

# Chromophoric Self-Assembled Superlattices

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The ubiquitous desire of chemists and materials scientists to design, fabricate, and understand the properties of ever more intricate molecular architectures and assemblies originates in the potential efficacy of such structures in photonic, catalytic, and biomimicking functions. While complex molecules and small aggregates of individual molecules are now increasingly accessible, controlling molecular assembly motifs on a larger scale is one of the most challenging problems in contemporary chemical synthesis.<sup>1</sup> These synthetic issues are significant in the design and realization of second-order nonlinear optical (NLO) materials,<sup>2</sup> light-harvesting molecular arrays,<sup>3</sup> artificial photosynthetic structures,<sup>4</sup> molecular ferromagnets<sup>5</sup> and superconductors,<sup>6</sup> as well as numerous biomolecule ensembles,<sup>7</sup> and a host of other fascinating products of supramolecular science. In the present Account, we discuss the evolution of molecular self-assembly strategies in the field of second-order nonlinear optical (NLO) materials and the relevance of such strategies to related areas of molecular engineering.

Organic NLO materials<sup>2</sup> currently attract considerable scientific and technological (e.g., in frequency-doubling and high-speed optical signal processing devices) interest due to the demonstrated large responses to input light, low dielectric constants/losses (necessary for high-speed operation), ultrafast response times (also necessary for high-speed operation), relatively high optical damage thresholds, and the intrinsic tunability of molecular structures. Electronic delocalization and polarization in organic and metal-organic molecular building blocks is the origin of the NLO response and offers significant attractions over inorganic materials where the response is ionic motion in nature.<sup>8</sup> The principle requirement for molecule-based second-order NLO materials is a *noncentrosymmetric organization* of the constituent active species. *A priori*, single crystals of molecular chromophores are candidates for such applications; however, they are arduous to grow, frequently crystallize in centrosymmetric space groups,<sup>2d</sup> and are difficult to fabricate as device-applicable (waveguiding) thin films. An attractive film-forming class of NLO materials are glassy

polymers in which acentric microstructure (polar organization) is induced by alignment of the chromophore dipoles in an electric field (poling). Here increased chromophore concentrations and improved temporal stability of polar alignment are current objects of intensive study.<sup>2a-c</sup> Layer-by-layer Langmuir-Blodgett film deposition techniques provide alternative structures with high chromophore concentrations; however, issues such as light-scattering microdomains, fragility, low structural stability, and centrosymmetric chromophore aggregate formation remain unresolved issues.<sup>2d</sup> Clearly, an alternative to poled polymers and Langmuir-Blodgett films would be attractive. We discuss here a promising and informative strategy employing sequential layer-by-layer construction of covalently self-assembled chromophoric multilayers.<sup>9</sup>

The purpose of this Account is thus to review recent molecular self-assembly research at Northwestern University. We begin with a discussion of synthetic and physicochemical design strategies, followed by an account of multilayer construction techniques aimed at second-order NLO materials. We then show how the self-assembly kinetics and structural dynamics provide tools to manipulate the resulting structures.

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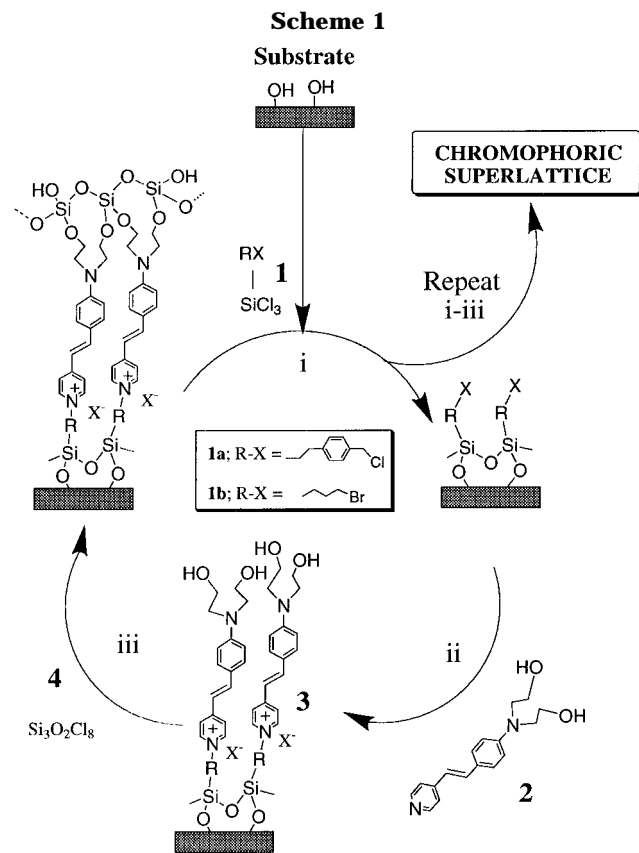
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Finally, photophysical properties are discussed along with fabrication of a prototype device.

### A Synthetic Strategy for Intrinsically Acentric Chromophoric Superlattices

The present approach utilizes siloxane condensation reactions originally developed by Sagiv<sup>10</sup> (for other purposes) and subsequently refined by Whitesides,<sup>11</sup> Ulman,<sup>12</sup> and others.<sup>13</sup> Chemisorption of alkyl or benzyl halide containing trichlorosilane coupling agents **1** (step i, Scheme 1) onto flat, hydroxy-terminated surfaces (e.g., glass, silicon, organic polymers) provides functionalized surfaces for the polar anchoring of bifunctional chromophore precursor **2** (Scheme 1). The quaternization/anchoring process (step ii, Scheme 1) converts the NLO-inactive precursor **2** into NLO-active chromophore **3** having a very large molecular second-order NLO response (hyperpolarizability,  $\beta_{zzz}^{\text{calcd}}$ , estimated by a semiempirical quantum chemi-

cal approach<sup>14</sup> to be  $950 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ ). Step ii also creates surface hydroxyalkyl functionalities that are subsequently used to "lock in" the polar structure with capping agent **4** via three-dimensional siloxane-network formation. This "capping" reaction (step iii) planarizes the structure, exposes silanol functionalities mimicking the original SiO<sub>2</sub> interface, and thus allows superlattice construction by iteration of steps i-iii.

The course of multilayer formation on clean glass substrates is monitored by optical spectroscopy (shift in  $\lambda_{\text{max}}$  of **2** from 390 nm to that of **3** at 480 nm); XPS (X-ray photoelectron spectroscopy; initial decrease in Si and O signals; increase and persistence of C, N, Cl/Br signals); advancing contact angles (expected changes in surface wettability of the various surface functionalities in each i-iii step); X-ray reflectivity and ellipsometry (yielding film thicknesses in accord with expected layer dimensions); and second-order NLO response characteristics. The films are strongly chemisorbed to the substrate and are insoluble in common organic solvents and mineral acids.

### Chromophoric Self-Assembled Monolayer Formation Kinetics

Understanding the kinetics of monolayer self-assembly is important in establishing a protocol for the efficient construction of reproducible, closely packed, complete monolayers and is essential when multilayer construction is desired. Surface silylation using different coupling agents (**1** in Scheme 1) was optimized first. While aliphatic trichlorosilane **1b** reacts rapidly (as expected<sup>10-12</sup>) to form a complete monolayer, aromatic trichlorosilanes (e.g., **1a**) require multiple immersions and longer reaction times for complete reaction.

*In situ* SHG (second harmonic generation: doubling of the input light frequency) spectroscopy<sup>15</sup> is a sensitive tool for probing surface chemical events, and this technique was employed here to better understand rate-limiting chromophore incorporation step ii by monitoring the chemisorptive quaternization process in real time.<sup>16</sup> The large change in molecular hyperpolarizability ( $\beta_{zzz}^{\text{calcd}} = 950 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$  for **3** vs  $33 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$  for **2** at an input wavelength,  $\lambda_0$ , of 1064 nm) allows direct monitoring of the self-assembly process and distinguishes it from simple physisorption.<sup>17</sup> No shift in the optical absorption spectrum is observed for chromophore **3** in solution versus as a thin, self-assembled solid film. Such a shift could be taken as evidence of centrosymmetric aggregation, which is common in certain dye-containing LB films,<sup>18</sup> and is also a potential concern in zirconium phosphate/phosphonate derived multilayers.<sup>13e,f</sup> In

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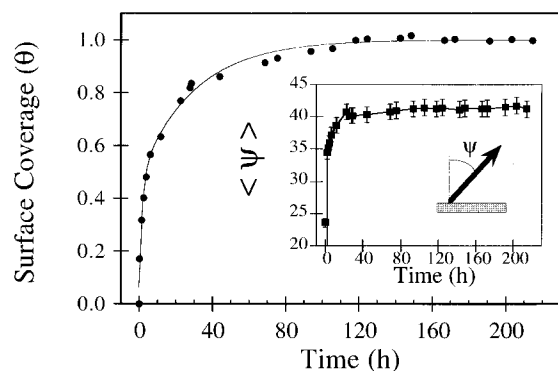
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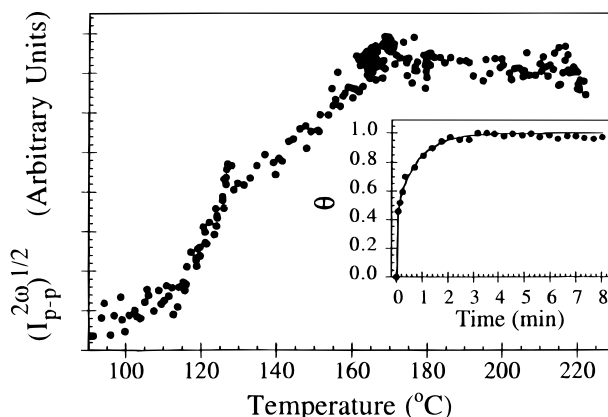
**Figure 1.** Solution *in situ* SHG evolution as a function of time at 60 °C in *n*-PrOH for chromophore quaternization reaction (step ii, Scheme 1) for a benzyl chloride (**1a**)-functionalized surface (step i, Scheme 1); the solid line is a theoretical fit to eq 1. The inset shows the average chromophore tilt angle from the surface normal as a function of reaction time (the line is a guide to the eye).

the present case, the monolayer SHG signal and its polarization directly reflect the number and orientation, respectively, of molecules adsorbed on the surface. Figure 1 depicts the quaternization reaction kinetics for step ii in the Scheme 1 (eq 1) and the average tilt (eq 2)<sup>19</sup> as a function of reaction time. Here

$$(I_{p-p}^{2\omega})^{1/2}(t) = (I_{p-p}^{2\omega})^{1/2}(t=\infty)(1 - \alpha_1 e^{-k_1 t} - \alpha_2 e^{-k_2 t}) \quad (1)$$

$$\frac{\chi_{zzz}^{(2)}}{\chi_{zyy}^{(2)}} = 2 \cot^2 \bar{\Psi} \quad (2)$$

$I_{p-p}^{2\omega}$  is the relevant SHG response intensity (intensity of frequency-doubled light),  $\alpha_1$  and  $\alpha_2$  are constants,  $k_1$  and  $k_2$  are kinetic rate constants, and ( $\bar{\Psi}$ ) is the average tilt angle of the chromophore molecular axes from the surface normal. Interestingly, the kinetics do not conform to a classical Langmuir chemisorption model,<sup>20</sup> but rather are better described by a two-stage process involving a rapid ( $k_1 \approx 10^{-4}$  (s<sup>-1</sup>)) initial coverage followed by a slower ( $k_2 \approx 10^{-5}$  (s<sup>-1</sup>)) second phase. Biphasic growth in alkylthiol self-assembly kinetics on gold<sup>12</sup> and coverage-dependent kinetic behavior in other chemisorption processes are not unprecedented.<sup>22</sup> In the present case,  $\bar{\Psi}$  increases rapidly in the early stages of monolayer formation and then plateaus. A significant tilt angle increase with increasing chromophore coverage suggests a cooperative response to electrostatic and steric packing forces. The surface chromophore density can also be evaluated using this information and, in combination with  $\beta_{zzz}^{\text{calcd}}$  and a 25 Å estimated film thickness, yields  $\sim 2 \times 10^{14}$  molecules/cm<sup>2</sup>. The 49 Å<sup>2</sup>/molecule "footprint"



**Figure 2.** Solid-state *in situ* SHG measurements of topotactic chromophore quaternization (step ii, Scheme 1) for a propyl bromide (**1b**)-functionalized surface (step i, Scheme 1) as a function of temperature. Inset: evolution of stilbazolium chromophore coverage as a function of time at 180 °C in air; the solid line is theoretical curve fit to eq 1.

compares favorably with that for LB films containing a similar chromophore substituent.<sup>24</sup>

These *in situ* SHG studies indicate that the rate-limiting step in the *solution phase* self-assembly process is the quaternization reaction, which is only complete after  $\sim 100$  h of reaction time. Although S<sub>N</sub>2 reactions are in principle more rapid in polar solvents, significant side reactions of **2** are observed in polar solvents.<sup>25</sup> While nonpolar solvents result in films with greater NLO response,<sup>26</sup> the assembly process is slowed by the lower solubility and lower reactivity of **2**. A solution to this dilemma was to devise *solvent-free* approaches in which chromophore precursor concentration is maximized and this pseudo-first-order reaction thus accelerated. A *topotactic* approach to molecular self-assembly was developed to address such a synthetic problem.<sup>27</sup> Solventless topochemical quaternization can be effected in two ways: "solid-state" or chemical vapor deposition (CVD) routes. The "solid-state" assembly is effected by simply spin-coating a thin film ( $\sim 100$  nm) of **2** on a prefunctionalized (**1b**) substrate followed by mild heating *in vacuo*. For CVD, **2** is passed directly in the vapor phase over the heated, prefunctionalized substrate.

*In situ* SHG studies were conducted in the "solid-state" mode in which the prefunctionalized substrate was placed on the hot stage of the SHG measurement apparatus<sup>27a</sup> at room temperature in air. The temperature was ramped at 3 °C/min to 160 °C, held for 1.0 h, and then ramped at 2 °C/min to 230 °C. The quaternization reaction is initiated at  $\sim 110$  °C (Figure 2), and the SHG response shows no decay after 1.0 h at 160 °C and no decrease on ramping to 230 °C. This is an improvement over LB films which are thermally

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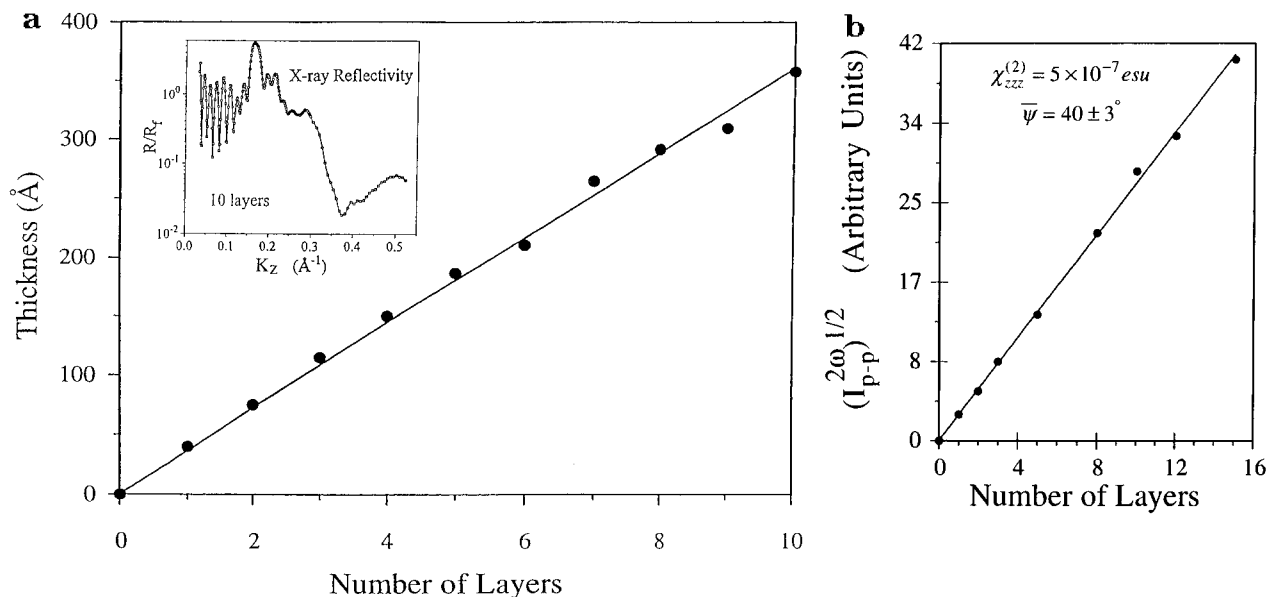
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**Figure 3.** Plot of (a) X-ray reflectivity derived thicknesses and (b) the square root of the SHG response versus the number of chromophoric layers in a toptotactically-derived (1b) stilbazolium superlattice. The lines are linear least-squares fits to the data. Inset of panel a: normalized X-ray reflectance plotted versus the incidence X-ray wave vector ( $K_z$ ) for a 10-layer specimen.

unstable at temperatures barely above 25 °C and Zr-PO<sub>3</sub>/PO<sub>4</sub> self-assembled materials where decomposition begins near 150 °C.<sup>13e</sup> A preliminary investigation of the “solid-state” quaternization reaction kinetics was carried out at 180 °C (inset, Figure 2). The reaction is complete in ~3 min, and no decay in SHG is observed for the next 80 min when the sample is maintained at 180 °C in air. At an input light wavelength of  $\lambda_0 = 1064$  nm, this film exhibits a bulk, second-order NLO response,  $\chi_{zzz}^{(2)}$  of  $7 \times 10^{-7}$  esu, which is comparable to the highest responses obtained for poled polymers<sup>2</sup> as well as for the far slower solution phase self-assembly process.<sup>25</sup> The kinetics of the “solid-state” process can also be fitted to eq 1 where the rapid initial chemisorption stage occurs with  $k_1 = 21(4) \text{ s}^{-1}$ , and a second, slower process with  $k_2 = 1.1(1) \text{ s}^{-1}$ . Thus, the toptotactic self-assembly process is approximately 5 orders of magnitude more rapid than the analogous process in solution. The rapidity does not allow detailed investigation of microstructural evolution;<sup>16</sup> however, upon completion of the chemisorption, the average chromophore tilt angle is  $40 \pm 3^\circ$ , comparable to the solution phase result.

### Superlattice Construction

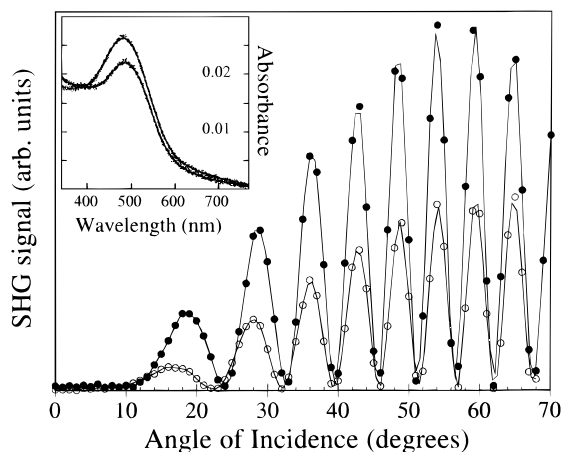
Self-assembled multilayer structures are accessible with simple hydrocarbon and fluorocarbon chains.<sup>28</sup> However, attempts to assemble more complex, functional structures via metal–ligand interactions<sup>13e,29</sup> or alternate deposition of polymers having opposite charges<sup>30</sup> have frequently resulted in less than perfect heterostructures. Our efforts to refine the chemistry

of superlattice self-assembly are directed toward development of versatile synthetic tools for more complex multifunctional structures. A first-generation synthetic approach to NLO-active multilayers (Scheme 1 with poly(vinyl alcohol) (PVA) as an interlayer spacer between steps iii and i) yielded assemblies containing up to five chromophoric layers.<sup>9a</sup> A second-generation solution phase approach effected without PVA planarization produced superlattices with up to nine chromophoric layers.<sup>9c</sup> Capping step iii was found to be essential for stable, acentric multilayers in spite of the fact that the reaction chemistry can tolerate omission of that step (reaction of the trichlorosilane coupling agent with the chromophore hydroxyalkyl units). The aforementioned *topotactic* process<sup>27</sup> now enables rapid and efficient construction of chromophoric superlattices with excellent NLO performance and structural regularity. The superlattice thicknesses calculated from X-ray reflectivity experiments (Figure 3a) exhibit a monotonic increase as a function of the total number of assembled layers, demonstrating regular periodicity. Data for a 10-layer sample (inset, Figure 3a) exhibit a maximum at  $K_z = 0.17 \text{ \AA}^{-1}$ , which is a “Bragg” peak due to X-ray scattering from individual layers. The derived interlayer spacing of  $36 \pm 1 \text{ \AA}$  is in good agreement with other thickness data and molecular models. Figure 3b shows that the SHG signal intensity depends quadratically on the number of layers, demonstrating not only structural regularity but also preservation of noncentrosymmetric packing as subsequent layers are added. A  $\chi^{(2)}$  value of  $\sim 5 \times 10^{-7}$  esu ( $\sim 200 \text{ pm V}^{-1}$ ) at  $\lambda_0 = 1064$  nm is deduced from the slope. The adherence to quadratic  $I^{2\omega}$  behavior and the distinctive X-ray reflectivity data are characteristic of a periodic structure without net centrosymmetry of the molecular building blocks. Thus, it is possible to maintain a high degree of acentric chromophore alignment and interlayer spacing *via* this growth process. Atomic force microscopy (AFM) measurements indicate relatively smooth surfaces with RMS roughness on the order of 12 Å for a 10-layer (360 Å) sample.<sup>27d</sup>

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**Figure 4.** SHG intensity as a function of fundamental light beam incident angle (normal to the glass surface) from a glass slide having a self-assembled **1a**-derived stilbazolium monolayer on either side before (○) and after (●) ion exchanging chloride for ethyl orange (eq 3). The interference patterns arise from the phase difference between the SHG light waves generated at either face of the glass slide during propagation of the fundamental light wave. Inset: monolayer UV-vis absorption spectra before (lower curve) and after (upper curve) ion exchange.

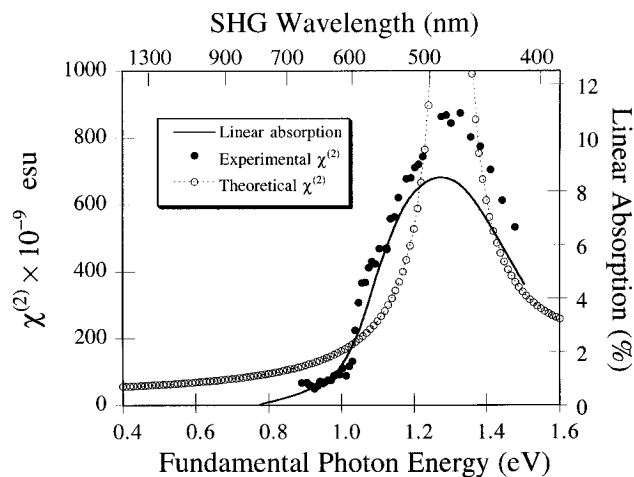
### Descriptive Chemistry. Ion-Exchange Processes

The stilbazolium halide chromophores in these self-assembled structures have a salt-like nature (Scheme 1), raising the question of whether the anion exchange can be used to tailor microstructure and optical response by metathesis with anions of differing size, shape, and hyperpolarizability. Such ion-exchange methodology<sup>31</sup> would represent a novel technique to manipulate film properties and to investigate chromophore environmental effects. Facile ion exchange of the chloride ions in **1a**-derived monolayers can be effected with iodide and *p*-aminobenzenesulfonate anions, as well as with anionic dyes, such as ethyl orange and Eosin-B,<sup>26</sup> which have substantial  $\beta$  values of their own. This leads to significant enhancement of the SHG response efficiency ( $\sim 50\%$  increase in  $\chi_{zzz}^{(2)}$ ) of the films (Figure 4). The average chromophore tilt angles does not change significantly on ion exchange ( $40 \pm 2^\circ$  before vs  $42 \pm 2^\circ$  after). The charge-transfer transitions of the stilbazolium and ethyl orange components (sodium salt,  $\lambda_{\max} = 474$  nm) overlap; thus, an increase in optical absorption is observed (inset, Figure 4) upon exchange of chloride for ethyl orange. Under room temperature exchange conditions, the maximum extent of chloride exchange is  $\sim 50\%$ .<sup>31</sup>

The origin of  $\chi_{zzz}^{(2)}$  enhancement in the ion-exchanged stilbazolium-containing monolayers has been explored theoretically<sup>32</sup> using a semiempirical quantum chemical approach.<sup>14</sup> The cation-anion environmental effects on SHG response were studied for iodide and *p*-aminobenzenesulfonate interactions with the stilbazolium cation. It is found that different anion-cation packing configurations are responsible for the greater SHG response. In particular, decreases

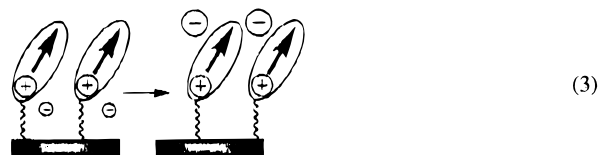
(31) (a) Roscoe, S. B.; Yitzchaik, S.; Kakkar, A. K.; Marks, T. J.; Lin, W.; Wong, G. K. *Langmuir* **1994**, *10*(4), 1337–1339. (b) Roscoe, S. B.; Yitzchaik, S.; Kakkar, A.; Marks, T. J.; Xu, Z.; Zhang, T.; Lin, W.; Wong, G. K., submitted for publication.

(32) Di Bella, S.; Fragalà, I.; Ratner, M. A.; Marks, T. J. *Chem. Mater.* **1995**, *7*, 400.



**Figure 5.** Experimental and calculated fundamental input light energy dependence of the second-order bulk NLO response,  $\chi_{zzz}^{(2)}$ , and the experimental linear absorption spectrum ( $\lambda_{\max} = 480$  nm), for a self-assembled film derived from stilbazolium chromophore **3**.

in the distances between stilbazolium donor substituent and bulkier anions lead to increased molecular hyperpolarizabilities and thus greater bulk SHG responses (eq 3).



It is found that ion-exchange processes are facile only in films having relatively low chromophore number densities ( $\geq 100 \text{ \AA}^2/\text{molecule}$ : about 50% coverage) and which are uncapped (monolayers without siloxane networks connecting the head groups). These results demonstrate that monolayers prepared under optimal conditions are dense, that the anions are trapped in such structures, and that the capping agent indeed protects the chromophores with a dense siloxane overlayer. The utility of surface anion metathesis to engineer optical properties of thin film materials offers possibilities of tailoring the local environment on the molecular level, for example, creating refractive index gradients for waveguides. Moreover, mild exchange reactions could be utilized in cases where direct anion insertion reactions might deform a chemically delicate building block.

### $\chi_{zzz}^{(2)}$ Dispersion and a Prototype Device for Doubling the Frequency of Input Light

An optical parametric amplifier (OPA)<sup>33</sup> was used to provide a tunable light source for studying the SHG response of the self-assembled films over a broad range of input light frequencies (the dispersion).<sup>34</sup> Such measurements are important for understanding the basic mechanism of NLO response as well as for acquiring device design information. As seen in Figure 5, the output signal of the second-order SHG

(33) (a) Lundquist, P.; Yitzchaik, S.; Zhang, T.; Kanis, D. R.; Ratner, M. A.; Marks, T. J.; Wong, G. K. *Appl. Phys. Lett.* **1994**, *64*, 2194. (b) Yitzchaik, S.; Lundquist, P.; Lin, W.; Kanis, D. R.; Ratner, M. A.; Marks, T. J.; Wong, G. K. *Mater. Res. Soc. Symp. Proc.* **1994**, *351*, 119.

(34) For an alternative approach, see: Shi, R. F.; Wu, M. H.; Yamada, S.; Cai, Y. M.; Garito, A. F. *Appl. Phys. Lett.* **1993**, *63*, 1173.

response ( $I^{2\omega}$ ) closely tracks the linear absorption spectrum, with the film  $\lambda_{\max} = 480$  nm ( $2\omega = 2.6$  eV) corresponding to the resonant (i.e., near  $\lambda_{\max}$  which provides an enhancement mechanism)  $\chi^{(2)}_{\max} = 9 \times 10^{-7}$  esu, an exceptionally large response for organic thin films.<sup>2</sup> The high values of  $\chi^{(2)}$  away from  $\lambda_{\max}$  ("off resonance"  $\sim 10^{-7}$  esu) suggest the potential use in NLO waveguiding device applications (*vide infra*).

The origin of the  $\chi^{(2)}$  dispersion was investigated theoretically using the aforementioned quantum chemical approach<sup>16</sup> for calculating the hyperpolarizability as a function of fundamental input frequency. A classical "two-level" description<sup>2,14a</sup> assumes that a single chromophore charge-transfer transition (usually HOMO  $\rightarrow$  LUMO), describes the hyperpolarizability ( $\beta_t$ , eq 4), where  $f_{ge}$  is the oscillator strength,  $\hbar\omega_{ge}$  is the energy of the charge-transfer excitation between ground state (g) and first excited state (e), and  $\Delta\mu_{ge}$  is the difference in dipole moment between the two states. This model predicts resonances (enhance-

$$\beta_t = \frac{3e^2}{2} \frac{\hbar\omega_{ge}f_{ge}\Delta\mu_{ge}}{[(\hbar\omega_{ge})^2 - (\hbar\omega)^2][(\hbar\omega_{ge})^2 - (2\hbar\omega)^2]} \quad (4)$$

ments) in the hyperpolarizability at frequencies  $\omega$  and  $2\omega$ , the latter of which is clearly visible in Figure 5. However, the experimental results exhibit a somewhat broader  $\chi^{(2)}$  response. The origin of the narrower calculated response is attributed to the neglect of vibrational effects.<sup>33b</sup>

A hybrid "sandwich" waveguide configuration<sup>35</sup> was next used with the chromophoric superlattices to

(35) (a) Yitzchaik, S.; Lundquist, P.; Lin, W.; Marks, T. J.; Wong, G. K. *SPIE Conf. Proc.* **1994**, 2285, 282. (b) Lundquist, P.; Yitzchaik, S.; Lin, W.; Wong, G. K.; Marks, T. J. Submitted.

(36) (a) Risk, W. P.; Lau, S. D.; Fontana, R.; Lane, L.; Nadler, Ch. *Appl. Phys. Lett.* **1993**, 63, 1301. (b) Flörshheimer, M.; K pfer, M.; Bosshard, C.; Looser, H.; G nter, P. *Adv. Mater.* **1992**, 4, 795.

fabricate a simple device which doubles the frequency of incident laser light over a long confined interaction path. Thus, a planar waveguide was constructed in which an optically linear polystyrene guiding layer was coated on top of an NLO-active layer assembled on glass. The linear guide (polystyrene) has good transparency for both fundamental input light ( $\omega$ ) and SHG light ( $2\omega$ ) without scattering or absorption losses. The self-assembled NLO region exhibits very high SHG conversion efficiencies ( $\chi_{zzz}^{(2)} = 5\text{--}7 \times 10^{-7}$  esu) and can thus be used in far thinner films (3–50 nm) than in typical SHG waveguide devices.<sup>2</sup> This multicomponent SHG waveguide exhibits SHG efficiencies<sup>35</sup> comparable to Langmuir–Blodgett film based devices having far thicker NLO-active layers.<sup>36</sup>

## Summary and Outlook

The approaches to and properties of the present self-assembled chromophoric superlattices should serve as prototypes for numerous fascinating possibilities in the field of supramolecular architectures. They complement routes involving mild solid-state syntheses<sup>1</sup> and secondary (noncovalent) aggregation<sup>2</sup> forces and should be considered in the future design of functional multimolecular assemblies. Such highly regular structures are intrinsically anisotropic in electrical and optical properties and thus may prove useful in a multitude of organic heterostructure-based molecular electronic and photonic devices.

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