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Applications of functionalized ionic liquids

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Abstract Recent developments of the synthesis and applications of functionalized ionic liquids (including dual-functionalized ionic liquids) have been highlighted in this review. Ionic liquids are attracting attention as alternative solvents in green chemistry, but as more functionalized ILs are prepared, a greater number of applications in increasingly diverse fields are found.

Keywords: ionic liquids, functionalized ionic liquids, dual-functionalized ionic liquids, reaction media, asymmetric synthesis, nano-materials, porous materials, lubricants, flue-gas desulfurization, oil desulfurization.

1 Introduction

The green chemistry research since the late 90s of the 20th century is a strategy to eliminate pollution from the headstream of chemical process and provides a solution for environmental protection and sustainable development of society and economy^[1]. The currently wide-used toxic and volatile organic solvents in chemical industry always breach the green chemistry spirit. In searching for the substitute for organic solvents, room temperature ionic liquids were found to have high thermal stability, negligible vapour pressure, wide liquid range, controllable polarity^[2] and excellent solubility for a wide range of substances. All these properties enable them as alternative solvent for chemical reactions (especially the catalytic ones), and thus the green revolution of the process becomes possible. The research of ionic liquids is developed at a

booming speed during the past decade^[3–14]. The transformation of imidazolium-based ionic liquid to carbene complexes^[15,16] and also stabilize nanoparticles^[17] has provided information on the mechanism of the reactions carried out in ionic liquid as solvent and helps to explain differences with organic solvents. The investigation of ionic liquid chemophysical properties can provide the basic data for such theoretical research and has become another hot point in ionic liquids study^[18]. With more and more ionic liquids becoming commercially available, they show the promising perspectives in diverse applications including catalysis, materials science, and separation technology^[19], etc. In addition, in turn such applications have promoted the design and synthesis of many new ILs. According to the statistical prediction, the kind number of ionic liquid can reach 10^{18} by cation/anion combination, while the commonly used organic solvents are only 300–400 kinds. Such a huge family of ionic liquid defi-

nately suggests broad application potentials.

The majority of research concerned with ionic liquids has been limited to a relatively small group of salts, typically with cations containing saturated hydrocarbon substituents. However, there is need to be construed by this limitation and since the properties of ionic liquids, such as melting point, viscosity, density and solubility within them are determined by the substituents on the organic component and by the counter anion, ionic liquid may be developed for a specific organic reaction, or for a specific application. A strategy of ionic liquid functionalization was firstly proposed by Kou, i.e. functionality introduction into the cation or anion of the ILs, such functionality enables specialized properties that can interact with the solutes in IL, and in turn the optimization of the special process can be achieved^[12]. For example: acidic ionic liquid used in previous literature was usually based on AlCl_3 , which was not stable, and the reusability was also difficult^[20–23], but in some cases these can be replaced by Brønsted acidic IL with appended carboxylic or sulfonic acid groups were recently reported, as was their use as solvent-catalysts for esterification and other organic reactions^[24–26]. Meanwhile, direct combination of HX and 1-methylimidazole to form acidic ionic liquids was also reported^[27]. Another example, imidazolium based ILs are unsuitable for reactions involving either active metals (i.e. Na or K) or in solutions that involve strong bases since these reagents react with the imidazolium salts, for this purpose, phosphonium based ILs have been developed recently, in which even Grignard reaction can be performed^[28].

So far, functionalised ILs are generally recognised as ILs with functional groups in the cation. Functionalization of the cation requires in most cases only a single reaction process, making them relatively easy to prepare. Now, however, ILs containing functionalised cations usually have higher viscosities compared to conventional ionic liquids with the same anions. Viscosity is an extremely important parameter, especially in large-scale applications and electrochemical device application like solar cells. To overcome this problem, functionalised anions have been shown to lower the viscosity. Recent research shows that asymmetrical anions with higher content of fluorine atoms can reduce significantly the viscosity of the resulting ionic liquid. From the conventional ionic liquid chemistry, it

is commonly accepted that the anion structure controls the properties of the ionic liquid. However, efforts in developing new ILs with functional anions have not inspired many interests so far. Compared to functionalized ILs with functional groups in the cations, only a very few dual-functional ILs are known, elucidating the functionalities of the anion-functionalised ionic liquids are even rarer to see in the literature. Functionalization of the anions usually needs multi-step reactions and requires more knowledge and skills in organic synthesis, and better understanding in the relationship of the physical properties and the structural features of the ILs. This is probably the reason why anion functionalised ILs have lagged far behind.

There are already plenty of excellent reviews and books covering the field of conventional ILs and its applications^[29–40], however, a review setting a point view from functionalization is needed. Herein this review paper, we will highlight recent developments towards exploring functionalised ILs as reaction media, possibly recyclable catalytic systems that exhibit higher activities than the classical ILs. Some other areas including using functionalised ILs for preparation nanoparticles, organometallic ionic liquids, porous materials and application as lubricant, absorption of SO_2 will also be highlighted. These applications sound somewhat exotic compared to applications as reaction media, but they have, we think, huge potential in industrial applications.

2 Functionalization of ionic liquids

The most commonly reported procedures for the preparation of functional cations are as follows: (1) Starting from 1-alkyl imidazole and functionalized alkyl halides using standard quaternization method gives the desired functionalised imidazolium halides in good yield; (2) Deprotonation of imidazole by HNa/HK followed by addition of two equivalents of functionalised alkyl halides or heating a mixture of 1-trimethylsilylimidazole and two equivalents of functionalised alkyl halide gave similarly high yield of the desired 1,3-bisfunctionalized-imidazolium halides^[41,42]. Most functional groups can be introduced directly to the imidazolium moiety using these methods^[43–56]. Fig. 1 gives an overview of functionalised imidazo-

lithium cations that have been reported. It is important to note that most of the imidazolium salts are inert and the attached functionalised groups can be varied again for synthesis of further ILs.

The functionalized halide precursors react with the salt of the targeted anion sodium or lithium salts can result in low melting point ionic liquids, and the sodium

or lithium halides will be precipitated as by-products. However, complete precipitation of the halides by-product is very difficult and this is known to influence strongly the physical and chemical properties as well, for example, poisoning catalysts dissolved in ILs^[57,58]. Considerable efforts have therefore been devoted to developing methods to eliminate halides con-

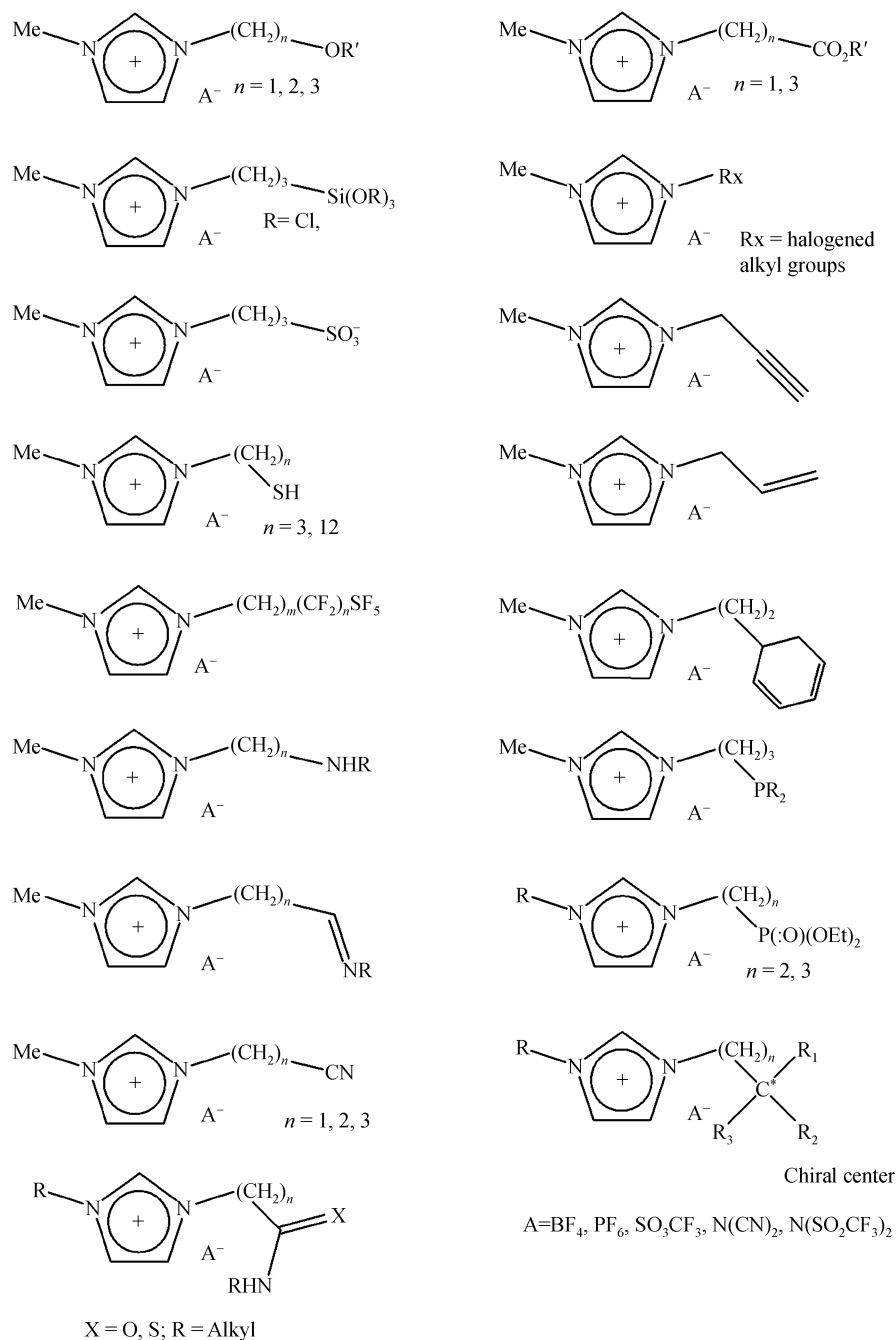


Fig. 1. The reported functionalized ILs on cations.

Notably, despite the diversity of the chemical structure that composes the ionic liquid cation, the preparation of the precursors and ILs themselves requires plenty of “non-green” chemical compounds and organic solvents. In other words, the preparation process of such “green solvent” is not “green”. Recently, Kou and co-workers reported the first example of ionic liquids generated from biomass^[77]. The protonation of natural α -amino acid and α -amino acetate and then combination with a variety of anions form a new family of ionic liquids. Compared with the conventional ionic liquids, such ionic liquids possess three advantages: (1) They can be bio-regenerated and bio-degraded; (2) the chirality in bio-precursor can be maintained in ILs; (3) further functionalization is possible. This strategy represents the new development direction of “greener” ionic liquids.

Much less effort has been devoted to the synthesis of functionalized anions, and most examples are based on readily available materials (Fig. 3), such as transition metal oxides^[78], aminoacids and transition metal carbonyl^[79–83]. Some alkene-substituted anions have also been introduced for synthesis of polymeric materials^[84,85]. Very recently, there are also few anions based on triazole backbone reported^[86–88]. They have higher melting points and viscosities, but have potential applications in energetic materials. Zhou synthesized a series of perfluoroalkyltrifluoroborates $[R_fBF_3]^-$ via an improved fluorination method. Anions exchange of these perfluoroalkyltrifluoroborates $[R_fBF_3]^-$ with imidazolium halides gave a series of ILs with very low viscosities^[89,90]. The reaction of SeO_2 with 0.5 equivalent of K_2CO_3 in methanol gave $[KSeO_2(OCH_3)]$. The reaction of the potassium salts with imidazolium chlorides gave a series of selenium based ILs. Treatment of these selenium based ILs with $HOCH_2CF_3$ gave new ILs with viscosity being as low as 15 cP, and these ILs can be applied as solvent for oxidative carbonylation reactions of aromatic amines^[91]. We recently synthesized a series dual functionalised ILs with an asymmetrical anion that also decrease viscosities^[92]. The synthetic strategy involves the preparation of the functionalized anion initially as a potassium salt, followed by anion metathesis with various imidazolium halides. The first step of the anion synthesis involves hydroboration of allyl cyanide using boron trichloride and triethylsilane, then addition of water to afford the

boronic acid that is subsequently stirred with KHF_2 in ether/ H_2O at ambient temperature. Recently a highly fluoro-anion based IL has also been reported, which can be partially dissolved in non-polar solvents and can be used in biphasic catalysis involving substrates such 1-alkenes^[93].

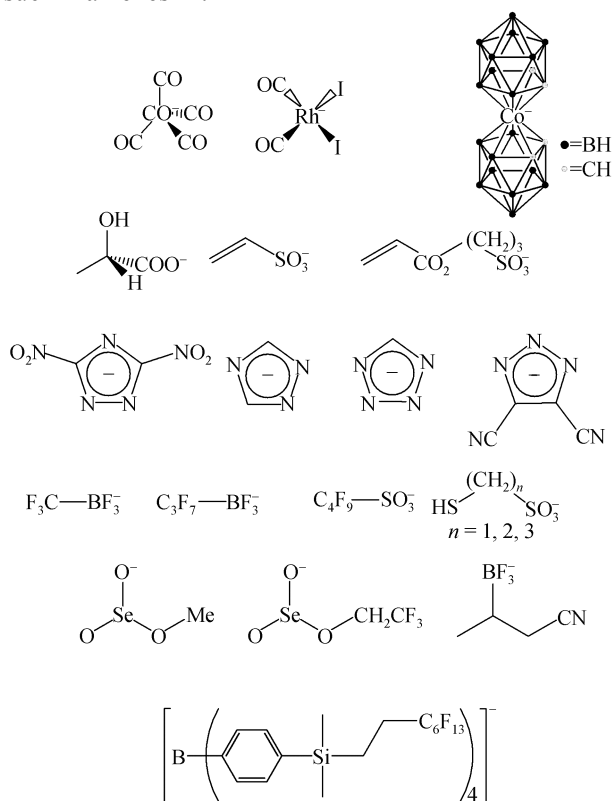


Fig. 3. Common functionalized anions.

It should be noted that despite a huge number of reports collected on functionalised ILs, their physical properties are not investigated routinely or systematically. The influence of the functional groups on the physical properties of the functionalised ILs is poorly understood.

3 Functional ILs for reaction media

Design and synthesis of ILs require knowledge on organic synthesis. Identifying the application of a special IL requires more understanding of the ILs and catalytic mechanism. In the last few years, many innovative concepts have been created in utilizing the specific properties of a specific IL for special reaction^[94–98]. Focused on the investigation of non-functionalized molecular structure and catalytic perform-

ance relationship, a great deal of work was reported by Dyson's group^[99–109]. In the last few years, many innovative concepts have been created in utilizing the specific properties of a specific IL for special reaction.

3.1 Ionic liquid-coordinated complexes for better immobilization in ILs

The design and synthesis of ILs for use as reaction media that can serve as both immobilization and as coordinating ligand for the catalysis in the process involving homogeneous catalysis is a worthwhile objective: such system would be useful in avoiding catalysts leaching from the ionic layer, which is especially significant for expensive transition metals and expensive ligands. The coordinating ability of the conventional ionic liquid is often very poor. Shreeve designed a coordination ligand and tested the activities as solvent for Heck reactions and observed that this catalyst ionic liquid solution could be recycled at least 10 times without significant decrease in catalytic performance^[110]. The most important feature of the catalytic system is that this catalyst is part of the ionic liquid and therefore not easily lost during extraction of the product.

A more effective catalytic system is the CN-functionalized pyridinium based ILs systems (Fig. 4). They have higher activity and can be reused up to 9 times with slightly increased activities^[111] (Fig. 5). The

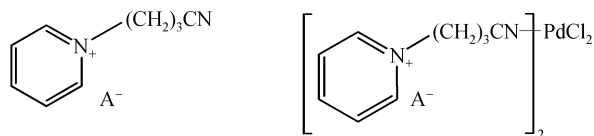


Fig. 4. Catalyst immobilization by CN functionalized ionic liquids.

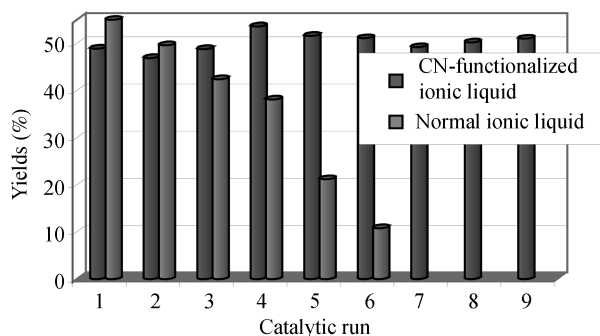


Fig. 5. Comparison of Heck catalytic runs in CN-functionalized IL and normal IL.

superiority of the nitrile-functionalized system compared to the alkyl-pyridinium ionic liquid-based one appears to be due to several factors. Inductive coupled plasma spectroscopy (ICP) was used to analyze the organic fractions after catalysis for palladium content. In addition, a cyclohexadiene functionalized ionic liquid was successfully used in ruthenium catalyzed transfer hydrogenation^[112].

CN functionalized ILs were also found to stabilize reaction intermediate in glycosidation reactions (C-O coupling) reactions^[113] (Fig. 6). It was suggested that the cyano group in the side chain of the imidazolium cation coordinated with the oxonium intermediate more effectively than trifluoromethanesulfonimide anion and increased the stereoselectivity of the product.

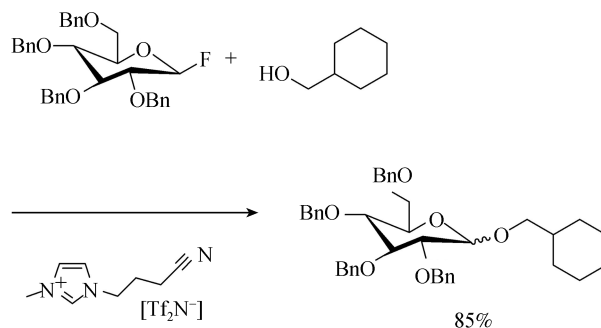


Fig. 6. Glycosidation reactions in CN-functionalized ionic liquids.

3.2 Chiral ionic liquids and asymmetric synthesis

It has been quite a long time since the start of asymmetric synthesis research in conventional ionic liquids^[114–116] and the work is under way^[117]. In all these tryouts, the chiral catalysts or ligands were necessary. The purpose of chiral ionic liquid synthesis is quite obvious: to carry out asymmetric synthesis in chiral ionic liquid and achieve high enantioselectivity by using expensive chiral ligands. Currently, various methodologies for chiral ionic liquids preparation exist but basically were based on the chiral starting materials, for example, the chiral anion alkaline salt or through imidazolium chiral alkylation^[118,119].

Full evaluations of the potential of these chiral ILs in synthetic and analytic applications are developing at an incredible rate. For example, the Baylis-Hillman reaction's enantioselectivity was enhanced with participation of chiral ionic liquid^[120] (Fig. 7).

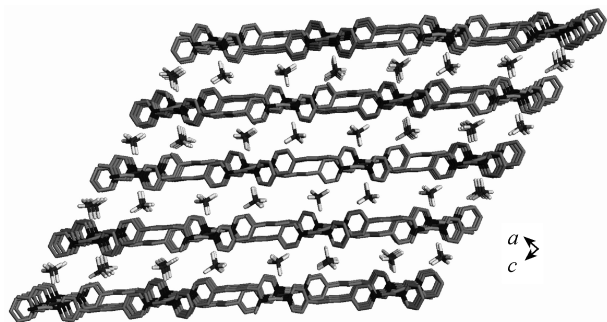


Fig. 9. Solvothermal methods using ionic liquid to form porous materials.

formed during the reaction, the NH_4^+ cation formed on the partial decomposition of urea acts to template the structure and balance the charge distribution of the framework, and the procedure is termed as “ionothermal” synthesis for distinguishing from other preparations.

The choline chloride/urea eutectic mixture was also employed as solvent for a zinc coordination polymer in a recent report^[130]. $\text{Zn}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ and $\text{H}_2\text{O}_3\text{PCH}_2\text{CO}_2\text{H}$ reacted in the choline chloride/urea eutectic mixture to give a $\text{Zn}(\text{O}_3\text{PCH}_2\text{CO}_2)\text{NH}_4$. The reaction took place at 80°C while no reaction was observed at ambient temperature. This may suggest that the *in situ* formation of structure NH_4^+ occurring at high temperature is crucial to the reaction. The NH_4^+ also enters the final structure as charge balancing agents.

While the above mentioned examples all use ILs as solvent at ambient pressure, heating is still required to generate the structure-directing template, and all require prolonged reaction times. The very recent report from our lab shows that an imidazolium based acidic ionic liquid/water can react with elemental zinc^[131], cobalt^[132], or main group/transition metal carbonates, the zwitterionic anion can be generated even at room temperature or even lower temperature, and the reaction is very quick (Fig. 10).

The use of ionic liquids and eutectic mixtures as solvent and template opens up many new possibilities in the preparation of polymeric porous materials. By using the right combination of the cations and anions, it is possible to target special frameworks for special applications. One example is the selective incorporation of small molecules or anions into the pores of the

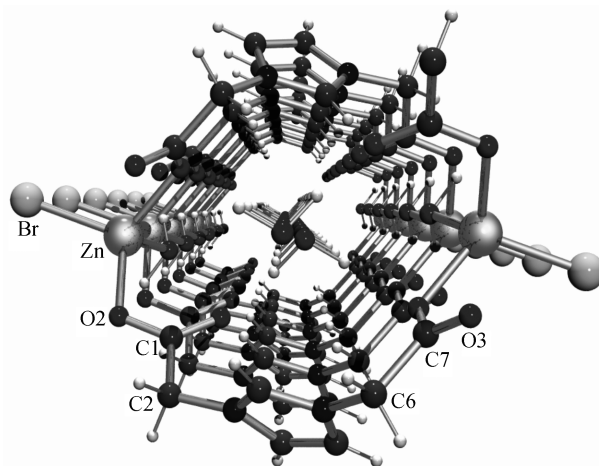


Fig. 10. Zinc coordination polymer containing water channel.

resulting porous framework. They will have potential applications, for example, for ion exchange.

5 Application of functional ILs in surface science

Ionic liquid interacts with solid surface such as silica gel and molecular sieves and tunability of hydrophilicity and hydrophobicity (wettability) of ILs has led to their use as surface modification agents^[133]. The fact that ILs are composed of cations and anions has made it possible to control the surface wettability using ILs by simple anion exchange, which is not possible using the traditional method based on organic solvents.

Submersing the Au substrate (the Au substrates were prepared by thermal evaporation of 100 nm of Au onto polished Si (100) with a 20 nm Ti adhesion layer and cut into 1 cm^2 pieces) in 1 mmol/L ethanol solution containing the thiol-functionalized ILs with Br^- as anions, results in the formation of well ordered self-assembled monolayer on the gold surface^[134]. Ellipsometric measurements show a film of about 19 Å in thickness, supporting the formation of monomolecular film, i.e. monolayer and not multilayer, and the water contact angle was found at 23° . If the surface was immersed in an aqueous solution of containing NaBF_4 and NaPF_6 , anion exchange was achieved. Thiol-functionalized ILs with anions of BF_4^- and PF_6^- thus modified the surface of the gold substrate. Using the same method, the bromide anion could also be replaced by NO_3^- , ClO_4^- , CF_3SO_3^- or $(\text{CF}_3\text{SO}_2)_2\text{N}^-$. The

water contact angle of the thus obtained systems increased in the order: $\text{Br}^- > \text{BF}_4^- > \text{NO}_3^- > \text{ClO}_4^- > \text{CF}_3\text{SO}_3^- > \text{PF}_6^- > (\text{CF}_3\text{SO}_2)_2\text{N}^-$, increasing significantly on progressing from Br^- to $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (Fig. 11).

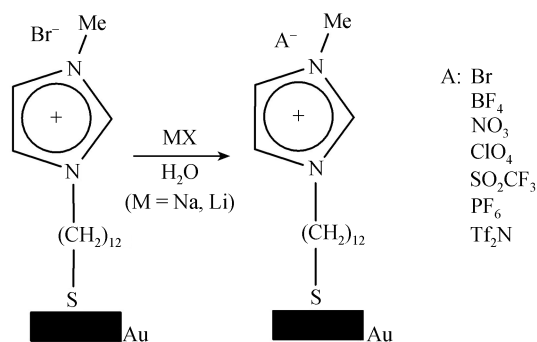


Fig. 11. Anion exchange on the gold surface.

Measurements of water contact angles could provide quantitative information on the effects of counter anions on the IL-modified surface wettability. The thiol-functionalized IL family are able to modify selectively the surface properties of self-assembled monolayer on gold. Modulation of surface properties such as wettability has important implications in both fundamental and technological advances; the anion effect offered by functionalized ILs on surface wettability is of practical significance to the adsorption on molecular surfaces and can be used for design of micro fluidics and micro devices used in anion sensing and in biomedical areas.

The IL cations also have an influence on the surface properties. In 1-alkyl-3-(3-silylpropyl)imidazolium and Si/SiO₂ surface systems, it was found that the anion effect was the main factor that determines the surface water wettability when the alkyl group was methyl. However, if the methyl group was replaced by butyl group, no significant changes in the contact angle of Si/SiO₂ surfaces upon the anion exchange were observed, and the wettability was mainly controlled by the butyl group and not affected by the anions^[135].

6 Ionic liquids and mechanical lubrication

Many commonly used lubricants raise significant concerns especially when they are used under extreme conditions. The low vapour pressure of ionic liquid

has made for example alkylimidazolium tetrafluoroborate as promising versatile lubricant for contacts of steel/metal, steel/SiO₂, Si₃N₄/SiO₂, steel/ceramics systems; they show excellent friction reduction, anti-wear performance and high load-carrying capacity^[136,137]. Under the same conditions, the friction coefficient of 1-methyl-3-hexylimidazolium tetrafluoroborate is significantly lower than the commonly used commercial products: fluorine-containing phosphazene and perfluoropolyether. The ILs exhibit superior tribological behaviour because of the unique dipolar structure of the molecules. Thus they can be absorbed easily on the sliding surface of friction pairs.

To improve the lubricating ability of ILs, the phosphorus ester group *O,O*-diethylphosphate was introduced into the imidazolium cation^[138] (Fig. 12). The resulting functionalized IL has generally better friction-reducing ability than the conventional 1-ethyl-2-hexylimidazolium hexafluorophosphate. This is especially prominent at a relatively high load, which indicates that the phosphorus ester functionalised ILs could be promising candidates as novel high-temperature liquid lubricant. Moreover, they show better anti-wear abilities than 1-ethyl-2-hexylimidazolium hexafluorophosphate for Al-on-Steel system. It was also found that the antiwear abilities of the phosphorus functionalised ILs for Al-on-Steel contact are related to the length of the alkyl chain.

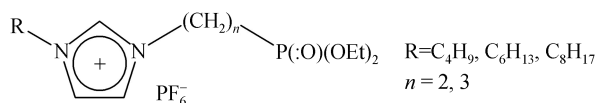


Fig. 12. Phosphorus ester ionic liquids for mechanical lubrication.

The superiority of the functionalized ILs compared to the conventional ILs is believed to be because that the phosphorus group in the alkyl side-chain can partially undergo hydrolyse in the presence of atmosphere moisture and react with freshly exposed aluminium or iron during the sliding process to form stable compounds which probably are dissolved in the ILs. The hypotheses are supported by the observation of the residue lubricants after the tests. The residue of phosphorus ester functionalized ILs remains transparent, while that of the conventional ILs visibly decompose.

7 Ionic liquids and nanotechnology

The combination of ionic liquid and nanotechnology is a perfect marriage in the modern advanced chemistry. Using conventional 1,3-di-*n*-butylimidazolium based ILs as reaction media, Srinivasan reported the isolation of palladium nanoparticles in 2001 formed in a Heck-reaction (catalyst: Pd(OAc)₂, PdCl₂) and characterized for the first time these nanoparticles by means of transmission electron microscopy (TEM)^[139]. In 2002, Dupont also reported the isolation and characterization of iridium nanoparticles from a biphasic hydrogenation reaction (catalyst: [IrCl(cod)]₂, cod = 1,5-cyclooctadiene) using imidazolium based ionic liquid [BMI]PF₆ as reaction media^[140]. The isolated iridium nanoparticles can be reused as catalysts in [BMI]PF₆ ILs and the efficiency is maintained for up to at least seven recycles. Nanoscale platinum(0) particles have been also prepared in imidazolium based ILs [BMI]PF₆ from an organometallic precursor. Reduction of Pt₂(dba)₃ (dba = bis-dibenzylidene acetone) with molecular hydrogen in [BMI]PF₆ leads to stable and isolable platinum (0) nanoparticle, which can be used as catalyst in hydrogenation reactions with high activities and recyclabilities^[141]. In electrochemistry research, ionic liquids were applied combined with various nanomaterials^[142,143].

The palladium nanoparticles were immobilized by ionic liquid onto molecular sieve and showed high catalytic activity in solvent-free alkene hydrogenation^[144].

Using CN functionalized pyridinium ILs, palladium nanoparticles can also be isolated from a Stille reaction process, and they are different from that isolated from non-functionalized pyridinium based ILs. The CN group in the cation can be weakly coordinated to zero covalent palladium and hence prevent the aggregation, which was observed in other reactions using conventional alkyylimidazolium ILs (Fig. 13)^[111].

Nanoparticles consist of metallic nanocrystal cores

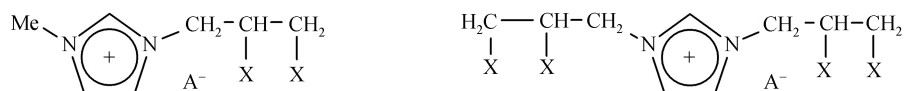


Fig. 14. The ionic liquids containing thiol functionality.

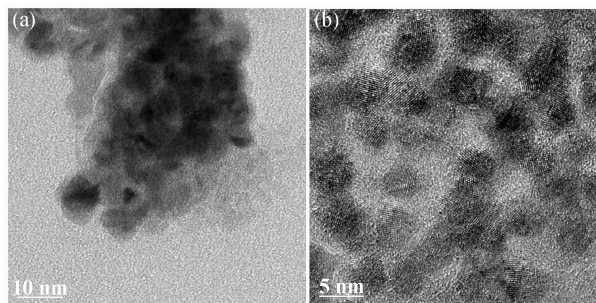


Fig. 13. Comparison of Pd NPs in CN-IL (a) and conventional IL (b).

and organic monolayer shells, and they have promising technological application applications, for example as chemosensor^[145]. Alkylthiol compounds are known to stabilize gold nanoparticles^[146–148]. However, the water-based synthesis of nanoparticles is fraught with inherent problems such as ionic interaction, low reactant concentration, and difficulty in removing the residue of stabilizers after synthesis. In this context, thiol-functionalized ionic liquids represent potentially good candidates as stabilizers since the ionic properties of ILs could enable better interaction of ILs and transition metals such as Au and Pt in ionic species salts than those in conventional solvents. Additionally, they can also be easily designed to be hydrophilic or hydrophobic by combining the cations with the appropriate anions.

The precise control of nanoparticle size and size distribution and a better understanding of the chemical behaviour of nanoparticles are becoming increasingly important and have been recognized as key research tasks in order to expand their utility. In a recent report, ILs with one, two, or more thiol groups were prepared in order to rationalize their effects on the size and distribution of nanoparticles (Fig. 14)^[149]. In addition, thiol groups were also introduced into the anion of the imidazolium based ILs, forming a dual-functionalised system, which was also evaluated in nanoparticle synthesis.

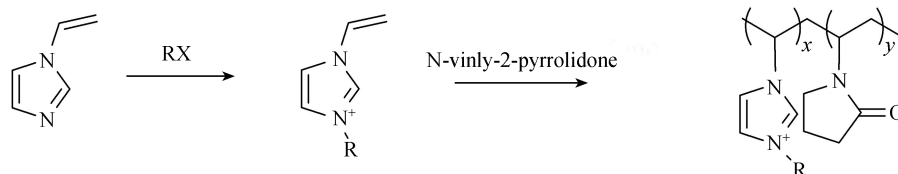


Fig. 15. PVP polymer containing ionic liquid moiety.

Gold and platinum nanoparticles prepared from these thiol-functionalised ILs are highly dispersible in aqueous salute. The nanoparticle size and stability were affected by the position and number of thiol groups in the cation and anion, and therefore the chemical and physical interaction between the ILs and metals plays a decisive role in determining the nanoparticle structure. Moreover, the nanoparticle size could be tuned according to the nature of cation and anion. The diameter of the nanoparticles was observed to decrease as the number of thiol groups increased on the cation, and the diameter decreased when a sulfite anion with a thiol group was employed. Furthermore, the nanoparticles encapsulated by these ILs were more stable towards agglomeration. Accordingly, the IL's functional groups in the cation and anion behaved as selective gates to allowing control of the size and uniformity of the encapsulated nanoparticles.

Polymer such as polyvinylpyrrolidone (PVP) is also commonly used nanoparticles stabilizer. The platinum, palladium and rhodium NPs were prepared by Kou and co-workers in [bmim][PF₆] (Fig. 14)^[150].

However, the low polarity of PVP makes it hard to dissolve in high polar ionic liquids, thus the application as stabilizer in IL is limited. Recently, Kou and co-workers designed a “ionic liquid-like” PVP polymer^[151], which can be successfully used as Rh NP stabilizer for high performance hydrogenation (Fig. 15).

Such Rh NPs can be used as catalyst for aromatic compound hydrogenation carried out in [bmim][BF₄]. The total turnover value reached 20,000 and the synergistic interaction of modified PVP and ionic liquid is considered the reason for the long life of catalyst.

Since chloride-contamination has a significant impact on the properties of the nanoparticle obtained from ILs^[152,153], a method for the production of nanoparticle has been developed using chloride-free functional ILs^[143]. Reduction of bis-(dibenzylideneacetone) platinum [Pt(dba)₂] (dissolved in thf) with

molecular hydrogen in chloride free ILs 4,5-dicyanotriazolium tetraoctylammonium IL (known as “Armand's Ligand”, Fig. 16) affords Pt nanoparticles that are soluble in THF and have Pt content of 15.6% according to the elemental analysis. Using a mixture of Pt(dba)₂ and Ru(cod)(cot) (cod = 1,5 cyclooctadiene; cot = 1,3,5-cyclooctatriens) in 1:1 molar ration, mixed PtRu-nanoparticles (Pt:Ru = 1:1) can be obtained in a similar manner. All these nanoparticles show excellent methanol oxidation catalytic activities.

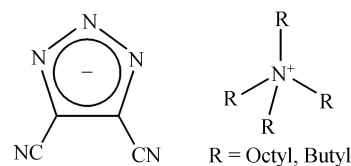


Fig. 16. Halide free ionic liquids for nanoparticle preparation.

8 Ionic liquids and clean technology

Ionic liquids, which show up as alternative solvent for green process, are now not only used for replacement of traditional solvents, but as applied as material for other clean technology, for example the fuel desulfurization and flow gas desulfurization.

The sulfur containing fuel is the main course of the atmosphere pollution and the sulfur mission has been strictly controlled all around the world. For instance, many western countries have set to limit the fuel sulfur mission from 500 mg/L down to 10–50 mg/L^[154]. Therefore, the deep desulfurization of fuel draws great attention in academic and industrial fields. The earliest ionic liquid application for desulfurization was reported in 2001^[155]. Wasserscheid and co-workers used ionic liquids of different molecular structure in the diesel desulfurization. It was found that after multi-step process by AlCl₃ ionic liquids, the sulfur concentration was reduced from 500 mg/L down to 235 mg/L. Meanwhile, the industrial equipment was designed for such process^[156]. At present, the approach

of ionic liquid desulfurization is to use ionic liquids as simply the extractor^[157] or combined chemical desulfurization (such as oxidation)^[158].

Chinese scientists also reported the [bmim][CuCl₂] as extractor for fuel desulfurization^[159]. It was found that [bmim][Cl] and CuCl₂ can form ionic liquid when mixed by 1:2, and by FAB-MS analysis, the anions were found to be CuCl₂⁻, Cu₂Cl₃⁻ and Cu₃Cl₄⁻. There is no oxide found in MS, indicating this kind of ionic liquids are moisture stable compared with AlCl₃ ionic liquids. The sulfur concentration of gasoline can be reduced maximally 37% by this ionic liquid. Besides, the ionic liquid has no strong Lewis acidity, then the polymerization of gasoline content is avoided. The desulfurization mechanism is speculated to be the formation of π -complex by Cu(I) compound and thiophene.

The ionic liquid application for fuel desulfurization is only at the starting stage, and the mechanism is not clear so far. On the other hand, there exist the problems of ionic liquid regeneration, negative effects on fuel quality, and so on. Therefore, work that is more detailed is needed in this area.

SO₂ is the most harmful gas in atmosphere with strong corrosiveness and toxicity, and is the main course of acid rain. The current dry, wet and semi-dry methods for flue gas desulfurization have problems such as high energy and water consuming, great waste water quantity and by-product. Han and co-workers

prepared a basic guanidinium ionic liquid for SO₂ adsorption from atmosphere (Fig. 17)^[160]. The SO₂ adsorption to ionic liquid can reach 0.305 g SO₂/g IL. The adsorbed SO₂ can be de-adsorbed at 40°C under vacuum. The desulfurization mechanism was investigated by NMR technique (Fig. 18). Using acidic/basic functionality of ionic liquid to treat harmful contents in atmosphere has the following advantages: the wide liquid range, the moderate interaction of ionic liquid between harmful contents that enables the controllable adsorption/de-adsorption, opens a new pathway for atmosphere pollution control.

9 Outlook

The endless functionality combination of cation/anion indicates the enormous application potentials for functionalized ionic liquids. Such magic liquid starting from green chemistry research now has been applied in further broader fields, and such trend is being continued. At present, the majority of ionic liquid research is now only limited in molecular design and lab investigation, and both academic and industrial chemists are expecting a huge revolution of ionic liquid replacement for traditional organic solvent in signification process. However, we are still confident that with the boundless possibility of physical/chemical properties endowed from functionalization, the opportunity and prospective for functionalized ionic liquid will be unlimited.

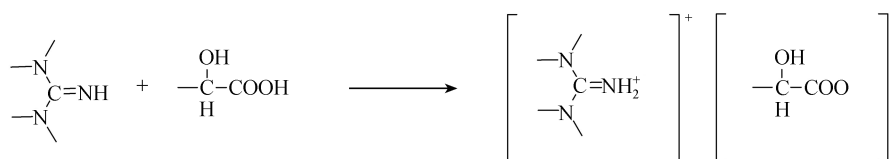


Fig. 17. Preparation of guanidinium ionic liquid.

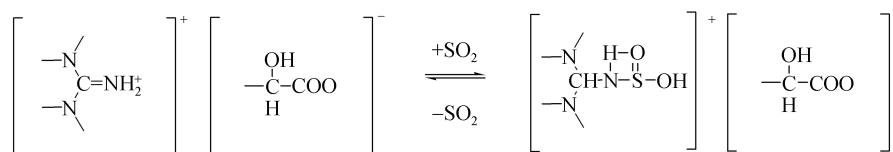


Fig. 18. The speculated desulfurization mechanism of guanidinium ionic liquid.

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