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Mixed Self-Assembled Monolayers of Highly Polar Rigid Biphenyl Thiols

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Mixed self-assembled monolayers (SAMs) of 4′-nitro-4-mercaptobiphenyl (**I**) and 4′-(dimethylamino)-4-mercaptobiphenyl (**III**) have been compared with that of 4′-nitro-4-mercaptobiphenyl (**I**) and 4′-methylmercapto-4-mercaptobiphenyl (**II**). The composition of the mixed SAMs was determined by external reflection Fourier transform infrared (ER−FTIR) spectroscopy and showed that both the magnitude and direction of dipole moment determined the final composition of mixed SAMs. In toluene, with a dielectric constant of 2.4, a significant enhancement dipolar interaction is observed. The composition of mixed SAMs of **I** and **II** showed a plateau at 40% surface concentration of **I**. These results can be explained by simple calculation based on the Hammett equation. The experimental results indicate that the equilibrium concentration of the two components in the mixed SAM$_{\mathbf{I/II}}$, in a nonpolar solvent, is driven by the formation of a two-dimensional assembly with zero net dipole moment.

Mixed SAMs[1] are ideal systems for studying the competition of absorption between two different molecules. Recently we have shown that the dipole moment of the adsorbing 4′-substituted-4-mercaptobiphenyl and the solvent polarity control the composition of mixed SAMs in equilibrium.[2] There we used 4′-trifluoromethyl-4-mercaptobiphenyl and 4′-methyl-4-mercaptobiphenyl, both having molecular dipoles that are relatively small. We also presented evidence that these mixed SAMs provide excellent model systems for studies of wetting, because of their long-term stability.[3] The motivation for the present studies is to examine the extent of dipolar interactions on adsorption of mixed SAMs, when the two dipolar molecule have significantly larger dipole moments (Figure 1). We expected that the driving force for forming a one-to-one ratio in the mixed SAMs will be maximized when the two 4′-substituents are nitro (NO_2, **I**), and dimethylamino ($(CH_3)_2N$, **II**), that represent a strong electron attracting, and a strong electron donor group, respectively. As a comparative simple dilution study we examined mixed SAMs of **I** and **III**, where the latter can be assumed to have a zero dipole moment due to the two mercapto-groups at the 4- and 4′-positions.

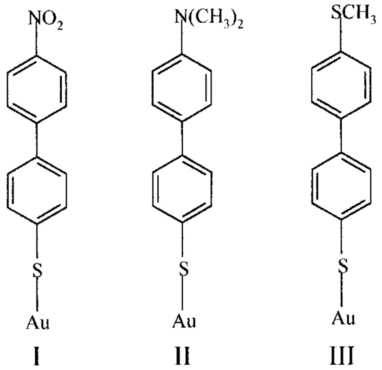

Figure 1. 4′-Substituted-4-mercaptobiphenyls.

Freshly cleaned gold substrates[4] were immersed into the toluene (HPLC grade) solution ($c_{\text{thiol}} = 10\ \mu$M) and kept there under nitrogen overnight. The substrates were removed from solution, rinsed with toluene, and blown dry by a jet of nitrogen. Mixed SAMs were prepared the same way, with a total thiol concentration of 10 μM. Monolayers were stored in toluene of HPLC grade for later studies. The thickness of all SAMs and mixed SAMs, established by ellipsometry[5] was 14 ± 1 Å.

Figure 2 shows transmission IR spectra of **I** in KBr, and external reflection Fourier transform infrared (ER−FTIR) of SAMs on gold made for acetonitrile, ethanol and toluene solutions.[6] In SAMs prepared from acetonitrile and ethanol solutions, the symmetric NO_2 vibration (ν_s(NO_2)) appears at 1348−1349 cm^{-1}, which is similar to the position of this band in the solid. The asymmetric NO_2 vibration (ν_{as}(NO_2)) is clearly observed, suggesting that

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[1] For a review on SAMs of thiols on gold see: (a) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir−Blodgett to Self-Assembly*, Academic Press: Boston, MA, 1991. (b) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.

[2] Kang, Jung F.; Ulman, Abraham; Liao, Sheng; Jordan, Rainer *J. Am. Chem. Soc.* **1998**, *120*, 9662.

[3] Kang, Jung F.; Jordan, Rainer; Ulman, Abraham *Langmuir* **1998**, *14*, 3983.

[4] Glass slides were baked overnight in a vacuum (10B7 Torr) at 300 °C. Gold (99.99%) evaporation was carried out at the same temperature, using a constant deposition rate of 3 Å/s, followed by annealing for 18 h. X-ray studies show that these gold substrates have (111) surfaces. Reproducible ellipsometric constants for gold substrates prepared according to this procedure are NS = 0.186 ± 0.01, and KS = 3.400 ± 0.05. Using these gold substrates, SAMs of biphenyl thiols show contact angle hysteresis of ~5°. In comparison, the same SAMs on gold substrates prepared at room temperature without annealing show a contact angle hysteresis of ~20°.

[5] 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.

[6] 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). 2500 scans were collected for each spectrum, with resolution of 1 cm^{-1}. The deviation of band position in consecutive experiments of the same sample was ~0.3 cm^{-1}. The spectra of bulk samples were collected over 200 scans.

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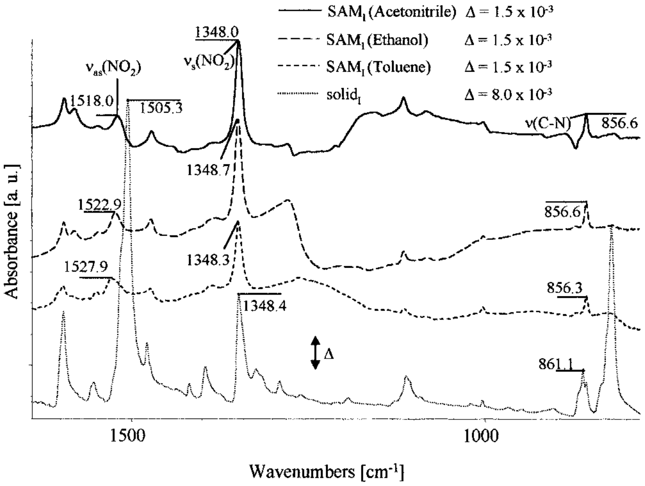

Figure 2. IR spectra of 4′-nitro-4-mercaptobiphenyl, in KBr, and in SAMs on gold adsorbed from acetonitrile, ethanol, and toluene solutions.

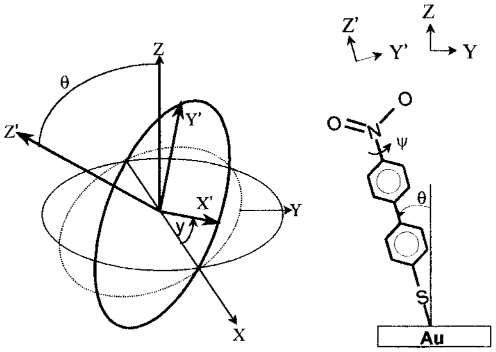

Figure 3. A tilted 4′-nitro-4-mercaptobiphenyl molecule in its SAM on gold. θ is the tilt angle and ψ is the angle of rotation about the molecular axis. Also presented are Euler's Angles.

the biphenyl moieties are tilted with respect to the surface normal. Thus, even in ethanol and acetonitrile, polar solvents with dielectric constants of 25.3 and 36.6, respectively,[7] the interaction of solvent molecules with the SAM is not sufficient to stabilize a two-dimensional assembly of such strong molecular dipole, and the molecules tilt to decrease the net dipole of the monolayer.[2] Interestingly, the position of the ($\nu_{as}(NO_2)$ band is solvent dependent, shifting from 1527.9 cm^{-1} in toluene to 1518.0 cm^{-1} in acetonitrile. This suggests that solvent polarity affects the intermolecular interactions of surface NO$_2$ groups.

Figure 3 presents a tilted 4′-nitro-4-mercaptobiphenyl molecule in its SAM on gold with the definitions of the tilt angle (θ) and the angle of rotation about the molecular axis (ψ). Also presented are Euler's angles.[8] X' is the aromatic C–H wagging axis, Y' is the $\nu_{as}(NO_2)$ axis, and Z' is the 1,4-axis, which is also the $\nu_s(NO_2)$ axis. The tilt and rotation angles are defined as

$$\frac{A_{x'}}{A_{y'}} = \tan^2 \psi, \quad \frac{A_{x'}}{A_{z'}} = \sin^2 \psi \tan^2 \theta, \quad \frac{A_{y'}}{A_{z'}} = \cos^2 \psi \tan^2 \theta$$

where the reduced absorbance A_i is defined as $A_i = A_{i,\mathrm{RA-FTIR}}/A_{i,\mathrm{transmission}}$. Thus, $A_{x'}$, $A_{y'}$, and $A_{z'}$ are directly attained from the ratios of the absorbance of the band in the RA–FTIR spectrum to that in transmission IR spectrums. Table 1 presents the calculated tilt and rotation angles for SAMs on **I** adsorbed from toluene, ethanol and acetonitrile. Notice that while the tilt angles are practically the same, within experimental error, the rotation angles differ significantly in polar and nonpolar solvents. That the tilt angles are similar is because the large molecular dipole moment is the dominating factor in defining molecular tilt, and solvent polarity has insignificant effect on the molecular tilt angle. If we assume that the nitro group is coplanar with the biphenyl system, molecular tilt does not produce attractive NO$_2$···NO$_2$ surface interactions, since the tilt is defined in the molecular plane. However, after rotation, attractive NO$_2$···NO$_2$ surface interactions can be established. That rotation brings nitro groups from neighboring molecules to interaction distance is especially important in nonpolar solvents, where solvent interactions cannot stabilize surface dipoles. This is why the angle of rotation is 46° for SAMs assembled from toluene but only 30° for SAMs assembled from acetonitrile and ethanol (Table 1).

Table 1. Tilt Angle (θ) and Rotation Angle (ψ) in Different Adsorption Solvents

	ethanol	toluene	acetonitrile
ψ (deg)	30	46	31
θ (deg)	14	17	14

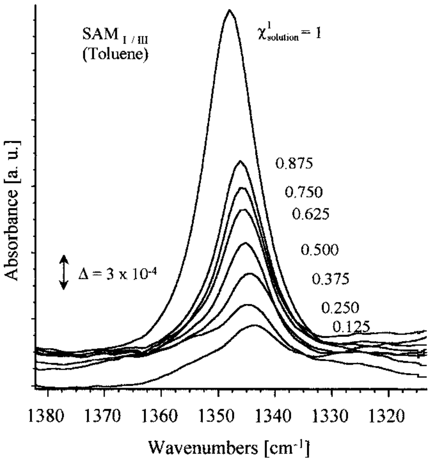

Figure 4. $\nu_s(NO_2)$ band at ~1349 cm^{-1} for mixed SAMs$_{I/III}$ made in toluene.

Figure 4 shows ER–FTIR spectra of **I/III** mixed SAMs, while Figures 5 and 6 present different regions in the spectra of **I/II** mixed SAMs. The 1348 cm^{-1} band is associated with NO$_2$ symmetric stretching ($\nu_s(NO_2)$). This strong band is useful for a quantitatively composition analysis of the mixed SAMs. The average absorbance integrals of the $\nu_s(NO_2)$ band for the two mixed SAMs ($\chi^I_{surface}$) are plotted in Figure 7 as a function of the molar fraction of **I** in solution. Notice, that for SAM$_{I/III}$, neglecting $\chi^I_{solution} = 0$ and $\chi^I_{solution} = 1$, there is a linear relationship between the surface and solution composition of **I**, where the deviation from theoretical composition increases with the increasing $\chi^I_{solution}$. Thus, at $\chi^I_{solution} = 0.9$, the surface concentration of nitro groups is only ~50%. This is a manifestation of the fact that toluene cannot stabilize a two-dimensional assembly of strong dipoles, and hence the driving force for dilution is significant. Another factor that affects $\chi^I_{surface}$ is the relative adsorption and desorption rates of the two components. Quartz crystal microbalance (QCM) studies reveal that the rate of adsorption is the fastest for nonpolar 4-mercaptobiphenyl derivatives. This explains the preferential adsorption of **III**, but cannot

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(7) *Handbook of Chemistry and Physics*; 75th ed.; Lide, D. R., Ed.; CRC Press: Boca Roton, FL, 1985.

(8) March, J. *Advanced Organic Chemistry*, 3rd edl; Mcgraw-Hill: New York, 1985, p 244.

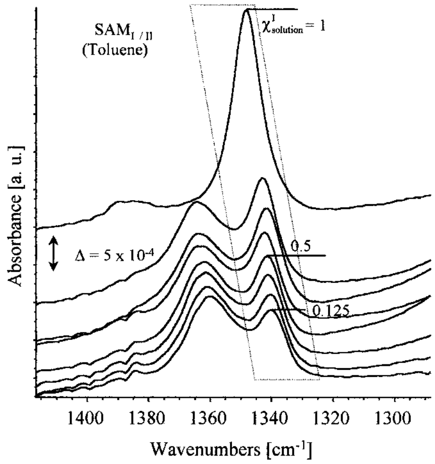

Figure 5. $\nu_s(NO_2)$ band at ~1349 cm^{-1}, and the ν(C−N) band at ~1362 cm^{-1} for mixed SAMs$_{I/II}$ made in toluene.

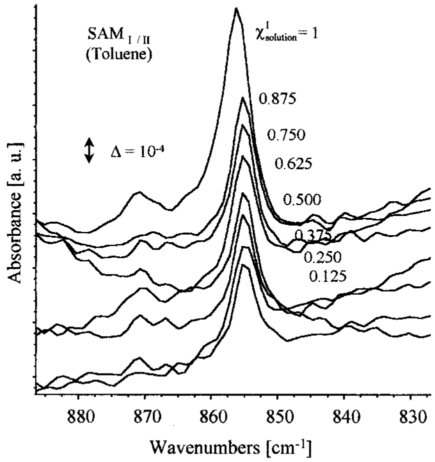

Figure 6. ν(C−N) band at ~856 cm^{-1} for different solution concentrations of **I**, for mixed SAMs$_{I/II}$ prepared in toluene.

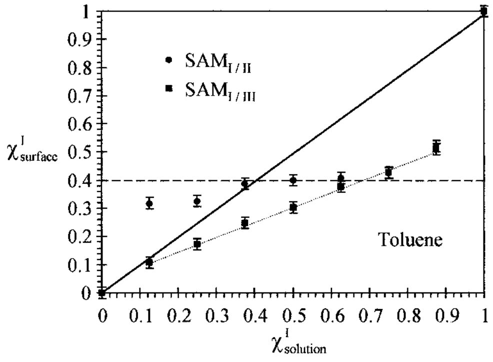

Figure 7. Integrated area under the $\nu_s(NO_2)$ band, for mixed SAMs$_{I/II}$ and SAMs$_{I/III}$ vs the molar fraction of **I** in solution, for adsorption from toluene.

explain the linear relationship. We have observed before the preferential adsorption of **III**, but never this kind of a linear behavior.[2]

For SAM$_{I/II}$, the $\nu_s(NO_2)$ band for **I**, which overlaps with neighboring aryl C−N stretching band for **II** (Figure 5) as well as the ν(C−N) band are effective for quantitative composition analysis. This requires a deconvolution procedure so that the two bands can be used for a direct analysis. In examining Figure 7 one observed the preferential adsorption of **I** is when $\chi^{I}_{solution} < 0.4$, and that between $\chi^{I}_{solution} = 0.1$ and $\chi^{I}_{solution} = 0.7$ the surface concentration of NO_2 groups is for $\chi^{I}_{surface} = 0.3-0.4$. The latter phenomenon is due to the stabilization of the mixed SAM by the attraction of opposite dipoles.

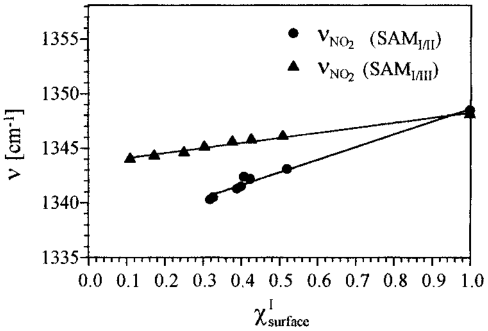

Figure 8. Frequency shifts of the $\nu_s(NO_2)$ band for mixed SAMs$_{I/II}$ and SAMs$_{I/III}$, vs the integrated area under the $\nu_s(NO_2)$ band.

The Hammett equation[9] for compounds with two groups X and X′ para-substituted on one ring has been applied to the quantitative treatments of the effect of substitutes on dipole moment determined by the electronic state of SAMs molecules.[10] The values of σ_p for $-NO_2$ are 0.778[11] and 0.81,[7] for $-N(CH_3)_2$, the numbers in the literature are −0.83[8] and −0.63.[7] To calculate the theoretical surface composition of **I** in the mixed SAMs, we assume that the total dipole moment of the mixture should be zero. If we use the $\sigma_p = 0$ for the thiolate-gold, the equation is

$$(1 - X)(\sigma_p(\mathbf{I})) + X(\sigma_p(\mathbf{II})) = 0 \qquad (1)$$

where X is the surface concentration of **I**. Using this equation and the two sets of values mentioned above for **I** and **II**, eq 1 gives $X = 0.45-0.5$, clearly higher than the plateau in Figure 7. This suggests that the thiolate contribution must be taken into account, and hence $\Delta\sigma$ has to be used, replacing eq 1 with

$$(1 - X)(\Delta\sigma(\mathbf{I})) + X(\Delta\sigma(\mathbf{II})) = 0 \qquad (2)$$

where $\Delta\sigma = \sigma_p(NO_2 \text{ or } N(CH_3)_2) - \sigma_p(S{-}Au)$. To account for the contribution of the S−Au to the dipole moment we have selected the $\sigma_p{}^{+}$ value for SCH_3, −0.164.[8] Since the thiolate is a π-donor, its contribution increases the molecular dipole in **I**, and decreases it in **II**. If the effect of electronic state on dipole moment of the para-substituted compound is considered to be simply additive,[12] $\Delta\sigma(\mathbf{I}) = 0.942$, $\Delta\sigma(\mathbf{II}) = -0.666$, and eq 2 gives $X = 0.4$, well within the experimental result. Thus, the experimental results indicate, that the equilibrium concentration of the two components in the mixed SAM, in a nonpolar solvent, is driven by the formation of a two-dimensional assembly with zero net dipole moment.

The frequency shifts of the $\nu_s(NO_2)$ band with respect to surface composition of **I** in mixed SAM$_{I/II}$ and SAM$_{I/III}$ are plotted in Figure 8. The slope of concentration-dependent shifts for $\nu_s(NO_2)$ band is larger for the mixed SAM$_{I/II}$, in agreement with the effective dipolar interaction of the two components, compared with the simple dilution effect in SAM$_{I/III}$.

In conclusion, we have prepared SAMs of 4′-nitro-4-mercaptobiphenyl (**I**) and 4′-(dimethylamino)-4-mercap-

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[9] Ulman A. *J. Phys. Chem.* **1988**, *92*, 2385.

[10] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972; p 146.

[11] Debye, P. *The Dipole Moment and Chemical Structure*; Blackie & Son Limited: London and Glasgow, 1931.

[12] Debe, M. K. *Appl. Surf. Sci.* **1982**, *14*, 1.

tobiphenyl (**III**) and compared their properties to those of mixed SAMs of 4′-nitro-4-mercaptobiphenyl (**I**) and 4′-methylmercapto-4-mercaptobiphenyl (**II**). The composition of the mixed SAMs was determined by external reflection ER−FTIR spectroscopy. The experimental results suggest, that both the magnitude and direction of dipole moment determined the final composition of mixed SAMs. In toluene, with a dielectric constant of 2.4, a significant enhancement of intermolecular dipolar interaction is observed. The composition of a mixed SAM of **I** and **II** showed a plateau at 40% surface concentration of **I**, which is in agreement with a simple calculation based on the Hammett equation. The equilibrium concentration of the two components in the mixed SAM$_{\mathbf{I/II}}$ is driven by the formation of a two-dimensional assembly with zero net dipole moment.

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