Supplementary Information

Protic ionic liquids based on phosphonium cations: comparison with ammonium analogues

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Sample preparation

Synthesis of Protic Phosphonium cation based ILs

Tributyl phosphonium bis(trifluoromethane sulphonyl) amide ($P_{444H}NTf_2$) was synthesized via reaction scheme 1.

Scheme 1

A typical procedure for synthesis of $P_{444H}NTf_2$ is as follows: 6.0 g (0.021 mol) $LiNTf_2$ (3M, all chemicals were used as received, except as otherwise specified) was dissolved in 5 ml distilled water, 5.0 g (0.021 mol) tri-isobutyl phosphonium chloride (Cytec) was dissolved in 20 ml distilled water, these two solutions were mixed and the mixture was stirred at room temperature for about 3 hrs; $P_{444H}NTf_2$ was deposited as white solid from the solution, separated by filtering and washed with distilled water for three times; the product was dried by vacuum at ~70 °C; 9 g of $P_{444H}NTf_2$ was obtained with a yield of 92 %. Electrospray mass spectroscopy (cone ±35V), m/z (relative intensity, %): ES$^+$, 203.3 ([C_4H_9]$_3$HP$^+$, 100); ES$^-$, 279.9 ([CF_3SO_2]$_2$N$^-$, 100). H^1 NMR (400.13 MHz in CDCl$_3$, δ/ppm relative to TMS): 6.67-5.10 (2 sets of multiple peaks, 1H, J_{P-H} = 462 Hz, it was reported[1] that the coupling constant between phosphorus and the directly bound proton (J_{P-H}) is 475Hz for (n-C_4H_9)$_3$PH-Br in ^{1}H-NMR), 2.25-2.19 (m, 6H), 2.13-2.02 (m, 3H,), 1.14-1.12 (m, 18H).

Tributyl phosphonium trifluoromethane sulphonate ($P_{444H}SO_3CF_3$) was synthesized with the same method as $P_{444H}NTf_2$, using $NaSO_3CF_3$ instead of $LiNTf_2$. Electrospray mass spectroscopy (cone ±35V), m/z (relative intensity, %): ES$^+$, 203.3 ([C_4H_9]$_3$HP$^+$, 100); ES$^-$, 149.1 (CF$_3$O$_2$SO$^-$, 100). H^1 NMR (400.13 MHz in CDCl$_3$, δ/ppm relative to TMS): 6.77-5.61 (2 sets of multiple peaks, 1H, J_{P-H} = 464 Hz), 2.34-2.27 (m, 6H), 2.14-2.01 (m, 3H,), 1.15-1.13 (m, 18H).

Tributyl phosphonium methane sulphonate

($P_{444H}SO_3CH_3$) was synthesized via reaction scheme 2.

Scheme 2

A typical procedure for synthesis of $P_{444H}SO_3CH_3$ is as follows: 3.67 g (0.018 mol) AgSO$_3$CH$_3$ (Aldrich) was dissolved in 20 ml distilled water, 4.29 g (0.018 mol) tri-isobutyl phosphonium chloride (Cytec) was added and the mixture was stirred at room temperature for overnight; AgCl was deposited from the solution, removed by filtering and the product was obtained by rotator-distillation; the product was dried by vacuum at ~70 °C; 3.1 g of $P_{444H}SO_3CH_3$ was obtained with a yield of 58 %. Electrospray mass spectroscopy (cone ±35V), m/z (relative intensity, %): ES$^+$, 203.2 ([C_4H_9]$_3$HP$^+$, 100); ES$^-$, 95.0 (CH$_3$O$_2$SO$^-$, 100). H^1 NMR (400.13 MHz in CDCl$_3$, δ/ppm relative to TMS): 10.79-10.76 (m, 1H,) 6.96-5.78 (2 sets of multiple peaks, 1H, J_{P-H} = 471 Hz), 2.91 (s, 3H), 2.34-2.28 (m, 6H), 2.14-2.05 (m, 3H,), 1.17-1.11 (m, 18H).

Tributyl phosphonium nitrate ($P_{444H}NO_3$) was synthesized via the same method as $P_{444H}SO_3CH_3$, using AgNO$_3$ instead of AgSO$_3$CH$_3$. Electrospray mass spectroscopy (cone ±35V), m/z (relative intensity, %): ES$^+$, 203.1 ([C_4H_9]$_3$HP$^+$, 100); ES$^-$, 62.0 (O$_2$NO$^-$, 100). H^1 NMR (400.13 MHz in CDCl$_3$, δ/ppm relative to TMS): 12.16 (s, 1H) 7.25-6.07 (2 single peaks, 1H, J_{P-H} = 473 Hz), 2.34-2.30 (m, 6H), 2.16-2.03 (m, 3H,), 1.15-1.10 (m, 18H).

Synthesis of Protic Ammonium cation based Ionic Liquids

The synthesis of protic ionic liquids based on tributylammonium cation was made by using proton transfer reaction. In the literature, some of the tributylammonium based protic ionic liquids such as *tributylammonium triflate*, *Tributylammonium methane sulphonate* have been reported[2] ; however *tributylammonium bis(trifluoromethane sulphonyl) amide and tributylammonium nitrate* have not been reported and the procedure for the synthesis is given below.

Tributyl ammonium bis(trifluoromethane sulphonyl) amide ($N_{444H}NTf_2$) was made by stirring the aqueous solutions of tributyl amine (Sigma, 99% pure) and HTFSA (99% pure)for 2 hours. Typically the reaction involves a slow addition of aqueous solution of HTFSA (6.02 g, 0.021 moles) to the aqueous solution of tributyl amine (3.97 g, 0.021 moles) kept in an ice bath. After 2 hours of stirring, the hydrophobic product separates out from the mixture. The product in the organic layer was separated out, washed with water to remove the impurities. Then the product was dissolved in dichloromethane and the solvent was removed by distillation. The final product was dried under vacuum at 60 °C for two days and the yield of pale yellow crystalline product was found to be 96%. Electrospray mass spectroscopy (cone

±35V), m/z (relative intensity, %): ES$^+$, 186.2 ([C$_4$H$_9$]$_3$HN$^+$, 100); ES$^-$, 279.9 ([CF$_3$SO$_2$]$_2$N$^-$, 100). H^1 NMR (400.13 MHz in CDCl$_3$, δ/ppm relative to TMS): 7.17 (s, 1H), 3.10-3.05 (m, 6H), 1.71-1.37 (m, 12H), 1.00-0.94 (m, 9H,). **^{19}F NMR** shows a strong signal for the fluorine atom of *bis(trifluoromethane sulphonyl) amide* anion, noticed at -78.8ppm.

***Tributyl ammonium nitrate* (N$_{444H}$NO$_3$)** was synthesized by a slow addition of aqueous solution of nitric acid (2.53 g, based on 100 % nitric acid, 0.040 moles) to aqueous solution of tributylamine (7.46 g, 0.040 moles) in an ice bath. The reaction mixture was stirred for about an hour and water was rotoevaporated at 70°C under reduced pressure. The product obtained (pale yellowish orange liquid) is dried under vacuum at 60° C for two days and the yield was calculated to be 98%. Electrospray mass spectroscopy (cone ±35V), m/z (relative intensity, %): ES$^+$, 186.2 ([C$_4$H$_9$]$_3$HN$^+$, 100); ES$^-$, 62.0 (O$_2$NO$^-$, 100). H^1 NMR (400.13 MHz in CDCl$_3$, δ/ppm relative to TMS): 10.2 (s, 1H) 3.12-3.08 (m, 6H), 1.73-1.35 (m, 12H), 0.98-0.92 (m, 9H,).

TGA Measurement

The thermal stability and moisture content in materials were investigated by employing Thermogravimetric Analysis (TGA) technique in a flowing dry Argon atmosphere (50 mL min^{-1}) by using a Perkin-Elmer Pyris TG/DTA 6300 1 instrument between a temperature range of 25 to 700 °C at a heating rate of 10 °C min^{-1}.

DSC Measurement

The thermal properties of materials were studied using a TA differential scanning calorimeter (DSC) model Q 100 over a temperature range of −120 to 300 °C at a scanning rate of 10 °C min^{-1}. The samples were sealed in the Aluminium pans under the dry N$_2$ gas in glove box to avoid any moisture absorption. The entropy changes (ΔS) reported in (**Table S1**) are calculated from the enthalpy change (ΔH) occurring at each transition, which is obtained from the area under the DSC transition peaks. The DSC traces were analyzed using the TA instruments universal analysis 2000 program.

Conductivity Measurement

The ionic conductivities of all samples were measured using AC impedance spectroscopy using a frequency response analyzer (FRA, Solartron, 1296), impedance software version 3.2.0. The conductivities were obtained by measurement of the complex impedance spectra between 10 MHz and 0.01 Hz on a Solartron SI 1296 Dielectric interface and Solartron SI 1270 frequency response analyzer using two shielded BNC connectors. A Eurotherm 2204e temperature controller under serial control was used to control a 240 V cartridge heater for some experiments. The Eurotherm was under Solatron impedance measurement software control. A 240 V cartridge heater and K type thermocouple, mounted in a brass block, were used to control the sample temperature.
All sample handling was conducted within a nitrogen filled dry box to avoid any moisture uptake. The temperature range over which the impedance is measured is different for different proton ionic liquids and salts between a temperature range of −30 °C to 130 °C.

Cyclic Voltammetry

All voltammetric experiments were undertaken inside a homemade nitrogen-filled glove-box using an Epsilon electrochemical workstation (Bioanalytical System, West Lafayette, IN). A standard three electrode arrangement was used in voltammetric studies with a glassy carbon (GC) or platinum (Pt) as working disk electrodes (Cypress Systems, Inc., Lawrence, KS), a Pt wire counter electrode, and a Pt wire, separated from the test solution with a frit, was employed as the quasi-reference electrode (QRE). However, all potentials were initially obtained versus the Fc$^{0/+}$ couple in order to minimize the problems associated with potential drift encountered with use of the QREs. The voltage axis in the cyclic voltammograms was then rescaled using the known conversion constants between Fc$^{0/+}$ and the Normal Hydrogen Electrode (NHE)[1].

Prior to each experiment, the working electrodes were polished with 0.30 μm alumina (Buehler, Lake Bluff, IL) on a clean polishing cloth (Buehler), sequentially rinsed with distilled water and acetone, and then dried with lint free tissue paper. Effective electrode area of 7.24×10^{-3} cm^2 for the GC electrode and 7.34×10^{-3} cm^2 for the Pt electrode were determined from the peak current for the oxidation of a 1.00 mM Ferrocene, Fc, solution in CH$_3$CN (0.10 M Bu$_4$NPF$_6$) degassed with N$_2$ and use of the Randles-Sevcik relationship. A diffusion coefficient of 2.30×10^{-5} cm^2 s^{-1} for Fc was used in these calibrations.[2]
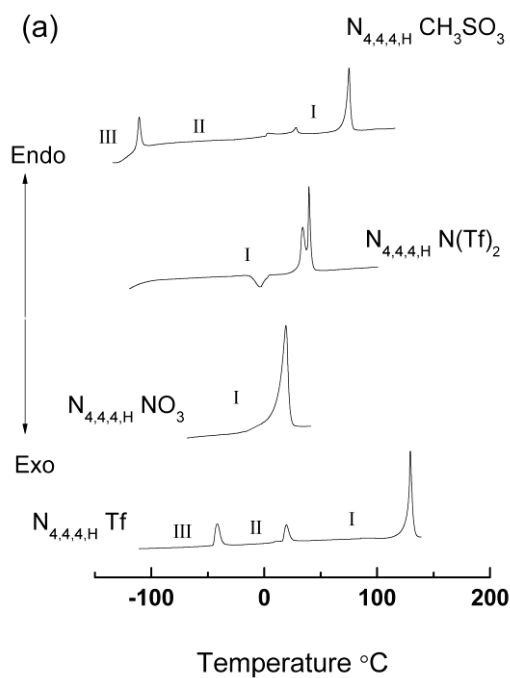
Figures and Tables

5 **Table S1.** Enthalpy and entropy values for different phase transitions calculated from the peak areas of DSC thermograms pure phosphonium and ammonium Protic Ionic liquids (PILs).

Materials	III>>II $\Delta H/$ kJ mol^{-1} ($\pm10\%$)	II>>I $\Delta H/$ kJ mol^{-1} ($\pm10\%$)	I>>melt $\Delta H/$ kJ mol^{-1} ($\pm10\%$)	III>>II $\Delta S/$ kJ mol^{-1} ($\pm10\%$)	II>>I $\Delta S/$ kJ mol^{-1} ($\pm10\%$)	I>>melt $\Delta S/$ kJ mol^{-1} ($\pm10\%$)
$P_{4,4,4,H}$ N(Tf)$_2$		6.1	10.7		20.7	36.3
$P_{4,4,4,H}$ Tf	5.0	2.8	17.6	16.8	9.3	59.5
$P_{4,4,4,H}$ CH$_3$SO$_3$						
$P_{4,4,4,H}$ NO$_3$						
$N_{4,4,4,H}$ N(Tf)$_2$			3.1			10.5
$N_{4,4,4,H}$ Tf	4.3	3.1	15.3	14.7	10.6	51.5
$N_{4,4,4,H}$ CH$_3$SO$_3$	0.7	0.2	1.6	2.3	0.6	5.5
$N_{4,4,4,H}$ NO$_3$		3.2	5.5		10.6	18.6

Table S2. Acid/Base pairs used in this work and their corresponding pK_a^{aq} values.

Acid/Conjugate base	pK_a^{aq} *
HN(Tf)$_2$/ N(Tf)$_2^{-1}$	~ - 14[#]
HTf/ Tf^{-1}	-14
HNO$_3$/ NO$_3^{-1}$	-1.3
CH$_3$SO$_3$H/ CH$_3$SO$_3^{-1}$	-2.6
$P_{4,4,4,H}^+$/ $P_{4,4,4,H}$	7.9
$N_{4,4,4,H}^+$/ $N_{4,4,4,H}$	10.9

10 * The pKa^{aq} values of acids from Evan's pK_a^{aq} table; pK_a^{aq} values for tri n-butylamine and tri-iso-butylphosphine from literature[3] # estimated pK_a^{aq} value of HN(Tf)$_2$ based on relatively close pK_a^{aq} value of HTf and HN(Tf)$_2$ measured in acetic acid[4].

(a)

(b)

Endo

$P_{4,4,4,H}$ CH_3SO_3

$P_{4,4,4,H}$ $N(Tf)_2$

II   I

$P_{4,4,4,H}$ NO_3

Exo

$P_{4,4,4,H}$ Tf   III   II

I

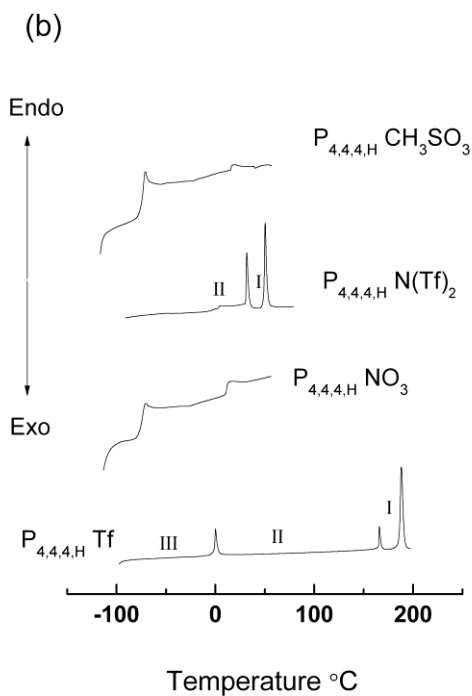-100   0   100   200

Temperature °C

Figure S1. DSC thermograms of (a) tributyl ammonium containing protic ionic liquids and (b) tributyl phosphonium containing protic ionic liquids. The roman numerals I, II and III indicate different solid phases with phase I being the highest temperature solid phase.
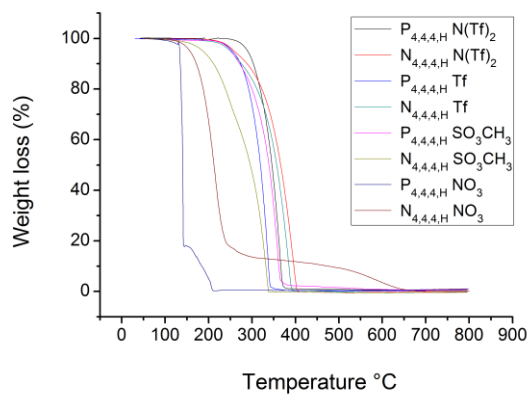
Weight loss (%)

—	$P_{4,4,4,H}$ $N(Tf)_2$
—	$N_{4,4,4,H}$ $N(Tf)_2$
—	$P_{4,4,4,H}$ Tf
—	$N_{4,4,4,H}$ Tf
—	$P_{4,4,4,H}$ SO_3CH_3
—	$N_{4,4,4,H}$ SO_3CH_3
—	$P_{4,4,4,H}$ NO_3
—	$N_{4,4,4,H}$ NO_3

0 100 200 300 400 500 600 700 800 900

Temperature °C

Figure S2. TGA traces of tributyl phosphonium and tributyl ammonium salts
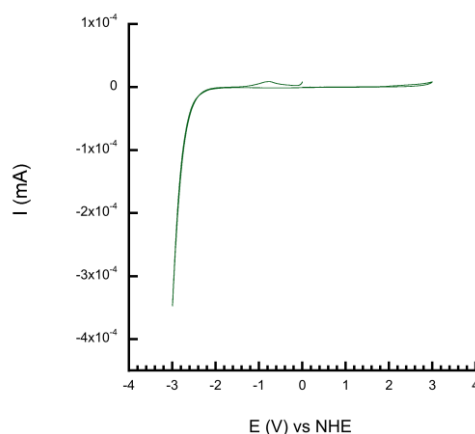
Figure S3. CV obtained at $v = 0.1$ Vs^{-1} with a Pt working electrode for 0.10 M Bu$_4$PF$_6$ in acetonitrile (without IL) as supporting electrolyte; The oxidation peak observed around -1 V is not seen if we only scan from 0V positive towards oxidation side. Therefore, it must be related to the reduction products formed during the reverse cycle.

Refernces

1. V. V. Pavlishchuk and A. W. Addison, *Inorganica Chimica Acta*, 2000, **298**, 97-102.

2. A. A. J. Torriero, A. I. Siriwardana, A. M. Bond, I. M. Burgar, N. F. Dunlop, G. B. Deacon and D. R. MacFarlane, *The Journal of Physical Chemistry B*, 2009, **113**, 11222–11231.

3. Pka of bases (amines and phosphines) are taken from (a) G. D. Fasman, *Handbook of biochemistry and molecular biology. CRC press cleveland*, 1976, pp. 305-351. (b) W. A. Henderson and C. A. Streuli, *J. Am. Chem. Soc.*, 1960, **82**, 5791-5794.b). Whereas, the pka values of acids are taken from evan's table (see http://www2.lsdiv.harvard.edu/labs/evans/.).

4. C. H. Cheon and H. Yamamoto, *Chemical Communications*, 2011, **47**, 3043-3056.