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Ecofriendly Fast Synthesis of Hydrophilic Poly(ethyleneglycol)-Ionic Liquid Matrices for Liquid-Phase Organic Synthesis.

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Abstract:

New, hydrophilic poly(ethyleneglycol)-ionic liquids have been synthesized and investigated, based on 1,3-disubstituted imidazolium cations and fluorinated anions (BF_4^-, PF_6^-, $(CF_3SO_2)_2N^-$, or NTf_2^-). A series of typical solvent-free reactions have been safely realized using a focused microwave reactor for the preparation of imidazolium chloride precursors in yields ranging from 73 to 94% followed by quantitative anion metathesis exchanges. The poly(ethyleneglycol)-ionic liquid matrices were also characterized by NMR (^1H, ^{13}C), mass spectrometry (MS), and their dynamic viscosity was determined at 25 °C. These poly(ethyleneglycol)-ionic liquid phases (PEG-ILPs) as task-specific ionic liquids are promising tools for synthetic applications in liquid-phase combinatorial chemistry.

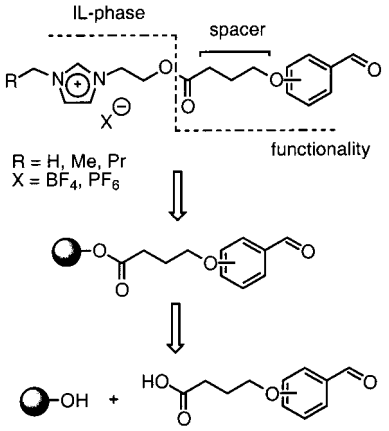

Figure 1. **Grafted ionic liquid phases for liquid-phase organic synthesis (LPOS).**

Introduction

Owing to their interesting chemical and physical properties, room-temperature ionic liquids[1] (RTILs) are attracting increasing interest as solvent alternatives, mainly as a substitute for conventional volatile organic compounds (VOCs). They have been also referred as "designer solvents";[2] by a judicious combination of cation and anion and changes in IL, physical properties[3] have been accomplished by altering the length of alkyl chain attached to the organic cation,[4] allowing for fine-tuning hydrophobicity, viscosity, and melting points. Because of their lack of vapor pressure and ease of reuse, ILs have been more and more applied in noncatalytic reactions[5] (in this case the IL is used as a green solvent) and catalytic reactions.[6]

Recent work from our laboratory has shown that benzaldehyde bound to ILs (Figure 1) can be used as a novel matrix in liquid-phase organic synthesis[7] potentially compatible with high-throughput synthesis and automation technology.[8] The advantages offered by the use of ionic liquid phases (ILPs) in liquid-phase organic synthesis (LPOS) are the following: (1) ILPs allow standard analytical methods (NMR, TLC) to be used to monitor reaction progress, (2) the routine product isolation is simple because the side product is removed by extraction and washings from the separated IL-phase, (3) it is possible to reuse the IL-phase in another cycle of synthesis, and (4) the IL-phases are easy to prepare and are compatible with a broad spectrum of reactions.

We report in this contribution our results in the preparation of new hydrophilic ionic liquid-phases on which poly-

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(ethyleneglycol) units[9] (PEG) are grafted, using solventless reaction conditions, assisted by focused microwave technology.[10]

Results and Discussion

Liquid imidazolium salts are generally obtained by anion exchange from imidazolium halide precursors. For the preparation of 1,3-dialkyl imidazolium halides via conventional heating methods in refluxing solvents, the major drawbacks of these common methods are the long reaction time (12−72 h) to afford reasonable yields and also the use of a large excess of the irritant volatile alkyl halides/organic solvents as reaction medium. In view of our general interest in solventless organic synthesis mediated by microwave ($\mu\omega$), we decided to explore the preparation of the imidazolium chlorides **3** and **6** using solvent-free conditions with a focused microwave[11] reactor (Synthewave 402).[12] This reactor operates with an adjustable power range 0−300 W and may be monitored either in power or in temperature or both.

For this study, the commercial 1-alkyl imidazoles employed were 1-methyl imidazole **1a** (R = H) and 1-butyl imidazole **1b** (R = Pr); the chloro alcohols **2** and **5** used were 2-chloroethanol **2a** (n = 1), 2-(2-chloroethoxy)ethanol **2b** (n = 2), 2-[2-(2-chloroethoxy)ethoxy]ethanol **2c** (n = 3), and 3-chloropropanol **5**. We have examined the effect of microwave power on a series of reactions using the chloro alcohols **2(a−c)**, **5**, and 1-alkyl imidazole **1(a,b)** as reactants. Under focused microwave irradiation, the imidazolium salt formed readily, and this increases the polarity of the reaction mixture, thereby increasing the rate of microwave absorption. At elevated power levels, it is possible to observe evaporation of chloro alcohol **2a** (or **5**) and partial decomposition of the imidazolium salt by microwave absorption, which results in lower yields. To overcome this problem, the reactions were conducted with intermittent microwave heating and continuous mixing at a moderate power level. For example (Table 1), the 1-(2-hydroxy-ethyl)-3-methylimidazolium chloride ([PEG$_1$mim][Cl]) **3a** and the 1-(3-hydroxy-propyl)-3-methylimidazolium chloride ([hypmim][Cl]) **6** were obtained under irradiation after 5 min at 20% power level in the first irradiation period (this first period was necessary to reach the plateau value of the bulk-imposed temperature at 180 °C), and then this microwave heating period was repeated at the same power level.

Results of the synthesis of a series of imidazolium chloride **3(a−e)** and **6** using optimized microwave reaction conditions (temperature, reaction time, and power level) are outlined in Table 1.

Table 1. **Optimized reaction conditions for the preparation of (PEG)$_n$-imidazolium chlorides 3(a−e) and 6 using a focused microwave reactor (Synthewave 402, Prolabo)**

salt	R	n	reaction conditions: MW/time/temp/power level (min/°C/%)	yield[a] (%)
3a[b]	H	1	(5/180/20) + (5/180/20)	94[d]
3b[c]	H	2	(2/90/20) + (4/120/5) + (24/120/15)	93
3c[c]	H	3	(2/90/20) + (4/120/5) + (24/120/15)	95
3d[c]	Pr	1	(2/90/20) + (4/120/5) + (24/120/15)	74
3e[c]	Pr	3	(2/90/20) + (4/120/5) + (24/120/15)	73
6[c]	H	-	(5/180/20) + (5/180/20)	94

[a] Isolated yields. [b] **3a:** mp = 86−88 °C. [c] At room temperature, the imidazolium chloride is liquid. [d] Recrystallization from anhydrous acetonitrile gave **3a** in 80% yield as colourless needles.

It should be noted that the preparation of the imidazolium chlorides **3(b−e)** was optimized using three irradiation heating periods with continuous stirring: 2 min were necessary to reach 90 °C at 20% power level, followed by 4 min at 120 °C (P = 5%), and then at the same reaction temperature (120 °C), the reaction mixture was irradiated for 24 min at 15% power level.

All the synthesized imidazolium chlorides **3** and **6** remain liquid for weeks (excepted for **3a** which crystallizes at room temperature at the end of the reaction); they appear to be very hygroscopic and hence were stored in an inert atmosphere at 4 °C after drying under high vacuum (10^{-2} Torr) at 60 °C for 8 h. Their purity[13] has been established by acquisition of clean ^{1}H and ^{13}C NMR as well as by FAB-MS (the purity of the chloride salt can be also controlled by the simple colorimetric Seddon's method[14]), and water contents were measured by Karl Fisher titration.

It is probably noteworthly here that the imidazolium salts **3(a−e)** and **6** were efficiently synthesized in yields ranging from 73 to 96% by simple exposure of neat reactants in the reactor to microwaves. This solventless method requires few minutes of reaction time (10−30 min) in contrast to several hours under classical heating conditions which use an excess of reactants.

In our chemical applications of ionic liquids for liquid-phase organic synthesis, the length of the alkyl chain attached to the imidazolium cation influences the physical properties (viscosity, hydrophobicity) of the (PEG)$_n$-ionic liquid phases (PEG-ILPs). It appears also that the counteranion has an effect on these physical properties. Driven by the need to find new PEG-ILPs with various viscosity and miscibility[15] properties, we have prepared a new series of ILPs by anion metathesis exchange of the previous imidazolium chlorides **3(a−e)** and **6**. For the anion-exchange reactions (Scheme 1), the corresponding weakly coordinating anions used were BF_4^-, PF_6^-, and bis((trifluoromethyl)sulfonyl)amide anion[16] [NTf_2] from the respective commercially available starting salts NH_4BF_4, KPF_6, and $LiN(CF_3SO_2)_2$ (or $LiNTf_2$). All the anion-exchange reactions were carried out in dry acetonitrile

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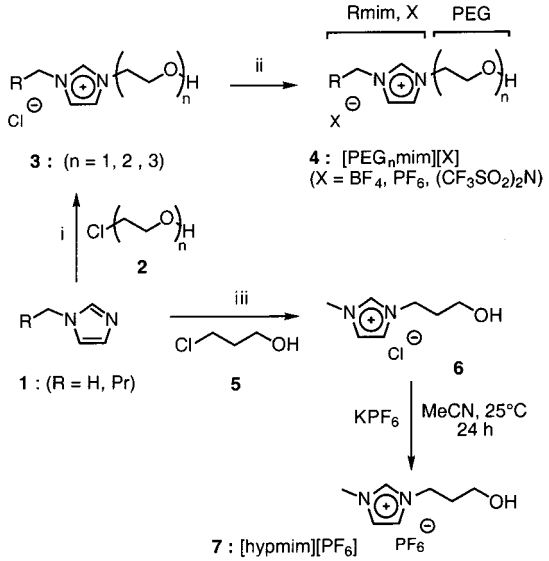
Scheme 1[a]



[a] *Reagents and reaction conditions:* (i) **3** 1 equiv, $\mu\omega$, 120 or 180 °C, 10−30 min. (ii) NH_4BF_4 or KPF_6 or $LiN(CF_3SO_2)_2$ ($LiNTf_2$) 1 equiv, dry MeCN, 25 °C, 24 h. (iii) **5** 1 equiv, $\mu\omega$, 10 min, 180 °C.

Table 2. **Dynamic viscosity at 25 °C (cP (0.01 g·cm^{-1}·s^{-1}) of salts 4(a−m) and 7 which are liquids at 25 °C after anion metathesis exchange**

salt	R	*n*	X^-	abreviation of cation	yield[a] (%)	viscosity[b] (cP)
4a	H	1	BF_4	[PEG$_1$mim][c]	98	86
4b	H	1	PF_6	[PEG$_1$mim][c]	98	336
4c	H	1	NTf_2	[PEG$_1$mim][c]	91	541
4d	H	2	BF_4	[PEG$_2$mim][d]	98	201
4e	H	2	PF_6	[PEG$_2$mim][d]	95	370
4f	H	2	NTf_2	[PEG$_2$mim][d]	92	922
4g	H	3	BF_4	[PEG$_3$mim][e]	92	391
4h	H	3	PF_6	[PEG$_3$mim][e]	95	864
4i	H	3	NTf_2	[PEG$_3$mim][e]	83	2249
4j	Pr	1	BF_4	[PEG$_1$bim][f]	83	204
4k	Pr	1	PF_6	[PEG$_1$bim][f]	86	542
4l	Pr	1	NTf_2	[PEG$_1$bim][f]	99	—[i]
4m	Pr	3	PF_6	[PEG$_3$bim][g]	98	923
7	H	-	PF_6	[hypmim][h]	90	538

[a] Isolated yield of salt. [b] Dynamic viscosity (cP) at 25 °C, estimated error = ±5%. [c] [PEG$_1$mim]: 1-(2-hydroxy-ethyl)-3-methylimidazolium. [d] [PEG$_2$mim]: 1-[2-(2-hydroxy-ethoxy)-ethyl]-3-methylimidazolium. [e] [PEG$_3$mim]: 1-{2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethyl}-3-methylimidazolium. [f] [PEG$_1$bim]: 3-butyl-1-(2-hydroxy-ethyl)imidazolium. [g] [PEG$_3$bim]: 3-butyl-1-{2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethyl}imidazolium. [h] [hypmim]: 1-(3-hydroxy-propyl)-3-methyl-imidazolium. [i] mp ≈ 30 °C.

stirred at room temperature under nitrogen for 24 h with conventional glassware. After filtration on a pad of Celite to remove NH_4Cl or KCl or LiCl followed by evaporation of the solvent in vacuo, the new PEG-ILPs **4(a−n)** and **7** were isolated in good yields (83−98%) (Table 2) as mobile oils at room temperature (excepted for **4l**, but this matrix has a low melting point, mp ≈ 30 °C). Then, the PEG-ILPs **4** and **7** were dried under high vacuum at 80 °C for 12 h without decomposition.

The dynamic viscosities of the $(PEG)_n$-ILPs (Table 2) are difficult to correlate with the chemical composition. Usually, the viscosities of the room-temperature ionic liquids[17] are governed by van der Waals interactions and H-bonding. It appears from the examination of the same imidazolium series that the viscosity depends on the nature of the anions. For example, with the 3-methylimidazolium series **4(a−c)** (**4a** : [PEG$_1$mim][BF_4], **4b** : [PEG$_1$mim][PF_6], **4c**: [PEG$_1$mim]-[NTf_2]), the viscosity increases as follows: $BF_4^- < PF_6^- < NTf_2^-$. Alkyl chain lengthening in the N-3 position of the imidazolium moiety has the same effect (**4(a−c)** and **4(j−l)** series), due to reduced rotation freedom. The high viscosities obtained with the NTf_2^- salts in each series are probably due to strong H-bonding between the hydroxyl group of the N-1 side chain attached to the imidazolium cation with the NTf_2^- counteranion which has moderate basicity. The NTf_2^- anion[18] appears more coordinating than the PF_6^- and BF_4^- anions. In the same way, the poly(ethyleneglycol) unit lengthening in N-1 position of the imidazolium cation makes also the ILPs more viscous (from PEG$_1$mim to PEG$_3$mim series). The salt **4a** ([PEG$_1$mim][BF_4]) presents the lowest dynamic viscosity as it combines minimal anion weight with weak coordinating properties and the shortest side chain for the cation with moderate cation weight; in this case it seems possible that the van der Waals interactions dominates the H-bonding.

In summary, the poly(ethyleneglycol) ionic liquid-phases $(PEG)_n$-ILPs based on imidazolium cation and three different anions have been studied and prepared in two steps with good yields: the first step involves an efficient solventless quaternization under focused microwave irradiations followed by a facile anion metathesis exchange which produces the expected task-specific ionic liquids.[19] Future studies are directed to the evaluation and the scope of PEG-ILPs in combinatorial chemistry[20] mediated by microwave irradiations.[21]

Experimental Section

General. Melting points were determined on a Kofler melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC 300 P (300 MHz) spectrometer, ^{13}C NMR spectra on a Bruker AC 300 P (75 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Unless otherwise stated, δ values refer to singlet absorptions. Data are given in the following order: δ value, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), number of protons, coupling constants *J* are given in Hertz. The mass spectra (HRMS) were taken on a Varian MAT 311 at a ionizing potential of 70 eV in the Centre Régional de Mesures Physiques de l'Ouest (CRMPO, Rennes). For the dynamic viscosity, the measure-

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ments were carried out at 25 °C on the AR 1000 microviscosimeter (TA Instruments) with a stainless cone plate geometry (diameter, 40 mm; angle, 1° 1′). A flow procedure was applied from 0.06 to 200 s^{-1} in 3 min with 20 points by decade. Water contents were determined by Karl Fischer coulometry using a Metrohm 652 KF coulometer. Solvents were evaporated with a Buchi rotary evaporator. All reagents were purchased from Acros, Aldrich, Avocado, and were used without purification. 1-Methylimidazole **1a** and 1-butylimidazole **1b** were distilled from CaH_2 prior to use.

Standard Procedure Using a Focused Microwave Oven for $(PEG)_n$-Imidazolium Chlorides 3(a−c) and 6. *1-(2-Hydroxy-ethyl)-3-methylimidazolium Chloride [PEG_1mim][Cl] (**3a**).* A mixture of freshly distilled 1-methylimidazole **1a** (15 g, 182.6 mmol) and 2-chloroethanol **2a** (14.70 g, 182.6 mmol) was placed in a cylindrical quartz reactor (Ø = 4 cm). The reactor was then introduced into a Synthewave 402 Prolabo microwave reactor [2.45 GHz, adjusted power within the range 0−300 W and a waveguide (single mode T_{01}) fitted with a stirring device and an IR temperature detector]. The stirred liquid mixture was irradiated twice at 20% power level for 5 min at 180 °C. Then the mixture was allowed to cool, and a white solid formed rapidly (∼5 min.) at 25 °C. The crude solid formed was filtered off (under nitrogen), washed successively with anhydrous ether (3 × 30 mL) and dry acetonitrile (2 × 20 mL) and vacuum-dried in a desiccator over $CaCl_2$ for 1 h. The solid salt [PEG_1-mim][Cl] **3a** was further dried under high vacuum (10^{-2} Torr) at 60 °C for 8 h and was stored (23.44 g, 94% yield) in the dark at 4 °C under nitrogen. Recrystallization from dry MeCN gave **3a** in 80% yield as colourless needles (mp = 86−88 °C).

Standard Experimental Procedure for the Preparation of Liquid $(PEG)_n$-Imidazolium Matrix 4 and 7 by Anion Exchange. *(a) From NH_4BF_4 and KPF_6.* A mixture of $(PEG)_n$-imidazolium chloride **3** or **6** (1 equiv) and NH_4BF_4 or KPF_6 (1 equiv) in dry acetonitrile (1:10 w/v) was stirred vigorously at 25 °C under nitrogen for 24 h. After elimination of the precipitated salt (NH_4Cl or KCl) on a filter paper, the resulting filtrate was quickly refiltered through a short column of Celite to remove some residual salt and finally concentrated by rotary evaporation that gave a mobile liquid. The ionic liquid phase **3** or **7** with BF_4^- or PF_6^- as counteranion were further dried under high vacuum (10^{-2} Torr) at 60 °C for 6 h. It is recommended to handle the $(PEG)_n$-ionic liquid phase **3** or **7** in the dark under an inert atmosphere at 4 °C.

(b) From Lithium Bis((trifluoromethyl)sulfonyl)amide $LiNTf_2$. The $(PEG)_n$-ionic liquid phases **4c**, **4f, 4i**, and **4l** were prepared from a solution of $(PEG)_n$-imidazolium chloride **3** (1 equiv) and lithium bis((trifluoromethyl)sulfonyl)amidure (1 equiv) in anhydrous acetonitrile (1:10 w/v). The solution was magnetically stirred at 25 °C under nitrogen for 24 h. After removal of solvent under reduced pressure, dry acetone was added to the crude reaction mixture for compounds **4c**, **4f**, and **4i** (or dry methylene chloride for **4l**). The resulting solution was rapidly filtered through a short column of Celite to remove the precipitated LiCl, then the filtrate was refiltered to ensure the complete elimination of LiCl, and the solvent was removed on a Rotavapor. For drying, the same procedure was used as for the $(PEG)_n$-ionic liquid phases obtained from NH_4BF_4 or KPF_6.

*Selected spectral data of 1-(2-hydroxy-ethyl)-3-methylimidazolium tetrafluoroborate [PEG_1mim][BF_4] (**4a**):* ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS) δ 3.92 (t, 3H, J = 4.8 Hz); 4.01 (s, 3H); 4.22 (br s, 1H, OH); 4.38 (t, 3H, J = 5.1 Hz); 7.63 (t, 1H, J = 1.55 Hz, H-5). 7.68 (t, 1H, J = 1.58 Hz, H-4); 8.85 (broad s, 1H, H-2). ^{13}C NMR (75 MHz, $(CD_3)_2$-CO, TMS) δ 36.40 (q, J = 144 Hz); 52.82 (t, J = 144 Hz); 60.95 (t, J = 143 Hz); 123.71 (dm, J = 203 Hz, C-5); 124.34 (dm, J = 203 Hz, C-4); 137.71 (dd, J = 222 Hz, C-2). HRMS *m*/*z*: 127.0871 found (calcd for $C_6H_{11}N_2O$, M^+ requires: 127.0871).

*1-(2-Hydroxy-ethyl)-3-methylimidazolium hexafluorophosphate [PEG_1mim][PF_6] (**4b**).* ^{1}H NMR (300 MHz, $(CD_3)_2$-CO, TMS) δ 3.92 (t, 3H, J = 4.8 Hz); 4.01 (s, 3H); 4.22 (br s, 1H, OH); 4.38 (t, 3H, J = 5.1 Hz); 7.63 (t, 1H, J = 1.55 Hz, H-5). 7.68 (t, 1H, J = 1.58 Hz, H-4); 8.85 (broad s, 1H, H-2). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, TMS) δ 36.40 (q, J = 144 Hz); 52.82 (t, J = 144 Hz); 60.95 (t, J = 143 Hz); 123.71 (dm, J = 203 Hz, C-5); 124.34 (dm, J = 203 Hz, C-4); 137.71 (dd, J = 222 Hz, C-2). HRMS *m*/*z*: 399.1384 found (calcd for $C_{12}H_{22}N_4O_2F_6P$, $[2C^+, PF_6^-]^+$ requires: 399.1385).

*1-[2-(2-Hydroxy-ethoxy)-ethyl]-3-methylimidazolium hexafluorophosphate [PEG_2mim][PF_6] (**4e**).* ^{1}H NMR (300 MHz, $(CD_3)_2CO$ TMS) δ 3.63 (dtd, 4H, J = 24.3, 5.8, 0.86 Hz); 3.81 (br s, 1H, OH); 3.90 (t, 2H, J = 6 hz); 4.00 (s, 3H); 4.48 (t, 2H, J = 5.7 Hz); 7.60 (t, 1H, J = 1.7 Hz, H-4); 7.70 (t, 1H, J = 1.7 Hz, H-5); 8.90 (s, 1H, H-2). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, TMS) δ 36.55 (q, J = 144 Hz); 50.43 (t, J = 144 Hz); 61.78 (tt, J = 142, 2.6 Hz); 69.30 (tqt, J = 144, 3.1 Hz); 73.33 (tqt, J = 141, 2.2 Hz); 123.93; 124.28 (dm, J = 204 Hz, C-4, C-5); 137.89 (dm, J = 122 Hz, C-2). HRMS *m*/*z*: 487.1899 found (calcd for $C_{16}H_{30}N_4O_4F_6P$, $[2C^+, PF_6^-]^+$ requires: 487.1909).

*1-{2-[2-(2-Hydroxy-ethoxy)-ethoxy]-ethyl}-3-methyl imidazolium bis((trifluoromethyl)sulfonyl)amide [PEG_3mim][NTf_2] (**4i**).* ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS) δ 3.55−3.73 (m, 8H); 3.94 (t, 2H, J = 4.9 Hz); 4.06 (s, 3H); 4.18 (br s, 1H, OH); 4.53 (t, 2H, J = 4.9 Hz); 7.67 (t, 1H, J = 1.7 Hz, H-4); 7.77 (t, 1H, J = 1.7 Hz, H-5); 9.13 (s, 1H, H-2). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, TMS) δ 36.62 (q, J = 143 Hz); 50.34 (t, J = 144 Hz); 61.73 (tt, J = 141, 2.6 Hz); 69.31 (tt, J = 145, 3.1 Hz); 70.73 (tt, J = 141, 2.9 Hz); 70.81 (tt, J = 142, 3.5 Hz); 73.16 (tt, J = 143, 2.6 Hz); 120.93 (q, J = 321 Hz, CF_3); 123.97 (dm, J = 202 Hz, C-4); 124.30 (dm, J = 202 Hz, C-5); 138.05 (dm, J = 225 Hz, C-2). HRMS *m*/*z*: 215.1396 found (calcd for $C_{10}H_{19}N_2O_3$, M^+ requires: 215.1396).

*3-butyl-1-(2-hydroxy-ethyl)imidazolium hexafluorophosphate [PEG_1bim][PF_6] (**4k**).* ^{1}H NMR (300 MHz, $(CD_3)_2$-CO, TMS) δ 0.95 (t, 3H, J = 7.4 Hz); 1.39 (sext, 2H, J = 7.3 Hz); 1.93 (quint, 2H, J = 7.6 Hz); 3.97 (t, 2H, J = 4.9 Hz); 4.16 (br s, 1H, OH); 4.35 (t, 2H, J = 7.3 Hz); 4.42 (t, 2H, J = 5.1 Hz); 7.72 (s, 1H, H-4); 7.73 (s, 1H, H-5); 8.95 (s, 1H, H-2). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, TMS) δ 13.70

(qt, $J = 125$ Hz); 19.97 (tsext, $J = 125$, 4.1 Hz); 32.74 (tm, $J = 125$ Hz); 50.24 (tm, $J = 145$ Hz); 53.08 (t, $J = 143$ Hz); 60.94 (tt, $J = 144$, 2.9 Hz); 123.24 (dm, $J = 202$ Hz, C-4); 124.00 (dm, $J = 202$ Hz, C-5); 137.07 (dm, $J = 222$ Hz, C-2). HRMS *m*/*z*: 483.2328 found (calcd for $C_{18}H_{34}N_4O_2F_6P$, $[2C^+, PF_6^-]^+$ requires: 483.2324).

*3-Butyl-1-{2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethyl}-imidazolium hexafluorophosphate [PEG$_3$bim][PF$_6$] (**4m**).* ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS) δ 0.95 (t, 3H, $J = 7.4$ Hz); 1.38 (sext, 2H, $J = 7.5$ Hz); 1.92 (quint, 2H, $J = 7.6$ Hz); 3.52−3.70 (m, 8H); 3.92 (t, 2H, $J = 4.7$ Hz); 3.98 (br s, 1H, OH); 4.36 (t, 2H, $J = 7.3$ Hz); 4.49 (t, 2H, J 4.9 Hz); 7.71 (t, $J = 1.8$ Hz, H-4); 7.75 (t, 1H, $J = 1.8$ Hz, H-5); 9.02 (s, 1H, H-2). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, TMS) δ 13.65 (qt, $J = 125$, 3.9 Hz); 19.91 (tsext; $J = 125$, 4.1 Hz); 32.70 (tm, $J = 129$ Hz); 50.16 (tm, $J = 145$ Hz); 50.37 (t, $J = 145$ Hz); 61.89 (tt, $J = 140$, 2.6 Hz); 69.19 (tt, $J = 145$, 3.2 Hz); 70.80 (tm, $J = 140$ Hz); 70.83 (tm; $J = 140$ Hz); 73.37 (tt, $J = 140$, 2.8 Hz); 123.01 (dm, $J = 202$ Hz, C-4); 124.07 (dm, $J = 202$ Hz, C-5); 137.25 (dm, $J = 225$ Hz, C-2). HRMS *m*/*z*: 659.3369 found (calcd for $C_{26}H_{50}N_4O_6F_6P$, $[2C^+, PF_6-]^+$ requires: 659.3372).

1-(3-Hydroxy-propyl)-3-methylimidazolium hexafluorophosphate [hypmim][PF$_6$] (7). ^{1}H NMR (300 MHz, $(CD_3)_2CO$, TMS) δ 2.12 (quint, 2H, $J = 6.9$ Hz); 3.63 (t, 2H, $J = 5.9$ Hz); 3.78 (br s, 1H, OH); 4.01 (s, 3H); 4.43 (t, 2H, $J = 7.1$ Hz); 7.64 (t, 1H, $J = 1.6$ Hz, H-4); 7.70 (t, 1H, $J = 1.6$ Hz, H-5); 8.88 (s, 1H). ^{13}C NMR (75 MHz, $(CD_3)_2CO$, TMS) δ 33.21 (tm, $J = 128$ Hz); 36.49 (q, $J = 144$ Hz); 47.62 (tm, $J = 142$ Hz); 58.83 (tquint, $J = 142$, 3.9 Hz); 123.46 (dm, $J = 202$ Hz, C-4); 124.60 (dm, $J = 202$ Hz, C-5); 137.50 (dm, $J = 222$ Hz, C-2). HRMS *m*/*z*: 427.1694 found (calcd for $C_{14}H_{26}N_4O_2F_6P$, $[2C^+, PF_6^-]^+$ requires: 427.1698).

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