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Single Reactor Route to Polar Superlattices. Layer-by-Layer Self-Assembly of Large-Response Molecular Electrooptic Materials by Protection−Deprotection

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Molecule-based photonic components such as electrooptic (EO) modulators promise greatly increased rates of information transmission by enhancing network speed, capacity, and bandwidth for data networking and telecommunications.[1] For these reasons, the synthesis and characterization of new organic EO materials with excellent optical, thermal, and chemical properties is a topic of great current scientific interest.[1−5] Of the synthetic approaches investigated,[1−4] efficient new self-assembly (SA) techniques are particularly promising and challenging because the resulting materials offer the potential of far higher EO coefficients and lower dielectric constants than those of established inorganic materials (e.g., $LiNbO_3$) and, because they are intrinsically acentric, they do not require electric field poling.[4] Moreover, growing robust chromophore arrays directly on silicon or related substrates would allow ready device integration. Chemisorptive siloxane-based SA[6] can yield robust, densely packed organic films.[4,6,7] However, while mono- and multilayer structures are known for simple hydro- or fluorocarbon chains,[7c] efficient fabrication of complex, structurally tailored *photonically/electronically functional* superlattices, and those with nanoscale control over polarity, has presented a far greater, largely unrealized goal.[4,7c,8,9]

It is known that stilbazolium-based multilayers exhibiting large EO responses ($\chi^{(2)} = 150-200$ pm/V) can be obtained by a laborious, iterative three-step procedure, the second of which involves inefficient spin-coating and vacuum treatment.[4a,b,9] Indeed, synthetic approaches available for assembling multilayers are limited in comparison to the great variety of applicable solution phase reactions. Importantly, monolayers containing nonpolar end groups are chemically inert toward many reagents, while iterative multilayer growth necessarily requires *continual regeneration of a constant and/or a large density of reactive surface sites*.[7a] Although several promising surface functionalization procedures have been reported,[10] there has been limited application to multilayers and none to optically/electronically functional siloxane-based structures. In this paper, we communicate a new all-"wet-chemical" protection−deprotection approach for the straightforward SA of large-response functional EO superlattices.

The present method involves iterative combination of (i) polar chemisorption of high-β chromophore monolayers, (ii) selective removal of chromophore *tert*-butyldimethylsilyl (TBDMS) protecting groups to gener-

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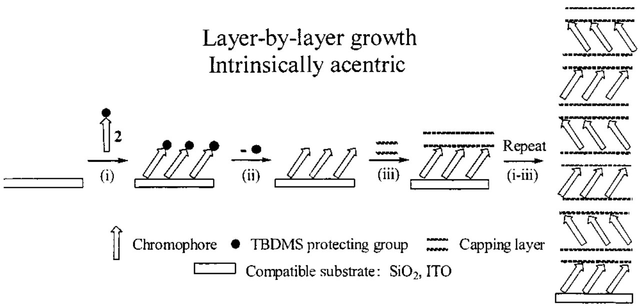
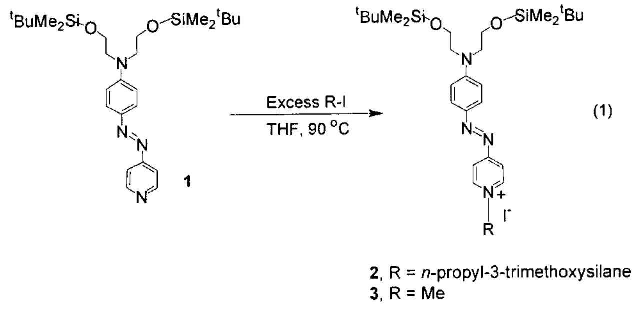


Figure 1. Schematic representation of the SA of **2**-based chromophoric superlattices by $^{n}Bu_4NF$ deprotection of the TBDMS-derivatized chromophore monolayers and "capping" of the resulting film with $Si_3O_2Cl_8$.

ate a large density of reactive hydroxyl sites, and (iii) capping of each "deprotected" chromophore layer with octachlorotrisiloxane (Figure 1). This latter step deposits a thin polysiloxane film (~8 Å thick) and is essential for stabilizing/planarizing acentric microstructures by providing interchromophore cross-linking.[4a,b,9] The present layer-by-layer construction can be efficiently carried out in a single reaction vessel, presaging ready automation.[11] The thermally and photochemically robust superlattices exhibit very large EO responses ($\chi^{(2)}$ ~ 220 pm/V), adhere strongly to glass, silicon, or indium tin oxide (ITO)-coated glass substrates, and are insoluble in common organic solvents.

Reaction of chromophore precursor 4-[[4-[*N*,*N*-bis-[(*tert*-butyldimethylsiloxy)ethyl]amino]phenyl]azo]-pyridine (**1**) with 1-iodo-*n*-propyl-3-trimethoxysilane results in quantitative formation of the new purple 4-[[4-[*N*,*N*-bis[(*tert*-butyldimethylsiloxy)ethyl]amino]phenyl]-azo]-1-*n*-propyl-3-trimethoxysilylpyridinium iodide salt (**2**; eq 1), which was fully characterized by conventional analytical techniques. Analogous 1-methylpyridinium



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salt **3** can be prepared using methyl iodide and has similar spectroscopic properties (e.g., the optical spectra of **2** and **3** in toluene exhibit a characteristic 93 nm red shift of the charge-transfer band vs chromophore precursor **1**).

The iterative chemisorptive SA process and the resulting multilayer structural regularity have been characterized by a full complement of physicochemical techniques: optical (UV–vis) spectroscopy, advancing contact angle (CA) measurements, X-ray photoelectron spectroscopy (XPS), synchrotron X-ray reflectivity (XRR), atomic force microscopy (AFM), and angle-dependent polarized second harmonic generation (SHG). The hydroxyl group deprotection (Figure 1, step ii) was examined by specular XRR, XPS, and CA measurements, which unequivocally reveal TBDMS group removal. XRR and XPS measurements on a **2**-based monolayer reveal an initial film thickness of 14.5 ± 0.5 Å and Si/N ~ 0.75, respectively. Treatment with $^{n}Bu_4NF$ in THF for 4 min at 25 °C results in a decrease of: (i) the film thickness by ~2.6 to 11.9 ± 0.5 Å and (ii) the electrons per unit area by ~16%, while XPS measurements reveal Si/N ~ 0.42. Complete TBDMS removal is expected to result in a ~32% decrease of electrons per unit area and Si/N ~ 0.25. Therefore, our observations indicate loss of ~50% of the TBDMS protecting groups. Further evidence of hydroxyl deprotection is obtained from aqueous CA measurements showing a decrease in θ_a of ~35° to 51 ± 4°. Because treatment of **1** with $^{n}Bu_4NF$ in solution results in quantitative formation of 4-[[4-[*N*,*N*-bis(hydroxyethyl)amino]phenyl]azo]pyridine by selective cleavage of *both Si–O bonds*,[9f] we suggest that the two TBDMS groups of each surface-bound chromophore **2** are chemically inequivalent (i.e., in many sites only one TBDMS group is present near the surface), resulting in a sterically less accessible TBDMS moiety. In support of this hypothesis, XRR reveals that the surface roughness ($\sigma_{\text{film-air}}$) *decreases* by ~1.3 to 3.8 ± 0.5 Å upon $^{n}Bu_4NF$ treatment of a **2**-based monolayer. Remarkably, the XRR-derived $\sigma_{\text{film-air}}$ width of the deprotected **2**-based monolayer is comparable to that of a highly ordered self-assembled octadecyltrichlorosilane film on silicon,[7b,12] demonstrating that this "protection–deprotection" approach affords smooth, well-organized

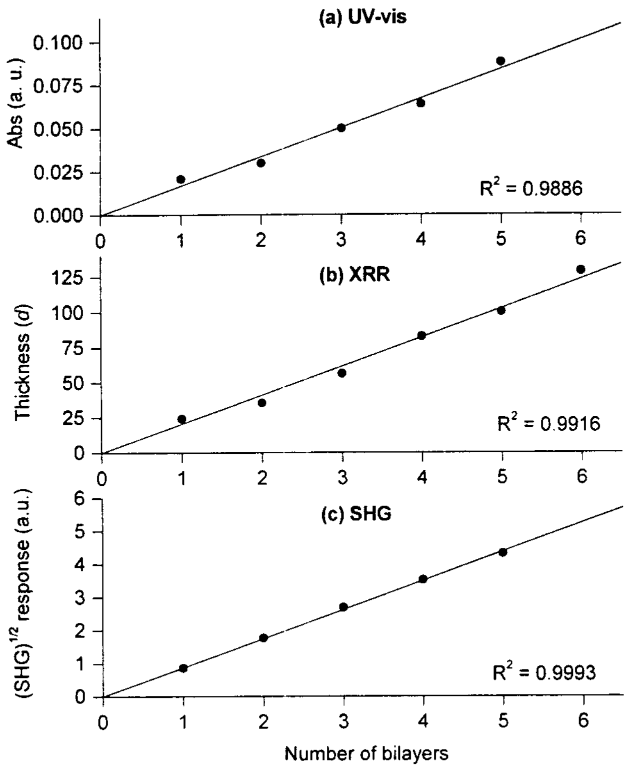

Figure 2. Linear dependence with the number of bilayers of three chromophoric superlattice physical properties: (a) Transmission optical absorbance (abs: arbitrary units) at λ = 580 nm. (b) Thickness (*d*) in angstroms derived from specular X-ray reflectivity measurements. (c) Square root of the 532 nm SHG intensity ($I^{2\omega}$; arbitrary units).

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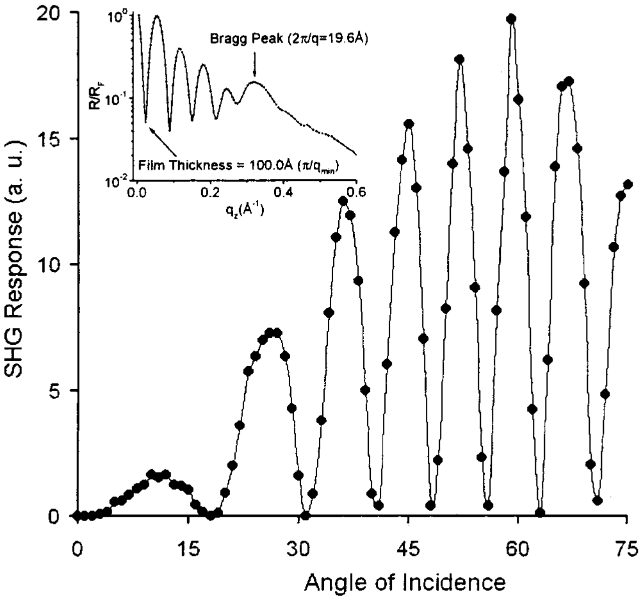

Figure 3. SHG response intensity as a function of the fundamental beam incident angle from a float glass slide having a SA multilayer ($n = 5$) on either side. Inset: Normalized X-ray reflectance plotted vs the wave vector for a sample with five bilayers.

films without affecting the Si−O bonds attached to the substrate.

The linear dependence of the HOMO−LUMO CT absorbance at 580 nm and the XRR-derived film thickness on the number of bilayers unambiguously demonstrates that equal densities of uniformly oriented chromophores are deposited in each assembled layer (Figure 2a,b). From the slope of the XRR data, an average interlayer spacing of 20.52 ± 0.45 Å is deduced. The "Bragg" peak maximum in the reflectivity data due to scattering from essentially identical layers ($K_z = 0.32$ Å^{-1}; Figure 3, inset) yields an interlayer spacing of 19.6 ± 1 Å. Advancing aqueous CA measurements support the expected surface wettabilities and repeat regularly with each SA step: TBDMS (i), ~86°; ethanolamine (ii), ~51°; −Si−OH (iii), ~25°.[9] AFM measurements on a six-bilayer sample reveal a smooth, essentially featureless surface with an root mean square roughness <8%, consistent with high structural regularity within each individual layer.

Polarized angle-dependent SHG measurements were made at $\lambda_0 = 1064$ nm in the transmission mode. For a regular, polar multilayer, the intensity ($I^{2\omega}$) should scale quadratically with the number of layers,[13] because the incident light wavelength is large compared to the film thickness ($l = 20.52\ (\pm 0.45) \times n$ Å; n = number of bilayers). The observed linear dependence of $I^{2\omega}$ indicates uniform chromophore polar alignment and structural regularity in layer thickness (Figure 2c), in full agreement with the aforementioned optical and XRR data (Figure 2a,b). The characteristic SHG interference pattern for each bilayer demonstrates that the quality and uniformity of the organic film is identical on both sides of the substrate and can be fit to eq 2,[13] where Ψ is the average orientation angle between the surface normal and the principal molecular tensor component (Figure 3; $n = 5$). A large nonlinear susceptibility, $\chi^{(2)}{}_{zzz} \sim 5.3 \times 10^{-7}$ esu (~220 pm/V) and $\Psi \sim 36°$, is obtained by calibration vs quartz. The macroscopic EO coefficient, $r_{33} \sim 80$ pm/V, is estimated using the index of refraction, $n = 1.51$ at $\lambda = 1064$ nm (eq 3).[1] An average chromophore surface density N_s of $\sim 2 \times 10^{14}$ molecules/cm^2 is then estimated for each bilayer using the ZINDO-derived molecular hyperpolarizability (β_{zzz}) value of 984 $\times 10^{-32}$ esu at 1064 nm,[9f] the experimental $\chi^{(2)}_{zzz}$, and the average interlayer spacing l (eq 4). The derived N_s corresponds to an average 'footprint' of ~50 Å^2/chromophore.

$$\chi^{(2)}_{zzz}/\chi^{(2)}_{zyy} = 2 \cot^2 \Psi \qquad (2)$$

$$r_{33} = -2\chi^{(2)}_{zzz}/n^4 \qquad (3)$$

$$N_s = l\chi^{(2)}_{zzz}/(\beta_{zzz} \cos^3 \Psi) \qquad (4)$$

These results with a known model chromophore demonstrate an efficient new "one-pot" approach to assembling organic superlattices having excellent EO response properties. The present results argue that selective desilylation of protected functional groups[14] to generate reactive surfaces represents a new application of such proctective agents and will prove useful for assembly of many types of photonically/electronically functional siloxane multilayers. Moreover, the present physicochemical measurements clearly show that robust EO thin films can be constructed with subnanometer level control of the layer dimensions and with microstructural acentricity completely preserved as assembly progresses.

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Supporting Information Available: Synthesis and characterization of compounds **2** and **3** and the formation of chromophoric superlattices. This material is available free of charge via the Internet at http://pub.acs.org.

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