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New ionic liquids with the bis[bis(pentafluoroethyl)phosphinyl]imide anion, $[(C_2F_5)_2P(O)]_2N^-$—Synthesis and characterization

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ABSTRACT

A new series of low melting and hydrophobic ionic liquids (ILs) containing the bis[bis(pentafluoroethyl)phosphinyl]imide anion, $[(C_2F_5)_2P(O)]_2N^-$ (FPI), and ammonium, phosphonium, imidazolium, pyridinium or pyrrolidinium cations were prepared and characterized. Their density, viscosity, melting point, glass transition temperature, decomposition temperature and conductivity are discussed. Many of these ionic liquids are liquids at room temperature with melting points below 15 °C, viscosities below 110 $mm^2\,s^{-1}$ and thermal stabilities above 300 °C.

1. Introduction

Salts that are liquid at temperatures below 100 °C are called ionic liquids (ILs). They attract considerable interest, e.g. as new media for chemical reactions [1,2] and catalysis [3–5], in separation processes and analytical techniques [6]. Due to their good electrical conductivity, ionic liquids can serve as electrolytes in various electrochemical devices [7] or in electrochemical processes, for instance in electro deposition of metals [8]. These applications are due to their advantageous properties such as: negligible vapour pressure, non-flammability, high thermal stability and liquid state over a wide temperature range. For electrochemical applications their low viscosity and high electrochemical stability are of importance.

Recently, we have demonstrated that the properties of ionic liquids, in particular their viscosity, are strongly dependent on the anion–cation interaction [9]. Weakly coordinating anions in combination with mono-cations, having the charge well delocalized, result in room temperature ionic liquids with low viscosity. Since the last decade thousands of ionic liquids have been synthesized, but only a few of them possess the required properties: low viscosity, good electrical conductivity, and high chemical, thermal and electrochemical stability [10,11]. These properties exhibit in particular the new generation of ionic liquids with bis(trifluoromethylsulfonyl)imide, [TFSI] [12–15], tris(pentafluoroethyl)trifluorophosphate [FAP] [16] or tetracyanoborate [17] anions. Ionic liquids with the bulky FAP anion are hydrolytically stable and highly hydrophobic [16], probably the most hydrophobic ones among known ionic liquids. FAP is a complex anion derived from the corresponding Lewis acid, tris(perfluoroalkyl)difluoro-phosphorane [16,18]. Therefore FAP salts react with Lewis acids which are stronger than tris(perfluoroalkyl)difluoro-phosphorane. This restricts the application of FAP ionic liquids in processes catalysed with strong Lewis acids (for example Friedel–Crafts alkylation or acylation), e.g. with $AlCl_3$ or SbF_5. Therefore search for new weakly coordinating anions with improved stability against strong Lewis acids is advised.

Recently we have developed a convenient synthesis of the strong N-H acid bis[bis(pentafluoroethyl)phosphinyl]imide, $[(C_2F_5)_2P(O)]_2NH$, and some of its metal salts [19]. The $[(C_2F_5)_2P(O)]_2NH$ acid, [HFPI], and the Na or K salts are suitable starting materials for the synthesis of new hydrophobic ionic liquids with the bis[bis(perfluoroethyl)phosphinyl]imide [FPI] anion. The syntheses of FPI ionic liquids were carried out in a very simple way by mixing aqueous solutions of $[(C_2F_5)_2P(O)]_2NH$ (or its sodium or potassium salt), with ammonium, phosphonium, imidazolium, pyridinium or pyrrolidinium chlorides or bromides

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(see Section 3). Ionic liquids with the FPI anion are highly hydrophobic and can be easily separated from the aqueous phase. After washing with water and drying, these ionic liquids are obtained in a very high purity.

Here, we describe the preparation and characterization of some ionic liquids with the FPI anion.

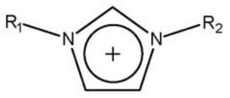
2. Results and discussion

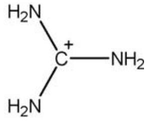
2.1. Synthesis of ionic liquids with the FPI anion

ILs with the bis[bis(pentafluoroethyl)phosphinyl]imide anion can be synthesized via metathesis reactions. The acid (HFPI) and Cat^+A^-, A = Cl, Br, OH were dissolved separately in a small quantity of water. Both aqueous solutions were then mixed together and stirred at room temperature. The obtained ionic liquid is insoluble in water and precipitate as a dense phase on the bottom of the reactions flask. Vigorous stirring is essential for the reaction to proceed quantitatively. The bottom phase was separated (in some cases diluted with CH_2Cl_2) and washed several times with water. If a solid material is formed, it can be filtered off and washed with water until the test for chloride (or bromide) with silver nitrate is negative. To avoid any excess of the FPI acid in the ionic liquid, the washing water should contain small amount of K_2CO_3.

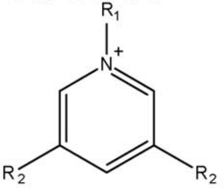
$$Cat^+A^- + [(C_2F_5)_2P(O)]_2NH \rightarrow Cat^+[(C_2F_5)_2P(O)]N^- + HA \qquad (1)$$

Here are the chosen cations

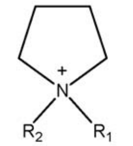




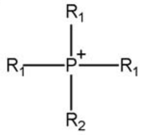
$R_1 = CH_3$,
$R_2 = C_2H_5$, C_4H_9, C_6H_{13}, $C_{10}H_{21}$, $C_{18}H_{37}$



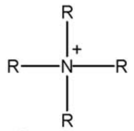
$R_1 = C_4H_9$, $R_2 = H$
$R_1 = C_4H_9$, $R_2 = CH_3$



$R_1 = C_4H_9$, $R_2 = CH_3$



$R_1 = C_4H_9$, $R_2 = C_4H_9$
$R_1 = C_6H_{13}$, $R_2 = C_{14}H_{29}$
$R_1 = C_6H_5$, $R_2 = CH_2C_6H_5$



$R = C_2H_5$, C_4H_9.

To remove the residual water, the FPI ILs were dried at 70 °C for 12–48 h under stirring in vacuum. The FPI ionic liquids are soluble in alcohol, acetone, acetonitrile, chloroform, dichloromethane, but immiscible with water, toluene and hexane.

The ionic liquids with the FPI anion were characterized by ^1H, ^{19}F, ^{31}P NMR spectroscopy and elemental analysis. The content of halide was controlled to be below 30 ppm.

2.2. Physico-chemical properties of ionic liquids with the FPI anion

2.2.1. Hydrolytic stability of FPI ionic liquids

The ionic liquids with FPI anion are stable against hydrolysis in water at room temperature for more than 2 months. However, after keeping an aqueous emulsion of 1-ethyl-3-methyl imidazolium FPI for 5 days at 100 °C we observed in the ^{19}F NMR spectrum a small signal which belongs to the hydrolysis product – bis(pentafluoroethyl)phosphinate.

Under basic conditions (6% aqueous KOH) at room temperature the hydrolysis of 1-ethyl-3-methyl imidazolium FPI proceeds much faster and within 10 days about 40% of the ionic liquid is hydrolyzed to the phosphinate.

2.2.2. Viscosity and density

The viscosity is an important property of ionic liquids, because it strongly influences the diffusion of species, which are dissolved or dispersed in the ionic liquid. This is especially important for electrochemical applications of ionic liquids. In general, the viscosity of ILs is essentially influenced by the cation–anion interaction, hydrogen bonding, as well as by the coordinating ability and symmetry of the ions [20].

It should be mentioned that the presence of water or other impurities (for instance residual organic solvents) reduces the viscosity of ionic liquids substantially. Therefore, we controlled carefully the water content in all FPI ILs by Karl-Fischer titration prior to viscosity measurement. In all studied ionic liquids the water content was below 50 ppm which should not have a substantial influence on the viscosity. To avoid the influence of the halide impurities, all ionic liquids were purified as described above, until the halide content was less that 30 ppm, controlled by ion-chromatography.

Ionic liquids with the FPI anion possess kinematic viscosity which is of comparable magnitude to the viscosity of ILs with the TFSI or FAP anion. For example, the viscosity of 1-hexyl-3-methylimidazolium IL with the TFSI anion is 44 [16], with the FAP anion is 74 [16] and with the FPI anion is 103 $mm^2\ s^{-1}$. All three ILs show low kinematic viscosity in comparison with 1-hexyl-3-methylimidazolium PF_6 (548 $mm^2\ s^{-1}$ [16]). Hence, the viscosity of ionic liquids is dominated by the nature of the anion. On the other side in the series [$C_n$mim][FPI] with different alkyl groups (n = 2, 4, 6) the viscosities are very similar: [emim][FPI] has the viscosity 171, [bmim][FPI] 151, and [hmim][FPI] 159 mPa s (see Fig. 1). For these three ionic liquids the influence of the cation size on the viscosity is minimal, because the bulky FPI anion occupies the major volume in the ionic liquid and carries the largest part of the molar mass (see Table 1).

Recently it was shown that there is a strong relationship between the molecular volumes V_m of ILs and their viscosity, conductivity and density [21]. According to Eq. (2) the volume of the FPI anion is estimated to be 0.467 nm^3 by using V_m = 0.58 nm^3 (available from single crystal X-ray diffraction of $[(CH_3)_4N][(C_2F_5)_2P(O)]_2N$ [19]) and

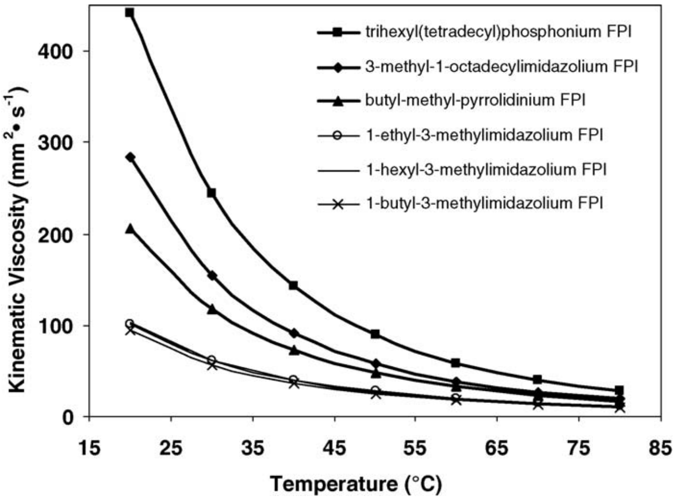


Fig. 1. Viscosity of a series of FPI ILs as a function of temperature.

Table 1
Dynamic and kinematic viscosity and density of ionic liquids with the FPI anion.

Ionic liquid	M.W.	Part of FPI anion in the molecular weight of IL %	Dynamic viscosity η/mPa s (20 °C)	Kinematic viscosity ν/mm^2 s^{-1} (20 °C)	Density ρ/g cm^{-3}
[emim][FPI]	695.17	84	171	102	1.68
[bmim][FPI]	723.22	80.7	151	95	1.59
[hmim][FPI]	751.28	77.7	159	103	1.54
[dmim][FPI]	807.38	72.3	199	137	1.45
[omim][FPI]	919.60	63.5	376	285	1.32
[bmpl][FPI]	726.27	80.4	325	206	1.58
[p(h3)t][FPI]	1061.82	55	536	443	1.21

[emim] = 1-ethyl-3-methylimidazolium; [bmim] = 1-butyl-3-methylimidazolium; [hmim] = 1-hexyl-3-methylimidazolium; [dmim] = 1-decyl-3-methylimidazolium; [omim] = 1-octadecyl-3-methylimidazolium; [bmpl] = butyl-methylpyrrolidinium; [p(h3)t] = trihexyltetradecylphosphonium.

the volume for the $[(CH_3)_4N]^+$ cation $V_{ion}(C^+) = 0.113\ nm^3$ [22].

$$V_m = V_{\text{ion}}(A^-) + V_{\text{ion}}(C^+) \tag{2}$$

This anion volume is double than that for $[TFSI]^-$ ($0.232\ nm^3$) [23] and the large size of the FPI anion influences the viscosity of ionic liquids (see Table 1).

Fig. 1 presents the viscosity of different FPI ILs plotted as a function of the temperature. The difference in the viscosities of FPI ionic liquids with various cations becomes very small at 80 °C. It looks that above 80 °C the weak interaction between FPI anion and organic cations is completely broken. In terms of the viscosity it means that in Eq. (3) [9], which describes the influence of the cation, anion and ion-pair diffusivity on the viscosity of ionic liquids, the last component becomes very small (3a) due to the high degree of ion-pairs self dissociation at high temperature.

$$\eta^{IL} = \frac{k \cdot T}{b_A \cdot D_A \cdot r_A + b_C \cdot D_C \cdot r_C + b_{A,C} \cdot D_{A,C} \cdot r_{A,C}} \tag{3}$$

where η—dynamic viscosity; r—radius of the anion, cation or sum (cation + anion); D_A—self-diffusion coefficient of anion; D_C—self-diffusion coefficient of cation; $D_{A,C}$—self-diffusion coefficient of ion-pair; $b_A = n_A\,4.5\pi$ [24]; $b_C = n_C\,3.5\pi$ [24]; $b_{A,C} = n_{A,C}\,6.0\pi$; n = transference number

$$\eta^{IL} = \frac{k \cdot T}{b_A \cdot D_A \cdot r_A + b_C \cdot D_C \cdot r_C + \boxed{\cancel{b_{A,C} \cdot D_{A,C} \cdot r_{A,C}}}} \equiv \frac{k \cdot T}{b_A \cdot D_A \cdot r_A + b_C \cdot D_C \cdot r_C} \tag{3a}$$

It seems that the viscosity of FPI ionic liquids at high temperature (>80 °C) depends on the mobility (diffusivity) of the cations and anions only. At >80 °C the dependence of the ILs viscosity on the anion or cation size becomes insignificant by the reason that $D_A{\cdot}r_A$ and $D_C{\cdot}r_C$ remains practically constant at a certain temperature. At the temperature of above 80 °C the viscosity of FPI ionic liquids practically does not depend on the size of the cation (see Fig. 1). It means that in Eq. (3a) all parameters at fixed temperature (above 80 °C) are constant; if η^{IL} is constant and the parameters: $k{\cdot}T$ and $b_A{\cdot}D_A{\cdot}r_A$ (belongs to the FPI anion) are constant as well, the parameter $b_C{\cdot}D_C{\cdot}r_C$ should be also constant. Assuming that the transference number n_C of the cations in the case of ionic liquids with the same anion (in our case FPI anion) is constant (it means $b_C = n_C{\cdot}3.5\pi$ is constant) we can conclude that $D_C{\cdot}r_C$ should be constant as well according to Eq. (3a).

The Arrhenius plot of the viscosity against temperature for the FPI ionic liquids is non-linear (Fig. 2). This is similar to that described previously for other ionic liquids [24]. In the critical point at high temperature the viscosities of different ionic liquids become very similar.

The density of FPI ionic liquids decreases slowly with increasing the length of the alkyl chain (see Table 1). Again, that is probably due to the dominant influence of the bulky and heavy FPI anion on the density.

2.2.3. Melting point and glass transition temperature

Table 2 presents the melting points of FPI salts in comparison to analogous compounds with other anions. The melting point and temperature of crystallization for the FPI ionic liquids were measured by difference scanning calorimetry (DSC), in the temperature range between −120 and 600 °C (see Table 3). A typical thermogram is shown in Fig. 3 for [bmpl]FPI. This ionic liquid shows a weak glass transition point at about −80 °C, followed by the crystallization at −35 °C and the melting point at about 7 °C. For [hmim]FPI, [dmim]FPI and [p(h3)t]FPI there are no indications for any melting points on the DSC curves. For some FPI

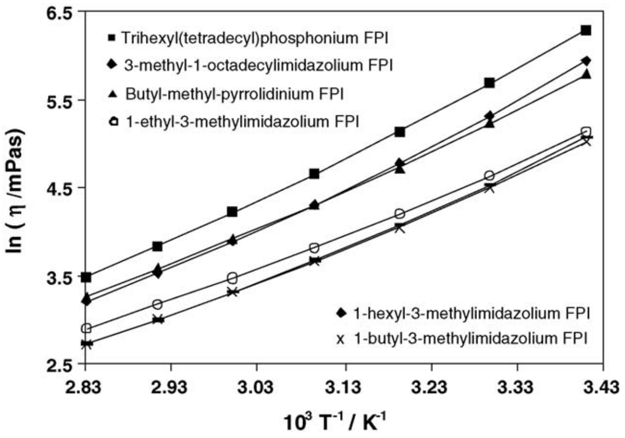


Fig. 2. Arrhenius plots of viscosity of a series of FPI ILs.

Table 2
Melting points (T_m) of FPI salts in comparison to related salts with different anions.

Cation	Anion	T_m (°C)	Ref.
TEA	Cl	110	[25]
	TFSI	104	[26]
	FAP	95	[16]
	FPI	46–47	a
TBP	Cl	62–64	[27]
	TFSI	65	[28]
	FAP	74	[16]
	FPI	145	a
TBA	Cl	41	[29]
	TFSI	90	[26]
	FAP	62	[16]
	FPI	150	a
C_4Py	Cl	103/162	[30]/[31]
	TFSI	26	[32]
	FPI	49	a

TEA = tetraethylammonium; TBP = tetrabutylphosphonium; TBA = tetrabutylammonium; C_4Py = N-butylpyridinium; TFSI = bis(trifluoromethylsulfonyl)imide; FAP = tris(pentafluoroethyl)trifluorophosphate; a = this work.

Table 3
The melting point (T_m), crystallization temperature (T_{cc}) and decomposition temperature (T_d) for ionic liquids containing the FPI anion.

Compound[a]	T_m/°C (DSC)	T_{cc}/°C (DSC)	T_m/°C (visual)	T_d/°C (TGA)
[emim][FPI]	+13	−52	17–18	300
[bmim][FPI]	+7	–	[b]	320
[hmim][FPI]	–	–	[b]	320
[dmim][FPI]	10–15	–	[b]	300
[omiml][FPI]	+14	–	16–17	300
[bmpl][FPI]	+7	−34	6–7	300
[p(h3)t][FPI]	−2	–	[b]	300
[3,5-mPyr][FPI][c]	+19	−31	18	280

[a] For abbreviations see Table 1.
[b] Glass state, no melting point observed.
[c] [3,5-mPyr] = N-butyl-3,5-dimethylpyridinium.

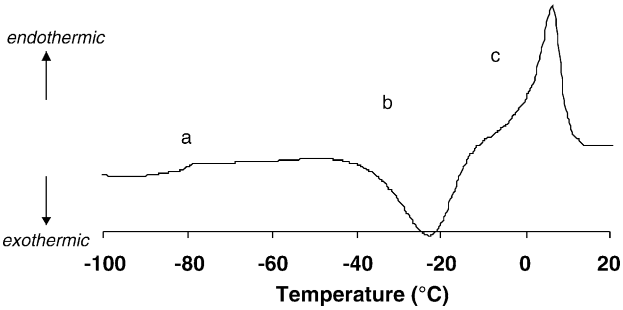


Fig. 3. DSC curve for [bmpl]FPI: (a) weak glass transition (−80 °C); (b) crystallization temperature (−34 °C); (c) melting point (7 °C).

salts the glass state can be also observed visually by heating from −80 °C to room temperature in sealed glass capillary tubes. The difference in the visually observed melting points and those obtained by DSC measurements may be due to differences in the heating rates.

2.2.4. Thermal stability

Figs. 4 and 5 show characteristic TGA curves for FPI salts with organic cations. The samples were heated in an inert atmosphere (N_2) at a rate of 10 °C per min. The TGA measurements indicate that FPI ionic liquids possess high thermal stability as the respective FAP ionic liquids [16]. FPI ILs containing different imidazolium cations shows rather similar thermal behaviour with a continuous mass loss between 280 and 400 °C (Fig. 4) and a T_{onset} of above 320 °C. The decomposition temperature T_d presented in Table 3 is the temperature at which 2% weight loss occurred at a heating rate of 10 °C per min (at isothermal conditions the decomposition temperatures are much lower). Above 450 °C the mass loss becomes more than 90% and the weight of the residue remains almost constant. The decomposition products of the FPI ILs were not investigated.

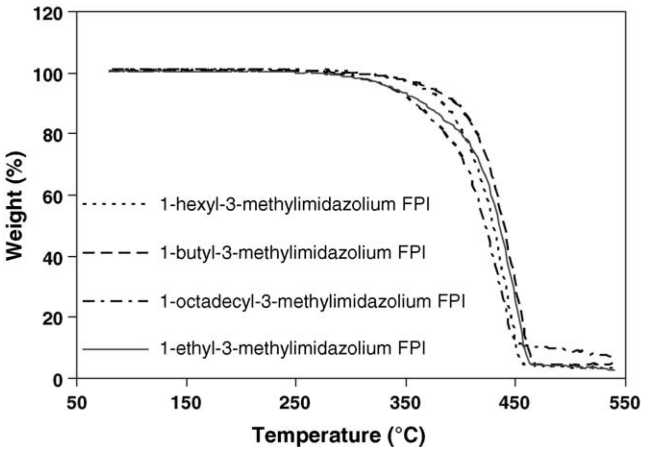


Fig. 4. TGA for selected imidazolium room temperature ionic liquids with the FPI anion.

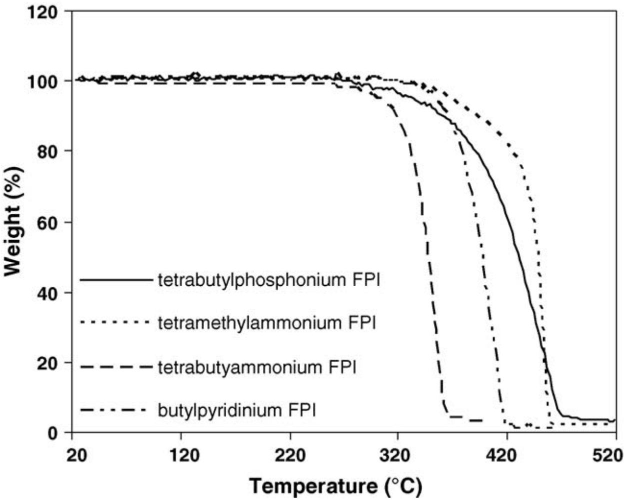


Fig. 5. TGA for some solid salts with the FPI anion.

It can be concluded that the thermal stability of ILs with the bis[bis(pentafluoroethyl)phosphinyl]imide anion is high and comparable with those of ionic liquids with other weekly coordinating anions, like bis(trifluoromethylsulfonyl)imide (TFSI) or tris(pentafluoroethyl)trifluorophosphate, (FAP) anions [16].

2.2.5. Electrochemical stability

The electrochemical stability was determined by cyclic voltammetry. The salts with bis[bis(pentafluoroethyl)phosphinyl]imide anion (FPI) posses high electrochemical stability (see Fig. 6). For example, tetrabutylammonium FPI has an electrochemical window of about 7 V, higher than the reported value of 5.5 V for trimethylpropyl ammonium bis(trifluoromethyl)sulfonylimide (TFSI) [33], but close to the value reported for tetrabutylammonium tris(pentafluoroethyl)trifluorophosphate (FAP) [16]. High electrochemical stability makes the salts with FPI anion attractive for application in electrochemical devices.

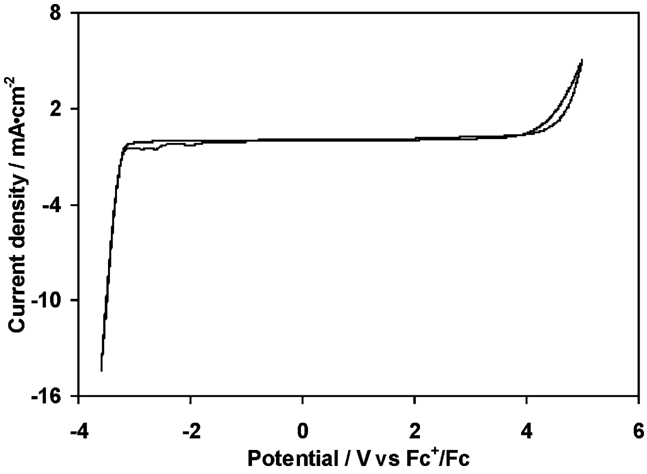


Fig. 6. Cyclic voltammogram of tetrabutylammonium FPI on a disc (Ø 3 mm) glassy carbon electrode (surface area: 7.065×10^{-2} cm^2) at room temperature (23 °C); scan rate: 20 mV s^{-1}; auxiliary electrode is Pt and reference electrode is Ag/$AgNO_3$ (CH_3CN). The potential values are normalized to E° of ferrocene.

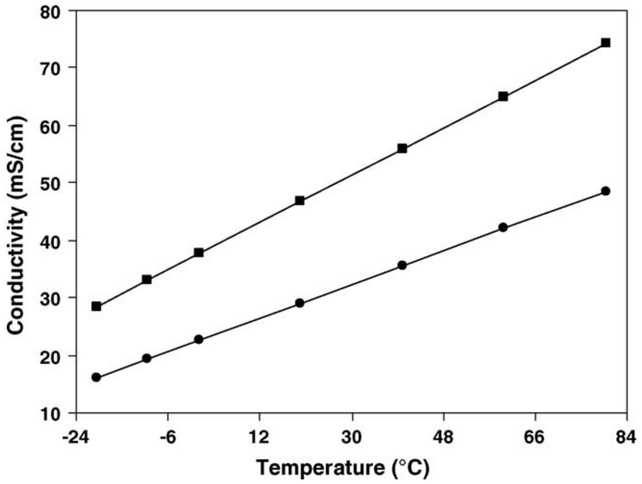


Fig. 7. The conductivity curve for [emim]FAP (■) and for [emim]FPI (●) in acetonitrile solution ($c = 0.83$ mol L^{-1}).

2.2.6. Conductivity

The conductivity of 0.83 mol L^{-1} solution of [emim]FPI in acetonitrile is linearly increasing with increasing temperature (in the temperature range −20 to 80 °C, see Fig. 7).

The conductivity of [emim]FAP is higher then the conductivity of [emim]FPI, because the FAP anion is less bulky than the FPI anion.

3. Experimental

3.1. General experimental procedures

NMR spectra of all compounds were measured in CD_3CN solution at room temperature on a Bruker Avance DRX-400 (^{1}H, 400.13 MHz; ^{19}F, 376.49 MHz; ^{31}P, 161.97 MHz) spectrometer. The chemical shifts were referenced to external TMS (^{1}H), $CFCl_3$ (^{19}F) and H_3PO_4 (^{31}P).

Elemental analysis was performed using a HEKATECH EA 3000 elemental analyser and the Callidus software.

Impurities in all FPI salts were detected by measuring of residual water by Karl-Fischer titration (831 KF-Coulometer, Metrohm) and of chloride or bromide by ion-chromatography (Metrohm Advanced IC System with Metrosep A Supp 5-150). Viscosities and densities of ionic liquids in the temperature range between 20 and 80 °C were measured using the Viscosimeter SVM 3000 Anton Paar.

Thermo analytical measurements were performed with a Netzsch DSC 204 and a TG STA 409 instrument. About 25–40 mg of the samples were weighed and sealed in aluminium crucibles or in ceramic pans for DSC or TG measurements, respectively. A temperature range between −120 and 600 °C with a heating rate of 10 °C min^{-1} under an atmosphere of dry nitrogen was employed. The data were processed with the Netzsch Proteus 4.0 software.

The electrochemical stability of the ILs were measured using an Autolab PGSTAT 30 (Eco Chemie). Cyclic voltamogramms were recorded for 0.1 mol L^{-1} solutions in CH_3CN at glassy carbon (gc) working electrode; auxiliary electrode was Pt and Ag/$AgNO_3$ (CH_3CN) was used as reference electrode. The potential values were normalized to E° of ferrocene.

Conductivities data were obtained using a Conductometer 703 (Knick). The cell constant was calibrated at room temperature by measuring the conductance of several standard solutions of KCl with concentrations ranging from 0.1 to 0.01 mol L^{-1}.

3.2. Tetraethyl ammonium bis[bis(pentafluoroethyl)phosphinyl]imide, $[(C_2H_5)_4N]^+$ $[(C_2F_5)_2P(O)]_2N^-$

A 20% aqueous solution of tetraethylammonium hydroxide (5.55 g, 7.53 mmol) was slowly added to the solution of bis[bis(-pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (4.41 g, 7.53 mmol) in 15 mL water by stirring and cooling of the reaction mixture with an ice water bath until the reaction mixture was neutral. The reaction mixture was stirred additionally 30 min at room temperature. The resulting mixture was concentrated in a rotary evaporator. The residue was dissolved and stirred in 10 mL dioxane for 30 min. After the dioxane was distilled off, a hygroscopic colourless solid remains in the reaction flask. The product (5 g, yield 94%) was dried at 60 °C in vacuum for ca. 12 h and subsequently 12 ppm of water was detected by Karl-Fischer titration. M.p. 46–47 °C.

Anal. Calcd for $C_{16}H_{20}F_{20}N_2O_2P_2$: C 26.91; H 2.82; N 3.92. Found: C 26.92; H 2.76; N 3.98.

^{19}F NMR, δ: −81.1 s (4CF$_3$); −123.7 m (4CF$_a$); −126.8 m (4CF$_b$); $^2J_{P,Fa} = 80.8$ Hz; $^2J_{P,Fb} = 86.8$ Hz; $^2J_{Fa,Fb} = 320$ Hz.
^{31}P NMR, δ: −8.2 quin,m (2P, $^2J_{P,F} = 80$ Hz).
^{1}H NMR, δ: 3.1 q (4CH$_2$, $^3J_{H,H} = 7.1$ Hz); 1.2 t,m (4CH$_3$, $^3J_{H,H} = 7.1$ Hz).

3.3. Tetra(n-butyl)ammonium bis[bis(pentafluoroethyl) phosphinyl]imide, $[(C_4H_9)_4N]^+$ $[(C_2F_5)_2P(O)]_2N^-$

To the solution of tetra(*n*-butyl)ammonium bromide, $[(C_4H_9)_4N]^+Br^-$ (1.23 g, 3.8 mmol) in 5 mL of water a solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (2.23 g, 3.8 mmol) in 5 mL of water was slowly added under stirring at room temperature. The mixture was left stirring for 30 min and the liquid bottom phase was extracted with 10 mL of CH_2Cl_2. The extract was washed four times with 40 mL of water until the test for bromide with $AgNO_3$ was negative. The CH_2Cl_2 solvent was evaporated and the residue was dried 18 h in vacuum ($<10^{-3}$ mbar) at 60 °C. Yield 87%, m.p. 150–151 °C.

Anal. Calcd for $C_{24}H_{36}F_{20}N_2O_2P_2$: C 34.88; H 4.39; N 3.39. Found: C 34.95, H 4.55, N 3.34.

^{19}F NMR, δ: −81.2 s (4CF$_3$); −123.7 m (4CF$_a$); −126.8 m (4CF$_b$); $^2J_{P,Fa} = 76.3$ Hz; $^2J_{P,Fb} = 82.4$ Hz; $^2J_{Fa,Fb} = 329.5$ Hz.
^{31}P NMR, δ: −8.4 quin,m (2P, $^2J_{P,F} = 79$ Hz).
^{1}H NMR, δ: 3.07 m (4CH$_2$); 1.59 m (4CH$_2$); 1.34 q,t (4CH$_2$, $^3J_{H,H} = 7.3$ Hz); 0.95 t (4CH$_3$, $^3J_{H,H} = 7.4$ Hz).

3.4. Tetra(n-butyl)phosphonium bis[bis(pentafluoroethyl) phosphinyl]imide, $[(C_4H_9)_4P]^+$ $[(C_2F_5)_2P(O)]_2N^-$

A solution of tetra(*n*-butyl)phosphonium bromide, $[(C_4H_9)_4P]^+Br^-$ (1.15 g, 3.38 mmol) in 10 mL of water was slowly added to the stirred solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (1.99 g, 3.4 mmol) in 10 mL of water at room temperature. The mixture was left stirring for 30 min and the white precipitate was filtered off and washed three times with 30 mL of water. After drying, 2.47 g of a white solid material was obtained. Yield 86%, m.p. 143–145 °C.

Anal. Calcd for $C_{24}H_{39}F_{20}NO_2P_3$: C 34.18; H 4.30; N 1.66. Found: C 34.42; H 4.71; N 1.65.

^{19}F NMR, δ: −81.1 s (4CF$_3$); −123.7 m (4CF$_a$); −126.8 m (4CF$_b$); $^2J_{P,Fa} = 78.8$ Hz; $^2J_{P,Fb} = 88.7$ Hz; $^2J_{Fa,Fb} = 322.5$ Hz.
^{31}P NMR, δ: 34.9 m (1P); −8.3 quin,m (2P, $^2J_{P,F} = 80$ Hz).

^{1}H NMR, δ: 2.0–2.1 m ($4CH_2$); 1.47 m ($8CH_2$); 0.93 t ($4CH_3$, $^3J_{H,H}$ = 7.1 Hz).

3.5. Benzyl(triphenyl)phosphonium bis[bis(pentafluoroethyl)phosphinyl]imide, $[(C_6H_5)_3P(CH_2C_6H_5)]^+[(C_2F_5)_2P(O)]_2N^-$

To the stirred solution of benzyl(triphenyl)phosphonium chloride, $[(C_6H_5)_3P(CH_2C_6H_5)]^+Cl^-$ (0.83 g, 2.1 mmol) in 5 mL of water, a solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (1.25 g, 2.1 mmol) in 5 mL of water was slowly added at room temperature. The mixture was kept stirring for 1 h at room temperature. The water insoluble material was extracted with CH_2Cl_2 and washed with water two times. After evaporation of CH_2Cl_2 and drying, 1.48 g of a pure white solid $[(C_6H_5)_3P(CH_2C_6H_5)]^+[(C_2F_5)_2P(O)]_2N^-$ was obtained. Yield 75%, m.p. 110 °C.

Anal. Calcd for $C_{33}H_{22}F_{20}NO_2P_3$: C 42.28; H 2.37; N 1.49. Found: C 42.55; H 0.56; N 1.50.

^{19}F NMR, δ: −81.1 s ($4CF_3$); −123.7 m ($4CF_a$); −126.8 m ($4CF_b$); $^2J_{P,Fa}$ = 77.7 Hz; $^2J_{P,Fb}$ = 85.4 Hz; $^2J_{Fa,Fb}$ = 320 Hz.

^{31}P NMR, δ: 23.7 s (1P); −8.3 quin,m (2P, $^2J_{P,F}$ = 80 Hz).

^{1}H NMR, δ: 7.9 m (3CH, $^3J_{H,H}$ = 7.6 Hz); 7.6 m (6CH); 7.5 m (6CH); 7.3 m (CH); 7.2 t (2CH, $^3J_{H,H}$ = 7.6 Hz); 6.9 d, m (2CH, $^3J_{H,H}$ = 7.1 Hz); 4.61 d (CH_2P, $^2J_{P,H}$ = 14.7 Hz).

3.6. Trihexyl(tetradecyl)phosphonium bis[bis(pentafluoroethyl) phosphinyl]imide, $[(C_6H_{13})_3P(C_{14}H_{29})]^+$ $[(C_2F_5)_2P(O)]_2N^-$

To the stirred solution of 4.11 g (7.9 mmol) trihexyl(tetradecyl)phosphonium chloride, $[(C_6H_{13})_3P(C_{14}H_{29})]^+Cl^-$ in 13 mL of ethanol, 4.62 g (7.9 mmol) bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ in 20 mL of water was added. The mixture was kept stirring for 1 h. After the ethanol was distilled off in vacuum, the liquid material was washed with water three times. After drying, 7.24 g of a liquid material was obtained. Yield 86%.

Anal. Calcd for $C_{40}H_{68}F_{20}NO_2P_3$: C 44.99; H 6.42; N 1.31. Found: C 44.83; H 5.88; N 1.62.

^{19}F NMR, δ: −81.04 s ($4CF_3$); −123.6 m ($4CF_a$); −126.7 m ($4CF_b$); $^2J_{P,Fa}$ = 74 Hz; $^2J_{P,Fb}$ = 80 Hz; $^2J_{Fa,Fb}$ = 318 Hz.

^{31}P NMR, δ: 34.73 m (1P); −8.3 quin,m (2P, $^2J_{P,F}$ = 80 Hz).

^{1}H NMR, δ: 2.01–2.08 m ($4CH_2$); 1.4–1.54 m ($8CH_2$); 1.28–1.33 m ($16CH_2$); 0.86–0.91 m ($4CH_3$).

3.7. Guanidinium bis[bis(pentafluoroethyl)phosphinyl]imide, $[(NH_2)_3C]^+[(C_2F_5)_2P(O)]_2N^-$

To the stirred solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (1.8 g, 3.1 mmol) in 5 mL water solid guanidinium carbonate was slowly added, $[(NH_2)_3C]_2{}^+CO_3{}^{2-}$ (0.28 g, 1.5 mmol) and the reaction mixture was cooled in an ice bath to 0 °C. The reaction mixture was stirred at that temperature for 30 min. The precipitate was separated by filtration and washed with cold water three times. After drying, 1.68 g of a very hygroscopic white solid was obtained. Yield 84%, m.p. 52 °C.

Anal. Calcd for $C_9H_6F_{20}N_4O_2P_2$: C 16.78; H 0.94; N 8.70. Found: C 16.83; H 0.86; N 8.54.

^{19}F NMR, δ: −81.2 s ($4CF_3$); −123.9 m ($4CF_a$); −126.8 m ($4CF_b$); $^2J_{P,Fa}$ = 85.8 Hz; $^2J_{P,Fb}$ = 80.6 Hz; $^2J_{Fa,Fb}$ = 316 Hz.

^{31}P NMR, δ: −6.5 quin,m (2P, $^2J_{P,F}$ = 81.7 Hz).

^{1}H NMR, δ: 5.92 br.s ($3NH_2$).

3.8. 1-n-Butyl-1-methylpyrrolidinium bis[bis(pentafluoroethyl) phosphinyl]imide $[C_9H_{20}N]^+$ $[(C_2F_5)_2P(O)]_2N^-$

To the stirred solution of 1-*n*-Butyl-1-methylpyrolidinium chloride, (1.46 g, 8.2 mmol) $[C_9H_{20}N]^+Cl^-$ in 4 mL of water, a solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (4.83 g, 8.2 mmol) in 10 mL of water was slowly added. The reaction proceeds within few minutes. The water insoluble material was extracted with CH_2Cl_2 and washed with water three times. After drying, 5 g of liquid 1-*n*-butyl-1-methylpyrrolidinium FPI was obtained (84%).

Anal. Calcd for $C_{17}H_{20}F_{20}N_2O_2P_2$: C 28.11; H 2.78; N 3.86. Found: C 28.15; H 2.25; N 4.22.

^{19}F NMR, δ: −81 s ($4CF_3$); −123.7 m ($4CF_a$); −126.8 m ($4CF_b$); $^2J_{P,Fa}$ = 78.2 Hz; $^2J_{P,Fb}$ = 89 Hz; $^2J_{Fa,Fb}$ = 318 Hz.

^{31}P NMR, δ: −7.9 quin,m (2P, $^2J_{P,F}$ = 80.6 Hz).

^{1}H NMR, δ: 3.38 m ($2CH_2$); 3.21 m (CH_2); 2.92 s (CH_3); 2.13 m ($2CH_2$); 1.70 m (CH_2); 1.35 q,t (CH_2, $^3J_{H,H}$ = 7.4 Hz); 0.95 t (CH_3, $^3J_{H,H}$ = 7.3 Hz).

3.9. N-butylpyridinium bis[bis(pentafluoroethy)lphosphinyl]imide, $[C_9H_{14}N]^+[(C_2F_5)_2P(O)]_2N^-$

A solution of N-butylpyridinium chloride, $[C_9H_{14}N]^+Cl^-$ (2.03 g, 11.8 mmol) in 5 mL water was added to a vigorously stirred solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (7 g, 11.9 mmol) in 10 mL water. The reaction mixture was diluted with 25 mL water and stirred additionally 30 min. The resulting solid precipitate was collected by filtration and washed three times with water until a pH 6–7 was obtained and the test for chloride with $AgNO_3$ was negative. After drying in vacuum for 18 h at 80 °C, a white solid material (8 g) was obtained. Yield 94%, m.p. 49 °C.

Anal. Calcd for $C_{17}H_{14}F_{20}N_2O_2P_2$: C 28.35; H 1.96; N 3.89. Found: C 27.91; H 1.82; N 3.88.

^{19}F NMR, δ: −81.1 s ($4CF_3$); −123.7 m ($4CF_a$); −126.8 m ($4CF_b$); $^2J_{P,Fa}$ = 69 Hz; $^2J_{P,Fb}$ = 79 Hz; $^2J_{Fa,Fb}$ = 314 Hz.

^{31}P NMR, δ: −8.2 quin,m (2P, $^2J_{P,F}$ = 79.8 Hz).

^{1}H NMR, δ: 8.67 d (2CH, $^3J_{H,H}$ = 6.1 Hz); 8.48 t (CH, $^3J_{H,H}$ = 7.8 Hz); 8 t (2CH, $^3J_{H,H}$ = 6.6 Hz); 4.5 t (CH_2, $^3J_{H,H}$ = 7.6 Hz); 1.92 m (CH_2); 1.35 q,t (CH_2, $^3J_{H,H}$ = 7.4 Hz); 0.94 t (CH_3, $^3J_{H,H}$ = 7.4 Hz).

3.10. 1-Butyl-3,5-dimethylpyridinium bis[bis(pentafluoroethy) lphosphinyl]imide, $[C_{11}H_{18}N]^+$ $[(C_2F_5)_2P(O)]_2N^-$

To the stirred solution of 1-butyl-3,5-dimethylpyridinium chloride, $[C_{11}H_{18}N]^+Cl^-$ (2.11 g, 10.5 mmol) in 5 mL of water, bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (6.2 g, 10.6 mmol) in 10 mL of water was added at room temperature. After 10 min two phases were formed. The reaction mixture was stirred for 30 min. The upper phase, containing unreacted starting material and HCl was removed from the mixture. The bottom phase was collected and approximately equal volume of CH_2Cl_2 was added. This solution was transferred to a separatory funnel and washed several times with water. The CH_2Cl_2 solvent was evaporated and the residue was dried for 18 h in vacuum at 60 °C resulting in a liquid material (6.9 g). Yield 88%.

Anal. Calcd for $C_{19}H_{18}F_{20}N_2O_2P_2$: C 30.5; H 2.42; N 3.74. Found: C 29.90; H 2.24; N 3.72.

^{19}F NMR, δ: −81.1 s ($4CF_3$); −123.7 m ($4CF_a$); −126.8 m ($4CF_b$); $^2J_{P,Fa}$ = 74 Hz; $^2J_{P,Fb}$ = 83 Hz; $^2J_{Fa,Fb}$ = 314 Hz.

^{31}P NMR, δ: −8.2 quin,m (2P, $^{2}J_{P,F}$ = 79.8 Hz).
^{1}H NMR, δ: 8.35 s (2CH); 8.11 s (CH); 4.4 t (CH_2, $^{3}J_{H,H}$ = 7.6 Hz); 2.45 s ($2CH_3$); 1.92 m (CH_2); 1.34 q,t (CH_2, $^{3}J_{H,H}$ = 7.4 Hz); 0.94 t (CH_3, $^{3}J_{H,H}$ = 7.4 Hz).

3.11. 1-Ethyl-3-methylimidazolium bis[bis(pentafluoroethy)lphosphinyl]imide $[C_6H_{11}N_2]^+$ $[(C_2F_5)_2P(O)]_2N^-$

A solution of 1-ethyl-3-methylimidazolium chloride, $[C_6H_{11}N_2]^+Cl^-$ (2.49 g, 16.9 mmol) in 10 mL of water was added to the solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (9.93 g, 16.9 mmol) in 30 mL of water at room temperature. After 1 h stirring the water insoluble material was extract with CH_2Cl_2 and washed few times with water containing of few mg of K_2CO_3. After evaporation of CH_2Cl_2 the residue was dried 24 h in vacuum at 70 °C. A liquid material (9.8 g) was obtained. Yield 83%.

Anal. Calcd for $C_{14}H_{11}F_{20}N_3O_2P_2$: C 24.19; H 1.59; N 6.04. Found: C 24.12; H 1.6; N 6.16.

^{19}F NMR, δ: −81.19 s ($4CF_3$); −123.7 m ($4CF_a$); −126.8 m ($4CF_b$); $^{2}J_{P,Fa}$ = 76.3 Hz; $^{2}J_{P,Fb}$ = 82.4 Hz; $^{2}J_{Fa,Fb}$ = 326 Hz.
^{31}P NMR, δ: −7.9 quin,m (2P, $^{2}J_{P,F}$ = 80 Hz).
^{1}H NMR, δ: 8.46 s (CH); 7.38 s (CH); 7.32 s (CH); 4.15 q (CH_2, $^{3}J_{H,H}$ = 7.3 Hz); 3.80 s (CH_3); 1.44 t (CH_3, $^{3}J_{H,H}$ = 7.1 Hz).

3.12. 1-Butyl-3-methylimidazolium bis[bis(pentafluoroethy)lphosphinyl]imide, $[C_8H_{15}N_2]^+$ $[(C_2F_5)_2P(O)]_2N^-$

To the stirred solution of 1-butyl-3-methylimidazolium chloride, $[C_8H_{15}N_2]^+Cl^-$ (1.13 g, 6.4 mmol) in 5 mL of water, the solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$, (3.78 g, 6.4 mmol) in 10 mL of water was slowly added at room temperature. The mixture was left stirring for 30 min and the bottom liquid phase was extracted with CH_2Cl_2 and washed with water until the test for chloride was negative. After evaporation of CH_2Cl_2, the residue was dried 48 h at 70 °C in vacuum. 3.65 g of pure 1-butyl-3-methylimidazolium FPI was obtained. Yield 79%.

Anal. Calcd for $C_{16}H_{15}F_{20}N_3O_2P_2$: C 26.57; H 2.09; N 5.81. Found: C 26.96; H 2.55; N 5.76.

^{19}F NMR, δ: −81.2 s ($4CF_3$); −123.7 m ($4CF_a$); −126.8 m ($4CF_b$); $^{2}J_{P,Fa}$ = 76.3 Hz; $^{2}J_{P,Fb}$ = 85.4 Hz; $^{2}J_{Fa,Fb}$ = 329.6 Hz.
^{31}P NMR, δ: −8.08 quin,m (2P, $^{2}J_{P,F}$ = 79.5 Hz).
^{1}H NMR, δ: 8.42 s (CH); 7.35 s (CH); 7.31 s (CH); 4.1 t (CH_2, $^{3}J_{H,H}$ = 7.38 Hz); 3.80 s (CH_3); 1.79 quin (CH_2, $^{3}J_{H,H}$ = 7.4 Hz); 1.32 q,t (CH_2, $^{3}J_{H,H}$ = 7.4 Hz); 0.92 t (CH_3, $^{3}J_{H,H}$ = 7.4 Hz).

3.13. 1-Hexyl-3-methyl imidazolium bis[bis(pentafluoroethyl)phosphinyl]imide, $[C_{10}H_{19}N_2]^+$ $[(C_2F_5)_2P(O)]_2N^-$

To the stirred solution of 1-hexyl-3-methylimidazolium chloride, $[C_{10}H_{19}N_2]^+Cl^-$ (2.8 g, 13.8 mmol) in 5 mL of water a solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (8.10 g, 13.8 mmol) in 30 mL of water was slowly added at room temperature. After 1 h stirring the water insoluble material was extract with CH_2Cl_2 and washed few times with water containing a few mg of K_2CO_3. After evaporation of CH_2Cl_2 and drying the residue 24 h in vacuum at 70 °C, 8.4 g of a liquid material was obtained. Yield 81%.

Anal. Calcd for $C_{18}H_{19}F_{20}N_3O_2P_2$: C 28.78; H 2.55; N 5.59. Found: C 29.11; H 2.65; N 6.07.

^{19}F NMR, δ: −81.16 s ($4CF_3$); −123.7 m ($4CF_a$); −126.8 m ($4CF_b$); $^{2}J_{P,Fa}$ = 76.3 Hz; $^{2}J_{P,Fb}$ = 85.4 Hz; $^{2}J_{Fa,Fb}$ = 329.6 Hz.
^{31}P NMR, δ: −8 quin,m (2P, $^{2}J_{P,F}$ = 79.5 Hz).
^{1}H NMR, δ: 8.4 s (CH); 7.35 s (CH); 7.31 s (CH); 4.1 t (CH_2, $^{3}J_{H,H}$ = 7.4 Hz); 3.80 s (CH_3); 1.9 t,t (CH_2, $^{3}J_{H,H}$ = 6.8 Hz); 1.3 m ($3CH_2$); 0.87 t (CH_3, $^{3}J_{H,H}$ = 6.4 Hz).

3.14. 1-Decyl-3-methyl imidazolium bis[bis(pentafluoroethyl)phosphinyl]imide, $[C_{14}H_{27}N_2]^+$ $[(C_2F_5)_2P(O)]_2N^-$

To the stirred solution of 1-decyl-3-methylimidazolium chloride, $[C_{14}H_{27}N_2]^+Cl^-$ (3.08 g, 11.8 mmol) in 15 mL of water a solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (7 g, 11.9 mmol) in 5 mL of water was slowly added at room temperature. After 30 min stirring the water insoluble material was extracted with CH_2Cl_2 and washed few times with water containing a few mg of K_2CO_3. After evaporation of CH_2Cl_2 and drying 16 h in vacuum at 60 °C, 8.98 g of a liquid material was obtained. Yield 94%.

Anal. Calcd for $C_{22}H_{27}F_{20}N_3O_2P_2$: C 32.73; H 3.37; N 5.20. Found: C 32.17; H 3.32; N 5.08.

^{19}F NMR, δ: −81.15 s ($4CF_3$); −123.7 m ($4CF_a$); −126.8 m ($4CF_b$); $^{2}J_{P,Fa}$ = 73.3 Hz; $^{2}J_{P,Fb}$ = 82.4 Hz; $^{2}J_{Fa,Fb}$ = 326.5 Hz.
^{31}P NMR, δ: −8 quin,m (2P, $^{2}J_{P,F}$ = 79.5 Hz).
^{1}H NMR, δ: 8.4 s (CH); 7.36 s (CH); 7.32 s (CH); 4.09 t (CH_2, $^{3}J_{H,H}$ = 7.4 Hz); 3.80 s (CH_3); 1.26 s ($8CH_2$); 0.86 t (CH_3, $^{3}J_{H,H}$ = 6.4 Hz).

3.15. 1-Octadecyl-3-methylimidazolium bis[bis(pentafluoroethyl)phosphinyl]imide, $[C_{22}H_{43}N_2]^+$ $[(C_2F_5)_2P(O)]_2N^-$

A solution of 1-octadecyl-3-methylimidazolium chloride, $[C_{22}H_{43}N_2]^+Cl^-$ (3.25 g, 8.7 mmol) in 10 mL of ethanol was added at room temperature to the stirred solution of bis[bis(pentafluoroethyl)phosphinyl]imide, $HN[P(O)(C_2F_5)_2]_2$ (5.1 g, 8.7 mmol) in 10 mL of ethanol. The mixture was left stirring for 0.5 h. The solvent was removed in vacuum and the residue was washed with water until the test for chloride was negative. The obtained substance was dried 48 h at 60 °C in vacuum and 6.51 g of pure 1-octadecyl-3-methylimidazolium FPI was obtained. Yield 81%.

Anal. Calcd for $C_{30}H_{43}F_{20}N_3O_2P_2$: C 39.18; H 4.71; N 4.57. Found: C 40.19; H 5.38; N 4.57.

^{19}F NMR, δ: −81.1 s ($4CF_3$); −123.7 m ($4CF_a$); −126.2 m ($4CF_b$); $^{2}J_{P,F}$ = 74.2 Hz; $^{2}J_{P,F}$ = 86.4 Hz; $^{2}J_{Fa,Fb}$ = 317 Hz.
^{31}P NMR, δ: −8 quin,m (2P, $^{2}J_{P,F}$ = 79.5 Hz).
^{1}H NMR, δ: 8.4 s (CH); 7.35 m (CH); 7.32 m (CH); 4.1 t (CH_2, $^{3}J_{H,H}$ = 7.38 Hz); 3.80 s (CH_3); 1.8 q,t (CH_2, $^{3}J_{H,H}$ = 7.4 Hz); 1.26 m ($15CH_2$); 0.87 t (CH_3, $^{3}J_{H,H}$ = 6.8 Hz).

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