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Communications to the Editor

Chromophoric Self-Assembled Multilayers. Organic Superlattice Approaches to Thin-Film Nonlinear Optical Materials

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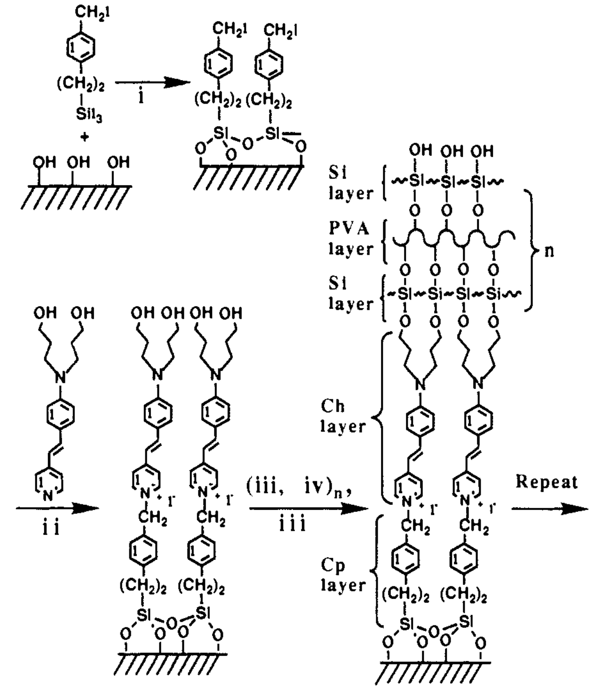
Poled polymer[1-3] and acentric Langmuir–Blodgett[4] films represent promising approaches to high-efficiency second harmonic generation (SHG) materials.[5] Nevertheless, net achievable nonlinear optical (NLO) chromophore alignments, number densities, and alignment temporal stabilities are significant issues in the former materials,[6] as are scattering microdomains, structural stability, and structural regularity, in the latter.[7] We communicate here an alternative approach to thin-film NLO materials utilizing the sequential construction of covalently self-assembled chromophore-containing multilayer structures.[8]

Scheme I[a]



[a]Conditions: (i) benzene, 25 °C; (ii) reflux in *n*-PrOH; (iii) $Cl_3SiOSiCl_2OSiCl_3$ in THF; (iv) poly(vinyl alcohol) in DMSO.

The general synthetic strategy (Scheme I) is based on self-assembly technology originally developed by Sagiv.[9,10] Noteworthy features include a stilbazole chromophore precursor[11] in which layer-building quaternization (step ii)[12] affords both an anchored high-β center[13] and diagnostic changes in the optical spectrum.[14] In addition, soft polymeric layers are introduced

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(11) (a) Prepared by coupling[2a,11b–d] *p*-(*N*,*N*-diallylamino)benzaldehyde with γ-picoline *N*-oxide, followed by 9-BBN hydroboration/reduction and H_2O_2/NaOH. High-resolution MS calcd for $C_{19}H_{24}N_2O_2$ 312.1838, found $M^+/e = 312.1852$. ^1H NMR (DMSO-d_6): δ 8.44 (2 H, d, $J = 6$ Hz), 7.44 (2 H, d, $J = 6$ Hz), 7.42 (2 H, d, $J = 9.2$ Hz), 7.38 (1 H, d, $J = 16.4$ Hz), 6.88 (1 H, d, $J = 16.4$ Hz), 6.69 (2 H, d, $J = 9.2$ Hz), 4.56 (1 H, t, $J = 16.4$ Hz), 3.44 (4 H, t, $J = 6$ Hz), 3.37 (4 H, t, $J = 7.6$ Hz), 3.34 (1 H, s), 3.31 (1 H, s), 1.67 (4 H, m). Anal. Calcd for $C_{19}H_{24}N_2O_2 \cdot 0.5H_2O$: C, 71.00; H, 7.84; N, 8.72. Assignments involving OH groups were confirmed by D_2O exchange. Found: C, 71.52; H, 7.69; N, 8.55. $\lambda_{max} = 390$ nm (MeOH). (b) Tournilhac, F.; Micoud, J. F.; Simon, J.; Weber, P.; Guillon, D.; Skoulios, A. *Mol. Cryst. Liq. Cryst.* **1987**, *2*, 55–61. (c) Lu, T. H.; Lee, T. J.; Wong, C.; Kuo, K. T. *J. Chin. Chem. Soc.* (*Taipei*) **1979**, *26*, 53–56. (d) Kuo, K. T. *J. Chin. Chem. Soc.* (*Taipai*) **1978**, *25*, 131–139.

(12) $ICH_2C_6H_4(CH_2)_2SiI_3$ was prepared in situ from NaI + the corresponding chloride (commercially available para + meta mixture) in CH_3CN.

(13) (a) β_{vec}(calcd) = 382×10^{-30} cm^5 esu^{-1} ($\hbar\omega = 1.17$ eV) by PPP-SCF-MECI techniques.[13b–d] (b) Li, D.; Marks, T. J.; Ratner, M. A. *Chem. Phys. Lett.* **1986**, *131*, 370–375. (c) Li, D.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1707–1715. (d) Li, D.; Marks, T. J.; Ratner, M. A., to be published.

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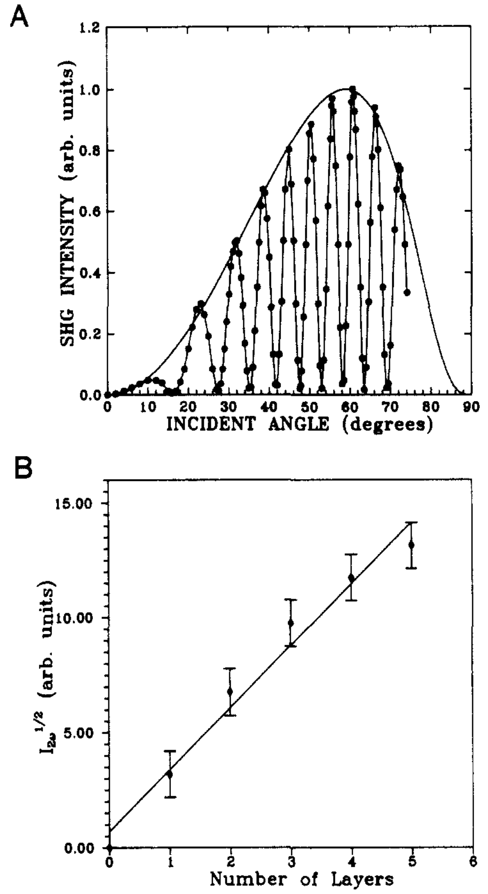

Figure 1. (A) SHG intensity as a function of fundamental beam incident angle from a glass slide having a self-assembled CpCh monolayer on either side. The interference pattern arises from the phase difference between the SHG waves generated at either side of the substrate during propagation of the fundamental wave. The solid envelope is a theoretical curve generated for $\chi_{zzz}^{(2)}/\chi_{zyy}^{(2)} = 3$. (B) Plot of the square root of SHG intensity versus the number of chromophore layers in the multilayer superlattice. The straight line is the linear least-squares fit to the experimental data.

transverse to the stacking direction (steps iii and iv, where n = 2 has so far afforded films of the most consistent quality)[15] to promote structural stability. The course of multilayer evolution on clean[16] SiO_2 substrates is readily monitored by optical spectroscopy (growth of chromophore absorption at 510 nm); XPS spectroscopy (initial diminution of Si and O signals; growth and persistence of C, N, and I signals); advancing contact angles, which are in accord with expected surface functionalities[9,10,17] and which repeat in each i–iv cycle (reaction product, $\theta_a(H_2O)$: clean SiO_2, 15°; i, 82°; ii, 55°; iii, 17°; iv, 17°); preliminary null ellipsometry, which is in accord with expected layer dimensions (approximate thickness in notation of Scheme I: CpChSi ≈ 34 Å; CpChSiPVASiPVASiCpChSiPVASiPVASiCpChSiPVASiPVASi ≈ 235 Å);[18] and NLO characteristics (vide infra). These multilayer films adhere strongly to glass, are insoluble in common organic solvents and strong acids, and can only be effectively removed by diamond polishing.

Transmission SHG measurements in the p-polarized geometry employed the 1064-nm output of a Q-switched Nd:YAG laser.[2] No in-plane anisotropy in the signal was detected as samples were rotated about the film normal. This indicates that these films possess uniaxial symmetry about the normal and that the distribution of chromophore molecular orientations does not have an azimuthal dependence. Figure 1A shows the SHG intensity as a function of incident angle for a glass slide coated on both sides with a self-assembled monolayer (CpCh). Two features are noteworthy and are observed in all multilayer samples. First, nearly complete destructive interference of SHG waves from the two monolayers is evident. This destructive interference is observed over many randomly selected spots on the films. It indicates that the quality of the structures on the two sides of the substrate is nearly identical and uniform, suggesting that the present self-assembly method is capable of generating excellent quality multilayers in a reproducible way. Second, excellent fits of the transmission SHG data envelopes can be obtained for $\chi_{zzz}^{(2)}/\chi_{zyy}^{(2)}$ in the range 3–4. For Figure 1A, the fit is shown for $\chi_{zzz}^{(2)}/\chi_{zyy}^{(2)} = 3$. Assuming a one-dimensional chromophore (i.e., one characterized by a single, dominant β component) and minimal dispersion, the relationship in eq 1 obtains.[19] Here, $\bar{\psi}$ is the average of the orientation angles, ψ, of the chromophore dipoles with respect to the substrate surface normal. Our results thus suggest that $\bar{\psi}$ is in the range 35°–39° for the present self-assembled chromophoric superlattices.

$$\chi_{zzz}^{(2)}/\chi_{zyy}^{(2)} = 2\cot^2\bar{\psi} \qquad (1)$$

By calibrating the SHG data against quartz, we obtain $\chi_{zzz}^{(2)} = 2 \times 10^{-7}$ esu for a typical superlattice film, and therefore, $\chi_{zzz}^{(2)} = 6 \times 10^{-7}$ esu for a single ChCp layer of 22-Å estimated thickness. This SHG efficiency considerably exceeds that of poled polymers,[1-3] compares favorably with high-quality LB films,[4,7] and is consistent with high chromophore number densities and degrees of acentric alignment.[20] Moreover, the large magnitude of $\chi_{zzz}^{(2)}$ suggests that the formation of centrosymmetric aggregates, which commonly occurs in LB films[7a,b,d] and which greatly depresses achievable $\chi_{zzz}^{(2)}$ values, is not important in the present self-assembled materials. Temporal stability studies reveal less than 10% decline in the SHG efficiency of a five-layer structure in the course of a month.

Since the present multilayers are extremely thin in comparison to λ = 1064 nm light and hence to the expected coherence length, the intensity of the SHG signal should scale quadratically with the number of chromophore layers.[21] This is an NLO diagnostic commonly employed to assess the structural regularity of LB films.[4,7] As can be seen in Figure 1B, the adherence of the present multilayer structures to quadratic behavior is good, indicating that it is possible to maintain the same degree of noncentrosymmetric chromophore ordering in the additions of successive layers.

In summary, these results demonstrate that self-assembly techniques represent a promising approach to the synthesis of thin-film materials having high second-order optical nonlinearities, and also that SHG experiments are informative structural probes thereof. Further synthetic elaboration and physical characterization efforts are in progress.

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(14) λ_{max} = 510 nm (monolayer) vs 529 nm (1,2-dichloroethane) for the model chromophore 4-[4-(*N*,*N*-dimethylamino)styryl]-1-benzylpyridinium iodide.[2a]

(15) Completion of this reaction is promoted by gentle sonication.

(16) Cleaning procedure: detergent + ultrasound (10 min), aqueous base (10 min), water, acetone, O_2 plasma (3 h).

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(20) Regarding the possibility that the λ = 1064 nm $\chi_{zzz}^{(2)}$ results may include significant resonant enhancement, supplementary SHG measurements were also carried out at λ = 1900 nm. These yield completely nonresonant $\chi_{zzz}^{(2)}$ values only ca. 40% smaller than the above data.

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