Preparation and Characterization of New Phosphonyl-Substituted Imidazolium Ionic Liquids

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A new series of diethoxyphosphinyl-substituted imidazolium 'room-temperature ionic liquids' (RTILs) were synthesized and characterized. The new compounds **1**–**12** (*Table 1*) were shown to have similar densities, but higher viscosities, than common ionic liquids. The new materials remain liquid over a broad temperature range, possess extremely low vapor pressures, display relatively high thermal stabilities (up to 325°), and decompose in a two-step process. Analysis of the solid/liquid phase transition showed that all of the new RTILs possess low glass-transition temperatures (T_g) associated with an intense change in molar heat capacity (ΔC_{pm}).

1. Introduction. – The so-called 'room-temperature ionic liquids' (RTILs) have attracted significant and growing interest, especially 1-alkyl-3-methylimidazolium cations [1], which display intrinsically useful properties such as good thermal stabilities, high ionic conductivities, negligible vapor pressures, and a wide electrochemical window. RTILs have found applications in synthesis, catalysis, and as components of batteries and fuel cells. They may also be used as embalming fluids [2] and lubricants [3], in ion drivers for space travel [4], and for the desulfurization of fuels [5].

Some RTILs can be used as 'designer solvents' [6] by making use of a judicious combination of cation and anion, and changes in ionic liquids. The physical properties, *e.g.*, hydrophobicity, viscosity, or melting point, can be readily tailored by altering the length of the alkyl chain attached to the organic cation. The design and synthesis of some task-specific RTILs has been extensively investigated [7]. For example, some new dense fluoroalkyl-substituted imidazolium-based ionic liquids [8] and a new series of imidazolium-based RTILs [9] containing ether and OH functions on alkyl side-chains have been successfully prepared. Such task-specific RTILs have been used for the extraction of metal ions from aqueous solutions [10], as promising tools in liquid-phase combinatorial chemistry [11], for chiral recognition [12], or as recyclable reaction media in catalyzed esterifications [13].

Here, we report the synthesis, characterization, and properties of a new series of imidazolium-based RTILs with a diethoxyphosphinyl functional group on the alkyl side chain.

2. Results and Discussion. – 2.1. *Synthesis.* The structures and abbreviated names of the new ionic liquids **1**–**12** are shown in *Table 1.* They were prepared by a previously reported methodology [1b], as shown in the *Scheme*. The alkylation of 1-alkylimidazoles **A** with diethyl bromoalkylphosphonates **B** was carried out at a moderate temperature (80°) in the absence of solvent for 24 h, and afforded the corresponding *N*-alkylated products **C** in good yields (typically above 90%). When the reaction was run for several days, the yield could not be further increased. Finally, the counter ion (Br^-) was exchanged by addition of a slight excess of $NaBF_4$, KPF_6, or NH_4PF_6. The volatile components were then removed by stirring the crude RTILs at 100° for 24 h *in vacuo*. All RTILs were thus obtained in medium-to-high yields. Thereby, the total yield was related to the length of the alkyl chain R: with decreasing chain length, the yield decreased. This observation was rationalized by the observation that ionic liquids bearing shorter alkyl chains are more readily water soluble and, thus, were partly lost during the subsequent aqueous washing step[1]. The new RTILs were stable in air, H_2O, and common organic solvents such as acetone, CH_2Cl_2, AcOEt, or EtOH.

Scheme

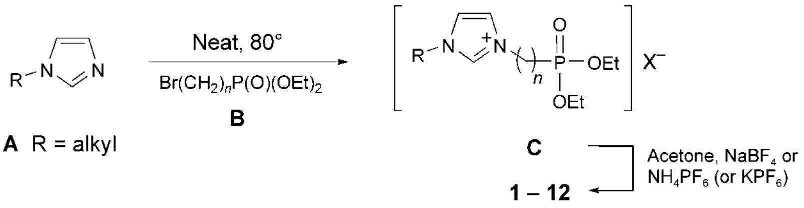
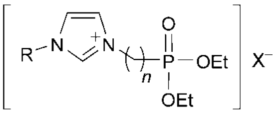


Table 1. *Structures of the New Ionic Liquids* **1**–**12**. The following conventions were used for abbreviated-name construction (from left to right): *DP*, diethoxyphosphinyl; *E* or *P* for ethyl or propyl (*n* = 2 or 3), resp.; *B*, *H*, or *O* for R = butyl, hexyl, or octyl, resp.; and *IM* for imidazolium.



1 – 12

Compound	Abbreviation	R	*n*	X
1	[DPEBIM][BF_4]	C_4H_9	2	BF_4
2	[DPEBIM][PF_6]	C_4H_9	2	PF_6
3	[DPPBIM][BF_4]	C_4H_9	3	BF_4
4	[DPPBIM][PF_6]	C_4H_9	3	PF_6
5	[DPEHIM][BF_4]	C_6H_{13}	2	BF_4
6	[DPEHIM][PF_6]	C_6H_{13}	2	PF_6
7	[DPPHIM][BF_4]	C_6H_{13}	3	BF_4
8	[DPPHIM][PF_6]	C_6H_{13}	3	PF_6
9	[DPEOIM][BF_4]	C_8H_{17}	2	BF_4
10	[DPEOIM][PF_6]	C_8H_{17}	2	PF_6
11	[DPPOIM][BF_4]	C_8H_{17}	3	BF_4
12	[DPPOIM][PF_6]	C_8H_{17}	3	PF_6

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[1] Indeed, ionic liquids bearing Me or Et side chains are fully miscible with H_2O.

2.2. *Density and Viscosity.* The densities of **1**–**12** at 25° are collected in *Table 2*. It can be seen that all compounds exhibited density values similar to those of the common ionic liquids [$C_n$mim][X] (*Table 2*, *Entries 13* and *14*). Generally, RTILs containing PF_6^- anions showed higher densities than those with BF_4^-, in agreement with literature data [1a]. As expected, longer alkyl chains R gave rise to a decrease in density (butyl > hexyl > octyl). In contrast, the length of the spacer ($n = 2$ or 3) between the P-atom and the imidazolium *N*-atom had little influence on the densities (*Entries 1–6 vs. 7–12*, resp.).

Table 2. *Density and Dynamic-Viscosity Data of Selected Ionic Liquids*

Entry	Compound	Density [kg m^{-3}] [a])	Viscosity [mm^2 s^{-1}] [b])
1	[DPEBIM][BF_4]	1214.1	160.2
2	[DPEHIM][BF_4]	1150.7	194.4
3	[DPEOIM][BF_4]	1121.4	388.8
4	[DPEBIM][PF_6]	1353.0	826.3
5	[DPEHIM][PF_6]	1277.8	644.5
6	[DPEOIM][PF_6]	1221.2	505.9
7	[DPPBIM][BF_4]	1208.9	540.1
8	[DPPHIM][BF_4]	1172.6	571.9
9	[DPPOIM][BF_4]	1142.4	447.3
10	[DPPBIM][PF_6]	1307.0	700.7
11	[DPPHIM][PF_6]	1265.0	759.7
12	[DPPOIM][PF_6]	1227.7	690.9
13	[C_8mim][BF_4] [c])	1080.0 [14]	129.0 [3d]
14	[C_8mim][PF_6] [c])	1190.0 [14]	232.2 [3d]

[a]) Measured at 25°. [b]) Measured at 40°. [c]) [C_8mim] = 1-octyl-3-methyl-1*H*-imidazolium.

The dynamic viscosities of **1**–**12** measured at 40° are given in *Table 2*. The new ionic liquids generally displayed higher viscosities than conventional RTILs. Compounds with BF_4^- anions (*Entries 1–3* and *7–9*) showed lower viscosities than those with PF_6^- anions (*Entries 4–6* and *10–12*), which is in agreement with related literature data [1b]. Also, the cation structure of a given RTIL strongly influences its viscosity, which is governed essentially by *Van der Waals* interactions and H-bonding ability. Lengthening of alkyl chains, thus, makes the RTILs more viscous due to increased *Van der Waals* interactions. Furthermore, attachment of the $(EtO)_2P(O)(CH_2)n$ group enhances the molecules' H-bonding capacity, which increases the viscosity.

2.3. *Thermal Stability.* Thermogravimetric-analysis (TGA)[2]) experiments were conducted to determine the thermal stabilities of the novel RTLIs. In the *Figure* shown below, the TGA curves of [DPPHIM][PF_6] (**8**) and [DPPOIM][PF_6] (**12**) indicate that these two ionic liquids are stable up to temperatures of *ca.* 300° (basically no weight loss). At 325°, both TGA curves showed inflections, indicating *ca.* 30.0 and 25.3% weight loss, respectively. These data suggest that, at 325°, loss of the $(EtO)_2P(O)$ groups takes place (calculated weight loss: 28.8 and 27.2%, resp.) by means of C–P bond cleavage. Further heating to 400° then leads to a gradual, nonspecific decomposition.

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[2]) Heating rate of 10°/min, under N_2 gas.

The other RTILs, *i.e.*, **1**–**7** and **9**–**11**, were stable up to *ca.* 300°, and decomposed rapidly below 400° at a constant rate. Thereby, the thermal stability generally increased with longer alkyl chains R.

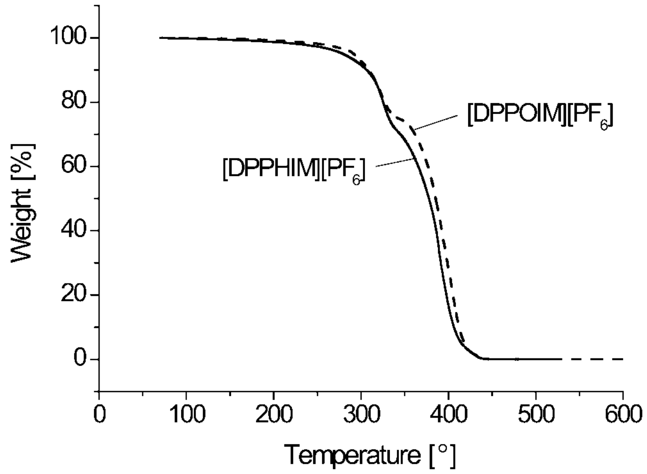

Figure. *Thermogravimetric analysis of the new ionic liquids [DPPHIM][PF$_6$]* (**8**) *and [DPPOIM][PF$_6$]* (**12**)

2.4. *Glass Transition and Change in Heat Capacity.* In general, low melting points, which can be achieved by creating low symmetry and good charge distribution with respect to the cation, are advantageous for ionic liquids. The phase-transition temperatures (midpoints of glass transitions) for **1**–**12** were determined by differential scanning calorimetry (DSC; *Table 3*). We observed substantial supercooling, since the glass-transition temperatures (T_g) of the samples were significantly lower than the melting points (m.p.). The relationship between the structure and chemical composition of an ionic liquid and its T_g value clearly illustrates that the cations strongly influence the phase transition. For example, for compounds with the PF_6^- anion and either propyl ($n=3$) or ethyl ($n=2$) spacers, T_g decreased from −58.7 to −67.3 to −96.1 and from −55.7 to −68.8 to −73.2°, respectively, upon varying the R group from butyl to hexyl to octyl. Interestingly, however, there was no obvious trend in T_g for compounds with BF_4^- anions (*Table 3*).

Another interesting feature of the new RTILs is that they showed a strong change in the molar[3]) heat capacity C_{pm} at the glass transition. In all cases, ΔC_{pm}, was higher than 190 J mol^{-1} K^{-1}. These high values indicate that many degrees of freedom are released at temperatures above T_g [9]. A very high ΔC_{pm} value at T_g appears to be a specific feature of ionic liquids. This can be rationalized by the fact that each molecular unit is in fact, composed of two subunits (the cation and the anion) that possess an appreciable relative mobility in the supercooled state [9].

3. Conclusions. – A new series of 'room-temperature ionic liquids' (RTLIs) have been synthesized and characterized. All compounds possess similar densities, but

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[3]) Subscript 'm' for *molar.*

Table 3. *Differential-Scanning-Calorimetry* (DSC) *Data for the New Ionic Liquids.* The melting points (m.p.) are given, together with the glass-transition temperatures (T_g) and the associated changes in (molar) heat capacity (ΔC_p or ΔC_{pm}).

Compound	M.p. [°]	T_g [°]	ΔC_p [J g^{-1} K^{-1}]	ΔC_{pm} [J mol^{-1} K^{-1}] [3]
[DPEBIM][BF_4]	– 80.5	– 84.9	0.753	283
[DPEHIM][BF_4]	– 82.6	– 83.3	0.650	263
[DPEOIM][BF_4]	– 79.8	– 84.8	1.211	523
[DPEBIM][PF_6]	– 50.2	– 55.7	0.483	210
[DPEHIM][PF_6]	– 62.3	– 68.8	0.680	314
[DPEOIM][PF_6]	– 64.2	– 73.2	0.485	238
[DPPBIM][BF_4]	– 64.3	– 67.2	0.623	243
[DPPHIM][BF_4]	– 75.5	– 78.1	0.892	373
[DPPOIM][BF_4]	– 64.5	– 71.7	0.433	193
[DPPBIM][PF_6]	– 52.5	– 58.7	0.521	233
[DPPHIM][PF_6]	– 66.2	– 67.3	0.612	291
[DPPOIM][PF_6]	– 92.5	– 96.1	0.410	207

higher viscosities, then conventional ionic liquids. Moreover, they display relatively high thermal stabilities, are liquid over a broad temperature range, have low vapor pressures, display a metastable supercooled liquid state when cooled from the equilibrium liquid state down to low temperatures without crystallizing, and are characterized by a significant change in molar heat capacity associated with the glass transition.

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Experimental Part

General. All reagents were commercially available and purified before use. IR Spectra of the neat liquids were recorded on *IFS66V/S* FT-IR spectrophotometer as dispersed films; in cm^{-1}. ^{1}H-NMR Spectra were recorded on a *Brucker* spectrometer at 300 MHz; chemical shifts δ in ppm rel. to Me_4Si (=0 ppm) or rel. to residual solvent signals ($CHCl_3$), coupling constants J in Hz. TGA and DSC experiments were performed with a *Perkin-Elmer 7* apparatus at a heating (or cooling) rate of 10°/min under N_2 (TGA) or Ar (DSC) atmosphere. DSC Experiments were performed in sealed Al pans, and the data were analyzed with a *Netzsch DSC-200* PC analyzer to derive T_g and ΔC_{pm} values.

*Typical Synthetic Procedure: 3-[3-(Diethoxyphosphinyl)propyl]-1-octyl-1*H-*imidazolium Hexafluorophosphate* ([DPPOIM][PF_6]; **12**)[4]. Under N_2, diethyl 3-bromopropylphosphonate (25.90 g, 0.10 mol) and 1-octyl-1*H*-imidazole (18.0 g, 0.10 mol) were added to a round-bottomed flask fitted with a condenser, and stirred for 24 h at 80°. The mixture was then cooled to r.t., washed with anh. Et_2O (3 × 30 ml), and concentrated and thoroughly dried *in vacuo*. The resulting imidazolium bromide (41.95 g, 95.6%) of type **C** (see the *Scheme*) was transferred to a flask, and acetone (150 ml) and $NH_4^+PF_6^-$ (21.19 g, 0.13 mol) were added sequentially. The resulting mixture was stirred at r.t. for 2 h, which resulted in the precipitation of a waxy solid. The latter was collected by filtration and extracted thoroughly with acetone (3 × 50 ml). The org. extract was collected, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford **12** (47.31 g, 98.2%) as a colorless liquid. IR (film): 3161, 3116, 2930, 2859, 1567, 1467, 1393, 1238, 1166, 1099, 1028, 966, 839, 643, 558. ^{1}H-NMR ($CDCl_3$): 8.72 (*s*, 1 H); 7.47 (*s*, 1 H); 7.37 (*s*, 1 H); 4.33 (*t*, *J* = 13.5, 2 H); 4.17 (*t*, *J* = 14.7, 2 H); 4.09 (*m*, *J* = 16.8, 4 H); 2.18 (*m*, *J* = 29.4, 2 H); 1.84 (*m*, *J* = 22.2, 2 H); 1.74 (*m*, *J* = 15.3, 2 H); 1.35 (*m*, 16 H); 0.87 (*t*, *J* = 12.3, 3 H). Anal. calc. for $C_{18}H_{36}F_6N_2O_3P_2$: C 42.86, H 7.14, N 5.56; found: C 42.59, H 7.23, N 5.53.

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[4] The synthesis of the BF_4-based ionic liquids was performed in analogy to the procedure given for **12**, but with $Na^+BF_4^-$ instead of $NH_4^+PF_6^-$ as the ion-exchange reagent.

*1-Butyl-3-[2-(diethoxyphosphinyl)ethyl]-1*H*-imidazolium Tetrafluoroborate* ([DPEBIM][BF_4]; **1**). Yield: 79.6%. IR (film): 3154, 3119, 2965, 2939, 2877, 1568, 1466, 1393, 1241, 1167, 1052, 965, 849, 764, 639, 522. ^{1}H-NMR ($CDCl_3$): 8.92 (*s*, 1 H); 7.40 (*s*, 1 H); 7.35 (*s*, 1 H); 4.49 (*t*, *J* = 13.5, 2 H); 4.18 (*m*, 6 H); 2.45 (*m*, *J* = 27.3, 2 H); 1.81 (*t*, *J* = 14.4, 2 H); 1.36 (*m*, 8 H); 0.98 (*t*, *J* = 13.5, 2 H). Anal. calc. for $C_{13}H_{26}BF_4N_2O_3P$: C 41.49, H 6.91, N 7.45; found: C 41.14, H 7.11, N 7.82.

*1-Butyl-3-[2-(diethoxyphosphinyl)ethyl]-1*H*-imidazolium Hexafluorophosphate* ([DPEBIM][PF_6]; **2**). Yield: 93.3%. IR (film): 3164, 3117, 2969, 2941, 2878, 1568, 1465, 1409, 1243, 1164, 1097, 1026, 968, 834, 757, 638, 557. ^{1}H-NMR ($CDCl_3$): 8.71 (*s*, 1 H); 7.49 (*s*, 1 H); 7.38 (*s*, 1 H); 4.47 (*t*, *J* = 13.5, 2 H); 4.13 (*m*, 6 H); 2.45 (*m*, *J* = 25.8, 2 H); 1.86 (*t*, *J* = 15.3, 2 H); 1.35 (*m*, 8 H); 0.96 (*t*, *J* = 14.7, 3 H). Anal. calc. for $C_{13}H_{26}F_6N_2O_3P_2$: C 35.94, H 5.99, N 6.45; found: C 35.25, H 5.55, N 6.61.

*1-Butyl-3-[3-(diethoxyphosphinyl)propyl]-1*H*-imidazolium Tetrafluoroborate* ([DPPBIM][BF_4], **3**). Yield: 92.1%. IR (film): 3152, 3114, 2965, 2938, 2876, 1566, 1466, 1392, 1239, 1168, 1055, 965, 787, 643, 521. ^{1}H-NMR ($CDCl_3$): 8.99 (*s*, 1 H); 7.55 (*s*, 1 H); 7.47 (*s*, 1 H); 4.38 (*t*, *J* = 13.5, 2 H); 4.23 (*t*, *J* = 14.7, 2 H); 4.09 (*m*, 4 H); 2.19 (*m*, *J* = 14.1, 2 H); 1.88 (*m*, *J* = 14.7, 2 H); 1.76 (*m*, *J* = 18.6, 2 H); 1.34 (*m*, 8 H); 0.97 (*t*, *J* = 14.4, 3 H). Anal. calc. for $C_{14}H_{28}BF_4N_2O_3P$: C 43.08, H 7.18, N 7.18; found: C 43.34, H 7.30, N 7.28.

*1-Butyl-3-[3-(diethoxyphosphinyl)propyl]-1*H*-imidazolium Hexafluorophosphate* ([DPPBIM][PF_6]; **4**). Yield: 93.6%. IR (film): 3162, 3116, 2967, 2939, 2877, 1567, 1466, 1369, 1238, 1170, 1099, 1027, 966, 839, 755, 643, 558. ^{1}H-NMR ($CDCl_3$): 8.67 (*s*, 1 H); 7.46 (*s*, 1 H); 7.38 (*s*, 1 H); 4.33 (*t*, *J* = 14.1, 2 H); 4.18 (*t*, *J* = 14.4, 2 H); 4.09 (*m*, 4 H); 2.17 (*m*, *J* = 29.4, 2 H); 1.86 (*m*, *J* = 22.8, 2 H); 1.73 (*m*, *J* = 33.3, 2 H); 1.39 (*m*, 8 H); 0.95 (*t*, *J* = 14.7, 3 H). Anal. calc. for $C_{14}H_{28}F_6N_2O_3P_2$: C 37.50, H 6.25, N 6.25; found: C 37.36, H 6.58, N 6.60.

*3-[2-(Diethoxyphosphinyl)ethyl]-1-hexyl-1*H*-imidazolium Tetrafluoroborate* ([DPEHIM][BF_4]; **5**).Yield: 94.1%. IR (film): 3153, 3118, 2958, 2933, 2862, 1568, 1467, 1381, 1285, 1242, 1167, 1057, 847, 764, 640, 521. ^{1}H-NMR ($CDCl_3$): 8.93 (*s*, 1 H); 7.44 (*s*, 1 H); 7.36 (*s*, 1 H); 4.51 (*t*, *J* = 20.7, 2 H); 4.20 (*m*, 6 H); 2.49 (*m*, *J* = 25.8, 2 H); 1.87 (*t*, *J* = 11.4, 2 H); 1.30 (*m*, 12 H); 0.86 (*t*, *J* = 13.5, 3 H). Anal. calc. for $C_{15}H_{30}BF_4N_2O_3P$: C 44.55, H 7.43, N 6.93; found: C 45.15, H 7.50, N 6.98.

*3-[2-(Diethoxyphosphinyl)ethyl]-1-hexyl-1*H*-imidazolium Hexafluorophosphate* ([DPEHIM][PF_6]; **6**). Yield: 95.1%. IR (film): 3164, 3121, 2959, 2935, 2863, 1568, 1467, 1409, 1217, 1164, 1091, 1028, 837, 740, 639, 558. ^{1}H-NMR ($CDCl_3$): 8.52 (*s*, 1 H); 7.48 (*s*, 1 H); 7.39 (*s*, 1 H); 4.45 (*t*, *J* = 13.5, 2 H); 4.17 (*m*, 6 H); 2.46 (*m*, *J* = 18.9, 2 H); 1.85 (*t*, *J* = 9.3, 2 H); 1.30 (*m*, 12 H); 0.86 (*t*, *J* = 12.9, 3 H). Anal. calc. for $C_{15}H_{30}F_6N_2O_3P_2$: C 38.96, H 6.49, N 6.06; found: C 38.83, H 6.52, N 5.96.

*3-[3-(Diethoxyphosphinyl)propyl]-1-hexyl-1*H*-imidazolium Tetrafluoroborate* ([DPPHIM][BF_4]; **7**). Yield: 92.9%. IR (film): 3151, 3114, 2958, 2933, 2863, 1566, 1466, 1392, 1368, 1239, 1167, 1056, 965, 787, 643, 493. ^{1}H-NMR ($CDCl_3$): 8.98 (*s*, 1 H); 7.54 (*s*, 1 H); 7.43 (*s*, 1 H); 4.38 (*t*, *J* = 13.8, 2 H); 4.21 (*t*, *J* = 14.7, 2 H); 4.13 (*m*, 4 H); 2.20 (*m*, *J* = 28.8, 2 H); 1.86 (*m*, *J* = 19.8, 2 H); 1.76 (*m*, *J* = 17.7, 2 H); 1.33 (*m*, 12 H); 0.87 (*t*, *J* = 9.3, 2 H). Anal. calc. for $C_{16}H_{32}BF_4N_2O_3P$: C 45.93, H 7.66, N 6.70; found: C 44.50, H 7.50, N 6.57.

*3-[3-(Diethoxyphosphinyl)propyl]-1-hexyl-1*H*-imidazolium Hexafluorophosphate* ([DPPHIM][PF_6]; **8**). Yield: 96.8%. IR (film): 3161, 3116, 2959, 2934, 2863, 1566, 1467, 1369, 1238, 1166, 1099, 1028, 967, 841, 741, 643, 558. ^{1}H-NMR ($CDCl_3$): 8.69 (*s*, 1 H); 7.44 (*s*, 1 H); 7.31 (*s*, 1 H); 4.35 (*t*, *J* = 13.8, 2 H); 4.17 (*t*, *J* = 15.3, 2 H); 4.10 (*m*, 4 H); 2.19 (*m*, *J* = 30.3, 2 H); 1.87 (*m*, *J* = 23.4, 2 H); 1.77 (*m*, *J* = 25.8, 2 H); 1.37 (*m*, 12 H); 0.88 (*t*, *J* = 13.5, 3 H). Anal. calc. for $C_{16}H_{32}F_6N_2O_3P_2$: C 40.34, H 6.72, N 5.88; found: C 39.69, H 6.67, N 6.00.

*3-[2-(Diethoxyphosphinyl)ethyl]-1-octyl-1*H*-imidazolium Tetrafluoroborate* ([DPEOIM][BF_4]; **9**). Yield: 96.0%. IR (film): 3154, 3118, 2929, 2858, 1615, 1568, 1467, 1379, 1285, 1167, 1060, 854, 765, 641, 521. ^{1}H-NMR ($CDCl_3$): 8.92 (*s*, 1 H); 7.44 (*s*, 1 H); 7.35 (*s*, 1 H); 4.51 (*t*, *J* = 15.3, 2 H); 4.18 (*m*, 6 H); 2.42 (*m*, *J* = 23.4, 2 H); 1.85 (*t*, *J* = 12.9, 2 H); 1.32 (*m*, 16 H); 0.86 (*t*, *J* = 7.2, 3 H). Anal. calc. for $C_{17}H_{34}BF_4N_2O_3P$: C 47.22, H 7.87, N 6.48; found: C 48.35, H 7.04, N 6.32.

*3-[2-(Diethoxyphosphinyl)ethyl]-1-octyl-1*H*-imidazolium Hexafluorophosphate* ([DPEOIM][PF_6]; **10**). Yield: 98.7%. IR (film): 3163, 3120, 2930, 2859, 1568, 1467, 1408, 1219, 1165, 1028, 971, 839, 741, 640, 558. ^{1}H-NMR ($CDCl_3$): 8.57 (*s*, 1 H); 7.48 (*s*, 1 H); 7.34 (*s*, 1 H); 4.45 (*t*, *J* = 14.7, 2 H); 4.12 (*m*, 6 H); 2.41 (*m*, *J* = 22.8, 2 H); 1.85 (*t*, *J* = 13.5, 2 H); 1.31 (*m*, 16 H); 0.86 (*t*, *J* = 12.3, 3 H). Anal. calc. for $C_{17}H_{34}F_6N_2O_3P_2$: C 41.63, H 6.94, N 5.71; found: C 41.95, H 6.97, N 5.66.

*3-[3-(Diethoxyphosphinyl)propyl]-1-octyl-1*H*-imidazolium Tetrafluoroborate* ([DPPOIM][BF_4]; **11**). Yield: 97.3%. IR (film): 3151, 3115, 2956, 2930, 2858, 1566, 1467, 1393, 1368, 1239, 1167, 1057, 965, 786, 643, 493. ^{1}H-NMR ($CDCl_3$): 8.92 (*s*, 1 H); 7.57 (*s*, 1 H); 7.48 (*s*, 1 H); 4.37 (*t*, *J* = 14.1, 2 H); 4.21 (*t*, *J* = 14.7, 2 H); 4.10 (*m*, 4 H); 2.19 (*m*, *J* = 48.6, 2 H); 1.89 (*m*, *J* = 19.5, 2 H); 1.77 (*m*, *J* = 18.3, 2 H); 1.26 (*m*, 16 H); 0.87 (*t*, *J* = 9.3, 3 H). Anal. calc. for $C_{18}H_{36}BF_6N_2O_3P$: C 48.43, H 8.07, N 6.28; found: C 48.78, H 7.91, N 6.44.

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