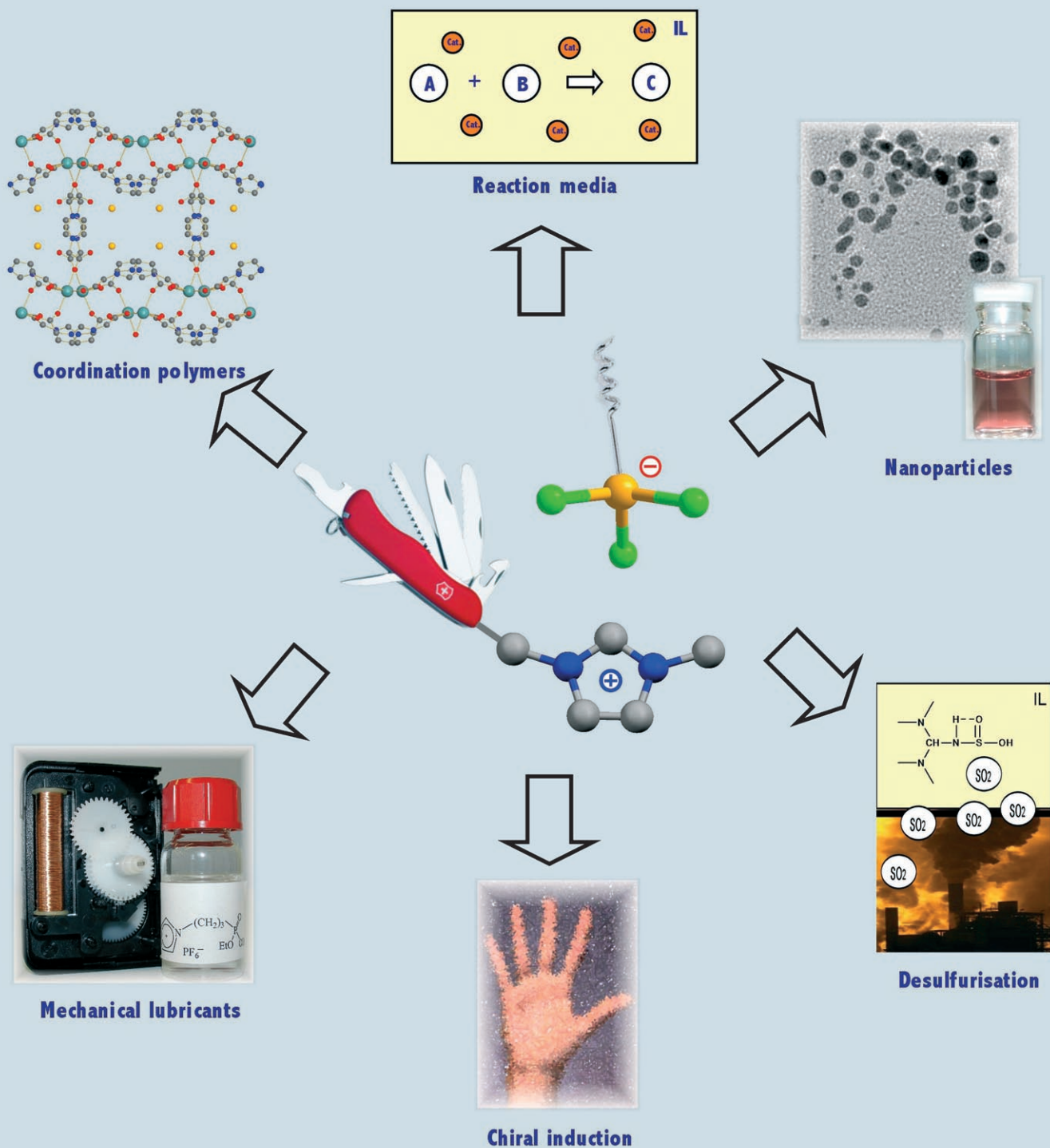


Delivering Solutions with Functionalised Ionic Liquids



From Dysfunction to Bis-function: On the Design and Applications of Functionalised Ionic Liquids

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Abstract: Some of the recent developments concerning the synthesis, properties and applications of functionalised ionic liquids are highlighted. Various strategies are presented, including functionalisation of the cation, anion or both cation and anion in the same ionic liquid, leading to what has been termed dual-functionalised ionic liquids. Particular attention is given to the application of functionalised ionic liquids as reaction media, to stabilise nanoparticles/modify surfaces and to generate porous materials.

Keywords: anions · cations · ionic liquids · nitrogen heterocycles

Introduction

Interest in ionic liquids has increased considerably over the last few years, fuelled by the development of new synthetic routes to ionic liquids, the preparation of new ionic liquids, together with an ever increasing range of potential applications. Initially developed for electrochemical purposes and subsequently regarded predominantly as alternative, environmentally benign reaction media, ionic liquids have in recent years found many other potential applications, which now span from, for example, storage media for toxic gases,^[1] lubricants,^[2] performance additives in pigments^[3] through to propellants in satellites.^[4] But while the areas where ionic liquids can be applied continue to expand, the majority of research concerned with ionic liquids has so far been limited to a relatively small group of salts, typically composed of imidazolium- or pyridinium-based cations containing satu-

rated hydrocarbon substituents. However, there is no reason for ionic liquids to be restricted in this way, especially as the introduction of functional groups is often relatively facile, allowing for marked changes of the physicochemical properties of the liquid. To maximise the benefits from using these new solvents, the development and application of so-called “task-specific”^[5] ionic liquids is desirable. The presence of functional groups imparts a particular reactivity pattern to the ionic liquid, enhancing the capacity for interactions with specific solutes. So far, most studies reporting on functionalised ionic liquids have focused on the derivatisation of the cationic component, but ionic liquids containing functionalised anions are starting to attract interest and nascent investigations of ionic liquids in which both the cation and anion are functionalised have also been reported.^[6] In this concept article we illustrate how functional groups can be introduced to ionic liquids and provide some examples that illustrate possible applications of such designer solvents.

Synthesis of Functionalised Ionic Liquids

Most ionic liquids with functionalised cations have been prepared by quaternisation of 1-alkylimidazole with a functionalised alkyl halide affording the desired functionalised imidazolium halide in usually good yield. Deprotonation of imidazole with NaH or KH followed by the addition of two equivalents of a functionalised alkyl halide, as well as heating a mixture of 1-trimethylsilylimidazole with two equivalents of a functionalised alkyl halide, both afford 1,3-bis-functionalised imidazolium halides.^[7] Most functional groups can be introduced directly to the imidazolium moiety using these methods,^[8] and Figure 1 provides a selection of functionalised imidazolium cations that have been reported. It is worth noting that some of the functional groups attached to the imidazolium (or pyridinium) salts can be modified further to yield other new salts including those derivatised with metal fragments.^[8d,9] Subsequent metathesis of the functionalised imidazolium halides with salts, such as Na[BF₄] or Li-[Tf₂N], affords, in many cases, low-melting salts that can be

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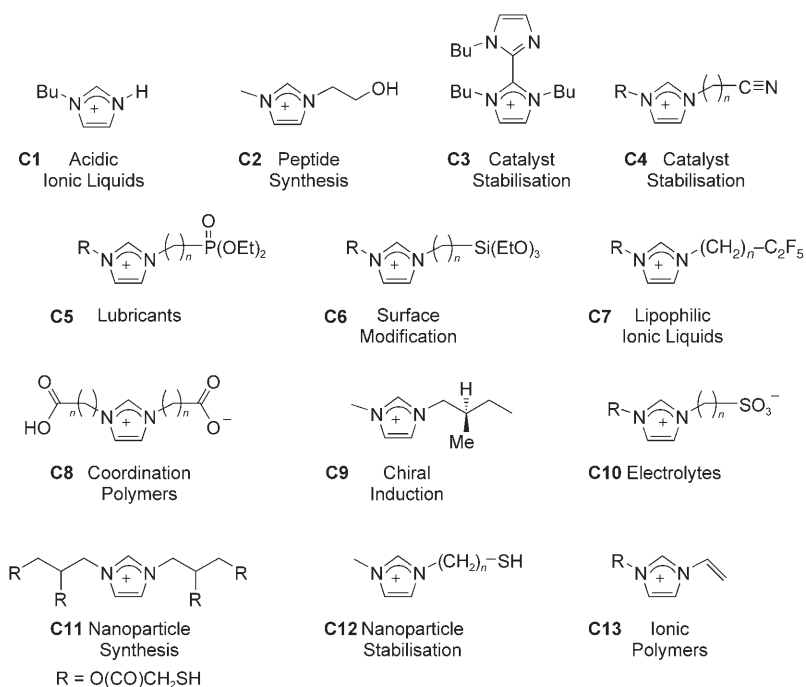


Figure 1. Examples for functionalised imidazolium cations and their potential applications.

classified as ionic liquids. In addition to the commonly used imidazolium salts, pyridium-, pyridazinium-, pyrrolidinium-, 1,2,4-triazolium-, guanidinium- and phosphazene-based ionic liquids have also been investigated in the last few years, to name but a few.^[10] There has also been increased interest in chiral,^[11] sulfonium,^[12] quaternary ammonium^[13] and phosphonium salts;^[14] these last being stable to the highly basic conditions necessary for Grignard reactions.^[15]

While a plethora of functionalised cations are now available, much less effort has been devoted to the synthesis of task-specific anions, although a selection is provided in Figure 2. Most examples are based on readily available materials, such as metal-carbonyl anions (**A1** and **A2**)^[16,17], carboranes (**A3**)^[18] and amino acids (**A4**).^[19] Highly fluorinated (stable) anions, (**A15**)^[20] alkene-derivatised anions (**A13** and **A14**)^[21] and anions based on a triazole backbone (**A11** and **A12**)^[4] have also been developed, each with specific applications in mind.

Most of the commonly employed anions are highly symmetric, almost spherical molecules. Increasing their asymmetry appears to have a marked effect on the melting point and

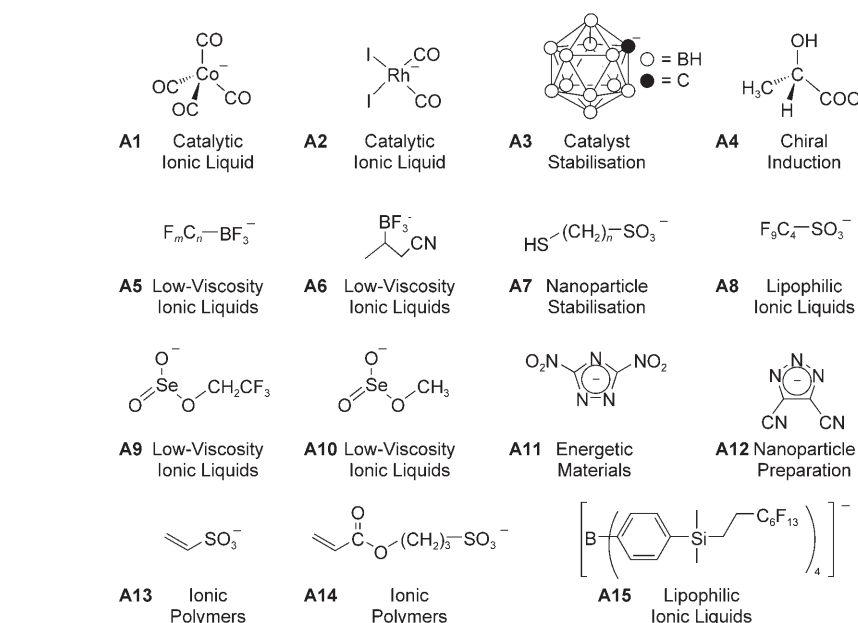


Figure 2. Selection of functional anions incorporated in ionic liquids.

viscosity of the resulting ionic liquid. Zhou and co-workers described a series of perfluoroalkyltrifluoroborate anions (**A5**) prepared by means of an improved fluorination method, leading to a series of ionic liquids with low viscosities.^[22] The selenite anions **A9** and **A10** also afford low-viscosity ionic liquids in combination with imidazolium cations and have been used as media for oxidative carbonylation of aromatic amines.^[23] A series of ionic liquids containing a nitrile-functionalised anion have also been reported, some exhibiting low viscosities.^[6] Notably, the nitrile anion **A6** was combined with functionalised imidazolium cations affording what has been termed “dual-functionalised ionic liquids”. There is considerable need for low-viscosity

ionic liquids in many applications, but perhaps most importantly in dye-sensitised solar cells, in which they are used as electrolytes.^[24] One limitation to the efficiency of solar cells is the viscosity of the electrolyte and it is likely that innovative new ionic liquids with lower viscosities than those currently available will find applications in the solar cells of the future.

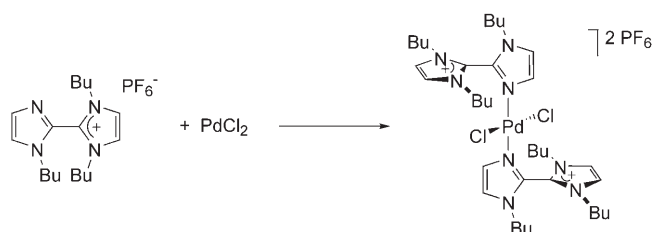
Despite a large number of functionalised ionic liquids reported, their physical properties are not routinely or system-

atically investigated, although spectroscopic methods are being increasingly employed to study ionic liquids.^[25] Nonetheless, the influence of the functional groups on the physical properties of the functionalised ionic liquids remain poorly understood.

Functionalised Ionic Liquids as Reaction Media

The use of functionalised ionic liquids in synthesis and catalysis is still very much in its infancy. In principle the ionic liquid might serve any of the following purposes: 1) assist in the activation of the catalyst, 2) generate a novel catalytic species, 3) improve the stability of the catalyst, 4) optimise immobilisation and recyclability, 5) facilitate product isolation and 6) influence the selectivity of the reaction. These points will be illustrated in the examples provided below. In addition, the functionalised ionic liquid has to meet certain requirements to be of use in synthesis and most important is their inertness with respect to the reaction in question. Also, the right balance between catalyst stabilisation and activation has to be found and this might require careful tuning of the reaction conditions.

The simplest functionalised ionic liquids are probably amphiphilic ionic liquids, bearing very long alkyl chains, and protic ionic liquids such as **[C1][BF₄]** (see Figure 1). The latter has been employed, for example, in the dimerisation of methyl acrylate with Pd(acac)₂ as a catalyst precursor. Increased reaction rates of 220 mol mol⁻¹ h⁻¹ (cf. 72–100 mol mol⁻¹ h⁻¹ in **[C₄C₁im][BF₄]**; C₄C₁im = 1-butyl-3-methylimidazolium) were obtained as this acidic liquid acts as proton reservoir for the protonation of the acetyl acetonate ligand in Pd(acac)₂, thereby activating the catalyst.^[26]



Scheme 1.

Superior catalyst stability relative to common ionic liquids was obtained when PdCl₂ was immobilised in a 2,2'-imidazole–imidazolium ionic liquid, **[C3][PF₆]**, which serves both as solvent and ligand, leading to the bis-imidazole complex shown in Scheme 1.^[8f] The resulting palladium species was demonstrated to be an active and highly recyclable catalyst in Heck coupling reactions and very good conversion was observed even when aryl chlorides were used as substrate.

The key feature to this catalytic system is that the catalyst ligand is part of the ionic liquid and therefore not easily lost during extraction of the product.

In this respect a series of phosphine ligands bearing, for example, charged imidazolium or guanidinium moieties, have been prepared, and some are shown in Figure 3.^[27] In general these do not serve as the reaction medium, but facilitate reactions conducted in nonfunctionalised ionic liquids through coordination to the metal.

Induction of chirality by means of chiral solvents is not a new concept, but one which has received new input with the synthesis of chiral ionic liquids.^[28] In a recent example, a range of chiral ionic liquids (**IL1–IL4**, in Scheme 2) have

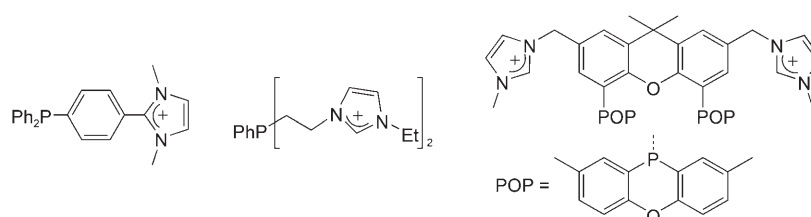
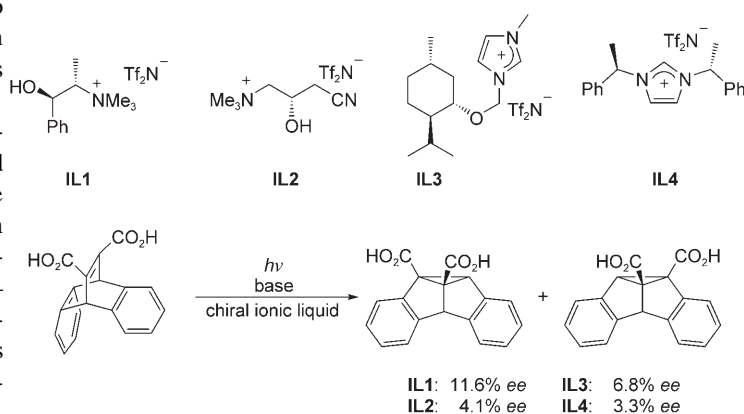


Figure 3. Examples of imidazolium-tagged phosphines

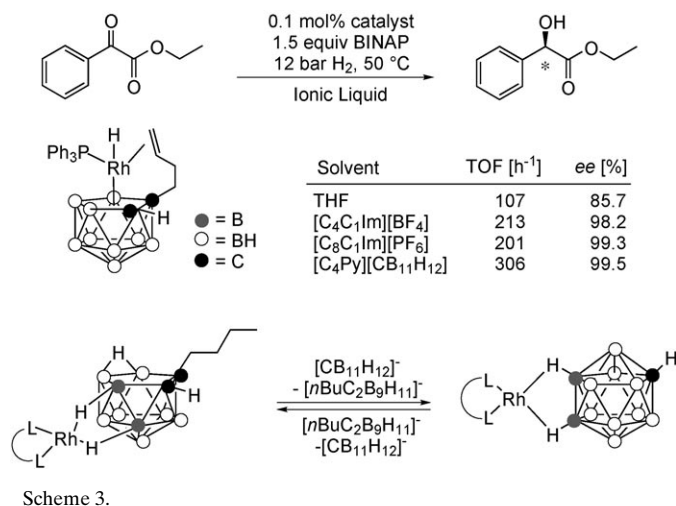


Scheme 2.

been evaluated as solvents for the photodimerisation of dibenzobicyclo[2.2.2]octatrienes.^[29] Although the observed enantioselectivities are only very modest in an absolute sense, they are among the highest achieved for unimolecular photochemical reactions conducted in a chiral environment. It was suggested that following deprotonation of the acid, chiral induction takes place through ion-pairing interactions.

Another example stems from enantioselective Heck arylation in a chiral ionic liquid, **[C9][PF₆]**, also with very low ee (<5%).^[30] However, it ought to be pointed out that markedly higher enantioselectivities (44% ee) have been observed with chiral ionic liquids in Baylis–Hillman coupling reactions, although in that case the ionic liquid served as co-catalyst rather than as solvent.^[31a]

An example of the beneficial effect of a task-specific anion is illustrated in Scheme 3. Here, a rhodacarborane cat-



alyst precursor containing what is termed a suicide alkene ligand, [*closo*-1,3- $\{\mu$ -(η^2 -3-CH₂=CHCH₂CH₂))-3-H-3-PPH₃-3,1,2-RhC₂B₉H₁₀], has been used to promote the enantioselective reduction of ketones in an ionic liquid comprised of a pyridinium cation and a 1-carbadodecaborate anion, [C₄py][A₃] (C₄py = *N*-butylpyridium).^[31b] Higher reaction rates were observed relative to the reaction in more conventional ionic liquids, such as either [C₈C₁im][BF₄] (C₈C₁im = 1-octyl-3-methylimidazolium) or [C₄C₁im][PF₆], which in turn were superior to THF. It was proposed that the carborane anion of the ionic liquid can interact with the metal centre to give a carborane complex that might act as the precursor to a catalytically active species.

Functionalised ionic liquids can also serve as supports for the synthesis of a desired molecule thereby facilitating purification and isolation. In a recent example, a hydroxy-functionalised imidazolium ionic liquid, [C₂][BF₄], was utilised for the synthesis of a pentapeptide, as outlined in Scheme 4.^[32] Advantages in using a functionalised ionic



Scheme 4.

liquid relative to other supports lies in their lower cost (as compared to perfluorinated or polymeric supports), their high loading capacity and facile analysis of the intermediates by spectroscopic methods. In contrast, product isolation relative to solid supports is probably less straightforward and the suitability for the synthesis of longer peptide chains has yet to be established.

Ionic liquids bearing functional groups may also be used to prepare surface-modified silica gels containing covalently anchored ionic liquid fragments, leading to supported ionic-liquid phase (SILP) catalysts that have been used, for example, in the hydroformylation of 1-hexene^[33] and the epoxidation of olefins.^[34] In both cases the solid support was treated

with 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium, [C₆][PF₆], affording a SiO₂ surface on which the ionic liquid is covalently bound, as depicted in Figure 4. Further examples for the interaction of ionic liquids with solid surfaces are given in the subsequent sections.

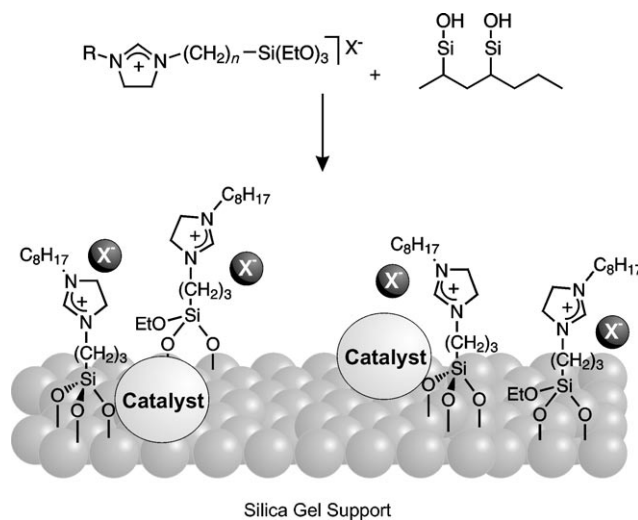


Figure 4. Modification of a silica surface with a covalently bound ionic liquid used to immobilise catalytic species.

Functionalised Ionic Liquids for Nanoparticle Synthesis and Stabilisation

The precise control of nanoparticle size and distribution together with a better understanding of the chemical behaviour of nanoparticles are becoming increasingly important in order to expand the utility of nanoparticles in various applications. There appear to be a number of interesting features of nanoparticles suspended or prepared in ionic liquids compared to other reaction media, and the amalgamation of ionic liquids with nanotechnology could result in some major advances in materials science. Nanoparticles suspended in ionic liquids have been demonstrated in various instances to be highly active catalysts for hydrogenation, hydroformylation or C–C cross-coupling reactions and their activity is usually superior relative to when they are employed in molecular solvents.^[35,36] Despite such promise, the presence of additional stabilising moieties may nevertheless be desirable to avoid long-term deactivation of the particles.

Nitrile-functionalised ionic liquids have been effectively used in this regard, for example, in Stille coupling reactions and their usefulness become apparent upon catalyst recycling. While in conventional *N*-butyl pyridinium ionic liquid, [C₄py][Tf₂N], the activity rapidly decreased to zero, little change was observed in the *N*-butyronitrile pyridinium analogue, [C₃CN][Tf₂N]. The superior activity in the nitrile-

functionalised ionic liquid is due to improved catalyst retention and improved catalyst stability.^[10e] While the nanoparticles immobilised in $[C_4py][Tf_2N]$ aggregated, those dissolved in $[C_3CN][Tf_2N]$ remained evenly distributed, as can be seen from the TEM pictures of the isolated particles shown in Figure 5.

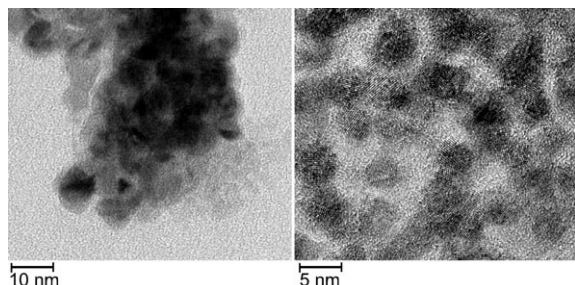
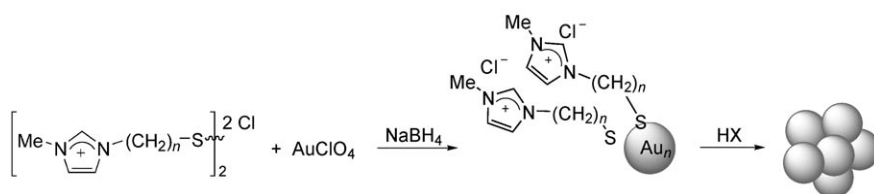


Figure 5. TEM images of the palladium nanoparticles isolated after the Stille reaction between iodobenzene and tributylphenyltin in $[C_4py][Tf_2N]$ (left) and $[C_3CN][Tf_2N]$ (right).

Of the many functional groups that can be employed to stabilise nanoparticles, thiol moieties have been shown to work particularly well in conjunction with ionic liquids. The synthesis of thiol-stabilised nanoparticles in aqueous solution can be problematic due to ionic interactions, low solubility of reactants and difficulties in removing residual stabiliser after the synthesis.^[37,38] In this context, thiol-functionalised ionic liquids based on **C11** and **C12** represent good candidates as solvent/stabiliser, since their intrinsic ionic nature could enable more conducive interactions between the ionic liquid and the nanoparticle. Additionally, they can easily be modified to be hydrophilic or hydrophobic by combining the cations with the appropriate anions, which could also prove useful.

Naka and co-workers designed a disulfide-functionalised imidazolium salt that can be reduced to a thiol with the ability to stabilise gold nanoparticles, as shown in Scheme 5.^[39] The resulting gold nanoparticles are coated with the thiol-functionalised chloride salt and are highly water-soluble and stable towards Brønsted acids such as HCl, HBr and HBF_4 . In contrast, agglomeration (as evidenced by TEM) occurred when either HI or HPF_6 was added, resulting in a colour change of the solution, an effect that might be utilised in an optical sensor for anions. It is proposed that with the latter acids, due to anion exchange, the particles are rendered hy-



Scheme 5.

drophobic and therefore agglomerate. Such anion metathesis can be utilised to transfer thiol-stabilised particles from an aqueous to an ionic-liquid phase by simply adding, for example, $[C_6C_1im][PF_6]$ and HPF_6 to the aqueous solution.

In a recent report, ionic liquids based on imidazolium cations like **C11**, bearing one, two or more thiol groups were prepared in order to rationalise their effects on the size and distribution of nanoparticles.^[40] In addition, thiol groups have also been attached to the anion, forming a dual-functionalised system, which was also evaluated in nanoparticle synthesis. Gold and platinum nanoparticles prepared from these thiol-functionalised systems are highly dispersible in aqueous solutions. Both the size and stability of the formed nanoparticles are influenced by the position and number of thiol groups in the cation and anion. The diameter of the nanoparticles was found to decrease as the number of thiol groups on the cation increases, as well as in the presence of the functionalised anion. Thus, the chemical and physical interaction between the ionic liquid and the metal plays a decisive role in controlling the size and structure of the nanoparticles.

Since chloride contamination has a significant impact on the properties of the nanoparticles obtained from an ionic liquid,^[41] chloride-free functionalised ionic liquids are desirable for the synthesis of nanoparticles.^[42] Reduction of a solution of $[Pt_2(dba)_3]$ (dba = dibenzylideneacetone) in THF with molecular hydrogen in the chloride-free ionic liquids tetraalkylammonium 4,5-dicyanotriazolium (anion **A12** in Figure 2) affords Pt nanoparticles that are soluble in THF. Heteronuclear nanoparticles prepared from $[Pt(dba)_2]$ and $[Ru(cod)(cot)]$ (cod = 1,5-cyclooctadiene; cot = 1,3,5-cyclooctatriene) in a 1:1 molar ratio, were also prepared, and shown to be excellent catalysts for methanol oxidation.

Surface Modification Using Functionalised Ionic Liquids

Ionic liquids can interact with solid surfaces on materials such as silica gel or molecular sieves,^[43] and the tunability of hydrophilicity and hydrophobicity (wettability) of ionic liquids has led to their use as surface modification agents. The fact that ionic liquids are composed of cations and anions has made it possible to control the surface wettability by simple anion exchange, which is not possible by using traditional methods based on organic solvents. Modulation of such surface properties is of fundamental and technological importance. The anion effect offered by functionalised ionic liquids on surface wettability is of practical significance with respect to adsorption on molecular surfaces and has potential applications, for example, in the fabrication of anion detectors.

Thiol-functionalised ionic liquids (with bromide as the

anion) form highly ordered self-assembled monolayers on gold surfaces.^[44] Ellipsometric measurements show a film with a thickness of roughly 19 Å with a water contact angle of 23°. Immersion of the surface in an aqueous solution containing [BF₄]⁻, [PF₆]⁻ or other suitable anions, results in exchange of the bromide. This led to an alternation of the water contact angle, which increases significantly on progressing from Br⁻ to [Tf₂N]⁻, as shown in Figure 6.

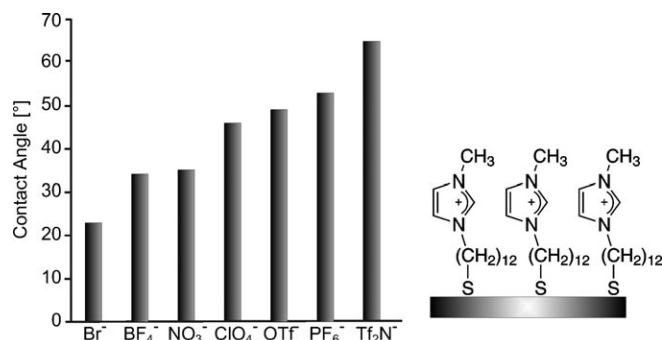


Figure 6. Change of the water contact angle on thiol-ionic liquid modified gold surface as a function of the type of anion present.

Self-assembled monolayers were also observed upon modification of silica with 1-alkyl-3-(3-triethoxysilylpropyl)imidazolium chloride, as outlined in Figure 4. It was found that the surface water wettability not only depends on the nature of the anion, but is also influenced by the length of the alkyl group present.^[45] The longer the alkyl chain on the imidazolium the less pronounced the anion effects.

Ionic liquids also exhibit useful tribological properties, showing excellent friction reduction, antiwear performance and high load-carrying capacity for various contacts.^[46] Introduction of a phosphorus ester group onto the imidazolium cation, affording species like [C5][PF₆] results in superior friction-reducing properties compared to conventional ionic liquids.^[47] The superiority of the functionalised ionic liquids compared to the conventional ionic liquids is believed to be due to the fact that the phosphorus group in the alkyl side chain can undergo partial hydrolysis in the presence of moisture. It can also react with freshly exposed aluminium or iron during the sliding process to form stable compounds, which are believed to dissolve in the ionic liquid.

From Ionic Liquids to Porous Materials

Porous materials such as zeotype frameworks are usually prepared in aqueous solution in a sealed autoclave at high temperature and pressure (hydrothermal synthesis).^[48] The reaction mixture commonly includes an organic template, such as ammonium or phosphonium salts, or solvent molecules. Because of the low vapour pressure, synthesis in ionic liquids can take place at ambient pressure, eliminating the complications associated with high hydrothermal pressures.

In principle, the ionic liquids can also be recycled for further use, reflecting a further advantage of ionic liquids compared to other solvents.

The first synthesis of mesoporous materials by using novel ionic liquid templates in water was reported in 2001,^[49] albeit in aqueous solution containing only a small amount of a dialkylimidazolium ionic liquid. A coordination polymer of the formula [Cu(bpp)][BF₄] (bpp = 1,3-bis(4-pyridyl)propane) was reported shortly afterwards by using [C₄C₁im][BF₄] as both solvent and scaffold with the tetrafluoroborate anion acting as template directing the formation of the coordination network, although remaining in the final structure to compensate for the charge.^[50] Other examples include the synthesis of aluminophosphate zeotype frameworks by using [C₂C₁im]Br (C₂C₁im = 1-ethyl-3-methylimidazolium) as solvent and template, as well as a choline chloride/urea eutectic mixture as solvent in the preparation of a new coordination polymer.^[51] So-called amphiphilic ionic liquids, bearing very long alkyl chains, have been used for the creation of microporous lamellar silica nanostructures.^[52]

Apart from serving as a template, ionic liquids or ionic liquid precursors can form highly interesting macrostructures, with, for example, imidazolium phosphonacetate forming a nanochannel architecture upon crystallisation.^[53] Alternatively, functionalised ionic liquids can react with metals or metal salts to form polymeric materials. A strontium-imidazolium polymer was obtained from the reaction of the zwitterion 1,3-bis(carboxymethyl)imidazolium derived from [C8H]Br, with SrCO₃ in water, affording a material in which the polymer layers are separated by water sheets, as shown in Figure 7a.^[54] When C8 was treated with zinc metal in water, a water-filled nanotube formed, see Figure 7b.^[55] Both structures illustrate the potential that ionic liquids have as ligands; this could conceivably find applications in many different areas of chemistry and materials science.

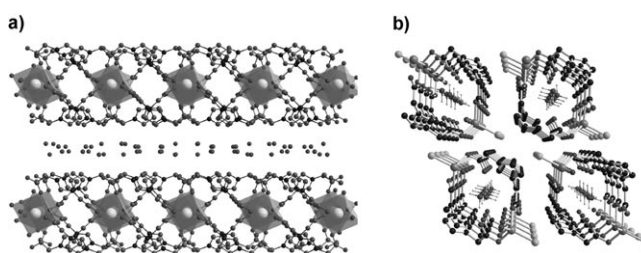


Figure 7. a) Water-sheet separating layers of an imidazolium carboxylate-strontium coordination polymer. b) Water-filled nanotube formed from an imidazolium carboxylate-zinc polymer.

Outlook

The pairing of functional cations and anions is unlimited and the potential of such ionic liquids has been recognised in a wide range of applications. While the development of such functionalised ionic liquids has been largely a process of design, the huge potential of their application remains largely unexplored. The opportunity for designing variants

with improved physical and chemical properties for specific applications is enormous.

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