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Simple method of preparation of novel hydrophobic ionic liquid with a per-fluoro-*tert*-butoxide anion

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Electronic Supplementary Information

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1 Synthesis and characterization of novel hydrophobic ionic liquid

1.1 Materials

1-butyl-3-methylimidazolium acetate, [C_4C_1im][OAc] (purity > 98 wt%) and 1-butyl-3-methylimidazolium chloride, [C_4C_1im]Cl (purity > 98 wt%) were obtained from Iolitec. Prior to the synthesis, these chemicals were further purified (to reduce the content of water and impurities) by drying under vacuum at 313.15 K and 0.1 Pa under constant stirring for at least 48h. After this procedure, ^{1}H and ^{13}C NMR analyses confirmed the purity of the [C_4C_1im][OAc] and [C_4C_1im]Cl samples as stated by the supplier. *Per*-fluoro-*tert*-butanol, C_4HF_9O (purity > 97 wt%) was purchased from fluorochem, United Kingdom, and was used without further purification.

1.2 Synthesis of novel hydrophobic ionic liquid

To a round-bottom flask containing 1 equimolar of aqueous solution of [C_4C_1im][OAc] was added 1.05 equimolar of *per*-fluoro-*tert*-butanol. The flask was fitted with condenser, thus allowing refluxing the mixture at 313.15 K. The reaction was monitored by Thin Layer Chromatography method, using silica sheet and methanol : ethylacetate (1:1) as eluent. After 24 hours, the reaction was assumed to be completed. The mixture was then transferred to another round-bottom flask specially designed to dry the IL under vacuum and was let under vacuum at 0.1 P and at 313.15 K under constant stirring for at least 48 h to ensure complete removal of water and possible unreacted materials. The synthesized IL was kept in sealed bottle with PTFE septum. For the characterization and thermophysical properties measurement, required amount of IL sample was taken using syringe equipped with needle, through the PTFE septum.

The purity of the synthesized IL was determined using nuclear magnetic resonance (NMR) spectroscopy. In this way, approximately 5 mg of sample was dissolved in 0.6 ml deuterated DMSO with tetramethyl silane (TMS) as an internal standard. The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at room temperature using Bruker AMX 300 operating at 300.13 and 75.45 MHz, respectively. The water content of the synthesized

IL was measured using KF method, described above, and was found to be lower than 200 ppm.

Table ESI 1. ^{1}H NMR and ^{13}C NMR chemical shifts (δ, ppm) of the novel IL 1-butyl-3-methylimidazolium *per*-fluoro-*tert*-butoxide at 298K under 0.1MPa.

Atom	^{1}**H**	^{13}**C**	^{19}**F**
10	0.92 (t, 3H, J_{HH} = 7.3 Hz)	13.35 (J_{CH} = 125 Hz)	-
9	1.29 (sext, 2H, J_{HH} = 7.3 Hz)	19.12 (J_{CH} = 126 Hz)	-
8	1.80 (quin, 2H, J_{HH} = 7.3 Hz)	31.78 (J_{CH} = 122 Hz)	-
6	3.87 (s, 3H)	35.91 (J_{CH} = 143 Hz)	-
7	4.18 (t, 2H, J_{HH} = 7.2 Hz)	48.91 (J_{CH} = 145 Hz)	-
11	-	80.71	-
12	-	122.54 (J_{CF} = 295 Hz)	- 97.38
5 [1]	7.73 (t, 1H, J_{HH} = 1.7 Hz)	123.99 (J_{CH} = 203 Hz)	-
4 [1]	7.80 (t, 1H, J_{HH} = 1.8 Hz)	122.67 (J_{CH} = 202 Hz)	-
2	9.30 (s, 1H)	137.16 (J_{CH} = 221 Hz)	-

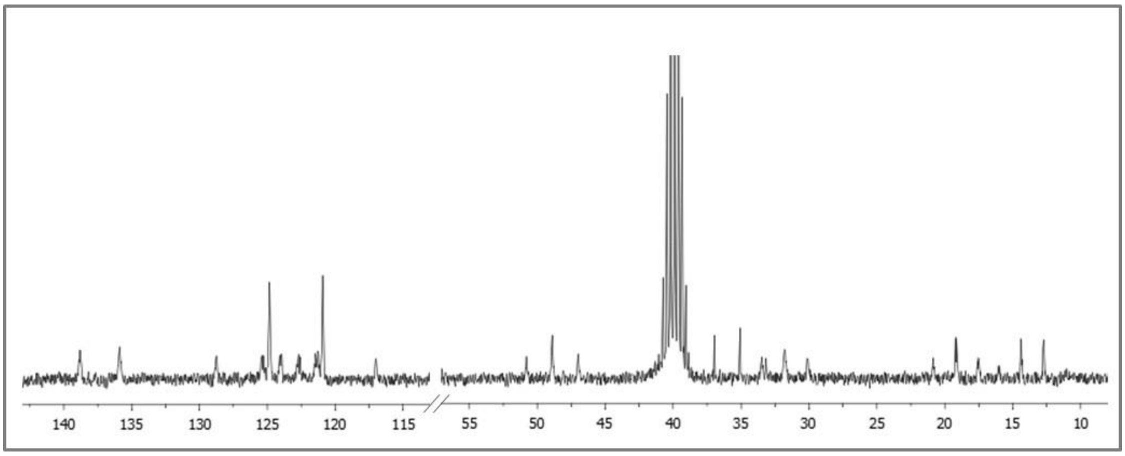

Figure ESI 1. ^{13}C NMR spectra of the novel IL 1-butyl-3-methylimidazolium *per*-fluoro-*tert*-butoxide without proton decoupling.

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[1] The assignment of these lines is supported by the 2D ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC NMR sequences performed for the 1-butyl-3-methylimidazolium cation (reference 1).

1.3 Physical Properties

The density, ρ, and viscosity, η, of the synthesized IL were determined using an automated SVM 3000 Anton-Paar rotational Stabinger viscometer-densimeter at temperature 298.15 K and at atmospheric pressure. Prior to the measurement, the equipment was calibrated using the standard solution given by the supplier and was further validated by measuring the density and viscosity of several ILs for which the data have been established by our research group. The accuracy of the density measurements was found to be better than 0.5 $kg \cdot m^{-3}$, whereas the relative uncertainty in dynamic viscosity was found to be ± 1%. The relative uncertainty in temperature is within ± 0.02 K.

The refractive index, n_D, of the studied IL was measured at 589.3 nm using an automated Abbemat 500 Anton Paar refractometer, enabling to measure either liquid or solid samples. The refractive index measurements were carried at temperature 298.15 K and at atmospheric pressure.

Double-distilled water, used for the water solubility measurement, was passed by a reverse osmosis system and further treated with a MilliQ plus 185 water purification apparatus. The purity analyses revealed resistivity values of 18.2 MΩ·cm and a Total Organic Carbon content smaller than 5 $\mu g \cdot dm^{-3}$. The analyte used for the coulometric Karl-Fischer (KF) titration was Hydranal® - Coulomat AG from Riedel-de Haen.

The surface tension of was determined through the analysis of the shape of a pendant drop and measured using a Dataphysics contact angle system OCA-20. Drop volumes of (10 ± 1) µL were obtained using a Hamilton DS 500/GT syringe connected to a Teflon coated needle placed inside an aluminium air chamber. The temperature was attained by circulating water in a double jacketed aluminium cell by means of a Julabo F-25 water bath. The temperature inside the aluminium chamber was measured with a Pt100 within ± 0.1 K, placed at a distance of approximately 2 cm to the liquid drop. Silica gel was kept inside the air oven to assure a dry environment and to avoid moisture absorption during the equilibration period. For the surface tensions determination, at each temperature and for each IL, at least 5 drops were formed and measured. For each drop, an average of 200 images was captured. The analysis of the drop shape was performed with the software module SCA 20 where the gravitational acceleration (g = 9.8018 m·s^2) and latitude (lat = 40º) were used according to the location of the assay.

The thermogravimetric analysis was determined using a thermal analysis on a thermogravimetric analyzer (TGA) with differential scanning calorimetric (DSC) capacity (Mettler Toledo, model TGA/DSC 1 LF) using the STAR analysis software. The samples were prepared in the aluminum pans and heated from (303.15 to 873.15) K, with a heating rate of 5 K·min^{-1} and under nitrogen gas flow of 40 mL·min^{-1}. The standard uncertainty of temperature is 0.2 K. The decomposition temperatures presented are the onset temperatures, which are the intersection of the baseline below the decomposition temperature with the tangent to the mass loss versus the temperature plots in the TGA profiles. The results are expressed as the average of duplicate measurements.

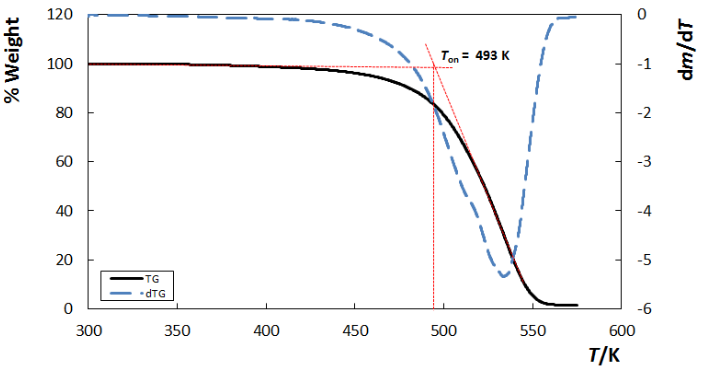

Figure ESI 2. Thermogravimetric analysis of [C_4C_1im][OAc]

1.4 Standard Microtox® liquid-phase assays

To evaluate the ecotoxicity of the synthesized novel hydrophobic ILs, several Standard Microtox® liquid-phase assays were carried out. Microtox® was used to evaluate the inhibition of the *Vibrio fischeri* (strain NRRL B-11177) luminescence followed by its exposure to each IL solution. The indications of the manufacturer on the standard 81.9 test protocol were followed.[2] The bacteria was exposed to a range of diluted aqueous solutions relative to the previously prepared stock solution, with a known concentration (0-81.9 wt%) of each IL. After 5, 15, and 30 minutes of exposure to each IL aqueous solution, the bacterial bioluminescence emission of *Vibrio fischeri* was measured and compared with the bioluminescence emission of a blank control sample. The corresponding 5 min-, 15 min- and 30 min-EC_{50} values (estimated concentration yielding a 50% of inhibition effect) were evaluated through the Microtox® Omni™ software version 4.1.[2] The EC_{50} values, plus the corresponding 95 % confidence intervals were estimated for each IL tested by non-linear regression, using the least-squares method to fit the data to the logistic equation.

2 Partial Charge Analysis

The geometries *tert*-butanol and *per*-fluoro-*tert*-butanol in the gas phase were optimized using the triple-ζ valence polarized basis set (TZVP) basis set and non-local BP exchange/correlation functional as implemented in Gaussian 03 Rev D.02.[3] The optimized geometry having the lowest energy and with the absence of imaginary or negative frequencies,[4] was used as the global minimum for the subsequent calculations. Thereafter, on the obtained minima, atomic charges of the isolated cation composing the studied compounds were retrieved by electrostatic surface potential (ESP) fits, using the CHelpG algorithm[5] to the electron densities obtained at the BP_TZVP level of theory.

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