

SUPPLEMENTAL MATERIAL for *Mechanism of Reactive Wetting and Direct, Visual Determination of the Kinetics of Self-Assembled Monolayer Formation*.

1. Experimental Details.

Chemicals. 11-Mercaptoundecanoic acid ($\text{HS}(\text{CH}_2)_{10}\text{COOH}$), 11-Mercapto-1-undecanol ($\text{HS}(\text{CH}_2)_{11}\text{OH}$), 1-Undecanethiol ($\text{CH}_3(\text{CH}_2)_{10}\text{SH}$), (11-Mercapto-1-undecyl)tri(ethylene glycol) ($\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_3\text{OH}$), fluorescein asymmetric disulfide ($\text{HOOC}-(\text{CH}_2)_{10}\text{S}-\text{S}(\text{CH}_2)_{10}\text{CONH}-\text{C}_{21}\text{H}_{11}\text{NO}_5\text{S}$; cf. Figure 1b), and triphenylimidazole-terminated thiol ($\text{HS}-(\text{CH}_2)_{11}-\text{O}-\text{C}_{21}\text{N}_2\text{H}_{15}$; cf. Figure 1b) were all of “Ultrapure Grade” (>99.5%) and were a generous gift of ProChimia Poland (www.prochimia.com).

Gold slides were prepared by e-beam evaporation of a 10 nm Ti adhesion layer followed by 50 nm of Au onto plasma-cleaned glass slides. Following evaporation, the slides were rinsed with hexane and ethanol and stored under ethanol until use.

Stamps were fabricated by casting a hot, 6% w/w solution of high-gel-strength agarose (OmniPur Agarose, Darmstadt Germany) in deionized water against oxidized poly(dimethyl siloxane) (PDMS) masters micropatterned in bas-relief. After further degassing under vacuum and gelation at room temperature, the agarose layer was gently peeled off and cut into approximately 1-2 cm x 1-2 cm x 2-5 mm rectangular blocks (“stamps”) patterned with the negative of the array of features in the PDMS master. Prior to stamping, the stamps were soaked overnight in large excess (50 mL of solution per stamp) of 0.01 – 5.0 mM solutions of thiols/disulfides in reagent grade ethanol (VWR). They were then blotted dry on filter paper for 5 minutes and allowed to rest on a clean glass slide for 5 minutes to equilibrate any hydration gradients that might have developed during drying. The stamps were then applied to nitrogen-dried gold slides and were covered with a Petri dish (to avoid stamp drying) for times ranging from 1 sec to 17 hr. After stamping, the surface was washed with ethanol and dried under nitrogen stream immediately prior to microscopic analysis. NOTE: The uniformly soaked stamp constituted a reservoir from which the molecules could be resupplied to compensate for those that had been delivered onto the metal surface. Given the macroscopic dimensions of the stamp and the concentrations of thiols/disulfides used, changes in the reservoir concentration could be neglected to good approximation (e.g., there are 10^{16} - 10^{18} molecules in a 1 cm^3 stamp vs. $\sim 10^{14}$ molecules needed to build 1 cm^2 of a densely packed SAM).

Etching and Fluorescent Marking. To visualize the locations of the spreading front and the density of the SAM formed behind it, the patterned gold slides were either (i) etched by immersing in a freshly prepared solution of a cyanide base etchant¹⁵ (1 M KOH, 0.1 M K₂S₂O₃, 0.01 M K₃Fe(CN)₆, and 0.001 M K₄(Fe(CN)₆) for 30 min (ii) soaked in a 1.0 mM solution of an asymmetric fluorescent disulfide or a fluorescent triphenylimidazole-terminated thiol for at least three hours. The etched slides were examined by optical microscopy while the fluorescently labeled gold surfaces were imaged by fluorescence microscopy on a Leica DM IRB inverted fluorescence microscope with a Hg lamp.

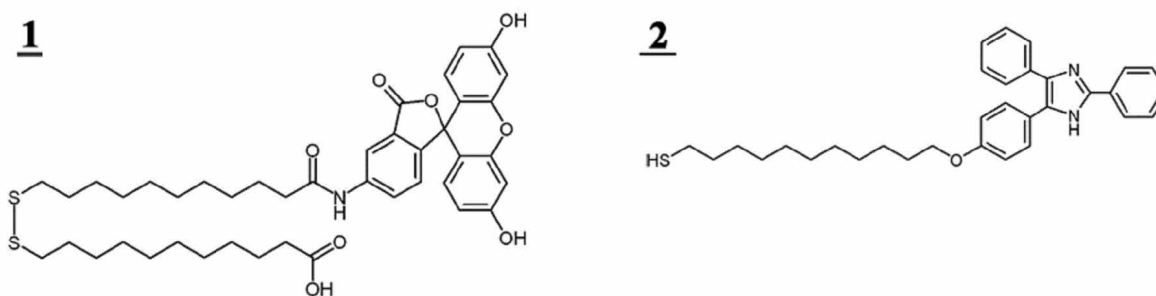


Figure S1: Alkyl disulfide terminated in a fluorescent group (**1**) used to visualize spreading patterns (cf. Fig. 1b, *right*). Fluorescence marking was also done with thiol **2** to confirm that steric effects (e.g., “bulkiness” and slower absorption of disulfides) do not influence the readout.

2. Comment on “Reaction-Control” during SAM formation. Spreading is controlled by the rate of SAM formation. To see this, note that according to our experimental data, the speed of the spreading front is maximal at the distance $x_{max} \sim 10 \mu\text{m}$ from the stamp and reaches the value $v_{max} \sim 10^{-2} \mu\text{m/s}$. It follows that the maximal rate of “consumption” of the thiol/disulfide molecules is $\kappa_{\text{reac}} = v_{max} \Sigma u$, where $\Sigma = 10^{15} \text{ cm}^{-2}$ [A. Ulman, *Chem. Rev.* **96**, 1533 (1996).] is the surface density of the molecules in the SAM, and u is the length of the spreading front line. The molecules are supplied from the stamp to the TPL through diffusion. All molecules contained in the volume $\delta u x_{max}$ are transported to the TPL, within the time $t_{\text{diff}} = x_{\text{max}}^2 / 2D$, where $D \sim 10^{-5} \text{ cm}^2/\text{s}$ [O. Dannenberger, M. Buck, and M. Grunze *J. Phys. Chem. B* **103**, 2202 (1999); L.S. Jung and C.T. Campbell *J. Phys. Chem B* **104**, 11168 (2000)] is the diffusion coefficient, and $\delta \sim 10$

μm is the characteristic thickness of the spreading layer (δ is commensurate with the height of the stamps' features, $H = 50\text{ }\mu\text{m}$, cf. Figure 3). Because the flux of molecules $\kappa_{diff} = Cx_{max}\delta u/t_{diff}$ is – even for the smallest thiol/disulfide concentration, $C = 0.01\text{ mM}$ – is larger than κ_{reac} ($\kappa_{diff}/\kappa_{reac} \sim 10^2$) the process is reaction-controlled. Furthermore, because the volume of thiol/disulfide solution flowing onto the surface is small compared to the total volume contained in the stamp, the energetic cost of solution transfer from the stamp is small compared to the surface energies involved. Consequently, it is reasonable to assume that the pressure difference between the inside and the outside of the stamp and the curvature-related energy terms can be neglected.

3. Comment on the irreversibility of surface reactions. The approximation of the surface kinetics as irreversible is congruent with previous literature reports [e.g., Schwartz, D.K. *Ann. Rev. Phys. Chem.* **2001**] and is further validated by our experiments. To see this, consider the case of reversible adsorption kinetics, for which the reaction rate equation becomes $d\vartheta(x,t)/dt = k_a(1 - \vartheta(x,t)) - k_d\vartheta$, where k_a and k_d are the forward (adsorption) and reverse (desorption) rate constants, respectively. Solving this equation, the fractional surface coverage, ϑ , can be expressed as a function of time as $\vartheta(x,t) = k_a/(k_a + k_d)(1 - \exp(-(k_a + k_d)\chi(x,t)t))$. Furthermore, while the forward rate constant is expected to depend on the bulk thiol concentration as $k_a(C) \sim kC^\lambda$, the reverse rate constant should be independent of C . Examining the equilibrium coverage, $\vartheta(t \rightarrow \infty) = k_a(C)/(k_a(C) + k_d)$, we note that under such circumstances the coverage – and thereby the surface energy, $\sigma_{LS}(x,t)$, and equilibrium spreading distance, x_{Eq} – could vary with C . This, however, is not what we observe experimentally, and it thus follows that for the concentrations studied, $k_a(C) \gg k_d$ and adsorption can be described by irreversible kinetics with $\vartheta(t \rightarrow \infty) = 1$. This statement is further supported by the fluorescence and etching results in which SAMs do not desorb even after prolonged soaking/etching.

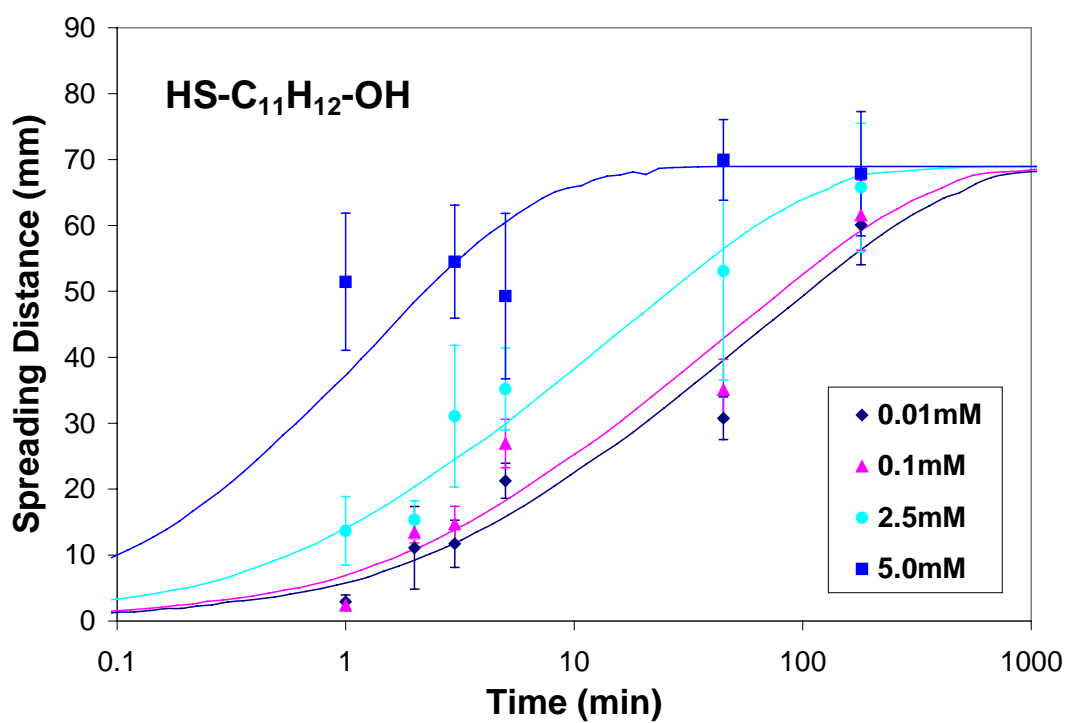
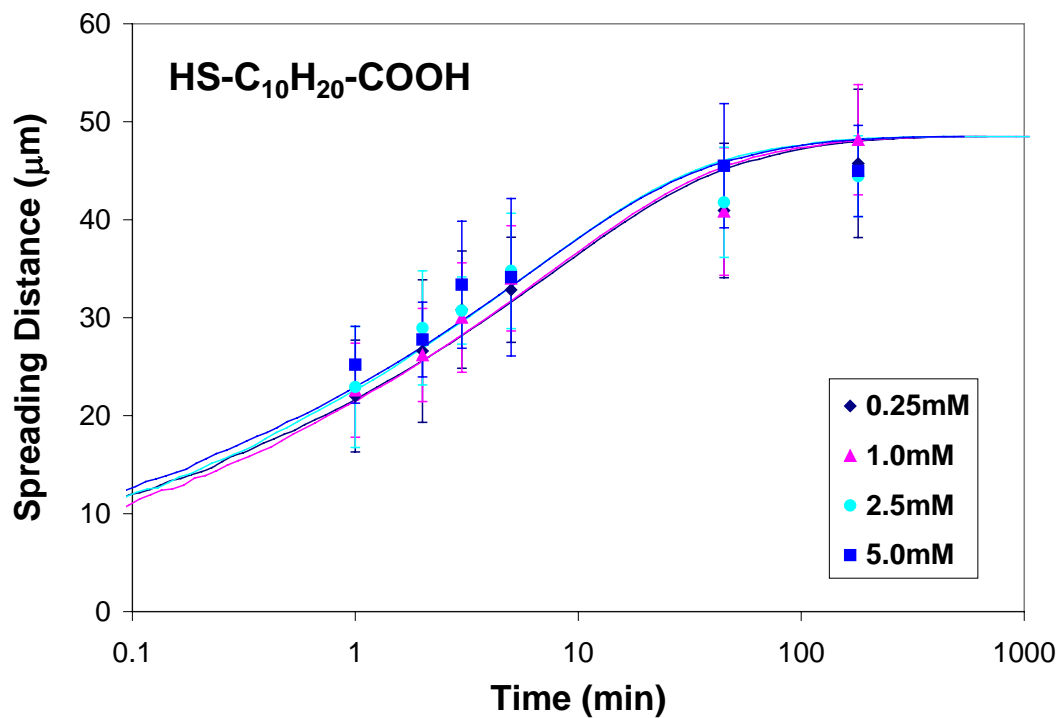
4. Fitting solutions of the Master Equation to the Experimental Dynamics Curves. The theoretical spreading curves, $\tilde{h}_0(\tilde{t})$, obtained from the “master” LD equations were fitted to the

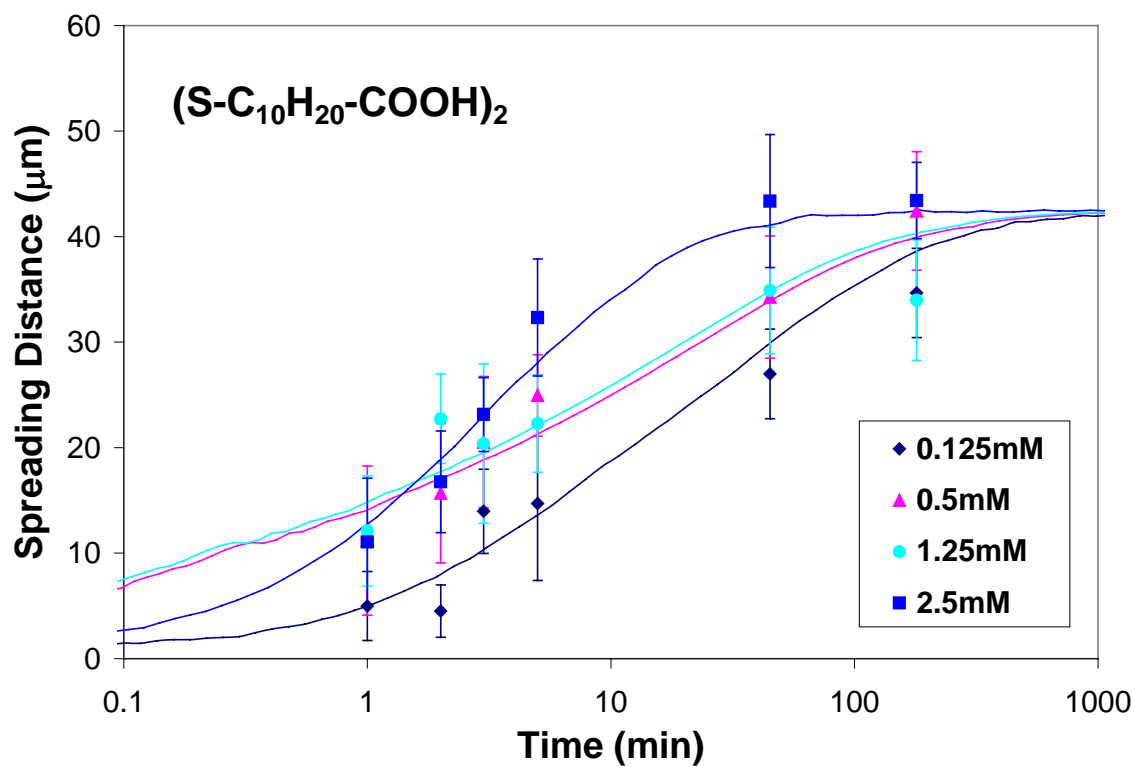
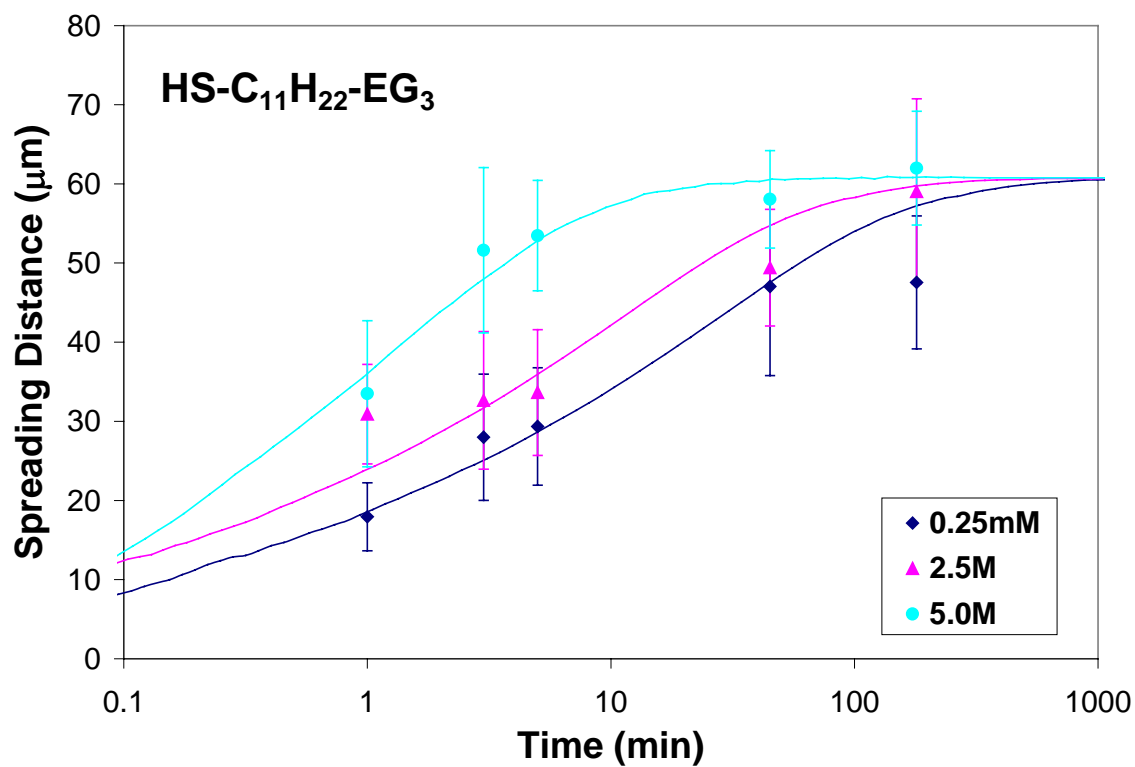
experimental data points using the least squares fitting method. In the fitting procedure, the quantities \tilde{k}_{eff} and τ were the only free parameters, and the rate constants were determined unambiguously from the formula $k_{eff} = \tilde{k}_{eff} / \tau$. Modeling was further simplified by the fact that (i) the values of the rescaled surface energies for all SAMs studied were determined from experimentally observed equilibrium spreading distances, x_{eq} , and (ii) the values of the liquid-gas surface tension, σ_{LG} , determined by stalagmometry, were approximately constant for a given thiol/disulfide over the range of concentrations $C = 0.01 - 5.0$ mM.

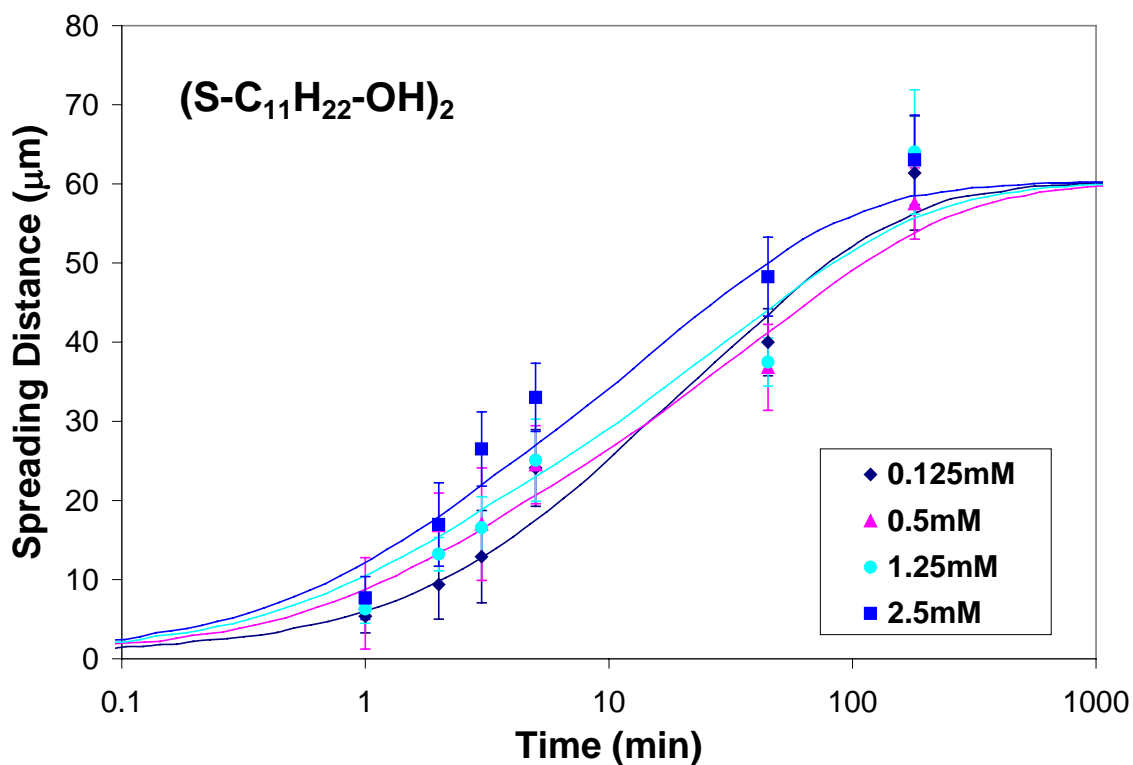
The LD equations were integrated numerically for $N = 100$ layers using the first order Euler scheme with the mesh size $\Delta\tilde{h} = 0.1$, time step $\Delta\tilde{t} = 0.4$, and the noise amplitude $\varepsilon = 1.0$. For each type and concentration of thiol/disulfide, the results of simulations were averaged over 100 different noise realizations. The length scale, h , was set based on the height of the stamp's features used. The rescaled surface energies, $\tilde{\sigma}_{LS}^{Au}$ and $\tilde{\sigma}_{LS}^{SAM}$, were determined, respectively, from the equilibrium spreading distances of pure ethanol, and each thiol/disulfide solution. The only fitting (free) parameters in the model were the rescaled surface reaction rate, \tilde{k}_{eff} , and the time scale, τ .

5. Comprehensive Experimental Data and Model Fits:

Note: the time axes in the figures below are plotted on a logarithmic scale to show the entire experimental range.







Finally, the figure below shows the summary of the kinetic curves with *linear* time axis (to emphasize that the curves plateau) fitted using the master equation. Lines: for thiols, — = 5.0 mM, — — = 2.5 mM, — — — = 1 mM, - - - = 0.25 mM, - - - - = 0.1 mM, — — — — = 0.01 mM; for disulfides, — = 2.5 mM, — — = 1.25 mM, — — — = 0.5 mM, - - - = 0.125 mM. Solid black line indicates ethanol.

