Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Halogen-bond mediated efficient storage of extremely volatile perfluoroiodides in ionic liquids

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General materials and methods

Unless otherwise stated, all chemicals were purchased from either Sigma-Aldrich or TCI (UK) 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 dry acetonitrile. FTIR spectra were obtained at room temperature on a PerkinElmer Spectrum 100 (ATR-IR).

TGA: The temperature of decomposition was measured on a TA instrument TGA Q5000 with a heating rate of 10 °C min^{-1} under dinitrogen atmosphere. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature.

DSC: Thermal profiles of the ionic liquids were obtained using a TA DSC Q2000 model with a TA Refrigerated Cooling System 90 (RCS), equipped with an auto-sampler. A cooling and heating ramp of 2 °C min^{-1} was used, ranging between -100 °C and 120 °C, depending on the ionic liquid system.

Synthesis of ionic liquids

The ionic liquids, [bmim]Cl, [bmim]Br, [bmim]I, [bmim][NTf_2] and [bmim][CH_3OSO_3] were synthesised using procedures reported in the literature.[1] Four ionic liquids, [bmim][OAc], [bmim][CF_3CO_2], [bmim][SCN] and [bmim][CF_3SO_3] were donated to us by Merck.

All ionic liquids were dried at 60 °C on a high vacuum line for 24 h and stored in a desiccator over $CaCl_2$.

Notes: It is noteworthy that [bmim][NTf_2] and $CF_3CF_2CF_2CF_2I$ did not mix at the molar ratio that was used in this work. A clear phase separation was observed and hence, [bmim][NTf_2] was eliminated from the study.

Synthesis of ionic liquid (**1**)

Tris[2-(2-methoxyethoxy)ethyl]amine (3.23g, 10 mM) was taken up in CH_3CN (5 cm^3) in a screw cap tube to which iodomethane (1.7g, 12 mM) was added, then sealed with a screw cap and heated at 50 °C for 24 h. The reaction mixture was cooled, the solvent and the excess iodomethane were removed on a Rotavap to yield a light brown liquid which was further dried on high vacuum line at 60 °C to obtain (**1**) as a pale yellow liquid.

(1): ^{1}H NMR (400 MHz, in $CDCl_3$): δ 4.05-3.95 (brm, 12H, 6xOCH_2), 3.71-3.68 (m, 6H, 3xOCH_2), 3.54- 3.52 (m, 6H, 3xN^+CH_2), 3.44 (s, 3H, N^+CH_3), 3.36 (s, 9H, 3xOCH_3).

^{13}C NMR (101 MHz, in $CDCl_3$): δ 71.48, 70.31, 64.86, 63.33, 58.86, 50.93.

ESMS: For cation [$C_{16}H_{36}NO_6$] requires 338.2543; observed 338.2519

For anion [I] requires 126.9045; observed 126.9041

NMR spectra of new ionic liquids:

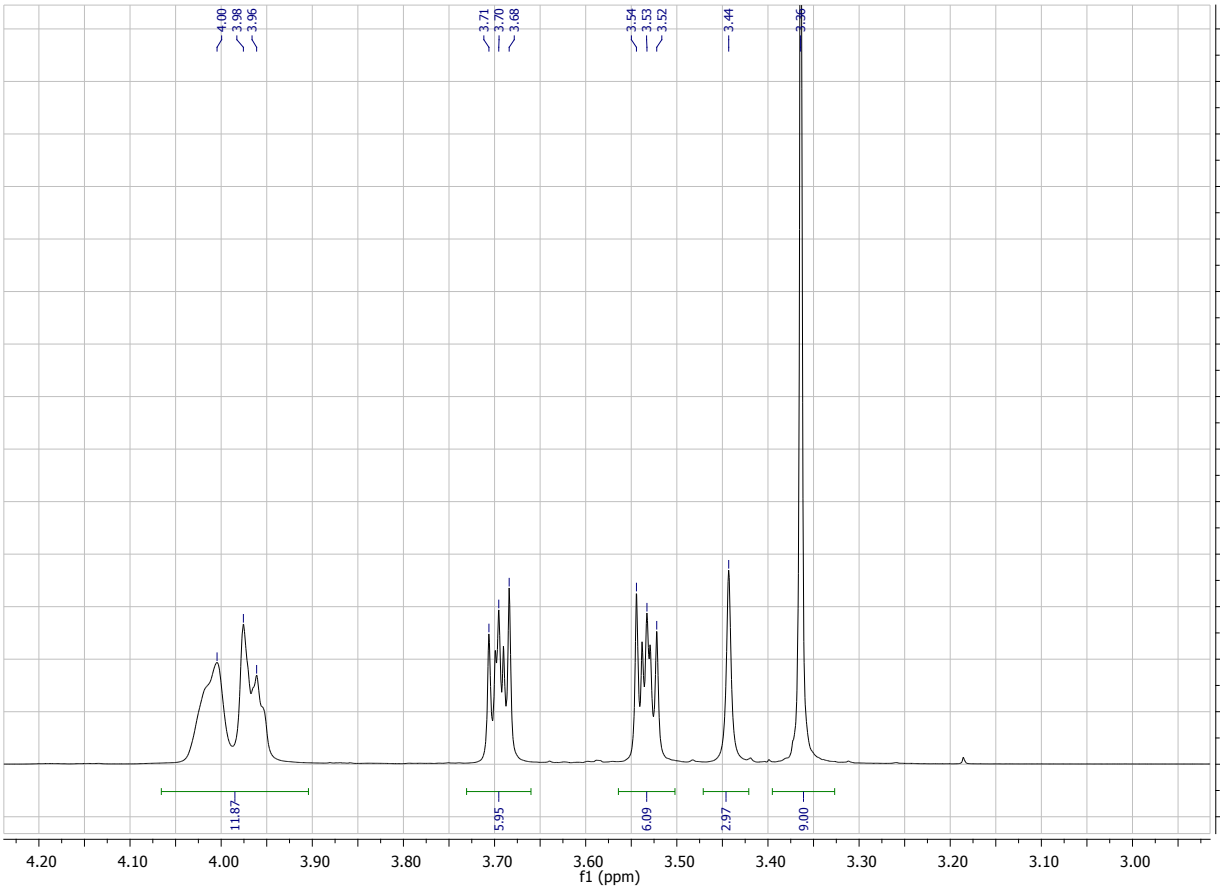

Figure S1: ^{1}H NMR (400 MHz) of ionic liquid (**1**) in $CDCl_3$

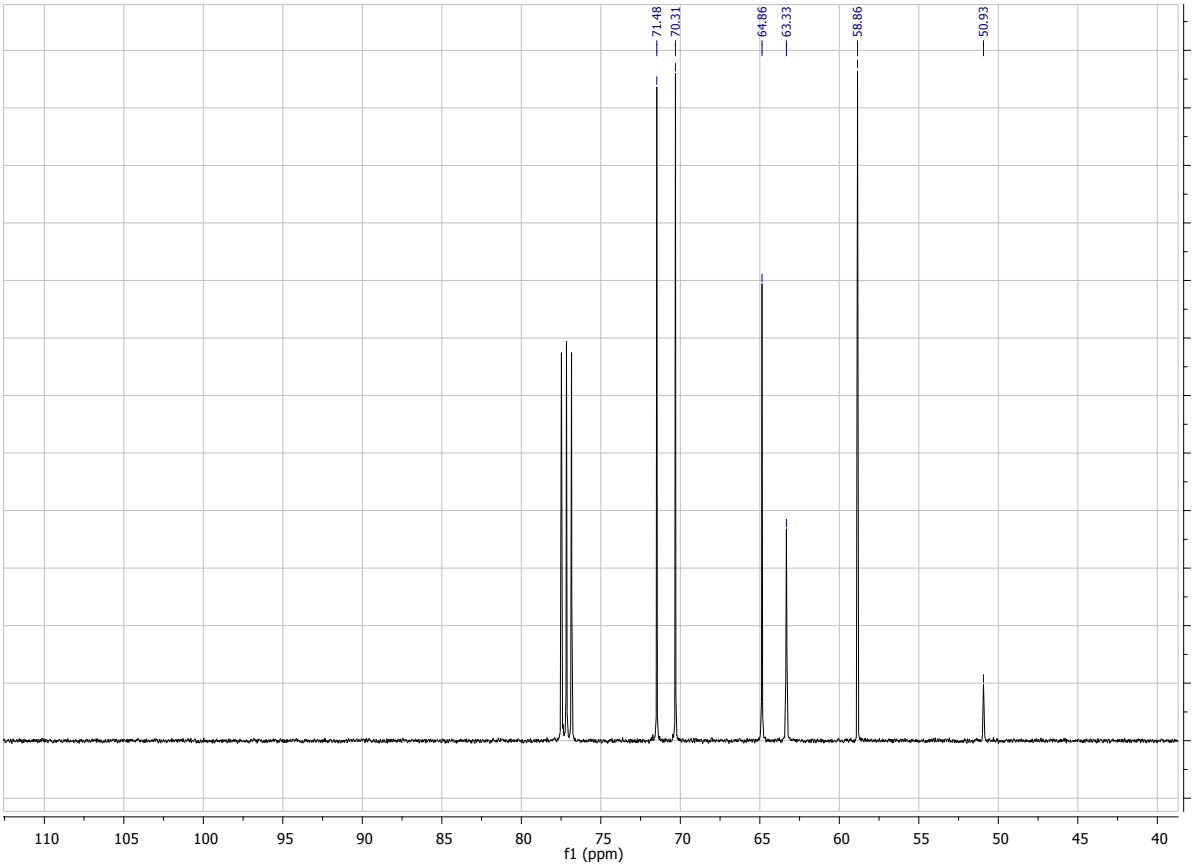

Figure S2: ^{13}C NMR (101 MHz) of ionic liquid (**1**) in $CDCl_3$

DSCs and TGAs of new ionic liquids

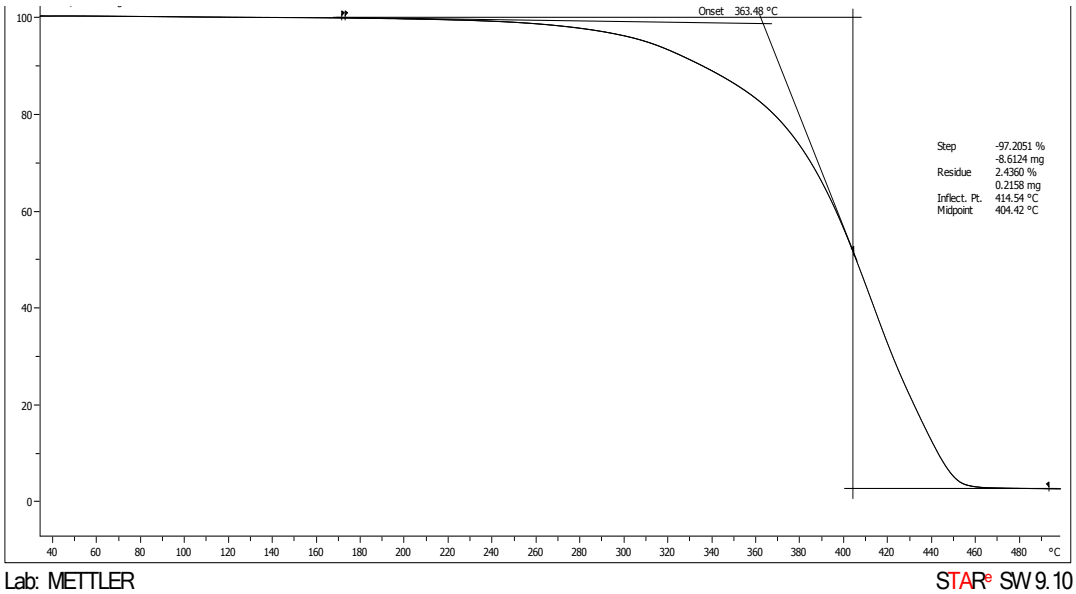

Figure S3: The Thermogravimetric analysis data of (**1**) (scan rate was set at 10 °C m^{-1})

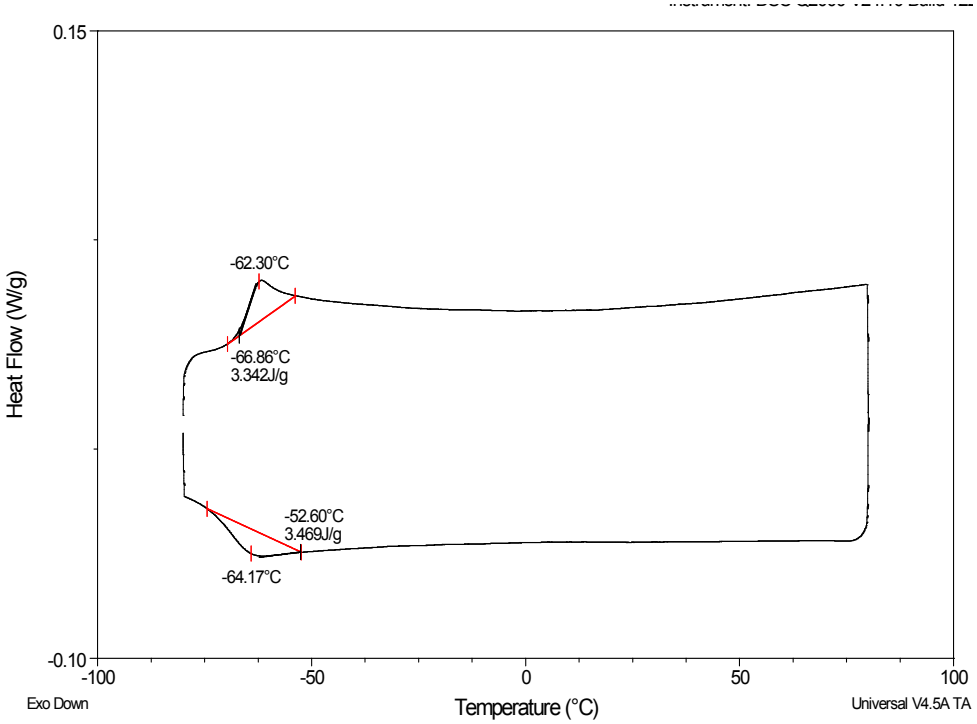

Figure S4: Differential scanning calorimetry of (**1**) (scan rate 5 °C m^{-1})

Apparatus for conducting the experiments related to release of the perfluoroiodide from an ionic liquid matrix

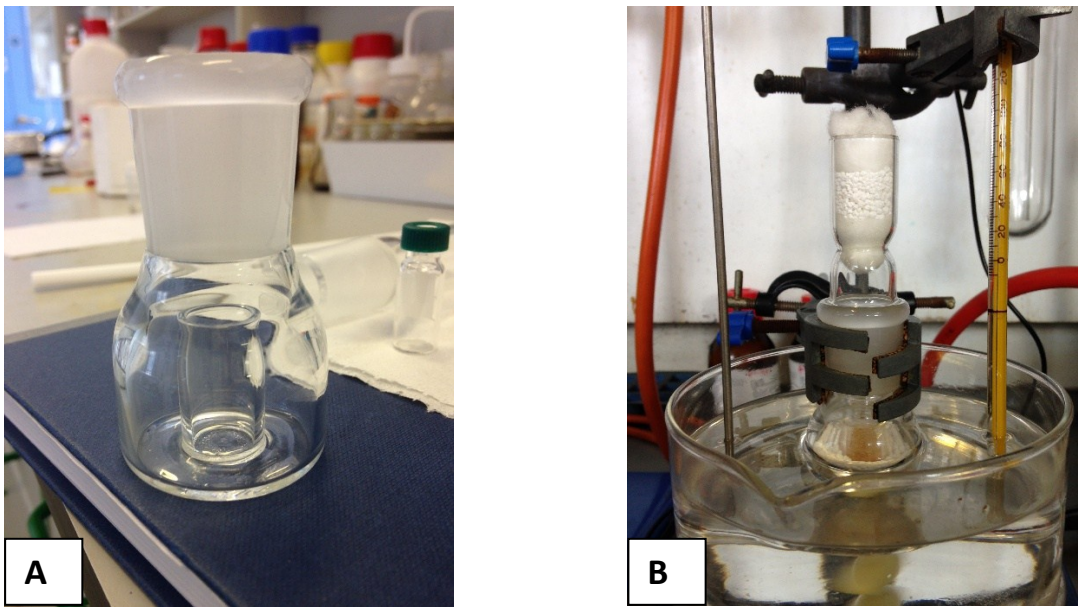

Figure S5: A; Glass jar with an inner compartment to house the GC-vial containing a mixture of ionic liquid and perfluoroiodide, **B**; final setup in a thermostatic oil bath with a drying tube attachment.

Additional gravimetric experiments:

(a) C_4F_9I (1 eq.) dissolved in ionic liquid (**1**; 1.2 eq.) can be heated to 50 °C in the apparatus shown in figure S5 and the released perfluoroiodide can be collected in a tube, cooled in dry ice, connected via the ground glass joint of the main apparatus. All the 'release' experiments were carried out in an efficient fumehood.

(b) In a screw capped glass bottle, ionic liquid (**1**; 5 mM, 2.33g) was loaded with C_4F_9I (4 mM, 1.38g) was kept in a fumehood at room temperature. The total weight of the bottle containing ionic liquid and perfluoroiodide were measured at appropriate time intervals.

Total weight of bottle + IL+ C_4F_9I = 29.71 g (t= 0 days)
= 29.70 g (t= 7 days)
= 29.67 g (t= 30 days)
= 29.63 g (t= 90 days)

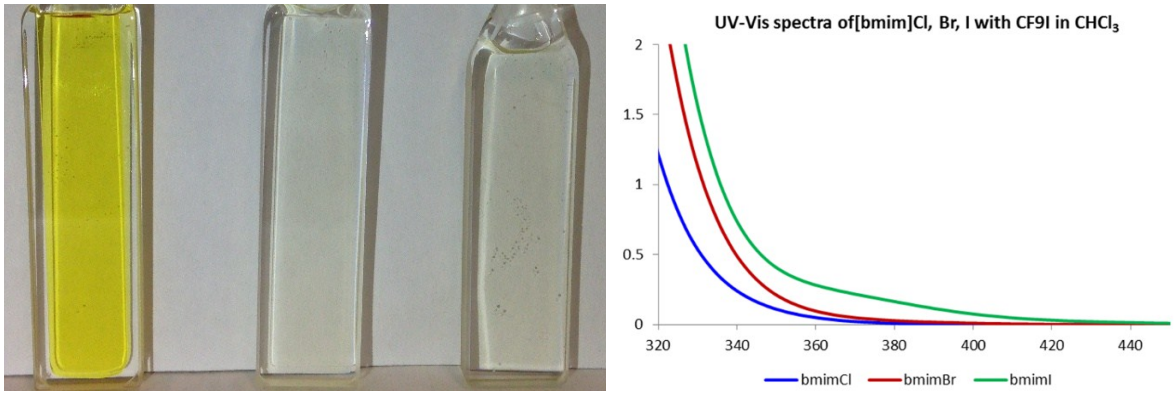

Figure S6: A; Glass jar with an inner compartment to house the GC-vial containing a mixture of ionic liquid and perfluoroiodide, B; final setup in a thermostatic oil bath with a drying tube attachment.

References

1. *Ionic Liquids in Synthesis***,** P. Wasserscheid and T. Welton, John Wiley & Sons, 25 Jun 2008**;** A. K. Burrell, R. E. Del Sesto, S. N. Baker, T. M. McCleskey and G. A. Baker, *Green Chem.,* 2007, **9**, 449–454