Synthesis of Chromophores with Extremely High Electro-optic Activities. 2. Isophorone- and Combined Isophorone–Thiophene-Based Chromophores

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Four new isophorone and combined isophorone and thiophene bridged chromophores have been synthesized. All of these new high $\mu\beta$ chromophores possess our newly synthesized tricyanovinyldihydrofuran acceptors. Because of our unique acceptor design, all of our chromophores show high solubility in all organic solvents due to minimized chromophore–chromophore electrostatic interactions. These chromophores have also been studied with respect to their solvatochromism and thermal behavior by TGA in air. Preliminary EO characterization of one of these chromophores in polycarbonate has demonstrated an extremely high r_{33} of 70 pm/V at 1550 nm. We believe that this is the largest r_{33} reported at this wavelength.

Introduction

We report here the synthesis of several new high $\mu\beta$ electro-optic (EO) chromophores and, for one compound, characterization of the r_{33} value through contact poling. Recently, significant progress has been made in the synthesis and subsequent processing of these new materials into high-speed devices.[1,2] Devices using these newly reported high $\mu\beta$ chromophores have brought polymer EO devices to the brink of commercialization. With the renewed interest in organic-based EO materials, even more new high $\mu\beta$ chromophores with unique structures have been developed, showing even higher electro-optic (EO) coefficients.[3] But to be accepted for use in a commercial device, organic NLO materials must meet very stringent environmental requirements. High electro-optic activity is not the only criterion for use in a device format; it must also show good thermal and photochemical stability. The host material must possess optical transparency at communication wavelengths. It also must include the ability to maintain the aligned chromophores in a noncentrosymmetric fashion after poling and maintain its high EO coefficient. Theoretical calculations and experimental results have born out that high $\mu\beta$ chromophores are difficult to align due to the chromophore's high ground-state dipole moment interactions.[3] Preventing chromophore–chromophore antiparallel interaction at the molecular level should lead to significant improvement of the poling process and therefore achieve the necessary high EO coefficients. To minimize this antiparallel packing, the nondendrimeric chromophores reported to date have been designed with floppy side chains attached to the flat conjugated structure. This approach seems to be successful based on the latest published data for what are known as the CLD and FTC type of chromophores[4,5] (Figure 1).

An alternative approach that has proven to be efficient in preventing chromophore antiparallel packing is the use of dendrimeric structures that bury the chromophore inside, physically separating them with bulky chains.[6] Previously, we published in this journal a series of bulky three-dimensional tricyanovinyldihydrofuran type of acceptors[7] (Figure 2).

The intent of this work is that when R_1 and R_2 are both above and below the chromophore's plane of conjugation, we should significantly increase the solubility and decrease the chromophore dipolar packing. To test this hypothesis further, we have designed various donor bridges to couple with our acceptors, making several new novel chromophores. It has been reported that the CLD type of chromophores have exhibited some solubility problems.[8] Our conjecture is crystallization occurs due to the strong ground-state dipole moment induced by the very flat (when R_1 and R_2 are methyl) tricyanovinyldihydrofuran (TCF) acceptor being incorporated into a larger rigid flat structure. The CLD type of structure with the isophorone-based bridge does not have the bulky alkyl groups in the center to help prevent crystallization. By modification of the TCF type of acceptor, we have been able to overcome

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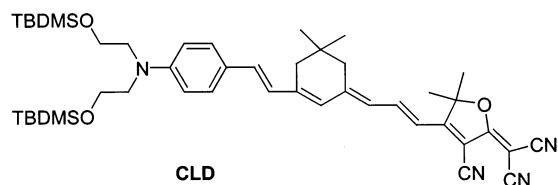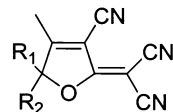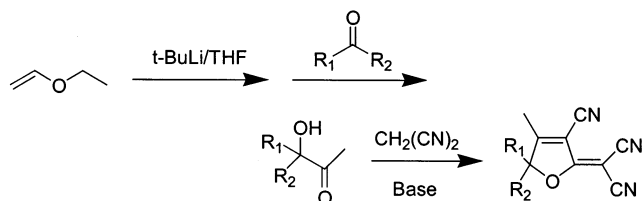(3) Dalton, L. R. *Opt Eng.* **2000**, *39* (3), 589.

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Figure 1.

Figure 2. General acceptor structure.

Scheme 1. Synthesis of Acceptors

this problem. When comparing our chromophores to CLD, we found that all of our chromophores can be easily doped into polycarbonate (PC) up to about 35 wt % chromophore level or even higher. We also are able to eliminate the bulky *tert*-butyldimethylsilyl (TBDMS) groups from our chromophores, which are known to aid solubility of high $\mu\beta$ chromophores in doped polymer systems. By elimination of the TBDMS groups, the C−H bond count is significantly decreased, possibly lowering the optical loss at communication wavelengths.
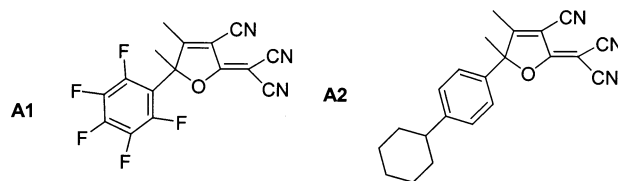
Results and Discussions

Our synthetic approach for making new chromophores is based on our unique acceptors.[7] Previously, we reported the synthesis of these novel acceptors; included here is a brief overview of the synthesis shown in Scheme 1.

Models of the acceptors we have synthesized show that R_1 and R_2 are both well out of the conjugation plane of the furan structure. We intentionally designed our acceptors to have R_1 and R_2 very different with respect to each other, the concept being that a large size difference will make the chromophore more soluble. It is clear there is a chiral center at the carbon shared by R_1 and R_2 and we believe by not resolving the enantiomers, it results in better solubility of the chromophore in solvents and, more importantly, the polymer matrix. Of course, we plan to investigate the effects associated with a chiral center when a pure enantiomer is incorporated into a chromophore. We currently are separating optically pure chiral acceptors and will publish the results when available. The acceptor structures used in this study are listed in Figure 3. The chromophores were synthesized based on two different donor bridge systems.

One set is aminobenzene donor and isophorone bridge-based chromophores as compared to the aminobenzene donor and thiophene bridge compounds outlined in part 1 of this study.

Replacing the thiophene ring bridge with a polyene or ring-locked polyene such as isophorone has been

Figure 3. Acceptors.

shown to result in dramatic increases of the molecular nonlinearity.[9,10] However, there are some drawbacks when this substitution takes place. The most obvious disadvantage of a polyene bridge is lower chromophore thermal stability as observed through TGA testing in air. When a ring-locked structure is compared to a polyene, the molecular nonlinearity tends to decrease, but thermal stability tends to increase.[11,12] This will be addressed in detail in a later section. Two isophorone only bridge-based chromophores were synthesized to directly compare a thiophene-based bridge with isophorone-based bridges.[14] Because of our unique acceptor designs, our chromophores were not found to have solubility problems.

The synthesis of this type of chromophore was conducted as shown in Scheme 2.

Compound **2** was synthesized following a recent reference.[13] No matter which synthetic method was chosen in our laboratories, compound **3** was always obtained as a cis−trans isomer mixture. Details concerning the amounts of trans and cis isomers have been reported by Zhang et al.[8]

The second type of compounds are aminobenzene donor, isophorone−thiophene double-bridge-based chromophores.

Previously, Jen and co-workers[15] reported the synthesis of a long conjugated chromophore containing an isophorone−thiophene combination bridge. It is expected that when the overall conjugation length has been extended, the chromophore should have a larger $\mu\beta$ value. Also, it is expected that by extension of the conjugation length, the chromophore solubility will decrease significantly. We have found that with a modified thiophene bridge and our very anisotropically shaped acceptors we were able to prepare two soluble chromophores containing both isophorone and thiophene units as a combination bridge shown in Figure 4. This good overall solubility allowed us to investigate in more detail the effects of conjugation length.

The synthesis of chromophores **6** and **7** are based on our previously described intermediates.[14] Compounds **1** and **3** were used to react with compound **8** in $NaOC_2H_5/HOC_2H_5$ solution. These intermediates were then further reacted with butyllithium/DMF to prepare

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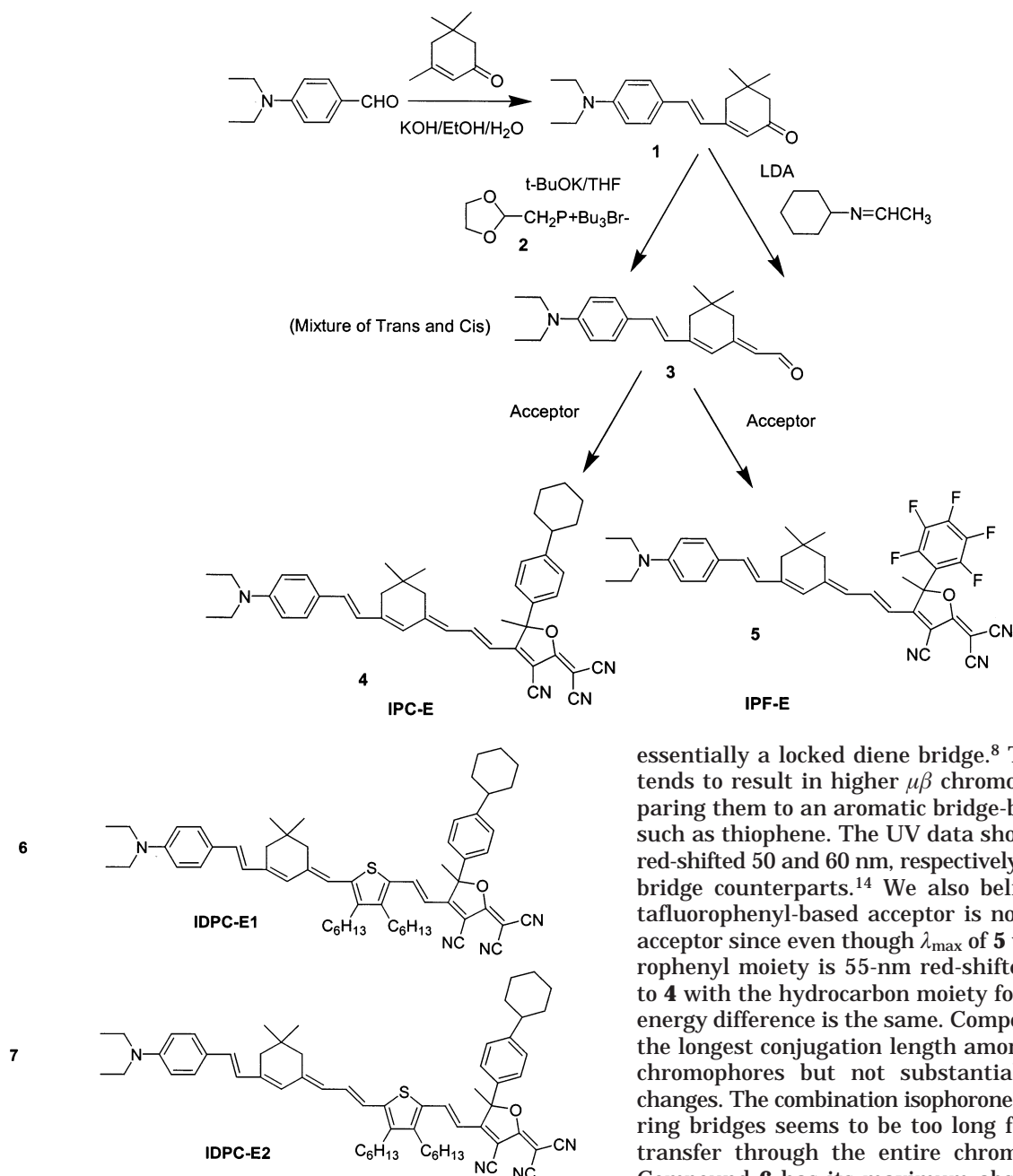
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Scheme 2

KOH/EtOH/H$_2$O

1

t-BuOK/THF

CH$_2$P+Bu$_3$Br-

2

LDA

N=CHCH$_3$

(Mixture of Trans and Cis)

3

Acceptor

Acceptor

4

IPC-E

5

IPF-E

6

IDPC-E1   C$_6$H$_{13}$ C$_6$H$_{13}$

7

IDPC-E2   C$_6$H$_{13}$ C$_6$H$_{13}$

Figure 4. Isophorone and thiophene double-bridge based chromophores.

the corresponding aldehydes. These aldehydes were easily coupled with our acceptors to form the chromophores (Scheme 3).
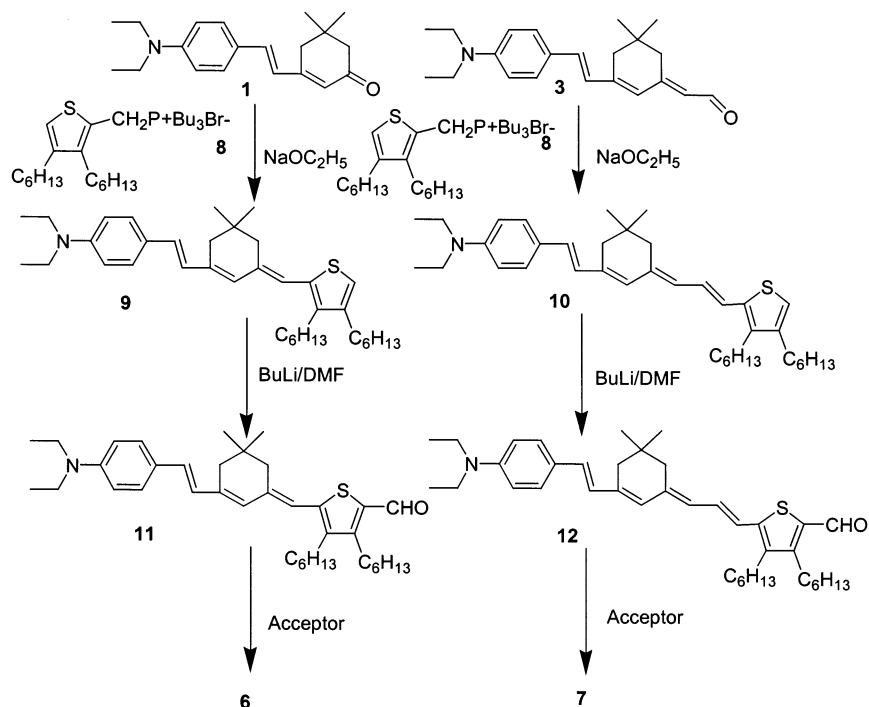
UV–Vis–NIR Studies of the Chromophores. All of our chromophores can be dissolved into both chloroform and toluene; the absorption spectra have been obtained in both solvents to determine the wavelength of the maximum absorption of the charge-transfer band. The chromophores were also given letter names in our laboratory to simplify identification within the group. All of the names along with the corresponding compound numbers are included in Table 1.

Again, as found in part 1, longer conjugation length does not always lead to a greater solvatochromic energy shift. Chromophores **4** and **5** both have an isophorone bridge that a previous reference has mentioned to as

essentially a locked diene bridge.[8] This type of bridge tends to result in higher $\mu\beta$ chromophores when comparing them to an aromatic bridge-based chromophore such as thiophene. The UV data show that **4** and **5** are red-shifted 50 and 60 nm, respectively, to their thiophene bridge counterparts.[14] We also believe that the pentafluorophenyl-based acceptor is not a much stronger acceptor since even though λ_{max} of **5** with the pentafluorophenyl moiety is 55-nm red-shifted when compared to **4** with the hydrocarbon moiety for both solvents the energy difference is the same. Compounds **6** and **7** have the longest conjugation length among our entire set of chromophores but not substantially higher energy changes. The combination isophorone–thiophene double-ring bridges seems to be too long for effective charge transfer through the entire chromophore π system. Compound **6** has its maximum absorption at 742 nm with an additional peak at 389 nm, while **7** has its maximum absorption at 760 nm and an additional peak at 407 nm as shown in Figure 5. Both of these additional absorption peaks at 389 and 407 nm appear at shorter wavelengths for both solvents, an effect not seen for any of the other compounds. We believe the charge transfer through the π system from end to end is not complete with some charge remaining on the aromatic thiophene ring creating the shorter wavelength absorption peak. The UV–Vis spectrum of the donor double-bridge compound **9** seems to verify our assumption having its absorption maximum at the same wavelength, 400 nm, that the new absorption peak appears.

It is well-known that solvatochromic effects are indicative of the chromophore's $\mu\beta$ value and several recent review articles have been written on the subject.[16,17] On the basis of simple solvent studies using polar chloroform and less polar toluene, we found that
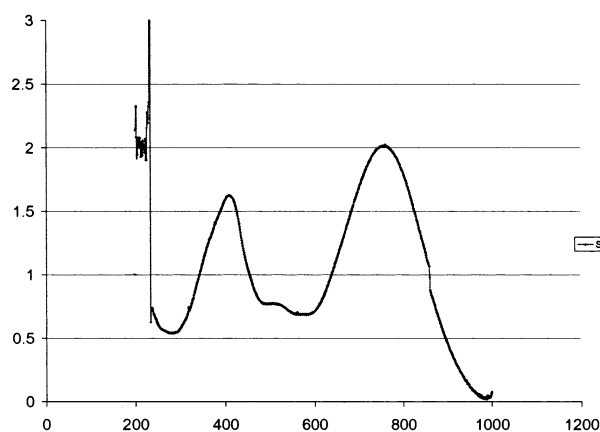
Scheme 3

Chromophore 7 in Chloroform

Figure 5. UV spectra of chromophore 7 in chloroform.

Table 1. Maximum Absorption of Chromophores

compd	chloroform λ_{max} (nm)	λ_{max} (cm^{-1})	toluene λ_{max} (nm)	λ_{max} (cm^{-1})	change (eV)	lab. name
4	705.8	14 168.3	664.9	15039.8	0.108	IPC-E
5	760.2	13 154.4	713.1	14023.3	0.108	IPF-E
6	742.1	13 475.3	702.7	14230.8	0.094	IDPC-E1
	389.4		389.4			
7	760.2	13 154.4	722.2	13846.6	0.086	IDPC-E2
	407.6		413.5			
9	407.6		407.0		N/A	N/A

chromophores **4** and **5** show the largest energy shift of the charge-transfer band (0.108 eV) while the longer chromophores **6** and **7** have 0.094 and 0.086 eV changes, respectively. It was also noted that TBDMS, used to protect the hydroxy functions on the chromophores, shows a bigger change in the charge-transfer band when

Table 2. TGA Test of Chromophore Thermal Stability

chromophore	lab. name	5% weight loss (°C)	melting point (°C)
4	IPC-E	270.3	214−216
5	IPF-E	251.6	180−182
6	IDPC-E1	264.9	118−120
7	IDPC-E2	291.0	134−136

compared to the analogous hydroxyl-containing chromophores.[14]

Thermal Stability of Chromophores. TGA testing of the chromophores has been performed in an air atmosphere. The test results are listed in Table 2 and the results are shown in Figures 5 and 6.

Comparing the onset of weight loss of chromophores **4**−**5** from Figure 5, we found **4** to be much more stable since **4** begins to decompose around 200 °C, where **5** begins thermal decomposition around 100 °C. We believe this is caused by the strong electron withdrawal of the pentafluorophenyl ring-containing acceptor; being a good leaving group, this corresponds to our previous hypothesis since we noticed the same behavior in our thiophene-based chromophores in a previous study.[14] Figure 6 clearly shows that **5** begins to decompose much earlier than its hydrocarbon counterpart.

At this time we do not have clear mechanistic evidence for this behavior but we think it is due to the following reasons. (1) The strong electron-withdrawing pentafluorophenyl ring causes the furan structure to be unstable with respect to either ring opening or a pentafluorophenyl radical leaving group, resulting in easier decomposition. (2) We know that the additional electron-withdrawing ability has made a large (55 nm) red shift in the chromophore's absorption peak, lowering the energy levels of the HOMO and LUMO which may facilitate molecular rearrangements. (3) Because fluorine withdraws electron density so strongly, the fluorinated benzene ring may separate from the tricyanofuran ring-forming radicals that further decompose. Chro-

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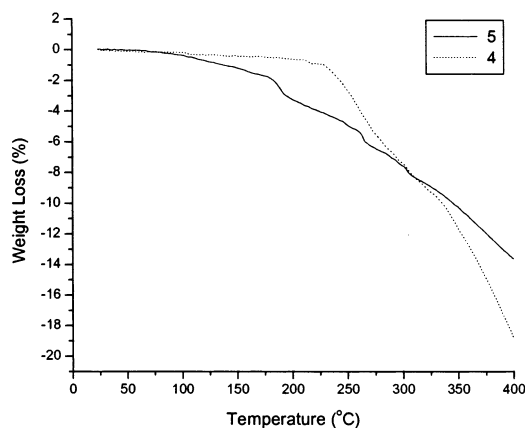
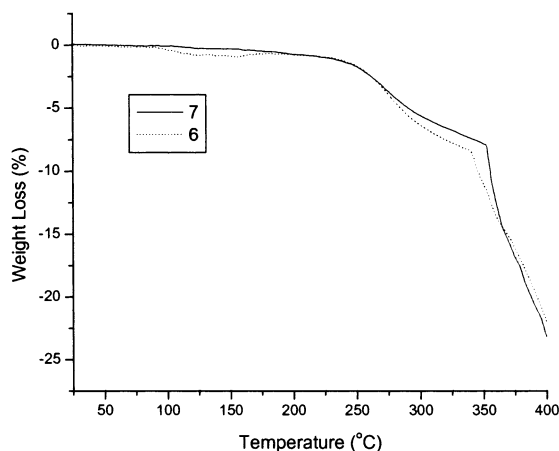**Figure 6.** TGA of chromophores **4** and **5**.

Figure 7. TGA of chromophores **6** and **7**.

mophores **6** and **7** both have an isophorone−thiophene double-ring bridge. We initially thought that these two compounds would be the least thermally stable of the set due to their extremely long conjugation length. But TGA tests in air have shown that they both are very stable with respect to breaking into smaller fragments as seen in Figure 7. The 5% weight loss by TGA is 264.9 °C for **6** and 291.0 °C for **7**.

Electro-optic Characterization. We selected **4** as the first chromophore on which to evaluate the electrooptic coefficient since it has the most pronounced "fishhook" shape. This shape was expected to give high solubility and low chromophore−chromophore pairing, facilitating poling. Evaluation of the chromophore nonlinear strength consisted of the following procedure. First, the chromophore was doped at 35 wt % into purified polycarbonate (Aldrich poly[Bisphenol A carbonate-*co*-4,4′-(3,3,5-trimethylcyclohexylidene)diphenol carbonate]). 35% chromophore loading was used based on observing no haze in cast films prior to poling; at higher concentrations the films became hazy. Solutions of 10% total solids were prepared in 1,2-dichloroethane and 3−5-μm-thick films spun-cast onto ITO/glass substrates. After drying overnight in a vacuum oven at room temperature, 200-nm-thick gold electrodes were thermally evaporated onto the top surface of the film. This sample preparation allows contact poling of the films and immediate ellipsometer measurements[18] to
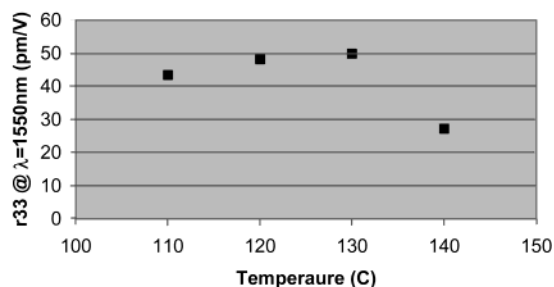
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Figure 8. r_{33} dependence on poling temperature for a constant poling field of 100 V/μm for compound **4**.
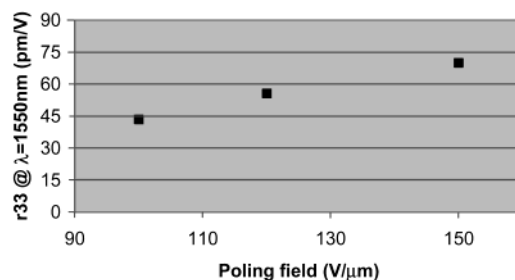

Figure 9. r_{33} dependence on poling field for a constant poling temperature of 130 °C.

determine the electro-optic coefficient. Measurements of r_{33} were performed at both 1550- and 1300-nm wavelengths.

Determining the optimum poling conditions consisted of two steps. First, films were contact-poled for 30 min at 100 V/μm but at varying temperatures. Figure 8 shows the measured r_{33} values as a function of temperature.

Optimum poling occurred at 130 °C for 35% of **4** in polycarbonate. Next, the films were poled at the optimum temperature found by the proceeding experiment but with successively higher field strengths until dielectric breakdown of the film occurred. Figure 9 shows the maximum r_{33} (λ = 1550 nm) value of 70 pm/V was obtained for compound **4** by poling at 150 V/μm and 130 °C. We typically poled samples under 200 V/μm because some samples break down at that level. This value is twice the value of LiNbO$_3$. The r_{33} values measured at 1300 nm were on the average 14% higher than the measured values at 1550 nm. This is close to the 22% increase predicted by the wavelength dispersion of β. The difference is likely due to measurement error. To our knowledge, this is the best r_{33} value reported at 1550 nm to date. We believe that there are mainly two reasons that contribute to this result. First, our unique acceptor design allows us to have very differently sized R$_1$ and R$_2$ groups. This size difference generates a chromophore with a fishhook shape that creates a great increase in chromophore solubility, resulting in an increased doping concentration. Second, the three-dimensional fishhook structure helps to keep chromophore−chromophore electrostatic interactions to a low level, resulting in more efficient poling.

Conclusion

We have successfully synthesized four new high $\mu\beta$ chromophores. These chromophores possess isophorone and combined isophorone−dialkylthiophene bridges. All chromophores take advantage of our newly synthesized

novel acceptors, rendering them very soluble in nonpolar solvents and polycarbonates. Since these acceptors have unique furan ring structures including spiro ring junctions, by selection of R_1 and R_2 groups of different sizes, electronic properties, and flexibility, all our newly synthesized chromophores have good solubility and high processibility. UV spectra show all the chromophores exhibit large solvatochromic effects, implying these new chromophores possess very large $\mu\beta$ values. Preliminary EO characterization demonstrates that chromophore **4** has an extremely high EO activity with a value of 70 pm/V r_{33} being achieved at 1550 nm as measured by elipsometry. Thermal testing indicates the chromophores are very stable with the majority of them stable to over 250 °C in air. Good thermal stability allows us more choices of how to process these chromophores into different polymer matrixes. We are continuing to characterize these chromophores and are actively working on obtaining pure enantiomers from the racemate. We will continue to report our results as they become available.

Experimental Section

General Information. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR were obtained with a Varian Unity Inova 300-MHz system. TMS was used as the internal standard. CDCl$_3$ was 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 and the deviation between these two mass values in Daltons and in parts per million are reported. All deviations were found to be less than 10 ppm for all cases. In this paper, the exact mass of protonated adduct will be given. Additional results have been supplied in the Supporting Information. Melting points were obtained from A Mel-Temp 3.0 device and are uncorrected. UV−Vis−NIR spectra were obtained using a Perkin-Elmer Lambda 900 spectrometer. TGA were performed 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 of 2.5−3.5 mg; 5% weight loss was taken as the onset of decomposition to avoid any residual solvent in the sample leading to error in the data.

3-(*p*-N,N-Diethylaminostyryl)-5,5-dimethylcyclohex-2-enone (1). 4-Diethylaminobenzaldehyde (17.7 g, 0.10 mol), isophorone (13.8 g, 0.10 mol), NaOH (8.0 g, 0.20 mol), ethanol (100 mL), and water (50 mL) were mixed at room temperature. The mixture was stirred at room temperature for 96 h. Solid formed in the reaction solution after 3 days of stirring. After filtering the solid from the reaction mixture, the solid was redissolved into ethyl acetate (300 mL) and washed with brine (100 mL) and water (2 × 50 mL) and dried over anhydrous MgSO$_4$. After the solvent was evaporated, the solid was slurred by adding ether to the flask. The solid was then collected by vacuum filtration to yield 17.8 g, 59.9%. mp 95.2−97.0 °C. ^{1}H NMR: δ 8.04 (d, 1H), 7.54 (d, 2H), 7.55−7.479 (m, 1H), 7.38

(m, 1H), 6.76 (d, 2H), 3.42 (q, 4H), 2.87 (s, 2H), 2.49 (s, 2H), 1.20 (t, 6H), 1.09 (s, 6H). Molecular formula: C$_{20}$H$_{27}$NO. Exact mass + H: calculated, 298.2171; observed, 298.2172.

Tributyl(1,3-dioxolan-2-ylmethyl)phosphonium Bromide (2). Compound **2** was made following the method from ref 19. 1,3-Dioxolan-2-ylmethyl bromide was reacted with tributylphosphine quantitatively at 90 °C to yield the salt as a glass without needing further purification. ^{1}H NMR: δ 5.28 (t, 1H), 4.10 (m, 4H), 3.13 (d, 2H), 2.50 (m, 6H), 1.48 (m, 12H), 0.94 (t, 9H).

3-{3-(*p*,N,N-Diethylaminostyryl)-5,5-dimethylcyclohex-2-enylidene}-2-butenal (3). *Method A*: To a solution of compound **1** (12.0 g, 0.041 mol) and compound **21** (0.048 mol) in THF (200 mL), potassium *tert*-butoxide (60 mL, 0.06 mol, 1 M in THF) was added dropwise. The mixture was refluxed overnight and the solvent was then removed. The organic material was extracted with ethyl ether (3 × 100 mL) from its water mixture. The combined organic extracts were washed with brine (2 × 100 mL) and water (100 mL) and dried over anhydrous MgSO$_4$. Aldehyde **3** was obtained as cis−trans isomers from a silica gel chromatograph column (10% ethyl acetate in hexane) to yield 5.3 g, 40.0%.

Method B: A solution of butyllithium (16.2 mL, 0.041 mol, 2.5 M in hexane) was added dropwise to a solution of diisopropylamine (4.08 g, 0.041 mol) in dry ether at 0 °C. This fresh LDA solution was stirred for 10 min at 0 °C and cooled to −78 °C. *N*-Cyclohexylacetaldimine (5.06 g, 0.041 mol) was added dropwise to the above LDA solution. The mixture was then slowly warmed to −10 °C and cooled back to −78 °C. Compound **1** (10.0 g, 0.034 mol) dissolved in 30 mL of ethyl ether was added dropwise to the Vilsmeier reagent. This final mixture was allowed to slowly warm to room temperature, stirred overnight, at room temperature, and poured into water (100 mL). The organic product was extracted with ethyl ether (2 × 100 mL). The combined organic layers were washed with brine (2 × 100 mL) and water (2 × 50 mL) and dried over anhydrous MgSO$_4$. After removal of the solvent, the cis−trans isomers of **3** were obtained from a silica gel chromatography column (10% ethyl acetate in hexane) to yield 5.7 g of **3**, 52.4%. The aldehyde proton peak at 10.23 is the cis isomer and the proton peak at 10.06 is the trans isomer. The NMR estimate of cis/trans is 34:64%. This result was obtained for both methods. Mixed isomers mp 88.0−91.0 °C. Trans isomer ^{1}H NMR: δ 10.06 (d, 1H), 7.35 (d, 2H), 6.76 (s, 2H), 6.05 (d, 2H), 6.26 (s, 1H), 5.92 (dd, 1H), 3.40 (q, 4H), 2.68 (d, 2H), 2.35 (s, 2H), 1.22 (t, 6H), 1.06 (s, 6H). Molecular formula: C$_{22}$H$_{29}$NO. Exact mass + H: calculated, 324.2327; observed, 324.2330.

2-{[3-[2(4-(Diethylamino)phenyl]ethenyl]-5,5-dimethyl-2-cyclohexen-1-ylidene]methyl}thiophene (9). Sodium ethoxide (50 mL, 0.05 mol, 1 M in ethanol) was added dropwise to a mixture of compound **1** (10.0 g, 0.034 mol) and **8** (22.3 g, 0.041 mol) in DMF (50 mL). The mixture was heated to 100 °C and stirred for 48 h before being poured into water (200 mL). The organic mixture was extracted with ethyl ether (3 × 100 mL). The combined organic layers were washed with brine (2 × 50 mL) and water (2 × 50 mL) and dried over anhydrous MgSO$_4$. Pure compound **9** was obtained from a silica gel chromatography column (5% ethyl acetate in hexane) to yield 11.0 g, 59.8%. ^{1}H NMR: δ 7.32 (d, 2H), 6.85 (s, 1H), 6.76−6.48 (m, 3H), 6.65 (d, 2H), 6.29 (s, 1H), 3.76 (q, 4H), 2.52 (m, 6H), 2.23 (s, 2H), 1.65−1.27 (m, 16H), 1.19 (t, 6H), 1.03 (s, 6H), 0.90 (m, 6H). Molecular formula: C$_{37}$H$_{55}$NS. Exact mass + H: calculated, 546.4133; observed, 546.4156.

2-{[3-[2[4-(Diethylamino)phenyl]ethenyl]-5,5-dimethyl-2-cyclohexen-1-ylidene]3-propylidene}thiophene (10). Compound **10** was made according to the method outlined for compound **9**. Compound **3** (1.43 g, 0.0044 mol), **9e** (2.9 g, 0.0053 mol), and sodium ethoxide (7.0 mL, 0.007 mol) yielded compound **10** (1.8 g, 71.6%). ^{1}H NMR: δ 7.31 (d, 2H), 6.71 (s, 1H), 6.91 (m, 1H), 6.70−6.61 (m, 3H), 6.52−6.44 (m, 1H), 6.64 (d, 2H), 6.19 (s, 1H), 3.37 (q, 4H), 2.56 (t, 2H), 2.47 (t, 2H), 2.31

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(s, 2H), 2.23 (s, 2H), 1.61−1.27 (m, 16H), 1.17 (m, 6H), 1.02 (s, 6H), 0.90 (m, 6H). Molecular formula: $C_{39}H_{57}NS$. Exact mass + H: calculated, 572.4290; observed, 572.4283.

5-{[3-[2[4-(Diethylamino)phenyl]ethenyl]-5,5-dimethyl-2-cyclohexen-1-ylidene]methyl}-2-thiophenecarboxaldehyde (11). Compound **9** (10.4 g, 0.019 mol) was mixed with dry THF (50 mL). Butyllithium (8 mL, 0.020 mol) was added dropwise at −78 °C. The mixture was warmed to −20 °C and cooled back to −78 °C again. DMF (3 mL) was then added. The final mixture was allowed to warm followed by stirring at room temperature overnight before the THF was removed. The residue was poured into water (100 mL) and extracted with ethyl ether (3 × 50 mL). The combined organic layers were washed with brine (2 × 50 mL) and water (2 × 50 mL) and dried over anhydrous MgSO₄. Pure **11** was obtained from a silica gel chromatography column (10% ethyl acetate in hexane) to yield 9.3 g, 85.3%. ¹H NMR: δ 9.98 (s, 1H), 7.33 (d, 2H), 6.84 (m, 1H), 6.65 (d, 2H), 6.63 (m, 2H), 6.46 (s, 1H), 3.39 (q, 4H), 2.85 (t, 2H), 2.58 (t, 2H), 2.56 (s, 2H), 2.27 (s, 2H), 1.62−1.31 (m, 16H), 1.18 (t, 6H), 1.05 (s, 6H), 0.91 (m, 6H). Molecular formula: $C_{38}H_{55}NOS$. Exact mass + H: calculated, 574,4083; observed, 574.4103.

5-{[3-[2[4-(Diethylamino)phenyl]ethenyl]-5,5-dimethyl-2-cyclohexen-1-ylidene]-3-propylidene}-2-thiophenecarboxaldehyde (12). Compound **12** was made following the procedure outlined for compound **11**. Compound **10** (5.71 g, 0.01 mol), butyllithium (6 mL, 0.015 mol), and DMF (1.5 mL) were used in the reaction to yield compound **12** (5.67 g, 94.7%). ¹H NMR: δ 9.94 (s, 1H), 7.32 (d, 2H), 7.23 (m, 1H), 6.83 (m, 1H), 6.68 (m, 3H), 6.65 (d, 2H), 6.23 (s, 1H), 3.38 (m, 4H), 2.84 (t, 2H), 2.55 (t, 2H), 2.32 (s, 2H), 2.27 (s, 2H), 1.61−1.32 (m, 16H), 1.17 (m, 6H), 1.03 (s, 6H), 0.91 (m, 6H). Molecular formula: $C_{40}H_{57}NOS$. Exact mass + H: calculated, 600.4239; observed, 600.4259.

General Procedure of Chromophore Synthesis. The desired donor bridge aldehyde (1 equiv) and desired acceptor (1−1.2 equiv) were dissolved into THF and ethanol (80:20 in volume) and then 3−5 drops of piperidine from a 23 gauge syringe needle was added as catalyst. The mixture was heated at reflux for 24−72 h and the solvents removed on a rotary evaporator. The residues were dissolved into ethyl acetate and precipitated from hexane. Solid could either be re-crystallized from ethyl acetate and hexane solution or purified through a silica chromatography column (10−60% ethyl acetate in hexane depending on the specific chromophore functional groups) to yield pure chromophore.

[3-Cyano-2-dicyanomethylidene-4-{*trans,trans,trans*-[3-(2-(4-N,N-diethylaminophenyl)vinyl)cyclohex-2-enylidene]-1-propenyl}-5-methyl-5-(4-cyclohexylphenyl)-2,5-dihydrofuran (4). Following the general procedure of compound **3** (5.75 g, 17.8 mmol), compound **A5** (6.7 g, 19.5 mmol), and piperidine (catalyst) were reacted in 100 mL of the THF/ethanol mixture. After 48 h, the solvent was removed and a solid was precipitated from ethyl acetate and hexane mixture (10% acetate). This solid was precipitated three times from the hexane 10% ethyl acetate solvent system to clean out impurities. Pure **4** was obtained via recrystallization from 60% acetate/hexane solution to yield 9.4 g, 81.7%. mp 220−222 °C. ¹H NMR, solvent CD₂Cl₂: δ 7.35 (m, overlap, 7H), 6.80 (m, overlap, 4H), 6.30 (m, 3H), 3.40 (q, 4H), 2.58 (t, broad OH, 1H), 2.34 (s, 2H), 2.07 (s, 3H), 2.29 (m, 6H), 1.86 (s, 2H), 1.62−1.41 (m, 4H), 1.17 (t, 6H), 1.00 (s, 3H), 0.95 (s, 3H). ¹³C NMR: 177.17, 173.97, 156.24, 151.28, 149.78, 149.22, 145.92, 134.97, 134.31, 129.77, 129.61, 128.36, 127.86, 126.64, 125.84, 124.31, 116.23, 113.19, 112.72, 112.18, 98.93, 95.11, 55.22, 45.05, 44.87, 40.21, 39.83, 34.93, 34.87, 31.71, 29.17, 28.08, 27.33, 26.61, 25.07, 13.01. Molecular formula: $C_{44}H_{48}N_4O$. Exact mass + H: calculated, 649.3906; observed, 649.3900.

[3-Cyano-2-dicyanomethylidene-4-{*trans,trans,trans*-[3-(2-(4-N,N-diethylaminophenyl)vinyl)cyclohex-2-enylidene]-1-propenyl}-5-methyl-5-(4-perfluorophenyl)-2,5-dihydrofuran (5). Compound **3** (1.0 g, 3.09 mmol), **A4** (1.3 g, 3.7 mmol), and piperidine (catalyst) were reacted together following the general procedure. Pure **5** was obtained from a silica gel column (50% ethyl acetate in hexane) to yield 1.1 g, 37.7%. mp 180−182 °C. ¹H NMR, solvent CD₂Cl₂: δ 7.62 (t, 1H), 7.40 (d, 2H), 6.94 (d, 1H), 6.75 (d, 1H), 6.66 (d, 2H), 6.38 (s, 1H), 6.31 (dd, 2H), 3.41 (q, 4H), 2.41 (s, 2H), 2.35 (s, 2H), 2.16 (s, 3H), 1.18 (t, 6H), 1.04 (s, 3H), 0.98 (s, 3H). ¹⁹F NMR: −138.35(2F), −150.27(1F), −160.50(2F). ¹³C NMR: 176.33, 169.92, 157.70, 151.64, 149.36, 148.07, 144.69, 140.37, 136.17, 129.78, 127.78, 125.57, 124.07, 114.71, 112.61, 112.04, 94.44, 93.76, 60.57, 56.16, 44.91, 40.17, 39.74, 31.69, 28.50, 26.65, 21.13, 14.39, 12.81. Molecular formula: $C_{38}H_{33}F_5N_4O$. Exact mass + H: calculated, 657.2653; observed, 657.2632.

4-{5-{[3-[2[4-(Diethylamino)phenyl]ethenyl]-5,5-dimethyl-2-cyclohexen-1-ylidene]methyl}-2-thienyl}-3-cyano-2-dicyanomethylidene-5-methyl-5-(4-perfluorophenyl)-2,5-dihydrofuran (6). Compound **11** (2.0 g, 3.48 mmol), **A5** (1.56 g, 4.53 mmol), and piperidine (catalyst) were reacted together in THF/ethanol (30 mL) following the general procedure. Chromophore **6** was obtained from a silica gel chromatography column (15% ethyl acetate in hexane) to yield 1.8 g, 57.6%. mp 118−120 °C. ¹H NMR, solvent CD₂Cl₂: δ 7.40−7.30 (m, overlap, 8H), 6.73−6.61 (m, overlap, 6H), 3.39 (q, 4H), 2.51 (m, 4H), 2.39 (s, 2H), 2.30 (s, 2H), 2.12 (s, 3H), 1.83−0.89 (m, 45H). ¹³C NMR: 176.31, 172.97, 152.53, 150.77, 147.80, 146.74, 143.86, 143.31, 142.04, 138.90, 134.11, 133.62, 130.30, 128.07, 127.91, 126.05, 124.33, 119.21, 112.58, 112.11, 111.59, 110.37, 98.18, 94.77, 44.34, 41.33, 38.44, 34.21, 31.55, 31.03, 30.48, 29.46, 28.53, 27.47, 26.72, 25.99, 24.64, 22.63, 13.81, 12.41. Molecular formula: $C_{60}H_{74}N_4OS$. Exact mass + H: calculated, 899.5661; observed, 899.5653.

4-{5-{[3-[2[4-(Diethylamino)phenyl]ethenyl]-5,5-dimethyl-2-cyclohexen-1-ylidene]-3-propylidene }-2-thienyl}-3-cyano-2-dicyanomethylidene-5-methyl-5-(4-perfluorophenyl)-2,5-dihydrofuran (7). Compound **12** (2.09 g, 3.48 mmol), **A5** (1.43 g, 4.18 mmol), and piperidine were reacted together in THF/ethanol (30 mL) following the general procedure. Chromophore **7** was obtained from column chromatography on silica gel (20% ethyl acetate in hexane) to yield 1.73 g, 53.8%. mp 134−136 °C. ¹H NMR, solvent CD₂Cl₂: 7.36−7.29 (m, overlap, 8H), 6.70−6.59 (m, overlap, 7H), 6.25 (m, 1H), 3.38 (q, 4H), 2.51 (m, 4H), 2.39 (s, 2H), 2.30 (s, 2H), 2.12 (s, 3H), 1.84 (m, 6H), 1.44−0.89 (m, 39H). ¹³C NMR: 175.86, 172.57, 153.33, 150.50, 148.71, 147.34, 143.27, 142.25, 140.68, 138.08, 133.14, 130.66, 129.18, 127.61, 125.71, 124.20, 120.88, 112.11, 111.69, 111.29, 110.96, 97.95, 95.17, 54.58, 43.99, 38.96, 33.86, 31.20, 30.49, 30.20, 29.11, 27.89, 27.12, 26.39, 25.66, 24.28, 22.28, 13.47, 12.08. Molecular formula: $C_{62}H_{76}N_4OS$. Exact mass + H: calculated, 925.5818; observed, 925.5758.

Supporting Information Available: General experimental data exact MS analyses of compounds **1−12** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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