SUPPORTING INFORMATION

**Materials.** Gold shot (99.99%) was obtained from J&J Materials, and silicon (100) wafers were purchased from Montico Silicon. Chromium-coated tungsten rods were obtained from R.D. Mathis. Deionized water (16.7 MΩ) was purified using a Modu-Pure filtration system and 200 proof ethanol was used as received from Aaper. The following chemicals were obtained from Sigma-Aldrich and used as received, 2-aminoethanethiol, mercaptoacetic acid (MAA), terephthaldialdehyde (TPDA), 1-octanethiol, N-hydroxysuccinimide (NHS), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI), sodium ascorbate (NaAs), and 2,6 dichloroindophenol (DCIP). Triton X-100 was obtained from Fisher Scientific. 1-Docosanethiol was purchased from Narchem.

**Preparation of SAMs.** Gold-coated silicon wafers were prepared by first evaporating a 100 Å layer of chromium followed by ~1250 Å of gold at a base pressure of 5 x 10^{-6} torr. The SAMs were prepared by immersing gold-coated silicon samples into 1 mM ω-terminated alkyl thiol solutions for 24 h at room temperature. Carboxyl-terminated SAMs were further modified by immersing the samples in 5 mM NHS and 20 mM EDCI aqueous solution for 1 h. Amine-terminated SAMs were further modified by immersing the samples in a 1mM TPDA aqueous solution for 1 h. The samples were rinsed with ethanol and water and dried under a stream of nitrogen following SAM formation and modification.
**Atomic Force Microscopy.** Gold-coated substrates suitable for AFM characterization were prepared by first evaporating a ~1250 Å layer of gold at a base pressure of 5 x 10^{-6} torr onto freshly cleaved mica. Using a similar procedure reported by Hegner et. al.\(^1\), we transferred the smooth gold film to a silicon wafer by gluing it face-down using Defcon epoxy as an adhesive, creating a Si/epoxy/Au/mica structure. The mica was removed by physically delaminating it to generate a clean, smooth gold surface for further modification. A PSI film was deposited on the freshly exposed gold surface using the vacuum-assembly method and imaged using atomic force microscopy (AFM). As shown in Figure S1, the vacuum-assembly method produces a smooth, dense PSI monolayer with a rms roughness of 1.9 nm.

**Docosanethiol Backfilling.** We have recently shown that docosanethiol (C\(_{22}\)SH) will displace a thin, underlying SAM in areas that are not coated by PSI whereas the presence of PSI acts to block this displacement reaction.\(^2\) As further confirmation that this PSI film is indeed a dense monolayer rather than a sparse multilayer, we have applied the displacement reaction to our PSI films. To prepare the PSI films we exposed an amine-terminated SAM, prepared from adsorption of 2-aminoethanethiol onto gold, to a

![AFM image of a 10 µm by 10 µm section of a PSI monolayer film assembled using the vacuum approach with a diagonal line scan depicting the surface topology.](image)
1 mM solution of terephthalldialdehyde (TPDA) in ethanol for 1 h (Figure 1). An aqueous solution of PSI (~1.9 \cdot 10^{-5} \text{ mol/L}) containing 0.2 M phosphate buffer and 0.9 mM Triton X-100 was then deposited onto the TPDA-modified SAM and placed under vacuum (~30 mTorr) for 30 min. For the replacement reaction, we then exposed the PSI film to a 1 mM solution of C_{22}SH in ethanol for 2 h. Figure S2 (a) displays PM-IRRA spectra of a PSI film attached through a TPDA SAM before (faded spectra) and after (dark spectra) exposure to C_{22}SH for 2 h. As a control, Figure S2 (b) shows a TPDA SAM (no PSI) before (faded) and after (dark) exposure to C_{22}SH for 2 h. The TPDA SAM is replaced significantly by C_{22}SH as evidenced by the increased absorbance of asymmetric and symmetric methyl stretching at 2964 cm^{-1} and 2879 cm^{-1}, respectively, and the asymmetric and symmetric methylene stretching at 2924 cm^{-1} and 2852 cm^{-1}, respectively (Figure S2 (b)). However, replacement by C_{22}SH is significantly inhibited by the dense PSI film as shown by weak changes in absorbance in Figure S2(a).

**Experimental Details**

**Infrared Spectroscopy.** Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) data were collected using a Bruker PMA-50 attachment to a
Bruker Tensor 26 infrared spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instruments PEM-90 photoelastic modulator. The source beam was modulated at a frequency of 50 kHz with half-wavelength ($\lambda/2$) retardation and set at 80° incident to the sample surface. Spectra for SAMs on gold substrates were collected over 10 min (760 scans) at a resolution of 4 cm$^{-1}$. The differential reflection spectra ($\Delta R/R$) were calculated from the s- and p-polarized signals simultaneously collected by a lock-in-amplifier. All reported IR spectra were repeated at least twice using independent sample preparations. The estimated error in reported spectra based on the standard deviations of band absorbances measured after these independent preparations was less than 10%.

**Spectroscopic Ellipsometry.** Film thickness was determined using a J. A. Woollam M-2000 ellipsometer. The optical source beam was varied from 400 nm and 700 nm and set at a 75° incident angle to the sample surface. Thickness measurements were extrapolated using a one parameter Cauchy model with an index of refraction of 1.45. Reported values and errors are the averages and standard deviations, respectively, of at least three independently prepared samples.

**Photochronoamperometry.** Light-induced chronoamperometric data were collected using a custom three-electrode electrochemical cell. A Ag/AgCl (saturated KCl) electrode was used as a reference electrode, and a Pt mesh was used as a counter electrode. The electrolyte medium contained 5 mM phosphate buffer, 100 mM sodium chloride, 250 µM 2,6 dichloroindophenol, and 5 mM sodium ascorbate. A 500 lumens Leica KL2500 cold lamp equipped with a red light filter was used as a light source. The working electrode was set to a -0.11 V potential bias during data collection.
**PSI Extraction.** Commercial spinach leaves were used for thylakoid and PSI isolation, using a modified procedure to that reported by Reeves and Hall.\(^3\)-\(^6\) Briefly, spinach leaves were finely cut and homogenized in grinding medium (0.33 M sorbitol, 10 mM Na\(_4\)P\(_2\)O\(_7\), 4 mM MgCl\(_2\), 2 mM ascorbic acid, pH 6.5), and then filtered and centrifuged to separate the chloroplast pellet. The pellet was resuspended in a resuspension buffer (0.33 M sorbitol, 2 mM EDTA, 1 mM MgCl\(_2\), 1 mM MnCl\(_2\), 50 mM HEPES, Triton X-100, pH 7.6) and centrifuged. The resulting suspension was loaded onto a hydroxylapatite column, washed with column buffer (10 mM phosphate buffer, pH 7), and eluted with elution buffer (0.2 M phosphate buffer, pH 7, with 1 mM Triton X-100). Chlorophyll concentration was analyzed using the methods described by Shiozawa et al.\(^3\) and Markwell et al.\(^7\) The P700 concentration was determined using methods described by Baba et al.\(^8\) The final suspension containing approximately 20 µM PSI in elution buffer was stored at -80 °C.


