Supporting Information

Esterification of self-assembled carboxylic acid-terminated thiol monolayers in acid environment: A time dependent study

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Infrared characterization- MHDA. To investigate if the carboxyl groups are transformed into an ester also after SAM formation, a freshly prepared MHDA SAM surfaces were immersed in EtOH with 1% 1M HCl. The surfaces were taken up after different time intervals to monitor the formation of an ester. In Figure S1 the RA spectra are displayed. From these spectra the integral of the CH_3 peak at ~2983 cm⁻¹ was calculated to follow the esterification rate, the figure of these results are shown in Figure 5B.

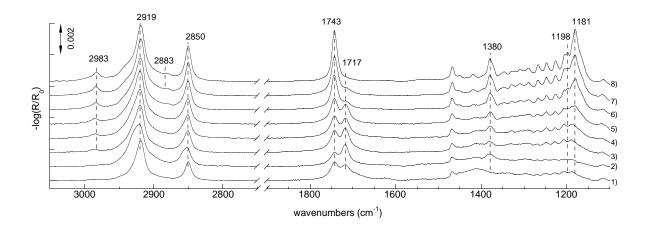


Figure S1. RA spectra of MHDA SAMs. 1) Freshly prepared MHDA SAM. Thereafter follows MHDA SAMs after incubation in EtOH with 10 mM HCl for 2) 1h, 3) 12h, 4) 24h, 5) 48h, 6) 5 days, 7) 2 weeks and 8) 4 weeks.

Treatment of a carboxylic acid SAM in HCl, followed by immersion for 2 h in Milli-Q water, Figure S2.

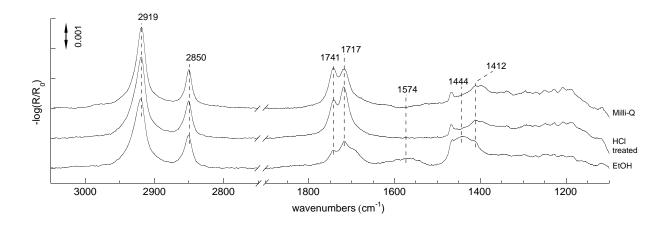


Figure S2. RA spectra of a freshly prepared MHDA SAM, after a 10 s rinse in HCl and after 2 h immersion in Milli-Q.

Infrared characterization – **EG**₆**COOH.** To investigate the structuring of the EG₆COOH SAMs even further RA measurements were done for SAMs prepared from EtOH with 2% TFA. Spectra of SAMs adsorbed from fresh, 2 weeks and 4 weeks old solutions are displayed in Figure S3. The EtOH and HCl RA spectra are identical to those prepared displayed in Figure 8 of the paper. The results for HCl and TFA are identical.

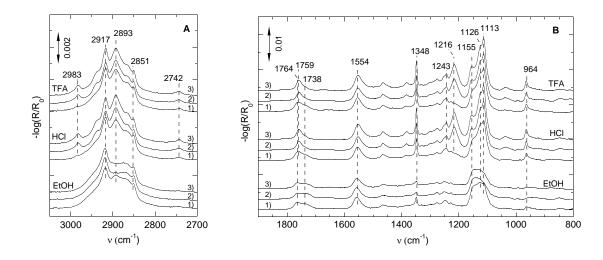


Figure S3. Comparison of IRAS data of EG_6COOH SAMs formed from thiol solutions in pure EtOH, EtOH with HCl or EtOH with TFA. 1), 2) and 3) in the graphs corresponds to SAMs adsorbed from fresh, 2 weeks old and 4 weeks old thiol solutions, respectively.