SUPPORTING INFORMATION

Physical Properties and Solid-Liquid Equilibria for Hexafluorophosphate-based Ionic Liquid Ternary Mixtures and their Corresponding Subsystems

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I. Experimental DSC data for the binary and ternary mixtures of ionic liquids, for mole fraction x, transition temperature T and pressure p = 102.0 kPa

For all DSC measurements, one cooling run was followed by one heating run, and only the thermal transitions of the heating run are reported. The following notations are used: $[C_4mpy][PF_6]$ (1), $[C_4mpip][PF_6]$ (2), and $[C_4mpyrr][PF_6]$ (3).

Table S1: Experimental DSC data for the binary subsystems

(2) + (1)		(1) + (3)		(2) + (3)	
x_1	T(K)	x_3	T(K)	x_3	T(K)
0.11	318.5	0.10	315.2	0.11	321.9
0.20	290.8	0.20	314.9	0.11	351.5
0.20	318.6	0.30	308.6	0.21	321.1
0.30	291.8	0.70	296.7	0.21	351.2
0.50	293.2	0.70	308.8	0.31	320.8
0.70	291.2	0.80	305.4	0.31	350.9
0.70	315.4	0.80	320.9	0.40	318.0
0.70	311.1	0.90	305.4	0.40	349.9
0.81	314.8	0.90	337.5	0.42	318.4
0.88	313.7			0.42	350.5
				0.63	312.7
				0.63	351.3
				0.71	310.2
				0.71	352.3
				0.80	308.4
				0.80	352.8
				0.90	296.1
				0.90	312.9
				0.90	353.9

Table S2: Experimental DSC data for the (1) + (2) + (3) ternary system

Isoplethal section $x_1 = 0.4$		**Isoplethal section** $x_3 / (x_3 + x_2) = 0.6$	
x_3	T(K)	x_1	T(K)
0.06	287.8	0.10	298.6
0.12	289.0	0.10	329.9
0.18	283.6	0.20	312.1
0.24	294.6	0.29	292.1
0.30	257.9	0.50	298.2
0.30	254.5	0.60	296.9
0.36	253.5	0.60	303.9
0.42	258.5	0.69	310.3
0.42	295.1	0.80	304.4
0.48	260.7	0.90	314.4
0.54	259.5		

II. Experimental liquidus temperature data for the binary mixtures of ionic liquids using complementary techniques (visual and capillary methods) for mole fraction *x*, transition temperature *T* and pressure *p* = 102.0 kPa

Most of the reported liquidus temperature data were obtained on completely recrystallized samples using an automatic capillary device. The temperatures were taken as the average of triplicate measurements. For a few biphasic mixtures (marked with *), a visual method using a temperature-controlled oil bath was used. The following notations are used: $[C_4mpy][PF_6]$ (1), $[C_4mpip][PF_6]$ (2), and $[C_4mpyrr][PF_6]$ (3).

Table S3: Experimental liquidus data for the binary mixtures (visual and capillary methods)

(2) + (1)		(1) + (3)		(2) + (3)	
x_1	T(K)	x_3	T(K)	x_3	T(K)
0	354.7	0	324.8	0.11	352.5
0.11	337.2*	0.10	319.2*	0.21	351.2
0.81	312.7*	0.20	314.2*	0.31	351.6
0.88	317.2*	0.80	319.2*	0.39	350.9
1	324.8	0.90	340.7*	0.42	350.9
		1	359.7	0.63	351.6
				0.71	352.9
				0.80	353.6
				0.90	356.3

III. Thermal behavior of [C_4mim][PF_6]

DSC thermograms were obtained for three independent samples of [C_4mim][PF_6]. For each sample, at least 3 repeated cycles of (cooling-)heating-cooling were performed. The transition temperatures and enthalpies were calculated using the average of all heating cycles (except the first one) for all samples studied. The cooling and heating rates were respectively 5 K/min and 2 K/min. Each temperature was taken as the peak temperature upon heating.

The thermogram of one sample is provided as an example in Figure S1 and the temperatures and enthalpies of the observed transitions are reported in Table S4. A detailed discussion of the thermal behavior of [C_4mim][PF_6] is given below.

Table S4: Fusion and solid-solid transition properties of [C_4mim][PF_6]

Transition	Enthalpy (kJ/mol)	Temperature (°C)
α → β	1.5 ± 0.1	-20.9 ± 0.3
β → L	14 ± 1	7.3 ± 0.3

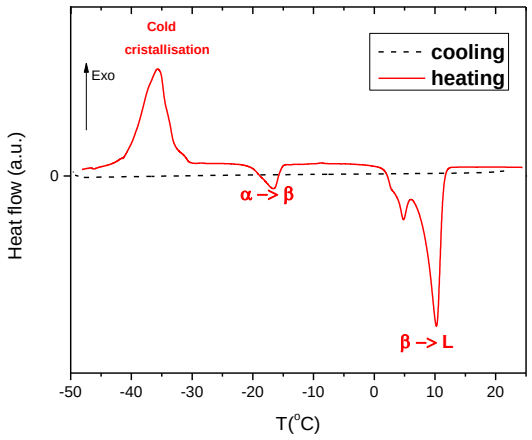

Figure S1: Thermogram of $[C_4mim][PF_6]$ (no DSC signal was observed upon cooling)

In the known case of $[C_4mim][PF_6]$, which has been extensively studied before [1-13], three distinct conformers are possible, leading to polymorphism [8]. On the thermogram of $[C_4mim][PF_6]$ (Figure S1), two close peaks can be observed during heating. This ionic liquid, known for its complex thermal behavior, has been extensively investigated [8, 10, 12, 14] and it was shown through Raman spectroscopic data and single X-ray diffraction analysis that there are at least 3 different polymorphs with different crystal structures and dominant $[C_4mim]^+$ conformer in the solid phase: α (space group *Pbca*) with conformer *gauche-trans*, β (space group $P\overline{1}$) with conformer *trans-trans* and γ (space group $P\overline{1}$) with conformer *gauche'-trans* [14]. The latter is the most thermodynamically stable. According to [10], upon heating after the cold crystallisation of the supercooled liquid to the phase α at around -46 °C, a reversible solid-solid transition to the β phase occurs at -23°C, independently of the scanning speed. Then, a tiny endothermic peak at 3°C precedes the melting occurring at around 12°C. That small endothermic peak was attributed to the transformation from the phase β to a phase designated as β', because of their identical Raman spectra. The β' phase is not fully identified yet, and it was assumed to be a disordered phase of β [8]. Depending on the thermal history, an exothermic peak around -18°C is observed, which indicates the irreversible transformation from the phase β to the thermodynamically stable phase γ melting at around the same temperature as β. The major difference between those two phases mostly stems from their melting enthalpies: around 13 kJ/mol and 20.9 kJ/mol for the β and γ phases, respectively.

In this work, both the cold crystallisation and the solid-solid transition from α to β were observed. The small endothermic peak, which seems to correspond to the transformation from β to β', overlapped the melting peak and made it necessary to perform a deconvolution to integrate both peaks. The enthalpy of

fusion obtained by integration and summation of the areas of both peaks (Table S4) is close to what is typically reported for the β polymorph (12.0-13.3 kJ/mol) [10]. The transition from β to β' was ignored in the present work as it is not fully understood. The fact that the Raman spectra for both phases were identical, added to the narrow temperature range of existence of β', seem to indicate that this peak could actually be associated with stepwise melting of the β phase, in which the non-polar domains would melt before the polar domains, similarly to what is observed for example for $[S_{222}][NTf_2]$ (S_{222} = triethylsulfonium) [15]. Broad melting peaks and pre-melting phenomena were also observed for $[C_4mim]Br$ and $[C_4mim]Cl$ and were attributed to the cooperative change between different conformations of the butyl chain [16]. Varying the cooling and heating rates coupled to structural studies (Raman, XRD…) would enable us to distinguish between different stable and metastable polymorphs and correctly assign the phases observed for $[C_4mim][PF_6]$.

IV. Experimental density data (in g/cm^3) for pure ionic liquids (IL) and their mixtures at temperature *T* (in K) and at *P* = 102.0 kPa

All density data were measured using an automated Stabinger viscometer-densimeter SVM3001. These were obtained upon heating and only once, except for the compositions close to the eutectic which were measured thrice. In that case, the results were taken as the average of triplicates. As an example, the densities of the $[C_4mpip][PF_6]$-$[C_4mpy][PF_6]$ binary mixtures investigated are displayed in Figure S2.

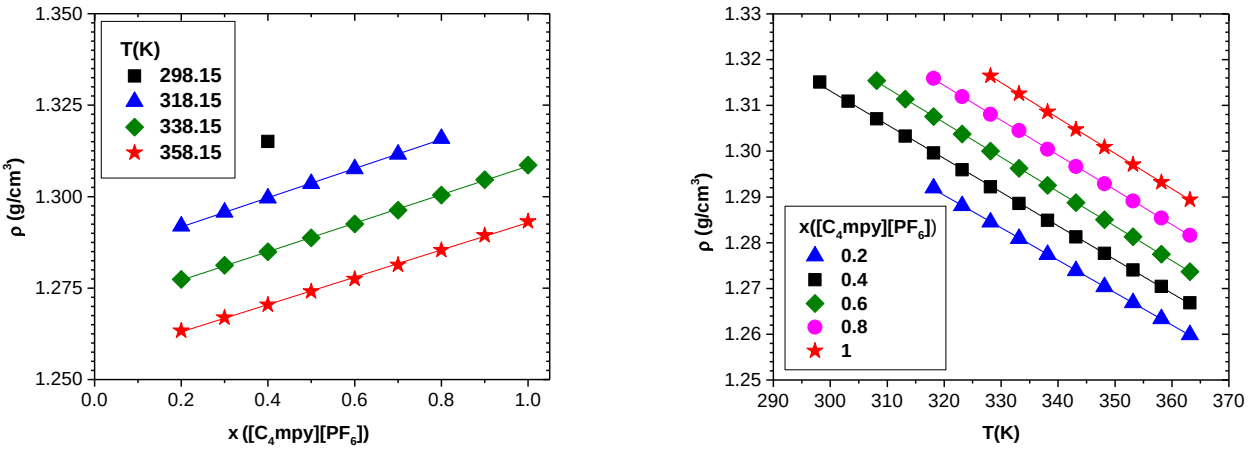

Figure S2: Density of the $[C_4mpip][PF_6]$-$[C_4mpy][PF_6]$ binary mixtures as a function of: (a) mole fraction of $[C_4mpy][PF_6]$ at different temperatures and (b) temperature at different compositions. Lines are linear fits to the density.

Table S5: Density of pure ionic liquids

IL / *T*(K)	**[C_4mpy][PF_6]**	**[C_4mim][PF_6]**
	ρ (g/cm³)	
288.15		1.375
293.15		1.371
298.15		1.367
303.15		1.363
308.15		1.358
313.15		1.354
318.15		1.350
323.15		1.346
328.15	1.316	1.342
333.15	1.313	1.338
338.15	1.309	1.334
343.15	1.305	1.330
348.15	1.301	1.326
353.15	1.297	1.322
358.15	1.293	1.318
363.15	1.289	1.314

Table S6: Density of [C_4mpip][PF_6] (1)-[C_4mpy][PF_6] (2) binary mixtures

x_2 / T(K)	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
				ρ (g/cm^3)				
298.15			1.315					
303.15			1.311	1.315				
308.15		1.303	1.307	1.311	1.315			
313.15		1.299	1.303	1.307	1.311			
318.15	1.292	1.296	1.300	1.304	1.308	1.312	1.316	
323.15	1.288	1.292	1.296	1.300	1.304	1.308	1.312	1.317
328.15	1.285	1.288	1.292	1.296	1.300	1.304	1.308	1.313
333.15	1.281	1.285	1.289	1.292	1.296	1.300	1.305	1.308
338.15	1.277	1.281	1.285	1.289	1.293	1.296	1.300	1.305
343.15	1.274	1.278	1.281	1.285	1.289	1.293	1.297	1.301
348.15	1.270	1.274	1.278	1.282	1.285	1.289	1.293	1.297
353.15	1.267	1.270	1.274	1.278	1.281	1.285	1.289	1.293
358.15	1.263	1.267	1.270	1.274	1.277	1.281	1.285	1.289
363.15	1.260	1.263	1.267	1.270	1.274	1.278	1.282	1.286

Table S7: Density of [C_4mpy][PF_6] (1)-[C_4mpyrr][PF_6] (2) binary mixtures

x_2 / T(K)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
				ρ (g/cm^3)				
303.15						1.322		
308.15				1.322	1.320	1.317		
313.15			1.321	1.318	1.316	1.314	1.311	
318.15		1.320	1.317	1.315	1.312	1.310	1.307	
323.15	1.318	1.316	1.313	1.311	1.308	1.306	1.304	
328.15	1.314	1.312	1.309	1.307	1.304	1.302	1.300	1.297
333.15	1.310	1.308	1.306	1.303	1.301	1.299	1.296	1.294
338.15	1.307	1.304	1.302	1.299	1.297	1.295	1.292	1.290
343.15	1.302	1.300	1.298	1.296	1.293	1.291	1.289	1.287
348.15	1.299	1.296	1.294	1.292	1.289	1.287	1.285	1.283
353.15	1.295	1.293	1.290	1.288	1.286	1.284	1.281	1.279
358.15	1.291	1.289	1.287	1.284	1.282	1.280	1.278	1.276
363.15	1.287	1.285	1.283	1.281	1.279	1.276	1.274	1.272

Table S8: Density of [C_4mpy][PF_6](1)-[C_4mpip][PF_6](2)-[C_4mpyrr][PF_6](3) ternary mixtures at constant x_1 = 0.4

x_3 / T(K)	0.06	0.12	0.18	0.24	0.30	0.36	0.42	0.48	0.54
					ρ (g/cm^3)				
298.15	1.316	1.317	1.318	1.319	1.320	1.321			
303.15	1.312	1.313	1.314	1.315	1.316	1.317	1.318	1.319	1.320
308.15	1.308	1.309	1.310	1.311	1.312	1.313	1.314	1.315	1.316
313.15	1.304	1.305	1.306	1.307	1.308	1.309	1.310	1.311	1.312
318.15	1.301	1.302	1.303	1.304	1.304	1.306	1.306	1.308	1.308
323.15	1.297	1.298	1.299	1.300	1.301	1.302	1.303	1.304	1.304
328.15	1.293	1.294	1.295	1.296	1.297	1.298	1.299	1.300	1.301
333.15	1.290	1.291	1.291	1.292	1.293	1.294	1.295	1.296	1.296
338.15	1.286	1.287	1.288	1.289	1.289	1.291	1.291	1.293	1.293
343.15	1.282	1.283	1.284	1.285	1.285	1.287	1.288	1.289	1.289
348.15	1.279	1.280	1.280	1.281	1.282	1.283	1.284	1.285	1.285
353.15	1.275	1.276	1.277	1.278	1.278	1.280	1.280	1.282	1.282
358.15	1.271	1.272	1.273	1.274	1.274	1.276	1.277	1.278	1.278
363.15	1.268	1.269	1.270	1.271	1.271	1.272	1.273	1.274	1.274

Table S9: Density of [C4mpy][PF6](1)-[C4mpip][PF6](2)-[C4mpyrr][PF6](3) ternary mixtures at constant $x_3 / (x_2 + x_3) = 0.6$

x_1 / T(K)	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
			ρ (g/cm^3)					
298.15			1.321					
303.15			1.317					
308.15		1.310	1.313	1.316	1.319			
313.15		1.306	1.309	1.312	1.315	1.319		
318.15	1.300	1.303	1.306	1.309	1.312	1.315	1.318	
323.15	1.296	1.299	1.302	1.305	1.308	1.311	1.314	1.318
328.15	1.292	1.295	1.298	1.301	1.304	1.307	1.310	1.313
333.15	1.289	1.291	1.295	1.297	1.300	1.303	1.306	1.309
338.15	1.285	1.288	1.291	1.294	1.297	1.300	1.303	1.306
343.15	1.281	1.284	1.287	1.290	1.293	1.296	1.299	1.302
348.15	1.278	1.281	1.283	1.287	1.289	1.292	1.295	1.298
353.15	1.274	1.277	1.280	1.282	1.285	1.288	1.291	1.294
358.15	1.271	1.273	1.276	1.279	1.281	1.285	1.287	1.291
363.15	1.267	1.270	1.273	1.275	1.278	1.281	1.284	1.286

V. Experimental viscosity data (in mPa.s) for pure ionic liquids (IL) and their mixtures at temperature T (in K) and at P = 102.0 kPa

Most viscosity data were measured using an automated Stabinger viscometer. These were obtained upon heating and only once, except for the compositions close to the eutectic which were measured thrice. In that case, the results were taken as the average of triplicates.

Some viscosity data (identified with *) were measured with a rotational rheometer at 50 s^{-1}.

Table S10: Viscosity of pure ionic liquids

IL / *T*(K)	[C_4mpy][PF_6]	[C_4mim][PF_6]	[C_4mpyrr][PF_6]	[C_4mpip][PF_6]
		η (mPa.s)		
288.15		525		
293.15		374		
298.15		273		
303.15		203		
308.15		154		
313.15		119		
318.15		94		
323.15		75		
328.15	93	61		
333.15	74	50		
338.15	60	41		
343.15	49	35		
348.15	40	29		
353.15	33	25		
358.15	28	22		201*
363.15	24	19	66*	159*
368.15			56*	
373.15			47*	103*
378.15			40*	
383.15			35*	70*

Table S11: Viscosity of [C4mpip][PF6] (1)-[C4mpyrr][PF6] (2) binary mixtures

x_2 / T(K)	0.3	0.5	0.7
	η (mPa.s)		
353.15	194*	154*	126*
363.15	125*	101*	85*
373.15	84*	68*	58*
383.15	59*	48*	41*

Table S12: Viscosity of [C4mpy][PF6] (1)-[C4mpyrr][PF6] (2) binary mixtures

x_2 / T(K)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
				η (mPa.s)				
303.15						746		
308.15				427	480	535		
313.15			277	313	352	390	448	
318.15		190	208	234	262	290	334	
323.15	130	146	159	178	199	220	253	
328.15	102	113	123	138	153	170	195	221
333.15	80	89	97	108	121	133	153	173
338.15	65	71	78	87	96	106	121	138
343.15	53	58	63	70	78	86	98	110
348.15	43	48	52	57	63	70	79	90
353.15	36	40	43	48	53	58	65	74
358.15	30	33	36	40	44	48	55	61
363.15	26	28	31	34	37	41	46	51

Table S13: Viscosity of [C_4mpip][PF_6] (1)-[C_4mpy][PF_6] (2) binary mixtures

x_2 / T(K)	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
				η *(mPa.s)*				
298.15			3274					
303.15			2113	1526				
308.15		1967	1398	1031	763			
313.15		1328	952	713	537			
318.15	1272	916	666	505	386	304	238	
323.15	890	648	477	367	284	227	179	145
328.15	635	468	350	272	213	172	137	113
333.15	463	346	262	205	163	133	107	89
338.15	344	260	199	158	127	104	85	71
343.15	260	199	154	124	100	83	68	57
348.15	200	155	122	98	80	67	55	47
353.15	157	123	97	79	65	55	46	39
358.15	124	98	79	65	54	45	38	33
363.15	100	80	64	53	45	38	32	28

Table S14: Viscosity of [C_4mpy][PF_6](1)-[C_4mpip][PF_6](2)-[C_4mpyrr][PF_6](3) ternary mixtures at constant x_1 = 0.4

x_3 / T(K)	0.06	0.12	0.18	0.24	0.30	0.36	0.42	0.48	0.54
				η (mPa.s)					
298.15	2945	2615	2332	2084	1857	1666			
303.15	1917	1714	1544	1390	1248	1130	964	916	794
308.15	1278	1152	1045	948	859	783	680	648	568
313.15	875	795	727	664	606	556	488	467	413
318.15	615	563	518	476	437	404	358	344	306
323.15	444	408	378	349	323	300	268	258	232
328.15	327	302	281	261	243	227	204	197	178
333.15	246	228	214	199	186	175	158	153	139
338.15	188	176	165	155	145	137	125	121	111
343.15	146	137	129	122	115	109	100	97	89
348.15	116	109	103	97	92	87	81	78	72
353.15	93	88	83	79	75	71	66	64	60
358.15	75	71	68	65	62	59	55	53	50
363.15	62	59	56	54	51	49	46	45	42

Table S15: Viscosity of [C4mpy][PF6](1)-[C4mpip][PF6](2)-[C4mpyrr][PF6](3) ternary mixtures at constant $x_3 / (x_2 + x_3) = 0.6$

x_1 / T(K)	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
				η (mPa.s)				
298.15			1686					
303.15			1143					
308.15		964	791	648	534			
313.15		684	561	465	385	325		
318.15	596	495	407	340	284	241	206	
323.15	439	365	302	253	213	182	157	136
328.15	329	274	229	192	163	140	121	106
333.15	250	210	176	149	127	109	95	84
338.15	194	163	138	117	100	87	76	67
343.15	152	129	109	93	80	70	61	54
348.15	121	103	88	75	65	57	50	45
353.15	98	84	72	62	54	47	42	37
358.15	80	69	59	51	45	39	35	31
363.15	66	57	49	43	38	33	30	27

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