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Structural Modification of Polymer-Supported Ionic Liquids as Catalysts for Nucleophilic Substitution Reactions Including Fluorination

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Abstract: A polymer-supported ionic liquid (PSIL) system was reported to be a highly efficient catalyst in nucleophilic fluorination and other nucleophilic substitution reactions using metal salts. In this study we have prepared structurally modified PSIL systems and examined their catalytic activity in nucleophilic fluorination and other substitution reactions in dependence on the length of the alkyl chain linker, counteranion, and the ionic liquid loading in the resin. The PSIL system with a longer alkyl linker had better catalytic activity, and the PSIL system with tetrafluoroborate (BF_4^-) as the counteranion showed the best catalytic activity among the other counteranions. The nucleophilic fluorination of 2-(3-methanesulfonyloxypropyl)naphthalene (**2**), as a model compound, with cesium fluoride in the presence of a 0.5 equivs. of an ionic liquid portion of PS[domim][BF_4] (polymer-supported 1-*n*-dodecyl-3-methylimidazolium tetrafluoroborate) was completed within 2.5 h, affording the fluoroalkane **3** (96%). The PSIL system with a higher ionic loading as a catalyst produced a better fluorination, while the PSIL system with a lower loading produced a better bromination. In addition, these PSIL systems had good swelling properties in polar aprotic solvents such as DMF (7.2 mL/g), DMSO (6.5 mL/g) and acetonitrile (5.2 mL/g). Based on the swelling of PSIL, nucleophilic acetoxylation and fluorination reactions were carried out in four different solvents. It was found that the PSIL with a longer alkyl linker had superior catalytic activity due to the longer distance between the polystyrene backbone and ionic liquid portion. The PSIL system with tetrafluoroborate (BF_4^-) as the counteranion shows the best catalytic activity compared with PSIL systems with other counteranions. These PSIL systems absorb polar aprotic solvents and swell considerably, which is a favorable characteristic in new types of resins for other applications.

Keywords: fluorination; ionic liquids; nucleophilic substitution; polymer-supported ionic liquid

Introduction

The immobilization of a catalyst and reagents on a variety of polymeric supports is attracting considerable attention in both industrial and laboratory chemical processes under the umbrella of "green chemistry" due to their ease of recycling, easy handling and the unique microenvironment caused by the reactants within the polymeric support.[1] In particular, polystyrenes as a polymeric support are the most popular materials for these purposes on account of their facile functionalization, stability, chemical inertness, and low expense.[1a]

Although metal salts are generally abundant in nature and are potent sources of nucleophiles in nucleophilic substitution processes, their limited solubility and low reactivity in organic reaction media can make nucleophilic substitution processes difficult.[2] Over the past several decades, a number of phase-transfer protocols[3,4] to facilitate product isolation and enable catalyst recovery by simple filtration, including solid-supported phase-transfer catalysts,[5] have been developed to enhance the solubility and reactivity of metal salts in organic media systems, and accelerate the reaction rate. However, these phase-transfer catalysts still show ineffective catalytic activity in the case of metal salts, which form a tight ion pair. In addition, solid-supported phase-transfer catalysts have a relatively low activity compared with the corresponding non-immobilized catalysts.[3–5]

Over the last decade, there has been increasing use of ionic liquids containing imidazolium and its coun-

ter anions in many research fields such as alternative reaction media, separation science, and material synthesis.[6] Recently, we successfully developed novel methodologies for various nucleophilic substitution reactions performed in the presence of ionic liquids such as fluorination using metal fluorides,[7a–c] hydroxylation using water,[7d] dealkylation,[7e] *C*-alkylation of pyrrole,[7f] alkylation of carbonate[7g] etc.[7h,i] The results were superior to those of conventional protocols. We had no problems in the purification of nonpolar compounds which are used in the nucleophilic substitution reactions in ionic liquid. However, the separation of the polar products containing many heteroatoms such as pharmaceuticals from the ionic liquid is hindered by the difficult extraction of the polar products.

More recently, a polystyrene-based polymer-supported ionic liquid (PSIL) system was introduced as a highly efficient catalyst for nucleophilic fluorination and other nucleophilic substitution reactions using metal salts. This PSIL system not only had many practical qualities such as ease of purification, recovery, and handling, but it also considerably enhanced the reactivity of the alkali metal salts. In particular, the PSIL system had a much higher catalytic activity than the reactions in the free ionic liquid. Furthermore, the PSIL could be reused several times without any decomposition or loss of activity.[8] Currently, a new concept of supported ionic liquid catalysis has also attracted a great deal of attention. Accordingly, there have been many attempts at preparing an immobilized ionic liquid for various purposes due to their considerable potential applications.[9] This study used structurally-modified polystyrene-supported ionic liquids to investigate their catalytic activity in nucleophilic substitution reactions. The length of the alkyl chain linker, counteranion and ionic liquid loading in the resin were examined with regard to their influence on the effectiveness of the optimized PSIL system (Figure 1). For these purposes, structural modified PSIL systems were prepared, and some nucleophilic substitution reactions such as fluorinations,[10] brominations, and acetoxylations of mesyloxyalkanes or bromoalkanes were examined in the presence of PSIL. The degree to which a resin bead swells, as a result of the absorption of a specific solvent, is considered to be a good measure of the site accessibility and the reaction rate.[11] Therefore, the swelling properties of the PSIL systems in several solvents was also surveyed.

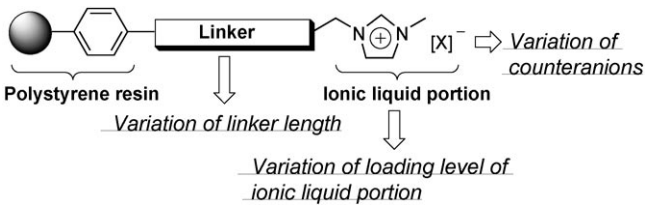
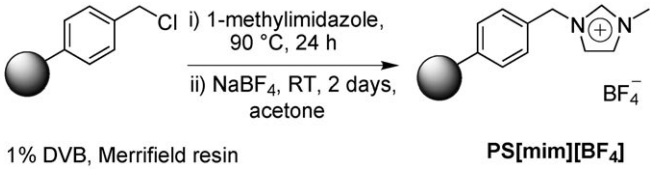


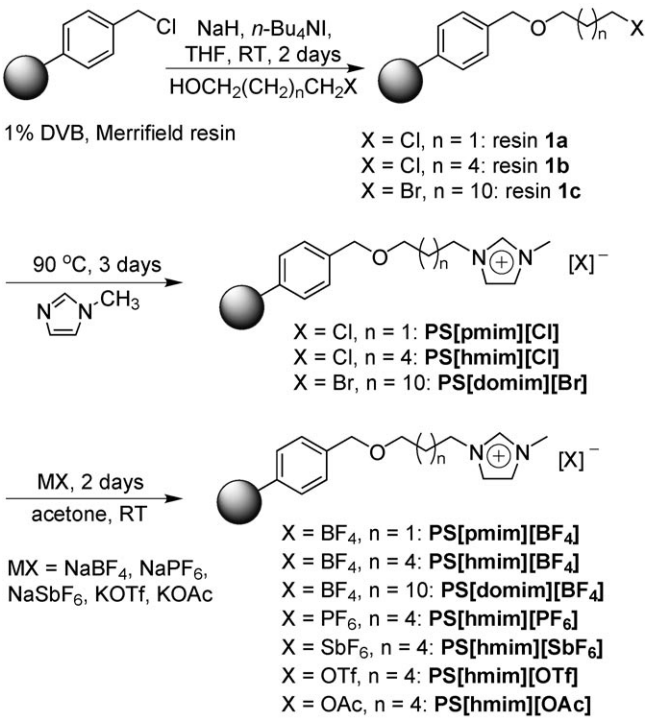
Figure 1. Structural modification of the polystyrene supported ionic liquids.

Results and Discussion

Many PSIL systems with different alkyl chain lengths as linkers, counteranions, and loading levels of ionic portion from Merrifield peptide resins were prepared.[12] The PS[mim][BF_4] (PS = polymer support; min = 1-methylimidazolium cation), which has no alkyl chain as a linker, was prepared using the procedure, as shown in Scheme 1. Merrifield resin (1% divinylbenzene, 4.5 mmol Cl/g) was reacted with 1-methylimidazole at 90 °C for 24 h to obtain PS[mim][Cl]. A further treatment of PS[mim][Cl] with $NaBF_4$ in acetone for 2 days afforded PS[mim][BF_4] (3.0 mmol of the ionic liquid portion per gram of polymer-supported product obtained). In addition, the other PSIL systems containing different lengths of alkyl chain linkers and counteranions such as PS-[pmim][X], PS[hmim][X] and PS[domim][X] (pmim = 1-*n*-propyl-3-methylimidazolium, hmim = 1-*n*-hexyl-3-methylimidazolium, domim = 1-*n*-dodecyl-3-methylimidazolium), were prepared using the procedure shown in Scheme 2. Different lengths of alkyl chain linkers were introduced by carrying out an alkoxylation reaction of the Merrifield resin with 3-chloro-1-propanol, 6-chloro-1-hexanol and 12-bromo-1-dodecanol in the presence of NaH in THF, affording resins **1a**, **1b** and **1c**, respectively. The PS[pmim][Cl], PS-[hmim][Cl] and PS[domim][Br] were prepared using the direct reaction of resins **1a–c** and 1-methylimidazole at 90 °C for 3 days. Further treatments of PS-[pmim][Cl], PS[hmim][Cl] and PS[domim][Br] with either $NaBF_4$, $NaPF_6$, $NaSbF_6$, KOTf or KOAc in acetone for 2 days afforded PS[pmim][BF_4] (2.4 mmol ionic liquid portion/g), PS[hmim][BF_4] (2.2 mmol ionic liquid portion/g), PS[domim][BF_4] (1.9 mmol ionic liquid portion/g), PS[hmim][PF_6] (2.1 mmol ionic liquid portion/g), PS[hmim][SbF_6] (1.6 mmol ionic liquid portion/g), PS[hmim][OTf] (2.1 mmol ionic liquid portion/g), or PS[hmim][OAc] (2.3 mmol ionic liquid portion/g). These PSIL systems were char-



Scheme 1. Preparation of the polymer-supported ionic liquids without a linker: PS[mim][BF_4].



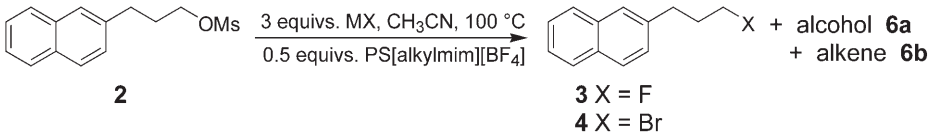
Scheme 2. Preparation of the structure modified polymer-supported ionic liquids: PS[alkylmim][X].

acterized by ^{13}C and ^{19}F solid-state NMR spectroscopy, and elemental analysis.

The catalytic activities of PSIL for nucleophilic substitution reactions such as fluorination and bromination according to the length of the alkyl chain as a linker in the PSIL system were examined by carrying out the nucleophilic fluorination and bromination of a model compound, 2-(3-methanesulfonyloxypropyl)-naphthalene (**2**), using 3 equivs. of CsF or KBr in the presence of 0.5 equivs. of the PSIL systems with various lengths of alkyl chain linkers such as PS[mim][BF_4], PS[pmim][BF_4], PS[hmim][BF_4], and PS-[domim][BF_4] at 100 °C in CH_3CN, as shown in Table 1. Entries 4 and 8 indicate that both the nucleophilic fluorination and bromination using PS[domim][BF_4], which has the longest linker among those tested, proceeded the fastest, affording both the desired products, fluoroalkane (**3**), and bromoalkane (**4**), almost quantitatively (in 96 and 99 % yields, respectively). Consequently, the PSIL system with the longer alkyl chain as a linker had a better catalytic activity in both reactions. It is believed that the long distance between the polystyrene backbone and the ionic liquid portion of the PSIL allowed the reagents to approach the ionic liquid portion easily.[5] Although the reactivities of PS[hmim][BF_4] and PS-[domim][BF_4] are basically the same by comparison of entries 3 and 4, enties 7 and 8, there is a trend in reactivity on increasing the chain length of the linkers from methyl to dodecyl. But the morphology of PS-[hmim][BF_4] has a better effect than that of PS-[domim][BF_4].

The nucleophilic acetoxylation of bromoalkane **4** with 2-(3-acetoxypropyl)naphthalene using potassium acetate at 90 °C in the presence of 0.5 equivs. of various PS[hmim][X] with different counteranions such as tetrafluoroborate (BF_4), hexafluorophosphate (PF_6), hexafluoroantimonate (SbF_6), triflate (OTf), and acetate (OAc) was next examined to determine what counteranion of the PSIL has the best catalytic activity in a nucleophilic substitution reaction, as shown in entries 1–5 of Table 2. The acetoxylation reaction rate using PS[hmim][BF_4] was faster than that using PF_6, SbF_6 and OTf as the counteranion. Moreover, PS-[hmim][BF_4] worked reasonably well as a catalyst in

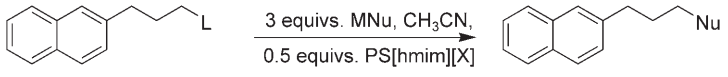
Table 1. Nucleophilic substitution of mesylate **2** with MX using PS[alkylmim][BF_4] of various alkyl linker lengths as a catalyst.[a]



Entry	Ionic resin (0.5 equivs.)[b]	MX	Time [h]	Yield [%][c]	Comments
1	PS[mim][BF_4]	CsF	6.0	93	trace alcohol
2	PS[pmim][BF_4]	CsF	3.5	95	trace alcohol
3	PS[hmim][BF_4]	CsF	3.0	97	-
4	PS[domim][BF_4]	CsF	2.5	96	trace alkene
5	PS[mim][BF_4]	KBr	1.5	97	-
6	PS[pmim][BF_4]	KBr	1.0	97	trace SM
7	PS[hmim][BF_4]	KBr	1.0	99	-
8	PS[domim][BF_4]	KBr	0.8	99	-

[a] All reactions were carried out on a 1.0 mmol reaction scale of mesylate **2** using 3.0 mmol of MX at 100 °C in 3 mL of CH_3CN.
[b] Equivs. denotes the number of moles of the ionic liquid portion, not the PS[hmim][BF_4].
[c] Yield of isolated product.

Table 2. Nucleophilic acetoxylation and fluorination using PS[hmim][X] of various counteranions as a catalyst.[a]



4: L = Br, **2**: L = OMs Nu = OAc, F

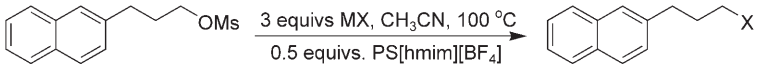
Entry	X	Reactant	MNu	Temperature [°C]	Time [h]	Yield [%][b]
1[c]	BF_4	**4**	KOAc	90	1.0	98
2	PF_6	**4**	KOAc	90	5.5	98
3	SbF_6	**4**	KOAc	90	2.5	99
4	OTf	**4**	KOAc	90	4.0	99
5	OAc	**4**	KOAc	90	1.5	99
6	PF_6	**2**	CsF	100	5.0	94
7	SbF_6	**2**	CsF	100	4.5	96
8	OTf	**2**	CsF	100	6.0	92[d]

[a] Mesylate **2** or bromoalkane **4** (1.0 mmol), MNu (3.0 mmol), and 0.5 equivs. of the ionic portion of PS[hmim][X] were used in 3 mL of CH_3CN.
[b] Yield of isolated product.
[c] Ref.[8]
[d] With 5% alcohol by-product.

comparison with the reaction with PS[hmim][OAc], of which the counteranion, acetate, is a good nucleophile source itself. A comparison of entry 3 in Table 1 and entries 6–8 in Table 2 shows that a PSIL system containing BF_4 as the counteranion is the best catalyst for the fluorination of the mesylate **2** to the fluoroalkane **3** using CsF as well as acetoxylation.

The catalytic activity of PSIL according to its ionic liquid loading in the resin was investigated using nucleophilic fluorination and bromination reactions with PS[hmim][BF_4] at various concentrations, 2.2, 1.2, 0.9, and 0.6 mmol/g, which were prepared with 4.5, 3.0, 1.75 and 0.95 mmol Cl/g of Merrifield peptide resin, respectively, under the same conditions as shown in Table 1 with the exception that the solvent for the reaction mixture, CH_3CN (10 mL), was stirred vigorously. Interestingly, the nucleophilic bromination with KBr using the PS[hmim][BF_4], which has a lower ionic liquid loading (0.6 mmol/g) had a faster reaction rate, converting mesylate **2** to bromoalkane **4** almost quantitatively (entries 6–9). In contrast, the fluorination with CsF using the PS[hmim][BF_4] which has a higher ionic liquid loading (2.2 mmol/g), had a faster reaction rate, as shown in entries 1–4 of Table 3. However, the polystyrene with no ionic liquid portion had no catalytic activity in either reaction. These results

Table 3. Nucleophilic substitution of the mesylate with MX using various loading levels of PS[hmim][BF_4] as a catalyst.[a]



2 **3** X = F
4 X = Br

Entry	Loading level of PSIL (mmol/g) (0.5 equivs.)[b]	MX	Time [h]	Yield of product [%][c] **2**	**3** or **4**
1	2.2	CsF	4.5	5	90
2	1.2	CsF	4.5	16	82
3	0.9	CsF	4.5	17	78
4	0.6	CsF	4.5	29	67
5	0[d]	CsF	4.5	79	14
6	2.2	KBr	110 (min)	-	97
7	1.2	KBr	90 (min)	-	99
8	0.9	KBr	90 (min)	trace	96
9	0.6	KBr	80 (min)	-	98
10	0[d]	KBr	1.0	80	14

[a] All reactions were carried out in 10 mL of CH_3CN for reaction media using lower loading PSIL to be stir.
[b] Equivs. indicates the mole of ionic liquid portion.
[c] Yield of isolated product.
[d] 500 mg of polystyrene resin (1% DVB) was used.

suggest that the fluorination reaction of PSIL is influenced by the matrix effect,[13] while the bromination reaction is influenced by both the matrix and site-isolated effects.[14]

Table 4 compares the swelling properties of some PSIL systems, PS[hmim][Cl], PS[hmim][BF_4], and PS-[hmim][OTf], with the same bead size (100–200 mesh) and approximately the same loading (0.9 mmol/g) in solvents typically used for organic synthesis with the commonly used Merrifield peptide resin (100–200 mesh, 0.9 Cl mmol/g). The immobilization of the ionic liquid at the polystyrene beads gave PS[hmim][BF_4] and PS[hmim][OTf] outstanding swelling constants in polar aprotic solvents such as CH_3CN, DMF, DMSO and acetone compared with the Merrifield resin. Moreover, the extent of PSIL swelling was dependent on its counteranion, i.e., its swelling can be controlled by the counteranion. For example, while PS[hmim][Cl] showed less swelling in the polar aprotic solvent compared with PS[hmim]-[BF_4] and PS[hmim][OTf], it was quite swollen in protic media such as methanol and H_2O/acetone (1:1). It is expected that these favorable characteristics will allow the development of a new type of resin for solid phase organic synthesis. However, the swelling properties of these PSIL systems were unsatisfactory in benzene and ether-type solvents such as THF and 1,4-dioxane in comparison with the Merrifield resin.

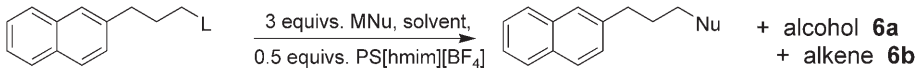
Table 4. Volumes of the swollen polystyrene-supported ionic liquids (mL/g).[a]

Solvent	Merrifield resin	PS[hmim][Cl]	PS[hmim][BF_4]	PS[hmim][OTf]
THF	6.2 (6.4[b])	4.3	4.4	4.7
acetone	2.6	3.0	4.7	4.6
H_2O/acetone (1:1)	1.8	3.6	3.1	3.0
benzene	6.0 (6.6[b])	4.0	3.6	4.0
CH_3CN	1.7 (1.8[c])	2.7	5.2	4.1
DMF	4.6 (4.8[b])	6.0	7.2	6.9
1,4-dioxane	5.8 (6.0[b])	3.9	3.7	4.1
CH_2Cl_2	5.9 (6.0[b])	6.2	5.5	5.9
methanol	1.8 (1.8[c])	4.0	1.9	2.7
DMSO	1.7 (1.8[c])	5.6	6.5	6.2

[a] Volumes were measured in syringes equipped with a sintered frit after equilibrating for 1 h using 100 mg of Merrifield resin (0.9 mmol/g), PS[hmim][Cl] (1.0 mmol/g), PS-[hmim][BF_4] (0.9 mmol/g), or PS[hmim][OTf] (0.9 mmol/g). All resins had dry volumes of approximately 1.5 mL/g.
[b] Ref.[11b]
[c] Ref.[11a]

From a survey of the swelling properties of PSIL, an acetoxylation reaction using KOAc in the presence of PS[hmim][BF_4] was carried out in different solvents with different swelling properties, as shown in entries 1–3 of Table 5. As expected, acetoxylation using DMF as a reaction media showed a significantly faster reaction rate (15 min, entry 1) than when using 1,4-dioxane and benzene (6 h; entry 2 and 14 h; entry 3, respectively), affording product **5** in almost quantitative yield. This reaction involved not only solvent effect itself but also the good site accessibility caused by the swelling of PS[hmim][BF_4]. However, DMF is not good reaction media for fluorination reactions using this CsF and PSIL due to the formation of alcohol **6a** as a by-product, even though the reaction rate was fast, as shown in entry 4 of Table 5. Entries 5 and 6 of Table 5 show that the reactions in 1,4-

Table 5. Nucleophilic acetoxylation and fluorination using PS[hmim][BF_4] in various solvents.[a]



2 L = OMs
4 L = Br

3 Nu = F
5 Nu = OAc

Entry	Solvent	Substrate	MNu	Temperature [°C]	Time [h]	Yield of product [%][b] SM[c]	TM[d]	**6a**	**6b**
1	DMF	**4**	KOAc	90	15 (min)	-	99	-	-
2	1,4-dioxane	**4**	KOAc	90	6.0	-	98	-	-
3	benzene	**4**	KOAc	90	14	-	98	-	-
4	DMF	**2**	CsF	100	1.5	-	68	21	trace
5	1,4-dioxane	**2**	CsF	100	6.0	-	74	17	trace
6	benzene	**2**	CsF	100	6.0	19	65	-	5[e]

[a] Mesylate **2** or bromoalkane **4** (1.0 mmol), MNu (3.0 mmol), and 0.5 equivs. of the ionic portion of PS[hmim][BF_4] were used in 3 mL of solvent.
[b] Isolated yield.
[c] Starting material.
[d] Target material
[e] NMR determined yield.

dioxane and benzene were also slow with the formation of by-products such as alcohol **6a** or alkene **6b**. Overall, CH_3CN was found to be the best reaction media for fluorination using this combination system.

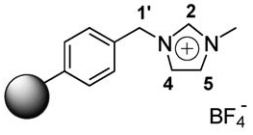
Conclusions

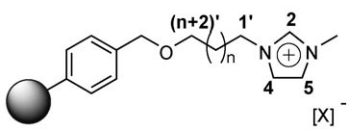
Structurally modified, polymer-supported ionic liquids, which act as highly efficient catalysts for nucleophilic fluorination and other substitution reactions, were prepared in an attempt to develop a more efficient PSIL system by examining their catalytic activity in dependence on the length of the alkyl chain linker, the counteranion and the loading level of ionic liquid portion on the resin. It was found the PSIL with a longer alkyl linker had superior catalytic activity due to the longer distance between the polystyrene backbone and ionic liquid portion. In addition, the PSIL system with tetrafluoroborate (BF_4^-) as the counteranion shows the best catalytic activity compared with PSIL systems with other counteranions. The PSIL system with a higher ionic portion showed better catalytic activity in fluorination reactions due to the matrix effect, while that with a lower ionic portion showed better catalytic activity in bromination reactions, which was attributed to both the matrix and site isolation effects. These PSIL systems absorb polar aprotic solvents and swell considerably, which is a favorable characteristic in new types of resins for other applications. The practical merits and unique characteristics of these PSIL systems may be useful in industrial chemical processes. However, further studies on the application of these PSIL systems to other reactions and the development of a new type of resin by introducing functional sites on the PSIL for solid-phase chemistry will be needed.

Experimental Section

Materials

The ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer at room temperature, and the chemical shifts are reported in δ units (ppm) relative to tetramethylsilane (TMS). The solid-state ^1H, ^{13}C, and ^{19}F NMR spectra were also recorded on a 600 MHz spectrometer at room temperature. TLC analysis was performed using a glass plate with silica gel 60 F_{254}. Flash chromatography was performed using 230–400 mesh silica gel. All other known compounds including the ionic liquids were commercially available.





Polystyrene-Supported 1-Methylimidazolium Tetrafluoroborate (PS[mim][BF_4])

Merrifield peptide resin (4.0 g, 18.0 mmol, 1.0 equiv., 1% DVB, 4.5 mmol Cl/g) in 1-methylimidazole (250 mL) was stirred for more than 24 h at 90 °C. The mixture was then cooled to room temperature. The resin was filtered and washed successively with dichloromethane, methanol, and finally acetone, and added to $NaBF_4$ (15.8 g, 144 mmol, 8 equivs.) in acetone (250 mL). The resulting mixture was stirred for more than 2 days at 25 °C. After filtration, the resin was washed repeatedly with acetone, acetone-water (1:1), water, acetone-water (1:1), acetone, and finally diethyl ether. After drying under high vacuum, PS[mim][BF_4] was obtained and identified by solid state NMR and elemental analysis; yield: 6.1 g. ^{13}C NMR (solid state): $\delta = 37$ (N-CH_3), 41 (aliphatic polystyrene skeleton), 53 (C1′), 130 (C4, C5, aromatic polystyrene skeleton), 137 (C2), 147 (aromatic polystyrene skeleton); ^{19}F NMR (solid state): $\delta = -147$; anal.: N 8.3 (3.0 mmol ionic liquid portion/g), Cl 0.2.

Synthesis of Resin 1a

3-Chloro-1-propanol (17.0 g, 180 mmol, 8 equivs.) was added to a suspension of NaH (60% in mineral oil, 7.2 g, 180 mmol, 8 equivs.) in anhydrous THF at 0 °C, and stirred for 30 min at 0 °C. Merrifield peptide resin (5.0 g, 22.5 mmol, 1.0 equiv., 1% DVB, 4.5 mmol Cl/g) was then added to the reaction mixture, which was followed by the addition of tetra-*n*-butylammonium iodide (8.3 g, 22.5 mmol, 1.0 equiv.). The reaction mixture was then stirred for more than 2 days at 25 °C. After filtration, the resin was washed repeatedly with THF, water, acetone, water, methanol, and finally dichloromethane. After drying under high vacuum, resin **1a** was obtained and identified by solid state NMR and elemental analysis; yield: 5.9 g. ^{13}C NMR (solid state): $\delta = 33$ (C2′), 41–43 (aliphatic polystyrene skeleton and C1′), 67 (C3′), 73 (*O*-benzylic carbon), 128–146 (aromatic polystyrene skeleton); anal.: Cl 13.2 (3.7 mmol Cl/g), N none.

Resin 1b: Resin **1b** was prepared according to the procedure used for resin **1a** except for the use of 6-chloro-1-hexanol instead of 3-chloro-1-propanol. ^{13}C NMR (solid state): $\delta = 27$–34 (C2′–C5′), 41 (aliphatic polystyrene skeleton), 46 (C1′), 72 (*O*-benzylic carbon and C6′), 129–146 (aromatic polystyrene skeleton); anal.: Cl 11.4 (3.2 mmol Cl/g), N none (from 4.5 mmol Cl/g of Merrifield peptide resin); anal.: Cl 5.0 (1.4 mmol Cl/g), N none (from 3.0 mmol Cl/g of Merrifield peptide resin); anal.: Cl 3.4 (1.0 mmol Cl/g), N none. (from 1.75 mmol Cl/g of Merrifield peptide resin); and anal.: Cl 3.1 (0.9 mmol Cl/g), N none (from 0.90 mmol Cl/g of Merrifield peptide resin).

Resin 1c: Resin **1c** was prepared according to the procedure used for resin **1a** except for the use of 12-bromo-1-dodecanol instead of 3-chloro-1-propanol. ^{13}C NMR (solid state): $\delta = 27$–33 (C2′–C11′), 41 (aliphatic polystyrene skeleton), 46 (C1′), 64–72 (*O*-benzylic carbon and C12′), 128–146 (aromatic polystyrene skeleton); anal.: Br 15.9 (1.9 mmol Br/g), N none.

Polystyrene-Supported 1-*n*-Propyl-3-methylimidazolium Chloride (PS[pmim][Cl])

Resin **1a** (3.7 mmol Cl/g; 5.0 g, 18.5 mmol) in 1-methylimidazole (300 mL) was stirred for more than 3 days at 90 °C. The mixture was then cooled to room temperature. The resin was filtered and washed successively with dichloromethane, methanol, acetone-water (1:1), water, methanol, acetone, and finally diethyl ether. After drying under high vacuum, PS[pmim][Cl] was obtained and identified by solid state NMR and elemental analysis; yield: 6.1 g. ^{13}C NMR (solid state): $\delta = 31$ (C2′), 37 (N-CH_3), 40 (aliphatic polystyrene skeleton), 49 (C1′), 68 (C3′), 73 (*O*-benzylic carbon), 125–128 (C4, C5, aromatic polystyrene skeleton), 138 (C2), 146 (aromatic polystyrene skeleton); anal.: N 7.6 (2.7 mmol ionic liquid portion/g), Cl 9.4.

Polystyrene-Supported 1-*n*-Hexyl-3-methylimidazolium Chloride (PS[hmim][Cl])

PS[hmim][Cl] was prepared according to the procedure used for PS[pmim][Cl] except for the use of resin **1b** instead of resin **1a**. ^{13}C NMR (solid state): $\delta = 27$–31 (C2′–C5′), 38 (N-CH_3), 41 (aliphatic polystyrene skeleton), 50 (C1′), 73 (*O*-benzylic carbon and C6′), 130 (C4, C5, aromatic polystyrene skeleton), 138 (C2), 146 (aromatic polystyrene skeleton); anal.: N 7.1 (2.5 mmol ionic liquid portion/g), Cl 8.1. (from 3.2 mmol Cl/g of resin **1b**); anal.: N 3.5 (1.3 mmol ionic liquid portion/g), Cl 4.6 (from 1.4 mmol Cl/g of resin **1b**); anal.: N 2.6 (0.9 mmol ionic liquid portion/g), Cl, 3.2 (from 1.0 mmol Cl/g of resin **1b**); and anal.: N 2.0 (0.7 mmol ionic liquid portion/g), Cl 3.0 (from 0.8 mmol Cl/g of resin **1b**).

Polystyrene-Supported 1-*n*-Dodecyl-3-methylimidazolium Bromide (PS[domim][Br])

PS[domim][Br] was prepared according to the procedure used for PS[pmim][Cl] except for the use of resin **1c** instead of resin **1a**. ^{13}C NMR (solid state): $\delta = 30$–38 (C2′–C11′ and N-CH_3), 40 (aliphatic polystyrene skeleton), 49–80 (C1′, C6′, and *O*-benzylic carbon), 126 (C4, C5, aromatic polystyrene skeleton), 138 (C2), 146 (aromatic polystyrene skeleton); anal.: N 5.3 (1.9 mmol ionic liquid portion/g), Br 15.7.

Polystyrene-Supported 1-*n*-Propyl-3-methylimidazolium Tetrafluoroborate (PS[pmim][BF_4])

$NaBF_4$ (13.0 g, 118 mmol, 8 equivs.) was added to 5.5 g (14.8 mmol, 1 equiv.) of PS[pmim][Cl] (2.7 mmol ionic liquid portion/g) in acetone (250 mL), and the mixture was stirred for more than 2 days at 25 °C. After filtration, the resin was washed repeatedly with acetone, acetone-water (1:1), water, acetone-water (1:1), acetone, and finally diethyl ether. After drying under high vacuum, PS[pmim][BF_4] was obtained and identified by solid state NMR and elemental analysis; yield: 6.1 g. ^{13}C NMR (solid state): $\delta = 30$ (C2′), 36 (N-CH_3), 41–50 (aliphatic polystyrene skeleton and C1′), 68 (C3′), 72 (*O*-benzylic carbon), 129 (C4, C5, aromatic polystyrene skeleton), 137 (C2), 146 (aromatic polystyrene skeleton); ^{19}F NMR (solid state): $\delta = -147$; anal.: N 6.8 (2.4 mmol ionic liquid portion/g), Cl 0.2.

Polystyrene-Supported 1-*n*-Hexyl-3-methylimidazolium Tetrafluoroborate (PS[hmim][BF_4])

PS[hmim][BF_4] was prepared according to the procedure used for PS[pmim][BF_4] except for the use of PS[hmim][Cl] instead of PS[pmim][Cl]. ^{13}C NMR (solid state): $\delta = 27$–31 (C2′–C5′), 37 (N-CH_3), 41 (aliphatic polystyrene skeleton), 50 (C1′), 72 (*O*-benzylic carbon and C6′), 128 (C4, C5, aromatic polystyrene skeleton), 137 (C2), 146 (aromatic polystyrene skeleton); ^{19}F NMR (solid state): $\delta = -148$; anal.: N 6.2 (2.2 mmol ionic liquid portion/g), Cl, 0.1 (from 2.5 mmol ionic portion/g of PS[hmim][Cl]); anal.: N 3.3 (1.2 mmol ionic liquid portion/g), Cl 0.4 (from 1.3 mmol ionic portion/g of PS[hmim][Cl]); anal.: N 2.6 (0.9 mmol ionic liquid portion/g), Cl 0.2 (from 0.9 mmol ionic portion/g of PS[hmim][Cl]); and anal.: N 1.7 (0.6 mmol ionic liquid portion/g), Cl 0.2 (from 0.7 mmol ionic portion/g of PS[hmim][Cl]).

Polystyrene-Supported 1-*n*-Dodecyl-3-methylimidazolium Tetrafluoroborate (PS[domim][BF_4])

PS[domim][BF_4] was prepared according to the procedure used for PS[pmim][BF_4] except for the use of PS[domim][Br] instead of PS[pmim][Cl]. ^{13}C NMR (solid state): $\delta =$ 30–36 (C2′–C11′ and N-CH_3), 40 (aliphatic polystyrene skeleton), 50–80 (C1′, C6′, and *O*-benzylic carbon), 129 (C4, C5, aromatic polystyrene skeleton), 137 (C2), 146 (aromatic polystyrene skeleton); ^{19}F NMR (solid state): $\delta = -147$; anal.: N 5.4 (1.9 mmol Cl/g), Br 0.6.

Polystyrene-Supported 1-*n*-Hexyl-3-methylimidazolium Hexafluorophosphate (PS[hmim][PF_6])

PS[hmim][PF_6] was prepared according to the procedure used for PS[hmim][BF_4] except for the use of $NaPF_6$ instead of $NaBF_4$. ^{13}C NMR (solid state): $\delta = 26$–30 (C2′–C5′), 36 (N-CH_3), 41 (aliphatic polystyrene skeleton), 50 (C1′), 72 (*O*-benzylic carbon and C6′), 128 (C4, C5, aromatic polystyrene skeleton), 137 (C2), 146 (aromatic polystyrene skeleton); ^{19}F NMR (solid state): $= \delta\ -69$; anal.: N 6.0 (2.1 mmol ionic liquid portion/g), Cl 0.5.

Polystyrene-Supported 1-*n*-Hexyl-3-methylimidazolium Hexafluoroantimonate (PS[hmim][SbF_6])

PS[hmim][SbF_6] was prepared according to the procedure used for PS[hmim][BF_4] except for the use of $NaSbF_6$ instead of $NaBF_4$. ^{13}C NMR (solid state): $\delta = 26$–30 (C2′–C5′), 37 (N-CH_3), 41 (aliphatic polystyrene skeleton), 50 (C1′), 72 (*O*-benzylic carbon and C6′), 129 (C4, C5, aromatic polystyrene skeleton), 137 (C2), 146 (aromatic polystyrene skeleton); ^{19}F NMR (solid state): $\delta = -110$; anal.: N 4.6 (1.6 mmol ionic liquid portion/g), Cl 0.4.

Polystyrene-Supported 1-*n*-Hexyl-3-methylimidazolium Triflate (PS[hmim][OTf])

PS[hmim][OTf] was prepared according to the procedure used for PS[hmim][BF_4] except for the use of KOTf instead of $NaBF_4$. ^{13}C NMR (solid state): $\delta = 27$–31 (C2′–C5′), 37 (N-CH_3), 41 (aliphatic polystyrene skeleton), 52 (C1′), 72 (*O*-benzylic carbon and C6′), 129 (C4, C5, aromatic polystyr-

ene skeleton), 138 (C2), 147 (aromatic polystyrene skeleton); ^{19}F NMR (solid state): $\delta = -77$; anal.: N 5.8 (2.1 mmol ionic liquid portion/g), Cl 0.2.

Polystyrene-Supported 1-*n*-Hexyl-3-methylimidazolium Acetate (PS[hmim][OAc])

PS[hmim][OAc] was prepared according to the procedure used for PS[hmim][BF_4] except for the use of NaOAc instead of $NaBF_4$. ^{13}C NMR (solid state): $\delta = 26$–30 (C2′–C5′), 37 (N-CH_3), 41 (aliphatic polystyrene skeleton), 50 (C1′), 71 (*O*-benzylic carbon and C6′), 124–128 (C4, C5, aromatic polystyrene skeleton), 138 (C2), 147 (aromatic polystyrene skeleton); anal.: N 6.4 (2.3 mmol ionic liquid portion/g), Cl 0.2.

2-(3-Hydroxypropyl)naphthalene (6a)

Butyllithium (105.4 mmol) in hexane (42.0 mL) was added dropwise over 40 min to a well stirred solution of 2-methylnaphthalene (10.0 g, 70.4 mmol) and potassium *tert*-butoxide (11.8 g, 105.4 mmol) in dried THF (250 mL) at 0 °C under a nitrogen atmosphere. After 1 h at 0 °C, 1-bromo-2-*tert*-butyldimethylsilyloxyethane (25.2 g, 105.4 mmol) was added to the mixture portionwise at 0 °C. The reaction mixture was stirred at 25 °C for 5 h, poured into water (350 mL) and extracted from the aqueous phase with EtOAc (350 mL × 3). The organic layer was dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by short flash column chromatography (100 % EtOAc) to obtain the crude product. The solvent was evaporated under reduced pressure. Tetrabutylammonium fluoride (33.3 g, 105.4 mmol) was added to the crude product in THF (300 mL), and stirred at 25 °C for 12 h. The reaction mixture was dissolved in water (300 mL) and extracted from the aqueous phase with EtOAc (300 mL × 3). The organic layer was dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by flash column chromatography (30 % EtOAc/hexane) to afford 2-(3-hydroxypropyl)naphthalene (**6a**) as a white solid; yield: 10.5 g (56.3 mmol, 80 %); mp 41.2–41.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.41$ (s, 1H), 1.96–2.03 (m, 2H), 2.89 (t, $J = 7.6$ Hz, 2H), 3.72 (t, $J = 6.4$ Hz, 2H), 7.34–7.37 (m, 1H), 7.41–7.48 (m, 2H), 7.65 (s, 1H), 7.77–7.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 32.17$, 34.05, 62.23, 125.16, 125.92, 126.40, 127.24, 127.37, 127.58, 127.94, 131.98, 133.58, 139.28; MS (EI): $m/z = 186$ (M^+), 142 (100); HR-MS (EI): $m/z = 186.1049$, calcd. for $C_{13}H_{14}O$ (M^+): 186.1045.

2-(3-Methanesulfonyloxypropyl)naphthalene (2) as a Starting Material

Triethylamine (9.0 mL, 64.4 mmol) and methanesulfonyl chloride (5.0 mL, 64.4 mmol) were added to alcohol **6a** (10.0 g, 53.6 mmol) in dichloromethane (250 mL) at 0 °C. The mixture was stirred at 25 °C for 6 h, and evaporated under reduced pressure to remove the dichloromethane. The residue was dissolved in water (300 mL) and extracted from the aqueous phase with EtOAc (300 mL × 3). The organic layer was dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by flash column chromatography (20 % EtOAc/hexane) to give 2-(3-methanesulfonyloxypropyl)naphthalene (**2**) as a colorless oil; yield: 11.6 g (43.9 mmol, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.14$–2.21 (m, 2H), 2.93 (t, $J = 7.6$ Hz, 2H), 2.99 (s, 3H), 4.26 (t, $J = 6.4$ Hz, 2H), 7.32–7.35 (m, 1H), 7.44–7.50 (m, 2H), 7.65 (s, 1H), 7.79–7.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 30.45$, 31.59, 37.24, 69.10, 125.39, 126.07, 126.62, 126.92, 127.36, 127.57, 128.18, 132.06, 133.48, 137.68; MS (EI): $m/z = 264$ (M^+), 168 (100), 141; HR-MS (EI): $m/z = 264.0831$, calcd. for $C_{14}H_{16}O_3S$ (M^+): 264.0820.

Typical Procedure for Fluorination

CsF (454 mg, 3 mmol) was added to a mixture of mesylate **2** (264 mg, 1.0 mmol), PS[hmim][BF_4] (227 mg, 0.5 mmol) and acetonitrile (3 mL) in a reaction vial. The mixture was stirred for more than 3.0 h at 100 °C. The reaction time was determined by TLC. The reaction mixture was filtered and washed with ethyl acetate. The filtrate was evaporated under reduced pressure. Short flash column chromatography (20 % EtOAc/hexanes) of the filtrate afforded 2-(3-fluoropropyl)naphthalene (**3**) as a colorless oil; yield: 182 mg (0.97 mmol, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.07$–2.20 (m, 2H), 2.95 (t, $J = 7.6$ Hz, 2H), 4.52 (dt, $J = 47.6$, 6.0 Hz, 2H), 7.37–7.39 (m, 1H), 7.45–7.53 (m, 2H), 7.68 (s, 1H), 7.84–7.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 31.41 (d, $J = 5.4$ Hz), 31.89 (d, $J = 19.7$ Hz), 83.05 (d, $J =$ 163.7 Hz), 125.26, 125.97, 126.57, 127.17, 127.40, 127.58, 128.02, 132.03, 133.57, 138.54; MS (EI): $m/z = 188$ (M^+), 141 (100), 115; HRMS (EI): $m/z = 188.1001$, calcd. for $C_{13}H_{13}F$ (M^+): 188.1001.

Typical Procedure for Bromination

Potassium bromide (357 mg, 3 mmol) was added to a mixture of mesylate **2** (264 mg, 1.0 mmol), PS[domim][BF_4] (263 mg, 0.5 mmol) and acetonitrile (3 mL) in a reaction vial. The mixture was stirred over 0.8 h at 100 °C. The reaction time was determined by TLC. The reaction mixture was filtered and washed with ethyl acetate. The filtrate was evaporated under reduced pressure. Short flash column chromatography (20 % EtOAc/hexanes) of the filtrate afforded 2-(3-brompropyl)naphthalene (**4**) as a colorless oil; yield: 246 mg (0.99 mmol, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.24$–2.31 (m, 2H), 2.97 (t, $J = 7.2$ Hz, 2H), 3.44 (t, $J = 6.6$ Hz, 2H), 7.34–7.37 (m, 1H), 7.44–7.51 (m, 2H), 7.67 (s, 1H), 7.80–7.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 33.09$, 33.97, 34.20, 125.31, 126.01, 126.74, 127.12, 127.40, 127.58, 128.09, 132.07, 133.53, 137.96; MS (EI): $m/z = 250$ (M^+), 248 (M^+), 141, 115; HR-MS (EI): $m/z = 248.0200$, calcd. for $C_{13}H_{13}{}^{79}Br$ (M^+): 248.0201.

Typical Procedure for Acetoxylation

Potassium acetate (294 mg, 3 mmol) was added to a mixture of 2-(3-bromopropyl)naphthalene (**4**, 249 mg, 1.0 mmol), PS-[hmim][OAc] (217 mg, 0.5 mmol) and acetonitrile (3 mL) in a reaction vial. The mixture was stirred at 90 °C for 1.5 h. The reaction time was determined by TLC. The reaction mixture was filtered and washed with ethyl acetate. The filtrate was evaporated under reduced pressure. Short flash column chromatography (50 % EtOAc/hexanes) of the filtrate afforded 2-(3-acetoxypropyl)naphthalene as a colorless oil; yield: 226 mg (0.99 mmol, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.04$–2.11 (m, 5H), 2.88 (t, $J = 7.6$ Hz, 2H), 4.16

(t, $J=6.6$ Hz, 2H), 7.34–7.36 (m, 1H), 7.45–7.50 (m, 2H), 7.65 (s, 1H), 7.79–7.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); $\delta=20.91$, 30.02, 32.26, 63.79, 125.19, 125.92, 126.39, 127.06, 127.35, 127.54, 127.96, 131.98, 133.52, 138.62, 171.09; MS (EI): $m/z=228$ (M^+), 168 (100), 141, 115; HR-MS (EI): $m/z=228.1156$, calcd. for $C_{15}H_{16}O_2$ (M^+): 228.1150.

Procedure for Measuring the Swelling Volume of the PSIL Systems.[11a]

The corresponding dry resin (100 mg) was added to a 1.0 mL syringe equipped with a polypropylene filter. A plunger was inserted after adding the appropriate solvent to the syringe (1 mL). The resin and solvent were mixed well by vortexing the mixture for 30 s, and allowing it to stand for 1 h for equilibration. The mixture was then vortexed again, extra solvent was removed using another syringe *via* a Luer-lock connector, and the volume of the swollen resin bead was recorded. In their dry state, the volume of all resins was approximately 1.5 mL/g. The level of swelling did not change significantly during the 24 h observation period.

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