating the CO₂ affinity and separation selectivity. However, how to optimize the permeability/selectivity of SILMs by harnessing the large tunability of ILs properties and their interaction with CO₂ still needs further efforts.

4.3 Ionic liquid/porous scaffold composite membranes in CO₂ separation

The integration of ILs with porous materials offers a promising approach to address the inherent viscosity-mass transfer decoupling bottleneck associated with ILs-based membranes. The intrinsic porosity of porous materials facilitates rapid molecular diffusion and mass transfer, synergistically combining with the superior CO₂ capture and selectivity characteristics of ILs. Traditionally, porous carbon and polymeric materials have been the most common and cost-effective choices for these systems.^{238, 270, 280-283} More recently, structurally well-defined materials such as metal-organic framework (MOF)^{257, 284, 285}, covalent organic framework (COF)^{271, 286} and covalent triazine framework (CTF)²⁸⁷⁻²⁹⁰ have also been proven significant potential in membrane separations. However, ensuring the stability of ILs within these porous supports is a critical prerequisite for the successful construction of such composite systems, especially under high-pressure conditions that may be encountered during practical separation processes.

The ILs can be incorporated into porous supports via two primary strategies: (1) embedding ILs homogeneously confined within the channels, and (2) physically impregnating ILs into porous supports. The former approach offers greater stability but often limits the intrinsic advantages of the ILs due to their quasi-solid behavior in such matrices, typically leading to lower permeability and

selectivity. Conversely, the latter approach relies on capillary action to immobilize the ILs within the pore channels, allowing for better retention of their absorption and mass transfer properties. However, larger pore channels can result in the overflow and loss of ILs, especially under high-pressure conditions.

A “brick-and-mortar” strategy was deployed to fabricate an ordered mesoporous carbon membrane, characterized by a narrow pore size distribution of 7.3-11.3 nm, which greatly strengthened the stability of ILs-carbon membranes compared to conventional mesoporous polymer membranes with broader pore size distributions.²⁷² The imidazolium-based ILs were then physically loaded onto these carbon membranes, and the results demonstrated that the CO₂ permeability remained stable even under a pressure of 1000 kPa for these composite membranes.

With the same goal of avoiding the ILs loss, a novel gas-phase cross-linking method was developed to form a polyamide (PN) network on the surface of polymer membranes (Figure 33).²⁷³ As shown in Figure 33A, the synthesis approach involves pre-dispersing trimesoyl chloride (TMC) into an SLM consisting poly(vinylidene fluoride-co-hexafluoropropylene) with the IL, followed by vapor-phase treatment with amine linkers. This process induces a catalyst-free interfacial cross-linking reaction, forming a polyamide network (PN) layer with gas selective diffusion channel on the surface structure. This modification preserved the mechanical integrity of the polymer while the relatively dense PN layer significantly reduced the risk of IL leakage. Their results showed that these membranes achieved both high permeability and selectivity (Figure 33B and 33C), surpassing the Robeson upper bound at the time.

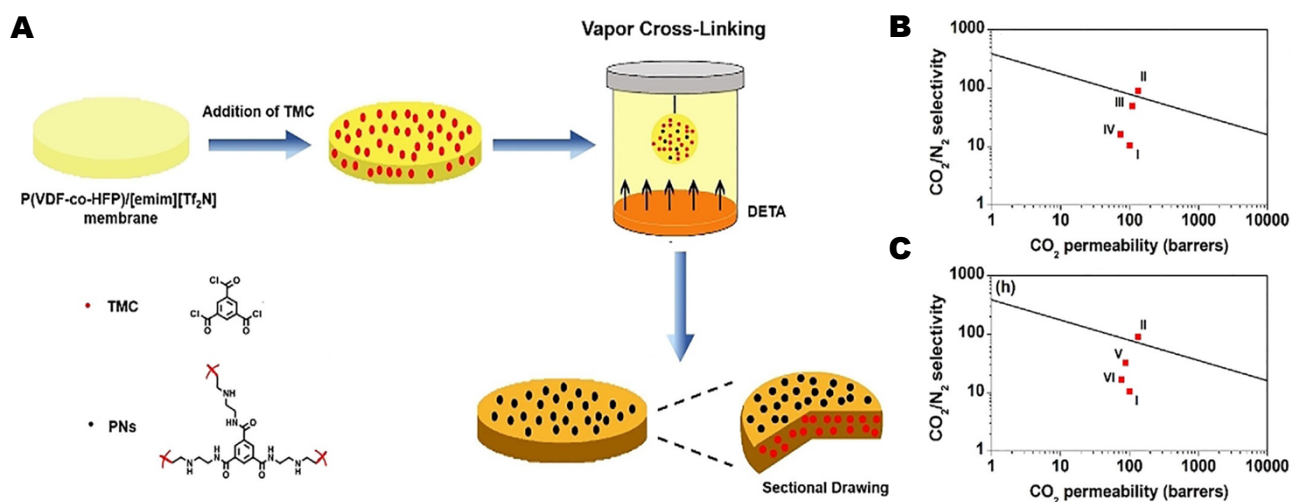


Figure 33. (A) The preparation of the composite membranes based on [Emim][Tf₂N] by vapor cross-linking strategy. Robeson plots (B, C) of the pristine (I) and the PN composed poly(vinylidene fluoride-co-hexafluoropropylene)/[Emim][Tf₂N] membrane (II, III, IV) at 298 K.²⁷³ Reproduced with permission from Ref 273. Copyright 2017 John Wiley & Sons.

Apart from embedding or impregnating ILs into porous channels, a more straightforward method involves coating the ILs directly onto the surface of the porous supports.^{274, 291, 292} Theoretically, a thin IL layer can be applied onto a porous support with ultralow thickness even the single-atom-thick graphene layer, dramatically reducing mass-transfer resistance while maintaining excellent CO₂ selectivity. An innovative ion-gating strategy was proposed that involved physically coating ILs onto

polyimide-derived carbon molecular sieve (CMS) membranes (Figure 34A and 34B), creating a “selective filter” to enhance CO₂ selectivity.²⁹¹ These ion-gated membranes exhibited enhanced diffusion selectivity due to the presence of interfacial ions at the pore entrances, which acted as molecular sieves. It was found that IL layers of near single-molecular thickness provided high CO₂ recognition ability with minimal diffusion resistance. This ion-gating sieving effect not only introduced new possibilities for improved separation but also offered valuable insights into the fundamental properties of ILs at the molecular level. Building on this, the IL gating creation approach was extended to monolayer nanoporous graphene (NPG) membranes (Figure 34C), which possess appropriate pore sizes (~1 nm) with high pore density ($1.1 \times 10^{12} \text{ cm}^{-2}$), with imidazolium-based ILs retaining on the membrane surfaces (Figure 34D).²⁹² These membranes demonstrated dynamic control over pore size to modify the transport of both CO₂ and N₂. The synergistic interplay between the porous structure of the graphene and the fluidic properties of the ILs enabled these composite membranes to exhibit excellent permeability and selectivity (Figure 34E). This novel approach provides a new frontier in the design and preparation of the ultrathin membranes for the CO₂/N₂ separation.

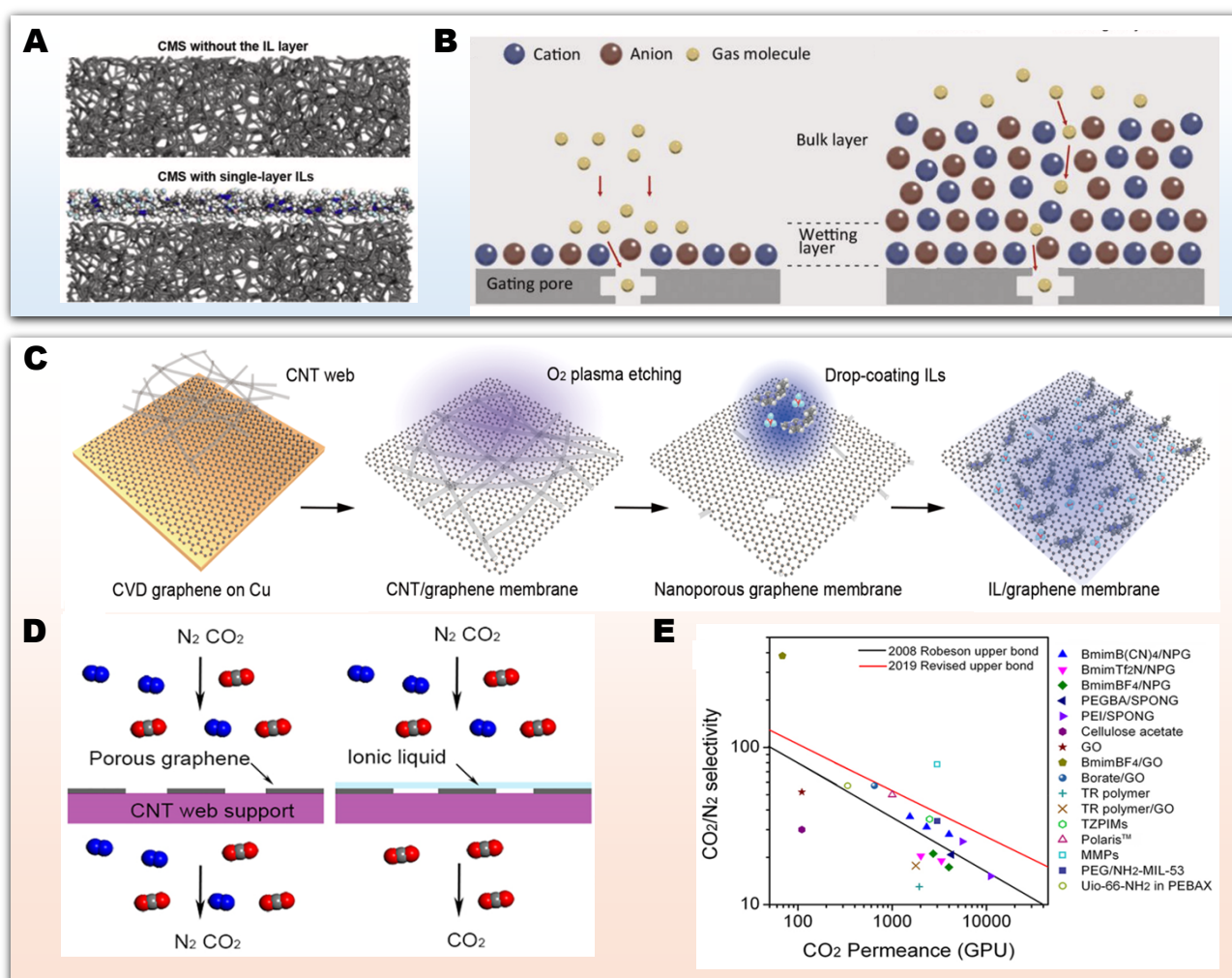


Figure 34. (A) Simulations of the gas transport through carbon molecular sieve structure. (B) Illustration of the gas molecule diffusion mechanism on the bulk and wetting layer of IL structure on the membrane surface.²⁹² Reproduced with permission from Ref 292. Copyright 2020 Elsevier. (C) The membrane fabrication process for the monolayer nanoporous graphene composite structure with

ILs. (D) The gas transport mechanism of CO₂ and N₂ through the nanoporous graphene pristine and composite membranes. (E) Separation performance of the nanoporous graphene composite membrane.²⁹¹ Reproduced with permission from Ref 291. Copyright 2020 American Chemical Society.

In addition to the CO₂/N₂ separation, IL (or composite) membranes have also been extensively investigated for the separation of other small gas molecules including H₂,^{293, 294} O₂,^{295, 296} and SO₂.^{278, 297} These studies show that IL membranes provide a promising alternative for selective gas separations due to their unique tunability, high chemical stability, and the ability to incorporate functionalized components for improved selectivity. For example, SILMs and PIL derived mixed matrix membranes (MMMs) have been explored for the CO₂/H₂ separation,²⁹³ which is particularly relevant for hydrogen purification from syngas and pre-combustion carbon capture. Some metal-containing ILs containing O₂ reactive Co(salen) (*N,N'*-bis(salicylidene)ethylenediamine) composite were synthesized and further formed O₂ affinity membranes. The O₂ permeability of these membranes were notably enhanced compared with the conventional polymer and fixed-O₂ carrier membranes.²⁹⁶ On the other hand, some task-specific ILs with high SO₂ affinity can be incorporated into membranes for selective SO₂ removal from flue gas streams.²⁹⁷

Apart from the advanced studies mentioned above, which were conducted under controlled laboratory settings, addressing real-world application demands requires evaluation under realistic gas feeds, long-term cycling, and impurity conditions. In several typical solid-supported ILMs composed of imidazole-based ILs, the separation performance of CO₂/CH₄ and CO₂/N₂ mixed-gas (CO₂ composition in the range of 0-66%) was well maintained at 303 K over more than 100 days under dry conditions with no decline in selectivity or permeability.²⁹⁸ The impact of water on CO₂ separation using SILM systems is also an important consideration. Some studies have suggested that water may influence CO₂ solubility through competitive adsorption equilibrium. For example, at an elevated pressure of 57 bar, it was demonstrated that CO₂ solubility in ILs decreased by up to 76% with water involving; however, this effect was negligible at 1 bar.²⁹⁹ Therefore, for SILMs, which typically operate at low pressures, this minimal influence on CO₂ solubility results in limited influence on separation performance. It was observed that the CO₂ permeability of [Emim][Tf₂N]-based SILMs remained largely invariant across a wide range of relative humidity values under low-pressure conditions. Other relevant works also consider the influence of other impurities such as H₂S.³⁰⁰ For the separation of CO₂/CH₄/H₂S mixtures using acetate-based SILMs, sustained CO₂/CH₄ selectivity (12-15) was obtained across multiple adsorption-desorption cycles in humid environments.³⁰¹ Overall, these studies confirm that hydrophobic or polymer-supported SILM designs can withstand realistic mixed gas feeds, cyclic operation, and humidity while preserving structural integrity and CO₂ separation performance, which is critical criteria for industrial deployment.

4.4 Modeling and simulations of CO₂ transport in ionic liquids

A key factor governing CO₂ solubility in non-reactive ILs is free volume. Modifying cation-anion interactions within the IL is an effective strategy to enhance CO₂ solubility. Two recent approaches involve macrocyclic cation ILs and dicationic ILs.^{302, 303} In the former, the conductor-like screening model (COSMO) for real solvents, integrated with MD simulations, were used to calculate fractional free volume, while in the latter, cavity size distribution was directly measured. The free volume

analysis of dicationic ILs revealed numerous cavities sufficiently large to accommodate CO₂. Additionally, CO₂ molecules are enveloped by the dication through the PEG bridge, where one oxygen atom engaging to one cationic moiety of the dual-charged system (Figure 35A-35D).

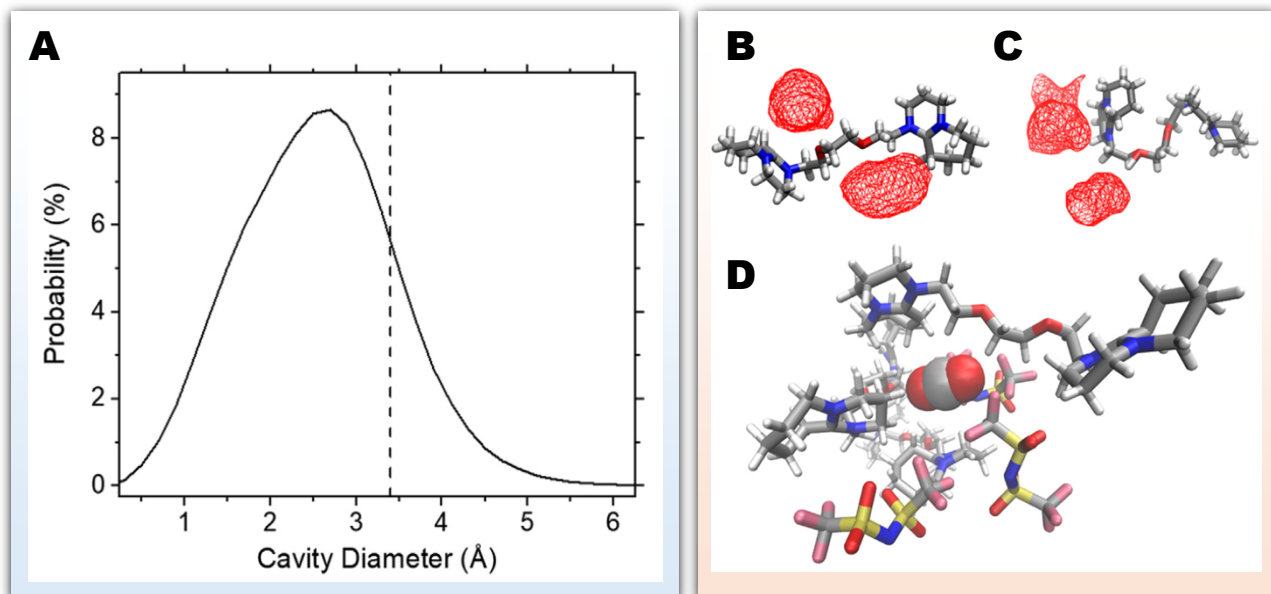


Figure 35. (A) Distribution of cavity in [DBU-PEG][Tf₂N]₂ IL, the dashed black line indicating the CO₂ kinetic diameter. (B, C) The spatial probability distribution of CO₂ (red wireframe) near the expanded and contracted [DBU-PEG]²⁺ configurations. (D) A characteristic snapshot depicting the CO₂ coordination in [DBU-PEG][Tf₂N]₂ IL.³⁰² Reproduced with permission from Ref 302. Copyright 2021 Elsevier.

Incorporating ILs with MOFs, COFs, basic metal oxides, mesoporous silica, and other porous scaffolds to create supported IL composite sorbents and membranes is an effective way to improve CO₂ capture performance for gas separation. Various computational approaches have been utilized to investigate these composites and optimize their CO₂ separation performance. The dispersion behavior of [BMIM][SCN] was examined across eight COFs and five MOFs with different chemical properties and pore structures using GCMC (grand canonical Monte Carlo) and classical MD simulations. The findings revealed that MOFs with stronger Coulombic interactions promoted more effective IL dispersion than COFs, leading to greater improvements in separation performance (Figure 36A). Furthermore, ILs exhibited higher dispersion in 3D pore structures than in 1D or 2D frameworks.³⁰⁴ Molecular simulations were used to examine CO₂ adsorption in mesoporous MOF MIL-100(Fe) impregnated with IL [Bmim][PF₆] and [Bmim][Tf₂N]. The results showed that IL incorporation increases CO₂ uptake by introducing new adsorption sites with a broader range of interaction energies (Figure 36B).³⁰⁵ Experimental data combined with high-throughput molecular simulations used to evaluate CO₂/N₂ separation in 1,085 IL/MOF composites. A strong correlation between experimental and simulation results confirmed the validity of the computational approach (Figure 36C). The screening identified [BMIM][BF₄] as significantly enhancing CO₂ adsorption across numerous MOFs. Structural analysis revealed that composites featuring low porosity, narrow pores, and high IL loading exhibited superior CO₂/N₂ selectivity.³⁰⁶

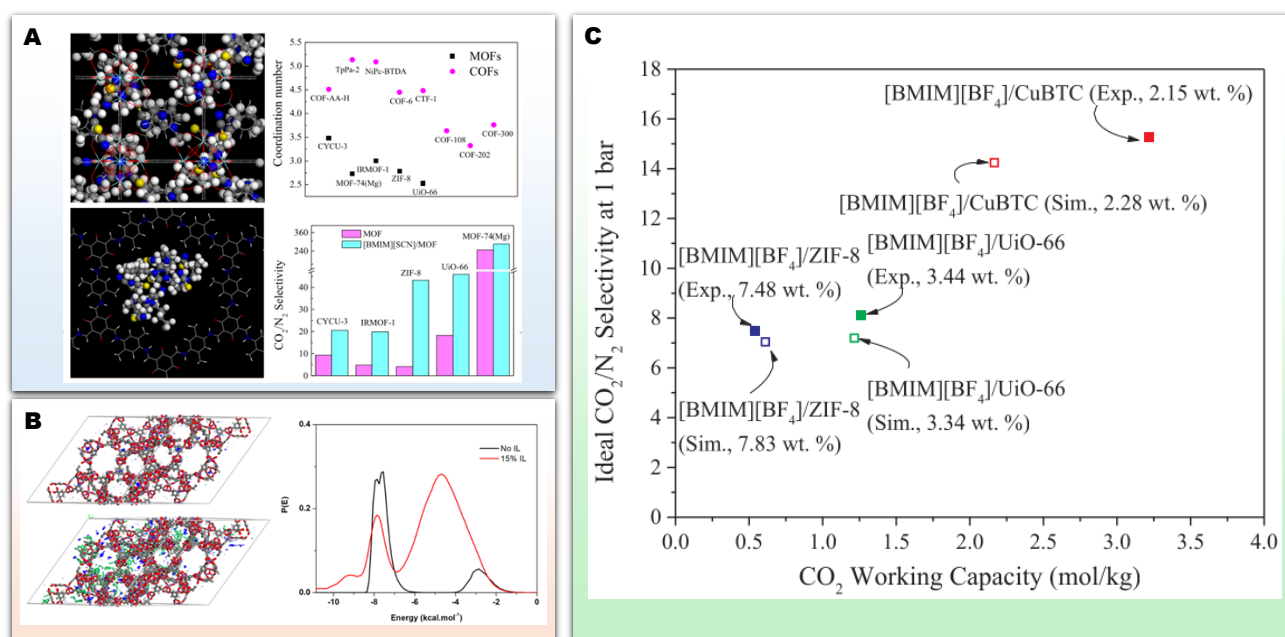


Figure 36. (A) Snapshots depicting ILs/MOFs and ILs/COFs structures from MD simulation: [BMIM][SCN]/UiO-66 (upper left), [BMIM][SCN]/TpPa-2 (lower left). The upper right illustrates the coordination number of ILs in MOFs and COFs, while the lower right presents the adsorption selectivities of MOFs and ILs/MOFs composites.³⁰⁴ Reproduced with permission from Ref 304. Copyright 2016 Elsevier. (B) Density map and energy plot (right) for CO₂ adsorption in non-impregnated (upper left) and impregnated (lower left) MIL-100 (Fe) at 150 K and 0.5 kPa.³⁰⁵ Reproduced with permission from Ref 305. Copyright 2019 American Chemical Society. (C) Comparison of CO₂/N₂ selectivity and CO₂ capacity between experimental and simulated results for ILs/MOFs composites.³⁰⁶ Reproduced with permission from Ref 306. Copyright 2020 Elsevier.

5. Ionic liquid-modified sorbents for low concentration CO₂ sorption

Technologies focus on extracting diluted CO₂ from the atmosphere and diverse gas streams is essential and challenge in gas separation procedures.³⁰⁷⁻³¹⁰ Among these, direct air capture (DAC) stands out as one of the most challenging and attractive procedures to capture CO₂ from air atmosphere, which has lower demand for land and water compared to natural methods.^{311, 312} However, current DAC technologies face significant hurdles on the path to commercialization at scale. The challenges are twofold, stemming from both the low concentration of CO₂ in air (approximately 415 ppm) and the open nature of the DAC process. These factors pose formidable difficulties for sorbent and process design. To effectively capture CO₂ from this low partial pressure (about 0.4 mbar), state-of-the-art sorbents typically incorporate amine, hydroxide, or oxide species as strong binding sites that selectively integrate CO₂. However, these current approaches encounter inherent issues: CO₂ capture is often associated with the generation of carbamate or bicarbonate species, relying heavily on the formation of strong chemical bonds and extensive intramolecular hydrogen bonding networks. The high stability of these CO₂-saturated products leads to energy-intensive sorbent regeneration cycles, and the harsh conditions required for CO₂ release exacerbate thermal and chemical degradation of the sorbents. A promising solution is the crystal engineering approach utilizing guanidine-derived sorbents in aqueous solutions. This method effectively enhances DAC of CO₂ by leveraging the rapid precipitation of CO₂-integrated products as the driving force. The extensive hydrogen bonding formed

between guanidinium cations, bicarbonate anions, and water molecules plays a critical role in facilitating continuous CO₂ chemisorption from diluted resources.³¹³ Furthermore, the guanidine-derived sorbents' fast precipitation behavior can be combined with aqueous amino acids or peptides to streamline CO₂ release and sorbent regeneration, with assistance from thermal treatment or solar energy.^{314,315} Given that DAC processes are generally conducted in open environments, solid sorbents are preferred, particularly those with high surface areas that promote rapid CO₂ sorption kinetics.

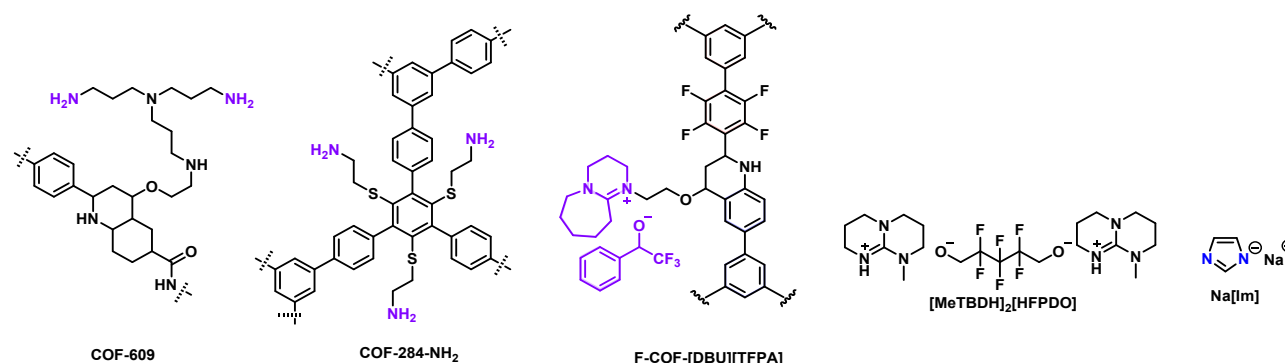
ILs possess unique properties, particularly their ability to be finely tuned for various interaction strengths with CO₂. This makes them excellent candidates for enhancing the active sites in the creation of solid sorbents aimed at the DAC of CO₂. This section will summarize and compare solid sorbents incorporating AILs and SILs in DAC applications (Table 4), juxtaposing them with amine- and metal oxide-derived sorbents. The comparison will be organized by substrate categories, including covalent organic frameworks (COFs) (Section 5.1), metal-organic frameworks (MOFs) (Section 5.2), carbon materials (Section 5.3), and silica supports (Section 5.4). In the developed solid sorbents, ILs or ionic pairs are integrated into the porous scaffolds through processes such as impregnation or covalent bond formation. This strategic incorporation leverages the complementary properties of ILs and the porous supports to enhance CO₂ capture from diluted resources effectively. The overall performance of these materials is influenced by several factors, including the chemical composition and structural characteristics of the support materials, the specific ILs utilized, and the modification methodologies employed. It should be clarified that, in this context, supported ILs refer to ILs that are either physically coated onto the surface of porous scaffolds or covalently grafted onto porous networks, resulting in solid sorbents suitable for CO₂ chemisorption. In contrast, certain PLs are synthesized by modifying porous scaffolds (e.g., MOFs) with specific cation–anion pairs; however, the resulting materials exhibit liquid-like, flowable behavior. This distinction is primarily governed by the structural and physicochemical properties of the incorporated IL components.

Table 4. The performance of selected IL-modified sorbents in the DAC of CO₂.

Sorbents ^a	Modifier and IL loading amount	Capacity (mmol CO ₂ /g sorbents)	Test conditions	CO ₂ releasing	Stability	Ref
COF-609	-	1.50	150 mbar CO ₂	-	-	316
COF-284-NH ₂	-	0.1	400 ppm	-	-	317
F-COF-[DBU][TFPA]	-	0.76	25 °C, 400 ppm, dry	He, 90 °C	Stable after 5 cycles	318
SIL ([MeTBDH] ₂ [HFPDO])-doped Ni-MOF	SIL, 1.74 mmol/g MOF	0.58	25 °C, 400 ppm, dry	He, 80 °C	Stable after 5 cycles	153

SIL ([MeTBDH] ₂ [HFPDO])- doped OMC	SIL, 30 wt %	0.655	25 °C, 400 ppm, dry	He, 80 °C	-	319
MCM41-CaO-[Na][Im]	IL, 20 wt %	0.97	25 °C, 400 ppm, dry	He, 80 °C	Stable after 10 cycles	320

^aAmine- or IL-based porous sorbents:



5.1 Ionic liquid-modified covalent organic framework sorbents

Solid sorbents with ordered structures and low density are preferred in DAC of CO₂, which can benefit the reaction mechanism study via x-ray- and neutron-based techniques combining computational chemistry. COFs are one of the most extensively studied porous materials in gas separation, which are composed of light elements, possess good crystallinity, have high surface area, and are featured by their permanent porous and ordered channels. To ensure effective performance in DAC of CO₂, it is crucial to have active sites that demonstrate strong interaction with CO₂ to facilitate its absorption from diluted sources, which will rely on the modification of COF scaffolds by basic moieties. For instance, the COF precursor COF-609-Im, synthesized via imine bond formation, underwent a successive cycloaddition and amination modification to incorporate amino sites into the scaffolds for enhanced CO₂ capture from diluted sources.³¹⁶ The tris(3-aminopropyl)amine-attached COF sorbent (denoted as COF-609) has exhibited largely improved (1360-fold) CO₂ uptake capacity than the unmodified COF precursor (denoted as COF-609-Im) under 0.4 mbar CO₂ pressure at 298 K and shown the capability to enrich CO₂ from diluted resources. However, the amorphous nature of the COF-609 sorbents was observed after step-by-step structure modification and amine moieties integration. The trimerization of acetyl group and C-F bond involved monomer in the presence of trifluoromethanesulfonic acid (TfOH) afforded fluorinated polyphenylene-linked COFs, which was then deployed as the precursor to attach -NH₂ moieties via C-S bond formation in the designed post-modification procedure.³¹⁷ The as-afforded amino-functionalized COF (COF-284-NH₂) with improved surface area and crystallinity achieved the uptake capacity of 0.1 mmol g⁻¹ at 0.4 mbar CO₂ pressure under ambient environment.

Modification of COFs by IL components is a promising methodology to afford efficient and stable COF sorbents for 400 ppm CO₂ capture, which could harness the combined advantages of ILs and

COF materials. The challenge is to develop an efficient synthesis procedure affording COF sorbents capable of integrating CO₂ from diluted sources (e.g., about 415 ppm in air) and maintaining the high crystallinity for a detailed reaction mechanism study. Instead of amine moieties, ionic pairs with improved thermal/chemical stability and significantly adjustable interaction strength with CO₂ were deployed to modify the COF skeletons and provide active sites to enrich CO₂ from diluted sources.³¹⁸ To obtain high-quality sorbents, a stable COF precursor capable of withstanding the basic and highly ionic conditions during the modification was required. Anionic sites with moderate interaction strength balancing the CO₂ sorption capacity and energy consumption in sorbent regeneration was preferred. A detailed modification procedure was established utilizing fluorinated COF (F-COF) with the imine bond as the precursor. To stabilize this bond, the imine was transformed into tetrahydroquinoline (THQ), resulting in the formation of alkyl halide sites. These sites were then reacted with the organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to introduce ionic pairs through nucleophilic attack. The anion exchange of Cl⁻ with deprotonated-(trifluoromethyl)benzyl alcohol ([TFPA]) afforded the targeted F-COF-[DBU][TFPA] for DAC of CO₂ application (Figure 37A). The well-maintained crystallinity was confirmed by the PXRD patterns and the x-ray atomic pair distribution functions (PDFs), in the latter spectra, intense peaks corresponding to the bonding connections and interlayer correlations were observed, as well as the damping behavior of the PDF signal at long *r*, corresponding to the crystalline domain size of at least 6 nm (Figure 37B). The complete anion exchange was demonstrated by elemental mapping, with no Cl⁻ shown up in the F-COF-[DBU][TFPA] sorbent. The F-COF-[DBU][TFPA] sorbent exhibited a BET surface area of 41 m² g⁻¹ and featured ultra-micropores measuring between 0.45 and 10 Å following modification. The 400 ppm CO₂ uptake capacity obtained at 298 K via the fixed-bed breakthrough assessment was 0.76 mmol g⁻¹. This capacity remained stable at 0.8 mmol g⁻¹ when tested with simulated air containing 400 ppm CO₂ (Figure 37C), benefiting from the ultra-high selectivity of CO₂/N₂ (beyond 5000 as calculated using the IAST method). Complete CO₂ releasing was achieved at 363 K under He flow, and good recyclability was observed within at least five cycles. The energy efficient sorbent regeneration benefited from the moderate interaction strength. Thermodynamic study revealed a reaction enthalpy of -39.56 kJ mol⁻¹, which was much lower than the hydroxide- (around -150 kJ mol⁻¹) and amine-derived sorbents (-70 to -90 kJ mol⁻¹) (Figure 37D). Both diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) under air atmosphere and operando solid NMR monitoring revealed the O-C bond formation between F-COF-[DBU][TFPA] and CO₂, leading to carbonate product formation. Furthermore, the CO₂ uptake capacity under DAC conditions could be enhanced to 1.86 mmol g⁻¹ by increasing the density of the anionic [TFPA] sites, with recyclability being effectively maintained over five cycles.

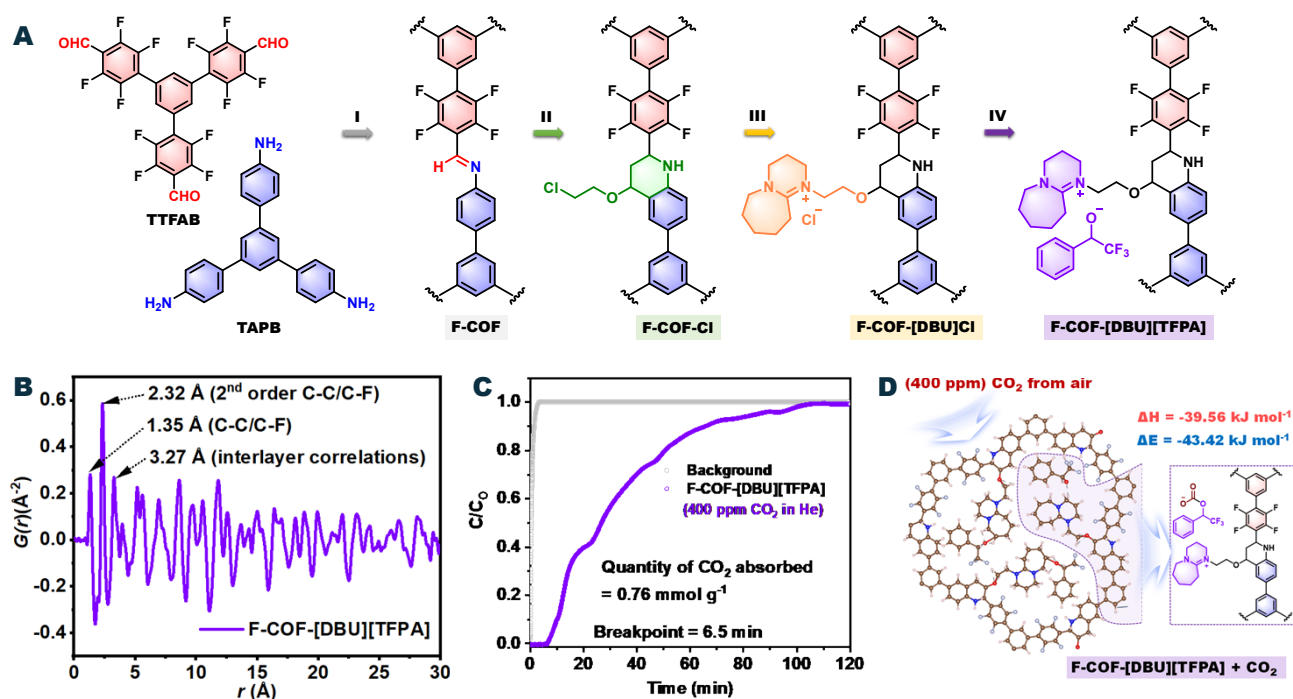


Figure 37. (A) Synthetic procedure of the ionic pair-derived F-COF scaffolds for DAC of CO_2 . (B) Atomic pair distribution function (PDF) of the F-COF-[DBU][TFPA] sorbent. (C) The breakthrough test at 298 K of F-COF-[DBU][TFPA] with 400 ppm CO_2 . (D) The thermodynamic parameters and reaction pathway of F-COF-[DBU][TFPA] sorbent with CO_2 .³¹⁸ Reproduced with permission from Ref 318. Copyright 2024 John Wiley & Sons.

5.2 Ionic liquid-modified metal organic framework sorbents

MOFs are another category of porous materials with highly crystalline architecture, high surface area, and tunable porosity to afford high gas uptake capacity and selectivity.³²¹ Integration of basic sites within the MOF scaffolds (e.g., zinc hydride and hydroxide) could absorb CO_2 under high temperature conditions (>200 °C) or low CO_2 partial pressure.^{322, 323} In terms of low concentration CO_2 capture, amine-modified MOF sorbents have exhibited attractive performance and large tunability by controlling the structure of amines and MOF substrates.³²⁴ The diamine-modified MOF sorbents exhibited unique stepped CO_2 uptake isotherms with different onsite CO_2 breakthrough uptake pressures relevant to the interaction between the amine-metal nodes and the sorption temperature.⁹⁸ Upon reacting with CO_2 and the ammonium carbamate product formation, the amine moieties were re-organized and formed chain structures. The unique behavior could be harnessed to diminish the energy consumption in CO_2 releasing via temperature control. A series of tetraamine-modified MOF sorbents was then developed, exhibiting stepped CO_2 uptake isotherms and good stability under humid (about 2.6% water content) flue gas conditions.⁹⁹ The sorbent regeneration could be achieved quickly using humid CO_2 as the sweeping gas at 180 °C, demonstrating robust CO_2 capture stability within over 1000 cycles. The uptake capacity and utilization efficiency of the amine functionalities could be further improved by tuning the steric hindrance of the carboxylate ligands in the MOF scaffolds and structure of the doped amines, supported by in situ NMR studies and theoretical simulation.^{325, 326} A CO_2 uptake capacity of amino acid (AA) anions- or polyamine (PA) species-modified MOF scaffolds

(MOF-808) with Zr node is $0.612 \text{ mmol g}^{-1}$, which could be further enhanced to $1.205 \text{ mmol g}^{-1}$ under humid conditions at relative humidity (RH) of 50% via bicarbonate formation.³²⁷ In addition to the reactive properties of the basic sites, the rigid scaffolds can be further utilized to adjust the CO_2 insertion behavior. Metal hydroxide generally possessed strong interaction with CO_2 , but the as-formed bicarbonate products with high stability led to energy-intensive sorbent regeneration. The rigid structure of MOF derived from the reaction of γ -cyclodextrin and potassium salts could encapsulate segregated hydroxide sites, which showed the capability to capture diluted CO_2 and avoided the formation of extensive hydrogen bonding network.³²⁸ Complete CO_2 release was achieved at 80°C under N_2 flow.

MOF sorbents involving ILs as the reactive sites in DAC of CO_2 applications were also explored via modification by SILs. To create high-quality MOF sorbents, it is essential to use MOF scaffolds that are robust in highly ionic environments with basicity. A fluorinated Ni-MOF with a high surface area ($1592 \text{ m}^2 \text{ g}^{-1}$), microporosity, small particle size of approximately 30 nm, and stability in SILs, which was synthesized from a fluorinated pyrazolate ligand and nickel acetate (Figure 38A).¹⁵³ The synthesis of SIL ($[\text{MeTBDH}]_2[\text{HFPDO}]$) using fluorinated alcohol 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (HFPDOH) in combination with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MeTBD) involves the deprotonation of HFPDOH and proton transfer. This SIL was chosen for modifying the Ni-MOF due to its strong ability to integrate CO_2 through O-C bond formation. Different amounts of SIL were doped in Ni-MOF via a wet-impregnation procedure. The crystalline skeleton of Ni-MOF was well maintained after SIL doping, as revealed by the PXRD patterns. The porosity of the SIL/Ni-MOF composites was evaluated by N_2 and CO_2 uptake isotherm, which demonstrated the presence of ultra-micropore (around 0.46 nm), allowing the penetration of CO_2 within the pores to facilitate gas transport and absorption. The small-angle X-ray scattering (SAXS) results on Ni-MOF before and after SIL doping exhibited a shortened distance between the ions of SIL in the composite materials compared with that of the free SIL phase (Figure 38B). The SIL-doped Ni-MOF demonstrated a significant increase in CO_2 uptake in the low-pressure region and exhibited the ability to facilitate CO_2 chemisorption at a pressure of 0.4 mbar (Figure 38C). The as-calculated energy distribution curves derived from the CO_2 uptake isotherms illustrated the strong CO_2 chemisorption nature benefiting from SIL doping, with the peak corresponding to reaction energy around 67.0 kJ mol^{-1} shown up. The optimal 400 ppm CO_2 uptake capacity of the SIL/Ni-MOF sorbent is 0.58 mmol g^{-1} via breakthrough evaluation at 298 K (Figure 38D). Sorbent regeneration was performed at 353 K, and fully recovered CO_2 uptake was demonstrated with at least five cycles. The influence of humidity was studied via RH value in the range of 2.5% to 10%, with a general trend of enhanced CO_2 uptake capacity but inferior absorption kinetics shown up. The CO_2 integration mechanism was further studied via DRIFTS (under air atmosphere) and NMR (using ^{13}C -labeled CO_2), confirming the carbonate formation pathway and its reversible nature. Theoretical simulations suggest that the SIL penetrates the pores of the Ni-MOF, with the alkoxide anions of the SIL positioned close to the cations instead of interacting with the Ni nodes. Compared to the reaction of CO_2 with free SIL ($\Delta H = -87.8 \text{ kJ mol}^{-1}$), the confined SIL in Ni-MOF possessed stronger interaction strength with CO_2 ($\Delta H = -113 \text{ kJ mol}^{-1}$).

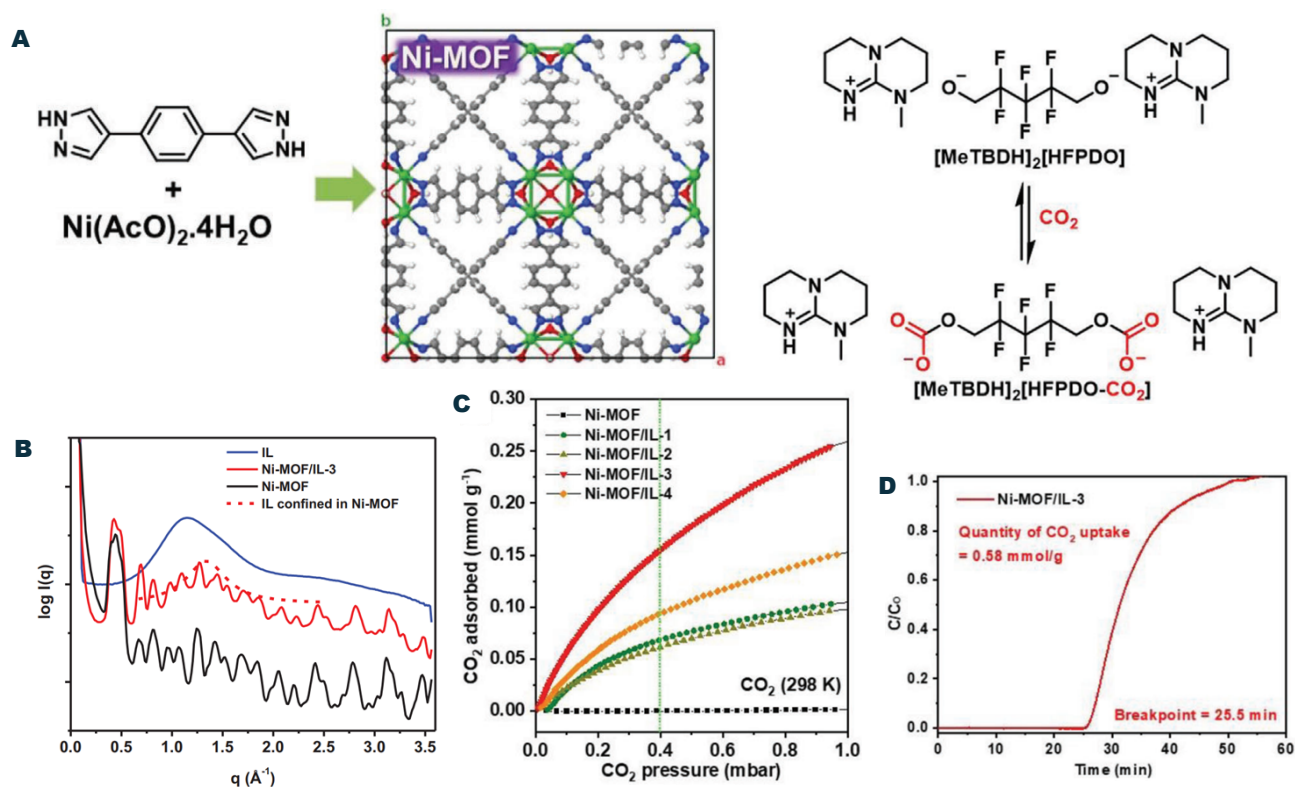


Figure 38. (A) The synthesis and structural characteristics of the Ni-MOF and [MeTBDH]₂[HFPDO] SIL, along with the reaction mechanism of the SIL with CO_2 . (B) The SAXS patterns of the composite Ni-MOF/SIL material, Ni-MOF, and SIL. (C) The CO_2 uptake isotherm at 298 K of the composite Ni-MOF/SIL sorbents and Ni-MOF. (D) The breakthrough curve at 298 K of Ni-MOF/SIL using He with 400 ppm CO_2 .¹⁵³ Reproduced with permission from Ref 153. Copyright 2023 John Wiley & Sons.

5.3 Ionic liquid-modified carbon-derived sorbents

Carbon materials are attractive in gas separation, particularly those with high surface areas ($> 4000 \text{ m}^2 \text{ g}^{-1}$), tunable porosity, and modified surface properties.³²⁹⁻³³² In addition, majority of the carbon materials are fabricated under high temperature conditions via pyrolysis, affording them with robust nature in practical DAC applications. AAILs were encapsulated in carbon capsules that have a micro/mesoporous shell structure and a hollow core. This process produced stable sorbents for CO_2 capture (aa-ENILs).³³³ The morphology of the hollow carbon capsules, which had a uniform diameter of around 700 nm, was confirmed by transmission electron microscopy (TEM) images (Figure 39A). The ammonium IL (1-butyl-3-methyl imidazolium methioninate ([Bmim][MET])) was used to provide active sites capable of absorbing CO_2 through ammonium carbamate formation (Figure 39A). The gravimetric CO_2 capture experiment using neat AAILs was challenging due to the slow diffusion rate and long equilibrium time required, leading to low CO_2 uptake capacity (Figure 39A). Comparatively, when aa-ENILs were employed, a significant enhancement in CO_2 absorption rates was observed, largely improving the utilization efficiency of AAILs. A carbon fiber precursor, designated as fiber600 and consisting exclusively of ultra-micropores around 0.45 nm in size, was used as the support (Figure 39B).³³⁴ ILs with phosphonium cations and either basic or neutral anions were deployed as modifiers for comparison (Figure 39B). The [P₆₆₆₁₄][NTf₂] IL exhibited only CO_2 physisorption capabilities. The CO_2 uptake capacity of the SIL ([P₆₆₆₁₄][Triz]) was measured at $0.95 \text{ mol mol}^{-1}$ under a CO_2 pressure

of 1 bar at 298 K, indicating efficient CO₂ chemisorption through the formation of N-C bonds. Additionally, the reaction enthalpy associated with CO₂ absorption was found to be $-56.4 \text{ kJ mol}^{-1}$.⁶⁷ The IL and SIL was applied to create a thin coating layer on the fiber surface, avoiding penetration into the pores. The calculated energy distribution curves displayed an obvious peak around 55.6 kJ mol^{-1} within the chemisorption region (Figure 39B). The CO₂ sorption behavior of pure ILs, fiber600, and fibers with IL-coating were assessed through thermogravimetric analysis and volumetric methods. The SIL-coated fibers demonstrated an enhanced CO₂ uptake capacity compared to fiber600 without SIL coating, coupled with improved sorption kinetics, especially with ILs featuring strong interaction sites for CO₂ binding (Figure 39B). The methods and findings highlight the effectiveness of ILs in enhancing porous scaffolds, substantially improving carbon capture performance, especially for low-concentration CO₂ applications. Additionally, the composite sorbent made from microporous carbon fiber and the basic IL (1-butyl-3-methylimidazolium acetate) demonstrated strong performance in diluted carbon capture and promising recyclability, with the porosity and surface area of the carbon fiber and IL loading significantly influencing CO₂ uptake capacity and kinetics.³³⁵

Using SIL as modifier, the effect of the porosity of the carbon substrates of the as-afforded sorbents was studied on the DAC performance by deploying ordered mesoporous carbon (OMC) materials with different porosity, including micro- and mesopores as the substrates.³¹⁹ The synthesis of ordered OMC substrates using the soft-template method involving phloroglucinol-formaldehyde resin and pluronic F127 copolymer, undergoing self-assembly in the acidic medium (Figure 39C). The carbon material was subsequently activated with potassium hydroxide (KOH) to create micropores and increase the surface area in OMC-A. The incorporation of [MeTBDH]₂[HFPDO] led to improved CO₂ uptake performance in both OMC and OMC-A, especially in the low-pressure region. Detailed porosity analysis of the IL/carbon composite materials revealed that the doped ILs preferentially occupied micropores and form thin layers on the surfaces of mesopores. The π - π interactions between the aromatic components of the IL and the carbon framework enhance their mutual interaction. This reinforcement is crucial for maintaining the integrity of the coating during use and modulating the interaction with CO₂. The 400 ppm CO₂ uptake capacity of 0.65 mmol g^{-1} of the OMC-A/SIL sorbents was achieved at 298 K (Figure 39C).

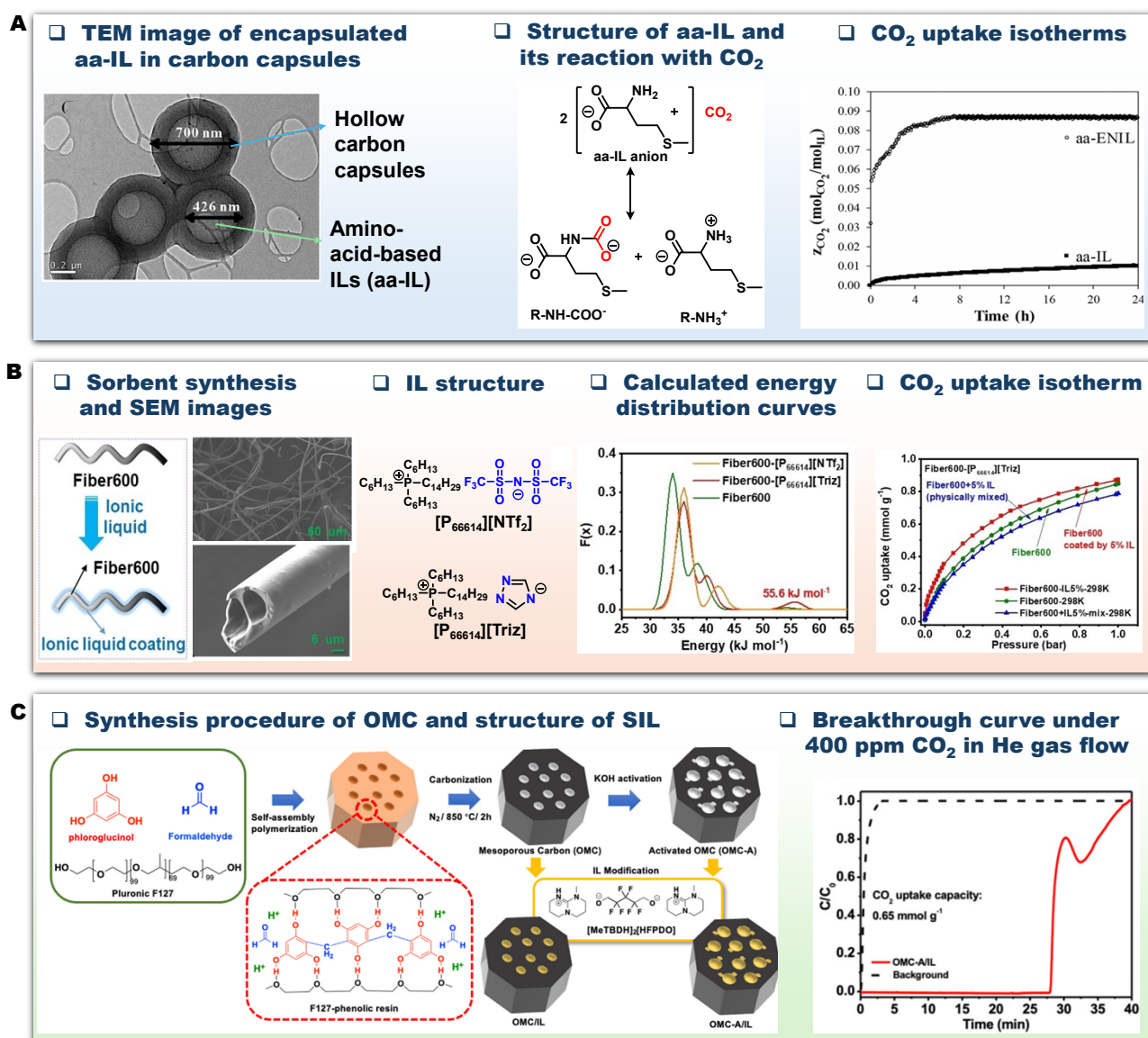


Figure 39. (A) TEM image of hollow carbon capsule-encapsulated aa-IL; Structure of aa-IL and its reaction pathway with CO₂; Kinetic CO₂ uptake isotherms of pure aa-IL and aa-IL/carbon capsule composite sorbent at 301.5 K and CO₂ pressure of 0.3 bar.³³³ Reproduced with permission from Ref 333. Copyright 2018 American Chemical Society. (B) SEM images of carbon fiber; Structure of ILs; The calculated energy distribution curves of different sorbents; CO₂ uptake isotherms (up to 1 bar at 298 K) of IL/carbon fiber sorbents.³³⁴ Reproduced with permission from Ref 334. Copyright 2022 John Wiley & Sons. (C) Synthesis of mesoporous carbon supports with different porosity and structure of the SIL; The breakthrough curve of SIL/OMC-A using He with 400 ppm CO₂.³¹⁹ Reproduced with permission from Ref 319. Copyright 2024 John Wiley & Sons.

5.4 Ionic liquid-modified silica-derived sorbents

Porous silica is another category of widely used supports in solid sorbent development, which possess rigid and porous architectures, tunable porosity, and facile surface modification.³³⁶⁻³³⁹ Amine-modified silica sorbents, via physically coating or covalent bond formation with the surface hydroxyl groups, have been widely researched in carbon capture. However, the extensive hydrogen bonding network formation and inferior chemical/thermal stability of amine moieties led to sluggish sorption

kinetics and performance decay particularly in the presence of water and oxidative gas impurities.^{309, 340, 341} IL-modified silica sorbents have the potential to afford improved performance, as they have higher thermal/chemical stability, can achieve hydrogen-bonding-free CO₂ chemisorption, and possess tunable interaction strength with CO₂ to search for the balance between uptake capacity and energy input for regeneration. The mesoporous SBA-15 with varying pore lengths was deployed as support, which after modification with SIL [P₆₆₆₁₄][Triz], to afford hybrid materials in CO₂ capture (Figure 40A).³⁴² Compared to the time needed by the other three mixed adsorbents, SBA-15 (4.3)–50% IL exhibited the fastest dynamic CO₂ absorption, achieving equilibrium in just 20 minutes. This improved absorption rate is attributed to the short pore length with 120 nm and large cross-sectional area of SBA-15 (4.3), which enhance the diffusion and reaction efficiency of CO₂ with the SIL within the pore channels (Figure 40A). In contrast, SBA-15 with longer pore lengths showed decreased absorption efficiency, as CO₂ faced greater diffusion resistance to react with the SIL. The pore structure (e.g., length and size) of porous supports plays a crucial role in the dispersion of liquid absorbents and CO₂ diffusion, which are vital for effective CO₂ absorption.

Mesoporous silica (MCM-41) was used as the support for synthesizing SIL-engineered sorbents, with SILs containing imidazolate ([Im]) or triazolate ([Triz]) anions serving as active sites for CO₂ integration. This approach aimed to investigate the influence of cation and anion basicity in SILs on the DAC performance of modified silica sorbents. (Figure 40B).³²⁰ To safeguard the basic SIL sites from deactivation by hydroxyl groups on the silica surface, a thin layer of CaO was applied to the mesoporous channels of the MCM-41 support. [P₄₄₄₄][Im] SIL, [Na][Im] along with [Na][Triz]) sodium salts were utilized as modifiers to produce SIL- and CaO-modified MCM-41 sorbents through a wet impregnation method. The coating of sodium salts enhanced the CO₂ uptake performance, particularly at the low-pressure region, and [Im] anion with stronger basicity led to more improvement than the [Triz] one (Figure 40B). Particularly, at CO₂ pressure of 0.4 mbar close to DAC condition, the involvement of [Im] sites exhibited enhanced CO₂ sorption capability. The reaction enthalpies for CO₂ capture were determined to be -89.9 kJ mol⁻¹ for [Im] and -56.4 kJ mol⁻¹ for [Triz]. The MSC-[Na][Im] and MSC-[P₄₄₄₄][Im] achieved maximum 400 ppm CO₂ uptake capacities of approximately 1.02 mmol g⁻¹ and 0.65 mmol g⁻¹, respectively at 298 K (Figure 40B).

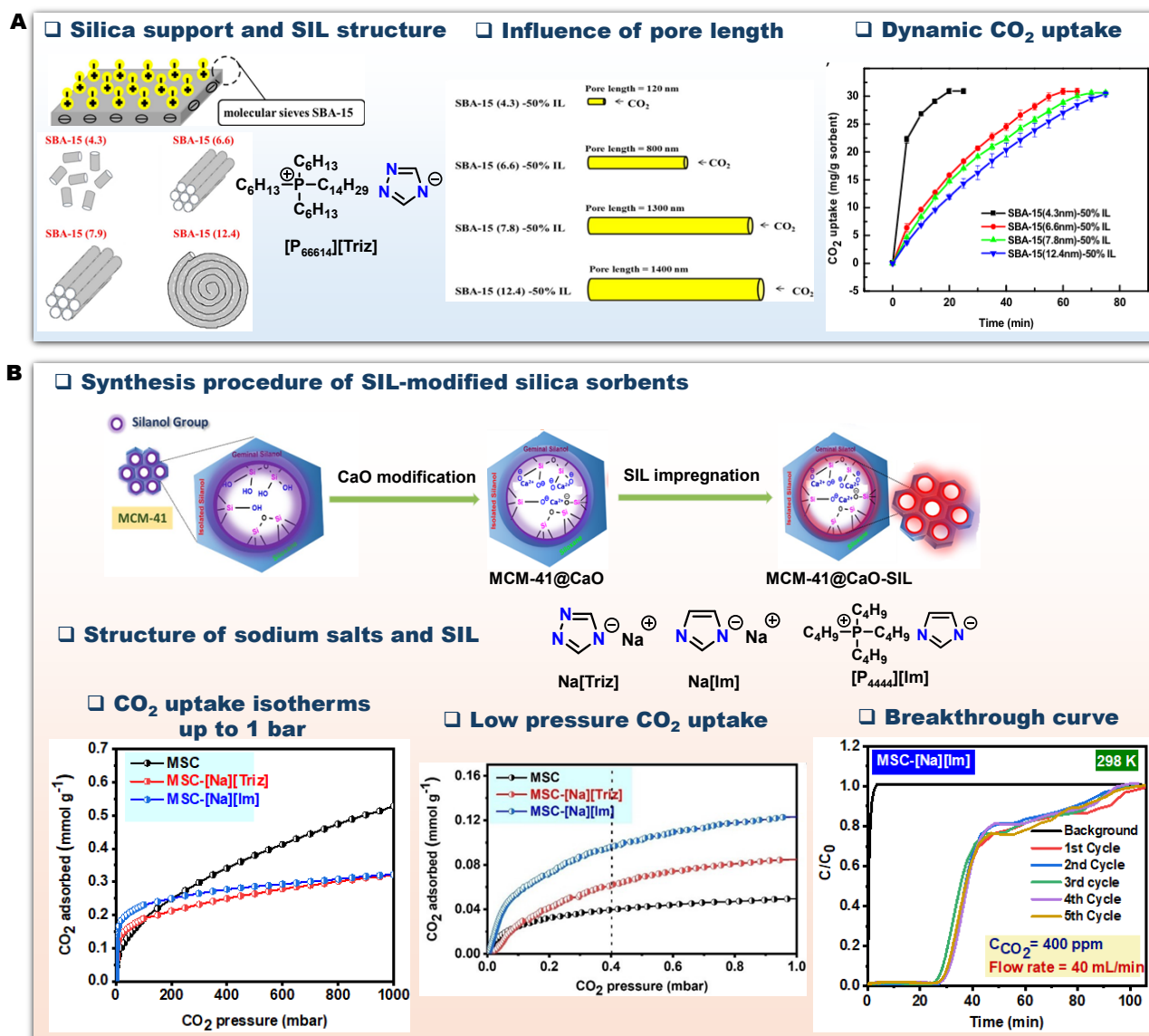


Figure 40. (A) Synthetic procedures of silica support and structure of the doped SIL; Pictures showing the different kinetics of CO₂ capture varying pore length; Dynamic CO₂ uptake isotherm using different SIL-modified silica sorbents.³⁴² Reproduced with permission from Ref 342. Copyright 2018 Elsevier. (B) Synthesis procedure of SIL- and CaO-modified silica sorbents; Structure of the basic sodium salts and SIL containing [Im] and [Triz] anion; CO₂ uptake isotherms of different silica support collected with CO₂ pressure up to 1 bar or 1 mbar; The CO₂ breakthrough at 298 K of MSC-[Na][Im] under He with 400 ppm CO₂.³²⁰ Reproduced with permission from Ref 320. Copyright 2023 John Wiley & Sons.

6. Utilization of ionic liquids in CO₂, H₂ or O₂-involved catalysis process

The unique properties of ILs, particularly their nonvolatility, excellent thermal and chemical stability, and highly tunable structures, make them attractive media and catalyst for gas-involved catalytic processes, enabling the integration of CO₂ capture and conversion.^{343, 344} The earliest attempt to use ILs in catalysis dates back to 1986 when acidic ILs containing AlCl₄⁻ and Al₂Cl₇⁻ anions were employed in Friedel-Crafts acylation reactions.³⁴⁵ Since then, a wide range of ILs, acidic,^{346, 347}

basic,^{348, 349} neutral,^{350, 351} and chiral,^{352, 353} have been explored as catalysts or reaction media in diverse catalytic applications, including hydrogenation, oxidation, cross-coupling, metathesis, polymerization, biocatalysis, photocatalysis, and electrocatalysis.^{354, 355} In CO₂ utilization via thermo-catalysis, ILs have demonstrated promising activity as metal-free catalysts, particularly in the cycloaddition of CO₂ with epoxides and aziridines. This is attributed to their enhanced CO₂ solubility compared to the conventional organic solvents, highly charge density, ability to act as hydrogen bond donor (e.g., cations of protic ILs), and nucleophilic anions (e.g., halide).^{4, 356-358} Beyond physisorption, ILs facilitate CO₂ chemisorption via O-C, N-C, and C-C bond formation, transforming CO₂ from a non-polar linear molecule into polar bent structure. The synergistic enrichment and pre-activation effect enables efficient CO₂ conversion into urea derivatives, quinazoline-2,4(1H,3H)-diones and benzimidazolones.^{4, 52, 118, 359, 360} Beyond non-reductive CO₂ valorization, ILs also catalyze reductive CO₂ transformations using organosilane,^{361, 362} or act as stabilizers and activity modulators for metal catalysts in hydrogenation reactions using H₂, yielding formamides, aldehydes, acids, alcohols, and hydrocarbons.^{4, 56, 363} In the hydrogenation of unsaturated substrates (e.g., dienes and ketones), ILs can modulate the electronic properties of metal active sites and stabilize polar intermediates, enhancing selectivity.^{364, 365} Similarly, ILs function as modifiers, reaction media, or platforms for integrating catalytic sites in oxidation reactions, improving both activity and selectivity.³⁶⁶⁻³⁶⁸ In CO₂ electroreduction, ILs serve as efficient alternatives to traditional aqueous or organic electrolytes, enhancing catalytic activity, selectivity, and recyclability.^{55, 369, 370} Likewise, in photocatalytic CO₂ reduction, ILs stabilize catalytic sites and influence product distribution between CO and hydrocarbons.^{371, 372} This section will present case studies of ILs-assisted catalytic processes for CO₂ valorization, categorized by reaction type: thermo-catalysis involving non-reductive CO₂ utilization (Section 6.1), CO₂ reduction with hydrosilanes or H₂ (Section 6.2), ILs in other hydrogenation (Section 6.3) and oxidation reactions (Section 6.4), and the role of ILs in CO₂ electroreduction (Section 6.5) and photoreduction (Section 6.6).

6.1 Ionic liquid facilitated non-reductive CO₂ utilization via thermo-catalysis

The cycloaddition of CO₂ with epoxides to form cyclic carbonates is one of the most extensively studied reactions in CO₂ conversion. ILs play a crucial role in this process by enriching CO₂ in the liquid phase, activating epoxides through hydrogen bonding, and promoting the ring-opening of epoxides (Figure 41).^{52, 373} Early applications of ILs in cyclic carbonate synthesis employed imidazolium-based ILs paired with [BF₄] anion to catalyze the cycloaddition reaction under neat conditions simplifying product separation.^{374, 375} ILs composed of halide anions (e.g., Br⁻ and I⁻) paired with imidazolium cations efficiently promote this reaction due to the strong nucleophilicity of halides and the coordination between the proton at the C-2 position of the imidazolium cation and the oxygen atom of epoxides.^{356-358, 376} The introduction of hydrogen bonding donors (e.g., -NH₂, -OH, and -COOH groups) on imidazolium cations further enhances catalytic activity by facilitating the ring-opening step via hydrogen bonding formation with the epoxide substrate.³⁷⁶ The presence of multiple Bronsted acidic sites in imidazolium cations enables solvent- and additive-free CO₂ reactions with a variety of epoxide substrates, with catalytic activity tunable by adjusting the distance between acidic moieties.³⁷⁷ Due to the CO₂-philic nature of PEG, incorporating PEG chains into IL cations enhances catalytic activity in cyclic carbonate synthesis. Such ILs can also couple with the transesterification of cyclic carbonates with alcohols, enabling one-pot dimethyl carbonate synthesis.³⁵⁸ Furthermore, ILs containing protonated DBU cations, alcoholates, and halide anions have demonstrated catalytic

activity for CO₂ conversion from simulated flue gas (15% CO₂) with epoxides at 303 K.³⁷⁸ Beyond small IL molecules functioning as homogeneous catalysts, PIL catalysts, synthesized from free radical polymerization of vinyl-functionalized IL precursors or polymerization of precursors containing multiple bases and alkyl halides, effectively promote cyclic carbonates formation. The catalytic activity of PILs can be tuned by modifying the ionic backbone structure, ionic pair density, porosity, and hydrophilicity toward epoxide substrates and carbonate products.^{379, 380} The particle size of PILs composed of phosphonium cations paired bromide anion and acrylic acid moieties could be controlled through microfluidic synthesis, leading to size-dependent activity variations in cyclic carbonate synthesis.³⁸¹ Another heterogenization strategy involves supporting active IL species on porous scaffolds, such as inorganic silica and organic materials like chitosan, cellulose, and polymers. These porous frameworks enhance the utilization efficiency of ionic species, facilitate mass transport, and improve catalyst separation and recyclability after CO₂ cycloaddition reactions.^{382, 383} Notably, ILs (e.g., [Bmim]Br) provide an integrated platform for olefin epoxidation and subsequent CO₂ cycloaddition, enabling one-pot cyclic carbonate synthesis using tertbutyl hydroperoxide (TBHP) as the oxidant.³⁷⁶ Additionally, imidazolium ILs with bicarbonate anions exhibit catalytic activity for both epoxidation and cycloaddition where in situ-generated carbenes interact with CO₂, enriching and activating it in the reaction medium (Figure 41).³⁸⁴ Aziridines, the nitrogen analogs of epoxides, display similar reactivity with CO₂, forming oxazolidinones with diverse structures in the presence of ILs (Figure 41).^{385, 386}

facilitating nucleophilic attack by the carbonate (formed via CO₂ reaction) on the carbon of the triple bond.³⁸⁸ The final cyclic reaction yielded α -methylene cyclic carbonates while generating the active anion sites. The incorporation of metal salts (e.g., Cu and Ag) or CO₂-philic moieties (e.g., C-F bonds) further enhanced catalytic activity, enabling α -methylene cyclic carbonate production under ambient conditions.³⁸⁹⁻³⁹¹

SILs have proven effective in promoting CO₂ utilization for synthesizing aza-fused ring compounds. For example, [Bmim]OH catalyzed the reaction of CO₂ with aliphatic primary amines, leading to disubstituted urea formation via dehydration.³⁹² Additionally, replacing [Bmim]OH with [Bmim]Cl in combination with an inorganic base expanded the scope to both aliphatic and aromatic amines.³⁹³ Another basic anion system, containing phenolate and triazolide sites connected by azo bridges, facilitated urea production from CO₂ and amines.³⁹⁴ The use of polystyrene-supported imidazolium ILs with bicarbonate anions improved catalyst stability and separation.³⁹⁵ The urea synthesis was further extended to cyclic structures through CO₂ reactions with *o*-phenylenediamines, leading to benzimidazolone formation in the presence of a SIL composed of protonated DBU cation ([DBUH]) and acetate anion ([OAc]) (Figure 42A).³⁹⁶ The reaction mechanism revealed that [OAc] activated *o*-phenylenediamine via hydrogen bonding, while CO₂ formed an adduct with the nitrogen site on [DBUH]. This interaction led to ammonium carbamate intermediate formation, followed by isocyanate stabilization via ionic pairing. The final step involved nucleophilic attack by -NH₂ on the isocyanate, forming cyclic urea products and regenerating the SIL catalyst. A SIL composed of a phosphonium cation paired with a 2-methylimidazolate anion ([MIm]) facilitated benzimidazolone formation under ambient CO₂ pressure.³⁸⁷ Additionally, the reaction of CO₂ with 2-aminobenzonitriles was explored using various SILs with hydroxide, acetate, fluorinated alcoholate, and azolide anions to produce quinazoline-2,4(1H,3H)-dione derivatives. Notably, a SIL composed of [DBUH] cation paired with trifluoroetholate ([TFE]) anion effectively activated CO₂ through carbonate formation and simultaneously activated the 2-aminobenzonitrile substrate via hydrogen bonding. This synergistic interaction promoted cyclization under ambient conditions (Figure 42B).¹¹⁸

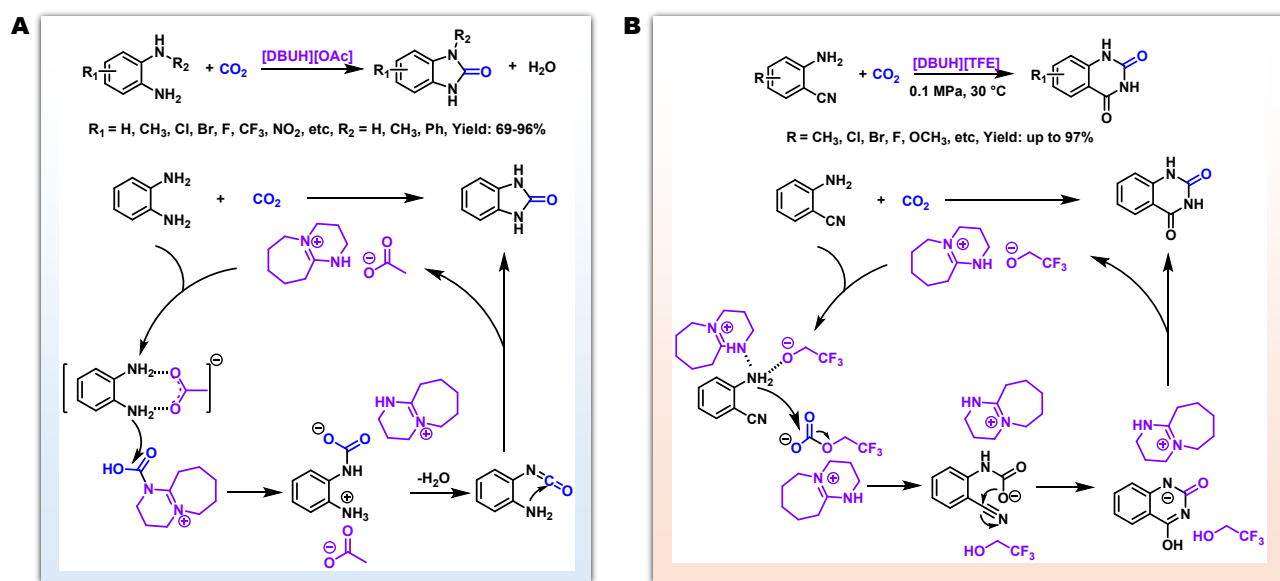


Figure 42. (A) Synthesis of benzimidazolones from *o*-phenylenediamine and CO₂ catalyzed by [DBUH][OAc].³⁹⁶ Reproduced with permissions from ref 396. Copyright 2013 American Chemical

Society. (B) Synthesis of quinazoline-2,4(1H,3H)-diones from 2-aminobenzonitriles and CO₂ catalyzed by [DBUH][TFE].¹¹⁸ Reproduced with permissions from ref 118. Copyright 2014 John Wiley & Sons.

6.2 Ionic liquid facilitated CO₂ reduction via thermal catalysis

CO₂, the most oxidized form of carbon, can be selectively reduced to acids, aldehydes, alcohols, hydrocarbons, or coupling products, depending on the catalyst, reducing reagent, and reaction conditions. Reductive CO₂ valorization via thermo-catalysis has been explored using hydrosilanes, hydroboranes, and H₂ gas as reductants. In the presence of amines, CO₂ reduction can yield formamides, amins, or methylamines with tunable selectivity when IL catalysts and hydrosilane serve as the hydrogen source (Figure 43A).^{397, 398} ILs can activate hydrosilanes via hydrogen bonding, facilitating CO₂ insertion and the formation of formoxysilane intermediates. The carbonyl group in these intermediates is subsequently attacked by amines, generating formamides along with silanol byproducts. For instance, ILs composed of [Bmim] cation and halide anions catalyze the reaction of CO₂ with aliphatic and aromatic amines in the presence of phenylsilane at ambient temperature, achieving formamide yields of up to 99%.³⁹⁹ When aldehydes are introduced as additional substrates, [Bmim]Cl catalyzes an integrated CO₂ reduction and coupling reaction, leading to unsymmetric N,N-disubstituted formamides.⁴⁰⁰ This reaction proceeds via imine intermediate formation from amines and aldehydes, which subsequently react with formoxysilane to introduce formyl groups through C-N bond formation. Further reduction of formamides in the presence of excess hydrosilane leads to methylamine formation. Selective control between formamide and methylamine products can be achieved using ILs with acetylcholine cations and carboxylate anions, with phenylsilane as the reducing agent (Figure 43B).^{361, 397, 401} The reaction temperature plays a crucial role, formylation occurs at 303 K while methylation takes place at 323 K. Additionally, the reaction pathway is influenced by the basicity of the amine substrates: low-basicity amines favor CO₂ insertion into hydrosilane, forming formoxysilane intermediates, whereas high-basicity amines first form ammonium carbamate, which is subsequently reduced by hydrosilane to generate silylcarbamate. Besides formamide and methylamine, hydrosilane-assisted CO₂ reduction can also yield amins when IL glycine betaine is used as a catalyst, with product selectivity controlled by reaction temperature and CO₂ pressure.³⁶¹ In this process, IL-activated hydrosilane reacts with CO₂ to generate silylformate and subsequently silylactal, which, upon reaction with amines, forms amins. Under excess hydrosilane and elevated temperatures, amins can be further reduced to methylamines. Conversely, at high CO₂ pressure (e.g., 10 bar) and lower temperatures (323 K), formamides dominate, while methylamine formation is hindered due to hydrosilane consumption by excess CO₂. Another pathway for amina formation involves CO₂ reduction in the presence of polymethylhydrosiloxane (PMHS), catalyzed by an IL composed of tetrabutylammonium cation and acetate anion ([ⁿBu₄N][OAc]) (Figure 43C).⁴⁰² Additionally, when 2-aminothiophenols serve as substrates, hydrosilane-promoted CO₂ reduction coupled with cycloaddition, catalyzed by [Bmim][OAc], enables benzothiazole production via C-S bond formation.³⁶² CO₂ reduction using hydrosilanes in combination with aromatic halides, supported Pd nanoparticles or Pd-phosphine ligand complexes provides an efficient approach for synthesizing aromatic aldehydes through C-C bond formation. Designed ILs, particularly those with basic functional groups, have the potential to enhance catalytic activity and fine-tune product selectivity.^{403,}

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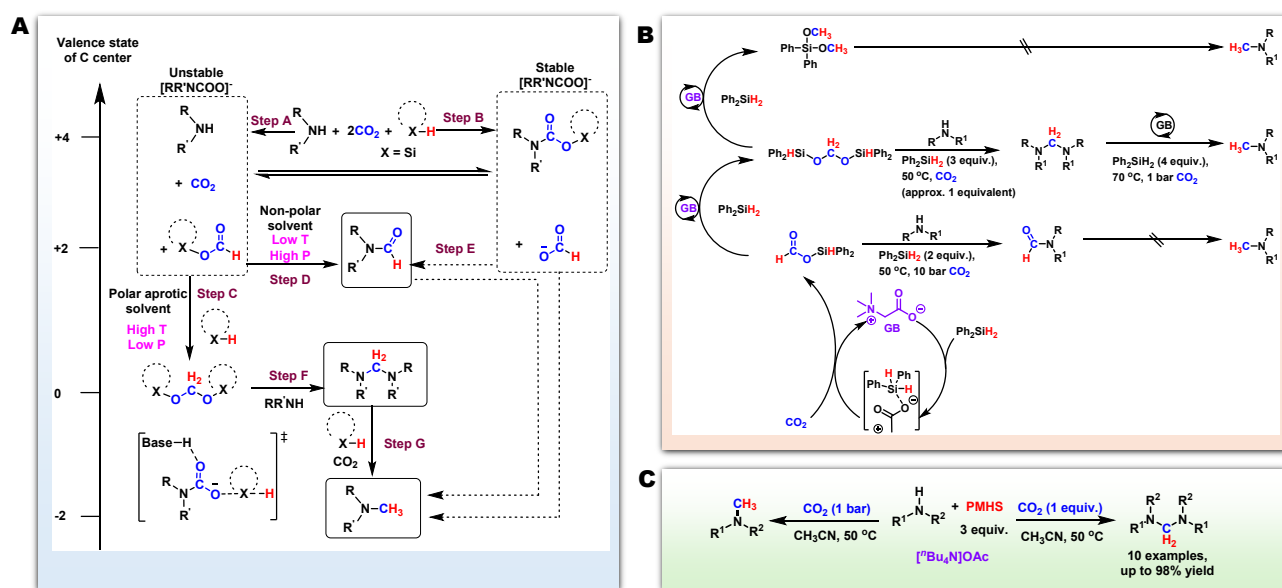


Figure 43. (A) IL-promoted CO₂ reduction with amines in the presence of hydrosilane, leading to selective N-formylation, N-methylation, or aminal formation depending on catalytic activity and reaction conditions.^{397, 398} Reproduced with permissions from refs 397, 398. Copyright 2022 American Chemical Society, 2018 American Chemical Society. (B) Selective CO₂ reduction and coupling with amines catalyzed by glycine betaine (GB).^{361, 397} Reproduced with permissions from refs 361, 397. Copyright 2017 John Wiley & Sons, 2022 American Chemical Society. (C) Controlled production of methylamines or aminals via reaction condition tuning in $[nBu_4N][OAc]$ -catalyzed CO₂ reduction.⁴⁰²

As discussed, hydrosilanes with active hydride species have demonstrated high efficiency in selective CO₂ hydrogenation with amines, catalyzed by ILs under mild conditions, albeit generating large amounts of silanol byproducts. In contrast, H₂ is a more sustainable reducing agent, particularly when derived from water electrolysis, as it primarily forms H₂O as a byproduct. However, H₂ is more inert than hydrosilanes, necessitating metal catalysts and harsher conditions to achieve reasonable CO₂ conversion and product yields. CO₂ hydrogenation with H₂ can yield carbon monoxide (CO), formic acid (HCOOH), methanol, hydrocarbons, or even C₂₊ coupling products, with ILs playing a crucial role in modulating metal site activity and product selectivity (Table 5). The reverse water gas shift (RWGS) reaction is widely used to convert CO₂ and H₂ into CO and water.⁴⁰⁵ IL coatings can confine and stabilize Ru sites, while their solvation effects enhance CO₂ and H₂ adsorption, improving RWGS performance.⁴⁰⁶ Additionally, integration Ru sites within IL anions, paired with phosphine ligand-functionalized cations, creates efficient catalysts for CO₂-to-CO conversion in the presence of H₂.⁴⁰⁷

HCOOH synthesis via CO₂ hydrogenation represents a sustainable pathway for CO₂ valorization and H₂ storage, as HCOOH can serve as a hydrogen carrier or be upgraded to alcohols and hydrocarbons.^{408, 409} ILs with basic functionalities enhance HCOOH production by complexing with metal catalysts and shifting reaction equilibrium through formate salts formation.^{410, 411} ILs with tertiary amine groups, such as [Mammim][TfO] and [DAMI][OTf], promote HCOOH synthesis when combined with SiO₂-supported RuCl₃-PPh₃ catalysts.^{412, 413} Fluorinated anions paired with [DAMI] cation further improve HCOOH production using bare Ru nanoparticles (NPs) or mesoporous silica-supported Ru catalyst.^{414, 415} More readily synthesized ILs, such as [Bmim][OAc] and [Bmmim][OAc], have been widely used as solvents for CO₂ hydrogenation to HCOOH. For example, [Bmim][OAc]

combined with $\text{Ru}_3(\text{CO})_{12}$ facilitates high HCOOH concentrations and turnover numbers (TON), assisting Ru-H intermediate formation and neutralizing free HCOOH to drive the reaction forward.⁴¹¹ Ru and Ir complexes in $[\text{Bmmim}][\text{OAc}]$ further improve efficiency under milder conditions.^{410, 416} IL-promoted CO_2 hydrogenation has also been demonstrated in heterogeneous catalytic systems, such as RuFe alloys or Pd/C catalyst.^{417, 418} Comparatively, when neutral ILs without basic sites were deployed, although they can still facilitate HCOOH formation from CO_2 reaction with H_2 , extra organic base or harsh reaction conditions were required to obtain reasonable yield.^{419, 420} Further reducing HCOOH to methanol (CH_3OH) is significantly more challenging, and IL applications in this area remain underexplored. Current studies indicate that ILs as reaction media, combined with commercial heterogeneous catalysts, can enhance CO_2 conversion and methanol selectivity in batch or membrane flow reactor.^{421, 422}

Further reductive cleavage of C-O bond in methanol leads to methane (CH_4) formation from CO_2 hydrogenation, with Ru-based catalysts being the most widely used in ILs-assisted systems (Table 5). Homogeneous Ru complexes can generate Ru NPs stabilized in the IL phase, where CO_2 -philic ILs containing imidazolium cations and $[\text{NTf}_2]$ or $[\text{CF}_3(\text{CF}_2)_3\text{SO}_3]$ anions enhance CO_2 and H_2 solubility, promoting CH_4 as the major product.^{423, 424} Applying a thin IL layer ($[\text{Bmim}][\text{BF}_4]$) to Ru NPs supported on silica further improves CO_2 -to- CH_4 conversion in the gas phase.⁴²⁵ Introducing additional metal sites alongside Ru can enhance C-C coupling, shifting the reaction pathway toward to C_{2+} hydrocarbon formation. CO_2 -philic ILs play a critical role in tuning gas diffusion and adsorption strength, facilitating hydrocarbon synthesis. Both homogeneous Pd-Fe catalyst systems and heterogeneous RuFe and RuNi alloys have demonstrated good C_{2+} hydrocarbon yields when paired with imidazolium ILs containing $[\text{PF}_6]$ and $[\text{NTf}_2]$ anions.^{417, 426, 427} The tunability of ILs in CO_2 hydrogenation is exemplified by the RuFe alloy system: in the presence of basic $[\text{Bmim}][\text{OAc}]$ at lower temperatures, HCOOH dominates, whereas switching to neutral $[\text{Bmim}][\text{NTf}_2]$ and increasing temperature shifts selectively toward $\text{C}_2\text{-C}_4$ hydrocarbons.⁴¹⁷

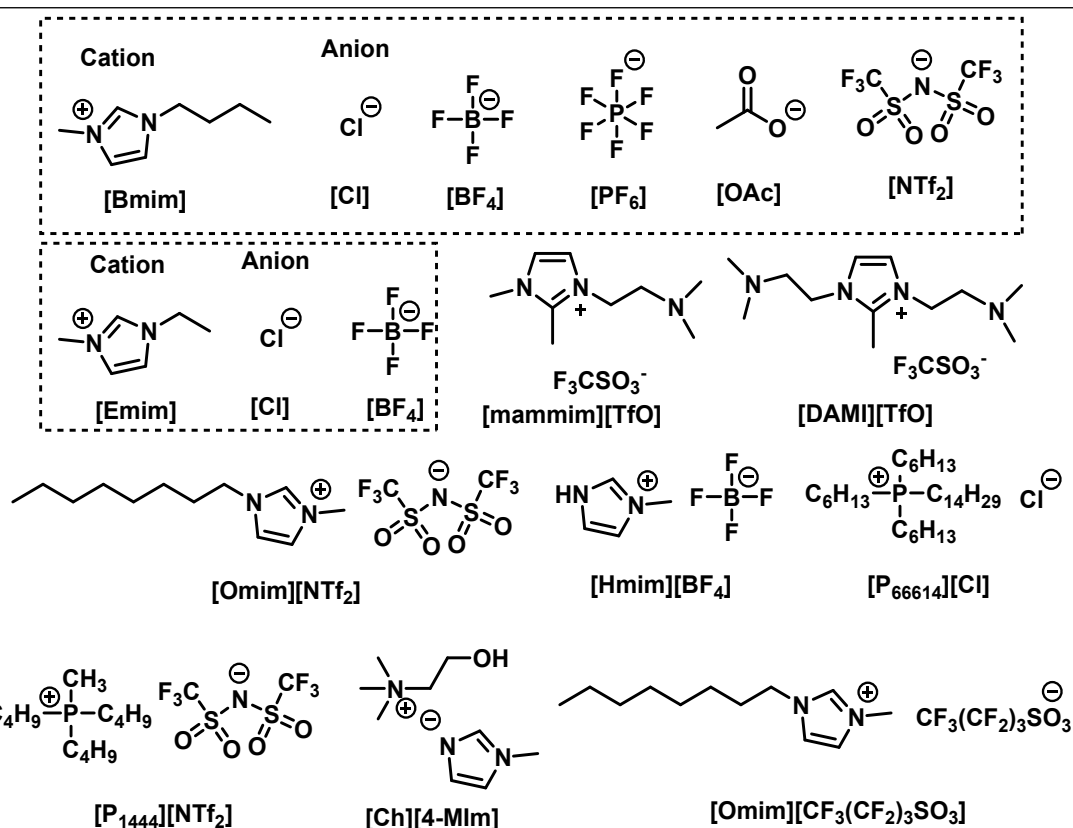
Incorporating additional substrates besides CO_2 and H_2 enables coupling reactions that integrate reduced CO_2 moieties into value-added chemicals (Table 5). ILs have shown exceptional tunability in formylation and methylation of amines via CO_2 reduction with hydrosilanes. Similar tunability is observed in catalytic systems using H_2 as the reducing agent. Choline-based SIL with basic imidazolate anions promote formamide formation using CuCl as a catalyst in CO_2/H_2 system.⁴²⁸ In Pd/C-catalyzed reactions using $[\text{Bmim}][\text{BF}_4]$ as the reaction medium, CO_2 , H_2 , and amines can yield formamides, methylamines, and 1,2-bis(N-heterocyclic)ethanes, with ILs playing a key role in activating amine substrates and formamide intermediates while controlling selectivity via reaction conditions.⁴²⁹ In the presence of alkene substrates, hydroformylation reactions occur, leading to alcohol formation. Imidazolium-based ILs with $[\text{Cl}]$, $[\text{NTf}_2]$, or $[\text{BF}_4]$ anions are commonly used in these processes, with $\text{Ru}_3(\text{CO})_{12}$ serving as the catalyst. Here, in situ CO generation is facilitated by ILs, which enhance gas solubility and stabilize Ru-H active sites, improving the coupling reaction and alcohol yield.⁴³⁰⁻⁴³² Furthermore, in IL media containing lithium halide additives and ether substrates, acetic acid can be produced via an in situ CH_3OH -to- CH_3I transformation, following by coupling with CO to form longer chain oxygenates.^{433, 434}

Table 5. Selected examples of IL-involved catalyst systems in CO₂ reduction using H₂ as the reducing agent.

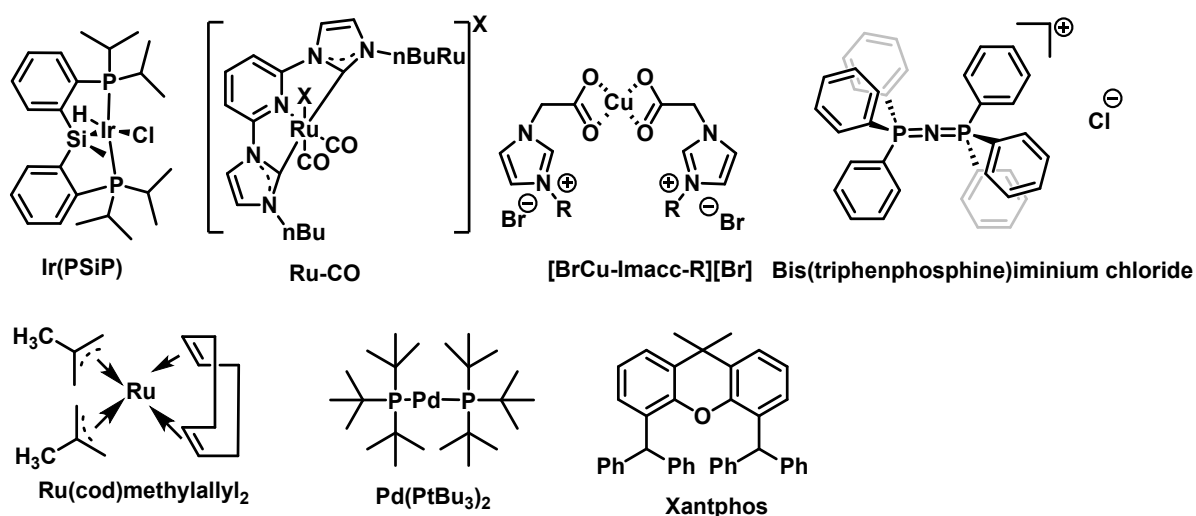
ILs ^a	Catalyst ^b	Reaction condition	Results	Ref
CO₂ reduction product: CO				
[C ₄ mim]Cl	[RuCl ₂ (CO) ₃] ₂ /IL/Silica	Catalyst 1.0 g, H ₂ 6 MPa, CO ₂ 2 MPa, 170 °C	TON: 250	406
[PPN][RuCl ₃ (CO) ₃]	-	Ru complex, PPNCI 0.1 mmol, NMP 2 mL, H ₂ 6 MPa, CO ₂ 2 MPa, 160 °C, 5 h	TON: 96	407
CO₂ reduction product: HCOOH				
[Mammim][OTf]	SiO ₂ -RuCl ₃ -PPh ₃	Catalyst 0.3 g, IL 1.5 g, H ₂ O 5 g, H ₂ 9 MPa, CO ₂ 9 MPa, 60 °C, 2 h	TOF: 103	412
[DAMI][OTf]	SiO ₂ -RuCl ₃ -PPh ₃	Catalyst 0.3 g, IL 0.4 g, H ₂ O 3 g, H ₂ 9MPa, CO ₂ 9 MPa, 80 °C, 2 h	TON: 1840	413
[DAMI][OTf]	Ru NPs in IL	CO ₂ /H ₂ 40 MPa, 100 °C, 5 h	TON: 1225	414
[DAMI][CF ₃ CF ₂ CF ₂ CF ₂ SO ₃]	Ru/MCM-41	Catalyst 0.15 g, IL 150 uM in 2 mL H ₂ O, CO ₂ /H ₂ 1:1 4 MPa, 80 °C, 5 h	TON: 178.2	415
[Bmim][OAc]	Ru ₃ (CO) ₁₂	Catalyst 7.8 μmol, IL 0.7 g, DMSO 67 mmol, H ₂ O 13.2 mmol, CO ₂ /H ₂ 1:1 4 MPa	TON: 17000	411
[Bmmim][OAc]	Ru-CO	Catalyst 2.8 μM, IL 3.3 mmol, dioxane 6 mL, H ₂ O 0.3 mL, H ₂ 3 MPa, CO ₂ 3 MPa, 140 °C	TON: 163000	410
[Bmmim][OAc]	Ir(PSiP)	Catalyst 1.6 μmol, IL 200 mg, DMSO 4.35 g, CO ₂ /H ₂ 1:2 6 MPa, 30 °C, 18 h	TON: 2475	416
[Bmim][OAc]	RuFe alloy	Catalyst 5 mg, IL 36 mg, D ₂ O 33 mg, DMSO 2.84 g, CO ₂ /H ₂ (1:2, 3 MPa), 60 °C, 24 h	TON: 34	417
[Bmim][OAc]	Pd/C	Catalyst 10 mg, IL 1 mmol; CO ₂ 3 MPa, H ₂ 5 MPa, 40 °C, 24 h	TON: 594	418
[P ₆₆₆₁₄][Cl]	Poly(urea)-Ru catalyst	CO ₂ /H ₂ 14.4 MPa, 70 °C	TOF: 11900	419
[Cu-Imace-C ₁][Br]	-	Catalysts 0.02 mmol, DBU 20 mmol, THF 5 mL, CO ₂ 2 MPa, H ₂ 2 MPa, 100 °C, 21 h	TON: 420	420
CO₂ reduction product: Methanol				
Li[NTf ₂] (20 wt%) doped [P ₁₄₄₄][NTf ₂]	Cu/ZnO/Al ₂ O ₃	H ₂ /CO ₂ 3:1 7.5 MPa, 250 °C, 24 h	25%	421
[Emim][BF ₄]	Cu-based catalyst (MK-	Membrane reactors	-	422

CO₂ reduction product: Hydrocarbons				
[Omim][NTf ₂]	Ru NPs	Ru(cod)methylallyl ₂ as precursor, IL 1 mL, total pressure 8 MPa, 150 °C	CH ₄ 69%	423
[Omim][CF ₃ (CF ₂) ₃ SO ₃]	Ru NPs	Ru(cod)methylallyl ₂ as precursor, H ₂ /CO ₂ 1:1 8 MPa, 150 °C, 24 h	CH ₄ 63%	435
[Bmim][BF ₄] IL coating	Ru/IL(1 : 10)/SiO ₂	H ₂ /CO ₂ 4:1, GHSV 2400 h ⁻¹ . gas phase, 250 °C	CH ₄ (CO ₂ conversion 70%)	425
[Bmim][PF ₆]	Pd(P ^t Bu ₃) ₂ , FeCl ₂ , Xantphos	IL 0.5 mL, CO ₂ 3 MPa, H ₂ 6 MPa, 180 °C, 12 h	C ₂ -C ₄ 98%	426
[Bmim][NTf ₂]	RuFe NPs	Catalyst 20 mg, IL 0.5 g, CO ₂ /H ₂ 1/4 0.85 MPa, 150 °C, 64 h	C ₂ -C ₄ 57%	417
[Bmim][NTf ₂]	RuNi NPs	Catalyst 20 mg, IL 0.5 mL, CO ₂ /H ₂ 1:4, 0.85 MPa, 150 °C, 60 h	C ₂ -C ₄ 65%	427
CO₂ reduction product: formamide or methylamine				
[Ch][4-MIm]	CuCl	morpholine 1 mmol; CuCl 50 mg, Ch-IL, 0.5 mmol; CO ₂ 3 MPa, H ₂ 5 MPa, 24 h	Formamide >99%	428
[Bmim][BF ₄]	Pd/C	amine 0.5 mmol, Pd/C 20 mg, IL 5 mmol, CO ₂ 2 MPa, H ₂ 3 MPa, 120 °C, 6 h (formylation); CO ₂ 4 MPa, H ₂ 6 MPa, 160 °C, 6 h (methylation)	Formamide, 1,2-bis(N-heterocyclic)ethane, methylamine	429
CO₂ reduction product: C₂+ oxygenates				
[Bmim][Cl]/[Bmim][NTf ₂]	Ru ₃ (CO) ₁₂	Catalyst 0.1 mmol, IL 9.4 mmol, 1-Hexene 20 mmol, CO ₂ 4 MPa, H ₂ 4.0 MPa, 160 °C, 10 h	n-C ₆ H ₁₃ OH 82%	430
[Bmmim]Cl	Ru ₃ (CO) ₁₂	Alkene 20 mmol, H ₃ PO ₄ , CO ₂ /H ₂ 1:1 6 MPa, 120 °C, 17 h	Alcohol up to 99%	431
[Emim]Cl	Ru ₃ (CO) ₁₂	Gas phase, propene/CO ₂ /H ₂ 4.0/23.7/72.3 flow rate 42.5 mL/min, pressure 8.6 MPa, 170 °C	n-C ₄ H ₉ OH 42%	432
[Bmim]Cl	Ru ₃ (CO) ₁₂	LiI, LiCl, methanol 3.7 mmol, CO ₂ 3 MPa, H ₂ 6 MPa, 160 °C, 15 h	CH ₃ CH ₂ OH, CO, CH ₄	433
[Hmim][BF ₄]	Ru ₃ (CO) ₁₂ +Rh ₂ (CO) ₄ Cl ₂	Lignin 200 mg, Ru catalyst 40 mmol), Rh catalyst 40 mmol, LiI 3 mmol, IL 3 g, CO ₂ 3 MPa, H ₂ 3 MPa, 140 °C, 12 h	CH ₃ COOH	434

^aStructures of ILs used in CO₂ hydrogenation:



^bStructures of catalysts:



6.3 Ionic liquid facilitated hydrogenation reactions via thermal catalysis

Hydrogenation is a widely employed technique for synthesizing saturated molecules and evaluating catalyst performance. Extensive research has explored the use of ILs as reaction media in the presence of both homogeneous and heterogeneous catalysts for the hydrogenation of various substrates.^{436, 437} This process involves the addition of hydrogen to the double bonds of alkenes and aromatic rings, yielding alkane products essential for fuel production and pharmaceutical synthesis. Typically, transition metals such as palladium (Pd), platinum (Pt), and nickel (Ni) serve as catalysts, enabling controlled and selective hydrogenation while preserving other functional groups. Early

attempts at hydrogenating alkenes in ILs utilized soluble rhodium (Rh) and ruthenium (Ru) metal complexes as catalysts under biphasic conditions. In these systems, imidazolium-based ILs acted as liquid supports to immobilize the metal complexes and assess hydrogenation efficiency.⁴³⁸ Additionally, ILs such as [Bmim][NTf₂] have been shown to stabilize heterogeneous metal NPs. By tuning the particle size of Ru NPs, selective hydrogenation of dienes was achieved, with a remarkable 97% selectivity for the conversion of 1,3-cyclohexadiene to cyclohexene.⁴³⁹

Besides serving as reaction media, ILs can be designed to incorporate active metal sites within their cation or anion structures, thereby modulating electronic properties and enhancing stability. For instance, in phenol and furfural hydrogenation for alcohol formation, IL has demonstrated the ability to stabilize Ru/CoO nanocatalysts via complexation. By replacing the anion with [P(C₆H₄-*m*-SO₃)₃]³⁻ (TPPT) (Figure 44A), the stability and activity of the catalyst were improved.⁴⁴⁰ Moreover, the catalytic properties of nanocomposites can be fine-tuned by altering the alkyl chain length and PEG molecular weight.⁴⁴¹ A notable advantage of these IL-based catalysts in their recyclability via thermoregulated phase separation. The IL-RuCoO_x catalyst, insoluble in 2-propanol at room temperature, dissolves upon heating, forming a uniform black solution. This property enables simple catalyst recovery: upon cooling to approximately 0 °C, the catalyst precipitates out, facilitating easy separation and reuse. A rhodium single atom (SA) catalyst was successfully integrated into a Keggin polyoxometalate (POM)-based IL and applied in the hydroformylation of olefins using CO and H₂.⁴⁴² This IL, composed of an ammonium cation ([N₁₈₈₈]) and a [SiW₁₁O₃₉Rh] anion, exhibited a melting point of approximately 95 °C. The Rh SA catalyst demonstrated enhanced stability, maintaining efficiency even after six months of air exposure. Metal-incorporated [Bmim]-based ILs have also been widely studied for the selective partial hydrogenation of benzene and toluene. A highly efficient catalytic system, combining Lewis acidic [Bmim][AlCl₄] with Pd/C, facilitated the hydrogenation of hydrocarbon-based aromatic substrates, including benzene and C₆₀ fullerene, under ambient H₂ pressure at room temperature.⁴⁴³ Experimental and computational studies indicated that the IL provides both kinetic and thermodynamic stabilization for the arenium intermediate. Furthermore, selective benzene hydrogenation to 1,3-cyclohexadiene was achieved using a catalytic system composed of core-shell RuPt nanoparticles in [Bmim][PF₆].⁴⁴⁴ Leveraging structure similarities, Ru NPs were successfully dispersed in nitrile-functionalized ILs for benzonitrile hydrogenation.⁴⁴⁵ The introduction of a nitrile group into the imidazolium cation improved selectivity toward imine product formation while preventing arene hydrogenation (Figure 44B). Besides liquid phase IL applications, IL moieties can also be employed as surface modifiers to tune support properties and enhance interactions with metal NPs. For example, imidazolium-based ILs paired with [NTf₂] anion were used as coating layers for silica supports, effectively stabilizing anchored RuFe and RuCo NPs. These catalysts demonstrated high efficiency in the selective hydrogenation of benzylideneacetone (Figure 44C).⁴⁴⁶

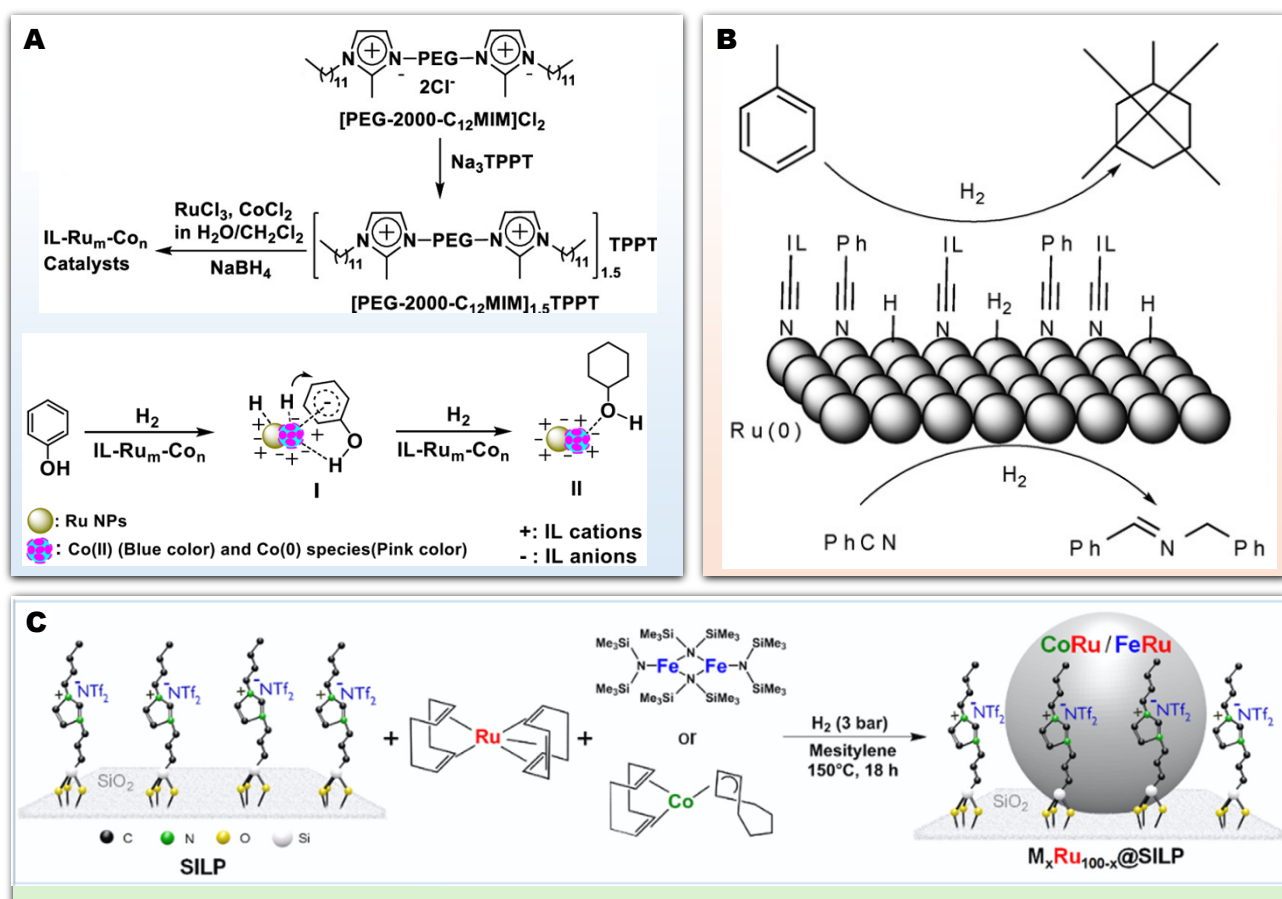


Figure 44. (A) Structure of Ru sites-involved in IL and its application in phenol hydrogenation.⁴⁴⁰ (B) Selectivity tuning in Ru-catalyzed phenylacetonitrile hydrogenation using nitrile-functionalized IL as the reaction medium.⁴⁴⁵ Reproduced with permission from Ref 445. Copyright 2009 Elsevier. (C) Synthesis of supported RuFe and RuCo catalysts on a silica support with IL as a modifier.⁴⁴⁶ Reproduced with permission from Ref 446. Copyright 2022 Elsevier.

6.4 Ionic liquid facilitated oxidation reactions via thermal catalysis

ILs have demonstrated exceptional catalytic performance in oxidation reactions due to their chemical stability under oxidative conditions and their ability to stabilize metal catalysts in high oxidation states. Among the most extensively studied ILs for oxidation are those based on imidazolium salts containing metal anions, such as Cu, Fe, and polyoxometalates (POMs). A series of amphiphilic peroxophosphomolybdates, [C_nmim]₃PMo₄O₂₄ (n = 4, 8, 16), were synthesized by mixing H₃PMo₁₂O₄₀·13H₂O with imidazolium chloride ILs in the presence of H₂O₂.⁴⁴⁷ These ILs exhibited excellent catalytic performance in the oxidative desulfurization of dibenzothiophene (DBT) using H₂O₂ as the oxidant, maintaining high activity with minimal loss over eight cycles. Similarly, an IL composed of ammonium cation ([n-Bu₄N]) and picolinate anion ([Pic]) effectively coordinated and stabilized vanadium oxo-clusters, enabling efficient oxidation of cyclohexane using H₂O₂.⁴⁴⁸ Incorporating active oxidation sites directly into IL structures not only enhances catalyst stability but also improves selectivity. For instance, the imidazolium IL [Omim]₂[WO₄] efficiently catalyzed the epoxidation of cyclooctene while suppressing H₂O₂ decomposition.^{449, 450} In contrast, using [Omim][BF₄] with Na₂WO₄ in an aqueous phase resulted in severe H₂O₂ decomposition. For oxidation reactions involving gaseous O₂, an IL catalyst was developed by combining CuCl with an

imidazolium-based IL containing TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) as the cation, paired with [NTf₂] anion. This catalyst effectively promoted the oxidation reaction of 5-hydroxymethylfurfural, yielding 2,5-diformylfuran.⁴⁵¹

6.5 Ionic liquid facilitated CO₂ electroreduction reactions

The electroreduction of CO₂ represents a promising method for converting intermittent energy sources into high-energy chemicals, potentially decreasing our reliance on fossil fuels and mitigating atmospheric pollution.³⁶⁹ However, CO₂ is the most oxidized state of carbon possessing intrinsic thermodynamic stability and kinetic inertness, leading to the requirement of harsh reaction conditions (e.g., high pressure, high temperature, or high overpotential) to afford satisfied electroreduction efficiency.^{409, 452} Developing electro-catalytic systems capable of activating CO₂ preferably under ambient pressure and converting CO₂ into fuel-related organic molecules is challenging.⁴⁵³ The products formed upon electrochemical CO₂ reduction by complex electron-proton transfer steps under different applied voltages including C1 compounds (CO, formate or HCOOH, methanol, formaldehyde, methane) and C₂₊ compounds (e.g., ethylene, ethanol, acetic acid, oxalate, ethane, and propyl alcohol).⁴⁵⁴ The electrocatalytic reduction of CO₂ to these products involves complex multi-electron and proton coupling steps, which typically lead to slow kinetics.⁴⁵⁵ As a result, the reaction usually undergoes low current density, inadequate selectivity, and a significant overpotential.

The significant overpotential required for CO₂ reduction is due to the considerable reorganization energy necessary for converting linear CO₂ into the bent radical anion [CO₂^{•-}] (CO₂ + e⁻ → ·CO₂⁻). This necessitates a very negative reduction potential of approximately -1.9 V versus the normal hydrogen electrode (NHE),⁴⁵⁵ rendering the reduction process significantly energy inefficient. Materials or compounds that can form complexes with CO₂ in a non-linear configuration can reduce this reorganization energy, thereby enhancing the efficiency of the electroreduction of CO₂.⁴⁵⁶ ILs have become promising candidates for CO₂ capture and separation due to their unique molecular structures and exceptional properties, including ultralow volatility, high thermal stability, low flammability, tunability, and strong CO₂ affinity.^{2, 44, 457} Notably, their relatively intrinsic ionic conductivity, high CO₂ solubility and broad potential windows make ILs especially advantageous as attractive electrolyte components for CO₂ electroreduction.⁴⁵⁸ Up to now, most of the ILs involved in the process for electroreduction of CO₂ are imidazolium types (e.g., [Bmim]⁺; [Emim]) with non-coordinating anions, i.e., Br⁻, BF₄⁻, PF₆⁻, and OAc⁻ (Figure 45).^{55, 458} The introduction of ILs was demonstrated to be capable of reducing the overpotential for CO₂ reduction in comparison with the aqueous or organic solvent systems, suppressing the competing H₂ evolution, and stabilizing the intermediates and regulating the local microenvironment to improve the product selectivity.⁴⁵⁸

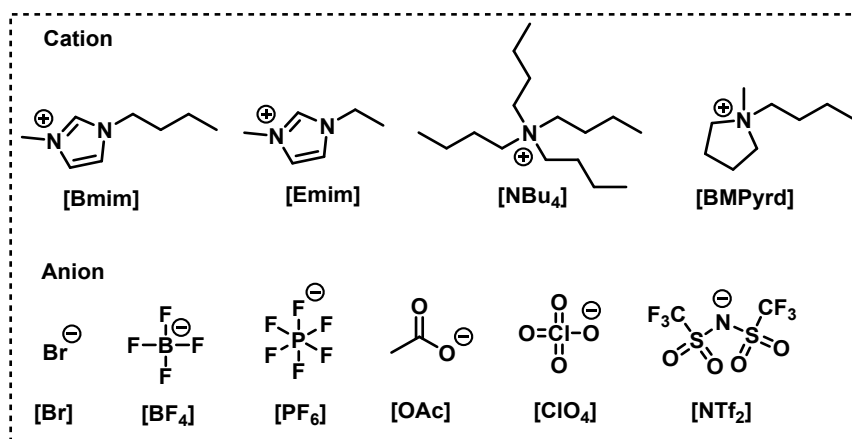


Figure 45. Typical ILs involved in the process for electroreduction of CO₂.^{55, 458}

The configuration of the imidazolium cation, particularly the delocalized 3-center 4-electron conjugation across the N1-C2-N3 moiety and the double bond between C4 and C5, is essential to its functionality. The slight delocalization in the central region enables these cations to efficiently extract and stabilize electrons, a property that can be strategically harnessed in a range of catalytic systems. In 2004, the electrosynthesis of syngas was introduced, involving the electrolysis of supercritical CO₂ and water using [Bmim][PF₆] as both solvent and electrolyte.⁴⁵⁹ This process not only generated CO involves a two-electron transfer process and H₂ but also produced trace amounts of HCOOH. Later, Rosen et al. developed an electrocatalytic system utilizing a silver (Ag) cathode along with a [Emim][BF₄] electrolyte in 2011.⁴⁶⁰ This configuration aimed to reduce the energy associated with the (CO₂)⁻ intermediate during the electroreduction of CO₂ to CO, thereby lowering the initial reduction barrier, as illustrated in [Figure 46A](#). The CO₂ to CO reduction process demonstrated a Faradaic efficiency (FE) of 96% over a duration of at least 7 hours, with an overpotential maintained below 0.2 V. Except the electroreduction of CO₂ to CO, CO₂ can be electro reduced to HCOOH on a pre-anodized platinum electrode using [Emim][NTf₂] as the electrolyte, with HNTf₂ serving as the proton source.⁴⁶¹ Besides, traditional Pb or Sn electrodes can achieve CO₂ electroreduction to HCOOH with a FE greater than 90% using a [Bmim][PF₆] (30 wt%)-H₂O (5 wt%)-MeCN electrolyte (refer to [Figure 46B-C](#)).⁴⁶² When the same IL is used as a supporting electrolyte, indium-doped carbon-supported MoP nanomaterials (MoP/In@C) serve as the cathode electrocatalyst, enhancing the FE_{HCOOH} to 96.5% at a current density of 43.8 mA cm⁻².⁴⁶³ Furthermore, the in-situ synthesized three-dimensional branched Cu catalyst has been shown to further improve both the FE and current density for HCOOH production to 98.2% and 102.1 mA cm⁻², respectively.⁴⁶⁴

In addition to the IL with purely physical absorption of CO₂, [Bmim][OAc] demonstrates high CO₂ solubility through chemical interactions with CO₂. The electroreduction of CO₂ in [Bmim][OAc] involves a chemically irreversible one-electron transfer to form the radical anion CO₂^{-•}, potentially leading to the subsequent production of oxalate, CO, and carbonate.⁴⁶⁵ The anions in ILs can also adsorb and stabilize intermediates from the CO₂ electroreduction, effectively controlling the selectivity of different two-electron transfer products, such as CO or HCOOH. Phosphonium-based SILs, such as [P₆₆₆₁₄][Triz] and [P₆₆₆₁₄][NTf₂], have been shown to exhibit distinct selectivity for CO₂ reduction products when utilized with an Ag electrode. For instance, The [P₆₆₆₁₄][Triz]-chemisorbed/activated CO₂ to formate by electrochemical reduction at low overpotentials (~0.17 V), while IL with NTf₂⁻

anion only produced CO (Figure 46D).⁴⁵⁶

Among the products generated through electrochemical CO₂ reduction, methanol is a highly sought-after target due to its high energy density and compatibility with existing infrastructures, making it a viable substitute for fossil fuels.⁴⁵⁴ The electrocatalytic conversion of CO₂ to methanol involves complex 6-electron and proton coupling steps ($\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$), which leads to slow kinetics.⁴⁵⁵ Consequently, this reaction typically experiences low current density, insufficient selectivity, and a significant overpotential. Integrating the electrocatalyst with an IL electrolyte is an effective approach to enhance this process. Imidazolium-based ILs, such as [Bmim][PF₆] and [Bmim][BF₄], paired with various metal catalysts—including Mo-Bi bisulfides,⁴⁶⁶ Pd-Cu gels,⁴⁶⁷ Cu₂-xSe,⁴⁶⁸ and Sn₁/CuO⁴⁶⁹—can facilitate the electrochemical CO₂ reduction to methanol. A proposed reaction pathway for the CO₂ electroreduction to methanol was illustrated over Cu₂-xSe catalyst, utilizing a ternary electrolyte system consisting of [Bmim][PF₆] (30 wt%)-H₂O (5 wt%)-MeCN (Figure 46E).⁴⁶⁸

The direct electroreduction of CO₂ to CH₄ involves an 8-electron process that presents significant scientific challenges due to its complex transformation pathways and difficulties in controlling selectivity. Recent advancements have utilized imidazolium-based IL electrolytes, including [Bmim][BF₄], [Bmim][PF₆], and [Bmim][ClO₄], in conjunction with layered MOFs derived from ZnCl₂ and trimesic acid (Zn-MOF) as catalysts. Operating at a voltage of -2.2 V (vs. Ag/Ag⁺), the Zn-MOF catalyst has demonstrated high selectivity for methane, achieving a FE greater than 80% (Figure 46F).⁴⁷⁰

The increased complexity during the CO₂ electroreduction to C₂⁺ products involves complex reaction mechanisms and C-C coupling, which increases the requirements for electrolytes and electrocatalytic materials. Current research continues to emphasize Cu-based catalysts,^{471, 472} where IL electrolyte systems play a key role in managing current density and product selectivity. For example, the synthetic influence of CO₂ electroreduction is enhanced by the use of alkaline ILs, such as 1-aminopropyl-3-methylimidazolium bromide ([C₃NH₂MIm][Br]), in Cu catalysts to facilitate the reduction of CO₂ to C₂⁺ chemicals (Figure 46G-H).⁴⁷² Additionally, the inclusion of alkaline IL can elevate the surface pH, which inhibits the production of H₂. Alkaline IL could establish hydrogen bonds with the *CO₂⁻ and other critical intermediates formed during the CO₂ reduction, potentially lowering the activation overpotential for CO₂ and promoting the C-C coupling process (Figure 46I).

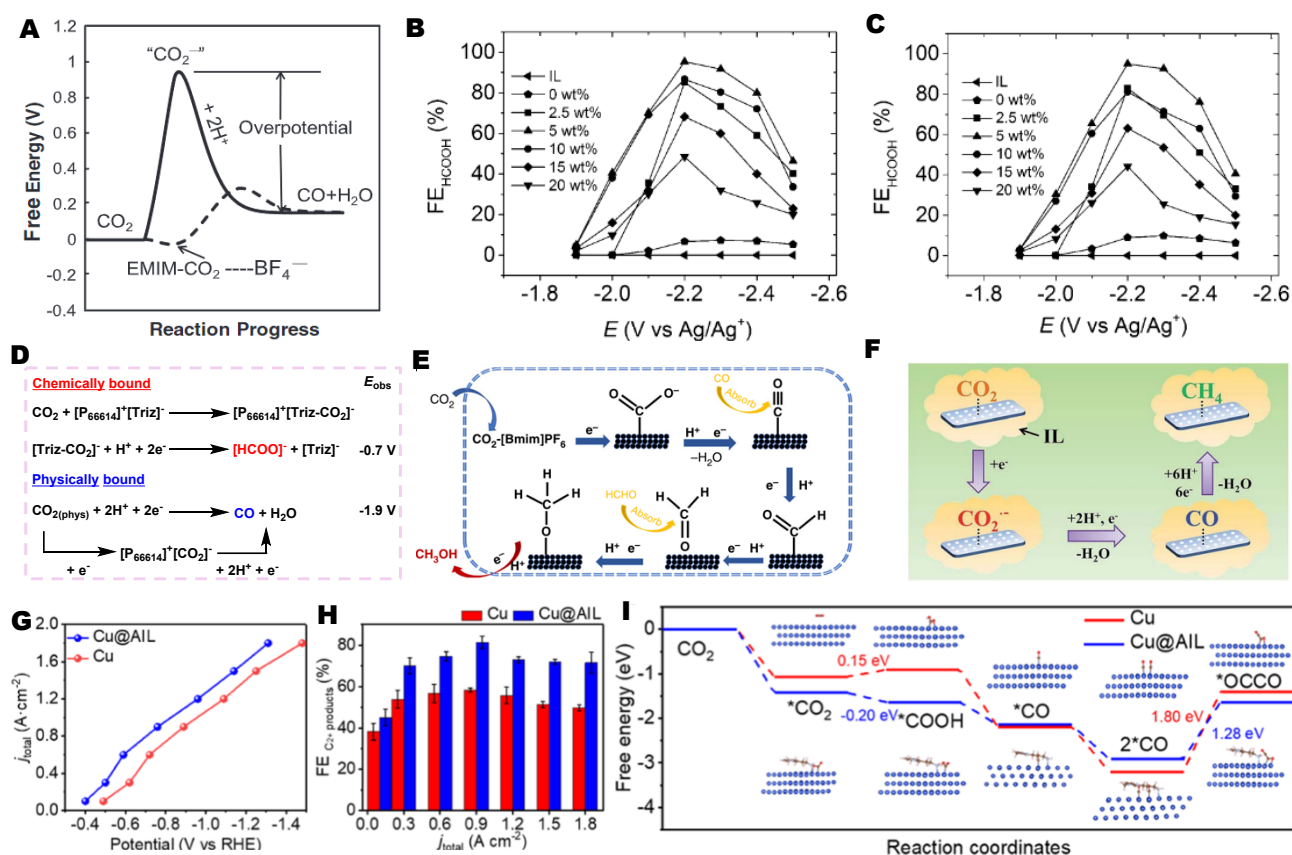


Figure 46. (A) The free energy of the system varies throughout the CO₂ electroreduction in water or acetonitrile or [Emim][BF₄].⁴⁶⁰ Reproduced with permission from Ref 460. Copyright 2011 The American Association for the Advancement of Science. (B-C) FE_{HCOOH} using [Bmim][PF₆]-MeCN-H₂O electrolytes with different H₂O contents on (B) Pb and (C) Sn electrodes.⁴⁶² Reproduced with permission from Ref 462. Copyright 2016 John Wiley & Sons. (D) Proposed reduction pathway at polarized Ag electrode in SILs, such as [P₆₆₆14][Triz] and [P₆₆₆14][NTf₂] saturated with CO₂. (E) Mechanism study of CO₂ electroreduction to methanol.⁴⁶⁸ Reproduced with permission from Ref 468. Copyright 2019 Springer Nature. (F) Mechanism study of CO₂ electroreduction to CH₄.⁴⁷⁰ Reproduced with permission from Ref 470. Copyright 2016 Royal Society of Chemistry. (G-H) The current density and FE_{C2+} of CO₂ electroreduction using alkaline ILs and Cu catalyst. (I) The mechanism of CO₂ electroreduction to C₂⁺ chemicals.⁴⁷² Reproduced with permission from Ref 472. Copyright 2023 American Chemical Society.

The electrochemical reduction of CO₂ represents a promising strategy for carbon recycling and sustainable fuel production. However, conventional processes typically rely on pure CO₂ feeds, incurring significant energy costs for capture and purification. To address this, some advanced catalyst systems incorporating the ILs have been developed to enable efficient CO₂ electroreduction directly from low-concentration CO₂ sources such as industrial flue gas typically composed of a low concentration of CO₂ at 5-15%. For instance, the nanoconfined ILs were introduced into porous Ni-N-C catalysts to enhance CO₂ solubility and local concentration at active sites (Figure 47A).⁴⁷³ The optimized Ni-N-C/[Bmim][PF₆] IL composite demonstrated nearly 100% Faradaic efficiency for CO production and up to 2.7-fold enhancement in current density under pure CO₂ (Figure 47B). Notably,

when operated with 5-10% CO₂, this system maintained high efficiency and stability for over 30 h, significantly outperforming the IL-free counterpart. Mechanistic insights suggested that the hydrophobic alkyl chains of the IL enrich CO₂ near the active sites, while the in situ generated CO₂•⁻ intermediate forms a complex with [Bmim]⁺ cations, facilitating the formation of a [Bmim]-CO₂ adduct (Figure 47C). This dual function as both CO₂ concentrator and cocatalyst offers a low-energy pathway for converting dilute CO₂ to CO. In addition, a bismuth–poly(ionic liquid) (Bi-PIL) hybrid catalyst was engineered, achieving over 90% Faradaic efficiency for formate production across a broad potential range, even at 15% CO₂ concentration (Figures 47D-G).⁴⁷⁴ The PIL component, featuring biphenyl groups, provides hydrophobicity and high ionic conductivity, suppressing electrode flooding and acting as a CO₂ concentrator and co-catalyst. Integration of the Bi-PIL catalyst into a solid-state electrolyte enabled continuous production of pure HCOOH directly from flue gas, with techno-economic analysis indicating a significant cost advantage over traditional methods. These studies highlight the potential of IL-based catalyst systems to overcome the challenges of low-concentration CO₂ utilization, offering integrated and scalable routes for the efficient conversion of CO₂ into valuable chemicals and fuels.

Notably, the direct electroreduction of diluted CO₂ from ambient air primarily relies on porous catalysts with high specific surface areas, catalysts functionalized with amine groups, or hybrid systems coupled with components such as ILs to enhance local CO₂ concentration and increase the CO₂ partial pressure.⁴⁷⁵ ILs are particularly promising in this context, as IL-derived sorbents can effectively capture CO₂ from air with long-term stability (see Section 5), while also enriching CO₂ near active sites and modulating their electronic properties.

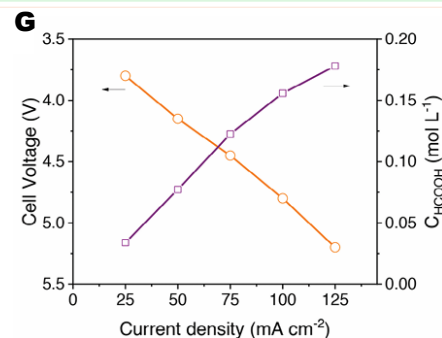
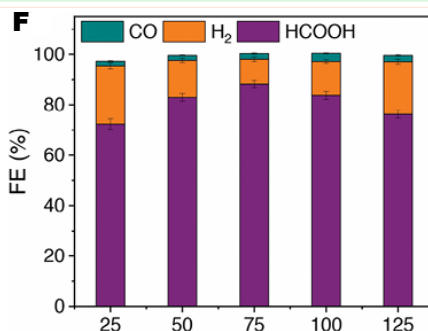
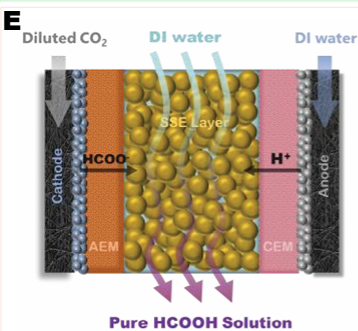
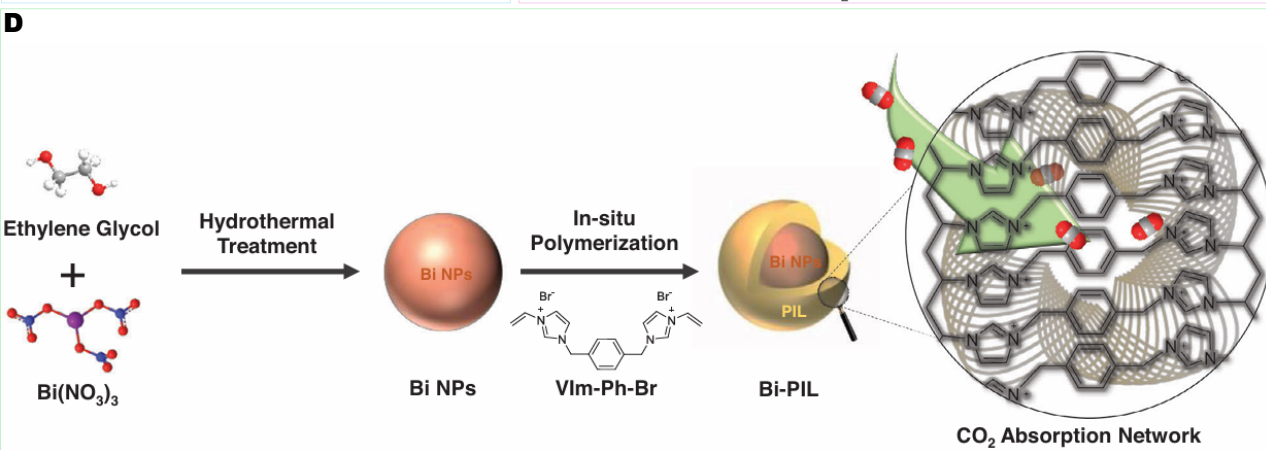
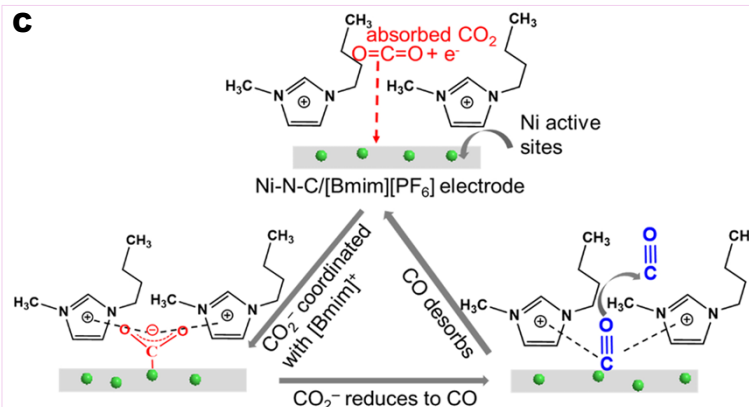
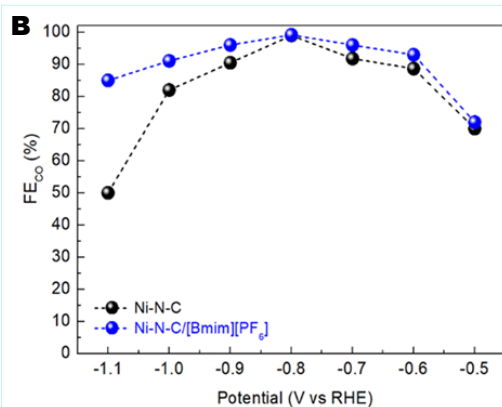
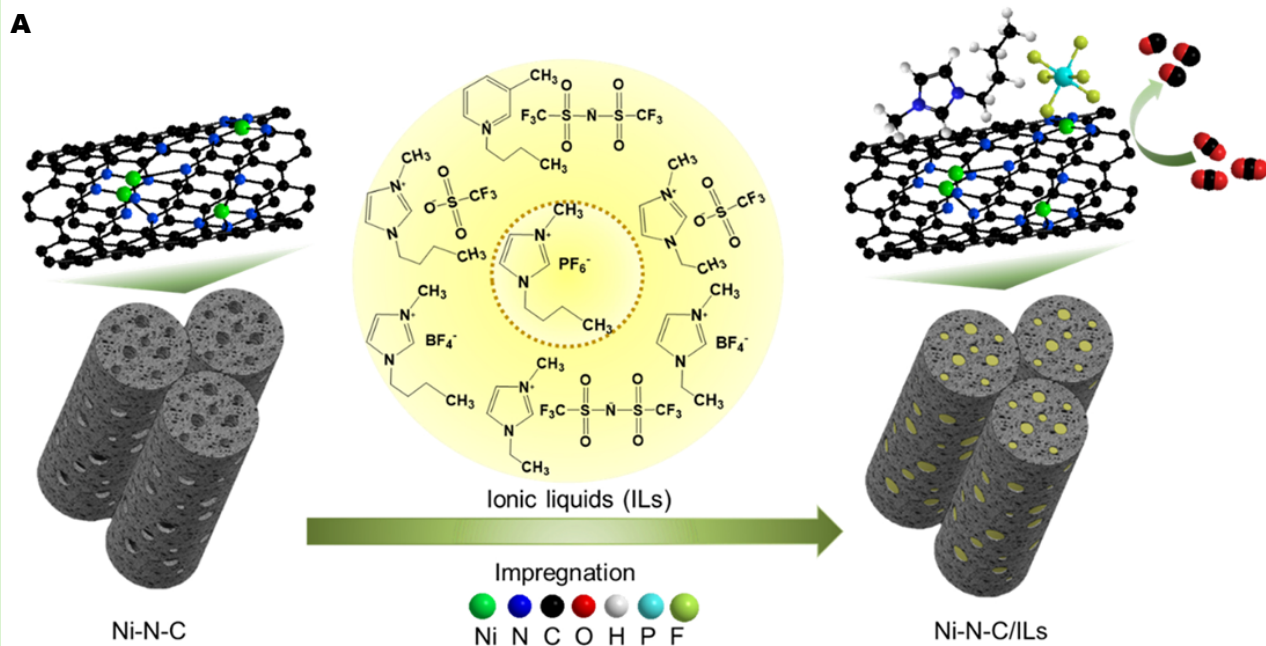


Figure 47. (A) Preparation of Ni-N-C/[Bmim][PF₆] Ni single atoms in Ni-N-C/[Bmim][PF₆].⁴⁷³ (B) FE_{CO} [Bmim][PF₆] of Ni-N-C catalyst and Ni-N-C/[Bmim][PF₆] electrodes.⁴⁷³ (C) Proposed mechanism of electroreduction of CO₂.⁴⁷³ Reproduced with permission from Ref 473. Copyright 2022 Elsevier. (D) Schematic illustration for the synthesis of Bi-PIL hybrids.⁴⁷⁴ (E) Schematic diagram of solid-state electrolyte electrolyzer.⁴⁷⁴ (F) FE of Bi-PIL-(VIm-Ph)-DVB at different current densities under flue gas conditions.⁴⁷⁴ (G) Cell voltage and concentration of produced formic acid at different current densities.⁴⁷⁴ Reproduced with permission from Ref 474. Copyright 2024 John Wiley & Sons.

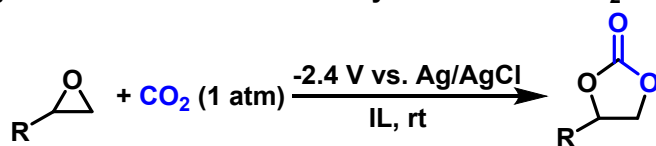
6.6 Ionic liquid facilitated CO₂-involved electro-organic transformation

IL-assisted CO₂ reduction reactions via electrocatalysis yield small molecular products such as CO, HCOOH, and methanol. Furthermore, CO₂ acts as a carbon source in IL-facilitated electrocatalytic organic synthesis, enabling the production of more complex chemical products, mainly including organic carbonates and carboxylation products.

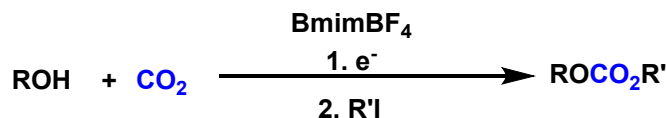
Cyclic carbonates were produced using a sacrificial Mg or Al anode under ambient conditions through the electrocatalytic reaction of CO₂ with epoxides (**Figure 48A**). This method operates without the need for additional catalysts or supporting electrolytes and utilizes ILs such as [Emim][BF₄], [Bmim][BF₄] and [Bmim][PF₆].⁴⁷⁶ Notably, [Bmim][BF₄] demonstrates superior performance by effectively stabilizing the CO₂^{•-} radical intermediate, which enables the formation of various cyclic carbonates with good yields. Furthermore, organic carbonates can be produced from CO₂ and organic alcohols through a two-step electrochemical process in a CO₂-saturated [Bmim][BF₄] electrolyte, again without the necessity for any supplementary electrolytes or catalysts.⁴⁷⁷ As illustrated in **Figure 48B**, under a pressure of 1.0 atm CO₂ and at 55°C, both primary and secondary alcohols can be efficiently transformed into their corresponding carbonates with commendable yields, while tertiary alcohols and phenol show no reactivity. Mechanistic investigations indicate that the generated CO₂^{•-} radical anion acts as a crucial intermediate that interacts with alcohols to yield carbonates upon the addition of an alkylating agent. Notably, the electrochemical facilitation of C-N bond formation in organic carbamates from CO₂ and amines has been successfully achieved (**Figure 48C**).⁴⁷⁸ This process entails the selective cathodic reduction of CO₂ followed by the introduction of ethyl iodide (EtI) as an alkylating agent in CO₂-saturated [Bmim][BF₄] solutions containing amines.

The electrocarboxylation of a variety of substrates—including alkenes, alkynes, ketones, halides, imines, epoxides, and dienes—was conducted using CO₂ in ILs such as [Bmim][BF₄] and tetraalkyl ammonium halides (e.g., Bu₄NBr), which function as both electrolytes and cocatalysts.^{479, 480} For example, the 2-arylsuccinic acids were synthesized from aryl-substituted alkenes with CO₂ using Al or Mg as the anode and non-noble Ni as the cathode (**Figure 48D**). The dicarboxylation occurred at 4 MPa CO₂ pressure and ambient temperature with an n-Bu₄NBr-DMF electrolyte, resulting in 2-arylsuccinic acids with high selectivity and good yields in the absence of additional catalysts. Furthermore, the electrocarboxylation of acetophenone has been investigated in two dry ILs, [Bmim][BF₄] and [BMPyrd][NTf₂].⁴⁸¹ Under a CO₂ atmosphere in dry [Bmim][BF₄], the electroreduction of acetophenone produces a mixture of products, including 1-phenylethanol, 2-hydroxy-2-phenylpropionic acid and dimers. In contrast, in dry [BMPyrd][NTf₂], which has low proton availability, the major reduction product is 2-hydroxy-2-phenylpropionic acid, revealing that [BMPyrd][NTf₂] serves as an effective medium for electrocarboxylation.

A. Cyclic carbonates: Electrocatalytic reaction of CO₂ with epoxides

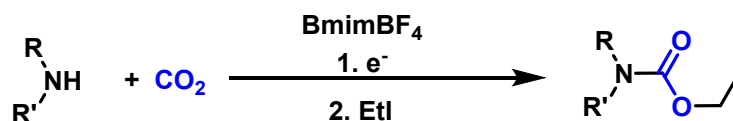


B. Organic carbonates: Electrocatalytic reaction of CO₂ with organic alcohols



R = CH₃, C₂H₅, *n*-C₄H₉, *sec*-C₄H₉, *tert*-C₄H₉, PhCH₂, Ph(CH₂)₂, Ph
 R' = CH₃, C₂H₅

C. Organic carbonates: Electrocatalytic reaction of CO₂ with amines



D. Electrochemical carboxylation of alkenes with CO₂

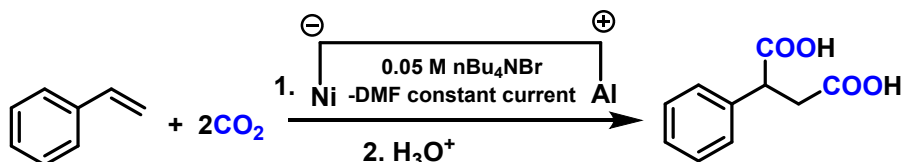


Figure 48. (A) Electrosynthesis of cyclic carbonates from epoxides and CO₂.⁴⁷⁶ (B) Electrosynthesis of organic carbonates from alcohols and CO₂.⁴⁷⁷ (C) Electrochemically promoted C-N bond formation from amines and CO₂ in ([Bmim][BF₄]).⁴⁷⁸ (D) Electrochemical carboxylation of alkenes with CO₂.⁴⁷⁹

6.7 Ionic liquid facilitated the synthesis of photocatalysts

Artificial photosynthesis for converting CO₂ into small energetic molecules such as CO, CH₃OH, CH₄, C₂H₄, CH₃CH₂OH, etc., is a promising approach to achieving carbon neutrality. This process mimics natural photosynthesis and utilizes sunlight to drive the conversion of CO₂, leveraging different mechanisms compared to electro-catalytic CO₂ reduction reactions. Although the underlying chemical transformations share similarities, artificial photosynthesis relies on solar energy as the primary driving force, highlighting its potential for sustainable energy production and carbon capture. A major challenge is effectively capturing and activating CO₂. ILs offer a solution due to their diverse ion pairs, which enhance the synthesis and morphology of photocatalysts, increasing active site exposure. Their tunable hydrophilicity and hydrophobicity assist in controlling the transport of reactants and products to these sites. Additionally, selecting specific IL cations and anions can adjust the photocatalyst's electronic structure, lowering the activation energy barrier for CO₂ and optimizing reaction pathways.

The changes in nanomaterial morphology influenced by IL concentration are linked to the diffusion-limited aggregation process, which is affected by organic or inorganic additives. In a reaction mixture, ILs with bulky organic cations and smaller anions could be interacted with primary nuclei, resulting in anisotropic growth due to restricted particle diffusion and uneven adsorption stability. By adjusting IL concentrations or structures, it is possible to control the morphology of nanomaterials

(Figure 49A).⁴⁸² For example, the IL [Bmim][BF₄] serves as a template for regulating the size of Cu nanoparticles (NPs), yielding sizes between 3-5 nm with a Cu content of 6.8% (Figure 49B).⁴⁸³ It also facilitates the synthesis of CuNi bimetallic nanoparticles. When combined with TiO₂, these materials effectively promote the CO₂ photoreduction to methanol. Furthermore, the synthesis of zinc oxide through the hydrolysis of imidazolium trichlorozincate IL results in catalytically active nanostructured materials (Figure 49C).⁴⁸⁴ The size and shape of these materials—such as NPs, nanorods, and nanosheets—are influenced by the synthetic conditions, specifically the varying ratios of IL to ZnCl₂ and the concentrations of the sodium hydroxide used, then showing excellent activities in the photoactivation of water and methane. Additionally, the concentration of Co single atoms in the Co single-atom modified Bi₂₄O₃₁Br₁₀ atomic layers could be easily controlled by the metal-based IL.⁴⁸⁵ These low-coordinated Co single atoms effectively lowered the activation energy and energy barriers, thereby enhancing the catalyst's CO₂ reduction activity.

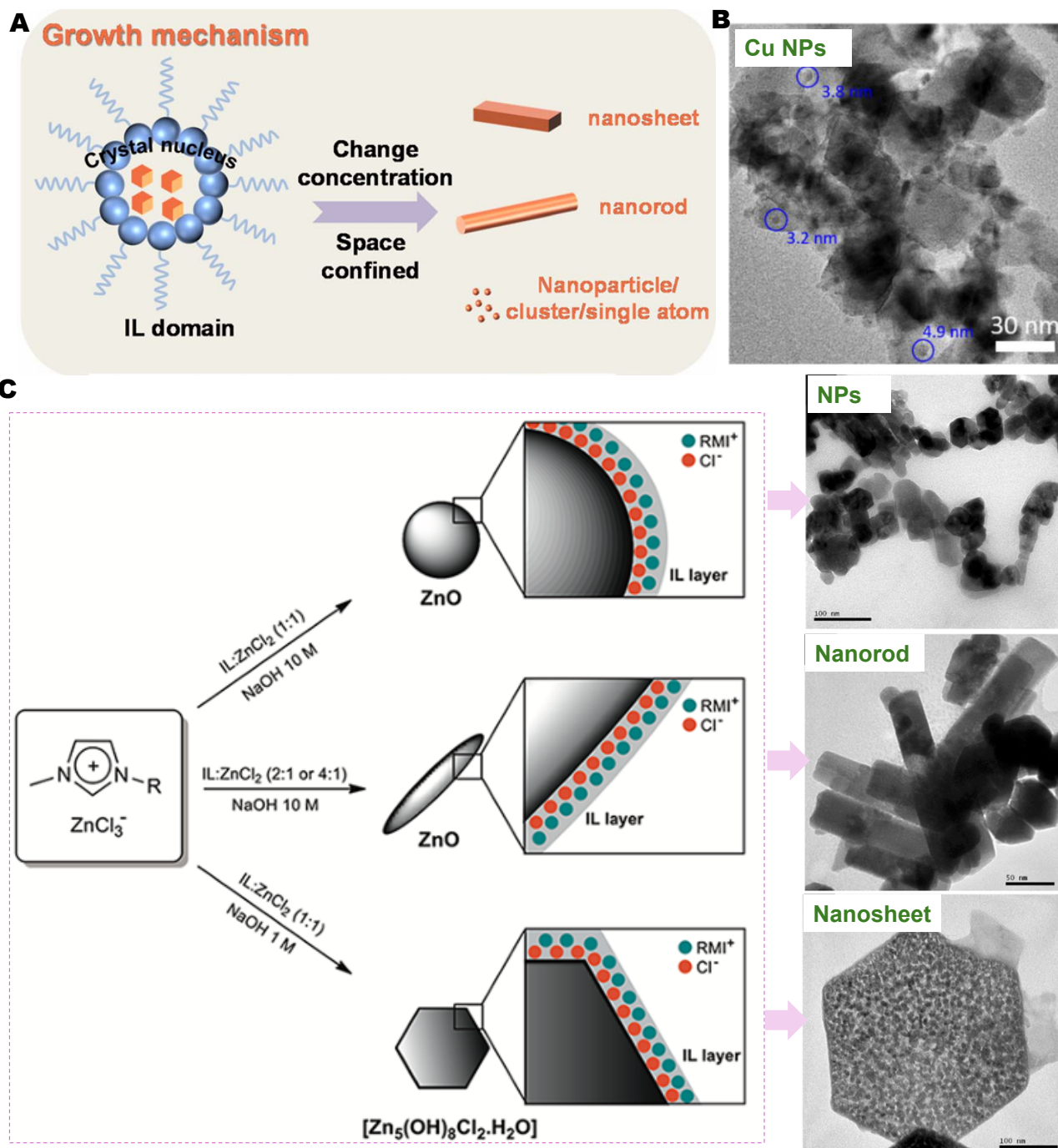


Figure 49. (A) The synthesis and morphology of photocatalysts assisted by ILs.⁴⁸² Reproduced with permission from Ref 482. Copyright 2025 Royal Society of Chemistry. (B) The synthesis of Cu NPs embedded in TiO₂ facilitated by IL for the CO₂ photoreduction to methanol.⁴⁸³ Reproduced with permission from Ref 483. Copyright 2021 Elsevier. (C) The synthesis of zinc oxide nanostructures through the hydrolysis of imidazolium trichlorozincate IL with ZnCl₂.⁴⁸⁴ Reproduced with permission from Ref 484. Copyright 2019 American Chemical Society.

6.8 Ionic liquid facilitated CO₂ photoreduction reactions

Imidazolium-based ILs, such as [Emim][BF₄], have been shown to reduce the initial barrier for CO₂ reduction while simultaneously suppressing the competing hydrogen evolution reaction (HER).

The C(2)-H group in the imidazole ring tends to form complexes with CO₂ rather than H₂O, thereby inhibiting competitive hydrogen evolution and promoting CO₂ reduction. This results in improved selectivity for CO₂ reduction products, which is a crucial factor in designing efficient electrocatalytic CO₂ reduction processes.⁴⁶⁰ The imidazolium-based ILs can also serve as a surface modifier for semiconductors, enhancing the separation of photogenerated electron-hole pairs. This improves the lifetime of photogenerated electrons and enables selective CO₂ reduction in green-light-driven photocatalytic systems, facilitating the conversion of CO₂ and H₂O into energetic small molecules. For instance, [Emim][NTf₂] and CoOx clusters were used as spatially separated redox sites to enhance the BiVO₄/graphitic carbon nitride (g-C₃N₄) Z-scheme heterojunction CN (CoO_x-BVO/CN-IL) (Figure 50A).⁴⁸⁶ The [Emim][NTf₂] interacts with g-C₃N₄ through hydrogen bonding and is capable of accepting photoexcited electrons to efficiently activate the adsorbed CO₂, facilitating its selective reduction to CO. The crucial participation of CoOx and the [Emim][NTf₂] in redox co-catalysis via a cascade Z-scheme charge transfer was demonstrated, with holes promoting water oxidation and electrons facilitating CO₂ reduction (Figure 50B). In addition, ultrathin g-C₃N₄ (CN) nanosheets were co-loaded with [Emim][BF₄] through hydrogen bonding interactions, along with borate-anchored cobalt single atoms, to create IL/Co-bCN nanocomposites (Figure 50C).³⁷² These nanocomposites formed distinct spatially separated domains for reduction and oxidation processes. The optimal nanocomposite demonstrated a 9-fold and 42-fold increase in photocatalytic CO₂ conversion rates compared to borate-modified CN and pristine CN, respectively, achieving CO₂ reduction with CO and CH₄ as the main products. The [Emim][BF₄] was found to effectively extract electrons, facilitating selective CO₂ reduction, while the single cobalt atoms trapped holes and catalyzed water oxidation. Moreover, a linear relationship was observed between the electron transfer rate and the quantity of IL loading in IL-catalyzed CO₂ photoreduction. In this mechanism, CO₂ binds to the C₂ atom of a reduced [Emim]⁺, forming a CO₂-[Emim] adduct. After further reduction and protonation, this leads to the formation of a CO-[Emim] adduct and a water molecule. The final protonation step releases CO, and [Emim]⁺ is regenerated. A minor portion of the CO-[Emim] adduct undergoes further reduction and protonation to produce CH₄ (Figure 50D).

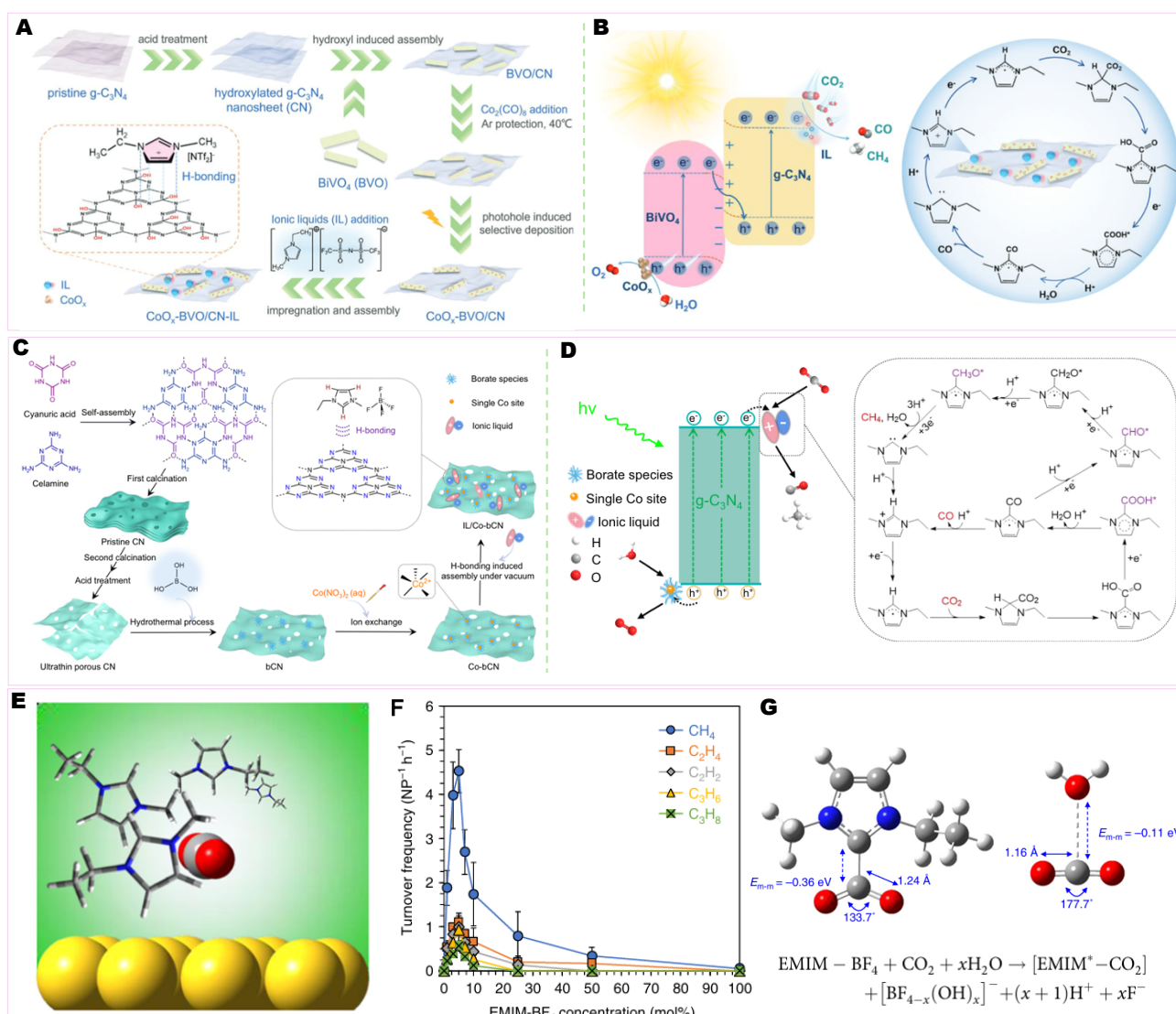


Figure 50. (A) The synthesis process of spatially separated CoO_x and IL-modified BVO/CN.⁴⁸⁶ (B) The proposed photocatalytic mechanism of CO_2 photoconversion over CoO_x -BVO/CN-IL.⁴⁸⁶ Reproduced with permission from Ref 486. Copyright 2023 John Wiley & Sons. (C) The synthetic procedures of IL/Co-bCN photocatalysts. (D) The proposed CO_2 photoconversion mechanism over IL/Co-bCN.³⁷² Reproduced with permission from Ref 372. Copyright 2023 Springer Nature. (E) Diagram illustrating CO_2 conversion on plasmon-excited Au nanoparticles facilitated by $[\text{Emim}][\text{BF}_4]$.⁴⁸⁷ (F) Turnover frequencies of hydrocarbon products generated during CO_2 reduction plotted using the concentration of $[\text{Emim}][\text{BF}_4]$.⁴⁸⁷ (G) The optimized geometries of $[\text{H}_2\text{O}-\text{CO}_2]$ and $[\text{Emim}^+-\text{CO}_2]$ by simulation.⁴⁸⁷ Reproduced with permission from Ref 487. Copyright 2019 Springer Nature.

The synergy between plasmonic excitation of NPs and the stabilizing role ILs provides a novel approach to CO_2 activation and reduction, enabling the production of valuable C1–C3 hydrocarbons (Figure 50E).⁴⁸⁷ At the core of this strategy is the use of plasmonic Au NPs, which, upon green-light excitation, generate the NPs/solution interface with a charge-rich environment. The IL $[\text{Emim}][\text{BF}_4]$ acts as a stabilizer for charged intermediates, such as CO_2 radicals, formed at the interface between the plasmonically excited Au nanoparticles and the solution. The $[\text{Emim}][\text{BF}_4]$ not only stabilizes these

reactive species but also facilitates multi-step electron transfer processes, which are crucial for the reduction of CO₂ into more complex hydrocarbons. Moreover, the IL promotes C–C coupling, a key step in producing higher hydrocarbons like ethylene, acetylene, propane, and propene. CO₂ reduction reaction activity, as measured by turnover frequencies (TOFs) of the hydrocarbon products, shows a marked increase with the concentration of [Emim][BF₄]. The highest activity was observed at a concentration of 5 mol% [Emim][BF₄] (Figure 50F). However, further increases in the IL concentration led to a sharp decline in CO₂RR activity, suggesting that an optimal balance between stabilization and electron transfer must be maintained for maximum efficiency. DFT calculations reveal the structure of the [Emim*–CO₂] complex, in which the C atom of CO₂ binds with the C2 position of the imidazole ring of [Emim][BF₄], exhibiting an intermolecular interaction energy of –0.36 eV (Figure 50G). This interaction is stronger than that of CO₂ with H₂O, underscoring the superior ability of [Emim][BF₄] to stabilize CO₂ during the reduction process. The IL facilitates the photogenerated electrons transfer from the Au nanoparticles to the adsorbed CO₂, effectively addressing a significant kinetic limitation. Furthermore, the CO₂•– generated via photo-induced electron transfer exhibits an extended lifetime on the Au surface due to solvation or complexation with the [Emim]⁺ cation. This extended radical lifetime is critical for the multi-electron reduction process required for hydrocarbon synthesis. These findings suggest that imidazolium-based ILs, especially when used in tandem with other catalytic components such as metal single atoms, represent a promising class of materials for enhancing photocatalytic CO₂ reduction. By stabilizing electrons and facilitating the selective reduction of CO₂, these ILs not only improve the overall efficiency of the system but also open up new pathways for designing highly selective and efficient catalytic processes for CO₂ conversion.

6.9 Modeling and simulations of ionic liquids in CO₂ conversion

DFT calculations on CO₂ conversion using IL catalysts provide valuable insights into the activation role of ILs. The reaction mechanism for the cyclization of CO₂ and 2-aminobenzonitriles forming quinazoline-2,4(1H,3H)-diones was investigated, with [BzTMA][Suc] as the catalyst.⁴⁸⁸ Theoretical calculations (Figure 51A) indicate that the [Suc] anion activates the –NH₂ group on 2-aminobenzonitrile, leading to the generation of the carboxylate intermediate CP3-2 (Figure 51B). Additionally, [Suc] promotes C–O bond cleavage by activating the –COO group (TS3-3, Figure 51A and 51B). The ring-closing step, which forms quinazoline-2,4(1H,3H)-diones, serves as the rate-determining process. While the [BzTMA] cation does not directly participate in the catalytic cycle, it acts as a donor of hydrogen-bond, stabilizing intermediates. The reaction mechanism of cycloaddition of CO₂ with epichlorohydrin (ECH) was explored, catalyzed by a novel dual-IL, [TMGH][O₂MEPZ][Br] (ILPT), in the presence of water to produce chloropropylene carbonate (CPC).⁴⁸⁹ The calculations reveal that CO₂ is initially activated by the –NH₂ group of the [TMGH] cation, followed by ECH ring-opening, which enables the migration of the activated –COO group. The final step is ring-closure to form CPC (Figure 51C). The addition of water plays a crucial role by creating space for CO₂ activation via the –NH₂ group of [TMGH] rather than the –COO[–] group of [O₂MEPZ], which dominates in water-lean conditions. Water also affects the rate-limiting process: without it, the ECH ring-opening step has an activation barrier of 18.2 kcal mol^{–1}, whereas in the hydrated system, the controlling process shifts to the ring-closure, reducing barrier to 5.8 kcal mol^{–1} (CO₂ addition without ECH, TS2-2) and 4.0 kcal mol^{–1} (CO₂ addition with ECH, TS3-2) (Figure 51D).

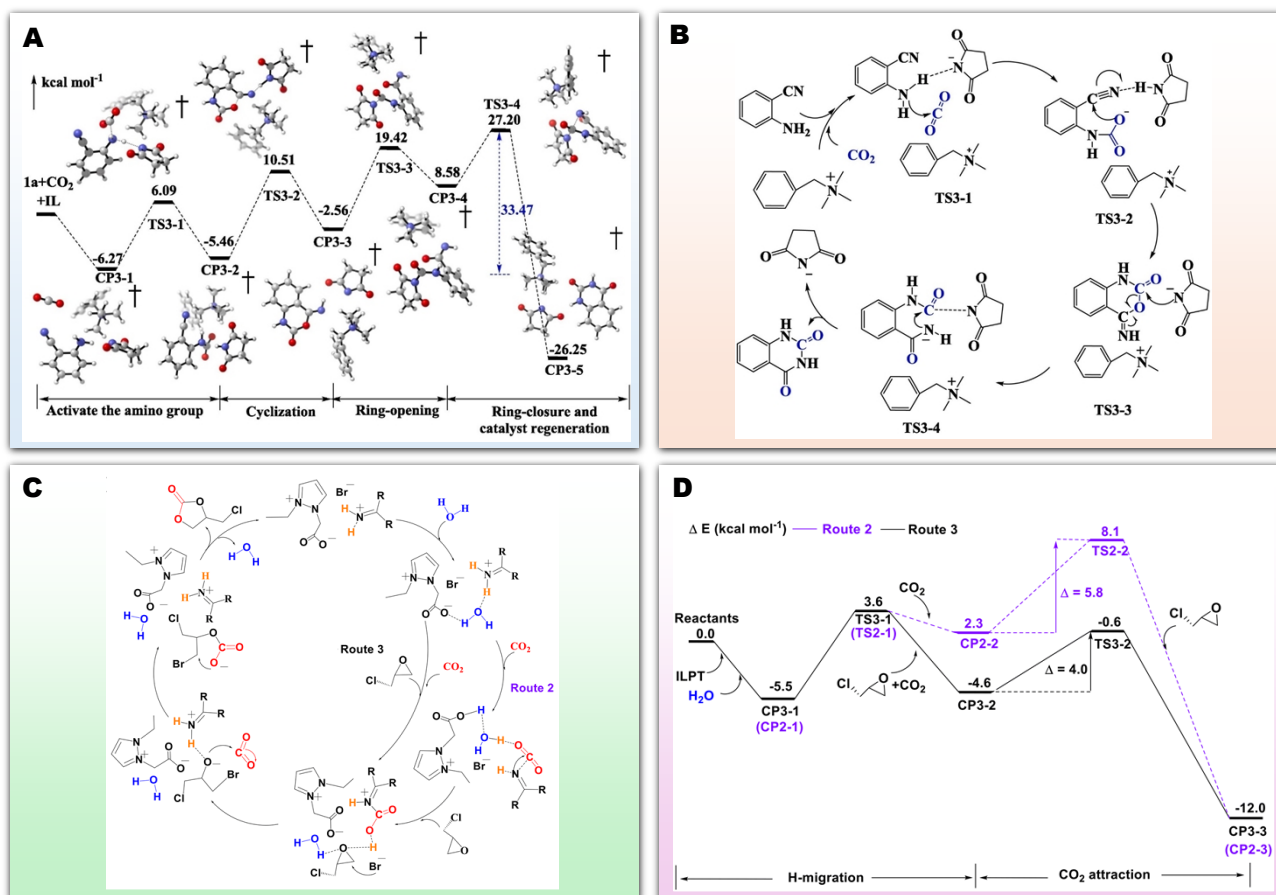


Figure 51. (A) Potential energy profile and optimized structures, and (B) reaction scheme for the cyclization from CO₂ and 2-aminobenzonitriles to generate quinazoline-2,4(1H,3H)-diones, catalyzed by [BzTMA][Suc].⁴⁸⁸ Reproduced with permission from Ref 488. Copyright 2022 Elsevier. (C) Proposed reaction mechanism and (D) potential energy profile illustrating the cycloaddition of CO₂ with epichlorohydrin, catalyzed by [TMGH][O₂MEPZ][Br] (ILPT) with water addition to produce chloropropylene carbonate.⁴⁸⁹ Reproduced with permission from Ref 489. Copyright 2023 Royal Society of Chemistry.

DFT calculations have demonstrated the role of ILs as solvents or supporting electrolytes on the electrode surfaces, influencing both catalytic activity and selectivity in electrochemical CO₂ reduction (CO₂RR). The introduction of IL ([BMIM][PF₆]) on the Cu[511] surface enhanced CO₂RR reactivity of by stabilizing key intermediates *CO and *CHO (Figure 52A).⁴⁹⁰ Meanwhile, the Gibbs free energy barrier for *CO hydrogenation to *CHO was lowered compared to *CO dimerization to *OCCO*, steering selectivity toward CH₄ over C₂H₄. The charge transfer interactions between Cu and [BMIM][NO₃] were studied (Figure 52B), further supporting the catalytic enhancement by ILs.⁴⁹¹ Similarly, through study over the effect of [BMIM][PF₆] on a NiFe dual-atom catalyst supported on nitrogen-doped carbon (NiFe@NC) for CO₂RR,⁴⁹² the DFT calculated free energy profiles (Figure 52C) showed a 0.35 eV reduction in the rate-limiting step for *CO₂⁻ formation. This improvement was attributed to electronic structure modifications, where NiFe@NC/[BMIM][PF₆] exhibited a lower LUMO energy level and a narrower HOMO-LUMO gap (Figure 52D), facilitating charge transfer and promoting CO₂RR.

The IL effects on the molecular catalyst [Rh(bpy)(HCp*)]⁻ was explored,⁴⁹³ and the calculations

indicated that while the presence of the [EMIM]⁺ cation had little impact on the free energy barrier for HCOO⁻ formation, it increased the hydrogen evolution reaction (HER) barrier by 5 kcal/mol (Figure 52E). This was attributed to π - π stacking between [EMIM]⁺ and the bipyridine ring, which hindered H₂O₅⁺ proton approach, thereby favoring HCOO⁻ over H₂. CO₂ photoreduction by modifying CdS/NH₂-UIO-66 with IL [M2070][IPA] was investigated.²⁰² DFT calculations demonstrated that IL incorporation significantly lowered the free energy barrier to for *COOH formation over *HCOO (Figure 52F), shifting the reaction pathway from CO₂-to-CH₄ (without IL) to CO₂-to-CO conversion (with IL).

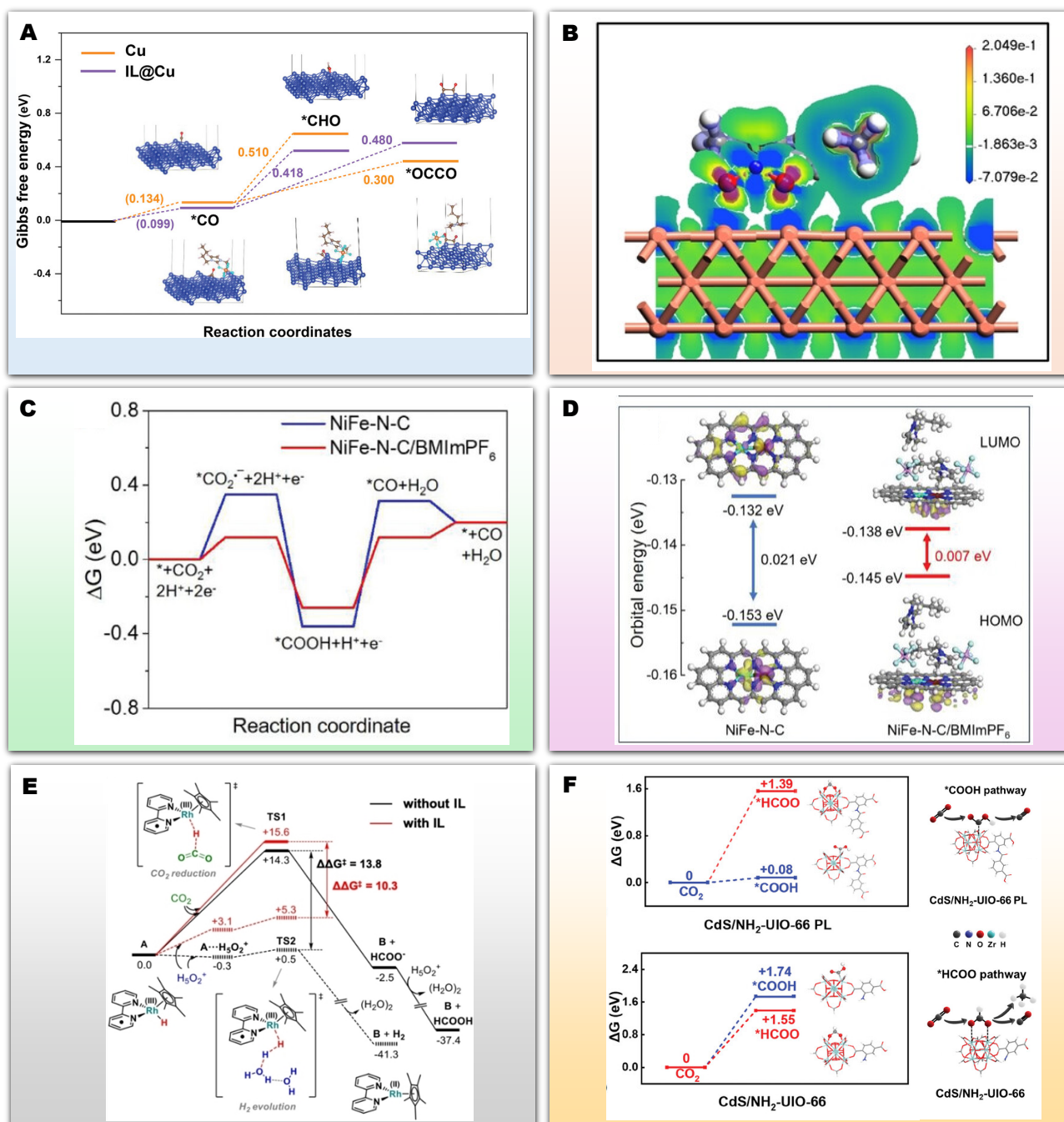


Figure 52. (A) Free energy profile for CO₂ electrochemical reduction on Cu[511] and [BMIM][PF₆]₂@Cu[511].⁴⁹⁰ Reproduced with permission from Ref 490. Copyright 2024 John Wiley

& Sons. (B) Differential charge density of [BMIM][NO₃]₂@Cu.⁴⁹¹ Reproduced with permission from Ref 491. Copyright 2022 John Wiley & Sons. (C) Free energy profile for CO₂RR in NiFe@NC and NiFe@NC/[BMIM][PF₆]. (D) Orbital energy profile of HOMO and LUMO for NiFe@NC and NiFe@NC/[BMIM][PF₆].⁴⁹² Reproduced with permission from Ref 492. Copyright 2023 John Wiley & Sons. (E) Free energy profile for CO₂RR (solid lines) and HER (dashed lines) for [Rh(bpy)(HCp*)]⁺ without (black) and with (red) [EMIM]⁺.⁴⁹³ Reproduced with permission from Ref 493. Copyright 2022 John Wiley & Sons. (F) Free energy profiles for CO₂ reduction pathways over CdS/NH₂-UIO-66 PL (top) and CdS/NH₂-UIO-66 (bottom).²⁰² Reproduced with permission from Ref 202. Copyright 2024 John Wiley & Sons.

7. Conclusions and perspective

ILs have shown significant potential in CO₂ sorption benefiting from their structural versatility and unique features to accommodate diverse gas pressures, temperatures, and impurities. However, several critical challenges persist in optimizing ILs for CO₂ capture, particularly in enhancing their scalability, sorption efficiency, and long-term durability. While the industrial production and application of certain ILs at scale have been demonstrated in metal processing and biomass valorization,⁵ their use in carbon capture remains limited to bench-scale experiments. Cost-effective and simple synthesis methods are still needed to produce IL sorbents with excellent capacity, stability, and low energy consumption for regeneration. This may require the development of continuous synthesis techniques, aided not only by thermal heating but also by microwave and ultrasonication. Large scale implementation of IL sorbents for CO₂ capture will also require tailored sorption processes. These should leverage some aspects of existing infrastructure used for amine-derived sorbents but must also accommodate the viscosity and sorption characteristics of ILs. On the fundamental level, current research on the reaction mechanisms primarily focuses on bonding formation and cleavage related to CO₂ molecules and CO₂-saturated systems. However, understanding the intermediate structure is equally crucial, which necessitates sophisticated control over CO₂ dosing. Advanced characterization techniques beyond conventional spectroscopy should be utilized, such as inelastic neutron scattering (INS) for detecting hydrogen-involved bonding variation and quasi-elastic neutron scattering (QUENS) for measuring gas diffusivity. In addition to the traditional basicity-driven CO₂ capture, recent discoveries of ILs with multiple active sites and proton-transfer-promoted CO₂ insertion mechanisms show great promise for enhancing CO₂ capture. However, these remain case studies. There is still a lack of comprehensive guidelines for designing ILs that can integrate CO₂ via in situ generation of extra active sites, a challenge that will require the support of theoretical simulation to expedite the screening process.

PLs, a quite new class of porous materials, have hold immense potential for applications in gas storage, separation, catalysis, and beyond. Among the various strategies for designing porous liquids, the use of ILs as the liquid phase has emerged as a particularly promising approach, benefiting from their tunable physicochemical properties, low volatility, and high thermal stability, and diverse functionalities. Incorporating functional groups into ILs can impart additional properties, such as catalytic activity or selective gas adsorption, thereby enhancing the functionality of the resulting porous liquid. More opportunities, challenges, and future directions in the development of PLs using ILs as the liquid phase will be discussed from a forward-looking perspective. 1) Customized design strategies for IL-based PLs. Tailoring the synthesis of smart PLs with multiple responsive properties to meet diverse application needs is highly appealing. This requires more efficient and precise design

of IL structures, for which machine learning could be an excellent option. Additionally, combining ILs with other solvents or additives to optimize the balance between porosity and fluidity represents an alternative strategy for constructing PLs. 2) Applications of IL-based PLs. Although IL-based PLs present a range of applications like gas adsorption, separation, catalysis, and conduction, there is still significant promise in expanding their use to fields such as energy storage, environmental remediation, drug delivery, and smart materials. 3) Advanced characterization techniques. A deeper understanding of how the molecular structure of ILs and porous hosts influences the overall properties of the porous liquid is needed to guide rational design. To investigate pore accessibility and fluid behavior at the molecular level, as well as to monitor the solid–liquid interface, advanced and sophisticated characterization techniques remain essential.

Despite significant advancements in IL-based membranes for CO₂ separation, several key challenges remain unresolved. The rational design of highly selective membrane-based separation processes is imperative for the efficient sequestration of anthropogenic CO₂. As the demand for energy-efficient CO₂ capture technologies continues to grow, developing high-performance IL membranes that overcome the inherent trade-off between permeability and selectivity remains an active and evolving research area. By integrating functionalized ILs into membrane architectures, researchers have begun to explore new avenues in CO₂ capture, leveraging the structural diversity of ILs and the scalability of membrane-based separation. The tunability of IL structures allows for precise control over CO₂ interactions, ranging from weak physical sorption to strong chemical binding. As discussed in Sections 4.1 and 4.2, state-of-the-art SILMs primarily rely on ILs that interact with CO₂ via a solution-diffusion mechanism, where gas transport is driven by physical solubility and diffusivity. Alternatively, facilitated transport IL membranes introduce mobile carriers, allowing ILs to form transient CO₂ complexes that diffuse across the membrane, significantly enhancing selectivity. A promising direction in IL-based CO₂ separation involves the incorporation of superbase-derived or amino-functionalized ILs, which exhibit high CO₂ uptake via chemisorption mechanisms. However, despite their superior CO₂ affinity, these ILs remain underutilized in membrane-based separations due to their intrinsically high viscosity, which hinders mass transport and reduces diffusion kinetics. Since gas permeability in IL membranes is fundamentally governed by the product of gas solubility (thermodynamic factor) and diffusivity (kinetic factor), it is essential to strategically engineer ILs to balance strong CO₂ interactions with optimal mass transport properties. Designing ILs that enable facilitated CO₂ transport without excessive viscosity constraints is a key challenge for advancing the field. To fully exploit the potential of IL-based membranes for CO₂ separation, future research efforts should focus on the following synergistic strategies aimed at addressing fundamental challenges in IL structure-function relationships: 1) designing ILs for fast CO₂ transport, overcoming viscosity-related transport limitations by tailoring IL molecular structures to enhance diffusivity while maintaining strong CO₂ binding; 2) optimizing the physical/chemical sorption balance, tuning CO₂ transport mechanisms in SILMs to maximize selective sorption and desorption kinetics; 3) engineering the local organization of IL ions in the membrane, modifying membrane chemical building blocks to control the spatial arrangement of IL ions, thereby facilitating gas transport; 4) regulating surface charges for ion-gated separation, designing membrane surface functionalities that interact with ILs to modulate ion-gated transport phenomena; 5) enhancing CO₂ sorption selectivity at the IL/porous membrane interface, controlling IL-membrane interfacial interactions to improve selective CO₂ uptake and diffusion efficiency. Addressing these fundamental questions requires an interdisciplinary approach, integrating molecular design, membrane engineering, and transport modeling systematically optimize

IL-based CO₂ separation technologies. By precisely tuning IL structures and membrane architectures, future research can bridge the gap between high CO₂ selectivity and practical membrane performance, ultimately accelerating the deployment of next-generation CO₂ separation membranes for industrial applications.

Ongoing research into SILs as modifiers in the synthesis and design of IL-derived absorbents for DAC of CO₂ presents a promising frontier in carbon capture technology. Significant progress has been made with SIL-modified silica, MOFs, and OMCs, offering advantages in terms of porosity and stability. The current methodologies have improved CO₂ uptake capacity through variations in active site coatings and surface areas of support precursor, greater insight into the precise mechanics of CO₂-sorbent interactions could lead to further breakthroughs. A deeper understanding of the mechanisms governing CO₂-absorbent interactions is crucial. Studying the molecular dynamics at the interface between CO₂ and absorbent materials could reveal new pathways to further improve capture efficiency. To thoroughly examine CO₂ insertion mechanisms, particularly in conjunction with simulations, recent research has focused on highly crystalline ionic-pair modified absorbents based on COF scaffolds. These materials have demonstrated promising performance in capturing 400 ppm CO₂ and have provided valuable insights into CO₂ reaction pathways and structural alterations during interactions. However, additional fundamental studies are essential, particularly for materials with basic active sites that exhibit robust properties and can be easily prepared. The development of COFs and MOFs that incorporate oxygen-based nucleophiles—such as alcohols, oxides, hydroxides, and alkoxides—represents a promising strategy for CO₂ capture. These materials can reversibly react with CO₂ to form carbonate species, enhancing their effectiveness in carbon capture applications. A significant advantage of these oxygen-based nucleophiles is their enhanced oxidative stability compared to traditional amine-based materials, primarily due to the higher electronegativity of oxygen. This attribute makes COFs and MOFs using these nucleophiles more robust and well-suited for practical applications in various environmental conditions. Traditionally, CO₂-releasing has relied on thermal heating, which poses challenges in terms of energy consumption and cost. Exploring alternative release methods, such as ultrasonication, photo-irradiation, electric treatment and magnetic induction, could make the DAC process more energy-efficient while reducing operational costs. Furthermore, the potential to convert captured CO₂ into value-added chemicals is crucial for establishing a circular carbon economy. Future research should prioritize developing absorbents that not only effectively capture CO₂ but also facilitate its conversion into chemicals under mild conditions. Advancing energy-efficient release mechanisms, tailoring sorbent designs, and creating synergies between carbon capture and utilization are vital for achieving commercial viability and large-scale implementation of DAC technologies.

Beyond gas storage and separation, ILs have emerged as versatile catalysts and reaction media in the field of CO₂ utilization, significantly enhancing the efficiency and selectivity of various catalytic processes. From facilitating the physisorption and chemisorption of CO₂ to serving as catalysts for both thermocatalytic and electrocatalytic reactions, ILs demonstrate remarkable properties that leverage their unique chemical characteristics. In thermocatalysis, ILs have showcased their ability to effectively enhance the solubility of CO₂ compared to traditional organic solvents through the formation of O-C, N-C, and C-C bonds, leading to successful reactions such as the cycloaddition of CO₂ with epoxides and aziridines. Their highly charged nature and hydrogen bonding capabilities further contribute to their catalytic activity, enabling the production of valuable compounds such as

urea derivatives and quinazoline-2,4(1H,3H)-diones. In addition to non-reductive CO₂ valorization, ILs play a crucial role in the reductive transformation of CO₂ when paired with organosilanes or metal catalysts. Their ability to stabilize polar intermediates and tune the electronic environment around active metal sites facilitates efficient hydrogenation reactions. This characteristic enhances selectivity in the production of formamides, aldehydes, acids, and hydrocarbons. Electrochemical CO₂ reduction is another area where ILs demonstrate significant potential, acting as alternatives to conventional aqueous or organic electrolytes. They enhance catalytic activity and selectivity, particularly in producing high-energy chemicals. Simultaneously, in photocatalytic CO₂ reduction, ILs used in tandem with other catalytic components, represent a promising class of materials for enhancing photocatalytic CO₂ reduction. By stabilizing electrons and facilitating the selective reduction of CO₂, ILs not only improve the overall efficiency of the system but also open up new pathways for designing highly selective and efficient catalytic processes for CO₂ conversion. The integration of ILs in CO₂ utilization processes represents not only a promising avenue for sustainable chemical production but also a significant step toward addressing global CO₂ emissions. The unique properties of ILs allow for tailored interactions with CO₂ and catalytically favorable conditions for various chemical transformations. The continued exploration of functionalized ILs with enhanced properties for specific reactions holds great promise for unlocking new pathways in CO₂ utilization. By designing ILs with tailored functional groups, we can optimize their interactions with both CO₂ and catalytically active sites, thereby improving overall catalytic performance. A deeper understanding of the mechanisms through which ILs facilitate CO₂ reactions is crucial for optimizing reaction conditions and enhancing selectivity. Conducting detailed studies on IL-catalyst interactions and the underlying reaction pathways will be essential for advancing this field. It is equally important to focus on the practical scalability of IL-assisted CO₂ utilization processes. Investigating the economic feasibility of these processes and developing methodologies that can be seamlessly integrated into existing industrial operations will be vital for achieving real-world applications. Furthermore, there is significant potential in developing integrated systems that combine CO₂ capture with various transformation procedures, including thermocatalysis, electrocatalysis, and photocatalysis. This integrated approach could streamline the process and enhance efficiency.

Despite the progress on ILs utilization in CO₂ separation and valorization, the large-scale application of ILs in related fields remains limited by several core challenges, particularly in terms of production cost and sustainability.⁴⁹⁴ Large-scale synthesis of ILs has been achieved via advanced industrial routes such as alkyl carbonate-based approaches, representing a halide-free, waste-minimized method that operates from kilogram to ton scale.^{6, 495} Continuous-flow technology is adopted to synthesize and purify ILs at scale, leveraging the superior heat/mass transfer, easier scaling, and better yield, selectivity, and purity versus batch methods. These improved synthesis approaches largely improved the purity of ILs and reduce the cost, allowing the applications of ILs as acid scavenger, as catalyst in epoxy-butene isomerization and oil refining. However, the large-scale commercial deployment of ILs for CO₂ separation and valorization remains elusive, with current applications limited to pilot or demonstration scale. This is primarily due to challenges such as low mass-transfer rates, relatively high production costs, and a lack of long-term performance data. Particularly, ILs possessing good CO₂ chemisorption behavior, especially in terms of DAC application, structure design and modification are required to achieve promising performance. The sophisticated structure modification involves complex, multi-step procedures and expensive precursors, contributing to significantly higher costs compared to traditional solvents such as aqueous amines. Among

emerging candidates, superbase-derived ILs show significant promise, offering advantages such as facile synthesis via acid-base neutralization, effective CO₂ chemisorption, and good recyclability. To enable the transition of these ILs to industrial scale, advancements in synthesis methodologies, rigorous sorption performance optimization, and long-term durability assessments are critical. Moreover, the energy consumption in regeneration of ILs after CO₂ absorption is another barrier to large-scale application. Although ILs possess benefits in low volatility and high thermal stability, the regeneration procedure can be energy-intensive due to high viscosity and strong CO₂ binding enthalpies in some ILs systems. In contrast, conventional solvents, though less stable and more corrosive, typically offer lower regeneration energy requirements and well-established industrial handling protocols. Searching the goldilocks between cost, capture capacity, stability, and energy input in a whole cycle is required to move forward. Additionally, from a sustainability perspective, comprehensive life cycle assessments (LCA) of ILs are still scarce, and concerns persist regarding their environmental persistence, toxicity, and end-of-life treatment. Addressing these issues through green synthesis, improved recyclability, and performance-cost optimization is critical for the broader deployment of ILs in gas separation technologies.

The studies highlighted above showcase the critical role of modeling and simulations in understanding the structure, reactivity, and dynamics of ILs for gas separation. Despite significant advancements, several key challenges remain. First, accurately simulating condensed-phase reactions remains difficult, particularly for reactive systems designed for CO₂ capture and conversion. This challenge arises from the need to sample reaction pathways while accounting for the explicit solvation environment and molecular fluctuation. To address this, multiscale approaches such as hybrid QM/MM simulations are essential. Second, the complex multiscale nature of many ILs poses additional challenges for molecular simulations. While a CO₂ molecule spans only a few angstroms, porous ILs can feature hollow spheres up to 50 nm in diameter with micropores as small as 1 nm in length scales, necessitate advanced multiscale simulation techniques to accurately model gas adsorption and transport behavior.

Notes

The authors declare no competing financial interest.

Biographies

Liqi Qiu is a postdoctoral researcher in the Department of Chemistry at the University of Tennessee, Knoxville, USA. She earned her Ph.D. in the Department of Chemistry from Nankai University in Tianjin, China, in 2022, where her research focused on solar energy utilization and the photo/electrocatalytic conversion of CO₂ into valuable chemicals. During her doctoral studies, she served as a visiting scholar in the Department of Chemistry at the University of Tennessee, Knoxville, USA. Currently, her research concentrates on the development of novel ionic liquids, porous ionic liquids, and nanomaterials for CO₂ capture, conversion, and membrane separation.

Errui Li is a postdoctoral researcher in the Department of Chemistry at the University of Tennessee, Knoxville, USA. He received his Ph.D. in Chemistry from Zhejiang University in 2021. His primary research interests include porous liquids, porous cages, and their applications in gas adsorption and separation.

Tian Ke is a postdoc of Chemistry Department in University of Tennessee (UT) at Knoxville, U.S. He received his Ph.D. from the College of Chemical and Biological Engineering, Zhejiang University (ZJU), in China, followed by a research assistant and postdoc in ZJU from 2021 to 2024. His central research interests include the rational design and synthesis of porous materials for advanced separation and energy applications.

Qingju Wang is currently a postdoc at the University of Tennessee, Knoxville. She received her BS in Chemical Engineering and Technology (2016) from Xiamen University, and PhD in Chemical Engineering and Technology (2021) from Zhejiang University. Her current research interest focusses on the design of multifunctional materials and their applications in separation and catalysis.

Yujing Tong is a Ph.D. student in Chemical and Biomolecular Engineering at Vanderbilt University in Nashville, USA. He received his M.S. in Chemistry from the University of California, Riverside, in 2022, following his B.S. degree from the University of Science and Technology of China in 2020. His research focuses on the computational exploration of 2D materials and functional interfaces for efficient molecular transport and separation.

Bo Li is a Research Assistant Professor at the Department of Chemical and Biomolecular Engineering at Vanderbilt University. He received his Ph.D. in Theoretical Chemistry from the Technical University of Munich, Germany in 2015. He was a postdoctoral scholar at the University of California, Riverside (from 2016 to 2020), and a postdoctoral research associate at Los Alamos National Laboratory (from 2020 to 2023). His research focuses on developing and applying advanced computational chemistry methods and machine learning techniques to discover and design novel materials and processes for renewable energy applications.

Hongjun Liu is an Assistant Research Professor of Chemical Engineering at Vanderbilt University. He received his Ph.D. in Chemical Engineering from Columbia University, and took several postdoctoral trainings at University of Notre Dame, Oak Ridge National Laboratory, and University of Tennessee. His research focuses on molecular simulations of soft matter materials.

De-en Jiang holds the H. Eugene McBrayer Chair in Chemical Engineering in the Department of Chemical and Biomolecular Engineering at Vanderbilt University as well as a courtesy appoint in the Department of Chemistry. He earned his B.S. and M.S. degrees in Chemistry from Peking University and a Ph.D. in Chemistry in 2005 from UCLA. Dr. Jiang's research centers on computational materials and chemistry, with a focus on applications in energy and the environment. He is a Fellow of the American Association for the Advancement of Science (AAAS). Dr. Jiang's scholarly influence is reflected in his recognition as a Clarivate Highly Cited Researcher in both 2023 and 2024. In addition to his research achievements, he serves as a Senior Editor for The Journal of Physical Chemistry published by ACS.

Shannon Mahurin is a Distinguished Staff Scientist and the Group Leader of the Nanomaterials Chemistry Group in the Chemical Sciences Division at Oak Ridge National Laboratory (ORNL). He received his Ph.D. in Chemical Physics from the University of Tennessee, Knoxville in 2000 and

joined ORNL as a Postdoctoral Research Associate in 2001. He became a staff member in the Environmental Sciences Division at ORNL and then moved to the Chemical Sciences Division. Current research interests include new materials for separations processes with particular emphasis on understanding mechanisms of gas separation and transport in ionic liquids and porous liquids, CO₂ conversion to carbon products, and structure and transport in high temperature molten salts.

Zhenzhen Yang is currently a Staff Scientist in the Chemical Sciences Division at Oak Ridge National Laboratory. She earned her Ph.D. in Organic Chemistry from Nankai University in 2013. Following her doctorate, she worked at the Institute of Chemistry, Chinese Academy of Sciences, as an Assistant and later Associate Staff Scientist from 2013 to 2018. She then joined the University of Tennessee Knoxville as a Postdoctoral Researcher from 2018 to 2020. Her research primarily focuses on developing functionalized nanomaterials for efficient adsorption, separation, activation, and transformation of small gas molecules.

Sheng Dai is currently a corporate fellow and section head overseeing four research groups in the areas of separations and polymer chemistry at Chemical Sciences Division, Oak Ridge National Laboratory and a Professor of Chemistry at the University of Tennessee, Knoxville. His current research interests include ionic liquids, porous materials, and their applications for separation sciences and energy storage as well as catalysis by nanomaterials. He is a Fellow of Material Research Society and Fellow of the American Association for the Advancement of Science.

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