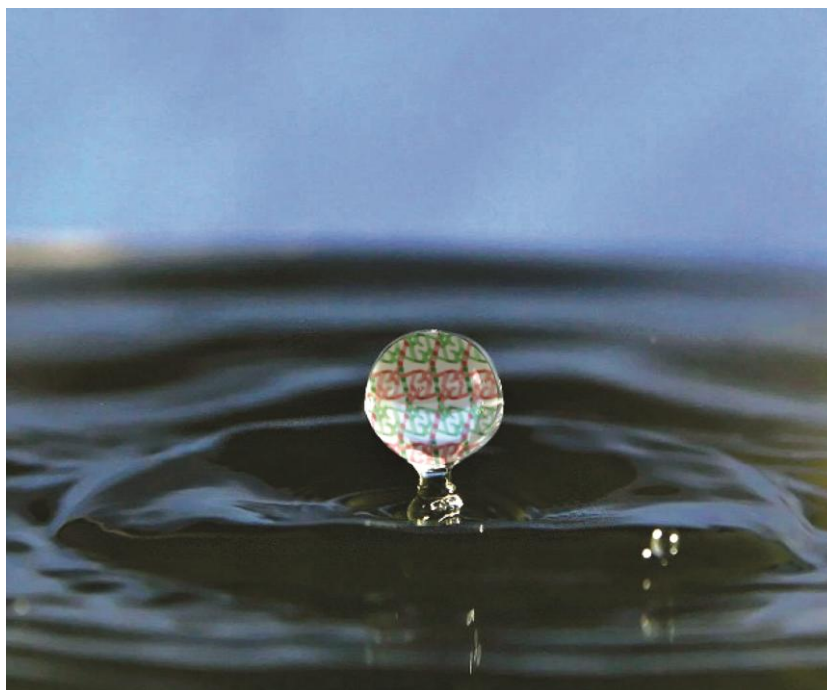


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Crystal Engineering with Ionic Liquids

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HIGHLIGHT

Ionic liquids as crystallisation media for inorganic materials

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Ionic liquids (ILs) have made a great impact on materials science and are being explored for potential applications in several disciplines. In this article, we briefly highlight the current state-of-the-art techniques employing ILs as new crystallisation media, working as neutral solvent, template or charge compensating species. The use of an IL as environmental friendly solvent offers many advantages over traditional crystallisation methods. The change from molecular to ionic reaction media leads to new types of materials being accessible. Room temperature ILs have been found to be excellent solvent systems for the crystallisation of a wide range of substances and morphologies ranging from nanoscopic crystals to micro- and even to macroscopic crystals. Moreover, high temperature routes, such as crystallisation from melts or gas phase deposition, have been replaced by convenient room or low temperature syntheses, employing ILs as reaction media.

Introduction

ILs are basically low melting salts ($T_m < 100\text{ }^\circ\text{C}$) which have highly interesting physical (such as wide liquid range, negligible vapour pressure, large electrochemical window, and high electric conductivity) and chemical (e.g. solvent) properties.^{1–3} Owing to their distinctive

features, ILs have found potential applications in organic and inorganic synthesis,^{1,4} separation techniques,⁵ lubrications,⁶ electrodeposition,⁷ spectroscopic studies,⁸ as electrolyte in photovoltaic devices (solar cells),⁹ and in crystal engineering of a wide range of substances.^{10–16} It has been observed that the inclusion of selected transition metal atoms or functional

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his doctorate in 2011, working on the synthesis of metal clusters and main group polycations from ionic liquids. Currently he is a postdoctoral researcher and his research interest is focused on crystal engineering of polynuclear main group compounds from room temperature ionic liquids.

Ejaz Ahmed studied Chemistry at Quaid-i-Azam University Islamabad, Pakistan and received an M.Sc. and an M.Phil. degree. In 2007, he was awarded a Ph.D. scholarship by the Higher Education Commission of Pakistan and the German Academic Exchange Service (DAAD) then he joined the research group of Prof. Ruck at the Dresden University of Technology. He completed



Joachim Breternitz

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Joachim Breternitz studied chemistry at the Dresden University of Technology. In the course of a double-degree programme under an ERASMUS scholarship, he visited Ecole Nationale Supérieure de Chimie de Rennes in France. He also had a short research stay in the group of Prof. Patzke at the University of Zurich in June 2011. He returned to Dresden at the end of 2011 and joined the research group of Prof. Ruck as a master

groups into the components of ILs can also render additional specific properties, such as inherent magnetism, chirality, optical, and catalytic activity, which depend primarily on the incorporated metal atoms or functional groups.^{17–20} The proper selection of ILs' components may possibly facilitate problem solving. For example, by choosing a suitable combination of ions capable of solubilising specific solutes, the solubility critical to crystallisation processes can be controlled. Therefore, several features of many currently investigated ILs may be helpful in the crystallisation of a desired product.

ILs have a wide liquid range (in some cases as large as -90 to 300 °C),¹ combined with low melting points, and the potential for tailoring size, shape, and functionality offers opportunities for thermal operating windows and control in reactivity that are not available with conventional molecular solvents. Thus, ILs provide unique prospects to use much higher and much lower temperatures for a reaction in a single reaction medium. ILs have higher viscosities than traditional organic solvents. High viscosity is important in crystal engineering of compounds when slow crystal growth from diffusing co-solvents is desired.¹⁰

ILs' solvent properties can be adjusted by modifying the intermolecular and interionic interactions present in the solvent. Some interesting observations can be explained by the ILs' solvent properties, *e.g.* the formation of liquid clathrates with aromatic compounds, the

selectivity and acceleration of organic and inorganic reactions, and the higher solubilities of a variety of inorganic materials.^{4,21} Hydrogen bonding ability of ILs is one of the important solvent properties for crystallisation.¹⁰

Recent studies on the interactions in the solid and liquid state suggests a loose ion lattice similar to a crystal lattice of a salt, where a cation is surrounded by several anions and *vice versa*.²² Consequently, ILs are not recommended to be treated as totally 'free' ions charge-separated solvent systems. Moreover, in comparison with conventional organic solvents, it has been observed that ILs are typically more structured.^{10,22}

Since the chemical and physical properties of inorganic materials often depend on their morphology and dimensionality, two main strategies for the fabrication of shape-controllable inorganic solids have been developed. The first approach is the template method, which employs a polymeric core support while the second is the soft method which makes use of ILs.^{23,24} The latter is in fact the template-free method, which is facile and efficient compared with the template method. The addition of a template to the reaction system involves a complicated process because of the incomplete removal of the template which may be responsible for some impurities. Therefore, ILs-based synthetic strategy was found to be more attractive and promising because the operations are relatively simple, environmental friendly, economical, and the overall product yield is high.^{18,23d}

In 2006, Rogers and co-workers for the first time demonstrated some interesting aspects of ILs as a new crystallisation media.¹⁰ They discussed different problems associated with crystallisation from ILs and suggested their possible solutions, *e.g.*

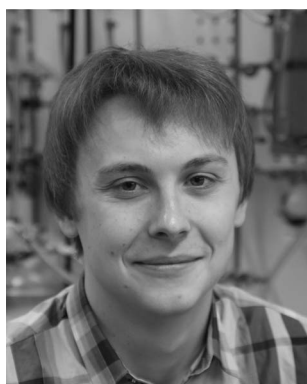
- Thermal shifts method to crystallise a variety of inorganic materials having low or high melting points at their respective freezing temperatures in an IL.

- The use of volatile co-solvents to increase the solubility of many metal salts in ILs and to facilitate crystal growth.

- Solvothermal or more appropriate ionothermal techniques using ILs with negligible vapour pressure and high thermal stability (this high temperature synthesis in ILs may not require any pressure vessels, making this technique more widely applicable).

- Slow diffusion technique to make use of the high viscosities of ILs whereby a solute in an IL solution is carefully layered onto a second (same or different) IL solution of another reagent to grow high quality crystals by allowing slow mixing.

These strategies were proven to be very useful to isolate or crystallise different products from ILs. The present article aims to highlight some of the more interesting and recent state-of-the-art techniques employing ILs (Table 1) as the crystallisation media, working as neutral solvent, template or charge compensating species. Primarily, the crystallisation of a wide range of substances and



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Matthias F. Groh studied chemistry at the Dresden University of Technology. In 2008, he was awarded a short term scholarship by the DAAD in corporation with the National Science Foundation (NSF) then he joined the group of Prof. Shores at Colorado State University. Before obtaining his master degree in 2011, he went to the National University of Mongolia for another short term program in 2010. Currently he is a Ph.D. student in the research group of Prof. Ruck and his research deals with the synthesis of metal-rich compounds from ionic liquids, structural determination, and quantum chemical calculations.



Michael Ruck

Michael Ruck obtained his diploma in chemistry in the group of Hartmut Bärnighausen at the University of Karlsruhe (Germany) in 1989. Then he joined the group of Arndt Simon at the Max Planck Institute for Solid State Research working on cluster compounds of rare earth metals and completing his doctoral degree in 1991. He returned to Karlsruhe, where he completed his habilitation on ternary bismuth subhalogenides in 1997. Since 2000 he holds the Chair for Inorganic Chemistry at Dresden University of Technology. His research interests concern subvalent compounds, low-dimensional systems, metastable phases, and low temperature syntheses of inorganic materials.

Table 1 List of abbreviations for different ionic liquids and ions

Ionic Liquid	Abbreviation
1-Methyl-1-propylpyrrolidinium bis(trifluoromethyl)sulfonylimide	[MPPYR][Tf ₂ N]
<i>N,N</i> -Dimethyloctadecylammonium bis(trifluoromethyl)sulfonylamide	[Me ₂ D ₂ N][Tf ₂ N]
1-Butyl-1-methyl-pyrrolidinium bis(trifluoromethyl)sulfonylimide	[BMPYR][Tf ₂ N]
Trifluoromethanesulfonate	[OTf] ⁻
Tetrapropylammonium bromide	[Pr ₄ N]Br
1-n-Butyl-3-methylimidazolium tetrachloridoaluminate	[BMIM][AlCl ₄]
1-Ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	[EMIM][Tf ₂ N]
1-n-Butyl-3-methylimidazolium L-aspartate	[BMIM][L-AspH]
1-Ethyl-3-methylimidazolium tetrafluoroborate	[EMIM][BF ₄]
1-Ethyl-3-methylimidazolium L-lactate	[EMIM][L-lactate]
1,1-(1,4-Butanediy)-bis(imidazole)	Bbi
1-Octyl-3-methylimidazolium trifluoroacetate	[OMIM]TA
1-Ethyl-2,3-dimethylimidazolium bromide	[EDMIM]Br

morphologies that range from nanoscopic crystals to micro- and even to macroscopic crystals will be discussed. Briefly, the modes of synthesis of new inorganic materials, morphologies, properties, and their possible applications will be highlighted. Moreover, we would like to point out some new directions and challenges of the future research. For convenience, the selected inorganic materials are categorised and discussed with respect to their average crystallite size. This highlight aims to provide a general overview of the field and to prompt future research efforts in crystal growth or crystal engineering from ILs.

Nanosopic crystals

In 2003, Antonietti *et al.* reported for the first time the synthesis of very fine anatase nanocrystals in IL under mild conditions.²⁵ The synthesis was carried out in the IL [BMIM]BF₄ *via* hydrolysis of TiCl₄ to obtain TiO₂ nanocrystals with an average diameter of 2–3 nm. The nanocrystals of TiO₂ were observed to build a self-assembly towards sponge-like spherical aggregates. The high crystallinity of the obtained particles underlines the unique advantages of the IL method compared to other synthetic pathways towards TiO₂ nanocrystals. The titania nanosponge shows structural mesoporosity with considerably high surface area and narrow pore size distribution, rendering the material interesting for solar cell conversion, catalysis, and electronic devices.

Yang *et al.* obtained nanoparticles of the Co-Pt system by high temperature synthesis in the IL [BMIM]Tf₂N.²⁶ Making use of the high thermal stability of the IL, they carried out the processes

at 350 °C, which was found to be indispensable for the formation of the intermetallic phases. They obtained the crystalline Co-Pt intermetallics in the form of single crystalline nanorods (Fig. 1). The Co/Pt ratio of 3 : 1 was determined by micro-electron diffraction. Further, they have also established that the use of IL is of great importance for the synthesis of Co-Pt nanorods because a reference synthesis in trioctylamine could not lead to the nanorods formation.

The synthesis of YVO₃:Eu nanocrystals of 12–15 nm diameter and of YVO₃:Eu@YF₃ core-shell nanocrystals was described by Feldmann and co-workers.²⁷ They successfully verified the possibility of re-crystallisation of nanoparticles in the IL [MeBu₃N][N(SO₂CF₃)₂]. The YVO₃:Eu nanocrystal formation consisted of two steps; in the first step, nanoparticles were formed in an IL–alcohol mixture and in the next step, crystallisation was achieved in the IL at 200 °C. The use of a co-solvent is necessary to lower the viscosity of the system and to enhance the solubility of the starting materials. The use of an IL as solvent resulted in the synthesis of monodispersed, nonagglomerated, and redispersible nanocrystals. The core-shell nanoparticles exhibit photoluminescence which could propose their possible use in optics.

The synthesis of single crystalline nanorods of α -FeOOH was reported by Kang and co-workers.^{28a} The preparation of the α -FeOOH nanocrystals was conducted under hydrothermal conditions in the presence of a certain amount of the IL [BMIM]Cl. The obtained α -FeOOH nanorods were analysed by selected area electron diffraction and found to be single-crystalline with dia-

mers of 50–65 nm (Fig. 2). The as-prepared nanorods of α -FeOOH were transformed into single crystalline porous α -Fe₂O₃ nanorods *via* a thermal degradation process. The role of the IL was described as a template and a capping agent due to the capability of the cation to form a hydrogen bond network. The magnetic and photocatalytic properties of α -Fe₂O₃ nanorods were investigated. The latter is found to be strongly surface dependent and it is believed that α -Fe₂O₃ nanorods could be utilised in green photocatalysis.

Chen *et al.* demonstrated a new approach for the synthesis of ZnO nanocrystals stabilised by the IL [Me₂D₂N][Tf₂N].^{28b} They prepared a composite of IL–ZnO nanocrystal directly from an IL salt containing Zn(II) cations. It has been observed that the size and the photoluminescent properties of the ZnO nanocrystals can be tuned by varying the reaction conditions. The nanomaterials emit blue to yellow light efficiently both in the solvated and in the solvent-free states. Furthermore, high thermal stability and good processability in both the solvated and solvent-free state make these composites highly applicable as new luminescent materials.

Li *et al.* reported the synthesis of CuO nanocrystals with different morphologies (from flower-like to leaf-like) in the IL [OMIM]TA.²⁹ Using the microwave-technique, they also explained the performance of the IL with respect to the high ionic conductivity and polarity. During their studies, they obtained different morphologies of CuO nanocrystals as a function of the reaction temperature and the IL concentration. Moreover, they have also determined the role of the IL in crystallisation and controlling the particles morphology by performing a similar reaction in an IL-free reference experiment. In contrast to the results of Zhu and co-workers,³⁰ who successfully synthesised CuO nanocrystals employing the IL [BMIM]BF₄, Li *et al.* showed a simple way to remove the IL by washing with distilled water and absolute alcohol, which was verified by IR spectra. The band gaps of flower-like and leaf-like CuO nanocrystals were estimated to be 1.68 and 1.70 eV, respectively. Therefore, CuO nanocrystals could find wide applications in various fields such as photonics and catalysis.

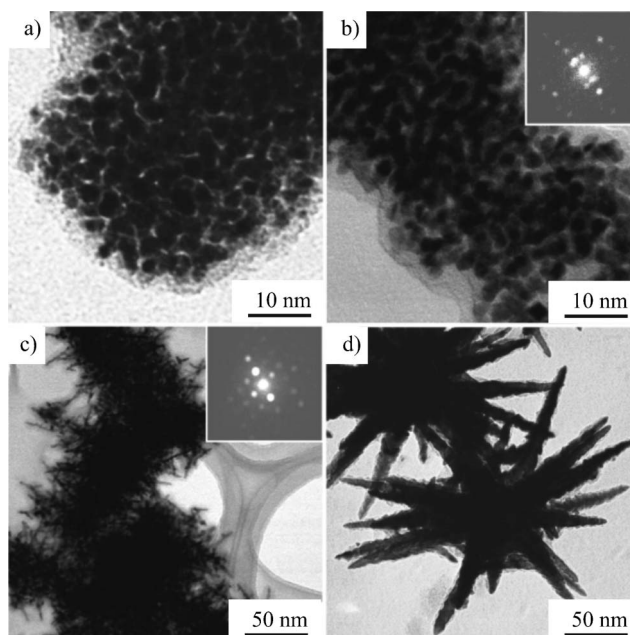


Fig. 1 TEM images of the Co/Pt nanomaterials obtained at the different reactant molar ratios of Pt(acac)₂ : Co(acac)₂ : CTAB: (a) 3 : 1 : 3, (b) 1 : 1 : 3, (c) 1 : 3 : 3 and (d) 1/9 : 1/3 : 3. Insets show micro-electron diffraction patterns from a single nanoparticle (panel b) and part of an individual nanowire (panel c) obtained using the UHV-STEM system. Reproduced from ref. 26 with permission from the American Chemical Society (copyright 2005).

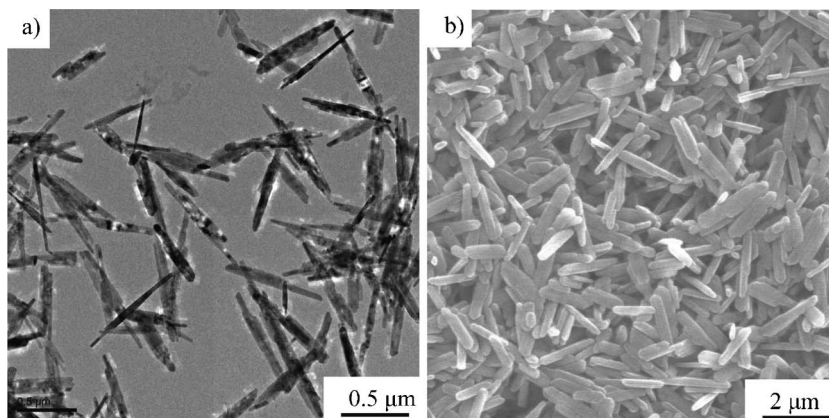


Fig. 2 (a) TEM image and (b) SEM image of α -FeOOH nanorods at 423 K. Reproduced from ref. 28a with permission from the American Chemical Society (copyright 2011).

A detailed study on the formation and crystallisation process of manganese-containing aluminophosphate nanocrystals was performed by Mintova and co-workers.³¹ They investigated the synthesis mechanism of MnAlPO-5 nanocrystals under ionothermal conditions, using the IL [EDMIM]Br. The reaction mixture consisting of aluminum isopropoxide, manganese(II) acetate dehydrate, [EDMIM]Br, and phosphoric acid was treated up to 150 °C for 5 h, which first resulted in the formation of an amorphous phase, which subsequently crystallised to discrete MnAlPO-5 nanocrystals

of 60–80 nm diameter after a heat treatment up to 90 h. The transformation process from an amorphous to intermediate and then to the crystalline MnAlPO-5 nanoparticles shows that the nucleation begins at the solid–liquid interface and continues through surface-to-core reversed growth until the entire amorphous solid is transformed into discrete nanocrystals. They have demonstrated a dual role of the IL; both as solvent and template for the crystallisation. Such inorganic materials are well known for their suitability as molecular sieves.

Yu *et al.* reported the synthesis of Bi₂S₃ nanoflowers in a mixed water/IL-templated system.³² The synthesis was carried out in two steps; a prior ultrasonic treatment, which is then followed by a heating process. They observed the crystallisation of Bi₂S₃ nanocrystals with a diameter of 60–80 nm, during the heating treatment at 120 °C. They have proposed the formation mechanism of the Bi₂S₃ flowers. Furthermore, upon aging, the flower-like structures tend to become loose and fall off from the mother flowers, which resulted in formation of the individual nanowires (Fig. 3).

Yu *et al.* have also demonstrated that the shape evolution and phase transformation strongly depend on the reaction conditions, *e.g.* pH value, reaction temperature, and the reaction time.

An IL-assisted process was reported by Zheng and co-workers to synthesise CdSe nanocrystals having nanospheres and dendrites morphologies.^{33a} They used a Se-containing IL [BMIM][SeO₂(OCH₃)] as a new Se precursor to prepare CdSe nanocrystals. They found that the sizes and morphologies of the crystals depended on the concentration of the IL. The as-prepared CdSe nanospheres show a fine dispersion with a uniform average diameter of about 15 nm with low concentration of IL. It is believed that the CdSe dendrites are obtained by self-assembly form nanospheres with high concentration of IL. They have anticipated that [BMIm][SeO₂(OCH₃)] could be used to prepare other nanoscale metal selenides with special morphologies and improved properties on a large scale.

Yan *et al.* developed a rapid microwave-assisted approach to prepare nanocrystals of NaYF₄ in the IL [BMIM]BF₄.^{33b} It was observed that small nanoparticles could form spontaneously in [BMIM]BF₄ by the microwave irradiation, and then spherical cubic NaYF₄ nanoclusters could be obtained by the self-assembly of these primary nanoparticles. The effect of different precursors or ILs was also studied and it was concluded that ILs played key

roles, such as the solvent for the reaction, the absorbent of microwave irradiation, and the source of fluoride ions for the formation of NaYF₄ nanocrystals. By the investigation of different thermal treatment methods, it has also been found that higher crystallinity and uniformity of the nanocrystals could be achieved in the microwave-accelerated system. The studies of the upconversion properties of the Ln³⁺ codoped NaYF₄ indicate that the synthesised nanoclusters in [BMIM]BF₄ exhibit excellent luminescent properties. Therefore, the rare earth fluoride nanoclusters were anticipated to be applied in solid-state lasers, three-dimensional flat-panel displays, and light emitting diodes.

A prominent recent review article by Neouze describes various classical and non-classical ways (*e.g.* microwave, gamma rays or ultrasound activation) for the synthesis of nanoparticles in imidazolium ILs and discussed the multiple role of ILs (*e.g.* solvent, microwave absorber, template, and stabiliser).^{34a} Moreover, the use of task-specific IL as reducing agent for the synthesis of silver or gold nanoparticles has also been established, *e.g.* imidazolium ILs containing hydroxyl functionalities are found to be good stabilizing and reducing agents for different metal salts and nanoparticles. Such hydroxyl functionalized imidazolium ILs have been applied for the synthesis of silver^{34b} and gold^{34c}

nanoparticles in aqueous medium. It has also been observed that the size of the silver or gold nanoparticles depend on the hydroxyl functionalized imidazolium ILs' concentration. In these ILs, the alcohol functionality is oxidized to an aldehyde while the noble metal ion is finally reduced to a metal.

Although several synthetic strategies have been developed for the morphological control of nanoparticles, rods, and wires of semiconductors, metals, and metal oxides *etc.*, the ILs-based approach is found to be superior due to mild reaction conditions, process economics, simple treatment, high yield, and low environmental impact.^{23,34} The morphological control is important for the outstanding catalytic, magnetic, and other properties. This emerging approach coupled with ultrasonic- and microwave-treatment opens new prospects to control morphogenesis and crystallisation of inorganic materials.

Microscopic crystals

Taubert *et al.* synthesised gold microcrystals *via* the reduction of HAuCl₄ with cellulose in the IL [BMIM]Cl, and systematically studied the effects of reaction temperature and cellulose concentration on size and morphology of the microparticles (Fig. 4).³⁵ They represented a simple and sustainable approach using cellulose, a reducing agent/template

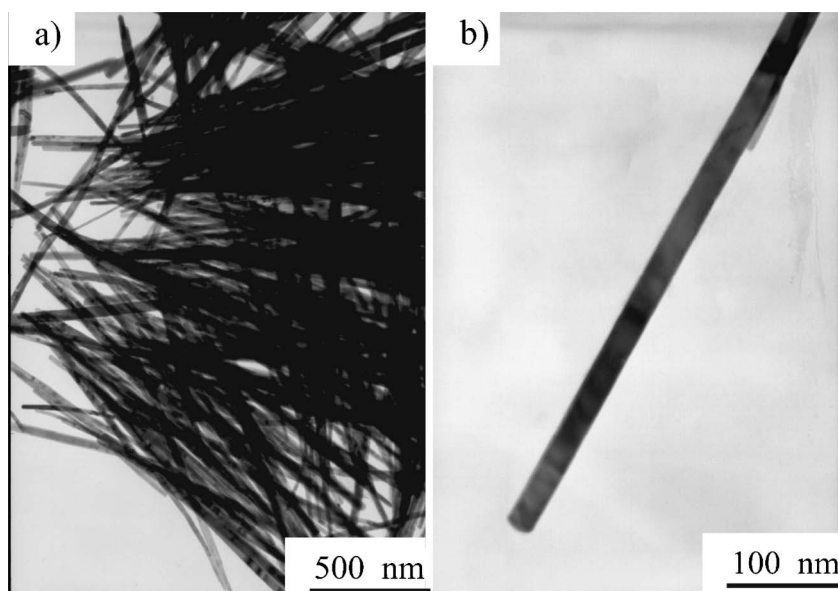


Fig. 3 TEM images of Bi₂S₃ nanowires, obtained in the IL system after reaction at 120 °C for 3 h. The sample was observed after ultrasonic treatment. Reproduced from ref. 32 with permission from the American Chemical Society (copyright 2005).

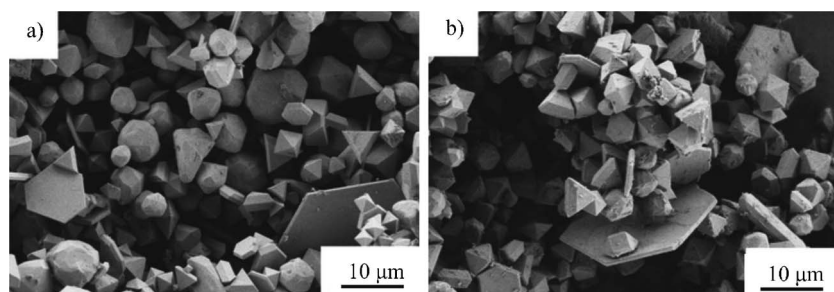


Fig. 4 SEM images of gold crystals prepared at different cellulose concentrations: (a) 40 mg of cellulose, (b) 100 mg of cellulose per g of [BMIM]Cl. Reproduced from ref. 35 with permission from the Royal Society of Chemistry.

from renewable raw material, and an IL, which could be recovered after the reaction. They showed that cellulose is an integral part of the reaction and an increased amount of cellulose increases the reduction rate of Au(III) to Au(0) and consequently enhances the nucleation efficiency of gold microcrystals. Moreover, cellulose drives the crystallisation towards polyhedral particles or large thick plates with diameters over 15 μm , obtained at 160 and 200 $^{\circ}\text{C}$.

A facile route for the preparation of wurtzite ZnO hexagonal micro-pyramids was demonstrated by Xie and co-workers using an IL (a mixture of oleic acid and ethylenediamine).^{36a} They carried out the thermal decomposition of zinc acetate in air employing IL as solvent which resulted in the high yield synthesis of ZnO hexagonal micro-pyramids whose surfaces are enclosed by polarized basal (000 $\bar{1}$) and side surface {10 $\bar{1}$ 1} planes. The base size and the height of the wurtzite ZnO hexagonal micro-pyramids are in the range of 1–1.5 μm (Fig. 5). Moreover, they explained the growth mechanism of the hexagonal micro-pyramid is due to IL lowering the surface energy of the polar surfaces. The experi-

mental results have shown that only in the presence of IL the ZnO hexagonal micro-pyramids could be grown.

An IL-based simple and one-step route for the synthesis of hollow titania microspheres was demonstrated by Kimizuka *et al.*^{36b} They performed an interfacial sol-gel reaction in the IL [BMIM]PF₆ to obtain hollow TiO₂ microspheres. It has been observed that the size of hollow spheres can be controlled by physical conditions such as stirring rate and temperature. Imidazolium molecules act not only as the solvent but also as stabilisers for the hollow microspheres. Moreover, they have also established that the hollow titania gels could be simultaneously modified with functional carboxylic acids and metal nanoparticles. It was also proposed that the asymmetric modification of the inner and outer surfaces of TiO₂ microspheres with photofunctional molecules and metal colloids could lead to a new family of photocatalytic systems.

Zheng *et al.* prepared dispersible ZnSe hollow microspheres by a novel, simple, and mild process using the IL [BMIM]Br-assisted complex-solvothermal method.³⁷ The uniform ZnSe micro-

spheres have the zinc blende structure with an average diameter of about 1.0 μm . It was observed that the IL and the pH have played important roles in controlling the morphology of ZnSe. The relatively high ionic conductivity and low surface tension of the IL, has affected the morphologies of the products and allowed the reactions to be carried out under milder conditions (at 140 $^{\circ}\text{C}$). Especially, the lower interface tension results in a high nucleation rate for the growth of ZnSe microcrystals. On the basis of their novel photonic properties, Zheng *et al.* have proposed these materials as potential building blocks for optoelectronic devices. Microaggregation, microcubes, and nanoplates of CoCO₃ were also successfully synthesised by Zheng *et al.* employing an IL [BMIM]Cl.³⁸

They have observed that the sizes and the morphologies of the CoCO₃ crystals depend on the concentration of the IL as well as the reaction temperature. The uniform CoCO₃ microcubes are obtained at 180 $^{\circ}\text{C}$ with a side length range of almost 3 μm while nanoplates are obtained at 120 $^{\circ}\text{C}$. Remarkably, the CoCO₃ microcrystals exhibit monodisperse characteristics. Further, Zheng

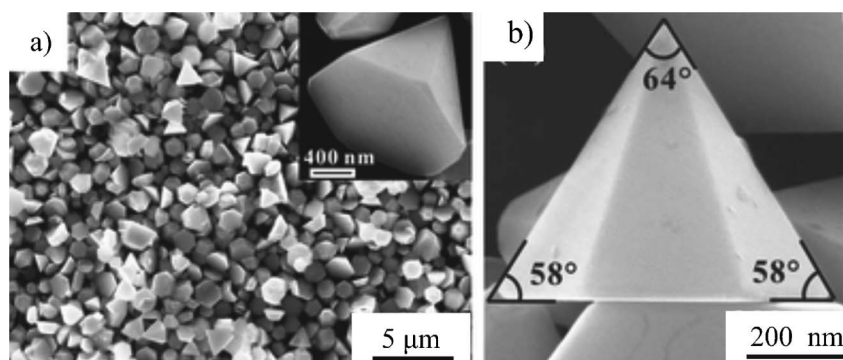


Fig. 5 (a) SEM image of the morphology of the ZnO micro-pyramids, an enlarged SEM image (inset) and (b) SEM image of an individual ZnO hexagonal micro-pyramid. Reproduced from ref. 36a with permission from the Royal Society of Chemistry.

et al. have used CoCO_3 microcrystals as a useful precursor to obtain porous Co_3O_4 particles with similar morphology through calcinations.

Huang and co-workers synthesised different morphologies of AgX (X = Cl, Br) microcrystals in a single-step *via* an ILs-assisted hydrothermal method (1.2–1.3 mmol of ILs were added in 90 ml of water).³⁹ The growth mechanism of AgX crystals was studied systematically under the influence of ILs $[\text{C}_n\text{MIM}]\text{X}$ with different alkyl chains ($n = 4, 8, 12$, and 16). They have shown that the morphology and size of AgX microcrystals could be tuned by using different ILs. The long aliphatic chains principally restrict the size (200 nm to 2 μm) and dispersion of the particles. With the increase in the length of the alkyl chain, the size of samples prepared under the same conditions will decrease, and the morphology tends to be uniform (Fig. 6). The near-spherical microcrystals with convex faces were obtained by employing ILs $[\text{C}_{16}\text{MIM}]\text{X}$ as a halogenide source and stabiliser. It has also been investigated that near-spherical Ag@AgX exhibit a superior plasmonic photocatalytic activity.

Lin and co-workers obtained binary YF_3 and rare earth fluoride REF_3 (RE = La–Lu) nano/microcrystals with multi-form crystal structures (hexagonal and orthorhombic) and different morphologies (nanodisks, secondary aggregates constructed from nanoparticles, and elongated nanoparticles) *via* a fast and facile microwave-assisted IL method.^{40a} The experi-

mental results show that the products formation depends entirely on the use of microwave irradiation and the IL $[\text{BMIM}]\text{BF}_4$. Microwave irradiation accelerates significantly the reaction rate and shortens the reaction time while the IL serves multiple functions simultaneously as solvent, reactant, and reaction template. In addition, Lin and co-workers investigated the magnetic and luminescent properties of the fluoride materials and proposed their possible applications, *e.g.* the multifunctional properties of $\text{GdF}_3:\text{Ce}^{3+}/\text{Ln}^{3+}$ make such materials applicable in the fields of light display systems, lasers, optoelectronic devices, and MRI.

Ying and co-workers synthesised decahedral CdMoO_4 microcrystals by reacting CdCl_2 and Na_2MoO_4 at 60 $^\circ\text{C}$ in the presence of the IL $[\text{BMIM}]\text{Cl}$ as a surfactant.^{40b} It has been observed that IL and reaction time are key factors for the formation of decahedral CdMoO_4 microcrystals. The photoluminescence spectrum of the as-synthesised decahedral CdMoO_4 microcrystals exhibits a strong and broad emission in the visible region which indicates that these kinds of inorganic solids could be used in solar cells, photoelectric and photocatalytic applications.

Macroscopic crystals

Mudring *et al.* conducted several studies⁴¹ to synthesise and isolate macrocrystals from ILs, *e.g.* a novel salt-like compound $[\text{MPPYR}][\text{NdI}_6]$, composed of

octahedral $[\text{NdI}_6]^{3-}$ anions and $[\text{MPPYR}]^+$ cations from the IL $[\text{MPPYR}][\text{TF}_2\text{N}]$.^{41a} Increasing the alkyl chain of the cation to butyl resulted in the formation of new compound $[\text{BMPYR}]_4[\text{NdI}_6][\text{TF}_2\text{N}]_4$, crystallised exclusively containing also the $[\text{TF}_2\text{N}]^-$ anion in addition to the cation. Therefore, it has been observed that the cation of the IL changes not only the crystal structure by itself but also can suppress or enable the co-crystallisation of the anion. To get good crystalline samples, they fully dissolved the educts at higher temperature and then cooled slowly to room temperature (thermal shift method). In another study^{41b} Mudring *et al.* crystallised europium with the weakly coordinating anion $[\text{OTf}]^-$ in its direct coordination sphere with the help of acetonitrile after cooling down the reaction in an IL.

Feldmann and coworkers synthesised several polyhalides in ILs.⁴² They summarised their recent results with some relevant literature in a comprehensive review, describing critically the new prospects for inorganic syntheses in ILs.⁴³ For the synthesis of the polybromides, they used a mixture of two ILs, whereas one of them is utilised as solvent and bromine source and the other as co-solvent to keep the eutectic mixture below the melting points of the polybromide compounds in the range of -20 to 10 $^\circ\text{C}$. The cations of the ILs function as counterions for the polybromides and are partly structure-directing. They have suggested that new polybromides could be used for saving, storage, handling the reactive halogens and interhalogens, and for future high power batteries.^{42a} Following them, Riedel *et al.*⁴⁴ achieved the first crystallisation of a higher polybromide monoanion $[\text{Br}_9]^-$ by condensing bromine into the single IL $[\text{Pr}_4\text{N}]\text{Br}$. After a couple of days, they obtained crystals at room temperature. These examples show the possibility of handling highly reactive compounds like bromine in synthesis through the usage of ILs.

Recently, we introduced a soft and sustainable chemical route for the synthesis of transition metal clusters and main group polycations in ILs at room temperature.^{4,45} Such cluster or polycationic compounds had traditionally been synthesised *via* high-temperature routes by performing reactions in melts or by

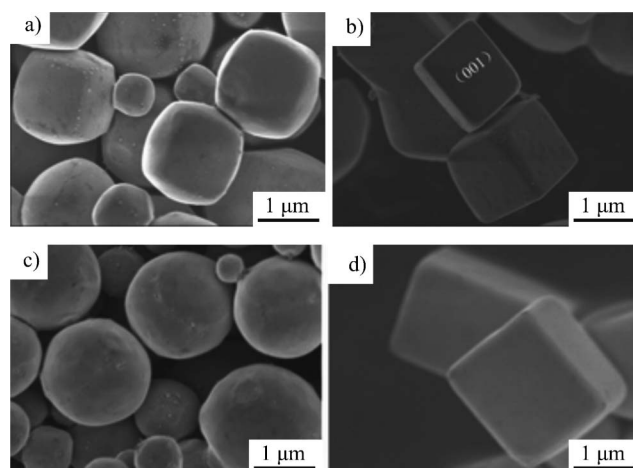


Fig. 6 (a) SEM images of near-spherical AgCl microcrystals prepared by using IL $\text{C}_{16}\text{MIMCl}$, (b) the cubic AgCl prepared by the traditional hydrothermal method, (c) SEM images of samples of the near-spherical AgBr prepared in water, and (d) the cubic AgBr prepared in $\text{C}_{16}\text{MIMBr}$ -glycol ether. Reproduced from ref. 39 with permission from the Royal Society of Chemistry.

chemical vapour transport, at room temperature or lower temperature by using so-called superacid solvents or liquid SO₂, and at room temperature in benzene.⁴ Considering the major problems associated with higher temperature routes (*e.g.* long annealing time, risk of product decomposition, and low yield) and taking into account the toxicity of benzene and SO₂, we developed an IL-based soft and sustainable chemical approach. We applied mostly Lewis-acidic IL [BMIM][AlCl₄] which proved to be highly advantageous for the rapid growth of good quality crystals in high yield, *e.g.* in the synthesis of a trinuclear tungsten compound Sn[SnCl][W₃Cl₁₃], we have utilised for the first time tin as a reducing agent to convert WCl₆ into a trinuclear [W₃Cl₁₃]³⁻ cluster.^{45c} Sn turned out to be a very effective reductant for the convenient room temperature preparation of a new polynuclear cluster compound from WCl₆ (Fig. 7). Among the main group polycations, the first mixed antimony/selenium polycation (Sb₁₀Se₁₀)²⁺ was also obtained by reacting Sb, Se, and SeCl₄ at room temperature in [BMIM][AlCl₄].^{45a} In the salt-like compound (Sb₁₀Se₁₀)[AlCl₄]₂, the centrosymmetric polycyclic cation (Sb₁₀Se₁₀)²⁺ consists of two realgar-like [Sb₄Se₄] cages, which are connected through positively charged, three-bonded selenium atoms with a central [Sb₂Se₂] ring (Fig. 8).

This new approach has not only provided new cluster compounds *via* redox reactions but also made it possible to carry out substitution/transformation reactions, *e.g.* a new bismuth–ruthenium–bromine cluster compound (Fig. 9) through the substitution of Bi₈²⁺ with Bi₅⁺ polycations at 140 °C with subsequent slow cooling of the IL (thermal shift method).^{45g} This reaction is based on the existence of different bismuth polycations in the reaction mixture in the IL.

Dyson *et al.*⁴⁶ recrystallised 18-crown-6 complexes of potassium and barium from IL [EMIM][Tf₂N] at the water interface, making use of the different solubilities of the complexes in water–IL as well as the immiscibility of the solvents. The [Tf₂N]⁻ anion substituted the original anions of the complexes and decreased the solubility in water. Therefore, this study could lead to new

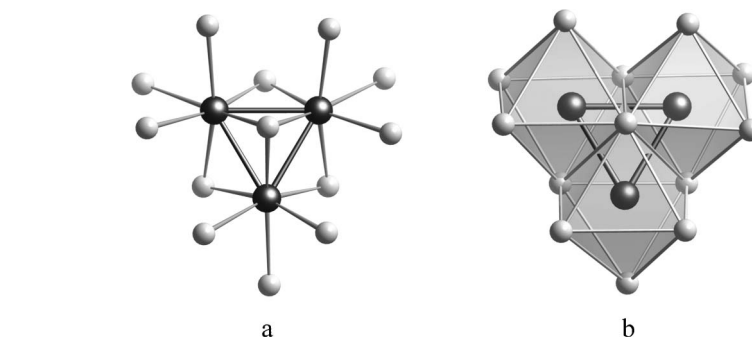


Fig. 7 a) The trinuclear [W₃(μ₃-Cl)(μ-Cl)₃Cl₉]³⁻ cluster anion, W atoms are shown as black and Cl atoms as light gray; b) polyhedral representation emphasising the edge-sharing of coordination octahedra.

techniques for extraction of alkaline and alkaline earth elements.

Morris and co-workers contributed several publications on the synthesis of inorganic materials, especially, coordination polymers from ILs and introduced the concept of ionothermal synthesis.⁴⁷ It is worth mentioning that they have synthesised novel homochiral frameworks, using achiral building blocks in the chiral IL [BMIM][L-AspH]. By using an achiral anion for the IL, the product was also found to be achiral. Moreover, using D-aspartate instead of L-form, the resulting framework crystallised with the opposite chirality.^{47b} Furthermore, they isolated several vanadium fluorides and oxyfluorides from ILs, whereas no part of the IL was incorporated into the structure.⁴⁸ One example of these oxyfluorides is [NH₄]₂[C₇H₁₄N][V₇O₆F₁₈], which consists of magnetic frustrated *S* = 1/2 kagomé networks of d¹ V⁴⁺ ions (Fig. 10).^{48a} In addition, Wragg and Morris *et al.* prepared aluminium and gallium phosphate chains by ionothermal reactions.⁴⁹ The use of zinc acetate improved the crystallinity of the products when [EMIM]Br was used as IL. However, the zinc acetate was not incorporated into the structure in contrast to the organic cation of the IL. Longer heating times disfavoured the chains in comparison to three dimensional framework phases.

Bu and co-workers produced several low-connectivity homochiral and achiral frameworks with eight-coordinated indium(III) sites as the tetrahedral node in an ionothermal synthesis and discussed the different roles of the ILs during the formation of the com-

pounds.⁵⁰ The ILs act not only as solvents but also in some cases as cationic or cationic/anionic structure-directing agents through encapsulation. It has also been observed that using [Pr₄N]Br as a reagent, the cationic structure directing function of the ILs could be suppressed.

Wang *et al.* isolated crystals of a 3D zinc(II) carboxylate coordination polymer in an ionothermal reaction using a mixture of two ILs, [EMIM][BF₄] and [EMIM][L-lactate].⁵¹ The compound incorporates the [EMIM]⁺ cation into the structure but none of the anions of the ILs. Nevertheless, the presence of both anions of the ILs is essential during the reaction. By using only one of the ILs, the coordination polymer was not formed.

Huang and co-workers synthesised open-framework selenidostannates from the elements and isolated single crystals of several millimetre length.⁵² By using hydrazine monohydrate as support for the ILs, they were successful in crystallising different selenidostannates depending on the molar ratios of the amine and the ILs. Without using hydrazine monohydrate, only nanoparticles or binary SnSe₂ were achieved. The molar ratio of tin and selenium was kept constant in all the cases and the effect of the ILs and the co-solvent hydrazine monohydrate was found to be structure directing. The channels of the frameworks are filled with the cations of the ILs (Fig. 11). For microporous selenidostannates, interesting applications like ion exchange, photocatalysis, and fast ion conductivity were proposed.

Recently, the synthesis of polyoxometalates (POMs) has received great interest

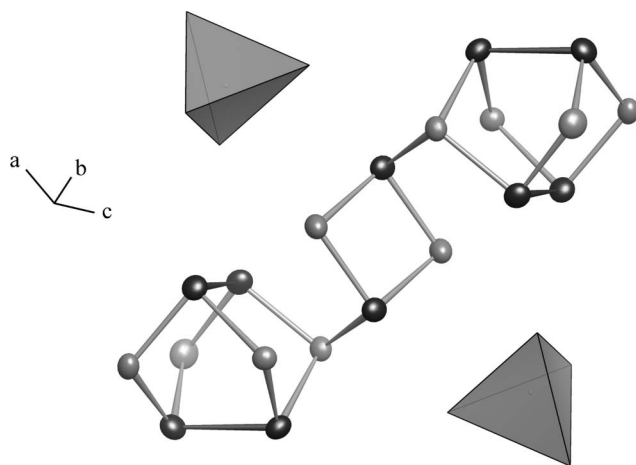


Fig. 8 Crystal structure of $(\text{Sb}_{10}\text{Se}_{10})[\text{AlCl}_4]_2$. Sb atoms are shown as black and Se as dark gray. $[\text{AlCl}_4]^-$ anions are shown as polyhedra.

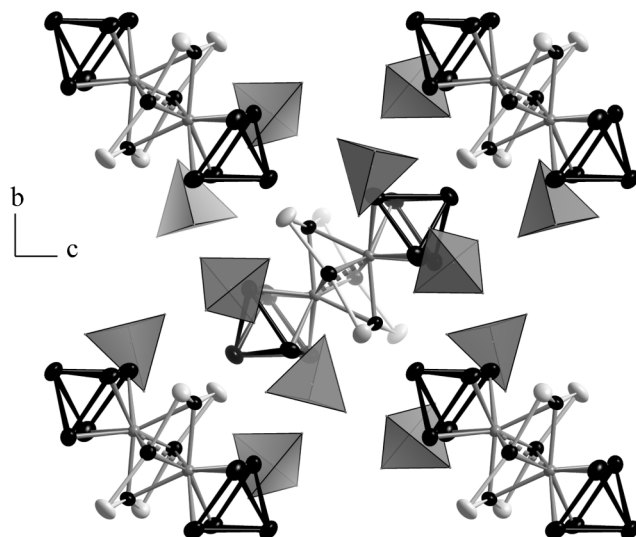


Fig. 9 Crystal structure of $[\text{Ru}_2\text{Bi}_{14}\text{Br}_4][\text{AlCl}_4]_4$. Bi atoms are black, Ru atoms grey and Br atoms are white and $[\text{AlCl}_4]^-$ anions are shown as tetrahedra.

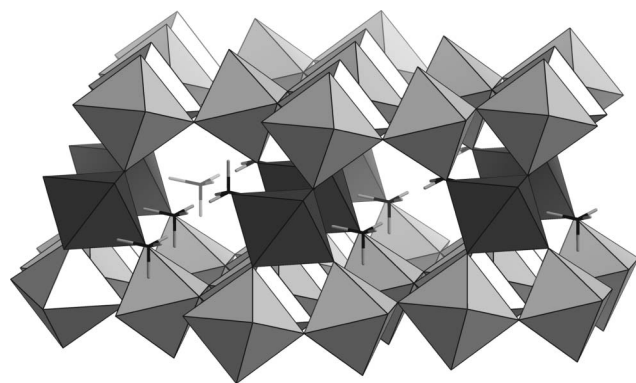


Fig. 10 $[\text{V}_7\text{O}_6\text{F}_{18}]^{3-}$ double layer in the crystal structure of $[\text{NH}_4]_2[\text{C}_7\text{H}_{14}\text{N}][\text{V}_7\text{O}_6\text{F}_{18}]$. The V^{4+} -centred polyhedra are light grey, V^{3+} -centred as dark grey, and ammonium cations are shown as sticks.

due to their extensive potential applications such as in catalysis, storage, separation, and chemical sensing *etc.*^{53,54} Following the concept of ionothermal synthesis, Wang and co-workers ionothermally produced several new POMs and discussed multiple factors in synthesis and crystallisation.⁵⁵ In some cases, they have observed that an increase in the reaction temperature (above 150 °C) and a decrease in the reaction time (below 10 days) is crucial for the crystallisation of POMs. Moreover, by using NaVO_3 or $\text{Ce}(\text{NO}_3)_3$, the crystallinity and yield of the products were greatly increased, although neither vanadium nor cerium were incorporated into the final crystal structures.^{55a} Sometimes, the cations of the partly disintegrated ILs were incorporated as counterions to crystallise those POMs which could not be isolated using other solvents like water under similar reaction conditions.^{55b} In addition Wang and co-workers achieved the first ionothermal syntheses of PMOFs (polyoxometalates-based metal-organic frameworks)^{55c}. $\text{Cu}^{\text{II}}(\text{Bbi})_{1.5}(\text{H}_2\text{Bbi})_2[\text{P}_2\text{W}_{18}\text{O}_{62}]$ is one of these materials, which was synthesised in $[\text{BMIM}]\text{Br}$, shown in Fig. 12.^{55c} The field of ionothermal synthesis of POMs is at its early stages and is expected to grow rapidly. Therefore, new functional materials with desirable properties are anticipated.

Summary and outlook

In this account, the ILs-based current state-of-the-art techniques *e.g.* ionothermal, solvothermal, hydrothermal, ultrasonic- and microwave-assisted strategies for inorganic materials synthesis and crystallisation are briefly highlighted. Moreover, some classical methods, *e.g.* the use of a co-solvent and thermal shift (where ILs may be chosen with a wide liquid range allowing both high and low temperature crystallisation in the same solvent) are also described which could also speed up the crystal growth. The use of ILs as new crystallisation media, working as neutral solvent, template or charge compensating species has provided a promising and more efficient strategy to synthesise a variety of inorganic materials. Depending on their average crystallite size, these crystalline materials are divided into three categories: nanoscopic crystals, micro- and

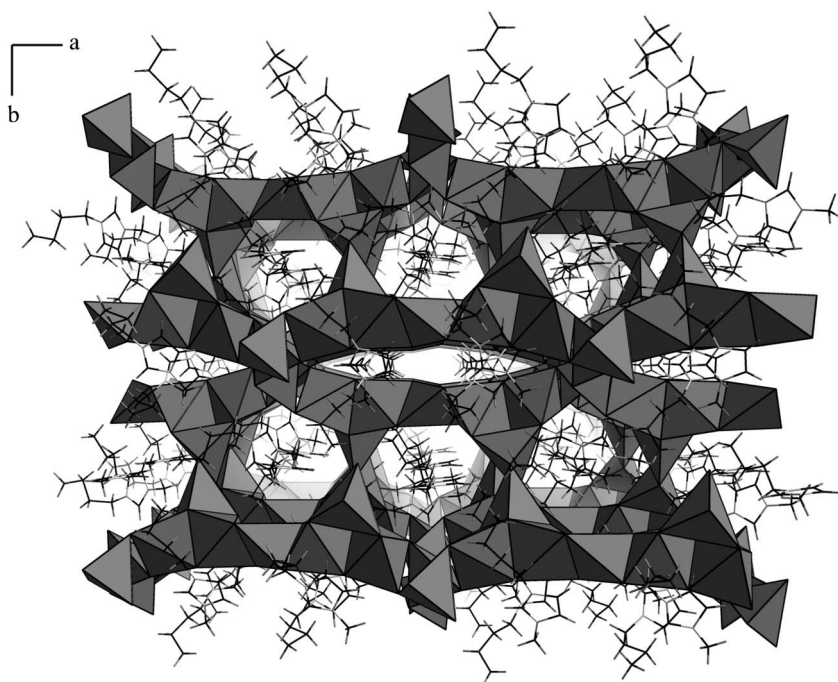


Fig. 11 Crystal structure of $[\text{BMIM}]_4[\text{Sn}_9\text{Se}_{20}]$. Se and Sn atoms are shown as polyhedra and $[\text{BMIM}]^+$ cations as wires/sticks.

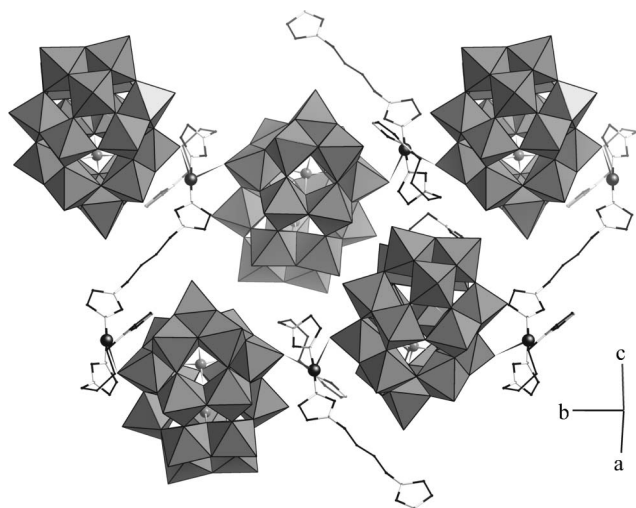


Fig. 12 Crystal structure of $\text{Cu}^{\text{II}}(\text{Bbi})_{1.5}(\text{H}_2\text{Bbi})_2[\text{P}_2\text{W}_{18}\text{O}_{62}]$. W and O atoms are shown as polyhedra, the organic molecules as wires/sticks, Cu atoms are black, and P atoms as grey.

macroscopic crystals. The few examples presented in this contribution, using ILs as crystallisation media, highlight the utility and effectiveness of these novel solvent systems. The current remarkable efforts point out that unique results are possible with ILs applying different strategies, and in future, further improvements for controlled crystallisation in ILs may be possible through a greater understanding of the nature of ILs themselves. The growing knowledge of the interactions between ILs and metals, ligands,

organic reagents, *etc.* will lead to new prospects in crystallisation and in crystal engineering.

The significance of the present study is manifold. First, the reactions in ILs provide principally an efficient, simple, and predominantly one-step route to inorganic materials. The size and morphology of crystals can be controlled by chemical (such as nature and concentration of ILs and other reagents) and physical (such as stirring rate, irradiations and temperature *etc.*) means.

Imidazolium based-ILs act not only as the solvent and templates for the nanocrystal growth but also as stabilisers especially for the hollow microspheres and metal nanoparticles. Second, the as-prepared microcrystals can serve as a useful precursor to obtain porous particles with almost similar morphology by means of calcinations. Third, the high thermal stability of ILs facilitates reactions to be conducted at various temperatures, which further allows the tuning of the reaction in terms of particle sizes, shapes, and connectivity. Fourth, various ILs-based approaches highlighted here present simple, soft, and sustainable strategies towards a range of inorganic materials with defined properties. In principle, ILs can be recycled, although purification may cause some difficulties due to the presence of organic or inorganic ions.

The unique character of ILs to have different combinations of cation/anion allows the fine-tuning of the properties and extends their application to other difficult crystallisation cases, and provides new opportunities for the synthesis of materials with unique morphologies and controlled crystalline phases. The recent development of inorganic materials synthesis in ILs reviewed in this article clearly shows that ILs added great value to materials science. The distinctive adaptability and flexibility of ILs provide a powerful tool for the fabrication of novel, interesting, and highly sophisticated structures *via* chemical approaches. Further research on developing the approach and investigating the span of ILs' application to design and synthesise different inorganic materials will benefit the scientific community.

It is believed that the development of new ILs, composed of metal ions or task-specific functional groups will result in the synthesis of new inorganic materials with novel structures and interesting properties. The acid–base properties of ILs and the catalytic properties of metal or metal oxide catalysts could be exploited to design multifunctional catalysts. Such unique catalysts may be able to tune the selectivity in organic reactions. Moreover, ILs based on biodegradable materials can also be employed to improve the environmental friendly nature of the synthetic approach.²³ This contribution highlights the recent

developments in materials chemistry and is expected to convince the readers that the synthesis of inorganic materials in ILs is a fascinating research field. It is anticipated that the existing achievements and many expected future results will have fundamental and practical impacts on materials science.

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