

Ionic Liquids

Electrostatic and Non-covalent Interactions in Dicationic Imidazolium–Sulfonium Salts with Mixed Anions

Zhaofu Fei,^[a] Dun-Ru Zhu,^[b] Ning Yan,^[a] Rosario Scopelliti,^[a] Sergey A. Katsuba,^[c] Gabor Laurenczy,^[a] Danielle M. Chisholm,^[d] J. Scott McIndoe,^{*,[d]} Kenneth R. Seddon,^[e] and Paul J. Dyson^{*,[a]}

Abstract: A series of thioether-functionalised imidazolium salts have been prepared and characterized. Subsequent reaction of the thioether-functionalised imidazolium salts with iodomethane affords imidazolium–sulfonium salts composed of doubly charged cations and two different anions. Imidazolium–sulfonium salts containing a single anion type are obtained either by a solvent extraction method or by anion exchange. The imidazolium–sulfonium salts undergo a methyl-transfer reaction on exposure to water, giving rise

to a new, singly charged imidazolium salt with iodide introduced at the 2-position of the imidazolium ring. Crystal structures of some of the imidazolium–sulfonium salts were determined by X-ray crystallography providing the topology of the interactions between the dications and the anions. Electrospray ionization mass spectrometry and quantum-chemical calculations were used to rationalise the relative strength of these interactions.

Introduction

Interest in ionic liquids (ILs) has grown rapidly^[1,2] with the introduction of task-specific^[3] (now commonly referred to as functionalised)^[4] ionic liquids giving the field a further boost.^[5] Theoretical investigations combined with spectroscopic studies (such as electronic absorption, vibrational, and NMR) have provided a deeper understanding of the nature of ionic liquids.^[6,7] Diffraction techniques such as X-ray crystallography and neutron scattering have provided quantitative information on the distances between the cations and the anions in ionic liquids,^[8,9] and their dynamic motions, etc.^[10]

The vast majority of the studies on ionic liquids are based on singly charged systems, and although a number of multiply

charged systems have been reported, they have not been investigated systematically.^[11,12,13] Shreeve and co-workers^[14] reported unsymmetric dicationic salts incorporating imidazolium and triazolium functionalities connected by alkyl and fluoroalkyl chains, and used these salts as reaction media for C–C coupling reactions. The same group also reported some bipyridinium^[15] and dicationic imidazolium salts.^[16] It has also been found that dicationic imidazolium salts with polyethylene glycol linkers exhibit high thermal stability and good lubricity allowing them to be used as high-pressure lubricants.^[17] Armstrong and co-workers have prepared dicationic pyrrolidinium salts connected by hydrocarbon chains,^[18,19] also with thermal stabilities exceeding their monocationic counterparts. Interestingly, the high stability of dicationic ionic liquids has enabled them to be used as reaction media for reactions that require forcing conditions.^[20] Dicationic ionic liquids have also been evaluated as stationary phases for gas chromatography,^[21,22] for extraction purposes^[23] and as electrolytes.^[24]

Despite the recent growth in reports of dicationic systems, the emphasis has been on their applications, and little effort has been directed towards understanding the interactions between the dications and the anions, although quantum-chemical calculations on multi-charged models have been reported.^[25,26] Only a few imidazolium salts with thioether moieties have been reported, and to the best of our knowledge, none have been converted into imidazolium–sulfonium dicationic salts.^[27] Consequently, in this paper, we describe a fundamental study centred on the synthesis and characterisation of some dicationic imidazolium–sulfonium salts with mixed anions. By combining one dication with two different anions, it has been possible to assess the relative strength of the interactions of the dication and the individual anions.

[a] Dr. Z. Fei, Dr. N. Yan, Dr. R. Scopelliti, Prof. G. Laurenczy, Prof. P. J. Dyson
Institut des Sciences et Ingénierie Chimiques
Ecole Polytechnique Fédérale de Lausanne (EPFL)
1015 Lausanne (Switzerland)
E-mail: paul.dyson@epfl.ch

[b] Prof. D.-R. Zhu
State Key Laboratory of Materials-Oriented Chemical Engineering
College of Chemistry and Chemical Engineering
Nanjing Tech University, Nanjing 210009 (P. R. China)

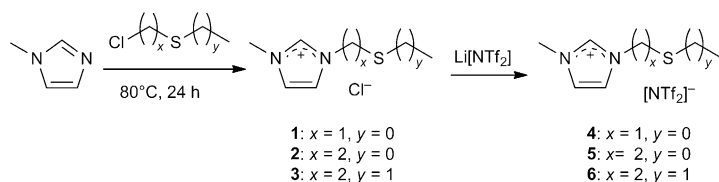
[c] Prof. S. A. Katsuba
A. E. Arbuzov Institute of Organic and Physical Chemistry of Kazan
Scientific Centre of the Russian Academy of Sciences
Arbuzov str. 8, 420088 Kazan (Russia)

[d] Dr. D. M. Chisholm, Prof. J. S. McIndoe
Department of Chemistry, University of Victoria
P.O. Box 3065, Victoria, BC, V8W 3V6 (Canada)
E-mail: mcindoe@uvic.ca

[e] Prof. K. R. Seddon
QUILL Centre, The Queen's University of Belfast
Stranmillis Road, Belfast BT9 5AG (UK)

Results and Discussion

Reaction of 1-methylimidazole with $\text{ClCH}_2\text{SCH}_3$ affords the imidazolium chloride $[\text{C}_1\text{SC}_1\text{mim}]\text{Cl}$, **1**, in high yield (Scheme 1). The product was obtained as a waxy solid, which was soluble in water and polar organic solvents. Similarly, reaction of $\text{ClCH}_2\text{CH}_2\text{SCH}_3$ and $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_3$ with 1-methylimidazole gave the corresponding compounds $[\text{C}_1\text{SC}_2\text{mim}]\text{Cl}$, **2**, and

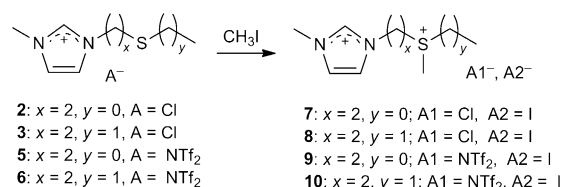


Scheme 1. Synthesis of imidazolium salts **1–6**.

$[\text{C}_2\text{SC}_2\text{mim}]\text{Cl}$, **3**, also as wax-like solids. Exchange of the chloride anion in **1–3** by $[\text{NTf}_2]^-$ ($\text{NTf}_2 = \text{bis}(\text{trifluoromethylsulfon-yl})\text{amide}$) by metathesis with $\text{Li}[\text{NTf}_2]$ afforded ionic liquids **4–6**, which are liquid at room temperature. Compared to their oxygen-containing analogues,^[28] the viscosities of the thioether ionic liquids **4–6** are slightly lower (Table 1), presumably owing

The ^1H NMR spectrum shows that methylation occurs at the sulfur centre. The IR spectra of **7–10** contain peaks in the range $2850\text{--}2910\text{ cm}^{-1}$ that are indicative of $\text{C–H}\cdots\text{halide}$ hydrogen bonds, with the absorptions of **9** and **10** (containing $[\text{NTf}_2]^-$ and I^- anions) being weaker than those of **7** and **8** (containing Cl^- and I^- anions).

The ESI mass spectra of **7**, **8**, **9** and **10** display peaks at m/z $[1/2(\text{dication})]^+$ and $[(\text{dication})(\text{anion})]^+$. The relative heights of the peaks are dependent on the anion and the nature of the solvent used for analysis. ESI-MS has been previously used to estimate the relative strength of cation/anion interactions in ionic liquids.^[30,31] In the ESI process, the analyte solution disperses into a fine spray of charged droplets, and the solvent evaporates from the droplets until a certain charge density is reached, the droplet then reduces further in size, either by fission or by ion evaporation



Scheme 2. Imidazolium-sulfonium salts **7–10** with mixed anions.

4		44		50
5		39		59
6		40		48

to the lower electronegativity of the sulfur atom compared with that of oxygen leading to weaker intra- and intermolecular hydrogen-bonding interactions.

The ^1H NMR (CD_3CN) spectra of **1–6** are as expected with the signal for the proton in the 2-position of the ring in the range $8.75\text{--}9.70\text{ ppm}$, with no significant difference observed compared with their ether analogues.^[28] The IR spectra of **1–3** display the expected aromatic C–H absorptions between 3000 and 3150 cm^{-1} and vibrations in the range $2850\text{--}2950\text{ cm}^{-1}$ attributable to $\text{C–H}\cdots\text{Cl}$ hydrogen-bonding interactions.^[29]

Reaction of **2**, **3**, **5** or **6** with an excess of iodomethane gave the dicationic imidazolium-sulfonium salts **7–10**, containing two different anions (Scheme 2). Under similar conditions, **1** and **4** did not react with iodomethane, presumably owing to the closer proximity of the sulfur atom to the electron-withdrawing imidazolium moiety, decreasing its nucleophilicity.^[4]

(the release of a solvated ion from the surface of the droplet). Ions that are most strongly solvated and/or ion-paired tend to occupy the interior of the droplet, whereas weakly solvated ions are located at the surface. The ions that are detected are those that are lost first in the process, rather than those that are paired up with counterions and removed as neutral species by the vacuum pump.^[32,33] The effect of hydrophobicity on the detection limit for different ionic liquids has been previously studied, with the more hydrophobic (surface-active) systems having the lowest detection limits and thus highest sensitivity.^[34] Consequently, in a solution of **10** (containing the I^- and $[\text{NTf}_2]^-$ anions) in ethanenitrile, the hydrophobic ions, $[(\text{dication})(\text{NTf}_2)]^+$, reside preferentially on the surface of the droplet whereas the iodide ions are strongly solvated and confined to the droplet interior. As such, when the charge density rises sufficiently that ion evaporation occurs, the species to be lost from the droplet are $[(\text{dication})(\text{NTf}_2)]^+$ ions (formed by a dication accompanied by a $[\text{NTf}_2]^-$ anion). For the same reasons, for the sample of **9** in ethanenitrile, the observed main peak is also the $[(\text{dication})(\text{NTf}_2)]^+$ ion.

The positive-ion ESI-MS of **10**, $[\text{C}_9\text{H}_{18}\text{N}_2\text{S}][\text{I}][\text{NTf}_2]$, in ethanenitrile shows the $[(\text{C}_9\text{H}_{18}\text{N}_2\text{S})]^+$ ion to have an intensity 95% that of the $[(\text{C}_9\text{H}_{18}\text{N}_2)(\text{NTf}_2)]^+$ ion (Figure 1). However, in propanone, the proportion drops to 50%, in methanol to 9% and in water to less than 1%.

This order is roughly consistent with the ability of the solvent to solvate the iodide ion. A strongly solvated iodide ion is likely to be present in the interior of the droplets, and hence be underrepresented in the spectrum. Because methanol and

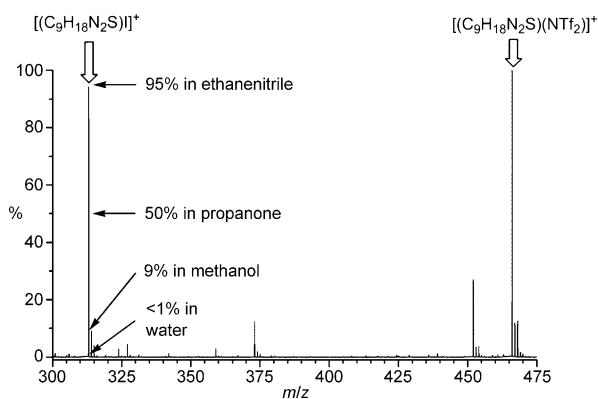


Figure 1. Positive-ion ESI-MS of **10** in ethanenitrile. The relative intensities of the $[(C_9H_{18}N_2S)]^+$ ion in various other solvents are indicated on the spectrum.

ethanenitrile have similar dielectric constants, but very different behaviour in this context, hydrogen bonding is clearly playing a significant role. Overall, the response factor of different dication/anion aggregate ions in these ESI-MS experiments reveals more about the solvation of the ionic liquid ions in a particular solvent than about the strength of the cation–anion ion pair in the neat ionic liquid.

To examine the cation–anion interactions in more detail, quantum-chemical calculations were carried out on the possible structures and interaction energies of the ion pairs involving the dication and individual anions, I^- , $[PF_6]^-$ and $[NTf_2]^-$. Initially, the conformational behaviour of the isolated ions was studied.

The conformation of the dication is determined by the torsion angles, τ_1 , τ_2 and τ_3 : $\tau_1 = C1-N1-C4-C5$ (for the numbering system, see Figure 2), and in a stable conformation it has

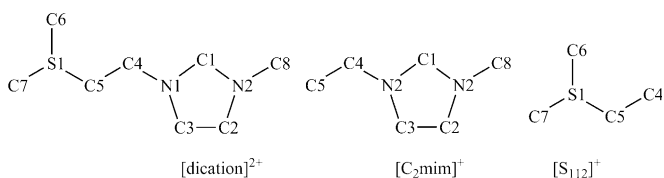


Figure 2. The numbering system of the $[dication]^{2+}$, $[C_2mim]^+$ and $[S_{112}]^+$.

a value of approximately $\pm 90^\circ$; $\tau_2 = N1-C4-C5-S1$, and can be approximately 180° in the *anti* conformation, approximately 60° in the *gauche* or approximately -60° in the (*–*)-*gauche* conformation; $\tau_3 = C4-C5-S1-C6$, and can have approximate values of -60° , 60° or 180° for the *anti*, the *gauche* and the (*–*)-*gauche* conformations, respectively, relative to the lone electron pair on the sulfur atom. According to literature data, $\tau_1 \approx 90^\circ$ corresponds to a global minimum of the potential energy surface (PES) of 1-alkyl-3-methylimidazolium cations, whereas $\tau_1 \approx 0^\circ$ corresponds to a local minimum.^[35] It was not possible to localize this latter minimum on the PES of the dication, and the energy difference between the minima with $\tau_1 \approx 90^\circ$ and $\tau_1 \approx -90^\circ$ did not exceed 0.4 kJ mol^{-1} , which suggests that these minima are almost equally populated. Thus,

only two torsion angles (τ_2 and τ_3) are essential for description of the conformational behaviour of the dication.

According to B3LYP/6–31G(d) computations, the lowest-energy conformer is *anti,gauche* (AG) with $\tau_2 \approx 170^\circ$ and $\tau_3 \approx 80^\circ$. The energy gaps between the AG form and the *gauche,gauche* (GG), the *anti,(–)gauche* (A,*–*G) and the *anti,anti* (AA) conformers are about 6.3, 7.1 and 10.5 kJ mol^{-1} , respectively. In crystals of **11**, **13**, **14** and **16** (see below), only the AG and the GG conformations of the dication are observed, a fact that suggests that the *gauche* conformation about the S–CH₂ bond is preferable, not only for the isolated species, but also in the bulk. According to these B3LYP/6–31G(d) computations, the *gauche* conformer of the model cation, ethyldimethylsulfonium, $[S_{112}]^+$ (Figure 2), is also more energetically stable than the *anti* form, although the energy gap of 2.5 kJ mol^{-1} is almost three times smaller than for the dication.

These computations and numerous literature data^[35] demonstrate that the *trans* conformation of the $[NTf_2]^-$ anion of C_2 symmetry with CF₃ groups on the opposite sides with respect to the S–N–S plane is energetically preferable relative to the *cis* conformer, in which the both CF₃ groups lie on the same side of the S–N–S plane. This conformation is also observed in crystals of **13** and **14**, although the *cis* conformation has also been reported for a few salts.^[36]

Based on the above computations of the isolated counterions, the interaction energies (E_{int}) of the dication and the anions were calculated. To avoid a basis-set superposition error (BSSE), E_{int} were counter-poise corrected by using a standard approach by Boys and Bernardi.^[37] The final expression for the $E_{int,cp}$ was as follows:

$$E_{int,cp} = E(AC,r_c)^{AC} - E(A,r_c)^{AC} - E(C,r_c)^{AC} + E_{def} \quad (1)$$

with

$$E_{def} = [E(A,r_c) - E(A,r_e)] + [E(C,r_c) - E(C,r_e)] \quad (2)$$

Here the deformation energy, E_{def} describes deformation of the anions, **A**, and cations, **C**, from their equilibrium structures to those assumed in the ion pair (r_e to r_c), and is calculated in the corresponding ion (**A** or **C**) basis set only whereas all other energy terms in Eq. (1) are calculated in the full basis set of the ion pair (AC).

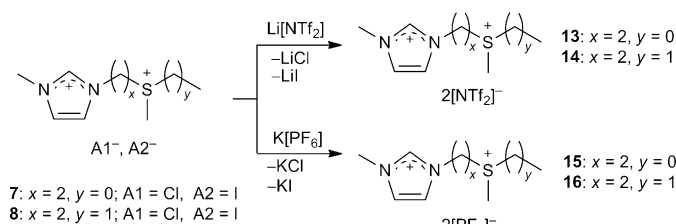
About twenty different types of ion pairing of singly charged imidazolium-based cations with I^- , $[PF_6]^-$ and $[NTf_2]^-$ anions have been revealed by X-ray crystallography^[38] and from quantum-chemical studies.^[28,39] This number should be much larger in the case of ion pairs of the dication with the same anion, and an attempt to localize computationally all minima on the potential energy surfaces of these systems would be extremely demanding. About thirty different ion pairs of the dication with I^- , $[PF_6]^-$ and $[NTf_2]^-$ anions were optimized by using either (a) the X-ray structures or (b) the optimized geometries of the individual ions in their lowest-energy conformation as a starting point. In all cases, the variant (b) resulted in the more energetically stable forms of the ion pairs with larger $E_{int,cp}$ [Eq. (1)] relative to the variant (a). Maximal values of the

Table 2. Interaction energies, $E_{\text{int,cp}}$ [kJ mol⁻¹] [Eq. (1)], computed for various ion pairs.

	[PF ₆] ⁻	[NTf ₂] ⁻	I ⁻
[dication] ²⁺	626.3	626.8	652.3
[C ₂ mim] ⁺	320.3	325.3	332.9
[S ₁₁₂] ⁺	296.8	315.7	348.3

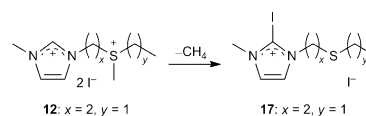
interaction energy, found for every type of the ion pairs as described above, are shown in Table 2 where they are compared with the corresponding values computed for the ion pairs of the same anions with the 1-ethyl-3-methylimidazolium ([C₂mim]⁺) and ethyldimethylsulfonium ([S₁₁₂]⁺) cations. The magnitude of the interaction energy follows the trend: I⁻ > [NTf₂]⁻ > [PF₆]⁻ irrespective of the type of cation and a similar trend for alkylimidazolium cations was found.^[39,40] The computational analysis indicates that the ion pairing in the dication-based systems is qualitatively similar to the case of monocation systems, in agreement with the ESI-MS experiments, with the solvation effects resulting in changes in the relative intensities in the ESI-MS spectra.

The single-anion-containing salts **11–14** can be isolated in pure anionic form by simply washing **9** and **10** with propanone. This process results in the precipitation of the iodide-containing salts **11** and **12**, leaving the [NTf₂]⁻ salts **13** and **14** in solution. Alternatively, water may be used in place of propanone to separate the salt mixtures, with **13** and **14** precipitating and **11** and **12** remaining in the aqueous phase. Salts **13** and **14** and the hexafluorophosphate-containing salts **15** and **16** may also be obtained from **7** and **8** by metathesis with two equivalents of Li[NTf₂] or K[PF₆], respectively (Scheme 3).



Scheme 3. Alternative routes to **13–16**.

Salts **11–16** are solids at room temperature; **13** and **14** have melting points of 85 °C and 75 °C, respectively, and can be considered as ionic liquids according to the commonly accepted definition (≤ 100 °C).^[41] Salts **11–16** are stable when stored under an inert atmosphere, but decompose over a prolonged time when exposed to air. In an attempt to crystallize **12**, the 2-iodoimidazolium derivative **17** was obtained in low yield as colourless crystals, presumably with the concomitant release of methane (Scheme 4). Similar decomposition reactions of sulfonium salts have been reported previously.^[42]



Scheme 4. Spontaneous reaction to form **17**.

Crystals of **11**, **13**, **14**, **16** and **17** suitable for X-ray analysis were obtained at room temperature by slow diffusion of diethyl ether into ethanenitrile solutions of the salts. With the exception of the diiodide salt, **11**, all structures show some disorder. In **13**, only one [NTf₂]⁻ anion is disordered, whereas there is significant disorder in **14** and **16** in the positions of both the sulfonium moiety and the anions. In **14**, two independent cations are present, both of which are disordered.

The structures of **11**, **13**, **14** and **16** are illustrated in Figure 3 and selected bond parameters are summarized in Table 3. The

Table 3. Selected bond lengths [Å] and angles [°] for **11**, **13**, **14** and **16**.

	11	13	14	16
C1–N1	1.327(7)	1.317(11)	1.324(6)	1.320(6)
C1–N2	1.348(7)	1.340(11)	1.376(5)	1.311(6)
N1–C4	1.487(7)	1.458(10)	1.490(5)	1.471(6)
C4–C5	1.535(8)	1.549(11)	1.443(7), 1.574(8)	1.528(7)
N2–C8 (for 11 , 13)	1.462(7)	1.473(13)		
N2–C9 (for 14 , 16)			1.471(6)	1.464(6)
S1–C5	1.809(6)	1.808(7)	1.792(5), 1.820(7)	1.857(5), 1.738(7)
S1–C6	1.801(5)	1.791(9)	1.794(6), 1.799(8)	1.785(6), 1.808(9)
S1–C7	1.794(5)	1.793(10)	1.823(7), 1.810(8)	1.840(9), 1.789(10)
C1–N1–C2	108.1(5)	106.8(8)	108.6(4)	108.1(4)
C5–S1–C6	101.6(3)	100.4(4)	100.5(3), 98.1(5)	101.8(3), 96.3(8)
C5–S1–C7	100.6(3)	102.3(4)	100.5(3), 103.6(5)	103.4(4), 100.0(8)
C6–S1–C7	102.6(3)	101.1(5)	103.6(3), 101.5(6)	113.9(5), 107.1(10)

bond angles and lengths around the imidazolium moiety in **11**, **13**, **14** and **16** are as expected.^[43] The presence of the sulfonium moiety relatively close to the imidazolium ring does not appear to exert any marked influence on the bond parameters within the imidazolium ring, whereas the bond lengths and angles around the sulfur atoms are slightly different to those of monocationic alkyl sulfonium centres.^[44] For example, the S–C bond lengths in **11** are 1.794(5), 1.801(5) and 1.809(6) Å, with the C–S–C angles of 100.6(3), 101.6(3) and 102.6(3)°, defining a distorted pyramidal geometry about the sulfonium centre.

Bond parameters within the imidazolium moieties in **13** and **14** are comparable with those observed in **11**. Notably, in the imidazolium ring of **13**, the N–C bonds N1–C4 (1.458(10) Å) and N2–C8 (1.473(13) Å) are almost the same length, whereas in the diiodide salt **11**, the N1–C4 (1.487(7) Å) bond length is longer than the N2–C8 (1.462(7) Å) one. In **13**, the C–S–C angles are 100.4(4), 101.1(5) and 102.3(4)°, and the S–C bond lengths are 1.791(9), 1.793(10) and 1.808(7) Å: these values are similar to those found in **11**. The extensive disorder in **14** and **16** precludes an analysis of their bond parameters.

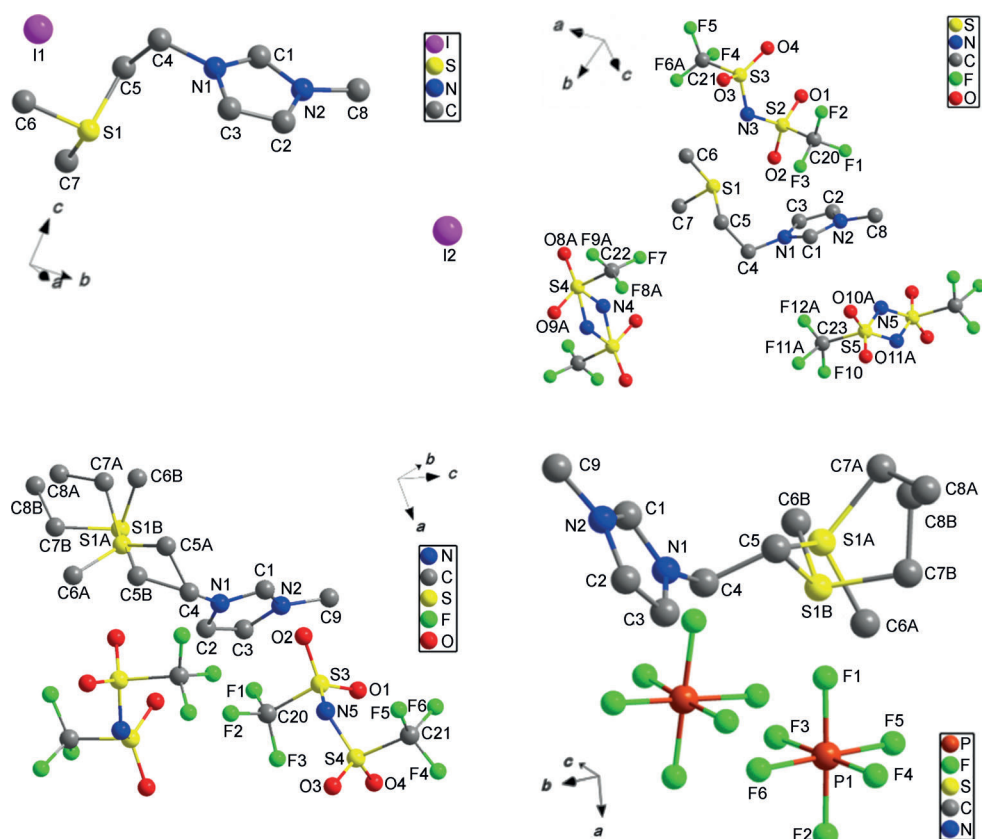


Figure 3. Structures of **11** (top left), **13** (top right), **14** (bottom left) and **16** (bottom right). Hydrogen atoms are omitted for clarity.

Although numerous structures of salts composed of transition-metal cations with the $[\text{NTf}_2]^-$ anion have been reported, only a few salts containing the imidazolium cation have been characterized crystallographically. In the handful of examples of imidazolium salts with $[\text{NTf}_2]^-$ anions, the C–S bonds in the anion usually adopt a *transoid* conformation^[45] and only a few examples with a *cisoid* conformation are known.^[36,38] Interestingly, all the *cisoid* conformations contain either transition metals or acidic hydrogen atoms able to adopt *O,O*-chelating interactions, through which the *cisoid* conformations are stabilized. The $[\text{NTf}_2]^-$ anions in **13** and **14** adopt a *transoid* conformation, an observation that is in agreement with the computational study (see above).

As expected, extensive hydrogen-bond interactions are found in **11**, **13**, **14** and **16** in the solid state (Figure 4 and Tables 4–7). The hydrogen atoms from the imidazolium ring

Table 4. Principle hydrogen bond parameters in 11 .				
D–H...A	<i>d</i> (D–H) [Å]	<i>d</i> (H...A) [Å]	<i>d</i> (D...A) [Å]	∠D–H...A [°]
C1–H1...I1 ^[a]	0.9500	2.9200	3.801(6)	155.00
C3–H3...I2 ^[b]	0.9500	3.0400	3.882(6)	149.00
C5–H5A...I1 ^[c]	0.9900	3.0400	3.964(6)	156.00
Symmetry codes: [a] 1/2– <i>x</i> , <i>y</i> , 1/2+ <i>z</i> ; [b] <i>x</i> , <i>y</i> –1, <i>z</i> ; [c] 1/2+ <i>x</i> , 1– <i>y</i> , <i>z</i> .				

interact with the anion and, in addition, the hydrogen atoms from the alkyl substituents surrounding the positively charged sulfur atom are also involved in hydrogen bonding.

In **13**, strong hydrogen bonds are observed that involve the oxygen atom in the anion and the C–H bonds in the imidazolium ring and the CH₂ moieties in the side chain with the C–H...O distances ranging from 2.27 to 2.60 Å (Table 5). However, owing to the disorder, a more exact examination of the distances is not possible. Both the O and F atoms in the anions in **14** are involved in hydrogen bonding (2.23 to 2.54 Å) with the dication (Table 6), whereas in **16** only the F atoms in the anion are involved in the hydrogen bonding with distances of 2.41 to 2.55 Å (Table 7). In some imidazolium salts, head-to-tail interactions are observed in which electronegative elements interact with the positively charged imidazolium ring. For example, in a nitrile

Table 5. Principle hydrogen bond parameters in 13 .				
D–H...A	<i>d</i> (D–H) [Å]	<i>d</i> (H...A) [Å]	<i>d</i> (D...A) [Å]	∠D–H...A [°]
C1–H1...O11A ^[a]	0.9500	2.5500	3.280(16)	133.00
C2–H2...N3 ^[b]	0.9500	2.6000	3.488(12)	156.00
C3–H3...O8A ^[c]	0.9500	2.3400	3.26(2)	162.00
C3–H3...O8B ^[c]	0.9500	2.5900	3.447(18)	150.00
C4–H4B...O3 ^[d]	0.9900	2.5700	3.405(11)	142.00
C5–H5A...O2 ^[e]	0.9900	2.5400	3.162(11)	121.00
C5–H5A...O11A ^[a]	0.9900	2.4900	3.172(14)	126.00
C5–H5B...O1 ^[c]	0.9900	2.5700	3.235(11)	124.00
C5–H5B...O4 ^[c]	0.9900	2.3800	3.313(10)	157.00
C6–H6A...O9B ^[f]	0.9800	2.2700	3.020(16)	133.00
C7–H7A...O1 ^[c]	0.9800	2.5000	3.120(11)	121.00
C7–H7C...O9A ^[g]	0.9800	2.5200	3.256(16)	132.00
C8–H8C...O11B ^[h]	0.9800	2.6000	3.378(16)	137.00
F12B...π (N1,N2)			3.158	

Symmetry codes: [a] 1–*x*, –*y*, 2–*z*; [b] –*x*, –*y*, 1–*z*; [c] 1–*x*, 1–*y*, 1–*z*; [d] –*x*, 1–*y*, 1–*z*; [e] 1–*x*, –*y*, 1–*z*; [f] 2–*x*, 1–*y*, 1–*z*; [g] *x*, *y*–1, *z*; [h] –*x*, –*y*, 2–*z*.

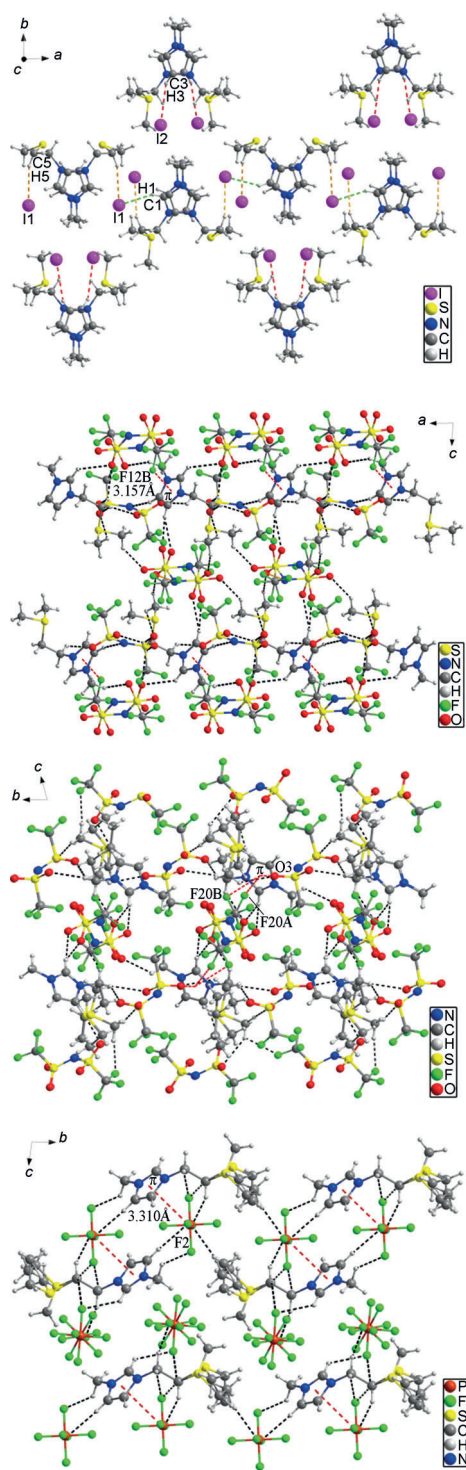


Figure 4. Hydrogen bonds in 11, 13, 14 and 16 (from the top).

served (S...I distances $> 4 \text{ \AA}$). In contrast, in salts 13, 14 and 16, interactions between the F atom from the anion with the imidazolium ring are observed with the F... π (N1,N2) distances ranging from 3.16 to 3.31 \AA (Figure 4).

The crystal structure of 17, containing two molecules in the asymmetric unit, is shown in Figure 4. Replacement of the hydrogen atom in the 2-position of the imidazolium ring by an iodine atom results in slight changes to the geometry of the

Table 6. Principle hydrogen bond parameters in 14.

D–H...A	$d(\text{D–H})$ [\AA]	$d(\text{H...A})$ [\AA]	$d(\text{D...A})$ [\AA]	$\angle \text{D–H...A}$ [$^\circ$]
C1–H1...O15A ^[a]	0.9500	2.2600	3.086(7)	144.00
C1–H1...O15B ^[a]	0.9500	2.2500	3.197(7)	173.00
C5 A–H5 A1...O3	0.9900	2.3800	3.083(6)	127.00
C2–H2...O7 ^[b]	0.9500	2.4400	3.313(6)	154.00
C6 A–H6 A2...F12	0.9800	2.5200	3.054(6)	114.00
C6 A–H6 A2...O8 ^[b]	0.9800	2.5400	3.319(8)	137.00
C4–H4 A...O15A ^[a]	0.9600	2.5100	3.333(7)	143.00
C4–H4B...O9	0.9600	2.3300	3.182(5)	148.00
C4–H4B...O11	0.9600	2.4500	3.172(5)	132.00
C6 A–H6 A3...O10 ^[c]	0.9800	2.4300	3.374(7)	161.00
C11–H11...O13A ^[d]	0.9500	2.2300	3.066(7)	146.00
C11–H11...O13B ^[d]	0.9500	2.2600	3.212(7)	176.00
C12–H12...O5	0.9500	2.4200	3.337(5)	161.00
C14–H14 A...O1 ^[e]	0.9600	2.4000	3.231(5)	145.00
C14–H14 A...O4 ^[e]	0.9600	2.4900	3.248(5)	136.00
C14–H14B...O13A ^[d]	0.9600	2.5200	3.341(7)	144.00
C15 A–H15B...O12	0.9900	2.4600	3.150(6)	127.00
C16 A–H16 A...O2 ^[f]	0.9800	2.4100	3.375(8)	167.00
C16 A–H16B...F7	0.9800	2.3900	3.315(8)	158.00
O3... π (N1,N2)			3.192	
F20 A... π (N1,N2)			3.296	
F20B... π (N1,N2)			3.305	

Symmetry codes: [a] 1– x , 1– y , 1– z ; [b] 1– x , 1– y , – z ; [c] x –1, y , z ; [d] 1– x , – y , 1– z ; [e] x , y –1, z ; [f] 1 + x , y –1, z .

Table 7. Principle hydrogen bond parameters in 16.

D–H...A	$d(\text{D–H})$ [\AA]	$d(\text{H...A})$ [\AA]	$d(\text{D...A})$ [\AA]	$\angle \text{D–H...A}$ [$^\circ$]
C1–H1...F10A ^[a]	0.9500	2.4900	3.208(7)	132.00
C2–H2...F2 ^[b]	0.9500	2.4100	3.325(6)	162.00
C4–H4 A...F7 A ^[a]	0.9900	2.5000	3.371(12)	146.00
C4–H4B...F3 ^[c]	0.9900	2.4500	3.324(6)	146.00
C5–H5 A...F1 ^[c]	0.9900	2.4300	3.322(7)	150.00
C5–H5B...F3	0.9900	2.5300	3.444(7)	154.00
C5–H5B...F10A ^[a]	0.9900	2.5400	3.260(8)	130.00
C8 A–H8 A2...F1 ^[d]	0.9800	2.5100	3.416(13)	153.00
C9–H9B...F4 ^[e]	0.9800	2.5500	3.299(6)	133.00
F2... π (N1,N2)			3.310	

Symmetry codes: [a] x , y , 1 + z ; [b] 1– x , 2– y , 1– z ; [c] 1 + x , y , z ; [d] – x , 1– y , 1– z ; [e] – x , 2– y , 1– z .

rings. In addition, the C–S–C bond angle in 17 is increased to 103.7° (cf. 101 – 102° in 11, 13, 14 and 16, see Table 3). The hydrogen-bonding interactions are significantly weakened compared to those in the crystal of 11, with the shortest C–H...I bond being 2.97 \AA (Table 8). The I...I distances between the iodine atom bonded to the imidazolium ring and the free iodide anion range from 3.36 to 3.37 \AA . These values are rather short, but still within the range found in structurally similar compounds.^[47,48] There are also interactions between the C–I bond and the imidazolium ring with the C–I... π distances lying between 3.75 and 3.91 \AA (Figure 5). No hydrogen bonds involving the S centre are observed, an observation that contrasts with ether-functionalised systems in which the oxygen atoms are involved in intermolecular interactions with the hy-

Table 8. Principle hydrogen bond parameters in 17.

D–H...A	<i>d</i> (D–H) [Å]	<i>d</i> (H...A) [Å]	<i>d</i> (D...A) [Å]	∠D–H...A [°]
C4–H4A...I2	0.9900	3.0300	3.504(9)	111.00
C9–H9A...I4 ^[a]	0.9800	2.9700	3.925(10)	164.00
C13–H13B...I3	0.9900	3.0500	3.574(9)	114.00
I1...π ^[b] (N1, N2)			3.875	
I1...π ^[c] (N3, N4)			3.911	
I4...π ^[c] (N1, N2)			3.751	
I1...I2 ^[d]			3.358	
I3...I4 ^[e]			3.373	

Symmetry codes: [a] *x*, 1 + *y*, *z*; [b] 3 – *x*, 1 – *y*, 1 – *z*; [c] 1.5 – *x*, *y* – 0.5, *z*; [d] 3.5 – *x*, *y* – 0.5, *z*; [e] 0.5 – *x*, 0.5 + *y*, *z*.

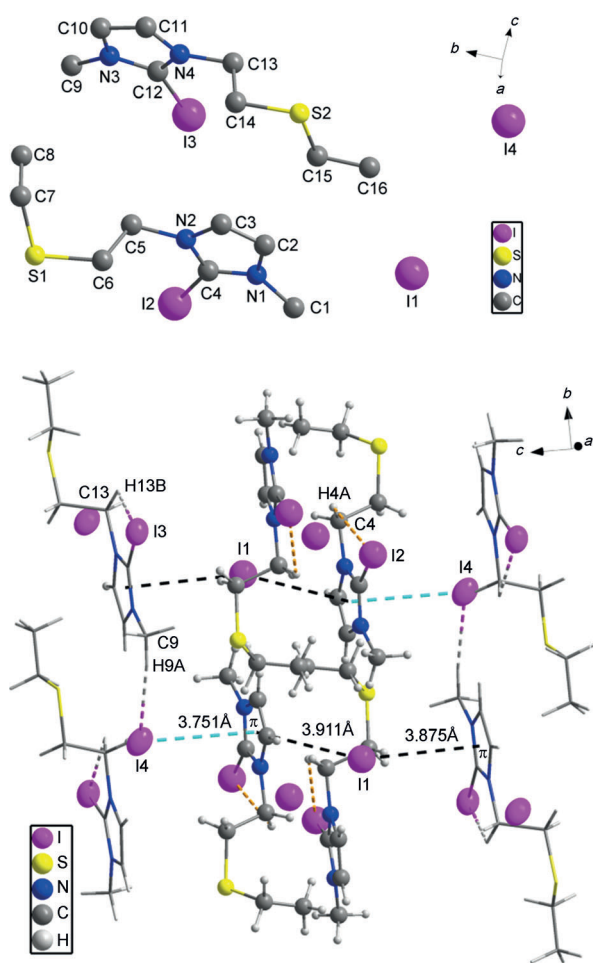


Figure 5. Molecular structure of 17 (top) and hydrogen-bonding patterns in 17 (bottom). Selected bond lengths [Å] and angles [°]: I2–C4, 2.093(8); I3–C12, 2.105(8); N1–C1–N2, 107.0(7); C6–S1–C7, 103.7(5).

drogen atoms from the imidazolium ring and the side-chains.^[28]

In conclusion, we have prepared a series of imidazolium–sulfonium salts that can be separated and purified in a simple manner according to the relative hydrophilicity/hydrophobicity of the anions and the strength of their interactions with the dications. Whereas other dicationic and multicationic salts are

room-temperature liquids,^[11–16] all the salts described herein are solid at room temperature although two may be classified as ionic liquids as they melt below 100 °C. However, as this definition is arbitrary,^[49] dating back to 1914 (before the term ionic liquids was introduced),^[50] we would consider all the materials described here to be ionic liquids, as there is no philosophical, empirical or theological reason to distinguish between the classification of a salt melting at 90 °C and one melting at 190 °C. The main reason for the elevated melting points of these salts appears to be the higher electrostatic interaction owing to the presence of the dication.^[51] ESI-MS of the salts showed the greatest affinity to the cation with anions that are less well solvated by the solvent used for analysis, rather than to the strongest ion pair. Consequently, the mass spectra are highly dependent on the solvent used for analysis. The crystal structures of some of the compounds reported represent the first structures of this class of salt. In most of the crystals, extensive disorder is observed, which is believed to be partially responsible for the low-melting nature of certain ionic liquids.^[52]

Experimental Section

General

All starting materials were obtained from commercial sources and used as received. The synthesis of the imidazolium salts was performed under an inert atmosphere of dry dinitrogen by using standard Schlenk techniques in solvents dried by using a solvent-purification system manufactured by Innovative Technology, Inc. IR spectra were recorded on a Perkin–Elmer FT-IR 2000 system. NMR spectra were measured on a Bruker DMX 400 spectrometer, using SiMe₄ as an external standard at 20 °C. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ™ Deca XP Plus quadrupole ion trap instrument for samples diluted in methanol by using a literature method.^[28] The ESI-MS experiments conducted in different solvents were performed on a Micromass QTOF *micro*. Elemental analysis was carried out at the EPFL. Viscosities were measured with a Brookfield DV-II+ viscometer using 0.5 mL of sample at 21 °C.

Synthesis of 1

Chloromethyl methyl sulfide (10.6 g, 0.11 mol) was added dropwise to a stirred solution of 1-methylimidazole (8.2 g, 0.1 mol) in diethyl ether (30 mL) at 0 °C. The reaction mixture was stirred at room temperature (20 °C) for a further 8 h, then the excess chloromethyl methyl sulfide and diethyl ether were removed under vacuum. The remaining waxy solid was washed with diethyl ether (3 × 5 mL) and dried under vacuum. Yield: 97%. ¹H NMR (400 Hz, CD₃CN): δ = 9.75 (s, 1 H), 7.69 (s, 1 H), 7.50 (s, 1 H), 5.50 (s, 2 H), 3.92 (s, 3 H), 2.00 ppm (s, 3 H); IR (neat) $\tilde{\nu}$ = 3115, 3091, 3065, 2981, 2954, 2900, 2850, 2845 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 143 [cation]⁺; elemental analysis calcd (%) for C₆H₁₁ClN₂S (178.69): C 40.33, H 6.20, N 15.68; found: C 40.89, H 6.28, N 15.52.

Synthesis of 2

Chloroethyl methyl sulfide (12.1 g, 0.11 mol) was added to 1-methylimidazole (8.2 g, 0.1 mol) at 0 °C in diethyl ether (30 mL) with stirring. The reaction mixture was stirred at room temperature for

a further 8 h. The excess of chloroethyl methyl sulfide and diethyl ether were removed under vacuum. Yield: 95%. ¹H NMR (400 Hz, CD₃CN): δ = 9.50 (s, 1H), 7.68 (s, 1H), 7.48 (s, 1H), 4.40 (t, 2H, *J* = 6.50 Hz), 3.90 (s, 3H), 3.02 (t, 2H, *J* = 6.50 Hz), 2.20 ppm (s, 3H); IR (neat): $\tilde{\nu}$ = 3120, 3070, 3051, 2978, 2900, 2850, 2840 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 157 [cation]⁺; elemental analysis calcd (%) for C₇H₁₃ClN₂S (192.71): C 43.63, H 6.80, N 14.54; found: C 43.71, H 6.86, N 14.52.

Synthesis of 3

2-Chloroethyl ethyl sulfide (13.1 g, 0.105 mol) was added to 1-methylimidazole (8.2 g, 0.1 mol, 10 mL) at 0 °C in diethyl ether (30 mL) with stirring. The reaction mixture was heated under reflux for 24 h, then the excess of 2-chloroethyl ethyl sulfide and diethyl ether were removed under vacuum. The remaining waxy solid was washed with diethyl ether (3 × 5 mL) and dried under vacuum. Yield: 97%. ¹H NMR (400 Hz, CD₃CN): δ = 9.70 (s, 1H), 7.70 (s, 1H), 7.60 (s, 1H), 4.44 (t, 2H, *J* = 6.40 Hz), 3.90 (s, 3H), 3.02 (t, 2H, *J* = 6.40 Hz), 2.62 (q, 2H, *J* = 7.00 Hz), 1.20 ppm (t, 3H, *J* = 7.00 Hz); IR (neat): $\tilde{\nu}$ = 3100, 3070, 3041, 2968, 2905, 2845, 2830 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 171 [cation]⁺; elemental analysis calcd (%) for C₈H₁₅ClN₂S (206.7395): C 46.48, H 7.31, N 13.55; found: C 46.51, H 7.34, N 13.52.

Synthesis of 4

A mixture of **1** (9.0 g, 0.05 mol) and Li[N(Tf)₂] (14.35 g, 0.05 mol) in water (20 mL) was stirred at room temperature for 2 h. The lower IL phase was separated, washed with water (2 × 5 mL) and dried under vacuum at 100 °C for 24 h to afford the product. Yield: 72%. ¹H NMR (400 Hz, CD₃CN): δ = 8.73 (s, 1H), 7.55 (s, 1H), 7.50 (s, 1H), 5.10 (s, 2H), 3.85 (s, 3H), 2.12 ppm (s, 3H); IR (neat): $\tilde{\nu}$ = 3110, 3091, 3055, 2980 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 143 [cation]⁺, negative ion 280 [Tf₂]⁻; elemental analysis calcd (%) for C₈H₁₁F₆N₃O₄S₃ (423.38): C 22.70, H 2.62, N 9.92; found: C 22.80, H 2.63, N 9.91.

Synthesis and characterisation of 5 and 6

Compounds **5** and **6** are prepared in a similar manner to that described for **4**.

5: Yield: 86%. ¹H NMR (400 Hz, CD₃CN): δ = 8.62 (s, 1H), 7.46 (s, 1H), 7.38 (s, 1H), 4.42 (t, 2H, *J* = 6.50 Hz), 3.88 (s, 3H), 2.96 (t, 2H, *J* = 6.50 Hz), 2.16 ppm (s, 3H); IR (neat): $\tilde{\nu}$ = 3111, 3070, 3030, 2970, 2901 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 157 [cation]⁺, negative ion 280 [Tf₂]⁻; elemental analysis calcd (%) for C₉H₁₃F₆N₃O₄S₃ (437.41): C 24.77, H 3.00, N 9.61; found: C 24.80, H 3.03, N 9.60.

6: Yield: 84%. ¹H NMR (400 Hz, CD₃CN): δ = 8.65 (s, 1H), 7.55 (s, 1H), 7.45 (s, 1H), 4.45 (t, 2H, *J* = 6.40 Hz), 3.88 (s, 3H), 3.05 (t, 2H, *J* = 6.40 Hz), 2.54 (q, 2H, *J* = 7.00 Hz), 1.20 ppm (t, 3H, *J* = 7.00 Hz); IR (neat): $\tilde{\nu}$ = 3120, 3070, 3040, 2948, 2905 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 171 [cation]⁺, negative ion 280 [Tf₂]⁻; elemental analysis calcd (%) for C₁₀H₁₅F₆N₃O₄S₃ (451.4352): C 26.61, H 3.35, N 9.31; found: C 26.80, H 3.38, N 9.29.

General procedure for the synthesis of 7–10

Iodomethane (14.1 g, 0.1 mol) was added to a solution containing **2**, **3**, **5** or **6** (1.92 g, 0.01 mol) in dichloromethane (20 mL) at 0 °C under stirring. The reaction mixture was heated under reflux for 24 h. After cooling to room temperature, diethyl ether (20 mL) was

added, forming a suspension. After filtration, the solid product was washed with diethyl ether (2 × 5 mL) and dried in vacuo.

7: Yield: 96%. ¹H NMR (400 Hz, CD₃CN): δ = 8.60 (s, 1H), 7.5 (s, 1H), 7.48 (s, 1H), 4.60 (t, 2H, *J* = 6.80 Hz), 3.90 (s, 3H), 3.60 (q, 2H, *J* = 6.80 Hz), 2.90 ppm (s, 6H); IR (neat cm⁻¹): $\tilde{\nu}$ = 3115, 3075, 3050, 2975, 2848 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 86 [1/2(dication)]⁺; elemental analysis calcd (%) for C₈H₁₆ClIN₂S (334.65): C 28.71, H 4.82, N 8.37; found: C 28.69, H 4.96, N 8.62.

8: Yield: 95%. ¹H NMR (400 Hz, CD₃CN): δ = 8.60 (s, 1H), 7.50 (s, 1H), 7.48 (s, 1H), 4.60 (t, 2H, *J* = 6.50 Hz), 3.90 (s, 3H), 3.60 (m, 2H), 3.45 (m, 2H), 2.90 (s, 3H), 1.50 ppm (t, 3H, *J* = 6.50 Hz); IR (neat): $\tilde{\nu}$ = 3120, 3070, 3051, 2970, 2838 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 93 [1/2(dication)]⁺; elemental analysis calcd (%) for C₉H₁₈ClIN₂S (348.67): C 31.00, H 5.20, N 8.03; found: C 31.09, H 5.26, N 8.02.

9: Yield: 98%. ¹H NMR (400 Hz, CD₃CN): δ = 8.60 (s, 1H), 7.50 (s, 1H), 7.48 (s, 1H), 4.60 (t, 2H, *J* = 6.80 Hz), 3.90 (s, 3H), 3.60 (q, 2H, *J* = 6.80 Hz), 2.90 ppm (s, 6H); IR (neat): $\tilde{\nu}$ = 3118, 3071, 3038, 2969 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 452 [(dication)(NTf₂)]⁺; elemental analysis calcd (%) for C₁₀H₁₆F₆IN₃O₄S₃ (579.34): C 20.73, H 2.78, N 7.25; found: C 20.69, H 2.76, N 7.32.

10: Yield: 96%. ¹H NMR (CD₃CN): δ = 8.50 (s, 1H), 7.51 (s, 1H), 7.49 (s, 1H), 4.60 (t, 2H, *J* = 6.50 Hz), 3.90 (s, 3H), 3.60 (m, 2H), 3.45 (m, 2H), 2.85 (s, 3H), 1.49 ppm (t, 3H, *J* = 6.50 Hz); IR (neat): $\tilde{\nu}$ = 3100, 3060, 3051, 2978 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 466 [(dication)(NTf₂)]⁺; elemental analysis calcd (%) for C₁₁H₁₈F₆IN₃O₄S₃ (593.37): C 22.27, H 3.06, N 7.08; found: C 22.69, H 3.16, N 7.12.

General procedure for the synthesis of 11 and 13

Compound **9** (5.80 g, 0.01 mol) was suspended in propanone (10 mL). It was filtered and the solid was washed with propanone (2 × 5 mL). The solid was then dried under vacuum for 24 h at 40 °C to give compound **11** as a white powder. The combined filtrates were evaporated and the resulting solid washed with water (2 × 5 mL) and dried under vacuum for 24 h at 40 °C to afford **13** as a white powder.

11: Yield: 59%. M.p.: 161 °C; ¹H NMR (400 Hz, CD₃CN): δ = 8.70 (s, 1H), 7.55 (s, 1H), 7.58 (s, 1H), 4.61 (t, 2H, *J* = 6.80 Hz), 3.90 (s, 3H), 3.60 (q, 2H, *J* = 6.80 Hz), 2.95 ppm (s, 6H); IR (neat): $\tilde{\nu}$ = 3105, 3065, 3050, 2978, 2880 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 86 [1/2(dication)]⁺; elemental analysis calcd (%) for C₈H₁₆I₂N₂S (426.09): C 22.55, H 3.78, N 6.57; found: C 22.69, H 3.86, N 6.62.

13: Yield: 61%. M.p.: 85 °C; ¹H NMR (400 Hz, CD₃CN): δ = 8.70 (s, 1H), 7.55 (s, 1H), 7.58 (s, 1H), 4.61 (t, 2H, *J* = 6.80 Hz), 3.90 (s, 3H), 3.60 (q, 2H, *J* = 6.80 Hz), 2.95 ppm (s, 6H); IR (neat): $\tilde{\nu}$ = 3115, 3065, 3050, 2978 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 452 [(dication)(NTf₂)]⁺; elemental analysis calcd (%) for C₁₂H₁₆F₁₂N₄O₈S₅ (732.59): C 19.67, H 2.20, N 7.65; found: C 19.73, H 2.26, N 7.62.

Synthesis and characterisation of 12 and 14

Compounds **12** and **14** were obtained from compound **10** by using the procedure described for **11** and **13**.

12: Yield: 54%. M.p.: 135 °C; ¹H NMR (400 Hz, CD₃CN): δ = 8.50 (s, 1H), 7.51 (s, 1H), 7.49 (s, 1H), 4.60 (t, 2H, *J* = 6.50 Hz), 3.90 (s, 3H), 3.60 (m, 2H), 3.45 (m, 2H), 2.85 ppm (s, 3H), 1.49 (t, 3H, *J* = 6.50 Hz); IR (neat): $\tilde{\nu}$ = 3120, 3070, 3051, 2978, 2850 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 93 [1/2(dication)]⁺; elemental analysis calcd (%) for C₉H₁₈I₂N₂S (440.12): C 24.56, H 4.12, N 6.36; found: C 24.69, H 4.16, N 6.42.

14: Yield: 59%. M.p.: 75 °C; ¹H NMR (400 Hz, CD₃CN): δ = 8.50 (s, 1H), 7.51 (s, 1H), 7.49 (s, 1H), 4.60 (t, 2H, *J* = 6.50 Hz), 3.90 (s, 3H), 3.60 (m, 2H), 3.45 (m, 2H), 2.85 (s, 3H), 1.49 ppm (t, 3H, *J* = 6.50 Hz); IR (neat): $\tilde{\nu}$ = 3100, 3050, 3000, 2970 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 466 [(dication)(NTf₂)⁺]; elemental analysis calcd (%) for C₁₃H₁₈F₁₂N₄O₈S₅ (746.6188): C 20.91, H 2.43, N 7.50; found: C 20.99, H 2.46, N 7.52.

General procedure for the synthesis of 15 and 16

Compound **7** (3.34 g, 0.01 mol) and K[PF₆] (3.68 g, 0.02 mol) were mixed in water (10 mL) and the resulting suspension was stirred at room temperature for 30 min. The suspension was filtered and the solid was washed with water (2 × 5 mL). The solid was then dried under vacuum for 24 h at 40 °C to give **15** as white powder. Compound **16** was obtained from reaction of compound **8** and K[PF₆] by using the same procedure.

Compounds **13** and **14** can also be prepared by using a similar procedure by reacting **7** and **8** with Li[NTf₂] in water.

15: Yield: 69%. M.p.: 123 °C; ¹H NMR (400 Hz, CD₃CN): δ = 8.70 (s, 1H), 7.55 (s, 1H), 7.58 (s, 1H), 4.61 (t, 2H, *J* = 6.80 Hz), 3.90 (s, 3H), 3.60 (q, 2H, *J* = 6.80 Hz), 2.95 ppm (s, 6H); IR (neat): $\tilde{\nu}$ = 3120, 3070, 3051, 2978 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 315 [(dication)(PF₆)⁺]; elemental analysis calcd (%) for C₈H₁₆F₁₂N₂P₂S (462.22): C 20.79, H 3.49, N 6.06; found: C 20.69, H 3.55, N 6.12.

16: Yield: 65%. M.p.: 115 °C; ¹H NMR (400 Hz, CD₃CN): δ = 8.50 (s, 1H), 7.51 (s, 1H), 7.49 (s, 1H), 4.60 (t, 2H, *J* = 6.50 Hz), 3.90 (s, 3H), 3.60 (m, 2H), 3.45 (m, 2H), 2.85 (s, 3H), 1.49 ppm (t, 3H, *J* = 6.50 Hz); IR (neat): $\tilde{\nu}$ = 3110, 3090, 3055, 2975 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 329 [(dication)(PF₆)⁺]; elemental analysis calcd (%) for C₉H₁₈F₁₂N₂P₂S (476.25): C 22.70, H 3.81, N 5.88; found: C 22.69, H 3.86, N 5.92.

Synthesis of 17

A solution of **12** (4.46 g, 0.01 mol) in water (10 mL) was maintained at room temperature in the air. After slow evaporation of the solvent over six days, colourless crystals formed. The solid crystals were washed with propanone and collected by filtration.

17: Yield: 15%. M.p.: 135 °C; ¹H NMR (400 Hz, CD₃CN): δ = 7.65 (s, 1H), 7.60 (s, 1H), 4.44 (t, 2H, *J* = 6.50 Hz), 3.90 (s, 3H), 3.02 (t, 2H, *J* = 6.50 Hz), 2.62 (q, 2H, *J* = 7.00 Hz), 1.20 ppm (t, 3H, *J* = 7.00 Hz); IR (neat): $\tilde{\nu}$ = 3100, 3070, 3041, 2968, 2905 cm⁻¹ (C–H); ESI-MS (CH₃CN): *m/z* (%): positive ion 296 [cation]⁺; elemental analysis calcd (%) for C₈H₁₄I₂N₂S (424.08): C 22.66, H 3.33, N 6.61; found: C 22.69, H 3.36, N 6.72.

Crystallography

Crystals suitable for X-ray diffraction studies of **11**, **13**, **14**, **16** and **17** were obtained by slow diffu-

sion of diethyl ether into ethanenitrile solutions at room temperature. Data collection for the X-ray structure determinations was performed on a KUMA CCD (**11**, **13**, **16** and **17**) and a Bruker Apex (**14**), using graphite-monochromated Mo_{Kα} (λ = 0.71070 Å) radiation and a low-temperature device [*T* = 140(2) K]. Data reduction was performed by CrysAlis RED (**11**, **13**, **16** and **17**)^[53] and EVALCCD (**14**).^[54] The structures of **11**, **13**, **14**, **16** and **17** were solved with SHELX97,^[55] refinement was performed by using the SHELX97 software package, and graphical representations of the structures were made with Diamond.^[56] All structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against *F*²), except for **11**, which was solved by using Patterson methods. An empirical absorption correction was applied to **11** and **13** (DELABS).^[57] All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. In **13** and **14**, there is disorder in the [NTf₂]⁻ anion and some fluorine, oxygen and nitrogen atoms were split over two positions and the DELU instructions applied to all oxygen atoms, and the SIMU instruction applied to all fluorine atoms. In **14** and **16**, there is disorder in the sulfonium moiety, which was split over two positions and the bond lengths were restrained using the DFIX instruction. Relevant details for the structure refinements of **11**, **13**, **14**, **16** and **17** are listed in Table 9.

CCDC-948992 (**11**), 948993 (**13**), 948994 (**14**), 948995 (**16**) and 948996 (**17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 9. Crystallographic data for **11**, **13**, **14**, **16** and **17**.

Compound	11	13	14	16	17
formula	C ₈ H ₁₆ I ₂ N ₂ S	C ₁₂ H ₁₆ F ₁₂ N ₄ O ₈ S ₅	C ₁₃ H ₁₈ F ₁₂ N ₄ O ₈ S ₅	C ₉ H ₁₈ F ₁₂ N ₂ P ₂ S	C ₈ H ₁₄ I ₂ N ₂ S
<i>M_r</i>	426.09	732.59	746.61	476.25	424.07
crystal system	orthorhombic	triclinic	triclinic	triclinic	orthorhombic
space group	<i>Pca</i> 2(1)	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> [Å]	15.2071(10)	7.9541(8)	8.6757(8)	6.5452(14)	10.5454(8)
<i>b</i> [Å]	9.8744(11)	8.7238(10)	17.528(2)	11.4307(19)	15.0752(15)
<i>c</i> [Å]	9.4091(6)	19.608(2)	19.271(2)	11.9928(18)	32.705(3)
α [°]	90	79.435(9)	75.061(10)	96.285(13)	90
β [°]	90	85.271(8)	77.637(9)	93.649(15)	90
γ [°]	90	85.182(9)	88.937(9)	93.281(15)	90
<i>V</i> [Å ³]	1412.9(2)	1329.7(2)	2763.6(5)	888.2(3)	5199.3(8)
<i>Z</i>	4	2	4	2	16
ρ_c [g cm ⁻³]	2.003	1.830	1.794	1.781	2.167
μ [mm ⁻¹]	4.57	0.57	0.55	0.48	4.96
<i>F</i> (000)	800	736	1504	480	3168
crystal size [mm ³]	0.30 × 0.20 × 0.18	0.40 × 0.24 × 0.22	0.46 × 0.36 × 0.34	0.23 × 0.22 × 0.13	0.22 × 0.14 × 0.10
θ range	3.3–25.0	3.2–25.0	3.3–25.0	3.4–25.0	3.4–26.0
reflins collected	7806	7626	52974	5058	65736
independent reflins	2355 [0.047]	4015 [0.062]	9679 [0.045]	2669 [0.042]	5093 [0.060]
[<i>R</i> _{int}]					
reflins obs. [<i>I</i> > 2 σ (<i>I</i>)]	2160	2736	7573	1836	4682
data/restraints/parameters	2355/1/122	4015/54/463	9679/130/948	2669/18/332	5093/78/240
GoF on <i>F</i> ² [^b]	0.0935	1.139	1.109	1.128	1.251
<i>R</i> / <i>wR</i> [<i>I</i> > 2 σ (<i>I</i>)] ^[a]	0.0220/0.0429	0.0845/0.2189	0.0729/0.1920	0.0655/0.1924	0.0482/0.1341
<i>R</i> / <i>wR</i> (all data)	0.0250/0.0435	0.1126/0.2290	0.0948/0.2027	0.0860/0.2603	0.0551/0.1375
Max., Min. $\Delta\rho$ (eÅ ⁻³)	0.57, -0.43	0.62, -0.56	1.83, -1.00	0.86, -0.43	1.76, -0.99

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; [b] $\text{GoF} = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

Computations

All quantum-chemical calculations were carried out by using the Gaussian 03 suites of programs.^[58] Structure optimisations were performed at the B3LYP/6–31G(d) level of theory. All stationary points were characterised as minima by analysis of the Hessian matrices. MP2/6–311G(d)/B3LYP/6–31G(d) single-point calculations were used for estimation of ion-pair binding energies (E_{int}). MP2/6–311+G(3df,2p) level of theory recommended for this purpose in literature^[59] was beyond our technical capability, and we used the smaller basis set 6–311G(d) because Tsuzuki et al.^[35] have demonstrated that MP2/6–311G(d) produced interaction energies within 4 kJ mol⁻¹ accuracy as compared to those of the benchmark method, CCSD(T)/6–311G(d).

Acknowledgements

We thank EPFL and Swiss National Science Foundation for financial support. J.S.M. thanks NSERC for financial support. D.R.Z. thanks the National Natural Science Foundation of China (No. 21171093) for financial support.

Keywords: dications · electrospray ionization mass spectrometry · ionic liquids · quantum-chemical calculations · X-ray spectroscopy

- [1] J. S. Wilkes, *Green Chem.* **2002**, *4*, 73–80.
- [2] a) P. J. Dyson, *Appl. Organomet. Chem.* **2002**, *16*, 495; b) M. Freemantle, *An Introduction to Ionic Liquids*, RSC, Cambridge, **2010**; c) J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508–3576; d) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123–150.
- [3] a) *Envisioning the Second Generation of Ionic Liquid Technology: Design and Synthesis of Task-Specific Ionic Liquids (TSILs)*, A. Wierzbicki, J. H. Davis, Jr., Paper No. 14F, in *Proceedings of the Symposium on Advances in Solvent Selection and Substitution for Extraction*, March 5–9, **2000**, Atlanta, Georgia, AIChE, New York, **2000**; b) A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, Jr., R. D. Rogers, *Chem. Commun.* **2001**, 135–136.
- [4] S. A. Forsyth, U. Fröhlich, P. Goodrich, H. Q. N. Gunaratne, C. Hardacre, A. McKeown, K. R. Seddon, *New J. Chem.* **2010**, *34*, 723–731.
- [5] a) J. H. Davis, Jr., *Chem. Lett.* **2004**, *33*, 1072–1077; b) Z. Fei, T. J. Geldbach, D. Zhao, P. J. Dyson, *Chem. Eur. J.* **2006**, *12*, 2122–2130; c) H. Xue, R. Verma, J. M. Shreeve, *J. Fluorine Chem.* **2006**, *127*, 159–176; d) Z. Fei, P. J. Dyson, *Chem. Commun.* **2013**, *49*, 2594–2596.
- [6] a) A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon, T. Welton, *J. Chem. Soc. Dalton Trans.* **1994**, 3405–3413; b) A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton, J. A. Zora, *J. Chem. Soc. Dalton Trans.* **1995**, 3467–3472.
- [7] a) S. A. Katsyuba, P. J. Dyson, E. E. Vandyukova, A. Vidiš, *Helv. Chim. Acta* **2004**, *87*, 2556–2565; b) I. Krossing, J. M. Slattery, C. Daguene, P. J. Dyson, A. Oleinikova, H. Weingärtner, *J. Am. Chem. Soc.* **2006**, *128*, 13427–13434; c) A. Wulf, K. Fumino, R. Ludwig, *Angew. Chem.* **2010**, *122*, 459–463; *Angew. Chem. Int. Ed.* **2010**, *49*, 449–453; d) S. A. Katsyuba, T. P. Griaznova, A. Vidiš, P. J. Dyson, *J. Phys. Chem. B* **2009**, *113*, 5046–5051; e) E. E. Zvereva, S. A. Katsyuba, P. J. Dyson, *Phys. Chem. Chem. Phys.* **2010**, *12*, 13780–13787.
- [8] E. Sloutskin, B. M. Ocko, L. Tamam, I. Kuzmenko, T. Gog, M. Deutsch, *J. Am. Chem. Soc.* **2005**, *127*, 7796–7804.
- [9] a) A. Triolo, O. Russina, V. Arrighi, F. Juranyi, S. Janssen, C. M. Gordon, *J. Chem. Phys.* **2003**, *119*, 8549–8557; b) S. M. Urahata, M. C. C. Ribeiro, *J. Chem. Phys.* **2004**, *120*, 1855–1863; c) Y. Wang, G. A. Voth, *J. Am. Chem. Soc.* **2005**, *127*, 12192–12193.
- [10] a) W. Zhao, F. Leroy, B. Heggen, S. Zahn, B. Kirchner, S. Balasubramanian, F. Müller-Plathe, *J. Am. Chem. Soc.* **2009**, *131*, 15825–15833; b) F. Domert, K. Wendler, R. Berger, L. D. Site, C. Holm, *ChemPhysChem* **2012**, *13*, 1625–1637.
- [11] a) H. Q. N. Gunaratne, P. Nockemann, S. Olejarz, S. M. Reid, K. R. Seddon, G. Srinivasan, *Aust. J. Chem.* **2013**, *66*, 607–611; b) F. D'Anna, H. Q. N. Gunaratne, G. Lazzara, R. Noto, C. Rizzo, K. R. Seddon, *Org. Biomol. Chem.* **2013**, *11*, 5836–5846.
- [12] a) Z. X. Zhang, H. Y. Zhou, L. Yang, K. Tachibana, K. Kamijima, J. Xu, *Electrochim. Acta* **2008**, *53*, 4833–4838; b) A. Lesimple, X. He, T.-H. Chan, O. Mamer, *J. Mass Spectrom.* **2007**, *43*, 35–41.
- [13] S. Yeganegi, A. Soltanabadi, D. Farmanzadeh, *J. Phys. Chem. B* **2012**, *116*, 11517–11526.
- [14] R. Wang, C.-M. Jin, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2006**, *45*, 6396–6403.
- [15] R. P. Singh, J. M. Shreeve, *Chem. Commun.* **2003**, 1366–1367.
- [16] Z. Zeng, B. S. Phillips, J.-C. Xiao, J. M. Shreeve, *Chem. Mater.* **2008**, *20*, 2719–2726.
- [17] C.-M. Jin, C. Ye, B. S. Phillips, J. S. Zabinski, X. Liu, W. Liu, J. M. Shreeve, *J. Mater. Chem.* **2006**, *16*, 1529–1535.
- [18] J. L. Anderson, R. Ding, A. Ellern, D. W. Armstrong, *J. Am. Chem. Soc.* **2005**, *127*, 593–604.
- [19] T. Payagala, J. Huang, Z. S. Breitbach, P. S. Sharma, D. W. Armstrong, *Chem. Mater.* **2007**, *19*, 5848–5850.
- [20] X. Han, D. W. Armstrong, *Org. Lett.* **2005**, *7*, 4205–4208.
- [21] K. Huang, X. Han, X. Zhang, D. W. Armstrong, *Anal. Bioanal. Chem.* **2007**, *389*, 2265–2275.
- [22] M. Qi, D. W. Armstrong, *Anal. Bioanal. Chem.* **2007**, *388*, 889–899.
- [23] Q. Liu, F. van Rantwijk, R. A. Sheldon, *J. Chem. Technol. Biotechnol.* **2006**, *81*, 401–405.
- [24] Z. Zhang, L. Yang, S. Luo, M. Tian, K. Tachibana, K. Kamijima, *J. Power Sources* **2007**, *167*, 217–222.
- [25] F. D'Anna, F. Ferrante, R. Noto, *Chem. Eur. J.* **2009**, *15*, 13059–13068.
- [26] H. Sun, D. Zhang, C. Liu, C. Zhang, *J. Mol. Struct.* **2009**, *900*, 37–43.
- [27] a) A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, Jr., R. D. Rogers, *Environ. Sci. Technol.* **2002**, *36*, 2523–2529; b) N. K. Sharma, M. D. Tickell, J. L. Anderson, J. Kaar, V. Pino, B. F. Wicker, D. W. Armstrong, J. H. Davis, Jr., A. J. Russell, *Chem. Commun.* **2006**, 646–648; c) A. A. J. Torriero, A. I. Siriwardana, A. M. Bond, I. M. Burgar, N. F. Dunlop, G. B. Deacon, D. R. MacFarlane, *J. Phys. Chem. B* **2009**, *113*, 11222–11231; d) A. Bhadani, S. Singh, *Langmuir* **2011**, *27*, 14033–14044.
- [28] Z. Fei, W. H. Ang, D. Zhao, R. Scopelliti, E. E. Zvereva, S. A. Katsyuba, P. J. Dyson, *J. Phys. Chem. B* **2007**, *111*, 10095–10108.
- [29] a) K. M. Dieter, C. M. Dymek, Jr., N. E. Heimer, J. W. Rovang, J. S. Wilkes, *J. Am. Chem. Soc.* **1988**, *110*, 2722–2726; b) J. Grondin, J.-C. Lassegues, D. Cavagnat, T. Buffeteau, P. Johansson, R. Holomb, *J. Raman Spectrosc.* **2011**, *42*, 733–743.
- [30] R. Bini, O. Bortolini, C. Chiappe, D. Pieraccini, T. Siciliano, *J. Phys. Chem. B* **2007**, *111*, 598–604.
- [31] a) P. J. Dyson, J. S. McIndoe, D. Zhao, *Chem. Commun.* **2003**, 508–509; b) P. J. Dyson, I. Khalaila, S. Luettgen, J. S. McIndoe, D. Zhao, *Chem. Commun.* **2004**, 2204–2205.
- [32] L. Tang, P. Kebarle, *Anal. Chem.* **1993**, *65*, 3654–3668.
- [33] N. B. Cech, C. G. Enke, *Mass Spectrom. Rev.* **2001**, *20*, 362–387.
- [34] B. L. Milman, Z. B. Alfassi, *Eur. J. Mass Spectrom.* **2005**, *11*, 35–42.
- [35] a) J. P. Lassègues, J. Grondin, R. Holomb, P. Johansson, *J. Raman Spectrosc.* **2007**, *38*, 551–558; b) K. Fujii, Y. Soejima, Y. Kyoshoin, S. Fukuda, R. Kanzaki, Y. Umebayashi, T. Yamaguchi, S.-i. Ishiguro, T. Takamuku, *J. Phys. Chem. B* **2008**, *112*, 4329–4336 and references cited therein.
- [36] J. D. Holbrey, W. M. Reichert, R. D. Rogers, *Dalton Trans.* **2004**, 2267–2271.
- [37] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566.
- [38] a) Y. U. Paulechka, G. J. Kabo, A. V. Blokhin, A. S. Shaplov, E. I. Lozinskaya, D. G. Golovanov, K. A. Lyssenko, A. A. Korlyukov, Y. S. Vygodskii, *J. Phys. Chem. B* **2009**, *113*, 9538–9546; b) S. M. Dibrov, J. K. Kochi, *Acta Crystallogr. Sect. C* **2006**, *62*, o19–o21; c) A. R. Choudhury, N. Winterton, A. Steiner, A. I. Cooper, K. A. Johnson, *CrystEngComm* **2006**, *8*, 742–745; d) A. R. Choudhury, N. Winterton, A. Steiner, A. I. Cooper, K. A. Johnson, *J. Am. Chem. Soc.* **2005**, *127*, 16792–16793; e) J. Fuller, R. T. Carlin, H. C. De Long, D. Haworth, *J. Chem. Soc. Chem. Commun.* **1994**, 299–300; f) C. M. Gordon, J. D. Holbrey, A. R. Kennedy, K. R. Seddon, *J. Mater. Chem.* **1998**, *8*, 2627–2636.
- [39] a) S. Tsuzuki, H. Tokuda, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* **2005**, *109*, 16474–16481; b) S. A. Katsyuba, E. E. Zvereva, A. Vidiš, P. J.

- Dyson, *J. Phys. Chem. A* **2007**, *111*, 352–370; c) P. A. Hunt, I. R. Gould, B. Kirchner, *Aust. J. Chem.* **2007**, *60*, 9–14; d) N. R. Dhupal, *Chem. Phys.* **2007**, *342*, 245–252.
- [40] S. Tsuzuki, R. Katoh, M. Mikami, *Mol. Phys.* **2008**, *106*, 1621–1629.
- [41] *Ionic Liquids in Synthesis* (Eds.: P. Wasserscheid, T. Welton), 2nd ed., Wiley-VCH, Weinheim, **2008**.
- [42] a) A. L. Maycock, G. A. Berchtold, *J. Org. Chem.* **1970**, *35*, 2532–2538; b) K. Ohkubo, T. Yamabe, *J. Org. Chem.* **1971**, *36*, 3149–3155; c) F. D. Saeva, *Tetrahedron* **1986**, *42*, 6123–6129; d) F. D. Saeva, B. P. Morgan, H. R. Luss, *J. Org. Chem.* **1985**, *50*, 4360–4362.
- [43] Examples of imidazolium salts characterised by single-crystal X-ray diffraction include: a) R. Ozawa, S. Hayashi, S. Saha, A. Kobayashi, H.-o. Hamaguchi, *Chem. Lett.* **2003**, *32*, 948–949; b) Y. S. Vygodskii, E. I. Lozinskaya, A. S. Shaplov, K. A. Lyssenko, M. Y. Antipin, Y. G. Urman, *Polymer* **2004**, *45*, 5031–5045; c) M. Nakakoshi, M. Shiro, T. Fujimoto, T. Machinami, H. Seki, M. Tashiro, K. Nishikawa, *Chem. Lett.* **2006**, *35*, 1400–1401; d) A. K. Abdul-Sada, A. M. Greenway, P. B. Hitchcock, T. J. Mohammed, K. R. Seddon, J. A. Zora, *J. Chem. Soc. Chem. Commun.* **1986**, 1753–1754.
- [44] For examples of sulfonium salts, see: a) O. Knop, A. Linden, B. R. Vincent, S. C. Choi, T. S. Cameron, R. J. Boyd, *Can. J. Chem.* **1989**, *67*, 1984–2008; b) O. Knop, T. S. Cameron, P. K. Bakshi, A. Linden, S. P. Roe, *Can. J. Chem.* **1994**, *72*, 1870–1881; c) H. Stegemann, K.-F. Tebbe, L. A. Bengtsson, *Z. Anorg. Allg. Chem.* **1995**, *621*, 165–170; d) L. Bengtsson-Kloo, J. Berglund, H. Stegemann, C. Svensson, P. H. Svensson, *Acta Crystallogr. Sect. C* **1996**, *52*, 3045–3047; e) L. Bengtsson-Kloo, J. Berglund, H. Stegemann, C. Svensson, P. H. Svensson, *Acta Crystallogr. Sect. C* **1998**, *54*, 1851–1853; f) A. Babai, A.-V. Mudring, *Inorg. Chem.* **2005**, *44*, 8168–8169; g) D. Zhao, Z. Fei, W. H. Ang, P. J. Dyson, *Int. J. Mol. Sci.* **2007**, *8*, 304–315.
- [45] Y. Funasako, M. Noshio, T. Mochida, *Dalton Trans.* **2013**, *42*, 10138–10143.
- [46] D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* **2004**, *43*, 2197–2205.
- [47] V. Stenzel, J. Jeske, W.-W. du Mont, P. G. Jones, *Inorg. Chem.* **1995**, *34*, 5166–5170.
- [48] M. Bremer, P. S. Gregory, P. v. R. Schleyer, *J. Org. Chem.* **1989**, *54*, 3796–3799.
- [49] K. R. Seddon, in *Molten Salts and Ionic Liquids: Never the Twin?* (Eds.: M. Gaune-Escard, K. R. Seddon), Wiley, New York, **2010**, xiii–xv.
- [50] P. Walden, *Bull. Acad. Imper. Sci. St. Petersburg* **1914**, *8*, 405–422.
- [51] A. F. Kapustinskii, *Quart. Rev.* **1956**, *10*, 283–294.
- [52] A. S. Larsen, J. D. Holbrey, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2000**, *122*, 7264–7272.
- [53] Oxford Diffraction Ltd., Abingdon, OX14 4RX, UK, **2003**.
- [54] A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220–229.
- [55] G. M. Sheldrick, SHELX-97, Structure Solution and Refinement Package, Universität Göttingen, **1997**.
- [56] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565–566.
- [57] N. Walker, D. Stuart, *Acta Crystallogr. Sect. A* **1983**, *39*, 158–166.
- [58] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
- [59] E. I. Izgorodina, U. L. Bernard, D. R. MacFarlane, *J. Phys. Chem. A* **2009**, *113*, 7064–7072.

Received: September 6, 2013

Revised: January 9, 2014

Published online on March 3, 2014