

SUPPORTING INFORMATION

A thermophysical and structural characterization of ionic liquids with alkyl and perfluoroalkyl side chains

N. S. M. Vieira,^a P. M. Reis,^a K. Shimizu,^b O. A. Cortes,^a I. M. Marrucho,^a J. M. M. Araújo,^a J.

M. S. S. Esperança,^a J. N. Canongia Lopes,^{*,a,b} A. B. Pereiro,^{*,a} and L. P. N. Rebelo^a

^a Instituto de Tecnologia Química e Biológica António Xavier, www.itqb.unl.pt, Universidade Nova de Lisboa, Apartado 127, 2780-157, Oeiras, Portugal.

^b Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

EXPERIMENTAL SECTION

Materials, Methods and characterization of the Fluorinated Ionic Liquids

In order to avoid inorganic contaminations usually present in the alkaline synthetic route, the synthesis of fluorinated ionic liquids were made through ion exchange resin method, as developed by *Ohno et al.*^{S1} and also implemented in our laboratory.^{S2} Briefly, in this procedure an anion exchange resin in the OH form (SUPELCO AMBERLITE IRN78) was used to prepare the different aqueous solutions of imidazolium hydroxides from imidazolium chlorides or bromides. Imidazolium hydroxides were then neutralized by the dropwise addition of adequate fluorinated acid solution.

All the isolated products were completely characterized by ¹H and ¹⁹F NMR, electrospray ionisation mass spectrometry (ESI-MS) and elemental analysis in order to check their expected structures and final purities. NMR studies also elucidate the expected cation/anion correlations by a quantitative integration of their characteristic ¹H and ¹⁹F resonance peaks, using 1,4-Difluorobenzene (99%; Alfa Aesar, Karlsruhe, Germany) as internal standard. Additionally, there were no peaks assigned to impurities in the ¹H and ¹⁹F NMR spectra. All the fluorinated ionic liquids were dried under vacuum (3×10^{-2} Torr) and vigorously stirred at 323.15 K for at least 2 days, immediately prior to use. The water content, determined by Karl Fischer titration, was less than 100 ppm. Experimental and characterization details about prepared fluorinated ionic liquids are detailed below.

For synthesis of 1-ethyl-3-methylimidazolium trifluoroethanoate ($[\text{C}_2\text{C}_1\text{Im}][\text{CF}_3\text{CO}_2]$), $\text{Ag}(\text{CF}_3\text{COO})$ was synthesized by reaction of 6.0 g Ag_2O (0.0259 mol, M.W = 231.74 g/mol) with trifluoroacetic acid 4.0 mL (0.0518 mol; M.W = 114.02 g/mol; $d = 1.48$ g/mL, 99%) in

water. After $\text{Ag}(\text{CF}_3\text{COO})$ 4.0 g (0.0181 mol; M.W = 220.88 g/mol) reacts with 1-ethyl-3-methylimidazolium bromide ($[\text{C}_2\text{C}_1\text{Im}][\text{Br}]$ 3.46 g (0.0181 mol, M.W = 191.07 g/mol) in water, to obtain $[\text{C}_2\text{C}_1\text{Im}][\text{CF}_3\text{COO}]$. The solution was filtered and then evaporated in rotavapour. The oil obtained was dried in vacuum line and was obtained a colourless liquid. The colourless liquid was washed with diethyl ether.

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 9.96 (s, 1H, $\text{N}=\text{CH}-\text{N}$); 7.80 (d, 2H, $\text{N}-\text{CH}=\text{CH}-\text{N}$); 4.41 (q, 2H, $\text{CH}_3\text{CH}_2\text{C}_1\text{Im}$); 4.05 (s, 3H, CH_3N); 1.54 (t, 3H, $\text{CH}_3\text{CH}_2\text{C}_1\text{Im}$).

^{19}F NMR (376 MHz, $(\text{CD}_3)_2\text{CO}$): δ -75.19.

Elemental analysis calculated (found): %C 42.86 (42.50); % H 4.95 (5.36); % N 12.50 (12.71).

ESI-MS: m/z (+)111; m/z (-)113.

For synthesis of 1-methyl-3-octylimidazolium trifluoroethanoate ($[\text{C}_8\text{C}_1\text{Im}][\text{CF}_3\text{CO}_2]$), 2.30 mL (0.0299 mol; M.W = 114.02 g/mol; $d = 1.48$ g/mL, 99%) of trifluoroacetic acid was dissolved in water. Then, 6.60 g of 1-methyl-3-octylimidazolium chloride ($[\text{C}_8\text{C}_1\text{Im}][\text{Cl}]$ (M.W = 230.78 g/mol; 0.0286 mol)) was dissolved in water and added to an anionic exchange resin. The solution was titrated until $\text{pH} = 7$ and was added a few portion of methanol during the process, because the solution become cloudy. The solution was then evaporated in rotavapour. The oil obtained was dried in vacuum line and was obtained a colourless liquid. The colourless liquid was washed with diethyl ether.

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 10.01 (s, 1H, $\text{N}=\text{CH}-\text{N}$); 7.80 (d, 2H, $\text{N}-\text{CH}=\text{CH}-\text{N}$); 4.38 (t, 2H, $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{C}_1\text{Im}$); 4.07 (s, 3H, CH_3N); 1.94 (qt, 2H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{C}_1\text{Im}$); 1.35-1.28 (m, 10H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{C}_1\text{Im}$); 0.89 (t, 3H, $\text{CH}_3\text{CH}_2\text{C}_1\text{Im}$).

^{19}F NMR (376 MHz, $(\text{CD}_3)_2\text{CO}$): δ -74.98

Elemental analysis calculated (found): %C 54.53 (54.70); % H 7.52 (7.85); % N 9.09 (9.12).

ESI-MS: m/z (+)195; m/z(-)113.

For synthesis of 1-ethyl-3-methylimidazolium perfluoropentanoate ($[\text{C}_2\text{C}_1\text{Im}][\text{C}_4\text{F}_9\text{CO}_2]$), 2.28 mL (0.0143 mol; M. W = 264.05 g/mol; d = 1.713 g/mol, 97%) of perfluoropentanoic acid was dissolved in water. Then, 2.73g of ($[\text{C}_2\text{C}_1\text{Im}][\text{Br}]$) (M.W = 191.07 g/mol; 0.0143 mol) was dissolved in water and added to an anionic exchange resin. The solution was titrated until pH = 7 and evaporated in rotavapour. The oil obtained was dried in vacuum line and was obtained a colourless liquid. The colourless liquid was washed with diethyl ether.

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 9.86 (s, 1H, N=CH-N); 7.77 (d, 2H, N-CH=CH-N); 4.41 (q, 2H, $\text{CH}_3\text{CH}_2\text{C}_1\text{Im}$); 4.06 (s, 3H, CH_3N); 1.54 (t, 3H, $\text{CH}_3\text{CH}_2\text{C}_1\text{Im}$).

^{19}F NMR (376 MHz, $(\text{CD}_3)_2\text{CO}$): δ -63.37; -81.95; -116.29; -123.45; -126.21.

Elemental analysis calculated (found): %C 35.31 (34.80); % H 2.96 (3.32); % N 7.49 (7.57).

ESI-MS: m/z (+)195; m/z(-)263.

For synthesis of 1-methyl-3-octylimidazolium perfluoropentanoate ($[\text{C}_8\text{C}_1\text{Im}][\text{C}_4\text{F}_9\text{CO}_2]$), 2.76 mL (0.0179 mol; M. W = 264.05 g/mol; d = 1.713 g/mol, 97%) of perfluoropentanoic acid was dissolved in water. Then, 4.0 g of 1-methyl-3-octylimidazolium chloride ($[\text{C}_8\text{C}_1\text{Im}][\text{Cl}]$) (M.W = 230.78 g/mol; 0.0173 mol) was dissolved in water and added to an anionic exchange resin. The solution was titrated until pH = 7 and was added a few portion of methanol during the process, because the solution become cloudy. The solution was then evaporated in rotavapour and was possible to see the formation of two phases. The oil obtained was dried in vacuum line and was obtained a colourless liquid. The colourless liquid was washed with diethyl ether.

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 9.90 (s, 1H, $\text{N}=\text{CH}-\text{N}$); 7.79 (d, 2H, $\text{N}-\text{CH}=\text{CH}-\text{N}$); 4.38 (t, 2H, $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{C}_1\text{Im}$); 4.06 (s, 3H, CH_3N); 1.94 (qt, 2H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{C}_1\text{Im}$); 1.35-1.27 (m, 10H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2\text{C}_1\text{Im}$); 0.88 (t, 3H, $\text{CH}_3\text{CH}_2\text{C}_1\text{Im}$).

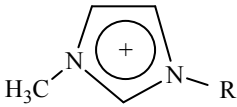
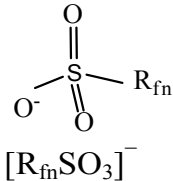
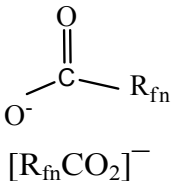
^{19}F NMR (376 MHz, $(\text{CD}_3)_2\text{CO}$): δ -63.22; -81.97; -116.26; -123.45; -126.53.

Elemental analysis calculated (found): %C 44.55 (44.30); %H 5.06 (5.41); %N 6.11 (6.16).

ESI-MS: m/z (+)195; m/z (-)263.

The structures of the FILs based on imidazolium cations conjugated with different sulfonate and carboxylate anions studied in this work are shown in Table S1.

Table S1. Fluorinated ionic liquids studied in this work

cation structure	anion structure
 $[\text{RC}_1\text{Im}]^+$ 1-Alkyl-3-methylimidazolium cation	 $[\text{R}_{\text{fn}}\text{SO}_3]^-$ Perfluoroalkyl sulfonate anion
	 $[\text{R}_{\text{fn}}\text{CO}_2]^-$ Perfluoroalkyl carboxylate anion
R = C₂ (ethyl); C₆ (hexyl), C₈ (octyl) or C₁₂ (dodecyl); R_{fn} = CF₃ (trifluoromethane), C₄F₉ (perfluorobutane) or C₈F₁₇ (perfluorooctane)	

RESULTS

For each property measurement the necessary quantity of fluorinated ionic liquid was taken from the respective schlenk flask with a syringe. To prevent humidity sampling was made under a nitrogen flow and was immediately placed in the respective apparatus.

The thermal properties (thermal stabilities, decomposition temperatures, melting points and glass transition temperatures) of the fluorinated ionic liquids studied in this work are summarized in Table S2.

Table S2. Thermal properties of selected fluorinated ionic liquids: starting temperature, T_{start} , onset temperature, T_{onset} , decomposition temperature, T_{dec} and melting temperature, T_{m} .

	$T_{\text{start}}^{\text{a}} / \text{K}$	$T_{\text{onset}}^{\text{a}} / \text{K}$	$T_{\text{dec}}^{\text{a}} / \text{K}$	T_{m} / K
$[\text{C}_2\text{C}_1\text{Im}][\text{CF}_3\text{SO}_3]$	577.95	609.56	633.26	260.41
$[\text{C}_8\text{C}_1\text{Im}][\text{CF}_3\text{SO}_3]$	575.45	606.06	628.95	284.14
$[\text{C}_2\text{C}_1\text{Im}][\text{C}_4\text{F}_9\text{SO}_3]$	593.85	627.17	668.17	293.11
$[\text{C}_{12}\text{C}_1\text{Im}][\text{C}_4\text{F}_9\text{SO}_3]$	567.55	616.75	636.38	310.66
$[\text{C}_2\text{C}_1\text{Im}][\text{C}_8\text{F}_{17}\text{SO}_3]$	567.44	616.21	642.93	367.72
$[\text{C}_2\text{C}_1\text{Im}][\text{CF}_3\text{CO}_2]$	373.15	413.72	431.86	255.07
$[\text{C}_8\text{C}_1\text{Im}][\text{CF}_3\text{CO}_2]$	404.18	423.51	438.15	279.45
$[\text{C}_2\text{C}_1\text{Im}][\text{C}_4\text{F}_9\text{CO}_2]$	374.85	391.58	408.58	277.63
$[\text{C}_8\text{C}_1\text{Im}][\text{C}_4\text{F}_9\text{CO}_2]$	379.23	399.22	419.57	297.18

^a Note that these values are from scanning TGA, and do not represent isothermal stabilities.

The experimental density, dynamic viscosity, refractive index and ionic conductivities of fluorinated ionic liquids as a function of temperature are listed in Tables S3 and S4.

Table S3. Density, ρ , dynamic viscosity, η , refractive index, n_D , and ionic conductivity, k , of the fluorinated ionic liquids as a function of temperature.

T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	n_D	$k/\text{mS}\cdot\text{cm}^{-1}$	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	n_D	$k/\text{mS}\cdot\text{cm}^{-1}$
[C ₂ C ₁ Im][CF ₃ SO ₃]					[C ₈ C ₁ Im][CF ₃ SO ₃]				
293.15	1.38899	51.40	1.43451	6.91	293.15	1.19204	305.1	1.44460	0.436
298.15	1.38473	42.60	1.43290	9.12	298.15	1.18822	226.1	1.44319	0.576
303.15	1.38051	35.72	1.43151	10.6	303.15	1.18442	170.6	1.44179	0.743
308.15	1.37634	30.29	1.43012	12.2	308.15	1.18064	131.1	1.44037	0.937
313.15	1.37216	25.86	1.42870	14	313.15	1.17688	102.8	1.43890	1.18
318.15	1.36801	22.40	1.42730	15.8	318.15	1.17316	81.42	1.43735	1.46
323.15	1.36386	19.52	1.42593	18	323.15	1.16946	65.59	1.43582	1.78
328.15	1.35973	17.13	1.42460	-	328.15	1.16578	53.52	1.43425	-
333.15	1.35567	15.10	1.42325	-	333.15	1.16211	44.38	1.43273	-
338.15	1.35157	13.45	1.42132	-	338.15	1.15848	36.94	1.43128	-
343.15	1.34749	12.04	1.42007	-	343.15	1.15485	31.16	1.42981	-
348.15	1.34342	10.82	1.41878	-	348.15	1.15124	26.53	1.42853	-
353.15	1.33935	9.749	1.41751	-	353.15	1.14763	22.90	1.42714	-
[C ₂ C ₁ Im][C ₄ F ₉ SO ₃]					[C ₁₂ C ₁ Im][C ₄ F ₉ SO ₃]				
293.15	1.55201	217.7	1.39970	-	293.15	-	-	-	-
298.15	1.54658	163.0	1.39834	1.60	298.15	-	-	-	-
303.15	1.54121	124.7	1.39696	2.00	303.15	-	-	-	-
308.15	1.53593	97.20	1.39560	2.47	308.15	1.25146	390.0	-	0.155

313.15	1.53067	77.10	1.39424	2.99	313.15	1.24699	280.9	1.41616	0.205
318.15	1.52544	62.12	1.39291	3.59	318.15	1.24254	207.3	1.41467	0.264
323.15	1.52025	50.77	1.39155	4.36	323.15	1.23810	156.7	1.41317	0.339
328.15	1.51509	42.02	1.39024	-	328.15	1.23368	120.8	1.41171	-
333.15	1.50995	35.19	1.38894	-	333.15	1.22930	95.08	1.41026	-
338.15	1.50485	29.79	1.38760	-	338.15	1.22493	75.55	1.40880	-
343.15	1.49977	25.46	1.38632	-	343.15	1.22060	61.11	1.40734	-
348.15	1.49470	21.95	1.38505	-	348.15	1.21628	50.05	1.40590	-
353.15	1.48967	19.09	1.38378	-	353.15	1.21199	41.62	1.40447	-

[C₂C₁Im][CF₃CO₂]

[C₈C₁Im][CF₃CO₂]

293.15	1.29592	38.16	1.44335	7.42	293.15	1.11859	214.3	1.45010	0.525
298.15	1.29190	31.24	1.44182	9.95	298.15	1.11492	159.6	1.44863	0.696
303.15	1.28790	26.15	1.44047	11.7	303.15	1.11127	120.9	1.44716	0.901
308.15	1.28393	22.16	1.43911	13.5	308.15	1.10764	93.43	1.44572	1.14
313.15	1.27997	19.04	1.43776	15.6	313.15	1.10404	73.72	1.44425	1.43
318.15	1.27604	16.43	1.43644	17.4	318.15	1.10046	58.71	1.44279	1.76
323.15	1.27212	14.34	1.43512	20.0	323.15	1.09692	47.61	1.44135	2.14
328.15	1.26821	12.62	1.43378	-	328.15	1.09339	39.11	1.43993	-
333.15	1.26434	11.22	1.43250	-	333.15	1.08988	32.64	1.43850	-
338.15	1.26047	9.98	1.43123	-	338.15	1.08639	27.37	1.43709	-
343.15	1.25660	8.95	1.42992	-	343.15	1.08291	23.24	1.43573	-
348.15	1.25276	8.08	1.42869	-	348.15	1.07944	19.91	1.43432	-
353.15	1.24892	7.37	1.42736	-	353.15	1.07597	17.29	1.43295	-

[C ₂ C ₁ Im][C ₄ F ₉ CO ₂]					[C ₈ C ₁ Im][C ₄ F ₉ CO ₂]				
293.15	1.49213	141.3	1.39878	1.46	293.15	1.29656	424.3	1.41303	0.166
298.15	1.48678	107.5	1.39736	1.87	298.15	1.29184	307.9	1.41152	0.225
303.15	1.48148	83.32	1.39595	2.35	303.15	1.28713	224.9	1.41002	0.295
308.15	1.47624	65.87	1.39454	2.88	308.15	1.28244	167.8	1.40851	0.392
313.15	1.47103	52.80	1.39315	3.50	313.15	1.27778	128.7	1.40702	0.491
318.15	1.46585	43.09	1.39173	4.19	318.15	1.27316	98.79	1.40551	0.624
323.15	1.46071	35.63	1.39036	4.96	323.15	1.26855	77.73	1.40403	0.779
328.15	1.45559	29.80	1.38900	-	328.15	1.26399	62.09	1.40255	-
333.15	1.45049	25.27	1.38760	-	333.15	1.25944	50.84	1.40113	-
338.15	1.44541	21.51	1.38626	-	338.15	1.25490	41.23	1.39962	-
343.15	1.44034	18.51	1.38493	-	343.15	1.25038	34.21	1.39818	-
348.15	1.43527	16.06	1.38360	-	348.15	1.24586	28.68	1.39677	-
353.15	1.43017	14.06	1.38225	-	353.15	1.24134	24.61	1.39560	-

Table S4. Fitting parameters for the density (equation 1), refractive index (equation 2), fluidity (inverse viscosity, equation 3) and ionic conductivity (equation 4) as a function of temperature for fluorinated ionic liquids. Standard deviations (S.D.) (equation 5) are also shown.

[C ₂ C ₁ Im][CF ₃ SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.50614$	$A_1 = -6.0587 \cdot 10^{-4}$	–	S.D. = $3.1 \cdot 10^{-5}$
n_D	$A_0 = 1.51765$	$A_1 = -2.8398 \cdot 10^{-4}$	–	S.D. = $1.29 \cdot 10^{-4}$
$\eta/\text{mPa}\cdot\text{s}$	$\eta_0 = 0.156$	$B = 867.09$	$T_0 = 143.58$	S.D. = $2.3 \cdot 10^{-2}$
$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 81.9$	$B' = 122.8$	$T_0' = 243.13$	S.D. = $2.0 \cdot 10^{-1}$
[C ₈ C ₁ Im][CF ₃ SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.36095$	$A_1 = -6.3236 \cdot 10^{-4}$	–	S.D. = $6.0 \cdot 10^{-5}$
n_D	$A_0 = 1.53120$	$A_1 = -2.9514 \cdot 10^{-4}$	–	S.D. = $1.0 \cdot 10^{-4}$
$\eta/\text{mPa}\cdot\text{s}$	$\eta_0 = 0.076$	$B = 1095.83$	$T_0 = 161.20$	S.D. = $2.4 \cdot 10^{-1}$
$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 1370.6$	$B' = 1143.3$	$T_0' = 151.17$	S.D. = $2.3 \cdot 10^{-3}$
[C ₂ C ₁ Im][C ₄ F ₉ SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.63948$	$A_1 = -6.8246 \cdot 10^{-4}$	–	S.D. = $9.5 \cdot 10^{-5}$
n_D	$A_0 = 1.47750$	$A_1 = -2.6571 \cdot 10^{-4}$	–	S.D. = $6.3 \cdot 10^{-5}$
$\eta/\text{mPa}\cdot\text{s}$	$\eta_0 = 0.130$	$B = 913.69$	$T_0 = 170.14$	S.D. = $4.3 \cdot 10^{-2}$
$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 13649.2$	$B' = 1827.4$	$T_0' = 96.24$	S.D. = $1.7 \cdot 10^{-2}$
[C ₆ C ₁ Im][C ₄ F ₉ SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.53816$	$A_1 = -6.9537 \cdot 10^{-4}$	–	S.D. = $7.5 \cdot 10^{-5}$
[C ₈ C ₁ Im][C ₄ F ₉ SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.50038$	$A_1 = -6.9859 \cdot 10^{-4}$	–	S.D. = $4.1 \cdot 10^{-5}$
[C ₁₂ C ₁ Im][C ₄ F ₉ SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.44379$	$A_1 = -7.1236 \cdot 10^{-4}$	–	S.D. = $2.8 \cdot 10^{-5}$
n_D	$A_0 = 1.50760$	$A_1 = -2.9213 \cdot 10^{-4}$	–	S.D. = $2.5 \cdot 10^{-5}$
$\eta/\text{mPa}\cdot\text{s}$	$\eta_0 = 0.102$	$B = 995.78$	$T_0 = 187.37$	S.D. = $1.3 \cdot 10^{-1}$
$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 1945.5$	$B' = 1570.2$	$T_0' = 141.75$	S.D. = $6.1 \cdot 10^{-4}$
[C ₂ C ₁ Im][CF ₃ CO ₂]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.43954$	$A_1 = -6.1528 \cdot 10^{-4}$	–	S.D. = $2.6 \cdot 10^{-5}$
n_D	$A_0 = 1.52064$	$A_1 = -2.6442 \cdot 10^{-4}$	–	S.D. = $8.9 \cdot 10^{-5}$
$\eta/\text{mPa}\cdot\text{s}$	$\eta_0 = 0.214$	$B = 669.68$	$T_0 = 163.85$	S.D. = $5.8 \cdot 10^{-2}$

$k / \text{mS} \cdot \text{cm}^{-1}$	$k_0 = 79.8$	$B' = 104.1$	$T_0' = 249.02$	S.D. = $2.6 \cdot 10^{-1}$
$[\text{C}_8\text{C}_1\text{Im}][\text{CF}_3\text{CO}_2]$				
$\ln \rho / \text{g} \cdot \text{cm}^{-3}$	$A_0 = 0.30158$	$A_1 = -6.4680 \cdot 10^{-4}$	–	S.D. = $5.9 \cdot 10^{-5}$
n_D	$A_0 = 1.53389$	$A_1 = -2.8613 \cdot 10^{-4}$	–	S.D. = $6.0 \cdot 10^{-5}$
$\eta / \text{mPa} \cdot \text{s}$	$\eta_0 = 0.088$	$B = 977.74$	$T_0 = 167.75$	S.D. = $1.9 \cdot 10^{-1}$
$k / \text{mS} \cdot \text{cm}^{-1}$	$k_0 = 686.6$	$B' = 884.8$	$T_0' = 169.84$	S.D. = $1.3 \cdot 10^{-3}$
$[\text{C}_2\text{C}_1\text{Im}][\text{C}_4\text{F}_9\text{CO}_2]$				
$\ln \rho / \text{g} \cdot \text{cm}^{-3}$	$A_0 = 0.60689$	$A_1 = -7.0535 \cdot 10^{-4}$	–	S.D. = $5.5 \cdot 10^{-5}$
n_D	$A_0 = 1.47944$	$A_1 = -2.7545 \cdot 10^{-4}$	–	S.D. = $5.6 \cdot 10^{-5}$
$\eta / \text{mPa} \cdot \text{s}$	$\eta_0 = 0.118$	$B = 881.87$	$T_0 = 168.73$	S.D. = $5.3 \cdot 10^{-2}$
$k / \text{mS} \cdot \text{cm}^{-1}$	$k_0 = 562.5$	$B' = 693.3$	$T_0' = 176.67$	S.D. = $3.8 \cdot 10^{-3}$
$[\text{C}_8\text{C}_1\text{Im}][\text{C}_4\text{F}_9\text{CO}_2]$				
$\ln \rho / \text{g} \cdot \text{cm}^{-3}$	$A_0 = 0.47213$	$A_1 = -7.2477 \cdot 10^{-4}$	–	S.D. = $3.8 \cdot 10^{-5}$
n_D	$A_0 = 1.49896$	$A_1 = -2.9352 \cdot 10^{-4}$	–	S.D. = $1.0 \cdot 10^{-4}$
$\eta / \text{mPa} \cdot \text{s}$	$\eta_0 = 0.047$	$B = 1191.10$	$T_0 = 162.46$	S.D. = 1.3
$k / \text{mS} \cdot \text{cm}^{-1}$	$k_0 = 978.8$	$B' = 1203.9$	$T_0' = 154.51$	S.D. = $2.9 \cdot 10^{-3}$

Table S5. Density, ρ , of the pure fluorinated ionic liquids as a function of temperature.

T/K	$\rho/g\cdot cm^{-3}$	T/K	$\rho/g\cdot cm^{-3}$
[C ₆ C ₁ Im][C ₄ F ₉ SO ₃]		[C ₈ C ₁ Im][C ₄ F ₉ SO ₃]	
293.15	1.39711	293.15	-
298.15	1.39221	298.15	-
303.15	1.38732	303.15	-
308.15	1.38246	308.15	1.32998
313.15	1.37762	313.15	1.32531
318.15	1.37282	318.15	1.32063
323.15	1.36805	323.15	1.31600
328.15	1.36331	328.15	1.31141
333.15	1.35861	333.15	1.30684
338.15	1.35393	338.15	1.30230
343.15	1.34927	343.15	1.29779
348.15	1.34463	348.15	1.29329
353.15	1.34001	353.15	1.28881

Table S6. Values of calculated molar volume, V_m , and molar refraction, R_m , as a function of temperature for selected fluorinated ionic liquids.

T/K	$V_m/\text{cm}^3\cdot\text{mol}^{-1}$	$R_m/\text{cm}^3\cdot\text{mol}^{-1}$	T/K	$V_m/\text{cm}^3\cdot\text{mol}^{-1}$	$R_m/\text{cm}^3\cdot\text{mol}^{-1}$
[C ₂ C ₁ Im][CF ₃ SO ₃]			[C ₈ C ₁ Im][CF ₃ SO ₃]		
293.15	187.34	48.84	293.15	288.90	76.83
298.15	187.92	48.83	298.15	289.83	76.86
303.15	188.49	48.84	303.15	290.76	76.90
308.15	189.06	48.85	308.15	291.69	76.93
313.15	189.64	48.86	313.15	292.62	76.95
318.15	190.22	48.87	318.15	293.55	76.96
323.15	190.80	48.88	323.15	294.48	76.97
328.15	191.37	48.89	328.15	295.41	76.97
333.15	191.95	48.90	333.15	296.34	76.98
338.15	192.53	48.86	338.15	297.27	76.99
343.15	193.11	48.88	343.15	298.20	77.00
348.15	193.70	48.89	348.15	299.14	77.04
353.15	194.29	48.91	353.15	300.08	77.07
[C ₂ C ₁ Im][C ₄ F ₉ SO ₃]			[C ₆ C ₁ Im][C ₄ F ₉ SO ₃]		
293.15	264.31	64.03	293.15	333.77	82.67
298.15	265.24	64.06	298.15	334.95	82.71
303.15	266.16	64.09	303.15	336.13	82.75
308.15	267.08	64.12	308.15	337.31	82.79
313.15	268.00	64.14	313.15	338.50	82.82
318.15	268.92	64.17	318.15	339.68	82.86
323.15	269.83	64.19	323.15	340.86	82.87
328.15	270.75	64.22	328.15	342.05	82.93
333.15	271.67	64.25	333.15	343.23	82.96
338.15	272.60	64.27	338.15	344.42	83.00
343.15	273.52	64.29	343.15	345.61	83.03
348.15	274.45	64.32	348.15	346.80	83.07
353.15	275.37	64.35	353.15	348.00	83.10

[C ₈ C ₁ Im][C ₄ F ₉ SO ₃]			[C ₁₂ C ₁ Im][C ₄ F ₉ SO ₃]		
308.15	371.75	92.08	-	-	-
313.15	373.06	92.13	313.15	441.45	110.82
318.15	374.38	92.18	318.15	443.03	110.86
323.15	375.69	92.22	323.15	444.62	110.91
328.15	377.01	92.26	328.15	446.21	110.96
333.15	378.33	92.30	333.15	447.80	111.01
338.15	379.65	92.34	338.15	449.40	111.06
343.15	380.97	92.37	343.15	451.00	111.10
348.15	382.29	92.40	348.15	452.60	111.15
353.15	383.62	92.44	353.15	454.20	111.19
[C ₂ C ₁ Im][CF ₃ CO ₂]			[C ₈ C ₁ Im][CF ₃ CO ₂]		
293.15	172.98	45.89	293.15	275.64	74.09
298.15	173.51	45.89	298.15	276.54	74.12
303.15	174.05	45.91	303.15	277.45	74.15
308.15	174.59	45.93	308.15	278.36	74.19
313.15	175.13	45.95	313.15	279.27	74.22
318.15	175.67	45.97	318.15	280.18	74.25
323.15	176.21	45.99	323.15	281.08	74.28
328.15	176.76	46.01	328.15	281.99	74.31
333.15	177.30	46.03	333.15	282.90	74.34
338.15	177.84	46.06	338.15	283.81	74.37
343.15	178.39	46.07	343.15	284.72	74.40
348.15	178.94	46.10	348.15	285.64	74.43
353.15	179.49	46.12	353.15	286.55	74.47
[C ₂ C ₁ Im][C ₄ F ₉ CO ₂]			[C ₈ C ₁ Im][C ₄ F ₉ CO ₂]		
293.15	250.76	60.62	293.15	353.49	88.15
298.15	251.66	60.65	298.15	354.78	88.19
303.15	252.56	60.68	303.15	356.08	88.23
308.15	253.46	60.70	308.15	357.38	88.26
313.15	254.35	60.73	313.15	358.69	88.30
318.15	255.25	60.75	318.15	359.99	88.33

323.15	256.15	60.77	323.15	361.30	88.37
328.15	257.05	60.79	328.15	362.60	88.40
333.15	257.95	60.81	333.15	363.91	88.44
338.15	258.86	60.84	338.15	365.23	88.47
343.15	259.77	60.87	343.15	366.55	88.50
348.15	260.69	60.89	348.15	367.87	88.54
353.15	261.62	60.92	353.15	369.22	88.64

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