On the evaporation, bonding, and adsorbate capture of an ionic liquid on Au(111)

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Electronic Supplementary Information

1. Ultra-high vacuum ionic liquid evaporator

Ultra-thin layers of the IL $[C_2C_1Im][Tf_2N]$ were formed on the gold crystal by vapour phase deposition. Congruent evaporation (where the vapour has the same stoichiometric composition as the liquid, without decomposition) has been demonstrated for $[C_2C_1Im][Tf_2N]$ adsorption on Au(110)¹. The IL was produced from the evaporator, shown schematically in Figure S1. It consisted of a glass vial with an outer diameter of 11 mm and a length of 36 mm. The vial was enclosed by a copper tube, and secured in position by ferry alloy shims. A 20 W, 12 V, halogen light bulb was positioned within the tube but separated from the vial by a copper partition. Temperature measurements were made with a type K thermocouple in contact with the bottom of the glass vial. The assembly was mounted on a 70 mm OD conflat flange with electrical connections for the light bulb and connections for the thermocouple. The apparatus was mounted horizontally, and set back from the main chamber in a tube behind a moveable baffle, as shown in Figure S1. The vial was angled so that it pointed slightly upwards, such that IL would not spill out. The evaporator was directed at the gold sample, which was turned to face it. The light bulb heated the copper tube which heated the glass vial, but the light bulb did not irradiate the IL.



Figure S1. Schematic of the evaporator. With the baffle open, IL can evaporate into the main chamber. Not to scale.

The baffle could be rotated to either allow IL vapour emanating from the evaporator to enter the main chamber (the "open" position), or to prevent IL vapour from entering the chamber by blocking the direct line of sight (the "closed" position). The procedure for evaporating IL was as follows. Firstly, the evaporator was heated with

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the baffle in the "closed" position until a stable evaporator temperature was achieved. The baffle was then rotated to the "open" position for a defined period of time with the evaporator temperature remaining stable. Finally, the baffle was rotated back to the "closed" position.

2. Line of Sight Mass Spectrometry, LOSMS

LOSMS was used in this study to ensure that the only species detected were those originating from the sample position. In LOSMS a pulse counting mass spectrometer is shrouded by a cryopump (liquid nitrogen, 77 K) with two apertures which establish a line of sight between the ionisation volume of the mass spectrometer and a patch at the sample surface ²⁻⁵. Only species flying by line of sight from the sample, through both apertures, to the ionisation volume (the LOS molecular beam) are detected, all other trajectories are terminated by cryopumping on the shroud. The mass spectrometer, and hence the TPD experiment, are therefore blind to all gas sources external to the mass spectrometer except for the emitting area within its line of sight.

3. Enthalpy of vaporisation of acetone

Reference $\overline{}^{6}$ gives the following empirical relationship between enthalpy of vaporisation ($\Delta_{vap}H_T$) in J kmol⁻¹ and temperature (*T*) for acetone between the melting temperature and the critical temperature (*T_c*),

 $\Delta_{vap}H_T(J \text{ kmol}^{-1}) = (4.215 \times 10^7)(1-T_r)^{0.3397},$

where $T_r = T/T_c$ and $T_c = 508.2$ K for acetone. At T = 125 K, $\Delta_{vap} H_T = 38.3 \times 10^6$ J kmol⁻¹ i.e. 38 kJ mol⁻¹.

4. Determination of E_a and A_{θ} for [C₂C₁Im][Tf₂N] from zero order kinetics.

An example of $\ln(counts)$ versus 1/T for $\theta=4.23$ is shown in Fig.S2. The data has been fitted over the initial part of the curve (see Fig.S2 inset) where the coverage is high and hence zero order kinetics are obeyed. An activation energy of 126 ± 5 kJ mol⁻

¹ was determined from this and other experiments yielding $\Delta_{vap}H_{380}=129\pm5$ kJ mol⁻¹ at the average temperature of 380 K.



Figure S2. $\ln(counts)$ vs 1/T for θ =4.23 data from Fig.2A. The inset shows the part of the data (red) used for the straight line fit.

Figure S3 shows the same TPD data fitted using simulated zero order kinetics. The exponentially increasing part of the curve has been fitted across the temperature range where zero order kinetics hold (see straight line and inset in fig. S2). E_a was fixed at 125 kJ mol⁻¹ and A_θ varied for the best fit. The same method was has been used for zero order desorption of acetone from the gold surface and the IL surface.



Figure S3. Background-subtracted LOSMS signal (m/z = 111) versus T_s plot for TPD of IL on Au(111) for $\theta = 4.23$, from the desorption data shown in Fig.2A and S2. Note that the simulation uses initial coverage $\theta=3.23$, because the monolayer desorbs

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separately at higher T_s . Heating rate 1 Ks⁻¹. Also shown is a simulated TPD trace, assuming zero-order desorption kinetics and E_a =125 kJ mol-1. A_{θ} has been varied to get the best fit.

5. Surface densities and structures for particular planes in crystalline $[C_2C_1Im][Tf_2N]$

 $[C_2C_1Im][Tf_2N]$ crystallizes in the Pca2₁ space, group which is orthorhombic with three mutually perpendicular unit cell translation vectors of lengths *a*=18.499 Å, *b*=8.626 Å and *c*=19.255 Å.⁷ A single *ab* plane is shown in plan and side view in Fig.7A of the paper. The unit mesh is rectangular with dimensions *a*=18.499 Å, *b*=8.626 Å, giving an area of 159.57 Å² which contains two ion pairs, giving a density of 1.253 x 10¹⁸ ion pairs m⁻². One side of the plane has oxygens and imidazolium groups with the rings of the imidazolium groups parallel to the *ab* plane. The other side of the plane has CF₃ groups and imidazoliums groups, with the CF₃ groups projecting higher than the rings. If we assume that this IL layer lies immediately on top of the gold surface, it is probably orientated with the oxygen and aromatic imidazolium rings adjacent to the gold surface, with the CF₃ groups away from the surface. RGJ Evap Bonding and Ads Capture of an IL on Au(111) ESI 29-Mar-13 5

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