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Hexaalkylguanidinium Salts as Ionic Liquids – New Applications in Titanium and Aluminium Alcoholates Assisted Synthesis and as Electrolytes for Electrodeposition of Metals

Dissertation

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List of abbreviations

APIs	Active Pharmaceutical Ingredients
AES	Auger Electron Spectroscopy
BASIL	Biphasic Acid Scavenging Utilising Ionic Liquids
BINOL	1,1'-Bi-2-naphthol
BMIm	1-Butyl-3-methylimidazolium
BMPyr	*N*-Butyl-*N*-methylpyrrolidinium
Bn	Benzyl
Bu	Butyl
*t*Bu	*tert*-Butyl
CHN	Elemental analysis
CI	Chemical Ionisation
CV	Cyclic Voltammetry
d	day(s)
DLS	Dynamic Light Scattering
DMC	Dimethyl carbonate
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
DSSC	Dye-Sensitised Solar Cell
EC	Ethylene carbonate
EDX	Energy-Dispersive X-ray analysis
EIS	Electrochemical Impedance Spectroscopy
EMIm	1-Ethyl-3-methylimidazolium
Et	Ethyl
FAP	Tris(perfluoroalkyl)trifluorophosphate
FSI	Bis(fluorosulfonyl)imide
GC	Glassy Carbon
Gu	Guanidinium
h	hour(s)
Hex	Hexyl

*c*Hex	Cyclohexyl
HMBC	Heteronuclear Multiple Bond Correlation
HMMIm	1-Hexyl-2,3-dimethylimidazolium
HOPG	Highly Oriented Pyrolytic Graphite
HSQC	Heteronuclear Single Quantum Correlation
IFP	Institut Francais du Petrole
IL(s)	Ionic Liquid(s)
IR	Infrared Spectroscopy
LAB	Linear Alkylbenzenes
LED	Light-Emitting Diode
LIB	Lithium-Ion Batteries
LSV	Linear Sweep Voltammetry
Me	Methyl
MPPip	*N*-Methyl-*N*-propylpiperidinium
MS	Mass Spectrometry
MEA	Monoethanolamine
MW	microwave
NAA	Neutron Activation Analysis
NHC	N-Heterocyclic Carbene
NMR	Nuclear Magnetic Resonance
NSAID	Non-Steroidal Anti-Inflammatory Drug
PenMeIm	1-Pentyl-3-methylimidazolium
PEs	Polymer Electrolytes
PMIm	1-Propyl-3-methylimidazolium
PMPyr	*N*-Propyl-*N*-methylpyrrolidinium
ppm	parts per million
Pr	Propyl
RTIL	Room Temperature Ionic Liquid
scCO_2	supercritical carbon dioxide
SEI	Solid Electrolyte Interface
SILP	Supported Ionic Liquid Phase
STM	Scanning Tunnelling Microscope

T_{dec}	Decomposition temperature
TEM	Transmission Electron Microscopy analysis
TFSI	Bis(trifluoromethanesulfonyl)imide
T_g	Glass transition temperature
TGA	Thermal Gravimetric Analysis
T_m	Melting point temperature
TSIL	Task Specific Ionic Liquid
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Table of contents

1. Introduction

Chemists all over the world are persuaded in the necessity of application of green solvents in industry. Green solvents are supposed to be environmentally friendly, having low health and safety risks. Traditional organic solvents are a significant source of hazardous waste due to their volatility. Ionic liquids represent an excellent substitute to the traditional solvents with "greener" properties.

Ionic liquids (ILs) are a class of compounds consisting entirely of ions and having a melting temperature below the boiling point of water.[1] Besides almost not-measurable vapour pressure, ILs possess other unique properties, such as non-flammability, high thermal and electrochemical stability, relatively high ionic conductivity, tunable miscibility with other solvents. ILs have received great attention from the scientific community as potential replacements for volatile organic solvents. Their specific properties make them desirable alternatives for many industrial applications.

Over 50 000 publications, including over 7 000 patents, appeared (status on 10.10.2013, results obtained from *SciFinder*), describing besides synthesis and physicochemical properties of ionic liquids also the variety of applications of ILs in organic synthesis, electrochemistry, analytical chemistry, separation techniques, nanotechnology, as engineering liquids etc. Ionic liquids showed an impetuous extension in the beginning of the 21st century in many fields, what is proven by the rash increase of publications and patents. For example, until 1999 only 1127 references on ILs, including 66 patents, can be retrieved in *SciFinder*.

Ionic liquids are of interest as novel solvent systems and reaction media, with good solubility for many organic and organometallic compounds (in particular transition-metal complexes, which are useful for catalysing organic transformations). Products of chemical reactions carried out in an IL can often be extracted with an unpolar organic solvent (in special cases also with water) or distilled from the reaction mixture, so that the ionic liquid (often also with a catalyst) can be recycled and reused.[1–4]

In the meantime, the solvent properties of ionic liquids have even attracted the attention of industrial chemists. Some examples of the use of ILs in industrial production of chemicals do exist (BASIL process of BASF SE, etc.).[1,5] Other (potential) applications of ILs include their use as engineering fluids, for gas separation techniques, metal extraction and in head-space chromatography.[6–8]

Another important property of many ILs is the large electrochemical window (often up to 6 V). This means that the electrochemical deposition of a wide range of metals, from ignoble to noble metals, from solutions of their salts or complexes in ionic liquids, should be possible. It should be kept in mind, that electrodeposition of metals such as the alkali metals, earth-alkali metals, or aluminium, tantalum and titanium from aqueous solutions of their salts is not possible. In fact, a number of applications of ILs for electrochemical processes and devices have been described. For example, ILs have been proposed as electrolytes and used in batteries, for metal plating, in fuel cells, in solar cells, in capacitors.[1,5,8–11]

In spite of a big number of publications on ILs a relative small amount of them deals with guanidinium-based ionic liquids. At the same time, hexaalkylguanidinium salts possess a high thermal stability and a better chemical stability than some of the other common classes of ILs, mainly, due to the effective dissipation of the positive charge in the cation. They are also inert against common nucleophiles and bases in comparison to widespread 1,3-dialkylimidazolium salts.

This work is concerned with the synthesis of hexaalkylguanidinium ionic liquids, their application as reaction media and as electrolytes. As the catalytic recyclable system in dehydrating cyclocondensation reactions, metal alkoxide/guanidinium-based IL mixtures were investigated. Along with the study of common electrochemical properties of diverse hexaalkylguanidinium salts, their possible application to metal electrodeposition, as well as to an electrolyte for Li-ion batteries were examined.

2. Overview: synthesis, physicochemical properties and selected application fields of ionic liquids

This chapter describes some topics, relevant for the present work, such as synthesis of guanidinium-based ionic liquids, properties of ILs and how to modify them, uses of ILs as reaction media and as electrolytes, as well as some industrial applications. At the beginning some basic information about ionic liquids and their historical development is provided.

2.1 Historical aspects of ionic liquids

The history of ionic liquids may be viewed as a relatively recent one or one extending back to the 19th century, when the scientists supposed that the obtained salts were not pure enough to be solid. The starting point in the history depends on the definition of "ionic liquid" and how deeply one looks for progenitors of the present materials. That is also the explanation why different authors chose diverse birthdates of ionic liquids.

Perhaps, one of the first reported observations of ionic liquids was the so-called "red oil" obtained during Friedel-Crafts reactions. Nevertheless, the structure of this oil was determined only recently by *Prof. J. Atwood* of the University of Missouri with the help of NMR spectroscopy to be a protonated benzene derivative, i.e. a cyclohexa-2,4-dien-1-ium heptachlorodialuminate (**Figure 1**).[1,12]

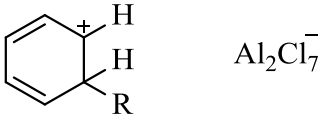
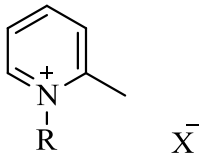


Figure 1. *Constitution of the "red oil" described by J. Atwood.*[12]

Another early observation of ionic liquids was described by *P. Murrill* in 1899.[13] By alkylation of picoline, he synthesised a number of *N*-alkylpicolinium halides (**Figure 2**), with melting points which classify them as room-temperature ionic liquids (RTILs). Even earlier (1876), some members of this class of salts have been prepared as syrupy liquids by the later Nobel laureate *W. Ramsay*.[14]



R = alkyl

Figure 2. *Structure of N-alkylpicolinium halides.*

Other progenitors of ILs, quaternary anilinium salts, were reported at the beginning of the 20th century.[15] Generally, these early reports are rarely mentioned. The beginning of the IL history is most commonly dated back to 1914 and the work of *P. Walden* on the use of alkylammonium nitrates.[16] He "disclosed his investigations on the electric conductivity, and derived from the capillarity constant, the molecular size of some organic ammonium salts".[16] As a result of the search for anhydrous low-melting salts, he obtained ethylammonium nitrate by neutralisation of ethylamine with nitric acid, with a melting point of 13-14 °C.

In 1934 a patent appeared,[17] which described the dissolution of cellulose in *N*-substituted pyridinium chlorides. These solutions enabled the derivatisation of cellulose and isolation of these derivatives. This patent is a herald of what scientists are trying to achieve nowadays using cellulose.[5] Several chloroaluminates were discovered in the following years. The aluminium electroplating from mixtures of ethylpyridinium bromide and metal chlorides was reported by *F. Hurley* and *T. Wier*[18] in 1951. U. S. Air Force Academy, interested in replacement of the LiCl-KCl molten salt electrolyte used in thermal batteries, investigated the fundamental properties and applications of pyridinium chloroaluminates.[19] As the pyridinium cation is easily reduced, more electrochemically stable cations were in demand. In 1982 *J. Wilkes* and *C. Hussey*[20] presented 1,3-dialkylimidazolium chloroaluminates, which was not only more stable to reduction but also possessed a wider liquid range. Nevertheless, all these salts suffer from extreme sensitivity to moisture. Furthermore, a product of the reaction with water is corrosive hydrogen chloride.

A major step forward was made by *J. Wilkes* and *M. Zaworotko*[21] in the early 1990's, with the report on moisture stable ionic liquids created by replacing the aluminium chloride with other anions, such as tetrafluoroborate or hexafluorophosphate. These were called the ionic liquids of second generation. Later, the ILs with these two anions have been explored more extensively, and it was stated that they must be treated with the greatest caution as they are fairly readily hydrolysed to boric acid and phosphate respectively, eliminating highly corrosive hydrogen fluoride.[1,22]

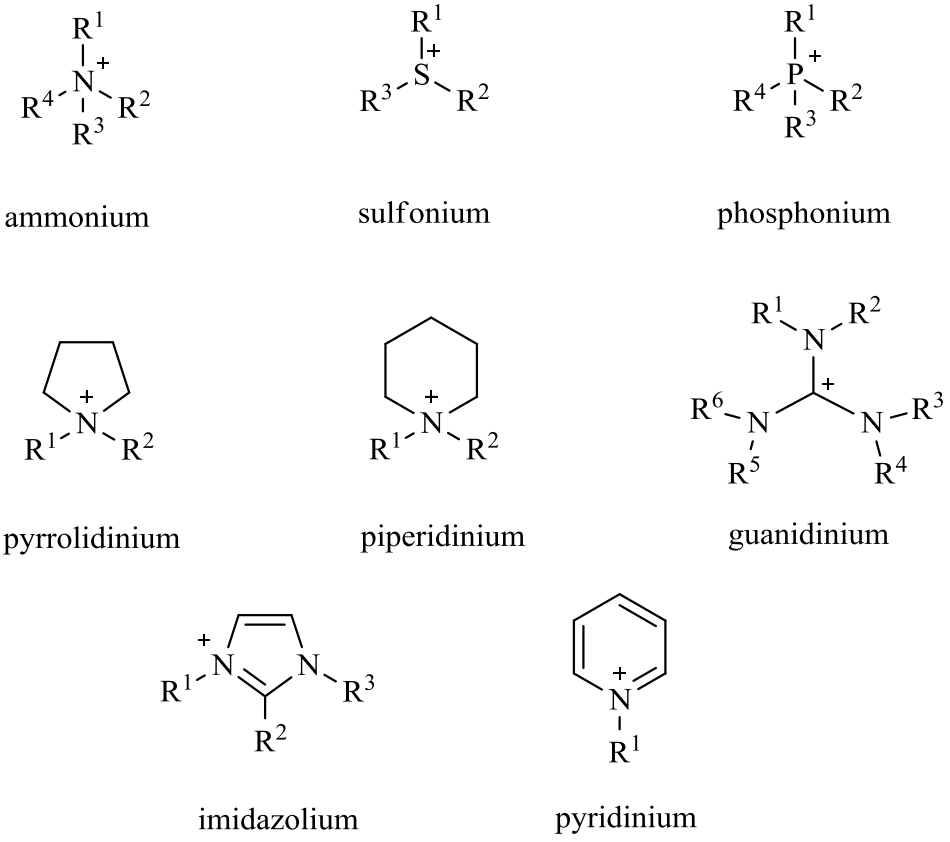


Figure 3. *Structures of the common cations used in ionic liquids.*

Since the report by *J. Wilkes* and co-workers, the family of RTILs has seen explosive growth. Starting with imidazolium cations, the cationic component has been varied to include pyridinium, ammonium, piperidinium, guanidinium, phosphonium, sulfonium, thiazolium and several other species (**Figure 3**).[23] In general, these cations have been combined with weakly coordinating anions to give low-melting ILs or RTILs. Common examples include tetrafluoroborate, hexafluorophosphate, trifluoromethanesulfonate (triflate), bis(trifluoromethylsulfonyl)imide (bistriflimide, triflamide) and dicyanamide (**Figure 4**). The

list of possible anionic components continues to grow rapidly. As an example, recently ionic liquids with hydrophobic tris(perfluoroalkyl)trifluorophosphate (FAP) anions (**Figure 4**) have been developed by Merck KGaA (Darmstadt, Germany).[24] To address the disadvantage of the hexafluorophosphate anion, the replacement of some fluorine atoms by hydrophobic perfluoroalkyl groups was a solution to increase the hydrolytic stability of fluorophosphates. Nevetheless, the ILs with FAP anion show relative high viscosity (and low conductivity) in comparison to wide-spread water-stable bistriflimides, however the electrochemical stability is comparable to that of bistriflimides.

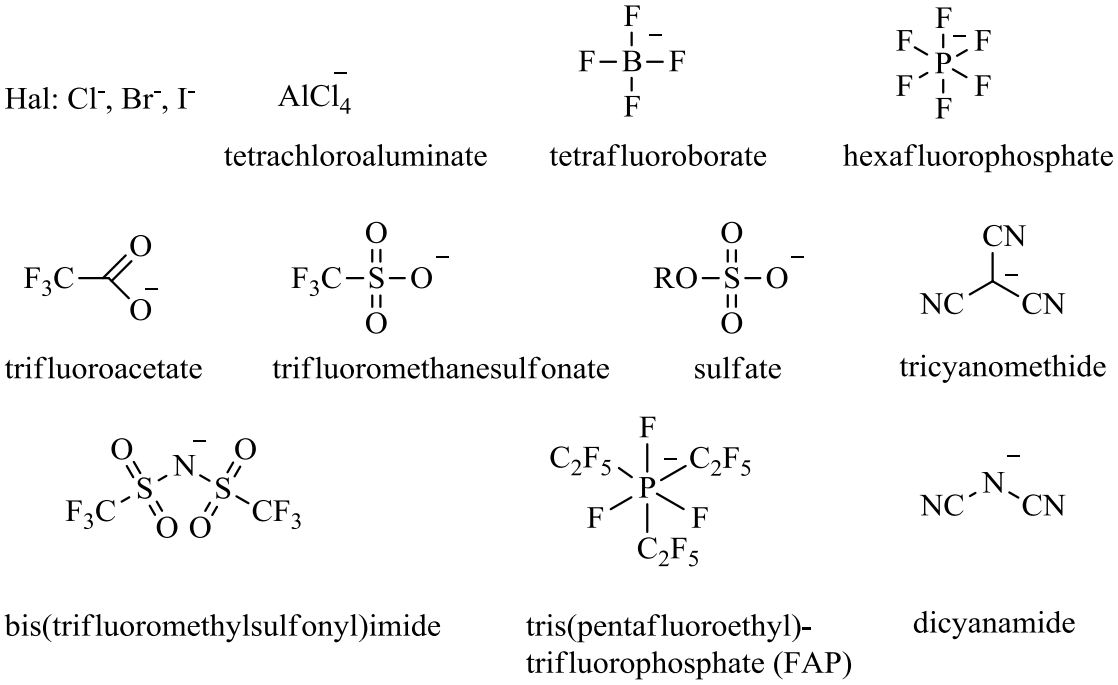


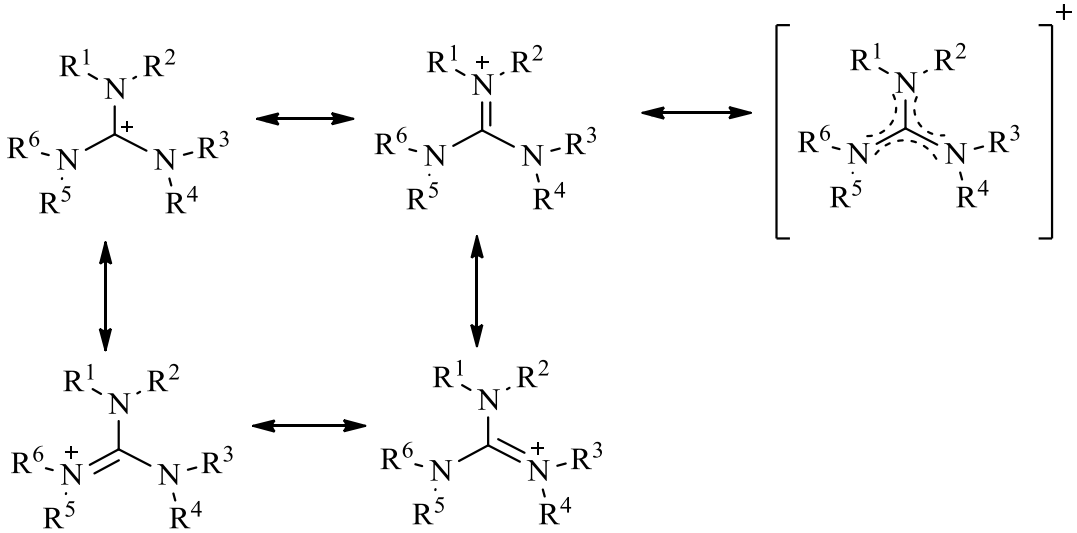
Figure 4. *Structures of the common anions used in ionic liquids.*

It seems obvious that the table of existing cation and anion will be further extended; the chemists work hard to introduce new features and useful properties to ionic liquids. It is also noteworthy to mention the concept of TSILs (task-specific ionic liquids), which was introduced by *J. Davis*.[25] These are ionic liquids in which a functional group (amino-, hydroxyl-, thio-, ether-, carbonyl-groups etc.) is covalently tethered to the cation or anion (or both) of the IL.[1] At the same time this incorporated functionality is intended to provide the IL with some peculiar properties to allow its application not just as a solvent or a reaction medium but as a catalyst in some reactions or as an IL with some special task. For example, a

thiourea-appended TSIL has been used for the extraction of Hg^{2+} and Cd^{2+} from IL-immiscible aqueous phases.[26] Chiral ILs can also be considered as TSILs.

2.2 Methods of synthesis of hexaalkylguanidinium-based ILs

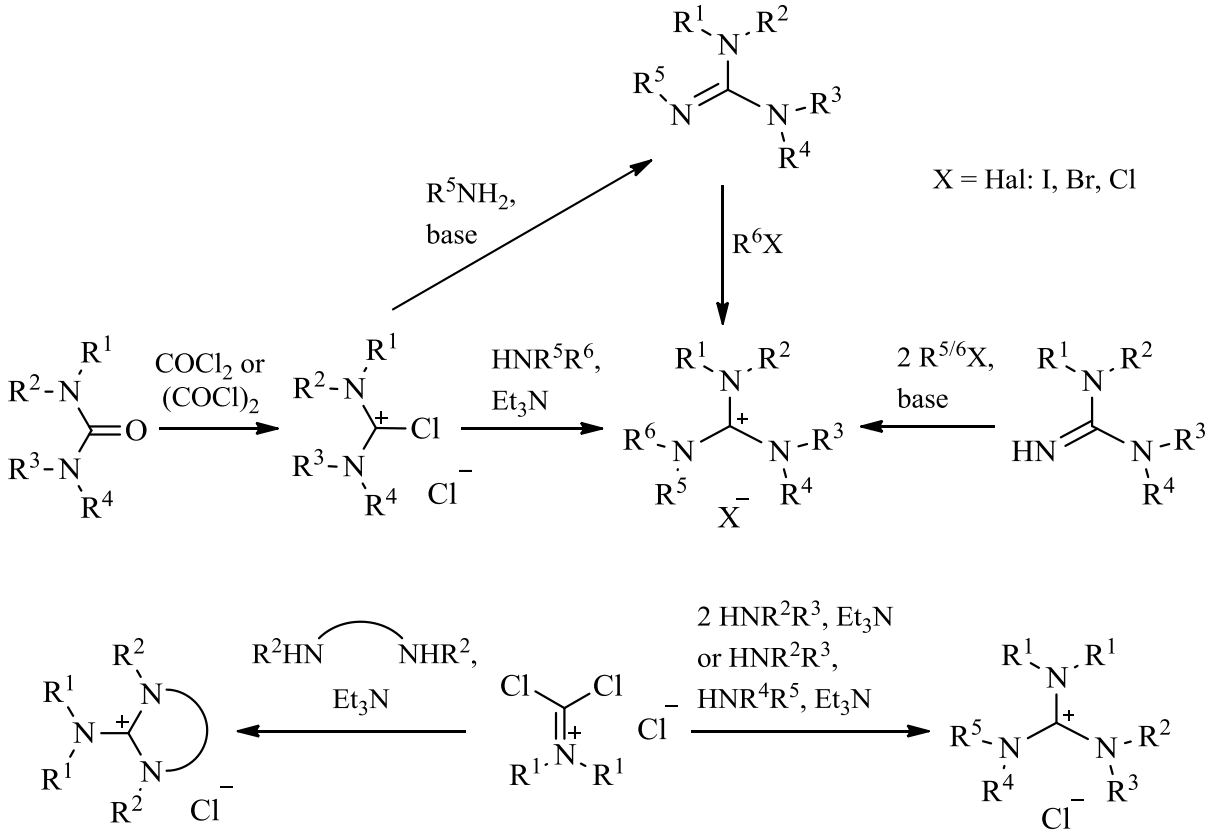
For most applications of ionic liquids, room-temperature ILs are the most desirable. The key role in liquid range of the IL and the aggregate state at room temperature is played by the anion. At the same time good charge stabilisation in the cation provides a high thermal stability. Although a lot of charge-stabilised cations are known (*N*,*N*'-dialkylimidazolium, *N*-alkylpyridinium, *N*,*N*-dialkylpyrrolidinium, tetraalkylammonium etc.), the guanidinium cation is known for a superior positive charge stabilisation and delocalisation. Resonance structures of the hexaalkylguanidinium cation are presented in **Scheme 1**.



Scheme 1. *Resonance structures of a hexaalkylguanidinium cation.*

Moreover, hexasubstituted guanidinium ILs have a better chemical stability than some other classes of ILs, particularly against bases. For example, *N*,*N*'-dialkylimidazolium cation under the basic conditions can form a highly reactive carbene (in the position 2).[27] Furthermore, the guanidinium core bearing six substituents provides a great variety of possibilities to obtain the required properties.

The main approaches to hexaalkylguanidinium salts are summarised in **Scheme 2**. Probably, the shortest way to the guanidinium core is the pathway developed by *W. Kantlehner* and co-workers[28,29] and consisting in the reaction of chloroformamidinium chloride with a *sec*-amine in the presence of triethylamine. Chloroformamidinium salts are available by chlorinating tetraalkylureas with phosgene, oxalyl chloride, phosphorus oxychloride or thionyl chloride.[30] *W. Kantlehner et al.* were the first to use the phosgene route to prepare peralkylated guanidinium salts from tetraalkylureas.



Scheme 2. *Synthetic pathways to hexaalkylguanidinium salts [modified according to lit. [31]].*

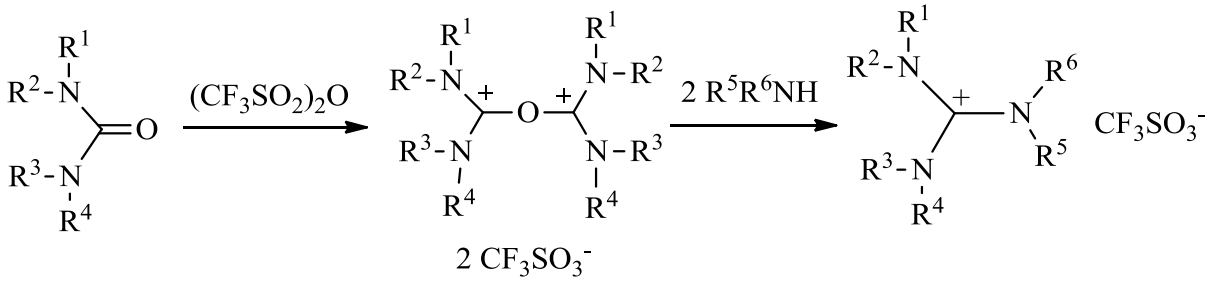
Hexaalkylguanidinium halides can also be obtained through a two-step procedure from chloroformamidium chloride with a subsequent alkylation.[28] This procedure allows higher variability of the R^5/R^6 substituents; it is especially beneficial when the appropriate *sec*-amines are not available. Contrary, a twofold alkylation (for example, with alkyl halides or dimethyl sulfate) of tetraalkylguanidines is chosen for the preparation of guanidinium salts with equal R^5/R^6 substituents.[32–34]

Another method to synthesise hexaalkylsubstituted guanidinium chlorides is the reaction of *N*,*N*-dialkylphosgeniminium chloride with 2 equivalents of *sec*-amines or 1 equivalent of bis(*sec*-amine). Successive addition of two different *sec*-amines provides a structural diversity of the guanidinium core.[35,36]

As ionic liquids with halide anions are very hygroscopic, anion exchange is usually performed to assign the IL properties necessary for particular application. Anions are usually introduced with other salts by anion metathesis (sometimes with acids); the reaction can be carried out in organic solvents or in water. Anion exchangers can also be used for guanidinium salts.[30]

Recently, some chloride-free pathways to guanidinium salts have been developed. Noteworthy, ionic liquids are often regarded as green chemistry solvents, but the non-"green" preparation of the ILs is rarely taken into account. Avoiding the use of halogenated solvents and halogen-containing intermediates are the key requirements for environmentally friendly synthesis. Moreover, avoiding chloride intermediates provides ionic liquids without halide impurities, what is essential for electrochemical applications.

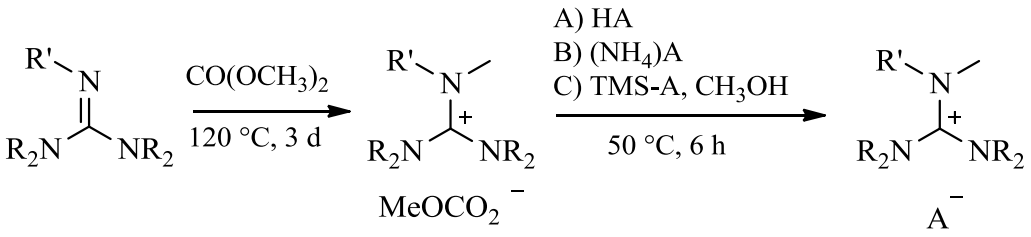
One of the chloride-free procedures was introduced by *H. Kunkel* and *G. Maas et al*.[31,37] This method consists in the preparation of hexaalkylguanidinium triflates from tetraalkylureas, triflic anhydride and dialkylamines in two steps (**Scheme 3**). It was shown that this synthesis can also be carried out as a one-pot procedure in non-chlorinated solvent, so in a completely chloride-free manner, what is beneficial in the context of green chemistry.



Scheme 3. *Chloride-free pathway to hexaalkylguanidinium triflates.*

Another promising halide-, solvent- and metal-free procedure was reported by *B. Oelkers* and *J. Sundermeyer*.[38] Their "methylcarbonate route" uses pentaalkylmethylguanidinium

methylcarbonate as an intermediate to obtain guanidinium ILs with other anions. Dimethyl carbonate is applied as a methylating agent for the pentaalkylguanidine (**Scheme 4**). However, this reaction does not work in the case of less crowded guanidinium cations, such as hexamethylguanidinium cation, where it leads to tetramethylammonium methylcarbonate and tetramethylurea. The obtained guanidinium methylcarbonates react with acids HA, their corresponding ammonium salts $(NH_4)A$ or with their silylated synthetic equivalents TMS-A in methanol to form ILs with anions, which are less basic than methylcarbonate (acetate, trifluoroacetate, thiocyanate, methanesulfonate, tetrafluoroborate, hexafluorophosphate, bistriflimide and some others). As a disadvantage of this method one should mention the use of a toxic and corrosive superacid bis(trifluoromethane)sulfonimide (Tf_2NH) or fluoroboric acid (HBF_4).



Scheme 4. *"Methylcarbonate route" to hexaalkylguanidinium salts.*[38]

2.3 Selected physical properties of the ILs

Ionic liquids are usually called "designer solvents". Modifying the structure of the IL makes it suitable for particular applications. Changing ion type, substitution and composition produces new ionic liquid systems, each with a unique set of properties. For the effective and rapid development of the required IL it is important to determine how the properties depend on anion, cation and substitution patterns, and how the properties can be changed in a systematic predictable way.

Here the most important physical properties are described, which are relevant for the present work.

2.3.1 Melting point

The melting point (T_m) is surely the most important characteristic of the ionic liquid, according to the definition. So if a salt has a melting point below 100 °C it is called an ionic liquid, if it is liquid at ambient temperature it is called a room-temperature IL (RTIL). For most of the applications liquid ILs are preferred. So in the development process of an IL some basic trends are to be taken into account. Both cations and anions contribute to the low melting points of ionic liquids. The main factors, which are responsible for lowering the melting point of an IL, are low symmetry, low intermolecular interaction (also absence of hydrogen bonds), good delocalisation of the charge (also existence of π electron orbitals), increased cation or anion size,[10,39] which all contribute to lowering the electrostatic interaction and prevent efficient packing into a crystal structure. The effect of side chain length was discussed by *K. Seddon*[40] on the example of *N*-substituted-*N'*-methylimidazolium tetrafluoroborates. He proved that the melting point at first decreases with the increase of the number of carbon atoms in the alkyl chain, but with a carbon number larger than 9 the ILs represent solids, the melting point of which increases with the chain length. A similar tendency was also observed for the guanidinium salts.[28,31]

The quanidinium cation is a good example of an effective charge delocalisation (**Scheme 1**). At the same time, six substituents in the core allow a lot of variations to build an unsymmetrical cation. Branched substituents also lead to lower melting points. Weakly coordinating anions with good charge delocalisation (usually due to stabilization by the electron-withdrawing effect of the halogen atoms), such as tetrafluoroborate, hexafluorophosphate, triflate, bistriflimide, triflamide and dicyanamide, are known to give low-melting ILs after anion exchange from respective high-melting halides.

Many ILs also show a glass transition temperature. The glass transition temperature (T_g) is generally understood to be the temperature where segmental motion begins on heating from the quenched amorphous solid.[10] The T_g is important because the ionic conductivity and viscosity of many ILs are a function of T_g.

2.3.2 Vapour pressure and thermal stability

Most of the ionic liquids are known to be non-distillable. This fact makes the purification of the ILs more difficult, because it is not possible to use the common purification technique – distillation. On the other hand, this peculiar property allows removal of water by simple heating under vacuum and can be successfully used in a row of applications, for example usage of ILs in organic synthesis instead of volatile solvents and in electronic devices instead of volatile electrolytes, distillation of the product from a reaction mixture etc. Low vapour pressure of the ILs, which is almost not possible to measure (*A. Heintz* managed to determine the vapour pressure of [BMIM]PF_6 to be 10^{-10} Pa at 298 K[41]), contributes also to the safety of the processes.

Some cases of distillation of ILs were reported (see for example lit. [42,43]), but they needed a prolonged distillation time. Details of the evaporation mechanism are not yet clear. Protic ILs, synthesised by the neutralisation of protic acid and organic base, easily evaporate on heating and can be recondensed at lower temperatures without decomposition. For ILs composed of quarternised onium cations a dealkylation mechanism is thought to be plausible; as a proof the transalkylation was observed in several cases.[10,39] *K. Seddon et al*. showed that ILs with low-nucleophilic anions can be distilled at 200 °C under high vacuum (less than 0.1 mbar) without decomposition. A cluster ion model has been proposed for this case because it is hardly conceivable that individual anions and cations are vaporized.[10,42]

A high thermal stability (up to 300-400 °C) allows to carry out processes at higher temperatures; but there are also some reports that long time exposure to high temperatures leads to decomposition.[44] The decomposition temperature (T_{dec}) depends on both cation and anion. Usually the temperature at the highest decomposition rate in the thermal gravimetric measurements (TGA) is ascribed to T_{dec}, but there are also publications, where authors take the temperature at 5% mass loss. For the anions the general stability order differs in the literature, here is the one presented in lit. [1]: $[NTf_2]^- > [PF_6]^- \sim [BF_4]^- > [Cl]^-$. In the case of a halide anion a cation may suffer a nucleophilic attack by the anion, what leads to a low decomposition temperature.

2.3.3 Viscosity

Viscosity is an important property of ILs used as electrolyte solutions or media for organic reactions. Viscosity of the fluid arises from the internal friction of the fluid, and it manifests itself externally as the resistance of the fluid to flow.[1] All the ILs reported were found to be Newtonian fluids, i.e. the viscosity of ILs is constant for different rates of shear and does not change with time. The values of the most established ionic liquids range from 10 to 500 cP, which is 10-100 times higher than that of water or organic solvents. The existing problem in this field is that the reported viscosity values are not always the same for any given IL owing to water content, impurities, synthetic route, starting materials and measurement method.[1,10]

Certainly, both cation and anion structures influence the viscosity. The trend for the greater viscosity is the larger cation; highly asymmetric substitution has been identified as important to obtain low viscosities.[1,44] The general order of increasing viscosity with respect to the anion is: $[NTf_2]^- < [BF_4]^- < [CF_3COO]^- < [TfO]^- < [CH_3COO]^- < [CH_3OSO_2]^-$.[1] Along with van der Waals forces and hydrogen bonding, electrostatic forces also determine the viscosity of ionic liquids.[10,39,44,45]

Even a small increase of the temperature leads to a drastic decrease of the viscosity. Another possibility to reduce the viscosity value is to add a small amount of organic solvent. This is not used that often, because it can have a negative impact on the flaming point of the system and, therefore, on the safety of the hole process.

2.3.4 Electrochemical stability

The electrochemical stability is a key criterion in the use of ILs in electrochemical applications, such as in electrodeposition of metals, in batteries, conductors, solar cells etc. This is determined by the electrochemical window, which is defined as the electrochemical potential range in which the electrolyte is neither reduced nor oxidised at an electrode.[44] Cathodic and anodic limits of pure ILs are attributed to the oxidative decomposition of the anion and the reductive decomposition of the cation, respectively. However, the comparison of the data on the electrochemical stability of the ionic liquids is difficult as reference systems

are different (glassy carbon (GC), platinum (Pt), ferrocene (Fc)/ferrocenium (Fc^+) are among the most common). The electrochemical window is also governed by the sweep rate of the potential, temperature, impurities and so on. Impurities, especially water and halide anions, drastically narrow the potential window.[1,9,10] Cyclic voltammetry and linear sweep voltammetry (LSV) are commonly used to estimate the electrochemical windows of the ILs, as in the case of the conventional electrolytes. The cut-off current density differs between many laboratories and ranges between 0.1-1.0 $mA \cdot cm^{-2}$.

The electrochemical stability of the ILs was found to be up to 6-7 V, which is several times higher than for water (the potential window of water is 1.2 V[44]). The large electrochemical windows have opened the door to electrodeposition of metals and semiconductors at room temperature which were formerly obtained only from high temperature molten salts (Al, Mg, Ta, Si, Ge).[44] The apparent overall trend in the electrochemical stability of the ionic liquid cations follows the order:[1] benzotriazolium < pyridinium < pyrrolinium < imidazolium ≤ pyrazolium ≤ sulfonium ≤ pyrrolidinium ≤ piperidinium ≈ ammonium ≈ morpholinium. The anion stability towards oxidation appears to follow the order:[1] halides < chloroaluminates < fluorinated anions ($[PF_6]^-$, $[AsF_6]^-$) ≤ triflate/triflyl ions ($[CF_3SO_3]^-$, $[(CF_3SO_2)_2N]^-$) ≈ fluoroborates ($[BF_4]^-$, $[C_2F_5BF_3]^-$). For the better overview, potential windows of some of the commonly used ILs are presented in **Table 1**.

Table 1. *Electrochemical windows of some ionic liquids.*

ILs	Cathodic limit, V	Anodic limit, V	Electrochemical window, V	Working electrode	Ref. electrode	References
$[EMIm]NTf_2$	-2.0	2.1	4.1	GC	Ag wire	[46]
$[BMIm]NTf_2$	-2.0	2.6	4.6	Pt	Ag/Ag^+ in DMSO	[47]
$[BMIm]BF_4$	-1.8	2.4	4.2	Pt	Ag/Ag^+ in DMSO	[47]
$[BMIm]PF_6$	-1.9	2.5	4.4	Pt	Ag/Ag^+ in	[47]

					DMSO	
[PenMeIm]FAP	-2.6	3.9	6.5	GC	Fc/Fc^+	[24]
$[PMPyr]NTf_2$	-2.5	2.8	5.3	Pt	Ag wire	[48]
$[Me_3BuN]NTf_2$	-3.3	2.5	5.8	GC	Fc/Fc^+	[49]
$[Bu_4N]FAP$	-3.3	3.7	7.0	GC	Fc/Fc^+	[24]
$[MPPip]NTf_2$	-3.3	2.5	5.8	GC	Fc/Fc^+	[50]
$[N_{11}N_{11}N_{33}Gu]NTf_2$	-2.1	2.2	4.3	GC	Ag wire	[51]

2.3.5 Conductivity

The conductivity of an electrolyte is a measure of available charge carriers and their mobility.[1] As the ILs are composed solely of ions, one would suppose that the ILs show high conductivities. In reality, they are significantly less conductive than concentrated aqueous electrolytes. This can be attributed to reduction of available charge carriers due to ion pairing and/or ion aggregation, and to the reduced ion mobility resulting from the large ion size (mainly cation size) found in many ionic liquids.[1,44] For example, one would expect an increase in conductivity by replacement of the bulky bis(trifluoromethylsulfonyl)imide anion with the less bulky triflate anion and, in particular, with trifluoroacetate. But the differences in conductivity between these three ionic liquids are negligible. It appears, that the interaction between the weakly coordinating anions, like FAP and bis(trifluoromethylsulfonyl)imide, with the cationic part is indeed weak. The triflate anion, and especially the trifluoroacetate anion coordinate more strongly to the cation, and this hinders their mobility and reduces the conductivity of ionic liquids with these anions.[24] Nevertheless, generally ILs possess reasonably good ionic conductivities, comparable to the non-aqueous solvent/electrolyte systems (~10 $mS \cdot cm^{-1}$).[1]

The conductivity of ILs is inversely linked to their viscosity. Thus, increasing the temperature lowers the viscosity and increases the conductivity.[10,44] It was also shown that impurities have a significant impact on conductivity.[1]

For the application of ionic liquids in Li-ion batteries the conductivity of lithium salt/IL solution is more important than of the pure IL. Generally, the ionic conductivity of such

solutions is lower than of the pure ionic liquid, although, the number of ions in system is higher. This is attributed to the increase in viscosity and T_g and also possible aggregation of the lithium ions in the IL.[10]

2.3.6 Impact of the ILs on environment and living organisms

Because of the negligible vapour pressure and non-flammability, ionic liquids were claimed to be "green" and non-toxic. Today there is a growing awareness of the impact of the ILs on the environment and living organisms. It is unquestionable that, due to their general properties, the vast majority of ionic liquids do not present any risk of atmospheric contamination; however, considering their industrial exploitation, they may present ecotoxicological risks to both aquatic and soil environments (due to accidental discharge).[52]

To be "green" the ILs should comply with the Twelve Principles of Green Chemistry[53] during the whole lifecycle, from synthesis to disposal. First of all, the synthesis of ILs should be considered, including the usage of solvents, hazard precursors and renewable resources, number of stages, atom economy. To satisfy these points, a number of renewable easily obtainable amino acid-based ionic liquids with nitrates and saccharinates as anions were described.[54,55]

A great number of testing models has been already applied to evaluate the ecotoxicology of ILs: bacteria, fungi, crustaceans, algae, plants, mammalian cell lines and animals (representing the five Kingdoms in the classification of living organisms).[52] Today a large number of reviews on toxicity and environmental acceptability exists.[52,54,56–59] It was shown that the effect of the tested anions was secondary to the effect of the cations on the observed toxicities, yet their broad diversity does not allow a conclusive analysis of their effects.[52] However, the stable bistriflimide anion is considered to be the most toxic one.[52,54,56,58] It is commonly accepted that toxicity is correlated with the lipophilicity of the cation (and also of anions in some cases), suggesting that interaction with the surface of the microbial cells plays a major role.[52] So the ILs with longer alkyl chains in the cation possess higher toxicities. Introduction of the oxygen atom in the side chain of the cation was reported to reduce significantly the toxicity and enhance primary biodegradability.[52,56] On the other hand, ionic

liquids were also synthesised to serve as antimicrobials, herbicides, fungicides,[54] as well as active pharmaceutical ingredients (APIs).[60]

An excellent review on biodegradability was given by *D. Coleman* and *N. Gathergood*.[61] To enhance the biodegradability, incorporation of the following structural features can be helpful: esters, amides, hydroxyl, aldehyde, carboxylic acid groups, linear alkyl chains.[52,62] Faster degradation was observed for the alkylsulfates, saccharinates, acesulfamates and alkanoates.[52] It should be noted that although reuse and recycle do enhance the overall green rating of the process, they only postpone ultimate disposal.[54]

Ionic liquids, as designable solvents, are supposed to fulfil the requirements of the specific application to provide the enhanced technical performance, to be non-hazardous for the environment and non-toxic for the living organisms. Unfortunately, it is almost not possible to combine all the parameters in one ideal ionic liquid, especially when contrary approaches should be used to achieve different characteristics of the IL. Nevertheless, for a relatively young field tremendous progress has been made in the direction of Green Chemistry, and taking into consideration that interest to the field of ionic liquids is ever-growing, the improvement of the diverse properties of the ILs will continue and make them more environmentally friendly, non-toxic and effective.

2.4 ILs as reaction media

Over the past decade ionic liquids have received a great deal of attention as possible “green” replacements for volatile organic solvents. Reaction types successfully performed in ILs include Diels–Alder, Friedel–Crafts, olefin hydrogenation, hydroformylation, oligomerization and Heck and Suzuki coupling reactions, to name just a few. ILs can act as solvents, as well as multifunctional compounds in catalytic reactions, like solvents and ligands, solvents and catalysts, stabilising agents for catalysts or intermediates. They can have positive impact on chemo-, regio-, stereo- and enantioselectivity, increase the yield, enhance the reaction rate, facilitate separation of products and catalyst recovery. Usually, extraction or distillation of the product is applied, so that the catalyst is retained in the ionic liquid phase. This allows then multiple use of the catalyst/solvent system, what is saving the costs and disposal of the

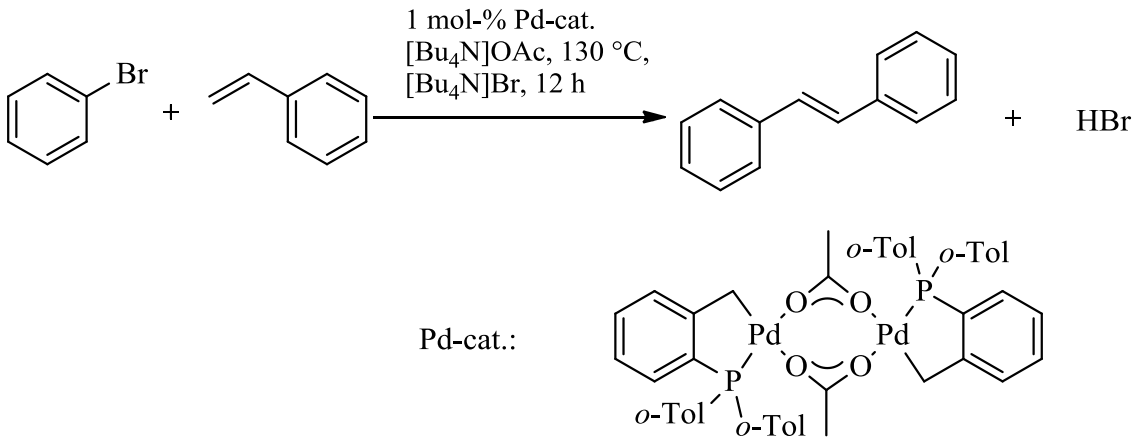
chemicals. Because many transition metal complexes are well soluble in ionic liquids, the ILs are particular suited for homogeneous catalysis and isolation of the catalyst in biphasic systems.

A number of reviews[2,4,39,63–65] and books[1,66,67] exist overviewing the achievements of the application of ILs in synthesis and catalysis. Here, only some classical reactions of organic chemistry, performed in ionic liquids, will be presented. At the same time, the examples given attempt to demonstrate a variety of possible functions of ILs and how they can be used to solve the problems/imperfections, usually observed in traditional organic solvents.

2.4.1 Heck reaction in ILs

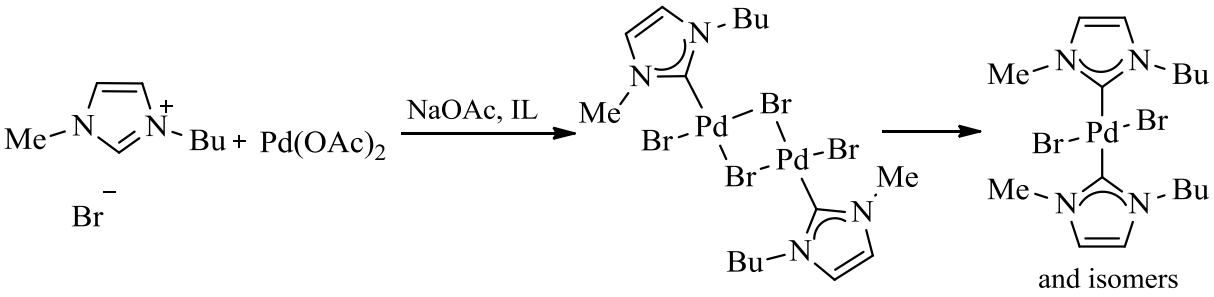
Heck reaction and other related transformations for selective C-C couplings have received a great deal of attention among synthetic chemists due to their versatility for fine chemical synthesis.[1] As the proof of their importance, the Nobel Prize in Chemistry 2010 was awarded jointly to *R. Heck*, *E. Negishi* and *A. Suzuki* "for palladium-catalysed cross-couplings in organic synthesis". It is not surprising that these reactions have been widely investigated in ILs by a number of research groups.

Already in 2000 *V. Böhm* and *W. Herrmann*[68] described a highly effective (yields over 90%), reusable (up to 13 times) catalytic system for the synthesis of stilbenes with distillative product separation (**Scheme 5**). In the same publication, the stabilising and activating impact of the ionic liquid in comparison to commonly applied polar solvents was demonstrated. For example, in the reaction of bromobenzene with styrene using diiodo-bis(1,3-dimethylimidazolin-2-ylidene)palladium(II) as catalyst the yield of stilbene could be increased from 20% (DMF) to over 99% ($[Bu_4N]Br$) under otherwise identical conditions. Moreover, it was stated that the Pd-catalysts decompose later in $[Bu_4N]Br$ – if they do at all – than they do in DMF under conditions *ceteris paribus*. Amazingly, the catalytical activity of ligand-less systems with $PdCl_2$ and $Pd(OAc)_2$ was also observed, however with lower reaction rates.



Scheme 5. *Synthesis of stilbene in recyclable phospha-palladacycle/[Bu$_4$N]Br system.*

J. Xiao et al.[69] found that the Heck reaction of aryl halides with acrylates or styrene in [BMIm]Br with $Pd(OAc)_2$ as the catalyst proceeds more efficiently in comparison to analogous [BMIm]BF_4. It was explained with the formation of a Pd-carbene complex in bromide melt under the reaction conditions, which was also isolated (**Scheme 6**), while precipitation of palladium black was observed in the tetrafluoroborate IL. In the case of [BMIm]Br the imidazolium ion can react with a catalyst precursor to form *N*-heterocylic carbene complexes via deprotonation in the imidazolium-based ionic liquids under catalytic conditions, and the carbene complexes so generated are active for C-C bond coupling reactions. So the ionic liquid showed to act not only as a solvent for starting materials, but also as a ligand and a catalyst stabilising medium in this system.



Scheme 6. *Formation of a Pd-carbene complex in [BMIm]BF_4.*

Interestingly, with [HMMIm]Cl (HMMIm = 1-hexyl-2,3-dimethylimidazolium) where the blocked C-2 position prevents carbene complex formation, $[PdCl_4]^{2-}$ is formed rather than Pd(0). This is clearly the result of the relative coordination strength of the Cl^- anion in comparison to $[BF_4]^-$ and $[PF_6]^-$.[1,70]

K. Seddon et al.[71] described different Heck reactions in [BMIm]PF_6 with a triphasic system [BMIm]PF_6/water/cyclohexane for extraction of products and salts formed as by-products. At the same time, Pd-catalyst remained in the ionic liquid and could be reused for five more times without loss of activity. However, from the contemporary view this protocol looks suspicious, because of the proneness of the PF_6-salt to hydrolysis, what was not taken into consideration in 1999.

Guanidinium-based ionic liquids were also reported to act as a multi-function reaction medium for Heck reaction of aryl halides and olefins, namely as a ligand, a base and a polar solvent, stabilising the Pd-catalyst and increasing the reaction rate.[72] The catalytical activity was attributed to the complex (such as L_2PdCl_2), obtained from protic *N*-butyl-*N',N',N'',N''*-tetramethylguanidinium acetate with $PdCl_2$ or $Pd(OAc)_2$ without extra addition of a base. This system could be reused five times.

Once an ionic catalyst solution with required selectivity and production rate was obtained, it is desirable to ascertain its stability. Metal/catalyst leaching from the system, especially in the case of extraction of the products, is of great concern as this can contaminate products and prevent the system from recycling and reuse. When immobilisation of the catalyst by dissolution/dispersion/complexation in ionic liquid is not efficient enough (IL as a liquid support), immobilisation on the solid support can be helpful (supported ionic liquid phase SILP concept). For this, solution of a metal catalyst in ILs is confined on the surface of a highly-porous solid by various methods such as physisorption, tethering or covalent anchoring of ionic liquid fragments.[73] SILP catalysts can be easily applied in continuous-flow-operated fixed-bed processing (substrate and products should be preferably gaseous) or facilitate separation of the catalyst phase from the organic product phase in batch synthesis.

D. Enders and co-workers[74] proposed an N-heterocyclic carbene (NHC) palladium/ionic liquid matrix on the silica surface (**Figure 5**), which showed high activity in Heck cross-coupling reaction of haloarenes with olefins in several cycles without Pd leaching. Pd-NHC complexes were generated in an imidazolium-type ionic liquid matrix (which was prefunctionalised with a trimethoxysilylpropyl group) and then the whole system was grafted on the surface of silica. TEM (transmission electron microscopy analysis) coupled with EDX

(energy-dispersive X-ray analysis) analysis indicated the formation of Pd nanoparticles within the immobilised IL layer. This is not surprising, as other authors also observed the stabilising effect of IL on Pd nanoparticles. For example, *K. Seddon et al.*[75] reported that Pd nanoparticles were responsible for the catalysis in the Heck coupling, used for the synthesis of the fragrance β-lilial in ionic liquids.

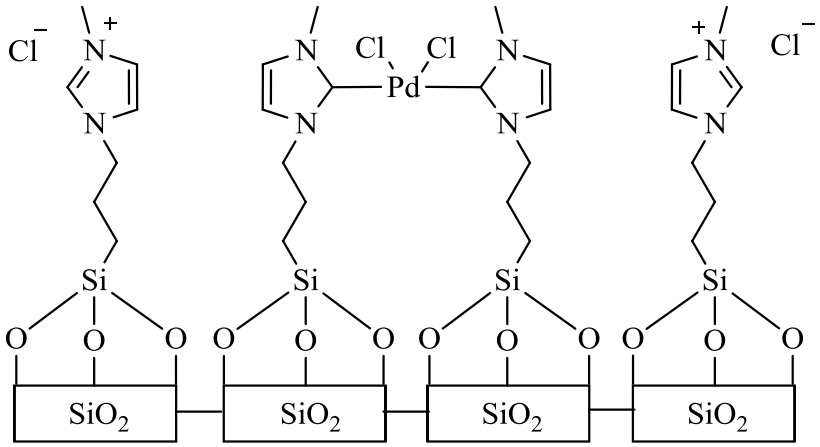


Figure 5. *Structure of NHC-Pd complex/IL matrix immobilised on silica.*

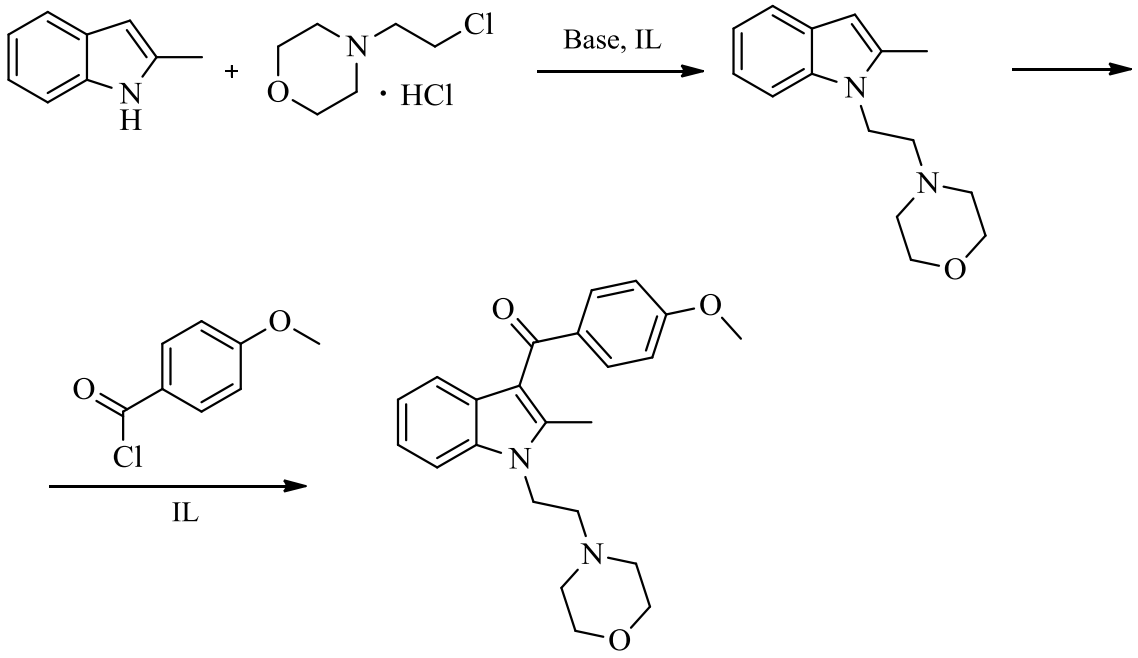
A non-covalent immobilisation of Heck catalyst on silica has been realized by *H. Hagiwara et al.*[76] $Pd(OAc)_2$ dissolved in $[BMIm]PF_6$, supported on silica surface, was applied to the Mizoroki-Heck reaction of aryl halides with cyclohexyl acrylate without a ligand in *n*-dodecane as a solvent. The procedure could be repeated six times with the same catalyst with only 0.24% of Pd leaching, what is acceptable for heterogeneous catalysts.

2.4.2 Miscellaneous reactions in ILs

Heck reactions are perhaps the most widely investigated reactions in ILs, but these reactions are not the only examples of a successful multi-task application of ILs in organic synthesis.

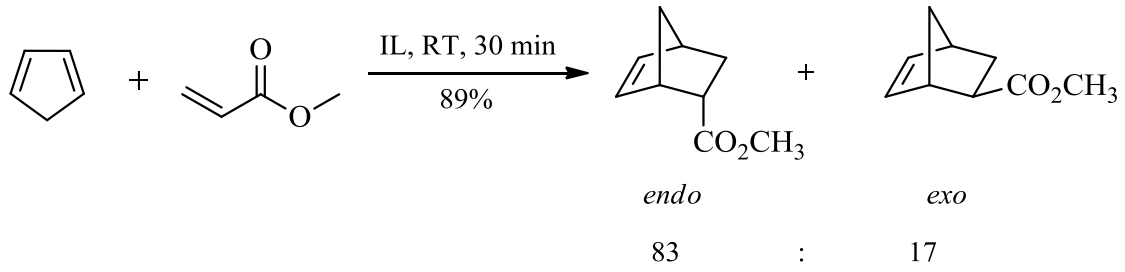
A two-step synthesis of the non-steroidal anti-inflammatory drug (NSAID) pravadoline is a good demonstration of a complete synthesis of a pharmaceutical in an ionic liquid, combining a Friedel-Crafts reaction and a regioselective nucleophilic reaction (**Scheme 7**).[77] The reaction takes place in $[BMIm]PF_6$ with 90-94% overall isolated yield. The acylation step was found to work without Lewis acids, and consequently without all the associated waste

aluminium disposal problems of a conventional Friedel-Crafts reaction. Moreover, the IL could be recovered and reused.



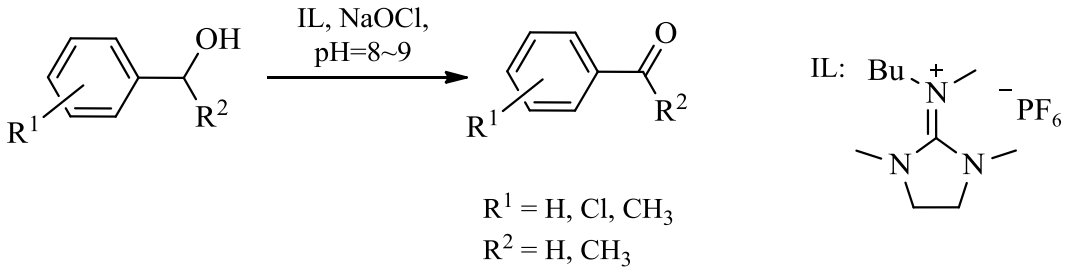
Scheme 7. *Synthesis of Pravadoline in ionic liquid [BMIm]PF_6.*

Ionic liquids have also been used with success as solvents for Diels-Alder reaction. In the reaction of cyclopentadiene with methyl acrylate, RTILs can give substantial increases in *endo*-selectivity and associated rate enhancements, when compared to non-polar solvents.[1,78] *T. Welton* and co-workers[78] found that the greatest selectivities characterise ILs with the strongest hydrogen-bond donor cation coupled with the weakest hydrogen-bond accepting anion. The *endo*-selectivity has been explained by the ability of the cation to hydrogen bond methyl acrylate. Nevertheless, perhaps one of the best *endo*-selectivities for the synthesis of methyl 5-norbornene-2-carboxylate was achieved in binary zinc(II) halide-containing salts. This reaction, performed in IL composed of choline chloride/$ZnCl_2$ (1:2), is shown in **Scheme 8**.[79] In this case the liquid products are easily separated by decantation from the IL, which can be reused.



Scheme 8. *Diel-Alder reaction of cyclopentadiene with methyl acrylate in choline chloride/$ZnCl_2$ (1:2).*

A cyclic hexaalkylguanidinium salt has been successfully applied as a reaction milieu in the selective oxidation of a series of substituted benzyl alcohols with sodium hypochlorite as the oxidant (**Scheme 9**).[80] A guanidinium ionic liquid was chosen because of its greater stability, especially under basic conditions and its phase transfer catalyst properties. Products were extracted with diethyl ether and the recovered IL was recycled five times with no appreciable decrease in yield.

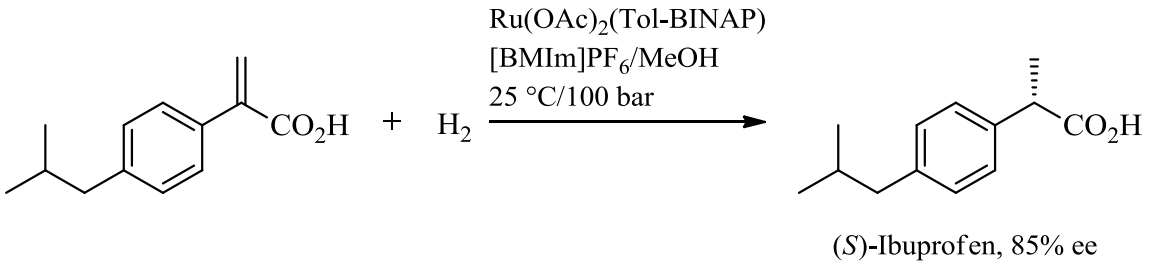


Scheme 9. *The NaOCl oxidation of benzyl alcohols in a guanidinium IL.*

The SILP concept in combination with a guanidinium-based IL was used for a solvent-free hydrogenation of cyclohexene, 1-hexene and 1,3-cyclohexadiene.[81] These reactions were catalysed by Pd nanoparticles immobilised on molecular sieves by 1,1,3,3-tetramethylguanidinium lactate, which showed unprecedented activity and stability. Later the same research group presented a method to prepare Ru nanocatalysts using 1,1,3,3-tetramethylguanidinium trifluoroacetate and montmorillonite. In this method the IL is first exchanged with the ions in the clay, and then Ru^{3+} ions are loaded onto the IL-exchanged montmorillonite. The final Ru/montmorillonite nanocatalyst is obtained after hydrogen treatment. This catalyst shows very high activity for the hydrogenation of benzene and is very

stable, due to the excellent synergistic effects of guanidinium IL, montmorillonite and Ru nanoparticles.[82]

P. Jessop et al.[83] proposed the asymmetric hydrogenation of isobutylatropic acid to furnish the anti-inflammatory drug ibuprofen (**Scheme 10**), followed by a product extraction with *sc*CO_2 (supercritical carbon dioxide). The product was separated from the ionic liquid and catalyst, and the catalyst/ionic liquid solution was then reused repeatedly without significant loss of enantioselectivity or conversion. Noteworthy, the use of the *sc*CO_2 for extraction of the product from the IL reaction medium can be very helpful, when extraction with traditional solvents and distillation do not work.

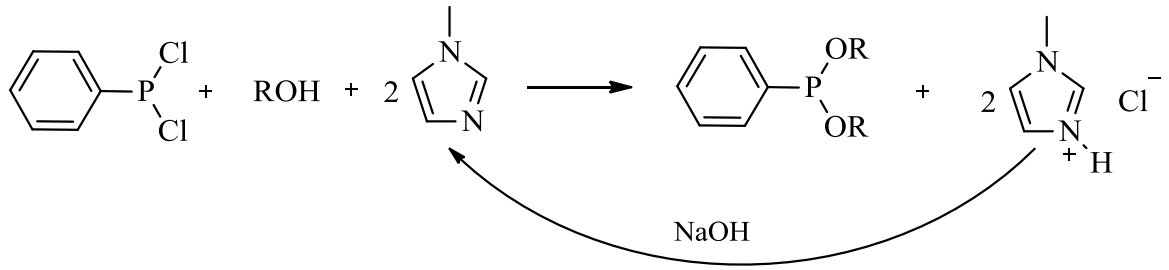


Scheme 10. *Synthesis of ibuprofen in [BMIm]PF_6.*

2.4.3 Applications of ILs in chemical processes

The Institut Francais du Petrole (IFP) (especially Nobel laureate *Y. Chauvin* and *H. Olivier-Bourbigou*) was the first to develop an ionic liquid-based process to a pilot scale. This is the DIFASOL technology which can be used for the dimerization of olefins, namely of butenes. The produced low-branched octenes are good starting materials for isononane production (intermediates in the plasticiser industry). The DIFASOL process can be considered as the biphasic analogue of monophasic DIMERSOL-X process, where the Ni catalyst remains immobilised in IL and the product is separated by simple decantation of two phases. As IL (acting as a solvent and co-catalyst) slightly acidic chloroaluminate ionic liquids with small amounts of aluminium alkyls were used. The main DIFASOL benefits can be summarised in the following aspects: the overall yield is higher in the biphasic process, the nickel consumption is lower, easy separation and no IL detected in products, improved dimer selectivity of the process, continuous flow process with a much smaller reactor.[1,5,65]

Perhaps one of the most well-known industrial applications of ILs is the BASIL (Basic Acid Scavenging utilising Ionic Liquids) process, developed by BASF SE and introduced in Ludwigshafen (BASF) already in 2002. Here, 1-methylimidazole substituted the classical tertiary amine used as an acid scavenger in the synthesis of alkoxyphenylphosphanes (**Scheme 11**). Alkoxyphenylphosphanes are precursors for the manufacture of photoinitiators (BASF's Lucirines®) to cure coatings and printing inks by exposure to UV light. In the case of 1-methylimidazole, the product can be easily separated from the formed 1-methylimidazolium chloride by decantation, and 1-methylimidazole can be regenerated. In the former case with a *tert*-amine, a slurry was obtained, which needed a complicated work-up lowering the yield and capacity of the process. Moreover, BASF was able to perform this reaction in a little jet reactor, which drastically increased the productivity of the process. Its success was almost immediately recognised: the process won the ECN Innovation Award in 2004.[1,5,65]



Scheme 11. *BASIL process.*

Some more examples of application of ILs in chemical industry were given to publicity. Among them are isomerisation by East Chemical Company, hydrosilylation by Degussa, Sonogashira reaction by Central Glass Company (Japan), Ionikylation (alkylation of isobutene) by PetroChina, ether cleavage by Eli Lilly, LAB (linear alkylbenzenes) production by Akzo-Nobel, chlorination by BASF and extractive distillation by BASF.[1,5,65]

The examples demonstrated above show that ionic liquids have a great potential for applications in industry. Higher cost-effectiveness can result from improved rate and selectivity, associated with more efficient catalyst recovery and better environmental compatibility, as well as easier and more energy-efficient technologies. ILs appear to be novel solutions to the chemical industry. Nevertheless, for industrial use of ILs also other aspects

should be addressed, such as IL's synthesis scale-up, purity, stability, toxicity, recycling, disposal and price, which may prevent ILs from process commercialisation.

2.5 ILs as electrolytes

2.5.1 Electrodeposition of metals from ILs

Ionic liquids represent promising and unique electrolytes for the electrodeposition mainly due to a wide electrochemical window combined with a good solubility for most of the metal salts and semiconductor precursors. ILs allow to deposit a range of metals, which are impossible to obtain in water, such as Li, Mg, Al, Ta etc. Many technical processes, such as electrowinning of rare earth metals and refractory metals (Mg, Al and several others) are performed in high-temperature molten salts. So deposition from ILs is a possible solution to perform the process at low-temperatures (even at room temperature), in a less corrosive solution and at lower costs. Ionic liquids allow conducting the process under (almost) water-free conditions, what also means the opportunity to electroplate the metals on water-sensitive materials. Moreover, because of the absence of water no hydrogen embrittlement is observed, what leads to higher quality of the deposits. Easier preparation of alloys, as well as preparation of some new alloys, which are not possible to obtain in water, are enabled in ionic liquids, while metal ion electrodeposition potentials are much closer together in ILs. Ionic liquids could also represent an alternative to environmentally hazardous processes such as the use of chromic acid for the electrodeposition of chromium or the use of cyanide for silver plating.[1,10,84,85]

Several reviews[85–89] and books[9,10] on electrodeposition of metals in ILs and its theoretical and practical aspects have been published. In the recent review of *A. Abbott et al.* [87] a table with the state of the art of deposited elements was presented (**Figure 6**). In this overview the achievements of electrodeposition from ionic liquids will be exemplified for aluminium, tantalum and chromium.

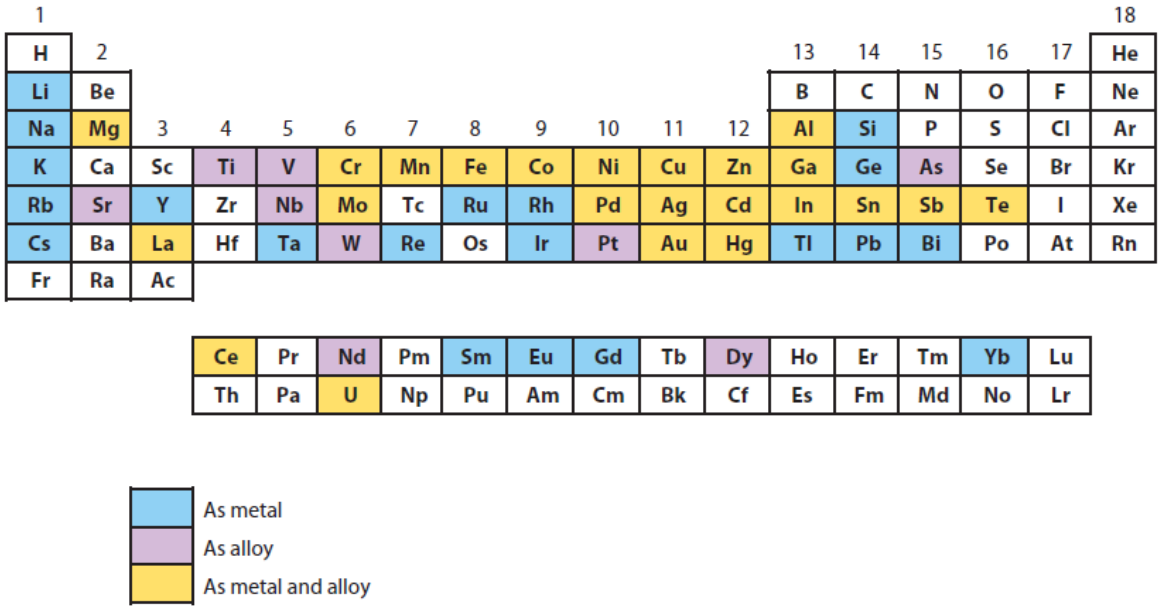


Figure 6. *The elements deposited from RTILs.*[87]

2.5.1.1 Electrodeposition of aluminium from ILs

Electrodeposition of aluminium has a great potential in industrial applications. Aluminium reacts with oxygen to form dense layers of aluminium oxide, which protect metals from corrosion. It is possible to electroplate aluminium from a complex aluminium–organic salt dissolved in toluene (SIGAL-process). As a source of aluminium triethylaluminium is used, which is highly flammable.

R. Osteryoung and *J. Robinson*[90] were the first, already in 1980, to describe the electrodeposition of aluminium on platinum and glassy carbon from an acidic composition of butylpyridinium chloride and $AlCl_3$ and from the same melt where 50% benzene was added. Afterwards a deal of publications appeared concerning electroplating of aluminium from $AlCl_3$-containing melts.

A very interesting observation on the electrodeposition of nano- and microcrystalline electrodeposition of aluminium from water- and air-stable ionic liquids was reported by *F. Endres*.[91,92] The ionic liquids [BMPyr]Tf_2N and [EMIm]Tf_2N show biphasic behaviour in the $AlCl_3$ concentration range from 1.6 to 2.5 mol·L^{-1} and 2.5 to 5 mol·L^{-1}, respectively.

Interestingly, the electroplating of aluminium proceeded only from the upper phases of the mixtures. It was found that nanocrystalline aluminium can be deposited in [BMPyr]Tf_2N saturated with $AlCl_3$. The deposits (**Figure 7**, left) obtained were generally uniform, dense, shining and adherent with very fine crystallites in the nanometer size regime. However, coarse cubic-shaped aluminium particles in the micrometer range (**Figure 7**, right) were obtained in the ionic liquid [EMIm]Tf_2N.[92] The particle size increased significantly with increasing temperature. This curious observation cannot be explained with the viscosity effect alone. Perhaps, the $[BMPyr]^+$ cation acts as a grain refiner and plays its role by adsorption on the substrates and on growing nuclei, thus hindering the further growth of crystallites.[10]

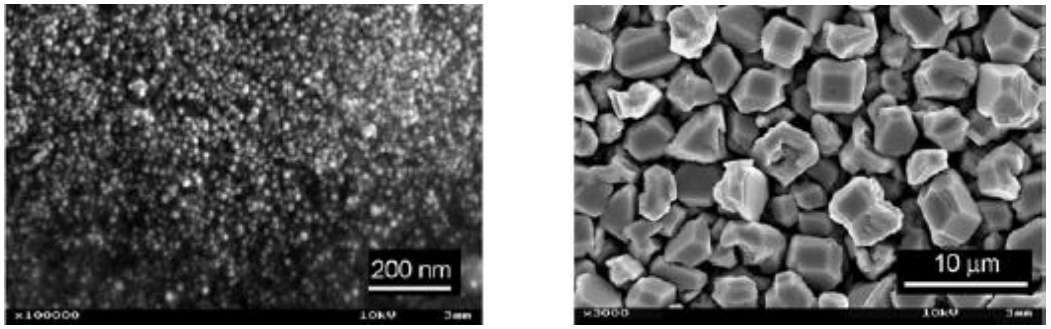


Figure 7. *SEM micrographs of electrodeposited Al films on gold formed in the upper phase of the mixture $AlCl_3$/[BMPyr]Tf_2N (left, part of Figure 2 in lit. [92]) and $AlCl_3$/[EMIm]Tf_2N (right, part of Figure 6 in lit. [92]) after potentiostatic polarisation at -0.45 V (vs. Al) for 2 h (left)/at -0.05 V (vs. Al) for 1 h (right) at 100 °C.*[92]

Later *F. Endres*[93] and *D. MacFarlane*[94] and co-workers tried to understand the electrodeposition and electrochemical behaviour in these mixtures and to characterise the aluminium species, which are responsible for the electrodeposition of aluminium from the upper phase. Both research groups suggested mixed $[AlCl_x(Tf_2N)_y]^-$ species to be electrochemically active. The possible formation of these species was proposed as described in **Figure 8**. The upper phase was reported to contain mainly [cation]$AlCl_4$, and the lower phase was formed from "free" $[Tf_2N]^-$ and $Al(NTf_2)_3$.

$$0.5x\ Al_2Cl_6 + x\ [Tf_2N]^- \rightarrow [AlCl_{(4-x)}(Tf_2N)_x]^- + (x\text{-}1)\ [AlCl_4]^-$$

Figure 8. *Formation of $[AlCl_x(Tf_2N)_y]^-$ species.*[93]

2.5.1.2 Electrodeposition of tantalum from ILs

Tantalum has unique properties that make it useful for many applications, from electronics to mechanical and chemical systems. Its high melting point, ductility, toughness, and excellent corrosion resistance make it an attractive coating material for components exposed to high temperature, wear and severe chemical environments. In addition, as tantalum is almost completely resistant to body fluids and non-irritating for human tissue, it has been widely used for making appliance and implants. The corrosion resistance of tantalum is attributed to a thin protective oxide film that forms spontaneously in air and that exhibits a high stability in most mineral acids.[95]

F. Endres et al.[95] was the first to electrodeposit tantalum in RTILs. It was found that electrodeposition of tantalum is not a straightforward process, as it has a tendency to form non-stoichiometric subhalide species. After a number of unsuccessful efforts to obtain crystalline tantalum from $TaCl_5$, it was substituted with TaF_5. At room temperature only black deposits were obtained. However, at higher temperature and especially in the presence of LiF metallic tantalum (up to 300 nm thick layers) with improved adherence was electrodeposited. The authors attributed these results to the ionic polarizability of Li^+, which can destabilize the Ta–F bonds leading to a facilitation of Ta deposition. **Figure 9** (right) shows the cyclic voltammogram of [BMPyr]Tf_2N containing 0.25 M TaF_5 and 0.25 M LiF on a Pt electrode at 200 °C. Three cathodic peaks are recorded in the forward scan before reduction of the organic cation of the ionic liquid sets in. This observation indicates that the reduction of Ta(V) to Ta metal obviously occurs in at least three steps and not in two steps as in the case of LiF absence (**Figure 9**, left).[95] It is noteworthy that low current density is required to obtain metallic tantalum.[10]

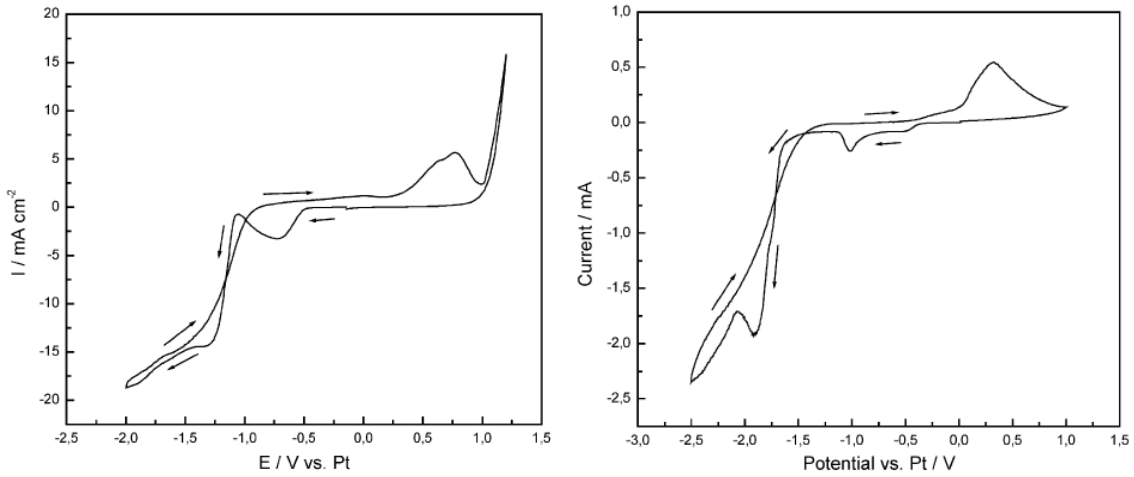


Figure 9. *Cyclic voltammograms of [BMPyr]Tf_2N containing 0.5 M TaF_5 (left, Figure 6 in lit.[95])/0.25 M TaF_5 (right, Figure 10 in lit. [95]) and without LiF (left)/with 0.25 M LiF (right) on a Pt electrode at 200 °C.*[95]

Further study[96] on the complex electrodeposition of Ta from TaF_5 in [BMPyr]Tf_2N on gold (polycrystalline gold and gold(111)) at room temperature showed that the reduction process takes four subsequent steps. First TaF_5 is reduced to TaF_3, subsequently TaF_3 is reduced via (at least) TaF_2, $TaF_{1.5}$, Ta_2F to elemental tantalum.

In order to study the effect of the cation, Ta electrodeposition was investigated in three ILs: [BMPyr]Tf_2N, [EMIm]Tf_2N and [PMIm]Tf_2N. It was found that no elemental Ta can be obtained from [EMIm]Tf_2N containing 0.5 M TaF_5 neither at room temperature nor at temperatures higher than 100 °C. The authors concluded[97] that the conditions of deposition, in terms of temperature, potential or current density chosen as well as the IL used as an electrolyte influence the deposition process and the morphology of the deposits.

2.5.1.3 Electrodeposition of chromium from ILs

Chromium is widely used as a coating material, due to its optical properties, high corrosion resistance and good thermal stability. These coatings are usually obtained by electrodeposition from aqueous solutions based either on CrO_3/H_2SO_4 or trivalent chromium salts/complexing agents. Both of these solutions have their limitations primarily due to the competing hydrogen evolution process, which limits the current efficiency and leads to hydrogen embrittlement of

the substrate, but also because of the highly cracked deposit that is produced.[98] The high toxicity of Cr(VI) is also an issue for serious health and environmental concerns.

A. Abbott et al.[98] proposed the eutectic composition, consisting of 1:2 choline chloride/chromium (III) chloride hexahydrate, ChCl/$CrCl_3 \cdot 6H_2O$, as an electrolyte for Cr electroplating. The electrodeposition of thick (27 μm), adherent, crack-free amorphous pale blue/grey chromium films was demonstrated from this ionic liquid, and it was shown that the waters of hydration are highly coordinated in the liquid and are not significantly electroactive within the potential window of the liquid.[98] This procedure could offer an efficient and environmentally more acceptable process for electrodeposition of chromium.

The addition of LiCl to the electrolyte allows obtaining black coatings with nanocrystalline structure and high corrosion resistance,[99] while bright metallic coatings were obtained by electrodeposition from a similar solution containing proprietary additives.[100] Recently several publications[101–103] appeared describing electrodeposition of black chromium from ILs with the tetrafluoroborate anion.

2.5.2 Application of ILs in Li-ion batteries

2.5.2.1 Conventional Li-ion batteries

A battery generally provides two functions – the ability to supply power over duration of time and the ability to store power. These are defined by two operations, charge/discharge (progress of the reaction) and storage/stop (termination of the reaction). In other words, a battery is a device that provides two functions, namely, energy storage and energy conversion (from chemical to electrical, and *vice versa*).[104]

Lithium-ion batteries (LIB), first introduced to market in 1991 by Sony, are currently one of the most popular battery technologies in the world. Although widely used in various portable electronic devices, only recently lithium-ion batteries have entered into the commercial electric vehicle market.[105] Conventional Li-ion batteries are based on a graphite anode, a lithium cobalt oxide cathode and liquid, organic carbonate electrolytes. At extreme

operational conditions, such as at the upper limit of the charge process, oxygen may be released from the layered $LiCoO_2$ cathode and, in the case of local overheating, it may react with the flammable organic liquid electrolyte, giving rise to thermal runaway effects, if not even to explosions.[106] The battery, the development of which is a task of high importance in many electrochemical laboratories, should possess high specific energy (high voltage joined with high specific capacity), high rate capability, high safety and low cost.

Li-ion batteries are light, compact and work with a voltage of the order of 4 V with a specific energy ranging between 100 $Wh \cdot kg^{-1}$ and 150 $Wh \cdot kg^{-1}$.[107] In its most conventional structure, a lithium-ion battery contains a graphite anode, a cathode formed by a lithium metal oxide ($LiMO_2$, e.g. $LiCoO_2$) and an electrolyte consisting of a solution of a lithium salt (e.g. $LiPF_6$) in mixed organic solvents (e.g. ethylene carbonate–dimethyl carbonate (EC-DMC)) embedded in a separator felt, such as glass fibre mats. **Figure 10** shows a typical lithium-ion battery configuration operating in the process, which involves the reversible extraction and insertion of lithium ions between the two electrodes with concomitant removal and addition of electrons.[107,108]

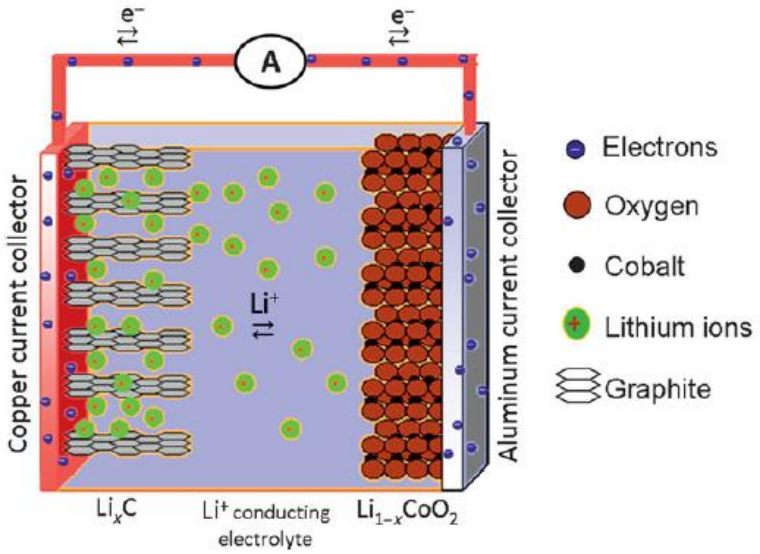


Figure 10. *Scheme and principles of functioning of a common lithium-ion battery.*[108]

The anode, cathode and electrolyte are three basic parts of any LIB, being the subject of extensive research. Metallic lithium has a very high-energy density, amounting to 3860 $mAh \cdot g^{-1}$.[109] However, due to the instability of the Li/electrolyte interface, with the

formation of dendrites forming pathways resulting in short-cuts, it has been replaced by carbon materials, which are able to intercalate lithium with the formation of the C_6Li compound (reversible capacity of ca. 370 $mAh \cdot g^{-1}$). Graphite is usually used as an anode for the Li-ion batteries with different types of electrolytes, including ionic liquids. Cathodes may be of the spinel type LiM_2O_4 (for example $LiTi_2O_4$, $LiMn_2O_4$ or $LiMnCoO_4$), olivine type $LiMPO_4$ (for example $LiFePO_4$ or $LiFe_{0.5}Mn_{0.5}PO_4$), Nasicon type $Li_2M_2SO_4$ or $Li_3M_2(PO_4)_3$ (for example $Li_2Fe_2(SO_4)_3$ or $Li_xTiNb(PO_4)_3$), of lamellar lattice (for example Li_xTiS_2). This leads to a high number of possible anode–cathode combinations.[109]

The worldwide research and development efforts in LIB are mostly focused along two main directions: (1) the replacement of graphite and of $LiCoO_2$ with alternative, higher capacity, lower cost anode and cathode materials; (2) the replacement of the organic carbonate liquid electrolyte solutions with safer and more reliable electrolyte systems.[107]

2.5.2.2 Li-ion batteries using ILs as electrolytes

The unique combination of favourable properties, such as non-volatility, non-flammability, possibility of safe operation in a wide temperature range, make ILs very appealing materials as stable and safe electrolyte media in lithium-ion batteries. One drawback of ionic liquids is in their cost, which is still prohibitively high, although price reduction is expected if the production will be scaled up.[107]

The route of implementation of ILs in LIB is still a long one. For instance, the structure of the IL/electrode interface is still unknown despite the fact that its full understanding is of key importance in view of battery applications.[106,110] The presence of graphitised carbon anode materials in the present Li-ion batteries has restricted the use of ILs in such systems. This is because unstable formation of a solid electrolyte interface (SEI) layer on graphite occurs.[108] The SEI is a passive layer formed on the surface of the electrode, such as oxides formed on the metals, which are responsible for their stability in contact with the electrolyte solution.[109] The widely investigated class of ILs based on the bis(trifluoromethylsulfonyl)imide (TFSI) anion is generally prone to side reactions, such as cation intercalation, leading to the exfoliation of the graphite layer and to IL decomposition during the first reduction. This

becomes a source of extremely large, irreversible capacity.[108] Considerable effort has been made on obtaining a stable SEI layer through which lithium ions can diffuse at a high rate in IL-containing LIB. Besides varying on the chemical nature of both IL cation and anion to control their final properties, another strategy consists of the inclusion of film-forming additives, such as vinylene carbonate or ethylene carbonate. Hybrid electrolytes based on mixtures of ILs and carbonate solvents proved to favour the formation of a stable SEI and reduce the viscosity with respect to pure IL solutions while retaining less flammability.[108,109] This strategy has been applied to a number of ILs with different cations: pyrrolidinium,[111–113] piperidinium,[112,114,115] imidazolium.[116,117]

The conductivity of IL–Li salt mixtures is connected to their viscosity, which, in turn, is dominated by the radius of the ions forming the IL. The use of a lighter anion such as bis(fluorosulfonyl)imide (FSI) is thus highly desirable.[108] *M. Ishikawa*[118] and co-workers first reported new IL systems based on the FSI anion (*N*-methyl-*N*-propylpiperidinium and 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imides) as having very good ionic conductivity and providing a stable, reversible capacity for a graphitised negative electrode at an ambient temperature without any additives. The same approach was later used for IL systems with other cations.[119–122] Electrolytes formed by dissolving LiTFSI in FSI-based ILs have been reported to allow reversible lithium insertion/deinsertion in graphite electrodes. Unfortunately, the high cost, due to the more difficult purification of the FSI anion with respect to TFSI, prevents the usage of the FSI-based ILs on a larger scale.[108]

Recently, *J. Reiter*[123,124] and co-workers reported a successful application of lithium bis(fluorosulfonyl)imide (LiFSI) solution in bis(trifluoromethanesulfonyl)imide-based IL as an electrolyte for graphite composite anodes in lithium-ion batteries operating at an elevated temperature of 55 °C. This success is explained by the ability of the FSI anions to create a stable solid electrolyte interface on graphite.

As already mentioned, quite a lot of anode and cathode materials exist, as well as a great number of their combinations. Ionic liquids have been applied not only with carbon materials but also with other materials, broadly used as electrodes in batteries. For instance, hexaalkylguanidinium-based ILs have already been tried as electrolytes for Li/$LiCoO_2$[125,126]

and Li/$LiFePO_4$[127,128] cells, but there were no reports on their compatibility with graphite. Although the Li/$LiCoO_2$ cells with guanidinium-based electrolytes had good capacities, they exhibited unfavourable cycle properties. On the other hand, good cycle properties at a charge-discharge current rate of 0.1 C were observed in Li/$LiFePO_4$ cells. These cells showed good rate capabilities after edition of 10% vinylene carbonate or γ-butyrolactone. Moreover, the experiments revealed that also IL (in this case guanidinium-based ILs) with low cathodic stability and without any additives can provide plating/stripping of lithium due to the formation of SEI film, and they can be successfully used in LIB.

Further improvements, in terms of safety and reliability, can be achieved by moving from liquid solutions to polymer electrolytes (PEs). Although many properties related to the nature of PEs are favourable for LIB, among which is negligible electrolyte leakage, there are also problems delaying their development, which include low conductivity of most solid PEs at ambient temperature and reactivity with the lithium electrode in solvent plasticised polymer systems. From this viewpoint, polymer electrolytes, resulting from a polymer matrix together with an IL, represent an attractive strategy, since they combine the mechanical and chemical stability of the polymer component with the intrinsic good conductivity, non-flammable nature and high thermal stability of the IL component.[108] Recently, application of a polymer electrolyte, composed of poly(vinylidene fluoride-*co*-hexafluoropropylene) PVdF-HFP microporous membrane incorporating guanidinium IL with $LiNTf_2$, was reported in Li/$LiFePO_4$ batteries.[129] The cells delivered the capacity of 142 $mAh \cdot g^{-1}$ at the 100th cycling (0.1 C) at 25 °C, what is a good stability of the discharge capacity cycle for this type of cells. The same authors developed polymer electrolytes based on polymeric IL as polymer host and incorporating guanidinium IL, $LiNTf_2$ and nano-scale silica.[130]

2.6 Miscellaneous applications of ILs

2.6.1 Application of ILs in biomass processing

Cellulose is the most abundant renewable resource, and its use has been made more accessible through the use of ionic liquids.[54,131] Traditionally, cellulose dissolution processes include volatile toxic (xanthate process) and expensive (Lyocell process) solvents, and require relatively harsh conditions. Dissolution of cellulose with ionic liquids allows the comprehensive utilisation of cellulose by combining two major green chemistry principles: using environmentally preferable solvents and bio-renewable feedstocks.[132]

Already in 1934 *C. Graenacher*[17] discovered that halide salts of nitrogen-containing bases (1-benzylpyridinium chloride, 1-ethylpyridinium chloride etc.) can be used to dissolve cellulose. With the use of 1-butyl-3-methyl-imidazolium chloride, *R. Rogers*[131] from the University of Alabama was the first to be able to dissolve cellulose in technically useful concentrations by physical dissolution in an inert solvent without using any auxiliaries. In 2005, BASF licensed the exclusive use of various intellectual property rights from the University of Alabama.[5,133] In China, the Institute of Process Engineering, Chinese Academy of Sciences and Wuliangyi Corporation have jointly launched a program to produce an anti-bacterial fibre applying the wool keratin/cellulose composite technology (using IL as a solvent).[132]

Cellulose can be dissolved, without derivatsation, in some hydrophilic ionic liquids, such as 1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride. Microwave heating significantly accelerates the dissolution process. Cellulose can be easily regenerated from its ionic liquid solutions by addition of water, ethanol or acetone. After its regeneration, the ionic liquids can be recovered and reused.[131,132] Fractionation of lignocellulosic materials, preparation of cellulose derivatives and composites, production of biofuels are some typical applications.

The dissolution process seems to be mainly influenced by the anion of the ionic liquid. Anions such as halides, carboxylates or phosphates seem to be able to very effectively break down interchain hydrogen bonds within the cellulose structures. The presence of water decreases the solubility through competitive hydrogen bonding processes.[131,133]

Recently, a German patent[134] (*W. Kantlehner* and *S. Saur*) appeared describing extraction of lignin, tannin, cellulose and hemicellulose from biogenic materials using guanidinium-based ionic liquids.

2.6.2 Application of ILs in dye-sensitised solar cells

The first successful demonstration of a nanocrystalline dye-sensitised solar cell (DSSC) in 1991 introduced an innovative approach for low-cost alternatives to traditional inorganic photovoltaic devices.[135] The most efficient DSSCs are based on nanostructured TiO_2 as a semiconductor, ruthenium(II) bipyridyl complexes as sensitisers and electrolytes consisting of volatile organic solvents with an iodide/triiodide redox couple.[136] The long-term instability of DSSCs remains one of the most important factors limiting their industrialisation.

The potential of room-temperature ionic liquids as solvents for electrolytes for dye-sensitised solar cells has been investigated during the last decades. The non-volatility, good solvent properties and high electrochemical stability of ionic liquids make them attractive solvents in contrast to volatile organic solvents. Despite this, the relatively high viscosity of ionic liquids leads to mass-transport limitations.[136,137]

The first ionic liquids tested belong to the imidazolium family, and these are most commonly investigated as electrolytes in DSSCs. However, some reports on the application of guanidinium-based IL have been made. DSSCs with hexaalkylguanidinium or cyclic guanidinium iodides as electrolytes can achieve power conversion efficiency of ca. 6%.[138,139] Triaryl-substituted guanidinium salts were also tested as hole-conductor materials in DSSCs.[43]

Very little effort has been devoted to the optimal adaption of the electrode materials or the sensitising dye to this new class of electrolytes.[136] Thus, interfacing the development of IL systems, DSSC materials and perhaps DSSC construction can lead to effective and long-time stable solar cells.

2.6.3 Other applications

Ionic liquids count a great number of applications also in non-synthetic fields, which are being broadly discussed, developed and already applied. Among them are the already mentioned electrochemical applications, such as the use of ILs as electrolytes in batteries, in supercapacitors and fuel cells, in dye-sensitised solar cells, as well as for electrodeposition of metals/semiconductors. Analytical applications include the use of ILs as active component in sensors, as matrix for mass spectrometry, and as stationary phase for gas chromatography. The growing area of engineering liquid applications encloses material processing with ionic liquids, separation technologies and applications in process machinery.[1] For example, ILs are used for the dispersion of nano-materials at IOLITEC, Air Products uses ILs instead of pressurised cylinders as a transport medium for reactive gases, ION Engineering is commercialising technology using ILs and amines for CO_2 capture and natural gas sweetening, and many others.[140]

For all these kinds of new applications the chemical industry as provider of ionic liquids can act as a driving force that fosters ionic liquid-based innovations in many of its customer industries.[1]

3. Motivation

Ionic liquids are potential alternative solvents in many industrial applications. Due to negligible vapour pressure, ionic liquids are not released to the environment by evaporation. They are easy to recycle and show remarkably high thermal stabilities. Because of their peculiar physical properties, which can be fine-tuned by variations of the cation as well as the anion, they represent innovative materials holding great promise for various different applications in chemical synthesis and technology.

This Ph. D. work is directed to develop the application of hexaalkylguanidinium-based ionic liquids in synthetic organic chemistry and in electrochemistry. Although hexasubstituted guanidinium salts possess superior delocalisation in the cation and therefore high thermal and chemical stability, they are still not available on the market. The advantage of guanidinium ionic liquids consists in the possibility to vary six substituents to adjust the properties of the IL to a spesific task. Thus, a number of guanidinium-based ionic liquids with different anions will be synthesised, its physical properties will be as far as possible completely investigated. Several methods of synthesis of guanidinium salt have already been described by *W. Kantlehner*,[28] *G. Maas*,[31] *C. A. M. Afonso*[35] (see chapter 2.2). These protocols will be applied and adopted for the synthesis of new representatives of the guanidinium family.

In this Ph.D. project, a new approach will be taken, which avoids working with metal halides. Instead, metal alcoholates will be employed. Metal alcoholates are known for many metals, including magnesium, aluminium, titanium and tantalum. They are commonly considered to hydrolyse quickly, but this reactivity can be moderated by the introduction of longer alkyl chains (i.e. butyl or higher) in the alcoholate. So far, synthetic chemistry using alcoholates in IL as reaction media has found little attention, and hardly anything is known about the electrochemical behaviour of metal alcoholates in ILs.

Titanium alkoxides $Ti(OR)_4$ have been widely applied as mild Lewis acids, for example in crossed aldol reactions, in Mukayama reactions of allylsilanes, Paal-Knorr reaction and for the formation of lactams. Titanium tetraisopropanolate is also a reagent for the famous Sharpless

asymmetric epoxidation of allylic alcohols. It will be interesting to learn whether ionic liquids as reaction media have an impact on the reaction course and/or the effectiveness of the reaction.

For this purpose, solutions of metal alcoholates (Ti, Al) in a range of ionic liquids, mainly hexaalkylguanidinium-based ionic liquids, will be prepared and investigated. Hexaalkylguanidinium cations are expected not to react with these alcoholates, since they are known to be stable also against hydroxide ions at room temperature. The most stable solutions will be applied as reaction media in some typical reactions of organic synthesis, mainly dehydrating cyclocondensation reactions leading to formation of various heterocyclic systems, catalysed by mild Lewis acids. The influence of ionic liquids as solvents on the course of organic reactions, as well as the possibility to reuse the catalyst/IL system, will be studied.

Moreover, ionic liquids have already been employed as the media for the electrodeposition of a considerable number of metals. This procedure helps to avoid many problems related with electrodeposition from molten salts (which is performed at high temperatures that consequently leads to high costs of energy) or limitations of electrolysis of metal salts in aqueous or organic solutions. From this standpoint electrodeposition of metals from solutions of metal alcoholates $M(OR)_n$ in ionic liquids is expected to be more convenient and can be carried out at room or near room temperature. This method is also able to provide safer conditions in comparison to electrodeposition from solutions of respective salts in ionic liquids avoiding the use of halogens. The use of metal alcoholates instead of metal halides should also decrease the hygroscopicity of the solution. The novelty of this part of research work will consist in the application of metal alcoholates for metal electrodeposition with ionic liquids as the electrolyte. The possibility of electrodeposition of other metals, which cannot be electroplated from water, will also be investigated. In these cases metal salts will be also tried as substrates.

For better understanding of the electrochemical processes, conducted with guanidinium-based ionic liquids, basic properties of metal (substrate)/IL interface, electrochemical stability of ILs should be studied.

Ionic liquids, due to their peculiar physical properties, represent a potential class of electrolytes in Li-ion batteries,[127,128] which can lend LIB safer characteristics. Several hexaalkylguanidinium bis(triflyl)imides have already been used as electrolytes for Li-ion batteries, but were tested only with a few electrode materials. The reported results suggested guanidinium ILs for further investigations in this field. In this work guanidinium-based ionic liquids should be modified to adress the actual demands in application of IL electrolytes, such as compatibility with electrodes (especially in the case of graphite), high electrochemical stability (to provide effective and long life of LIB), and high conductivity (to improve the battery capacities).

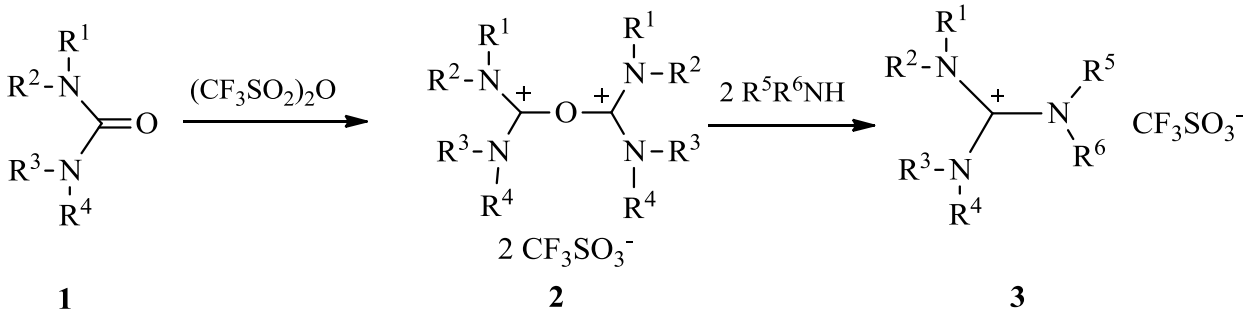
4. Results and discussion

4.1 Synthesis of guanidinium-based ionic liquids

The aim of this work was to investigate the possibilities of application of guanidinium-based ionic liquids (ILs) as a solvent in organic synthesis and as an electrolyte for metal electrodeposition, Li-batteries, DSSC and LED devices. It is well known, that it is possible to modify the structure and therefore the properties of the ILs according to the specific application. Peculiar physical properties of ionic liquids (thermal stability, melting point, viscosity, tunable miscibility with other solvents) can be fine-tuned by variations of the cation as well as the anion. So, first of all, a good number of ionic liquids had to be synthesised.

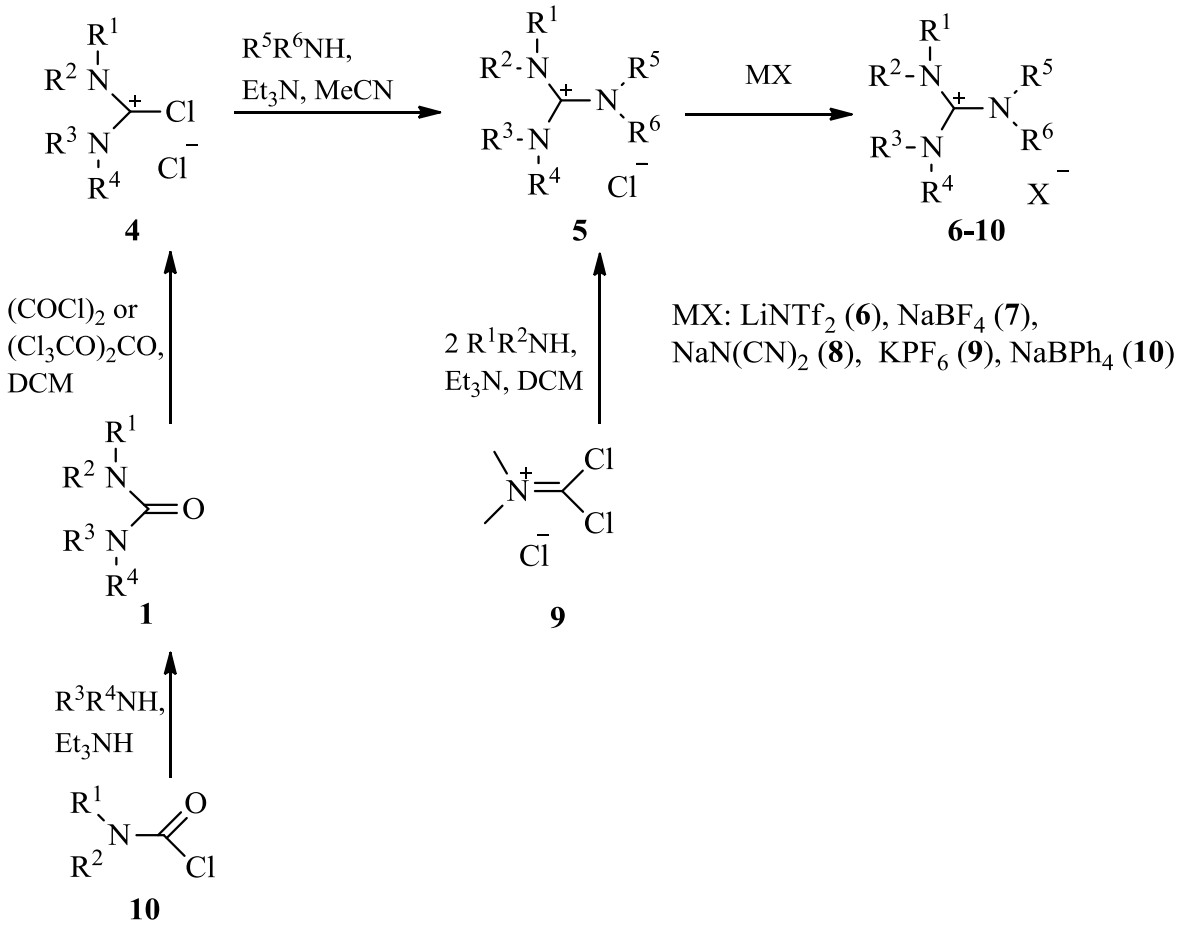
For the investigations, ILs with different cations and anions had to be prepared. The focus was laid on hexaalkylguanidinium salts, because many of them have a high thermal stability and, due to the effective dissipation of the positive charge in the cation, a better chemical stability than some of the other common classes of ILs. Some selected and promising guanidinium-based ionic liquids were prepared by the routes[31,35,141,43,28] shown in **Scheme 12**.

Method A (**1** → **2** → **3**):



1 **2** **3**

Methods B (**1** → **4** → **5**) and C (**9** → **5**):



Scheme 12. *Synthesis of guanidinium-based ILs.*

Hexaalkylguanidinium trifluoromethanesulfonates **3** (triflates, TfO; **Table 2**) were obtained on a halogen-free route from the corresponding ureas in two steps (see method A, **Scheme 12**). Most of these ILs have already been reported in literature,[31] but some of them (**3d,3g, 3h, 3i**, underlined in **Table 2**) represent new ionic liquids. Reaction of **2a** (R^1=R^2=Me) with diisopropylamine failed, perhaps due to sterical hindrance.

Most of the hexaalkylguanidinium bis(trifluoromethylsulfonyl)imides (bis(triflyl)imides, Tf_2N; **Table 2**) were also prepared from the corresponding teraalkylureas **1** in three steps. The main procedure followed was taken from *W. Kantlehner et al.*,[28] but, instead of highly toxic gaseous phosgene, easier-to-handle and therefore less dangerous oxalyl chloride or in some cases solid triphosgene were used to chlorinate the urea. However, in the case of *N,N*-dibutyl-*N',N'*-diethylurea no acceptable yields were obtained either with oxalyl chloride nor with

thionyl chloride or triphosgene. The highly hygroscopic chloroamidinium salt **4** was thoroughly washed with dry diethyl ether, so that the excess of oxalyl chloride or unreacted urea could be removed, as well as some coloured impurities. This work-up facilitates the decolouration at the further stages of the synthesis. Some of the chloroformamidinium chlorides **4** as a solution in acetonitrile were kindly provided by *Prof. W. Kantlehner* (Hochschule Aalen, Germany). The nucleophilic substitution of **4** with *sec*-amines led to hexaalkylguanidinium chlorides. It should be mentioned that this route (method B, from **1** to **5**) is limited to the availability of the ureas, whereas method C can be applied instead. Phosgene iminium chloride **9** is a commercially available chemical. So this method is applicable for symmetric cations, where two mole equivalents of *sec*-amine are applied[35] (however, the synthesis of the salt **6m** through this route failed; the salt **6m** was obtained from 1,1-carbonyldipiperidine by method B), but also some unsymmetric guanidinium chlorides can be obtained by subsequent addition of two different *sec*-amines.[36] As disadvantages of this route, more intensive colouration of the reaction mixture can arise (may be due to some impurities in the purchasable phosgene iminium chloride **9** or/and its high moisture sensibility) and in some cases along with a desired unsymmetric cation unselective formation of two symmetric cations occurs (when two molecules of the same amine are used for the formation of the guanidinium core). In these cases (**6u** and **6v**) the bypath over urea was taken (method B, from **10** to **1**, **Scheme 12**). The desired urea could be easily obtained from an *N*,*N*-dialkylcarbamoylchloride[142] and then the required guanidinium chloride was synthesised in the usual way.

The purity of the ionic liquids is a very important point for most applications, especially electrochemical ones.[1,9] As it is almost impossible (at least in a reasonable time span) to distill the prepared ionic liquid (with bistriflimide, triflate, tetrafluoroborate, sulfonate etc. anions), it is essential to take a pure halide (chloride in this work) for an anion exchange. Because of this aspect, some modifications in the work-up procedure for the guanidinium chlorides were developed to achieve a satisfactory purity of the products. After the reaction mixture was filtered from triethylammonium chloride and the solvent was distilled off, 0.1 M aqueous NaOH solution was added to adjust pH 9-10. The basic medium was needed to effectively transform all remaining ammonium salts in the amine form. Then the water solution was extracted with diethyl ether several times in order to remove the formed amines

and some of the coloured impurities (in many cases the diethyl ether phase was intensively coloured; after evaporation, NMR analysis showed only amines and undefined products, perhaps these coloured impurities, and no guanidinium salt). The next step was different depending on the distribution coefficient of the salt in water or dichloromethane. In cases where the salt was not or only partly soluble in dichloromethane, water was distilled off, the oily residue was dried at 40 °C/0.05 mbar. Dry acetonitrile and diethyl ether (2:1, v/v) were added and the precipitate (NaCl, excess NaOH) was filtered off. After removal of the solvents on the rotary evaporator the remaining guanidinium chloride was intensively dried at 50-70 °C/0.05 mbar. If the guanidinium salt was well soluble in dichloromethane, the NaCl-saturated water phase was extracted several times with dichloromethane. The organic phase was dried over Na_2SO_4, the solvent was evaporated and the remaining guanidinium chloride was dried as written earlier. This work-up has an advantage to spare the guanidinium salt multiple heating procedures and tremendous water distillation. Moreover, this work-up is also time-saving. So the second procedure was tested at first for the synthesised guanidinium chlorides. If it didn't work in the proper way, the first procedure was applied.

The anion exchange reaction was carried out in water analogous to lit. [43]. Special attention was devoted to washing the IL with deionized water to remove all Li^+ and Cl^- ions. The control was made with 0.2 % aqueous $AgNO_3$ solution. Chloride ions can be disturbing in electrochemical applications and lead to false information about electrochemical properties of ILs (electrochemical window, conductivity etc.). The residual chloride content of one of the synthesised hexaalkylguanidinium triflamides **6a** was measured by neutron activation analysis (NAA) by *Dr. I. Sziklai-László* (Nuclear Analysis and Radiography Department, Centre for Energy Research, Hungarian Academy of Sciences) to be 10 ppm, what proves that this IL conforms to the demands of electrochemistry. The second important point for electrochemical applications is a low water content. It was achieved with the vacuum-drying in a bulb-to-bulb apparatus for several hours and was measured to be less than 10 ppm with a Karl-Fischer titrator. For the electrochemical studies the ILs used should be of a high degree of purity. Cooperative work with the Institute of Electrochemistry (*C. Berger*, University of Ulm) showed that for the discolouration purposes a work-up with activated coal is to be preferred to a work-up with Al_2O_3.

Dicyanamides **8**, tetrafluoroborates **7** and hexafluorophosphates **9** were synthesised by anion exchange between guanidinium chlorides and an appropriate salt in dichloromethane analogous to *C. Afonso et al*.[35,141]

Table 2. *Synthesised guanidinium-based ionic liquids.*[a,b]

	R^1	R^2	R^3	R^4	R^5	R^6	Abbreviation
3a	Me	Me	Et	Et	Bu	Bu	$[N_{11}N_{22}N_{44}Gu]OTf$
3b	Et	Et	Bu	Bu	Hex	Hex	$[N_{22}N_{44}N_{66}Gu]OTf$
3c	Me	Me	Et	Et	$MeO(CH_2)_2$	$MeO(CH_2)_2$	$[N_{11}N_{22}N_{1O21O2}Gu]OTf$
3d	Me	Me	Me	Me	$MeO(CH_2)_2$	$MeO(CH_2)_2$	$[N_{11}N_{11}N_{1O21O2}Gu]OTf$
3e	Me	Me	Me	Me	Me	Bu	$[N_{11}N_{11}N_{14}Gu]OTf$
3f	Me	Me	Me	Me	Et	Et	$[N_{11}N_{11}N_{22}Gu]OTf$
3g	Me	Me	Me	Me	Pr	Pr	$[N_{11}N_{11}N_{33}Gu]OTf$
3h	Me	Me	Me	Me	Bu	Bu	$[N_{11}N_{11}N_{44}Gu]OTf$
3i	Me	Me	Me	Me	Hex	Hex	$[N_{11}N_{11}N_{66}Gu]OTf$
3j	Bu	Bu	Bu	Bu	Bu	Bu	$[N_{44}N_{44}N_{44}Gu]OTf$
6a	Me	Me	Et	Et	Bu	Bu	$[N_{11}N_{22}N_{44}Gu]NTf_2$
6b	Et	Et	Bu	Bu	Hex	Hex	$[N_{22}N_{44}N_{66}Gu]NTf_2$
6c	Me	Me	Et	Et	$MeO(CH_2)_2$	$MeO(CH_2)_2$	$[N_{11}N_{22}N_{1O21O2}Gu]NTf_2$
6d	Me	Me	Me	Me	$MeO(CH_2)_2$	$MeO(CH_2)_2$	$[N_{11}N_{11}N_{1O21O2}Gu]NTf_2$
6e	Me	Me	Me	Me	Me	Me	$[N_{11}N_{11}N_{11}Gu]NTf_2$
6f	Me	Me	Me	Me	Me	Bu	$[N_{11}N_{11}N_{14}Gu]NTf_2$
6g	Me	Me	Me	Me	Bu	Bu	$[N_{11}N_{11}N_{44}Gu]NTf_2$
6h	Me	Me	Me	Me	Hex	Hex	$[N_{11}N_{11}N_{66}Gu]NTf_2$
6i	Me	Me	Me	Bu	Me	Bu	$[N_{11}N_{14}N_{14}Gu]NTf_2$
6j	Me	Me	Hex	Hex	Hex	Hex	$[N_{11}N_{66}N_{66}Gu]NTf_2$
6k	Et	Et	Bu	Bu	Bu	Bu	$[N_{22}N_{44}N_{44}Gu]NTf_2$
6l	Me	Me	Me	Me	$-(CH_2)_5-$		$[N_{11}N_{11}N_{pip}Gu]NTf_2$
6m	Me	Me	$-(CH_2)_5-$		$-(CH_2)_5-$		$[N_{11}N_{pip}N_{pip}Gu]NTf_2$
6n	$-(CH_2)_5-$		$-(CH_2)_5-$		$-(CH_2)_5-$		$[N_{pip}N_{pip}N_{pip}Gu]NTf_2$
6o	Me	Me	Me	Me	$-(CH_2)_4-$		$[N_{11}N_{11}N_{pyr}Gu]NTf_2$
6p	Me	Me	Me	Me	$-(CH_2)_2O(CH_2)_2-$		$[N_{11}N_{11}N_{mor}Gu]NTf_2$
6q	Me	Me	Et	Et	$-(CH_2)_5-$		$[N_{11}N_{22}N_{pip}Gu]NTf_2$
6r	Me	Me	Pr	Pr	$-(CH_2)_5-$		$[N_{11}N_{33}N_{pip}Gu]NTf_2$
6s	Me	Me	Hex	Hex	$-(CH_2)_5-$		$[N_{11}N_{66}N_{pip}Gu]NTf_2$

6t	Me	Me	Me	*c*Hex	-$(CH_2)_5$-		$[N_{11}N_{1cHex}N_{pip}Gu]NTf_2$
6u	Me	Me	Me	Bu	-$(CH_2)_5$-		$[N_{11}N_{14}N_{pip}Gu]NTf_2$
6v	Me	Me	$MeO(CH_2)_2$	$MeO(CH_2)_2$	-$(CH_2)_5$-		$[N_{11}N_{1O21O2}N_{pip}Gu]NTf_2$
6w	Me	Me	Me	Me	Me	*c*Hex	$[N_{11}N_{11}N_{1cHex}Gu]NTf_2$
6x	Me	Me	Me	Me	2-EtHex	2-EtHex	$[N_{11}N_{11}N_{EHEH}Gu]NTf_2$
7a	Et	Et	Bu	Bu	Hex	Hex	$[N_{22}N_{44}N_{66}Gu]BF_4$
7b	Me	Me	Me	Me	-$(CH_2)_5$-		$[N_{11}N_{11}N_{pip}Gu]BF_4$
7c	Me	Me	Me	Me	Hex	Hex	$[N_{11}N_{11}N_{66}Gu]BF_4$
7d	Me	Me	Hex	Hex	-$(CH_2)_5$-		$[N_{11}N_{66}N_{pip}Gu]BF_4$
8a	Me	Me	Et	Et	Bu	Bu	$[N_{11}N_{22}N_{44}Gu]N(CN)_2$
8b	Et	Et	Bu	Bu	Hex	Hex	$[N_{22}N_{44}N_{66}Gu]N(CN)_2$
9a	Me	Me	Hex	Hex	-$(CH_2)_5$-		$[N_{11}N_{66}N_{pip}Gu]PF_6$
10a	Me	Me	Me	Me	Me	*c*Hex	$[N_{11}N_{11}N_{1cHex}Gu]BPh_4$

a) **3** – Trifluoromethanesulfonates; **6** – bis(trifluoromethylsulfonyl)imides; **7** – tetrafluoroborates; **8** – dicyanamides; **9** – hexafluorophospates; **10** – tetraphenylborates; **5** – chlorides (not presented in this table), numbering analogous to **6**.

b) Compounds with underlined numbers were newly prepared in this work.

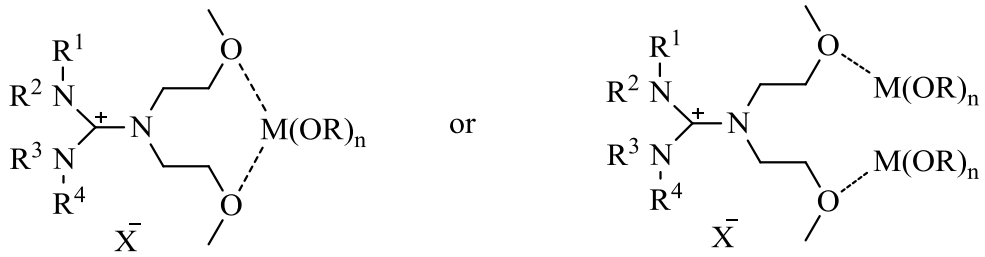
For the application of ionic liquids as solvents in organic synthesis or as electrolytes it is important that the source reagents for the preparation of ILs are readily available, and also that the ILs possess appropriate properties such as melting point, viscosity, solubility, conductivity, electrochemical stability. These reasons prompted us to spread the range of guanidinium-based ILs, among which new ILs (underlined in **Table 2**) as well as others, that have already been mentioned in periodicals or patents but not always fully described, were obtained and characterised. The major attention was paid to ILs with a bis(triflimide) anion because of their higher electrochemical and thermal stability, lower viscosity, higher conductivity and also hydrophobicity and good solubility characteristics for titanium and aluminium alcoholates. The full list of synthesised guanidinium-based ILs is presented in **Table 2**. The structures of these ionic liquids and literature references for the known ILs are provided in **Appendix 2**.

Ionic liquids are known to be “tunable” for each specific application. That is the explanation why a good number of guanidinium-based ionic liquids was generated to find the proper one for each task. An advantage of a guanidinium cation upon imidazolium and ammonium

cations is the opportunity to introduce six different substituents and in this way to influence the physical, electrochemical and chemical properties of the IL.

One of the main applications for guanidinium ILs in this work was their use as solvents for metal alcoholates as catalysts in organic synthesis. Another project of the metal alcoholate/guanidinium IL system was metal electrodeposition from ILs in cooperation with the Institute of Electrochemistry (University of Ulm). For both applications the homogeneous solution is favourable to provide an effective mass transport. So in the first step the solubility of the metal alcoholates in ILs was investigated, and the ILs which gave homogeneous, highly concentrated solutions were chosen as potentially applicable. For these studies hexaalkylguanidinium triflates, bistriflamides, dicyanamides and tetrafluoroborates as well as 1-butyl-3-methylimidazolium (BMIm) bistriflamide and *n*-hexyltrimethylammonium (Me_3HexN) bistriflamide for comparison were synthesised. *n*-Hexyltrimethylammonium iodide ([Me_3HexN]I), used as a precursor for [Me_3HexN]NTf_2, was prepared according to *D. MacFarlane et al.*[143]

The variety of guanidinium cations included cations with different chain length or symmetry, and those with ether function (this could be profitable for complex formation with metal alcoholates, see **Scheme 13**).



Scheme 13. *Possible complexes between ether-functionalised IL and metal alcoholates.*

Some hexaalkylguanidinium liquids were provided for preliminary electrochemical investigations, namely electrochemical stability and surface interaction of ionic liquids with single crystalline gold surfaces. The work was done in the Institute of Electrochemistry (University of Ulm, *C. Berger, M. Gnahm, Prof. Dr. D. M. Kolb, Prof. Dr. T. Jacob*). It was found that the bis(triflyl)imides possess wider electrochemical window in comparison to

triflates and dicyanamides,[144] but it is still not as wide as that of some commercially available ILs based on other organic cations. Some of the ionic liquids, which are commonly used in electrochemistry, include piperidinium, pyrrolidinium, pyridinium, morpholinium cations. In hopes to improve the electrochemical stability, one or more of these structural moieties were integrated in the guanidinium cation (**6l-v**, **Table 2**).

As *N,N,N',N'*-tetramethyl-*N'',N''*-pentamethyleneguanidinium bis(trifluoromethyl-sulfonyl)imide (**6l**) showed good electrochemical stability, the series of guanidinium ILs containing a piperidinium structure was extended to **6m,n,q-v**. Some of them were tested as electrolytes in Li-ion batteries (LIB) in cooperation with TUM CREATE in Singapore (*N. Bucher, S. Hartung, Prof. Dr. H. E. Hoster*). For another project with ZSW (Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, *S. Hess, Dr. M. Wachtler*) two ILs **6w** and **6x** with sterically demanding cations were synthesised and also applied in LIB.

For the multi-purpose cooperation with Siemens AG (*Dr. A. Kanitz, Dr. M. Rührig*) the salts with different anions were prepared. Among the purposes of cooperation were applications of guanidinium ILs in LEC devices, in condensators, in metal electrodeposition.

In this work several diverse applications of hexaalkylguanidinium ionic liquids were tested. For each application the guanidinium cation was "fine-tuned" as well as the appropriate anion was taken according to a specific task.

4.2 Restricted rotation in hexaalkylguanidinium salts

All synthesised ionic liquids were characterised by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy. In many cases we could observe more ^{1}H and ^{13}C signals as one would expect for the symmetrical cation. This is attributed to the restricted rotation around the $C^{+}–NR_2$ partial double bonds, which leads to a chiral non-planar propeller-like structure of the hexasubstituted guanidinium cation, first studied by *A. Santoro* and *G. Mickevicius*.[32] Hindered rotation gives rise to the magnetic non-equivalence of the chemically equivalent nuclei in the two alkyl chains of a symmetrically substituted NR_2 group.[31,32] For example, we

could observe such behaviour of methyl groups in symmetric guanidinium bis(triflyl)imides **6g,h,l,p**, where instead of one two signals were detected; methyl groups in **6q-s,v** also were observed to be non-equivalent. Similar rotamers of persubstituted guanidinium salts were also observed by other authors.[31,35,38] Analogous studies have been carried out for pentasubstituted guanidinium salts[145–147] and L-arginine.[148] Moreover, the presence of one unsymmetrical NR^1R^2 group can evoke *E*/*Z* isomerism around the iminium partial double bond, herewith several diastereomers can be formed.[31]

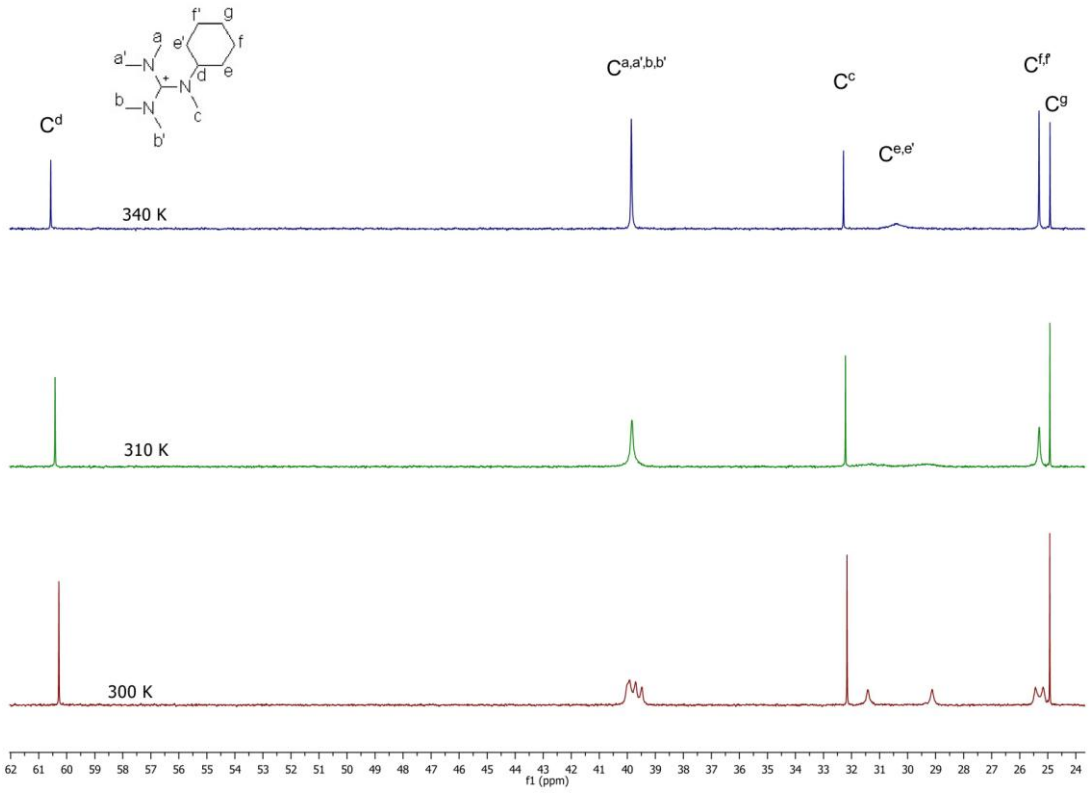


Figure 11. *^{13}C NMR spectrum of N-cyclohexyl-N,N',N',N'',N''-pentamethylguanidinium chloride (**5w**).*

Hindered rotation was observed among others also for **6w** and **6x** and for the corresponding chlorides. The rotation around the C–N partial double bonds was very slow on the NMR timescale at room temperature, what resulted in additional ^{13}C NMR signals. In order to correlate the signals, high-temperature NMR spectra were recorded for both chloride salts. At higher temperature, rotational barriers could be overcome which led to the "collapse" of signals of rotamers/diastereomers into the spectrum of an average cation structure. **Figure 11**

and **Figure 12** show temperature-dependent ^{13}C NMR spectra of *N*-cyclohexyl-*N,N',N',N'',N''*-pentamethylguanidinium chloride (**5w)** (**Figure 11**) and *N,N*-bis(2-ethylhexyl)-*N',N',N'',N''*-tetramethylguanidinium chloride (**5x)** (**Figure 12**).

Noteworthy, in the ^{13}C NMR spectrum of **5x** at 340 K (**Figure 12**) only the beginning of the coalescence is detected, but not yet the fast exchange resulting in the formation of a spectrum with averaged chemical shifts.

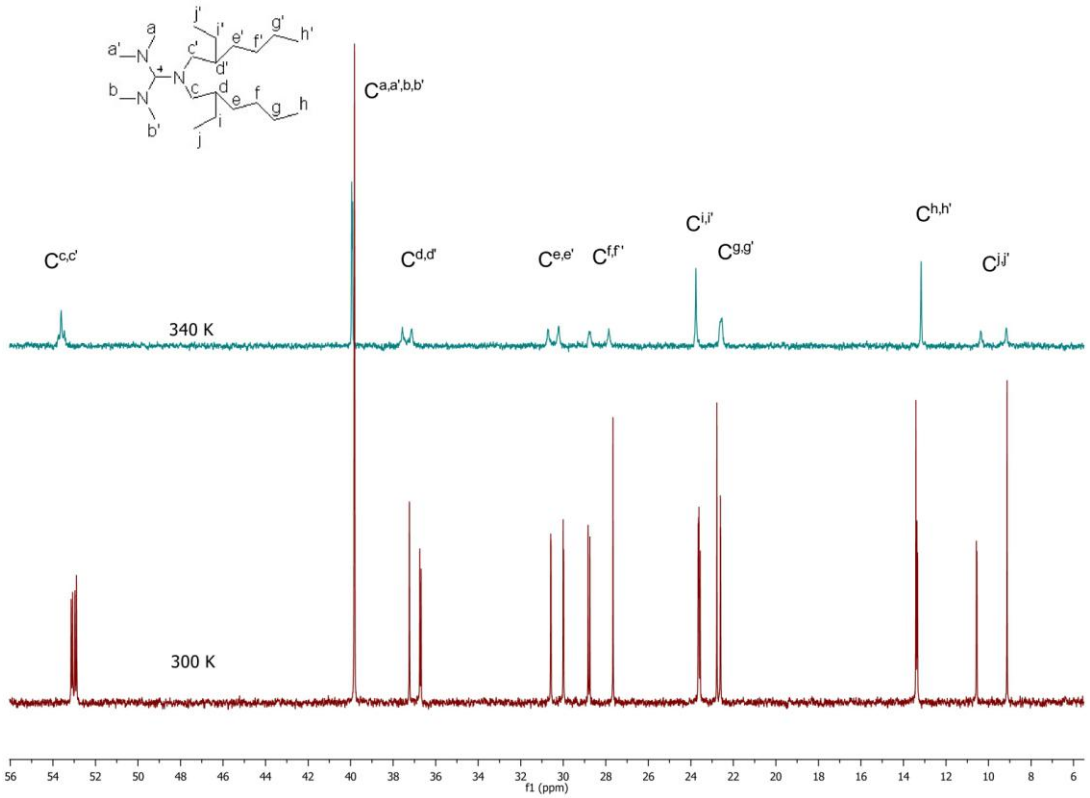


Figure 12. *^{13}C NMR spectrum of N,N-bis(2-ethylhexyl)-N',N',N'',N''-tetramethylguanidinium chloride (**5x**).*

High temperature NMR spectra of **5w** proved the restricted rotation in the cation and made the correlation of the signals easier. Overlapping ^{1}H NMR signals could be then assigned with the help of 2D $^{1}H,^{13}C$-HSQC experiments. For the proper assigning of the ^{13}C signals of **5x,** $^{1}H,^{13}C$-HSQC as well as HMBC experiments were necessary. In an HMBC spectrum only two couplings of the least shielded protons of CH_3 group (H^{j} or $H^{j'}$) are observed, namely with $C^{i,i'}$ (at $\delta \approx 23.5$ ppm) and $C^{d,d'}$ (at $\delta \approx 37$ ppm). Similar behaviour of an isooctyl substituent was also noticed by *B. Oelkers* and *J. Sundermeyer*.[38]

4.3 Crystal structure of *N*-cyclohexyl-*N,N',N',N'',N''*-pentamethylguanidinium chloride

Guanidinium chlorides, as well as other ILs containing halide anions, are known to be hygroscopic. This may be a reason why not that many crystal structures of hexaalkylguanidinium halides were determined. Usually chloride is exchanged to more water and air stable anions, for example tetraphenylborate, which are easier to handle. Nevertheless, along with diverse penta- and persubstituted guanidinium tetraphenylborates,[149–151] hexafluorophosphates,[152] some crystal structures of guanidinium chlorides[38,150–153] and bromides[150,154] have been published. In this work the X-ray structure of *N*-cyclohexyl-*N,N',N',N'',N''*-pentamethylguanidinium chloride (**5w)** is presented (**Figure 13**).

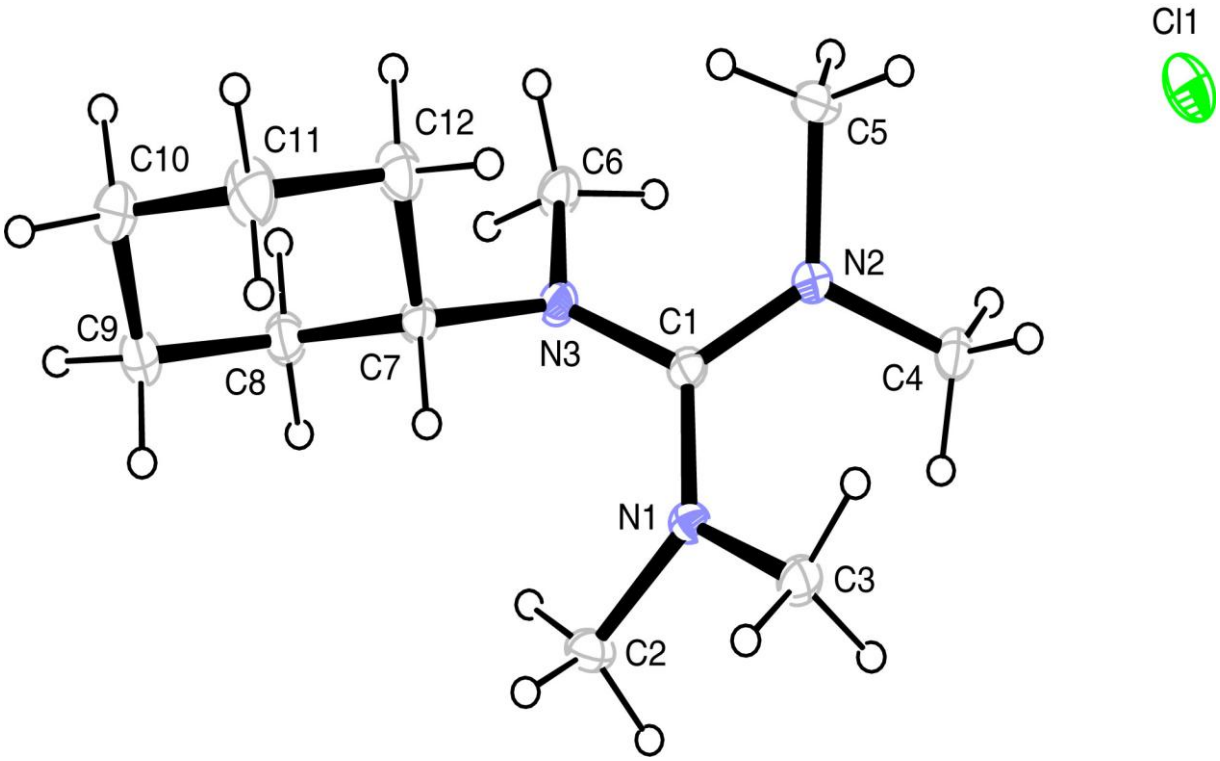


Figure 13. *Structure of N-cyclohexyl-N,N',N',N'',N''-pentamethylguanidinium chloride (**5w**) in the solid state.*

Suitable single crystals were obtained by crystallisation from ethyl acetate–DMF, and the crystals were washed with diethylether. The crystals were kept under inert atmosphere or under silicon oil.

Table 3. *Some selected bond lengths [Å] and angles [°].*

N(1)-C(1)	1.338 (16)	N(2)-C(1)-N(1)	119.95 (11)
N(2)-C(1)	1.334 (17)	N(2)-C(1)-N(3)	120.31 (11)
N(3)-C(1)	1.358 (16)	N(1)-C(1)-N(3)	119.74 (11)

As expected, the obtained data confirm the good charge delocalisation in the guanidinium cation. The central carbon atom (C1) has a trigonal-planar coordination (sum of NCN bond angles = 360.0°) (**Table 3**). The C–N bond lengths are in the typical range of C–N partial double bonds. Similar to hexamethylguanidinium salts, such as *N,N,N',N',N'',N''*-hexamethylguanidinium chloride ($[N_{11}N_{11}N_{11}Gu]Cl$),[38] the guanidinium cation exhibits a three-blade propeller-shaped geometry, but the torsion angle at the cyclohexyl-substituted C1–N3 bond is significantly larger than at the dimethyl-substituted C1–N1 and C1–N2 bonds (45.1 vs. 32.4 and 33.2 ^{o}). The less symmetrical and sterically more demanding nature of the cation obviously leads to a less close packing than for $[N_{11}N_{11}N_{11}Gu]Cl$, which is considered as a decisive factor for the drastically lowered melting point of **5w** compared to $[N_{11}N_{11}N_{11}Gu]Cl$.

Full crystallographic data is given in **Appendix 1**.

4.4 Selected physical properties of the synthesised guanidinium-based ILs

Perhaps one of the most important characteristics of an ionic liquid is its melting point. By definition IL should melt below 100 °C. This work was concentrated mostly on room-temperature ionic liquids, so in the case of high melting guanidinium chlorides the anion exchange was carried out to obtain in most cases room-temperature ionic liquids (RTILs). Decomposition temperatures (temperature of the highest decomposition gradient at the

heating rate of 10 K/min), melting points and glass transition temperatures are summarised in **Table 3**. The common rule was confirmed, that the melting point is raised by a higher molecular weight and a more symmetrical cation. On the examples of **3g, 3h, 3i** and **5f, 5g, 5h**, respectively, one can notice that with the extension of the chain length the melting point goes at first down, but then again up. This is attributed to the tendency of long alkyl chains to assume a close parallel orientation. Concerning the influence of the anion, halides possess the highest melting point, followed by tetrafluoroborates, hexafluorophospates and triflates; dicyanamides and bistriflimides have the lowest melting point.

Frequently encountered properties of ionic liquids, namely good thermal stability along with low vapour pressure and inflammability, recommend them for many fields of application. Among all synthesised ILs chlorides and dicyanamides are the least stable ones. ILs with other anions reached decomposition temperatures of up to 450 °C and higher. Such good thermal stability of guanidinium-based ionic liquids is due to an effective dissipation of the positive charge in the cation. Moreover, if another cycle is introduced in this cation (for example, piperidine, morpholine) the salt becomes slightly more thermally stable (**Table 4**). This can be also explained with the better delocalisation of the positive charge by the participation of the neighbouring ring. Another observation was made for the salts containing a methoxyethyl substituent. Some of them were found to be less stable than alkyl-substituted ones. The same behaviour was also determined for ILs with other cations and also for the guanidinium cation.[128] *H. Zhao et al.* suggest that this is due to the weakened cation–anion electrostatic interaction enabling the anions to act as nucleophiles.[155]

Another important physical characteristic of an ionic liquid is its viscosity. Unfortunately, it was impossible to get reliable data for the new guanidinium ILs because of the absence of the proper equipment. But it is obvious that ILs containing an ether function are distinctly less viscous. *J.-M. Lee et al.* ascribed the alkoxy chain effect on decreasing viscosity to the increased free volume, which results from the high conformational flexibility of the ether moieties and provides more available holes for the convenience of mass transport and low viscosity.[156]

Table 4. *Thermal properties of synthesised guanidinium-based ionic liquids.*[a,b]

	R^1	R^2	R^3	R^4	R^5	R^6	T_{dec}	T_m/T_g
3d	Me	Me	Me	Me	$MeO(CH_2)_2$	$MeO(CH_2)_2$	408	67/-
3e	Me	Me	Me	Me	Me	Bu	453	59/-93
3f	Me	Me	Me	Me	Et	Et	462	195/-
3g	Me	Me	Me	Me	Pr	Pr	455	162/-92
3h	Me	Me	Me	Me	Bu	Bu	456	-/-73
3i	Me	Me	Me	Me	Hex	Hex	438	47/-
5d	Me	Me	Me	Me	$MeO(CH_2)_2$	$MeO(CH_2)_2$	305	83/-
5e	Me	Me	Me	Me	Me	Me	329	291/-
5f	Me	Me	Me	Me	Me	Bu	310	91/-46
5g	Me	Me	Me	Me	Bu	Bu	302	-/-59
5h	Me	Me	Me	Me	Hex	Hex	299	103/-
5l	Me	Me	Me	Me	$-(CH_2)_5-$		330	158/-47
5m	Me	Me	$-(CH_2)_5-$		$-(CH_2)_5-$		322	205/-
5n	$-(CH_2)_5-$		$-(CH_2)_5-$		$-(CH_2)_5-$		332	202/-[c]
5o	Me	Me	Me	Me	$-(CH_2)_4-$		332	152/-63
5p	Me	Me	Me	Me	$-(CH_2)_2O(CH_2)_2-$		326	187/-47
5q	Me	Me	Et	Et	$-(CH_2)_5-$		315	126/-55
5r	Me	Me	Pr	Pr	$-(CH_2)_5-$		311	94/-
5s	Me	Me	Hex	Hex	$-(CH_2)_5-$		302	-/-52
5t	Me	Me	Me	cHex	$-(CH_2)_5-$		307	175/-
5u	Me	Me	Me	Bu	$-(CH_2)_5-$			solid/-48
5v	Me	Me	$MeO(CH_2)_2$	$MeO(CH_2)_2$	$-(CH_2)_5-$		292	92/-59
5w	Me	Me	Me	Me	Me	cHex	305	142/-41
5x	Me	Me	Me	Me	2-EtHex	2-EtHex	292	160/-
6d	Me	Me	Me	Me	$MeO(CH_2)_2$	$MeO(CH_2)_2$	445	7/-57
6e	Me	Me	Me	Me	Me	Me	467	88/-
6f	Me	Me	Me	Me	Me	Bu	465	-/-85
6g	Me	Me	Me	Me	Bu	Bu	464	-/-80
6h	Me	Me	Me	Me	Hex	Hex	460	-/-82
6i	Me	Me	Me	Bu	Me	Bu	469	63/-71[d]
6k	Et	Et	Bu	Bu	Bu	Bu	457	68/-
6l	Me	Me	Me	Me	$-(CH_2)_5-$		470	3/-75
6m	Me	Me	$-(CH_2)_5-$		$-(CH_2)_5-$		461	-/-62

6n	-$(CH_2)_5$-		-$(CH_2)_5$-		-$(CH_2)_5$-		462	63/-69
6o	Me	Me	Me	Me	-$(CH_2)_4$-		455	9/-
6p	Me	Me	Me	Me	-$(CH_2)_2O(CH_2)_2$-		473	47/-61[e,f]
6q	Me	Me	Et	Et	-$(CH_2)_5$-		470	-/-76
6r	Me	Me	Pr	Pr	-$(CH_2)_5$-		475	-/-73
6s	Me	Me	Hex	Hex	-$(CH_2)_5$-		475	-/-72
6t	Me	Me	Me	*c*Hex	-$(CH_2)_5$-		453	-/-52
6u	Me	Me	Me	Bu	-$(CH_2)_5$-		473	-/-74
6v	Me	Me	MeO$(CH_2)_2$	MeO$(CH_2)_2$	-$(CH_2)_5$-		447	-/-79
6w	Me	Me	Me	Me	Me	*c*Hex	431	-/-67
6x	Me	Me	Me	Me	2-EtHex	2-EtHex	448	-/-75
7a	Et	Et	Bu	Bu	Hex	Hex	462	-/71
7b	Me	Me	Me	Me	-$(CH_2)_5$-		468	107/-
7c	Me	Me	Me	Me	Hex	Hex	459	33/-60[e]
7d	Me	Me	Hex	Hex	-$(CH_2)_5$-		472	-/-59
8a	Me	Me	Et	Et	Bu	Bu	371	-/-60
8b	Et	Et	Bu	Bu	Hex	Hex	373	-/-57
9a	Me	Me	Hex	Hex	-$(CH_2)_5$-		467	-/-54
10a	Me	Me	Me	Me	Me	*c*Hex	409	233/-107

a) **3** – Trifluoromethanesulfonates; **5** – chlorides; **6** – bis(trifluoromethylsulfonyl)imides; **7** – tetrafluoroborates; **8** – dicyanamides; **9** – hexafluorophospates; **10** – tetraphenylborates.

b) Compounds with underlined numbers were newly prepared in this work.

c) The quantity of the salt was not enough for DSC measurements.

d) T_g is seen only during second heating.

e) On the DSC curve some peaks were detected, which can be attributed to the melting point, which is lower as measured with a melting point apparatus. It can be explained with water content in the probe or hydrate formation. T_g refers in this case to the hydrate.

f) T_g is seen only during first heating.

4.5 Solubility of metal alcoholates in ionic liquids

To obtain a full picture of alcoholate solubility, RTILs with different cations and anions were taken, which are presented in **Figure 14**. As anions triflate, bistriflimide and dicyanamide were chosen; as cations those with a guanidinium core were mostly investigated. While

bistriflimides showed the most promising results in terms of solubility, imidazolium and tetraalkylammonium bis(triflyl)imides were additionally synthesised to see how the nature of the cation influences the solubility of alcoholates in ILs.

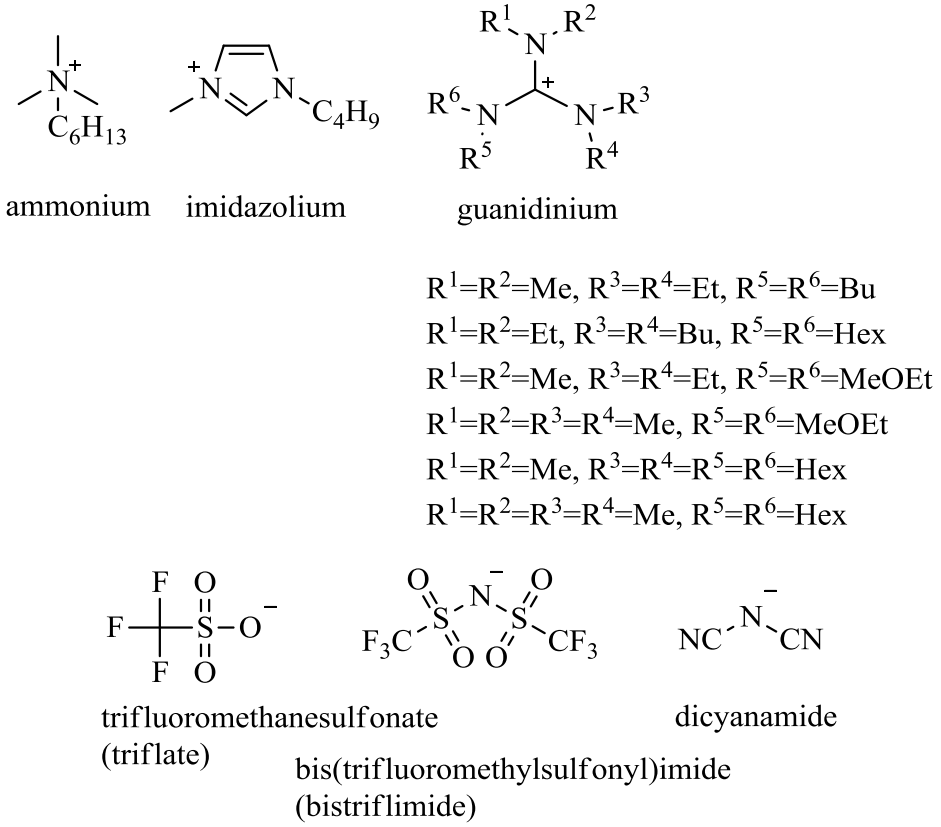


Figure 14. *Structures of cations and anions applied in solubility studies.*

Preliminary work on the polarity of guanidinium triflates and triflamides was carried out. Solvent polarity, i. e., the overall solvation capability for solutes, is an important criterion for choosing the appropriate solvent for a particular chemical reaction and in our case for the preparation of a stable metal alcoholate solution. The results of polarity studies using Reichardt's dye lead to the conclusion that the polarity of hexaalkylguanidinium-based ionic liquids is exceptionally sensitive to the nature of the anionic component in these salts.[157]

The purpose of solubility experiments was to examine the solubility of metal alkoxides in the selected ILs, to recognize regularities in solubility and to choose the most stable solutions for further applications. As the metal alcoholates are extremely water sensitive, the ILs were thoroughly dried before solution experiments. The alkoxides used were freshly distilled.

First experiments have shown that the solid aluminium isopropoxide is generally less soluble than liquid titanium isopropoxide (**Table 5**). With the aim to obtain a solution of aluminium alcoholate in IL, aluminium *sec*-butoxide, a liquid aluminium alcoholate, was also tested. But the majority of aluminium alkoxide mixtures both in triflates and bistriflimides were heterogeneous (two oily phases) and crystallised within several days. Treatment with ultrasound didn't affect the solubility properties. Dynamic light scattering (DLS) measurements, which could have helped us to understand the nature of these dispersions, appeared not to be a suitable tool. The probable reason could be a high viscosity of the guanidinium-based IL. The data obtained from optical microscopy did not provide us with reliable information because the particles seen in the microscope were supposed to be aluminium oxide, which could have precipitated after the contact with air moisture. To conclude, aluminium isopropoxide is almost insoluble at room temperature in all tested ILs, but in guanidinium IL it can be dissolved at 0.1-0.5 mol/L concentrations at 120-130 °C.

Titanium isopropoxide showed good solubility (up to 1 M, **Table 5**) in hexaalkylguanidinium bistriflimides. For example, the 0.84 M solution in *N,N*-dibutyl-*N',N'*-diethyl-*N'',N''*-dihexylguanidinium bis(trifluoromethylsulfonyl)imide (**6b**) remained stable in a closed flask for more than six months. As titanium isopropoxide was badly soluble in triflates, more bistriflamides were synthesised and used in these experiments. Although the ether group in the side chain of guanidinium cations **6c** and **6d** (**Scheme 13**) was expected to increase the solubility of alkoxides by complexation, titanium isopropoxide could only be dissolved in these ILs by heating. Hexaalkylguanidinium dicyanamides also form transparent solutions with titanium tetraisopropoxide (approx. 0.4 mol/L), which are also stable for several months. To sum up, titanium isopropoxide was better soluble in guanidinium bistriflimides with longer alkyl chains in the cation. This can be explained with better wan der Waals interactions between the substituents of the cation and the alcoholate.

To analyse the influence of the cation's core on the dissolution properties, 1-butyl-3-methylimidazolium and hexyltrimethylammonium bistriflamides were also tested. Their mixtures with metal alcoholates remained turbid at room temperature, also at low alcoholate content (0.04-0.05 mol/L for $Al(O\textit{i}Pr)_3$ and 0.20-0.39 mol/L for $Ti(O\textit{i}Pr)_4$, **Table 5**), and cleared only by heating.

For further investigations a system of hexaalkylguanidinium bistriflimides and titanium tetraisopropoxide was selected as the most concentrated and stable one. As ILs *N,N*-dibutyl-*N',N'*-diethyl-*N'',N''*-dihexylguanidinium bis(trifluoromethylsulfonyl)imide (**6b**) or more easily obtainable *N,N*-dihexyl-*N',N',N'',N''*-tetramethylguanidinium bis(trifluoromethyl-sulfonyl)imide (**6h**) were chosen.

Table 5. *Concentrations[a] (mol/L) of the prepared solutions of metal alcoholates in ILs.*

	IL	Al(O*sec*Bu)$_3$	Al(O*i*Pr)$_3$	Ti(O*i*Pr)$_4$
3a	[$N_{11}N_{22}N_{44}$Gu]OTf		0.01 (turbid)	0.17 (turbid)
3c	[$N_{11}N_{22}N_{2O12O1}$Gu]OTf	0.12 (turbid)	0.16 (turbid)	0.05 (turbid)
6a	[$N_{11}N_{22}N_{44}$Gu]NTf_2		0.06 (turbid)	**0.11 (clear)**
				0.40 (turbid)
6b	[$N_{22}N_{44}N_{66}$Gu]NTf_2	0.37 (turbid)	0.44 (turbid)	**0.84 (clear)**
				3.00 (turbid)
6c	[$N_{11}N_{22}N_{2O12O1}$Gu]NTf_2		0.01 (turbid)	0.31(turbid)
6d	[$N_{11}N_{11}N_{2O12O1}$Gu]NTf_2	0.24 (turbid)	0.13 (turbid)	0.17 (turbid)
6h	[$N_{11}N_{11}N_{66}$Gu]NTf_2			**0.67 (clear)**
				1.00 (turbid)
6j	[$N_{11}N_{66}N_{66}$Gu]NTf_2	0.14 (turbid)	0.15 (turbid)	**0.53(clear)**
8b	[$N_{22}N_{44}N_{66}$Gu]$N(CN)_2$		0.32 (turbid)	**0.44 (clear)**
	[BMIm]NTf_2		0.06 (turbid)	0.20 (turbid)
	[Me_3HexN]NTf_2		0.04 (turbid)	0.39(turbid)

a) Mass proportion of the components in the suspension or immiscible liquids.

For electrochemical studies a number of Ti(O*i*Pr)$_4$ solutions in guanidinium-based ILs were prepared in a glove-box (**Table 6**). Homogenous as well as two-phase systems were obtained and investigated. Two-phase systems represented a saturated solution of titanium isopropoxide in IL (no interaction between IL ions and Ti(O*i*Pr)$_4$ was observed in the NMR spectra) as the lower layer and pure Ti(O*i*Pr)$_4$ as the upper layer.

Table 6. *Concentrations[a] (mol/L) of the prepared solutions of $Ti(OiPr)_4$ in ILs.*

	IL	Concentration[a]	Remark
6h	$[N_{11}N_{11}N_{66}Gu]NTf_2$	0.67	clear
		1.00-1.34	turbid
		2.00	two phases
6l	$[N_{11}N_{11}N_{pip}Gu]NTf_2$	0.10	clear
		0.17-0.84	turbid
		1.51	two phases
7c	$[N_{11}N_{11}N_{66}Gu]BF_4$	0.10-1.17	turbid
		1.84	two phases
	$[BMIm]NTf_2$	0.16	clear
		0.33	two phases

a) Mass proportion of the components in the immiscible liquids.

Because of the low solubility of aluminium alcoholates in ionic liquids, no suitable solutions could be obtained for the electrochemical studies.

4.6 Condensation reactions in guanidinium-based ionic liquids

A large number of publications have appeared recently describing that ILs can be applied with success as solvents for organic reactions. The following advantages of using ILs in organic synthesis and catalysis can be mentioned: opportunity to tune the reaction conditions (wide temperature range, designable solvent properties), immobilisation of the catalyst and reusability of the IL/catalyst system, easy work-up procedure, avoidance of some disadvantages associated with organic solvents (e.g. volatility, flammability, disposal of chlorinated solvents etc.). It has been also highlighted that the use of ionic liquids is not merely an environmentally friendly alternative, but can have considerable additional consequences on reactivity in the form of significant variations in reaction rates and selectivities.[1,158]

All named aspects also extend to hexaalkylguanidinium-based ILs, and this type of ILs has already found some applications in organic synthesis and catalysis as reaction media. Among them, guanidinium-based phosphotungstates were used for epoxidation of olefins,[159] guanidinium acetates as a medium for the palladium-catalyzed Heck reaction,[72] Lewis acidic guanidinium ILs for aminolysis of epoxides.[160] Hexaalkylguanidinium ILs as reaction media have been reported for oxidation of benzyl alcohols,[80] nucleophilic substitution reactions,[161] CO_2 fixation,[162] Sharpless dihydroxylation[163,164] and asymmetric aldol reaction.[165,166] Intramolecular carbenoid C–H insertion of an α-methoxycarbonyl-α-diazoacetamide was successfully performed by rhodium and ruthenium catalysts in hexaalkylguanidinium triflates.[167]

4.6.1 Reaction of lactamisation

Cyclocondensation of ω-amino acids in the presence of titanium-based Lewis acids is one of the ways to obtain macrocyclic lactams.[168] *P. Helquist* and co-workers have investigated the lactamisation reaction of some amino acids (**Scheme 14**) and applied the elaborated method to the synthesis of streptogramin A family antibiotics.[168,169] Madumycin I (**Figure 15**) is a representative member of the type A streptogramin series which comprises several antibiotics having wide-ranging applications.

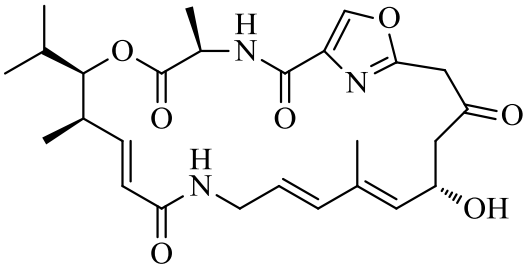
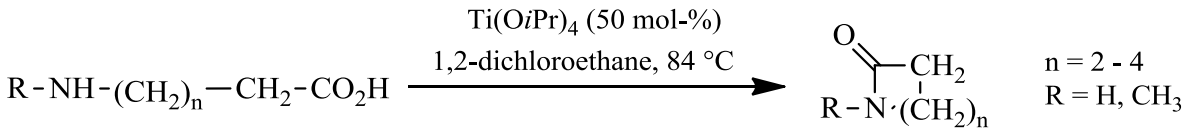


Figure 15. *Structure of madumycin I.*

We have carried out the cyclisation of some amino acids in guanidinium-based ILs in order to avoid the disadvantages of the described procedure concerned with usage of halogenated organic solvents. Our attention was attracted mostly by bistriflimide-ILs, which are among the most hydrophobic ILs. This could have a positive impact on the stability and therefore activity of the catalyst and on the easier procedure to recover and regenerate the IL.



Scheme 14. *Reaction of lactamisation.*[168]

Titanium alkoxides ([$Ti(OR)_4$ and $MeTi(OR)_3$] have been widely applied as Lewis acids, for example in aldol reactions,[170,171] in Kulinkovich cyclopropanation,[172] and in the formation of lactams. Titanium tetraisopropanolate is also a reagent for the famous Sharpless asymmetric epoxidation of allylic alcohols.[173]

First of all, screening and optimisation reactions were carried out with 4-aminobutyric acid in the transparent system $Ti(OiPr)_4/[N_{22}N_{44}N_{66}Gu]NTf_2$ (**6b)** (**Table 7**). The experiments allowed us to make the following conclusions:

- with the same amount of catalyst (50 mol-%) at the same temperature (84 °C) the reaction in IL demands the same time as in 1,2-dichloroethane (3 h);
- at higher temperatures the velocity of the reaction increases;
- the reaction proceeds also with a smaller amount of catalyst but needs prolonged time or elevated temperatures;
- the nature of guanidinium-based IL influences not significantly the time of the reaction (along with $[N_{22}N_{44}N_{66}Gu]NTf_2$ (**6b)**, $[N_{11}N_{22}N_{44}Gu]NTf_2$ (**6a)**, $[N_{11}N_{11}N_{66}Gu]NTf_2$ (**6h)** and $[N_{22}N_{44}N_{66}Gu]N(CN)_2$ (**8b)** were also tested and showed similar results; a dicyanamide-IL was not applied for the further studies because of its lower thermal stability);
- an extractive work-up procedure (with cyclohexane or diethyl ether) gave only moderate yields, with the maximum yield of 62 % (usually about 40 %), however when a cycle of reactions was carried out in the same system IL/catalyst the yield increased with the number of cycles (35 % – 65 % – 70 % – 89 % for **6a**); in many cases it was impossible to obtain selective extraction: IL and the catalyst leached into the organic solvent and a part of the product remained in the reaction mixture. The best yields (45–62 %) were achieved after extraction with dry cyclohexane from guanidinium bistriflimides, followed by distillation of the solvent and further extraction of the product with water from the residue;
- excellent yields of γ-butyrolactam (pure by elemental analysis) were obtained after bulb-to-bulb distillation.

Table 7. *Optimisation of the lactamisation reaction of γ-aminobutyric acid (monitored by ^{1}H NMR spectroscopy) in **6b**.*

	Temperature, °C			
Ti(O*i*Pr)$_4$, mol-%	40	80	100	120
50	> 8 h	3 h	2 h	
20			4 h	2 h
10		> 10 h		3h
5				5 h
0				—

The results obtained from cyclisation of a number of amino acids under optimised IL conditions (10 mol-% catalyst, 120 °C, distillative work-up) and under "traditional" conditions (halogenated organic solvent) are compared in **Table 8**. For a better collation, the experiments were also carried out with the same quantity of catalyst in an organic solvent (1,2-dichloroethane).

Table 8. *Reaction conditions and yields of the lactamisation reaction (see **Scheme 14**).*[a,b]

n, R	Ti(O*i*Pr)$_4$ (50 mol-%), DCE, 84 °C [168]	Ti(O*i*Pr)$_4$ (10 mol-%), DCE, 84 °C	Ti(O*i*Pr)$_4$ (10 mol-%), IL, 120 °C	Ti(OSiMe$_3$)$_4$ (10 mol-%), IL, 120 °C	Al(O*i*Pr)$_3$ (10 mol-%), IL, 120 °C
2, H	93% (3 h)	85% (3 h)	85% (3 h)	88% (3 h)	89% (3 h)
2, Me	85% (5 h)	41% (5 h)	82% (3 h)	88% (1 h)	84% (1 h)
3, H	75% (4 h)	87% (4 h)	82% (2 h)	94% (2 h)	94% (3 h)
4, H	35% (26 h)	9% (26 h)	58% (26 h)	62% (26 h)	26% (26 h)

a) DCE = 1,2-dichloroethane. IL: [$N_{11}N_{11}N_{66}$]NTf_2 (**6h**) or [$N_{22}N_{44}N_{66}$]NTf_2 (**6b**)**.**

b) ILs **6h** and **6b** gave similar yields under the same conditions.

In most cases we succeeded in increasing the yield along with decreasing the reaction time. The system metal alcoholate/guanidinium IL was especially effective for the synthesis of the *N*-substituted lactam (the reaction duration was five times lower) and for caprolactam (during the same time the double yield was obtained).

Along with titanium isopropanolate we have tried other Lewis acids, which are less moisture sensitive. For example, titanium trimethylsilanolate has this advantage and showed to be a bit more catalytically active in comparison to isopropanolate. Titanium 2-ethylhexanolate, which is more viscous than isopropanolate and trimethylsilanolate, is somewhat less active than the others. This is why the reactions with titanium 2-ethylhexanolate were not extended. Aluminium isopropanolate did not show good solubility, but its catalytic activity is comparable to that of titanium trimethylsilanolate with only one exception (synthesis of caprolactam).

In order to accelerate the reaction we added molecular sieves 4 Å to adsorb the water produced in the condensation reaction and to prevent the hydrolysis of the catalyst. Unfortunately it had no impact on the reaction.

Another major advantage of our IL strategy is given by the fact that the IL/catalyst system could be reused in the subsequent cycles with little or no reduction in yield (**Table 9**).

Table 9. *Yields of the lactamisation reaction (see **Scheme 14**) in four subsequent cycles.*[a]

n, R	Catalyst	Yields in 4 cycles, %
2, H	$Al(O\textit{i}Pr)_3$	89 – 89 – 89 – 95
2, H	$Ti(O\textit{i}Pr)_4$	85 – 85 – 94 – 85
2, H	$Ti(OSiMe_3)_4$	88 – 91 – 89 – 85
2, H	$Ti(O(CH_2)_4CH(C_2H_5)CH_3)_4$	75 – 75 – 54 - 50
2, Me	$Ti(O\textit{i}Pr)_4$	82 – 92 – 94 – 77
2, Me	$Ti(OSiMe_3)_4$	88 – 90 – 87 – 94

3, H	$Al(OiPr)_3$	94 – 96 – 95– 95
3, H	$Ti(OiPr)_4$	82 – 79 – 74 – 72
3, H	$Ti(OSiMe_3)_4$	94 – 98 – 96 – 96

a) For reaction conditions, see **Table 8**.

Moreover, the possibility of phase separation into a product phase and catalyst/IL phase was investigated, what could facilitate the work-up procedure. For this, the concentration of the amino acid in IL was increased. Unfortunately, the formed lactam did not appear as a separate phase and the typical distillation work-up was required. Three times higher concentration of the γ-aminobutyric acid resulted in 96% yield of butyrolactam instead of 85%.

To test the scope of the developed method, the cyclodehydration of 11-aminoundecanoic acid was tried. The experiment failed, apparently due to the low solubility of the amino acid in IL (ring strain in the lactam could also be one of the reasons for the failure). Cyclisation of the optically active L-lysine was also attempted, but the reaction with 10 mol-% of $Ti(OiPr)_4$ took almost two days and yielded less than 18 % of α-amino-ε-caprolactam, not in pure form. The reaction with 100 mol-% of the same catalyst gave 27 % of impure product, so the racemisation of the product could not be studied.

Obviously, the lactamisation is catalysed only by metal alcoholates or species derived therefrom. Without catalyst no reaction takes place, also not after 5 h at 120 °C. NMR spectra of the reaction mixture before the second cycle no longer contained signals of the isopropyl substituent. The reason could be the hydrolysis of $Ti(OiPr)_4$ with possible formation of TiO_2. Nevertheless, the solid species formed (formation of a precipitate was observed several minutes after the start of the reaction) is active for the next cycles.

To gain an insight into the reaction mechanism and interaction between the metal alcoholates and bistriflimide anion (may be titanium is complexed with the IL anion?), we performed ^{1}H-, ^{13}C- and ^{19}F-NMR studies of the concentrated solutions of titanium isopropanolate with *N,N*-dihexyl-*N',N',N'',N''*-tetramethylguanidinium bis(trifluoromethylsulfonyl)imide (**6f)** in $CDCl_3$. Interestingly, no indication for complexation of titanium by the anion was found. On

the contrary, all signals correlate to the pure substances. So the IL performs the only role of inert (also thermally stable, inflammable, not volatile etc.) solvent.

So some more experiments were needed to understand the nature of the catalyst. To this end, several mixtures of ionic liquids and precipitate, which remained after the product isolation (after bulb-to-bulb distillation and extraction) were diluted in dichloromethane and filtered. The precipitate was dried and the NMR and IR spectra were collected. In this way aminobutanoic acid could be detected in the admixture with the precipitated TiO_2. This powder was washed with water to remove the acid. X-ray diffraction (XRD) measurements of the solid so obtained showed that it was only amorphous material. After calcination at 550 °C for 4 h the XRD-spectrum of pure anatase was collected (**Figure 16**).

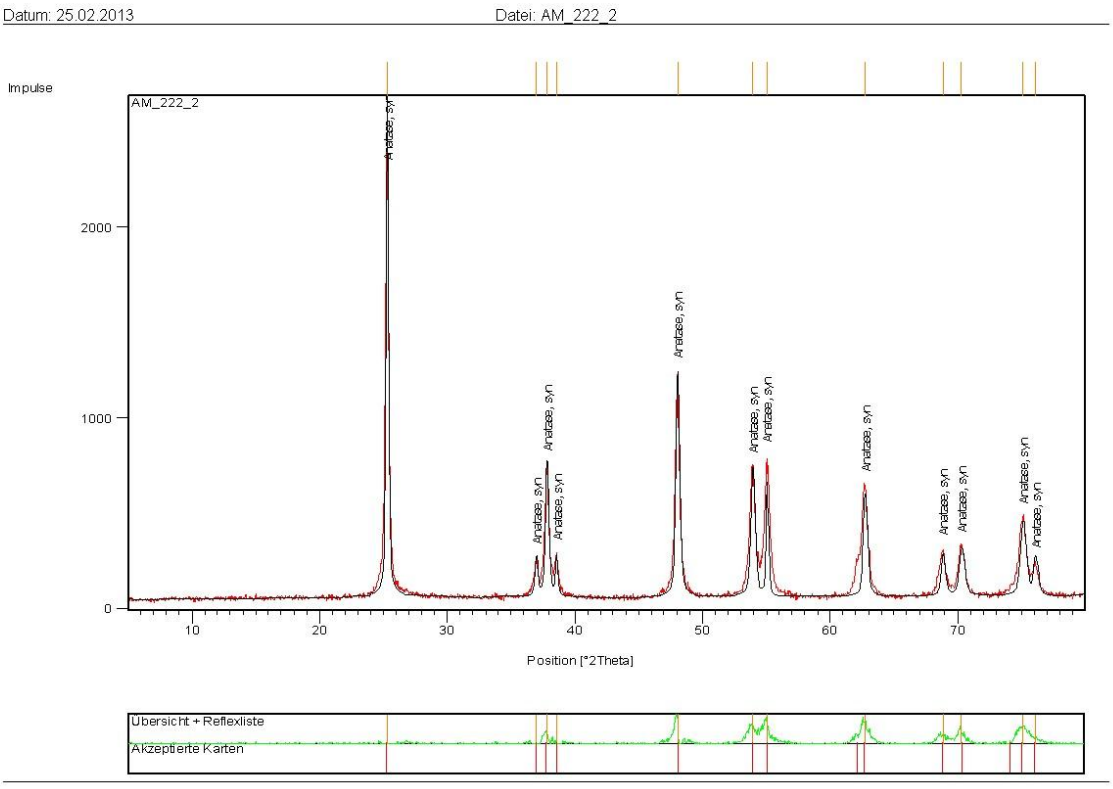


Figure 16. *XRD-spectrum of the calcinated catalytically active powder.*

Actually, it is not surprising to obtain anatase particles as a side product of the reaction. It has been reported by many authors that diverse ionic liquids are effective for the synthesis of TiO_2

anatase nanoparticles from titanium alcoholates.[174–177] Therefore, it was also interesting to get information on the size of particles obtained after the catalysis. The TEM images of the anatase (obtained after calcination) are presented in **Figure 17** (above). Most particles are nanoparticles with a size of 30-60 nm. The images below show the particles obtained after filtration from the catalyst/IL system. It is seen that they are bigger in size, the majority of them is conglomerated, and the single particles have very porous structure.

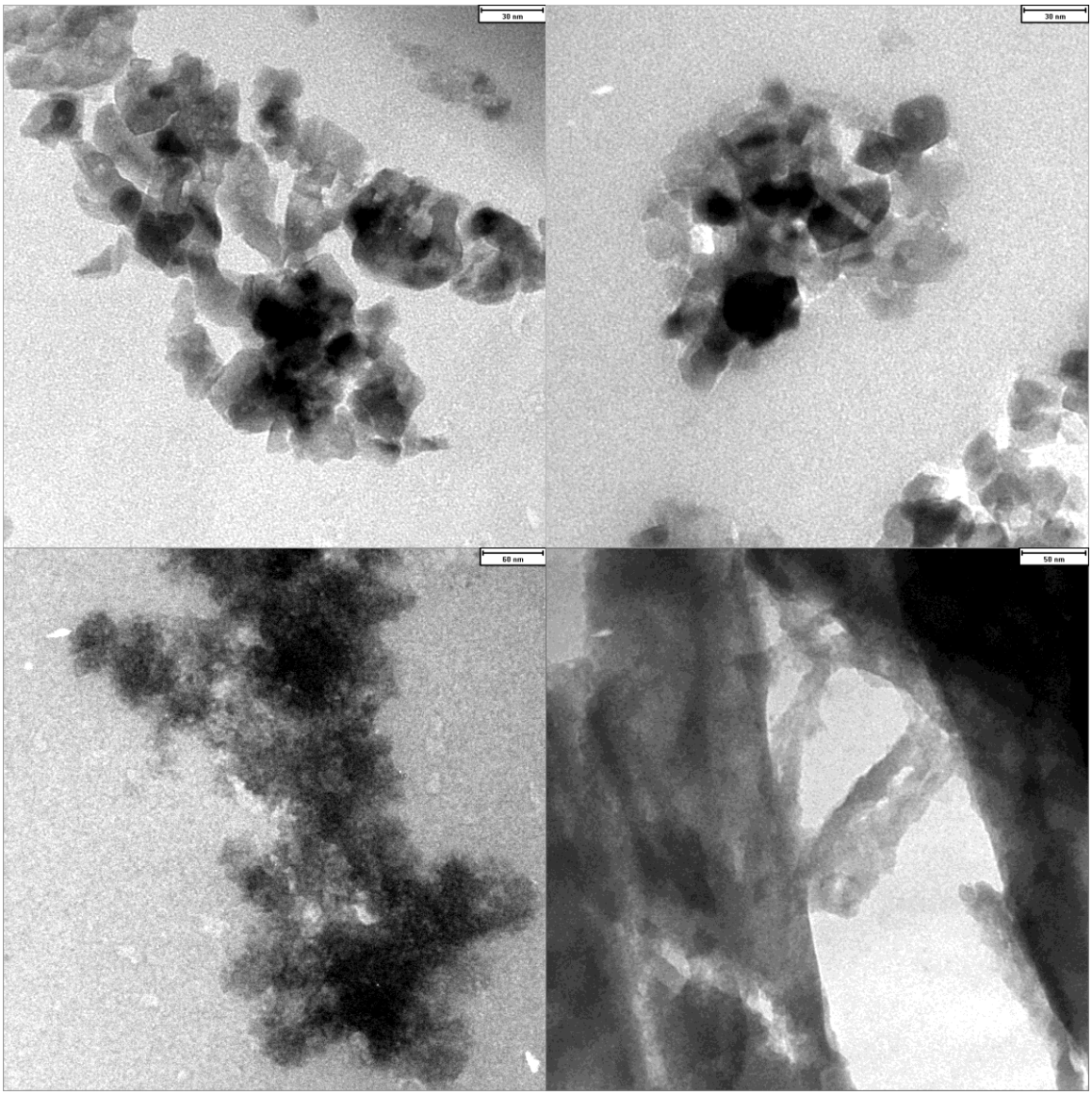


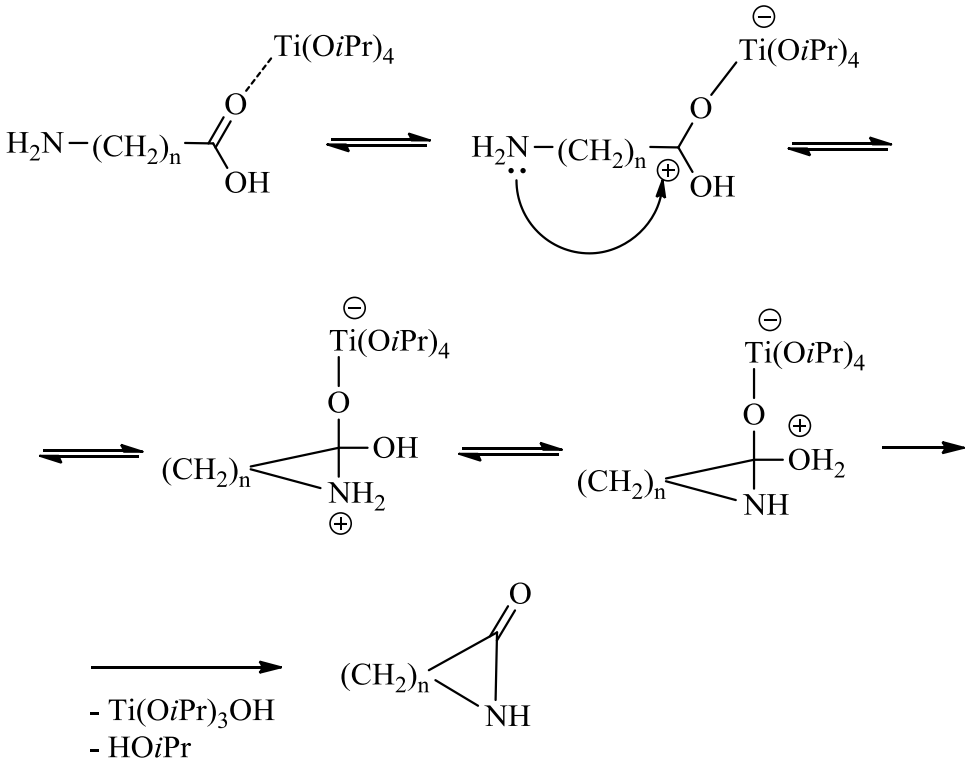
Figure 17. *TEM images of anatase particles (above; the same probe but different sites (left and right), length scale corresponds to 30 nm) and catalyst particles (below; the same probe but different sites (left and right), length scale corresponds to 60 (left) and 50 (right) nm).*

Is the titanium dioxide the active catalytic species? To answer this question the experiment with 10 mol-% anatase as a catalyst was carried out, but no reaction was observed. Interestingly, after addition of several drops of water the reaction began but very slowly. On the other side, when the powder obtained by filtration from the reaction mixture (when $Ti(O\textit{i}Pr)_4$ was used as catalyst) was applied one more time, the reaction was fast as usual. With the precipitate (TiO_2) washed with water only a slow reaction was observed. There was no reaction in the IL sample remaining after filtration.

So the possible catalyst could be a) the freshly precipitated $Ti(OH)_4$, its dimers or trimers or freshly obtained TiO_2 (further TiO_2*), b) the named compounds complexed with amino acid. For clarification, the lactamisation reaction of γ-aminobutanoic acid was carried out in the presence of a separately prepared TiO_2*-amino acid complex (from $Ti(O\textit{i}Pr)_4$, γ-aminobutanoic acid in isopropanol at reflux for 3 h with subsequent filtration of the catalyst). After 3 h the conversion of 58 % instead of expected 99 % was detected by NMR. Further experiments with freshly precipitated TiO_2* (from $Ti(O\textit{i}Pr)_4/H_2O$ in isopropanol) and *in situ* precipitated TiO_2* in IL (from $Ti(O\textit{i}Pr)_4/H_2O$ in IL) showed the same catalytic activity of the prepared powders as in the original reaction.

Concluding everything written above, it seems that the first steps of the reaction are catalysed by the Lewis acidic $Ti(O\textit{i}Pr)_4$ (**Scheme 15**). Afterwards, water is formed as the side-product. Titanium tetraisopropanolate, which is already sensitive to traces of water, is hydrolysed to $Ti(OH)_4$, what finally results in titanium dioxide. It is also known that titanium alcoholate and titanium hydroxide are prone to form oligomers.[178–180] So a number of species could act as a catalyst, but the most likely under these conditions (high temperature, vacuum distillation) is titanium dioxide, which represents nanoparticles with porous structure (**Figure 17**, below). Water is known to adsorb both associatively and dissociatively (as HO^-) on reduced Ti cations and to oxidize the surface,[181,182] thus blocking the coordinatively unsaturated sites at the TiO_2 surface. It is also possible that the amino acid adsorbs on the surface of titanium dioxide, where the reaction takes place. Moreover, TiO_2 reveals Lewis acidic properties, as well as Lewis basic properties.[183] In any case, the chemical behaviour of both Ti^{4+} (Lewis acid) and O^{2-} (Lewis base) ions depends on the surface structure.[184] It seems that in this

reaction we deal with mildly Lewis acidic titanium dioxide as catalytic species. Moreover, Lewis acid activity of TiO_2 nanoparticles has already been reported.[185,186]



Scheme 15. *Proposed mechanism of Ti(OiPr)$_4$–catalysed lactamisation.*

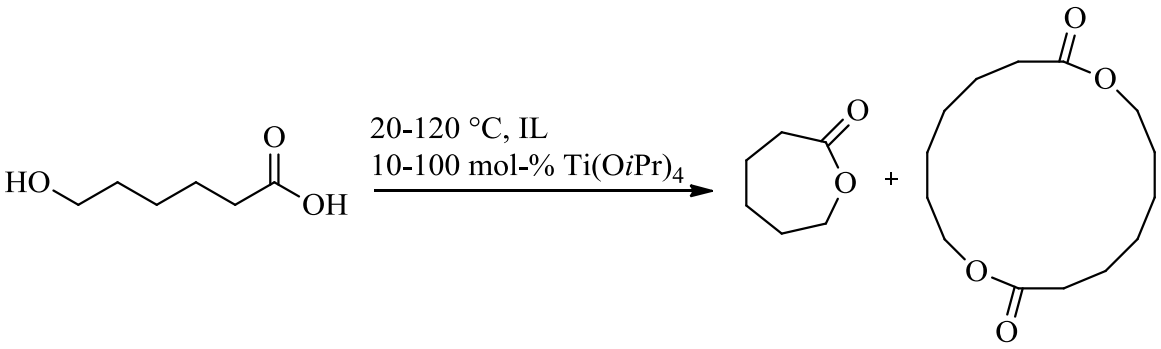
With the application of hexaalkylguanidinium bistriflimides as solvents we managed: a) to lower the amount of the catalyst significantly, b) to reduce the duration of the reaction (since the IL allows a higher reaction temperature), c) to use an easier work-up procedure (vacuum distillation of the product from the reaction mixture), d) to carry out several cycles without regeneration of IL, without extra addition of new catalyst before the next cycle, e) to improve yields in some cases and f) to avoid the use of organic solvents and some disadvantages associated with them (e.g. volatility, flammability, disposal of chlorinated solvents etc.).

The developed procedure for the lactamisation reaction in a guanidinium-IL reaction medium is convenient and efficient. Compared to usual conditions (in an organic solvent) much lower amounts of catalyst could be used and the catalyst could be reused. This aspect is very promising from the viewpoint of atom economy, as the solvent (IL) and the catalyst

immobilised in it can be used in many cycles and the only by-product formed is water. This is a significant step towards Green Chemistry synthesis.

4.6.2 Reactions of lactonisation

The procedure developed for intramolecular amidation was also applied for the intramolecular esterification. For the cyclisation of 6-hydroxycaproic acid (**Scheme 16**) and 15-hydroxypentadecanoic acid it was found that the reaction could not be completed under the chosen conditions even after several days. For example, condensation of 6-hydroxycaproic acid catalysed by 70 % of Ti(O*i*Pr)$_4$ at 120 °C gave after one day the 1:0.4 ratio of acid to lactam. Unfortunately, increasing the catalyst amount (from 10 to 100 mol-%) or the reaction temperature (room temperature → 120 °C), varying the catalyst (Ti(O*i*Pr)$_4$, Ti(OSi(Me)$_3$)$_4$, Al(O*i*Pr)$_3$), prolonging the reaction time (up to 5 days) and performing the reaction under MW conditions did not lead to the completion of the reaction and unconsumed hydroxy acid was distilled together with the product. In all cases the yields were moderate. The methylester of 6-hydroxycaproic acid, as a more active reagent, was also tried in this reaction at 40 and 120 °C but without success.



Scheme 16. *Cyclisation of 6-hydroxycaproic acid in IL **6h**.*

Two reasons for the failure of lactonisation could be mentioned. Firstly, the competitive dimer formation, which was also observed in controlling NMR spectra. Along with signals of the ε-caprolactone in ^{1}H NMR spectrum in D_2O (at δ = 4.32 ppm (m, CH_2O) and at δ = 2.67 ppm (m, $CH_2C(O)$) signals with lower chemical shifts appear (at δ = 4.08 ppm (m, CH_2O) and at δ = 2.38 ppm (m, $CH_2C(O)$), which were attributed to the dimer, shown in **Scheme 16** (other

signals of the product and by-product were overlaped by the signals of IL). This side reaction could perhaps be suppressed by carrying out the reaction with a low concentration of hydroxy acid, but in the case of ionic liquids this is not reasonable because of the high cost of the solvent. Another reason could be the relatively low Lewis acidity of the employed alcoholates in combination with lower nucleophilicity of the oxygen of the hydroxy acid compared to nitrogen of the amino acid.

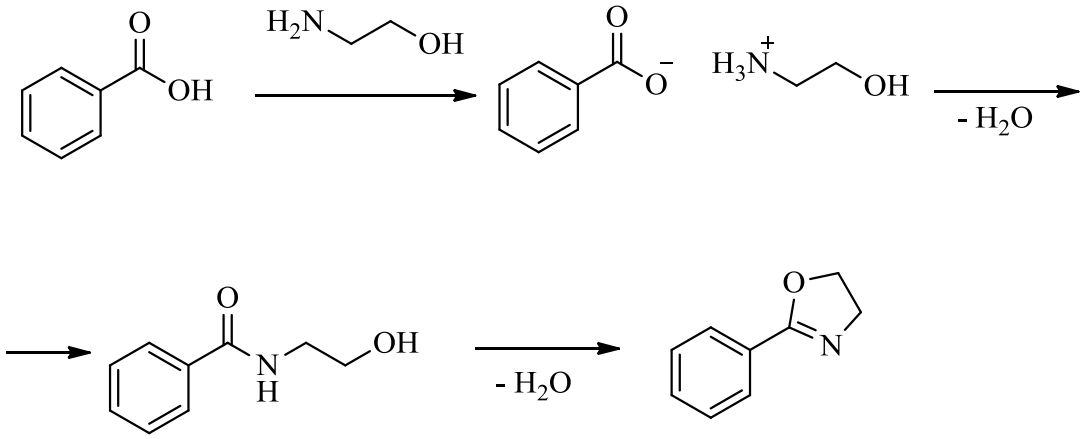
4.6.3 Synthesis of oxazolines

2-Oxazolines are an important class of heterocycles, widely present in natural products. 2-Oxazolines are structural entities in naturally occurring iron chelators, cytotoxic cyclic peptides, antiinflamantory, antimitotic and neuroprotective agents.[187,188] They are intermediates in drug syntheses.[189,190] Oxazolines are well-known as protected form of carboxylic acids as well as amino alcohols and are also widely utilised as chiral auxiliaries. Chiral bis(oxazoline) ligands have broad application in asymmetric hydrosilylation, carbenoid cyclopropantion reaction, Friedel-Crafts reaction, Diels-Alder reaction, Aldol addition, Michael reaction, Henry reaction, allylic oxidation, 1,3-dipolar cycloaddition, and so on.[191]

Methods of synthesis of 2-oxazolines have been extensively explored. Most of them suffer from using such harsh reagents as thionyl chloride and the necessity of high temperature conditions (up to 230 °C).[192,193] Several milder approaches have also been developed, including the preferable one-pot procedure as well. Perhaps one of the most facile one-pot protocols is the one applying a tetranuclear zinc cluster in refluxing toluene,[194] so that a number of oxazolines could be obtained in good and excellent yields after chromatographic work-up. Another approach consists in the use of a [BMIm]Cl/$InCl_3$ system, which affords 60-80 % yields under mild conditions (60 °C, 3 h).[195] Nevertheless, to obtain the pure products organic solvents were needed and nothing was reported about the possibility of recycling the catalyst/IL system.

In order to develop an efficient (organic) solvent-free procedure with recyclable catalyst system, we explored $Ti(O\mathit{i}Pr)_4$/$[N_{11}N_{11}N_{66}Gu]NTf_2$ (**6h**) as a milieu for the direct dehydrating condensation. This system has already been identified as an effective catalyst for cyclic

amidation (lactamisation, see chapter 4.6.1) and direct amidation (*S. Eichel*[196]), thus it was expected to catalyse at least the first step in the oxazoline synthesis, namely amide formation (**Scheme 17**). The application of thermally more stable guanidinium bistriflimide IL (instead of imidazolium chloride) would provide the possibility to work at higher temperatures (by distillation of the product or reaction temperature).



Scheme 17. *The stepwise formation of 2-phenyl-4,5-dihydro-1,3-oxazole.*

For the initial studies the reactions of benzoic acid with either monoethanolamine (MEA) or 2-amino-2-methyl-1-propanol were taken. In refluxing chlorobenzene the reactions needed 67 h (MEA) and 120 h (2-amino-2-methyl-1-propanol) to give after chromatographic work-up the oxazolines in yields of only 40 and 50 %, respectively (**Table 10**). The first experiments (benzoic acid with monoethanolamine) in IL showed that at 120 °C solely benzamide is formed. However, the oxazolines could be obtained after bulb-to-bulb distillation at 200 °C instead of 120 °C during several hours (the yield in brackets refers to the yield obtained after distillation at 200 °C). This means that the cyclic product was built during distillation. In another experiment the reaction was conducted at 200 °C; formation of the oxazoline was observed in the NMR spectra, but only poor yields could be isolated. Moreover, longer duration at 200 °C prompted the formation of by-products. To lower the time needed for the reaction to proceed, the reaction mixture was at first kept at 120 °C for the amide formation, and then the temperature was increased to 200 °C. Unfortunately, all deviations of this procedure led only to poor yields. A higher amount of catalyst ($Ti(O\textit{i}Pr)_4$) was found to be beneficial for the acceleration of the reaction, however higher temperatures still were needed for the oxazoline formation. As a disadvantage, the titanium tetraisopropoxide was distilled

off together with the product; this means that the catalyst was not immobilised in the IL and therefore could not be used once more. In addition, the product had to be separated from the catalyst, and so the application of organic solvents was unavoidable.

This reaction suffers from poor yields and necessity of high temperatures, likely because the Lewis acid used is not strong enough to activate the carboxylic acid. To improve the reaction conditions, an attempt with MW irradiation was made, but also after several hours only benzamide was produced. Aluminium isopropanolate and titanium tetrakis(trimethylsilanolate) were found to be less effective than titanium tetraisopropoxide. Some Ti-complexes were tested in the reaction of benzoic acid and MEA, namely *in situ* formed Ti isopropoxide/acetylacetonate complex and Ti isopropanolate/HOTf combination (1:2). But it had no influence on the reaction time and promoted the formation of by-products. The complex isolated from Ti(O*i*Pr)$_4$/HOTf (1:2) was also not effective.

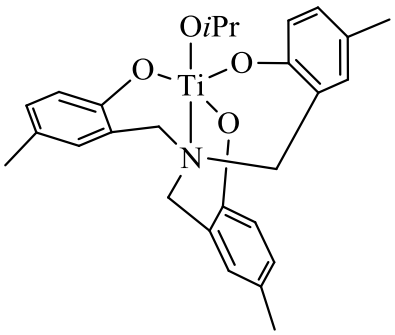
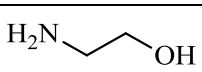
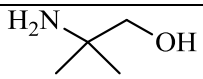


Figure 18. *Titanium(IV) complex of trianionic amine triphenolate ligand [modified according to lit. [*197*]].*

In the reaction of benzoic acid with isobutanolamine, a titanium(IV) complex of trianionic amine triphenolate ligand was explored. This complex (**Figure 18**), derived from a bulkier tripodal ligand, shows a better resistance to hydrolysis.[197] Therefore, it could be more stable and active in the dehydration/condensation reaction. The ligand was synthesised from 2,4-dimethylphenol and hexamethylenetetramine (urotropine) according to lit. [198]. The complex was formed in a dichloromethane/IL solution, the organic solvent was distilled off, and the remaining orange solution was used as a catalytic milieu (20 % of Ti-complex compared to reagents) for the condensation. After 7 h at 170 °C (at this temperature the reaction mixture was clear, at higher temperatures the sublimation of ammonium salt was

observed, see **Scheme 17**) only a 30 % yield of 4,4-dimethyl-2-phenyl-4,5-dihydrooxazole could be achieved (some traces of the ligand were noticed in the NMR spectrum as well). So the application of various Ti complexes had no positive impact.

Table 10. *Synthesis of 2-oxazolines from carboxylic acids (or dimethyl malonate) and amino alcohols.*

Amine										
Acid	Solvent[a]	Cat.[b], %	Temp., °C	Durat., h	Yield[c], %	Solvent[a]	Cat.[b], %	Temp., °C	Durat., h	Yield, %
PhCOOH	PhCl	50	140	67	40	PhCl	50	140	120	51
	IL	50	120	8	0(57)	IL, 4Å MS	50	a)120 b)200	3 1,5	50
	IL	50	120	13	0(41)	IL, 4Å MS	50	200	5,5	50
	IL	50	200	20	23[d]	IL, 4Å MS	50	a)120 b)200	1 8,5	67
	IL, 4Å MS	50	a)120 b)200	3 1,5	18(31[d])	IL, 4Å MS	-	200	7	49
	IL, 4 Å MS	50	a)120 b)200	3 3	16(23[d])	IL	-	200	7	18
	IL, 4 Å MS	50	200	10	(16[d])					
	IL, 4 Å MS	50	a)120 b)200	1 6	(29[d])					
	IL, 4 Å MS	50	a)120 b)200	4 12	(30[d])					
	IL, 4 Å MS	-	a)120 b)200	1 15	0					
	IL	250	a)120 b)200	2 7	52					

$PhCH_2COOH$	IL, 4 Å MS	50	200	6	11(72)	IL, 4 Å MS	50	a)120 b)200	1 7	63
$H_3COOCCH_2COOCH_3$						IL, 4 Å MS	50	a)120 b)200	4 7	34

a) IL = $[N_{11}N_{11}N_{66}Gu]NTf_2$ (**6h**).

b) Catalyst = $Ti(OiPr)_4$.

c) In parentheses: the yield refers to the yield obtained after distillation at 200 °C.

d) Obtained not in pure form, chromatographic purification or distillation was needed.

As the reaction needed 200 °C in all cases, the question arose, whether the reaction was catalysed or was simply promoted by the temperature and/or molecular sieves. In the case with monoethanolamine no reaction took place without the catalyst; in the case of isobutanolamine, unexpectedly, 49 % yield was obtained with molecular sieves and 18 % without molecular sieves and catalyst. The first conclusion is that the catalyst plays only a limited role in this reaction, the second – the nucleophilicity of the amine is the key factor for the reaction under these conditions.

Nevertheless, with the $Ti(OiPr)_4$/IL system we were able to obtain 34 % of bis(4,4-dimethyl-4,5-dihydrooxazol-2-yl)methane (**Figure 19**) from dimethyl malonate after fractional distillation, what is still acceptable, when considering the multi-step traditional synthesis of bis(oxazolines) involving hazardous acid chlorides and halogenating agents.

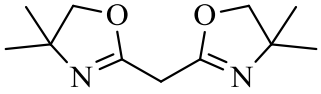
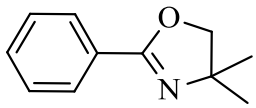
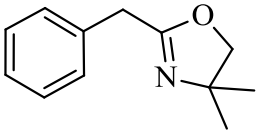


Figure 19. *Structure of bis(4,4-dimethyl-4,5-dihydrooxazol-2-yl)methane.*

Moreover, in the cases with acceptable yields the catalyst systems were successfully reused. For the subsequent cycles less time was necessary to complete the reaction (**Table 11**).

Table 11. *The synthesis of 2-oxazolines in three subsequent cycles.*

Oxazoline	Reaction conditions of the first cycle	Reaction conditions of the next cycles	Yields in three subsequent cycles, %
	IL, 4Å MS, 50 % $Ti(OiPr)_4$, 1 h at 120 °C, 8.5 h at 200 °C	Catalyst/IL system from the first cycle, 7 h at 200 °C	67 – 63 – 63
	IL, 4Å MS, 50 % $Ti(OiPr)_4$, 1 h at 120 °C, 7 h at 200 °C	Catalyst/IL system from the first cycle, 5 h at 200 °C	63 – 60 – 59

To conclude, satisfactory conditions and yields of the 2-oxazoline synthesis were not achieved. Too high temperatures, low yields of oxazolines in many cases and the presence of the corresponding amide as a side-product do not promote this procedure for a wide application, taking into account that some methods of oxazoline synthesis with high atom economy already exist. However, the low price of titanium tetraisopropoxide can in some cases be more favourable in comparison to more effective but also more expensive catalysts.

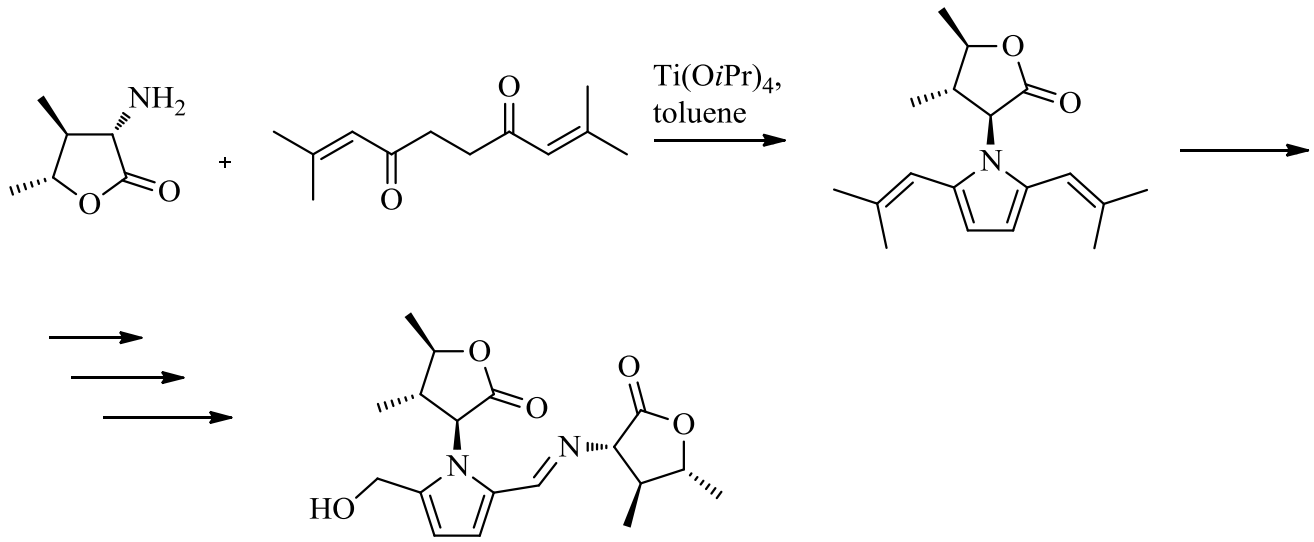
4.6.4 Paal-Knorr synthesis

Pyrroles and their derivatives are one of the most important classes of heterocyclic compounds. They exhibit broad biological and pharmacological properties. Many pyrrole derivatives possess antibacterial, antiinflammatory, antioxidant, antitumor, antifungal and immune suppressant activities.[199] Highly functionalised pyrroles are subunits of heme, chlorophyll, vitamin B_{12} and pyrrole alkaloids isolated from marine sources.[199,200] One of the best selling drugs, atorvastatin (trade name Lipitor), a drug for lowering cholesterol, bears a pyrrole core in its structure.[201]

Up to day a great number of pyrrole syntheses exists, but Paal-Knorr condensation is the most simple straightforward reaction, including acid-catalysed cyclisation from a 1,4-dicarbonyl compound and ammonia or primary amines. Although this reaction was first reported concurrently by *C. Paal*[202] and *L. Knorr*[203] already in 1884, it still awakes the interest of researchers, who continue to develop new catalysts and solvents to make the reaction "green". Noteworthy, a Paal-Knorr condensation is one of the steps in the total synthesis of atorvastatin.[201,204]

Both Brønsted and Lewis acids catalyse the Paal-Knorr reaction. The moderate Lewis acid titanium tetraisopropoxide was employed in the synthesis of the alkaloid funebrine[205,206] (**Scheme 18**). It suggested itself as a suitable catalyst, which would not catalyse polymerisation of pyrrole and decomposition of the aminolactone, as in the case of stronger Lewis acids.[206,207]

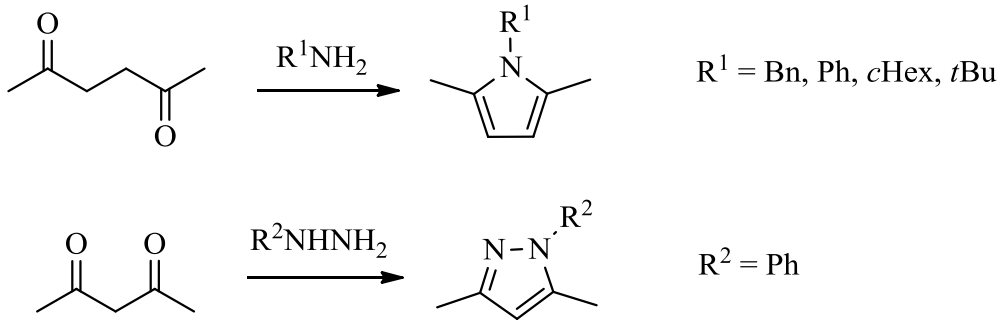
Although imidazolium-based ionic liquids have already been applied in the Paal-Knorr pyrrole synthesis,[208,209] no ionic liquids with triflamide anion were used. We tried our reusable IL/catalyst system in this type of reactions.



funebrine

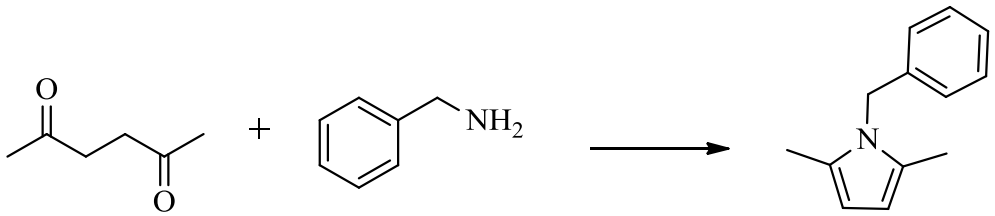
Scheme 18. *Paal-Knorr pyrrole condensation in the synthesis of funebrine.*[206]

For the preliminary studies the condensation between 2,5-hexanedione and benzylamine was investigated (**Scheme 19**, **Table 12**). It was found that this reaction can be completed without catalyst at room temperature in the IL $[N_{11}N_{11}N_{66}Gu]NTf_2$ **(6h)** within 24 h, what is nearly twice as effective as in the traditional solvent (benzene). The reaction could be accelerated not only at higher temperature, but also at ambient temperature by addition of 10 mol-% of Ti(O*i*Pr)$_4$. Bulb-to-bulb distillation provided pure product without tedious work-up.



Scheme 19. *Investigated Paal-Knorr reactions.*

Table 12. *Preliminary optimisation of the Paal-Knorr reaction.*



Solvent	Ti(O*i*Pr)$_4$, mol-%	Temperature, °C	Time, h	Yield, %
IL **6h**	0	20	24	86
IL **6h**	0	120	0.5	90
Benzene	0	20	24	50[a]
IL **6h**	10	20	2	93

a) Conversion of dicarbonyl compound (determined by NMR).

Further reactions were carried out with other, less nucleophilic (aniline) and more steric hindered (*t*BuNH$_2$, *c*HexNH$_2$), amines to reveal the scope of the IL/catalyst system (**Table 13**). If the reaction was not over after 24 h at room temperature, the catalyst amount was increased to 50 mol-%. In some cases higher temperatures were needed. The reaction conditions were optimised for each case to achieve good and excellent yields. Notably, the

Paal-Knorr reaction failed completely when *tert*-butylamine was used as an amine component. It is known that the Paal-Knorr reaction is a classic synthesis of pyrroles from ammonia or primary amines, whereas sterically hindered *tert*-alkylamines are not prone to form pyrroles under mild conditions.[210]

The Paal-Knorr pyrrole synthesis was also successfully extended to the synthesis of 1-phenylpyrazole from 2,4-pentanedione and phenylhydrazine (**Scheme 19**).

Table 13. *Paal-Knorr reaction in IL **6h** with different substrates.*[a]

Diketone	Amine	Cat.[b], mol-%	Temp., °C	Time, h	Yield, %
$CH_3CO(CH_2)_2COCH_3$	**$BnNH_2$**	**10**	**20**	**2**	**93**
$CH_3CO(CH_2)_2COCH_3$	$PhNH_2$	10	20	22	56[c]
$CH_3CO(CH_2)_2COCH_3$	**$PhNH_2$**	**50**	**20**	**48**	**94**
$CH_3CO(CH_2)_2COCH_3$	*c*$HexNH_2$	10	20	22	32[c]
$CH_3CO(CH_2)_2COCH_3$	*c*$HexNH_2$	50	20	20	45[c]
$CH_3CO(CH_2)_2COCH_3$	***c*$HexNH_2$**	**10**	**120**	**3**	**73**
$CH_3CO(CH_2)_2COCH_3$	*t*-$BuNH_2$	10	20	24	0
$CH_3CO(CH_2)_2COCH_3$	*t*-$BuNH_2$	100	20	24	0
$CH_3COCH_2COCH_3$	**$PhNHNH_2$**	**10**	**20**	**24**	**95**

a) Optimised conditions are indicated in bold.

b) Catalyst = $Ti(OiPr)_4$.

c) Conversion of 1,4-diketone (determined by NMR).

In all cases the catalyst/IL mixture remaining after product distillation could be reused several times without losing activity considerably (**Table 14**).

Table 14. *Performing the Paal-Knorr reaction in several subsequent cycles.*[a]

Diketone	Amine	Yield in 3 subsequent cycles, %
$CH_3CO(CH_2)_2COCH_3$	$BnNH_2$	93 – 99 – 99
$CH_3CO(CH_2)_2COCH_3$	$PhNH_2$	94 – 86 – 95
$CH_3CO(CH_2)_2COCH_3$	*c*$HexNH_2$	73 – 79 – 64
$CH_3COCH_2COCH_3$	$PhNHNH_2$	95 – 97 – 99

a) For reaction conditions see **Table 13.**

The catalytic system of $Ti(OiPr)_4$ in the hexaalkylguanidinium bistriflimide **6h** proved to be an effective and mild milieu for the Paal-Knorr reaction with all the advantages, which were also achieved by performing lactamisation reaction in guanidinium ILs (see chapter 4.6.1). Pyrroles and pyrazoles can easily be obtained by the developed method.

In comparison to the procedure described by *B. Wang et al.*,[208] which demonstrated the preparation of pyrroles in [BMIm]I at room temperature with the following extraction of the product with diethylether, this procedure avoids the use of flammable organic solvents. On the other hand, [BMIm]I system allows synthesis of pyrroles from more steric hindered amines, such as *tert*-butylamine and isopropylamine.

The developed guanidinium-based IL/$Ti(OiPr)_4$ system is more advantageous to the $Bi(OTf)_3$/[BMIm]BF_4 system proposed by *Y. S. Yadav et al.*[209] because the catalyst used is considerably cheaper and triflamide-based IL is water-stable compared to tetrafluoroborate IL.

4.6.5 Friedel-Crafts acylation

Friedel-Crafts reactions were among the earliest examples of catalytic reactions performed in room-temperature ionic liquids. Imidazolium chloroaluminate ionic liquids act both as a catalyst and as a solvent in Friedel-Crafts acylations and alkylations, as was demonstrated by *J. Wilkes and co-workers* already in 1986.[211] Recently a number of publications and patents appeared describing the use of metal catalysts in room-temperature ionic liquids in this type of reactions.[2,212,213] Several titanium alkoxide triflamide complexes (for example, $Ti(OiPr)_2(HOiPr)_2(Tf_2N)_2$) were reported to catalyse the Friedel-Crafts acylation.[214,215]

Chloride-free mild catalytic system, titanium tetraisopropoxide in guanidinium-based ionic liquid **6h,** was used in the acylation of anisole. As no reaction with benzoic acid as an acylating agent with 10 mol-% of catalyst at 120 °C was observed, stronger electrophiles were tried, namely methyl benzoate, benzoyl chloride and acetic anhydride. Despite of increasing the concentration of $Ti(OiPr)_4$ (until 200 mol-%) all reactions failed. In a number of cases, especially when more than 50 mol-% of the catalyst was utilised, the esterification product (isopropyl benzoate) instead of Friedel-Crafts product (4-methoxybenzophenone or

acetophenone) was formed. The explanation could be that titanium alkoxide is a too weak Lewis acid for the Friedel-Crafts reaction irrespective of the strength of the electrophile used. To increase the activity of the Lewis acid, *in situ* obtained BINOL/Ti isopropanolate complex (1:1) was used in the reaction of anisole with benzoyl chloride in IL. This reaction was carried out with 20 mol-% of Ti complex for 2 h at room temperature, followed by 22 h at 120 °C and resulted in isopropyl benzoate. For the arene acylation strong Lewis acids such as metal chlorides, triflates or bistriflimides should be used. As an alternative, a task-specific ionic liquid with Lewis acidic properties could perform a recyclable media for these reactions.

4.7 Electrochemical properties and applications

4.7.1 Study of the electrochemical behaviour of guanidinium-based ILs

A number of hexaalkylguanidinium ionic liquids (triflates, bistriflamides, dicyanamides) were investigated in the Institute of Electrochemistry at the University of Ulm (*Prof. Dr. D. M. Kolb, Prof. Dr. T. Jacob, Dr. M. Gnahm, Dipl.-Chem. C. Berger*). Basic properties of the metal/IL interface were studied such as double-layer capacitance and potentials of zero-charge; to this end, electrochemical impedance spectroscopy as well as cyclic voltammetry were used. The metal surface was also studied with *in situ* scanning tunneling microscopy in order to describe the structures of adsorbates on the metal surface at various potentials. *In situ* STM studies suggest no ad-structure of the cation of the ILs at negative potentials on Au(100) as well as on Au(111) in contrast to imidazolium-based ILs. The observed phenomena could be interesting for the planned electrodeposition of metals. The detailed results are described in the Diploma Thesis of *C. Berger* (2011),[216] the Doctoral Thesis of *M. Gnahm* (2012)[217] and in a full research paper [144].

With the aim to enlarge the electrochemical window, a number of guanidinium-based ILs were synthesised. Their cyclovoltammetric data is given in **Table 15**. It was stated that triflate- and dicyanamide-based ionic liquids are less electrochemically stable. The bistriflimide salts provided the broadest windows. These results are in agreement with expectations, based on literature data of electrochemical stability of other ILs. Because of higher electrochemical stability, water stability, hydrophobicity and lower viscosity, the bis(triflyl)imide salts were investigated more intensively. For applications, such as metal electrodeposition or lithium-ion batteries, cathodic stability of the IL-electrolyte is more important than anodic stability. Mainly, the stability of the cation is responsible for the cathodic limit. So the substituents in the guanidinium core have been varied to find the most electrochemically stable IL (see chapter 4.1). Only liquid ILs were chosen for the electrochemical investigations. The cathodic stability of guanidinium bistriflimides with alkyl substituents showed almost no coherence with the length of the alkyl chain. But the presence

of a cycle (6-ring) improved the cathodic stability considerably. Electrochemical windows of some ILs turned out to be as broad as those of widely used commercially available salts (e.g. imidazolium and piperidinium ILs).

Table 15. *Cyclovoltammetric data of different guanidinium-based ionic liquids.*[a]

	Ionic liquid	Cathodic limit [V]	Anodic limit [V]	Electrochemical window [V]
3a	$[N_{11}N_{22}N_{44}Gu]OTf$	-0.6	0.6	1.2
3h	$[N_{11}N_{11}N_{44}Gu]OTf$	-1.0	1.2	2.2
6a	$[N_{11}N_{22}N_{44}Gu]NTf_2$	-1.8	1.0	2.8
6b	$[N_{22}N_{44}N_{66}Gu]NTf_2$	-1.8	0.8	2.6
6g	$[N_{11}N_{11}N_{44}Gu]NTf_2$	-2.2	0.7	2.9
6h	$[N_{11}N_{11}N_{66}Gu]NTf_2$	-1.8	1.7	3.5
6l	$[N_{11}N_{11}N_{pip}Gu]NTf_2$	-2.5	0.8	3.3
6m	$[N_{11}N_{pip}N_{pip}Gu]NTf_2$	-2.1	1.5	3.6
6o	$[N_{11}N_{11}N_{pyr}Gu]NTf_2$	-1.2	1.4	2.6
7a	$[N_{22}N_{44}N_{66}Gu]BF_4$	-2.2	1.0	3.2
7c	$[N_{11}N_{11}N_{66}Gu]BF_4$	-2.2	1.6	3.8
8a	$[N_{11}N_{22}N_{44}Gu]N(CN)_2$	-1.5	0.6	2.1
8b	$[N_{22}N_{44}N_{66}Gu]N(CN)_2$	-1.5	0.6	2.1
	$[BMIm]NTf_2$[b]	-1.9	1.3	3.2
	$[MPPip]NTf_2$[b]	-2.5	1.5	4.0

a) All potentials were measured on the Au(111) surface, with respect to the Ag/AgCl pseudo-reference electrode in the Institute of Electrochemistry at the University of Ulm (*C. Berger*). A cut-off current density of 20 $\mu A \cdot cm^{-2}$ was assumed as anodic and cathodic limits.

b) 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($BMIMTf_2N$) and 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)amide ($MPPipTf_2N$) were purchased from Merck.

IL $[N_{11}N_{11}N_{pip}Gu]NTf_2$ (**6l)** turned out to be the cathodically most stable IL and therefore the most promising for various electrochemical applications. This behaviour of the guanidinium salt containing a piperidinium moiety is likely due to the ability of the piperidine substituent to effectively dissipate the positive charge in the cation. Moreover, the proper piperidinium

ILs are well known to have a broad potential window. Comparison of cyclic voltammograms of piperidinium-containing guanidinium IL **6l** and hexaalkylguanidinium IL **6h** is presented in **Figure 20**.

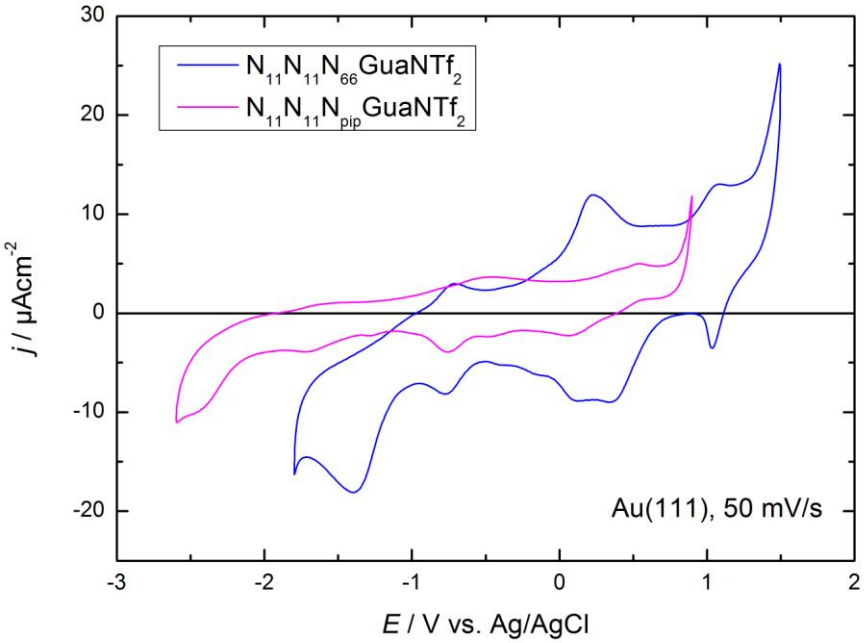


Figure 20. *Cyclic voltammograms of ILs* ***6l*** *and* ***6h*** *(C. Berger, Institute of Electrochemistry, University of Ulm).*

4.7.2 Electrodeposition from guanidinium-based ILs

Room temperature ionic liquids are promising non-aqueous electrolytes for the electrodeposition of various metals because they have the merits of both organic electrolytes and high-temperature molten salts. Ionic liquids can be used in a wide temperature range, and temperature influences such phenomena as surface diffusion, electrocrystallisation and nucleation, associated with the electrodeposition of metals.[9] In addition, the process can be carried out safely because ionic liquids are neither flammable nor volatile if they are kept below thermal decomposition temperature.

Currently room temperature ionic liquids are widely investigated as media for metal electrodeposition. A high cathodic limit allows depositing of less noble metals such as

lithium, zinc, aluminium, iron, titanium, tantalum and rhenium. Electrodeposition of metals from solutions of metal alcoholates [$M(OR)_n$] in ionic liquids is expected to be more convenient. This method is able to provide safer conditions in comparison to electrodeposition from solutions of respective salts in ionic liquids avoiding the use of halogens. Hexaalkylguanidinium ILs with complex anions such as triflamide are easier to handle than hygroscopic haloaluminate ILs. The novelty of this part of research work consists in the application of metal alcoholates as substrates for metal electrodeposition from ionic liquids as the reaction media. It should be kept in mind that electrodeposition of metals such as the alkali metals, earth-alkali metals, aluminium, tantalum and titanium from aqueous solutions of their salts is not possible.

4.7.2.1 Titanium electrodeposition

Electrodeposition of titanium is of great interest for the coating of medicinal implants. It was reported that titanium nanowires have been deposited electrochemically, with *in situ* monitoring by scanning tunneling microscopy, at the step edge of highly oriented pyrolytic graphite (HOPG) at room temperature from 0.24 M $TiCl_4$ in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide.[218] On the other hand, *F. Enders et al.* showed that from titanium halides in different ionic liquids (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, 1-butyl-1-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)amide and trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide) instead of elemental titanium only non-stoichiometric halides are formed.[219] Recently the formation of Ti-Al alloys in imidazolium chloride was reported.[220,221]

In this project, a new approach is taken, which avoids working with hazardous and corrosive metal halides. Instead, metal alcoholates are employed, which should decrease the hygroscopicity of the reaction medium and provide reproducible electrodeposition of metals. Moreover, the guanidinium cation, which has a different electrochemical behaviour compared to common commercially available ILs,[144] could have a positive influence on the metal deposition.

Based on the results of solubility experiments (see chapter 4.5), polarity[157] and the electrochemical studies, solutions of titanium alcoholates in several hexaalkylguanidinium bis(trifluoromethylsulfonyl)imides were chosen. For the electrodeposition experiments a number of solutions of titanium isopropanolate, trimethylsilanolate and 2-ethylhexanolate with different concentrations (up to 0.1 M) in hexaalkylguanidinium bistriflimides **6a** and **6b** were prepared. We were not able to deposit titanium from these ionic liquids. The reasons could be a narrow electrochemical window of these ILs, the inescapable presence of moisture or unfavourable properties as a precursor of the titanium alcoholates themselves. Another explanation could be a complicated stepwise reduction of Ti^{4+} to Ti^{0} through several oxidation states.

The experiments on titanium electrodeposition were continued with new ILs with a higher electrochemical stability, namely with ILs **6h, 6l, 7a**. Solutions, emulsions and two-phase systems were prepared in the glove-box (see chapter 4.5) in order to examine the tendency and the possibility of the titanium deposition from different systems. Cyclic voltammograms revealed comparable behaviour of clear and turbid systems. However, the turbid solutions could not be investigated with *in situ* STM because of the presence of disturbing particles. Although, a reduction peak was observed in the CV (**Figure 21**), no further proof of deposited titanium metal could be found. All *in situ* STM measurements failed so far, mainly, due to complexity of the device construction and sensitivity of the titanium-containing solutions to the air moisture. Although the measurements were performed under inert atmosphere, a very short contact to the air could lead to the hydrolysis of the titanium alcoholate. Assuming that a small amount of solution is distributed over a large surface, it seems feasible that the unavoidable traces of air hydrolyse the titanium alcoholate. The particles observed in *in situ* STM, presumably formed titanium dioxide, were disturbing during the measurements. On the other hand, the cyclic voltammograms of titanium isopropanolate solutions in [BMIm]NTf_2 were considered to be more promising and were chosen for further investigations.

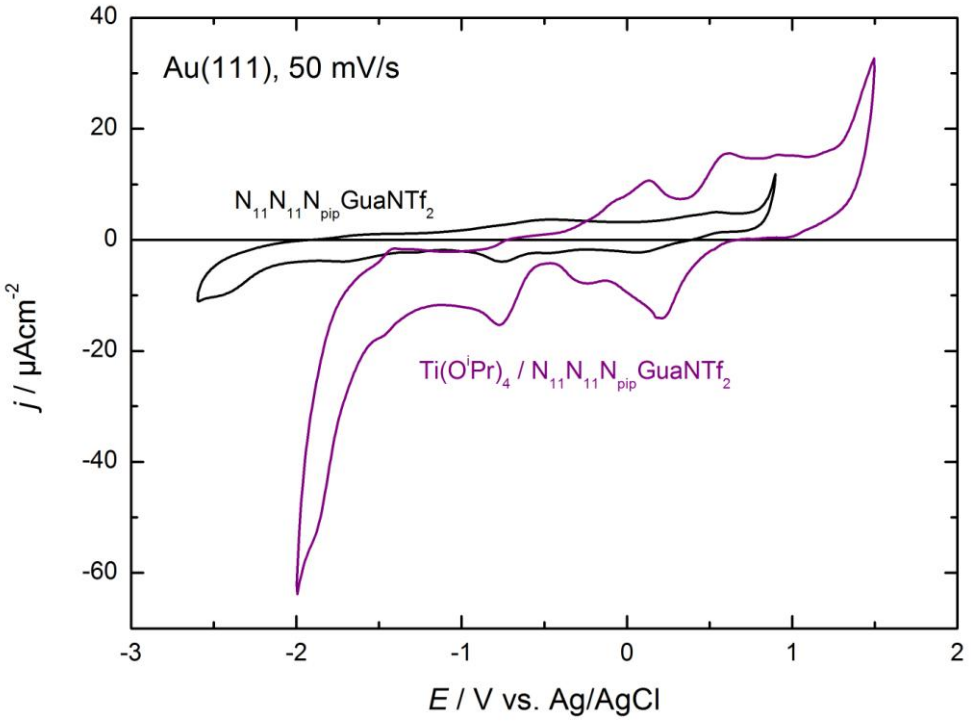


Figure 21. *Cyclic voltammogram of $[N_{11}N_{11}N_{pip}Gu]NTf_2$ **(6l)** containing $Ti(OiPr)_4$ on Au(111) substrate (C. Berger, Institute of Electrochemistry, University of Ulm).*

4.7.2.2 Dysprosium electrodeposition

Dysprosium (Dy) is a rare-earth element and a lanthanide. Due to its profitable properties, such as the highest magnetic moment per atom and highest saturation magnetization, Dy is also one of the most important elements for high-tech industries. It is often used in neodymium magnets as an additive element that prevents them from demagnetizing at high temperature. Dysprosium cannot be electroplated from aqueous solutions due to its negative electrode potential. In addition, dysprosium reacts very fast with the components of the atmosphere, water and oxygen. A cost efficient electroplating of Dy also would be of great industrial interest.[222,223] Some investigations on electrodeposition of metallic dysprosium have already been reported. *H. Gores et al.*[222] managed to obtain Dy from $Dy(TfO)_3$ solution (0.25 mol·kg^{-1}) in dimethylpyrrolidinium trifluoromethanesulfonate/dimethylformamide solution (1.00 mol kg^{-1}). *A. Kurachi*[223] and co-workers observed irreversible dysprosium

electrodeposition from solution of $Dy(NTf_2)_3$in triethylpentylphosphonium bistriflimide (0.075 M) at 100-150 °C.

In a cooperation with Siemens AG (Erlangen) and the Institute of Electrochemistry at the University of Ulm, dysprosium was successfully electrodeposited from guanidinium-based ionic liquids already at room temperature at first on Au(111) substrate, and then on NdFeB-magnets. Cyclic voltammetry, *in situ* STM, XPS, AES measurements were used to characterise the obtained deposits, where both dysprosium metal and dysprosium oxide (Dy_2O_3) were present. Details of this research cannot be given here due to a confidentiality agreement.

4.7.2.3 Iron electrodeposition

Iron was successfully electrodeposited from a saturated solution of iron(II) chloride in *N*,*N*-dibutyl-*N'*,*N*'-diethyl-*N*'',*N*''-dimethylguanidinium bis(trifluoromethylsulfonyl)imide (**6a**), as was proven by XPS measurements and described by *in situ* STM measurements.[216] *In situ* STM measurements determined formation of Fe-isles, which grew to Fe-layers after several hours. The cyclic voltammogram is presented in **Figure 22**.

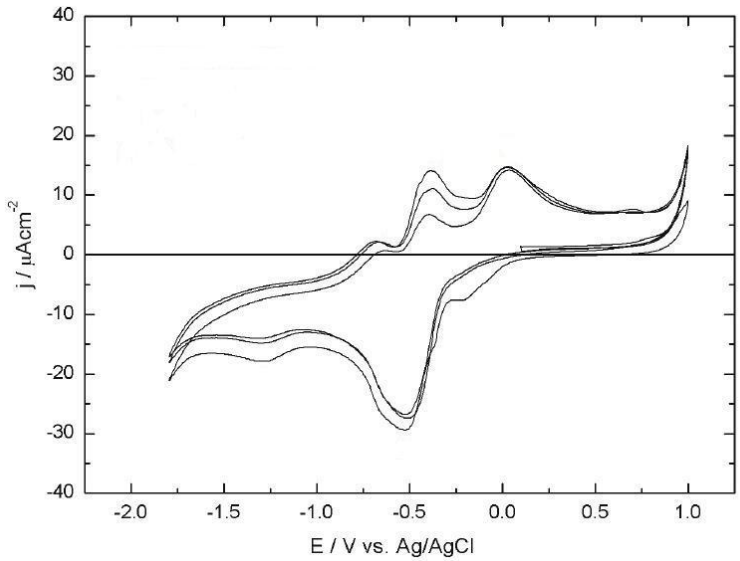


Figure 22. *Cyclic voltammogram of $[N_{11}N_{22}N_{44}Gu]NTf_2$ (**6a**) containing $FeCl_2$ on Au(111) substrate (C. Berger, Institute of Electrochemistry, University of Ulm).*[216]

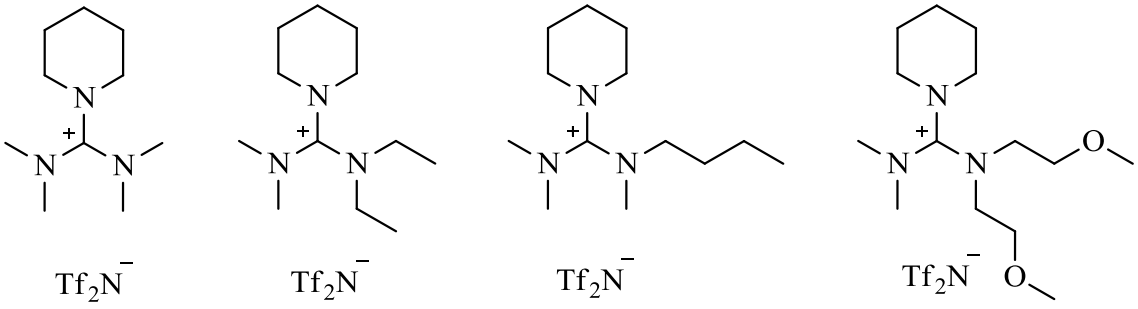
4.7.3 Application of guanidinium-based ILs in batteries

Several peralkylated guanidinium ILs were examined as electrolytes in Li-ion batteries. Guanidinium ILs containing a piperidinium moiety were investigated in TUM CREATE, Singapore (*N. Bucher, S. Hartung, M. Arkhipova, P. Kratzer, X. Wu, Prof. Dr. H. Hoster*). Two ILs containing sterically demanding substituents were explored in the Centre for Solar Energy and Hydrogen Research Baden-Württemberg (Zentrum für Sonnenenergie- und Wasserstoffforschung Baden-Württemberg, ZSW), Ulm (*S. Hess, Dr. M. Wachtler*).

4.7.3.1 Guanidinium ILs containing a piperidinium moiety

At first, some primary studies important for application of ILs in batteries were performed, such as measurements of viscosity, (Li-)ion conductivity, thermal and electrochemical stability. A 0.5 M solution of $LiNTf_2$ in $[N_{11}N_{11}N_{pip}Gu]NTf_2$ (**6l**) was tested as an electrolyte for Li-ion batteries. These experiments included cycles of Li deposition/dissolution on stainless steel and (de-) intercalation into/from $LiFePO_4$ electrodes. The performance tests in Li/$LiFePO_4$ cells were carried out at various C-rates (*i. e.* charge/discharge rate, which specifies charge and discharge current as a multiple of the capacity;[224] for example a 1000 mAh battery that is discharged at 1C rate should under ideal conditions provide a current of 1000 mA for one hour) and two different temperatures for a better quantitative comparison to other electrolyte systems. So at room temperature (approx. 25 °C) a charge/discharge capacity of 143 $mAh \cdot g^{-1}$ could be reached at 0.05 C, while at 55 °C a capacity of 148 $mAh \cdot g^{-1}$ was detected already at 0.2 C C-rate. The salt **6l** outperforms other common guanidinium and piperidinium based ionic liquids with regard to achieved capacities of Li/$LiFePO_4$ cells. The obtained results are the subject of paper.[225]

The obtained results prompted us to enlarge the series of ILs with such structure. ILs **6q, 6u, 6v** with unsymmetrically substituted cations were synthesised to see the influence of the cation structure of the guanidinium ILs and their corresponding viscosities on the battery performance (**Figure 23**).



6l **6q** **6u** **6v**

Figure 23. *Structures of guanidinium ILs, containing a piperidinium moiety (**6l**, **6q**, **6u**, **6v**), used in this work.*

IL $[N_{11}N_{14}N_{pip}Gu]NTf_2$ (**6u**) and ether-functionalised $[N_{11}N_{1O21O2}N_{pip}Gu]NTf_2$ (**6v**) have been investigated for battery application during my five-week stay in Singapore at TUM CREATE. Ether function was introduced in the structure of IL **6v** to reduce the viscosity and to enhance Li transport, what was also achieved. Linear sweep voltammograms, performed in a two-electrode coin cell with stainless steel as the working electrode and lithium as the counter and reference electrode, are presented in the **Figure 24**. It was found that IL **6v** and unsymetric IL **6u** show the higher electrochemical stabilities in comparison to the earlier tested IL **6l** (**Table 16**), but the ether-functionalised IL **6v** possesses the lowest thermal stability (T_{dec}(**6u**) = 465 °C, T_{dec}(**6v**) = 423 °C, T_{dec}(**6l**) = 463 °C, measured in TUM CREATE). However, this value is not limiting and the IL **6v** is still applicable in the usual temperature range of batteries.

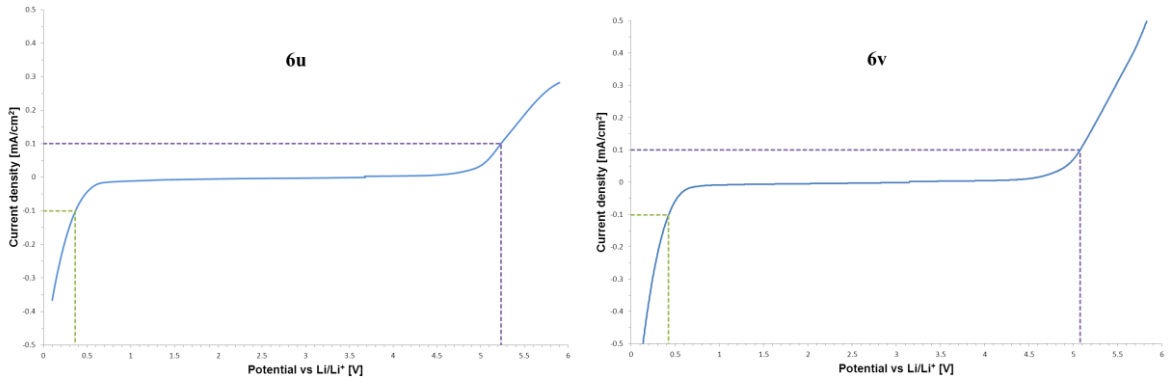


Figure 24. *Linear sweep voltammograms (LSVs) of $[N_{11}N_{14}N_{pip}Gu]NTf_2$ (**6u**) and $[N_{11}N_{1O21O2}N_{pip}Gu]NTf_2$ (**6v**) (scan rate: 10 mV·s^{-1}).*

Table 16. *Electrochemical windows of several guanidinium ILs.*[a]

IL	Cathodic limit, V	Anodic limit, V	Electrochemical window, V
$[N_{11}N_{11}N_{pip}Gu]NTf_2$ (**6l**)[b]	0.44	4.88	4.44[225]
$[N_{11}N_{22}N_{pip}Gu]NTf_2$ (**6q**)[b]	0.44	5.04	4.60
$[N_{11}N_{14}N_{pip}Gu]NTf_2$ (**6u**)	0.36	5.23	4.87
$[N_{11}N_{1O21O2}N_{pip}Gu]NTf_2$ (**6v**)	0.43	5.07	4.65

a) LSV measurements were performed in a Li/stainless steel coin cell with 10 $mV \cdot s^{-1}$ scan rate and a cut-off current of 0.1 $mA \cdot cm^{-2}$, TUM CREATE, Singapore.

b) The measurements were carried out by *N. Bucher, S. Hartung, P. Kratzer, X. Wu.*

In agreement with Walden's rule, – more viscous ILs possess lower conductivity, – $[N_{11}N_{14}N_{pip}Gu]NTf_2$ (**6u**) has relatively low conductivity (0.65 mS/cm, **Table 17**) and $[N_{11}N_{1O21O2}N_{pip}Gu]NTf_2$ (**6v**) – a little bit higher value (0.79 mS/cm), which is still lower by a factor of almost 2 than for $[N_{11}N_{11}N_{pip}Gu]NTf_2$ (**6l**) (1.46 mS/cm). For the battery applications, the conductivity values of electrolytes are more important, as they are known to be lower than of pure ILs. While the conductivities of new pure ILs were already low, the concentration of the Li salt was reduced to 0.3 M. These data are also presented in **Table 17**.

Table 17. *Conductivity data of several guanidinium IL and electrolytes based on them.*[a]

IL	Conductivity, $mS \cdot cm^{-1}$	Electrolyte	Conductivity, $mS \cdot cm^{-1}$
$[N_{11}N_{11}N_{pip}Gu]NTf_2$ (**6l**)[b]	1.46[225]	0.5 M LiTFSI in **6l**[b]	0.74[225]
$[N_{11}N_{22}N_{pip}Gu]NTf_2$ (**6q**)[b]	1.10	0.5 M LiTFSI in **6q**[b]	0.47
$[N_{11}N_{14}N_{pip}Gu]NTf_2$ (**6u**)	0.65	0.3 M LiTFSI in **6u**	0.43
$[N_{11}N_{1O21O2}N_{pip}Gu]NTf_2$ (**6v**)	0.79	0.3 M LiTFSI in **6v**	0.46

a) The measurements were performed in a glove-box at 28 °C using a conductivity meter (Eutech Instruments, CyberScan 600 Series), TUM CREATE, Singapore.

b) The measurements were carried out by *N. Bucher, S. Hartung, P. Kratzer, X. Wu.*

Electrochemical Impedance Spectroscopy (EIS) measurements, performed with 0.3 M electrolytes in a symmetric lithium coin cell set-up (Li|electrolyte|Li), indicated that the SEI formation (SEI = Solid Electrolyte Interphase) was finished after 10 h and stayed stable

afterwards (**Figure 25**). Similar behaviour was observed for the 0.3 M **6v**-containing electrolyte.

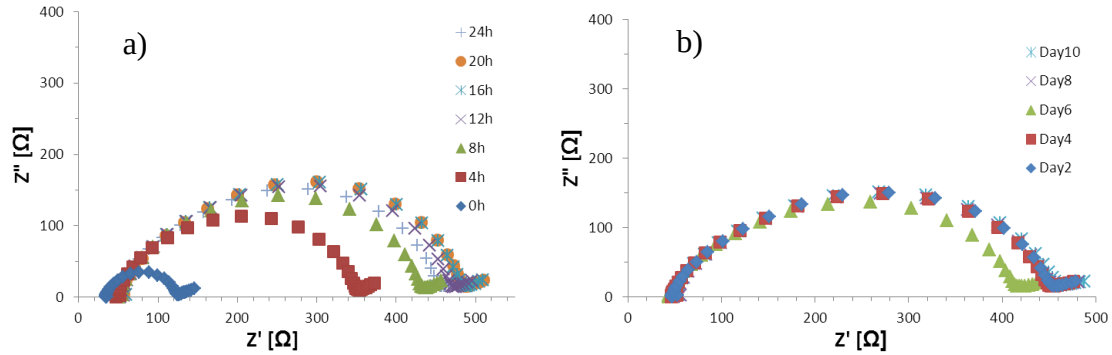


Figure 25. *Impedance response of a symmetrical Li|0.3 M LiTFSI in **6u**|Li cell stored at room temperature during the first (a) 24 hours, (b) 10 days.*

The applied ILs show a limited cathodic stability. Therefore, the reversibility of plating/stripping of Li should have been inspected. These experiments have been performed in coin cell with stainless steel and lithium as working and combined counter&reference electrode, respectively. **Figure 26** shows cyclic voltammogram of 0.3 M **6v**-containing electrolyte. Although plating and stripping can be observed, they are not completely reversible. This happens presumably due to the partial decomposition of IL, which can be accompanied with the formation of a passivation layer in the first cycle. This layer (also SEI) can prevent electrolyte decomposition in further cycles. Similar behaviour was also observed by other IL-containing electrolytes, as well as by guanidinium ones.[126,225] This assumption can be supported by the presence of the cathodic peak at approx. 1.5 V only in the first cycle, so when the SEI layer should be formed. The system seems to be stabilised during the further cycles. Although the absolutely reversible plating/stripping is desirable for battery application, the batteries do not operate at such low voltages. Usually charge/discharge operations for the cells with $LiFePO_4$ electrodes are performed at 2.8-4.0 V. As seen from the cyclic voltammogram the investigated electrolyte is stable up to 0 V vs. Li and even a bit lower.

Battery tests are the most important and meaningful experiments in the development of batteries. They generally consist of two experiments: charge/discharge cycling at different C-rates to determine the rate capabilities and cycling at a constant rate to study the cycle

properties. At TUM CREATE only charge/discharge cycling at different C-rates has been performed, but at two different temperatures (room temperature and 55 °C, **Figure 27**).

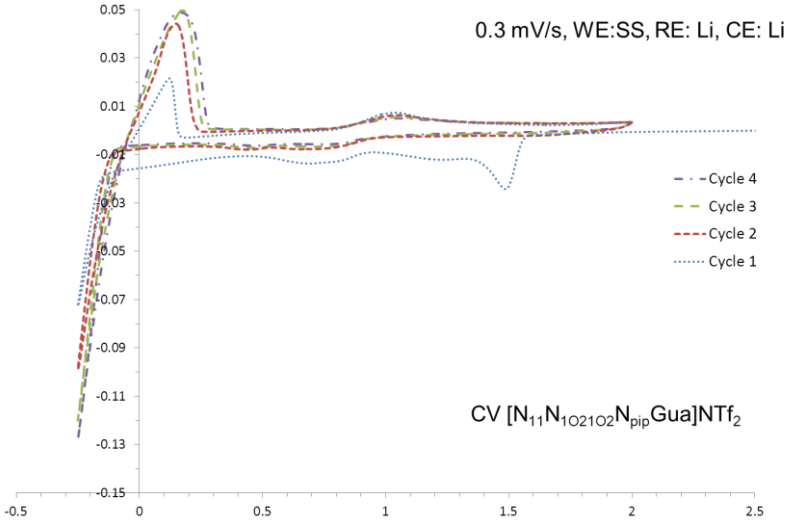


Figure 26. *Cyclic voltammogram of 0.3 M LiTFSI in $[N_{11}N_{1O21O2}N_{pip}Gu]NTf_2$ (**6v**) electrolyte.*

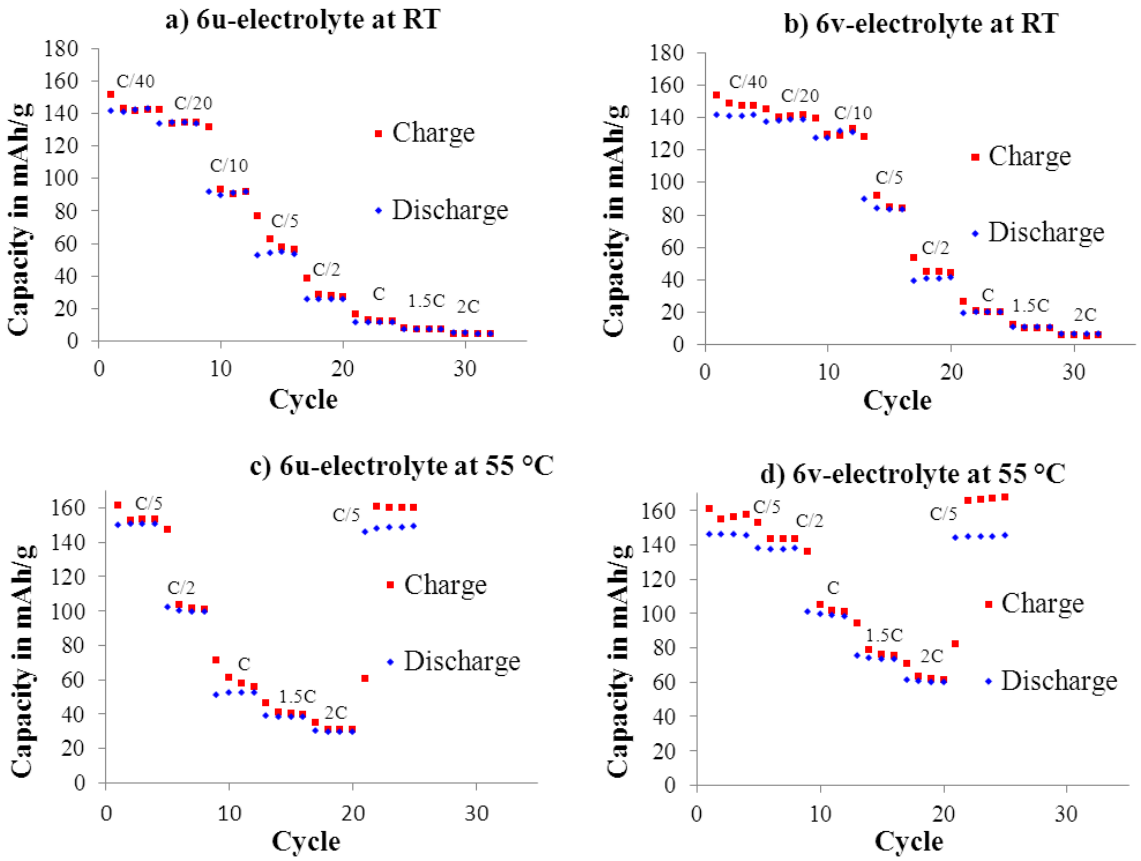


Figure 27. *Rate capability of the Li/$LiFePO_4$ cells incorporating 0.3 M LiTFSI in ILs: (a) **6u** and (b) **6v** at room temperature; (c) **6u** and (d) **6v** at 55 °C.*

The obtained results are summarised in **Table 18** and **Table 19**. The capacities achieved with the new ILs in most cases increased in comparison to the first tested guanidinium-based IL (**6l**), this is seen especially at higher C-rates. The reported capacities of guanidinium and piperidinium-based electrolytes allow the conclusion that guanidinium ILs containing a piperidinium moiety are more efficient as electrolytes in LIB than the ILs containing only a guanidinium or piperidinium moiety in the cation.

Table 18. *Comparison of the capacity [mAh·g^{-1}] in Li/LiFePO$_4$ cells at room temperature.*[a]

C-rate	**6u**	**6v**	**6l**[b]	**6q**[b]	$[N_{11}N_{11}N_{14}Gu]NTf_2$[127][c]	[BMPip]NTf_2[226][d]
C/40	142	141	154	146		
C/20	135	138	143	143		94
C/10	92	131	101	136	75	

a) The measurements were conducted in a Li/LiFePO$_4$ cells at 24 °C using 0.3 M LiTFSI solution for **6u** and **6v**, and 0.5 M LiTFSI solution for **6l** and **6q**, TUM CREATE, Singapore.

b) The measurements were performed by *N. Bucher, S. Hartung, P. Kratzer, X. Wu.*

c) 0.3 mol·kg^{-1} LiTFSI solution in IL was used.

d) 0.32 mol·kg^{-1} LiTFSI solution in IL was used.

The cycling experiments at 55 °C proved the ILs **6v** and **6q** to be the most promising among the tested ones for the application in Li-ion batteries (**Table 19**). However, the low-viscous ether-functionalised guanidinium-based electrolyte **6v** demonstrated higher capacity value at C-rate of 1C. Notably, for a comparison the concentration of the Li salt should also be taken into account. Obviously, viscosity and conductivity influence the effectiveness of the cells, but they are not the only factors important for good performance. According to a common rule, the larger the substituents the higher is the viscosity. The same was observed in the case with guanidinium ionic liquids with the exception of IL **6v**, containing ether groups. Perhaps, the reduction of the viscosity of the electrolyte (by adding the additives, such as vinylene carbonate) or the ILs (by changing the anion to bis(fluorosulfonyl)imide) can improve the performance characteristics of the cells.

Table 19. *Comparison of the capacity [mAh·g^{-1}] in Li/LiFePO$_4$ cells at 55 °C.*[a]

C-rate	**6u**	**6v**	**6l**[b]	**6q**[b]	$[N_{11}N_{11}N_{2O12O2}Gu]NTf_2$[128][c]
C/5	151	146	148	146	
C/2	99	138	82	135	
1C	52	98	41	106	125
2C	30	60	26	69	

a) The measurements were conducted in a Li/LiFePO$_4$ cells at 55 °C using 0.3 M LiTFSI solution for **6u** and **6v**, and 0.5 M LiTFSI solution for **6l** and **6q**, TUM CREATE, Singapore.

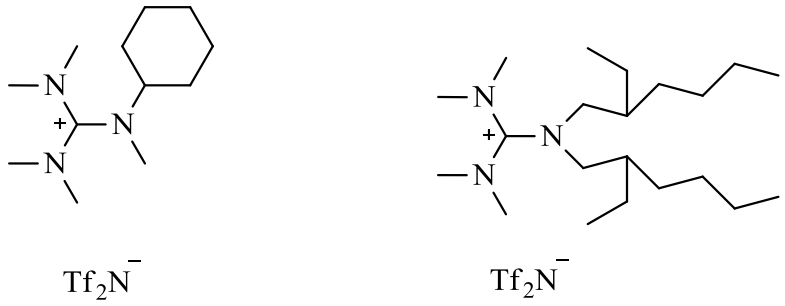
b) The measurements were performed by *N. Bucher, S. Hartung, P. Kratzer, X. Wu.*

c) 0.6 mol·kg^{-1} LiTFSI solution in IL was used.

The cooperation with the research group of *Prof. H. Hoster* at TUM CREATE showed, that guanidinium ILs with piperidinium moiety in the cation successfully combine the advantages of guanidinium and piperidinium ionic liquids for battery electrolyte applications. Nevertheless, the improved results are still not comparable with standard organic electrolytes (for example, 1 M LiPF6 in EC:DMC). But IL-electrolytes provide safer operating of the batteries. More efforts are needed to bring IL-based Li-ion batteries on the level of contemporary LIB.

4.7.3.2 Guanidinium ILs containing sterically more demanding substituents

Two new guanidinium-based ILs, *N*-cyclohexyl-*N*,*N*',*N*',*N*'',*N*''-pentamethylguanidinium bis(trifluoromethylsulfonyl)imide (**6w**) and *N*,*N*-bis(2-ethylhexyl)-*N'*,*N*',*N*'',*N*''-tetramethylguanidinium bis(trifluoromethylsulfonyl)imide (**6x**) (**Figure 28**) with sterically rather demanding substituents (cyclohexyl and 2-ethylhexyl) were incorporated in the cation in hopes to prevent the cation intercalation in the graphite, when used as an electrolyte in Li-ion batteries.



Tf_2N^- Tf_2N^-

6w **6x**

Figure 28. *Structures of guanidinium ILs, containing sterically rather demanding substituents (**6w**, **6x**), used in this work.*

Compared to the carbonate-based (1 M $LiPF_6$ in ethylene carbonate-dimethyl carbonate (EC-DMC), 1:1 w/w) and 1-butyl-1-methylpyrrolidinium bistriflimide-based reference electrolytes, guanidinium-based electrolytes showed higher viscosities, lower conductivities, similar cathodic stabilities and lower anodic stabilities (about 4.8 V vs. Li/Li^+). However, the anodic stability is high enough for application with state-of-the-art 3 V and 4 V cathode materials, and it could be shown that they can be used with $LiFePO_4$. As for the anode, they are compatible with $Li_4Ti_5O_{12}$, but are not compatible with graphite. Presumably, no adequate SEI is formed on graphite, which results in intercalation of the guanidinium cation and rapid blocking and destruction of the graphite electrode. The addition of SEI forming additives to the guanidinium-based electrolytes might improve the cycling behaviour of graphite – this was however outside of the scope of this investigation. Another idea is to use the bis(fluorosulfonyl)imide as anion of ionic liquid or Li salt.

Despite the broad electrochemical window and the compatibility with the mentioned electrode materials the application in lithium-ion batteries is probably hampered by the low conductivities and resulting low rate capabilities.

A paper with the explicit results of this cooperation has recently been submitted.[227]

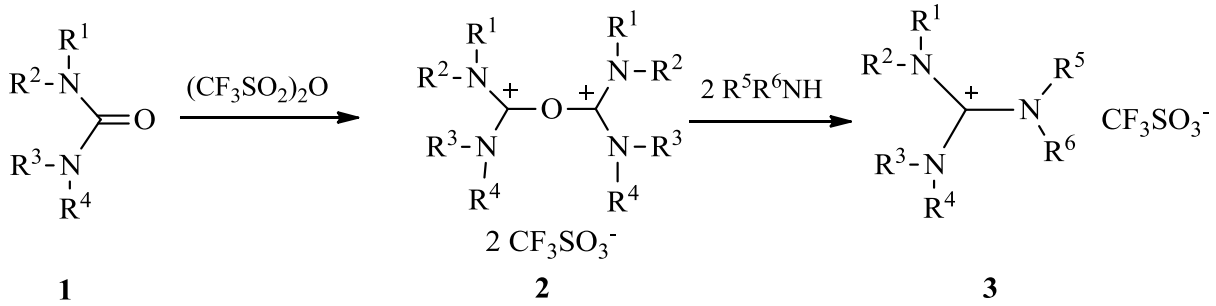
5. Summary

The objective of this work was to investigate the possible fields of application of hexasubstituted guanidinium-based ionic liquids in organic chemistry and in electrochemistry. Specific properties of ILs, such as non-volatality, non-flammability, chemical and thermal stability, have been advantageously used. Solutions of metal alkoxides (Ti, Al) have been prepared and applied as catalytic recyclable media for some dehydrating cyclocondensation reactions. Another approach consisted in application of such solutions for metal electrodeposition. Electrochemical investigations have been carried out in cooperation with the Institute of Electrochemistry, Universtity of Ulm. Along with the basic electrochemical behaviour of guanidinium-based ionic liquids, electroplating of titanium, dysprosium and iron has been studied. The third part of the work was devoted to the application of peralkylated guanidinium salts as electrolytes in lithium-ion batteries. As a result two projects with different approaches, namely the use of guanidinium ILs containing a piperidinium moiety or containing sterically more demanding substituents, to improve the characteristics of LIB have been developed.

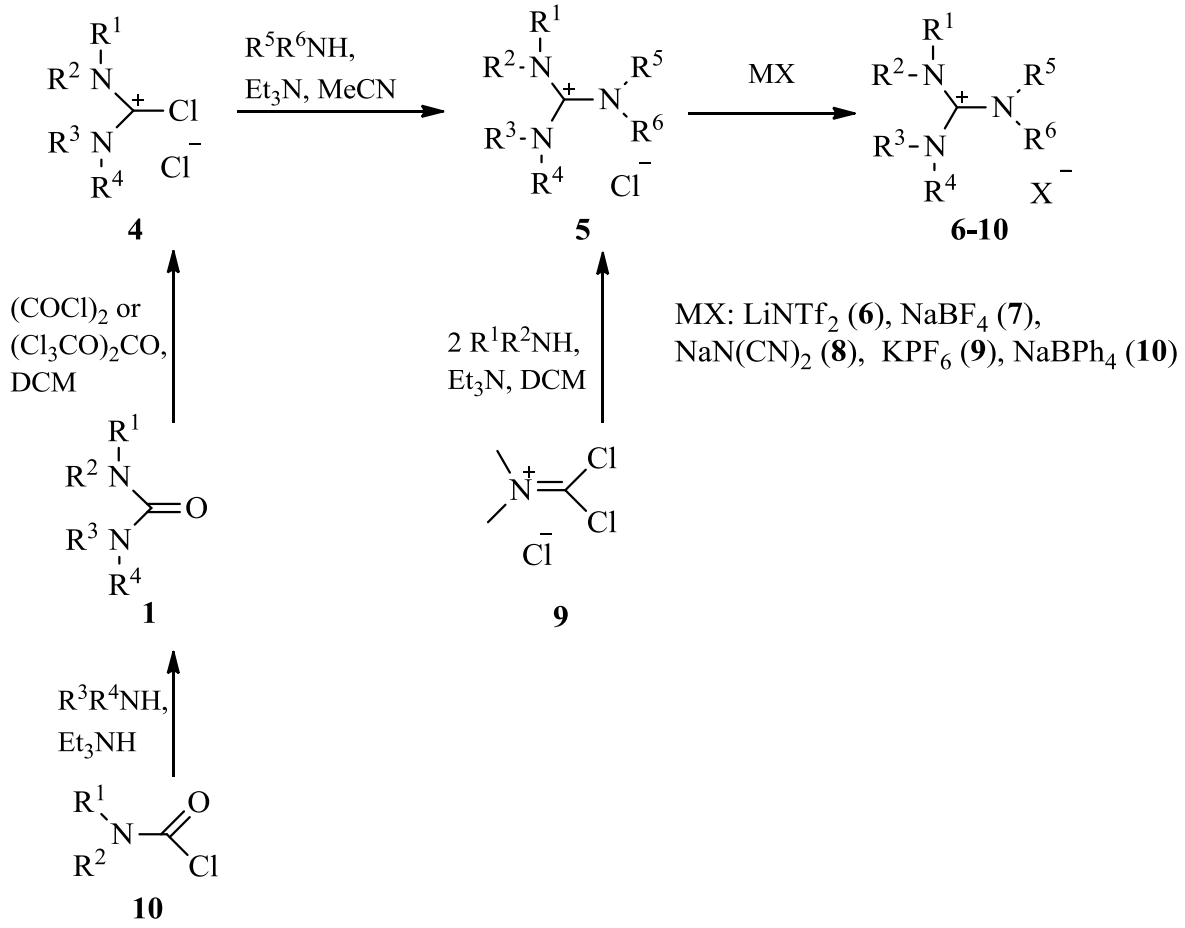
A good number of hexasubstituted ionic liquids with various anions (bis(trifluoromethylsulfonyl)imide, trifluoromethanesulfonate, tetrafluoroborate, hexafluorophosphate, dicyanamide, tetraphenylborate) has been prepared according to described procedures[28,31,35,43,141] (**Scheme 20**), while over twenty new ionic liquids have been obtained. Peralkylated guanidinium salts containing cyclic mojeties, such as piperidinium, pyrrolidinium or morpholinium structural units, have been attained. The work-up procedures have been partially modified with the focus on high purity and colourlessness of the ILs. These aspects are especially important for the electrochemical applications.

The obtained ionic liquids have been characterised with NMR, IR, MS, DSC and TGA methods. For some of the synthesised guanidinium chlorides, restricted rotation could be observed in NMR spectra. The crystal structure was determined for *N*-cyclohexyl-*N,N',N',N'',N''*-pentamethylguanidinium chloride (**5w**).

Method A (**1** → **2** → **3**):



Methods B (**1** → **4** → **5**) and C (**9** → **5**):

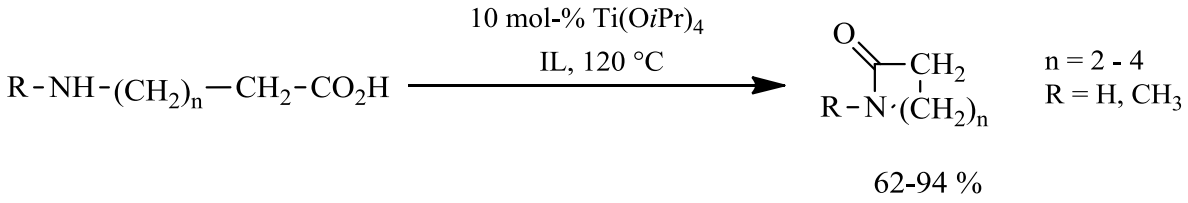


Scheme 20. *Synthesis of guanidinium-based ILs.*

Solubility tests have shown that aluminium isopropoxide is not soluble in hexaalkylguanidinium ILs at room temperature and can be dissolved only at 120-130 °C, whereas titanium isopropoxide dissolves readily in guanidinium bistriflimides with longer alkyl chains in the cation at room temperature. NMR experiments suggest that there is no interaction between titanium alcoholate and ionic liquid. Interestingly, in the ether-

functionalised guanidinium salts metal alcoholates are only sparingly soluble, although it was expected that formation of hydrogen bonds would favour the dissolution.

Solutions of titanium and aluminium isopropanolates in **6b** and **6h** have been chosen for further investigations and applied as mild catalytic media for some typical reactions of organic chemistry.



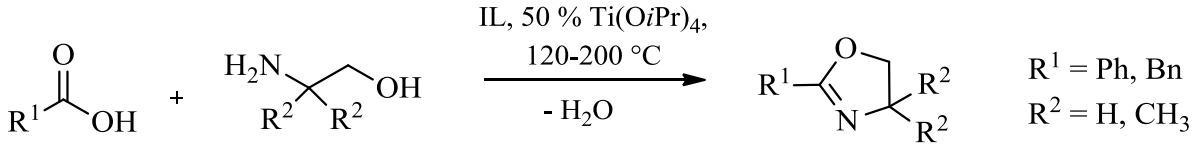
Scheme 21. *Reaction of lactamisation in hexaalkylguanidinium bistriflimides.*

With the application of hexaalkylguanidinium bistriflimides as solvents in the reaction of lactamisation (**Scheme 21**) we managed: a) to lower the amount of the catalyst significantly in comparison to the procedure in a chloro-containing organic solvent, b) to reduce the duration of the reaction (since the IL allows a higher reaction temperature), c) to use an easier work-up procedure (vacuum distillation of the product from the reaction mixture), d) to carry out several cycles without regeneration of IL, without extra addition of new catalyst before the next cycle and with little or no reduction in yield, e) to improve yields in some cases and f) to avoid the use of organic solvents and some disadvantages associated with them (e.g. volatility, flammability, disposal of chlorinated solvents etc.).

However, the titanium isopropoxide, used as a catalyst for lactamisation, was hydrolysed by the formed water, the precipitated porous TiO_2 could promote the next cycles. Interestingly, isolated precipitate presented amorphous material, which after calcination furnished pure anatase with a particle size of 30-60 nm (as determined by XRD and TEM). Noteworthy, the reaction of lactonisation with the same catalyst/IL system failed.

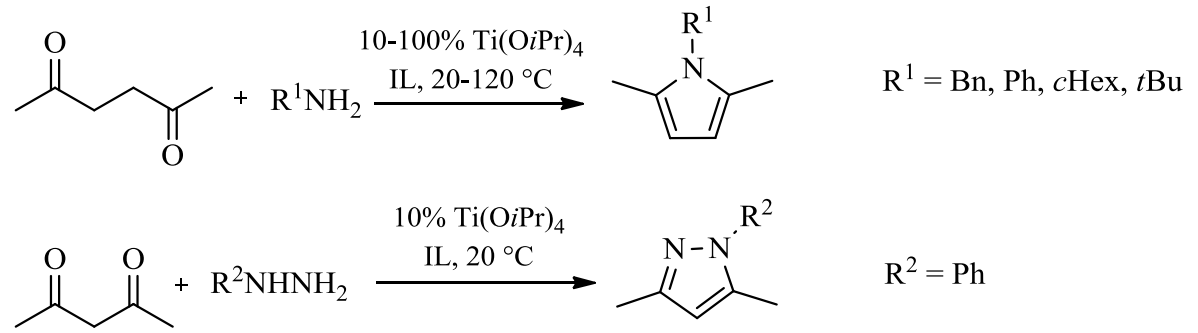
Inspired by the results of lactamisation reactions and direct amidation[196] of carboxylic acids in guanidinium ionic liquids, synthesis of 2-oxazolines (**Scheme 22**) has been investigated. Optimisation experiments revealed that the used catalyst is very weak for this type of reaction,

and increasing the temperature and the use of molecular sieve do not lead to acceptable yields. However, in the case of more nucleophilic amine (isobutanolamine) the reactions proceeded smoother, and the catalyst/IL system could be reused two more times with yields in the range 59-67 %. As satisfactory procedure with acceptable yield was not achieved for this reaction type, the use of a stronger Lewis acid is proposed.



Scheme 22. *Synthesis of 2-oxazolines in guanidinium-based ionic liquids.*

Paal-Knorr syntheses in a Ti(O*i*Pr)$_4$/IL system (**Scheme 23**) perform well when a mild Lewis acidic catalyst is needed. In the case of more sterically hindered amines (cyclohexylamine) higher ammounts of catalyst or elevated temperatures were needed. Notably, the reaction with *tert*-butylamine failed completely. The Paal-Knorr pyrrole synthesis was also successfully extended to the synthesis of 1-phenylpyrazole from 2,4-pentanedione and phenylhydrazine.



Scheme 23. *Investigated Paal-Knorr reactions.*

The developed procedures for the lactamisation reaction and Paal-Knorr synthesis in a guanidinium-IL reaction medium are convenient and efficient. It should be kept in mind that the developed procedures are only applicable when mild Lewis acidity of the catalyst is desirable. Compared to usual conditions (in an organic solvent) much lower amounts of catalyst could be used and the catalyst could be reused. This aspect is very promising from the viewpoint of atom economy, as the solvent (IL) and the catalyst immobilised in it can be

applied in many cycles and the only by-product formed is water. This is a significant step towards Green Chemistry synthesis.

Electrochemical studies, performed in the Institute of Electrochemistry at the University of Ulm, demonstrated that hexaalkylguanidinium ionic liquids are electrochemically less stable than widely applied and commercially available imidazolium and piperidinium salts. However, the introduction of a piperidinium moiety in the guanidinium cation improved the cathodic stability of the IL. At the same time, guanidinium bistriflimides have been chosen for further electrochemical applications, as more electrochemically stable, hydrophobic and less viscous ILs.

The electroplating of titanium from Ti(O*i*Pr)$_4$/guanidinium IL failed. The failture was attributed to the high moisture-sensitivity of the titanium isopropoxide in combination with the complexicity of the performed experiments (especially the performance of STM measurements). Otherwise, the electrodeposition of dysprosium from guanidinium-based ionic liquids on the Au(111) surface and a NeFeB-magnet (in the context of a cooperation with Siemens AG and Institute of Electrochemistry at the University of Ulm), as well as electrodeposition of iron has been successfully demonstrated.

Two further cooperations with TUM CREATE (Singapore) and Centre for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW, Ulm) concerned the application of hexasubstituted guanidinium bis(triflyl)imides in electrolytes of lithium-ion batteries. The IL-containing cells have been described with the help of Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), cycling tests have been performed as well. The cooperation with TUM CREATE showed that guanidinium ILs with a piperidinium moiety (**6l, 6q, 6u, 6v**) in the cation successfully combine the advantages of guanidinium and piperidinium ionic liquids for battery electrolyte applications, exemplified on Li/$LiFePO_4$ cells. Cooperation with ZSW stated that the anodic stability of the guanidinium salt, containing sterically more demanding substituents (**6w, 6x**), is high enough for application with state-of-the-art 3 V and 4 V cathode materials, and that they can be used with $LiFePO_4$. As for the anode, they are compatible with $Li_4Ti_5O_{12}$, but not with graphite.

6. Experimental part

6.1 General remarks

All reactions with potentially water-sensitive compounds were carried out under inert atmosphere. Argon from the firm MTI (purity grade 4.6, 99.996%) was used as inert atmosphere. The glass appliances were heated in vacuum and purged with argon before use. The two-stage rotary vane vacuum pump (Vakuumbrand RZ6, 5.7/6.8 m^3/h) was connected to a cooling trap and gave a total vacuum of 10^{-2} mbar.

All solvents used were distilled on the rotary evaporator before use. The solvents were dried according to standard procedures:[228] diethyl ether, pentane and cyclohexane were dried with natrium/benzophenone and subsequently distilled. Acetonitrile was at first distilled from KOH, then from P_2O_5. Dichloromethane and dichloroethane were predried with $CaCl_2$, filtered, distilled and refluxed with P_2O_5, followed by distillation. Ethyl acetate and *N*,*N*-dimethylformamide were refluxed with P_2O_5 and subsequently distilled. Solvents were stored in Schlenk vessels with 3 or 4 Å molecular sieves under argon.

All amines were stirred over one week with KOH, filtered, refluxed with a fresh portion of KOH for several hours and distilled. Amines were stored in Schlenk flasks under argon. Ureas were freshly distilled in vacuum with a Vigreux column. Oxalyl chloride was distilled before use. Carboxylic acids and amino acids were dried in vacuum. Metal alcoholates were distilled in vacuum and stored in Schlenk flasks under argon. Other chemicals were used without purification if not otherwise mentioned.

A bulb-to-bulb distillation of products and drying of ionic liquids was performed on the bulb-to-bulb distillation apparatus (Büchi, GKR 50).

Microwave synthesis was carried out in a microwave from the company MLS GmbH.

6.1.1 Analytic methods

The following equipment was applied to characterise the synthesised compounds.

^{1}H NMR spectroscopy	Bruker Avance 400 (400.13 MHz)
^{13}C NMR spectroscopy	Bruker Avance 400 (100.62 MHz)
	Bruker Avance 500 (125.77 MHz)
^{19}F NMR spectroscopy	Bruker Avance 400 (376.46 MHz)
IR spectroscopy	Bruker, Vektor 22 TFIR spectrometer, He-Ne-Laser (632.82 nm)
CI-MS	Finnigan MAT, SSQ-7000
Elemental analysis	Heraeus vario EL
	Elementar vario MICRO cube
Melting point	Büchi Melting point B540
Thermogravimetry	Mettler-Toledo TGA/SDTA 851
	Mettler Toledo STARe TGA/DSC1
Differential scanning calorimetry	Perkin Elmer DSC 7
Column chromatography	Silica gel 60 (0.063-0.200 mm), Merck
Thin layer chromatography	Alugram® Xtra SIL G/UV$_{254}$
Karl Fischer titration	Mettler Toledo DL36 KF Coulometer
X-ray structure analysis	Oxford Xcalibur diffractometer (SuperNova, Dual Source, Atlas CCD) using Cu-K$_\alpha$ radiation (λ = 1.5184 Å) at 180(2) K, software for structure solution and refinement: CrysAlis PRO, SHELXL-97; molecule plot: ORTEP-3
Transmission electron microscopy	TEM Zeiss EM10, accelerating voltage 80 kW, CCD-camera (TVIPS 1K·1K)

NMR

The chemical shifts are reported in parts per million (ppm) on the δ-scale. If not otherwise mentioned, the measurements were made at 300 K. ^{1}H NMR spectra are referenced to the

residual proton signal of the solvent ($\delta(CDCl_3)$ = 7.26 ppm, $\delta(CD_3CN)$ = 1.94 ppm, $\delta(CD_3OD)$ = 3.31 ppm, $\delta(D_2O)$ = 4.80 ppm). ^{13}C spectra are referenced to the solvent signal ($\delta(CDCl_3)$ = 77.00 ppm, $\delta(CD_3CN)$ = 118.26 ppm, $\delta(CD_3OD)$ = 49.00 ppm), and ^{19}F spectra to external C_6F_6 ($\delta(C_6F_6)$ = −162.9 ppm).

The coupling constants are given in Herz (Hz). The following abbreviations are applied to characterise the splitting pattern of the NMR signals: s = singlet, d = doublet, t = triplet, ψt = pseudotriplet, q = quartet, m = multiplet, bs = broad singlet).

In some cases $^{1}H,^{13}C$-HSQC, HMBC spectra were measured for the assignment of the signals.

IR

The solid compounds were pressed in KBr pellets. Liquid samples were sandwiched between two plates of sodium chloride. Some samples (both solid and liquid) were measured on a ATR headpiece. The intensity of the adsorption bands is abbreviated as follows: vs = very strong, s = strong, m = medium, w = weak, br = broad.

Mass spectrometry

The mass spectrometry measurements were performed at the service center of mass spectrometry (University of Ulm).

Elemental analysis

The elemental analyses were conducted at the Institute of Organic Chemistry I as well as at the service center of elemental analysis (University of Ulm). Some samples were measured in the Institute of Organic Chemistry at the University of Stuttgart.

Differential scanning calorimetry (DSC)

The measurements were carried out between -140 and 40 °C with the heating/cooling rate of 10 °C/min. DSC was performed in the Institute of Inorganic Chemistry I.

Thermogravimetry (TG)

The measurements were carried out between 30 and 800 °C with the heating rate of 10 °C/min under nitrogen atmosphere. TG was performed in the Institute of Inorganic Chemistry I. The decomposition behaviour of ILs **6l**, **6q**, **6u**, **6v** was also measured in TUM CREATE, Singapore.

6.1.2 Starting compounds

Starting compounds were purchased from the chemical suppliers (Merck, ABCR, Alfa Aesar, Acros organics, VWR and Iolitec) or synthesised according to the referenced procedures.

Tetramethylurea
Butylmethylamine
Dihexylamine
Bis(2-methoxyethyl)amine
N-Cyclohexyl-*N*-methylamine
(Dichloromethylene)dimethylamminium chloride
Oxalyl chloride
N,*N*-Dimethylcarbamoylchloride (96%)
1,1'-Carbonyldipiperidine
Lithium bis(trifluoromethylsulfonyl)imide
Potassium hexafluorophospate
Sodium dicyanamide
Titanium(IV) isopropoxide
Tetrakis(trimethylsilyloxy)titanium
Titanium(IV) 2-ethylhexoxide
Aluminium triisopropanolate
Aluminium *sec*-butoxide
2,5-Hexanedione
4-Aminobutyric acid
6-Aminohexanoic acid
Triflic anhydride[229]
Bis(*N*,*N*-diethyl-*N',N'*-dimethylamidinio) ether bis(trifluoromethanesulfonate)[31]

Bis(*N*,*N*-dibutyl-*N',N'*-diethylamidinio) ether bis(trifluoromethanesulfonate)[31]

Bis(*N,N,N',N'*-tetrabutylamidinio) ether bis(trifluoromethanesulfonate)[31]

N,*N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dimethylguanidinium trifluoromethanesulfonate[31]

N,*N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dihexylguanidinium trifluoromethanesulfonate[31]

N,*N*-Diethyl-*N',N'*-bis(methoxyethyl)-*N'',N''*-dimethylguanidinium trifluoromethanesulfonate[31]

N,*N*,*N',N',N'',N''*-Hexabutylguanidinium trifluoromethanesulfonate[31]

N,*N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dimethylguanidinium chloride[43,144]

N,*N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dihexylguanidinium chloride[43,144]

N,*N*-Diethyl-*N',N'*-bis(methoxyethyl)-*N'',N''*-dimethylguanidinium chloride[43]

N,N'-Dibutyl-*N,N',N'',N''*-tetramethylguanidinium chloride[35]

N,N,N',N'-Tetrahexyl-*N'',N''*-dimethylguanidinium chloride[35]

N,*N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dimethylguanidinium bis(trifluoromethylsulfonyl)-imide[43,144]

N,*N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dihexylguanidinium bis(trifluoromethylsulfonyl)-imide[43,144]

N,*N*-Diethyl-*N',N'*-bis(methoxyethyl)-*N'',N''*-dimethylguanidinium bis(trifluoromethylsulfonyl)imide[43]

N,N'-Dibutyl-*N,N',N'',N''*-tetramethylguanidinium bis(trifluoromethylsulfonyl)imide[35]

N,N,N',N'-Tetrahexyl-*N'',N''*-dimethylguanidinium bis(trifluoromethylsulfonyl)imide[35]

N-Methyl-γ-aminobutyric acid[230]

5-Aminopentanoic acid[231]

Some of the ureas and solutions of *N*,*N*-dibutyl-*N',N'*-diethylchloroformamidinium chloride, *N*,*N*-dibutyl-*N',N'*-dihexylchloroformamidinium chloride, *N*,*N*-dimethyl-*N',N'*-dipropylchloroformamidinium chloride in acetonitrile were kindly provided by *Prof. Dr. W. Kantlehner* (FH Aalen).

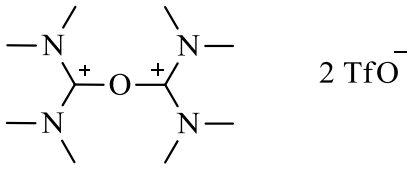
The chemicals not mentioned above were available in the Institute of Organic Chemistry I.

6.2 Synthetic procedures

6.2.1 Synthesis of hexaalkylguanidinium trifluoromethanesulfonates

6.2.1.1 Synthesis of dication ether salts

6.2.1.1.1 Synthesis of bis(*N,N,N',N'*-tetramethylamidinio) ether bis(trifluoromethanesulfonate) (2a)



Tetramethylurea	29.7 mmol	7.12 mL
Triflic anhydride	59.4 mmol	5.00 mL
Dichloromethane		100 mL

Prepared according to the procedure given in [31]. To a solution of triflic anhydride in 60 mL of dry dichloromethane, which was placed in a Schlenk flask, tetramethylurea in 40 mL of dry dichloromethane was added dropwise under argon atmosphere and cooling to 0 °C. After the addition was complete, the reaction mixture was stirred at 0 °C for 1 h, brought to room temperature and finally heated at reflux for 6 h. After cooling to room temperature, the colourless precipitate was filtered off, washed with dry dichloromethane and dried in vacuum for several hours (20 °C/0.01 mbar).

Yield: 12.2 g (80%); m.p. 254–256 °C.

^{1}H NMR (CD_3CN): δ = 3.17 (s, 24 H, NCH_3) ppm.

^{13}C NMR (CD_3CN): δ = 42.1 (NCH_3), 157.0 (CN_2O) ppm.

^{19}F NMR ($CDCl_3$): δ = -74.9 ppm.

IR (ATR): ν = 2965 (w), 1711 (s), 1686 (s), 1518 (m), 1472 (m), 1415 (m), 1263 (s), 1225 (s), 1158 (s), 1031 (s), 882 (w), 765 (m), 639 (s) cm^{-1}.

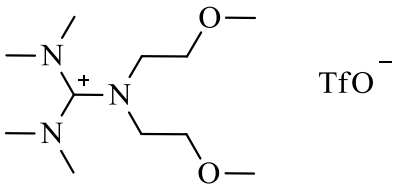
CHN (in %): $C_{12}H_{24}F_6N_4O_7S_2$ (514.46 g/mol)

Calcd.	C 28.02	H 4.70	N 10.89
Found	C 27.88	H 4.79	N 11.01

6.2.1.2 Synthesis of hexaalkylguanidinium trifluoromethanesulfonates

General procedure, according to lit. [31]. A suspension of a bis(amidinio)ether bis(trifluoromethanesulfonate) in dry dichloromethane was prepared and cooled with an ice bath to 0 °C. A solution of a *sec*-amine (2–2.05 equiv.) in dry dichloromethane was added. After 30 min at 0 °C, the mixture was stirred for 1 h at room temperature and finally heated at reflux for 1–40 h. After cooling the solution was concentrated on the rotary evaporator, and *n*-pentane (10 mL) was added in order to extract the formed urea. The lower (oily) phase was dissolved in dichloromethane and washed with 0.1 M NaOH; the organic phase was dried with Na_2SO_4. The solvent was evaporated, and the salt was dried on the bulb-to-bulb apparatus to remove the remaining traces of volatiles (solvents, amines) for 8 h at 60 °C/0.01 mbar.

6.2.1.2.1 Synthesis of *N,N*-bis(2-methoxyethyl)-*N',N',N",N"*-tetramethylguanidinium trifluoromethanesulfonate (3d)



Dication ether salt **2a**	9.70 mmol	5.00 g
Bis(methoxyethyl)amine	19.44 mmol	2.85 mL
Dichloromethane		60 mL

Prepared according to the general procedure, refluxed for 40 h. The product was obtained as a light yellow solid.

Yield: 3.1 g (84%); m.p. = 67 °C; T_{dec} = 408 °C.

^{1}H NMR ($CDCl_3$): δ = 2.95 and 3.00 (2 s, each 6 H, NCH_3), 3.32 (s, 6 H, OCH_3), 3.27-3.47 (m, 6 H, NCH_2CH_2 and NCH_2), 3.57-3.67 (m, 2 H, NCH_2CH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 39.9 and 40.2 (NCH_3), 49.2 (NCH_2), 58.8 (CH_3O), 68.8 (NCH_2CH_2), 118.2 and 121.4 (CF_3), 164.4 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -74.7 ppm.

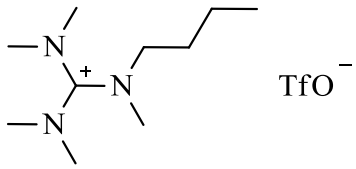
IR (ATR): ν = 2922 (w), 2804 (w), 1599 (vs), 1471 (m), 1403 (s), 1262 (m), 1169 (m), 1146 (m), 1070 (m), 905 (s) cm^{-1}.

MS (CI): *m*/*z* = 232 (100%, $[cation]^+$).

CHN (in %): $C_{12}H_{26}F_3N_3O_5S$ (381.41 g/mol)

Calcd.	C 37.79	H 6.87	N 11.02
Found	C 37.83	H 7.19	N 11.11

6.2.1.2.2 Synthesis of *N*-butyl-*N,N',N',N'',N''*-pentamethylguanidinium trifluoromethanesulfonate (3e)



Dication ether salt **2a**	7.78 mmol	4.00 g
Butylmethylamine	15.56 mmol	1.84 mL
Dichloromethane		45 mL

Prepared according to the general procedure, refluxed for 3 h. The product was obtained as a yellow solid.

Yield: 1.8 g (70%); m.p. = 59 °C; T_{dec} = 453 °C, T_g = -93 °C.

^{1}H NMR ($CDCl_3$): δ = 0.90-0.94 (t, ^3J = 7.2 Hz, 3 H, CH_3CH_2), 1.20-1.70 (several m, 4 H, $CH_3CH_2CH_2CH_2N$), 2.94 and 2.96 (2 overlapped s, 15 H, NCH_3), 3.05-3.25 (m, 2 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.6 (CH_3CH_2), 19.8 ($CH_3CH_2CH_2CH_2N$), 29.5($CH_3CH_2CH_2CH_2N$), 37.8 ($N(C_4H_9)CH_3$), 40.2 (broad, 4 NCH_3), 52.4 (NCH_2), 119.2 and 122.4 (CF_3), 163.4 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -74.7 ppm.

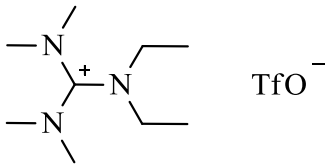
IR (ATR): ν = 2973 (w), 1597 (s), 1576 (s), 1475 (m), 1409 (s), 1250 (vs), 1225 (s), 1152 (vs), 1026 (vs), 891 (s) cm^{-1}.

MS (CI): *m*/*z* = 186 (100%, $[cation]^+$).

CHN (in %): $C_{11}H_{24}F_3N_3O_5S$ (335.39 g/mol)

Calcd.	C 39.39	H 7.21	N 12.53
Found	C 39.37	H 7.41	N 12.54

6.2.1.2.3 Synthesis of *N*,*N*-diethyl-*N'*,*N'*,*N"*,*N"*-tetramethylguanidinium trifluoromethanesulfonate (3f)



Dication ether salt **2a**	3.31 mmol	1.71 g
Diethylamine	6.62 mmol	0.69 mL
Dichloromethane		20 mL

Prepared according to the general procedure, refluxed for 1 h. The product was obtained as a light yellow solid.

Yield: 0.43 g (40%); m.p. = 195 °C; T_{dec} = 462 °C.

^{1}H NMR ($CDCl_3$): δ = 1.21-1.25 (t, ^3J = 7.2 Hz, 6 H, CH_3CH_2), 2.98 and 3.03 (2 s, 12 H, NCH_3), 3.24-3.29 (q, ^3J = 7.2 Hz, 4 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 12.9 (CH_3CH_2), 40.3 and 40.4 (NCH_3), 43.5 (NCH_2), 163.4 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -74.7 ppm.

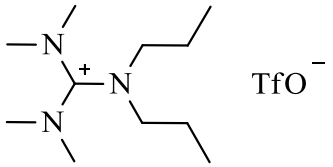
IR (ATR): ν = 2922 (w), 1599 (vs), 1471 (m), 1403 (s), 1262 (m), 1217 (m), 1168 (m), 1146 (m), 1069 (m), 904 (s) cm^{-1}.

MS (CI): *m*/*z* = 172 (100%, $[cation]^+$).

CHN (in %): $C_{10}H_{22}F_3N_3O_5S$ (321.36 g/mol)

Calcd.	C 37.37	H 6.90	N 13.08
Found	C 37.25	H 6.99	N 13.02

6.2.1.2.4 Synthesis of *N,N*-dipropyl-*N',N',N",N"*-tetramethylguanidinium trifluoromethanesulfonate (3g)



Dication ether salt **2a**	1.94 mmol	1.00 g
Dipropylamine	3.88 mmol	0.53 mL
Dichloromethane		15 mL

Prepared according to the general procedure, refluxed for 3 h. The product was obtained as a colourless solid.

Yield: 0.24 g (36%); m.p. = 162 °C; T_{dec} = 455 °C, T_g = -92 °C.

^{1}H NMR ($CDCl_3$): δ = 0.93-0.97 (t, ^3J = 7.3 Hz, 6 H, C*H*$_3$CH$_2$), 1.45-1.75 (several m, 4 H, CH$_3$C*H*$_2$CH$_2$N), 2.99 and 3.03 (2 s, 12 H, NCH_3), 3.00-3.25 (m, 4 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 11.2 (C*H*$_3$CH$_2$), 20.9 (CH$_3$*C*H$_2$CH$_2$N), 40.4 and 40.5 (NCH_3), 51.1 (NCH_2), 163.4 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -74.7 ppm.

IR (ATR): ν = 2968 (w), 2880 (w), 1568 (s), 1454 (m), 1410 (m), 1262 (vs), 1225 (s), 1137 (s), 1030 (vs), 888 (m) cm^{-1}.

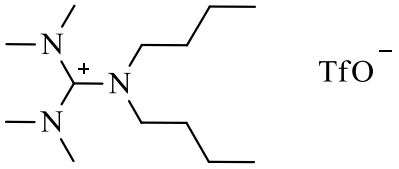
MS (CI): *m*/*z* = 200 (100%, $[cation]^+$).

CHN (in %): $C_{12}H_{26}F_3N_3O_5S$ (349.41 g/mol)

Calcd.	C 41.25	H 7.50	N 12.03

Found	C 41.20	H 7.60	N 12.00

6.2.1.2.5 Synthesis of *N,N*-dibutyl-*N',N',N",N"*-tetramethylguanidinium trifluoromethanesulfonate (3h)



Dication ether salt **2a**	9.7 mmol	5.0 g
Dibutylamine	19.4 mmol	3.3 mL
Dichloromethane		60 mL

Prepared according to the general procedure, refluxed for 2 h. The product was obtained as a light yellow oil.

Yield: 2.87 g (78%); T_{dec} = 456 °C, T_g = -73 °C.

^{1}H NMR ($CDCl_3$): δ = 0.93-0.96 (t, ^3J = 7.3 Hz, 6 H, C*H*$_3$CH$_2$), 1.20-1.65 (several m, 8 H, CH$_3$C*H*$_2$C*H*$_2$CH$_2$N), 2.98 and 3.03 (2 s, each 6 H, NCH$_3$), 3.05-3.20 (m, 4 H, NCH$_2$) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.7 (C*H*$_3$CH$_2$), 20.0 (CH$_3$*C*H$_2$CH$_2$CH$_2$N), 29.6 (CH$_3$CH$_2$*C*H$_2$CH$_2$N), 40.4 (NCH$_3$), 49.3 (NCH$_2$), 163.3 (CN$_3$) ppm.

^{19}F NMR ($CDCl_3$): δ = -74.7 ppm.

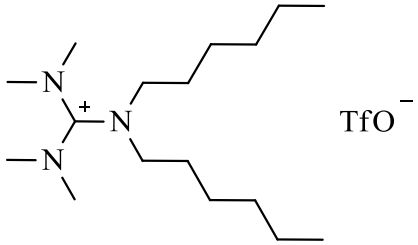
IR (NaCl): ν = 2962 (s), 2936 (s), 2876 (m), 1593 (s), 1568 (s), 1464 (m), 1435 (m), 1411 (m), 1268 (s), 1224 (m), 1150 (s), 1032 (s), 897 (s) cm^{-1}.

MS (CI): *m*/*z* = 228 (100%, [cation]$^+$).

CHN (in %): $C_{14}H_{30}F_3N_3O_5S$ (377.47 g/mol)

Calcd.	C 44.55	H 8.01	N 11.13
Found	C 44.59	H 8.49	N 11.15

6.2.1.2.6 Synthesis of *N,N*-dihexyl-*N',N',N",N"*-tetramethylguanidinium trifluoromethanesulfonate (3i)



Dication ether salt **2a**	3.9 mmol	2.0 g
Dihexylamine	7.8 mmol	1.8 mL
Dichloromethane		25 mL

Prepared according to the general procedure, refluxed for 6 h. The product was obtained as a light yellow solid.

Yield: 0.9 g (53%); m.p. = 47 °C, T_{dec} = 438 °C.

^{1}H NMR ($CDCl_3$): δ = 0.87-0.91 (ψt, 6 H, C*H*$_3$CH$_2$), 1.20-1.70 (several m, 16 H, CH$_3$(C*H*$_2$)$_2$CH$_2$N), 2.98 and 3.04 (2 s, each 6 H, NCH$_3$), 3.05-3.20 (m, 4 H, NCH$_2$) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.7 (C*H*$_3$CH$_2$), 20.0 (CH$_3$*C*H$_2$CH$_2$CH$_2$N), 29.6 (CH$_3$CH$_2$*C*H$_2$CH$_2$N), 40.4 (NCH$_3$), 49.3 (NCH$_2$), 163.3 (CN$_3$) ppm.

^{19}F NMR ($CDCl_3$): δ = -74.7 ppm.

IR (ATR): ν = 2963 (m), 2930 (m), 2863 (m), 1593 (m), 1562 (s), 1409 (m), 1258 (s), 1223 (m), 1147 (s), 1030 (s), 897 (w) cm^{-1}.

MS (CI): *m*/*z* = 284 (100%, [cation]$^+$).

CHN (in %): $C_{18}H_{38}F_3N_3O_5S$ (433.57 g/mol)

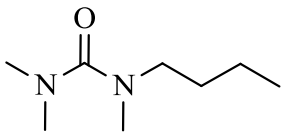
Calcd.	C 49.86	H 8.83	N 9.69
Found	C 49.88	H 8.86	N 9.67

6.2.2 Synthesis of hexaalkylguanidinium chlorides

6.2.2.1 Synthesis of tetraalkylureas

General procedure, analog to lit. [142]. Triethylamine (1 mol) and the corresponding secondary amine (1 mol) were dissolved in dry acetonitrile (500 mL). To this solution *N*,*N*-dialkylcarbamoylchloride (1 mol) was added dropwise and with stirring at –10 °C. The temperature of the mixture was kept by cooling with a sodium chloride/ice bath. Then the cooling bath was removed and the mixture was stirred for 16 h. The separated triethylamine hydrochloride was filtered off and the acetonitrile was removed in a rotary evaporator from the filtrate. Dry ether was added to the residue (400 mL) and the mixture was set aside in a refrigerator (2 °C) for 16 h. The separated salt was filtered off. From the filtrate the ether was distilled. The residue was distilled through a Vigreux-column with fractionation.

6.2.2.1.1 Synthesis of *N*-butyl-*N*,*N*',*N*'-trimethylurea (1a)



Triethylamine	84.9 mmol	11.8 mL
Butylmethylamine	84.9 mmol	10.0 mL
N,*N*-dimethylcarbamoylchloride	84.9 mmol	7.8 mL
Acetonitril		50 mL

Prepared according to the general procedure, distilled in water-jet vacuum at overhead temperature 91-93 °C. The product was obtained as a colourless oil.

Yield: 11.86 g (88%).

^{1}H NMR ($CDCl_3$): δ = 0.89-0.93 (t, 3 H, ^3J = 7.3 Hz, $CH_3(CH_2)_3N$), 1.23-1.33 (m, 2 H, $CH_3CH_2(CH_2)_2N$), 1.47-1.55 (m, 2 H, $CH_3CH_2CH_2CH_2N$), 2.77 (s, 9 H, NCH_3), 3.11-3.15 (t, 2 H, ^3J = 7.5 Hz, $CH_3(CH_2)_2CH_2N$) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.9 ($CH_3(CH_2)_3N$), 20.0 ($CH_3CH_2(CH_2)_2N$), 29.7 ($CH_3CH_2CH_2CH_2N$), 36.3 ($N(CH_3)C_4H_9$), 38.7 ($N(CH_3)_2$), 50.1 ($CH_3(CH_2)_2CH_2N$), 165.6 (N_2CO) ppm.

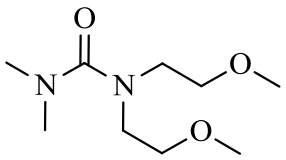
IR (ATR): ν = 2957 (m), 2931 (m), 2870 (m), 1649 (s), 1497 (m), 1383 (m), 1142 (m), 1092 (w), 913 (w), 783 (w) cm^{-1}.

MS (CI): *m*/*z* = 159 (94%, $[M+H]^+$).

CHN (in %): $C_8H_{18}N_2O{\cdot}0.20H_2O$ (158.24 + 3.60 g/mol)

Calcd.	C 59.04	H 11.46	N 17.21
Found	C 59.07	H 11.33	N 17.25

6.2.2.1.2 Synthesis of *N*,*N*-bis(2-methoxyethyl)-*N'*,*N'*-dimethylurea (1b)



Triethylamine	108.6 mmol	15.1 mL
Bis(2-methoxyethyl)amine	108.6 mmol	15.9 mL
N,*N*-dimethylcarbamoylchloride	108.6 mmol	10.0 mL
Acetonitril		50 mL

Prepared according to the general procedure, distilled at overhead temperature 85-95 °C/0.06 mbar. The product was obtained as a colourless oil.

Yield: 22.4 g (83%).

^{1}H NMR ($CDCl_3$): δ = 2.79 (bs, 6 H, NCH_3), 3.31 (bs, 6 H, OCH_3), 3.36-3.39 (ψt, 4 H, ^3J = 5.9 Hz, $CH_3OCH_2CH_2N$), 3.47-3.50 (t, 4 H, ^3J = 6.0 Hz, $CH_3OCH_2CH_2N$) ppm.

^{13}C NMR ($CDCl_3$): δ = 38.7 ($N(CH_3)_2$), 48.4 ($CH_3OCH_2CH_2N$), 58.8 ($CH_3OCH_2CH_2N$), 70.9 ($CH_3OCH_2CH_2N$), 165.2 (N_2CO) ppm.

IR (NaCl): ν = 2928 (m), 2882 (m), 1647 (s), 1491 (m), 1390 (m), 1187 (m), 1118 (s), 1014 (w), 966 (w), 781 (w) cm^{-1}.

MS (CI): *m*/*z* = 205 (43%, $[M+H]^+$).

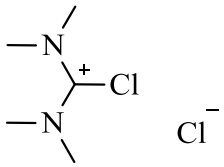
CHN (in %): $C_9H_{20}N_2O_3$ (204.27 g/mol)

Calcd.	C 52.92	H 9.87	N 13.71
Found	C 52.92	H 9.92	N 13.88

6.2.2.2 Synthesis of chloroformamidinium chlorides

General procedure, modified analogous to the procedure given in lit. [232]. *N,N,N',N'*-Tetraalkylchloroformamidinium chloride was obtained by adding dropwise tetraalkylurea to freshly distilled oxalyl chloride (10% excess) dissolved in dry dichloromethane under argon atmosphere. The solution was stirred overnight at room temperature or refluxed (evolution of CO-gas), and then the solvent was removed under water-jet vacuum. The remaining solid was washed several times with dry diethylether until the washing ether was colourless (to remove the excess of oxalyl chloride, the unreacted urea and coloured impurities). A solid or liquid moisture-sensitive product was dried for 3 h at 20 °C/0.05 mbar.

6.2.2.2.1 Synthesis of *N,N,N',N'*-tetramethylchloroformamidinium chloride (4a)



Tetramethylurea	167.0 mmol	20.0 mL
Oxalyl chloride	183.0 mmol	15.7 mL
Dichloromethane		70 mL

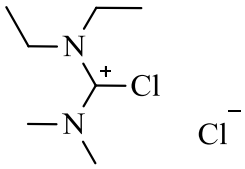
Prepared according to the general procedure. The product was obtained as a white moisture-sensitive powder.

Yield: 27.09 g (95%); m.p. = 159-161 °C.

^{1}H NMR ($CDCl_3$): δ = 3.55 (s, 12 H, NCH_3) ppm.

^{13}C NMR ($CDCl_3$): δ = 44.8 (NCH_3), 159.0 ($C^+Cl[N(CH_3)_2]_2$) ppm.

6.2.2.2.2 Synthesis of *N,N*-diethyl-*N',N'*-dimethylchloroformamidinium chloride (4b)



N,N-diethyl-*N',N'*-dimethylurea	96.7 mmol	15.0 mL
Oxalyl chloride	106.4 mmol	9.1 mL
Dichloromethane		60 mL

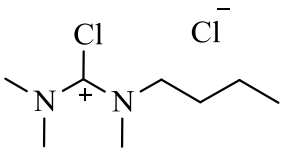
Prepared according to the general procedure after 4 h under reflux. The product was obtained as a light yellow moisture-sensitive powder.

Yield: 18.0 g (93%); m.p. = 80-82 °C.

^{1}H NMR ($CDCl_3$): δ = 1.37-1.41 (ψt, 6 H, C*H*$_3$CH$_2$N), 3.59 (bs, 6 H, NCH$_3$), 3.85-3.95 (m, 4 H, CH$_3$C*H*$_2$N) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.2 (*C*H$_3$CH$_2$N), 45.5 (NCH$_3$), 49.3 (CH$_3$*C*H$_2$N) ppm.

6.2.2.2.3 Synthesis of *N*-butyl- *N,N',N'*-trimethylchloroformamidinium chloride (4c)



N-butyl-*N,N',N'*-trimethylurea	62.1 mmol	9.8 g
Oxalyl chloride	68.3 mmol	5.9 mL
Dichloromethane		50 mL

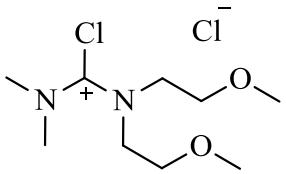
Prepared according to the general procedure after 3 h under reflux. The product was obtained as a light yellow moisture-sensitive powder.

Yield: 10.8 g (81%); m.p. = 110-112 °C.

^{1}H NMR ($CDCl_3$): δ = 0.88-0.94 (t, 3 H, ^{3}J = 7.3 Hz, CH_3(CH_2)$_3$N), 1.30-1.39 (m, 2 H, CH_3CH_2(CH_2)$_2$N), 1.68-1.75 (m, 2 H, CH_3CH_2CH_2CH_2N), 3.56 (bs, 6 H, N(CH_3)$_2$), 3.58 (bs, 3 H, N(CH_3)C_4H_9), 3.69-3.73 (m, 2 H, CH_3(CH_2)$_2$CH_2N) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.5 (*C*H_3(CH_2)$_3$N), 19.7 (CH_3*C*H_2(CH_2)$_2$N), 28.8 (CH_3CH_2*C*H_2CH_2N), 42.7 (N(*C*H_3)C_4H_9), 45.2 (N(CH_3)$_2$), 56.7 (CH_3(CH_2)$_2$*C*H_2N), 158.7 (N_2CCl) ppm.

6.2.2.2.4 Synthesis of *N,N*-bis(2-methoxyethyl)-*N',N'*-dimethylchloroformamidinium chloride (4d)



Method A:

N,N-bis(2-methoxyethyl)-*N',N'*-dimethylurea	9.8 mmol	2.0 g
Oxalyl chloride	10.8 mmol	0.9 mL
Dichloromethane		20 mL

Prepared according to the general procedure after 3 h under reflux. The product was obtained as a yellow moisture-sensitive powder.
Yield: 1.7 g (67%).

Method B:

N,N-bis(2-methoxyethyl)-*N',N'*-dimethylurea	68.5 mmol	14.0 g
Oxalyl chloride	122.3 mmol	10.5 mL
Dichloromethane		140 mL

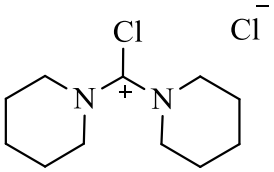
Prepared according to the general procedure after 14 h under reflux. The product was obtained as a light yellow moisture-sensitive powder.
Yield: 16.3 g (92%).

M.p. = 68-70 °C.

^{1}H NMR ($CDCl_3$): δ = 3.35 (bs, 6 H, NCH_3), 3.57 (bs, 6 H, OCH_3), 3.68-3.74 (t, 4 H, ^{3}J = 4.8 Hz, $CH_3OCH_2CH_2N$), 4.11-4.14 (t, 4 H, ^{3}J = 4.8 Hz, $CH_3OCH_2CH_2N$) ppm.

^{13}C NMR ($CDCl_3$): δ = 45.4 ($N(CH_3)_2$), 54.2 ($CH_3OCH_2CH_2N$), 59.1 ($CH_3OCH_2CH_2N$), 69.5 ($CH_3OCH_2CH_2N$) ppm.

6.2.2.2.5 Synthesis of *N,N,N',N'*-bis(pentamethylene)chloroformamidinium chloride (4e)



1,1-Carbonyldipiperidine	16.6 mmol	3.3 g
Oxalyl chloride	18.3 mmol	1.6 mL
Dichloromethane		30 mL

Prepared according to the general procedure after 9 h under reflux. The product was obtained as a yellow moisture-sensitive powder.

Yield: 4.0 g (95%).

^{1}H NMR ($CDCl_3$): δ = 1.75-1.90 (m, 6 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.95-4.05 (m, 4 H, 2-H_{pip}, 6-H_{pip}) ppm.

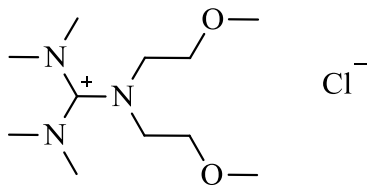
6.2.2.3 Synthesis of hexaalkylguanidinium chlorides

General procedure A, modified analogous to the procedure given in lit. [28,43]. To a solution of tetraalkylchloroformamidinium chloride in dry acetonitrile was added a solution of *sec.* amine (1 equiv.) and triethylamine (1 equiv.) in dry diethyl ether under argon atmosphere at room temperature. The mixture was stirred overnight, the precipitated ammonium salt was filtered off, and the volatiles were evaporated at 40 °C/180 mbar. In order to destroy remaining ammonium salt(s), 0.1 M aqueous NaOH was added to the residual oil until the pH

was slightly alkaline. To remove the coloured impurities, the aqueous solution was washed several times with diethylether. Water and triethylamine were distilled off on the rotary evaporator (40 °C/70 mbar), and the remaining residue was subsequently dried at 50 °C/0.05 mbar. Afterwards it was dissolved in dry acetonitrile/diethylether (2:1, v/v) and the solid was filtered off. The organic solvents were evaporated. Washing with a dry diethyl ether was effective to provoke the crystallisation of the product and to remove some colourful impurities. The product was dried for 8 h at 80 °C/0.05 mbar.

General procedure B, modified analogous to the procedure given in lit. [28,36,43]. The salt was prepared from a *sec*-amine, triethylamine and tetraalkylchloroformamidinium chloride as described in general procedure A. The mixture was stirred overnight at room temperature. The precipitated triethylammonium chloride was filtered off, and the solvents were removed in a rotary evaporator at 40 °C/180 mbar. To the residual oil a 0.1 M aqueous NaOH solution was added until the pH was slightly alkaline. To remove the coloured impurities, the aqueous solution was washed several times with diethyl ether. Then it was saturated with NaCl and extracted several times with dichloromethane. The combined organic phases were dried with Na_2SO_4. The solvent was removed and the product was dried for 8 h at 80 °C/0.05 mbar.

6.2.2.3.1 Synthesis of *N,N*-bis(2-methoxyethyl)-*N',N',N",N"*-tetramethylguanidinium chloride (5d)



Tetramethylchloroformamidinium chloride	**(4a)**	23.4 mmol	4.0 g
Bis(2-methoxyethyl)amine		23.4 mmol	3.4 mL
Triethylamine		23.4 mmol	3.3 mL
Acetonitrile			30 mL
Diethyl ether			15 mL

Prepared according to the general procedure A. The product was obtained as a colourless hygroscopic solid.

Yield: 4.3 g (69%); m.p. = 83 °C, T_{dec} = 305 °C.

^{1}H NMR ($CDCl_3$): δ = 3.06 and 3.08 (2 s, each 6 H, NCH_3), 3.33 (s, 6 H, OCH_3), 3.42-3.55 (m, 6 H, NCH_2CH_2 and NCH_2), 3.65-3.75 (m, 2 H, NCH_2CH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 40.2 and 40.6 (NCH_3), 49.4 (NCH_2), 58.9 (CH_3O), 69.2 (NCH_2CH_2), 164.4 (CN_3) ppm.

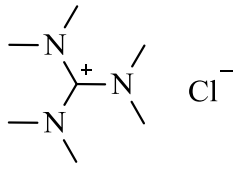
IR (KBr): ν = 2937 (m), 2903 (m), 2829 (w), 1602 (vs), 1565 (vs), 1458(m), 1432 (m), 1409 (s), 1115 (s), 1064 (w), 1012 (w), 893 (w) cm^{-1}.

MS (CI): *m*/*z* = 232 (20%, $[cation]^+$).

CHN (in %): $C_{11}H_{26}ClN_3O_2 \cdot 0.5H_2O$ (267.80 + 9.00 g/mol)

Calcd.	C 47.73	H 9.83	N 15.18
Found	C 47.75	H 10.07	N 15.21

6.2.2.3.2 Synthesis of *N,N,N',N',N'',N''*-hexamethylguanidinium chloride (5e)



Tetramethylchloroformamidinium chloride	**(4a)**	59.3 mmol	10.2 g
N,*N*-dimethyl(trimethylsilyl)amine		65.2 mmol	10.5 mL
Chloroform			70 mL

Prepared according to a modified procedure given in lit. [232]. Tetramethylchloroformamidinium chloride was dissolved in dry chloroform and cooled to 0 °C. A solution of dimethyl(trimethylsilyl)amine (10% excess) in dry chloroform was added in small portions under argon atmosphere. Then the reaction mixture was refluxed for 3 h and cooled down. All volatile components were evaporated in a rotary evaporator (40 °C/40 mbar). The remaining solid was recrystallised from acetonitrile/dimethylformamide (1:1, v/v). The colourless crystals were dried for 8 h at 80 °C/0.05 mbar.

Yield: 9.4 g (84%); m.p. = 290 °C, T_{dec} = 329 °C.

^{1}H NMR ($CDCl_3$): δ = 3.09 (s, 18 H, NCH_3) ppm.

^{13}C NMR ($CDCl_3$): δ = 40.6 (NCH_3), 163.2 (CN_3) ppm.

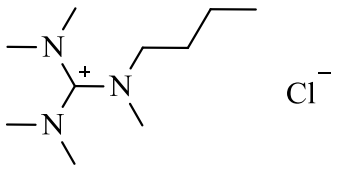
IR (ATR): ν = 2923 (w), 2907 (w), 1602 (s), 1585 (s), 1473 (m), 1403 (s), 1262 (m), 1168 (m), 1146 (m), 1071 (m), 906 (s) cm^{-1}.

MS (CI): *m*/*z* = 144 (100%, $[cation]^+$).

CHN (in %): $C_7H_{18}ClN_3 \cdot 0.5H_2O$ (179.69 + 8.00 g/mol)

Calcd.	C 44.56	H 10.15	N 22.27
Found	C 44.68	H 10.74	N 22.55

6.2.2.3.3 Synthesis of *N*-butyl-*N*,*N*',*N*',*N*",*N*"-pentamethylguanidinium chloride (5f)



Tetramethylchloroformamidinium chloride	**(4a)**	20.0 mmol	3.4 g
Butylmethylamine		20.0 mmol	2.4 mL
Triethylamine		20.0 mmol	2.8 mL
Acetonitrile			25 mL
Diethyl ether			15 mL

Prepared according to the general procedure A. The product was obtained as a light yellow hygroscopic solid.

Yield: 3.2 g (73%); m.p. = 91 °C, T_{dec} = 310 °C, T_g = -46 °C.

^{1}H NMR ($CDCl_3$): δ = 0.93-0.97 (t, 3 H, ^{3}J = 7.3 Hz, $N(CH_2)_3CH_3$), 1.20-1.60 (several m, 4 H, $N(CH_2)_2CH_2CH_3$ and $NCH_2CH_2CH_2CH_3$), 3.04-3.11 (several overlapped s, 12 H, NCH_3), 3.18 (bs, 3 H, $N(CH_3)C_4H_9$), 3.20-3.24 (t, 2 H, ^{3}J = 7.5 Hz, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.5 ($N(CH_2)_3CH_3$), 19.7 ($N(CH_2)_2CH_2CH_3$), 29.4 ($NCH_2CH_2CH_2CH_3$), 38.1 ($N(CH_3)C_4H_9$), 40.2 and 40.6 (NCH_3), 52.3 (NCH_2), 163.1 (CN_3) ppm.

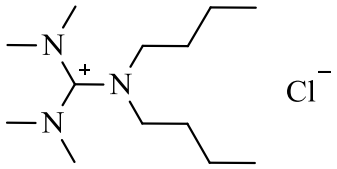
IR (ATR): ν = 2926 (w), 2954 (w), 2872 (w), 1603 (m), 1575 (s), 1405 (s), 1255 (m), 1153 (m), 1074 (w), 897 (m) cm^{-1}.

MS (CI): *m*/*z* = 186 (100%, $[cation]^+$).

CHN (in %): $C_{10}H_{24}ClN_3 \cdot 0.14H_2O$ (221.77 + 2.57 g/mol)

Calcd.	C 53.54	H 10.91	N 18.73
Found	C 53.65	H 11.02	N 18.72

6.2.2.3.4 Synthesis of *N,N*-dibutyl-*N',N',N",N"*-tetramethylguanidinium chloride (5g)



Method A:

Tetramethylchloroformamidinium chloride	**(4a)**	49.7 mmol	8.6 g
Di-*n*-butylamine		49.7 mmol	8.4 mL
Triethylamine		49.7 mmol	6.9 mL
Acetonitrile			40 mL
Diethyl ether			20 mL

Prepared according to the general procedure A. The product was obtained as a light yellow hygroscopic oil.

Yield: 5.6 g (43%).

Method B:

Tetramethylchloroformamidinium chloride	56.7 mmol	9.7 g
Di-*n*-butylamine	56.7 mmol	9.6 mL
Triethylamine	56.7 mmol	7.9 mL
Acetonitrile		60 mL
Diethyl ether		20 mL

Prepared according to the general procedure B. The product was obtained as a light yellow hygroscopic oil.

Yield: 11.6 g (78%).

T_{dec} = 302 °C, T_g = -59 °C.

^{1}H NMR ($CDCl_3$): δ = 0.91-0.95 (t, 6 H, ^3J = 7.3 Hz, $N(CH_2)_3CH_3$), 1.25-1.67 (m, 8 H, $N(CH_2)_2CH_2CH_3$ and $NCH_2CH_2CH_2CH_3$), 3.05 and 3.18 (2 s, each 6 H, NCH_3), 3.15-3.18 (m, 4 H, $NCH_2(CH_2)_2CH_3$) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.7 ($N(CH_2)_3CH_3$), 20.0 ($N(CH_2)_2CH_2CH_3$), 29.8 ($NCH_2CH_2CH_2CH_3$), 40.6 and 40.9 (NCH_3), 49.4 ($NCH_2(CH_2)_2CH_3$), 163.2 (CN_3) ppm.

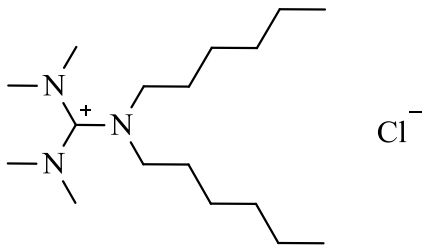
IR (NaCl): ν = 2957 (s), 2872 (s), 1597 (s), 1560 (s), 1466 (m), 1432 (m), 1408 (m), 1250 (m), 1193 (m), 1050 (m), 1113 (w), 1068 (w), 897 (w) cm^{-1}.

MS (CI): *m*/*z* = 228 (100%, $[cation]^+$).

CHN (in %): $C_{13}H_{30}ClN_3 \cdot 1.5H_2O$ (263.85 + 27.01 g/mol)

Calcd.	C 53.68	H 11.44	N 14.45
Found	C 53.41	H 11.92	N 14.31

6.2.2.3.5 Synthesis of *N*,*N*-dihexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidinium chloride (5h)



Tetramethylchloroformamidinium chloride	**(4a)**	73.8 mmol	12.6 g
Di-*n*-hexylamine		73.8 mmol	17.1 mL
Triethylamine		73.8 mmol	10.3 mL
Acetonitrile			100 mL
Diethyl ether			50 mL

Prepared according to the general procedure A, recrystallised from dry cyclohexane/ethyl acetate (5:2, v/v). The product was obtained as a colourless hygroscopic solid.

Yield: 16.3 g (69%); m.p. = 103 °C, T_{dec} = 299 °C.

^{1}H NMR ($CDCl_3$): δ = 0.87-0.91 (ψt, 6 H, $N(CH_2)_5CH_3$), 1.25-1.70 (several m, 16 H, $NCH_2(CH_2)_4CH_3$), 3.06 and 3.21 (2 s, both 6 H, NCH_3), 3.10-3.20 (m, 4 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.9 ($N(CH_2)_5CH_3$), 22.5 ($N(CH_2)_4CH_2CH_3$), 26.5 ($N(CH_2)_3CH_2CH_2CH_3$), 27.7 ($N(CH_2)_2CH_2(CH_2)_2CH_3$), 31.4 ($NCH_2CH_2(CH_2)_3CH_3$), 40.7 and 41.0 ($NCH_3$), 49.7 ($NCH_2$), 163.2 ($CN_3$) ppm.

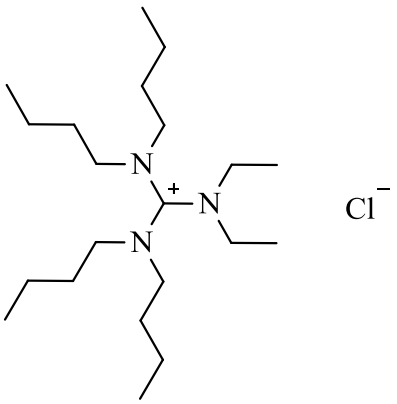
IR (ATR): ν = 2929 (m), 2856 (m), 1590 (s), 1559 (s), 1428 (m), 1403 (s), 1373 (m), 1271 (w), 1244 (w), 1121 (w), 1068 (m), 893 (m) cm^{-1}.

MS (CI): *m*/*z* = 284 (16%, $[cation]^+$).

CHN (in %): $C_{17}H_{38}ClN_3$ (319.92 g/mol)

Calcd.	C 63.82	H 11.97	N 13.13
Found	C 63.79	H 12.15	N 13.18

6.2.2.3.6 Synthesis of *N*,*N*,*N'*,*N'*-tetrabutyl-*N"*,*N"*-diethylguanidinium chloride (5k)



N,*N*-Dibutyl-*N'*,*N'*-diethylchloroformamidinium chloride	20.0 mmol	5.7 g
Di-*n*-butylamine	20.0 mmol	3.4 mL
Triethylamine	20.0 mmol	2.8 mL
Acetonitrile		30 mL
Diethyl ether		10 mL

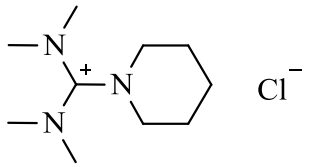
Prepared according to the general procedure A. The product was obtained as a colourless hygroscopic solid.

Yield: 6.3 g (84%).

^{1}H NMR ($CDCl_3$): δ = 0.92-0.97 (overlapped t, 12 H, $N(CH_2)_3CH_3$), 1.24-1.72 (several m, 22 H, NCH_2CH_3 and $NCH_2(CH_2)_2CH_3$), 3.02-3.49 (several m, 12 H, NCH_2CH_3, $NCH_2(CH_2)_2CH_3$) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.0 (NCH_2CH_3), 13.54 and 13.58 ($N(CH_2)_3CH_3$), 19.95 and 19.96 ($NCH_2CH_2CH_2CH_3$), 29.42 and 29.50 ($NCH_2CH_2CH_2CH_3$), 44.0 (NCH_2CH_3), 49.35 and 49.37 ($NCH_2(CH_2)_2CH_3$), 163.7 (CN_3) ppm.

6.2.2.3.7 Synthesis of *N,N,N',N'*-tetramethyl-*N'',N''*-pentamethyleneguanidinium chloride (5l)



Tetramethylchloroformamidinium chloride	**(4a)**	25.0 mmol	4.3 g
Piperidine		25.0 mmol	2.5 mL
Triethylamine		25.0 mmol	3.5 mL
Acetonitrile			45 mL
Diethyl ether			20 mL

Prepared according to the general procedure A, recrystallised from dry ethyl acetate/dimethylformamide (2:1, v/v). The product was obtained as a colourless hygroscopic solid.

Yield: 4.2 g (77%); m.p. = 158 °C, T_{dec} = 330 °C, T_g = -47 °C.

^{1}H NMR ($CDCl_3$): δ = 1.25–1.50 (m, 6 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.77 (s, 12 H, NCH_3), 2.97–3.13 (m, 4 H, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 22.6 (4-C_{pip}), 24.5 (3-C_{pip}, 5-C_{pip}), 40.05 and 40.09 (NCH_3), 49.3 (2-C_{pip}, 6-C_{pip}), 161.9 (CN_3) ppm.

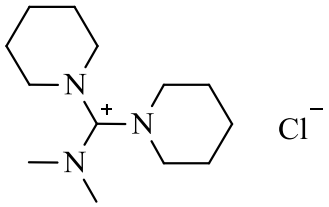
IR (ATR): ν = 2930 (m), 2856 (m), 1564 (s), 1435 (m), 1407 (s), 1365 (m), 1277 (m), 1253 (m), 1214 (m), 1136 (m), 1026 (m), 922 (m), 879 (m) cm^{-1}.

MS (CI): *m*/*z* = 184 (27%, $[cation]^+$).

CHN (in %): $C_{10}H_{22}ClN_3 \cdot 0.75H_2O$ (219.75 + 13.50 g/mol)

Calcd.	C 51.49	H 10.15	N 18.01
Found	C 51.48	H 10.27	N 17.94

6.2.2.3.8 Synthesis of *N,N*-dimethyl-*N',N',N'',N''*-bis(pentamethylene)guanidinium chloride (5m)



N,N,N',N'-Bis(pentamethylene)chloroformamidiniumchloride **(4e)**	4.5 mmol	1.1 g
N,N-Dimethyl(trimethylsilyl)amine (18.5% excess)	4.95 mmol	0.8 mL
Chloroform		15 mL

Prepared analogous to *N,N,N',N',N'',N''*-hexamethylguanidinium chloride with 18.5% excess of *N,N*-dimethyl(trimethylsilyl)amine, refluxed for 1.5 h, recrystallised from dry ethyl acetate/dimethylformamide (2:1, v/v). The product was obtained as a colourless hygroscopic solid.

Yield: 0.9 g (79%); m.p. = 205 °C, T_{dec} = 322 °C.

^{1}H NMR ($CDCl_3$): δ = 1.55–1.75 (m, 12 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.04 (s, 6 H, NCH_3), 3.20–3.40 (m, 8 H, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 23.2 (4-C_{pip}), 25.0 and 25.1 (3-C_{pip}, 5-C_{pip}), 40.9 (NCH_3), 50.1 and 50.2 (2-C_{pip}, 6-C_{pip}), 162.3 (CN_3) ppm.

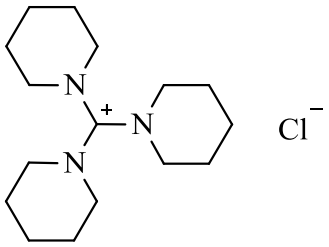
IR (ATR): ν = 2936 (m), 2854 (m), 1577 (s), 1552 (s), 1446 (m), 1416 (m), 1379 (m), 1283 (m), 1258 (m), 1212 (w), 1136 (w), 1027 (w), 1016 (w), 919 (w), 862 (m) cm^{-1}.

MS (CI): *m*/*z* = 224 (52%, $[cation]^+$).

CHN (in %): $C_{13}H_{26}ClN_3 \cdot 0.5H_2O$ (259.81 + 9.00 g/mol)

Calcd.	C 58.08	H 10.12	N 15.63
Found	C 58.25	H 10.35	N 15.75

6.2.2.3.9 Synthesis of *N,N,N',N',N'',N''*-tris(pentamethylene)guanidinium chloride (5n)



N,N,N',N'-Bis(pentamethylene)chloroformamidinium chloride **(4e)**	4.5 mmol	1.1 g
Piperidine	4.5 mmol	0.4 mL
Triethylamine	4.5 mmol	0.6 mL
Acetonitrile		10 mL
Diethyl ether		5 mL

Prepared according to the general procedure A, washed with dry diethyl ether/dichloromethane (2:1, v/v). The product was obtained as a light yellow hygroscopic solid.

Yield: 0.4 g (27%); m.p. = 202 °C, T_{dec} = 332 °C.

^{1}H NMR ($CDCl_3$): δ = 1.70–1.80 (m, 18 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.40–3.50 (m, 12 H, 2-H_{pip}, 6-H_{pip}) ppm.

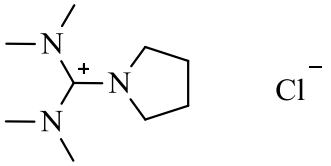
^{13}C NMR ($CDCl_3$): δ = 25.3 (4-C_{pip}), 31.0 (3-C_{pip}, 5-C_{pip}), 50.6 (2-C_{pip}, 6-C_{pip}) ppm.

MS (CI): *m*/*z* = 264 (57%, $[cation]^+$).

CHN (in %): $C_{16}H_{30}ClN_3 \cdot 0.33H_2O$ (299.88 + 5.94 g/mol)

Calcd.	C 62.82	H 10.11	N 13.74
Found	C 62.75	H 9.92	N 13.88

6.2.2.3.10 Synthesis of *N,N,N',N'*-tetramethyl-*N'',N''*-tetramethyleneguanidinium chloride (5o)



Tetramethylchloroformamidinium chloride	**(4a)**	30.4 mmol	5.2 g
Pyrrolidine		30.4 mmol	2.5 mL
Triethylamine		30.4 mmol	4.2 mL
Acetonitrile			40 mL
Diethyl ether			10 mL

Prepared according to the general procedure A. The product was obtained as a light beige hygroscopic solid.

Yield: 3.8 g (61%); m.p. = 152 °C, T_{dec} = 332 °C, T_g = -63 °C.

^{1}H NMR ($CDCl_3$): δ = 1.95–2.10 (m, 4 H, 3-H_{pyr}, 4-H_{pyr}), 3.05 (s, 12 H, NCH_3), 3.50–3.60 (m, 4 H, 2-H_{pyr}, 5-H_{pyr}) ppm.

^{13}C NMR ($CDCl_3$): δ = 25.2 (3-C_{pyr}, 4-C_{pyr}), 40.07 (NCH_3), 49.7 (2-C_{pyr}, 5-C_{pyr}), 160.1 (CN_3) ppm.

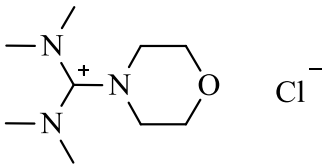
IR (ATR): ν = 2929 (w), 2857 (w), 1564 (s), 1436 (m), 1407 (s), 1365 (m), 1276 (m), 1253 (m), 1215 (m), 1136 (m), 1026 (m), 922 (m), 879 (m) cm^{-1}.

MS (CI): *m*/*z* = 170 (100%, $[cation]^+$).

CHN (in %): $C_9H_{20}ClN_3 \cdot 0.2H_2O$ (205.73 + 3.60 g/mol)

Calcd.	C 51.64	H 9.82	N 20.07
Found	C 51.64	H 10.22	N 20.10

6.2.2.3.11 Synthesis of 4-(bis(dimethylamino)methylidene)morpholinium chloride (5p)



Tetramethylchloroformamidinium chloride	**(4a)**	18.4 mmol	3.1 g
Morpholine		18.4 mmol	1.6 mL
Triethylamine		18.4 mmol	2.6 mL
Acetonitrile			20 mL
Diethyl ether			10 mL

Prepared according to the general procedure A, recrystallised from dry ethyl acetate/acetonitrile (4:5, v/v). The product was obtained as a colourless hygroscopic solid.

Yield: 2.6 g (63%); m.p. = 187 °C, T_{dec} = 326 °C, T_g = -47 °C.

^{1}H NMR ($CDCl_3$): δ = 3.12 and 3.13 (2 s, 12 H, NCH_3), 3.40–3.60 (m, 4 H, 3-H_{mor}, 5-H_{mor}), 3.83–3.90 (t, 4 H, ^3J = 4.7 Hz, 2-H_{mor}, 6-H_{mor}) ppm.

^{13}C NMR ($CDCl_3$): δ = 40.9 and 41.1 (NCH_3), 49.1 (3-C_{mor}, 5-C_{mor}), 66.2 (2-C_{mor}, 6-C_{mor}), 162.9 (CN_3) ppm.

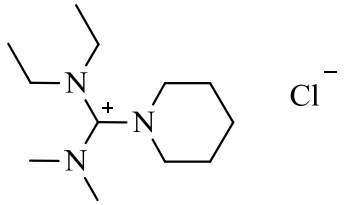
IR (ATR): ν = 2970 (w), 2911 (w), 2864 (w), 1569 (s), 1435 (m), 1408 (s), 1356 (m), 1271 (s), 1107 (s), 1065 (m), 822 (s) cm^{-1}.

MS (CI): *m*/*z* = 186 (8%, $[cation]^+$).

CHN (in %): $C_9H_{20}ClN_3O \cdot 0.125H_2O$ (221.73 + 2.25 g/mol)

Calcd.	C 48.26	H 9.11	N 18.76
Found	C 48.44	H 9.13	N 18.89

6.2.2.3.12 Synthesis of *N,N*-diethyl-*N',N'*-dimethyl-*N",N"*-pentamethyleneguanidinium chloride (5q)



N,N-Diethyl-*N',N'*-dimethylchloroformamidinium chloride **(4b)**	90.3 mmol	18.0 g
Piperidine	90.3 mmol	8.9 mL
Triethylamine	90.3 mmol	12.6 mL
Acetonitrile		80 mL
Diethyl ether		20 mL

Prepared according to the general procedure A, recrystallised from dry ethyl acetate/dimethylformamide (10:1, v/v). The product was obtained as a colourless hygroscopic solid.

Yield: 15.4 g (69%); m.p. = 126 °C, T_{dec} = 315 °C, T_g = -55 °C.

^{1}H NMR ($CDCl_3$): δ = 1.15-1.21 (2 overlapped t, 6 H, NCH_2CH_3), 1.58-1.78 (m, 6 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.04 and 3.13 (2 s, each 3 H, NCH_3), 3.20–3.55 (2 m, 8 H, 2-H_{pip}, 6-H_{pip}, NCH_2CH_3) ppm.

^{13}C NMR ($CDCl_3$): δ = 12.7 and 12.9 (NCH_2CH_3), 23.1 (4-C_{pip}), 24.8 and 25.0 (3-C_{pip} and 5-C_{pip}), 40.5 and 40.6 (NCH_3), 43.4 and 43.5 (NCH_2CH_3), 50.1 (2-C_{pip}, 6-C_{pip}), 162.5 (CN_3) ppm.

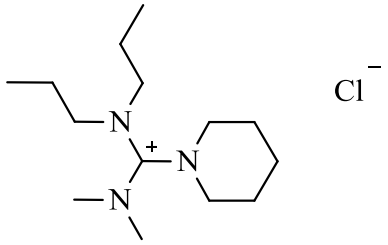
IR (ATR): ν = 2939 (m), 2862 (w), 1584 (s), 1552 (s), 1450 (m), 1421 (m), 1380 (w), 1295 (m), 1255 (m), 1070 (w), 1028 (w), 987 (w), 877 (w) cm^{-1}.

MS (CI): *m*/*z* = 212 (100%, $[cation]^+$).

CHN (in %): $C_{12}H_{26}ClN_3$ (221.73 g/mol)

Calcd.	C 58.16	H 10.58	N 16.96
Found	C 58.26	H 10.69	N 17.04

6.2.2.3.13 Synthesis of *N,N*-dimethyl-*N',N'*-pentamethylene-*N",N"*-dipropylguanidinium chloride (5r)



N,N-Dimethyl-*N',N'*-dipropylchloroformamidinium chloride	34.3 mmol	7.8 g
Piperidine	34.3 mmol	3.4 mL
Triethylamine	34.3 mmol	4.8 mL
Acetonitrile		30 mL
Diethyl ether		10 mL

Prepared according to the general procedure A, recrystallised from dry ethyl acetate. The product was obtained as a colourless hygroscopic solid.

Yield: 7.2 g (76%); m.p. = 94 °C, T_{dec} = 311 °C.

^{1}H NMR ($CDCl_3$): δ = 0.93-0.97 (t, 6 H, $NCH_2CH_2CH_3$), 1.45-1.83 (2 m, 10 H, $NCH_2CH_2CH_3$, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.10 and 3.20 (2 s, each 3 H, NCH_3), 3.13–3.17 (ψt, 4 H, $NCH_2CH_2CH_3$), 3.25-3.66 (several m, 4 H, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 11.2 and 11.4 ($NCH_2CH_2CH_3$), 20.9 and 21.1 ($NCH_2CH_2CH_3$), 23.4 (4-C_{pip}), 25.2 and 25.3 (3-C_{pip} and 5-C_{pip}), 40.9 and 41.2 (NCH_3), 50.3, 50.5, 51.3 and 51.4 ($NCH_2CH_2CH_3$, 2-C_{pip}, 6-C_{pip}), 162.9 (CN_3) ppm.

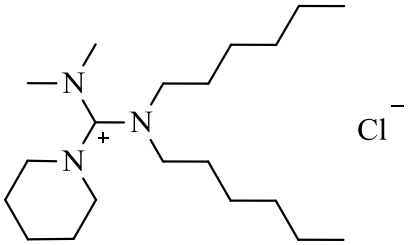
IR (ATR): ν = 2931 (m), 2873 (w), 1580 (s), 1544 (s), 1450 (m), 1410 (s), 1374 (m), 1288 (m), 1248 (m), 1153 (m), 1070 (m), 1023 (m), 945 (m), 864 (m) cm^{-1}.

MS (CI): *m*/*z* = 240 (34%, $[cation]^+$).

CHN (in %): $C_{14}H_{30}ClN_3$ (275.86 g/mol)

Calcd.	C 60.95	H 10.96	N 15.23
Found	C 60.95	H 11.01	N 15.23

6.2.2.3.14 Synthesis of *N,N*-dihexyl-*N'*,*N'*-dimethyl-*N"*,*N"*-pentamethyleneguanidinium chloride (5s)



Dichloromethylenedimethyliminium chloride	10.0 mmol	1.6 g
Di-*n*-hexylamine	10.0 mmol	2.3 g
Triethylamine	20.0 mmol	2.8 mL
Piperidine	10.0 mmol	1.0 mL
Dichloromethane		30 mL

Prepared according to the modified procedure given in lit. [35,36]. To a suspension of dichloromethylenedimethyliminium chloride in anhydrous dichloromethane at 0 °C (ice bath) was added dropwise a mixture of dihexylamine (1 equiv.) and triethylamine (1 equiv.) in dichloromethane. After 1 h a mixture of piperidine (1 equiv.) and triethylamine (1 equiv.) was added dropwise at 0 °C, and the reaction was stirred at room temperature for 4 h. The work-up was performed analogous to the general procedure A. In some cases the product was purified chromatographically (silica gel, dichloromethane/methanol, 9:1, v/v). The product was obtained as a yellow hygroscopic oil.

Yield: 1.6 g (43%); T_{dec} = 302 °C, T_g = - 52°C.

^{1}H NMR ($CDCl_3$): δ = 0.85-0.92 (ψt, 6 H, $N(CH_2)_5CH_3$), 1.18-1.85 (several m, 22 H, $NCH_2(CH_2)_4CH_3$, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.08 and 3.20 (2 s, each 3 H, NCH_3), 3.13–3.20 (ψt, 4 H, $NCH_2(CH_2)_4CH_3$), 3.23-3.67 (several m, 4 H, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.9 ($N(CH_2)_5CH_3$), 22.4 and 22.5 ($N(CH_2)_4CH_2CH_3$), 23.4 (4-C_{pip}), 25.2 and 25.3 (3-C_{pip} and 5-C_{pip}), 26.4 and 26.5 ($N(CH_2)_3CH_2CH_2CH_3$), 27.6 and 27.7 ($N(CH_2)_2CH_2(CH_2)_2CH_3$), 31.3 and 31.4 ($NCH_2CH_2(CH_2)_3CH_3$), 40.9 and 41.2 ($NCH_3$), 49.6, 49.7, 50.2 and 50.4 ($NCH_2(CH_2)_4CH_3$, 2-C_{pip}, 6-C_{pip}), 162.8 (CN_3) ppm.

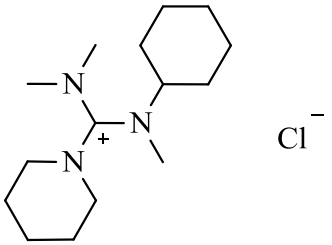
IR (NaCl): ν = 2933 (s), 2858 (s), 1585 (s), 1546 (s), 1452 (m), 1420 (m), 1379 (m), 1275 (m), 1255 (m), 1139 (m), 1026 (m), 922 (w), 879 (w) cm^{-1}.

MS (CI): *m*/*z* = 324 (20%, $[cation]^+$).

CHN (in %): $C_{20}H_{42}ClN_3 \cdot 0.67H_2O$ (360.02 + 12.00 g/mol)

Calcd.	C 64.57	H 11.74	N 11.29
Found	C 64.66	H 11.86	N 11.38

6.2.2.3.15 Synthesis of *N*-cyclohexyl-*N*,*N'*,*N'*-trimethyl-*N"*,*N"*-pentamethylene-guanidinium chloride (5t)



Dichloromethylenedimethyliminium chloride	11.7 mmol	1.9 g
N-Cyclohexyl-*N*-methylamine	11.7 mmol	1.5 g
Triethylamine	23.4 mmol	3.3 mL
Piperidine	11.7 mmol	1.2 mL
Dichloromethane		40 mL

Prepared analogous to *N*,*N*-dihexyl-*N',N'*-dimethyl-*N",N"*-pentamethyleneguanidinium chloride **(5s)**, recrystallised from dry ethyl acetate/dimethylformamide (5:3, v/v). The product was obtained as a colourless hygroscopic solid.

Yield: 1.4 g (42%); m.p. = 175 °C, T_{dec} = 307 °C.

^{1}H NMR ($CDCl_3$): δ = 1.05-2.03 (several m, 16 H, 2-H_{cHex}, 3-H_{cHex}, 4-H_{cHex}, 5-H_{cHex}, 6-H_{cHex}, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.92, 2.96, 3.06, 3.13, 3.16 and 3.22 (6 overlapped s, 9 H, NCH_3), 3.25–3.58 (several m, 5 H, 1-H_{cHex}, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 23.3 and 23.4 (4-C_{pip}, rotamers), 24.9, 25.2, 25.4 and 25.7 (3-C_{pip}, 5-C_{pip}, 3-C_{cHex}, 4-C_{cHex}, 5-C_{cHex}, rotamers), 29.5, 31.7 and 31.9 (2-C_{cHex}, 6-C_{cHex}, rotamers), 33.3

(N(C*H*$_3$)*c*Hex), 40.6, 41.2 and 41.3 (NCH$_3$, rotamers), 49.7, 50.4, 50.5 and 50.7 (2-C$_{pip}$, 6-C$_{pip}$, rotamers), 61.0 and 61.3 (1-C$_{cHex}$, rotamers), 163.4 and 163.5 (CN$_3$, rotamers) ppm.

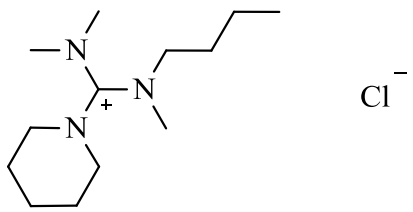
IR (ATR): ν = 2933 (s), 2848 (m), 1589 (s), 1545 (s), 1450 (m), 1409 (m), 1268 (m), 1161 (m), 1069 (w), 1024 (w), 927 (w), 879 (w) cm^{-1}.

MS (CI): *m*/*z* = 252 (45%, [cation]$^+$).

CHN (in %): C$_{15}$H$_{30}$ClN$_3$·0.2H$_2$O (287.87 + 3.60 g/mol)

Calcd.	C 61.81	H 10.51	N 14.42
Found	C 61.75	H 10.77	N 14.41

6.2.2.3.16 Synthesis of *N*-butyl-*N,N',N'*-trimethyl-*N'',N''*-pentamethyleneguanidinium chloride (5u)



N-Butyl-*N,N',N'*-trimethylchloroformamidinium chloride	**(4c)**	8.5 mmol	1.8 g
Piperidine		8.5 mmol	0.8 mL
Triethylamine		8.5 mmol	1.2 mL
Acetonitrile			15 mL
Diethyl ether			5 mL

Prepared according to the general procedure B. The product was obtained as a colourless hygroscopic solid.

Yield: 2.0 g (90%); T_{dec} = 313 °C, T_g = -48 °C.

Due to high hygroscopicity of the salt, it was impossible to determine the m.p.

^{1}H NMR (CDCl$_3$): δ = 0.91-0.96 (2 overlapped t, 3 H, N(CH$_2$)$_2$C*H*$_3$, rotamers), 1.22-1.85 (several m, 10 H, NCH$_2$(C*H*$_2$)$_2$CH$_3$, 3-H$_{pip}$, 4-H$_{pip}$, 5-H$_{pip}$), 3.05, 3.07, 3.09, 3.12 and 3.17 (several overlapped s, 9 H, NCH$_3$), 3.18–3.52 (several m, 6 H, NC*H*$_2$(CH$_2$)$_2$CH$_3$, 2-H$_{pip}$, 6-H$_{pip}$) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.6 and 13.7 ($N(CH_2)_3\mathit{C}H_3$, rotamers), 19.9 and 20.0 ($N(CH_2)_2\mathit{C}H_2CH_3$, rotamers), 23.4 (4-$C_{pip}$), 25.2, and 25.3 (3-$C_{pip}$ and 5-C_{pip}, rotamers), 29.5 and 29.6 ($NCH_2\mathit{C}H_2CH_2CH_3$, rotamers), 38.7 ($N(C\mathit{H}_3)Bu$), 40.6, 40.8, 41.1 and 41.2 (NCH_3, rotamers), 50.0, 50.2, 50.4, 52.6 and 53.4 ($N\mathit{C}H_2(CH_2)_2CH_3$, 2-$C_{pip}$, 6-$C_{pip}$, rotamers), 163.07 and 163.13 (CN_3, rotamers) ppm.

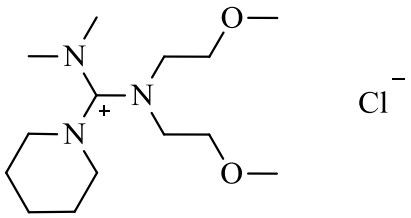
IR (ATR): ν = 2935 (s), 2864 (m), 1562 (s), 1451 (m), 1410 (m), 1274 (m), 1137 (w), 1027 (w), 882 (w) cm^{-1}.

MS (CI): *m*/*z* = 226 (100%, $[cation]^+$).

CHN (in %): $C_{13}H_{28}ClN_3 \cdot 1.3H_2O$ (261.83 + 24.00 g/mol)

Calcd.	C 54.62	H 10.81	N 14.70
Found	C 54.71	H 11.12	N 14.79

6.2.2.3.17 Synthesis of *N*,*N*-bis(2-methoxyethyl)-*N'*,*N'*-dimethyl-*N"*,*N"*-pentamethylene-guanidinium chloride (5v)



N,*N*-Bis(2-methoxyethyl)-*N'*,*N'*-dimethylchloroformamidinium chloride **(4d)**

	6.6 mmol	1.7 g
Piperidine	6.6 mmol	0.6 mL
Triethylamine	6.6 mmol	0.9 mL
Acetonitrile		20 mL
Diethyl ether		5 mL

Prepared according to the general procedure B, aqueous solution was additionally washed with dichloromethane before adding NaCl (to remove coloured impurities and *N*,*N*-bis(2-methoxyethyl)-*N'*,*N'*-pentamethyleneurea formed as a side product), recrystallised from dry ethyl acetate/dimethylformamide (10:1, v/v). The product was obtained as a colourless hygroscopic solid.

Yield: 1.1 g (54%); m.p. = 92 °C, T_{dec} = 292 °C, T_g = - 59 °C.

^{1}H NMR ($CDCl_3$): δ = 1.52-1.82 (several m, 6 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.03 and 3.04 (2 overlapped s, 6 H, NCH_3), 3.27 and 3.28 (2 overlapped s, 6 H, $NCH_2CH_2OC\mathit{H}_3$), 3.18–3.70 (several m, 12 H, $NC\mathit{H}_2CH_2OC\mathit{H}_3$, $NCH_2C\mathit{H}_2OCH_3$, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 23.5 (4-C_{pip}), 24.9 and 25.2 (3-C_{pip} and 5-C_{pip}, rotamers), 40.2 and 40.9 (NCH_3, rotamers), 49.2, 49.6, 49.9 and 50.2 ($NCH_2CH_2OCH_3$, 2-C_{pip}, 6-C_{pip}, rotamers), 58.7 and 57.8 ($NCH_2CH_2OCH_3$, rotamers), 69.0 and 69.1 ($NCH_2CH_2OCH_3$, rotamers), 163.9 (CN_3) ppm.

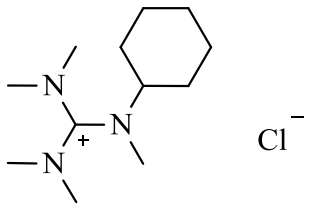
IR (KBr): ν = 2940 (s), 2864 (m), 1587 (vs), 1549 (vs), 1451 (s), 1420 (s), 1369 (m), 1291 (m), 1254 (m), 1115 (s), 1064 (m), 1011 (m), 859 (m) cm^{-1}.

MS (CI): *m*/*z* = 272 (66%, $[cation]^+$).

CHN (in %): $C_{14}H_{30}ClN_3O_2 \cdot 0.33H_2O$ (307.86 + 5.94 g/mol)

Calcd.	C 53.57	H 9.85	N 13.39
Found	C 53.45	H 9.85	N 13.41

6.2.2.3.18 Synthesis of *N*-cyclohexyl-*N,N',N',N'',N''*-pentamethylguanidinium chloride (5w)



N,N,N',N'-Tetramethylchloroformamidinium chloride **(4a)**	19.9 mmol	3.4 g
N-Cyclohexyl-*N*-methylamine	19.9 mmol	2.6 mL
Triethylamine	19.9 mmol	2.8 mL
Acetonitrile		30 mL
Diethyl ether		15 mL

Prepared according to the general procedure A, recrystallised from dry ethyl acetate/dimethylformamide (3:1, v/v). The product was obtained as a colourless hygroscopic solid.

Yield: 3.6 g (73%); m.p. = 142 °C, T_{dec} = 305 °C, T_g = - 41 °C.

^{1}H NMR ($CDCl_3$): δ = 1.05–1.20 (m, 1 H, 4-H$_{cHex}$), 1.28–1.48 (m, 2 H, 3-H$_{cHex}$, 5-H$_{cHex}$), 1.50–1.75 (m, 4 H, 2-H$_{cHex}$, 6-H$_{cHex}$), 1.77–2.05 (m, 3 H, 3-H$_{cHex}$, 4-H$_{cHex}$ and 5-H$_{cHex}$), 2.91 (s, 3 H, N(*c*Hex)C*H*$_3$), 3.05 and 3.15 (2 overlapped broad s, 13 H, NCH_3 and 1-H$_{cHex}$) ppm.

^{13}C NMR ($CDCl_3$): δ = 24.9 (4-C$_{cHex}$), 25.46 and 25.64 (3-C$_{cHex}$ and 5-C$_{cHex}$), 29.59 and 31.79 (2-C$_{cHex}$ and 6-C$_{cHex}$), 33.0 (N(*c*Hex)*C*H$_3$), 40.3 and 41.0 (NCH_3), 61.0 (N(1-C$_{cHex}$), 163.7 (CN_3) ppm.

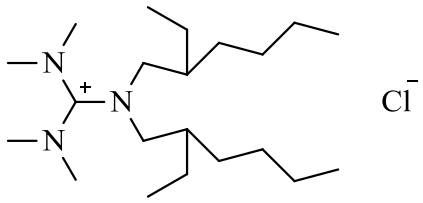
IR (KBr): ν = 2933 (s), 2858 (m), 1597 (s), 1584 (s), 1468 (m), 1408 (s), 1256 (m), 1151 (m), 1104 (m), 1064 (w), 998 (w), 900 (m) cm^{-1}.

MS (CI): *m*/*z* = 212 (100%, [cation]$^+$).

CHN (in %): $C_{12}H_{26}ClN_3 \cdot 0.125H_2O$ (247.81 + 2.25 g/mol)

Calcd.	C 57.56	H 10.58	N 16.78
Found	C 57.40	H 10.90	N 16.68

6.2.2.3.19 Synthesis of *N,N*-bis(2-ethylhexyl)-*N',N',N",N"*-tetramethylguanidinium chloride (5d)



N,N,N',N'-Tetramethylchloroformamidinium chloride **(4a)**	33.1 mmol	5.6 g
Bis(2-ethylhexyl)amine	33.1 mmol	9.9 mL
Triethylamine	33.1 mmol	4.6 mL
Acetonitrile		40 mL
Diethyl ether		15 mL

Prepared according to the general procedure B, recrystallised from dry ethyl acetate/dimethylformamide (2:1, v/v). The product was obtained as a colourless hygroscopic solid.

Yield: 10.0 g (81%); m.p. = 160 °C, T_{dec} = 292 °C.

^{1}H NMR ($CDCl_3$): δ = 0.80–0.94 (m, 12 H, 4 CH_3 of (2-Et)Hex), 1.05–1.60 (m, 18 H, $NCH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 2.90–3.25 (several m, 16 H, NCH_3 and NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 9.9, 11.2, 13.9 and 14.1 (4 CH_3 of (2-Et)Hex), 22.83, 22.95, 23.91 and 23.94 (CH_2CH_3 of (2-Et)Hex), 28.21, 28.25, 29.08 and 29.12 ($CH_2CH_2CH_3$, rotamers), 30.4 and 31.0 ($CH_2CH_2CH_2CH_3$), 37.23, 37.26, 37.65 and 37.67 (NCH_2CH, rotamers), 40.56, 40.60, 41.30, 41.36 and 41.42 (NCH_3, rotamers), 53.1, 53.3, 53.5 and 53.7 (NCH_2, rotamers), 163.7 (CN_3) ppm.

IR (KBr): ν = 2957 (s), 2929 (s), 2870 (m), 1593 (s), 1568 (s), 1462 (m), 1404 (m), 1262 (m), 1168 (m), 1148 (m), 1071 (m), 895 (m) cm^{-1}.

MS (CI): *m*/*z* = 340 (63%, $[cation]^+$).

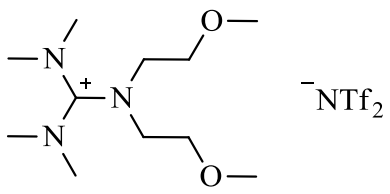
CHN (in %): $C_{21}H_{46}ClN_3 \cdot 0.125H_2O$ (247.81 + 2.25 g/mol)

Calcd.	C 67.07	H 12.33	N 11.17
Found	C 67.19	H 12.28	N 11.16

6.2.3 Synthesis of hexaalkylguanidinium bis(trifluoromethyl-sulfonyl)imides

General procedure, analogous to the procedure given in lit. [43,144]. Hexaalkylguanidinium chloride and lithium bis(trifluoromethylsulfonyl)imide were dissolved in deionised water. The solutions were combined resulting in two phases. After stirring the mixture at 70 °C for 30 min, it was cooled to room temperature and dichloromethane was added. The organic phase was separated and washed with several portions of deionised water until a test on chloride ions in the rinsing water ($AgNO_3$) was negative. The organic phase was dried with Na_2SO_4, stirred over charcoal for 15 min and filtered. The solvent was removed in a rotary evaporator, and the product was dried for 8 h at 120 °C/0.05 mbar in the bulb-to-bulb apparatus.

6.2.3.1 Synthesis of *N,N*-bis(2-methoxyethyl)-*N',N',N",N"*-tetramethyl-guanidinium bis(trifluoromethylsulfonyl)imide (6d)



Salt $[N_{11}N_{11}N_{1O21O2}Gu]Cl$ (**5d)**	7.3 mmol	2.0 g
$LiNTf_2$	7.3 mmol	2.1 g
H_2O (deionised)		35 mL

Prepared according to the general procedure. The product was obtained as a light yellow oil.

Yield: 3.2 g (84%); m.p. = 7 °C, T_{dec} = 445 °C, T_g = -57 °C.

^{1}H NMR ($CDCl_3$): δ = 2.95 and 3.00 (2 s, each 6 H, NCH_3), 3.32 (s, 6 H, OCH_3), 3.32-3.65 (several m, 8 H, NCH_2CH_2 and NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 39.8 and 40.2 (NCH_3), 49.3 (NCH_2), 58.7 (CH_3O), 68.7 (NCH_2CH_2), 118.3 and 121.3 (CF_3), 164.4 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.2 ppm.

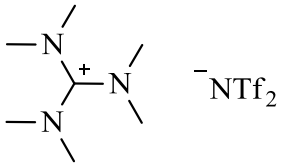
IR (NaCl): ν = 2939 (m), 2902 (m), 2834 (m), 1602 (s), 1568 (s), 1456 (m), 1435 (m), 1411 (s), 1352 (s), 1190 (s), 1136 (s), 1058 (s), 1014 (m), 894 (m) cm^{-1}.

MS (CI): *m*/*z* = 232 (100%, $[cation]^+$).

CHN (in %): $C_{13}H_{26}F_6N_4O_6S_2$ (512.49 g/mol)

Calcd.	C 30.47	H 5.11	N 10.93
Found	C 30.50	H 5.59	N 11.26

6.2.3.2 Synthesis of *N,N,N',N',N'',N''*-hexamethylguanidinium bis(trifluoromethylsulfonyl)imide (6e)



Salt $[N_{11}N_{11}N_{11}Gu]Cl$ **(5e)**	6.1 mmol	1.1 g
$LiNTf_2$	6.1 mmol	1.8 g
H_2O (deionised)		30 mL

Prepared according to the general procedure. The product was obtained as a colourless solid.

Yield: 2.0 g (77%); m.p. = 88 °C, T_{dec} = 467 °C.

^{1}H NMR ($CDCl_3$): δ = 2.99 (s, 18 H, NCH_3) ppm.

^{13}C NMR ($CDCl_3$): δ = 40.2 (NCH_3), 118.2 and 121.4 (CF_3), 163.2 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

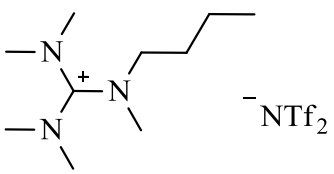
IR (ATR): ν = 2957 (w), 1596 (s), 1577 (m), 1474 (w), 1410 (m), 1347 (m), 1333 (m), 1167 (s), 1144 (s), 1053 (s), 897 (m) cm^{-1}.

MS (CI): *m*/*z* = 144 (100%, $[cation]^+$).

CHN (in %): $C_9H_{18}F_6N_4O_4S_2$ (424.38 g/mol)

Calcd.	C 25.47	H 4.28	N 13.20
Found	C 25.48	H 4.42	N 13.32

6.2.3.3 Synthesis of *N*-butyl-*N,N',N',N'',N''*-pentamethylguanidinium bis(trifluoromethylsulfonyl)imide (6f)



Salt $[N_{11}N_{11}N_{14}Gu]Cl$ **(5f)**	5.0 mmol	1.1 g
$LiNTf_2$	5.0 mmol	1.6 g
H_2O (deionised)		30 mL

Prepared according to the general procedure. The product was obtained as a light yellow oil.

Yield: 1.7 g (75%); T_{dec} = 465 °C, T_g = -85 °C.

^{1}H NMR ($CDCl_3$): δ = 0.92-0.96 (t, 3 H, ^3J = 7.3 Hz, $N(CH_2)_3CH_3$), 1.23-1.72 (several m, 4H, $N(CH_2)_2CH_2CH_3$ and $NCH_2CH_2CH_2CH_3$), 2.90-3.02 (several overlapped s, 15 H, NCH_3 and $N(CH_3)C_4H_9$), 3.10-3.18 (m, 2 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.5 ($N(CH_2)_3CH_3$), 19.9 ($N(CH_2)_2CH_2CH_3$), 29.5 ($NCH_2CH_2CH_2CH_3$), 37.8 ($N(CH_3)C_4H_9$), 40.2 (bs, NCH_3), 52.6 (NCH_2), 118.3 and 121.5 (CF_3), 163.5 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

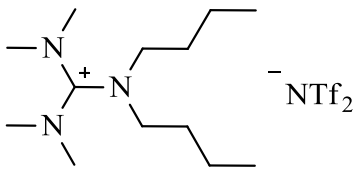
IR (NaCl): ν = 2964 (w), 2940 (w), 2878 (w), 1582 (s), 1410 (m), 1352 (s), 1227 (m), 1192 (s), 1137 (s), 1058 (s), 899 (w) cm^{-1}.

MS (CI): *m*/*z* = 186 (100%, $[cation]^+$).

CHN (in %): $C_{12}H_{24}F_6N_4O_4S_2$ (466.46 g/mol)

Calcd.	C 30.90	H 5.19	N 12.01
Found	C 30.71	H 5.05	N 12.25

6.2.3.4 Synthesis of *N*,*N*-dibutyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidinium bis(trifluoromethylsulfonyl)imide (6g)



Salt $[N_{11}N_{11}N_{44}Gu]Cl$ **(5g)**	10.9 mmol	2.9 g
$LiNTf_2$	10.9 mmol	3.2 g
H_2O (deionised)		50 mL

Prepared according to the general procedure. The product was obtained as a light yellow oil.

Yield: 5.0 g (90%); T_{dec} = 464 °C, T_g = -80 °C.

^{1}H NMR ($CDCl_3$): δ = 0.90-0.93 (t, 6 H, ^3J = 7.3 Hz, $N(CH_2)_3CH_3$), 1.20-1.65 (m, 8 H, $N(CH_2)_2CH_2CH_3$ und $NCH_2CH_2CH_2CH_3$), 2.93 and 2.95 (2 s, each 6 H, NCH_3), 2.98-3.20 (several m, 4 H, $NCH_2(CH_2)_2CH_3$) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.5 ($N(CH_2)_3CH_3$), 19.8 ($N(CH_2)_2CH_2CH_3$), 29.5 ($NCH_2CH_2CH_2CH_3$), 40.1 and 40.2 (NCH_3), 49.3 ($NCH_2(CH_2)_2CH_3$), 115.0, 118.2, 121.4 and 124.6 (CF_3), 163.2 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

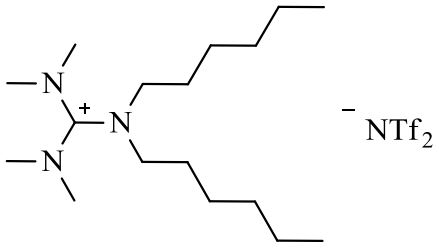
IR (NaCl): ν = 2964 (m), 2939 (m), 2878 (m), 1593 (s), 1568 (s), 1411 (m), 1352 (s), 1227 (m), 1190 (s), 1138 (s), 1059 (s), 897 (m) cm^{-1}.

MS (CI): *m*/*z* = 228 (100%, $[cation]^+$).

CHN (in %): $C_{15}H_{30}F_6N_4O_4S_2$ (508.54 g/mol)

Calcd.	C 35.43	H 5.95	N 11.02
Found	C 35.53	H 5.91	N 11.03

6.2.3.5 Synthesis of *N,N*-dihexyl-*N',N',N'',N''*-tetramethylguanidinium bis(trifluoromethylsulfonyl)imide (6h)



Salt $[N_{11}N_{11}N_{66}Gu]Cl$ **(5h)**	13.3 mmol	4.3 g
$LiNTf_2$	13.3 mmol	3.8 g
H_2O (deionised)		50 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 7.1 g (94%); T_{dec} = 460 °C, T_g = -82 °C.

^{1}H NMR ($CDCl_3$): δ = 0.87-0.91 (ψt, 6 H, $N(CH_2)_5CH_3$), 1.20-1.68 (several m, 16 H, $NCH_2(CH_2)_4CH_3$), 2.97 and 3.01 (2 s, both 6 H, NCH_3), 3.04-3.20 (m, 4 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.9 ($N(CH_2)_5CH_3$), 22.4 ($N(CH_2)_4CH_2CH_3$), 26.4 ($N(CH_2)_3CH_2CH_2CH_3$), 27.5 ($N(CH_2)_2CH_2(CH_2)_2CH_3$), 31.3 ($NCH_2CH_2(CH_2)_3CH_3$), 40.31 and 40.34 ($NCH_3$), 49.6 ($NCH_2$), 118.3 and 121.4 ($CF_3$), 163.2 ($CN_3$) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.2 ppm.

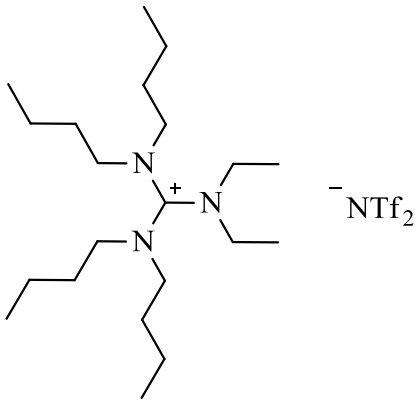
IR (NaCl): ν = 2958 (m), 2935 (m), 2863 (m), 1594 (s), 1566 (s), 1411 (m), 1352 (s), 1333 (s), 1190 (s), 1138 (s), 1059 (s), 897 (m) cm^{-1}.

MS (CI): *m*/*z* = 284 (100%, $[cation]^+$).

CHN (in %): $C_{19}H_{38}F_6N_4O_4S_2$ (564.65 g/mol)

Calcd.	C 40.42	H 6.78	N 9.92
Found	C 40.36	H 6.69	N 10.01

6.2.3.6 Synthesis of *N,N,N',N'*-tetrabutyl-*N'',N''*-diethylguanidinium bis(trifluoromethylsulfonyl)imide (6k)



Salt $[N_{22}N_{44}N_{44}Gu]Cl$ **(5k)**	10.0 mmol	3.7 g
$LiNTf_2$	10.0 mmol	2.9 g
H_2O (deionised)		40 mL

Prepared according to the general procedure, the obtained solid was washed with deionised water until a test on chloride ions in the rinsing water ($AgNO_3$) was negative. The product was obtained as a colourless solid.

Yield: 5.8 g (94%); m.p. = 68 °C, T_{dec} = 457 °C.

^{1}H NMR ($CDCl_3$): δ = 0.91-0.95 (overlapped t, 12 H, $N(CH_2)_3CH_3$), 1.17-1.77 (several m, 22 H, NCH_2CH_3 and $NCH_2(CH_2)_2CH_3$), 2.95-3.40 (several m, 12 H, NCH_2CH_3, $NCH_2(CH_2)_2CH_3$) ppm.

^{13}C NMR ($CDCl_3$): δ = 12.7 (NCH_2CH_3), 13.48 and 13.53 ($N(CH_2)_3CH_3$), 19.92 and 19.94 ($NCH_2CH_2CH_2CH_3$), 29.38 and 29.46 ($NCH_2CH_2CH_2CH_3$), 43.8 (NCH_2CH_3), 49.3 and 49.4 ($NCH_2(CH_2)_2CH_3$), 118.3 and 121.5 (CF_3), 163.8 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.2 ppm.

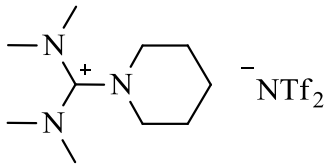
IR (ATR): ν = 2967 (m), 2938 (m), 2878 (m), 1535 (s), 1457 (m), 1344 (s), 1197 (s), 1177 (s), 1136 (s), 1049 (s), 789 (m), 740 (m) cm^{-1}.

MS (CI): *m*/*z* = 340 (100%, $[cation]^+$).

CHN (in %): $C_{23}H_{46}F_6N_4O_4S_2$ (620.75 g/mol)

Calcd.	C 44.50	H 7.47	N 9.03
Found	C 44.55	H 7.55	N 9.10

6.2.3.7 Synthesis of *N,N,N',N'*-tetramethyl-*N",N"*-pentamethyleneguanidinium bis(trifluoromethylsulfonyl)imide (6l)



Salt $[N_{11}N_{11}N_{pip}Gu]Cl$ **(5l)**	10.0 mmol	2.2 g
$LiNTf_2$	10.0 mmol	2.9 g
H_2O (deionised)		40 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 4.4 g (95%); m.p. = 3 °C, T_{dec} = 470 °C, T_g = -75 °C.

^{1}H NMR ($CDCl_3$): δ = 1.65–1.80 (m, 6 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.98 and 2.99 (2 s, 12 H, NCH_3), 3.20–3.35 (m, 4 H, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 23.4 (4-C_{pip}), 25.1 (3-C_{pip}, 5-C_{pip}), 40.32 and 40.35 (NCH_3), 50.0 (2-C_{pip}, 6-C_{pip}), 118.2 and 121.4 (CF_3), 162.8 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

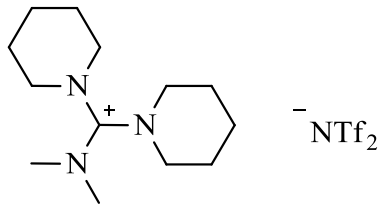
IR (ATR): ν = 2951 (m), 2864 (m), 1569 (s), 1436 (m), 1411 (s), 1347 (s), 1330 (s), 1277 (m), 1176 (s), 1134 (s), 1053 (m), 922 (m), 879 (m) cm^{-1}.

MS (CI): *m*/*z* = 184 (100%, $[cation]^+$).

CHN (in %): $C_{12}H_{22}F_6N_4O_4S_2$ (464.44 g/mol)

Calcd.	C 31.03	H 4.77	N 12.06
Found	C 31.03	H 4.68	N 12.25

6.2.3.8 Synthesis of *N,N*-dimethyl-*N',N',N'',N''*-bis(pentamethylene)-guanidinium bis(trifluoromethylsulfonyl)imide (6m)



Salt [$N_{11}N_{pip}N_{pip}$Gu]Cl **(5m)**	2.3 mmol	0.6 g
$LiNTf_2$	2.3 mmol	0.7 g
H_2O (deionised)		10 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 1.0 g (86%); T_{dec} = 461 °C, T_g = -62 °C.

^{1}H NMR ($CDCl_3$): δ = 1.63–1.78 (m, 12 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.99 (s, 6 H, NCH_3), 3.20–3.35 (m, 8 H, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 23.4 (4-C_{pip}), 25.0 and 25.2 (3-C_{pip}, 5-C_{pip}), 40.6 (NCH_3), 50.17 and 50.18 (2-C_{pip}, 6-C_{pip}), 118.6 and 121.1 (CF_3), 162.5 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.2 ppm.

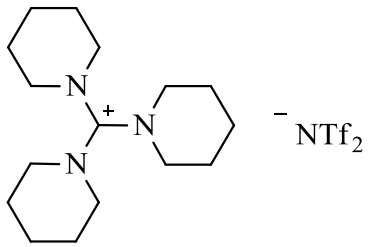
IR (NaCl): ν = 2946 (s), 2868 (s), 1560 (s), 1449 (s), 1428 (s), 1350 (s), 1285 (s), 1259 (s), 1187 (s), 1135 (s), 1057 (s), 1015 (m), 920 (m), 872 (m) cm^{-1}.

MS (CI): *m*/*z* = 224 (100%, $[cation]^+$).

CHN (in %): $C_{15}H_{26}F_6N_4O_4S_2$ (504.51 g/mol)

Calcd.	C 35.71	H 5.19	N 11.11
Found	C 35.68	H 5.20	N 11.19

6.2.3.9 Synthesis of *N,N,N',N',N",N"*-tris(pentamethylene)guanidinium bis(trifluoromethylsulfonyl)imide (6n)



Salt $[N_{pip}N_{pip}N_{pip}Gu]Cl$ **(5n)**	1.2 mmol	0.4 g
$LiNTf_2$	1.2 mmol	0.3 g
H_2O (deionised)		6 mL

Prepared according to the general procedure. The product was obtained as a colourless solid.

Yield: 0.6 g (76%); m.p. = 63 °C, T_{dec} = 462 °C, T_g = -69 °C.

^{1}H NMR ($CDCl_3$): δ = 1.62–1.78 (m, 18 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.24–3.38 (m, 12 H, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 23.4 (4-C_{pip}), 25.1 (3-C_{pip}, 5-C_{pip}), 50.4 (2-C_{pip}, 6-C_{pip}), 118.3 and 121.5 (CF_3), 162.3 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.2 ppm.

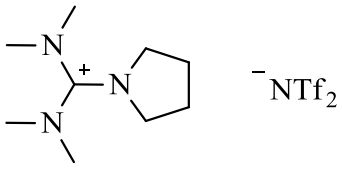
IR (ATR): ν = 2945 (w), 2864 (w), 1550 (s), 1442 (m), 1346 (s), 1289 (m), 1182 (vs), 1137 (s), 1058 (s), 1015 (m), 917 (w), 856 (w) cm^{-1}.

MS (CI): *m*/*z* = 264 (100%, $[cation]^+$).

CHN (in %): $C_{18}H_{30}F_6N_4O_4S_2$ (544.57 g/mol)

Calcd.	C 39.70	H 5.55	N 10.29
Found	C 39.69	H 5.79	N 10.37

6.2.3.10 Synthesis of *N,N,N',N'*-tetramethyl-*N",N"*-tetramethylene-guanidinium bis(trifluoromethylsulfonyl)imide (6o)



Salt $[N_{11}N_{11}N_{pyr}Gu]Cl$ **(5o)**	9.7 mmol	2.0 g
$LiNTf_2$	9.7 mmol	2.8 g
H_2O (deionised)		40 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 3.7 g (85%); m.p. = 9 °C, T_{dec} = 455 °C.

^{1}H NMR ($CDCl_3$): δ = 1.95–2.07 (m, 4 H, 3-H_{pyr}, 4-H_{pyr}), 2.94 (s, 12 H, NCH_3), 3.40–3.47 (m, 4 H, 2-H_{pyr}, 5-H_{pyr}) ppm.

^{13}C NMR ($CDCl_3$): δ = 25.0 (3-C_{pyr}, 4-C_{pyr}), 40.2 (NCH_3), 49.5 (2-C_{pyr}, 5-C_{pyr}), 118.2 and 121.4 (CF_3), 160.0 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

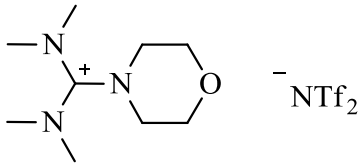
IR (ATR): ν = 2965 (w), 1573 (s), 1436 (w), 1410 (m), 1348 (s), 1331 (s), 1228 (m), 1173 (vs), 1133 (s), 1053 (vs), 899 (m) cm^{-1}.

MS (CI): *m*/*z* = 170 (100%, $[cation]^+$).

CHN (in %): $C_{11}H_{20}F_6N_4O_4S_2$ (450.42 g/mol)

Calcd.	C 29.33	H 4.48	N 12.44
Found	C 29.42	H 4.89	N 12.72

6.2.3.11 Synthesis of 4-(bis(dimethylamino)methylidene)morpholinium bis(trifluoromethylsulfonyl)imide (6p)



Salt $[N_{11}N_{11}N_{mor}Gu]Cl$ **(5p)**	6.8 mmol	1.5 g
$LiNTf_2$	6.8 mmol	1.9 g
H_2O (deionised)		20 mL

Prepared according to the general procedure. The product was obtained as a colourless solid.

Yield: 2.1 g (68%); m.p. = 47 °C, T_{dec} = 473 °C, T_g = -61 °C.

^{1}H NMR ($CDCl_3$): δ = 2.98 and 3.01 (2 s, 12 H, NCH_3), 3.28–3.43 (m, 4 H, 3-H_{mor}, 5-H_{mor}), 3.75–3.87 (m, 4 H, 2-H_{mor}, 6-H_{mor}) ppm.

^{13}C NMR ($CDCl_3$): δ = 40.46 and 40.47 (NCH_3), 48.9 (3-C_{mor}, 5-C_{mor}), 65.9 (2-C_{mor}, 6-C_{mor}), 118.2 and 121.3 (CF_3), 162.6 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.4 ppm.

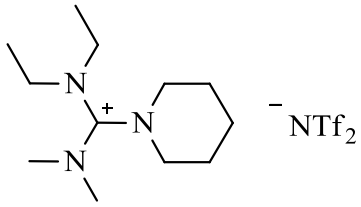
IR (ATR): ν = 2915 (w), 2868 (w), 1607 (m), 1572 (s), 1470 (w), 1413 (m), 1347 (s), 1333 (s), 1274 (m), 1173 (vs), 1138 (s), 1114 (s), 1049 (vs), 885 (s) cm^{-1}.

MS (CI): *m*/*z* = 186 (100%, $[cation]^+$).

CHN (in %): $C_{11}H_{20}F_6N_4O_5S_2$ (466.42 g/mol)

Calcd.	C 28.33	H 4.32	N 12.01
Found	C 28.57	H 4.32	N 12.09

6.2.3.12 Synthesis of *N*,*N*-diethyl-*N'*,*N'*-dimethyl-*N"*,*N"*-penta-methyleneguanidinium bis(trifluoromethylsulfonyl)imide (6q)



Salt $[N_{11}N_{22}N_{pip}Gu]Cl$ **(5q)**	42.4 mmol	10.5 g
$LiNTf_2$	42.4 mmol	12.2 g
H_2O (deionised)		150 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 19.1 g (92%); T_{dec} = 470 °C, T_g = -76 °C.

^{1}H NMR ($CDCl_3$): δ = 1.15-1.21 (2 overlapped t, 6 H, NCH_2CH_3), 1.62-1.80 (m, 6 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.95 and 3.00 (2 s, each 3 H, NCH_3), 3.15–3.40 (m, 8 H, 2-H_{pip}, 6-H_{pip}, NCH_2CH_3) ppm.

^{13}C NMR ($CDCl_3$): δ = 12.6 and 12.8 (NCH_2CH_3), 23.4 (4-C_{pip}), 24.9 and 25.1 (3-C_{pip} and 5-C_{pip}), 40.3 and 40.4 (NCH_3), 43.4 and 43.6 (NCH_2CH_3), 50.0 and 50.2 (2-C_{pip}, 6-C_{pip}), 115.1, 118.3, 121.4 and 124.6 (CF_3), 162.9 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

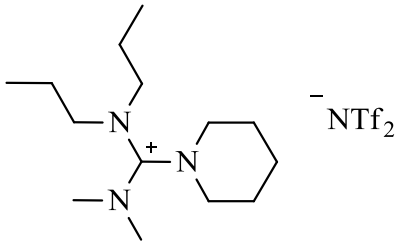
IR (NaCl): ν = 2946 (m), 2866 (w), 1583 (s), 1553 (s), 1452 (m), 1424 (m), 1352 (s), 1297 (m), 1256 (m), 1188 (s), 1139 (s), 1058 (s), 790 (w) cm^{-1}.

MS (CI): *m*/*z* = 212 (100%, $[cation]^+$).

CHN (in %): $C_{14}H_{26}F_6N_4O_4S_2$ (492.50 g/mol)

Calcd.	C 34.14	H 5.32	N 11.38
Found	C 34.15	H 5.16	N 11.51

6.2.3.13 Synthesis of *N,N*-dimethyl-*N',N'*-pentamethylene-*N",N"*-dipropylguanidinium bis(trifluoromethylsulfonyl)imide (6r)



Salt $[N_{11}N_{33}N_{pip}Gu]Cl$ **(5r)**	15.1 mmol	4.2 g
$LiNTf_2$	15.1 mmol	4.3 g
H_2O (deionised)		50 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 7.2 g (92%); T_{dec} = 475 °C, T_g = -73 °C.

^{1}H NMR ($CDCl_3$): δ = 0.91-0.95 (2 overlapped t, 6 H, $NCH_2CH_2CH_3$), 1.42-1.83 (2 m, 10 H, $NCH_2CH_2CH_3$, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.96 and 3.01 (2 s, each 3 H, NCH_3), 3.03–3.42 (several m, 8 H, $NCH_2CH_2CH_3$, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 11.0 and 11.2 ($NCH_2CH_2CH_3$), 20.8 and 20.9 ($NCH_2CH_2CH_3$), 23.4 (4-C_{pip}), 25.0 and 25.2 (3-C_{pip} and 5-C_{pip}), 40.50 and 41.54 (NCH_3), 50.2, 51.3 and 51.5 ($NCH_2CH_2CH_3$, 2-C_{pip}, 6-C_{pip}), 118.3 and 121.5 (CF_3), 162.9 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

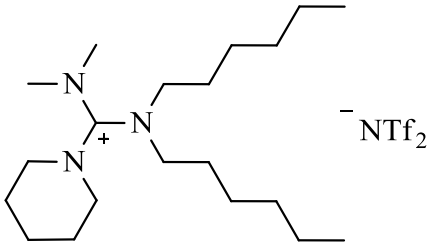
IR (NaCl): ν = 2944 (m), 2879 (w), 1581 (s), 1551 (s), 1453 (m), 1423 (m), 1353 (s), 1227 (m), 1191 (s), 1139 (s), 1059 (s), 788 (m) cm^{-1}.

MS (CI): *m*/*z* = 240 (100%, $[cation]^+$).

CHN (in %): $C_{16}H_{30}F_6N_4O_4S_2$ (520.55 g/mol)

Calcd.	C 36.92	H 5.81	N 10.76
Found	C 37.11	H 5.82	N 10.90

6.2.3.14 Synthesis of *N*,*N*-dihexyl-*N'*,*N'*-dimethyl-*N"*,*N"*-penta-methyleneguanidinium bis(trifluoromethylsulfonyl)imide (6s)



Salt $[N_{11}N_{66}N_{pip}Gu]Cl$ **(5s)**	5.0 mmol	1.8 g
$LiNTf_2$	5.0 mmol	1.4 g
H_2O (deionised)		20 mL

Prepared according to the general procedure. The product was obtained as a yellow viscous oil.

Yield: 2.4 g (80%); T_{dec} = 475 °C, T_g = - 72°C.

^{1}H NMR ($CDCl_3$): δ = 0.85-0.93 (ψt, 6 H, $N(CH_2)_5CH_3$), 1.20-1.83 (several m, 22 H, $NCH_2(CH_2)_4CH_3$, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.95 and 3.01 (2 s, each 3 H, NCH_3), 3.03–3.43 (several m, 8 H, $NCH_2(CH_2)_4CH_3$, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.9 ($N(CH_2)_5CH_3$), 22.4 ($N(CH_2)_4CH_2CH_3$), 23.4 (4-C_{pip}), 25.0 and 25.2 (3-C_{pip} and 5-C_{pip}), 26.3 and 26.5 ($N(CH_2)_3CH_2CH_2CH_3$), 27.4 and 27.5 ($N(CH_2)_2CH_2(CH_2)_2CH_3$), 31.3 ($NCH_2CH_2(CH_2)_3CH_3$), 40.5 ($NCH_3$), 49.6, 49.8 and 50.2 ($NCH_2(CH_2)_4CH_3$, 2-$C_{pip}$, 6-$C_{pip}$), 118.2 and 121.5 ($CF_3$), 162.9 ($CN_3$) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

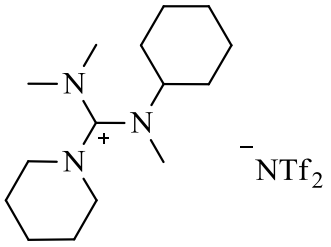
IR (NaCl): ν = 2936 (s), 2864 (m), 1580 (s), 1550 (s), 1453 (m), 1423 (m), 1353 (s), 1285 (m), 1227 (m), 1190 (s), 1139 (s), 1059 (s), 788 (w) cm^{-1}.

MS (CI): *m*/*z* = 324 (100%, $[cation]^+$).

CHN (in %): $C_{22}H_{42}F_6N_4O_4S_2$ (604.71 g/mol)

Calcd.	C 43.70	H 7.00	N 9.27
Found	C 43.64	H 7.49	N 9.26

6.2.3.15 Synthesis of *N*-cyclohexyl-*N*,*N*',*N*'-trimethyl-*N*",*N*"-pentamethyleneguanidinium bis(trifluoromethylsulfonyl)imide (6t)



Salt $[N_{11}N_{1cHex}N_{pip}Gu]Cl$ **(5t)**	4.2 mmol	1.2 g
$LiNTf_2$	4.2 mmol	1.2 g
H_2O (deionised)		30 mL

Prepared according to the general procedure. The product was obtained as a colourless viscous oil.

Yield: 1.8 g (81%); T_{dec} = 453 °C, T_g = - 52 °C.

^{1}H NMR ($CDCl_3$): δ = 1.05-2.00 (several m, 16 H, 2-H_{cHex}, 3-H_{cHex}, 4-H_{cHex}, 5-H_{cHex}, 6-H_{cHex}, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.82, 2.83, 2.91 and 2.98 (several overlapped s, 9 H, NCH_3), 3.08–3.38 (several m, 5 H, 1-H_{cHex}, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 23.4 and 23.5 (4-C_{pip}, rotamers), 25.0, 25.1, 25.3 and 25.7 (3-C_{pip}, 5-C_{pip}, 3-C_{cHex}, 4-C_{cHex}, 5-C_{cHex}, rotamers), 29.4, 31.6 and 31.8 (2-C_{cHex}, 6-C_{cHex}, rotamers), 32.8 and 33.0 (N(CH_3)*c*Hex, rotamers), 40.1, 40.5, 40.8 and 40.9 (NCH_3, rotamers), 49.7, 50.1, 50.4 and 50.6 (2-C_{pip}, 6-C_{pip}, rotamers), 61.1 and 61.5 (1-C_{cHex}, rotamers), 115.1, 118.3, 121.5 and 124.7 (CF_3), 163.4 and 163.5 (CN_3, rotamers) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

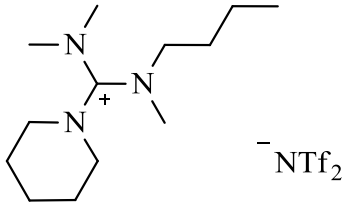
IR (NaCl): ν = 2939 (s), 2863 (m), 1579 (s), 1550 (s), 1453 (m), 1413 (m), 1352 (s), 1260 (m), 1186 (vs), 1138 (s), 1058 (s), 789 (w) cm^{-1}.

MS (CI): *m*/*z* = 252 (100%, $[cation]^+$).

CHN (in %): $C_{17}H_{30}F_6N_4O_4S_2$ (532.56 g/mol)

Calcd.	C 38.34	H 5.68	N 10.52
Found	C 38.32	H 5.74	N 10.64

6.2.3.16 Synthesis of *N*-butyl-*N*,*N*',*N*'-trimethyl-*N*",*N*"-pentamethylene-guanidinium bis(trifluoromethylsulfonyl)imide (6u)



Salt $[N_{11}N_{14}N_{pip}Gu]Cl$ **(5u)**	31.7 mmol	8.3 g
$LiNTf_2$	31.7 mmol	9.1 g
H_2O (deionised)		100 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 14.0 g (87%); T_{dec} = 473 °C, T_g = -74 °C.

^{1}H NMR ($CDCl_3$): δ = 0.94-0.96 (2 overlapped t, 3 H, $N(CH_2)_2CH_3$, rotamers), 1.22-1.85 (several m, 10 H, $NCH_2(CH_2)_2CH_3$, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.94, 2.95, 2.98 and 3.01 (several overlapped s, 9 H, NCH_3), 3.10–3.35 (several m, 6 H, $NCH_2(CH_2)_2CH_3$, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.6 ($N(CH_2)_3CH_3$), 19.9 and 20.0 ($N(CH_2)_2CH_2CH_3$, rotamers), 23.4 (4-C_{pip}), 25.1 and 25.2 (3-C_{pip} and 5-C_{pip}), 29.4 and 29.5 ($NCH_2CH_2CH_2CH_3$, rotamers), 38.0 and 38.2 ($N(CH_3)Bu$, rotamers), 40.3, 40.4, 40.5 and 40.6 (NCH_3, rotamers), 50.0, 50.1, 52.5 and 52.6 ($NCH_2(CH_2)_2CH_3$, 2-C_{pip}, 6-C_{pip}, rotamers), 118.3 and 121.4 (CF_3), 163.1 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

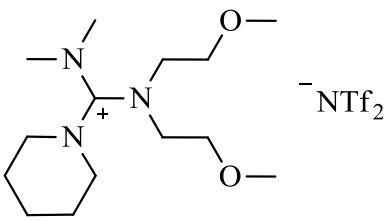
IR (NaCl): ν = 2943 (m), 2869 (m), 1566 (s), 1454 (m), 1413 (s), 1353 (s), 1190 (s), 1138 (s), 1058 (s), 881 (m), 788 (m) cm^{-1}.

MS (CI): *m*/*z* = 226 (100%, $[cation]^+$).

CHN (in %): $C_{15}H_{28}F_6N_4O_4S_2$ (506.53 g/mol)

Calcd.	C 35.57	H 5.57	N 11.06
Found	C 35.56	H 5.43	N 11.20

6.2.3.17 Synthesis of *N*,*N*-bis(2-methoxyethyl)-*N'*,*N'*-dimethyl-*N"*,*N"*-pentamethyleneguanidinium bis(trifluoromethylsulfonyl)imide (6v)



Salt $[N_{11}N_{1O21O2}N_{pip}Gu]Cl$ **(5v)**	25.5 mmol	7.9 g
$LiNTf_2$	25.5 mmol	7.3 g
H_2O (deionised)		80 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 14.1 g (90%); T_{dec} = 447 °C, T_g = -79 °C.

^{1}H NMR ($CDCl_3$): δ = 1.60-1.85 (several m, 6 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.03 and 3.04 (2 overlapped s, 6 H, NCH_3), 2.97 and 3.00 (2 s, 6 H, NCH_3), 3.15–3.65 (several m, 12 H, $NCH_2CH_2OCH_3$, $NCH_2CH_2OCH_3$, 2-H_{pip}, 6-H_{pip}), 3.31 and 3.32 (2 overlapped s, 6 H, $NCH_2CH_2OCH_3$) ppm.

^{13}C NMR ($CDCl_3$): δ = 23.5 (4-C_{pip}), 24.9 and 25.1 (3-C_{pip} and 5-C_{pip}), 40.0 and 40.6 (NCH_3), 49.2, 49.5, 49.9 and 50.2 ($NCH_2CH_2OCH_3$, 2-C_{pip}, 6-C_{pip}), 57.8 ($NCH_2CH_2OCH_3$), 68.8 and 68.9 ($NCH_2CH_2OCH_3$), 118.3 and 121.5 (CF_3), 163.9 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.2 ppm.

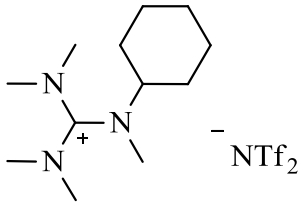
IR (NaCl): ν = 2942 (m), 2867 (m), 1586 (s), 1550 (s), 1454 (m), 1422 (m), 1353 (s), 1292 (m), 1191 (vs), 1138 (s), 1058 (s), 860 (w), 789 (w) cm^{-1}.

MS (CI): *m*/*z* = 272 (100%, $[cation]^+$).

CHN (in %): $C_{16}H_{30}F_6N_4O_6S_2$ (552.55 g/mol)

Calcd.	C 34.78	H 5.47	N 10.14
Found	C 34.79	H 5.31	N 10.34

6.2.3.18 Synthesis of *N*-cyclohexyl-*N,N',N',N'',N''*-pentamethyl-guanidinium bis(trifluoromethylsulfonyl)imide (6w)



Salt $[N_{11}N_{11}N_{1cHex}Gu]Cl$ **(5w)**	14.4 mmol	3.6 g
$LiNTf_2$	14.4 mmol	4.1 g
H_2O (deionised)		50 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 5.8 g (82%); T_{dec} = 431 °C, T_g = -67 °C.

^{1}H NMR ($CDCl_3$): δ = 1.05–1.20 (m, 1 H, 4-H_{cHex}), 1.28–1.45 (m, 2 H, 3-H_{cHex}, 5-H_{cHex}), 1.55–1.75 (m, 4 H, 2-H_{cHex}, 6-H_{cHex}), 1.80–2.05 (m, 3 H, 3-H_{cHex}, 4-H_{cHex} and 5-H_{cHex}), 2.84 (s, 3 H, N(*c*Hex)CH_3), 2.93 and 2.99 (2 overlapped bs, 12 H, NCH_3), 3.10-3.20 (m, 1 H, 1-H_{cHex}) ppm.

^{13}C NMR ($CDCl_3$): δ = 25.0 (4-C_{cHex}), 25.6 and 25.7 (3-C_{cHex} and 5-C_{cHex}), 29.5 and 31.8 (2-C_{cHex} and 6-C_{cHex}), 32.7 (N(*c*Hex)*C*H_3), 40.0 and 40.6 (NCH_3), 61.2 (N(1-C_{cHex})), 118.3 and 121.4 (CF_3), 163.9 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

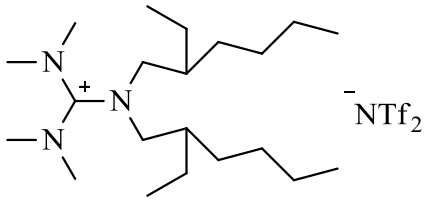
IR (NaCl): ν = 2939 (m), 2863 (m), 1594 (s), 1566 (s), 1456 (m), 1411 (m), 1353 (s), 1190 (s), 1139 (s), 1058 (s), 899 (m) cm^{-1}.

MS (CI): *m*/*z* = 212 (100%, $[cation]^+$).

CHN (in %): $C_{12}H_{26}F_6N_4O_4S_2$ (492.50 g/mol)

Calcd.	C 34.14	H 5.32	N 11.38
Found	C 34.12	H 5.33	N 11.46

6.2.3.19 Synthesis of *N*,*N*-bis(2-ethylhexyl)-*N'*,*N'*,*N"*,*N"*-tetramethyl-guanidinium bis(trifluoromethylsulfonyl)imide (6x)



Salt $[N_{11}N_{11}N_{2\text{-}6\ 2\text{-}6}Gu]Cl$ **(5x)**	12.0 mmol	4.5 g
$LiNTf_2$	12.0 mmol	3.4 g
H_2O (deionised)		50 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 6.6 g (89%); T_{dec} = 448 °C, T_g = -75 °C.

^{1}H NMR ($CDCl_3$): δ = 0.80–0.95 (m, 12 H, 4 CH_3 of (2-Et)Hex), 1.05–1.65 (m, 18 H, $NCH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$), 2.85–2.95 and 3.05–3.15 (several m, 4 H, NCH_2), 3.00 (s, 12 H, NCH_3) ppm.

^{13}C NMR ($CDCl_3$): δ = 9.6, 11.1, 13.92 and 13.98 (4 CH_3 of (2-Et)Hex), 22.8, 22.9, 23.7 and 23.8 (CH_2CH_3 of (2-Et)Hex), 28.0 and 29.0 ($CH_2CH_2CH_3$), 30.2 and 30.9 ($CH_2CH_2CH_2CH_3$), 37.1, 37.2 and 37.7 (NCH_2CH, rotamers), 40.3 and 40.5 (NCH_3), 53.2, 53.4, 53.5 and 53.8 (NCH_2, rotamers), 118.3 and 121.5 (CF_3), 163.7 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -75.3 ppm.

IR (NaCl): ν = 2962 (s), 2933 (s), 2875 (m), 1586 (s), 1564 (s), 1463 (m), 1412 (m), 1353 (s), 1189 (s), 1139 (s), 1059 (s), 894 (m) cm^{-1}.

MS (CI): *m*/*z* = 340 (100%, $[cation]^+$).

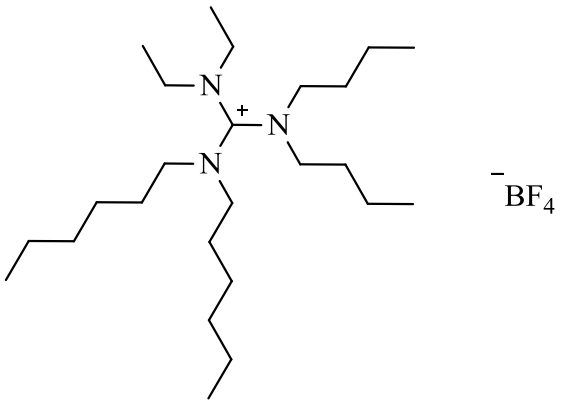
CHN (in %): $C_{21}H_{46}F_6N_4O_4S_2$ (620.76 g/mol)

Calcd.	C 44.50	H 7.47	N 9.03
Found	C 44.50	H 7.34	N 9.16

6.2.4 Synthesis of hexaalkylguanidinium tetrafluoroborates

General procedure, modified procedure given in lit. [35]. Hexaalkylguanidinium chloride (1 equiv.) was dissolved in dry dichloromethane. Sodium tetrafluoroborate (1.4 equiv.) was added. The suspension was stirred at room temperature for 24 h. The precipitate was filtered off and washed with dichloromethane. The mother liquid was dried with Na_2SO_4, stirred over charcoal for 15 min and filtered. The solvent was removed in a rotary evaporator, and the product was dried for 8 h at 80 °C/0.05 mbar in the bulb-to-bulb apparatus.

6.2.4.1 Synthesis of *N,N*-dibutyl-*N',N'*-diethyl-*N'',N''*-dihexylguanidinium tetrafluoroborate (7a)



Salt $[N_{22}N_{44}N_{66}Gu]Cl$ **(5b)**	11.6 mmol	5.0 g
$NaBF_4$	16.7 mmol	1.8 g
Dichloromethane		20 mL

Prepared according to the general procedure. The product was obtained as a colourless oil.

Yield: 4.9 g (88%); T_{dec} = 462 °C, T_g = -71 °C.

^{1}H NMR ($CDCl_3$): δ = 0.84–0.98 (several overlapped t, 12 H, 4 CH_3 of Hex and Bu), 1.18–1.78 (several m and t, 30 H, NCH_2CH_3, $NCH_2(CH_2)_2CH_3$ and $NCH_2(CH_2)_4CH_3$), 2.98–3.44 (several m, 12 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 12.76, 12.77, 13.60, 13.63, 13.87 and 13.88 (CH_3), 19.99, 20.03, 22.46, 22.48, 26.47, 26.51, 27.36, 27.38, 29.44, 29.49, 31.23 and 31.28 ((CH_2)$_2$$CH_3$ and (CH_2)$_4$$CH_3$), 43.80 and 43.83 (N$CH_2$$CH_3$), 49.32, 49.40, 49.56 and 49.58 (NCH_2 of Hex and Bu), 163.9 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -150.18, -150.23 ppm.

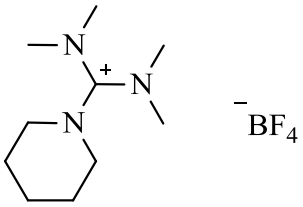
IR (NaCl): ν = 2958 (s), 2933 (s), 2873 (m), 1539 (s), 1460 (m), 1440 (m), 1380 (m), 1311 (m), 1056 (s), 792 (w) cm^{-1}.

MS (CI): *m*/*z* = 396 (100%, $[cation]^+$).

CHN (in %): $C_{25}H_{54}BF_4N_3$ (483.52 g/mol)

Calcd.	C 62.10	H 11.26	N 8.69
Found	C 61.96	H 12.07	N 8.75

6.2.4.2 Synthesis of *N,N,N',N'*-tetramethyl-*N'',N''*-pentamethylene-guanidinium tetrafluoroborate (7b)



Salt [$N_{11}N_{11}N_{pip}$Gu]Cl **(5l)**	9.1 mmol	2.0 g
$NaBF_4$	12.7 mmol	1.4 g
Dichloromethane		25 mL

Prepared according to the general procedure. The product was obtained as a colourless solid.

Yield: 2.3 g (94%); m.p. = 107 °C, T_{dec} = 468 °C.

^{1}H NMR ($CDCl_3$): δ = 1.68–1.78 (m, 6 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.98 and 2.99 (2 s, 12 H, NCH_3), 3.25–3.35 (m, 4 H, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 23.5 (4-C_{pip}), 25.2 (3-C_{pip}, 5-C_{pip}), 40.32 and 40.36 (NCH_3), 49.9 (2-C_{pip}, 6-C_{pip}), 163.0 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -149.97, -150.02 ppm.

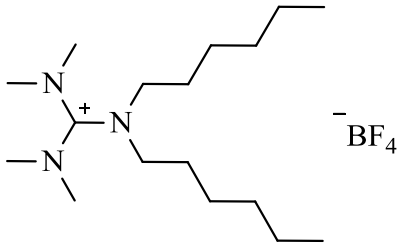
IR (ATR): ν = 2938 (w), 2868 (w), 1569 (s), 1412 (m), 1277 (m), 1093 (m), 1070 (m), 1033 (vs), 921 (m), 878 (m) cm^{-1}.

MS (CI): *m*/*z* = 184 (100%, $[cation]^+$).

CHN (in %): $C_{10}H_{22}BF_4N_3$ (271.11 g/mol)

Calcd.	C 44.30	H 8.18	N 15.50
Found	C 44.18	H 8.28	N 15.35

6.2.4.3 Synthesis of *N,N,N',N'*-tetramethyl-*N",N"*-dihexylguanidinium tetrafluoroborate (7c)



Salt $[N_{11}N_{11}N_{66}Gu]Cl$ **(5h)**	6.3 mmol	2.0 g
$NaBF_4$	8.8 mmol	1.0 g
Dichloromethane		20 mL

Prepared according to the general procedure. The product was obtained as a colourless oil, which crystallised after several months.

Yield: 2.0 g (87%); m.p. = 33 °C, T_{dec} = 459 °C, T_g = -60 °C.

^{1}H NMR ($CDCl_3$): δ = 0.82-0.88 (ψt, 6 H, $N(CH_2)_5CH_3$), 1.17-1.65 (several m, 16 H, $NCH_2(CH_2)_4CH_3$), 2.93 and 2.97 (2 s, both 6 H, NCH_3), 2.98-3.18 (m, 4 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.9 ($N(CH_2)_5CH_3$), 22.5 ($N(CH_2)_4CH_2CH_3$), 26.4 ($N(CH_2)_3CH_2CH_2CH_3$), 27.5 ($N(CH_2)_2CH_2(CH_2)_2CH_3$), 31.4 ($NCH_2CH_2(CH_2)_3CH_3$), 40.26 and 40.32 ($NCH_3$), 49.5 ($NCH_2$), 163.3 ($CN_3$) ppm.

^{19}F NMR ($CDCl_3$): δ = -149.70, -149.75 ppm.

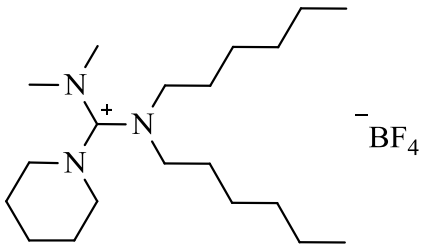
IR (NaCl): ν = 2932 (s), 2860 (m), 1597 (s), 1566 (s), 1467 (m), 1435 (m), 1411 (m), 1058 (s), 897 (m) cm^{-1}.

MS (CI): *m*/*z* = 284 (100%, [cation]$^+$).

CHN (in %): $C_{17}H_{38}BF_4N_3$ (371.31 g/mol)

Calcd.	C 54.99	H 10.32	N 11.32
Found	C 54.97	H 10.50	N 11.30

6.2.4.4 Synthesis of *N*,*N*-dihexyl-*N'*,*N'*-dimethyl-*N"*,*N"*-pentamethylene-guanidinium tetrafluoroborate (7d)



Salt $[N_{11}N_{66}N_{pip}Gu]Cl$ **(5s)**	2.9 mmol	1.0 g
$NaBF_4$	4.0 mmol	0.4 g
Dichloromethane		15 mL

Prepared according to the general procedure. The product was obtained as a yellow viscous oil.

Yield: 0.9 g (79%); T_{dec} = 472 °C, T_g = -59 °C.

^{1}H NMR ($CDCl_3$): δ = 0.87-0.93 (ψt, 6 H, $N(CH_2)_5CH_3$), 1.20-1.80 (several m, 22 H, $NCH_2(CH_2)_4CH_3$, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.97 and 3.03 (2 s, each 3 H, NCH_3), 3.03–3.45 (several m, 8 H, $NCH_2(CH_2)_4CH_3$, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 14.0 ($N(CH_2)_5CH_3$), 22.5 ($N(CH_2)_4CH_2CH_3$), 23.5 (4-C_{pip}), 25.1 and 25.2 (3-C_{pip} and 5-C_{pip}), 26.4 and 26.5 ($N(CH_2)_3CH_2CH_2CH_3$), 27.4 and 27.5 ($N(CH_2)_2CH_2(CH_2)_2CH_3$), 31.3 and 31.4 ($NCH_2CH_2(CH_2)_3CH_3$), 40.5 ($NCH_3$), 49.4, 49.6, 50.0 and 50.1 ($NCH_2(CH_2)_4CH_3$, 2-C_{pip}, 6-C_{pip}), 163.0 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -150.05, -150.10 ppm.

IR (NaCl): ν = 2933 (s), 2860 (m), 1583 (s), 1549 (s), 1455 (m), 1423 (m), 1380 (w), 1284 (m), 1255 (m), 1055 (s), 789 (w) cm^{-1}.

MS (CI): *m*/*z* = 324 (100%, [cation]$^+$).

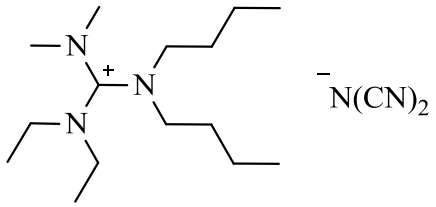
CHN (in %): $C_{20}H_{42}BF_4N_3$ (411.37 g/mol)

Calcd.	C 58.39	H 10.29	N 10.21
Found	C 58.67	H 10.49	N 10.13

6.2.5 Synthesis of hexaalkylguanidinium dicyanamides

General procedure, modified procedure given in lit. [141]. Hexaalkylguanidinium chloride (1 equiv.) was dissolved in dry dichloromethane. Sodium dicyanamide (1.4 equiv.) was added. The suspension was stirred at room temperature for 24 h. The precipitate was filtered off and washed with dichloromethane. The mother liquid was dried with Na_2SO_4, stirred over charcoal for 15 min and filtered. The solvent was removed on a rotary evaporator, and the product was dried for 8 h at 80 °C/0.05 mbar in the bulb-to-bulb apparatus.

6.2.5.1 Synthesis of *N,N*-dibutyl-*N',N'*-diethyl-*N'',N''*-dimethylguanidinium dicyanamide (8a)



Salt $[N_{11}N_{22}N_{44}Gu]Cl$ **(5a)**	16.3 mmol	4.8 g
$NaN(CN)_2$	22.8 mmol	2.1 g
Dichloromethane		25 mL

Prepared according to the general procedure. The product was obtained as a light yellow oil.

Yield: 4.6 g (87%); T_{dec} = 371 °C, T_g = -60 °C.

^{1}H NMR ($CDCl_3$): δ = 0.93–0.98 (2 overlapped t, 6 H, $CH_2(CH_2)_2CH_3$), 1.21–1.70 (several m, 14 H, NCH_2CH_3, $CH_2(CH_2)_2CH_3$), 3.03 and 3.04 (2 s, 3 H each, NCH_3), 3.01–3.38 (several m, 8 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 12.8, 13.1, 13.6 and 13.7 ($(CH_2)_nCH_3$, n = 0, 1, 3), 20.0 and 20.1 ($CH_2CH_2CH_2CH_3$), 29.5 and 29.7 ($CH_2CH_2CH_2CH_3$), 40.4 and 40.5 (NCH_3), 43.5 and 44.1 (NCH_2CH_3), 49.1, 49.7 ($NCH_2(CH_2)_2CH_3$), 119.9 (CN, anion), 163.4 (CN_3) ppm.

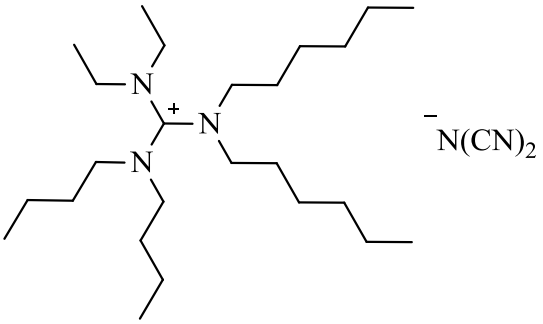
IR (NaCl): ν = 2961 (s), 2875 (s), 2222 (s), 2187 (m), 2127 (s), 1580 (s), 1549 (s), 1460 (s), 1421 (s), 1382 (m), 1302 (s), 1182 (w), 1112 (w), 897 (w) cm^{-1}.

MS (CI): *m*/*z* = 256 (100%, $[cation]^+$).

CHN (in %): $C_{17}H_{34}N_6$ (322.49 g/mol)

Calcd.	C 63.31	H 10.63	N 26.06
Found	C 63.42	H 10.67	N 26.02

6.2.5.2 Synthesis of *N,N*-dibutyl-*N',N'*-diethyl-*N'',N''*-dihexylguanidinium dicyanamide (8b)



Salt $[N_{22}N_{44}N_{66}Gu]Cl$ **(8b)**	6.4 mmol	2.8 g
$NaN(CN)_2$	9.0 mmol	0.8 g
Dichloromethane		15 mL

Prepared according to the general procedure. The product was obtained as a light yellow oil.

Yield: 2.8 g (93%); T_{dec} = 373 °C, T_g = -57 °C.

^{1}H NMR ($CDCl_3$): δ = 0.88–0.99 (several overlapped t, 12 H, 4 CH_3 of Hex and Bu), 1.23–1.80 (t and several m, 30 H, NCH_2CH_3, $NCH_2(CH_2)_2CH_3$ and $NCH_2(CH_2)_4CH_3$), 3.01–3.45 (several m, 12 H, NCH_2) ppm.

^{13}C NMR ($CDCl_3$): δ = 12.91, 12.92, 13.64, 13.67, 13.88 and 13.90 (CH_3), 20.06, 20.08, 22.47, 22.48, 26.50, 26.56, 27.44, 27.49, 29.50, 29.59, 31.23 and 31.26 ($(CH_2)_2CH_3$ and

(CH_2)$_4$$CH_3$), 43.87 and 43.90 (N$CH_2$$CH_3$), 49.41, 49.47 and 49.65 (NCH_2 of Hex and Bu), 120.0 (CN, anion), 163.8 (CN_3) ppm.

IR (NaCl): ν = 2933 (s), 2873 (s), 2222 (s), 2187 (m), 2126 (s), 1538 (s), 1456 (s), 1380 (m), 1302 (m), 1112 (w), 901 (w) cm^{-1}.

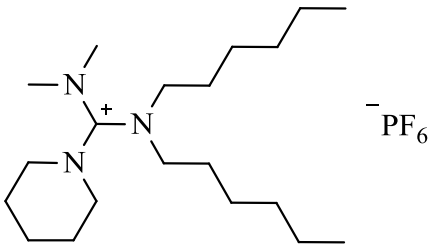
MS (CI): *m*/*z* = 397 (100%, $[cation]^+$).

CHN (in %): $C_{27}H_{54}N_6$ (462.75 g/mol)

Calcd.	C 70.08	H 11.76	N 18.16
Found	C 70.07	H 11.53	N 18.05

6.2.6 Synthesis of hexaalkylguanidinium hexafluorophosphates

6.2.6.1 Synthesis of *N,N*-dihexyl-*N',N'*-dimethyl-*N",N"*-pentamethylene-guanidinium hexafluorophosphate (9a)



Salt $[N_{11}N_{66}N_{pip}Gu]Cl$ (**5s)**	5.9 mmol	2.1 g
KPF_6	8.3 mmol	1.5 g
Dichloromethane		20 mL

Prepared according to modified procedure given in lit. [35]. Hexaalkylguanidinium chloride **5s** (1 equiv.) was dissolved in dry dichloromethane. Potassium hexafluorophosphate (1.4 equiv.) was added. The suspension was stirred at room temperature for 24 h. The precipitate was filtered off and washed with dichloromethane. The mother liquid was dried with Na_2SO_4, stirred over charcoal for 15 min and filtered. The solvent was removed on a rotary evaporator, and the product was dried for 8 h at 80 °C/0.05 mbar in the bulb-to-bulb apparatus. The product was obtained as a yellow viscous oil.

Yield: 2.4 g (86%); T_{dec} = 467 °C, T_g = -54 °C.

^{1}H NMR ($CDCl_3$): δ = 0.85-0.92 (ψt, 6 H, $N(CH_2)_5CH_3$), 1.20-1.82 (several m, 22 H, $NCH_2(CH_2)_4CH_3$, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.95 and 3.00 (2 s, each 3 H, NCH_3), 3.00–3.42 (several m, 8 H, $NCH_2(CH_2)_4CH_3$, 2-H_{pip}, 6-H_{pip}) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.9 ($N(CH_2)_5CH_3$), 22.46 and 22.49 ($N(CH_2)_4CH_2CH_3$), 23.4 (4-C_{pip}), 25.1 and 25.2 (3-C_{pip} and 5-C_{pip}), 26.3 and 26.5 ($N(CH_2)_3CH_2CH_2CH_3$), 27.4 and 27.5 ($N(CH_2)_2CH_2(CH_2)_2CH_3$), 31.3 and 31.4 ($NCH_2CH_2(CH_2)_3CH_3$), 40.5 ($NCH_3$), 49.5, 49.7, 50.1 and 50.2 ($NCH_2(CH_2)_4CH_3$, 2-C_{pip}, 6-C_{pip}), 162.9 (CN_3) ppm.

^{19}F NMR ($CDCl_3$): δ = -68.8, -70.7 ppm.

IR (NaCl): ν = 2933 (s), 2861 (m), 1581 (s), 1553 (s), 1455 (m), 1424 (m), 1380 (w), 1255 (w), 1138 (w), 1026 (w), 922 (w), 838 (s) cm^{-1}.

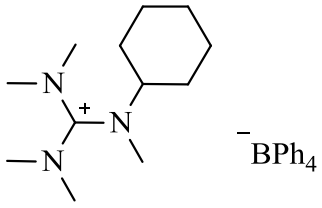
MS (CI): *m*/*z* = 324 (100%, $[cation]^+$).

CHN (in %): $C_{20}H_{42}F_6P$ (469.53 g/mol)

Calcd.	C 51.16	H 9.02	N 8.95
Found	C 51.32	H 9.08	N 8.97

6.2.7 Synthesis of hexaalkylguanidinium tetraphenylborate

6.2.7.1 Synthesis of *N*-cyclohexyl-*N,N',N',N'',N''*-pentamethylguanidinium tetraphenylborate (10a)



Salt $[N_{11}N_{11}N_{1cHex}Gu]Cl$ **(5w)**	5.9 mmol	2.1 g
$NaBPh_4$	8.3 mmol	1.5 g
Dichloromethane		20 mL

Hexaalkylguanidinium chloride **5w** and sodium tetraphenylborate were dissolved in deionised water. The solutions were combined resulting in two phases. The mixture was stirred at room

temperature for 24 h. The precipitate was filtered off, washed at first with deionised water, then with diethyl ether. The product was recrystallized from ethyl acetate/acetonitrile (3:1, v/v) and dried for 8 h at 100 °C/0.05 mbar in the bulb-to-bulb apparatus. The product was obtained as a colourless solid.

Yield: 1.6 g (86%); m.p. = 233 °C, T_{dec} = 409 °C, T_g = -107 °C.

^{1}H NMR (CD_3CN): δ = 1.07–1.20 (m, 1 H, 4-H_{cHex}), 1.30–1.45 (m, 2 H, 3-H_{cHex}, 5-H_{cHex}), 1.50–1.70 (m, 4 H, 2-H_{cHex}, 6-H_{cHex}), 1.75–1.94 (m, 3 H, 3-H_{cHex}, 4-H_{cHex} and 5-H_{cHex}), 2.74 (s, 3 H, N(*c*Hex)CH_3), 2.80-2.95 (several overlapped s, 12 H, NCH_3), 3.17-3.27 (m, 1 H, 1-H_{cHex}), 6.83-6.87 (t, 4 H, 4-H_{Ph}), 6.98-7.02 (t, 8 H, 3-H_{Ph} and 5-H_{Ph}), 7.24-7.30 (m, 8 H, 2-H_{Ph} and 6-H_{Ph}) ppm.

^{13}C NMR (CD_3CN): δ = 25.8 (4-C_{cHex}), 26.2 and 26.4 (3-C_{cHex} and 5-C_{cHex}), 30.1 and 32.3 (2-C_{cHex} and 6-C_{cHex}), 33.0 (N(*c*Hex)*C*H_3), 40.5 and 40.8 (NCH_3), 61.4 (N(1-C_{cHex}), 122.7 (4-C_{Ph}), 126.49, 126.52, 126.55, 126.57 (3-C_{Ph} and 5-C_{Ph}), 136.66, 136.68 (2-C_{Ph} and 6-C_{Ph}), 164.0, 164.5, 164.9, 165.0 and 165.5 (1-C_{Ph} and CN_3) ppm.

IR (KBr): ν = 3051 (m), 3001 (m), 2929 (m), 2855 (m), 1567 (s), 1405 (m), 1147 (m), 896 (m), 737 (s), 705 (vs) cm^{-1}.

MS (CI): *m*/*z* = 212 (100%, $[cation]^+$).

CHN (in %): $C_{36}H_{46}BN_3$ (531.58 g/mol)

Calcd.	C 81.34	H 8.72	N 7.90
Found	C 81.53	H 8.95	N 8.00

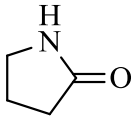
6.2.8 Reactions in guanidinium-based ionic liquids

6.2.8.1 Reaction of lactamisation

General procedure. Dried IL **6b** or **6h** (2 g) was placed in the round-bottom flask with a three-way Claisen adaptor, argon inlet and a drying tube. Catalyst (10 mol-%) and then 0.4 g amino acid were added. The mixture was stirred for some hours at 120 °C. The reaction was controlled by NMR (in D_2O). The product was then separated by bulb-to-bulb distillation at 120-140 °C/0.05 mbar. For the next cycle the new portion of the amino acid was added and the procedure was repeated. For exact conditions and yields, see **Tables 8** and **9**.

The procedure with higher concentration of amino acid in IL. Dry IL **6h** (2.5 mL) was placed in the round-bottom flask with a three-way Claisen adaptor, argon inlet and a drying tube. Catalyst (10 mol-% $Ti(O\textit{i}Pr)_4$, 0.43 mL) and then 1.5 g (14.5 mmol) 4-aminobutyric acid were added. So much IL was taken that smooth stirring was achieved (2.5 mL). After 3 h of stirring at 120 °C the mixture was cooled to room temperature. Since no phase separation was observed, the product was separated by vacuum distillation as in the general procedure. The reaction yielded 96% of γ-butyrolactam.

6.2.8.1.1 γ-Butyrolactam (2-pyrrolidone)



4-Aminobutyric acid	3.90 mmol	0.40 g
Titanium tetraisopropoxide	0.39 mmol	0.12 mL
IL **6h**		2 g

The product was obtained as a colourless liquid.

^{1}H NMR ($CDCl_3$): δ = 2.10-2.18 (m, 2 H, 4-H), 2.28-2.32 (t, 2 H, 3-H), 3.38-3.42 (t, 2 H, 5-H), 5.91 (bs, 1 H, NH) ppm.

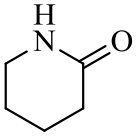
^{13}C NMR ($CDCl_3$): δ = 20.7 (4-C), 30.4 (3-C), 42.2 (5-C), 179.4 (C=O) ppm.

Obtained NMR data is in agreement with lit. [233].

CHN (in %): C_4H_7NO (85.05 g/mol)

Calcd.	C 56.45	H 8.29	N 16.46
Found	C 56.46	H 8.14	N 16.68

6.2.8.1.2 δ-Valerolactam (2-piperidinone)



5-Aminopentanoic acid	3.40 mmol	0.40 g
Titanium tetraisopropoxide	0.34 mmol	0.10 mL
IL **6h**		2 g

The product was obtained as a white powder, m.p. 40 °C (lit. 39-40 °C[234]).

^{1}H NMR (CD_3OD): δ = 1.70-1.85 (m, 4 H, 4-H, 5-H), 2.29-2.32 (t, 2 H, 3-H), 3.26-3.29 (t, 2 H, 6-H) ppm.

^{1}H NMR ($CDCl_3$): δ = 1.66-1.76 (m, 4 H, 4-H, 5-H), 2.27-2.31 (t, 2 H, 3-H), 3.23-3.27 (t, 2 H, 6-H), 7.16 (bs, 1 H, NH) ppm.

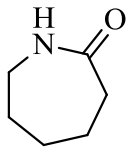
^{13}C NMR (CD_3OD): δ = 21.7 (4-C), 23.1 (5-C), 32.0 (3-C), 43.0 (6-C), 174.9 (C=O) ppm.

Obtained NMR data is in agreement with lit. [233].

CHN (in %): $C_5H_9NO \cdot 0.125$ (99.13 + 2.25 g/mol)

Calcd.	C 59.23	H 9.20	N 13.82
Found	C 59.26	H 9.18	N 13.88

6.2.8.1.3 ε-Caprolactam (hexahydro-2-azepinone)



6-Aminohexanoic acid	3.10 mmol	0.40 g
Titanium tetraisopropoxide	0.31 mmol	0.09 mL
IL **6h**		2 g

The product was obtained as a white powder, m.p. 70 °C (lit. 69-70 °C[235]).

^{1}H NMR ($CDCl_3$): δ = 1.60-1.75 (m, 6 H, 4-H, 5-H, 6-H), 2.43-2.46 (ψt, 2 H, 3-H), 3.17-3.20 (m, 2 H, 7-H), 6.51 (bs, 1 H, NH) ppm.

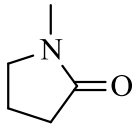
^{13}C NMR ($CDCl_3$): δ = 23.2 (5-C), 29.7 and 30.6 (4-C and 6-C), 36.6 (3-C), 42.8 (7-C), 179.1 (C=O) ppm.

Obtained NMR data is in agreement with lit. [233].

CHN (in %): $C_5H_{11}NO$ (113.16 g/mol)

Calcd.	C 63.68	H 9.80	N 12.38
Found	C 63.60	H 9.94	N 12.27

6.2.8.1.4 *N*-Methyl-2-pyrrolidone



N-Methyl-4-aminobutyric acid	3.40 mmol	0.40 g
Titanium tetraisopropoxide	0.34 mmol	0.10 mL
IL **6h**		2 g

The product was obtained as a colourless liquid.

^{1}H NMR ($CDCl_3$): δ = 1.97-2.03 (m, 2 H, 4-H), 2.34-2.39 (t, 2 H, 3-H), 2.83 (s, 3 H, NCH_3), 3.35-3.39 (t, 2 H, 5-H) ppm.

^{13}C NMR ($CDCl_3$): δ = 17.5 (4-C), 29.5 (CH_3), 30.6 (3-C), 49.3 (5-C), 174.9 (C=O) ppm.

Obtained NMR data is in agreement with lit. [236].

CHN (in %): $C_5H_9NO{\cdot}0.31H_2O$ (99.13 + 5.63 g/mol)

Calcd.	C 55.96	H 9.31	N 13.05
Found	C 55.96	H 9.30	N 13.07

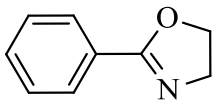
6.2.8.2 Reaction of lactonisation

General procedure. Dried IL **6b** or **6h** (2 g) was placed in the round-bottom flask with a three-way Claisen adaptor, argon inlet and a drying tube. Catalyst (10-100 mol-%) and then 0.2 g hydroxy acid were added. The mixture was stirred for some hours at 20-120 °C. The reaction was controlled by NMR (in D_2O). The product was then separated by bulb-to-bulb distillation at 120-130 °C/0.05 mbar. The obtained mixtures of lactone/hydroxy acid were not further separated.

6.2.8.3 Synthesis of 2-oxazolines

General procedure. Dried IL **6h** (2 g) was placed in the round-bottom flask, provided with reflux condenser, a three-way Claisen adaptor, argon inlet and a drying tube. Catalyst (50-250 mol-%) and then acid (3 mmol), amino alcohol (3.6 mmol) and 1 g of molecular sieves 4Å were added. The mixture was stirred for some hours at 120 °C, then at 200 °C. The reaction was controlled by NMR (in $CDCl_3$ or CD_3OD). The product was separated by bulb-to-bulb distillation at 120-140 °C/0.05 mbar. For the next cycle the new portions of the acid and amino alcohol were added and the procedure was repeated. For exact conditions and yields, see **Tables 10** and **11**.

6.2.8.3.1 2-Phenyl-4,5-dihydrooxazole



Benzoic acid	3.00 mmol	0.36 g
Monoethanolamine	3.60 mmol	0.22 mL
Titanium tetraisopropoxide	1.50 mmol	0.45 mL
Molecular sieves 4Å		1 g
IL **6h**		2 g

The product was obtained as a colourless liquid.

^{1}H NMR ($CDCl_3$): δ = 4.03-4.08 (t, ^3J = 9.5 Hz, 2 H, 4-H_{ox}), 4.40-4.45 (t, ^3J = 9.4 Hz, 2 H, 5-H_{ox}), 7.38–7.49 (several m, 3 H, 3-H_{Ph}, 4-H_{Ph}, 5-H_{Ph}), 7.92-7.95 (m, 2 H, 2-H_{Ph} and 6-H_{Ph}) ppm.

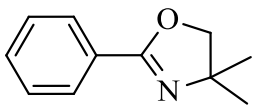
^{13}C NMR ($CDCl_3$): δ = 54.9 (4-C_{ox}), 67.5 (5-C_{ox}), 127.7 (1-C_{Ph}), 128.1 and 128.3 (2-C_{Ph}, 3-C_{Ph}, 5-C_{Ph}, 6-C_{Ph}), 131.2 (4-C_{Ph}), 164.6 (2-C_{ox}) ppm.

Obtained NMR data is in agreement with lit. [237].

CHN (in %): $C_9H_9NO{\cdot}0.14H_2O$ (147.17 +2.57 g/mol)

Calcd.	C 71.98	H 6.26	N 9.33
Found	C 72.03	H 6.37	N 9.23

6.2.8.3.2 4,4-Dimethyl-2-phenyl-4,5-dihydrooxazole



Benzoic acid	3.00 mmol	0.36 g
2-Amino-2-methyl-1-propanol	3.60 mmol	0.35 mL
Titanium tetraisopropoxide	1.50 mmol	0.45 mL
Molecular sieves 4Å		1 g
IL **6h**		2 g

The product was obtained as a colourless liquid.

^{1}H NMR (CD_3OD): δ = 1.38 (s, 6 H, CH_3), 4.20 (s, 2 H, 5-H_{ox}), 7.43–7.56 (several m, 3 H, 3-H_{Ph}, 4-H_{Ph}, 5-H_{Ph}), 7.89-7.91 (d, 2 H, ^{3}J = 7.3 Hz, 2-H_{Ph} and 6-H_{Ph}) ppm.

^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 6 H, CH_3), 4.10 (s, 2 H, 5-H_{ox}), 7.37–7.48 (several m, 3 H, 3-H_{Ph}, 4-H_{Ph}, 5-H_{Ph}), 7.92-7.95 (m, 2 H, 2-H_{Ph} and 6-H_{Ph}) ppm.

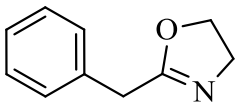
^{13}C NMR (CD_3OD): δ = 28.6 (CH_3), 68.5 (4-C_{ox}), 80.5 (5-C_{ox}), 129.4, 129.7 (1-C_{Ph}, 2-C_{Ph}, 3-C_{Ph}, 5-C_{Ph}, 6-C_{Ph}), 133.0 (4-C_{Ph}), 164.9 (2-C_{ox}) ppm.

Obtained NMR data is in agreement with lit. [238].

CHN (in %): $C_{11}H_{13}NO{\cdot}0.17H_2O$ (175.23 + 3.00 g/mol)

Calcd.	C 73.88	H 7.55	N 7.83
Found	C 73.73	H 7.56	N 7.81

6.2.8.3.3 2-Benzyl-4,5-dihydrooxazole



Phenylacetic acid	3.00 mmol	0.41 g
Monoethanolamine	3.60 mmol	0.22 mL
Titanium tetraisopropoxide	1.50 mmol	0.45 mL
Molecular sieves 4Å		1 g

IL **6h**		2 g

The product was obtained as a colourless liquid.

^{1}H NMR ($CDCl_3$): δ = 3.57 (s, 2 H, CH_2-Bn), 3.77-3.82 (t, ^{3}J = 9.4 Hz, 2 H, 4-H_{ox}), 4.16-4.21 (t, ^{3}J = 9.3 Hz, 2 H, 5-H_{ox}), 7.19–7.30 (several m, 5 H, Ar-H) ppm.

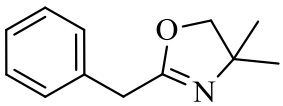
^{13}C NMR ($CDCl_3$): δ = 34.6 (CH_2-Bn), 54.4 (4-C_{ox}), 67.5 (5-C_{ox}), 126.9 (4-C_{Ph}), 128.5 and 128.9 (2-C_{Ph}, 3-C_{Ph}, 5-C_{Ph}, 6-C_{Ph}), 135.1 (1-C_{Ph}), 166.9 (2-C_{ox}) ppm.

Obtained NMR data is in agreement with lit. [239].

CHN (in %): $C_{10}H_{11}NO{\cdot}0.29H_2O$ (161.20 + 5.14 g/mol)

Calcd.	C 71.32	H 7.06	N 8.32
Found	C 71.17	H 6.99	N 8.54

6.2.8.3.4 4,4-Dimethyl-2-benzyl-4,5-dihydrooxazole



Phenylacetic acid	3.00 mmol	0.41 g
2-Amino-2-methyl-1-propanol	3.60 mmol	0.35 mL
Titanium tetraisopropoxide	1.50 mmol	0.45 mL
Molecular sieves 4Å		1 g
IL **6h**		2 g

The product was obtained as a colourless liquid.

^{1}H NMR ($CDCl_3$): δ = 1.30 (s, 6 H, CH_3), 3.61 (s, 2 H, CH_2-Bn), 3.93 (s, 2 H, 5-H_{ox}), 7.24–7.37 (several m, 5 H, Ar-H) ppm.

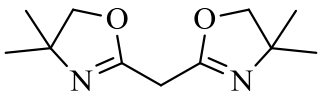
^{13}C NMR ($CDCl_3$): δ = 28.3 (CH_3), 34.9 (CH_2-Bn), 67.0 (4-C_{ox}), 79.3 (5-C_{ox}), 126.9 (4-C_{Ph}), 128.6 and 128.7 (2-C_{Ph}, 3-C_{Ph}, 5-C_{Ph}, 6-C_{Ph}), 135.3 (1-C_{Ph}), 164.2 (2-C_{ox}) ppm.

Obtained NMR data is in agreement with lit. [240].

CHN (in %): $C_{12}H_{15}NO$ (189.25 g/mol)

Calcd.	C 76.16	H 7.99	N 7.40
Found	C 75.92	H 8.23	N 7.67

6.2.8.3.5 Bis(4,4-dimethyl-4,5-dihydrooxazol-2-yl)methane



Phenylacetic acid	3.00 mmol	0.41 g
2-Amino-2-methyl-1-propanol	7.20 mmol	0.69 mL
Titanium tetraisopropoxide	1.50 mmol	0.45 mL
Molecular sieves 4Å		1 g
IL **6h**		2 g

The product was obtained as a colourless liquid.

^{1}H NMR ($CDCl_3$): δ = 1.27 (s, 12 H, CH_3), 3.30 (s, 2 H, CH_2), 3.96 (s, 4 H, 5-H_{ox}) ppm.

^{13}C NMR ($CDCl_3$): δ = 28.2 (CH_3), 28.6 (CH_2), 67.3 (4-C_{ox}), 79.5 (5-C_{ox}), 160.1 (2-C_{ox}) ppm.

Obtained NMR data is in agreement with lit. [241].

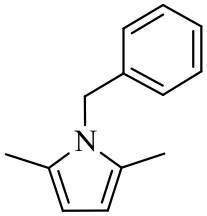
CHN (in %): $C_{11}H_{18}N_2O_2 \cdot 0.33H_2O$ (210.27 + 5.94 g/mol)

Calcd.	C 60.25	H 8.73	N 12.78
Found	C 60.26	H 8.66	N 12.64

6.2.8.4 Paal-Knorr synthesis

General procedure. Dried IL **6h** (2 g) was placed in a round-bottom flask equipped with a three-way Claisen adaptor, argon inlet and a drying tube. Catalyst (10-100 mol-%) and then 1,3- or 1,4-diketone (0.3 mL) and amine (1 equiv.) were added. The mixture was stirred for 2-48 h at 20-120 °C. The reaction was controlled by NMR (in $CDCl_3$). The product was separated by bulb-to-bulb distillation at 100-130 °C/0.05 mbar. For the next cycle new portions of the 1,3- or 1,4-diketone and amine were added and the procedure was repeated. For exact conditions and yields, see **Tables 13** and **14**.

6.2.8.4.1 1-Benzyl-2,5-dimethyl-1*H*-pyrrole



2,5-Hexanedione	2.56 mmol	0.30 mL
Benzylamine	2.56 mmol	0.28 mL
Titanium tetraisopropoxide	0.256 mmol	0.076 mL
IL **6h**		2 g

The product was obtained as a white powder, m.p. 44-45 °C (lit. 44.5-45 °C[242]).

^{1}H NMR ($CDCl_3$): δ = 2.15 (s, 6 H, CH_3), 5.00 (s, 2 H, CH_2), 5.89 (s, 2 H, 3-H_{pyr}, 4-H_{pyr}), 6.88-6.90 (d, 2 H, 2-H_{Ph}, 6-H_{Ph}), 7.19-7.30 (several m, 3 H, 3-H_{Ph}, 4-H_{Ph}, 5-H_{Ph}) ppm.

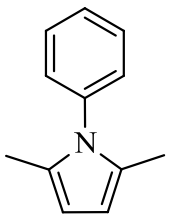
^{13}C NMR ($CDCl_3$): δ = 12.3 (CH_3), 46.5 (CH_2), 105.3 (3-C_{pyr}, 4-C_{pyr}), 126.8 and 127.8 (4-C_{Ph} and 2-C_{pyr}, 5-C_{pyr}), 125.5 and 128.6 (2-C_{Ph}, 3-C_{Ph}, 5-C_{Ph}, 6-C_{Ph}), 138.4 (1-C_{Ph}) ppm.

Obtained NMR data is in agreement with lit. [243].

CHN (in %): $C_{13}H_{15}N$ (185.26 g/mol)

Calcd.	C 84.28	H 8.16	N 7.56
Found	C 84.22	H 8.25	N 7.41

6.2.8.4.2 2,5-Dimethyl-1-phenyl-1*H*-pyrrole



2,5-Hexanedione	2.56 mmol	0.30 mL
Aniline	2.56 mmol	0.23 mL
Titanium tetraisopropoxide	0.256 mmol	0.076 mL

IL **6h**	2 g

The product was obtained as a white powder, m.p. 52 °C (lit. 50-52 °C[244]).

^{1}H NMR ($CDCl_3$): δ = 2.04 (s, 6 H, CH_3), 5.92 (s, 2 H, 3-H_{pyr}, 4-H_{pyr}), 7.21-7.23 (d, 2 H, 2-H_{Ph}, 6-H_{Ph}), 7.38-7.49 (several m, 3 H, 3-H_{Ph}, 4-H_{Ph}, 5-H_{Ph}) ppm.

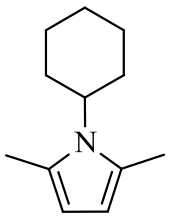
^{13}C NMR ($CDCl_3$): δ = 13.0 (CH_3), 105.5 (3-C_{pyr}, 4-C_{pyr}), 127.6 (4-C_{Ph}), 128.2 and 129.0 (2-C_{Ph}, 3-C_{Ph}, 5-C_{Ph}, 6-C_{Ph}), 128.8 (2-C_{pyr} and 5-C_{pyr}), 138.9 (1-C_{Ph}) ppm.

Obtained NMR data is in agreement with lit. [243].

CHN (in %): $C_{12}H_{13}N$ (171.24 g/mol)

Calcd.	C 84.17	H 7.65	N 8.18
Found	C 83.97	H 7.66	N 8.00

6.2.8.4.3 1-Cyclohexyl-2,5-dimethyl-1*H*-pyrrole



2,5-Hexanedione	2.56 mmol	0.30 mL
Cyclohexylamine	2.56 mmol	0.29 mL
Titanium tetraisopropoxide	0.256 mmol	0.076 mL
IL **6h**		2 g

The product was obtained as a colourless liquid, which crystallised after several hours in freezer at -20 °C, m.p. 41-43 °C (lit. 47-48 °C[245]).

^{1}H NMR ($CDCl_3$): δ = 1.15-2.00 (several m, 10 H, *c*Hex-H), 2.31 (s, 6 H, CH_3), 3.88-3.94 (m, 1 H, 1-H_{cHex}), 5.75 (s, 2 H, 3-H_{pyr}, 4-H_{pyr}) ppm.

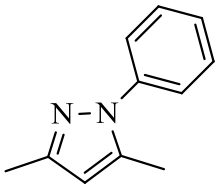
^{13}C NMR ($CDCl_3$): δ = 14.4 (CH_3), 25.6 (4-C_{cHex}), 26.6 (3-C_{cHex} and 5-C_{cHex}), 32.4 (2-C_{cHex} and 6-C_{cHex}), 56.4 (1-C_{cHex}), 106.0 (3-C_{pyr}, 4-C_{pyr}), 127.8 (2-C_{pyr} and 5-C_{pyr}) ppm.

Obtained NMR data is in agreement with lit. [246].

CHN (in %): $C_{12}H_{19}N$ (177.29 g/mol)

Calcd.	C 81.30	H 10.80	N 7.90
Found	C 81.07	H 11.07	N 7.82

6.2.8.4.4 3,5-Dimethyl-1-phenyl-1*H*-pyrazole



Acetylacetone	2.92 mmol	0.30 mL
Phenylhydrazine	2.92 mmol	0.29 mL
Titanium tetraisopropoxide	0.292 mmol	0.087 mL
IL **6h**		2 g

The product was obtained as a light yellow liquid.

^{1}H NMR ($CDCl_3$): δ = 2.30 (s, 6 H, CH_3), 5.99 (s, 1 H, 4-H_{pyr}), 7.31-7.37 (m, 1 H, 2-H_{Ph}), 7.41-7.46 (m, 4 H, Ar-H) ppm.

^{13}C NMR ($CDCl_3$): δ = 13.4 and 13.5 (CH_3), 106.9 (4-C_{pyr}), 127.2 (4-C_{Ph}), 124.7 and 128.9 (2-C_{Ph}, 3-C_{Ph}, 5-C_{Ph}, 6-C_{Ph}), 139.3 and 139.9 (3-C_{pyr} and 5-C_{pyr}), 148.9 (1-C_{Ph}) ppm.

Obtained NMR data is in agreement with lit. [247].

CHN (in %): $C_{11}H_{12}N_2 \cdot 0.09H_2O$ (172.23 + 1.64 g/mol)

Calcd.	C 75.92	H 7.07	N 16.10
Found	C 75.94	H 7.10	N 16.16

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8. Appendix

8.1 Crystallographic data of *N*-cyclohexyl-*N,N',N',N'',N''*-pentamethylguanidinium chloride (5w)

Table 1. *Crystal data and structure refinement for MA195 (**5w**).*

Identification code	ma195	
Empirical formula	C12 H26 Cl N3	
Formula weight	247.81	
Temperature	180(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	*P* 2(1)/*n*	
Unit cell dimensions	*a* = 5.97719(19) Å	α = 90°.
	b = 29.5775(10) Å	β = 96.494(3)°.
	c = 8.2483(2) Å	γ = 90°.
Volume	1448.86(8) Å^3	
Z	4	
Density (calculated)	1.136 Mg/m^3	
Absorption coefficient	2.169 mm^{-1}	
F(000)	544	
Crystal size	0.30 x 0.27 x 0.18 mm^3	
Theta range for data collection	2.99 to 72.53°.	
Index ranges	-7<=*h*<=6, -36<=*k*<=35, -10<=*l*<=4	
Reflections collected	4971	
Independent reflections	2803 [*R*(int) = 0.0145]	
Completeness to theta = 72.53°	97.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2803 / 0 / 150	
Goodness-of-fit on F^2	1.135	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0331, *wR*2 = 0.0900	
R indices (all data)	*R*1 = 0.0346, *wR*2 = 0.0910	
Largest diff. peak and hole	0.294 and -0.357 e.Å^{-3}	

Table 2. *Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for MA195 (**5w**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
Cl(1)	2811(1)	740(1)	7734(1)	37(1)
N(1)	7200(2)	644(1)	1880(1)	22(1)
N(2)	7753(2)	837(1)	4616(1)	24(1)
N(3)	9591(2)	1242(1)	2730(1)	23(1)
C(1)	8177(2)	906(1)	3081(2)	20(1)
C(2)	8277(2)	526(1)	432(2)	29(1)
C(3)	4983(2)	436(1)	1938(2)	27(1)
C(4)	7478(2)	384(1)	5291(2)	29(1)
C(5)	7676(2)	1205(1)	5797(2)	30(1)
C(6)	11519(2)	1363(1)	3903(2)	29(1)
C(7)	8967(2)	1546(1)	1322(2)	24(1)
C(8)	11001(2)	1688(1)	484(2)	31(1)
C(9)	10271(3)	2000(1)	-962(2)	36(1)
C(10)	8974(3)	2408(1)	-451(2)	40(1)
C(11)	6960(3)	2264(1)	388(2)	43(1)
C(12)	7688(3)	1959(1)	1856(2)	35(1)

Table 3. *Bond lengths [Å] and angles [°] for MA195 (**5w**).*

N(1)-C(1)	1.3384(16)	C(10)-C(11)	1.516(2)
N(1)-C(2)	1.4619(17)	C(11)-C(12)	1.533(2)
N(1)-C(3)	1.4663(16)		
N(2)-C(1)	1.3344(17)	C(1)-N(1)-C(2)	123.16(11)
N(2)-C(5)	1.4654(16)	C(1)-N(1)-C(3)	122.63(11)
N(2)-C(4)	1.4668(16)	C(2)-N(1)-C(3)	114.17(10)
N(3)-C(1)	1.3575(16)	C(1)-N(2)-C(5)	122.68(11)
N(3)-C(6)	1.4628(16)	C(1)-N(2)-C(4)	122.79(11)
N(3)-C(7)	1.4823(16)	C(5)-N(2)-C(4)	114.40(11)
C(7)-C(8)	1.5241(19)	C(1)-N(3)-C(6)	120.06(10)
C(7)-C(12)	1.5320(19)	C(1)-N(3)-C(7)	120.24(10)
C(8)-C(9)	1.5318(19)	C(6)-N(3)-C(7)	118.67(10)
C(9)-C(10)	1.520(2)	N(2)-C(1)-N(1)	119.95(11)

N(2)-C(1)-N(3)	120.31(11)
N(1)-C(1)-N(3)	119.74(11)
N(3)-C(7)-C(8)	112.31(11)
N(3)-C(7)-C(12)	110.35(11)
C(8)-C(7)-C(12)	111.05(11)
C(7)-C(8)-C(9)	110.36(12)
C(10)-C(9)-C(8)	111.81(12)
C(11)-C(10)-C(9)	111.08(13)
C(10)-C(11)-C(12)	110.90(13)
C(7)-C(12)-C(11)	110.44(12)

Table 4. *Anisotropic displacement parameters ($Å^2$ x 10^3) for MA195. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	33(1)	50(1)	29(1)	9(1)	6(1)	10(1)
N(1)	22(1)	22(1)	22(1)	-2(1)	3(1)	-3(1)
N(2)	29(1)	22(1)	21(1)	-1(1)	4(1)	-3(1)
N(3)	25(1)	22(1)	22(1)	2(1)	-1(1)	-5(1)
C(1)	20(1)	19(1)	22(1)	1(1)	1(1)	1(1)
C(2)	30(1)	31(1)	27(1)	-9(1)	7(1)	-1(1)
C(3)	23(1)	28(1)	28(1)	0(1)	1(1)	-6(1)
C(4)	35(1)	26(1)	27(1)	5(1)	5(1)	-5(1)
C(5)	35(1)	30(1)	23(1)	-6(1)	4(1)	1(1)
C(6)	27(1)	29(1)	28(1)	3(1)	-3(1)	-7(1)
C(7)	28(1)	22(1)	21(1)	2(1)	1(1)	-3(1)
C(8)	35(1)	29(1)	29(1)	4(1)	11(1)	2(1)
C(9)	48(1)	36(1)	27(1)	7(1)	11(1)	-1(1)
C(10)	57(1)	28(1)	35(1)	10(1)	5(1)	1(1)
C(11)	49(1)	40(1)	41(1)	14(1)	9(1)	17(1)
C(12)	38(1)	36(1)	32(1)	8(1)	11(1)	10(1)

Table 5. *Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for MA195 (**5w**).*

	x	y	z	U(eq)
H(2A)	9787	659	516	43
H(2B)	7373	643	-543	43
H(2C)	8393	197	352	43
H(3A)	5159	108	2075	40
H(3B)	4027	499	918	40
H(3C)	4283	561	2858	40
H(4A)	7655	156	4451	44
H(4B)	5975	357	5649	44
H(4C)	8621	335	6223	44
H(5A)	9027	1194	6589	44
H(5B)	6334	1171	6368	44

H(5C)	7616	1495	5223	44
H(6A)	11254	1659	4382	43
H(6B)	12881	1377	3345	43
H(6C)	11715	1134	4768	43
H(7)	7925	1375	507	29
H(8A)	11748	1416	95	46
H(8B)	12096	1848	1275	46
H(9A)	11621	2104	-1449	55
H(9B)	9313	1828	-1806	55
H(10A)	9982	2599	300	60
H(10B)	8455	2591	-1426	60
H(11A)	5878	2099	-397	64
H(11B)	6193	2535	760	64
H(12A)	8667	2131	2685	52
H(12B)	6344	1858	2356	52

Table 6. *Torsion angles [°] for MA195 (**5w**).*

C(5)-N(2)-C(1)-N(1)	-146.57(12)
C(4)-N(2)-C(1)-N(1)	37.76(18)
C(5)-N(2)-C(1)-N(3)	33.17(18)
C(4)-N(2)-C(1)-N(3)	-142.50(13)
C(2)-N(1)-C(1)-N(2)	-147.83(12)
C(3)-N(1)-C(1)-N(2)	29.74(18)
C(2)-N(1)-C(1)-N(3)	32.42(18)
C(3)-N(1)-C(1)-N(3)	-150.01(12)
C(6)-N(3)-C(1)-N(2)	33.60(18)
C(7)-N(3)-C(1)-N(2)	-134.63(12)
C(6)-N(3)-C(1)-N(1)	-146.65(12)
C(7)-N(3)-C(1)-N(1)	45.12(17)
C(1)-N(3)-C(7)-C(8)	-145.14(12)
C(6)-N(3)-C(7)-C(8)	46.47(16)
C(1)-N(3)-C(7)-C(12)	90.37(14)
C(6)-N(3)-C(7)-C(12)	-78.03(15)
N(3)-C(7)-C(8)-C(9)	179.85(11)
C(12)-C(7)-C(8)-C(9)	-56.05(15)
C(7)-C(8)-C(9)-C(10)	55.46(17)

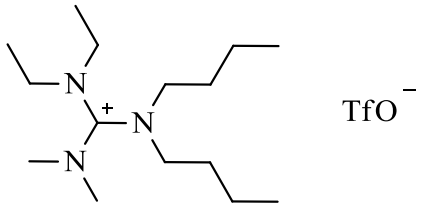
C(8)-C(9)-C(10)-C(11)	-55.74(19)
C(9)-C(10)-C(11)-C(12)	56.16(19)
N(3)-C(7)-C(12)-C(11)	-177.77(12)
C(8)-C(7)-C(12)-C(11)	57.02(17)
C(10)-C(11)-C(12)-C(7)	-56.81(18)

8.2 Structural formulas of synthesised guanidinium-based ionic liquids

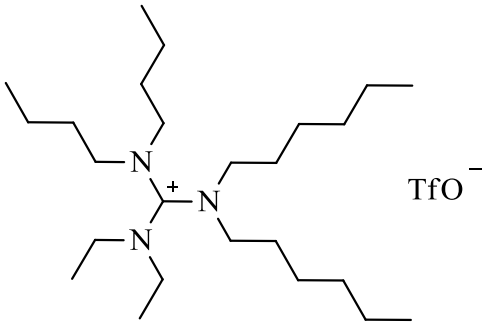
References are provided for the ionic liquids, which have already been reported.

8.2.1 Guanidinium-based trifluoromethanesulfonates

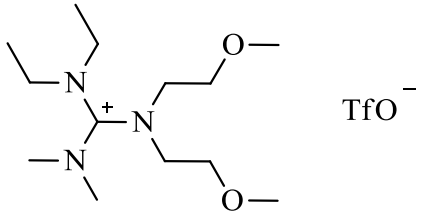
3a: $[N_{11}N_{22}N_{44}Gu]OTf$ [31,43]



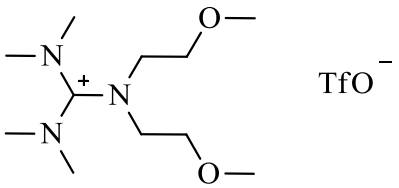
3b: $[N_{22}N_{44}N_{66}Gu]OTf$ [31,43]



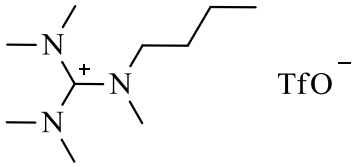
3c: $[N_{11}N_{22}N_{1O21O2}Gu]OTf$ [31,43]



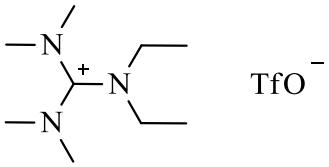
3d: $[N_{11}N_{11}N_{1O21O2}Gu]OTf$



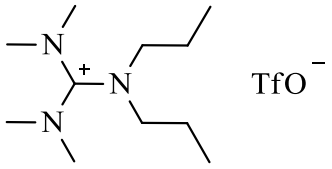
3e: $[N_{11}N_{11}N_{14}Gu]OTf$ [248]



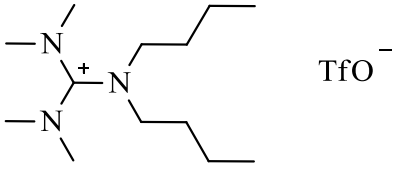
3f: $[N_{11}N_{11}N_{22}Gu]OTf$ [249]



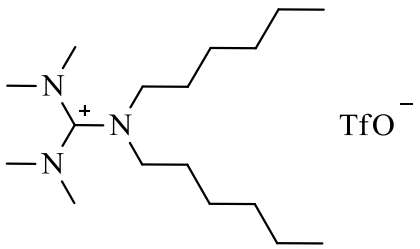
3g: $[N_{11}N_{11}N_{33}Gu]OTf$



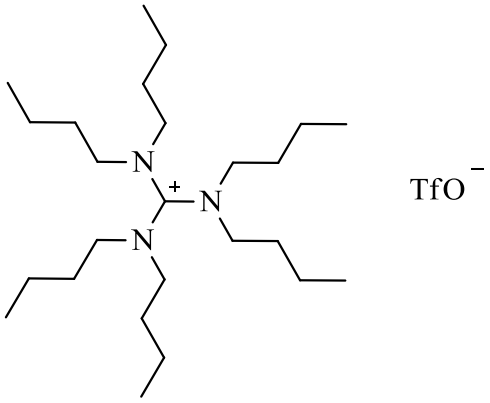
3h: $[N_{11}N_{11}N_{44}Gu]OTf$



3i: $[N_{11}N_{11}N_{66}Gu]OTf$

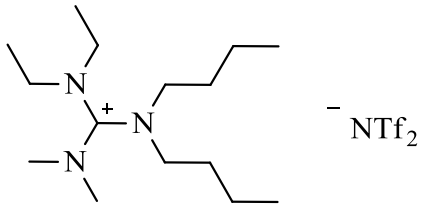


3j: $[N_{44}N_{44}N_{44}Gu]OTf$ [31,43]

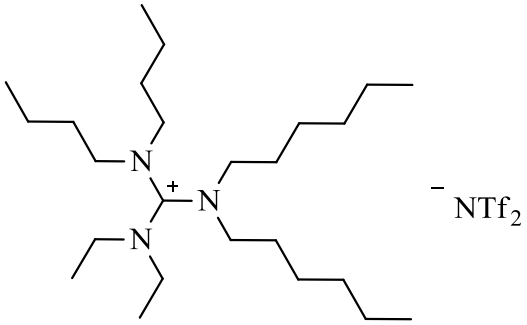


8.2.2 Guanidinium-based bis(trifluoromethylsulfonyl)imides

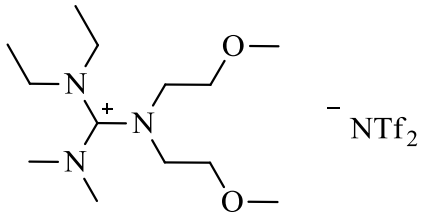
6a: $[N_{11}N_{22}N_{44}Gu]NTf_2$ [43]



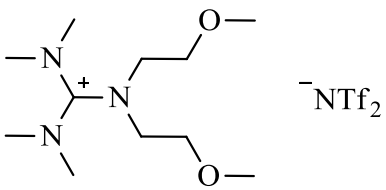
6b: $[N_{22}N_{44}N_{66}Gu]NTf_2$ [43]



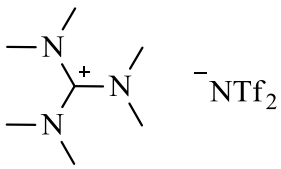
6c: $[N_{11}N_{22}N_{1O21O2}Gu]NTf_2$ [43]



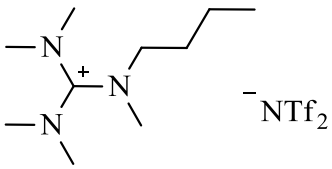
6d: $[N_{11}N_{11}N_{1O21O2}Gu]NTf_2$ [128]



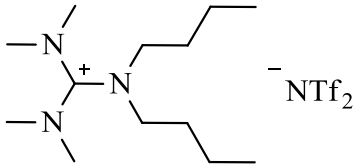
6e: $[N_{11}N_{11}N_{11}Gu]NTf_2$ [51]



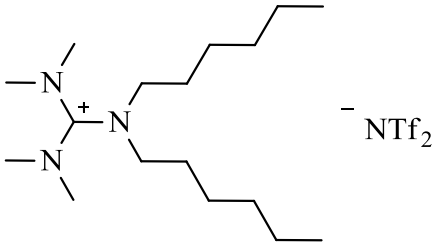
6f: $[N_{11}N_{11}N_{14}Gu]NTf_2$ [51]



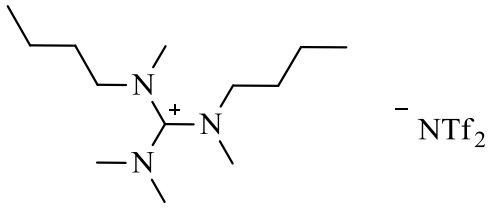
6g[$N_{11}N_{11}N_{44}Gu$]NTf_2 [51,250]



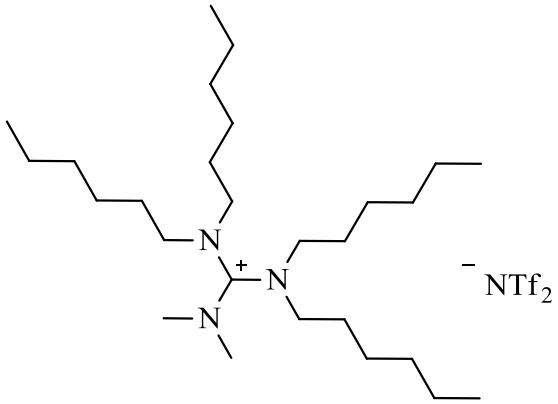
6h: [$N_{11}N_{11}N_{66}Gu$]NTf_2



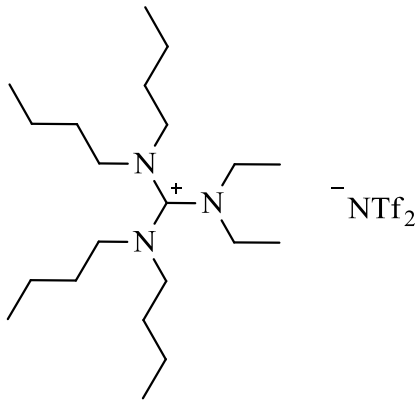
6i: [$N_{11}N_{14}N_{14}Gu$]NTf_2 [35,251]



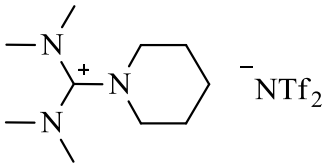
6j: [$N_{11}N_{66}N_{66}Gu$]NTf_2 [35]



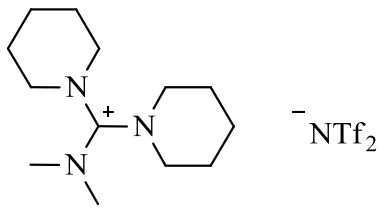
6k: [$N_{22}N_{44}N_{44}Gu$]NTf_2



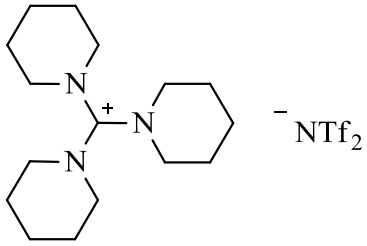
6l: [$N_{11}N_{11}N_{pip}Gu$]NTf_2



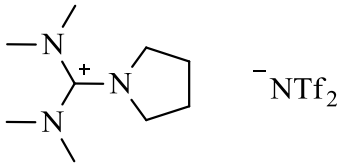
6m: [$N_{11}N_{pip}N_{pip}Gu$]NTf_2



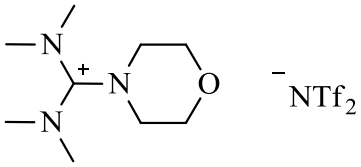
6n: [$N_{pip}N_{pip}N_{pip}Gu$]NTf_2



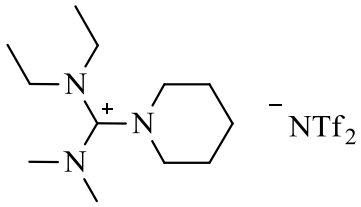
6o: $[N_{11}N_{11}N_{pyr}Gu]NTf_2$ [252]



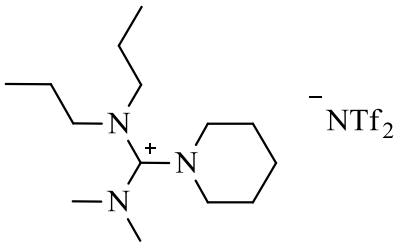
6p: $[N_{11}N_{11}N_{mor}Gu]NTf_2$



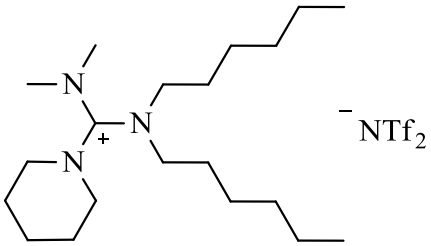
6q: $[N_{11}N_{22}N_{pip}Gu]NTf_2$



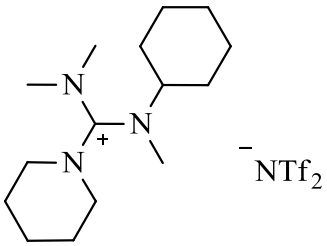
6r: $[N_{11}N_{33}N_{pip}Gu]NTf_2$



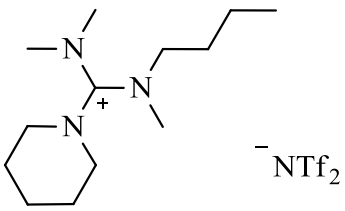
6s: $[N_{11}N_{66}N_{pip}Gu]NTf_2$



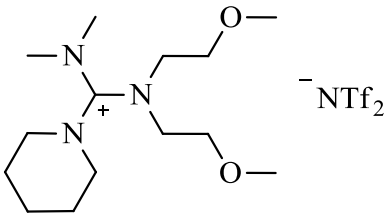
6t: $[N_{11}N_{1cHex}N_{pip}Gu]NTf_2$



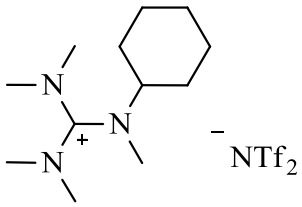
6u: $[N_{11}N_{14}N_{pip}Gu]NTf_2$



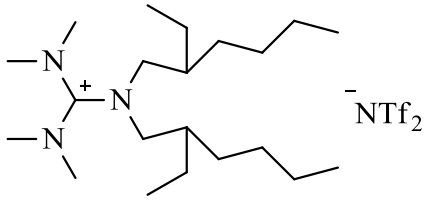
6v: $[N_{11}N_{1O21O2}N_{pip}Gu]NTf_2$



6w: $[N_{11}N_{11}N_{1cHex}Gu]NTf_2$

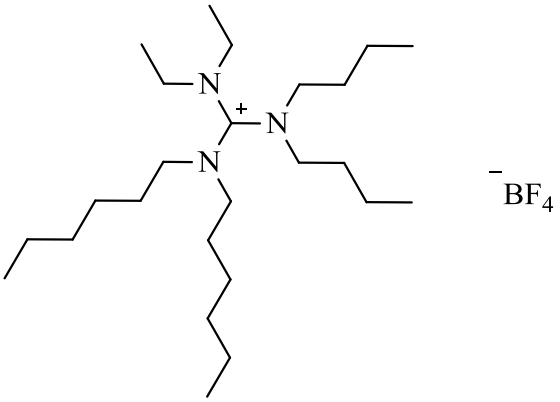


6x: $[N_{11}N_{11}N_{EHEH}Gu]NTf_2$

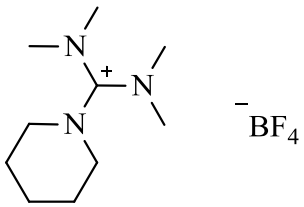


8.2.3 Guanidinium-based tetrafluoroborates

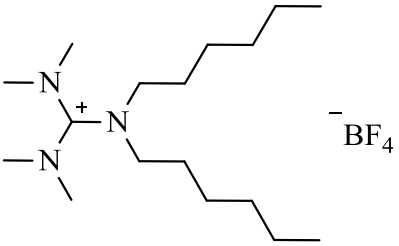
7a: $[N_{22}N_{44}N_{66}Gu]BF_4$



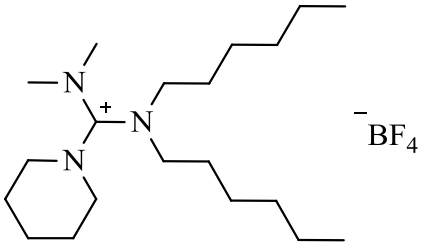
7b: $[N_{11}N_{11}N_{pip}Gu]BF_4$



7c: $[N_{11}N_{11}N_{66}Gu]BF_4$ [253]

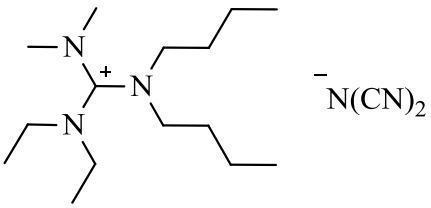


7d: $[N_{11}N_{66}N_{pip}Gu]BF_4$ [254]

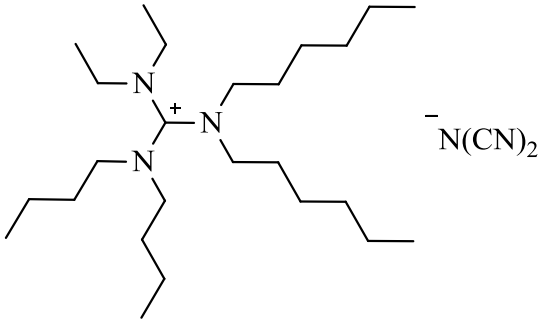


8.2.4 Guanidinium-based dicyanamides

8a: $[N_{11}N_{22}N_{44}Gu]N(CN)_2$ [144]

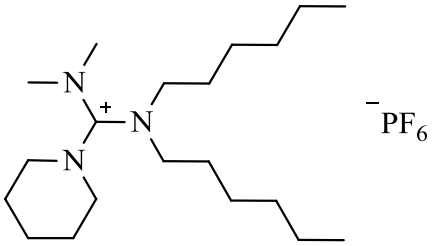


8b: $[N_{22}N_{44}N_{66}Gu]N(CN)_2$ [144]



8.2.5 Guanidinium-based hexafluorophosphates

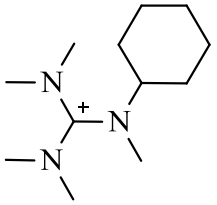
9a: $[N_{11}N_{66}N_{pip}Gu]PF_6$ [254]



$^{-}PF_6$

8.2.6 Guanidinium-based tetraphenylborates

10a: $[N_{11}N_{11}N_{1cHex}Gu]BPh_4$



$^{-}BPh_4$

Arkhipova Maria

Curriculum Vitae

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Place of birth: Leningrad (St. Petersburg), Russian Federation

Education:

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04/2013 – 05/2013	Visiting researcher at TUM CREATE (6 weeks); Singapore. Theme: *"Application of guanidinium-based ionic liquids in Li-ion batteries"*.
10/2011 – 02/2012	Participation in the seminar *"Entwicklung, Zulassung und Überwachung von Arzneimitteln"* (Development, admission and control of drugs) organised by Ratiopharm GmbH and University of Ulm.
08/2009 – 01/2010	Visiting researcher at the University of Ulm, Institute of Organic Chemistry I (DAAD-Fellowship); Ulm, Germany. Theme: *"Synthesis of N,S-containing heterocycles upon interaction of thiohydroxamic acid with oxalyl and malonyl chlorides"*.
09/2008 – 07/2009	Ph.D. student at the Department of Organic Chemistry at St. Petersburg State Chemical Pharmaceutical Academy; St. Petersburg, Russia. Theme: *"Synthesis of N,O-containing heterocycles upon interaction of hydroxamic acid and amidoximes with oxalyl and malonyl chlorides"*.
09/2003 – 06/2008	St. Petersburg State Chemical Pharmaceutical Academy, Faculty of industrial drug technology, St. Petersburg, Russia. Speciality: **engineer in Biotechnology** (Diploma with honours). Theme: *"Synthesis, biological activity of new N,S-containing heterocyclic compounds and development of a new antifungal uncture"*.
09/1995 – 06/2003	School № 13 with advanced study of English (Certificate with honours, gold medal); St. Petersburg, Russia.
09/1993 – 08/1995	School № 343; St. Petersburg, Russia.

Der Teil des Lebenslaufs wurde aus Gründen des Datenschutzes entfernt.

22 May 2014, Ulm Arkhipova Maria

List of scientific publications and presentations

Publications:

Process for preparation, crystal structure and antimicrobial activity of 2-[(1Z)-1-(3,5-diphenyl-1,3,4-thiadiazol-2(3H)-ylidene)methyl]-3,5-diphenyl-1,3,4-thiadiazol-3-ium chloride, N. N. Kuz'mich, M. V. Arkhipova, I. P. Yakovlev, E. P. Anan'eva, RU 2402550, **2009**.

Empirical Polarity Parameters for Hexaalkylguanidinium-based Room-temperature Ionic Liquids, M. G. Bogdanov, I. Svinyarov, H. Kunkel, C. Steinle, M. Arkhipova, W. Kantlehner, G. Maas, *Z. Naturforsch.* **2010**, *65b*, 791–797.

The electrochemical interface of gold in a hexaalkylsubstituted guanidinium ionic liquid, M. Gnahm, C. Berger, M. Arkhipova, H. Kunkel, T. Pajkossy, G. Maas, D. M. Kolb, *Phys. Chem. Chem. Phys.* **2012**, *14*, 10647–10652.

A novel ionic liquid for Li ion batteries – uniting the advantages of guanidinium and piperidinium cations, N. Bucher, S. Hartung, D. Yu, M. Arkhipova, P. Kratzer, G. Maas, M. Srinivasan, H. E. Hoster, *RSC Advances* **2014**, *4*, 1996–2003.

Synthesis and Characterization of New Guanidinium-Based Ionic Liquids as Possible Electrolytes in Lithium-Ion Batteries, M. Wachtler, S. Hess, M. Arkhipova, M. Wohlfahrt-Mehrens, G. Maas, *J. Electrochem. Soc.*, submitted.

Poster presentations:

09/2013	11th Iminium salt Conference ImSaT-11; Goslar, Germany.
09/2011	10th Iminium salt Conference ImSaT-10; Bartholomä, Germany.
06/2009	International Conference in Organic Chemistry (InterYCOS); St. Petersburg, Russia.

05/2012	Participation in the 111th General Assembly of German Bunsen-Society of Physical Chemistry; Leipzig, Germany.
10/2011 – 02/2012	Participation in the seminar *"Entwicklung, Zulassung und Überwachung von Arzneimitteln"* (Development, admission and control of drugs) organised by Ratiopharm GmbH and University of Ulm.

Die Danksagung wurde aus Gründen des Datenschutzes entfernt.

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Erklärung

Ich versichere hiermit, dass ich die Arbeit slbstständig angefertigt habe und keine anderen als die angegebenen Quellen und Hilfmittel benutzt sowie die wörtlich oder inhaltlich übernommenen Stellen als solche kenntlich gemacht habe.

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Maria Arkhipova