Macromolecules **2001,** *34,* 253−261

Progress toward Device-Quality Second-Order Nonlinear Optical Materials. 4. A Trilink High $\mu\beta$ NLO Chromophore in Thermoset Polyurethane: A “Guest−Host” Approach to Larger Electrooptic Coefficients

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Received September 7, 2000; Revised Manuscript Received November 13, 2000

ABSTRACT: A novel trilinkable thiophene-containing second-order nonlinear optical (NLO) chromophore [$(HO)_3$FTC] was synthesized from a trilinkable donor bridge and a tricyanofuran electron acceptor (TCF). The TCF acceptor was modified with two butyls which greatly increased solubility and processability of the trihydroxy-functionalized chromophore and inhibited strong chromophore−chromophore interaction. A thermal stability study of $(HO)_3$FTC indicates that the free hydroxyl group located close to the cyano acceptor causes the chromophore to decompose at a much lower temperature than FTC chromophores with no free hydroxyl groups. Significantly improved thermal stability of the chromophore in polyurethane film was obtained by masking the free hydroxyl groups with toluene diisocyanate. New polyurethane prepolymer synthetic schemes were designed and studied in detail to improve electric field induced dipole alignment. Enhancement of over 150% in poling efficiency was achieved by reducing the degree of chromophore attachment to polymer backbone before applying an electric poling field through a “guest−host” approach. It was found to be critical to allow isocyanate and hydroxyl cross-linkers to react at higher temperature for a longer time to form a partially cross-linked prepolymer before the −NCO masked trilink chromophore was added. By anchoring chromophores to a three-dimensional cross-linked polyurethane network at three points, the thermal stability of poling-induced electrooptic activity was enhanced by 33 °C.

Introduction

Organic second-order nonlinear optical (NLO) materials have received increasing attention for application in electrooptic devices characterized by large bandwidth (>100 GHz), low drive voltage (<5 V), and facile integration with very large-scale integration semiconductor electronics.[1,3] Device-quality materials must satisfy several requirements including (1) large electrooptic (EO) coefficients (r_{33}), (2) high thermal stability of poling induced EO activity, (3) good processability, etc.[3] Realization of any individual above-mentioned requirement is not difficult; simultaneously, optimization of all properties is not an easy task.[3−7] To obtain large EO coefficients, chromophores with high molecular hyperpolarizability (β) must be employed. High β chromophores are typically characterized by large dipole moments and extended π-conjugation. Strong chromophore−chromophore electrostatic interactions not only lead to poor solubility and poor processability but also interfere with dipole alignment. Thermal stability and poling efficiency are also interrelated. Optimization of one often causes the attenuation of the other.[6,8]

Thermal stability of poling-induced chromophore dipole alignment can be improved by covalent incorporation of functionalized NLO chromophores into various polymer systems. It can be further increased by increasing the number of points by which the chromophore is attached to the matrix. It has been demonstrated that an additional cross-linking site on a chromophore can enhance thermal stability by 20−30 °C.[6,9] We have reported a dilink FTC chromophore (Figure 1, middle) which has a $\mu\beta$ value of 17 600 at 1.9 μm.[10,11] The chromophore was incorporated into polyurethane yielding a thermal stability of 90 °C and an average EO coefficient of 36 pm/V.[10] To improve the thermal stability of the FTC material, we developed a synthetic scheme to introduce a third hydroxyl group on the thiophene ring of the aminophenylvinylenethienyl donor bridge to obtain a trilink chromophore $(HO)_3$FTC (Figure 1). In previous studies, we have already observed that the EO coefficient obtained for the dilink FTC polyurethane (PU) material was lower than that obtained from the guest−host FTC/PMMA material (36 vs 57 pm/V).[10] It is expected that a decent poling efficiency is even more difficult to obtain for cross-linked materials of the trilink chromophore due to increased chain entanglement. In this work, we investigated the synthesis of the trilink FTC chromophore, and the incorporation of the chromophore into polyurethane systems, and found that an enhancement of >150% in EO coefficient could be achieved by using a “guest−host” approach instead of the conventional polyurethane synthesis and processing procedures.

Results and Discussion

Synthesis and Characterization of $(HO)_3$FTC. So far, only very few trifunctionalized chromophores have been prepared, and none have very high $\mu\beta$ values (greater than 5000×10^{-48} esu at 1.9 μm). In Figure 1

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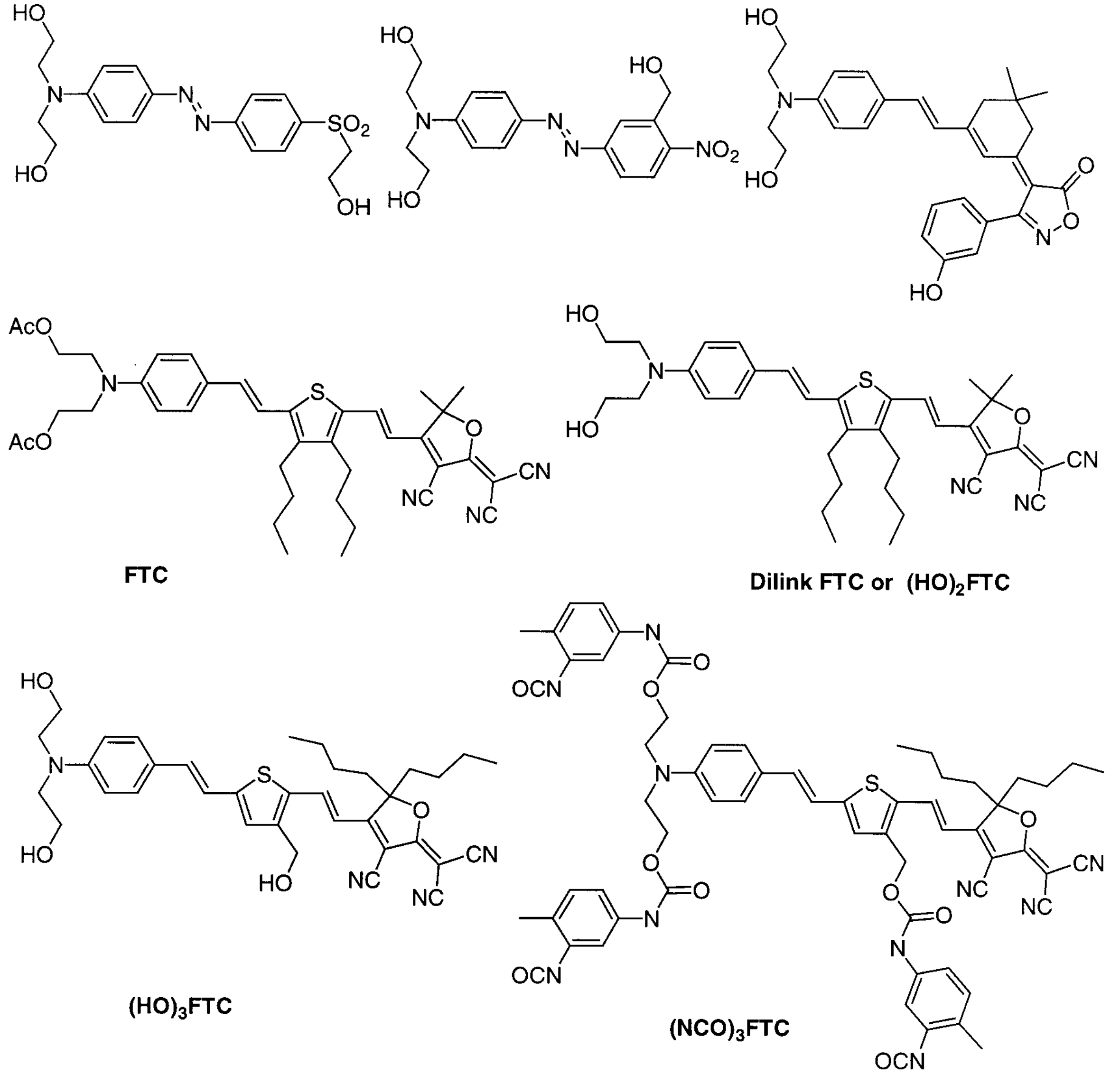


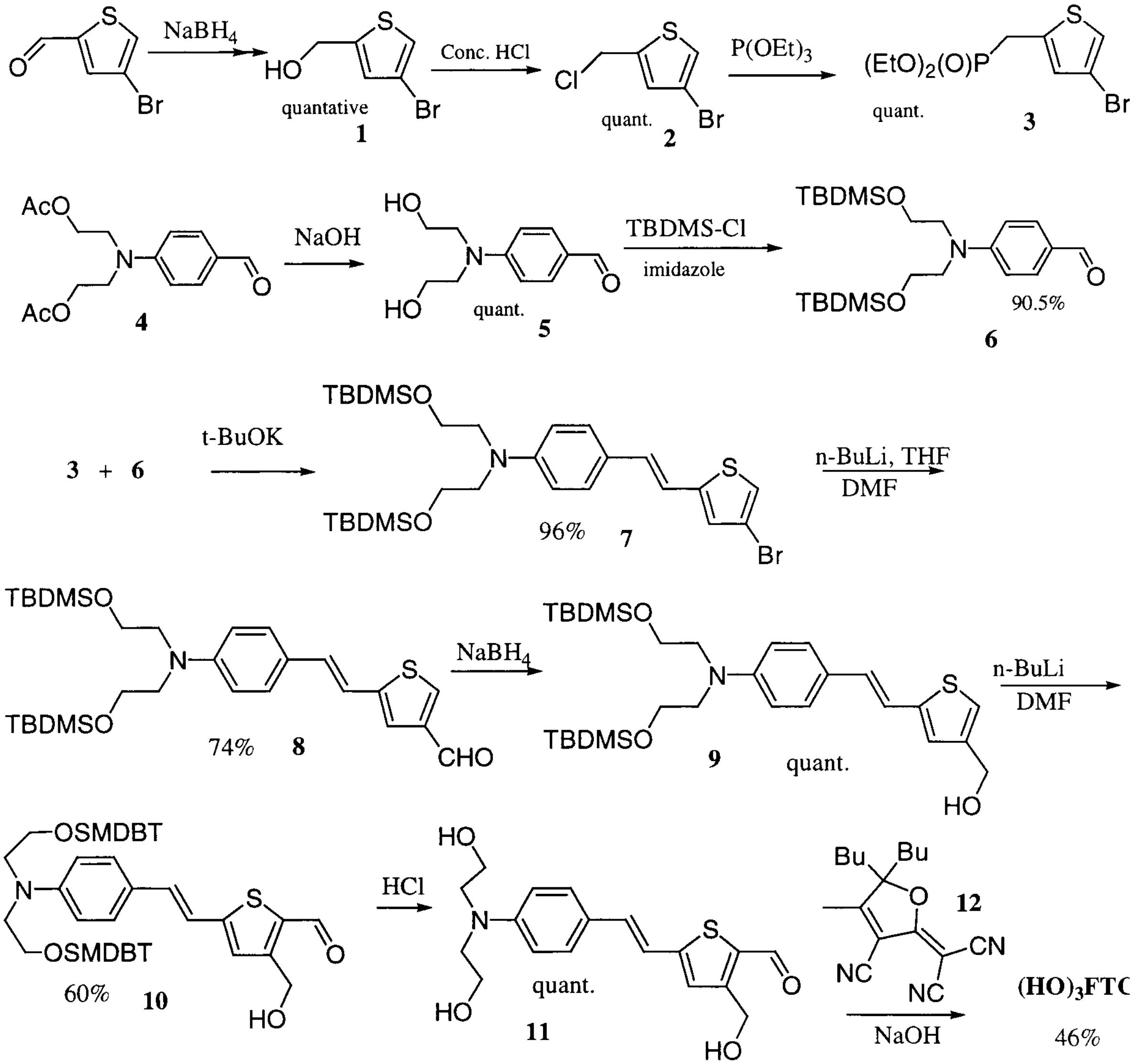
Figure 1. Top: some representative literature trilink chromophores. Middle: FTC and dilink FTC we have recently reported. Bottom: trilink FTCs synthesized in the present work.

(top) we list representative trifunctional chromophores found in the literature.[6,10,12] In these chromophores, two hydroxyl groups are realized by adopting a commercial dihydroxylaniline donor. The same electron donor is used for the synthesis of the trihydroxy-functionalized FTC chromophore $(HO)_3$FTC. The third hydroxyl group is introduced as a side group on the thiophene ring. The synthetic scheme of $(HO)_3$FTC is shown in Scheme 1. 4-Bromothiophene-2-carboxaldehyde was reduced to the corresponding alcohol quantitatively. Subsequent treatment with concentrated hydrochloric acid afforded 4-bromo-2-thienylmethyl chloride. Arbuzov reaction of the chloride with diethyl phosphite gave the phosphonate intermediate **3**. The synthesis of the dihydroxy-functionalized donor (compound **5**) has been reported earlier.[4] **5** was then reacted with TBDMS−Cl to protect the hydroxyl groups. **3** and **6** were coupled by the Hornor−Emmons reaction in 96% yield. The formylation of the resulting bromide **7** was effected with *n*-butyllithium and DMF in 74% yield. In this reaction, the isomeric aldehyde (−CHO on C5 of the thiophene ring), which resulted from the migration of lithium from C4 to C5, was identified as the major side product. It was found that a short reaction time for the lithiation was critical to suppress the side product. The aldehyde **8** was reduced by sodium borohydride to afford an alcohol that was then formylated directly with BuLi/DMF to produce the desired donor bridge. The TBDMS protecting groups were cleaved with HCl/acetone to yield trihydroxy-functionalized donor bridge **11**.

High $\mu\beta$ chromophores generally have poor solubility especially when they carry free hydroxyl groups. Because of strong interchromophore hydrogen bonding, simple trilink FTC is not processable if it is not modified with solublizing side chains. To address the solubility problem, a dibutyl-substituted version of the TCF acceptor, namely, 3-cyano-5,5-dibutyl-2-dicyanomethylene-4-methyl-2,5-dihydrofuran (compound **12** in Scheme 1, denoted DBTCF), was synthesized. The trilink FTC based on DBTCF (denoted $(HO)_3$FTC) is shown in Figure 1.

The acceptor 3-cyano-5,5-dibutyl-2-dicyanomethylene-4-methyl-2,5-dihydrofuran was synthesized using a modified literature method[13] and was coupled to the donor bridge by Knovenegal condensation to afford $(HO)_3$FTC in 46% yield. $(HO)_3$FTC has an all-trans conformation as evidenced by the large coupling constants in ^{1}H NMR (see Figure 3).

Scheme 1. Synthesis of (HO)$_3$FTC



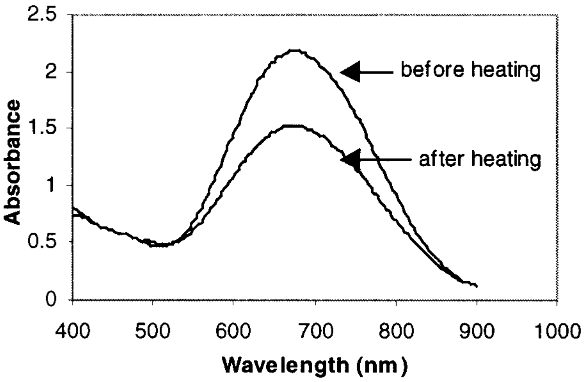


Figure 2. UV–vis absorption of (HO)$_3$FTC polyurethane film before and after heating at 140 °C for 1 h.

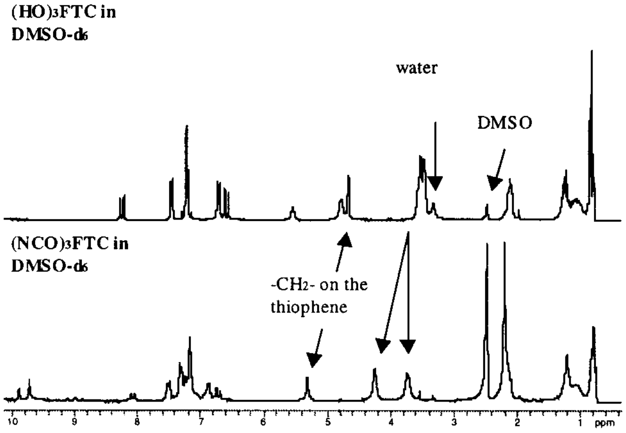


Figure 3. NMR spectra of (HO)$_3$FTC and (NCO)$_3$FTC.

Physical Properties of (HO)$_3$FTC and Its Polyurethane (PU) Thin Films. The two butyl groups of (HO)$_3$FTC are excellent at preventing chromophore dipoles from forming a tightly packed crystalline structure. The chromophore has excellent solubility in common organic solvents such as acetone, THF, methanol, dioxane, methylene chloride, etc. The UV–vis absorption maximized at 639 nm in chloroform and at 622 nm in dioxane. The λ_{max} difference in dioxane and chloroform is only 17 nm, which is much lower than the usual λ_{max} differences (~50 nm) of chromophores with similar $\mu\beta$ values to FTC. The apparently low bathochromism of (HO)$_3$FTC is due to the formation of hydrogen bonding between hydroxyl groups and dioxane solvent.[5]

The thermal stability of (HO)$_3$FTC was studied by differential thermal analysis (DTA). A sharp melting endotherm was observed at 207 °C, and the onset

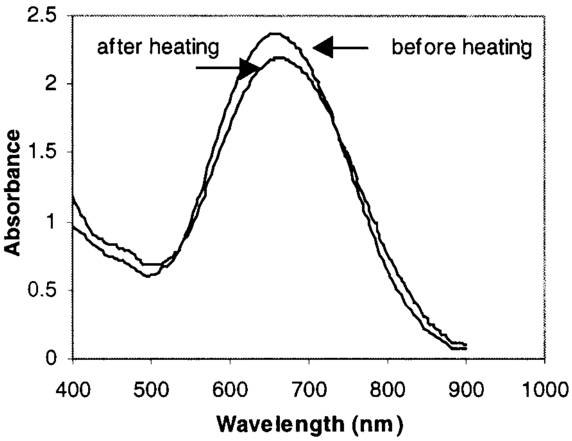


Figure 4. UV−vis absorption of $(NCO)_3FTC$ polyurethane film before heating and after heating at 140 °C for 1 h.

decomposition temperature was observed to be 240 °C. $(HO)_3FTC$ and cross-linkers toluene diisocyanate (TDI) and triethanolamine (TEA) were mixed in a drybox and reacted for 20 min at 80 °C to form an oligomeric prepolymer solution with a molecular weight $M_n = 1753$. Despite the oligomeric nature, the solution was viscous enough to spin uniform films of 1.5−2 μm thickness. The thermal stability of $(HO)_3FTC$ in polyurethane film was studied by UV−vis absorption spectroscopy. After heating at 140 °C for 1 h, the peak absorbance dropped by 40% (see Figure 2). After heating at 120 °C it dropped by 21%. The changes in chromophore absorption maximum indicate that the chromophore decomposes severely at temperatures required for the poling/curing processes. Since FTC is stable to 361 °C in N_2 atmosphere[10] and the $(HO)_2FTC$ polyurethane material was stable in air at 130 °C during film processing,[11] we conclude that the intramolecular reaction between the cyano group(s) and the hydroxyl group on the thiophene ring was responsible for $(HO)_3FTC$ decomposition.

Synthesis and Physical Properties of $(OCN)_3FTC$. To overcome the stability problem associated with the free hydroxyl group, $(HO)_3FTC$ was reacted with a large excess of TDI to mask each of the $(HO)_3FTC$ hydroxyl groups with a TDI, forming a tri-NCO-functionalized FTC variant—$(OCN)_3FTC$. After precipitation and reprecipitation from THF/hexane, the proton NMR spectrum of $(NCO)_3FTC$ was recorded and is shown in Figure 3 together with that for $(HO)_3FTC$. Hydroxyl proton peaks are no longer seen in the $(NCO)_3FTC$ ^1H NMR spectrum, indicating that the TDI protection is complete. The difference between the integrations of aromatic peaks in the region of 6.95−6.0 ppm in $(NCO)_3FTC$ and $(HO)_3FTC$ ^1H NMR spectra is nine protons, which is consistent with the number of protons on the three TDI moieties.

The thermal stability of $(NCO)_3FTC$ in polyurethane was also studied by UV−vis absorption spectroscopy. Polyurethane films were prepared in a manner similar to that used for $(HO)_3FTC$. UV−vis absorption spectra of films were taken before and after 1 h thermal curing at 140 °C. Only a 7.6% percent drop in peak absorption was observed (Figure 4), indicating that thermal stability of trilink FTC can be greatly improved by masking the hydroxyls with TDI.

Conventional Method of $(OCN)_3FTC$/PU Synthesis and Its Modification. In previous studies of thermoset polyurethane NLO materials, we have established polyurethane NLO material synthesis and processing conditions.[6] The hydroxy-functionalized chromophore is reacted first with TDI at 80 °C for 40 min, followed by addition of trilinker TEA and subsequent reaction at 80 °C for 20−30 min. In this scheme the overall ratio of NCO/OH is controlled to be unity. Dilink FTC chromophore has been incorporated into TDI/TEA polyurethane at 15 wt % loading level using this condition, and an average r_{33} of 36 pm/V was obtained. However, when this procedure was adopted to prepare the $(TDI)_3FTC$ prepolymer, the resulting films could not be poled efficiently. A typical r_{33} value obtained was 10 pm/V.

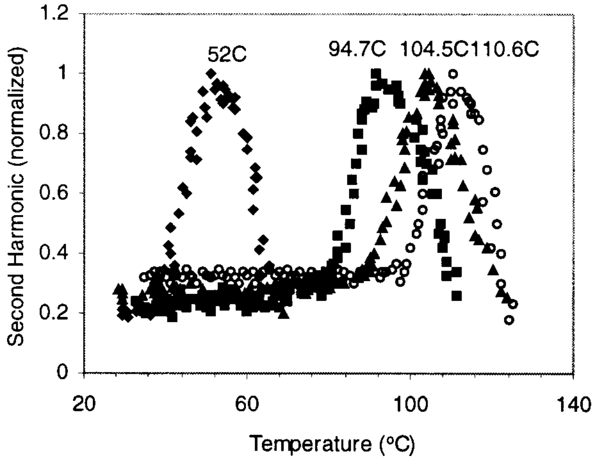


Figure 5. In-situ poling of (NCO)3FTC/PU films: (◆) fresh film, (■) 120 °C precured for 3 min, (▲) 140 °C precured for 3 min, (○) 160 °C precured for 3 min.

The poor poling performance of $(NCO)_3FTC$ is attributed to its very limited mobility in polyurethane matrix. In newly spun films, the chromophore molecules were not fully attached to polymer chains due to the oligomeric nature of the prepolymer. However, in the subsequent room temperature vacuum-drying and the precuring processes, unreacted cross-linkers and chromophores further reacted to form a rather hardened lattice, greatly reducing the mobility of chromophore. The trilink nature of $(NCO)_3FTC$ renders it locked in place even earlier than the dilink FTC, thus resulting in reduced ability of chromophore dipoles to align along the poling field.

To improve poling efficiency of the trilink FTC−PU material, we modified the above procedure. In the modified scheme, the overall ratio of NCO/OH was still controlled to be unity. But the cross-linkers TDI and TEA were reacted first at a much higher temperature (100 °C) for 30 min to form an oligomeric prepolymer (denoted **PP1**). $(NCO)_3FTC$ was then simply dissolved in the prepolymer solution at 80 °C within a minimum amount of time (about 5 min). The prepolymer solution was viscous enough to spin-coat uniform films of 1.5−2 μm thickness. Films were dried in a vacuum oven at ambient temperature for 9 h. An in-situ poling technique and FTIR spectroscopy were used to study the matrix hardening process and the influence of thermal precuring on poling behavior. Figure 5 shows the second-harmonic responses of the films as a function of ramping temperature. The temperatures corresponding to SH peaks are defined as optimal poling temperatures (T_{opt}). Below T_{opt}, films cannot be efficiently poled. Beyond this temperature, the soft film cannot support a high poling field.

Unprecured fresh films had a very low T_{opt} (e.g., ~52 °C). From the above discussion, it is clear that the best

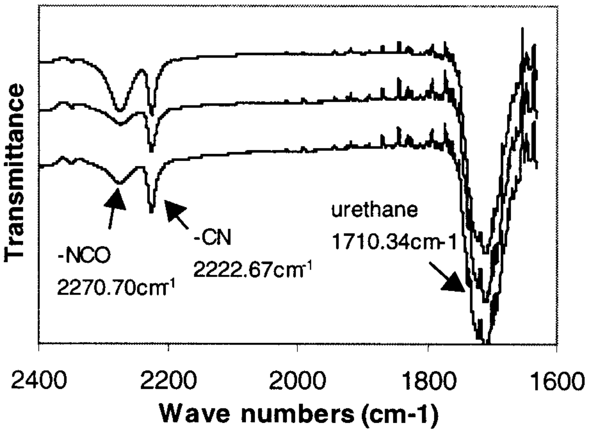


Figure 6. FTIR spectra of PP1/(HO)$_3$FTC films: top, unprecured film; middle, 80 °C, 1 h; bottom, 120 °C, 3 min.

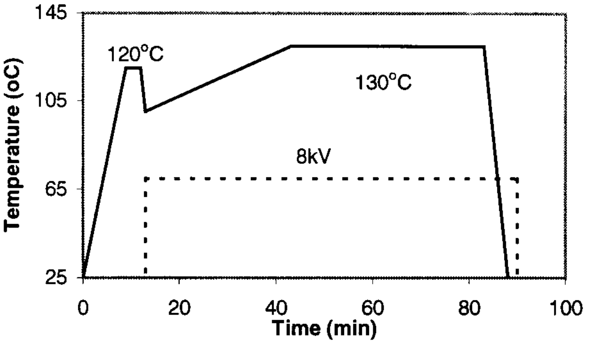


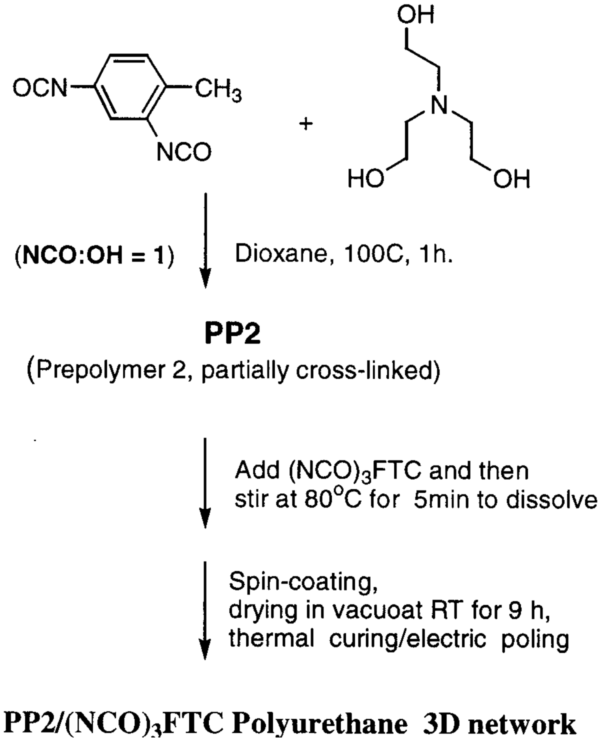
Figure 7. Poling profile for PP1/(NCO)$_3$FTC film.

poling efficiency would be obtained if the fresh film was poled without precuring and poling temperature was increased from its T_{opt} (52 °C) at a rate that matches the change of T_{opt}. However, this poling strategy is not practical. First, the poling/curing will take very long time to reach final lattice hardening. In Figure 6, we show that a significant amount of isocyanate still existed in the film after being heated at 80 °C for 1 h. Second, poling over a long period of time will allow atmospheric moisture to react with isocyanate, leading to poor film quality and reduced thermal stability.[6]

A short period of precuring (3 min) at elevated temperatures significantly increased optimal poling temperatures. For films precured at 120, 140, and 160 °C, T_{opt}'s reached 94.2, 104.5, and 110.6 °C, respectively. By comparing the relative intensity of the −NCO peak at 2270.7 cm^{-1} in IR spectra of unprecured and 120 °C precured films (Figure 6), we found that the amount of remaining isocyanate was reduced by about 50%. This indicated that the cross-linking reaction in solid polyurethane film proceeded quite rapidly at a temperature of 120 °C. On the basis of these observations, a stepwise poling scheme (Figure 7) was designed, and a r_{33} value of 18.7 pm/V was obtained.

A Novel "Guest−Host" Approach. By using the modified method of prepolymer preparation, the EO coefficient was improved by more than 70%. However, it was still only half of the r_{33} value achieved for dilink FTC−PU material. Cross-linking during the drying and precuring processes still locked up the chromophore molecules to a large degree.

Scheme 2. "Guest−Host" Approach to Incorporate (NCO)$_3$FTC into Thermoset Polyurethane



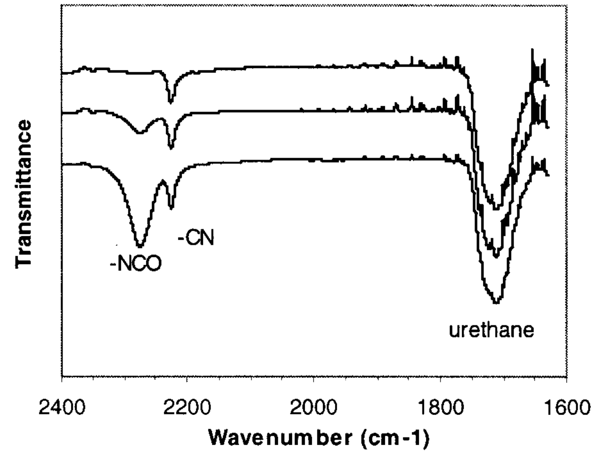


Figure 8. FTIR spectra of PP2/(NCO)$_3$FTC films. From bottom to top: unprecured film; 120 °C, 3 min; 130 °C, 40 min.

To further improve the poling efficiency of the (NCO)$_3$FTC polyurethane material, we proposed a "guest−host" method, which is shown in Scheme 2. A mixture of cross-linkers (TDI and TEA) with a unity ratio of cross-linking functional groups (−OH and −NCO) is heated at sufficiently high temperature (100 °C) for a period of time (1 h) to form a substantially cross-linked prepolymer (denoted PP2) as the host, then the trifunctionalized chromophore (NCO)$_3$FTC is added, and the mixture is stirred at 80 °C for a minimum amount of time (5 min) to form a solution for film spin-coating without forming substantial cross-linking between the chromophore and the "host" prepolymer. PP2 could precipitate from methanol solution, and the precipitate was not fully soluble in acetone. This is in sharp contrast to the behavior of PP1, which could not be precipitated from methanol, and its fresh film (after a few minutes vacuum-drying) was fully soluble in acetone. The different behavior indicates that PP2 had a much higher molecular weight than PP1. The IR spectra of unprecured PP2/(NCO)$_3$FTC films (after being vacuumed for 9 h) are shown in Figure 8. These show a much higher −NCO peak than the unprecured PP1/

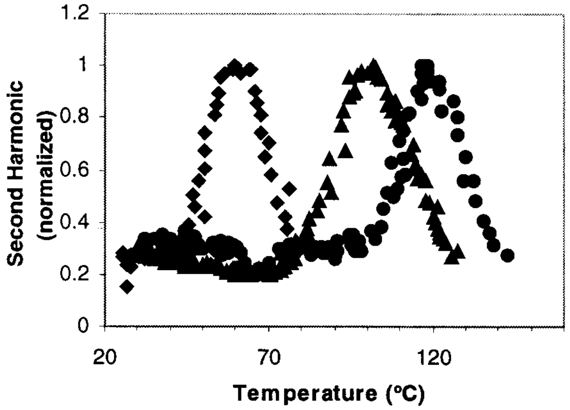


Figure 9. In-situ poling of PP2/(NCO)$_3$FTC films: (◆) unheated, (▲) 120 °C precured for 3 min, (●) 160 °C precured for 3 min.

(NCO)$_3$FTC film (Figure 6), which was expected since there was less unreacted −OH in fresh PP2/(NCO)$_3$FTC film, and more −NCO of (NCO)$_3$FTC survived the room-temperature drying process.

Such a “guest−host” system is different from the conventional guest−host systems in that the large amount of N−H group in the formed urethane structures and the remaining unreacted hydroxy groups in the prepolymer “host” could still cross-link with the chromophore at elevated temperatures. The phase separation encountered in the conventional guest−host systems is not observed. Two factors are attributed to this: first, the chromophore carries bulky side groups which prevent the chromophore from aggregating easily; second, the affinity of the chromophore to the “host” is stronger than in the conventional guest−host systems due to the hydrogen bonding between chromophore −NCO groups and “host” urethane groups and due to the fact that some chromophores are already partially linked to the “host”.

The in-situ poling technique was used again to study the poling/curing behavior of PP2/(NCO)$_3$FTC films under different thermal treatment. The results are shown in Figure 9. Unprecured films had a T_{opt} of 60 °C. After 3 min precuring at 120 and 160 °C, T_{opt} increased to 102 and 118 °C, respectively. The higher T_{opt} of the fresh film compared to that of fresh PP1/(NCO)$_3$FTC film suggested that the PP2/(NCO)$_3$FTC film was more robust. The increased hardness of the new film allowed electric poling without precuring. However, films were still sensitive to high poling voltage, especially at the early stage when cross-linking was incomplete. For example, when the film was poled using a poling temperature and voltage profile in Figure 10a, severe film bleaching was visually observed. The UV−vis spectrum of bleached film is shown in Figure 11 (bottom). The low refractive index (1.622 at 1.06 μm compared to 1.65 of unbleached films) was further evidence of chromophore decomposition. Interestingly, despite the severe bleaching of the film, an r_{33} value of 26.4 pm/V was still obtained. To reduce the damage to chromophore, we adopted a milder poling scheme (Figure 10b) in which corona discharge voltage was increased gradually. An r_{33} of 28 pm/V was obtained. The UV−vis spectrum of the poled film is also shown in Figure 11. The order parameter was calculated to be 0.25 with estimation that the chromophore decomposition caused ~5% drop in absorbance. The dynamic thermal stability of such poled films was measured by monitoring second-harmonic intensity as a function of ramping temperature. A typical result is shown in Figure 12 together with thermal stability data of dilink FTC polyurethane materials poled/cured under two different temperature profiles. Trilink FTC polyurethane shows a dynamic stability of 113 °C, which is 23 °C higher than the dilink FTC/PU material poled/cured using same final curing temperature (130 °C). If we compared stability of both materials poled/cured under their optimal conditions which is 120 °C precuring and 110 °C poling for dilink FTC/PU, the gain in dynamic stability is 33 °C.

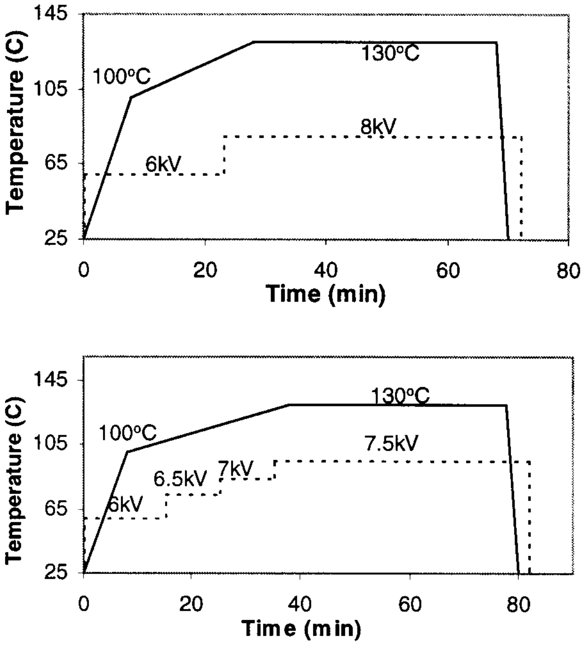


Figure 10. Corona poling/curing voltage and temperature profiles: (a, top) a profile that caused film bleaching; (b, bottom) a stepwise profile that produced 28 pm/V without bleaching the film.

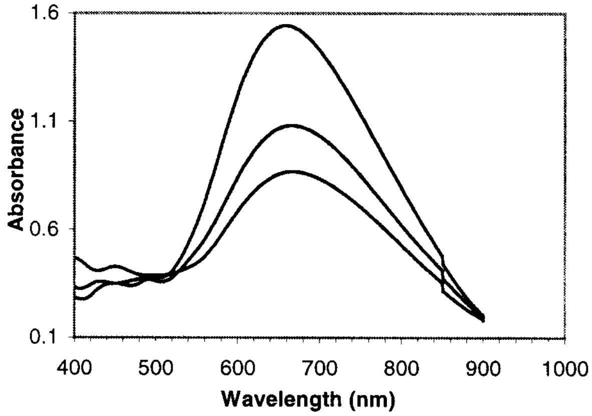


Figure 11. UV−vis absorption spectra of PP2/(NCO)$_3$FTC films: top, unheated film; middle, film poled using profile b in Figure 10; bottom, film poled using profile a in Figure 10.

Experimental Section

Chromophore Synthesis. All chemicals were purchased from Aldrich and were used as received. All reactions were carried out under argon unless otherwise specified. All reactions were monitored by thin-layer chromatography; therefore, the reaction yields were optimized unless otherwise stated. Only reactions appearing in the schemes depicted in Figures 4.3, 4.4, and 4.5 will be described in the synthesis section. ^{1}H

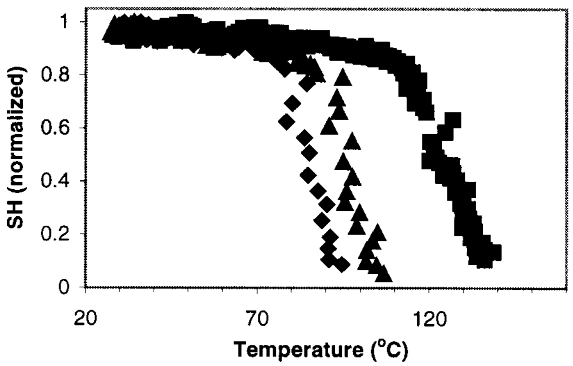


Figure 12. Thermal stability of PP2/(NCO)$_3$FTC and (HO)$_2$-FTC/PU materials: (◆) (HO)$_2$FTC/PU, precured at 120 °C for 3 min, poled at 110 °C for 1 h; (▲) (HO)$_2$FTC/PU, precured at 140 °C for 3 min, poled at 130 °C for 1 h; (■) PP2/(NCO)$_3$FTC poled using profile b in Figure 10.

NMR and ^{13}NMR were taken on a Bruker-250 FT NMR spectrometer, and tetramethylsilane was added to all NMR solvents as an internal standard unless otherwise stated. UV−vis spectra were obtained from a Perkin-Elmer Lambda-4C UV/vis spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Inc. Mass spectroscopy analyses were done at UC Riverside Mass Spectrometer Center. Thermal analyses were performed on a Shimadzu differential thermoanalyzer under nitrogen atmosphere at a heating rate of 10 °C/min. Melting points were determined in capillary tubes on a Mel-Temp II melting point apparatus unless otherwise indicated. Melting points were not corrected. Polymer molecular weights were determined using Waters GPC instrument. IR measurements were performed on a Perkin-Elmer FT-IR spectrometer, Spectrum 2000.

4-Bromo-2-thiophenemethanol (**1**). A solution of 4-bromo-2-thiophenecarboxaldehyde (0.424 mol, 90 g) in methanol (220 mL) was added to a solution of sodium borohydride (0.157 mol, 6.06 g) in dilute aqueous NaOH solution (40 mL, 0.2 N). The reaction was cooled with ice bath to keep the temperature below 5 °C. After the addition the mixture was stirred at room temperature for 1 h. A usual work-up afforded a quantitative yield. ^{1}H NMR (CDCl$_3$): δ 7.16 (s, 1H), 6.86 (s, 1H), 4.69 (s, 2H), 3.05 (br s,1H, alcoholic proton) ppm. ^{13}C NMR (CDCl$_3$): δ 145.12, 127.60, 122.51, 109.18, 59.41 ppm. Anal. Calcd for $C_5H_5Br_1O_1S_1$: C, 31.11; H, 2.61; Br, 41.39; S, 16.61. Found: C, 31.10; H, 2.55; Br, 41.53; S, 16.49.

5-Bromo-2-chloromethylthiophene (**2**). 4-Bromo-2-thiophenemethanol (**1**) (0.424 mol) was dropped into concentrated hydrochloric acid (700 mL, 37%) over 5 min, which was cooled with −2 °C bath. The reaction mixture was warmed to 5 °C over 2 h. Then the organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic solution was washed twice with a small amount of water (100 mL × 2), dried with MgSO$_4$, and condensed via rotary evaporation. The residue was distilled under reduced pressure to yield a clear liquid with a nearly quantitative yield: 0. 42 mol. ^{1}H NMR (CDCl$_3$): δ 7.19 (s, 1H), 6.98 (s, 1H), 4.70 (s, 2H) ppm. ^{13}C NMR (CDCl$_3$): δ 141.25, 129.83, 123.78, 109.26, 39.57 ppm. Anal. Calcd for $C_5H_4Br_1Cl_1S_1$: C, 28.39; H, 1.91; Br, 37.78; Cl, 16.76; S, 15.16. Found: C, 28.30; H, 1.85; Br, 37.91; Cl, 16.69, S, 15.10.

Diethyl 5-Bromo-2-thienylmethylphosphonate (**3**). A mixture of 5-bromo-2-chloromethylthiophene (**2**) (0.42 mol, 88.8 g) and triethyl phosphite (0.46 mol) was heated at 140 °C overnight. Rotary evaporation in vacuo gave the product in quantitative yield. ^{1}H NMR (CDCl$_3$): δ 7.09 (s, 1H), 6.90 (d, 3.6 Hz, 1H), 4.09 (m, 4H) ppm. 3.32 (d, 20.8 Hz, 2H), 1.30 (t, 6.5 Hz, 6H). ^{13}C NMR (CDCl$_3$): δ 134.13 (d, 39 Hz), 129.60 (d, 33 Hz), 121.82, 109.04, 62.31 (d, 23 Hz), 27.83 (d, 285 Hz), 16.18 (d, 20 Hz) ppm. Anal. Calcd for $C_9H_{14}Br_1O_3P_1S_1$: C, 34.52; H, 4.51; Br, 25.52; S, 10.24. Found: C, 34.34; H, 4.49; Br, 25.78; S, 10.06.

***p*-Bis(2-hydroxyethyl)aminobenzaldehyde** (**5**). *N*-Phenyldiethanolamine was treated with acetic anhydride and then followed by formylation to give *p*-bis(2-acetoxyethyl)aminobenzaldehyde (**4**). Deacetylation of compound **4** was conducted using the standard condition to give quantitative yield of **5**. The product was used in the next reaction after usual work-up and removal of solvents in vacuo without further purification. ^{1}H NMR (DMSO-d_6): δ 9.68 (s, 1H), 7.70 (d, 8.88 Hz, 2H), 6.86 (d, 8.97 Hz, 2H), 4.92 (t, 5.40 Hz, 1H), 3.61 (m, 8H) ppm. ^{13}C NMR (DMSO-d_6): δ 190.03, 153.33, 132.12, 124.73, 111.43, 58.50, 53.63 ppm.

***p*-Bis(2-*tert*-butyldimethylsiloxyethyl)amimobenzaldehyde** (**6**). The literature method of TBDMS protection was followed with minor modification: *tert*-butyldimethylsilyl chloride (0.648 mol) was added in portions to a mixture of *p*-bis-(2-hydroxyethyl)amimobenzaldehyde (**5**) (0.27 mol), dimethylformamide (140 g), and imidazole (1.35 mol). The reaction mixture was stirred at room temperature for 36 h. The mixture was then poured to 500 mL of water and extracted with hexane (100 mL × 3). The combined extract was dried over MgSO$_4$ and condensed via rotary evaporation. The residue was purified with flash chromatography on silica gel using 1 EtOAc/3 hexane as eluent to afford 106.97 g of light yellow oil: 90.5%. ^{1}H NMR (CDCl$_3$): δ 9.70 (s, 1H), 7.68 (d, 8.80 Hz, 2H), 6.72 (d, 9.11 Hz, 2H), 3.79 (t, 6.11 Hz, 4H), 3.60 (t, 6.03 Hz, 4H), 0.86 (s, 18H), 0.01 (s, 12H) ppm. ^{13}C NMR (CDCl$_3$): δ 190.03, 152.80, 132.05, 125.08, 110.94, 60.11, 53.41, 25.80, 18.17, −5.47 ppm. Anal. Calcd for $C_{23}H_{43}N_1O_3Si_2$: C, 63.10; H, 9.90; N, 3.20. Found: C, 63.20; H, 9.82; N, 3.31.

3-Bromo-5-{4-[*N*,*N*-bis(2-(*tert*-butyldimethylsiloxy)-ethyl)amino]styryl}thiophene (**7**). A solution of potassium *tert*-butoxide (12.16 g, 0.105 mol) in 200 mL of THF was added to a mixture of *p*-bis(2-hydroxyethyl)amimobenzaldehyde (**6**) (40.00 g, 91.37 mmol), diethyl 5-bromo-2-thienylmethylphosphonate (**3**) (31.47 g, 100.5 mmol), and 30 mL of THF over 10 min with mechanic stirring. Stirring was continued for 10 min after the addition, and the reaction mixture was poured into a saturated sodium bicarbonate solution. After separation of the organic layer the aqueous phase was extracted with hexane two times (100 mL × 2). The combined organic solution was dried over MgSO$_4$ and condensed via rotary evaporation. The residue was purified by column spectroscopy on silica gel using 1 EtOAc/20 hexane as eluent to give 52.42 g of product: yield 96%. ^{1}H NMR (CDCl$_3$): δ 7.33 (d, 8.78 Hz, 2H), 7.00 (d, 1.31 Hz, 1H), 6.94 (d, 16.12 Hz, 1H), 6.89 (d, 1.41 Hz, 1H), 6.84 (d, 16.00 Hz, 2H), 6.69 (d, 8.88 Hz, 2H), 3.80 (t, 6.81 Hz, 4H), 3.57 (t, 6.44 Hz, 4H), 0.93 (s, 18H), 0.08 (s, 12H) ppm. ^{13}C NMR (CDCl$_3$): δ 147.86, 144.90, 129.84, 127.84, 126.19, 123.89, 119.66, 115.77, 111.53, 109.95, 60.25, 53.47, 25.91, 18.26, −5.34 ppm. Anal. Calcd for $C_{28}H_{46}Br_1N_1O_2S_1Si_2$: C, 56.35; H, 7.77; N, 2.35, Br, 13.39, S, 5.37. Found: C, 56.53; H, 7.76; N, 2.34; Br, 13.49; S, 5.26.

5-{4-[*N*,*N*-Bis(2-(*tert*-butyldimethylsiloxy)ethyl)-amino]styryl}thiophene-3-carboxaldehyde (**8**). A solution of compound **7** (16.23 g, 27.2 mmol) in THF (130 mL) was cooled to −95 °C with an ether/liquid N$_2$ bath. *N*-Butyllithium (28.83 mmol, 11.5 mL, 2.5 M in hexane) was added through a syringe over 5 min, followed immediately with the addition of DMF (35.3 mmol, 2.7 mL) over 3 min. The reaction mixture was warmed to −70 °C in 10 min and then quenched with aqueous ammonium acetate solution. The organic layer was separated, and the aqueous phase was extracted with 100 mL of hexane. The combined organic solution was condensed, and the residue was purified with column chromatography on silica gel using 1/8 ethyl acetate/hexane to afford 10.84 g: yield 73%. ^{1}H NMR (CDCl$_3$): δ 9.82 (s, 1H), 7.87 (s,1H), 7.34 (s, 1H), 7.33 (d, 8.45 Hz, 2H), 6.97 (d, 15.90 Hz, 1H), 6.87 (d, 15.93 Hz, 1H), 3.77 (t, 6.45 Hz, 4H), 3.54 (t, 6.59 Hz, 4H), 0.90 (s, 18H), 0.04 (s, 12H) ppm. ^{13}C NMR (CDCl$_3$): δ 184.91, 148.01, 145.96, 143.32, 134.63, 130.94, 127.89, 123.70, 120.91, 115.88, 111.52, 60.22, 53.44, 25.88, 18.24, −5.37 ppm. Anal. Calcd for $C_{29}H_{47}N_1O_3S_1Si_2$: C, 63.80; H, 8.68; N, 2.57; S, 5.87. Found: C, 63.91; H, 8.73; N, 2.55; S, 5.76.

5-{4-[*N*,*N*-Bis(2-(*tert*-butyldimethylsiloxy)ethyl)-amino]styryl}thiophene-3-methanol (**9**). The aldehyde **8**

was reduced to the alcohol **9** in a manner similar to the reduction of compound **1** in quantitative yield. ^{1}H NMR (CDCl$_3$): δ 7.33 (d, 8.88 Hz, 2H), 7.00 (d, 15.5 Hz, 1H), 6.98 (s, 1H), 6.97 (s, 1H), 6.85 (d, 16.22 Hz, 1H), 6.69 (d, 8.83 Hz, 2H), 4.59 (s, 2H), 3.79 (t, 6.52 Hz, 4H), 3.56 (t, 6.49 Hz, 4H), 0.94 (s, 18H), 0.08 (s, 12H) ppm. ^{13}C NMR (CDCl$_3$): δ 147.49, 144.69, 142.57, 128.75, 127.58, 124.39, 123.90, 119.28, 117.06, 111.46, 60.68, 60.21, 53.41, 25.87, 18.16, −5.38 ppm. Anal. Calcd for $C_{29}H_{49}N_1O_3S_1Si_2$: C, 63.57; H, 9.01; N, 2.56; S, 5.85. Found: C, 63.66; H, 8.04; N, 2.54; S, 5.73.

5-{4-[*N*,*N*-Bis(2-(*tert*-butyldimethylsiloxy)ethyl)-amino]styryl}-3-hydroxymethylthiophene-2-carboxaldehyde (10). Compound **9** (18.76 mmol, 10.28 g) was dissolved in 40 mL of THF. The solution was cooled to −30 °C and then was treated with *n*-butyllithium (40.25 mmol, 16.1 mL, 2.5 M in hexane). After the addition the reaction temperature was raised to 0 °C and was maintained at this temperature for 2 h. Then, DMF (24.4 mmol, 1.89 mL) was added through syringe over 5 min. The mixture was stirred at room temperature for 30 min and worked up with water and ether extraction. The ether extract was dried over MgSO$_4$ and condensed via rotary evaporation. The residue was purified with column chromatography on silica gel using 1/8 ethyl acetate/hexane to afford 8.1 g of red solid: yield 75%. ^{1}H NMR (CDCl$_3$): δ 9.80 (s, 1H), 7.34 (d, 8.65 Hz, 2H), 7.07 (d, 16.02 Hz, 1H), 7.04 (s, 1H), 6.93 (d, 15.82 Hz, 1H), 6.68 (d, 8.67 Hz, 2H), 4.82 (br, 2H), 3.77 (t, 6.28 Hz, 4H), 3.67 (br, 1H, the alcoholic proton), 3.55 (t, 6.21 Hz, 4H), 0.89 (s, 18H), 0.03 (s, 12H) ppm. ^{13}C NMR (CDCl$_3$): δ 182.24, 154.08, 151.27, 148.66, 133.91, 133.72, 128.59, 126.48, 123.22, 115.46, 111.61, 60.24, 59.48, 53.44, 25.88, 18.25, −5.37 ppm. Anal. Calcd for $C_{30}H_{49}N_1O_4S_1Si_2$: C, 62.56; H, 8.58; N, 2.43; S, 5.57. Found: C, 63.76; H, 8.55; N, 2.43; S, 5.42.

5-{4-[*N*,*N*-Bis(2-hydroxyethyl)amino]styryl}-3-hydroxymethylthiophene-2-carboxaldehyde (11). Compound **10** (3.07 g, 5.33 mmol) was dissolved in 20 mL of acetone. Dilute hydrochloric acid (3 mL, 0.75 N) was added, and the mixture was stirred at room temperature for 1.5 h. Triethylamine (3 mmol) was added to neutralize the acid. Then, 10 mL of water was added slowly to precipitate out the product. The product was collected by filtration, washed, and dried in vacuo to give a quantitative yield. ^{1}H NMR (DMSO-d_6): δ 10.03 (s, 1H), 7.48 (d, 8.72 Hz, 2H), 7.26 (s, 1H), 7.23 (d, 15. 3 Hz, 1H), 7.13 (d, 15.80 Hz, 1H), 6.84 (d, 8.18 Hz, 2H), 5.15 (br, 3H), 4.80 (s, 2H), 3.54 (m, 8H) ppm. ^{13}C NMR (DMSO-d_6): δ 182.56, 154.06, 151.72, 147.78, 133.74, 132.99, 128.58, 126.95, 123.82, 116.14, 112.33, 57.87, 57.22, 53.64 ppm. Anal. Calcd for $C_{18}H_{21}N_1O_4S_1$: C, 62.23; H, 6.09; N, 4.03; S, 9.23. Found: C, 62.30; H, 6.14; N, 3.90; S, 9.10.

Chromophore (HO)$_3$FTC. Compound **11** (1.76 mmol, 0.61 g), 3-cyano-5,5-dibutyl-2-dicyanomethylene-4-methyl-2,5-dihydrofuran (1.94 mmol), sodium hydroxide (0.53 mmol), and anhydrous ethanol (20 mL) were mixed and refluxed for 3 h. Ethanol was then removed via rotary evaporation, and the residue was taken up with ethyl acetate. Flash column chromatography (EtOAc) and recrystallization from CH$_3$OH/water twice and EtOAc once afforded 0. 5 g of shiny crystals: yield 46%. ^{1}H NMR (DMSO-d_6): δ 8.25 (d, 15.60 Hz, 1H), 7.46 (d, 8.47 Hz, 2H), 7.26 (d, 15.41 Hz, 1H), 7.23 (s, 1H), 7.17 (d, 15.87 Hz, 1H), 6.72 (d, 9.06 Hz, 2H), 6.59 (d, 15.48 Hz, 1H), 5.55 (t, 4.1 Hz, 1H), 4.79 (s, 2H), 4.67 (d, 3.62 Hz, 2H), 3.51 (m, 8H), 2.12 (t, 8.53 Hz, 4H), 1.24 (m, 4H), 1.08 (m, 4H), 0.835 (t, 7.07 Hz) ppm. ^{13}C NMR (DMSO-d_6): δ 177.32, 172.75, 154.36, 152.82, 149.11, 137.97, 134.93, 132.17, 129.12, 128.35, 122.85, 115.65, 112.93, 112.54, 112.24, 111.59, 111.39, 110.88, 103.41, 58.13, 57.83, 53.15, 52.18, 37.34, 24.33, 21.88, 13.67 ppm. Anal. Calcd for $C_{35}H_{40}N_4O_4S_1$: C, 68.60; H, 6.58; N, 9.14; S, 5.23. Found: C, 68.64; H, 6.59; N, 9.00; S, 5.12.

Prepolymer Synthesis and Film Fabrication. Masking (HO)$_3$FTC with TDI. In a drybox 1 g of (HO)$_3$FTC, and 6 mol equiv of TDI was dissolved in 6 mL of anhydrous THF. The mixture was stirred at 70 °C for 12 h. It was then condensed to 3 mL, and hexane was added to precipitate the product (NCO)$_3$FTC. It was reprecipitated from hexane one more time to get rid of TDI. ^{1}H NMR (DMSO-d_6) is shown in Figure 3.

PP1/(NCO)$_3$FTC Prepolymer Solution. In a drybox, a solution of 34.4 mg, 0.197 mmol TDI, 28.2 mg, 0.189 mmol TEA in 725 mg of dioxane (−OH is 14.7% in excess −OH) was stirred at 100 °C for 30 min to produce prepolymer PP1. 22 mg, 0.0388 mmol of (NCO)$_3$FTC was then added, and the mixture was stirred at 80 °C for 5 min to fully dissolve the chromophore. The overall ratio of NCO:OH is 1. The weight percentage loading of (NCO)$_3$FTC was 27.8 wt %; the number density was the same as the 15 wt % dilink FTC polyurethane material we reported earlier.[10]

PP2/(NCO)$_3$FTC Prepolymer. In a drybox, a solution of 36.2 mg, 0.208 mmol TDI, 20.7 mg, 0.139 mmol TEA in 725 mg dioxane (NCO:OH = 1) was stirred at 100 °C for 60 min to produce prepolymer PP1. 22 mg, 0.0388 mmol of (NCO)$_3$FTC was then added, and the mixture was stirred at 80 °C for 5 min to fully dissolve the chromophore. The weight percentage loading of (NCO)$_3$FTC was 27.8 wt %; the number density was the same as the 15 wt % dilink FTC polyurethane material we reported earlier.[10]

Film Preparation, Electrical Poling, and NLO Measurements. Without delay, the above solutions were filtered through 0.2 mm Teflon syringe filters and spin-coated onto indium−tin oxide coated glass substrates and KBr substrates to produce films of around 2 μm thickness. The films were dried in vacuo for 9 h at room temperature. In situ electric field poling/second-harmonic generation was performed on a SHG setup[14] coupled with a corona discharge needle mounted 1.5 cm above the film. The poling voltage was fixed at 6−7 kV while the temperature was ramped at a rate of 10 °C/min. EO coefficient and refractive index measurements were performed on a ATR setup using a 1.06 μm diode laser.[6]

Conclusions

A novel trilinkable donor bridge was synthesized and was coupled to a TCF acceptor to give a trilinkable FTC chromophore. Introduction of dibutyl groups inhibited chromophore−chromophore interaction and thus increased solubility of the trihydroxyl chromophore. The thermal stability of the trilink chromophore was studied by differential thermal analysis and UV−vis. It was found that the free hydroxyl group that is located close to the cyano-derivatized acceptor caused the chromophore to decompose at a temperature much lower than the T_d of a FTC chromophore that carries no free hydroxyl groups. Masking the free hydroxyl groups turned (HO)$_3$FTC chromophore into a triisocyanate-functionalized chromophore, which showed much improved thermal stability. New polyurethane prepolymer synthetic schemes were designed and studied in detail to improve electric field induced dipole alignment efficiency by reducing the degree of chromophore attachment to the polymer backbone before applying the electric poling field. Enhancement of over 150% in poling efficiency was achieved by adopting a “guest−host” approach of incorporating the trilink chromophore into a difficult-to-control thermoset polyurethane network. It was found critical to allow isocyanate and hydroxyl cross-linkers to react at higher temperature for longer time to form partially cross-linked prepolymer solutions before the −NCO masked trilink chromophore was mixed in. By anchoring chromophores to three-dimensional cross-linked polyurethane network by three points of attachment, the thermal stability of poling induced electrooptic activity was enhanced by 33 °C.

Acknowledgment. We gratefully acknowledge support for this work by the National Science Foundation and by the U.S. Air Force Office of Scientific Research.

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MA001561D