Supporting Information

Enrichment Effects of Ionic Liquid Mixtures at Polarized Electrode Interfaces Monitored by Potential Screening

Sunghwan Shin,[#,*] *ORCID:* 0000-0002-2773-7649, Francesco Greco,[#] *ORCID: 0000-0001-8399-8475*, Florian Maier, *ORCID:* 0000-0001-9725-8961 and Hans-Peter Steinrück *ORCID:* 0000-0003-1347-8962

Lehrstuhl für Physikalische Chemie 2, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

In the following, we show the experimental data collected during the potential screening measurements. The data were obtained with a symmetric two-electrode electrochemical cell setup comprising two wires of identical metal (ϕ= 0.25 mm for Au, and ϕ=0.30 mm for Pt) as electrodes with identical contact area to the electrolyte. At a specific applied cell voltage, $U_{applied}$, the potential screening at the anode and cathode is determined through the binding energy shift of IL-related core level signals at the IL/vacuum interface by XPS (that is, F 1s for all systems containing more than 10 mol% $[C_8C_1Im][Tf_2N]$, N 1s for the rest).

Measurements were performed for different mixtures of $[C_8C_1Im][Tf_2N]$ and $[C_8C_1Im]Cl$, denoted as $[C_8C_1Im][Tf_2N]_xCl_{1-x}$, with Au and Pt electrodes; see Figures S2-S15. In each case, the binding energy of the F 1s (or N 1s) core level vs. applied potential is shown in (a) for applied cell voltages of -2 V to +2 V, with the working electrode (WE) grounded (black squares) and the counter-electrode (CE) grounded (blue triangles). The dashed lines indicate the ideal behavior, that is, equal potential drops at the anode/cathode interfaces (±0.5 eV/V). Also shown is the corresponding residual current during the XPS measurements (b), as measured at constant external voltages applied. The residual currents are estimated by averaging the current of each chronoamperogramm after 60 s at a constant voltage applied. The chronoamperometric measurements of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01) with Au electrodes are shown in Figure S1. A rapid decrease of current is observed within 1 s, which originates from the capacitive charging process during the EDL formation. After applying the voltage, we waited 60 s before starting the XPS measurement. The negligible residual currents of typically well below 0.2 μA confirm the absence of faradaic processes and an equilibrium state during

XPS (note that the remaining ±0.4 µA current of the ±2 V curves shown in Fig. S1 is due to leakage or parasitic currents in some of our electrochemical cells. Notably, for pure $[C_8C_1Im]Cl$ no such current is present (see Figure S9)).

For each studied mixture, the quantitative analysis of all IL-related core levels is shown in a separate Table (Tables S1-S14). Thereby, the experimental mol % is determined by the weighted amount of the two ILs in the mixtures, and the XPS mol % is obtained by the ratio of the areas of the Cl 2p and F 1s peaks. The nominal and experimental ratios are given in number of atoms of the various elements in the IL mixture.

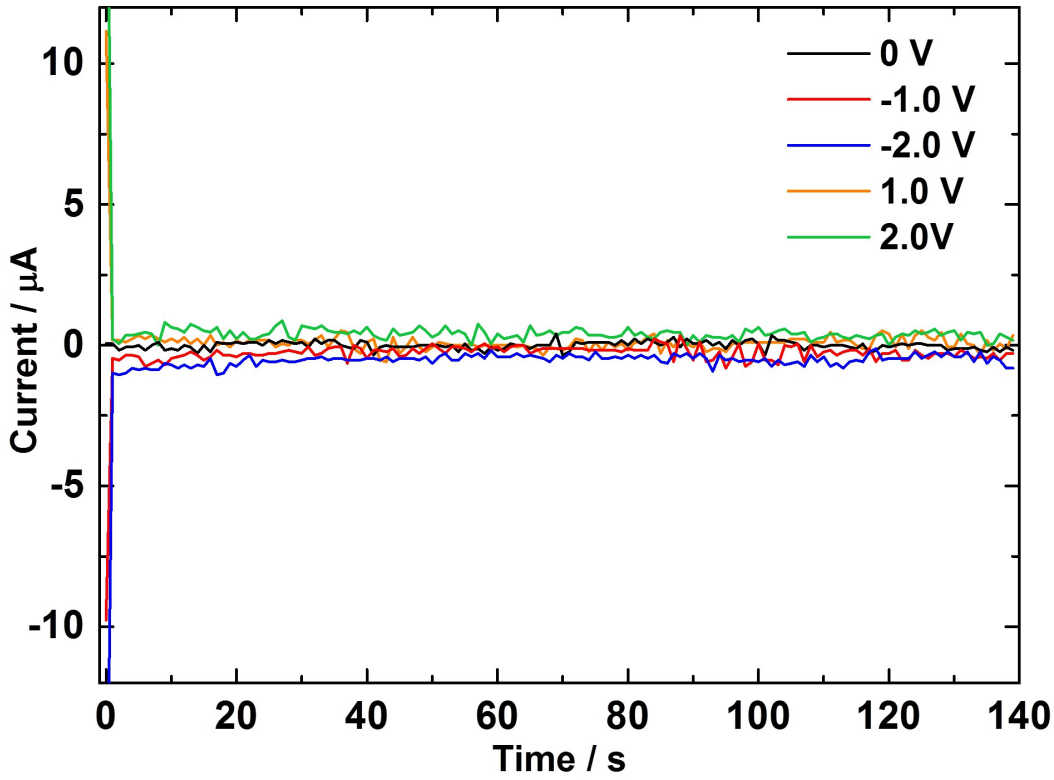

Figure S1. Current between Au electrodes in $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01) with a constant applied potential. The charging current for an EDL formation decreased rapidly within 1 s. All XPS measurements were started after the EDL formation and the residual current during the measurement was less than 0.2 µA; note that for this specific cell a residual leakage current of ±0.4 µA was present at the highest voltage of ±2V.

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 1.0) on Au electrodes

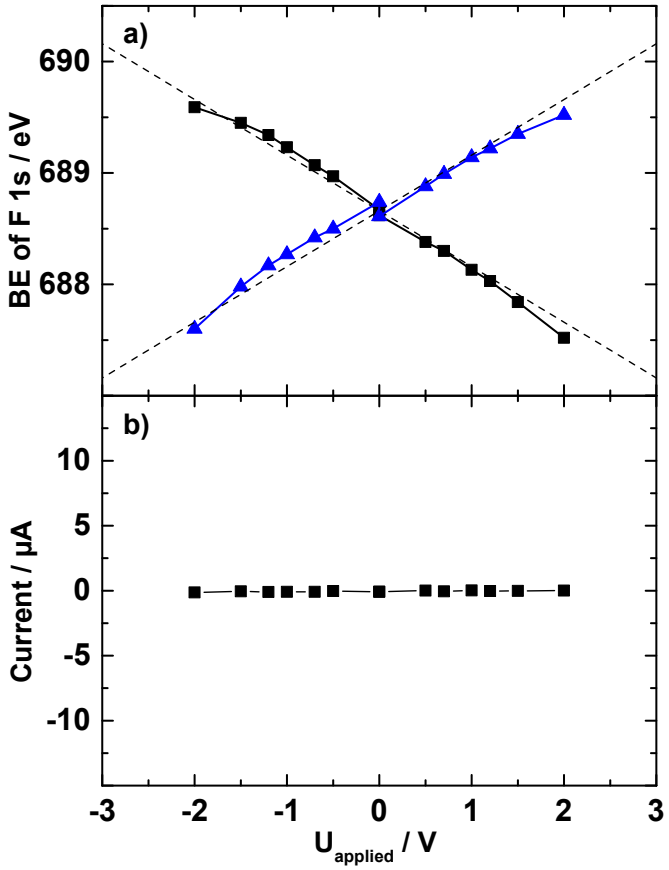

Figure S2. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 1) on Au. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S1. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 1) on Au.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 1.0)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**100**					**0**
XPS mol %										
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	6.0	4.0	1.0	2.0	2.0	-/-
Exp. ratio	1.9	1.0	4.0	6.8	6.1	4.0	1.0	2.1	1.9	-/-

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.999) on Au electrodes

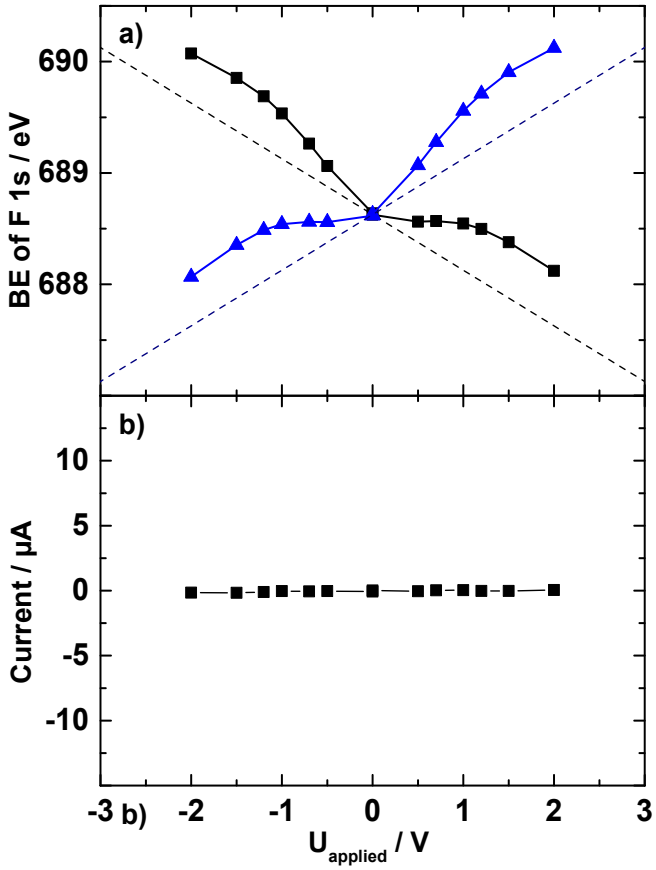

Figure S3. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.999) on Au. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S2. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.999) on Au.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.999)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**99.91**					**0.09**
XPS mol %					-/-					-/-
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	6.0	4.0	1.0	2.0	2.0	0.001
Exp. ratio	2.0	1.0	4.0	6.8	6.1	4.1	1.0	1.9	2.0	-/-

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.99) on Au electrodes

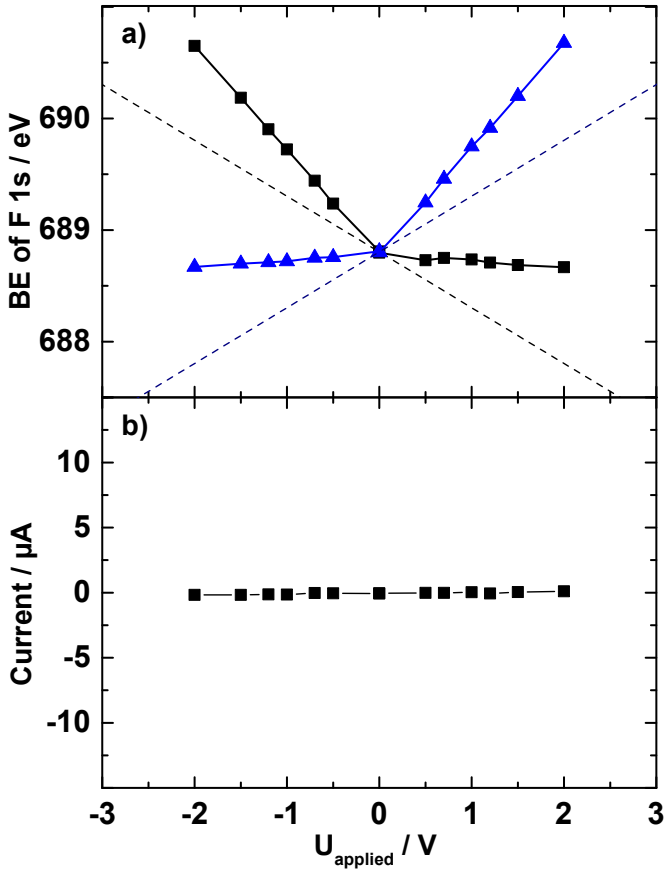

Figure S4. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.99) on Au. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S3. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.99) on Au.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.99)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**99.0**					**1.0**
XPS mol %					-/-					-/-
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	6.0	4.0	1.0	2.0	2.0	0.01
Exp. ratio	2.0	1.0	4.0	6.9	6.1	4.1	1.0	2.0	2.0	-/-

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.9) on Au electrodes

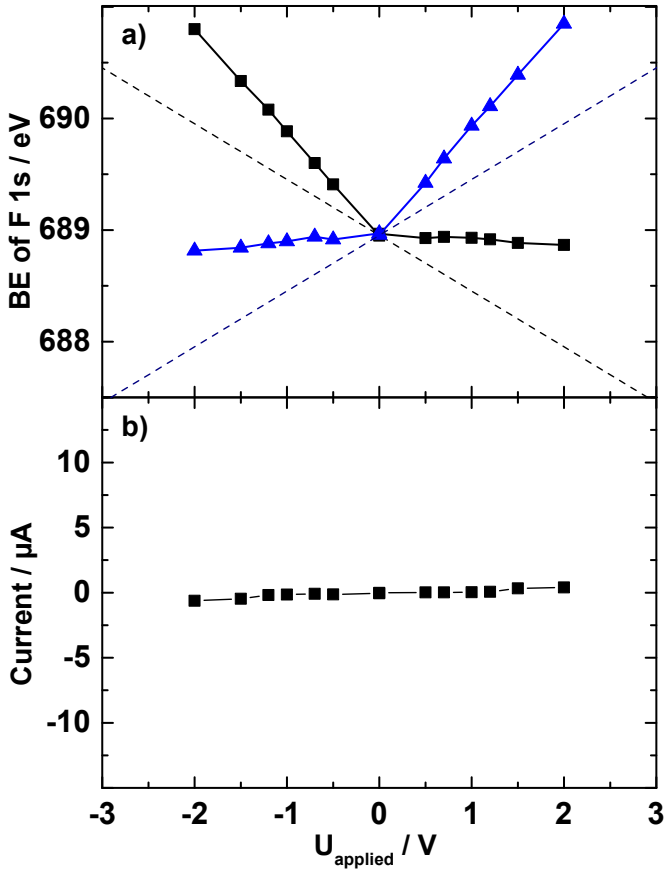

Figure S5. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.9) on Au. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S4. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.9) on Au.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.9)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**90.1**					**9.9**
XPS mol %					**90.3**					**9.7**
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	5.4	3.6	0.9	1.8	1.8	0.1
Exp. ratio	2.0	1.0	4.0	6.9	5.3	3.8	1.0	1.8	1.8	0.1

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.5) on Au electrodes

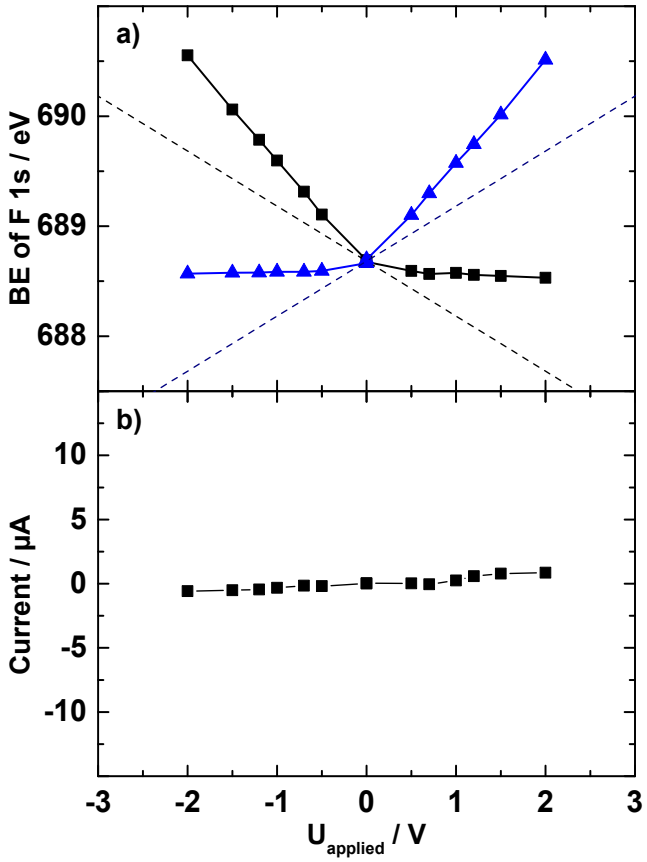

Figure S6. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.5) on Au. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S5. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.5) on Au.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.5)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**49.2**					**50.8**
XPS mol %					**51.4**					**48.6**
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	3.0	2.0	0.5	1.0	1.0	0.5
Exp. ratio	2.0	1.0	3.9	7.1	2.9	2.3	0.6	1.1	1.0	0.5

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.1) on Au electrodes

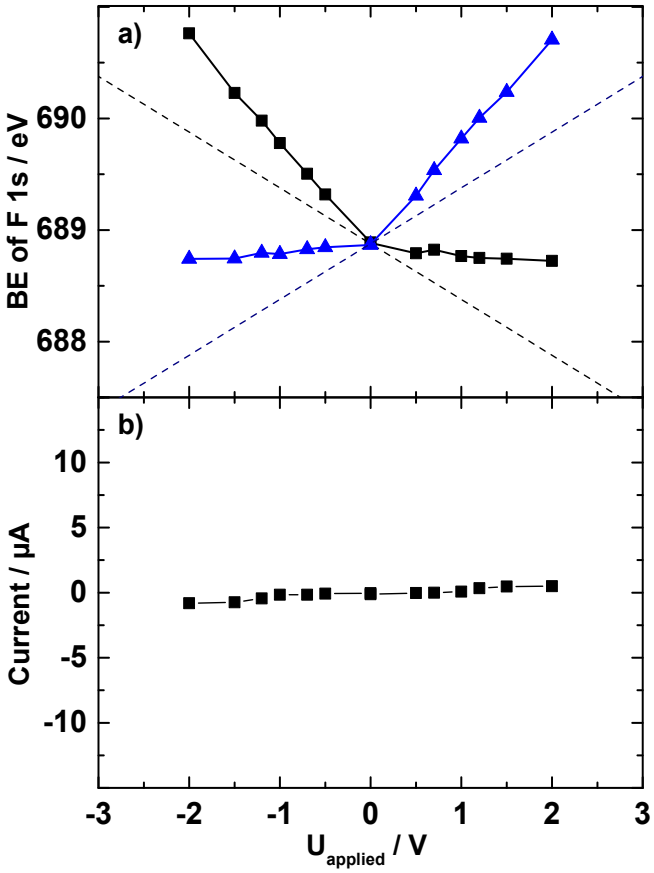

Figure S7. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.1) on Au. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S6. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.1) on Au.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.1)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**11.0**					**89**
XPS mol %					**14.7**					**85.3**
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	0.6	0.4	0.1	0.2	0.2	0.9
Exp. ratio	1.8	0.9	3.6	6.8	0.8	1.0	0.2	0.3	0.3	0.8

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01) on Au electrodes

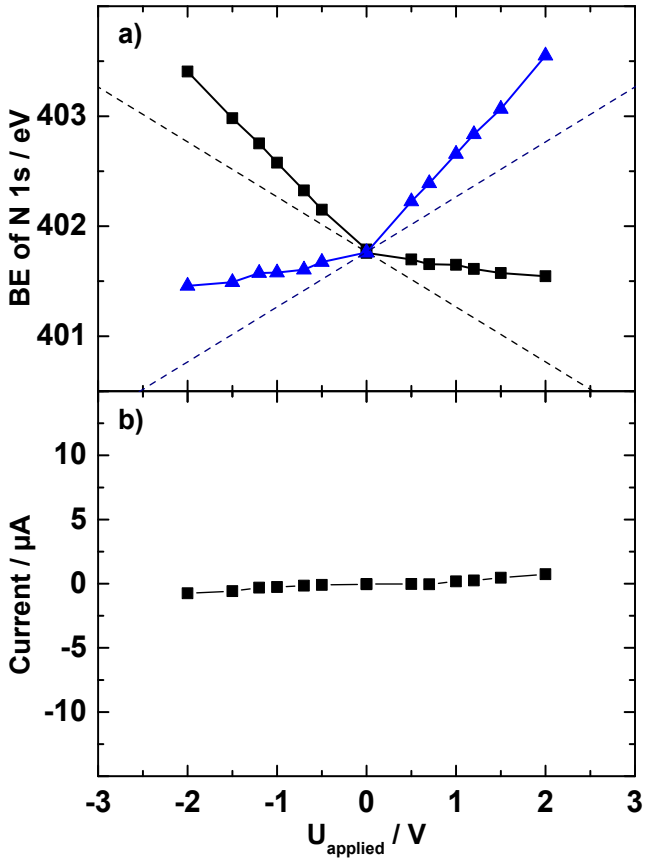

Figure S8. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01) on Au. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S7. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01) on Au.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**1.3**					**98.7.**
XPS mol %					**3.3**					**96.7**
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	0.06	0.04	-/-	-/-	0.02	0.99
Exp. ratio	2.0	1.0	3.9	7.0	0.19	0.16	-/-	-/-	0.05	0.95

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0) on Au electrodes

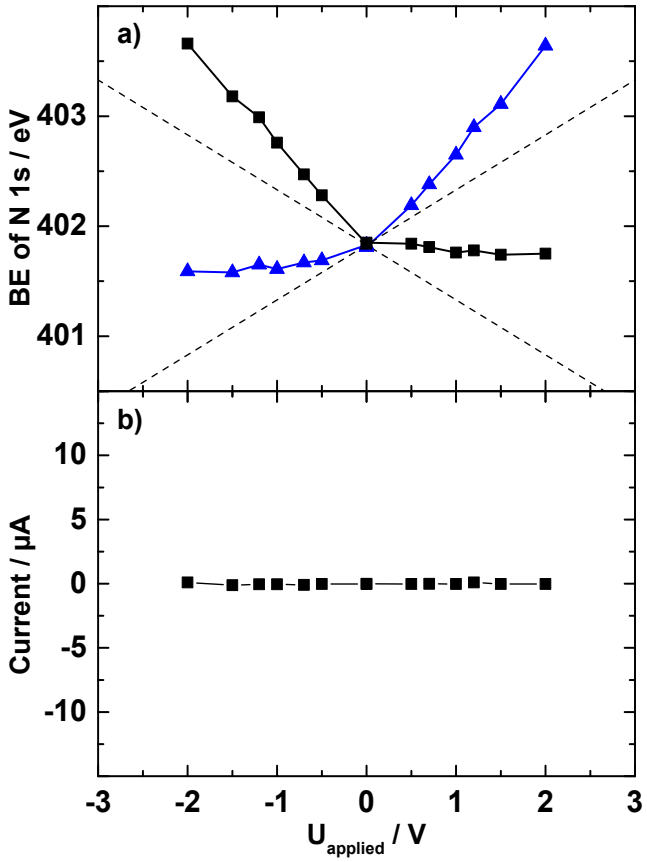

Figure S9. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0) on Au. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S8. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0) on Au.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**0**					**100**
XPS mol %										
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	-/-	-/-	-/-	-/-	-/-	1.0
Exp. ratio	1.9	1.0	4.0	7.1	-/-	-/-	-/-	-/-	-/-	1.0

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 1.0) on Pt electrodes

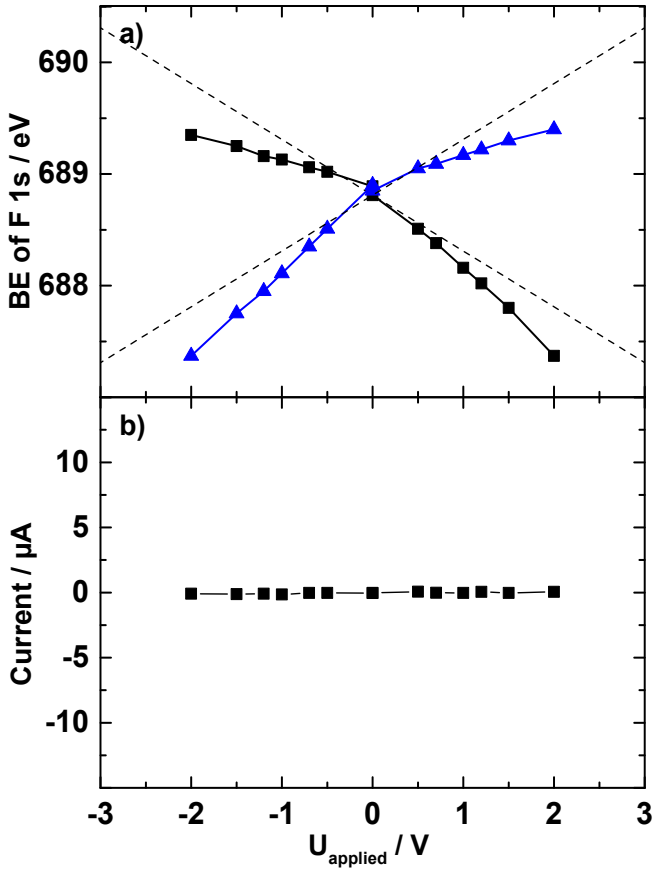

Figure S10. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 1.0) on Pt. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S9. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 1.0) on Pt.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 1.0)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**100**					**0**
XPS mol %										
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	6.0	4.0	1.0	2.0	2.0	-/-
Exp. ratio	1.0	1.0	4.0	6.8	6.1	4.1	1.0	2.0	2.1	-/-

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.99) on Pt electrodes

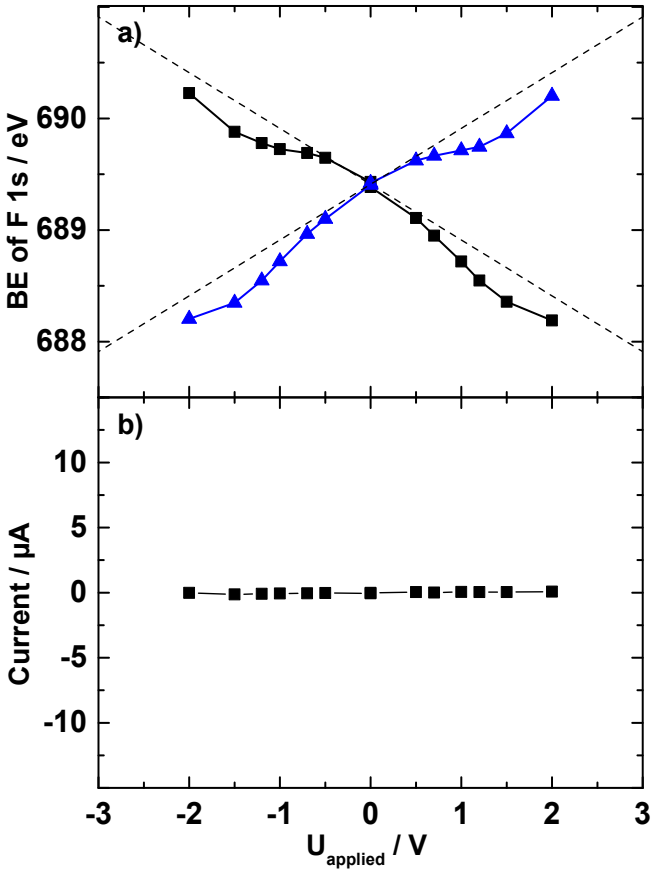

Figure S11. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.99) on Pt. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S10. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.99) on Pt.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.99)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**99.0**					**1.0**
XPS mol %					-/-					-/-
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	6.0	4.0	1.0	2.0	2.0	0.01
Exp. ratio	2.0	1.0	4.0	6.9	6.1	4.1	1.0	2.0	2.0	-/-

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.9) on Pt electrodes

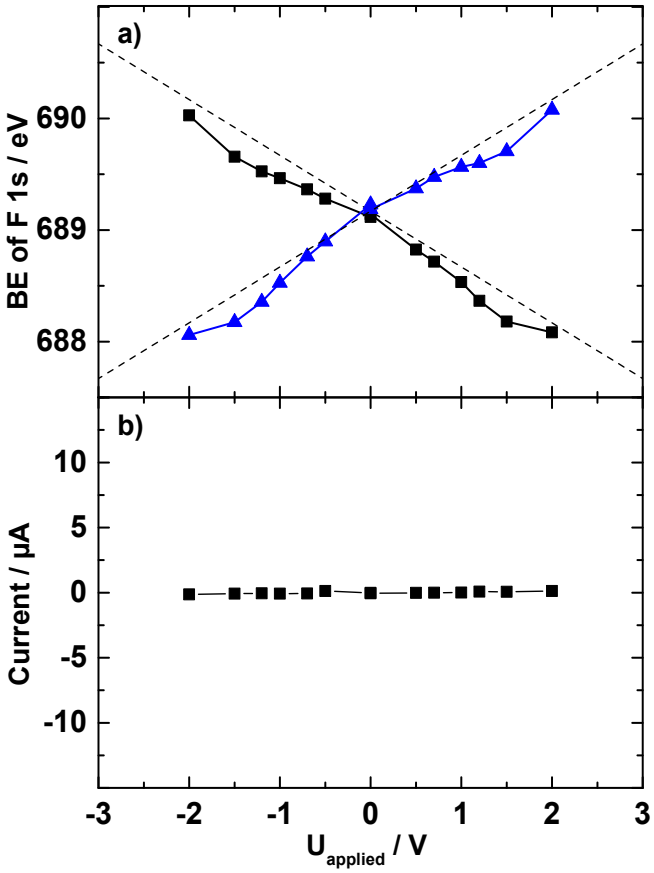

Figure S12. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.9) on Pt. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S11. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.9) on Pt.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.9)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**90.1**					**9.9**
XPS mol %					**88.0**					**12.0**
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	5.4	3.6	0.9	1.8	1.8	0.1
Exp. ratio	1.9	1.0	4.1	6.9	5.1	4.0	0.9	1.7	1.8	0.1

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.5) on Pt electrodes

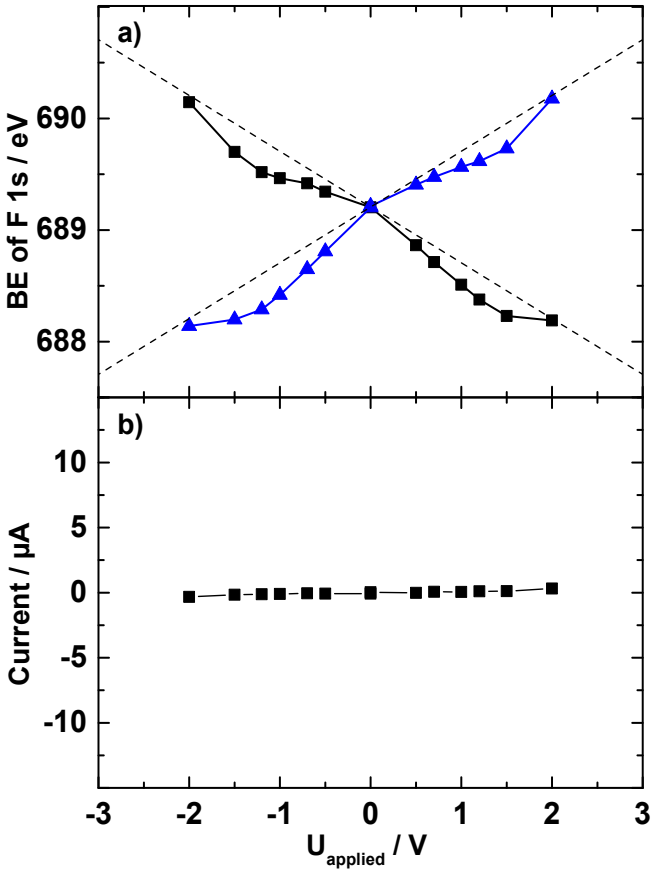

Figure S13. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.5) on Pt. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S12. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.5) on Pt.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.5)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**50.0**					**50.0**
XPS mol %					**44.1**					**55.9**
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	3.0	2.0	0.5	1.0	1.0	0.5
Exp. ratio	2.0	1.0	4.1	7.1	2.3	2.9	0.5	0.9	0.9	0.5

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.1) on Pt electrodes

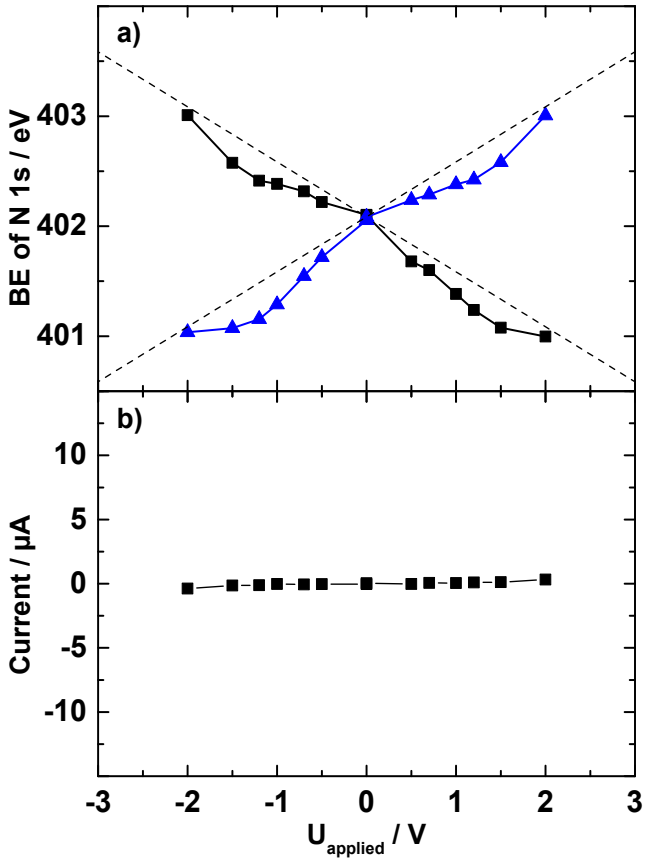

Figure S14. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.1) on Pt. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S13. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.1) on Pt.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.1)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**11.0**					**89.0**
XPS mol %					**10.2**					**89.8**
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	0.6	0.4	0.1	0.2	0.2	0.9
Exp. ratio	1.9	1.0	4.0	6.9	0.6	0.5	0.1	0.4	0.2	0.9

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01) on Pt electrodes

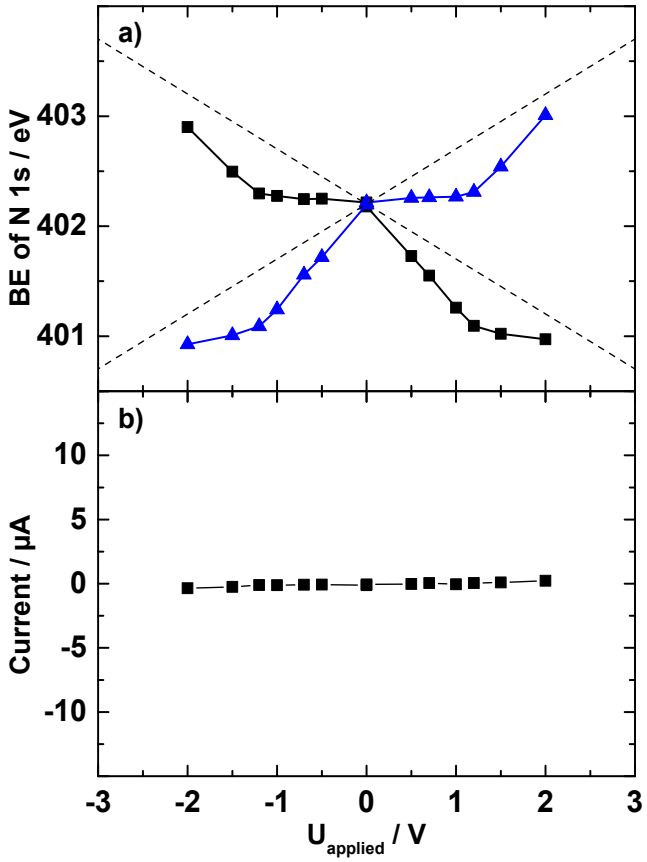

Figure S15. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01) on Pt. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S14. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01) on Pt.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0.01)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**1.3**					**98.7**
XPS mol %					**2.5**					**97.5**
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	0.06	0.04	-/-	-/-	0.02	0.99
Exp. ratio	2.0	1.0	4.0	6.9	0.15	0.11	-/-	-/-	0.05	0.96

$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0), on Pt electrodes

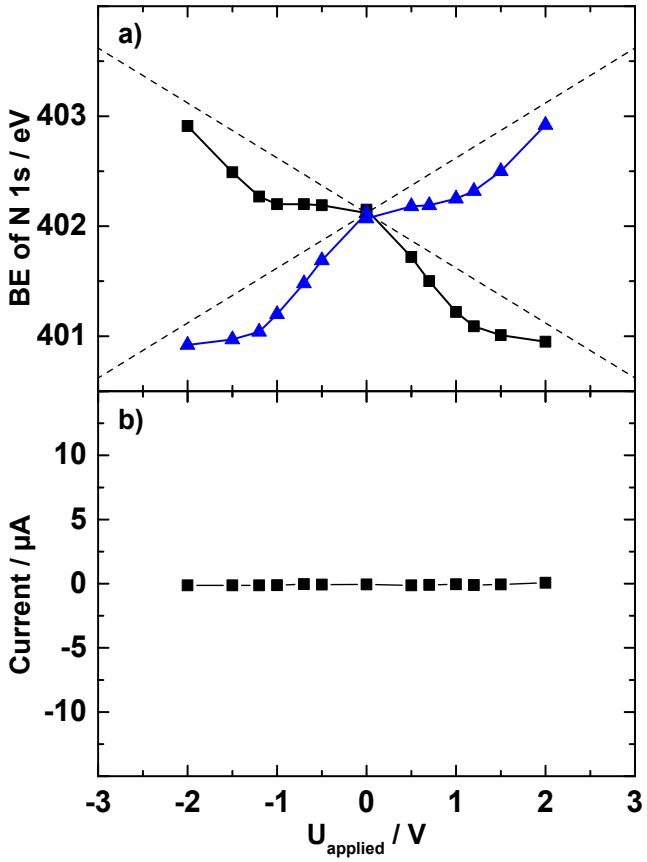

Figure S16. (a) Data for $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0) on Pt. (b) Residual current during the XPS measurements at constant external voltages applied.

Table S15. Quantitative analysis of the XP spectra of $[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0) on Pt.

	$[C_8C_1Im][Tf_2N]_xCl_{1-x}$ (x = 0)									
Ions	**$[C_8C_1Im]^+$**				**$[Tf_2N]^-$**					**Cl^-**
Exp. mol %					**0**					**100**
XPS mol %										
XPS regions	**N 1s N_{Im}**	**C 1s C_2**	**C 1s C_{het}**	**C 1s C_{alk}**	**F 1s F_{Tf2N}**	**O 1s O_{Tf2N}**	**N 1s N_{Tf2N}**	**C 1s C_{Tf2N}**	**S 2p S_{Tf2N}**	**Cl 2p**
Nominal ratio	2.0	1.0	4.0	7.0	-/-	-/-	-/-	-/-	-/-	1.0
Exp. ratio	2.0	1.0	4.0	7.0	-/-	-/-	-/-	-/-	-/-	1.0