Supporting information

Adsorption and Thermal Evolution of $[C_1C_1Im][Tf_2N]$ on Pt(111)

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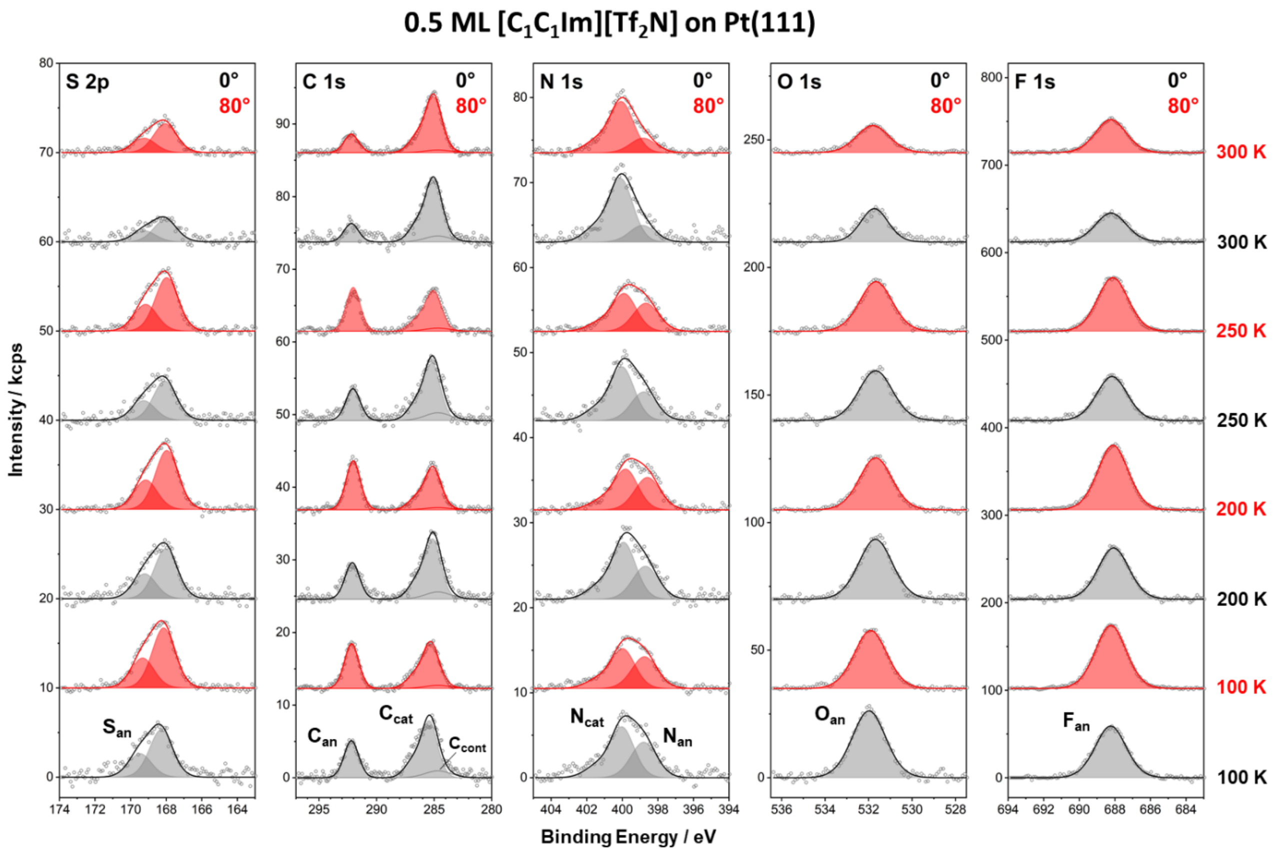

Figure S1: S 2p, C 1s, N 1s, O 1s and F 1s spectra of **0.5 ML** [C_1C_1Im][Tf_2N] on Pt(111), including peak fitting. Measured at 0° (black) and 80° (red) emission angle, after low temperature deposition and heating to the denoted temperatures (the 100 K film was deposited at 100 K, the other films at 200 K); for each temperature, a new layer was freshly prepared (the exact coverages of the individual layers varied between 0.46 and 0.54 ML; see Table S6). In the C 1s spectra, a small contamination of the surface (C_{cont}) was taken into account. Note that the spectra are the same as shown in Figure 6 without fitting.

Table S1: Quantitative analysis of the composition of **0.5 ML** [C_1C_1Im][Tf_2N] on Pt(111) at different temperatures, as derived from the XP spectra shown in Figure S1 at 0° (black) and 80° (red) emission angle.

	S_{an}	C_{an}	C_{cat}	N_{cat}	N_{an}	O_{an}	F_{an}	Σ
nominal	**2**	**2**	**5**	**2**	**1**	**4**	**6**	**22**
300 K, 80°	1.0	1.0	4.1	1.8	0.5	1.8	4.4	14.5
300 K, 0°	0.8	1.0	4.4	2.2	0.5	1.8	3.8	14.5
250 K, 80°	1.9	2.1	3.1	1.3	0.9	3.2	6.9	19.3
250 K, 0°	1.4	1.7	4.3	1.9	0.9	3.3	5.7	19.3
200 K 80°	2.1	2.7	3.1	1.4	1.0	3.4	8.4	22
200 K, 0°	1.8	2.0	4.5	2.0	1.0	4.0	6.7	22
100 K, 80°	2.1	2.4	3.3	1.4	1.0	3.7	8.1	22
100 K, 0°	1.7	2.0	4.2	1.8	1.1	4.5	6.7	22

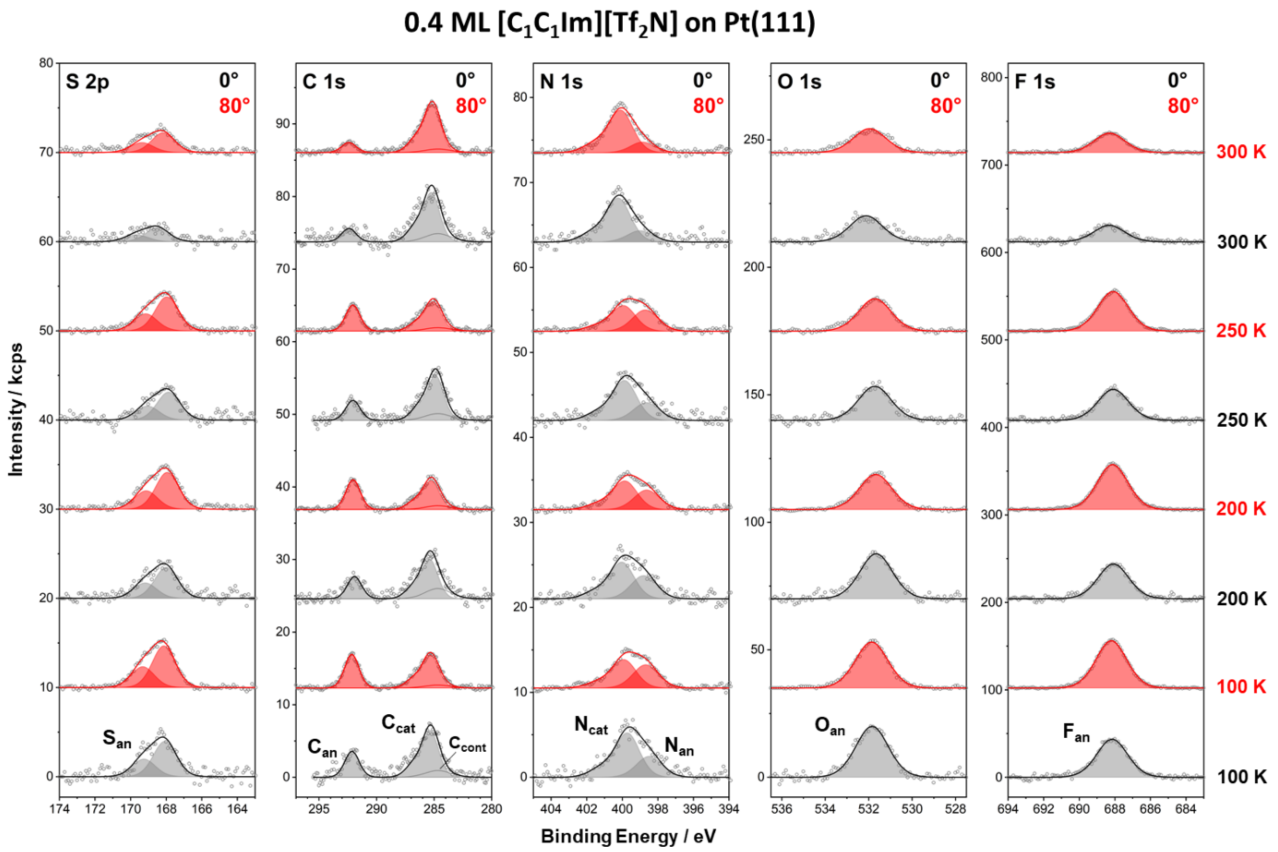

Figure S2: S 2p, C 1s, N 1s, O 1s and F 1s spectra of **0.4 ML** $[C_1C_1Im][Tf_2N]$ on Pt(111), including peak fitting. Measured at 0° (black) and 80° (red) emission angle, after deposition at 100 K and heating to the denoted temperatures; for each temperature, a new layer was freshly prepared (the exact coverages of the individual layers varied between 0.35 and 0.39 ML; see Table S6). In the C 1s spectra, a small contamination of the surface (C_{cont}) was taken into account. Note that the spectrum at 200 K (0°) is the same as shown in Figure 3c.

Table S2: Quantitative analysis of the composition of **0.4 ML** $[C_1C_1Im][Tf_2N]$ on Pt(111) at different temperatures, as derived from the XP spectra shown in Figure S2 at 0° (black) and 80° (red) emission angle.

	S_{an}	C_{an}	C_{cat}	N_{cat}	N_{an}	O_{an}	F_{an}	Σ
nominal	**2**	**2**	**5**	**2**	**1**	**4**	**6**	**22**
300 K, 80°	0.9	0.7	4.7	1.9	0.4	2.0	3.3	14.0
300 K, 0°	0.7	1.0	4.9	2.0	0.5	2.2	2.9	14.0
250 K, 80°	1.6	1.9	2.9	1.2	0.9	2.8	6.8	18.0
250 K, 0°	1.3	1.4	4.4	1.8	0.7	2.9	5.4	18.0
200 K 80°	1.9	2.4	3.2	1.5	0.9	3.4	8.7	22
200 K, 0°	1.6	1.8	4.4	1.9	1.1	4.4	6.8	22
100 K, 80°	1.9	2.4	3.3	1.3	1.0	3.9	8.2	22
100 K, 0°	1.6	1.9	4.6	2.0	0.9	4.4	6.6	22

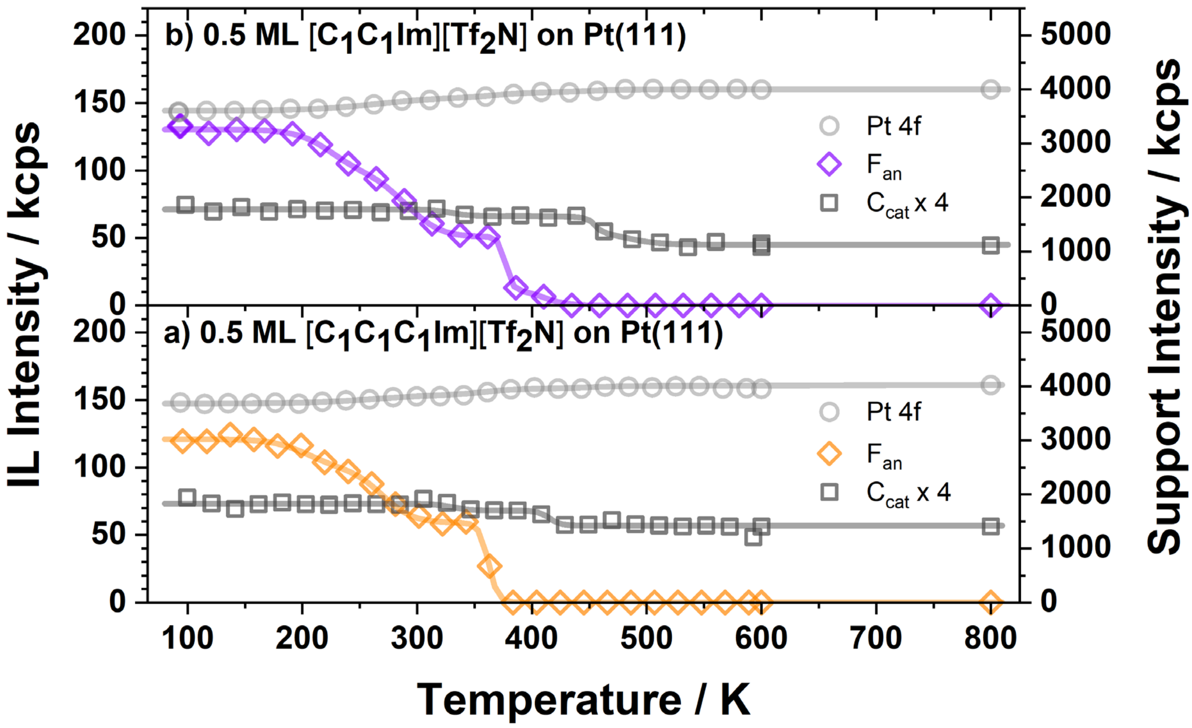

Figure S3: Comparison of the thermal evolution of (a) 0.5 ML $[C_1C_1C_1Im][Tf_2N]$ and (b) 0.5 ML $[C_1C_1Im][Tf_2N]$ on Pt(111), for the Pt 4f (light grey circles), F_{an} (orange (a) and violet (b) diamonds) and C_{cat} (dark grey squares) intensities during heating on Pt(111). The IL films were first deposited onto the sample at 100 K via PVD; thereafter, XP spectra were recorded while heating with a linear heating rate of 2 K/min up to 600 K; after flashing the samples to 800 K, a last data set was also recorded. The intensity scale for the Pt 4f signal is given on the right side and that of the F_{an} and C_{cat} signals on the left. Note that the data for $[C_1C_1Im][Tf_2N]$ (b) correspond to those in Figure 4b.

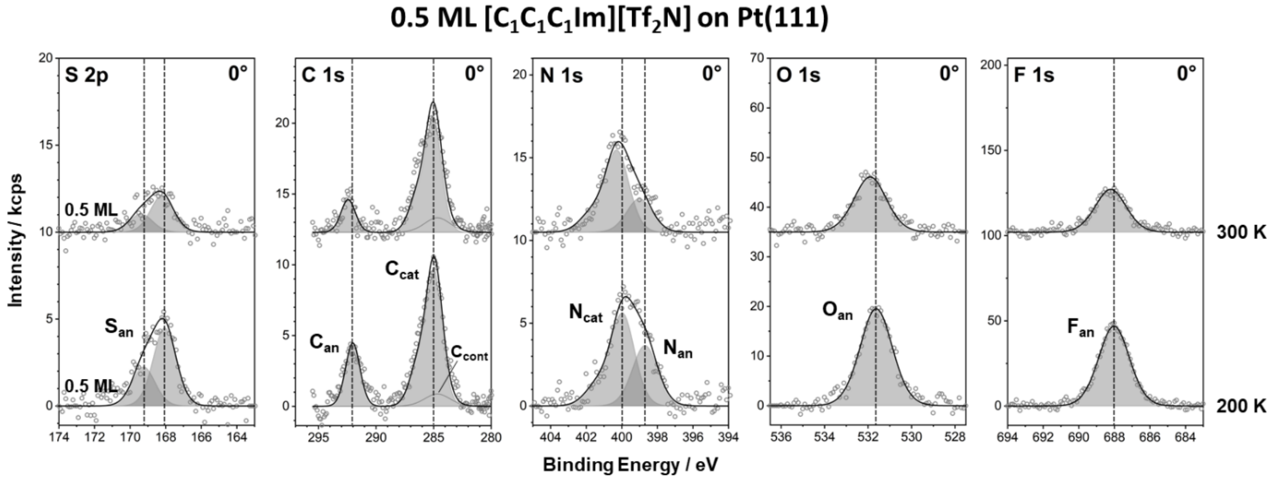

Figure S4. S 2p, C 1s, N 1s, O 1s and F 1s spectra of 0.5 ML $[C_1C_1C_1Im][Tf_2N]$ on Pt(111) at 200 K (deposited at 200 K) and 300 K (deposited at 100 K, followed by heating to 300 K). The exact coverages are 0.48 and 0.46 ML for 200 and 300 K, respectively, see Table S6. In the C 1s spectra, a small contamination of the surface (C_{cont}) was taken into account. The dotted lines indicate the binding energy positions of the film at 200 K.

Table S3: Quantitative analysis of the composition of **0.5 ML** $[C_1C_1C_1Im][Tf_2N]$ on Pt(111) at 200 and 300 K, as derived from the XP spectra shown in Figure S4.

	S_{an}	C_{an}	C_{cat}	$N_{cat, sum}$	N_{an}	O_{an}	F_{an}	Σ
nominal	**2 (2)**	**2 (2)**	**6**	**2**	**1 (1)**	**4 (4)**	**6 (6)**	**23 (15)**
300 K, 0°	0.7 (1.5)	1.0 (2.0)	4.8	1.6	0.6 (1.2)	2.0 (4.0)	3.1 (6.3)	13.7 (15)
200 K, 0°	1.7 (1.7)	2.1 (2.1)	6.2	1.9	1.1 (1.1)	3.7 (3.8)	6.3 (6.3)	22 (15)

Table S4: Fitting parameters for 0.4/0.5 ML thick films of $[C_1C_1Im][Tf_2N]$ and $[C_1C_1C\ _1Im][Tf_2N]$ on Pt(111). The S 2p doublet is separated by 1.18 eV, and the N_{cat} and N_{an} signals are separated by 1.21 eV. The C_{cat} signal was fitted with an additional shoulder at 1.52 eV higher binding energy (BE), with 25 % intensity of the main peak, and the N_{cat} signal with an additional shoulder at 1.50 eV higher BE, with 20 % intensity (10 % intensity for the film deposited at 300 K) of the main peak; this procedure reproduces the asymmetric line shapes of the cation signals. The absolute BEs in eV are not constrained and are given in Table 2.

0.4/0.5 ML	S_{an}	C_{an}	C_{cat}	N_{an}	N_{cat}	O_{an}	F_{an}
Fwhm /eV	1.53	1.48	1.67	1.70	1.60	1.75	2.04

Table S5: Summary of preparation conditions and file IDs for the shown STM images. After deposition of 0.5 ML IL at T_{prep}, onto clean Pt(111) and an optional annealing step to T_{max}, the sample was imaged at T_{meas}. The tunneling bias (U_{bias}) is applied to the substrate.

Figure	T_{meas}	T_{max}	T_{prep}	U_{bias}	I_{set}	**File_ID** [YYMMDD_##-##]
1a	110 K	157 K	157 K	1.2 V	0.3 nA	20210901_57-2
1b	110 K	157 K	157 K	1.2 V	0.3 nA	20210901_58-1
1c	110 K	157 K	157 K	1.2 V	0.4 nA	20210901_40-2
1d	110 K	200 K	157 K	1.2 V	0.3 nA	20210901_131-1
1e	110 K	200 K	157 K	1.2 V	0.3 nA	20210901_175-1
1f	110 K	200 K	157 K	1.2 V	0.3 nA	20210901_175-1
1g	110 K	250 K	157 K	1.2 V	0.5 nA	20210903_203-1
1h	110 K	250 K	157 K	1.2 V	0.2 nA	20210903_123-1
1i	110 K	250 K	157 K	1.2 V	0.3 nA	20210903_194-1
1j	110 K	300 K	157 K	1.2 V	0.3 nA	20210903_236-1
1k	110 K	300 K	157 K	1.2 V	0.2 nA	20210903_294-1
1l	110 K	300 K	157 K	1.2 V	0.2 nA	20210903_294-1

Table S6: Overview of the preparation/measuring conditions and file IDs for all XP spectra.

Figure		**File_ID** [YYMMDD-##]	**Coverage / ML**
2	100 K	221221-08 & -07 220628-07 & -08 230210-04 & -05 230206-04 & -05	4.3 0.37 0.46 0.54
	180 K	220711-06 to -25 220712-05 to -24	0.07 – 1.7 0.08 – 2.1
	200 K	230111-05 & -06 230207-04 & -05	3.3 0.54
3	a)	230111-05	3.3
	b)	230124-04	0.51
	c)	220614-03	0.35
4	c) 1.3 ML	220726-04 to -06	1.3
	b) 0.5 ML	230213-04 to -06	0.51
	a) 0.4 ML	220622-04 to -06	0.39
5	300 K, top	230321-05	0.47
	300 K	230126-03	0.49
	250 K	230125-04	0.50
	200 K	230124-04	0.51
	100 K	230127-03	0.52
6 & S1	300 K, 80°	230209-07	0.46
	300 K, 0°	230126-03	0.49
	250 K, 80°	230208-06	0.48
	250 K, 0°	230125-04	0.50
	200 K, 80°	230207-05	0.54
	200 K, 0°	230224-04	0.51
	100 K, 80°	230210-05	0.46
	100 K, 0°	230127-03	0.52
7		230313-03 to -14	0 – 3.3

S2	300 K, 80°	220705-07	0.39
	300 K, 0°	220519-04	0.39
	250 K, 80°	220704-05	0.37
	250 K, 0°	220601-03	0.37
	200 K, 80°	220629-06	0.36
	200 K, 0°	220614-03	0.35
	100 K, 80°	220628-08	0.37
	100 K, 0°	220524-05	0.38
S3	b)	230213-04 to -06	0.51
	a)	221026-03 to -05	0.46
S4	300 K	221020-06	0.46
	200 K	221019-04	0.48