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Evolution of Orientation in the Growth of Azo Dye Zirconium Phosphate−Phosphonate Multilayers

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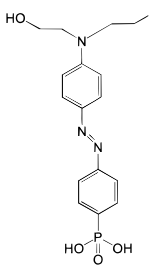
We report here the first observation of a change in the orientation of a chromophore with number of layers deposited using zirconium phosphate−phosphonate interlayer chemistry.

The potential of organic thin films for use in nonlinear and electrooptical applications has resulted in extensive research efforts directed toward improved design and understanding of these thin films.[1−8] Most applications require that the films be organized on some length scale.[9,10] Since molecular orientation plays a key role in many of the interesting properties of organic thin films, the term "organized" often refers to some degree of uniformity in molecular orientation. Organic chromophores incorporated into zirconium phosphate−phosphonate ($Zr-PO_x$) interlayers are excellent examples of mixed inorganic/organic molecular systems that exhibit interesting optical and electrical properties. Mallouk and co-workers first demonstrated multilayer formation of organic thin films based on self-assembly of $Zr-PO_x$ interlayers.[1,2] Katz et al. utilized $Zr-PO_x$ interlayers to assemble a multilayered structure of a polar azo dye (**I**) that exhibited second-order nonlinear optical properties.[3] Since then several molecular systems based on $Zr-PO_x$ chemistry have been developed and characterized.[4−8]



I

Second harmonic generation (SHG) studies of $Zr-PO_x$ interlayers with **I** indicate some degree of polar order that does not change as more layers are deposited.[3] However, the same film does not exhibit linear dichroism.[4] In addition, X-ray diffraction studies indicate the absence of a well-structured surface.[4] Ellipsometry studies of the interlayer system for **I** on silicon indicate that each layer deposited is approximately 16 Å thick, which is 4 Å thinner than calculated based on typical bond lengths.[3] The difference in layer thickness was attributed to nonideal packing and an average molecular tilt angle (with respect to surface normal) of ~35°. Some of these inconsistencies in observed characteristics may be due to the fact that Zr^{4+} is only loosely bound to the surface; as determined by X-ray photoelectron spectroscopic studies, rinsing may lead to removal of Zr^{4+} from the surface.[4] "Self-healing", or the filling in of lost Zr^{4+} sites during subsequent exposure to layer formation solutions, was postulated by Putvinski et al.[5]

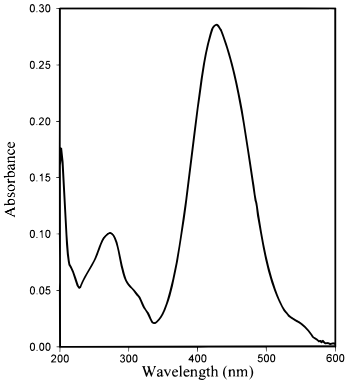


Figure 1. Absorbance spectrum of 4-{4-[*N*,*N*-bis(2-hydroxyethyl)amino]-phenylazo}benzylphosphonic acid in methanol.

In this study, angle-resolved photoacoustic spectroscopy (ARPAS) was used to probe the orientation of **I** in $Zr-PO_x$ interlayers as a function of number of layers. ARPAS relies on the acoustic signal generated when excited state molecules decay nonradiatively. By varying the incident angle of plane polarized light from a pulsed laser source with respect to the surface upon which molecules have been deposited, it is possible to extract the mean tilt angle of the molecule with respect to the lab *z*-axis, or surface normal. For example, for molecules uniaxially aligned along the surface normal, and a transition dipole aligned along the molecular long axis, the absorbance should increase as the electric field vector is rotated from parallel to perpendicular to the surface. Conversely, a transition dipole aligned perpendicular to the molecular long axis in the example just given would exhibit a decreasing signal. The advantages of ARPAS include the nearly universal applicability of absorbance with sensitivity comparable to fluorescence. Complete descriptions of the experimental apparatus, data collection, and fitting procedure were published previously.[11]

Figure 1 shows both the chemical structure and the absorbance spectrum for **I**, the azo dye used in this study.[12] On the basis of semiempirical calculations (ZNDO/S and Pariser−Parr−Pople), as well as previous assignments,[13,14] the transition centered at 270 nm is most likely an $^1A \rightarrow {}^1H^+$ (Platt notation) and polarized orthogonal to the molecular long axis. However, an alternative assignment, in which the transition dipole moment is directed at 45° with respect to the molecular long axis, has also been suggested.[13,14] The low energy side of the transition centered near 410 nm has been assigned to $^1A \rightarrow {}^1B$, which is polarized along the long axis of the molecule.[13,14] Complementary information could be obtained if both the long and short axis transitions were

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[12] The azo dye, 4-{4-[*N*,*N*-bis(2-hydroxyethyl)amino]phenylazo}-benzylphosphonic acid, was synthesized from 4-aminophenylphosphonic acid (H. Katz) and *N*-phenyldiethanolamine (Aldrich) with a published procedure.[3] The molecular weight with fast atom bombardment and a glycerin/HCl matrix gave a molecular ion (M) of 365 *m/e*, and M + 1 of 366 *m/e*. ^1H NMR analysis of the product, using *p*-dioxane as an external reference and D_2O as the solvent, yielded a multiplet at δ 3.7 (4Hs), a doublet at δ 6.9 (2Hs), and a multiplet at δ 7.6 (6Hs), in agreement with previously published results.

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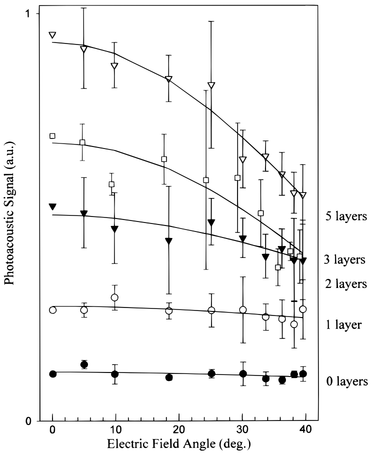

Figure 2. Normalized photoacoustic signal for representative data as a function of electric field angle (defined with respect to surface normal) of the excitation beam. The data points are an average of three measurements at each point and error bars are ±1 s. The solid lines are nonlinear regressions to eq 8 of ref 11. Although no significant photodegradation was observed for this system, the order in which data points were acquired as a function of angle was varied to avoid systematic error.

probed.[10] Due to source wavelength limitations, this study utilizes only 266 nm excitation.[15] However, future studies are planned which will include both transitions.

Mono- and multilayer structures of **I** were deposited on quartz by following a published procedure.[3,16] Five separate studies were conducted over a time period of several weeks (i.e., five separate quartz substrates were used to form multilayer films). For each multilayer study, the UV−vis absorbance spectrum of the surface was taken after each exposure to the layer formation solutions.[17] Absorbance for both 406 and 266 nm was found to be linear with the number of dye layers deposited; as an example, for one particular multilayer system the slopes of linear regressions to absorbance versus number of layers were 0.004(±0.0003), $R = 0.99$, and 0.004(±0.0002), $R = 0.99$, respectively. For this particular film the maximum absorbance of the film (6 layers) was 0.02, thus the film was not optically thick. Molecular orientation and packing density can both influence the extinction of relative transitions in the molecule; thus, the absorbance as a function of wavelength when the surface is probed with unpolarized light does not provide quantitative information. However, the fact that the relative absorbance at 266 and 406 nm is significantly different than it is for an isotropic solution (Figure 1) does provide qualitative evidence for molecular orientation within the film. The photoacoustic amplitude as a function of layer number exhibited a slight degree of curvature and appeared to approach an asymptote above 6 layers. The amplitude was measured with plane polarized light at normal incidence. In this configuration, measurement of the photoacoustic amplitude is sensitive to molecular orientation and would not be expected to be linear if orientation changes as a function of layer number.

Figure 2 shows the trend in photoacoustic amplitude as a function of both electric field angle (with respect to surface normal) and number of layers. An isotropic sample should exhibit a flat response and yield a mean tilt angle of 54.7°, the magic angle (with respect to surface normal). Such was the case for the blank quartz, as shown in Figure 2. Note that the curvature in the angular response increased as layers were added to the surface, indicating a change in molecular orientation as a function of coverage. While this experimentally observed trend is independent of the transition moment assignment, quantitative evaluation of molecular orientation angles requires use of the transition moment vector. Assuming that the transition excited at 266 nm is orthogonal to the molecular long axis (which is the most likely orientation[13,14]), regressions of the raw data from five separate experiments to eq 8 in ref 11 yield the following average transition moment tilt angles for 1−6 layers: 58° ± 4°, 66° ± 2°, 71° ± 7°, 66° ± 6°, 76° ± 6°, and 75° ± 5°. The trend indicates that as the layer formation procedure is repeated, the dye molecules tilt, on average, more toward surface normal with the respective molecular tilt angles being 32°, 24°, 19°, 24°, 14°, and 15°, for 1−6 layers. The possibility that the transition moment probed at 266 nm is directed at 45° with respect to the molecular long axis was rejected since the calculated (from fit) expectation values for the higher coverages yielded nonphysical tilt angles.[18] Several control studies were conducted to rule out contributions from physisorbed dye.

The observed trend is best explained by a combination of layer formation and "self-healing". There is extensive experimental evidence that the chemistry used in this study results in multilayer formation.[3−6] However, it is unlikely that multilayer formation alone enhances the degree of orientation for the dye molecule, since no change in orientation was observed upon "end-capping" the terminal dye layer with a Zr−PO$_x$ interlayer. Thus, it seems likely that a change in tilt angle toward the surface normal with subsequent layers is due to improved packing within the layers. In this study, the exposure times to the interlayer formation solutions (POCl$_3$ followed by ZrOCl$_2$) were relatively short (∼5−10 min) in comparison to other procedures.[7] It is postulated that incomplete interlayers are formed during each exposure and that subsequent exposures result in improved coverage for the bottom layer as well as formation of an incomplete upper layer.[5]

The observation in this study of a change in molecular orientation as a function of "layer number" is contradictory to previous studies.[3,6−8] For example, Katz et al. found no change in polar order, using SHG, as a function of increasing layer number.[3] Using FTIR, Corn and co-workers found no change in the conformational band intensities or widths of an alkyl functional group as a function of additional layers.[8] While differences in solution chemistry and (or) substrate, such as a lack of amino terminated primer at the surface, may account for the observed differences in orientation, it is noteworthy that SHG and FTIR do not necessarily provide a direct measurement of molecular orientation. Furthermore, unpolarized UV−vis absorbance cannot differentiate between layer formation and improved packing within layers, since molecules are added to the surface in both cases. As pointed out in ref 7, ellipsometry also provides insufficient information when the measured thickness is less than expected, since the technique cannot distinguish between an average thickness and a combination of high and low thickness domains. Clearly, further studies are necessary to develop a complete picture of multilayer film growth.

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[15] The fourth harmonic of a Q-switched Spectra Physics Nd:YAG (GCR-11) laser was used for excitation. Film extinction at 355 nm (the third harmonic of the laser) was too small at low coverages for orientation measurements.

[16] The aminopropyltrimethoxysilane primer was omitted from the procedure for quartz substrates based on a discussion with H. Katz. The quartz substrates were cleaned and "primed" by a ∼5 min immersion in piranha followed by a thorough rinse in doubly distilled water.

[17] UV−vis absorbance spectra were acquired on an HP 8452a diode array spectrometer. The light source is unpolarized.

[18] Assuming all rotation angles about the molecular z-axis are equally probable (reasonable considering the general vertical orientation, with respect to the surface of this particular molecular system), then $\langle cos^2\ \theta_f\rangle = {}^1/_2[1 - \langle cos^2\ \theta_z\rangle]$ for a transition moment angle of 90° with respect to the molecular long axis; where θ_f is the angle between the transition moment and the surface normal and θ_z is the angle between the molecular long axis and the surface normal. For a transition moment angle of 45° with respect to the molecular long axis $\langle cos^2\ \theta_f\rangle = {}^1/_4[1 + \langle cos^2\ \theta_z\rangle]$. Thus, the values for θ_f, calculated using a delta function distribution, must be between 45° and 90° if the transition moment angle is orthogonal to the molecular long axis and between 45 ° and 60° if the transition moment angle is at 45° with respect to the molecular long axis. The data for 5 layers (Figure 2) yield a θ_f value of ∼90°.