Ionic Liquids and Poly(ionic liquid)s for Morphosynthesis of Inorganic Materials

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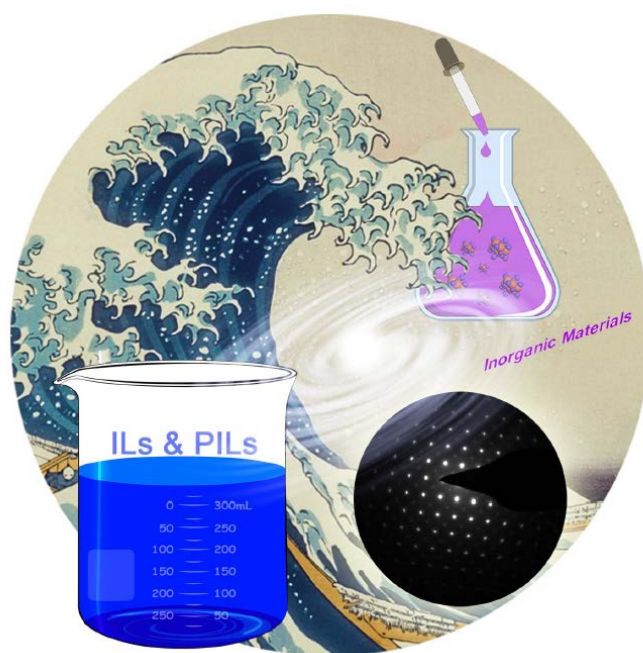
Ionic liquids and poly(ionic liquid)s have demonstrated great potential as "designer solvents and addictives" for advanced inorganic synthesis. This review surveys recent key progress in this exciting research field and speculates on possible future directions.

Abstract: Ionic liquids (ILs) are new, innovative ionic solvents with rich physicochemical properties and intriguing pre-organized solvent structures, which offer great potentials to impact across versatile areas of scientific research, for example, the synthetic inorganic chemistry. Recent use of ILs as precursors, templates, and solvents has led to inorganic materials with tailored sizes, dimensionalities, morphologies and functionalities that are difficultly, or even not accessible, with conventional solvents. Poly(ionic liquid)s (PILs) polymerized from ILs monomers also raise the prospect of modifying nucleation, growth and crystallization of inorganic objects, shedding light on the synthesis of a wide range of new materials. Here we survey recent key progress in using ILs and PILs in the field of synthetic inorganic chemistry. As well as highlighting the unique features of ILs and PILs that enable advanced synthesis, the effects of adding other solvents on the final products, along with the emerging applications of created inorganic materials were discussed. We finally provide an outlook on several development opportunities that could lead to new advancements of this exciting research field.

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1. Introduction

Ionic liquids (ILs) are liquids composed entirely of ions with melting point below 100 $^\circ$C, were first discovered by Paul Walden in 1914[1], and found great interest in both academia and industry. Meanwhile, we observed breakthroughs in organic synthesis of ILs that are—among others—moisture- and air-stable[2] as well as cost-effective[3]. Today, combining various cations and anions through Coulombic interactions is likely to produce more than 10^{18} ILs with versatile physical and chemical profile (Figure 1). This offers opportunities for science and technology in a very broad variety of fields including energy (CO_2/SO_2 capture[4]; Li, Na, Mg-ion batteries;[5] fuel cells;[6] dye-sensitized solar cells,[7] water splitting,[4c, 8] *etc.*), synthesis,[9] biomass pretreatment,[10] catalysis,[9e, 11] pharmaceuticals,[4c] explosives,[12] lubricants[13] and many others.[14] The polymerization of IL monomers leads to a new class of polymers, *i.e.*, poly(ionic liquid)s or polymerized ionic liquids (PILs), which inherited as polymers some unique features of ILs depicted in Figure 1, combined to polymer properties such as multivalency and processability.[15] PILs thereby enabled additional applications in materials science,[15c, 16] membrane science,[15a, 17] catalysis,[15b] electrochemical devices,[15c] actuator[18] and many more.

Although ILs as reaction media and catalysis for organic synthesis have been broadly used since the 1980s,[9f] their use for inorganic materials preparation starts more lately from early 2000 but has rapidly advanced ever since.[9a, 9b] The unique solvent potential of ILs enables processes that are difficult or even impossible in conventional solvents to become viable: the high polarity offers ILs the ability to dissolve versatile precursors and to realize smooth crystallization of the products;[19] redox-robust ILs with electrochemical windows potentially spanning from -4 V to +4 V (some cases even up to 7V overall) allow the electrodeposition of very reactive elements such as titanium and aluminium as well as of semiconductors;[20] the ionic feature and high polarizability make ILs excellent microwave adsorbers for creating new inorganic materials *via* microwave heating.[21] This is to be seen combined with a low toxicity in some species, negligible vapor pressure and high thermal stability of ILs which permit chemical reactions to be performed in non-pressurized vessels at high temperatures.[9c] ILs-involved synthesis has become extremely powerful route for the production of diverse inorganic materials—ranging from metals, carbons, silicas, metal oxides and chalcogenides, metal salts, to open-framework materials (Figure 2).[9a-c, 19]

In this review, we want to focus on an attractive subfield of this research and highlight key advances of inorganic synthesis of crystalline materials, namely polymorph and morphology/size control ("morphosynthesis"), which is essentially based on the ability of ILs and PILs to nucleate, stabilize or interact with very special crystal faces, which ends in new species and new nanostructures. As the amount of ILs required in such interfacial operations is low, we also discuss the effects of adding co-solvents to the final reaction mixtures, and finish by spotlighting some exciting applications of the as-prepared materials. We also offer a brief prospect on the promises of PILs for inorganic synthesis, and speculate on possible future directions.
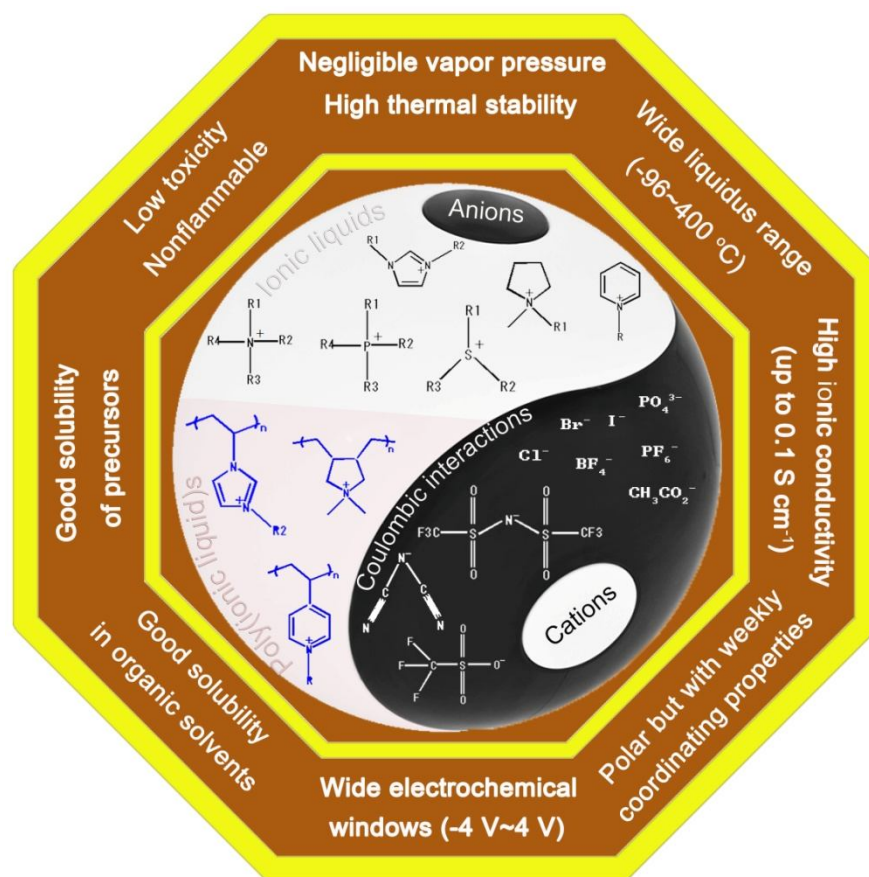

Figure 1. The "Yin and Yang" diagram illustrates the interaction between representative anions (Yin) and cations (Yang) that creates ILs and PILs with unique properties.

2. Synthesis of inorganic materials from ILs/PILs

2.1. Why inorganic synthesis using ILs/PILs?

Conventional molecular media such as water and organic solvents, while being technologically successful for conducting chemical reactions, pose drawbacks in terms of a narrow range of

liquidus and poor solubility of precursors with different polarity; organic solvents show high vapor pressures, toxicity and are flammable as well,[9b] which not only lead to synthetic failures, but also environmental and safety problems. Reactions in classical molten salts are restricted to high temperatures and are destructive for many fragile precursors.[22] In contrast, ILs are almost "universal" solvents to dissolve matters, including ILs themselves.[23] Being ionic, the large enthalpy of vaporization (ΔH_{vap}) endows ILs with low vapor pressure, which makes them "green" alternatives to volatile organic solvents.[9a, 9c] As well as electrochemical stability, ILs also possess high thermal stability and a wide liquidus range, in some cases they are stable liquid even up to 400 °C. These unique properties have placed ILs as a preferable solvation media for a broad swath of material preparations and have stimulated the development of many synthetic techniques, for examples, ionothermal synthesis, sol-gel synthesis, microwave synthesis and electrodeposition.[24]
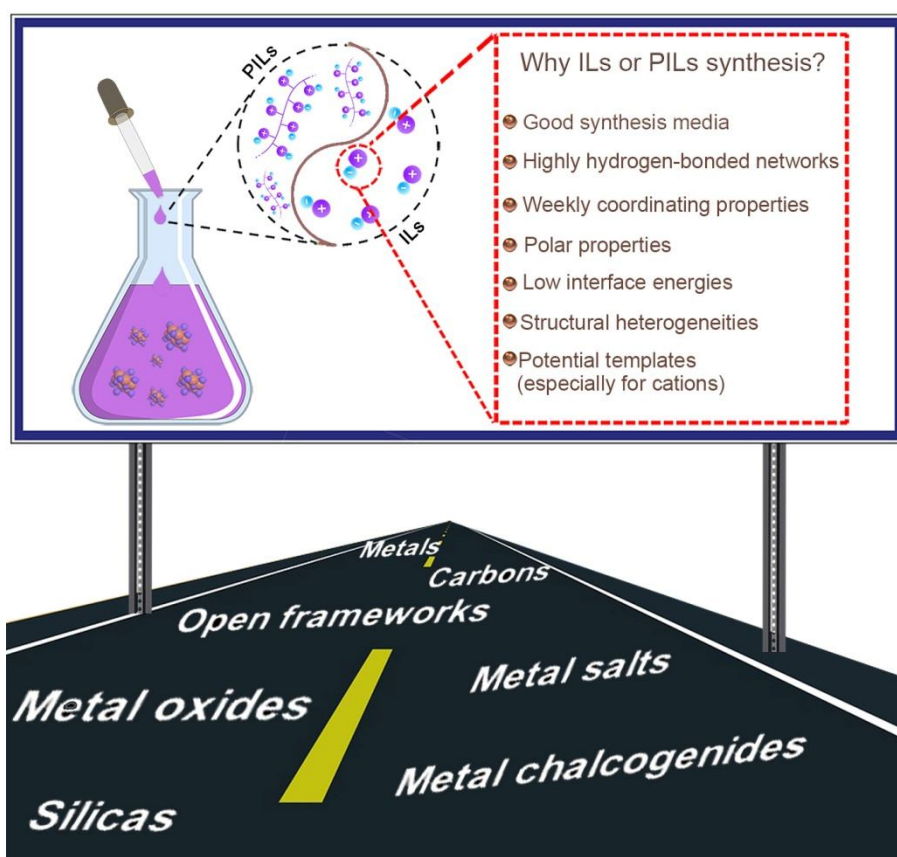

Figure 2. Illustration of the key properties of ILs and PILs that open the way for the synthesis of versatile inorganic crystalline materials.

Structurally, ILs are cations (big and asymmetrical) and anions (small and flexible) that kept together by strong electrostatic interactions.[23] The combination of these opposing properties results

in their low melting points[25] and affects the viscosity,[26] which determines the transport of solutes in ILs and thus is important to crystal growth of inorganic materials.[27] The interactions within IL solvents can be summed up to be "very complicated": except for the obvious Coulombic interactions, other intermolecular forces such as hydrogen bonding, dipole-dipole, van der Waals and dispersion forces are also comparably strong, enabling the diverse regulation of local structures in ILs.[28] For example, imidazolium ILs can form extended hydrogen-bond networks, making them highly structured, and therefore present an entropic contribution for spontaneous, well defined and higher order self-assembled nanostructures.[9a, 28a, 29] Moreover, ILs are prone to spatial heterogeneity as a result of microphase demixing of hydrophilic and hydrophobic fragments (such as alkyl-chain aggregation), typically for imidazolium ILs when the alkyl chains are longer than propyl.[20b] Studies have demonstrated that, using the segregated polar and non-polar domains in ILs to partition the precursors, this heterogeneity exhibits the ability of controlling growth rates, particle sizes and potential morphologies in materials synthesis.[28b]

Interface tension is another important physicochemical component that directly affects the kinetics process of crystal growth, including crystal nucleation and ripening. Even polar ILs have sometimes surprisingly low interface free energies, allowing for faster nucleation-to-growth rates and thereby generating very small primary crystalline seeds.[9a] Low interface tension also allows ILs to form emulsions *via* mechanical agitation, thus forming microheterogeneous systems to solubilize polar and non-polar substances for inorganic synthesis.[24, 30] It is worth noting that ILs are often low coordinating solvents, especially the ones with perfluorinated anions (*e.g.*, $[BF_4]^-$, $[PF_6]^-$, $[SiF_6]^-$, and $[Al(OR^F)_4]^-$; R^F is fluoroalkyl).[9d, 31] Unlike reactions in conventional polar solvents, this coordinative inertness permits weak interactions between bonding partners, thus providing access to low-valent metal cations, compounds with metal-metal bonds and clusters, and new network compounds.[9d] We also note that ILs with quaternary ammonium and imidazolium cations often directly enable to template preparation of zeolites and metal organic frameworks (MOFs).[9c, 25]

From this short highlight of some of the unique properties of ILs, it is already indicated how they may affect the synthesis of inorganic materials (Figure 2). Indeed, ILs were observed to serve as solvents, surfactants, precursors, stabilizers and structure-directing agents to realize a unusually high-level control of inorganic objects. This is nicely complemented by recent attempts of effective

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materials synthesis controlled by using PILs as additives, owing to their unique features inherited from ILs as well as their incoming polymer properties. Details of the related achievements in ILs/PILs-directed materials synthesis will be discussed in the next sections.

2.2. Synthesis of inorganic materials in pure ILs

The unique solvent potential makes ILs remarkable synthetic media for a wider range of well-defined functional materials, for example metal nanoparticles. Nanoparticulate metals are, owing to their exotic physicochemical properties compared to their bulk counterparts, interesting in versatile applications. Dupont and co-workers[32] reported in 2002 a pioneering work on preparing Ir nanoparticles in [BMIM]PF$_6$ ([BMIM] = 1-butyl-3-methylimidazolium) through reduction of [IrCl(cod)]$_2$ (cod = 1,5-cyclooctadiene) by H$_2$, which stimulated subsequent studies of preparing various metal nanoparticles in imidazolium-based ILs.[9b, 31] A striking feature of these prepared nanoparticles is that they are often very small and uniform, benefiting from the stabilization effect and low interface tensions of ILs.[9a, 31]

Different from classical salts, ILs bear pre-organized structures through the extended hydrogen-bond networks. Recent molecular simulation[33] has revealed that, for imidazolium ILs, both a continuous 3D network of ionic channels and non-polar domains exist (Figure 3a and b), which affect the solvation of the ILs and their ability to interact with various species, but also strongly influence entropic effects. These non-polar domains allow the use of non-polar metal precursors (*e.g.*, organometallic), while polar species favour the polar regions of ILs. The volume of these nano-regions in ILs enables the modulation of size and shape of prepared nanoparticles.[31, 34] The metal nanoparticles formed in imidazolium ILs are in addition stabilized by hydrogen-bond supramolecular interactions of the type $\{[BMIM]_x(X)_{x-n}\}^{n+}[(BMIM)_{x-n}(X)_x]^{n-}\}_m$ (where X is the anion), rather than by isolated cations and anions.[31]

Another trend for the synthesis and stabilization of metal nanoparticles worth noting is the use of functionalized ILs, or so-called "task-specific" ILs.[35] ILs can be modified by functional groups such as thiol, nitrile, amine, the presence of which sometimes allows a better control of the size and morphology of resultant metal nanoparticles by specific chemical interactions.[36] For example, Wang and co-workers[36b] found that ultra-small Au nanoparticles (~1.7 nm) can be synthesized and stabilized by 1-(3-aminopropyl)-3-methylimidazolium bromide (IL-NH$_2$) (Figure 3c). It turns out

that the IL-NH$_2$ terminal group affords effective interaction between N and Au, leading to these very tiny, uniform Au nanoparticles that remain stable in air even up to 8 months.[36b]
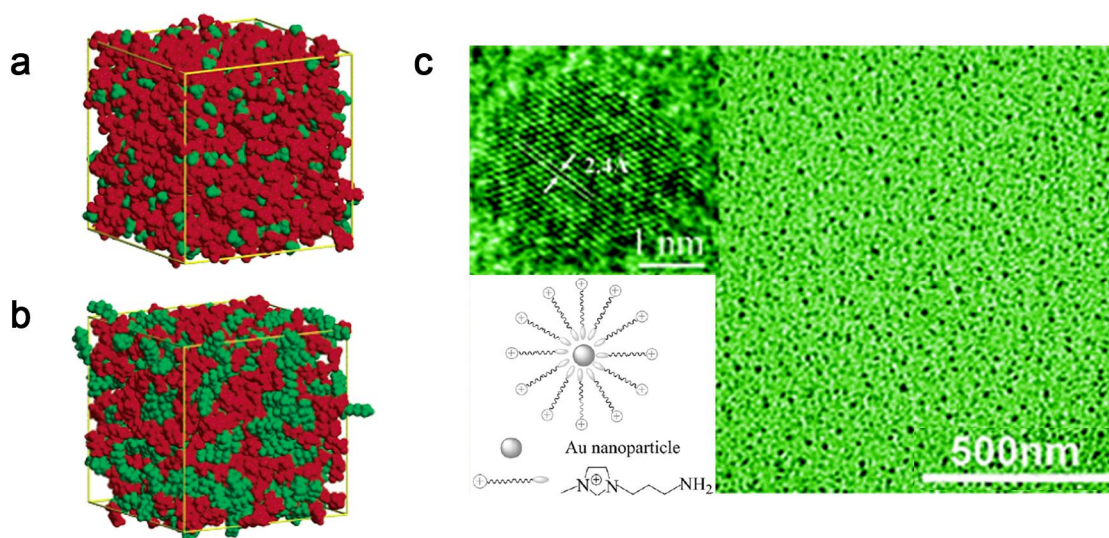

Figure 3. a, b) Simulation study of imidazolium-based ILs (boxes contain 700 ions) showing the polar (red) and non-polar (green) domains for a) [EMI][PF$_6$] (1-ethyl-3-methylimidazolium hexafluorophosphate) and b) [OMI][PF$_6$] (1-methyl-3-*n*-octylimidazolium hexafluorophosphate), *l* = 54.8 Å. *l* is the length of the box side. As seen, increased IL side chains result in larger non-polar domains. Reprinted from the Ref. [33] with permission from the American Chemical Society. c) Transmission electron microscopy (TEM) image of the Au nanoparticles prepared in the presence of IL-NH$_2$. The insets in c) are high-resolution TEM image (up) showing lattice spacing of a typical gold nanoparticle, and the structure illustration (down) of the resulting Au-IL nanoparticles. Reprinted from the Ref. [36b] with permission from the Royal Society of Chemistry.

This approach is by no means restricted to noble metal nanoparticles. A very systematic approach to extend IL media to inorganic solid state synthesis was presented by Ruck *et al*.[27] As the focus of this review is on morphosynthesis, we will only mention works relevant to this subfield. In a very exciting piece of work, the group for instance extended phosphorous chemistry to ILs.[37] Red phosphorus is usually far less reactive than the white allotrope. In the Lewis-acidic [BMIM]Cl·2AlCl$_3$, red phosphorus could however be shown to form spontaneously nanoscale particles. These particles, because of their highly increased surface area, then can be conveniently used for a whole range of phosphorous chemistry.

Also for bismuth, the IL seems to favour and stabilize the presence of low valent cluster structures.[38] At room temperature, elemental bismuth and bismuth(III) cations synproportionate in the Lewis-acidic [BMIM]Cl/AlCl$_3$ within minutes. The existence of bismuth polycations in the dark

colored solution was proven by Raman spectroscopy. Dark-red crystals of $Bi_5(AlCl_4)_3$ could be isolated from the IL. The method allows the synthesis of bismuth cluster compounds under milder conditions than in high-temperature melts and more conveniently and environmental friendly than in liquid SO_2 with strongly oxidizing, toxic agents like SbF_5 or AsF_5.

This work was later extended to inorganic solid state syntheses that rely conventionally on very high temperatures, which could be brought down by ILs to near room temperature and be run in a much sustainable fashion.[39] This included low-valent crystalline halogenides Te_2Br, alpha-Te_4I_4, Bi_6Cl_7, and Bi_6Br_7, as well as of $WSCl_4$ and $WOCl_4$. Compared to the published conventional approaches, reduction of reaction time (up to 80%) and temperature (up to 500 K) and, simultaneously, an increase in yield were achieved. In the majority of cases, the solid products were phase-pure. It was also proven by X-Ray diffraction on single crystals that the quality of the crystals made in ILs was comparable to that of products obtained by chemical transport reactions. In a similar fashion, a whole range of complex, well defined polyoxometalates could be easily synthesized.[40]

ILs as reaction media also surprise sometimes throughout the simplest reactions. For titania (TiO_2), for instance, a room temperature synthesis of brookite as a majority component was described.[41] Brookite is a rare polymorph of TiO_2, and usually not found in sol-gel syntheses. Only because of the special properties of ILs, chemists now could access such nanoparticulate brookite species (2~4 nm) for a variety of purposes, easily. Superior use of as-prepared product in Li-intercalation was demonstrated in this work. Many of these approaches with a focus on complex inorganic cluster synthesis were summarized in an early review in 2012.[27]

Besides nanoparticles, ILs also enable the morphogenesis of other inorganic nanomaterials with dimensions spanning from 1D to 3D, thus allowing to tailor their properties. The IL structures can adapt to many species, as they provide hydrophobic/hydrophilic regions and a high directional polarizability, which can be oriented parallel or perpendicular to the embedded species.[9a] This leads to reactions in ILs are like reactions in a pure "universal" ligand,[9a] therefore in principle, ILs are "designer solvents" for the access of micro/nano-structured materials. A large body of work has demonstrated that template-assisted electrodeposition in ILs is efficient for making 1D nanostructures.[42] An example from Al-Salman and co-workers[42a] showed that well-defined germanium nanowires with diameters of 90-400 nm (Figure 4a) can be made through this technique

in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Py$_{1,4}$]Tf$_2$N). Key advantage that enables this success is the wide electrochemical window of [Py$_{1,4}$]Tf$_2$N (Figure 4b), which is hardly accessible in this way with conventional solvents. In appropriate ILs, similar deposition also leads to silicon,[42a] silver,[42b] cobalt,[42c] aluminium[42d] and even very reactive titanium[42e] 1D nanostructures. Remarkably, the morphology and size of deposited materials exhibited an interesting ion effect, presumably because that tuning ions in ILs can alter the mechanism of nucleation and growth of the deposit.[43] This intrinsically results from the solvation layers—depending upon the IL selected and metal salt dissolved—forming at the interface between ILs and the electrode, which, however, has not been well clarified and needs further investigation.[20a] Other preparation strategies using ILs as solvents, capping reagent and/or structure-directing agents also led to a series of high-quality 1D crystals, for examples, tellurium nanorods and nanowires from microwave-assisted synthesis in *N*-butylpyridinium tetrafluoroborate ([BuPy]BF$_4$);[44] CoPt nanorods from hot-injection method in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl ([BMIM]Tf$_2$N),[45] and many others.[46]
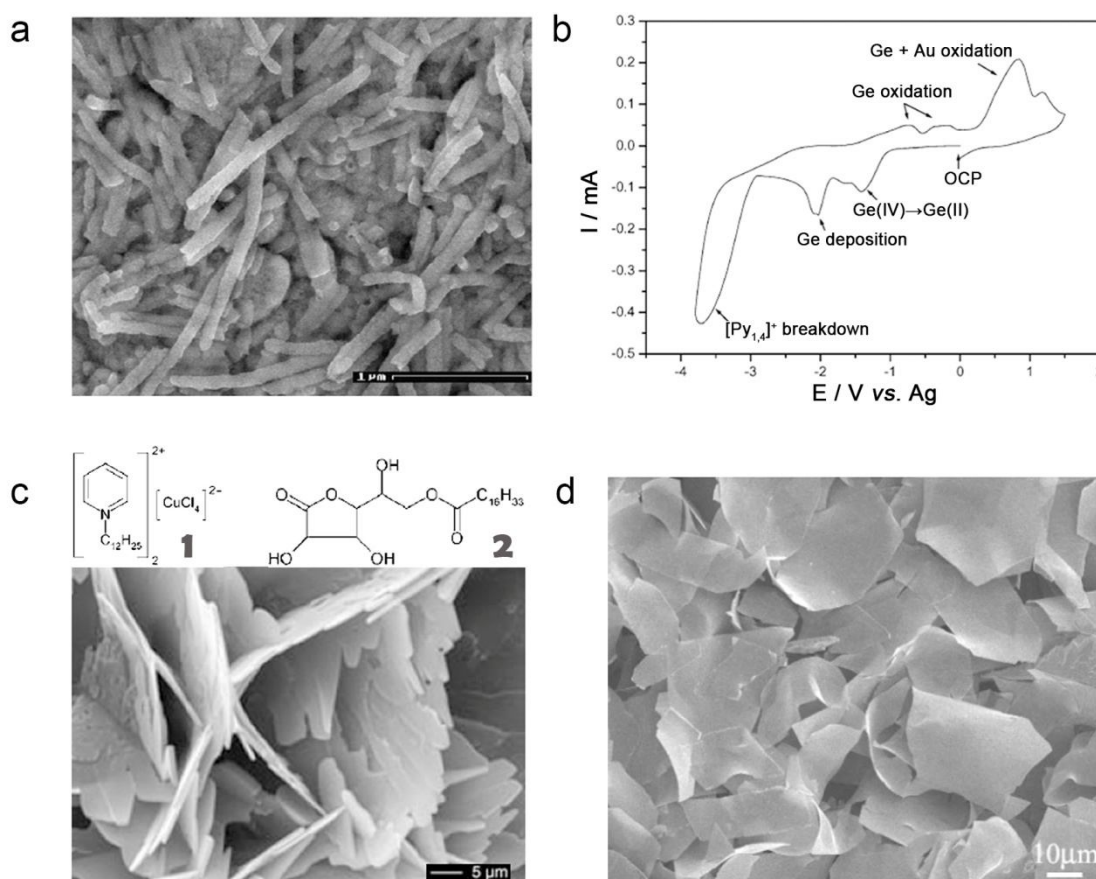
Figure 4. a) High-resolution scanning electron microscopy (SEM) image of germanium nanowires prepared by electrodeposition in [Py$_{1,4}$]Tf$_2$N. b) Cyclic voltammogram of 0.1 M GeCl$_4$ in [Py$_{1,4}$]Tf$_2$N inside the M90 PC membrane with an Au sputtered film on one side of the membrane at working electrode. Scan rate: 10 mV s^{-1}, at room temperature. Reprinted from the Ref. [42a] with permission from the Royal Society of Chemistry. c) SEM image of CuCl nanoplatelets prepared from a 1:1 mixture of bis(dodecyl pyridinium) tetrachlorocuprate (1) and 6-O-palmitoyl ascorbic acid (2) at 85 $^\circ$C. Reprinted from the Ref. [48a] with permission from the Wiley-VCH. d) SEM image of Au nanosheets prepared by the microwave heating of HAuCl$_4$ dissolved in [BMIM]BF$_4$ or [BMIM]PF$_6$. Reprinted from the Ref. [48c] with permission from the American Chemical Society.

2D materials such as graphene and layered transition metal dichalcogenides are fundamentally and technologically intriguing.[47] The morphology of inorganic crystals can also be shaped into 2D structures applying ILs as crystallization media,[48] offering opportunities for creating new inorganic 2D materials. Figure 4c shows CuCl nanoplatelets prepared by Taubert in a 1:1 mixture of bis(dodecyl pyridinium) tetrachlorocuprate (**1**) and 6-O-palmitoyl ascorbic acid (**2**).[48a] This mixture is an IL composed of ordered domains with layered architecture that templates the formation of unusual plate-like CuCl crystals. Meanwhile, it also serves as solvent and Cu precursor, pointing to an "all-in-one (*i.e.*, solvent-template-reactant)" synthesis concept.[48a] The "all-ion-one" strategy also enabled the synthesis of CdF$_2$ nanoflakes,[48b] and inorganic crystals with other morphologies.[24, 49] Highly structured ILs were further witnessed to tailor 2D crystals at micro-scale.[48c, 48d] Uniform single-crystal Au nanosheets with thickness of ~50 nm and size larger than 30 μm were prepared by microwave heating of HAuCl$_4$·3H$_2$O dissolved in [BMIM]BF$_4$ or [BMIM]PF$_6$ (Figure 4d).[48c] Again, the structure pattern of imidazolium ILs, taking as long-range hydrogen-bonded supramolecular template, has resulted in the interesting 2D micro-size structures.[29, 48c]

Moving forward to 3D architectures, ILs also demonstrated their ability of unusual morphogenetic control, in view of their functionalities as solvents, stabilizers and crystal growth modifiers. Very unusual, uniform ZnO micro-pyramids with exposed polar surfaces (*i.e.*, ±(0001) and {10-11} planes) were fabricated in a mixture of oleic acid and ethylenediamine (Figure 5).[50] According to the reaction R-COOH + R-NH$_2$→R-COO$^-$ +R-NH$_3^+$, the mixture can be taken as a self-organized IL that stabilizes the high energy polar surfaces. Similar polyhedral crystals with exposed polar surfaces were reported for Au prepared in [BMIM]BF$_4$ medium.[48d] Recently, appropriate ILs have been employed to tailor a series of 3D inorganic crystals, such as star-like

Pd,[51] AuZn alloy dendrites,[52] ZnO multipods,[53] SnS$_2$ flowers,[54] and PbSe dendrites.[48g]
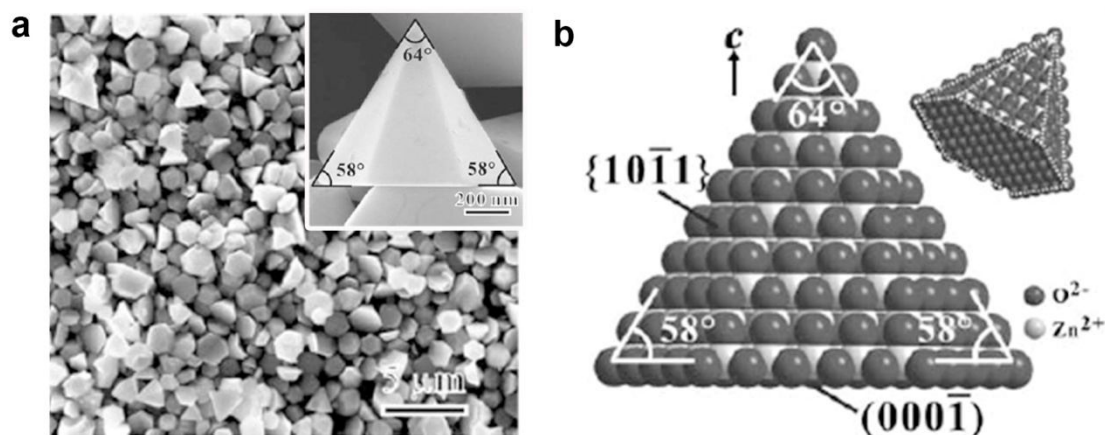

Figure 5. a) SEM image of ZnO hexagonal micro-pyramids prepared within a mixture of oleic acid and ethylenediamine as the solvent. The inset in a) shows an enlarged SEM image of a typical ZnO hexagonal micro-pyramid. b) Schematic model of a ZnO hexagonal micro-pyramid. Reprinted from the Ref. [50] with permission from the Royal Society of Chemistry.

Beyond dense crystalline nanostructures, IL-based synthesis of porous, open-framework crystals such as zeolites and inorganic-organic frameworks has also achieved great success.[9c, 25, 55] Conventional routes to these crystalline porous solids are hydro/solvothermal synthesis, often performing in sealed autoclaves under autogenous pressure.[55] Improved or at least simplified synthesis of open-framework crystals may come by using ILs or eutectic mixture as solvent and structure-directing agent, a process called ionothermal synthesis which was introduced by Cooper and co-workers in 2004.[56] The switch from water or organic solvents to ILs offers the advantage of missing volatility, which allows reactions to be conducted in open vessels. Meanwhile, the structure-patterned ILs can serve as structure-directing agent to template the size, topology and crystallinity of desired open-frameworks.[9c, 25, 55] This ionothermal approach has led to a number of high-quality zeolites, zeotype materials and MOFs that not only contained the already known structures but also create new ones.[9b, 9c, 25, 55, 57] Benefiting from ambient pressure environment provided by ionothermal synthesis, Cai and co-workers prepared a highly oriented SAPO-11 film using 1-methyl-3-ethylimidazolium bromide ([EMIM]Br) as both solvent and template (Figure 6), which exhibits excellent anti-corrosion coatings for different types of alloys.[58] In contrast, zeolites prepared hydrothermally in sealed vessels are often impractical for large, oddly shaped and cut pieces of metal.[25, 58] One more aspect is noteworthy that some "impurities", such as water, often

exist in ILs, may profoundly influence the ionothermal process[25, 55] and potentially other synthetic processes, which will be discussed below.
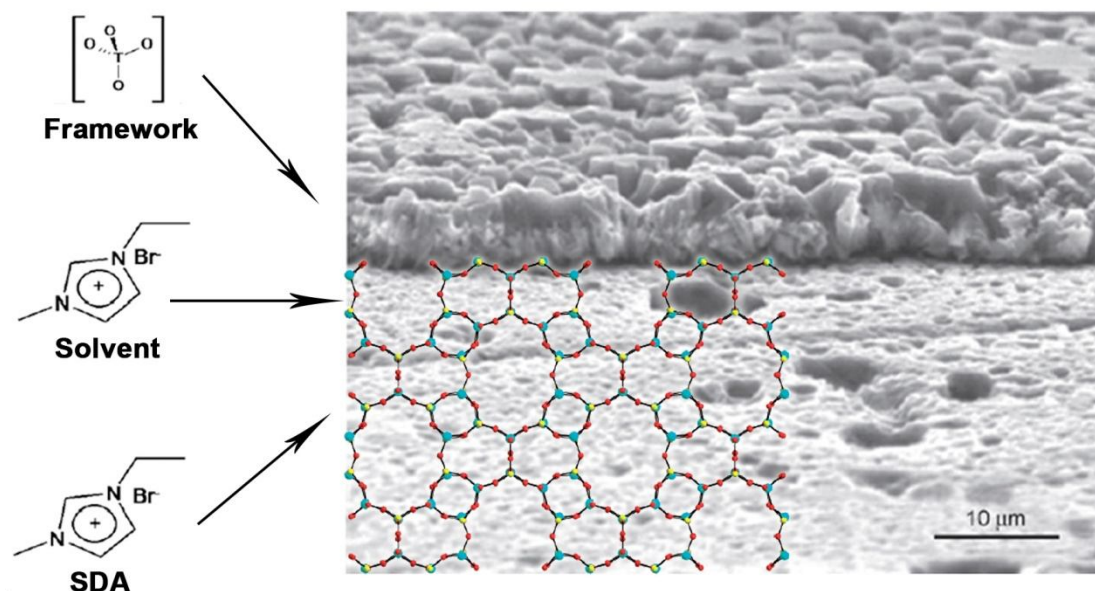

Figure 6. Ambient pressure ionothermal synthesis of zeolite coatings offers great promise in anti-corrosion applications. The SEM image shows a cross section of the SAPO-11 (AEL) coating on aluminum alloy, with the corresponding AEL zeolite framework topology as inset. Red, blue, and yellow balls correspond to O, Al and P, respectively. Reprinted from the Ref. [58] with permission from the Wiley-VCH.

2.3. Synthesis of inorganic materials in IL-based mixed solvents

Perhaps most ILs of interest for inorganic materials synthesis are moisture- and air-stable. It is important to note that many of these ILs are hygroscopic and are able to absorb water from the atmosphere.[55, 59] This also includes highly hydrophobic ILs such as [BMIM]Tf$_2$N, for which 474 ppm water was detected even after a vigorous drying process.[60] As a consequence the properties of ILs such as viscosity, conductivity and the electrochemical window are often altered to a certain extent depending on the content of water in ILs. [20b] Moreover, the pre-organized solvent structure of ILs is likely to be modified with the presence of water, as it can tightly bind to the hydrogen-bonded networks of ILs.[9a] As a result, the structural outcome of such syntheses exhibits a strong water content-dependent behavior. It is worth mentioning that, even at high concentrations, water in ILs is molecularly dispersed or present only as small clusters with water-anion interactions, while that in organic solvents usually leads to phase segregation on the microscopic scale.[55] Therefore, water in such aggregate states functions more likely as a classical "surfactant" with a

strong tendency towards highly ordered self-organization.[9a] The strong interaction between water and anions also results in significant deactivation of water in ILs because of reduced nucleophilicity and thus decreases ligand strength and hydrolysis activity, offering a new chemistry in such "wet" ILs.[55] Many reactions were found to greatly benefit from the presence of water in ILs. For examples, a reactant quantity of water in ionothermal synthesis can act as a mineralizer to prepare the desired zeolite structure.[25] Sol-gel synthesis under water-rich environment can enable the formation of IL/silica self-organized mesostructure at a higher order as compared with the one prepared in water-poor medium.[9a, 61] This results in modified syntheses by deliberately adding controlled amounts of water in ILs, thereby realizing an optimized or improved control of targeted inorganic objects.[61-62] Besides water, many other solvents, both polar and non-polar, were mixed with ILs as reaction media, including ethanol,[63] 1-propanol,[64] ethylene glycol,[65] acetone,[66] hexane,[67] dimethylformamide,[68] ethylenediamine,[69] other amines,[70] and even other kinds of ILs.[28a] Although the role of added solvents is very complex and the understanding of their effects on the structure and chemistry of parent ILs are underdeveloped, these modified synthetic media provide new opportunities for the synthetic inorganic chemistry and have already led to exciting results.

Organized inorganic matters such as mesostructured silica can be effectively made through sol-gel chemistry when organizational processes are incorporated.[71] In 2000, Dai and co-workers reported the first work of using IL (*i.e.*, [EMIM]Tf$_2$N) as solvent for sol-gel preparation of silica aerogel.[72] This was a non-hydrolytic sol-gel process, where [EMIM]Tf$_2$N interacted with sol particles, acts to solvate aerogel precursors effectively and form a homogeneous sol-gel network without shrinkage over a long aging time. Things become more interesting when some reaction water was added, which often aids in forming crystalline and highly ordered structures.[9a, 61] Zhou *et al.* have applied the nanocasting technique onto self-organized IL structures for the preparation of super-microporous lamellar silica (Figure 7a), using 1-hexadecyl-3-methyl-imidazolium chloride ([C$_{16}$MIM]Cl) as a template.[61] The presence of water modifies the pattern of IL self-organization, especially at higher water content, which leads to a layer-like L$_\beta$- nanostructure (Figure 7b) that templates the formation of the highly ordered lamellar product. Silica synthesized in the exact same reaction with a tenfold less of water, however, crystallized in a 2D hexagonal mesophase,[9a] evidencing the ability of modulating the structural pattern of ILs by water. In another study it was

shown that combining polymer latexes and amphiphilic [C$_{16}$MIM]Cl in water-rich environment can template the formation of bimodal porous silica with both inverse opal microstructure and super-microporous lamellar nanostructure.[62f]

As described above, water in ILs is molecularly dispersed or present only as small clusters with water-anion interactions *via* hydrogen bonds. The strength of such interaction depends significantly on the type of anions, following the order of [PF$_6$]$^-$ < [SbF$_6$]$^-$ < [BF$_4$]$^-$ < [(CF$_3$SO$_2$)$_2$N]$^-$ < [ClO$_4$]$^-$ < [CF$_3$SO$_3$]$^-$ < [NO$_3$]$^-$ < [CF$_3$CO$_2$]$^-$.[73] This offers the possibility of tuning the effects of water on the ILs' structure by using different anions, especially when cations act as templates. In general, ILs with short-chain cations were originally not supposed to self-assemble into an ordered micelle structure or liquid crystalline phase in solution, like the way that long-chain surfactants do.[61] Unexpectedly, an interesting mesoporous silica with wormlike pores (Figure 7c) was reported using a short-chain [C$_4$MIM]BF$_4$ as template *via* sol-gel nanocasting technique, pointing to the pronounced self-organization already of that species.[62o] Owing to the special structure and property of [C$_4$MIM]BF$_4$, the hydrogen bonds between water and [BF$_4$]$^-$ anions are weak, which permits the formation of hydrogen bonds between silano group of tetramethyl orthosilicate and [BF$_4$]$^-$, thus inducing the oriented arrangement of the [BF$_4$]$^-$ anion along the pore walls (Figure 7d). Meanwhile, the neighboring imidazolium rings drive the formation of rigid, oriented π-π stacking structure (Figure 7d). These developed structures point to a possible hydrogen-bond-co-π-π mechanism, suggesting how IL acts as the replication phase for creating long vermiculate mesopore,[62o] and potentially other mesoporous structures.
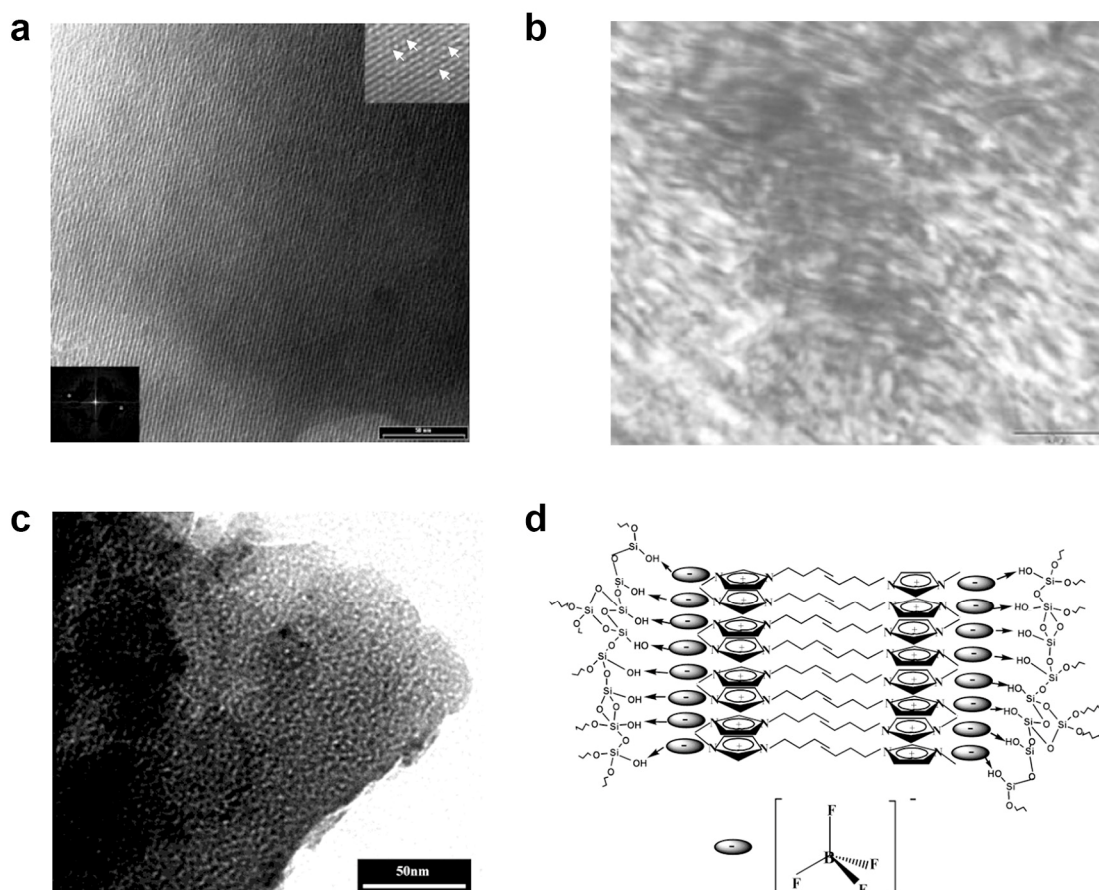
Figure 7. a) TEM image of super-microporous lamellar SiO_2 prepared in $[C_{16}MIM]Cl$ through the nanocasting technique. The insets are the $1.5\times$ magnification (up) and the corresponding Fourier transform (down) of the image, respectively. The scale bar is 50 nm. b) Polarized light optical microscopy image of the mesophase of $[C_{16}MIM]Cl$ between crossed polarizers in TMOS, water, and HCl. Scale bar: 20μm. Reprinted from the Ref. [61] with permission from the Wiley-VCH. c) TEM image of the mesoporous SiO_2 prepared in $[C_4MIIM]BF_4$ through the nanocasting technique. d) Schematic of the proposed π-π stacking model that explains the formation of mesoporous SiO_2. In this model, the silanol groups interact with $[BF_4]^-$ anions to form hydrogen bonds. Reprinted from the Ref. [62o] with permission from the American Chemical Society.

Later, this work was expanded to the synthesis of mesoporous, electrochromic and crystalline WO_3 films.[74] These films were obtained *via* evaporation-induced self-assembly using long-chain ILs such as $[C_{16}MIM]Cl$, $[C_{16}MIM]Br$, cetyltrimethylammonium chloride and bromide as additives. Owing to the presence of the ionic structure-directing agents, the WO_3 films crystallize in a preferred orientation along the *a*-axis on different substrates, as evidenced by X-ray diffraction. The WO_3 films with this IL-induced orientation show improved electrochromic properties when compared to films with a lower degree of crystallographic orientation, prepared in an analogue fashion.

Substantial efforts have been devoted to the preparation of high-quality TiO_2 materials with controlled morphology, size, structure and phase, for which ILs are beginning to play a part.[62k, 62l, 75] Similar to silica, TiO_2 materials can be synthesized with the sol-gel route from hydrolysis of a titanium precursor.[76] However, this process under water-rich environment usually causes, *via* the formation of $Ti(OH)_4$,[76] amorphous products that need to be calcined above 350 °C to result in the desired crystalline products.[9a] Recently it was shown that spherical spongelike TiO_2 superstructures assembled from crystalline nanoparticles can be made by hydrolyzing titanium tetrachloride in ILs (*i.e.*, $[C_4MIM]BF_4$) in water-poor conditions (Figure 8a).[62l] The resulting anatase sample had a unparalled high surface area of 554 m^2 g^{-1}; this is due to the very high nucleation rate of TiO_2 in such water-poor IL system, leading to the formation of very tiny crystalline nanoparticles (2~3 nm) because of the low interface energy and surface stabilization by the adaptability of ILs. In another example, Nakashima *et al.* reported the synthesis of interesting hollow TiO_2 microspheres in ILs *via* an interfacial sol-gel route (Figure 8b and c).[62k] It was found that the water content in ILs must be limited to 2 wt% or smaller, as otherwise the obtained products start to contain rough and irregular TiO_2 microparticles. This again demonstrates the significant role of water in ILs that affects the prepared products, here however from its unfavorable side. Nowadays, it is still not clear how water exactly modifies the structure and chemistry of ILs, and how it affects the related reaction process. A recent set of experiments supported the finding that adding reagent quantities of water in ILs can significantly enhance the crystallization kinetics of molecular sieves in an ionothermal synthesis,[62n] but a fundamental mechanistic understanding is still lacking.
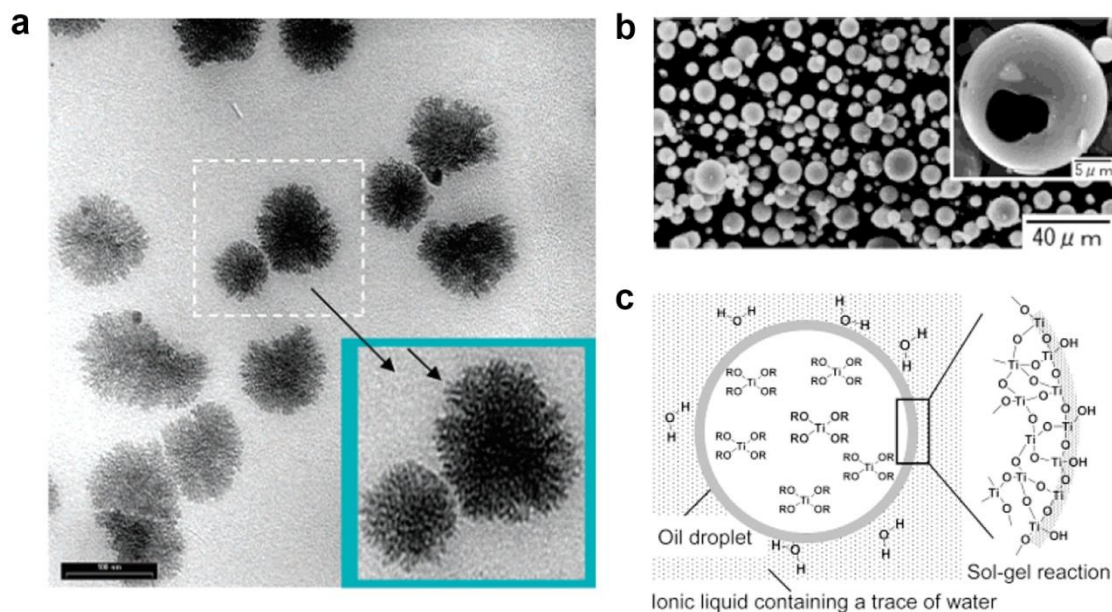
Figure 8. a) TEM image of spherical TiO$_2$ sponges composed of tiny TiO$_2$ nanoparticles formed in [BMIM]BF$_4$. The inset is a 2× magnification of the selected region. The scale bar is 100 nm. Reprinted from the Ref. [62l] with permission from the American Chemical Society. b) SEM images of hollow TiO$_2$ gel microspheres prepared in [C$_4$MIM]PF$_6$. The inset presents a fractured TiO$_2$ microsphere. c) Schematic of the proposed formation mechanism of hollow TiO$_2$ microspheres at the interface of oil droplet and IL. Reprinted from the Ref. [62k] with permission from the American Chemical Society.

Apart from water, many other solvents (both polar and non-polar) have been mixed with ILs as modified solvation media for conducting reactions. An interesting work from Wang and co-workers studied the addition of amines in IL (*i.e.*, [BMIM]Br) that affected the crystallization process of molecular sieves synthesis.[70c] Adding amines (Figure 9a) in the recipe or not (Figure 9b) clearly led to different crystallization dynamics and selectivity towards two types of molecular sieves, *i.e.*, AlPO$_4$-11 (AEL structure) and AlPO$_4$-5 (AFI structure). The structural change of prepared molecular sieves suggested that amines have a structure-directing effect, along with the IL. This was supported by ^{1}H nuclear magnetic resonance spectra where the formation of hydrogen bonds between amines and IL could be documented, resulting in modified self-organization patterns and supramolecular structure of IL, and eventually different crystallization behaviors.[70c] Although recent studies provide some guidance for developing materials synthesis through adding foreign solvents (including ILs themselves) in ILs as reaction media,[28a, 55, 62n, 70c] further material optimization may improve from a better understanding of structure, properties and chemistry of these mixed solvents, especially the behavior of solutes that "dissolve" in them. Besides

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experimental efforts, computational tools and atomistic simulation of these states between order and disorder will be required to help us to gain insights on these important issues.
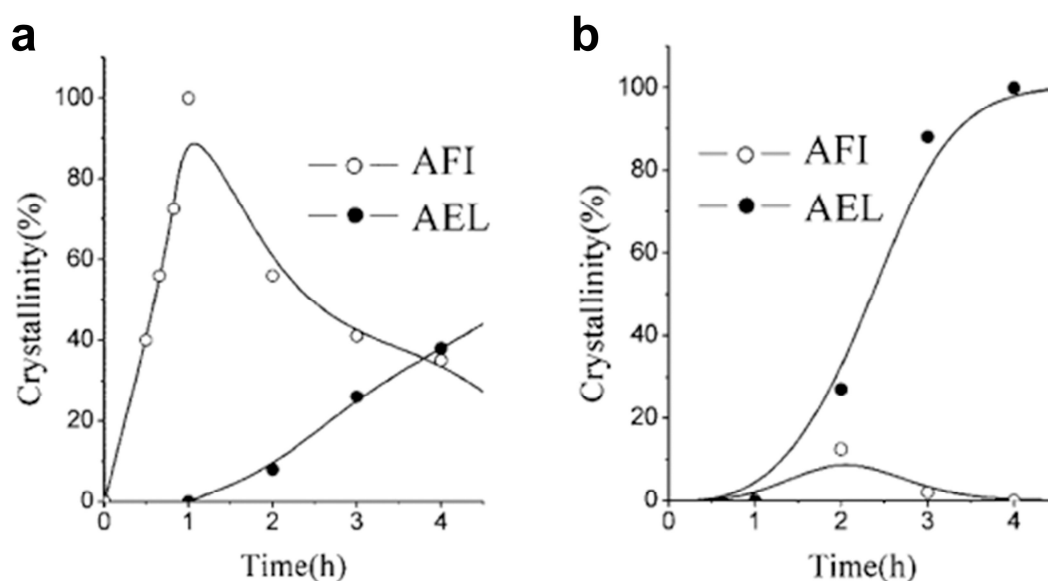

Figure 9. Crystallization curves show that AFI and AEL structures evolved at 190 °C using synthesis mixtures composed of $Al_2O_3 : 2.55P_2O_5 : 0.6HF : 20-[BMIM]Br : xn$-dipropylamine, where a) $x = 1.5$ and b) $x = 0$. Reprinted from the Ref. [70c] with permission from the American Chemical Society.

2.4. Synthesis of inorganic materials controlled by PILs

The polymerization of IL monomers created a new family of polymers (*i.e.*, PILs) with a charged group (cation or anion) as a repeating unit (Figure 10a). Although the first research of PILs could be dated back to 1970s,[77] a focused effort on PILs was re-initiated after Ohno and co-workers' work of designing solid electrolytes that indeed could replace ILs for electrochemical applications.[78] PILs inherit their unique properties from ILs, and polymer side brings new functionalities such as enhanced shape stability, improved processability, flexibility, as well as improved control over the meso-to nanostructures.[15] Most important concept in the present context is the "multifunctionality",[79] which is by the repeat of an interaction motif, the exerted control *via* binding gets amplified, until completely orders of interaction can be reached (note that using a Boltzmann approach of interaction, the repeat number enters the exponential of the binding constant).

The scientific and technological importance of PILs meanwhile spans a wide range of applications and was reviewed before.[15-18] Here we only discuss their role as morphosynthesis

agents, in analogy to the ILs above. It is well known that conventional polymers can be used as effective crystal growth modifiers that can control the architectures of inorganic materials at various hierarchy levels.[80] For example, synthetic double-hydrophilic block copolymers have shown great advance as additives for generating new crystalline minerals, where the functional block can be tailored for specific polymer-crystal interactions.[80b] The low solubility of these polymers in all other media than water however limits their applications for the synthesis of a wide range of inorganic materials. PILs on the other hand can dissolve easily in many organic solvents, and choice of counter ions even allows adaption of solubility to a given reaction medium.[15a, 15b] This combines with other intriguing merits of PILs enables them to be very effective additives for the preparation of inorganic objects with controlled morphology and structural specialty. Nevertheless, only relatively limited reports regarding this strategy have been documented,[81] leaving it a very promising research field.

Zhang and co-workers demonstrated that PILs are effective to improve conventional hydrothermal carbonization process, realizing the easy preparation of nanostructured porous nitrogen-doped carbon materials (S_{BET} up to 572 m^2g^{-1}) (Figure 10b and c).[82] Without PILs, the exact same carbonization process yielded micrometer sized carbon particles with low Brunauer-Emmett-Teller surface area (<10 m^2g^{-1}) (Figure 10d).[82] These surface-active PILs (*e.g.*, poly(3-cyanomethyl-1-vinylimidazolium) bromine (PCMVImBr)) act as stabilizers that restrict further growth of carbon nanoparticles formed at early stage; while the charges in the backbone introduce electrostatic repulsion to avoid their agglomeration in solution, thus reducing the particle size from micro-scale to nano-scale. Moreover, PILs here play roles of pore-generating agent and nitrogen sources that functionalize prepared carbon products with porosity and nitrogen-doping.[82] Very recently, Gao and co-workers introduced PILs as effective additives that enable a remarkable level of control over morphogenesis of Bi_2S_3 crystals.[83] For example, very unusual high-crystalline mesoporous Bi_2S_3 sheets were prepared using the imidazolium-based PILs as crystal growth modifiers (Figure 10e and f), enabling the arrival at this novel 2D structure although Bi_2S_3 itself has strong tendency toward 1D growth.[84] It is reasonable to assume that with the coming efforts focus on PILs, the next few years will bring new advancements in materials synthesis that allows for the access of inorganic crystals with tailored architectures and properties.
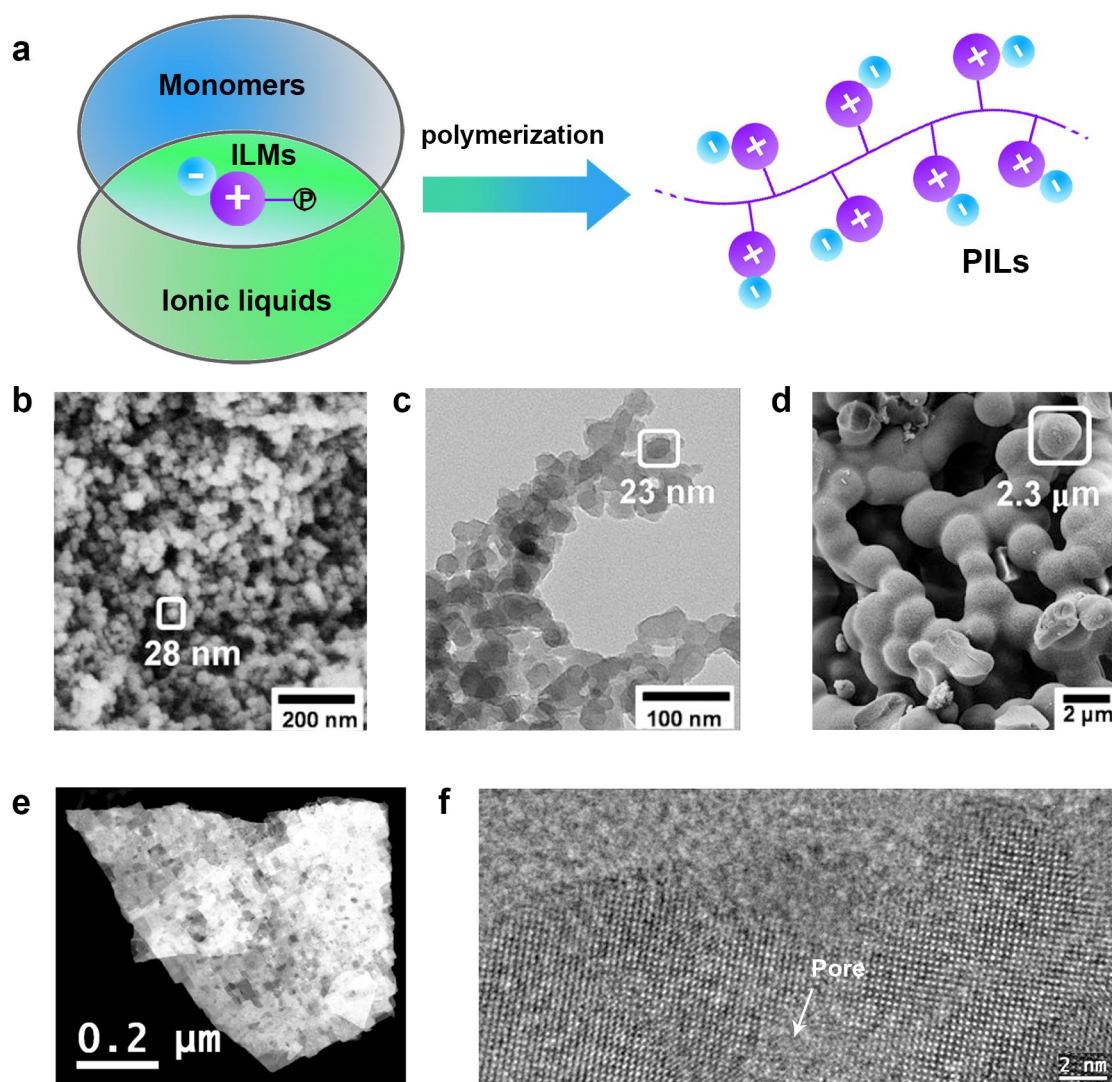
Figure 10. a) Schematic of the relationship between ILs and PILs. ILMs: IL monomers and "P": polymerizable group. b, c) SEM and TEM images of carbon materials prepared by HTC of 0.9 g D-Fructose with the presence of 0.3 g PCMVImBr at 160 ^{o}C for 23 h, respectively. d) SEM image of carbon materials prepared using the same process as that for b, c), but without PILs during the synthesis. Reprinted from the Ref. [82] with permission from the Wiley-VCH. e) High-angle annular dark field scanning transmission electron microscopy image of Bi$_2$S$_3$ mesoporous nanosheets prepared using PCMVImBr as additive. f) HRTEM image shows the high-crystalline Bi$_2$S$_3$ crystal with mesoporous structure. Reprinted from the Ref. [83] with permission from the Wiley-VCH.

3. Applications of inorganic materials from ILs/PILs

The various inorganic compounds with novel morphology and/or structurally special characters that are hardly or inaccessible through conventional synthetic chemistry open of course massive application potential in fields spreading from energy storage, catalysis and optics to medicine and others.[48g, 62n, 70b, 85] It is important to note that inorganic materials prepared within/with ILs/PILs

not only preserve the original properties but that the ILs/PILs usually add characteristics or lead to improved performances. For example, in 2003, Fukushima and co-workers prepared physical gels by grounding imidazolium ILs with single-walled carbon nanotubes (CNTs), creating the first gelatinous carbon material—called bucky gels.[86] They later described the electromechanical application of such CNT-IL hybrid as bucky gel actuators (Figure 11a).[87] IL in this device acted as not only an internal electrolyte but also a conducting material that binds with CNTs. Under the stimulus of an applied voltage, imidazolium cations and BF_4^- anions can form an electric double layer with oppositely charged CNTs, which leads to swelling and shrinkage at the cathode and anode layers, respectively, and eventually the mechanical bending (Figure 11a).[87a] Guo and co-workers reported an interesting hybrid material of CNTs/ILs/Pt, where ultra-small Pt nanoparticles (~3 nm) with uniform dispersion adhere to the surface of 1-(3-aminopropyl)-3-methylimidazolium bromide-functionalized CNTs (Figure 11b).[85a] Such amine-terminated IL-linked hybrid exhibits superior electrocatalytic activity towards methanol oxidation reactions as compared with commercial Pt/C catalyst and CNT/Pt hybrid using poly(diallyldimethylammonium chloride) (PDDA) as linkers (Figure 11c).

Thermoelectric devices are based on semiconducting materials that enable electricity generation or cooling applications directly from a heat source.[88] Although its discovery can date back to 1950s, no candidate materials bearing Seebeck coefficient larger than 3 are on the horizon.[89] Also in field, ILs have stepped in the synthesis of new materials for enhanced thermoelectric properties.[48g, 65, 90] Semiconducting metal chalcogenide films and crystals with tailored size, shape and structure were prepared in appropriate ILs and demonstrated potential performance gains.[65, 90a-c] Biswas and co-workers reported that $[Bi_2Te_2Br](AlCl_4)$ and $[Sb_2Te_2Br](AlCl_4)$ compounds—thermoelectric materials with extended layered structures and anisotropic electrical transport properties—can be prepared in a Lewis acidic IL, $[EMIM]Br-AlCl_3$.[90f] Ding and co-workers[48g] described the use of tetrabutylphosphonium halide ($[P_{4444}]X$, X = Cl, Br) ILs for dissolving chalcogen elements, which allows for the rapid reaction between chalcogens and metal powders under microwave heating that leads to various micro-/nano-structured metal chalcogenides (Figure 11d). Of note, the phosphonium halide ILs also simultaneously enable the halogen atoms to be doped in metal chalcogenides for n-type thermoelectric materials. This results in a PbTe material prepared in $[P_{4444}]Br$ exhibits a relatively high power factor as compared to other counterparts,[91]

owing to its high Seebeck coefficient (Figure 11e and f).[48g] Other kinds of efficient thermoelectric materials made from ILs can be anticipated.

Recent activities in materials research also witnessed low-cost and high-performance storage electrodes enabled by ILs.[92] For example, olivine $LiFePO_4$ has limitations due to the very low electronic conductivity.[93] In recent reports, Tarascon and co-workers described the use of ILs to enable the preparation of $LiFePO_4$ with controlled size and morphology, at temperatures at least 200 °C lower than those needed for conventional ceramic approaches.[85b, 94] The nanosized $LiFePO_4$ made in [EMIM]TFSI was found to perform satisfactorily with sustainable reversible capacities of 150 mAh g^{-1} at a C/10 rate (Figure 11g, inset left) and 80% of the delivered capacity at a 1C discharge rate (Figure 11g, inset right).[85b] It fits to the discussed context that the low-temperature ionothermal synthesis obviously permits $LiFePO_4$ to crystallize at nanocale (without amorphous surface layers), which offers exceptionally short transport lengths and significantly reduced Li ion diffusion time, thereby resulting in the enhanced battery performance.

The ionothermal for making open-framework crystals was already discussed above, while exploration of special applications is still in its infancy.[9c, 9d, 25] The limited existing examples already reveal advanced applications of porous materials prepared from ILs: Cai and co-workers found that a high-quality coating of SAPO-11 zeolite film onto metal surface can be realized in imidazolium ILs (Figure 6), which shows very good corrosion-resistant properties.[58] Fu *et al.* reported that a family of (Mo_8O_{26})-based porous MOFs can be prepared using [EMIM]Br as solvent (Figure 11h), where the weak coordinating ability of the used IL facilitates the self-assembly of polyoxoanions.[95] After activation (*i.e.*, bulky organic cations within the nanosized channels were replaced by transition-metal ions *via* a cation-exchange process), the IL-prepared MOFs show N_2 and H_2 uptakes of 276 cm^3 g^{-1} and 176 cm^3 g^{-1} (at standard temperature and pressure), respectively, comparing favorably with documented porous materials such as zeolite Y, mesoporous silica, and ZIF-8 (Figure 11i).[95] Furthermore, such MOFs can exhibit CO_2 uptake capacity at saturation of 165 cm^3 g^{-1} (7.4 mmol g^{-1}, 231.6 L L^{-1}) at 195 K and 87.7 cm^3 g^{-1} (3.9 mmol g^{-1}, 122.5 L L^{-1}) at 273 K, performing comparable to the highest value of classical zeolite-like MOFs.[95]
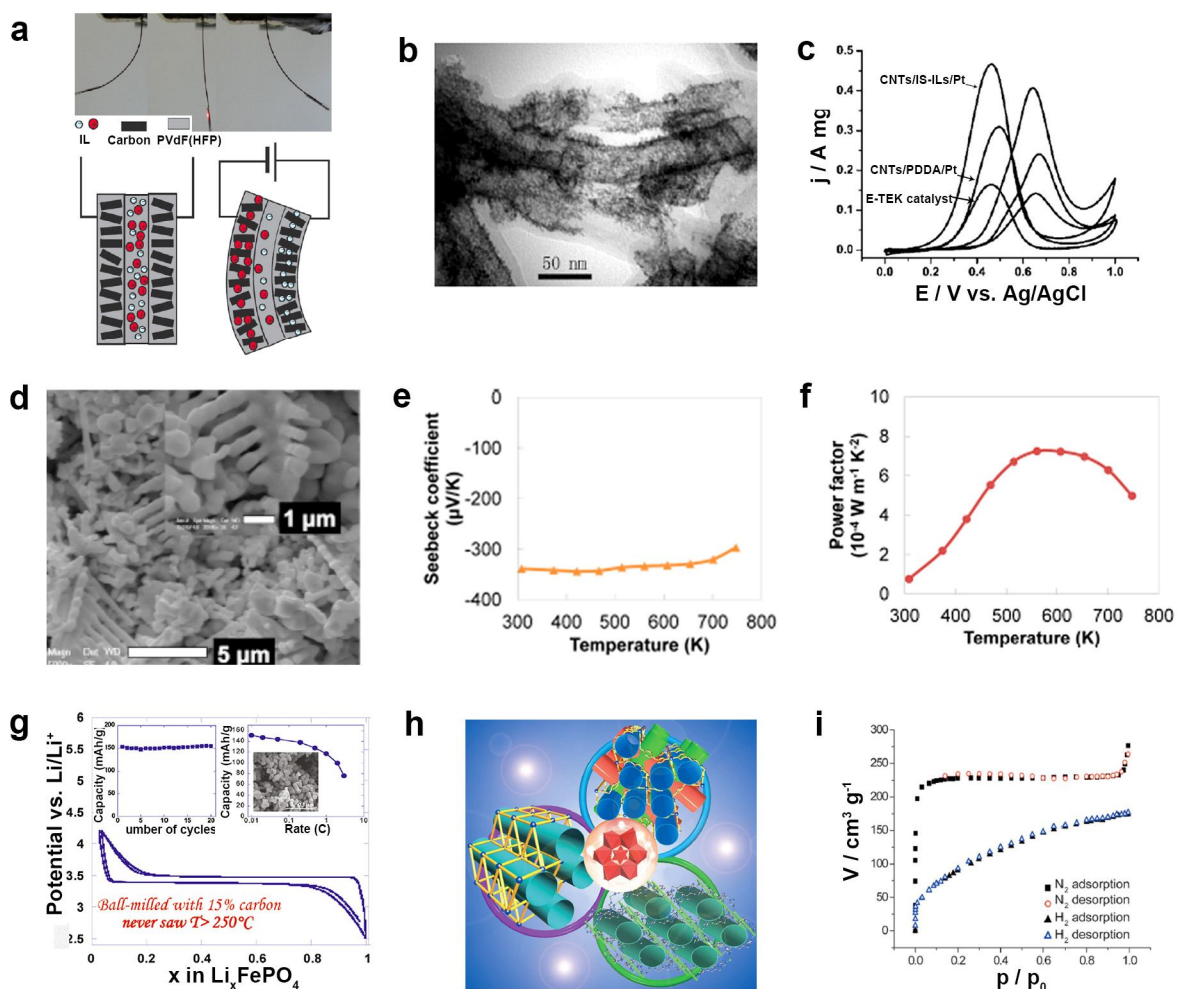
Figure 11. a) Performances of bucky-gel actuator in response to alternating square-wave voltages; bending motion of the actuator strip at an applied voltage of ±3.5 V with a frequency of 0.005 Hz (up), and schematic of the response modeling of the bucky-gel actuator based on the ion transfer mechanism (down). Reprinted from the Ref. [87a] with permission from the Elsevier. b) TEM image of CNTs/ILs/Pt hybrid nanostructure. c) Cyclic voltammograms of modified glass carbon electrodes comprising the E-TEK Pt/C catalyst, CNTs/PDDA/Pt hybrid, and CNTs/ILs/Pt hybrid at the scan rate of 50 mV s^{-1}. Reprinted from the Ref. [85a] with permission from the Wiley-VCH. d) SEM image of PbTe prepared by microwave heating of corresponding elemental precursors in [P$_{4444}$]Cl. Inset shows a enlarged SEM image. e, f) Thermoelectric property measurement of PbTe materials prepared in [P$_{4444}$]Br after spark plasma sintering: temperature dependence of e) Seebeck coeffient and f) power factor. Reprinted from the Ref. [48g] with permission from the American Chemical Society. g) Voltage-composition profile along with the capacity retention (inset left) and power rate (inset right) for Li/LiFePO$_4$ half cells assembled with nanometric LiFePO$_4$ powders prepared in [EMIM]TFSI. Cycling rate is C/10. Reprinted from the Ref. [85b] with permission from the American Chemical Society. h) Schematic of the three (Mo$_8$O$_{26}$)-based porous MOF materials made through ionothermal synthesis. i) Gas sorption isotherms of activated (TBA)$_2$[Cu^{II}(BBTZ)$_2$(α-Mo$_8$O$_{26}$)] (TBA = tetrabutylammonium cation, BBTZ = 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene) for N$_2$ and H$_2$ at 77 K. Reprinted from the Ref. [95] with permission from the Wiley-VCH.

4. Conclusion and a Personal Outlook

ILs, although known for over a century, experienced in the last years increasing research interests from material chemistry and are full of promises for a range of critical applications. Remarkably, ILs have demonstrated great potential to provide a substantial impact on synthetic inorganic chemistry by offering a complementary tools that are hardly or inaccessible through conventional ways using water or organic solvents as media. In this review, we highlighted key advances in IL research regarding morphology and polymorph control for the access of inorganic crystalline materials with tailed size, dimensionalities, morphologies and functionalities. We extended this approach shortly by introducing also the polymeric counterparts, PILs as additives. Moreover, various applications ranging from actuators and electrocatalysis to energy storage were spotlighted, which illustrate that crystalline materials created from ILs/PILs usually enable improved functionalities and performance.

It should be noticed that the research of synthesizing inorganic crystalline materials based on ILs/PILs is now in its early stage and needs to be systematized and quantified. Besides gaining further knowledge on the structure of ILs/PILs close to mineral surfaces, it is important to have in-depth understandings on how ILs/PILs species interact with solutes and reactants; how they influence the nucleation, growth, crystallization and/or self-assembly process. Fundamental insights on the structure of the electric double layer at IL-based electrodes are highly desired to continue advancing electrochemical synthesis. Advancements are also needed for the development of "greener and biodegradable" ILs/PILs, which thereby would permit the applications of the as-prepared hybrids to consumers, and potentially also to bioscience and medicine. Several other aspects those are worth exploring include the use of task-specific ILs for creating unusual structures such as chiral inorganic materials; developing new types of ILs/PILs as alternatives to commonly used imidazolium-based ILs; and mixtures of ILs and how they increase the synthetic flexibility; as well as lowing the cost of ILs/PILs for economically viable synthesis. For all that, the future of ILs/PILs in materials science is bright!

Acknowledgements

Biographies

Min-Rui Gao received his Ph.D. degree from the University of Science and Technology of China in 2012 in Nano Chemistry under the supervision of Prof. Shu-Hong Yu. He then did postdoctoral research at University of Delaware and Argonne National Laboratory in USA during 2012-2015. After that, he worked in the Department of Colloid Chemistry, directed by Prof. Markus Antonietti in the Max Plank Institute of Colloids and Interfaces in Potsdam, Germany (2015-2016). His research interest involves the development of nanostructured materials and their applications in energy fields.

Jiayin Yuan studied chemistry in Shanghai Jiao Tong University, China in 1998. He received his master degree in the University of Siegen in 2004, and doctoral degree (summa cum laude) in the University of Bayreuth, Germany in 2009. He then joined the Max Plank Institute of Colloids and Interfaces in Potsdam as a postdoc supervised by Professor Markus Antonietti, where he was promoted to a research group leader in 2011. He received the ERC Starting Grant in 2014 and Dr. Hermann-Schnell Award in 2015. His current interest focuses on poly(ionic liquid)-derived functional (nano)materials.

Markus Antonietti studied chemistry in Mainz, where he also received his Ph.D. in 1985 and his Habilitation in 1990. Since 1993 he has been the director of the Max Plank Institute of Colloids and Interfaces. His work deals with modern materials chemistry, energy materials, and sustainability issues within those topics. He published around 650 papers and issued 90 patents, his H-index is

128. Besides being a devoted chemist and a higher academic teacher, he is also a passionate chef specialized in fusion cuisine and performs in a Rock 'n' Roll band.

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