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Syntheses, structures and properties of 1-ethyl-3-methylimidazolium salts of fluorocomplex anions †

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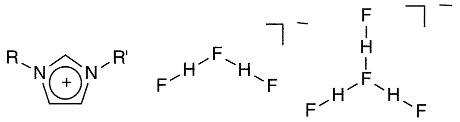
Fluoroacid–base reactions of a room-temperature ionic liquid, 1-ethyl-3-methylimidazolium fluorohydrogenate (EMIm(HF)$_{2.3}$F, EMIm = 1-ethyl-3-methylimidazolium cation), and Lewis fluoroacids (BF_3, PF_5, AsF_5, NbF_5, TaF_5 and WF_6) give EMIm salts of the corresponding fluorocomplex anions, EMImBF$_4$, EMImPF$_6$, EMImAsF$_6$, EMImNbF$_6$, EMImTaF$_6$ and EMImWF$_7$, respectively. Attempts to prepare EMImVF$_6$ by both the acid–base reaction of EMIm(HF)$_{2.3}$F with VF_5 and the metathesis of EMImCl with KVF_6 failed due to the strong oxidizing power of the pentavalent vanadium, whereas EMImSbF$_6$ was successfully prepared only by the metathesis of EMImCl and $KSbF_6$. EMImBF$_4$, EMImSbF$_6$, EMImNbF$_6$, EMImTaF$_6$ and EMImWF$_7$ are liquids at room temperature whereas EMImPF$_6$ and EMImAsF$_6$ melts at around 330 K. Raman spectra of the obtained salts showed the existence of the EMIm cation and corresponding fluorocomplex anions. IR spectroscopy revealed that strong hydrogen bonds are not observed in these salts. EMImAsF$_6$ (mp 326 K) and EMImSbF$_6$ (mp 283 K) are isostructural with the previously reported EMImPF$_6$. The melting point of the hexafluorocomplex EMIm salt decreases with the increase of the size of the anion ($PF_6^- < AsF_6^- < SbF_6^- < NbF_6^- \approx TaF_6^-$).

Introduction

Molecular design, synthesis and characterization of room-temperature ionic liquids (RTILs, also called room-temperature molten salts) are of current interest as electrolytes and green solvents because of their negligibly small vapor pressure and chemical stability over a wide range of temperatures.[1] The functionality of an RTIL strongly depends on the cationic or anionic species and their combinations. After the synthesis of air-stable 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$) by Wilkes and Zaworotko,[2] a number of reports have been made on salts composed of organic cations and bulky fluoroanions such as PF_6^- or $(CF_3SO_2)_2N^-$.[3] The alkylimidazolium-based RTILs often exhibit a low melting point and viscosity. However, limited to EMIm salts, the relationship between the physical properties and the molecular size or geometry of the anions is still unclear. BF_4^-, PF_6^- and AsF_6^- are known today as highly symmetric anions for the EMIm salts.[2–4] EMImSbF$_6$ has been reported without its physical properties; only the application as reaction solvent for organic synthesis has been discussed.[5] The salt of a larger anion appears to have a lower melting point as a result of the decrease of the electrostatic interactions between the cation and anion. However, in fact, the melting point of EMImBF$_4$ (288 K) is much lower than those of EMImPF$_6$ and EMImAsF$_6$ (333 and 326 K, respectively).[2–4] This contradiction is probably caused by the difference of the molecular geometries of the anions. Systematic study is necessary to clarify the relationship between the structures and properties of EMIm salts of fluorocomplex anions. Furthermore, alternative preparative routes should be developed to obtain RTILs with high purities. Recently, a series of alkylimidazolium fluorohydrogenate (RR′Im(HF)$_{2.3}$F) have been reported,[6] which is the combination of RR′Im cation and $(HF)_nF^-$ anions ($n = 2, 3$) where the non-integer figure of 2.3 for the room-temperature vacuum stable salt results from the existence of both the $(HF)_2F^-$ and $(HF)_3F^-$ anion in this liquid (Scheme 1).[7]



Scheme 1 RR′Im(HF)$_{2.3}$F.

In the present study, EMIm(HF)$_{2.3}$F is used as a fluorobase to react with some binary fluorides (MF_m) which act as fluoroacids to give fluorocomplex salts, EMImMF$_{m+1}$. We confirmed that this method effectively works for some binary fluorides.[8] The physical properties of the obtained EMImMF$_{m+1}$ are reported as well as their solid-state structures and thermal properties.

Results and discussion

Syntheses of EMImMF$_m$ by fluoroacid–base reactions

Although EMImX (X = Cl, Br, I) are known, EMImF has never been isolated as a pure unsolvated compound and is considered to be unstable at room temperature. EMImMF$_{m+1}$ cannot be prepared by the simple acid–base reaction of EMImF and MF_m without forming any byproduct as in the case of alkylimidazolium–chloroaluminate system.[9] EMIm(HF)$_{2.3}$F itself is an RTIL in which F^- is stabilized by making a covalent bond with HF to form fluorohydrogenate anions such as $(HF)_2F^-$ and $(HF)_3F^-$.[6,7] HF is a weak fluoroacid and is liberated by the interaction of EMIm(HF)$_{2.3}$F with MF_m to give EMImMF$_{m+1}$ according to the reaction below (Scheme 2).

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† Electronic supplementary information (ESI) available: Raman and IR assignments. See http://www.rsc.org/suppdata/dt/b3/b310162b/
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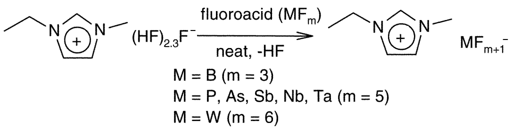
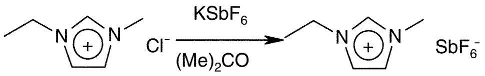


Scheme 2 Syntheses of $EMImMF_{m+1}$ by fluoroacid–base reactions.

There are two common methods for the synthesis of dialkylimidazolium-based RTILs.[1] Metathesis such as the reaction of EMImCl and MBF_4 (M = ammonium, alkali metal or silver) in water–ethanol to prepare $EMImBF_4$ is a popular synthetic route but has a problem of contamination by the byproduct MCl. Preparation using an aqueous solution of protonic acid such as the reaction of EMImCl and HBF_4 (aq.) is applied for the preparation of $EMImBF_4$. However, this method is not suitable for reactive metal fluorides which are hydrolyzed or reduced by water. The benefit of the present method is that the byproduct HF is volatile and easily removed by evacuation at elevated temperatures, giving high purity of the reaction product. All the reactions are highly exothermic and the reaction vessel should be cooled occasionally by refrigerant. The reactions with BF_3, PF_5, AsF_5, NbF_5, TaF_5 and WF_6 gave the expected salts of singly charged anions. No trace of HF was detected by IR spectroscopy or cyclic voltammetry of the obtained salts. $EMIm(HF)_{2.3}F$ and VF_5 violently reacted to give black products due to the strong oxidizing power of VF_5. The metathesis of EMImCl and KVF_6 in acetone also produced black products without giving $EMImVF_6$. In the case of the reaction of $EMIm(HF)_{2.3}F$ with SbF_5, the color of the liquid immediately turned wine-red just after the addition of SbF_5, suggesting partial decomposition. In the Raman spectrum of the liquid after the evacuation at 298 K, some peaks were observed at the higher side of the strong peak at 655 cm^{-1}. These peaks are typical for the polynuclear anions such as $Sb_2F_{11}^-$.[10] Successive heating under a dynamic vacuum to eliminate the byproduct HF and the excess SbF_5 changed the color of the sample to black. Thus the direct reaction of $EMIm(HF)_{2.3}F$ with SbF_5 is not preferable to synthesize $EMImSbF_6$. The metathesis previously reported for other salts, the reaction of EMImCl and $KSbF_6$ in acetone, is the only viable method for the synthesis of $EMImSbF_6$ (Scheme 3).[5]



Scheme 3 Synthesis of $EMImSbF_6$.

Properties of $EMImMF_{m+1}$

$EMImBF_4$ is miscible with water whereas the solids $EMImPF_6$ and $EMImAsF_6$ are not. $EMImSbF_6$ is immiscible with water and sinks to the bottom of the vessel. However, the interface gradually disappeared after contact with water overnight, probably due to the slow hydrolysis of $EMImSbF_6$. $EMImNbF_6$ and $EMImTaF_6$ are miscible with water. $EMImWF_7$ rapidly reacts with water to give a blue liquid.

Selected physical properties of $EMImMF_6$ are summarized in Table 1. The conductivity of $EMImSbF_6$ is a little lower than that of $EMImN(SO_2CF_3)_2$ (8.8 mS cm^{-1}) or of $EMImSO_3CF_3$ (9.2 mS cm^{-1}).[3,11] $EMImWF_7$ is a viscous RTIL with a viscosity of 171 cP. $EMImBF_4$ possesses the highest conductivity (13.6 mS cm^{-1}) among the salts in the present study.[12] Although the conductivities of $EMImSbF_6$, $EMImTaF_6$ and $EMImNbF_6$ increase in this order, the differences are not significant. The conductivity of the RTIL of the largest anion, $EMImWF_7$, is the lowest among those of the salts in the present study. Cyclic voltammograms at Pt electrodes in $EMImBF_4$, $EMImSbF_6$, $EMImNbF_6$ and $EMImTaF_6$, and a glassy carbon electrode in $EMImWF_7$ are shown in Fig. 1. Their anodic limit potentials are almost the same, +1.5 V *vs.* Ag^+/Ag. The EMIm cation is reported to be reduced at around −3.0 V *vs.* Ag^+/Ag.[13] The cathodic limits of $EMImBF_4$ and $EMImTaF_6$ are around −3.0 V, probably assigned to the reduction of EMIm cation, whereas in the cases of $EMImSbF_6$, $EMImNbF_6$ and $EMImWF_7$, the anions in the RTILs are more easily reduced than the cation and their electrochemical windows are narrower than those of $EMImBF_4$ and $EMImTaF_6$.[13]

Table 1 Selected physical properties of $EMImMF_{m+1}$

	$T_m{}^a$/K	ρ^a/g cm^{-3}	σ^a/mS cm^{-1}	η^a/cP
$EMImBF_4{}^b$	288	1.28	13.6	32
$EMImPF_6{}^c$	333	1.56	–	–
$EMImAsF_6$	326	1.78	–	–
$EMImSbF_6$	283	1.85	6.2	67
$EMImNbF_6{}^d$	272	1.67	8.5	49
$EMImTaF_6{}^d$	275	2.17	7.1	51
$EMImWF_7$	258	2.27	3.2	171

[a] T_m: Melting point, ρ: density at 298 K (the densities of $EMImPF_6$ and $EMImAsF_6$ are crystallographically determined), σ: conductivity at 298 K, η: viscosity at 298 K. [b] Ref. 12. [c] Ref. 3. [d] Ref. 8.

Table 2 Summary of crystal data and refinement results for $EMImAsF_6$ and $EMImSbF_6$ with crystal data of $EMImPF_6$

	$EMImAsF_6$	$EMImSbF_6$	$EMImPF_6{}^c$
Formula	$H_{11}C_6N_2F_6As$	$H_{11}C_6N_2F_6Sb$	$H_{11}C_6N_2F_6P$
M_r	300.09	346.92	255.24
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	8.871(10)	8.942(8)	8.757(2)
b/Å	9.424(2)	9.390(8)	9.343(2)
c/Å	13.786(2)	13.849(12)	13.701(3)
β/°	102.985(14)	101.680(12)	103.05(3)
V/Å³	1123.04(3)	1138.8(17)	1092.02
Z	4	4	4
D_c/g cm^{-3}	1.775	2.024	1.558
T/K	298	200	283–303
$R_1{}^a$	0.0388	0.0390	–
$wR_2{}^b$	0.1039	0.0939	–

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w[|F_o|^2 - |F_c|^2]^2/\Sigma w|F_o|^2]^{1/2}$. [c] Ref. 3.

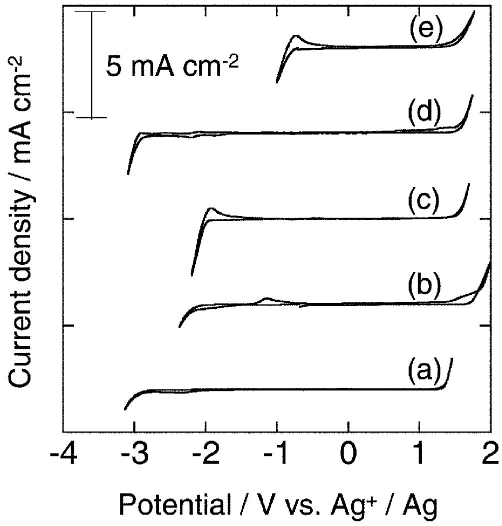


Fig. 1 Cyclic voltammograms of Pt electrodes in (a) $EMImBF_4$, (b) $EMImSbF_6$, (c) $EMImNbF_6$, (d) $EMImTaF_6$ and a glassy carbon electrode in (e) $EMImWF_7$: scan rate = 30 mV s^{-1}.

Structures and thermal properties of $EMImMF_6$

Details of the data collection parameters and other crystallographic information for $EMImAsF_6$ and $EMImSbF_6$ are

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Table 3 Selected bond lengths and bond angles in $EMImAsF_6$ and $EMImSbF_6$ (Å, °)

$EMIm^+$	$EMImAsF_6$	$EMImSbF_6$	MF_6^- (M = As, Sb)	$EMImAsF_6$	$EMImSbF_6$
N1–C2	1.304(5)	1.310(8)	M–F1	1.681(3)	1.857(4)
C2–N3	1.314(5)	1.313(7)	M–F2	1.684(3)	1.842(5)
N3–C4	1.364(5)	1.351(8)	M–F3	1.703(3)	1.876(4)
C4–C5	1.326(7)	1.334(10)	M–F4	1.663(3)	1.824(5)
C5–N1	1.359(6)	1.368(8)	M–F5	1.685(3)	1.844(5)
N1–C6	1.472(5)	1.472(7)	M–F6	1.671(3)	1.840(5)
C6–C7	1.498(7)	1.504(9)			
N3–C8	1.461(5)	1.460(8)	F1–M–F2	91.7(2)	90.8(2)
			F1–M–F3	179.68(17)	179.67(19)
N1–C2–N3	110.0(4)	109.9(5)	F1–M–F4	88.8(2)	90.2(3)
C2–N3–C4	107.7(4)	107.9(5)	F1–M–F5	87.61(17)	88.8(2)
N3–C4–C5	106.8(4)	107.7(6)	F1–M–F6	91.87(18)	90.8(2)
C4–C5–N1	108.2(4)	107.1(6)	F2–M–F3	88.2(2)	89.2(2)
C5–N1–C2	107.3(4)	107.5(5)	F2–M–F4	178.8(3)	179.0(3)
C2–N1–C6	126.3(4)	126.4(5)	F2–M–F5	89.5(3)	90.6(4)
C5–N1–C6	126.3(4)	126.1(5)	F2–M–F6	89.0(2)	89.2(3)
N1–C6–C7	111.4(4)	110.7(5)	F3–M–F4	91.4(2)	89.8(2)
C2–N3–C8	126.4(4)	125.7(5)	F3–M–F5	92.10(17)	90.8(2)
C4–N3–C8	125.9(4)	126.5(5)	F3–M–F6	88.42(17)	89.5(2)
C2–N1–C6–C7	112.2(6)	116.6(9)	F4–M–F5	89.4(3)	89.6(4)
			F4–M–F6	92.1(3)	90.6(3)
			F5–M–F6	178.4(2)	179.6(3)

provided in Table 2. Selected bond distances and angles are listed in Table 3. Both of the compounds are isostructural with $EMImPF_6$ of which the crystal data reported by Fuller *et al.* are jointly listed in Table 2.[3] Neither $EMImAsF_6$ nor $EMImSbF_6$ exhibit any thermal peaks corresponding to phase transitions in the DSC curves (above 163 K), the structure being considered to be maintained below their melting points. The ORTEP[14] diagram of $EMImAsF_6$ is shown in Fig. 2. $EMImAsF_6$ and $EMImSbF_6$ are composed of EMIm cations and expected octahedral MF_6^- anions (*cis*-F–M–F angular distortion < 2.4° for AsF_6^- and < 1.2° for SbF_6^-). Typical bond lengths and bond angles are observed in the EMIm cations determined here. The β-carbon of the ethyl group is out of the plane of the imidazolium five-membered ring with C2–N1–C5–C6 torsion angles of 112.2(6) and 116.6(9)° for $EMImAsF_6$ and $EMImSbF_6$, respectively. The cations are placed parallel to each other but not in a stacked arrangement. The formula unit volumes for $EMImPF_6$, $EMImAsF_6$ and $EMImSbF_6$ are 273.0 at 273 K, 280.8 at 273 K and 284.7 Å^3 at 200 K, respectively, changing with the size of the anion, although the cell parameters of $EMImSbF_6$ were determined at 200 K. The hydrogen-bond geometries in $EMImAsF_6$ and $EMImSbF_6$ are summarized in Table 4. In general, relatively large complex anions in EMIm salts make weaker hydrogen bonds with EMIm cation than small anions such as halides.[3,15] In $EMImAsF_6$ and $EMImSbF_6$, the hydrogen-bond distances between H atoms in the cation including methyl groups and F atoms of MF_6^- are not less than 2.5 Å, indicating that the hydrogen bonds in these salts are not strong in terms of the van der Waals criterion (2.7 Å),[16] the coulombic force dominating the interaction between the cation and anion. This observation agrees with the case of $EMImPF_6$ and the results of IR spectra discussed below.[3] Unfortunately, the structure determination of $EMImNbF_6$ and $EMImTaF_6$ failed due to the poor quality of the crystals. The relationship between the melting points and the sizes of the anions for the fluorocomplex salts are shown in Fig. 3, where the radius of the central atom in the fluorocomplex anion reported by Shannon is plotted on the horizontal axis.[17] The radius of seven-coordinated Mo(VI) is used for the unavailable data for W(VI) of seven coordination since the similarity is crystallographically known for the radii of these atoms with the same oxidation state and coordination environment. There is a tendency for the melting point of the salt to decrease with increase in size of the anion except for $EMImBF_4$. The tetrahedral BF_4^- anion is considered to have a different interaction with the cation from those of hexa- or heptafluoroanions and they cannot be treated in the same manner as a singly charged rigid sphere.

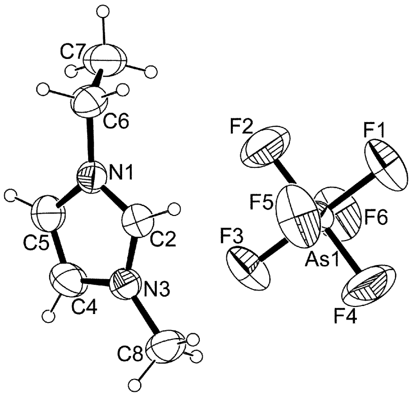

Fig. 2 ORTEP[14] diagram of the EMIm cation and AsF_6 anion in the $EMImAsF_6$ structure.

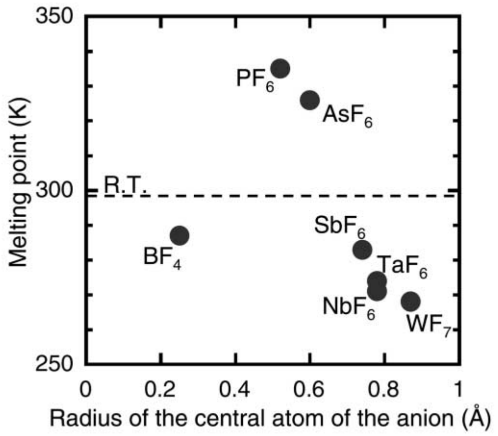

Fig. 3 Relationship between the size of anion and melting point for $EMImMF_{m+1}$. The horizontal axis is referenced to the value of the radius of the central atom of the anion reported by Shannon and the radius of seven-coordinated Mo(VI) is used for that of WF_7^-.[17]

Vibrational spectra

Raman and IR frequencies of the obtained salts with their assignments are summarized as ESI.† Vibrational spectra of EMIm cations in some salts are well-characterized in previous

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Table 4 Hydrogen-bond geometries for $EMImAsF_6$ and $EMImSbF_6$ (Å, °)

	$EMImAsF_6$				$EMImSbF_6$			
D–H ··· A	D–H	H ··· A	D ··· A	D–H ··· A	D–H	H ··· A	D ··· A	D–H ··· A
C(2)–H(2) ··· F(1)	0.93	2.59	3.254(4)	129	0.93	2.51	3.228(5)	134
C(2)–H(2) ··· F(5)	0.93	2.67	3.137(4)	112	0.93	2.68	3.108(7)	109
C(8)–H(8b) ··· F(1)	0.96	2.54	3.396(3)	148	0.96	2.55	3.345(6)	140
C(8)–H(8c) ··· F(3)	0.96	2.62	3.300(3)	128	0.96	2.71	3.304(6)	121
C(8)–H(8a) ··· F(6)	0.96	2.69	3.221(4)	115	0.96	2.59	3.129(7)	116

reports.[18] Assignment below 600 cm^{-1} contains some ambiguities due to the overlap of C–H bending and ring bending modes. The Raman spectra of the obtained salts (< 1200 cm^{-1}) are shown in Fig. 4. Peaks assigned to the EMIm cation are essentially the same as observed in the spectrum of EMImCl (Fig. 4(h)). The positions of the peaks except for those of EMIm cation are in good agreement with the fundamental modes of the corresponding fluorocomplex anions reported in the literature.[19] Their IR spectra also exhibit the fundamental modes of the fluorocomplex anions. Three candidates for the geometry of a seven-coordinated molecule; the pentagonal bipyramid (D_{5h}), the monocapped octahedron (C_{3v}) and the monocapped trigonal prism (C_{2v}) have similar energy levels and the environment around the molecule determines the preferable geometry.[20] The first report of the Raman and IR spectra of $CsWF_7$ suggested that WF_7^- has D_{5h} geometry.[21] However, a single crystal X-ray diffraction study performed nineteen years later revealed that the actual geometry of WF_7^- in $CsWF_7$ was C_{3v}.[22] WF_7^- with the geometry of the monocapped trigonal prism (C_{2v}) was found in $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot CH_3CN$.[23] Raman spectra of the two geometries are similar to each other and characterized by a strong peak at around 700 cm^{-1} with several small peaks. The appearance of the Raman spectrum of $EMImWF_7$ is close to that of $CsWF_7$ rather than $[WF_4(bipy)_2]^{2+}\cdot 2[WF_7]^-\cdot CH_3CN$. Therefore WF_7^- is exposed to a weaker ionic field in the liquid state than that in the solid and may be concluded to have the C_{3v} symmetry. The seven equivalent F atoms in $EMImWF_7$ detected by ^{19}F NMR spectroscopy indicates the presence of intramolecular ligand exchange on the NMR time scale.

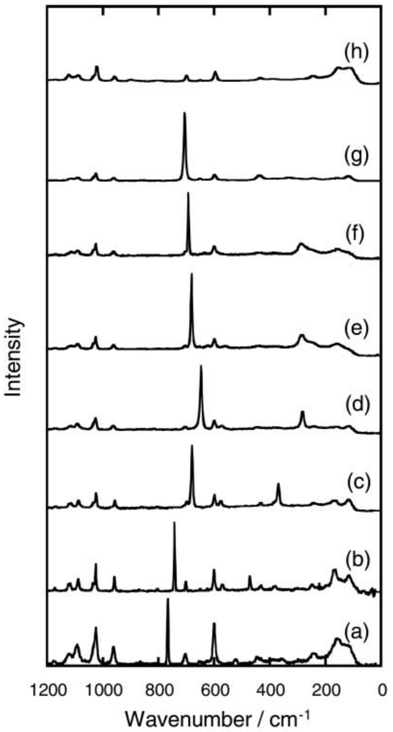

Fig. 4 Raman spectra of (a) $EMImBF_4$, (b) $EMImPF_6$, (c) $EMImAsF_6$, (d) $EMImSbF_6$, (e) $EMImNbF_6$, (f) $EMImTaF_6$, (g) $EMImWF_7$ and (h) EMImCl.

Hydrogen bonds in EMIm salts are often discussed based on the IR spectra in the range 3000–3200 cm^{-1}. The IR spectra of this region for the present salts are shown in Fig. 5. A strong hydrogen bond between the ring proton and anion is reflected in the shift of the C–H stretching of the ring proton. In solid EMImCl or basic EMImCl–$AlCl_3$ ionic liquid for example, the C–H stretching of the ring proton is observed between 3000 and 3100 cm^{-1} due to the strong hydrogen bond between the ring proton and anions, whereas the C–H stretching of EMIm cation in the weak hydrogen bond system is observed between 3100 and 3200 cm^{-1}.[18] As shown in Fig. 5, the absorption bands of C–H aromatic stretchings in the IR spectra of all the present fluorocomplex salts were observed in the latter region, suggesting that the hydrogen bonds *via* ring protons are not strong in these salts.

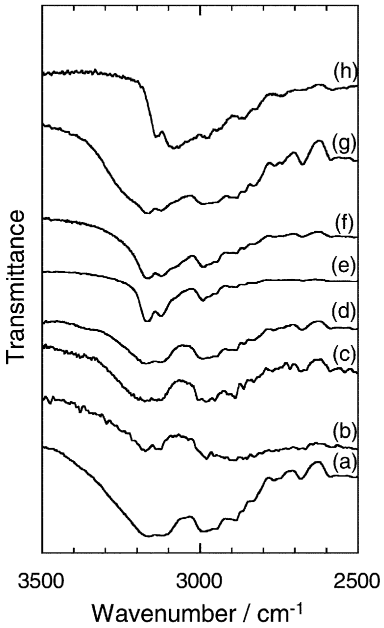

Fig. 5 IR spectra of (a) $EMImBF_4$, (b) $EMImPF_6$, (c) $EMImAsF_6$, (d) $EMImSbF_6$, (e) $EMImNbF_6$, (f) $EMImTaF_6$, (g) $EMImWF_7$ and (h) EMImCl in the region between 2500–3500 cm^{-1}

Experimental

Materials and methods

Volatile materials were handled in a vacuum line constructed of SUS316 stainless steel and PFA (tetrafluoroethylene–perflurоalkyl vinyl ether copolymer). Nonvolatile materials were handled under argon atmosphere in a glove-box. A PFA reaction tube combined with a stainless steel valve was used as a reaction vessel for volatile materials. A T-shaped reactor constructed of tubes and a T-joint made of PFA were used for the reaction of nonvolatile materials. Anhydrous HF (Daikin Industries, Co. Ltd., purity >99%) was treated with K_2NiF_6 (Ozark–Mahoning) for several days prior to use to remove

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water. **CAUTION**: Anhydrous HF and some fluorides below are highly toxic and must be handled using appropriate apparatus and protective gear. Acetone dehydrated (Wako Pure Chemical Industries, water content <50 ppm), BF_3 (Nippon Sanso, purity 99.99%), PF_5 (Nippon Sanso, purity 99%), SbF_5 (PCR, purity >97%), NbF_5 (Ozark–Mahoning, purity 99%), TaF_5 (Ozark–Mahoning, purity 99.5%), WF_6 (Central Glass, purity 99.999%) were used as supplied. AsF_5 was prepared by the reaction of As_2O_3 (Wako Pure Chemical Industries, purity >98%) and F_2 gas (Daikin Industries, purity 99.7%) at 573 K. VF_5 was prepared by the reaction of vanadium metal powder (Nilaco, purity 99.5%) and F_2 gas at 573 K. KVF_6 was prepared by the reaction of KF (Wako Pure Chemical Industries, purity >98%) and VF_5 in aHF. $KSbF_6$ (Aldrich, purity 99%) was used as supplied. EMImCl (Sanko Chemical Industry, purity 98.5%) was purified by recrystallization in acetonitrile solution by adding ethyl acetate. EMIm$(HF)_{2.3}F$ was synthesized by the reaction of EMImCl and anhydrous HF.[6] EMIm$(HF)_{2.3}F$ is involatile and inert against borosilicate glassware at ambient conditions, however, contact with reducing metals such as aluminium should be avoided.

Synthesis of EMImBF$_4$

EMIm$(HF)_{2.3}F$ (9.88 mmol) and a large excess of BF_3 were reacted in a PFA tube. A colorless liquid was obtained after the removal of liberated HF and excess BF_3 under dynamic vacuum at 343 K. Spectroscopic methods and elemental analysis identified the liquid as EMImBF$_4$ (9.84 mmol). Anal. Calc. for $BC_6F_4H_{11}N_2$: C, 36.38; H 5.56; N, 14.15. Found: C, 36.38; H 5.42; N, 14.30%. ^{1}H NMR (neat), δ 8.35 (s, 1H, H(2)), 7.30 (s, 1H, H(4)), 7.23 (s, 1H, H(5)), 3.97 (q, 2H, $J = 21.6$ Hz, H(6)), 3.66 (s, 3H, H(8)), 1.19 (t, 3H, $J = 14.7$ Hz, H(7)). ^{19}F NMR (neat), δ −150.35 (s, BF_4).

Synthesis of EMImPF$_6$

EMIm$(HF)_{2.3}F$ (6.51 mmol) and a large excess of PF_5 were reacted in a PFA tube. A white powdered sample was obtained after the removal of liberated HF and excess PF_5 under dynamic vacuum at 343 K. Spectroscopic methods and chemical analysis identified the solid as EMImPF$_6$ (6.69 mmol). Anal. Calc. for $C_6F_6H_{11}N_2P$: C, 28.13; H 4.30; N, 10.94. Found: C, 28.23; H 4.33; N, 10.91%. ^{1}H NMR (DMSO-d$_6$), δ 9.07 (s, 1H, H(2)), 7.75 (t, $J = 3.6$ Hz, H(4)), 7.66 (t, $J = 3.6$ Hz, H(5)), 4.17 (q, $J = 22.2$ Hz, H(6)), 3.83 (s, H(8)), 1.40 (t, $J = 14.7$ Hz, H(7)). ^{19}F NMR (DMSO-d$_6$), δ −70.7 (d, $J = 704$ Hz, PF_6).

Synthesis of EMImAsF$_6$

The reaction of EMIm$(HF)_{2.3}F$ (3.97 mmol) and a large excess of AsF_5 in the same manner as for EMImPF$_6$ gave a white powder of EMImAsF$_6$ (4.12 mmol). Anal. Calc. for $AsF_6C_6H_{11}N_2$: C, 24.01; H 3.67; N, 9.34. Found: C, 23.84; H 3.61; N, 9.25%. ^{1}H NMR (DMSO-d$_6$), δ 9.08 (s, 1H, H(2)), 7.76 (t, $J = 3.3$ Hz, H(4)), 7.67 (t, $J = 3.3$ Hz, H(5)), 4.17 (q, $J = 22.2$ Hz, H(6)), 3.83 (s, H(8)), 1.40 (t, $J = 14.7$ Hz, H(7)). ^{19}F NMR (DMSO-d$_6$), δ −68.4 (q, $J = 2788$ Hz, AsF_6). The salt was recrystallized from a cooled methanol solution at 268 K and provided for single-crystal X-ray diffraction.

Synthesis of EMImSbF$_6$

EMImCl (93.1 mmol) and $KSbF_6$ (93.1 mmol) were reacted in dehydrated acetone. After stirring for 72 h, the reaction mixture was filtered through a glass frit. The precipitate was identified as KCl by X-ray powder diffraction. The filtrate was dried by evacuation at 343 K in a PFA vessel. A colorless liquid was obtained. Spectroscopic methods and elemental analysis identified the liquid as EMImSbF$_6$ (74.7 mmol, yield 80.2%). Anal. Calc. for $F_6C_6H_{11}N_2Sb$: C, 20.76; H, 3.17; N, 8.07. Found: C, 20.74; H, 3.09; N, 8.18%. ^{1}H NMR (neat), δ 7.88 (s, 1H, H(2)), 6.95–6.91 (m, 1H, H(4)), 6.88–6.85 (m, 1H, H(5)), 3.71 (q, 2H, $J = 21.9$ Hz, H(6)), 3.40 (s, 3H, H(8)), 1.01 (t, 3H, $J = 14.7$ Hz, H(7)). ^{19}F NMR (neat), δ −113.69 (s, SbF_6). The salt was recrystallized from the neat salt at 273 K and provided for single-crystal X-ray diffraction.

Synthesis of EMImNbF$_6$

EMImNbF$_6$ was synthesized in the same manner as previously reported.[8] Anal. Calc. for $C_6F_4H_{11}N_2Nb$: C, 22.65; H, 3.46; N, 8.81. Found: C, 22.95; H 3.27; N, 8.80%. ^{1}H NMR (neat), δ 8.99 (br s, 1H, H(2)), 7.70 (br s, 1H, H(4)), 7.64 (br s, 1H, H(5)), 4.40 (br s, 2H, H(6)), 4.09 (br s, 3H, H(8)), 1.64 (br s, 3H, H(7)). ^{19}F NMR (neat), δ −127.25 (br s, NbF_6).

Synthesis of EMImTaF$_6$

EMImTaF$_6$ was synthesized in the same manner as previously reported.[8] Anal. Calc. for $C_6F_4H_{11}N_2Nb$: C, 17.74; H 2.71; N, 6.90. Found: C, 17.89; H 2.60; N, 6.85%. ^{1}H NMR (neat), δ 8.34 (br s, 1H, H(2)), 7.30 (br s, 2H, H(4), H(5)), 4.12 (br s, 2H, H(6)), 3.81 (br s, 3H, H(8)), 1.42 (br s, 3H, H(7)). ^{19}F NMR (neat), δ −191.48 (s, TaF_6).

Synthesis of EMImWF$_7$

EMIm$(HF)_{2.3}F$ (3.34 mmol) and a large excess of WF_6 were reacted in a PFA tube. After the reaction, phase separation of the excess WF_6 beneath the liquid of the reaction mixture was observed. A yellow liquid EMImWF$_7$ (3.31 mmol) was obtained after the removal of liberated HF and excess WF_6 under dynamic vacuum at 343 K. Anal. Calc. for $C_6F_7H_{11}N_2W$: C, 16.83; H, 2.57; N, 6.55. Found: C, 17.09; H, 2.74; N, 6.67%. ^{1}H NMR (neat), δ 8.47 (br s, 1H, H(2)), 7.51 (br s, 1H, H(4)), 7.46 (br s, 1H, H(5)), 4.24 (br s, 2H, H(6)), 3.93 (br s, 3H, H(8)), 1.50 (br s, 3H, H(7)). ^{19}F NMR (neat), δ −90.61 (s, WF_7).

X-Ray diffraction analysis

For EMImAsF$_6$, X-ray diffraction data were collected using a Nonius KappaCCD diffractometer with a CCD area detector and monochromated Mo-Kα radiation at 298 K. The single crystal which was fixed in a quartz capillary under argon atmosphere was mounted on a goniometer head. The obtained data were processed by the program DENZO-SMN.[24] The program SORTAV was used for the absorption correction.[25] For EMImSbF$_6$, X-ray diffraction data were collected using a Rigaku AFC7 diffractometer with a Mercury CCD area detector and monochromated Mo-Kα radiation at 200 K. The single crystal fixed on a glass fiber in a cooled oil ($C_{10}F_{18}$) was mounted on the goniometer head. The obtained data were processed by the program CRYSTAL CLEAR.[26] The SHELX-97 suite of programs were used for the solution and refinement of the structures.[27] All the non-hydrogen atoms were determined by the direct method and difference Fourier synthesis by introducing anisotropic displacement parameters, whereas all the hydrogen atoms were refined using appropriate riding models, with C–H distances of 0.97 Å for CH_2, 0.96 Å for CH_3 and 0.93 Å for aromatic groups. The displacement parameters of H atoms were fixed at $1.2U_{eq}$ of their parent atoms ($1.5U_{eq}$ for methyl groups).

CCDC reference numbers 217826 and 217827.

See http://www.rsc.org/suppdata/dt/b3/b310162b/ for crystallographic data in CIF or other electronic format.

Spectroscopic and thermal analyses

The Raman spectra of solid and liquid samples were obtained by FTS-175C (BIO-RAD Laboratories) using 1064 nm line of Nd:YAG laser as an excitation line at room temperature. The samples for Raman spectroscopy were loaded in NMR Pyrex test tubes. The IR spectra of solid and liquid samples were

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obtained by FTS-165 (BIO-RAD Laboratories). The samples were sandwiched by a pair of AgCl windows fixed in a stainless airtight cell. ^{1}H NMR measurements of the samples were performed using a Varian Mercury-300BB NMR spectrometer (300 MHz) and the obtained spectra were referenced to tetramethylsilane. ^{19}F NMR measurements of the samples were performed using a Varian Mercury-300BB NMR spectrometer (282 MHz) and the obtained spectra were referenced to trichlorofluoromethane; C_6D_6 was used as an external standard for the measurements of the neat salts. All the data were recorded as chemical shifts. Differential scanning calorimetric analysis (DSC) was performed on the sample in a platinum cell under nitrogen gas flow using a Shimadzu DSC-60. A scanning rate 5 K min^{-1} was used.

Measurement of electrochemical and physical properties

Electrochemical measurements were performed using a Pt or glassy carbon working electrode, and a glassy carbon counter electrode with the aid of Hokuto Denko, HZ-3000 electrochemical measurement system. The reference electrode was made of silver wire immersed in EMImBF$_4$ containing 0.05 M AgBF$_4$ which was separeted from the electrolyte by Polyflon filter (Advantec). Conductivities were measured by the impedance technique using a cell with platinum disk electrodes calibrated by KCl standard aqueous solution. Viscosity measurements were performed using an Ostwald viscometer made of PFA. Densities were measured by weighing samples in a PFA vessel whose volume was calibrated by distilled water.

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