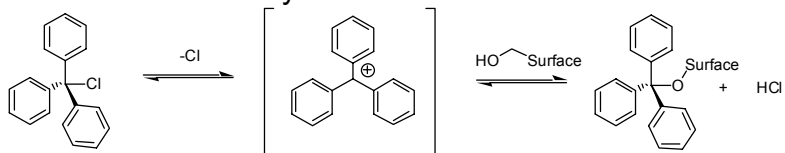


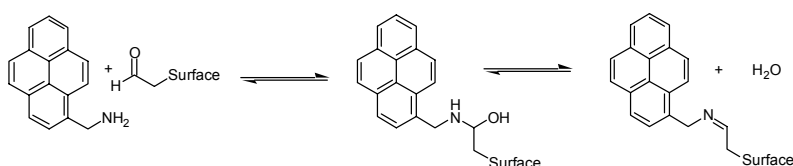
Supporting information

Proposed mechanisms of covalent attachment of chromophores to different functional groups on a SAM surface.

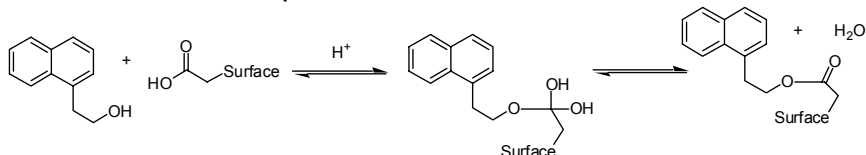
1. Attachment of trityl to OH.



2. Attachment of pyrene to CHO.



3. Attachment of naphthalene to COOH.



Experimental

- 1. Monolayer Preparation:** Octadecyltrichlorosiloxane (OTS) SAMs were prepared on oxidized Si(111) wafers (p-type, 50 Ω cm), initially cleaned with RCA SC1 (NH₄:H₂O₂:H₂O, 4:1:1) at 80°C for 45 minutes. The substrates were immersed in 10⁻³M solutions of OTS (95%, Acros) in toluene (GR grade, EM science). Monolayers were characterized through IR amplitude (3.5 \pm 0.2 O.D. @ 2918 cm⁻¹ in CH₂ antisymmetric stretch mode), IR peak frequency (2918 \pm 1 cm⁻¹ in CH₂ antisymmetric stretch mode) and contact angle (>110°) to determine fullness and compactness. Full monolayers were cleaned by sonication in acetone and CHCl₃. The samples were then irradiated in a home-made UV chamber with a low pressure Hg/Ar lamp (Oriel Instruments) with a total intensity of \sim 2mW/cm² at a working distance of 3 cm. Post irradiation, the samples were placed in reaction mixtures appropriate to the functional group to be detected.
- 2. Chromophore Chemisorption:** μ M solutions were prepared of either triphenylmethylchloride (98%, Aldrich) in dimethylformamide (DMF, ACS grade, Baker), 1-pyrenemethylamine (95%, Aldrich) in ethanol (ACS grade, Pharmaco) or 1-naphthaleneethanol (99%, Aldrich) in methylenechloride (ACS grade, Fisher). The first two reactions were run at room temperature for two hours. The third reaction was refluxed for two hours with a catalytic amount of hydrochloric acid (CMOS grade, Baker).
- 3. UV measurements:** were carried out using a Perkin-Elmer Lambda 19 UV-Vis spectrometer in 1mm path length cells.
- 4. Fluorescence measurements:** were performed on a Jobin Yvon Horiba Spex Fluorolog 3 with 5nm bandpass and 5 scan averages with samples oriented at a 45° incident angle. Excitation and emission monochromators are double grating and detection is accomplished using a PMT. Fluorescent signals for all samples were corrected for lamp fluctuations by recording the ratio of the sample fluorescence signal to the source reference photodiode.

5. **Post Reaction Cleaning Procedure:** Following chromophore grafting, the sample surfaces were rinsed with neat solvent. The samples were then sonicated in successively less polar solvents (CH_2Cl_2 , methanol or acetone, and hexane) to remove residual reactant species from the surface.
6. **Control Issues:** In order to provide controls to determine success of chromophore grafting both bare oxidized silicon and full OTS monolayers grown on oxidized silicon were incorporated into the initial set of reactions. Conveniently, SAMs are grown on both sides of the silicon wafer. Since only the side of the wafer directly in the path of the UV light is phototransformed¹, the rear side of the sample served as a built in control to monitor cleaning procedures.
7. **Calibration:** The calibration sample (Unirradiated SAM on Si) was marked with a diamond scribe defining the boundaries of the spot (4mm x 6mm) illuminated by the fluorometer. This marking facilitated realignment of the sample and ensured that the solution spread only in the defined area. A 5 μL drop of dilute solution was placed on the marked area of the sample and the solvent was allowed to evaporate. To monitor cleaning of the sample between drops, fluorescence measurements were made.
8. **XPS Measurements:** XPS data obtained before and after 15 minute UV/ O_3 treatment of full OTS monolayer grown on the native oxide of silicon. Loss of carbonaceous material is apparent but the signal from oxygenated carbon, which appears a possible shoulder peak near binding energy 286-288eV, is very small, which makes quantification impossible.
9. **FTIR Measurement:** were performed on a Brüker Tensor 27 FTIR spectrometer. FTIR data below is obtained after 30 minute irradiation of full OTS SAM. Based on an IR cross-section for carbonyl of $8.4 \times 10^{-19} \text{cm}^2$, calculated from NIST webbook IR data of acetone², a FULL monolayer of aldehyde groups ($\sim 4 \times 10^{14}$ molecules/ cm^2) at the surface would result in an IR absorbance of 2×10^{-4} OD. Clearly detection of submonolayer coverages of carbonyl is at best challenging. FLOSS provides several orders of magnitude improvement in sensitivity.

Additional DATA

1. XPS data

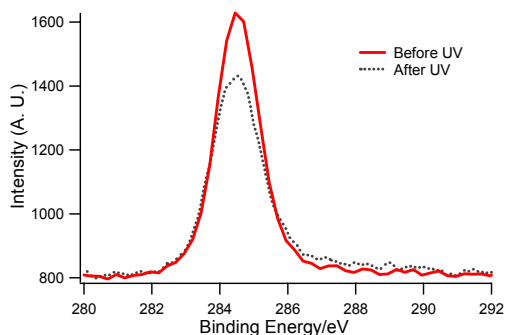


Figure 1 C(1s) region XPS spectra of ODS SAM before and after 15min of UV irradiation.

2. FTIR

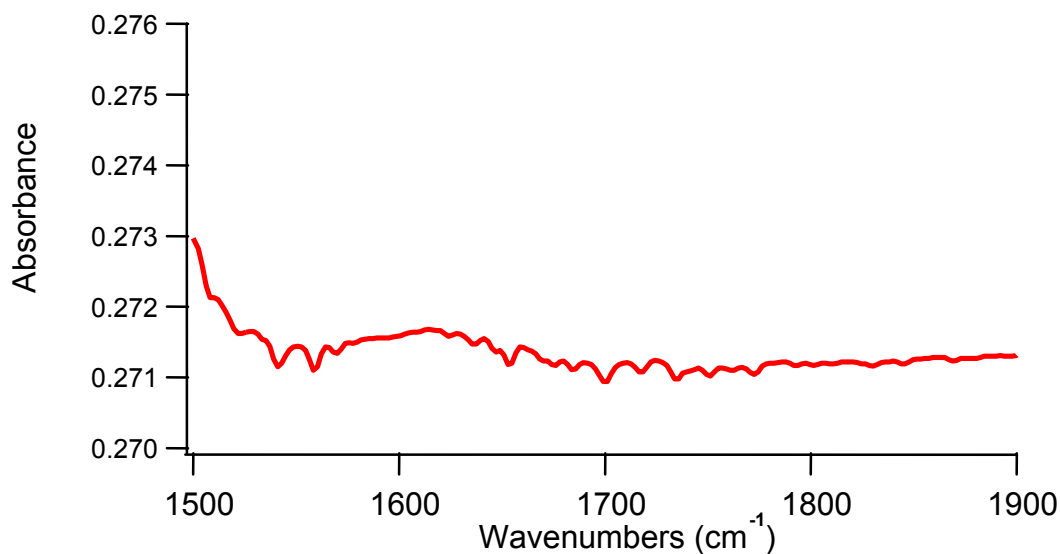


Figure 2 FTIR data collected from ODS SAM irradiated for 30 minutes

3. **Intrinsic Substrate Fluorescence:** Baseline fluorescent signals of silicon were established by both RCA SC1 (4:1:1, H₂O:NH₄OH:H₂O₂) and UV/O₃ cleaning samples of Si(111) with native oxide. In both cases a very low fluorescent signal was seen on the order of 4000-6000 c/s depending on excitation wavelength (Figure3 and 4).

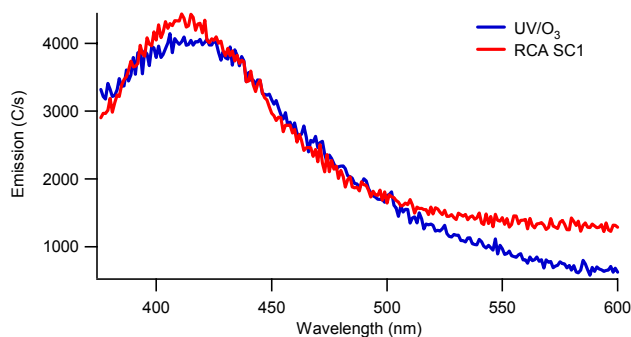


Figure 3 Fluorescence baseline for Si(111)/SiO₂. Excitation wavelength 342nm

4. **Calibration curves:** can be seen below for the chromophores (Figures 4-5).

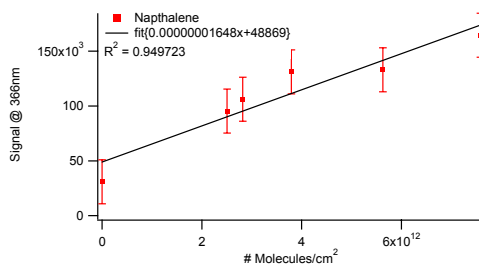


Figure 4 Calibration curve for naphthaleneethanol

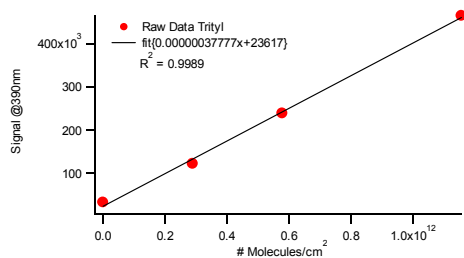


Figure 5 Calibration curve for tritylchloride

- (1) Ye, T.; Wynn, D.; Dudek, R.; Borguet, E. *Langmuir* **2001**, *17*, 4497-4500.
- (2) Stein, S. E. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69* (<http://webbook.nist.gov>); Mallard, W. G., Ed.; National Institute of Standards and Technology: Gaithersburg MD, 20899, 2003.