SUPPORTING INFORMATION

Effects of Alkyl Chain Length and Anion Size on Thermal and Structural Properties for 1-Alkyl-3-methylimidazolium Hexafluorocomplex Salts (C_xMImAF_6, x = 14, 16, and 18; A = P, As, Sb, Nb, and Ta)

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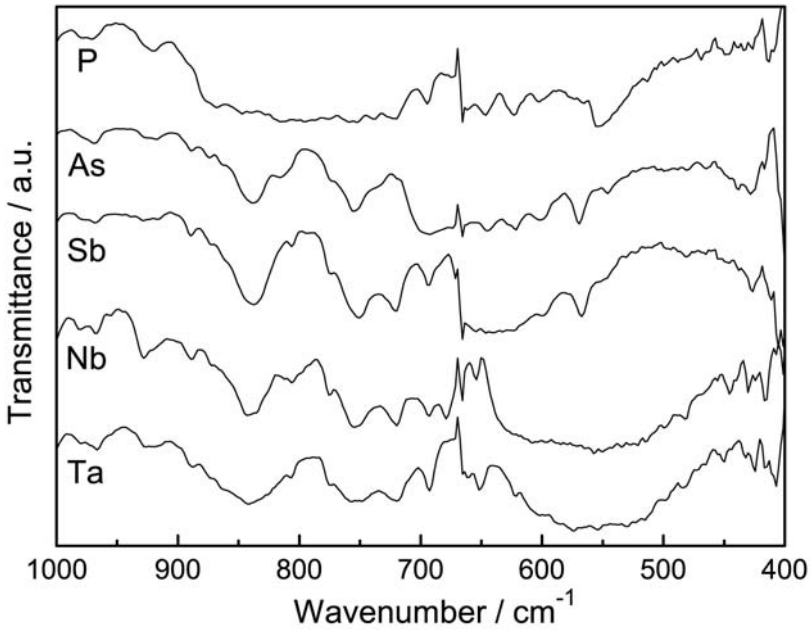

Figure S1 Infra-red spectra of $C_{14}MImAF_6$ (A = P, As, Sb, Nb, and Ta).

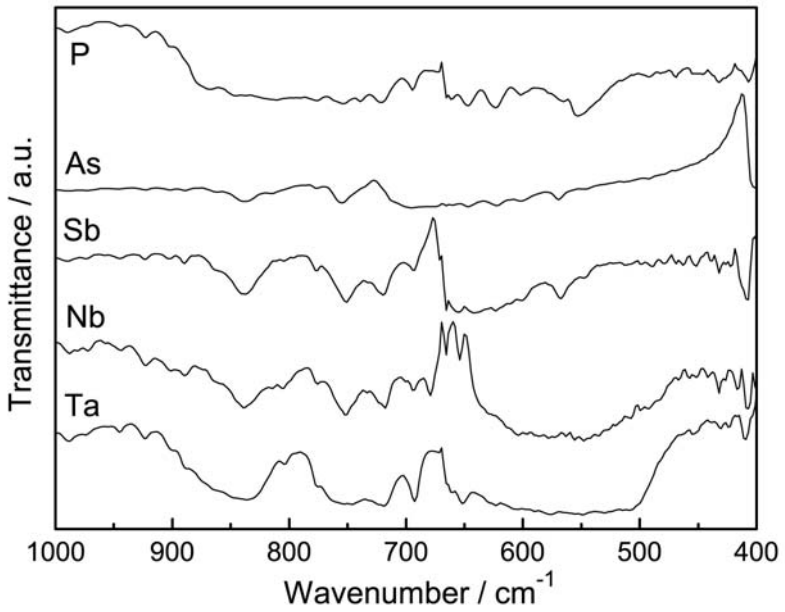

Figure S2 Infra-red spectra of $C_{16}MImAF_6$ (A = P, As, Sb, Nb, and Ta).

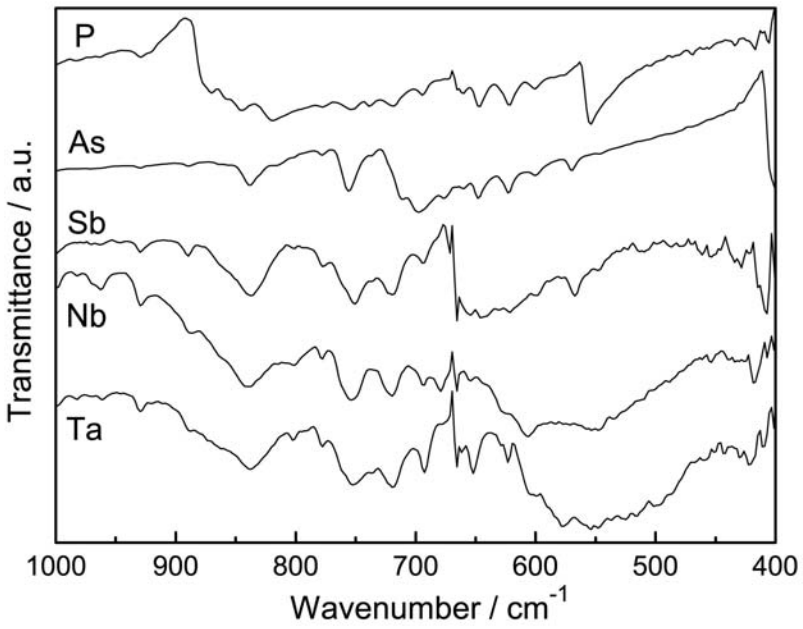

Figure S3 Infra-red spectra of $C_{18}MImAF_6$ (A = P, As, Sb, Nb, and Ta).

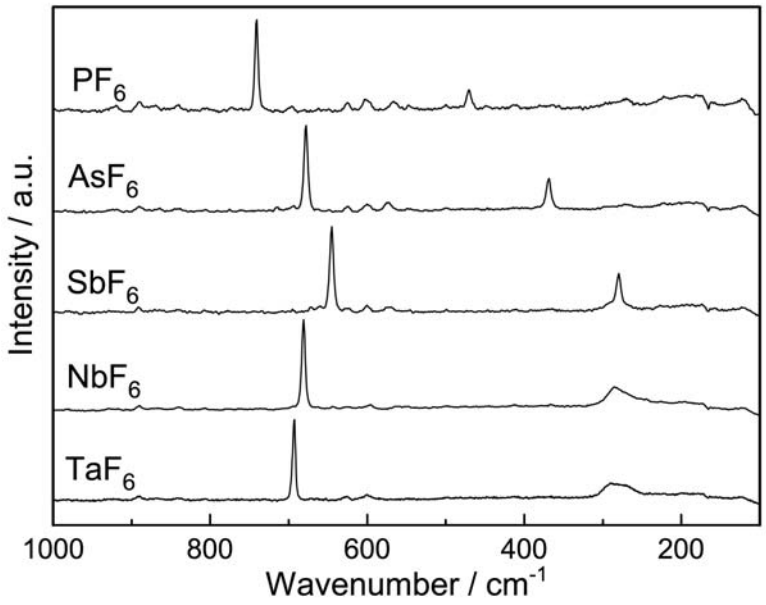

Figure S4 Raman spectra of $C_{14}MImAF_6$ (A = P, As, Sb, Nb, and Ta).

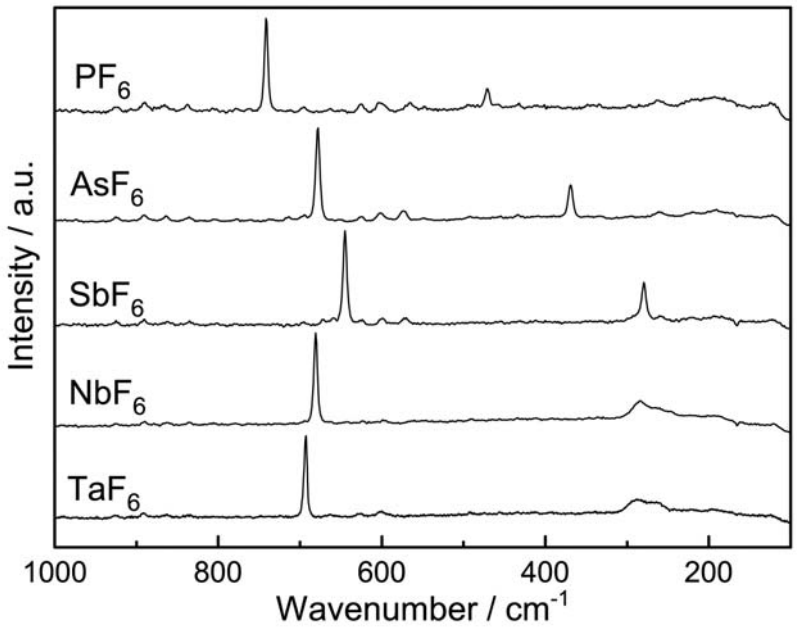

Figure S5 Raman spectra of $C_{16}MImAF_6$ (A = P, As, Sb, Nb, and Ta).

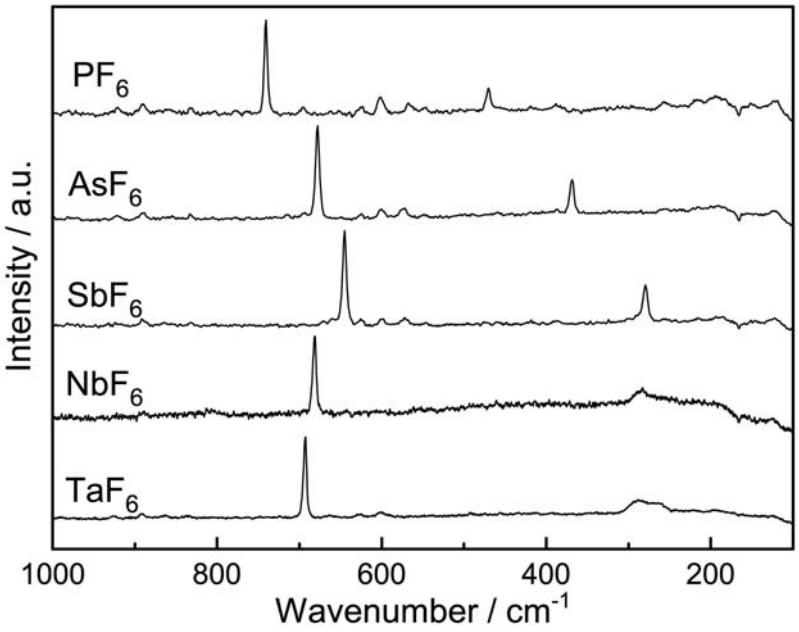

Figure S6 Raman spectra of $C_{18}MImAF_6$ (A = P, As, Sb, Nb, and Ta).

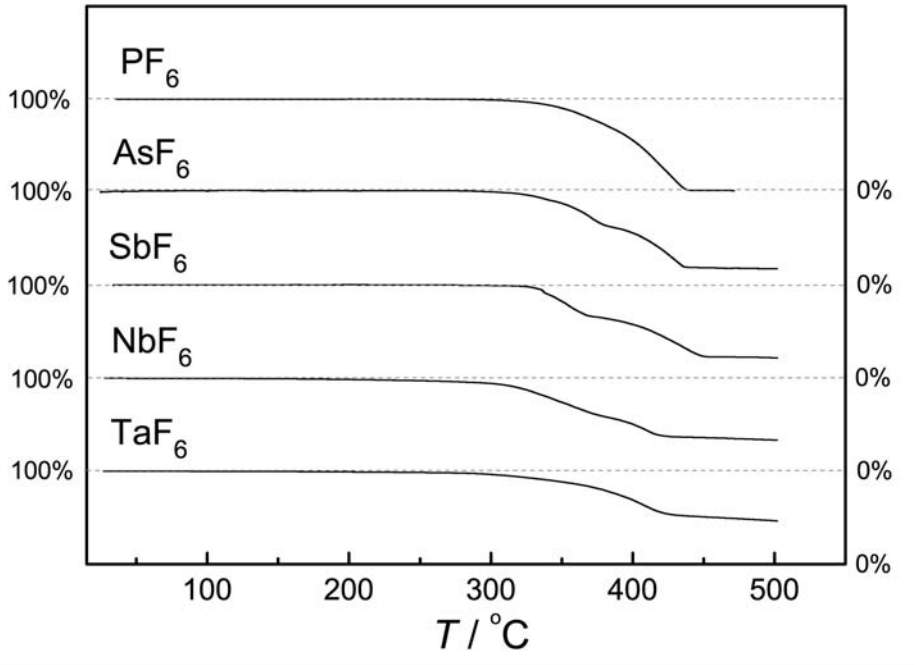

Figure S7 Thermogravimetric curves of $C_{14}MImAF_6$ (A = P, As, Sb, Nb, and Ta). The temperatures where the samples lose 10 % weight are 351.0 °C for $C_{14}MImPF_6$, 345.6 °C for $C_{14}MImAsF_6$, 340.5 °C for $C_{14}MImSbF_6$, 328.5 °C for $C_{14}MImNbF_6$, and 342.5 °C for $C_{14}MImTaF_6$.

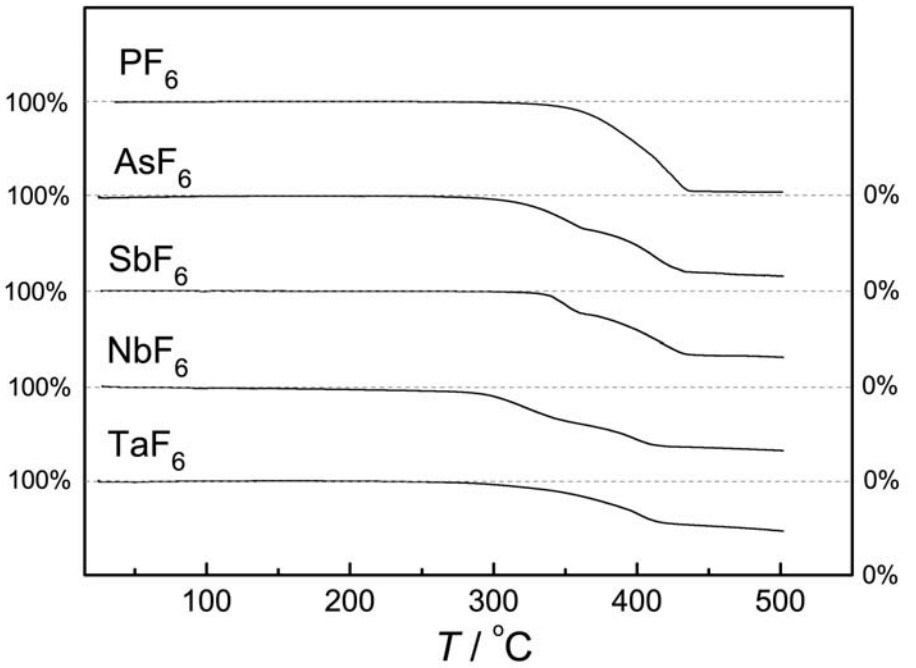

Figure S8 Thermogravimetric curves of $C_{16}MImAF_6$ (A = P, As, Sb, Nb, and Ta). The temperatures where the samples lose 10 % weight are 351.2 °C for $C_{16}MImPF_6$, 336.2 °C for $C_{16}MImAsF_6$, 345.2 °C for $C_{16}MImSbF_6$, 307.8 °C for $C_{16}MImNbF_6$, and 337.2 °C for $C_{16}MImTaF_6$.

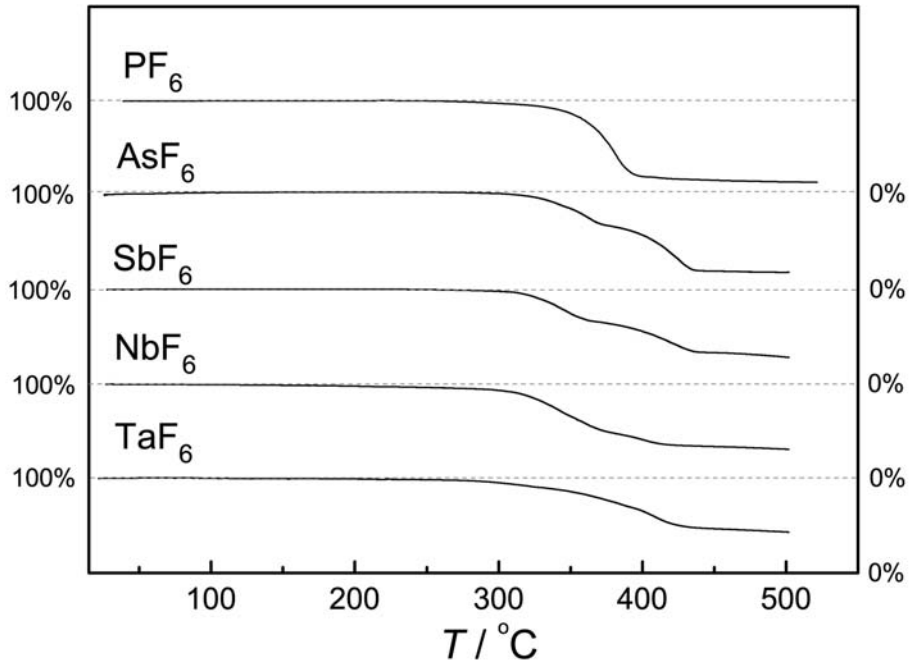

Figure S9 Thermogravimetric curves of $C_{18}MImAF_6$ (A = P, As, Sb, Nb, and Ta). The temperatures where the samples lose 10 % weight are 343.5 °C for $C_{18}MImPF_6$, 342.7 °C for $C_{18}MImAsF_6$, 329.3 °C for $C_{18}MImSbF_6$, 314.9 °C for $C_{18}MImNbF_6$, and 332.3 °C for $C_{18}MImTaF_6$.

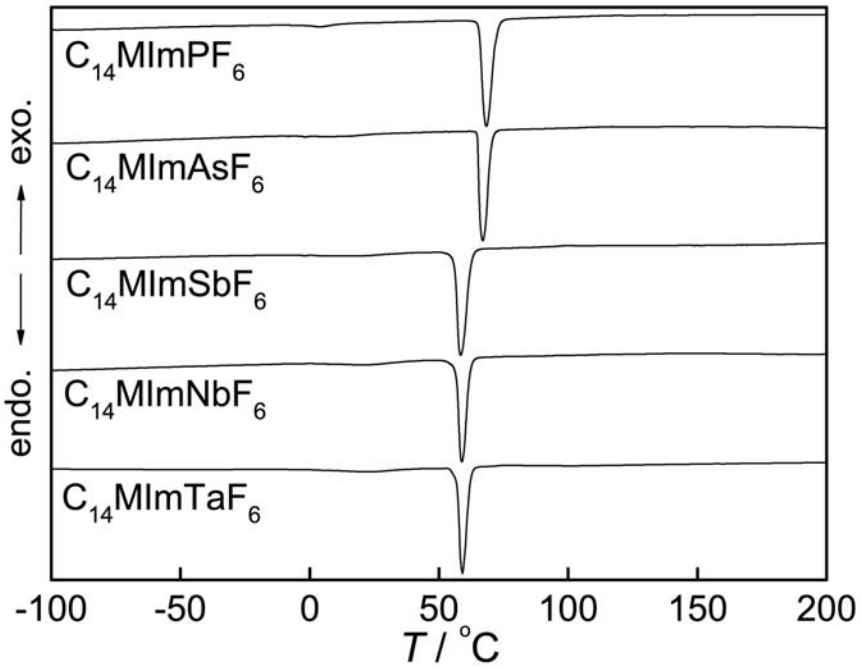

Figure S10 Differential scanning calorimetric curves (heating process) for $C_{14}MImAF_6$ (A = P, As, Sb, Nb, and Ta).

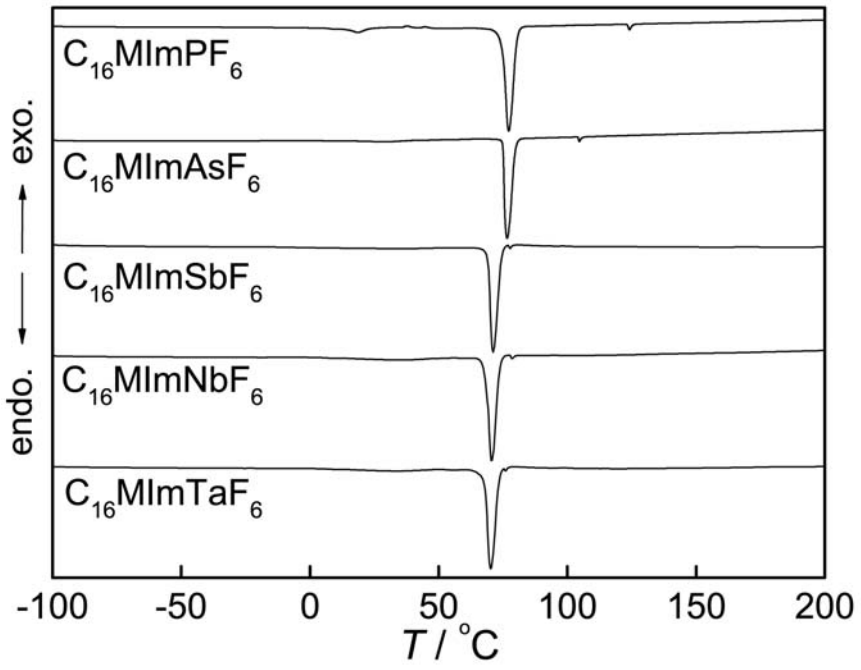

Figure S11 Differential scanning calorimetric curves (heating process) for $C_{16}MImAF_6$ (A = P, As, Sb, Nb, and Ta).

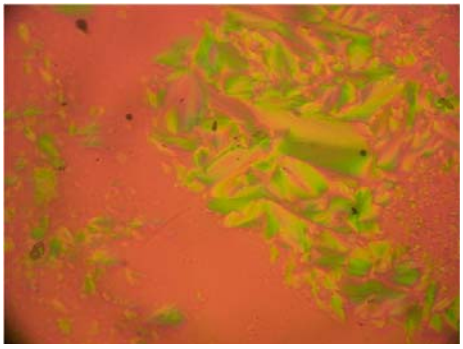

Figure S12 Polarized optical microscopic textures of $C_{14}MImPF_6$ (67 °C).

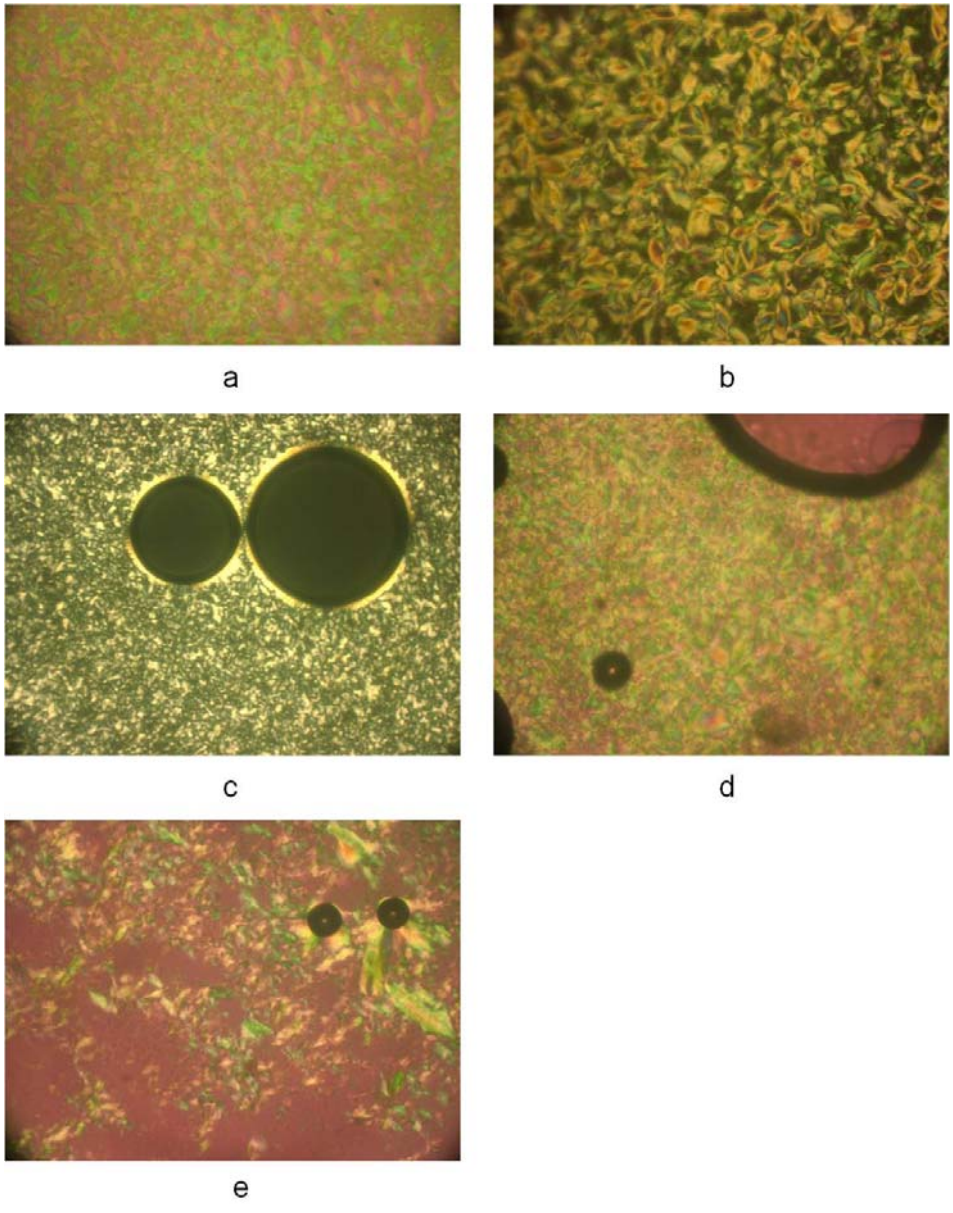

Figure S13 Polarized optical microscopic textures of (a) $C_{16}MImPF_6$ at 100 °C, (b) $C_{16}MImAsF_6$ at 100 °C, (c) $C_{16}MImSbF_6$ at 68 °C, (d) $C_{16}MImNbF_6$ at 70 °C, and $C_{16}MImTaF_6$ at 70 °C.

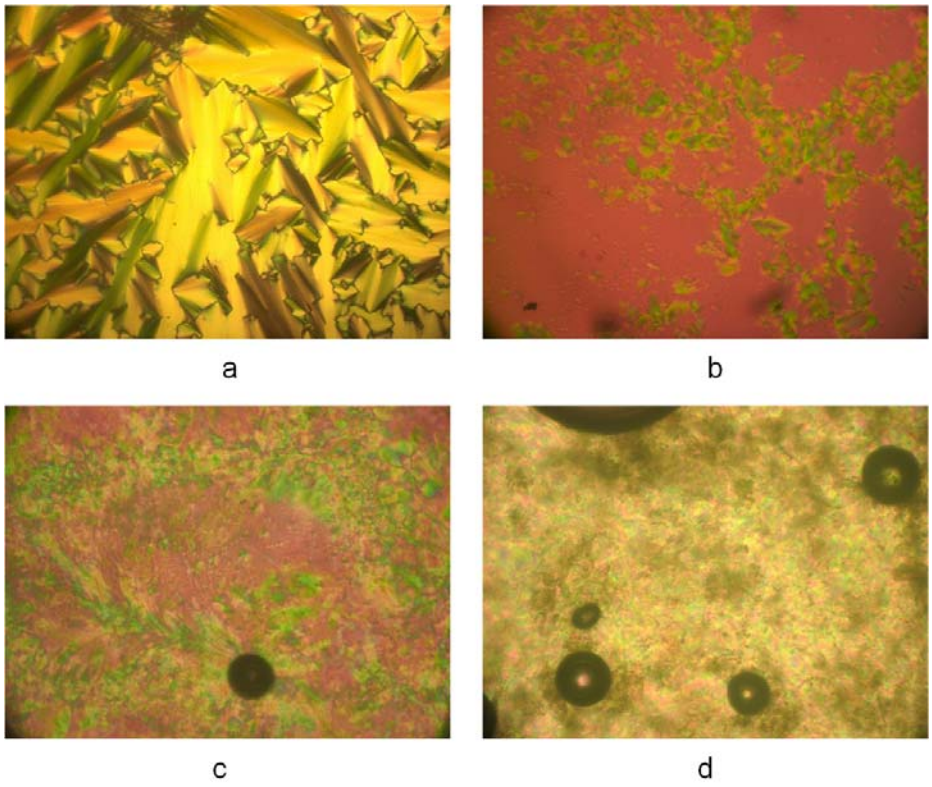

Figure S14 Polarized optical microscopic textures of (a) $C_{18}MImPF_6$ at 100 °C, (b) $C_{18}MImAsF_6$ at 100 °C, (c) $C_{18}MImSbF_6$ at 100 °C, and (d) $C_{18}MImNbF_6$ at 100 °C.

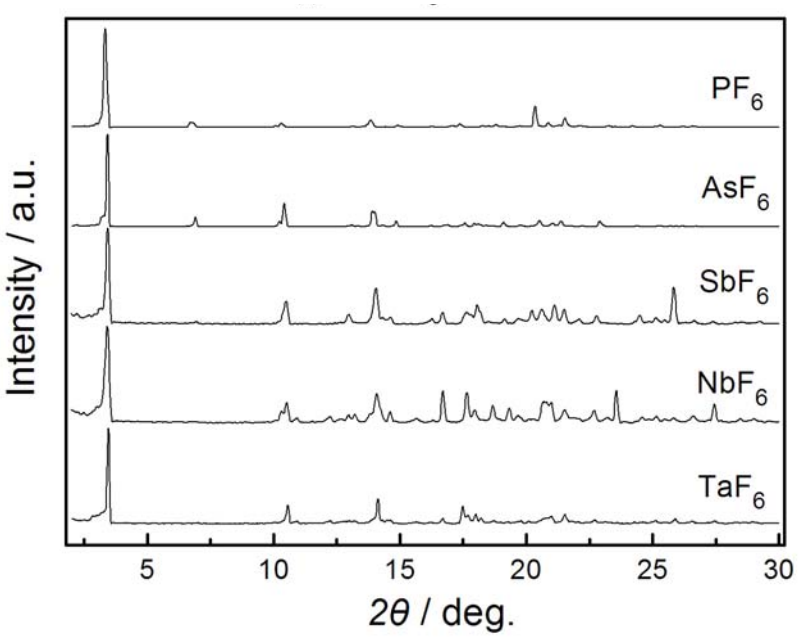

Figure S15 X-ray diffraction patterns ($2° < 2\theta < 30°$) for $C_{14}MImAF_6$ (A = P, As, Sb, Nb, and Ta) in the crystalline phase at 40 °C.

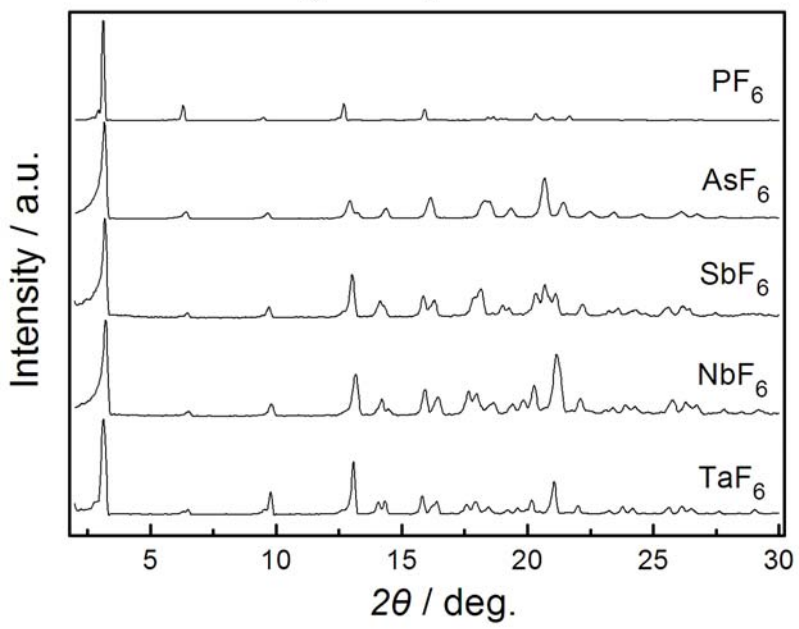

Figure S16 X-ray diffraction patterns ($2° < 2\theta < 30°$) for $C_{16}MImAF_6$ (A = P, As, Sb, Nb, and Ta) in the crystalline phase at 40 °C.

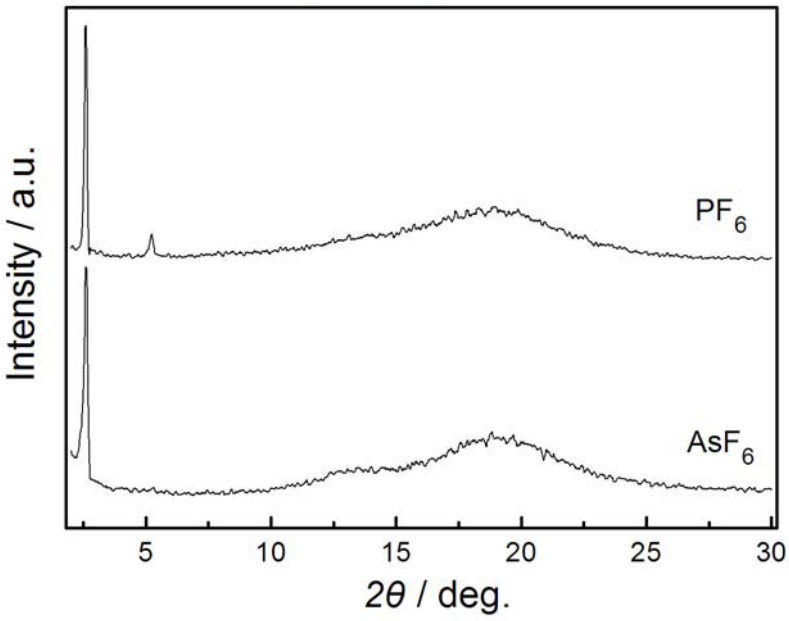

Figure S17 X-ray diffraction patterns ($2° < 2\theta < 30°$) for $C_{16}MImAF_6$ (A = P and As) in the liquid crystalline mesophase at 100 °C.

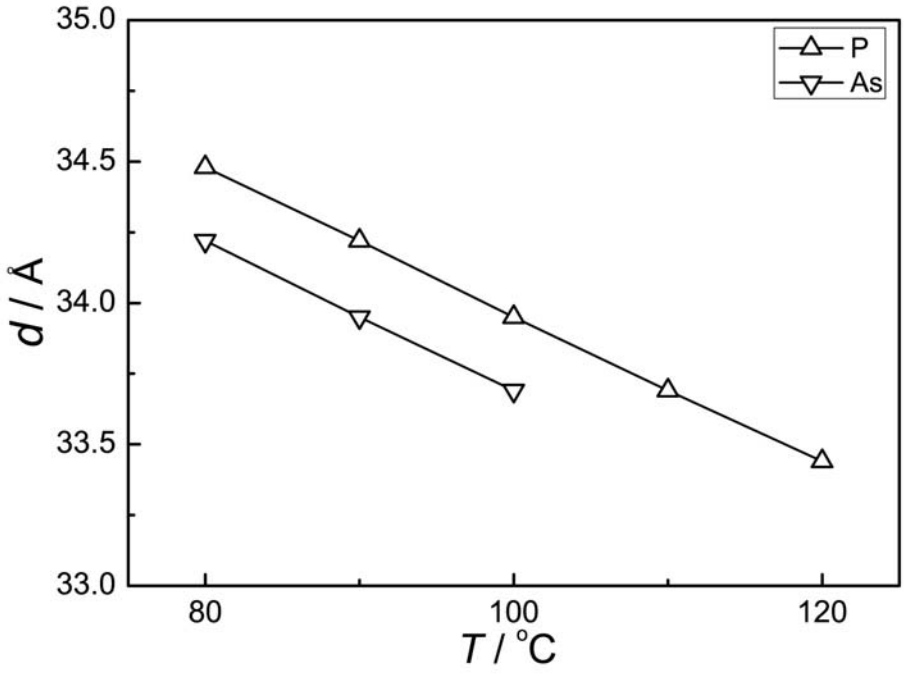

Figure S18 Layer spacings of $C_{16}MImAF_6$ (A = P and As) in the liquid crystalline mesophase.

Table S1 Summary of crystal data and refinement results for $C_{18}MImAF_6$ (A = P, As, Sb, Nb, and Ta) at 25 °C.

	P	As	Sb	Nb	Ta
formula	$C_{22}H_{43}N_2F_6P$	$C_{22}H_{43}N_2F_6As$	$C_{22}H_{43}N_2F_6Sb$	$C_{22}H_{43}N_2F_6Nb$	$C_{22}H_{43}N_2F_6Ta$
fw	480.55	524.50	571.34	542.49	630.53
crystal color	colorless	colorless	colorless	colorless	colorless
crystal size, mm	0.80×0.30×0.05	0.70×0.20×0.05	0.75×0.30×0.03	0.70×0.30×0.05	0.43×0.13×0.04
T/°C	25	25	25	25	25
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a/Å	9.6506(16)	9.5645(13)	9.6973(7)	9.5882(11)	9.6813(8)
b/Å	9.5436(17)	9.8620(15)	9.9933(7)	10.0041(14)	10.0074(9)
c/Å	29.633(5)	28.969(4)	28.991(2)	28.871(3)	29.014(3)
β/°	92.169(4)	94.400(3)	95.2424(16)	95.094(3)	95.112(2)
V/Å^3	2727.3(8)	2724.5(7)	2797.8(3)	2758.4(6)	2799.8(4)
Z	4	4	4	4	4
ρ_{calcd}/g cm^{-3}	1.170	1.279	1.356	1.306	1.496
F(000)	1032	1104	1176	1136	1264
μ/mm^{-1}	0.152	1.299	1.036	0.487	3.976
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
reflns collected/unique	18736/4276	20574/4779	21577/4925	21340/4855	20501/4902
$R_1(F_o)^a$	0.1039	0.0886	0.0500	0.0885	0.0469
$wR_2(F_o^2)^b$	0.3062	0.2720	0.1514	0.2576	0.1136
R_{int}	0.0524	0.0546	0.0302	0.0551	0.0524

^{a} $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$ for $I > 2\sigma(I)$. ^{b} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$ for $I > 2\sigma(I)$.

Table S2 Summary of crystal data and refinement results for $C_{18}MImAF_6$ (A = P, As, Sb, Nb, and Ta) at 55 °C.

	P	As	Sb	Nb	Ta
formula	$C_{22}H_{43}N_2F_6P$	$C_{22}H_{43}N_2F_6As$	$C_{22}H_{43}N_2F_6Sb$	$C_{22}H_{43}N_2F_6Nb$	$C_{22}H_{43}N_2F_6Ta$
fw	480.55	524.50	571.34	542.49	630.53
crystal color	colorless	colorless	colorless	colorless	colorless
crystal size, mm	0.80×0.30×0.05	0.70×0.20×0.05	0.75×0.30×0.03	0.70×0.30×0.05	0.43×0.13×0.04
T/°C	55	55	55	55	55
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a/Å	9.740(2)	9.7983(11)	9.9860(13)	9.838(3)	9.9490(10)
b/Å	9.526(2)	9.6239(13)	9.8314(14)	9.772(3)	9.7952(10)
c/Å	29.916(7)	29.575(3)	29.360(4)	29.126(8)	29.289(3)
β/°	90.578(5)	91.6869(18)	92.795(2)	93.286(6)	92.810(2)
V/Å^3	2775.5(11)	2787.6(6)	2879.0(7)	2795.5(13)	2850.9(5)
Z	4	4	4	4	4
ρ_{calcd}/g cm^{-3}	1.150	1.250	1.318	1.289	1.469
F(000)	1032	1104	1176	1136	1264
μ/mm^{-1}	0.150	1.270	1.007	0.480	3.905
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
reflns collected/unique	17469/3979	21446/4899	22176/5061	18406/4671	22069/5006
$R_1(F_o)^a$	0.1341	0.0853	0.0691	0.0832	0.0495
$wR_2(F_o^2)^b$	0.3577	0.2410	0.2048	0.2090	0.1190
R_{int}	0.0494	0.0526	0.0485	0.0639	0.0505

^{a} $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$ for $I > 2\sigma(I)$. ^{b} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$ for $I > 2\sigma(I)$.

Table S3 Summary of geometrical parameters related to overlapped alkyl chain lengths in the C_xMImPF_6 (x = 12, 14, and 18) crystal structures.

	x = 12 (–150 °C)	x = 14 (–98 °C)	x = 18 (–100 °C)
$l_{N1\text{-}Cterminal}$ (= bond length of N1-$C_{teminal}$) / Å [a]	14.302	16.848	21.945
$l_{Cterminal'\text{-}N1}$ (= bond length of $C_{teminal}$-N1') / Å	5.364	5.416	5.425
$\alpha_{N1\text{-}Cterminal\text{-}N1'}$ (= bond angle of N1-$C_{teminal}$-N1') / °	104.63	104.45	104.18
$\alpha_{Cterminal\text{-}N1\text{-}Cterminal'}$ (= bond angle of $C_{teminal}$-N1-$C_{teminal}$') / °	75.37	75.55	75.82
l_{over} (= overlapped alkyl chain length) / Å [b]	12.947	15.497	20.616
l_{alkyl} (= alkyl chain interspacing) / Å [c]	5.190	5.245	5.260

[a] $C_{teminal}$ is the carbon atom at the end of the long alkyl chain.

[b] The overlapped alkyl chain length l_{over} was calculated by the following equation:

$l_{over} = l_{N1\text{-}Cterminal} - l_{Cterminal'\text{-}N1} \times \cos(\alpha_{Cterminal\text{-}N1\text{-}Cterminal'})$.

[c] The alkyl chain interspacing l_{alkyl} was calculated by the following equation:

$l_{alkyl} = l_{Cterminal'\text{-}N1} \times \sin(\alpha_{Cterminal\text{-}N1\text{-}Cterminal'})$.

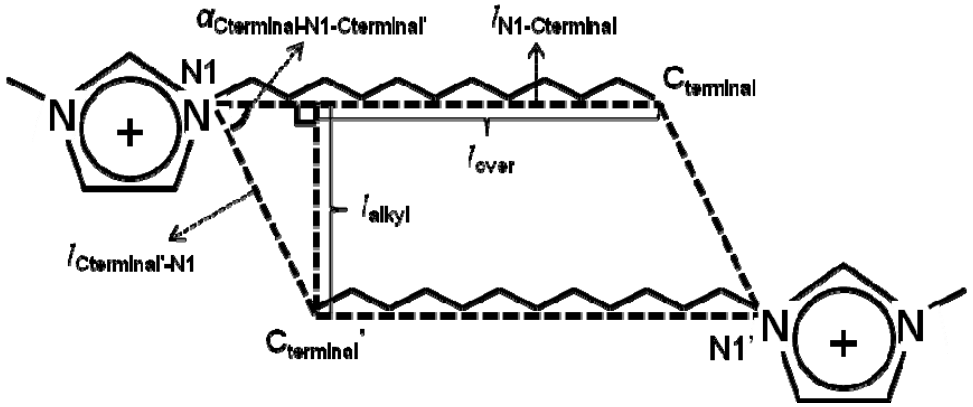

Table S4 Summary of geometrical parameters related to overlapped alkyl chain lengths for the $C_{18}MImAF_6$ (A = P, As, Sb, Nb, and Ta) crystal structures at –100 °C.

	P	As	Sb	Nb	Ta
$l_{N1\text{-}C23}$ (= bond length of N1-C_{23}) / Å	21.945	21.933	21.907	21.889	21.886
$l_{C23'\text{-}N1}$ (= bond length of C_{23}-N1') / Å	5.425	5.443	5.500	5.490	5.506
$\alpha_{N1\text{-}C23\text{-}N1'}$ (= bond angle of N1-C_{23}-N1') / °	104.18	103.25	101.38	101.35	100.93
$\alpha_{C23\text{-}N1\text{-}C23'}$ (= bond angle of C_{23}-N1-C_{23}') / °	75.82	76.75	78.62	78.65	79.07
l_{over} (= overlapped alkyl chain length) / Å [a]	20.616	20.685	20.822	20.809	20.842
l_{alkyl} (= alkyl chain interspacing) / Å [b]	5.260	5.298	5.392	5.383	5.406
$c \times \sin\beta$	28.343	27.985	25.939	27.069	26.536

[a] The overlapped alkyl chain length l_{over} was calculated by the following equation:
$l_{over} = l_{N1\text{-}C23} - l_{C23'\text{-}N1} \times \cos(\alpha_{C23\text{-}N1\text{-}C23'})$.

[b] The alkyl chain interspacing l_{alkyl} was calculated by the following equation:
$l_{alkyl} = l_{C23'\text{-}N1} \times \sin(\alpha_{C23\text{-}N1\text{-}C23'})$.