Reports

Polar Orientation of Dyes in Robust Multilayers by Zirconium Phosphate-Phosphonate Interlayers

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Polar orientation of molecules in solids leads to materials with potentially useful properties such as nonlinear optical and electrooptical activity, electrochromism, and pyroelectricity. A simple self-assembly procedure for preparing such materials is introduced that yields multiple polar dye monolayers on solid surfaces joined by zirconium phosphate-phosphonate interlayers. Second harmonic generation (SHG) shows that the multilayers have polar order that does not decrease with increasing numbers (up to a large number) of monolayers in the film. The inorganic interlayers, as determined by SHG, impart excellent orientational stability to the dye molecules, with the onset of orientational randomization above 150°C.

HE SEQUENTIAL POLAR DEPOSITION of monomolecular layers to form "multilayers" is a promising route to the use of such materials as thin films. A known way to form polar multilayers is the Langmuir-Blodgett (L-B) procedure (1-3), in which monolayers at the air-water interface are mechanically transferred to a solid substrate. Because of a reliance on van der Waals interactions to maintain the polar orientation of the component molecules, the polar structure is not stable at elevated temperatures in conventional L-B films. An alternative "self-assembly" strategy, in which mechanical manipulation of monolayers and reliance on dispersive interactions to maintain orientation are avoided, is based on the repeated formation of monolayers by the irreversible chemisorption of molecules from homogeneous solutions (4). To assure layer-by-layer deposition, the chemisorption process is designed to be self-limiting at one monolayer, and a subsequent chemical treatment is used to reactivate the surface for chemisorption of the next monolayer.

Using a version of this self-assembly strategy, Li et al. (5) recently reported the formation of polar dye multilayers by a complex sequence of substitution reactions at Si and C atoms to form dye monolayers joined by "soft" polymer interlayers. We use a simpler self-assembly procedure (6) to form multiple polar dye monolayers joined by relatively immobile Zr phosphate-phosphonate interlayers (Fig. 1). The construction of related nonpolar multilayers was demon-

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strated by Mallouk and co-workers (7) on the basis of analogy with the solid-state structure of bulk Zr diphosphonates (8). Second harmonic generation (SHG) estab-

lishes that our multilayers have uniform polar order that does not decrease with increasing numbers of monolayers in the film. Most significantly, as determined by SHG, the inorganic interlayers impart orientational stability to the dye molecules up to at least 150°C. In fact, with the particular dye used, thermal degradation of the nonlinear optical activity of the multilayer most likely occurs by dye decomposition rather than by the usual process of molecular reorientation.

Silicon and glass substrates were treated with aminopropyltrimethoxysilane under conditions optimized previously (9). To form each monolayer, we phosphorylated the amine-terminated surface (or hydroxylterminated in the case of latter layers) for 5 to 10 min in 0.2 M POCl₃-0.2 M collidine in acetonitrile at room temperature, rinsed the surface with water, zirconated it for 5 min in 5 mM aqueous ZrOCl₂ at room temperature, rinsed it again with water, immersed it for 10 min in solutions of 1.5 mM 4-{4-[N,N-bis(2-hydroxyethyl)amino] phenylazo}phenylphosphonic acid [1 (10)]in ethanol held just below the boiling point, and finally rinsed it extensively with ethanol.



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structure of dye multilayer film based on known structures of Zr(HOPO₃)₂ and related organic Zr phosphonate salts (8), which feature Zr (IV) in pseudo-octahedral sites between opposed hexagonal layers of phosphate or phosphonate.

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Multilayers were formed by repetition of this sequence.

A plot of ellipsometric thickness versus number of layers of 1 deposited on Si is shown in Fig. 2A. The thickness per layer, 16 Å (11), is consistent with, but somewhat less than, the sum of the thickness generated from a Corey-Pauling-Koltun model, 13 Å for 1 in its most extended conformation, and the assumed thickness of 7 Å(8) for the interlayer of Zr flanked by two phosphates. The deviation may indicate tilting or lessthan-ideal packing of the dye molecules. A plot of absorbance at 420 nm versus layer number on glass is shown in Fig. 2B; Fig. 3 shows the absorption spectrum of a multi-



Fig. 2. Thickness, absorbance, and SHG as a function of the number of monolayers in multilayer samples. (A) Ellipsometric thickness determined in reflection from polished Si wafers assuming a film refractive index of 1.54. The best fit line through the origin is shown; slope, 15.7 Å per layer. (B) Absorbance determined from transmission at 420 nm at normal incidence on soda lime glass with half of the layers on either side of the substrate. The best fit line through the origin is shown; slope, 0.0072 per layer. (\mathbf{C}) Square root of the transmitted SHG intensity of the multilayers used in (B) relative to quartz (12) for the three distinct polarizations of the fundamental and the SHG. The angle of incidence used (61°) is one of the angles that gives completely constructive interference between the SHG from the two sides of the glass substrate. Completely destructive interference was observed at other angles, demonstrating that the SHG is fully coherent. Lines are best fits through the origin. \blacktriangle , Fundamental *p*-polar-ized, SHG *p*-polarized, slope 2.3 \times 10⁻³ per layer; \bullet , fundamental *s*-polarized, SHG *p*-polar-ized, slope 1.4×10^{-3} per layer; \blacksquare , fundamental polarized at 45° to the plane of incidence, SHG s-polarized, slope 1.1 \times 10⁻³ per layer.

layer film. Samples for Fig. 2, A through C, were prepared with the same numbers of depositions, but the data in Fig. 2, B and C, cover twice as many layers because both sides of the substrates are probed. The linearity of the plots in Fig. 2, A and B, indicates that the same amount of dye is deposited during each deposition cycle. This consistency is a prerequisite for a viable multilayer deposition technique.

Figure 2C shows the square root of the intensity of transmitted second harmonic light at 532 nm versus the number of layers of films on glass for three combinations of the polarizations of the fundamental and the second harmonic (12). The intensities of SHG at other polarizations follow the expected function of the intensities of these three polarizations (13). The three plots are linear, as expected for a coherent, secondorder process from uniformly polar films, and the slope of the data is proportional to the effective nonlinearity of the film for that polarization (14). We conclude that the dye molecules in all layers have the same degree of polar orientation and do not reorient after they are covered by subsequent dye layers. This is the first demonstration of such reproducibility over more than ten self-assembled or L-B layers. No second harmonic light was observed from layers of a centrosymmetric dye, quaterthiophenediphosphonic acid (9), consistent with the expectation that a polar dye is necessary for SHG.

The SHG intensities in Fig. 2C are referenced to the SHG intensity from a quartz crystal (12) to allow us to determine the magnitude of the nonlinearity of these films and thus gauge the potential of this deposition technique for the preparation of more nonlinear materials using dyes better optimized for hyperpolarizability. We obtain the following nonlinear coefficients d_{iik} from the slopes of the three plots in Fig. 2C and the layer thickness determined in Fig. 2A (13):

$$|(2d_{xxz} + d_{zxx})\cos^2\theta_{\rm f}|$$

$$+ d_{zzz} \sin^2 \theta_{\rm f} = 12 \text{ pm/V} \qquad (1)$$

$$|d_{zxx}| = 7 \text{ pm/V} \tag{2}$$

$$|d_{xxx}| = 10 \text{ pm/V} \tag{3}$$

where θ_f is the angle of refraction in the film (34.6°).

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These nonlinearities are of the same order of magnitude as those of LiNbO₃, one of the widely used inorganic nonlinear materials, for which the nonzero coefficients range from 2 to 44 pm/V (15) and are a couple of orders of magnitude less than the values for L-B monolayers of the stilbazolium dyes (3), which have very high second-order susceptibilities (16). Given that the dye used here, which incorporates the relatively weakly



Fig. 3. Absorbance spectrum of a ten-layer film.

electron-withdrawing phosphonate group, is not optimized for its hyperpolarizability, the magnitude of the nonlinearity is encouraging. However, the relatively large values of d_{xxxx} and d_{xxxx} are surprising and suggest that it may be inappropriate to view this dye as an isolated linear molecule with a single large hyperpolarizability along its long axis, an approximation that has commonly been made for aromatic systems with coupled electron-donating and electron-withdrawing groups.

More significant than the degree of nonlinearity of these films is the thermal stability of that nonlinearity. We found that the SHG intensity did not significantly diminish after 3 hours at 150°C in air. Orientational randomization occurs at much lower temperatures in most L-B films (2) and poled polymers (17). Furthermore, the reduction in SHG that does eventually occur at higher temperatures or after much longer times at 150°C appears to be due only to thermal degradation of the dye, not molecular reorientation, because the proportionality between the square root of the SHG intensity and the optical density of the film is unchanged. Because the dye used here was selected for ease of synthesis rather than stability to degradation, there is a good possibility that dyes can be found for which the films are stable at even higher temperatures.

We have prepared polar dye molecules of many monomolecular layers with the same degree of orientation in each layer, considerable second-order optical nonlinearity, and excellent thermal stability. The deposition requires neither intricate mechanical processes nor difficult chemical reactions. Further details of film preparation, experimental results, and optical analysis will be reported elsewhere (18).

REFERENCES AND NOTES

- 1. R. Popovitz-Biro et al., J. Am. Chem. Soc. 112, 3498 (1990); C. Bossard et al., Proc. SPIE 1273, 70 (1990); R. C. Hall et al., ibid. 824, 121 (1988); B. L. Anderson et al., Synth. Met. 28, D683 (1989);
 O. A. Aktsipetrov, N. N. Akhmediev, E. P. Mishina, . R. Novak, JETP Lett. 37, 207 (1983).
- 2. N. J. Geddes, M. C. Jurich, J. D. Swalen, R. Tweig,
- J. F. Rabolt, J. Chem. Phys. 94, 1603 (1991). 3. I. R. Girling et al., J. Opt. Soc. Am. B 4, 950

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(1987); D. B. Neal et al., Electron. Lett. 22, 460 (1986); D. Lupo et al., J. Opt. Soc. Am. B 5, 300 (1988).

- A. Ulman, Adv. Mater. 2, 573 (1990).
- 5. D. Q. Li et al., J. Am. Chem. Soc. 112, 7389 (1990)
- 6. T. M. Putvinski et al., Langmuir 6, 1567 (1990). H. Lee, L. J. Kepley, H.-G. Hong, T. E. Mallouk, J. Am. Chem. Soc. 110, 1567 (1988); H. Lee, L. J. Kepley, H.-G. Hong, S. Akhter, T. E. Mallouk, J. Phys. Chem. **92**, 2597 (1988).
- 8. M. B. Dines, P. M. DiGiacomo, Inorg. Chem. 20, 92 (1981); M. B. Dines et al., in Chemically Modified Surfaces in Catalysis and Electrocatalysis, J. S. Miller, Ed., no. 192 of ACS Symposium Series (American Chemical Society, Washington, DC, 1982), pp. 223 - 240
- 9. H. E. Katz, M. L. Schilling, C. E. D. Chidsey, T. M. Putvinski, R. S. Hutton, Chem. Mater. 3, 699 (1991).
- Sodium nitrite (0.76 g, 0.011 mol) in 3 ml of H_2O 10. was added dropwise to a suspension of 4-aminophenylphosphonic acid (1.70 g, 0.01 mol) in HCl (4.5 ml) and H_2O (20 ml) cooled to 0°C. As the addition was completed, the solution became homogeneous, and stirring at low temperature was continued for 15 min. Bis(2-hydroxyethyl)aniline (1.8 g, 0.01 mol) was then added, and the solution immediately began turning red, and it continued to darken as the aniline dissolved. After stirring at 0°C for 2 hours, we added solid sodium acetate (1.6 g, 0.02 mol), and the vigorously stirred solution was brought up to room temperature over 1 hour. The mixture was then refrigerated overnight. After being warmed to room temperature, the solution was filtered, and a red-purple solid was collected that was washed with copious amounts of H2O and dried to give the product, 3.1 g (85% yield). ¹H nuclear magnetic resonance (NMR) (CD₃OD): δ 3.87 (m, 4H, CH₂O, CH₂N), δ 7.15 (d, 2H, ArH), δ 7.90 (m, 6H, ArH). Analysis calculated for $C_{16}H_{20}N_3PO_5 + 0.5 H_2O$: C, 48.98%; H, 5.90%; N, 10.71%; P, 7.89%. Found: C, 49.15; H, 5.52; N, 10.60; P, 7.84.
- 11. The ellipsometric thicknesses are determined with the refractive index of 1.54 suggested by Mallouk and co-workers (7). The actual value might be somewhat higher because of the presence of the azo dve, but it is difficult to measure in such thin films.
- 12. All SHG data for the multilayers were referenced to the $\chi^{(2)}_{xxxx}$ tensor component of quartz, which was determined by SHG from an antireflection-coated, y-cut quartz single crystal with both the fundamental and SHG polarized along the quartz x-axis. The angle of incidence was chosen to give the first SHG maximum away from normal incidence [that is, the first Maker fringe maximum (19)]. The quartz flat was adequately parallel as judged by the completely destructive interference at the Maker fringe minima. The data were corrected for the polarization response of the spectrometer.
- 13. The intensity of p- and s-polarized SHG are, respectively:

$$\begin{split} & f_{p}^{2\omega}(\gamma) = I_{pp \to p}^{2\omega} \cos^4 \gamma + I_{ss \to p}^{2\omega} \sin^4 \gamma \\ & + \left[I_{pp \to p}^{2\omega} f_{ss \to p}^{2\omega} \right]^{1/2} \cos \phi \sin^2 2\gamma \\ & I_{s}^{2\omega}(\gamma) = I_{sp \to s}^{2\omega} \sin^2 2\gamma \end{split}$$

(4)

(5)

where γ is the angle of polarization of the fundamental with respect to the plane of incidence, ϕ is the phase between the p-polarized SHG fields due to the p- and s-components of the fundamental, and ω is the angular frequency of the light. In transmission, the SHG intensities for the three distinct combinations of polarizations are related to the SHG intensity from quartz by:

$$\begin{split} I_{pp \rightarrow p}^{2\omega} &= C(\theta) \left| (2d_{xxx} + d_{zxx}) \cos^2 \theta_{\rm f} + d_{zxx} \sin^2 \theta_{\rm f} \right|^2 \\ & (6) \\ I_{ss \rightarrow p}^{2\omega} &= C(\theta) \cos^4 (\theta_{\rm f} - \theta) \left| d_{zxx} \right|^2 \\ I_{sp \rightarrow s}^{2\omega} &= C(\theta) \cos^2 (\theta - \theta_{\rm s}) \\ & \times \cos^2 (\theta_{\rm s} - \theta_{\rm f}) \cos^2 (\theta_{\rm f} - \theta) \left| d_{xxx} \right|^2 \\ & (8) \end{split}$$

where:

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$$C(\theta) = \left[\frac{\pi}{2} \frac{l_{\rm f}}{l_{\rm quartz}}\right]^2 \left[\frac{n_{\rm quartz}}{n_{\rm f}}\right]^3 \frac{I_{\rm quartz}^{2\alpha}}{|d_{\rm quartz}|^2} \times [T_p^{a \to f}(\theta)]^2 T_p^{f \to s}(\theta) T_p^{s \to a}(\theta) \frac{\sin^2 \theta_{\rm f} \cos \theta}{\cos^3 \theta_{\rm f}} \qquad (9)$$

 θ is the angle of incidence, θ_f and θ_s are, respectively, the angles of refraction in the film and the substrate (derived from θ with Snell's law), l_f is the film thickness per layer, l_{quartz} is the coherence length of quartz [20.65 µm (20)], n_{quartz} and n_{f} are the refractive indices of quartz [1.45 (15)] and the film [1.54 (11)], respectively, d_{quartz} is the nonlinear coefficient of quartz when both the fundamental and second harmonic are polarized along the quartz x-axis [0.32 pm/V (15)], and $T_p^{i\to j}(\theta)$ is the transmissivity for *p*-polarized light of the interface be-tween phases *i* and *j*, where a, f, and s refer to air, film, and substrate (soda-lime glass with a refractive

index of 1.52). All of the p-transmissivities are essentially unity for the angle of incidence used here.

- 14. B. Dick, A. Gieralski, G. Marowsky, G. A. Reider, Appl. Phys. B 38, 107 (1985).
- S. Singh, in CRC Handbook of Laser Science and Technology, M. J. Weber, Ed. (CRC Press, Boca Raton, FL, 1986), pp. 3–220.
 G. R. Meredith, in Nonlinear Optical Properties of
- Organic and Polymeric Materials, D. J. Williams, Ed. (American Chemical Society, Washington, DC, 1983), pp. 27–56
- 17. D. Jungbauer et al., Appl. Phys. Lett. 56, 2610 D. jungbauet et al., $2 \times 2^{n} \times 2^{n}$ (1990). W. L. Wilson et al., in preparation. P. D. Maker, R. W. Terhune, M. Nisenoff, C. M.
- Savage, Phys. Rev. Lett. 8, 21 (1962). 20 J. Jerephagnon and S. K. Kurtz, Phys. Rev. B 1, 1739 (1970).

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Tuning High-T_c Superconductors via Multistage Intercalation

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Multistage intercalation has been used to tune the interaction between adjacent blocks of CuO_2 sheets in the high- T_c (high superconducting transition temperature) superconductor Bi₂Sr₂CaCu₂O_x. As revealed by atomic-resolution transmission electron microscopy images, foreign iodine atoms are intercalated into every nth BiO bilayer of the host crystal, resulting in structures of stoichiometry IBi2"Sr2"Ca"Cu2"O. with stage index n up to 4. An expansion of 3.6 angstroms for each intercalated BiO bilayer decouples the CuO₂ sheets in adjacent blocks. A comparison of the superconducting transition temperatures of the pristine host material and intercalated compounds of different stages suggests that the coupling between each pair of adjacent blocks contributes ~ 5 K to T_c in Bi₂Sr₂CaCu₂O_x.

LTHOUGH IT IS GENERALLY BElieved that the critical structural units in the highest $T_{\rm c}$ superconductors are the CuO2 planes, the significance of coupling between the planes is poorly understood. It was recently demonstrated that, like many other two-dimensional materials, Bi-based high- T_c superconducting oxides can be intercalated with foreign species (1). For stage-1 iodine-intercalated Bi₂Sr₂CaCu₂O_x, guest iodine atoms are introduced between every pair of weakly bonded BiO bilayers, thus affecting the coupling between identical host blocks containing the double CuO2 planes. In some intercalation compounds, higher stage structures are possible; a stage-n structure has n identical host layers or blocks sandwiched be-

tween each pair of intercalant layers. Highstage single-phase graphite intercalation compounds can be synthesized with n as high as 8 (2), but in other layered compounds it is difficult to achieve single-phase intercalation with n > 1. The possibility of using intercalants to vary the strength of interlayer interactions and possibly modify microscopic charge transfer makes the intercalation of high- T_c compounds attractive. Systematic investigation of the superconductivity mechanism and its relation to crystal structure is possible if different intercalants can be incorporated and higher stage compounds can be generated.

We here examine interblock interactions in the high- T_c superconductor Bi₂Sr₂CaCu₂O_x by using multistage iodine intercalation to "tune" the coupling between adjacent CuO2containing blocks. Atomic resolution realspace transmission electron microscopy (TEM) images identify stage structures with $n \leq 4$. Correlations between the crystal structure and $T_{\rm c}$ allow us to determine the contributions to T_c of interblock CuO₂ plane interactions and to evaluate various models for the superconductivity mechanism.

In the intercalation of pristine Bi2Sr2Ca-

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