

Supporting Information for: Electrochemical Stability of Thiolate Self-Assembled Monolayers on Au, Pt, and Cu

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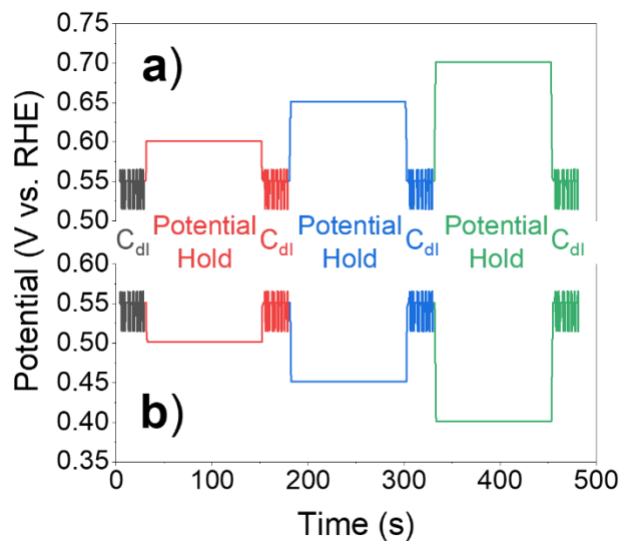


Figure S1. Potential hold method for probing oxidative (a) and reductive (b) desorption of C3 on various electrodes. Shown in black is the initial identification of the full SAM C_{dl} . Then the potential is scanned at 100 mV/s to the first potential tested and held for two minutes before scanning back to test the electrode C_{dl} . This repeated with increasing or decreasing potential holds in 50 mV increments. The first three potential holds tested in the sequence are shown in red, blue, and green.

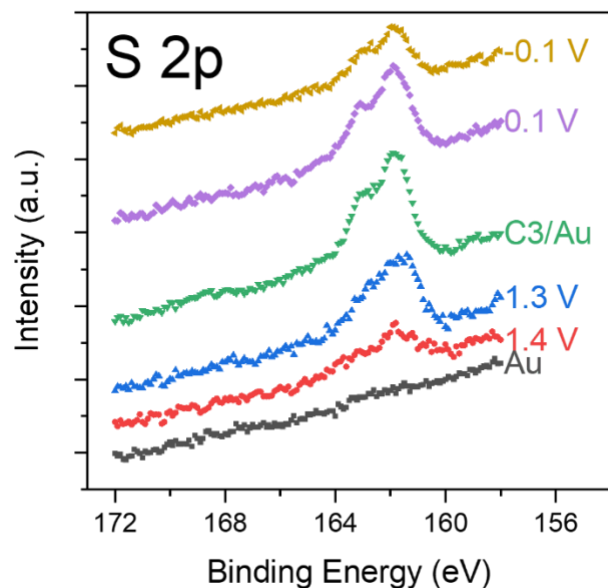


Figure S2. XPS conducted on six different Au substrates: C3/Au taken to -0.1 V (yellow left triangles), C3/Au taken to 0.1 V (purple diamonds), a full SAM 1-propanethiol (C3/Au, green downward triangles), C3/Au taken to 1.3 V (blue upward triangles), C3/Au taken to 1.4 V (red circles), and unmodified clean Au (black squares).

Details: X-ray photoelectron spectroscopy (XPS) was used on a subset of samples to validate the methodology of using capacitance to characterize the stability and coverage of SAMs. XPS measurements (Kratos Axis Supra) were conducted with a monochromatic Al K α source with a power of 225 W (emission current of 15 mA, accelerating voltage of 15 kV). Samples were measured in a large sample area of 700 μm x 300 μm in the S 2p region from 172 to 158 eV with a pass energy of 80 eV, a step size of 0.1 eV, dwell time of 425.53 ms, and 10 sweeps (5 sweeps for 1.3 V and 1.4 V). CasaXPS (version 2.3.25) was used to fit the S 2p $_{3/2}$ and S 2p $_{1/2}$ peaks using a Lorentzian asymmetric lineshape and a linear background. Peaks were constrained to have equal full width half maxima (FWHM) and S 2p $_{3/2}$ to have double the area of S 2p $_{1/2}$.

Samples were prepared for XPS following the procedures outlined in the main text. Briefly, six Au foils were electrochemically cleaned in 0.1 M HClO $_4$ followed by modification of five of them with 1-propanethiol. Two of these substrates were then taken through the two-minute potential hold sequence for oxidation (**Figure S1a**) up to either 1.3 V or 1.4 V, while two more of these substrates were taken through the two-minute potential hold sequence for reduction (**Figure S1b**) down to either 0.1 V or -0.1 V. Each sample was stored in a glove box after preparation to limit SAM degradation by air exposure. Between sample preparation and XPS measurements, air exposure was a maximum of twenty minutes.

XPS spectra from the six samples are shown in **Figure S2**. Peaks at 162 eV and 163 eV are assigned to S 2p $_{3/2}$ and S 2p $_{1/2}$, indicating that the thiols are covalently bound and not physically adsorbed.¹ Air oxidation of the SAM was not observed, as demonstrated by the lack of any other S 2p peaks. Species such as sulfonates/sulfonates should exhibit an oxidized sulfur peak at higher binding energies, and the absence of these features also suggests such species do not remain after

applying oxidative potential. If oxidized sulfur species do form, they are most likely only physically adsorbed and quickly dissolved by electrolyte or the rinsing procedure after electrochemical treatment.

Analysis of **Figure S2** shows an obvious qualitative trend in sulfur signal. With more oxidizing potentials, sulfur signal decreases from the full SAM (C3/Au) to greater degrees of removal at 1.3 V and 1.4 V. Likewise, sulfur signal decreases with more reducing potentials at 0.1 and -0.1 V. The thiol removal is correlated with the redox features of the C3/Au surface in Figure 1 of the main text. C3/Au was used to calibrate the area of the S 2p peaks to the maximum surface coverage. The estimated fraction of a saturating monolayer, θ_{XPS} , was compared to the apparent surface coverage calculated by double layer capacitance, θ_{Cdl} (**Table S1**). These measurements are in fair agreement and demonstrate the sufficiency of C_{dl} as an indicator of electrochemical stability for thiolate layers.

Table S1. Comparison of SAM surface coverage determined by C_{dl} and XPS

Removal Type	Potential (V vs. RHE)	θ_{Cdl}	θ_{XPS}
Reduction	-0.1	0.48	0.44
Reduction	0.1	0.95	0.89
Oxidation	1.3	0.83	0.94
Oxidation	1.4	0.54	0.45

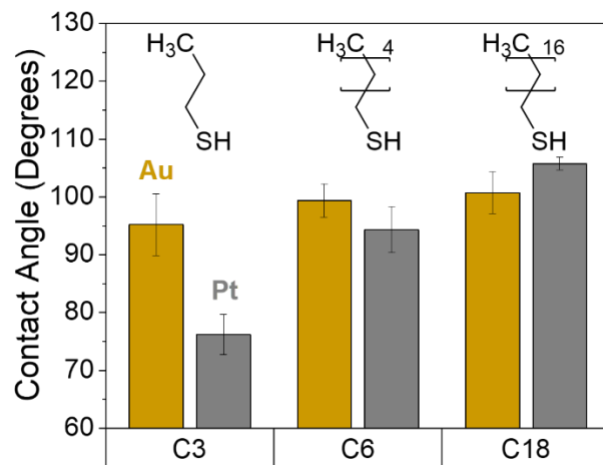


Figure S3. Static contact angle measurements of water on different thiolate SAMs on Au (gold) and Pt (gray) using the sessile drop method.

Details: Contact angle measurements were used to confirm the formation of SAMs and demonstrate relative degrees of ordering (**Figure S3**). With increasing chain length of alkanethiol from C3 to C6 to C18, the contact angle increases. In the case of Au, the angle plateaus with chain length soon after C6, consistent with a high general degree of ordering on this surface.^{2,3} Interestingly on Pt, the contact angle monotonically increases, not showing a plateau like Au. This could be explained by the fact that Pt surfaces do not reconstruct upon thiol modification, resulting in more defective SAMs than Au, especially for shorter chain thiols.⁴

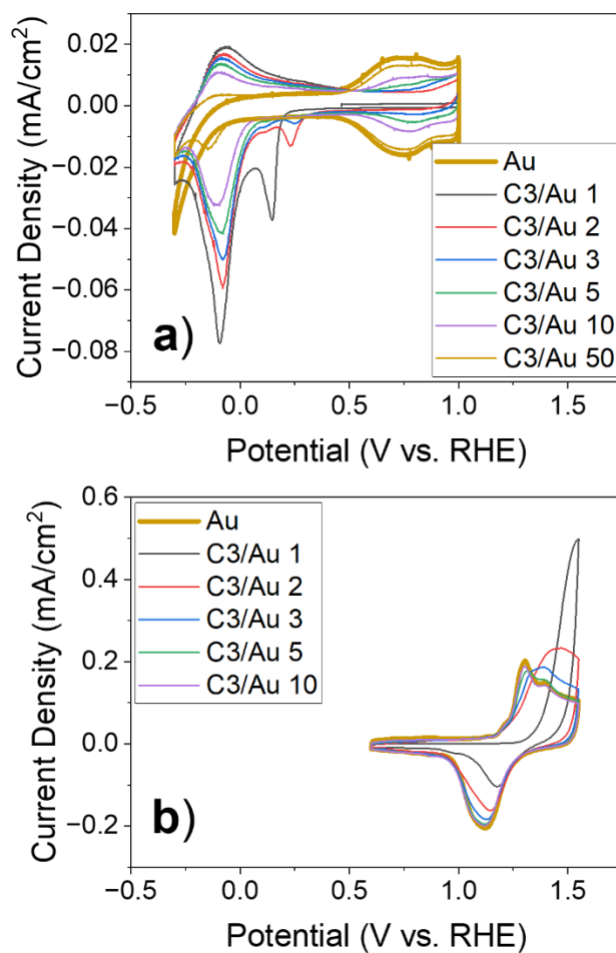


Figure S4. Consecutive direct desorption cyclic voltammograms (CVs) for (a) reduction and (b) oxidation of C3 on Au in 0.1 M KOH at 100 mV/s, compared to bare Au (gold color) over the same range. The CV cycle number is indicated for the C3/Au CVs.

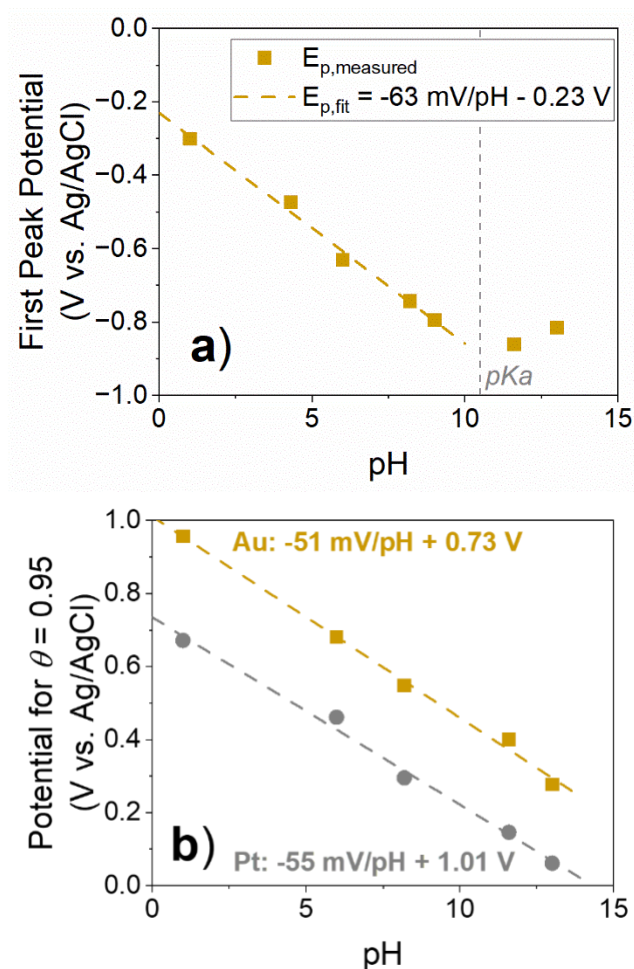


Figure S5. Desorption potential plotted vs. pH for the (a) reductive (peak potential for reductive desorption on Au) and (b) oxidative (95% coverage) desorption of C3. Data from (a) comes from Figure 3a. Data from (b) comes from Figures 3b and 3c. Best fit lines (dashed) are reported with associated slope and intercept. For (a), the best fit line only goes through pHs < pKa.

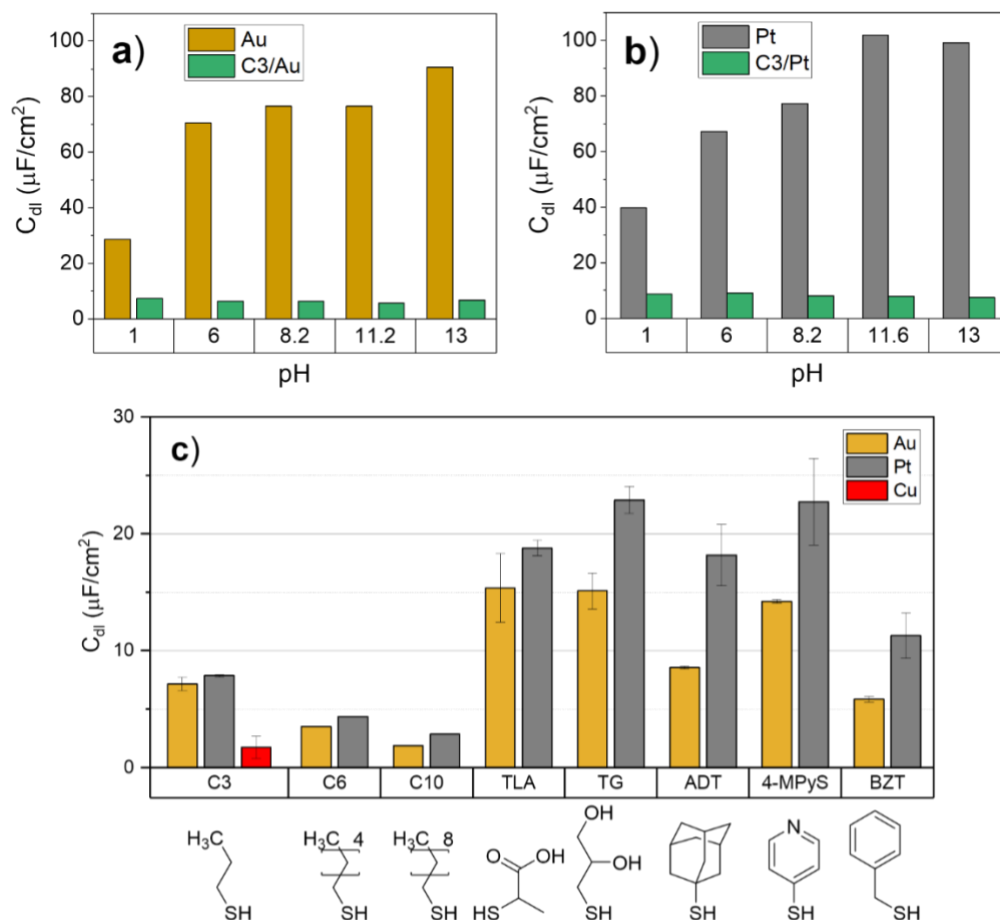


Figure S6. Double-layer capacitance measurements as measured by cyclic voltammetry at different scan rates. C3 at different pHs on (a) Au and (b) Pt. The capacitance of the unmodified electrodes generally increases with pH, partly due to the shift in non-Faradaic potential window (vs. PZC) to take this measurement (c.f. Figures S5a and S5b). (c) Capacitance of different thiol-coated SAM surfaces in 0.1 M KOH.

Details: **Figure S6c** shows the C_{dl} of different thiols on Au, Pt, and Cu, which are all in reasonable agreement with literature, suggesting we form a full SAM on each system. There are a few general trends to comment on. As expected, SAMs from alkanethiols (C3, C6, C10) monotonically decrease in C_{dl} with increasing carbon chain length. In addition, we observe that SAM capacitances on Pt are higher than on Au. This has been attributed to greater disorder of SAMs on Pt compared to Au (further demonstrated by contact angle measurements, **Figure S3**), presumably due to the lack of surface reconstruction on Pt.⁴ Another observation is that the non-alkanethiols we studied generally have a higher C_{dl} than all the alkanethiols (except for BZT/Au which we discuss in the main text). This is expected to be the case as most functionalized and branching thiols have greater difficulty of forming a close-packed intermolecular stabilizing monolayer.^{5,6} Furthermore, the addition of electron donating groups (or hydrogen bonding groups) such as nitrogen, oxygen, and hydroxyls increases the solubility of water and ions within the monolayer, increasing C_{dl} compared to alkanethiols.

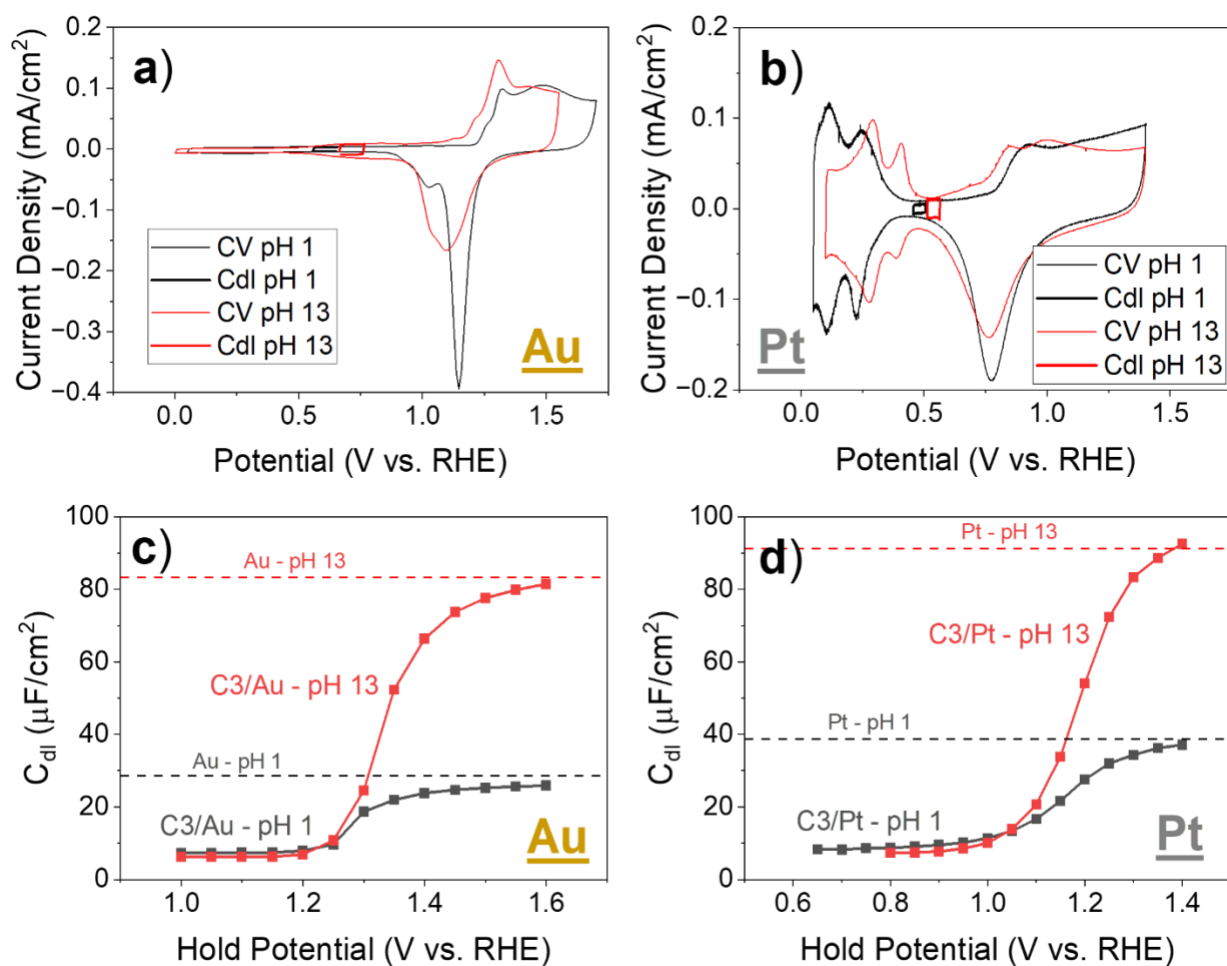


Figure S7. Wide range (thin lines) and double layer region (thick lines) cyclic voltammograms of unmodified (a) Au and (b) Pt at pH 1 (black) and pH 13 (red). For both electrodes, capacitance measured by CV is greater at pH 13 than 1. Capacitance is also shown for C3 SAMs as a function of hold potential at pH 1 (black) and 13 (red) for (c) Au and (d) Pt.

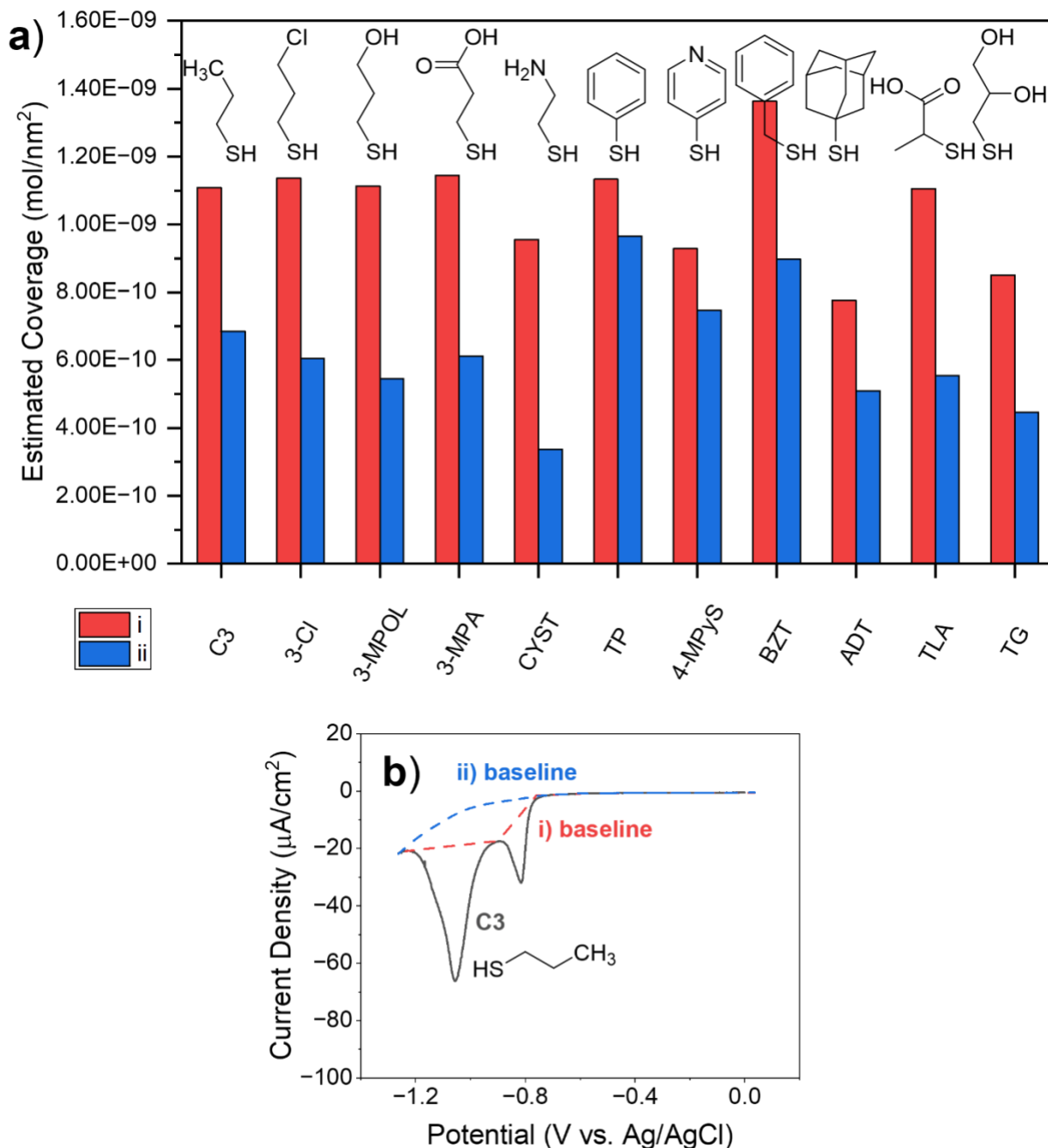


Figure S8. Additional analysis of reductive desorption of SAMs from Au. (a) Estimated surface coverage of each SAM reported as moles of thiol per nm^2 of Au, calculated from two different methods: (i) Smooth spline baseline connecting double layer region of SAM to the onset of HER; (ii) Linear baseline capturing only the peak area of the two major peak regions, with baseline connection at the minimum between the two peaks. Since thiol desorption from higher coordinated sites (second peak) slightly overlaps HER and the capacitance of the electrode changes during the linear sweep voltammogram, accurate determination of the absolute surface coverage is difficult; but, comparison of trends between different thiols should hold. (b) Linear sweep voltammogram of C3/Au showing the different methods of integration, (i) and (ii), used in (a).

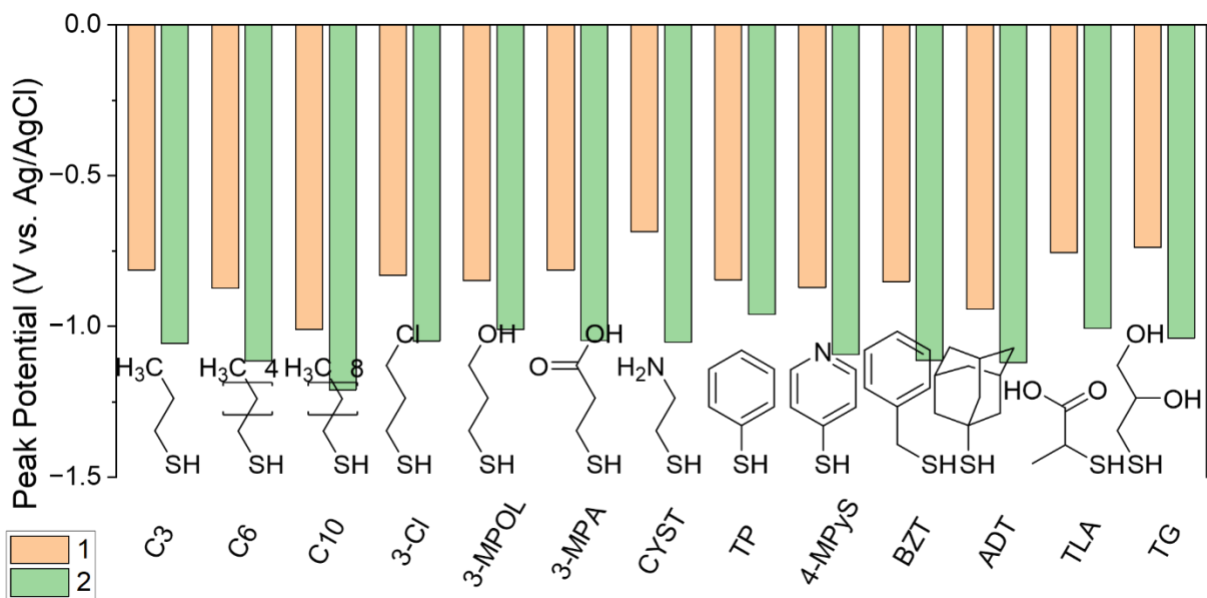


Figure S9. Peak potential for the major first (less negative) and second (more negative) desorption peaks. The peak positions correlate with the electrochemical stability windows reported the main text.

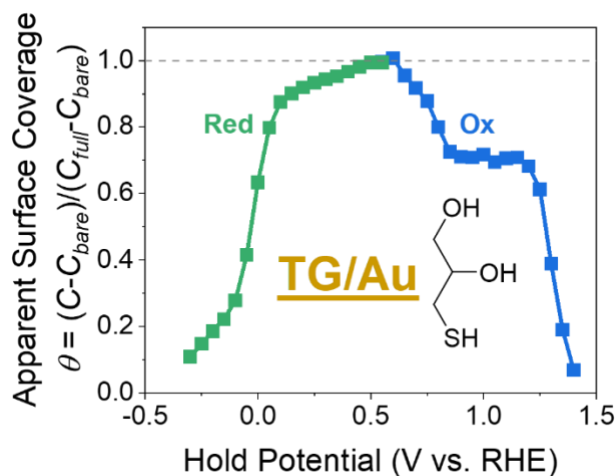


Figure S10. Apparent surface coverage of thioglycerol on Au determined from potential hold experiments.

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