Supporting information for:

Properties of ionic liquids on Au surfaces: Non conventional anion exchange reactions with carbonate

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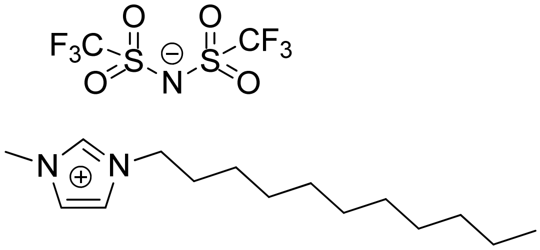
Experimental Section

MDMI-Br was synthesized as previously described by Lee *and al.* [1]. The MDMI-carboxylate was synthesized as described by Voutchkova and al [2]. Gold-coated glass slides were prepared by deposition of 1 nm Cr and 50 nm Au by sputter deposition. The RT-IL SAM was formed by soaking the Au-coated slides in a 5 mM solution of 1-(12-mercaptododecyl)-3-methylimidazolium bromide (MDMI-Br) in ethanol for 16 hours at 4°C. Thereafter, the gold slides were immersed in a salt solution (10 mM in water) to exchange the bromide anion with BF_4^-, PF_6^- or NTf_2^-. Immersing the Au slides coated with RT-IL-X (X = Br^-, BF_4^-, PF_6^- or NTf_2^-) in a bicarbonate buffer (20 mM $NaHCO_3$, 9g/L NaCl and pH = 7.60) for 16 hours resulted in anion exchange. To evaluate if the metathesis is reversible to the initial counter anion, the Au slides were immersed once again in the respective salt solution (10 mM in water) for 16 hours. Aqueous contact angle was measured for all samples. A 30 µL drop of water was deposited on the RT-IL SAM. A picture of the droplet was acquired with a digital camera and the contact angle was measured using Image J (freeware available on the website of the National Institutes of Health – NIH). Mid-IR analysis of the RT-IL SAM and the anion exchange process was performed on a FTIR equipped with a Ge attenuated total reflection accessory (Bruker optics) with 4 cm^{-1} resolution. XPS measurements were performed using an ESCALAB 3 MKII with a Mg K_a source at a power of 206 W and a 0.05 eV resolution. The XPS data were obtained by averaging four identically prepared samples.

For MS analysis, 10 mg/mL solution of 2,5-dihydroxybenzoic acid dissolved in 1:1 ethanol/H_2O + 0.1% trifluoroacetic acid (TFA) was spotted directly on the gold layer modified with the RT-IL SAM. The analyses were performed by MALDI-TOF MS using an UltrafleXtreme mass spectrometer operated by Flex Control 3.0 software (Bruker Daltonics, Billerica, MA). Data acquisition was carried out in reflectron geometry under optimized delayed extraction conditions with a source accelerating voltage of + 0 – 25 kV in the *m/z* range between 10 – 2000. Flex Analysis software (Bruker Daltonics) was then used for the analyses of the mass spectra. In each case, the measurements for contact angle, mid-IR, XPS, and MS were performed on the RT-IL with the original anion and after exchange in bicarbonate buffer.

Au NPs were synthesized by citrate reduction of $AuCl_4^-$ [3]. Thereafter, the RT-IL was self-assembled on the gold nanoparticles by exposing the citrate-capped Au NPs to MDMI-Br. To 10 mL of gold nanoparticle solution (5 to 10 nM), 20 µL of MDMIBr (450 µM) was added and stirred for one hour. Then, 32 µL of a 1 mM solution (Au NP agglomerate in 10 mM) specific counter anion (BF_4^-, PF_6^- or NTf_2^-) was added to the reaction mixture and stirred overnight. The Au NP reacted with the RT-IL was centrifuged and decanted to recuperate the Au NP. A first portion of the Au NP was set aside as a control for analysis by Raman spectroscopy. The second portion exposed to 5 mL of HCO_3^- (1 mM, 0.45 g/L NaCl, pH = 7.40) overnight. Each sample was centrifuged and decanted for analysis by Raman spectroscopy after anion exchange. The Raman spectra were acquired on a Renishaw InVia Raman microscope with a 633 nm excitation laser. Each Raman spectrum was acquired at 10% laser power (approximately 2-3 mW at the sample) with an integration time of 10 s.

1-undecyl-3-methylimidazolium bistrifluoromethanesulfonimide

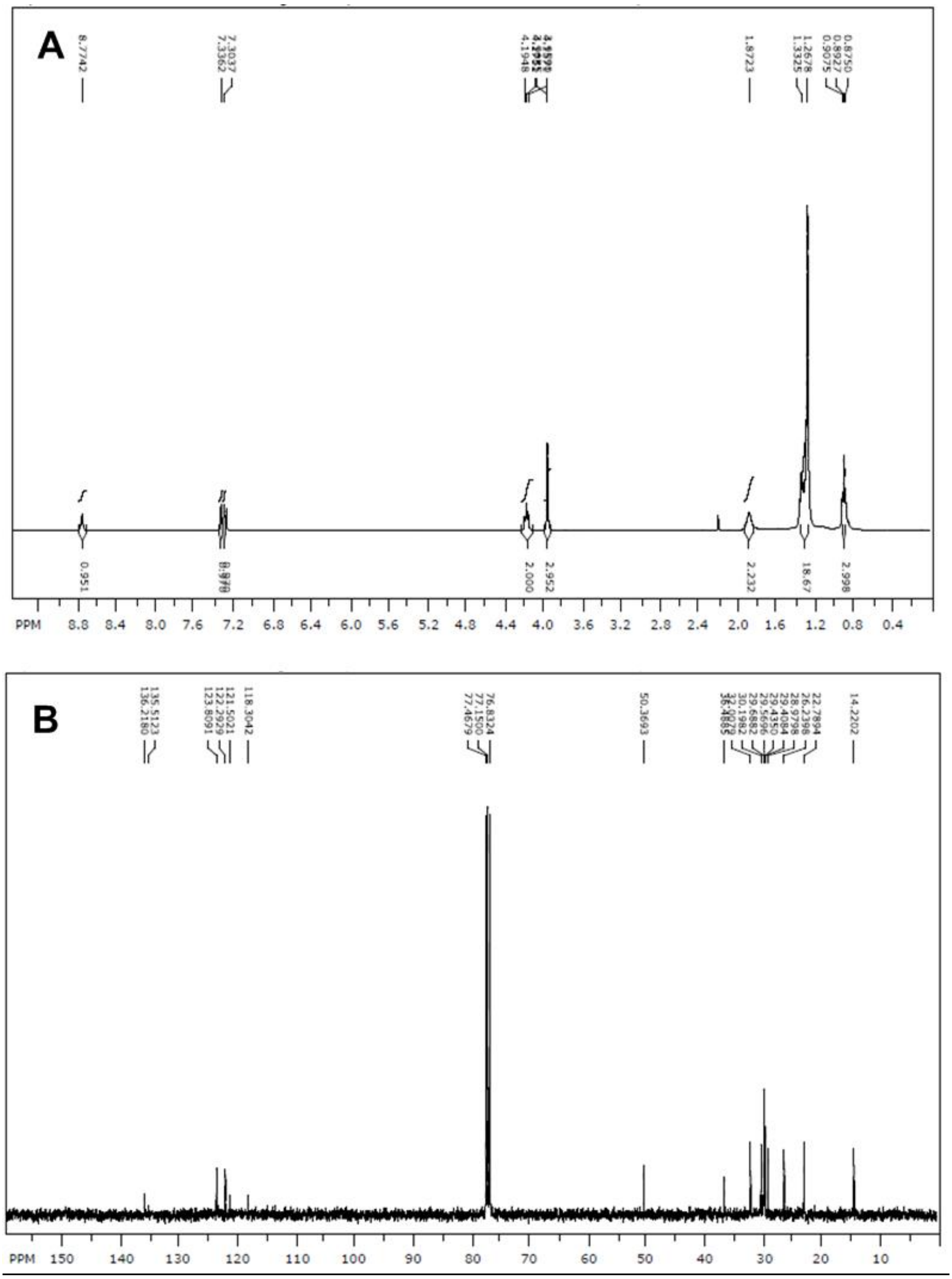


^{1}H-NMR (400 MHz, $CDCl_3$): (δ, ppm): 0.84-0.90 (t, *J*=7.0 Hz, 3H), 1.21-1.34 (m, 18H), 1.78-1.90 (m, 2H), 3.94 (s, 3H), 4.11-4.19 (t, *J*=7.0 Hz, 2H), 7.28 (s, 1H), 7.31 (s, 1H), 8.75 (s, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): (δ, ppm): 14.2, 22.8, 26.2, 29.0, 29.4, 29.4, 29.6, 29.7, 30.2, 32.0, 36.5, 50.4, 118.3-121.5 (d, $J_{C\text{-}F}$= 320 Hz), 122.3, 123.8, 136.2.

^{19}F-NMR (160 MHz, $CDCl_3$): (δ, ppm): -79.5.

Supplementary figures and tables: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1.8723
1.2678
1.3325
0.8750
0.8927
0.9075
0.951
2.000
2.952
2.232
18.67
2.998
PPM
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
B
135.5123
136.2180
121.5021
122.2929
123.8091
118.3042
76.8324
77.1500
77.4679
50.3693
36.4885
30.1982
29.6882
29.5696
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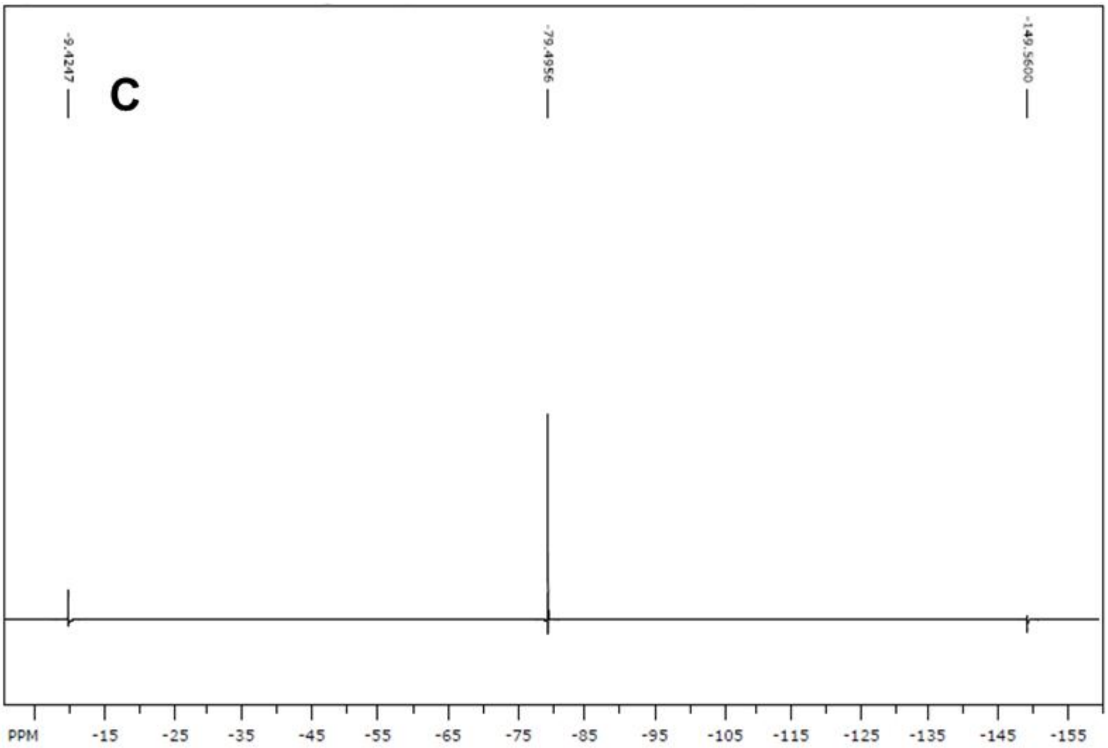

Figure S1: (A) ^{1}H NMR, (B) ^{13}C NMR, and (C) ^{19}F NMR spectra of 1-undecyl-3-methylimidazolium NTf_2^- following the exposition of a solution to HCO_3^-. The NMR spectra are identical to the starting material, indicating that the metathesis did not occur with exposure to bicarbonate.

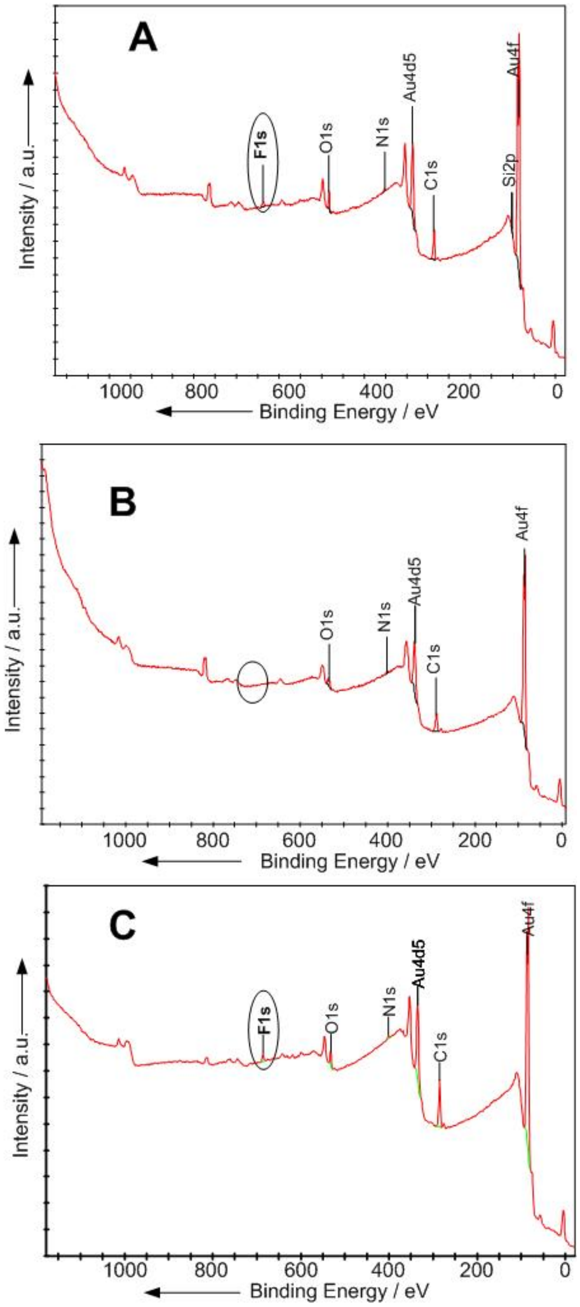

Figure S2: XPS spectra acquired at different steps of the anion metathesis reaction for MDMI-BF_4 SAM. (A) XPS spectrum of the initial surface prepared with MDMI-BF_4 SAM. (B) XPS spectrum of MDMI-carbonate. The exchange is evident from the peak at 690 eV, representing the fluorine 1s orbital, which disappears after anion exchange in the HCO_3^- solution. (C) XPS spectrum of the reversibility of the anion exchange, for a surface prepared as for (B) after it was exposed to BF_4^-. Table S1 exposes the peak area of the normalized fluorine fraction for every step.

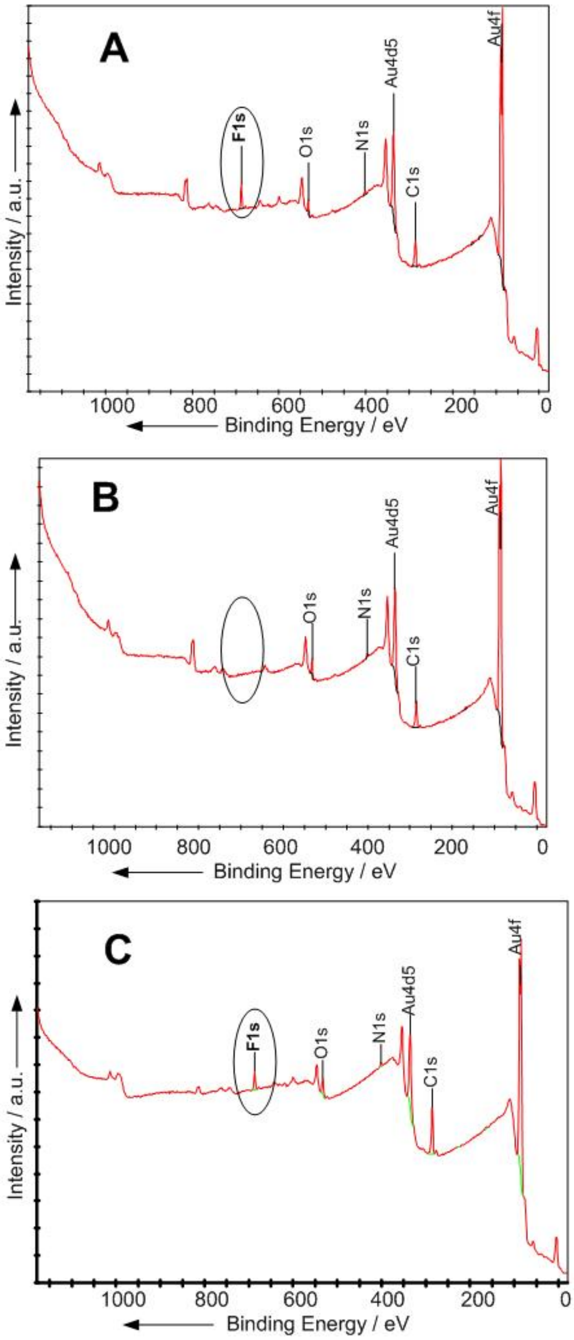

Figure S3: XPS spectra acquired at different steps of the anion metathesis reaction for MDMI-PF_6 SAM. (A) XPS spectrum of the initial surface prepared with MDMI-PF_6 SAM. (B) XPS spectrum of MDMI-carbonate. The exchange is evident from the peak at 690 eV, representing the fluorine 1s orbital, which disappears after anion exchange in the HCO_3^- solution. (C) XPS spectrum of the reversibility of the anion exchange, for a surface prepared as for (B) after it was exposed to PF_6^-. Table S1 exposes the peak area of the normalized fluorine fraction for every step.

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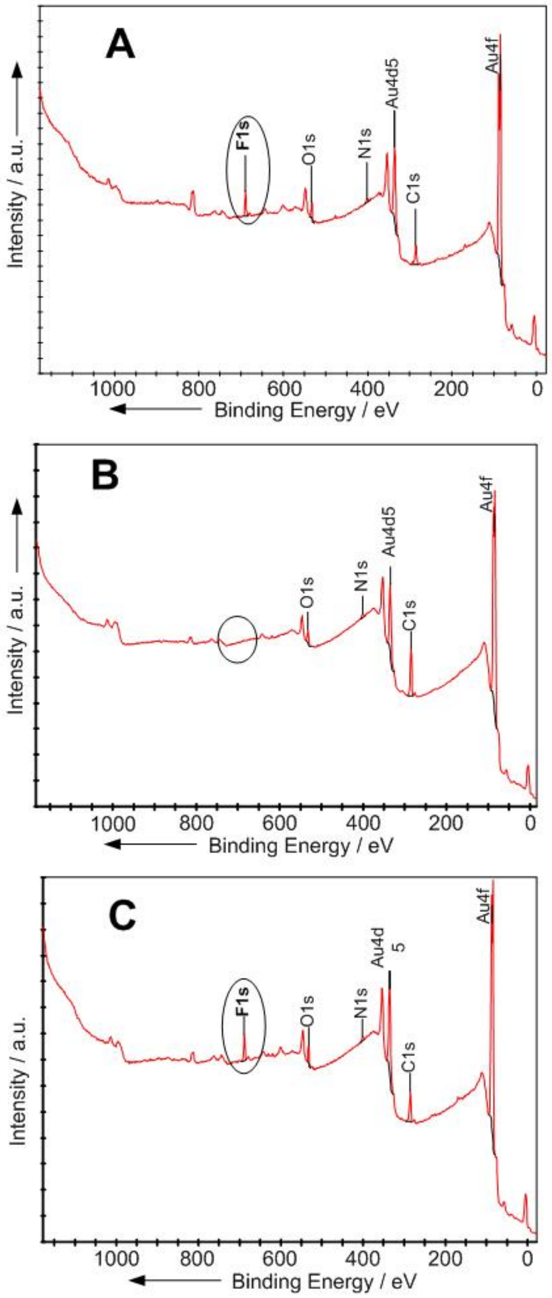

Figure S2: XPS spectra acquired at different steps of the anion metathesis reaction for MDMI-NTf_2 SAM. (A) XPS spectrum of the initial surface prepared with MDMI-NTf_2 SAM. (B) XPS spectrum of MDMI-carbonate. The exchange is evident from the peak at 690 eV, representing the fluorine 1s orbital, which disappears after anion exchange in the HCO_3^- solution. (C) XPS spectrum of the reversibility of the anion exchange, for a surface prepared as for (B) after it was exposed to NTf_2^-. Table S1 exposes the peak area of the normalized fluorine fraction for every step.

Table S1: XPS analysis of the fraction of fluorine for MDMI-X^- IL-SAM

Counter anion	As deposited	After HCO_3^- exposure	After exposure to initial anion
Br^-	0.000	0.000	0.000
BF_4^-	0.038 ± 0.003	0.000	0.037 ± 0.005
PF_6^-	0.11 ± 0.01	0.000	0.075 ± 0.004
NTf_2^-	0.11 ± 0.02	0.000	0.096 ± 0.009

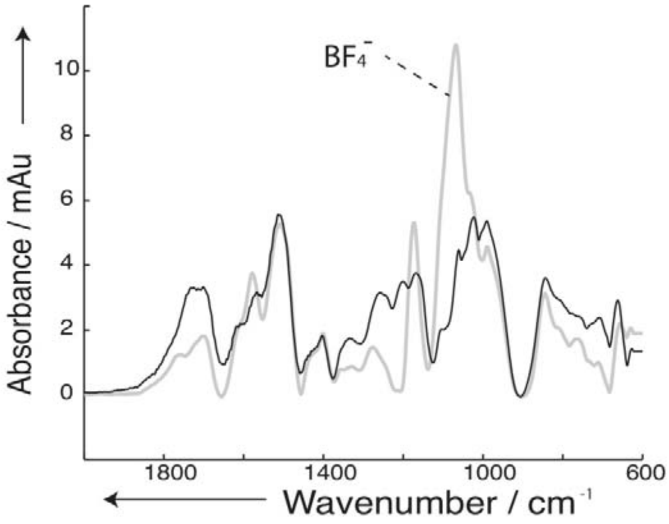

Figure S5: Mid-IR spectrum of the anion nion metathesis on MDMI-BF_4^- SAM after HCO_3^- exposure. The 1074 cm^{-1} peak, representing the B-F vibration (gray), disappears after anion exchange in the HCO_3^- solution (black).

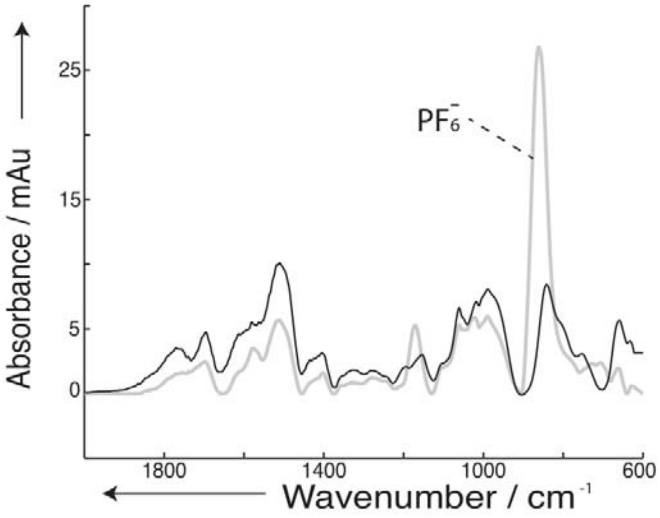

Figure S6: Mid-IR spectrum of the anion metathesis on MDMI-PF_6^- SAM after HCO_3^- exposure. The 866 cm^{-1} peak, representing the P-F vibration (gray), disappears after anion exchange in the HCO_3^- solution (black).

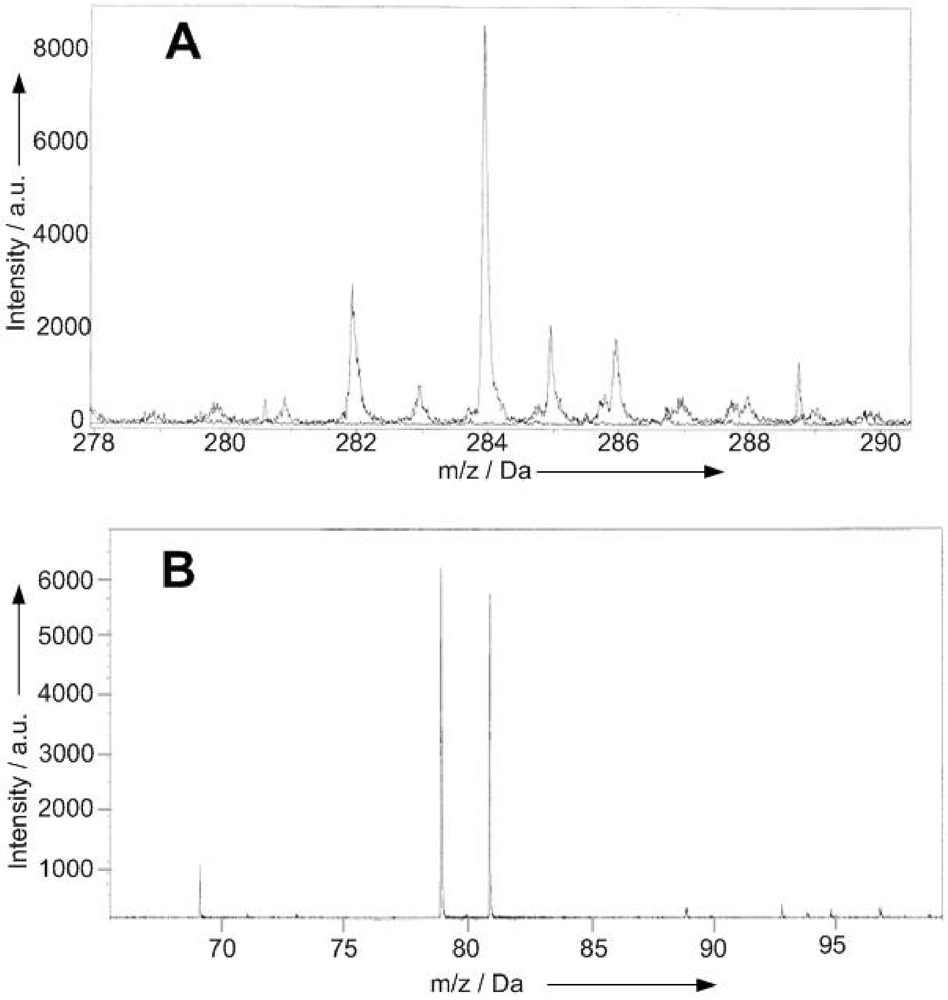

Figure S7: (A) MDMI$^+$ self-assembled on gold surface is characterized by the peak at m/z of 283.8 in the positive ionization mode of the mass spectrum and (B) by the peaks for Br$^-$ at m/z of 79 and 81 in negative ionization mode.

References

(1) Lee, B. S.; Chi, Y. S.; Lee, J. K.; Choi, I. S.; Song, C. E.; Namgoong, S. K.; Lee, S. G. *J. Am. Chem. Soc.* **2004**, *126*, 480.

(2) Voutchkova, A. M.; Feliz, M.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 12834.

(3) Turkevich, J. H., J.; Stevenson, P.C. *Discuss. Faraday Soc.* **1951**, *11*, 55.