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ARTICLE

Click chemistry mediated synthesis of bio-inspired phosphonyl-functionalized ionic liquids

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This study focuses on the synthesis of a class of novel biologically-inspired ionic liquids coupled with a phosphonate group containing short to long side chains (C₃–C₁₁) via Pudovic reaction. The ionic liquids exhibited very low glass transition temperatures and were hydrophobic in character. This method has the attributes of "click" chemistry with outstanding efficiency, simplicity, yields and regioselectivity. The results of their calcium (II) ligating capability are also presented.

Introduction

Task-specific ionic liquids (TSILs) or functionalized ionic liquids are a unique subclass of conventional ionic liquids that incorporate an ion-tethered functionality tailored for specific applications ranging from organic synthesis and metal extraction to material and pharmaceutical sciences.¹ The introduction of a functional group on a cation and/or anion allows for marked changes of the physicochemical properties of ionic liquids and conveys a particular reactivity pattern to them. The continued success of TSILs in a wide variety of applications presents challenges toward developing practical synthetic routes for these functional organic materials. Since functional groups on TSILs are generally heteroatom-based, the challenge is to develop a highly efficient, atom-economical and orthogonal methodologies, such as "click" chemistry.² Underlying these synthetic goals is the additional desire to develop scalable reactions that fall within the philosophical realm of green chemistry for the synthesis of ILs.^{2e}

Functional groups can either be coupled to the cation, anion or both through a linker, which is generally used for minimizing interaction between a reactive functionality and an ionic moiety. In fact, modulation of a functionality's reactivity can be expected as a function of the length and structure of the linker. Ionic liquids containing long linkers ($\geq C_8$) exhibit a high degree of self-organization and mobility that increases with the extension of the side chains. Ionic liquids containing long chain appendages recently have been exploited in a broad spectrum of applications such as biomaterials,³ phase transfer catalysts,⁴ Ni-NHC catalyzed olefin dimerization,⁵ biomass dissolution,⁶ zeolites⁷ and metallic nanoparticles^{8,9} syntheses. Regrettably, the melting points of ionic liquids begin to increase significantly once an appended *N*-substituted linker exceeds seven carbon atoms in length for several homologous series of 1-*n*-alkyl-3-methylimidazolium ionic

liquids.^{3a,b} Therefore, synthesis of ionic liquids that incorporate more hydrophobic structural elements, while keeping their melting points below room temperature, continues to be a challenge.

Phosphonic acids and their analogue esters, phosphonates, are a valuable class of organophosphorus compounds employed in a variety of chemical and biological functions due to their structural similarities with phosphates (including DNA and RNA)¹⁰ and phosphonopeptides.¹¹ Their positions as crucial constituents of many major biomolecules,¹² pro-drugs¹³ and materials¹⁴ have resulted in the development of various synthetic methodologies designed to generate phosphonates and phosphonic acids as a mimic of the parent phosphate.¹⁵ From a synthetic viewpoint, the additions of phosphorus-centered radicals across the *ene* and *yne* substrates are one of the most versatile pathways for the formation of carbon-phosphorus bonds. The reactivity has been extensively studied using various activation methods or catalysts such as AIBN/heat,¹⁶ AIBN/UV,^{16a} Et₃B/O₂,¹⁷ microwave,¹⁸ phosphine–borane,¹⁹ transition metals²⁰ and NiL_{*n*}.²¹ Recently, Li *et al.* reported a radical-based phosphonofluorination of unactivated alkenes using AgNO₃/Selectfluor reagent as a catalytic system, which led to formation of β -fluorinated alkylphosphonates with high stereoselectivity.²²

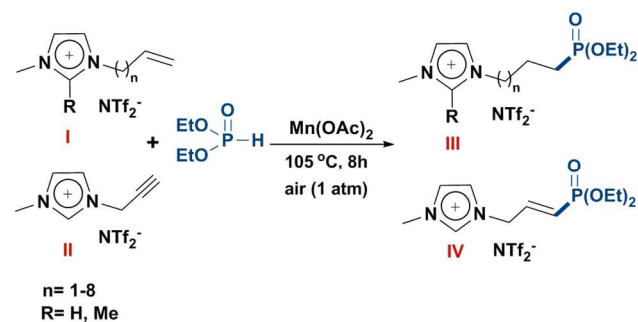
Phosphonyl and phosphinoyl-functionalized TSILs are typically synthesized by the nucleophilic substitution of 1-alkylimidazole with diethyl haloalkylphosphonates and haloalkyldiphenyl phosphinate (alkyl = ethyl and propyl), respectively.^{23,25} They were reported as an adaptive ligand for the complexation of 4*f* metals,^{23b-g} deep desulfurization process of diesel fuel,²⁴ lubricants²⁵ and corrosion inhibitors for reactive metals.²⁶ Liu *et al.*^{23a,25} and Srinivasan *et al.*^{23f} separately reported the synthesis of phosphoryl-based ILs containing short side chains (C₂–C₃) via nucleophilic substitution of 1-alkylimidazoles with diethyl bromoalkylphosphonates at high temperature in 24–40h. Phosphoramidate-functionalized imidazolium salts were synthesized

by the Davis group *via* nucleophilic substitution of phosphorus (V) oxyhalides and 1-(3-aminopropyl) imidazole in DCM and then quarternized at the imidazole N(3) by the reaction of EtI, followed by metathesis.^{23b} Likewise, Quadi *et al.* reported preparation of ammonium-type phosphoramidate/phosphonate TSILs using similar approach by the reaction of corresponding amine/alcohol with dichlorophosphate in Et₂O followed by the quarternization by alkyl iodide and metathesis.^{23d} Synthesis of P=O functionalized imidazolium salts as intermediates toward nucleophilic heterocyclic carbene-phosphine complexes of Pd(II) was reported by Danopoulos *et al.*²⁷ They observed the reductive elimination of methylimidazolium salts from complex palladium and phosphine or phosphate followed by oxidative addition. The ligand synthetic strategy is based upon the quarternization of 1-arylimidazoles with (ω -bromoalkyl) diphenylphosphine oxide at 150–160 °C followed by reduction with SiHCl₃ in refluxing chlorobenzene. Nockemann *et al.* reported a multi-step approach to make the phosphine oxide-functionalized ionic liquids with moderate-sized linkers (C₂–C₈) in moderate yields (~70%) by nucleophilic addition of alkyl bromide-bearing imidazolium ionic liquids with potassium diphenylphosphine followed by the oxidation with hydrogen peroxide.²⁸ Due to use of KPPH₂ as a strong base and presence of acidic proton at C2 position of imidazolium ring, only C2-substituted imidazolium cations were used, which limited the number of possible ILs that could be made via this methodology. Generally, in the case of above-mentioned nucleophilic substitution methods, only phosphonyl/phosphinoyl-based ILs containing short to moderate linkers (C₂–C₈) are synthesizable.

Dupont and Moores groups recently reported a radical-mediated preparation of phosphine-functionalized ionic liquids as versatile ligands toward the second generation of Grubbs catalysts for RCM reaction²⁹ and palladium nanoparticles for biphasic hydrogenation of olefins,⁸ respectively. In fact, according to the Etemad-Moghadam's report,^{16a} the major disadvantages of the photoactivation methods are long reaction time and poor yield/regioselectivity and reaction needs to be carried out under argon atmosphere. Likewise, Grubbs and Daefler described a method to produce Wittig triphenylphosphonium salts *via* the radical-mediated photoaddition of [HPPH₃][BF₄] across unactivated olefins.³⁰ Forsyth *et al.* reported the preparation of a number of tetraalkylphosphonium cations coupling with phosphate and phosphinate anions and their sulfur analogs that displayed a high thermal stability (above 200 °C) and were used for corrosion protection of reactive metals.²⁶

Despite the wide range of the potential applications of P=O bearing ionic liquids, very few investigations into an efficient synthesis methodology have been reported to date. Notably, the reported synthetic methods suffer from one or more drawbacks such as harsh reaction conditions,^{27,28} laborious and complex work-up/purification procedures,^{23a, 27} use of volatile organic solvents in the preparation/workup process,^{23a,27,28} ability to form limited numbers of ILs,^{23,27-29} long reaction time,^{8,23a,23f} necessity of an expensive inert gas atmosphere like argon,^{26,29,30} moderate yields with the occurrence of side reactions.^{23,28} To further develop this important class of TSILs, the exploitation of additional robust, efficient and orthogonal "click" reactions is desirable. To this intent, we sought to take advantage of the well-documented and atom-

economical addition of phosphonyl radicals across *ene* and *yne* substrates – hydrophosphonylation or the Pudovik reaction – using a non-precious catalyst, Mn(OAc)₂, to synthesize a novel class of bio-inspired phosphonyl-functionalized ILs (Scheme 1, **III** and **IV**) with C₃–C₁₁ linkers and low glass transition temperatures (Chart 1).



Scheme 1. Aerobic hydrophosphonylation of various *ene* and *yne*-bearing ILs (**I** and **II**) catalyzed by Mn(OAc)₂ to form the phosphonyl-functionalized ionic liquids (**III** and **IV**).

Experimental

Materials and methods

For the present study, all of the chemicals employed including 1-methylimidazole (98% purity), diethyl phosphite (98% purity), and 1,2-dimethylimidazole (98% purity) were commercially available in high purity and were purchased from Acros Organics and were used without further purification. Solvents were used as received, without further purification. Potassium bistriflimide, employed for metathesis reactions, was prepared *via* neutralization (pH = 7.0) of HNTf₂ (Iolitec GmbH, 80%) with KOH followed by the removal of water.

Characterization of the products using ¹H, ¹³C and ³¹P NMR was performed on a JEOL 500 MHz NMR with multi-nuclear capabilities using DMSO-*d*₆. Chemical shifts are reported relative to TMS as the internal reference at 0.00 ppm for both the ¹H, ¹³C and ³¹P NMR data. ESI-MS analyses were performed by flow-injection on a Thermo Scientific ion trap mass spectrometer using HPLC grade acetonitrile. As our interest was in the cations of these salts, data was collected in positive ion mode. Glass transition temperatures were determined by using a Q2000 TA differential scanning calorimeter, with a heating rate of 10 min⁻¹. The reported data represents the average of at least three trials, and were reproducible to within 1 °C.

General synthetic procedure

A mixture of diethyl phosphite (6–9 mmol), Mn(OAc)₂ (0.3 equiv. relative to each *ene* or *yne* group) was stirred at room temperature until a homogenous mixture was observed. Then *ene* or *yne*-bearing ionic liquids (1 mmol) were added to the mixture and were stirred at 105 °C for 8 hours. After completion of the reactions (¹H NMR monitoring on a sample of crude mixture), the residues were washed with hexanes (5 × 10 mL) and then H₂O (1 × 5 mL). Removal of residual solvents *in vacuo* yielded ILs **1–19** in 81–96%.

Ene and *yne*-bearing ILs were prepared in good yields using multi-step reactions with high-purity bromoalkenes or propargyl bromide with corresponding 1-methylimidazole, 1,2-dimethyl imidazole, trialkylamine or triphenylphosphine as starting materials followed by the metathesis reaction with KNTf_2 , which was reported in reference 3b. These ILs were subjected to standard silver-ion tests to ensure the completeness of the exchange of halide for the NTf_2^- anion. All gave negative results, indicating that residual halide anion content in the salts were below the accepted threshold levels.

Results and discussion

Synthesis and characterization. The ideal catalyst should not contain precious elements and should bring reactions to completion in a few hours through operationally simple procedures. In this context, the primary focus of this work was to design an operationally simple, high-yielding and non-precious metal catalyzed addition of P–H across *ene* and *yne*-bearing ILs (Scheme 1, **I** and **II**). Our initial studies concentrated on the coupling reaction of 1-allyl-3-methyl imidazolium IL (Scheme 1, **I**, $n = 1$, $R = \text{H}$) with diethyl phosphite as a model reaction to optimize the reaction conditions by examining the effects of initiator/catalyst, solvent and temperature (Table 1). The preliminary screening of various non-precious metal catalysts (NPMCs) revealed that the catalytic amount of $\text{Mn}(\text{OAc})_2$ (0.3 equiv./alkene) activated at 105 °C in the presence of air and in the absence of solvent was the most effective reaction conditions, which led to complete conversion to product **1** in anti-Markovnikov fashion (Table 1, entry 12). Remarkably, when the reaction was performed in an open-flask manner, the complete conversion was observed (Table 1, entry 12), whereas the yield of the obtained product was very low in the absence of air (Table 1, entry 13). This methodology is the modification of previously reported reaction by Ishii *et al.*³¹ for the hydrophosphonylation of alkenes (Table 1, entries 10 and 11) with longer reaction time and higher temperature. Using Ishii's reaction conditions (Table 1, entry 10), led to the low yield (58%).

In order to generate the required P-centered radical under oxidative reaction condition, $\text{Mn}(\text{OAc})_2$ catalyst was used. The requisite Mn(III) was generated *in situ* from the reaction of Mn(II) with the oxygen from the air and oxidized diethyl phosphite to the corresponding phosphonyl radical, which then was efficiently added across double bond. In terms of sustainability, O_2 is the ideal terminal oxidant because it is readily available and H_2O is the by-product of this catalytic oxidation reaction. Our preliminary experiments demonstrated the combination of Mn(II) and air to be potentially able to generate the chain process of P-centered radical addition to [allylmim][NTf_2] as an *ene*-bearing ionic liquid. The Mn(II)-catalyzed click reaction is an idea synthesis platform to systematically probe properties of ionic liquids due to its facile synthesis process, benign reaction conditions, excellent molecular control and fidelity. This methodology that using $\text{Mn}(\text{OAc})_2$ as an efficient catalyst in the presence of air was reported by Ishii *et al.* for hydrophosphonylation of alkenes (Table 1, entries 10 and 11).³¹

Table 1. Optimization Studies.

1

entry	conditions	conversion (%) ^a	ref.
1 ^b	AIBN (0.2 equiv.), cyclohexane, 80 °C, 60h, N ₂	0	16b
2 ^c	ABCN (0.2 equiv.), cyclohexane, 80 °C, 60h, N ₂	0	27
3	Et ₃ B (0.3 equiv.), MeOH, RT, 60h, air	0	17b
4	Et ₃ B (0.3 equiv.), cyclohexane, RT, 60h, air	0	17c
5	Et ₃ B (0.3 equiv.), cyclohexane, 80 °C, 60h, air	0	-
6 ^d	Microwave, 80 °C, 5h, air/N ₂	0	18b
7 ^e	NiCl ₂ (0.3 equiv.)/dppe (0.5 equiv.), CH ₃ CN, 82 °C, 2h	89	21e
8	NiCl ₂ (0.3 equiv.), CH ₃ CN, 82 °C, 2h	73	21e
9	Ni(OAc) ₂ (0.3 equiv.), CH ₃ CN, 82 °C, 2h	23	-
10	Mn(OAc) ₂ (0.3 equiv.), 90 °C, 1h, air	58	31
11	Mn(OAc) ₂ (0.3 equiv.)/Co(OAc) ₂ (0.1 equiv.), 90 °C, 1h, air	51	31
12 ^f	Mn(OAc)₂ (0.3 equiv.), 105 °C, 8h, air	100	-
13	Mn(OAc) ₂ (0.3 equiv.), 105 °C, 8h, N ₂	<10	-

^aConversion measured by ¹H NMR; ^bAIBN: azobis(isobutyronitrile); ^cABCN: azobis(cyclohexanecarbonitrile); ^ddecomposed product was obtained; ^edppe: bis(diphenylphosphino)ethane; ^freaction conditions: [allylmim][NTf_2] (1 mmol), diethyl phosphite (6 mmol), $\text{Mn}(\text{OAc})_2$ (0.3 mmol) under open-flask conditions.

Encouraged by these initial results, the scope of hydrophosphonylation of *ene* and *yne*-bearing ILs was investigated to create a library of novel phosphonyl-functionalized ionic liquids (Chart 1). The hydrophobic and weakly coordinating anion bis(trifluoromethanesulfonyl)imide [NTf_2^-], which is highly stable from both thermal and hydrolytic standpoints, is paired with the cations. First, the radical additions of diethyl phosphite to a number of aromatic (imidazolium) and non-aromatic (ammonium and phosphonium) *ene*-bearing ionic liquids containing C₃–C₁₁ side chains were investigated. Near quantitative yields (84–96%) along with exclusive anti-Markovnikov orientation were achieved under the optimized reaction conditions outlined above (Chart 1, ILs **1–12** and **14–16**). The key objective of this work is to develop bio-inspired materials that are highly lipophilic while being low melting salts. This is the first time a highly efficient construction of phosphonyl-functionalized ionic liquids with long aliphatic structural units ($\geq \text{C}_8$), while maintaining them liquid at ambient temperature, was achieved (Chart 1, ILs **6–12**). Subsequently, the scope of the study was expanded to ionic liquids with cations bearing more than one *ene* group. These *ene* ILs were prepared according to a general method reported by Welton *et al.*³² Reacting these ILs with diethyl phosphite under the same conditions provided

the desired polyadducts (Chart 1, ILs **13** and **17**) quantitatively and isolated in very good yields (**13**: 85%; **17**: 81%). Both the ^1H and ^{13}C NMR spectra of each **1**–**19** clearly illustrate complete hydrophosphonylation, which was readily ascertained on the basis of peak integration (^1H NMR) and the disappearance of the olefinic peaks (^1H , ^{13}C) of the starting cation. This was further corroborated by its the ESI-MS spectrum; however, in the ESI-MS of **17** the expected parent ion of $m/z = 730.34$ is not observed. Instead, it produces a high-mass ion with $m/z = 458.32$, consistent with a structure in which two of the four phosphonyl moieties have been cleaved, leaving two intact while regenerating two of the original *N*-tethered allyl moieties. To fully probe the efficiency of this process, the addition of the phosphonyl radical to imidazolium-type ionic liquids containing *N*-substituted triple bond was investigated (Scheme 1, II). Both the mono and bis *yne*-functionalized ionic liquids smoothly underwent mono-hydrophosphonylation, reaching high yields with complete anti-Markovnikov selectivity (Chart 1, **18** and **19**).

Interestingly, the solubility characteristic of the ionic products along with the efficient nature of the Pudovik reaction creating no byproducts allowed all of the ionic liquids to be purified simply by washing with hexanes and cold water. Notably, this means no chromatographic purification was required. Indeed, the residual/excess diethyl phosphite was readily removed by washing the reaction residue with hexanes, in which none of the starting or product ionic liquids are soluble. Likewise, any residual catalyst was easily removed by washing with H_2O , with which those ionic liquids are immiscible. Final products were isolated in >80% recovered yields as viscous clear liquids. It is noteworthy to mention that the purification process does not involve the use of halogenated solvents nor chromatographic separation. Indeed, the total obtained yields were related to the length of the linkers. As observed, the yields of the ILs with long linkers are higher in comparison to ionic liquids containing shorter linkers and multiple phosphonate groups. This observation can be rationalized by the fact that ionic liquids bearing shorter linkers and multiple phosphonate functionality are more readily water soluble due to the H-bond formation capability of

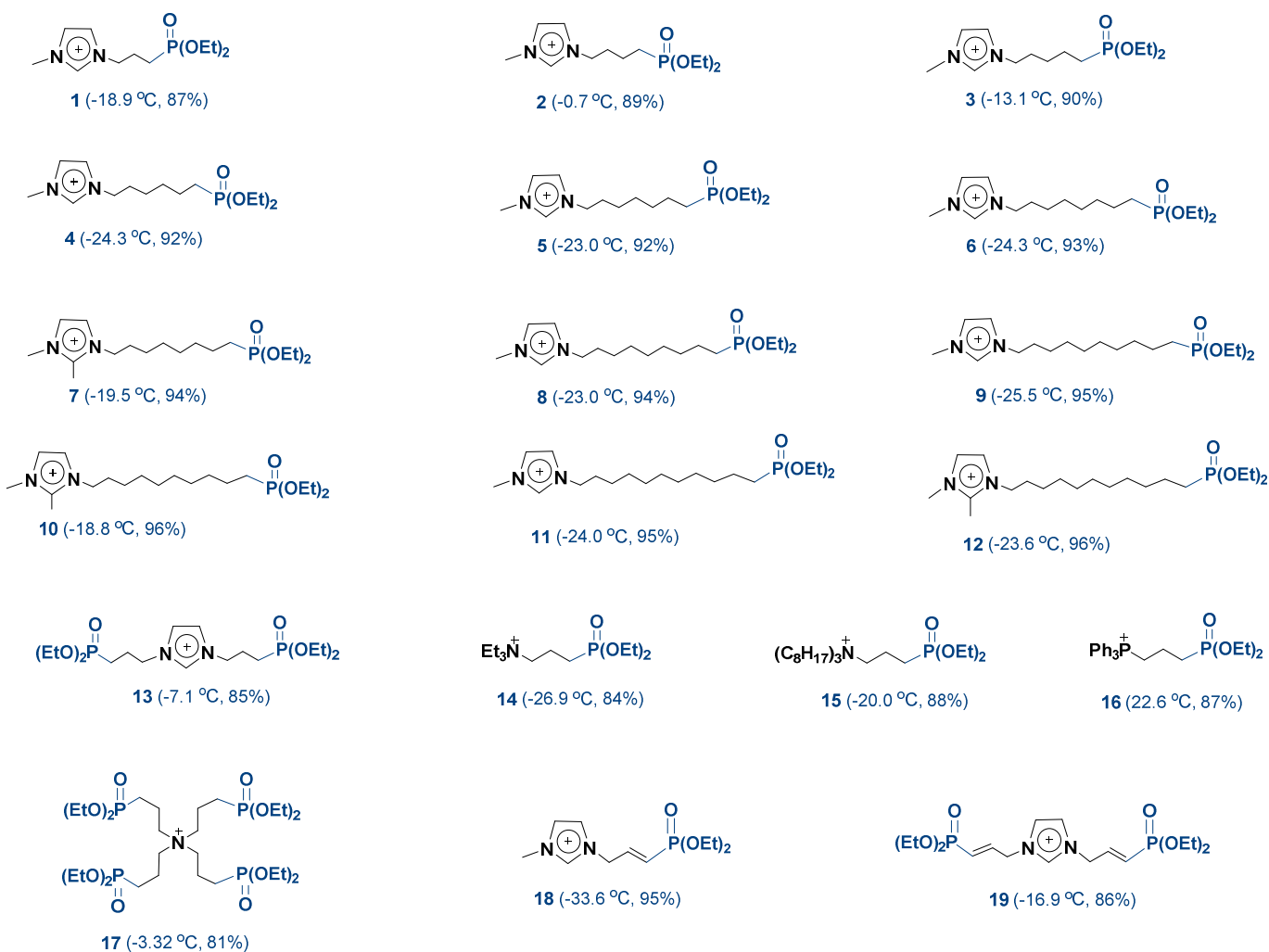


Chart 1. A library of phosphonyl-functionalized ionic liquids including their glass transition temperatures (°C) and recovered yields (%). Only the structures of cations are present and the anion, NTf_2^- is not shown.

phosphonate group, thus were partially lost during the subsequent aqueous washing step.

The P=O stretching vibration in IR spectra of all ionic liquids demonstrated characteristic absorption peaks ranging between 1194–1197 cm^{-1} and was not greatly affected by the length of the linkers and presence of a α,β -double bonds. On the other hand, the ^{31}P NMR spectra showed the P=O singlet chemical shift increased with increasing linker length ranging from 30.93 to 32.68 ppm in ILs **1–12**. For all of the synthesized TSILs, the P=O characteristic peaks were partially split due to the formation of hydrogen bonds. According to Nockemann's report, a H-bond was formed between the P=O functionality as an acceptor with protons on the α carbon to phosphorus of adjacent cations. Despite considerable effort, an X-ray crystal structure was not obtained since the ILs could not be isolated most likely because phosphonyl group diminishes the crystallinity of IL.

Thermophysical properties. The thermal properties of these new ionic liquids were determined by differential scanning calorimetry (DSC), and only a glass transition temperature (T_g ; midpoints of phase transitions), no melting or crystallization points, was observed upon heating. The resulting glass transition temperature (T_g) data was in Chart 1. All of the synthesized TSILs are viscous liquids at ambient temperature and exhibited well-defined T_g at a very low temperature ranging from -33.6 to 22.6 $^{\circ}\text{C}$ without melting (Chart 1). Indeed, the O=P(OEt)₂ group is the main structural feature of the new ionic liquids that appears to have an important impact upon their physical state. The overall depressions in the glass transition points brought about by the inclusion of phosphonate moiety are substantial regardless of whether the latter is H- or Me-bearing at the imidazolium C2 position. A comparison of the T_g values of phosphonyl-based ionic liquids with T_m of corresponding all-carbon reference ionic liquids containing the same number of side-chain carbons, shows the dramatic impact of the presence of phosphonate functionality upon the phase transition temperatures of the ionic liquids, which demonstrably decreases the T_g values of new TSILs. For instance, [C₁₂C₁im][NTf₂] comprising a saturated C₁₂ side chain, has a T_m value of 34.9 $^{\circ}\text{C}$ reported by Mudring *et al.*,⁹ however, replacement with a phosphonyl unit (IL **11**) yields T_g of -24.0 $^{\circ}\text{C}$ and converts a crystalline solid to an amorphous liquid. It is reasonable to assume that the introduction of phosphonyl functional group lowered the tendency for crystallization. Indeed, introduction of phosphonyl group caused the suppression of a clear melting temperature, and only glass transitions were observable (chart 1). Likewise, while reference [C₁₀C₁im][NTf₂] has a T_m of 18.9 $^{\circ}\text{C}$,^{3a} its counterpart IL **8** has T_g of -23.0 $^{\circ}\text{C}$. Not surprisingly, the viscosities of ILs **8** and **11** tangibly greater than reference ILs, likely because of the more H-bonding potential inherent in their cations. The melting point is controlled by three main factors: intermolecular forces, molecular symmetry and the conformational degrees of the freedom of molecule.³³ The likely explanation for the observed complete disappearance of crystallinity and very low T_g values is that the heightened rotational freedom of the chain caused the reduced lattice energy of the ionic liquids, which high chain flexibility predominates over the high polarity of phosphonyl groups. Besides, Rothenberg

et al. have proposed the former domain constitutes a *symmetry-breaking region*, the impact of which is eventually outweighed by that of the cumulative inter-chain dispersion forces of progressively longer alkyl groups.³³ Therefore, the low symmetry and relatively large size of the cations combined with effective charge distribution of the anion led to the destabilization of the packing efficiency of the crystal lattice of the ionic liquids. Generally, elongation of the cation's alkyl side chain leads to an increase in melting point. However, in this case the trend of increasing in T_g values with the number carbons on the side chain was not observed. For the imidazolium-based ionic liquids the hydrogen bonding between the cation and the anion is mainly determined by the most acidic hydrogen at the cation in the position C2.³⁴ As such, the methylation at C2 position removes the hydrogen bond between the cation and anion, remarkably affecting the melting point of ionic liquids, which is the most important feature of ionic liquids, as well as the viscosity.³⁵ As observed, higher melting points were obtained for the C2-methylated ionic liquids relative to their C2-protonated counterparts. As proposed by Ludwig *et al.*, formation of strong HBs between the H2 position of the imidazolium cation and anion introduces "defects" into the their Columbic network and destabilize the whole system, which leads to a lower melting point and viscosity.³⁶ However, another explanation, which was assessed by theoretical and experimental studies, emphasizes on the determinant role of entropy.³⁷⁻³⁹ In this light, the replacement of the acidic C2 hydrogen at the imidazolium ring by a methyl group, decreases the entropy of the ionic liquids in the liquids phase. As a result, the loss of entropy is the main reason for their relative higher melting points and enhanced viscosities. In our study, this phenomenon is evident when comparing the T_g values of ILs **7** and **10** with ILs **8** and **11**, where the effect of methyl substituting at C2 position can be observed. The C2-methylated ILs **7** and **10** are the structural isomers of their C2-protonated counterparts (ILs **8** and **11**) and the sole structural difference between them is the presence of a methyl group at C2 position of imidazolium ring. ΔT_g values for the C2-methylated ILs/C2-protonated ILs such as **7/8** and **10/11** are 3.5 $^{\circ}\text{C}$ and 5.2 $^{\circ}\text{C}$, respectively. IL **16**, as a functionalized alkytriphenylphosphonium salt, shows the greatest T_g in this series due to the large cation size. Interestingly, inclusion of the phosphonate group to allytriphenylphosphonium-based IL turn a crystalline solid salt to an amorphous ionic liquid, which is liquid at room temperature ($T_g = 22.6$ $^{\circ}\text{C}$). According a recent Davis's report, arylphosphonium-based ionic liquids are generally more thermally stable than their imidazolium and ammonium counterparts under various conditions.⁴⁰

Molecular modeling. The molecular modeling was performed using IL **1** as the model. The structure of **1** was optimized using the B3LYP exchange–correlation functional⁴¹ and the 6-311++G (d,p) basis set as implemented in the Gaussian09 suite of programs.⁴² Stable structures were confirmed by computing analytic vibrational frequencies. Figure 2 displays the most stable conformation for IL **1**. Only front-conformations were obtained, while no top conformation was found due to the presence of the flexibility of the bulky NTf₂ anion. The free energy associated with the formation of IL **1**

amounts to -63.1 kcal/mol. In addition, the electron density isosurface of IL 1 is shown in the electrostatic potential energy map in Figure 1. The ESP mapping illustrates the polarization of the cation with the imidazolium ring as the blue region and phosphonyl group as the least positive charge region (red).

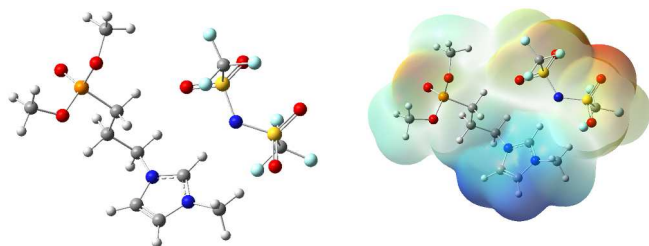


Figure 1. Right: the most stable conformation of IL 1. Left: the electrostatic potential energy map of complex of IL 1. The ethyl group was modeled by methyl group.

Calcium affinity. One the objectives of the research are also to investigate the calcium complexation process by using selected phosphonyl-functionalized ILs. Normally, water-soluble calcium ions are separated from hydrocarbonaceous feedstock by using strong acids, which highly corrosive. The separation of oil-soluble calcium ions (calcium naphthenate, calcium phenol, fatty acid calcium) require the usage of organic solvents and organic decalcifying agents, which are usually toxic, flammable and volatile organic compounds (VOCs). Their usage raises serious environmental and safety concerns. Therefore, ionic liquids have been proposed as suitable alternatives due to their unique physical properties and environmental compatibility.^{1h,k} However, the main drawback associated with using classical ionic liquids for metal extraction procedures is finding extractant molecules that remain only in the IL phase as well as understanding the increased complexity of the system upon the addition of solutes, prompting the studies of the functionalized ionic liquids concept for metal extraction using IL. For the first time, the Rogers and Davis groups introduced the concept of TSILs designed for the extraction of specific metal ions.⁴³ Attaching a metal ion coordinating group directly to the imidazolium cation makes the extractant an integral part of the hydrophobic phase and greatly diminishes the chance for loss to the aqueous phase. In other words, other than using ILs as eco-friendly solvents for metal separation, the functional ILs consisting extracting entities (functionalities), which are grafted onto the structures of cations and combine unique physical and chemical properties of ionic liquids. Functionalized ionic liquids were also derived to include the task specific functionalities, such as metal ligating groups that when used as part of the solvent dramatically enhance the extraction of targeted metal ions. These TSILs behave both as non-volatile solvents and extractants, overcoming the potential issues encountered through solvent/extractant miscibility and facilitating the solvent/extractant recovery process.

The affinity of the synthesized phosphonyl-functionalized ionic liquids for calcium ions was examined by utilizing them as complexing agents to bond to the calcium ions present in bone char, which consists mainly of tricalcium phosphate and calcium

carbonate. We hypothesized the calcium in the stationary phase would immobilize the ionic liquids by means of chelation between the phosphonate functionality and calcium salts. A chromatographic column was prepared with 1.00 g of bone char powder. ILs were separately massed (4.1 mmol for each IL) and dissolved in dichloromethane before running the ionic liquids through the column. Once the ILs eluted the column, dichloromethane was used to wash out non-bonded ionic liquids. The solvent was evaporated and the remained ionic liquids were massed to determine the amount retained in the column (Figure 2). As shown in Figure 2, interestingly, the increasing length of the linker between the cation and phosphonate group appeared to increase the binding ability of the ligand toward calcium salts. Nockemann's report gives support to these findings since increasing the length of the linker between the cation core and phosphonate functional group appeared to profoundly enhance the binding ability of the ligand with transition metals.²⁸ Additionally, the phosphonyl-bearing ionic liquids with longer linkers showed stronger adsorption on the metallic surface and have better anti-wear ability rather than shorter chains ionic liquids, according to the Liu's report. These TSILs displayed a high thermal stability up to *ca.* 300 °C and their thermal stabilities improved with longer linkers.²⁵ Moreover, polyfunctionalized ionic liquids 13, 17 and 19 as bi- or tetradentate ligands, demonstrated the maximal bone affinities, which are related to their ability for simultaneously binding/chelating with more than one calcium site per compound.

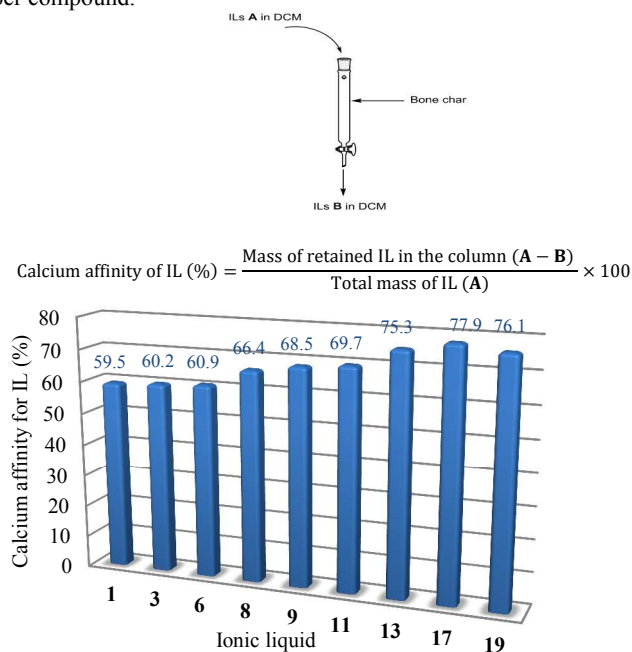


Figure 2. Calcium (II) affinity of selected phosphonyl-bearing ionic liquids.

Organic chelating agents such as EDTA are used to bind metal ions (Ca^{2+} , Cu^{2+} , Pb^{2+} , Co^{3+} and Fe^{3+}) in controlling water hardness and chelation therapy *e.g.* for treating mercury and lead poisoning. Due to the cost the environmental hazard, great efforts have been made to replace EDTA with citric acid, inorganic polyphosphates *e.g.* pentasodium tripolyphosphate (STPP), nitrilotriacetic acid (NTA) and organic polymers *e.g.* polyacrylic acid.⁴⁴

Polyphosphates and NTA were found to potentially cause environmental issues and be carcinogenic.⁴⁵ We also conducted the above-mentioned test to compare the calcium binding power of ILs **11**, **13** and **17** with some standard calcium agents (Table 2). As shown in Figure 3, although citric acid has considerable higher calcium (II) affinity (83.4%) than ILs, bi- and tetradentate ILs (**13** and **17**) showed the better binding affinity to calcium (II) ions in comparison to EDTA (77.0%) and STPP (72.1%), making them “greener” alternatives for calcium (II) traditional solvent/chelator systems.

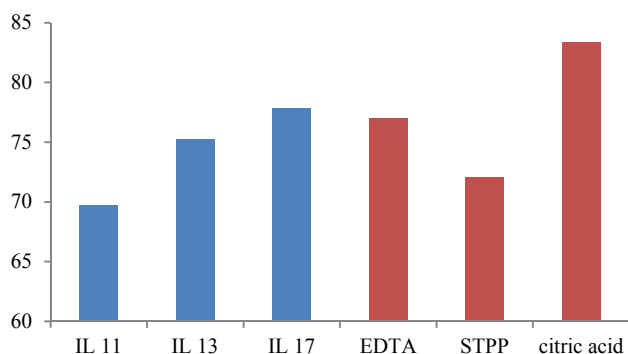


Figure 3. Comparison of calcium (II) binding power of ILs (blue) and common chelating agents (red).

Conclusions

In summary, we have reported the synthesis of a series of novel bio-inspired ionic liquids containing phosphonyl functional groups as a stable linkage for the connection of chemical and biological components was reported. Simple reaction conditions were used to provide good to quantitative yields. The construction of functionalized ionic liquids using the Pudovic "click" reaction offers considerable promise as a facile method to create structurally elaborated IL ions, which result from the modular nature of the reaction coupled with synthetically powerful characteristics *e.g.* regioselectivity, quantitative yields, simple and non-chromatographic purification/workup procedure and solvent-free conditions. $\text{Mn}(\text{OAc})_2$ was employed as a non-precious metal catalyst in these transformations. Accordingly, our research has assured a progressive direction in the development of the new ionic liquids containing phosphonate group and long aliphatic tail structures, which are generally similar to the corresponding phospholipids. Additionally, the preliminary results were described in terms regarding their tunability toward calcium ligation abilities. Increasing length of linkers between the cations and phosphonate groups appeared to enhance the binding ability of ligands to calcium ions. These novel TSILs have a great potential to use in the calcium separation/extraction process (*e.g.* decalcification of crude oil) and also development synthetic bone-seeking compounds with calcium antiresorptive and mineralization potencies. Further studies involving their thermal stability, density/viscosity and temperature-dependent miscibility of IL/water with emphasize on the demetallization of crude oil are currently in progress.

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Notes and references

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The key objective of this work is to develop bio-inspired ionic liquids that are highly lipophilic *via* “click” chemistry.

Graphical abstract:

