Ionothermal Synthesis of Zeolites, Metal–Organic Frameworks, and Inorganic–Organic Hybrids

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ABSTRACT

Ionothermal synthesis, the use of ionic liquids as both solvent and template (structure-directing agent), has been used to prepare zeolites and inorganic–organic hybrids such as metal–organic frameworks. The underlying properties of the ionothermal method are discussed, and it is compared with traditional hydrothermal preparative methods. The materials resulting from ionothermal synthesis are described, and any structural features that can be related to the ionic liquid used as the solvent are discussed. Future areas of potential interest are also considered.

Introduction

The search for new porous solids remains at the forefront of synthetic materials science as their architectures continue to be of interest for many established and emerging applications.[1–3] Until relatively recently, the field of crystalline porous solids was dominated by aluminosilicate zeolites, but since the 1980s, many other fascinating materials have been produced, ranging from aluminophosphates[4] to metal–organic frameworks[5,6] and other inorganic–organic hybrids.[7,8] In general, these materials are made in a so-called solvothermal synthesis, often in sealed autoclaves under autogenous pressure. By far the most common solvent used is water, giving rise to hydrothermal synthesis,[9] but many other solvents have been tried.[10] This Account details the recent developments in ionothermal synthesis of open framework structures, where the solvent used is predominantly an ionic liquid or eutectic mixture, which also acts, in many cases, as the template provider.

In the 1940s, Barrer[11] and Milton[12] hydrothermally synthesized the first zeolites. Synthetic hydrothermal zeolite formation involves mixing the reagents, usually the tetrahedral atom source or sources, an organic structure-directing agent (SDA, often called the template), a mineralizer, and the solvent. The mixture is then heated (<220 °C) in a polytetrafluoroethylene (PTFE)-lined steel autoclave at high autogeneous pressure for a period of time. To date, approximately 40 natural zeolite structures[13] and more than 130 synthetic frameworks[14] have been identified.

The first class of molecular sieves synthesized that contained no silica consisted of the aluminophosphates (AlPOs), synthesized by Flanigen and co-workers in the early 1980s.[4] The search for more exotic structures led swiftly to the exploration of materials such as berylo- and zincophosphates.[15] Today a wide range of elements have been incorporated into phosphates and many new zeolite analogues synthesized.

An alternative route to hydrothermal synthesis uses nonaqueous solvents rather than water. The role of the solvent in, for example, a zeolite synthesis is to ensure efficient transport of reactants but without interacting too strongly with any of the individual components of the mixture. Since the inorganic precursors of zeolites and most inorganic–organic hybrid materials are ionic, the best solvents tend to be relatively polar in nature. To find suitable organic solvents for zeolite synthesis, their tendency to form hydrogen bonds must be considered. If the solvent forms hydrogen bonds which are too strong, this will prevent the framework species and template from interacting, thus preventing nucleation. Intermediate hydrogen bonding organic solvents, such as hexanol, propanol, glycol, glycerol, and pyridine, are therefore preferred.[10]

Ionic liquids[16] are a class of organic solvents with high polarity and a preorganized solvent structure. Room-temperature (or near-room-temperature) ionic liquids are classically defined as liquids at ambient temperatures (or <100 °C) that consist only of ions.[17] They have excellent solvating properties, little measurable vapor pressure, and high thermal stability. In the area of materials science, there have been several reports of ionic liquids being used as solvents with very little or controlled amounts of water involved in the synthesis.[18] Most of these studies concentrated on amorphous materials and nanomaterials.

In 2004, Cooper et al.[19] reported a new type of solvothermal synthesis in which an ionic liquid[20] or eutectic mixture[21] was used as both the solvent and the SDA in the synthesis of zeolites. This new synthesis methodology has been termed ionothermal synthesis and is currently receiving a growing amount of interest within the zeolite community. Recent publications using ionothermal synthesis have reported the formation of aluminophosphates,[19,22–27] cobalt aluminophosphates,[28] gallium phosphates,[23] and organic–inorganic hybrid materials.[29–35] Many of these structures are new, demonstrating the

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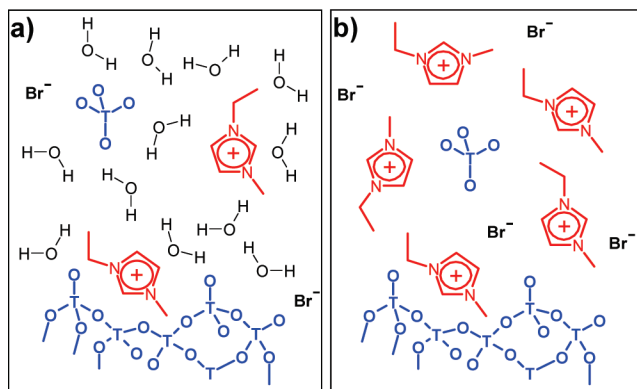
FIGURE 1. Schematic comparison between (a) hydrothermal and (b) ionothermal synthesis. In panel a, interactions between the excess solvent (water) and the template or framework dominate, while in panel b, the template–framework interactions dominate.[22]

potential of ionothermal synthesis in the discovery of novel materials. This Account will concentrate on summarizing the work to date in this area.

The Idea behind Ionothermal Synthesis

The unique feature of ionothermal synthesis is that the ionic liquid acts as both the solvent and the template provider. Many ionic liquid cations are chemically very similar to species that are already known as good templates (alkylimidazolium-based, pyridinium-based ionic liquids). Many are relatively polar solvents, making them suitable for the dissolution of the inorganic components required for the synthesis. One of the defining properties of ionic liquids is their lack of a detectable vapor pressure which effectively results in the elimination of the safety concerns associated with high hydrothermal pressures and has also led to their use in microwave synthesis.

For the purpose of ionothermal synthesis, a broader definition of an ionic liquid is used: a salt that melts below the temperatures used in the synthesis of zeolites, typically 150–220 °C. Since there are no other solvents added to the reaction mixture, the theory holds that there are no other molecules present to act as space fillers during zeolite synthesis. This means that ionothermal synthesis ideally removes the competition between template–framework and solvent–framework interactions that are present in hydrothermal preparations (Figure 1). This, however, is the idealistic scenario, which is not always attainable due to the possible decomposition of a small fraction of the ionic liquid cations, resulting in smaller template cations which may preferentially act as the SDA in the ionic liquid solvent.[25]

Recent molecular modeling studies indicate that the structures of ionic liquids are characterized by long range correlations and distributions that reflect the asymmetric structures of the cations.[16] Long-range asymmetric effects of this kind potentially increase the likelihood of transferring chemical information from the template cation to the framework, a situation that is desirable if full control over the templating process is to be achieved.

Deep Eutectic Mixtures

Eutectic mixtures have been used in ionothermal synthesis as an alternative to ionic liquids. A eutectic mixture is a mixture of two or more compounds which has a melting point lower than that of either of its constituents.[21] Eutectic mixtures exhibit unusual solvent properties that are very similar to those exhibited by the ionic liquids. High solubility can be observed (depending on the eutectic mixture used) for inorganic salts, salts that are sparingly soluble in water, aromatic acids, amino acids, and several metal oxides. Advantages of eutectic mixtures over ionic liquids are their ease of preparation in the pure state and their relative nonreactivity with water. Many are biodegradable, and the toxicology of the components may be well-characterized. Eutectic mixtures based on urea and choline chloride are also far less costly than ionic liquids.

Role of Water and Fluoride in Ionic Liquids

In ionothermal synthesis, the reaction takes place in an ionic environment, which differentiates it from hydrothermal or solvothermal techniques, where the solvent is predominantly molecular. It should be noted, however, that this does not preclude the presence of small amounts of water since many ionic liquids are hygroscopic and can absorb significant amounts of water from the atmosphere.[36] Dialkylimidazolium bis[(trifluoromethyl)sulfonyl]amides (Tf_2N^-) are reported to be hydrophobic,[37] but they still contain some water, even after a vigorous drying process. Rogers et al.[38] carried out studies on the water content of dried hydrophobic and hygroscopic ionic liquids. As an example, 1-butyl-3-methylimidazolium (BMIm) Tf_2N is classified as a hydrophobic ionic liquid but after drying contains 474 ppm water; BMImCl is hygroscopic and after drying contains 2200 ppm water. This water content is possibly beneficial to zeolite formation as water can act as a mineralizer when present in only reactant quantities. Recent work in the structure and chemistry of "wet" ionic liquids also indicates some other very interesting potential applications of ionothermal synthesis for the preparation of unusual solids. Particularly interesting is the deactivation of water through strong interaction with the anions in the IL.[36,39] It is now relatively well known that wet ionic liquids (containing as much as 7 M water depending on the actual ionic liquid) behave as if the water is less reactive than one would expect it to be. Yasaka et al. showed, using H–D exchange reactions, that water is significantly deactivated in ionic liquids,[40] and Hardacre and co-workers showed that highly sensitive molecules like PCl_3 can be stored for extended periods in various ionic liquids without hydrolysis.[41] The reason for this deactivation of water is that even at significant concentrations the water is molecularly dispersed or present only as small clusters, and the strong water–anion interactions reduce the nucleophilicity of the water and decrease its hydrolysis activity. In contrast, water in organic solvents often phase segregates on a microscopic scale to form hydrophilic regions that exhibit

normal water reactivity. As the water content is increased in an ionic liquid, the water tends to form larger hydrogen-bonded clusters and networks and behaves much more like other wet solvents. The amount of water present is therefore of great importance in determining the outcome of a synthesis.

Mineralizers, such as fluoride or hydroxide ions, added to the reaction mixtures in the correct quantities are often vital for crystallization of the desired molecular sieve products. Fluoride in particular has recently been an extremely useful mineralizer in aluminophosphates[42] and silicate synthesis.[43] In addition to helping solubilize the starting materials under the reaction conditions, fluoride itself can play a structure-directing role[44,45] and is intimately involved in template ordering in certain materials.[46]

In ionothermal synthesis, the addition of water or fluoride seems to be important in determining the phase selectivity of the reaction (see below). The ability to add either of these two important additives to the synthesis allows a level of control in ionothermal synthesis that is often absent in other methods.

Ionothermal Synthesis of Aluminophosphates, Cobalt Aluminophosphates (CoAlPOs), and Silicates

The first report of zeotype materials synthesized ionothermally used the ionic liquid 1-ethyl-3-methylimidazolium bromide (EMImBr), which is a relatively polar solvent that solubilizes the starting materials almost completely at the reaction temperatures.[19] This indicates that the synthesis mechanism is a crystallization from solution rather than a solid-to-solid transformation. SIZ-1 (St Andrews Ionothermal Zeolite-1) and SIZ-6 (Figure 2) are new zeotype structures and were produced without the addition of fluoride. Both structures have hanging P–O bonds and aluminium coordinated to more than four oxygens.[19,24] SIZ-3 (AEL) and SIZ-4 (CHA) were produced with the addition of HF and consist of fully condensed frameworks. SIZ-5 (AFO) was produced with the addition of water and can be classified as hydrothermal synthesis due to the quantity of water used being greater in molar terms than the quantity of ionic liquid.

The apparent dependence of the products on water and HF gives some clues about the possible mechanism of the reaction; however, further clarification is required with the need for additional experimental studies. With little water and no HF to act as mineralizers, targeting of interrupted framework structures such as SIZ-1 and SIZ-6 appears to be possible. Upon addition of HF or water, condensed structures, for example, SIZ-3, SIZ-4, and SIZ-5, are formed with no hanging P–O bonds. The ionic liquids are good solvents on their own, but the addition of fluoride or water as a mineralizer appears to increase their solvating power and leads to the possible targeting of condensed frameworks. It also appears that the addition of water or fluoride increases the efficiency of formation of the Al–O–P bond
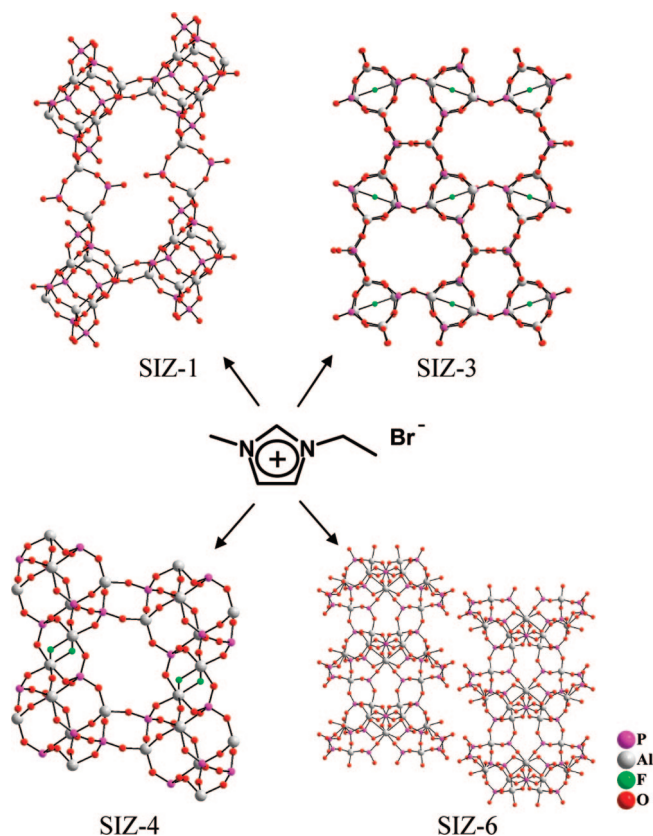

FIGURE 2. Ball-and-stick diagrams of the ionothermally synthesized aluminophosphates SIZ-1, SIZ-3, SIZ-4, and SIZ-6. The SDAs have bee omitted for clarity.[25]

as suggested for mineralizer function in hydrothermal synthesis.[47]

An obvious way to control phase selectivity is to change the template. By changing the ionic liquid cation, for instance, altering the chain on the alkylmethylimidazolium, one hopes that different framework topologies would result, as demonstrated by Zones in his hydrothermal synthesis, where templates of similar chemistry were used.[48] However, the SIZ-4 (CHA) and SIZ-6 structures appear to be default structures that form when the cation is altered slightly (Figure 3 summarizes the results).[25] The single-crystal XRD and NMR results showed that the templates occluded in the AlPO–CHA materials were not the original cations from the ionic liquid, but the 1,3-dimethylimidazolium cation formed at some point in situ during the reaction process. It also appeared that the addition of fluoride as a mineralizer seemed to aid in the decomposition to this cation. The stability of ionic liquids is currently of great interest as it impacts their potential applications. Chowdhury et al.[49] showed that heating several ionic liquids to 435 °C leads to the breakage of the N-alkyl bonds in these materials and that this reaction is susceptible to catalytic enhancement. It seems likely that in the presence of fluoride some of the N-alkyl bonds in the imidazolium cations are broken and re-formed under ionothermal synthesis conditions and that the 1,3-dimethylimidazolium cations are formed via a metathesis of the alkyl groups.
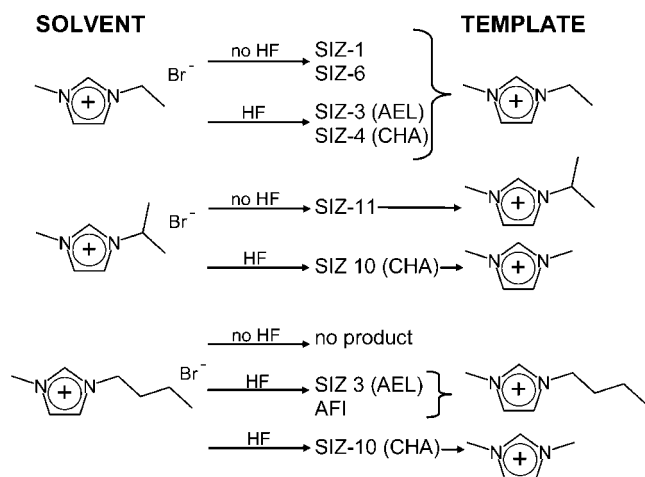
FIGURE 3. Summary of the ionic liquid solvent, AlPO product, and final template incorporated into the structure.

Interestingly, the metathesis seems not to occur during microwave heating or when open vessels are used. Xu et al. report the use of BMImBr as a solvent and template in the microwave-enhanced synthesis of a mixture of AlPO-5 (AFI) and AlPO-11 (AEL) at ambient pressure.[27] Microwave heating has several advantages over conventional heating such as fast crystal growth and higher selectivity.[50] These results have also been produced on the benchtop in a round bottom flask using an oil bath to heat the reaction mixture.[51] The template in both structures is confirmed by ^{13}C MAS NMR to be the BMIm cation. In an open vessel, any methyl bromide (boiling point of 4 °C) or butyl bromide (boiling point of 102 °C) produced upon N-alkyl bond cleavage would evaporate quickly under the reaction conditions, so the metathesis is unlikely to take place. Also reported is the possible structure directing role of several amines added to the ionothermal synthesis.[51] While the addition of the amine appears to affect the crystallization process and result in better selectivity, it does not however, become occluded into the framework pores. This work adds another interesting variable to be considered in ionothermal synthesis.

It is apparent that despite the large number of ionic liquids that are available, they will not all necessarily produce new zeotype structures. The synthesis of zeolites is, in general, very sensitive to the various reaction conditions, including the type of reaction vessel used, the nature of the heat source, the addition of HF, and the addition of organics. The SIZ-4 and SIZ-10 (CHA) frameworks have different templates, indicating that the organic is acting more as a space filler than a structure-directing agent according to the definition by Davis and Lobo.[13] The same is true of SIZ-6 or SIZ-11, where the organic cation can be EMIm or 1-isopropyl-3-methylimidazolium, respectively. The AlPO-11 (AEL) structure can also occlude either the EMIm or BMIm cation. To date, the AlPO-5 structure has only been produced ionothermally occluding the BMIm cation; this, however, may change as the research into other ionic liquids continues.

The cobalt aluminophosphates SIZ-7 (SIV), SIZ-8 (AEI), and SIZ-9 (SOD) were all synthesized ionothermally using EMImBr.[28] All have framework topologies different from those of the aluminophosphates previously reported by the ionothermal method. This indicates that the cobalt hydroxide added to the synthesis mixture may contribute an additional structure directing effect on top of that supplied by the organic cation of the ionic liquid. The addition of cobalt hydroxide will also have altered the pH and water content. The hydroxide may react with the phosphoric acid or the acidic hydrogen on the imidazolium ring between the two nitrogen atoms to produce water. Subtle changes in reaction conditions can alter the product selectivity markedly.

The synthesis of the three Co-AlPOs is an indication that the ionothermal synthesis method is suitable for the preparation of transition metal-functionalized frameworks that may be useful for applications such as catalysis or gas adsorption. The preparation of the novel framework topology, SIZ-7, is a further indication of the potential of ionothermal synthesis in the production of new zeotype materials, and it has been given the code SIV by the International Zeolite Association. SIZ-7 can be described as consisting of double-crankshaft chains which run parallel to the crystallographic *a*-axis. This same double-crankshaft chain is found in the frameworks of PHI, GIS, and MER, and how the chains are connected defines the type of framework that is formed (Figure 4).

It is clear that AlPOs and CoAlPOs are accessible using ionothermal techniques, but what about silicates? Most of the industrially relevant zeolite materials are based on silicon, but it is a much more difficult problem for synthetic chemistry as the solubility of silicon species is much trickier to control than that of Al or P. However, the production of a new silicate polymorph framework has been reported as isolated crystals among amorphous material.[52] This result shows that it is possible to ionothermally synthesise pure silicates. The SIZ-12 structure is made up of distorted double-crankshaft chains illustrated in bold in Figure 5. These chains form a layer with each chain being a mirror image of the next. The layers are joined together in an ABAB sequence to give a three-dimensional structure. SIZ-12 has a framework density of 23.92 Si/1000 Å^3 which is comparable to that of quartz, cristobalite, and tridymite which have framework densities of 26.52, 23.33, and 22.61 Si/1000 Å^3, respectively.[47]

Initially, ionothermal synthesis of zeotype materials was investigated using ionic liquids with a bromide anion. Investigations carried out involving the replacement of the bromide anion with PF_6^- resulted in the formation of β-NH_4AlF_4.[53] This was only formed with the addition of phosphoric acid (85 wt % in H_2O), indicating that the water was required for the PF_6^- to undergo hydrolysis to produce HF and PO_4^{3-} before crystallization could take place. The template in this reaction was ammonium. Again, this illustrates how the HF may catalyze the decomposition of the ionic liquid over time.

In an attempt to overcome the effect of HF on the ionic liquid, the anion was changed to TF_2N^-.[26] To date, TF_2N^- has been found to be one of the anions which produces
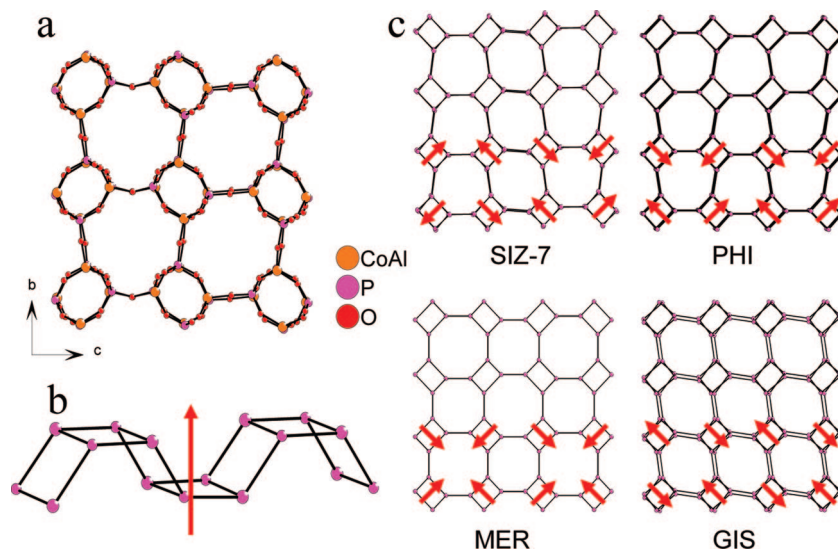
FIGURE 4. Structure of SIZ-7 (a). The crankshaft chains (b) run into the plane of the paper, and the red arrows indicate the relative orientations of the chains in the various related structures (c). For clarity, only the tetrahedral nodes in the structures are shown in panel c.[28]
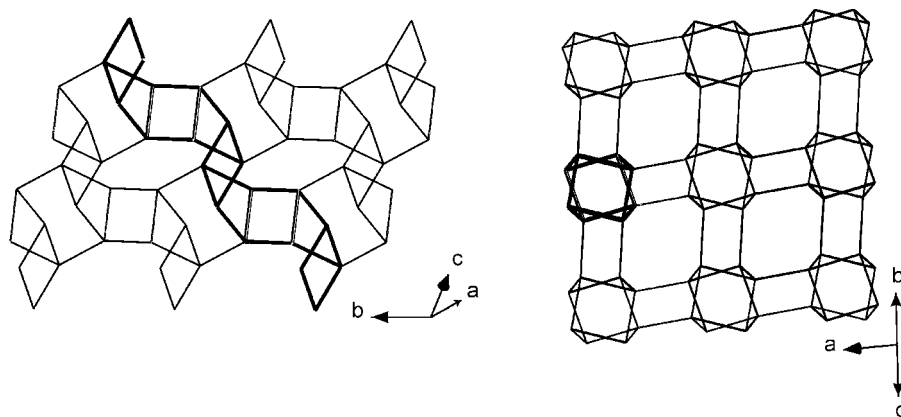

FIGURE 5. Line diagrams of SIZ-12 where each line represents a Si–O–Si linkage: (a) a layer through the structure illustrating the distorted double-crankshaft chain in bold and (b) the three-dimensional structure.[52]

the more thermally stable ionic liquids, with many being stable to well over 500 °C.[54] The chain structure produced, $Al(H_2PO_4)_2F$, however, did not contain any template. This may be due to the ionic liquid being a relatively less polar solvent than the ionic liquid formed using the Br^- anion, reducing the solubility of the starting materials.

Aluminophosphates Synthesized in Eutectic Mixtures

The replacement of the ionic liquid solvent with a eutectic mixture provides a new mechanism by which the solvent also acts as a template delivery agent. The urea derivative slowly decomposes under the reaction conditions to yield a cationic species that acts as the SDA. There are only a few examples in the literature of zeotypes and zeolite analogues synthesized by the in situ generation of a template within the reaction vessel.[55–58] The use of eutectic mixtures allows the control of mineralizer concentration, e.g., water and HF, to be retained while also

providing a new mechanism by which the template is delivered to the reaction mixture.

This synthesis technique has been shown to be very versatile, delivering a number of different templates to aid in the preparation of both AlPOs and GaPOs.[23] Figure 6 illustrates just a small selection of the structures that are formed. Several hundred functionalized ureas are commercially available, and many of these will probably be suitable for this type of work, illustrating the scope of this methodology. The ease of preparation of eutectic mixtures and the different chemistry involved, as evidenced by, for example the first non-fluoride preparation of gallium phosphate Zeolite-A,[23] indicate that this route may be particularly useful for targeting materials that are difficult to prepare in traditional hydrothermal synthesis.

The use of eutectic mixtures in the ionothermal synthesis of aluminophosphates also leads to phases that have been postulated but never isolated in hydrothermal synthesis.[23] Ozin and co-workers[59] postulated that such phases (termed "parent chains") are important in the
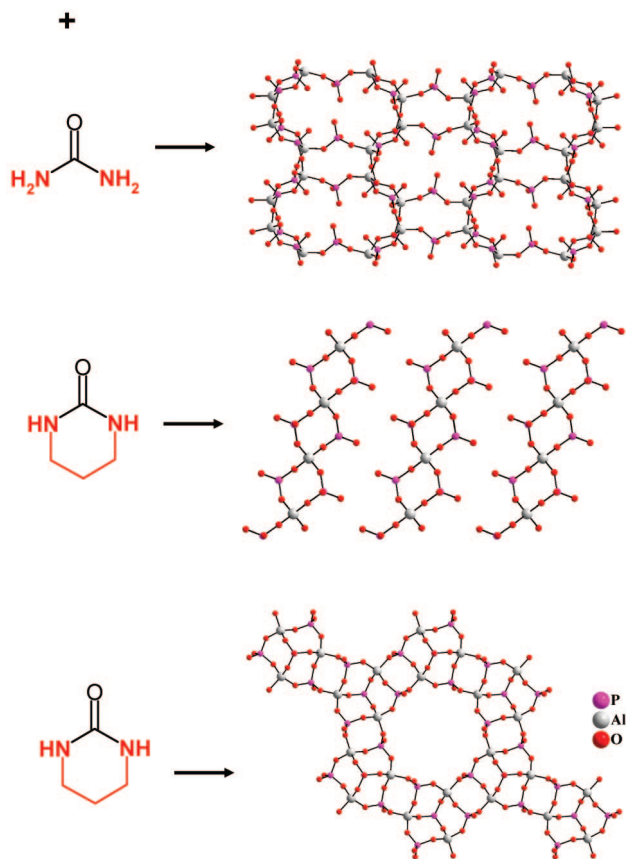
Choline Chloride

+

FIGURE 6. Examples of urea derivatives and the products formed by ionothermal synthesis. Highlighted in red is the section of the urea derivative which acts as the SDA; however, the SDAs have been omitted from the final structures for clarity.[19,23]

mechanism of AlPO formation and suggested that their nonisolation was due to them being hydrolytically unstable. The isolation of several parent chain structures when a eutectic mixture is used as both the solvent and the template provider points to hydrolysis conditions rather milder than those in hydrothermal or solvothermal synthesis, probably a result of water deactivation as described above. The addition of mineralizers such as water and HF can again be carefully controlled, with more water leading to the formation of two- and three-dimensional structures.

Ionothermal Synthesis of Organic–Inorganic Hybrids and Metal–Organic Frameworks

In recent years, the all-inorganic framework solids have been augmented by a vast array of organic–inorganic materials, of which metal–organic frameworks (MOFs) are the most famous. Organic–inorganic hybrids are usually coordination polymers of multifunctional oxygen- or nitrogen-based ligands. Such ligands range from organophosphonates and carboxylates to 2,2′-bipyridine and mixed ligands. The nomenclature of such organic–inorganic hybrid solids has not yet been standardized. However, common usage seems to be that all such materials

are coordination polymers and that MOFs constitute a subset of such materials where the polymerization produces three-dimensional connectivity. Some metal organic frameworks can be made porous by removal of any guest molecules in the voids inside the three-dimensional frameworks.

The first organic–inorganic hybrid material synthesized ionothermally used $BMImBF_4$ as the solvent to synthesize $Cu(bpp)BF_4$ [bpp = 1,3-bis(4-pyridyl)propane].[30] The BF_4^- anions were incorporated into the extended one-dimensional coordination polymer as charge-compensating species, and the $BMIm^+$ remained in solution. The first three-dimensional MOF organic–inorganic hybrid material was synthesized with the same ionic liquid as the solvent and provider of the charge-compensating species, BF_4^-. The structure, $Cu_3(tpt)_4(BF_4)_3 \cdot (tpt)_{2/3} \cdot 5H_2O$ [tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine], has large channels (~5 Å in diameter) which are filled with noncoordinating free tpt, H_2O, and BF_4^-.[31] Figure 7 illustrates both of these structures.

Recent work by Liao et al.[34] reports the ionothermal synthesis of the anionic metal–organic framework EMIm-Cd(BTC) (BTC = 1,3,5-benzenetricarboxylate), using microwave heating. The ionic liquid used as the solvent was EMImBr. Lin et al.[29] similarly synthesized $(EMIm)_2Ni_3$-$(TMA)_2(OAc)_2$ using EMImBr as the solvent. In contrast to the previously mentioned examples of organic–inorganic hybrids synthesized in ionic liquids, these examples incorporate the ionic liquid cation as the SDA and charge-balancing species. This could possibly be due to the different characteristics of the ionic liquids based upon the different anions. It seems that, as with the aluminophosphate solids described above, the more hydrophobic the ionic liquid (those with BF_4^- and Tf_2N^-), the less likely the organic cation is to be incorporated as a template in the final material.

Organic–Inorganic Hybrids and Metal–Organic Frameworks Synthesized in Eutectic Mixtures

Liao et al.[33] reported the synthesis of a novel coordination polymer, $Zn(O_3PCH_2CO_2) \cdot NH_3$, where the solvent was the eutectic choline chloride/urea mixture. The urea partially decomposes and acts as the template delivery agent to produce the structure-directing ammonium ions. Work has also been carried out by Lii et al. using a eutectic choline chloride/malonic acid mixture as the solvent to produce two new open-framework iron oxalatophosphates, $Cs_2Fe(C_2O_4)_{0.5}(HPO_4)_2$ and $CsFe(C_2O_4)_{0.5}(H_2PO_4)$-$(HPO_4)$,[35] and two new metal oxalatophosphonates, $Na_2M_3(C_2O_4)_3(CH_3PO_3H)_2$ (M = Fe^{II} and Mn^{II}).[60] In these syntheses, the eutectic mixture did not form part of the organic–inorganic hybrid material. Both the work by Liao et al. and the work by Lii et al. demonstrate again the versatility and ease of using eutectic mixtures as solvents for the synthesis of open-framework structures.
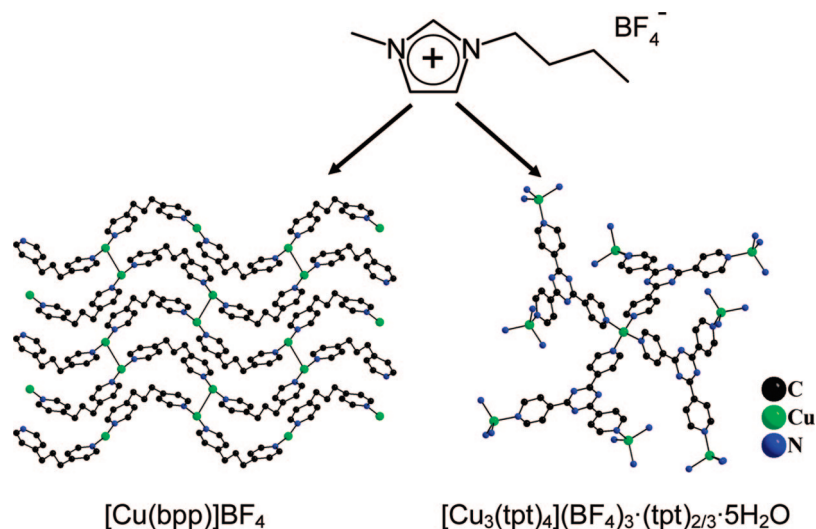
FIGURE 7. Ball-and-stick diagrams for illustrating the two-dimensional and three-dimensional cationic MOF formed using an ionic liquid as the solvent. The guest molecules and charge-compensating molecules have been omitted for clarity.[30,31]

Conclusions and Future

The production of zeotype structures with hanging P–O bonds (e.g., SIZ-1, SIZ-2, and SIZ-6) and one-dimensional chains suggests that ionothermal synthesis may have a slower rate of hydrolysis than in other methods. This may make ionothermal synthesis of zeotypes an ideal methodology for "lego chemistry", i.e., taking a secondary building unit such as a gallophosphate double-4-ring (D4R)[61] as a starting material for the production of three-dimensional zeotype structures. Perhaps under these milder conditions the D4R building units will stay intact and join together to form three-dimensional zeotype structures. This would lead to an attractive mechanistic idea for the design and preparation of molecular sieves that has thus far appeared to be unsuccessful in hydrothermal/solvothermal synthesis.[44]

Another interesting idea is the use of a mixture of different ionic liquids[62] as the solvent and template in zeolite synthesis. As described earlier, changing anions (e.g., from Br^- to Tf_2N^-) leads to great differences in the properties of the ionic liquids. Mixed anion ionic liquids have intermediate properties, which might lead to further control over the products in ionothermal synthesis. Like mixed anion ionic liquid systems, the cations can also be mixed. This would be an interesting study to carry out to see if two products were formed using the different cation templates or if competition of templates leads to just one product being formed.

Perhaps one of the more potentially important areas for future work in ionothermal synthesis is the possibility of synthesizing chiral materials using chiral ionic liquids. Currently, many chiral zeolite frameworks have been hypothetically modeled, but none have been synthesized or found naturally as homochiral materials. If a chiral ionic liquid is used as a solvent and template, is there the possibility of inducing chirality into the zeolite framework or the inorganic–organic hybrid material? Recently, it has been shown that the use of a chiral ionic liquid can induce chirality in the resulting solid (in this case, a coordination polymer), opening a great many possibilities in this area.[63]

At present, ionothermal synthesis has concentrated on the synthesis of porous materials. In principle, ionothermal methods could be used in any of the situations where hydrothermal or solvothermal methods have been used successfully in the past. The range of properties of ionic liquids is very wide indeed, and there should be an ionic liquid that suits almost every possible synthesis, especially when combined with different possible mineralizers. Already, some workers are using ionothermal-like methods to produce interesting new materials, such as unusual germanium semiconducting clathrates.[64]

In conclusion, ionothermal synthesis is a novel methodology for the synthesis of zeotype materials and inorganic–organic hybrid materials. The scope of the synthesis has been demonstrated in this Account with examples, including the synthesis of novel AlPOs, CoAlPOs, GaPOs, MOF, and coordination polymers. Interest in this methodology is growing, and it can be expected that in the near future there will be further publications reporting new and exciting structures and developments.

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