Approaches to crystallization from ionic liquids: complex solvents–complex results, or, a strategy for controlled formation of new supramolecular architectures?

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There are now more than 1200 papers a year describing research results using the 'neoteric' solvents, known as ionic liquids (ILs). If ILs are such highly studied solvents, why has there been so comparatively little research in their use in crystallization? Here we explore this question and discuss possible strategies for utilization of the mundane and the unique aspects of ILs for novel crystallization strategies including crystallization of high and low melting solids using thermal shifts; "solvothermal" techniques; slow diffusion; electrocrystallization; and use of a co-solvent. The results presented here and those appearing in the literature indicate both the complex nature of these solvents and their promise in delivering unique solvation, metal ion coordination numbers, coordination polymer motifs, and metal–anion interactions, to name but a few. These complex, but fascinating, results and the promise of much more intimate control over crystallization processes will drive a growing interest in using ILs as crystallization solvents.

What are ionic liquids anyway?

The most generally accepted definition of an ionic liquid (IL) is an ionic salt that melts below 100 °C. ILs are not new materials of course—they have been known for over 100 years[1]—but a renewal of interest arose from a new way of thinking about these low melting salts as solvents, specifically as VOC replacements.[2–5] Now, the current research areas are quite diverse, with applications in such areas as battery electrolytes, separations, lubrications, life sciences, and catalytically active

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solvents for synthetic chemistry, to name but a few.[5–8] The research in these areas has led to increased understanding of the features required to produce ILs and a resulting phenomenal growth in the discovery of different types of salts that can support low melting IL phases.

Common examples of cations and anions, which have been most widely investigated as ILs, are shown in Fig. 1, however, this list is by no means exhaustive, many new ILs are being identified and studied almost on a daily basis. Hundreds of ILs are commercially available from major sources, such as BASF, Merck KGaA/EMD Chemicals, Aldrich, Solvent Innovations, *etc*. As we will discuss below, the choice of IL cation and anion to be studied should be based upon the type of process one is to employ and the specific interactions desired, and not based on what is in popular usage.

One of the unique attributes of ILs is the ability to fine-tune their physical (*e.g.*, density, viscosity, melting point) and chemical (*e.g.*, solvent) properties by selection of the appropriate cations and anions.[9,10] Control of the properties of an IL is based on manipulating the interactions between the ions; suppression of these interactions reduces lattice energies and extreme suppression of these interactions leads to glass formation upon cooling, polymorphism, multiple phase transitions, and ion dissociation.[11,12] An understanding of the physical and chemical properties of ILs allows the proper selection of a specific IL for a given application. Thus, for example, by choosing ionic components capable of solubilizing specific solutes, one can control solubility critical to crystallization processes.

Several properties of many currently studied ILs may be advantageous in a crystallization process. ILs have a tendency to supercool, which gives many of them fairly wide liquidus operating ranges (in some cases as large as 200–300 °C) and provides thermal operating windows not possible with conventional solvents. Thus, ILs may provide unique opportunities to use much higher and much lower temperatures for a process in a single solvent.

ILs also typically possess higher viscosities than traditional organic solvents, a potential process advantage or disadvantage. The increase in viscosity, while not attractive for bulk crystallizations, can be important in crystal engineering, where slow crystal growth from diffusing solvents is an advantage.

Along with the tunability of the physical properties, IL solvent properties can also be tuned to suit a particular crystallization need by adjusting the intermolecular and interionic interactions present in the solvent. Published analyses of IL solvent properties, although limited to date, allow some insight into the nature of these interactions. The solvent properties of ILs can be used to explain such diverse observations as the formation of liquid clathrates with aromatic compounds,[13] selectivity and accelerated reaction times of organic reactions,[14] and the unique solubilities of some materials in the ILs.[15]

One solvent property important for crystallization is the ILs' hydrogen bonding ability. Just as indicated above for the IL physical properties, the solvent properties can also be modified based on the choices of cation and anion components. Thus, when it is desirable to match a known solvent such that an IL can be used as a replacement or where unique solvation is needed, IL solvent properties can be adjusted to increase or decrease the interactions between the IL and the solute.

It is important to note here that it is the unique and tunable physical and solvent properties which separate this class of liquids from molecular liquids and electrolyte solutions. A comparison of the solvent properties of organic solvents and ILs shows that ILs are typically more structured than organic solvents.[16] While ILs are indeed composed of ions, the structure of the liquid depends on the many interactions specific to the cations and anions present. Imidazolium-based ILs with short alkyl chains form coulombic materials, while

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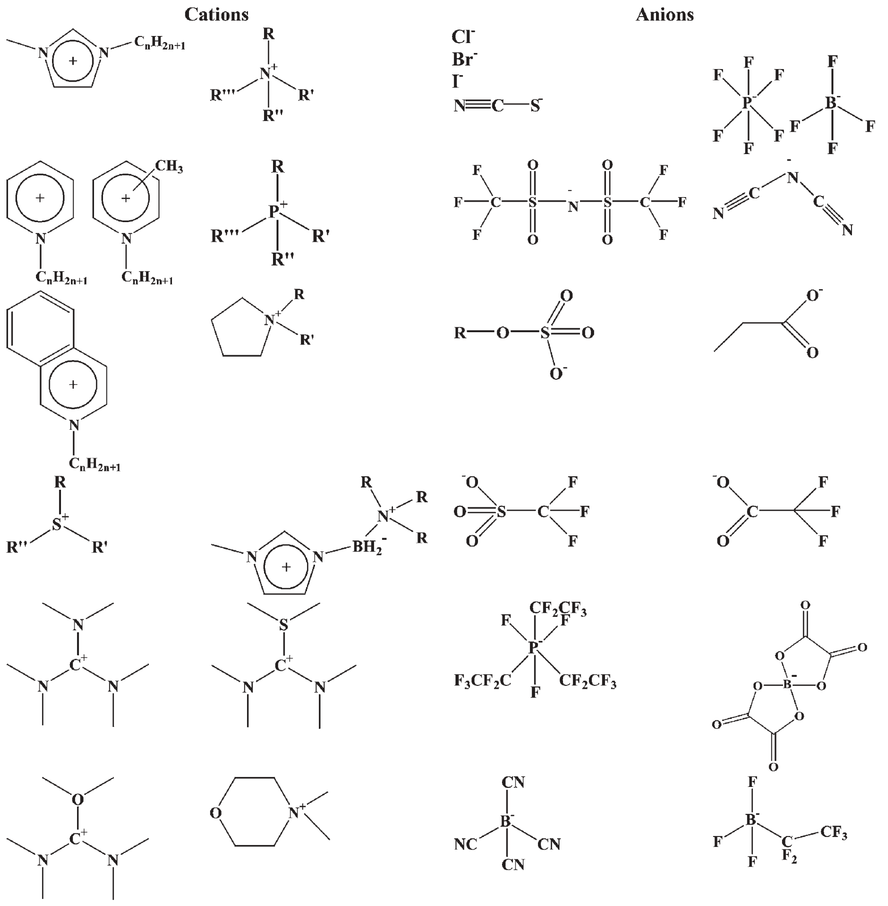

Fig. 1 A sampling of commonly used cations and anions in the formation of ionic liquids.

separation of the ions by changes to the cation and anion can lead to liquids with weaker coulombic interactions.[9,17] Current analysis of the interactions present in certain ILs in the solid state and liquid state, suggest a loose ion lattice similar to that found in salt crystal lattices, a cation surrounded by several anions and *vice versa*.[18,19] It is also becoming increasingly apparent that ILs should not necessarily be considered as totally charge-separated 'free' ions.

The unique physical and solvent properties of ILs and the ability to tune these properties lead one to the conclusion that the investigation of crystallization approaches and processes from IL solutions is both necessary and desirable. There is every expectation that such studies could lead to controlled crystallizations, enhanced processes, and formation of new supramolecular architectures. This leads to our next question:

Why, then, has there not been more[20] extensive study of the use of ILs for crystallization?

There actually may be several answers to the stated question. The first, rather simplistic, view is that the much hyped, non-volatility of many ILs is not conducive to crystallization studies from the many practitioners that use evaporation of solvents (slow or fast) to purify reaction products. However, just because ILs are not volatile does not mean they cannot be used as crystallization solvents!

There are challenges and opportunities for the use of any crystallization solvent and ILs are no exception. One challenge to the use of many ILs is indeed non-volatility under normal conditions. IL solvents usually cannot be purified before or after use by distillation and crystallization (although a recent paper by Rebelo, Seddon *et al.* showed that, under extreme conditions, ILs could in fact be distilled and therefore purified),[21] and the presence of even minor impurities in an IL solvent is known to dramatically affect the physical and solvent properties of the IL.[22] Perhaps even more importantly for crystallizations, such impurities could result in crystallizations that are not reproducible. Even now, one has to wonder if these impurities (and ILs are sometimes notoriously difficult to purify) are responsible for the limited crystallization results reported in the literature.

Although perhaps challenging at times, ILs are in fact recyclable, with the techniques used based on the impurities to be removed. Two such techniques under current investigation include use of supercritical CO_2[23] and "salting out",[24] although one can envision the use of ion exchange resins, pervaporation (for volatile impurities),[25] solvent extraction, *etc.*, to name but a few. Needless to say, new techniques and approaches for purification of ILs are currently being investigated in many labs worldwide.

Perhaps more challenging reasons for the limited study of ILs as crystallization solvents have their origins in just the type of advantages discussed in the opening section of this article.

The complexity of IL solvents (even pure ILs) makes it difficult to predict how crystallizations will behave; and the sheer number of possible ILs makes a rational choice of crystallization solvent a process sure to lead to a headache! The many possible interactions between the ions and between the ions and the solute can lead to unexpected results, making predicting the resulting crystal structure very difficult, and thus increasing the difficulty of crystallization, much less crystal engineering, in the short term.

Why then should ILs be studied as crystallization solvents?

The proper choice of IL ions allows one to use a solvent which consists of an 'unsolvated ion'-rich environment, where one or both ions can be chosen to have specific intermolecular (or interionic) interactions, and thus be, for example, highly solvating or essentially non-coordinating. This means unique environments can be created for solutes allowing for tailored solubility, novel crystallization strategies, and perhaps access to unique solid-state environments. Recently, Mudring and co-workers have illustrated the unique environment ionic liquids provide for lanthanide chemistry.[26–28]

In addition to the unique interionic interactions and solute environments that are possible with ILs, another aspect deserves some attention when considering using ILs for crystallization: ion shape. Many IL ions are bulky, of low symmetry, and flexible by design; these properties being understood to contribute to low lattice energies due to poor packing, and thus to the characteristic low melting points of these salts. The effects of these ion properties on crystallizations are yet additional design advantages (or yes, potential disadvantages as well).

Let us consider briefly the well-studied IL ion, the 1-butyl-3-methylimidazolium cation ($[C_4mim)]^+$) and the popular hydrophobic anion bis(trifluoromethanesulfonyl)imide ($[NTf_2]^-$), both depicted in Fig. 2. The ions' flexibility can inhibit the formation of crystalline solids (which is why many ILs have the tendency to form supercooled liquids), and lead to polymorphic solids as observed for $[C_4mim]Cl$.[29,30] However, this same ion flexibility can also provide unique opportunities for crystallization strategies. The rotational flexibility and variability of ion size can create unique templating[31] effects or cavities in the formation of unique crystal lattices. In addition, one may chose appropriate IL components to create unique ion-rich solvent environments, which may help stabilize, for example, polyanionic or polycationic frameworks.

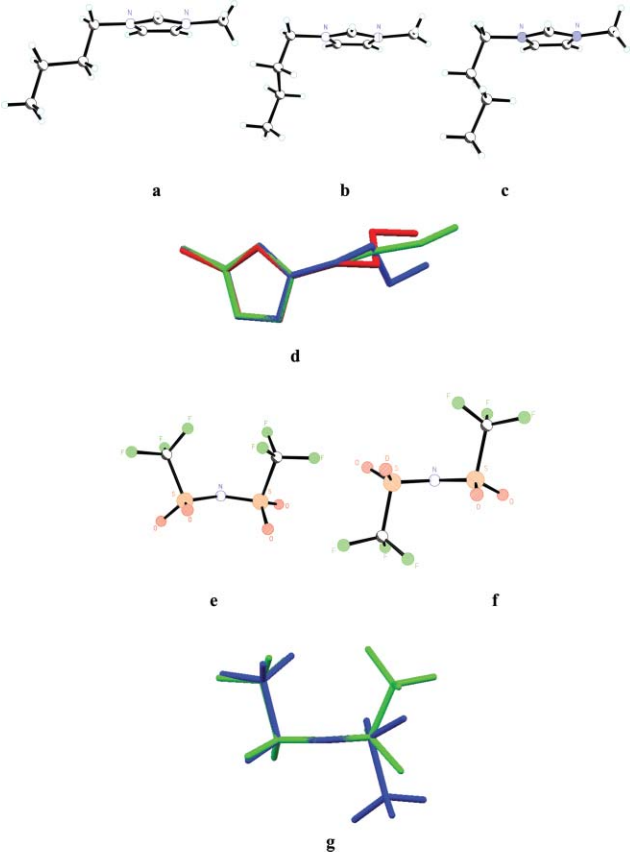

Fig. 2 Representations of the orientational flexibility of a common IL cation and anion: (a) $[C_4mim]^+$ found in the monoclinic polymorph of $[C_4mim]Cl$;[30] (b) $[C_4mim]^+$ found in the orthorhombic polymorph of $[C_4mim]Cl$;[30] (c) $[C_4mim]^+$ found in $[C_4mim][PF_6]$;[32] (d) overlay of (a) (green), (b) (blue), and (c) (red); (e) *cis* conformation of the anion in $[C_1mim][NTf_2]$; (f) *trans* conformation of the anion in $[C_2C_2C_2im][NTf_2]$;[33] (g) overlay of (e) (green) and (f) (blue).

If you can't evaporate ILs, how can they be used in crystallization strategies?

A list of the relatively few crystallization techniques explored to date in the literature, and indeed in our labs, would include (a) solvothermal (or ionothermal) techniques[34,35] (where ILs may have the advantages of high thermal stability and low vapor pressures); (b) use of thermal shifts (where ILs may be chosen with a large liquid window allowing both high and low temperature crystallization in the same solvent); (c) use of a co-solvent to help increase solubility and allow evaporation to reduce solubility (where ILs may be chosen which have a wide range of dissolving powers); (d) slow diffusion (where the relatively high viscosity and densities of many common ILs can be used to advantage); (e) electrocrystallization (where the conducting nature of the solvent could be used to advantage), and; (f) use in the preparation of nanoparticles and zeolites[31,36] (where ILs may stabilize particles uniquely or serve as templates in crystallizations). The list of possible crystallization techniques is, of course, much more extensive, and perhaps limited at this point only by one's imagination in using the unique properties of ILs to accomplish a given crystallization.

No matter which crystallization technique is employed, the first step is to find an IL in which the solute or reagents are soluble or partially soluble. This may actually be harder than anticipated, despite the much-touted ability of ILs to dissolve practically anything! What is often missed in these statements, is the fact that it is not a single IL that will dissolve everything, rather that one can find a specific IL to dissolve almost any solute. Thus, the initial selection of IL (*e.g.*, hydrophilic, hydrophobic, strong hydrogen bond donor/acceptor, coordinating/non-coordinating, *etc.*) is actually a critical first step in the successful use of an IL in any crystallization strategy.

In some instances, a solute may be introduced into an IL by the use of a co-solvent. That is an organic solvent (*e.g.*, acetonitrile) can be used to solubilize (for example) a metal salt, which is then introduced into the IL. The amount of co-solvent can typically be very small in relation to the IL, just enough to solubilize the desired amount of solute. The co-solvent may then be evaporated (at almost any temperature since the properly chosen IL will not evaporate!) or retained for the subsequent crystallization strategy.

Once an IL with the appropriate physical and chemical properties is selected, the easiest and most underutilized (or recognized) method of crystallization is simply employing heating and cooling to shift solubility and induce crystallization. A potential reason for overlooking the full potential of ILs using thermal shifts, is that we simply are not used to using solvents which have such a large (perhaps as high as 400 °C) liquid window. There are a few papers which detail some high temperature crystallizations and a few which utilize low temperature crystallization, however, no one has yet utilized the range of accessible temperatures in an effective way (as for example, in the control of polymorphism) with a single IL.

ILs may have specific advantages over traditional solvents when used at high or low temperatures. For example, high temperature 'solvothermal' techniques usually result in high pressure build up which has restricted the use of this technique with volatile solvents to special vessels. For those ILs with negligible vapor pressure and high thermal stability, such high temperature routes may not require pressure vessels, making this crystallization technique more widely available.

Given the often high viscosity of ILs, slow diffusion techniques can easily be employed for crystal engineering, where, for example, a solute in IL solution is carefully layered onto a second IL solution of another reagent. Interestingly, the second IL solution may be the same or a different IL.

What is certainly clear at this point, is that a more detailed knowledge of the type of interactions possible within an IL and between IL ions and solutes, and detailed solubility studies in ILs, are needed to provide insight into choosing the proper IL for a specific crystallization strategy. With this increased fundamental knowledge, crystallizations and crystal engineering in these unique solvents will become easier and predicting structures prior to experimentation more common place. Until we reach that level of understanding, however, a more Edisonian approach will be followed by necessity. Here then, lets explore a few early results from our laboratories and, where appropriate, some examples appearing in the literature.

What do the early IL crystallization and crystal engineering results tell us?

Zaworotko and co-workers published one of the earliest crystallizations from an IL medium, metal ion complexes were crystallized and characterized.[37] An Fe(III) complex, *trans*-difluorotetrakis(1-methylimidazole)iron(III) tetrafluoroborate, was crystallized from a reaction of $CpFe(CO)_2I$ and $AgBF_4$ in the protonated IL 1-methyl-3-*H*-imidazolium tetrafluoroborate, $[MeHim][BF_4]$ (Fig. 3a), at 100 °C for 10 h. The reaction revealed that the IL cations were deprotonated and coordinated the metal centers, resulting in the isolation of a metal complex with BF_4^- counterions.

The Mo(II) compound, [1-methylimidazolium]$_2$[*cis*-MoO_2(salicylato-O^1,O^2)$_2$] was crystallized from a molten mixture of 1-methyl-3-*H*-imidazolium salicylate (Fig. 3b) and $Mo(CO)_6$ held at 90 °C for 4 days. In this case, the salicylate anion coordinated to the metal center forming a complex anion.

These early reactions in ILs with crystallization from the IL of unintended products, illustrate one of the challenges in utilizing ILs for crystallization (and indeed as solvents in general): not all ILs are as non-coordinating as they are touted to be. Multi-component ILs are often not innocent bystanders and can play a bigger role in the chemistry than just as the solvent, and examples of the incorporation of the cation or the anion or both in crystal structures have been observed in our research. We will discuss this in more detail later, but first, let us look at the early specific uses of ILs to crystallize solutes or prepare crystal engineered solids.

Crystallization using thermal shifts

One of the easiest IL crystallization strategies is to change the temperature of the solvent in order to change the solubility of the solute. Although there are currently not enough data to reliably predict how changes in temperature affect the solubility of solutes in ILs, this is a major focus of research in many laboratories. In the meantime, the very wide liquid range and thermal stability of many ILs makes this crystallization methodology exceptionally appealing. Indeed, because of the possible wide liquidus window, crystalline materials with high or low melting points can be crystallized at their respective freezing temperatures in an IL solution. Let us examine two simple examples involving high (catechol) and low (acetophenone) melting points.

Catechol: crystallization of higher melting solids.[38] Catechol is an aromatic molecule that one would expect to have high solubility in many hydrophobic ILs based upon the ready formation of liquid clathrates with aromatic solvents and ILs.[13] However, at room temperature, catechol (mp 105 °C) is only slightly soluble, if at all, in such ILs, with no noticeable dissolution in the IL 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_8mim][NTf_2]$) after stirring for 1 h.[39] Heating a mixture of solid catechol (as a dull grey to black solid) and ($[C_8mim][NTf_2]$ to 110 °C resulted in melting and subsequent dissolution of the catechol to form a homogeneous

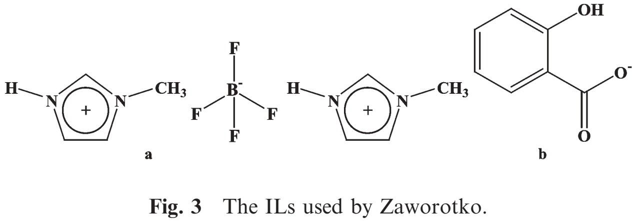

Fig. 3 The ILs used by Zaworotko.

single phase. Slow cooling of the solution from 110 °C to 90 °C over 8 h using a programmable oven, yielded long colorless needles of catechol, which were recovered from the IL by filtration. Subsequent single crystal XRD analyses of the isolated crystals confirmed the original structure as published by Brown[40] and later by Wunderlich and Mootz.[41] The IL did not disrupt or change the hydrogen bond network found in crystalline catechol.

Acetophenone: crystallization of lower melting solids. Due to the wide liquid range available to many ILs, low temperature crystallizations are also possible. One such example is the crystallization of acetophenone (mp 20 °C) from the same IL utilized above, [C_8mim][NTf_2]. At room temperature, acetophenone is soluble in the IL and upon cooling the solution, to approximately 0 °C, crystallizes from the IL.[42]

Using a thermal shift to crystallize a solute around its melting point is, of course, only one way to induce crystallization. A more common approach would be to use temperature to change the solute's solubility and induce crystallization in this fashion. In either case, however, the possibility for relatively large changes in temperature (at least compared to many volatile organic solvents) opens the door to some unique crystallization strategies.

Purification strategies can be envisioned using crystallization from an IL at higher or lower than 'normal' solvent temperatures at atmospheric pressure with no loss or crystallization of the solvent. ILs may also have a role in the investigation of metastable polymorphs, where, for example, McCrone has suggested the use of high boiling solvents.[43] The low or negligible vapor pressures of many ILs also open up new applications for crystallization in a vacuum.

"Solvothermal" techniques

There have been a few papers describing the use of IL solvents for reaction and crystallization at high temperature in a sealed, evacuated vessel, essentially solvothermal crystallization techniques. In 2002, Jin *et al.*[34] reacted a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ and 1,3-bis(4-pyridyl)propane (bpp) in [C_4mim][BF_4] in a sealed glass tube under vacuum. The reaction was carried out at 140 °C for 3 days, leading to the isolation of the metal coordination complex [Cu(bpp)][BF_4], a product of reduction of Cu(II) to Cu(I), coordination, and ion exchange. The structure consists of cationic polymeric layers of $[Cu(bpp)]^+{}_n$ where adjacent layers alternate directions, with the $[BF_4]^-$ anions separating the layers. This arrangement forms alternating sheets of polymeric cation/ligand and anions with closest contacts to the metal centers of *ca.* 2.57 Å.

In 2004, Dybtsev, *et al.*[35] carried out essentially the same reaction using 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tptz) rather than bpp. $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in [C_4mim][BF_4] with tptz was sealed in a glass tube at 170 °C for 2 days resulted in violet crystals of $[Cu_3(tptz)_4][BF_4]_3 \cdot (tptz)_{2/3} \cdot 5H_2O$. The polymeric Cu–tptz structure is more complex than the simple components would first imply. The structure is composed of tetrahedral Cu^+ metal centers and tptz nodes connecting the metal centers. The extended 3D framework forms cavities throughout the structure, composed of four metal centers and four ligands. Once again, the IL solvent provides an anion for the final crystalline product. We will address this issue of IL participation again later.

Both of the above studies illustrate an IL's ability to serve as a thermally stable solvent and provide examples of the complex nature of ILs, which makes predicting crystal structures more difficult. One wonders, however, if sealed and evacuated conditions (normal for solvothermal techniques) are required for IL solvents and the term 'ionothermal' may indeed be more appropriate as suggested by Cooper, *et al.*[31]

Slow diffusion

Crystal engineering strategies that rely on the coordination of, for example, a metal and ligand with controlled crystallization of a polymeric framework, can take advantage of the high densities and viscosities of many ILs by making use of the very slow mixing and diffusion of the reactants. The reactants can be dissolved in different, complementary, or even identical ILs and then layered such that they slowly diffuse together or that the reactants slowly diffuse into a common homogenous phase. The relatively high viscosities of the ILs can help promote the growth of high quality crystals by allowing slow mixing and controlled rates of crystal growth.

Certainly, the use of different ILs would yet again increase the complexity of the solvent system, however, this may be a viable alternative allowing the required solubility of the metal or ligand. Indeed, the complex nature of the ionic system may create unique crystallization environments as will be discussed below.

$[Co(H\text{–}tptz)Cl_3] \cdot H_2O$: a coordination complex and effects of impurities.[44] First, let us explore an attempted crystallization of a Co(II)/2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) coordination complex. Layering a solution of $CoCl_2$ dissolved in *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ([C_4C_1pyr][NTf_2]) onto a solution of tptz in the same IL, resulted in a progressive color change at the interface from blue (Co solution) to orange-red, and finally in formation of yellow-orange crystals of $[Co(H\text{–}tptz)Cl_3] \cdot H_2O$.[44]

The crystal structure revealed the protonation of the uncoordinated pyridyl group in the tptz ligand and the incorporation of water of hydration. While this result does indicate such simple crystallization experiments are quite readily performed, it also illustrates one of the well known limitations of the utilization of ILs as solvents; many ILs are very difficult to dry completely and are most often intrinsically hydroscopic; exposure to the atmosphere typically results in adsorption of some water.

$[Co(OH_2)_2(bipy)_2][NTf_2]_2 \cdot [C_4mim][NTf_2]$: coordination polymers, ion exchange, and IL "solvates".[45] This complex was prepared by layering 0.1 M 4,4′-bipyridyl (bipy) in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_4mim][NTf_2]) onto a 0.1 M solution of $Co(BF_4)_2 \cdot 6H_2O$ in the same IL. As the two layers slowly mixed, pale pink rectangular crystals of $[Co(OH_2)_2(bipy)_2][NTf_2]_2 \cdot [C_4mim][NTf_2]$ formed at the interface. The structural analysis of this coordination polymer reveals some subtle, yet interesting differences from a similar structure reported in the literature.

The complex (whose asymmetric unit is shown in Fig. 4), consists of an octahedral Co^{2+} center coordinated to four bipy ligands (forming a polycationic 2D grid) and to two *trans* water molecules which reside above and below the plane of the grid. Several features of the crystalline product illustrate more potential pitfalls and opportunities in the utilization of IL crystallization solvents.

First, crystallization occurred with the more hydrophobic (for this particular structure) and most abundant anion, $[NTf_2]^-$, rather than the minor BF_4^- component. (While perhaps a $Co(NTf_2)_2$ salt could have be used in the synthesis, this would have been dramatically more expensive; nonetheless, this strategy would have eliminated any uncertainty about which anion would crystallize with the product.) Second, in addition to the $[NTf_2]^-$ anions, which balance the charge carried by the cationic framework, one formula unit of the IL itself, is present per Co^{2+} metal center. (We shall examine later, whether we should call this a 'solvate' or not!)

The alkyl chain in the $[C_4mim]^+$ cation adopts an all *trans* configuration similar to that observed for this cation in the monoclinic form of $[C_4mim]Cl$ (Fig. 2a), but with a slightly different twist in the alkyl chain as depicted in Fig. 5. The difference can be quantified by the C–N–C–C torsion angle of -83.1° (blue) in the monoclinic $[C_4mim]Cl$ structure and -98.2° (green) in this structure.

All three of the unique $[NTf_2]^-$ anions have the higher energy *cis* conformation (Fig. 5b) with small differences in the dihedral C–S···S–C angles, 28.4(6), −32.1(4), and −49.2(5)°. (We have discussed previously[33] how close interactions between the IL ions can force the $[NTf_2]^-$ anion into the *cis* conformation, which is more commonly observed in the crystal structures of this anion with Group 1 metals.[46]) Even in these closely related conformations, structural variations are evident (Fig. 5b).

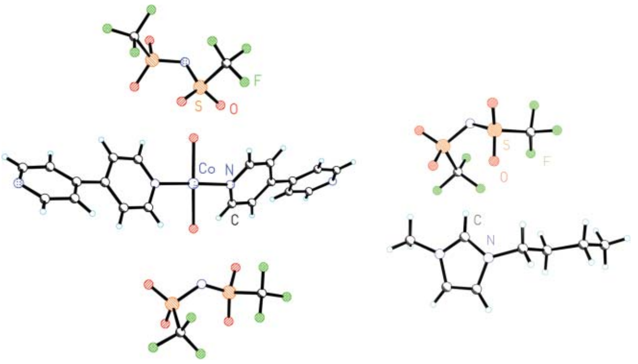

Fig. 4 Asymmetric unit observed for $[Co(OH_2)_2(bipy)_2][NTf_2]_2\cdot[C_4mim][NTf_2]$. (Hydrogen atoms were not located for the two coordinated water molecules.)

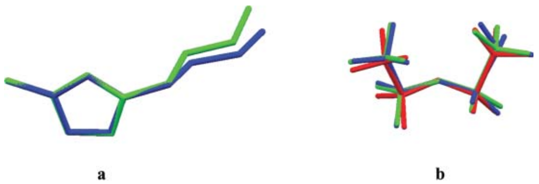

Fig. 5 Overlay of (a) the imidazolium cations in $[C_4mim]Cl$ (monoclinic form, blue) and in $[Co(OH_2)_2(bipy)_2][NTf_2]_2\cdot[C_4mim][NTf_2]$ (green), and (b) overlay of the three unique anions in the latter structure.

The three unique anions and one imidazolium cation per Co^{2+} metal center, provide a rather unique mix of charges and ions. As a result, the 2D Co^{2+}–bipy polycationic grid is similar to, but subtly different from that found by Felloni *et al.* using a 6 : 1 ligand to metal ratio of $Co(NO_3)_2$ and bipy in hot methanol with diffusion of Et_2O vapor to crystallize $[Co(OH_2)_2(bipy)_2][NO_3]_2\cdot 2(bipy)\cdot 2H_2O$.[47] A comparison of the two Co^{2+}–bipy grids is provided in Fig. 6.

The metal···metal distances in the IL structure (Fig. 6 left) are symmetrical at 11.43 Å through either ligand; however, in the Felloni structure these distances are longer and have small variations (11.48 Å *vs.* 11.50 Å). The differences appear to be a result of differences in the twist of the bridging bipy ligands. The torsion angles between the two 6-membered rings of each ligand are more nearly the same in the IL structure (36.8, 25.6°) than observed by Felloni (−27.4, −0.1°).[47]

Viewed side-on to the sheet (Fig. 6 middle), the IL structure (left) shows the angular twist of both bipy ligands and is the same from either direction. The Felloni structure (right) shows a similar angular twist when viewed down one axis, but viewed down the other axis, the more nearly planar bipy ligand orientation is obvious. The differences in separations between the metal ions within the grid for the Felloni structure also result in the observed offset of the location of the water molecules when the grid is viewed edge on (Fig. 6 middle right).

Both structures pack in layers (Fig. 6 bottom) and include solvent or uncomplexed molecules in the crystal structure. However, the IL structure crystallizes with IL-like layers separating the 2D polycationic grids (and an additional anion more closely associated with the grids). This results in a layer-to-layer separation of 10.11 Å for the IL structure, while the layers in the Felloni structure are only 7.86 Å apart. Clearly, the use of different ILs and solutes could result in grids with variable interlayer separations, similar to what one observes for clay-like systems.

Use of a co-solvent

As stated earlier, it is not always easy to find an IL that will dissolve every desired solute. ILs are often designed to not be strongly solvating. However, in such cases, it is often possible to use a volatile co-solvent, which will dissolve a reactant solid, overcoming the lattice energy, at which point this solution can be added to the IL and the co-solvent kept or removed by, for example, evaporation. As shown below, the addition of small amounts of a co-solvent like acetonitrile can increase the solubility of many metal salts in a given IL but, at the same time, the addition can add more complexity to an already complex solvent system.

$[Pd(pyrimidine)_2(OAc)_2]$: IL and co-solvent in the crystallization of a solvent-free monomeric coordination compound.[48] Palladium(II) acetate could not be dissolved directly in pure $[C_4mim][NTf_2]$, however, the addition of a small amount of

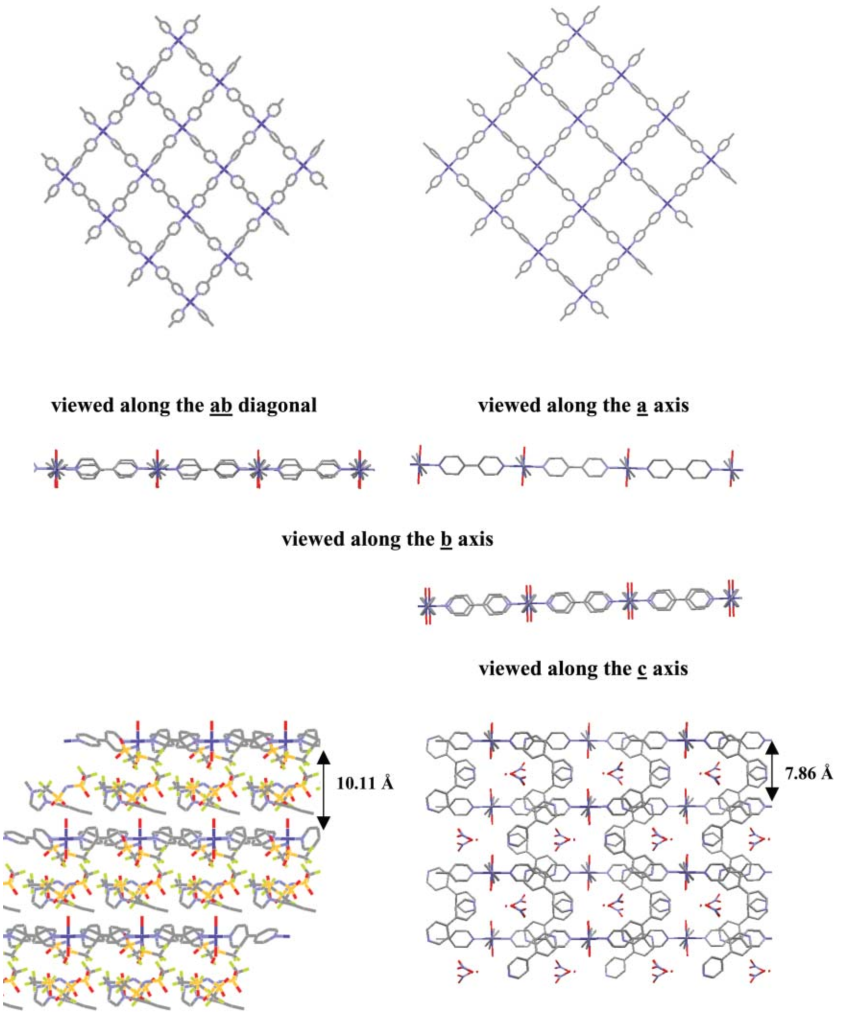

Fig. 6 A comparison of the 2D Co^{2+}–bipy cationic grids and their stacking in $[Co(OH_2)_2(bipy)_2][NTf_2]_2\cdot[C_4mim][NTf_2]$ (left) and $[Co(OH_2)_2(bipy)_2][NO_3]_2\cdot 2(bipy)\cdot 2H_2O$[47] (right). (Hydrogen atoms have been omitted for clarity.)

CH_3CN (12 : 1 IL : CH_3CN) allowed the preparation of a 0.33 M $Pd(OAc)_2$ solution in the mixed solvent. This solution was mixed with a 0.33 M solution of pyrimidine dissolved in $[C_4mim][NTf_2]$ to a final 1 : 1 molar ratio. As the acetonitrile was slowly evaporated, crystals grew from the solution.

Neither the weakly coordinating IL nor the co-solvent appears in the final structure (Fig. 7). The square planar Pd^{2+} is coordinated to two *trans* monodentate acetate anions and two *trans* pyrimidines. The Pd–O distance is 1.997(1) Å, while the uncoordinated oxygen atoms reside 3.065(2) Å from the metal center. The metal coordination complexes exhibit π-stacking (pyrimidine···pyrimidine close contacts at 3.8 Å) and close contacts between the uncoordinated oxygen and pyrimidine hydrogen atoms from neighboring complexes at a distance of 2.39(3) Å.

$[Ag(pyrimidine)][NO_3]$: IL and co-solvent in the crystallization of solvent-free "crystal engineered" squares available from traditional routes.[49] In 1998, we[50] reported the crystallization of Ag–pyrimidine supramolecular squares by the slow diffusion of a methanolic solution of pyrimidine layered over $AgNO_3$ in CH_3CN (Fig. 8). In an attempt to repeat that synthesis in an IL, a small amount of CH_3CN (12 : 1 IL : CH_3CN) was added to $[C_4mim][NTf_2]$ to effect dissolution of $AgNO_3$ in the IL. Since pyrimidine is directly soluble in this IL, a 0.33 M solution of pyrimidine in the IL without any co-solvent was slowly added to the Ag^+ solution (to a final molar ratio of 1 : 1 Ag : pyrimidine) and the CH_3CN allowed to slowly evaporate.

Crystals of $[Ag(pyrimidine)][NO_3]$ formed at the air/IL interface and were determined by complete XRD analysis to be the same structure as we published previously. Thus, even in relatively complex solvent systems, it is possible to mimic crystal engineering strategies utilizing traditional organic solvents.

$[Ag(pyrimidine)_2][PF_6]\cdot 0.5H_2O$: two different ILs and co-solvent resulting in anion exchange, but without "solvent" inclusion.[51] In another attempt to develop unique supramolecular motifs from ILs, 0.0005 moles of $AgClO_4$ were dissolved in 3 mL of $[C_4mim][PF_6]$ containing a small amount of CH_3CN (12 : 1 IL : CH_3CN) and a 0.33 M solution of pyrimidine in $[C_4mim][NTf_2]$ was added to give a final molar metal : ligand ratio of 1 : 2. Despite the complexity of the

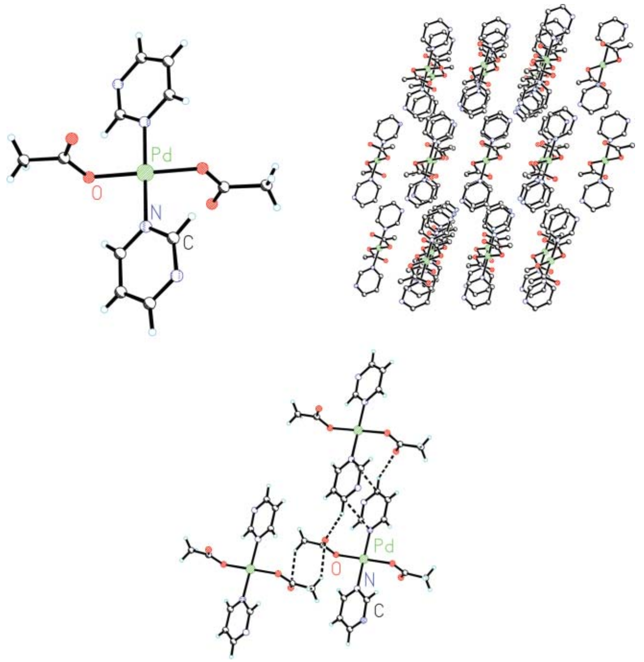

Fig. 7 $[Pd(pyrimidine)_2(OAc)_2]$ (top left), packing diagram (top right), and close contacts between the complexes (bottom).

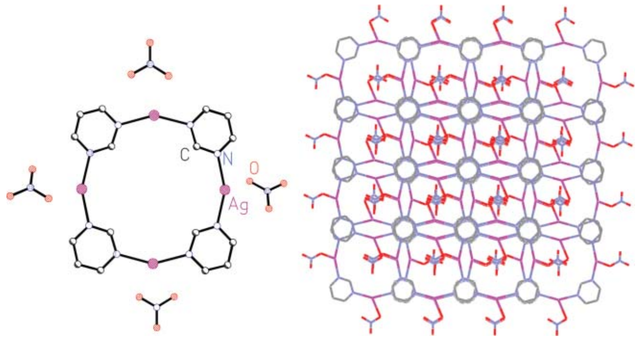

Fig. 8 Tetracationic squares and packing diagram of $[Ag(pyrimidine)][NO_3]$ obtained here from ILs and in ref. 50 from conventional solvents.

medium used, the resulting structure, $[Ag(pyrimidine)_2][PF_6]\cdot 0.5H_2O$ is identical to that we obtained earlier by the layering of methanolic solutions of pyrimidine and $AgPF_6$ in a metal : ligand ratio of 1 : 2 (Fig. 9).[52]

$[Ag(CH_3CN)(bipy)][NTf_2]\cdot CH_3CN$: IL and co-solvent resulting in anion exchange and inclusion of the co-solvent.[53] Using the same strategy as noted earlier for $[Ag(pyrimidine)][NO_3]$, but substituting 4,4′-bipyridine (bipy) for pyrimidine, resulted in the crystallization of a linear cationic polymer comprised of three coordinate Ag^+ with terminal N-coordinated CH_3CN and two bridging bipy ligands (Fig. 10a). The $[NTf_2]^-$ anions (in the *cis* conformation) and non-coordinated CH_3CN molecules complete the structure.

The Ag–bipy chains interact with neighboring chains *via* $Ag^+\cdots\pi$ (*ca.* 3.61 Å) and $\pi\cdots\pi$ (*ca.* 3.56 Å) interactions, resulting in 2D layers approximately one bipy wide. The closest anion contacts are Ag···O interactions (*ca.* 2.96 Å) and H(bipy)···O contacts (*ca.* 2.46 Å). The anions and coordinated and uncoordinated CH_3CN molecules form a double layer between the 2D layers of stacked Ag–bipy polymers with a large 14.8 Å separation (Fig. 10c).

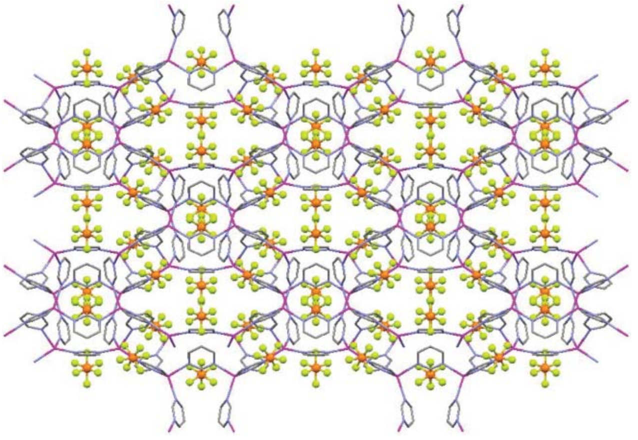

Fig. 9 Packing diagram of $[Ag(pyrimidine)_2][PF_6]\cdot 0.5H_2O$. obtained here from ILs and in ref. 52 from conventional solvents. Two different four coordinate Ag^+ nodes result in tetracationic and octacationic supramolecular assemblies and the extended packing depicted here along the *c* axis.

The Ag–bipy chain is related to similar chains observed in $[Ag(bipy)NO_3]_n$[54] and $[Ag(CH_3CN)(bipy)][BF_4]\cdot H_2O$ (Fig. 10b).[55] In the former, *trans* monodentate coordination of the Ag^+ ions to the anions precludes any interchain interaction, however, in the latter, the chains are offset and close pack as a result of both $Ag^+\cdots\pi$ and $\pi\cdots\pi$ (edge overlap) interactions.

Comparison of $[Ag(CH_3CN)(bipy)][NTf_2]\cdot CH_3CN$ and $[Ag(CH_3CN)(bipy)][BF_4]\cdot H_2O$ reveals significant differences in how the polymers pack (Fig. 10). The Ag–bipy chains are nearly identical, even the torsion angles between the pyridine planes of the bipy ligand are similar at $-21.5°$ in the NTf_2^- structure and $-23.3°$ in the BF_4^- structure. However, the CH_3CN molecules are more closely associated with the Ag^+ ion in the IL-derived structure ($Ag–NCCH_3$ = 2.61 Å *vs.* 2.76 Å) and are aligned in opposite directions alternating down the chain (Fig. 10a *vs.* 10b).

The $\pi\cdots\pi$ interactions in the BF_4^- structure are limited to an edge overlap and the Ag–bipy chains are offset resulting in a thicker sheet and a much smaller double layer (comprised of BF_4^-, CH_3CN, and H_2O) of approximately 10.51 Å (Fig. 10c *vs.* 10d). Interestingly, the BF_4^- anion is common in IL usage and one might expect that a similar structure could be isolated directly from an IL based on this anion.

Silver nanotubes, $[Ag(pyrimidine)_2]_3[BF_4][NTf_2]_2$: IL and co-solvent resulting in templating, increasing complexity, partial ion exchange, but a unique structure.[56] Utilizing the same strategy as discussed above for $[Ag(pyrimidine)][NO_3]$, but substituting $AgBF_4$ for the nitrate salt and using a 1 : 2 (Ag : pyrimidine) molar ratio, a rather unique mixed anion structure was obtained, $[Ag(pyrimidine)_2]_3[BF_4][NTf_2]_2$ (Fig. 11). As observed in the 3D network coordination complex $[Ag(pyrimidine)_2][PF_6]$, there are different orientations of the

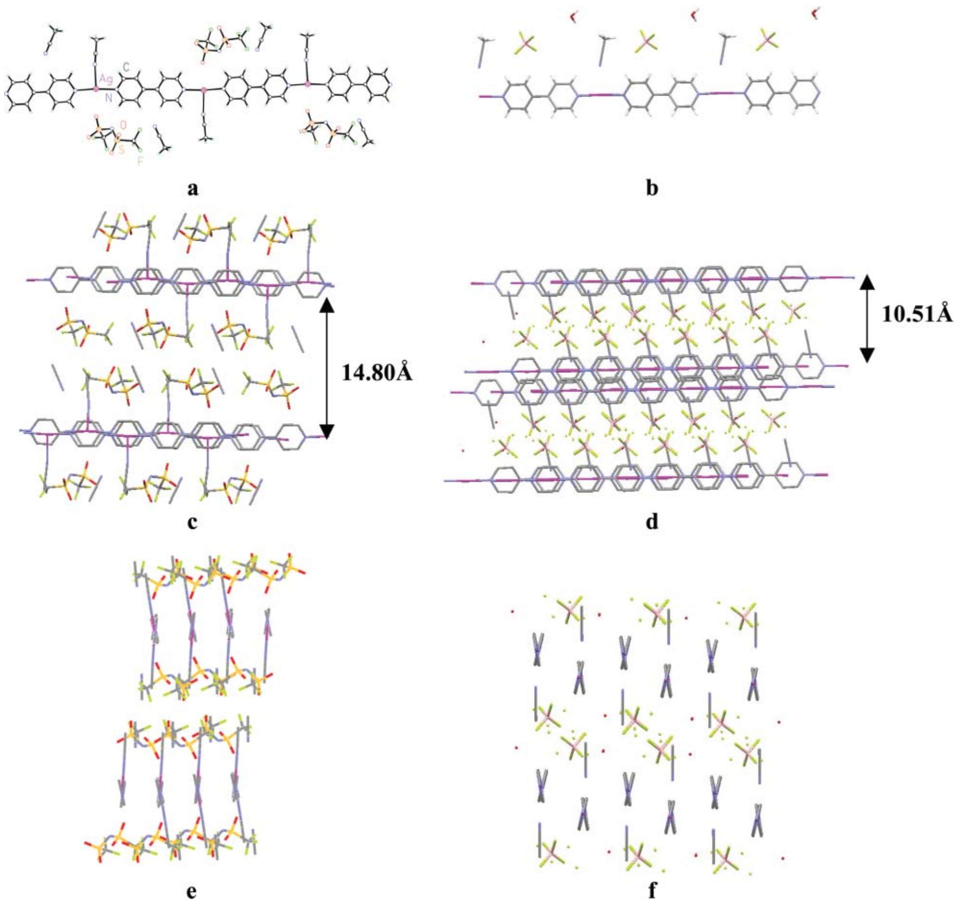

Fig. 10 A comparison of $[Ag(CH_3CN)(bipy)][NTf_2]\cdot CH_3CN$ (a, c, e) and $[Ag(CH_3CN)(bipy)][BF_4]\cdot H_2O$[55] (b, d, f).

ligands at each unique Ag^+ ion. Both Ag^+ nodes are tetrahedral with unique Ag–N distances ranging from 2.251(12)–2.370(11) Å and N–Ag–N angles ranging from 94.1(3)–119.7(3)°.

Interestingly, tricationic rings are linked perpendicularly by one pyrimidine ligand from each of the three metal ions in the ring resulting in nanotubes of *ca.* 6.1 Å width, which are aligned along the *a* axis and propagate throughout the structure. The nanotubes pack in alternating directions (Fig. 11c) along the *c* axis. Two $[NTf_2]^-$ anions and one $[BF_4]^-$ anion provide charge balance, but each anion also plays a unique structural role. The $[BF_4]^-$ anions in the nanotube cavities suggest a templating effect (Fig. 11b). The $[NTf_2]^-$ anions (in their low energy *trans* configuration) appear to play a key role in crystallization of the nanotubes with six columns of these anions insulating the nanotubes, decreasing electrostatic repulsions, and leaving very little void space in the structure (Fig. 11d–e).

When is a solvate a solvate?

One aspect of the use of ILs for crystallization strategies that will deserve some attention is nomenclature. The term 'solvate' is rather well defined (except perhaps when considering the so-called 'pseudo-polymorphs'![57]), however, when one uses an IL 'solvent' for crystallization, one faces the potential for total or partial ion exchange of either or both ions, and the possibility of including the entire IL formula unit into the resulting crystal structures. This was illustrated above with:

- Anion exchange: $[Ag(pyrimidine)_2][PF_6]\cdot 0.5H_2O$
- Partial anion exchange: $[Ag(pyrimidine)_2]_3[BF_4][NTf_2]_2$
- Anion exchange and inclusion of an entire IL formula unit: $[Co(OH_2)_2(bipy)_2][NTf_2]_2\cdot[C_4mim][NTf_2]$

Certainly, additional possibilities will result as many more scientists attempt crystallizations from IL solutions. The results to date do not yet, however, suggest a clear resolution to nomenclature issues, since even IL nomenclature itself is open to debate!

What have we learned so far about crystallizations using ILs?

The few examples presented here, and those now appearing in the literature in greater numbers using ILs as crystallization solvents, readily highlight both the utility and complexity of these novel solvents. Given the high interest in developing new IL or IL-like systems, we can expect both the complexity and the unique solvent properties to be expanded even further, as illustrated, for example, by the use of eutectic mixtures to dissolve metal oxides recently demonstrated by Abbott *et al.*[58]

What we hope to also see, is an increase in the utilization of the unique properties of ILs in crystallization strategies. Current results have tended to arise from using ILs as solvent replacements rather than taking advantage of the uniqueness

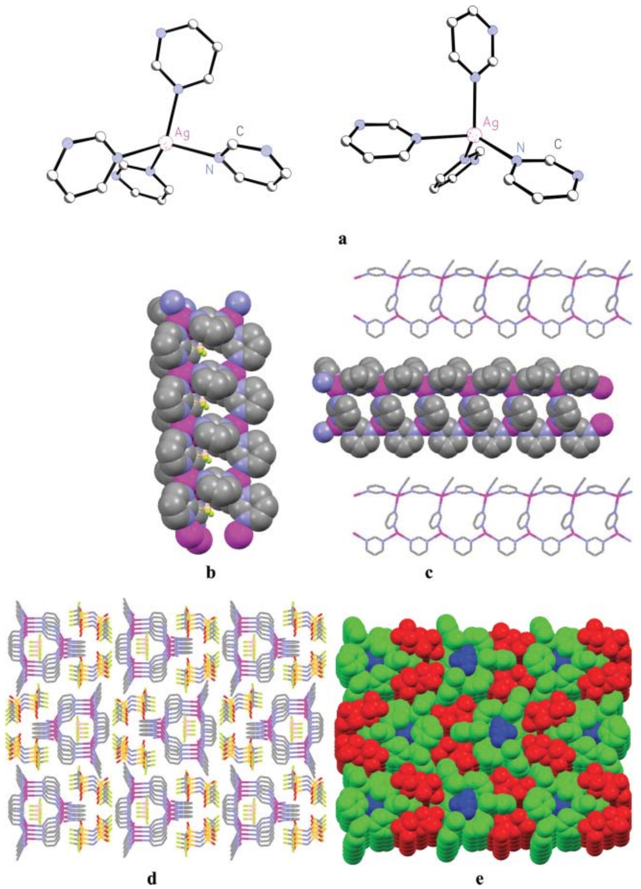

Fig. 11 Illustrations of the (a) two different Ag$^+$ nodes; (b) the tubes surrounding BF$_4^-$ anions; (c) alternating directions in the nanotube packing; (d) packing diagram; and (e) space filling model of the nanotubes (green), and BF$_4^-$ (blue) and NTf$_2^-$ (red) anions.

of the IL solvents (*e.g.*, the accessibility of dramatically larger liquidus ranges, their conductivity, *etc.*). We, for example, are trying to take advantage of the conductivity of ILs to access unique structures *via* electrocrystallizations and recently isolated a uranyl tetramer, $[C_6mim]_4[(UO_2)_4(O_2)_2(NO_3)_2(CH_3COO)_4]_2\cdot 4H_2O$, *via* crystallization in a U-tube electrocell at 1.8 V in the presence of air.[59] Unfortunately, this result is not yet reproducible.

Perhaps we have learned that ILs add unnecessary complexity in crystal design strategies given that we really do not know how to provide complete strategies for crystal design from the organic solvents that have been around for centuries. On the other hand, the current results would seem to indicate unique results are possible using ILs and future control of IL complexity may be possible through a greater understanding of the nature of ILs themselves.

The growing understanding of the interactions between metals, ligands, organics, *etc.*, and ILs will lead to new possibilities in crystallization and in crystal engineering, if we are patient during the rather Edisonian experimental stage and sift through the large number of variable, complex, and captivating results. Regardless of the conclusions one draws from the current results, patience will be rewarded and, in the meantime, a fascinating period of exploration awaits us in this growing field. Let the crystallizations continue!

Acknowledgements

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49 $[\mathrm{Ag(pyrimidine)}][\mathrm{NO_3}]$. In a 20 mL glass vial, 0.001 moles of $\mathrm{AgNO_3}$ was dissolved in 3 mL of a $[\mathrm{C_4mim}][\mathrm{NTf_2}] : \mathrm{CH_3CN}$ (12 : 1) solution with heating. A 0.33 M solution of pyrimidine in $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ was slowly added to give a final 1 : 1 (Ag : pyrimidine) molar ratio. The vial was placed in an isolated area with the cap left askew. As the $\mathrm{CH_3CN}$ slowly evaporated, colorless platelet crystals formed at the air/liquid interface.

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51 $[\mathrm{Ag(pyrimidine)_2}][\mathrm{PF_6}]\cdot 0.5\mathrm{H_2O}$. In a 20 mL glass vial, 0.0005 moles of $\mathrm{AgClO_4}$ was dissolved in 3 mL of a $[\mathrm{C_4mim}][\mathrm{PF_6}] : \mathrm{CH_3CN}$ (12 : 1) solution with heating. 3 mL of a 0.1 M pyrimidine solution in $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ was slowly added to give a final 1 : 2 (Ag : pyrimidine) molar ratio. The vial was placed in an isolated area with the cap left askew and as the $\mathrm{CH_3CN}$ slowly evaporated, suitable single crystals formed at the air/liquid interface. These were harvested and subjected to single crystal XRD analysis.

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53 [Ag(CH_3CN)(bipy)][NTf_2]·CH_3CN. In a 20 mL glass vial, $AgNO_3$ was dissolved in [C_4mim][NTf_2] : CH_3CN (12 : 1) with heating resulting in a 0.33 M solution. A 0.33 M 4,4′-bipyridine solution in [C_4mim][NTf_2] was slowly added to give a final 1 : 1 (Ag : bipy) molar ratio. The vial was placed in an isolated area with the cap left askew, and as the CH_3CN slowly evaporated, colorless platelet crystals suitable for single crystal XRD analysis formed at the air/liquid interface. Formula: $C_{16}H_{14}AgF_6N_5O_4S_2$, *M*: 626.31, space group: monoclinic $P2_1/c$, *a*: 8.439(6), *b*: 29.12(2), *c*: 10.064(8) Å, *β*: 113.611(12)°, *T*: 173 K, *V*: 2266(3) Å^3, *Z*: 4, D_{calc}: 1.836 g cm^{-3}, independent/observed reflections: 3170 (R_{int}: 0.0985)/2948 [$I > 2\sigma(I)$], GooF: 1.067, R_1, wR_2 [$I > 2\sigma(I)$]: 0.0263, 0.0621, R_1, wR_2 (all data): 0.0293, 0.0635. CCDC 611319. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608496f.

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