



Thermal properties of *N*-alkyl-*N*-methylpyrrolidinium and *N*-butylpyridinium fluorometallates and physicochemical properties of their melts

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ABSTRACT

A series of *N*-alkyl-*N*-methylpyrrolidinium (RMPyr⁺, where R = E: ethyl, B: butyl, and H: hexyl) and *N*-butylpyridinium (BPy⁺) salts based on the fluoro-complex anions, BF₄⁻, PF₆⁻, SbF₆⁻, NbF₆⁻, TaF₆⁻, and WF₇⁻, have been synthesized and their thermal behavior has been investigated. The melting points of the RMPyr⁺ salts are above room temperature with the trend; BMPyrAF₆ < HMPyrAF₆ < EMPyrAF₆ for the hexafluoro-complex salts. Some of the salts containing BMPyr⁺ and HMPyr⁺ exhibit phase transitions in the solid states. Similar melting points of BPy⁺ salts of PF₆⁻, SbF₆⁻, NbF₆⁻, TaF₆⁻, and WF₇⁻ are observed at around 350 K. Ionic conductivity and viscosity for BMPyrNbF₆ (3.0 mS cm⁻¹ and 164 cP at 328 K) are similar to those for BMPyrTaF₆ (3.0 mS cm⁻¹ and 165 cP at 328 K), resulting from the similarity of the anions in size. The activation energies of ionic conductivity for the NbF₆⁻ and TaF₆⁻ salts are 18 and 20 kJ mol⁻¹, and those for viscosity are 23 and 25 kJ mol⁻¹, respectively calculated by Arrhenius equation in the temperature range between 328 and 348 K. Electrochemical windows of BMPyrNbF₆, BMPyrTaF₆, and BMPyrWF₇ are about 4.0, 5.0 and 3.1 V, respectively.

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1. Introduction

Ionic liquids (ILs) attract more and more attention in various fields, such as electrochemistry and organic chemistry, because of their unique properties such as low volatility, nonflammability, wide liquid-phase temperature ranges, and wide electrochemical windows [1–5]. Compared to the salts based on the cations such as imidazolium and pyridinium, nonaromatic cation-based salts often exhibit high melting points and sometimes decompose without melting. On the other hand, the high electrochemical and chemical stabilities of the nonaromatic cation-based salts are large benefits in various applications including electric double layer capacitors (EDLCs), fuel cells, lithium batteries, and solar cells [6–11]. Dialkylpyrrolidinium cations are nonaromatic, however, exceptionally give low temperature ionic liquids in the combination with selected anions such as fluorohydrogenate ((FH)_nF⁻) and bis(trifluoromethylsulfonyl)amide (TFSA⁻) anions [12,13]. The pyrrolidinium cation-based salts also have received attention since they often form a plastic crystal phase [14–18] which are potential electrolytes in solar cells and Li-batteries [8].

Among the reported synthetic routes for ILs [19], fluoroacid–base reaction between fluorohydrogenate ILs and binary fluorides (AF_m) is one of the effective methods to reduce possible impurities

such as water and chloride or bromide from raw materials. A series of 1-ethyl-3-methylimidazolium (EMIm⁺) cation-based fluoro-complex salts of BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, NbF₆⁻, TaF₆⁻, and WF₇⁻ were synthesized with this method and characterized by spectroscopic, physical, chemical, and electrochemical methods [20]. The melting points of the series of the EMIm⁺ salts decrease with increasing the size of the anion from the PF₆⁻ salt (333 K) to the WF₇⁻ salt (258 K) except for the BF₄⁻ salt (288 K).

In the present study, we report the syntheses of a series of *N*-alkyl-*N*-methylpyrrolidinium (RMPyr⁺, where R = E: ethyl, B: butyl, and H: hexyl) and *N*-butylpyridinium (BPy⁺) salts based on the fluoro-complex anions, BF₄⁻, PF₆⁻, SbF₆⁻, NbF₆⁻, TaF₆⁻, and WF₇⁻ by fluoroacid–base reactions. Thermal behaviors of the obtained salts are also reported. The physical and electrochemical properties of the three salts with low melting temperatures, BMPyrNbF₆, BMPyrTaF₆, and BMPyrWF₇, are discussed in detail.

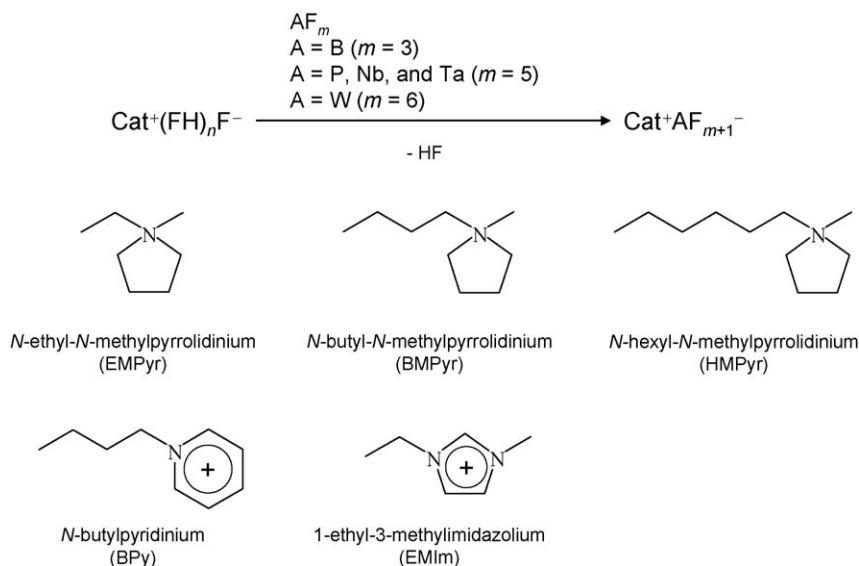
2. Results and discussion

2.1. Synthesis and vibrational spectroscopy

All the present fluoro-complex salts were prepared by the fluoroacid–base reactions of a fluorohydrogenate ionic liquid and the corresponding fluorides (Scheme 1) as previously reported [20] except SbF₆⁻ salts that were synthesized by the conventional ion exchange reactions of the corresponding chloride salts and KSBF₆

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Scheme 1. Preparation of the fluoro-complex salts and the structures of the cations used in the current study.

since the pyrrolidinium and pyridinium cations are not stable against the oxidation by SbF_5 . For all the salts obtained above, the corresponding cation and anion were confirmed by vibrational spectroscopy, while only the spectroscopic features of BMPyrNbF₆, BMPyrTaF₆, and BMPyrWF₇ are briefly described here (see Section 3 for the other salts).

Figs. 1 and 2 show IR and Raman spectra, respectively, for BMPyrNbF₆, BMPyrTaF₆, and BMPyrWF₇. The vibrational modes of the BMPyr cation are observed at the expected positions in the spectra [14,15]. For BMPyrNbF₆ and BMPyrTaF₆, the ν_3 mode of the

anion is observed in the IR spectra at 615 and 561 cm^{-1} , respectively, and the ν_1 and ν_5 modes are observed in the Raman spectra (670 and 283 cm^{-1} for BMPyrNbF₆ and 683 and 287 cm^{-1} for BMPyrTaF₆) [21]. The Raman active ν_2 and IR active ν_4 mode are too weak to be detected in the present salts. Although the molecular geometry of WF_7^- in BMPyrWF₇ is unknown, the possible three candidates, monocapped octahedron, monocapped trigonal prism, and pentagonal bipyramid, are considered to give a strong peak at $\sim 700 \text{ cm}^{-1}$ in the Raman spectrum as reported in the previous literatures [22–24]. The absorption band observed

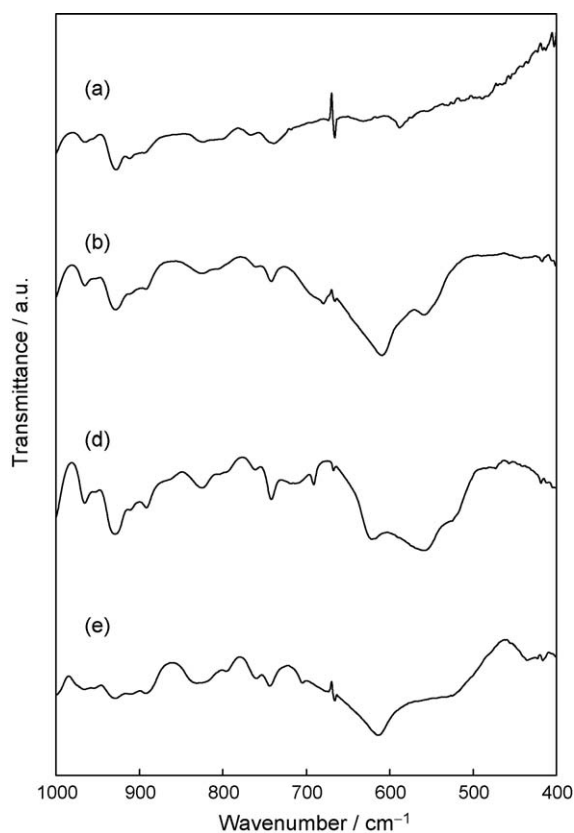


Fig. 1. IR spectra of (a) BMPyrCl, (b) BMPyrNbF₆, (c) BMPyrTaF₆, and (d) BMPyrWF₇.

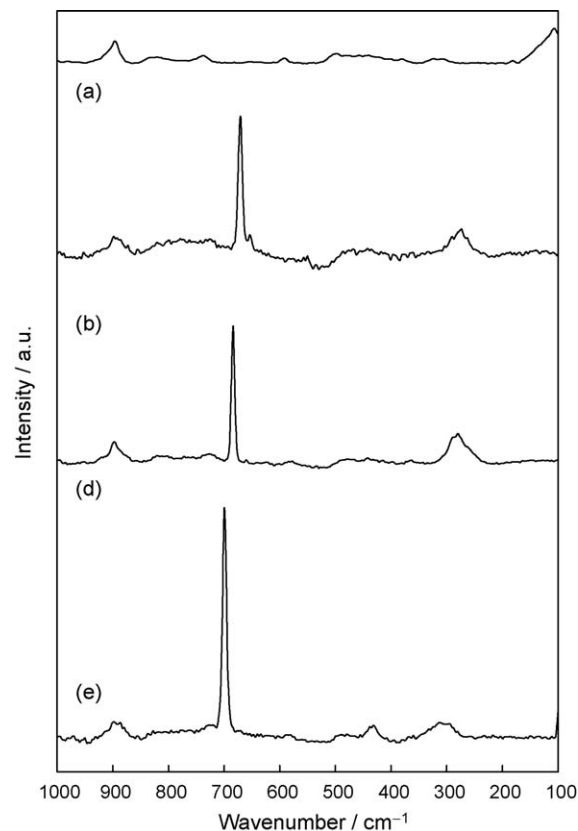


Fig. 2. Raman spectra of (a) BMPyrCl, (b) BMPyrNbF₆, (c) BMPyrTaF₆, and (d) BMPyrWF₇.

Table 1
Melting points and decomposition temperatures of RMPyr and BPy fluorocomplex salts.

	M.W.	T_m /K	T_d /K
EMPy _r			
BF ₄ ⁻	201	567	697
PF ₆ ⁻	259	534	657
SbF ₆ ⁻	350	–	651
NbF ₆ ⁻	321	–	663
TaF ₆ ⁻	409	–	670
WF ₇ ⁻	431	–	659
BMPyr			
SbF ₆ ⁻	378	326	633
NbF ₆ ⁻	349	320	639
TaF ₆ ⁻	437	323	637
WF ₇ ⁻	459	322	635
HMPyr			
BF ₄ ⁻	259	345	613
PF ₆ ⁻	315	467	608
SbF ₆ ⁻	406	453	623
NbF ₆ ⁻	377	439	623
TaF ₆ ⁻	465	448	673
WF ₇ ⁻	487	456	710
BPy			
PF ₆ ⁻	281	351	518
SbF ₆ ⁻	371	351	603
NbF ₆ ⁻	343	357	573
TaF ₆ ⁻	431	351	633
WF ₇ ⁻	453	348	603

M.W.: molecular weight; T_m : melting point; T_d : decomposition temperature.

around 580 cm⁻¹ in the IR spectrum also agrees with the band observed in other WF₇⁻ salts [20].

2.2. Thermal behaviors

The melting points and decomposition temperatures of a series of RMPyr and BPy salts are listed in Table 1. In the cases of EMPyr salts, the BF₄⁻ and PF₆⁻ salts exhibit melting points of 567 and 534 K, respectively, whereas the other salts of SbF₆⁻, NbF₆⁻, TaF₆⁻, and WF₇⁻ decompose without melting. Although the melting point of HMPyrBF₄ is 345 K, the other HMPyr⁺ salts of PF₆⁻, SbF₆⁻, NbF₆⁻, TaF₆⁻, and WF₇⁻ exhibit much higher melting points of around 450 K. The aromatic cation-based salts of BPy⁺ based on PF₆⁻, SbF₆⁻, NbF₆⁻, TaF₆⁻, and WF₇⁻ exhibit melting points of around 350 K regardless of the anionic species. The pyrrolidinium cation-based salts, HMPyrBF₄ and BMPyrAF_n (A = Sb, Nb, Ta (n = 6), W (n = 7)), exhibit several solid–solid transitions. Fig. 3 and Table 2 show the DSC heating traces and phase transition temperature of BMPyr⁺ salts of NbF₆⁻, TaF₆⁻, and WF₇⁻ anion, respectively. In the

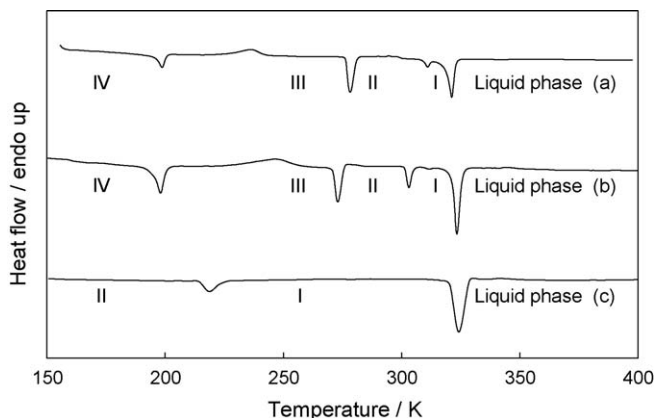


Fig. 3. DSC curves for (a) BMPyrNbF₆, (b) BMPyrTaF₆, and (c) BMPyrWF₇.

Table 2
Summary of thermal transition temperatures for BMPyr salts.

	T_{IV-III} /K	T_{III-II} /K	T_{II-I} /K	T_m /K	ΔH_f /kJ mol ⁻¹	ΔS_f /J K ⁻¹ mol ⁻¹
BMPyrNbF ₆	195	278	305	320	2.44	7.6
BMPyrTaF ₆	198	273	303	323	3.27	10.1
BMPyrWF ₇	–	–	202	322	4.09	12.7

T_m : melting temperature; ΔH_f : enthalpy change of fusion; ΔS_f : entropy change of fusion.

solid state, both NbF₆⁻ and TaF₆⁻ salts exhibit four solid phases. The broad exothermic peak observed for the NbF₆⁻ and TaF₆⁻ salts between the phases IV and III are assigned to the crystallization of a supercooled domain. On the other hand, the WF₇⁻ salt exhibits two solid phases assigned to the phase I and II, with a phase transition temperature of 202 K. The enthalpy and entropy changes of fusion, ΔH_f and ΔS_f , are also shown in Table 2. The ΔS_f value is calculated using the relationship $\Delta S_f = \Delta H_f/T_m$, where T_m is the melting point. Timmermans pointed out that plastic crystal phases typically have an entropy change of fusion, lower than 20 J K⁻¹ mol⁻¹ [25]. This appears to be the cases for NbF₆⁻ of 7.6 J K⁻¹ mol⁻¹, TaF₆⁻ of 10.1 J K⁻¹ mol⁻¹, and WF₇⁻ salts of 12.7 J K⁻¹ mol⁻¹, suggesting that the solid phase I for the present NbF₆⁻, TaF₆⁻, and WF₇⁻ salts is a plastic crystal phase [16,17].

Fig. 4 shows the melting points of the prepared salts as a function of the ionic radii of central atoms of the anions [20,26]. The data for EMImAF_m (A = P, As, Sb, Nb, Ta (m = 6), and W (m = 7)) [20] are also plotted for comparison. In the cases of BMPyr⁺ salts, the melting point decreases with increase in size of the central atom, from 411 K for BMPyrBF₄ to 316 K for BMPyrWF₇. On the other hand, the melting points of BPyPF₆, BPyNbF₆, BPyTaF₆, and BPyWF₇ are not different significantly, 351, 357, 351, and 348 K, respectively. Comparing BMPyr⁺ salts of NbF₆⁻, TaF₆⁻, and WF₇⁻ to the corresponding BPy⁺ salts, BMPyr⁺ salts exhibit melting points about 30 K lower than those of the BPy⁺ salts. The melting points of these salts are determined by several factors, including lattice energy that is related to the crystal structure and interaction energy between an ion and its adjacent ions in the liquid state. The BF₄⁻ anion tends to show a lower melting point in spite of its small size, which is probably due to the different coordination

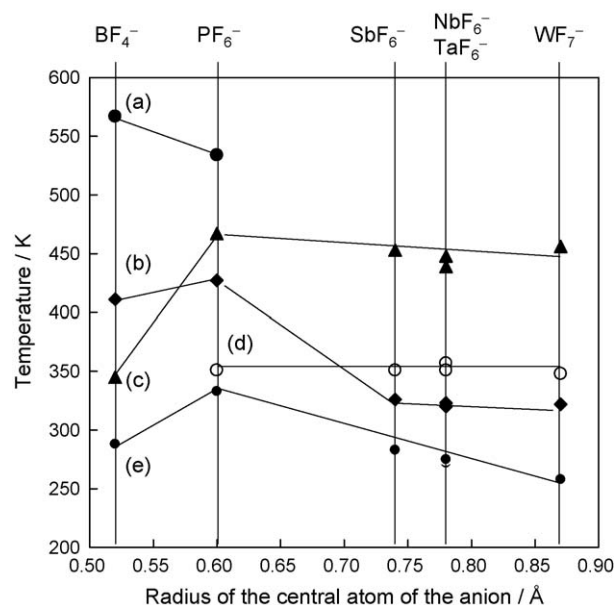


Fig. 4. Relationship between the melting point and radius of the central atom of the anion for the fluorocomplex salts: (a) EMPyr, (b) BMPyr, (c) HMPyr, (d) BPy, and (e) EMIm.

Table 3

Summary of ionic conductivity and viscosity of BMPyrNbF₆ and BMPyrTaF₆ in the temperature range of 328–348 K.

	Temperature/K				
	328	333	338	343	348
BMPyrNbF ₆					
η/cP	164	126	106	87	74
σ/mS cm ⁻¹	3.0	3.5	4.2	4.8	5.5
BMPyrTaF ₆					
η/cP	165	128	110	89	70
σ/mS cm ⁻¹	3.0	3.5	4.2	5.1	5.8

η: viscosity; σ: ionic conductivity.

environment around its tetrahedral shape from the larger hexa- or heptacoordinated anions. Further discussion requires the crystal structures and thermodynamic data for these compounds.

2.3. Physical and electrochemical properties

Table 3 lists ionic conductivity and viscosity for BMPyrNbF₆ and BMPyrTaF₆ in the temperature range from 328 to 348 K. The ionic conductivity and viscosity of BMPyrNbF₆ are similar to those of BMPyrTaF₆. Fig. 5 shows the Arrhenius plots of viscosity and conductivity for BMPyrNbF₆ and BMPyrTaF₆. The activation energies of ionic conductivity for the NbF₆⁻ and TaF₆⁻ salts are 18 and 20 kJ mol⁻¹, and those for viscosity are 23 and 25 kJ mol⁻¹, respectively, calculated by Arrhenius equation in the temperature

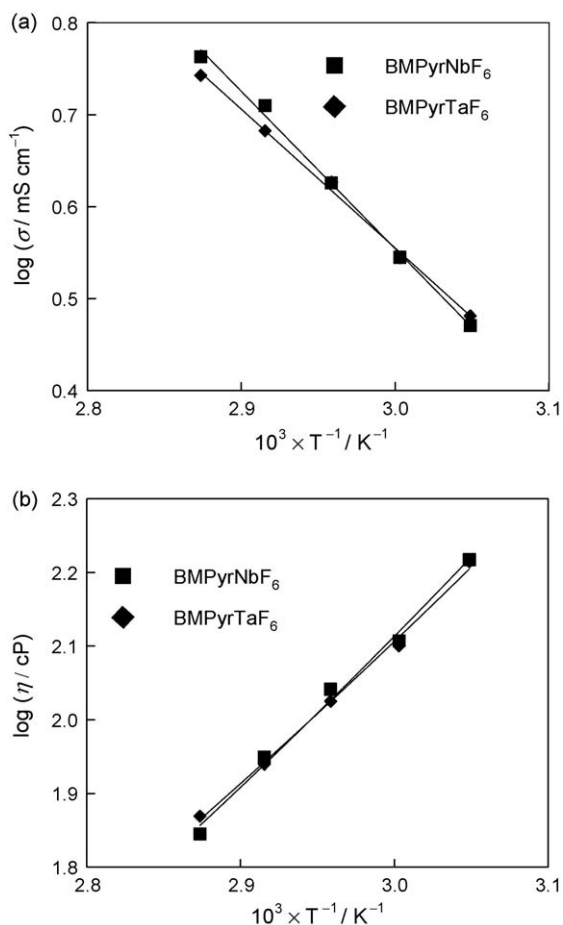


Fig. 5. Temperature dependency of viscosity and ionic conductivity for BMPyrNbF₆ and BMPyrTaF₆ in the temperature range of 325–353 K.

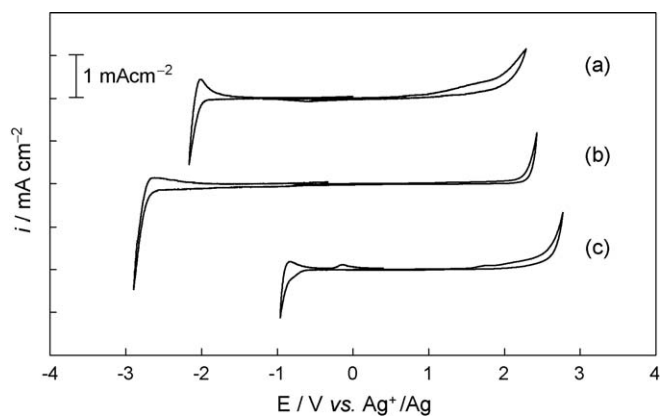


Fig. 6. Cyclic voltammograms of a glassy carbon electrode in (a) BMPyrNbF₆, (b) BMPyrTaF₆, and (c) BMPyrWF₇.

range between 328 and 348 K. The similarity in these values is considered to be the results of the similar size of the anions. Fig. 6 shows the cyclic voltammograms of a glassy carbon electrode in BMPyrNbF₆, BMPyrTaF₆, and BMPyrWF₇ at 343 K. The cathode limits of NbF₆⁻, TaF₆⁻, and WF₇⁻ salts are -2.0, -2.8, and -0.8 V vs. Ag⁺/Ag, respectively. These limits are assigned to the reductions of anions, because the reduction of BMPyr⁺ is observed at around -3.0 V vs. Ag⁺/Ag [17,27]. Although the reactions at the cathode limits for the three BMPyr⁺ salts are unknown, the difference of the reduction potential is due to the difference in stability of the anion against reduction, which is supported by the similar reduction potentials to the cases of the EMIm⁺ salts of NbF₆⁻, TaF₆⁻, and WF₇⁻ (-2.0, -2.9, and -0.8 V vs. Ag⁺/Ag, respectively) [20]. On the other hand, the anode limits of NbF₆⁻, TaF₆⁻, and WF₇⁻ were +2.0, +2.2, and +2.3 V vs. Ag⁺/Ag, respectively, and assigned to the oxidations of BMPyr⁺. In conclusion, the electrochemical windows of BMPyrNbF₆, BMPyrTaF₆, and BMPyrWF₇ are 4.0, 5.0 and 3.1 V, respectively.

3. Experimental

3.1. General experimental procedure

Moisture sensitive materials were handled in a glove box under a dry Ar atmosphere. All the reactions involved with anhydrous HF (aHF, Daikin Industries, purity >99%) were performed in PFA reactors. Anhydrous HF was dried over K₂NiF₆ (Ozark-Mahoning) for several days prior to use. The starting chlorides, RMPyrCl and BPyCl, were prepared by the reactions of the corresponding amine and chloroalkane. The fluorohydrogenate salts were prepared by the reactions of the chloride and a large excess of aHF. Volatile materials were pumped off at room temperature after the reaction. Boron trifluoride (Nippon Sanso, purity 99.99%), PF₅ (Nippon Sanso, purity 99%), antimony pentafluoride (SbF₅, PCR, purity >97%), K₂SbF₆ (Aldrich, purity 99%), NbF₅ (Aldrich, purity 99%), TaF₆ (Aldrich, purity 99.5%), and WF₆ (Central Glass, purity 99.999%) were used as supplied.

3.2. Spectroscopic measurement

Raman spectra of solid and liquid samples were obtained by LabRAM300 (Horiba Jobin Yvon) using 632 nm line of He-Ne 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 obtained by FTS-165 (BIO-RAD Laboratories). The samples were sandwiched by a pair of AgCl windows fixed in a stainless airtight cell.

3.3. Measurement of physical and electrochemical properties

Differential scanning calorimetric (DSC) analysis was performed on the sample in an aluminium sealed cell under dry Ar gas flow using a Shimadzu DSC-60. The scanning rate of 10 K min⁻¹ was used. Conductivity and electrochemical window were measured by AC impedance spectroscopy and cyclic voltammetry, respectively, with the aid of HZ-3000 electrochemical measurement system (Hokuto Denko). The cell for conductivity measurement was made of PFA and polytetrafluoroethylene (PTFE) with platinum disk electrodes and was calibrated by a KCl standard aqueous solution. The working and counter electrodes for electrochemical window measurement were glassy carbon, on the other side, reference electrode was Ag wire immersed in EMIMBF₄ containing 0.05 M AgBF₄. Viscosity was measured by a cone-plate rheometer DV-II + Pro (Brookfield Engineering Laboratories Inc.).

3.4. Synthesis

3.4.1. Synthesis of EMPyrBF₄

Boron trifluoride was condensed on EMPyr(FH)_{2.3}F (5.58 mmol) at 77 K in a PFA tube. After warming up to room temperature, the mixture was mixed well. This procedure was repeated several times until the reaction finishes. A colorless solid was obtained after the removal of liberated HF and excess BF₃ under dynamic vacuum at 300 K. Anal. Calcd. for C₇F₄H₁₆N₁B₁: C, 41.83; H, 8.02; N, 6.97. Found: C, 41.79; H, 7.94; N, 6.99. Raman (frequency/cm⁻¹ (relative intensity)): 739(s) (BF₄⁻, ν₁). IR (frequency/cm⁻¹ (relative intensity)): 1049(s) (BF₄⁻, ν₃), 524(s) (BF₄⁻, ν₄). Here, s and w for relative intensity denote strong and weak, respectively.

3.4.2. Synthesis of EMPyrPF₆

The same procedure as for EMPyrBF₄ was used. Anal. Calcd. for C₇F₆H₁₆N₁P₁: C, 32.44; H, 6.22; N, 5.40. Found: C, 32.16; H, 5.94; N, 5.41. Raman (frequency/cm⁻¹ (relative intensity)): 738(s) (PF₆⁻, ν₁). IR (frequency/cm⁻¹ (relative intensity)): 845(s) (PF₆⁻, ν₃), 559(s) (PF₆⁻, ν₄).

3.4.3. Synthesis of EMPyrSbF₆

EMPyrCl (5.58 mmol) and equivalent KSbF₆ (5.56 mmol) were reacted in acetone, and most amount of by-product KCl was eliminated by filtration. After removing acetone, water and dichloroethane were added to the EMPyrSbF₆ and KCl mixture for extraction. A white powder of BMPyrSbF₆ was obtained by removing water containing KCl, and dichloroethane under dynamic vacuum at 300 K. Anal. Calcd. for C₇F₆H₁₆N₁Sb₁: C, 24.02; F, 32.57; H, 4.61; N, 4.00. Found: C, 23.54; F, 32.08; H, 4.43; N, 3.91. Raman (frequency/cm⁻¹ (relative intensity)): 645(s) (SbF₆⁻, ν₁), 278(w) (SbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 663(s) (SbF₆⁻, ν₃).

3.4.4. Synthesis of EMPyrNbF₆

EMPyr(FH)_{2.3}F (4.82 mmol) and equimolar NbF₅ (4.82 mmol) were reacted in a T-shaped PFA reactor. A colorless powder sample was obtained after the removal of liberated HF under dynamic vacuum at 340 K. Raman and IR spectroscopy and elemental analyses identified the solid was BMPyrNbF₆. Anal. Calcd. for C₇F₆H₁₆N₁Nb₁: C, 26.18; F, 35.50; H, 5.02; N, 4.36. Found: C, 25.55; F, 35.11; H, 4.77; N, 4.30. Raman (frequency/cm⁻¹ (relative intensity)): 676(s) (NbF₆⁻, ν₁), 278(w) (NbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 617(s) (NbF₆⁻, ν₃).

3.4.5. Synthesis of EMPyrTaF₆

The same procedure as for EMPyrNbF₆ was used. Anal. Calcd. for C₇F₆H₁₆N₁Ta₁: C, 20.55; F, 27.86; H, 3.94; N, 3.42. Found: C, 20.00;

F, 27.05; H, 3.72; N, 3.38. Raman (frequency/cm⁻¹ (relative intensity)): 691(s) (TaF₆⁻, ν₁), 282(w) (TaF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 578(s) (TaF₆⁻, ν₃).

3.4.6. Synthesis of EMPyrWF₇

The same procedure as for EMPyrBF₄ was used. Anal. Calcd. for C₇F₇H₁₆N₁W₁: C, 19.51; F, 30.85; H, 3.74; N, 3.25. Found: C, 20.98; F, 23.00; H, 4.22; N, 3.51. Raman (frequency/cm⁻¹ (relative intensity)): 629(s) (WF₇⁻). IR (frequency/cm⁻¹ (relative intensity)): 615(s) (WF₇⁻).

3.4.7. Synthesis of BMPyrSbF₆

The same procedure as for EMPyrSbF₆ was used. Anal. Calcd. for C₇F₆H₁₆N₁Sb₁: C, 28.60; F, 30.16; H, 5.33; N, 3.71. Found: C, 28.65; F, 29.62; H, 5.32; N, 3.77. Raman (frequency/cm⁻¹ (relative intensity)): 645(s) (SbF₆⁻, ν₁), 570(vw) (SbF₆⁻, ν₂), 279(m) (SbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 653(s) (SbF₆⁻, ν₃). Here, m and vw for relative intensity denote medium and very weak, respectively.

3.4.8. Synthesis of BMPyrNbF₆

The same procedure as for EMPyrNbF₆ was used. Anal. Calcd. for C₉F₆H₂₀N₁Nb₁: C, 30.96; F, 32.65; H, 5.77; N, 4.01. Found: C, 30.69; F, 32.55; H, 5.60; N, 4.02. Raman (frequency/cm⁻¹ (relative intensity)): 670(s) (NbF₆⁻, ν₁), 283(w) (NbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 615(s) (NbF₆⁻, ν₃).

3.4.9. Synthesis of BMPyrTaF₆

The same procedure as for EMPyrNbF₆ was used. Anal. Calcd. for C₉F₆H₂₀N₁Ta₁: C, 24.73; F, 26.07; H, 4.61; N, 3.20. Found: C, 25.85; F, 25.30; H, 4.68; N, 3.47. Raman (frequency/cm⁻¹ (relative intensity)): 683(s) (TaF₆⁻, ν₁), 290(w) (TaF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 586(s) (TaF₆⁻, ν₃).

3.4.10. Synthesis of BMPyrWF₇

The same procedure as for EMPyrBF₄ was used. Anal. Calcd. for C₉F₇H₂₀N₁W₁: C, 23.55; F, 28.97; H, 4.39; N, 3.05. Found: C, 24.00; F, 26.80; H, 4.48; N, 3.16. Raman (frequency/cm⁻¹ (relative intensity)): 700(s), 307(w) (WF₇⁻). IR (frequency/cm⁻¹ (relative intensity)): 619(s) (WF₇⁻).

3.4.11. Synthesis of HMPyrBF₄

The same procedure as for EMPyrBF₄ was used. Anal. Calcd. for C₁₁F₄H₂₄N₁B₁: C, 51.38; H, 9.41; N, 5.45. Found: C, 49.47; H, 9.09; N, 5.26. Raman (frequency/cm⁻¹ (relative intensity)): 764(s) (BF₄⁻, ν₁). IR (frequency/cm⁻¹ (relative intensity)): 1072(s) (BF₄⁻, ν₃), 524(w) (BF₄⁻, ν₄).

3.4.12. Synthesis of HMPyrPF₆

The same procedure as for EMPyrBF₄ was used. Anal. Calcd. for C₁₁F₆H₂₄N₁P₁: C, 41.9; H, 7.67; N, 4.44. Found: C, 41.94; H, 7.72; N, 4.40. Raman (frequency/cm⁻¹ (relative intensity)): 738(s) (PF₆⁻, ν₁). IR (frequency/cm⁻¹ (relative intensity)): 849(s) (PF₆⁻, ν₃), 559(s) (PF₆⁻, ν₄).

3.4.13. Synthesis of HMPyrSbF₆

The same procedure as for EMPyrSbF₆ was used. Anal. Calcd. for C₁₁F₆H₂₄N₁Sb₁: C, 32.54; F, 28.07; H, 5.96; N, 3.45. Found: C, 30.48; F, 28.2; H, 5.53; N, 3.29. Raman (frequency/cm⁻¹ (relative intensity)): 644(s) (SbF₆⁻, ν₁), 278(w) (SbF₆⁻, ν₅). IR (frequency/cm⁻¹ (relative intensity)): 659(s) (SbF₆⁻, ν₃).

3.4.14. Synthesis of HMPyrNbF₆

The same procedure as for EMPyrSbF₆ was used. Anal. Calcd. for C₁₁F₆H₂₄N₁Nb₁: C, 35.02; F, 30.22; H, 6.41; N, 3.71. Found: C, 34.77; F, 28.74; H, 6.35; N, 3.70. Raman (frequency/cm⁻¹ (relative

intensity): 677(s) (NbF_6^- , ν_1), 274(w) (NbF_6^- , ν_5). IR (frequency/ cm^{-1} (relative intensity)): 774(s) (NbF_6^- , ν_3).

3.4.15. Synthesis of HMPyrTaF₆

The same procedure as for EMPyrNbF₆ was used. Anal. Calcd. for C₁₁F₆H₂₄N₁Ta₁: C, 28.4; F, 24.5; H, 5.20; N, 3.01. Found: C, 29.37; F, 24.4; H, 5.27; N, 3.09. Raman (frequency/ cm^{-1} (relative intensity)): 687(s) (TaF_6^- , ν_1), 282(w) (TaF_6^- , ν_5). IR (frequency/ cm^{-1} (relative intensity)): 598(s) (TaF_6^- , ν_3).

3.4.16. Synthesis of HMPyrWF₇

The same procedure as for EMPyrBF₄ was used. Anal. Calcd. for C₁₁F₇H₂₄N₁W₁: C, 27.12; F, 27.30; H, 4.97; N, 2.88. Found: C, 28.17; F, 20.61; H, 5.33; N, 3.04. Raman (frequency/ cm^{-1} (relative intensity)): 703(s) (WF_7^-). IR (frequency/ cm^{-1} (relative intensity)): 632(s) (WF_7^-).

3.4.17. Synthesis of BPyPF₆

The same procedure as for EMPyrBF₄ was used. Anal. Calcd. for C₇F₆H₁₆N₁P₁: C, 38.44; H, 5.02; N, 4.98. Found: C, 38.32; H, 4.80; N, 4.99. Raman (frequency/ cm^{-1} (relative intensity)): 728(s) (PF_6^- , ν_1). IR (frequency/ cm^{-1} (relative intensity)): 839(s) (PF_6^- , ν_3), 549 (PF_6^- , ν_4).

3.4.18. Synthesis of BPySbF₆

The same procedure as for EMPyrSbF₆ was used. Anal. Calcd. for C₇F₆H₁₆N₁Sb₁: C, 29.06; F, 30.65; H, 3.79; N, 3.77. Found: C, 28.86; F, 30.15; H, 3.71; N, 3.76. Raman (frequency/ cm^{-1} (relative intensity)): 643(s) (SbF_6^- , ν_1), 581(w) (SbF_6^- , ν_2), 284(m) (SbF_6^- , ν_5). IR (frequency/ cm^{-1} (relative intensity)): 645(s) (SbF_6^- , ν_3).

3.4.19. Synthesis of BPyNbF₆

The same procedure as for EMPyrNbF₆ was used. Anal. Calcd. for C₇F₆H₁₆N₁Nb₁: C, 31.51; F, 33.22; H, 4.11; N, 4.08. Found: C, 32.02; F, 33.10; H, 4.04; N, 4.19. Raman (frequency/ cm^{-1} (relative intensity)): 687(s) (NbF_6^- , ν_1), 287(w) (NbF_6^- , ν_5). IR (frequency/ cm^{-1} (relative intensity)): 608(s) (NbF_6^- , ν_3).

3.4.20. Synthesis of BPyTaF₆

The same procedure as for EMPyrNbF₆ was used. Anal. Calcd. for C₇F₆H₁₆N₁Ta₁: C, 25.07; F, 26.44; H, 3.27; N, 3.25. Found: C, 25.11; F, 26.31; H, 3.09; N, 3.20. Raman (frequency/ cm^{-1} (relative intensity)): 687(s) (TaF_6^- , ν_1), 292(w) (TaF_6^- , ν_5). IR (frequency/ cm^{-1} (relative intensity)): 570(s) (TaF_6^- , ν_3).

3.4.21. Synthesis of BPyWF₇

The same procedure as for EMPyrBF₄ was used. Anal. Calcd. for C₇F₇H₁₆N₁W₁: C, 23.86; F, 29.35; H, 3.11; N, 3.09. Found: C, 24.97; F, 22.69; H, 3.34; N, 3.23. Raman (frequency/ cm^{-1} (relative intensity)): 705(s) (WF_7^-). IR (frequency/ cm^{-1} (relative intensity)): 619(s) (WF_7^-).

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