# Supporting Information

## Experimental

Bromoundecanol, ferrocenecarboxaldehyde, ethanol, dimethyformamide, sodium azide, sodium ascorbate, and decanethiol were purchased and used as received. Copper sulfate pentahydrate was isolated by crystallization of anhydrous copper sulfate from water. Methylene chloride was distilled over calcium hydride. Methanol was distilled over magnesium turnings. Tetrahydrofuran was distilled over sodium benzophenone ketyl.

### Synthesis of 1-Azidoundecan-11-thiol (1):

Adapted from a previously published procedure.[i]

### Synthesis of 1-Azidoundecan-11-ol

To 150mL of DMF, 10g of $Br(CH_2)_{11}OH$ and 2.86g of $NaN_3$ were added. The flask containing the mixture was evacuated, refilled with $N_2$, and refluxed under $N_2$ for 24 hours. After cooling to room temperature, 150mL of $H_2O$ was added after which the mixture was extracted three times with diethyl ether. The organic phase was washed with water three times and dried over $MgSO_4$. Rotary Evaporation yielded a pale yellow oil. 87% Yield. $^1$HNMR ($CDCl_3$, 400MHz): 3.63, (q, 2H); 3.24 (t, 2H); 1.57 (m, 4H); 1.22-1.4 (m 14H).

## Synthesis of 1-Azidoundecan-11-methylsulfonate

To 1g of $N_3(CH_2)_{11}OH$ 35mL of THF (from still) and 1mL of methanesulfonyl chloride were added. In a separate vial, 1.27g of triethylamine was dissolved in 5mL THF. The triethylamine solution was slowly added to the stirring $N_3(CH_2)_{11}OH$ solution over 5 minutes. The reaction progressed at room temperature for 2 hours. 35mL of ice-cold water was added, and the organic phase was separated from the aqueous phase. The aqueous phase was extracted twice with diethyl ether (2x35mL). The combined organic phases were then combined and washed with 1M HCl, $H_2O$, $NaHCO_3$, and $H_2O$. After drying over $MgSO_4$, the solvent was removed via rotary evaporation yielding a pale yellow oil. 87% Yield. $^1$HNMR ($CDCl_3$, 400MHz): 4.21, (t, 2H); 3.24 (t, 2H); 2.99 (s, 3H); 1.74 (m, 2H); 1.59 (m, 2H); 1.22-1.42 (m, 14H);

## Synthesis of 1-Azidoundecan-11-thioacetate

1g of $N_3(CH_2)_{11}OSO_2C$ and 0.775g of potassium thioacetate was dissolved in 30mL of methanol. The solution was degassed and refluxed under $N_2$ for three hours. After cooling to room temperature, excess methanol was removed via rotary evaporation and ice cold water (30mL) was added. The mixture was extracted 3 times with diethyl either (30mL) and washed three times with water (3x30mL). The solution was dried over $MgSO_4$ and the solvent removed by rotary evaporation yielding a yellow oil. $^1$HNMR ($CDCl_3$, 400MHz): 3.24 (t, 2H); 2.85 (t, 2H); 2.31 (s, 3H); 1.5-1.61 (m, 4H); 1.22-1.4 (m, 14H).

Synthesis of 1-Azidoundecane-11-thiol (1):

To 300mg of $N_3(CH_2)_{11}SCOCH_3$, 20mL of methanol was added. The solution was degassed thoroughly and backfilled with $N_2$. 1 mL conc HCl was added, and the entire mixture was refluxed for 5hrs. The reaction mixture was quenched with water and extracted twice with diethyl ether. The organic phase was washed twice with water (2x20mL) and dried over $MgSO_4$. Rotary evaporation yielded a yellow oil. 80% Yield $^1$HNMR ($CDCl_3$, 400MHz): 3.24 (t, 2H); 2.51 (q, 2H); 1.59 (m, 4H); 1.22-1.41 (m, 14H).

Synthesis of Ferrocene Acetylenes:

Ethynylferrocene (2) and 1-ferrocenyl-2-propyn-1-one (3) were synthesized using previously established synthetic methods.[ii]

Substrate Preparation:

The gold substrates were prepared by electron-beam evaporation of a titanium adhesion layer (99.99% purity) followed by gold (99.99% purity) onto 4-inch silicon wafers. Silicon was pre-cleaned for 10 minutes in hot piranha (1:3 $H_2O_2/H_2SO_4$), and rinsed in deionized water (**Warning**: Piranha solution reacts violently, even explosively, with organic materials. It should not be stored or combined with significant quantities of organic material.)

. The deposition was carried out in a cryogenically pumped deposition chamber. Titanium thicknesses (monitored with a quartz oscillator) were on the order of 15-20nm and gold thicknesses were on the order of 150-200nm. After deposition, the chamber was backfilled with purified argon.

Formation of Mixed SAMs

Gold substrates were cleaned by immersion into 1:3 $H_2O_2/H_2SO_4$ for 1 minute, followed by rinsing with copious amounts of deionized water. This was followed by a quick rinse in concentrated HCl. The substrate was rinsed again with deionized water followed by ethanol. Deposition solutions were made by dissolving the desired ratio of decanethiol and 1-azidoundecan-11-thiol in ethanol. The total thiol concentration was always 1mM. Cleaned gold substrates were then immersed in the deposition solution for 24-36 hours. After deposition, SAM's were rinsed in ethanol and water in order to remove excess absorbate and dried with $N_2$ to remove residual solvent.

Formation of Ferrocene Terminated Monolayers:

In a typical prep, mixed monolayers of $N_3(CH_2)_{11}SH$ and $CH_3(CH_2)_9SH$ were completely submerged in a 1mM ferrocene acetylene solution (solvent 2:1 water ethanol). If catalyst was desired, 15 mol% of either sodium ascorbate or ascorbic acid was added, followed by 1 mol% of $CuSO_4$ $5H_2O$. The reaction chamber was covered in foil and stored inside a drawer for the duration of the reaction in order to prevent photo-oxidation of the monolayer. After reaction, monolayers were rinsed with copious amounts of ethanol, water, methylene chloride, and then water again to ensure that any physisorbed ferrocenes were washed off.

Electrochemical measurements:

The electrochemical cell area was defined by pressing down on the sample with a cylindrically bored Teflon™ cone (4mm inner diameter) pressed against the sample. The bore was filled with 1M aqueous perchloric acid. A platinum counter electrode and a glass frit-isolated Ag/AgCl/KCl reference electrode were suspended above the cell. The cell potential was controlled and the cell current converted to a potential signal by a conventional potentiostat (PAR 273). Potential program signal to the potentiostat was generated by a Wavetek 395 function generator, and the current response signal from the potentiostat was recorded using a Tektronix TDS 520 digital oscilloscope. All measurements were performed at room temperature with no exclusion of air.

Infrared external reflection spectroscopy:

Spectra were obtained using a Mattson RS 10000 FT-IR spectrometer with external optics enclosed in a plexiglass box and bathed by dry, $CO_2$-free air. A narrow-band MCT detector cooled with liquid nitrogen was used to detect the light. The light was incident on the sample at 86° from normal. Only p-polarized light was collected (light polarized in the plane of incidence). 256 scans were recorded at a $8cm^{-1}$ resolution. The moving mirror speed was 3.1cm/sec (HeNe laser modulation frequency = 50kHz) in the forward and reverse directions. The SAM spectra were ratioed against a background spectrum of bare gold cleaned by immersion into 1:3 $H_2O_2/H_2SO_4$ for 1 minute, followed by rinsing with copious amounts of deionized water. This was followed by a quick rinse in concentrated HCl. The substrate was rinsed again with deionized water followed by ethanol and then blown dry with $N_2$.

## Optical ellipsometry:

Ellipsometric measurements were made with a Gaertner variable angle ellipsometer L116A using a helium-neon laser of wavelength 632.8 nm and an incidence angle of 70°. The Gaertner GC5A+SubCA+SC6A+SC7A automatic ellipsometry program for an IBM PC was used to calculate film thicknesses. A refractive index of 1.45 was assumed for the monolayer films.[iii] Five measurements of the bare substrates optical constants $N_s$ and $K_s$ were made at random positions on the gold surface and averaged. Thickness measurements were made at five random positions immediately after film formation, and the averaged value was reported.

## Monolayer capacitance

Measurement of the capacitance in the double layer charging region gauges the change in quality of the monolayers before and after reaction.[3] An increase in capacitance can result from increased permeation of ions and is indicative of damage to the film. Unreacted monolayers exhibit typical capacitance values at 0 V vs. Ag/AgCl/KCl of $1.97 \times 10^{-6}$ F/cm$^2$. For monolayers terminated in 2, the capacitance increased to $3.11 \times 10^{-6}$

F/cm$^2$. Monolayers derivatized with 3, however, showed no change in capacitance. The differences between 2 and 3 probably reflect the differences in required reaction times. This demonstrates that reaction conditions are mild enough to prevent significant damage to the film though lengthy reaction causes minor increases in the monolayer permeability. These increases are most notable at potentials positive of the ferrocene oxidation where we presume that the postively charge pendant ferrocenium ion is repelled from the surface helping to open up free volume in the monolayer and promoting permeation, the more so as damage accumulates in the film. The mild reaction conditions employed for "click" chemistry lead to only modest increases in this permeation.

## References

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