

## Vapor Phase Self-Assembly of Electrooptic Thin Films via Triple Hydrogen Bonds

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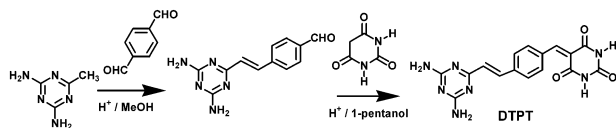
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Molecule-based electrooptic (EO) materials represent a promising direction in the quest to develop novel technologies for greatly increased optical data network speed, capacity, and bandwidth.<sup>1</sup> Microstructural acentricity is a key, yet synthetically daunting, challenge for such materials, with electric-field poling of chromophoric glassy polymers,<sup>2</sup> Langmuir–Blodgett (LB) film transfer,<sup>3</sup> and layer-by-layer formation of covalent self-assembled superlattices (SAs)<sup>4,5</sup> representing the principal avenues pursued to date. In addition to attractions, each approach also poses challenges ranging from the inherent thermodynamic instability of poled dipole-containing glasses,<sup>2</sup> to the modest efficiency of most layer-by-layer growth techniques,<sup>3–6</sup> to the fragility of amphiphilic lattices enforced principally by van der Waals interactions.<sup>3</sup> We report here an alternative, vapor phase approach which utilizes robust patterns of directed triple hydrogen bonds to assemble microstructurally acentric, EO-active films in an expeditious growth process.

Although directed multiple H-bonds are widely used in crystal engineering,<sup>7,8</sup> few reports describe thin film deposition using H-bonding constituents.<sup>9</sup> “Oblique incidence organic molecular beam deposition” produces preferentially oriented thin films<sup>10</sup> with single H-bonds used to align pyridylbenzoic acid chromophore molecules. However, in this case, the molecular dipoles are aligned parallel to the substrate, and only in-plane directional ordering is achieved (disadvantageous for conventional thin film waveguiding devices).<sup>2,4</sup> The present approach utilizes specifically designed intermolecular longitudinal triple H-bonding interactions to align chromophore molecules head-to-tail and preferentially perpendicular to the substrate, as thin solid films from the vapor phase. Out-of-plane noncentrosymmetric microstructures are thereby achieved in smooth, optically clear, thermally robust films which can be grown in a few hours. Parallel theoretical work shows that such minimal energy head-to-tail chromophore orientations also afford intermolecular cooperative effects which substantially enhance the effective molecular hyperpolarizability.<sup>11</sup> The chromophore 5-{4-[2-(4,6-diamino-[1,3,5]triazin-2-yl)-vinyl]-benzylidene}-pyrimidine-2,4,6-trione (DTPT) containing H-bond/electron donor and H-bond/electron acceptor modules was synthesized in two steps (Scheme 1)

**Scheme 1.** Synthesis of 5-{4-[2-(4,6-Diamino-[1,3,5]triazin-2-yl)-vinyl]-benzylidene}-pyrimidine-2,4,6-trione (DTPT)

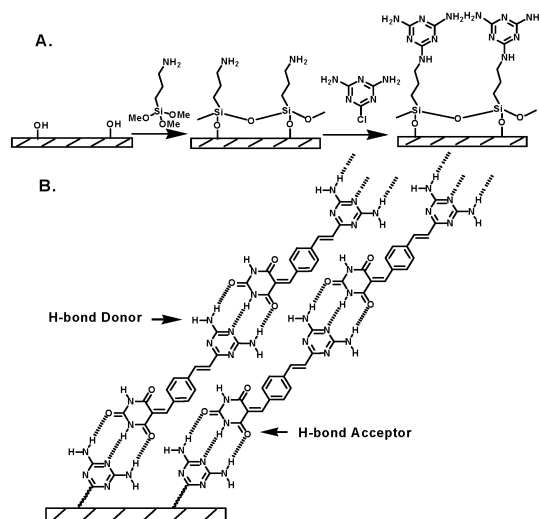


and characterized by conventional analytical/spectroscopic techniques.<sup>12</sup> The pyrimidine-2,4,6-trione and 4,6-diamino-1,3,5,-

triazine-2-yl moieties form longitudinally directed donor–acceptor triple H-bonds between neighboring molecules. The basic structural and thermodynamic characteristics of such linkages have been well-characterized.<sup>7,8</sup>

In film growth experiments, a melamine template was first anchored to the cleaned glass or Si (100) substrate (Scheme 2, A),

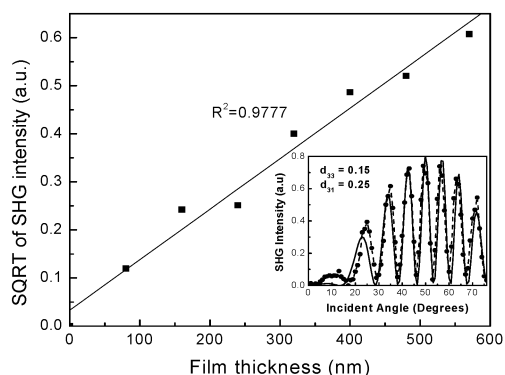
**Scheme 2.** (A) Substrate Functionalization for DTPT Self-Assembly; (B) Scheme for DTPT Self-Assembly



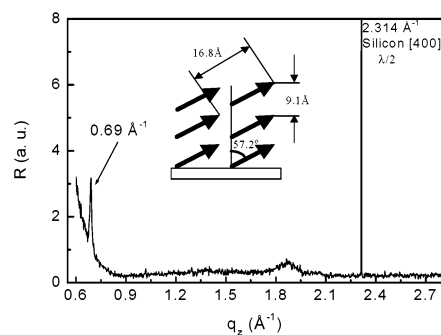
and the functionalized substrates were characterized by XPS. A Denton Vacuum DV-502 deposition apparatus ( $10^{-5}$ – $10^{-6}$  Torr) was then used to fabricate DTPT films at an optimized substrate temperature of 100 °C and growth rate of 0.5–2.0 Å/s. A calibrated quartz crystal sensor was used to monitor the film growth rate and approximate thickness. The resulting films are optically transparent ( $\alpha \approx 10 \text{ cm}^{-1}$  at 640–1800 nm,  $\lambda_{\text{max}} = 332 \text{ nm}$ ) and smooth by contact mode AFM (rms roughness = 1.7 nm over a 25  $\mu\text{m}^2$  area for a 1.22  $\mu\text{m}$ -thick film). Polarized transmission second harmonic generation (SHG) measurements at  $\lambda_0 = 1064 \text{ nm}$  were carried out on samples placed on a computer-controlled rotation stage.<sup>6</sup> Angle-dependent interference patterns for glass substrates coated on both sides (Figure 1 inset) demonstrate that identical film quality and uniformity on both sides of the substrates is achieved. The quadratic dependence of the 532 nm light output intensity ( $I^{2\omega}$ ) on film thickness (Figure 1) further demonstrates the uniformity of the chromophore orientation and that the response is a bulk rather than interface effect. Calibrating the data (Figure 1, inset) versus quartz yields  $d_{33} = 0.15 \text{ pm/V}$  and  $d_{31} = 0.25 \text{ pm/V}$ , values consistent with the modest computed molecular hyperpolarizability [ $\beta_{\text{tot}}(\omega = 0.0 \text{ eV}) = 81 \times 10^{-30} \text{ esu}$  for a linear trimer].<sup>11</sup> Using

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**Figure 1.** Square-root of the second harmonic generation response  $(I^{2\omega})^{1/2}$  as a function of DTPT film thickness. Inset:  $I^{2\omega}$  as a function of the fundamental beam incident angle. The dashed line is drawn as a guide to the eye. The solid line is the fitting result.



**Figure 2.** Specular synchrotron X-ray diffraction pattern for a thick (0.75  $\mu\text{m}$ ) DTPT film grown on a template-functionalized Si(100) substrate. Inset: Proposed molecular alignment in film.

standard assumptions,<sup>13</sup> the SHG analysis yields an average chromophore tilt angle of  $\sim 56.7^\circ$  with respect to the substrate normal.

Synchrotron X-ray diffraction (XRD) techniques<sup>14</sup> were employed to probe film microstructural regularity. The data reveal a specular feature at  $0.69 \text{ \AA}^{-1}$ , which corresponds to a repeat distance of  $9.1 \text{ \AA}$  (Figure 2). DFT-level molecular modeling<sup>11</sup> shows that the repeat distance between DTPT molecules in a H-bonded chain is  $\sim 16.8 \text{ \AA}$ , which, combined with the XRD data, yields a molecular tilt angle from the substrate normal of  $\sim 57^\circ$  in the films (Figure 2, inset). This result is in good agreement with the tilt angle derived from SHG data (vide supra) and shows that out-of-plane ordering of chromophore molecules has been achieved.

In summary, the donor–acceptor  $\pi$  electron chromophore DTPT was designed and synthesized. Triple H-bonding interactions direct self-assembled chromophore alignment in the desired molecular head-to-tail direction using a straightforward vapor phase deposition process. Angle-dependent SHG interference patterns for glass substrates coated on both sides and the quadratic dependence of the  $2\omega$  light output intensity on DTPT film thickness demonstrate high, uniform film quality and polarity. XRD also demonstrates long-range microstructural order and yields a molecular tilt angle in good agreement with polarized SHG data, demonstrating out-of-plane ordering of chromophore alignment. Future work will explore the scope of this growth process with second-generation chromophores.

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**Supporting Information Available:** Details of DTPT synthesis, film growth, and characterization (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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