

Imidazolium-based ionic liquids grafted on solid surfaces

Cite this: *Chem. Soc. Rev.*, 2014, **43**, 7171

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Supported ionic liquids (SILs), which refer to ionic liquids (ILs) immobilized on supports, are among the most important derivatives of ILs. The immobilization process of ILs can transfer their desired properties to substrates. Combination of the advantages of ILs with those of support materials will derive novel performances while retaining properties of both moieties. SILs have been widely applied in almost all of fields involving ILs, and have brought about drastic expansion of the ionic liquid area. As green media in organic catalytic reactions, based on utilizing the ability of ILs to stabilize the catalysts, they have many advantages over free ILs, including avoiding the leaching of ILs, reducing their amount, and improving the recoverability and reusability of both themselves and catalysts. This has critical significance from both environmental and economical points of view. As novel functional materials in surface science and material chemistry, SILs are ideal surface modifying agents. They can modify and improve the properties of solids, such as wettability, lubricating property, separation efficiency and electrochemical response. With the achievements in the field of ILs, using magnetic nanoparticles (MNPs) to SILs has drawn increasing attention in catalytic reactions and separation technologies, and achieved substantial progress. The combination of MNPs and ILs renders magnetic SILs, which exhibit the unique properties of ILs as well as facile separation by an external magnetic field. In this article, we focus on imidazolium-based ILs covalently grafted to non-porous and porous inorganic materials. The excellent stability and durability of this kind of SILs offer a great advantage compared with free ILs and IL films physically adsorbed on substrates without covalent bonds. Including examples from our own research, we overview mainly the applications and achievements of covalent-linked SILs in catalytic reactions, surface modification, separation technologies and electrochemistry.

Received 19th May 2014

DOI: 10.1039/c4cs00172a

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1. Introduction

In recent decades, room-temperature ionic liquids (RT-ILs), especially imidazolium-based ionic liquids, have been central to many areas of chemistry. RT-ILs are a special class of molten salts composed of large asymmetric organic cations and inorganic or organic anions, which melt at or below 100 °C, usually close to room-temperature.^{1,2} The special structure and interaction of ions determine their unique physicochemical properties, such as negligible vapor pressure, chemical, thermal and photocatalytic stability, nonflammability, relatively high ionic conductivity, and a wide electrochemical potential window. Moreover, RT-ILs can be designed to desired structures for specific applications through varying the cations and anions. Hence, they are often referred to as “designer liquids”. As a result, RT-ILs open up new horizons in

many areas, such as organometallic catalysis, surface modification, biocatalysis, chemical sensors, analytical techniques as well as electrochemistry, *etc.* There have been many reviews which have presented comprehensive overviews on these topics.^{3–6}

The facile designability and functionalization of ILs can lead to many innovations. Supported ionic liquids (SILs) are among the most important branches in the IL community, and have drawn great attention in both fundamental research and practical applications.^{7–10} Supported ionic liquids refer to ILs that are immobilized on solid, polymer, liquid or aerogel supports by either covalent or noncovalent bonds using various methods, including simple physisorption, self-assembly or polymerization.^{11–13} The unique physicochemical properties of ILs can be transferred to substrates. They not only retain the advantages of ILs and supports but also derive a series of new performances and novel properties due to the synergistic effect of ILs and supports, while also overcoming many of negative aspects of conventional ILs (*e.g.*, leaching and disarrangement, poor recovery and so on). The dramatic advantages of SILs have inspired drastic re-evaluation of the ionic liquid area. Over the last decade, SILs have been used as green media and functional

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materials for supports of catalysts, surface modifying agents, stationary phases in separation technologies, and electrodes in electrochemistry.^{14–17}

In this critical review, our interest centres on imidazolium-based ILs covalently linked to non-porous and porous inorganic materials. We summarize mainly the achievements of covalently-linked supported ionic liquids in related areas. Section 2 gives the concept of SILs and their derivatives, and describes their synthetic methods and routes. In Section 3, the applications and advances of SILs in organic chemistry are described with discussion of SILs and catalysts. Section 4 presents the modulation of wetting and lubricating behaviors of substrates through covalently anchoring ILs on their surfaces, and the effect of anions and cations of SILs is discussed. Referring also to our group's work, we describe the synthesis of stably dual-stimuli-responsive IL superhydrophobic surfaces. Section 5 summarizes the advances of SILs in separation technology. Covalent bonds between ILs and substrates can enhance the stability and avoid the disarrangement of SIL films. In addition, SILs can tailor the electrochemical properties of materials, with approaches appending covalently ILs on electrodes and electrolytes being described in Section 6. Finally, we offer conclusions about this review and an outlook on the future and perspective of the domain of SILs. Considering the rapid developments in this topic, we would like to point out that the achievements of SILs presented here approximately covers the period from 2002 to March 2014.

2. Supported ionic liquids and relatively derivative concepts

In catalytic reactions, aggregation and poor recovery of transition-metal catalysts, and the difficult separation of products from reaction mixtures are the great challenges from both environmental and economical points of view. RT-ILs have the ability to overcome these limitations to a great degree, and

they are suitable reaction media for numerous catalytic reactions.¹⁸ However, the leaching of ionic liquid themselves from reaction systems and the large amount needed have hindered their widespread practical applications due to their expense and potential toxicity to the environment.

Under this background, the concept of “immobilized ionic liquids” on solid surfaces *via* covalent bonds is derived from the term “immobilized liquids”.¹¹ In 2002, Mehnert *et al.*¹⁹ covalently anchored 1-*n*-butyl-3-[3-(triethoxysilanyl)propyl]-4,5-dihydroimidazolium onto silica gel surface *via* the reaction between trimethoxysilyl functional group in ILs and the abundant silanol groups on silica gel, forming supported ionic liquids (Scheme 1). In organic catalytic reactions, the reaction phase to dissolve the catalyst is necessary, and the added free ILs are absorbed in the SIL layer. The mixture of bonded and mobile phases of ILs forms supported ionic liquid phases (SILPs),⁹ as excellent stabilizers for the catalysts and media of reactions. In SILPs, Mehnert *et al.* dissolved the active Rh catalyst, denoted as supported ionic liquid catalyst (SILC), which successfully catalyzed hydroformylation reaction with high yields using only a small amount of ILs.

Although it can be argued that ILs once bound to a solid support, that the cation–anion pair no longer constitutes a true IL, the unique properties of ILs still remain in SILs. Covalently linked ILs on supports offer a highly attractive strategy to circumvent the leaching of ILs, minimize the amount needed and improve the stability,²⁰ while displaying other desirable performances applicable in other areas. When they are employed in separation technologies, SIL films are often denoted as supported ionic liquid membranes (SILMs).⁸

Supported-mono-ILs composed of one imidazolium moiety, which refer generally to self-assembled monolayers of imidazolium ion (SAMIMs) (Scheme 1 and Fig. 1a), often present low density, and result in poor performances in the modified solids. Thus, in organic reactions, supported-multi-ILs (Fig. 1b) which have two or three imidazolium moieties in side chains are grafted on supports with different counteranions, and can offer more catalytic active centres than supported-mono-ILs.²¹



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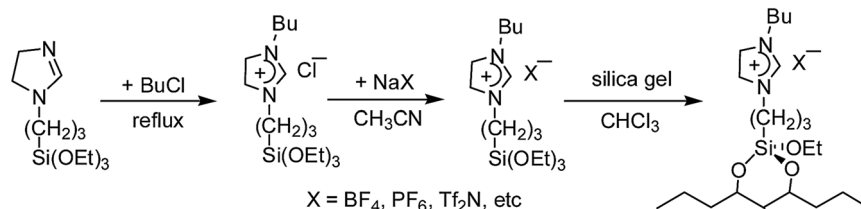
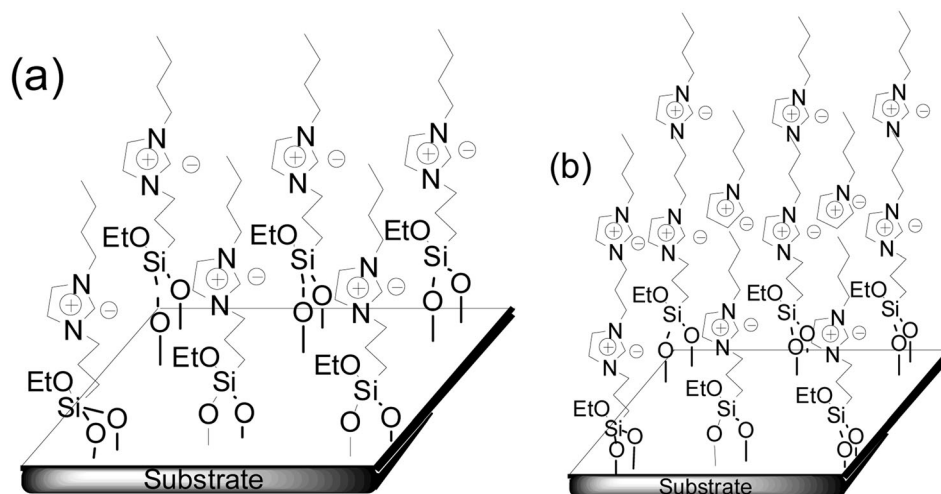
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Jingcheng Hao

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His research focuses on colloid and interfacial sciences, including surfactants in solution and self-assembly at all scales in bulk solutions and at surfaces.

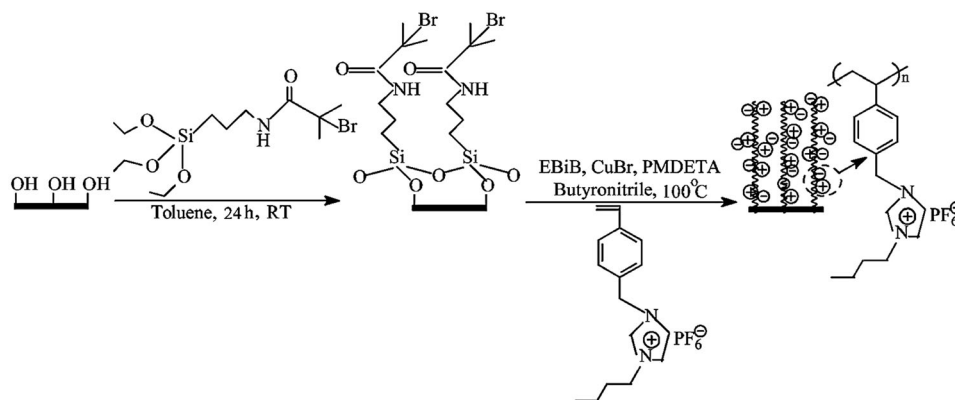
Scheme 1 Preparation of SILs via covalent bonds.¹⁹Fig. 1 Supported-mono-ILs (a)¹⁹ and supported-multi-ILs (b)²¹ on supports.

In parallel fascinating developments of both SILs and poly(ionic liquid)s (PILs) in recent years,²² supported poly(ionic liquid)s (SPILs) have significantly increased in surface chemistry and material science. For example, [1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate] ([PVBIm]PF₆) brushes are grafted from the surface of silicon wafer *via* surface-initiated atom transfer radical polymerization (ATRP) technique, as shown in Scheme 2.²³ The diversity of ILs induces a variety of SPILs, and many experiments prove that they can offer higher density and uniformity than SILs, and enhance the performances to a substantial degree.

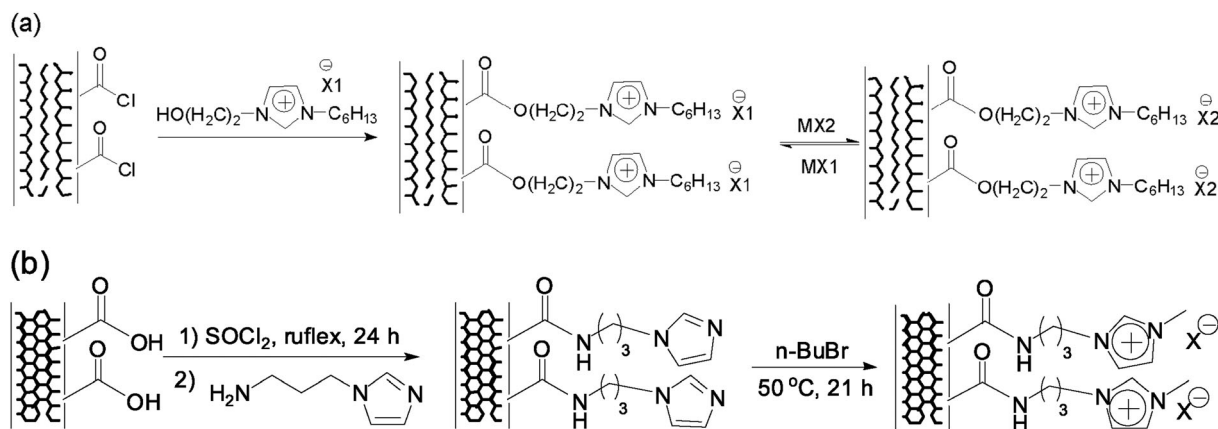
Different supports can form different interactions with ILs.^{5,24} The majority of supports which immobilize ILs are often mesoporous silica materials, zeolites and clays (*e.g.*, montmorillonite), carbon nanotubes (CNTs) and metal/metal oxide nanoparticles (NPs) and other materials.^{24,25} Among them, silica-based materials, including silica gel, MCM-41 and MCM-48 are the most popular supports due to their large surface areas, high thermal and mechanical stability, on which many studies of immobilizing ILs are reported.²⁶ In addition, CNTs and graphenes are considered as another type of promising building blocks for ILs because of their inherent advantageous properties, such as good mechanical strength, high chemical stability and large surface area-to-volume ratio.²⁷ Within the area of SILs, magnetic iron oxide nanoparticles are becoming one of the most attractive supports. One reason is that they are easily separated from mixtures by applying an external magnetic field due to their magnetic property.²⁸ The other reason is that they are readily prepared and functionalized, and have been

derived to hydroxyapatite-encapsulated $\gamma\text{-Fe}_2\text{O}_3$, $\text{SiO}_2\text{@Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4\text{@SiO}_2$ NPs, *etc.*^{29–31}

Though both cations and anions of ILs have the capability to react with functional groups of solid surfaces, immobilization of cations is the main type in SILs.¹¹ The covalent strategy is accomplished by the reaction between pre-functionalized solid surfaces and imidazolium-based ILs with special functional groups, such as trimethoxysilyl-, thiol-, ether-, carboxylic acid-, amino- and hydroxyl-group.⁹ Generally, different substrates need different pre-functionalizing processes. Upon treatment with Piranha solvent, the surfaces of silica-based materials and some metal or metal oxides form a large number of hydroxyl groups,²⁴ and trimethoxysilyl group is realized to be the most stable linking group between ILs and them, while thiol-groups are often used to link Au with ILs.¹⁶ For CNTs, the common functionalizing process is that oxidize them in aqueous HNO₃ to yield carboxylic acid groups on the surface,²⁷ and IL-NH₂ or IL-OH is introduced to the surface *via* -CONH- or -COO- bonds, forming IL-CNT systems. Nowadays, grafting ILs onto substrates can be achieved by two synthetic routes according to the literature (Scheme 3),^{32–34} (i) ILs are prepared first and then self-assembled on the substrate surfaces directly (Scheme 3a).^{32,33} However, the purification of ILs is very difficult, and a small quantity of impurities can produce disordering and defective films, and result in the poor reproducibility. Alternatively, (ii) the imidazolyl moiety is first self-assembled on the substrate surfaces *via* covalent bonds, and followed by the preparation of ILs directly on substrate surfaces (Scheme 3b).³⁴ This route avoids



Scheme 2 Preparation of supported [PVBIm]PF₆ via ATRP technique.²³



Scheme 3 Schematic depiction of the modification of CNTs with functionalized ILs. (a) preparing ILs first, and then self-assembling on the substrate surface via covalent bonds,³³ (b) anchoring imidazolyl moiety on surfaces first, followed by the preparation of ILs directly.³⁴

the purification process of ILs, and the reproducibility is better than that of the first method. Fortunately, the coating of graphene oxide (GO) with ILs is easier than that of CNTs. GO has plentiful and reactive epoxy groups, and nucleophilic ring-opening reaction can introduce amino-terminated ILs to graphene sheets.³⁵

SILs and derivatives have been studied in catalytic reactions, surface modification, separation technologies and electrochemistry. Here we systematically describe the performance of the cations, counteranions of ILs and their supports in many applications.

3. Applications of SILs in organic reactions

The leaching and high consumption of free ILs have stimulated the rapid development of SILs, which are proved to be superior green media relative to free ILs. First, the most advantageous feature of SILs is that they possess higher stability and need less IL than free ILs. Secondly, SILPs can retain the ability of ILs to immobilize transition-metal or metal-free catalysts, having the capability to avoid the leaching of catalysts. Thirdly, SILPs combine the advantages of homogeneous with heterogeneous catalysis, with the advantage of facile separation. Therefore,

they can effectively resolve the difficulties in separation of products, and achieve high recoverability and reusability of catalysts. Further studies show that ILs grafted on supports can modify the process of catalytic reactions, affecting reaction rate, production, yield and even enantioselective activity of asymmetric reactions.¹⁸ In more than one decade, a large range of SILs have been prepared and have been comprehensively investigated in many catalytic reactions.⁷

De Vos *et al.*⁹ have given a definition about the combining types among catalysts, ILs and solid supports, including covalent and noncovalent linkages. Considering the chemical bonds between ILs and supports in this article, we discuss mainly two combining approaches. One type refers to dissolved catalysts in SILPs, and the other type is with the catalyst as a component of ILs, as either cation moiety or counteranion.

3.1. Dissolving catalysts in SILPs

Following the formation of SILPs, transition metals are dissolved and efficiently circumvented into SILPs by virtue of the high interfacial area between SILPs and catalysts, forming the catalyst/IL/IL-support system.⁹ That is, the system acts as not only solvent but also immobilizing agent of the catalyst. Both the compositions of supported ILs and supports can affect the

properties of catalysts and the reaction process, such as stability, recoverability and activity, *etc.*

3.1.1. Effect of compositions of supported ILs on the catalytic properties

(1) *Effect of cations of SILs on catalytic properties.* Supported-mono-ILs with imidazolium side chains have featured in the research of SILs since 2002 (Fig. 1a).

Many catalysts, such as Rh, Pd, Zn, Mn, Au complexes and corresponding metal NPs as well as metal-free catalysts have been studied in SILPs.^{36–38} Taking Rh catalytic species for instance, many experiments prove that utilization of SILPs to immobilize Rh complexes can avoid their aggregation and facilitate separation. More importantly, the study on the reaction mechanism reveals that rhodium concentration in SILPs is improved at the large reaction interface. The activity of the [Rh]/IL/IL-SiO₂ system (turnover frequency (TOF) of 3360–3600 h^{–1}) in hydroformylation reaction is almost three times higher than those for the biphasic [Rh]–[bmim]BF₄ system (TOF of 1320–1380 h^{–1}).^{9,19} The other highlight in SILPs is the reaction types. Until now, almost all of catalytic reactions have been evaluated in SILPs, such as Suzuki reaction,^{37,39,40} hydrogenation reaction,⁴¹ Baeyer–Villiger reaction,⁴² even multi-component reactions^{38,43} and continuous fixed-bed reactors.⁴⁴ The experimental results demonstrate that SILPs present excellent recoverability and reusability and affect the catalytic activity.

Moreover, this strategy shows a favourable availability in asymmetric catalysis reactions.^{45–47} Asymmetric reactions have been of central importance in the synthesis of natural products and pharmaceutical compounds over recent decades. Chiral species are very expensive and difficult to synthesize, and air-sensitivity can result in the loss of chiral characteristics, and thus steps to make them stable and facilitate their recycling are very desirable. Many experiments have demonstrated that SILPs can overcome these limitations to a great degree due to their promising ability to stabilize chiral catalysts as well as avoiding catalysts leaching. Lou^{48,49} designed a catalytic system through solubilising a chiral Ru complex into IL-modified mesoporous materials, and used it to catalyze hydrogenation of aromatic ketones and acetophenone as heterogeneous catalysts (Fig. 2). Although this catalytic system only exhibited comparable conversions and enantiomeric excess (ee) values to previous reports, it showed high stability and could be recycled at least four times without noticeable decrease in catalytic and enantioselective activity, which was superior to other asymmetric catalytic systems. Thus the advancement of catalyst/IL/IL-support system is very desirable in asymmetric reactions.

Supported-mono-ILs systems, however, often can not offer effective catalytic activity. Wei's group⁵⁰ studied the reaction mechanism and found that the amount of catalytic active centres was insufficient in this kind of catalytic system. They thus synthesized SiO₂-bisILs with bis-imidazolium moieties and SiO₂-triILs with tri-imidazolium moieties in the IL fragments (Fig. 1b). The experimental results revealed that both SiO₂-bisIL[PF₆[–]]₂Pd⁰ and SiO₂-bisILs[PdEDTA]^{2–} achieved nearly 100% yield and selectivity in hydrogenation reactions of nitrobenzene (Scheme 4)⁵¹ and Suzuki cross-coupling reaction,²¹ respectively. Moreover, the

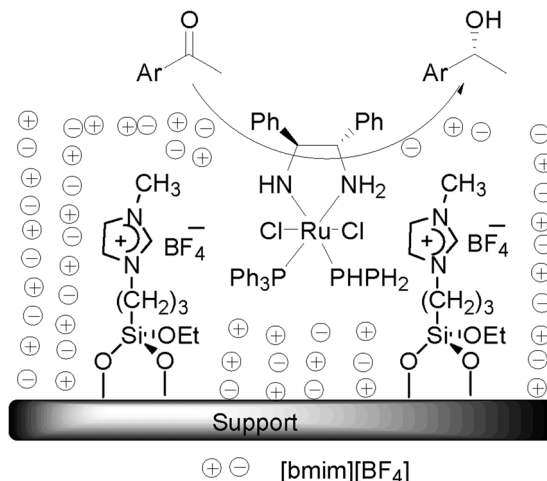
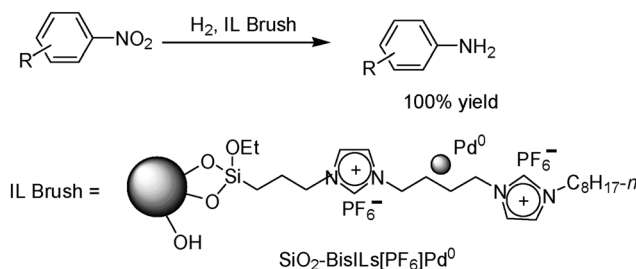


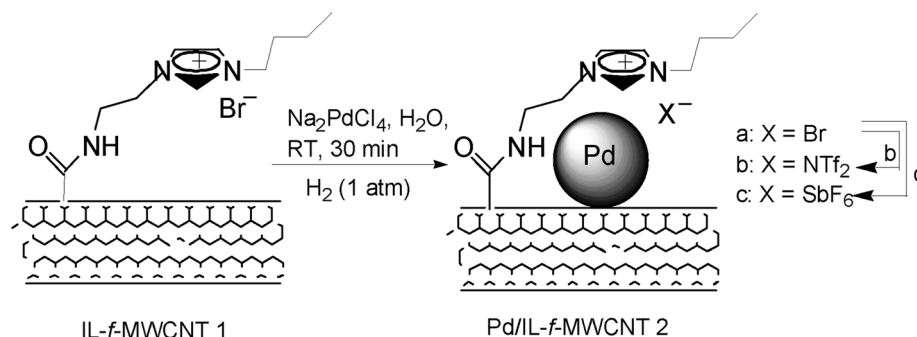
Fig. 2 Chiral [RuCl₂(PPh₃)₂(S,S-DPEN)], DPEN = 1,2-diphenylethylenediamine, solubilized in SILPs and used in the asymmetric hydrogenation of acetophenone.⁴⁹

catalysts of supported-multi-ILs could be recycled 10 times in the Suzuki reaction,²¹ which was much larger than free ILs and the catalytic systems of supported-mono-ILs. Obviously, compared with the traditional supported-mono-ILs, supported-multi-ILs have more prominent three-dimensional environment characteristics, and provide an increased number of active centres for catalysts, reactants and active species.

(2) *Effect of counteranions of SILs on catalytic properties.* Counteranions in SILs retain their facile exchange function, and can tailor the properties of SILs. Lee *et al.*⁵² studied the effect of a series of counteranions on catalytic activities in hydrogenation of *trans*-stilbene based Pd@IL-MWCNTs (multiwalled carbon nanotube) hybrids (Scheme 5). They found that Pd/IL-*f*-MWCNT with SbF₆[–] anion showed superior catalytic activity compared with hybrids having Br or Tf₂N[–] ((CF₃SO₂)₂N[–]) anions, and led to 50 times recycling with high catalytic activity. Moreover, the counteranion exchange can tailor the solubility of palladium NPs, and thus influence their dispersion and aggregation. Therefore, the catalytic activity, separation and recycling of catalysts can be adjusted based on the exchange of counteranions, which provides an ideal approach on the separation and reusability of catalysts. Similar results are also found in asymmetric catalytic reactions. The efficiency and enantioselectivity of chiral catalysts can be



Scheme 4 SiO₂-bisIL[PF₆[–]]₂-Pd⁰ in hydrogenation reactions of nitrobenzene.⁵¹

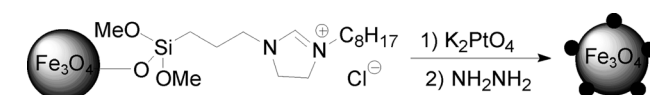


Scheme 5 Synthesis of palladium NPs supported on IL-MWCNTs with different counteranions.⁵²

tuned *via* exchange of counteranions. For example, aldol reaction in a catalytic system composed of SiO₂-immobilized imidazolium-PF₆/proline system affords aldol product only in 15% yield with 52% ee. However, upon simple exchange with BF₄ anion, for SiO₂-IL-BF₄/proline, the yield is increased to 51% with 64% ee.⁴⁶

3.1.2. Effect of supports in SILs on catalytic properties. It is well-known that various supports can form diverse interactions with ILs and catalytic species, and their BET surface area and pore morphology can provide different reservoirs for catalyst species, affecting the catalyst loading.²⁴ SILs possess combined advantages of ILs and supports, and using different supports to control catalytic properties is a further strategy for optimization. The leaching of rhodium from the IL/IL-SiO₂ system is a substantial problem. In 2008, Serp *et al.*²⁷ used MWCNT instead of SiO₂ as a support to prepare an [Rh]/IL/IL-MWCNT system. In the hydrogenation of 1-hexene, Rh/MWCNT-SIL (55% of IL w/w) could be reused five times without any loss of catalytic activity, showing more than twice the catalytic activity of Rh/SiO₂-SIL. The results reveal that the Rh/CNT-SIL catalytic system can offer higher stability and superior catalytic efficiency than the IL-SiO₂ system, with elimination of Rh leaching. This advantage is probably related to the very open structure of MWCNT aggregates that facilitates mass transport and improves the kinetics.

Using magnetic nanoparticles (MNPs) to support ILs *via* covalent bonds is an attractive strategy in the SIL area, and the resulting MNP-IL systems have been used to support transition-metal catalysts (*e.g.*, Pt, Pd and other metal NPs).^{29,53,54} Abu-Reziq *et al.*⁵⁵ reduced K₂PtO₄ to Pt NPs by NH₂NH₂, and deposited them on the MNP-ILs surface, preparing a novel MNP-IL-C₈-Pt hybrid catalyst (Scheme 6). It was found to be an excellent selective catalyst for the hydrogenation of alkynes and α,β -unsaturated aldehydes. With diphenylacetylene as substrate, this catalytic system could give 100% conversion, in which *cis*-stilbene selectivity reached up to 95% and *trans*-stilbene only 5%. In terms of recycling, the recycling process of magnetic MNP-IL-C₈-Pt catalyst was very simple. After each recycling run by applying an external magnetic field to attract the catalyst, the catalyst was washed twice with methanol, and it could be re-used for the next run after dissolving in the same solvent. Recycle times were up to four cycles without significant loss in activity or selectivity. Magnetic MNP-IL-Pd hybrid catalysts are also promising catalytic systems, and have successfully catalyzed Suzuki reactions^{56,57} and



Scheme 6 Supporting Pt NPs onto MNPs using IL as a surface modifier.⁵⁵

even one-pot dehydration/hydrogenation reactions of benzylic alcohols.⁵⁸ More importantly, after the MNP-IL-Pd catalyst is separated magnetically from the reaction mixture, it can be directly applied to catalyze other reactions, such as carbonylation of iodoarenes, Suzuki and Heck coupling reactions. This strategy can open up a significant method to recycle heavy metals in the area of reusing industrial effluent.

As discussed above, the strategy of dissolving transition-metal catalysts in supported imidazolium-based ILs is an effective approach for improving the properties of catalysts. The aggregation and leaching of catalysts and loss of activity, however, is still a problem in some cases. Hence, immobilizing catalysts to SILs *via* either covalently anchoring on cations or as counteranions are of importance, and have advantages over simply dissolving catalysts into SILs systems in improvement of the catalyst stability.

3.2. Catalysts as component moiety of SILs

Catalysts can be designed to be components of cation moieties or counteranions of SILs, obtaining “designer catalysts”.

3.2.1. Cations of SILs as catalysts. One case is that the cations of supported ionic liquid themselves are catalysts. This kind of typical SILCs mainly involves supported sulfonic acid-, salen and metal-free functionalized ILs. Generally, -SO₃H, or -SO₂Cl functionalized ILs are immobilized onto silica materials, ZrO₂, TiO₂ or Al₂O₃. They show good performance in many organic transformations, such as esterification, nitration of benzene, Michael reaction, one-pot multi-component synthesis, *etc.*^{59–62} For example, a novel SILC which consists of -SO₃H functionalized benzimidazolium-based IL is immobilized on a silica-based solid support. As an efficient heterogeneous catalyst for solventless synthesis of 1-amidoalkyl naphthols from 2-naphthol, amides and aldehydes, 95% yield is obtained. In comparison with other catalyst systems employed for this synthesis, supported benzimidazolium-based IL-SO₃H shows a much higher activity in terms of short reaction time and use of mild conditions. In addition, the catalyst is recovered and

reused five times giving good to excellent yields of the products.⁶¹ Recently, some hybrid magnetic NPs, including Fe₃O₄ anchored onto SiO₂ or silica-coated Fe₃O₄ NPs, have been fabricated and used as supports for Brønsted acidic ILs.^{30,31} This method offers practical convenience in catalyst separation and recycling as well as avoiding large amounts of acidic wastes.

Metal-free chiral organocatalysts, such as L-proline, pyrrolidine and urea (thiourea)-based compounds, are also attached onto the cations of SILs,⁶³ and are often used to catalyze asymmetric catalysis reactions.⁶⁴ Supported pyrrolidine-based chiral ILs were used fairly to catalyze Michael addition reaction of ketones with nitrostyrenes.⁶⁵ Along with ideal recycling, this catalyst with a chiral cation can lead to up to 94% yield with excellent enantioselectivities (up to >99% ee) and high diastereoselectivities (up to >99:1 dr) (Scheme 7). Recently, Huang *et al.*⁶⁶ immobilized lipase covalently on SILs. This strategy greatly promotes the enzymatic properties, including activity, thermal and storage stability and reusability.

It is well known that the chiral salen catalytic system plays an important role in asymmetric catalysis reactions.^{67,68} Up to now, chiral metal salen complexes of Cr, Mn and V as substituents have been appended to supported imidazolium cations. For example, SIL-(salen) Mn(III) compounds have been applied to catalyze asymmetric epoxidation of unfunctionalized olefins, as shown in Fig. 3. As well as showing comparable or even higher enantioselectivity than homogeneous counterparts, the most prominent of these catalysts are very stable and can be recycled five times without loss of activity, superior to the homogeneous systems.⁶⁹

3.2.2. Counteranions of SILs as catalysts. The other effective method to immobilize transition-metal catalysts is to transform them to anionic species to act as counteranions.⁷⁰ Friedel–Crafts alkylations of aromatic compounds are heavily polluting reactions due to stoichiometry of acidic chloroaluminates needed in reactions. How to avoid their leaching and overcome their contamination has been a critical topic from a green chemistry standpoint. One of the most effective methods is to immobilize chloroaluminates in different ratios containing [AlCl₄][−], [Al₂Cl₇][−], [Al₃Cl₁₀][−] on IL-modified solid inorganic materials, which is one of the earliest studied systems.¹¹ Based on these results, a series of similar SILCs containing Lewis acid

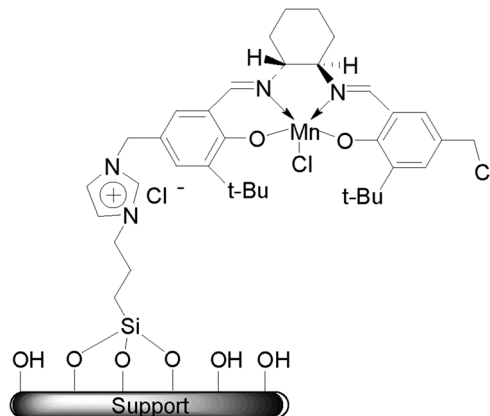


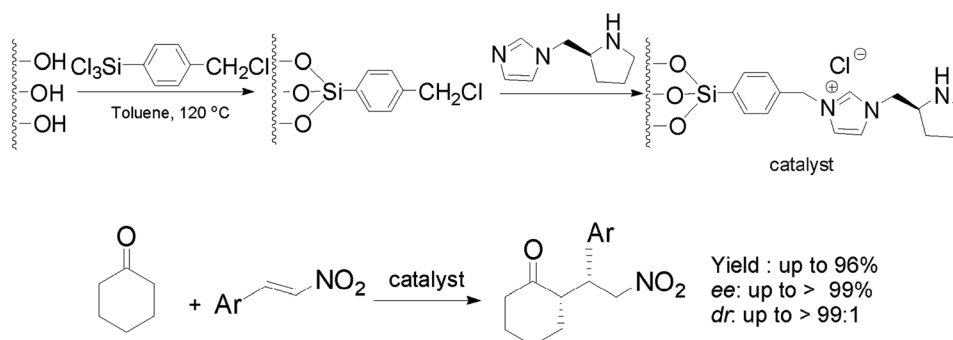
Fig. 3 Structure of SIL-(salen) Mn(III) compounds.⁶⁹

anions, [PdCl₄]^{2−}, [NiCl₄]^{2−}, [CuCl₄]^{2−}, [SnCl₅][−], [CoCl₄]^{2−}, [NiCl₄]^{2−}, are prepared *via* ion-exchange reaction of SiO₂–ILs.⁷⁰ They exhibit efficiently catalytic activity and reusability when evaluated in Friedel–Crafts reactions, Knoevenagel condensations, Kharasch addition reaction and Baeyer–Villiger reaction. This technique is very significant in terms of environmental factors.

Similarly, catalytic species [W₂O₃(O₂)₄]^{2−}, [α-PW₁₂O₄₀]^{3−}, [PMo₁₀V₂O₄₀]^{5−}, [RuO₄][−] and [PdEDTA]^{2−} often act as counteranions of SILCs.^{21,71–73} The side chains of imidazolium moieties grafted onto supports can provide hydrophobic microenvironments, and the anionic metal catalysts and reactants are entrapped in them, forming an essentially homogeneous catalytic system while retaining the advantages of a heterogeneous system. When selective oxidation of sulfide is catalyzed by peroxotungstate immobilized on IL-modified silica with aqueous hydrogen peroxide, the yield reaches up to 94.8%, and the catalyst can be reused six times.⁷¹

4. Applications of SILs in surface modification

In surface sciences, the wetting and lubricating behaviours are very important in both fundamental research and practical applications. Many cases need to be modulated by modifying



Scheme 7 Synthesis of supported pyrrolidine-based chiral IL and application in asymmetric Michael addition to nitrostyrenes.⁶⁵

agents according to the practical requirement. Unique properties of ILs, especially tunable property and facile linking with solids make them fascinating hydrophobic agents and lubricants.

4.1. Modulating the surface wettability of substrates

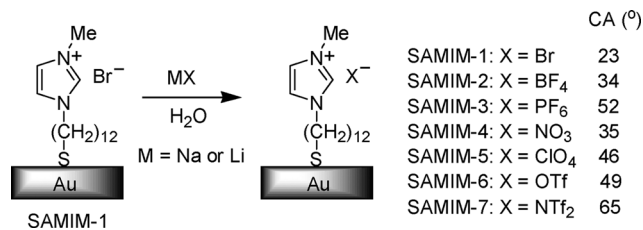
Wettability of a solid surface is an important property, which is governed by surface chemistry and morphology.^{74–76} ILs are found to have potential ability to be wettability controlling agents. First, it is well-known that surface tension (γ) of imidazolium-based ILs has the value between organic solvents (e.g., pentane: $\gamma = 16.0 \text{ N m}^{-1}$, dodecane: $\gamma = 25.6 \text{ N m}^{-1}$, at 20 °C) and water ($\gamma = 72.7 \text{ N m}^{-1}$ at 20 °C),^{77,78} and it decreases with an increase of the length of the side chain in the imidazolium moiety. Secondly, supported ILs can offer tunable properties towards substrates through exchange of cations or counteranions, and act as on-off agents to obtain reversibly switchable wettability. Thirdly, their unique stability towards acid, base and high temperature is superior to other hydrophobic materials, and can induce long-term durability. Therefore, ILs as one kind of novel hydrophobizing agents are highlighted.⁷⁹ Up to now, many hydrophobic IL films have been fabricated using self-assembly technique,^{16,80,81} layer-by-layer method,⁸² electrospinning,⁸³ and so on. Among them, the strategy of grafting ILs on substrates by covalent bonds can provide superior stable and durable films to be engineered.

4.1.1. Effect of counteranions of SILs on the wettability.

As smart modifying agents, ILs can tailor the wetting behaviour of substrates through the exchange of counteranions. In 2004, Choi's group¹⁶ modified SAMIMs on Au surfaces by submersing an Au sheet into a thiol-terminated IL solution for indicated times. To reveal the effect of anions on the surface wettability, they exchanged a series of counteranions through directly immersing the SAMIM-1 with Br^- in aqueous solutions containing the exchanging anion, including BF_4^- , PF_6^- , Tf_2N^- , $\text{CF}_3\text{SO}_2\text{O}^-$ (OTf^-), ClO_4^- and NO_3^- . As shown in Scheme 8, the SAMIM-1 with Br^- has a relatively hydrophilic property (water contact angle (CA) about $23 \pm 1^\circ$), whereas the SAMIM-7 with Tf_2N^- exhibits the highest CA with $65 \pm 1^\circ$. Other SAMIMs bearing different anions display intermediate CA values. The effect of counteranions on hydrophobicity of SAMIMs is in the following order: $\text{Tf}_2\text{N}^- > \text{PF}_6^- > \text{OTf}^- > \text{ClO}_4^- > \text{NO}_3^- > \text{BF}_4^- > \text{Br}^-$. Almost simultaneously, Itoh *et al.*⁸⁴ used this strategy to accomplish the phase-transfer of Au NPs, which simplified their separation and extraction. Further, the tuning of the wetting behaviour can adjust the aggregation state of gold NPs in water, and control the colour change of solutions, offering a smart optical sensor for anions.

Exchanging counteranions on SAMIM surfaces are one kind of potential approaches for manipulating surface wetting behavior, and has been applied to tune the behaviour of CNTs, GO, silica-based materials and magnetic iron oxide NPs in many areas,^{32,54,80} similarly to Au sheet and NPs.

CNTs are ideal materials in sensors. However, the poor solubility in a wide range of solvents hinders their widespread



Scheme 8 The process of the exchange of anions and the CA values of SAMIMs with different anions.¹⁶

applications. In order to improve their compatibility and create more opportunity for applications, chemical modification of CNTs has been studied with various materials. As excellent modifying agents, ILs not only highlight the unique physical properties of CNTs but also tune their wetting behaviour *via* exchanging the counteranions.³² Compared with other materials, ILs offer a simple and convenient approach in CNT purification and processability. The interest in modification of CNTs is driving a rapid increase to graphene-based materials. Anchoring ILs on GOs achieves their transfer into the organic phase by changing their properties from hydrophilic to hydrophobic, and improves their stabilization in water, DMF and DMSO due to tunable solubility and protecting function by the IL units.^{35,85} IL-modified CNTs and GOs extend their applications in materials science and electro-analytical chemistry.

Silica-based materials are widely used in many areas, as mentioned-above in Section 2, and their modification has been a hot issue in surface science for many years. As expected, ILs are ideal modifier agents.^{80,86} Following manipulating the wettability of Au, Choi *et al.*⁸⁰ adopted a similar method to control the wetting behaviour of Si/SiO₂ surface, and the results were rapidly extended to flat silicon substrates and glasses, which are widely applied in microfluidics, separation techniques and self-cleaning surfaces for solar energy equipment, cars and buildings.

Although the exchange of counteranions of ILs can tailor the values of CA, many studies find that the effect of anions on the wetting behaviour of ILs is determined by the size of counteranions in some cases,⁸⁰ and the imidazolium-based cations have superior ability relative to counteranions on tailoring surface wettability because they can alter their length and composition of the chain with more scope than anions.

4.1.2. Effect of cations of SILs on the wettability. Long-chain ILs are favourable hydrophobic materials,⁷⁷ while the inherently hydrophobic and oleophobic nature of fluorine can result in ILs having perfluoroalkyl chains possessing high hydrophobicity.^{87,88} To synthesize superhydrophobic IL monolayers, it is necessary to incorporate long chains in imidazolium-based ILs or use fluorinated ILs to decrease further the surface tension, combining with hierarchical architectures of substrates.^{74–76} In 2012, our group⁸⁹ prepared SAMs of long-chained substituent containing fluorinated alkyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium ions ($[\text{C}_n\text{Ftespim}]\text{X}^{80}$) on rough Al surfaces. It was found that the CAs of SAMs of $[\text{C}_n\text{Ftespim}]\text{X}$ increased with the

increase of the chain length of substituents, and could be tuned by the exchange of counteranions. Superhydrophobic SAMs of $[C_n\text{Ftespim}]X$ ($X = \text{PF}_6^-$ and TF_2N^-) with CAs above 160° were obtained at $n \geq 6$. Recently, we⁹⁰ prepared novel superhydrophobic $\text{ZnO}-[C_n\text{Ftespim}]X$ hybrid materials. ZnO particles were first deposited on a glass surface, and then $[C_n\text{Ftespim}]X$ was grafted *via* $-\text{Si}-\text{O}-$ covalent bonds, in which ZnO provided surface roughness while ILs acted as lower surface tension material. Wettability measurements revealed that CAs of $\text{ZnO}/[C_8\text{Ftespim}]I$ films were $140.7 \pm 2.0^\circ$. Exchange of counteranion from I^- to PF_6^- increased the CA up to $153.7 \pm 2.0^\circ$. The superhydrophobic $\text{ZnO}-[C_8\text{Ftespim}]X$ hybrid materials have two important properties. On the one hand, ZnO micro/nanostructures can impart their photoresponsive property to ZnO/IL films,⁹¹ and can induce them to possess UV-induced reversible wettability. On the other hand, the photo-induced stability of ILs renders them to be promising coatings of photocatalytic ZnO films,⁹² which can replace the degradable common coatings (*e.g.*, (fluoroalkyl)silane (FAS), $(\text{CH}_3\text{O})_3\text{SiC}_{18}\text{H}_{37}$ (ODS)). From the standpoint of stability and benign environment, ILs as coatings of ZnO or TiO_2 films are clearly significant. The synergistic action of ILs and ZnO NPs results in light/anion dual-stimuli-responsive superhydrophobic surfaces with high stability, and could be very significant in intelligent on-off and self-cleaning materials.

The reproducibility to obtain superhydrophobic SAMIMs is poor due to their low density on surfaces. Thus, in recent years, supported poly(ionic liquid)s have drawn attention to achieve high hydrophobicity, and are becoming increasingly studied.^{23,93–96} Vinyl-, vinylbenzyl- and allyl-substituted imidazolium-based ILs are grafted onto the solid surfaces through radical reactions. Generally, mercapto group is often used to modify silica as linker to tether PILs through surface radical chain-transfer addition. Elemental analysis reveals that the amount of imidazolium groups bonded to silica materials is very high, and the wettability of Si-vinyl-based IL bearing PF_6^- anion reaches 131° ,⁹³ which is higher than the CAs of SAMIM mentioned above. More importantly, the reproducibility of SPILs in wettability is better than that of SILs.

4.2. Modulating the lubricating property of substrates

The potential advantages of IL thin films, such as the stability to environment and high endurance, make them of potential use as lubrication oils, additives and thin films. Liu's group^{97,98} has investigated the tribological property of IL films. However, the ultrathin IL films formed on silicon surfaces by the way of weak physisorption freely migrate on the substrate surface,

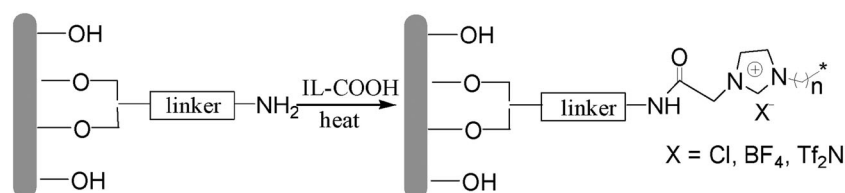
leading to rupture and poor durability. To reduce this limitation, it is necessary to link ILs with chemical bonds to the surface. Wang *et al.*⁹⁹ and Zhou *et al.*¹⁰⁰ adopted a two-step process to construct SIL films on engineered material surfaces. Firstly, amino-terminated compounds, including (3-aminopropyl)-triethoxysilane (APS), *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (DA) and dopamine, were employed as linkers to graft on a hydroxylated silicon surface, respectively. Then, imidazolium-based $\text{IL}-\text{COOH}$ was chemically anchored onto amino-terminated SAMs by heat treatment, forming ultrathin IL films, as shown schematically in Scheme 9. Additionally, mobile ILs were absorbed into the supported-IL layer, and the synergistic action between the bonded and mobile phases of ILs has the capability to further improve their tribological properties, anti-rupture performance and durability.

SPILs are also used as lubricants. Takahara¹⁰¹ anchored poly(1-(2-methacryloyloxy)ethyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide) (PMIS) and poly(*n*-hexyl methacrylate) (PHMA) brushes onto silicon wafers, and investigated their friction coefficient in dry nitrogen atmosphere, water, or 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIMTFSI). It was found that PMIS was superior to PHMA in the friction coefficient and friction cycles, in which the $-\text{COOH}$ group in PMIS played an important role.

As mentioned above, ILs supported in the substrates can modulate the surface properties, including the wetting and lubricating behaviours, and even antibacterial properties to protect surfaces.¹⁰² Indeed, SILs have been widely used in separation technologies as stationary phases.^{10,17}

5. Applications of SILs in separation technologies

As novel functional materials, ILs have been applied in analytical chemistry for more than two decades.^{17,103} The main advantages of employing ILs stem from their unique properties. First, the special interactions in ILs, including the intermolecular interactions among ILs molecules and the electrostatic interactions between the cation moieties and counteranions within ILs, induce analytes in mixtures to present different distribution coefficients and solubilities in ILs. Therefore, ILs have remarkable advantages to separate a wide variety of mixtures, such as metal NPs and ions, nonpolar and polar organic molecules, and even enantiomers from racemic mixtures. Secondly, the diverse and designable structures of ILs make the stationary phases smart, and alteration of counterions can tune



Scheme 9 SIL films in lubrication, in which APS, DA⁹⁹ and dopamine¹⁰⁰ act as linkers.

the selectivity according to the analytes' properties. Thirdly, the thermal stability and low volatility of ILs make them ideal candidates for separation technologies.

Initially, most imidazolium-based ILs stationary phases were prepared *via* coating IL layers on the support surfaces without chemical bonds.^{10,104} However, the driving of a mobile phase can disarrange IL films when they flow through physically adsorbed ionic liquid membranes, and then render them unstable. The concept of SILs linked covalently on stationary phase has propelled an advance of separation technologies.¹⁰⁵ Such SILs have been used in solid-phase extraction (SPE), liquid chromatography (LC), gas chromatography (GC) and capillary electrochromatography (CEC), gas capture and mass spectrometry.^{106,107}

5.1. Application of SILs in solid-phase extraction

Solid-phase extraction is a technique which uses solid sorbents to extract sample analytes from liquid mixtures. Since ILs were introduced onto commercial silica *via* chemical modification as extraction agents in SPE at the beginning of the 21st century,¹⁰⁸ a number of SILs, each possessing different functionalities, have been widely applied in SPE for the pre-concentration of organic compounds and trace heavy metals from waste water on the basis of economic criteria and possible toxicological concerns. It has been reported that Pb(II), Sc(III), sudan dyes, acids, amines, aldehydes and phenols have been extracted from aqueous matrixes.^{17,108} Furthermore, utilization of SILs has led to the isolation of biological matrices, such as the extraction of cryptotanshinone, tanshinone I and tanshinone IIA from *Salvia Miltiorrhiza* Bunge, the separation of oxymatrine from *Sophora flavescens* Ait as well as the competitive adsorption of matrine from oxymatrine.¹⁰⁹ Aside from the higher extraction efficiencies obtained compared to conventional sorbents, higher recovery is shown than that in traditional silica cartridges.¹¹⁰

In extraction, one is concerned with the extraction efficiencies, which is mainly determined by the compositions of SILMs. It is observed that the stationary phase surface coverage with ILs is low and the selectivity and sensitivity of SILs is not sufficiently high.¹¹¹ SPILs have thus been introduced and have been systematically investigated in SPE and solid-phase micro-extraction (SPME). Anderson's group^{112–114} coated a series of polymeric ionic liquids on silica supports as selective SPME sorbent coatings, and successfully achieved the analysis of alcohols, aldehydes, esters, alkyl halides and aromatics as well as the separation of genotoxic impurities from aqueous solutions, and even the selective extraction of CO₂. Similarly, Feng *et al.*^{115–117} and Pang *et al.*¹¹⁸ used SPILs as sorbent materials to coat stainless steel fibers for the separation of organic compounds. Compared with supported-ILs containing the same anions, SPIL-based sorbents exhibit high extraction efficiency due to the high coating density and uniformity of films. In addition, the effect of counteranions was studied. Feng's group¹¹⁶ fabricated a PIL-based SPME sorbent composed of PF₆ anion and an analogous PIL containing naphthalene sulfonate anion. They applied them for the extraction of PAHs

in hair spray and nail polish. The sensitivity of the novel aromatic functionalized PIL was superior to PIL-PF₆. In addition, PIL containing both polymerizable cation and anion, namely, [VC₈IM] *p*-styrenesulfonate is also tethered through covalent linkages to a stainless steel substrate for the analysis of anilines, phenols and phthalate esters in water samples.¹¹⁷ This kind of double-confined PIL sorbent coating offers better resistance to high ionic strength aqueous samples compared to a PIL containing no polymerizable anions.

The other focus in SPE is the collection of the sorbents after adsorbing analytes. Following IL-modified silica, carbon nanotubes and steel substrates, IL-modified MNPs are shown to be favorable extraction sorbents, in which facile separation and efficient extraction capability have attracted great attention. Fe₃O₄ NPs and SiO₂@Fe₃O₄ microspheres coated with ILs by covalent immobilization have been used in SPE, and successfully achieved the extraction of organic compounds and metal NPs (*e.g.*, extracting polycyclic aromatic hydrocarbons (PAHs) and chlorophenols from water samples).^{119,120} Under the optimal conditions, high recoveries (70.3–88.8%) are achieved with satisfactory relative standard deviations of less than 6.0%.

With the rapid development of biphasic IL-supercritical fluid continuous flow systems, the combination of SILPs with supercritical CO₂ has led to highly attractive fixed-bed flow systems.^{4,44,121} This technique achieves not only continuous catalytic reactions but also extraction, in which supported ILs act as reactors and the stationary phase (fixed-bed) while supercritical fluids are the mobile phase. This technique can avoid IL dispersing, accelerate the mass transfer in ILs, while providing good catalyst performance and the facile separation of products.

5.2. Applications of SILs in chromatographic separation techniques

For several decades, chromatographic techniques, such as LC, GC and CEC, have become the most popular methods for the separation and identification of analytes in complex samples according to their different migration rate.¹²²

Since 2004, Liu and co-workers¹²³ covalently anchored ILs onto LC chromatographic columns as stationary phases, and successfully separated ephedrine mixture with methanol/water mobile phases, utilization of IL-modified LC stationary phases has been a hot research topic and contributed to the rapid evolution of LCs. Until now, various IL-modified columns have been prepared *via* covalently tethering different imidazolium-based ILs onto the pre-activated stationary phase, and have achieved the effective separation of anions, hydrophobic compounds and small polar molecules in multi-mode chromatography techniques, including ion-exchange, reversed-phase, and hydrophilic interaction liquid chromatographies.^{124–126}

The drastic achievements of SILs in chromatography have been highlighted in a number of recent review articles.^{122,127,128} In 2012, Afonso *et al.*¹²⁹ summarized IL-modified silica stationary phases in high performance liquid chromatography (HPLC),

including their preparation and physicochemical characterization, chromatographic behavior, and analytical performance.

Similar to in SPE, SPILs have been engaged in LC stationary phases in recent years. SPILs present multiple interactions including hydrophobic, π - π , and ion-dipole interactions with different components, in which one can obtain a special selectivity and sensitivity superior to a commercially available monomeric octadecylated silica column in multi-mode stationary phase (Fig. 4).¹³⁰ For example, Qiu *et al.*¹²⁶ used 1-allyl-3-butylimidazolium bromide to modify mercaptopropyl-functionalized silica through surface radical chain-transfer addition. The obtained IL-modified silica could be used as a stationary phase in reversed-phase LC, and separated a mixture of PAHs containing positional isomers using methanol (60%, v/v) as mobile phase.

As a continuation of their work, Qiu's group^{131–133} studied the effect of counteranions on the separation ability of SILs. 1-Vinyl-3-octadecylimidazolium bromide was polymerized on porous silica particles, forming Sil-PImC₁₈-Br, and exchanged counteranions by using methyl orange (MO), with Sil-PImC₁₈-MO being obtained. It was found that Sil-PImC₁₈-MO as the stationary phase offered higher shape selectivity for constrained isomers of PAHs than Sil-PImC₁₈-Br both in reversed- and normal-phase HPLC. Obviously, methyl orange dye with large size and π - π interaction as counteranion plays an important role in high selectivity. The reason is that the interposition of MO molecules results in a highly oriented arrangement between the octadecyl imidazolium chains and the rigid segment of MO, as shown in Fig. 5. The π - π interactions among aromatic ring of MO, PAHs and imidazolium moieties can modulate different distribution coefficients to different components, whereas Br⁻ does not show this capability.

Based on these studies, Qiu's group^{134,135} introduced polymerizable ionic liquid pairs to LC. Both polycation and polyanion are copolymerized on silica to prepare multifunctional hybrid materials in hydrophobic and hydrophilic interaction chromatographies. This strategy enhances further the selectivity and stability of HPLC.

Anion exchangeable technique is another important chromatographic mode. As expected, the immobilization of ILs on the stationary phase can transfer their facile exchange of anions to SILs, and form promising anion exchangeable layered materials to provide anion exchangeable sites. The experimental results demonstrate that imidazolium salts 1-butyl (or 1-octyl)-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride grafted onto layered octosilicate exhibit a high capacity for sorption of sulfasalazine, and the release behavior of the accommodated

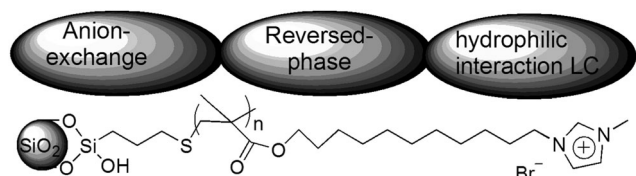


Fig. 4 Poly(ionic liquid)-grafted silica in multi-mode stationary phase.¹³⁰

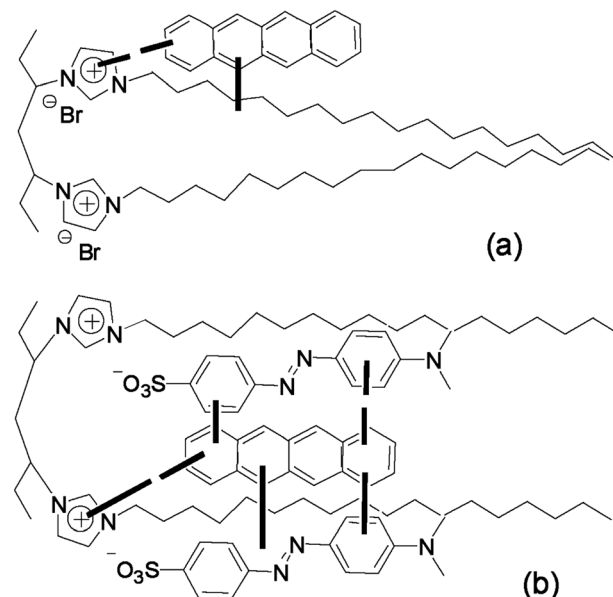


Fig. 5 The effect of MO on the oriented arrangement of octadecylimidazolium chain and the interaction among them, (a) Sil-PlmC₁₈-Br, (b) Sil-PlmC₁₈-MO.¹³²

sulfasalazine is largely dependent on the pH values, which is potentially applicable to drug delivery systems.¹³⁶ More interestingly, Gushikem *et al.*¹³⁷ successfully used this technique to obtain gold NPs. They first grafted imidazolium-based IL with Cl[−] anion on the surface of SBA-15 mesoporous silica, and then exchanged with AuCl₄[−] *via* anion exchange. Subsequently, solids containing AuCl₄[−] ions were submitted to a chemical reduction process with NaBH₄, converting the anionic gold species into supported gold NPs. Obviously, ion-exchange property of SILs creates a new pathway for various practical applications.

GC is one of the most popular techniques to separate volatile and semivolatile analytes in complex samples. ILs are thermally stable at high temperatures, provide high-efficiency separations, and form multiple interactions with molecules. Therefore, imidazolium-based IL membranes are ideal GC stationary phases.¹³⁸ Generally, ILs are often coated physically on GC columns. However, the non-uniform film thickness on the wall of the capillary at high temperatures has limited their use. As early as 2005, Anderson *et al.*¹³⁹ cross-linked a class of ionic liquid monomers by free-radical reactions to provide a more durable and robust stationary phase which was able to endure high temperatures. Subsequently, the potential of ILs covalently bound in capillary inner wall of the GC is further demonstrated, and some covalent-linked SILs and SPILs are used as stationary phases.¹⁴⁰ However, the inner diameter of capillary columns of GC is so small that the development of the surface-bonded IL stationary phases in GC is slower than that in LC.

As an inevitable development results, IL-bonded silica hybrid monolithic columns can be employed as stationary phase in CEC, which uses an electric field to separate mixtures.

The first attempt was done by Qin's group, who covalently bonded propylmethylimidazolium chloride to a silica capillary in 2002.¹⁴¹ They found that the high conductivity and tunable miscibility of ILs reduced interaction between analytes and many mixtures as well as the capillary wall. Subsequently, positively charged pharmaceutical molecules, DNA fragments, alkyl phosphonic acids, esters and metallic cations have been successfully separated.^{142–145} Compared with an analogous column without IL modification, the electro-osmotic flow (EOF) reversal, better separation efficiency and improved peak shapes are observed for the IL-bonded column.¹⁴⁶

5.3. Applications of SILs in gas separation and capture

Gases (*e.g.*, CO₂, SO₂, and other gases) capture and removal from power plants are critical issues in both industry and academia from the viewpoint of economic development and environmental protection. Among them, CO₂ is a greenhouse gas, and its separation, capture and storage are very important concerning worldwide sustainable development. In recent years, SILMs have been found to be ideal capturing agents of gases due to their high selectivity, negligible vapour pressures, high thermal stabilities and tunable properties.^{104,147,148} A number of investigations have shown that supported “task-specific” ionic liquids, including amino acid-based ILs and phenol-based ILs which have been popular adsorbents and absorbents for CO₂, and the selectivity for CO₂/N₂ and CO₂/CH₄ separations is higher than that of other absorbents. Until now, the achievements in CO₂ capture by SILMs have been summarized in many reviews.^{149,150} Similar to other separation technologies, SILMs through physisorption have some inherent limitations, facile disarrangement, non-uniformity, poor reusability and so on. Therefore, using covalent bonds to link ILs and adsorbents is of potential importance. In this area of study, how to enhance CO₂ absorption capacity, reduce CO₂ absorption enthalpy, and improve CO₂ absorption kinetics are crucial issues. Romanos *et al.*¹⁵¹ proposed an advanced strategy to combine the separation with creation of CO₂ from CO₂–CO mixture with high efficiency. They firstly anchored 1-(silylpropyl)-3-methylimidazolium hexafluorophosphate onto siliceous supports and then dispersed ultrasmall (2–3 nm) and well-stabilized Au NPs onto the SILP acting as a heterogeneous catalyst. CO₂/CO separation values above 50 were obtained in cases where liquid crystalline ordering of the IL layers and extended pore blocking had occurred. The SILPs–Au NPs hybrids captured CO₂ while oxidizing CO to CO₂ *in situ*.

Hence bonded ILs on solid-phase supports have propelled the development of separation technologies. However, the choice of suitable SILs with high selectivity to a variety of mixtures has been a big challenge because different mixtures present different selectivity in SILs.

6. Applications of SILs in electrochemistry

ILs have been used in electroanalytical chemistry since 2000.¹⁵² Owing to their high ionic property and wide electrochemical

potential window, ILs have ability to provide a remarkably increased electron transfer rate at interfaces, cause significantly decrease in the over-potential, and thus enhance the electrochemical responses in detection. Up to now, ILs have been utilized in both electrodes and electrolyte gels.^{6,153}

Using ILs to modify electrodes is a promising strategy. Because their widespread solubility in solutions can drive IL components to easily diffuse into electrolyte in the case of physically mixing to electrodes, the ideal approach is to append ILs on electrodes *via* covalent bonds. As shown in Fig. 6, some forms of IL-modified electrodes are described.¹⁵³ Imidazolium-based ILs have been used to modify a series of electrodes, such as Au, different forms of carbon, and boron-doped diamond electrodes.^{153,154} Both cations and counteranions have an influence on the properties of electrodes, and several examples are described below.

The main performance of binding ILs is to improve the conductivity of electrodes. Au-based electrodes are widely used in electroanalytical chemistry. In 2010, Chi and co-workers¹⁵⁵ attached ILs on Au electrode *via* Au–S bonds. The introduction of ILs enhanced the hydrophobicity and conductive properties of Au. At the Au–IL electrode|water interface the electrochemiluminescence (ECL) intensity of the luminol–O₂ system was much larger and more stable than that at Au|water interface, resulting in a sensitive and stable ECL response. This could be a promising strategy to construct O₂-related biosensors.

Another important performance of SILs on electrodes is to induce the deposition of noble-metal NPs to electrodes. The strategy of coating noble-metal NPs on electrodes is a common tool in many applications ranging from advanced sensors to highly efficient fuel cells, which increase the efficiency, specificity and selectivity of electrodes. However, there are usually insufficient binding sites for anchoring the precursors of metal ions or metal NPs on common electrodes, which leads to poor dispersion. Therefore, surface functionalization of electrode is necessary.

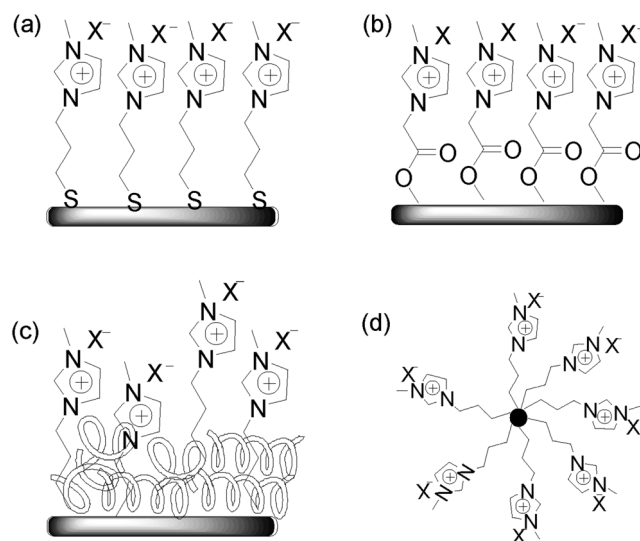


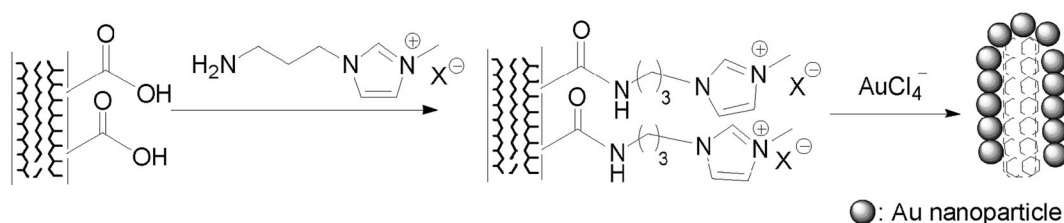
Fig. 6 Schematic depiction of electrodes or electrode materials prepared from appended IL.¹⁵³

CNT–Au hybrid NPs are well studied and established electrodes. During the preparation procedure of CNT/Au from CNTs, common methods which deposit Au NPs on CNT surfaces involve tedious assembly processes and multi-step reactions, and often load low density of NPs so limiting many practical applications. Ionic liquids, as stabilizers of metal NPs, can offer more binding sites for the precursors of metal ions. Niu's group¹⁵⁶ grafted IL–NH₂ to MWCNT surfaces to create more opportunity to capture AuCl₄[−], and obtained MWCNT–IL–gold NP hybrid materials (Scheme 10). This kind of electrode can increase the electrocatalytic activity of MWCNT toward reduction of oxygen. This good property may result from two factors. First, the average diameter of gold NPs is about 3.3 nm in the hybrid of MWCNT–IL–Au, which is much smaller than that in the MWCNT–thionine–Au hybrid, and the distribution is also quite uniform. As known, the electrocatalytic property of gold NPs is size-dependent, and the smaller size will lead to higher activity.¹⁵⁷ Secondly, the presence of ILs also plays a significant role in the good electrocatalysis of MWCNT–IL–Au hybrid because the high conductivity of ILs facilitates electron transfer for oxygen reduction. With the developments of SILs, SPILs are also used to modify electrodes, similar to other areas. As an example of vinyl-substituted imidazolium-based ILs, the grafting of 1-vinyl-3-ethylimidazolium tetrafluoroborate onto the CNT surface can form CNT–PIL hybrids.¹⁵⁸ This kind of SPILs can introduce a large number of surface functional groups on the CNTs, and has been used to capture a variety of precursors of metal ions, such as [PtCl₆]^{2−} and RuCl₃. Finally, a uniform PtRu or Pt NP layer grows on the CNTs–PIL surface with ethylene glycol as reductant. The PtRu or Pt/CNTs–PIL catalyst offers a higher electrochemical surface area and

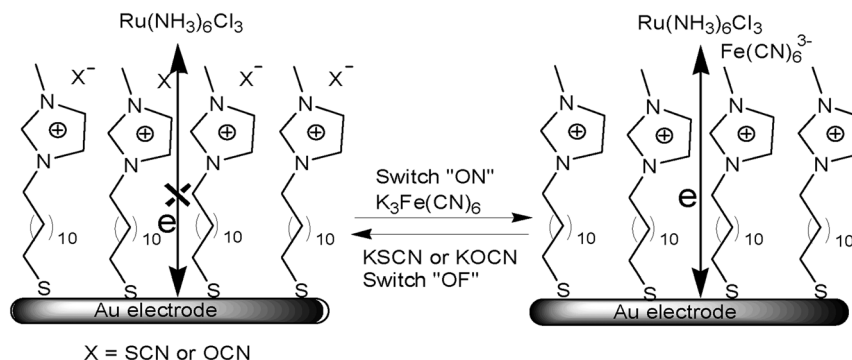
better performance for methanol electrooxidation than PtRu/CNTs (or Pt/CNTs) catalyst.

Anchoring ILs onto electrodes *via* covalent bonds can offer another important function. The tunable property of SILs *via* exchanging counteranions can be transferred to electrodes, and presents great advantages over other electrodes in selective electron-transfer toward redox-probe molecules. For instance, electrodes containing IL–SWCNTs (single-walled carbon nanotubes) can display unusual tunable wettability and charge-transfer activity, which has opened up a novel kind of electrodes. Lee *et al.*^{14,159} exchanged counteranions between Fe(CN)₆^{3−} and other anions on SILs, and found that electron-transfer occurred in the presence of Fe(CN)₆^{3−} (anionic redox-probe molecule) but did not occur in the presence of Ru(NH₃)₆³⁺ (cationic redox-probe molecule). The SAMIM having Fe(CN)₆^{3−} as an anion showed electron transfer toward Ru(NH₃)₆³⁺, and the Ru^{3+/2+} redox-switchable SAM was generated by reversible anion exchange between Fe(CN)₆^{3−} and SCN[−] (or OCN[−]) (Scheme 11).

Besides modifying electrodes, SILs are becoming important components of electrolytes. To improve both thermal and mechanical properties of electrolytes modified by ILs, it is necessary to alter ILs to gel states through polymerization or grafting onto inorganic nanoparticles.^{86,160} They not only maintain most of the attractive features of the untethered ILs but also exhibit substantially improved conductive and mechanical properties of electrolytes. For example, anchoring 1-trimethoxysilyl-C₁₁–3-butyliimidazolium–Tf₂N on ZrO₂ nanostructures can lead to solventless electrolytes.¹⁶⁰ These hybrid fluids exhibit exceptional redox stability windows, excellent thermal stability, good lithium transference numbers, and long-term interfacial stability in the presence of a lithium anode. These materials offer exciting



Scheme 10 Illustration of the procedure for preparing MWCNT–IL–Au hybrids.¹⁵⁶



Scheme 11 Anion-directed Ru^{3+/2+} redox-switchable surfaces.¹⁵⁹

opportunities for applications in electrochemical storage and conversion devices.

7. Conclusions and outlook

In this critical review, we have given an overview of the recent achievements and applications of SILs, and presented a systematic and full discrimination of this class of ILs against free ILs and other supported IL systems through physisorption. Immobilizing ILs on solid supports have derived many novel functions, forming a variety of functional materials. Until now, SILs have been involved in all fields where ILs can be used. They bring great prospects in catalytic reactions, surface science, separation techniques and electrochemistry.

SILs have significantly increased in recent years, and the designability of ILs and supports offers fascinating opportunity for novel functional materials. Nowadays, MNPs-SILs and SPILs present significant developments. Magnetic NPs-supported ILs combine the advantages of MNPs with ILs, simplifying the recycling handling as well as improving efficiency. Meanwhile, the high loading density and uniformity of SPILs can optimize the qualities of films, and can be applied in more widespread fields.

Compared with the achievements in catalytic reactions and separation technologies, applications of SILs in surface science are still at a preliminary stage. In the wake of new developments in the wettability of solids, smart surfaces that are reversibly switched between superhydrophobicity and superhydrophilicity *via* external stimuli have aroused great interest. Grafting ILs onto M_xO_y (*e.g.*, TiO_2 , ZnO , WO_3 , V_2O_5 , SnO_2 , *etc.*) with photoresponsive property through covalent bonds can construct dual-stimuli-responsive superhydrophobic surfaces with reversible switching by both anion exchange of ILs and photo-induction of M_xO_y . Moreover, the photocatalytic stability of imidazolium-based ILs can mend the photocatalytic degradation of common coatings (FAS, ODS, *etc.*) of M_xO_y films with photocatalytic property. We believe that ILs-modified stimuli-responsive superhydrophobic films will have many innovative uses.

Abbreviations

SIL	Supported ionic liquid
IL	Ionic liquid
RTIL	Room-temperature ionic liquid
SILP	Supported ionic liquids phase
SILC	Supported ionic liquid catalyst
SILM	Supported ionic liquid membrane
SAMIM	Self-assembled monolayers of imidazolium ion
PIL	Poly(ionic liquid)
SPIL	Supported poly(ionic liquid)
[PVBIm]PF ₆	[1-(4-Vinylbenzyl)-3-butylimidazolium hexafluorophosphate]
ATRP	Atom transfer radical polymerization
CNT	Carbon nanotube
NP	Nanoparticle

GO	Graphene oxide
TOF	Turn over frequency
ee	Enantiomeric excess
MWCNT	Multiwalled carbon nanotube
DPEN	1,2-Diphenylethylenediamine
Tf ₂ N	(CF ₃ SO ₂) ₂ N
MNP	Magnetic nanoparticle
OTf	CF ₃ SO ₂ O
CA	Water contact angle
FAS	(Fluoroalkyl)silane
ODS	(CH ₃ O) ₃ SiC ₁₈ H ₃₇
APS	(3-Aminopropyl)triethoxysilane
DA	N-[3-(Trimethoxysilyl)propyl]ethylenediamine
PMIS	Poly(1-(2-methacryloyloxy)ethyl-3-butylimidazolium-bis(trifluoromethanesulfonyl)imide)
PHMA	Poly(<i>n</i> -hexyl methacrylate)
EMImTFSI	1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
SPE	Solid-phase extraction
LC	Liquid chromatography
GC	Gas chromatography
CEC	Capillary electrochromatography
PAH	Polycyclic aromatic hydrocarbon
HPLC	High-performance liquid chromatography
SPME	Solid-phase microextraction
MO	Methyl orange
ECL	Electrochemiluminescence
SWCNT	Single-walled carbon nanotube

Acknowledgements

This work was financially supported by the NSFC (Grant No. 21033005 & 21273134) and the NSF of Shandong Province (Grant No. ZR2013EML003).

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