

Synthesis of New Electrooptic Chromophores and Their Structure–Property Relationship[†]

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Several new high $\mu\beta$ chromophores have been synthesized. These chromophores were intentionally designed to study structure–property relationships. The synthetic strategy that was followed has been described in our previous publications. Chromophore photostability was investigated from a structural point of view. Contact and corona poling of the chromophores have also been accomplished with a 70 pm/V r_{33} being achieved at $\lambda = 1550$ nm. The same chromophores were also studied in two different polymer host systems to compare their dependence of the electrooptic coefficient and stability on the matrix material.

Introduction

Electrooptic (EO) chromophores are the basic element for polymeric second-order nonlinear optical (NLO) materials. Chromophores with very high $\mu\beta$ values have been intensively pursued in the past several years.^{1–7} Devices that have over 100 GHz modulation frequencies and a sub-1-V halfwave drive voltages have been demonstrated using the FTC chromophore (Figure 1).^{8,9} However, achieving a commercially usable all polymeric modulator still requires a more fundamental understanding of the structure–property relationships of these new chromophores. Previously, we reported in a series of publications a new acceptor and chromophore system.^{4,5,10} All of our acceptors have a structure where the sp^3 hybridized carbon in the acceptor ring forces the two R groups above and below the plane of the chromophore's conjugated long axis. We believe this results in an increase of free space around the highly polar tricyanofuran ring (Figure 1). This structure helps prevent chromophore–chromophore electrostatic interactions. The fact that the final product is left as a racemic mixture may also aid in the chromophore's solubility. On the basis of these acceptors, we have successfully synthesized several new “fishhook” shaped NLO chromophores. These chromophores possess either single alkylthiophene, dialkylthiophene, isophorone, or combined isophorone–dialkylthiophene bridges. All chromophores contain our newly synthesized novel acceptors, rendering them very soluble in nonpolar solvents. Because these acceptors have a unique modifiable furan ring structure including spiro ring functions, we can select R_1 and R_2 groups of different sizes, electronic properties, and flexibility affecting the final characteristics of the chromophore. All the chromophores show unique solubility, processibility, and absorption band characteristics that are dependent on the choice of R_1 and R_2 . UV spectra in polar and nonpolar solvents show that all of the chromophores have large solvatochromic effects, implying that all chromophores possess very large $\mu\beta$ values.^{4,5} Preliminary EO characterization of one chromophore has demonstrated an extremely high EO value of 70 pm/V r_{33} being achieved at 1550 nm, as measured by ellipsometry.¹¹ Thermal testing also indicates the chromophores are very stable with the majority of them stable to over 250 °C in air.^{4,5}

In this paper, we followed our previously published methods and synthesized several new chromophores.^{4,5,10} We intention-

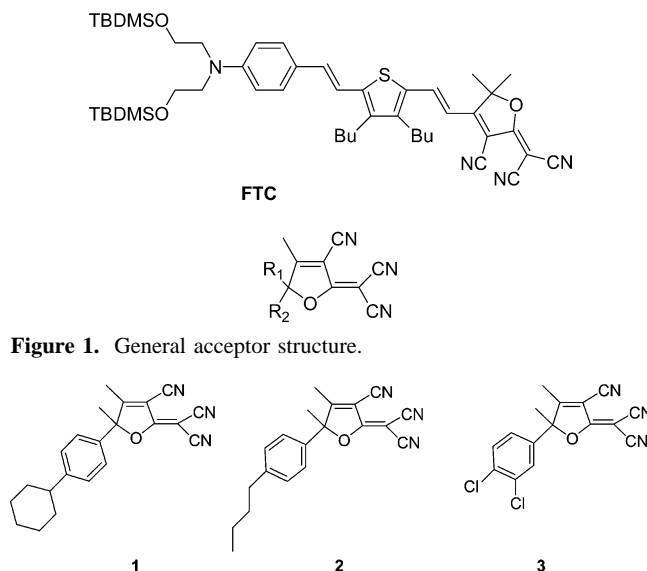


Figure 1. General acceptor structure.

Figure 2. Acceptors.

ally changed acceptors, donors, and bridges in a systematic manner to understand their structure–property relationships.

Results and Discussions

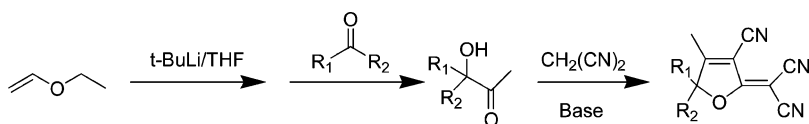
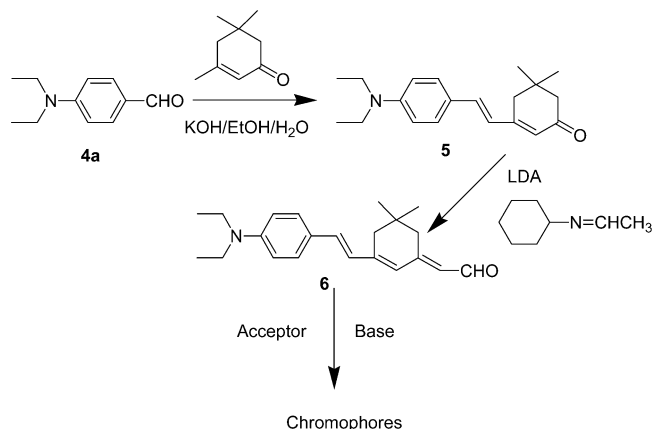
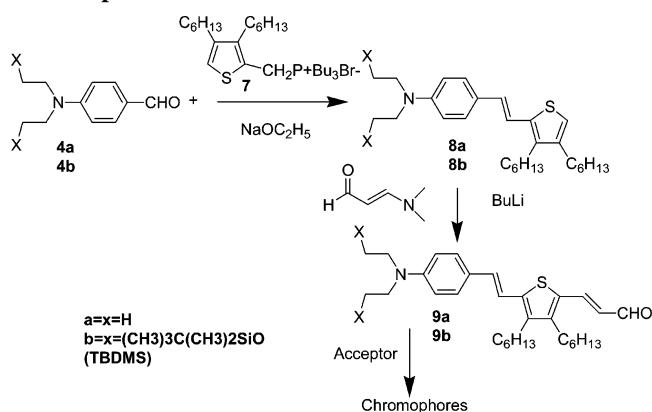
(1) Synthesis. The general synthetic scheme of the chromophores was accomplished in the following order: (1) synthesis of the acceptors and (2) synthesis of the donor bridge systems followed synthesis of the final chromophores. The syntheses of the acceptors was accomplished according to Scheme 1; and the detailed procedure can be found in our previous paper.¹⁰

In this paper, we have chosen to use the three different acceptors shown in Figure 2 for our chromophore study.

Acceptor **1** has a cyclohexyl ring in the para position with respect to the furan ring acceptor, making this R group of the acceptor large and rigid. Acceptor **2** has a butyl group in place of the cyclohexyl ring, making it as large but less rigid. Both of these should have similar electronic properties when incorporated into the chromophore. Acceptor **3** has two chlorine atoms in the para and meta positions of the benzene ring making it electron withdrawing with respect to the other two acceptors we studied. All of these three acceptors have similar charac-

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SCHEME 1: General Procedure of Synthesis of Acceptors**SCHEME 2: Synthesis of Isophorone Bridge Chromophores****SCHEME 3: Disubstituted Thiophene Bridge Chromophores**

teristic in that one R group is aromatic and significantly larger than the methyl attached to the same carbon of the ring. Because the sp^3 carbon forces both R groups out of the plane of the ring, this helps prevent π – π stacking of acceptors.

Two general types of chromophores that differ at the bridge have been synthesized according to our previously published method.^{4,5} The synthetic scheme using isophorone as the bridge component of the chromophore is shown in Scheme 2.

Chromophores with a disubstituted thiophene bridge structure were synthesized as shown in Scheme 3.

All the chromophores synthesized for this study are listed in Table 1.

(2) Photostability. In our previous papers, we discussed in detail our experiments related to the chromophore's thermal stability. In most cases, our chromophores are very stable up to 200–300 °C depending on the specific structure. We have noticed that thiophene bridged chromophores are more stable than isophorone bridged chromophores. We believe that this additional stability is due to the thiophene's aromatic structure. It is also possible that because the isophorone bridge contains allylic protons, it can more easily generate radicals, leading to less stable chromophores.

To further understand the structure–property relationships, we also studied the photobleaching of our chromophores at

TABLE 1: Synthesized Chromophores

Chromophore Name	Structure
IPC-E	
IPCI-E	
IPB-E	
SIPC-B	
DPC-E	
DPCI-E	
DPC-T	

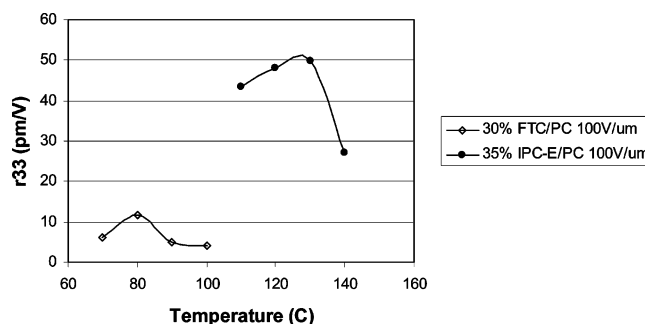
telecommunication wavelengths. There have been some reports about photostability of organic EO materials, but a systematic comparison of EO chromophore photostability according to their structures has not been seen.^{12–14} We used a novel fiber optic pump–probe test to measure the photostability of the chromophores. Fiber samples were prepared by cleaving a 1 m segment of a SMF-28 single-mode fiber. The chromophores were dissolved into polysulfone (Udel, Amoco) using dichlo-

TABLE 2: Relative Photostability of EO Chromophores in Polymer Host with 100 MW at 1550 nm Incident in Air

chromophore	stability in polysulfone	stability in polycarbonate
IPC-E	1	0.61
IPB-E	2.1	
IPCl-E	4.6	
SIPC-B	4.5	
DPC-E	5.8	
DPCl-E	9.5	
DPC-T	18.6	5.2

roethane. The fiber end was dipped into this solution to obtain a 5–10 μm thick coating over the cleaved end. The exact thickness of the film is not important for this test. The experimental setup allowed us to expose the film to a continuous 1550 nm pump beam to induce photobleaching whereas a low power 660 nm probe beam was used to monitor the decrease in the magnitude of the main absorption band of the chromophore. Because the bleaching is measured relative to the first absorption measurement, the exact thickness of the film is not critical. The experimental details of the photobleaching experiments are being published separately.¹⁵ Other factors such as photobleaching in air versus inert atmosphere, the addition of antioxidants and other factors are to be discussed in a separate publication. Here we report only the relative photostability of the chromophores of our series, so we can relate these results to our chromophore structures. We believe these results can help guide the design of new chromophores, reducing the risk of photobleaching at the main communication wavelengths. The relative photostability data are listed in Table 2.

Looking at the structures in Table 2, we can explain the photostability results as related to our chromophore structures. First, the chromophores IPC-E, IPB-E, and IPCl-E all contain the same donor and bridge system. The differences of the three chromophores is found in the acceptors. IPB-E is 2.6 times more stable than IPC-E, and IPCl-E is 4.6 times more stable than IPC-E. The acceptor of IPC-E, the least stable of the group, has a cyclohexyl ring that contains a benzylic tertiary carbon combination in a position that can easily form a free radical by losing a proton. The acceptor of chromophore IPC-B with intermediate stability, has an *n*-butyl group in place of the cyclohexyl ring. The phenyl ring still has a benzylic position but it is now a secondary instead of tertiary carbon. The secondary benzylic carbon is not as susceptible to forming a radical as the tertiary carbon of IPC-E. In contrast, IPCl-E has no alkyl group on the phenyl ring, and accordingly this chromophore was found to be the most stable chromophore in this group. When we compare chromophores SIPC-B and IPC-E, the only difference in structure is the donor group. SIPC-B has a sulfur donor whereas IPC-E has an amino donor. Though the data indicate that the sulfur donor is more stable than the amino donor, it may simply be due to the fact that the sulfur donor is a weaker donor than the amino donor. The chromophore SIPC-B has a wider band gap than IPC-E, as indicated by the blue shifted charge-transfer band and lower r_{33} value. Therefore, we cannot conclude that a sulfur donor is more stable than an amino donor. There may be other electronic factors playing a significant role in this case. The chromophores DPC-E and DPC-T are the same with the only difference being DPC-T has two TBDMS (*tert*-butyldimethylsilyl) moieties on the end of the amino's alkyl groups. We think these large bulk groups somehow help protect the amino donor from oxidation. Chromophores DPCl-E and DPC-E contain the same donor and thiophene bridge with the phenyl cyclohexyl and dichloro phenyl

**Figure 3.** Determinations of best poling temperature (contact poled and ellipsometer measurement at $\lambda = 1550$ nm).

R groups on the acceptor. Again, these two acceptors show the same trend as before in the IPX-E series. DPCL-E is almost twice as stable as DPC-E. When the thiophene bridge chromophores are compared as a group to all the isophorone based chromophores, they are more photostable than the isophorone based chromophores. This result is consistent with our previously published thermal stability data.^{4,5}

We also compared photostability of the chromophores in two different polymer hosts. Because the chromophores were found to be less stable in polycarbonate (PC) than polysulfone, only two chromophores were studied in polycarbonate. The chromophores that were the least and most stable in polysulfone were also studied in PC, and the results are shown in Table 2. IPC-E in polysulfone was found to be 1.7 times more stable in polysulfone than in polycarbonate with DPC-T being 3.6 times more stable in polysulfone than in PC. We also noticed a difference in the r_{33} obtained with two host systems, which is presented in the following section.

(3) Poling Results. We performed both contact and corona poling for the chromophore IPC-E. The reason we chose this chromophore is due to its particularly large, rigid “fishhook” shape, and that we were also able to effectively scale-up the synthesis. Comparisons of the IPC-E and FTC chromophores in both polysulfone and polycarbonate hosts were obtained from initial contact poling/ellipsometer measurements. Subsequent corona poling/ATR measurements were used for comparing IPC-E with our other chromophores. The switch to using corona poling/ATR measurements was made to reduce the required sample preparation.

For our contact poling experiments, the chromophores were doped at 30–35 wt % into purified polycarbonate (Aldrich poly-[Bisphenol A carbonate-co-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate]). At a loading of 30–35%, we observed no haze in solution 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 were spun-cast onto clean 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 to determine the electrooptic coefficient.¹¹

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 3 shows the measured r_{33} values as a function of temperature. Second, the films were poled at the optimum temperature found by the preceding experiment but with successively higher field strengths until dielectric breakdown of the film occurred. Measurements of r_{33} were performed at a wavelength of 1550 nm. The best poling results of IPC-E and FTC in PC are shown in Figure 4.

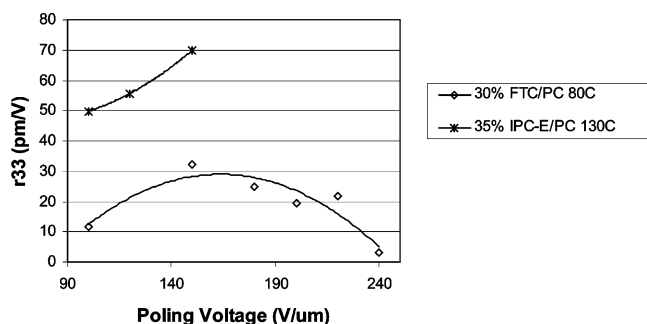


Figure 4. Poling results in polycarbonate (contact poled and ellipsometer measurement at $\lambda = 1550$ nm).

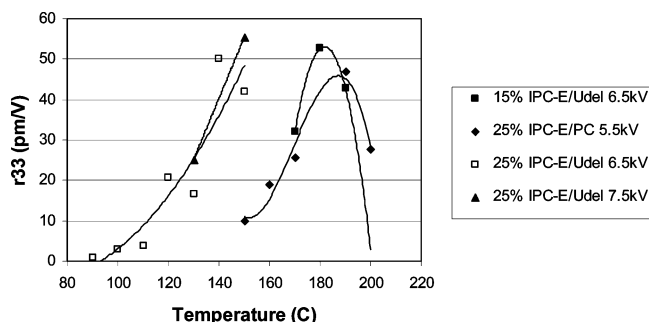


Figure 5. IPC-E poled at different temperatures (corona poled and ATR measurement at $\lambda = 1064$ nm).

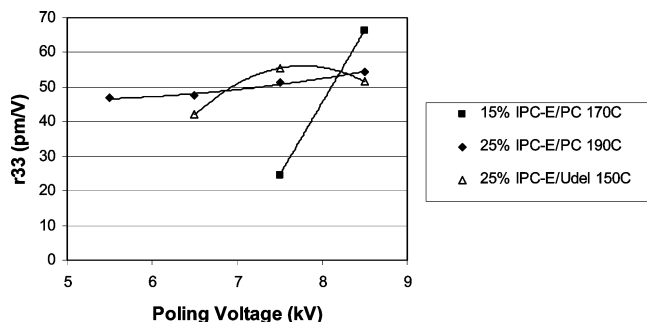


Figure 6. IPC-E poled at different voltages (corona poled and ATR measurement at $\lambda = 1064$ nm).

An r_{33} value slightly more than 70 pm/V was achieved for IPC-E. We also obtained a value over 30 pm/V for the FTC chromophore at 1550 nm; this number is consistent with the previously reported value of 55 pm/V at 1064 nm.⁶

For corona poling, the polymer films were made the same way as the contact poling films; however, none of the ITO is etched off and no deposited Au electrode is needed. The thickness should be measured before poling the film in the same manner as the contact films. This information is mainly used to determine if the film will support at least two waveguide modes at $\lambda = 1064$ nm that are required for an independent calculation of index and thickness.

To corona pole a sample, the film was placed on a heating pad aligned with predetermined marked lines for proper placement under a corona discharge needle. The grounding electrode was connected from the power supply to a wire that was previously soldered to the ITO. The lid was closed on the enclosing chamber, covered with a black cloth, and the chamber was allowed to purge with nitrogen for 1 min. The voltage was turned on and the temperature controller started. The voltage source applies a positive voltage to the corona poling needle which causes positive ions to be deposited on the film surface. Typically, the films were heated at a rate of 10 °C/min, held at the desired temperature and poled for 30 min, allowed to cool

TABLE 3: Results of Poled Chromophores

chromophore	wt %	host	poling temp, °C	poling voltage, kV	r_{33} (1064 nm), pm/V
DPC-T	25	PC	220	6.5	52
IPCI-E	25	PC	170	6.5	60
SIPC-B	25	PC	190	6.5	20
DPC-E	25	PC	190	7.5	46

with the voltage on, and removed when the temperature had reached <40 °C again.

The poling results of IPC-E in PC and polysulfone are illustrated in Figures 5 and 6. Our best poling results obtained for IPC-E were 53 pm/V in Udel and 66 pm/V in PC. The actual values are below our contact poling results. After dispersion is considered, consistency of the two results is observed when the difference in chromophore loading density is taken into account. The contact and corona poled samples produced only slightly different poling efficiencies. These measurement results are described in detail separately.¹⁶

We have corona poled several of our other chromophores in polycarbonate for comparison. Results from ATR measurements are summarized in Table 3.

Although all of these poling results have not been optimized using a temperature voltage matrix, they still indicate that the relative EO activities for the two isophorone based chromophores IPCI-E and IPC-E are comparable, and the two thiophene bridged chromophores DPC-E and DPC-T exhibit slightly lower r_{33} values under similar conditions. The chromophore that has a sulfur donor gave the lowest EO coefficient of the set.

Conclusions

Several new high $\mu\beta$ chromophores have been synthesized according to our previously published methodology. These chromophores were intentionally designed to satisfy our search for a better understanding of structure–property relationships within EO chromophores. Photostability tests have demonstrated that EO chromophores can be rationally designed to avoid photobleaching. This could be the major barrier for using these chromophores in practical commercial devices. Avoiding structures that contain benzylic or allenic carbons can greatly increase the chromophore's stability.

Chromophore thermal stability is somewhat consistent with the photostability results when compared to our prior studies of thermal decomposition. These results show that for these types of chromophores, thermal decomposition can be best avoided if the structure has very little chance for radical generation. Amino donors are the best donors available for high EO coefficients, but these could be problematic when oxygen is present. The thiophene based bridge system is more stable than the isophorone based bridge, but thiophene bridged chromophores give slightly lower EO coefficients when the rest of the structure is kept the same. The photostability of the chromophores has also been found to be dependent on the polymer host. We have experimentally demonstrated that polysulfone is a better host than polycarbonate in regards to photostability.

We have also poled IPC-E and our other chromophores in different hosts under different conditions to look for relative trends. We have achieved an r_{33} of 70 pm/V in polycarbonate from our contact poling experiments. This is the best value obtained at 1550 nm to date for any chromophore observed. Corona poling experiments were also conducted and show that the r_{33} values for IPC-E in polysulfone and PC are slightly

different but within the range of measurement error. Poling results for our other chromophores indicate that the r_{33} value of IPCI-E is comparable to IPC-E, but IPCI-E is more photostable. We found thiophene bridge based chromophores to have slightly lower EO coefficients than the corresponding isophorene based chromophores, but the thiophene based chromophores tend to have better photostability and thermal stability.

Experimental Section

General Information. ^1H 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 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 spectrometry. Twenty micrograms of each of the samples of interest was dried under a stream of nitrogen. The samples were then dissolved in a saturated solution of 2,5-dihydroxybenzoic acid in tetrahydrofuran for subsequent matrix-assisted laser desorption/ionization (MALDI) mass spectrometric analysis. Samples were irradiated with a Nd:YAG laser operating at 355 nm. An IonSpec (Irvine, CA) Ultima II Fourier transform ion cyclotron resonance (FTICR) mass spectrometer was utilized in the analysis. Analysis conditions are unique to each set of mass spectral experiments and are available upon request. For all samples, the predominant ionization mechanism was as their sodiated $(\text{M} + \text{Na})^+$ adduct. For all samples, the observed exact mass values were in excellent agreement with theoretical values ($\Delta < 10$ ppm). Prior to analysis the instrument was externally calibrated with a solution of poly(ethylene glycol) 1000 (PEG 1000) (Sigma Chemical Corp.). So as to demonstrate the improved accuracy through internal calibration, the samples IPB-E and DPC-E were analyzed initially with an external followed by an internal calibration event. For the internal calibration experiments, the standard, PEG 1000 was co-added to the sample-containing matrix.

Compounds **1–3** were synthesized following the procedure of our previous publication.¹⁰ Compounds **4a**, **5**, and **6** were synthesized as found in our previous paper.⁵ Compounds **4b**, **7**, **8a**, **8b**, **9a**, and **9b** were prepared on the basis of ref 4.

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 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 be either recrystallized from ethyl acetate and hexane solution or was purified using a silica gel chromatography column (10–60% ethyl acetate in hexane depending on the chromophore) to yield pure chromophores.

3-Cyano-2-(dicyanomethylidene)-4-{*trans,trans,trans*-[3-(2-(4-(*N,N*-diethylamino)phenyl)vinyl)cyclohex-2-enylidene]-1-propenyl}-5-methyl-5-(4-cyclohexylphenyl)-2,5-dihydrofuran (IPC-E) and the chromophore **4-[(1*E*,3*E*)-4-[5-[(1*E*)-2-[4-[bis(2-*tert*-butyldimethylsiloxy)ethyl]amino]phenyl]ethenyl]-3,4-dihexyl-2-thienyl]butenyl]-3-cyano-5-methyl-5-(4-cyclohexylphenyl)-2(5*H*)-furanlylidene]propanedinitrile (DPC-T)** were prepared as found in our previous references.^{4,5}

3-Cyano-2-(dicyanomethylidene)-4-{*trans,trans,trans*-[3-(2-(4-(*N,N*-diethylamino)phenyl)vinyl)cyclohex-2-enylidene]-1-propenyl}-5-methyl-5-(4-*n*-butylphenyl)-2,5-dihydrofuran (IPB-E) was synthesized following the general procedure.

Compound **6**, 3.0 g (9.3 mmol), and 2-(dicyanomethylene)-3-cyano-4,5-dimethyl-5-(4-*n*-butylphenyl)-2,5-dihydrofuran (**2**), 3.5 g (11.2 mmol), were reacted in THF/ethanol and purified using column chromatography silica gel (ethyl acetate 20% in hexane). After chromatography, 1.5 g of IPE-B was obtained. Yield: 26.0%. ^1H NMR (solvent CD_2Cl_2): δ 7.31 (m, 7H), 6.79 (m, 2H), 6.62 (m, 2H), 6.37 (m, 2H), 6.25 (m, 1H), 3.40 (q, 4H), 2.64 (t, 2H), 2.34 (s, 2H), 2.09 (m, 2H), 2.07 (s, 3H), 1.60–1.36 (m, 4H), 1.17 (t, 6H), 1.00 (s, 3H), 0.92 (t, 3H), 0.85 (s, 3H). ^{13}C NMR: 177.16, 174.00, 156.19, 149.74, 149.23, 146.25, 145.94, 134.94, 134.27, 129.94, 129.77, 129.61, 127.86, 126.63, 125.88, 124.35, 116.27, 113.19, 112.71, 112.20, 98.92, 95.24, 55.32, 45.06, 39.84, 35.83, 34.08, 31.73, 29.18, 28.05, 22.91, 14.24, 13.00. Molecular formula: $\text{C}_{42}\text{H}_{46}\text{N}_4\text{O}$. Exact mass + Na: calcd 645.3569, obsd 645.3559. Deviation (ppm): 0.6.

3-Cyano-2-(dicyanomethylidene)-4-{*trans,trans,trans*-[3-(2-(4-(*N,N*-diethylamino)phenyl)vinyl)cyclohex-2-enylidene]-1-propenyl}-5-methyl-5-(3,4-dichlorophenyl)-2,5-dihydrofuran (IPCI-E). Following the general procedure, compound **6**, 3 g (9.3 mmol), and 2-(dicyanomethylene)-3-cyano-4,5-dimethyl-5-(3,4-dichlorophenyl)-2,5-dihydrofuran (**3**), 3.68 g (11.2 mmol), were reacted as above and purified using silica gel column chromatography (ethyl acetate 30% in hexane). After chromatography, 2.4 g of IPCI-E was obtained. Yield: 40.5%. ^1H NMR (solvent CD_2Cl_2): δ 7.55 (d, 2H), 7.51 (d, 1H), 7.36 (d, 2H), 7.21 (dd, 1H), 6.85 (q, 2H), 6.66 (d, 2H), 6.34 (d, 2H), 6.25 (d, 1H), 3.40 (q, 4H), 2.39 (s, 2H), 2.25 (m, 2H), 2.06 (s, 3H), 1.18 (t, 6H), 1.03 (s, 3H), 0.93 (s, 3H). ^{13}C NMR: 176.71, 171.81, 157.33, 151.01, 149.32, 145.87, 137.55, 135.10, 134.09, 131.87, 129.77, 128.69, 127.95, 126.12, 125.73, 124.18, 115.53, 112.90, 112.16, 97.14, 94.32, 55.78, 45.05, 40.33, 31.83, 28.21, 25.01, 12.99. Molecular formula: $\text{C}_{38}\text{H}_{36}\text{Cl}_2\text{N}_4\text{O}$. Exact mass + Na: calcd 657.2164; obsd 657.2103. Deviation (ppm): 9.1.

3-Cyano-2-(dicyanomethylidene)-4-{*trans,trans,trans*-[3-(2-(4-butylthiophenyl)vinyl)cyclohex-2-enylidene]-1-propenyl}-5-methyl-5-(4-cyclohexylphenyl)-2,5-dihydrofuran (SIPC-B). 3-{3-(*p-n*-Butylstyryl)-5,5-dimethylcyclohex-2-enylidene}-2-butenal was made following Marder's method.¹⁷ Then 3.4 g (10.0 mmol) and compound **1**, 4.1 g (12.0 mmol), were reacted according to the general procedure. The chromophore was purified by column chromatography (15% ethyl acetate in hexane on silica gel). After chromatography, 2.3 g of SIPC-B was obtained. Yield: 34.6%. ^1H NMR (solvent CD_2Cl_2): δ 7.34 (m, 9H), 6.87 (m, 2H), 6.44 (d, 1H), 6.36 (s, 1H), 6.28 (d, 1H), 2.95 (t, 2H), 2.33 (s, 2H), 2.26 (m, 2H), 2.08 (s, 3H), 1.86–1.38 (m, 15H), 1.00 (s, 3H), 0.92 (t, 3H), 0.85 (s, 3H). ^{13}C NMR: 176.88, 174.25, 154.50, 153.90, 151.44, 147.05, 145.50, 139.15, 134.43, 133.88, 132.38, 131.77, 130.49, 128.60, 128.41, 127.85, 126.63, 117.61, 112.74, 111.70, 99.27, 97.03, 56.46, 44.85, 40.08, 39.66, 34.85, 33.09, 31.61, 29.13, 28.03, 27.30, 26.58, 24.95, 22.54, 13.95. Molecular formula: $\text{C}_{44}\text{H}_{47}\text{N}_3\text{OS}$. Exact mass + Na: calcd 688.3338; obsd 688.3359. Deviation (ppm): 3.0.

4-[(1*E*,3*E*)-4-[5-[(1*E*)-2-[4-(diethylamino)phenyl]ethenyl]-3,4-dihexyl-2-thienyl]butenyl]-3-cyano-5-methyl-5-(4-cyclohexylphenyl)-2(5*H*)-furanlylidene]propanedinitrile (DPC-E). Compound **9a**, 2.8 g (5.8 mmol), was reacted with compound **1**, 2.4 g (7.0 mmol), following the general procedure. The chromophore was purified using silica gel column chromatography (15% ethyl acetate in hexane). After chromatography, 1.4 g of DPC-E was obtained. Yield: 29.8%. ^1H NMR (solvent CD_2Cl_2): δ 7.32 (m, 7H), 7.16 (d, 1H), 7.05 (d, 1H), 6.99 (d, 1H), 6.67 (m, 3H), 6.43 (d, 1H), 3.41 (q, 4H), 2.58 (m, 4H), 2.08 (s, 3H), 1.85 (m, 5H), 1.51–1.24 (m, 22H), 1.18 (t, 6H),

0.89 (m, 6H). ^{13}C NMR: 176.93, 173.17, 154.59, 151.31, 150.74, 150.21, 148.91, 145.90, 141.96, 139.38, 138.06, 133.92, 133.47, 133.14, 129.05, 128.40, 126.65, 125.98, 124.21, 117.03, 115.23, 114.48, 113.01, 112.17, 99.44, 96.14, 55.31, 45.03, 34.82, 32.17, 31.53, 29.92, 27.35, 26.62, 24.92, 23.18, 14.41, 12.99. Molecular formula: $\text{C}_{53}\text{H}_{64}\text{N}_4\text{OS}$. Exact mass + Na: calcd 827.46985; obsd 827.4680. Deviation (ppm): 2.2.

4-[(1E,3E)-4-[5-[(1E)-2-[4-(diethylamino)phenyl]ethenyl]-3,4-dihexyl-2-thienyl]butenyl]-3-cyano-5-methyl-5-(3,4-dichlorophenyl)-2(5H)-furanlydene]propanedinitrile (DPCI-E). Compound **9a**, 3.1 g (6.5 mmol), was reacted with compound **3**, 2.6 g (7.8 mmol), following the general procedure. The chromophore was purified by column chromatography on silica gel (25% ethyl acetate in hexane). After chromatography, 1.8 g of DPCI-E was obtained. Yield: 35.3%. ^1H NMR (solvent CD_2Cl_2) δ 7.61 (d, 1H), 7.52 (d, 1H), 7.41 (d, 2H), 7.29–7.21 (m, 3H), 7.03 (d, 2H), 6.67 (m, 3H), 6.41 (d, 1H), 3.43 (q, 4H), 2.62 (m, 4H), 2.10 (s, 3H), 1.49–1.34 (m, 16H), 1.20 (t, 6H), 0.92 (m, 6H). ^{13}C NMR: 176.49, 171.26, 151.62, 150.40, 149.02, 147.01, 142.21, 138.89, 137.11, 135.31, 134.29, 133.85, 133.69, 131.98, 129.19, 128.97, 126.28, 125.92, 124.13, 116.32, 114.94, 112.77, 112.19, 112.18, 111.88, 97.61, 95.69, 56.34, 45.04, 32.16, 31.52, 29.94, 28.01, 27.44, 24.88, 23.16, 14.40, 12.99. Molecular formula: $\text{C}_{47}\text{H}_{52}\text{Cl}_2\text{N}_4\text{OS}$. Exact mass + Na: calcd 813.3137; obsd 813.3139. Deviation (ppm): 0.2.

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Supporting Information Available: Table of masses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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