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A Molecular Architectural Approach to Novel Electro-Optical Materials

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The goal is to construct polar multilayers with nonlinear optical coefficients larger than classical inorganic crystals such as KDP or quartz. The strategy is to use various chemical interactions such as covalent bonds or hydrogen bonding to build polar structures. We have synthesized novel barbituric acid and melamine derivatives that will spontaneously self-assemble into a supramolecular ribbon according to their complementary H-bond motif. This supramolecular ribbon can then stack into a polar multilayer structure as verified by sum frequency generation ($\omega_1+\omega_2$) or second harmonic generation (when $\omega_1 = \omega_2$). Second harmonic generation yields a value of $d_{33} = 3.2$ pm/V for the self-assembled films and sum frequency generation shows a net polar orientation of the methyl groups in the multilayer along the surface normal. X-ray diffraction confirms the layered structure and produces the periodicity of ~41 Å, which corresponds well to the width of the supramolecular ribbons (~40 Å).

Background and Research Objectives

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 the 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

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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 report, 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. The spontaneously self-assembled, polar multilayer film (Figure 1) was grown by drop casting on a silica substrate. Using single wavelength ellipsometry to measure film thickness,[8] the average molecular orientation of the chromophores is also determined. 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.

Importance to LANL's Science and Technology Base and National R&D Needs

This project supports several Laboratory core competencies and missions. First, advanced materials remain as one of the core competencies at Los Alamos National Laboratory because the fundamental of materials structures and materials properties is critical in many important applications, including defense-related applications. Understanding materials structures and ordering at the molecular level is the key to solving issues in existing materials applications and to predict future high performance materials.

Secondly, self-assembled materials are closely related to biological systems. Therefore, understanding molecular self-assemblies, their structures, and their physical properties would lead to new design principles of chemical sensors or biosensors. Both chemical sensors and biosensors are playing a key role in the on-going thrust area of Threat Reduction here at the Laboratory. Interactions of molecular self-assemblies at device surfaces are vital to information transduction of sensor technology. This project provides fundamental scientific understanding and insights into molecular interactions, ordering, and their collective effects.

Thirdly, nonlinear optical materials hold great potential applications in optical computing. Therefore this project indirectly supports the effort to build a base of scientific knowledge in advanced computing at the Laboratory. A principal example of the potential application for these electro-optic materials is in optical switching and data transmission. Successes in preparation of these materials would allow faster and cheaper routing of information along fiber-optic networks and enable users to interconnect economically to high-quality telecommunication systems.

This work will build a fundamental understanding of new synthetic approaches to electro-optic materials to address limitations of existing materials. Major industries such as IBM, Rockwell International, and Bell Labs have pilot programs in organic electro-optic devices as part of their strategic business plan. DOE and DoD also could benefit directly from the results of this research.

Several Los Alamos groups have a unique perspective on designing, constructing, and modeling superior thin-film-based materials with optimized nonlinear optical properties. We have developed a unique technique—molecular self-assembly—in which molecules are organized into ordered arrays by covalently bonding to the substrate. Self-assembly technology represents a new and exciting approach to constructing super-structures on two-dimensional surfaces in molecular architectures. To realize the promise of this materials synthesis approach, a comprehensive understanding of the physical mechanisms responsible for self-assembly must be developed. While essential for the development of electro-optic materials, this understanding will also have an impact on the development of optimized thin films for applications including chemical and biological sensors, light harvesting materials, and charge and energy transport systems.

Scientific Approach and Accomplishments

The major accomplishment in this project is the advances in fundamental understanding of molecular self-assemblies. Theoretical calculations were carried out on the assemblies of synthetic polymers using a rigid-rod model. The modeling results agree with the experimental observation in the x-ray reflectivity measurements. We found that x-ray reflectivity is a very valuable technique at understanding the molecular structures of the self-assembled systems. Critical parameters such as film thickness, roughness, and electron density can be deduced from these measurements. In addition, electronic transport properties in these self-assembled systems were also investigated and novel electronic transport properties were observed. Molecular self-assemblies based on covalent bonding, ionic interactions, or hydrogen bonding were investigated. In this report, we will only discuss the hydrogen bonding system; the readers are referred to the list of publications for further information on other systems.

Figure 1 outlines the synthesis of a pair of building blocks that have a perfect match to each other via hydrogen bonding; namely, 5-(4-dodecyloxylbenzylidiene)-2,4,6-(1H,3H)-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 is asymmetric because ADT has twice as many alkyl chains as DPB. Bragg diffraction (x-ray) was observed at $2\theta = 2.16$ and 4.28 degrees, which shows that the BDP-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 three-dimensional modeling. The asymmetric BDP-ADT ribbon can pack into either a symmetric structure; i.e., a head-to-head and tail-to-tail arrangement or an asymmetric structure; i.e., a head-to-tail motif. It is found that the asymmetric BDP-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 6 H-bonds, and secondarily by hydrophobic chain - chain and π -π interactions.

The second harmonic generation (SHG) experimental procedure and method for deducing the second-order tensors have been described elsewhere[9-11] and here we will only summarize the sum-frequency generation (SFG) experiment. SFG spectra were obtained by overlapping tunable mid-IR and 1064 nm beams at the sample surface. A Nd:YAG laser provided ~50 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 parametric generation (OPG) and amplification (OPA) in BBO and KTP nonlinear crystals.[12-14] 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 photomuliplier tube (PMT) and gated integrator.

The transmitted p-polarized SH intensity from the multilayer film grown on one side of a silica substrate for both s- and p-polarized incident excitation is shown in Figure 2. 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 2(b)). 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.[9,10] These films typically have uniaxial symmetry about the surface normal,[11,15] 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 (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 chromophores is approximately $45°$ with respect to the surface normal.

The relative SH intensity increased with film thickness, suggesting that the BDP-ADT multilayer retains an ordered structure within the bulk. Thicker films were prepared by increasing the number of drops on the substrate. The absorbance (A) at ~400 nm increased approximately linearly from 1 to 5 drops. This is as expected since A increases linearly with film thickness. Figure 3 shows the SH intensity at an incident angle of $50°$ versus A. The expected quadratic dependence (SH intensity proportional to A^2) is not observed although the bulk of the multilayer film remains *asymmetric* or polar. The attenuation of the SHG response at thicker films indicates that the degree of polar order is decreasing as the films become thicker. 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 ($\upsilon_a = 2916$, and $\upsilon_s = 2849$ cm^{-1}) increased by 2 cm^{-1} when the incident angle is varied from $75°$ to $20°$. At a high incident angle the IR beam probes mostly the structure of the film at the interface, whereas the beam penetrates the bulk at low 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 conclude that the alkyl chains along with barbituric acid and melamine derivatives become more disordered away from the Ge substrate. Both SHG and FTIR data support the conclusion that the layers near the interface are more ordered. SHG data obtained as the fundamental beam was scanned across the sample (8 mm) allowed the uniformity of the film to be assessed. In addition, it was found that annealing the sample or allowing the solvent to evaporate slowly improved the quality of the film. Drop casting from certain solvents such as a 1:1 mixture of ethanol and acetone also enhanced the film quality.[16]

The FTIR-ATR spectrum of the film grown on Ge and the SFG spectrum of the film grown on Si(100) are shown in Figure 4(a) and 4(b), respectively. The SFG spectrum in the C-H stretching region was fitted using a Voigt function to obtain the positions of the vibrational resonances. The fit to the spectrum is shown by the solid line in Figure 4(b). The four dashed 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 4(a)). 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 alkyl thiols chemisorbed on gold.[17] The weak shoulder near 2850 cm^{-1} is assigned to the symmetric (d^+) methylene resonance.[18] The broad feature between 2900 cm^{-1} 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 features has been observed before in the SFG spectrum of surfactant films.[19] 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[19] and Conboy[20] *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 are not localized, but random along the chain. Thus, the variation in the local environment of the SFG-active methylene groups would lead to inhomogenous (Gaussian) broadening of the linewidth.[18,21,22]

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.[23] 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.

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 phenylene-carbon double-bond

linkage, 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 than in the opposite direction. The relatively weak methylene resonances in the *thin* films show that the alkyl chains in the multilayer are nearly all-*trans* with few *gauche* defects.

Publications

1. Yang, X., Smilowitz, L., Buscher, C. T., McBranch, D., Robinson, J., and Li, D., "A Molecular Architectural Approach to Self-Assembled Monolayers as NLO Materials,"*Mat. Res. Soc. Symp. Proc*, **413**, 123 (1997)

2. Li, D. and Ramos, O., "Fundamentals and Applications of Molecular Self-Assemblies on Surfaces," in *Electrical and Optical Polymer Systems: Fundamentals, Methods, and Applications*, World Scientific Publishing Co. Pte. Ltd. (Invited Book Chapter). Chapter 20, pp 795-845 (1998).

3. Li, D., Yang, X., and McBranch, D., "A Molecular Architectural Approach to Nonlinear Optical Materials," *Technical Digest Series*, Optical Society of America, **11**, 409-11 (1996)

4. Li, D., Yang, X., and McBranch, D., "Self-Assembled, Molecular and Macromolecular π-Conjugated Optical Materials and Their Nonlinear Optical Properties," *Synthetic Metal*, **86(#1-3)**, 1849-1850 (1997).

5. Smilowwitz, L., Jia, Q. X., Yang, X., Li, D., McBranch, D., Bulow, S. J., and Robinson, J. M., "Imaging Nanometer-Thick Patterned Self-Assembled Monolayers Via 2nd-Harmonic Generation Microscopy," *J. Appl. Phys.* **81(5)**, 2051(1997).

6. Lütt, M., Fitzsimmons, M., and Li, D., "X-Ray Reflectivity Study of Self-assembled Multilayers of Macrocycles and Macromolecules," *J. Phys. Chem. B,* **102 (2),** 400-405 (1998)

7. Li, D., Lütt, M., Fitzsimmons, M., Synowicki, R., Haley, M. E., and Brown, G. W., "Preparation, Characterization, and Properties of Mixed Organic and Polymeric Self-Assembled Multilayers," *J. Am. Chem. Soc.* **120**, 8797-8804(1998)

8. Shi, X., Li, D., Lütt, M., Fitzsimmons, M., and VanPattern, G. P., "Self-Assembled Multilayers and Photoluminescence Properties of a New Water Soluble Poly(para-Phenylene)," in "Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials IV," J. R. Reynolds, A. K-Y. Jen, M. F. Rubner, L. R. Dalton Eds., *Mat. Res. Soc. Symp. Proc*, **488**, 133-138 (1998)

9. Li, D., Lütt, M., Shi, X., and Fitzsimmons, M.R., "Multilayer Self-Assemblies as Electronic and Optical Materials," in "Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials IV," J. R. Reynolds, A. K-Y. Jen, M. F. Rubner, L. R. Dalton Eds., *Mat. Res. Soc. Symp. Proc*, **488**, 133-138 (1998).

10. Li, D., Bishop, A., Gim, Y., Shi, X. B., Fyzsimmons, M. R., and Jia, Q. X., "Conduction Properties of Metal/Organic Monolayers/Semiconductor Heterostructures," *Appl. Phys. Lett.* **73(#18),** 2645-2647 (1998)

11. Mashl, R. J., Ku, L., Grønbech-Jensen, N., Fitzzsimmons, M., Lütt, M.,and Li, D., "Theoretical and Experimental Adsorption Studies of Synthetic Polymers on an Oppositely Charged Surface," *J. Chem Phys.* **110,** 2219 (1999)

12. Johal, M. S., Parikh, A. N., Lee, Y., Casson, J. L., Foster, L., Swanson, B. I., McBranch, D. W., Li, D. Q., and Robinson, J. M., "A Study of the Conformational Structure and Cluster Formation in an LB Film Using Second-Harmonic Generation, Second Harmonic Microscopy and FT-IR Spectroscopy," submitted to *Langmuir.* 1999

13. Johal, M. S., Cao, Y.W., Chai, X.D., Smilowitz, L. B., Robinson, J. M., Li, T. J., McBranch, D. W., and Li, D. Q., "Second-Harmonic and Sum-Frequency Generation Studies of Spontaneously Self-Assembled H-Bonded Asymmetric Polar Multilayers," submitted to *Chem Mater.*

References

[1] Kajiyama, T.; Aizawa, M. (Ed.) *New Developments in Constructions and Functions of Organic Thin Films*, Elsevier Science B.V., Amsterdam, 1996.

[2] Li, D.; Marks, T. J.; Zhang, C.; Wang, G. W. *Synth. Metals* **1991**, *41-43*, 3157.

[3] Aldrovandi, S.; Borsa, F.; Lascialfari, A.; Tongnetii, V. J. *J. Appl. Phys.* **1991**, *67*(9,2A), 5914.

[4] Shen, Y. R. *The Principles of Nonlinear Optics*, John Wiley & Sons, Inc., New York, 1984.

[5] Zernike, F.; Midwinter, J. E. *Applied Nonlinear Optics*, John Wiley & Sons, Inc., 1973.

[6] Ulman, A. An Introduction to Ultrathin Organic Films from Langmuir Blodgett to Self Assembly, Academic Press Inc., San Diego, 1991.

[7] See, for example, Yang, X.; McBranch, D.; Swanson, B.; Li, D. Q. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*(5), 538.

[8] The experimental details of film thickness determination by single wavelength ellipsometry can be found in Johal, M. S.; Parikh, A.; Lee, Y.; Casson, J. L.; Foster, L.; Swanson, B.; McBranch, D. W.; Li, D. Q.; Robinson, J. M. submitted to *Langmuir*.

[9] Li, D.; Swanson, B. I.; Robinson, J. M.; Hoffbauer, M. A. *J. Amer. Chem. Soc.* **1993**, *115*, 6975.

[10] Li, D.; Swanson, B. I.; Robinson, J. M.; Hoffbauer, M. A. *Nonlinear Optics III* **1992**, *1626*, 424.

[11] Li, D.; Ratner, M. A.; Marks, T.J.; Zhang, C.; Yang, Y.; Wang, G. K. *J. Amer. Chem. Soc.* **1990**, *112*, 7389.

[12] An excellent account of mid-IR production using OPG/OPA in BBO and KTP nonlinear crystals can be found in Zhang J.; Huang, J. Y.; Shen, Y. R. *Optical Parametric Generation and Amplification*, Laser Science and Technology, vol 19, Harwood Academic Publishers, 1995.

[13] Tang, C. L.; Cheng, L. K. *Fundamentals of Optical Parametric Processes and Oscillators*, Laser Science and Technology, vol 20, Harwood Academic Publishers, 1995.

[14] The mid-IR and residual 1064nm beams copropagating from the OPG/OPA were separated using a sapphire beam splitter, and focused on the sample. The phase matching of the beams at the sample was calculated using $f_{SFG}\sin\phi_{SFG} = f_{1064nm}\sin\phi_{1064nm} - f_{mid-IR}\sin\phi_{mid-IR}$.

[15] Katz, H. E.; Scheller, G.; Putvinski, T. M.; Schilling, M. L.; Wilson, W. L.; Chidsey, C. E. D. *Science* **1991**, *254*, 1485.

[16] These results were presented at *Organic Thin Films for Photonics Applications*, Optical Society of America, **1997**, *14*, 155, Longbeach, California.

[17] Johal, M. S.; Usadi, E. W.; Davies, P. B. *J. Chem. Soc,. Faraday Trans.* **1996**, *92*(4), 573.

[18] Johal, M. S. *Ph.D. Thesis, University of Cambridge, 1997.*

[19]   Ward, R.N.; Duffy, D.C.; Davies, P.B.; Bain, C.D. *J. Phys. Chem.* **(1994)**, <u>98</u>, 8536.

[20]   Conboy, J.C.; Messmer, M.C.; Richmond, J. *J. Phys. Chem.* **(1996)**, <u>100</u>, 7617.

[21]   Gadzuk, G. W.; Luntz, A. C. *Surf. Sci.*, **1984**, *114*, 429.

[22]   Miragliotta, J. M.; Polizotti, R. S.; Rabinowitz, P.; Cameron, S. D.; Hall, R. B. *Chem. Phys.* **1990**, *143*, 123.

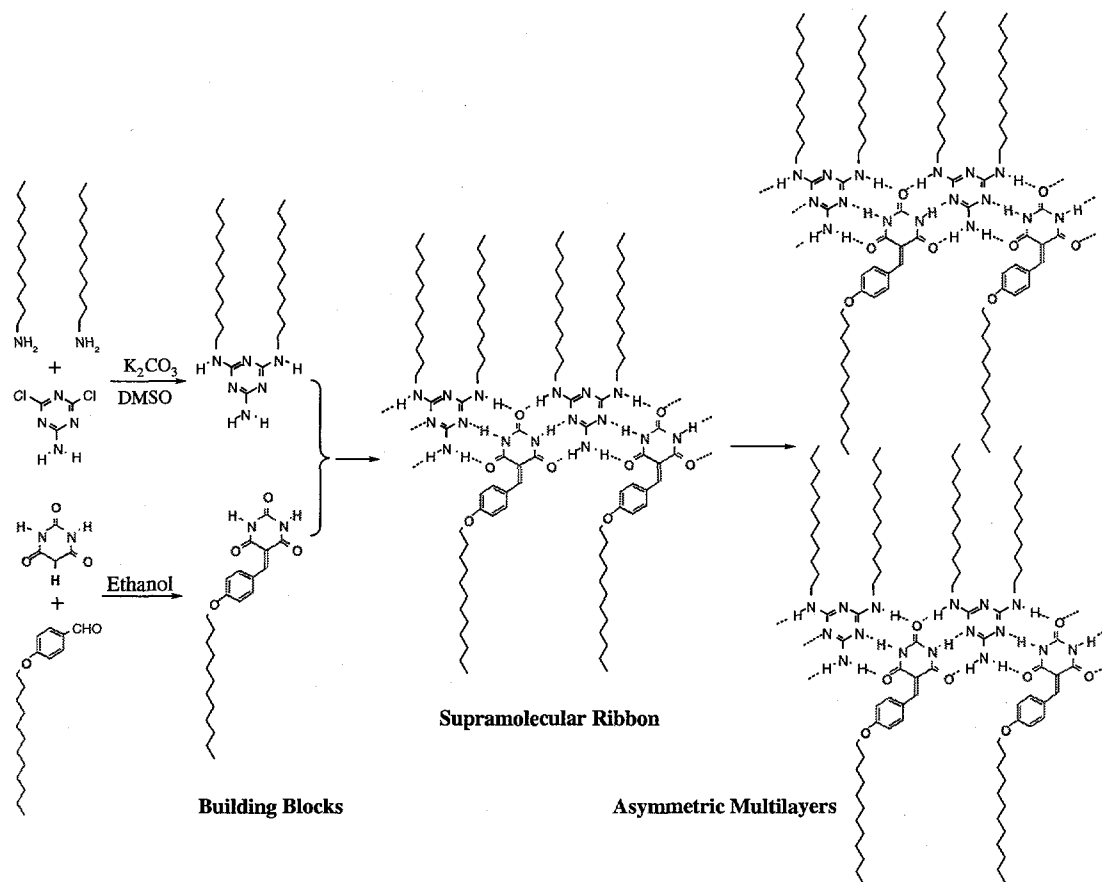[23]   Ong, T. H.; Davies, P. B.; Bain, C. D. *Langmuir* **1993**, *9*, 1836.

Figure 1. Synthesis of the supramolecular building blocks BDP and ADT, and the formation of asymmetric multilayer BDP-ADT structure.
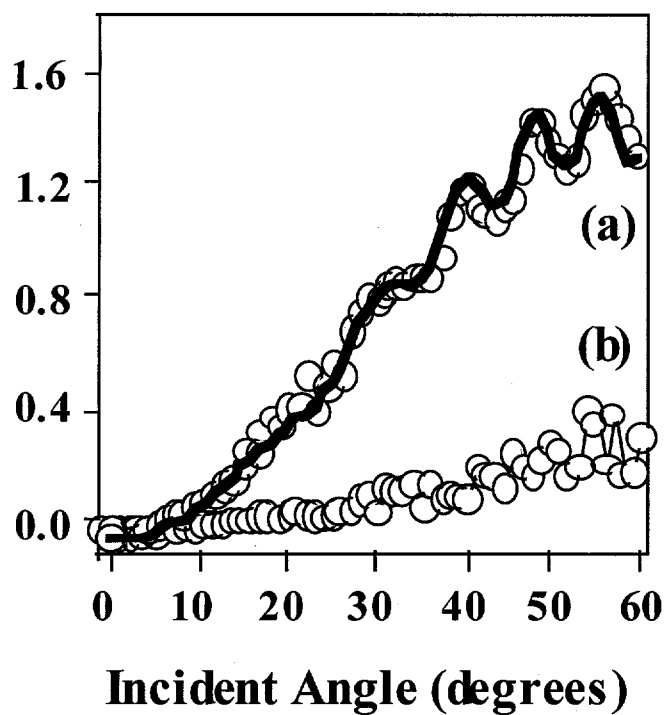
Figure 2. (a) The p-in, p-out and (b) s-in, p-out polarized SHG data of the multilayer drop-cast on a silica substrate as a function of incident angle. The solid line in (a) is a fit to the data points as discussed in the text.
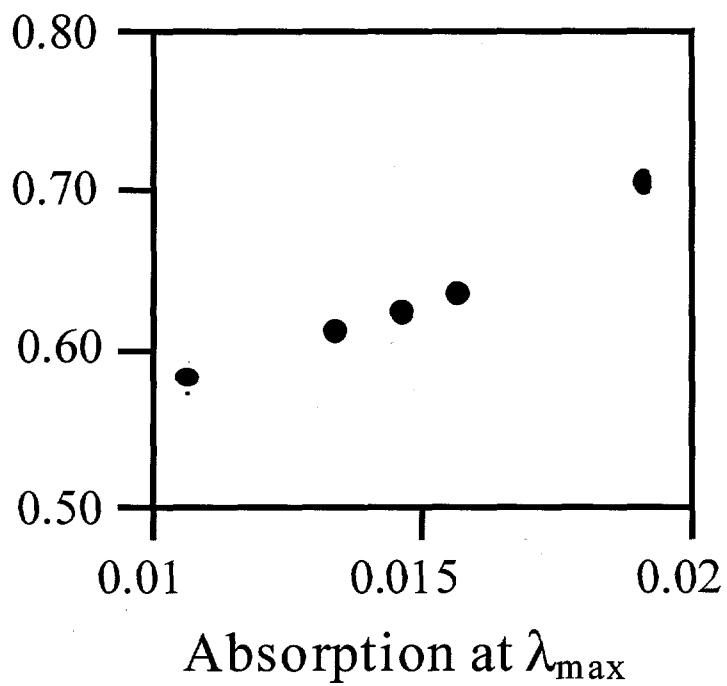
Figure 3. Plot of the SH intensity as a function of absorption at λ_{max} = 400 nm. The incident angle of the fundamental beam was 50°.
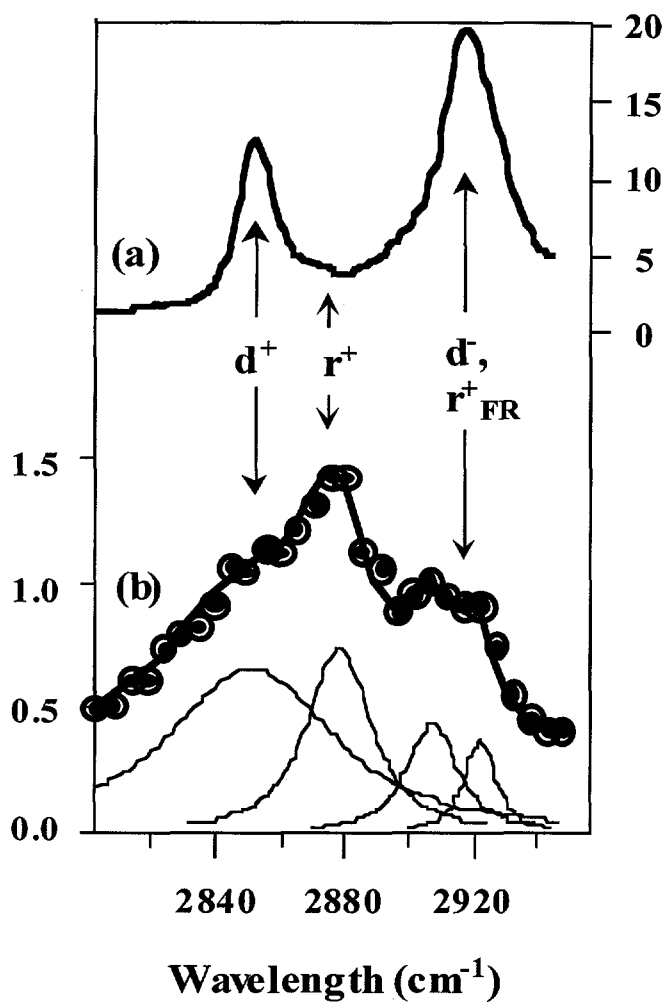
Figure 4. (a) The FTIR-ATR spectrum of the BDP-ADT multilayer from a single p-polarized reflection at the flat surface of a hemisphere Ge internal reflection element. (b) The ppp-polarized vibrational SFG spectrum of the multilayer. The main feature in the SFG spectrum is the symmetric methyl resonance (r^+). The solid line is a fit to the SFG data points. The deconvolved resonance profiles (dashed lines) are shown below the SFG spectrum. All spectra were obtained at room temperature.