Ionic liquids for efficient hydrogen sulfide and thiol scavenging

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Electronic Supplementary Information

Materials and general methods

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used without further purifications. ^{1}H NMR and ^{13}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 Lamda 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.

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_3CN (4 cm^3) 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^3 portions) and diethyl ether discarded. The resulting gummy product was dried at 50 °C under high vacuum, overnight yielding (**1**; 1.5 g, 91%). ^{1}H-NMR (CD_3CN): δ 9.4 (s, 1H, Py^{2}**H**), 9.1 (d, 1H, Py^{6}**H**), 8.9 (d, 1H, Py^{4}**H**), 8.5 (s, 1H, alkene-**H**), 8.2 (t, 1H, Py^{5}**H**), 4.7 (q, 2H, O**CH$_2$**), 4.3 (q, 2H, N**CH$_2$**), 2.4 (s, 3H, **CH$_3$**SO_3), 1.65 (t, 3H, **CH$_3$**), 1.3 (s, 1H, OCH_2**CH$_3$**); 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^3) 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 $NCCH_2CO_2Et$ (0.41 g, 3.6 mM) were dissolved in ethanol (4 cm^3) 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.

^{1}H-NMR ($CDCl_3$): δ 8.17 (s, 1H, alkene-**H**), 7.99 (d, 1H, Ar**H**), 6.99 (d, 1H, Ar**H**), 4.37 (q, 2H, O**CH$_2$**), 4.13 (t, 2H, O**CH$_2$**), 2.90 (t, 2H, OCH_2**CH$_2$**), 2.65 (q, 4H, 2xN**CH$_2$**), 1.39 (t, 3H, OCH_2**CH$_3$**), 1.08 (t, 6H, 2x**CH$_3$**).

The yellow oil (0.68 g, 0.26 mM) was dissolved in diethyl ether (5 cm^3), treated with dimethyl sulfate (0.27 g, 0.26 mM) and stirred overnight that resulted in formation of two layers. Diethyl ether was decanted of 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%. ^{1}H-NMR (CD_3CN): δ 8.28 (s, 1H, alkene-**H**), 8.09 (d, 2H, Ar**H**), 7.17 (d, 2H, Ar**H**), 4.52 (t, 2H, O**CH$_2$**), 4.35 (q, 2H, O**CH$_2$**), 3.73 (t, 2H, OCH_2**CH$_2$**), 3.54 (s, 3H, N**CH$_3$**), 3.45 (q, 4H, 2xN**CH$_2$**), 3.06 (s, 3H, SO_3O**CH$_3$**), 1.37 (t, 6H, 2xCH_2**CH$_3$**); ESMS; cation: calculated, 331.20217; observed: 331.2023.

Synthesis of ionic liquid (3)

To a solution of 2-(dimethylamino)ethyl propen-2-oate (1.43 g, 10 mM) in CH_3CN (2 cm^3) 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 $Li[N(SO_2CF_3)_2]$ (5.2 mM) in water/CH_2Cl_2 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%. ^{1}H-NMR (CD_3CN): δ 6.44 (d, 1H, alkene-H), 6.21 (dd, 1H, alkene-H), 5.99 (d, 1H, alkene-H), 4.52 (m, 2H, OCH_2), 3.59 (m, 2H, N^+CH_2), 3.41 (q, 2H, N^+CH_2), 3.05 (s, 6H, N^+Me_2), 1.35 (t, 3H, NCH_2**CH$_3$**); ^{13}C NMR δ 164.7, 131.5, 127.2, 121.3, 117.5 (NTf_2 group), 61.6, 60.7, 57.2, 50.4, 7.24; ESMS; cation: calculated, 172.1338; observed: 172.1337.

For NMR experiments, approximately 100 mM solutions in CD_3CN were prepared and either H_2S was bubbled through for 5-15 minutes or appropriate thiol was added the NMRs were run on 400 MHz NMR spectrometer. Same solutions were subjected to ESMS analysis as well.

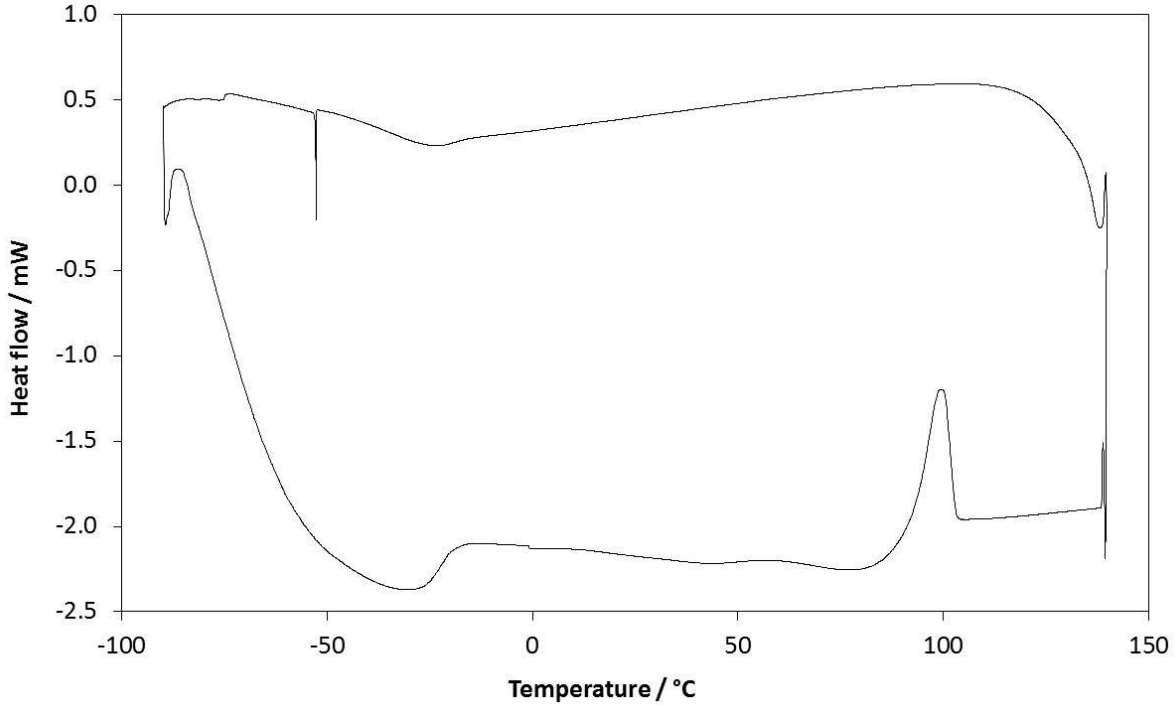

Figure 1: DSC (second scan) of ionic liquid (**2**), run at 5 °C min^{-1}

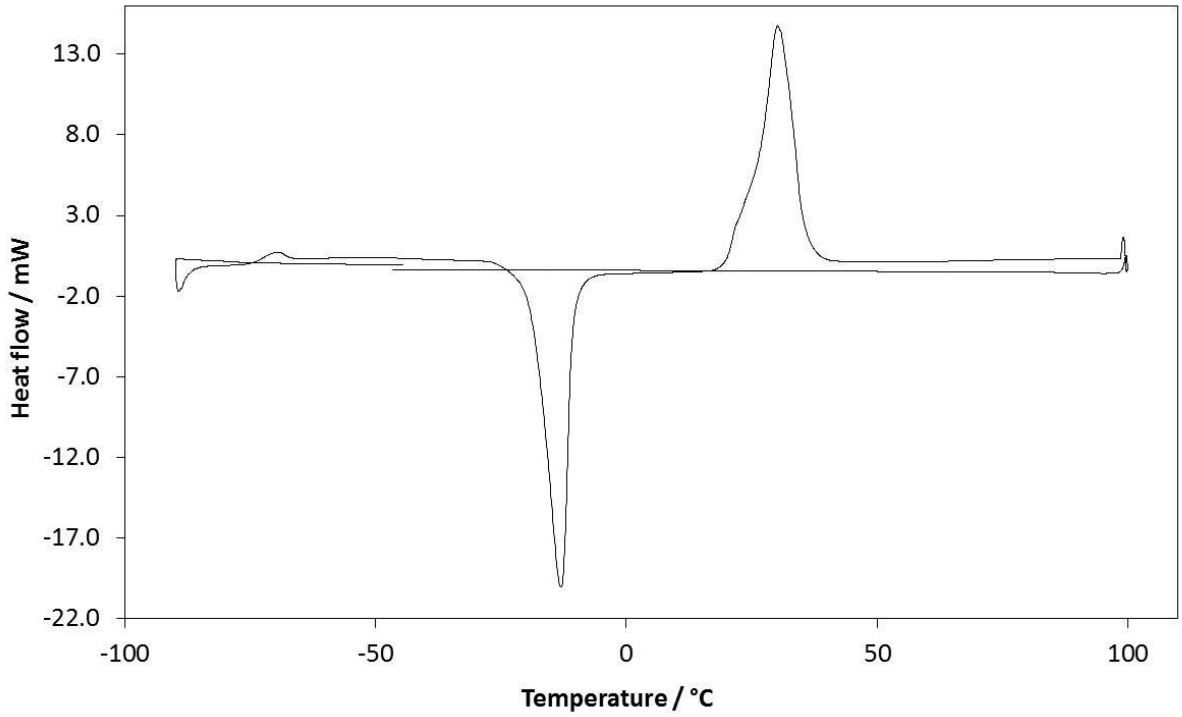

Figure 2: DSC (second scan) of ionic liquid (**3**), run at 5 °C min^{-1}

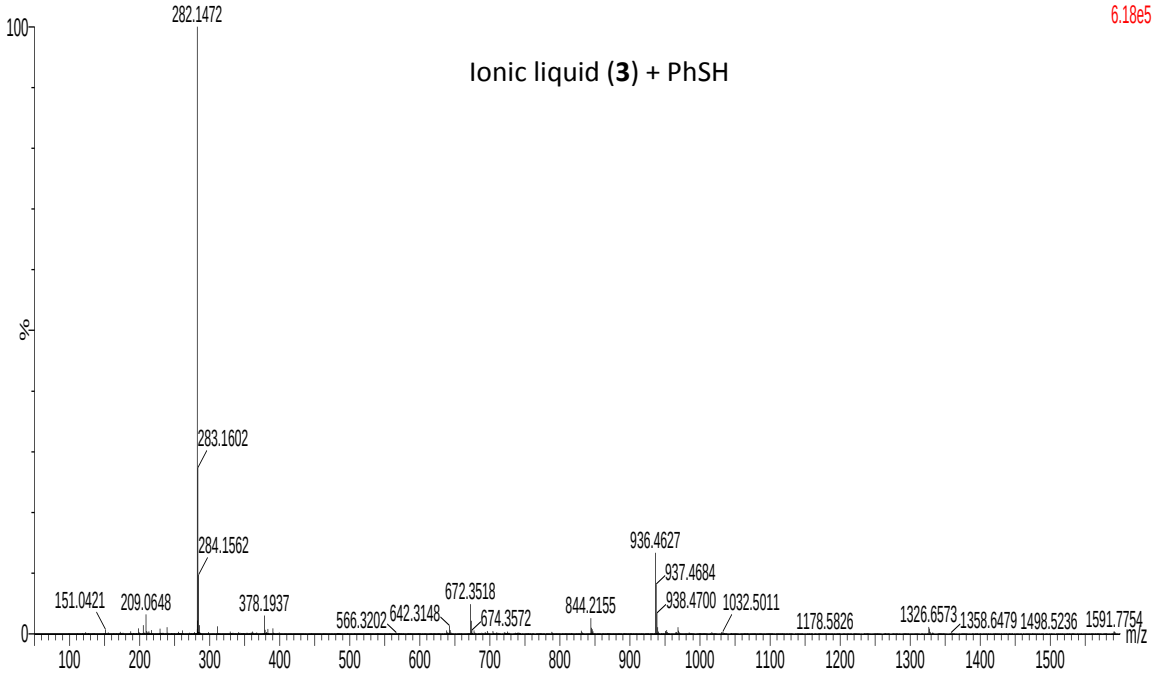

Figure 3: ESMS of a CD_3CN solution containing ionic liquid (**3**) and PhSH

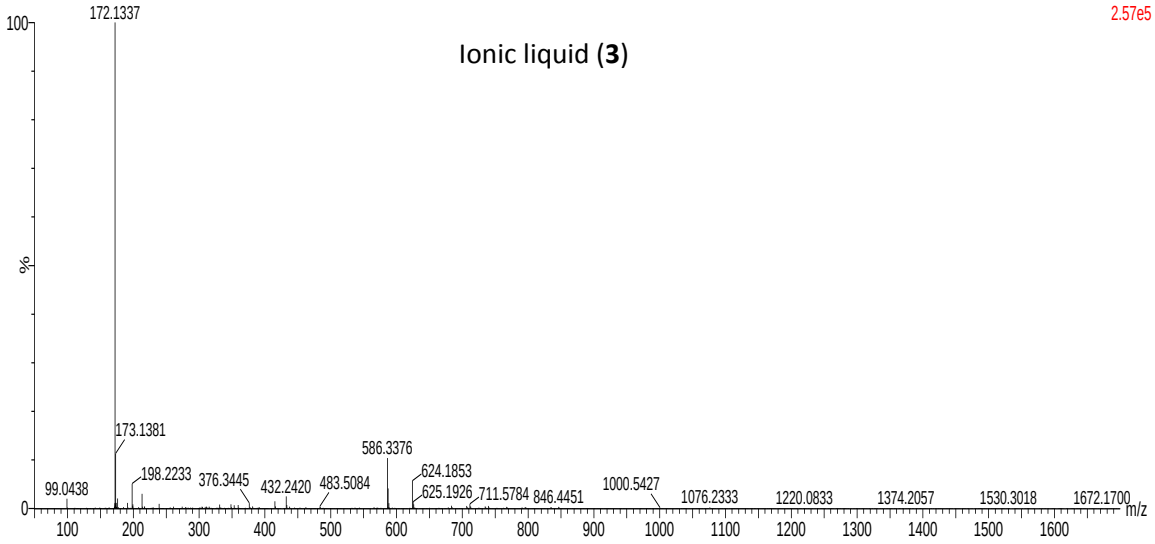

Figure 4: ESMS of a CD_3CN solution containing ionic liquid (**3**)

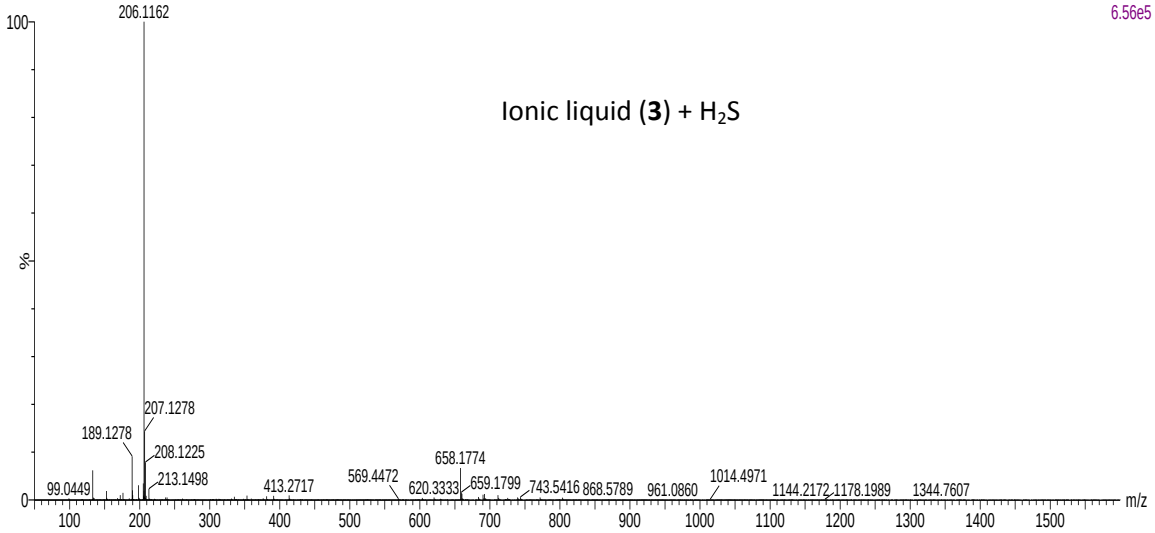

Figure 5: ESMS of a CD_3CN solution containing ionic liquid (**3**) and H_2S

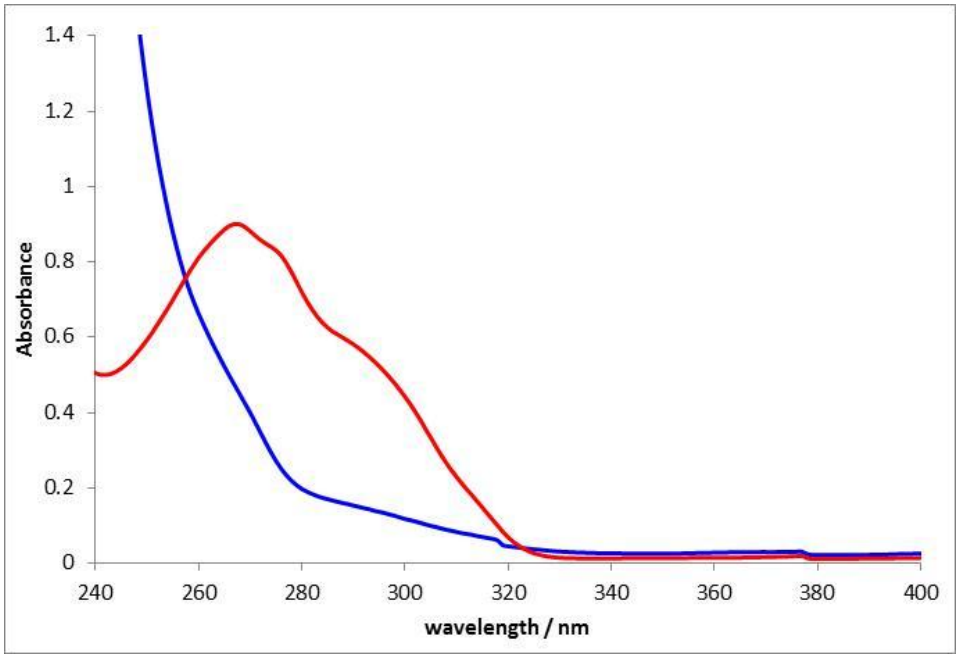

Figure 6: Electronic absorption spectra of (a) — ionic liquid (**1**) in CH_3CN; (b) — solution of ionic liquid (**1**) with 1.1eq. of $HOCH_2CH_2SH$ in CH_3CN