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SYNTHESIS OF NOVEL FLUOROUS IMIDAZOLIUM IONIC LIQUIDS

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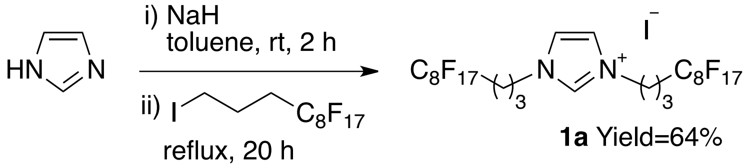
Abstract – The synthesis of a novel class of fluorous ionic liquids was investigated. The 1,3- and 1,2-diperfluoroalkylated imidazolium salts **1** and **2** were successfully prepared. Unfortunately, most of them were solids and had low fluorophilicity. On the other hand, most imidazolium salts **3-8** possessing one or two tris(perfluoroalkyl)silyl groups in cation moiety were liquids at room temperature and had high fluorophilicity independent of the kind of anion moiety. Additionally, dicationic bisimidazolium ionic liquids **10** having two tris(tridecafluorooctyl)silylpropyl groups were also prepared and showed good fluorophilicity.

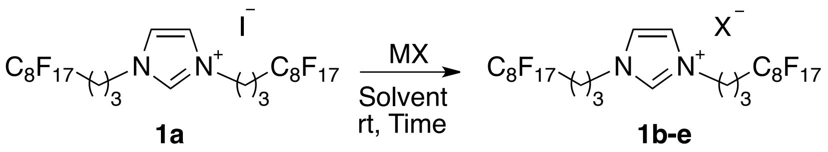
Fluorous chemistry[1] has been expected as one of the promising fields of green chemistry.[2] In particular the synthesis of fluorous ionic liquids possessing perfluoroalkyl groups in anions and/or cations has received growing attention since they will be an alternative to perfluoroalkane based fluorous biphasic systems.[3] We have also been intrigued by the synthesis of these compounds in the last few years. As the results of research on it, the efficient synthetic methods of the highly fluorous piperidinium, and pyridinium ionic liquids have been reported recently.[4] On the other hand, there are few reports about perfluoroalkylated imidazolium ionic liquids,[5-8] despite imidazoliums are one of the most popular and versatile cation classes used to form ionic liquids. For instance, Davis and Christoffers prepared imidazolium ionic liquids having one or two perfluoroalkyl groups on nitrogen atom without mention of their fluorophilicity.[5,6] Although Kvíčala reported highly fluorous imidazolium ionic liquids, the perfluorinated polyether group used as their fluorous tag needed multistep approach to prepare.[7] Deelman showed the synthetic method of imidazolium ionic liquid having perfluoroalkyl groups in anionic site and its solubility in perfluorohexane as a fluorous solvent, but fluorophilicity was not detailed.[8] In this paper, we describe the convenient synthetic methods of a novel class of highly fluorinated room-temperature imidazolium ionic liquids with a good solubility in perfluorinated solvents.

Initially the synthesis of imidazolium ionic liquids possessing two perfluoroalkyl groups was carried out. First of all, the reaction of imidazole with 1H,1H,2H,2H,3H,3H-heptadecafluoroundecyl iodide was examined to lead to the formation of the corresponding 1,3-diperfluoroalkylated imidazolium iodide **1a** (Scheme 1). Though Christoffers et al. have already reported the synthetic method for 1,3-diperfluoroalkyl substituted imidazolium ionic liquids,[6] here we used more convenient procedure to prepare them.[9] The treatment of imidazole with sodium hydride followed by the reaction with perfluoroundecyl iodide gave imidazolium iodide **1a** in moderate yield. The melting point of the obtained iodide was very high (280 °C). Then we examined the possibility to reduce the melting point by anion exchange and to increase the fluorophilicity by introduction of further perfluoroalkyl groups to the salt. The anion exchange reactions of **1a** with an excess of lithium bis(trifluoromethylsulfonyl)imide, sodium tetrafluoroborate, potassium hexafluorophosphate, or sodium tetrakis[*p*-{dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl}phenyl]borate,[8] respectively gave the corresponding bis(trifluoromethylsulfonyl)-imide **1b**, tetrafluoroborate **1c**, hexafluorophosphate **1d**, or tetrakis[*p*-{dimethyl(1H,1H,2H,2H-

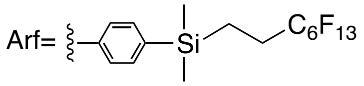


Scheme 1. Synthesis of 1,3-diperfluoroalkylated imidazolium iodide **1a**

Table 1. Anion exchange of imidazolium iodide **1a**



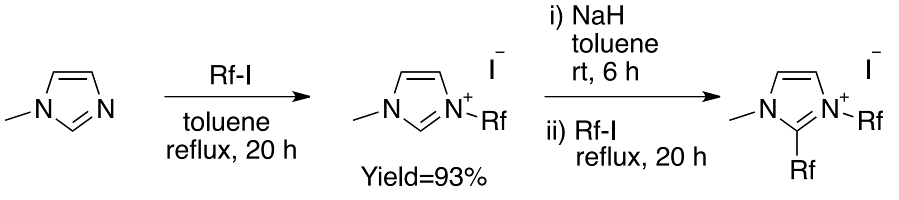
Entry	MX	Solvent	Time (h)	**1**	Yield (%)[a]	mp (°C)[b]
1	$LiN(CF_3SO_2)_2$	acetone/water	5	**1b**	92	89
2	$NaBF_4$	acetone/water	5	**1c**	83	153
3	KPF_6	acetone/water	5	**1d**	93	145
4	$NaB(Arf)_4$	acetone	48	**1e**	83	liquid[c]



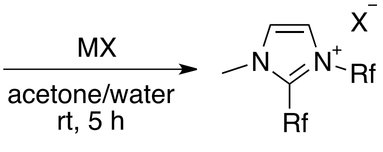
[a] Isolated yield.
[b] Measured by DSC.
[c] Liquid at ordinary temperature (20-25 °C).

perfluorooctyl)silyl}phenyl]borate **1e** in good yields.[10] The results were summarized in Table 1. Regrettably all these salts except borate **1e** were solids at room temperature and insoluble in perfluoromethylcyclohexane, which is a representative fluorous solvent.

Next, the synthesis of 1,2-diperfluoroalkylated imidazolium iodide **2a** was carried out. The reaction of 1-methylimidazole with perfluoroundecyl iodide proceeded smoothly to afford the corresponding iodide in good yields (Scheme 2). The treatment of the resulting iodide with sodium hydride and the following reaction with second perfluoroundecyl iodide gave the desired 1,2-diperfluoroalkyl substituted salt **2a** in moderate yield. The melting point of iodide **2a** was too high (166 °C) to say that this compound is ionic liquid. Then the anion exchange reactions of **2a** with an excess of lithium bis(trifluoromethylsulfonyl)imide, sodium tetrafluoroborate, or potassium hexafluorophosphate were examined. The resulting salts **2b-d** have lower melting points than **2a**. Unfortunately, a series of 1,2-diperfluoroalkyl imidazolium salts **2** were practically insoluble in representative polar organic solvents (e.c. methanol, chloroform, tetrahydrofuran, and acetone) and perfluoromethylcyclohexane.



2a Yield=56%



2b-**d**

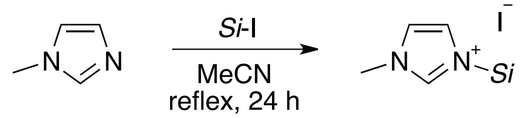
MX	2	Yield (%)[a]	mp (°C)[b]
$LiN(CF_3SO_2)_2$	**2b**	96	liquid[c]
$NaBF_4$	**2c**	91	58
KPF_6	**2d**	98	48

[a] Isolated yield.
[b] Measured by DSC.
[c] Liquid at ordinary temperature (20-25 °C).

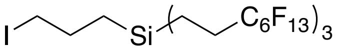
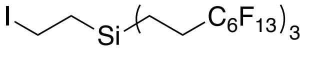
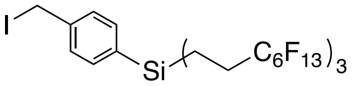
Scheme 2. Synthesis and anion exchange of 1,2-diperfluoroalkylated imidazolium iodide **2a**

Next, the addition of silylpropyl iodide having three perfluoroalkyl groups on the silicon atom to nitrogen atom of imidazole derivative was explored to yield imidazolium ionic liquids possessing three or more perfluoroalkyl groups. Strašák et al. have reported the synthesis of highly fluorous imidazolium ionic liquids by using fluorous ponytail such a tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl substituent.[11] The tris(tridecafluorooctyl)silylpropyl iodide, tris(tridecafluorooctyl)silylethyl iodide, and 4-tris(tridecafluorooctyl)silylbenzyl iodide were prepared as reported in the literature.[11,12] Then the reaction of 1-methylimidazole with the obtained silyl substituted alkyl iodides resulted in the formation of the corresponding imidazolium iodides **3-5a** in good yields. The results were summarized in Table 2. While the introduction of tris(tridecafluorooctyl)silylpropyl group was to prepare the already known reference compounds, tris(tridecafluorooctyl)silylethyl group was used to increase fluorine weight ratio, that would be to increase the fluorophilicity of ionic liquids. Moreover, tris(tridecafluorooctyl)silylbenzyl group was introduced to reduce the melting point of imidazolium salts with increasing molecular volume. Though the obtained iodides **3a** and **4a** were liquids at ordinary temperatures and pressures (Entries 1 and 2), the iodide **5a** having silylphenyl group was solid contrary to expectations (Entry 3). The presence of the phenyl group in **5a** will provide the force of the face-to-face π-π stacking interaction on molecular packing leading to higher melting point.

Table 2. Synthesis of imidazolium iodides having a tris(tridecafluorooctyl)silyl group **3-5a**



3-5a

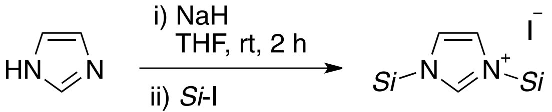
Entry	*Si*-I	Product	Yield (%)[a]	mp (°C)[b]
1		**3a**	96	liquid[c]
2		**4a**	84	liquid[c]
3		**5a**	83	71

[a] Isolated yield.
[b] Measured by DSC.
[c] Liquid at ordinary temperature (20-25 °C).

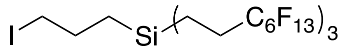
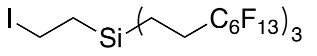
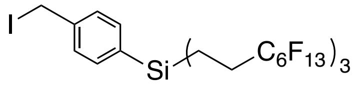
In order to introduce much further fluorous alkyl groups, the reaction of imidazole and the excess amounts of silyl substituted alkyl iodides was carried out. The treatment of imidazole with sodium hydride and the following reaction with two equivalents of silyl substituted alkyl iodides afforded the corresponding disubstituted iodides **6-8a** respectively. The results were summarized in Table 3. The iodides **6a** and **7a** having silylalkyl groups were yielded as liquids (Entries 1 and 2), but the **8a** possessing silylbenzyl groups was obtained as solid state in analogy with mono-substituted iodide **5a** (Entry 3).

The resulted iodides **3-8a** were converted to the corresponding bis(trifluoromethylsulfonyl)imides **3-8b**, tetrafluoroborates **3-8c**, hexafluorophosphates **3-8d**, or tetrakis[*p*-{dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl}phenyl]borates **3e** by anion exchange reactions as mentioned before. The yields of anion exchange reaction and the melting points of the resulted salts were compiled in Table 4. The

Table 3. Synthesis of imidazolium iodides having two tris(tridecafluorooctyl)silyl groups **6-8a**



6-8a

Entry	*Si*-I	Product	Yield (%)[a]	mp (°C)[b]
1		**6a**	65	liquid[c]
2		**7a**	45	liquid[c]
3		**8a**	35	115

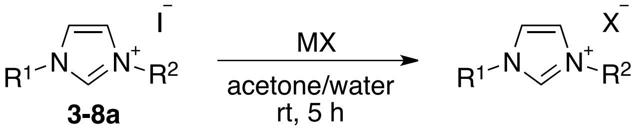
[a] Isolated yield.
[b] Measured by DSC.
[c] Liquid at ordinary temperature (20-25 °C).

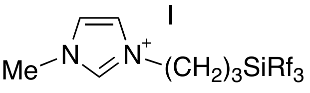
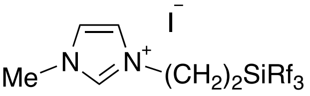
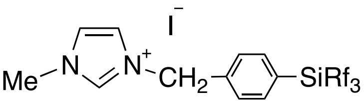
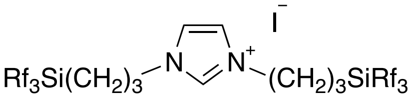
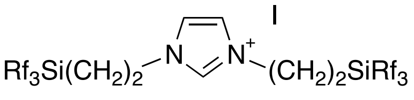
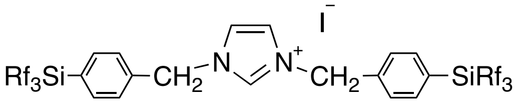
imidazolium salts **3**, **4**, **6**, and **7** having one or two tris(tridecafluorooctyl)silylalkyl groups were liquids, in spite of the kind of anion species (Entries 1-7, and 11-16). It is noteworthy that the salts having a silylbenzyl group **5b**-**d** were liquids (Entries 8-10), although the corresponding iodide **5a** was solid (Table 2, Entry 3). On the other hand, dibenzylimidazolium imide **8b** was liquid as was the case with **5b** (Entry 17), but tetrafluoroborate **8c** and hexafluorophosphate **8d** were solids having lower melting points than the starting iodide **8a** (Entries 18 and 19).

Additionally, the synthesis of dicationic bisimidazolium salts having perfluoroalkyl groups was explored. It has been known that the thermal stabilities of geminal dicationic ionic liquids are greater than those of most traditional monocationic ionic liquids.[13] Moreover, their properties are easily modified by varying the linker chains, so geminal dicationic ionic liquids are used to improve properties of dye sensitized solar cells, lubricants and more.[14,15] Firstly 1,10-bis(imidazol-1-yl)decane was prepared.[16] Imidazole was treated with sodium hydride and reacted with 1,10-dibromodecane to furnish the corresponding bis(imidazol-1-yl)decane in good yield (Scheme 3). The following reaction of the obtained imidazolyldecane with perfluoroundecyl iodide gave the desired geminal dicationic iodide **9a**. However, the resulted iodide **9a** containing two perfluoroalkyl substituents had high melting point (161 °C). On the other hand, the reaction with tris(tridecafluorooctyl)silylpropyl iodide afforded the corresponding geminal dicationic imidazolium iodide **10a** as a liquid at ordinary temperatures and pressures.

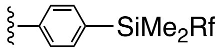
The following anion exchange reaction of imidazolium iodides **9a** and **10a** was carried out as before. These results were shown in Table 5. In these reactions, the corresponding geminal dicationic imidazolium ionic liquids were afforded in good yields, except the sulfonylimide **9b** (Entry 1).

Table 4. Anion exchange of silyl substituted imidazolium iodides **3-8a**



Entry	Substrate	MX	Product	Yield (%)[a]	mp (°C)[b]
1	 **3a**	$LiN(CF_3SO_2)_2$	**3b**	99	liquid[d]
2		$NaBF_4$	**3c**	98	liquid[d]
3		KPF_6	**3d**	100	liquid[d]
4[c]		$NaB(Arf)_4$	**3e**	86	liquid[d]
5	 **4a**	$LiN(CF_3SO_2)_2$	**4b**	87	liquid[d]
6		$NaBF_4$	**4c**	92	liquid[d]
7		KPF_6	**4d**	88	liquid[d]
8	 **5a**	$LiN(CF_3SO_2)_2$	**5b**	98	liquid[d]
9		$NaBF_4$	**5c**	100	liquid[d]
10		KPF_6	**5d**	100	liquid[d]
11	 **6a**	$LiN(CF_3SO_2)_2$	**6b**	100	liquid[d]
12		$NaBF_4$	**6c**	97	liquid[d]
13		KPF_6	**6d**	90	liquid[d]
14	 **7a**	$LiN(CF_3SO_2)_2$	**7b**	100	liquid[d]
15		$NaBF_4$	**7c**	81	liquid[d]
16		KPF_6	**7d**	99	liquid[d]
17	 **8a**	$LiN(CF_3SO_2)_2$	**8b**	99	liquid[d]
18		$NaBF_4$	**8c**	98	92
19		KPF_6	**8d**	100	94

$Rf=CH_2CH_2C_6F_{13}$ Arf=

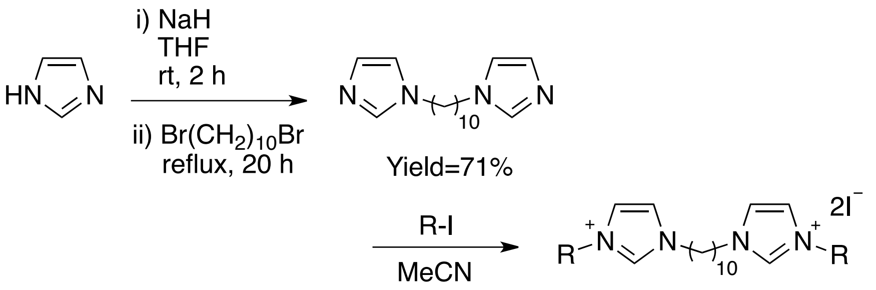


[a] Isolated yield.

[b] Measured by DSC.

[c] Reaction was carried out in acetone for 48 h.

[d] Liquid at ordinary temperature (20-25 °C).



9a, **10a**

Compound	R	Yield (%)[a]	mp (°C)[b]
9a	$(CH_2)_3C_8F_{17}$	60	161
10a	$(CH_2)_3Si(CH_2CH_2C_6F_{13})_3$	75	liquid[c]

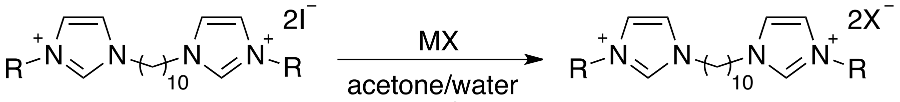
[a] Isolated yield.

[b] Measured by DSC.

[c] Liquid at ordinary temperature (20-25 °C).

Scheme 3. Synthesis of geminal dicationic imidazolium iodides **9a** and **10a**

Table 5. Anion exchange of dicationic imidazolium iodides **9a** and **10a**



9a or **10a**

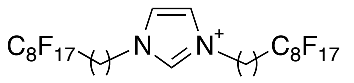
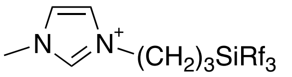
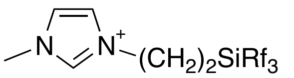
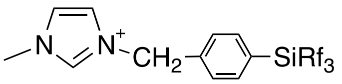
Entry	R	MX	Product	Yield (%)[a]	mp (°C)
1	$(CH_2)_3C_8F_{17}$	$LiN(CF_3SO_2)_2$	**9b**	93	waxy solid
2[b]		$NaB(Arf)_4$	**9e**	56	liquid[c]
3	$(CH_2)_3Si(CH_2CH_2C_6F_{13})_3$	$LiN(CF_3SO_2)_2$	**10b**	100	liquid[c]
4		$NaBF_4$	**10c**	98	liquid[c]
5		KPF_6	**10d**	95	liquid[c]

[a] Isolated yield.

[b] Reaction was carried out in acetone for 48 h.

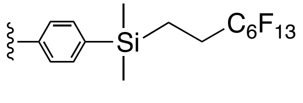
[c] Liquid at ordinary temperature (20-25 °C).

Table 6. Fluorophilicity of imidazolium ionic liquids **1-5**

Entry	Ionic liquid			Fluorine weight ratio (%)	$P_{PFMC/Tol}$	f
		Cation	Anion			
1	**1e**		B(Arf)$_4^-$	55.9	122	4.80
2	**3a**		I$^-$	56.1	234	5.46
3	**3b**		N(CF$_3$SO$_2$)$_2^-$	58.0	121	4.80
4	**3c**		BF$_4^-$	63.8	75	4.32
5	**3d**		PF$_6^-$	63.9	90	4.50
6	**3e**		B(Arf)$_4^-$	55.2	125	4.83
7	**4a**		I$^-$	56.7	243	5.49
8	**4b**		N(CF$_3$SO$_2$)$_2^-$	58.6	231	5.44
9	**4c**		BF$_4^-$	64.5	76	4.33
10	**4d**		PF$_6^-$	64.6	78	4.35
11	**5b**		N(CF$_3$SO$_2$)$_2^-$	56.2	252	5.53
12	**5c**		BF$_4^-$	61.5	82	4.41
13	**5d**		PF$_6^-$	61.7	80	4.38

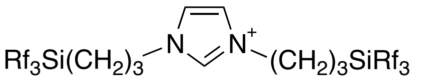
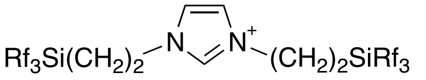
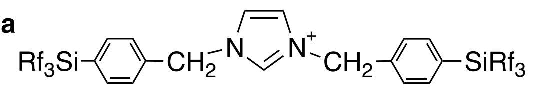
$SiRf_3=Si(CH_2CH_2C_6F_{13})_3$

Arf=



To quantify the fluorophilicity (f=ln P)[17] of the obtained molten ionic liquids **1**–**10** possessing perfluoroalkyl groups in cation (and anion) moiety, perfluoro(methylcyclohexane) (PFMC)/toluene (Tol) partition coefficients ($P_{PFMC/Tol}$)[18] were measured. The data are summarized in Tables 6-8. All of the ionic liquids **1**–**10** possessing three or more perfluoroalkyl groups contain >55 wt% fluorine and exhibited very high fluorophilicity with positive f values.[17] To investigate the existence effect of perfluoroalkyl groups in anion moiety on fluorophilicity of ionic liquids, the partition coefficients of silylpropyl imidazolium

Table 7. Fluorophilicity of imidazolium ionic liquids **6-8**

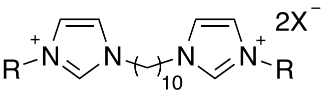
Entry	Ionic liquid			F weight ratio (%)	$P_{\mathrm{PFMC/Tol}}$	f
	Cation		Anion			
1	**6a**		I^-	61.3	259	5.56
2	**6b**		$N(CF_3SO_2)_2^-$	62.1	150	5.01
3	**6c**		BF_4^-	65.5	123	4.82
4	**6d**		PF_6^-	65.5	35	3.55
5	**7a**		I^-	62.0	245	5.50
6	**7b**		$N(CF_3SO_2)_2^-$	63.2	124	4.82
7	**7c**		BF_4^-	66.3	114	4.73
8	**7d**		PF_6^-	66.3	80	4.39
9	**8a**		I^-	59.0	245	5.50
10	**8b**		$N(CF_3SO_2)_2^-$	59.9	47	3.86
11	**8c**		BF_4^-	63.0	29	3.37
12	**8d**		PF_6^-	63.1	75	4.31

$SiRf_3=Si(CH_2CH_2C_6F_{13})_3$

salts **3a**–**e** containing three perfluoroalkyl groups on silicon atom were measured (Table 6, Entries 2-6). Then all ionic liquids showed good fluorophilicity independent of the kind of anion moiety. Notably, the imidazolium iodides **3-8a** and **10a** indicated critically high fluorophilicity independent of a kind of structure on cation moieties. Inconveniently, it is unclear at present why only the iodides have high fluorophilicity. When the fluorine weight ratios and *f* values were compared between ionic liquids **3** and **4**, there was no definite direct correlation with them (Entries 2-5 and Entries 7-10). Thus, it became clear that the tris(perfluoroalkyl)silyl groups should be involved to exhibit high fluorophilicity of imidazolium ionic liquids.

In conclusion, synthesis of fluorous imidazolium ionic liquids has been described. The reaction of imidazole with perfluoroundecyl iodide and the following anion exchange gave 1,3-diperfluoroalkylated

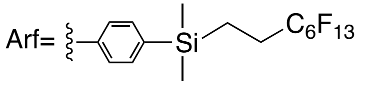
Table 8. Fluorophilicity of imidazolium ionic liquids **9** and **10**



9, 10

Entry	Ionic liquid			F weight ratio (%)	$P_{PFMC/Tol}$	*f*
		R	Anion			
1	**9e**	$(CH_2)_3C_8F_{17}$	$B(Arf)_4^-$	52.2	84	4.43
2	**10a**	$(CH_2)_3SiRf_3$	I^-	56.5	235	5.46
3	**10b**		$N(CF_3SO_2)_2^-$	57.5	81	4.39
4	**10c**		BF_4^-	60.3	53	3.97
5	**10d**		PF_6^-	60.4	77	4.31

$SiRf_3=Si(CH_2CH_2C_6F_{13})_3$



imidazolium salts **1**. Only the phenylborate **1e** having perfluoroalkyl groups in anion moiety was a molten ionic liquid with high fluorophilicity. Unfortunately, 1,2-diperfluoroalkyl imidazolium salts **2** were practically insoluble in representative polar organic solvents and perfluoromethylcyclohexane. On the other hand, most imidazolium salts **3-8** possessing one or two tris(perfluoroalkyl)silyl groups were liquids at room temperature and had high fluorophilicity independent of the kind of anion moiety. Furthermore, dicationic bisimidazolium ionic liquids **10** having two tris(tridecafluorooctyl)silylpropyl groups were prepared and showed good fluorophilicity. Further studies aimed at application of the resulting ionic liquids into chemical reaction and device development are now in progress in our laboratory. The results will be reported in due course.

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SUPPORTING INFORMATION

Supplementary (synthesis of the starting azides, HPLC chromatograms, IR, ^{1}H and ^{13}C NMR, MS spectra, etc.) data associated with this article can be found, in the online version, at URL:

https://www.heterocycles.jp/newlibrary/downloads/PDFsi/26252/101/1.

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