Mixed Self-assembled Monolayers of Rigid Biphenyl Thiols: Impact of Solvent and Dipole Moment

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Abstract: The formation of mixed self-assembled monolayers (SAMs) of different 4′-substituted-4-mercaptobiphenyl (with X = CH_3, CF_3, and SCH_3) on gold, from different solvents, has been investigated. Monolayer thickness values, estimated by ellipsometry, contact angle measurements, and external reflection absorption infrared (ERFTIR) spectroscopy confirms that >90% of the monolayer is formed after 1 h of adsorption. The dielectric constant of the solvent, the permanent dipole moment of the substituted mercaptobiphenyl, their adsorption and desorption kinetics, and their intermolecular dipole−dipole interactions in the SAM were all found to play a crucial role in the final composition of the mixed SAMs.

Introduction

Mixed self-assembled monolayers (SAMs)[1,2] have become ideal model systems for the study of surface properties, given the possibility for fine control of the concentrations of surface functional group. Our interest in SAMs has been as model surfaces for the studies of wetting,[3] adhesion,[4] and friction,[5] and as substrates for surface-initiated ionic polymerization.[6] As model surfaces, SAMs must fulfill at least three requirements: (1) to be strongly attached to the substrate, so that surfaces will withstand environmental chemical and physical effects; (2) to be homogeneous and closely packed, so that model surfaces will have a given, and well-defined composition, and (3) to allow a diverse range of surface functional groups to be present. Alkanethioles have been the molecules of choice since they readily give homogeneous, ordered, and chemically and mechanically stable SAMs.[1,2] However, chain dynamics in SAMs made of flexible alkyl derivatives result in surface reconstruction because of the possibility of trans−gauche conformational changes in chain-termina. Recent studies of sum-frequency generation spectroscopy[7] show that the structure of such a surface is clearly perturbed when it interacts strongly with another condensed phase (e.g., hexadecane). Thus, surface reorganization processes must be considered, especially if very polar surface groups, such as hydroxyl, are present.[8] In such

cases, the perturbation can be significant,[9] and not confined only to the surface.[8] Consequently, surface engineering using ω-functionalized alkanethiolate SAMs may not result in surfaces of desired stability to allow reproducible, detailed, and systematic studies of wetting and adhesion.

To overcome this shortcoming, we have synthesized a large variety of 4′-substituted-4-mercaptobiphenyls, which have the following advantages: First, SAMs of thiolates on Au(111) have been studied more than any other SAM, and many structural and physical properties of these systems are understood.[1,2] Second, the preparation of thiophenols, which are non-moisture-sensitive solid compounds, is straightforward.[10] Third, the potential epitaxial adsorption of the thiolate-addlayer on the gold surface offers the possibility that different underlying lattices (e.g., {111}, {100}) may provide SAM surfaces with different symmetries. Last, the adsorbing properties of the thiophenol group may be altered by using different substituents at the 4′-position of the biphenyl molecule.

Differences in adsorption kinetics become important when mixed monolayers are prepared, since surface concentration can differ significantly from solution concentration because of competitive adsorption and desorption processes. Thus, we have carried out detailed adsorption kinetics studies, by means of quartz crystal microbalance (QCM), of several 4′-substituted-4-mercaptobiphenyls.[11] Interestingly, although we found no correlation between the measured adsorption kinetics and the Hammet constants of the 4′-substituents, there was a strong correlation between adsorption kinetics and the molecular dipole moment. The fastest adsorbing molecule in this series was the 1,4-dimercaptobiphenyl, and applying either an electron-donating or an electron-attracting 4′-substituent—e.g., $N(CH_3)_2$, or

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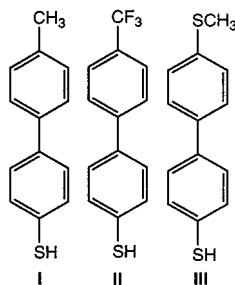
Figure 1. 4′-Substituted-4-mercaptobiphenyls.

CF_3, respectively—resulted in a rate decrease, probably attributable to the increasing repulsive intermolecular interactions in the forming SAM.

That the 4′-substituent defines the dipole moment along the molecular axis is not surprising, given the effectively complete conjugation along the entire molecule, since both aromatic rings are in-plane in the solid state at temperatures >40 K.[12] Therefore, the formation of SAMs from biphenylthiols derivatives can be considered as the assembly of dipoles, and since the biphenylthiols series provides molecules with a variety of dipole moments, systematic studies of polar interaction and their effects on adsorption kinetics, self-assembly mechanism, and the resulting monolayer structure are now possible for the first time. Here we give a detailed account of the preparation of mixed SAMs. The question we pose is whether the molecular dipole moments, and the intermolecular dipole—dipole interactions, in the SAM play a role in the formation, composition, and structure of mixed SAMs. Here we address in detail the part of the question dealing with monolayer composition. In forthcoming papers we shall discuss kinetic effects,[11] and band shifts in the external reflection Fourier transform infrared (ERFTIR) spectra of mixed SAMs.[13]

To answer the question posed, we have selected 4′-trifluoromethyl-4-mercaptobiphenyl (**II**) as one of the components in mixed SAMs (Figure 1). This thiol has a very strong IR absorption band for the CF_3 group, and by mixing it with other biphenyl thiols that have either CH_3 (**I**) or SCH_3 (**III**) groups at the 4′-position, the formation of mixed SAMs can be monitored quantitatively in various solvents. Because the biphenyl moieties in the SAMs are presumably perpendicular to the monolayer surface,[14,15] and the molecules lack conformational freedom, IR spectroscopy can be used to quantitatively determine the surface concentration of CF_3 groups.

Experimental Section

Materials. Details of synthesis, purification, and analysis of the 4′-substituted-4-mercaptobiphenyls will be published elsewhere.[16] Toluene, anhydrous ethanol, 1,2-dichloroethane, and acetonitrile (all ACS-grade) were obtained from Aldrich, Quantum Chemicals, or EM Science and were used as received.

Gold Substrate Preparation. Glass slides (Fisher) were cleaned in ethanol at 40 °C for 10 min in an ultrasonic bath. The slides were then treated in an argon plasma chamber for 30 min at an argon pressure of 0.1 Torr. Slides were mounted in the vacuum evaporator (Key High Vacuum) on a substrate holder, which is placed ∼15 cm above the gold source. They were baked overnight in a vacuum (10^{-7} Torr) at 300 °C with a halogen lamp heater (Ushio Oregon Inc.). The lamp

was mounted 10 cm above the back of the substrates, and the temperature was controlled with an OMEGA CN8500. Gold (purity 99.99%) was evaporated at a rate of 3−5 Å/s, and the evaporation rate and film thickness were monitored with a quartz crystal microbalance (model TM100 from Maxtek Inc.). The gold substrates were annealed in a vacuum at 300 °C for 18 h. After cooling to room temperature, the chamber was filled with nitrogen, and the substrates were stored in a vacuum desiccator for later use. Reproducible optical constants for gold substrates prepared in this manner are $N_S = 0.186 \pm 0.01$, and $K_S = 3.400 \pm 0.05$. Atomic force microscopy (AFM) studies revealed terraces of Au(111) with typical crystallite sizes of 0.5−1 μm^2.

Monolayer Preparation. Gold substrates were cleaned by argon plasma for 30 s (argon pressure = 0.1 Torr), before immersion into the thiol solution ($c = 10\ \mu M$) in ethanol. The substrates were kept in the thiol solution for 18 h under nitrogen. 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 a total thiol concentration of 10 μM. SAM-covered substrates were stored in pure ethanol for later analysis. Ellipsometry, contact angle measurements and IR spectroscopy (see below) all suggest that >90% of the SAM is formed after 1 h. Experiments carried out in our laboratory indicate that after 18 h in the thiol solution, the structures represent equilibrium SAMs.

Exchange Experiments. SAMs were immersed in a solution of thiols ($c = 10\ \mu M$) in ethanol, under nitrogen. Every time a sample was taken out for thickness and ERFTIR measurements, it was rinsed with ethanol and blown dry by a jet of nitrogen. After the measurements were completed, the sample was returned to the thiol solution.

Thickness Measurements. Thickness was estimated by ellipsometry with a Rudolph Research AutoEL ellipsometer (He−Ne laser, angle of incidence 70°). At least three individual points were measured on each sample, with an assumed refractive index of 1.462 for the organic film. The estimated thickness of the SAMs of **I**, **II**, and **III** was 14, 14, and 15 Å, respectively (all ±1 Å).

Contact Angle Measurements. Static contact angles were determined at room temperature by the sessile drop method with use of a Ramé−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, we examined 20-μL droplets that were formed at the end of blunt-ended needle of a syringe. Advancing and receding angles were measured by tilting the sample stage. The stage tilt was increased until the droplet started to move on the surface, at which time the tilt was 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°. Stored images of droplet were analyzed by using software from NIH. Advancing water contact angle for SAMs of **I**, **II**, and **III** are 80°, 81°, and 86°, respectively.

ERFTIR. The IR data were obtained with a Nicolet MAGNA-IR 760 spectrometer equipped with an MCT-A detector cooled with liquid nitrogen. The sample compartment was purged with CO_2-free dry air by use of a Whatman laboratory gas generator. Spectra were collected in a grazing angle mode with a Spectratech FT-80 attachment (angle of incidence 80°). We collected 2500 scans for each spectrum, at a spectral resolution of 1 cm^{-1}. The certainty of band maxima in consecutive experiments of the same sample was ∼± 0.005 cm^{-1}.

Results and Discussion

The preparation of biphenylthiolate SAMs and mixed SAMs is highly reproducible. Monolayers are generally stable, as was apparent from thickness and contact angle measurements taken after 1 week and 1 month. However, the SAM of **II** on gold is less stable when no polar solvent is present. On the other hand, all mixed SAMs of **I** and **II** are stable for at least 1 month. This observation is in agreement with arguments made below, and manifests the need for stabilization of an assembly of dipoles.

SAMs of II. Figure 2 presents the infrared spectra of **II** in KBr, in solution (5 mM, CCl$_4$), and in a SAM on gold, formed

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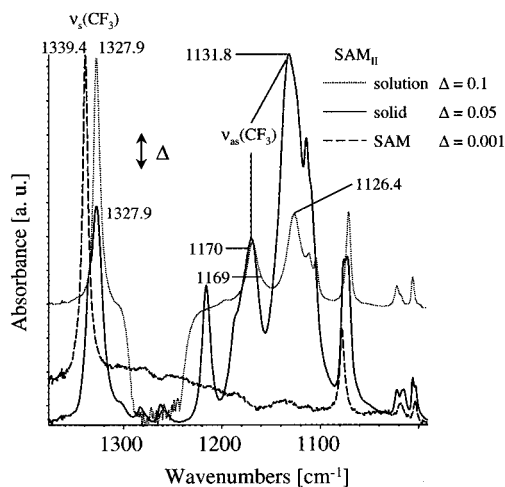(16) Kang, J. F.; Jordan, R.; Ulman, A. Manuscript in preparation.

Figure 2. IR spectra of 4′-trifluoromethyl-4-mercaptobiphenyl in KBr, in solution (5 mM in CCl$_4$), and in a SAM on gold.
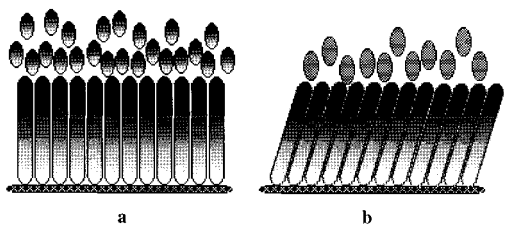

Figure 3. Idealized picture of a polar SAM stabilized by polar solvent molecules (a), and of a SAM with tilted molecules because of the absence of external polar interactions (b).

from ethanol (dielectric constant = 25.3[17]). Notice that the spectrum is dramatically simplified in the SAM, and the band maxima are shifted to higher energy. The band at 1003 cm^{-1} is assigned as an aromatic parallel C−C−C bending mode.[18] The band at 1339 cm^{-1} is the symmetrical CF$_3$ stretching vibration [ν_s(CF$_3$)], while that at 1072 cm^{-1} is the biphenyl b$_{1u}$ band. No asymmetrical CF$_3$ band [ν_{as}(CF$_3$)] has been observed in SAMs made from ethanol or acetonitrile (dielectric constant = 36.6). This is in agreement with molecules that are perpendicular to the SAM surface.[14,15] In this orientation, the gold−S−C angle is 180°, and the hybridization of the thiolate sulfur is sp.[19] Therefore, the first mechanism for the stabilization of a polar SAM is dipolar interactions with polar solvent molecules (Figure 3a).

On the other hands, when adsorption is carried out from toluene (dielectric constant = 2.4[17]) or from 1,2-dichloroethane (dielectric constant = 10.4[17]), two ν_{as}(CF$_3$) bands, at 1132 and 1174 cm^{-1}, are observed (Figure 4).[20] In addition, the ν_s(CF$_3$) is shifted from 1339 to 1335 cm^{-1}, and the area under the peak is about half of the value measured for the same SAM made from ethanol. Furthermore, the area of the b$_{1u}$ band is also about one-half of its value (see Figure 4). These observations suggest that the molecules in this SAM are tilted away from the normal surface, and that the gold−S−C angle is not 180°. The exact packing and ordering of biphenylthiolates in the SAMs adsorbed from ethanol and from toluene are currently under investigation by using second-harmonic-generation spectroscopy. Once the tilt angle in a SAM made from toluene is known, it will become

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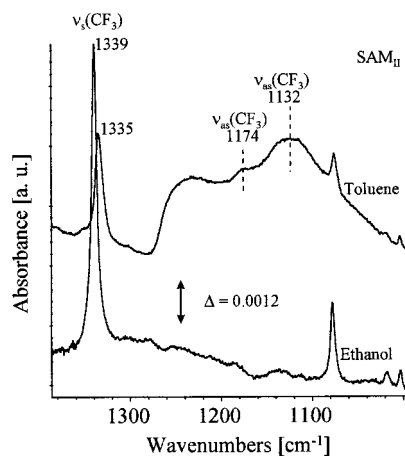(20) Randle, R. R.; Whiffen, D. M. *J. Chem. Soc.* **1955**, 1311.

Figure 4. IR spectra of 4′-trifluoromethyl-4-mercaptobiphenyl in SAMs on gold prepared from ethanol and from toluene.

possible to estimate coverage. Notice that the experimental thicknesses of SAMs from ethanol and from toluene are the same, within experimental error. This may result from the small theoretical difference between the two thicknesses (≤2 Å when the tilt angle is 30°), as well as from an unaccounted-for difference in the refractive index of the SAM.

Because of the electron donor properties of the thiolate sulfur and the electron acceptor properties of the trifluoromethyl group, **II** has a significant permanent dipole moment, and its monolayer can be viewed as a two-dimensional array of dipoles. Therefore, in the absence of stabilization from polar solvent molecules, the second stabilization mechanism for a polar SAM is molecular tilt, which results in a less polar monolayer (Figure 3b).

Tao and co-workers[21] have argued, on the basis of electrochemical studies, that SAMs of thiophenolates are less stable from those of alkanethiolates, because of the sp-hybridization imposed on the thiolate sulfur when the molecules are perpendicular to the gold surface. Our theoretical calculations[19] of alkanethiolate SAM systems, on the other hand, suggest very small energy difference between the sp- and sp^3-hybridizations, and indicate that rehybridization of the thiolate sulfur may be involved in the packing and ordering processes of the SAMs. If the hybridization of the thiolate sulfur in SAMs adsorbed from toluene is sp^3, it verifies our suggestion[19] that the surface−S−C angle may be influenced by the intermolecular interaction. What is interesting, and probably unique to aromatic thiols, where there is conjugation between the headgroup and the substituent at the 4′-position, is that the solvent may have a role in defining this angle as well, given the SAM−solvent dipole−dipole interactions.

Mixed SAMs of I and II. Figure 5 shows that as the concentration of **II** in its mixed SAMs with **I** decreases, the intensity of the ν_s(CF$_3$) bands decreases monotonically, and is uniformly shifted to lower frequencies. This rules out the existence of phase-separated monodomains. Also, corroborative AFM studies do not reveal any domains.[22] The IR spectra of SAMs of **I** and **II** show a common band at 1003 cm^{-1}, with equal areas. All mixed SAMs also show the same common

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(22) We carried out topographical as well as lateral force measurements on all SAMs and mixed SAMs, using the Topometrix Explorer instrument. A domain formation should be visible in lateral force measurements, since friction forces of **I**, **II**, and **III** SAMs are significantly different. We did not observe such domains in scans ranging from 100 × 100 μm down to 0.5 × 0.5 μm.
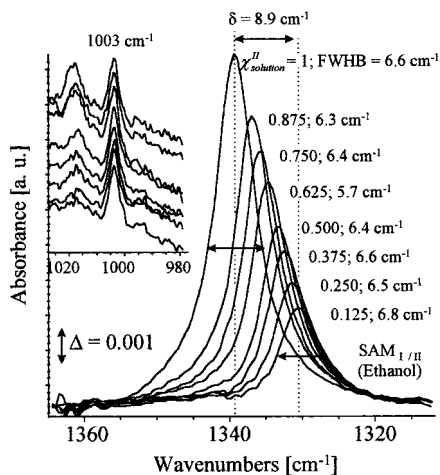
Figure 5. The $\nu_s(CF_3)$ band for **I** and **II** mixed SAMs made in ethanol. The insert shows a common band at 1003 cm^{-1}, with the same integrated area, suggesting that all mixed SAMs have the same coverage.

Figure 6. The $\nu_s(CF_3)$ band for **I** and **II** mixed SAMs made in toluene.

band and the same integral absorption area, suggesting that an identical surface density is formed in all molecular ratios.

Since in the ERFTIR spectra the intensity of the methyl vibration is much smaller than that of the CF_3 group, this vibration cannot be used as a reliable band to extract complementary information on orientation and packing behavior. Notwithstanding, we note that depolarization effects have to be considered,[23] for they not only cause band shifts in mixed SAMs,[13] but may also influence the integral absorption area of bands under investigation. The data presented here, however, is self-consistent when integral band areas are concerned. Furthermore, in a related study, we have investigated mixed SAMs of 4′-methyl-4-mercaptobiphenyl and 4′-hydroxy-4-mercaptobiphenyl on gold.[24] There, we used the trifluoroacetate ester to quantitatively measure surface OH concentration, by ERFTIR spectroscopy and observed a perfect linear relationship between areas under three different CF_3 bands and surface CF_3 concentration ($\chi^{II}_{surface}$.) Therefore, the ERFTIR results provide reliable information on the surface CF_3 concentration. We plan detailed XPS investigations to study the relationship between surface composition obtained from XPS data and from ERFTIR data.

Figure 6 shows that when mixed SAMs of **I** and **II** are prepared from toluene, the integral absorption areas of the $\nu_s(CF_3)$ band level into a plateau as the **II**:**I** concentration ratio in solution increases. This becomes clear in Figure 7, where the integrated absorption [$\nu_s(CF_3)$] as a function of the molar fraction of **II** in solution ($\chi^{II}_{solution}$) is presented for adsorption from ethanol and from toluene. The dashed line represents the case where surface and solution concentrations are equal.

When a mixed SAM of **I** and **II** is prepared in ethanol, with $\chi^{II}_{solution} = 0.12$, the surface CF_3 concentration after 16 h in solution is $\chi^{II}_{surface} = 0.26$. This is unexpected, since **II** is more polar then **I**, and therefore should be more stabilized by a polar solvent. To understand fully the adsorption of mixed SAMs, one should consider three effects: the relative adsorption and desorption kinetics, the polarity of the individual components, and the final electronic structure of the resulting SAM. Quartz crystal microbalance studies have revealed that while **I** adsorbs faster than **II** ($k_a = 36.23 \pm 9.24$ vs 8.69 ± 1.63, in toluene),
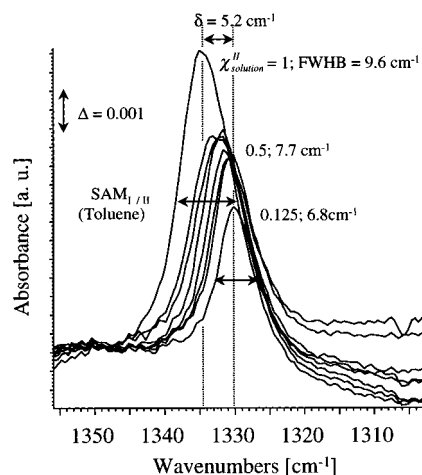
it also desorbs faster [$k_d = 2.14 \pm 1.39) \times 10^{-3}$, vs ($1.09 \pm 0.32) \times 10^{-3}$.[11] This implies that the observed preferential adsorption of **II** may be partly the result of the preferential desorption of **I**. However, another contribution to the observed preferential adsorption of **II** may be the fact that **I** and **II** are both polar, and that their permanent dipole moment are in opposite directions, although that of **I** is smaller. Thus, a mixed SAM of **I** and **II** can be viewed as an assembly of oppositely directed dipoles (Figure 8).

The exchange of **I** for **II** in the SAM has been confirmed by studies of mixed SAMs that were removed from solution after 60 min of adsorption. IR spectroscopy showed $\chi^{II}_{surface} = 0.12$ for the CF_3 group, confirming that the observed $\chi^{II}_{surface} = 0.26$ results from postadsorption equilibrium. Thus, there is a driving force for the formation of mixed SAMs, presumably attributable to the partial cancellation of dipoles by nearest neighbors. This is the third mechanism for the stabilization of SAMs made of polar molecules.

As the concentration of **II** in ethanol increases, its preferential adsorption decreases, and for a molar fraction of **II** above $\chi^{II}_{solution} = 0.5$, **I** shows preferential adsorption (Figure 7). Intuitively, one may suggest the repulsion among polar **II** molecules as the sole mechanism for the observed trend. Hence, as the concentration of **II** in the mixed SAM increases beyond 50%, net intermolecular repulsion balances the adsorption−desorption kinetics effect, and dominates. However, this probably is not the complete explanation, because in mixed SAMs prepared from toluene, a plateau in the surface CF_3 concentration in the region of $\chi^{II}_{surface} = 0.5-0.6$ is noticeable (Figure 7). Therefore, the equilibrium surface composition is obviously affected by the polarity of the solvent.

That the $\chi^{II}_{surface}$ in SAMs made in toluene is initially larger than for SAMs made in ethanol can be justified by the lower stabilization of **II** in the toluene solution, which adds to the driving force to mix the two thiols in their two-dimensional assembly. Similar behavior was observed in the formation of mixed SAMs from OH- and CH_3-terminated alkanethiols.[1,2] In that case, OH-terminated alkanethiols were preferentially adsorbed from nonpolar solvents. However, the significant plateau in Figure 7 suggests that a unique stabilization is achieved by mixing **I** and **II** because of the attractive dipolar interactions (Figure 8). Thus, in a polar solvent (ethanol or acetonitrile), where a polar SAM can be stabilized by solvent interactions (Figure 4), preferential adsorption may dominate, and no, or a very small plateau will be observed. In a nonpolar solvent, on

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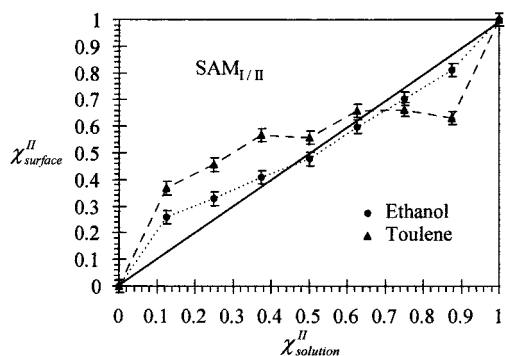(24) Kang, J. F.; Jordan, R.; Ulman, A. *Langmuir* **1998**, *14*, 3983.

Figure 7. Integrated area under the $\nu_s(CF_3)$ band, in mixed SAMs of **I** and **II**, vs the molar fraction of **II** in solution, for adsorption from ethanol and from toluene.
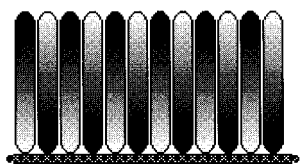

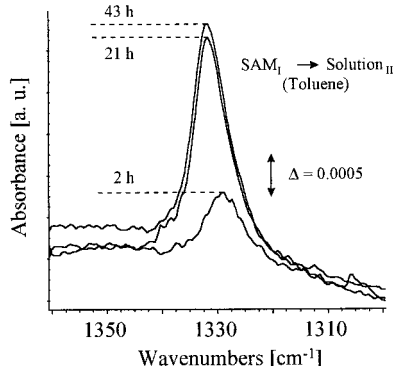**Figure 8.** An idealized picture of a mixed SAM with a 1:1 ratio of oppositely arranged dipoles.

Figure 9. Changes in the $\nu_s(CF_3)$ band when a SAM of **I** is in contact with a 10 μM solution of **II** in toluene.

the other hand, the reduced stability of a polar SAM results in a mixed monolayer with an ∼1:1 ratio of **I** and **II**.

To examine this hypothesis, we carried out experiments where SAMs of **I** were exposed to a solution of **II** and vice versa. Figure 9 presents the result of one such experiment, where SAMs of **I** were exposed to a 10 μM solution of **II** in toluene. Notice that after 2 h there already is significant exchange of **I** by **II**. Also, the position of $\nu_s(CF_3)$ in the final SAM is exactly the same as that for a mixed SAM prepared from a 10 μM solution with $\chi_{solution}^{II} = 0.5$. This implies that these SAMs are probably similar in their degree of randomness and in their structure.

Since we suggested that the small desorption rate constant of **II** is partly responsible for its preferential adsorption, a crucial experiment is to study what happens when SAMs of **II** are exposed to a 10 μM solution of **I** in toluene. Here, the relative significance of preferential adsorption and intermolecular dipolar interaction can be investigated. Figure 10 shows the results of one such experiment. Notice that the expected decrease in the intensity of the $\nu_s(CF_3)$ band is observed, but no band shift occurred. In other words, the position of the $\nu_s(CF_3)$ band is the same in the SAM of **II** and in this mixed SAM. One possible explanation is that molecules of **I** and **II** are phase-separated. However, if this is the case, the domains of **II** must be very small, since wetting hysteresis is not significantly larger
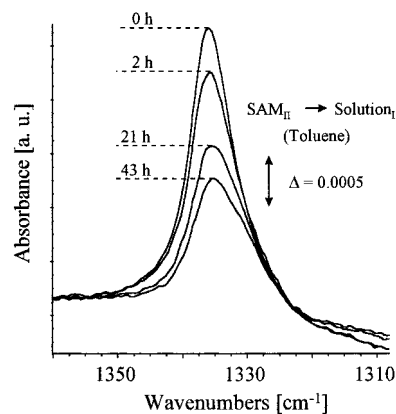

Figure 10. Changes in the $\nu_s(CF_3)$ band when a SAM of **II** is in contact with a 10 μM solution of **I** in toluene.
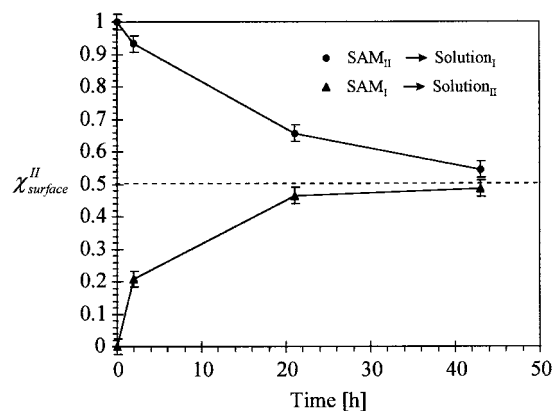

Figure 11. Integrated area under the $\nu_s(CF_3)$ band for the experiments in Figures 7 and 8 as a function of time.

than in regular mixed SAMs, and AFM studies reveal patternless SAM surfaces.[22] Another possible explanation is that the structure of a SAM of **II** is different from that of **I**, and that this structure is retained after exchange, suggesting that the different structures of the two mixed SAMs—obtained from the two exchange experiments—are the source of the observed differences in their ERFTIR spectra. At present, we cannot provide experimental data to support this hypothesis. Although the structure of a SAM of **I** has been studied,[15] no structural information is yet available about the SAM of **II**. Figure 11 summarizes the two exchange experiments. Finally, the question of how much driving force in the mixing of **I** and **II** is provided by entropy increase cannot be addressed without theoretical calculations.

We have shown that the composition of a mixed SAM of **I** and **II** is affected by the dielectric constant of the solution from which they adsorbed. Therefore, to study the solvent effect on the formation of mixed SAMs from thiols **I** and **II**, we have carried out further experiments, using 1,2-dichloroethane and acetonitrile. Figure 12 presents the absorption area under the $\nu_s(CF_3)$ band, in mixed SAMS of **I** and **II**, versus $\chi_{solution}^{II}$, for adsorption from 1,2-dichloroethane and acetonitrile. Notice the absence of a plateau, and the small preferential adsorption of **II** for all values of $\chi_{solution}^{II}$ in acetonitrile. This is in agreement with the high dielectric constant of acetonitrile, which allows the stabilization of a highly polar SAM (Figure 3).

1,2-Dichloroethane has a dielectric constant between that of toluene and ethanol. Figure 12 also shows the absorption area under the $\nu_s(CF_3)$ band versus $\chi_{solution}^{II}$. Two interesting trends are noted. First, there is a plateau in the concentration of **II** in the mixed SAMs, but it is in $\chi_{surface}^{II}$ values that are higher than
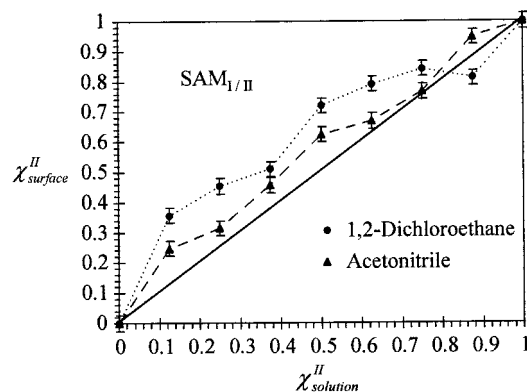
Figure 12. Integrated area under the $\nu_s(CF_3)$ band, in mixed SAMs of **I** and **II** vs the molar fraction of **II** in solution, for adsorption from 1,2-dichloroethane and acetonitrile.

Figure 13. Integrated area under the $\nu_s(CF_3)$ band in mixed SAMs of **II** and **III** vs the molar fraction of **II** in solution, for adsorption from ethanol and toluene.

in the corresponding SAMs adsorbed from toluene, in agreement with the higher dielectric constant of the solvent. Second, the effects that govern the composition of the mixed SAMs are, again, the preferential adsorption of **II** because of its small desorption kinetics constant, its stabilization in solution that is smaller than in acetonitrile or ethanol, and the stabilization of the mixed SAMs owing to partial dipole cancellation.

We have discussed so far mixed SAMs of **I** and **II**, and argued that SAM composition is defined by the balance between the stabilization of **II** in solution, its desorption kinetics constant, and the stabilization of a resulting polar SAM. The thiol **III** is practically a nonpolar molecule, which has an adsorption kinetics constant higher than that of **I** ($k_a = 106.12 \pm 18.43$), with a similar desorption kinetics constant [$(k_d = 2.90 \pm 2.7) \times 10^{-3}$]. Therefore, we expected a significant preferential adsorption of **III** in the preparation of mixed SAMs with **II**. Figure 13 shows the integral absorption of the $\nu_s(CF_3)$ band of mixed SAM of **II** and **III**, versus $\chi_{solution}^{II}$, for adsorption from ethanol and toluene. The fast adsorption of **III** dominates, but its concentration in the mixed SAMs is, again, higher in ethanol then in
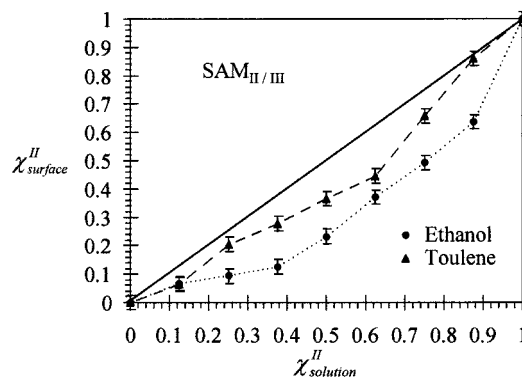
toluene. These results further corroborate the arguments presented in this paper.

Conclusions

The formation of mixed self-assembled monolayers (SAMs) of different 4′-substituted-4-mercaptobiphenyls (e.g., with CH_3, CF_3, and SCH_3) on gold, from different solvents, has been investigated. Monolayer thickness values, estimated by ellipsometry, contact angle measurements, and ERFTIR spectroscopy confirm that >90% of the monolayer is formed after 1 h of adsorption. We found that the dielectric constant of the solvent, the permanent dipole moment of the substituted mercaptobiphenyl, adsorption and desorption kinetics, and intermolecular dipole−dipole interactions in the SAM play a crucial role in the final composition of the mixed SAMs.