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The Changing State of Porous Materials

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Abstract

Porous materials contain regions of empty space into which guest molecules can be selectively adsorbed and sometimes chemically transformed. This has made them useful in both industrial and domestic applications, ranging from gas separation, energy storage, and ion exchange to heterogeneous catalysis and green chemistry. Porous materials are often ordered (crystalline) solids. Order—or uniformity—is frequently held to be advantageous, or even pivotal, to our ability to engineer useful properties in a rational way. Here we highlight the growing evidence that topological disorder can be useful in creating alternative properties in porous materials. In particular, we highlight here several concepts for the creation of novel porous liquids, rationalise routes to porous glasses, and provide perspectives on applications for porous liquids and glasses.

Nanoporous materials span a fascinating array of different chemistries, ranging from classical inorganic zeolites to molecular organic and hybrid framework solids.¹ Their microporous and mesoporous architectures find widespread practical use² for applications such as environmental remediation, heterogenous catalysis, medicine, and energy generation.^{3,4}

Extensive work on the formation of crystalline inorganic zeolitic frameworks from aluminosilicate gels started in the 1940s,⁵ that is, nearly three decades after amorphous porous solids such as activated charcoal were employed by Harrison and Zelinsky in respirators during World War 1,⁶ and twenty years after the patenting of silica xerogel formation.⁷ Those early zeolites had pore sizes that were typically below 8 Å, but the work also laid the foundations for the discovery in the 1990's of mesoporous silica solids with pores sizes approaching 100 Å.⁸

Examples of the function-led synthesis of amorphous porous materials can also be found in the organic domain. For example, internal void space was created within so-called polymers of intrinsic microporosity (PIMs) by relying upon inefficient packing of rigid, contorted polymer units.⁹ Subsequently, order was introduced by linking organic units via covalent bonds, which ultimately gave rise to rigid, amorphous porous aromatic frameworks (PAFs)¹⁰ and crystalline covalent organic frameworks (COFs).¹¹ Likewise, early work on amorphous organometallic polymers influenced the subsequent formation of ordered three-dimensional framework materials based on the self-assembly of inorganic and organic components.¹² More than 70,000 such metal-organic frameworks, or MOFs, have now been reported in the pure crystalline state, with their robust and ordered frameworks allowing some materials to reach specific pore volumes in excess 5.02 cm³ g⁻¹.¹³

As well as extended solids, discrete organic molecules have been fabricated that possess cage structures. These cages can assemble into either crystalline or amorphous materials, which may retain accessible porosity.¹⁴ Discrete cages may also take the form of inorganic compounds, such as polyoxometalates, or be formed by coordination bonding between inorganic and organic units. Metal-organic polyhedra (MOPs), or metal-organic cages (MOCs), for example, are formed from the directed assembly of a range of inorganic and organic 'building blocks'.^{15,16}

To date, much of the research effort to realise the potential of porous materials has focused on the rational design of the crystalline solid state. This predilection toward order has prevailed despite the utility of order-disorder transitions in hybrid solids, the potential processing advantages of disordered materials (e.g., soluble PIMs), and the success of design techniques to control porosity in amorphous polymers.⁹ This stems, in part, from the ease of characterization of crystalline solids at the laboratory scale by X-ray diffraction, which has been key to the explosive development of the chemistry of metal-organic frameworks.¹⁷ It is also manifested in a large number of high-throughput screening studies and the generation of databases of hypothetical periodic frameworks.¹⁸ As this field has matured, the presence of defects in these crystalline structures was noted as providing an additional 'handle' to tune their properties, or to introduce extra functionality that is not otherwise present in the parent framework. The controlled introduction and

characterization of elements of disorder in crystalline frameworks¹⁹ was shown to be key in controlling the catalytic properties of mixed-metal framework materials.²⁰ Such work also prompted studies on order–disorder phase transitions,²¹ and the past few years have seen increased efforts to control the most fundamental of all properties of porous materials—their physical state (**Figure 1**). The goal is to bridge the huge gap in behaviour between solids and liquids by introducing functional disorder in a controlled manner, while retaining some of the desirable properties of porous frameworks.

The solid state, both crystalline and amorphous, provides advantages over liquids in several respects. For example, in heterogeneous catalytic processes where the separation of catalyst from liquid phase substrate is necessary, and in the use of activated carbon with pressure-swing adsorption processes in the production of H₂ from natural gas streams.²² It is also true that, at present, porous solids incur generally lower energy penalties than liquids in CO₂ adsorption-desorption processes.²³

In other settings, however, the lack of fluidity in porous solids means that they cannot be incorporated into continuous flow processes, and the liquid state may then prove more useful. For example, liquid alkylamine or dialkylether liquid technologies are currently employed the removal of acidic gases from waste streams in the upgrading of synthesis or natural gas, and the large-scale capture of CO₂.²⁴ Such processes could prove to be conceptually easier to upgrade with porous liquid technologies, which might also offer better heat management possibilities, easier handling properties, and improved processability when compared to porous solids.

In this perspective, we focus on recent key advances in the design and introduction of topological disorder into porous materials. A dual and complementary view is emerging: rather than retro engineering topological disorder into existing ordered frameworks, we might instead search to introduce and control porosity new, heavily disordered materials, such as liquids. We discuss in particular the formation of amorphous solid and liquid states, the control over their nano- and micro-structures, and efforts to tailor their physical and chemical properties. We extend the existing classification system of porous liquids,²⁵ and propose strategies to populate the resulting unexplored areas of materials space. We highlight glasses as the intersection between the area of porous solids and liquids, and provide a perspective on this rapidly evolving field.

Porous liquids

The synthesis of porous liquids (PLs) stems from a desire to create materials that possess both porosity and fluidity. Classification of PLs into three categories has remained standard since their conceptualization (**Figure 2**). **Type 1** PLs are defined as discrete, molecular ‘host’ materials with intrinsic porosity, which are liquid in their neat state. Initial difficulties in engineering large host molecules to form liquids in their neat states were overcome by adding flexible alkyl tails to organic

cage hosts, whilst Dai and Mahurin *et al* have rendered hollow silica nanospheres fluid by grafting polymers onto the exterior surfaces.²⁶ This strategy requires navigation of a delicate balance; increasing alkyl chain lengths lower melting point, yet also allow occupation of the host cavity with the flexible tails, compromising porosity.²⁷ The use of ionic interactions to imbue liquidity to a porous material has also proven useful. Dai *et al.* for example synthesized a potassium salt of a negatively charged organic cage host, before adding dicyclohexano-18-crown-6 to complex the potassium ion.²⁸ The absence of a long alkyl tail in this case meant that the cages remained empty, as indicated by both positron annihilation lifetime spectroscopy (PALS) and their high gas uptake. Combination of the two strategies is also possible, as demonstrated by Nitschke *et al.* in the addition of flexible tails with positively charged end groups to a charged metal-organic cage.²⁹

Type 2 PLs avoid the difficulties in forming pure liquid phases, by having the hosts dissolved in a solvent rather than existing in their neat state. Requirements here are (i) the host must exhibit a very high solubility to provide a high concentration of empty cavities and (ii) the chosen solvent must be too sterically hindered to fit inside the host. These considerations mean that the creation of Inorganic **Type 2** species is difficult, though we suggest that the approaches taken by Akutagawa *et al.* in solubilizing giant Mo ring species with organic surface groups may be a transferable route forward in this area.³⁰

Turning to organic liquids, an early example made use of organic cages functionalised on the outside with crown ether groups in order to provide high solubility. Here, 15-crown-5 was employed as a (somewhat unconventional) solvent, given its size and very low surface curvature. Remarkably, using this approach clear solutions could be obtained that consisted of up to 48 wt% of the host (a cage to solvent mole ratio of only 12). Also, the uptake of methane, an industrially important gas, was found to increase by a factor of 8 due to the presence of the empty cavities. This dramatic increase in gas uptake is consistent with the prediction that the thermodynamic cost of dissolution in conventional liquids is dominated by the energy required to form a notional cavity in which solute molecules can be accommodated.³¹ In the case of a porous liquid, the thermodynamic work to produce the empty cavities is already done during the synthesis (and/or activation) of the material, so that the solute, in a sense, has less work to do when it is dissolved. This early work in the field thus pointed to the potential of porous liquids to act as 'super-solvents' for gases.

In the aforementioned examples, substituents were grafted onto the outside of the hosts to make them highly soluble. An alternative strategy to increase solubility is to generate a mixture of less symmetrical hosts that differ subtly from each other in having substituents randomly placed at different positions. Effectively, each cage in the scrambled mixture then has a different shape, and this frustrates crystallisation of the material, making it more soluble. For example, a mixture of cage

3 (1,2-cyclohexanediamine vertices) and cage 13 (1,2-diamino-2-methyl-propane vertices), led to the scrambled cage 3³:13³ as the dominant component in the mixture, in which 3 cyclohexane vertices of each cage were replaced with a propyl group. The products proved to be highly soluble in 2-hydroxyacetophenone and exhibited permanent porosity. Later, similar materials were identified involving more scalable solvents by using a robotic screening technique.³²

The need for low melting points and/or high solubilities is removed altogether in **Type 3** porous liquids, since these take the form of suspensions rather than neat liquids or solutions. Specifically, particles of porous solids (*e.g.*, silica, zeolites, MOFs etc.) are agitated until they form a suspension in a liquid whose molecules are unable to enter the pores. However, the nature of the solid-liquid interactions and/or the particle size may need to be controlled if a highly stable suspension is to be obtained. For example, Moro *et al.* have formed suspensions of silica nanoparticles in water, though surface hydrophobization was necessary to prevent the ingress of solvent into the porous cavities.³³ Size excluded dispersions have also been investigated, first by Liu *et al.*, who suspended ZIF-8 in a mixture of liquid glycol and 2-methylimidazole to form a slurry. Although there was no direct evidence that the ZIF-8 pores remained unoccupied by the solvent, this slurry exhibited unusually high CO₂ sorption capacity and selectivity.³⁴ It has been noted that the gas uptakes of **Type 3** PLs are predictable – typically being simple weighted averages of the uptakes of the solid and liquid in their pure states.³⁵

Very recently, several *extended* metal-organic framework species with intrinsic porosity have been isolated in the liquid form; that is, reported to melt at temperatures lower than their decomposition point. The zeolitic imidazolate family consists of over 100 different known frameworks based on tetrahedral metal nodes connected by imidazolate based linkers.³⁶ Several species undergo partial coordination bond (Zn–N) breakage at *ca.* 400 °C, followed by rapid interchange of metal-ligand coordination partners. Interestingly, this results in a liquid which possesses 95% accessible porosity, compared to 74% in the microporous solid form.³⁷ The absence of a second component in such systems, coupled with the fact that they are not discrete molecular species, leads us to propose that these species belong to a new category of porous liquid: **Type 4**. In effect, they are solid materials of extended connectivity in 3 dimensions which, in the liquid state, retain intrinsic porosity due to the strong constraints of their instantaneous coordination (**Figure 2**); that is, the local order imposed by the associated nature of the liquid.

Supercooled Porous Liquids and Glasses

The move towards fluid porosity provides an intriguing opportunity to look deeper into possibilities in an area that bridges both liquid and solid states: that is, supercooled liquids, or glasses (**Figure 3**). Cooling a liquid causes an increase in viscosity, and a corresponding decrease in molecular

motion of the components present in the system. Slow cooling (compared to molecular motion) results in the first order phase transition known as crystallisation, though relatively high rates of cooling may result in a slowdown of molecular motion, until no further changes in movement on observable timescales are observed.³⁸ The range over which this slowdown in molecular motion occurs is a general kinetic phenomenon, referred to as the glass transition T_g (**Figure 3a**). We therefore suggest the possible existence of porous glasses corresponding to the categories of the porous liquids in **Figure 2**.

In the strictest sense, **Figure 3a** only provides a route to form glasses from **Type 1** and **Type 4** porous liquids, in which the liquid state can be regarded as pure. Whilst reports of the latter exist (formed by quenching liquids from the ZIF family), the extension in the case of **Type 1** is less clear. Here, iminospherand-based (non-porous) liquids have been demonstrated to possess reversible glass transitions at around 50 °C, with the glasses produced retaining the high transparency of their liquid phases upon cooling, and possessing the ability to be drawn into fibres.³⁹ However, the occupation of cage pores by the externally functionalized long alkyl species in the liquid state is also likely to persist in the glass, given the enthalpic stabilization afforded to the system by long chain – pore wall dispersive interactions. Interestingly, liquids formed from similar cages functionalized with shorter alkyl chains possess 30% empty cages, though their glass forming ability has not yet been investigated,³⁹ whilst the crown-ether anionic covalent cages highlighted in **Figure 2** also form a glass, though only below room temperature.²⁸ The prospect of a **Type 1** liquid possessing a glass temperature T_g above room temperature, while retaining porosity in the glass state, is therefore exciting, though for now elusive.

Unlike the other types described above, extending this approach to form **Type 2** porous glasses is significantly more complicated. For example, highly concentrated porous liquids are most sought after for the purposes of application; however, these will be the most vulnerable to precipitation of the discrete organic as temperature is lowered and solubility decreases. Moreover, the presence of solvent has been observed to decrease the T_g in the case of both discrete organic molecules,⁴⁰ and inorganic systems.^{40,41,42} A detailed study on the effect of concentration on T_g in **Type 2** porous liquids formed from a variety of solvents would thus be highly informative in perhaps identifying a useful trade-off between concentration of cage, and the stability of the glass at room temperature.

The absence of a fixed stoichiometry means that the compositional variance of glasses is huge compared to crystalline solids, allowing control over the resultant material properties. Even in a straightforward case, such as the ternary calcium aluminosilicate system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ which is useful for display applications, a database of 231 different compositions predicts Young's moduli values which span from 60 to 160 GPa (**Figure 3b**).⁴³

Taking a broader perspective, the freezing of colloidal suspensions occurs naturally in a variety of processes such as sea ice growth, and has been utilized to generate controlled porosity in a variety of materials including alloys, silica, water-soluble polymers, clays, and bone substitutes.^{44,45} Deville *et al.* have shown extensively that such processes can be harnessed in structuring complex composite materials (**Figure 3c**)⁴⁶. Such methods should also prove applicable to other porous liquids, where they would lead to the generation of tuneable hierarchical porosity combining intrinsic and ice-templated porosity.

The glass phase analogy of polymorphism, called *polyamorphism*, may also be harnessed to effect transformations between different glasses of identical chemical composition but different physical and chemical properties.⁴⁷ The transit between two glass states commonly occurs through the application of pressure, and results in sudden changes in material density and properties; this has been demonstrated in a host of different systems including $Y_2O_3-Al_2O_3$,⁴⁸ GeO_2 and molecular organics.⁴⁹ The existence of different amorphous states of the ZIF-62 glass forming system has already been probed (**Figure 3d**), though the different properties of the amorphous states have not been explored.

Proposed Applications

Many of the suggested applications for porous liquids thus far centre on chemical separation technologies. Currently, acid gas separations are performed using scrubbing agents such as ethanolamines and polyethylene glycol dialkyl ethers that absorb a target gas, and are later regenerated through typically energy intensive processes.⁵⁰ The use of organic cage-based liquids for key separations of soluble gases⁵¹ would require higher selectivities than available at present, but could be advantageous in terms of reductions in the energy required for recycling due to improved heat management.

Several important problems still need to be addressed in using porous liquids for such processes. Greenaway *et al.* demonstrated appreciable gas uptake in a range of porous liquids, notably through scrambling techniques (**Figure 4a**), but also found that the dynamic equilibria between bound and unbound guest molecules led to leaching of the guest over several days.⁵² The synthesis of porous liquids of lower volatilities may prove particularly beneficial in overcoming this loss through regular thermal or pressure swing processes.

Overall, **Type 3** PLs in particular have some attractive aspects with regard to real world applications: *i.* they can be prepared economically by forming a dispersion of two commercially-available components, *ii.* they have predictable gas uptakes, and *iii.* they are a diverse and modular platform technology consisting of thousands of potential variants, with a correspondingly wide

range of tuneable properties. PLs might even be drop-in replacements for existing solvent-based gas separation processes, if they are found to be superior in terms of economics and performance.

Examples have been tailored toward gas separations such as CO₂/CH₄ separation, which is of interest for natural gas sweetening and biogas upgrading, thus demonstrating their potential for application. In this regard, a dispersion of the MOF Al(OH)(fumarate) in polydimethylsilicone oil was found to have greater CO₂ capacity than the industrially used solvent Genosorb. A further exciting possibility is that PLs can be tailored toward gas separations for which no selective solvent currently exists, such as ethane/ethane separation.⁵³ In such applications, the liquid state could allow manufacture of free-standing or supported liquid membranes.⁵⁴

Applications in gas separations may also be opportunities for **Type 4** glasses, such as those formed from ZIFs. For example, Jiang *et al.* have recently utilized the glass forming process by first forming a crystalline ZIF-62 layer upon an Al₂O₃ substrate, before melt-quenching (**Figure 4b**).⁵⁵ Interestingly, they found separation factors for H₂/CH₄, CO₂/N₂ and CO₂/CH₄ mixtures exceeding those for the crystalline material. Although the molecular mechanism is still unclear, the high selectivities reported for the ZIF-62 glass membrane should promote much further exploration into the guest capture and selectivity properties of porous glass materials in general.

Porous liquids may find application beyond carbon capture and storage – for example, in the subsequent utilization of the captured feedstock. Electrochemical reduction and catalytic conversion processes have been observed to produce a range of value-added chemicals such as formic acid, methanol and ethylene.⁵⁶ A range of electrolytes have been investigated, including KOH/MeOH mixtures, and ionic liquids.⁵⁷ Porous liquids might present a unique opportunity to overcome problems of low CO₂ solubility while at the same time acting as a catalyst for the reductive processes.

More speculatively, many crystalline framework materials have shown that their strong local order can lead to stimuli-responsive properties, making them “smart materials” whose *chemical* properties may be switched through stimulation with, for example, temperature, pressure, or light. The switching of *physical* structure through application of external stimuli is also a concept widely used in information storage.⁵⁸ We predict this may be extended to porous materials. For example, the design glasses and liquids by incorporating photoresponsive moieties, such as an azobenzene backbone, would render it possible to change the physical and chemical properties using light. Mochida *et al.* have provided proof of concept in controlling the reversible transition of a ruthenium-based solid coordination polymer to an ionic liquid of identical composition (**Figure 4c**).⁵⁹

Novel Materials Discovery

The relative novelty of the field of porous liquids and glasses compared to corresponding solid-state studies promises much excitement in the area of new materials discovery. Here, it is already

clear that we need to move from serendipity-based discovery of new states of porous materials to an era of designability and the creation of new materials with targeted properties. Motivation to guiding research into improved **Type 1**, **2** and **3** materials will for example be improvements in the concentration of pore generators. This might be pursued in **Type 1** inorganic and inorganic-organic liquids for example by borrowing from the strategy used in **Type 1** organic liquids,²⁶ with porous counter-ions such as crown ethers in place of long alky chains or smaller, non-porous counterions such as NTf₂. Improvements in the capacity of **Type 2** and **Type 3** liquids on the other hand clearly necessitate an increase in solubility of the porous component. The results of Greenaway *et al.*,⁵² provide some directions on this. The field may pay particular attention to scrambled, achiral cages and asymmetrical porous materials which exist in topologically disordered solid states, and link the higher solubilities observed to the same logic employed in amorphous pharmaceuticals. Further research into the creation of Type 3 PLs through the heating of (low T_g) MMMs may also be of interest.

Such experimental efforts would be made more efficient from the development of computational techniques to accurately predict the structures and properties of hypothetical porous liquids. Extending the plethora of high-throughput computational studies focusing on the uptake capacities and separation abilities for different gas species, to topologically disordered liquid and glasses would therefore present an interesting challenge.⁶⁰ This should, however, also go hand in hand with the adaptation and application of theoretical tools for systematic characterization of molecular cages and porous molecular materials,^{61,62} such as crystal structure prediction.⁶³

Type 4 liquids present an entirely different problem, which at the outset is one of first developing some guiding principles to allow their formation across different chemical families (**Figure 2**). Far less work has been performed in this area, though we would suggest that controlling the hierarchy of bond energies within porous materials is a key requirement to the formation of Type 4 liquids, regardless of chemistry. Specifically, clear differences in the strength of bonding leads to the possibility of selective bond breaking at sufficiently high temperatures while maintaining some local order, which seems to be crucial to obtain a porous liquid. Considerations in each case would be the residual diffusivity of framework components after melting, limiting the size of the rigid unit which may be used, lest the molten fluid be too viscous or glassy; and also the stabilization of the ionic components after the initial decoordination (in the case of salts).

For example, the ADOR process in zeolites relies upon the chemical destruction of mixed metal zeolites, followed by chemical structuring and reconfiguration of the components into a different framework.⁶⁴ Similarly, hydrogen-bonded organic frameworks (HOFs) such as triptycene trisbenzimidazolone are also formed from rigid organic molecules that crystallize through supramolecular interactions based on hydrogen bonding, which is typically an order of magnitude weaker than covalent bonds.⁶⁵ The design of Type 4 associative liquid HOFs may be challenging,

however, because of the typically very high melting points of these materials, their inherent propensity to crystallize, or because of sublimation/decomposition before melting.

Finally, we also note that non covalent interactions with strong local order (*i.e.*, preferential coordination) have been observed to play a critical role in excellent glass forming systems such as B_2O_3 .⁶⁶ There, the strongly associated nature of the trigonal BO_3 units, combined with the large number of possible three-connected networks energetically quasi-degenerate, favours the vitrification and the formation of a macroscopically disorder material. Such systems, modified to feature a larger and bulkier motif, are also good candidates for **Type 4** porous liquids.

Understanding and Designing

There are substantial gaps in our fundamental understanding of existing porous liquids and glasses, which must be filled at a fundamental level if we are to make progress in their applications. Further research into how kinetic factors such as cooling rates and sample sizes influence their melting/vitrification behaviour is likely to yield pathways to accurately controlling the density (and therefore porosity) of all porous glass categories, while a combination of simulated thermodynamic energy landscapes with experimental pressure-temperature diagrams would allow significant control to be exerted over new structure discovery in a parameter space of larger dimension with tuneable variables such as chemical composition, pressure, and temperature.

The nature of the transitions between ordered and disordered states is a second area in which our current knowledge is lacking. We have highlighted here the routes to forming porous liquids, and speculate on routes to novel porous glasses. Many interesting questions also lie in the reversibility of the transition from liquid to glass, and also the transition from ordered crystalline materials to topologically disordered states. For example, fast interchange between ordered crystalline chalcogenide domains and topologically disordered glasses form the basis of research into improved data storage.⁶⁷ This is facilitated by significant differences in electrical resistance between ordered and disordered states, which we note has been observed within examples of amorphous and crystalline MOFs.⁶⁸ It is possible that the chemical complexity of such systems provide more shallow energy landscapes, and the existence of a plethora of degenerate states which allow for increased storage capacity.

One may also consider direct transitions between the crystalline and liquid states, particularly within low T_m systems such as those in Type 1 and Type 2 categories. The latent heat of the solid-liquid phase transition in both inorganic and organic systems is used to store, and release, thermal energy near the transition temperature.⁶⁹ The use of hybrid crystalline systems has (very recently) been proposed,⁷⁰ as have crystalline-liquid transitions in metal-organic systems.⁷¹ Other uses may also be found for such transitions, for example in gas storage where we borrow inspiration from ionic liquids.⁷² Here, the reaction of room temperature solids with guest molecules results in the

reduction of their inherent T_m , and the subsequent ability to use the enthalpy of fusion to offset energy losses in absorbent regeneration.

The complexity of topologically disordered porous solids and liquids presents significantly greater challenges in both fundamental and applied domains when compared with their crystalline counterparts, which are themselves difficult systems to understand in detail – for example, in terms of the effects of defects. However, topologically disordered porous solids and liquids also provide new opportunities to engineer processability and to harness significant, reversible changes in both chemical and physical properties that simply cannot be attained in porous crystalline frameworks.

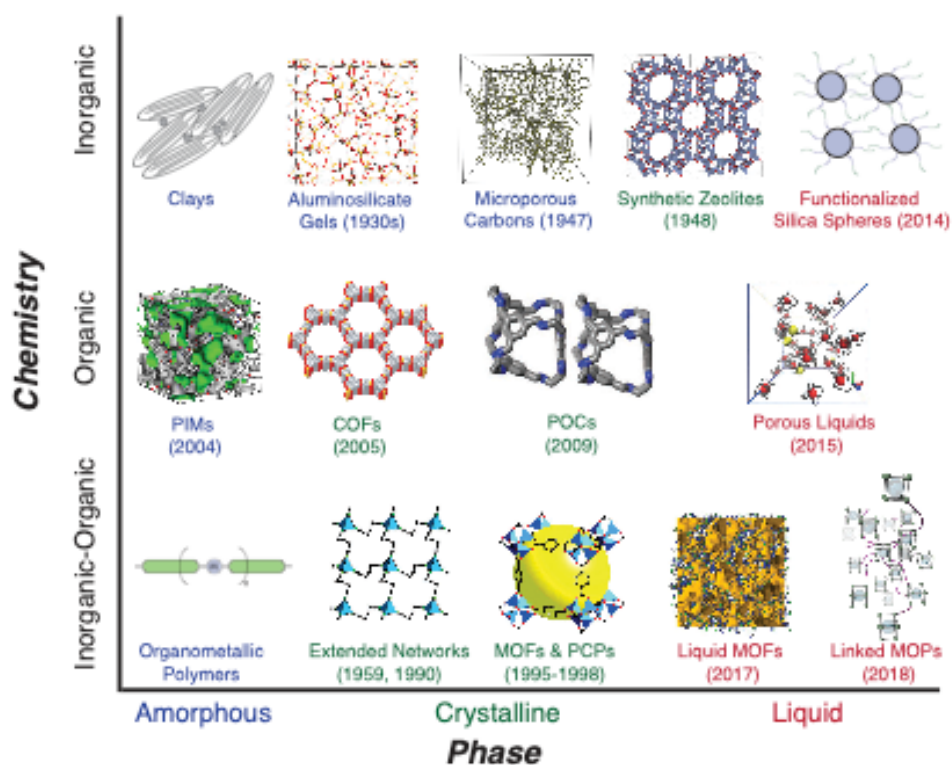


Figure 1. The evolution of atomic arrangement in porous materials science. This figure highlights the evolution in focus from selected amorphous solids, through to the crystalline state, and onwards to the liquid state, spanning organic, inorganic and hybrid materials. **References:** PIMs,⁹ COFs,¹¹ POCs,⁷³ porous liquids,⁷⁴ organometallic polymers,¹² extended networks,^{75,76} MOFs & PCPs,^{77,78} liquid MOFs,³⁷ functionalized silica spheres,²⁶ linked MOPs,¹⁶ aluminosilicate gels,⁷⁹ clays,⁸⁰ microporous carbons,⁸¹ synthetic zeolites.⁵ **Figures:** PIMs,⁸² COFs,¹¹ POCs,⁷³ porous liquids,⁷⁴ extended networks,⁸³ MOFs & PCPs,⁸⁴ liquid MOFs,³⁷ functionalized silica spheres,²⁶ linked MOPs,¹⁶ aluminosilicate gels,⁸⁵ microporous carbons.⁸⁶



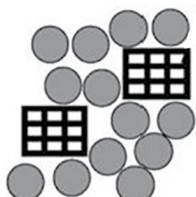
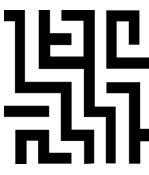
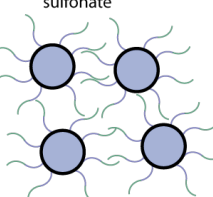
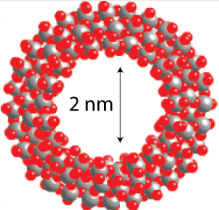
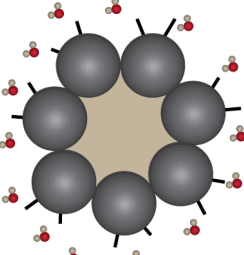
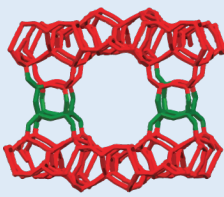
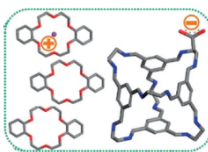
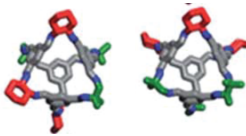
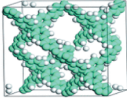
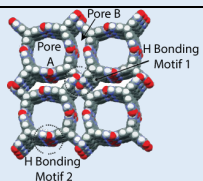
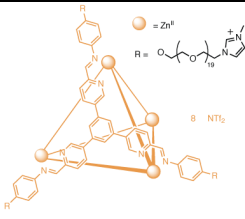
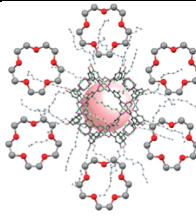
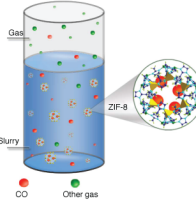
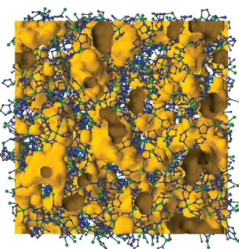
	Type			
	1	2	3	4
				
Inorganic	<ul style="list-style-type: none"> ● Hollow SiO₂ — Organosilane — Poly(ethylene glycol) sulfonate  <p><i>Functionalised SiO₂</i></p>	 <p><i>Functionalized Mo₁₅₄-rings</i></p>	 <p><i>Hydrophobic hollow SiO₂ in Water</i></p>	 <p><i>Mixed Si/Ge Zeolites</i></p>
Organic	 <p><i>Crown-ether anionic covalent cages</i></p>	 <p><i>Scrambled organic cages</i></p>	 <p><i>PAFs in oil</i></p>	 <p><i>Triptycene-trisbenzimidazolone (or other HOFs)</i></p>
Inorganic-Organic	 <p><i>Functionalized metal-organic polyhedra</i></p>	 <p><i>Metal-organic polyhedra in crown ether</i></p>	 <p><i>ZIF-8 in glycol-2-methylimidazole</i></p>	 <p><i>Liquid ZIF-4</i></p>

Figure 2. Updated classification of porous liquids. The 1st row shows a schematic depicting PL types. **Type 1** PLs consist of intrinsically porous hosts (hollow circles). In **Type 2** PLs, these are dissolve in sterically hindered solvents (solid circles). **Type 3** PLs consist of microporous hosts (square grids) within a sterically hindered solvent. **Type 4** PLs are neat microporous hosts which form transient, strongly associated liquids. Examples of known materials are given, alongside suggestions (in blue), for some categories not yet populated, on which discovery of the first examples may be based. Figure references. Schematics.²⁵ | Type 1 (adapted).²⁶ O Type 1.²⁸ IO Type 1.²⁹ | Type 2.³⁰ O Type 2.³² IO Type 2.⁸⁷ | Type 3 (adapted).³³ O Type 3.^{10,53} IO Type 3.³⁴ | Type 4.⁶⁴ O Type 4.^{65,88} IO Type 4.³⁷ Categories shaded in blue are discussed in the outlook section.

We note that the example in I Type 1 posed a problem for us in classification terms. We placed this in the inorganic category, rather than the inorganic-organic category because although functionalisation with an organic is necessary for the liquid state, the main body of the material is inorganic in nature.

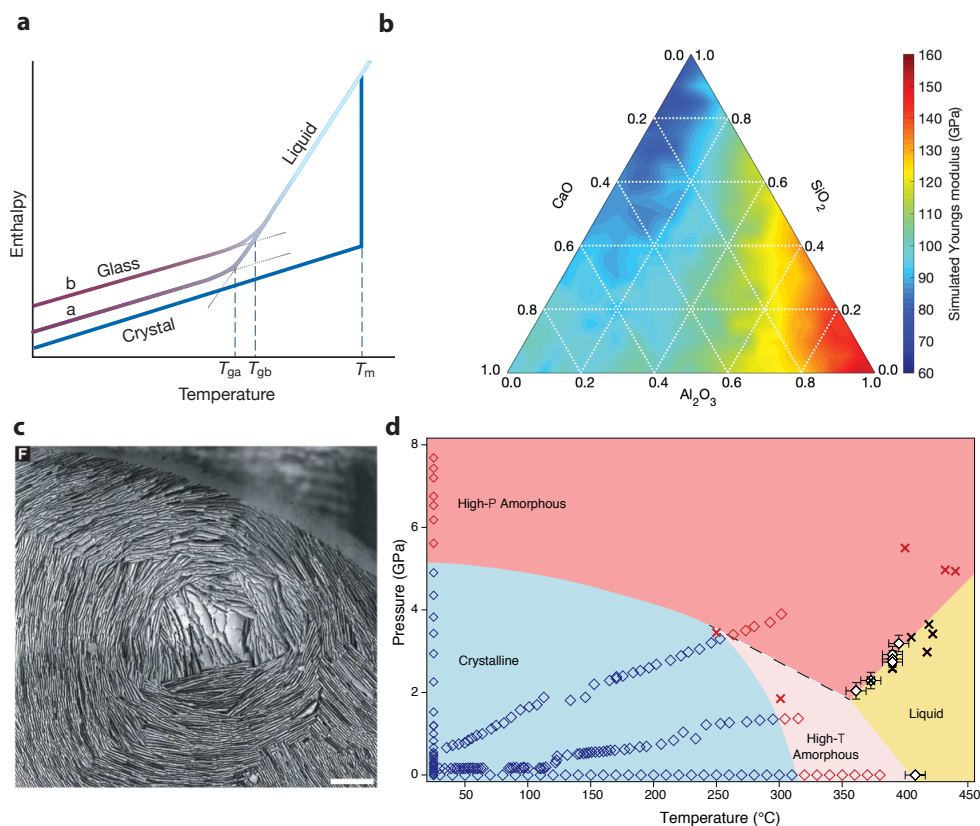


Figure 3. Solid-Liquid Transformations. (a) Schematic representation of enthalpy as a function of temperature for a liquid state capable of both crystallisation and vitrification, depending on cooling rate.⁸⁹ The glass transition is dependent upon rate of cooling – faster cooling leads to lower T_g values than slower cooling rates. T_g is however commonly defined using heating and cooling rates of 10 K/min for standardization between materials. (b) Ternary diagram showing the Young's modulus values predicted by high-throughput molecular dynamics simulations as a function of composition in the CaO – Al_2O_3 – SiO_2 glass system.⁴³ (c) Ice-templated mesostructure of alumina (scale bar = 500 μm).⁴⁶ (d) The pressure–temperature (P , T) phase diagram of ZIF-62. Blue: stability domain of crystalline ZIF-62, tracing the results of the phase transition analysis from PXRD (blue and red diamonds). Red: two distinct amorphous phases with high (dark red) and low (light red) densities relative to each other. Yellow: domain of liquid ZIF-62, defined by melting points from the crystalline ZIF-62 (observed optically at high P and using DSC at ambient P). Crosses indicate conditions from which samples were quenched for morphological analysis.⁹⁰

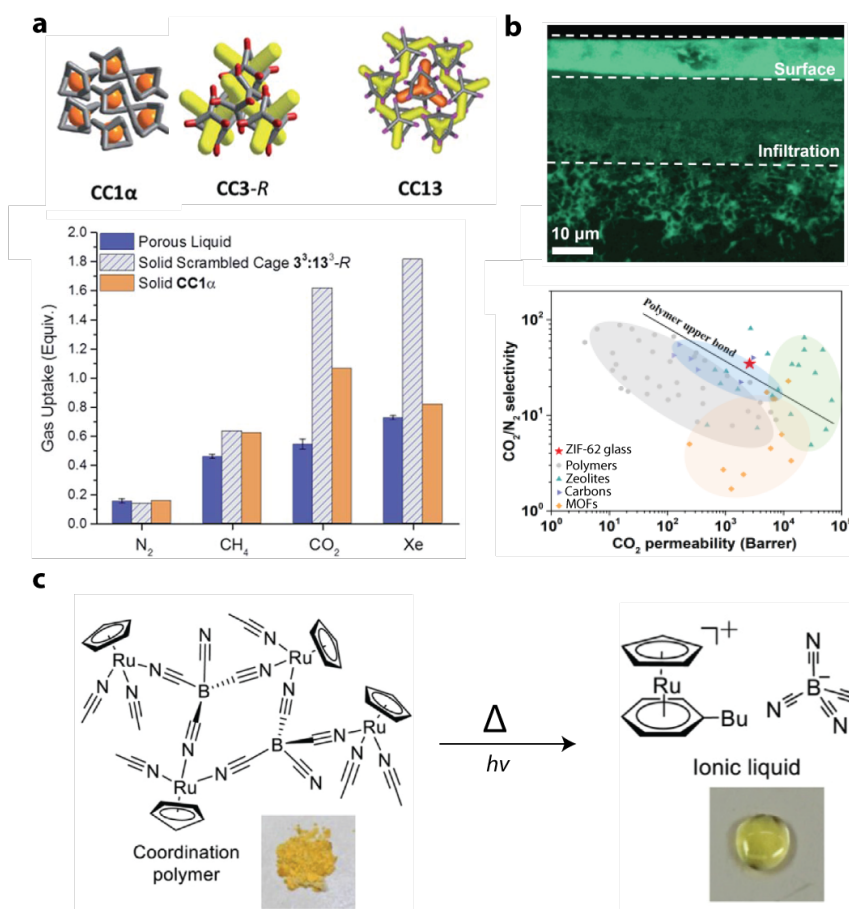


Figure 4. Applications of porous liquids. (a) Schematic structures of porous cages, alongside comparison of the molecular equivalents of gas uptake per cage for porous liquids.⁵² CC1 α packs in a window-to-arene fashion and contains only isolated voids within the cage itself (grey $\frac{1}{4}$ core cage structure; orange $\frac{1}{4}$ isolated cage voids). Crystalline CC3-R and CC13 have interconnected pore networks (yellow); crystalline CC13 also has some formally isolated cage voids (orange); grey = core cage structure; red = cyclohexane vertices; pink = methylpropane vertices. (b) EDX mapping of a ZIF-62 glass membrane on a porous Al₂O₃ support, and comparison of the separation for CO₂/N₂ separations with literature data.⁵⁵ (c) Transformation of a Ruthenium-based amorphous coordination polymer to an ionic liquid.⁹¹

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Competing Interests

The authors declare no competing interests.