Functionalized imidazolium salts for task-specific ionic liquids and their applications

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Recent developments in task specifically functionalized imidazolium salts, which can be used for specific tasks ranging from catalysts recycling, supports for organic synthesis, catalysis, separation of specific metal ions from aqueous solution, and construction of nanostructures and ion conductive materials, have been reviewed.

Introduction

Since the first report on water-stable imidazolium cation-based ionic liquids, ethylmethylimidazolium tetrafluoroborate ([emim][BF_4]), by Wilkes and Zaworotko in 1992,[1] various 1,3-dialkylimidazolium salts containing a wide variety of anions such as PF_6^-, $(CF_3SO_2)_2N^-$, $CF_3SO_3^-$, CF_3COO^-, CH_3COO^- *etc.* have been synthesized, that are currently receiving a great deal of attention as novel media in organic synthesis, catalysis, and in preparation of nanostructured materials.[2] Due to their negligible vapor pressure and non-flammable nature, they are regarded as eco-friendly alternatives to volatile organic media. Moreover, their properties such as hydrophilicity/hydrophobicity and miscibility with organic solvents or water can be varied by changing the *N*-alkyl substituents and/or anion. Thus, these tailor-made materials can be designed to have specific properties. Pioneering works by Wilkes on chloroaluminate ionic liquids consisting of mixtures of 1,3-dialkylimidazolium chloride and aluminium chloride demonstrated that the ionic liquids could act both as solvent and catalyst for Friedel–Crafts reactions.[3] Recently, many attempts have been made to explore functional ionic liquids through incorporation of additional functional groups as a part of the cation and/or anion. The incorporation of functional groups can impart a particular capability to the ionic liquids, enhancing their capacity for catalyst reusability as exemplified with imidazolium salt-functionalized phosphine–metal complexes, which showed dramatically increased reusability and stability in ionic liquids compared with the unfunctionalized ones (see later). Moreover, specific functional groups can also be incorporated for task-specific purposes. For example, a primary amine functionalized imidazolium salt can separate CO_2 from gas streams,[4] while ionic liquids bearing appended sulfonic acid groups were used as solvent-catalyst for esterifications.[5] During the last five years, various types of functionalized ionic liquids expressly categorized as being "task-specific" ionic liquids (TSILs) have been designed and synthesized for specific purposes such as catalysis, organic synthesis, separation of specific materials as well as for the construction of nanostructure materials and ion conductive materials *etc.*[6] Many of them were focused on the incorporation of functionality into a branch appended to the cation, especially imidazolium cation (Fig. 1). In this article, recent development of these functionalized imidazolium salts for TSIL and other novel materials will be reviewed with special attention on new structures, properties and applications. The imidazolium salts are defined as TSILs when they are the following: (i) ionic liquids in which a functional group is covalently tethered to the cation or anion (or both) of the imidazolium salts, which behave not only as a reaction medium but also as a reagent or catalyst. (ii) A conventional ionic liquid solution of a functionalized imidazolium salt, which is not a liquid form at ambient temperature, could also be defined as a TSIL since the functionalized imidazolium salt become integral elements of the overall ionic liquid solution

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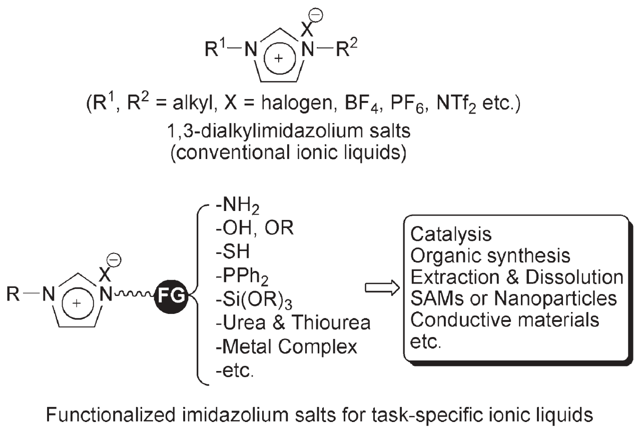


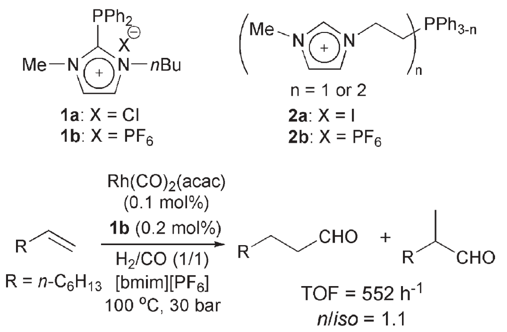
Fig. 1 Imidazolium salts for conventional ionic liquids and functionalized imidazolium salts for task-specific ionic liquids.

and can introduce a functional group into the liquid. The functionalized imidazolium salts, which are designed for specific purposes and can be used as a precursor for specific materials such as self-assembled monolayers and nanoparticles are also included in this article.

Task-specific ionic liquids for catalysis

To facilitate the separation and subsequent reuse of catalysts, methods for immobilizing homogeneous catalysts have been pursued for decades. One of the promising approaches is the use of two-phase systems, in which the phase of preference of the catalyst differs from that of the substrate, allowing facilitation of catalyst recovery from products by phase-separation. In this context, the use of ionic liquids to immobilize homogeneous catalysts has been one of the most fruitful areas of ionic liquids research to date. In many cases, the catalysts can easily be immobilized in ionic liquids, and thus, separated by simple phase separation and recycled. In spite of their high potential as vehicles for catalyst immobilization, these systems still have a tendency to leach dissolved catalyst into the co-solvent used to extract the product of the reaction from the ionic liquid. To overcome or reduce the catalyst leaching, the imidazolium salt motif was incorporated into the ligand, catalyst-precursor or support materials, resulting in enhancement of the catalyst reusability as well as in some cases, activity in conventional ionic liquids.

Hydroformylation. Hydroformylation of alkenes is an important process for the manufacture of alkanals. Many efforts have been devoted for aqueous biphasic system using water-soluble rhodium complexes such as the sodium salt of trisulfonated triphenylphosphine (tppts). However, due to the low solubility of the long chain olefins in water, the aqueous biphasic system is limited to shorter than C_5 olefins. Since the first application of ionic liquids by Parshall in 1972,[7] various ionic liquid biphasic catalytic systems have been employed to circumvent problems arising from the aqueous biphasic catalytic systems.[2f] However, immobilization of neutral catalysts such as $Rh(CO)_2(acac)(PPh_3)$ were not successful,[8] and leaching of the catalysts into the organic phase occurred. To avoid the leaching problem, several different types of cationic phosphine ligands (cobaltcenium, guanidinium or pyridinium *etc.*) have been developed.[9] Wasserscheid and co-workers specially designed the phosphine-functionalized imidazolium salts **1** or **2** for Rh-catalyzed hydroformylation of olefins in ionic liquid biphasic systems.[10] Dissolution of the metal complex of the ionic ligands into a conventional ionic liquid gives rise to a task-specific ionic liquid since the metal complex ion becomes an integral part of the ionic medium, and remained there when the reaction products are extracted into a co-solvent. The imidazolium phosphines **1** and **2** (Scheme 1) could be synthesized starting from commercially available ionic liquids, 1-*n*-butyl-3-methylimidazolium (bmim) salts and 1-vinylimidazole,[11] respectively. The phosphine-functionalized imidazolium salts showed a pronounced solubility in ionic liquids. For example, the solubility of **2b** in an ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]), was as high as 310 g kg^{-1} at 45 °C. In Rh-catalyzed hydroformylation of oct-1-ene in [bmim][PF$_6$] biphasic system, the ligand **1b** showed higher activity (TOF = 552 h^{-1}) in comparison with **2b** (n = 2) (TOF = 32 h^{-1}), but no selectivity (n/iso = 1.1). The ligands **1b** and **2b** may coordinate with metal in different manners, *i.e.* the ligand **1b** could possibly chelate as monodentate whereas **2b** acts in a P-carbene bidentate manner. These task-specific Rh-catalysts were immobilized effectively in an ionic liquid, and can be recycled several times without significant leaching of Rh to the organic phase.



Scheme 1

Cole-Hamilton and co-workers synthesized anion functionalized imidazolium salts **3** and **4** (Fig. 2), and used them together with $Rh_2(OAc)_4$ as the catalyst precursor for biphasic hydroformylation of non-1-ene or oct-1-ene in [bmim][PF$_6$]/scCO$_2$ in a continuous flow process.[12] Although the selectivities (n/iso = 3.8) were not high, the catalyses proceeded at a constant rate for >20 h, in which the substrate, gases and products were transported in and out of the reactor dissolved

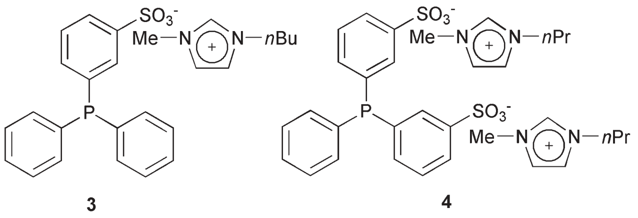


Fig. 2

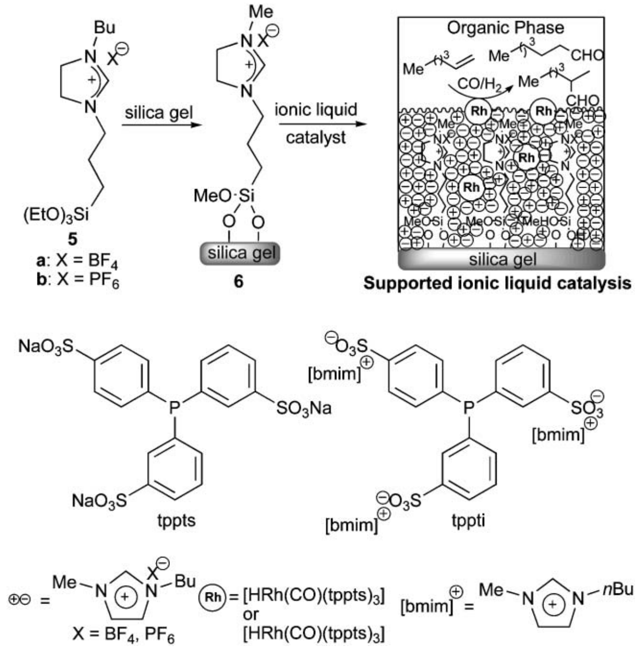


Fig. 3

in $scCO_2$. Moreover, analysis of the recovered products revealed that <1 ppm Rh was leached into the organic phase.

Another interesting recent development is the rhodium-catalyzed supported ionic liquid hydroformylation of hex-1-ene reported by Mehnert *et al.*[13] The task-specifically designed alkoxysilyl-functionalized 4,5-dehydroimidazolium salts **5a,b** were grafted onto the silica gel to give the corresponding the surface-modified silica gels **6a** and **6b**, which upon treatment with additional conventional ionic liquid resulted in the formation of a multiple layer of free ionic liquid on the support. These layers serve as the supported ionic liquid phase in which the homogeneous catalyst was dissolved (Fig. 3). In Rh-catalyzed hydroformylation of hex-1-ene, as shown in Table 1, the supported-ionic liquid phase catalytic system exhibited a slightly enhanced activity (TOF = 65 min^{-1}, entry 1) with comparable selectivity to the biphasic ionic liquid system (TOF = 23 min^{-1}, entry 4). The improved activity might be attributed to a higher concentration of the active rhodium species at the interface in comparison to the biphasic system. However, both the supported and the biphasic ionic liquid systems showed lower catalytic activity compared to the homogeneous system (TOF of 400 min^{-1}, entry 6), and also exhibited similar rhodium leaching behavior (2.1% from [bmim][BF_4], 0.07% from [bmim][PF_6]), which may be largely due to solubility of ionic liquids in the organic phase. The loss of rhodium could be suppressed through keeping the aldehyde concentration below 50 wt% and an increase of the phosphine ligand concentration.

Table 1 Rh-Catalyzed hydroformylation of 1-hexene using supported ionic liquid phases, biphasic and homogenous catalysis

Entry	Condition	Solvent	*t*/min	Yield (%)	n/iso	TOF/min^{-1}
1	Silica/tppti	[bmim][BF_4]	300	33	2.4	65
2	Silica/tppts	[bmim][BF_4]	240	40	2.4	56
3	Silica/tppti	[bmim][PF_6]	270	46	2.4	60
4	Biphasic/tppti	[bmim][BF_4]	230	58	2.2	23
5	Biphasic/tppti	[bmim][PF_6]	180	70	2.5	22
6	Homog./PPh_3	Toluene	120	95	2.6	400

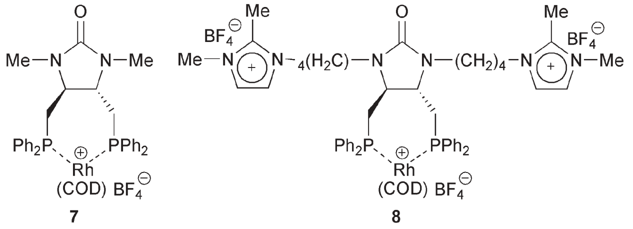
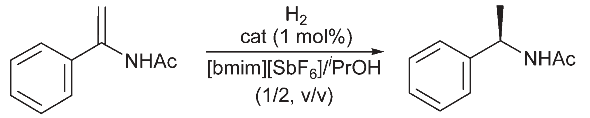


Fig. 4

Asymmetric hydrogenation. Catalytic asymmetric hydrogenation reactions in ionic liquids are of particular interest as they could provide a means for facile recycling of the air-sensitive and expensive chiral ligands. Since the first report on catalytic asymmetric hydrogenation reactions in ionic liquids by the group of Chauvin in 1995,[8] several research groups have studied catalytic asymmetric hydrogenations in ionic liquids.[2] The chiral Ru complexes of BINAP or BINAP analogs were efficiently immobilized in ionic liquids, and reused several times in the hydrogenation of olefins or ketones without significant loss of catalytic efficiencies.[14] In contrast to Ru-complexes, the catalytic activity of air-sensitive chiral Rh–diphosphine complexes such as the Rh–(*R*,*R*)-Me-DuPhos complex was largely decreased after first run.[15] Recently, we found that incorporation of the imidazolium ionic tag into the chiral diphosphine not only avoided catalyst leaching but also increased the stability of catalyst in ionic liquid.[16] The Rh-complex of diphosphine Me-BDPMI **7**, which showed excellent catalytic activity in asymmetric hydrogenations,[17] was modified task-specifically with imidazolium salt to give chiral diphosphine–Rh complex **8** (Fig. 4), and applied as a catalyst for asymmetric hydrogenation of an enamide in an ionic liquid biphasic system. As shown in Table 2, the catalytic efficiency of the Rh complex **7** in an ionic liquid dropped significantly after two cycles (entries 1–3), thus, the conversion

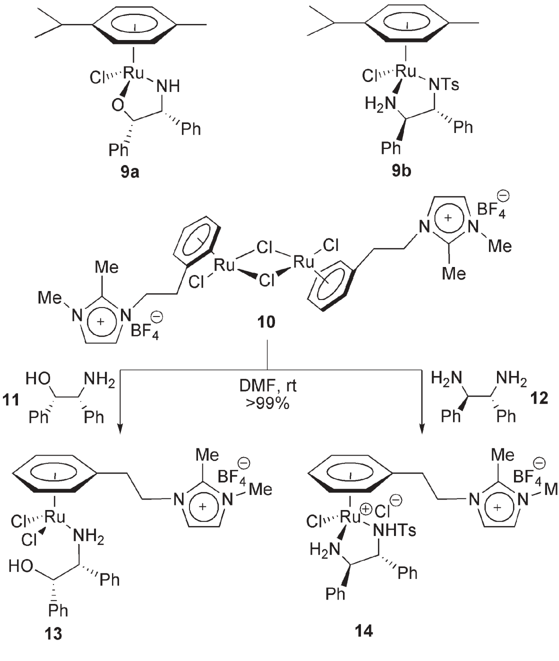
Table 2 Rh-Catalyzed asymmetric hydrogenation of *N*-acetylphenylethenamine using **7** and **8** in [bmim][SbF_6]–^{i}PrOH two-phase solvent systems



Entry	Cat.	Run	*t*/h	Conv. (%)	Ee (%)
1	**7**	1	1	100	95.8
2		2	1	100	95.1
3		3	1	78	94.2
4		4	1	51	91.4
5		4	12	85	88.0
6	**8**	1	1	100	97.0
7		2	1	100	96.6
8		3	1	100	96.2
9		4	1	82	95.4
10		4	8	100	95.4

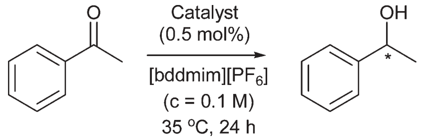
and enantioselectivity were decreased in the third (78%, entry 3) and fourth (51%, entry 4) runs. The reactions were not complete even after prolonged reaction time (entry 5). In contrast, the imidazolium ion tagged Rh-complex **8** was successfully immobilized in the ionic liquid, which can be reused three times without any loss of catalytic activity. Although in the fourth run, the catalytic activity was slightly decreased, the reaction was completed when the reaction time was prolonged to 8 h. The enantioselectivity was also not decreased significantly. ICP-AES analyses of the ^{i}PrOH layer separated from the first runs clearly indicated that no Rh (<1 ppm) and no phosphorus (<3 ppm) was found within detection limits indicating the appended imidazolium ion tag increased the preferential solubility of the Rh-complex in the ionic liquid.

Asymmetric transfer hydrogenation. Quite recently, Dyson *et al.* synthesized a dinuclear Ru complex **10** bearing η^6-arenes with pending imidazolium salt tags, which could be regarded as a versatile starting material for the synthesis of a wide range of Ru catalysts.[18] As a proof of demonstration, the imidazolium salt-functionalized Ru-complex **10** used for the task-specific modification of the well-known η^6-arenes Ru complexes **9a,b**,[19] and thus, reacted with optically pure amino alcohol **11** and diamine **12** to give the cationic Ru-complexes **13** and **14**, respectively (Scheme 2). Asymmetric transfer hydrogenations of acetophenone in an ionic liquid, [bddmim][PF_6] (bddmim = 1-butyl-2,3-dimethylimidazolium), using **9a**, **9b**, **13** and **14** as catalysts showed that the reusability of the catalyst in ionic liquid was largely dependent on the reaction conditions (Table 3). When the transfer hydrogenations were conducted in ^{i}PrOH/KOH conditions, relative to the neutral complexes **9a** and **9b**, catalyst loss was up to 10 times (compare entries 2 with 6, and 4 with 8) lower in the cationic analogous **13** and **14**, demonstrating the positive effects of the imidazolium salt tag. The diamine derived Ru-complexes **9b** and **14** showed superior stability in an ionic liquid compared with the amino alcohol derived Ru-complexes **9a** and **13**, which deactivated quickly, and reuse of the ionic liquid phases was not viable. In contrast, the diamine complex **14** in [bddmim][PF_6] was stable for at least 72 h and recycling of the ionic liquid phase was feasible. Nevertheless, the conversion was still reduced upon reuse the recovered ionic liquid phase, *i.e.* from 80% in the first cycle to 21% in the fourth cycle (entries 7–10). Interestingly, when a formic acid/triethylamine azeotrope was used as a proton source, the reusability of the catalyst system composed of **9b**/[bddmim][PF_6] was much superior to the TSIL catalytic system composed of **14**/[bddmim][PF_6]. However, as the formic acid/triethylamine azeotrope forms a homogeneous phase together with [bddmim][PF_6], the reaction volume was gradually increased. Accordingly, the solution containing the catalyst required washing with water after product extraction with hexane or Et_2O, and drying in vacuum prior to the next catalytic cycle. In this manner, an ionic liquid solution containing **9b** could be reused five times without significant decrease in activity. The catalyst solution could be stored for days without any effect on activity or enantioselectivity. However, this procedure was not applicable to complex **14**, which was too soluble in water and consequently extracted from the ionic liquid.



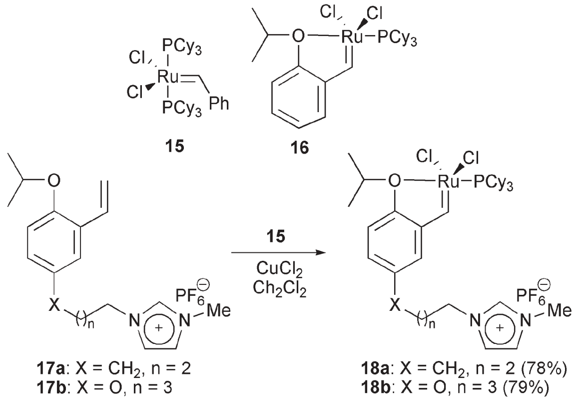
Scheme 2

Table 3 Asymmetric transfer hydrogenation of acetophenone in ^{i}PrOH/KOH catalyzed by Ru-complexes **9a**, **9b**, **13** and **14** in [bddmim][PF_6]



Entry	Catalyst	Run	Conv. (%)	Ee (%)	Leaching (%)
1	**9a**	1	97	58	61
2		2	1		
3	**9b**	1	95	98	63
4		2	5		
5	**13**	1	95	27	5
6		2	15		
7	**14**	1	80	98	8
8		2	66		
9		3	57		
10		4	21		

Ring-closing metathesis (RCM). Ring-closing metathesis (RCM) catalyzed by metal–cerbene complexes such as Grubbs-type **15** and Hoveyda's catalyst **16**, is a powerful synthetic method to generate new C=C bonds.[20] However, only limited RCMs in ionic liquids have reported. Buijsman *et al.* have reported for the first time that the Grubbs's Ru catalyst precursor **15** dissolved in [bmim][PF_6] promoted the RCM of dienes for at least three cycles.[21] However, due to the leaching of the catalyst to the organic phase, low conversion was obtained at the last cycle. Similarly, Dixneuf and co-workers also found that the Ru allenylidene salt in [bmim][PF_6] could be a recyclable catalytic system, but the catalyst proved to be efficient only for the first two cycles.[22] In

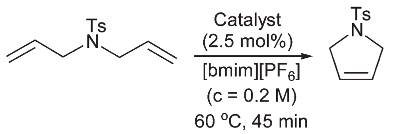


Scheme 3

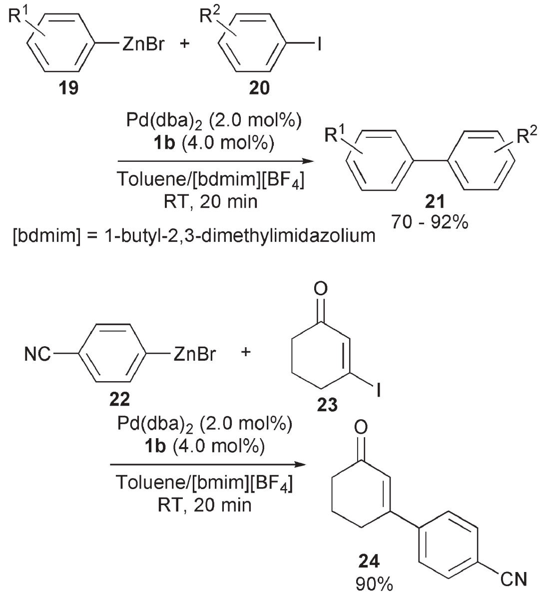
2003, Guillemin and co-workers[23] and Yao[24] independently have reported that a task-specific modification of the Ru–carbene complex **16** brings about an immense improvement in their performance as recyclable catalysts for RCM in ionic liquids (Scheme 3). The air-stable solid form of imidazolium salt-functionalized Ru–carbene complexes **18a** and **18b** were easily synthesized by reaction of **17** with Grubbs's catalyst **15**. In RCM of dienes using **18a** and **18b** in ionic liquids, the TSIL catalytic systems can be recycled effectively. As shown in Table 4, the catalytic activity of the TSIL catalytic system composed of catalyst **18a**/[bmim][PF$_6$] in RCM of *N*,*N*-bisallyl *p*-toluenesulfonamide was retained up to nine cycles. In contrast, the activities of the unmodified catalysts **15** and **16** immobilized in [bmim][PF$_6$] were dramatically decreased after the first run. These results clearly showed the importance of attaching an imidazolium salt tag to the catalyst not only to avoid its leaching from the ionic liquid phase but also to increase its stability in ionic liquid. The TSIL catalytic system can be stored for several months without loss of activity as demonstrated by the fact that the catalytic activity of the catalyst **18a** in [bmim][PF$_6$] recovered from the eighth run was retained for three months providing the result of ninth run in Table 4.

C–C Coupling reactions. Since the first report by Kaufmann *et al.* on the Pd-catalyzed Heck coupling in an ionic liquid in 1996,[25] many related metal-catalyzed C–C coupling reactions in imidazolium cation-based ionic liquids have been investigated, and provided superior catalytic efficiencies in ionic liquids compared to organic solvents. It was also noted that palladium complexes of imidazolylidene carbenes, formed by reaction of the base with the imidazolium cation, may be implicated in these reactions, but not all cases. Knochel and co-workers specifically designed and synthesized the 2-imidazolium-phosphine **1b** for Pd-catalyzed C–C bond forming reactions in ionic liquids.[26] In Ngishi cross-coupling reactions between arylzinc reagents **19** with aryl halides **20** in [bdmim][BF$_4$]/toluene biphasic system, the **1b**–Pd-complex exhibited high catalytic activity. In most cases, the reaction proceeded at room temperature within a few minutes to give the coupling products **21** with high yields (70–92%). The Pd-complex in [bmim][BF$_4$]/toluene can also be an active catalyst for cross-coupling of 3-iodo-2-cyclohexen-1-one (**23**) with the arylzinc reagent **22**, and afforded the 3-substituted cyclohexenone **24** within 20 min at room temperature in 90% yield (Scheme 4). However, it was observed that the catalytic activity of the recovered Pd-complex immobilized in ionic liquid was significantly decreased after the third cycle (20% lower yield and tripled reaction time).

Table 4 Comparative recycling and reuse in [bmim][PF$_6$] of **18a** and catalysts **15** and **16** in the RCM of diene **15**

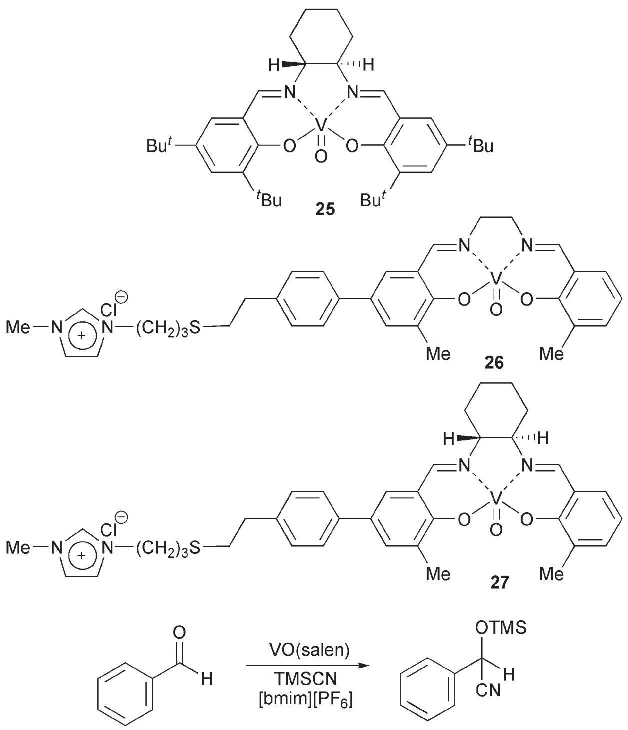


	Run								
Catalyst	1	2	3	4	5	6	7	8	9
18a	>98	>98	>98	>98	>98	96	92	92	92
15	>98	20	—	—	—	—	—	—	—
16	>98	40	20	—	—	—	—	—	—



Scheme 4

Cyanosilylation of aldehydes catalyzed by vanadium salen complexes. Cyanosilylations of aldehydes or ketones are important synthetic methods for cyanohydrins, which are versatile synthetic intermediates in the synthesis of α-hydroxy acids and β-hydroxyamines.[27] A recent study by Corma and co-workers proved the feasibility of the ionic liquids as reaction medium as well as liquid support for unmodified chiral vanadium salen complex **25** in cyanosilylation of aldehydes.[28] Although the reusability of the catalyst immobilized in an ionic liquid, [bmim][PF$_6$], was promising, leaching of the catalyst could not be avoided. To overcome the catalyst leaching problem, the same authors task-specifically designed new vanadyl salen complexes **26** and **27**, which covalently anchored to imidazolium salts (Fig. 5).[29] The imidazolium salt-functionalized achiral vanadyl salen complex **26** was not

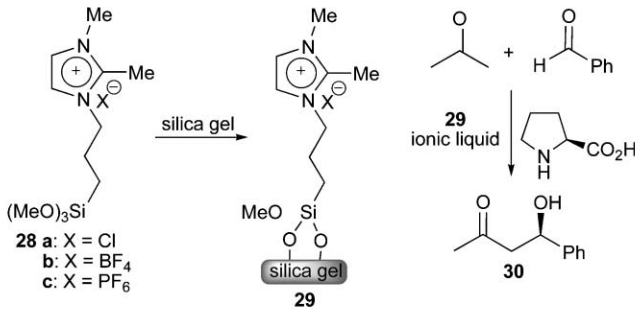


with **25**: 85%, 89% ee
with **26**: 88-91% (6 runs)
with **27**: 88%, 57% ee

Fig. 5

soluble in hexane and diethyl ether, which was used for the product extraction, but completely soluble in an ionic liquid, [bmim][PF$_6$]. The cyanosilylation of benzaldehyde with TMSCN using complex **26** in [bmim][PF$_6$] proceeded highly efficiently, and the catalyst immobilized in the ionic liquid could be reused six times without loss of catalytic activity. Unfortunately, the covalent functionalization with imidazolium salt negatively affected the ability of the chiral complex **27** to asymmetric induction, and showed relatively lower enantioselectivity (88% conversion, 57% ee) compared to the ee (85% conversion, 89% ee) obtained from the complex **25** in [bmim][PF$_6$].

Proline-catalyzed direct asymmetric aldol reaction. L-Proline catalyzed direct aldol reaction between aldehydes and ketones has recently received a great deal of attention from the point of view of atom economy.[30] However, the turnover number (*ca.* 3) was too low for practical application of the reaction. Hence, several attempts have been made to immobilize the proline on a silica or poly(ethylene glycol) (PEG), but a significant reduction in enantioselectivity was observed.[31] Recently, three research groups reported independently the use of L-proline in ionic liquid as a reusable catalyst system, and showed that the yields and enantioselectivities were quite comparable with those obtained in organic solvents.[32] Quite recently, Gruttadauria and co-workers carried out proline catalyzed direct asymmetric aldol reaction between acetone and aldehydes in a supported ionic liquid phase.[33] The trimethoxysilyl-functionalized ionic liquids **28** were immobilized on silica gel to form silica gels **29** modified with ionic liquids, and added a conventional ionic liquid to generate supported ionic liquid phases (Scheme 5). Table 5 summarizes the results obtained from L-proline catalyzed direct aldol reaction between benzaldehyde and acetone with various catalytic systems. It was found that the catalytic efficiency of the supported ionic liquid system was quite comparable with other catalytic systems, and was largely dependent on the anion of the supported ionic liquid phase. For example, aldol reaction in a catalytic system composed of **29b**/[bmim][BF$_4$]/proline afforded aldol product **30** in 51% yield with 64% ee (entry 1) whereas the **29c**/[bmim][PF$_6$]/proline system afforded **30** only in 15% yield with 52% ee (entry 4). An important role of imidazolium moiety on silica gel was also observed by comparison with the result obtained with the unmodified silica gel/[bmim][BF$_4$]/proline catalytic system, in which the catalytic efficiency was dramatically decreased (entry 3). The **29b**/[bmim][BF$_4$]/proline catalytic system could be reused three times without loss of catalytic activity.

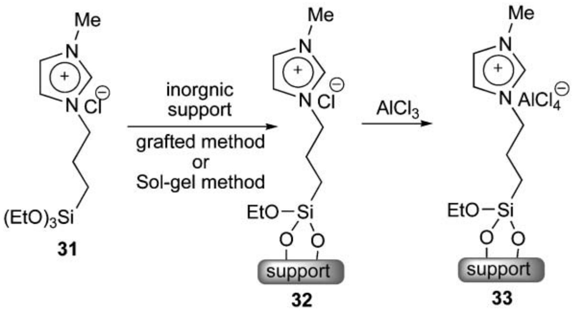


Scheme 5

Table 5 Direct Aldol reaction between acetone and benzaldehyde with different L-proline catalyst forms

Entry	Catalyst	Yield (%)	Ee (%)	Ref.
1	**29b**/[bmim][BF$_4$]/proline	51	64	33
2	**29b**/proline	40	64	33
3	SiO$_2$/[bmim][BF$_4$]	38	12	33
4	**29c**/[bmim][PF$_6$]/proline	15	52	33
5	**29a**/proline	59	40	33
6	Proline/DMSO	62	60	31*a*
7	Proline/[bmim][PF$_6$]	58	71	32*b*
8	Proline/[bmim][PF$_6$]	55	76	32*a*
9	PEG-proline/DMF	45	59	31*b*

Lewis and Brønsted acid catalyzed reactions. Since many Lewis or Brønsted acid catalyzed reactions generally involve cationic intermediates such as carbenium or acylium ions, substantial rate enhancements in ionic liquids would be expected. As mentioned earlier, Lewis acidic imidazolium chloroaluminate, [emim][AlCl$_4$], can function as both a catalyst and a solvent for Friedel–Crafts reactions. More recently, the chloroaluminate ionic liquids were used as catalysts for Knoevenagel condensations[34] and microwave-assisted tetrhydropyranyl protection of alcohols and phenols.[35] To facilitate the catalyst separation, Hölderich and co-workers immobilized the chloroaluminate ionic liquids on inorganic supports (SiO$_2$, Al$_2$O$_3$, TiO$_2$, ZrO$_2$) using triethoxysilyl-functionalized imidazolium salts.[36] Immobilizations of

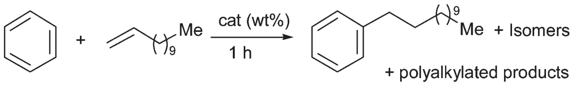


Scheme 6

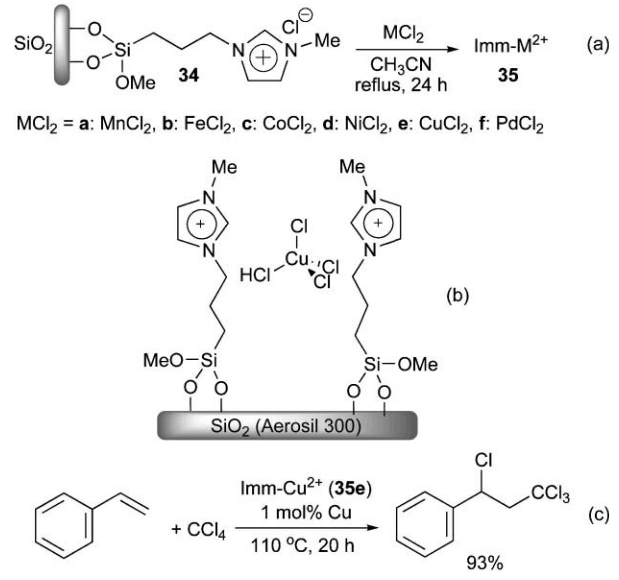
triethoxysilyl-functionalized ionic liquid **31** on amorphous silica (SiO_2) and MCM 41 have been conducted either by the grafting method (NLAC I) or the sol–gel method (NLAC II), followed by addition of $AlCl_3$ to form novel Lewis acid catalysts **33** (Scheme 6). As shown in Table 6, the grafted chloroaluminate NLAC I (entries 1 and 2) showed superior catalytic activity to that prepared by the sol–gel method (NLAC II) (entry 3) in Friedel–Crafts alkylation of benzene with dodecene. The NLAC I grafted on MCM 41 was by far the most active supported chloroaluminate catalyst (entry 2). Even at room temperature almost complete conversion could be achieved using 1 wt% catalyst within 1 h with very high selectivity (entry 5).

Very recently, Iwasawa and co-workers also prepared supported ionic liquids containing various metal ions. Grafting of the trimethoxysilyl-functionalized imidazolium chloride onto the silica (**34**), followed by addition of $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ or $PdCl_2$ afforded **35a–f** (Imm-M^{2+}), respectively (Scheme 7(a)).[37] There is interest in the immobilization mode of the $CuCl_2$ onto the supported ionic liquid. Comparison of the EXAFS data of the Imm-Cu^{2+} (**35e**) with those of the single-crystal structure of the $[bmim]_2CuCl_4$ clearly suggested that the Imm-Cu^{2+} (**35e**) has a sandwiched $CuCl_4^{2-}$ moiety (Scheme 7(b)). The catalytic activity of the Imm-M^{2+} materials (**35a–f**) was investigated for the Kharasch reaction between styrene and CCl_4, and it was found that only the immobilized copper catalyst (Imm-Cu^{2+}, **35e**) was very active (under optimized condition: 93% yield) (Scheme 7(c)). The catalytic activity of Imm-Cu^{2+} (**35e**) was superior to SiO_2-$CuCl_2$ (0.3% yield) or $[bmim]_2CuCl_4$ (68% yield).

Table 6 Results for the alkylation of benzene with dodecene catalyzed NLACs: molar ratio benzene:dodecene = 10:1



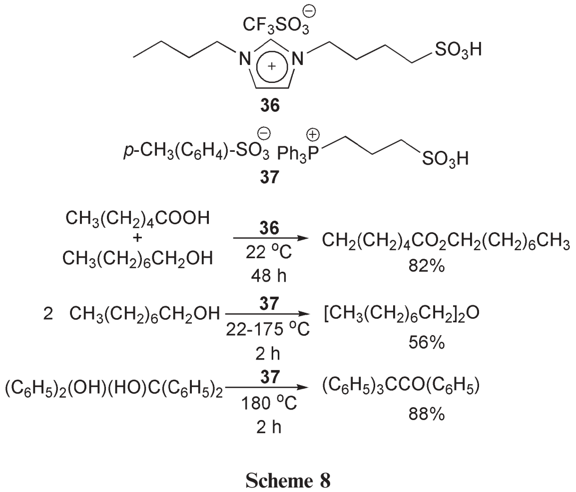
Entry	**33**	*T*/°C	Cat. (wt%)	Conv. (%)	Isomer (%)	Mono (%)	Poly (%)
1	SiO_2/NLAC **I**	80	6	92.3	22.3	76.2	1.5
2	MCM 41/NLAC **I**	80	6	100	12.6	85.6	1.8
3	MCM 41/NLAC **II**	80	6	74	17.8	82.2	0
4	SiO_2/NLAC **I**	20	1	46.8	7.6	90.7	1.8
5	MCM 41/NLAC **I**	20	1	92.8	0	92.3	7.7



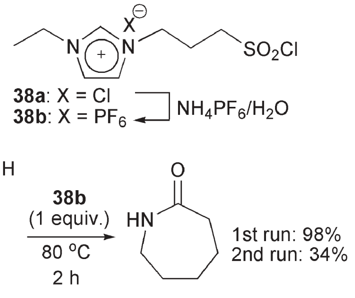
Scheme 7 (a) Synthesis of Imm-M^{2+} (**35**), (b) schematic illustration of Imm-Cu^{2+} (**35e**) and (c) Kharasch reaction catalyzed by Imm-Cu^{2+} (**35e**)

Davis and co-workers reported novel sulfonic acid-functionalized TSILs, imidazolium salt **36** and phosphonium salt **37**.[5] These TSILs act as dual solvent-catalysts for several classical acid-catalyzed organic reactions such as Fischer esterification, alcohol dehydrodimerization and pinacol rearrangement (Scheme 8). The TSIL **37** could be recycled five times without loss of activity in the synthesis of ethyl acetate from ethanol and acetic acid. Interestingly, the presence of a threshold quantity of water in the ionic liquid contributed to higher dehydration reaction yields, but the role of water is not clear yet.

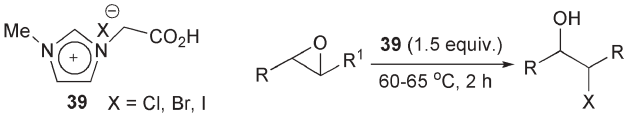
Many synthetically important rearrangement reactions are catalyzed by Lewis or Brønsted acids, and hence, may benefit from using TSILs as solvent-catalysts. Sun and co-workers reported Beckmann rearrangement of various ketoximes using a TSIL **38** appended sulfonyl chloride.[38] Surprisingly, the authors claimed that the sulfonyl chloride functional group, which is generally known to be liable toward water, was stable in water, and the TSIL **38** was immiscible with water, which allowed easy separation of the product, especially



Scheme 8



Scheme 9



Scheme 10

ε-caprolactam having good solubility in water. Thus, cyclohexanone oxime was smoothly transformed to ε-caprolactam in high yield at *ca.* 80 °C, however, recycling of the recovered TSIL reduced the conversion to 34% (Scheme 9).

Another interesting example of a TSIL is carboxylic acid-functionalized imidazolium salts **39**, which acted as a reagent and catalyst for the epoxide ring opening.[39] The carboxylic acid group activates the epoxide ring and the halide anion acts as a nucleophile, and thus various epoxides were converted to vicinal-halohydrine with good to excellent yields (Scheme 10). The same authors have investigated the role of ionic liquids as catalysts and reaction media in Michael addition of thiols and active methylenes to conjugated carbonyl and nitriles.[40]

Task-specific ionic liquids as supports for organic synthesis

Owing to their nonvolatile nature, TSILs can be thought of as liquid versions of solid supports. The use of TSILs as supports in organic synthesis is expected to have a number of advantages over solid supports. For example, the properties of the ionic liquid supports could easily be controlled to allow a solution like behavior. The loading capacity could easily be evaluated using standard analytical methods such as NMR and HPLC/MS *etc.* Moreover, the high polarity of the IL-phase may be suitable for microwave dielectric heating, allowing microwave-assisted reactions. The alcohol-functionalized TSILs have been extensively studied as replacements for solid polymer supports in the heterogeneous-phase synthesis of organic molecules. Bazureau and co-workers synthesized various alcohol-functionalized TSILs, [R-PEG$_n$mim][X] **40**, from *N*-alkylimidazole and Cl(CH_2CH_2O)$_n$OH in high yields (73–99%) (Fig. 6) using microwaves.[41] The melting temperatures or dynamic viscosities of [R-PEG$_n$mim][X] **40** are summarized in Table 7.

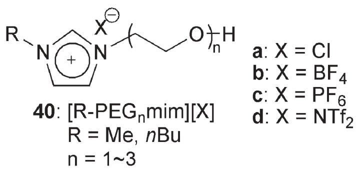


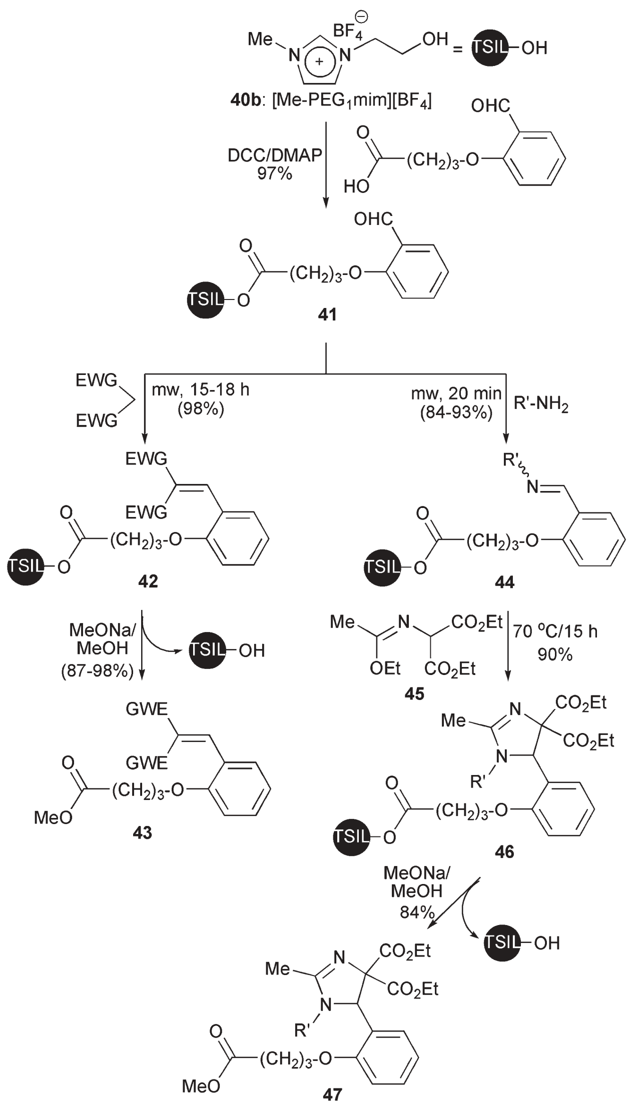
Fig. 6

Extensive studies by the group of Bazureau clearly demonstrated the potential of alcohol-functionalized TSILs **40** as liquid supports in ionic liquid-phase Knovenagel reactions, 1,3-dipolar cycloaddition and generation of a small libraries of thiazolidines and 2-thioxotetrahydropyrimini-4-(1*H*)-ones.[42] For example, as shown in Scheme 11, esterification of the TSIL **40b**, [Me-PEG$_1$mim][BF_4], with a carboxylic acid-functionalized benzaldehyde moiety, afforded the benzaldehyde **41** bound covalently onto TSIL support. The benzaldehyde **41** was used as a starting material for microwave-assisted Knovenagel reactions and formation of aldimine to form **42** and **44**, respectively, in high yields. 1,3-Dipolar cycloaddition of aldimine **44** with the imidate **45** afforded the cycloadduct **46**. The TSIL-bound products were purified by simple washing with organic solvents such as Et_2O to remove the unreacted reagents. Cleavage of the TSIL phase with MeONa in MeOH afforded the reaction products **43** and **47**, and the recovered TSIL **40b** could be reused. Similarly, Miao and Chan also utilized the TSIL **40b** as a liquid support for Suzuki coupling reactions, and demonstrated its advantage over conventional solution phase synthesis.[43] Recently, Grée and co-workers further modified the TSIL **40b** to Wang resin-type TSILs **48**,[44] and coupled with electrophilic alkenes provided new ionic liquid-grafted reagents **49**, which can be used for various ionic liquid-phase reactions such as Diels–Alder cycloadditions **50**, 1,4-additions **51**, Heck couplings **52** and Stetter reactions **53**, which converted to 2-pyridyllactone by $NaBH_4$ reduction, followed by intramolecular cyclization (Scheme 12). The TSIL support **48** could be easily separated and recovered by cleavage of the ester bond with MeONa.

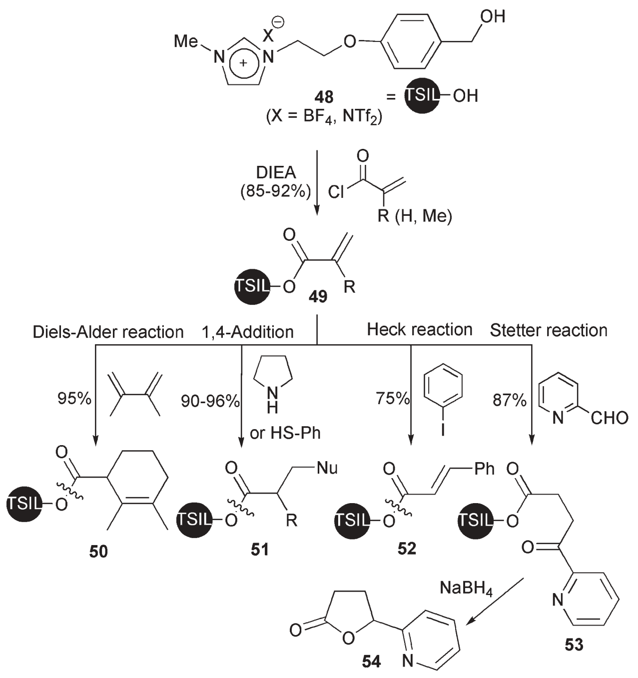
Table 7 Melting temperatures or dynamic viscosity at 25 °C (cP: 0.01 g cm^{-1} s^{-1}) of TSILs **40**

40 [R-PEG$_n$mim][X]	Mp[a,]/°C) or viscosity[b]	**40** [R-PEG$_n$mim][X]	Mp[a,]/°C or viscosity[b]
[Me-PEG$_1$mim][Cl]	86–88[a]	[Me-PEG$_2$mim][PF_6]	370[b]
[Me-PEG$_2$mim][Cl]	Liquid	[Me-PEG$_2$mim][NTf_2]	922[b]
[Me-PEG$_3$mim][Cl]	Liquid	[Me-PEG$_3$mim][BF_4]	391[b]
[Bu-PEG$_1$mim][Cl]	Liquid	[Me-PEG$_3$mim][PF_6]	846[b]
[Bu-PEG$_3$mim][Cl]	Liquid	[Me-PEG$_3$mim][NTf_2]	2249[b]
[Me-PEG$_1$mim][BF_4]	86[b]	[Bu-PEG$_1$mim][BF_4]	204[b]
[Me-PEG$_1$mim][PF_6]	336[b]	[Bu-PEG$_1$mim][PF_6]	542[b]
[Me-PEG$_1$mim][NTf_2]	541[b]	[Bu-PEG$_1$mim][NTf_2]	~30[a]
[Me-PEG$_2$mim][BF_4]	201[b]	[Bu-PEG$_3$mim][NTf_2]	923[b]

[a] Not measured. [b] Not observed.



Scheme 11 Application of TSIL **40b** in Knovenagel and 1,3-dipolar cycloaddition reactions.



Scheme 12 Wang-type TSILs and their applications.

Task-specific ionic liquids for extraction and dissolution

Extraction of metal ions from aqueous solutions. Extraction of specific metal ion species from aqueous waste is a major challenge in mining, nuclear fuel and waste reprocessing. However, most hydrated metal ions are more soluble in water than in water-immiscible ionic liquids, and do not partition into the ionic liquid from water. To increase the affinity of the metal ion in ionic liquids, the hydration environments of the metal ions have been changed either by using organic ligands[45] or inorganic anions that form more extractable anionic complexes with the metal.[46] Unfortunately, the drawbacks associated with these approaches lie in finding extractant molecules that remain exclusively in the ionic liquid under all processing conditions. Davis and Roger introduced the concept of task-specific ionic liquids for the first time to describe ionic liquids **55a–f** (Fig. 7), which were designed specifically to extract heavy metal ions.[47] Metal ion-ligating groups such as thioether (**55a**), thiourea (**55b–c**) and urea (**55d–f**) were incorporated into the imidazolium cation, and these TSILs can be used directly as solvent or may be doped as an extractant into conventional ionic liquids such as [bmim][PF$_6$] in liquid/liquid separations of mercury(II) and cadmium(II). Table 8 summarizes the physical properties of the TSILs **55**. When the metal ion-ligating group appended TSILs **55** was used, the metal ion distribution ratios increased several orders of magnitude, regardless of whether the TSILs were used as the sole extracting phase or doped into a conventional ionic liquid, [bmim][PF$_6$] to form a 1:1 solution. In general, the distribution ratios of Cd^{2+} were lower than the ratios observed for Hg^{2+}. It

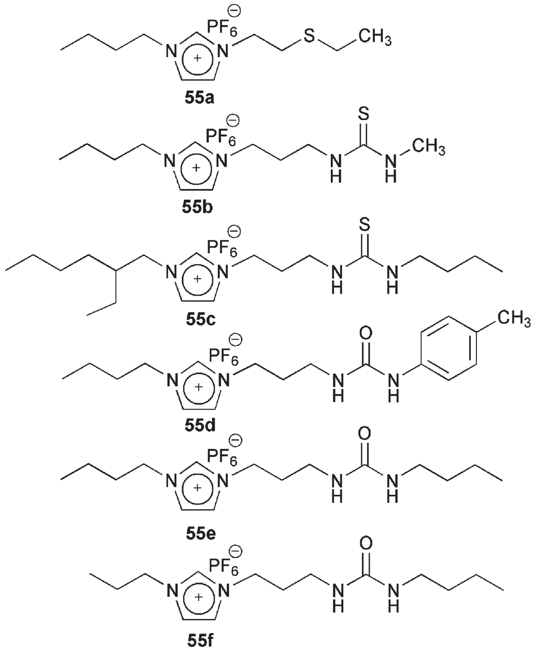


Fig. 7

Table 8 Physical properties of the TSILs **55a–f**

					Viscosity/cP	
TSIL **55**	Mp/°C	Fp/°C	T_g/°C	Decomp./°C	25 °C	90 °C
55a	−12.8	−55.2	−62.6	300	[a]	[a]
55b	−18.7	−75.1	−52.4	300	[a]	[a]
55c[c]	[b]	−49.3	−17.4	225	964	661
55d[c]	[b]	17.7	−12.6	200	873	552
55e[c]	46.2	[b]	−45.0	225	799	523
55f[c]	64.5	[b]	−59.4	225	801	510

[a] Not measured. [b] Not observed. [c] 1:1 mixture of **55c–f** with [bmim][PF_6]; fp = freezing point.

was also found that both the appended functional group and the alkyl group appeared to effect the extraction. Overall, the distribution ratios for Hg^{2+} are the highest with the TSIL having urea (**55d–f**) > thiourea with the 'tail' **55c** > thioether **55a** > thiourea **55b** functional groups, while those for Cd^{2+} decrease from **55c** > **55a** > **55d–f** > **55b**.

Davis also synthesized the phosphoramide-functionalized imidazolium salt **56** to remove actinides and salicylaldehyde-derived imidazolium salt **57** to extract Ni^{2+} ions from aqueous solutions (Fig. 8).[48] He described the preliminary results suggesting that the partition coefficient for Am^{3+}, UO^{2+} and Pu^{4+} with the phosphoramide-functionalized imidazolium salt **56** were in the same range as those found for Hg^{2+} and Cd^{2+} with the urea- and thiourea-functionalized imidazolium salts **55**. Similarly, a solution of **57** in [hmim][PF_6] quickly decolorized green aqueous solutions containing Ni^{2+}, and the color moved completely into the ionic liquid phase suggesting formation of a Ni-TSIL **57** complex.

CO_2 capture. A number of investigations have shown that CO_2 is remarkably soluble in imidazolium-based ionic liquids, and suggested the possibility of CO_2 separation using ionic liquids.[49] Davis and co-workers specifically designed and synthesized the primary amine-functionalized TSIL **58** as a CO_2 capture agent (Fig. 9).[4] Compared to the conventional ionic liquid, the amine-functionalized TSIL **58** showed superior ability for CO_2 capture. The molar uptake of CO_2 per mole of TSIL **58** during the 3 h exposure period approached 0.5, which is the theoretical maximum value for CO_2 sequestration as an ammonium carbamate salt **59**. This per mole uptake of CO_2 by the amine-functionalized TSIL **58** is quite comparable to those of the standard sequestering amines such as monoethanolamine or diisopropanol amine. Comparison of both the IR and NMR spectra of the CO_2-untreated (no carbamate C=O stretch) and CO_2-treated materials (carbamate C=O stretch and resonance at 1666 cm^{-1} in IR and δ 158.11 in ^{13}C NMR) clearly indicated that the sequestration of CO_2 by the TSIL **58** occurred *via* its fixation as an ammonium carbamate as shown in Fig. 9. Moreover, the process of CO_2 uptake is reversible, CO_2 being excluded upon heating (80–100 °C) for several hours under vacuum. The recovered TSIL **58** has been repeatedly recycled for CO_2 uptake (five cycles) with no observed loss of efficiency.

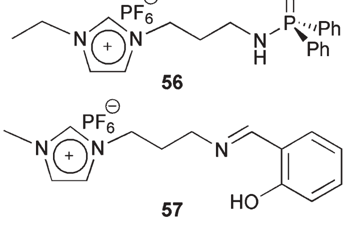


Fig. 8

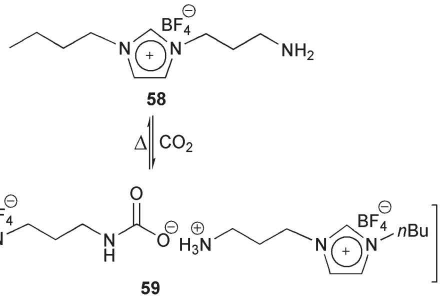


Fig. 9

Dissolution of carbohydrates. Kimizuka and Nakashima developed ether-containing "sugar-philic" TSILs **60a,b** by reaction of *N*-methylimidazole with the corresponding bromides (Fig. 10).[50] These sugar-philic ionic liquids homogeneously dissolved carbohydrates such as β-D-glucose (solubility in **60**, 450 mg mL^{-1}), α-cyclodextrin (350 mg mL^{-1}), amylase (30 mg mL^{-1}) and agarose (20 mg mL^{-1} in **60a**, 10 mg mL^{-1} in **60b**) by heating. Dissolution of amylose in these TSILs is noteworthy since it is only slightly soluble in pure water (less than 0.5 mg mL^{-1}). Glucose oxidase was also soluble in these ionic liquids (concentration, 1 mg mL^{-1}), however, the other proteins such as cytochrome c, myoglobin, hemoglobin, and catalase were insoluble. Dispersion of glycoliphids in **60** formed stable bilayer membranes, which displayed reversible thermal transformation from fibrous assemblies to vesicles. It was also found that the sugar-philic TSIL **60** formed ionogels with amide-group-enriched glycolipids. Pernak *et al.* synthesized a series of 3-alkoxymethyl-1-methylimidazolium salts **61**, and screened their anti-microbial activities against cocci, rods and fungi.[51] Their anti-microbial activities were greatly affected by the alkyl chain length in the alkoxymethyl substituents (longer alkyl-chain showed higher activity) but did not depend on the type of anion. The melting temperatures of the ether-containing TSILs **61a–l** are summarized in Table 9. Recently, Lin *et al.* utilized **61k** (X = Cl) as a template for the preparation of tubular shaped silica nanoparticles, which was used for controlled release of the ether-containing TSIL **61k** (X = Cl) exhibiting antibacterial activity.[52]

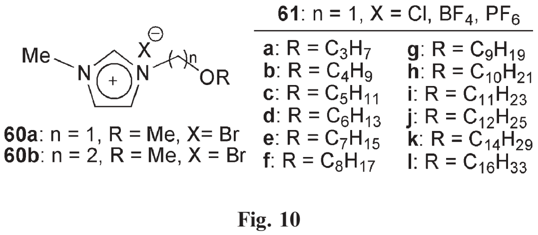


Fig. 10

Table 9 Melting temperatures (°C) of the ether-functionalized sugar-philic TSILs **61**

	X		
R	Cl	BF_4	PF_6
C_3H_7 (**61a**)	Oil	Liquid	Liquid
C_4H_9 (**61b**)	Oil	Liquid	Liquid
C_5H_{11} (**61c**)	Oil	Liquid	Liquid
C_6H_{13} (**61d**)	Grease	Liquid	Liquid
C_7H_{15} (**61e**)	Grease	Liquid	37–38
C_8H_{17} (**61f**)	Grease	Liquid	48–50
C_9H_{19} (**61g**)	Grease	Liquid	47–49
$C_{10}H_{21}$ (**61h**)	Grease	56–57	46–47
$C_{11}H_{23}$ (**61i**)	66–68	61–62	52–53
$C_{12}H_{25}$ (**61j**)	67–70	62–64	61–63
$C_{14}H_{29}$ (**61k**)	70–73	65–67	67–69
$C_{16}H_{33}$ (**61l**)	73–75	68–69	71–73

Task-specific ionic liquids for nano-sized materials

Formation of self-assembled monolayers on Au and Si/SiO$_2$. Modulation of surface properties such as wettability, adhesion, and biocompatibility has important implications in both fundamental and technological advances.[53] We could transfer the tunable physical properties of the ionic liquids onto the solid surfaces *via* formation of self-assembled monolayers (SAMs) with thiol-functionalized imidazolium salts. The properties of the SAMs, especially water wettability, could be adjusted by variation of the length of alkyl chain of imidazolium cation and/or the counter anions. Various thiol-functionalized imidazolium bromides **62**, were synthesized and formed well-ordered, closed-packed self-assembled monolayers (C_nSAMIM-a) with 19 Å thickness on gold surfaces (Fig. 11).[54] It was found that "direct" exchange of anion on the SAM surfaces could be possible providing C_nSAMIM-a–f having various counter anions, and investigated the effects of anion and alkyl chain on the surface wettability. Measurements of water contact angles of the C_nSAMIM-a–f indicated that water wettability of the SAM surfaces was largely dependent not only on counter anions (Fig. 12) but also on the length of alkyl chains. In the case of C_{1-4}SAMIMs, the anions played a significant role in determining water wettability of the surfaces. It was qualified that the effects of counteranions on the surface hydrophobicity of the C_1SAMIMs a–g was in the following order: $NTf_2 > PF_6 > CF_3SO_3 > ClO_4 > NO_3 > BF_4 > Br$.

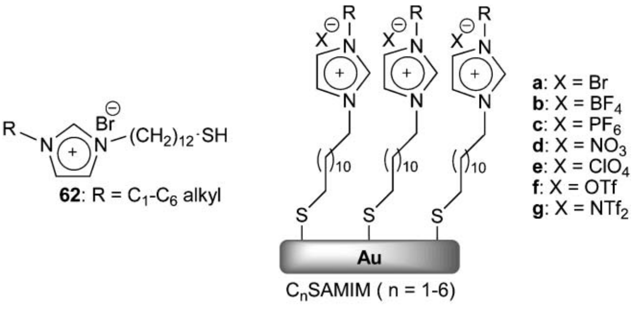


Fig. 11 Thiol-functionalized imidazolium salt and self-assembled monolayer on gold surfaces

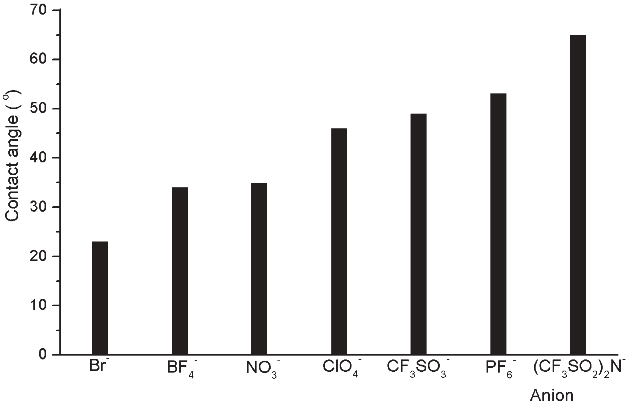


Fig. 12 Effects of counter anion on water-contact angle of C_1SAMIM-a–g

More recently, we observed that the C_1SAMIMs on gold electrodes exhibited a selective electron-transfer toward redox-probe molecules, *i.e.* the electron transfer occurred in the presence of $Fe(CN)_6{}^{3-}$ (anionic redox-probe molecule) but did not occur in the presence of $Ru(NH_3)_6{}^{3+}$ (cationic redox-probe molecule).[55] The C_1SAMIM having $Fe(CN)_6{}^{3-}$ as an anion showed electron transfer toward $Ru(NH_3)_6{}^{3+}$, and the $Ru^{3+/2+}$ redox-switchable SAM was generated by reversible anion exchange between $Fe(CN)_6{}^{3-}$ and SCN^- (or OCN^-) (Fig. 13). The anion effect on the electron transfer demonstrated in this paper could advantageously be incorporated into the design of integrated molecular switch nanodevices.

We also formed self-assembled monolayers (SAMs) presenting imidazolium moiety on Si/SiO$_2$ surfaces using triethoxylsilyl-functionalized imidazolium salts **31** ($C_n$tespims), which were made by reaction of *N*-methyl- or *N*-butylimidazole with triethoxysilylchloropropane in good yields.[56] The well-ordered SAMs (thickness, Me-SAM-Si/SiO$_2$: 6 Å, Bu-SAM-Si/SiO$_2$: 8 Å) were formed by immersing freshly cleaned Si/SiO$_2$ substrates in a 1% toluene solution of **31** at 100 °C for 24 h (Fig. 14). As we found with the C_nSAMIMs (Fig. 11) formed with the thiol-functionalized TSILs **62** on gold surfaces, the water wettability of the SAMs surfaces was also affected by the anions and the length of the alkyl chain. Water contact angles of the Me-SAM-Si/SiO$_2$-a–c samples were 24, 30 and 42°, respectively, which clearly showed that water wettability of the Me-SAM-Si/SiO$_2$ was also determined by counter anions. In

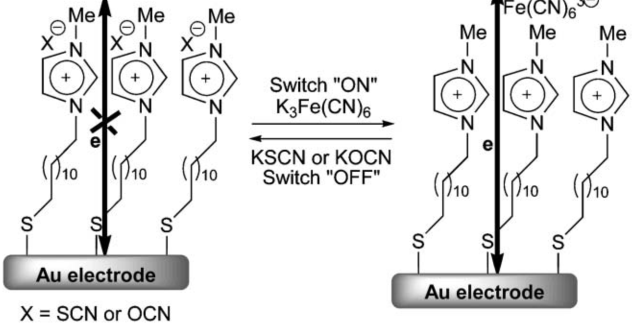


Fig. 13 Anion-directed $Ru^{3+/2+}$ redox-switchable surfaces

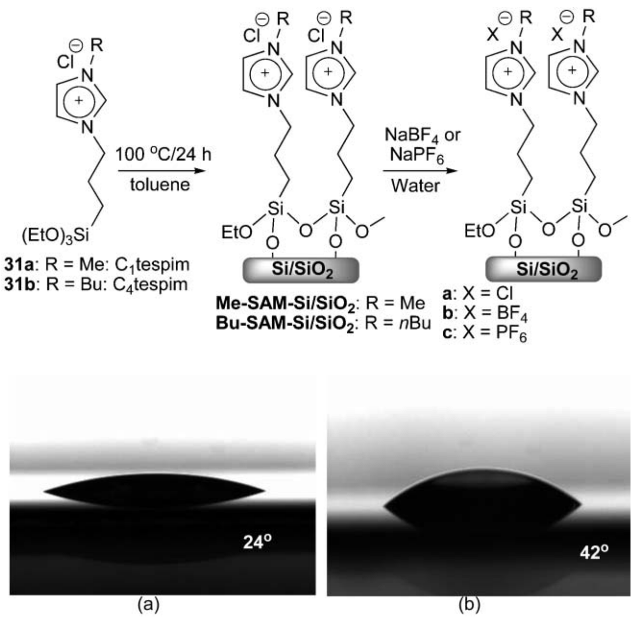


Fig. 14 Self-assembled monolayers formed with trialkoxysilyl-functionalized TSILs **31** on Si/SiO$_2$ surfaces and images of water droplets onto the Me-SAM-Si/SiO$_2$-a and Me-SAM-Si/SiO$_2$-c.

contrast, we observed relatively small (or no) changes in the contact angles of the Bu-SAM-Si/SiO$_2$ surfaces: the water contact angles of Bu-SAM-Si/SiO$_2$-a–c were 51, 51 and 52°, respectively.

Metal nanoparticles

Chuji and co-workers synthesized gold nanoparticles **64** (X = Cl, average diameter: 5 nm) the surfaces of which were modified with disulfide-functionalized imidazolium chloride **63** (Fig. 15).[57] The property of the gold nanoparticles changed from hydrophilic to hydrophobic by anion exchange of the imidazolium salt coated on the surface, *i.e.* the nanoparticle **64a** having Cl anion was soluble in water whereas **64b** having PF$_6$ anion was immiscible with water, and phase-transferred from water to an ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate *via in situ* anion exchange by addition of HPF$_6$ to **64a**. Such gold nanoparticles can be used as exceptionally high extinction dyes for colormetric sensing of anions in water. Larger red shifts were observed in the order of $PF_6^- > I^- > BF_4^-$.

Similarly, Lee and co-workers utilized poly-thiol-functionalized TSILs **65a,b** and **66** (Fig. 16) for the preparation of Au and Pt nanoparticles.[58] It was found that the particle size and uniformity were dependent on the number of thiol groups. Thus, the average size of the nanoparticles decreased with increases in the number of thiol groups in the TSILs **65a**, **65b** and **66** (average diameters: 3.5, 3.1 and 2.0 nm for Au and 3.2, 2.2 and 2.0 nm for Pt).

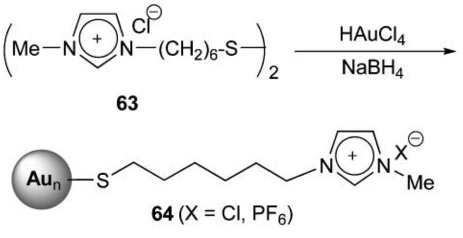


Fig. 15 Synthesis of gold nanoparticles **64** with TSIL **63**.

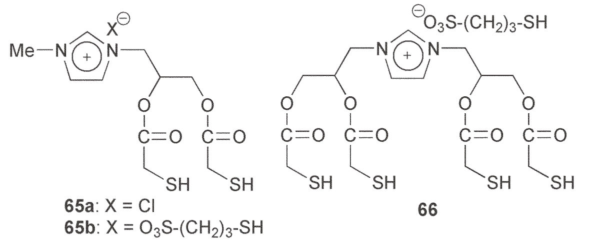


Fig. 16

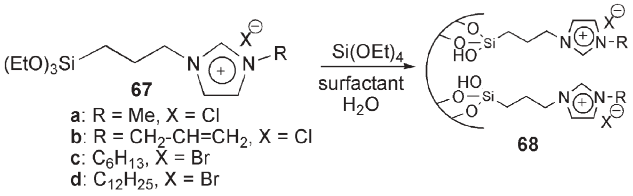


Fig. 17

Nanostructured silicas. As found by Moreau *et al.*, a template directed hydrolysis-polycondensation of Si(OEt)$_4$ with triethoxysilyl-functionalized imidazolium salts **67a–d** formed ordered mesoporous nanostructured silicas **68** containing covalently linked ionic species (Fig. 17).[59] The structural morphology of the materials was largely dependent on the alkyl appendage. Whereas materials incorporating imidazolium salts with rather short alkyl substituents **67a** and **67b** showed lamellar structures, longer alkyl groups attached on the imidazolium ring **67d** led to nanostructured silica hybrid materials with hexagonal symmetry, which may attributed to the modification of the micellar arrangement of the surfactant molecules (hexadecylpyridinium chloride) in the hydrolysis-condensation mixture. The hydrophilic methyl- and allylimidazolium cations interacted only with the polar head of the surfactant molecules, whereas the dodecylimidazolium cation can behave as an amphiphilic molecule and may be incorporated in the micellar arrangement. Table 10 summarizes the BET surface area and XRD *d*-spacings of the nanostructured silicas **68**. Quite recently, various C_2-symmetric trimethoxysilyl-functionalized mono- and bis-imidazolium salts have been synthesized by Bedford and co-workers, and it is expected that these trialkoxysilyl-functionalized imidazolium salts will be useful TSILs having potential applications for heterogeneous *N*-heterocyclic catalysis and sol–gel materials.[60]

Table 10 BET surface areas and XRD *d*-spacings of the nanostructured silicas **68**

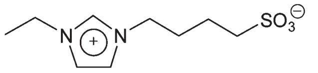
	BET surface area/m^{2}g^{-1}	100	110	200
68a	415	5.55	—	2.74
68b	502	6.41	—	3.24
68c	734	4.78	—	2.83
68d	853	4.62	2.68	2.31

Task-specific ionic liquids for ion conductive materials

The early history of ionic liquids research was dominated by their electrochemical applications as electrolytes. They have excellent electrochemical properties such as high ion content, high ionic conductivity, wide electrochemical windows, non-volatility and non-flammability, and thus, attracted the attention as electrolyte solutions for lithium ion batteries, fuel cells, solar cells, and capacitors.[61] Although ionic liquids show excellent ionic conductivities of over 10^{-2} S cm^{-1} at room temperature, this derives from the component ions themselves, which are mostly useless as target ions such as lithium cations, protons, or iodide anions.[62] Even when target ions were added to the ionic liquid, the ionic liquid component ions can also migrate along the potential gradient. Furthermore, addition of other salts induced increase in both T_g and viscosity, and accordingly ionic conductivity was considerably decreased. To overcome the component ion migration along the potential gradient, various zwitterionic compounds, in which both cation and anion are tethered, have been designed and synthesized by the group of Ohno.[63] Although most of the zwitterions melt above 100 °C, when an equimolar amount of lithium salt such as LiOTf, $LiNTf_2$, $LiBF_4$ or $LiClO_4$ was added to the zwitterions, the mixture showed only a glass transition temperature T_g. For example, an equimolar mixture of sulfonate-containing zwitterion **69** and $LiNTf_2$ showed a T_g value of −37 °C, and high ionic conductivity of 8.9 × 10^{-4} S cm^{-1} at 100 °C. Table 11 summarizes the thermal behavior of sulfonate-containing zwitterion **69** with an equimolar amount of lithium salt. It was also reported that the zwitterionic compounds are shown to act as dissociation enhancers in polyelectrolyte materials.[64] Currently, many efforts to investigate the ion-conductivity of the variety of zwitterionic ionic liquids are under way, and will provide a chance to development of novel, efficient ion conductive materials.

Recently, Kato and Ohno synthesized corroboratively a new class of task-specific ionic liquids **70** exhibiting fluid-organized structures, and one-dimensional ion conduction has been achieved for columnar liquid crystal materials, which are oriented uniaxially.[65] DSC and X-ray measurements indicated that the hexagonal columnar phases were maintained over wide temperature ranges including room temperature. Table 12 shows the thermal properties of the TSILs **70**. The X-ray patterns of **70a,b** at 25 °C showed that the intercolumnar distances were 3.5 and 3.8 nm, respectively. The ion conductivities parallel to the columnar axis ($\sigma_{\rm II}$) for **70** are higher than those perpendicular to the axis, and the highest ion conductivity of 4.8 × 10^{-4} S cm^{-1} ($\sigma_{\rm II}$) was achieved for **70a** at 130 °C in the columnar phase. Moreover, the incorporation of the lithium salts in these columnar materials lead to the enhancement of the ionic conductivities as well as the liquid crystallinity. For example, columnar material **70b** containing $LiBF_4$ (molar ratio of $LiBF_4$ to **70b**: 0.25) showed a conductivity of 7.5 × 10^{-5} S cm^{-1} ($\sigma_{\rm II}$) and the columnar phase from 17 to 193 °C, while those of **70b** alone were conductivity of 3.1 × 10^{-5} S cm^{-1} ($\sigma_{\rm II}$) and the columnar phase from 17 to 183 °C.

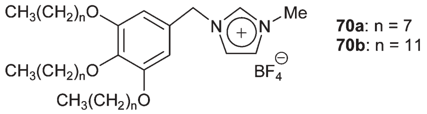
Table 11 Thermal behavior of zwitterion **69** with an equimolar amount of LiX, where LiBETI = lithium bis(perfluoroethylsulfonyl) imide



69

	T_m/°C	T_g/°C
Neat **69** (2nd heating)	175	18
+$LiNTf_2$	—	−37
+LiBETI	—	−5
+LiOTf	—	19
+$LiBF_4$	—	5
+$LiClO_4$	—	24

Table 12 Thermal properties of **70a** and **70b**



	Phase transition behaviour				
70a	Glassy	−29 °C	Columnar	133 °C	Isotropic
70b	Crystalline	17 °C	Columnar	183 °C	Isotropic

Other functionalized imidazolium salts

The type of functional groups incorporated into imidazolium salts need not to be those described above. Davis *et al.* synthesized new ionic liquids **71** containing imidazolium cation with long, appended fluorous tails, which function as surfactants when added to a conventional ionic liquid facilitating the emulsification of fluoroalkanes with ionic liquid phases.[66] As exemplified by the work of Leclerc and co-workers, the incorporation of polymerizable thiophene functional groups provided new polymers **72** bearing imidazolium salts, which can be used as chemosensors for the specific detection of iodide over a wide range of other anions.[67]

Concluding remarks

The results discussed here demonstrated that many of the functionalized imidazolium salts are capable of accomplishing specific tasks ranging from catalyst immobilization, liquid-supported organic reactions, metal extraction from aqueous solutions to construction of nanoassemblies and ion conduction *etc*. However, research in task-specific ionic liquids is still young and there is a lot to explore. Obviously, design and synthesis of novel functionalized imidazolium salts for task-specific purposes will be extended, with nearly limitless possibilities. Indeed, the task-specific ionic liquids will find their way in many applications in the areas of catalysis, organic synthesis as well nanostructured materials and ion transformation *etc*.

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