

Supporting information

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Background subtraction in the N 1s region:

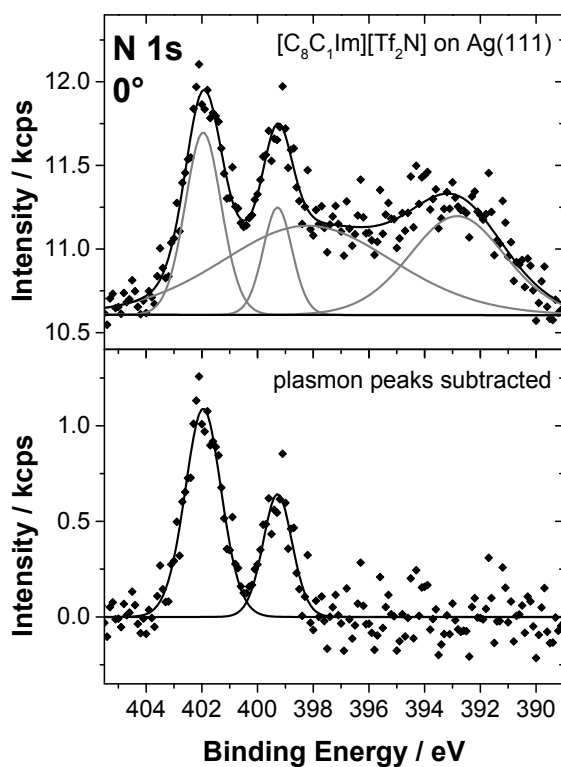


Figure S1: N 1s signal in 0° emission of 2.8 nm of $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ on Ag(111). The peak at higher BE corresponds to the two N atoms in the cationic imidazolium ring and the peak at lower BE to the single N atom in the anion. The peaks overlap strongly with satellites of the Ag 3d line of the substrate. A least-squares fit of the N 1s peaks together with the satellites was used to deal with the complicated background. The lower spectrum shows the IL related N 1s spectrum after subtraction of the substrate contributions of the spectra.

Composition of IL films on Ag(111) from PVD compared to macroscopic films

Table S1: Film composition as measured by XPS of a 3.7 nm thin film of [C₁C₁Im][Tf₂N] on Ag(111) (left) and a macroscopic droplet (right) at RT in 0° emission. Nominal ratios are given in brackets.

component	C _{het} 1s	C _{an} 1s	N _{cat} 1s	N _{an} 1s	O 1s	F 1s	S 2p
atom ratio	5.3 / 4.9 (5)	2.0 / 2.1 (2)	1.8 / 2.1 (2)	1.2 / 1.1 (1)	4.1 / 3.9 (4)	5.9 / 5.9 (6)	1.8 / 2.0 (2)
FWHM / eV	1.9 / 1.7	1.5 / 1.3	1.4 / 1.4	2.0 / 1.4	1.7 / 1.5	2.0 / 1.9	1.8 / 1.4
BE / eV	287.0 / 287.0	293.1 / 293.0	402.2 / 402.3	399.6 / 399.6	532.8 / 532.8	689.0 / 688.9	169.0 / 169.1

Table S2: Film composition as measured by XPS of a 2.9 nm thin film of [C₈C₁Im][Tf₂N] on Ag(111) (left) and a macroscopic droplet (right) at RT in 0° emission. Nominal ratios are given in brackets.

component	C _{alk} 1s	C _{het} 1s	C _{an} 1s	N _{cat} 1s	N _{an} 1s	O 1s	F 1s	S 2p
atom ratio	6.8 / 7.3 (7)	4.9 / 5.1 (5)	1.9 / 2.1 (2)	2.1 / 2.0 (2)	1.1 / 1.0 (1)	4.0 / 3.9 (4)	6.4 / 5.7 (6)	1.8 / 1.9 (2)
FWHM / eV	1.5 / 1.4	1.7 / 1.6	1.4 / 1.4	1.6 / 1.4	1.4 / 1.5	1.5 / 1.5	1.9 / 1.9	1.4 / 1.3
BE / eV	285.0 / 285.0	286.9 / 286.9	292.9 / 293.0	402.1 / 402.2	399.5 / 399.6	532.7 / 532.8	688.9 / 688.9	169.0 / 169.1

RT LEED study for sub-ML coverages of $[C_1C_1Im][Tf_2N]$ on Ag(111):

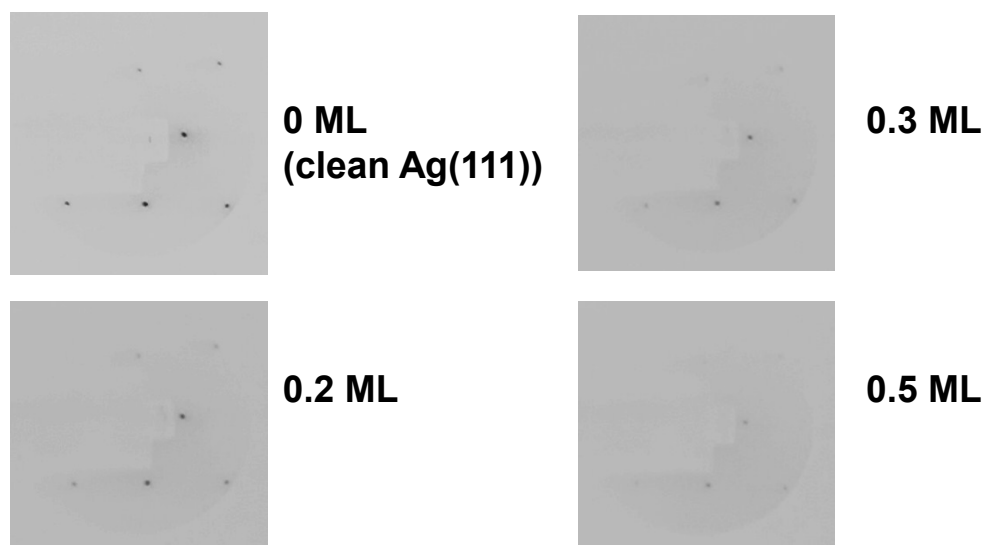


Figure S2: LEED series for sub-ML coverages of $[C_1C_1Im][Tf_2N]$ on Ag(111) at 300 K. The weak feature on the left side of the pictures is the shadow of the sample holder.

Reference experiment with low X-ray exposure after deposition of $[C_1C_1Im][Tf_2N]$ on Ag(111):

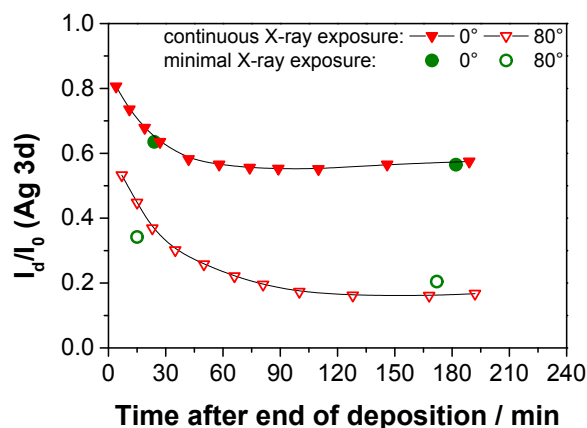


Figure S3: Time-dependent ARXPS of the IL film after ending the deposition of $[C_1C_1Im][Tf_2N]$ on Ag(111) at RT. The red triangles represent the data of Figure 8a. The green circles show data for a reference experiment with much lower exposure to X-rays, in which the sample was moved out of the X-ray beam between the scans in order to reduce the exposure for the measurements at ~ 180 min by more than a factor of 4.

