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Wetting and Fourier Transform Infrared Spectroscopy Studies of Mixed Self-Assembled Monolayers of 4′-Methyl-4-mercaptobiphenyl and 4′-Hydroxy-4-mercaptobiphenyl

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Mixed self-assembled monolayers (SAMs) of 4′-methyl-4-mercaptobiphenyl and 4′-hydroxy-4-mercaptobiphenyl were prepared on gold (111) surfaces. The composition of the mixed SAMs could be precisely determined by external reflection Fourier transform infrared (ER−FTIR) spectroscopy and showed direct correlation with their wetting properties. Contact angles of water, glycerol and diiodomethane showed small hysteresis, and their values did not change after 1 month, suggesting that these mixed SAMs are stable and can be utilized as model systems for the study of surface phenomena.

Chain dynamics in self-assembled monolayers (SAMs)[1,2] of alkanethiolates on gold results in surface reconstruction due to *trans−gauche* conformational changes in chain-termina. This process is especially noticeable in hydroxy-terminated SAMs, as was shown both by experimental means[3] and by molecular dynamics simulations.[4] Driven by the formation of correlated H-bonds, and to minimize surface free energy, terminal hydroxy groups get buried in the surface, resulting in an increase of the measured water contact angle from ∼20° to ∼60°, and in hydroxyl groups less available for chemical reactions, such as esterification.[3]

Mixed SAMs are ideal systems for studies of surface phenomena. However, if SAM surfaces change with time, as a result of stimuli such as temperature and solvents with different dielectric constants, they do not fit to serve as model surfaces, since surface properties are influenced by the dynamic processes. The motivation for the studies presented in this paper is the search for rigid, stable model surfaces, so that surface reconstruction can be prevented and the chemical foundation of surface properties can be established. This was the driving force for our extensive synthetic efforts to prepare a large variety of 4′-substituted-4-mercaptobiphenyls.

Recent helium diffraction studies of a SAM of **I** showed a diffraction peak even at room temperature,[5] and quartz crystal microbalance studies of water vapor adsorption on a SAM of **II** suggest that these surfaces are robust.[6] In this paper we present detailed studies of mixed SAMs of 4′-methyl-4-mercaptobiphenyl and 4′-hydroxy-4-mercaptobiphenyl (Figure 1) on gold (111) surfaces. We have selected these thiols, because the pure SAMs provide the most hydrophilic and most hydrophobic surfaces in this series. The mixed SAMs provide molecular-level control of surface OH concentration, thus allowing systematic studies of wetting.

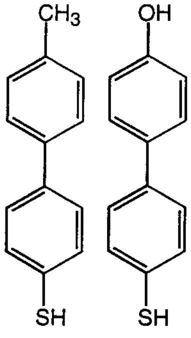
I II

Figure 1. 4′-Substituted-4-mercaptobiphenyls.

Freshly cleaned gold substrates[7] were immersed into the thiol solution ($c_{\text{thiol}} = 10\ \mu$M, anhydrous ethanol)[8] and kept there under nitrogen overnight. The substrates were removed from solution, rinsed with ethanol, and blown dry by a jet of nitrogen. Mixed SAMs were prepared the same way, with total thiol concentration being 10 μM.[9] Monolayer were stored in anhydrous ethanol for later studies. The thickness of all SAMs and mixed SAMs, as established by ellipsometry,[10] was 13 ± 1 Å.

Figure 2 shows external reflection Fourier transform infrared (ER-FTIR)[11] spectra of the trifluoroacetylated[12]

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(7) A detailed procedure has been published before. In short, Glass slides were baked overnight in a vacuum (10^{-7} Torr) at 300 °C. Gold (99.99%) evaporation was carried out at the same temperature, using a constant deposition rate of 1−2 Å/s. The gold substrates were further annealed in a vacuum at 300 °C for 18 h. X-ray studies show that these gold substrates have Au(111) surfaces. Reproducible ellipsometric constants for gold substrates prepared according to this procedure are $N_S = 0.186 \pm 0.01$, and $K_S = 3.400 \pm 0.05$. Using these gold substrates, SAMs of biphenyl thiols show contact angle hysteresis of ≤6°. In comparison, the same SAMs on gold substrates prepared at room temperature without annealing show contact angle hysteresis of ≤20°. All substrates were cleaned using argon plasma for 30 s immediately before immersion into the thiol solution.

(8) Details of synthesis, purification and analysis of 4′-substituted-4-mercaptobiphenyl will be published elsewhere. Ethanol (anhydrous) and trifluoroacetic anhydride were obtained from Aldrich and used as received.

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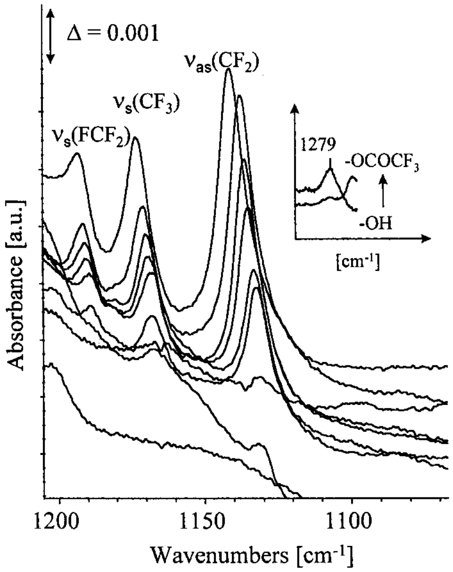

Figure 2. Midrange IR spectra of trifluoroacetylated mixed SAMs of **I** and **II**. The insert shows the ν_{C-O} band before and after trifluoroacetylation.

mixed SAMs. Notice in the insert the 1279 cm^{-1} band associated with ν_s(C$-$O) mode. According to the reduction of its area, the transformation of surface $-$OH groups to $-$OCOCF$_3$ groups was carried out with 96% yield. Thus, this surface functionalization reaction is effective for quantitative composition analysis of the mixed SAMs. There are three pronounced C$-$F stretching bands at 1141, 1173, and 1193 cm^{-1} in Figure 2.[13] The average absorbance integrals of these bands is plotted in Figure 3 as a function of the molar fraction of **II** in solution. Notice that preferential adsorption of **I** persists, probably due to the stabilization of **II** in the ethanol solution.

The frequency shifts of the three bands are plotted in Figure 4 vs surface composition. This is in agreement with the findings of Liedberg and co-workers who observed concentration-dependent shifts in the ER-FTIR spectra of trifluoroacetylated mixed SAMs.[14] We have observed similar frequency changes as a function of surface composition in mixed SAMs of **I** with 4′-trifluoromethyl-4-mercaptobiphenyl and found excellent agreement between theory and experiments, when a classical electromagnetic model was used.[15] Notice the linear relationship for the three bands, and that the three lines have the same slope. This suggests that the same dipolar interactions in the two-dimensional assemblies are responsible for the band shifts.

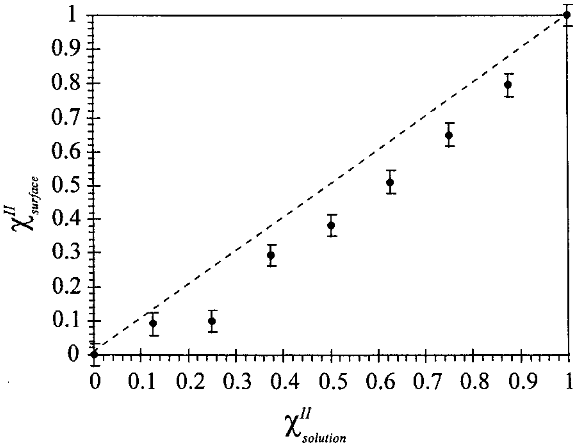

Figure 3. Average integrated areas under the ν_s(CF$_3$) and ν_{as}(CF$_2$) bands, in mixed SAMs of **I** and **II**, vs the molar fraction of **II** in solution, for adsorption from ethanol.

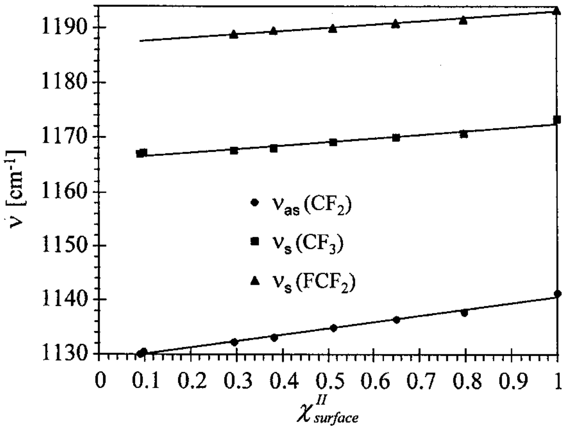

Figure 4. Frequency shifts of the ν_s(FCF$_2$), ν_s(CF$_3$), and ν_{as}(CF$_2$) bands are vs surface composition.

The contact angles[16] of water, glycerol, and diiodomethane provide additional information about the mixed SAM surfaces. The surface tension (γ_{lv}) of these three liquids is 72, 63, and 50 dyn/cm^2, respectively. Figure 5 shows linear relationships between cos θ of advancing and receding water contact angles and surface composition. These results are in agreement with the Cassie equation[17] predicting that the contact angle of heterogeneous surfaces is an area average of the contact angles of the two homogeneous surfaces

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(9) Some precautions were taken to reduce errors associated with solution preparation. First, 0.1 mM stock solutions of the two thiols were prepared in ethanol, bubbled with nitrogen, and stored in the refrigerator. Second, nine pieces of gold were cut from same batch of gold substrates. Finally, nine solutions of 0%, 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5%, and 100% **II** mixed with **I** were prepared out of stock solution. All stock solutions were saved for no longer than 2 weeks. Errors were established after repetition of experiments and measurements.

(10) Thickness was estimated by ellipsometry using a Rudolph Research AutoEL ellipsometer (He$-$Ne laser, angle of incidence 70°). Measurements of three separate points were carried out on each sample, using an assumed refractive index of 1.462.

(11) The FTIR spectra were obtained using a Nicolet MAGNA-IR 760 spectrometer equipped with an MCT-A detector that is cooled with liquid nitrogen. The sample compartment was purged with CO$_2$-free dry air using a Whatman laboratory gas generator. Spectra were collected in a grazing angle mode using an angle of incidence 80° (SpectraTech FT-80 attachment). Two thousand five hundred scans were collected for each spectrum, with a spectral resolution of 1 cm^{-1}. The deviation of band position in consecutive experiments of the same sample was about $\pm$0.3 cm^{-1}.

(12) The SAMs were introduced into a 50-mL jar containing a few drops of trifluoroacetic anhydride.[3a] The jar was sealed, and the SAMs were allowed to react with the anhydride vapor for 18 h. The samples were removed from the jar, blown by a jet of dry nitrogen to remove adsorbed anhydride, and immediately studied by FTIR spectroscopy.

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(16) Contact angles were determined at room temperature by the sessile drop method using a Rame-Hart model 100 goniometer, equipped with a high-resolution CCD-IRIS color video-camera (Sony) connected to a computer. To measure the advancing and receding angles, a 20 μL droplet was formed at the end of blunt-ended needle of a syringe. Obtained images of the droplet were evaluated using NIH software. Advancing and receding angles were measured by tilting the sample stage. Thus, the tilt angle was increased until the droplet started to move on the surface and immediately decreased to a point where the droplet stopped moving. Maximum advancing and minimum receding contact angles for water were found at a tilt angle of ~40°.

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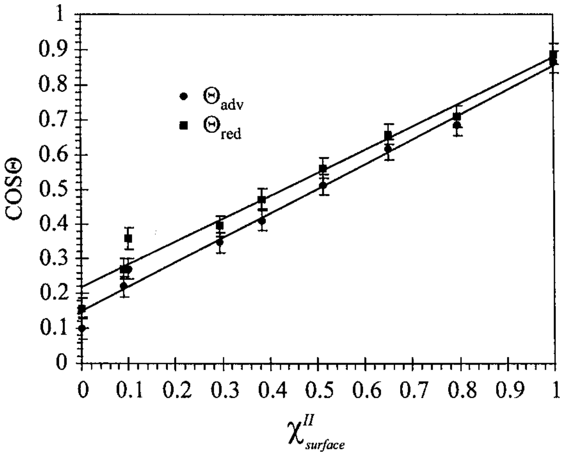

Figure 5. Advancing and receding water cantact angles on mixed SAMs of **I** and **II**.

$$\cos \theta_{obs} = f_1 \cos\theta_1 + f_2 \cos\theta_2$$

where θ_1 is the contact angle of a SAM of **I**, θ_2 is the contact angles of a SAM of **II**, and f_1 and f_2 are the fractional coverages of **I** and **II** in the mixed SAMs, respectively.

A comparison of the wetting of the mixed SAMs by the three liquids is shown in Figure 6. Notice that none of these wetting experiment showed a wetting transition such as the one observed for the wetting of mixed SAMs of 11-hydroxyundecane-1-thiol and dodecanethiol by hexadecane, bicyclohexyl, and methoxyethanol.[18] The latter three liquids could not be used in the present studies because they completely wet all mixed SAM surfaces.

To further analyze the mixed SAMs we have used the geometric-mean method[19] to calculate their total surface free energy (γ_s^{exp}), as well as the dispersive (γ_s^d), and polar (γ_s^p) components from the advancing contact angles of diiodomethane and water. From Figure 7, it is apparent that γ_s^p grows linearly with the surface OH concentration, keeping up with the change of γ_s^{exp}, while γ_s^d remains about the same for all compositions.

We have followed the water contact angles of the mixed SAMs for a month and did not detect any change, withing experimental error (±1°). Measurements carried out after 16 months did not show any decrease in contact angles.

In conclusion, we have prepared mixed self-assembled monolayers of 4′-methyl-4-mercaptobiphenyl and 4′-hydroxy-4-mercaptobiphenyl on annealed gold (111) surfaces. The composition of the mixed SAMs was determined by ER-FTIR spectroscopy and showed good correlation with their wetting properties. Contact angles of water, glycerol, and diiodomethane showed small hysteresis, and their values did not change with time. This suggests that these mixed SAMs do not undergo surface reconstruction processes, as observed for their aliphatic counterparts, and thus can be utilized as model surfaces.

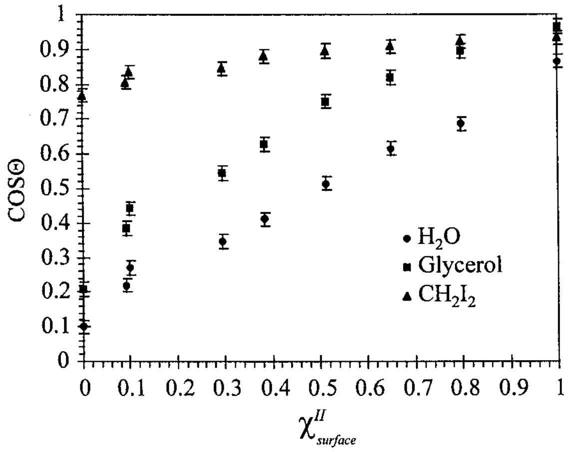

Figure 6. Contact angles of water, glycerol, and diiodomethane on mixed SAMs of **I** and **II**.

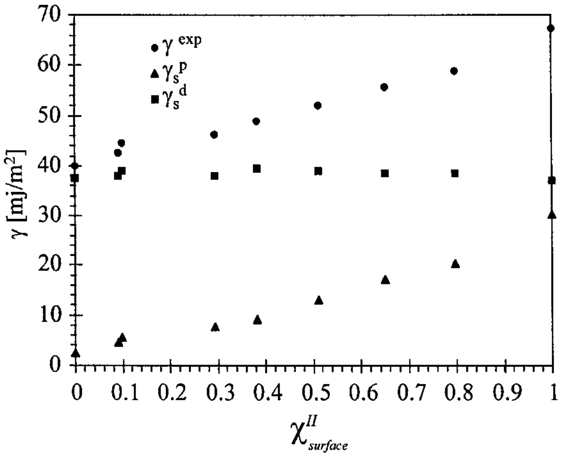

Figure 7. A plot of of γ_s^{exp}, γ_s^d, and γ_s^p, vs for mixed SAMs of **I** and **II** vs surface composition.

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