Supporting Information

Comparative Study of M[N(SO_2F)(SO_2CF_3)]–[*N*-butyl-*N*-methylpyrroridinium][N(SO_2F)(SO_2CF_3)] (M = Li, Na, K, Rb, Cs) Ionic Liquid Electrolytes

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Table S1 Viscosities (mPa s) of $[C_4C_1pyrr][FTA]$ (Pure IL) and M[FTA]–$[C_4C_1pyrr][FTA]$ ionic liquids (x(M[FTA]) = 0.20; M = Li, Na, K, Rb, Cs).

T / K	Pure IL	M = Li	M = Na	M = K	M = Rb	M = Cs
273	159	492	729	547	476	362
278	122	349	505	393	345	266
283	96.0	258	364	287	261	200
288	76.6	195	262	214	196	153
293	62.0	150	196	164	151	120
298	51.0	117	149	128	119	97.4
303	42.7	92.5	119	102	96.3	77.7
308	35.9	75.1	94.2	82.2	78.2	63.5
313	30.4	61.8	76.0	66.9	64.2	52.6
318	26.1	50.6	61.9	55.2	54.0	43.7
323	22.5	42.7	50.9	46.1	44.9	37.4
328	19.5	36.1	42.9	38.7	38.9	31.7
333	17.1	31.0	35.9	31.8	33.2	27.0
338	15.1	26.7	30.4	27.2	28.7	23.4
343	13.4	23.3	25.8	23.5	25.2	20.4
348	11.9	20.4	22.7	20.5	22.2	18.0
353	10.7	17.8	19.8	18.0	19.8	16.1
358	9.7	16.0	17.6	15.9	17.5	14.2
363	8.8	14.2	15.3	14.2	15.3	12.8
368	8.0	12.9	14.1	12.8	14.0	11.5
373	7.4	11.6	12.6	11.6	13.0	10.5
378	6.8	10.6	11.4	10.5	11.8	9.6
383	6.2	9.5	10.3	9.5	10.6	8.7
388	5.7	8.7	9.2	8.7	9.6	8.0

Table S2 Ionic conductivities (mS cm^{-1}) of $[C_4C_1pyrr][FTA]$ (Pure IL) and M[FTA]–$[C_4C_1pyrr][FTA]$ ionic liquids (x(M[FTA]) = 0.20; M = Li, Na, K, Rb, Cs).

T / K	Pure IL	M = Li	M = Na	M = K	M = Rb	M = Cs
268	1.2	0.37	0.26	0.40	0.45	0.55
273	1.5	0.52	0.38	0.56	0.62	0.75
278	2.0	0.72	0.54	0.78	0.85	1.0
283	2.5	1.0	0.7	1.0	1.1	1.3
288	3.0	1.3	1.0	1.4	1.4	1.7
293	3.7	1.6	1.3	1.7	1.8	2.1
298	4.4	2.0	1.7	2.2	2.3	2.6
303	5.3	2.5	2.1	2.7	2.8	3.2
308	6.2	3.1	2.6	3.3	3.4	3.8
313	7.2	3.7	3.2	4.0	4.1	4.5
318	8.2	4.4	3.9	4.7	4.8	5.3
323	9.4	5.1	4.6	5.6	5.6	6.2
328	10.6	6.0	5.4	6.5	6.5	7.1
333	11.9	6.9	6.3	7.5	7.5	8.1
338	13.3	7.8	7.3	8.6	8.5	9.2
343	14.8	8.9	8.4	9.7	9.7	10.4
348	16.4	10.0	9.5	10.9	10.9	11.7
353	18.1	11.2	10.7	12.3	12.2	13.0
358	19.8	12.5	12.0	13.6	13.6	14.4
363	21.7	13.9	13.4	15.1	15.1	16.0
368	23.5	15.2	14.9	16.6	16.6	17.6
373	25.5	16.7	16.4	18.1	18.3	19.3
378	27.6	18.2	18.1	19.8	20.1	21.2
383	29.7	19.8	19.8	21.5	22.1	23.2
388	31.9	21.5	21.5	23.3	24.1	25.3

Table S3 Densities (g cm^{-3}) and their fitting parameters of [C_4C_1pyrr][FTA] (Pure IL) and M[FTA]–[C_4C_1pyrr][FTA] ionic liquids (x(M[FTA]) = 0.20; M = Li, Na, K, Rb, Cs).[a]

T / K	Pure IL	M = Li	M = Na	M = K	M = Rb	M = Cs
273	1.379	1.439	1.449	1.454	1.487	1.517
278	1.374	1.435	1.445	1.449	1.482	1.512
283	1.370	1.430	1.440	1.445	1.477	1.508
288	1.366	1.426	1.436	1.440	1.473	1.503
293	1.361	1.421	1.431	1.436	1.468	1.498
298	1.357	1.416	1.427	1.431	1.464	1.494
303	1.353	1.412	1.422	1.427	1.459	1.489
308	1.349	1.407	1.418	1.422	1.454	1.484
313	1.345	1.403	1.413	1.418	1.450	1.480
318	1.340	1.399	1.409	1.414	1.445	1.475
323	1.336	1.394	1.404	1.409	1.441	1.471
328	1.332	1.390	1.400	1.405	1.437	1.466
333	1.328	1.385	1.396	1.400	1.432	1.462
338	1.324	1.381	1.391	1.396	1.428	1.457
343	1.320	1.377	1.387	1.392	1.423	1.453
348	1.316	1.373	1.383	1.388	1.419	1.448
353	1.312	1.368	1.378	1.383	1.415	1.444
358	1.308	1.364	1.374	1.379	1.410	1.439
363	1.304	1.360	1.370	1.375	1.406	1.435
368	1.300	1.356	1.366	1.371	1.402	1.431
$A_\rho \times 10^4$	–8.291	–8.811	–8.827	–8.777	–8.946	–9.103
B_ρ	1.605	1.679	1.690	1.693	1.730	1.765

[a] Density values were fitted by the following equation; $\rho = A_\rho T + B_\rho$

Table S4 Molar concentrations (mol dm^{-3}) and their fitting parameters of alkali metal cations (M^+; M = Li, Na, K, Rb, Cs) in M[FTA]–[C_4C_1pyrr][FTA] ionic liquids (x(M[FTA]) = 0.20).[a]

T / K	M = Li	M = Na	M = K	M = Rb	M = Cs
273	0.8336	0.8317	0.8267	0.8235	0.8189
278	0.8309	0.8290	0.8241	0.8210	0.8163
283	0.8282	0.8264	0.8215	0.8184	0.8137
288	0.8256	0.8238	0.8189	0.8158	0.8112
293	0.8229	0.8212	0.8163	0.8132	0.8086
298	0.8203	0.8186	0.8138	0.8107	0.8061
303	0.8177	0.8160	0.8112	0.8082	0.8036
308	0.8151	0.8134	0.8087	0.8057	0.8011
313	0.8125	0.8109	0.8062	0.8032	0.7987
318	0.8099	0.8083	0.8037	0.8007	0.7962
323	0.8074	0.8058	0.8012	0.7982	0.7937
328	0.8049	0.8033	0.7987	0.7957	0.7913
333	0.8023	0.8008	0.7962	0.7933	0.7889
338	0.7998	0.7983	0.7938	0.7909	0.7864
343	0.7974	0.7958	0.7913	0.7884	0.7840
348	0.7949	0.7933	0.7889	0.7860	0.7816
353	0.7924	0.7909	0.7865	0.7836	0.7793
358	0.7899	0.7884	0.7840	0.7812	0.7769
363	0.7875	0.7860	0.7816	0.7788	0.7745
368	0.7851	0.7836	0.7792	0.7764	0.7722
$A_C \times 10^4$	–5.103	–5.065	–4.990	–4.956	–4.913
B_C	0.9725	0.9697	0.9626	0.9585	0.9527

[a] Molar concentration values were fitted by the following equation; $C(M^+) = A_C T + B_C$

Table S5 Molar ionic conductivities (S cm^2 mol^{-1}) of $[C_4C_1pyrr][FTA]$ (Pure IL) and M[FTA]–$[C_4C_1pyrr][FTA]$ ionic liquids (x(M[FTA]) = 0.20; M = Li, Na, K, Rb, Cs).

T / K	Pure IL	M = Li	M = Na	M = K	M = Rb	M = Cs
273	0.41	0.12	0.091	0.14	0.15	0.18
278	0.53	0.17	0.13	0.19	0.21	0.25
283	0.67	0.23	0.18	0.25	0.27	0.32
288	0.83	0.31	0.24	0.33	0.36	0.41
293	1.01	0.39	0.32	0.43	0.45	0.52
298	1.22	0.50	0.41	0.54	0.57	0.65
303	1.45	0.62	0.52	0.67	0.70	0.79
308	1.70	0.75	0.65	0.82	0.85	0.95
313	1.98	0.91	0.80	0.99	1.02	1.13
318	2.29	1.08	0.96	1.18	1.20	1.33
323	2.62	1.27	1.15	1.39	1.41	1.55
328	2.97	1.48	1.35	1.63	1.64	1.80
333	3.35	1.71	1.58	1.88	1.89	2.06
338	3.75	1.96	1.83	2.16	2.16	2.34
343	4.19	2.23	2.10	2.46	2.46	2.65
348	4.64	2.52	2.40	2.78	2.77	2.98
353	5.13	2.83	2.71	3.12	3.11	3.34
358	5.64	3.16	3.05	3.48	3.48	3.72
363	6.19	3.52	3.42	3.86	3.87	4.12
368	6.74	3.87	3.80	4.27	4.28	4.55

Table S6 VTF parameters of viscosity and ionic conductivity, and α and C' (= $\log(\lambda\eta^{\alpha})$) parameters for $[C_4C_1pyrr][FTA]$ (Pure IL) and M[FTA]–$[C_4C_1pyrr][FTA]$ ionic liquids (x(M[FTA]) = 0.20; M = Li, Na, K, Rb, Cs). Concerning the right column, the α and C' values correspond to the slopes and vertical intercepts of the Walden plots, and the B_σ/B_η values are calculated from the VTF fitting parameters.

	Viscosity			Ionic conductivity			Walden plot		
	$A_\eta\times10^3$ / mPa s $K^{-1/2}$	B_η / K	$T_{0\eta}$ / K	$A_\sigma\times10^{-4}$ / mS cm^{-1} $K^{1/2}$	B_σ / K	$T_{0\sigma}$ / K	α	B_σ/B_η	C' (= $\log(\lambda\eta^{\alpha})$)
Pure IL	4.73	1040	137	2.79	958	136	0.93	0.92	−0.19
M = Li	6.74	977	157	2.08	900	157	0.94	0.92	−0.25
M = Na	5.98	1002	161	2.42	916	162	0.94	0.91	−0.22
M = K	8.56	927	161	1.99	852	162	0.91	0.92	−0.18
M = Rb	6.50	1029	151	2.82	973	151	0.94	0.95	−0.18
M = Cs	4.73	1086	144	3.12	1013	144	0.93	0.93	−0.21

Table S7 Summary of the redox potentials of M^+/M ($E(M^+/M)$; M = Li, Na, K, Rb, Cs) in various electrolytes at 298 K.

Electrolyte	E (M^+/M) / V vs. Ag^+/Ag					Ref.
	$E(Li^+/Li)$	$E(Na^+/Na)$	$E(K^+/K)$	$E(Rb^+/Rb)$	$E(Cs^+/Cs)$	
M[FTA]–[C_4C_1pyrr][FTA]*	−3.48	−3.36	−3.67	−3.71	−3.83	This study
M[FSA]–[C_3C_1pyrr][FSA]**	−3.46	−3.35	−3.71	n/a	n/a	a
1 mol dm^{-3} M^+/PC	−3.78	−3.55	−3.87	−3.94	−4.09	b
1 mol dm^{-3} M^+/MeCN	−3.29	−3.12	−3.44	−3.44	−3.53	b
1 mol dm^{-3} M^+/Water	−3.839	−3.513	−3.735	−3.742	−3.826	b
1 mol dm^{-3} M^+/EtOH	−3.78	−3.42	−3.62	−3.63	−3.72	b
1 mol dm^{-3} M^+/DMF	−3.72	−3.39	−3.62	−3.62	−3.72	b
1 mol dm^{-3} M^+/NMP	−3.93	−3.40	−3.58	−3.56	−3.66	b
1 mol dm^{-3} M^+/DMSO	−3.64	−3.29	−3.51	−3.49	−3.60	b

PC = propylene carbonate, MeCN = acetonitrile, EtOH = ethanol, DMF = *N*,*N*-dimethylformamide, NMP = *N*-methylpyrrolidone, DMSO = dimethyl sulfoxide

* Values of M[FTA]–[C_4C_1pyrr][FTA] were measured at the molar concentration of M[FTA] of 0.820 mol dm^{-3} for Li[FTA], 0.819 mol dm^{-3} for Na[FTA], 0.814 mol dm^{-3} for K[FTA], 0.811 mol dm^{-3} for Rb[FTA], 0.806 mol dm^{-3} for Cs[FTA].

** Values of M[FSA]–[C_3C_1pyrr][FSA] were measured at the molar concentration of M[FSA] of 1.0 mol dm^{-3} for Li[FSA],[c] 0.98 mol dm^{-3} for Na[FSA],[d] and 0.98 mol dm^{-3} for K[FSA].[a]

(a) Yamamoto, T.; Matsumoto, K.; Hagiwara, R.; Nohira, T. Physicochemical and Electrochemical Properties of K[$N(SO_2F)_2$]–[N-Methyl-N-propylpyrrolidinium][$N(SO_2F)_2$] Ionic Liquids for Potassium-Ion Batteries. *J. Phys. Chem. C* **2017**, *121*, 18450–18458.

(b) Marcus, Y. Thermodynamic Functions of Transfer of Single Ions from Water to Nonaqueous and Mixed Solvents, PART 3: Standard Potentials of Selected Electrodes. *Pure Appl. Chem.* **1985**, *57*, 1129–1132.

(c) Yoon, H.; Best, A. S.; Forsyth, M.; MacFarlane, D. R.; Howlett, P. C. Physical properties of high Li-ion content *N*-propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide based ionic liquid electrolytes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4656–4663.

(d) Matsumoto, K.; Okamoto, Y.; Nohira, T.; Hagiwara, R. Thermal and Transport Properties of Na[$N(SO_2F)_2$]–[*N*-Methyl-*N*-propylpyrrolidinium][$N(SO_2F)_2$] Ionic Liquids for Na Secondary Batteries. *J. Phys. Chem. C* **2015**, *119*, 7648−7655.

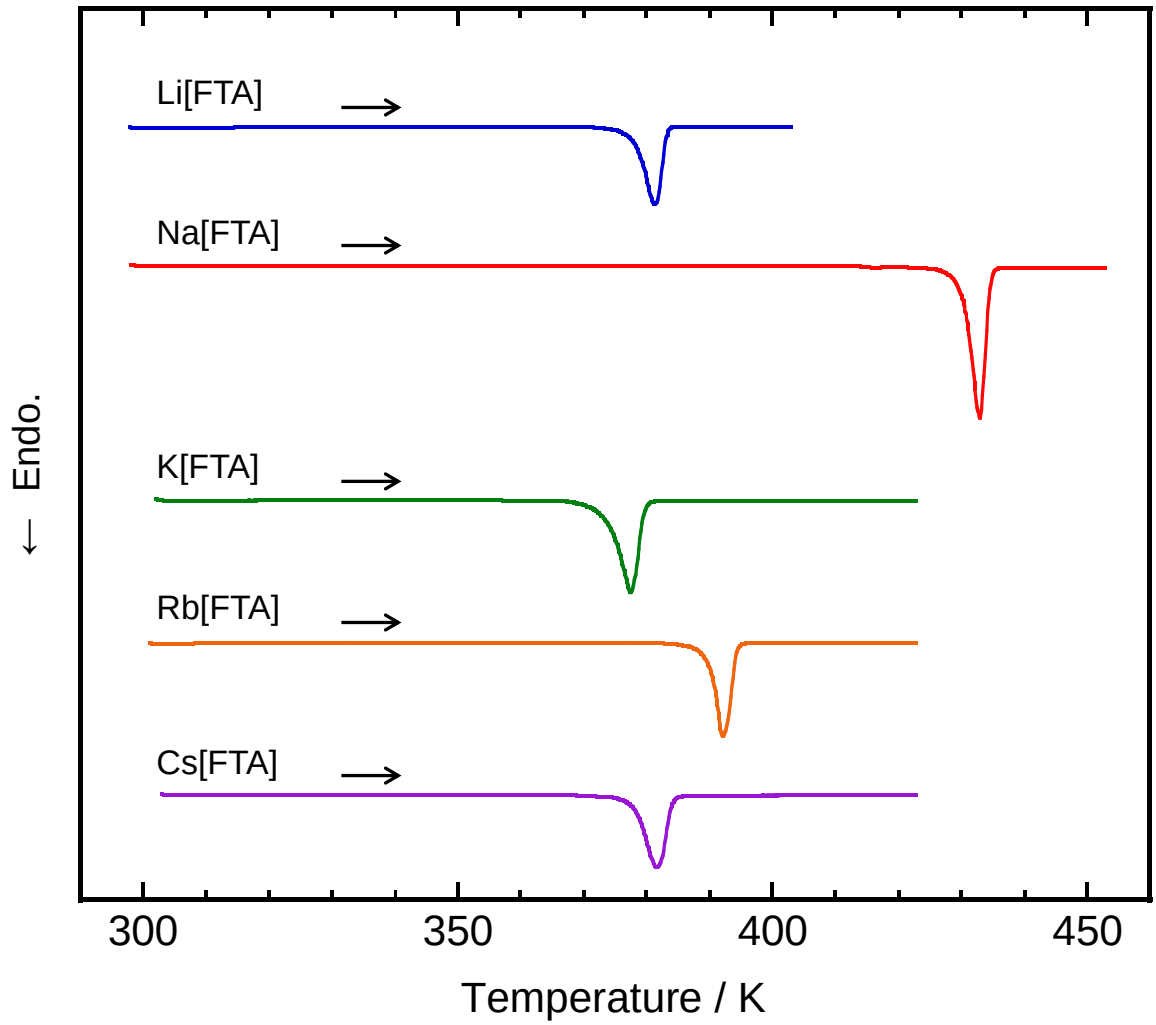

Fig. S1 DSC curves of M[FTA] salts (M = Li, Na, K, Rb, Cs). Scan rate: 2 K min^{-1}.

The onset and end temperatures of melting are found to be 378 and 383 K for Li[FTA], 430 and 435 K for Na[FTA], 373 and 380 K for K[FTA], 390 and 395 K for Rb[FTA], and 378 and 384 K for Cs[FTA], respectively. These results are almost consistent with the previous report.[e] The small deviations might be attributed to the difference of the measurement conditions.

(e) Kubota, K.; Nohira, T.; Hagiwara, R.; Matsumoto, H. Thermal Properties of Alkali (Fluorosulfonyl)(trifluoromethylsulfonyl)amides. *Chem. Lett.* **2010**, *39*, 1303–1304.