Biodegradable ionic liquids: Part I. Concept, preliminary targets and evaluation

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The design, preparation and evaluation of biodegradable ionic liquids containing ester or amide groups in the alkyl side chain are presented. Factors improving the biodegradation of surfactants were successfully applied to ionic liquids. These novel ionic liquids can be prepared from readily available starting materials in high yield. The introduction of a group susceptible to enzymatic hydrolysis greatly improves the biodegradation (OECD 301D 'Closed Bottle Test') compared with the commonly used dialkylimidazolium ionic liquids, bmimBF₄ and bmimPF₆. For the 3-methyl-1-(alkyloxycarbonylmethyl)imidazolium bromide series, the greatest biodegradation was observed when alkyl = butyl, pentyl, hexyl and octyl. The corresponding amide analogs proved to be poorly biodegradable.

Introduction

Ionic liquids (ILs) have been the subject of considerable interest as media for a wide range of synthetic and analytical processes.^{1,2} They are considered in a 'green chemistry' context due to their low vapour pressure, ease of recovery facilitating recycling³ and applicability to catalytic processes.⁴ ILs possess a number of interesting properties such as high polarity and ionic conductivity, a wide window of electrochemical potential and excellent chemical and thermal stability. However, it is this stability that has led us to question the potential for ILs to accumulate in the environment.⁵ When the ionic liquid has served its operational use, disposal becomes an issue. As the pressure to reduce incineration and landfill waste increases the requirement for chemicals which are biodegradable increases.⁶ Within the field of green chemistry it is unacceptable to produce large quantities of waste which have high ecotoxicity or biological activity.⁷ Seddon reported the first industrial process where ionic liquids were used on a multi-tonne scale.⁸ As ionic liquids advance from academic curiosities the need to study their toxicity and biodegradation is paramount.

Toxicity to humans and other organisms has obvious significance, while toxicity to micro organisms has the potential to limit biodegradation. Like biodegradability, the assessment of IL toxicity is only now being addressed. There have been a few articles stating that there is a need to test the biodegradation of ionic liquids⁵ however experimental results to ascertain these properties have been surprisingly lacking.

In a preliminary communication⁹ we reported the first investigation into the biodegradability of the dialkylimidazolium ionic liquids. We chose the dialkylimidazolium ILs as a starting point and incorporated features which have been found to improve the biodegradability of other classes of compounds such as surfactants. Since this initial disclosure of our findings no biodegradation data on ILs has been published, although a few preliminary toxicology results have been reported.

Jastorff and co-workers subsequently reported a theoretical environment risk analysis on a test set of dialkylimidazolium ILs.¹⁰ This multidimensional analysis was based on five ecotoxicological indicators; release, spatiotemporal range, bioaccumulation, biological activity and uncertainty. The current lack of detailed experimental data on the biodegradability of ILs complicated

predictions on bioaccumulation and spatiotemporal range and resulted in a high uncertainty level.

Our inspiration for this work came from the development of biodegradable surfactants. We now report our progress towards preparing a readily biodegradable ionic liquid.

History of surfactants

The development of biodegradable surfactants¹¹ has been of significant commercial interest since the 1940's when synthetic surfactants were developed as a replacement for soap in many laundry products. Tetrapropylene alkyl benzene sulfonates (TPBS)¹² were manufactured extensively but due to their poor biodegradation lead to major problems in sewage treatment and contamination of river waters.¹³

Modification of the highly branched alkyl chain to the linear secondary alkyl group gave linear alkylbenzene sulfonate surfactants (LAS) with greatly improved biodegradation.¹⁴ In the 1960's TPBS were phased out and replaced with LAS in the United States.¹²

On further examination of the literature regarding biodegradation of surfactant compounds we noticed a close resemblance between many quaternary ammonium compounds as well as surfactants based around an imidazolium core. These derivatives have a striking resemblance to the structure of many of the most important ILs prepared to date and we felt that much of the work developing biodegradable surfactants would be relevant to the design of a biodegradable ionic liquid. In particular is the development of biodegradable surface active quaternary ammo-

nium compounds (QACs). The most popular QAC used initially was the dialkyl dimethyl ammonium salt (**1**), however the biodegradation of **1** in aquatic sediments is low and this coupled to its ecotoxicity has led to its replacement by dialkyl QACs based on the imidazolium and ethoxylated ethanaminium QACs (compounds **2** and **3**).¹⁵ The presence of the amide bonds led to improved biodegradation properties due to an extra hydrolysis degradation pathway. Ester derivatives (**4** and **5**) and related compounds have also been prepared and show good biodegradation.^{15,16c}

Design

Boethling¹⁵ identified three factors which are important in the design of biodegradable compounds; (i) the presence of potential sites of enzymatic hydrolysis (for example, esters and amides), (ii) the introduction of oxygen in the form of hydroxyl, aldehyde or carboxylic acid groups, and (iii) the presence of unsubstituted linear alkyl chains (especially ≥ 4 carbons) and phenyl rings, which represent possible sites for attack by oxygenases. These principles have been followed during the development of biodegradable surfactants.^{16–18}

Not all of these structural features are appropriate for ILs. The incorporation of oxygen containing functional groups such as alcohols, aldehyde and carboxylic acids would severely limit the ILs usefulness as reaction media, while the introduction of phenyl groups is known to produce compounds with elevated melting points.¹⁹ As a result, we chose to prepare dialkylimidazolium ILs with ester or amide functionality in one of the side chains. It was deemed important to limit branching in the side chains so only linear alkyl groups attached to the ester and amide were chosen. An important feature of this design is that although there are a very large number of possible ionic liquids that can theoretically be prepared based on the imidazolium core, within the limits suggested in the design segment of this paper, the number of potential hot targets is reasonably small. The incorporation of an ester or amide group was postulated to be a balance between reduced chemical stability and increased biodegradability.

A major concern at the design stage of this project was the physical properties of these modified imidazolium ionic liquids. Points which needed to be addressed were 1) melting points and 2) solubility and the effect of the ester/amide alkyl length on these properties. If the inclusion of an ester or amide bond into the side chain lead to increased order and crystallinity these target ionic liquids would only be liquids at elevated temperatures. A key property of PF₆[−] and NTf₂[−] based ILs is their hydrophobic nature. If the hydrogen bonding possible with the ester or amide in the side chain was sufficient to remove this hydrophobic character then their use as alternatives for BmimPF₆ and BmimNTf₂ would be compromised.

Results and discussion

Syntheses of the ILs described in this manuscript were based on standard approaches for the preparation of imidazolium ILs.^{19,20} This process involved alkylation of methyl imidazole with the appropriate ester or amide derivative of bromoacetic acid.

The esters or amide derivatives of bromoacetic acid were either commercially available or formed in one step *via* the reaction of bromoacetyl bromide with the appropriate alcohol or amine.²¹ An advantage of this route is that a wide range of ester and amide side chains can be prepared easily. For ionic liquids with anions other than bromide, a metathesis reaction was employed to introduce the counter ion of choice (Scheme 1). Metathesis of the halide anion to

Scheme 1 IL synthesis [compounds in parentheses are solids at room temperature].

BF₄[−], PF₆[−], NTf₂[−] and N(CN)₂[−] proceeded in good to excellent yield. BF₄[−] ionic liquids were prepared by counter-ion exchange with NaBF₄ in acetonitrile. Removal of the solvent gave IL contaminated with trace NaBF₄ as shown by ¹⁹F NMR. Clean samples could be isolated after a simple work-up. Compound **9h** was prepared by counter-ion exchange with KPF₆ in acetonitrile. PF₆[−] and NTf₂[−] based ionic liquids (except **9h**) were prepared by mixing an aqueous solution of the bromide salt with KPF₆ or LiNTf₂, respectively. The hydrophobic IL phase was separated, washed and residual water removed under high vacuum to give pure samples. N(CN)₂[−] ionic liquids were prepared by counter-ion exchange with NaN(CN)₂ in acetonitrile analogously to the BF₄[−] ionic liquid examples.²²

Imidazolium salts with ester containing side chains were generally found to be liquids at room temperature; 21 of the 23 ester containing compounds proved to be liquids at room temperature, though compound **8a** and all ILs with the bromide counter ion were viscous at room temperature. ILs with amide containing side chains were less likely to be room temperature ionic liquids; 6 of the 12 examples prepared were solids at room temperature. The secondary amide derivatives **7h** and **9h** were solids, presumably due to increased intermolecular forces resulting from H-bonding. Imidazolium salts with *N,N*-diethyl amide side chains (compounds **7j**, **9j** and **10j**) were solids, while *N*-butyl-*N*-methyl amides (compounds **7i**, **8i**, **10i**, **11i**) were liquids at room temperature.

There are two main features of the *N*-butyl-*N*-methyl amides (**7i**–**11i**) which affect their macroscopic properties. Firstly, the unsymmetrical environment around the nitrogen of the amide (*cf.* with solid *N,N*-diethyl amide examples **7j**, **9j** and **10j**), as symmetry has previously been reported as important regarding melting point.^{1,23} Secondly, the *N*-butyl-*N*-methyl amides (**7i**–**11i**) prepared exist as a 1 : 1.3 mixture of rotomers around the amide bond and it

is proposed that this isomeric mixture leads to a depression of the melting point.²⁴

All the ionic liquids prepared in this paper have melting points below 100 °C, a benchmark which has been set to determine their classification as ILs.⁸

All PF₆ and NTf₂ ILs containing an ester or amide in the side chain were hydrophobic except for the secondary amide derivative **9h**. The introduction of the polar functional group did not significantly affect the water solubility of the IL. The use of PF₆ ionic liquids outside of the research laboratory has been questioned due to their propensity to evolve HF if not stored and handled carefully.^{5c} The authors note that for the ionic liquids presented within, HF formation would lead to decomposition. The PF₆ ILs were prepared to study their properties however their suitability as industrial chemicals seems limited.

Biodegradation testing data

Two samples (**7b** and **8b**) were evaluated in a commercial laboratory²⁵ using a modified Sturm test (OECD 301B). In this test, the chemical being evaluated is added to aerobic aqueous medium inoculated with wastewater micro organisms and the evolution of CO₂ is measured for a defined period and reported as a percentage of the theoretical maximum. The Organisation for Economic Cooperation and Development (OECD) has approved this modified Sturm test as one means of assessing biodegradability.²⁶ Compounds which evolve more than 60% of the total CO₂ are considered to be a pass (OECD 301B). This test was applied to two dialkylimidazoles with ester containing side chains (compounds **7b** and **8b**) and bmimPF₆. All three examples appeared to be relatively close to the pass level (**7b** = 48%, **8b** = 59% and bmimPF₆ = 60%). After these preliminary results a more comprehensive biodegradation study was initiated.

A larger panel of ionic liquids with functionalised side chains were evaluated using the 'Closed Bottle Test' (OECD 301D).²⁷ In this test the IL was added to an aerobic aqueous medium inoculated with wastewater micro organisms and the depletion of dissolved molecular oxygen was measured for a defined period of time and reported as a percentage of the theoretical maximum. Duplicate bottles of each series were analysed at the start of the test for dissolved oxygen and the remaining bottles were incubated at 20 °C ± 1 °C in the dark. Bottles of all series were withdrawn in duplicate for dissolved oxygen analysis over the 28-day incubation period. A control with inoculum, but without test chemicals was run in parallel for the determination of oxygen blanks. Sodium *n*-dodecyl sulfate (SDS) was used as reference substance. Compounds which reached a biodegradation level higher than 60% are referred to as readily biodegradable. Readily biodegradable has been defined as "an arbitrary classification of chemicals which have passed certain specified screening tests for ultimate biodegradability; the conditions in these tests are so stringent – relatively low density of non-acclimatized bacteria, relatively short duration, absence of other compounds – that such chemicals will rapidly and completely biodegrade in aquatic environments under aerobic conditions".¹¹

The data showed significant differences between the biodegradability of the ionic liquids incorporating an ester group and those containing an amide linker in the side chain. ILs incorporating different alkyl esters (from methyl to octyl) in the side chain presented similar biodegradation profiles (Fig. 1).

It appears that the biodegradation increased slightly with increasing alkyl chain length for the lowest alkyl esters and later remained relatively constant (Fig. 2). Regarding the structure of ionic liquids containing an ester group in the chain side, it seems reasonable that the biodegradation of these molecules may be initiated by enzymatic cleavage of the ester bond leading to the separation of the imidazolium fragment and the corresponding primary alcohol that can readily be metabolized *via* the pathway of fatty acid β -oxidation.¹⁷

Fig. 1 Biodegradation curves of the ionic liquids containing an ester group in the cation side chain (3-methyl-1-(alkyloxymethylcarbonyl)-imidazolium bromides): Me (●), Et (▲), Pr (▼), Bu (◆), Pent (+), Hex (×), Oct (*); reference substance: SDS (■).

Fig. 2 Biodegradation (28-day period) of 3-methyl-1-(alkyloxymethyl)imidazolium bromides as a function of the number of carbon atoms of the alkyl chain.

No evidence for some extent of ultimate biodegradation was detected for ILs containing an amide linker in the side chain (Fig. 3).

Fig. 3 Biodegradation curves of ionic liquids incorporating an amide group in the cation side chain: N(Et₂) (●), N(BuH) (▲), N(BuMe) (▼); reference substance: SDS (■).

The two most widely used ionic liquids in academia and industry are based on the 1-*n*-butyl-3-methylimidazolium core. *i.e.* bmimBF₄ and bmimPF₆. These ILs, with bmimBr, were also tested for biodegradation by the 'Closed Bottle Test' (OECD 301D). BmimBF₄ and bmim PF₆ were found to show no biodegradation (0%) in this test. BmimBr was found to have negligible biodegradation as measured by the Closed Bottle Test (1%). Comparison of compounds **7a–j** and bmimBr shows that the incorporation of the ester functional group has greatly improved the biodegradation properties of the IL. A more detailed study of counter-ion effect on biodegradation is in progress.

The results obtained from the Closed Bottle Test differed from those obtained using the modified Sturm test, with the latter

indicating higher levels of biodegradation. Such differences may be related to the inoculum that was used. Biodegradation is intimately bound up with bacterial growth, nutrition and metabolism, and factors which affect these bacterial functions will also affect the biodegradability assessments. The nature and quantity of the inoculum play an important role in biodegradability assessment; the inoculum is probably the biggest single factor in the success of the batch test. Although the Closed Bottle and modified Sturm test have a number of similarities, the inoculum cell densities in these tests methods vary considerably (Closed Bottle Test; 10^1 – 10^3 cells mL^{-1} , modified Sturm test; 10^4 – 10^6 cells mL^{-1}). The bacterial cell density in the medium determines, to a large extent, the length of the lag period and also whether sufficient test substance is degraded within the duration of the test. If the number of cells capable of degrading the test substance is relatively high, the density will soon reach a value which makes a significant reduction in the concentration of the substance. However, when the initial cell density is relatively low, the lag period before a significant density is reached may be longer than the period of the test (28 days). Thus, the large differences found in the extent of ultimate biodegradation applying these two biodegradation methods could be reasonably attributed to significant variability in cell density.

The biodegradation data should be interpreted with caution taking into account the features both of the biodegradation test applied as well of the chemicals studied. Screening methods have been used in many studies on the biodegradability of quaternary ammonium compounds, namely surfactants such as alkyltrimethyl ammonium salts and benzylalkyldimethyl ammonium salts.^{28,29} It has been found that degradation rates of these compounds in screening methods significantly underestimated the rate and the extent of degradation occurring in natural environmental systems.^{30,31} Since imidazolium compounds are similarly charged ammonium ion-species similar results would be expected.

The toxicity of the ionic liquids may also have a negative impact on their biodegradation. Many quaternary ammonium salts are potential biocides and could inhibit growth of micro organisms capable of degrading quaternary ammonium salts.^{32–35} Ranke *et al.*³⁶ recently conducted the first comprehensive study on the biological effects of dialkylimidazolium ionic liquids. Cytotoxic effects of IL were determined against two mammalian cell lines (the promyelocytic leukaemia rat cell line IPC-18 and the rat glioma cell line C6) while acute toxicity was measured using a luminescent bacteria (*Vibrio fischeri*) assay. In general the toxicity of the ILs was found to be some orders of magnitude lower than that of the conventional solvents such as acetone, acetonitrile, methanol and methyl *tert*-butyl ether. The length of the alkyl chains was found to influence the toxicity of the dialkylimidazolium ILs, with longer chain lengths proving to be more toxic. A search of the literature shows that the biological properties of these biocides is related to their long alkyl chain length.^{37,38}

The anti-microbial activity of a series of 3-alkoxymethyl-1-methylimidazolium ionic liquids (**13**, $\text{R} = \text{C}_3\text{H}_7$ – $\text{C}_{16}\text{H}_{33}$, $\text{X} = \text{Cl}$, BF_4 , PF_6) has also been investigated.³⁷ ILs with shorter alkoxy substituents lacked activity against cocci, rods and fungi, while those with longer alkoxy chains (> 10 carbon atoms) proved to be very active. These findings have implications for the use of such IL as media for biotransformations as well as their degradation by micro organisms. A study of soft antimicrobials including 1-[(*n*-dodecanoyloxy)methyl]-3-methylimidazolium chloride (**14**) by Bodor *et al.* showed that the long chain ester derivatives of methyl imidazole (including **14**) show effective antimicrobial activity at ppm concentrations.³⁹ Similarly, other alkyl substituted imidazolium compounds (*e.g.* **15**) have also been found to possess biological activity.⁴⁰

Therefore, the biodegradation results found could be related to the inhibitory effects of the quaternary ammonium salts on the bacterial populations. In light of these results, further investigations on biodegradability and potential toxicity of ionic liquids should be carried out.

Conclusions

ILs containing an ester in the side-chain were generally found to be liquids at room temperature, independent of the counter-ion. The amide derivatives were solids at room temperature except for the *N*-butyl-*N*-methyl series. NTf_2 and PF_6 ILs containing an ester in the side chain exhibited the same hydrophobic character as bmimNTf_2 and bmimPF_6 .

The Bmim derived ILs and examples containing an amide in the side chain were found to show poor to negligible biodegradation as measured by the Closed Bottle Test (OECD 301D). The incorporation of an ester in the side chain resulted in a significant increase in biodegradation. Esters of type **7** with an alkyl chain length of ≥ 4 proved to be the most biodegradable. It is postulated that this improved biodegradation is due in part to an enzymatic hydrolysis step which initiates a pathway to further breakdown products. Significant enhancement in the biodegradation of methylimidazolium ILs has been achieved. The factors which improved the biodegradation of surfactants have successfully been applied to ionic liquids.

Experimental

Methyl bromoacetate, ethyl bromoacetate, propyl bromoacetate were purchased from Aldrich and used without further purification. Butyl bromoacetate, pentyl bromoacetate, hexyl bromoacetate, octyl bromoacetate, *N,N*-diethyl-2-bromo-acetamide, *N*-butyl-2-bromoacetamide and *N*-butyl-*N*-methyl-2-bromoacetamide were prepared as described below, and purified by distillation. Ethyl chloroacetate was purchased from Fluka and used without further purification. 1-Methylimidazole (99%, Aldrich) was distilled before use to remove impurities detrimental to all ILs prepared. All organic solvents were dried and distilled before use. ILs were washed with distilled water. 3-Methyl-1-(methoxycarbonylmethyl)imidazolium bromide (**3a**) was prepared according to the literature [mp = 131 – 133 °C].¹⁹ 1-*n*-Butyl-3-methylimidazolium BF_4 , PF_6 and NTf_2 were prepared according to the literature. All NMR spectra of ILs were recorded in CD_3CN (Aldrich 15,180–7, 99.8 atom %D) on a Bruker Avance DPX 300 spectrometer. ^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75.4 MHz respectively. NMR spectra of the ester and amide derivatives of bromoacetic were recorded in CDCl_3 . Melting points are uncorrected. All room temperature ionic liquids were placed in the fridge (2 °C) and freezer (-18 °C) to further evaluate their melting points. Unless indicated in the experimental data below (see **8g** and **9g**) all the room temperature ionic liquids did not crystallise at -18 °C. However, the viscosity of the ionic liquids at this temperature was significantly increased. A study of glass transition temperatures was not attempted with these materials. Determination of the physical properties of the ionic liquids prepared is still in progress (*e.g.* solubility, thermal stability, viscosity, density and stability to hydrolysis⁴¹) and will be reported in due course.

3-Methyl-1-(ethoxycarbonylmethyl)imidazolium bromide (7b)

To a stirred solution of 1-methylimidazole (4.1 g, 4.0 mL, 50 mmol) in THF (50 mL) at -5°C under a nitrogen atmosphere was added dropwise ethyl bromoacetate (10.0 g, 6.7 mL, 60 mmol). The reaction mixture was stirred vigorously at -5°C for 1 h, then at rt for 3 h. The THF top phase was decanted and the IL washed with diethyl ether (3×10 mL), then residual solvent removed *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 98% yield (12.2 g, 49 mmol). ^1H NMR (300 MHz, CD_3CN) δ 9.38 (s, 1H), 7.64 (s, 1H), 7.51 (s, 1H), 5.30 (s, 2H), 4.23 (q, $J = 7.0$ Hz, 2H), 3.93 (s, 3H), 1.25 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz) δ 167.80, 138.72, 124.82, 124.10, 63.23, 51.06, 37.40, 14.63. MS (ESI): m/z , 169.1 $[\text{M}-\text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(propoxycarbonylmethyl)imidazolium bromide (7c)

This compound was prepared analogously to **7b** using 1-methylimidazole (2.11 g, 2.05 mL, 25 mmol) and propyl bromoacetate (5.46 g, 3.90 mL, 30 mmol) to give a clear viscous hygroscopic oil in 96% yield (6.31 g, 24 mmol). ^1H NMR (300 MHz, CD_3CN) δ 9.57 (s, 1H), 7.78 (s, 1H), 7.63 (s, 1H), 5.42 (s, 2H), 4.10 (q, $J = 7.0$ Hz, 2H), 3.94 (s, 3H), 1.62 (tt, $J = 7.0, 7.0$ Hz, 2H), 0.89 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.93, 138.89, 124.81, 124.40, 68.73, 51.08, 37.40, 22.68, 10.75. MS (ESI): m/z , 183.1 $[\text{M}-\text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(butoxycarbonylmethyl)imidazolium bromide (7d)

This compound was prepared analogously to **7b** using 1-methylimidazole (3.86 g, 3.75 mL, 47 mmol) in diethyl ether (50 mL) and butyl bromoacetate (11.0 g, 56.4 mmol) to give a clear viscous hygroscopic oil in 98% yield (12.75 g, 47 mmol). ^1H NMR (300 MHz, CD_3CN) δ 9.44 (s, 1H), 7.66 (s, 1H), 7.53 (s, 1H), 5.33 (s, 2H), 4.18 (t, $J = 7.0$ Hz, 2H), 3.93 (s, 3H), 1.62 (tt, $J = 7.5, 7.5$ Hz, 2H), 1.38 (tt, $J = 7.5, 7.5$ Hz, 3H), 0.92 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.58, 138.76, 124.66, 124.23, 66.94, 66.20, 50.90, 37.16, 31.15, 19.63, 13.89. MS (ESI): m/z , 197.2 $[\text{M}-\text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(pentoxycarbonylmethyl)imidazolium bromide (7e)

This compound was prepared analogously to **7b** using 1-methylimidazole (4.93 g, 4.78 mL, 60 mmol) in diethyl ether (50 mL) and pentyl bromoacetate (15.0 g, 71.8 mmol) to give a clear viscous hygroscopic oil in 97% yield (16.98 g, 58 mmol). ^1H NMR (300 MHz, CD_3CN) δ 9.49 (s, 1H), 7.69 (s, 1H), 7.55 (s, 1H), 5.36 (s, 2H), 4.16 (t, $J = 7.0$ Hz, 2H), 3.94 (s, 3H), 1.61 (tt, $J = 7.5, 7.5$ Hz, 2H), 1.38–1.28 (m, 4H), 0.89 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.56, 138.75, 124.62, 124.18, 67.16, 50.87, 37.13, 28.76, 28.48, 22.84, 14.17. MS (ESI): m/z , 211.1 $[\text{M}-\text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(hexoxycarbonylmethyl)imidazolium bromide (7f)

To a stirred solution of 1-methylimidazole (2.11 g, 2.05 mL, 25 mmol) in diethyl ether (25 mL) at -5°C under a nitrogen atmosphere was added dropwise hexyl bromoacetate (6.70 g, 5.31 mL, 30 mmol). The reaction mixture was stirred vigorously at -5°C for 1 h, then at rt for 3 h. The diethyl ether top phase was decanted and the IL washed with diethyl ether (3×10 mL) then residual solvent removed *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 92% yield (7.01 g, 23.0 mmol). ^1H NMR (300 MHz, CD_3CN) δ 9.49 (s, 1H), 7.69 (s, 1H), 7.56 (s, 1H), 5.36 (s, 2H), 4.15 (t, $J = 7.0$ Hz, 2H), 3.93 (s, 3H), 1.67–1.57 (m, 2H), 1.40–1.25 (m, 6H), 0.87

(t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.95, 139.03, 124.95, 124.54, 67.51, 51.20, 37.50, 32.32, 29.36, 26.35, 23.48, 14.60. MS (ESI): m/z , 225.2 $[\text{M}-\text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(octoxycarbonylmethyl)imidazolium bromide (7g)

This compound was prepared analogously to **7f** using 1-methylimidazole (0.84 g, 0.82 mL, 10.3 mmol) and octyl bromoacetate (3.01 g, 12.0 mmol) to give a clear viscous hygroscopic oil in 95% yield (3.26 g, 9.8 mmol). ^1H NMR (300 MHz, CD_3CN) δ 9.41 (s, 1H), 7.64 (s, 1H), 7.53 (s, 1H), 5.32 (s, 2H), 4.17 (t, $J = 7.0$ Hz, 2H), 3.94 (s, 3H), 1.70–1.60 (m, 2H), 1.40–1.20 (m, 10H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.97, 139.08, 125.00, 124.59, 67.58, 51.23, 37.52, 32.84, 30.23, 30.18, 29.48, 26.75, 23.68, 14.73. MS (ESI): m/z , 253.3 $[\text{M}-\text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(*N*-butylcarbamoylmethyl)imidazolium bromide (7h)

This compound was prepared analogously to **7f** using 1-methylimidazole (0.42 g, 0.41 mL, 5.0 mmol) and *N*-butyl-2-bromoacetamide (1.16 g, 6.0 mmol) to give an oil in 94% yield (1.30 g, 4.7 mmol). The oil slowly crystallised at room temperature. ^1H NMR (300 MHz, CD_3CN) δ 9.11 (s, 1H), 8.39 (bs, 1H, NH), 7.56 (s, 1H), 7.45 (s, 1H), 5.14 (s, 2H), 3.90 (s, 3H), 3.15 (q, $J = 7.0$ Hz, 2H), 1.52–1.40 (m, 2H), 1.40–1.37 (m, 2H), 0.87 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz) δ 166.12, 138.89, 124.99, 124.58, 52.70, 40.48, 37.62, 32.55, 21.28, 14.57. MS (ESI): m/z , 196.1 $[\text{M}-\text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(*N*-butyl-*N*-methylcarbamoylmethyl)-imidazolium bromide (7i)

To a stirred solution of 1-methylimidazole (821 mg, 0.80 mL, 10 mmol) in THF (15 mL) at -5°C under a nitrogen atmosphere was added dropwise *N*-butyl-*N*-methyl-2-bromoacetamide (2.50 g, 12 mmol, 1 : 1.3 mixture of isomers) in THF (5 mL). The reaction mixture was stirred vigorously at -5°C for 1 h, then at rt for 48 h. The THF top phase was decanted and the IL washed with THF (2×5 mL), then residual solvent removed *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 95% yield (2.76 g, 9.51 mmol). * denotes both isomers. ^1H NMR (300 MHz, CD_3CN) δ 8.78 (s, 1H, minor), 8.74 (s, 1H, major), 7.43–7.35 (m, 2H*), 5.22 (s, 2H, major), 5.19 (s, 2H, minor), 3.90 (s, 3H*), 3.37 (t, $J = 7.0$ Hz, 2H, major), 3.30 (t, $J = 7.0$ Hz, 2H, minor), 3.02 (s, 3H, major), 2.92 (s, 3H, minor), 1.70–1.25 (m, 4H*), 0.99 (t, $J = 7.0$ Hz, 3H, minor), 0.93 (t, $J = 7.0$ Hz, 3H, major). ^{13}C (75 MHz) δ 165.85 (major), 165.53 (minor), 138.89 (minor), 138.72 (major), 125.01 (minor), 124.91 (major), 123.75 (minor), 123.72 (major), 51.70 (major), 51.33 (minor), 49.64 (minor), 48.53 (major), 37.19*, 34.96 (major), 34.24 (minor), 30.86 (minor), 29.94 (major), 20.69 (minor), 20.58 (major), 14.25*. MS (ESI): m/z , 210.2 $[\text{M}-\text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(*N,N*-diethylcarbamoylmethyl)imidazolium bromide (7j)

This compound was prepared analogously to **7b** using 1-methylimidazole (1.05 g, 1.02 mL, 12.8 mmol) and *N,N*-diethyl-2-bromoacetamide (2.98 g, 15.4 mmol) to give a crystalline solid in 99% yield (3.51 g, 12.7 mmol). mp = $66\text{--}68^{\circ}\text{C}$; ^1H NMR (300 MHz, CD_3CN) δ 9.27 (s, 1H), 7.60 (s, 1H), 7.47 (s, 1H), 5.44 (s, 2H), 3.91 (s, 3H), 3.37 (q, $J = 7.0$ Hz, 2H), 3.34 (q, $J = 7.0$ Hz, 2H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.06 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 165.17, 139.25, 125.54, 124.14, 51.80, 42.60, 41.97, 37.55, 14.86, 13.67. MS (ESI): m/z , 196.1 $[\text{M}-\text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(methoxycarbonylmethyl)imidazolium BF₄ (8a)

A dry flask was charged with 3-methyl-1-(methoxycarbonylmethyl)imidazolium bromide (**7a**) (702 mg, 3.0 mmol) and acetonitrile (2 mL) under a nitrogen atmosphere. NaBF₄ (362 mg, 3.3 mmol) was added in one portion and the suspension was stirred vigorously for 4 days at rt. The fine white precipitate was filtered quickly in air and washed with dry acetonitrile (2 × 1 mL). The filtrate and washings were combined, solvent removed by rotary evaporation then *in vacuo*. The product was dried at 60 °C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 96% yield (0.70 g, 2.9 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.58 (s, 1H), 7.40 (s, 2H), 5.02 (s, 2H), 3.89 (s, 3H), 3.78 (s, 3H). ¹³C (75 MHz) δ 168.33, 138.75, 125.15, 125.00, 54.33, 51.18, 37.63. ¹⁹F (254 MHz) δ -151.6 (BF₄⁻). MS (ESI): *m/z*, 155.1 [M-BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(ethoxycarbonylmethyl)imidazolium BF₄ (8b)

This compound was prepared analogously to **8a** using 3-methyl-1-(ethoxycarbonylmethyl)imidazolium bromide **7b** (1.79 g, 6.3 mmol) and NaBF₄ (0.69 g, 6.3 mmol) to give a clear viscous hygroscopic oil in 92% yield (1.51 g, 5.9 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.66 (s, 1H), 7.44 (s, 1H), 7.40 (s, 1H), 5.30 (s, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.83, 138.80, 125.16, 124.93, 63.90, 51.31, 37.64, 14.83. ¹⁹F (254 MHz) δ -151.6 (BF₄⁻). MS (ESI): *m/z*, 169.1 [M-BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(propoxycarbonylmethyl)imidazolium BF₄ (8c)

This compound was prepared analogously to **8a** using 3-methyl-1-(propoxycarbonylmethyl)imidazolium bromide **7c** (722 mg, 2.8 mmol) and NaBF₄ (333 mg, 3.0 mmol) to give a clear viscous hygroscopic oil in 98% yield (727 mg, 2.7 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.55 (s, 1H), 7.41 (s, 2H), 7.40 (s, 1H), 5.00 (s, 2H), 4.17 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.70 (qt, *J* = 7.0, 7.0 Hz, 2H), 0.95 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.90, 138.76, 125.15, 124.9, 69.24, 51.22, 37.58, 23.00, 10.96. ¹⁹F (254 MHz) δ -151.5 (BF₄⁻). MS (ESI): *m/z*, 183.1 [M-BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(hexoxycarbonylmethyl)imidazolium BF₄ (8f)

This compound was prepared analogously to **8a** using 3-methyl-1-(hexoxycarbonylmethyl)imidazolium bromide **7f** (758 mg, 2.25 mmol) and NaBF₄ (247 mg, 2.50 mmol) to give a clear viscous hygroscopic oil in 90% yield (630 mg, 2.0 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.63 (s, 1H), 7.43 (s, 2H), 7.40 (s, 1H), 5.02 (s, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.70-1.60 (m, 2H), 1.42-1.28 (m, 6H), 0.91 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.85, 138.76, 125.17, 124.94, 67.87, 51.30, 37.64, 32.55, 29.56, 26.58, 23.72, 14.77. ¹⁹F (254 MHz) δ -151 (BF₄⁻). MS (ESI): *m/z*, 225.2 [M-BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(octoxycarbonylmethyl)imidazolium BF₄ (8g)

This compound was prepared analogously to **8a** using 3-methyl-1-(octoxycarbonylmethyl)imidazolium bromide **7g** (350 mg, 1.05 mmol) and NaBF₄ (127 mg, 1.16 mmol) to give a clear viscous hygroscopic oil in 97 % yield (346 mg, 1.02 mmol). The oil crystallised in the freezer at -18 °C. ¹H NMR (300 MHz, CD₃CN) δ 8.50 (s, 1H), 7.40 (s, 2H), 7.38 (s, 1H), 4.98 (s, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.70-1.60 (m, 2H), 1.42-1.25 (m, 10H), 0.91 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.87, 138.79, 125.16, 124.95, 67.85, 51.25, 37.60, 30.38, 30.32, 29.59, 26.89, 23.83, 14.88. ¹⁹F (254 MHz) δ -151.4 (BF₄⁻). MS (ESI): *m/z*, 253.3 [M-BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(*N*-butylcarbamoylmethyl)imidazolium BF₄ (8h)

This compound was prepared analogously to **8a** using 3-methyl-1-(*N*-butylcarbamoylmethyl)imidazolium bromide **7h** (128 mg, 0.45 mmol) and NaBF₄ (50 mg, 0.50 mmol) in acetonitrile (1 mL) to give a clear viscous hygroscopic oil in 86% yield (110 mg, 0.39 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.55 (s, 1H), 7.39 (s, 1H), 7.35 (s, 1H), 7.05 (bs, 1H, NH), 4.85 (s, 2H), 3.86 (s, 3H), 3.20 (q, *J* = 7.0 Hz, 2H), 1.55-1.40 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.40-1.28 (qt, *J* = 7.0, 7.0 Hz, 2H), 0.92 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 165.73, 138.65, 125.10, 124.59, 52.39, 20.54, 37.50, 32.52, 21.11, 14.45. ¹⁹F (254 MHz) δ -151.7 (BF₄⁻). MS (ESI): *m/z*, 196.1 [M-BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(*N*-butyl-*N*-methylcarbamoylmethyl)imidazolium BF₄ (8i)

This compound was prepared analogously to **8a** using 3-methyl-1-(*N*-butyl-*N*-methylcarbamoylmethyl)imidazolium bromide **7i** (256 mg, 0.88 mmol, 1 : 1.3 mixture of isomers) and NaBF₄ (107 mg, 0.97 mmol) to give a clear viscous hygroscopic oil in 98% yield (256 mg, 0.86 mmol, 1 : 1.3 mixture of isomers). * denotes both isomers. ¹H NMR (300 MHz, CD₃CN) δ 8.46 (s, 1H, minor), 8.44 (s, 1H, major), 7.40-7.30 (m, 2H*), 5.08 (s, 2H, minor), 5.05 (s, 2H, major), 3.88 (s, 3H*), 3.37 (t, *J* = 7.0 Hz, 2H, major), 3.28 (t, *J* = 7.0 Hz, 2H, minor), 3.00 (s, 3H, major), 2.92 (s, 3H, minor), 1.70-1.25 (m, 4H*), 0.99 (t, *J* = 7.0 Hz, 3H, minor), 0.93 (t, *J* = 7.0 Hz, 3H, major). ¹³C (75 MHz) δ 166.05 (major), 165.79 (minor), 139.14 (minor), 139.04 (major), 125.48 (minor), 125.44 (major), 124.43*, 121.42* (q, *J* = 320 Hz, CF₃), 51.76 (major), 51.51 (minor), 50.01 (minor), 49.15 (major), 37.41*, 35.07 (major), 34.65 (minor), 31.21 (minor), 30.35 (major), 21.10 (minor), 21.09 (major), 14.74 (major), 14.69 (minor). ¹⁹F (254 MHz) δ -152.10 (BF₄⁻). MS (ESI): *m/z*, 210.2 [M-BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(*N,N*-diethylcarbamoylmethyl)imidazolium BF₄ (8j)

This compound was prepared analogously to **8a** using 3-methyl-1-(*N,N*-diethylcarbamoylmethyl)imidazolium bromide **7j** (552 mg, 2.0 mmol) and NaBF₄ (242 mg, 2.2 mmol) to give a clear viscous hygroscopic oil in 92% yield (520 mg, 1.84 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.55 (s, 1H), 7.38 (s, 2H), 5.10 (s, 2H), 3.83 (s, 3H), 3.30 (m, 4H), 1.19 (t, *J* = 7.0 Hz), 1.07 (t, *J* = 7.0 Hz). ¹³C (75 MHz) δ 163.72, 137.68, 124.10, 122.95, 50.22, 41.12, 40.58, 36.01, 13.25, 12.21. ¹⁹F (254 MHz) δ -150.8 (BF₄⁻). MS (ESI): *m/z*, 196.1 [M-BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(methoxycarbonylmethyl)imidazolium PF₆ (9a)

A flask was charged with 3-methyl-1-(methoxycarbonylmethyl)imidazolium bromide **7a** (702 mg, 3.0 mmol) and distilled water (2 mL). KPF₆ (607 mg, 3.3 mmol) in distilled water (1 mL) was added in one portion and the suspension was stirred vigorously for 4 h at rt. The top aqueous layer was removed, the IL washed with water (3 × 1 mL) then the solvent removed *in vacuo*. The product was dried at 60 °C at 0.01 mmHg for 72 h to give a crystalline solid in 67% yield (0.61 g, 2.0 mmol). mp = 76-78 °C; ¹H NMR (300 MHz, CD₃CN) δ 8.49 (s, 1H), 7.39 (s, 2H), 4.99 (s, 2H), 3.88 (s, 3H), 3.79 (s, 3H). ¹³C (75 MHz) δ 168.32, 138.67, 125.14, 125.02, 54.35, 51.18, 37.64; ¹⁹F (254 MHz) δ -73.0 (d, *J*_{P-F} = 707 Hz, PF₆⁻); MS (ESI): *m/z*, 155.1 [M-PF₆⁻]⁺; MS (ESI): *m/z*, 144.9 [PF₆⁻].

3-Methyl-1-(ethoxycarbonylmethyl)imidazolium PF₆ (9b)

This compound was prepared analogously to **9a** using 3-methyl-1-(ethoxycarbonylmethyl)imidazolium bromide **7b** (0.55 g, 2.2 mmol) and KPF₆ (0.41 g, 2.2 mmol) to give a clear viscous oil in

68% yield (0.47 g, 1.5 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.47 (s, 1H), 7.39 (s, 2H), 4.97 (s, 2H), 4.26 (q, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.29 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.80, 138.65, 125.18, 125.00, 63.98, 51.30, 37.63, 14.84. ^{19}F (254 MHz) δ -72.5 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-). MS (ESI): m/z , 169.1 $[\text{M}-\text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(propoxycarbonylmethyl)imidazolium PF_6 (9c)

This compound was prepared analogously to **9a** using 3-methyl-1-(propoxycarbonylmethyl)imidazolium bromide **7c** (0.60 g, 2.3 mmol) and KPF_6 (464 mg, 2.5 mmol) to give a clear viscous oil in 78% yield (585 mg, 1.8 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.47 (s, 1H), 7.39 (s, 2H), 4.98 (s, 2H), 4.17 (t, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.69 (qt, $J = 7.0, 7.0$ Hz, 2H), 0.95 (t, $J = 7.0$ Hz, 3H); ^{13}C (75 MHz) δ 167.84, 138.65, 125.18, 124.99, 69.32, 51.28, 37.64, 23.03, 10.98; ^{19}F (254 MHz) δ -72.7 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-); MS (ESI): m/z , 183.1 $[\text{M}-\text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(hexoxycarbonylmethyl)imidazolium PF_6 (9d)

This compound was prepared analogously to **9a** using 3-methyl-1-(hexoxycarbonylmethyl)imidazolium bromide **7d** (762 mg, 2.3 mmol) and KPF_6 (458 mg, 2.5 mmol) to give a clear viscous oil in 89% yield (0.76 g, 2.1 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.49 (s, 1H), 7.39 (s, 2H), 4.98 (s, 2H), 4.20 (t, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.70–1.60 (m, 2H), 1.40–1.30 (m, 6H), 0.90 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.78, 138.62, 125.17, 124.97, 67.89, 51.28, 37.62, 32.54, 29.56, 26.57, 23.71, 14.77. ^{19}F (254 MHz) δ -71.94 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-). MS (ESI): m/z , 225.2 $[\text{M}-\text{PF}_6^-]^+$ MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(octoxycarbonylmethyl)imidazolium PF_6 (9g)

This compound was prepared analogously to **9a** using 3-methyl-1-(octoxycarbonylmethyl)imidazolium bromide **7g** (528 mg, 1.58 mmol) and KPF_6 (321 mg, 1.74 mmol) to give a colourless oil in 81% yield (508 mg, 1.27 mmol). The oil crystallised in the fridge at 2 °C. ^1H NMR (300 MHz, CD_3CN) δ 8.46 (s, 1H), 7.39 (s, 2H), 4.96 (s, 2H), 4.19 (t, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.72–1.60 (m, 2H), 1.42–1.25 (m, 10H), 0.90 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.77, 138.57, 125.15, 124.96, 67.88, 51.26, 37.62, 32.99, 30.38, 30.31, 29.58, 26.89, 23.84, 14.86. ^{19}F (254 MHz) δ -72.67 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-); MS (ESI): m/z , 253.3 $[\text{M}-\text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(*N*-butylcarbamoylmethyl)imidazolium PF_6 (9h)

A dry flask was charged with 3-methyl-1-(*N*-butylcarbamoylmethyl)imidazolium bromide **7h** (120 mg, 0.43 mmol) and acetonitrile (1 mL) under a nitrogen atmosphere. KPF_6 (96 mg, 0.52 mmol) was added in one portion and the suspension was stirred vigorously for 4 days at rt. The fine white precipitate was filtered quickly in air and washed with dry acetonitrile (2×1 mL). The filtrate and washings were combined, solvent removed by rotary evaporation then *in vacuo*. The product was dried at 60 °C at 0.01 mmHg for 72 h to give a clear crystalline solid in 99% yield (145 mg, 0.42 mmol). mp = 64–66 °C; ^1H NMR (300 MHz, CD_3CN) δ 8.46 (s, 1H), 7.36 (s, 2H), 6.78 (bs, 1H, NH), 4.80 (s, 2H), 3.87 (s, 3H), 3.21 (q, $J = 7.0$ Hz, 2H), 1.60–1.30 (m, 4H), 0.93 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 165.87, 138.66, 125.15, 124.69, 52.36, 40.68, 37.51, 32.53, 21.14, 14.55. ^{19}F (254 MHz) δ -72.46 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-); MS (ESI): m/z , 196.1 $[\text{M}-\text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(*N*-butyl-*N*-methylcarbamoylmethyl)-imidazolium PF_6 (9i)

This compound was prepared analogously to **9a** using 3-methyl-1-(*N*-butyl-*N*-methylcarbamoylmethyl)imidazolium bromide **7i** (265 mg, 0.91 mmol, 1:1.3 mixture of isomers) and KPF_6 (185 mg, 1.0 mmol) to give a crystalline solid in 70% yield (225 mg, 0.63

mmol, 1 : 1.3 mixture of isomers). mp = 62–64 °C; * denotes both isomers. ^1H NMR (300 MHz, CD_3CN) δ 8.42 (s, 1H, minor), 8.40 (s, 1H, major), 7.40–7.30 (m, 2H*), 5.06 (s, 2H, major), 5.03 (s, 2H, minor), 3.88 (s, 3H*), 3.37 (t, $J = 7.0$ Hz, 2H, major), 3.28 (t, $J = 7.0$ Hz, 2H, minor), 3.00 (s, 3H, major), 2.92 (s, 3H, minor), 1.70–1.25 (m, 4H*), 0.99 (t, $J = 7.0$ Hz, 3H, minor), 0.93 (t, $J = 7.0$ Hz, 3H, major); ^{13}C (75 MHz) δ 165.75 (major), 165.48 (minor), 138.93 (minor), 138.85 (major), 125.51 (minor), 125.45 (major), 124.42*, 51.86 (major), 51.61 (minor), 50.00 (minor), 49.18 (major), 37.50*, 35.05 (major), 34.59 (minor), 31.28 (minor), 30.36 (major), 21.11*, 14.69 (major), 14.65 (minor). ^{19}F (254 MHz) δ -72.38 (d, $J_{\text{P-F}} = 710$ Hz, PF_6^-); MS (ESI): m/z , 210.2 $[\text{M}-\text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(*N,N*-diethylcarbamoylmethyl)imidazolium PF_6 (9j)

This compound was prepared analogously to **9a** using 3-methyl-1-(*N,N*-diethylcarbamoylmethyl)imidazolium bromide **7j** (828 mg, 3.0 mmol) and KPF_6 (607 mg, 3.3 mmol) to give a crystalline solid in 66% yield (0.68 g, 2.0 mmol). mp = 64–66 °C; ^1H NMR (300 MHz, CD_3CN) δ 8.43 (s, 1H), 7.33 (s, 2H), 5.04 (s, 2H), 3.88 (s, 3H), 3.37 (q, $J = 7.0$ Hz, 2H), 3.34 (q, $J = 7.0$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 3H), 1.10 (t, $J = 7.0$ Hz, 3H); ^{13}C (75 MHz) δ 164.80, 138.85, 125.47, 124.34, 51.71, 42.50, 42.00, 37.54, 14.65, 13.55; ^{19}F (254 MHz) δ -72.8 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-); MS (ESI): m/z , 196.1 $[\text{M}-\text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(methoxycarbonylmethyl)imidazolium NTf_2 (10a)

A flask was charged with 3-methyl-1-(methoxycarbonylmethyl)imidazolium bromide **7a** (702 mg, 3.0 mmol) and distilled water (2 mL). LiNTf_2 (947 mg, 3.3 mmol) in distilled water (1 mL) was added in one portion and the suspension was stirred vigorously for 4 h at rt. The top aqueous layer was removed, the IL washed with water (3×1 mL) then the solvent removed *in vacuo*. The product was dried at 60 °C at 0.01 mmHg for 72 h to give a clear viscous oil in 93% yield (1.21 g, 2.8 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.49 (s, 1H), 7.39 (bs, 2H), 4.99 (s, 2H), 3.88 (s, 3H), 3.79 (s, 3H). ^{13}C (75 MHz) δ 168.23, 138.59, 125.22, 125.09, 121.39 (q, $J = 320$ Hz, CF_3), 54.31, 51.19, 37.64. ^{19}F (254 MHz) δ -80.15 (CF_3). MS (ESI): m/z , 155.1 $[\text{M}-\text{NTf}_2^-]^+$; MS (ESI): m/z , 279.9 $[\text{NTf}_2^-]$.

3-Methyl-1-(ethoxycarbonylmethyl)imidazolium NTf_2 (10b)

This compound was prepared analogously to **10a** using 3-methyl-1-(ethoxycarbonylmethyl)imidazolium bromide **7b** (0.53 g, 2.1 mmol) and LiNTf_2 (0.60 g, 2.1 mmol) to give a clear viscous oil in 90% yield (0.85 g, 1.9 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.46 (s, 1H), 7.39 (s, 2H), 4.96 (s, 2H), 4.26 (q, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.29 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.70, 138.66, 125.19, 124.98, 123.53 (q, $J = 320$ Hz, CF_3), 63.98, 51.33, 37.64, 14.81. ^{19}F (254 MHz) δ -80.05 (CF_3). MS (ESI): m/z , 169.1 $[\text{M}-\text{NTf}_2^-]^+$; MS (ESI): m/z , 279.9 $[\text{NTf}_2^-]$.

3-Methyl-1-(propoxycarbonylmethyl)imidazolium NTf_2 (10c)

This compound was prepared analogously to **10a** using 3-methyl-1-(propoxycarbonylmethyl)imidazolium bromide **7c** (0.95 g, 3.6 mmol) and LiNTf_2 (1.15 g, 4.0 mmol) to give a clear viscous oil in 92% yield (1.55 g, 3.4 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.49 (s, 1H), 7.39 (s, 2H), 4.99 (s, 2H), 4.17 (t, $J = 7.0$ Hz, 2H), 3.87 (s, 3H), 1.68 (tq, $J = 7.0, 7.0$ Hz, 2H), 0.95 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.89, 138.82, 125.27, 125.02, 121.44 (q, $J = 320$ Hz, CF_3), 69.44, 51.32, 37.63, 23.03, 11.03. ^{19}F (254 MHz) δ -80.06 (CF_3). MS (ESI): m/z , 183.1 $[\text{M}-\text{NTf}_2^-]^+$; MS (ESI): m/z , 279.9 $[\text{NTf}_2^-]$.

3-Methyl-1-(hexoxycarbonylmethyl)imidazolium NTf₂ (10d)

This compound was prepared analogously to **10a** using 3-methyl-1-(hexoxycarbonylmethyl)imidazolium bromide **7d** (680 mg, 2.0 mmol) and LiNTf₂ (637 mg, 2.2 mmol) to give a clear viscous oil in 89% yield (0.90 g, 1.8 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.47 (s, 1H), 7.39 (s, 2H), 4.97 (s, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 3.87 (s, 3H), 1.70–1.60 (m, 2H), 1.40–1.30 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.74, 138.60, 125.16, 124.97, 121.39 (q, *J* = 320 Hz, CF₃), 67.90, 51.30, 37.65, 32.53, 29.55, 26.57, 23.70, 14.74. ¹⁹F (254 MHz) δ –80.20 (CF₃). MS (ESI): *m/z*, 225.2 [M–NTf₂–]⁺; MS (ESI): *m/z*, 279.9 [NTf₂–].

3-Methyl-1-(octoxycarbonylmethyl)imidazolium NTf₂ (10g)

This compound was prepared analogously to **10a** using 3-methyl-1-(octoxycarbonylmethyl)imidazolium bromide **7g** (548 mg, 1.64 mmol) and LiNTf₂ (520 mg, 1.81 mmol) to give a clear viscous oil in 93% yield (0.81 g, 1.52 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.48 (s, 1H), 7.39 (s, 2H), 4.97 (s, 2H), 4.20 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.70–1.60 (m, 2H), 1.40–1.20 (m, 10H), 0.90 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.76, 138.72, 125.21, 124.27, 121.20 (q, *J* = 320 Hz, CF₃), 67.95, 51.28, 37.60, 33.06, 30.43, 30.40, 29.62, 26.96, 23.89, 14.95. ¹⁹F (254 MHz) δ –80.05 (CF₃). MS (ESI): *m/z*, 253.3 [M–NTf₂–]⁺; MS (ESI): *m/z*, 279.9 [NTf₂–].

3-Methyl-1-(*N*-butyl-*N*-methylcarbamoylmethyl)-imidazolium NTf₂ (10i)

This compound was prepared analogously to **10a** using 3-methyl-1-(*N*-butyl-*N*-methylcarbamoylmethyl)imidazolium bromide **7i** (302 mg, 1.04 mmol, 1 : 1.3 mixture of isomers) and LiNTf₂ (329 mg, 1.15 mmol) to give a clear viscous oil in 80% yield (410 mg, 0.84 mmol, 1 : 1.3 mixture of isomers). * denotes both isomers. ¹H NMR (300 MHz, CD₃CN) δ 8.42 (s, 1H, minor), 8.40 (s, 1H, major), 7.40–7.30 (m, 2H*), 5.06 (s, 2H, minor), 5.02 (s, 2H, major), 3.88 (s, 3H*), 3.37 (t, *J* = 7.0 Hz, 2H, major), 3.28 (t, *J* = 7.0 Hz, 2H, minor), 3.00 (s, 3H, major), 2.92 (s, 3H, minor), 1.70–1.25 (m, 4H*), 0.99 (t, *J* = 7.0 Hz, 3H, minor), 0.93 (t, *J* = 7.0 Hz, 3H, major). ¹³C (75 MHz) δ 165.72 (major), 165.47 (minor), 139.01 (minor), 138.93 (major), 125.55 (minor), 125.48 (major), 124.38*, 121.42* (q, *J* = 320 Hz, CF₃), 51.90 (major), 51.65 (minor), 50.07 (minor), 49.24 (major), 37.49*, 35.07 (major), 34.62 (minor), 31.29 (minor), 30.36 (major), 21.10*, 14.67 (major), 14.61 (minor). ¹⁹F (254 MHz) δ –79.90 (CF₃). MS (ESI): *m/z*, 210.2 [M–NTf₂–]⁺; MS (ESI): *m/z*, 279.9 [NTf₂–].

3-Methyl-1-(*N,N*-diethylcarbamoylmethyl)imidazolium NTf₂ (10j)

This compound was prepared analogously to **10a** using 3-methyl-1-(*N,N*-diethylcarbamoylmethyl)imidazolium bromide **7j** (828 mg, 3.0 mmol) and LiNTf₂ (947 mg, 3.3 mmol) to give a crystalline solid in 83% yield (1.18 g, 2.48 mmol). mp = 43–45 °C; ¹H NMR (300 MHz, CD₃CN) δ 8.47 (s, 1H), 7.34 (s, 2H), 5.06 (s, 2H), 3.88 (s, 3H), 3.37 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 7.0 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 164.81, 138.89, 125.47, 124.33, 121.39 (q, *J* = 320 Hz, CF₃), 51.72, 42.51, 42.00, 37.53, 14.65, 13.55. ¹⁹F (254 MHz) δ –80.03 (CF₃). MS (ESI): *m/z*, 196.1 [M–NTf₂–]⁺; MS (ESI): *m/z*, 279.9 [NTf₂–].

3-Methyl-1-(ethoxycarbonylmethyl)imidazolium N(CN)₂ (11b)

A dry flask was charged with 3-methyl-1-(ethoxycarbonylmethyl)imidazolium bromide (**7b**) (1.50 g, 6.0 mmol) and acetonitrile (3 mL) under a nitrogen atmosphere. NaNCNCN (641 mg, 7.2 mmol) was added in one portion and the suspension was stirred vigorously for 4 days at rt. The fine white precipitate was filtered quickly in air

and washed with dry acetonitrile (2 × 1 mL). The filtrate and washings were combined, solvent removed by rotary evaporation then *in vacuo*. The product was dried at 60 °C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 96% yield (1.35 g, 5.73 mmol). ¹H NMR (300 MHz, CD₃CN) δ 9.06 (s, 1H), 7.53 (s, 1H), 7.45 (s, 1H), 5.18 (s, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.92 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.90, 138.99, 125.02, 124.64, 63.67, 51.26, 37.53, 14.77. Peaks for NCNCN[–] not cited. MS (ESI): *m/z*, 169.1 [M–NCNCN[–]]⁺; MS (ESI): *m/z*, 66.0 [NCNCN[–]].

3-Methyl-1-(*N*-butyl-*N*-methylcarbamoylmethyl)-imidazolium N(CN)₂ (11i)

This compound was prepared analogously to **11b** using 3-methyl-1-(*N*-butyl-*N*-methylcarbamoylmethyl)imidazolium bromide **7i** (208 mg, 0.71 mmol, 1:1.3 mixture of isomers) and NaNCNCN (77 mg, 0.86 mmol) to give a clear viscous hygroscopic oil in 96% yield (189 mg, 0.68 mmol, 1 : 1.3 mixture of isomers). * denotes both isomers. ¹H NMR (300 MHz, CD₃CN) δ 8.75 (s, 1H, minor), 8.71 (s, 1H, major), 7.50–7.35 (m, 2H*), 5.20 (s, 2H, major), 5.18 (s, 2H, minor), 3.90 (s, 3H*), 3.37 (t, *J* = 7.0 Hz, 2H, major), 3.30 (t, *J* = 7.0 Hz, 2H, minor), 3.02 (s, 3H, major), 2.92 (s, 3H, minor), 1.70–1.25 (m, 4H*), 0.99 (t, *J* = 7.0 Hz, 3H, minor), 0.93 (t, *J* = 7.0 Hz, 3H, major). ¹³C (75 MHz) δ 165.85 (major), 165.54 (minor), 138.99 (minor), 138.85 (major), 125.19 (minor), 125.11 (major), 123.94*, 51.78 (major), 51.43 (minor), 49.78 (minor), 48.75 (major), 37.29*, 35.03 (major), 34.36 (minor), 31.02 (minor), 30.09 (major), 20.85 (minor), 20.77 (major), 14.41*. Peaks for NCNCN[–] not cited. MS (ESI): *m/z*, 210.2 [M–NCNCN[–]]⁺; MS (ESI): *m/z*, 66.0 [NCNCN[–]].

Butyl bromoacetate (12d)⁴²

To a stirred solution of triethylamine (41.6 mL, 300 mmol), butan-1-ol (18.3 mL, 14.82 g, 200 mmol) and dichloromethane (300 mL) at –78 °C under a nitrogen atmosphere was added dropwise bromoacetyl bromide (17.4 mL, 40.37 g, 200 mmol). After stirring at –78 °C for 3 h the reaction mixture was allowed to warm up to –20 °C and quenched by addition of water (50 mL). The organic phase was washed with distilled water (3 × 50 mL), saturated ammonium chloride (3 × 50 mL), saturated sodium bicarbonate (3 × 50 mL) and brine (2 × 50 mL) then dried over magnesium sulfate, filtered and solvents removed *via* rotary evaporation. The crude product (28 g, clean by ¹H NMR) was distilled to give a pale yellow oil in 59% yield (23.1 g, 118 mmol). ¹H NMR (300 MHz, CDCl₃) δ 4.17 (t, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 1.64 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.40 (tt, *J* = 7.0, 7.0 Hz, 2H), 0.93 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.17, 66.01, 30.33, 25.77, 18.87, 13.49.

Pentylbromoacetate (12e)^{42,43}

This compound was prepared analogously to butylbromoacetate using pentan-1-ol (21.7 mL, 17.6 g, 200 mmol) to give a pale yellow oil in 72% yield (29.9 g, 143 mmol). ¹H NMR (300 MHz, CDCl₃) δ 4.16 (t, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 1.64 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.45–1.25 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.16, 66.28, 27.99, 27.76, 25.77, 22.12, 13.79.

Hexylbromoacetate (12f)

This compound was prepared analogously to butylbromoacetate using triethylamine (20.8 mL, 150 mmol), hexan-1-ol (12.4 mL, 10.2 g, 100 mmol), dichloromethane (200 mL) and bromoacetyl bromide (8.7 mL, 20.2 g, 100 mmol) to give a crude product (21.6 g) which was distilled to give a colourless oil in 65% yield (14.5 g, 65 mmol). ¹H NMR (300 MHz, CDCl₃) δ 4.17 (t, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 1.64 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.40–1.20 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.20, 66.34, 31.24, 28.28, 25.77, 25.30, 22.38, 13.84. NMR data in agreement with literature.⁴⁴

Octylbromoacetate (12g)

This compound was prepared analogously to butylbromoacetate using triethylamine (20.8 mL, 150 mmol), octan-1-ol (15.8 mL, 13.0 g, 100 mmol), dichloromethane (200 mL) and bromoacetyl bromide (8.7 mL, 20.2 g, 100 mmol) to give a crude product (18.7 g) which was distilled to give a colourless oil in 24% yield (6.0 g, 24 mmol). ^1H NMR (300 MHz, CDCl_3) δ 4.16 (t, $J = 7.0$ Hz, 2H), 3.82 (s, 3H), 1.64 (tt, $J = 7.0, 7.0$ Hz, 2H), 1.40–1.20 (m, 10H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.13, 66.27, 31.62, 29.00, 29.01, 28.30, 25.74, 25.62, 22.48, 13.91. NMR data in agreement with literature.⁴⁵

N-Butyl-2-bromoacetamide (12h)⁴⁶

This compound was prepared analogously to butylbromoacetate using triethylamine (20.8 mL, 150 mmol), butylamine (9.8 mL, 7.3 g, 100 mmol), dichloromethane (200 mL) and bromoacetyl bromide (8.7 mL, 20.2 g, 100 mmol) to give a crude product (18.0 g) which was distilled to give a light brown oil, which crystallized on standing, in 39% yield (7.5 g, 39 mmol). Mp = 35–37 °C. Lit. Mp = 38–39 °C.⁴⁶ ^1H NMR (300 MHz, CDCl_3) δ 6.50 (bs, 1H, NH), 3.87 (s, 2H), 3.28 (q, $J = 7.0$ Hz, 2H), 1.52 (tt, $J = 7.0, 7.0$ Hz, 2H), 1.37 (tt, $J = 7.0, 7.0$ Hz, 2H), 0.93 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 165.35, 39.85, 31.18, 29.17, 19.86, 13.55.

N-Butyl-N-methyl-2-bromoacetamide (12i)⁴²

This compound was prepared analogously to butylbromoacetate using triethylamine (20.8 mL, 150 mmol), N-methyl-butylamine (11.8 mL, 8.72 g, 100 mmol), dichloromethane (200 mL) and bromoacetyl bromide (8.7 mL, 20.2 g, 100 mmol) to give a crude product (21.0 g) which was distilled to give a pale yellow oil in 54% yield (11.37 g, 54 mmol). ^1H NMR (300 MHz, CDCl_3) δ 3.84 (s, 2H, minor), 3.83 (s, 2H, major), 3.35 (t, $J = 7.0$ Hz, 2H, major), 3.30 (t, $J = 7.0$ Hz, 2H, minor), 3.04 (s, 3H, major), 2.92 (s, 3H, minor), 1.65–1.25 (m, 4H, major and minor), 0.94 (t, $J = 7.0$ Hz, 3H, minor), 0.91 (t, $J = 7.0$ Hz, 3H, major). ^{13}C (75 MHz) δ 166.30, 50.55, 47.88, 35.89, 33.61, 30.41, 28.84, 26.57, 25.89, 19.75, 13.66.

N,N-Diethyl-2-bromoacetamide (12j)

This compound was prepared analogously to butylbromoacetate using triethylamine (20.8 mL, 150 mmol), diethylamine (10.4 mL, 7.30 g, 100 mmol), dichloromethane (200 mL) and bromoacetyl bromide (8.7 mL, 20.2 g, 100 mmol) to give a crude product (14.5 g) which was distilled to give a pale yellow oil in 31% yield (6.01 g, 31 mmol). ^1H NMR (300 MHz, CDCl_3) δ 3.83 (s, 2H), 3.378 (q, $J = 7.0$ Hz, 2H), 3.383 (q, $J = 7.0$ Hz, 2H), 1.25 (t, $J = 7.0$ Hz, 3H), 1.13 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 165.65, 42.78, 40.36, 26.39, 14.20, 12.34. NMR data in agreement with literature.⁴⁷

Closed Bottle Test

Sodium *n*-dodecyl sulfate (SDS) was used as reference substance. Solutions containing 2 mg L⁻¹ of the test ionic liquids and the reference chemical as sole sources of organic carbon were prepared, separately, in previously aerated mineral medium. The solutions were then inoculated with secondary effluent collected from an activated sludge treatment plant and each well-mixed solution was carefully dispensed into a series of BOD bottles so that all the bottles were completely full. A control with inoculum, but without test chemicals was run parallel for the determination of

oxygen blanks. Duplicate bottles of each series were analysed immediately for dissolved oxygen and the remaining bottles were incubated at 20 °C $\pm$ 1 °C in the dark. Bottles of all series were withdrawn in duplicate for dissolved oxygen analysis over the 28-day incubation period. The biodegradation after *n* days was expressed as the ratio of the biochemical oxygen demand (BOD) to the chemical oxygen demand (COD) both of them expressed as mg O₂/mg compound. The chemical oxygen demand was determined by the dichromate reflux method.⁴⁸ For the calculation of the biochemical oxygen demand the determined oxygen depletions were divided by the concentration of ionic liquid.

References

- (a) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (b) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (c) J. D. Holbury and K. R. Seddon, *Clean Prod. Process.*, 1999, **1**, 223; (d) P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168.
- (a) J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765; (b) L. Blanchard, D. Nancu, E. J. Bechman and J. F. Bennecke, *Nature*, 1999, **399**, 28; (c) A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin and R. D. Rogers, *Ind. Eng. Chem. Res.*, 2000, **39**, 3596.
- (a) P. J. Scammells, N. Gathergood and J. Ripper, *PCT Int. Appl.*, 2002, 25 pp. WO 0216367; (b) I. Hemeon, N. W. Barnett, N. Gathergood, P. J. Scammells and R. D. Singer, *Aust. J. Chem.*, 2004, **2**, 125.
- R. Sheldon, *Chem. Commun.*, 2001, **23**, 2399.
- (a) W. M. Nelson, *Ionic liquids: industrial applications for green chemistry*, *ACS Symp. Ser. 818*, ed. R. D. Rogers and K. R. Seddon, 2002, pp. 30–41; (b) T. Laird, S. A. Hermitage and U. Tilstam, *Org. Process Res. Dev.*, 2002, **6**, 338; (c) R. P. Swatloski, J. D. Holbrey and R. D. Rogers, *Green Chem.*, 2003, **5**, 361.
- M. J. Scott and M. N. Jones, *Biochim. Biophys. Acta*, 2000, **1508**(1–2), 235.
- (a) R. Freer and A. Curzon, *NATO Sci. Ser. II: Math. Phys. Chem.*, 2003, **92**, 129; (b) J. D. Holbury, *Ionic liquids: industrial applications for green chemistry*, *ACS Symp. Ser. 818*, ed. R. D. Rogers and K. R. Seddon, 2002, pp. 446–4458.
- K. R. Seddon, *Nat. Mater.*, 2003, **2**(6), 363. In this efficient case methyl imidazole is converted to the ionic liquid (the hydrochloride salt of methyl imidazole), then the methyl imidazole is regenerated and recycled.
- N. Gathergood and P. J. Scammells, *Aust. J. Chem.*, 2002, **55**, 557.
- B. Jastorff, R. Störmann, J. Ranke, K. Mölter, F. Stock, B. Oberheitmann, W. Hoffmann, J. Hoffmann, M. Nüchter, B. Ondruschka and J. Filser, *Green Chem.*, 2003, **5**, 136.
- Biodegradability of Surfactants*, ed. D. R. Karsa and M. R. Porter, Blackie Academic & Professional, London, 1995.
- R. D. Swisher, *Surfactant Biodegradation*, 2nd edn., *Surfactant Science Series Vol 18*, Marcel Dekker, New York, 1987.
- H. A. Painter, *The Handbook of Environmental Chemistry*, ed. O. Hutzinger, Springer-Verlag, Berlin, Germany, 1992, **vol. 3F**, pp. 1–88.
- R. A. Rapaport and W. S. Eckhoff, *Environ. Toxicol. Chem.*, 1990, **9**, 1245.
- (a) R. S. Boethling, *Designing Safer Chemicals*, *ACS Symp. Ser. 640*, 1996, 156; (b) P. H. Howard, R. S. Boethling, W. Stiteler, W. Meylan and J. Beauman, *Sci. Total Environ.*, 1991, **109/110**, 635; (c) R. S. Boethling, *Cationic Surfactants*, *Surfactant Science Series Vol. 53*, Marcel Dekker, New York, 1994, pp. 95–135.
- (a) G. E. Wenter, J. McGrady, E. P. Gosselink and W. A. Cilley, *Eur. Pat. Appl.*, 1981, 36; (b) W. E. Gledhill and V. W. Saeger, *J. Ind. Microbiol.*, 1987, **2**(2), 97; (c) J. Waters, H. H. Kleiser, M. J. How, M. D. Barratt, R. R. Birch, R. J. Fletcher, S. D. Haugh, S. G. Hales, S. J. Marshall and T. C. Pestell, *Tenside, Surfactants, Deterg.*, 1991, **28**(6), 460; (d) B. Durif-Varambon, C. Bocard, C. Gatellier and B. Sillion, *Ger. Offen.*, 1976, DE 2558907 19760708.
- For review, see ⁶.
- (a) W. McGucken, *Biodegradable: detergents and the environment*, 1st edn., 1991, Texas A&M University Press, USA; (b) *Biodegradability of Surfactants*, ed. D. R. Karsa and M. R. Porter, Blackie Academic and Professional, London, 1995.
- D. S. McGuinness and K. J. Cavell, *Organometallics*, 2000, **19**, 741.
- (a) Y. Matsuda, H. Gotou, K. Katou, H. Matsumoto, M. Yamashita, K. Takahashi, S. Ide, K. Furuno and K. Torisu, *Hetrocycles*, 1991, **32**(11),

- 2217; (b) R. A. Jones, J. Sepulveda Arques, E. Zaballos Garcia, P. A. Bates and M. B. Hutthouse, *J. Chem. Soc., Chem. Commun.*, 1986, **24**, 1745.
- 21 Ethyl chloroacetate was also reacted with 1-methylimidazole to give 3-methyl-1-(ethoxycarbonylmethyl)imidazolium chloride as a viscous oil in 98% yield.
- 22 D. R. MacFarlane, J. Golding, S. Forsyth, M. Forsyth and G. B. Deacon, *Chem. Commun.*, 2001, **16**, 1430.
- 23 S. V. Dzyuba and R. A. Bartsch, *Chem. Commun.*, 2001, **16**, 1466.
- 24 This ratio of tautomers is derived from the condensation of *N*-methylbutylamine with bromoacetyl bromide yielding *N*-butyl-*N*-methyl-2-bromoacetamide. Heating the ionic liquids (**7g–11g**) at 60 °C for 72 h did not affect the ratio of amide rotomers, suggesting that this ratio is the thermodynamic equilibrium.
- 25 Sturm tests were performed by Leeder Consulting, 192 Station St, Fairfield VIC 3078, Australia, <http://www.leederconsulting.com>.
- 26 Test Guideline 301B: *Ready Biodegradability: Modified Sturm Test in OECD Guidelines for the Testing of Chemicals*, 1981, Organisation for Economic Cooperation and Development (OECD), Paris.
- 27 OECD Chemical Group, 1993. *Ready Biodegradability: Modified OECD Screening Test*. Method 301 E. *OECD Revised Guidelines for Tests for Ready Biodegradability*, Paris, France.
- 28 C. G. Van Ginkel and M. Kolvenbach, *Chemosphere*, 1991, **23**, 281.
- 29 M. T. García, I. Ribosa, T. Guindulain, J. Sánchez-Leal and J. Vives-Rego, *Environ. Pollut.*, 2001, **111**, 169.
- 30 R. J. Larson, *Residue Rev.*, 1983, **85**, 159.
- 31 R. J. Larson, *Dev. Ind. Microbiol.*, 1983, **24**, 425.
- 32 R. M. Ventullo, *Appl. Environ. Microbiol.*, 1986, **51**, 356.
- 33 D. M. Tubbing and W. Admiraal, *Appl. Environ. Microbiol.*, 1991, **57**, 3616.
- 34 (a) Jpn. Kokai Tokkyo Koho 1980 JP 55151578; (b) B. W. Kaplan, 1980 US 4201786.
- 35 (a) K. Ikura, K. Katsuura, M. Mizuno and T. Nishibe, Jpn. Kokai Tokkyo Koho, 1979, JP 54079278; (b) P. N. Edwards, 1979, CH 608490; (c) Japan. Kokai 1974, JP 49127968; (d) P. N. Edwards Brit., 1975, GB 1408344; (e) Austrian, 1975, AT 322546; (f) Neth. Appl., 1974, NL 7304808.
- 36 J. Ranke, K. Mölter, F. Stock, U. Bottin-Weber, J. Poczobutt, J. Hoffmann, B. Ondruschka, J. Filser and B. Jastorff, MI CPS: biochem/0303001.
- 37 J. Pernak, K. Sobaszekiewicz and I. Mirska, *Green Chem.*, 2003, **5**, 52.
- 38 D. L. Fredell, *Cationic Surfactants, Surfactant Science Series Vol. 53*, Marcel Dekker, New York, 1994, pp. 31–60.
- 39 (a) N. Bodor, J. J. Kaminski and S. Selk, *J. Med. Chem.*, 1980, **23**(5), 469; (b) N. Bodor and J. J. Kaminski, *J. Med. Chem.*, 1980, **23**(5), 566; (c) Bodor, R. Woods, C. Raper, P. Kearney and J. J. Kaminski, *J. Med. Chem.*, 1980, **23**(5), 474; (d) N. Bodor 1976 US 39897111; (e) N. Bodor, 1979 US 4160099.
- 40 Jpn. Kokai Tokkyo Koho, 1987, JP 62294603.
- 41 P. Wasserscheid, R. von Hal and A. Bösmann, *Green Chem.*, 2002, **4**, 400.
- 42 No NMR data previously reported.
- 43 Pentylbromoacetate has been previously synthesized by the esterification of bromoacetic acid and pentanol, Z. Zhang, H. Pan, C. Hu, F. Fu, Y. Sun, R. Willem and M. Gielen, *Appl. Organomet. Chem.*, 1991, **5**(3), 183.
- 44 L. Gil, Y. Han, E. E. Opas, G. A. Redan, R. Ruel, J. G. Seedor, P. C. Tyler and R. N. Young, *Bioorg. Med. Chem.*, 1999, **7**(5), 901.
- 45 (a) J.-F. Chollet, L. Miginiac, G. Picotin and P. Miginiac, *Synth. Commun.*, 1989, **19**(11–12), 2167; (b) D. P. Arnold, J. P. Bartley and D. A. James, *Aust. J. Chem.*, 1992, **45**(8), 1191.
- 46 I. Kruglik and Y. G. Gololobov, *J. Org. Chem. USSR (Engl. Transl.)*, 1978, **14**, 690.
- 47 M. A. P. Martins and R. Rittner, *Org. Magn. Reson.*, 1980, **14**(6), 522.
- 48 APHA (American Public Health Association), AWWA (American Water Works Association), and WPCF (Water Pollution Control Federation), 1985, *Method 508 B. Standard Methods for the Examination of Water and Wastewater*, 16th edn., Washington, pp. 532–537.