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LETTERS

The Structure of a Tetraazapentacene Molecular Monolayer

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Langmuir molecular monolayers of a unique tetraazapentacene zwitterionic amphiphile were found to form stripe-like domains that responded strongly to an applied magnetic field. These stripe domains were transferred as Langmuir–Blodgett (LB) films to glass substrates, where they were structurally characterized using five complementary imaging techniques, including scanning second-harmonic generation (SHG) microscopy and capacitance force microscopy. The molecular orientations of adjacent single striped domains of a tetraazapentacene monolayer were determined by SHG polarization measurements. Those structures were shown to be consistent across the various imaging techniques.

Molecular monolayer films are utilized in a host of passive and active scientific and technological applications, such as monolayer surfactants,¹ liquid crystal films,² and chemically tailored surfaces designed for (bio)chemical recognition³ and selection.⁴ The chemical nature of molecular monolayers ranges from that of model amphiphiles, such as eicosanoic acid, to molecular monolayers designed with complex structure and function, such as chip-based genomic sequences, biosensors, or molecular electronics components. As the complexity of the molecular film increases, characterization of that film becomes an increasingly difficult challenge. Measurements of single parameters, such as the angle of the molecular tilt axis, the surface wetting contact angle, etc., are just single pieces of a much larger puzzle. As a result, a number of techniques, including various forms of scanning probe microscopy (SPM),⁵ fluorescence microscopy,⁶ and Brewster angle microscopy (BAM),⁷ have been developed for molecular film characterization.

In this paper, we report on the characterization of unique, striped domains that were observed in monolayers of a tetraazapentacene amphiphile (Figure 1). This molecule, which exhibits high-temperature liquid-crystalline phases, is also an acid—base indicator and can exist in either a zwitterionic or a protonated form, where each form is characterized by a colorimetric signature. The tetraazapentacene amphiphile was designed to exhibit "flathead amphiphilic" properties (in contrast to traditional amphiphiles, such as phosphatidyl choline). In previous work,⁸ we showed that the tetraazapentacenes prefer the zwitterionic, rather than a diradical, singlet ground state. High-level calculations revealed that the calculated dipole moment of the tetraazapentacene molecule is 9.1 D.

When this molecule was spread onto a basic subphase of a Langmuir trough, the tetraazapentacene zwitterion (TAZ) spontaneously forms domains that, when viewed using Brewster angle microscopy (BAM), appear as alternating striped features (labeled dark and bright stripes) and exhibit a refractive index contrast with each other and with the surrounding film. These stripes, which are a minority component of an otherwise featureless monolayer, also exhibited a strong translational response to a static magnetic field.⁹ We successfully transferred these domains as Langmuir–Blodgett (LB) films to an ap-

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Figure 1. The amphiphilic tetraazapentacene zwitterion (TAZ) used in this study. The area of the TAZ molecule, as defined by the X-ray of the crystal structure, excepting the long alkyl chain, is shown in the dotted line. The molecular x and z axes are indicated on the scale bars.

propriately prepared glass substrate. For this transfer, BAM was employed as the common characterization tool for both the Langmuir monolayer and the LB films. We then interrogated the striped domains of the LB film using the following imaging techniques: scanning second-harmonic generation (SHG) imaging with full polarization control, scanning two-photon fluorescence (2PF) images (cocollected with the SHG images), and cocollected topographic and capacitance force scanning probe microscopy (SPM) analysis imaging. The frequency dependence of the 2PF images indicated the presence of the zwitterionic form of the tetraazapentacene. SHG microscopy was the principal structural technique used here, and analysis of polarization-dependent SHG images led to an elucidation of the two principal molecular polarizability axes with respect to the laboratory coordinates. This fitted structure generated certain predictions as to the relative structure and orientation of the bright and dark stripes. Those predictions were shown to be consistent with results from the SPM images, which reveal both a topographic contrast and a dipole at the interface between the bright and dark stripes.

The scanning SHG microscope utilized here has been previously described,¹⁰ but the particular application described here is new for this apparatus and constitutes the principle experimental component of this paper. SHG is highly interface selective¹¹⁻¹³ and is based on the coherent mixing of optical wave vectors with the hyperpolarizability tensors of the interfacial material. Certain structural parameters, such as molecular orientation and tilt angle, can be directly measured, and applications of SHG microscopy toward the determination of molecular orientation at surfaces are well established.¹⁴ Such measurements have traditionally probed areas that are large compared to the size of molecular domains and have represented an average over many domains. The application of SHG microscopy toward the structural investigation of molecular films was suggested by Boyd et al.¹⁵ Since that time, SHG microscopy has been applied to single-crystal surfaces, magnetic surface domains, biological interfaces, molecular film structure, and quantum dot monolayers, as discussed in a review by Simpson.¹⁶ In particular, molecular film structure has been qualitatively studied by SHG microscopy in the far field¹⁷⁻²¹ and near field.²²⁻²⁴ Various experimental configurations for SHG microscopy in the far field have been explored by Florscheimer,^{14,21} who has applied that technique to quantitatively determine the molecular orientation in single domains of the model amphiphile 2-docosylamino-5-nitropyridine.

The SHG signal is proportional to the square of nonlinear susceptibility (χ) of a molecular film at an interface. In turn, χ is a linear combination of the molecular hyperpolarizability (β) parameters. If the β tensor components are known, then SHG measurements can yield structural parameters of a molecular monolayer. In considering the SHG signal from a molecular monolayer, there are 18 independent β components,²⁵ and a determination of all 18 components represents a formidable

challenge. Model molecules, characterized by only one or two dominant β components or by a narrow distribution of tilt angles (θ), have been the focus of most investigations. For such systems, the average value of the tilt axis, θ , may be extracted from SHG measurements.^{26–28}

An SHG-based determination of the absolute 3-D molecular orientation requires that the molecule itself must have more than two dominant β components or multiaxial β components and that the resolution of SHG microscope must be able to resolve single molecular domains. Wudl et al.⁸ reported the absorption and fluorescence spectra for a similar tetraazapentacene in which the long alkyl chains in Figure 1 were replaced by phenyl groups. Sharp absorption features, observed around 420 and 750 nm, were tentatively assigned as $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively. Thus, this molecule should have multiple transition dipole directions and, correspondingly, multiple dominant β components. In our experimental setup, the illumination area of the nonlinear optical microscope allows us to readily resolve, at stepped input and output polarizations, the SHG response from single domains, so that a complete data set could be recorded for each domain. An alternative approach would be to rotate the actual sample itself at a few fixed input and output polarization values.²⁹ We employ the first approach because it avoids the problem of keeping a single domain under the illumination while the sample is rotated.

Experimental Details

Tetraazaacene Zwitterion Synthesis. The tetraazapentacene zwitterion (TAZ) was prepared according to Scheme 1. The product was obtained as a solid that is deep green in solution. Protonation with dilute acid produces a blue solution fluorescing to red. The material can be purified by "recrystallization" (reprecipitation) from chloroform solution with ethanol.

SCHEME 1



Langmuir monolayers of TAZ were prepared using a commercial NIMA 622 LB trough. The recrystallized TAZ molecules were dissolved in fresh (nonacidic) CH₃Cl and spread onto an aqueous pH 10 subphase (25 mM Na₂CO₃ and 25 mM NaHCO₃ in 18.2-M Ω H₂O, temperature controlled at 20 °C). The film was equilibrated on the water surface for approximately 30 min, and then the film was compressed at a rate of 2 cm²/ min. The film was transferred as an LB monolayer to a cleaned glass substrate at a surface pressure of 35 mN/m. Prior to deposition, the glass substrates were cleaned using piranha solution (5:1 concentrated H₂SO₄/30% H₂O₂), followed by an



Figure 2. Schematic diagram of the scanning nonlinear optical microscope utilized in this study. Figure abbreviations are as follows: $\lambda/2$ = half-waveplate, P = polarizer, LPF = long-wave pass filter, L = lens, DM = dichroic mirror, and F = filter.

exhaustive rinse in 18.2-M Ω H₂O. In acidic solution, TAZ may be protonated to either the mono- or biprotonated form, a change that is accompanied by a change in solution color.⁸ The TAZ was stored in CHCl₃ solution under Ar to prevent the CHCl₃ from degrading. The pH 10 subphase was utilized to suppress protonation of the TAZ during the film preparation process. The TAZ Langmuir monolayers and LB films (on glass) were interrogated by BAM. Regions containing striped domains were identified and orientation markers were inked onto the substrates.

The transferred sample on the glass substrate was investigated by our custom-built scanning nonlinear optical microscope, which has been greatly modified from its previous version¹⁰ (Figure 2). Briefly, a broad band Tsunami femtosecond laser system (Spectra Physics) was used as a illumination source with excitation coverage from 720 to 980 nm. The laser beam passes through a $\lambda/2$ plate and a polarizer and then is focused onto the sample at a 45° angle to a spot size of about 1.5 μ m diameter using aspheric molded gel lenses (Thorlab 350170, f = 6.16mm, 0.30 NA). A long pass filter was placed just before the input lens to block any SHG or fluorescence signals generated in the light passage. The reflected light was collimated by a second lens. Then, the fundamental laser beam was removed with short pass filters, and the SHG signal was separated from the two-photon fluorescence (2PF) signal with a dichroic mirror. Additional band-pass filters were installed in front of each detector to ensure that only the signals in the desired spectral regions were recorded. The average incident laser power (normally 1 MW/cm²) was controlled by a series of neutral density filters, and the direction of input polarization was varied by rotating the $\lambda/2$ plate. Sheet polarizers could also be added in front of the detectors to select the polarization of the output signals. The sample was mounted through a holder onto a pair of Burleigh inchworm piezoelectric stages, scanning in X and Y directions, and both the SHG and 2PF signals were recorded using photomultiplier tubes. The laser was chopped, so the preamplifiers of the photomultipliers were fed into digital lockin amplifiers.

Results and Discussion

Langmuir Isotherms and BAM Measurements. Langmuir isotherms were measured for TAZ monolayers, and the structure of the monolayer was monitored in situ by BAM. The surface pressure (π) began to increase around 105 Å²/molecule, and the monolayer collapsed near 47 Å²/molecule ($\pi = 50$ mN/m). For $\pi > 5$ mN/m, striped features with widths ranging from 10 to 200 μ m appeared in the BAM images. These stripes exhibited sharp (bright/dark) polarization-dependent contrast between adjacent stripes (Figure 3) that were retained in the (transferred) LB films. The contrast change between adjacent stripes was typically observed by changing the polarization of the reflected



Figure 3. Brewster angle micrograph of a TAZ Langmuir monolayer at a surface pressure (π) = 15 mN/m. The input polarization of the light is set at 0.75°, while output polarizations are set at (a) 34.3° and (b) 3.8°. The scale of image is 480 × 360 μ m. Nearly identical images were obtained from transferred LB monolayers on glass substrates.

light by $20^{\circ}-40^{\circ}$. Our BAM probes an area that is small compared with the size of the monolayer, so we do not know the coverage of the stripes. However, above a threshold pressure value, there was no clear correlation between the width and density of the stripes and the surface pressure. In general, the stripes were not uniformly distributed and were a minority component of about 5-15% of the entire monolayer. It was difficult to judge the length of the stripes, but for the ones that we could measure, the length typically exceeded 1 mm.

The LB films, transferred near 52 Å²/molecule, yielded identical polarization contrast behavior when probed by BAM. Qualitatively similar sharp contrast changes were observed in BAM images of a monolayer of 1-monopalmitoyl-*rac*-glycerol (MPG) by Knobler et al.³⁰ Those LB monolayers exhibited "star-shaped" domains, which were subdivided into seven wedge-shaped segments. Each edge showed different intensity in BAM, and the contrast between segments depended on the output polarization. An analysis of such domains demonstrated that molecules within each segment have the same tilt azimuth, which points outward in the direction parallel to the segment bisector. By analogy, we conclude that the stripe-shaped features are single TAZ molecular domains.

Magnetic Field Effects on the Langmuir Monolayer. The TAZ molecule has a permanent dipole along the *z*-axis, and a monolayer of these molecules does move across the water subphase. A moving dipole under the influence of a magnetic field can feel the following force:³¹

$$\mathbf{F} = \mathbf{v} \times [\nabla \times (\mathbf{B} \times \mathbf{d})] \tag{1}$$

where **v**, **B**, and **d** are the velocity of the dipole, the magnetic field, and the dipole moment. To explore the magnetic effect on TAZ monolayer, a neodynimium-iron-boron magnet was mounted on a translation stage and lowered to within a millimeter or so of the monolayer surface. The Wilhelmy balance was removed from the trough for these measurements. The BAM microscope was utilized to monitor the effect of the magnetic field on the monolayer film, although that microscope did not have video-capture capabilities. Movies of the response of these stripes to the magnetic field were therefore monitored by recording the cathode ray tube (CRT) screen output of the BAM using a video recorder. Those movies are available on the web as supplemental information to this paper.⁹ The BAM images revealed that the striped structures moved more than 10 times faster (240–380 μ m/sec) with the magnet in place than without the magnet $(10-20 \,\mu\text{m/sec})$. The drift of the stripes also changed direction from motion parallel to the moving direction of the barrier without the magnet to a more randomized drift with the magnet. These fast movements lasted for more than 5 min after placing the magnet above the surface, indicating that this effect is mainly due to the static magnetic field. A



Figure 4. Second-harmonic generation (SHG) (a) and two-photon fluorescence (2PF) images (b) collected at 800 nm excitation. SHG images are scaled as follows: (i) p-in-p-out (\times 1.8), (ii) s-in-p-out (\times 1.0), (iii) s-in-s-out (\times 1.7), and (iv) p-in-s-out (\times 2.5). 2PF images are taken at (i) p-in-u(unpolarization)-out, (ii) s-in-u-out, (iii) s-in-u-out, (iii) s-in-u-out.

quantitative physical picture of this magnetic effect has not been established. However, to our best knowledge, this observation of a magnetic influence on a molecular monolayer is without precedent, although eq 1 does provide a physical basis for this observation.

Nonlinear Optical Imaging. The absorption spectrum of the TAZ in ethanol solution exhibits features around 290, 420, and 750 nm.8 The 750-nm feature has a negative solvatochroism, shifting to 790 nm in toluene solution. Absorption spectroscopy on spin-cast thin films of TAZ indicated that there was appreciable absorption strength in the solid material at wavelengths longer than 800 nm. Therefore, we chose 800 and 860 nm as illumination wavelengths. Both wavelengths are onresonance at 2ω , but 860 nm is, at most, only weakly resonant at ω , while 800 nm is more strongly resonant. Dispersed fluorescence measurements from TAZ in CH₂Cl₂, excited at 446 nm, provided a guide for choosing an appropriate filter set for 2PF imaging. The protonated form of TAZ yields a strong fluorescence feature near 750 nm, while the dominant fluorescence feature from the zwitterionic form is centered near 550 nm. Thus, we collected the 2PF image using filters to select wavelengths between 450 and 650 nm.

The 2PF and SHG images, collected at various polarization combinations and at $\omega = 800$ nm, are presented in Figure 4. In our experiment, p-polarization is in the *X*-*Z* plane, while s-polarization is parallel to the *Y*-axis. For the SHG images, the signal level varied dramatically for different polarization conditions, so some of the SHG data are scaled for clarity of presentation.

The 2PF image reveals a stripe feature that is approximately five times more intense than the flat background. The relative intensity of the stripe can be attributed either to the direction of the two-photon transition dipole moment or to a concentration gradient of TAZ molecules. Topographic SPM analysis of these domains revealed a height variation across a dark/bright stripe boundary of only about 8 Å, which can explain a change in molecular orientation but not a concentration gradient. This orientation change was confirmed by SPM operating in surface potential (SP) mode, which revealed an electric field (presumably arising from a change in dipole orientations) at the bright/ dark stripe boundaries. The same stripe appears in the SHG image, although other stripes appear in what are the background regions of the 2PF image. All SHG features exhibited a strong polarization-dependent intensity.

The SHG signal depends on molecular hyperpolarizability β . In our experimental condition, there are two excited states, which locate 750 and 420 nm above the ground state and are

close to the fundamental and second harmonic frequencies. The expression for resonant β has been described by Corn²⁶ and Simpson.¹⁶ Using the formalism by Simpson and two excited states, we simplified resonant β as follows:

$$\begin{split} \beta_{ijk} &\propto \sum_{n=1,2} \left\{ \frac{\delta_{n0}^{i} m_{n0}^{j} m_{n0}^{k}}{\omega_{n0}^{2} - (\omega + i\Gamma_{n0})^{2}} + \\ & \frac{m_{n0}^{i} (\delta_{n0}^{j} m_{n0}^{k} + m_{n0}^{j} \delta_{n0}^{k}) (\omega_{n0}^{2} + 2\omega^{2})}{[\omega_{n0}^{2} - (2\omega + i\Gamma_{n0})^{2}] [\omega_{n0}^{2} - (\omega + i\Gamma_{n0})^{2}]} \right\} + \\ & \left\{ \frac{m_{12}^{i} (m_{20}^{j} m_{10}^{k} + m_{10}^{j} m_{20}^{k}) [\omega_{10} \omega_{20} - \omega^{2} + \Gamma_{10} \Gamma_{20} - i\omega(\Gamma_{10} + \Gamma_{20})]}{[\omega_{10}^{2} - (\omega + i\Gamma_{10})^{2}] [\omega_{20}^{2} - (2\omega + i\Gamma_{20})^{2}]} + \\ \frac{m_{20}^{i} (m_{10}^{j} m_{12}^{k} + m_{12}^{j} m_{10}^{k}) [\omega_{10} \omega_{20} + 2\omega^{2} - \Gamma_{10} \Gamma_{20} + i\omega(2\Gamma_{10} + \Gamma_{20})]}{[\omega_{10}^{2} - (\omega + i\Gamma_{10})^{2}] [\omega_{20}^{2} - (2\omega + i\Gamma_{20})^{2}]} + \\ \frac{m_{10}^{i} (m_{20}^{j} m_{12}^{k} + m_{12}^{j} m_{20}^{k}) [\omega_{10} \omega_{20} + 2\omega^{2} - \Gamma_{10} \Gamma_{20} + i\omega(\Gamma_{10} + 2\Gamma_{20})]}{[\omega_{20}^{2} - (\omega + i\Gamma_{20})^{2}] [\omega_{10}^{2} - (2\omega + i\Gamma_{10})^{2}]} \right\}$$

In eq 2, subscripts 0, 1, and 2 correspond to the ground and the first and second excited states. ω_{n0} and Γ_{n0} are the energy and the lifetime broadening term for the electronic transition between excited (*n*) and ground (0) states. δ_{nm}^i and m_{nn}^i are the difference in the permanent dipole moment and the transition dipole moment between the electronic state *n* and *n'* along the molecular axis *i*, respectively.

At 800 nm, both the fundamental and SHG frequencies are resonant with absorption bands of the TAZ. The 2PF process involves coherent two-photon absorption and incoherent onephoton emission, which can be explained by the transition dipole moment between electronic states. However, the SHG signal is a completely coherent process and retains information originating from not only the transition dipole moments but also the permanent dipole moment change as shown in eq 2. Therefore, it is not surprising to observe additional features in the SHG images.

We collected a full polarization data set of SHG signals at $\omega = 860$ nm with the newly prepared sample. In this sample, two long and wide adjacent stripe structures, identified with BAM after the transfer to glass substrate and oriented nearly parallel to the *X*-scan axis of the nonlinear optical microscope, were imaged so that data on dark and bright stripes could be collected in one experiment cycle. We arbitrarily labeled the stripes with high- and low-SHG signal (as measured at s-input/s-output polarizations), respectively, as bright and dark. Each data point was separated from adjacent points by a distance of 5 μ m to minimize photobleaching.

At seven output polarizations (Φ_{out}), SHG intensity was measured as a function of input polarization (Φ_{in}) at every 10° from 0° to 180°. A subset of that data is presented in Figure 5. In these plots, p- and s-polarization correspond, respectively, to 0° and 90°. Each plot shows two intensity lobes of varying intensity depending on the input polarization, separated by 90°. The polarization of an SHG signal, and its correlation to molecular parameters, has been explicitly derived by Feller et al.,²⁹ and we used that formalism to fit the data.

The SHG polarization plots can be fitted with various combinations of 18 independent molecular β tensor components and Euler angles (θ, ϕ, ψ), which are shown in the Appendix. In our particular experiment, the fundamental light (860 nm) and the doubled light (430 nm) is 70 nm (0.13 eV) or 10 nm (0.07 eV) away from the first and second electronic excitation of TAZ.



Figure 5. Representative plots at various output polarizations of the SHG signal vs the input polarization (Φ_{in}) from single bright and dark domains of the TAZ molecular monolayer. The filled squares are experimental data, and the solid lines are the fits.

 TABLE 1: Nonlinear Molecular Hyperpolarizability

 Tensors, Their Phases, and Euler Angles for Dark and

 Bright Domains^a

eta_{zzz}	β_{zxx}	β_{xxx}	β_{xzz}	β_{xxz}	β_{zzx}
1 (0°)	-0.19 (232°)	-0.25 (111°)	-0.81 (266°)	-0.11 (139°)	0.34 (40°)
		θ	φ	,	ψ
Bright stripe Dark stripe		$-48^{+3}_{-3}\\46^{+2}_{-2}$	12 -12	5^{+3}_{-4} 1^{+2}_{-2}	$-40^{+8}_{-5} \\ 23^{+5}_{-6}$

^{*a*} All β components and their phases are scaled with respect to β_{zzz} .

Therefore, ω and 2ω both have resonance character, so the β tensor components are complex numbers as shown in eq 2. They can, in principle, be determined by the transition dipole moment and permanent dipole moment change between the three electronic states. Because the ground state of TAZ has the zwitterionic form, these two electronic transitions will likely lead to a charge reorganization on the x-z molecular plane. Therefore, the six β tensors having x or z components and their corresponding phases were determined from a fit to the SHG data.

All fitted β tensor components, their phases, and Euler angles for the bright and dark stripes are listed in Table 1. The fitted SHG intensities are presented as solid lines in the Figure 5 plots. The scaled areas of the TAZ molecule, extracted from the fits, for bright- and dark-striped structures are shown in Figure 6. The angles between the stripe direction (*X*-axis) and the molecular planes (x-z plane) for the bright and dark stripes are, respectively, 86° and 41°, while the angle between these two planes is 64°.

Scanning Probe Microscopy Measurements. Scanning probe microscopy was performed in two modes using a commercial instrument (Digital Instruments): topographic mode and surface potential (SP) mode. These two modes gave complementary information; the SP measurement (Figure 7a) gives chemical information on the identity of the structure seen in the topographic image (Figure 7b). The instrument collects the two data sets in the following manner. First, a conventional topographical image is taken. For SP measurements, the cantilever tip is then raised several tens of a nanometer above



Figure 6. Molecular x-z planes of the bright (grey colored) and dark domains of the TAZ molecular monolayer drawn within the laboratory frame.



Figure 7. SPM images of a TAZ LB monolayer: (a) AFM image (topography); (b) surface potential images. The two images were collected simultaneously. The domain boundary imaged here was first identified by BAM techniques and later located by SPM using alignment markers.

the film, and the cantilever is rescanned at constant height over the same features previously scanned in topographical mode. During the SP scan, the mechanical vibrations are turned off and replaced by a sinusoidal ac voltage, thereby creating an oscillatory electric force. The oscillating force is proportional to the product of the driving amplitude of the sinusoidal voltage and the potential difference between the tip and the sample surface. When this difference is zero, the electric force felt by the cantilever tip is also zero and the tip voltage is then equal to the SP. The SP measured this way is directly related to the vertical component of the electric dipole moment in the film.

The topographical image of the stripe feature seen with BAM shows a sharp 8 Å step across the continuous boundary line separating two domains. The corresponding SP image also shows a boundary line, but it is offset from the step seen in the topographical image by a few angstroms into the domain that is lower in height. The SP on either side of this boundary seems to be the same, while the SP of the boundary region itself is reduced by about 50 mV. We interpret these results to mean that, while the SP measurement is not sensitive to the difference in the vertical projection of the dipole moment between the two domains on either side of the stripe boundary, it does detect the slight discontinuity in the electric field due to the change in tilt angle of the molecules at the interface of the stripes.

Discussion

The uniqueness of the structural fit to the SHG polarization data is questionable because of a lack of information on the β components. However, our fit does lead to certain predictions that can at least be checked for consistency with the other measurements reported here. First, the height difference between the bright and dark molecular domains is predicted to be about 8 Å, and this is in good agreement with the value measured by SPM in topographic mode. Second, the SP images indicate the presence of a field gradient at the interface of the two types of domains, and this is also predicted from the relative molecular orientations in the domains. Third, the projected molecular area onto the *X*-*Y* plane of the substrate is 39 and 45 $Å^2$ for bright and dark stripes, respectively. These values are at least consistent with the measured area per molecule (52 $Å^2$) from the isotherm, especially considering that this bulk isotherm measurement includes both the minority-component striped domains and the other, relatively featureless (by all imaging techniques) film components. Fourth, the contrast change between adjacent stripes was observed in BAM as the polarization of reflected light changed by $20^{\circ}-40^{\circ}$. If we assume that the permanent dipole orientation in the ground state of TAZ determines the direction of polarization of reflected light, then the observed contrast in the BAM images between adjacent stripes is determined by the angle describing the relative orientation of the two sets of dipoles. From the SHG fitted molecular orientation of adjacent stripes that is described in Figure 6, that angle difference is 23°. This compares favorably with the observed value from the BAM measurements of $20^{\circ}-40^{\circ}$.

The structure of a monolayer film of TAZ has been investigated by five different microscopies. Striped molecular domains with alternating, polarization-dependent dark and bright contrasts were found by BAM. A full polarization data set of the SHG signal was collected for both bright and dark stripes, and the data were fitted to extract the molecular structure parameters of these domains. The extracted structural picture was consistent across all imaging techniques. The demonstration here that the technique of scanning SHG microscopy can generate high-quality structural information is encouraging. We are engaged in other experiments that utilize molecular monolayers as the active switching components in solid state devices, and a future application of this technique will be to apply it toward interrogating the molecular mechanical changes that we have hypothesized as being responsible for the switching mechanisms. Carrying out such measurements within the context of a solid-state device setting is our current goal.

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Appendix

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The polarization-dependent SHG signal has been explicitly derived by Feller et al.²⁹ Briefly, it can be expressed as follows:

$$\text{SHG} \propto |\chi_{\text{eff}}^{(2)}|^2$$
 (A1)

$$\chi_{\rm eff}^{(2)} = [\hat{\mathbf{e}}(2\omega) \cdot \mathbf{L}(2\omega)] \chi^{(2)} : [\mathbf{L}(\omega) \cdot \hat{\mathbf{e}}(2\omega)] [\mathbf{L}(\omega) \cdot \hat{\mathbf{e}}(2\omega)] \quad (A2)$$

where $\hat{\mathbf{e}}(\Omega)$ and $\mathbf{L}(\Omega)$ are unit polarization vectors and local field correction factor tensors for $\Omega = \omega$ or 2ω . The unit polarization vectors for the incident and reflected SHG beam as defined in the laboratory *XYZ* coordinate (Figure 2) are given by

$$\hat{\mathbf{e}}(\omega) = (\cos \theta_{\text{in}}^* \cos \Phi_{\text{in}}, \sin \Phi_{\text{in}}, \sin \theta_{\text{in}}^* \cos \Phi_{\text{in}}) \quad (A3)$$
$$2\omega) = (-\cos \theta_{\text{out}}^* \cos \Phi_{\text{out}}, \sin \Phi_{\text{out}}, \sin \theta_{\text{out}}^* \cos \Phi_{\text{out}}) \quad (A4)$$

where θ_{in} and θ_{out} are 45° and $\Phi = 0^{\circ}$ and 90° correspond to p- and s-polarization, respectively. The local field correction factor tensors, which were derived by Feller et al, ²⁹ are given by

$$L_{XX}(\Omega) = \frac{2n_1(\Omega)\cos\theta_2(\Omega)}{n_2(\Omega)\cos\theta_{\rm in} + n_1(\Omega)\cos\theta_2}$$
(A5)

$$L_{YY}(\Omega) = \frac{2n_1(\Omega)\cos\theta_{\rm in}}{n_1(\Omega)\cos\theta_{\rm in} + n_2(\Omega)\cos\theta_2(\Omega)}$$
(A6)

$$L_{ZZ}(\Omega) = \frac{2n_1^2(\Omega)n_2(\Omega)\cos\theta_{\rm in}}{n_{\rm m}^2(\Omega)[n_2(\Omega)\cos\theta_{\rm in} + n_1(\Omega)\cos\theta_2(\Omega)]}$$
(A7)

$$\theta_2(\Omega) = \sin^{-1} \left[\frac{n_1(\Omega) \cdot \sin(\theta_{in})}{n_2(\Omega)} \right]$$
(A8)

Here, n_1 , n_2 , and n_m are indices of refraction of the air, glass, and the monolayer. Here, on the basis of literature precedent,^{29,32} we use $n_m = 1$, while $n_1 = 1$ and $n_2 = 1.51$ near 800–860 nm, and 1.53 around 400–430 nm. Finally, the nonlinear susceptibility, $\chi^{(2)}$, can be expressed as the linear combination of the molecular nonlinear polarizability, β , by

$$\chi_{ijk}^{(2)} \propto \sum_{l=1}^{3} \sum_{m=1}^{3} \sum_{n=1}^{3} \mathrm{ML}(\theta, \phi, \psi)_{i,l} \cdot \mathrm{ML}(\theta, \phi, \psi)_{j,m} \cdot \mathrm{ML}(\theta, \phi, \psi)_{k,n} \cdot \beta_{lmn}$$
(A9)

where *i*, *j*, and *k* are laboratory coordinates and *l*, *m*, and *n* are molecular coordinates. $ML(\theta, \phi, \psi)$ is the molecular-to-laboratory frame (Euler angle) transformation matrix and can be expressed as follows:

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ML(\theta,\phi,\psi) =
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 $[\]begin{pmatrix} \cos\phi\cdot\cos\psi - \sin\phi\cdot\cos\theta\cdot\sin\psi & -\cos\phi\cdot\sin\psi - \sin\phi\cdot\cos\theta\cdot\cos\psi & \sin\phi\cdot\sin\theta\\ \sin\phi\cdot\cos\psi + \cos\phi\cdot\cos\theta\cdot\sin\psi & -\sin\phi\cdot\sin\psi + \cos\phi\cdot\cos\theta\cdot\cos\psi & -\cos\phi\cdot\sin\theta\\ \sin\theta\cdot\sin\psi & \sin\theta\cdot\cos\psi & \cos\theta \end{pmatrix}$

Uncertainty of Angle Measurement. In our fitting program, the percent deviation from the measured SHG data was minimized. Using the hyperpolarizability shown in Table 1 as a fixed parameter, we monitored the sum of deviations as we changed one Euler angle and used the other two as fitting variables. When the amount of deviation was doubled from the best fit in Table 1, the angle difference was used for the uncertainty of Euler angle measurement.

References and Notes

(1) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.; Parikh, A. N.; Nuzzo, R. G. J. Am. Chem. Soc. **1991**, 113, 7152.

(2) Kato, K.; Tanaka, K.; Date, M. Electr. Commun. Jpn. Part II-Electr. 1998, 81, 32.

(3) Wu, D. G.; Cahen, D.; Grat, P.; Naaman, R.; Nitzan, A.; Shvarts, D. *Chem.-Eur. J.* **2001**, *7*, 1743.

(4) Fodor, S. P. A.; Read, J. L.; Pirrung, M. C.; Stryer, A. L. Yu.; Solas, D. Science **1991**, 251, 767.

(5) Rugar, D.; Hansma, P. Phys. Today 1990, 43, 23.

(6) Korlach, J.; Schwille, P.; Webb, W. W.; Feigenson, G. W. Proc. Natl. Acad. Sci. U.S.A. 1999, 96, 9966.

(7) Mobius, D. Curr. Opin. Colloid Interface Sci. 1998, 3, 137–142.
(8) Wudl, F.; Koutentis, P. A.; Weitz, A.; Ma, B.; Strassner, T.; Houk, K. N.; Khan, S. I. Pure Appl. Chem. 1999, 71, 295.

(9) A movie that illustrates the effect of a magnetic field upon the motion of the stripes may be viewed at http://www.chem.ucla.edu/~gregho/ heathgrp/members/hyeon/TAZ_files/frame.htm.

(10) Henrichs, S. E.; Sample, J. L.; Shiang, J. J.; Heath, J. R.; Collier, C. B.; Savkelly, B. L. J. Phys. Chem. B **1000**, 102, 2554

C. P.; Saykally, R. J. J. Phys. Chem. B 1999, 103, 3524.

(11) Shen, Y. R. Annu. Rev. Phys. Chem. 1989, 40, 327.

(12) Corn, R. M.; Higgins, D. A. Chem. Rev. **1994**, 94, 107.

(13) Eisenthal, K. Chem. Rev. 1996, 96, 1343.

(14) Florsheimer, M. Phys. Status Solidi A 1999, 173, 15.

(15) Boyd, G. T.; Shen, Y. R.; Hansch, T. W. Opt. Lett. 1986, 11, 97.
(16) Simpson, G. J. Appl. Spectrosc. 2001, 55, 16A.

(17) Smilowitz, L.; Jia, Q. X.; Yang, X.; Li, D. Q.; McBranch, D.;
 Buelow, S. J.; Robinson, J. M. J. Appl. Phys. **1997**, 81, 2051.

(18) Johal, M. S.; Parikh, A. N.; Lee, Y.; Casson, J. L.; Foster, L.;

Swanson, B. I.; McBranch, D. W.; Li, D. Q.; Robinson, J. M. *Langmuir* **1999**, *15*, 1275.

(19) Vydra, J.; Eich, M. Appl. Phys. Lett. 1999, 72, 275.

(20) Zeng, H.; Liu, C.; Tokura, S.; Kira, M.; Segawa, Y. J. Phys.: Condens. Matter 1999, 11, L333.

(21) Florsheimer, M.; Bootsmann, M–T; Fuchs, H. *Adv. Mater.* **2000**, *12*, 1918.

(22) Shen, Y.; Swiatkiewicz, J.; Winiarz, J.; Markowicz, P.; Prasad, P. N. *Appl. Phys. Lett.* **2000**, *77*, 2946.

(23) Shen, Y.; Markowicz, P.; Winiarz, J.; Swiatkiewicz, J.; Prasad, P.
 N. Opt. Lett. 2001, 26, 725.

(24) Schaller, R. D.; Roth, C.; Raulet, D. H.; Saykally, R. J. J. Phys. Chem. B 2000, 104, 5217.

(25) Andrews, D. L. In *Modern Nonlinear Optics, Part 2*; Evans, M., Kielich, S., Eds.; Advances in Chemical Physics, Vol. LXXXV, John Wiley & Sons, Inc.: New York, 1993; p 545.

(26) Corn, R. M.; Higgins, D. A. In *Characterization of Organic Thin Films*; Ulman, A., Ed.; Manning Publication Co.: Greenwich, U.K., 1995; p 227.

(27) Kikteva, T.; Star, D.; Zhao, Z.; Baisley, T. L.; Leach, G. W. J. Phys. Chem. B **1999**, 103, 1124.

(28) Kikteva, T.; Star, T. D.; Leach, G. W. J. Phys. Chem. B 2000, 104, 2860.

(29) Feller, M. B.; Chen, W.; Shen, T. R. *Phys. Rev. A* 1991, 43, 6778.
(30) Gehlert, U.; Fang, J.; Knobler, C. M. *J. Phys. Chem. B* 1998, 102, 2614.

(31) Wilkens, M. Phys. Rev. Lett. 1994, 72, 5.

(32) CRC Handbook of Chemistry and Physics, 68th ed.; CRC Press Inc.: Boca Raton, FL; 1987-1988; pp E-372.