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(54) Title: NOVEL IONIC LIQUIDS

(57) Abstract: The present invention provides for novel organic salts, more specifically ionic liquids and for methods for the preparation of such novel ionic liquids. The invention also provides for the use of the ionic liquids in chemistry applications, for example for the solubilization of metal oxides, hydroxides and salts, for the deposition of metals or for extraction procedures, among others. The invention furthermore provides for a method for the solubilization of metal oxides and metal salts, for the deposition of metals and for extraction procedures, this by using the novel ionic liquids. The present invention furthermore provides for materials obtained by the methods hereof.

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NOVEL IONIC LIQUIDS

FIELD OF THE INVENTION

The present invention provides for novel organic salts, more specifically ionic liquids and for
10 methods for the preparation of such novel ionic liquids. The invention also provides for the use of
the ionic liquids in chemistry applications, for example for the solubilization of metal oxides,
hydroxides and salts, for the deposition of metals or for extraction procedures, among others. The
invention furthermore provides for a method for the solubilization of metal oxides and metal
salts, for the deposition of metals and for extraction procedures, this by using the novel ionic
15 liquids. The present invention furthermore provides for materials obtained by the methods hereof.

BACKGROUND OF THE INVENTION

There is much current interest in ionic liquids. These compounds are examples of molten salts
20 that are liquid at temperatures below 100 °C or sometimes even at room temperature (Welton, T.
Chem. Rev. **1999**, *99*, 2071-2083). The much lower melting points of ionic liquids compared to
those of inorganic salts can be partially attributed to the bulky cationic groups, i.e. low charge
density and incompatibility of Coulombic attraction forces with steric hindrance. Ionic liquids
have very low vapor pressures, although it was recently shown that they are distillable (Earle,
25 M.J. *Nature* **2006**, *439*, 831-834). Therefore they do not produce hazardous vapors (in contrast to
many conventional solvents). Most ionic liquids have high ignition points and they do not
generate explosive air-vapor mixtures. They can act as solvents for chemical reactions, including
catalytic reactions (Parvulescu, V. I.; Hardacre, C. *Chem. Rev.* **2007**, *107*, 2615-2665). Ionic
liquids are an interesting reaction medium for the synthesis of unusual inorganic compounds
30 (Taubert, A.; Li, Z. *Dalton Trans.* **2007**, 723-727). They find use in electrochemical applications,
for example as electrolytes in batteries, and in photovoltaic devices, but also as a medium for
electrodeposition or electropolishing of metals.

Especially for electrochemical applications and for applications in solvent extraction
35 technology, ionic liquids should have a high solubilizing power for metal salts, including metal

5 oxides. To avoid leaching of the metal catalyst in catalytic reactions, it is of importance to have ionic liquids that can keep metals dissolved in them. A good solubility of metal salts is observed for ionic liquids based on aluminum chloride, such as mixtures of 1-ethyl-3-methylimidazolium chloride and aluminum chloride ($[\text{C}_2\text{mim}]\text{Cl} - \text{AlCl}_3$), and mixtures of 1-butylpyridinium chloride and aluminum chloride ($\text{BPC} - \text{AlCl}_3$). Unfortunately, these systems suffer from
10 extreme water sensitivity. Compounds like the 1-alkyl-3-methylimidazolium hexafluorophosphate, $[\text{C}_n\text{mim}][\text{PF}_6]$, are room temperature ionic liquids with a much lower sensitivity towards water. Unfortunately, these ionic liquids and related ones like the 1-alkyl-3-methylimidazolium tetrafluoroborates or the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides have a low solubility for metal salts. This can be explained by
15 the weakly-coordinating properties of the constituting anions and cations, so that the solvation energy is not high enough to break the binding interactions between the ions or molecules of the metal-containing compounds in the solid state.

To overcome the problems with the solubility of metal salts, researchers have developed
20 so-called “*task-specific ionic liquids*” (TSILs), which are ionic liquids with a functional group covalently tethered to the cationic or anionic part (Davis, J. H. Jr. *Chem. Lett.* **2004**, *33*, 1072-1077). When the functional group has the ability to coordinate to the metal ion (preferably as a bidentate or a polydentate ligand), it is easier to dissolve metal oxides or metal salts into the ionic liquid. As a rule, these task-specific ionic liquids are not used as single-component ionic liquids,
25 but they are mixed with more conventional ionic liquids. A rationale to use mixtures rather than pure task-specific ionic liquids is that the task-specific ionic liquids often have a higher melting point and a higher viscosity than conventional ionic liquids. Moreover, the conventional ionic liquids are in general much cheaper than the task-specific ionic liquids. An example of a task-specific ionic liquid is an imidazolium salt incorporating a thiourea moiety, which has been used
30 for the extraction of mercury(II) and cadmium(II) from an aqueous phase (Visser, A. E. et al. *Chem. Commun.* **2001**, 135-136). Task-specific ionic liquids with appended tertiary phosphine groups have been used to immobilize rhodium(I) organometallic catalysts in $[\text{C}_4\text{mim}][\text{PF}_6]$ (Kottsieper, K. W. et al. *J. Mol. Catal. A* **2001**, *175*, 285-288).

The major drawback of these task-specific ionic liquids is that they are often only
35 accessible after a multistep synthetic procedure. The time-consuming preparation of these ionic

5 liquids restricts their use in large-scale industrial applications. Therefore, the development of task-specific ionic liquids that can readily be prepared from cheap raw materials is an important research target. Task-specific ionic liquids that can be prepared from renewable natural resources would even be better. Abbott and coworkers obtained ionic liquids by mixing choline chloride with hydrated transition metal salts (Abbott, A. et al. *Chem. Eur. J.* **2004**, *10*, 3769-3774), or with
10 anhydrous zinc(II) chloride or tin(II) chloride (Abbott, A. P. et al. *Chem. Commun.* **2001**, 2010-2011; Abbott, A. P. et al. *Inorg. Chem.* **2004**, *43*, 3447-3452). The same research group also prepared ionic liquids by mixing choline chloride with urea in a 1:2 molar ratio (Abbott, A. P. et al. *Chem. Commun.* **2003**, 70-71). These mixtures of choline chloride and urea are called “*deep eutectic solvents*”. They can dissolve different types of metal oxides as well as metal salts, but the
15 solubility of the metal salts in these ionic-liquid-like mixtures is in general less than 1 wt.% (Abbott, A. P. et al. *Inorg. Chem.* **2005**, *44*, 6497-6499). *Choline chloride* (also known as 2-hydroxyethyltrimethyl ammonium chloride or vitamin B4) is a cheap commodity chemical that is produced annually on a multi-ton scale. Its main use is as an animal feed additive. Choline chloride itself is a solid with a high melting point (m.p. = 298-304 °C). Although ionic liquids
20 based on choline chloride have the advantages of being cheap, they are all hydrophilic and miscible with water or with polar solvents. This is a problem for applications like the extraction of metal ions from an aqueous phase or like the electrodeposition of reactive metals (e.g. aluminum, magnesium, tantalum and the rare earths). Metal complexes with the zwitterionic ligand betaine have been investigated for a long time, but none of these complexes contain the
25 bis(trifluoromethylsulfonyl)imide anion.

The closest prior art (WO 2004/029004) describes the compositions that contain ionic liquids and their use in organic synthesis, but does not describe the ionic liquids of the present invention.

Therefore, it is clear that there is a need for further alternative ionic liquids, which are cheap,
30 easy to produce, are obtained from renewable natural resources, are water immiscible, have good metal solubilization properties and/or are renewable. The present invention fulfils this need by the provision of novel ionic liquids.

5 SUMMARY OF THE INVENTION

The present invention provides for novel organic salts, more specifically ionic liquids and for methods for the preparation of such novel organic salts, more specifically ionic liquids. The invention also provides for the use of the organic salts, more specifically ionic liquids in chemistry applications. The invention furthermore provides for chemistry applications, like a method for the solubilization of metal oxides, by using the novel organic salts, more specifically ionic liquids. The present invention furthermore relates to compositions, (solutions, complexes or mixtures among others) comprising said organic salts, more specifically ionic liquids and to materials obtained by the methods using said organic salts, more specifically ionic liquids. The present invention also relates to the use of said compositions comprising said organic salts, more specifically ionic liquids or of the materials obtained by the methods using said organic salts, more specifically ionic liquids.

A first aspect of the present invention relates to novel organic salts, in a more particular case novel ionic liquids. The organic salts of the present invention have a quaternary ammonium, phosphonium, arsonium, or stibonium structure according to formula (I):



I

wherein

- Y is selected from N; P; As; or Sb;
- each of R^1 , R^2 and R^3 are independently selected from C_{1-12} alkyl; or C_{3-12} cycloalkyl; or each of R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 can be taken together to form a substituted or unsubstituted cyclic structure;
- R^4 is selected from a C_{1-12} alkyl-COOH; or C_{3-12} cycloalkyl-COOH; wherein alkyl is optionally substituted with at least one OH or comprises at least one carbonyl function;
- X^- is selected from organic sulfonates; organic sulfates; organic carboxylates; organic sulfonylimides; or tetrafluoroborate.

In a particular embodiment, R^1 , R^2 , R^3 , R^4 , Y and X^- are as described in formula I, but R^4 is not C_3 alkyl-COOH or C_2 alkyl-COOH when Y is N and R^1 , R^2 and R^3 are all methyl and X^- is

5 bis(trifluoromethylsulfonyl)imide (TF_2N^-). In a more particular embodiment, R^1 , R^2 , R^3 , R^4 , and Y are as described in formula I, and X^- is bis(trifluoromethylsulfonyl)imide but R^4 is not C_3 alkyl-COOH when Y is N and R^1 , R^2 and R^3 are all methyl.

In a particular embodiment, each of R^1 , R^2 and R^3 are independently selected from C_{1-8} alkyl and C_{3-8} cycloalkyl, yet more in particular are independently selected from C_{1-6} alkyl and C_{3-6} cycloalkyl, still more particularly are independently selected from C_{1-4} alkyl, yet more particularly from C_{1-3} alkyl. In a preferred embodiment, each of R^1 , R^2 and R^3 are the same and more particularly are methyl, ethyl, propyl, butyl, hexyl, or octyl.

In another particular embodiment, R^4 is selected from C_{1-8} alkyl-COOH and C_{3-8} cycloalkyl-COOH, still more in particular is selected from C_{1-6} alkyl-COOH and C_{3-6} cycloalkyl-COOH, yet more particularly is C_{1-4} alkyl-COOH or C_{1-3} alkyl-COOH and yet more preferably is C_{1-2} alkyl-COOH and even more preferably is $-\text{CH}_2\text{COOH}$. In another particular embodiment, R^1 , R^2 , R^3 , Y, and X^- are as described in formula I, and R^4 is C_1 or C_2 alkyl-COOH or C_{3-12} cyclo alkyl, more preferably is C_1 or C_2 alkyl-COOH, even more preferably is $-\text{CH}_2\text{COOH}$. In yet another particular embodiment, R^1 , R^2 , R^3 , and Y are as described in formula I, and R^4 is C_1 or C_2 alkyl-COOH more preferably is $-\text{CH}_2\text{COOH}$, and X^- is TF_2N^- .

In another particular embodiment, the present invention relates to an organic salt of formula I wherein Y is P, As or Sb, and R^1 , R^2 , R^3 and R^4 and X^- are as described in formula I, more preferably X^- is TF_2N^- .

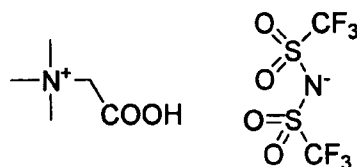
In a more preferred embodiment, $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{Y}^+$ is betaine, wherein Y is N, R^1 is $-\text{CH}_3$, R^2 is $-\text{CH}_3$, R^3 is $-\text{CH}_3$ and R^4 is $-\text{CH}_2\text{COOH}$.

In a particular embodiment, X^- is selected from organic sulfonates, preferably perfluorinated organic sulfonates; organic sulfates, preferably perfluorinated organic sulfates; organic sulfonylimides, preferably perfluorinated organic sulfonylimides ; or organic carboxylates, preferably perfluorinated organic carboxylates, such as methylsulfonate (CH_3SO_3^-), bis(trifluoromethylsulfonyl)imide (TF_2N^-), bis(pentafluoroethylsulfonyl)imide, bis(heptafluoropropylsulfonyl)imide, bis(nonafluorobutylsulfonyl)imide, bis(perfluoropentylsulfonyl)imide, bis(perfluorohexylsulfonyl)imide, triflate (TfO^-), pentafluorobenzoate ($\text{C}_6\text{F}_5\text{COO}^-$) and dodecylsulfate ($\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$). In another particular embodiment, X^- is selected from perfluoro- C_{1-12} alkyl-sulfonylimide (or more particularly from perfluoro- C_{1-6} alkyl-sulfonylimide, such as bis(pentafluoroethylsulfonyl)imide,

- 5 bis(heptafluoropropylsulfonyl)imide, bis(nonafluorobutylsulfonyl)imide, bis(perfluoropentylsulfonyl)imide, or bis(perfluorohexylsulfonyl)imide), more specifically is bis(trifluoromethylsulfonyl)imide (Tf_2N^-).

In a more preferred embodiment, the organic salt is betaine bis(trifluoromethylsulfonyl)imide. Such organic salts may be in protonated or unprotonated form. The structure of betaine

- 10 bis(trifluoromethylsulfonyl)imide in protonated form is according to formula II:



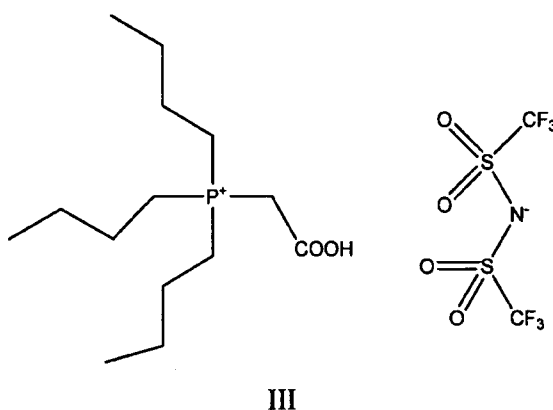
II

- In another particular embodiment, the present invention relates to an organic salt of formula I wherein Y is N or P, more preferably wherein Y is N. In another particular embodiment, the present invention relates to an organic salt of formula I wherein Y is P. In another particular embodiment, the present invention relates to an organic salt of formula I wherein Y is P and X^- is Tf_2N^- . In another particular embodiment, the present invention relates to an organic salt of formula I wherein Y is N and X^- is Tf_2N^- .

- 20 In another particular embodiment, the present invention relates to an organic salt of formula I wherein R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 form a substituted or unsubstituted cyclic structure, and wherein Y, R^4 , and X^- are as described in formula I, more preferably Y is N or P, even more preferably Y is N. In another particular embodiment, the present invention relates to an organic salt of formula I wherein R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 form a substituted or unsubstituted cyclic structure, and wherein R^4 is as described in formula I, and wherein Y is N and X^- is Tf_2N^- . In another particular embodiment, the present invention relates to an organic salt of formula I wherein Y is P, and R^1 , R^2 and R^3 are independently selected from C_{1-12} alkyl, and R^4 and X^- are as described in formula I, more preferably X^- is Tf_2N^- .

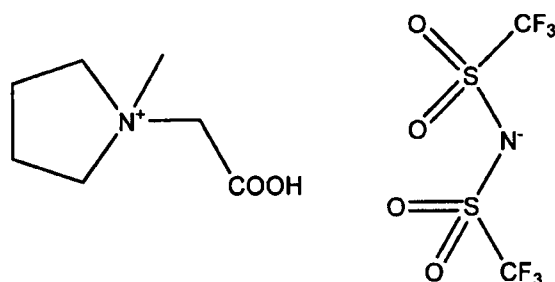
- In another particular embodiment, the present invention relates to an organic salt of formula I wherein Y is N, and R^1 , R^2 , R^3 and X^- are as described in formula I, and R^4 is a substituted C_{1-12} alkyl-COOH, more preferably R^4 is a C_{1-12} alkyl-COOH wherein at least one OH group is present in alkyl or at least one carbonyl ($\text{C}=\text{O}$) group is present in alkyl, more preferably one OH group is present in alkyl or one carbonyl ($\text{C}=\text{O}$) group is present in alkyl. In another particular

- 5 embodiment, the present invention relates to an organic salt of formula I, wherein Y is N and R⁴ is selected from a substituted C₁₋₃ alkyl-COOH wherein at least one OH group is present, or a C₁₋₃ alkyl-COOH which contains at least one carbonyl group. In another particular embodiment, the present invention relates to an organic salt of formula I wherein Y is N, and R¹, R² and R³ are as described in formula I, and R⁴ is a substituted C₁₋₁₂ alkyl-COOH, and X⁻ is Tf₂N⁻.
- 10 In another particular embodiment, the present invention relates to an organic salt of formula I wherein Y is P and R⁴ is -CH₂CH₂COOH or -CH₂COOH, and even more particularly Y is P and R⁴ is -CH₂COOH. In a more preferred embodiment, R¹R²R³R⁴Y⁺ is carboxymethyl-tributylphosphonium, wherein Y is P and R¹ is butyl, R² is butyl, R³ is butyl and R⁴ is -CH₂COOH. In another preferred embodiment, the organic salt is P-carboxymethyl-
- 15 tributylphosphonium bis(trifluoromethylsulfonyl)imide. The structure of this organic salt is according to formula III:



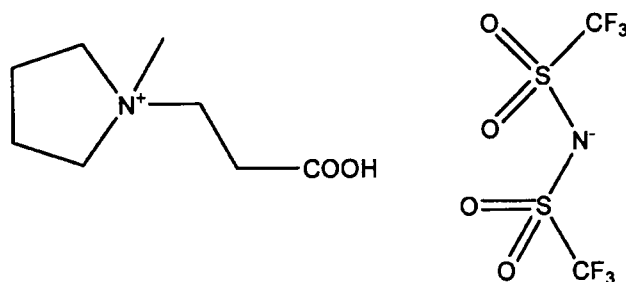
20

- In another particular embodiment, the present invention relates to an organic salt of formula I wherein R⁴ is as described herein, and Y is N and R¹ and R², or R¹ and R³, or R² and R³ forms a pyrrolidinium ring structure. In a more preferred embodiment, R¹R²R³R⁴Y⁺ is *N*-carboxymethyl-methylpyrrolidinium, wherein Y is N and together with R¹ and R², or R¹ and R³, or R² and R³ said
- 25 N forms a pyrrolidinium ring structure, and R⁴ is -CH₂COOH. In another preferred embodiment, the organic salt is *N*-carboxymethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, the structure of which is according to formula IV:



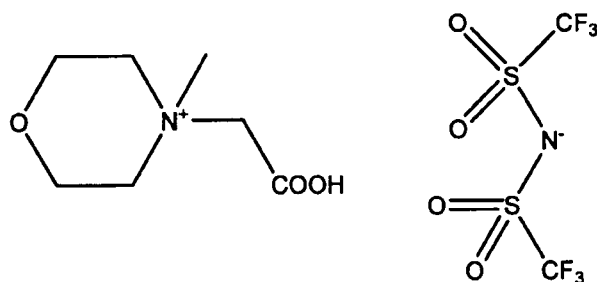
IV

In another preferred embodiment, $R^1R^2R^3R^4Y^+$ is *N*-carboxyethyl-methylpyrrolidinium, wherein *Y* is N and together with R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 said N forms a pyrrolidinium ring structure, and R^4 is $-\text{CH}_2\text{CH}_2\text{COOH}$. In another preferred embodiment, the organic salt is *N*-carboxyethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, the structure of which is according to formula V:



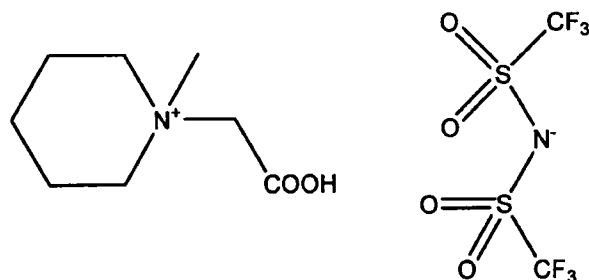
V

In another particular embodiment, the present invention relates to an organic salt of formula I wherein R^4 is as described herein, and *Y* is N and together with R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 said N forms a morpholinium ring structure. In a more preferred embodiment, $R^1R^2R^3R^4Y^+$ is *N*-carboxymethyl-methylmorpholinium, wherein *Y* is N and together with R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 said N forms a morpholinium ring structure, and R^4 is $-\text{CH}_2\text{COOH}$. In another preferred embodiment, the organic salt is *N*-carboxymethyl-methylmorpholinium bis(trifluoromethylsulfonyl)imide, the structure of which is according to formula VI:



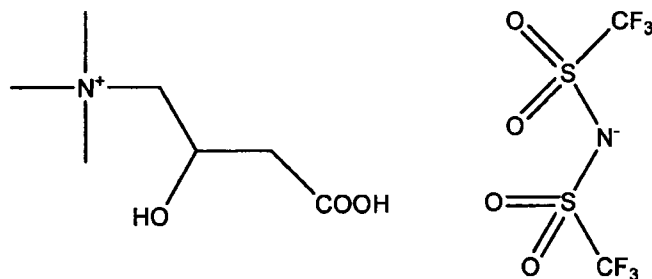
VI

In another particular embodiment, the present invention relates to an organic salt of formula I wherein R^4 is as described herein, and Y is N and together with R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 said N forms a piperidinium ring structure. In a more preferred embodiment, $R^1R^2R^3R^4Y^+$ is *N*-carboxymethyl-methylpiperidinium, wherein Y is N and together with R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 said N forms a piperidinium ring structure, and R^4 is $-\text{CH}_2\text{COOH}$. In another preferred embodiment, the organic salt is *N*-carboxymethyl-methylpiperidinium bis(trifluoromethylsulfonyl)imide, the structure of which is according to formula VII:



VII

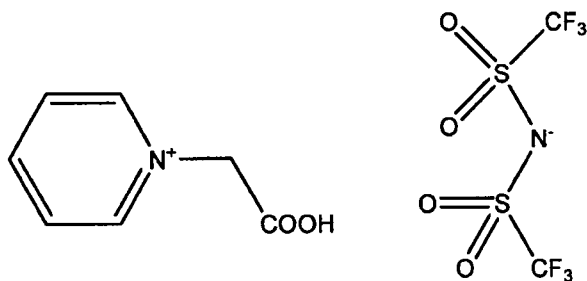
In yet another particular embodiment, the present invention relates to an organic salt of formula I wherein R^1 , R^2 and R^3 are as described herein, and R^4 is selected from C_{1-12} hydroxyalkyl-COOH, still more in particular is selected from C_{1-3} hydroxyalkyl-COOH, even more particularly is $-\text{CH}_2\text{CH}_2\text{OHCH}_2\text{COOH}$. In another preferred embodiment, $R^1R^2R^3R^4Y^+$ is carnitine. In another preferred embodiment, the organic salt is carnitine bis(trifluoromethylsulfonyl)imide, the structure of which is according to formula VIII:



VIII

In a particular embodiment carnitine is in L- or D-carnitine or a mixture of L- and D-carnitine, being a racemic mixture. In another particular embodiment carnitine is L-carnitine.

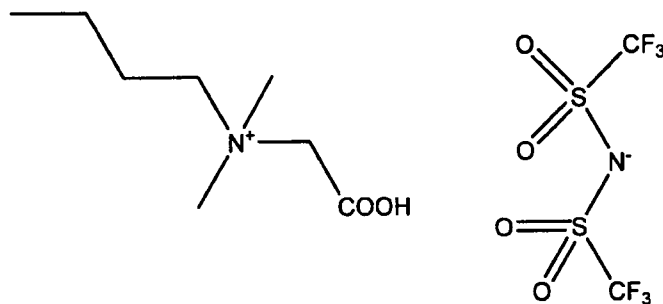
In another particular embodiment, the present invention relates to an organic salt of formula I wherein R^4 is as described herein, and Y is N and together with R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 said N forms a pyridinium ring structure. In a more preferred embodiment, $R^1R^2R^3R^4Y^+$ is *N*-carboxymethyl-methyl pyridinium, wherein Y is N and together with R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 said N forms a pyridinium ring structure, and R^4 is $-\text{CH}_2\text{COOH}$. In another preferred embodiment, the organic salt is *N*-carboxymethyl-methylpyridinium bis(trifluoromethylsulfonyl)imide, the structure of which is according to formula IX:



IX

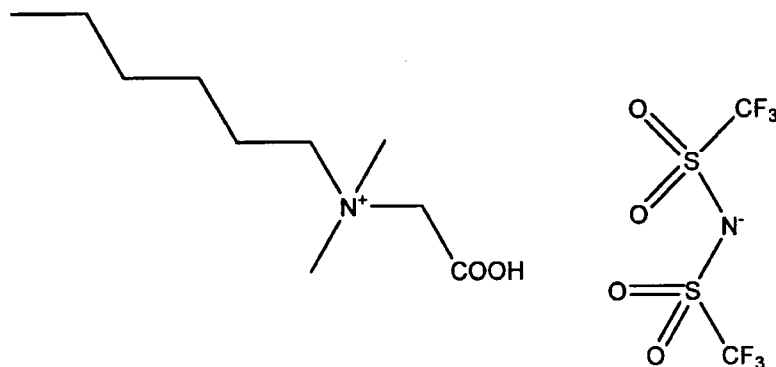
In another particular embodiment, the organic salt is *N*-dimethyl-*N*-butyl-betainium bis(trifluoromethylsulfonyl)imide, the structure of which is according to formula X:

5



X

In another particular embodiment, the organic salt is N-dimethyl-N-hexyl-betainium bis(trifluoromethylsulfonyl)imide, the structure of which is according to formula XI:



10

XI

For all embodiments of the invention, X^- is selected from bis(trifluoromethylsulfonyl)imide (Tf_2N^-), bis(pentafluoroethylsulfonyl)imide, bis(heptafluoropropylsulfonyl)imide, bis(nonafluorobutylsulfonyl)imide, bis(perfluoropentylsulfonyl)imide, bis(perfluorohexylsulfonyl)imide, more preferably X^- is bis(trifluoromethylsulfonyl)imide (Tf_2N^-).

15

The organic salts of the invention are in a 100% pure form or are not mixed with any other ionic liquids.

A second aspect of the present invention relates to a process for the preparation of the ionic liquids described herein, said process comprising the step of performing the metathesis reaction of $R^1R^2R^3R^4Y^+$ halogenide and salts of - preferably perfluorinated -organic sulfonate, organic sulfate, organic sulfonylimide anions or organic carboxylate anions in water. More particularly, the present invention relates to the preparation of betaine bis(trifluoromethylsulfonyl)imide by the metathesis reaction of betaine chloride or betaine bromide and lithium

20

5 bis(trifluoromethylsulfonyl)imide in water. The ionic liquid betaine bis(trifluoromethylsulfonyl)imide can also be prepared by the reaction between $R^1R^2R^3R^4Y^+$ hydroxide and the acid hydrogen bis(trifluoromethylsulfonyl)imide. Another aspect of the present invention relates to the products obtained by the process comprising the step of performing the metathesis reaction of $R^1R^2R^3R^4Y^+$ halogenide and salts of - preferably
10 perfluorinated - organic sulfonate, organic sulfate, organic sulfonylimide or organic carboxylate anions in water as described herein. In a more particular embodiment, the present invention relates to the organic salt obtained by mixing betaine halogenide and lithium bis(trifluoromethylsulfonyl)imide in water or by mixing betaine hydroxide and hydrogen bis(trifluoromethylsulfonyl)imide.

15

A third aspect of the present invention relates to the use of the organic salts of the present invention for general chemical applications at higher temperatures such as a solvent, for extraction procedures, as a reaction medium, for electrodeposition, among others.

In a particular embodiment, the present invention relates to the use the organic salts, more specifically of betaine bis(trifluoromethylsulfonyl)imide, as an ionic liquid and to the use of said
20 ionic liquids as described herein for industrial applications, more specifically chemical applications, yet more specifically chemical applications involving metals such as:

- the solubilization of organic or inorganic compounds, such as of metal oxides, metal hydroxides or metal salts;
- 25 - extraction procedures, more in particular for the extraction of metal ions from metallurgical slags or from pulverized mixtures of metal oxides with silicate or aluminosilicate rocks;
- decontamination of soils contaminated by heavy metals (especially with copper, nickel, zinc, cadmium, mercury or lead);
- for catalytic reactions wherein the ionic liquid serves as a solvent or as a catalyst;
- 30 - for electrodeposition of metal ions, wherein as an example, the ionic liquid serves as a solvent for the metal precursors;
- as a medium for electropolishing or for the cleaning of metal surfaces by for example the removal of surface oxidation layers;
- electrodeposition of (thin) metal layers on conductive surfaces;

- 5 - for the processing of spent nuclear fuel elements: dissolution of MOX or other oxides nuclear fuel elements for separation of fission products and fissile material;
- as electrolyte in batteries, fuel cells, photovoltaic devices and electrochromic devices;
- for recycling of noble metals from used catalysts and electronic circuits.

10 Another aspect of the present invention relates to methods for performing chemical applications by using the ionic liquids as described herein. The present invention thus relates to methods for:

- 15 - the solubilization of organic or inorganic compounds, such as of metal oxides, metal hydroxides or metal salts;
- extraction procedures, more in particular for the extraction of metal ions from metallurgical
slags or from pulverized mixtures of metal oxides with silicate or aluminosilicate rocks;
- decontamination of soils contaminated by heavy metals (especially with copper, nickel,
zinc, cadmium, mercury or lead);
- catalytic reactions wherein the ionic liquid serves as a solvent or as a catalyst;
- electrodeposition of metal ions, wherein as an example the ionic liquid serves as a solvent
20 for the metal precursors;
- electropolishing or for the cleaning of metal surfaces, by for example the removal of surface oxidation layers;
- electrodeposition of (thin) metal layers on conductive surfaces;
- the processing of spent nuclear fuel elements: dissolution of MOX or other oxides nuclear
25 fuel elements for separation of fission products and fissile material
- recycling of noble metals from used catalysts and electronic circuits;

by using the novel ionic liquids described herein.

The present invention furthermore relates to a method for performing chemical reactions and/or extractions by using the ionic liquids, more specifically betaine bis(trifluoromethylsulfonyl)imide

30 ionic liquid and comprising the steps of:

- mixing betaine bis(trifluoromethylsulfonyl)imide with one or more other liquids at higher temperatures (for example for a mixture with water at a temperature above 55.5 or 60 °C), alternatively further comprising other organic or inorganic compounds; and
 - separating betaine bis(trifluoromethylsulfonyl)imide from the other liquid(s) by cooling
35 the temperature to room temperature or slightly above (i.e. between 25 °C and 40 °C).

- 5 The present invention also relates to a method for performing chemical reactions and/or extractions by using the ionic liquids, more specifically betaine bis(trifluoromethylsulfonyl)imide ionic liquid and comprising the steps of:
- mixing betaine bis(trifluoromethylsulfonyl)imide with an alkali-hydroxide aqueous solution, alternatively further comprising other organic or inorganic compounds; and
 - 10 - separating betaine bis(trifluoromethylsulfonyl)imide from water by acidification, for example with inorganic acids such as a solution of hydrogen chloride.

Yet another aspect of the present invention relates to compositions, such as solutions, mixtures or complexes, comprising the organic salts, more specifically the ionic liquids described herein, in a particular embodiment comprising betaine bis(trifluoromethylsulfonyl)imide in protonated or unprotonated form.

In a particular embodiment, said compositions are complexes or solutions of the ionic liquids described herein, which are in a more particular embodiment metal complexes of the ionic liquids such as betaine bis(trifluoromethylsulfonyl)imides with zinc, cadmium, mercury, lead, copper, nickel, silver, gold, palladium, platinum, rhodium, rare earths (scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium), thorium, uranium, neptunium, plutonium, americium, curium, californium or berkelium.

In another particular embodiment, said compositions are mixtures of the ionic liquids described herein with one or more other liquids such as water, organic solvents (such as toluene) or other ionic liquids such as bis(trifluoromethylsulfonyl)imide comprising ionic liquids (i.e. choline bis(trifluoromethylsulfonyl)imide), among others. Such mixtures may be consisting of one phase or may be separated in two or multiple phases, this in a particular embodiment depending on the conditions such as the temperature or the pH. The mixtures may comprise the ionic liquids of the present invention in different ratios, ranging from 0.1% to 99.9%, or from 1% to 99 %, or from 5% to 95%.

Yet in another particular embodiment, said compositions are solutions of organic or inorganic compounds in the ionic liquids of the present invention.

5 Another aspect relates to the process for the preparation of compositions of the organic salts or ionic liquids described herein, comprising the step of mixing the organic salts or ionic liquids with other liquids, with gases or solid compounds. In a particular embodiment, the invention relates to the process for the preparation of metal complexes of betaine bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal hydroxides and mixing
10 them with betaine bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the process for the preparation of metal complexes of N-carboxymethyl-methylmorpholinium bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal hydroxides and mixing them with N-carboxymethyl-methylmorpholinium bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the
15 process for the preparation of metal complexes of N-carboxymethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal hydroxides and mixing them with N-carboxymethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the process for the preparation of metal complexes of N-carboxyethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imides starting
20 from metal oxides or metal hydroxides and mixing them with N-carboxyethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the process for the preparation of metal complexes of N-carboxymethyl-methylpiperidinium bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal hydroxides and mixing them with N-carboxymethyl-methylpiperidinium
25 bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the process for the preparation of metal complexes of N-carboxymethyl-methylimidazolium bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal hydroxides and mixing them with N-carboxymethyl-methylimidazolium bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the process for the preparation of metal
30 complexes of P-carboxymethyl-tributylphosphonium bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal hydroxides and mixing them with P-carboxymethyl-tributylphosphonium bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the process for the preparation of metal complexes of N-carboxymethylpyridinium bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal
35 hydroxides and mixing them with N-carboxymethylpyridinium

5 bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the process for the preparation of metal complexes of L-carnitine bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal hydroxides and mixing them with L-carnitine bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the process for the preparation of metal complexes of N-dimethyl-N-butyl-betainium
10 bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal hydroxides and mixing them with N-dimethyl-N-butyl-betainium bis(trifluoromethylsulfonyl)imide. In another particular embodiment, the invention relates to the process for the preparation of metal complexes of N-dimethyl-N-hexyl-betainium bis(trifluoromethylsulfonyl)imides starting from metal oxides or metal hydroxides and mixing them with N-dimethyl-N-hexyl-betainium
15 bis(trifluoromethylsulfonyl)imide.

Another particular aspect relates to the compositions (such as solutions, mixtures or complexes) obtained by the process of mixing the organic salts or ionic liquids described herein with other liquids, with gases or solid compounds (such as inorganic or organic compounds). In a particular
20 embodiment, the present invention relates to solutions prepared by dissolution of metal salts in the ionic liquids of the present invention. In a more preferred embodiment, the ionic liquid is betaine bis(trifluoromethylsulfonyl)imide.

Yet another aspect relates to the use of said compositions for industrial applications. A particular
25 embodiment relates to the use of said compositions in chemical applications, more in particular chemical applications involving metals such as metal oxides, metal hydroxides or metal salts. Another particular embodiment relates to the use of said compositions in chemical applications, wherein said chemical applications are selected from the list of as a solvent, for example for the solubilization of organic or inorganic compounds, such as of metal oxides, metal hydroxides or
30 metal salts; for extraction procedures, more in particular for the extraction of metal ions; for decontamination of soils contaminated by heavy metals especially with copper, nickel, zinc, cadmium, mercury or lead; for catalytic reactions wherein the ionic liquid serves as a solvent or as a catalyst; for electrodeposition of metal ions; as a medium for electropolishing or for the cleaning of metal surfaces; for deposition of metals onto conductive surfaces; for the processes of
35 spent nuclear fuel elements; as electrolyte in batteries, fuel cells, photovoltaic devices and

5 electrochromic devices and for recycling of noble metals from used catalysts and electronic circuits. One embodiment relates to the use of the lithium complex of betaine bis(trifluoromethylsulfonyl)imide as electrolyte in batteries, fuel cells, photovoltaic devices and electrochromic devices. Another embodiment relates to the use of lanthanide complexes of betaine bis(trifluoromethylsulfonyl)imide as ionic liquids.

10

BRIEF DESCRIPTION OF THE FIGURES

Figure 1: Temperature-dependent phase behavior of a binary [Hbet][Tf₂N] -water mixture. The bluish [Cu(bipy)Cl₂] complex (depicted as dark grey in Figure 1) was dissolved in the ionic liquid to accentuate the phase boundaries.

15

Figure 2: The liquid-liquid equilibrium phase diagram of the binary mixture [Hbet][Tf₂N] - water.

Figure 3: Illustration of the pH-dependent phase behavior of a binary [Hbet][Tf₂N] - water mixture. A two-phase system is obtained for acidic and neutral conditions, whereas a one-phase system is observed for alkaline conditions (pH ≥ 8). The dye methyl red was added to make the phase boundaries better visible (depicted as dark grey in Figure 3).

20

Figure 4: Transfer of copper(II) from the ionic liquid [Hbet][Tf₂N] to the aqueous phase upon acidification of the aqueous phase by a hydrogen chloride solution.

Figure 5: Phase diagram of a water / N-carboxymethyl-methylmorpholinium bis(trifluoromethylsulfonyl)imide system.

25

DETAILED DESCRIPTION OF THE INVENTION

Definitions and nomenclature.

30 We name the ionic liquid presented in formula I as protonated betaine bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N]. Here we represent the cation betaine by *Hbet* rather than by *bet*, because in [Hbet][Tf₂N] the carboxylate group is protonated. Protonated betaine is sometimes also named as betainium⁵⁸, but this name has not received widespread use. The anion bis(trifluoromethylsulfonyl)imide is also known as (CF₃SO₂)₂N⁻, PMS, BTFSI, TFSI, 35 Tf₂N or Tf₂N⁻.

- 5 However, it should be clear to a person skilled in the art that the organic salts described in the present invention can be in different forms, protonated or unprotonated or with different counterions.

10 In each of the following definitions, the number of carbon atoms represents the maximum number of carbon atoms generally optimally present in the substituent or linker; it is understood that where otherwise indicated in the present application, the number of carbon atoms represents the optimal maximum number of carbon atoms for that particular substituent or linker.

The term "C₁₋₁₂ alkyl" as used herein means normal, secondary, or tertiary hydrocarbon having 1 to 12 carbon atoms. Examples are methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-methyl-1-propyl(i-Bu), 2-butyl (s-Bu) 2-methyl-2-propyl (t-Bu), 1-pentyl (n-pentyl), 2-pentyl, 3-pentyl, 2-methyl-2-butyl, 3-methyl-2-butyl, 3-methyl-1-butyl, 2-methyl-1-butyl, 1-hexyl, 2-hexyl, 3-hexyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 3-methyl-3-pentyl, 2-methyl-3-pentyl, 2,3-dimethyl-2-butyl, 3,3-dimethyl-2-butyl, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. In a particular embodiment, the term can also include C₁₋₁₂ haloalkyl, which is a C₁₋₁₂ alkyl bearing at least one halogen. In another particular embodiment, the term can also include C₁₋₁₂ hydroxyalkyl, more preferably C₁₋₃ hydroxyalkyl, even more preferably 2-hydroxypropyl.

The term "substituted or unsubstituted cyclic structure" as used herein means a monocyclic saturated (aliphatic) or unsaturated (aromatic) or partly unsaturated ring structure having from 3 to 7 carbon atoms wherein at least one N, P, As or Sb atom is present and additionally at least one carbon atom can be replaced with a heteroatom, this heteroatom can be a N, P, As, Sb, O, S, Se, or Te in case of an aliphatic or partly unsaturated ring structure and can be N, P, As, or Sb in case of an aromatic or partly unsaturated ring structure. These cyclic structures can optionally be substituted with C₁₋₁₂ alkyl structures. Examples of this substituted or unsubstituted cyclic structure include, but are not limited to, pyridinium, imidazolium, pyrrolidinium, morpholinium, piperidinium, dihydropyridylum, thiazolylum, pyrrolylium, pyrazolylum, imidazolylum, tetrazolylum, piperidinylium, pyrrolidinylium, 2-pyrrolidonylium, pyrrolinylium, tetrahydropyranylium, bis-tetrahydropyranylium, azocinylium, triazinylium, 6H-1,2,5-thiadiazinylium, 2H,6H-1,5,2-dithiazinylium, 2H-pyrrolylium, isothiazolylum, isoxazolylum, pyrazinylium, pyridazinylium, pyrimidinylium, furazanylium, imidazolidinylium,

5 imidazolinylium, pyrazolidinylium, pyrazolinylium, piperazinylium, morpholinylium, or oxazolidinylium.

In a particular embodiment of each aspect of the invention the cyclic structures consist of the examples recited above.

As used herein and unless otherwise stated, the term "C₃₋₁₂ cycloalkyl" means a monocyclic
10 saturated hydrocarbon monovalent radical having from 3 to 12 carbon atoms, such as for instance cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl and the like, or a C₇₋₁₂ polycyclic saturated hydrocarbon monovalent radical having from 7 to 12 carbon atoms such as, for instance, norbornyl, fenchyl or adamantyl.

For the avoidance of doubt, when the terms C₁₋₈, C₁₋₆, C₁₋₄, C₁₋₃ or C₁₋₂ are used herein they
15 respectively refer to structures having from 1 to 8, 1 to 6, 1 to 4, 1 to 3 or 1 to 2 carbon atoms.

The term "ionic liquid" as used herein, means molten salts that are liquid at temperatures below 100°C.

As used herein and unless otherwise stated, the term halogen means any atom selected from the group consisting of fluorine, chlorine, bromine and iodine.

20 Any substituent designation that is found in more than one site in an organic salt of this invention shall be independently selected.

It is known to the person skilled in the art that certain isomeric structures like carnitine can have different isomeric forms (e.g. L- and D-form), thus it is clear to the person skilled in the art that these isomeric structures include all possible isomeric forms, including tautomeric and
25 stereochemical forms (stereoisomers) and racemic mixtures which may be present in the cation of the organic salts of the invention and position isomers are not included.

30 Novel ionic liquids

The present invention provides for organic salts having quaternary ammonium or phosphonium structure according to the following formula (I):

35



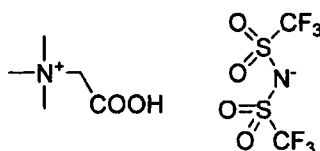
Wherein:

- Y is selected from N; P; As; or Sb;
- each of R^1 , R^2 and R^3 are independently selected from C_{1-12} alkyl; or C_{3-12} cycloalkyl; or
10 each of R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 can be taken together to form a substituted or unsubstituted cyclic structure;
- R^4 is selected from a C_{1-12} alkyl-COOH; or C_{3-12} cycloalkyl-COOH; wherein alkyl is optionally substituted with at least one OH or comprises at least one carbonyl function;
- X^- is selected from organic sulfonates, preferably perfluorinated organic sulfonates; organic
15 sulfates, preferably perfluorinated organic sulfates; organic carboxylates; organic sulfonylimides, preferably bis(perfluoroalkylsulfonyl)imides; or tetrafluoroborate.

These organic salts are ionic liquids and can be used as such. More preferably, the present invention provides for the ionic liquid betaine bis(trifluoromethylsulfonyl)imide in protonated or
20 unprotonated form. This invention shows that betaine is a useful starting material for the design of task-specific ionic liquids which can solubilize metal oxides.

In a search for cheap and easily accessible ionic liquids, we turned our attention to betaine. Betaine is a trivial name for 1-carboxy-*N,N,N*-trimethylmethanaminium (inner salt). It is also
25 known as *N,N,N*-trimethylglycine, *N*-trimethylglycine or trimethylglycine. Betaine has a zwitter-ionic structure. Betaine melts with decomposition at 310 °C. It readily reacts with mineral acids or organic acids whereby the carboxylate group gets protonated and the anionic part of the acid becomes the anion in the betaine salt. For instance betaine reacts with hydrochloric acid to form betaine hydrochloride, a salt with melting point of 232 °C. Betaine hydrochloride is a water-
30 soluble salt that can be used to prepare hydrophobic salts by a metathesis reaction. The difference between the choline and the betaine cation is that in the betaine cation the hydroxyl group of choline is replaced by a carboxylic acid group. In fact, betaine is a metabolite that is formed by oxidation of choline⁵⁹. The carboxylate group of betaine is a very good coordinating group towards metal ions, better than the aliphatic alcohol function of choline. The most important form
35 of betaine on the market is the hydrochloride salt, betaine hydrochloride. An aqueous solution of

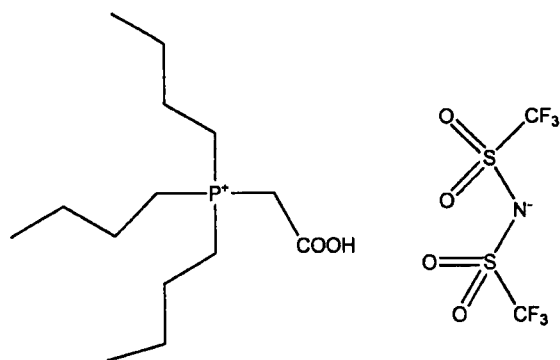
5 betaine hydrochloride reacts with an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide to form betaine bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N]. With this invention, we introduce protonated betaine bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N] (see formula I), as a new ionic liquid, more particularly also as a task-specific ionic liquid for selective solubilization of metal oxides and
 10 metal salts. The main physical and structural properties of this organic salt are presented. The temperature dependent miscibility of the ionic liquid with water has been studied. Of importance is the formation of a one-phase binary mixture at high temperature and a two-phase binary mixture at ambient temperatures. It will be shown that the phase behavior of [Hbet][Tf₂N] - water mixtures strongly depends on the pH conditions.



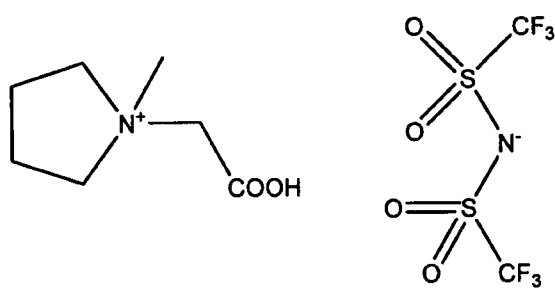
II

The positive charge on the quaternary nitrogen (or phosphor, arsenicum or antimony) atom has an inductive effect on the COOH-group. This effect is affected by the chain length in-between the COOH-group and the positively charged nitrogen (or phosphor, arsenicum or antimony) atom,
 20 respectively. The shorter the distance between these functional groups, the higher the acidity of the proton of the COOH-function. Therefore, one or two CH₂ groups in-between, and more preferably one CH₂ group in-between is favorable for the application of this invention: these ionic liquids exhibit a significantly higher solubilizing ability for metal oxides than ionic liquids with three or more CH₂-groups between the positively charged heteroatom and the COOH-
 25 function.

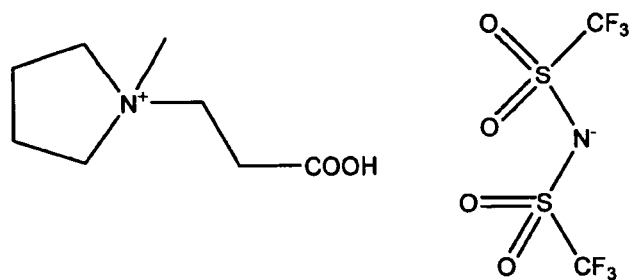
Building further on this concept, different other ionic liquids can be obtained, not only by extension of the alkyl chains of the groups R¹, R², R³, R⁴, but also by making R¹ and R² part of a cyclic system (which can contain in addition a heteroatom). Instead of ammonium cation, the corresponding phosphonium cations can be considered as well. Examples of such ionic liquids
 30 are shown in formulae III-IX:



III

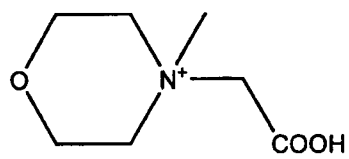


IV

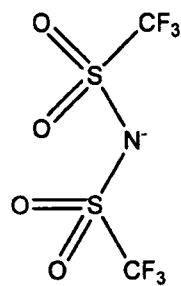


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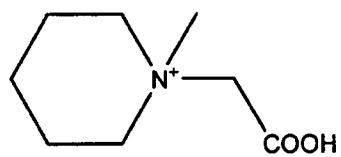
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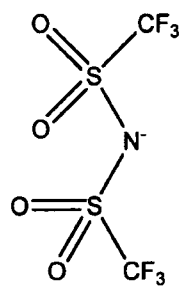
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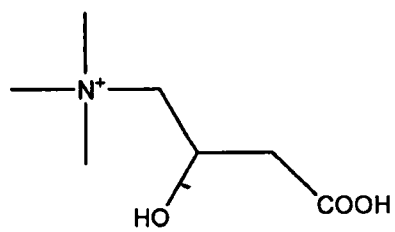
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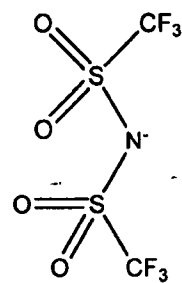
VII

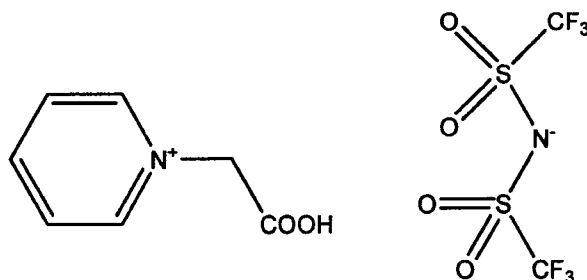


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VIII





IX

It has been shown that protonated betaine bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N], and related compounds are ionic liquids with the ability to dissolve large quantities of metal oxides. This metal solubilizing power is selective. Soluble are: oxides of the trivalent rare earths, uranium(VI) oxide, zinc(II) oxide, cadmium(II) oxide, mercury(II) oxide, nickel(II) oxide, copper(II) oxide, palladium(II) oxide, lead(II) oxide and silver(I) oxide. Insoluble or very poorly soluble are iron and manganese oxides, cobalt oxides, as well as aluminum oxide and silicon oxide. Also metal hydroxides can be solubilized in the ionic liquid. The metals can be stripped from the ionic liquid by treatment of the ionic liquid with an acidic aqueous solution. After transfer of the metal ions to the aqueous phase, the ionic liquid can be recycled for reuse. Betainium bis(trifluoromethylsulfonyl)imide forms one phase with water at high temperatures, whereas phase separation occurs below 55.5 °C (temperature switch behavior). The mixtures of the ionic liquid with water also show a pH-dependent phase behavior: two phases occur at low pH, whereas one phase is present under neutral or alkaline conditions.

In a particular embodiment, certain organic salts described herein are not ionic liquids according to the definitions (having melting points under 100°C), but still have a melting point around or under 200°C and therefore can be used for chemical applications at higher temperatures, such as: as a solvent, as a reaction medium, for electrodeposition of metals, among other applications.

Synthesis and preliminary analysis of the betaine salts

Protonated betaine bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N], is accessible via different synthetic routes.

The best method is by reaction of the zwitterionic betaine with the acid hydrogen bis(trifluoromethylsulfonyl)imide, Tf₂NH. This reaction involves a simple proton transfer from

- 5 the bis(trifluoromethylsulfonyl)imide to the more basic carboxylate group, so that the betaine will be protonated. This method is general applicable for the preparation of other betaine salts. For instance, we prepared by this method protonated betaine hexafluorophosphate, protonated betaine triflate, and protonated betaine pentafluorobenzoate. However, all these salts have melting points above 100 °C and can therefore not be considered as ionic liquids.
- 10 A second synthetic route to the protonated betaine bis(trifluoromethylsulfonyl)imide ionic liquid is by the metathesis reaction of betaine hydrochloride and lithium bis(trifluoromethylsulfonyl)imide (in 1:1 molar ratio) in aqueous solution. An aqueous solution of betaine hydrochloride reacts with an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide to form protonated betaine bis(trifluoromethylsulfonyl)imide,
- 15 [Hbet][Tf₂N]. The ionic liquid easily separates from the aqueous layer (due to its hydrophobicity). The ionic liquid prepared by the metathesis reaction has a melting point of 57 °C and the compound can easily be supercooled to room temperature. The fact that [(Hbet)₃(bet)][Tf₂N]₃ is formed besides [Hbet][Tf₂N], depending on the experimental conditions, leads to the assumption that an equilibrium between different species in solution is present. So
- 20 far, no detailed information on this equilibrium is available yet. The pure [(Hbet)₃(bet)][Tf₂N]₃ compound (m.p. = 70 °C) crystallizes from a solution of the mixture in the [C₄mim][Tf₂N] ionic liquid. Pure [Hbet][Tf₂N], free of [(Hbet)₃(bet)][Tf₂N]₃, can be obtained by mixing stoichiometric amounts of the betaine inner salt (bet) and the acid hydrogen bis(trifluoromethylsulfonyl)imide, H[Tf₂N]. Pure [Hbet][Tf₂N] melts at 69 °C.
- 25 The melting point of protonated betaine bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N], in equilibrium with [(Hbet)₃(bet)][Tf₂N]₃, as prepared by the metathesis reaction between lithium bis(trifluoromethylsulfonyl)imide and betaine chloride is 57 °C, but the liquid compound can be supercooled to room temperature. [Hbet][Tf₂N] shows a tendency to crystallize rather than to form a glass: after some time (hours to weeks) crystallization occurs. The viscosity of
- 30 [Hbet][Tf₂N] is 351 cP at 60 °C. [Hbet][Tf₂N] is a hydrophobic ionic liquid at room temperature; after addition of water, two separate phases are formed. Heating treatment of a mixture induced the formation of a one-phase-system at a critical temperature of 56 °C. Cooling of the one-phase mixture resulted again in phase separation. A similar temperature-dependent miscibility was observed for mixtures of [Hbet][Tf₂N] with toluene. [Hbet][Tf₂N] is miscible with ethanol, 1-
- 35 octanol (and other higher alcohols), benzonitrile, acetonitrile, DMSO, acetic acid and ethyl

5 acetate, but also with other ionic liquids containing the bis(trifluoromethylsulfonyl)imide anion like $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$. $[\text{Hbet}][\text{Tf}_2\text{N}]$ is immiscible with hexane, heptane, dichloromethane (DCM), chloroform, benzene, toluene and diethyl ether.

All trials to obtain ionic liquids of protonated betaine bis(trifluoromethylsulfonyl) imide with counter ions other than bis(trifluoromethylsulfonyl)imide failed and resulted in the formation of
10 solids with a high melting point: (1) protonated betaine hexafluorophosphate, $[\text{Hbet}][\text{PF}_6]$ (m.p. = 159 °C; this compound has been reported earlier); (2) protonated betaine triflate, $[\text{Hbet}][\text{OTf}]$ (m.p. = 125 °C); (3) protonated betaine pentafluorobenzoate, $[\text{Hbet}][\text{C}_6\text{F}_5\text{COO}]$ (m.p. = 144 °C); (4) betaine tetrafluoroborate (200 °C). Also analogues with non-fluorinated counter ions have widely been described in the literature, but all the reported compounds have a melting point well
15 above 100 °C.

A general approach to the synthesis of the other ionic liquids is by first quaternizing a tertiary amine (e.g. N-methylpyrrolidine, tributylamine) or a tertiary phosphine (e.g. tributylphosphine) by reaction with an ester of chloroacetic acid or bromoacetic acid (preferentially a methyl ester or an ethyl ester). After quaternization, the ester is converted to the corresponding acid, and the
20 chloride (or bromide) anion is exchanged by a metathesis reaction for a bis(trifluoromethylsulfonyl)imide anion. The ionic liquid separates from the water phase. The esters of chloroacetic acid or bromoacetic acid can be replaced by other esters of γ -bromoalkanoic acids or γ -chloroalkanoic acids. Lithium bis(trifluoromethylsulfonyl)imide can be replaced by other lithium bis(trifluoroalkylsulfonyl)imides.

25

Thermomorph behavior

Although we described hereinabove that $[\text{Hbet}][\text{Tf}_2\text{N}]$ forms a two-phase system with water, this statement is only true for mixtures at room temperature and slightly above. Upon heating the mixture, a one-phase-system with an upper consolute point at around 55.5 °C is formed. Cooling
30 of the one-phase mixture resulted again in phase separation. The phase separation is illustrated in Figure 1. The phase diagram of the binary system $[\text{Hbet}][\text{Tf}_2\text{N}]$ - water is shown in Figure 2. The phase diagram was measured by equilibrating the $[\text{Hbet}][\text{Tf}_2\text{N}]$ - water mixture at a given temperature, followed by analysis of the components in the $[\text{Hbet}][\text{Tf}_2\text{N}]$ rich phase (lower layer) and in the water-rich phase (upper layer). The composition of the phases was determined by

- 5 distilling out the water and comparing the original mass with the remaining (non-volatile) ionic liquid mass. At the critical concentration, the mass fraction of the ionic liquid is around 0.519.

pH-dependent phase behavior

When a biphasic mixture of protonated betaine bis(trifluoromethylsulfonyl)imide is treated with
10 (a solution of) alkali hydroxides such as LiOH, NaOH, or KOH, a monophasic mixture is obtained, because the alkali salts of betaine bis(trifluoromethylsulfonyl)imide are water soluble (Figure 3). Acidification of the solution leads to the regeneration of the hydrophobic protonated betaine bis(trifluoromethylsulfonyl)imide ionic liquid and thus to phase separation.

15 Solubility of metal oxides

An interesting property of betaine bis(trifluoromethylsulfonyl)imide is its ability to dissolve metal oxides. The metal oxides react with the carboxylic acid group of the ionic liquid to form carboxylate complexes and water. The following oxides were found to be soluble in the ionic liquid [Hbet][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃,
20 Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO, ZnO, CdO, HgO, CuO, Ag₂O, NiO, PdO and MnO. Oxides can be replaced by hydroxides as the starting material. In a typical experiment, the metal oxide is mixed with [Hbet][Tf₂N] and water, and the mixture is stirred for several hours. After evaporation of water under reduced pressure, a solution of the metal betaine complex in [Hbet][Tf₂N] is obtained. The solubility of metal oxides in protonated betaine
25 bis(trifluoromethylsulfonyl)imide is high because the ionic liquid can form stoichiometric compounds with the metals; i.e. so much metal oxide can be added to the [Hbet][Tf₂N] ionic liquid until all the ionic liquid is transformed into a metal complex. However, the presence of water is facilitating the dissolution of the metal oxide in the ionic liquid. It is more difficult to dissolve the ionic liquid in direct contact with the metal oxide. This can be due to the fact that
30 most metal oxides have a hydrophilic surface, whereas the ionic liquid is hydrophobic; therefore the wettability of the metal oxide by the pure ionic liquid is lower. Good direct dissolution (i.e. without addition of water) of a metal oxide in [Hbet][Tf₂N] was however also observed, for example for CuO. Not all metal oxides can be solubilized in [Hbet][Tf₂N]. Insoluble or very poorly soluble are iron and cobalt oxides, as well as aluminum oxide and silicon oxide. Besides
35 the metal oxides, also different metal salts like CuCl₂·2H₂O or EuCl₃·6H₂O are soluble in

5 [Hbet][Tf₂N]. For instance, [Hbet][Tf₂N] can dissolve 1.75 mol% of CuCl₂ and 6 mol.% of EuCl₃ (determined titrimetrically by EDTA). The dissolution process can be facilitated by working under moderate to high pressure conditions. Under these experimental conditions, it is possible to dissolve in the ionic liquid oxides that are otherwise insoluble in [Hbet][Tf₂N]. Examples of such oxides include Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃. To perform the
10 experiment, an equimolar ionic liquid/ water mixture is heated with the metal oxide in a PTFE-lined acid digestion bomb.

The metals can be stripped from betaine bis(trifluoromethylsulfonyl)imide by extracting the ionic liquid with an acidified aqueous solution (for instance with diluted hydrochloric acid or diluted nitric acid). The metal complex of protonated betaine bis(trifluoromethylsulfonyl)imide is
15 decomposed and the betaine bis(trifluoromethylsulfonyl)- imide ionic liquid is regenerated. The metal ion is thus transferred to the aqueous phase and betaine bis(trifluoromethylsulfonyl)imide is regenerated. For instance, a solution of copper(II) in [Hbet][Tf₂N] was extracted twice with a 37% HCl solution. The ratio of the metal content in the aqueous phase to the ionic liquid phase was determined by titration to be 82:1 after the first extraction. The metal was almost completely
20 extracted to the aqueous phase after a second extraction with the acidic solution. The transfer of copper(II) from the ionic liquid to the aqueous phase upon acidification of the aqueous layer is shown in Figure 4. The same extraction can also be done with other aqueous acids such as aqueous HNO₃ or H₂SO₄. A nearly quantitative removal of neodymium(III) from [Hbet][Tf₂N] could be obtained by two extractions of the ionic liquid with a 37% HCl solution. The
25 [Hbet][Tf₂N] ionic liquid can be reused after stripping of its metal content.

The metal complexes of betaine bis(trifluoromethylsulfonyl)imide have in general a high melting point (> 100 °C), but the rare-earth complexes of betaine bis(trifluoromethylsulfonyl)imide have melting points below 100 °C and can thus be considered as genuine ionic liquids.

30

35

5 **Table 1:** Melting points for the lanthanide complexes of [Hbet][Tf₂N].

Lanthanide complex	Melting point (°C)
Y ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	109
La ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	78
Pr ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	86
Nd ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₄	90
Sm ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	88
Eu ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	95
Gd ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	94
Tb ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	88
Dy ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	88
Ho ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	80
Er ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	94
Tm ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	97
Yb ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	89
Lu ₂ ((CH ₃) ₃ NCH ₂ COO) ₈ N(SO ₂ CF ₃) ₂) ₆ (H ₂ O) ₂	88

10 The metal complexes of betaine bis(trifluoromethylsulfonyl)imide can be dissolved in the ionic liquids choline bis(trifluoromethylsulfonyl)imide or the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides. Betaine bis(trifluoromethylsulfonyl)imide is also miscible in all molar ratios with choline bis(trifluoromethylsulfonyl)imide or the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides.

15 **Applicability of the ionic liquid**

Due to its properties, mainly the metal dissolving properties, [Hbet][Tf₂N] can be used for multiple purposes. We have shown that the [Hbet][Tf₂N] ionic liquid can be used for the selective dissolution of metal oxides in the ionic liquid, extraction and back extraction (stripping) of metals, cleaning of metal surfaces, dissolution of palladium oxide to show the potential for

5 recycling precious metals (platinum group metals) from catalysts and the electrodeposition of metals from the ionic liquid.

Subsequently, [Hbet][Tf₂N] can be used in the following sectors:

- Ore processing: extraction of precious metals for ores. The selective solubility of metal oxides has advantage for the extraction for metals from ores: valuable metals can be
10 extracted whereas the quartz, silicates, aluminosilicates, aluminum oxides and iron oxides are unaffected;
- Metal processing industry: electrodeposition of metals, electroplating, electropolishing. We have shown that metals can be deposited from solutions of the metal salts in protonated betaine bis(trifluoromethylsulfonyl)imide or of the metal complexes of betaine
15 bis(trifluoromethylsulfonyl)imide by electrolysis. After immersion of a zinc plate in an ionic liquid containing copper betaine bis(trifluoromethylsulfonyl)imide, the zinc plate is covered by a coating of metallic copper. By the same method, a copper plate can be coated with metallic silver by immersion in an ionic liquid containing silver betaine bis(trifluoromethylsulfonyl)imide;
- Energy sector: electrolytes for batteries, fuel cells and photovoltaic cells;
- Electrochromic displays;
- Nuclear sector: processing of spent nuclear fuel elements. Selective extraction of lanthanides and actinides from other fission products and from uranium;
- Environmental: cleaning of soils contaminated by heavy metals. The selective solubility of
25 metal oxides is herein also useful;
- Cleaning industry: removal of oxide coating on metals. The cleaning of oxidized metal surfaces is easily done with betaine bis(trifluoromethylsulfonyl)imide. For instance, we have shown that a copper sheet covered with a black coating of copper(II) oxide could be cleaned after short immersion in protonated betaine bis(trifluoromethyl-sulfonyl)imide;
- Recycling: recycling of precious metals (platinum group metals) from used catalysts (three-
30 way catalysts in automobile exhausts);
- Recovery of copper, zinc and lead.

5 As a summary, protonated betaine bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N], is a versatile ionic liquid that can be used for multiple purposes. It can be looked at as a task-specific ionic liquid that can be used for the selective solubilization of metal oxides, hydroxides and metal salts. Moreover, the ionic liquid can be switched from a hydrophobic one to a hydrophilic one by temperature or pH control. Although the melting point [Hbet][Tf₂N] is above room temperature, 10 it is miscible with room-temperature ionic liquids containing the [Tf₂N]⁻ anion and the mixtures are room-temperature ionic liquids as well. This widely broadens the applicability of this ionic liquid.

Examples

15

GENERAL DESCRIPTION OF THE MATERIALS AND METHODS USED

Elemental analyses (carbon, hydrogen, nitrogen) were made on a CE Instruments EA-1110 elemental analyzer. FTIR spectra were recorded on a Bruker IFS-66 spectrometer. The samples 20 were measured using the KBr pellet method or as a thin film between KBr windows. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz). The water content of the ionic liquids was determined by a coulometric Karl Fischer titrator (Mettler Toledo Coulometric Karl Fischer Titrator, model DL39). The viscosity of the ionic liquids was measured by the falling ball method (Gilmont Instruments). Differential scanning calorimetry (DSC) 25 measurements were made on a Mettler-Toledo DSC822e module (scan rate of 10 °C min⁻¹ under helium flow). The organic precursors were purchased from Acros Organics and lithium bis(trifluoromethylsulfonyl)imide from IoLiTec. All chemicals were used as received, without any additional purification step.

30 EXAMPLE 1: SYNTHESIS AND ANALYSIS OF BETAINES BIS(TRIFLUOROMETHYLSULFONYL)IMIDES.

A solution of betaine hydrochloride (1 mol, 153.61 g) in 250 mL of water was added under stirring to 500 mL of an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (1 mol, 35 287.08 g). The mixture was stirred for one hour at room temperature. The aqueous phase

5 separated from the ionic liquid. After separation of the phases, the ionic liquid phase was washed three times with small amounts of water until no chloride impurities could be detected by the silver nitrate test. The ionic liquid was evaporated to dryness at 120 °C in vacuo on a rotary evaporator. A water content of 35 ppm was determined by coulometric Karl Fischer titration. ¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ = 4.27 (s, 2H), 3.19 (s, 3 × CH₃). ¹³C-NMR ([D₆]DMSO, TMS): δ = 167.38 (COO), 125.99, 121.75, 117.52, 113.28 (2 × CF₃), 64.06 (N-CH₂), 54.16 (3 × CH₃). Elemental analysis calcd (%) for C₇H₁₂N₂O₆F₆S₂ (M_w = 398.302 g mol⁻¹): C 21.10, H 3.03, N 7.03; found: C 20.78, H 3.24, N 6.85. M.p. = 57 °C. Density: 1.531 g cm⁻³ (60 °C).
A viscosity of 351 cP (60°C) of the compound was measured by the falling ball method. Density: 1.554 g cm⁻³.

15 EXAMPLE 2: SYNTHESIS OF BETAINETETRAFLUOROBORATE

A solution of betaine hydrochloride (32.5 mmol, 5 g) in 20 mL of hot water was added under stirring to an aqueous solution of ammonium tetrafluoroborate (32.5 mmol, 3.412 g, 20 mL). The mixture was stirred for one hour at room temperature and no phase separation was observed. The solution was allowed to cool down in the refrigerator at 4°C. White crystals of betaine tetrafluoroborate, [Hbet][BF₄] precipitated. The product was filtered, washed with cold water, and dried under vacuum.

Melting point: 200 °C (onset).

25 EXAMPLE 3: SYNTHESIS OF BETAINEHXAFLUOROPHOSPHATE

A solution of betaine hydrochloride (32.5 mmol, 5 g) in 20 mL of hot water was added under stirring to an aqueous solution of potassium hexafluorophosphate (32.5 mmol, 5.98g, 20 ml). The mixture was stirred for one hour at room temperature, no phase separation was observed. The solution was allowed to cool down in the refrigerator at 4°C. White crystals of betaine hexafluorophosphate, [Hbet][PF₆], precipitated. The product was filtered, washed with cold water, and dried under vacuum.

Melting point (onset): 159 °C.

- 5 Note: the synthesis of this compound (but not the thermal behavior) was described by Coronado and coworkers in Eugenio Coronado et al., *Angewandte Chemie International Edition* **43** (2004) 6152-6156.

EXAMPLE 4: SYNTHESIS OF BETAINE TRIFLATE

10

A solution of betaine monohydrate (42.68 mmol, 5 g) in 20 mL of hot water was added under stirring to 20 mL of a hot aqueous solution of trifluoromethanesulfonic acid (42.68 mmol, 6.41 g). The mixture was stirred for one hour at room temperature, no phase separation was observed. The water was evaporated under vacuum. Betaine trifluoromethanesulfonate, [Hbet][OTf] was
15 obtained as a white solid.

Melting point (onset): 111°C.

EXAMPLE 5: SYNTHESIS OF BETAINE PENTAFLUOROBENZOATE

- 20 A solution of betaine monohydrate (42.68 mmol, 5 g) in 20 mL of hot water was added under stirring to 20 mL of a hot aqueous suspension of pentafluorobenzoic acid (42.68 mmol, 9.05 g). The mixture was stirred for one hour at room temperature and phase separation occurred. The aqueous phase was evaporated under vacuum. Betaine pentafluorobenzoate was obtained as a white solid.

- 25 Melting point (onset): 144 °C.

EXAMPLE 6: MISCIBILITY OF PROTONATED BETAINE BIS(TRIFLUOROMETHYLSULFONYL) IMIDE

- 30 • *With [Chol][Tf₂N]*:

[Hbet][Tf₂N] and [Chol][Tf₂N] are miscible in any molar ratio. A 1:1 mixture does not crystallize after cooling in a refrigerator at 4°C, so an eutectic mixture is formed.

- Choline bis(trifluoromethylsulfonyl)imide, [Chol][Tf₂N], was prepared as described in the prior
35 art. A solution of choline chloride (1 mol, 139.62 g) in 250 mL of water was added under stirring

5 to 500 mL of an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (1 mol, 287.08 g). The mixture was stirred for one hour at room temperature and the aqueous phase separated from the ionic liquid. After separation of the phases the ionic liquid phase was washed three times with small amounts of water until no chloride impurities could be detected after adding silver nitrate. Finally the ionic liquid choline bis(trifluoromethylsulfonyl)imide was evaporated to dryness at
 10 120°C on a rotary evaporator. A water content of 25 ppm was determined using a coulometric Karl Fischer Titrator (Mettler Toledo, model DL39). ¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ = 5.29 (t, 1H), 3.84 (m, 2H), 3.39 (m, 2H), 3.10 (s, 9H). ¹³C-NMR ([D₆]DMSO, TMS): δ = 124.27, 121.07, 117.87, 114.67 (2 × CF₃), 67.01 (N-CH₂), 55.13 (CH₂), 53.18 (3 × CH₃).

15 • ***With organic solvents:***

Protonated betaine bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N], is completely miscible with e.g. 1-octanol, benzonitrile, DMSO, acetonitrile, acetic acid, ethylacetate, ethanol and methanol. The compound is immiscible with hexane, dichloromethane (DCM), chloroform, benzene, diethylether. Toluene was found to exhibit a temperature dependent miscibility. While the
 20 solubility of toluene at room temperature is very low, the solubility increases markedly with temperature.. The ionic liquid is also miscible with other ionic liquids containing the bis(trifluoromethylsulfonyl)imide anion, like the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides.

25 Table 2. Miscibility of [Hbet][Tf₂N] with organic solvents

Miscible	Immiscible	Partially miscible
1-octanol	hexane	toluene
benzonitrile	DCM	
DMSO	chloroform	
acetonitrile	benzene	
acetic acid	diethylether	
ethylacetate		
ethanol		

• ***With water – dependence of temperature:***

5 [Hbet][Tf₂N] is a hydrophobic ionic liquid at room temperature. After addition of water, two separate phases are formed. Heating treatment of a mixture induced the formation of a one-phase-system at a critical temperature of 56 °C. The phase diagram of the [Hbet][Tf₂N]/water system is shown in Figure 2. By cooling down the mixture the two phases are recovered. So the system [Hbet][Tf₂N] /water is a temperature switchable one-phase/two-phase system.

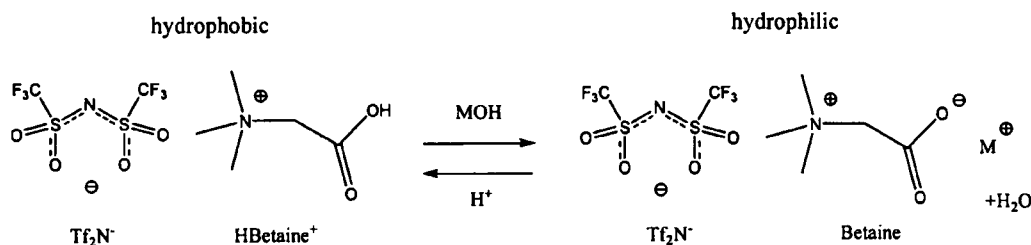
10

• *With water – dependence of pH:*

[Hbet][Tf₂N] contains an acidic hydrogen atom and can be deprotonated by addition of a base. [Hbet][Tf₂N] was mixed with different alkali metal hydroxides. 25 mmol of [Hbet][Tf₂N] was mixed with hot water and an aqueous solution of an alkali metal hydroxide was added dropwise
15 until pH 7. The hydrophobic phase disappears. After acidification of the solution, two phase-system was reformed. After evaporation of the water phase under reduced pressure, and after neutralization of the ionic liquid, a hydrophilic salt remained with melting points above 100°C.

Scheme 1: Neutralization of Betaine Tf₂N with an alkaline hydroxide.

20



Lithium salt

25 [Hbet][Tf₂N] (16.63 g; 41.75 mmol) was added to 10 mL of an aqueous solution of LiOH (1 g; 41.75 mmol) and stirred for 15 minutes. After filtration, the water was evaporated under vacuum. The colorless crystals were recrystallized from water and dried at 50°C in a vacuum oven. Elemental analysis: calcd (%) for Li((CH₃)₃NCH₂CO₂)(N(SO₂CF₃)₂) (M_w= 404.23 g mol⁻¹) C 20.80, H 2.74, N 6.92; found C 20.69, H 3.07, N 6.76.

30

5 **Sodium salt**

[Hbet][Tf₂N] (9.96 g; 25.0 mmol) was added to 10 mL of an aqueous solution of NaOH (1 g; 25.0 mmol) and stirred for 15 minutes. After filtration, the water was evaporated under vacuum. The colorless crystals were recrystallized from water and dried at 50°C in a vacuum oven. Elemental analysis: calcd (%) for Na((CH₃)₃NCH₂CO₂)(N(SO₂CF₃)₂)(H₂O) (M_w= 438.2 g mol⁻¹)

10 C 19.18, H 2.98, N 6.39; found C 19.78, H 2.97, N 6.38.

Potassium salt

[Hbet][Tf₂N] (7.10 g; 17.82 mmol) was added to 10 mL of an aqueous solution of KOH (1 g; 17.82 mmol) and stirred for 15 minutes. After filtration, the water was evaporated under vacuum.

15 The colorless crystals were recrystallized from water and dried at 50°C in a vacuum oven. Elemental analysis: calcd (%) for K((CH₃)₃NCH₂CO₂)(N(SO₂CF₃)₂)(H₂O) (M_w= 454.41 g mol⁻¹) C 18.50, H 2.88, N 6.16; found C 18.83, H 2.82, N 6.18.

Table 3: Melting points and CHN-results for some alkali metal salts of [Hbet][Tf₂N].

20

BASE	m.p. (°C)	Elemental analysis		
		% C	% H	% N
lithium hydroxide	127	20.69 (20.79)	3.07(2.74)	(6.93) 6.76
sodium hydroxide	109	19.82 (20.00)	2.97 (2.63)	6.43 (6.66)
potassium hydroxide	152	18.84 (19.26)	2.82 (2.54)	6.18 (6.42)

EXAMPLE 7: SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES IN A [Hbet][Tf₂N] – WATER MIXTURE

25

The following oxides were found to be soluble in the ionic liquid [Hbet][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO, ZnO, CdO, HgO, CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be soluble in the ionic liquid [Hbet][Tf₂N]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂,

- 5 Cu(OH)₂, Ni(OH)₂, Fe(OH)₂, Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂ LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂.

Yttrium(III) complex

10 Y₂O₃ (1 g; 4.42 mmol) was mixed with [Hbet][Tf₂N] (10.583 g; 26.5 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Y₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 2831.90 g mol⁻¹) C 22.05, H 3.27, N 6.92; found C 21.67, H 3.03, N 6.51.

15 ***Lanthanum(III) complex***

La₂O₃ (1 g; 3.06 mmol) was mixed with [Hbet][Tf₂N] (7.334 g; 18.4 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

20 Elemental analysis: calcd(%) for La₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₄ (M_w = 2967.93 g mol⁻¹) C 21.04, H 3.24, N 6.60; found C 20.58, H 3.24, N 6.19.

Praseodymium(III) complex

Pr₆O₁₁ (1 g; 0.97 mmol) was mixed with [Hbet][Tf₂N] (7.018 g; 17.6 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

25 Elemental analysis: calcd(%) for Pr₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₄ (2971.94 g mol⁻¹) C 21.02, H 3.26, N 6.53; found C 20.61, H 4.08, N 6.16.

Neodymium(III) complex

30 Nd₂O₃ (1 g; 2.97 mmol) was mixed with [Hbet][Tf₂N] (7.102 g; 17.8 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The purple crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Nd₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₄ (M_w = 2978.60 g mol⁻¹) C 20.96, H 3.24, N 6.58; found C 20.60, H 3.22, N 6.20.

35

5 *Samarium(III) complex*

Sm₂O₃ (1 g; 2.86 mmol) was mixed with [Hbet][Tf₂N] (6.852 g; 17.20 mmol) and 10 mL water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times. Elemental analysis: calcd(%) for Sm₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 2954.81 g mol⁻¹) C 21.13, H 3.13, N 6.60; found C 21.10, H 3.10, N 6.05.

Europium(III) complex

Eu₂O₃ (1 g; 2.84 mmol) was mixed with [Hbet][Tf₂N] (6.789 g ; 17.04 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times. Elemental analysis: calcd(%) for Eu₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 2958.01 g mol⁻¹) C 21.11, H 3.13, N 6.62; found C 20.25, H 3.08, N 6.32.

Gadolinium(III) complex

Gd₂O₃ (1 g; 2.75 mmol) was mixed with [Hbet][Tf₂N] (6.592 g; 16.5 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times. Elemental analysis: calcd(%) for Gd₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 2968.00 g mol⁻¹) C 21.04, H 3.10, N 6.60; found C 20.31, H 3.03, N 6.21.

Terbium(III) complex

Tb₄O₇ (1 g; 1.33 mmol) was mixed with [Hbet][Tf₂N] (6.398 g; 16.05 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times. Elemental analysis: calcd(%) for Tb₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 2971.94 g mol⁻¹) C 21.01, H 3.12, N 6.60; found C 20.70, H 3.17, N 6.18.

5

Dysprosium(III) complex

Dy₂O₃ (1 g; 2.68 mmol) was mixed with [Hbet][Tf₂N] (6.402 g; 16.08 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

- 10 Elemental analysis: calcd(%) for Dy₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 2979.09 g mol⁻¹) C 20.93, H 3.11, N 6.57; found C 20.74, H 3.69, N 6.20.

Holmium(III) complex

Ho₂O₃ (1 g; 2.64 mmol) was mixed with [Hbet][Tf₂N] (6.319 g; 15.8 mmol) and 10 mL of water.

- 15 The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The purple crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Ho₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 2983.95 g mol⁻¹) C 20.92, H 3.11, N 6.57; found C 20.30, H 3.47, N 6.33.

- 20 ***Erbium(III) complex***

Er₂O₃ (1 g; 2.61 mmol) was mixed with [Hbet][Tf₂N] (6.247 g; 15.6 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

- Elemental analysis: calcd(%) for Er₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 2988.61 g mol⁻¹) C 20.90, H 3.10, N 6.56; found C 20.67, H 3.01, N 6.16.
- 25

Thulium(III) complex

Tm₂O₃ (1 g; 2.59 mmol) was mixed with [Hbet][Tf₂N] (6.193 g; 15.5 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

- 30 Elemental analysis: calcd(%) for Tm₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 2991.96 g mol⁻¹) C 20.86, H 3.10, N 6.55; found C 20.54, H 3.26, N 6.13.

5

Ytterbium(III) complex

Yb₂O₃ (1 g; 2.53 mmol) was mixed with [Hbet][Tf₂N] (6.064 g; 15.2 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

- 10 Elemental analysis: calcd(%) for Yb₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 3000.17 g mol⁻¹) C 20.81, H 3.09, N 6.53; found C 20.60, H 3.22, N 6.20.

Lutetium(III) complex

Lu₂O₃ (1 g; 2.51 mmol) was mixed with [Hbet][Tf₂N] (6.005 g; 15.7 mmol) and 10 mL of water.

- 15 The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Lu₂((CH₃)₃NCH₂CO₂)₈(N(SO₂CF₃)₂)₆(H₂O)₂ (M_w = 3004.02 g mol⁻¹) C 20.78, H 3.08, N 6.53; found C 20.61, H 4.08, N 6.16.

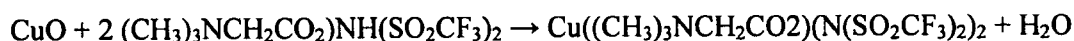
Copper(II) complex

CuO (1 g; 12.57 mmol) was mixed with [Hbet][Tf₂N] (10.014 g; 25.1 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The green crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Cu((CH₃)₃CO₂)N(SO₂CF₃)₂ (M_w = 858.14 g mol⁻¹).

- 25 C 19.59, H 2.58, N 6.52; found C 19.55, H 2.94, N 6.30.

Reaction:

***Zinc(II) complex***

- 30 ZnO (1 g; 12.3 mmol) was mixed with [Hbet][Tf₂N] (9.788g; 24.5 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Zn₄((CH₃)₃NCH₂CO₂)₁₀(N(SO₂CF₃)₂)₈(H₂O)₄ (M_w = 3746.27 g mol⁻¹) C 21.15 H 3.17, N 6.72; found C 20.47, H 3.48 N 6.42.

35

5 *Mercury(II) complex*

HgO (1 g; 4.6 mmol) was mixed with [Hbet][Tf₂N] (3.679g; 9.23 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Hg((CH₃)₃NCH₂CO₂)₂(N(SO₂CF₃)₂)₂ (M_w= 995.17 g mol⁻¹) C
10 16.89, H 2.23, N 5.62; found C 17.11, H 2.28, N 5.48.

Manganese(II) complex

MnO (1 g; 14.09 mmol) was mixed with [Hbet][Tf₂N] (11.2g; 28.1 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under
15 vacuum. The purple crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Mn((CH₃)₃NCH₂CO₂)₂(N(SO₂CF₃)₂)₂(H₂O) (M_w= 867.54 g mol⁻¹) C 19.38 H 2.78, N 6.45; found C 19.49, H 2.83, N 6.28.

Silver(I) complex

20 Ag₂O (1 g; 4.35 mmol) was mixed with [Hbet][Tf₂N] (1.733g; 4.35 mmol) and 10 mL of water. The mixture was stirred at room temperature and protected from light for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized 3 times from water.

Elemental analysis: calcd(%) for Ag₂((CH₃)₃NCH₂CO₂)₂(N(SO₂CF₃)₂)₂ (M_w= 505.16 g
25 mol⁻¹) C 16.64 H 2.19, N 5.54; found C 16.79, H 2.27, N 5.31.

Nickel(II) complex

NiO (1 g; 13.38 mmol) was mixed with [Hbet][Tf₂N] (10.66 g; 26.7 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under
30 vacuum. The green crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Ni₂((CH₃)₃NCH₂CO₂)₂(N(SO₂CF₃)₂)₂ (M_w = 1895.77 g mol⁻¹).
C 20.90, H 3.35, N 6.65; found C 20.93, H 3.23, N 6.46.

5 ***Palladium(II) complex***

PdO (1 g; 8.16 mmol) was mixed with [Hbet][Tf₂N] (6.508 g; 16.3 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The yellow crystals were recrystallized from water 3 times.

Elemental analysis: calcd(%) for Pd((CH₃)₃NCH₂CO₂)₃(N(SO₂CF₃)₂)₂(H₂O)₂ (M_w= 1054.19 g mol⁻¹) C 21.65, H 3.53, N 6.64; found C 21.31, H 3.02, N 6.80 %.

Lead complex

PbO (1 g; 8.16 mmol) was mixed with [Hbet][Tf₂N] (6.507g; 16.3 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The white crystals were recrystallized from water 3 times. Elemental analysis: calcd(%) for Pb₅((CH₃)₃NCH₂CO₂)₇(N(SO₂CF₃)₂)₈O(OH)(H₂O)₂ (M_w = 4166,24 g mol⁻¹). C 16.76, H 2.21, N 5.54; found C 15.33, H 2.81, N 4.72 %.

Mp.: 177 °C (peak) IR: 3437s, 1632m, 1493m, 1454m, 1397m, 1351m, 1193m, 1059w, 956w, 933m.

Table 4. Melting points of metal salts of [Hbet][Tf₂N]

Compound	Melting point (°C)
[Li(bet)][Tf ₂ N]	127
[Na(bet)][Tf ₂ N]·H ₂ O	109
[K(bet)][Tf ₂ N]·H ₂ O	152
[Cu ₃ (bet) ₈ (H ₂ O) ₄][Tf ₂ N] ₆	288
[Zn ₄ (bet) ₁₀][Tf ₂ N] ₈ (H ₂ O) ₄	117
[Ag ₂ (bet) ₂ (Tf ₂ N)][Tf ₂ N]	127
[Hg(bet) ₂][Tf ₂ N] ₂	111
[Y ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	109
[La ₂ (bet) ₈][Tf ₂ N] ₆ ·4H ₂ O	78
[Pr ₂ (bet) ₈][Tf ₂ N] ₆ ·4H ₂ O	86
[Nd ₂ (bet) ₈][Tf ₂ N] ₆ ·4H ₂ O	90
[Sm ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	88

[Eu ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	95
[Gd ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	94
[Tb ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	88
[Dy ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	88
[Ho ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	88
[Er ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	94
[Tm ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	97
[Yb ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	89
[Lu ₂ (bet) ₈][Tf ₂ N] ₆ ·2H ₂ O	88

5

The lanthanide-containing complexes described herein may be considered as ionic liquids, because the melting points of the compounds are below 100°C, in accordance with the definition of an ionic liquid. The melting points are specified in table 4. At room temperature these complexes can be described as highly viscous supercooled liquids.

10

These [Hbet][Tf₂N] complexes obtained by procedures described in this example 9 are easily soluble in the [Chol][Tf₂N] ionic liquid. As an example, 1.5 g (6.7 mol %) of Cu((CH₃)₃NCH₂CO₂)N(SO₂CF₃)₂)₂ (1.75 mmol) were stirred with 10 g of [Chol][Tf₂N] to give a transparent blue solution. Higher concentrations of the metal betaine complex in the [Chol][Tf₂N] ionic liquid can be achieved. Same concentrations can be dissolved of betaine complexes of e.g. Mn²⁺, Ni²⁺, Zn²⁺, Pd²⁺, Ag⁺, Cd²⁺, Hg²⁺, Pb²⁺, Y³⁺, La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Lu³⁺, UO₂²⁺.

15

EXAMPLE 8: SOLUBILITY OF METAL OXIDES AND SALTS IN PURE [Hbet][Tf₂N] AND EXTRACTION PROCEDURES

20

Metal oxides

Copper oxide is soluble in pure [Hbet][Tf₂N]. CuO (1g) was stirred with 10 g of [Hbet][Tf₂N] for 2 hours at 70°C. The copper oxide was found to dissolve completely and a blue transparent solution was obtained.

25

- 5 Also metal oxides of e.g. Mn^{2+} , Ni^{2+} , Zn^{2+} , Pd^{2+} , Ag^+ , Cd^{2+} , Hg^{2+} , Pb^{2+} , Y^{3+} , La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , Lu^{3+} , UO_2^{2+} can be dissolved in pure $[\text{Hbet}][\text{Tf}_2\text{N}]$.

Metal salts

- 10 Metal salts, like $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ are also soluble in $[\text{Hbet}][\text{Tf}_2\text{N}]$.
- a) Solubility of Cu^{2+} : An excess of copper chloride was added to $[\text{Hbet}][\text{Tf}_2\text{N}]$ (5g; 12.5 mmol). The mixture was stirred for 4 hours at 100 °C and the non-dissolved copper chloride was removed from the mixture. The metal content of the resulting solution was determined by titration with EDTA. 1.75 mol% CuCl_2 were found to dissolve in $[\text{Hbet}][\text{Tf}_2\text{N}]$.
- 15 b) Solubility of Eu^{3+} : An excess of europium chloride, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was added to $[\text{Hbet}][\text{Tf}_2\text{N}]$ (5g; 12.5 mmol). The mixture was stirred for 4 hours at 100 °C and the non-dissolved europium chloride was removed from the mixture. The metal content of the resulting solution was determined by titration with EDTA. 6 mol% $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were found to dissolve in $[\text{Hbet}][\text{Tf}_2\text{N}]$. The same can be performed for the metal chloride salts of e.g. Mn^{2+} , Ni^{2+} , Zn^{2+} , Pd^{2+} , Ag^+ , Cd^{2+} , Hg^{2+} , Pb^{2+} , Y^{3+} , La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , Lu^{3+} , UO_2^{2+} .
- 20

EXAMPLE 9: RECOVERY OF METALS AND IONIC LIQUIDS

- The dissolved metals can easily be recovered from the ionic liquid phase by an extraction with an aqueous acid solution. The metals are extracted into the aqueous phase while the ionic liquid phase is recovered and can be separated and reused.
- 25 As an example, CuO (1 g; 12.57 mmol) was mixed with $[\text{Hbet}][\text{Tf}_2\text{N}]$ (10 g; 25.1 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. The water was evaporated and the ionic liquid phase was extracted twice with a 37% HCl solution. The ratio of the metal content in the aqueous phase to the ionic liquid phase was determined by titration to be 82:1 after the first extraction. The metal was almost completely extracted to the aqueous phase after a second extraction with the acid. The same extraction can also be performed with HNO_3 or H_2SO_4 .
- 30 In another example, Nd_2O_3 (1 g; 2.97 mmol) was mixed with $[\text{Hbet}][\text{Tf}_2\text{N}]$ (7.102 g; 17.8 mmol) and 10 mL of water. The mixture was stirred under reflux for 12 hours. The water was evaporated and the ionic liquid phase was extracted twice with a 37% HCl solution. The neodymium ions
- 35

- 5 were almost completely extracted to the aqueous phase after a second extraction with the acid. The same extraction can also be performed with HNO₃.

EXAMPLE 10: DISSOLUTION AND DEPOSITION OF METALS

- 10 [Hbet][Tf₂N] (100 mL) was heated in a beaker at 70°C. An oxidized copper metal plate was immersed into the ionic liquid. After a few minutes the ionic liquid turned slightly blue and the copper plate was found to be bright and reflective all over its surface.

- Copper-containing [Hbet][Tf₂N] (100 mL) was heated in a beaker at 70 °C. A zinc or iron metal
15 plate was immersed into the ionic liquid. After a few minutes the copper metal was deposited on the surface of the zinc or iron plate, respectively.

- Silver-containing [Hbet][Tf₂N] (100 mL) was heated in a beaker at 70°C. A copper metal plate
20 was immersed into the ionic liquid. After a few minutes the silver metal was deposited on the surface of the copper plate.

EXAMPLE 11: SYNTHESIS OF N-CARBOXYMETHYL-METHYLPYRROLIDIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

- 25 To N-methylpyrrolidinium (0.5 mol, 42.5 g), ethyl chloroacetate (0.5 mol, 61.2 g) was slowly added on cooling in an ice bath. The mixture was stirred for 2 days. The crude product was washed with diethyl ether to remove unreacted starting materials. The solid compound was refluxed in 15% aqueous solution of hydrochloric acid for 7 hours. Water was evaporated under reduced pressure and the hydrochloride N-carboxymethyl-methylpyrrolidinium was recrystallized
30 from a mixture of acetonitrile and methanol. The recrystallized compound was redissolved in water and an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (0.5 mol, 143.5 g) was added. The ionic liquid separated from the water phase. The ionic liquid phase was washed several times with water until no chloride impurities could be detected with the silver nitrate test. The ionic liquid was then evaporated to dryness at 80 °C under vacuum on a rotary evaporator.

5 ^1H -NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 4.34 (s, 2H), 3.62 (d, 4H), 3.17 (s, N-CH₃), 2.09 (s, 4H). ^{13}C -NMR (100.62 MHz, $[\text{D}_6]\text{DMSO}$, TMS): δ = 167.11 (COOH), 126.22, 121.95, 117.69, 113.42 ($2 \times \text{CF}_3$), 65.02 (CH₂-N-CH₂), 62.15 (CH₂-COOH), 49.21 (N-CH₃), 21.49 (CH₂).

Elemental analysis calcd (%) for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_6\text{F}_6\text{S}_2$ ($M_w = 424.02 \text{ g mol}^{-1}$): C 25.47, H 3.33, N 6.60; found: C 26.07, H 4.30, N 6.44. IR (KBr pellet, cm^{-1}): 1747s, 1632w, 1478w, 1462m,

10 1422m, 1352m, 1062m.

Melting point (M.p.) = 49 °C.

The ionic liquid does not form one phase with water upon heating.

15 EXAMPLE 12: N-CARBOXYETHYL-METHYLPYRROLIDINIUM BIS(TRIFLUORO-METHYLSULFONYL)IMIDE

To N-methylpyrrolidine (0.5 mol, 42.5 g), bromopropionate ethyl ester (0.5 mol, 90.5 g) was slowly added on cooling in an ice bath. The mixture was stirred for 2 days. The crude product was washed with diethyl ether to remove unreacted starting materials. The solid compound was
20 refluxed in 15% aqueous solution of hydrochloric acid for 7 h. Water was evaporated under reduced pressure and the hydrochloride N-carboxyethyl-methylpyrrolidinium was recrystallized from a mixture of acetonitrile and methanol. The recrystallized compound was redissolved in water and an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (0.5 mol, 143.5 g) was added. The ionic liquid separated from the water phase. The ionic liquid phase was washed
25 several times with water until no chloride impurities could be detected with the silver nitrate test. The ionic liquid was then evaporated to dryness at 80 °C under vacuum on a rotary evaporator. Elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_6\text{F}_6\text{S}_2$ ($M_w = 438.36 \text{ g mol}^{-1}$): C 27.40, H 3.68, N 6.39; found: C 27.28, H 3.72, N 6.31.

M.p. = liquid at room temperature.

30 The ionic liquid does not form one phase with water upon heating.

5 EXAMPLE 13: N-CARBOXYMETHYL-METHYLMORPHOLINIUM BIS(TRI-
FLUOROMETHYLSULFONYL)IMIDE

To N-methyl morpholinium (0.5 mol, 50.05g), ethyl chloroacetate (0.5 mol, 61.2 g) was slowly added on cooling in an ice bath. The mixture was stirred for 2 days at room temperature. The
10 crude product was washed with diethyl ether to remove unreacted starting materials. The solid compound was refluxed in 15% aqueous solution of hydrochloric acid for 7 h. Water was evaporated under reduced pressure and the N-carboxymethyl-methylmorpholinium hydrochloride was recrystallized from a mixture of acetonitrile and methanol. The recrystallized compound was redissolved in water and an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (0.5
15 mol, 143.5 g) was added. The ionic liquid separated from the water phase. The ionic liquid phase was washed several times with water until no chloride impurities could be detected with the silver nitrate test. The ionic liquid was then evaporated to dryness at 80 °C under vacuum on a rotary evaporator. A water content of 320 ppm was determined by coulometric Karl Fischer titration.

¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ = 4.43 (s, 2H), 3.93 (s, 4H), 3.60 (m, 4 H), 3.33 (s,
20 3H). ¹³C-NMR (100.62 MHz, [D₆]DMSO, TMS): δ = 166.90 (COOH), 126.69, 122.43, 118.17, 113.92 (2 × CF₃), 62.00 (N-CH₂-COOH) 60.59 (4 C), 47.89 (N-CH₃).

Elemental analysis calcd (%) for C₉H₁₄N₂O₇F₆S₂ (M_w = 440.01 g mol⁻¹): C 24.55, H 3.20, N 6.36; found: C 24.71, H 4.07, N 6.13. IR (KBr-pellet, cm⁻¹): 1745s, 1628m, 1475w, 1426w, 1353m, 1058m.

25 M.p. = 55°C (onset).

A mixture of N-carboxymethyl-methylmorpholinium bis(trifluoromethylsulfonyl)imide and water (50/50 wt. %) forms one phase above 52 °C. Below 52 °C, phase separation takes place.

30 EXAMPLE 14: N-CARBOXYMETHYL-METHYLPYPERIDINIUM BIS(TRIFLUORO-
METHYLSULFONYL)IMIDE

To N-methyl piperidinium (0.5 mol, 49.55 g), ethyl chloroacetate (0.5 mol, 61.2 g) was slowly added on cooling. The mixture was stirred for 2 days. The crude product was washed with diethyl ether to remove unreacted starting materials. The solid compound was refluxed in 15% aqueous solution of hydrochloric acid for 7 h. Water was evaporated under reduced pressure and the
35 hydrochloride N-carboxymethyl-methylpiperidinium was recrystallized from a mixture of

5 acetonitrile and methanol. The recrystallized compound was redissolved in water and an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (0.5 mol, 143.5 g) was added. The ionic liquid separated from the water phase. The ionic liquid phase was washed several times with water until no chloride impurities could be detected with the silver nitrate test. The ionic liquid was then evaporated to dryness at 80 °C under vacuum on a rotary evaporator. The compound is
 10 a liquid at room temperature.

¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ = 4.27 (s, 2H), 3.53 (m, 4H), 3.02 (s, 3H), 1.79 (t, 4H), 1.53 (m, 2H). ¹³C-NMR (100.62 MHz, [D₆]DMSO, TMS): δ = 166.64 (COOH), 126.22, 121.95, 117.69, 113.42 (2 × CF₃), 61.25 (N-CH₂-COOH), 60.66 (2x CH₂), 20.94 (CH₂), 19.48 (2 x CH₂).

15 The ionic liquid does not form one phase with water upon heating.

EXAMPLE 15: P-CARBOXYMETHYL-TRIBUTYLPHOSPHONIUM BIS(TRI-FLUOROMETHYLSULFONYL)IMIDE

20 To tributyl phosphonium (0.5 mol, 101.1 g), ethyl chloroacetate (0.5 mol, 61.2 g) was slowly added on cooling in an ice bath under nitrogen atmosphere. The mixture was stirred for 2 days at room temperature. The crude product was washed with diethyl ether to remove unreacted starting materials. The solid compound was refluxed in 15% aqueous solution of hydrochloric acid for 7 h. Water was evaporated under reduced pressure and the hydrochloride P-carboxymethyl-
 25 tributylphosphonium was recrystallized from a mixture of acetonitrile and methanol. The recrystallized compound was redissolved in water and an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (0.5 mol, 143.5 g) was added. The ionic liquid separated from the water phase. The ionic liquid phase was washed several times with water until no chloride impurities could be detected with the silver nitrate test. The ionic liquid was then evaporated to
 30 dryness at 80 °C under vacuum on a rotary evaporator.

¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ = 3.62(d, 2H), 2.25 (m, 6H), 1.43 (m, 12 H), 0.90 (t, 9H). ¹³C-NMR (100.62 MHz, [D₆]DMSO, TMS): δ = 167.31 (COOH), 126.24 121.97, 117.70, 113.44 (2 × CF₃), 39.01 (CH₂-COOH) 26.82 (CH₂), 26.15 (CH₂), 23.75 (CH₂), 23.53 (CH₂), 23.32 (CH₂), 23.26 (CH₂) , 22.98 (CH₂), 18.23 (CH₂), 18.20 (CH₂), 13.51(3xCH₃)

5 Elemental analysis calcd (%) for $C_{16}H_{30}NO_6F_6S_2P$ ($M_w = 541.12 \text{ g mol}^{-1}$): C 35.48, H 5.58, N 2.58; found: C 36.91, H 5.57, N 2.28. IR (KBr-pellet, cm^{-1}): 2967m, 2939s, 2879m, 1712s, 1468w, 1348m, 1059m.

M.p. = 55 °C.

The phosphonium ionic liquid does not form one phase with water upon heating.

10

EXAMPLE 16: L-CARNITINE BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

A solution of L-carnitine (0.6 mol, 96.7g) in 100 mL of water was added under stirring to an aqueous solution of hydrogen bis(trifluoromethylsulfonyl)imide (0.5 mol, 142.1 g). The mixture
15 was stirred for one hour in an ice bath. The aqueous phase separated from the ionic liquid. After separation of the phases, the ionic liquid phase was dissolved in acetone, the excess of L - carnitine precipitates. The ionic liquid was evaporated to dryness at 80 °C in vacuum on a rotary evaporator.

$^1\text{H-NMR}$ (300 MHz, $[\text{D}_6]\text{DMSO}$, TMS): $\delta = 4.41$ (q, 1H), 3.35 (d, N- CH_2), 3.12 (s, 3 x CH_3),
20 2.41 (m, 2H). $^{13}\text{C-NMR}$ (100.62 MHz, $[\text{D}_6]\text{DMSO}$, TMS): $\delta = 171.56$ (COOH), 125.99, 121.75, 117.52, 113.28 (2 x CF_3), 69.50 (N- CH_2), 62.48 (C-OH), 53.46 (3 x CH_3) (40.42 ($\text{CH}_2\text{-COOH}$)).

Elemental analysis calcd (%) for $\text{C}_{25}\text{H}_{47}\text{N}_5\text{O}_{17}\text{F}_{12}\text{S}_4$ ($M_w = 1045.17 \text{ g mol}^{-1}$): C 28.67 H 4.62, N 6.69; found: C 28.66, H 4.57, N 6.43. IR (KBr-pellet, cm^{-1}): 1591s, 1481m, 1407m, 1349m, 1056m, 613s.

25 M.p. = 55 °C.

A mixture of l-carnitine bis(trifluoromethylsulfonyl)imide and water (50/50 wt. %) forms one phase above 8 °C. Below 8 °C, phase separation takes place.

30 EXAMPLE 17: N-CARBOXYMETHYLPYRIDINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

N-carboxymethylpyridinium (0.5 mol, 86.5) was dissolved in water (100 ml) and an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (0.5 mol, 143.5 g) was added. The ionic
35 liquid separated from the water phase. The ionic liquid phase was washed several times with

5 water until no chloride impurities could be detected with the silver nitrate test. The ionic liquid was then evaporated to dryness at 80 °C under vacuum on a rotary evaporator. A water content of 32 ppm was determined by coulometric Karl Fischer titration.

¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ = 9.02 (d, 2H), 8.65 (t, 1H), 8.19 (t, 2H), 5.52 (s, 2H).

Elemental analysis calcd (%) for C₉H₈N₂O₆F₆S₂ (M_w = 417.97 g mol⁻¹): C 25.84, H 1.93, N 6.70;
10 found: C 25.88, H 3.17, N 6.33. IR (KBr-pellet, cm⁻¹): 1747s, 1639m, 1493w, 1426w, 1353m, 1058m.

M.p. = 32 °C (onset temperature).

A mixture of N-carboxymethylpyridinium bis(trifluoromethylsulfonyl)imide and water (50/50 wt.%) forms one phase above 55 °C. Below 55 °C, phase separation takes place.

15

EXAMPLE 18: REDUCTION OF THE VISCOSITY OF THE TASK-SPECIFIC IONIC LIQUIDS

20 The task-specific ionic liquids with the COOH functional group are in general viscous liquids. To make these ionic liquids more easy to handle, they can be mixed (diluted) with other ionic liquids. For instance, the task-specific ionic liquid 1-carboxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was found to be miscible in all weight proportions with the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and these mixtures
25 have a lower viscosity than the task-specific ionic liquid itself.

1-Carboxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide had been described earlier by Bartsch, Richard A.; Dzyuba, Sergei V. Polarity variation of room temperature ionic liquids and its influence on a Diels-Alder reaction. ACS Symposium Series (2003), 856 (Ionic
30 Liquids as Green Solvents), 289-299.

This compound was prepared by us as follows:

Under an inert atmosphere of dry nitrogen a mixture of 1-methylimidazole (0.5 mol, 41.02 g) and ethyl chloroacetate (0.5 mol, 61.2 g) was stirred at RT for 1 h, during which time the reaction mixture turned to a solid. The solid was washed with diethyl ether (3 x 30 mL). The solid
35 compound was refluxed in 15% aqueous solution of hydrochloric acid for 7 h. Water was

- 5 evaporated under reduced pressure and the 1-carboxymethyl-3-methylimidazolium was recrystallized from a mixture of acetonitrile and methanol. The recrystallized compound was redissolved in water and an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (0.5 mol, 143.5 g) was added. The ionic liquid separated from the water phase. The ionic liquid phase was washed several times with water until no chloride impurities could be detected with the silver
- 10 nitrate test. The ionic liquid was then evaporated to dryness at 80 °C under vacuum on a rotary evaporator. A water content of 67 ppm was determined by coulometric Karl Fischer titration.
- ¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ = 9.05 (s, 1H), 7.67 (d, 2H), 5.11 (s, 2H), 3.90 (s, 3H).
¹³C-NMR (100.62 MHz, [D₆]DMSO, TMS): δ = 168.58 (COOH), 137.72 (NCN), 123.9 (C-C) 126.21, 121.95, 117.68, 113.42 (2 × CF₃), 49.97 (N-CH₂), 36.11 (N-CH₃).
- 15 Elemental analysis calcd (%) for C₈H₉N₃O₆F₆S₂ (M_w = 420.98 g mol⁻¹): C 22.81, H 2.15, N 9.97; found: C 22.22, H 2.12, N 9.17. IR (KBr-pellet, cm⁻¹): 1743s, 1579m, 1478w, 1425w, 1346m, 1056m.
- M.p. = liquid at room temperature.
- A mixture of 1-carboxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and water
- 20 (50/50 wt. %) forms one phase above 64 °C. Below 64 °C, phase separation takes place.

EXAMPLE 19: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN THE IONIC LIQUID N-CARBOXYMETHYL-METHYL-MORPHOLINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

- 25 N-carboxymethyl-methylmorpholinium bis(trifluoromethylsulfonyl)imide, [MHbetMor][Tf₂N] (5 g, 11.35 mmol) was mixed with an equimolar amount of the metal oxide or -hydroxide (or an excess of the metal oxide or -hydroxide) and 20 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The following oxides
- 30 were found to be soluble in the ionic liquid [MHbetMor][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO, ZnO, CdO, HgO, CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be soluble in the ionic liquid [MHbetMor][Tf₂N]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂, Fe(OH)₂, Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂,
- 35 Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂.

5

Characterization of the copper(II) complex: N-carboxymethyl-methylmorpholinium bis(trifluoromethylsulfonyl)imide, [MHbetMor][Tf₂N] (5 g, 11.35 mmol) was mixed with an equimolar amount of copper(II) oxide (11.35 mmol, 0.903 g) and 20 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum.

10 Elemental analysis: calcd(%) for Cu₂([MbetMor]₄[Tf₂N]₄) (C₉H₁₄CuF₆N₂O₁₀S₂) (Mw = 551.88 g mol⁻¹) C 19.58, H 2.55, N 5.07; found C 19.70, H 2.45, N 5.25.

EXAMPLE 20: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN

15 THE IONIC LIQUID N-CARBOXYMETHYL-METHYL-PYRROLIDINIUM
BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

N-carboxymethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [MHbetPyr][Tf₂N] (5 g, 11.78 mmol) was mixed with an equimolar amount of the metal oxide or -hydroxide (or an excess of the metal oxide or -hydroxide) and 20 mL of water. The mixture was stirred under
20 reflux for 12 hours. After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [MHbetPyr][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO, ZnO, CdO, HgO, CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be
25 soluble in the ionic liquid [MHbetPyr][Tf₂N]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂, Fe(OH)₂, Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂.

Characterization of the copper(II) complex: N-carboxymethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [MHbetPyr][Tf₂N] (5 g, 11.78 mmol) was mixed with an
30 equimolar amount of copper oxide (11.78 mmol, 0.936 g) and 20 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum.

Elemental analysis: calcd(%) for Cu₂([MbetPyr]₄[Tf₂N]₄) (C₃₆H₅₆Cu₂F₂₄N₈O₂₆S₈) (Mw = 1856.55 g mol⁻¹) C 23.29, H 3.04, N 6.03; found C 23.38, H 3.14, N 5.98.

5 EXAMPLE 21: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN
THE IONIC LIQUID N-CARBOXYETHYL-METHYL-PYRROLIDINIUM
BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

N-carboxyethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [MEHbetPyr][Tf₂N] (5
 10 g, 11.05 mmol) was mixed with an equimolar amount of the metal oxide or -hydroxide (or an
 excess of the metal oxide or -hydroxide) and 20 mL of water. The mixture was stirred under
 reflux for 12 hours. After filtration, water was evaporated under vacuum. The following oxides
 were found to be soluble in the ionic liquid [MEHbetPyr][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁,
 Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO,
 15 ZnO, CdO, HgO, CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be
 soluble in the ionic liquid [MEHbetPyr][Tf₂N]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂,
 Fe(OH)₂, Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂,
 Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂.

20 EXAMPLE 22: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN
THE IONIC LIQUID N-CARBOXYMETHYL-METHYL-PIPERIDINIUM
BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

N-carboxymethyl-methylpiperidinium bis(trifluoromethylsulfonyl)imide, [MHbetPip][Tf₂N] (5
 25 g, 11.40 mmol) was mixed with an equimolar amount of the metal oxide or -hydroxide (or an
 excess of the metal oxide or -hydroxide) and 20 mL of water. The mixture was stirred under
 reflux for 12 hours. After filtration, water was evaporated under vacuum. The following oxides
 were found to be soluble in the ionic liquid [MHbetPip][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁,
 Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO,
 30 ZnO, CdO, HgO, CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be
 soluble in the ionic liquid [MHbetPip][NTf₂]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂,
 Fe(OH)₂, Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂,
 Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂.

5 EXAMPLE 23: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN
THE IONIC LIQUID N-CARBOXYMETHYL-METHYL-IMIDAZOLIUM
BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

N-carboxymethyl-methylimidazolium bis(trifluoromethylsulfonyl)imide, [HbetMIM][Tf₂N] (5 g,
 10 11.86 mmol) was mixed with an equimolar amount of the metal oxide or -hydroxide (or an
 excess of the metal oxide or -hydroxide) and 20 mL of water. The mixture was stirred under
 reflux for 12 hours. After filtration, water was evaporated under vacuum. The following oxides
 were found to be soluble in the ionic liquid [HbetMIM][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁,
 Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO,
 15 ZnO, CdO, HgO, CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be
 soluble in the ionic liquid [HbetMIM][Tf₂N]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂,
 Fe(OH)₂, Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂,
 Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂.

20 EXAMPLE 24: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN
THE IONIC LIQUID P-CARBOXYMETHYL-TRIBUTYL-PHOSPHONIUM
BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

P-carboxymethyl-tributylphosphonium bis(trifluoromethylsulfonyl)imide, [HbetPhos][Tf₂N] (5 g,
 25 9.23 mmol) was mixed with an equimolar amount of the metal oxide or -hydroxide (or an excess
 of the metal oxide or -hydroxide) and 20 mL of water. The mixture was stirred under reflux for
 12 hours. After filtration, water was evaporated under vacuum. The following oxides were found
 to be soluble in the ionic liquid [HbetPhos][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃,
 Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO, ZnO, CdO, HgO,
 30 CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be soluble in the
 ionic liquid [HbetPhos][Tf₂N]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂, Fe(OH)₂,
 Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂,
 Sr(OH)₂ and Ba(OH)₂.

5 EXAMPLE 25: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN
 THE IONIC LIQUID N-CARBOXYMETHYL-PYRIDINIUM
 BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

N-carboxymethylpyridinium bis(trifluoromethylsulfonyl)imide, [HbetPy][Tf₂N] (5 g, 11.95
 10 mmol) was mixed with an equimolar amount of the metal oxide or -hydroxide (or an excess of
 the metal oxide or -hydroxide) and 20 mL of water. The mixture was stirred under reflux for 12
 hours. After filtration, water was evaporated under vacuum. The following oxides were found to
 be soluble in the ionic liquid [HbetPy][Tf₂N] : Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃,
 Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO, ZnO, CdO, HgO,
 15 CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be soluble in the
 ionic liquid [HbetPy][Tf₂N] : Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂, Fe(OH)₂,
 Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂,
 Sr(OH)₂ and Ba(OH)₂.

Characterization of the cadmium complex: N-carboxymethylpyridinium
 20 bis(trifluoromethylsulfonyl)imide, [HBETPy][Tf₂N] (5 g, 11.78 mmol) was mixed with an
 equimolar amount of cadmium oxide (11.78 mmol, 1.534 g) and 20 mL of water. The mixture
 was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum.

Elemental analysis: calcd(%) for Cd([MbetPy][Tf₂N]) (C₁₈H₁₄CdF₁₂N₄O₁₄S₄) (Mw = 979.02 mol⁻¹)
¹) C 22.08, H 1.44, N 5.72; found C 22.38, H 1.54, N 5.78.

25

EXAMPLE 26: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN
 THE IONIC LIQUID L-CARNITINE BIS(TRIFLUOROMETHYL-SULFONYL)IMIDE

L-carnitine bis(trifluoromethylsulfonyl)imide, [LCAR][Tf₂N] (5 g, 11.30 mmol) was mixed with
 30 an equimolar amount of the metal oxide or -hydroxide (or an excess of the metal oxide or -
 hydroxide) and 20 mL of water. The mixture was stirred under reflux for 12 hours. After
 filtration, water was evaporated under vacuum. The following oxides were found to be soluble in
 the ionic liquid [LCAR][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃,
 Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO, ZnO, CdO, HgO, CuO, Ag₂O,
 35 NiO, PdO, and MnO. The following hydroxides were found to be soluble in the ionic liquid

- 5 [LCAR][Tf₂N]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂, Fe(OH)₂, Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂.

10 EXAMPLE 27: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID N-CARBOXYMETHYL-METHYLPYPERIDINIUM BIS(TRIFLUOROMETHYL-SULFONYL)IMIDE UNDER HIGH PRESSURE

N-carboxymethyl-methylpyperidinium bis(trifluoromethylsulfonyl)imide, [MHbetPip][Tf₂N] (1 g, 2.28 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [MHbetPip][Tf₂N] under high pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

20 EXAMPLE 28: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID N-CARBOXYMETHYL-METHYLMORPHOLINIUM BIS(TRIFLUOROMETHYL-SULFONYL)IMIDE UNDER HIGH PRESSURE

N-carboxymethyl-methylmorpholinium bis(trifluoromethylsulfonyl)imide, [MHbetMor][Tf₂N] (1 g, 2.27 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [MHbetMor][Tf₂N] under high pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

30 EXAMPLE 29: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID N-CARBOXYMETHYL-METHYLPYRROLIDIINIUM BIS(TRIFLUOROMETHYL-SULFONYL)IMIDE UNDER HIGH PRESSURE

5 N-carboxymethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [MHbetPyr][Tf₂N] (1 g, 2.35 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [MHbetPyr][Tf₂N] under high
10 pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

EXAMPLE 30: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID N-CARBOXYETHYL-METHYLPYRROLIDINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE UNDER HIGH PRESSURE

15 N-carboxyethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [MEHbetPyr][Tf₂N] (1 g, 2.28 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [MEHbetPyr][Tf₂N] under high
20 pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

EXAMPLE 31: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID N-CARBOXYMETHYL-METHYLPYRROLIDINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE UNDER HIGH PRESSURE

25 N-carboxymethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [MHbetPip][Tf₂N] (1 g, 2.28 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [MHbetPip][Tf₂N] under high
30 pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

5 EXAMPLE 32: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID N-CARBOXYMETHYL-METHYLIMIDAZOLIUM BIS(TRIFLUOROMETHYL-SULFONYL)IMIDE UNDER HIGH PRESSURE

10 N-carboxymethyl-methylimidazolium bis(trifluoromethylsulfonyl)imide, [HbetMIM][Tf₂N] (1 g, 2.37 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [HbetMIM][Tf₂N] under high pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

15

EXAMPLE 33: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID P-CARBOXYMETHYL-TRIBUTYLPHOSPHONIUM BIS(TRIFLUOROMETHYL-SULFONYL)IMIDE UNDER HIGH PRESSURE

20 P-carboxymethyl-tributylphosphonium bis(trifluoromethylsulfonyl)imide, [HbetPhos][Tf₂N] (1 g, 1.84 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [HbetPhos][Tf₂N] under high
25 pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

EXAMPLE 34: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID N-CARBOXYMETHYL-PYRIDINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE
30 UNDER HIGH PRESSURE

N-carboxymethyl-pyridinium bis(trifluoromethylsulfonyl)imide, [HbetPy][NTf₂] (1 g, 2.39 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following
35

- 5 oxides were found to be soluble in the ionic liquid [HbetPy][Tf₂N] under high pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

EXAMPLE 35: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID L-CARNITINE BIS(TRIFLUOROMETHYLSULFONYL)IMIDE UNDER HIGH PRESSURE

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- L-carnitine bis(trifluoromethylsulfonyl)imide, [L-Car][Tf₂N] (1 g, 2.26 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were
15 found to be soluble in the ionic liquid [L-Car][Tf₂N] under high pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

EXAMPLE 36: SYNTHESIS OF N-DIMETHYL-N-BUTYL-BETAINIUM BIS (TRIFLUOROMETHYLSULFONYL)IMIDE

20

- 1-Bromobutane (0.1 mol, 13.7 g) reacted with the ethyl ester of glycine betaine (0.1 mol 13.1 g) for 7 hours at 50 °C. The product was washed with diethyl ether and refluxed for 7 hours in an aqueous HCl solution (15 %). The hydrobromide salt was recrystallized from methanol and dissolved in water and an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (0.1 mol,
25 28.7 g) was added. A hydrophobic phase separated from the water phase.

¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ = 3.57 (s, 2H), 3.28 (m, 2H), 3.05 (s, N-CH₃), 1.47 (m, 2H), 1.10 (m, 2H), 0.73 (t, 3H). ¹³C-NMR (100.62 MHz, [D₆]DMSO, TMS): δ = 166.73 (COOH), 126.22, 121.95, 117.69, 113.42 (2 × CF₃), 64.30 (CH₂-COOH), 61.26 (N-CH₂), 50.98 (2 × CH₃) 24.08 (CH₂), 19.42 (CH₂), 13.60 (CH₃).

- 30 Elemental analysis calcd (%) for C₁₀H₁₈N₂O₆F₆S₂ (M_w = 440.38 g mol⁻¹): C 27.27, H 4.12, N 6.36; found: C 27.32, H 4.07, N 6.45.

N-dimethyl-N-butyl-betainium bis(tri-fluoromethylsulfonyl)imide ([C4Hbet][Tf₂N]) was obtained as a viscous liquid, but the sample crystallized out at room temperature after a few weeks. The melting point of this solid was 58 °C (onset temperature).

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5 EXAMPLE 37: SYNTHESIS OF N-DIMETHYL-N-HEXYL-BETAINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

1-Bromohexane (0.1 mol, 16.5 g) reacted with the ethyl ester of glycine betaine (0.1 mol 13.1 g) for 7 h at 50 °C. The product was washed with diethyl ether and refluxed for 7 h in a 15 %
10 aqueous HCl solution. The hydrobromide salt was recrystallized from methanol and dissolved in water and an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (0.1 mol, 28.7 g) was added. A hydrophobic phase separated from the water phase.

¹H-NMR (300 MHz, [D₆]DMSO, TMS): δ = 4.16 (s, 2H), 3.43 (m, 2H), 3.16 (s, N-CH₃), 1.65 (m, 2H), 1.28 (m, 6H), 0.87 (t, 3H). ¹³C-NMR (100.62 MHz, [D₆]DMSO, TMS): δ = 166.72
15 (COOH), 126.22, 121.95, 117.69, 113.42 (2 × CF₃), 64.44 (N-CH₂-COOH), 61.33 (N-CH₂), 50.98 (2 × CH₃), 30.90 (CH₂), 25.66 (CH₂), 22.11 (CH₂), 22.01 (CH₂), 14.03 (CH₃).

Elemental analysis calcd (%) for C₁₂H₂₂N₂O₆F₆S₂ (M_w = 468.08 g mol⁻¹): C 30.77, H 4.73, N 5.98; found: C 30.84, H 4.85, N 6.02.

M.p.: below room temperature (highly viscous liquid).

20

EXAMPLE 38: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN THE IONIC LIQUID N-DIMETHYL-N-BUTYL-BETAINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

25 N-methyl-N-butyl-betainium bis(trifluoromethylsulfonyl)imide, [C₄Hbet][Tf₂N] (5 g, 11.35 mmol) was mixed with an equimolar amount of the metal oxide or -hydroxide (or an excess of the metal oxide or metal hydroxide) and 20 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [C₄Hbet][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃,
30 Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO, ZnO, CdO, HgO, CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be soluble in the ionic liquid [C₄Hbet][Tf₂N]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂, Fe(OH)₂, Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂.

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5 EXAMPLE 39: SOLUBILIZATION OF METAL OXIDES AND METAL HYDROXIDES IN THE IONIC LIQUID N-DIMETHYL-N-HEXYL-BETAINIUM BIS(TRIFLUOROMETHYL-SULFONYL)IMIDE

N-dimethyl-N-hexyl-betainium bis(trifluoromethylsulfonyl)imide, [C6Hbet][Tf₂N] (5 g, 11.35
 10 mmol) was mixed with an equimolar amount of the metal oxide or -hydroxide (or an excess of the metal oxide or -hydroxide) and 20 mL of water. The mixture was stirred under reflux for 12 hours. After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [C6Hbet][Tf₂N]: Sc₂O₃, Y₂O₃, La₂O₃, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₄O₇, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, UO₃, PbO, ZnO, CdO, HgO,
 15 CuO, Ag₂O, NiO, PdO, and MnO. The following hydroxides were found to be soluble in the ionic liquid [C6Hbet][Tf₂N]: Pb(OH)₂, Zn(OH)₂, Cd(OH)₂, Cu(OH)₂, Ni(OH)₂, Fe(OH)₂, Fe(OH)₃, Co(OH)₂, Cr(OH)₃, Mn(OH)₂, LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂.

20 EXAMPLE 40: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID N-DIMETHYL-N-BUTYL-BETAINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE UNDER HIGH PRESSURE

N-dimethyl-N-butyl-betainium bis(trifluoromethylsulfonyl)imide, [C4Hbet][Tf₂N] (1 g, 2.28
 25 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [C4Hbet][Tf₂N] under high pressure: Co₃O₄, CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

30 EXAMPLE 41: SOLUBILIZATION OF METAL OXIDES IN THE IONIC LIQUID N-DIMETHYL-N-BUTYL-BETAINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE UNDER HIGH PRESSURE

- 5 N-dimethyl-N-hexyl-betainium bis(trifluoromethylsulfonyl)imide, [C₆Hbet][Tf₂N] (1 g, 2.28 mmol) was mixed with an equimolar amount of metal oxide and 5 mL of water. The mixture was heated in an oven at 140°C for 24 hours in a PTFE-lined acid digestion bomb (No. 4744, 45 ml, Parr Instrument Company). After filtration, water was evaporated under vacuum. The following oxides were found to be soluble in the ionic liquid [C₆Hbet][Tf₂N] under high pressure: Co₃O₄,
 10 CoO, Co₂O₃, Cr₂O₃, FeO and Fe₂O₃.

EXAMPLE 42: INFLUENCE OF THE ALKYL CHAIN LENGTH ON THE PHYSICAL PROPERTIES OF BETAINIUM SALTS

- 15 Replacement of a methyl group in betainium bis(trifluoromethylsulfonyl)imide by a longer alkyl chain influences the polarity and thus the solubility of the resulting ionic liquids. This affects the solubility of the ionic liquids in water and in some organic solvents, and it also affects the hydropobicity of the ionic liquids. [Hbet][Tf₂N] is totally miscible with water at temperatures above 56 °C, but the butyl analogue [C₄Hbet][Tf₂N] and the hexyl analogue [C₆Hbet][Tf₂N] are
 20 at all temperatures insoluble in water. Whereas [Hbet][Tf₂N] and [C₄Hbet][Tf₂N] are insoluble in dichloromethane (DCM), [C₆Hbet][Tf₂N] is soluble in this solvent. [Hbet][Tf₂N] is insoluble in chloroform, [C₄Hbet][Tf₂N] is partially soluble and [C₆Hbet][Tf₂N] is soluble.
- It is preferred that R¹, R², and R³ are all C₁, C₂, or C₃ alkyl, in order to obtain ionic liquids with the following properties: miscible with water, in particular above 50°C, and insoluble in non-
 25 ionic organic solvents, more in particular dichloromethane or chloroform.
- More in particular, it is preferred that R⁴ is C₁ or C₂ alkyl-COOH, when R¹, R², and R³ are C₁, C₂, or C₃ alkyl. Moreover, the ionic liquids of this invention wherein R⁴ is C₁ or C₂ alkyl-COOH are easy to synthesize and cheap. The solubilization of metal oxides and metal hydroxides is increased when R⁴ is C₁ or C₂ alkyl-COOH compared to C₃ or more (>C₃) alkyl-COOH, more in
 30 particular the solubilization of metal oxides and metal hydroxides is the highest when R⁴ is -CH₂-COOH (C₁ alkyl-COOH). The positive charge on the quaternary nitrogen (or phosphor, arsenicum or antimony) atom has an inductive effect on the COOH-group. This effect is affected by the chain length in-between the COOH-group and the positively charged nitrogen (or phosphor, arsenicum or antimony) atom, respectively. The shorter the distance between these
 35 functional groups, the higher the acidity of the proton of the COOH-function. Therefore, one or

5 two CH₂ groups in-between, and preferably one CH₂ group in-between is favorable for the application of this invention: these ionic liquids exhibit a significantly higher solubilizing ability for metal oxides than ionic liquids with three or more CH₂-groups between the positively charged heteroatom and the COOH-function.

10 EXAMPLE 43: CARBOXYMETHYL-TRIBUTYLARSONIUM BIS(TRIFLUORO-METHYLSULFONYL)IMIDE

To tributylarsine (0.05 mol, 12.31 g), ethyl chloroacetate (0.05 mol, 6.12 g) is slowly added on cooling in an ice bath under nitrogen atmosphere. The mixture is stirred for 5 days at room
15 temperature. The crude product is washed with diethyl ether to remove unreacted starting materials. The solid compound is refluxed in 15% aqueous solution of hydrochloric acid for 7 h. Water is evaporated under reduced pressure and As-carboxymethyl-tributylarsonium hydrochloride is recrystallized from a mixture of acetonitrile and methanol. The recrystallized compound is redissolved in water and an aqueous solution of lithium
20 bis(trifluoromethylsulfonyl)imide (0.05 mol, 14.35 g) is added. The ionic liquid separates from the water phase. The ionic liquid phase is washed several times with water until no chloride impurities are detected with the silver nitrate test. The ionic liquid is then evaporated to dryness at 80 °C under vacuum on a rotary evaporator.

25 EXAMPLE 44: CARBOXYMETHYL-TRIOCTYLSTIBONIUM BIS(TRIFLUORO-METHYLSULFONYL)IMIDE

To trioctyl antimony (0.05 mol, 23.07 g), ethyl chloroacetate (0.05 mol, 6.12 g) is slowly added on cooling in an ice bath under nitrogen atmosphere. The mixture is stirred for 5 days at room
30 temperature. The crude product is washed with diethyl ether to remove unreacted starting materials. The solid compound is refluxed in 15% aqueous solution of hydrochloric acid for 7 h. Water is evaporated under reduced pressure and Sb-carboxymethyl-trioctylstibonium hydrochloride is recrystallized from a mixture of acetonitrile and methanol. The recrystallized compound is redissolved in water and an aqueous solution of lithium
35 bis(trifluoromethylsulfonyl)imide (0.05 mol, 14.35 g) is added. The ionic liquid separates from

5 the water phase. The ionic liquid phase is washed several times with water until no chloride impurities are detected with the silver nitrate test. The ionic liquid is then evaporated to dryness at 80 °C under vacuum on a rotary evaporator.

10 EXAMPLE 45: P-CARBOXYMETHYL-TRIHEXYLPHOSPHONIUM BIS(TRI-
FLUOROMETHYLSULFONYL)IMIDE

To trihexylphosphine (0.5 mol, 14.32 g), ethyl chloroacetate (0.05 mol, 6.12 g) is slowly added on cooling in an ice bath under nitrogen atmosphere. The mixture is stirred for 5 days at room temperature. The crude product is washed with diethyl ether to remove unreacted starting
15 materials. The solid compound is refluxed in 15% aqueous solution of hydrochloric acid for 7 h. Water is evaporated under reduced pressure and P-carboxymethyl-trihexylphosphonium hydrochloride is recrystallized from a mixture of acetonitrile and methanol. The recrystallized compound is redissolved in water and an aqueous solution of lithium
20 bis(trifluoromethylsulfonyl)imide (0.05 mol, 14.35 g) is added. The ionic liquid separates from the water phase. The ionic liquid phase is washed several times with water until no chloride impurities are detected with the silver nitrate test. The ionic liquid is then evaporated to dryness at 80 °C under vacuum on a rotary evaporator.

25 EXAMPLE 46: P-CARBOXYMETHYL-TRIOCTYLPHOSPHONIUM BIS(TRI-
FLUOROMETHYLSULFONYL)IMIDE

To trioctylphosphine (0.05 mol, 18.53 g), ethyl chloroacetate (0.05 mol, 6.12 g) is slowly added on cooling in an ice bath under nitrogen atmosphere. The mixture is stirred for 5 days at room temperature. The crude product is washed with diethyl ether to remove unreacted starting
30 materials. The solid compound was refluxed in 15% aqueous solution of hydrochloric acid for 7 h. Water is evaporated under reduced pressure and P-carboxymethyl-trioctylphosphonium hydrochloride is recrystallized from a mixture of acetonitrile and methanol. The recrystallized compound is redissolved in water and an aqueous solution of lithium
35 bis(trifluoromethylsulfonyl)imide (0.05 mol, 14.35 g) is added. The ionic liquid separates from the water phase. The ionic liquid phase is washed several times with water until no chloride

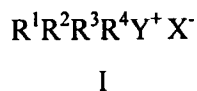
- 5 impurities are detected with the silver nitrate test. The ionic liquid is then evaporated to dryness at 80 °C under vacuum on a rotary evaporator.

EXAMPLE 47: DEHYDROCARNITINIUM BIS(TRIFLUOROMETHYLSULFONYL)-IMIDE

- 10 A solution of 3-carboxy-2-oxopropyl-trimethylammonium hydroxide inner salt (dehydrocarnitine) (0.05 mol, 7.96 g) in 100 mL of water is added under stirring to an aqueous solution of hydrogen bis(trifluoromethylsulfonyl)imide (0.05 mol, 14.21 g). The mixture is stirred for one hour in an ice bath. The aqueous phase separated from the ionic liquid. After separation of the phases, the ionic liquid phase is dissolved in acetone, the excess of dehydrocarnitine
15 precipitates. The ionic liquid is evaporated to dryness at 80 °C in vacuum on a rotary evaporator.
-

CLAIMS

1. An organic salt according to formula (I):



wherein

- Y is selected from N; P; As; or Sb;
 - each of R^1 , R^2 and R^3 are independently selected from C_{1-12} alkyl; or C_{3-12} cycloalkyl; or each of R^1 and R^2 , or R^1 and R^3 , or R^2 and R^3 can be taken together to form a substituted or unsubstituted cyclic structure;
 - R^4 is selected from a C_{1-12} alkyl-COOH; or C_{3-12} cycloalkyl-COOH; wherein alkyl is optionally substituted with at least one OH or comprises at least one carbonyl function;
 - X^- is selected from organic sulfonates; organic sulfates; organic carboxylates; organic sulfonylimides; or tetrafluoroborate.
2. The organic salt according to claim 1, wherein R^4 is selected from C_{3-12} cycloalkyl-COOH; $-\text{CH}_2\text{CH}_2\text{COOH}$; or $-\text{CH}_2\text{COOH}$ and $\text{Y} = \text{N}$.
3. The organic salt according to claim 1, wherein R^4 is $-\text{CH}_2\text{COOH}$ and $\text{Y} = \text{N}$.
4. The organic salt according to claim 1, wherein R^4 is selected from C_{3-12} cycloalkyl-COOH and $\text{Y} = \text{N}$.
5. The organic salt according to claim 1, wherein each of R^1 , R^2 and R^3 are independently selected from C_{1-12} alkyl and $\text{Y} = \text{P}$.
6. The organic salt according to claim 1, wherein each of R^1 , R^2 and R^3 are independently selected from C_{1-12} alkyl, R^4 is $-\text{CH}_2\text{COOH}$ and $\text{Y} = \text{P}$.

7. The organic salt according to claim 1, wherein Y is N, and R¹ and R², or R¹ and R³, or R² and R³ form a substituted or unsubstituted cyclic structure.
8. The organic salt according to claim 1, wherein Y is N, R¹ and R², or R¹ and R³, or R² and R³ form a substituted or unsubstituted cyclic structure, and R⁴ is -CH₂CH₂COOH or -CH₂COOH.
9. The organic salt according to claim 1, wherein Y is N and R⁴ is selected from a substituted C₁₋₁₂ alkyl-COOH wherein at least one OH group is present, or a C₁₋₁₂ alkyl-COOH which contains at least one carbonyl group.
10. The organic salt according to claims 1 to 9, wherein X⁻ is selected from perfluorinated organic sulfonate, perfluorinated organic sulfate, organic bis(perfluoroalkylsulfonyl)imide anions or perfluorinated organic carboxylates.
11. The organic salt according to claims 1 to 9, wherein X⁻ is a bis(perfluoro-C₁₋₁₂alkyl-sulfonyl)imide.
12. The organic salt according to claims 1 to 9, wherein X⁻ is bis(trifluoromethylsulfonyl)imide.
13. The organic salt according to claim 1, wherein the ionic liquid is selected from the group of betaine bis(trifluoromethylsulfonyl)imide, N-dimethyl-N-butyl-betainium bis(trifluoromethylsulfonyl)imide, N-dimethyl-N-hexyl-betainium bis(trifluoromethylsulfonyl)imide, carboxymethyl-tributylphosphonium bis(trifluoromethylsulfonyl)imide, N-carboxymethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, N-carboxyethyl-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, N-carboxymethyl-methylmorpholinium bis(trifluoromethylsulfonyl)imide, N-carboxymethyl-methylpiperidinium bis(trifluoromethylsulfonyl)imide, carnitine bis(trifluoromethylsulfonyl)imide, N-carboxymethyl-methylpyridinium bis(trifluoromethylsulfonyl)imide, carboxymethyl-

tributylarsonium bis(trifluoromethylsulfonyl)imide, carboxymethyl-trioctylstibonium
 bis(trifluoromethylsulfonyl)imide, P-carboxymethyl-trihexylphosphonium
 bis(trifluoromethylsulfonyl)imide, P-carboxymethyl-trioctylphosphonium
 bis(trifluoromethylsulfonyl)imide, and dehydrocarnitinium
 bis(trifluoromethylsulfonyl)imide.

14. A process for the preparation of the organic salts of claims 1 to 13, said process comprising the step of performing the metathesis reaction of $R^1R^2R^3R^4Y^+$ halogenide and salts of perfluorinated organic sulfonate, organic sulfate, bis(perfluoroalkylsulfonyl)imide or organic carboxylate anions in water.

15. A process for the preparation of the organic salts of claims 1 to 13, said process comprising the step of mixing of $R^1R^2R^3R^4Y^+$ hydroxide and perfluorinated organic sulfonic acid, organic sulfatic acid, organic carboxylic acids or organic hydrogen sulfonylimide in water.

16. The use of the organic salts according to claims 1 to 13 in chemical applications.

17. The use of organic salts according to claim 16, wherein said chemical applications are chemical applications involving metals such as metal oxides, metal hydroxides or metal salts.

18. The use of the organic salts according to claim 16 and 17, wherein said chemical applications are selected from the list of as a solvent, for example for the solubilization of organic or inorganic compounds, such as of metal oxides, metal hydroxides or metal salts; for extraction procedures, more in particular for the extraction of metal ions; for decontamination of soils contaminated by heavy metals especially with copper, nickel, zinc, cadmium, mercury or lead; for catalytic reactions wherein the organic salt serves as a solvent or as a catalyst; for electrodeposition of metal ions; as a medium for electropolishing or for the cleaning of metal surfaces; for deposition of metals onto conductive surfaces; for the processes of spent nuclear fuel elements; as electrolyte in

batteries, fuel cells, photovoltaic devices and electrochromic devices and for recycling of noble metals from used catalysts and electronic circuits.

19. Compositions comprising the organic salts according to claims 1 to 13 and further comprising another liquid, gas or organic or anorganic compound.

20. Compositions according to claim 19, wherein said composition further comprises metals.

21. Compositions according to claim 20, wherein said composition is selected from the list of $[\text{Li}(\text{bet})][\text{Tf}_2\text{N}]$, $[\text{Na}(\text{bet})][\text{Tf}_2\text{N}] \cdot \text{H}_2\text{O}$, $[\text{K}(\text{bet})][\text{Tf}_2\text{N}] \cdot \text{H}_2\text{O}$, $[\text{Cu}_3(\text{bet})_8(\text{H}_2\text{O})_4][\text{Tf}_2\text{N}]_6$, $[\text{Zn}_4(\text{bet})_{10}][\text{Tf}_2\text{N}]_8(\text{H}_2\text{O})_4$, $[\text{Ag}_2(\text{bet})_2(\text{Tf}_2\text{N})][\text{Tf}_2\text{N}]$, $[\text{Hg}(\text{bet})_2][\text{Tf}_2\text{N}]_2$, $[\text{Y}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$, $[\text{La}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 4\text{H}_2\text{O}$, $[\text{Pr}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 4\text{H}_2\text{O}$, $[\text{Nd}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 4\text{H}_2\text{O}$, $[\text{Sm}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$, $[\text{Eu}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$, $[\text{Gd}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$, $[\text{Tb}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$, $[\text{Dy}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$, $[\text{Ho}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$, $[\text{Er}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$, $[\text{Tm}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$, $[\text{Yb}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$ and $[\text{Lu}_2(\text{bet})_8][\text{Tf}_2\text{N}]_6 \cdot 2\text{H}_2\text{O}$.

22. Compositions according to claim 19, wherein said compositions are mixtures with other organic salts comprising perfluorinated organic sulfonate, perfluorinated organic sulfate, organic bis(perfluoroalkyl)sulfonylimide, organic carboxylate, or tetrafluoroborate anions.

23. A process for the preparation of compositions according to claim 19, comprising the step of mixing the organic salts with other liquids, with gases or solid compounds.

24. The use of compositions according to claims 19 to 22 in chemical applications.

25. The use of L-carnitine or D-carnitine as a cationic building block for obtaining chiral organic salts.

FIGURES

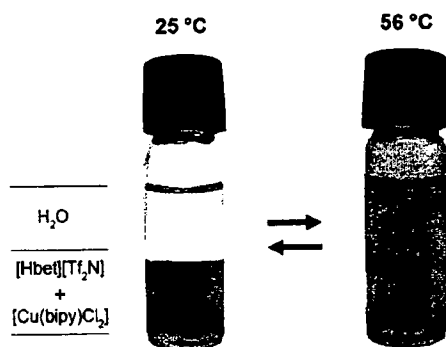


Figure 1

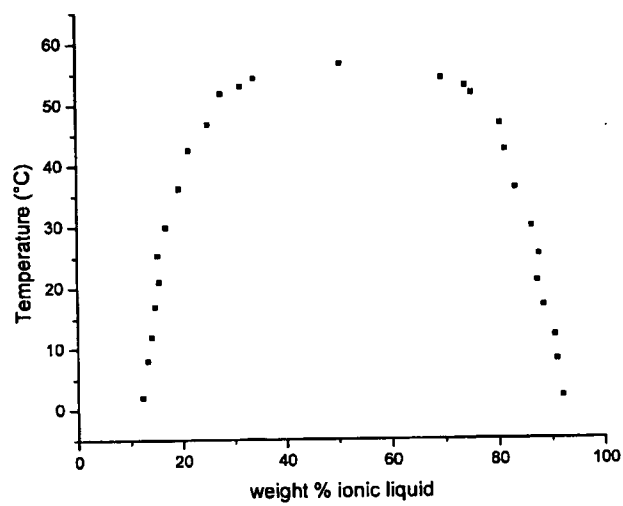


Figure 2

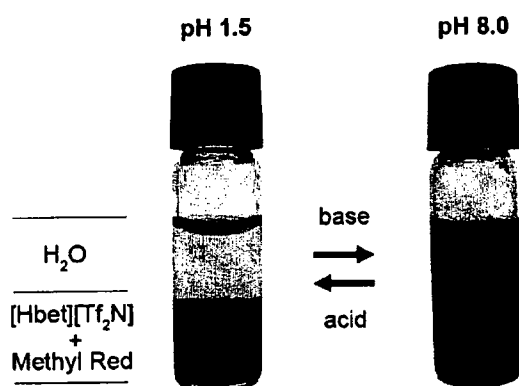


Figure 3

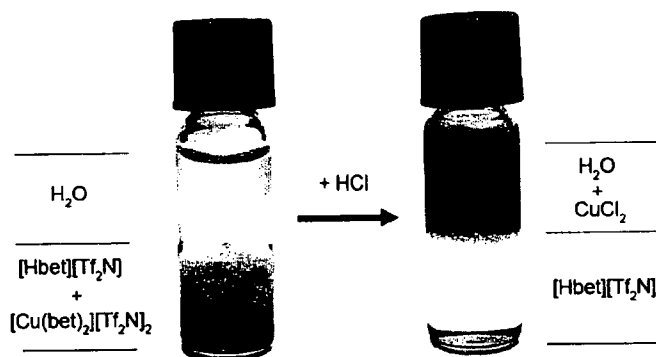


Figure 4

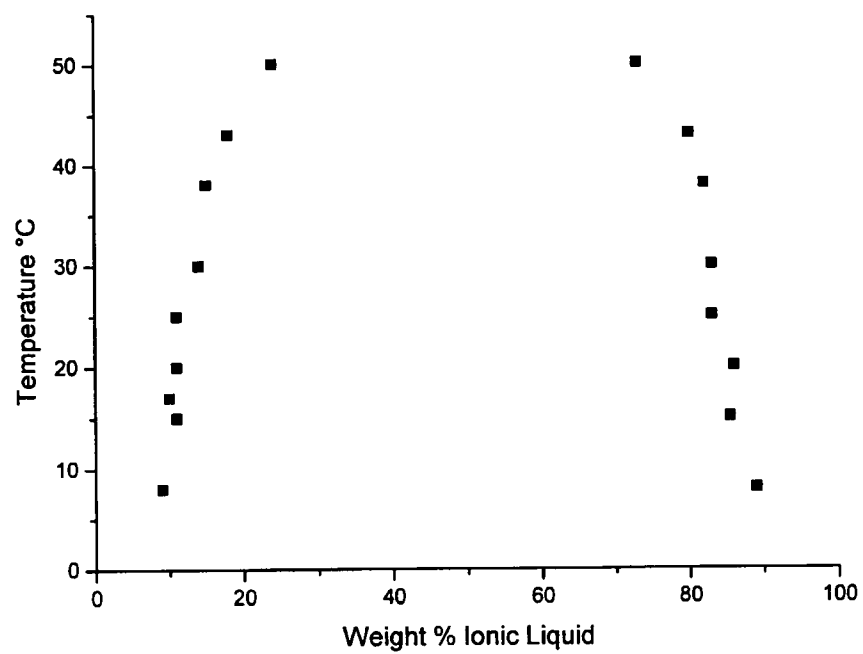


Figure 5.