

## 1. Supporting information

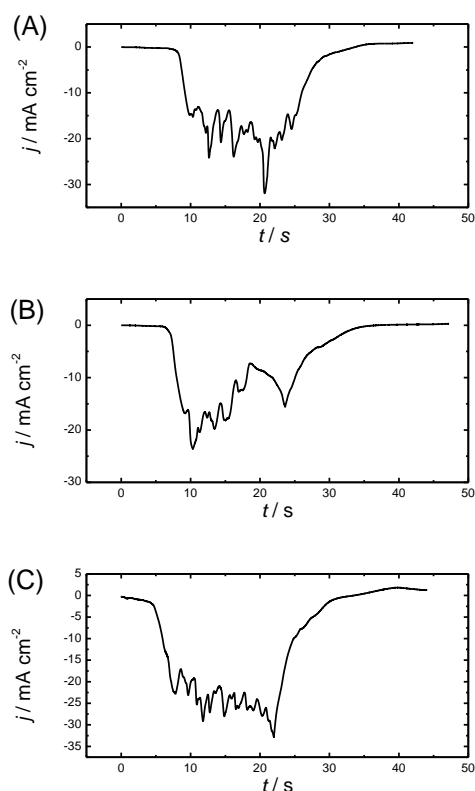
### 1.1. Preparation and characterisation of $[N^nBu_4][GeI_3]$

$GeI_2$  was purchased from Sigma and used as received.  $[N^nBu_4]I$  was purchased from Sigma and dried under vacuum at 373 K for 4 hours, then stored in a glove box.  $CH_2Cl_2$  was distilled from  $CaH_2$ ;  $Et_2O$  from a blue solution of Na/benzophenone ketyl.  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra were obtained on a Bruker AV II-400 spectrometer at 298 K and are referenced to the residual solvent signal. Elemental analysis was undertaken at London Metropolitan University.

A solution of  $[N^nBu_4]I$  (369 mg, 1.0 mmol) in  $CH_2Cl_2$  (10 mL) was added to a solution of  $GeI_2$  (326 mg, 1.0 mmol) in  $CH_2Cl_2$  (10 mL) and stirred for 16 hours. After this time the solution was filtered, concentrated to ~10 mL and  $Et_2O$  was layered on top. A dense red oil formed after ~16 hours, then the supernatant was decanted away and the oil dried in vacuo. Formation of a powdered solid was induced by triturating the oil. Yield: 633 mg of a red solid, 91%. Analysis: Calc. for  $C_{16}H_{36}GeI_3N$  (695.81): C, 27.62; H, 5.21; N, 2.01. Found: C, 27.74; H, 5.04; N, 2.10.  $^1H$  NMR ( $CD_3CN$ ): 3.15–3.24 (8H, m,  $NCH_2$ ), 1.62–1.72 (8H, m,  $NCH_2CH_2$ ), 1.47 (8H, sextet,  $J = 7.3$  Hz,  $CH_2CH_3$ ), 1.03 (12H, t,  $J = 7.3$  Hz,  $CH_3$ ) ppm.  $^{13}C\{^1H\}$  NMR: ( $CD_3CN$ ): 59.66 (t,  $J = 2.5$  Hz,  $NCH_2$ ), 24.64 ( $NCH_2CH_2$ ), 20.33 ( $CH_2CH_3$ ) 13.99 ( $CH_3$ ) ppm.

## 1.2. Charge integration upon the first voltammetric wave

Figure S1 shows chronoamperograms for  $[\text{GeCl}_3]^-$ ,  $[\text{GeBr}_3]^-$  and  $[\text{GeI}_3]^-$  corresponding to the cyclic voltammograms in Figure S1B, C and D with potential windows for each of +0.1 to -2.0 V, +0.34 to -2.0 V and +0.2 to -2.0 V, respectively.



**Figure S1.** Chronoamperometric traces for the first cycle voltammograms shown in Figure 1 B to D recorded for each species in supercritical fluid difluoromethane (358 K, 19.1 MPa) containing 60 mM  $[\text{N}^n\text{Bu}_4][\text{BF}_4]$ . Gold disc electrodes were employed with a scan rate of  $100 \text{ mV s}^{-1}$ , (A) 11 mM  $[\text{EMIM}][\text{GeCl}_3]$ , (B) 13 mM  $[\text{EMIM}][\text{GeBr}_3]$ , and (C) 16 mM  $[\text{EMIM}][\text{GeI}_3]$ .

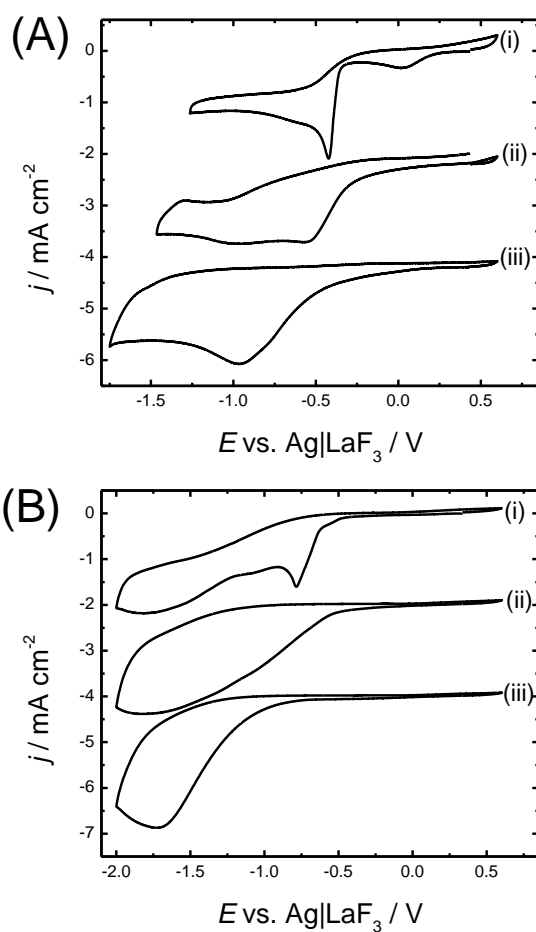
## 1.3. Voltammetry of $[\text{EMIM}][\text{GeI}_3]$ with $[\text{N}^n\text{Bu}_4][\text{BF}_4]$ in liquid $\text{CH}_2\text{F}_2$

Liquid difluoromethane and dichloromethane are close analogues to supercritical difluoromethane as solvents. At room temperature and pressure dichloromethane is a volatile liquid that can be easily employed as a solvent for electrochemistry. In contrast, at room temperature and pressure difluoromethane is a gas, however it can

be liquefied under modest pressure (vapour pressure 1.38 MPa at 293 K). The electrochemistry of  $[\text{GeI}_3]^-$  in dichloromethane has been reported previously.<sup>[1]</sup> Here we briefly report the electrochemistry in liquid  $\text{CH}_2\text{F}_2$ .

Figure S2A shows the voltammetry of 16 mM  $[\text{EMIM}][\text{GeI}_3]$  with 60 mM  $[\text{N}^n\text{Bu}_4][\text{BF}_4]$  in liquid difluoromethane at a gold electrode. On the first cycle, Figure S2A(i), there are reduction waves at  $E_{\text{peak}} = 0.02 \text{ V vs. Ag|LaF}_3$  and  $-0.42 \text{ V vs. Ag|LaF}_3$ . These correspond to the 2 electron reduction to form elemental Ge, with the first reduction corresponding to underpotential deposition of Ge onto gold, followed at more cathodic potential by bulk germanium deposition. Similar voltammetry was seen in dichloromethane.<sup>[1]</sup> On the anodic return scan there is no sign of a Ge stripping peak. With subsequent cycles the main reduction peak shifts cathodically (Figures S2A(ii) and (iii)) to  $E_{\text{peak}} = -0.55 \text{ V vs. Ag|LaF}_3$  and then  $E_{\text{peak}} = -0.96 \text{ V vs. Ag|LaF}_3$ .

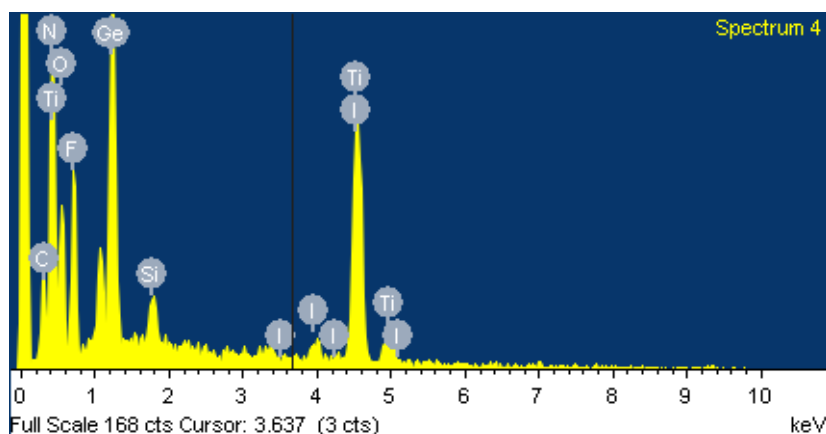
On TiN, Figure S2B, the results are similar, although the Ge deposition is shifted to a more anodic potential and there is no evidence for underpotential deposition on the first scan (compare Figures S2A(i) and S2B(i)).



**Figure S2:** Consecutive cyclic voltammograms recorded at  $100 \text{ mV s}^{-1}$  for  $16 \text{ mM}$   $[\text{EMIM}][\text{GeI}_3]$  in liquid  $\text{CH}_2\text{F}_2$ , containing  $60 \text{ mM}$   $[\text{N}^t\text{Bu}_4][\text{BF}_4]$  as background electrolyte. (A) Au disc electrode, (B) TiN flag electrode.

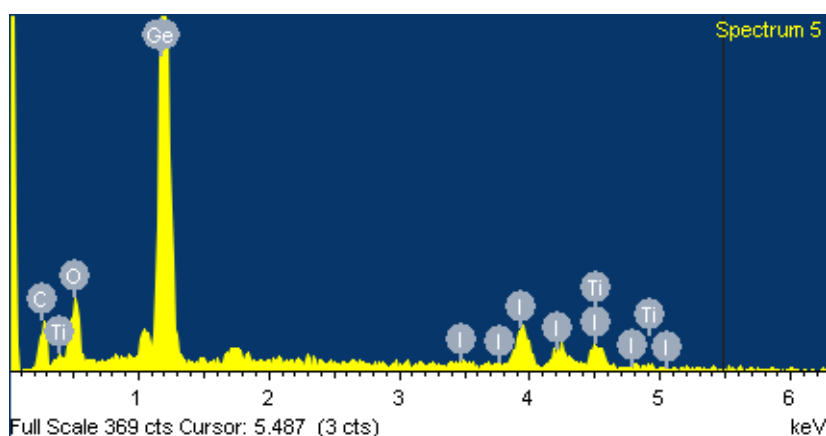
#### 1.4. Analysis of as-deposited thin films: EDX and XRD

EDX spectra of the films were recorded over  $60 \text{ s}$  using an accelerating voltage of  $10 \text{ keV}$  for the area of the low resolution SEM images shown in Figures 4C and 4E



Element	Atomic%
C K	4.14
N K	11.33
O K	10.14
F K	14.14
Si K	1.31
Ti K	37.69
Ge L	16.75
IL	4.50

**Figure S3:** EDS spectrum recorded for the as-deposited film formed by electrodeposition of Ge at -1.05 V vs. Ag|LaF<sub>3</sub> for 4000 s from a plating bath containing 16 mM [EMIM][GeI<sub>3</sub>] and 60 mM [EMIM][BF<sub>4</sub>] in supercritical difluoromethane at 358 K and 19.2 MPa. The corresponding SEM image is shown in Figure 2.



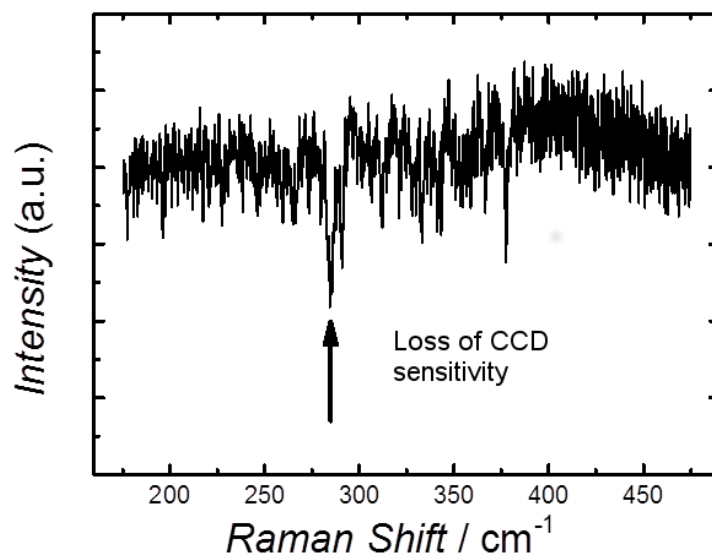
Element	Atomic%
C K	31.96
O K	18.57
Ti K	7.03
Ge L	32.09
IL	10.34

**Figure S4:** EDS spectrum recorded for the as-deposited film formed by electrodeposition of Ge at -1.05 V vs. Ag|LaF<sub>3</sub> for 4000 s from a plating bath containing 16 mM [N<sup>n</sup>Bu<sub>4</sub>][GeI<sub>3</sub>] and 60 mM [N<sup>n</sup>Bu<sub>4</sub>][BF<sub>4</sub>] in supercritical difluoromethane at 358 K and 19.2 MPa. The corresponding SEM image is shown in Figure 2.

### 1.5. Raman Spectra detector sensitivity

The spectral sensitivity of the CCD detector was evaluated between 175 and 475 cm<sup>-1</sup> under the same conditions used for measurements on the Ge samples. In this case, a white light source (effectivity emitting a black body radiation) was shone directly onto the CCD and the spectrum recorded. As shown in Figure S5 there is a loss of

sensitivity at  $284\text{ cm}^{-1}$  of band width of  $6\text{ cm}^{-1}$  which is also superimposed on the as-deposited Ge Raman spectra shown in Figure 4.



**Figure S5.** Raman spectrum recorded for a white light source showing the loss in sensitivity at  $284\text{ cm}^{-1}$ .

- [1] P. N. Bartlett, C. Y. Cummings, W. Levason, D. Pugh, G. Reid, *Chem. Eur. J.* **2014**, *20*, 5019-5027.