

Supplementary materials

Stability in ASW

Infrared Reflection-Absorption Spectroscopy (IRAS) was used to assess the stability of SAMs upon 4 days immersion in ASW. IRAS spectra from the chemisorption of HS-(CH₂)₁₅-N(CH₃)₃⁺ on a gold surface before and after immersion in ASW of SAM obtained are shown in Figure S1. The absorption at 1081 cm⁻¹ associated with C–N vibrational mode splits to give a stronger additional band at 1099 cm⁻¹. The bands at 1489 and 1375 cm⁻¹ arise from CH₃ symmetric and asymmetric stretching vibrations, respectively. The absorption at 1464 cm⁻¹ is due to the CH₂ scissoring deformation of the backbone chain.

Figure S2 shows the IRAS spectra of SAM obtained from HS-(CH₂)₁₅-COOH chemisorbed on gold. The peak at 1745 cm⁻¹ associated with C=O stretching mode of –COOH groups slightly decreases after immersion in ASW due to the dissociation of the acid groups at the pH of seawater. The band peaking at 1717 cm⁻¹ due to C=O stretching mode of COOH dimers (hydrogen bonded acids) also appears less intense after immersion and shifts to 1700 cm⁻¹. Accordingly, the asymmetric and symmetric COO⁻ bands at 1562 and 1470 cm⁻¹, respectively, appear to increase after immersion. Contributions to the broad symmetric carboxylate stretching band are also present peaking at 1440 cm⁻¹ which are assigned to the bending mode of CH₂ groups. The band at 1314 cm⁻¹ is assigned to C–O stretch of COOH groups.

In Figure S3 are shown IRAS spectra from the adsorption of HS-(CH₂)₁₅-CH₃ on gold, before and after

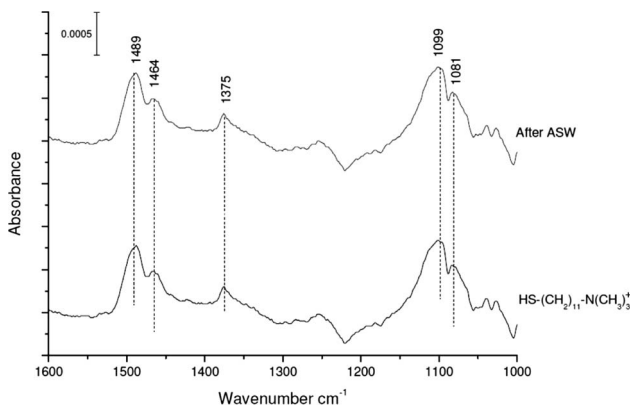


Figure S1. IRAS spectra of N(CH₃)₃⁺-terminated SAM in the region between 1600–1000 cm⁻¹ before and after 4 days immersion in ASW.

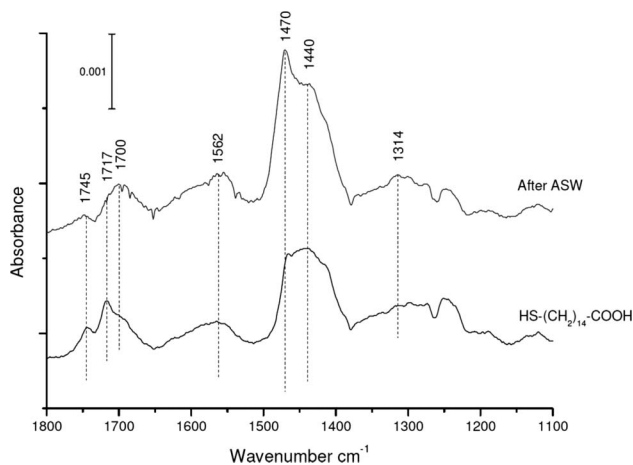


Figure S2. IRAS spectra of COOH-terminated SAM in the region between 1800–1100 cm⁻¹ before and after 4 days immersion in ASW.

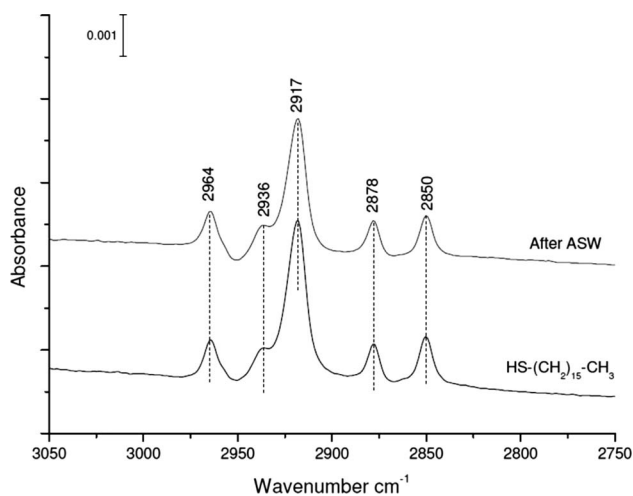


Figure S3. IRAS spectra of CH₃-terminated SAM in the region between 3050–2750 cm⁻¹ before and after 4 days immersion in ASW.

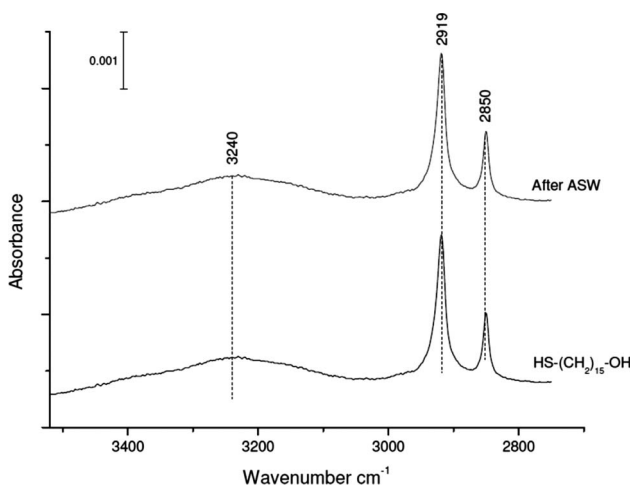


Figure S4. IRAS spectra of OH-terminated SAM in the region between 3500–2700 cm^{-1} before and after 4 days immersion in ASW.

immersion in ASW. The bands at 2964 and 2878 cm^{-1} are assigned to the CH_3 asymmetric ($\nu_{as}\text{CH}_3$) and ($\nu_s\text{CH}_3$) symmetric stretching modes, respectively. The bands at 2917 and 2850 cm^{-1} are assigned to the $\nu_{as}\text{CH}_2$ and $\nu_s\text{CH}_2$

modes, respectively. The band observed at 2936 cm^{-1} arises from the splitting of the $\nu_{as}\text{CH}_3$ band owing to Fermi resonance interactions with the lower frequency of the asymmetric CH_3 deformation mode.

IRAS spectra associated with the chemisorption of HS-(CH_2)₁₅-OH on a gold surface before and after immersion in ASW are shown in Figure S4. The bands at 2920 and 2850 cm^{-1} are assigned to the $\nu_{as}\text{CH}_2$ and $\nu_s\text{CH}_2$ modes, respectively. The broad adsorption peaking at 3050 cm^{-1} arises from the OH stretching vibration.

References

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