

SUPPORTING INFORMATION

Fluorinated Ionic Liquids: Properties and Applications

Ana B. Pereiro^{*,†}, João M. M. Araújo[†], Susana Martinho[†], Filipa Alves[†], Sara Nunes[†], Ana Matias[†], Catarina M. M. Duarte^{†‡}, Luis Paulo N. Rebelo[†], Isabel M. Marrucho^{†,§,*}

EXPERIMENTAL SECTION

Materials. 1-Methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium hexafluorophosphate, >97% mass fraction purity, 1-butyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium hexafluorophosphate, >97% mass fraction purity, tetrabutylammonium heptadecafluorooctanesulfonate, >97% mass fraction purity, tetrabutylammonium perfluorobutanesulfonate, >97% mass fraction purity, 1-ethyl-3-methylpyridinium perfluorobutanesulfonate, >97% mass fraction purity, 1-methyl-3-octylimidazolium perfluorobutanesulfonate, >99% mass fraction purity, 1-hexyl-3-methylimidazolium perfluorobutanesulfonate, >99% mass fraction purity, and 1-butyl-1-methylpyrrolidinium perfluorobutanesulfonate, 98% mass fraction purity were supplied by

* Corresponding authors. Tel.: +351 214469414; fax: +351 214411277. E-mail address: anab@itqb.unl.pt (A. B. Pereiro) and imarrucho@itqb.unl.pt (I. M. Marrucho).

[†] Instituto de Tecnologia Química e Biológica

[‡] Instituto de Biologia Experimental e Tecnológica

[§] Universidade de Aveiro

IoLiTec GmbH. All 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. Water content, determined by Karl Fischer titration, was less than 100 ppm. No further purification of the ILs was carried out. The purity of the final products was checked by $^1\text{H-NMR}$.

In the cytotoxicity assay, the CellTiter 96® AQueous One Solution Cell Proliferation Assay was obtained from Promega (San Luis Obispo, CA, USA); RPMI medium 1640, fetal bovine serum (FBS), L-Glutamine, penicillin-streptomycin solution, MEM medium, MEM non-essential amino acids (MEM-NEAA), sodium pyruvate (100x) and trypsin-EDTA solution came from Gibco (Invitrogen Corporation, Paisley, UK). For cell culture, human colon carcinoma Caco-2 cells were purchased from Deutsche Sammlung von Mikroorganismen und Zellkulturen (DSMZ, Braunschweig, Germany) and were routinely grown in RPMI 1640 supplemented with 10% of inactivated FBS, 2mM of glutamine and 5000U of penicillin-streptomycin. Human hepatocellular carcinoma cells were obtained from the European Collection of Cell Culture (ECACC, Wiltshire, UK) and were cultured in MEM with 10% of inactivated FBS, 2mM Glutamine, 1% MEM-NEAA and 1% sodium pyruvate. Stock cells were maintained as monolayers in 175 cm² culture flasks and incubated at 37°C in a 5% CO₂ humidified atmosphere.

Methods and Procedures. Each fluorinated ionic liquid was taken from the respective schlenk flask with a syringe under a nitrogen flow to prevent humidity and was immediately placed in the apparatuses.

Thermogravimetric analyses (TGA) were carried out with a TA instrument Model TGA Q50 and the thermal stabilities and decomposition temperatures of the fluorinated ionic liquids were measured. Nitrogen was used for the TGA measurements at a flow rate of 60 ml·min⁻¹. Samples were placed inside aluminium pans and heated to 873 K at a rate of 1 K·min⁻¹ until

complete thermal degradation was achieved. Universal Analysis, version 4.4A software, determined the onset (T_{onset}), the starting (T_{start}) and the decomposition (T_{dec}) temperatures corresponding to the temperature at which the baseline slope changed during heating, the weight loss was less than 1%, and the weight loss was 50%, respectively. A DSC Q200 Differential Scanning Calorimeter (TA Instrument) was used to measure the thermal properties of the fluorinated ionic liquids. The sample was continuously purged with 50 ml·min⁻¹ dinitrogen. About 5 to 10mg of fluorinated IL was crimped in an aluminum standard sample pan. Indium (m.p., T = 429.76 K) was used as the standard compound for the calibration of the DSC.

Cell toxicity assays were performed using human Caco-2 and HepG2 cells. Briefly, Caco-2 and HepG2 cells were seeded at a density of 2×10^4 cells/well and 6×10^4 cells/well, respectively in 96-well plates and their media was replaced every 48 h. Caco-2 cell experiments were performed using completely differentiated cells (after reaching confluence \pm 96 hours after seeding) and HepG2 cell experiments were performed 24 h after seeding. Stock solutions of the ILs were prepared in DMSO. All the ILs were homogenous in solution and diluted in 5% FBS culture medium with a maximum of 1% DMSO. Caco-2 and HepG2 cells were incubated for 4 h with the ILs in a 5% FBS medium. This length of time was chosen according to digestion time. Control cells contained culture medium with the percentage of DMSO used. After 4 hours of incubation, the samples were removed and 100 μ L of a CellTiter 96® AQueous One Solution Cell Proliferation Assay reagent (containing MTS and PES) was added to each well and left to react for 4 h. This solution reagent contains a tetrazolium compound (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium, inner salt; MTS and an electron-coupling reagent (phenazine ethosulfate, PES). PES has an enhanced chemical stability which allows it to be combined with MTS, leading to a stable solution. MTS is bio-reduced by

cells into a coloured formazan product that is soluble in tissue culture medium. Formazan was quantified spectrophotometrically at 490 nm in a BioTek FLx800 microplate reader (BioTek, USA). Each sample was incubated in six different wells and the obtained value was the average of three independent assays. Cell viability was determined by the ratio between the measured absorbance of ILs-contacted cells and the measured absorbance of control. Dose-dependent toxicity curves were determined presenting the toxicity trends for each FIL. Afterwards, the function that best fit the experimental data and the EC50 was estimated by interpolation.

Measurements of viscosity and density were performed in the temperature range between 283.15 and 353.15 K at atmospheric pressure using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The SVM 3000 uses Peltier elements for fast and efficient thermostability. The temperature uncertainty is ± 0.02 K. The precision of the dynamic viscosity measurements is $\pm 0.5\%$ and the absolute uncertainty of the density is $\pm 0.0005 \text{ g}\cdot\text{cm}^{-3}$. For each fluorinated ionic liquid, triplicates were measured and the reported result is the average value with a maximum relative standard deviation (RSD) of 0.51%.

The refractive index of the pure ionic liquids was determined by an ABBEMAT 500 Anton Paar automatic refractometer with a resolution of $\pm 10^{-6}$ and an uncertainty in the experimental measurements of $\pm 4\cdot 10^{-5}$. The apparatus was calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene (provided by the supplier) before each series of measurements.

A CDM210 Radiometer Analytical conductimeter was used to measure the ionic conductivities in a jacketed glass cell containing a magnetic stirrer. A water bath controlled to $\pm 0.01\text{K}$ was used to thermostatize the cell. Cell temperature was measured by means of a platinum resistance thermometer coupled to a Keithley 199 System DMM/Scanner. The thermometer was

calibrated against high-accuracy mercury thermometers (0.01 K). For the electrical conductivity measurements, 1.5 ml of the sample was added to the thermostatic cell and vigorously stirred. The cell was closed with screw caps to ensure a secure seal and flushed with dry nitrogen to prevent humidity. The conductimeter was calibrated at each temperature with certified 0.01 D and 0.1 D KCl standard solutions supplied by Radiometer Analytical. This technique was validated using the pure ionic liquids 1-ethyl-3-methylimidazolium and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The results were compared with published data using the impedance method showing maximum relative deviations of 2%. Every conductivity value was determined at least three times and the uncertainty of the measurements was estimated to be 1% in absolute value.

RESULTS

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 S1.

Table S1. Thermal Properties of Selected Fluorinated Ionic Liquids: Starting Temperature, T_{start} , Onset Temperature, T_{onset} , Decomposition Temperature, T_{dec} , Melting Temperature, T_{m} , and Glass Transition Temperature, T_{g} .

	$T_{\text{start}}^{\text{a}} / \text{K}$	$T_{\text{onset}}^{\text{a}} / \text{K}$	$T_{\text{dec}}^{\text{a}} / \text{K}$	T_{m} / K	T_{g} / K
[(EtPFHex)MeIm][PF ₆]	429.93	535.20	544.39	338.94	236.18
[(EtPFHex)BuIm][PF ₆]	420.52	519.75	557.73	362.57	–
[NBu ₄][(PFOc)SO ₃]	373.67	385.08	402.61	255.14	225.72
[NBu ₄][(PFBu)SO ₃]	545.07	587.04	619.21	327.13	234.45
[EtMepy][(PFBu)SO ₃]	574.13	629.10	651.89	277.85	–
[HexMeIm][(PFBu)SO ₃]	565.56	627.00	666.18	296.75	–
[OcMeIm][(PFBu)SO ₃]	581.98	621.41	655.78	308.13	–
[BuMepyr][(PFBu)SO ₃]	588.99	632.25	650.62	632.08	–

^aNote 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 Table S2. The temperature dependence of the density and refractive index was studied applying the following expression:

$$\ln \rho = A_0 + A_1 T \quad (1)$$

$$n_D = A_0 + A_1 T \quad (2)$$

where T is the absolute temperature and A_0 , and A_1 are adjustable parameters. The correlation parameters are given in Table S3 together with the standard deviations (S.D.). These deviations were calculated by applying the following expression:

$$\text{S.D.} = \left(\frac{\sum_i^{n_{\text{DAT}}} (z_{\text{exp}} - z_{\text{adjust}})^2}{n_{\text{DAT}}} \right)^{1/2} \quad (3)$$

where property values and the number of experimental and adjustable data are represented by z and n_{DAT} , respectively.

The refractive index can be used as a measure of the electronic polarizability of a molecule and can provide useful information when studying the forces between molecules or their behavior in solution.^{S1} The Lorenz–Lorentz equation relates the electronic polarizability, α_e , with the refractive index, n_D , and can also be expressed in terms of the molar refraction, or molar polarizability,^{S2} R_m , using the expression:

$$R_m = \frac{N_A \alpha_e}{3\epsilon_0} = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) V_m \quad (4)$$

where N_A is the Avogadro's constant, ϵ is the dielectric constant, and V_m is the molar volume.

Table S2. Density, ρ , Dynamic Viscosity, η , Refractive Index, n_D , and Ionic Conductivity, k , of the Pure 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	$k/\text{mS}\cdot\text{cm}^{-1}$
[NBu ₄][(PFOc)SO ₃]					[NBu ₄][(PFBu)SO ₃]				
283.15	–	–	1.40102	$1.28 \cdot 10^{-3}$	283.15	–	–	–	–
288.15	–	–	1.39946	$2.44 \cdot 10^{-3}$	288.15	–	–	–	–
293.15	1.3215	12159	1.39788	$4.41 \cdot 10^{-3}$	293.15	1.2371	28508	1.41696	–
298.15	1.3173	6690	1.39625	$7.39 \cdot 10^{-3}$	298.15	1.2335	15319	1.41547	–
303.15	1.3129	3879	1.39478	$1.22 \cdot 10^{-2}$	303.15	1.2301	8622	1.41400	–
308.15	1.3083	2340	1.39321	$1.89 \cdot 10^{-2}$	308.15	1.2266	5059	1.41249	–
313.15	1.3034	1464	1.39165	$2.86 \cdot 10^{-2}$	313.15	1.2230	3081	1.41101	–
318.15	1.2984	947.2	1.39006	$4.19 \cdot 10^{-2}$	318.15	1.2192	1946	1.40954	–
323.15	1.2934	631.9	1.38849	$5.95 \cdot 10^{-2}$	323.15	1.2152	1265	1.40814	–
328.15	1.2882	433.5	1.38692	–	328.15	1.2111	846.5	1.40669	–
333.15	1.2833	305.1	1.38535	–	333.15	1.2069	581.3	1.40522	–
338.15	1.2783	219.9	1.38373	–	338.15	1.2028	409.1	1.40364	–
343.15	1.2735	161.9	1.38205	–	343.15	1.1987	294.4	1.40231	–
348.15	1.2686	121.6	–	–	348.15	1.1944	216.2	–	–
353.15	1.2638	92.94	–	–	353.15	1.1899	161.8	–	–
[HexMeIm][(PFBu)SO ₃]					[OcMeIm][(PFBu)SO ₃]				
293.15	1.3967	570.0	1.40987	0.218	298.15	1.3381	374.6	1.41279	–

298.15	1.3918	401.7	1.40847	0.299	303.15	1.3332	344.9	1.41134	-
303.15	1.3871	290.2	1.40704	0.401	308.15	1.3287	252.9	1.40990	0.355
308.15	1.3824	214.4	1.40562	0.527	313.15	1.3242	189.2	1.40848	0.461
313.15	1.3778	161.6	1.40421	0.678	318.15	1.3197	144.3	1.40710	0.588
318.15	1.3732	124.1	1.40281	0.857	323.15	1.3153	111.9	1.40568	0.732
323.15	1.3686	96.98	1.40130	1.07	328.15	1.3109	88.21	1.40430	-
328.15	1.3639	76.95	1.40005	-	333.15	1.3065	70.53	1.40289	-
333.15	1.3593	61.92	1.39867	-	338.15	1.3020	57.15	1.40152	-
338.15	1.3546	50.49	1.39731	-	343.15	1.2976	46.88	1.40008	-
343.15	1.3499	41.66	1.39595	-	348.15	1.2931	38.89	-	-
348.15	1.3450	34.76	-	-	353.15	1.2885	32.61	-	-
353.15	1.3401	29.31	-	-	-	-	-	-	-
[EtMepy][(PFBu)SO ₃]									
283.15	1.5306	578.9	1.42439	0.405	323.15	1.4899	56.72	1.41250	2.97
288.15	1.5252	394.8	1.42290	0.565	328.15	1.4850	46.34	1.41082	-
293.15	1.5199	278.2	1.42142	0.765	333.15	1.4802	38.39	1.40934	-
298.15	1.5148	201.8	1.41997	1.01	338.15	1.4753	32.18	1.40790	-
303.15	1.5098	150.3	1.41850	1.30	343.15	1.4704	27.26	1.40651	-
308.15	1.5048	114.4	1.41703	1.64	348.15	1.4655	23.33	-	-
313.15	1.4998	88.98	1.41554	2.03	353.15	1.4607	20.15	-	-
318.15	1.4949	70.46	1.41405	2.48	-	-	-	-	-

Table S3. 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 Selected Fluorinated Ionic Liquids. Standard Deviations (S.D.) (Equation 5) are Also Shown.

[NBu ₄][(PFOc)SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.5008$	$A_1 = -7.547 \cdot 10^{-4}$	–	S.D. = $3.4 \cdot 10^{-4}$
n_D	$A_0 = 1.4902$	$A_1 = -3.150 \cdot 10^{-4}$	–	S.D. = $5.0 \cdot 10^{-5}$
$\phi/\text{mPa}^{-1}\cdot\text{s}^{-1}$	$\phi_0 = 3.75$	$B = 707.29$	$T_0 = 232.5$	S.D. = $7.7 \cdot 10^{-5}$
$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 1334.6$	$B' = 1349.7$	$T_0' = 186.4$	S.D. = $4.5 \cdot 10^{-4}$
[NBu ₄][(PFBu)SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.4037$	$A_1 = -6.482 \cdot 10^{-4}$	–	S.D. = $5.5 \cdot 10^{-4}$
n_D	$A_0 = 1.5029$	$A_1 = -2.934 \cdot 10^{-4}$	–	S.D. = $4.3 \cdot 10^{-5}$
$\phi/\text{mPa}^{-1}\cdot\text{s}^{-1}$	$\phi_0 = 2.14$	$B = 707.34$	$T_0 = 232.8$	S.D. = $9.0 \cdot 10^{-5}$
[HexMeIm][(PFBu)SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.5346$	$A_1 = -6.840 \cdot 10^{-4}$	–	S.D. = $1.5 \cdot 10^{-4}$
n_D	$A_0 = 1.4920$	$A_1 = -2.801 \cdot 10^{-4}$	–	S.D. = $6.1 \cdot 10^{-5}$
$\phi/\text{mPa}^{-1}\cdot\text{s}^{-1}$	$\phi_0 = 3.75$	$B = 705.46$	$T_0 = 203.34$	S.D. = $2.0 \cdot 10^{-4}$
$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 1376.8$	$B' = 1186.9$	$T_0' = 157.4$	S.D. = $1.4 \cdot 10^{-3}$
[OcMeIm][(PFBu)SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.5006$	$A_1 = -6.802 \cdot 10^{-4}$	–	S.D. = $3.4 \cdot 10^{-4}$
n_D	$A_0 = 1.4967$	$A_1 = -2.816 \cdot 10^{-4}$	–	S.D. = $2.7 \cdot 10^{-5}$
$\phi/\text{mPa}^{-1}\cdot\text{s}^{-1}$	$\phi_0 = 3.56$	$B = 706.04$	$T_0 = 205.01$	S.D. = $3.2 \cdot 10^{-4}$
$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 1381.1$	$B' = 1295.0$	$T_0' = 151.4$	S.D. = $1.8 \cdot 10^{-3}$
[EtMepy][(PFBu)SO ₃]				
$\ln\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.6136$	$A_1 = -6.648 \cdot 10^{-4}$	–	S.D. = $1.1 \cdot 10^{-4}$
n_D	$A_0 = 1.5094$	$A_1 = -3.001 \cdot 10^{-4}$	–	S.D. = $7.4 \cdot 10^{-5}$
$\phi/\text{mPa}^{-1}\cdot\text{s}^{-1}$	$\phi_0 = 4.12$	$B = 704.89$	$T_0 = 193.8$	S.D. = $1.3 \cdot 10^{-4}$
$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 1430.0$	$B' = 1028.1$	$T_0' = 156.5$	S.D. = $1.4 \cdot 10^{-2}$

The relation between the polarizability and the refraction index shown above can provide important information about the behavior of a liquid as a solvent media and constitutes a measure of the importance of the dispersion forces to the cohesion of the liquid. Therefore, solvents with a large index of refraction, and hence large polarizability, should enjoy particularly strong dispersion forces,^{S3} serving also as good solvents for species possessing high polarizabilities. Molar refractions can be considered as a measure of the hard-core molecular volumes because the electronic polarizability can be related to a spherical molecular radius,^{S1} a , by:

$$\alpha_e = 4\pi\epsilon_0 a^3 \quad (5)$$

and equation 4 can be expressed in the following form:^{S1}

$$n_D^2 - 1 = 3 \left(\frac{V_m}{R_m - 1} \right)^{-1} = 3 \left(\frac{R_m}{f_m} \right) \quad (6)$$

where f_m is the free volume defined as:

$$f_m = (V_m - R_m) \quad (7)$$

which means that the refractive index is directly proportional to the occupied part of the molar volume, R_m taken as the hard-core molecular volume.^{S4,S5} The values for the calculated molar refractions (from equation 4) and free volumes (from equation 7) of all the selected samples were calculated and are listed in Table S4.

Arrhenius fittings for fluidity (1/viscosity), ϕ , were well carried out by the Vogel-Fulcher-Tammann (VFT) equation:

$$\phi = \phi_0 \exp\left(\frac{-B}{T - T_0}\right) \quad (8)$$

Table S4. Values of Calculated Molar Volume, V_m , Molar Refraction, R_m , and Free Volume, f_m , as a Function of Temperature for Selected Fluorinated Ionic Liquids.

T/K	$V_m/\text{cm}^3 \cdot \text{mol}^{-1}$	$R_m/\text{cm}^3 \cdot \text{mol}^{-1}$	$f_m/\text{cm}^3 \cdot \text{mol}^{-1}$	T/K	$V_m/\text{cm}^3 \cdot \text{mol}^{-1}$	$R_m/\text{cm}^3 \cdot \text{mol}^{-1}$	$f_m/\text{cm}^3 \cdot \text{mol}^{-1}$
[NBu ₄][(PFOc)SO ₃]				[NBu ₄][(PFBu)SO ₃]			
293.15	561.12	135.39	425.73	293.15	437.73	110.07	327.66
298.15	562.93	135.33	427.60	298.15	439.01	110.04	328.97
303.15	564.82	135.34	429.47	303.15	440.22	110.01	330.22
308.15	566.80	135.34	431.46	308.15	441.48	109.97	331.51
313.15	568.93	135.37	433.56	313.15	442.78	109.94	332.84
318.15	571.12	135.40	435.72	318.15	444.16	109.94	334.22
323.15	573.33	135.44	437.89	323.15	445.62	109.97	335.66
328.15	575.62	135.49	440.13	328.15	447.13	109.99	337.14
333.15	577.85	135.52	442.32	333.15	448.69	110.03	338.66
338.15	580.08	135.54	444.54	338.15	450.22	110.02	340.20
343.15	582.29	135.53	446.77	343.15	451.76	110.08	341.68
[HexMeIm][(PFBu)SO ₃]				[OcMeIm][(PFBu)SO ₃]			
293.15	333.87	82.70	251.17	298.15	369.49	92.09	277.40
298.15	335.06	82.74	252.32	303.15	370.85	92.15	278.70
303.15	336.19	82.77	253.43	308.15	372.10	92.17	279.93
308.15	337.33	82.79	254.54	313.15	373.37	92.20	281.17

313.15	338.46	82.81	255.65	318.15	374.63	92.24	282.39
318.15	339.59	82.84	256.76	323.15	375.90	92.27	283.63
323.15	340.74	82.84	257.90	328.15	377.17	92.30	284.87
328.15	341.89	82.89	259.00	333.15	378.44	92.33	286.11
333.15	343.06	82.92	260.14	338.15	379.73	92.36	287.36
338.15	344.25	82.96	261.29	343.15	381.03	92.39	288.65
343.15	345.46	83.00	262.46	-	-	-	-
[EtMepy][(PFBu)SO ₃]							
283.15	275.21	70.28	204.92	318.15	281.78	70.42	211.36
288.15	276.19	70.32	205.88	323.15	282.73	70.43	212.30
293.15	277.14	70.34	206.80	328.15	283.66	70.40	213.25
298.15	278.08	70.37	207.71	333.15	284.59	70.41	214.18
303.15	279.01	70.39	208.62	338.15	285.52	70.42	215.10
308.15	279.93	70.40	209.53	343.15	286.48	70.45	216.03
313.15	280.86	70.41	210.45	-	-	-	-

where ϕ_0 , B , and T_0 are constants. The fitting parameters are summarized in Table S3.

Temperature dependence of ionic conductivity was also fitted with the VFT equation:

$$\kappa = \kappa_0 \exp\left(\frac{-B'}{T - T'_0}\right) \quad (9)$$

where σ_0 , B' , and T'_0 are adjustable parameters. Table S3 summarizes the best-fit parameters of ionic conductivity.

REFERENCES

- (S1) Tariq, M.; Forte, P. A. S.; Gomes, M. F. C.; Lopes, J. N. C.; Rebelo, L. P. N., Densities and refractive indices of imidazolium- and phosphonium-based ionic liquids: Effect of temperature, alkyl chain length, and anion. *J. Chem. Thermodyn.* **2009**, *41* (6), 790-798.
- (S2) Moldover, M. R., Measurement of the Thermodynamics Properties of Single Phases. In *IUPAC Experimental Thermodynamics Vol. VI: Measurement of the Thermodynamic Properties of Single Phases*, Elsevier: 2008; pp 435-451.
- (S3) Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*. 3 ed.; Wiley: 2003.
- (S4) Deetlefs, M.; Seddon, K. R.; Shara, M., Predicting physical properties of ionic liquids. *Phys. Chem. Chem. Phys.* **2005**, *8* (5), 642-649.
- (S5) Iglesias-Otero, M. A.; Troncoso, J.; Carballo, E.; Romani, L., Density and refractive index in mixtures of ionic liquids and organic solvents: Correlations and predictions. *J. Chem. Thermodyn.* **2008**, *40* (6), 949-956.

This information is available free of charge via the Internet at <http://pubs.acs.org/>.