Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Effects of the HF conrtent *n* in the $(FH)_nF^-$ anion on the formation of ionic plastic crystal phases of *N*-ethyl-*N*-methylpyrrolidinium and *N*,*N*-dimethylpyrrolidinium fluorohydrogenate salts

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S-1. Discussions about the phase transition from the region B to A and that from the region A to IPC (I)

The DSC curves in the cooling process for EMPyr(FH)$_n$F ($1.9 \leq n \leq 2.3$) are shown in Fig. S4. During the cooling process, several solid phases were observed separately, including IPC (II) phase (described below) between IPC (I) and the regions A or C. During the heating process, this IPC (II) phase was not observed through the phase transition from the region A to IPC (I). This behavior is caused by the overlap of the phase transition from IPC (II) to IPC (I) with that from the EMPyr(FH)$_2$F crystal to IPC (I) as shown in reference 18. The XRD patterns of EMPyr(FH)$_{1.9}$F at 213 K, EMPyr(FH)$_{2.0}$F at 183 K, and EMPyr(FH)$_{2.1}$F at 183 K are shown in Fig. S5. The samples for this XRD measurement were cooled from room temperature to the target temperature as performed in DSC analysis in Fig. S4. The XRD patterns in Fig. S5 are coincident with those of the IPC (II) in Fig. 8, indicating that the IPC (II) phase appears in the supercooled states for EMPyr(FH)$_{1.9}$F, EMPyr(FH)$_{2.0}$F, and EMPyr(FH)$_{2.1}$F. This behavior supports that the existence of IPC(II) in the region A in Fig. 3 with the EMPyr(FH)$_2$F crystal.

Table S1 Experimental and calculated *d* values and indices for the IPC (I) of EMPyr(FH)$_n$F.

h	*k*	*l*	$d_{obs.}$ / Å	$d_{calc.}$ [a] / Å
EMPyr(FH)$_{1.0}$F (298 K)				
1	1	1	5.59	5.61
2	0	0	4.87	4.86
2	2	0	3.45	3.44
a = 9.72 Å, V = 919 Å^3				
EMPyr(FH)$_{1.1}$F (298 K)				
1	1	1	5.62	5.62
2	0	0	4.87	4.87
2	2	0	3.43	3.44
a = 9.73 Å, V = 921 Å^3				
EMPyr(FH)$_{1.2}$F (298 K)				
1	1	1	5.66	5.65
2	0	0	4.90	4.90
2	2	0	3.46	3.46
a = 9.79 Å, V = 939 Å^3				
EMPyr(FH)$_{1.9}$F (273 K)				
1	1	1	5.84	5.86
2	0	0	5.09	5.07
2	2	0	3.58	3.59
a = 10.14 Å, V = 1043 Å^3				
EMPyr(FH)$_{2.0}$F (263 K)				
1	1	1	5.84	5.86
2	0	0	5.09	5.08
2	2	0	3.60	3.59
a = 10.16 Å, V = 1048 Å^3				
EMPyr(FH)$_{2.1}$F (243 K)				
1	1	1	5.84	5.86
2	0	0	5.09	5.08
2	2	0	3.60	3.59
a = 10.16 Å, V = 1048 Å^3				
EMPyr(FH)$_{2.2}$F (243 K)				
1	1	1	5.84	5.86
2	0	0	5.09	5.08
2	2	0	3.60	3.59
a = 10.16 Å, V = 1048 Å^3				
EMPyr(FH)$_{2.3}$F (213 K)				
1	1	1	5.88	5.88
2	0	0	5.09	5.09
2	2	0	3.60	3.60
a = 10.18 Å, V = 1054 Å^3				

[a]The d_{calc} values were calculated from the obtained a lattice constants.

Table S2 Experimental and calculated *d* values and indices for the IPC (I') of DMPyr(FH)$_n$F.

h	*k*	*l*	$d_{obs.}$ / Å	$d_{calc.}$ [a] / Å
DMPyr(FH)$_{1.0}$F (298 K)				
1	1	1	5.42	5.42
2	0	0	4.69	4.69
2	2	0	3.32	3.32
3	1	1	2.83	2.83
2	2	2	2.70	2.71
4	0	0	2.35	2.35
a = 9.39 Å, V = 827 Å^3				
DMPyr(FH)$_{1.1}$F (298 K)				
1	1	1	5.46	5.47
2	0	0	4.74	4.74
2	2	0	3.35	3.35
3	1	1	2.85	2.86
2	2	2	2.73	2.73
4	0	0	2.37	2.37
a = 9.47 Å, V = 849 Å^3				
DMPyr(FH)$_{1.2}$F (298 K)				
1	1	1	5.46	5.48
2	0	0	4.74	4.74
2	2	0	3.35	3.35
3	1	1	2.86	2.86
2	2	2	2.74	2.74
4	0	0	2.38	2.37
a = 948 Å, V = 852 Å^3				
DMPyr(FH)$_{1.3}$F (298 K)				
1	1	1	5.46	5.46
2	0	0	4.72	4.73
2	2	0	3.35	3.34
3	1	1	2.85	2.85
2	2	2	2.72	2.73
4	0	0	2.37	2.36
a = 9.45 Å, V = 844 Å^3				
DMPyr(FH)$_{1.4}$F (298 K)				
1	1	1	5.46	5.46
2	0	0	4.74	4.73
2	2	0	3.33	3.34
3	1	1	2.85	2.85
2	2	2	2.73	2.73
4	0	0	2.37	2.37
a = 9.46 Å, V = 846 Å^3				
DMPyr(FH)$_{1.5}$F (298 K)				
1	1	1	5.49	5.51
2	0	0	4.77	4.77
2	2	0	3.37	3.37
3	1	1	2.87	2.88
2	2	2	2.76	2.75
4	0	0	2.40	2.39

a = 9.54 Å, V = 868 Å^3				
DMPyr(FH)$_{1.6}$F (298 K)				
1	1	1	5.56	5.56
2	0	0	4.82	4.82
2	2	0	3.41	3.41
3	1	1	2.90	2.90
2	2	2	2.78	2.78
a = 9.63 Å, V = 893 Å^3				
DMPyr(FH)$_{1.7}$F (298 K)				
1	1	1	5.66	5.63
2	0	0	4.87	4.87
2	2	0	3.45	3.45
3	1	1	2.93	2.94
2	2	2	2.81	2.81
a = 9.75 Å, V = 926 Å^3				
DMPyr(FH)$_{1.8}$F (298 K)				
1	1	1	5.66	5.67
2	0	0	4.92	4.91
2	2	0	3.47	3.47
a = 9.82 Å, V = 948 Å^3				
DMPyr(FH)$_{1.9}$F (298 K)				
1	1	1	5.73	5.70
2	0	0	4.92	4.94
2	2	0	3.49	3.49
a = 9.88 Å, V = 964 Å^3				
DMPyr(FH)$_{2.0}$F (298 K)				
1	1	1	5.73	5.72
2	0	0	4.95	4.95
2	2	0	3.50	3.50
a = 9.91 Å, V = 973 Å^3				

[a] The d_{calc} values were calculated from the obtained a lattice constants.

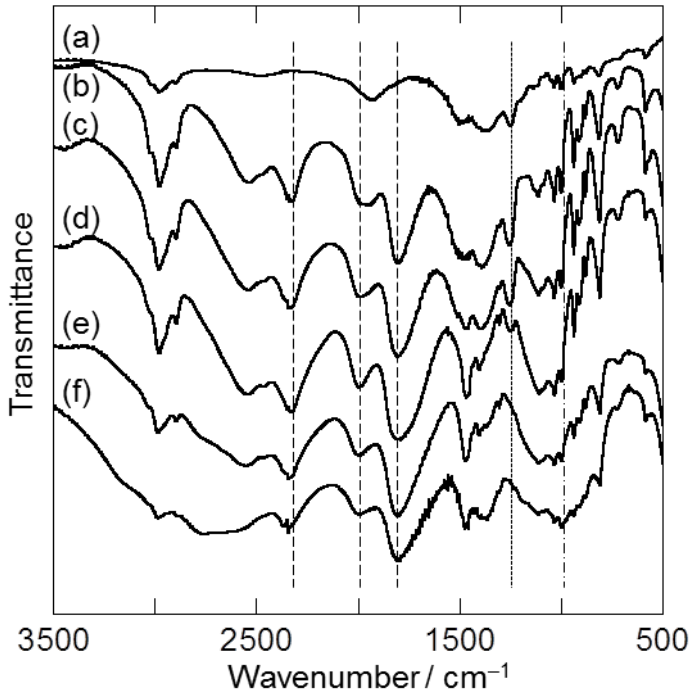

Fig. S1 Infrared spectra for EMPyr$(FH)_nF$; n = (a) 1.0, (b) 1.3, (c) 1.5, (d) 1.8, (e) 2.0, and (f) 2.3. The dotted line (·····), dashed lines (– – –), and long dashed dotted line (· − · −) denote the positions where $(FH)_1F^-$, $(FH)_2F^-$, and $(FH)_3F^-$ are supposed to be observed, respectively [11,16,17].

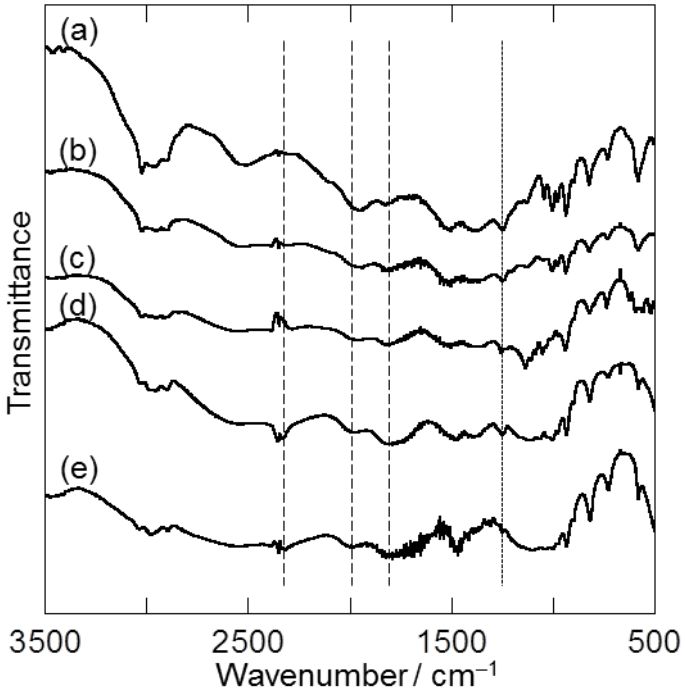

Fig. S2 Infrared spectra for DMPyr$(FH)_nF$; n = (a) 1.0, (b) 1.3, (c) 1.5, (d) 1.8, and (e) 2.0. The dotted line (·····) and dashed lines (– – –) denote the positions where $(FH)_1F^-$ and $(FH)_2F^-$ are supposed to be observed, respectively [11,16,17].

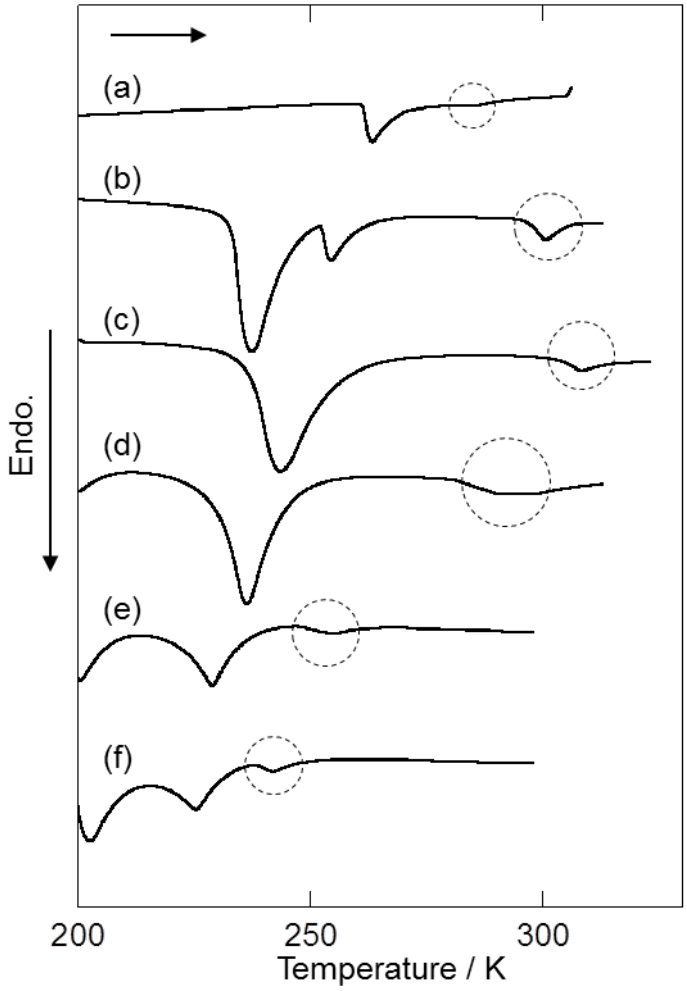

Fig. S3 The magnification of DSC curves (Fig. 2) for EMPyr$(FH)_nF$ in the range of $1.8 \leq n \leq 2.3$; (a) 1.8, (b)1.9, (c) 2.0, (d) 2.1, (e) 2.2, and (f) 2.3. The peaks surrounded by dotted circles denote melting.

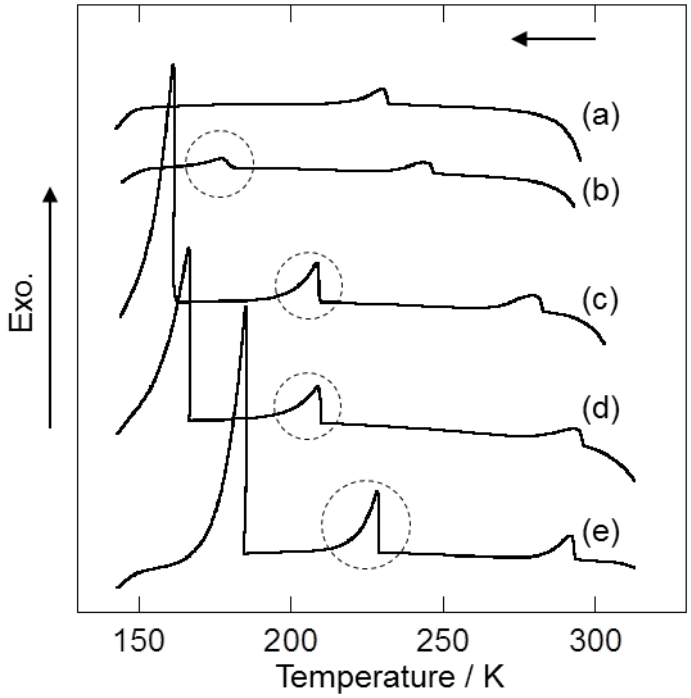

Fig. S4 Differential scanning calorimetric curves during the cooling process for EMPyr(FH)$_n$F in the range of $1.9 \leq n \leq 2.3$; (a) 2.3, (b) 2.2, (c) 2.1, (d) 2.0, and (e) 1.9. The dotted circles denote the exothermic peaks of the phase transition from IPC (I) to IPC (II).

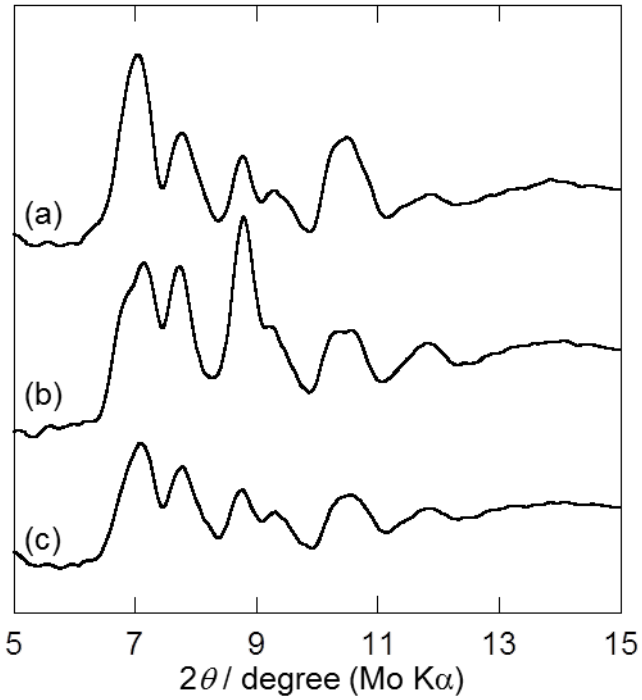

Fig. S5 X-ray diffraction patterns of EMPyr$(FH)_nF$; (a) n = 1.9 at 213 K, (b) n = 2.0 at 183 K, and (c) n = 2.1 at 183 K. The sample was cooled from room temperature to the target temperature as in the case of DSC in Fig. S4.

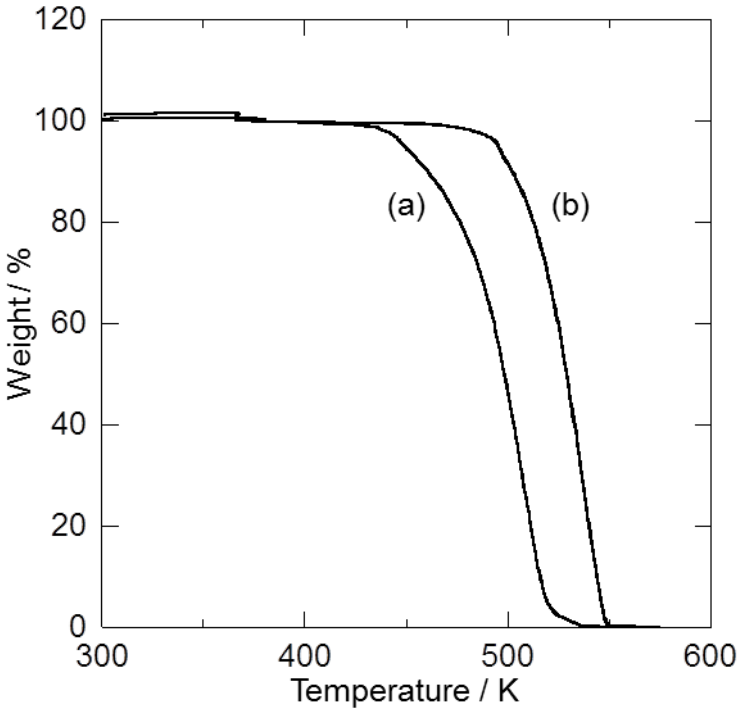

Fig. S6 Thermogravimetric curves of (a) EMPyr$(FH)_{1.0}F$ and (b) DMPyr$(FH)_{1.0}F$.

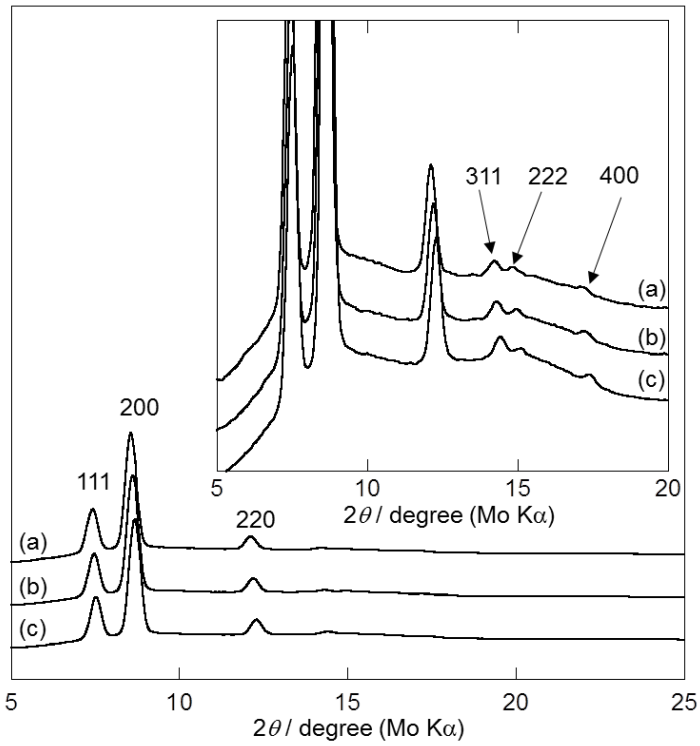

Fig. S7 X-ray diffraction patterns of DMPyr$(FH)_{1.0}$F at (a) 443 K, (b) 373 K, and (c) 298 K.