Supporting information for:

Ionic liquids enable electrospray ionisation mass spectrometry in hexane

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**General experimental details**

1 was purchased from Aldrich and used as provided but handled in an inert-atmosphere glovebox. Hexane and toluene were HPLC-grade, and were dried and purged of oxygen using an MBraun solvent-purification system. Pentane, cyclohexane and benzene were HPLC-grade. (C$_2$H$_4$O)$_6$ (“18-crown-6”) was purchased from Aldrich.

**Mass spectra of 1 in various non-polar solvents**

ESI-MS of 1 were collected in positive-ion mode in hexane, pentane, cyclohexane, benzene and toluene. Concentrations of 1 are noted on the spectra. “Ion intensity” refers to the ion current for the base peak. Spectra were collected for 1 minute in all cases, summing 60 individual mass spectra. Relatively high solvent flow rates tend to improve spectra quality; these spectra were collected at 10 µL min$^{-1}$ but flow rates of up to 40 µL min$^{-1}$ often improved the ion current significantly.
**Figure S11.** Positive-ion ESI mass spectra of 1 at differing concentrations in hexane. Each spectrum was collected over 1 minute (60 summed spectra). A stable spray and good spectra are obtained at a threshold of $\sim 10^{-5}$ mol L$^{-1}$. 
Figure SI2. Positive-ion ESI mass spectra of 1 at differing concentrations in pentane. Each spectrum was collected over 1 minute (60 summed spectra). A stable spray and good spectra are obtained at a threshold of $\sim 10^{-5}$ mol L$^{-1}$. 
Cyclohexane

Figure S13. Positive-ion ESI mass spectra of 1 at differing concentrations in cyclohexane. Each spectrum was collected over 1 minute (60 summed spectra). A stable spray and good spectra are obtained at a threshold of \( \approx 10^{-5} \text{ mol L}^{-1} \).
Figure SI4. Positive-ion ESI mass spectra of 1 at differing concentrations in benzene. Each spectrum was collected over 1 minute (60 summed spectra). A stable spray and good spectra are obtained at a threshold of ~10^{-5} mol L^{-1}, though the IL can be detected at a satisfactory signal-to-noise ratio at ~10^{-7} mol L^{-1}. 
Figure S15. Positive-ion ESI mass spectra of 1 at differing concentrations in toluene. Each spectrum was collected over 1 minute (60 summed spectra). A stable spray and good spectra are obtained at a threshold of ~10^{-5} mol L^{-1}, though the IL can be detected at a satisfactory signal-to-noise ratio at ~10^{-7} mol L^{-1}.
Figure S16. Positive-ion ESI mass spectrum of 3 in toluene. Similarly, the negative-ion spectrum shows no CA$_2^-$ ion, only A$^-$. 