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.

1H NMR and 13C 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][NTf₂] and [bmim][CH₃OSO₃] were synthesised using procedures reported in the literature.² Four ionic liquids, [bmim][OAc], [bmim][CF₃CO₂], [bmim][SCN] and [bmim][CF₃SO₃] 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 CaCl₂.

Notes: It is noteworthy that [bmim][NTf₂] and CF₃CF₂CF₂I did not mix at the molar ratio that was used in this work. A clear phase separation was observed and hence, [bmim][NTf₂] was eliminated from the study.

**Synthesis of ionic liquid (1)**

Tris[2-(2-methoxyethoxy)ethyl]amine (3.23g, 10 mM) was taken up in CH₃CN (5 cm³) 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)**: ¹H NMR (400 MHz, in CDCl₃): δ 4.05-3.95 (brm, 12H, 6xOCH₂), 3.71-3.68 (m, 6H, 3xOCH₂), 3.54-3.52 (m, 6H, 3xN+CH₂), 3.44 (s, 3H, N+CH₃), 3.36 (s, 9H, 3xOCH₃).

¹³C NMR (101 MHz, in CDCl₃): δ 71.48, 70.31, 64.86, 63.33, 58.86, 50.93.

**ESMS:** For cation [C₁₆H₃₆NO₆] 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 perfluoriodide 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 perfluoriodide, B; final setup in a thermostatic oil bath with a drying tube attachment.
Additional gravimetric experiments:

(a) \(\text{C}_4\text{F}_9\text{I} \ (1 \text{ eq.})\) dissolved in ionic liquid (1; 1.2 eq.) can be heated to 50 °C in the apparatus shown in figure S5 and the released perfluoriodide 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 \(\text{C}_4\text{F}_9\text{I} \ (4 \text{ mM, 1.38g})\) was kept in a fumehood at room temperature. The total weight of the bottle containing ionic liquid and perfluoriodide were measured at appropriate time intervals.

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\text{Total weight of bottle + IL+ C}_4\text{F}_9\text{I} = 29.71 \text{ g} \ (t= 0 \text{ days})
\]
\[
= 29.70 \text{ g} \ (t= 7 \text{ days})
\]
\[
= 29.67 \text{ g} \ (t= 30 \text{ days})
\]
\[
= 29.63 \text{ g} \ (t= 90 \text{ days})
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Figure S6: A; Glass jar with an inner compartment to house the GC-vial containing a mixture of ionic liquid and perfluoriodide, B; final setup in a thermostatic oil bath with a drying tube attachment.

References