1962 *Chem. Mater.* **1999,** *11,* 1962−1965

Spontaneously Self-Assembled Polar Asymmetric Multilayers Formed by Complementary H-Bonds

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Received March 16, 1999
Revised Manuscript Received May 17, 1999

Ordered molecular assemblies can lead to materials with extremely high second-order nonlinear optical (NLO) properties.[1−3] Although organic molecules with high nonlinearities are well-known,[4,5] it has been difficult to design *bulk* materials in which such molecules are well-aligned. Generating ordered assemblies by the Langmuir−Blodgett (LB) technique often leads to metastable films and is only possible for a narrow range of molecular species[6] while chemical synthesis of covalently bound supramolecular structures on surfaces can be difficult and time-consuming.[7] The formation of polar multilayers by drop-casting is an attractive alternative, especially if such structures lead to thermodynamically stable *asymmetric* (head-to-tail) assemblies. Asymmetric assemblies are more desirable because the inherent nonlinear optical properties of the molecular layers are additive, whereas in symmetric systems, the nonlinear response cancels within each symmetric bilayer due to destructive interference.

In this work, we describe the preparation of a novel asymmetric assembly and use sum-frequency generation ($\omega_1 + \omega_2$) and second-harmonic generation (where $\omega_1 = \omega_2$) to determine the degree of structural order and the second-order nonlinear susceptibility (d_{33}), respectively. Sum-frequency generation (SFG)[8] is a general second-order nonlinear optical process that probes *only* noncentrosymmetric regions such as interfaces. In a typical experiment, spatial and temporal overlap of visible (ω_1) and IR pulses (ω_2) at the sample gives rise to light at $\omega_1 + \omega_2$ and this signal can be used to measure either electronic spectra by varying the visible excitation (ω_1) or vibrational spectra by tuning the IR frequency (ω_2). The spontaneously self-assembled, polar multilayer films (Figure 1), which consist of a melamine and barbituric acid interlocked hydrogen bonding network,[9−12] were grown by drop-casting on a silica substrate. One of the interesting features of these materials is that they are initially formed by weak intermolecular interactions (hydrogen bonds) and yet ultimately yield thermodynamically stable and robust macroscale structures with a net polar orientation.

Figure 1 outlines the synthesis of 5-[4-(dodecyloxyl)-benzylidiene]-2,4,6-(1*H*,3*H*)-pyrimidinetrione (DBP) and 2-amino-4,6-(didodecylamino)-*S*-triazine (ADT). DBP was synthesized by refluxing 4-dodecyloxylbenzaldehyde with barbituric acid in ethanol; ADT was obtained by treating 2-amino-4,6-dichloro-*S*-triazine with dodecylamine in DMSO with K_2CO_3 present. DBP and ADT have complementary H-bonding codes and spontaneously form supramolecular ribbons when mixed in a 1:1 ratio in chloroform. The formation of H-bonds in the supramolecular ribbon was confirmed by FTIR spectroscopy as indicated by the shift of the carbonyl, amide, and amino IR bands. The resulting supramolecular ribbon assembled perpendicular to the surface. The ribbon is asymmetric because ADT has twice as many alkyl chains as DBP. Bragg diffraction (X-ray) was observed at $2\theta = 2.16$, 3.18, and 4.28°, which shows that the DBP:ADT system is a multilayered lamellar structure. The *d* spacing value obtained from X-ray diffraction is 41 Å, in agreement with the ~40 Å supramolecular ribbon width obtained from molecular 3D modeling. The asymmetric DBP:ADT ribbon can pack into either a symmetric structure (head-to-head and tail-to-tail) or an asymmetric structure (head-to-tail). It is found that the asymmetric DBP:ADT ribbons assemble into a polar multilayer head-to-tail structure (*vide infra*). It is extremely unusual to find a dipolar system that will self-assemble into a polar multilayer because dipole−dipole repulsion typically leads to energy-minimized head-to-head (or tail-to-tail) structures. The formation of these supramolecular self-assemblies is driven primarily by the interplay of encoded six H-bonds, and secondarily by substrate−film and hydrophobic chain−chain interactions.

The films were characterized by FTIR-ATR spectroscopy, sum-frequency generation, and second-harmonic generation (SHG). The FTIR spectra were taken at 20° angle of incidence with 1 cm^{-1} resolution. SFG spectra were obtained by overlapping tunable mid-IR and 1064-nm beams at the sample surface. A Nd:YAG laser provided ~35 ps pulses at 1064 nm. The energy density at the sample was ~1 mJ/mm^2. The mid-IR beam (100 μJ/pulse near 2.8 μm) was obtained by optical paramet-

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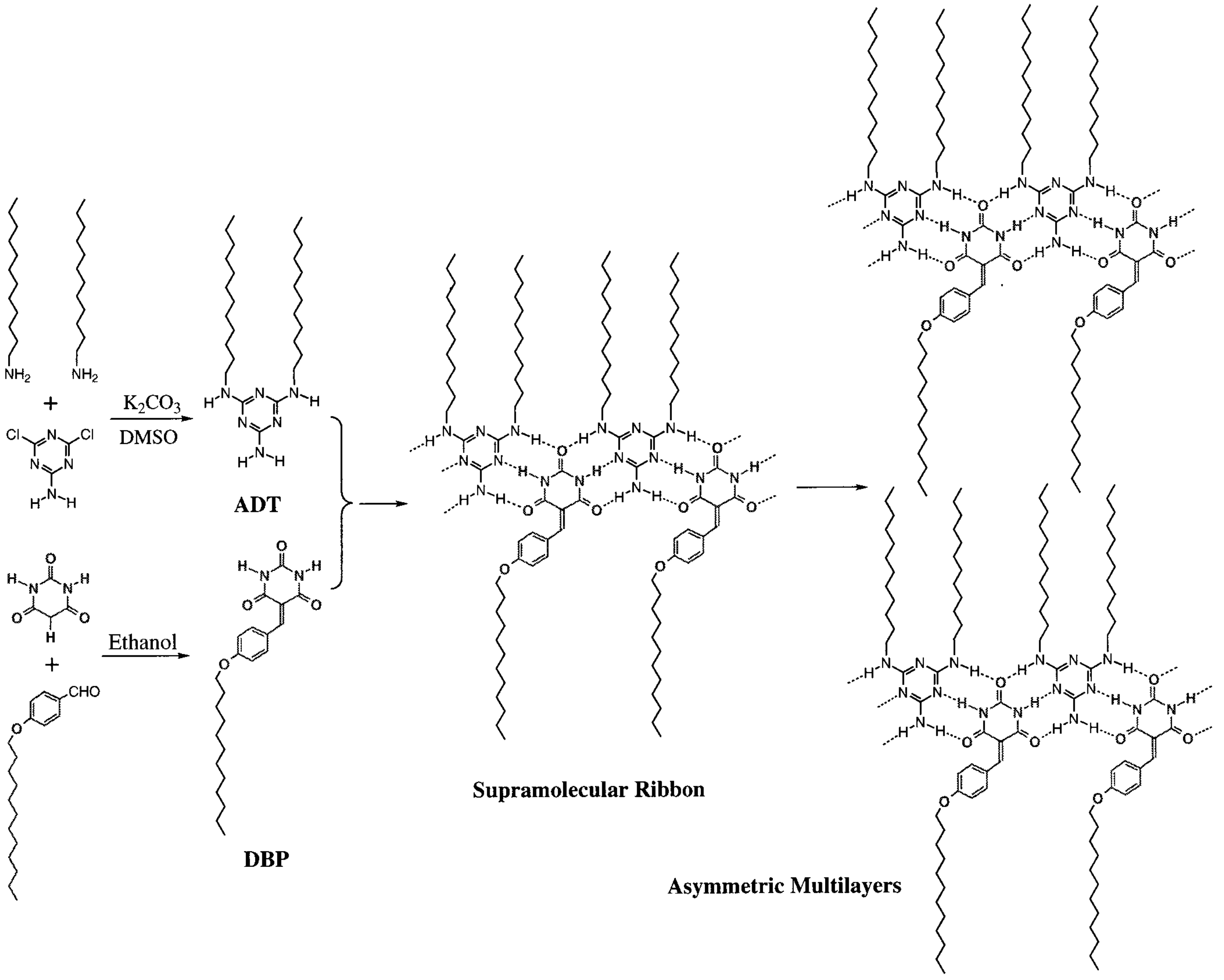

Figure 1. Synthesis of the supramolecular building blocks DBP and ADT, and the formation of asymmetric multilayer DBP: ADT structure.

ric generation (OPG) and amplification (OPA) in BBO and KTP nonlinear crystals.[13−15] All input beams were p-polarized. The transmitted p-polarized SFG signal in the red spectral range was spatially separated from the two input beams and detected using a PMT and gated integrator. The SHG experimental procedure and method for deducing the second-order tensors have been described elsewhere.[16−18]

The FTIR-ATR spectrum of the film grown on Ge and the SFG spectrum of the film grown on Si(100) are shown in parts a and b of Figure 2, respectively. The SFG spectrum in the C−H stretching region was fitted[19] to obtain the positions of the vibrational resonances. The fit to the spectrum is shown by the solid line in Figure 2b. The four curves shown below the spectrum are the deconvolved Voigt profiles, corresponding to the four resonances observed. All the observed SFG features correspond to vibrational resonances observed in the FTIR-ATR spectrum (Figure 2a). The broadened alkyl resonances in the SFG spectrum likely result primarily from the in-plane disorder which leads also to azimuthal symmetry of the SHG. The prominent infrared methyl symmetric stretch (r^+) in the SFG spectrum appears near 2875 cm^{-1}. This is exactly the same frequency of r^+ observed in the SFG spectra of close-packed alkanethiols chemisorbed on gold.[20] The weak shoulder near 2850 cm^{-1} is assigned to the symmetric (d^+) methylene resonance.[21] The broad feature between 2900 and 2940 cm^{-1} is probably due to the overlapping asymmetric methylene (d^-) and the Fermi resonance of the methyl (r^+_{FR}) stretches. The overlap of these fea-

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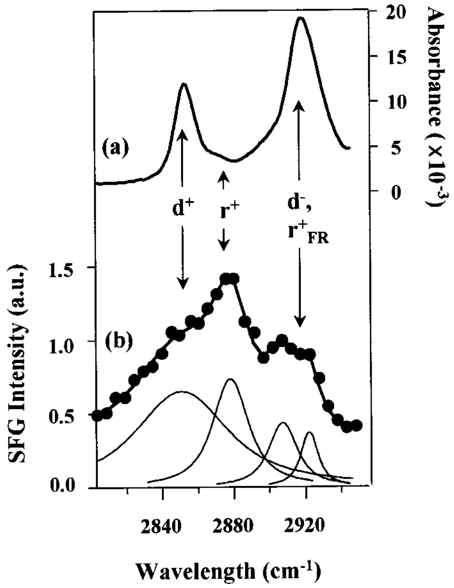

Figure 2. (a) FTIR-ATR spectrum of the DBP:ADT multilayer from a single p-polarized reflection at the center of the flat surface of a Ge hemisphere and (b) ppp-polarized vibrational SFG spectrum of the multilayer. The main feature in the SFG spectrum is the symmetric methyl resonance (r^+). The solid line is a fit to the SFG data points. The deconvolved resonance profiles are shown below the SFG spectrum. All spectra were obtained at room temperature.

tures has been observed before in the SFG spectra of surfactant films.[22] The symmetric methyl resonance appears as only a weak shoulder in the FTIR-ATR spectrum. In contrast, the methyl stretch is the dominant feature in the SFG spectrum, with relatively weak methylene resonances (intensity ratio $d^+/r^+ \ll 1$), despite the fact that the number ratio of methylene to methyl groups is 11. Ward[22] and Conboy[23] et al. found that the relatively strong methylene features (intensity ratio $d^+/r^+ \gg 1$) observed in SFG spectra are an indication of structural disorder in the alkyl chains. In contrast, the SFG spectrum in this work indicates that the bulk structure of the *thin* film normal to the surface is well-ordered with few gauche defects in the alkyl chains. The large broadening of d^+ suggests that the small population of gauche defects in the alkyl chains is not localized, but random along the chain. Thus, the variation in the local environment of the SFG-active methylene groups would lead to inhomogeneous (Gaussian) broadening of the line width.[21,24,25] The presence of the relatively strong methyl feature also demonstrates that there is a net polar orientation of methyl groups with respect to the surface. If the bulk molecular structure resulted in equal numbers of methyl groups pointing "up" and "down" (as in most multilayer LB films), one would expect complete cancellation of the signal from methyl groups with opposite orientations, resulting in zero observed SFG.[26] The fact that a prominent methyl resonance is observed is consistent with the packing structure of the self-assembly, i.e., twice as many methyl groups pointing in one direction than in the opposite direction (see Figure 1). The SFG spectrum, therefore, is consistent with the asymmetric arrangement of the methyl groups between stacked ribbons.

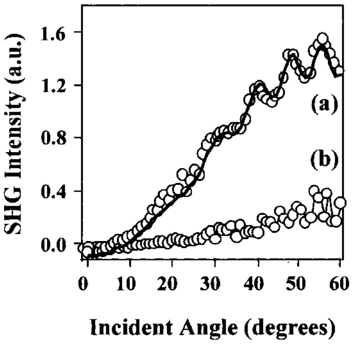

Figure 3. (a) The p-in, p-out and (b) s-in, p-out polarized SHG intensity from a 300 Å multilayer film drop-cast on a silica substrate as a function of incident angle at 532 nm. The solid line in a is a fit to the data points as discussed in the text.

The transmitted p-polarized second-harmonic (SH) intensity from the multilayer film drop-cast on one side of a silica substrate for both s- and p-polarized incident excitation is shown in Figure 3. As expected, no s-polarized SH signal was observed using s-polarized excitation. Very little p-polarized SH signal was observed using s-polarized excitation (Figure 3b). Two main features are observed in the data: the increase in SH signal at high angles of incidence and the weak interference fringes. The fringes are thought to arise from the interaction of the SH waves from the multilayer and the opposite surface of the silica substrate.[16,17] These films typically have uniaxial symmetry about the surface normal,[18,27] thus yielding only two independent tensor elements (d_{33} and d_{31}). With the film thickness determined to be 300 Å by single wavelength ellipsometry[28] (using a refractive index of 1.55 for the multilayer), the magnitude of the nonlinear susceptibility is $d_{33} = 3.2$ pm/V and the average angle of the chromophore dipoles is approximately 45° with respect to the surface normal.

The SH intensity from well-ordered thin films increases quadratically with the number of layers. Drop-casting does not readily allow layer-by-layer control of film thickness and drop-cast films are typically much thicker than films made in Langmuir–Blodgett troughs or by ionic assembly techniques, for example. We varied the film thickness by increasing the number of drops on the substrate. Figure 4 displays the square root of the SH intensity at an incident angle of 50° versus the observed absorbance, *A*, near 400 nm, a maximum in the absorption spectrum. The absorbance at 400 nm increased approximately linearly from 1 to 5 drops and is therefore directly proportional to thickness. Thus Figure 4 shows that the relative SH intensity increased with film thickness, suggesting that the DBP:ADT multilayer retains an ordered structure within the bulk. The attenuation of the SHG response from the thicker

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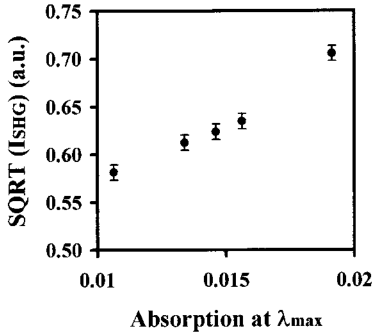

Figure 4. Plot of the square root of the SH intensity as a function of absorption at $\lambda_{max} = 400$ nm. The incident angle of the fundamental beam was 50°. The nonzero intercept indicates that these thick films are somewhat disordered, as described in the text. The error bars show the variation in the SH response from each film as the fundamental beam was scanned across the sample (8 mm) to assess the uniformity of the film. Annealing the sample or allowing the solvent to evaporate slowly improved the quality of the film as did drop-casting from certain solvents such as a 1:1 mixture of ethanol and acetone.

films indicates that the degree of polar order decreases somewhat with film thickness. This phenomenon is also observed in the FTIR studies. In an ATR experiment with a Ge hemisphere as the internal reflection element, both CH_2 vibration frequencies ($d^-= 2916$ and $d^+=2849$ cm^{-1}) increased by ~ 5 cm^{-1} when the incident angle was varied from 75° to 20°. The resolution of the FTIR was 1 cm^{-1}. At a large incident angle the IR beam probes mostly the structure of the film at the substrate–film interface, whereas the beam penetrates the bulk at small incident angles. Low CH_2 vibration frequencies at 75° indicate highly ordered alkyl chains while high CH_2 vibration frequencies at 20° suggest that there are more gauche structures introduced by the disorder. The FTIR results suggest that the alkyl chains, and therefore the attached chromophores, become more disordered away from the Ge substrate. Both the SHG and FTIR data support the conclusion that the layers near the film/substrate interface are more ordered.

In summary, we have shown that drop-cast films of a nonlinear chromophore spontaneously self-assemble into ordered NLO-active multilayers with a head-to-tail geometry. The relatively large magnitude of d_{33} can be attributed to the combination of polarizable, delocalized π-electrons associated with the DBP unit, as well as the spontaneous assembly into a relatively ordered, polar structure. The SFG spectrum from the film shows the appearance of prominent methyl resonances indicating a high degree of polar ordering, with twice as many methyl groups pointing in one direction as in the opposite direction. The relatively weak methylene resonances in the films show that the alkyl chains in the multilayer are nearly all-trans with few gauche defects.

Acknowledgment. We thank Dr. Atul Parikh (LANL) for his assistance with the ellipsometry measurements. This work was supported by Los Alamos National Laboratory Directed Research and Development, under the auspices of the U.S. Department of Energy.

CM990158M