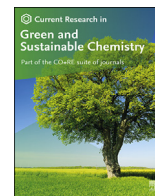


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Porous liquids – Future for CO₂ capture and separation?

Mohd Zamidi Ahmad^{a,*}, Alessio Fuoco^{b,**}

^a Organic Materials Innovation Center (OMIC), Department of Chemistry, University of Manchester, Oxford Road, M13 9PL, United Kingdom

^b Institute on Membrane Technology, National Research Council of Italy (CNR-ITM), via P. Bucci 17/C, Rende, CS, 87036, Italy



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ABSTRACT

Porous liquids form a new class of materials, which are liquid at room temperature and possess permanent porosity. The latter is a characteristic generally associated with solid-state only. Since the idea of porous liquid was exploited over a decade ago, the researchers see an opportunity of solving the solid material's limitation in gas capture and separation. In this discussion, we present the most recent developments on porous liquids and, in our perspectives, how they can tackle energy and environmental issues by their coupling with membrane technology.

In a broader context, the need to reduce greenhouse gas, chlorofluorocarbons and other gaseous emissions is essential for tackling climate change and to achieve the 2015 Paris Agreement goals. In addition, the energy used for chemical separations in industrial processes accounts for 10–15% of the world's energy consumption. Thus, improved separation technologies will reduce energy consumption and the spreading of negative-emission technologies such as carbon capture sequestration and utilization (CCSU). Despite the imperative necessity of CCSU, many candidates are still considered the key technology due to the complex balancing between economic, technical and ecological advantages and drawbacks. Porous materials, which are usually solids, are of great interest for absorption due to the presence of permanent cavities, but liquids are easier to handle at the industrial scale. Porous liquids are a good compromise between these two traditional classes of materials.

1. Introduction

Liquids are generally deemed non-porous fluid, albeit the presence of ill-defined shapes and spaces indeed occur due to the random molecular motion [1]. The introduction of new liquid molecules that exhibits permanent porosity while maintaining their fluidity properties, termed as 'porous liquid' in 2007 [2], changed our perspective on non-porous fluid and subverting the idea that only solid porous materials can be utilized for their size- and shape-selective adsorption and separation [3–5]. Porous liquids (PLs) emphasize their intrinsic porosity and are classified into three categories (Fig. 1) [2,6]; Type 1, neat host liquid that cannot collapse or interpenetrate, Type 2 and Type 3, which are rigid hosts or particles with microporous frameworks dispersed in sterically hindered solvents [2]. The distinctive fundamental difference between a porous liquid and a porous solid is fluidity [7], which opens up various process benefits. For example, a liquid with an appropriate viscosity can be pumped into a continuous system, hence easily implemented or retrofitted into the conventional circulated flow processes [8,9], and not restricted to the solid nature limitations (i.e., low wetting resistance,

limited adsorption capacities and difficulties in their regeneration and reuse [10,11]). In gas separation and capture, a porous liquid takes advantage of its liquid-like matrices (often low M_w polymer, ionic liquids, glycol) as a separation medium and the empty cavities as a gas transport pathway [12].

Type 2 and 3 can be achieved by combining a suitable solvent with porous scaffolds (e.g., porous cages, metal-organic frameworks, MOFs or metal-organic polyhedral, MOPs). The possibility of using porous scaffolds as PLs opens a new horizon for material development [2,13,14]. Contrarily to the network polymers and frameworks, these porous scaffolds are first synthesized and then assembled in a subsequent step in solid-state. This offers the solution-processing options that are not available for insoluble organic and inorganic frameworks and that is essential for scale-up. When synthesizing PLs from porous cages with ionic liquids (ILs) as the solvent, their advantages are synergistically combined, especially the ILs' high ionic conductivity, negligible volatility, and most importantly, its good solvation ability [12].

There are several targets with regards to PL research and development, proposed by Cooper [7]:

* Corresponding author.

** Corresponding author.

E-mail addresses: mohdzamidi.ahmad@manchester.ac.uk (M.Z. Ahmad), a.fuoco@itm.cnr.it (A. Fuoco).

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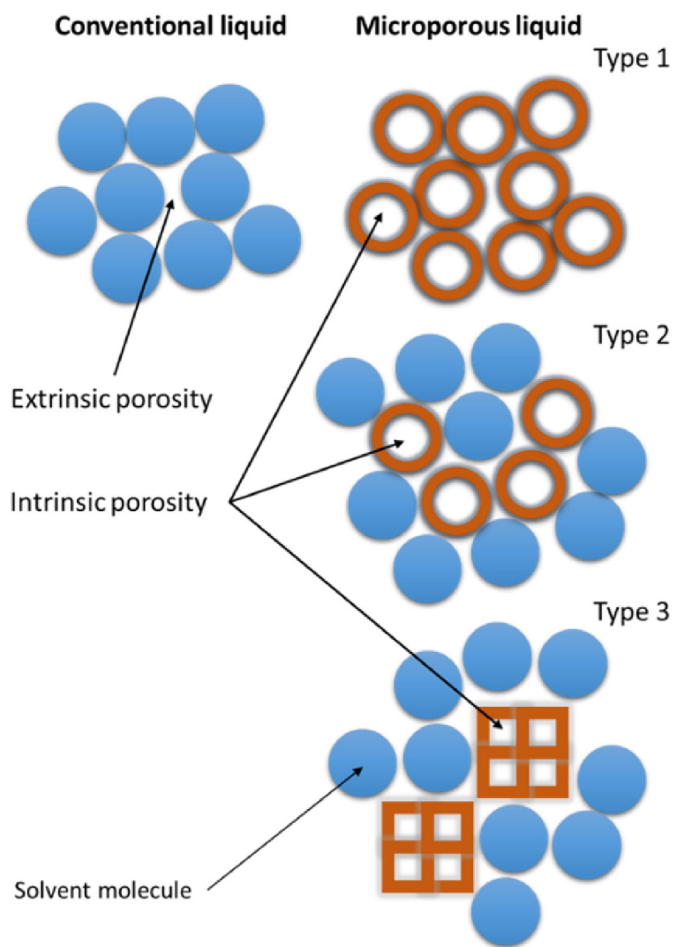


Fig. 1. Molecules representation in a conventional liquid, consisting of only extrinsic porosity (small, irregular, transient cavities) and microporous liquids that possess intrinsic porosity (molecule-sized, regular, permanent empty cavities) within the molecules. Illustration based on ref [2,6].

1. To benchmark the PLs against existing high free volume liquids, such as ionic liquids and polyethers (e.g., Solexol [15]);
2. To create PL with ideally zero volatility, similarly to the ionic liquid;
3. To explore and understand the guest adsorption and release kinetics [7,16] in order to facilitate pressure-swing or temperature-swing adsorption/desorption cycles in low- or zero-volatility porous liquids.

This review discusses the PL synthesis routes reported over the last years and their effectiveness for gas capture application. In the second section, we will also discuss their possible exploitation in membrane-based gas separation technologies, in the form of mixed matrix membranes (MMMs), or membrane contactors.

2. Porous liquid synthesis

2.1. Type 1

Type 1 PL is a neat liquid with intrinsic porosity. The liquid is expected to retain its microporosity if its constituent molecules have an internal cavity, which cannot collapse due to its rigidity, and incapable of intermolecular self-filling [2]. A few organic-based PLs, primarily cyclic molecules such as crown ethers, cyclodextrins, cucurbiturils, possess intrinsic porosity themselves in liquid state. However, they may require an elevated temperature to maintain a certain degree of fluidity.

Several of the Type 1 PLs are ZIF-based (ZIF = zeolitic imidazolate framework). Bennet et al. [17] reported the melting and quenching

below the decomposition temperature (T_d) of crystalline ZIF-4 [$\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$] without any mass loss, yielding a liquid phase melt-quenched glass ZIF-4 with extended Zn-im-Zn (im = imidazolate, $\text{C}_3\text{H}_3\text{N}_2^-$) coordination network. However, the kinetics-time stability of the fleeting liquid phase was not fully understood. Following this report, Gaillac et al. [18] demonstrated the retention of porosity in the liquid state of the molten ZIF-4 by both experimental and computational approaches (Fig. 2). The porosity was found to be larger than that of imidazolium ionic liquids, whose ions are roughly of the same size as the imidazolate anion, with featured void space size distribution typically above 1 Å in radius. Zhou et al. [19] investigated the melting of ZIF-76 [$\text{Zn}(\text{C}_8\text{H}_7\text{N}_2)_2$] with crystal cavities of 5.7 Å and 15.7 Å, and ZIF-76-mbim (mbim = 5-methyl benzimidazole) with crystal cavities of 5.8 Å and 15.6 Å, achieving a liquid with large and reversible porosity between 4 and 8 Å. The molten glass a_g ZIF-76 showed a single cavity at ca. 5 Å, whereas the glass a_g ZIF-76-mbim showed two cavities of 4.8 Å and 7.2 Å. This difference in cavities size and distribution leads to a difference in adsorption properties and while a_g ZIF-76 adsorbs reversibly in excess of 4 wt% CO_2 at 273 K, 1 bar – the a_g ZIF-76-mbim absorbed 7 wt% of CO_2 at the same condition, which is a confirmation of a remnant network of accessible and interconnected pores.

Type 1 PL is also designed based on pure host molecules using solvents or forming a eutectic solution so that the liquid is readily obtained at room temperature. Prof. Dai's group in 2015 introduced PL based on hollow silica spheres as pore generators [20], mono-dispersed in a low molar mass solvent by Stöber method [21], surface-engineered with suitable organic corona (covalently attached) and polymeric canopy (statically attracted) species. The pore generator is produced using a hard template (Fig. 3a), which has to be rigid and stable when the guest molecules are removed [6]. The removal method varies depending on the type of used hard template, e.g., thermal decomposition (calcination), acid dissolution, and solvent extraction. In their study [20], 14 nm diameter hollow silica spheres were synthesized from polymer beads as hard template and then attached to positively charged organosilane with chloride as the counter-ion, followed by anion exchange with poly(ethylene glycol) tailed sulfonate (PEGS) (Fig. 3b). The PL presented CO_2 permeability (P_{CO_2}) of 158 Barrer and CO_2/N_2 selectivity ($\alpha_{\text{CO}_2/\text{N}_2}$) of ~10. Following that, Shi et al. [22] investigated the effect of different nanospheres pore sizes on the PLs CO_2 adsorption capacity. The 9 nm CP hollow spheres (HS), 14 nm F108-HS, and 32 nm F127-HS were functionalized with the 3-(trihydroxysilyl)-1-propane sulfonic acid (SIT) as corona and the cheap industrial reagent polyether amine (M2070) as a canopy. All PLs showed thermal stability of up to about 250 °C, a temperature suitable for the regeneration process. PL with the biggest sphere core (F127-HS) shows the best CO_2 adsorption capacity of 2.2 $\text{mmol}\cdot\text{g}^{-1}$ at 2.5 MPa at 298 K.

Very recently, Liu et al. [23] prepared nanosized silicalite-1 (S-1) zeolite-based PL through the methodology presented in Fig. 3. The S-1 liquid showed CO_2 uptake of 0.474 wt.% (at 1 bar), at least twice the adsorption capacity of PEGS, and the former maintained better performance in the range of investigated pressures, i.e. up to 10 bar. Positron annihilation lifetime spectroscopy (PALS) and intelligent gravimetric analyzer (IGA) support the presence of permanent cavities in these materials. However, the concept was introduced a decade earlier, in 1994, by Cram et al. [24] when porous cages hemicarcerand (Fig. 4a) were synthesized and encapsulated around dimethylacetamide [$(\text{CH}_3)_2\text{NCOCH}_3$], functioned as a guest molecule and dissolved in sterically hindered diphenyl ether. Upon heating the solution at 195 °C for five days, empty pore hemicarcerand spheres were obtained. Much later, Dutasta et al. [25] reported cryptophane-111 (Fig. 4b), which is able to encapsulate small gas molecules (CH_4 , C_2H_6 , C_2H_4) in CDCl_3 as the solvent, and showed high affinity towards CH_4 . Rauffuss et al. [13] reported an inorganic 'molecular cage' Co_4Ru_4 , [$\{\text{Cp}(\text{Co}(\text{CN})_3\}^{15}_4$ (Cp^*Ru_4) (Fig. 4c), which can be crystallized in acetonitrile and the solvent remained outside of the cage cavities. Unfortunately, no adsorption isotherms were reported on these materials as direct evidence

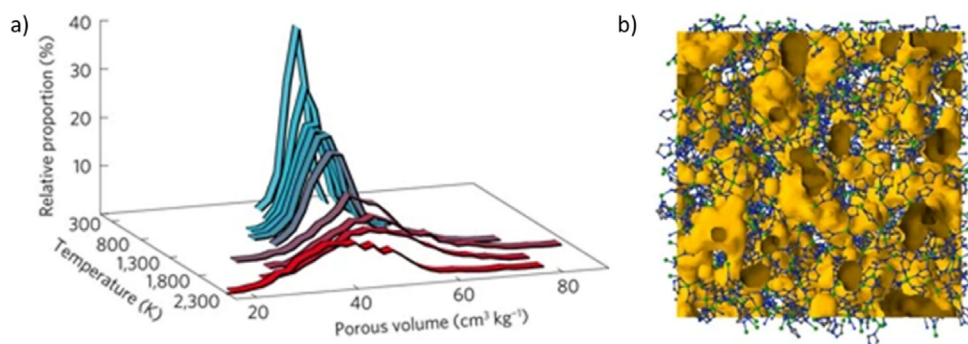


Fig. 2. (a) Total pore volume distribution against its melting temperature evolution, (b) atomic configuration of the melt ZIF-4 obtained from a reverse Monte Carlo modelling. Free volume is presented in orange. Figures obtained and rearranged with permission [18].

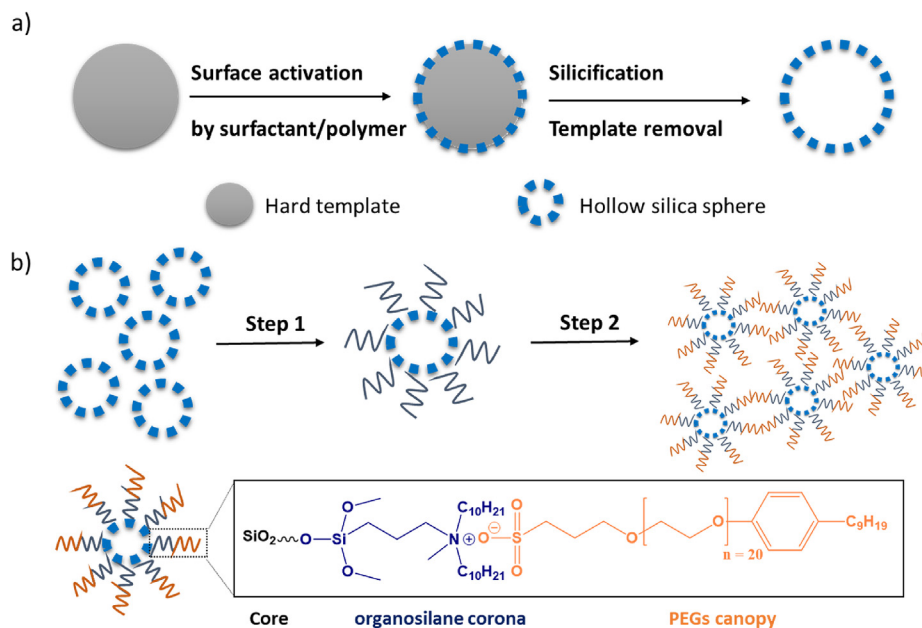


Fig. 3. (a) The preparation of hollow silica spheres from a hard template, (b) two-step PL synthesis procedure. Step 1; organosilane (positively charged) attachment to silica sphere surfaces act as the corona, and Step 2; anion exchange with poly(ethylene glycol) tailed sulfonate (PEGs), act as polymer canopy, a fluid medium. Figure adapted and reproduced with permission [20].

of the presence of intrinsic porosity.

A series of studies were reported on the rigid iminospherand cage, a molecule obtained from imine condensation between four 1,3,5-trifor-mylbenzene and six diamines, alkylated with various different chain length groups [26]. The study reported the first organic cages with measurable melting point (mp), and the medium-length alkyl tails effectively lowered the rigid iminospherand host's mp, presumed to be non-porous in the liquid state. In a continuation study [27], the same group emphasized that *n*-C₅ alkyl substituted caged forms a liquid with 30% empty cages at all times, according to molecular dynamic (MD) simulations. Not only that, the *n*-C₅ substituted cage's melting point (mp = 158 °C) was reduced very significantly when substituted with *n*-C₁₂ (mp = 40 °C). It is also concluded that long unbranched alkyl chains could rapidly enter the cavities and subsequently remove their porosity. However, terminally branched alkyl slowed down the inclusion rate, neo-C14 substituted iminospherand has almost 100% empty cages, i.e., porous in the liquid state, for the long simulation (100 ns) duration.

Type 1 PLs synthesis often leads to low yield and considering the harsh production conditions, they are not very industrially attractive [20]. For this reason, Type 2 and Type 3 porous liquids are generally favoured due to their lower environmental risk and relatively cheaper

starting materials. These two types of PLs are both based on the concept of porosity addition to a given liquid by using a porous scaffold and, consequently, increases the liquid's separation capacity. Type 2 molecular hosts are dissolved in size-excluded solvents, whereas Type 3 the porous scaffolds are only dispersed in solvents, where the solvent molecules are too bulky to enter in the host cavities [28].

2.2. Type 2

In 2015, James' group further investigated the same rigid iminospherand cage functionalized with six crown ether groups and dissolved it in a high concentration 15-crown-5 solvent, which is too big to enter its pore cavities [29] as PL Type 2. During the cage synthesis, a mixture of diamines was used and referred to as 'scrambled cages'. The scrambled cages formed a concentrated (>10 wt%) porous liquid in the bulky solvent hexachloropropene (PCP). Both MD and PALS analyses confirmed the presence of empty pores, i.e. intrinsic porosity, within the liquid. They presented a high CH₄ solubility at all studied temperatures, with an 8-fold increase compared to other molecular solutions with cavities [24, 25,30]. The storage capacity in these materials is in the order of CH₄ > CO₂ > N₂, which does not correlate to the gas kinetic sizes, meaning that

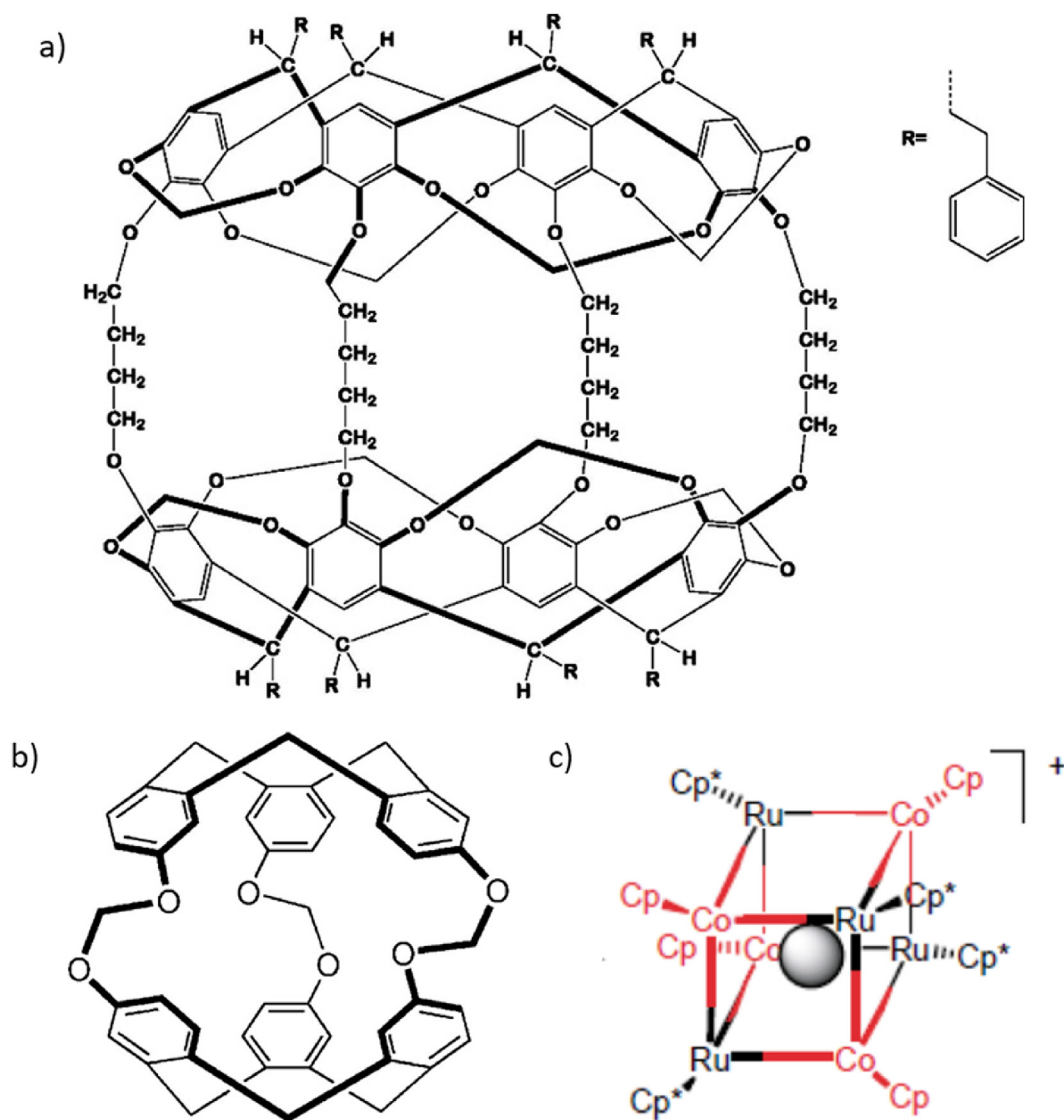


Fig. 4. The structure of (a) hemicarcerand molecule, (b) cryptophane-111, (c) inorganic 'molecular box' $[\{Cp(Co(CN)_3)_4(Cp^*Ru)_4\}^+]$ (Co_4Ru_4), filled with guest molecule. $\bullet = N_2H_5^+$, $MeNH_3^+$, NH_4^+ , Cs^+ , K^+ , Rb^+ , Tl^+ ; $\color{red}\text{---} = -CN$. Images reproduced with permission [6,13,25].

the storage capacity is governed by specific intermolecular interactions between the cage and the size/shape of the gas molecule. This scrambling strategy was introduced earlier by the same group [31], using porous organic cages (POCs) in PCP and became the basis of many following PL Type 2 studies. In this study, the mixture of different cage vertex functionalities (cage 1 and cage 3, Fig. 5a) produces a scrambled distribution of molecules that pack inefficiently. The amorphous scrambled also showed a substantial nitrogen sorption increase with a predominantly microporous BET surface area of $522\text{--}704\text{ m}^2\cdot\text{g}^{-1}$ (Fig. 5b) and improved H_2/N_2 selectivity (Fig. 5c). Their molecular simulations for the amorphous solids suggest that the porosity results from voids running both through and between the cage molecules (Fig. 5d–e).

To fully understand the structure/properties relationship, Zhang et al. [32] recently studied the thermodynamics and kinetics of gas storage in crown-ether cage porous liquids by using molecular simulations. Instead, Greenaway et al. [16] aimed to know better the role of the vertex disordered porous liquids. They started with the initial design strategy and extended to an in-depth study of the most porous liquid's physical properties. They concluded that porous organic cages' solubility could be increased by using a dynamic covalent scrambling strategy.

As mentioned, the basis of Type 2 PLs was POCs with crown-ether functionality; however, the resulting liquids are viscous and difficult to scale-up due to the difficult six-step synthesis [33]. While realizing the need to expedite the precursors screening process and to find non-chlorinated replacements for PCP (toxic and limited commercial availability), from the same group, Kearsy et al. [33] developed a high-throughput scramble cage library, consisting of three-component scrambled cage mixtures. They obtained 44 combinations (out of 61 possible mixtures) that gave sufficient scrambled cages conversion (solubility of $\geq 0.2\text{ g}$ and $\geq 80\%$ purity). Based on their previous success of $3^3:13^3$ PL in PCP (solubility of $200\text{ mg}\cdot\text{ml}^{-1}$) [31], five bulky solvents such as 2-hydroxyacetophenone (HAP) and 4-(trifluoromethoxy)benzyl alcohol (TBA) were determined to improve for $3^3:13^3$ solubility by $\sim 50\%$ ($\geq 300\text{ mg}\cdot\text{ml}^{-1}$). Upon setting a few other requirements (i.e., scramble cage's solubility of $\geq 300\text{ mg}\cdot\text{ml}^{-1}$, synthesis purity of $\geq 95\%$ without gel formation), only 29 PLs were tested for gas uptake measurement. Even though the gas uptakes vary depending on the solvent, the PLs showed a substantial adsorption increase compared to the parent solvent (example in Fig. 6). Upon component system modification (e.g., changing solvent system, cage component, and cage concentration), several scrambled

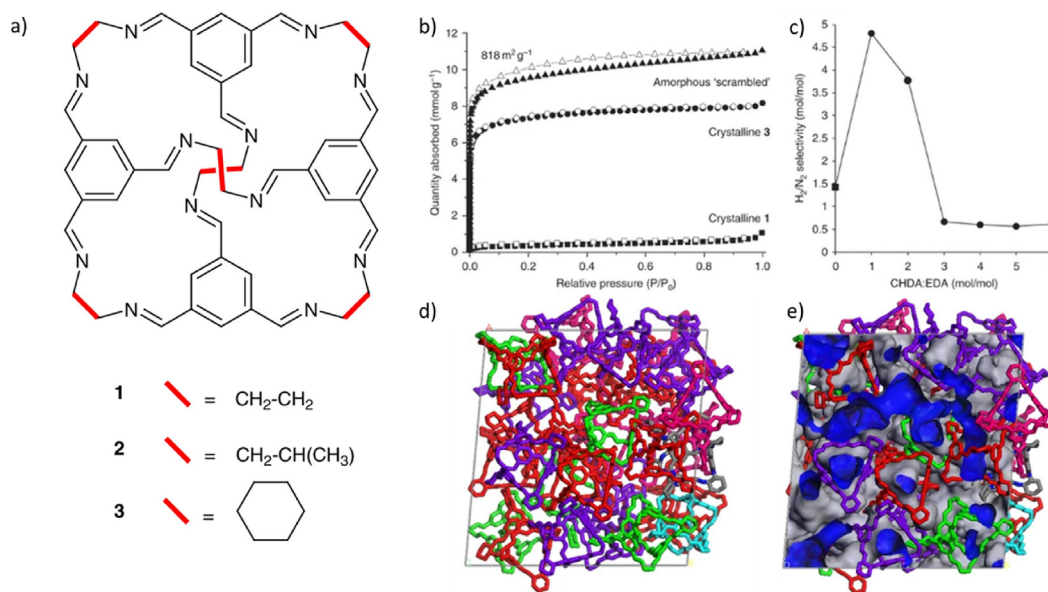


Fig. 5. (a) Chemical structures of imine-linked cages; (b) Nitrogen adsorption isotherms (filled symbols) and desorption isotherms (open symbols) for crystalline cages 1 and 3 and an amorphous sample; (c) H₂/N₂ selectivity of the amorphous cage mixtures compared with single-component crystalline analogues; (d) atomistic simulation for the amorphous, represent the molecular distribution; and (e) the as Connolly surface analysis, suggesting around 80% void volume generated by cavities between the cages, rather than the internal cage volume itself. The images were obtained, rearranged, and reproduced with permission [31].

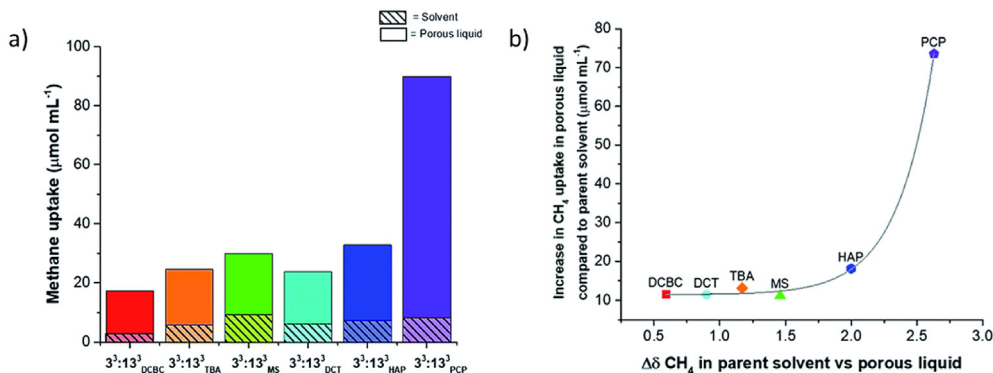


Fig. 6. Methane uptake in neat solvents and 3³:13³ porous liquids (20% w/v); (b) the difference in methane uptakes, plotted with respect to the neat solvent. The image is reproduced with permission [33].

systems showed very promising properties, such as the 27 wt% 3³:13³ in HAP, which presented a 93% increase in Xe solubility.

2.3. Type 3

As for Type 3 PLs development, the use of MOFs as porous hosts seems to be an accurate approach since the materials have already fascinated us for their limitless metal-ligand combinations [34], creating various 3D-MOFs with specific porosity to cater to specific interests in gas separation [35–40]. In CO₂ capture and separation, numerous MOFs show exceptional high CO₂ uptakes at high pressure [41–44], unfortunately giving low and meaningless adsorption at low CO₂ pressure (i.e., at 0.15 bar, common CO₂ concentration in the post-combustion flue gas).

In fact, ZIF-8 [Zn(C₄H₅N₂)₂], one of the most studied imidazolate-based MOFs for gas capture, was also the first explored for potential exploitation as a porous liquid. Unlike the previously discussed ZIFs, ZIF-8 cannot be melted as type 1 PL without it decomposes [18]. Thus, the attention naturally shifted into making it a type 3 PL. ZIF-8 nanoparticles were suspended in glycol and glycol-2-methylimidazolate, and the latter showed excellent selectivities for several gas pairs, e.g., CO₂/H₂ = 951, CO₂/N₂ = 394, and CO₂/CH₄ = 114 [45]. The high CO₂ adsorption is

mainly contributed by its high solubility in glycol and glycol-2-methylimidazolate. The ZIF-8-based PL can efficiently remove CO₂ from gas mixtures at normal pressure/temperature, and most importantly, the sorption enthalpy is only -29 kJ·mol⁻¹, indicating the low energy required for sorbent regeneration. The work encouraged others to disperse ZIF-8 in two ionic liquids: the 1,8-diazabicyclo(5.4.0) undec-7-ene DBU-based, [DBU-PEG][NTf₂] [46] and the *n*-butyl pyridinium bis-(trifluoromethyl sulfonyl) imide, [Bpy][NTf₂] [47]. In the first study, the incorporation of permanent porosity was confirmed by the in-situ pore-/void-volume characterization PALS analysis. The ZIF-8 (30%)/[DBU-PEG][NTf₂] also presented 4.7 times CO₂ adsorption capacity compared to the pure [DBU-PEG][NTf₂] at 10 bar and 298 K (Table 1) [46]. In the second study, pre-aggregation of ZIF-8 was avoided by using wet ZIF-8 nanoparticles in methanol, which formed a very stable colloidal solution, up to 7 months, when dispersed in the IL. The preservation of the porosity was proven by I₂ adsorption and release experiment, and accordingly to their lifetime parameters [47]. However, the adsorption analysis did not show a significant difference in CO₂ uptake between the pure IL and 20 mg·mL⁻¹ ZIF-8-[Bpy][NTf₂] colloid. Costa-Gomes et al. [48] further investigated ZIF-8 with other well-known MOFs, Mg-MOF-74 [Mg₂(-DOBDC)] and HKUST-1, dispersed in a

Table 1

The physicochemical properties of Type 3 PLs compared to their pristine materials' properties.

No	Material composition	Type	CO ₂ adsorption [cm ³ (STP)·g ⁻¹]	Ref.
1	ZIF-8 (30%)/[DBU-PEG][NTf ₂]	III	34.54 ^a	[46]
	[DBU-PEG][NTf ₂]	Solvent	7.31 ^a	
2	ZIF-8	MOF	132.84 ^a	[49]
	6 wt.% ZIF-67-IDip@mesitylene	III	2.89	
	Mesitylene	Solvent	2.13	
3	ZIF-67-IDip	MOF	33.1	[28]
	12.5 wt.% PAF-1@Genosorb®	III	16.13	
	Genosorb® 1753	Solvent	5.15	
	PAF-1	PAF	93.41	
	12.5 wt.% Al(fum)(OH)@PDMS 50 cst	III	8.06	
	PDMS 50 cst	Solvent	2.64	
	Al(fum)(OH)	MOF	48.61	
	12.5 wt.% ZIF-8@PDMS 50 cst	III	4.93	
	ZIF-8	MOF	18.82	
	12.5 wt.% Zeolite 5A@PDMS 50 cst	III	4.93	
Zeolite 5A	Zeolite	24.42		

n.p. = not presented.

^a Adsorption at 10 bar.

phosphonium based ionic liquid, trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) imide, [P_{6,6,6,14}][NTf₂]. MD simulations were performed to gain further insight into the suspension structures, and suspension free volumes were quantified by computing volumes and

surfaces of Voronoï polyhedral around individual atomic types.

Very recently, Knebel et al. [49] explored ZIF-67-based PLs. ZIF-67 is cobalt-substituted ZIF-8, which retains ZIF-8 tetrahedral SOD topology but with stiffer Co–N bonds than ZIF-8's Zn–N, which contributes to ZIF-67's slightly smaller effective pore apertures [50]. The outer surfaces of ZIF-67 were modified two different *n*-heterocyclic carbenes; 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene (IMes) and 1,3-bis(2,4,6-diisopropylphenyl)imidazole-2-ylidene (IDip). The IDip and IMes adsorption after removing an imidazole linker on the ZIF-67 surfaces are presented in Fig. 7. The modification successfully produced very stable dispersions of the relatively large ZIF-67 nanoparticles (264 ± 54 nm) when using comparatively large solvent molecules such as cyclohexane, cyclooctane, and 1,3,5-trimethylbenzene (mesitylene). The ZIF-67-IDip (1–6 wt.% loadings) in mesitylene showed a clear trend of a non-Newtonian behaviour liquid, with strongly increasing viscosity at low shear rates. In their methane and propylene break-through adsorption experiment using an in-house 'liquid sorbent bed', the PL (6 wt.% ZIF-67-IDip@mesitylene) showed longer retention time for propylene (8.4 min after methane) compared to the blank mesitylene (2.5 min after methane). The PL also showed a significant increase of CO₂ adsorption capacity (Table 1), higher than the mesitylene blank. The additional adsorption capacity in the PL is undoubtedly contributed by the high CO₂ adsorption capacity of pristine ZIF-67-IDip.

Another study demonstrated supramolecular polymerization of dirhodium paddlewheel based cuboctahedral metal-organic polyhedral (Rh-based MOP) using ditopic imidazolite bix (1,4-bis(imidazol-1-ylmethyl)benzene) linkers to form amorphous with permanent hierarchical porosity [51]. The polymerization was conducted stepwise and monitored through electronic absorption spectroscopy and dynamic light scattering (DLS) experiments (Fig. 8a). The authors produced size

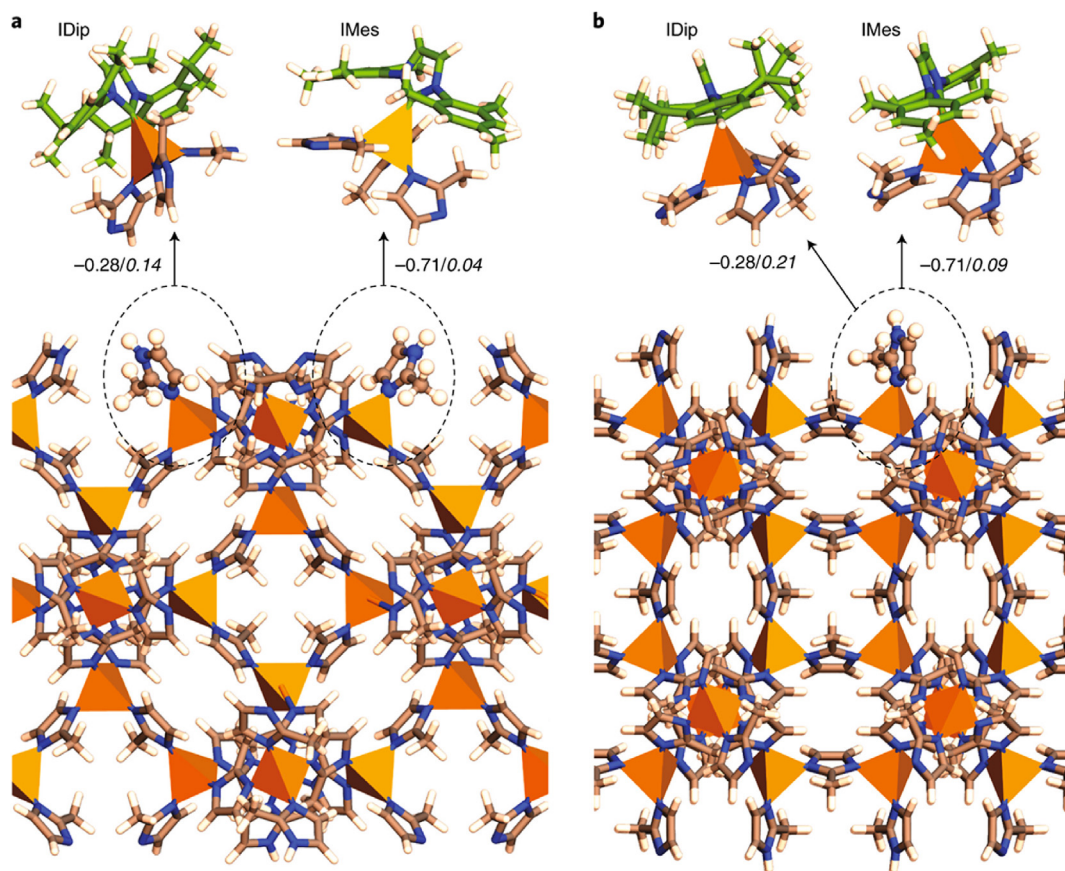


Fig. 7. IDip and IMes adsorption after removing an imidazole linker on the metal site of the ZIF-67 surfaces, from the slab geometry direction of (a) (100) and (b) (110). Atoms presentation, carbon atoms within MOFs = brown, carbon atoms within carbenes = green, nitrogen = blue, hydrogen = off-white and tetrahedral cobalt = orange. Imaged reproduced with permission [49].

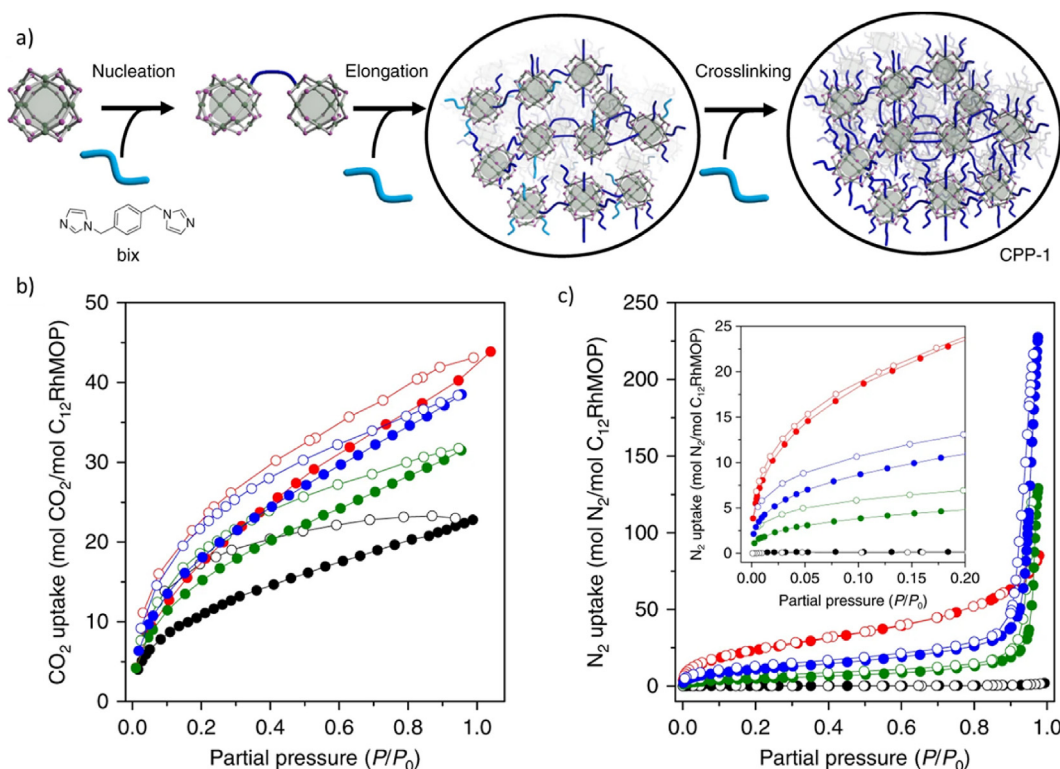


Fig. 8. (a) Schematic illustration of the stepwise polymerization of $C_{12}RhMOP$ with bix to yield CPP-1, which entails initial nucleation, followed by elongation in excess bix, and finally cross-linking. Dark blue bix represents the coordination of both imidazole rings, (b) CO_2 adsorption isotherm at 195 K, and (c) N_2 adsorption isotherm at 77 K of SAG-1 (red), CPP-1_small (blue), CPP-1_big (green), and $C_{12}RhMOP$ (black). Images reproduced with permission [51].

controllable spherical particles and three-dimensional interconnected colloidal by controlling the synthesis self-assembly pathway. The materials also showed high CO_2 and N_2 adsorption properties that increases with its internal microporosity contents (Fig. 8b–c), outperforming the porous monomer $C_{12}RhMOP$.

Cahir et al. [28] screened the dispersion of a number of microporous solids (MOFs, zeolites, PAF-1) in a diverse of chemically inert and thermally stable non-ionic liquid phases (silicone oils, polyethylene glycols, and natural triglyceride oils) that are sterically excluded from the pores of the solid. The produced materials were characterized accordingly, including gas solubility measurement, CO_2 uptake kinetic and PALS measurement. Several of the obtained PLs are presented in Table 1 for our discussion. To demonstrate the potential in a cyclic gas separation, where the ease of regeneration process is essential, two PLs (12.5 wt.% HKUST-1@PDMS, CO_2 uptake of $10.79 \text{ cm}^3 (\text{STP}) \cdot \text{g}^{-1}$, and 12.5 wt.% Al(fum)(OH)@PDMS, CO_2 uptake of $8.40 \text{ cm}^3 (\text{STP}) \cdot \text{g}^{-1}$) were subjected to regeneration test. The materials showed $\geq 75\%$ recovery in CO_2 uptake capacities only after 2 h of vacuum, whereas the conventional amine-based solution (12.5 wt.% MEA@H₂O) only showed $\sim 5\%$ recovery ($44.84 \text{ cm}^3 (\text{STP}) \cdot \text{g}^{-1}$ to $2.28 \text{ cm}^3 (\text{STP}) \cdot \text{g}^{-1}$ of CO_2 uptake only). These findings exhibit the possibility of an easy and low energy *in-situ* regeneration process for the PLs and definitely resolves one of the major drawbacks of amine-based CO_2 scrubbing technology that requires a large energy cost for regeneration. The authors also state that the temperature-based regeneration process (typically $<100 \text{ }^\circ\text{C}$) will not pose a problem since the solvents have high smoke points of $\geq 140\text{--}310 \text{ }^\circ\text{C}$. The authors further examined the physicochemical stability of the selected 12 wt.% Al(fum)(OH)@PDMS compared with dimethylether polyethylene glycol, a solvent better known by its commercial name, Genosorb® 1753 and used in natural gas sweetening. The PL not only has greater CO_2 capacity at low pressure ($8.74 \text{ cm}^3 (\text{STP}) \cdot \text{g}^{-1}$ vs. $2.69 \text{ cm}^3 (\text{STP}) \cdot \text{g}^{-1}$) but also a greater working capacity than Genosorb® 1753 ($18.37 \text{ cm}^3 (\text{STP}) \cdot \text{g}^{-1}$ vs. $14.11 \text{ cm}^3 (\text{STP}) \cdot \text{g}^{-1}$) under these simulated

temperature and pressure swing conditions (i.e., when operating between 348 K, 5 bar and 298 K, 1 bar).

The key issues that one should carefully consider when making Type 2 and Type 3 PLs are: (1) selection of suitable sterically hindered solvents to prevent possible pore penetration, which causes the PL to lose its permanent porosity, instantaneously or over time [6]; (2) to obtain a high synthesis yield [6]; and (3) to have cages with high solubility in a bulky solvent [16], which is challenging to achieve since porous scaffolds usually have modest solubilities [6,14]. Additionally, possible agglomeration and sedimentation issues arising from the solvent's inability to retain the particulates in the liquid phase should be considered. However, this limitation can be tackled by surface functionalization of the porous scaffolds.

3. PLs outlooks in CO_2 capture and gas separation

There are not many research papers on the use of PLs in gas separation. For instance, a search on Scopus using the combination keywords of “porous liquids” and “gas separation” gives 122 document results, of which many in 2020, and only one appears with “gas scrubbing” (Fig. 9). This can be highly misleading on the potential uses of this new class of materials in the CO_2 capture. Instead, their potential is confirmed by launching a spinout joint venture company between The University of Liverpool and Queen's University Belfast, called ‘Porous Liquid Technologies Ltd’ in 2018.

The strength of PLs relies on their capability to combine the separation performances of solid porous materials, but presented in the liquid phase, which is a typical trait and selling point for the use of amine solutions in the traditional industrial settings for CO_2 removal. CO_2 capture by amine solution is a well-established technology, which has its pillars back to 1930 [52], and many technological solutions could be easily transferred to systems using PLs. This means that the PLs can be easily retrofitted into the existing industrial plants without the need for

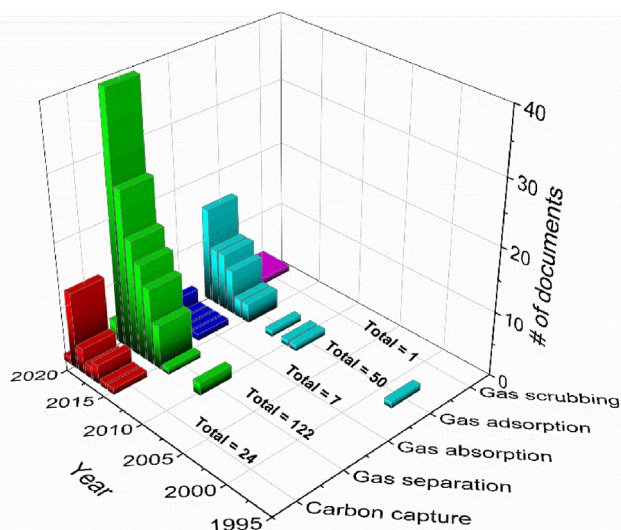


Fig. 9. Number of documents found on Scopus Search using keywords 'porous liquids' and carbon capture, gas separation, gas adsorption, gas adsorption, and gas scrubbing in all fields on 11/01/2021.

extensive and expensive setting updates. Moreover, the presence of permanent porosity in PLs will help in the transition from absorption to the adsorption process. In fact, one of the main drawbacks of the amine solution usage, similarly to ionic liquid usage, another novel class material and a candidate in the absorption process, is the high energy required for their regeneration. The process requires high temperature stripping gas, e.g., water vapour at 100–120 °C [53]. The transition to adsorption processes will drastically decrease the energy required for their regeneration [4,54]. This is an essential step to tackle the Paris agreement objectives after COP 21. For instance, energy usage in the separation process is about half of the overall energy used in the US industrial sector [55].

3.1. Their perspectives in membrane separation technology

We foresee that coupling PLs with membrane technology will boost their exploitation in gas separation. Membrane technology is well established in several fields such as nitrogen production or hydrogen recovery [56], and at the same time is emerging in other applications such as biogas upgrading [57] or carbon capture [58,59]. Its large and quick widespread is especially due to the advantages from a thermodynamic perspective [60], which decreases the energetic consumption of membrane-related processes, making them very attractive for economic and ecological reasons. PLs can make an outbreak in the membrane field in two ways: as a filler in the preparation of mixed matrix membranes or as a liquid phase in gas/liquid membrane contactors.

3.1.1. Mixed matrix membranes (MMMs)

A mixed matrix membrane (MMM) is a membrane composed of an insoluble filler dispersed into a polymeric matrix to benefit from the polymer material processability and the filler's enhanced separation performance [61–64]. Several porous materials (e.g., COFs, MOFs, PAFs) have been used in the last decades for their preparation, but the performances were below their true potentials due to the poor compatibility between rigid fillers and polymer matrixes [65,66] and often manageable at low particle loadings due to difficulties in maintaining the membranes' physical integrity (mechanical stability and brittleness) [67]. Nonetheless, the PLs can overcome these issues, associated with the advantages of their liquid nature and intrinsic microporosity, as readily observed in the fast booming of ionic liquid-based MMMs in the last decade [68].

Knebel et al. [49] demonstrated the advantages by fabricating 20–50 wt.% loading MMMs with ZIF-67-IDip in 6FDA-DAM and

6FDA-DHTM-Durene (2:8). The very high loadings were achieved due to the stable dispersion of ZIF-67-IDip that prevents the particle agglomeration in the processing stage, which often leads to detrimental effects. The ZIF-67-IDip based membrane shows much better adhesion and filler dispersion (Fig. 10a–b for 6FDA-DAM MMMs and Fig. 10d–e for 6FDA-DHTM-Durene MMMs). The observation was also confirmed by focused ion beam SEM analysis (see their Supplementary Video 1). In terms of gas separation, the authors presented higher propylene/propane selectivity (Fig. 10c and 10f) in MMMs with ZIF-67-IDip@mesitylene PL with respect to the pure polymer. It was concluded that the increase in selectivity is due to the substantial increase in propylene adsorption (thanks to the propylene preferential adsorption of ZIF-67-IDip@mesitylene PL) whereas the propane adsorption in the MMMs was comparable to that of the pure polymer. The final propylene permeability ($P_{C_3H_6}$) in PL MMMs was improved substantially, from the pristine 6FDA-DAM ($P_{C_3H_6} = 23.1$ Barrer) to 6FDA-DAM/ZIF-67, 34.5 wt.% ($P_{C_3H_6} = 46.3$ Barrer) to 6FDA-DAM/ZIF-67-IDip@mesitylene, 47.5 wt.% ($P_{C_3H_6} = 104.8$ Barrer).

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.crgsc.2021.100070>

To the best of our knowledge, the above-discussed paper is currently the only article on MMMs using a PL and it perfectly highlights the PLs potential in the membrane field. Additionally, we were already aware of the successful use of ionic liquid to reduce the non-selective interfacial defects between ZIF-67 and a polymer matrix [69]. For instance, PIM-1/UiO-66 MMMs show very interesting CO₂ properties [70,71] but also diffused interfacial defects [71], which can be overcome by the use of the recently synthesized porous liquid UiO-66-liquid [72], leading to a better performing membrane. This is only an example of the plethora of possible combinations between polymers and PLs, as demonstrated by the huge number of MMM investigations [3,56,61,73], and due to the very rich chemistry of PLs [74], which is similar to that of solid microporous materials [75–77].

3.1.2. Membrane contactors

Membrane contactor technology is the natural merger between scrubbing-like and membrane technologies. In this configuration, the two phases are partitioned by a membrane, which increases the contact area. Very recently, membrane contactors have been tested at a pilot plant scale for CO₂ capture from flue gas [78,79], showing that an increase in desorption efficiency would enhance this process's economic feasibility. This issue can be overcome in PLs with negligible vapour pressure, such as the liquid coordination cage proposed by Ma et al. [80], which was obtained by incorporating poly(ethylene glycol) (PEG)-imidazolium chains into a Zn-based tetrahedron. The negligible vapour pressure allows recycling the PLs using low vacuum pressure in the desorption chamber, simultaneously decreasing the energy consumption. Moreover, the proposed PL [80] also showed a higher affinity towards several alcohols such as *t*-butanol, *i*-butanol, and *i*-propanol with respect to their isomers *n*-propanol or *s*-butanol, which are the separation target in the industry. In addition, this novel coordinated cages-based PL can also capture chlorofluorocarbons, one of the major responsible for ozone depletion, and thus the climate change. The PL also has the potential to separate the molecules with a similar chemical structure to chlorofluorocarbons, which possess similar environmental threats, normally present in volatile anaesthetics for medical and surgical procedures [81]. Even though it is a completely unexplored field for the PLs, we forecast that the novel materials will also help in their recovery from the exhaled gas circuit of the anaesthesia machines or via lowering of CO₂ content in closed-loop anaesthesia circuits [82].

One of the major challenges in membrane contactors is the liquid intrusion into the membrane structure [83], which decreases the effective separation properties. The high modulability of the PLs' molecular shape will be a solution to this issue. The modulability also allows the users to tune the PL viscosity to allow a correct fluid dynamic in the apparatus, as demonstrated in a zeolite-based PL by Li et al. [84] and in a

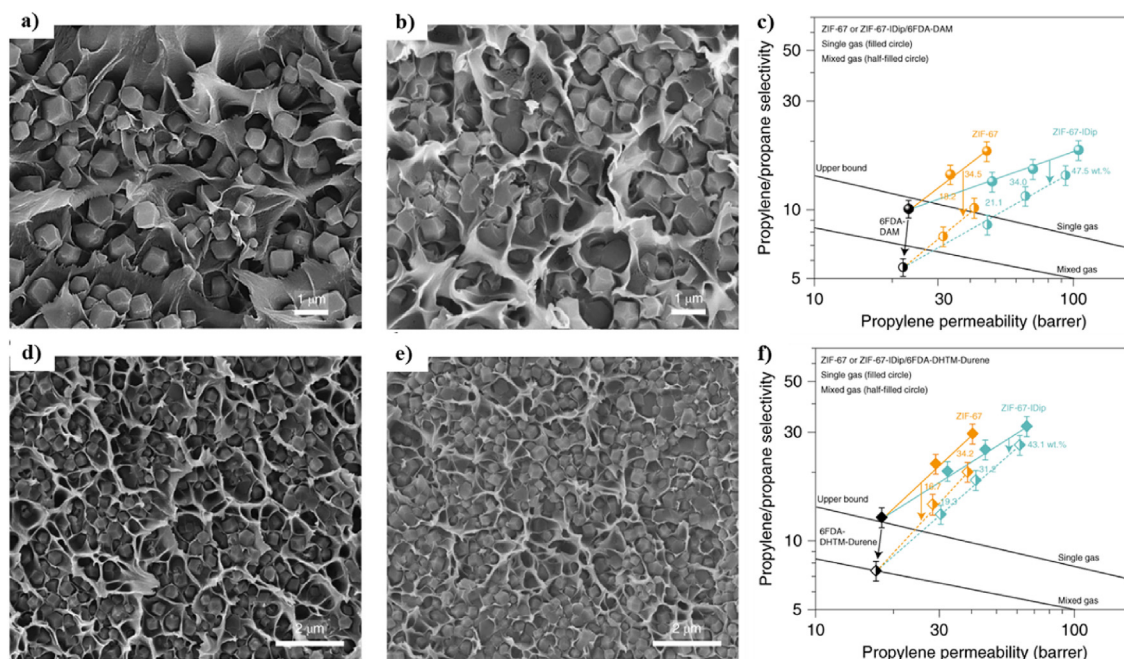


Fig. 10. Cross-sectional SEM images of 6FDA-DAM MMMs with (a) 34.5 wt.% ZIF-67 (b) 47.5 wt.% ZIF-67-IDip and (c) their single- and mixed-gas propylene/propane selectivity versus propylene permeability. Similar presentations for 6FDA-DHTM-Durene (a) 34.2 wt.% ZIF-67, (b) 47.5 wt.% ZIF-67-IDip and (c) their single- and mixed-gas propylene/propane selectivity versus propylene permeability. Image reproduced with permission [49].

porous organic cages-based PL by Egleston et al. [85]. The latter has also shown that the presence of methyl groups close to the cavity entrance, and the change from the solid to the liquid that suppresses the presence of extrinsic intermolecular pores, have a strong effect on Xe uptake, opening for instance, new routes in radioisotopes separations [86,87].

4. Conclusions

In conclusion, we can state that there is plenty of room in the empty cavities of the porous liquids. We forecast that novel functionalities and processes will fill it for energy and environmental solutions in the near future. The solution processability of the PLs will boost the exploitation of MMMs as a good compromise between pure polymeric and ceramic or solid crystalline membranes. Moreover, their cavities and functionalities will also be investigated as membrane contactors and reactors since they can be used both in the form of adsorbent liquid or as a catalyst.

Declaration of competing interest

There are no conflicts to declare.

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