Variable Index of Refraction Ultrathin Films Formed from Self-Assembled Zirconium Phosphonate Multilayers: Characterization by Surface Plasmon Resonance Measurements and Polarization/Modulation FT-IR Spectroscopy

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Ultrathin (submicrometer) organic films of specified index of refraction are constructed by the sequential deposition of self-assembled zirconium phosphonate (ZP) molecular monolayers that contain two different bisphosphonate ions, 1,10-decanediylbis(phosphonate) (DBP) and 4,4'-azobis[2-(methylene)benzophosphonate] (AZO). By varying the ratio of DBP to AZO monolayers in the ZP multilayer film, the index of refraction can be controlled. A combination of surface plasmon resonance (SPR) measurements and polarization/modulation Fourier transform infrared reflection–absorption spectroscopy (PM/FT-IR) is used to examine the structure of the ZP multilayers on vapor-deposited gold substrates, and ellipsometric measurements are utilized to determine the index of refraction of the ZP multilayers on transparent substrates. ZP films consisting of 100% DBP and 100% AZO molecules are found to have indices of refraction of 1.51 and 1.64, respectively, at an optical wavelength of 632.8 nm. In both the 100% DBP and the 100% AZO multilayers, an average monolayer thickness of 16 ± 0.5 Å is determined from the SPR measurements. The spectroscopic and ellipsometric data indicate that the index of refraction of mixed ZP multilayer films (i.e., films with both DBP and AZO self-assembled monolayers) can be varied systematically between 1.51 and 1.64, but that the average thickness of the self-assembled monolayers is greater in the mixed films than in either of the 100% DBP or 100% AZO multilayers.

The formation of ultrathin (submicrometer) organic films by the sequential deposition of molecular monolayers is currently being pursued as a means of fabricating thin-film optical devices such as optical waveguides, photonic switches, electrooptical components, and nonlinear optical films. The versatility of this deposition methodology stems from (i) the fine control of film thickness that can be achieved by forming the thin film one monolayer at a time and (ii) the ease with which different chemical functionalities can be incorporated into the thin film in order to control its linear and nonlinear optical properties. Currently, the most common method of forming ultrathin organic films one monolayer at a time is the Langmuir–Blodgett (LB) technique of repeatedly transferring monolayer structures from a water surface to a substrate. In 1988, Mallouk and co-workers demonstrated a new strategy for forming organic thin films on metal and oxide substrates by the spontaneous adsorption and self-assembly of zirconium phosphonate (ZP) multilayers. These films contained alternate layers of organic (n-alkyl) and inorganic (zirconium phosphonate) structures and appeared to be both thermally robust and highly reproducible. A variety of metal phosphonate multilayer structures are currently being examined for use as ultrathin organic films in both optical and chemical applications.
When creating a thin-film optical waveguide for a given wavelength, the film will consist of alternating self-assembled monolayers of AZO. For example, a 1:1 AZO/DBP film has alternating self-assembled monolayers of DBP. By varying the AZO/DBP ratio in the ZP multilayer, we can control the overall index of refraction of the thin film.

ZP multilayers formed on vapor-deposited gold substrates are characterized with a combination of polarization/modulation Fourier transform infrared reflection-absorption spectroscopy (PM/FT-IRRAS) for molecular structure information and surface plasmon resonance (SPR) measurements for the optical determination of film thickness. We recently employed this combination of techniques to characterize the adsorption of biopolymers onto self-assembled monolayers at gold surfaces, and both methods have been applied by a number of other research groups in the study of self-assembled monolayers.

In addition to the experiments on gold substrates, the indices of refraction for ZP multilayer films formed on transparent silica substrates were determined from ellipsometry. The combined spectroscopic characterization experiments reveal that the mixed ZP multilayer deposition strategy for the formation of variable index of refraction organic films is deceptively simple; while the index of refraction of the thin film varies in a systematic fashion, unexpected changes are observed in the molecular structure and thickness of the mixed ZP multilayers.

**EXPERIMENTAL CONSIDERATIONS**

**Materials.** Diethyl 4-aminobenzylphosphonate (99%), pyridine (99%), 2,4,6-collidine (99%), phosphorus oxychloride (99%), bromotrimethylsilane (97%), zirconium chloride octahydrate (98%), anhydrous octane (99+%), anhydrous tetrahydrofuran (THF) (99%), and lithium aluminum hydride (1 M in THF) were obtained from Aldrich. Other reactants and solvents included CuCl (Mallinckrodt), 10-carbomethoxydecyl)dimethylchlorosilane (United Chemical Technologies), methylene chloride and UV grade acetonitrile (Burdick and Jackson), ethyl acetate (Fisher), and absolute ethanol (Quantum). All chemicals were used as received. Mercaptoundecanediol (MUD) and 1,10-decanediylbis(phosphonic acid) (DBP) were synthesized as described previously. All aqueous solutions were prepared from 18 MQ-TM Millipore-filtered water.

**Synthesis of Azobis[(p-phenylene)methylene]bis(phosphonic acid) (AZO).** AZO was prepared from an autoxidation reaction of diethyl 4-aminobenzylphosphonate (2 g, 8.2 mmol in 20 mL of pyridine) and oxygen (bubbled through the solution at 10 psi) in the presence of CuCl (0.25 g, 2.5 mmol) as a catalyst. The reaction was determined to be complete in 3 h by TLC in 1:1 hexane/ethyl acetate. The pyridine solution was added to a separatory funnel containing 100 mL each of a 10% HCl aqueous solution and ethyl acetate; the ethyl acetate extract was subsequently dried with Na$_2$SO$_4$, and the solvent was removed by rotary evaporation to give a red crystalline solid. Hydrolysis of the bis-

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Figure 1. Schematic diagram for the construction of mixed zirconium phosphate multilayer films. The ZP films are created on vapor-deposited gold substrates that have been first primed with a self-assembled monolayer of phosphorylated 11-mercaptopoundecanediol (MUD) and one self-assembled monolayer of 1,10-decanediylbis(phosphonate) (DBP). Mixed multilayers are formed by the sequential self-assembly of either 1,10-decanediylbis(phosphonate) (DBP) or 4,4'-azobis([p-phenylene)methylene]bis(phosphonate) (AZO) molecules onto the surface. For example, the 1:1 AZO/DBP multilayer film will have alternating self-assembled monolayers of AZO and DBP.

Perhaps the two most fundamental characteristics of an ultrathin organic film are its thickness ($d$) and its index of refraction ($n$). For example, both $d$ and $n$ need to be specified when creating a thin-film optical waveguide for a given wavelength of light. In this paper, we demonstrate that the self-assembly of ZP multilayers can be used to construct ultrathin organic films with both a specific thickness and an index of refraction that can be set in a given range ($1.51 \leq n \leq 1.64$ at $\lambda = 632.8$ nm). To accomplish this, we create ZP multilayers which contain two different bisphosphonate ions, 1,10-decanediylbis(phosphonate) (DBP) and 4,4'-azobis([p-phenylene)methylene]bis(phosphonate) (AZO). As depicted in Figure 1, monolayers of either DBP or AZO are deposited sequentially onto a substrate primed with a trimethylsilane (99%), anhydrous octane (99+%), anhydrous tetrahydrofuran (THF) (99.9%), and lithium aluminum hydride (1 M in THF) were obtained from Aldrich. Other reactants and solvents included CuCl (Mallinckrodt), 10-carbomethoxydecyl)dimethylchlorosilane (United Chemical Technologies), methylene chloride and UV grade acetonitrile (Burck and Jackson), ethyl acetate (Fisher), and absolute ethanol (Quantum). All chemicals were used as received. Mercaptoundecanediol (MUD) and 1,10-decanediylbis(phosphonic acid) (DBP) were synthesized as described previously. All aqueous solutions were prepared from 18 MQ-TM Millipore-filtered water.

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(diester) was performed by reaction with bromotrimethylsilane (7.5 g, 49 mmol) in methylene chloride (30 mL) under N₂ at room temperature for 12 h. The solvent and excess bromotrimethylsilane were removed under vacuum to yield an ocre paste that was converted to a fine orange/brown precipitate upon the addition of 50 mL of a 10% HCl aqueous solution. This precipitate was extracted with ethyl acetate as in the case of the pyridine solution to yield a brown/orange powder (1.32 g, 87% yield): "H NMR (DMSO-d₆, δ 3.1 (d, 4 H, CH₂²), δ 7.45 (d, 4 H, ArH), δ 7.80 (d, 4 H, ArH); Raman (H₂O) 1616, 1477, 1433, and 1160 cm⁻¹; IR (KBr) 1602, 1499, 1433, and 581 cm⁻¹; UV–vis λ_max (aqueous, pH = 10) 348 nm.

Substrate Preparation and Primer Layer Formation. Gold substrates for the SPR and PM/FT-IRRAS measurements were prepared by the vapor deposition of thin (47 nm) gold films onto glass microscope slide covers as reported previously. Prior to ZP multilayer deposition, a monolayer of MUD was first self-assembled on the gold surface by immersion in a 1 mM ethanolic solution for 48–72 h. The resulting alcohol-terminated surface was then phosphorylated using previously described methods, followed by zirconation in 5 mM ZrOCl₂ aqueous solution and the self-assembly of one DBP monolayer (by immersion in a 1.2 mM aqueous solution for 16 h). The surface was rinsed thoroughly with Millipore-filtered water between all deposition steps. This resultant “primer layer” was prepared on all of the gold substrates prior to the formation of a ZP multilayer film. Silica substrates for the ellipsometry measurements were prepared from fused silica disks (Laser Optics, Inc., 1 in. diameter × 0.25 in., J/20). The silica surface was prepared according to the following procedure: (i) immersion in 150 mL of 30/70 (v/v) 30% H₂O₂/ concentrated H₂SO₄ (Fluka, puriss.) for 1 h with sonication (Caution: This solution is a highly oxidizing mixture that should only be prepared immediately before use and not stored!), (ii) extensive rinsing with water and absolute EtOH, (iii) heating at 110 °C for 4 h, (iv) silanization with a 10 mM (10-carboxyethoxy)dimethylchlorosilane solution in octane heated to reflux for 24 h under nitrogen, (v) rinsing in absolute EtOH for 1 h with sonication, (vi) heating at 110 °C for 1 h, and (vii) reaction with LiAlH₄ in THF for 2 min under nitrogen to reduce the terminal methyl ester on the silanized surface to an alcohol. As in the case of the gold substrates, prior to ZP multilayer formation, this alcohol-terminated surface was first phosphorylated, zirconated, and then coated with a single DBP monolayer.

ZP Multilayer Formation Methodology. ZP multilayers were assembled on the primed gold and silica substrates by alternate exposure of the surface to an aqueous 5 mM ZrOCl₂ solution (1–2 h) and an aqueous 1.2 mM bisphosphate (either DBP or AZO) solution (9–18 h). The surface was rinsed extensively with water after each deposition step. The extended exposure time to the DBP or AZO solution was required for complete self-assembly of the monolayer onto the surface at room temperature; shorter self-assembly times have been observed for elevated temperatures.

PM/FT-IRRAS Measurements on Gold Substrates. All PM/FT-IRRAS differential reflectance spectra (ΔAR/R) were obtained without a background or reference spectrum on a Mattson RS-1 spectrometer utilizing a methodology and optical layout that have been described previously. The differential reflectance spectra were converted to absorbance units in order to compare them with normal FT-IRRAS spectra. Spectra in the CH stretching region (3100–2700 cm⁻¹) were obtained with an InSb detector, and spectra in the mid-infrared region (1800–850 cm⁻¹) were obtained using a narrow band HgCdTe detector. All spectra were acquired at 2 cm⁻¹ resolution from 1024 interferometer scans.

SPR Measurements on Gold Substrates. SPR reflectivity measurements were obtained with an SPR apparatus that has been described previously. The thin gold film samples were brought into optical contact with a BK7 hemispherical prism using a drop of methyl salicylate (as an index matching fluid) between the prism and the back side of the gold-coated microscope slide cover. As shown schematically in the inset of Figure 2, the reflectivity of p-polarized light from a HeNe laser (632.8 nm, 1 mW, Newport Corp.) from the BK7/Au/ZP film sample was monitored as a function of incident angle, θ. Figure 2 plots a series of reflectivity curves obtained during the formation of a 20 monolayer DBP film. The reflectivity curves all exhibit a cusp at 41.3° corresponding to the critical angle of the BK7 hemispherical prism. Beyond the critical angle, a sharp dip in the reflectivity was observed that is associated with the formation of surface plasmons at the gold/ZP film surface. The position of the reflectivity minimum is denoted as the SPR angle and is shifted with the deposition of successive ZP multilayers onto the surface. The reflectivity curve
labeled "0 Layers" corresponds to a gold surface that has been modified with the primer layer mentioned above (phosphorylated MUD and 1 DBP monolayer). Shifts in the SPR angle (Δθ) after the deposition of subsequent DBP monolayers were defined relative to the SPR angle for this surface. These shifts in the SPR angle were modeled with a six-phase (BK7 (n = 1.52), Au (n = 0.154 + 3.55i), MUD (n = 1.45), DBP (n = 1.51), ZP film, air) complex Fresnel calculation using a Pascal program described previously.36

UV-Vis Absorption and Ellipsometry Measurements on Silica Substrates. The deposition of AZO molecules onto transparent substrates was monitored by UV-vis spectra obtained from a Hewlett-Packard Model 8452A diode array spectrophotometer. Micromolar aqueous AZO solutions exhibited an absorption maximum at 348 nm, and ZP multilayer films exhibited an absorption maximum at 340 nm. The amount of absorbance at 340 nm increased linearly with the number of AZO monolayers for the 100% AZO and the 1:1 AZO/DBP films. The slight blue shift in the absorption maximum upon deposition suggests that the AZO molecules are interacting slightly in the ZP multilayers. However, no UV photochemistry, i.e., trans to cis isomerization,55-57 was observed in any of the AZO multilayers, even though a large photoactivity was observed for AZO molecules in an aqueous solution. Ellipsometry measurements for the various ZP films on fused silica were obtained with a Rudolph Research Model AutoEL II ellipsometer employing 633 nm light at an incident angle of 70°. The ellipsometric parameters Δ (the phase difference upon reflection) and Ψ (the arctangent of the amplitude ratio for the s and p components of light upon reflection) were measured as a function of ZP film thickness. These Δ and Ψ values were then compared with the results of a three-phase [SiO₂ (n = 1.46), ZP film, air] Fresnel calculation to determine an index of refraction for the ZP film.

RESULTS AND DISCUSSION

Characterization of a 100% DBP Multilayer Film. The CH stretching and mid-IR regions of the PM/FT-IRRAS spectrum for a ZP multilayer formed from the sequential self-assembly of 20 DBP monolayers on a vapor-deposited thin gold film. The gold surface was primed with a self-assembled monolayer of phosphorylated MUD and one self-assembled DBP monolayer before the formation of the ZP films. The antisymmetric and symmetric methylene stretching bands occur at 2927 and 2854 cm⁻¹, respectively, in both of the ZP films. The integrated area for the 1:1 AZO/DBP film is 70% of the 100% DBP film, which is higher than expected.

(i) Single, sharp, well-defined phosphonate band is observed at 1080 cm⁻¹. The position of this band is representative of the structure of the inorganic portion of the ZP multilayer and becomes sharp and well-defined on densely packed primer monolayers.35

(ii) A broad and weak absorption band (corresponding to an intensity of ~1 × 10⁻⁴ AU/monolayer) is observed at 1654 cm⁻¹. This broad band is attributed to the bending vibration of water and indicates that some water molecules have been incorporated into the ZP multilayer (most likely in the inorganic portions of the film). The incorporation of water molecules into ZP multilayers has been observed previously.12 Heating the film to 105 °C for 72 h under vacuum did not alter the intensity of this band.

Table 1. Vibrational Band Frequencies and Assignments for the DBP and AZO Multilayers

<table>
<thead>
<tr>
<th>frequency (cm⁻¹)</th>
<th>DBP Film</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2927 ± 1</td>
<td>ν₁(CH₂)</td>
<td>methylene stretch</td>
</tr>
<tr>
<td>2854</td>
<td>ν₄(CH₃)</td>
<td>methylene stretch</td>
</tr>
<tr>
<td>1654</td>
<td>δ(H₂O)</td>
<td>water bending</td>
</tr>
<tr>
<td>1467</td>
<td>δ(CH₂)</td>
<td>CH₂ scissoring def.</td>
</tr>
<tr>
<td>1409</td>
<td>δ(α-CH₂)</td>
<td>α-CH₂ scissoring def.</td>
</tr>
<tr>
<td>1080</td>
<td>ν₃(PO₂⁻)</td>
<td>phosphonate stretch</td>
</tr>
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</table>

<table>
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<tr>
<th>frequency (cm⁻¹)</th>
<th>AZO Film</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3060</td>
<td>ν₂₀(C–H)</td>
<td>aromatic CH stretch</td>
</tr>
<tr>
<td>2930</td>
<td>ν₁(CH₂)</td>
<td>methylene stretch</td>
</tr>
<tr>
<td>2856</td>
<td>ν₄(CH₃)</td>
<td>methylene stretch</td>
</tr>
<tr>
<td>1653</td>
<td>δ(H₂O)</td>
<td>water bending</td>
</tr>
<tr>
<td>1604</td>
<td>ν₈(CC)</td>
<td>ring stretch</td>
</tr>
<tr>
<td>1508</td>
<td>ν₁₄(CC)</td>
<td>ring stretch</td>
</tr>
<tr>
<td>1415</td>
<td>δ(α-CH₂)</td>
<td>α-CH₂ scissoring def.</td>
</tr>
<tr>
<td>1102, 1065</td>
<td>ν₄(PO₂⁻)</td>
<td>phosphonate stretch</td>
</tr>
</tbody>
</table>

* Frequency modes and assignments follow the numbering convention of Wilson for para-substituted benzenes and azobenzenes.

Figure 5. Shifts in the SPR angle (Δθ) measured during the formation of a 20 monolayer 100% DBP film. The shifts Δθ were determined from SPR reflectivity curves such as those shown in Figure 2, with the SPR angle of the “0 Layer” surface defined as θ = 0. The three lines in the figure are the results of complex Fresnel calculations using an index of refraction of 1.51 (as determined from ellipsometric experiments) for the ZP multilayer and a DBP monolayer thickness of 15, 16, or 17 Å. From the experimental data, a DBP monolayer thickness of 16 ± 0.5 Å is determined.

In order to determine the thickness of the DBP multilayer film, a series of SPR measurements were performed during the film deposition process. Figure 5 plots the shift (Δθ) in the SPR angle observed after the addition of each self-assembled monolayer during the formation of a DBP multilayer film. As mentioned in the previous section, the SPR angle is determined from the minimum in the SPR reflectivity curve obtained with a HeNe laser at λ = 632.8 nm. In addition, the y-axis in the figure is defined as the number of monolayers that have been deposited onto a Au substrate. The changes in Δθ at either 1.50, 1.51, or 1.52. The experimental data clearly show that n for the DBP multilayer film is determined to be equal to 1.51 ± 0.01. Similar ellipsometric measurements were used to determine n for the other ZP multilayers described in this paper and are listed along with the value for the 100% DBP film in Table 2.

Now that it has been determined that the index of refraction for the DBP multilayers is equal to 1.51, the SPR angle shifts in Figure 5 can be analyzed to ascertain the thickness of the self-assembled DBP monolayers. Using a six-phase Fresnel calculation, the theoretical curves for Δθ as a function of the number of ZP monolayers are plotted in Figure 5 for monolayer thicknesses of 15, 16, and 17 Å. A comparison of the experimental data points

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and the theoretical $\Delta \theta$ curves demonstrate that a DBP monolayer thickness of $16 \pm 0.5$ Å can be obtained from the SPR measurements. This thickness agrees favorably with values reported previously.\(^2\) The accuracy of better than $\pm 1$ Å is typical for the SPR technique\(^3\) and is remarkable for an optical measurement at $\lambda = 632.8$ nm. On the basis of a space-filling model, the inorganic portion of the DBP monolayer from the center of the first carbon above to the first carbon below the layer is determined to be about 6.5 Å. In an all-trans configuration that is oriented perpendicular to the surface, the additional nine methylene groups contribute about 11.4 Å, for a total thickness of $\sim 17-18$ Å.\(^4\) An experimentally determined average monolayer thickness of 16 Å is plausible given the possibility of tilting and the presence of alkyl chain disorder in the DBP monolayer as observed in the PM/FT-IRRAS spectrum.

**Characterization of a 100% AZO Multilayer Film.** For comparison with the 100% DBP monolayer, a second ZP multilayer was created by the sequential self-assembly of AZO monolayers onto a primer layer on a gold substrate. The CH stretching region of the PM/FT-IRRAS spectrum for the 100% AZO multilayer (not shown) was dominated by the antisymmetric and symmetric methylene stretches of the primer layer at 2925 and 2852 cm\(^{-1}\), respectively. Moreover, the integrated area of these methylene stretches of the primer layer at 2925 and 2852 cm\(^{-1}\), due to local field effects were observed in the ultrathin ZP films, as expected given the relatively long wavelength of the infrared light, and is significant higher than the value of 1.51 observed for the DBP film. Using an index of refraction of 1.64, the six-phase Fresnel calculations can be used to analyze the SPR shifts and determine an average AZO monolayer thickness of 16 ± 0.5 Å, which is the same value obtained for the DBP monolayer. The similarity of these two numbers suggests that mixed monolayers of these two molecules may yield stable ZP multilayer films. On the basis of a space-filling model with an inorganic section thickness of 6.5 Å, the AZO monolayer in which the azobenzene is oriented perpendicular to the surface (9–10 Å) should have a total thickness of $\sim 17-18$ Å. The smaller experimentally determined value of 16 Å again suggests tilting and disorder in the ZP film.

**Characterization of a 1:1 AZO/DBP Multilayer Film.** Having determined that a DBP multilayer film has an index of refraction $n = 1.51$ and that an AZO multilayer film has an index of refraction $n = 1.64$, one would expect that a ZP multilayer film formed from alternating self-assembled monolayers of AZO and DBP would possess an index of refraction of $n = (1.64 + 1.51)/2 = 1.575$. Indeed, the ellipsometric measurements of a 1:1 AZO/DBP film were performed during the deposition of the AZO multilayer film, and the shift ($\Delta \theta$) in the SPR angle observed after the addition of each self-assembled monolayer is plotted as the squares in Figure 7. For comparison, the SPR data for the DBP film from Figure 5 are plotted in the figure as the triangles. A larger $\Delta \theta$ per monolayer is observed for the AZO multilayer film; this larger shift is attributed to a higher index of refraction of the AZO multilayer. As listed in Table 2, ellipsometric measurements of AZO multilayer films on a transparent substrate yield an index of refraction of $n = 1.64 \pm 0.01$. This value is within the range observed for azobenzene-derivatized polymers (1.623–1.758)\(^9\) and is significantly higher than the value of 1.51 observed for the DBP film. Using an index of refraction of 1.64, the six-phase Fresnel calculations can be used to analyze the SPR shifts and determine an average AZO monolayer thickness of 16 ± 0.5 Å, which is the same value obtained for the DBP monolayer. The similarity of these two numbers suggests that mixed monolayers of these two molecules may yield stable ZP multilayer films. On the basis of a space-filling model with an inorganic section thickness of 6.5 Å, the AZO monolayer thickness of 16 Å again suggests tilting and disorder in the ZP film.


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**Table 2. Monolayer Thicknesses and Indices of Refraction for the ZP Multilayer Films**

<table>
<thead>
<tr>
<th>Film</th>
<th>$n$ (^a)</th>
<th>$d$ (Å/layer) (^b)</th>
<th>$\Delta \theta$ (deg)</th>
<th>$d_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBP</td>
<td>1.51 ± 0.01</td>
<td>16 ± 0.5</td>
<td>6.36 ± 0.15 (^c)</td>
<td>320 ± 5</td>
</tr>
<tr>
<td>AZO</td>
<td>1.64</td>
<td>16</td>
<td>8.33</td>
<td>320</td>
</tr>
<tr>
<td>1:1 AZO/DBP</td>
<td>1.57</td>
<td>19</td>
<td>9.85</td>
<td>380</td>
</tr>
</tbody>
</table>

\(^a\) Determined by ellipsometry on fused silica substrates. \(^b\) Determined by SPR on vapor-deposited gold slides. \(^c\) Reported uncertainty is the standard deviation of three gold-ZP film samples.

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DBP multilayer film on a transparent substrate yield a value of \( n = 1.57 \) (see Table).

However, SPR measurements on the 1:1 AZO/DBP multilayer suggest that even though \( n = 1.57 \) as expected, the structure and thickness of the ZP film have changed. As with the previous two ZP films, SPR measurements were performed during the deposition of the 1:1 AZO/DBP multilayer film in order to determine the average monolayer thickness. The shift \( \delta \theta \) observed after the addition of each self-assembled monolayer is plotted as circles in Figure 7 along with the data from the DBP and AZO multilayers. Given that \( n = 1.57 \) for this film, one would expect that the \( \delta \theta \) curve for this film would fall in between the curves for the AZO and DBP multilayers. Unexpectedly, the data for the 1:1 AZO/DBP multilayer systematically show a larger \( \delta \theta \) shift than either of the other two films. Using \( n = 1.57 \), this \( \delta \theta \) curve corresponds to an average monolayer thickness of 19 Å, which is a 19% increase in the average thickness as compared to the 16 Å obtained for both the AZO and DBP monolayers. To demonstrate how unusual this number is, if the monolayer thickness is fixed at 16 Å, the \( \delta \theta \) curve for the 1:1 AZO/DBP multilayer can only be fit using an index of refraction of 1.70, which is clearly an unreasonable number given \( n = 1.64 \) for the 100% AZO multilayer.

What structural changes have occurred that result in a new average thickness of 19 Å/monolayer for the 1:1 AZO/DBP multilayers? The UV–vis experiments on the 1:1 AZO/DBP multilayers used to characterize the ZP film formation on the transparent substrates showed no unusual behavior: the absorption spectra were the same as those obtained from the 100% AZO monolayers except that the overall absorbance was half as intense, as expected. The PM/FT-IRRAS spectrum of the 1:1 AZO/DBP film, however, was not quite what was expected. The CH stretching region for the 1:1 AZO/DBP multilayer is plotted as the dashed line in Figure 3 along with the spectrum for the 100% DBP multilayer. The frequencies of the methylene bands are the same in the two samples, indicating that there are no large structural changes in the DBP monolayers of the mixed film. However, the integrated intensity of the methylene bands for the 1:1 film is 70% of that observed for the pure DBP multilayer. This value is ~20% higher than expected.63

The mid-IR region of the PM/FT-IRRAS spectrum for the 1:1 AZO/DBP multilayer is plotted in Figure 8 (the solid line) and confirms the discrepancy observed in the methylene stretching bands. Also plotted in the figure is a spectrum labeled “(AZO + DBP)/2” (the dashed line). This artificial spectrum is synthesized from the spectra of the 100% AZO and 100% DBP multilayers and represents what should have been observed if the picture in Figure 1 were correct. Instead, the phosphonate band at 1080 cm\(^{-1}\) and the DBP methylene scissoring band at 1466 cm\(^{-1}\) are more intense in the spectrum of the true 1:1 AZO/DBP multilayer by ~18%. Thearyl bands of the azobenzene functionality are about the same intensity in the two spectra, and the water band in the true spectrum is smaller than expected.

Note that only intensity changes are observed in the PM/FT-IRRAS spectrum of the 1:1 AZO/DBP multilayer. No changes in vibrational band frequencies are observed, indicating that there are no large changes in the molecular structure of the 1:1 AZO/DBP multilayer. The changes in band intensity can be attributed to one of two effects: either there has been a change in the orientation of the molecules in the AZO and DBP monolayers, or there has been a change in the number density of molecules in the ZP multilayers. Most of the change in intensity arises from changes in the vibrational bands associated with the DBP molecules; very little change is observed in the intensity of the vibrational bands of the AZO molecules in the ZP film. The SPR data clearly show that the average monolayer thickness has increased by 19% in the 1:1 AZO/DBP multilayer film. If this increase were to arise from a more perpendicular orientation of the DBP multilayers, one would expect to see a decrease in the intensity of the methylene stretching bands. Such decreases are often observed in the well-oriented samples of \( \pi \)-alkanethiol monolayers self-assembled onto gold surfaces.44,45 The fact that we instead observe an increase in the stretching band intensities (but no change in the band frequencies) implies that 19% more DBP has been incorporated into the 1:1 AZO/DBP film than the amount suggested in the simple picture in Figure 1. It is this additional DBP that must lead to the increased average film thickness of 19 Å/monolayer. In fact, a reexamination of the SPR data in Figure 7 also shows this to be true. The amount of shift in the SPR angle uniformly increases for the 1:1 AZO/DBP film with each additional monolayer deposition. If the same amount of AZO and DBP were deposited with each monolayer, we would expect to see a larger shift for the AZO monolayers (due to its higher index of refraction) than for the DBP monolayers.

How does the additional 19% of DBP get incorporated into the 1:1 AZO/DBP multilayer film? It is important to remember that all of the optical measurements employed in this paper to analyze the ZP films are average measurements over the entire surface. Thus an average monolayer thickness of 16 Å/monolayer could mean that a significant portion of a given DBP or AZO self-assembled monolayer has a thickness of 19 Å, while the rest of

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(60) The expected value for the CH stretching region is based on an artificial spectrum derived by taking the average of the 100% AZO and 100% DBP spectra. The integrated intensity of the methylene stretching bands for the synthesized spectrum is 57% of that observed for the pure DBP multilayer. This value is 20% lower than the intensity of the measured 1:1 AZO/DBP spectrum.

Figure 8. Mid-infrared region of the PM/FT-IRRAS spectrum of a 20 monolayer 1:1 AZO/DBP ZP film (solid line). The gold surface was primed with a self-assembled monolayer of phosphorylated MUD and one self-assembled DBP monolayer before the formation of the ZP film. This spectrum contains contributions from both the AZO and DBP portions of the multilayer, although the DBP bands are 18% more intense than expected. For comparison, a synthetic spectrum denoted as “(AZO + DBP)/2” (dashed line) that was generated from the spectra of the 100% DBP and 100% AZO multilayers is also plotted.
the film is significantly thinner; increasing the average film thickness just means that the amount of thicker monolayer regions has increased. Another possibility is that changes in the packing structure of the inorganic zirconium phosphonate lattice for the mixed monolayers are responsible for changes in the packing density of the organic sections of the monolayer. This may also provide a possible explanation for the observed decrease in the intensity of the water band at 1653 cm⁻¹, since it is likely that the water resides in the inorganic regions of the film. Similar arguments of changes in the structure of the zirconium phosphonate lattice for the mixed monolayers have been suggested by Byrd et al. and Zeppenfeld et al. in their studies of metal phosphonate multilayers. In addition, a third possibility is that excess DBP intercalates into the preceding AZO regions of the 1:1 AZO/DBP multilayer film. This results from the inability to form pure well-ordered AZO monolayers due to the azo dye substituent area being greater than that of the phosphate headgroup area of 24 Å². The incorporation of excess DBP molecules into the AZO regions may then cause both sets of molecules to stand straighter, i.e., more perpendicular, resulting in the observed larger 1:1 AZO/DBP multilayer film thickness. An analogous bulk system in which large tetramethyl biphenylphosphonate groups are surrounded by smaller phosphite groups has been reported by Alberti et al.

**SUMMARY AND CONCLUSIONS**

In summary, we have demonstrated that mixed zirconium phosphonate multilayer films can be used to create ultrathin organic films with a specified thickness and index of refraction. In particular, the two molecules DBP and AZO can be used to create mixed ZP multilayer films of index of refraction at 632.8 nm between 1.51 and 1.64. In principle, one could construct graded index of refraction ZP films by systematically changing the AZO/DBP ratio during the multilayer film formation. A second potential application of these DBP and AZO monolayers would be to mix them with SHG-active ZP multilayers in order to tune the index of refraction and phase matching characteristics of the resultant ZP multilayer. We are currently pursuing the synthesis and self-assembly of SHG-active ZP multilayers that employ an additional phosphorylation step during deposition, as first demonstrated by Katz et al.

The studies reported in this paper demonstrate that SPR and PM/FT-IRRAS measurements are a pair of well-matched, highly sensitive methods for determining the molecular structure and the thickness of the ZP multilayers. In particular, it was shown that the 1:1 mixed AZO/DBP monolayer did not exhibit the thickness expected from the 100% DBP and 100% AZO multilayers; additional DBP molecules are apparently incorporated into the mixed ZP multilayer film. In preliminary experiments on 2:1 and 1:2 AZO/DBP multilayer films, we have seen similar effects in the average film thickness. It is clear from these initial results that the optical and spectroscopic characterization measurements employed in this work are essential tools for the rational design of ultrathin optical films via the self-assembly of organic multilayers.

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