

**Supporting Information**  
for  
**Vapor Phase Self-Assembly of Electrooptic Thin Films via Triple Hydrogen Bonds**

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**Materials and methods.** Unless stated otherwise, chemicals were purchased from Aldrich Chemical Co. and used as received. Single-crystal silicon (100) substrates were purchased from Semiconductor Processing Company, Inc. NMR spectra were recorded on a Varian Mercury-400 MHz or Varian INOVA-500 MHz spectrometer. Mass spectra were recorded with a Micromass Quattro II Triple Quadrupole HPLC/MS/MS Mass Spectrometer. Elemental analyses were performed by Midwest Microlabs. UV-vis spectra were recorded on a Cary 1E spectrophotometer. Polarized second harmonic generation measurements were carried in the transmission mode with a Q-switched Nd:YAG laser operating at 1064 nm, with a pulse width of 3 ns at a frequency of 10 Hz. Atomic force microscopic images were recorded with a Nanoscope II instrument (Digital Instruments, Inc.).

**Synthesis of 4-[2-(4,6-diamino-[1,3,5]triazin-2-yl)-vinyl]-benzaldehyde.** To 107.2 g (800 mmol) of benzene-1,4-dicarboxaldehyde suspended in 450 mL methanol was added with stirring 294.0 g of 31% aqueous sulfuric acid (50 mL of concentrated sulfuric acid was added slowly to 200 mL of water while stirring). The solid dissolved and a yellow solution was obtained. The solution was heated to 80 °C with an oil bath, and 25.0 g (200 mmol) 6-methyl-[1,3,5]triazine-2,4-diamine powder was added. The solution was stirred at 80 °C for 8 h then cooled to room temperature. Next, 1.2 g of yellow byproduct (1,4-bis[4-[2-(4,6-diamino-[1,3,5]triazin-2-yl)-vinyl]]-benzene) was removed by filtration, and the filtrate was treated with 2000 mL water. The resulting solid was collected by filtration and washed with saturated aqueous NaHCO<sub>3</sub> and water until neutral. The excess benzene-1,4-dicarboxaldehyde was removed by sonicating and washing with acetone three times. Light yellow product (20.0 g, yield: 41%) was obtained. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ 9.992 (s, 1H), 7.894 (d, J = 8.0 Hz, 2H), 7.847 (d, J = 7.5 Hz, 2H), 7.806 (d, J = 15.5 Hz, 1H), 6.928 (d, J = 15.5 Hz, 1H), 6.806 (br, 4H). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>): δ 193.914, 193.417, 170.671, 167.847, 141.836, 136.833, 131.461, 130.688, 128.883.

**Synthesis of 5-{4-[2-(4,6-Diamino-[1,3,5]triazin-2-yl)-vinyl]-benzylidene}-pyrimidine-2,4,6-trione (DTPT).** To 7.29 g (30 mmol) of 4-[2-(4,6-diamino-[1,3,5]triazin-2-yl)-vinyl]-benzaldehyde suspended in 150 mL of 1-pentanol at 130 °C was cautiously added 75 mL of hot aqueous sulfuric acid (25 mL of concentrated sulfuric acid was added to 50 mL of water with cautious stirring). The solid dissolved immediately, and a yellow solution was obtained. To this solution, 4.61 g (36 mmol) of powdered barbituric acid was added while stirring vigorously at 140 °C. Yellow precipitate appeared immediately. The mixture was briefly refluxed at 140 °C for 10 min then filtrated while hot. The solid which collected was washed with 50 mL of warm 1-pentanol, then suspended in 300 mL of water and neutralized with saturated aqueous NaHCO<sub>3</sub>. The solid was collected by filtration and washed with water. Yellow product (9.72 g, yield: 88%) was obtained. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 11.519 (s, 1H), 11.375 (s, 1H), 8.378 (s, 1H), 8.234 (d, J = 8.0 Hz, 2H), 7.915 (d, J = 16.0 Hz, 1H), 7.857 (d, J = 8.0 Hz, 2H), 7.101 (br, 4H), 7.047 (d, J = 16.0 Hz, 1H). m.p. > 350 °C. EA found: C, 52.20; H, 3.86; N, 26.12. Calculated for C<sub>16</sub>H<sub>13</sub>N<sub>7</sub>O<sub>3</sub>·H<sub>2</sub>O: C, 52.03; H, 4.09; N, 26.55. MS (ESI, relative abundance): M<sup>+</sup>+1 (68), M<sup>++</sup>+2 (13), 242.1 (5), 217.1 (6), 179.0 (15), 157.0 (30), 101.0 (55), 79.1 (100). MS (high resolution, ESI): MH<sup>+</sup>(352.1158).

**Sublimation of DTPT.** To achieve further purification and to ascertain that DTPT is stable under sublimation conditions, the chromophore was gradient sublimed at 330 °C / ~ 3 × 10<sup>-8</sup> Torr for 24 h. The <sup>1</sup>H NMR spectrum of the sublimed material is identical to that prior to sublimation. EA found: C, 54.21; H, 3.61; N, 26.60. Calculated for C<sub>16</sub>H<sub>13</sub>N<sub>7</sub>O<sub>3</sub>: C, 54.70; H, 3.73; N, 27.91. This result shows that the water of crystallization is lost on sublimation.

### Preparation of functionalized substrates

**Cleaning of substrates:** Sodium lime glass, fused quartz, and silicon wafer substrates were cleaned by immersion in “piranha” solution (H<sub>2</sub>SO<sub>4</sub> / 30% H<sub>2</sub>O<sub>2</sub> 7:3 (v/v); *Caution: “Piranha” is an extremely dangerous oxidizing agent and should be handled with care using appropriate shielding*) at 80 °C for 1h. After cooling to room temperature, they were rinsed with deionized water and then subjected to an RCA-type cleaning protocol (NH<sub>3</sub> ·H<sub>2</sub>O/ H<sub>2</sub>O/ 30% H<sub>2</sub>O<sub>2</sub> 1:5:1 (v/v) at room temperature, 40 min). They were then washed with deionized water and dried in oven at 125 °C overnight.

**Self-Assembly of 3-aminopropyltrimethoxysilane.** A room temperature solution of 196 mL of 95% ethanol and 4 mL of 3-aminopropyltrimethoxysilane was allowed to stand for 10 min to ensure silanol formation. The substrates were then immersed in this solution for 10 min. They were next rinsed three times with 95% ethanol and dried in a dry N<sub>2</sub> dstream, and cured for 10 min in a vacuum oven at 110 °C.

**Surface functionalization with 6-chloro-1,3,5-triazine-2,4-diamine.** The reagent 6-chloro-1,3,5-triazine-2,4-diamine (0.15 g) was suspended in 50 mL of 1-pentanol at 150 °C. The 3-aminopropyltrimethoxysilane functionalized substrates were then loaded into the reactor. After refluxing for 24 h, they were cooled to room temperature and rinsed with 1-pentanol, deionized water, and acetone.