

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

P. Zhu<sup>1</sup>, H. Kang<sup>1</sup>, A. Facchetti<sup>1</sup>, G. Evmenenko<sup>2</sup>, P. Dutta<sup>2</sup>, and T.J. Marks<sup>1</sup>

<sup>1</sup>Department of Chemistry and <sup>2</sup>Department of Physics and Astronomy, Northwestern University

*Microstructural acentricity – the alignment of molecular dipole moments in a material – is one of the basic requirements for creating electrooptic (EO) materials useful for high-speed optical telecommunications. A new molecular chromophore, DTPT (5-{4-[2-(4,6-diamino-[1,3,5]triazin-2-yl)-vinyl]-benzylidene}-pyrimidine-2,4,6-trione), was designed and synthesized to create a precursor for the vapor phase growth of a high-response organic EO film. Triple H-bonding interactions between neighboring molecules direct self-assembled chromophore alignment in a head-to-tail orientation using a straightforward vapor-phase thin-film deposition process. Angle-dependent Second Harmonic Generation (SHG) interference patterns and the quadratic dependence of the output light intensity on the film's thickness demonstrate high, reproducible film quality and uniformity. Synchrotron x-ray diffraction (XRD) demonstrates long-range order in the film and yields a molecular tilt angle in good agreement with polarized SHG data. This shows that out-plane ordering of chromophore molecules – i.e. ordering perpendicular to the substrate – has been achieved.*

Organic EO materials represent a promising direction in the quest to develop novel technologies for increased optical data network speed, capacity, and bandwidth. Achieving microstructural acentricity is a key, yet synthetically daunting challenge for developing such materials. To date, the principle EO active films that have been developed are electric-field poled polymers, Langmuir-Blodgett films, and covalent self-assembled superlattices (SASs) formed layer by layer. In addition to advantages, each approach also poses challenges – ranging from the inherent thermodynamic instability of poled polymers, to the inefficiency of SAS growth techniques, to the fragility of amphiphilic (having both water-loving and water-hating components) lattices enforced principally by van der Waals interactions.

We reported an alternative, vapor phase approach that utilizes robust patterns of directed triple H-bonds to assemble microstructurally acentric, EO-active films in an expedited growth process. This approach utilizes specifically designed intermolecular longitudinal triple H-bonding interactions to align chromophore molecules head-to-tail and preferentially perpendicular to the substrate, forming thin solid films from the vapor phase. Out-plane non-centrosymmetric microstructures are thereby achieved in smooth, optically clear, thermally robust films, which can be grown in hours. Theoretical work shows that such head-to-tail orientations also produce intermolecular cooperative effects, which substantially enhance the effective molecular hyperpolarizability of the films. The chromophore DTPT (5-{4-[2-

(4,6-diamino-[1,3,5]triazin-2-yl)-vinyl]-benzylidene}-pyrimidine-2,4,6-trione), containing H-bond + electron donor and H-bond + electron acceptor modules,



Authors (left to right)  
Peiwan Zhu, Antonio Facchetti,  
Tobin J. Marks, and Hu Kang

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#### Contact information

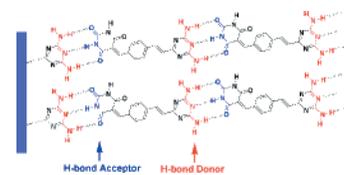
Tobin J. Marks  
Department of Chemistry,  
Northwestern University

Email: t-marks@northwestern.edu

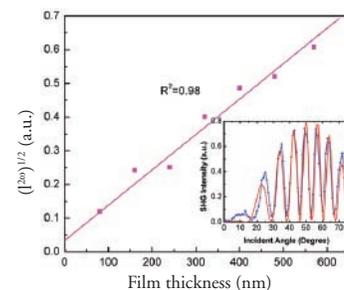
was synthesized and characterized using conventional analytical/spectroscopic techniques. The pyrimidine-2,4,6-trione and 4,6-diamino-1,3,5,-triazine-2-yl moieties of DTPT form longitudinally directed donor-acceptor triple H-bonds between neighboring molecules (**Figure 1**).

In this process, a melamine template was first anchored to a glass or Si (100) substrate. A Denton Vacuum DV-502 deposition apparatus ( $10^{-5}$  –  $10^{-6}$  Torr) was then used to fabricate films at 100 °C at a growth rate of 0.5 – 2.0 Å/s. The film growth rate and thickness was monitored with a quartz crystal sensor. The resulting films are optically transparent ( $\alpha \sim 10$  cm<sup>-1</sup> at 640 – 1800 nm) and smooth, as measured using atomic force microscopy (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 SHG measurements were carried out at  $\lambda_o = 1064$  nm. Angle-dependent interference patterns for glass substrates coated on both sides (**Figure 2a**, inset) demonstrate that identical film quality and uniformity on both sides of the substrate is achieved. The quadratic dependence of the 532 nm light output intensity ( $I^{2\omega}$ ) on film thickness (**Figure 2a**) further demonstrates the uniformity of the chromophore orientation. Calibrating the data (**Figure 2a**, inset) vs. quartz yields nonlinear optical coefficients of  $d_{33} = 0.15$  pm/V (picometers per volt) and  $d_{31} = 0.25$  pm/V. Using standard assumptions, the SHG analysis yields an average chromophore tilt angle of  $\sim 61.3^\circ$  with respect to the substrate normal.

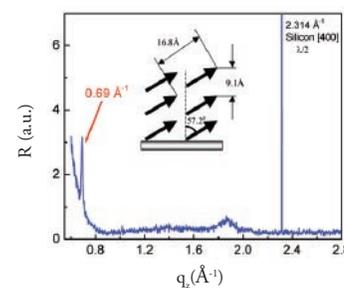
Synchrotron XRD techniques were employed to probe film microstructural regularity. The data reveal a specular (mirror-like) feature at  $0.69 \text{ \AA}^{-1}$ , which corresponds to a repeat distance of 9.1 Å (**Figure 2b**). Molecular modeling shows that the repeat distance between DTPT molecules in a H-bonded chain is  $\sim 16.8$  Å, which, combined with the XRD data, yields a molecular tilt angle relative to the substrate normal of  $\sim 57^\circ$  (**Figure 2b**, inset). This result is in good agreement with the tilt angle derived from SHG data and shows that out-plane ordering of chromophore molecules has been achieved. Importantly, these results demonstrate that appropriately designed molecule precursors can be used in gas phase film growth processes to produce smooth, robust, EO-active films with high microstructural acentricity.



**Figure 1.** Scheme for DTPT self-assembly.



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



**Figure 2b.** Specular synchrotron x-ray diffraction pattern for a DTPT film grown on a template-functionalized Si(100) substrate. Inset: Proposed molecular alignment in film.