Synthesis of Chromophores with Extremely High Electro-optic Activity. 1. Thiophene-Bridge-Based Chromophores

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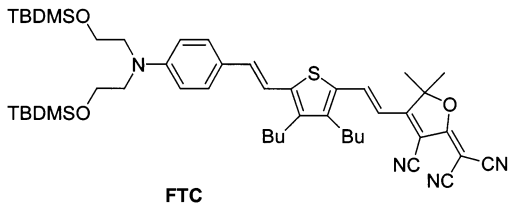
We have successfully synthesized several new substituted thiophene-based electro-optic chromophores. All of these chromophores have structures similar to FTC but they incorporated our newly designed tricyanovinyldihydrofuran acceptors. Since these acceptors possess an anisotropic structure, all of the chromophores are very soluble in a wide range of organic solvents. Thermal study of these chromophores by TGA shows all of them are very stable in air. UV spectra indicate the chromophores have a large solvatochromic effect, implying very large molecular nonlinearities.

Introduction

Over the past 5 years, a 100 GHz and a sub-1-volt halfwave modulator have been demonstrated using FTC as the electro-optic (EO) chromophore.[1,2] However, to be usable in a commercial telecom device, organic NLO materials must meet several critical criteria. First, the active component, the chromophore, must be thermally and photochemically stable. Second, the chromophore needs to have a high molecular nonlinearity while being compatible with the polymer host. Third, both the NLO chromophore and host materials must possess optical transparency at communication wavelengths. Fourth, the chromophore must be able to be aligned in a noncentrsymmentric fashion by poling and remain stable for many years retaining a high EO coefficient.

It is well-known that state of the art high $\mu\beta$ chromophores possess a strong ground-state dipole moment, leading to electrostatic interactions resulting in poor poling-induced alignment.[3] Therefore, the full potential of the intrinsic molecular high electro-optical coefficient is never obtained in a bulk poled material. A common structural characteristic of high $\mu\beta$ chromophores is their flat highly conjugated system. The resulting high dipole moment makes the chromophores aggregate and crystallize from the host polymers. During the past few years, attempts to physically separate the chromophores by attaching side chains to them have made great progress on achieving higher poled EO coefficients by lessening aggregation effects. An example of this design concept is shown by the chromophore known as FTC (Figure 1).[4]

An other method used to prevent chromophore pairing is accomplished by incorporating the chromophore



FTC

Figure 1.

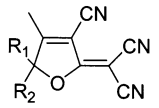


Figure 2.

inside a dendrimer structure, physically separating them with bulky peripheral chains.[5] We have previously submitted a paper reporting a new series of tricyanovinyldihydrofuran type acceptors designed to prevent chromophore aggregation.[6] These acceptors possess a highly anisotropic three-dimensional structure due to large size differences in R_1 and R_2.(Figure 2).

Structure modeling suggested that the out-of-plane R_1 and R_2 groups can effectively prevent chromophore−chromophore stacking due to the three-dimensional shape of the chromophore. The chromophores with R_1 = methyl and R_2 = 4-cyclohexyl-4′-phenyl, labeled DPC in Figure 5 have an overall shape similar to that of a fishhook. These "fishhook" chromophores we suspect will be more soluble and not crystallize from the host polymer as easily as other reported high $\mu\beta$ chromophores. To test this hypothesis, we have designed two series of thiophene-bridge-containing chromophores for comparison with the well-known FTC chromophore. We have found that all of our chromophores can routinely be doped into polycarbonate (PC) at 25−35 wt % or

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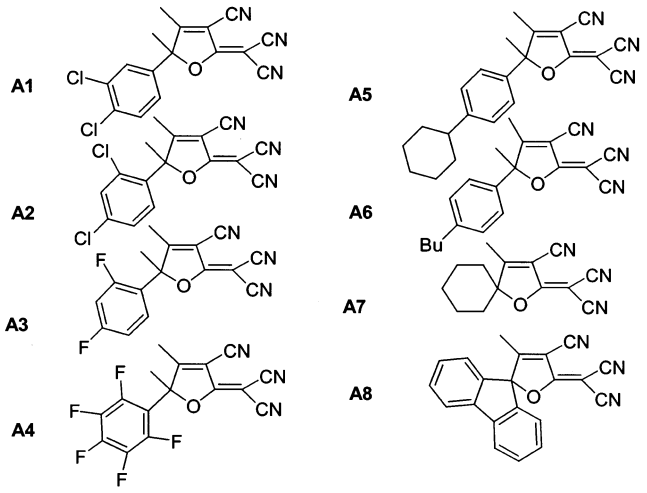
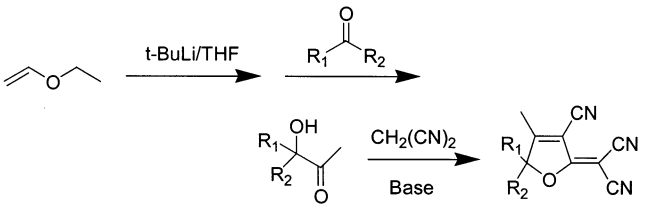


Figure 3. Acceptors.

Scheme 1. Synthesis of Acceptors



higher chromophore levels for poling studies. We report here the synthesis of those new chromophores.

Results and Discussions

Our synthetic approach to these new chromophores is based on our unique acceptors.[6] We have previously reported the synthesis of these novel acceptors, which is shown briefly in Scheme 1.

The acceptor structures we chose to incorporate into the chromophore for this study are listed in Figure 3.

The chromophores were synthesized using two different thiophene donor bridge systems. Type 1 consists of an aminobenzene donor and a regio-specific 3-alkylthiophene-based bridge. The purpose of synthesizing a chromophore with a thiophene bridge substituted on one side only is as follows: (1) Double alkyl substitution on the thiophene bridge may create a twist in the middle of the molecule, crowding the substituents affecting the conjugation. (2) To determine how single or dual substitution affects the chromophore's thermal stability. (3) Determine which substitution pattern enhances the chromophore's electronic properties.

Synthesis of the chromophores (Figure 4) was accomplished following the general procedures outlined below. *p*-*N*,*N*-bis(2-hydroxyethyl)aminobenzaldehyde was synthesized according to a well-known method.[7] *p*-*N*,*N*-bis(2-hydroxyethyl)aminocinnamaldehyde was synthesized by reacting *p*-*N*,*N*-bis(2-hydroxyethyl)benzene with *N*-bromosuccinimide (NBS). This product, *p*-*N*,*N*-bis(2-hydroxyethyl)aminobenzenebromide, was then reacted with butyllithium and 3-(dimethylamino)acrolein. Alternatively, aminobenzaldehyde was reacted with tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide to give

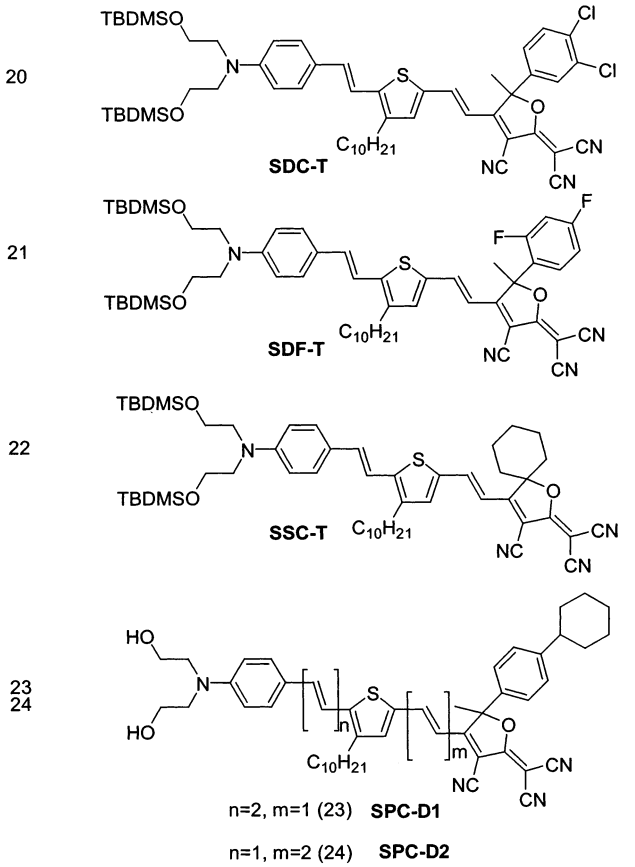


Figure 4. Aminobenzene- and 3-alkylthiophene-based chromophores.

the target compounds[8] (**3a**, **3**; Scheme 2). The thiophene bridge compounds were prepared in six steps to yield the Wittig salt. (**4f**; Scheme 3). After the final Wittig condensation of the thiophene ylide with the aldehyde, the desired donor bridges were prepared (**6a,b**; Scheme 4).

Donor bridges **6a,b** were reacted with butyllithium to form the lithiate anion followed by addition to DMF or acrolein to form the desired aldehyde or cinnamaldehyde function on the thiophene ring. The donor bridges were then reacted with the desired acceptor to yield the various chromophores (**20**−**24**; Scheme 5).

Type 2 donor bridge compounds consist of an aminobenzene and a 3,4-dialkylthiophene-based bridge (Figure 5).

Simple 3,4-dialkyl-substituted thiophenes have previously been used as the chromophore's bridge.[9] We have constructed several new chromophores by extending the chromophore one additional double bond between either the donor and the bridge or between the bridge and the acceptor. By incorporation of our new acceptors into the larger structures, the longer chromophores remain amorphous and soluble. The overall synthetic method for the 3,4-dialkylthiophene bridge is the same as that for the 3-alkylthiophene bridge except for how the Wittig salt is generated (**9e**; Scheme 6).

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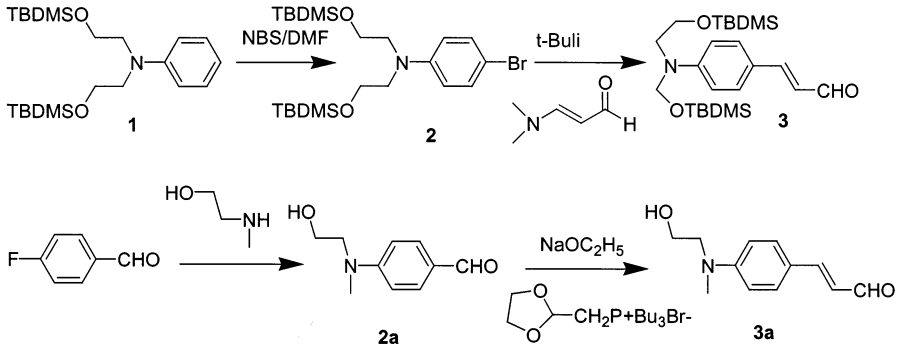
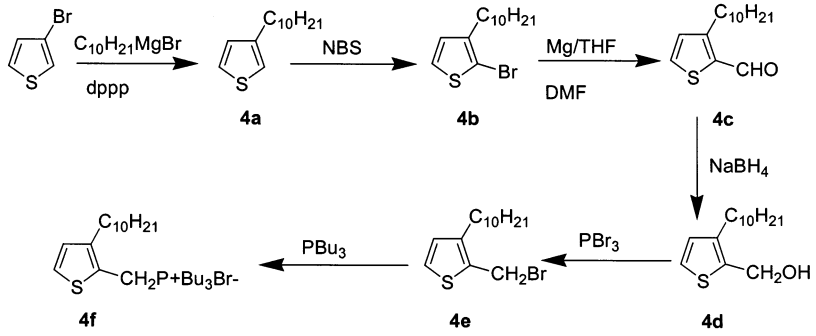
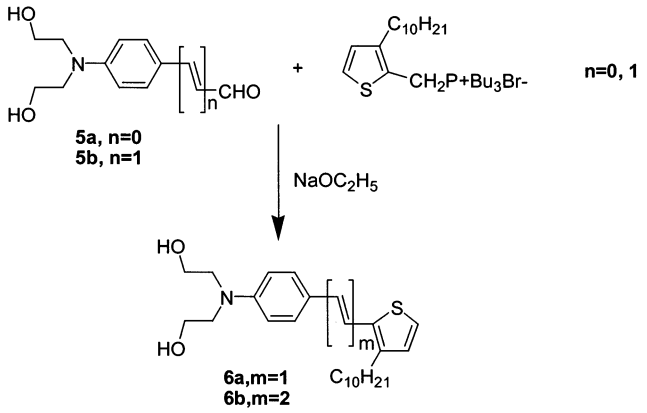
Scheme 2



Scheme 3



Scheme 4



Compound **9e** is reacted with *p*-*N*,*N*-bis(2-hydroxyethyl)aminobenzaldehyde or one of the other aldehydes to produce the donor bridges as described in Scheme 4 (Figures 6 and 7). Following Scheme 5, compounds **15**−**19** and chromophores **25**−**29** have been synthesized.

UV−Vis−NIR Studies of the Chromophores. All of our new chromophores can be dissolved into both chloroform and toluene. The absorption spectra have been obtained in both solvents to determine the wavelength of the maximum absorption peak for the charge-transfer band. The chromophores were also given letter names based on their structure in our laboratory to facilitate identification. All of the in-house laboratory names along with the corresponding compound numbers are included in Table 1.

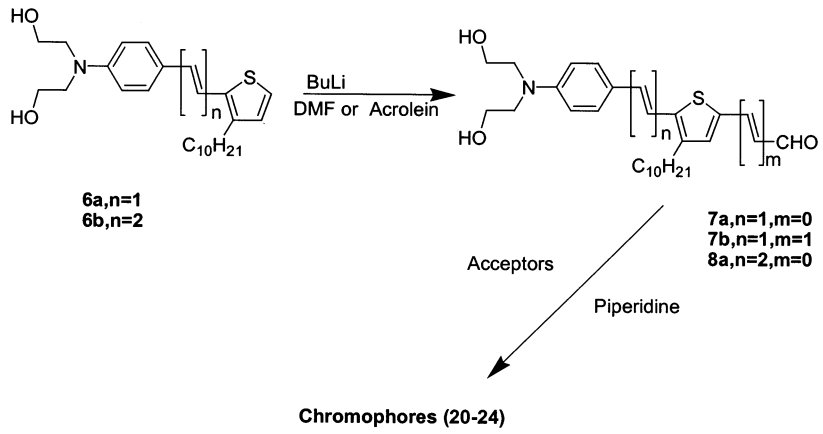
One immediately notices all the TBDMS-substituted compounds show the largest energy level difference between the two solvents. Out of the four compounds with the largest energy differences (0.1 eV or higher), three structures are compounds with only one double bond between the donor, bridge, and acceptor (**22**, **20**, and **21**). Therefore, the length of the conjugation alone is not the most important factor in generating a large hyperpolarizability. Compound **25**, with two double bonds between the bridge and our largest acceptor, also shows a large solvatochromic shift. The extension of the space between the bridge and this large acceptor most likely allows for less twisting of the conjugated system between the bridge and acceptor. Note how compound **25**, with the additional double bond between the bridge and acceptor, shows a larger shift than comparable compounds with the additional double bond between the donor and bridge (**26** and **27**). This trend is continued when compounds **23**, **24**, and **28** are compared. One side substitution on the thiophene bridge does not seem to have a significant impact on the hyperpolarizability (compounds **23** and **28**).

Thermal Stability of the Chromophores. TGA testing of all the chromophores has been performed in air. The results are listed in Table 2 and the weight loss diagrams are attached.

Chromophores **20**−**24** (Figure 8) all have incorporated into their structure the same 3-alkylthiophene bridge and show thermal stability over 250 °C. Incorporation of an extra double bond between the donor and the bridge or the bridge and the acceptor seems to have very little impact on the chromophore's overall thermal stability.

Chromophores **25**−**29** (Figure 9) all contain 3,4-dialkylthiophene bridges. All of these chromophores are also very stable, with the results generating one of each type as the two most stable structures. A previous literature report indicated that TBDMS-protected chromophores are more stable than the unprotected hydroxy counterparts. The authors believe this is due to the

Scheme 5



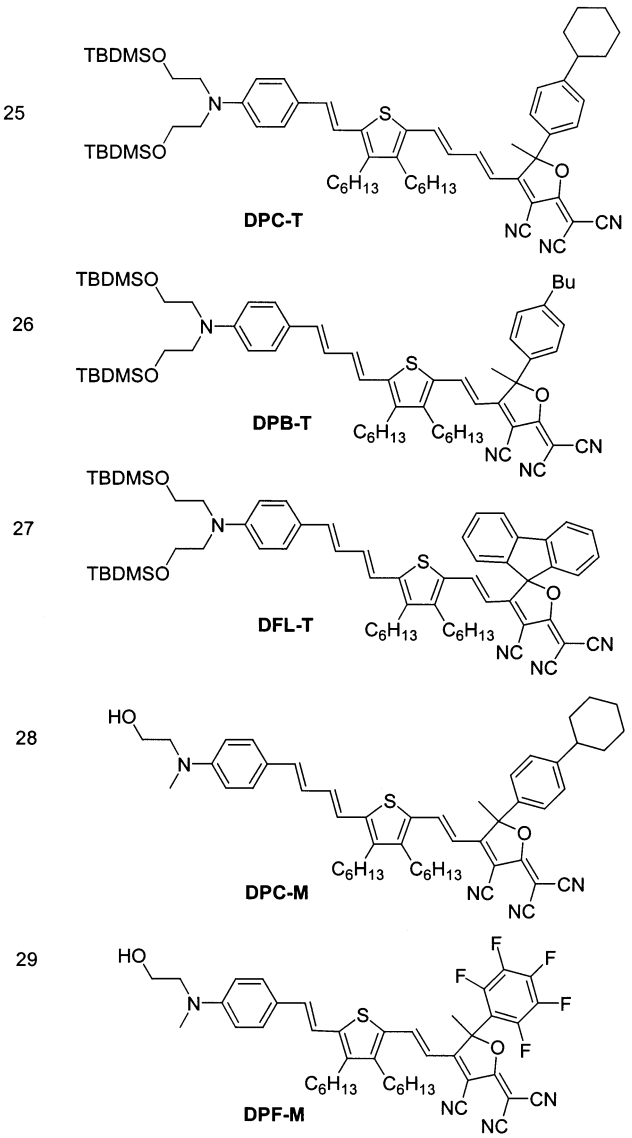


Figure 5. Aminobenzene- and 3,4-dialkylthiophene-based chromophores.

ability of the hydroxyl function to react with an acceptor cyano group when heated.[10] The second most stable chromophore does not include the TBDMS-protecting

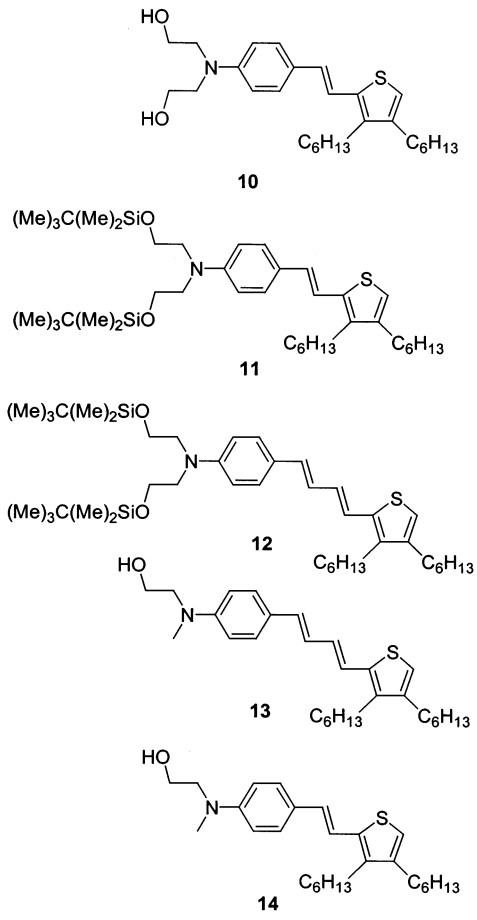
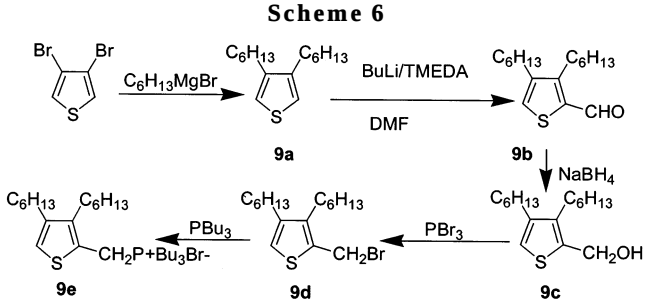


Figure 6. 3,4-Dihexylthiophene donor bridges.

Scheme 6



group, indicating this may not be the case. We also surprisingly noticed that chromophore **29**, containing the pentafluorophenyl group, has the lowest thermal

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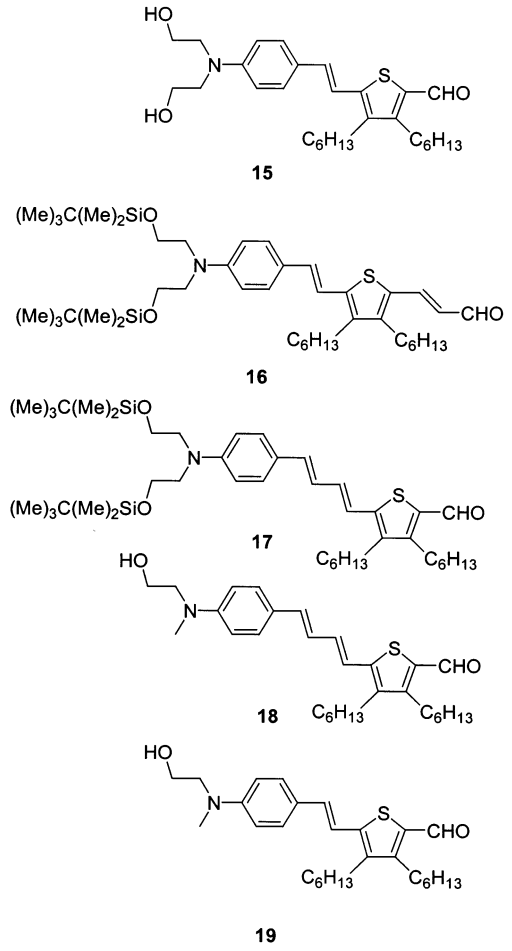

Figure 7. 3,4-Dihexylthiophene donor bridge aldehydes.

Table 1. Maximum Absorption of Chromophores

chromophore	chloroform (nm)	λ_{max} (cm^{-1})	toluene (nm)	λ_{max} (cm^{-1})	change (eV)	lab. name
22	677.6	14757.9	637.3	15691.2	0.116	SSC-T
20	721.9	13852.3	678.6	14736.2	0.110	SDC-T
25	713.8	14009.5	671.7	14887.6	0.109	DPC-T
21	697.7	14332.8	660.3	15144.6	0.100	SDF-T
26	701.8	14249.1	671.7	14887.6	0.079	DPB-T
27	713.8	14009.5	688.9	14515.9	0.063	DFL-T
29	708.4	14116.3	686.7	14562.4	0.055	DPF-M
24	659.5	15163.0	641.9	15578.8	0.052	SPC-D2
28	679.6	14714.5	662.6	15092.1	0.047	DPC-M
23	669.5	14936.5	654.5	15278.8	0.042	SPC-D1

Table 2. TGA Test of Chromophore Thermal Stability in Air

chromophores	lab. name	5% weight loss (°C)	melting point (°C)
20	SDC-T	273.9	139−141
21	SDF-T	277.4	181−183
22	SSC-T	292.6	80−82
23	SPC-D1	279.4	166−168
24	SPC-D2	266.2	107−109
25	DPC-T	264.1	77−79
26	DPB-T	262.1	55−57
27	DFL-T	278.9	101−103
28	DPC-M	290.2	120−122
29	DPF-M	256.5	161−164

stability of the group; this may be due to the ability of the pentafluorophenyl group to leave intact upon heating. TGA results in air do not account for degradation by pericyclic reactions or other types of reactions where no part of the molecule becomes a gas-phase leaving group. It does, however, point to certain functional groups that may be problematic during high-temperature poling like the pentafluorophenyl group.

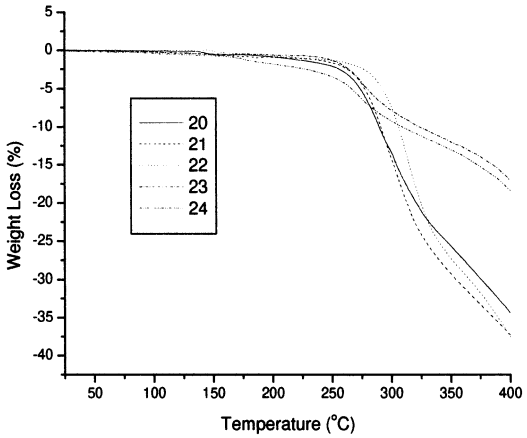

Figure 8. TGA of chromophores **20**−**24**.

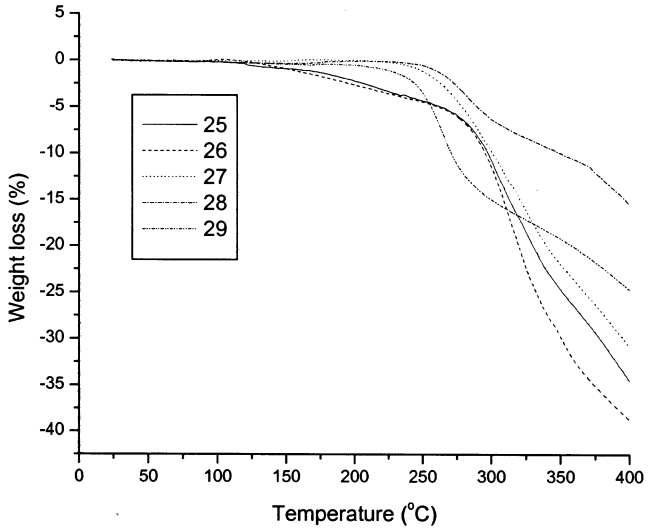

Figure 9. TGA of chromophores **25**−**29**.

Conclusions

We have successfully synthesized several new thiophene-bridge-based "fishhook"-shaped NLO chromophores. These chromophores possess either single alkylthiophene or dialkylthiohene bridges. All chromophores consist of our newly synthesized novel acceptors, rendering them very soluble in nonpolar solvents. Since these acceptors have a unique furan ring structure including spiro ring functions, by selecting R_1 and R_2 groups of different sizes, electronic properties, and flexibility, all the chromophores show unique solubility, processibility, and absorption band characteristics. UV spectra show that all of the chromophores have large solvatochromic effects. These results imply that all chromophores possess very large $\mu\beta$ values. The largest energy shift is more than twice the smallest of the compounds in this study. Thermal tests in air by TGA indicate that the chromophores are quite stable with respect to fragmentation with the majority of them showing less than 5% weight loss above 250 °C in air. Thermal stability data provides us with informed choices of which functional groups to couple together into these chromophores.

Experimental Section

Selected representative intermediates have been reported here, along with one final chromophore. The synthetic details of all the other intermediates and chromophores can be obtained in the Supporting Information.

General Information. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR were obtained using a Varian Unity Inova 300-MHz system. TMS was used as the internal standard. $CDCl_3$ or CD_2Cl_2 were used as solvent unless specified otherwise. Gas chromatography/mass spectrometry (GC/MS) data were obtained using a Varian Saturn 200 system. Matrix-assisted laser desorption ionization Fourier transform ion cyclotron resonance mass spectrometry (MALDI−FTICR/MS) was performed on an IonSpec Ultima II (IonSpec Corp., Irvine, CA) 7T Fourier transform mass spectrometer. The neat samples, dissolved in methylene chloride, were mixed with a 0.5 M solution of 2,5-dihydroxybenzoic acid and allowed to co-crystallize. External calibration with a standard of poly(ethylene glycol) (M_w = 1000) was provided. The theoretical exact mass for all the compounds was obtained as the protonated adduct, the sodium adduct, the carbon 13 satellite of the sodium adduct, and the theoretical exact mass for the radical cation formed by loss of an electron. The observed mass for the cation adduct, the observed mass for the protonated adduct, the observed mass for the sodium adduct, and the observed mass for the carbon 13 satellite of the sodium adduct as well the deviation between these two mass values in daltons and parts per million are reported and was found to be less than 10 ppm in all cases. In this paper, the exact mass of the protonated adduct only will be given. The additional results are supplied in the Supporting Information. Melting points were obtained from a Mel-Temp 3.0 device and are uncorrected. UV−Vis−NIR were obtained using a Perkin-Elmer Lambda 900 spectrometer. TGA were obtained using a Seiko TG/DTA 220. The conditions were as follows: atmosphere, air at 100 mL/min; heat cycle, 20−400 °C at 10 °C/min; sample size, 2.5−3.5 mg. A 5% weight loss was taken as the onset of decomposition to avoid any residual solvent in the sample leading to erroneous data.

***p*-*N*,*N*-Bis(2-*tert*-butyldimethylsiloxyethyl)aminobenzyl Bromide (2).** To a 1000-mL flask of *p*-*N*,*N*-bis(2-*tert*-butyldimethylsiloxyethyl)aminobenzene (172 g, 0.421 mol) in 300 mL of DMF, *N*-bromosuccinimide (NBS) (82.3 g) as a 20-mL DMF solution was added dropwise at room temperature in the dark. The mixture was stirred overnight and poured into water. The organic layer was extracted with ethyl ether (3 × 150 mL). The combined organic layers were washed using brine (2 × 100 mL) and water (100 mL) and dried over anhydrous $MgSO_4$. After the solvent was evaporated, the product was obtained by column chromatography on silica gel (5% ethyl acetate in hexane) to give 143 g of compound **2** as a solid, yield 70%. mp 34−36 °C. ^{1}H NMR: δ 7.24 (d, 2H), 6.57 (d, 2H), 3.73 (t, 4H), 3.47 (t, 4H), 0.86 (s, 18H), 0.03 (s, 12H). Exact mass + H: calculated, 488.2016; observed, 488.2029.

***p*-*N*-(2-Hydroxyethyl)-*N*-methylaminobenzaldehyde (2a). 2a** was made following the procedure from a U.S. patent.[7] Freshly distilled 4-fluorobenzylaldehyde (237 g, 1.91 mol), 2-methylaminoethanol (215.5 g, 2.87 mol), anhydrous sodium carbonate (304.2 g, 2.87 mol), and 18-crown-6 ether (catalytic amount) in dry DMSO (250 mL) were heated to 100 °C for 24 h. After following the literature procedure, the yellow solid was precipitated from ether solution to give 297 g, yield 89%. mp 70−72 °C. ^{1}H NMR: δ 9.73 (s, 1H), 7.74 (d, 2H), 6.79 (d, 2H), 3.89 (m, 2H), 3.62 (t, 2H), 3.12 (s, 3H), 1.69 (t, 1H, OH).

***p*-*N*,*N*-Bis(2-*tert*-butyldimethylsiloxyethyl)aminocinnamaldehyde (3).** *tert*- Butyllithium (74 mL, 0.122 mol) was added dropwise to a mixture of *p*-*N*,*N*-bis(2-*tert*-butyldimethylsiloxyethyl)aminobenzyl bromide (**2**) (30.3 g, 0.062 mol) and THF (200 mL) in a round-bottom flask at −78 °C. The mixture was allowed to warm to −30 °C, followed by cooling to −78 °C again. 3-(Dimethylamino)acrolein (6.83 g, 90% purity, 0.062 mol) was added dropwise. The mixture was stirred overnight at room temperature and water (50 mL) was added. After the THF was removed, the organic layer was extracted with ethyl ether (3 × 100 mL). The combined organic layers were washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. Compound **3** was obtained from a silica chromatography column (15% ethyl acetate in 85% hexane), yielding 20 g, 70.2%. ^{1}H NMR: δ 9.58 (d, 1H), 7.40 (d, 2H), 7.36 (d, 1H), 6.70 (d, 2H), 6.55 (dd, 1H), 3.76 (t, 4H), 3.56 (t, 4H), 0.86 (s, 18H), 0.03 (s, 12H). Exact mass + H: calculated, 464.3016; observed, 464.3013.

3-Decylthiophene (4a). To a mixture of 3-bromothiophene (81.5 g, 0.5 mol) and [1,3-bis(diphenylphosphino)propane]-dichloronickel(II) (dppp) in 300 mL of dry ethyl ether, decylmagnesium bromide (560 mL, 0.56 mol) was added dropwise. The mixture was then refluxed overnight and cooled in an ice bath. A 5% HCl solution was added to destroy the unreacted Grignard reagents. The organic layer was separated from the water layer in a separation funnel. The ether solution was then washed with $NaHCO_3$ solution (100 mL), brine (2 × 100 mL), and water (100 mL) and dried over anhydrous $MgSO_4$, After the ether was removed, the organic residue was vacuum-distilled (101 °C/3 mmHg) to give **4a**: 85 g, yield 75.9%. ^{1}H NMR: δ 7.23 (m, 1H), 6.93 (m, 1H), 2.62 (t, 2H), 1.64−1.26 (m, 16H), 0.88 (t, 3H). GC/MS: 223 (M − 1).

2-Bromo-3-decylthiophene (4b). *N*-bromosuccinimide (NBS) (37.6 g, 0.211 mol) was dissolved into 200 mL of DMF. This mixture was added dropwise to a mixture of **4a** (64 g, 0.211 mol) in DMF (300 mL) in the dark. The mixture was stirred overnight and poured into 1 L of water. The organic material was extracted with ethyl ether (3 × 150 mL). The combined organic extracts were washed with brine (2 × 100 mL) and water (100 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the remaining organic material was vacuum-distilled at 105 °C/1.2 mmHg to give 74 g of compound **4b**, yield 91.7%. ^{1}H NMR: δ 7.25 (d, 1H), 6.79 (d, 1H), 2.56 (t, 2H), 1.66−1.29 (m, 16H), 0.88 (t, 3H). GC/MS: 301 (M − 1).

3-Decylthiophene-2-carboxaldehyde (4c). Magnesium turnings (7 g, 0.292 mol) and dry THF (300 mL) were placed in a 1000-mL round bottom flask. 2- Bromo-3-decylthiophene (84 g, 0.277 mol) was added dropwise to the above solution. The mixture was stirred vigorously. After the reaction started to form the Grignard reagent, the mixture was kept at reflux until the magnesium metal almost disappeared. The mixture then was transferred to a clean flask and dry DMF (40 mL) was added dropwise to the Grignard reagent solution. The mixture was refluxed overnight and cooled in an ice bath. 5% HCl (100 mL) was added to stop the reaction. After removal of the THF, the organic layer was extracted with ethyl ether (3 × 100 mL). The combined organic layers were washed with saturated $NaHCO_3$ (100 mL), brine (100 mL), and water (100 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the aldehyde was purified by column chromatography on silica gel (5% ethyl acetate in hexane) to give **4c**: 53.6 g, yield 76.7%. ^{1}H NMR: δ 10.04 (s, 1H), 7.64 (d, 1H), 7.01 (d, 1H), 2.99 (t, 2H), 1.68−1.26 (m, 16H), 0.88 (t, 3H). GC/MS: 252 (M^+).

2-Hydroxymethyl-3-decylthiophene (4d). 3-Decylthiophene-2-carboxaldehyde (**4c**) (53 g, 0.21 mol) was dissolved into methanol (300 mL) in a round bottom flask. $NaBH_4$ powder (5.83 g, 0.155 mol) was added slowly to the above mixture. This mixture was stirred overnight and the methanol was evaporated. The organic material was extracted using ethyl ether (3 × 100 mL). The combined organic layers were washed with brine (2 × 100 mL) and water (100 mL). After the solution was dried over anhydrous $MgSO_4$, the solvent was evaporated and compound **4d** obtained (48.2 g, 90.4%). NMR identified it was pure enough to be used without further purification. ^{1}H NMR: δ 7.19 (d, 1H), 6.88 (d, 1H), 4.77 (s, 2H), 2.61 (t, 2H), 1.58−1.27 (m, 16H), 0.89 (t, 3H). GC/MS: 253 (M − 1).

2-Bromomethyl-3-decylthiophene (4e). 2-Hydroxymethyl-3-decylthiophene (**4d**) (48.2 g, 0.19 mol) was mixed with dry ethyl ether (300 mL) and cooled in an ice bath. PBr_3 (25.6 g, 0.095 mol) was added dropwise to the mixture. The mixture was stirred under a dry N_2 atmosphere overnight and then slowly poured into a saturated $NaHCO_3$ solution (300 mL). The ether layer was separated and washed with brine (2 × 100 mL) and water (100 mL) and dried over anhydrous $MgSO_4$.

Since compound **4e** was found to be very unstable in air, this compound was used immediately after the ether was evaporated. ^{1}H NMR indicated that the compound was of very good purity; further distillation was not required. Yield: 52.3 g, 86.1%. ^{1}H NMR: δ 7.21 (d, 1H), 6.83 (d, 1H), 4.72 (s, 2H), 2.60 (t, 2H), 1.64−1.27 (m, 16H), 0.88 (t, 3H).

3-Decyl-2-thienylmethyltributylphosphonium Bromide (4f). Compound **4e** (52.3 g, 0.165 mol) was mixed with tributylphosphine (33.3 g, 0.165 mol) in toluene (200 mL). The mixture was refluxed for 72 h. The toluene was evaporated, and the product **4f** was dissolved into DMF and used without further purification. mp 63−65 °C. The molecular formula without bromine is $C_{27}H_{52}PS$ since the bromine is not observed. Exact mass + H: calculated, 440.3606; observed, 440.3587.

General Procedures for Making a Donor Bridge Using Wittig Condensation Conditions. Aminobenzene−thiophene donor bridges were prepared as follows: The *N*,*N*-disubstituted aminobenzaldehyde (1.0 equiv) and the alkylated thienyltributylphosphonium bromide (1.0−1.2 equiv) were mixed in either DMF or ethanol. To these mixtures, $NaOC_2H_5$ (1.3−1.5 equiv) was added dropwise with stirring at 90−110 °C under N_2. These mixtures were stirred for 48−72 h, after which time aqueous HCl (10%) or water was added. The resulting mixtures were then stirred for 1 h. The organic materials were extracted with ethyl ether three times. The combined organic layers were washed with brine and water. After the solution was dried over anhydrous $MgSO_4$, pure compounds were obtained from chromatography on silica gel using mixed ethyl acetate and hexane as the eluting solvent.

4-[*N*,*N*-Di(2-hydroxyethyl)amino]benzaldehyde (5a) and 4-[*N*,*N*-Di(2-hydroxyethyl)amino]cinnamaldehyde (5b). **5a** and **5b** were obtained from hydrolysis of the TBDMS-protected aldehydes and used without purification according to the references.[11-12]

2-{4-[*N*,*N*-Di(2-hydroxyethyl)]aminophenylethenyl}-3-decylthiophene (6a). Compounds **5a** (26 g, 0.05 mol) and **4f** (12.6 g, 0.06 mol) were reacted together using sodium ethoxide (0.075 mol, 1 M in ethanol) following the general procedure. Pure **6a** eluted from a silica column using 50% ethyl acetate/hexane to yield 16 g of **6a**, 74.5%. mp 62.5−64.5 °C. ^{1}H NMR: δ 7.36 (d, 2H), 7.07 (d, 1H), 7.03 (d, 1H), 6.83 (d, 1H), 6.82 (d, 1H), 6.70 (d, 2H), 3.86 (t, 4H), 3.61 (t, 4H), 3.09 (s, broad, 2H, OH), 2.66 (t, 2H), 1.59−1.26 (m, 16H), 0.87 (t, 3H). Molecular formula: $C_{26}H_{39}NO_2S$. Exact mass + H: calculated, 430.2780; observed, 430.2792.

2-{4-[*N*,*N*-Di(2-hydroxyethyl)amino]phenylene-(3-decyl)-thien-5}-al (7a). To a solution of compound **6a** (16.6 g, 0.039 mol) in dry THF (100 mL), butyllithium (48 mL, 0.116 mol, 2.5 M in hexane) was added dropwise at −78 °C. The mixture then turned green and was allowed to slowly warm to −20 °C. After the mixture was cooled back down to −78 °C, 15 mL of DMF was added dropwise. The mixture was then slowly warmed to room temperature and stirred overnight at room temperature; 30 mL of water was added to quench the reaction. After the solvent was evaporated, the organic layer was extracted with ethyl ether (3 × 70 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL) and dried over anhydrous $MgSO_4$. Pure compound **7a** was obtained through column chromatography on silica gel (50% ethyl acetate in hexane) to yield 15 g of **7a**, 85.2%. ^{1}H NMR: δ 9.76 (s, 1H), 7.49 (s, 1H), 7.40 (d, 2H), 7.03 (d, 2H), 6.71 (d, 2H), 3.90 (t, 4H), 3.64 (t, 4H), 2.67 (t, 2H), 1.62−1.26 (m, 16H), 0.88 (t, 3H). Molecular formula: $C_{27}H_{39}O_3SN$. Exact mass + Na: calculated, 480.2548; observed, 480.2554.

Compounds **9a** and **9b** were synthesized by following exactly references 8 and 11. ^{1}H NMR peaks are listed below. **9c−e** were synthesized through the following procedure, but not purified prior to use in the next reaction.

3,4-Dihexylthiophene (9a). bp 115−117 °C/2 mmHg. ^{1}H NMR: δ 6.89 (s, 2H), 2.51 (t, 4H), 1.61 (m, 4H), 1.33 (m, 12H), 0.90 (t, 6H).

3,4-Dihexylthiophene-2-carboxldehyde (9b). bp 150−153 °C/0.2 mmHg. ^{1}H NMR: δ 10.0 (s, 1H), 7.30 (s, 1H), 2.91 (t, 2H), 2.52 (t, 2H), 1.64 (m, 4H), 1.33 (m, 12H), 0.91 (t, 6H). Molecular formula: $C_{17}H_{28}OS$. Exact mass + H: calculated, 281.1939; observed, 281.1937.

2-{4-[*N*,*N*-Di(2-(1,1,2,2-tetramethyl-1-silapropoxy)-ethyl)]aminophenylene}-3,4-dihexylthiophene (11). Compound **10** (8 g, 0.018 mol), *tert*-butyldimethylsilyl chloride (10.5 g, 0.07 mol), imidazole (9.5 g, 0.014 mol), and DMF (40 mL) were mixed with stirring at room temperature. The mixture was stirred overnight under N_2 and poured into water (200 mL). The organic layer was extracted with ethyl ether (3 × 50 mL). The combined organic layers were washed with water (3 × 100 mL) and dried over anhydrous $MgSO_4$. Pure compound **11** was obtained from silica gel chromatography (2% ethyl acetate in hexane) to yield 11.8 g, 98.3%, of **11**. mp 50.0−52.5 °C. ^{1}H NMR, solvent CD_2Cl_2: δ 7.37 (d, 2H), 7.21 (d, 1H), 6.84 (d, 1H), 6.75 (s, 1H), 6.71 (d, 2H), 3.82 (t, 4H), 3.58 (t, 4H), 2.67 (t, 2H), 2.54 (t, 2H), 1.65−1.39 (m, 16H), 0.95 (s, 24H), 0.03 (s, 12H). Molecular formula: $C_{40}H_{71}NO_2SSi_2$. Exact mass + H: calculated, 686.4822; observed, 686.4871.

General Procedure for the Chromophore Synthesis. Donor bridge aldehydes (1 equiv) and acceptors (1−1.2 equiv) were dissolved into a mixture of THF and ethanol (80:20 in volume). Piperidine was used as the catalyst. The mixtures were refluxed for 24−72 h and the solvents were removed on a rotary evaporator. The residues were dissolved into ethyl acetate and the solids precipitated from hexane. The solid obtained this way could either be recrystallized from ethyl acetate and hexane solution or be purified using a silica chromatography column (10−60% ethyl acetate in hexane depending on the chromophore's functional groups) to yield pure chromophores. Some chromophores were reacted with *tert*-butyldimethylsilyl chloride before or after column chromotography to protect the hydroxy functional groups. The protection reactions were conducted following the synthetic procedure of compound **11**.

4-[(1E)-2-[5-[(1E)-2-[4-[Bis(2-*tert*-butyldimethylsiloxy-ethyl)amino]phenyl]ethenyl]-4-decyl-2-thienyl]ethenyl]-3-cyano-5-methyl-5-(3,4-dichlorophenyl)-2(5H)-furanylidene] Propanedinitrile (20). 7a (1.0 g, 2.18 mmol) was reacted with *tert*-butyldimethylsilyl chloride following the procedure given for compound **11** to yield 1.5 g of TBDMS-protected aldehyde. Following the general procedure given above for the chromophore synthesis, the TBDMS-protected aldehyde (1.5 g, 2.18 mmol) and **A1** (0.8 g, 2.42 mmol) were mixed together in 20 mL of THF/ethanol solution. Piperidine (5 drops) was added as the catalyst. Crude **20** was purified by column chromatography on silica gel (15% ethyl acetate in hexane). The reaction yielded 0.88 g, 59.9%. mp 139−141 °C. ^{1}H NMR, solvent CD_2Cl_2: δ 7.59 (d, 1H), 7.50 (d, 1H), 7.38 (d, 2H), 7.30 (m, 2H), 7.14 (s, 1H), 7.04 (d, 2H), 6.72 (d, 2H), 6.60 (d, 1H), 3.80 (t, 4H), 3.59 (t, 4H), 2.62 (t, 2H), 2.11 (s, 3H), 1.31 (m, 16H), 0.88 (m, 21H), 0.027 (s, 12H). ^{13}C NMR: 175.96, 171.15, 150.88, 149.61, 143.12, 140.67, 140.29, 136.56, 136.20, 135.26, 135.10, 134.15, 131.84, 129.22, 128.76, 126.06, 123.96, 114.22, 112.17, 111.99, 111.90, 111.30, 97.29, 96.50, 60.70, 56.48, 32.22, 30.76, 29.91, 29.71, 29.63, 28.40, 25.95, 24.67, 23.00, 18.43, 14.21, −5.38. Molecular formula: $C_{55}H_{74}Cl_2N_4O_3SSi_2$. Exact mass + Na: calculated, 1019.4295; observed, 1019.4309. (Note: Mass + H is not available for this sample.)

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Supporting Information Available: General experimental data, exact MS analyses of compounds **1**−**29** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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