Porous liquids based on porous cages, metal organic frameworks and metal organic polyhedra

Anastasiya Bavykina[#], Amandine Cadiou[#] and Jorge Gascon^{*}

King Abdullah University of Science and Technology, KAUST Catalysis Center
(KCC), Advanced Catalytic Materials, Thuwal 23955, Saudi Arabia.

[#]These authors contributed equally

jorge.gascon@kaust.edu.sa

Abstract

The possibility of creating well controlled empty space into liquids is both, conceptually and, from the application point of view, very attractive. Since James, Cooper and co-workers coined the term porous liquid a few years ago, intense research effort has been put into this new class of materials. This review highlights most of the work published to date in this field, with special emphasis on the use of Metal Organic Frameworks, Porous Organic Cages and Metal Organic Polyhedra as pore generators. After discussing some general considerations on the fundamentals of porous liquids, we examine the different synthetic approaches proposed to date and the main challenges in terms of materials synthesis and characterization. Finally, our view on possible future research directions is outlined.

1. Introduction

According to the IUPAC, porosity is a concept related to texture that refers to the empty space in a material.¹ Porous materials contain cavities, interstices or channels and their properties vary depending upon the size, shape and configuration of these pores. Porosity is a crucial property with important implications for a great number of technologies (from catalysis to gas separation)²⁻⁷ and a naturally occurring phenomenon (*i.e.* porosity and permeability of a given soil are crucial in defining its properties).

Inevitably, when thinking about porous materials, we would normally think, exclusively, about solids. Indeed, the concept of a porous liquid may somehow strike as counterintuitive. However, since the pioneering works of James, Cooper and co-workers, the term porous liquid is gaining attention within the scientific community.⁸ This is not surprising, the possibility of adding well controlled empty space into liquids is very attractive in terms of potential applications: for instance, absorption processes based on liquids are easy to control, much more efficient from a heat transfer perspective and technologically mature. However, large heats of absorption **are the main drawback of this process because regeneration of the absorbent requires a considerable amount of energy.** If such absorptive processes could be turned into adsorptive ones, the consequences in terms of energy efficiency would be very important.

In order to make a porous liquid, the presence of empty spaces is necessary. This can either be achieved directly in certain liquids or by combining solvents and porous scaffolds. According to O'Reilly *et al.* (**Figure 1**),⁹ there are three types of porous liquids: Type 1 are neat liquids with intrinsic porosity. They have to be rigid, incapable of self-filling and have an internal cavity. When empty hosts are dispersed or dissolved in a

solvent that is sterically hindered and cannot penetrate the cages' voids, a type 2 porous liquid is formed. Finally, type 3 porous liquids comprise framework materials dispersed in a hindered solvent.

Figure 1. Cartoon representing molecules in a conventional liquid, which has only “extrinsic” porosity between the molecules (small, irregular, transient cavities), and microporous liquids that have “intrinsic” porosity within the molecules (molecule-sized, regular, permanent empty cavities). Type 1: neat liquid hosts that cannot collapse or inter- penetrate. Type 2: Rigid hosts dissolved in solvents that are too sterically hindered to occupy the cavities. Type 3: Particles of microporous frameworks dispersed in sterically hindered solvents. Reproduced with permission from reference⁹

From the designer point of view, type 2 and 3 porous liquids offer many more degrees of freedom and have obviously been the most studied. In this article, we review the recent efforts in the development of porous liquids by using either Metal Organic Frameworks (MOFs) or porous cages as porosity enablers. In doing so, we highlight

the main challenges in design, making special emphasis on challenges in the characterization of this peculiar class of materials.

2. Metal Organic Frameworks in porous liquids.

2.1. State of the art

Metal-organic frameworks are a fascinating class of hybrid materials that offers a myriad of structures due to the almost infinite combinations between inorganic nodes, which can be isolated metal, chains or cluster, ²⁻⁷ and organic linkers, which are typically based on carboxylates and/or azolates. ¹⁰⁻¹² The careful choice of these building blocks enables the access to MOFs with specific porosity, *i.e.* channels and/or cages, of particular interest for gas separation,¹³⁻¹⁷ storage,¹⁸⁻²² drug delivery, ^{23,24} catalysis ²⁵⁻²⁷ and other energy related applications.²⁸⁻³⁰ Although researchers have devoted a lot of effort to developing MOFs with remarkable potential, their industrial implementation is advancing at a slower pace.

Improving the separation capacity of a given liquid through the addition of porosity is a very attractive concept. Carbon capture represents an interesting case study, as the current state of the art technology involves absorption using amine solutions, with a quite important energy penalty mostly associated to the regeneration of the liquid. A “green” alternative to this technology would be the use of ionic liquids that, in addition to having high CO₂ solubility, would display high thermal and chemical stability as well as negligible vapor pressure.^{31,32} Unfortunately, enthalpies of absorption in ionic liquids are still higher than for solid adsorbents.³³ On the other hand, the high inefficiency of solid-solid heat exchangers precludes to a large extent the application of porous solids in the adsorptive separation of CO₂. In this spirit, the development of

hybrid processes where solid adsorbents were applied in the liquid phase could be an excellent solution to this long standing issue.^{34,35}

As defined previously, porous liquids can be divided into three types. In 2015, Bennett *et al.* observed that ZIF-4 (ZIF= Zeolitic Imidazole Framework) can be melted without any mass loss, leading to a liquid phase keeping an extended Zn-Im-Zn (Im=imidazolate) coordination network.³⁶ In 2018 this discovery was extended towards two other ZIFs – ZIF-76 and ZIF-76-mblm (mblm stands for 5-methylbenzimidazole). MOF liquids (named MOF glasses) were obtained from these MOFs and exhibited permanent and reversible porosity.³⁷ Recently, Gaillac *et al.* have studied the melting of ZIF-4 via experimental and computational means such as *in situ* variable temperature X-Ray diffraction, *ex-situ* neutron pair distribution function (PDF) and first-principles molecular dynamics (FPMD).³⁸ They demonstrated the retention of porosity in the liquid state (Figure 2). **This is, to the best of our knowledge, the only example of a porous liquid based on a MOF that resembles a type 1 porous liquid.**

Figure 2. Structure of a ZIF-4 crystal, glass, and structural evolution upon heating. a) A basic building unit from metal ion and linker. b) Representation of the cage topology. c) Crystalline structure. d) Atomic configuration of the melt-quenched glass gained from modelling synchrotron and neutron total scattering data. e) experimental neutron structure factor data and the fit from the configuration shown in d. Inset: X-ray data and fit. f) Experimental glass (top) and computational (bottom) X-ray structure factors upon heating. Reproduced with permission from reference ³⁸.

Another approach to synthesize porous liquids is to disperse and stabilize solid porous materials in hindered solvents that cannot enter the pores. The use of three dimensional (3D) frameworks like MOFs would lead to type 3 porous liquids.⁹

All 3D porous MOFs contain channels and/or cages. The ideal MOF should be highly selective and display a large adsorption capacity. One way to achieve this is to have small aperture to use the size/shape exclusion principle with large cages to maximize storage capacity. ZIF-8, structurally comparable to zeolites with the sodalite topology, exhibits small apertures (0.34 nm) but large cages (1.16 nm), making it an ideal platform for fundamental studies.³⁹ In 2014, Liu *et al.* used this MOF as the first example in the literature of a porous liquid based on MOFs.⁴⁰ They suspended ZIF-8 nanoparticles in a glycol and glycol-2-methylimidazole solution and demonstrated by adsorption and breakthrough experiments that the slurries exhibit higher selectivity compared to conventional technologies. Indeed, the slurry ZIF-8/glycol-2-methylimidazole reaches selectivities of 951, 394 and 114 for CO₂/H₂, CO₂/N₂ and CO₂/CH₄ respectively. Moreover, the CO₂ adsorption enthalpy is about -29 kJ mol⁻¹, much lower than for aqueous amines or ionic liquids.⁴¹ The authors explain this enhancement of selectivity compared to the solid phase of ZIF-8 by an increment of

CO₂ solubility in glycol and glycol-2-methylimidazole while the solubility of the other gases is much lower.

Figure 3. Separation performance of pure ZIF-8 and two porous liquids based on the same ZIF-8 crystals. Reproduced with permission from reference⁴⁰

Very recently, Shan *et al.* reported the coupling of ZIF-8 nanoparticles and [DBU-PEG] [NTf₂] IL.⁴² The obtained porous liquids are extremely stable thanks to the formation of chemical bonding at the solute-solvent interface.³³ Different loadings of ZIF-8 were analyzed. The incorporation of permanent micropores was confirmed by Positron Annihilation Lifetime spectroscopy (PALs). By comparison of the CO₂ adsorption-desorption measurement between the neat IL and different loadings of ZIF-8, it was

claimed that ZIF-8 porous liquid (30 wt%) exhibits approximately 4.7 times the CO₂ capacity of pure [DBU-PEG] [NTf₂] with an adsorption capacity of 1.56 mmol g⁻¹ at 10 bars and 298 K.

Nanocrystallites of ZIF-8 have also been dispersed in the IL [Bpy][NTf₂] (N-butyl pyridinium bis (trifluoromethyl sulfonyl)imide) by Liu *et al.*⁴³ They demonstrated that by using wet ZIF-8 in methanol instead of the dry ZIF-8 pre-aggregation can be avoided, leading to a colloidal solution with the ILs stable up to seven months. The preservation of the porosity was proven by I₂ adsorption/release experiments and, according to the comparison of their positron lifetime parameters on ZIF-8, [Bpy][NTf₂] and ZIF-8-[Bpy][NTf₂] colloid, ZIF-8 porosity remains intact in ILs.

Finally, Gomes *et al.* have provided the most recent example of a porous liquid, to the best of our knowledge.⁴⁴ ZIF-8 and Mg₂(DOBDC) (known as Mg-MOF-74) were chosen and dispersed in [P6,6,6,14][NTf₂] (trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide). Density measurements of the suspension revealed that the 5% w/w dispersion of ZIF-8 is significantly less dense than the pure IL, hinting at the presence of free volume unlike the suspension of MOF-74 which is much denser than the neat IL. Molecular dynamic (MD) simulations demonstrated that ions from IL do not occupy the pores of ZIF-8, while the cylindrical pores of Mg-MOF-74 are filled with liquid: in full agreement with experiments, thus demonstrating that a porous liquid is obtained with ZIF-8 but not with Mg-MOF-74. Gravimetric gas solubility measurements of CO₂, methane and nitrogen were performed, and it was claimed that ZIF-8 suspension (5% w/w) provoked a molar adsorption increase of 63% per mass of liquid in case of CO₂ and more than 100% for CH₄ and N₂, at 303 K and 5 bar. (Figure 4)

Figure 4. Dissolution of carbon dioxide, methane and nitrogen in a porous liquid. a) Structures of ZIF-8 and [P_{6,6,6,14}][NTf₂]. b) Solubility of carbon dioxide in the ZIF-8 suspensions at 303 K from atmospheric pressure up to 5 bar. c) Solubility of methane in the ZIF-8 suspensions at 303 K from atmospheric pressure up to 5 bar. d) Solubility of nitrogen in the ZIF-8 suspensions at 303 K from atmospheric pressure up to 5 bar. Reproduced with permission from reference

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To date and to the best of our knowledge, only the five publications reported in this review demonstrate the use of MOFs either to obtain a neat porous liquid (type 1) or dispersed in ionic liquids leading to type 3 porous liquids. (Table 1) Additionally, only three MOFs – ZIF-4, ZIF-8 and Mg-MOF-74 – were investigated and only two of them successfully formed porous liquids. It means that i) porous liquids based on MOFs are possible and feasible and ii) the door is now open for a new promising field.

Table 1. Porous liquid based on MOFs reported to date.

Composition		Porous liquid type	Characterizations	Ref
MOF	Solvent			
ZIF-4		I	<i>in situ</i> variable temperature X-Ray, <i>ex-situ</i> neutron pair distribution function (PDF) first-principles molecular dynamics calculation (FPMD)	38
ZIF-8	Glycol Glycol-2-methylimidazole	III	CO ₂ /H ₂ , CO ₂ /N ₂ and CO ₂ /CH ₄ separations measurements	40
ZIF-8	[DBU-PEG] [NTf ₂]	III	Thermogravimetric analysis Positron annihilation lifetime spectroscopy CO ₂ adsorption	42
ZIF-8	[Bpy][NTf ₂]	III	Positron annihilation lifetime spectroscopy I ₂ adsorption/desorption	43
ZIF-8	[P6,6,6,14][NTf ₂]	III	Molecular dynamic simulations Gravimetric gas solubility measurements	44

2.2 Perspectives

A lot of work has already been dedicated to shape MOFs as nanoparticles, feature that is an important prerequisite for their use in future porous liquids.⁴⁵ This is mainly achieved using either microwave assisted hydro(solvo)thermal synthesis, ultra-sound assisted synthesis or by using a specific additive.⁴⁶ In the meantime, a lot of effort has

been dedicated to the tuning of MOF porosity for different adsorptive applications. MOFs with high surface area and pore volume were firstly considered to tackle the CO₂ issue. As an example, MOF-177,⁴⁷ MIL-100 and MIL-101,⁴⁸ DUT-9⁴⁹ or PCN-426⁵⁰ amount other MOFs were tested and as expected display exceptional CO₂ uptake at high pressure. Unfortunately, at 0.15 bar, which represents the CO₂ concentration usually found in post-combustion flue gas, the uptake is quite low, rendering these high surface area materials useless for this application.^{17,51}

Consequently, researchers started exploring other design routes to capture CO₂ at low pressure. An applied strategy involved MOFs functionalization.^{52,53} This can take place either on open metal sites of the framework or at certain ligand functionalities such as perfluoroalkanes⁵⁴, amides⁵⁵ or amines.⁵⁶

The other explored possibility derives from the concept of reticular chemistry.⁵⁷⁻⁶¹ Basically, a MOF consists of a metal part and a ligand that assemble together leading to a 2 or 3 dimensional framework. This network possesses geometrical properties and there exists a spatial relation between vertexes, leading to a specific topology. Then, two cases can be considered. First, this topology remains unchanged if the same metal node is kept but the length of the linker is tuned.⁶² Therefore, it is possible to modify the aperture size of the cavities and adjust them for a targeted application. This strategy has been successfully employed on *fcu* and *ftw* platforms in order to reach challenging separations as butane/isobutene and propane/propylene.^{63,64} Second, the ligand is kept identical but metals are altered. As an example, one of the best materials for CO₂ capture, SiFSIX-3-Cu⁶⁵, was further tuned leading to materials with better CO₂ uptake at very low concentration such as SiFSIX-3-Ni^{66,67}, AIFIVE-1-Ni,⁶⁸ and NbOFFIVE-1-Ni.^{69,70} Their remarkable performance is associated with their ultramicroporosity (aperture size <4Å). This property seems essential for low pressure

CO₂ capture.⁷¹⁻⁷⁴ Accordingly, we believe that the reader can draw his inspiration from experimental but also theoretical results regarding possible candidates that already show high potential for CO₂ capture as bulk material.^{15,75-77} The combination of those MOFs with an adequate ionic liquid should lead to new porous liquids with high ability for CO₂ capture and separation.

3. Porous cages and metal organic polyhedral based porous liquids.

3.1. State of the art

Porous Organic Cages (POC)⁷⁸ and Metal Organic Polyhedra (MOP)⁷⁹ are two novel types of porous materials that have emerged over the last decade. In this Review both types, together with the well-known macrocycles, will be referred as Porous Cages since they have similar properties concerning the topic of this Review. Porous Cages are molecules with a rigid structure, accessible intrinsic cavities and, therefore, are promising in providing tunable void architectures. They are believed to have a potential in selective gas storage and/or separation, sensing and catalysis.⁸⁰

Type 2 porous liquids are formed when porous cages are used as pore generators.⁹ Such a pore generator has to fulfill a couple of requirements – the cage is to be rigid and stable when emptied from any guest within its structure. On top of that, the cage's cavity size has to maintain the required porosity: when dissolved, the selected solvent should not occupy its inner void.

One of the very first examples is dated back to 1994. Cram *et al.*⁸¹ demonstrated the concept of empty hosts dissolved in sterically hindered solvents. Hemicarcerand, the molecule depicted in **Figure 5**, has cavities sufficiently small to avoid diphenyl ether to enter but big enough to include smaller CH₂Cl₂ and (CH₃)₂NCOCH₃. When the

hemicarcerand molecule was synthesized around $(\text{CH}_3)_2\text{NCOCH}_3$ as a guest and heated up in diphenyl ether for five days at $195\text{ }^\circ\text{C}$, empty hemicarcarend spheres were obtained. The guest release was confirmed by ^1NMR , however, there was no direct evidence reported that the molecule's cavity was empty.

Figure 5. Hemicarcerand molecule. Reproduced with permission from reference ⁸¹

Rauchfuss *et al.* reported an inorganic “molecular box” $[\{\text{Cp}(\text{Co}(\text{CN})_3\}^{15}_4(\text{Cp}^*\text{Ru})_4]$ (Co_4Ru_4), **Figure 6**.⁸² There, Co_4Ru_4 is capable of including small guest molecules, *e.g.* CH_3NH_3^+ , K^+ , Cs^+ . It was possible to crystallize Co_4Ru_4 with acetonitrile. The window size of the Co_4Ru_4 is that small that acetonitrile remained outside of the host's cavity. The presence of empty voids was proven by ^1HMR , ESI-MS and crystallography.

Figure 6. Inorganic “molecular box” $[\{\text{Cp}(\text{Co}(\text{CN})_3\}^{15}_4(\text{Cp}^*\text{Ru})_4]$ (Co_4Ru_4). Reproduced with the permission from reference ⁸²

Dutasta *et al.* in 2009 reported on encapsulation of small gas molecules, such as methane, ethane and ethylene, by cryptophane-111 (**Figure 7A**) in an organic solution.⁸³ Cryptophane was dissolved in CDCl₃, which is large to fit within the cryptophane's cavity, inside NMR tubes. Guest species were then allowed to flow into the tube and equilibrate; ¹NMR spectra were collected in order to study the kinetics and thermodynamics of the host-guest complexation. No PALS or adsorption isotherms were reported as a direct evidence of the empty voids of the cryptophane.

A different approach was employed by the group of Dai. They reported on the fabrication of a type 3 porous liquid based not on the conventional cages, but on hollow silica spheres, **Figure 7B**.⁸⁴ Charged organosilane was used as a corona for the surface modification. The chloride counteranion, balancing the positively charged corona, was replaced by a poly(ethylene glycol)-tailed sulfonate canopy, yielding a transparent hollow silica based porous liquid. The inorganic silica units were homogeneously dispersed in the organic medium. Nitrogen adsorption isotherms' shape did not alter after the modification, suggesting that the hollow framework was well preserved. Thermogravimetric analysis showed that the liquid was solvent-free, as there was no evident mass loss until the temperature reached 260 °C. TEM and SEM images revealed monodispersed hollow spheres.

Figure 7. Different pore generators used in the preparation of porous liquids discussed in the text. A cryptophane-111, B hollow silica spheres, C iminospherand cage. Reproduced with permission from references ⁸³(a), ⁸⁴(b), ⁸⁵(c) respectively.

James and co-workers reported a series of papers on porous liquids. A rigid iminospherand cage, obtained from imine condensation between four 1,3,5-triformylbenzene molecules and six diamines, (**Figure 7C** and **Figure 8A**) was alkylated with groups of different chain length.⁸⁵ In 2012 it was found out that the medium length alkyl tails are effective in dramatically lowering the melting point of the rigid iminospherand host. These were the first organic cages that showed a measurable melting point. Melting points as low as 50 °C could be obtained and a fully Newtonian liquid phase was formed above 80 °C. These alkylated materials were non-porous in the glassy solid state and were believed to be nonporous in their liquid state due to the easy penetration of the cage cavities by mobile tail ends. In 2014 a thorough study on designing and understanding microporosity in liquids confirmed that increasing the chain length (**Figure 8A**) decreases the melting point and increases the diffusion coefficient of the cages in the fluid. *E.g.* the presence of *n*-C₁₂ lowered the melting point compared to *n*-C₅ from 158 °C to 40 °C. Despite its relatively high melting point, the *n*-C₅ substituted cage formed a liquid with 30% of its cages empty at any time according to MD simulations. Also, the influence of alkyl's terminal branching was explored. Branched chains were found in general to increase the melting point. However, long unbranched chains could rapidly enter the cage cavities and, therefore, remove the porosity from the liquid. Terminal branching slowed down the rate of entering the cage; *e.g.* the cage with neo-C₁₄ chain has almost all the cages empty for the duration of long simulation (100ns).⁸⁶

Figure 8. Rigid iminospherade cages. Reproduced with permission from references ⁸⁶(a), ⁸(b), ⁸⁷(c).

In 2015, the same group prepared a porous liquid from the same cage functionalized with six crown ether groups (**Figure 8B**). The obtained molecule was dissolved at high concentration in a 15-crown-5 solvent, which is too large to enter the pores.⁸ As a result of this design, a highly concentrated liquid phase (44 wt%) was obtained. It was the first report on a highly concentrated porous liquid – only 12 solvent molecules were needed to dissolve one cage. Both MD and PALS experiments confirmed the presence of empty pores in the liquid. They also suggested that the porous liquid might have a dramatically increased capacity to dissolve solute molecules up to ≈ 0.5 nm in diameter relative to the pure crown solvent. Methane solubility was examined and found to be higher at all studied temperatures in case of the porous liquid. It has to be noted that the cage synthesis yield was moderate, and, in order to be competitive with porous solids in terms of gas capacities, an alternative scale-up route was developed. There, during the synthesis of the cage, a mixture of diamines was used and a mixture of the so-called “scrambled cages” was obtained. This mixture could be prepared in multi-gram quantities from commercially available starting materials. The scrambled cages

formed a concentrated (>10 wt%) porous liquid in hexachloropropene (PCP), which is also big enough not to enter the pores. The obtained liquid was at least ten times less viscous at the comparable cage concentration because of the lack of bulky crown-ether substituents. Since the cavities were empty, small organic molecules of the correct size could compete with each other for the cavity. For a reader's amusement, a video is available online, where the addition of chloroform rapidly displays xenon from a sample of the scrambled-cage-based porous liquid that was saturated with xenon, whereas addition of a larger 1-*t*-butyl-3,5-dimethylbenzene, does not. Later, Qiao *et al.* used molecular simulations to study kinetics and thermodynamics for the storage of several gases in the crown ether substituted cage-based liquid. They concluded that the gas storage capacity follows the order $\text{CH}_4 > \text{CO}_2 > \text{N}_2$, which does not simply correlate with the gas molecule size.⁸⁸ The capacity of the gas storage was governed by nonelectrostatic (dispersive) intermolecular interactions between the gas and the cage and the size/shape of the gas molecule. The former controls the affinity of gas molecules for the cage, while the latter controls whether the inner space is used effectively.

The approach of using scrambled cages in porous liquids was explored further in 2017.⁸⁷ A series of vertex disordered porous liquids were reported (**Figure 8C**). 150 combinations of scrambled cages and different solvents were studied by a combination of measurement techniques, molecular simulations and control experiments. *E.g.* **3³:13³-R**, equal amines combination, depicted by number 3 in the **Figure 8C**, was discovered, which is more than 10 wt.% soluble in PCP. In general, it was shown that when there was no a suitable guest, the cage cavities remained unoccupied. The liquids could reversibly adsorb large quantities of gas – *e.g.* 72% and 74% for Xe and SF₆, respectively. The liquids were compared to the

corresponding porous organic cage solids and were found to have similar gas binding affinities, pointing that physical properties of the cage molecule were translated into the liquid state. However, some physical properties were different – while solid homochiral porous cages showed enantioselectivity for chiral aromatic alcohols, the equivalent homochiral porous liquids did not.

Recently Carne-Sanchez *et al.* reported the formation of a colloidal gel with hierarchical porosity.⁸⁹ They have demonstrated the supramolecular polymerization of Rh-based cuboctahedral MOPs using imidazole linkers to form amorphous polymers with permanent porosity. By controlling the self-assembly pathway, two distinct macroscopic morphologies selectively fabricated – (i) size controllable spherical particles, and (ii) three-dimensionally interconnected colloidal gels (**Figure 9**). The resulting amorphous materials showed that nitrogen and carbon dioxide adsorption properties arise indeed from the microporosity of the MOP's *internal* cavity. The macroscopic morphology was found to strongly influence the adsorption properties of the assemblies. The authors believe that their strategy can be generalized to any metal–organic polyhedron with appropriate coordination equilibria to linkers.

Figure 9. Schematic representation of the proposed mechanism for the formation of a supramolecular colloidal gel (SCG-1). Reproduced with permission from reference ⁸⁹

3.2. Perspectives

As is seen from the above-mentioned examples, very different cage types could be used as pore generators within a porous liquid. The field of Porous Cages is relatively new compared to the MOF field, while the importance of porous liquids is only being currently explored. That all said, it is obvious that only a small fraction of porous liquid design was tried and carried out, and many more are to come. Both porous organic cages and metal organic polyhedra are modular compounds and there are comprehensive reviews available describing their design routes.^{78,90} POCs themselves have already found applications in molecular separations showing selectivity for different gas pairs, e.g. SF₆-N₂²⁰, CO₂-N₂⁹¹, CO₂-CH₄⁹², H₂-N₂⁹³, rare gases separation^{94,95} as well as for water desalination^{96,97} and chiral hydrocarbon GC separations.^{98,99} There exists a number of examples where different POCs (i.e. cyclodextrins¹⁰⁰, Noria¹⁰¹, imine cages¹⁰²) were used as additives to a mix matrix membrane.¹⁰³ POCs were also employed in catalysis – e.g. Sun *et al.* employed an organic solubilized molecular cage as a support for Rh nanoparticles¹⁰⁴ and Yang *et al.* obtained Pd clusters with a great precision of a size control by encapsulating them within the open cavities of soluble POCs.¹⁰⁵

MOPs are also used as additives in mix matrix membranes (MMM), which might have some advantages over MOF based MMM – higher additive concentration can be achieved. *E.g.* when Perez *et al.* used MOP-18 [(Cu₂₄(ddbdc)₂₄(S)₂₄] dispersed in matrimid for MMM fabrication, MOP-18 molecules did not aggregate into large particles even at loadings as high as 80 wt%.¹⁰⁶ On the opposite side, Liu *et al.* fabricated a MMM from MOP-15 [Cu₂₄(NH₂-mBDC)] and 6FDA-DAM polymer matrix. There, the MOP loading was as low as 1.6 wt% , while a large performance enhancement in permeability, aging resistance, and selectivity was achieved

compared to a MOF based MMM.¹⁰⁷ Kitchin *et al.* reported a systematic study of a series of MOPs with varied organic chain length to produce anti-aging intercalated MMM. Aging was found to be slowed by a factor of three when the optimal ^tBu-MOP additive was used.¹⁰⁸ Currently, the majority of existing MOPs based MMM are fabricated from the Cu₂₄L₂₄ core reported by Eddaoudi *et al.* in 2001.^{109,110} This MOP consists of a copper based paddlewheel unit and dicarboxylate linker; many unexplored possibilities are present here with varying the MOP's chemistry, *i.e.* change of the metal of the unit or linker modification. Fulong *et al.* reported three different MOP fillers varying both architecture and metal ions.¹¹¹ The prosperity of both POCs and MOPs based MMMs suggests that the same POCs and MOPs based porous liquids have a huge potential in gas separation; these two materials are close conceptually, being differed only by the nature of the continuous matrix – solid for conventional MMMs and liquid for liquid membrane.

4. Conclusions and future perspectives

In spite of the relatively low number of publications to date, the field of porous liquids is rapidly evolving. When considering the different types, it is clear that the different design strategies largely depend on the porous liquid of choice. For instance, in order to make type 3 porous liquids based on MOFs, the choice of an appropriate sterically hindered solvent is going to be crucial. However, MOF surface functionalization in order to tune both pore aperture and affinity for the solvent may offer still unexplored possibilities.

To date, most MOF based porous liquids are based on ionic liquids and this indeed seems like a good approach: given the modular design of both MOFs and ILs, there

might be a plethora of potential combinations to be discovered. In this sense, the development of computational screening tools for this specific class of materials would be really helpful. On another note, we would not discard the possibility of realizing MOF based porous liquids based on other solvents and/or polymerization approaches such as the ones recently developed by Carmé- Sanchez *et al.*⁸⁹ This could lead to liquid “mixed matrix membrane” like materials with very interesting properties.¹⁰³

When porous cages are used as pore generators, the design of the cage *itself* is the focus of the liquid design. The cage has to be designed to be rigid, with a well-defined pore space, incapable of self-filling and highly soluble. In this sense, porous cages may offer more possibilities than bigger pore generators, although again unpredictability and the need for large synthetic efforts may hamper progress.

A very important aspect in the field will certainly be the way of characterizing this class of materials. From the above paragraphs, it is easy to realize that traditional methods for the characterization of porosity are not straightforward when it comes to porous liquids. One obvious issue is that adsorption isotherms are usually measured at very low pressures that may produce evaporation of the solvent. Such measurement can be done when an ionic liquid with nearly 0 vapor pressure is used as continuous phase, but not for most other solvents. PALS, on the other hand, is a more widely applicable technique that, regrettably not available to all researchers. We wonder if the use of more available spectroscopic techniques such as IR or Raman spectroscopies could help shed light into the actual porosity of porous liquids.

Last but not least, when it comes to the application of porous liquids, we believe that research to date has only scratched the surface in terms of potential. These materials are porous, fluid and tunable – having these features combined allows to customize them for a specific application more easily and implement the designed material into

an existing plant. Pore generator design, *i.e.* design of a specific MOF or POC, is a modular platform, and it has advanced drastically in recent years laying in front of us a fruitful field for a porous liquid design. Adsorptive separation is a clear application with a large potential, however, we would like to encourage the scientific community to look at other applications: *i.e.* liquid membranes based on porous liquids may offer high fluxes and moderate to good selectivities along with easy scale up for many industrially and environmentally important separations. Catalysis by porous liquids (not far from recent developments in the protection of homogeneous catalysts by porous cages ^{112,113}) may lead to unexpected selectivities and may help bridge the gap between homogeneous and heterogeneous catalysis. Even, if biocompatible solvents and pore generators could be used, the formulation of drug delivery fluids could be achieved.

In any case, given the current interest, the vast number of components that can be combined and the potential for application, we believe the next few decades are going to witness an explosion in the development of porous liquids and are looking forward to seeing where the imagination of the researchers involved in this field can bring the topic of porous liquids.

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