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# The changing state of porous materials

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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, rationalize routes to porous glasses and provide perspectives on applications for porous liquids and glasses.

anoporous materials span a fascinating array of different chemistries, ranging from classical inorganic zeolites to molecular organic and hybrid framework solids<sup>1</sup>. Their microporous and mesoporous architectures find widespread practical use<sup>2</sup> for applications such as environmental remediation, heterogeneous catalysis, medicine and energy generation<sup>3,4</sup>.

Extensive work on the formation of crystalline inorganic zeolitic frameworks from aluminosilicate gels started in the 1940s (ref. <sup>5</sup>), that is, nearly three decades after amorphous porous solids such as activated charcoal were employed by Harrison and Zelinsky in respirators during World War I (ref. <sup>6</sup>), and 20 years after the patenting of silica xerogel formation<sup>7</sup>. These early zeolites had pore sizes that were typically below 8 Å, but the work also laid the foundations for the discovery in the 1990s of mesoporous silica solids with pore sizes approaching 100 Å (ref. <sup>8</sup>).

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<sup>9</sup>. Subsequently, order was introduced by linking organic units via covalent bonds, which ultimately gave rise to rigid, amorphous porous aromatic frameworks<sup>10</sup> and crystalline covalent organic frameworks<sup>11</sup>. 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<sup>12</sup>. 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 of  $5.02 \, \text{cm}^3 \, \text{g}^{-1}$  (ref. <sup>13</sup>).

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<sup>14</sup>. 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, or metal–organic cages (MOCs), for example, are formed from the directed assembly of a range of inorganic and organic foundation blocks<sup>15,16</sup>.

To date, much of the research effort to realize 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 (for example soluble PIMs) and the success of design techniques to control porosity in amorphous polymers9. 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 MOFs<sup>17</sup>. It is also manifested in a large number of high-throughput screening studies and the generation of databases of hypothetical periodic frameworks<sup>18</sup>. 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 frameworks<sup>19</sup> was shown to be key in controlling the catalytic properties of mixed-metal framework materials<sup>20</sup>. Such work also prompted studies on order-disorder phase transitions<sup>21</sup>, and the past few years have seen increased efforts to control the most fundamental of all properties of porous materials-their physical state (Fig. 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  $H_2$  from natural gas streams<sup>22</sup>. It is also true that, at present, porous solids incur generally lower energy penalties than liquids in CO<sub>2</sub> adsorption–desorption processes<sup>23</sup>.

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 for the removal of acidic gases from waste streams in the upgrading of synthesis or natural gas, and the large-scale capture of

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**Fig. 1** The evolution of atomic arrangement in porous materials science. The evolution in focus from selected amorphous solids through to crystalline materials and onward to the liquid state, spanning organic, inorganic and hybrid chemistries: PIMs<sup>9</sup>, covalent organic frameworks (COFs)<sup>11</sup>, particulate organic carbons (POCs)<sup>73</sup>, porous liquids<sup>74</sup>, organometallic polymers<sup>12</sup>, extended networks<sup>75,76</sup>, MOFs and porous coordination polymers (PCPs)<sup>7778</sup>, liquid MOFs<sup>37</sup>, functionalized silica spheres<sup>26</sup>, linked metal-organic polyhedra (MOPs)<sup>16</sup>, aluminosilicate gels<sup>79</sup>, clays<sup>80</sup>, microporous carbons<sup>81</sup> and synthetic zeolites<sup>5</sup>. Credit: reproduced with permission from ref. <sup>82</sup>, Springer Nature Ltd (PIMs); ref. <sup>11</sup>, The American Association for the Advancement of Science (COFs); ref. <sup>74</sup>, Springer Nature Ltd (porous liquids); ref. <sup>83</sup>, John Wiley and Sons (extended networks); ref. <sup>84</sup>, The American Association for the Advancement of Science (MOFs and PCPs); ref. <sup>37</sup>, Springer Nature Ltd (liquid MOFs); ref. <sup>26</sup>, John Wiley and Sons (functionalized silica spheres); ref. <sup>16</sup>, under a Creative Commons license CC BY 4.0 (linked MOPs); ref. <sup>85</sup>, Royal Society of Chemistry (aluminosilicate gels); ref. <sup>86</sup>, AIP Publishing (microporous carbons); and adapted from ref. <sup>73</sup>, Springer Nature Ltd (POCs)

 $CO_2$  (ref. <sup>24</sup>). 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 with 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 in new, heavily disordered materials, such as liquids. We discuss in particular the formation of amorphous solid and liquid states, control over their nano- and microstructures, and efforts to tailor their physical and chemical properties. We extend the existing classification system of porous liquids<sup>25</sup>, 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 stems from a desire to create materials that possess both porosity and fluidity. Classification of porous liquids into three categories has remained standard since their conceptualization (Fig. 2). Type 1 porous liquids 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, Mahurin and co-workers have rendered hollow silica nanospheres fluid by grafting polymers onto the exterior surfaces<sup>26</sup>. This strategy requires navigation of a delicate balance: increasing alkyl chain lengths lower the melting point, yet also allow occupation of the host cavity with the flexible tails, compromising porosity<sup>27</sup>. The use of ionic interactions to imbue liquidity to a porous material has also proven useful. Dai and co-workers for example synthesized a potassium salt of a negatively charged organic cage host, before adding dicyclohexano-18-crown-6 to complex the potassium ion<sup>28</sup>. The absence of a long alkyl tail in this case meant that the cages remained empty, as indicated by both positron annihilation lifetime spectroscopy and their high gas uptake. Combination of the two strategies is also possible, as demonstrated by Nitschke and co-workers in the addition of flexible tails with positively charged end groups to a charged MOC<sup>29</sup>.

Type 2 porous liquids avoid the difficulties of forming pure liquid phases by having the hosts dissolved in a solvent rather than existing in their neat state. Requirements here are (1) the host must exhibit a very high solubility to provide a high concentration of empty cavities and (2) the chosen solvent must be too sterically hindered to fit inside the host. These considerations mean that the



**Fig. 2 | Updated classification of porous liquids.** First row: schematic depicting porous liquid types. Type 1 porous liquids consist of intrinsically porous hosts (open circles). In type 2 porous liquids, these are dissolved in sterically hindered solvents (filled circles). Type 3 porous liquids consist of microporous hosts (square grids) within a sterically hindered solvent. Type 4 porous liquids are neat microporous hosts that form transient, strongly associated liquids. Examples of known materials are given, alongside suggestions (shaded in blue) for some categories not yet populated, on which discovery of the first examples may be based. Categories shaded in blue are discussed in the 'Novel materials discovery' section. We note that the example in inorganic 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 functionalization with an organic is necessary for the liquid state the main body of the material is inorganic in nature. Credit: adapted with permission from ref. <sup>25</sup>, John Wiley and Sons (schematics); ref. <sup>28</sup>, John Wiley and Sons (O type 1); ref. <sup>29</sup>, Springer Nature Ltd (IO type 1); ref. <sup>30</sup>, American Chemical Society (I type 2); ref. <sup>32</sup>, Royal Society of Chemistry (O type 2); ref. <sup>87</sup>, John Wiley and Sons (IO type 2); ref. <sup>33</sup>, American Chemical Society (I type 3); ref. <sup>10</sup>, John Wiley and Sons, and ref. <sup>53</sup>, under a Creative Commons license CC BY 4.0 (O type 3); ref. <sup>34</sup>, under a Creative Commons license CC BY 4.0 (IO type 3); ref. <sup>44</sup>, Royal Society of Chemistry (I type 4); ref. <sup>45</sup>, John Wiley and Sons (O type 4); ref. <sup>37</sup>, Springer Nature Ltd (IO type 4); and reproduced with permission from ref. <sup>26</sup>, John Wiley and Sons (I type 1)

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<sup>30</sup>.

Turning to organic liquids, an early example made use of organic cages functionalized on the outside with crown ether groups 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 molar 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 marked 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<sup>31</sup>. 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 'supersolvents' 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 crystallization 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 3<sup>3</sup>:13<sup>3</sup> as the dominant component in the mixture, in which three 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<sup>32</sup>.

The need for low melting points and/or high solubilities is removed altogether for type 3 porous liquids, since these take the form of suspensions rather than neat liquids or solutions. Specifically, particles of porous solids (for example silica, zeolites, MOFs and so on) 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<sup>33</sup>. Size-excluded dispersions have also been investigated, notably by Liu et al., who suspended zeolitic imidazolate framework ZIF-8 particles 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 CO<sub>2</sub> sorption capacity and selectivity<sup>34</sup>. It has been noted that the gas uptakes of type 3 porous liquids are predictable-typically being simple weighted averages of the uptakes of the solid and liquid in their pure states<sup>35</sup>.

Very recently, several extended MOF 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<sup>36</sup>. Several species undergo partial coordination bond (Zn-N) breakage at about 400 °C, followed by rapid interchange of metalligand coordination partners. Interestingly, this results in a liquid that possesses 95% accessible porosity, compared with 74% in the microporous solid form<sup>37</sup>. 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 three dimensions, which, in the liquid state, retain intrinsic porosity due to the strong constraints of their instantaneous coordination (Fig. 2): that is, the local order imposed by the associated nature of the liquid.

#### Supercooled porous liquids and glasses

The move toward fluid porosity provides an intriguing opportunity to look deeper into possibilities in an area that bridges liquid and solid states: that is, supercooled liquids, or glasses (Fig. 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 with molecular motion) results in the first-order phase transition known as crystallization, 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<sup>38</sup>. The range over which this slowdown in molecular motion occurs is a general kinetic phenomenon, referred to as the glass transition (Fig. 3a). We therefore suggest the possible existence

of porous glasses corresponding to the categories of the porous liquids in Fig. 2.

In the strictest sense, Fig. 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<sup>39</sup>. 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<sup>39</sup>, whilst the covalent cages highlighted in Fig. 2 also form a glass, though only below room temperature<sup>28</sup>. 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 notably 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<sup>40</sup> and inorganic systems<sup>40–42</sup>. 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 the concentration of the 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 with crystalline solids, allowing control over the resultant material properties. Even in a straightforward case, such as the ternary calcium aluminosilicate system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, which is useful for display applications, a database of 231 different compositions predicts Young's modulus values which span from 60 to 160 GPa (Fig. 3b)<sup>43</sup>.

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<sup>44,45</sup>. Deville et al. have shown extensively that such processes can be harnessed in structuring complex composite materials (Fig. 3c)<sup>46</sup>. Such methods should also prove applicable to other porous liquids, where they would lead to the generation of tunable 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<sup>47</sup>. The transition 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<sub>2</sub>O<sub>3</sub> (ref. <sup>48</sup>), GeO<sub>2</sub> and molecular organics<sup>49</sup>. The existence of different amorphous states of the ZIF-62 glass-forming system has already been probed (Fig. 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



**Fig. 3** | **Solid-liquid transformations. a**, Schematic representation of enthalpy as a function of temperature for a liquid state capable of both crystallization and vitrification, depending on cooling rate<sup>88</sup>. The glass transition is dependent upon the rate of cooling—faster cooling leads to higher  $T_g$  values than slower cooling.  $T_g$  is however commonly defined using heating and cooling rates of 10 K min<sup>-1</sup> for standardization between materials. **b**, Ternary diagram showing Young's modulus values predicted by high-throughput molecular dynamics simulations as a function of composition in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass system<sup>43</sup>. **c**, Ice-templated mesostructure of alumina (scale bar, 500 µm)<sup>46</sup>. **d**, The pressure-temperature (*P*, *T*) phase diagram of ZIF-62. The phase boundary between the two amorphous phases is tentatively indicated with a dashed black line. Black diamonds represent melting points determined using an optical microscopy experiment. Blue: stability domain of crystalline ZIF-62, tracing the results of the phase transition analysis from powder X-ray diffraction (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 differential scanning calorimetry at ambient *P*). Crosses indicate conditions from which samples were quenched for morphological analysis<sup>89</sup>. Credit: adapted with permission from ref. <sup>88</sup>, Springer Nature Ltd (**a**); and reproduced with permission from ref. <sup>43</sup>, under a Creative Commons license CC BY 4.0 (**b**); ref. <sup>46</sup>, The American Association for the Advancement of Science (**c**); ref. <sup>89</sup>, Springer Nature Ltd (**d**)

and polyethylene glycol dialkyl ethers that absorb a target gas, and are later regenerated though typically energy-intensive processes<sup>50</sup>. The use of organic cage-based liquids for key separations of soluble gases<sup>51</sup> 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 (Fig. 4a), but also found that the dynamic equilibria between bound and unbound guest molecules led to leaching of the guest over several days<sup>52</sup>. 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 porous liquids in particular have some attractive aspects with regard to real-world applications: they can be prepared

economically by forming a dispersion of two commercially available components, they have predictable gas uptakes and they are a diverse and modular platform technology consisting of thousands of potential variants, with a correspondingly wide range of tunable properties. Porous liquids 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  $CO_2/CH_4$  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 polydimethylsiloxane was found to have greater  $CO_2$  capacity than the industrially used solvent Genosorb. A further exciting possibility is that porous liquids can be tailored toward gas separations for which no selective solvent currently exists, such as ethane/ethane separation<sup>53</sup>. In such applications, the liquid state could allow manufacture of free-standing or supported liquid membranes<sup>54</sup>.



**Fig. 4 | Applications of porous liquids. a**, Schematic structures of porous cages, alongside a comparison of the molecular equivalents of gas uptake per cage for porous liquids<sup>52</sup>. CC1α packs in a window-to-arene fashion and contains only isolated voids within the cage itself (grey, 1/4 core cage structure; orange, 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, Energy-dispersive X-ray mapping of a ZIF-62 glass membrane on a porous Al<sub>2</sub>O<sub>3</sub> support, and comparison of the separation for CO<sub>2</sub>/N<sub>2</sub> separations with literature data<sup>55</sup>. **c**, Transformation of a ruthenium-based amorphous coordination polymer to an ionic liquid<sup>90</sup>. Credit: adapted with permission from ref. <sup>52</sup>, under a Creative Commons license CC BY 4.0 (**a**); ref. <sup>55</sup>, John Wiley and Sons (**b**); ref. <sup>90</sup>, John Wiley and Sons (**c**)

Applications in gas separations may also be opportunities for type 4 glasses, such as those formed from ZIFs. For example, Jiang and co-workers have recently utilized the glass-forming process by first forming a crystalline ZIF-62 layer on an Al<sub>2</sub>O<sub>3</sub> substrate before melt-quenching (Fig. 4b)<sup>55</sup>. Interestingly, they found separation factors for H<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> 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 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<sup>56</sup>. A range of electrolytes have been investigated, including KOH/MeOH mixtures and ionic liquids<sup>57</sup>. Porous liquids might present a unique opportunity to overcome problems of low CO<sub>2</sub> 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 stimulus-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<sup>58</sup>. We predict that this may be extended to porous materials. For example, the design of glasses and liquids by incorporating photoresponsive moieties, such as an azobenzene backbone, would make it possible to change the physical and chemical properties using light. Mochida and co-workers have provided proof of concept in controlling the reversible transition of a ruthenium-based solid coordination polymer to an ionic liquid of identical composition (Fig. 4c)<sup>59</sup>.

#### Novel materials discovery

The relative novelty of the field of porous liquids and glasses compared with 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 novel 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<sup>26</sup>, with porous counterions such as crown ethers in place of long alky chains or smaller, non-porous counterions such as NTf<sub>2</sub>. 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.<sup>52</sup> provide some directions on this. Researchers in the field may pay particular attention to scrambled, achiral cages and asymmetrical porous materials that 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 porous liquids through the heating of  $(low-T_e)$  mixed matrix membranes (MMMs) may also be of interest.

Such experimental efforts would be made more efficient by 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 liquids and glasses would therefore present an interesting challenge<sup>60</sup>. This should, however, go hand in hand with the adaptation and application of theoretical tools for systematic characterization of molecular cages and porous molecular materials<sup>61,62</sup>, such as crystal structure prediction<sup>63</sup>.

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 (Fig. 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 lead 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 (assembly–disassembly–organization– reassembly) 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<sup>64</sup>. Similarly, hydrogen-bonded organic frameworks 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<sup>65</sup>. The design of type 4 associative liquid hydrogen-bonded organic frameworks may be challenging, however, because of the typically very high melting points of these materials, their inherent propensity to crystallize or sublimation/ decomposition before melting.

Finally, we also note that non-covalent interactions with strong local order (that is, preferential coordination) have been observed to play a critical role in excellent glass-forming systems such as  $B_2O_3$  (ref. <sup>66</sup>). There, the strongly associated nature of the trigonal BO<sub>3</sub> units, combined with the large number of possible energetically quasidegenerate three-connected networks, favours the vitrification and the formation of a macroscopically disordered 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 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 pressuretemperature diagrams would allow important control to be exerted over new structure discovery in a parameter space of larger dimension with tunable 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 glasses forms the basis of research into improved data storage<sup>67</sup>. This is facilitated by differences in electrical resistance between ordered and disordered states, which we note has been observed within examples of amorphous and crystalline MOFs<sup>68</sup>. It is possible that the chemical complexity of such systems provides more shallow energy landscapes, and the existence of a plethora of degenerate states, which allow for increased storage capacity.

We may also consider direct transitions between the crystalline and liquid states, particularly within low-melting temperature  $(T_m)$  systems such as those in the 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<sup>69</sup>. The use of hybrid crystalline systems has (very recently) been proposed<sup>70</sup>, as have crystalline–liquid transitions in metal–organic systems<sup>71</sup>. Other uses may also be found for such transitions, for example in gas storage, where we borrow inspiration from ionic liquids<sup>72</sup>. 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 remarkably 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.

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All authors contributed equally to the writing of the manuscript.

#### Competing interests

The authors declare no competing interests.

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