Electronic Supplementary information (ESI)

Liquids intermediate between "ionic" and "molecular" liquids - Liquid Ion Pairs?

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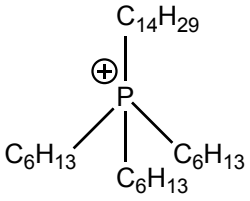
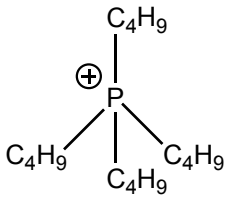
I. General

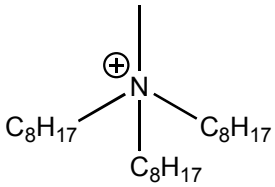
Fig S1: Structures of cations and anions investigated.



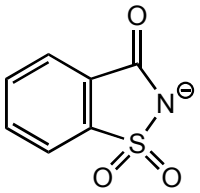
$[P_{6,6,6,14}]^+$



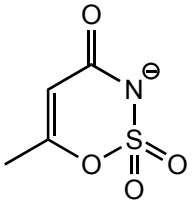
$[P_{4,4,4,4}]^+$



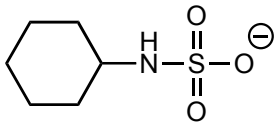
$[N_{1,8,8,8}]^+$



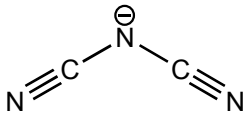
[Sacc]$^-$



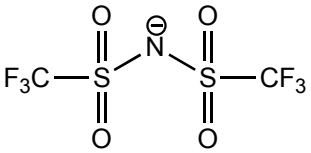
[Ace]$^-$



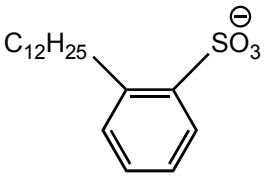
[Cyc]$^-$



[dca]$^-$



[NTf_2]$^-$



[dbsa]$^-$

Cl$^\ominus$

[Cl]$^-$

II. Experimental

Analysis

^{1}H, and ^{13}C NMR spectra were recorded on a Bruker DPX 300 at 300MHz spectrometer for solutions in $CDCl_3$. Positive and Negative ion electro spray mass spectra (ESMS) were recorded with a Micro mass Platform electro spray mass spectrometer for samples dissolved in methanol. Karl Fischer experiments were conducted on a 831 KF Coulometer which uses the coulometric titrator system. The titration solution used was Hydranal Coulomat AG. Ionode S10 ion selective electrodes $[Cl]^-$ were used to measure the chloride content. Calibration curves were measured using standard solutions of $[Nme_4][Cl]$ in 100ml methanol over the concentration range 1 ppm to 1000 ppm.

Thermal analysis: Pyrolysis GC-MS was carried out using a Varian CP-3800 gas chromatograph. Attached was a Varian Saturn 2200 CG/MS/MS unit. The capillary column used was a Varian factor four capillary column (VF-5ms 30M x 0.25mm ID DF=0.25). The pyrolysis probe used was a CDS pyroprobe 1000 series. 2 μL of sample (diluted into CH_3Cl_2) was injected and held in the probe for 30 seconds at 500 ^{o}C. The sample was loaded onto the capillary column at 0 ^{o}C and then subjected to the following temperature ramp: heat at 8 ^{o}C/min to 80 ^{o}C; 80 ^{o}C to 200 ^{o}C at 10 ^{o}C/min, 200 ^{o}C to 325 ^{o}C at 15 ^{o}C/min and finally held at 325 ^{o}C for 5mins.

Thermal analysis and temperature dependent phase behaviour was studied in the range of –150 °C to 200 °C by differential scanning calorimetry (T.A Q100 series) with samples between 5 -10mg. Thermal scans below room temperature were calibrated using the cyclohexane solid-solid transition and melting point at –87.0 °C and 6.5 °C respectively. Thermal scans above room temperature were calibrated using the indium melting point of 156.6 °C. Transition temperatures were recorded as the peak maximum of the thermal transition.

Thermogravimetric analysis was conducted using a Perkin-Elmer Pyris TGA 1 in a flowing dry nitrogen atmosphere (50 mL/min.) between 25 and 500 °C with a heating rate of 10 °C/min. The instrument was calibrated using the curie points of four reference materials, Alumel, perkin-alloy, iron and nickel. Platinum pans were used in all experiments with samples between 5 - 10 mg.

Transport properties: Density measurements were carried out using an Anton Paar DMA 5000 density meter. The density meter uses the 'oscillating U-tube principle" [1] to determine the density of the liquid. Viscosity measurements were carried out using an Anton Paar AMVn viscosity meter.

Conductance measurements were performed using a locally designed dip cell probe consisting of two platinum wires sheathed in glass. The cell constant was determined with a solution of 0.01 M KCl at 25 ºC. Conductivities were obtained by measurement of the complex impedance spectra between 1 MHz and 0.01 Hz on a Solartron SI 1296 Dielectric interface. The temperature was controlled at 10 ºC intervals (± 1 ºC) using a Eurotherm 2204e temperature controller interfaced to the Solatron and a cartridge heater set in a brass block with a cavity for the cell. A K-type thermocouple was set in the block adjacent to the cell. The conductance was determined from the first real axis touchdown point in the Nyquist plot of the impedance data.

Theoretical calculations: Standard *ab initio* molecular orbital theory and density functional theory (DFT) calculations were carried out using GAUSSIAN 03[2]. All ion pairs were optimised at the B3LYP/6-31+G(d)[3] level of theory. Binding energies (BE) were calculated using the second order Møller-Plesset perturbation theory (MP2) and a 6-311+G(2df,p) basis set. BE is defined as the difference of the total energies of the ion pair and the corresponding ions. The binding energies were corrected for the zero-point vibrational energies computed using scaled B3LYP/6-31+G(d) frequencies[4].

III. Synthesis

Tetradecyl(trihexyl)-phosphonium saccharinate [$P_{6,6,6,14}$][Sacc]

To a solution of tetradecyl(trihexyl)phosphonium chloride (7.78 g, 15 mmol) in 50 mL anhydrous acetone was added solid sodium saccharinate (3.07 g, 15 mmol) suspension stirred at 25 ^{o}C for 6 hrs. Precipitated sodium chloride was removed by filtration and solvent removed in vacuo, yielding a yellowish viscous liquid . The ionic liquid was decolorized by redissolution in 30 mL of acetone followed by treatment with activated charcoal (Darco-G60, Aldrich) at 40 ^{o}C overnight. Carbon was removed by flitration through alumina (acidic, Brockmann I, Aldrich) and solvent removed in vacuo to yield Tetradecyl(trihexyl)phosphonium saccharinate [$P_{6,6,6,14}$][Sacc] as a colourless liquid (9.2 g, 92%). ^{1}H NMR δ_{H} (300 MHz; $CDCl_3$) 7.84-7.94 (4H, m, CH_2), 2.0-2.3 (8H, m, CH_2), 1.4-1.5 (16H, m, CH_2), 1.2-1.3 (32H, m, CH_2), 0.79-0.85 (12H, m, CH_3) ppm.^{13}C NMR δ_c(300 MHz; $CDCl_3$): 131.6, 131.0, 123.3, 119.7, 32.0, 31.21, 31.19, 30.9 30.79, 30.65, 30.46, 29.8, 29.6, 29.5, 29.0, 22.46, 21.9, 19.5, 18.9, 14.2, 14.0, ppm.

ES-MS: ES^+ m/z 483 $[P_{6,6,6,14}]^+$. ES^- m/z 181 $[Sacc]^-$.

Water content (Karl-fischer): 230ppm

Cl content: < 100ppm

Tetradecyl(trihexyl)-phosphonium cyclamate [$P_{6,6,6,14}$][Cyc]

See previous. [$P_{6,6,6,14}$][Cl] (7.79g, 15 mmol) and sodium cyclamate (3.039 g, 15 mmol) afforded the title compound as a colourless liquid (9.0 g, 91%). ^{1}H NMR δ_{H}(300 MHz; $CDCl_3$) 3.6-3.8 (2H, m, CH_2), 3.2-3.4 (H, m CH), 2.2-2.3 (8H, m, CH_2), 2.1 (2H, m, CH_2), 1.6 (2H, m, CH_2), 1.4-1.5 (16H, m, CH_2), 1.2-1.3 (32H, m, CH_2), 0.79-0.85 (12H, m, CH_3) , ppm.

^{13}C NMR δ_c(300 MHz; $CDCl_3$): 193.6, 53.4, 31.9, 31.3, 31.1, 30.9, 30.8, 30.7, 30.5, 30.4, 29.6-29.7 29.5, 29.3, 29.0, 22.7, 22.5, 22.4, 22.0, ppm.

ES-MS: ES^+ m/z 483 $[P_{6,6,6,14}]^+$. ES^- m/z 178 $[Cyc]^-$.

Water content (Karl-Fischer): 170ppm

Cl content: < 100ppm

Tetrabutyl- phosphonium saccharinate [$P_{4,4,4,4}$][Sacc]

[$P_{4,4,4,4}$][Cl] was recrystalized from a solution of acetone / hexane before use. [$P_{4,4,4,4}$][Cl], 6.78 g, 23 mmol) and sodium saccharinate (4.720 g, 23 mmol) afforded the title compound as a colourless liquid (9.2g, 91%). ^{1}H NMR δ_H(300 MHz; $CDCl_3$) 7.84-7.94 (4H, m, CH_2), 2.1-2.2 (8H, m, CH_2), 1.36-1.41 (16H, m, CH_2), 0.8-0.85 (12H, m, CH_3) , ppm.

^{13}C NMR δ_c(300 MHz; $CDCl_3$): 143.3, 134.3, 130.8, 122.4, 120.5, 118.6, 22-23, 18.2, 17.5, 12.4, ppm.

ES-MS: ES^+ m/z 259 $[P_{4,4,4,4}]^+$. ES^- m/z 181 $[Sacc]^-$.

Water content (Karl-Fischer): 600ppm

Cl content: < 100ppm

Tetrabutyl- phosphonium acsesulfamate [$P_{4,4,4,4}$][Ace]

See previous. [$P_{4,4,4,4}$][Cl] (7.07g, 24 mmol) and potassium acesulfamate (4.833 g, 24 mmol) afforded the title compound as a white solid (9.3 g, 91%). ^{1}H NMR δ_H (300 MHz; $CDCl_3$) 5.5 (H, s, CH). 2.1-2.2 (8H, m, CH_2), 1.99 (3H, s, CH_3), 1.36-1.41 (16H, m, CH_2), 0.8-0.85 (12H, m, CH_3), ppm.

^{13}C NMR δ_c(300 MHz; $CDCl_3$): 168.7, 159.9, 100.7, 22-23, 18.8, 17.8, 17.2, 12.3, ppm.

ES-MS: ES^+ m/z 259 $[P_{4,4,4,4}]^+$ ES^- m/z 162 $[Ace]^-$.

Water content (Karl-Fischer): 374ppm

Cl content: < 100ppm

Tetrabutyl- phosphonium cyclamate [$P_{4,4,4,4}$][Cyc]

Same procedure as for [$P_{6,6,6,14}$][Sacc]. [$P_{4,4,4,4}$][Cl] (6.78 g, 23 mmol) and saodium cyclamate (4.60 g, 23 mmol) afforded the title compound as a colourless0. liquid (9.4 g, 93%).^{1}H NMR δ_H (300 MHz; $CDCl_3$) 3.25 (H, s, CH), 2.2-2.26 (2H, m, CH_2), 2.1-2.2 (8H, m, CH_2), 1.36-1.41 (20H, m, CH_2), 1.18 (5H, m, CH), 0.8-0.85 (12H, m, CH_3) , ppm.

^{13}C NMR δ_c(300 MHz; $CDCl_3$): 53.1, 52.9, 51.7, 49.6, 33.2, 29.6, 26.2, 24.7, 22-23, 18.0, 17.3, 12.4, ppm.

ES-MS: ES^+ m/z 259 $[P_{4,4,4,4}]^+$ ES^- m/z 178 $[Cyc]^-$.

Water content (Karl-Fischer): 293ppm

Cl content: < 100ppm.

Tetradecyl(trihexyl)-phosphonium chloride $[P_{6,6,6,14}][Cl]$

Purchased from Cytec Industries. The ionic liquid was decolorized by redissolution in 30 mL of acetone followed by treatment with activated charcoal (Darco-G60, Aldrich) at 40 ^oC overnight. Carbon was removed by flitration through alumina (acidic, Brockmann I, Aldrich) and solvent removed in vacuo at 60 ^oC for 24hrs at 0.1 Torr.

^1H NMR δ_H (300 MHz; $CDCl_3$) 2.0-2.3 (8H, m, CH_2), 1.4-1.5 (16H, m, CH_2), 1.2-1.3 (32H, m, CH_2), 0.79-0.85 (12H, m, CH_3) ppm.

ES-MS: ES^+ m/z 483 $[P_{6,6,6,14}]^+$ ES^- m/z 35.5 $[Cl]^-$.

Water content (Karl-Fischer): 189ppm.

Tetradecyl(trihexyl)-phosphonium bis(trifluoromethylsulfonyl)imide $[P_{6,6,6,14}][NTf_2]$

Purchased from Cytec Industries. Clean up as with $[P_{6,6,6,14}][Cl]$

^1H NMR δ_H (300 MHz; $CDCl_3$) 2.0-2.3 (8H, m, CH_2), 1.4-1.5 (16H, m, CH_2), 1.2-1.3 (32H, m, CH_2), 0.79-0.85 (12H, m, CH_3) ppm.

ES-MS: ES^+ m/z 483 $[P_{6,6,6,14}]^+$ ES^- m/z 279 $[NTf_2]^-$.

Water content (Karl-Fischer): 141ppm

Cl content: < 100ppm.

Tetradecyl(trihexyl)-phosphonium dodecylbenzenesulfonate $[P_{6,6,6,14}][dbsa]$

Purchased from Cytec Industries. Clean up as with $[P_{6,6,6,14}][Cl]$.

^1H NMR δ_H (300 MHz; $CDCl_3$) 7.8 (H, s, CH), 7.44 - 7.40 (2H, m, CH), 2.0-2.3 (7H, m, CH_2), 1.4 -1.8 (24H, m, CH_2), 1.16-1.3 (48, m, CH_2), 0.69-0.87 (15H, m, CH_3) ppm.

ES-MS: ES^+ m/z 483 $[P_{6,6,6,14}]^+$ ES^- m/z 325 $[dbsa]^-$.

Water content (Karl-Fischer): 172ppm

Cl content: < 100ppm.

Tetradecyl(trihexyl)-phosphonium dicyanamide [$P_{6,6,6,14}$][dca]

Purchased from Cytec Industries. Clean up as with [$P_{6,6,6,14}$][Cl]

^{1}H NMR δ_H(300 MHz; $CDCl_3$) 2.0-2.3 (8H, m, CH_2), 1.4-1.5 (16H, m, CH_2), 1.2-1.3 (32H, m, CH_2), 0.79-0.85 (12H, m, CH_3) ppm.

ES-MS: ES^+ m/z 483 $[P_{6,6,6,14}]^+$ ES^- m/z 66 $[dca]^-$.

Water content (Karl-Fischer): 186ppm

Cl content: < 100ppm.

IV. Thermal behaviour

Table S1: Phase transitions and decomposition temperatures for the salts.

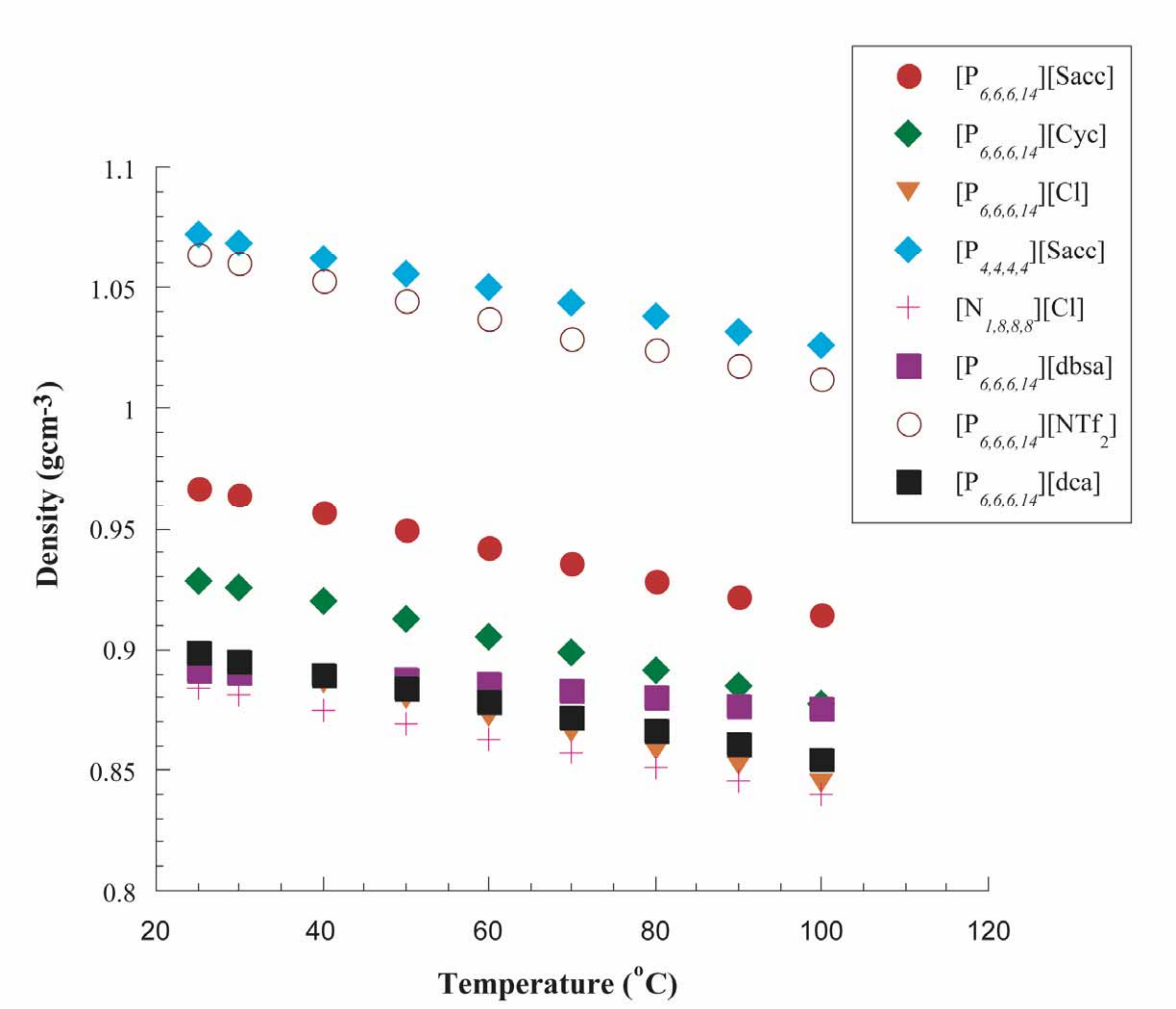
IL	**T_g / °C**	**T_{dec} / °C**
$[P_{6,6,6,14}]$[Sacc]	-56	197
$[P_{6,6,6,14}]$[Cyc]	-53	194
$[P_{6,6,6,14}][NTf_2]$*	-76	400
$[P_{6,6,6,14}]$[dca]*	-67	395
$[P_{6,6,6,14}]$[dbsa]	-70	--
$[P_{4,4,4,4}]$[Sacc]	-34	300
$[P_{4,4,4,4}]$[Ace]	-47 (Tg)	280
	5 (crystallisation)	
	42 (melt, ΔS_f = 43(10) $JK^{-1}mol^{-1}$)	
$[P_{4,4,4,4}]$[Cyc]	-32	280
$[N_{1,8,8,8}]$[Cl]	--	202

T_g = Glass transition (onset), T_{dec} = decomposition temperature measured by the step tangent method

* Taken from Del Sesto *et al*.[5]

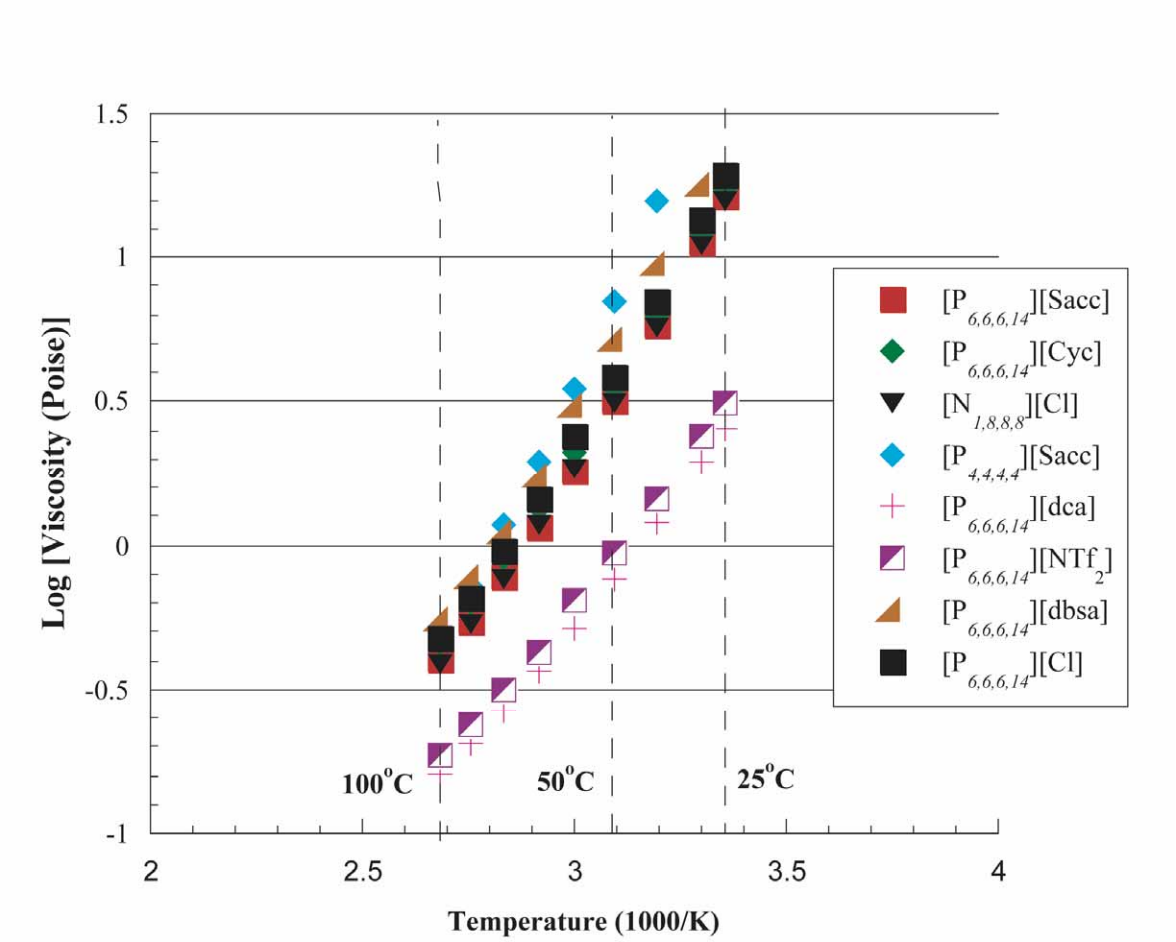
V. Density

Fig S2: Density of phosphonium salts and $[N_{1,8,8,8}][Cl]$ ranging from 25 – 100 ^{o}C



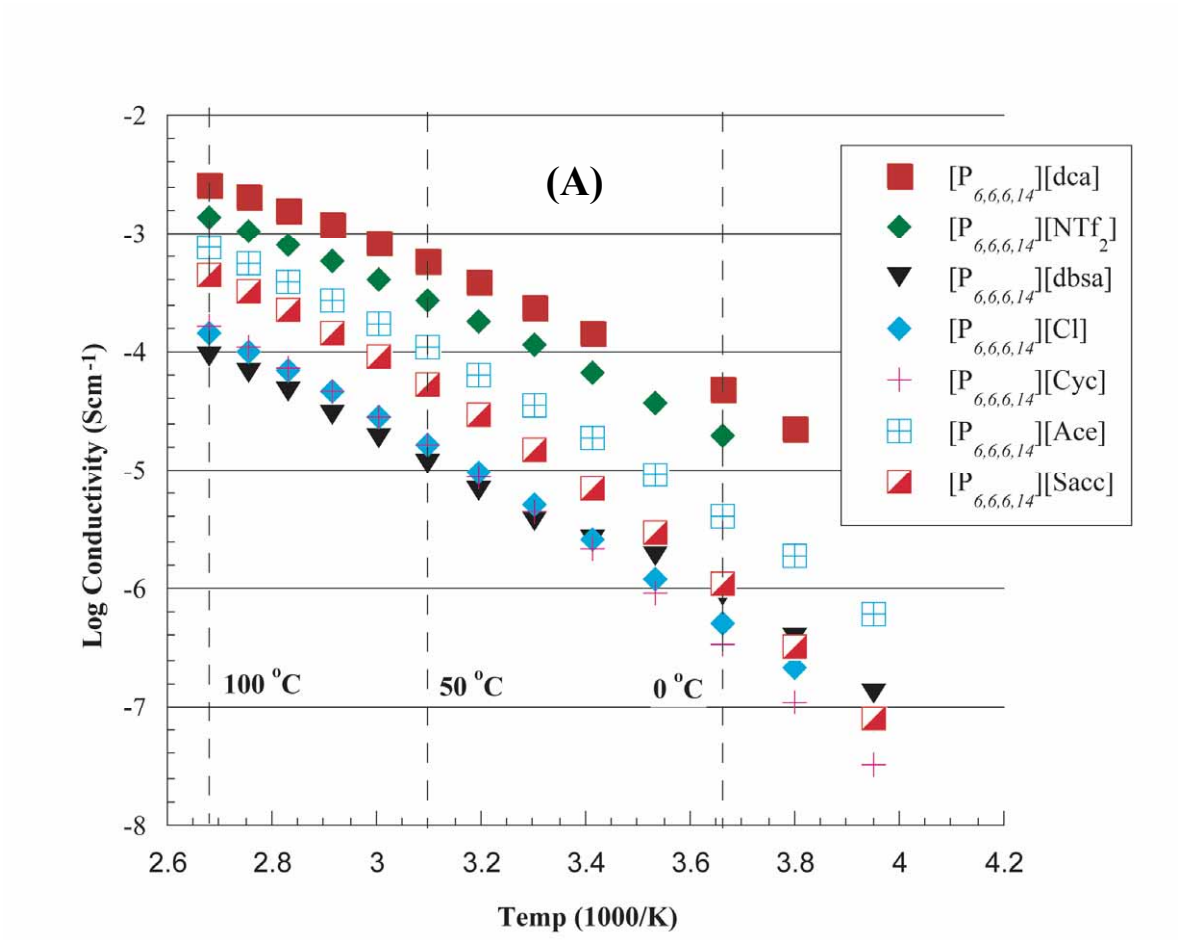
VI. Viscosity

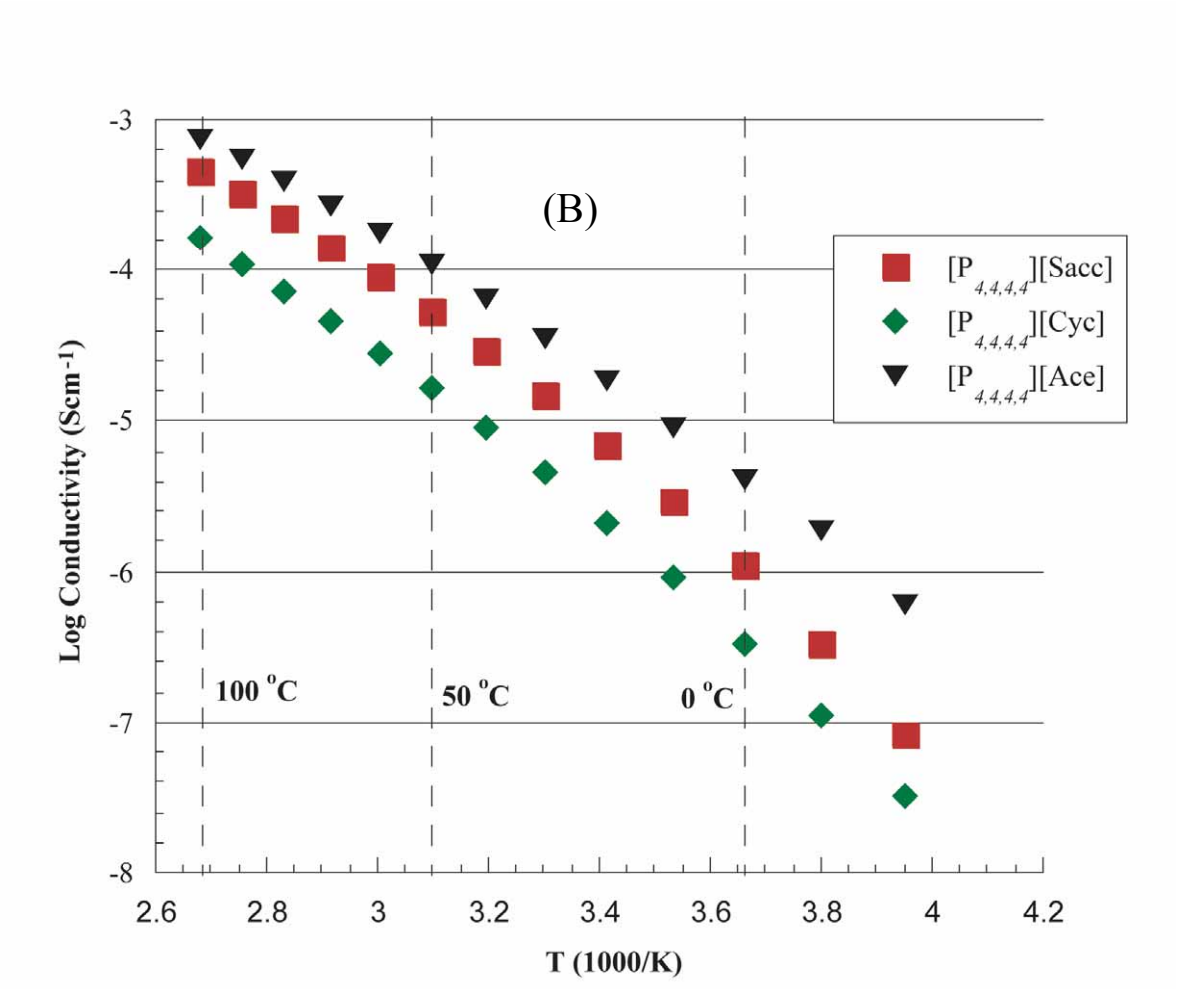
Fig S3: Viscosity Vs Temp over the range 25 – 100 ^{o}C for phosphonium based ILs.



VII. Conductivity

Fig S4: Conductivity in the temp range –20 – 100 °C for A: $[P_{6,6,6,14}]^+$ family and B: $[P_{4,4,4,4}]^+$ family




(B)
Log Conductivity (Scm-1)
T (1000/K)
100 °C
50 °C
0 °C
[P4,4,4,4][Sacc]
[P4,4,4,4][Cyc]
[P4,4,4,4][Ace]
-3
-4
-5
-6
-7
-8
2.6
2.8
3
3.2
3.4
3.6
3.8
4
4.2

VII. Theoretical calculations.

Table S2. B3-LYP/6-31+G(d) optimised geometries in the form of Gaussian archive entries for all ionic liquid ion pairs and the corresponding ions used to calculate interaction energies.

$[(n\text{-}C_4H_9)_4P^+][\ C_6H_{12}SO_3N^-]$ ($[P_{4,4,4,4}][Cyc]$)

1\1\GINC-AC16\FOpt\RB3LYP\6-31+G(d)\C22H48N1O3P1S1\EXI501\17-Nov-2006\
0\\#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt maxdisk=67108864
00\\opt\\0,1\C,0.4533502542,-0.6370959872,-1.6760749523\C,1.1392516097
,0.3566361873,-0.7232473614\C,2.6681750899,0.2856196131,-0.860639716\C
,3.3916186245,1.2298325659,0.1061315234\P,-1.3783201869,-0.6157785016,
-1.7069667946\C,-2.1264061727,-0.4946772316,-0.0377173275\C,-2.1645147
363,0.8970295341,0.6172962739\C,-2.8018798882,0.8339843434,2.014943305
2\C,-2.8513468615,2.200830993,2.7069210984\C,-1.8963682702,0.818921141
,-2.7403136768\C,-3.4092113945,0.9609399719,-2.9832559936\C,-3.7493130
093,2.2163329737,-3.802205946\C,-5.2519206233,2.364664202,-4.066928863
6\C,-1.9864444621,-2.1697752374,-2.4596085975\C,-1.2533165467,-2.62295
09991,-3.7336810775\C,-1.8669755342,-3.9124883449,-4.3016591319\C,-1.1
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3,-3.5122682839\H,-3.94352389,1.0006775161,-2.0245674607\H,-1.14922021
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4\H,-1.2805171908,-1.8388450313,-4.5058715929\H,-0.2001112494,-2.80982
78331,-3.4937911659\H,-3.8194253913,0.4263800263,1.9301091024\H,-2.235
9928556,0.1242307204,2.6319523331\H,-1.8416825598,-4.685512453,-3.5231
220151\H,-2.9271871144,-3.7393108979,-4.5384603805\H,2.9887943344,-0.7
47953088,-0.6780959633\H,2.9549970115,0.5260316826,-1.8951750382\H,-3.
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1.5934931278,-5.3335874121,-5.9341036213\H,-1.161473273,-3.6686337336,
-6.3579649892\H,-0.0836494107,-4.6330077827,-5.3309762251\H,4.47921483
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,-4.6510438117\H,-5.6438611469,1.5066397707,-4.6273600382\H,-5.8161898
945,2.4358667351,-3.1285703745\O,0.8630846571,-3.7008621763,-0.7489763
659\S,-0.0199276222,-3.6652569214,0.45327742\O,0.1499039748,-2.3952284
119,1.2407914916\O,-1.4587724739,-3.9392227052,0.1718115492\N,0.515579
6436,-4.9965528298,1.3724028641\H,1.5332776548,-4.9712516169,1.3789526
887\C,-0.0863998073,-5.1970839345,2.709128565\C,0.6161644225,-4.407867
5791,3.8372593132\C,2.012149821,-4.9658829513,4.1665080972\C,1.9656049
333,-6.4700570204,4.4833657477\C,1.2898387891,-7.2604144194,3.35017685
95\C,-0.1085713129,-6.7045562978,3.0349112961\H,-0.0117254994,-4.47109
6341,4.7395952269\H,0.6732062711,-3.3515527596,3.5544341995\H,2.443741
3956,-4.4108483759,5.0103307919\H,2.6935247746,-4.7950182044,3.3181473
176\H,2.9788286133,-6.8536413584,4.6660200838\H,1.3997223954,-6.623264
4594,5.415836144\H,1.2178368623,-8.3231674609,3.6181289785\H,1.9147423
499,-7.2150570189,2.4456020321\H,-0.7579965455,-6.8564400968,3.9108934
092\H,-0.5607814343,-7.243411957,2.1946268817\H,-1.1209333428,-4.85088
90643,2.6176702051\\Version=IA64L-G03RevD.01\State=1-A\HF=-1887.248235
2\RMSD=4.764e-09\RMSF=2.563e-06\Thermal=0.\Dipole=-1.3630457,3.3117949
,-1.7924827\PG=C01 [X(C22H48N1O3P1S1)]\\@

$[(n\text{-}C_4H_9)_4P^+][\ C_7H_4SO_3N^-]$ ($[P_{4,4,4,4}][Sacc]$)

1\1\GINC-AC6\FOpt\RB3LYP\6-31+G(d)\C23H40N1O3P1S1\EXI501\12-Jun-2007\0
\\#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt freq=noraman maxd
isk=5368709120\\opt\\0,1\C,-0.054130348,-0.1445492513,-0.0478493915\C,
-0.0368720297,-0.2211646569,1.4892152236\C,1.4021428862,-0.3193205412,
2.0222042764\C,1.4598741694,-0.4541829626,3.5477352401\P,-1.7039292945
,-0.0172891499,-0.8170550764\C,-2.5531942654,1.5152482444,-0.244723264
8\C,-1.8120794886,2.8358180915,-0.5174446686\C,-2.600019191,4.05521027
39,-0.0122661283\C,-1.8758304819,5.3805525873,-0.2745096911\C,-1.48965
4723,0.0366319647,-2.6295699317\C,-2.7687384409,-0.1291193331,-3.46929
39077\C,-2.4666317525,-0.0057136874,-4.9723822003\C,-3.7122163476,-0.2
139441201,-5.8405185754\C,-2.8057945374,-1.3849189632,-0.2830406287\C,
-2.302716816,-2.8203325329,-0.5187188547\C,-3.3269693717,-3.8576435708
,-0.0333581064\C,-2.8426056489,-5.2957667179,-0.2547597825\H,-3.762079
4733,-1.2226376178,-0.7988769107\H,-2.9990250057,-1.2142589716,0.78534
5974\H,-0.9941120876,0.9910784974,-2.8543069855\H,-0.7713003433,-0.766
0796198,-2.8513173432\H,0.4405666785,-1.0329443561,-0.4760574827\H,0.5
175387433,0.7256227067,-0.3991899325\H,-3.540375923,1.5269245712,-0.72
56711338\H,-2.7344754021,1.3978500559,0.8316004736\H,-0.5322709582,0.6
540640463,1.9356791707\H,-0.597652589,-1.1056460595,1.8206211324\H,-3.
2041455072,-1.1182949064,-3.2786192407\H,-3.527101016,0.6173669079,-3.
1874172323\H,-0.8268592537,2.8185487447,-0.0327446898\H,-1.6290517149,
2.9486052515,-1.5941747155\H,-2.0909714234,-2.9830192502,-1.5794586378
\H,-1.3496479183,-2.9695604308,0.0037075086\H,-3.5870950618,4.07298632
5,-0.4956753708\H,-2.7861830008,3.9441358759,1.0654567106\H,-3.5431766
638,-3.6970266181,1.0341024011\H,-4.2761774579,-3.7060024294,-0.568184
0272\H,1.8944379226,-1.1762456307,1.5469903283\H,1.9620235923,0.574162
3414,1.7100312772\H,-2.0375011566,0.9870856758,-5.1733882496\H,-1.7001
457376,-0.7419690167,-5.2438174955\H,-2.4614985369,6.2294217615,0.0960
246241\H,-0.8992292496,5.4062231948,0.2249334868\H,-1.7061384844,5.535
8426211,-1.347274476\H,-3.598495316,-6.0202068636,0.0712032374\H,-2.62
73860403,-5.476119622,-1.3138859386\H,-1.9230647133,-5.4933903437,0.31
03153531\H,2.4968077898,-0.515785785,3.8975543831\H,0.9906415452,0.404
1206897,4.0470045813\H,0.9425724402,-1.3611959522,3.8856971373\H,-3.46
74766936,-0.1150256825,-6.904168056\H,-4.1327027535,-1.2158404059,-5.6
906850588\H,-4.49528276,0.5204295531,-5.6074737579\N,0.2888092278,-2.6
487621174,-2.6710525242\S,-0.0677273767,-3.580275364,-3.9885948787\C,1
.2880318238,-3.18317465,-1.9289363694\C,1.8665358955,-4.4477884989,-2.
5262990603\C,1.2183123139,-4.8133468772,-3.7012898145\O,1.7006140813,-
2.7076098346,-0.8536076362\O,-1.4090158197,-4.1947796907,-3.8395169903
\O,0.1716268282,-2.8486598125,-5.2501128029\C,2.9152869027,-5.22449859
5,-2.0390115454\C,3.2902871952,-6.3643168154,-2.7605044326\C,2.6253733
314,-6.7181284853,-3.9436260922\C,1.5682931345,-5.9392308492,-4.433521
3988\H,1.0474917686,-6.2052181801,-5.3487503774\H,2.9334312751,-7.6068
907918,-4.488632619\H,4.1079563192,-6.9846159601,-2.4018401569\H,3.420
7031847,-4.9375387961,-1.1213835967\\Version=IA64L-G03RevD.01\State=1-
A\HF=-1920.5207602\RMSD=6.846e-09\RMSF=1.039e-06\Thermal=0.\Dipole=-1.
683269,2.9510936,2.6414955\PG=C01 [X(C23H40N1O3P1S1)]\\@

$[(n\text{-}C_4H_9)_4P^+][\ Cl^-]$ ($[P_{4,4,4,4}][Cl]$)

1\1\GINC-AC51\FOpt\RB3LYP\6-31+G(d)\C16H36Cl1P1\EXI501\10-Jun-2007\0\\
#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt freq=noraman maxdis
k=5368709120\\opt\\0,1\C,-0.0921967434,0.1949497952,-0.1544342428\P,-0
.262870752,0.1114667946,1.6799910046\C,1.3786815987,-0.0576924053,2.45
80725691\C,2.115150605,-1.3814059749,2.1956597776\C,3.4913631691,-1.39
68237253,2.881130085\C,4.241671857,-2.7176231413,2.6775804687\C,0.7403
475679,1.3696871382,-0.6968304319\C,0.8320294651,1.3544217607,-2.23114
82291\C,1.6572434472,2.51965122,-2.7888829269\C,-1.0489905472,1.631834

895,2.3111176812\C,-2.507198362,1.8635551733,1.8831283361\C,-3.0566724
514,3.1754056047,2.4672427926\C,-4.5221124968,3.4243155267,2.093856414
\C,-1.3113761585,-1.3681895546,1.9708638511\C,-1.6761079695,-1.7011845
129,3.4286418476\C,-2.5336077257,-2.9732569434,3.5080977934\C,-2.91996
87213,-3.328475301,4.9489387845\Cl,-0.0575200329,0.7161493526,5.449706
1816\H,1.1846013855,0.0993253827,3.5369417735\H,1.976462435,0.79856294
12,2.117098139\H,-2.2205712324,-1.2146216477,1.3727422065\H,-0.7784564
004,-2.2092624114,1.5056520596\H,0.3434627834,-0.7597272955,-0.4781547
673\H,-1.1083947801,0.2276846325,-0.5692479032\H,-0.9452338507,1.55292
67527,3.4106038245\H,-0.4100548337,2.468438189,1.9970666649\H,0.299379
4737,2.3216540358,-0.3727064373\H,1.7541347644,1.3363164212,-0.2762486
614\H,-0.7702295227,-1.8137460848,4.0330736984\H,-2.2056241994,-0.8593
596451,3.8871358488\H,-2.6015236878,1.889796025,0.7867486389\H,-3.1326
812592,1.0318725556,2.234133342\H,1.5190049539,-2.2181378597,2.5834831
616\H,2.2474056461,-1.5589537357,1.1173819213\H,-2.9477492024,3.149126
7834,3.5587992991\H,-2.4386916833,4.0135694933,2.1147531753\H,4.096732
7708,-0.5650927983,2.4931501372\H,3.3539209071,-1.2057720713,3.9528631
493\H,1.2728455707,0.4016558996,-2.5573952376\H,-0.1821634244,1.385769
1661,-2.654188661\H,-3.4451446846,-2.8424299372,2.9049522173\H,-1.9857
794427,-3.8146993763,3.0570276077\H,-4.8826246548,4.3665546868,2.52227
54379\H,-4.6553496526,3.4809274381,1.005348326\H,-5.1693369218,2.62116
85709,2.4685220658\H,5.2179195173,-2.6962834011,3.1754106265\H,3.67722
68718,-3.562671017,3.0917792734\H,4.4153355091,-2.9211326715,1.6125661
321\H,1.7043290422,2.4811963256,-3.8830887192\H,1.2212447333,3.4864717
138,-2.5078709265\H,2.6866537258,2.4954938263,-2.4100139926\H,-3.52906
17183,-4.2397715572,4.9807683715\H,-2.0298877536,-3.4927705902,5.56744
80863\H,-3.4952321942,-2.5195875241,5.4146148247\\Version=IA64L-G03Rev
D.01\State=1-A\HF=-1432.9970201\RMSD=2.417e-09\RMSF=1.400e-05\Thermal=
0.\Dipole=-0.233083,-0.7354895,-4.9781717\PG=C01 [X(C16H36Cl1P1)]\\@

$[(n\text{-}C_4H_9)_4P^+][C_6H_{13}\text{-}C_6H_5\text{-}SO_3^-]$ ($[P_{4,4,4,4}][dbsa]$)

1\1\GINC-AC54\FOpt\RB3LYP\6-31+G(d)\C28H53O3P1S1\EXI501\08-Aug-2007\0\
\#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt freq=noraman maxdi
sk=1342177280\\opt\\0,1\C,-0.0008809539,-0.0017804076,-0.0067215031\C,
-0.0032564126,-0.0105378483,1.3980677822\C,1.1878363519,-0.0110058141,
2.1227550367\C,2.4094599656,-0.0028093893,1.4435665661\C,2.4382291677,
0.0029568983,0.049520159\C,1.2365370247,0.0030504476,-0.6648447722\S,3
.9473191673,-0.0269085301,2.3890716275\O,3.9906294638,-1.3490624651,3.
0923510323\C,-1.2986855597,0.0412892712,-0.7854019592\C,-1.800438461,1
.4759446603,-1.0524336237\C,-3.1158126211,1.5183429969,-1.8414030791\C
,-3.6190286544,2.942338385,-2.1157546972\C,-4.9349719876,2.9891715301,
-2.9046620196\C,-5.4292203304,4.4155014545,-3.1747911306\O,5.054388959
2,0.1243623276,1.3891855659\O,3.8688801967,1.1203598133,3.3475087727\C
,6.1817444673,-1.043757894,5.4078504047\P,7.4557503417,-0.3334448754,4
.3030713837\C,7.0230243179,1.4088791916,3.9374243682\C,7.6849882903,2.
0423135343,2.7016628761\C,7.2829911087,3.5186989201,2.559479569\C,7.88
75149529,4.1761225251,1.3137448748\C,5.794159327,-0.1773822421,6.61826
75691\C,4.7407141743,-0.8768871247,7.4919131134\C,4.3058302473,-0.0259
241788,8.6902454227\C,9.0892015451,-0.3322429885,5.1549391535\C,9.5864
358049,-1.7004950471,5.6532866128\C,10.9785749818,-1.6116839544,6.2985
511131\C,11.4825110182,-2.9644622617,6.814242187\C,7.5260887451,-1.395
2722577,2.8103899858\C,8.7927502512,-1.3036525227,1.9417606732\C,8.696
4791402,-2.2358723667,0.723023635\C,9.9361569618,-2.1671033172,-0.1758
508499\H,1.1734474679,-0.0174038121,3.2086070641\H,6.5507879842,-2.027
1821555,5.7294324497\H,5.3080615185,-1.2199199941,4.7604008844\H,9.813
1389017,0.1067280872,4.4560679718\H,9.0056256427,0.3698684121,5.994867
8854\H,5.9294493387,1.4334086649,3.819376836\H,7.2701719732,1.97488669
73,4.8467253942\H,7.3770756239,-2.423726751,3.1654409027\H,6.631895298
6,-1.1290577287,2.2283023807\H,8.7815319927,1.9681504544,2.7534213202\
H,7.350972462,1.4991501256,1.8109133522\H,8.8775077386,-2.1091095441,6
.3853451462\H,9.6205063609,-2.4158473668,4.8206394939\H,8.9372096924,-
0.2748843481,1.5913790005\H,9.6867060639,-1.5670804584,2.5249931107\H,
6.6756362647,0.0573371052,7.2343808959\H,5.3830695749,0.7756896634,6.2

643423915\H,8.5483632476,-3.2689809488,1.068774877\H,7.8015762903,-1.9
729348633,0.1446218094\H,3.8686685032,-1.1138450989,6.8691182645\H,5.1
415761404,-1.8375057959,7.8473557714\H,6.1882478278,3.5803244948,2.516
3500433\H,7.5954706683,4.0724311171,3.4574243919\H,11.6915507721,-1.20
81531784,5.5656060816\H,10.947160706,-0.8901330012,7.1273200416\H,9.83
8597257,-2.8419374247,-1.0340744558\H,10.0875092938,-1.1528912122,-0.5
667208248\H,10.844408724,-2.4533242904,0.3708026291\H,3.5551534078,-0.
5492659092,9.2938381552\H,5.1555134104,0.2082590098,9.3452532397\H,3.8
652014884,0.9232315507,8.3609964191\H,7.5837310594,5.2266051216,1.2354
3312\H,8.9851586749,4.1476437897,1.3371615194\H,7.5576442468,3.6652847
027,0.400830818\H,12.4758230945,-2.8687896277,7.2672454881\H,10.807800
8828,-3.3767987936,7.5749555748\H,11.5563446468,-3.6977748188,6.001358
8004\H,3.3955855791,0.0076179154,-0.4615803587\H,1.263812915,0.0033602
326,-1.753363054\H,-0.9525823324,-0.0209824565,1.9310943212\H,-2.07516
24274,-0.5110976871,-0.2381679886\H,-1.1680356442,-0.4744364081,-1.746
7898781\H,-1.9283227021,1.9957565442,-0.0921753965\H,-1.0238632571,2.0
305841172,-1.5983055174\H,-2.982949077,0.990221908,-2.7982573244\H,-3.
8886004309,0.960398827,-1.2904295074\H,-3.7516592207,3.4713033486,-1.1
595471681\H,-2.846827545,3.5002904285,-2.6672289118\H,-4.8028614667,2.
4610637591,-3.8604750908\H,-5.7074506365,2.4330800252,-2.3533605158\H,
-6.369710127,4.4140304169,-3.7392623621\H,-5.6042316948,4.9586712958,-
2.2370278699\H,-4.693122888,4.9868491869,-3.755126003\\Version=IA64L-G
03RevD.01\State=1-A\HF=-2064.1651768\RMSD=9.618e-09\RMSF=2.323e-05\The
rmal=0.\Dipole=3.3877581,-0.4188397,1.6968183\PG=C01 [X(C28H53O3P1S1)]
\\@

$[(n\text{-}C_4H_9)_4P^+][(CN)_2N^-]$ ($[P_{4,4,4,4}][dca]$)

1\1\GINC-AC47\FOpt\RB3LYP\6-31+G(d)\C18H36N3P1\EXI501\23-May-2007\0\\#
P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt maxdisk=5368709120\\
opt\\0,1\C,-0.0490704085,-0.2089239795,0.0163916742\C,-0.0721518344,-0
.1686116052,1.554597711\C,1.3486458664,-0.2539764753,2.13689064\C,1.36
36463359,-0.2174440782,3.6690064375\P,-1.682989264,-0.1258860278,-0.79
62257296\C,-2.543844433,1.4252359529,-0.3195536231\C,-1.8419249498,2.7
219171144,-0.7684421109\C,-2.5924986613,3.9716724974,-0.2829350791\C,-
1.9173374615,5.2738780985,-0.7289779932\C,-1.4785694401,-0.1947249562,
-2.6099303605\C,-2.7813270282,-0.1297503139,-3.426485045\C,-2.49606889
54,-0.1764736146,-4.936937769\C,-3.7729624705,-0.1172799071,-5.7825591
382\C,-2.7365286413,-1.5201190743,-0.229355022\C,-2.1426437238,-2.9217
409155,-0.4710303232\C,-3.105934117,-4.0322307535,-0.0241497252\C,-2.5
287245454,-5.435513032,-0.2433965101\H,-3.7026480237,-1.4180497505,-0.
7412015867\H,-2.9340820274,-1.3629033272,0.8393108787\H,-0.8033740454,
0.6320962206,-2.8674165241\H,-0.920160907,-1.1171185913,-2.8179938167\
H,0.4228954535,-1.128966117,-0.3530160571\H,0.5380278615,0.6214236816,
-0.3975945611\H,-3.5589836853,1.3721587757,-0.734886709\H,-2.654748788
,1.4055692511,0.7727547755\H,-0.5463842117,0.7580004962,1.9075754052\H
,-0.6709651982,-1.0003542083,1.952035429\H,-3.4417809963,-0.9678854855
,-3.1630579462\H,-3.334497791,0.7919273547,-3.1964530511\H,-0.81047309
03,2.7443263251,-0.3974060656\H,-1.761371039,2.7451861132,-1.861804703
5\H,-1.8959276149,-3.0528211305,-1.5313185097\H,-1.1926109402,-3.02388
89456,0.0670729273\H,-3.6262525771,3.9452779702,-0.6579306216\H,-2.662
4469271,3.9505131966,0.8145245367\H,-3.3508643212,-3.896468595,1.03959
71906\H,-4.0538798804,-3.9342484743,-0.5732670046\H,1.8265886444,-1.17
68899695,1.7824939074\H,1.9492240277,0.5749143095,1.7394515775\H,-1.83
50838514,0.6590587576,-5.2030156188\H,-1.9393137146,-1.0942209561,-5.1
682495491\H,-2.4702431075,6.1478921499,-0.3658181098\H,-0.8920017051,5
.340443942,-0.3460295282\H,-1.865081517,5.3393754766,-1.8224527069\H,-
3.2374998179,-6.2069620174,0.0790848125\H,-2.299432268,-5.609305738,-1
.3015038993\H,-1.5994254885,-5.5751520422,0.3219878516\H,2.3881902423,
-0.2799969621,4.0528243413\H,0.9220662801,0.7120402911,4.0511531456\H,
0.7977973343,-1.0563038769,4.0946140389\H,-3.537040172,-0.1520248068,-
6.8521744479\H,-4.4383166265,-0.9619744577,-5.5616900755\H,-4.33361268
43,0.8078818065,-5.59606529\N,2.4278378177,-0.446179733,-2.9716420719\
C,1.7353539608,-1.5181894794,-2.669070923\C,1.8912139183,0.7201010756,

-2.7032233984\N,1.420081009,1.7732723385,-2.4499203175\N,1.1293153788,
-2.4917299521,-2.3859588198\\Version=IA64L-G03RevD.01\State=1-A\HF=-12
13.2208217\RMSD=3.635e-09\RMSF=2.650e-04\Thermal=0.\Dipole=-4.303665,0
.3391266,2.3411607\PG=C01 [X(C18H36N3P1)]\\@

$[(n\text{-}C_4H_9)_4P^+][(CF_3SO_2)_2N^-]$ ($[P_{4,4,4,4}][NTf_2]$)

1\1\GINC-AC51\FOpt\RB3LYP\6-31+G(d)\C18H36F6N1O4P1S2\EXI501\08-Jun-200
7\0\\#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt maxdisk=536870
9120\\opt\\0,1\C,-0.0003305918,0.0042023341,-0.0002215796\C,-0.0000224
106,0.0021782971,1.5390172989\C,1.4341433321,0.0041971912,2.0947672506
\C,1.4739814842,0.0312713581,3.6265272079\P,-1.6505824172,-0.056225488
8,-0.7786295197\C,-1.5149683046,0.0887525765,-2.5938695682\C,-2.851399
6505,0.066464383,-3.3575000134\C,-2.6273022781,0.1926736261,-4.8739428
897\C,-3.9368999887,0.1601100228,-5.6692720166\C,-2.4896056868,-1.6315
553762,-0.344642223\C,-1.7266744314,-2.9048373492,-0.7602215017\C,-2.5
239091622,-4.1783531033,-0.4369562598\C,-1.7723064167,-5.4569340003,-0
.825031979\C,-2.6934445491,1.306704398,-0.1226126056\C,-2.1573415851,2
.7219870162,-0.4112412423\C,-3.0573426614,3.8113181687,0.1932351186\C,
-2.5425988463,5.2270006956,-0.0911890614\N,1.7306623716,-0.0675973138,
-2.7444643043\S,2.0519192214,-1.4333283199,-3.5563019309\O,0.766631744
3,-2.152012109,-3.6512919971\S,2.6640131586,1.2583435828,-2.6757905186
\O,4.1021297513,1.0729074515,-2.8626268391\C,2.1009710355,2.2833508603
,-4.1625090211\F,2.3491590603,1.6577587495,-5.3162387191\O,2.164230299
6,2.0430157151,-1.532267163\F,0.7706673946,2.5249983889,-4.0900842143\
F,2.7378534542,3.4630633123,-4.1598601053\C,3.022570667,-2.4800038132,
-2.3151836155\F,2.3081026904,-2.640207303,-1.1750239732\O,2.9187882797
,-1.332812757,-4.7290350179\F,3.2514883461,-3.6948196885,-2.8341995943
\F,4.1901666999,-1.9146927505,-1.9991159352\H,-3.4808297652,-1.6055025
051,-0.8159599696\H,-2.6600583148,-1.6210500673,0.739899363\H,-0.96237
81947,1.0137424687,-2.7927267309\H,-0.8545243575,-0.7199897214,-2.9290
410672\H,0.55894999,-0.8495336898,-0.3968274121\H,0.5174766818,0.88598
7282,-0.3971501923\H,-3.6974283096,1.1813090856,-0.5483041661\H,-2.790
7336547,1.1457769732,0.9588157066\H,-0.5305346185,0.8855417944,1.92103
24682\H,-0.533699071,-0.8774729313,1.9272721918\H,-3.3900510899,-0.869
9484895,-3.1557042784\H,-3.5049886119,0.8845570896,-3.0222482657\H,-1.
1403140961,2.8279996046,-0.0126958256\H,-2.0798051628,2.8772684563,-1.
4950024212\H,-1.4965824818,-2.8791193487,-1.8323019178\H,-0.7593787329
,-2.9428359801,-0.2436519799\H,-4.0764844133,3.7022062953,-0.204831625
3\H,-3.1318809414,3.6575510077,1.2793652041\H,-2.7581778158,-4.1991554
506,0.6374146864\H,-3.4890063881,-4.1445628489,-0.9629247199\H,1.96303
5525,-0.8846418757,1.725634516\H,1.9733418856,0.8704861943,1.690576330
7\H,-2.0907255579,1.128322143,-5.0810837406\H,-1.9678190774,-0.6191597
194,-5.2063933256\H,-3.2014403436,5.9812373411,0.3537163417\H,-1.53726
89917,5.374920433,0.321465501\H,-2.490900123,5.4222371888,-1.169321842
7\H,-2.3659120304,-6.3477994788,-0.5902081371\H,-1.54766734,-5.4751519
614,-1.8980949594\H,-0.8203233533,-5.5370679657,-0.2862568358\H,2.5072
706613,0.029106778,3.9912078197\H,0.9842731876,0.9300057333,4.02329821
86\H,0.9679838805,-0.8429819785,4.0565356138\H,-3.7445576576,0.2533703
781,-6.7439776781\H,-4.4777349509,-0.7816359148,-5.5098031675\H,-4.603
5655612,0.982420191,-5.3783076595\\Version=IA64L-G03RevD.01\State=1-A\
HF=-2799.9816008\RMSD=3.086e-09\RMSF=1.007e-06\Thermal=0.\Dipole=-5.52
37915,0.0689009,3.2174794\PG=C01 [X(C18H36F6N1O4P1S2)]\\@

$C_7H_4SO_3N^-$ $[Sacc]^-$

1\1\GINC-AC2\FOpt\RB3LYP\6-31+G(d)\C7H4N1O3S1(1-)\EXI501\11-Jun-2007\0
\\#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt freq=noraman maxd
isk=2684354560\\opt\\-1,1\C,0.0666432013,0.0015216274,-0.0959711638\C,
0.021886292,-0.0372730524,1.2904812471\C,1.1674896874,-0.0475719493,2.
0758683847\C,2.4039642537,-0.016857046,1.4160715239\C,2.4658612654,0.0

225218476,0.0144511476\C,1.2947389837,0.0319941173,-0.7540024343\H,1.1
070914272,-0.0782465797,3.1606587625\H,3.324772643,-0.0236474301,1.996
3152153\H,3.4366336781,0.0458503124,-0.4773941114\H,1.3210516032,0.062
2320166,-1.8400942741\C,-1.3273839731,0.0044203182,-0.7149222953\N,-2.
3217960924,-0.0312198216,0.2080436042\S,-1.734246241,-0.0682722657,1.7
405040921\O,-1.4703758823,0.0371646146,-1.9470926641\O,-2.0593670623,1
.1614221039,2.5026851521\O,-2.0325364849,-1.3458529569,2.4317048139\\V
ersion=IA64L-G03RevD.01\State=1-A\HF=-947.8066356\RMSD=6.695e-09\RMSF=
2.509e-05\Thermal=0.\Dipole=3.4704724,0.0232619,0.4589096\PG=C01 [X(C7
H4N1O3S1)]\\@

$C_6H_{12}SO_3N^-$ [Cyc]$^-$

1\1\GINC-AC6\FOpt\RB3LYP\6-31+G(d)\C6H12N1O3S1(1-)\EXI501\15-Nov-2006\
0\\#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt freq=noraman max
disk=6710886400\\opt\\-1,1\C,-0.018899022,-0.1928520528,0.0939041376\C
,0.1704213505,-0.4005916958,1.6070694923\C,1.6340799461,-0.1962440159,
2.0350334802\C,2.165084678,1.1722845395,1.574248918\C,1.984095401,1.36
14233598,0.0592468781\C,0.5167513834,1.1776885694,-0.3878144669\H,0.52
53886544,-0.9885794797,-0.44177788\H,-1.074822804,-0.2689696517,-0.184
2344428\H,-0.1734886741,-1.4048350711,1.8945586432\H,-0.4688099531,0.3
045803975,2.1604217031\H,1.7342638014,-0.2995250439,3.1260156517\H,2.2
535392547,-0.9905952564,1.5866308949\H,3.2253564086,1.2797667929,1.847
5481044\H,1.6264405224,1.9722233068,2.1037342389\H,2.6084278443,0.6205
829225,-0.4677048182\H,2.322787325,2.3576126476,-0.2481536958\H,0.4907
365302,1.2003708734,-1.4825188358\N,-0.2813900878,2.336446169,0.045206
1078\S,-1.6706304571,2.7347041595,-0.9507276118\H,-0.6422155295,2.2345
078353,0.9927105572\O,-2.287045978,3.8412014581,-0.1729251794\O,-1.061
5958395,3.1123120589,-2.2530697774\O,-2.5204460498,1.5048584526,-1.027
5429351\\Version=IA64L-G03RevD.01\State=1-A\HF=-914.5264643\RMSD=4.888
e-09\RMSF=3.419e-05\Thermal=0.\Dipole=2.8913056,-2.4554524,2.0992025\P
G=C01 [X(C6H12N1O3S1)]\\@

C_6H_{13}-C_6H_5-SO_3^- [dbsa]$^-$

1\1\GINC-AC28\FOpt\RB3LYP\6-31+G(d)\C12H17O3S1(1-)\EXI501\22-Aug-2007\
0\\#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt freq=noraman max
disk=1342177280\\opt\\-1,1\C,0.0037836063,-0.0093723439,-0.008816951\C
,-0.0026841235,-0.0020274308,1.3925041629\C,1.2356106724,0.0024565842,
2.0565371928\C,2.4361066885,0.0045915298,1.3454807319\C,2.4251744592,0
.0012505227,-0.0535282205\C,1.2041434142,-0.0072297553,-0.7283779542\C
,-1.3030774571,0.0408854329,2.1689697746\C,-1.7796002677,1.4722348907,
2.4909935984\C,-3.0955385881,1.5127275875,3.2796074986\C,-3.5768142725
,2.9344419092,3.6013957382\C,-4.8926253375,2.9780796156,4.3907277766\C
,-5.3652771883,4.4025854511,4.70701037\S,4.0060638105,-0.0112191226,-0
.9739802967\O,4.7229558225,1.1990726267,-0.4757152238\O,4.6462363669,-
1.299109133,-0.5755043516\O,3.5991046663,0.0576328449,-2.407612045\H,3
.3882561634,0.0060510362,1.868672507\H,1.2120694947,-0.0144976967,-1.8
142848374\H,-0.9440469429,-0.0214639371,-0.5477965691\H,1.257276503,-0
.0006114026,3.1466679499\H,-1.1898595092,-0.5135959986,3.1122876071\H,
-2.0906729751,-0.4735152642,1.5990880316\H,-0.9931445408,1.991328577,3
.0572500794\H,-1.8946977017,2.0293629371,1.5502509967\H,-3.8774935497,
0.9865330493,2.7097037488\H,-2.974076402,0.9506492749,4.2189861324\H,-
2.7960398644,3.4615224775,4.1709774024\H,-3.6993398725,3.4969808256,2.
663112345\H,-5.6737194808,2.4523366756,3.8215955998\H,-4.7703966718,2.
4173189882,5.3293627557\H,-6.3067328922,4.3991554843,5.2710378209\H,-4
.6199808533,4.9432482132,5.3050215293\H,-5.5296601539,4.9784785533,3.7
86833432\\Version=IA64L-G03RevD.01\State=1-A\HF=-1091.4439511\RMSD=3.8
48e-09\RMSF=1.310e-05\Thermal=0.\Dipole=-7.0961826,1.5750408,4.2154714
\PG=C01 [X(C12H17O3S1)]\\@

$(CN)_2N^-$ [dca]$^-$

1\1\GINC-AC14\FOpt\RB3LYP\6-31+G(d)\C2N3(1-)\EXI501\22-Apr-2006\0\\#P
gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt freq=noraman maxdisk=2
68435456\\opt\\-1,1\N,0.2603274818,0.,0.1840793277\C,0.1075240642,0.,1
.4877246243\C,1.4384815819,0.,-0.3945335481\N,-0.1648302316,0.,2.63719
95432\N,2.4314321633,0.,-1.0344699471\\Version=IA64L-G03RevD.01\State=
1-A1\HF=-240.5141545\RMSD=3.081e-09\RMSF=1.180e-04\Thermal=0.\Dipole=-
0.3219748,0.,-0.2276706\PG=C02V [C2(N1),SGV(C2N2)]\\@

$(CF_3SO_2)_2N^-$ $[NTf_2]^-$

1\1\GINC-AC13\Freq\RB3LYP\6-31+G(d)\C2F6N1O4S2(1-)\EXI501\11-Sep-2006\
1\\#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) scf=tight freq=noram
an maxdisk=1342177280\\freq\\-1,1\C\F,1,fc2\F,1,fc3,2,fcf3\F,1,fc4,2,f
cf4,3,dih4,0\S,1,sc5,2,scf5,4,dih5,0\N,5,ns6,1,nsc6,2,dih6,0\S,6,sn7,5
,sns7,1,dih7,0\O,7,os8,6,osn8,5,dih8,0\O,5,os9,1,osc9,3,dih9,0\O,5,os1
0,1,osc10,3,dih10,0\O,7,os11,6,osn11,5,dih11,0\C,7,cs12,6,csn12,5,dih1
2,0\F,12,fc13,7,fcs13,6,dih13,0\F,12,fc14,7,fcs14,6,dih14,0\F,12,fc15,
7,fcs15,6,dih15,0\\fc2=1.343127\fc3=1.345942\fcf3=108.131\fc4=1.350893
\fcf4=107.984\dih4=-116.339\sc5=1.891746\scf5=111.695\dih5=-120.634\ns
6=1.618826\nsc6=102.59\dih6=-61.468\sn7=1.618616\sns7=125.166\dih7=93.
192\os8=1.46802\osn8=107.986\dih8=-158.604\os9=1.467998\osc9=102.985\d
ih9=-52.469\os10=1.468159\osc10=104.117\dih10=-177.582\os11=1.468159\o
sn11=117.343\dih11=-20.337\cs12=1.891736\csn12=102.619\dih12=93.05\fc1
3=1.350851\fcs13=109.643\dih13=178.88\fc14=1.343174\fcs14=111.696\dih1
4=-61.459\fc15=1.346023\fcs15=111.491\dih15=59.634\\Version=IA64L-G03R
evD.01\State=1-A\HF=-1827.2834748\RMSD=5.257e-09\RMSF=2.645e-05\ZeroPo
int=0.0521495\Thermal=0.066795\Dipole=-0.0988222,0.0415404,0.0672431
\Polar=88.3197745,1.1471676,109.2771419,1.1304714,-11.4903053,95.5044291
\PG=C01 [X(C2F6N1O4S2)]\\@

$(n\text{-}C_4H_9)_4P^+$ $[P_{4,4,4,4}]^+$

1\1\GINC-AC42\FOpt\RB3LYP\6-31+G(d)\C16H36P1(1+)\EXI501\15-Nov-2006\0\
\#P gfinput B3LYP/6-31+G(d) INT(grid=ultrafine) opt freq=noraman maxdi
sk=6710886400\\opt\\1,1\C,-0.0005856837,-0.0003289317,0.000485731\P,-0
.0000023703,-0.0000228127,1.8345428573\C,1.7475609234,0.0003109549,2.3
911296095\C,1.961896222,0.0003655598,3.917451296\C,3.4565383956,0.0007
915776,4.2815541031\C,-1.3900939041,-0.0004227974,-0.6664959311\C,-1.2
839317388,-0.0008150246,-2.2011801381\C,-0.8736967568,1.4807735961,2.4
730305719\C,-0.2861426286,2.8393572779,2.0433469247\C,-1.0868041069,4.
0154890392,2.6283098098\C,-0.8732878923,-1.4808466418,2.4735256197\C,-
0.285676544,-2.8394109812,2.0438588546\C,-1.0858163277,-4.0155694359,2
.6294814131\H,-0.8823271419,1.3937317558,3.5673202214\H,-1.918975763,1
.3935268063,2.1491461684\H,2.2232085896,-0.8779203591,1.9355095589\H,2
.2228331451,0.8787406561,1.9354994301\H,0.5777612732,0.8779283364,-0.3
146325144\H,0.5777207798,-0.8787327547,-0.3142991563\H,-0.8815358363,-
1.3936218876,3.5678039311\H,-1.918697158,-1.3938169812,2.1500046592\H,
-1.9616183367,-0.8815996804,-0.345829751\H,-1.9615156917,0.8809821183,
-0.3462756016\H,1.4830268426,0.8815146562,4.3648886348\H,1.4835355573,
-0.8810671466,4.3648726565\H,-0.2811025271,-2.9181872039,0.9485453206\
H,0.7596565207,-2.9179322823,2.3710485563\H,0.7590100206,2.9181547809,
2.3710438851\H,-0.2810340653,2.9178925126,0.9480177828\C,-0.5189251787
,-5.3776487753,2.214954361\H,-1.0935449667,-3.9364162071,3.7254406364\
H,-2.1327195548,-3.936660262,2.305106619\C,-0.5199593015,5.3775873132,
2.2137816404\H,-2.1335284293,3.9363145387,2.3034233799\H,-1.0950710869
,3.9365659155,3.7242818975\C,-2.6547999407,-0.0008982323,-2.8861463973
\H,-0.7098135626,0.8790165821,-2.5232618552\H,-0.7099247675,-0.8808789
641,-2.5228244948\C,3.693663295,0.0008358448,5.7955653882\H,3.93754315
32,-0.8790118831,3.8320740897\H,3.9370398188,0.880883655,3.832101174\H
,-1.1094466292,-6.1921396014,2.6471503335\H,-0.5310397118,-5.501225182
6,1.1251150248\H,0.5161499447,-5.5009745627,2.5563888648\H,-1.11085971
72,6.1920583792,2.6454966321\H,0.514915409,5.5011856569,2.5557252445\H
,-0.5315333349,5.5009253813,1.1239096042\H,-2.5448501646,-0.0011841652
,-3.9755568856\H,-3.2393006524,-0.8875171746,-2.6114955707\H,-3.239181

4957,0.8859401289,-2.6119501595\H,4.7651360196,0.001144086,6.021065623
5\H,3.2547118806,0.8874286503,6.2693186376\H,3.2552293498,-0.886028644
7,6.2692896977\\Version=IA64L-G03RevD.01\State=1-A\HF=-972.5939709\RMS
D=4.340e-09\RMSF=3.202e-05\Thermal=0.\Dipole=0.0000017,0.0000046,0.000
0024\PG=C01 [X(C16H36P1)]\\@

Table S3. MP2/6-311+G(2df,p) total electronic energies (E_{tot}, in Hartree) and B3-LYP/6-31+G(d) scaled zero-point vibrational energies (ZPVE, in Hartree) of the ions pairs and the corresponding ions used to calculate binding energies of the ion pairs.

Ionic species	E_{tot}	ZPVE
$(n\text{-}C_4H_9)_4P^+$	-970.500208	0.487302
$C_6H_{12}SO_3N^-$	-913.085914	0.186420
$C_7H_4SO_3N^-$	-946.340202	0.100793
Cl^-	-459.759138	0.0
$C_6H_{13}\text{-}C_6H_5\text{-}SO_3^-$	-1089.547004	0.267628
$(CN)_2N^-$	-240.0626223	0.020474
$(CF_3SO_2)_2N^-$	-1824.998197	0.051138
$[(n\text{-}C_4H_9)_4P^+][\ C_6H_{12}SO_3N^-]$	-1883.728723	0.675335
$[(n\text{-}C_4H_9)_4P^+][\ C_7H_4SO_3N^-]$	-1916.976481	0.589307
$[(n\text{-}C_4H_9)_4P^+][\ Cl^-]$	-1430.399051	0.486987
$[(n\text{-}C_4H_9)_4P^+][\ C_6H_{13}\text{-}C_6H_5\text{-}SO_3^-]$	-2060.188186	0.756369
$[(n\text{-}C_4H_9)_4P^+][(CN)_2N^-\ ]$	-1210.691977	0.508823
$[(n\text{-}C_4H_9)_4P^+][(CF_3SO_2)_2N^-]$	-2795.621855	0.539379

VIII. References

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