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Dye adsorption on self-assembled silane monolayers: optical absorption and modeling

Shilpa R. Tawde,[a] D. Mukesh,[b] J. V. Yakhmi*[a] and C. Manohar[a]

[a]*Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India. E-mail: yakhmi@magnum.barc.ernet.in*
[b]*ICI India Research and Technology Centre, Thane Belapur Road, Thane, India*

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A comparative study has been carried out on the adsorption of the Rhodamine 6G dye on glass slides covered with self assembled monolayers of phenyltrichlorosilane and uncoated plain glass. Optical absorption measurements indicate enhancement of the amount of dye adsorbed on silane coated glass as compared to uncoated glass, possibly due to the interaction of the phenyl group in the silane molecule with the dye. Experiments also indicate the formation of dimers of Rhodamine 6G and that the coverage of the dye on the silane modified surface is preferentially as monomers when compared to uncoated glass. Molecular modeling studies on this system support these results.

Introduction

The technique of depositing mono- and multi-layers on surfaces through self assembly techniques has gained importance recently in view of the ease with which these coatings can be deposited on a variety of surfaces of complex shapes and also because of the potential they hold for depositing these coatings on a large scale.[1] Alkylsilane monolayers are used for a wide variety of applications such as adhesion promoters,[2] surface modifiers,[3] antiglare photoresist coating,[4] non-linear optical devices,[5] *etc.* Phenylsilane modified silica is used for separation of CO_2 from flue gases to control air pollution.[6] A major hurdle in the development and use of self assembled monolayers (SAMs) is the lack of reproducibility during deposition.[7] Nevertheless, reliable self-assembled multilayer thin films of porphyrins have been synthesized on a quartz surface modified with alkyltrichlorosilanes,[8] and conducting polymers have been deposited on hydroxy-terminated surfaces with printed monolayers of alkylsiloxanes as templates.[9] An alternate way of depositing films is by the Langmuir–Blodgett technique. This technique has the advantage that the films can be deposited on plane surfaces as multilayers of predetermined thickness in a controlled way.[10] One of the important applications of thin films is in the area of electroluminescent display devices[11] which consist of thin films of organic dyes deposited in between two glass plates coated with transparent conducting tin oxide films. In comparison to inorganic semiconductor films the organic dyes have a higher quantum yield and should be able to give sufficient brightness even as monolayers with the proper choice of dye.

Here, we report the results of our attempts to develop the process of depositing monolayers of silanes on glass surfaces reproducibly using the self assembly technique. After depositing the film we attempted to adsorb Rhodamine 6G dye on to these surfaces which were investigated by optical absorption spectroscopy. A method of analyzing the spectra was developed to measure the fraction of the dye adsorbed as monomers or dimers. Molecular modeling studies were carried out to determine the minimum energy conformation and orientation of the dye on the silane surface. Molecular modeling of the surface silane layer on silica[12] and on glass fiber reinforced composites[13] has been reported in the literature for appropriate coupling agents with high adhesive strength.[14]

Experimental

Phenyltrichlorosilane ($PhSiCl_3$) was obtained from Fluka (>98%) and Rhodamine 6G was obtained from Merck, Darmstadt (Germany) and were used without further purification. Benzene and tetrachloromethane were obtained from SDS Fine Chemicals, India.

Preparation of solid substrate

The microscope glass slides used in this work were cleaned by dipping them chromic acid for two days. The slides were then rinsed with distilled water followed by sonication for 15 min in distilled water. Each slide was washed once again in a jet of distilled water and finally dried by blowing a stream of hot air on it. The cleaned slides showed hydrophilic behavior as seen from the uniform wetting of the glass surface by water. The slides were used within one day after cleaning. The cleaning of glass slides in this manner was found to be crucial to obtain reproducible results.

Coating method

A set of ten cleaned glass slides mounted on a slide holder was dipped in a solution containing 2 mM phenyltrichlorosilane in benzene–tetrachloromethane (7 : 3, v/v), sonicated for 10 min and allowed to stand for 45 min. The slides were removed from solution, dried by blowing with hot air and cured at 50 °C for 15 min in an oven. The coated slides now showed hydrophobic behavior as shown by contact angle measurements.

Adsorption of Rhodamine 6G

The slides mounted on a slide holder were dipped in aqueous 0.01–1.00 mM Rhodamine 6G solution. For steady state experiments, the slides were left in the solution for 24 h, while for the kinetics study the slides were removed at various time intervals. The excess dye solution on the slides was washed away with a jet of distilled water. All the experiments were repeated three times and an average of the values obtained is reported.

Characterization

The optical absorption measurements were performed on a Hitachi 330 spectrophotometer. The slides were coated with the silane on both sides so that the measured spectra represent the effect due to two independent layers. Contact angle measurements were carried out by magnifying 20 × the image of a water droplet (1 μL volume) placed on the surface.

Analysis of data

Solution spectra. In an aqueous solution Rhodamine 6G exists as aggregates, mostly as dimers.[15] The dissociation equilibrium of the dimer is given by $\mathrm{D}\xrightleftharpoons{K}2\,\mathrm{M}$ where D denotes the dimer and M the monomer and the equilibrium constant K is given by

$$K=\frac{2x^2c}{(1-x)} \tag{1}$$

where x is the mol fraction of monomer.

The observed absorption coefficient, $a(\lambda,c)$ has contributions from both the monomer and dimer:

$$a(\lambda,c)=A_{\mathrm{obs}}/cl=a_{\mathrm{m}}(\lambda)x+a_{\mathrm{d}}(\lambda)[(1-x)/2] \tag{2}$$

where A_{obs} is the measured absorbance, $a_{\mathrm{m}}(\lambda)$ and $a_{\mathrm{d}}(\lambda)$ are the absorption coefficients of pure monomer and dimer, respectively, at wavelength λ, c is the total concentration and l is the path length. Eqn. (2) assumes that each component of the solution separately obeys Beer's law. The procedure for analysis of data is the same as that adopted by Selwyn and Steinfeld.[15] The solution spectra were recorded for five different dye concentrations (c). Assuming a given value of K, five values of x were calculated using eqn. (1) for five c values [absorbance $A_{\mathrm{obs}}(\lambda,c)$ for these concentrations are known]. Eqn. (2) can be rearranged as

$$a(\lambda,c)=\{a_{\mathrm{m}}(\lambda)-[a_{\mathrm{d}}(\lambda)/2]\}x+[a_{\mathrm{d}}(\lambda)/2]=Px+Q \tag{2a}$$

where $P=\{a_{\mathrm{m}}(\lambda)-[a_{\mathrm{d}}(\lambda)/2]\}$ and $Q=a_{\mathrm{d}}(\lambda)/2$.

In eqn. (2a), for five calculated values of x, the corresponding five $a(\lambda,c)$ values are known (from recorded spectra). Hence P, Q and the correlation coefficient were calculated by a least squares fitting method.

The best value of K for each wavelength was selected based on the goodness of fit as measured by the correlation coefficient. From the corresponding P and Q values, $a_{\mathrm{m}}(\lambda)$ and $a_{\mathrm{d}}(\lambda)$ were calculated and this procedure was repeated for a variety of wavelengths.

Glass slide spectra. For Rhodamine 6G adsorbed on phenylsilane coated glass, the bulk concentration terms in eqn. (1) are replaced by surface concentration terms. Hence eqn. (1) and (2) are modified as

$$K_{\mathrm{a}}=\frac{2x^2c_{\mathrm{a}}}{(1-x)} \tag{3}$$

$$\text{and } a(\lambda,c_{\mathrm{a}})=\frac{A_{\mathrm{obs}}}{c_{\mathrm{a}}l}=a_{\mathrm{m}}(\lambda)x+a_{\mathrm{d}}(\lambda)[(1-x)/2] \tag{4}$$

It is assumed that the molar absorption coefficient measured in solution is not significantly changed upon adsorption onto the slide. Since the concentration of the dye on the surface (c_{a}) is not known, the corresponding absorption coefficient $a(\lambda,c_{\mathrm{a}})$ value required in eqn. (4) cannot be directly calculated from the absorbance. Hence eqn. (4) was modified by substituting the value of the concentration from eqn. (3) to obtain

$$\frac{2x^2\,A_{\mathrm{obs}}}{K_{\mathrm{a}}(1-x)}=a_{\mathrm{m}}(\lambda)x+a_{\mathrm{d}}(\lambda)\ (1-x)/2 \tag{5}$$

Solving for x we obtain,

$$x=\frac{(a_{\mathrm{m}}-a_{\mathrm{d}})+[(a_{\mathrm{m}}-a_{\mathrm{d}})^2+2a_{\mathrm{d}}\alpha]^{1/2}}{2\alpha} \tag{6}$$

$$\text{where } \alpha=\frac{2A_{\mathrm{obs}}}{K_{\mathrm{a}}}+a_{\mathrm{m}}-\frac{a_{\mathrm{d}}}{2}$$

For a particular K_{a} value, the value of x was estimated using eqn. (6) for five different bulk concentrations at a particular wavelength, λ_1. The corresponding five 'c_{a}' values for the concentration of adsorbed dye were estimated from eqn. (3). Surface concentration, c_{a}, and x values do not change with wavelength. Therefore the above values of x and c_{a} were substituted in eqn. (5) at a different wavelength, λ_2, to obtain the corresponding calculated absorbance $A_{\mathrm{calc}}(\lambda_2)$. The value of $A_{\mathrm{calc}}(\lambda_2)$ has to be same as the observed absorbance $A_{\mathrm{obs}}(\lambda_2)$. The above procedure was repeated by varying K values until the best value was obtained where the difference between $A_{\mathrm{calc}}(\lambda_2)$ and $A_{\mathrm{obs}}(\lambda_2)$ was minimal.

Molecular modeling methodology

Molecular modeling studies were carried out using HYPERCHEM software (Hypercube Inc., Gainesville, FL, USA) run on a Pentium computer. The methodology adopted for calculating the conformational energy of the molecules was similar to the molecular force field technique developed by Levitt.[16] The total energy is the sum of individual energies pertaining to bond stretching, angle bending, dihedral, van der Waals, out-of-plane bending and electrostatic attraction. These energy terms are estimated from analytical expressions. The molecular force field algorithm, MM+, which is suitable for organic molecules (and is considered superior to MM2) was used for energy calculations. The goal was to find a set of coordinates such that the potential energy of the molecules was minimized. Energy minimization is carried out in HYPERCHEM using the steepest descent and conjugate gradient algorithms. In our study, molecular mechanics (MM) calculations were performed for the following cases: (i) a single molecule of Rhodamine 6G (monomer); (ii) two molecules of Rhodamine 6G (dimer); (iii) a plain glass surface with a linear strand containing five silicon atoms connected through oxygen bridges and with twelve OH groups;[17,18] (iv) the same glass surface with the three OH groups replaced by phenyl groups (*i.e.* a silane coated surface); (v) monomer–plain glass system; (vi) monomer and silane coated glass surface; (vii) dimer–plain glass system; and (viii) dimer–silane coated glass system.

MM energy minimization was performed on the two molecules that were optimized separately. The system was also optimized by altering the relative initial distance and orientation of one molecule with respect to the other in order to be sure of obtaining the global minimum energy of the combined system. The energy values estimated are *in vacuo*.

Results and discussion

Optical studies

The silane treated slides showed higher contact angles (100 ± 1°) compared to plain glass (38 ± 2°) for drops of water having identical volume (1 μL). This shows that a silane coating makes the surface hydrophobic. We obtain an equilibrium constant of 3.4×10^{-4} mol dm^{-3} for the dissociation of dimers of Rhodamine 6G in aqueous solution based on the method described above, which matches reasonably well with the literature values of 5.9×10^{-4} mol dm^{-3}[15] and 4×10^{-4} mol dm^{-3}.[19] Fig. 1 shows the effect of bulk concentration on the mole fraction of monomer as estimated by the above method. As expected, the mole fraction of the monomer decreased (from 0.938 to 0.699) when the bulk concentration

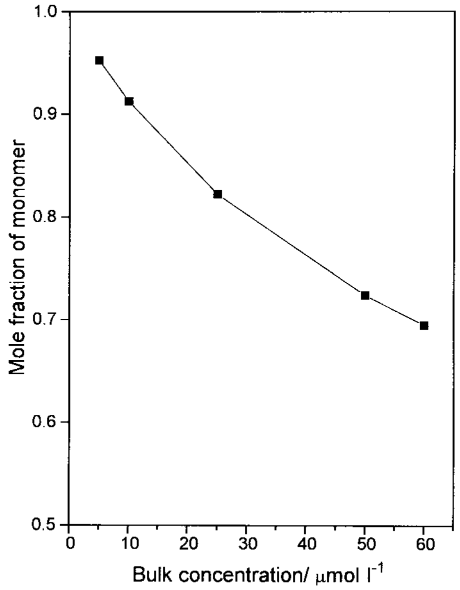

Fig. 1 Variation of mole fraction of monomer in an aqueous solution of Rhodamine 6G with bulk concentration.

was increased from 5 to 60 μM, indicating formation of dimers and an increase in their proportion with increasing concentration.

Fig. 2 shows the effect of bulk concentration on calculated surface concentration of the dye for both silane coated and uncoated glass slides. As expected, the surface concentration increases with increasing bulk concentration in this range. For variation of bulk concentration of the dye in the range 0.01–1.00 mM, the adsorbed dye concentration on the silane coated surface varies in the range $(1.2–1.6)\times 10^{-10}$ mol cm^{-2}. The cross-sectional area of a molecule of the dye as obtained from modeling studies was found to be 90.9 Å^2 (10.1 Å × 9 Å) in good agreement with values reported in the literature.[20] Using this data, the surface concentration for a closely packed monolayer of the dye was calculated to be 1.82×10^{-10} mol cm^{-2}. Hence, our results [$(1.2–1.6)\times 10^{-10}$ mol cm^{-2})] indicate that the dye is adsorbed as a monolayer with 66–88% coverage. On uncoated glass the surface concentration lies in the range $(0.56–0.76)\times 10^{-10}$ mol cm^{-2} for the same bulk concentrations. The increase by 2.5 to 3 times in the amount of dye adsorbed on silane coated relative to uncoated glass points to the important role played by the interaction of the phenyl group in the silane molecule with Rhodamine 6G. This is explained in more detail later in the discussion of the molecular modeling results. The value of the equilibrium constant, *K*, for dissociation of the dimer on silane coated slides is three times larger than that on the uncoated glass slides, implying that a higher proportion of monomer is present in the former case. This, at first sight, is surprising in view of the higher concentration of dye on the coated surface, but molecular modeling studies provide the rationale for this.

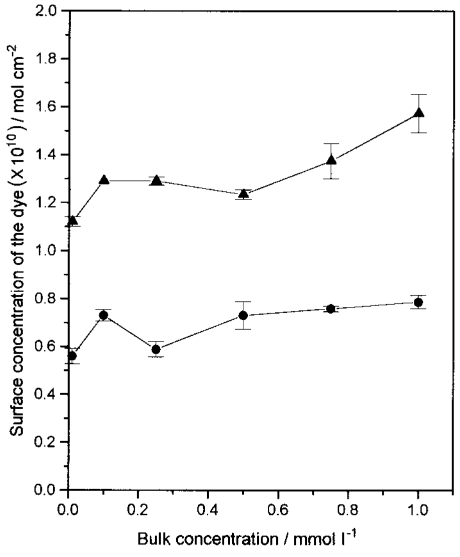

Fig. 2 Effect of bulk concentration of the dye on calculated surface concentration for silane coated glass (▲) and uncoated glass (●).

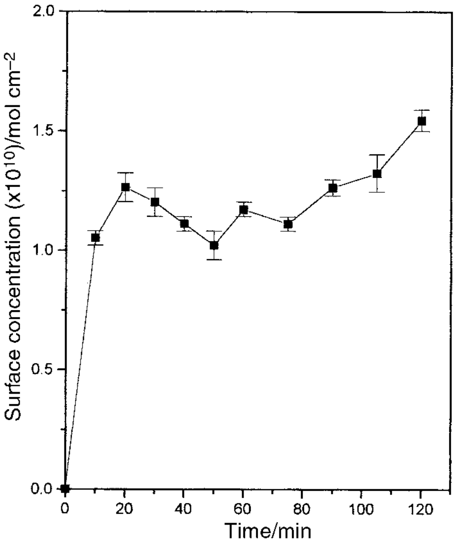

Fig. 3 Kinetics of adsorption of Rhodamine 6G on silane coated glass (bulk concentration = 1 mM).

Time dependent experiments were carried out for a bulk concentration of dye of 1 mM. Fig. 3 shows the changes in surface concentration of the dye on silane coated glass as a function of time (as estimated by the method described above) at a wavelength of 530 nm. Although there is an overall increase in the surface concentration of the dye with time, small fluctuations are observed. The fluctuations at each individual adsorption time (*i.e.* the random error) seem to be much smaller than the fluctuations around the common mean of all the points. This could arise from differences in orientation of the physisorbed dye molecules owing to the dynamic nature of adsorption. Similar fluctuations have been reported in the literature for adsorption of mixed monolayers of substituted cyanine dyes and arachidic acid on plain glass surfaces.[21]

Results of molecular modeling

The structure of the monomer of Rhodamine 6G obtained by MM optimization was found to be similar to that reported by Ilich *et al.*[22] based on NMR and modeling studies in aqueous solution. Table 1 gives the energy values obtained from mode-

Table 1 Molecular mechanics energies of the monomer and dimer of Rhodamine 6G on silane coated and uncoated glass

	MM energy/ kcal mol^{-1}	Reduction in combined energy/kcal mol^{-1}
Monomer	51.1	—
Dimer	68.6	33.6
Glass	6.0	—
Silane + Glass	−5.7	—
Monomer + Glass	48.8	8.3
Dimer + Glass	62.5	12.1
Monomer + Silane + Glass	23.9	21.5
Dimer + Silane + Glass	48.4	14.5

ling studies. The values in the second column are estimated by subtracting the combined energy from the sum of energies of the individual components, *e.g.* reduction in the energy of the dimer relative to the monomer is estimated as $(2 \times 51.1) - 68.6 = 33.6$ kcal mol^{-1} indicating that the formation of dimers is thermodynamically favored.

Interactions of the dye with silane coated and plain glass were studied. Plain glass was simulated/represented based on the silica structure reported[17] where the average distance between the silicon atoms in silica is *ca.* 3.6 Å and there is no order between these atoms at distances above 10 Å. The silica tetrahedra are attached at corners with a distribution of intertetrahedral angles in the range 130–180° with random twisting of adjacent tetrahedra.[18] A linear strand containing five SiO_4^- tetrahedra was thus selected to simulate the glass surface.

Phenylsilane coated glass was simulated by modifying the same glass structure. In the mechanism of formation of an alkyltrichlorosilane SAM,[7] all three chloro groups are hydrolyzed to –OH and bind to the glass substrate. Thus the base of the silane tetrahedron rests on the glass surface leaving the fourth group, *i.e.* the phenyl group, pointing outwards. As a consequence, all the phenyl groups point outwards from the surface and are arranged parallel to each other *via* π–π interactions. Hence, the –OH groups on glass were replaced by phenyl groups to represent the silane coated surface.

Interactions between the monomer/dimer and plain or silane coated glass leads to a decrease in combined energy, indicating that these interactions are also thermodynamically favored. Fig. 4 and 5 show the minimum energy conformation for the interaction of a monomer and dimer, respectively, on a silane coated surface. It can be seen that for the monomer–phenylsilane system, the xanthene ring of Rhodamine 6G orients itself in between two phenyl groups with its two nitrogen atoms pointing downwards. In the case of the dimer, while the xanthene ring of one of the dye molecules interacts with the phenyl groups of the silane, the other is perpendicular to this plane, showing a strong interaction with the former through the nitrogen atoms. Hence the dimer orients itself on the surface with the nitrogen atoms pointing upwards. Fig. 6 and 7 show the minimum energy conformation of the monomer and dimer, respectively, on plain glass. For plain glass, since there is no hindrance due to phenyl groups, the dye molecule orients itself with its nitrogen atoms pointing downwards. The decrease in the MM energy of the dimer–plain glass system (12.1 kcal mol^{-1}) is more than that for the monomer–plain glass system (8.3 kcal mol^{-1}), whereas, a reverse trend is seen for the silane coated glass system, *i.e.* the decrease in MM energy of the monomer–silane-glass system (21.5 kcal mol^{-1}) is more than that of the decrease in MM energy of the dimer–silane-glass system (14.5 kcal mol^{-1}). This suggests that Rhodamine 6G is adsorbed more favorably as the monomer than as the dimer on silane coated glass while the dimer is adsorbed more favorably than the monomer on plain glass. This conclusion is in line with our experimental observations.

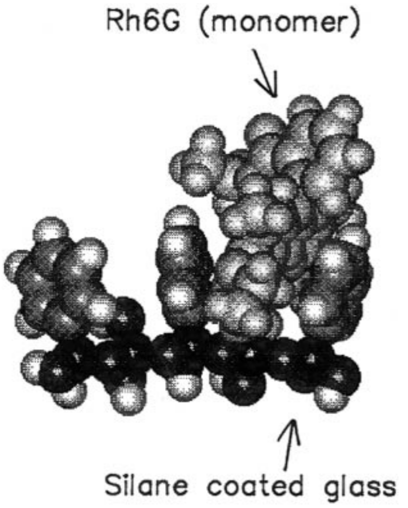

Fig. 4 Minimum energy conformation of Rhodamine 6G monomer on silane coated glass (represented by a linear strand of five silicon atoms each surrounded by oxygen atoms in a tetrahedral geometry. Phenyl groups are attached to the silicon atoms).

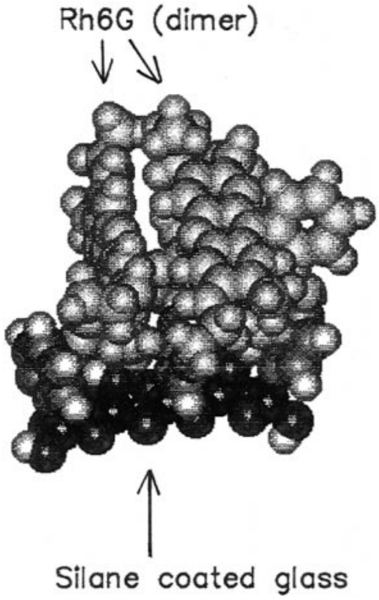

Fig. 5 Minimum energy conformation of Rhodamine 6G dimer on silane coated glass (represented by a linear strand of five silicon atoms each surrounded by three oxygen atoms in a tetrahedral geometry. Phenyl groups are attached to the silicon atoms).

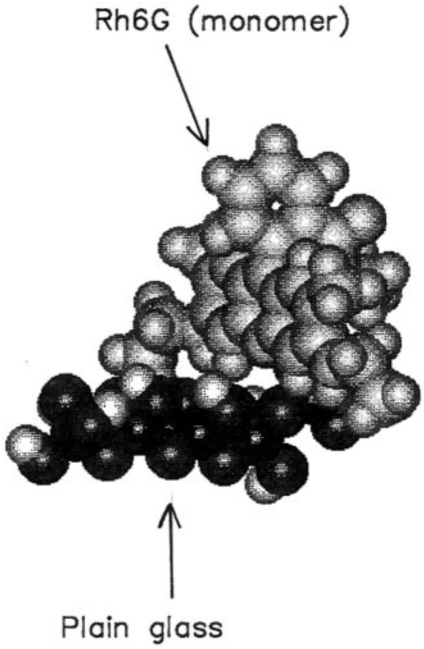

Fig. 6 Minimum energy conformation of Rhodamine 6G monomer on plain glass (represented by a linear strand of five silicon atoms each surrounded by four oxygen atoms in a tetrahedral geometry).

Conclusions

We have developed a method of depositing SAMs using silane coupling agents and adsorbing Rhodamine 6G dye on these

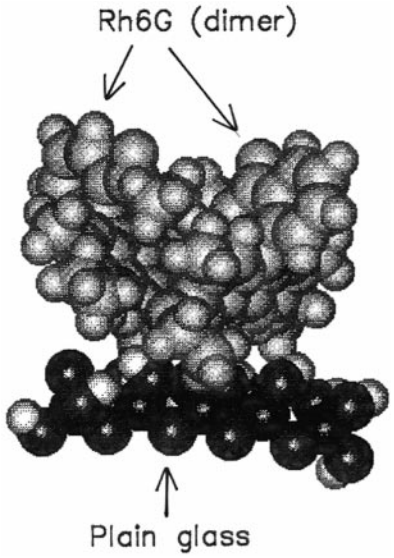

Fig. 7 Minimum energy conformation of Rhodamine 6G dimer on plain glass (represented by a linear strand of five silicon atoms each surrounded by four oxygen atoms in a tetrahedral geometry).

layers. The films deposited have been investigated by optical absorption spectroscopy and a method for analyzing the spectra has been developed which estimates the monomer and dimer fractions, surface concentrations and equilibrium constant for dimer dissociation. It is shown that the equilibrium constant for the monomer and dimer equilibrium is modified for the silane coated surface favoring the existence of the monomer. Using molecular modeling methods a rationale has been put forward for the deposition of Rhodamine 6G preferentially as the monomer on silane coated glass. It is proposed that the orientation of the dye molecules in the monolayers is responsible for this. Using the molecular dimensions of the dye molecule obtained from molecular modeling it was shown that the dye is adsorbed as a monolayer on a silane coated surface.

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