Ionic liquid *S*-alkylthiouronium salts†

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The preparation and characterisation of a series of ionic liquids based on *S*-alkylthiouronium cations prepared from thiourea, 1,3-dimethylthiourea, 1,3-diethylthiourea and 1,3-tetramethylthiourea coupled with bis{(trifluoromethane)sulfonyl}imide, bromide, methylsulfate or ethylsulfate anions are reported. All are liquids at room temperature or solids with melting points close to room temperature, except for the bromide salts, which have melting points below 92 °C. Systematic variation in the *N*- and *S*-alkyl substituents demonstrates how the physical properties of these ionic liquids can be readily controlled. The mutual miscibility limits of representative examples with octane, dodecane and toluene have been determined as a function of temperature, and the extraction of dibenzothiophene from dodecane as a model for desulfurisation of diesel has been investigated.

Ionic liquids[1] are of significant interest as alternative solvents for a wide range of applications from electrochemistry, through organic synthesis and catalysis to biomass processing and nanomaterial fabrication.[2] The reduced vapour pressure of ionic liquids, the potential to design in *a priori* low toxicity, availability of wide liquid ranges and high thermal and electrochemical stability provide this impetus. The search for, and investigation of, new ionic liquids is driven by efforts to understand the relationships between chemical structure and physical properties,[3] and to actively develop ionic liquids with specific, tailored functionality.[4]

While ionic liquids containing 1,3-dialkylimidazolium cations have been the most extensively studied, many other cation families are known and these can generally be categorised as unsaturated or saturated and cyclic or acyclic systems. Dialkylimidazolium, dialkylpyrrolidinium, and tetraalkylammonium cations are examples of cyclic aromatic (unsaturated), cyclic non-aromatic (saturated), and cyclic saturated cations, respectively, and along with pyridinium and phosphonium-based systems represent the bulk of known organic ionic liquids. In contrast, guanidinium, uronium and thiouronium cations (Fig. 1) have a planar, charge-delocalised acyclic core and represent the fourth type of cation configuration available. These systems have either six (guanidinium) or five (uronium, thiouronium) sites which can be used for structural modification, providing a large range of variables with which to change the properties of the salts.

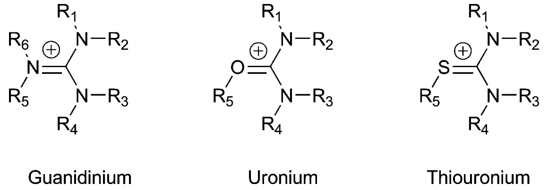

Fig. 1 Structures of guanidinium, uronium and thiouronium cations (showing a single canonical form in each case).

A number of examples of ionic liquids with guanidinium cations have been reported,[5] and have been studied as solvents for synthesis and catalysis,[6] as absorbents for gases,[7] and as dye-sensitized solar cell electrolytes.[8] The high nitrogen content of guanidinium cations leads to high energy density yet remarkable thermal and chemical stability providing interest as potential high-energy materials.[9]

The analogous uronium and thiouronium salts are well known and are used as peptide-coupling agents, intermediates in thiol and guanidine syntheses, metal-complexation, electroplating bath additives, stabilisers for vulcanised rubber, and in metal extraction and fixing (for example in photography). The salts can be conveniently synthesised by alkylation of ureas and thioureas under neutral or acidic conditions. It is worth noting that thiouronium salts readily undergo hydrolysis or aminolysis to ureas and guanidines, respectively, under basic conditions, with liberation of thiols.[10]

The tendency for *S*-methyl-*N*,*N*′-alkylthiouronium methylsulfate salts to form liquids rather than crystalline solids was first reported, in passing, in 1951,[11] however, only much more recently have a small number of ionic liquid thiouronium salts have been reported in the patent literature.[12,13] Bond and co-workers[14] have also recently synthesised and electrochemically characterised ten cyclic, aromatic *S*-alkyl thiolonium, thiotetrazolium, and thiobenzolium based ionic liquids prepared by alkylation of aromatic, cyclic thiones followed by protonation of the thioether functionalised heterocycle.

However, there is limited experimental data on the synthesis and physical properties of the acyclic sulfur-containing thiouronium-based ionic liquids. Here we describe the synthesis, characterisation, and measurement of physical, rheological, and electrochemical properties of thiouronium ionic liquids synthesised from four commercially available thioureas: thiourea, 1,3-dimethylthiourea, 1,3-diethylthiourea, and 1,3-tetramethylthiourea (Fig. 2). The ionic liquids, and starting

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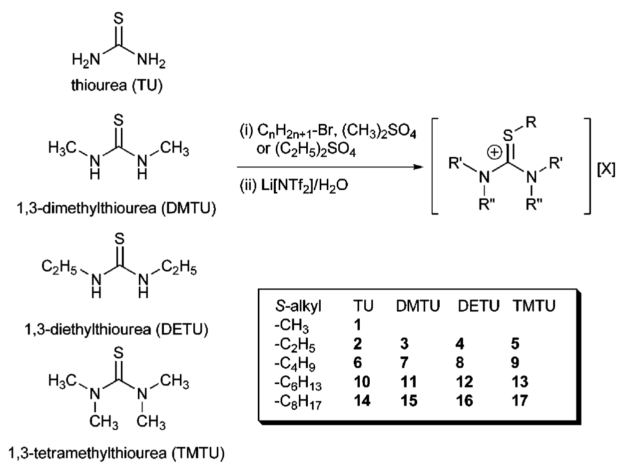

S-alkyl	TU	DMTU	DETU	TMTU
-CH_3	**1**			
-C_2H_5	**2**	**3**	**4**	**5**
-C_4H_9	**6**	**7**	**8**	**9**
-C_6H_{13}	**10**	**11**	**12**	**13**
-C_8H_{17}	**14**	**15**	**16**	**17**

Fig. 2 General synthesis and structures of the thiouronium cations (**1–17**) prepared from the four initial thioureas, thiourea, 1,3-dimethylthiourea, 1,3-diethylthiourea and 1,3-tetramethylthiourea, by alkylation with either dimethylsulfate (**1**), diethylsulfate (**2**, **3**, **5**) or bromoalkanes (**2–17**) followed by anion exchange with Li[NTf$_2$] in water.

materials, were chosen in order to examine the effects of the three structural variables, namely *S*-alkyl and *N*-alkyl substitution and anion, on the ionic liquid characteristics of a matrix of substituted thiouronium salts with hydrogen-, methyl-, and ethyl-substituents on the nitrogen positions and methyl, ethyl, butyl, hexyl and octyl groups on the sulfur of the cation (Table 1). Preliminary measurements of the mutual miscibility limits with octane, dodecane and toluene and the extraction of dibenzothiophene from dodecane with promising ionic liquids from within the matrix are also presented.

Results and discussion

Alkylated thiouronium salts (Table 1) were prepared with seventeen *S*-alkylthiouronium cations as either methylsulfate, ethylsulfate, bromide or bis{(trifluoromethane)sulfonyl}imide salts, by alkylation of thiourea, 1,3-dimethylthiourea, 1,3-diethylthiourea and 1,3-tetramethylthiourea with diethylsulfate or dimethylsulfate and/or bromoethane, bromobutane, bromohexane and bromooctane, followed by anion metathesis with Li[NTf$_2$] following the general scheme indicated in Fig. 2. The

Table 1 Experimental characterisation of the ionic liquids prepared. Glass transition temperatures and melting points were determined by DSC and decomposition temperatures by dynamic DSC under dinitrogen

	S-R	*N*-R′	*N*-R″	Anion	State (at rt)	$T_{mp}{}^a$/°C	T_g/°C	T_{dec}/°C	Potential window/V	Cathodic limit^b/V	Anodic limit^b/V
1	CH_3	H	H	[MeSO$_4$]	Solid	36	−61	200	4.0	−1.5	2.5
2	C_2H_5	H	H	Br	Solid	87	n/o^c	202	1.5	−1.5	0.0
		H	H	[EtSO$_4$]	Solid	~0–25^d	−56.2	183			
				[NTf$_2$]	Liquid	27	−69	258	4.0	−1.5	2.5
3		CH_3	H	Br	Solid	62	−42	166	1.3	−1.3	0.0
				[EtSO$_4$]	Solid	32	−65	~175	3.8	−1.5	2.3
				[NTf$_2$]	Liquid	19	−74^e	245	4.0	−1.5	2.5
4		CH_3	CH_3	Br	Solid	92	−25	131	−2.0	−2.0	0.0
				[NTf$_2$]	Liquid	—	−85^f	307	4.3	−2.0	2.3
5		C_2H_5	H	Br	Liquid	40	−49	150	1.5	−1.5	0.0
				[EtSO$_4$]	Liquid	—	−76.2	186	3.5	−1.5	2.0
				[NTf$_2$]	Liquid	—	−87	257	4.0	−2.5	1.5
6	C_4H_9	H	H	Br	Solid	83	−30	195	1.7	−1.5	0.2
				[NTf$_2$]	Solid	49	−60	257	4.0	−1.5	2.5
7		CH_3	H	Br	Solid	60	−29	161	1.5	1.5	0.0
				[NTf$_2$]	Liquid	—	−72	209	4.0	−1.5	2.5
8		CH_3	CH_3	Br	Solid	82	n/o^c	121			
				[NTf$_2$]	Liquid	—	−83	287	4.3	−2.0	2.3
9		C_2H_5	H	Br	Liquid	—	−47	150			
				[NTf$_2$]	Liquid	—	−81	175	4.1	−1.5	2.6
10	C_6H_{13}	H	H	Br	Solid	86	−30	196			
				[NTf$_2$]	Liquid	—	−66	240	3.9	−1.4	2.5
11		CH_3	H	Br	Solid	95	−41	157			
				[NTf$_2$]	Liquid	—	−77	256	4.0	−1.5	2.5
12		CH_3	CH_3	Br	Solid	73	n/o^c	121			
				[NTf$_2$]	Liquid	—	−87	314	4.3	−2.0	2.3
13		C_2H_5	H	Br	Liquid	49	−45	154			
				[NTf$_2$]	Liquid	—	−84	239	4.0	−1.5	2.5
14	C_8H_{17}	H	H	Br	Solid	96	−35	204	1.5	−1.5	0.0
				[NTf$_2$]	Liquid	—	−65	258	3.9	−1.4	2.5
15		CH_3	H	Br	Solid	54	−44	159			
				[NTf$_2$]	Liquid	—	−77	231	4.0	−1.5	2.5
16		CH_3	CH_3	Br	Solid	79^g	n/o^c	115			
				[NTf$_2$]	Liquid	—	−87	311	4.5	−2.0	2.5
17		C_2H_5	H	Br	Liquid	—	−56	150			
				[NTf$_2$]	Liquid	—	−81	175	4.1	−1.5	2.6

[a] mp and T_g recorded by DSC on heating, T_{dec} measured to the onset to 5 wt% decomposition by TGA; viscosities and densities at 25 °C except where noted. [b] Relative to Ag/Ag$^+$. [c] n/o indicates transition was not observed by DSC. [d] A reliable melting point could not be obtained visually, no crystallisation and melting was determined by DSC. [e] lit. −68 °C from ref. 12. [f] lit. −81 °C from ref. 12. [g] Crystal–crystal transition at −11 °C.

matrix of cations was prepared in order to systematically investigate the effects of *S*-alkyl and *N*-alkyl/hydrogen substitution on the ionic liquid-forming properties of the salts.

All new ionic liquids gave satisfactory microanalysis and had IR, NMR, and mass spectra consistent with the proposed structures. Phase transitions for all the salts were characterised by DSC and TGA, and are detailed in Table 1.

Melting and glass transition temperature

The four salts prepared with alkylsulfate anions all have relatively low melting points; **1**-$MeSO_4$ and **3**-$EtSO_4$ are hygroscopic crystalline solids at room temperature with melting points between 27–36 °C (Table 1). **2**-$EtSO_4$ crystallised slowly at 0 °C on seeding with crystals obtained by cooling a small sample to −15 °C and melted between 0–25 °C, **5**-$EtSO_4$ did not show any tendency to crystallise, either on standing in a freezer, or during the thermal cycles of the DSC measurements and only a glass transition was observed.

In general, ionic liquids with methyl- and ethylsulfate anions tend to have low melting points,[15] even with small, rigid cations such as 1,3-dimethylimidazolium methylsulfate (mp 43 °C). The melting points of the thiouronium salts here are largely comparable to those of the imidazolium systems. **1**-$MeSO_4$ has an even smaller rigid cation than that of 1,3-diethylimidazolium, with five non-hydrogen atoms and only a single methyl substituent and melts at 36 °C.

The bromide salts were isolated initially as liquids, all of which crystallised slowly on standing at room temperature as solids with the melting points between 40–100 °C except for **9**-Br (*S*-ethyl-*N*,*N*′-diethylthiouronium) and **17**-Br (*S*-octyl-*N*,*N*′-diethylthiouronium) which remained as viscous oils. All the bromide-containing ionic liquids formed glasses on cooling directly from the molten state, with glass transition temperatures between −25 to −56 °C except for longer-chain *S*-alkyl-*N*,*N*′-tetramethylthiouronium bromides (**8**-Br, **12**-Br and **16**-Br) and *S*-ethylthiouronium bromide (**2**-Br) which crystallised directly on cooling rather than forming a glass. For all the glass forming salts, cold crystallisation followed by melting transitions was observed during the DSC cycles. Melting points and glass transition temperatures for the bromide salts from Table 1 are plotted in Fig. 3 as a function of *S*-alkyl chain length.

The salts derived from both thiourea and tetramethylthiourea have melting points approximately 50 °C higher than those from dimethyl- and diethylthiourea with a single substituent on each nitrogen atom. This is presumably a result of the lower symmetries of the *N*,*N*′-dialkylthiouronium cations rather than any hydrogen-bonding effects. Little variation was observed in the melting points of the salts with increasing the size of the *S*-alkyl substituent. This contrasts markedly with the reduction in, and suppression of, melting points with increasing substituent chain length commonly observed for other ionic liquids.[16]

Metathesis to the $[NTf_2]^-$ salts resulted in a wide family of low melting ionic liquids, as anticipated. Only one of the bis{(trifluoromethyl)sulfonyl}imide salts (**6**-NTf_2) spontaneously crystallised at room temperature (mp 47 °C). **2**-NTf_2 and **3**-NTf_2 displayed sub-ambient crystallisation and subsequent melting points in the DSC experiments at 27 °C and 19 °C respectively. All the remaining bis{(trifluoromethyl)sulfonyl}-imide ionic liquids investigated were glass-forming liquids and could not be induced to crystallise, either by cooling to −15 °C for long periods, or in the DSC cooling cycles where only glass transitions were observed. Melting points and glass transition temperatures are plotted as a function of *S*-alkyl chain length in Fig. 4. In comparison to the corresponding bromide salts, the suppression of crystallisation is marked and the glass transition temperatures are also significantly lowered, ranging from −60 to −95 °C.

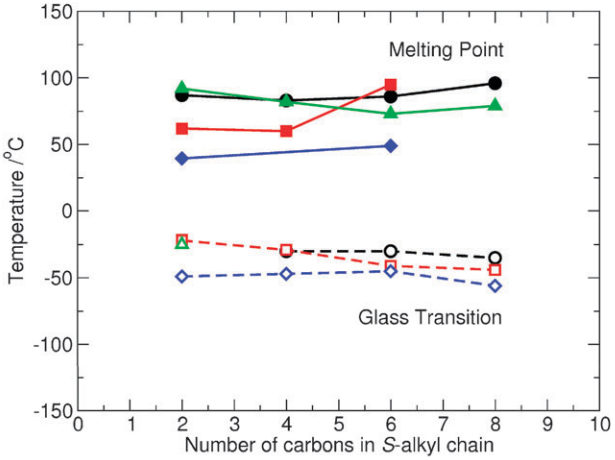

Fig. 3 Variation in the melting points and glass transition temperatures. *S*-alkyl-thiouronium (circle), *S*-alkyl-*N*,*N*′-dimethylthiouronium (square), *S*-alkyl-*N*,*N*′-diethylthiouronium (diamond), and *S*-alkyl-*N*,*N*′-tetramethylthiouronium (triangle) bromide salts synthesised as a function of the number of carbons in the *S*-alkyl substituent. Connecting lines (solid for melting points and dashed for glass transitions) are added as a visual aid.

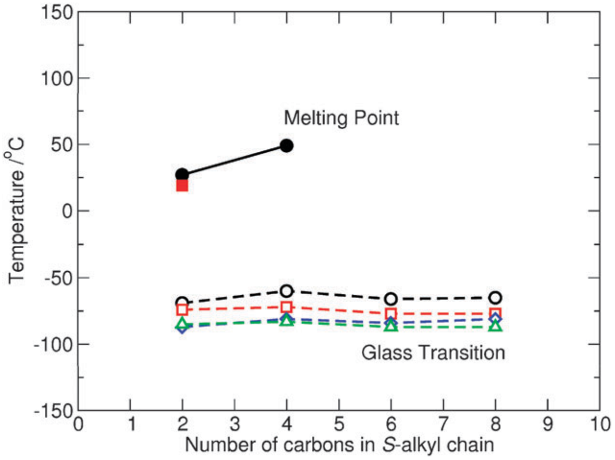

Fig. 4 Variation in the melting points and glass transition temperatures. *S*-alkyl-thiouronium (circle), *S*-alkyl-*N*,*N*′-dimethylthiouronium (square), *S*-alkyl-*N*,*N*′-diethylthiouronium (diamond), and *S*-alkyl-*N*,*N*′-tetramethylthiouronium (triangle) bis{(trifluoromethyl)sulfonyl}imide salts synthesised as a function of the number of carbons in the *S*-alkyl substituent. Connecting lines (solid for melting points and dashed for glass transitions) are added as a visual aid; only glass transitions were observed for most of the ionic liquids.

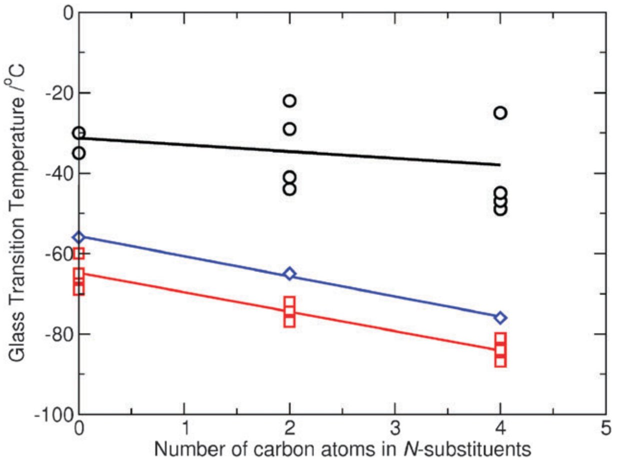

Fig. 5 Variation in glass transition temperature with the size of the *N*-alkyl substituents on the thiouronium salts grouped by anion type; Br^- (circle), $[EtSO_4]^-$ (diamond), and $[NTf_2]^-$ (square). For the $[NTf_2]^-$ and $[EtSO_4]^-$ salts, each carbon atom added to the *N*-substituent of the cation reduced T_g by *ca.* 5 °C.

Comparing the glass transition temperatures a small, but distinct step-wise reduction in the glass transition temperatures is apparent on changing the *N*-substitution in the thiouronium cations from –NH to $–NH(CH_3)$ to $–NH(C_2H_5)$ for the ionic liquids with ethylsulfate, bromide or bis{(trifluoromethyl)-sulfonyl}imide anions (Fig. 5). This is most clearly defined for the ethylsulfate and bis{(trifluoromethyl)sulfonyl}imide systems, where adding a CH_2 moiety to each *N*-site in the cation results in a reduction of the glass transition temperature of 5 °C. The comparable trend is less clearly defined for the bromide salts, with an increased spread in the observable glass transition temperatures and with a number of the salts crystallising directly on cooling rather than forming super-cooled glasses.

Thermal stability

Decomposition temperatures were investigated by dynamic TGA, scanning at 5 °C min^{-1} under nitrogen. The results, reported in Table 1, were determined from the onset to the initial 5% mass loss. All of the ionic liquids showed moderate thermal stability to at least 150 °C. The decomposition temperatures (T_{dec}) of the thiouronium ionic liquids increase with decreasing nucleophilicity of the anions present, roughly following the order $Br^- < [RSO_4]^- < [NTf_2]^-$, with mean onset of decomposition temperatures of 160 °C, 186 °C and 251 °C, respectively, for the three anion types. However, in general, the thiouronium salts showed poorer thermal stability compared to the corresponding simple alkylguanidinium ionic liquids.[17] This is probably associated with nuculeophilic based induced decomposition at the mercaptoether group of the cation.

Density and viscosity

Densities and viscosities were measured between 20–90 °C in the liquid regions for the ionic liquids with $[NTf_2]^-$ and $[RSO_4]^-$ anions and are shown in Tables 2 and 3 respectively. For all the ionic liquids investigated, the densities ranged between 1.20–1.50 g cm^{-3} at 25 °C and decreased linearly with increasing temperature. This is illustrated in Fig. 6 for the three ethylsulfate salts **2**-$EtSO_4$, **3**-$EtSO_4$ and **5**-$EtSO_4$ showing the systematic decrease in density as the number of methylene groups in the cation increases on substituting the thiouronium cations with *N*-methyl and *N*-ethyl groups.

The changes in densities of the different ionic liquids correlate directly with the group contribution descriptor models for thermophysical properties.[18] The coefficients of thermal expansion (α) are in the range −7 to -10×10^{-4} K^{-1}, typical for both ionic liquids[19] and molecular organic solvents. For each cation, the ionic liquids with $[NTf_2]^-$ anions had higher densities than the corresponding alkylsulfate salts.

Table 2 Densities (g cm^{-3}) of ionic liquids **2**-$EtSO_4$, **3**-$EtSO_4$, **3**-NTf_2, **4**-NTf_2, **5**-$EtSO_4$, **5**-NTf_2, **6**-NTf_2, **7**-NTf_2, **8**-NTf_2, **9**-NTf_2, **10**-NTf_2, **11**-NTf_2, **12**-NTf_2, **13**-NTf_2, **15**-NTf_2, and **17**-NTf_2 as a function of temperature

T/°C	**2**-$EtSO_4$	**3**-$EtSO_4$	**3**-NTf_2	**4**-NTf_2	**5**-$EtSO_4$	**5**-NTf_2	**6**-NTf_2	**7**-NTf_2
25	1.3033	1.2403	1.5085	1.4501	1.1782	1.4289		1.4293
35	1.2962	1.2325	1.4981	1.4404	1.1706	1.4189		1.4194
45	1.2888	1.2247	1.4876	1.4306	1.1631	1.4088		1.4094
55	1.2817	1.2172	1.4774	1.4212	1.1558	1.3990	1.4770	1.3997
65	1.2747	1.2099	1.4674	1.4119	1.1485	1.3894	1.4674	1.3901
75	1.2679	1.2027			1.1413		1.4580	1.3786
85	1.2616	1.2000			1.1336		1.4484	1.3611
α^a	−6.999	−7.468	−10.29	−9.56	−7.323	−9.89	−9.520	−9.810
R^2	0.9997398	0.9998574	0.9999	0.9999	0.9999631	0.9999	0.9999912	0.9999652
T range for fit	25–85	25–85	25–65	25–65	25–85	25–65	55–85	25–65

T/°C	**8**-NTf_2	**9**-NTf_2	**10**-NTf_2	**11**-NTf_2	**12**-NTf_2	**13**-NTf_2	**15**-NTf_2	**17**-NTf_2
25	1.3896	1.3527	1.4245	1.3739	1.3384	1.3207	1.3145	1.2478
35	1.3804	1.3432	1.4145	1.3643	1.3294	1.3112	1.3052	1.2386
45	1.3710	1.3336	1.4041	1.3546	1.3204	1.3002	1.2959	1.2296
55	1.3619	1.3241	1.3938	1.3451	1.3117	1.2825	1.2869	1.2208
65	1.3530	1.3068	1.3825	1.3353	1.3030	1.2653	1.2778	1.2137
75	1.3440	1.2868					1.2686	1.2053
85		1.2555					1.2509	1.1957
α^a	9.123	−9.540	−10.47	−9.64	−8.85	−13.95	−9.164	−8.529
R^2	0.99991	0.9999978	0.9995	0.9999	0.9999	0.9811	0.9999854	0.9994225
T range for fit	25–75	25–55	25–65	55–65	25–65	25–65	25–75	25–85

[a] Coefficient of thermal expansion ($\times 10^{-4}$ K^{-1}), where R^2 is the goodness of fit to the linear regression over the temperature range 25–85 °C.

Table 3 Viscosity (cP) for the ionic liquids **2**-EtSO$_4$, **3**-EtSO$_4$, **5**-EtSO$_4$, **5**-NTf$_2$, **6**-NTf$_2$, **7**-NTf$_2$, **8**-NTf$_2$, **9**-NTf$_2$, **11**-NTf$_2$, **12**-NTf$_2$, **14**-NTf$_2$, **15**-NTf$_2$, **16**-NTf$_2$, and **17**-NTf$_2$ as a function of temperature in their respective liquid regions within the temperature range 20–90 °C

T/°C	**2**-EtSO$_4$	**3**-EtSO$_4$	**5**-EtSO$_4$	**5**-NTf$_2$	**6**-NTf$_2$	**7**-NTf$_2$	**8**-NTf$_2$	**9**-NTf$_2$
20						143		116
25	2287	336	199	59			32	
30						85		72
35	1095	167	118	40			23	
40						53		48
45	569	96	73	27			17	
50					98	35		34
55	312	58	50				12	
60					63	25		25
65	187	38	36				9.0	
70					43			
75	120	26	26				6.9	
80					30			
85	82							
90					22			
T range for fit/°C	25–85	25–75	25–75	25–45	50–90	20–60	26–75	20–60
$\ln(A'/\mathrm{cP})^a$	−0.0728	−1.318	−0.8246	−1.1555	−0.9884	−0.8462	−1.496	−0.6056
B'^a/K	641.32	643.65	620.50	587.29	614.22	537.04	546.74	541.75
$T_0{}^a$/K	216.95	208.15	196.95	186.15	213.15	201.15	190.15	192.15
R^2	0.9973	0.9996	0.9997	0.9956	0.9997	0.9987	0.9973	0.9999

T/°C	**10**-NTf$_2$	**11**-NTf$_2$	**12**-NTf$_2$	**14**-NTf$_2$	**15**-NTf$_2$	**16**-NTf$_2$	**17**-NTf$_2$
20				561	171		274
25		30	19			23	
30			16	299	103		165
35		21	19			17	
40			11	170	64		102
45		14				12	
50				104	42		65
55	59					8.5	
60				66	30		44
65	38	6.7				6.4	
70				46	21		31
75	27	5.2	4.2			4.9	
80				34			24
85							
90				26			
T range for fit/°C	55–75	25–75	25–75	20–90	20–70	25–75	20–80
$\ln(A'/\mathrm{cP})^a$	−1.3385	−2.0391	−2.027	−0.5232	−0.9588	−1.9808	−0.9945
B'^a/K	654.37	561.83	561.83	588.52	595.49	582.87	673.51
$T_0{}^a$/K	207.15	196.15	186.15	208.15	196.15	186.15	192.15
R^2	0.9996	0.9935	0.9995	0.9985	0.9983	0.9932	0.9980

[a] Parameters from fitting the viscosity data to the VFT equation ($\eta = A'\exp(B'/T - T_0)$) where R^2 is the goodness of fit.

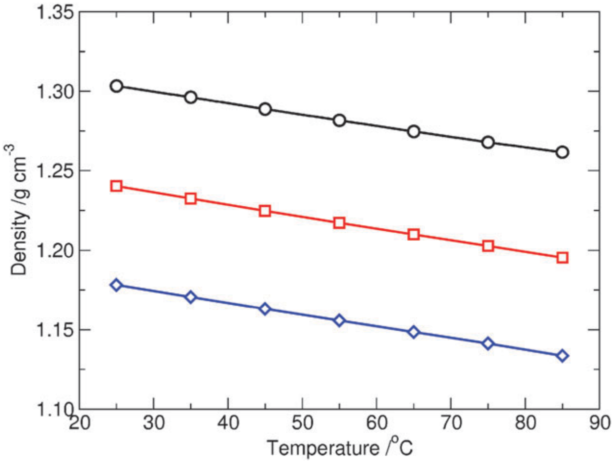

Fig. 6 Change in density for the three S-ethylthiouronium ethylsulfate ionic liquids **2**-EtSO$_4$ (circle), **3**-EtSO$_4$ (square), and **5**-EtSO$_4$ (diamond) with temperature, showing the linear decrease in density with increasing temperature and with increasing the number of methylene substituents on each thiouronium nitrogen from 0 for **2**-EtSO$_4$ to 2 for **5**-EtSO$_4$.

Viscosity measurements were made between room temperature, or the melting point of the ionic liquid, and 90 °C using a cone and plate viscometer. In all cases, the viscosity decreased with temperature and showed a good fit to the VFT equation[20] characteristic of ionic liquids.[21] The corresponding data are summarised in Table 3 as a function of temperature.

The ionic liquids with $[\mathrm{NTf_2}]^-$ anions and the shortest alkyl substituents on the cation S-position display the lowest viscosities. For those ionic liquids derived from 1,3-tetramethylthiourea (**8**-, **12**-, and **16**-NTf$_2$), the viscosities are comparable or lower than those for 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide.[22] It is notable, however, that the introduction of even one alkyl substituent on the cation N-positions provides sufficient disruption of the hydrogen-bond donating ability of the cations to reduce the ionic liquid viscosities significantly, providing potentially useful materials of moderate fluidity. For example the presence of a methyl or ethyl group in **3**-EtSO$_4$ and **5**-EtSO$_4$ compared to **2**-EtSO$_4$ reduces the viscosity by approximately an order of magnitude, from ∼2000 cP at 25 °C for **2**-EtSO$_4$ to ∼200 cP for **5**-EtSO$_4$.

This provides access to a wider array of ionic liquids with moderately high fluidity, derived from the dimethyl- and diethylthiourea starting materials in addition to those from tetramethylthiourea.

Electrochemical window

The electrochemical windows of all the ionic liquids were measured by cyclic voltammetry at 25 °C, the data are shown in Table 1. The cathodic reduction limit of the thiouronium cations occurs at −2.0 V for the pentaalkylated *S*-alkyl-*N*,*N′*-tetramethylthiouronium salts and at −1.5 V for those containing one or more hydrogens on the *N*-positions; provides electrochemical windows of up to ∼4.5 V depending on the anodic oxidation potential defined by the anion present. Typical cyclic voltammograms, for the ionic liquids **5**-Br, **5**-$EtSO_4$ and **5**-NTf_2, are presented in Fig. 7 and show the common reductive limit of −1.5 V *vs.* Ag/Ag^+ for the *S*-ethyl-*N*,*N′*-diethylthiouronium cation in each case and oxidative limits of 0.0 V (Br^-), 2.0 V ($[EtSO_4]^-$), and 2.5 V ($[NTf_2]^-$). Thiouronium cations are electrochemically less stable than imidazolium cations[23] and the cathodic limit is thus reduced from −2.5 to −1.5 V. When the cation is fully alkylated, the cathodic window extends to −2 V. The anodic limit is almost unaffected and is consistent with that of [emim][NTf_2].[24]

The relatively low viscosities of these thiouronium ionic liquids and the relatively good reductive stability of the cation may provide a new class of ionic liquid electrolytes for photovoltaic applications.

Miscibility with aliphatic and aromatic hydrocarbons

Binary phase compositions of **3**-NTf_2 and **5**-NTf_2 with octane, dodecane, and toluene were measured over the temperature range 25–85 °C using ^1H NMR spectroscopy to probe the miscibility and mutual solubility of each of the two components of the binary mixtures.

The data (Fig. 8) show high solubility of toluene in both ionic liquids, with the mutual miscibility limit forming at 73.9–75.0 mol% toluene in **3**-NTf_2 and at 76.5–78.3 mol% in **5**-NTf_2. These results are comparable with the saturation composition of toluene/1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide mixtures which show a maximum at 1 : 2.8 ionic liquid : toluene (*ca.* 74 mol% toluene).[25]

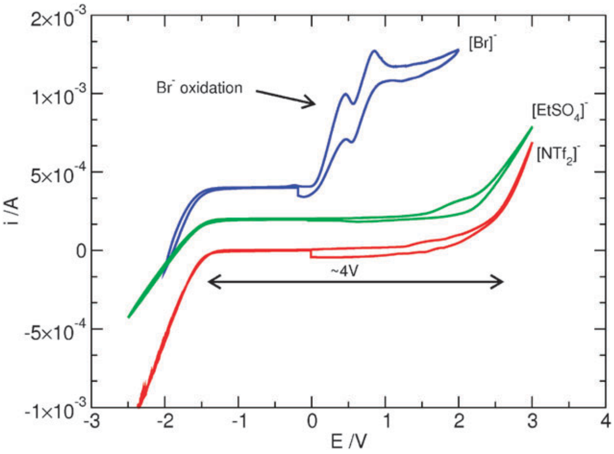

Fig. 7 Typical cyclic voltammograms of *S*-ethyl-*N*,*N′*-diethylthiouronium bromide, ethylsulfate and bis{(trifluoromethyl)sulfonyl}imide, all the ionic liquids showed a reduction limit of *ca.* −1.5 V (*vs.* Ag/Ag^+). The three data sets of vertically offset to aid visualisation.

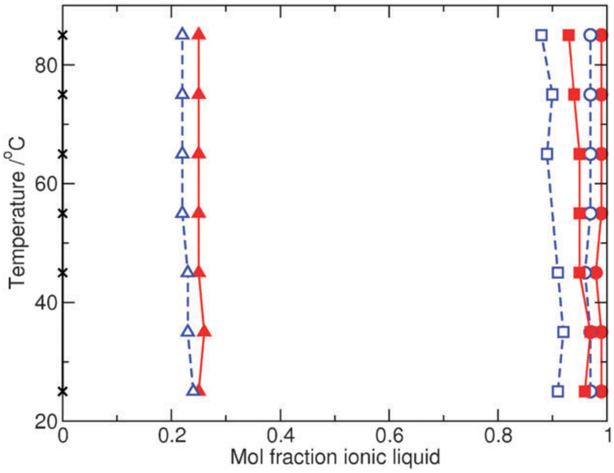

Fig. 8 Mutual miscibility limits as a function of temperature for **3**-NTf_2 (solid lines) and **5**-NTf_2 (dashed lines) with octane (square), dodecane (circle) and toluene (triangle). No ionic liquids were detected in the hydrocarbon phases (crosses) in any of the systems.

The solubility of toluene in imidazolium-based ionic liquids increases dramatically with increasing the total alkyl-chain component of the cation and for 1-hexyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, total miscibility with toluene is observed. In contrast, the two thiouronium systems described here have, respectively, four and six carbon atoms in the total alkyl-substituents, yet show almost identical mutual miscibility profiles.

The solubility of octane and dodecane in the ionic liquids examined was much lower than that of toluene, as anticipated. The mutual miscibility limits of octane and dodecane with **3**-NTf_2 varied from 3.0–6.9 mol% and 1.2–1.5 mol%, respectively, and from 6.4–11.9 mol% and 2.6–4.3 mol%, respectively, with **5**-NTf_2. In common with other ionic liquid systems reported,[26] octane showed higher miscibility with the ionic liquids than the longer chain dodecane, and on changing from *N*-methyl to *N*-ethyl substitution on the ionic liquid, the solubility of both alkanes increases. No ionic liquids were detected in the upper hydrocarbon phases during the measurements.

The vast differences in the solubilities of the aliphatic and aromatic hydrocarbons and the variation in relative miscibilities of aromatics and aliphatic hydrocarbons in the two different thiouronium-based ionic liquids studied could indicate the formation of specific, selective interactions with aromatics[27] that could lead to potential use in aliphatic/aromatic separation as has been studied using other types of ionic liquids.[28–31]

Polyaromatic sulfur extraction

We have previously demonstrated how increasing the size of the cations from pyridinium or imidazolium through picolinium to lutidinium and isoquinolinium in ionic liquids can enhance the extraction of polyaromatic sulfur compounds such as dibenzothiophene (DBT) from aliphatic hydrocarbons as a model desulfurisation process.[32] Extraction data were modelled using a QSPR approach with descriptors that indicated the importance of cation aromaticity and planarity in enhancing extraction. Thiouronium-based ionic liquids, which contain a flat, charge delocalised, yet non-aromatic cation, are not encompassed within the descriptor set used, so we were interested to compare how the ionic liquids described here performed as solvents for desulfurisation.

Three ionic liquids (**6**-NTf_2, **7**-NTf_2, and **9**-NTf_2) with –NH_2, –$NH(CH_3)$, and –$NH(C_2H_5)$ groups were tested for the extraction of DBT from dodecane as a model system using the procedures previously described.[32] The *S*-alkyl group was butyl in all three ionic liquids to remain comparable with the previous studies. DBT was extracted by all three ionic liquids, with **6**-NTf_2 removing 41.3% (std. dev. 0.7), whereas on adding an alkyl substituent to the nitrogens resulted in improved extraction, with **7**-NTf_2 removing 68.0% (std. dev. 0.3) and **9**-NTf_2 removing 64.1% (std. dev. 0.2) of the DBT present. When compared to the ionic liquids containing aromatic cations previously studied, the thiouroniums display extraction coefficients of comparable values. Most notably, **9**-[NTf_2] which is derived from diethylthiourea combines many good physical and rheological properties, simple preparation of the cations, and good extraction characteristics.

Conclusions

A range of *S*-alkylthiouronium ionic liquids accessible from relatively low cost readily available thioureas have been prepared and characterised. All the salts synthesised exhibited low melting points. All the bromides melted below 100 °C. Melting points and glass transition temperatures all show a general reduction on *N*-alkyl substitution, compared to the protonated thiouronium salts, and significantly lower melting points for bis{(trifluoromethyl)sulfonyl}imide anions compared to bromide. Monoalkylation of the *N*-sites of the cation reduces both melting and glass transition temperatures relative to the pentaalkyl analogues, although at a cost of a lower decomposition temperature, slightly reduced electrochemical window and an increase in viscosity. The physical properties (mp, T_g, T_{dec}, viscosity) and electrochemical windows are reasonable for many applications provided that basic conditions, under which thiouronium salts undergo hydrolysis, are avoided.

Experimental

Materials

Thioureas (thiourea, 1,3-dimethylthiourea, 1,3-diethylthiourea, and 1,3-tetramethylthiourea) and the alkylating agents (diethylsulfate, bromoethane, bromohexane, and bromooctane) were purchased from Aldrich and used as received, lithium bis{(trifluoromethyl)sulfonyl}imide was purchased from 3M. Initial alkylation of the thioureas either in toluene (dialkylsulfate) or ethanolic (bromoalkane) solution yielded thiouronium alkylsulfate and bromide salts in good yields. Anion metathesis of the water soluble alkylsulfate or bromide salts in water with lithium bis{(trifluoromethyl)sulfonyl}imide (Li[NTf_2]) gave the hydrophobic $[NTf_2]^-$ ionic liquids.

Synthesis

***S*-Methylthiouronium methylsulfate (1-$MeSO_4$).** Dimethylsulfate (16.2 g, 0.129 mol) was added dropwise to a slurry of thiourea (7.7 g, 0.129 mol) in toluene (50 cm^3) at 60 °C with the rate of addition controlled to maintain the reaction temperature at 60 ± 5 °C. After addition, the reaction mixture was stirred for 1 h, then allowed to cool to room temperature to give a biphasic mixture. The upper toluene layer was decanted off. The lower ionic liquid phase was washed with hexane (2 × 50 cm^3) and the remaining solvent was removed under reduced pressure at 60 °C to give a colourless liquid that solidified on standing at −15 °C: mp 36 °C (Found: C, 17.23; H, 5.37; N, 13.66; S, 31.57%. $[C_2H_7N_2S][CH_3SO_4]$ (mol. wt. 202.2) requires C, 17.82; H, 4.98; N, 13.85; S, 31.70%); δ_H (500 MHz, DMSO-d_6) 8.93 (br s, 4H, 2 × NH_2), 3.40 (3H, s, O-CH_3), 2.55 (3H, s, S-CH_3); δ_C (125 MHz, DMSO-d_6) 171.6 (SCN_2), 53.8 (O-CH_3), 13.6 (S-CH_3).

***S*-Ethylthiouronium bromide (2-Br).** Thiourea (4.09 g, 0.054 mol) was dissolved in ethanol with warming and bromoethane (6.15 g, 0.056 mol, 1.05 eq.) was added and the homogeneous solution heated at reflux overnight. Ethanol and unreacted bromoethane were removed under reduced pressure at 60 °C and the product was then dried *in vacuo* to yield **2**-Br as a clear, colourless oil that crystallised on cooling to room temperature as a colourless solid, mp 87 °C (Found: C, 19.67; H, 4.64; N, 15.4; S, 17.3; Br, 42.46%. $[C_3H_9N_2S]Br$ (mol. wt. 185.09) requires C, 19.47; H, 4.90; N, 15.14; S, 17.32; Br, 43.17%); δ_H (500 MHz, DMSO-d_6) 8.99 (4H, s), 3.15 (2H, q), 1.26 (3H, t); δ_C (125 MHz, DMSO-d_6) 169.6 (SCN_2), 24.6, 14.0 (terminal CH_3); ESI-MS (CH_3CN/H_2O) +ve mode: 105.0 (100%, $[C_3H_9N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Ethylthiouronium ethylsulfate (2-$EtSO_4$).** **2**-$EtSO_4$ was prepared using the same procedure as **1**-$MeSO_4$ from thiourea (15.8 g, 0.208 mol) and diethylsulfate (33.0 g, 1.05 eq.) in toluene (150 cm^3) as a colourless liquid after decanting the upper toluene phase, washing with hexane (2×) and drying under reduced pressure at 60 °C and finally *in vacuo*. A small sample was cooled to −15 °C overnight, yielding colourless crystals which were used to seed the bulk liquid, which then slowly crystallised as a hygroscopic colourless crystalline mass at 0 °C and melted on standing at room temperature. (Found: C, 23.75; H, 5.70; N, 11.95; S, 28.19%. $[C_3H_9N_2S][C_2H_5SO_4]$ (mol. wt. 230.3) requires C, 26.08; H, 6.13; N, 12.16; S, 27.84%); δ_H (500 MHz, DMSO-d_6) 9.02, 8.94 (4H, br d, J^1_{NH} = 38.5 Hz, 2 × NH_2), 3.77 (2H, q, O-CH_2CH_3), 3.14 (2H, q, S-CH_2CH_3), 1.25 (3H, t, O-CH_2CH_3), 1.11 (3H, t, S-CH_2CH_3); δ_C (125 MHz, DMSO-d_6) 170.2 (SCN_2), 62.0 (O-CH_2CH_3), 25.0 (S-CH_2CH_3), 15.4 (O-CH_2CH_3), 14.4 (S-CH_2CH_3); ESI-MS (CH_3CN/H_2O) +ve mode: 105.0 (100%, $[C_3H_9N_2S]^+$).

***S*-Ethylthiouronium bis{(trifluoromethyl)sulfonyl}imide (2-NTf_2).** The metathesis of **2**-Br (4.80 g, 0.026 mol) in water with Li[NTf_2] (7.44 g, 0.026 mol) in water resulted in the separation of **2**-NTf_2 as a colourless liquid, which was washed with water and dried *in vacuo*, mp 27 °C (Found: C, 15.63; H, 2.41; N, 11.11; S, 25.15%. $[C_3H_9N_2S][N(SO_2CF_6)_2]$ (mol. wt. 385.33) requires C, 15.59; H, 2.35; N, 10.91; S, 24.96%); δ_H (500 MHz, DMSO-d_6) 8.93 (4H, s), 3.13 (2H, q), 1.26 (3H, t); δ_C (125 MHz, DMSO-d_6) 169.7 (SCN_2), 119.4 (q, J_{CF} = 320 Hz), 24.7, 13.9 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 105.0 (100%, $[C_3H_9N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Ethyl-*N*,*N*′-dimethylthiouronium bromide (3-Br).** **3**-Br was prepared using the same procedure as **2**-Br from 1,3-dimethylthiourea (4.89 g, 0.047 mol) and bromoethane (5.37 g, 0.049 mol, 1.05 eq.) heated at reflux overnight. After removal of solvent and excess bromoethane, the product was dried *in vacuo* to yield **3**-Br as a colourless crystalline solid, mp 62 °C (Found: C, 28.20; H, 5.93; N, 14.01; S, 15.01; Br, 36.63%. $[C_5H_{13}N_2S]Br$ (mol. wt. 213.14) requires C, 28.18; H, 6.15; N, 13.14; S, 15.04; Br, 37.49%); δ_H (500 MHz, DMSO-d_6) 9.03 (2H, s), 3.24 (2H, q), 2.95 (6H, d), 1.28 (3H, t) δ_C (125 MHz, DMSO-d_6) 166.5 (SCN_2), 30.7 (N-C), 25.2, 13.7 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 133.1 (100%, $[C_5H_{13}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Ethyl-*N*,*N*′-dimethylthiouronium ethylsulfate (3-EtSO$_4$).** **3**-EtSO$_4$ was prepared using the same procedure as **1**-MeSO$_4$ from 1,3-dimethylthiourea (15.8 g, 0.208 mol) and diethylsulfate (33.0 g, 1.05 eq.) in toluene (100 cm^3), heating overnight at 60 °C. A homogeneous solution in toluene was obtained in contrast to **2**-EtSO$_4$. The solvents were removed under reduced pressure at 60 °C to give a colourless liquid which slowly crystallised on storing at −15 °C: mp ≈ 32 °C (Found: C, 32.06; H, 7.65; N, 10.44; S, 24.80%. $[C_5H_{13}N_2S][C_2H_5SO_4]$ (mol. wt. 258.4) requires C, 32.54; H, 7.02; N, 10.84; S. 24.82%); δ_H (500 MHz, DMSO-d_6) 8.95 (2H, b, 2 × N*H*), 3.75 (q, 2H, O-C*H*$_2$-CH$_3$), 3.20 (q, 2H, S-C*H*$_2$-CH$_3$), 2.94 (6H, d, J^2_{NH} = 17.4 Hz, 2 × N-C*H*$_3$), 1.29 (3H, t, OCH$_2$-C*H*$_3$), 1.11 (3H, t, SCH$_2$-C*H*$_3$); δ_C (125 MHz, DMSO-d_6) 167.1 (S*C*N$_2$), 61.6 (O-*C*H$_2$), 31.1 (N-*C*H$_3$), 31.0 (N-*C*H$_3$), 25.4 (S-*C*H$_2$), 15.5 (OCH$_2$-*C*H$_3$), 14.2 (SCH$_2$-*C*H$_3$).

***S*-Ethyl-*N*,*N*′-dimethylthiouronium bis{(trifluoromethyl)sulfonyl}imide (3-NTf$_2$).** The metathesis of **3**-Br (4.83 g, 0.023 mol) in water with Li[NTf$_2$] (6.5 g, 0.023 mol) in water resulted in the separation of **3**-NTf$_2$ as a colourless liquid, which was washed with water and dried *in vacuo*, mp 19 °C (Found: C, 20.41; H, 2.85; N, 10.55; S, 23.48%. $[C_5H_{13}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 413.38) requires C, 20.34; H, 3.17; N, 10.16; S, 23.27%); δ_H (500 MHz, DMSO-d_6) 8.96 (2H, s), 3.18 (2H, q), 2.93 (6H, d), 1.28 (3H, t); δ_C (125 MHz, DMSO-d_6) 166.8 (SCN_2), 119.4 (q, J_{CF} = 320 Hz), 30.6 (N-C) 25.1, 13.6 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 133.1 (100%, $[C_5H_{13}N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Ethyl-*N*,*N*′-tetramethylthiouronium bromide (4-Br).** **4**-Br was prepared using the same procedure as **2**-Br from 1,1,3,3-tetramethylthiourea (5.48 g, 0.041 mol) dissolved in ethanol at 60 °C and bromoethane (4.74 g, 0.044 mol, 1.05 eq.) as a colourless crystalline solid, mp 92 °C (Found: C, 34.64; H, 7.14; N, 11.61; S, 12.88; Br, 33.59%. $[C_7H_{17}N_2S]Br$ (mol. wt. 241.2) requires C, 34.86; H, 7.10; N, 11.61; S, 13.29; Br, 33.13%); δ_H (500 MHz, DMSO-d_6) 3.25 (12H, s), 3.06 (2H, q), 1.23 (3H, t); δ_C (125 MHz, DMSO-d_6) 173.7 (SCN_2), 43.4 (N-C) 28.4, 14.6 (terminal CH_3). ESI-MS (CH_3CN/H_2O); +ve mode: 161.1 (100%, $[C_7H_{17}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Ethyl-*N*,*N*′-tetramethylthiouronium bis{(trifluoromethyl)sulfonyl}imide (4-NTf$_2$).** The metathesis of **4**-Br (5.46 g, 0.023 mol) in water with Li[NTf$_2$] (6.5 g, 0.023 mol) in water resulted in the separation of **4**-NTf$_2$ as a colourless liquid, which was washed with water and dried *in vacuo* (Found: C, 24.69; H, 3.47; N, 9.86; S, 22.04%. $[C_7H_{17}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 441.44) requires C, 24.49; H, 3.88; N, 9.52; S, 21.79%); δ_H (500 MHz, DMSO-d_6) 3.25 (12H, s), 3.06 (2H, q), 1.23 (3H, t); δ_C (125 MHz, DMSO-d_6) 173.9 (SCN_2), 119.4 (q, J_{CF} = 320 Hz), 43.2 (N-C), 28.3, 14.5 (terminal CH_3). ESI-MS (CH_3CN/H_2O); +ve mode: 161.1 (100%, $[C_7H_{17}N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Ethyl-*N*,*N*′-diethylthiouronium bromide (5-Br).** **5**-Br was prepared using the same procedure as **2**-Br from 1,3-diethylthiourea (5.48 g, 0.041 mol) dissolved in ethanol at 60 °C and bromoethane (4.74 g, 0.044 mol, 1.05 eq.) as a colourless liquid which slowly solidified on standing, mp 40 °C (Found: C, 34.22; H, 6.86; N, 10.62; S, 13.03; Br, 32.51%. $[C_7H_{17}N_2S]Br$ (mol. wt. 241.2) requires C, 34.86; H, 7.1; N, 11.61; S, 13.29; Br, 33.13%); δ_H (500 MHz, DMSO-d_6) 9.34 (1H, s), 9.06 (1H, s), 3.43 (4H, m), 3.32 (2H, q), 1.25 (3H, t), 1.15 (6H, t); δ_C (125 MHz, DMSO-d_6) 164.4 (SCN_2), 25.9 (N-C), 14.6, 13.7, 13.1 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 161.1 (100%, $[C_7H_{17}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Ethyl-*N*,*N*′-diethylthiouronium ethylsulfate (5-EtSO$_4$).** **5**-EtSO$_4$ was prepared using the same procedure as **3**-EtSO$_4$ from 1,3-diethylthiourea and diethylsulfate in toluene yielding a homogeneous reaction solution. Toluene and unreacted excess diethylsulfate were removed under reduced pressure at 60 °C, and the resulting colourless ionic liquid was washed twice with hexane, and then finally dried *in vacuo* to yield the product as a colourless liquid. (Found: C, 37.63; H, 7.91; N, 9.29; S, 22.10%. $[C_7H_{17}N_2S][C_2H_5SO_4]$ (mol. wt. 286.4) requires C, 37.74; H, 7.74; N, 9.78; S, 22.35%); δ_H (500 MHz, DMSO-d_6) 9.14, 8.86 (2H, d, J^1_{NH} = 140 Hz, 2 × N*H*), 3.76 (4H, q, O-C*H*$_2$CH$_3$), 3.41 (4H, m, 2 × N-C*H*$_2$CH$_3$), 3.24 (2H, q, S-C*H*$_2$CH$_3$), 1.27 (3H, t, O-CH$_2$C*H*$_3$), 1.16 (6H, t, 2 × N-CH$_2$C*H*$_3$), 1.11 (3H, t, S-CH$_2$C*H*$_3$); δ_C (125 MHz, DMSO-d_6) 164.4 (SCN_2), 25.9 (N-C), 14.6, 13.7, 13.1 (terminal CH_3).

***S*-Ethyl-*N*,*N*′-diethylthiouronium bis{(trifluoromethyl)sulfonyl}imide (5-NTf$_2$).** The metathesis of **5**-Br (4.83 g, 0.023 mol) in water with Li[NTf$_2$] (6.5 g, 0.023 mol) resulted in the separation of **5**-NTf$_2$ as a colourless liquid, mp not detected (Found: C, 24.54; H, 3.78; N, 9.97; S, 21.8%. $[C_7H_{17}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 441.44) requires C, 24.49; H, 3.88; N, 9.52; S, 21.79%); δ_H (500 MHz, DMSO-d_6) 9.13 (1H, s), 8.87 (1H, s), 3.38 (4H, m), 3.22 (2H, q), 1.28 (3H, t), 1.16 (6H, t); δ_C (125 MHz, DMSO-d_6) 164.8 (SCN_2), 119.4 (q, J_{CF} = 320 Hz), 25.7 (N-C) 14.4, 13.6, 12.9 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 161.1 (100%, $[C_7H_{17}N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Butyl-thiouronium bromide (6-Br).** **6**-Br was prepared using the same procedure as **2**-Br from thiourea (17.0 g, 0.223 mol) and bromobutane (32 g, 0.234 mol) in ethanol heated at 60 °C for 48 h. Ethanol and excess bromobutane were removed under reduced pressure at 70 °C, and then *in vacuo* to yield a colourless crystalline solid, mp 83 °C (Found: C, 28.34; H, 5.82; N, 13.28; S, 14.80%. $[C_4H_{13}N_2S]Br$ (mol. wt. 213.1) requires C, 28.18; H, 6.15; N, 13.14; S, 15.04%); δ_H (500 MHz, $CDCl_3$) 7.42, 7.22 (br d, 2H, J_{NH} = 102 Hz, 2 × N*H*), 3.16 (t, 2H, S-CH_2), 1.51 (2H, q, SCH_2-CH_2), 1.34 (2H, q, SCH_2CH_2-CH_2), 0.85 (3H, t, -CH_3); δ_C (75 MHz, $CDCl_3$) 170.3 (S*C*N_2), 119.45 (J_{CF} = 320 Hz, -*C*F_3), 30.9, 29.5, 20.7, 12.9 (S-butyl chain). ESI-MS (CH_3CN/H_2O); +ve mode: 133.1 (100%, $[C_5H_{13}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Butyl-thiouronium bis{(trifluoromethyl)sulfonyl}imide (6-[NTf$_2$]).** The metathesis of **6**-Br (16.68 g, 0.04 mol) in water (100 cm^3) with Li[NTf$_2$] (14.4 g, 0.05 mol) resulted in the separation of **6**-NTf$_2$ as a colourless liquid which was isolated, dried under reduced pressure then *in vacuo*, and then stored at 4 °C overnight, resulting in solidification as a colourless crystalline mass, mp 49 °C (Found: C, 20.19; H, 3.50; N, 9.03; S, 23.39%. $[C_4H_{13}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 413.3) requires C, 20.34; H, 3.17; N, 10.17; S, 23.27%); δ_H (500 MHz, $CDCl_3$) 7.50, 6.82 (4H, br d, J_{NH} = 340 Hz, 2 × NH_2), 3.10 (2H, t, *J* = 7.3 Hz, S-CH_2), 1.73 (2H, q, *J* = 7.3 Hz, SCH_2-CH_2), 1.45 (2H, q, *J* = 7 Hz, SCH_2CH_2-CH_2), 0.92 (3H, t, *J* = 7.1 Hz, -CH_3). ESI-MS (CH_3CN/H_2O); +ve mode: 133.1 (100%, $[C_5H_{13}N_2S]^+$); −ve mode: 279.9 (100%, $[N(SO_2CF_3)_2]^-$).

***S*-Butyl-*N*,*N*′-dimethylthiouronium bromide (7-Br).** **7**-Br was prepared using the same procedure as **2**-Br from 1,3-dimethylthiourea (20 g, 0.2 mol) and bromobutane (32.7 g, 0.23 mol) in ethanol, heating at 60 °C overnight. The solvent and excess bromobutane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a colourless liquid that crystallised slowly on standing at room temperature as a colourless solid, mp 60 °C (Found: C, 34.63; H, 7.28; N, 11.33; S, 13.04%. $[C_7H_{17}N_2S]Br$ (mol. wt. 241.2) requires C, 34.86; H, 7.10; N, 11.61; S, 13.29%); δ_H (500 MHz, DMSO-d_6) 9.05 (b, 2H, 2 × N*H*), 3.23 (2H, t, S-CH_2), 2.95 (6H, d, J^2_{NH} = 11.6 Hz, 2 × N-CH_3), 1.60 (2H, m, SCH_2-CH_2), 1.40 (2H, m, SCH_2CH_2-CH_2), 0.90 (3H, t, -CH_3); δ_C (125 MHz, DMSO-d_6) 167.2, 31.2, 30.7, 30.4, 21.4, 13.7. ESI-MS (CH_3CN/H_2O); +ve mode: 161.1 (100%, $[C_7H_{17}N_2S]^+$); −ve mode: 78.9 (100%), $^{79}Br^-$; 80.9 (100%), $^{81}Br^-$).

***S*-Butyl-*N*,*N*′-dimethylthiouronium (7-NTf$_2$).** The metathesis of **7**-Br (24.6 g, 0.102 mol) in water (50 cm^3) with Li[NTf$_2$] (29.0 g, 0.101 mol) in water (25 cm^3) with stirring resulted in the separation of **7**-NTf$_2$ as a dense colourless liquid (33.8 g, 75% isolated yield) (Found: C, 24.85; H, 4.22; N, 9.63; S, 22.13%. $[C_7H_{17}N_2S][N(SO_2CF_3)]$ (mol. wt. 441.4) requires C, 24.49; H, 3.88; N, 9.52; S, 21.79%); δ_H (500 MHz, $CDCl_3$) 7.42, 7.22 (br d, 2H, J_{NH} = 102 Hz, 2 × N*H*), 3.11 (m, 8H, 2 × N-CH_3 + S-CH_2), 1.69 (2H, q, SCH_2-CH_2), 1.47 (2H, q, SCH_2CH_2-CH_2), 0.96 (3H, t, -CH_3).

***S*-Butyl-*N*,*N*′-tetramethylthiouronium bromide (8-Br).** **8**-Br was prepared from 1,3-tetramethylthiourea (9.82 g, 0.074 mol) and bromobutane (10.7 g, 0.078 mol) with heating at 80 °C overnight. The solvent and excess bromobutane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a colourless crystalline solid, mp 82 °C (Found: C, 39.59; H, 7.30; N, 10.79; S, 11.15%. $[C_9H_{21}N_2S]Br$ (mol. wt. 269.2) requires C, 40.15; H, 7.86; N, 10.40; S, 11.91%). δ_C (125 MHz, $CDCl_3$-d_6) 175.81, 44.86, 35.04, 31.37, 21.78, 13.52. ESI-MS (CH_3CN/H_2O); +ve mode: 189.1 (100%, $[C_9H_{21}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Butyl-*N*,*N*′-tetramethylthiouronium bis{(trifluoromethyl)-sulfonyl}imide 8-NTf$_2$.** The metathesis of **8**-Br (11.5 g, 0.043 mol) and Li[NTf$_2$] (12.2 g, 0.043 mol) in water (50 cm^3) resulted in the separation of **8**-NTf$_2$ as a pale yellow liquid (Found: C, 28.17; H, 4.96; N, 8.77; S, 20.12%. $[C_9H_{21}N_2S][N(SO_2CF_3]_2]$ (mol. wt. 469.5) requires C, 28.14; H, 4.51; N, 8.95; S, 20.49%); δ_H (500 MHz, $CDCl_3$) 3.30 (12H, s), 2.98 (2H, t, S-CH_2), 1.66 (2H, q, SCH_2-CH_2), 1.43 (2H, q, SCH_2CH_2-CH_2), 0.94 (3H, t, -CH_3). ESI-MS (CH_3CN/H_2O); +ve mode: 189.1 (100%, $[C_9H_{21}N_2S]^+$); −ve mode: 279.9 (100%, $[N(SO_2CF_3)_2]^-$).

***S*-Butyl-*N*,*N*′-diethylthiouronium bromide (9-Br).** **9**-Br was prepared from 1,3-diethylthiourea (39.8 g, 0.3 mol) and bromobutane (41.97 g, 0.3 mol) with heating at 80 °C overnight as a viscous liquid (Found: C, 39.89; H, 7.88; N, 10.16; S, 11.33%. $[C_9H_{21}N_2S]Br$ (mol. wt. 269.2) requires C, 40.15; H, 7.86; N, 10.40; S, 11.91%). δ_C (125 MHz, DMSO-d_6) 165.1, 31.4, 30.6, 21.7, 15.1, 13.7, 13.6. ESI-MS (CH_3CN/H_2O); +ve mode: 189.1 (100%, $[C_9H_{21}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Butyl-*N*,*N*′-diethylthiouronium bis{(trifluoromethyl)sulfonyl}-imide 9-NTf$_2$.** The metathesis of **9**-Br (23.5 g, 0.087 mol) and Li[NTf$_2$] (25 g) in water (150 cm^3) resulted in the separation of **9**-NTf$_2$ as a pale yellow liquid (Found: C, 29.98; H, 4.91; N, 9.36; S, 18.83%. $[C_9H_{21}N_2S][N(SO_2CF_3]_2]$ (mol. wt. 469.5) requires C, 28.14; H, 4.51; N, 8.95; S, 20.49%); δ_H (500 MHz, $CDCl_3$) 7.62, 7.17 (2H, br d, J_{NH} = 225 Hz, 2 × N*H*), 3.53 (4H, q, 2 × N-CH_2), 3.16 (2H, t, S-CH_2), 1.71 (2H, q, SCH_2-CH_2), 1.35 (2H, q, SCH_2CH_2-CH_2), 1.33 (t, 6H, 2 × NCH_2-CH_3), 0.96 (3H, t, -CH_3). ESI-MS (CH_3CN/H_2O); +ve mode: 189.1 (100%, $[C_9H_{21}N_2S]^+$); −ve mode: 279.9 (100%, $[N(SO_2CF_3)_2]^-$).

***S*-Hexylthiouronium bromide (10-Br).** **10**-Br was prepared using the same procedure as **2**-Br from thiourea (3.16 g, 0.042 mol) and bromohexane (7.19 g, 0.044 mol) in ethanol, heating at 60 °C overnight. The solvent and excess bromohexane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a colourless liquid that crystallised on cooling to room temperature as a colourless solid, mp 86 °C (Found: C, 34.8; H, 6.8; N, 11.1; S, 13.25; Br, 34.2%. $[C_7H_{17}N_2S]Br$ (mol. wt. 241.2) requires C, 34.86; H, 7.10; N, 11.61; S, 13.29; Br, 33.13%); δ_H (500 MHz, DMSO-d_6) 8.99 (4H, s), 3.13 (2H, t), 1.58 (2H, m), 1.3 (6H, m), 0.86 (3H, t). δ_C (125 MHz, DMSO-d_6) 169.8 (SCN_2), 30.4, 30.0, 28.2, 27.3, 21.8, 13.8 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 161.1 (100%, $[C_7H_{17}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Hexylthiouronium bis{(trifluoromethyl)sulfonyl}imide (10-NTf$_2$).** The metathesis of **10**-Br (5.46 g, 0.023 mol) in water with Li[NTf$_2$] (6.5 g, 0.023 mol) resulted in the separation of **10**-NTf$_2$ as a colourless liquid. (Found: C, 24.8; H, 3.82; N, 9.92; S, 22.08%. $[C_7H_{17}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 441.44) requires C, 24.49; H, 3.88; N, 9.52; S, 21.79%); δ_H (500 MHz, DMSO-d_6) 8.94 (4H, s), 3.12 (2H, t), 1.59 (2H, m), 1.28 (6H, m), 0.86 (3H, t); δ_C (125 MHz, DMSO-d_6) 169.8 (SCN_2), 119.4 (q, J_{CF} = 320 Hz), 30.4, 30.0, 28.2, 27.3, 21.8, 13.7 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 161.1 (100%, $[C_7H_{17}N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Hexyl-*N*,*N*′-dimethylthiouronium bromide (11-Br).** **11**-Br was prepared using the same procedure as **2**-Br from 1,3-dimethylthiourea (3.87 g, 0.037 mol) and bromohexane (6.44 g, 0.039 mol) in ethanol, heating at 60 °C overnight. The solvent and excess bromohexane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a colourless liquid that crystallised on cooling to room temperature as a colourless solid, mp 95 °C (Found: C, 40.25; H, 8.07; N, 10.67; S, 11.93; Br, 30.22%. $[C_9H_{21}N_2S]Br$ (mol. wt. 269.25) requires C, 40.15; H, 7.86; N, 10.40; S, 11.91; Br, 29.68%); δ_H (500 MHz, DMSO-d_6) 9.18 (1H, s), 9.02 (1H, s), 3.26 (2H, t), 2.94 (6H, s), 1.59 (2H, m), 1.3 (6H, m), 0.85 (3H, t); δ_C (125 MHz, DMSO-d_6) 166.8 (SCN_2), 30.6 (N-C), 30.4, 27.8, 27.4, 21.8, 13.7 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 189.1 (100%, $[C_9H_{21}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Hexyl-*N*,*N*′-dimethylthiouronium bis{(trifluoromethyl)sulfonyl}imide (11-NTf$_2$).** The metathesis of **11**-Br (5.74 g, 0.021 mol) in water with Li[NTf$_2$] (6.12 g, 0.021 mol) resulted in the separation of **11**-NTf$_2$ as a colourless liquid (Found: C, 28.19; H, 4.29; N, 9.32; S, 20.69%. $[C_9H_{21}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 469.49) requires C, 28.14; H, 4.51; N, 8.95; S, 20.49%; δ_H (500 MHz, DMSO-d_6) 8.95 (2H, s), 3.16 (2H, t), 2.93 (6H, d), 1.61 (2H, m), 1.29 (6H, m), 0.86 (3H, t); δ_C (125 MHz, DMSO-d_6) 166.8 (SCN_2), 119.4 (q, J_{CF} = 320 Hz), 30.6 (N-C), 30.4, 27.8, 27.4, 21.8, 13.7 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 189.1 (100%, $[C_9H_{21}N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Hexyl-*N*,*N*′-tetramethylthiouronium bromide (12-Br).** **12**-Br was prepared using the same procedure as **2**-Br from 1,3-tetramethylthiourea (4.45 g, 0.034 mol) and bromohexane (5.83 g, 0.035 mol) in ethanol, heating at 60 °C overnight. The solvent and excess bromohexane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a colourless liquid that crystallised on cooling to room temperature as a colourless solid, mp 73 °C (Found: C, 43.96; H, 8.71; N, 9.66; S, 10.73; Br, 25.51%. $[C_{11}H_{25}N_2S]Br$ (mol. wt. 297.30) requires C, 44.44; H, 8.48; N, 9.42; S, 10.78; Br, 26.88%; δ_H (500 MHz, DMSO-d_6) 3.23 (12H, s), 3.03 (2H, t), 1.58 (2H, m), 1.29 (6H, m), 0.87 (3H, t); δ_C (125 MHz, DMSO-d_6) 174.1 (SCN_2), 43.3 (N-C), 33.7, 30.5, 29.0, 27.4, 21.8, 13.7 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 217.2 (100%, $[C_{11}H_{25}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Hexyl-*N*,*N*′-tetramethylthiouronium bis{(trifluoromethyl)sulfonyl}imide (12-NTf$_2$).** The metathesis of **12**-Br (5.98 g, 0.02 mol) in water with Li[NTf$_2$] (5.78 g, 0.02 mol) resulted in the separation of **12**-NTf$_2$ as a colourless liquid (Found: C, 31.36; H, 5.26; N, 8.27; S, 19.32%. $[C_{11}H_{25}N_2S][N(SO_2CF_3)_3]$ (mol. wt. 497.55) requires C, 31.38; H, 5.06; N, 8.45; S, 19.33%); δ_H (500 MHz, DMSO-d_6) 3.23 (12H, s), 3.03 (2H, t), 1.58 (2H, m), 1.29 (6H, m), 0.87 (3H, t); δ_C (125 MHz, DMSO-d_6) 174.1 (SCN_2), 119.4 (q, J_{CF} = 320 Hz), 43.3 (N-C), 33.7, 30.5, 29.0, 27.5, 21.8, 13.7 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 217.2 (100%, $[C_{11}H_{25}N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Hexyl-*N*,*N*′-diethylthiouronium bromide (13-Br).** **13**-Br was prepared using the same procedure as **2**-Br from 1,3-diethylthiourea (4.45 g, 0.034 mol) and bromohexane (5.83 g, 0.035 mol) in ethanol, heating at 60 °C overnight. The solvent and excess bromohexane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a colourless liquid that crystallised on cooling to room temperature as a colourless liquid that solidified on standing at room temperature, mp 49 °C (Found: C, 44.33; H, 8.05; N, 8.97; S, 10.82; Br, 27.2%. $[C_{11}H_{25}N_2S]Br$ (mol. wt. 297.30) requires C, 44.44; H, 8.48; N, 9.42; S, 10.78; Br, 26.88%); δ_H (500 MHz, DMSO-d_6) 9.29 (1H, s), 9.03 (1H, s), 3.43 (4H, m), 3.27 (2H, t), 1.59 (2H, m), 1.28 (12H, m), 0.85 (3H, t); δ_C (125 MHz, DMSO-d_6) 164.7 (SCN_2), 31.2 (N-C) 30.4, 28.0, 27.3, 21.8, 14.6, 13.7, 13.1 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 217.2 (100%, $[C_{11}H_{25}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Hexyl-*N*,*N*′-diethylthiouronium bis{(trifluoromethyl)sulfonyl}imide (13-NTf$_2$).** The metathesis of **13**-Br (5.98 g, 0.02 mol) in water with Li[NTf$_2$] (5.77 g, 0.02 mol) resulted in the separation of **13**-NTf$_2$ as a colourless liquid (Found: C, 31.44; H, 4.86; N, 8.69; S, 19.04%. $[C_{11}H_{25}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 497.55) requires C, 31.38; H, 5.06; N, 8.45; S, 19.29%); δ_H (500 MHz, DMSO-d_6) 9.13 (1H, s), 8.88 (1H, s), 3.38 (4H, m), 3.2 (2H, t), 1.6 (2H, m), 1.28 (6H, m) 1.16 (6H, t), 0.86 (3H, t); δ_C (125 MHz, DMSO-d_6) 165.0 (SCN_2), 119.4 (q, J_{CF} = 320 Hz), 31.0 (N-C), 30.4, 27.9, 27.3, 21.8, 14.5, 13.7, 13.0 (terminal CH_3). ESI-MS (CH_3CN/H_2O); +ve mode: 217.2 (100%, $[C_{11}H_{25}N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Octylthiouronium bromide (14-Br).** **14**-Br was prepared using the same procedure as **2**-Br from thiourea (18.8 g, 0.194 mol) and bromooctane (37.5 g, 0.194 mol) in ethanol (100 cm^3) heating at 60 °C for 24 h. The solvent and excess bromohexane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a colourless liquid that crystallised on cooling to room temperature as a colourless liquid that solidified on standing at room temperature, mp 96 °C (Found: C, 39.94; H, 7.80; N, 10.10; S, 11.50%.

$[C_9H_{21}N_2S]Br$ (mol. wt. 269.2) requires C, 40.15; H, 7.86, N, 10.40, S, 11.91%); δ_H (500 MHz, DMSO-d_6) 9.07, 8.99 (4H, br d, 2 × NH_2), 3.15 (2H, t, S-CH_2), 1.57 (2H, q, SCH_2-CH_2), 1.35 (2H, m, S-CH_2CH_2-CH_2), 1.25 (8H, m, -$(CH_2)_4$-), 0.85 (3H, t, -CH_3); δ_C (125 MHz, DMSO-d_6) 170.3, 31.5, 30.5, 28.9, 28.7, 28.1, 22.4, 14.3. ESI-MS (CH_3CN/H_2O); +ve mode: 189.1 (100%, $[C_9H_{21}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Octylthiouronium bis{(trifluoromethyl)sulfonyl}imide (14-NTf_2).** The metathesis of **14**-Br (17.0 g, 0.063 mol) in water with Li[NTf_2] (18.1 g, 0.063 mol) resulted in the separation of **14**-NTf_2 as a colourless liquid (Found: C, 27.73; H, 4.64; N, 8.52; S, 20.19%. $[C_9H_{21}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 469.5) requires C, 28.14; H, 4.51, N, 8.95, S, 20.49%); δ_H (500 MHz, $CDCl_3$) 7.70, 6.98 (4H, br d, J_{NH} = 360 Hz, 2 × NH_2), 3.08 (2H, t, J = 7.3 Hz, S-CH_2), 1.68 (2H, q, J = 7.3 Hz, SCH_2-CH_2), 1.40 (2H, q, J = 7 Hz, SCH_2CH_2-CH_2), 1.29 (8H, br m, -$(CH_2)_4$-), 0.88 (3H, t, J = 7.1 Hz, -CH_3); δ_C (125 MHz, $CDCl_3$) 173.1 (SCN_2), 119.9 (q, J_{CF} = 320 Hz), 32.0 (N-C), 31.8, 29.3, 29.2, 28.7, 28.2, 23.0, 14.4 (terminal CH_3). ESI-MS (CH_3CN/H_2O); +ve mode: 189.1 (100%, $[C_9H_{21}N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Octyl-*N*,*N*′-dimethylthiouronium bromide (15-Br).** **15**-Br was prepared using the same procedure as **2**-Br from 1,3-dimethylthiourea (15.0 g, 0.15 mol) and bromooctane (32.0 g, 0.166 mol) in ethanol (75 cm^3) heating at 60 °C for 24 h. The solvent and excess bromohexane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a colourless liquid that crystallised on cooling to room temperature as a colourless liquid that solidified on standing at room temperature, mp 54 °C (Found: C, 44.61; H, 8.17; N, 9.13; S, 10.44%. $[C_{11}H_{25}N_2S]Br$ (mol. wt. 297.3) requires C, 44.44; H, 8.48; N, 9.42; S, 10.78%); δ_H (500 MHz, DMSO-d_6) 9.13, 9.94 (2H, br d, J_{NH} = 90 Hz, 2 × NH), 3.22 (2H, m, S-CH_2), 2.95 (6H, d, J^2_{NH} = 12.7 Hz, 2 × NCH_3), 1.61 (2H, m, SCH_2-CH_2), 1.37 (2H, m, SCH_2CH_2-CH_2), 1.26 (8H, m, -$CH_2)_4$-), 0.87 (3H, t, -CH_3); δ_C (125 MHz, DMSO-d_6) 167.2 (SCN_2), 31.5, 31.2, 31.1, 31.0, 28.9, 28.7, 28.4, 28.2, 22.4, 14.3 (terminal CH_3). ESI-MS (CH_3CN/H_2O); +ve mode: 217.2 (100%, $[C_{11}H_{25}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Octyl-*N*,*N*′-dimethylthiouronium bis{(trifluoromethyl)-sulfonyl}imide (15-NTf_2).** The metathesis of **15**-Br (12.5 g, 0.042 mol) in water (75 cm^3) with Li[NTf_2] (12.5 g, 0.043 mol) resulted in the separation of **15**-NTf_2 as a pale yellow liquid (17.8 g, 85% isolated yield). (Found: C, 31.02; H, 5.75; N, 8.41; S, 19.18%. $[C_{11}H_{25}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 497.5) requires C, 31.28; H, 5.06, N, 8.45, S, 19.33%); δ_H (500 MHz, DMSO-d_6) 7.43, 7.22 (2H, br d, J_{NH} = 105 Hz, 2 × NH), 3.11 (m, 8H, 2 × N-CH_3 + S-CH_2), 1.71 (2H, q, SCH_2-CH_2), 1.33 (2H, q, SCH_2CH_2-CH_2), 1.31 (8H, m, -$(CH_2)_4$-), 0.88 (3H, t, J = 7.2 Hz, -CH_3).

***S*-Octyl-1,1,3,3-tetramethylthiouronium bromide (16-Br).** **16**-Br was prepared using the same procedure as **2**-Br from 1,1,3,3-tetramethylthiourea (4.06 g, 0.031 mol) and bromooctane (6.23 g, 0.032 mol) ethanol (100 cm^3) heating at 60 °C for 24 h. The solvent and excess bromohexane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a colourless liquid that crystallised on cooling to room temperature as a colourless liquid that solidified on standing at room temperature, mp 79 °C (Found: C, 47.15; H, 9.2; N, 8.73; S, 9.81; Br, 24.41%. $[C_{13}H_{29}N_2S]Br$ (mol. wt. 325.36) requires C, 47.88; H, 8.98; N, 8.61; S, 9.86; Br, 24.56%); δ_H (500 MHz, DMSO-d_6) 3.23 (12H, s), 3.02 (2H, t), 1.58 (2H, t), 1.25 (10H, m), 0.86 (3H, t); δ_C (125 MHz, DMSO-d_6) 174.0 (SCN_2), 43.4 (N-C), 33.7, 31.1, 29.1, 28.3, 27.8, 22.0, 13.9 (terminal CH_3); ESI-MS (CH_3CN/H_2O); +ve mode: 245.2 (100%, $[C_{13}H_{29}N_2S]^+$); −ve mode: 78.9 (100%, $[Br]^-$).

***S*-Octyl-*N*,*N*′-tetramethylthiouronium bis{(trifluoromethyl)-sulfonyl}imide (16-NTf_2).** The metathesis of **16**-Br (6.19 g, 0.019 mol) in water (75 cm^3) with Li[NTf_2] (5.46 g, 0.019 mol) resulted in the separation of **16**-NTf_2 as a colourless liquid (Found: C, 34.61; H, 5.49; N, 7.92; S, 18.80%. $[C_{12}H_{29}N_2S][N(SO_2CF_3)_2]$ (mol. wt. 525.6) requires C, 34.28; H, 5.56; N, 8.00; S, 18.30%); δ_H (500 MHz, DMSO-d_6) 3.23 (12H, s), 3.02 (2H, t), 1.58 (2H, t), 1.25 (10H, m), 0.86 (3H, t); δ_C (125 MHz, DMSO-d_6) 174.22 (SCN_2), 119.4 (q, J_{CF} = 320 Hz), 43.3 (N-C), 33.7, 31.1, 29.1, 28.3, 27.8, 21.9, 13.8 (terminal CH_3). ESI-MS (CH_3CN/H_2O); +ve mode: 245.2 (100%, $[C_{13}H_{29}N_2S]^+$); −ve mode: 279.9 (100%, $[C_2NO_4F_6S_2]^-$).

***S*-Octyl-*N*,*N*′-diethylthiouronium bromide (17-Br).** **17**-Br was prepared using the same procedure as **2**-Br from 1,3-diethylthiourea (22.2 g, 0.16 mol) and bromooctane (32.0 g, 0.166 mol) in ethanol (100 cm^3) heating at 60 °C for 24 h. The solvent and excess bromohexane were removed under reduced pressure at 70 °C and then *in vacuo* to give the product as a clear golden liquid (Found: C, 47.89; H, 8.21; N, 8.52; S, 8.88%. $[C_{13}H_{29}N_2S]Br$ (mol. wt. 325.4) requires C, 47.99; H, 8.98, N, 8.61, S, 9.85%); δ_H (500 MHz, DMSO-d_6) 9.17 (2H, d, J_{NH} = 135 Hz, 2 × NH), 3.26 (4H, m, 2 × N-CH_2CH_3), 3.29 (2H, t, S-CH_2), 1.59 (2H, m, SCH_2-CH_2), 1.36 (2H, m, SCH_2CH_2-CH_2), 1.25 (8H, m, -$(CH_2)_4$-), 1.16 (6H, m, 2 × NCH_2-CH_3), 0.85 (3H, t, -CH_3); δ_C (125 MHz, DMSO-d_6) 165.2, 31.7, 31.5, 28.8, 28.7, 28.5, 28.1, 22.4, 15.1, 14.3, 13.6. ESI-MS (CH_3CN/H_2O); +ve mode: 245.2 (100%, $[C_{13}H_{29}N_2S]^+$); −ve mode: 78.9 (100%, $^{79}Br^-$), 80.9 (100%, $^{81}Br^-$).

***S*-Octyl-*N*,*N*′-diethylthiouronium bis{(trifluoromethyl)sulfonyl}-imide (17-NTf_2).** The metathesis of **17**-Br (19.3 g, 0.059 mol) in water (100 cm^3) with Li[NTf_2] (18.7 g, 0.065 mol) resulted in the separation of **17**-NTf_2 as a pale yellow liquid (Found: C, 37.00; H, 6.37; N, 7.85; S, 16.95%. $[C_{13}H_{29}N_2S][N(SO_2CF_3]_2]$ (mol. wt. 535.6) requires C, 34.28; H, 5.56, N, 7.99, S, 18.30%); δ_H (500 MHz, $CDCl_3$) 7.86, 7.35 (2H, br d, J_{NH} = 255 Hz, 2 × NH), 3.55 (4H, b, 2 × N-CH_2), 3.26 (t, 3H, S-CH_2), 1.68 (2H, q, J = 7.3 Hz, SCH_2-CH_2), 1.45 (2H, q, J = 7 Hz, SCH_2CH_2-CH_2), 1.28 (br m, 14H, 2 × NCH_2-CH_3 + -$(CH_2)_4$-), 0.88 (t, 3H, J = 7.1 Hz, -CH_3).

Analysis

Microanalyses and electrospray mass spectroscopy were performed by A.S.E.P., QUB. ^1H NMR spectra were recorded on Bruker Avance DRX 500 and DPX 300 spectrometers in either DMSO-d_6 or $CDCl_3$. Melting points and glass transition temperatures were determined by differential scanning calorimetry (TA DSC Q2000 with either liquid nitrogen cryostatic cooling or a refrigerated cooling system, 5–20 mg samples, 5 °C min^{-1} heating and cooling rates under nitrogen, scanning between −100 and +100 °C). Transitions above ambient were confirmed optically by hot-stage polarising optical microscopy (Olympus BX50 microscope equipped with a Linkam TH600 hot stage and TP92 temperature controller). Thermal decomposition profiles were collected by thermogravimetric analysis (TA TGA Q5000 using a 5 °C min^{-1} heating ramp under nitrogen). Densities were determined at 10 °C intervals between 20 and 90 °C, using a Metler Toledo DE40 oscillating tube densitometer. Sample size was 1 cm^3. Measurements of kinematic viscosity were carried out over the temperature range 20 to 95 °C using a Brookfield DV-II+ cone and plate viscometer, equipped with a Grant LTD6G circulating heater. Electrochemical experiments were carried out in a 10 cm^3 glass cell with 3 g of ionic liquid. Cyclic voltammogram experiments were recorded with a PC-controlled microAutolab Type III Potentiostat (Eco-Chemie, Netherlands), and performed in a three-electrode arrangement with a platinum (1.5 mm diameter) as the working electrode, a bright platinum coil as the counter electrode, and all potentials measured with respect to a 0.01 M Ag^+/Ag reference, with $AgNO_3$ dissolved in 1-butyl-3-methylimidazolium nitrate and separated from the bulk solution *via* a glass frit. The IR-drop was uncompensated. The platinum working electrode was polished using alumina slurry (Kemet, UK) of decreasing particle size (from 5 μm to 0.1 μm) on soft lapping pads. Prior to all experiments, solutions were purged by bubbling dry argon for at least 10 min. A positive pressure of inert gas was maintained above the surface of the electrolyte throughout the experiments.

For the experimental determination of the mutual miscibility limits of the immiscible binary mixtures of dodecane, octane and toluene with the ionic liquids, compositions lying on the immiscible region were introduced inside a jacketed glass cell. The temperature was controlled using a thermostated water bath and was checked by means of a thermometer with an accuracy of $\pm 1 \times 10^{-1}$ K. All the mixtures were vigorously stirred for at least 1 h, and then allowed to settle for a minimum of 4 h to guarantee that the equilibrium state was completely reached. The indicated times were fixed according to results from preliminary tests. A sample of each layer in equilibrium was withdrawn using glass syringes with coupled stainless steel needles. Then the samples were dissolved in DMSO-d_6 inside NMR-tubes, which were properly sealed. The composition of these samples was determined by proton nuclear magnetic resonance spectroscopy (^1H NMR) by comparison of the relative integrals of the signals from the cations and hydrocarbons.

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