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## COMMUNICATION

# Ionic liquids for efficient hydrogen sulfide and thiol scavenging

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Functionalised pyridinium and ammonium ionic liquids bearing a Michael acceptor are shown to scavenge H<sub>2</sub>S gas and various thiols, in most cases, without the aid of any added bases. Utilising the effective non-volatility of ionic liquids and ‘tagging’ malodourous substances to an ionic matrix renders them odourless.

## Introduction

Hydrogen sulfide gas occurs naturally in crude petroleum, natural gas, volcanic gases and hot springs. Petroleum oil and natural gas are the products of thermal conversion of decayed organic matter, known as kerogen, which is trapped in sedimentary rocks.<sup>1</sup> High-sulfur kerogens release hydrogen sulfide during decomposition, and this H<sub>2</sub>S stays trapped in oil and gas deposits.<sup>2</sup> Hydrogen sulfide gas also can result from industrial activities, such as food processing, coke ovens, Kraft paper mills, tanneries and petroleum refineries. Contaminants present in natural gas, which have to be removed at gas processing facilities, include water vapour, sand, dioxygen, carbon dioxide, and dinitrogen, helium, neon, and hydrogen sulfide: is by far the predominant impurity in natural gas.<sup>3</sup> Natural gas is classified as *sour* when H<sub>2</sub>S is present in larger (> 5.7 mg m<sup>-3</sup>) amounts which then is routinely *sweetened* at desulfurisation processing facilities.<sup>4</sup> 95% of the gas sweetening process involves removing the H<sub>2</sub>S by absorption in an amine (trialkyltriazene) solution<sup>5</sup>, presumably through a weak acid-weak base proton transfer equilibrium, while other methods include carbonate processes, solid bed absorbents, BASF’s aqueous glyoxal scrubber,<sup>6</sup> and physical absorption.<sup>7</sup>

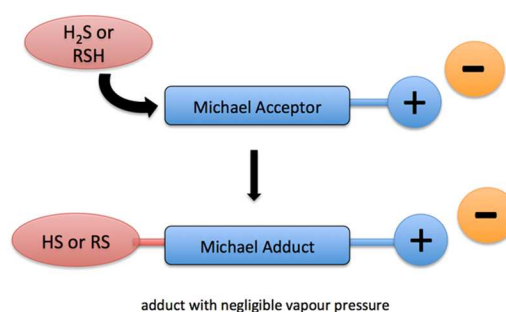
Recently, there has been a glut of publications on sensing for H<sub>2</sub>S and thiols with emphasis on sensory systems for biological systems.<sup>8</sup> Real-time monitoring of H<sub>2</sub>S fluxes in living cells and more complex specimens have received lot of attention by biologists and chemists alike.<sup>9</sup> However, much less focus and attention is paid to the scavenging of these undesirable odorous gases in the literature. Hence the removal/scavenging of H<sub>2</sub>S from petroleum gases, and also from the flue gases originating from petroleum refineries, is an essential step towards protecting the environment.<sup>10</sup> Consequently, the removal of H<sub>2</sub>S and other sulfurous materials from petroleum products has the beneficial effects of improving performance quality of the fuel.

There have been few reports on the usage of ionic liquids for removal of H<sub>2</sub>S mainly through physisorption and in some cases (carboxylate ionic liquids), partial chemisorption is suggested.<sup>7</sup>

Hydrogen sulfide can also result from bacterial breakdown of organic matter. Furthermore, substances containing thiol groups - edible materials such as durian fruit<sup>11</sup> and garlic<sup>12</sup>- also impart undesirable malodours. Indeed, human sweat contains a few thiols that are mainly responsible for its characteristic malodour.<sup>13</sup> Non-toxic and biodegradable materials (*e.g.* surfactants/ionic liquids) that are capable of scavenging thiols may be incorporated into personal care products in order to mask these malodours.<sup>14</sup>

## Results and discussion

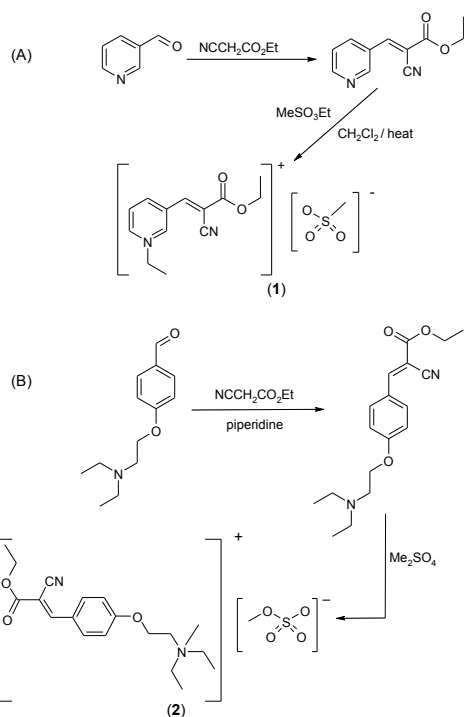
With these goals in mind, a class of ‘reactive’ ionic liquids is reported here that is capable of reacting with thiols and hydrogen sulphide completely *via* a reversible Michael addition to produce non-volatile ionic matrices with attached ‘odorous’ segments (see the illustration in Figure 1).



**Figure 1:** An illustration of the scavenging of volatile ‘sulfurous’ compounds by a non-volatile ionic liquid matrix

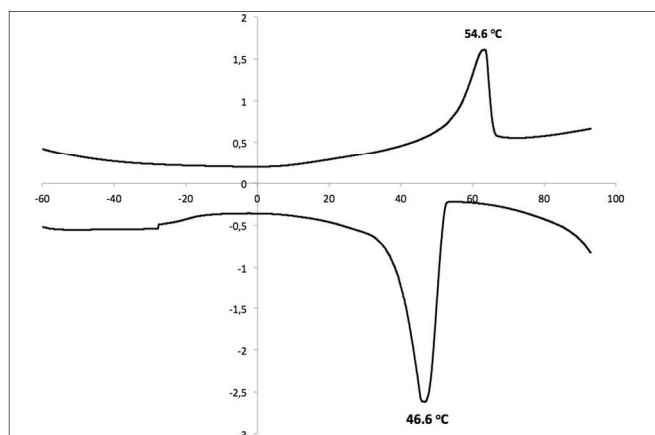
Since ionic liquids, by nature, have negligible vapour pressures<sup>15</sup> the resulting sulfur-bound salts would render no bad odours. These ionic liquids are capable of ‘mole *per* mole’ complete scavenging of H<sub>2</sub>S and thiols, unlike the cases described in the literature. Such ionic liquids were synthesised using a very simple reaction scheme that is depicted in Scheme 1.

Our synthetic strategy involves synthesising ionic liquids with a tethered Michael acceptor functionality. All 3- and 4-pyridinecarboxaldehydes and the functionalised benzaldehyde were treated with NCCH<sub>2</sub>CO<sub>2</sub>Et, using a catalytic amount of piperidine to produce  $\alpha,\beta$ -unsaturated cyano esters that carry a typical Michael acceptor. The ionic liquids were produced by quaternising the pyridine (Scheme 1A) or trialkylamine (Scheme 1B) nitrogen with a suitable alkylating agent such as ethyl methanesulfonate. Furthermore, all reactions were clean and relatively easy to perform at the multi-gram scale, starting from readily available chemicals. It was noticed that the ionic liquid originating from quaternising ethyl[2-(4-pyridyl)-1-cyano]prop-2-enoate with ethyl methanesulfonate lacked sufficient stability over a considerable period of time. Therefore, this compound was omitted from this study. However, ethyl[2-(3-pyridyl)-1-cyano] prop-2-enoate was very stable and that, in turn, was treated with ethyl methanesulfonate to produce the ionic liquid (1). The ionic liquid (1) given in Scheme 1A, has the positively charged pyridinium cation in close proximity to the Michael acceptor reaction site, whereas ionic liquid (2) shown in Scheme 1B, has the positive charge placed relatively far away from the reaction centre. Therefore, these two systems are expected to show some reactivity differences towards incoming nucleophiles.



**Scheme 1:** Reaction schemes for the synthesis of ionic liquids for scavenging H<sub>2</sub>S and thiols.

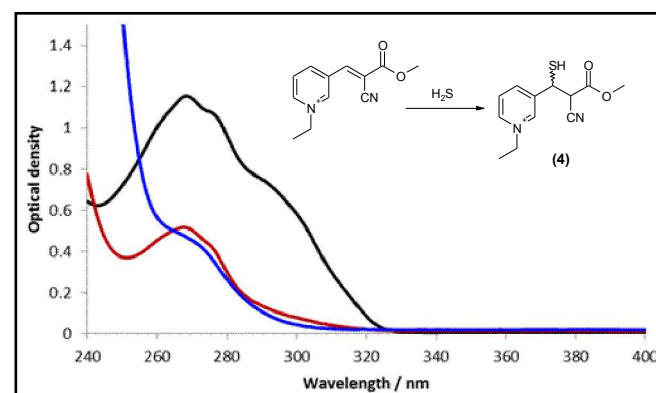
The differential scanning calorimetric (DSC) analysis of ionic liquid (1) is shown in Figure 2, displaying a melting point at 55 °C and a corresponding freezing point at 47 °C (these numbers correspond to peak values) falling within the conventional realm of ionic liquids.



**Figure 2:** The second DSC scan of ionic liquid (1), performed at a rate of 5 °C/min.

Catalytic thiol additions to 2-aryl-1-cyanoprop-2-enoate and corresponding amides are known.<sup>16</sup> Targeting non-catalytic cysteine residues with irreversible acrylamide-based inhibitors is a powerful approach for enhancing pharmacological potency and selectivity,<sup>17</sup> however, spontaneous addition of H<sub>2</sub>S to such electrophiles, to our knowledge, is not known in the absence of a catalyst.

In order to examine the gas uptake, a stream of H<sub>2</sub>S gas was passed through a CH<sub>3</sub>CN solution of ionic liquid (1) and was analysed by electronic absorption spectroscopy. Figure 3 clearly indicates the changes that occurred after passing H<sub>2</sub>S through the solution for 5-15 min. The UV-band had shifted to the far UV indicating the loss of conjugation.



**Figure 3:** Electronic absorption spectra of ionic liquid (1) in CH<sub>3</sub>CN before and after bubbling H<sub>2</sub>S at atmospheric pressure and at 20 °C; - (a) (1); - (b) (1) after bubbling H<sub>2</sub>S for 5 min; - (c) after bubbling H<sub>2</sub>S 15 min; the inset illustrates the reaction of H<sub>2</sub>S with the cation of (1).

These solutions in CD<sub>3</sub>CN were also examined by <sup>1</sup>H NMR spectroscopy. The results are shown in Figure 4, where the disappearance of the unique alkene proton is clearly seen indicating H<sub>2</sub>S addition across the double bond.

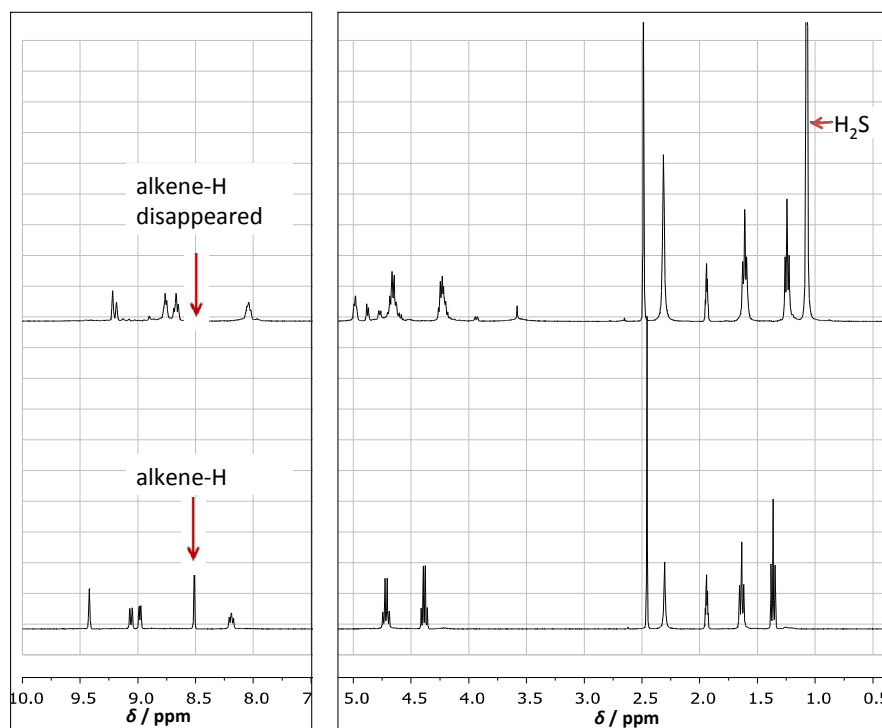


Figure 4: <sup>1</sup>H NMR spectra of ionic liquid (1) in CD<sub>3</sub>CN before and after bubbling H<sub>2</sub>S gas at atmospheric pressure and at 20 °C.

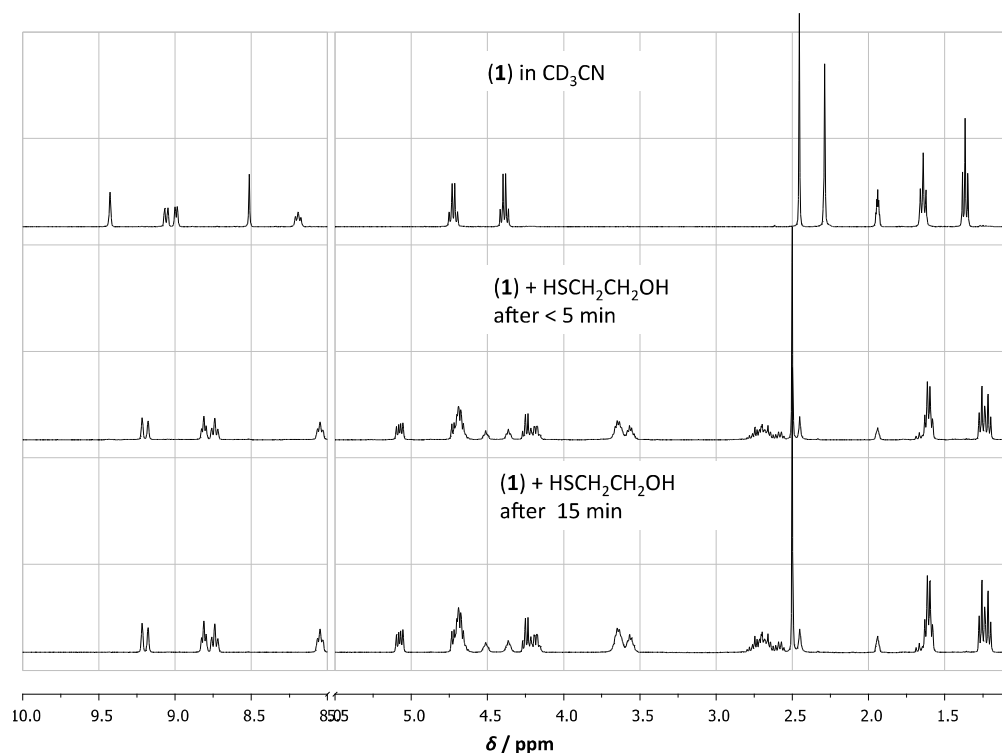
As expected, a mixture of diastereoisomers of the H<sub>2</sub>S adduct (4) was formed and the identity of the product (4) was verified by ESMS, exhibiting a molecular ion peak at *m/z* 265 (see inset, Figure 3). More detailed analysis of <sup>1</sup>H NMR reveals significant shifts of 4 signals associated with the pyridinium ring. As expected, H<sub>2</sub>S addition leads to deconjugation of the pyridinium ring and the double bond.

A similar experiment was carried out using a solution of (1) in CD<sub>3</sub>CN and replacing H<sub>2</sub>S with a small excess (1:1.4 eq.) of 2-mercaptoethanol. This solution was analysed by <sup>1</sup>H NMR spectroscopy. Figure 5 categorically shows that the addition of 2-mercaptothiol was clean, verified by the complete disappearance of the alkene proton, resulting in two diastereomeric adducts. It appears, in this case, that the two diastereomeric adducts are formed in near equal amounts. It is not very clear as to how significantly different steric factors could enforce the formation of vastly amounts of the two diastereoisomers.

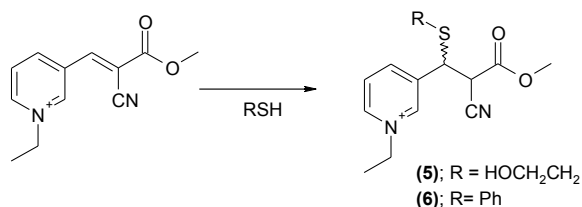
The scheme 2 depicts the chemistry involved in this Michael addition process. Further evidence also comes from the ESMS analysis of the resulting solution showing the presence of a peak at *m/z* 295 corresponding to 2-mercaptoethanol adduct (5). The presence of the pyridinium moiety in close proximity of the Michael acceptor could enhance the reactivity of the ionic liquid.

When PhSH was employed as the thiol nucleophile, very similar results were obtained through a spontaneous Michael addition to ionic liquid (1), generating (6). Again a diastereomeric mixture of thiophenate adducts were present in a CD<sub>3</sub>CN solution of (1) after the reaction is completed. The ionic liquid (2) was also subjected to a similar analysis by <sup>1</sup>H NMR. It was found that the ionic liquid in question did not react swiftly with H<sub>2</sub>S and an addition of a small amount of an amine<sup>18</sup> (NMe<sub>2</sub>Et) base was required for an efficient reaction. Trialkylphosphines<sup>19</sup> as catalysts for thiol additions to acrylate type Michael acceptors may also be used. Figure 6 shows <sup>1</sup>H NMR spectra of (2) before and after treatment with H<sub>2</sub>S gas.

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**Figure 5:** 2-6 and 7.5-10  $\delta$  Regions of  $^1\text{H}$  NMR spectra of ionic liquid (**1**) in  $\text{CD}_3\text{CN}$  before and post adding 1.1 eq. of  $\text{HOCH}_2\text{CH}_2\text{SH}$  after 5 and 15 min. time intervals at  $20^\circ\text{C}$ .

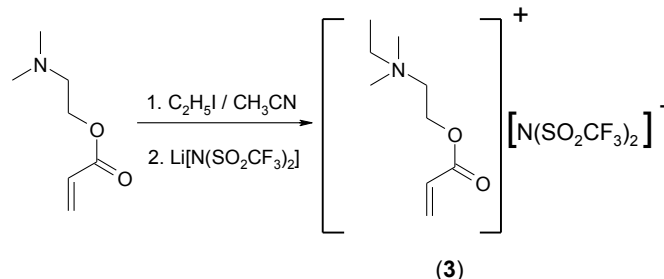


**Scheme 2:** A reaction scheme showing the products formed from reactions with the cation of ionic liquid (**1**) with  $\text{HOCH}_2\text{CH}_2\text{SH}$  and  $\text{PhSH}$  in  $\text{CH}_3\text{CN}$ .

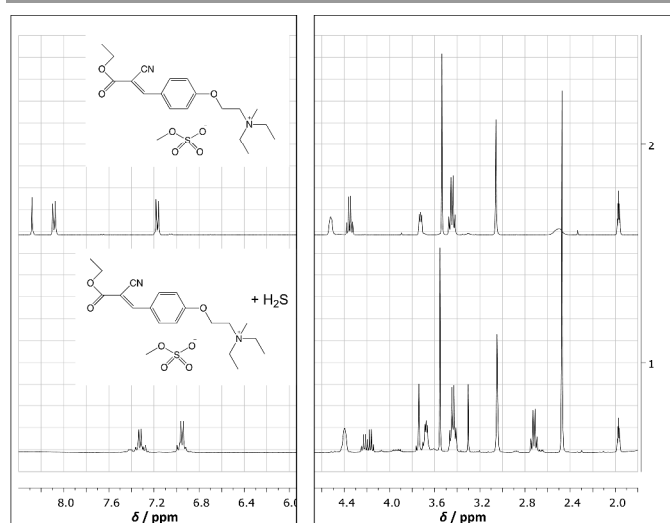
In the  $^1\text{H}$  NMR spectrum (in  $\text{CD}_3\text{CN}$ ), the absence of the alkene proton at  $\delta$  8.28, coupled with upfield shifting of all aromatic protons is noticeable, as a consequence of the addition of hydrogen sulfide across the double bond (Figure 6; bottom spectral traces). Deconjugation of the cyanoacrylate unit from the aromatic nucleus increases its electron density and hence accounts for the changes observed in the  $^1\text{H}$  NMR spectrum, post  $\text{H}_2\text{S}$  addition.

The ionic liquid (**3**), (Scheme 3), was synthesised as the bistriflamide salt,  $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$  in two steps using commercially available starting materials. The synthesis of (**3**)

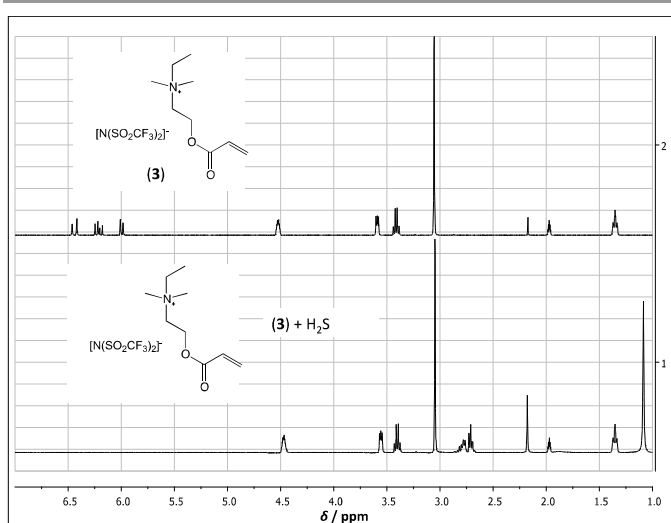
involves quaternisation with iodoethane followed by anion exchange with  $\text{Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$ . The ionic liquid (**3**) was shown to react cleanly, in  $\text{CD}_3\text{CN}$  solution, with hydrogen sulfide, thiophenol or 2-mercaptoethanol without an added base (see Figures 7 and 8).



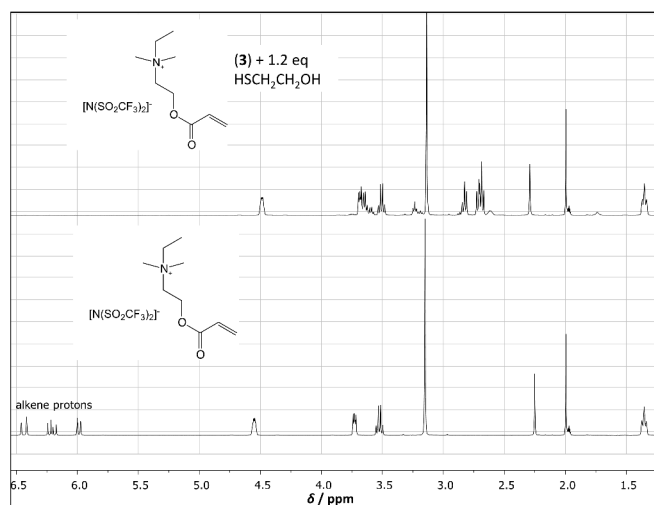
**Scheme 3:** The reaction scheme for the synthesis of ionic liquid (**3**) for scavenging  $\text{H}_2\text{S}$  and thiols.



**Figure 6:**  $^1\text{H}$  NMR spectra of ionic liquid (2) in  $\text{CD}_3\text{CN}$ , with a catalytic amount of  $\text{Me}_2\text{NEt}$ , before and after bubbling  $\text{H}_2\text{S}$  gas at atmospheric pressure and at  $20^\circ\text{C}$ .

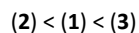


**Figure 8:**  $^1\text{H}$  NMR spectra of ionic liquid (3) in  $\text{CD}_3\text{CN}$ , before and after treating with hydrogen sulfide at  $20^\circ\text{C}$



**Figure 7:**  $^1\text{H}$  NMR spectra of ionic liquid (3) in  $\text{CD}_3\text{CN}$ , before and after treating with 1.2 eq. of 2-mercaptoethanol at  $20^\circ\text{C}$ .

The order of empirical reactivity of the cations, with either  $\text{H}_2\text{S}$  or  $\text{RSH}$ , is the same, and in the sequence of increasing reactivity:



Each of these cations was subjected to energy minimisation by DFT (density functional theory), and the bond lengths and bond orders of the formal double bonds were calculated, see Table 1. The observed reactivity mirrors the trend anticipated, namely that the shortest bond with the highest bond order is the most reactive, whilst the longest bond with the lowest bond order is the least reactive. This argument is supported by the fact that ionic liquids (1) and (3) react with  $\text{H}_2\text{S}$  and thiols without the aid of an added external base, whereas for (2) a catalytic amount of an amine base was needed for an efficient Michael addition.

**Table 1:** Computed bond lengths and bond orders for cations (1), (2) and (3)

	Bond order	Bond length / Å
(1)	1.73	1.358
(2)	1.68	1.362
(3)	1.86	1.337

## Conclusions

We have demonstrated the versatility of a class of reactive ionic liquids towards scavenging thiols and hydrogen sulphide completely, which are highly malodourous and toxic substances. Therefore the materials described here can contribute to the green advancement leading to environmental clean-up. Hydrogen sulfide, in particular, is a troublesome component omnipresent in oil and gas that contributes to degrading their quality. We show that the synthesis of these ionic liquids, which incorporate a Michael acceptor, is straightforward, and can be done utilising readily available chemicals. Ionic liquids will also facilitate separation from non-polar liquid hydrocarbons post-removal of  $\text{H}_2\text{S}$  and thiols, which may enable sulfur separation in industrial scale processes. The non-volatile nature of these ionic liquids qualifies them as supported materials for removal of  $\text{H}_2\text{S}$  from natural gases. We made use of much documented thiol-ene chemistry to capture thiols and  $\text{H}_2\text{S}$  and immobilise them into a non-volatile ionic matrix. Since the Michael addition is a reversible reaction, there is potential to recycle the ionic liquids after sulfur capture. Our findings have potential for applications in the oil and gas industries, and also in personal care products.

## Materials and methods

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used without further purifications.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz). ESMS-mass spectroscopy measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120 °C). Both positive and negative ions were detected, with an *m/z* range of 50 to 1500. Samples were injected as dilute solutions in acetonitrile. All DSC scans were obtained using a TA DSC Q2000 model with a TA Refrigerated Cooling System 90 (RCS) and an autosampler. Electronic absorption spectra were obtained using a Perkin Elmer Lambda 950 spectrophotometer using a cuvette with 1 cm path length. The computational chemistry package Spartan '10 for Windows was used with density functional theory (DFT), at the B3LYP level of theory utilising the 6-31G\* basis set, to calculate the equilibrium geometry of the cations (1), (2) and (3) in the gas phase.<sup>20</sup>

### Synthesis of ionic liquid (1)

Ethyl{2-cyano-3-(3-pyridyl)}prop-2-enoate (1.01 g, 5 mM) and ethyl methanesulfonate (0.63 g, 5 mM) in CH<sub>3</sub>CN (4 cm<sup>3</sup>) was heated at 50 °C, in screw-cap tube, for 16 h. The solvent was removed under reduced pressure; the resulting residue was sonicated with diethyl ether (2 x 5 cm<sup>3</sup> portions) and diethyl ether discarded. The resulting gummy product was dried at 50 °C under high vacuum, overnight yielding (1; 1.5 g, 91%). <sup>1</sup>H-NMR (CD<sub>3</sub>CN): δ 9.4 (s, 1H, Py<sup>2</sup>H), 9.1 (d, 1H, Py<sup>6</sup>H), 8.9 (d, 1H, Py<sup>4</sup>H), 8.5 (s, 1H, alkene-H), 8.2 (t, 1H, Py<sup>5</sup>H), 4.7 (q, 2H, OCH<sub>2</sub>), 4.3 (q, 2H, NCH<sub>2</sub>), 2.4 (s, 3H, CH<sub>3</sub>SO<sub>3</sub>), 1.65 (t, 3H, CH<sub>3</sub>), 1.3 (s, 1H, OCH<sub>2</sub>CH<sub>3</sub>); ESMS: **cation**; calculated: 231.11335, found: 231.1132; **anion**; calculated: 94.98029, found: 94.98025.

### Synthesis of ionic liquid (2)

(2-Chloroethyl)diethylammonium chloride (5.16 g, 30 mM) and 4-hydroxybenzaldehyde (3.3 g, 27 mM) was taken in dry propanone (100 cm<sup>3</sup>) to which potassium carbonate (12 g, 87 mM) was added and the resulting mixture was heated to reflux overnight. The cooled solution was passed through a short silica plug and the solvent evaporated to yield a yellow oil (4.48 g, 75%), which was used in the next step without further purification.

4-(Diethylaminoethoxy)benzaldehyde (0.8 g, 3.6 mM) and NCCH<sub>2</sub>CO<sub>2</sub>Et (0.41 g, 3.6 mM) were dissolved in ethanol (4 cm<sup>3</sup>) and a drop of piperidine added and then stirred overnight. The solvent and piperidine were removed under vacuum and the resulting yellow oil was used in the next step.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 8.17 (s, 1H, alkene-H), 7.99 (d, 1H, ArH), 6.99 (d, 1H, ArH), 4.37 (q, 2H, OCH<sub>2</sub>), 4.13 (t, 2H, OCH<sub>2</sub>), 2.90 (t, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 2.65 (q, 4H, 2xNCH<sub>2</sub>), 1.39 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 1.08 (t, 6H, 2xCH<sub>3</sub>).

The yellow oil (0.68 g, 0.26 mM) was dissolved in diethyl ether (5 cm<sup>3</sup>), treated with dimethyl sulfate (0.27 g, 0.26 mM) and

stirred overnight that resulted in formation of two layers. Diethyl ether was decanted off and the residue was washed twice with diethyl ether and then dried under high vacuum, at 50 °C, to remove traces of solvents. Yield 0.84 g, 88%. <sup>1</sup>H-NMR (CD<sub>3</sub>CN): δ 8.28 (s, 1H, alkene-H), 8.09 (d, 2H, ArH), 7.17 (d, 2H, ArH), 4.52 (t, 2H, OCH<sub>2</sub>), 4.35 (q, 2H, OCH<sub>2</sub>), 3.73 (t, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 3.54 (s, 3H, NCH<sub>3</sub>), 3.45 (q, 4H, 2xNCH<sub>2</sub>), 3.06 (s, 3H, SO<sub>3</sub>OCH<sub>3</sub>), 1.37 (t, 6H, 2xCH<sub>2</sub>CH<sub>3</sub>); ESMS; cation: calculated, 331.20217; observed: 331.2023.

### Synthesis of ionic liquid (3)

To a solution of 2-(dimethylamino)ethyl propen-2-olate (1.43 g, 10 mM) in CH<sub>3</sub>CN (2 cm<sup>3</sup>) added iodoethane (1.6 g, 10.2 mM) and stirred at room temperature overnight. After removing the solvent under vacuum, the residue was taken in ether to produce a pale yellow solid, which was filtered and dried. This iodide salt (5 mM) was subjected to metathesis with Li[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] (5.2 mM) in water/CH<sub>2</sub>Cl<sub>2</sub> system. The ionic liquid (3) was isolated in the usual manner and dried at 50 °C under high vacuum to leave a viscous product; Yield, 91%. <sup>1</sup>H-NMR (CD<sub>3</sub>CN): δ 6.44 (d, 1H, alkene-H), 6.21 (dd, 1H, alkene-H), 5.99 (d, 1H, alkene-H), 4.52 (m, 2H, OCH<sub>2</sub>), 3.59 (m, 2H, N+CH<sub>2</sub>), 3.41 (q, 2H, N+CH<sub>2</sub>), 3.05 (s, 6H, N+Me<sub>2</sub>), 1.35 (t, 3H, NCH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR δ 164.7, 131.5, 127.2, 121.3, 117.5 (NTf<sub>2</sub> group), 61.6, 60.7, 57.2, 50.4, 7.24; ESMS; cation: calculated, 172.1338; observed: 172.1337.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: additional DSC, NMR and MS data are included here. See DOI: 10.1039/b000000x/

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## Ionic liquids for efficient hydrogen sulfide and thiol scavenging

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Functionalised pyridinium and ammonium ionic liquids bearing a Michael acceptor are shown to scavenge H<sub>2</sub>S gas and various thiols, in most cases, without the aid of any added bases. Utilising the effective non-volatility of ionic liquids and ‘tagging’ malodourous substances to an ionic matrix renders them odourless.

