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Efficient Preparation of (Fluorosulfonyl)(pentafluoroethanesulfonyl)imide and Its Alkali Salts

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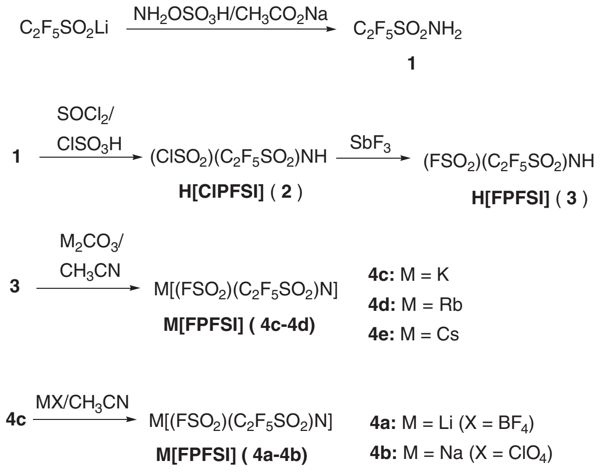
New alkali salts based on (fluorosulfonyl)(pentafluoroethanesulfonyl)imide {[(FSO_2)($C_2F_5SO_2$)N]$^-$, FPFSI$^-$} anion are introduced, together with a new effective preparation of $C_2F_5SO_2NH_2$ and H[FPFSI]. The former amide was prepared by amination of lithium pentafluoroethanesulfinate ($C_2F_5SO_2Li$) with NH_2OSO_3H, which was converted to the H[FPFSI] by sequential chlorosulfonation with $SOCl_2$/$ClSO_3H$, and fluorination by SbF_3.

Recently, there has been a growing interest in fluorosulfonimides as lithium salts, and ionic liquids (ILs) containing these anions, after the recognition that the archetype fluorosulfonimide salt, lithium bis(fluorosulfonyl)imide {Li[N(SO_2F)$_2$], LiFSI}, has desirable properties as solute, and its ILs are very low-viscosity ionic solvents for lithium-ion batteries (LIBs).[1] Thus far, while a large number of bis(perfluoroalkanesulfonyl)imides have been reported,[2] little attention has been paid to the asymmetric (fluorosulfonyl)(perfluoroalkanesulfonyl)imides [(FSO_2)(R_FSO_2)N]$^-$ ($R_F = C_mF_{2m+1}$, $m \geq 1$).[3] Furthermore, very few synthetic details and characterization data are available, as most of them are claimed in patents.[3] In particular, few of them are effective for preparation of asymmetric (fluorosulfonyl)(perfluoroalkanesulfonyl)imide salts, though they may have properties that neither symmetric Li[N(SO_2F)$_2$] nor Li[N(SO_2CF_3)$_2$] can provide.

Several methods have been described to prepare the asymmetric [(FSO_2)(CF_3SO_2)N]$^-$ anion: 1) $CF_3SO_2NH_2$ is treated with (highly toxic) fluorosulfonic acid anhydride ($(FSO_2)_2O$),[3b] or gaseous sulfurylfluoride (SO_2F_2) in the presence of weakly nucleophilic base,[3c] or treated with PCl_5, followed by FSO_3H;[3d,3e] 2) CF_3SO_3H is reacted with $ClSO_2NCO$,[3f] or CF_3SO_2NCO with $ClSO_3H$,[3g] followed by fluorination. However, no synthetic details and characterization data have been available for higher homologs {[(FSO_2)(R_FSO_2)N]$^-$ ($R_F = C_mF_{2m+1}$, $m > 1$}.[3b] For the $R_FSO_2NH_2$ precursors, they are mainly prepared by reacting perfluoroalkanesulfonyl fluorides (prepared from electrochemical fluorination) with ammonia.[2] Similar methods, however, cannot be used for the perfluoroalkanesulfonyl chloride (R_FSO_2Cl, $R_F = C_mF_{2m+1}$, $m > 1$) except for trifluoromethanesulfonyl chloride,[4] because of the competitive reduction of the former R_FSO_2Cl with a higher R_F group with ammonia or amine, and an appreciable amount of perfluoroalkanesulfinate forms as by-product.[5] With the ever-increasing demand for lithium salts and ILs with robust anions as electrolytes for advanced LIBs, there clearly remains a need for new effective methods toward accessing perfluoroalkanesulfonamides ($R_FSO_2NH_2$) and (fluorosulfonyl)(perfluoroalkanesulfonyl)imides {H[(FSO_2)(R_FSO_2)N], $R_F = C_mF_{2m+1}$}.



Scheme 1.

With the knowledge of the background described above, we wish to report here an effective synthetic approach for pentafluoroalkanesulfonamide ($C_2F_5SO_2NH_2$), and (fluorosulfonyl)(pentafluoroethanesulfonyl)imide (H[FPFSI]), as well as the preparation and characterization of alkali salts based on FPFSI$^-$ anion (Scheme 1) (The details of the preparation and characterization experiments can be seen in the Supporting Information).[6]

Amination of hydrocarbon (aliphatic and aromatic) sulfinate with hydroxylamine-*O*-sulfonic acid (NH_2OSO_3H) has been decribed.[7] Based on the same principle, we envisioned that perfluoroalkanesulfinate would be transformed to the corresponding sulfonamide. Indeed, $C_2F_5SO_2NH_2$ (**1**) was obtained in 70% yield and sufficient purity by amination of lithium pentafluoroethanesulfinate ($C_2F_5SO_2Li$) with NH_2OSO_3H under mild basic conditions at room temperature (Scheme 1). Taking into account the easily available perfluoroalkanesulfinate salts, we reasonably assume that perfluoroalkanesulfinates are a good alternative to perfluoroalkanesulfonyl halide to access perfluoroalkanesulfonamides.

On the basis of a similar principle for preparing ($ClSO_2$)$_2$NH by resorting to $SOCl_2$/$ClSO_3H$ and NH_2SO_3H,[2g] the (chlorosulfonyl)(pentafluoroethanesulfonyl)imide {H[ClPFSI], **2**} was similarly obtained in 85% yield by refluxing $C_2F_5SO_2NH_2$ (**1**) with $SOCl_2$/$ClSO_3H$ at 120–130 °C for 36 h. The H[FPFSI] (**3**) was prepared in 90% yield by fluorination of **2** with SbF_3. Different from the reported methods, the intermediate **3** was prepared without resorting to cumbersome or highly hazardous chemicals, such as (FSO_2)$_2$O,[3b] SO_2F_2,[3c] or $ClSO_2NCO$.[3f] We will show in a later report that this route can be used for all the perfluoroalkylated homologs of **3**.

Table 1. Physicochemical properties of (fluorosulfonyl)(pentafluoroethanesulfonyl)imide ($FPFSI^-$) alkali salts

Salts	T_c[a] /°C	T_{s-s}[a] /°C	T_m[a] /°C	ΔS_m[b] /$J\,mol^{-1}\,K^{-1}$	T_d[c] /°C
Li[FPFSI] (**4a**)	74		152	44.5	201
Na[FPFSI] (**4b**)		147	162	30.0	253
K[FPFSI] (**4c**)		0, 70	173	32.9	336
Rb[FPFSI] (**4d**)		76, 105	129	17.5	290
Cs[FPFSI] (**4e**)		84	118	47.6	302
Li[TFSI]			234,[d] 233[e]		384[e]
Na[TFSI]			257[e]		441[e]
K[TFSI]			205,[d] 199[e]		460[e]
Rb[TFSI]			177[e]		467[e]
Cs[TFSI]			122[e], 115[f]		472[e]

[a] Crystallization temperature (T_c), solid–solid transition temperature (T_{s-s}), and melting points (T_m) determined by DSC on heating. [b] Entropy of melting ($\Delta S_m = \Delta H_m/T_m$, where ΔH_m is melting enthalpy at T_m (K)). [c] Decomposition temperature (T_d) determined by TGA. [d] Data from Ref. 8b. [e] Data from Ref. 8a. [f] Data from Ref. 8c.

The alkali salts, K[FPFSI] (**4c**), Rb[FPFSI] (**4d**), and Cs[FPFSI] (**4e**), were prepared by an acid–base neutralization of **3** with a slight excess of the corresponding carbonate (M_2CO_3, M = K, Rb, and Cs) in CH_3CN at 0 °C.

The highly hygroscopic lithium (Li[FPFSI], **4a**) and sodium (Na[FPFSI], **4b**) salts were prepared by metathesis of **4c** with $LiBF_4$ and $NaClO_4$, respectively, in CH_3CN, and the insoluble by-products KBF_4 and $KClO_4$, were removed by filtration. The solvent-free salts, **4a** and **4b**, were obtained in nearly quantitive yields and high purity by removal of the solvent under high vaccum.

The physicochemical properties of the salts M[FPFSI] (M = Li, Na, K, Rb, and Cs), such as phase behavior (including crystallization temperature, solid–solid transition, and melting point, if appropriate), and thermal stability are summarized in Table 1. For comparison, the data for the melting points and thermal stability of the corresponding M[TFSI] (M = Li, Na, K, Rb, and Cs) salts are also included in Table 1,[8] wherein the structure of the symmetric $TFSI^-$ $\{[N(SO_2CF_3)_2]^-\}$ anion is isomeric with that of the asymmetric $FPFSI^-$.

Figure 1 shows the phase behavior of the alkali salts {M[FPFSI], **4**} measured by DSC. All of them show relatively low melting points below 180 °C. These values for the melting points of the M[FPFSI] (**4**) salts are lower than those for the corresponding salts with the isomeric and symmetric $TFSI^-$ anion (Table 1). It seems that the asymmetric factor of the $FPFSI^-$ anion plays a key role in achieving the low melting points of these salts.

Figure 2 shows the melting points of the M[FPFSI] (**4**) salts, as well as those for the corresponding $TFSI^-$ salts. For simple inorganic alkali salts, the melting points are generally higher for the smaller alkali cation. However, the melting points of M[FPFSI] (**4**) decrease in the irregular order: $Cs^+ < Rb^+ < Li^+ < Na^+ < K^+$. A similar trend was also observed for the five corresponding $TFSI^-$ salts (Table 1).[8a] This irregular trend would be attributable to the more complicated ion–ion interactions in these alkali salts containing a larger organic anion than those in the simple inorganic salts.

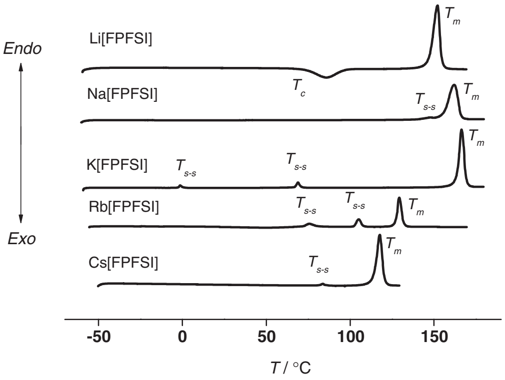


Figure 1. DSC traces of various alkali $FPFSI^-$ salts.

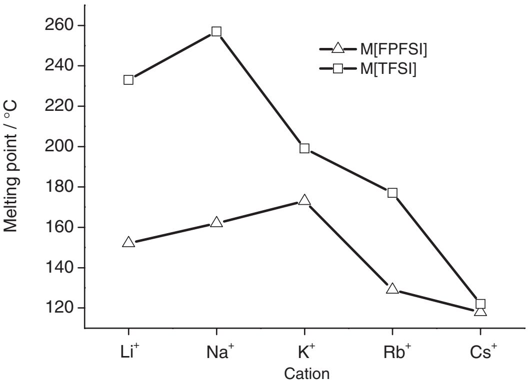


Figure 2. Melting points of various alkali $FPFSI^-$ and $TFSI^-$ salts.

The lithium salt **4a** shows a sharp melting point at 152 °C, indicating its high purity. The other four salts **4b**–**4e** display solid–solid transitions before melting, which can be classified as ionic plastic crystals. To our knowledge, these are the first examples of alkali salts displaying plastic crystalline-phases close to room temperature. Therefore, it opens the possibility to create novel lithium-ion conducting plastic crystals, or neat alkali-based ionic liquid electrolytes by doping the salts **4b**–**4e** with lithium salt **4a** in future work.

All the alkali salts **4** show stability ranging from 200 to 330 °C. These values for the thermal stability of the M[FPFSI] (**4**) salts are much lower than those for the corresponding salts containing the isomeric $TFSI^-$ anion. In addition, lower thermal stabilities were also observed for the FSI^- salts with alkali cations.[1g] These results indicated that introducing a FSO_2– group into the perfluorinated sulfonylimide anion generally causes a decrease in thermal stability, presumably due to the FSO_2– group being more liable to pyrolysis. Of the five alkali salts **4a**–**4e**, Li[FPFSI] (**4a**) shows the lowest thermal stability ≈200 °C, but which is still enough for electrolyte salts for LIBs.

In summary, we have developed new efficient preparative approaches for $C_2F_5SO_2NH_2$ and $(FSO_2)(C_2F_5SO_2)NH$ (H[FPFSI]). $C_2F_5SO_2NH_2$ was prepared from the corresponding sulfinates as precursors to react with NH_2OSO_3H under mild basic conditions. The H[FPFSI] was prepared by sequential chlorosulfonation, and fluorination with $SOCl_2/ClSO_3H$, and SbF_3. The alkali salts based on $FPFSI^-$ anion were prepared and characterized. They show relative low melting points due to low symmetry of the FPFSI$^-$ anion, good thermal stability, and plastic crystalline-phases close to room temperature. The desired properties of the lithium salt may allow it as electrolyte salt for advanced lithium batteries.

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