Strategies for design and synthesis of porous liquids toward carbon capture and separation

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Abstract: Porous liquids (PLs) represent a promising category of sorbents in carbon capture and separation capable of integrating the advantages of flowing liquid and porous solid systems. Well-defined pores were engineered into liquid sorbents via liquifying molecules with stiff interior voids, dissolving rigid porous hosts in flowing liquids, or dispersing porous frameworks in high steric hindrance solvents, producing type I, II, or III PLs, respectively. Unique features of PLs have triggered broad interest in exploring their applications in carbon capture and separation, in which diverse design strategies, synthesis approaches, and enhanced performance have been reported. In this minireview, recent progress in the design, synthesis, and structural engineering of PLs and efforts towards the optimization of their carbon capture and separation behavior will be summarized, including the comparison between PLs with varied types. Porosity engineering into liquid sorbents provides opportunities to resolve challenging issues in conventional sorption and separation systems.

Keywords: Porous liquids; Carbon dioxide; Carbon capture; Ionic liquids; Porous materials

Carbon capture and sequestration has been developed as one of the most promising approaches to alleviate the global warming issues caused by greenhouse gas emissions from fossil fuel combustion [1]. Aqueous amine solutions are currently used for CO_2 removal from low-pressure flue gas combinations but still have unsolved issues in evaporation, degradation, and high-energy consumption in cycling procedures [2]. Porous solid scaffolds with defined porous channels (e.g., zeolites, covalent organic frameworks (COFs), and metal–organic frameworks (MOFs)) are promising candidates to alleviate the energy penalty problem but may have difficulty in integrating them into existing flow pipelines [3]. Porous liquids (PLs) are a new type of liquid system with persistent porosity, which have steadily gained attention over the last decade after the concept was presented in 2007 by James et al. [4]. The combined features of porous solid and liquid fluidity in PLs illustrate the wide range of applications [5-7], particularly in selective sorption and separation of specific gas molecules. For example, benefiting from the superfluidity, PLs have a rapid heat dissipation rate and a high pumping capacity, which is preferred in the sorption and regeneration procedures. The advantages from the processable liquid feature allows for a variety of engineering solutions to address the issue of sluggish gas diffusion behaviors in liquid phases, such as spraying, agitation, and membrane contactors. Problems associated with sorbent materials as solids, such as mechanical fatigue, physical aging, and plasticization, are rarely encountered in PLs. The fluidity advantage of PLs will enable them to be included in contemporary industrial pump instruments [3, 8]. Rapid progresses related to PLs have been made in terms of design, synthesis, characterization and application [9-54]. The abundance of available advanced porous hosts, such as zeolites, COFs, MOFs, etc., combined with sterically hindered solvents (e.g., various classes of ionic liquids (ILs)), provide limitless opportunities for developing novel PLs towards diverse applications, and some of the works have been summarized in the reviews by our own and other groups [8, 55-58]. However, no complete assessment of the specific application of PLs in CO_2 capture and separation has been summarized. This review will highlight the recent progresses related to the design principle and structure engineering of task specific PLs towards enhanced carbon capture and separation (Figure 1). We hope the insights provided herein can provide guidance on the discovery of promising sorbents in carbon capture and separation with high uptake capacity, good selectivity, rapid sorption kinetics, and energy-efficient and long-term cycling stability.

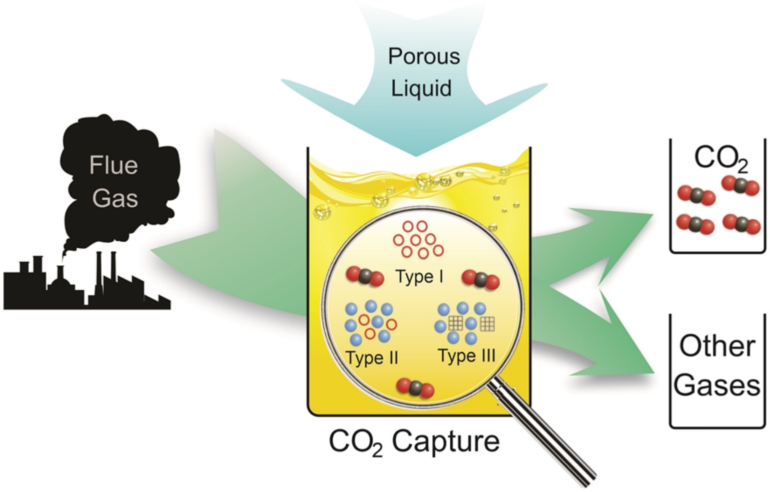

Figure 1 Utilization of porous liquids in carbon capture and separation.

State-of-the-art PLs could be classified into three categories using James's I–II–III systems. Type I PLs have stiff interior voids in their molecules, leading to larger pore volume and reduced volatility because there is no extra solvent [59]. In 2015, Dai et al. created a type I PL from engineering the out-sphere of hollow silica (HS) spheres with microporous shells, which could block the penetration of molecules larger than 1.9 nm via the molecular sieve effect (Figure 2A). To maintain open structures in the PL, the fluid medium must not self-fill voids. As a corona for surface modification, a positively charged organosilane moiety of 2.0 nm was utilized, and the content of inorganic hollow spheres was 17.5%, as determined by thermogravimetric analysis (TGA). The as-synthesized PL was then deployed for membrane-based CO_2 separation. The HS-derived PL has a CO_2 permeability of 158 Barrer, which was higher than that obtained by the liquid counterparts (75 Barrer) while both exhibited similar CO_2/N_2 selectivity of 10. This demonstrated that the hollow structures could speed up gas transport in dense liquids, but the gas selectivity was still controlled by the polymeric liquid chain structures [11]. The achievement that has been made in this work provide extra opportunities and guidance on further improving the CO_2 separation performance in membrane-based processes.

Then this PL synthesis strategy was extended to the fabrication of PLs with hallow carbon spheres (HCS) leveraging the electrostatic interaction between HCS and polymeric ILs, in which HCS with empty pores could be stabilized in a dense liquid phase (Figure 2B). The content of HCS was ~15% in the as-afforded PL. The CO_2 adsorption/desorption isotherms of the HCS-PL and the pure dense liquid counterparts were collected at 298 K up to 10 bar. At a CO_2 pressure of 1 bar, the HCS-PL with extra cavity displayed a CO_2 uptake capacity of 0.445%, which was higher than the liquid sorbents without HCS (< 0.261 wt.%). Enhanced CO_2 uptake by HCS-PL was also observed at high CO_2 pressure (10 bar), and 55.9 wt% of the adsorbed CO_2 was retained in HCS-PL during the desorption process, indicating the promising application of PL in gas storage [10]. PLs composed of HS spheres with different particle size were prepared via the surface modification by ionic pairs being synthesized from the reaction of 3-(trihydroxysilyl)-1-propanesulfonic acid as corona with polyether amine (M2070) as canopy (Figure 2C), which displayed good flowability and thermal stability. CO_2 capture study revealed that for PLs with similar grafting density, those with bigger pore size had a higher CO_2 uptake capacity at 298 K [13].

PL composed of polymer surfactant conjugated HS nanorods and bio-conjugated carbonic anhydrase enzyme (bCA) could achieve combined CO_2 capture and conversion, in which CO_2 could go through the porous wall and be stored in the HS nanorods, bCA could act as the catalyst for the conversion of slowly released CO_2 to HCO_3^- ions (Figure 2D). The CO_2 storage in PL was verified by the rapid transmittance decrease caused by the formation of $CaCO_3$ from $CaCl_2$ and the as-produced HCO_3^- [12]. The successful combination of CO_2 capture and conversion could extend the application of PL systems into efficient carbon capture and utilization (CCU). Theoretical calculation using density functional theory (DFT) demonstrated that for HS-derived PLs containing organosilane moiety cation (corona) and poly(ethylene glycol)-containing sulfonate anion (canopy), the as-involved CO_2-philic polyethylene glycol (PEG) units had the strongest interaction with CO_2, together with weak interaction provided by hydrogen bonding [14].

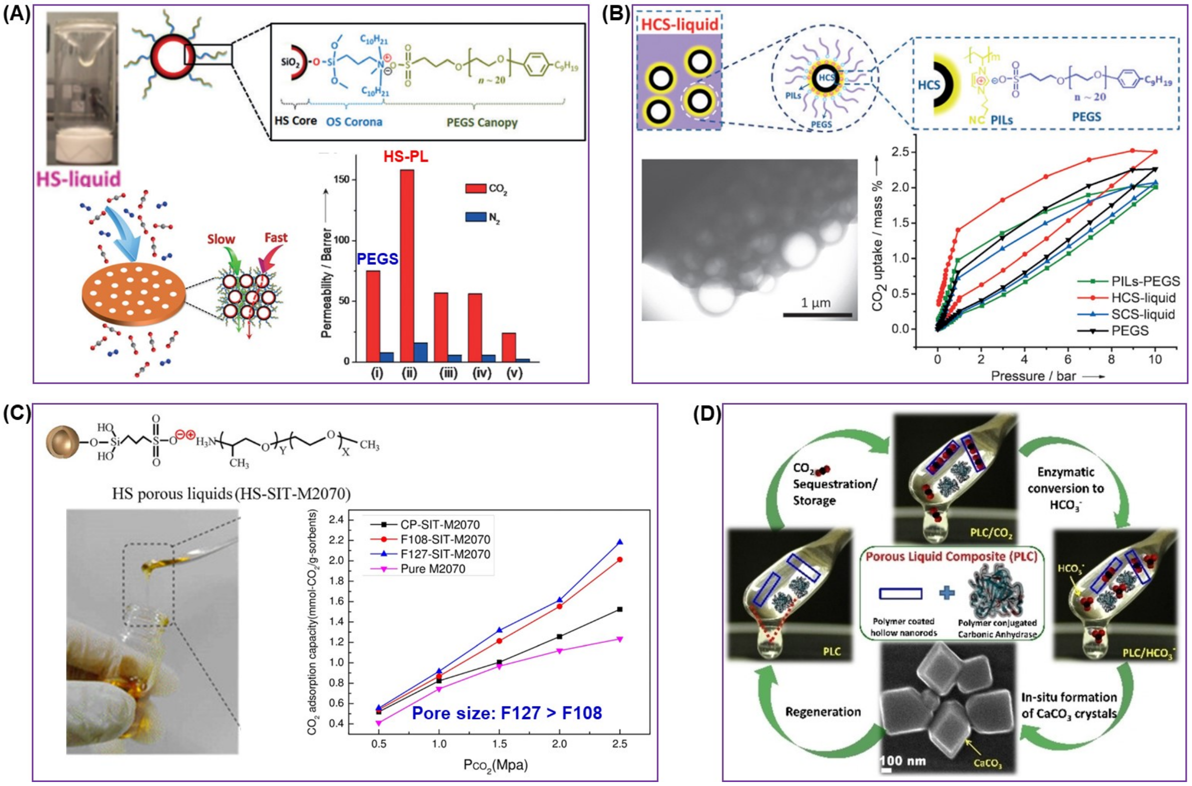

Figure 2 (A) Structures of HS-derived PL and its application in membrane-based CO_2 separation. Reproduced with permission.[11]Copyright 2015, Wiley-VCH. (B) Structures and TEM image of HCS-derived PL, and the CO_2 uptake isotherms at 298 K. Reproduced with permission.[10] Copyright 2017, Wiley-VCH. (C) PLs derived from HS with different pore size and their CO_2 uptake isotherms at 298 K. Reproduced with permission.[13] Copyright 2018, Wiley-VCH. (D) PLs for CO_2 capture and conversion. Reproduced with permission.[12] Copyright 2021, Wiley-VCH.

Type II PLs are composed of rigid and porous hosts being dissolved in selected solvents that are unable to enter the host cavities due to steric prevention [59]. Towards this aspect, Dai et al. created type I and type II PLs composed of anionic covalent cage host and crown ether solvents via the complexation approach in supramolecular systems (Figure 3). Simply combining 18-

crown-6 (18-C-6) with the as-synthesized anionic covalent cage with K^+ as a cation (KACC) resulted in Type I PL (denoted as 18-C-6-PL) including the anionic component of porous organic cages as and the cationic component of 18-crown-6-coordinated potassium ion. While adding excess amount of 15-crown-5 resulted in a Type II PL being formed by dissolving the 15-crown-5 (15-C-5)/KACC complex in excess 15-crown-5 solvent (denoted as 15-C-5-PL). CO_2 uptake behavior evaluation revealed that at 10 bar CO_2 pressure and 298 K, the CO_2 uptake capacity of 18-C-6-PL and 15-C-5-PL achieved 0.429 and 0.375 mmol g^{-1}, respectively, which was much higher compared with the pure crown ether solvent, demonstrating the existence of empty cavities in the PLs derived from the cages [15].

Theoretical study was conducted to provide guidance on the gas separation behavior of PL systems. For example, the Yang group recently investigated the separation behavior of some binary gas mixtures, such as N_2/CO_2 and CH_4/CO_2, using PLs formed by immersing a crown ether-containing cage molecule in 15-crown-5 solvent by molecular dynamics (MD) simulations. The results demonstrated that the adsorption and separation performance of type II PLs possessing a ratio of 1:12 (cage : solvent) was better than that achieved by the counterparts possessing a ratio of 1:91 and 1:170 when being deploying in the separation of CO_2/N_2 or CO_2/CH_4. The study using the spatial distribution function and trajectories indicated that the PLs had CO_2-philic property, resulting in CO_2 being trapped in the channels. While N_2 and CH_4 are, however, rarely absorbed into the bulk phase [16]. MD simulations further demonstrated that large size of the core in cage molecule was preferred for applications aiming to separate CO_2 and N_2. For the CO_2 storage inside a cage, the key step was primarily limited by the multiple CO_2 molecules packing into the core of the cage structure. Comparatively, the difficulty in N_2 storage was primarily caused by the weak interactions between N_2 and the cage host. Therefore, the corresponding cage structure engineering would greatly increase the uptake capacity towards CO_2 molecules [17].

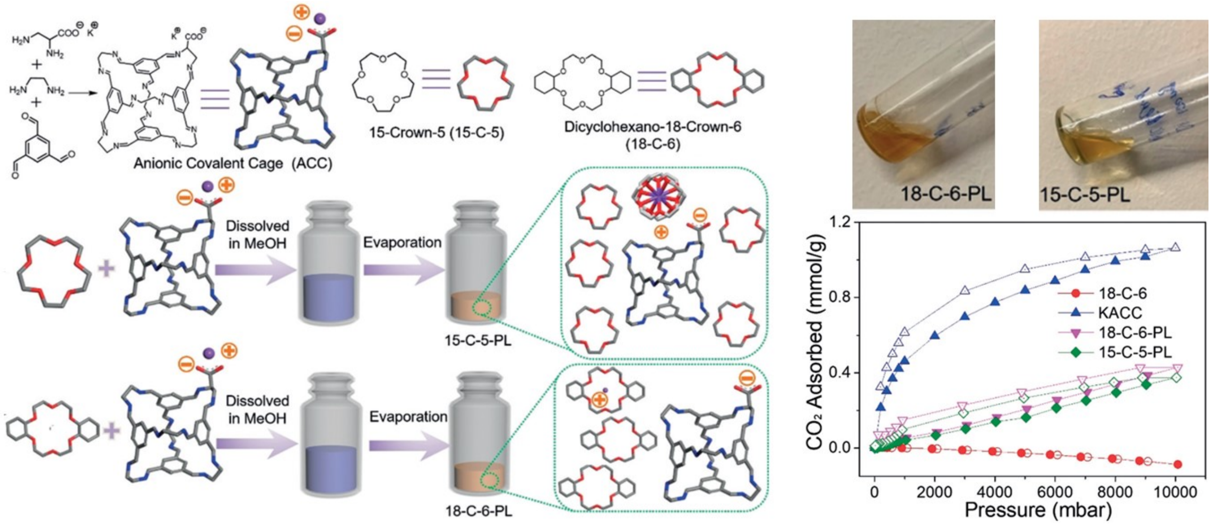

Figure 3 Synthesis of type I and type II PLs via a supramolecular complexation approach and their CO_2 uptake isotherms being collected at 298 K. Reproduced with permission.[15] Copyright 2019, Wiley-VCH.

Microporous frameworks being dispersed in solvents that are able to sterically inhibit their entering into the pores are classified as Type III liquids [59]. MOFs composed of diverse metal cores and coordination ligands and zeolites represent two types of widely used porous host to form PLs by choosing specific liquid fluidity, particularly after surface modification. For example, zeolites could be dispersed in ILs and stabilized by hydrogen bonding formation between the Brønsted sites in H-form zeolites and the alkyl chains in ILs. In addition, the mechanical bond derived from the long alkyl chain of the cation in ILs which could penetrate the channel of zeolite at the interface position could improve the stability. Besides structure and properties of the zeolites, counter anions in the ILs (e.g., NTf_2, BF_4, $CH_3CH_2SO_4$, etc.) could also influence the gas uptake behavior of the as-resulted type III PLs [24].

The large structural tunability in both the porous host and the liquid counterparts provide a large library for the development of type III PLs towards enhanced carbon capture. A straightforward way was to disperse selected MOF (ZIF-8) or zeolite (ZSM-5) featured by a small cage window and large sodalite cage into bulky ILs with a dication structure coupled with the NTf_2 anion (Figure 4A). The existence of permanent porosity in the as-formed PLs was verified by the CO_2 adsorption behavior and positron annihilation lifetime spectroscopy (PALS) measurement. Particularly, at ambient conditions, a substantial hysteresis loop in CO_2 sorption/desorption was observed, highlighting the promise to use these PLs for rationally controlling or gating gas sorption behavior [19]. IL composed of 1,6-bis(3-butylimidazolium-1-yl)hexane cation and bis(trifluoromethylsulfonyl)amide anion was also deployed as the fluidity composition to produce type III PL with ZIF-67 as the porous host, which displayed 55 times the CO_2 uptake capacity compared to the pure IL [22]. Other similar PL types included the combination of alkylphosphonium halides with ZIF-8 [23, 24].

Other solvents are also deployed in PL synthesis, together with the modification of the porous host to achieve long-term stable dispersion. Poly(dimethylsiloxane) (PDMS) was demonstrated as a good bulky solvent in PL synthesis. UiO-66 and those with $-NH_2$ or C-Br bonds in the frameworks with isoreticular structure could be well dispersed and stabilized in PDMS after being coated by a layer of a PDMS-tethered methacrylate polymer. CO_2 sorption demonstrated that PLs derived from UiO-66 or UiO-66-NH_2 exhibited higher CO_2 sorption capacity than a UiO-66-Br_2-derived PL and the PDMS liquid (Figure 4B) [21].

UiO-66 with hydroxyl groups or ZIF-8 with amino groups could act as the porous host to form PLs with flexible oligomer species being synthesized via the reaction of polyether amine (M2070) and organosilane (KH569). The as-formed oligomer could react with the -OH or $-NH_2$ functionalities within the MOF structures to stabilize the dispersion. CO_2 uptake isotherms and the breakthrough test revealed the improved CO_2 sorption and separation behavior of the as-produced PLs compared with the oligomer and the M2070 liquid sorbents (Figure 4C) [3].

UiO-66 containing imidazole functionalities could react with alkyl halides to form imidazolium halide-modified MOFs, which then after anion exchange with PEG-containing sulfonate, generate PLs with abundant cavities (Figure 4D). The as-prepared Im-UiO-PL achieved promising CO_2 uptake capacity, which was 14 times higher than that being obtained by the pure dense liquid counterpart. In addition, the captured CO_2 could be released at elevated temperatures and converted to cyclic carbonates [20]. Surface modification of ZIF-67 particles by basic N-heterocyclic carbenes allowed its stable dispersion in organic solvents with relatively large steric hindrance, such as cycloalkanes and mesitylene. The as-produced PLs performed well in CO_2 adsorption exceeding the uptake capacity obtained by the pure organic solvents (Figure 4E) [18].

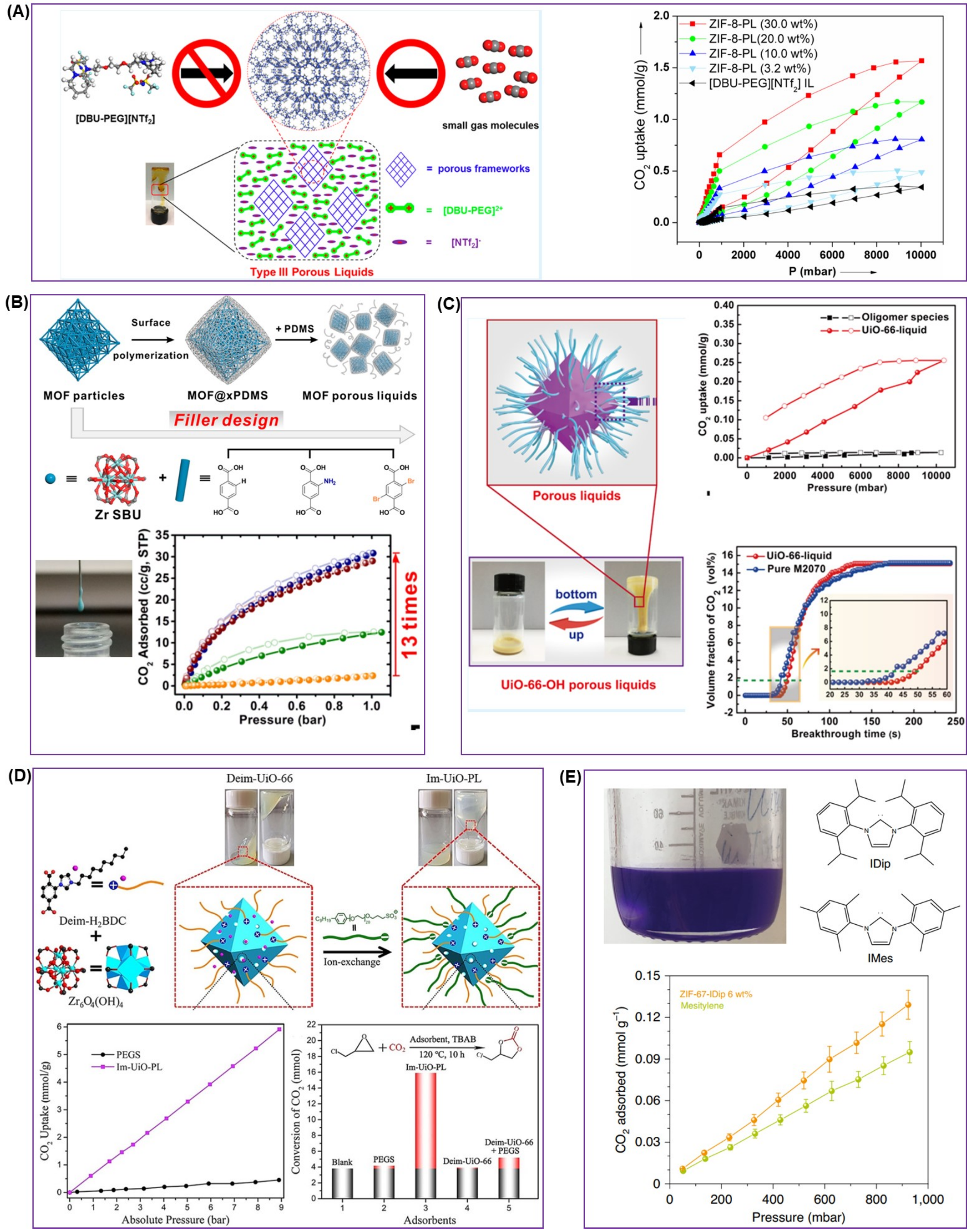

Figure 4 (A) Type III PL formed by dispersing MOFs or zeolites in bulky ionic liquid. Reproduced with permission.[19] Copyright 2018, American Chemical Society. (B) PL formation via the dispersion of surface modified UiO-66 into PDMS and the CO$_2$ sorption isotherms. Reproduced with permission.[21] Copyright 2019, American Chemical Society. (C) PLs composed of hydroxyl

group-modified UiO-66 as porous host and oligomer as the liquid phase. Reproduced with permission.[3] Copyright 2021, American Chemical Society. (D) Imidazolium ionic liquids-modified MOFs as PLs in CO_2 capture and conversion. Reproduced with permission. [20] Copyright 2021, Wiley-VCH. (E) PL formed by dispersing carbene-modified ZIF-67 in mesitylene and its CO_2 uptake isotherms. Reproduced with permission.[18] Copyright 2020, Springer Nature.

In the aspect of diverse porous hosts, a three-dimensional (3D) covalent organic framework (COF) could act as the rigid host with permanent cavity, which after colloidal modification by imidazolium ILs containing aldehyde functionalities and bulk anion (BAr^F), could be well dispersed and stabilized in bulky imidazolium ILs to afford type III PLs. Compared with the pure IL, CO_2 uptake capacity of the COF-derived PL was 10 times higher [25]. An extensive study demonstrated the synthesis of diverse type III PLs using MOFs, zeolites, or porous organic polymers (PAF-1) and the solid host and non-ionic liquids, including silicone oils, triglyceride oils, or PEGs as the liquid compositions. For all the diverse combinations, CO_2 solubility in the PLs all displayed improvement of 3-6 times compared to the liquid component [26]. The ionic liquid polymers being synthesized by neutralization reaction of M2070 with poly(4-styrene sulfonic acid) could act as a good bulky liquid phase to disperse and stabilize HCS for PL production and enhanced CO_2 capture [27].

In summary, diverse PLs (type I, II, and III) have been designed and synthesized that are composed of a rigid porous host (HS, HCS, cages, MOFs, zeolites, COFs, etc.) and a bulky liquid phase (ILs, organosilanes, bulky alkanes, etc.), and the CO_2 sorption/separation behaviors were evaluated by isotherm collection, breakthrough test, or membrane-based separation. Although the above-mentioned progress has been made, in most of the works, CO_2 uptake behavior was deployed as an indicator to show the benefits by introducing extra pore volumes into the liquid phase. Compared with the CO_2 capture investigation using ILs or porous scaffolds, studies on the CO_2 sorption/separation behaviors using PLs are still in the preliminary stage.

Some of the aspects requiring a deep understanding in future studies include: (1) although PLs displaying improved higher CO_2 uptake capacity than the dense liquid phase, they are still inferior compared to the porous host. (2) State-of-the-art fluidity counterparts in PLs synthesis are neutral components, but basic ILs (e.g., amino group-functionalized ILs [60, 61] and superbase-derived ILs [62, 63]) are more preferred in CO_2 capture and conversion. Rigid porous hosts capable of withstanding strong basicity are highly required. (3) Studies on membrane-based CO_2 separation using PLs are still limited. In traditional CO_2 separation using supported IL-based membranes

(SILMs), the gas permeability is the product of solubility and diffusivity [5]. Although diverse task-specific ILs (TSILs) towards CO_2 chemisorption have been developed to deliver much higher CO_2 solubility, the current SILMs were still limited to the physisorption ones, mainly owing to the relatively high viscosity (sluggish diffusivity) of the chemisorption ILs, particularly after CO_2 capture [64]. According to the Cohen-Turnbull equation, the gas diffusivity increases as the empty space increases by providing a fast transport pathway [65]. Therefore, considering the benefits of introducing porous volumes into the dense IL phase in CO_2 transport, PLs will provide a large tuning space to overcome the current limitations of basic TSILs and promote the CO_2 transport in SILMs surpassing the upper bound of the Robeson plot.

Acknowledgements

The research was supported financially by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy.

Authors contributions

N. Mokhtarinori wrote the first draft that was integrated by Z. Yang and S. Dai. All the authors contributed to the final version.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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