

Self-Assembled Electro-Optic Thin Films with Dramatically Blue-Shifted Optical Absorption Based on Novel X-Shaped Two-Dimensional Charge-Transfer Chromophores

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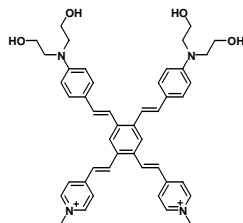
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INTRODUCTION

Molecule-based electro-optic (EO) materials have recently attracted intense research interest because of their potential applications in photonic technologies such as optical communications, integrated optics, and optical data processing and storage.^{1,2} Crucial prerequisites for achieving large bulk EO response are that the individual chromophores have large molecular hyperpolarizabilities (β) and that they are arranged in a noncentrosymmetric architecture.³ Typical EO chromophores are one-dimensional (1-D) π -conjugated systems end-capped with donor and acceptor moieties. Considerable efforts have been made to increase the molecular hyperpolarizability β by optimizing the D/A strength and/or the conjugation path of this kind of 1-D dipolar molecule. However, a major problem for these 1-D chromophores is the difficulty in optimizing the nonlinearity-transparency tradeoff. The increase in β of these chromophores is usually accompanied by bathochromic shifts of the optical maximum and a decrease in thermal stability, which limits their practical applications in photonics.^{1,2,4}

Beyond classical 1-D EO molecules, several new kinds of non-traditional chromophores with multi-dimensional charge-transfer such as "A-shaped",^{5,6} "X-shaped",^{7,8} and octapolar^{9,10} molecules have been being studied recently. Compared to 1-D dipolar molecules, these molecules take advantage of the off-diagonal components of the β tensor. They may offer an improved nonlinearity-transparency tradeoff. However, due to the synthetic challenges posed by these molecules, most research has focused on theoretical work and few experimental examples have been reported.^{11,12}

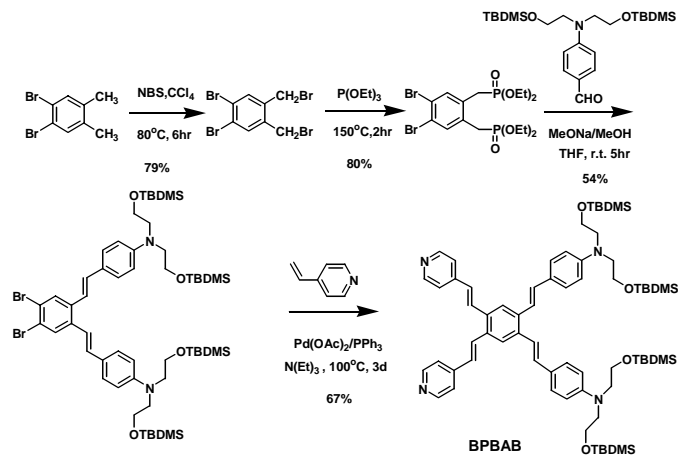
We report here the design, synthesis, and self-assembled thin film fabrication of a new type of "X-shaped" chromophore (**Scheme 1**). In this chromophore, the optical transition dipoles couple in such a manner as to drastically blue-shift the optical maximum while maintaining a large molecular hyperpolarizability. Computational results show that this chromophore possesses a very large β_0 of 407×10^{-30} esu and a rather blue-shifted λ_{\max} at 369nm. Moreover, when end-capped with two kinds of functional groups, the new chromophore can be employed in a covalent layer-by-layer self-assembly approach for the fabrication of intrinsically polar, robust, and structurally regular EO thin films.^{13,14}



Scheme 1. Molecular structure of the X-shaped chromophore.

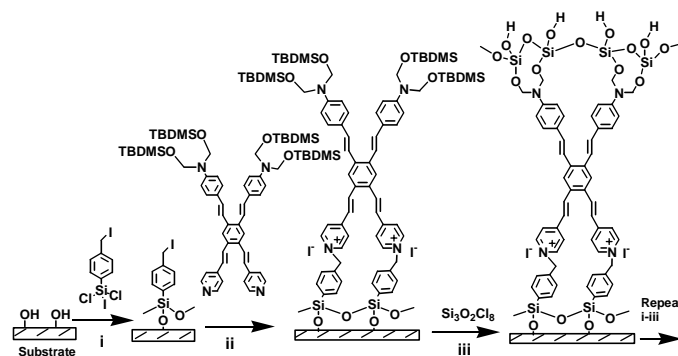
RESULTS AND DISCUSSION

The synthesis of chromophore precursor 1,2-bis-((E)-2-pyridin-4-yl-vinyl)-4,5-bis((E)-2-[p-N,N-bis(2-tert-butyl-dimethylsiloxyethyl)amino-phenyl]ethenyl)-benzene (**BPBAB**) is shown in **Scheme 2**, and the synthetic details will be published elsewhere. The new compounds were fully characterized by conventional analytical/spectroscopy techniques. Thermal analysis data show that the yellow crystalline chromophore precursor **BPBAB** is thermally very stable ($T_d > 340^\circ\text{C}$).



Scheme 2. Synthesis of X-shaped chromophore precursor **BPBAB**.

Films have been fabricated on a variety of substrates (glass, quartz, silicon) via the iterative three-layer process shown in **Scheme 3**: (i) hydrophilic substrates are immersed in a 15 mM solution of dichloro-iodo-(4-iodomethyl-phenyl)-silane in pentane for 30 min under rigorously anhydrous and anaerobic conditions, followed by rinsing and drying. A benzyl halide-functionalized surface is obtained via the self-limiting chemisorption of the silane; (ii) the functionalized substrates are spin-coated with a 5 mM **BPBAB** solution in toluene on both sides and cured at 120°C for 40 min in vacuum oven, then washed with toluene. The chromophore layer is thereby self-assembled via a quaternization reaction; (iii) the substrates are then dipped in a capping solution ($\text{Si}_3\text{O}_2\text{Cl}_2$:dry pentane; 1:150 v/v) for 30 min under rigorously anhydrous and anaerobic conditions. A polar structure is thereby locked in a three-dimensional siloxane network, and the active sites are also regenerated for subsequent layer deposition.



Scheme 3. Self-assembly of the X-shaped chromophore.

UV-visible spectroscopy (**Figure 1, inset**) shows that the λ_{\max} of the films is at the remarkably short wavelength of 325nm. The linear dependence of the absorbance at 325nm on the number of layers (**Figure 1**) indicates that essentially equal quantities of chromophore are deposited on the substrates in constructing each layer.

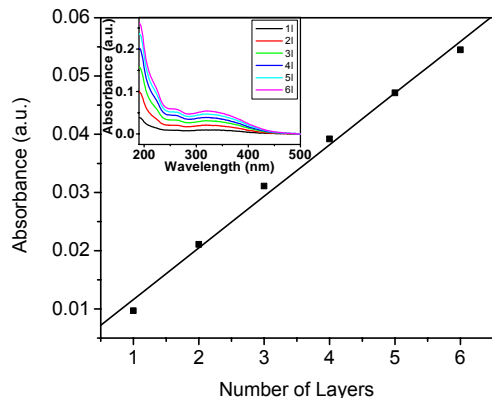


Figure 1. UV-vis absorbance of films at $\lambda_{\max} = 325$ nm as a function of the number of layers. **Inset:** UV-vis spectra of films grown on fused quartz.

Polarized transmission SHG measurements on the present films at $\lambda_0 = 1064$ nm show a quadratic dependence of the 532 nm light output intensity ($I^{2\omega}$) on the number of layers (**Figure 2**), indicating preservation of polar microstructure as layer-by-layer assembly progresses. The multilayer films exhibit large second-order macroscopic EO responses $\chi^{(2)} \sim 300$ pm/V and $r_{33} \sim 90$ pm/V at 1064 nm (obtained by calibration vs quartz). Angle-dependent SHG interference patterns for glass substrates coated on both sides demonstrate that the three-step deposition process affords identical film quality and uniformity on both sides of the substrate (**Figure 2 inset**).

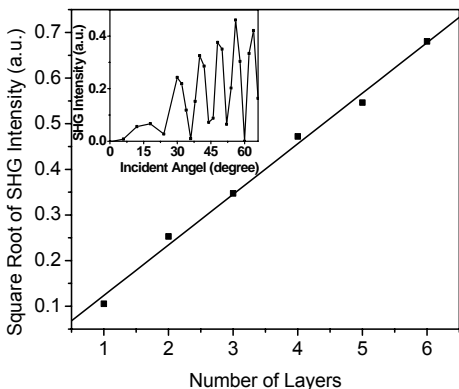


Figure 2. Square-root of film 532 nm second-harmonic generation (SHG) response ($I^{2\omega}$, arbitrary units) as a function of the number of layers. **Inset:** SHG response as a function of fundamental beam incident angle from a float glass slide having a film on either side.

Specular x-ray reflectivity is used to probe the microstructural evolution of these siloxane-based superlattices. Structural details are obtained by fitting the multilayer reflectivity data to a Gaussian-step electron density model. Typical reflectivity data for a five-layer sample are presented in **Figure 3 inset**. The films exhibit pronounced minima, “Kiessig fringes”, corresponding to destructive interference of reflections from the top and bottom of the film and indicate a narrow distribution of film thicknesses. The film thickness increases linearly as a function of the number of layers (**Figure 3**), underscoring the high structural regularity and efficiency of this approach. From the slope of

the XRR data, an average interlayer spacing of 67.3 Å can be deduced.

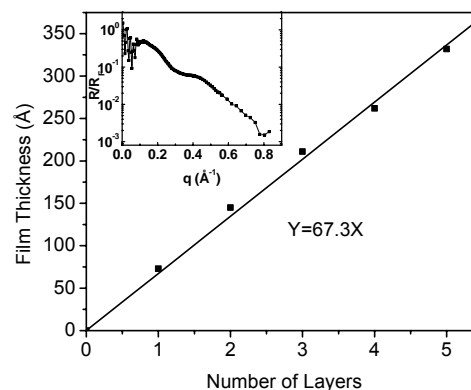


Figure 3. Specular X-ray reflectivity (XRR)-derived film thickness (Å) as a function of the number of layers. **Inset:** XRR data for a five-layer sample.

CONCLUSIONS

In summary, an “X-shaped” 2-D charge-transfer chromophore was designed and synthesized. The chromophore exhibits a dramatically blue-shifted optical maximum while maintaining a large molecular hyperpolarizability. Self-assembled thin films of this chromophore show excellent EO response and transparency. The λ_{\max} of the films is at a remarkably short wavelength of 325 nm. Estimated $\chi^{(2)} \sim 300$ pm/V and $r_{33} \sim 90$ pm/V at 1064nm have been obtained.

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