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Pyrene-Tagged Alcoholic Ionic Liquids as Phase Transfer Catalysts for Nucleophilic Fluorination

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Functional group−activity relationships of pyrene-tagged ionic liquid (PTIL)-based organocatalysts for nucleophilic fluorination using alkali metal fluorides (MFs) are described, which demonstrate that the pyrene, oligoether and alcohol moieties on the imidazolium ring are vital for efficient catalysis. Further investigation of these findings led to the discovery of new strategy, which showed superior catalyst separation process, *i.e.*, catalyst is effortlessly separated from the reaction mixture using reduced graphene oxide. The catalytic efficiency of the PTIL as a phase transfer catalyst was demonstrated by the high conversion of the reactants up to 98% fluorinated yield using MFs in CH_3CN or *t*-amyl alcohol. Importantly, the catalyst not only enhanced the reactivity of bimolecular nucleophilic substitutions (S_N2) within a short reaction time and reduces the formation of by-products but also affords high yield with easy isolation and separation under mild conditions.

Keywords: Ionic liquid, Fluorination, Phase transfer catalyst, Pyrene, Graphene oxide

Introduction

Due to the increase in environmental consciousness in chemical synthesis, the challenge for a sustainable environment calls for clean procedures that avoid the use of harmful chemicals. In recent years, ionic liquids (ILs) have attracted increasing interest and been successfully used for different purposes in various branches of pure and applied sciences as environmentally benign solvents and catalysts such as gas absorption,[1] liquid separation,[2] heat transfer fluids,[3] lubricants,[4] electrolytes,[5] and catalysts.[6] The most attractive features of ILs are organic salts that are composed entirely of ions and their negligible vapor pressure, as well as the ability to tune their physicochemical properties by varying the ion structure. These key features along with other characteristics make them excellent candidates for organocatalysis such as fluorination,[7] esterification,[8] aldol condensation,[9] polymerization,[10] dimerization,[11] oxidation,[12] and Knoevenagel condensation.[13] In particular, much attention is currently being focused on organic reactions with ILs as organocatalysts and many chemical reactions including bimolecular nucleophilic substitutions (S_N2) have been performed in ILs with excellent outcomes.[14,7] Recently, Chi *et al.* reported a *t*-alcohol-functionalized IL. Also, our group developed oligoether-functionalized imidazolium-based IL, which provided remarkable reactivity and selectivity in nucleophilic fluorination.[15]

Various ILs can be synthesized in many ways and most consist of heterocyclic organic molecules, such as imidazole, pyrrolidine, piperidine, pyridine, etc. Moreover, imidazolium-based ILs perform well as phase transfer catalyst (PTC) in S_N2 reactions (including fluorination). Unfortunately, most of these catalysts are still difficult to separate from the reaction mixture.[14] In particularly, if the product and IL show partial mutual solubility, the separation is much more complicated and satisfactory results were obtained in only limited cases.[16] Importantly, the catalytic activity, selectivity, and catalyst separation strategies are also important for the large-scale synthesis. Therefore, the development of active and typical separable catalysts for the S_N2 fluorination under mild conditions is highly desirable and a hot topic in both green chemistry and current organic synthesis.

As the unique properties of the fluorine atom,[17] synthesis of fluorinated biomolecules has attracted a lot of attention, and make it significant in pharmaceutical,[18,19,7b] agrochemical,[20] and material sciences.[21] However, nature produces only a limited number of structurally simple fluorine-containing natural molecules[22-24] that can potentially be used in medicinal chemistry and material sciences as fluorinated starting materials. Therefore, developments in these fields are closely related to the development of practical, selective, cost-effective, and efficient methodologies for the formation of C—F bonds onto biomolecules in the appropriate procedure. In this study, oligoethylene glycol or *t*-alcohol functionalized PTILs were synthesized and used as PTC for the nucleophilic fluorination of various substrates in CH_3CN or *t*-amyl alcohol. We studied in detail the roles of activity of pyrene, oligoether, and alcohol moieties attached to PTIL1 as well as the role of pyrene moiety for the separation of catalyst after reaction. It is well known that metal cations can bind with pyrene moiety

through the cation-π interaction[25,26] and they can form chelate with oligoether,[15b] and at the same time fluoride can make H-bonding with alcohol moiety,[15] thus metal fluoride (MF) Coulomb (electrostatic) attraction becomes weak and fluoride can work easily in fluorination reactions (Figure 1). On the other hand, the presence of pyrene moiety is interesting and desirable from a separation point of view due to noncovalent bonding (NCB) effect with graphene.[26,27]

Experimental

Synthesis of Pyrene-Tagged Ionic Liquid PTIL1. 4-(1-pyrenyl)butyl mesylate (**2**) was synthesized according to the literature procedure.[28] Typically, a solution of 1-pyrene-butanol (**1**) (0.78 g, 2.85 mmol), methylene chloride (20 mL) and triethylamine (1.0 g, 9.89 mmol) were cooled in an ice bath, then methane sulfonyl chloride (0.5 g, 4.38 mmol) was added dropwise under constant stirring. The mixture was stirred overnight and filtered off, then the solution was washed with sodium bicarbonate and brine, respectively. The organic layer was dried over sodium sulfate and evaporated to dryness at reduced pressure. The crude product was purified by column chromatography on silica gel using 50% mixture of dichloromethane and petroleum ether to afford the resulting compound **2** as a colorless oil (0.97 g, 98%). Further, 17-(1*H*-imidazol-1-yl)-3,6,9,12,15-pentaoxaheptadecan-1-ol (**3**) was synthesized from 17-bromo-3,6,9,12,15-pentaoxaheptadecan-1-ol and imidazole in acetone as described our earlier reported[7a] and was used as a precursor for synthesizing PTIL1. Subsequently, **3** (0.66 g, 2.0 mmol) was added drop-wise to the solution of **2** (0.70 g, 2.0 mmol) in CH_3CN (18 mL). The reaction mixture was stirred at 90°C for 24 h and evaporated under reduced pressure to remove CH_3CN. The residue was repeatedly washed with diethyl ether (10 mL × 5) and dried under high vacuum for 24 h at room temperature

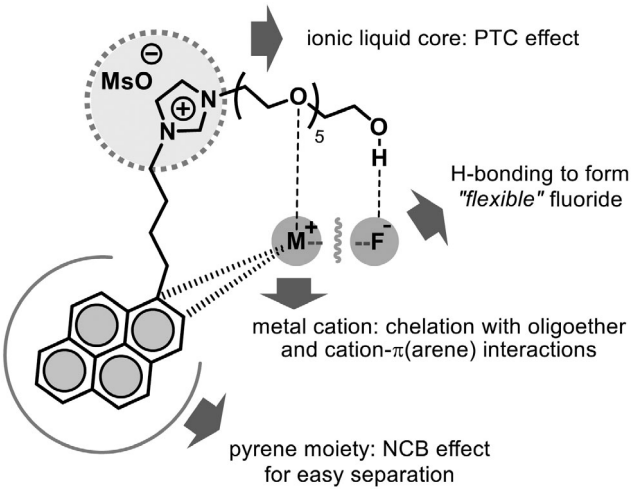


Figure 1. Concept of pyrene-tagged hexaethylene glycolic ionic liquids (PTIL1) as a phase transfer catalyst.

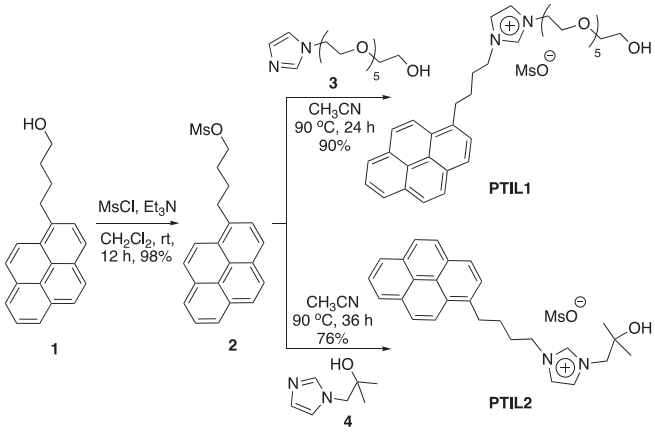
to afford 0.79 g (90%) of PTIL1 as a light yellow thick liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86–2.00 (m, 4H), 2.77 (s, 3H), 3.43–3.61 (m, 22H), 3.78 (t, J = 4.0 Hz, 2H), 4.22 (t, J = 8.0 Hz, 2H), 4.45 (t, J = 4.0 Hz, 2H), 7.10 (s, 1H), 7.55 (s, 1H), 7.81–8.19 (m, 9H), 9.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 29.8, 32.4, 39.5, 49.5 (d, J = 9.0 Hz), 61.2, 69.9, 70.0, 70.0, 70.1, 70.2, 70.2, 70.3, 70.4, 70.4, 70.4, 70.5, 121.0, 123.1, 123.5, 124.7, 124.7, 124.8, 124.9124.9, 125.8, 126.7, 127.3, 127.3, 127.4, 128.5, 129.9, 130.7, 131.3, 135.4, 137.5; IR (KBr) cm^{-1}: 3436 (w), 3033 (w), 2926 (w), 1603 (m), 1559 (s), 1194 (s), 1057 (s), 841 (s), 770 (m), 535 (m). HRMS (FAB TOF): *m/z* calcd for $C_{35}H_{45}N_2O_6$: $(M\text{-}X)^+$ 589.3278, found 589.3282; (X = [MsO]).

Synthesis of Pyrene-Tagged Ionic Liquid PTIL2. 1-(1*H*-imidazol-1-yl)-2-methylpropan-2-ol (**4**) was synthesized according to the literature procedure[15a] and was used as a precursor for synthesizing PTIL2. Subsequently, **4** (0.35 g, 2.5 mmol) was added dropwise to the solution of **2** (0.88 g, 2.5 mmol) in CH_3CN (20 mL). The reaction mixture was stirred at 90°C for 36 h and evaporated under reduced pressure to remove solvent. Finally, the residue was repeatedly washed several times with diethyl ether and dried under high vacuum for 24 h at 25°C to afford 0.90 g (76%) of PTIL2 as a colorless thick liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 6H), 1.77–2.12 (m, 4H), 2.74 (s, 3H), 3.31 (t, J = 7.2 Hz, 2H), 4.05–4.11 (m, 4H), 5.00 (s, 1H), 6.94 (s, 1H), 7.15 (s, 1H), 7.79 (s, 1H), 7.95–8.14 (m, 8H), 9.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 26.4, 27.8, 29.5, 32.3, 39.6, 49.6, 59.5, 68.4, 120.2, 121.4, 122.6, 123.0, 123.6, 124.8, 125.0, 125.9, 126.7, 127.2, 127.4, 127.5, 128.5, 129.9, 130.7, 131.3, 135.2, 138.1, 138.5; IR (KBr) cm^{-1}: 3417 (w), 3033 (w), 2925 (w), 1602 (m), 1558 (s), 1193 (s), 1058 (s), 840 (s), 771 (m), 536 (m); HRMS (FAB TOF): *m/z* calcd for $C_{27}H_{29}N_2O$: $(M\text{-}X)^+$ 397.2280, found 397.2281; (X = [MsO]).

General Procedure for the S_N2 Fluorination Reaction. Cesium fluoride (CsF, 456 mg, 3 mmol) was added to the mixture of a substrate (1.0 mmol) and PTIL1 (274 mg, 0.4 mmol) and solvent (4 mL) were added in a reaction vial. The reaction mixture was stirred at 100°C, and the reaction time was determined by monitoring thin layer chromatography (TLC). After completion of the reaction it was diluted with CH_2Cl_2 and then added reduced graphene oxide (rGO). The mixture was sonicated for 20 min and stirred for 1 h at 25°C. The organic layer was separated from mixture by simple filtration, and evaporated under reduced pressure. The crude reaction product was purified using column chromatography on silica-gel (230–400 mesh) afforded the corresponding products.

Results and Discussion

The multifunctional organocatalysts, PTILs were designed and prepared as shown in Scheme 1. First, 4-(1-pyrenyl) butyl mesylate (**2**) was synthesized from 4-(pyren-1-yl)



Scheme 1. Synthesis of pyrene-tagged ionic liquids: PTIL1 and PTIL2.

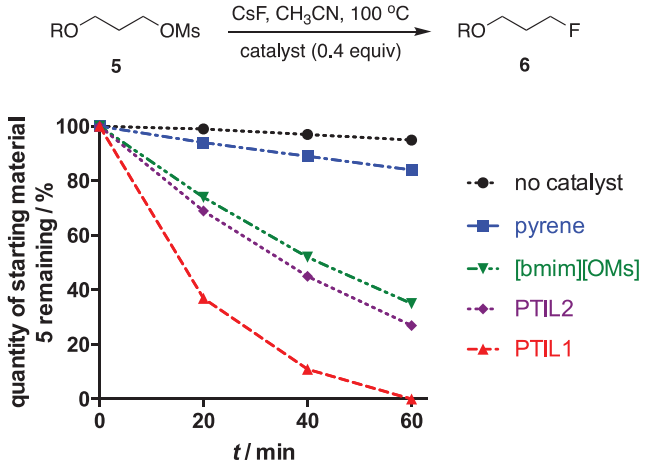


Figure 2. Nucleophilic fluorination of **5** with CsF in CH_3CN catalyzed by PTIL1, PTIL2, [bmim][OMs], pyrene, or without any catalyst. *R* = 4-nitrophenyl.

butan-1-ol (**1**) with methanesulfonyl chloride according to literature procedure.[28] Simultaneously, 17-(1*H*-imidazol-1-yl)-3,6,9,12,15-pentaoxaheptadecan-1-ol (**3**) was treated with **2** to afford pyrene-tagged ionic liquid, PTIL1, in 90% yield. Further, the treatment of 1-(1*H*-imidazol-1-yl)-2-methylpropan-2-ol (**4**) with **2** at 90°C for 36 h to obtain PTIL2 in 76% yield.

The catalytic activity of the prepared catalyst PTIL1 was tested with a representative set of primary and secondary mesylate and halide substrates. Initially, to investigate the catalytic activity of PTIL1 and PTIL2, a series of controlled experiments were carried out under exactly the same reaction conditions. Typically, the S_N2 fluorination of 3-(4-nitrophenoxy)propyl mesylate (**5**) was performed by using 3 equiv of CsF in the presence of the catalyst (0.4 equiv) at 100°C for 1 h in CH_3CN and the results are summarized in Figure 2. The nucleophilic fluorination in the absence of any catalyst or in the presence of only

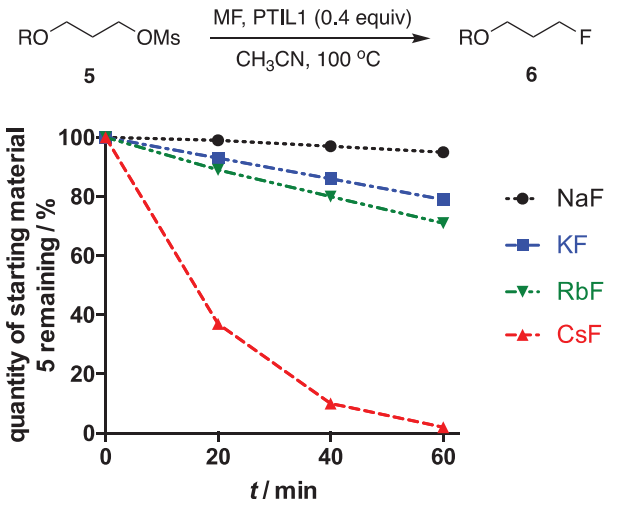


Figure 3. Nucleophilic fluorination of **5** with different MFs in CH_3CN catalyzed by PTIL1. *R* = 4-nitrophenyl.

pyrene hardly proceeded, whereas the same reaction condition in the presence of the commercial IL [bmim][OMs] (bmim =1-*n*-butyl-3-methylimidazolium) proceeded smoothly. Importantly, the use of pyrene substituted alcohol-functionalized ILs such as PTIL1 and PTIL2 showed much faster reaction rates than the use of [bmim][OMs] under the defined same reaction condition. According to literatures this may be due to the presence of pyrene moiety[26] and alcohol functional group[15] on ILs. Furthermore, PTIL1 contains oligoether moiety with same IL core and showed higher catalytic activity than PTIL2. These results were highly consistent with our hypothesis depicted in Figure 1, demonstrating that metal-cation-π interactions, the formation of "*flexible*" fluoride,[15] and the metal cation chelation along with oligoethers play a crucial role in enhancing the rate of reaction.

In order to obtain the optimized catalytic performance, S_N2 fluorination reactions were carried out with various MFs and different molar ratios of catalyst in a wide range of solvent systems. Initially, we performed the fluorination of **5** with various amounts of catalyst for screening the loading. As shown in Figure S1 (see Supporting information), the yield of product gradually increased with an increase of loading amount of catalyst (0–0.4 equiv). In addition, the reaction was completed within 1 h in the presence of 0.4 equiv of PTIL1 in CH_3CN. Therefore, 0.4 equiv loading of catalyst was determined to be the optimal loading for the S_N2 fluorinations. Subsequently, in a quick survey of MFs, CsF gave the best result whereas other MFs such as rubidium fluoride (RbF) and potassium fluoride (KF) demonstrated very low (29% or less) activities. Moreover, NaF was fully inactive (Figure 3).

Furthermore, we investigated the effect of solvent to obtain higher efficiency for the S_N2 fluorination reactions (Figure 4). PTIL1 showed poor catalytic activity (11% or less) when 1,4-dioxane was used as the solvent.

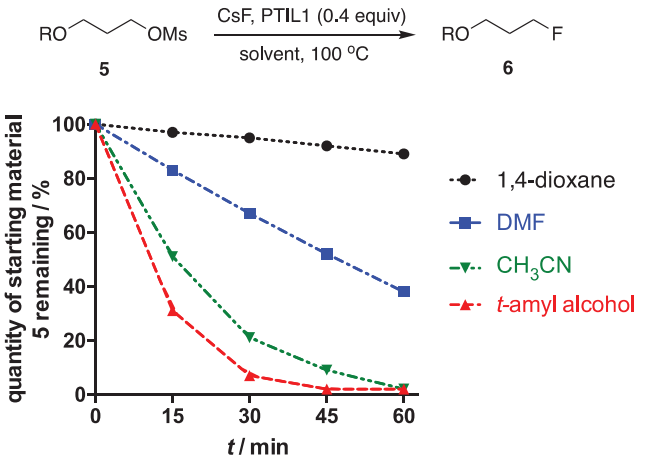


Figure 4. Nucleophilic fluorination of **5** using CsF in different solvent in the presence of PTIL1. *R* = 4-nitrophenyl.

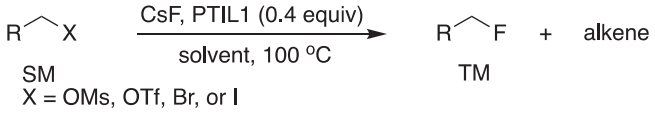
Dimethylformamide (DMF) was not good solvent in this reaction using PTIL1 compared with CH_3CN. On the other hand, in *t*-amyl alcohol medium, the fluorination had a significantly faster rate, affording the desired product **6** in excellent yield without the formation of any by-products under the defined reaction condition. The results showed that *t*-amyl alcohol along with CH_3CN were the best solvents for the catalytic activity of the solvent used. With these optimized results in hand, the reactions of various substrates with CsF were performed.

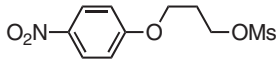
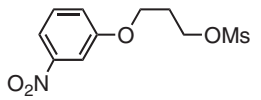
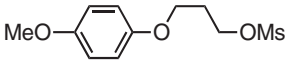
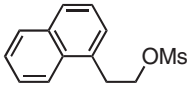
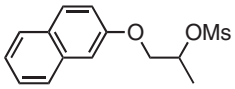
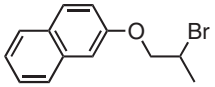
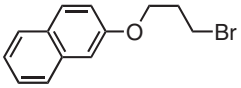
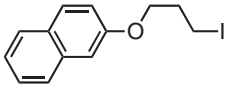
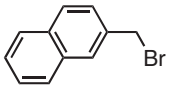
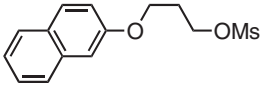
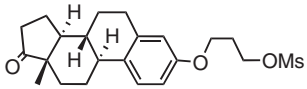
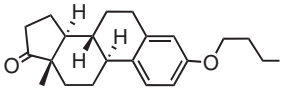
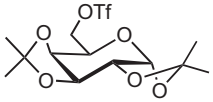
In order to extend the scope of the S_N2 fluorination catalyzed by PTIL1, we performed fluorination of various primary/secondary mesylate and halide substrates using CsF at 100°C (Table 1). In most cases, the fluorination reactions of primary mesylate substrates, such as 3-(4-nitrophenoxy)propyl, 3-(3-nitrophenoxy)propyl, 3-(4-methoxyphenoxy)propyl, and 3-(naphthalen-2-yloxy)propyl mesylate, proceeded smoothly to give the corresponding products in good yield in polar aprotic CH_3CN (entries 1–3 and 10; method A). However, the reaction of a secondary mesylate substrate demonstrated somewhat poor yield and chemoselectivity in CH_3CN (entry 5; method A). For further study on the influence of PTIL1 on the chemoselectivity in the S_N2 fluorination in CH_3CN, the fluorination was conducted using the base-sensitive substrate such as 2-(2-mesyloxyethyl)naphthalene. This reaction afforded a fluorinated product in only 50% yield along with 48% alkene by-product in CH_3CN (entry 4; method A). Furthermore, a bioactive molecule such as fluoropropyl estrone was prepared from the fluorination reaction of the corresponding estrone-mesylate substrate using CsF in excellent yield (97%) in the presence of PTIL1 (entry 11; method A) whereas the same reaction in the presence of a pyrene-tagged methylimidazolium mesylate (PIL), which has no hexaethylene glycolic moiety, proceeded slightly slow, affording the product in 91% yield with 6% of alkene by-product (entry 11; method C).[26] This result showed the hexaethylene glycolic moiety of PTIL1 could enhanc its catalytic activity as well as chemoselectivity in the reaction. In addition, the fluoro-sugar molecule is known to be difficult to extract from the ILs due to their solubility in the liquid salts. The reaction of a triflate sugar substrate using CsF in the presence of PTIL1 not only proceeded in a high yield, affording the fluoro-sugar products, but also allowed the products to be isolated and purified easily (entry 13).

Halides are known to be more challenging substrates for nucleophilic fluorination and demonstrated low or negligible reactivity under identical reaction conditions. Hence, we also performed the S_N2 fluorination of various iodide and bromide substrates using CsF in the presence of PTIL1 (entries 6–9 and 12). According to literature, the transformation of secondary alkyl bromide into the fluoride using the conventional PTC is very difficult because of a competing β-elimination side reaction.[29,30] Therefore, the fluorination of a secondary alkyl bromide such as 2-(2-bromopropoxy)naphthalene afforded the desired secondary alkyl fluoride product in only 27% with alkene (73%) in CH_3CN (entry 6; method A). The primary alkyl bromide substrates such as 2-(bromomethyl) naphthalene and 3-*O*-(3-bromopropyl)estrone proceeded smoothly to give the corresponding product in good yields (entries 9 and 12, respectively) whereas the same reaction of 2-(3-bromopropoxy)naphthalene showed a somewhat a low chemoselectivity and poor yield in CH_3CN (61%, entry 7; method A). The reaction of a primary iodo-substrate showed similar trends (50% yield, entry 8; method A). The synergistic effect of PTIL catalyst with protic *t*-alcohol solvent using *t*-amyl alcohol allowed the fluorination (in particular, using base-sensitive substrates) to proceeded highly chemoselectively enhancing reaction rate significantly (Table 1, method B).[29,30,15b] Under *t*-amyl alcohol medium, the reactions of all substrates proceeded much more selectively and faster, affording the corresponding fluoro-products (up to 98% isolated yield) in the presence of PTIL (Table 1, entries 1–8; method B). In particular, 2-(2-fluoroethyl)naphthalene could prepared in 94% yield along with only 5% alkene in *t*-amyl alcohol from the base-sensitive 2-(2-mesyloxyethyl)naphthalene. In a similarly manner, the primary and secondary halides could be converted to the corresponding fluoro-products in excellent yield by this fluorination protocol (entries 6–8, method B). In addition, PTIL1 was successfully removed by the interaction with commercially available rGO from the reaction mixture including the fluoro-product (even fluoro-products containing naphthalene).

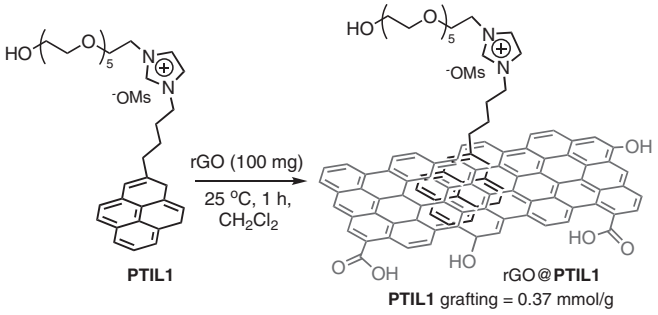
In the view of green chemistry, we then turned our attention to the separation of catalyst after reaction under mild condition. The crucial issue in an IL-based catalyst is the possibility that some ILs can mixed with products that can be difficult to separate. Herein, we report an efficient and convenient procedure for separation of ILs using rGO. The PTIL1 was anchor on the surface of rGO through noncovalent interaction.[26] Initially, we studied the PTIL1 grafting capacity on the graphitic surface. The exact grafting amount of PTIL1 onto rGO was 0.37 mmol/g measured by elemental analysis (Scheme 2). This result

Table 1. Nucleophilic fluorinations of the various substrates using CsF in the presence of PTIL1 as a catalyst.[a]



Entry	SM	Method[a]	Time (h)	Yield (%) TM[b]	Alkene[c]
1		A	1	91	8
		B	0.5	98	—
2		A	1	87	11
		B	0.5	98	—
3		A	1	93	5
		B	0.5	97	—
4		A	2	50	48
		B	0.6	94	5
5		A	2.5	85	13
		B	1.5	97	—
6		A	4	25	73
		B	1.5	98	—
7		A	2.5	61	37
		B	1	97	—
8		A	2.5	50	48
		B	0.6	90	9
9		A	1.5	98	—
10		A	1.5	98	—
11		A	3.5	97	—
		C[d]	4	91	6
12		A	6.5	93	6
13		A	3.5	98	—

[a] All reactions were carried out on a 1.0 mmol scale of substrate with 3.0 equiv of CsF at 100°C; method A in CH_3CN; method B in t-amyl alcohol; method C with 0.5 equiv of a pyrene-tagged methylimidazolium mesylate (PIL) instead of 0.4 equiv of PTIL1 in CH_3CN.
[b] Isolated yield.
[c] Determined by ^1H NMR integration.
[d] Ref. 26.



Scheme 2. Grafting of PTIL1 onto the graphitic surface.

indicated the beneficial noncovalent interaction of a graphene with pyrene moiety for ILs separation from the reaction mixture by simple filtration.

Conclusion

In conclusion, we have designed and developed oligoether-functionalized pyrene-tagged PTIL1 that act as highly efficient multifunctional organocatalysts for nucleophilic fluorination. This PTIL1 catalyst was demonstrated that a wide range of substrates can be successfully fluorinated under defined reaction condition. This PTC system could significantly enhance the reactivity of MFs. Moreover, the synergistic effect of PTIL catalyst with protic *t*-alcohol solvent allowed the fluorination to proceed highly chemoselectively. In particular, the pyrene moiety of PTIL1 played crucial roles in enhancing the rate of reaction and in separation of catalyst through noncovalent interaction. We strongly believe that this catalytic system, in combination with its efficiency in fluorinated reactions for different substrates, may inspire future research in the field of organic synthesis and catalytic engineering.

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Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

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