Supplemental Material for ELECTRICAL AND PHYSICAL CHARACTERIZATION OF BILAYER CARBOXYLIC ACID FUNCTIONALIZED MOLECULAR LAYERS

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Note: the identification of commercial equipment or vendor in this section is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

S1. Methods and Materials
   A. Au preparation

Ultrasmooth Au (uS Au) substrates were prepared according to Ref. 31, and details are provided in the supporting information document. Briefly, Au (60 nm to 120 nm thick) was evaporated (by either thermal or electron beam deposition) onto a fluorinated silane-treated silicon substrate. For device-scale measurements, a shadow mask with an array of 150 μm diameter circles was placed in front of the substrate.

   B. Monolayer formation

For thiol self-assembly, the uS Au substrates were cleaned by an isopropanol rinse, exposure to UV/O_3 for 10 minutes, deionized water rinse, ethanol soak and finally dried by N_2. Based on our previous experience and of those published[1,2], we do not expect the 10 minute UV/O_3 treatment to affect the roughness of our uS Au surface. Ethanol-based 1 mmol/L mercaptoundecanoic acid (C11) and mercaptohexadecanoid acid (C16) solutions were prepared in a N_2-filled glovebox, and the uS Au substrates were kept in solution overnight. After monolayer formation, the samples were rinsed in ethanol and dried with N_2.

For alkene (undecylenic acid, C'11) monolayer formation onto DSP silicon substrates, the substrates were cleaned by first rinsing in isopropanol and dried in streaming nitrogen. Next, they were etched in piranha solution using a 3:1 volume ratio of concentrated sulfuric acid to hydrogen peroxide (30 %) at 90 °C for 20 minutes, and then rinsed in deionized water and dried with N_2. Finally, the substrates were etched in buffer oxide etch (BOE; 6:1 of NH_4F to HF) for 30 seconds, rinsed with deionized water, and dried with N_2. The cleaned Si substrates were transferred to the glovebox within a few minutes.

The C'11 was gently heated (35 °C to 40 °C to ensure liquid state) in the N_2-filled glovebox, pipetted onto the clean Si surface, and photochemically reacted (UV lamp, λ = 254

nm) for 3 hours. After C'11 monolayer formation, the sample was rinsed in tetrahydrofuran, sonicated in dichloromethane and isopropanol for 10 minutes each, and dried with N_2.

To promote carboxylic acid terminated surfaces, the samples (C11, C16, and C'11) were dipped in HCl (2 mol/L, 65 °C) for 30 seconds and dried with N_2. Additionally, C11 and C16 samples were exposed to a Cu-containing solution. Copper perchlorate in ethanol (5 mmol/L) was prepared, and the samples were exposed to the solution for 30 seconds, and subsequently copiously rinsed in ethanol and dried in N_2.

C. Details of Infrared-based measurements

The reflection accessory has a fixed grazing angle (80°) reflection stage with a wire grid polarizer positioned before reaching the sample. For measurements in transmission, the silicon substrates were situated near Brewster's angle where the IR beam passed through a wire grid polarizer before reaching the sample. The sample compartment was purged with N_2, and spectra were collected at 4 cm^{-1} resolution. Monolayers formed on (uS) Au were measured by using the reflection set-up, while monolayers formed on Si were measured in transmission. A UV-O_3-cleaned uS Au on PET or Au/Si sample was used as references for reflection IR, while a BOE etched DSP Si served as reference for transmission measurements. As a reference for pb-RAIRS measurements, Au (150 nm) evaporated onto H-terminated DSP Si ($\rho = 10\ \Omega \cdot cm$ to $15\ \Omega \cdot cm$) was used.

D. X-ray Photoelectron Spectroscopy: measurement and fit analysis

Photoelectrons were collected normal to the sample surface. XPS spectra were deconvoluted by using a Voigt lineshape and a linear background. Spectra of the same photoemission (PES) line were fitted simultaneously, coupling the Gaussian (for identical measurement settings) and Lorentzian (for identical PES lines) widths.

E. Near Edge X-ray Absorption Fine Structure: measurement and fit analysis

NEXAFS spectra were collected in partial electron yield (PEY) mode at a grid voltage of -225 V; PEY spectra were normalized to the I_0 current (collected by a Au mesh upstream). The angle of incidence between the p-polarized X-ray photons and the sample was varied and resulted in angle-dependent NEXAFS spectra. Spectra were fitted simultaneously for the same sample at different measurement angles. Spectral components were convoluted by using an error function lineshape as the background (or edge-step; center and width are coupled) and spectral features were decomposed into Gaussian lineshapes (widths are coupled).

S2. S 2p XPS spectra and fit (S 2p spectra with and without Cu atoms)

The S 2p photoemission lines were measured for the MUA (mercaptoundecanoic acid) monolayer on Au/PET with and without copper incorporation (denoted as 'Cu-MUA'). The spectra from both samples were fitted employing a linear background and a Voigt lineshape to describe the $2p_{3/2}$ and $2p_{1/2}$ photoemission lines. The spectra from both samples were fitted simultaneously while coupling their Gaussian width, coupling their Lorentzian contribution for each spin-orbit PES line, and using the spin-orbit area constraint of 1:2 for intensity of $2p_{1/2}$ to $2p_{3/2}$. Based on the S 2p spectra, we find that the S atoms are in one chemical environment which

is consistent with bound Au-S[3] and that they remain in the same chemical environment after Cu incorporation.
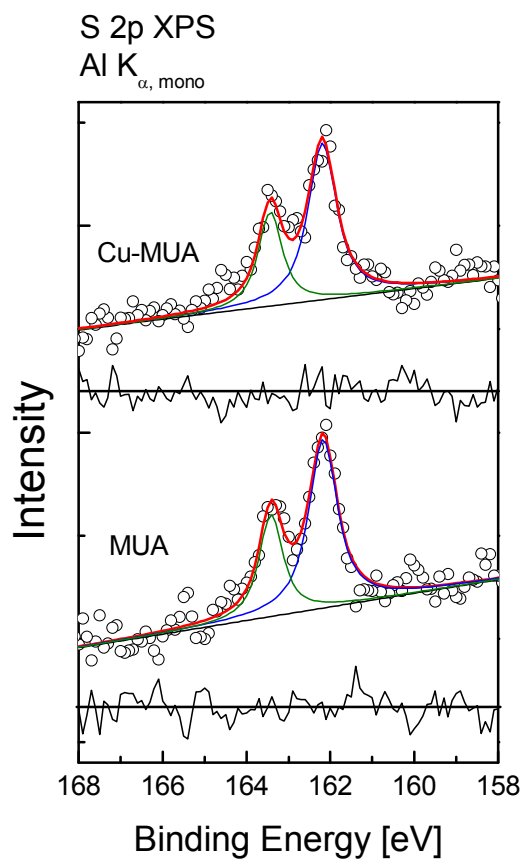

Fig. S1. XPS S 2p spectra of MUA before (bottom spectrum) and after (top spectrum) the incorporation of Cu atoms. Data is shown as open circles and the fits as solid lines. The difference between the fit and data (residuals) are shown directly below each spectrum and the solid horizontal line serves as a guide to the eye.

S3. Estimation of molecular and atomic density on surfaces using XPS

(a) For thiol-containing monolayers on Au substrates, we used the S 2p and Au 4f intensities from the same sample surface to estimate the density of S atoms on Au (and therefore, we can estimate the number of molecules). We used the following,

$$n_S' = \frac{I_{S2p}/(S_{S2p} \times T_{KE,S2p} \times IMFP_{KE,S\,2p})}{I_{Au4f}/(S_{Au4f} \times T_{KE,Au4f} \times IMFP_{KE,Au4f})} \times \frac{IMFP_{KE,Au4f} \times N_A \times M_{Au}}{\rho_{Au}} \times \frac{10^{-21}cm^2}{nm^2}$$

where:

n_s' ≡ number of S atoms nm^{-2}

I_{S2p} ≡ integrated XPS intensity of S2p transition

I_{Au4f} ≡ integrated XPS intensity of Au4f transition

$T_{KE,\,y}$ ≡ transmission function of the electron analyzer, dependent on kinetic energy of photoelectron detected

$IMFP_{KE,y}$ ≡ inelastic mean free path of photoelectron, dependant on kinetic energy of photoelectron

N_A ≡ Avogadro's constant [6.02 E23 atoms/mol]

M_{Au} ≡ molecular weight of gold [196.97 g/mol]

ρ_{Au} ≡ density of Au, at room temperature [19.3 g/cm^3]

With $I_{S2p}/(S_{S2p}\,T_{KE,S2p}\,IMFP_{KE,S2p})$ = 965.2 (for MUA), $I_{Au4f}/(S_{Au4f}\,T_{KE,Au4f}\,IMFP_{KE,Au4f})$ = 25347.6 (for MUA), and $IMFP_{KE,\,Au4f}$ = 1.577 nm (Au 4f electrons through Au)[4]. We find that we have about 3.5 – 4 molecules per nm^2 of Au surface.

(b) For estimating the grafted undecylenic acid (UDA) molecules onto Si, we used two methods. The first method is similar to that used in (a). Here, we calculated the surface density of carbon and oxygen atoms (n_C' and n_O') on the same UDA/Si sample. We used the C 1s, O 1s, and Si 2s PES lines with $IMFP_{KE,Si2s}$ = 3 nm (Si 2s electrons through Si)[4], M_{Si} = 28.1 g/mol, and ρ_{Si} = 2.3 g/cm^3. To find UDA surface density, we divided n_C' and n_O' by 11 and 2 (number of carbon and oxygen atoms in UDA), respectively. Thus, we calculated that we have 7.9 – 8.0 UDA molecules per nm^2 on Si. However, this method tends to overestimate our molecular density at the surface because of reactive nature of H-Si surface; there is some carbon and oxygen detected on the H-Si surface. After correcting for carbon and oxygen content found on a H-Si surface from that of the UDA/Si surface, we find that our UDA density is about 5.5 – 6.5 molecules per nm^2.

The second method we used to estimate the UDA coverage on Si was to determine the signal attenuation from the substrate (i. e., the Si PES lines). The PES intensity of a given core level is proportional to,

$$I \propto exp^{-d/IMFP} .$$

Thus for two samples that are identical but one contains an overlayer (e. g., molecular layer) and measured in identical experimental settings, the signal ratio is:

$$\frac{I_1}{I_O} = \frac{exp^{-\frac{d_1}{IMFP_1}}}{exp^{\frac{-d_O}{IMFP_O}}}$$

where the subscript "o" denotes the surface without a monolayer (H-Si) and "1" denotes the surface with UDA. We used the Si 2s intensities, $d_o = 0$, and $IMFP_1 = 3.55$ nm (for Si 2s electron through a C10 molecule)[4], we find that the average d_1 is 1.7 nm. And using,

$$n'_{UDA} = \frac{d_1 \times \rho_{UDA} \times N_A}{M_{UDA}} \times \frac{10^{-21} \ cm^2}{nm^2}$$

with $\rho_{UDA} = 0.912$ g/cm^3 and $M_{UDA} = 184.27$ g/mol, we estimate that we have 3.2 UDA molecules per nm^2.

(c) To estimate the ratio of Cu atoms to S atoms on the "Cu-incorporated" surface of the same sample, we used the following:

$$\frac{n_{Cu}}{n_S} = \frac{I_{Cu2p}/(S_{Cu2p} \times T_{KE,Cu \ 2p} \times IMFP_{KE,Cu \ 2p})}{I_{S2p}/(S_{S2p} \times T_{KE,S2p} \times IMFP_{KE,S2p})}$$

where $I_{S2p}/(S_{S2p} \ T_{KE,S2p} \ IMFP_{KE,S2p}) = 971.8$ and $I_{Cu2p}/(S_{Cu2p} \ T_{KE,Cu2p} \ IMFP_{KE,Cu2p}) = 573.4$, and results in one Cu atom to every two – three S atoms. Since there is one sulfur in MUA, we estimated that there is about one Cu atom for every two to three MUA molecules. We opted to count the Cu atoms with respect to the S atoms since S is directly related the SAM molecule. Counting S atoms with respect to the –COOH group (using either O 1s or C 1s contribution) would be ideal, but that method introduces additional sources of error since C and O atoms are present in ambient contamination.

S4. Contact angle (CA) and spectroscopic ellipsometry (SE) measurements

Spectroscopic ellipsometry (SE) measurements were performed on monolayers on Au/Si substrates by using a Woollam M2000. The angle of incidence was set to 75° with respect to the surface normal. The optical thickness of the monolayers was obtained by fitting the data to a Au/monolayer model where the optical properties of the monolayer were modeled as a Cauchy dispersion using n=1.5. A monolayer of octadecanethiol on Au/Si was used as the gold material reference with the assumption that the monolayer thickness is 2.3 nm and n=1.5 octadecanethiol. Measurements were performed on at least three different spots on the same sample.

Water contact angle (CA) were performed at ambient conditions using a First Ten Angstrom goniometer equipped with a video camera. Commerical software extracted the contact

angle values between the deionized water (18 MΩ·cm) droplet and the monolayer surface. This measurement was performed on at least three different spots within the same sample.

The average water CA and SE estimated thickness of the C11, Cu-C11, C16, and C'11 monolayers are summarized in the figure below. These CA values for carboxylic acid-containing monolayers are larger than values reported in the literature (e.g., Refs. 5 and 6), but we are confident that we have carboxylic acid groups present in our monolayer based on other physical characterizations (i.e., XPS and FTIR). When Cu is adsorbed to the C11 surface, the thickness is nearly the same but the CA changes considerably and is consistent with a previous report[5]. While the thiol-containing monolayers on Au have thicknesses that are consistent with fitted ellipsometry results for a range of lengths[7], the C'11 grafted on Si is significantly larger than C11 and the CA indicates more disorder. This could be due to the ellipsometric model used (Si substrate and Cauchy layer) which did not take into account a SiO_2 interlayer or possibly indicative of multilayer formation. The multilayer formation is unlikely given the results from XPS.
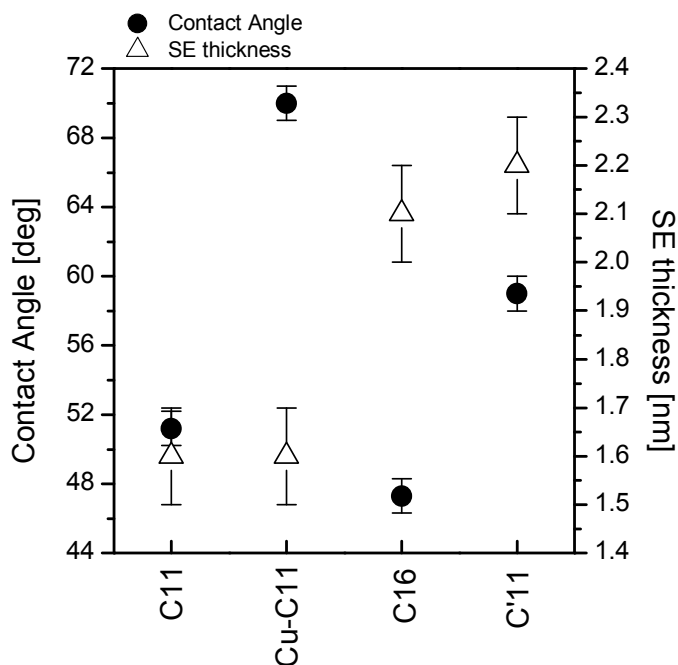

Fig. S2. Measured values of contact angle (left axis; filled circles) and SE thickness (right axis; open triangles) of C11, Cu-C11, C16, and C'11 monolayers. The standard deviation taken from at least five different measurements are represented as error bars.

S5. Infrared Spectra of Undecylenic acid (C'11) monolayer on Si

Spectra are shown from four different fabrication runs, and the data show the variability of the relative intensities of the carbonyl stretch and alkene stretch. Chemical selectivity is limited when grafting bifunctional molecules onto Si surfaces.
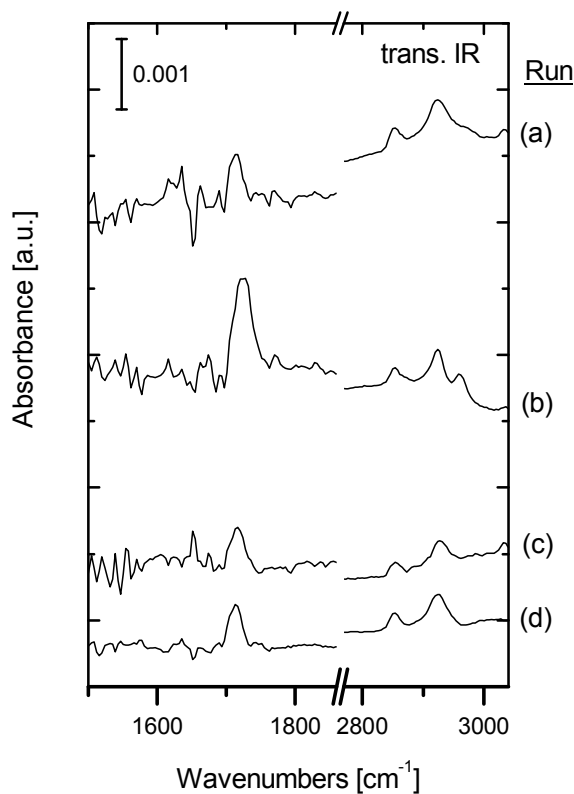

Fig. S3. Transmission infrared spectra of C'11 monolayer grafted onto Si subtrates from four different runs.

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