Developing New Inexpensive Room-Temperature Ionic Liquids with High Thermal Stability and a Greener Synthetic Profile

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ABSTRACT: Ionic liquids (ILs) have advantageous physical properties, which resulted in a rapid growth of research in this area in the past 15 years. One of the biggest challenges preventing the widespread use of ILs is the cost of production due to complex synthetic routes and/or expensive starting materials. Keeping in mind these industrial needs for scale-up and the desirable properties for applications in the lubrication area, here, we report the design and synthesis of four novel series of hydrophobic room-temperature ILs (RTILs) achieved from cheap and commercially available starting materials, namely, silicon-based, imidazolium-based, phosphonium-based, and monomer imidazolium-based. These syntheses were developed as expedited chemistry protocols and possess a greener synthetic profile compared to previously reported ILs of similar structures. All the RTILs were characterized by 1D NMR (1H NMR, 13C NMR, 31P NMR, 19F NMR, and 11B NMR) and 2D NMR (COSY, HSQC, and HMBC) analyses, high-resolution mass spectrometry, and chemical tests (primarily the silver nitrate test). Preliminary thermal analysis tests by thermogravimetric analysis show all novel RTILs display remarkably high thermal stabilities (386−474 °C). Differential scanning calorimetry data show low glass transitions ranging from −36 to −72 °C, which suggests good free volume and ion mobility.

INTRODUCTION

Ionic liquids (ILs) are materials entirely composed of ions with a melting point below of 100 °C.1−11 ILs have attracted considerable attention during the past two decades because of their capacity to possess a unique combination of physicochemical properties such as minimal volatility, high thermal stability, strong dissolution powers, low flash points, high chemical stabilities, catalytic activities, a tunable range of polarities, and relatively high electroconductivities.12−17 By changing the structures of cations and their combinations with a range of anions, the desired physicochemical properties can be tailored for a particular application.18−24

Mainly due to their recyclability and very low volatility, ILs were first proposed in the chemical industry as “green” alternatives to traditional volatile solvents, as catalysts25 and in biocatalytic reactions.26 These applications have now grown to include separation processes,27 electrochemical sensors,28 lithium batteries,29 fuel cells,30 and dye-sensitized solar cells,31 in production of nanomaterials,32 of porous and conductive polymers,33 in biomass processing,34,35 and in lubrication36 with some processes operating already at the industrial scale.37,38 Moreover, extraction of heavy metals with hydrophobic ILs is well documented.39

In view of this large and expanding landscape of applications, synthetic methodologies that minimize the generation of hazardous substances and provide more economical approaches for the preparation of novel ILs with improved physicochemical properties are greatly required. We are particularly interested in applications in the area of lubrication.

RESULTS AND DISCUSSION

Important cationic partners include ammonium (e.g., imidazolium) and phosphonium ions.

The imidazolium cation, in combination with weakly coordinating anions, exhibits a delocalized π-electron system with a pronounced aromatic bond character.40 This is one chemical characteristic that allows it to be used as a precursor to N-heterocyclic carbenes for successful transition-metal coordination41 and as a viable candidate for CO2 capture.42 It has been demonstrated that ILs with longer alkyl chains are strongly adsorbed on sliding surfaces and provide better lubrication properties than the shorter alkyl chains.43,44

ILs containing phosphonium cations tend to possess high thermal stabilities, which, for instance, was one of the desirable properties for the industrial adoption of the IL [P8,8,8,18]I45 as a Lewis basic IL in the isomerization process of 3,4-epoxybut-1-ene to 2,5-dihydrofuran instead of its ammonium ana-
Room-Temperature Silicon-Based ILs (RTSi-ILs).

Despite their application potential, phosphonium ILs have been less systematically studied than their nitrogen-based counterparts. In this report, we use traditional anions (NTf₂, PF₆, and BF₄⁻) and partner them with novel cations based on four main structural types described below. In this paper, we report on the design, synthesis, and purification of nine novel, hydrophobic, room-temperature ILs (RTILs) via expedited protocols from cheap, commercially available starting materials.

All protocols involve two synthetic steps: the first is the synthesis of chloride/bromide intermediate ILs, followed by the synthesis of the final product ILs. All chloride/bromide intermediate ILs were synthesized via S_N2 displacement reactions of amines with suitable alkyl chlorides (Scheme 1) or bromides (Schemes 2–4). This was followed by an anion exchange reaction, usually occurring in neat, water to afford the final ILs. The chloride/bromide intermediate ILs were not purified further as they were deemed to be of sufficient purity to be used in the next step. Through the anion exchange procedure, the impurities were efficiently eliminated from the final product.

The two-reaction protocol employed minimizes environmental impact and maximizes the friendliness to manufacture processes from both an energy-efficiency perspective and a pollutant-reduction perspective. This was achieved through, respectively, optimization of the reaction temperatures, which were reduced compared to structurally similar ILs reported in the literature, the avoidance of organic solvents (first reaction), the use of water as a solvent (second reaction), the use of equimolar amounts of the reagents in both reactions.

During protocol optimization, reaction progress was monitored by ¹H NMR analysis of the reaction mixtures at regular intervals and at a variety of temperatures. This ensured that optimal reaction times and temperatures were found (see Experimental Section). The novel RTILs reported in this work were characterized by several ¹H, ³¹C, and where applicable ¹¹B, ¹³C, and ³¹P) and 2D NMR (COSY, HSQC, and HMBC) techniques to ensure structural integrity (see Supporting Information), as well as high-resolution mass spectrometry (HRMS) of the ion couples. Purity was assessed through analysis of NMR spectra and the silver nitrate test. All reaction conditions are summarized in Table 2 along with reaction conditions of structurally similar ILs available from the chemical literature. The novel RTILs fall into the four main structural categories described below.

Room-Temperature Silicon-Based ILs (RTSi-ILs). Silicon oils are naturally occurring liquid siloxane polymers with branching organic side-chains, with the most industrially important one being polydimethylsiloxane. These polymers are of commercial interest because of their relatively high thermal stability and their lubricating properties. For the thermal stability, thermogravimetric analysis (TGA) of polydimethylsiloxane showed a degradation temperature starting at circa 400 °C. The effective lubrication of this IL type has also been investigated on stainless steel, where frictional behavior without a lubricant coating is above 0.8, while that of stainless steel coated with 0.1 μm thick silicone oil is less than 0.2. More recently, synthetic ILs containing the NTf₂ anion have found successful applications as additives to base oils for the lubrication of steel on aluminum. IL additives have distinct advantages over traditional lubricant additives, such as zinc dialkylthiophosphate, in that they are more stable at high temperatures, they are ashless upon decomposition and they are compatible with a wider range of surfaces. Silicone oils are inherently safe and nontoxic compounds that have been used in the treatment of complicated retinal detachments for over 30 years. There are currently no RTSi-ILs on the market, and those previously synthesized are often expensive to produce.

Here, we present the synthesis of two novel RTILs (Scheme 1) from cheap starting materials 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and (chloromethyl)-trimethylsilane to 1-(methyl trimethylsilane)-1,8-diazabicyclo[5.4.0]undec-7-ene chloride, [DBU-M-TMSi] Cl; and 1-benzyl-2-methylimidazole and (chloromethyl)-trimethylsilane to 1-benzyl-2-methyl-3-(methyl trimethylsilane)imidazolium chloride, [BM-M-TMSi-im] Cl. These chloride intermediates [DBU-M-TMSi] Cl and [BM-M-TMSi-im] Cl are, respectively, hydrophilic and partially hydrophilic. Hydrophilicity is linked to the use of chloride as a counter ion. In this first reaction, neat conditions and a temperature of 70 °C were appropriate to trigger the S_N2 displacement reaction between DBU and the hindered neopentyl carbon of (chloromethyl)trimethylsilane to smoothly afford the IL intermediate [DBU-M-TMSi] Cl in excellent yield.
nucleophilicity toward carbon electrophiles. The above was warranted because imidazole [BM-M-TMSi-im] Cl, the use of NaI as a Finkelstein catalyst for the preparation of the second chloride intermediate IL, occurs via N-alkylation by SN2 mechanism 1-bromo-3-methyl-Chain (RTim-ILs). The synthesis of these imidazolium ILs entry 1, 2, 10, 16, 22).

Room-Temperature Imidazolium-Based ILs with Small Chain (RTim-ILs). The synthesis of these imidazolium ILs occur via N-alkylation by S$_{n}$2 mechanism 1-bromo-3-methyl-butane, followed by anion exchange. The S$_{n}$2 reaction attained completion at 85 °C in 12 h. The anion exchange reaction occurred in water/CH$_2$Cl$_2$ (1:1) at room temperature in 1 h. The product, soluble in CH$_2$Cl$_2$, was collected in the bottom layer. All other reagents and salts remained in the water layer. This layer was decanted off efficiently, and the CH$_2$Cl$_2$ layer was further washed with water to afford the pure product [DMMB-im] BF$_4$. The anion exchange reaction using LiNTf$_2$ was carried out exclusively in water and was completed in 30 min. The product was washed with water three times to provide pure [DMMB-im] NTf$_2$.

On comparing the cation structure of [DMMB-im] BF$_4$ (Scheme 2) and of an RTim-IL with a long chain, such as [BMO-im] BF$_4$ (Scheme 5), it can be seen that by changing the cation alkyl chain length, the solubility in water can be effectively tuned. Synthetically, using the reaction conditions for the RTim-ILs presented in Scheme 2, we have shown an improvement in energy use and a shorter reaction time as compared to similar systems that have previously been reported (see Table 2, entries 3, 4, 11, 16–22).

Room-Temperature Phosphonium-Based IL (RTP-ILs). Phosphonium-based ILs have been reported to possess higher thermal stabilities than most ILs and excellent lubrication properties. They are also efficient media as solvents used in several reactions, including the mild nitration of arenes and the base-promoted Baylis–Hillman reaction through the stabilization of zwitterionic intermediates exerted by polar additives. Alkylidithiophosphate compounds with longer alkyl chain groups provide lower wear rates compared to compounds with shorter chains, as additives in base oil in the concentration range of 0.1–1.0 wt %.

The bulkiness of the cation weakens the electrostatic interactions with the anion, resulting in weaker interactions between the ions. The interplay of these interactions within IL structures and between ILs and surfaces are used to design ILs with tunable lubrication properties. Phosphonium cations, such as trialkylphosphines, as well as a limited number of tetraalkylphosphonium halides are currently commercially available.

Here, phosphonium IL [TBP$_{888}$] NTf$_2$ was synthesized as shown in Scheme 3. Compared to the synthesis of ILs of similar structures (see Table 2, entries 5, 12–15), our novel phosphonium-based RTPILs were synthesized through a synthetic protocol that massively reduces the reaction time (from 72 to 12 h), the use of solvents (pet ether vs solvent-free for the first step, CH$_2$Cl$_2$/water vs CH$_2$Cl$_2$ for the second step), and the energy expenditure (similar temperatures for the first step, but room temperature vs 40–60 °C for the second step) through the fine-tuning of reaction conditions. Preparation of the bromide intermediate IL [TBP$_{888}$] Br, was performed at 135 °C for 12 h in neat conditions. The anion exchange reaction to prepare [TBP$_{888}$] NTf$_2$ was performed at 40 °C in 18 h in water/CH$_2$Cl$_2$ (1:1) at RT for 30 min. CH$_2$Cl$_2$ was required to solubilize the cation (which is insoluble in water) and it was easier to remove thanks to its low boiling point, after the reaction attained completion. Both steps were carried out on a large research laboratory scale to afford 34 g of [TBP$_{888}$] NTf$_2$.

Room-Temperature Monomer Imidazolium-Based ILs (RTMim-ILs). Recently poly(ionic liquid) (PILs) or polymerized ILs have emerged for applications in materials science and polymer chemistry. PILs are polyelectrolytes that are made up of a polymerized IL block copolymer. IL monomers for PIL synthesis are becoming increasingly popular with applications in biphasic reaction catalysis, electromechanical actuator membranes and diluents, separation membranes, and water purification agents.
IL monomer species for use in PIL synthesis tend to be quite expensive. Literature syntheses to monomer intermediate ILs include reaction conditions of 110 °C for 48−72 h in toluene or at 82 °C for 48−72 h in acetonitrile.61 (Table 2, entries 6, 17−22).

Herein, the monomer ILs were achieved via a greener protocol, as shown in Scheme 4, and at a much lower cost in comparison with the current monomer ILs in the market.64 The intermediate monomer IL [ABM-im] Br was synthesized in acetonitrile at 40 °C in 4 h as monitored by 1H NMR analyses run at regular intervals. The anion exchange was then completed at RT, in 30 min, with water as the reaction medium. The bromide intermediate IL [ABM-im] Br is a hydrophilic material, however, product IL [ABM-im] NTf2 is a hydrophobic species.

**Room-Temperature Imidazolium Based ILs with Long Chain Cations (RTim ILs).** In petroleum science and technology, long alkyl chain ILs are used as surfactants to increase oil recovery.65 Furthermore, 1-decyl-3-methylimidazolium tetrafluoroborate in the oxidative desulfurization of diesel exhibited high catalytic activity for the removal of dibenzothiophene.66 1-Alkyl-3-methylimidazolium hydrogen sulfate ILs (with C6−C14-long alkyl chains) are also utilized as surfactants with catalytic activities67 and as fuel additives.36,68

In this work, the C8-long chain bromide intermediate IL [BMO-im] Br was prepared using low cost raw materials via the SN2 displacement reaction between 1-benzyl-2-methylimidazole and 1-bromooctane in acetonitrile at 70 °C (Scheme 5). Consequently, anion exchange in water at room temperature provided the corresponding hydrophobic RTILs [BMO-im] NTf2, [BMO-im] BF4, and [BMO-im] PF6 in 30 min. The anion exchange protocol was carried out on a 29 g scale for IL product [BMO-im] NTf2. Table 2 (entries 7−9, 17−22) compares our synthetic protocols to the ones for ILS of similar structures reported in the chemical literature.

**Thermal Decomposition by TGA.** For measurement of thermogravimetric data, TGA was carried out on a TA Instruments SDTQ600, and a derivative thermogravimetric analysis (DTG) was used for all TGA data obtained (Figure 1). TGA was used to ascertain the thermal stability of the ILs in the range of temperatures 25−600 °C (all data in Figure 1). All the novel ILs synthesized displayed relatively high TGA values for ILs, ranging from a minimum value of 380 °C for [BMO-im] BF4 to a maximum value of 474 °C for [DMMB-im] NTf2.

The two main structural parameters under analysis were the anion type and the cation type. The anion influence on the thermal stability of the ILs was studied by fixing the cation type (see Figure 1) and varying the anion. The order of thermal stability found here was [BMO-im] BF4 < [BMO-im] PF6 < [BMO-im] NTf2 and [DMMB-im] BF4 < [DMMB-im] NTf2. The thermal stability for these is consistent with the current literature data which provides the following thermal stability trend in anionic variations [BF4] < [PF6] < [NTf2].69

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The thermal stability of ILs with different anions decreases with the increase of nucleophilicity and hydrophilicity of the corresponding anion.70,71 The thermal decomposition temperature ($T_d$) values ranged from 386 °C for [BMO-im] BF4, to 393 °C for [BMO-im] PF6, and to 450 °C for [BMO-im] NTf2; likewise they increased from 442 °C for [DMMB-im] BF4 to 474 °C for [DMMB-im] NTf2.

The data also indicate that the [DMMB-im] cation provides a more thermally stable RTIL for the same anion (BF4) than [BMO-im], however their respective NTf2 RTILs possess very similar TGA values. The temperature range for the anion series was wider for the [BMO-im] cation than for the [DMMB-im] cation, where a much narrower temperature range was measured for TGA values. The influence of the cation was studied through fixing the anion and varying the cation. In Figure 1, the NTf2 series is shown with the TGA values for the imidazolium-based RTIL series increasing in the following way [ABM-im] NTf2 < [BM-M-TMSi-im] NTf2 < [BMO-im] NTf2 < [DMMB-im] NTf2. $T_d$ values ranged from 408 °C for [ABM-im] NTf2 to 430 °C for [BM-M-TMSi-im] NTf2, to 449 °C for [BMO-im] NTf2 and to 474 °C for [DMMB-im] NTf2. Structurally three of these four RTILs have the same benzyl group bonded to one of the methylimidazoliun N atoms, namely, [ABM-im], [BM-M-TMSi-im], and [BMO-im].

Therefore, the difference in $T_d$ values can be ascribed to the other side-chain present, which is an allyl group for [ABM-im], a methyl trimethylsilane group for [BM-M-TMSi-im], and an n-octane group for [BMO-im]. The increase in $T_d$ values can be rationalized in terms of the relative chemical stabilities of these groups in their bonding with benzyl methylimidazolium. The allyl group seems to be the least thermally stable, which is likely due to the presence of the isolated, terminal double bond, which upon temperature increase can undergo a number of reactions, including condensation, cycloaddition, rearrangement, addition, and isomerization without need for a catalyst.72 This is in agreement with literature values for allyl-based ILs, which tend to possess the lowest relative thermal stability.73

The second most thermally stable RTIL was the [BM-M-TMSi-im] cation, which has a silicon-containing branched alkane. Si-containing alkanes tend to be less thermally stable than their corresponding parent alkane. This can be seen with neopentane and tetramethylsilane flashpoints of −7 and −27 °C, respectively, and thermal decomposition of tetramethylsilane yielding alkanes.

Linear alkane chains such as n-octane in the [BMO-im] cation can establish van der Waals interactions with adjacent molecules more effectively than branched alkane derivatives, such as methyl trimethylsilane in [BM-M-TMSi-im], which stabilizes these long-chain alkane systems. Furthermore, they tend to be relatively unreactive because of stable σ-bonds between atoms of very similar or equal electronegativities.

The $T_d$ value for the [DBBM-im] cation was similar to that for the [BMO-im] cation as they both possess an alkane chain bonded to one of the N atoms of the methylimidazolium ring and the principal structural difference is the methyl group versus the benzyl group bonded to the second methylimidazolium N atom. Benzyl groups can undergo thermal decomposition too, aided by the formation of educts stabilized by aromaticity.74,75 For the BF4 series, we compared the cations [DMMB-im] and [BMO-im] and the thermal stabilities also followed the trend [BMO-im] BF4 < [DMMB-im] BF4.

Figure 1. TGA results for [DBU-M-TMSi]NTf2, [BM-M-TMSi-im]NTf2, [DMMB-im]BF4, [DMMB-im]NTf2, [TBP88]NTf2, [ABM-im]NTf2, [BMO-im]BF4, [BMO-im]PF6, [BMO-im]NTf2.
Hence, depending on the potential application of the ILs, when imidazolium is the core cationic component, aromatic structures covalently bonded to it play a prominent role in the IL thermal stabilities. The TGA values for the novel ILs demonstrate that their thermal stability is among the highest 5% reported for ILs.73,76

**Thermal Behavior of ILs.** The thermal behavior of the novel ILs was studied by differential scanning calorimetry (DSC), which gives information about phase transitions such as solid–solid phase transitions (e.g., glass transition), solid–liquid phase transitions (e.g., melting), and liquid–solid phase transitions (crystallization).77 In this study, DSC gives information on phase transitions of our pure novel ILs. Glass transition temperature (\(T_g\)) is one of the most important properties of ILs, where the IL transition from a hard and glassy state to a soft and rubbery state is monitored. At this transition, the IL does not melt, but undergoes a slight softening (phase change) at elevated temperatures.

Figure 2 shows the DSC results for the novel ILs with the \(T_g\) values summarized in Table 1. A comparison of the NTf2 anion containing ILs shows that \([DBU-M-TMSi]\) NTf2 displayed a lower \(T_g\) than \([BM-M-TMSi-im]\) NTf2: −56.3 °C as compared to −43.3 °C. This difference indicates that the \([DBU-M-TMSi]\) cation provides a lower viscosity, higher free volume, and ion mobility than the \([BM-M-TMSi-im]\) cation. These silicon-based ILs could be useful even for low temperatures as oil additives for lubrication applications.

Furthermore, due to the flat geometry of the imidazolium and benzene rings means the \([BM-M-TMSi-im]\) cations can more easily form a regular, crystalline lattice at lower temperatures. \([DMMB-im]\) NTf2 shows the lowest \(T_g\) (−72.4 °C) due to the small, asymmetrical cation, which provides more ion mobility as well as free volume and results in a lowering of the \(T_g\). \([TBP_{888}]\) NTf2 displays a similarly low \(T_g\) (−71.7 °C), even though it has a localized charge on the phosphonium cation. Its big and asymmetrical structure along with the free rotation of the benzyl ring may help to decrease its \(T_g\).

Comparing the \([BMO-im]\) cation series to determine the effect of changing the structure of anions reveals that, as the anion species becomes bigger and the charge more delocalized, its \(T_g\) shifts to lower values, which results in an increase of ion mobility, free volume, and/or less viscosity.

**Starting Materials and Yields.** In this work, low-cost, commercially available starting materials were used for the syntheses, such as technical grade 1-benzyl-2-methylimidazole (90%) and the reaction conditions were optimized to deliver high yields and highly pure IL products over two synthetic steps. These readily available starting materials, optimized synthetic and greener protocols are crucial to the large-scale commercialization of ILs. In this work, yields for all the novel ILs are provided in Figure 3. Furthermore, all IL products are liquids at room temperature, which for industrial use is a very advantageous physical property (e.g., for transportation) (Figure 4).

**Comparison with Previous Works.** We summarized the optimized synthetic methodologies for our ILs to protocols of structurally related and currently available ILs from the chemical literature in Table 2.

### CONCLUSIONS

Greener, safe, environmentally friendly, and expeditious synthetic methodologies were developed to produce novel series of imidazolium-, phosphine-, imidazolium monomer-, and silicon-based ILs in high yields, purities, and laboratory scales. Characterization of the ILs were carried out through the study of their 1D NMRs, namely, \(^1H\), \(^{13}C\), \(^{31}P\), \(^{19}F\), \(^{11}B\) NMR, and 2D NMRs, high-resolution mass spectra, thermal stabilities, and behaviors. One of the critical challenges for RTIL production that has been addressed in this paper is the very high manufacturing costs that currently limits their large-scale production in industry. Herein, the use of low cost and commercially available starting materials to synthesize RTILs possessing highly desirable purities and physical properties is reported. Furthermore, it is noted that silicon-based RTILs are not yet available on the market for either academic or industrial applications. These ILs have potential applications as lubricants or as additives for light-weight materials, such as aluminum.77,82,83

### EXPERIMENTAL SECTION

**General Experimental Section. Materials.** 1-Benzyl-2-methylimidazole (technical grade, 90%), DBU (98%), 1-bromo-3-methylbutane (96%), 1-bromooctane (99%), allyl bromide (99%), trioctylphosphate (97%), NaBF4 (98%), and benzyl bromide (98%) were purchased from Sigma Aldrich. Sodium iodide (99.5%), 1,2-dimethylimidazole (98%), and potassium hexafluoroarsenate (99%) were purchased from Alfa Aesar. (Chloromethyl)trimethylsilane (98%) was gifted by Wacker Co. The reagents were used as provided without further purification, with NMR analysis confirming an acceptable degree of purity and correct structural identity.

**Nuclear Magnetic Resonance Spectroscopy.** Nuclear magnetic resonance (NMR) Spectra were recorded on Bruker Ascend TM 400, in the deuterated solvent stated. Chemical

![Figure 2. DSC heating traces (10 °C min⁻¹) of novel ILs.](https://dx.doi.org/10.1021/acsomega.9b04091)

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**Table 1.** \(T_g\) Results of Novel ILs

| ILs          | \([DBU-M-TMSi]\) NTf2 | \([BM-M-TMSi-im]\) NTf2 | \([DMMB-im]\) NTf2 | \([TBP_{888}]\) NTf2 | \([ABM-im]\) NTf2 | \([BMO-im]\) PF6 | \([BMO-im]\) NTf2 |
|--------------|-----------------------|--------------------------|-------------------|---------------------|-----------------|----------------|----------------|
| \(T_g\)      | −56.3                 | −43.3                    | −72.4             | −71.7               | −59.3           | −42.5          | −36.1          | −59.3            |

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shifts (δ) are quoted in ppm and coupling constants (J) in Hz. Residual signals from the solvents were used as an internal reference, using the following reference chemical shifts: CDCl₃ at 7.26 ppm for ¹H NMR and 77.2 ppm for ¹³C NMR.

**Mass Spectrometry.** HRMS spectra were obtained at the Analytical and Biomolecular Research Facilities at the University of Newcastle, Australia, from samples resuspended in 1 mL of acetonitrile with 0.1% formic acid (∼1 mg/mL), before being further diluted to ∼10 ng/mL in 50% acetonitrile/water containing 0.1% formic acid. Samples were infused directly into the HESI source of a Thermo Scientific Q Exactive plus (QE+) using an on-board syringe pump at 5 mL/min. Data were acquired on the QE+ in both positive and negative ion mode at a target resolution of 70,000 at 200 m/z. Raw MS files were manually processed using Thermo Qualbrowser while the isotopic patterns of predicted chemical formula were modeled using Bruker Compass Isotope Pattern to give a predicted formula.

**Thermogravimetric Analysis.** TGAs were obtained on a SDTQ600 thermogravimetric analyzer (TA Instruments). Each IL sample (5−10 mg) was placed in an alumina pan under an atmosphere of nitrogen with a flow rate of 100 mL/min. Pyrolysis of each IL sample was then carried out over a temperature range 25−800 °C with a temperature ramp rate of 5 °C/min.

**Differential Scanning Calorimetry.** DSC measurements were made using a Netzsch DSC 214 Polyma instrument with liquid N₂ cooling, driven by Proteus 70 software. Samples (5−20 mg) were sealed in Al pans inside an argon-filled glovebox. Samples were cooled at 10 °C min⁻¹ from room temperature to −100 °C and, after an isothermal equilibration time of 10 min, heated to 60 or 80 °C at the same scan rate. Three thermal cycles were performed for samples with heat flow regulated to a rate of 10⁶/°C/min for all the samples.

**Drying of ILs.** In order to minimize water content, all ILs were dried for 6 h on a rotary evaporator at 60 °C as low as the pressure allowed to go (a few mbars). Then, they were dried under high vacuum overnight.

**Experimental Section.** RTSi-ILs. Preparation of 1-(Methyl trimethylsilane)-1,8-diazbicyclo[5.4.0]undec-7-ene Chloride [DBU-M-TMSi]Cl and of 1-(Methyl trimethylsilane)-1,8-diazabicyclo[5.4.0]undec-7-ene Bis(trifluoromethylsulfonfonyl)amide [DBU-M-TMSi] NTf₂. Under neat conditions, (chloromethyl)trimethylsilane (20.00 mmol, 2.453 g) was added dropwise to 1,8 diazabicyclo[4.5.0]undec-7-ene (20.00 mmol, 3.045 g) under an atmosphere of nitrogen at RT. After the addition was complete, the temperature was raised to 70 °C and the reaction stirred for 2 h. After completion of the reaction, monitored via ¹H NMR, the temperature was allowed to return to RT and the resulting product 1-(methyl trimethylsilane)-1,8-diazabicyclo[4.5.0]undec-7-ene chloride [DBU-M-TMSi] Cl was an off-white solid (5.344 g, 97%), which was used in succeeding reactions without further purification.

The [DBU-M-TMSi] Cl (19.44 mmol, 5.344 g) was dissolved in deionized water (5 mL) and stirred at RT. Bis(trifluoromethane)sulfonimide lithium (19.44 mmol, 5.581 g) dissolved in deionized water (5 mL) was added slowly to the stirred solution of [DBU-M-TMSi] Cl, dissolved in deionized water (10 mL) at RT. The resulting solution was stirred for a further 30 min at RT with immiscible colorless liquid forming at

![Figure 3. Yield of novel RTILs over two synthetic steps.](image)

![Figure 4. Images of selected novel RTILs. (Left) [TBP₈₈₈] NTf₂, (middle) [BMO-im] NTf₂, and (right) [DBU-M-TMSi] NTf₂. Photograph courtesy of Mahdi Ghorbani. Copyright 2020.](image)
### Table 2. Synthetic Methodology Comparison of Our Novel ILs vs Structurally Related, Currently Available ILs Reported in the Chemical Literature

| Entry | Class          | Intermediate IL Structure | Reaction Conditions | IL Product Structure | Reaction Conditions |
|-------|----------------|---------------------------|---------------------|----------------------|---------------------|
| 1     | RTSi-ILs       | [DBU-M-TMSi] Cl           | 70 °C, 2 h, solvent-free | [DBU-M-TMSi] NTf₂   | RT, 0.5 h, water    |
| 2     | 2. RTim-ILs    | [BM-M-TMSi-im] Br         | 80 °C, 12 h, Na₂Cl₄CN | [BM-M-TMSi-im] NTf₂ | RT, 0.5 h, CH₃Cl₂ water |
| 3     | 3. RTP-ILs     | [DMMB-im] Br              | 85 °C, 12 h, solvent-free | [DMMB-im] BF₄  | RT, 1 h, CH₃Cl₂ water |
| 4     | 4. RTMim-ILs   | [ABM-im] Br               | 40 °C, 4 h, CH₃CN   | [ABM-im] NTf₂     | RT, 0.5 h, water    |
| 5     | 5. RTMim-ILs   | [BMO-im] Br               | 70 °C, 72 h, CH₃CN   | [BMO-im] BF₄  | RT, 0.5 h, water    |
| 6     | 6. RTMim-ILs   | [BM-[CH₂]₄(OEt)₄]        | 60 °C, 24 h, CH₃Cl₂   | [BM-[CH₂]₄(OEt)₄] BF₄ | RT, 0.5 h, water    |
| 7     | 7. RTMim-ILs   | [P[8888]] Br              | 110 °C, 48°–72 h, toluene (or) | [P[8888]] Br  | RT, 24 h, water    |
| 8     | 8. RTMim-ILs   | [OM-im] Br               | 80 °C, 24 h, toluene  | [OM-im] F(CF₂)₄SO₃ | RT, 48 h, acetone, CH₃Cl₂ |
| 9     | 9. RTMim-ILs   | [TP(8888)] Br           | 70 °C, 12 h, tolune  | [TP(8888)] Br | RT, 24 h, water    |
| 10    | DBU derivatives cf. 1. RTIL | [DBU-Et] Br | 60 °C, 48 h, CH₃CN   | [DBU-Et] SCN    | RT, 24 h, CH₃Cl₂ water |
| 11    | cf. 2. RTim-ILs | [DHPA-im] Cl           | 130 °C, 48 h, solvent-free | [DHPA-im] NTf₂ | RT, N/A h, ethyl acetate, CH₃CN, water |
| 12    | cf. 3. RTP-ILs | [TPB] Cl²               | 120 °C, 72 h, pet. ether, water | [TPB] BF₄ | 62 °C, 18 h, CH₃Cl₂ |
| 13    | cf. 4. RTMim-ILs | [TOP] Cl²             | 120 °C, 72 h, pet. ether, water | [TOP] NTf₂ | 60 °C, 18 h, water; CH₃Cl₂ |
| 14    | [P[8888]] Br | 110 °C, 72 h, n-hexane | [P[8888]] Br | RT, 6 h, anion exchange exchange (Amberlites IRN-78), water/ethanol (1:2, v/v) |
| 15    | 16. cf. 1. RTSi-ILs | [TBP] Cl²               | 110 °C, 48°–72 h, toluene (or) | [TBP] Cl² | RT, 24 h, water    |
| 17    | 17. RTILs cf. 2. RTILs | [OM-im] Br²           | 80 °C, 24 h, toluene  | [OM-im] F(CF₂)₄SO₃ | RT, 48 h, acetone, CH₃Cl₂ |
| 18    | [TMHEDA] Br | 80 °C, 12 h, tolune | [TMHEDA] Br | RT, 48 h, acetone, CH₃Cl₂, water |
| 19    | [2MOPYR] Br | 70 °C, N/A h, CH₃CN | [2MOPYR] Br | RT, 24 h, CH₃CN, CH₃Cl₂, water |
| 20    | [F(CF₂)₄(CH₂)₄min] | 120 °C, 0.33 h, CH₃Cl₂, microwave, water, 3-layer separation | [F(CF₂)₄(CH₂)₄min] F(CF₂)₄SO₃ | reflux, 4 h, dry propanol, CH₃Cl₂ |
| 21    | [BCP] Br² | 135 °C, 18 h, solvent-free, wash with ethyl acetate | [BCP] NTf₂ | 70 °C, N/A h, water |
| 22    | [iPr₂N(CH₂)₂N¹¹¹¹]Cl | reflux, 24 h, CH₃CN, Na₂CO₃ | [iPr₂N(CH₂)₂N¹¹¹¹] Cl | RT, N/A h, CH₃Cl₂ water |

**Abbreviations used for IL cations retrieved from the chemical literature:** [TBP]: tributyl phosphate, [TOP]: tributyl(2,3-dihydroxypropyl)-phosphonium, [P[8888]]: 1-(2-diisopropylaminoethyl)dimethylethylammonium, [F-CF₂)₄(CH₂)₄min]: fluoroalkyl methylimidazolium, [BCP]: 1-buty1-4-cyanopyridinium. Other abbreviations: cf.: compare to, hr: hour/s, N/A: not available, RT: room temperature.

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the bottom of the reaction vessel. The water was decanted off and the liquid was washed with water (3 × 5 mL) and dried under vacuum to afford 9.796 g (97.0%) of pure [DBU-CH₂-TMSi-im] Cl as colorless liquid. H NMR (400 MHz, CDCl₃): δ (ppm) 0.12 (s, 9H), 1.67–1.74 (m, 6H), 2.05 (p, J = 5.9 Hz, 2H), 2.70 (d, J = 10.4 Hz, 2H), 3.09 (s, 2H), 3.38 (t, J = 5.6 Hz, 2H), 3.47 (t, J = 6.4 Hz, 2H), 3.55 (d, J = 9.6 Hz, 2H); 13C NMR (100 MHz, CDCl₃): δ (ppm) = 2.2, 19.7, 22.6, 25.8, 28.3, 28.6, 46.1, 48.7, 48.9, 55.0, 114.9, 118.1, 121.3, 124.5; 19F NMR (376 MHz, CDCl₃): δ (ppm) = 78.88; HRMS (FTMS ESI+): for [DBU-M-TMSi-im] (cation) [M⁺] requires, 239.19380; found, 239.19377; (FTMS ESI−): for NTf₂ (anion) [NTf₂] [M⁻] requires, 279.91675; found, 279.89721.

**RTILs. Preparation of 1-Benzyl-2-methyl-3-(methyl trimethylsilyl)imidazolium Chloride ([BM-M-TMSi-im] Cl) and of 1-Benzyl-2-methyl-3-(methyl trimethylsilyl)imidazolium bis(trifluoromethylsulfonyl)amide ([BM-M-TMSi-im] NTf₂).** To a stirring solution of 1-benzyl-2-methyl-imidazol (5.00 mmol, 0.861 g) in acetonitrile (3 mL), (chloromethyl)trimethylsilane (5.00 mmol, 0.613 g) was added dropwise and then NaI (20 mmol %, 0.150 g) under an atmosphere of nitrogen at RT. After the addition was complete, the temperature was raised to 80 °C and the reaction was allowed to stir for 12 h. After completion of the reaction, monitored via H NMR, the temperature was allowed to return to RT. The acetonitrile was evaporated in vacuo to give 1-benzyl-2-methyl-3-(methyl trimethylsilyl) chloride ([BM-M-TMSi-im] Cl) as an off-white powder, which was used in succeeding reactions without further purification.
Preparation of 1,2-Dimethyl-3-(3-methylbutane)-imidazolium Bromide [DMMB-im] Br and of 1,2-Dimethyl-3-(3-methylbutane)imidazolium Tetrafluoroborate [DMMB-im] BF₄. Under neat conditions, trioctylphosphine (25.00 mmol, 1.510 g) under an atmosphere of nitrogen at RT. The temperature was raised to 85 °C and the reaction allowed to stir for 12 h. After completion of the reaction, monitored via ¹H NMR, the temperature was allowed to return to RT and the product 1,2-dimethyl-3-(3-methylbutane)imidazolium bromide [DMMB-im] Br formed as a light orange solid, which was used in succeeding reactions without further purification.

[Bis(trifluoromethylsulfonyl)amide] [TBP₈₈₈] NTf₂. Under neat conditions, trioctylphosphine (25.00 mmol, 9.226 g) was added slowly to triethylbromoborate (25.00 mmol, 4.276 g) under an atmosphere of nitrogen at RT. The temperature was raised to 135 °C and the reaction allowed to stir for 12 h. After completion of the reaction, monitored via ¹H NMR, the temperature was allowed to return to RT and the product benzyltrietylphosphonium bromide [TBP₈₈₈] Br formed as a crystalline snowly solid, which was used in succeeding reactions without further purification.

The [TBP₈₈₈] Br was dissolved in CH₂Cl₂ (20 mL) and stirred at RT. Bis(trifluoromethane)sulfonimide lithium (25.00 mmol, 7.177 g), dissolved in deionized water (10 mL), was added slowly to the stirring solution of [TBP₈₈₈] Br, dissolved in deionized water (10 mL) at RT. The resulting solution was stirred for a further 30 min at RT with immiscible colorless liquid forming at the bottom of the reaction vessel. The vessel was decanted off, and the liquid was washed with water (3 × 10 mL) and dried under vacuum to afford 17.064 g (92.0%) of pure [TBP₈₈₈] NTf₂, as transparent colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.87 (t, J = 6.4 Hz, 9H), 1.24–1.42 (m, 36H), 2.03–2.09 (m, 6H), 3.60 (d, J = 14.4 Hz, 2H), 7.21–7.23 (m, 2H), 7.36–7.38 (m, 3H), ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 14.2, 18.4, 18.9, 21.5, 21.6, 22.7, 28.8, 29.0, 30.6, 30.7, 31.8, 124.9, 127.7, 127.8, 128.9, 129, 115.2, 118.5, 121.7, 129.8, 129.86, 129.88, 129.91; ¹⁵PF NMR (162 MHz, CDCl₃): 31.72; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) −78.75; HRMS (FTMS ESI⁺): for [TBP₈₈₈] (cation) [M]+ requires, 279.91675; found, 279.89856.

RTMim-ILs. Preparation of 1-Allyl-3-benzyl-2-methylimidazolium Bromide [ABM-im] Br and of 1-Allyl-3-benzyl-2-methylimidazolium Bis(trifluoromethylsulfonyl)amide [ABM-im] NTf₂ as Monomer ILs. A stirring solution of 1-benzyl-2-methylimidazolium lithium (5.00 mmol, 0.861 g) in acetonitrile (3 mL) was added dropwise to allyl bromide (5.00 mmol, 0.605 g) under an atmosphere of nitrogen at RT. After the addition was complete, the temperature was raised to 40 °C and the reaction allowed to stir for 4 h. After completion of the reaction, monitored via ¹H NMR, the temperature was allowed to return to RT. The acetonitrile was evaporated in vacuo to give 1-allyl-2-methylimidazolium bromide (5.00 mmol, 0.605 g) under an atmosphere of nitrogen at RT. After the addition was complete, the temperature was raised to 40 °C and the reaction allowed to stir for 4 h. After completion of the reaction, monitored via ¹H NMR, the temperature was allowed to return to RT. The acetonitrile was evaporated in vacuo to give 1-allyl-2-methylimidazolium bromide [ABM-im] Br as yellow viscous liquid that was used in succeeding reactions without further purification.

The product [ABM-im] Br was then dissolved in deionized water (3 mL) and stirred at RT. Bis(trifluoromethane)sulfonimide lithium (5.00 mmol, 1.435 g) dissolved in deionized water (3 mL) was added slowly to the stirring solution of [ABM-im] Br, dissolved in deionized water (5 mL) at RT. The resulting solution was stirred for a further 30 min at RT with immiscible pale yellow liquid forming at the bottom of the reaction vessel. The vessel was decanted off, and the liquid was washed with water (3 × 5 mL) and dried under vacuum to afford 4.162 g (93.0%) of pure 1,2-dimethyl-3-(3-methylbutane)imidazolium bis(trifluoromethylsulfonyl)amide as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.92 (d, 6.3 Hz), 1.62–1.64 (m, 3H), 2.54 (s, 3H), 3.73 (s, 3H), 3.99 (t, J = 9.6 Hz, 2H), 7.14 (dd, J = 2.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 9.4, 22.0, 25.5, 35.2, 38.2, 47.2, 115.0, 118.2, 120.7, 121.4, 122.5, 124.6, 143.7; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) −79.1; HRMS (FTMS ESI⁺): for [DMMB-im] (cation) [M]+ requires, 167.15482; found, 167.15418; (FTMS ESI⁺): for NTf₂ (anion) [NTf₂]⁻ [M]+ requires, 279.91765; found, 279.91799.

RTP-ILs. Preparation of Benzyltri-n-octylphosphonium Bromide [TBP₈₈₈] Br and of 3-Benzyltri-n-octylphosphonium Bis(trifluoromethylsulfonyl)amide [TBP₈₈₈] NTf₂. Under neat conditions, trioctylphosphine (25.00 mmol, 9.226 g) was added slowly to triethylbromoborate (25.00 mmol, 4.276 g) under an atmosphere of nitrogen at RT. The temperature was raised to 135 °C and the reaction allowed to stir for 12 h. After completion of the reaction, monitored via ¹H NMR, the temperature was allowed to return to RT and the product benzyltrietylphosphonium bromide [TBP₈₈₈] Br formed as a crystalline snowly solid, which was used in succeeding reactions without further purification.
Preparation of 1-Benzyl-2-methyl-3-octylimidazolium Hexafluorophosphate [BMO-im] PF6. 1-Benzyl-2-methyl-3-octylimidazolium bromide (17.00 mmol, 6.211 g) was dissolved in deionized water (10 mL) and stirred at RT. Potassium hexafluorophosphate (17.00 mmol, 3.129 g), dissolved in deionized water (20 mL), was added slowly to the stirring solution of [BMO-im] Br. The resulting solution was stirred for a further 30 min at RT with immiscible yellow liquid forming at the bottom of the reaction vessel. The water was decanted off, and the liquid was washed with water (3 × 5 mL) and dried under vacuum to afford 1.582 g (85.0%) of pure 1-benzyl-2-methyl-3-octylimidazolium hexafluorophosphate [BMO-im] PF6 as yellow compound. 

1H NMR (400 MHz, CDCl3): δ (ppm) 0.86 (t, J = 6.9 Hz, 3H), 1.23–1.28 (m, 10H), 1.75 (t, J = 6.8 Hz, 2H), 2.57 (s, 3H), 4.04 (t, J = 7.5 Hz, 2H), 5.28 (s, 2H), 7.23–7.27 (m, 4H), 7.33–7.35 (m, 3H); 13C NMR (100 MHz, CDCl3): δ (ppm) 9.8, 14.1, 22.6, 26.3, 29.01, 29.07, 29.7, 31.7, 48.7, 52.0, 121.2, 121.7, 126.9, 128.2, 120.0, 129.1, 129.4, 133.0, 143.8; 19F NMR (376 MHz, CDCl3): δ (ppm) 9.7, 14.2, 22.7, 26.3, 29.0, 29.1, 29.6, 31.8, 48.8, 52.1, 121.2, 121.6, 128.3, 129.3, 129.6, 132.7, 143.8; 13C NMR (100 MHz, CDCl3): δ (ppm) 73.65, 78.9; HRMS (FTMS ESI+): for [BMO-im] (cation) [M]+ requires, 279.23238; found, 279.23232. 

Preparation of 1-Benzyl-2-methyl-3-octylimidazolium Tetrafluoroborate [BMO-im] BF4. 1-Benzyl-2-methyl-3-octylimidazolium bromide (20.00 mmol, 5.742 g), dissolved in deionized water (5 mL), was added slowly to the stirring solution of [BMO-im] Br. The resulting solution was stirred for a further 30 min at RT with immiscible yellow and cloudy liquid forming at the bottom of the reaction vessel. The water was decanted off, and the liquid was washed with water (3 × 5 mL) and dried under vacuum to afford 9.728 g (86.0%) of pure [BMO] NTf2 as transparent crumbly solid, which was used in succeeding reactions without further purification.

The [BMO-im] Br was dissolved in deionized water (10 mL) and stirred at RT. Bis(trifluoromethyl)sulfonylimide lithium (20.00 mmol, 5.742 g), dissolved in deionized water (5 mL), was added slowly to the stirring solution of [BMO-im] Br. The resulting solution was stirred for a further 30 min at RT with immiscible yellow and cloudy liquid forming at the bottom of the reaction vessel. The water was decanted off, and the liquid was washed with water (3 × 5 mL) and dried under vacuum to afford 1.614 g (86.0%) of pure [BMO] NTf2 as transparent yellow liquid. 

1H NMR (400 MHz, CDCl3): δ (ppm) 0.86 (t, J = 6.8 Hz, 3H), 1.278 (m, 10H), 1.79 (t, J = 7.6 Hz, 2H), 2.58 (s, 3H), 4.04 (t, J = 7.6 Hz, 2H), 5.24 (s, 2H), 7.10 (d, J = 2.4 Hz, 1H), 7.20–7.23 (m, 3H), 7.38–7.40 (m, 3H); 13C NMR (100 MHz, CDCl3): δ (ppm) 9.9, 14.0, 22.5, 26.2, 28.8, 28.9, 29.5, 31.6, 48.9, 52.3, 118.2, 121.1, 121.4, 121.5, 124.6, 127.5, 128.1, 129.6, 132.3, 143.6; 19F NMR (376 MHz, CDCl3): δ (ppm) −78.9; HRMS (FTMS ESI+): for [BMO-im] (cation) [M]+ requires, 285.23253; found, 285.23238; (FTMS ESI−): for NTf2 (anion) [NTf2]− [M]− requires, 279.91675; found, 279.89726.

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