

Star-Shaped Azo-Based Dipolar Chromophores: Design, Synthesis, Matrix Compatibility, and Electro-optic Activity

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Abstract: Three new azo-benzene-based push-pull chromophores with dendritic architecture were synthesized as active materials for electro-optic applications. These chromophores were synthesized in six or seven synthetic steps with an overall yield of around 80% per step and high purity. UV-vis spectroscopy showed significant influence of the transient dipole moment on the observed r_{33} values. The chromophores were stable to photochemical oxidation in ambient light and air. The electrical poling conditions were optimized for each chromophore as the T_g of the composite material varied significantly. The highest EO coefficient achieved was 22–25 pm/V at 1550 nm wavelength. STEM analysis of the blends enabled the correlation of the activity of these large chromophores with the blend morphology. An amorphous polycarbonate host effectively disperses the chromophores in 2–20 nm aggregates in the active materials. However, macrophase separation into 200–500 nm aggregates was observed in a methacrylate host matrix.

Introduction

In recent years, organic and polymeric materials have emerged as viable alternatives to conventional inorganic crystalline materials in active photonic components such as electro-optic modulators. Polymer electro-optic modulators offer a number of advantages over the currently used lithium niobate modulator. In addition to the potential processing advantages and lower cost, the lower dielectric constant and higher electro-optic (EO) coefficient of organic/polymeric materials result in higher bandwidth compared to lithium niobate-based modulators. Recently we have demonstrated an organic EO modulator architecture with a large bandwidth of 150 GHz with a detectable terabit signal¹ using a simple nonlinear optical chromophore DR1 in a polymer host. This was based on the analysis of dielectric constants of various core and cladding materials to achieve the closest velocity match reported so far in a modulator configuration.² In terms of material properties this modulator architecture allows us in principle to utilize chromophores that provide an EO coefficient of at least 25–30 pm/V and still achieve V_π below 1 V. Dalton et al. have recently demonstrated modulators with V_π below 1 V by developing novel polyene-based chromophores (CLD dyes).^{3,4}

One of the most challenging aspects of designing novel EO chromophores is to balance the need for a high EO coefficient with synthetic ease and photochemical stability. At a molecular level, to achieve high r_{33} values through high electric field orientability requires maximizing the dipole moment of the chromophores, which in turn results in antiparallel aggregation of the dipoles. Hence the translation of microscopic to macroscopic nonlinearity depends on minimization of the electrostatic interaction between the dipoles.

Dendritic architecture is very effective in site isolation of the chromophores, hence reducing electrostatic interaction between the dipoles. With this approach there are dendritic chromophores reported to have EO coefficients as high as 60 pm/V at 1550 nm wavelength with good alignment stability at 80 °C⁵ and a side chain dendrimer NLO polymer with an EO coefficient of 97 pm/V at 1310 nm.⁶ Many of these chromophores with high EO coefficients involve 10–12 synthetic steps with overall low yields and poor photostability in air. Our interest is in incorporating azo-benzene-based push-pull chromophores in dendritic architectures as active materials for electro-optic applications. Compared with polyene- or stilbene-based systems, the advantages of using azo-benzene-based dendritic chromophores are the simple high-yielding synthetic steps and increased photostability in air.^{7a,b} Azo-benzene-containing dendritic benzyl aryl ethers have been extensively studied by

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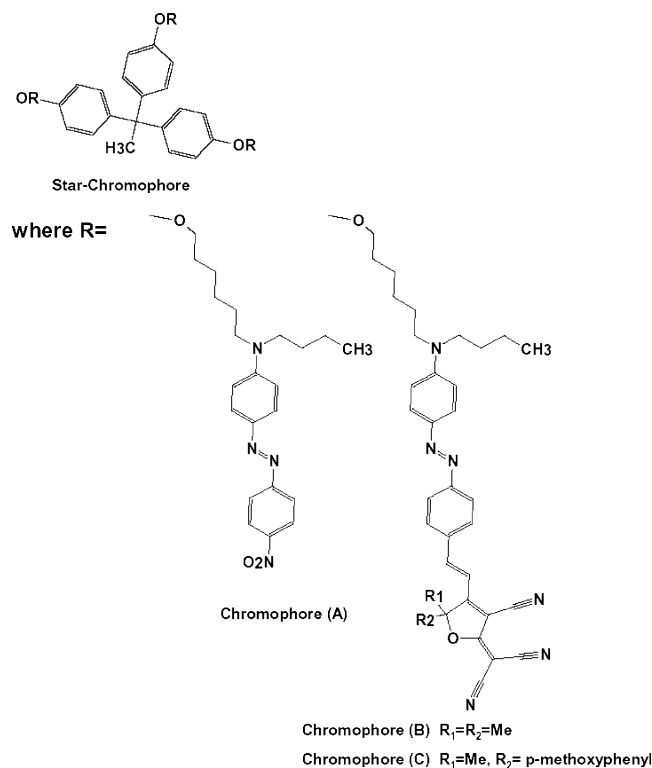


Figure 1. Structure of chromophores A, B, and C.

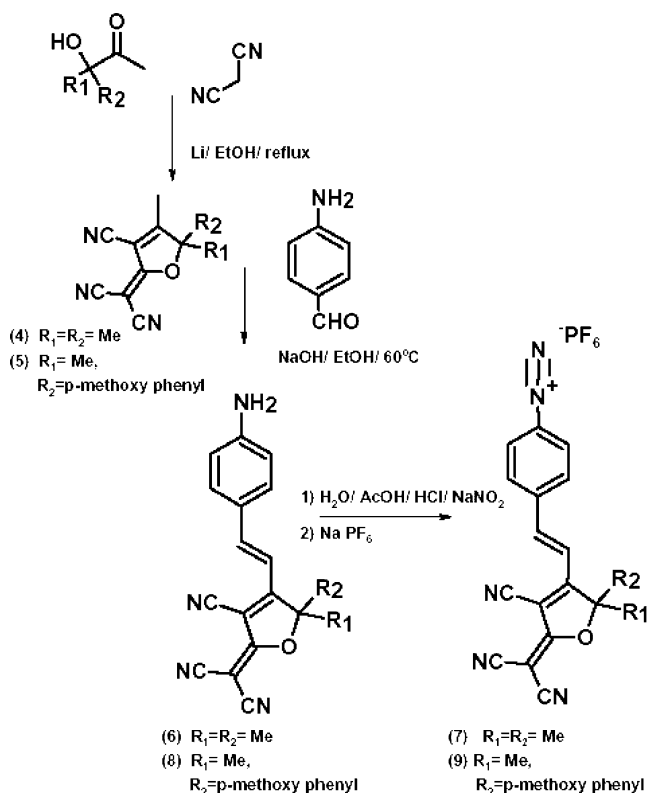
McGrath et al.,^{8a} mainly to study the photomodulation of dendrimer properties, and Yokoyama et al., for second-harmonic generation studies.^{8b} Use of three-dimensional molecules or dendrimers for control of functionality on nanometer length scales is one of the fastest growing areas of research in polymer chemistry.⁹ Attributes such as spherical shape, increased solubility, low viscosity, and monodisperse nature of dendritic molecules have been exploited in nanoelectronics, drug delivery systems,¹⁰ and nonlinear optics.⁵ We report the first example of star-shaped azo-benzene-based EO chromophores and our studies on some of the critical parameters such as blend morphology, poling conditions, and chromophore loading.

Results and Discussions

Synthesis. Our synthetic approach to these new star-shaped chromophores is to utilize simple high-yielding diazonium salt chemistry. The three new chromophores A, B, and C are shown in Figure 1. We synthesize the core starting from 1,1,1-tris(4'-hydroxyphenyl)ethane by etherification with *N*-(6-bromohexyl)-*N*-butylaniline in two steps (Scheme 2). The length of the flexible linker connecting the aniline to the core was kept as six carbons, which allows sufficient flexibility to allow the alignment of the chromophores in response to an applied field.

Chromophore A is synthesized by a simple coupling of commercially available 4-nitrophenyldiazonium tetrafluoroborate salt with the core. For chromophores B and C the acceptor part of the chromophore is synthesized by reacting either TCF or its derivative by a simple Knoevenagel reaction with *p*-aminobenzaldehyde. The resulting dye does not require any

Scheme 1. Synthesis of the Tricyanofuran Acceptor Derivative and the Diazonium Salt



purification since in the subsequent step the diazonium salt of that dye is isolated from the reaction medium as a pure solid in good yield. Once the diazonium salt is isolated, coupling in acetic acid in the presence of sodium acetate at room temperature with the core amine results in the desired star-shaped chromophore (Scheme 1). As outlined in an earlier publication,¹¹ isolation of the benzenediazonium salts derived from the (dicyanovinyl)- or in our case (tricyanofuran)anilines avoids the exposure of the aniline precursors to the reactive byproducts of the diazotization process. The azo coupling has also been successfully employed on polymer backbones such as in the synthesis of methacrylate copolymers with azo dye side chains. Hence it is not surprising that the isolated diazonium salt could be efficiently coupled at room temperature in acetic acid to all three amine functionalities of the core. This is further supported by lack of significant amount of partially functionalized core material as seen from TLC of crude product. However the coupling of diazonium salt **9** was less efficient than the diazonium salt **7** to the core, resulting in a yield of less than 65% of chromophore C as against 93% of chromophore B.

An alternate synthetic approach is to synthesize a monomeric chromophore by diazotization of *p*-aminobenzaldehyde and coupling to *N*-(1-bromohexyl)-*N*-butylaniline or *N*-(1-hydroxyhexyl)-*N*-butylaniline followed by Knoevenagel reaction with tricyanofuran. Subsequent coupling of this chromophore to the 1,1,1-tris(4'-hydroxyphenyl)ethane core by Mitsunobu reaction (using triphenylphosphine/DEAD) led to decomposition of the chromophore.

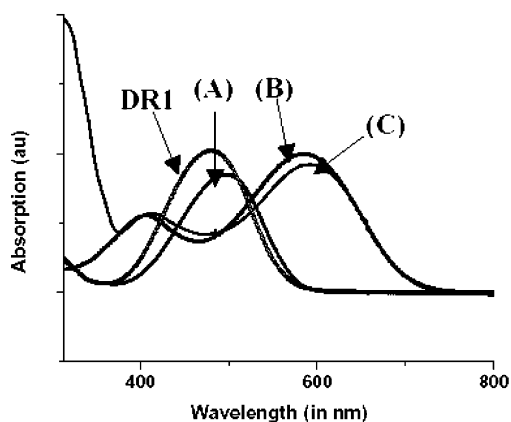
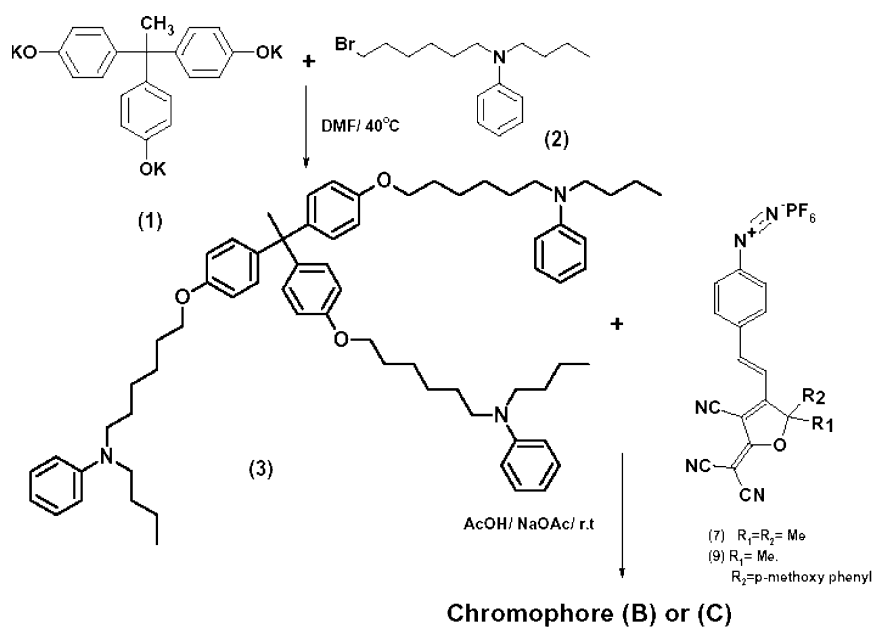
UV-Vis Studies and Evaluation of Dipole Moment of the Chromophores. The measured dipole moment per azo unit

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Scheme 2. Synthesis of the Core of the Chromophore and Subsequent Coupling to the Diazonium Salt to Yield the Star-Shaped Chromophore**Figure 2.** UV-vis spectrum of DR1 and chromophores A, B, and C in chloroform.

increases significantly from 8.5 D for the chromophore with nitro as the acceptor group (chromophore A) to 13.3 D for the tricyanofuran derivative as the acceptor group. This is as expected since the donor group is identical in these chromophores but the strength of the acceptor group increases in chromophores B and C. This is also consistent with expectations from monomeric dyes.

The absorption spectra for the three star-shaped chromophores were obtained in a polar solvent (chloroform) and a nonpolar solvent (toluene) to evaluate the solvatochromic effects. The absorption maxima for the charge-transfer band are reported in Table 1. Longer conjugation length in chromophore B and chromophore C leads to a red shift in the maximum absorption peak (Figure 2). This is also apparent from the color of the chromophore itself. Chromophore A is reddish-orange; chromophores B and C are bluish-violet in color. In C the presence of a *p*-methoxyphenyl substituent on the tricyanofuran ring, instead of the methyl group in B, leads to a red shift of 7 nm. The energy level difference in the two solvents is approximately 0.08 eV for all the chromophores. This indicates that variation of the acceptor group from nitro in chromophore A to a

tricyanofuran derivative in C does not lead to a significant difference in excitation-induced polarization or does not lead to a difference in the differential stabilization of the ground and excited states by the two solvents.

Poling Studies and Electro-optic Characterization. We started with chromophore A, which is the simplest structure for electro-optic characterization. This chromophore is essentially Disperse Red-1 (DR-1) except that three DR-1 units are linked together through an aromatic core. DR1 is known to show electro-optic activity in both polycarbonate and methacrylate matrix hosts. It is known that 20 wt % loading of DR-1 in a methacrylate host results in r_{33} (at 1550 nm) of 5–6 pm/V.¹² This amounts to a number density of 4.8×10^{20} molecules of DR1 in 1 g of polymer host. Hence we blended 38 wt % (equivalent to 4.8×10^{20} molecules) of chromophore A in 20 wt % solution of a methacrylate copolymer in cyclopentanone [PMMA-*co*-HEMA (9:1) where HEMA is hydroxyethyl methacrylate] containing a diisocyanate cross-linking agent. Films of 4–5 μm thickness were spin coated on ITO glass substrate and dried thoroughly in a vacuum oven overnight. These films were poled at 130 $^\circ\text{C}$ by direct DC poling (120 V/ μm), and the electro-optic coefficient was measured immediately. Measurement of r_{33} at 1550 nm showed an activity of less than 1 pm/V. The possible reason for low activity could be incompatibility between the host polymer and the large chromophore molecules, resulting in phase separation. To confirm this, we changed the host matrix to amorphous polycarbonate [poly(bisphenol A carbonate-*co*-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol)], commonly known as APC. Unlike the methacrylate host APC has an aromatic backbone similar to the chromophore core, which is likely to result in a more compatible blend. Chromophore A was dissolved in 12 wt % solution of APC in cyclopentanone [4.8×10^{20} chromophore molecules/g of polymer], spin coated on ITO substrate, and dried overnight. Contact poling at 150

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Table 1. UV–Vis Characterization of the Star-Shaped Chromophores

| chromophore | dipole moment (D) ^a | λ_{\max} (in CHCl ₃) | λ_{\max} (in toluene) | $\Delta\lambda$ | change (eV) |
|-------------|--------------------------------|------------------------------------------|-------------------------------|-----------------|-------------|
| A | 8.5 | 497 | 480 | 17 | 0.088 |
| B | 10.5 | 585 | 563 | 22 | 0.083 |
| C | 13.3 | 592 | 569 | 23 | 0.084 |

^a Measured in dioxane as solvent.

°C resulted in an r_{33} value of 6–7 pm/V. No significant relaxation was observed at room temperature, as the r_{33} value remained constant at 6–7 pm/V over the period of 3 months. The quality of the films obtained with APC as matrix was significantly better than the methacrylate matrix, as evidenced by a reduced number of pinholes, improved film uniformity, and more consistent poling conditions. Chromophores B and C also formed incompatible blends with methacrylate host matrix; hence all further studies were conducted with APC matrix. Varying weight % of chromophore B was blended in APC matrix, and films were spin coated (2–3 μm thick) and dried overnight at high temperature in a vacuum oven. The chromophore/APC blends were contact poled at 150 °C, and the electro-optic coefficient was measured immediately. Figure 3 shows the EO coefficients of poled chromophore B/APC films plotted as a function of number density of the chromophore. Results on the compound can be summarized as follows.

(a) A maximum r_{33} value of 22–25 pm/V was achieved at 1550 nm wavelength for a chromophore loading of 43 wt % (number density of 7.18×10^{20} chromophore molecules/g of polymer).

(b) Beyond the maximum, r_{33} drops to lower values. It is important to point out that at this stage we have a loading of almost 52 wt % of the chromophore in the polymer host, which will lead to increased electrostatic interactions. This observation is in agreement for similar maxima reported in the work by the Dalton group.¹³

(c) Chromophore B loading density (4.8×10^{20} molecules/g) equivalent to 20 wt % of DR-1 gives approximately 2.5 times the EO coefficient (15 pm/V) compared to DR-1 (6 pm/V).¹⁴ The two main factors that contribute toward the r_{33} are the dipole moment and the oscillator strength. The higher dipole moment of chromophore B compared to DR1 clearly would lead to enhanced orientation during poling. Integration of the area under the peak in the UV–vis spectrum for similar concentration in Figure 2 shows that the transition moment or the oscillator strength of the chromophore B is approximately double that of DR1, which translates into a higher β and hence explains the observed values of r_{33} .

(d) Only six high-yielding synthetic steps are involved in the synthesis of this simple star chromophore, which still provides an EO coefficient of around 25 pm/V. Substitution of the phenyl group by a thiophene ring is likely to approximately double the $\mu\beta$ value, and hence the r_{33} value is likely to double (i.e., close to 40–50 pm/V) with just one additional synthetic step, by close analogy with previous work.¹⁵ At room temperature the chromophores maintained their activity over a period of 3

months in ambient light, as no significant change (<10%) occurred in their measured EO values. This is consistent with the established photostability of azo dyes.^{7a,b} This is in contrast to polyenic dye samples, which lost most of their activity (and color) under identical conditions.

Chromophore C was harder to handle in terms of both purification and poling than the other star-shaped chromophores, and only preliminary conclusions can be drawn about it. Up to a loading density of 46 wt % (4.8×10^{20} molecules/g of polymer) the films could be poled at close to 140 °C. Beyond 46 wt % the contact gold electrodes on the film for poling start to crack at 130 °C, leading to electrical shorting of the sample. This indicated that the glass transition temperature T_g of the composite material containing more than 46 wt % of chromophore was significantly lower. We could not detect T_g by DSC analysis of the composite blends. This could also be attributed to possible thermal expansion mismatch between the polymer film and the gold electrode. Hence on the basis of the conditions under which the samples shorted, an optimal poling temperature of 95 °C was used. This allowed successful poling of the two higher concentrations with a number density of 9.6 and 11.9×10^{20} molecules of chromophore C/g of polymer. As discussed earlier, chromophore C was designed to have more solubility in the polymer host and reduce the electrostatic interactions due to the bulky *p*-methoxyphenyl side group at the acceptor end of the molecule. However, the measured values were found to be significantly lower than chromophore B. Incorporation of compound **5** in the azo-based star chromophore as the acceptor group instead of compound **4** has the following effects.

(1) Some of the samples showed a value of 20 pm/V at 1550 nm immediately after poling, but stabilized in 30 min to a value of 15 pm/V. The T_g of these blends is significantly depressed, leading to relaxation of the poled chromophores and hence lower r_{33} values.

(2) Solubility of the chromophore C is much higher than chromophore B in the host matrix. Up to 65 wt % of chromophore C can be loaded in the polymer host without any precipitation.

Previous theoretical work on the wavelength dispersion of the electro-optic coefficient has indicated an enhancement of r_{33} as the optical wavelength approaches a material resonance. For chromophores with absorption resonances in the 480–580 nm range, a simple two-level model predicts a 20–30% increase in r_{33} as the optical wavelength decreases from 1550 to 1310 nm.^{16,17} Experimentally, we have measured a 22% increase in r_{33} between 1550 and 1310 nm for chromophore B (which translates into a EO coefficient of around 30 pm/V at 1310 nm) and a 47% increase for chromophore A. While r_{33} is indeed observed to increase as the optical wavelength approaches a material resonance, there is only fair agreement with two-level predictions. This could be due to assumptions inherent in the model that are clearly not met in practice, such as complete dipolar alignment, as well as actual variations in molecular alignment from sample to sample.

Influence of Guest–Host Blend Morphology on the Electro-optic Activity. The drastic difference in the electro-

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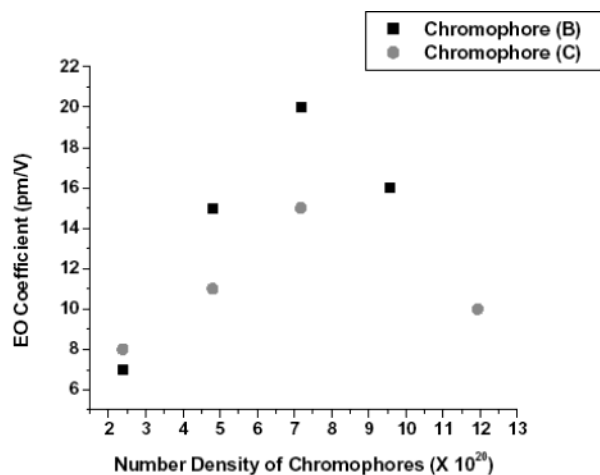


Figure 3. Measured EO coefficient for chromophores B and C as a function of chromophore loading.

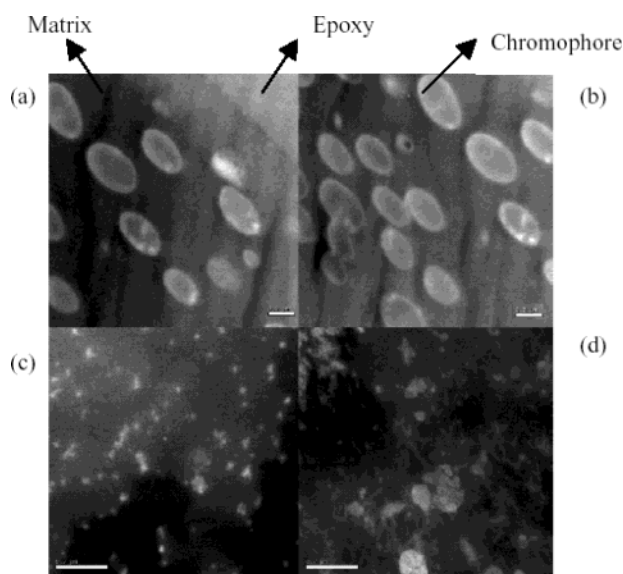


Figure 4. Annular dark field STEM images of chromophore A: (a and b) in acrylate host; (c and d) in APC host. Scale bar is $0.2 \mu\text{m}$ in all images.

optic activity of these star-shaped chromophores in different host matrixes prompted us to examine the morphology of these blends using ADF-STEM. It is known that chromophore phase separation is one of the most important factors governing the activity in a guest–host system. However, to the best of our knowledge, no systematic study has been conducted to correlate the blend morphology and the electro-optic activity. We looked at the simplest system of chromophore A in both methacrylate and APC matrix. In both blends the chromophore loading was the same (number density of 4.8×10^{20}).

The ADF-STEM images are shown in Figure 4. From Figure 4a and b it is clear that the chromophore macrophase separates into oval aggregates of 100–200 nm length scales in the methacrylate host. The bright region is the chromophore and the dark region is the methacrylate host. These phase-separated systems would have light-scattering losses that would make them unusable in an actual device. Figure 4c with the chromophore in APC host shows bright spots of length scale 2–20 nm, which is drastically smaller than the oval aggregates seen in the methacrylate host. Figure 4d is from a different spot of the same sample, which shows string-like domains a few nanometers in

diameter of the chromophore dispersed in the APC host. These observations correlate well with the measured r_{33} values of <1 pm/V for the methacrylate host and 7 pm/V in the APC host. From the STEM images it can be inferred that for maximizing the EO activity of the chromophores it is essential to disperse the chromophores on 2–20 nm length scales and prevent their aggregation and subsequent macrophase separation. Even in the best blends, we can see isolated larger aggregates, which are around 100 nm in diameter. The presence of these larger aggregates in the chromophore/APC blends suggests that use of compatibilizing agents for uniform dispersion can further improve the blend morphology. It should be noted that the free hydroxy groups in the methacrylate copolymer host are completely cross-linked by the diisocyanate in the final blend, yet the overall higher polarity of the methacrylate host compared to the APC host could be one of the reasons for the phase separation.

Conclusions

In this work we have demonstrated a simple high-yielding synthetic procedure involving three to six steps for the first star-shaped azo-based electro-optic chromophores with high r_{33} values. These chromophores could be poled in a polycarbonate host to achieve an EO coefficient as high as 25 pm/V at 1550 nm. UV–vis spectroscopy shows a significant influence of transition dipole moments on the observed r_{33} values. These values were found to be stable at room temperature for at least 3 months and did not require stringent handling conditions. STEM studies to correlate blend morphology with the electro-optic activity indicates that these high molecular weight chromophores form incompatible blends in methacrylate copolymer, whereas they disperse predominantly into 2–20 nm domains in an amorphous polycarbonate matrix.

Currently we are designing heterocycles containing azobenzene-based dendritic chromophores, which is likely to double the observed r_{33} values. We are also investigating the introduction of cross-linking groups at the acceptor end of the chromophore C, which would impart orientational stability at higher temperature.

Experimental Section

General Methods of Material Characterization. All the chemicals were purchased from Aldrich and were used without further purification. ^1H NMR was taken on a Bruker 360 MHz with tetramethylsilane as internal standard. UV–vis spectra were obtained from a HP 8453 UV–vis system. Elemental analyses were performed by Robertson Microlit Laboratories, NJ. Thermal analysis was performed under N_2 on a Perkin-Elmer DSC-7 at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. The dipole moment of the chromophore was obtained by measuring the differential capacitance as a function of concentration. Measurements using *p*-dioxane solutions were performed at 1 kHz, using a high-precision capacitance bridge.

Electron microscopy was performed in a JEOL 2010F-ARP operated at 200 kV as a scanning transmission electron microscope with a 0.16 nm spot size.¹⁸ Samples were prepared for electron microscopy by microtoming to 50 nm thick sections, which were then placed on ac support grids. The samples were not stained. The images are recorded on a Fischione annular dark field (ADF) detector with single-electron sensitivity.¹⁹ The ADF signal produces an incoherent image where the scattered intensity scales approximately as the density times the atomic

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number $Z^{1.7}$ (close to the asymptotic Rutherford scattering limit of Z^2).^{19–21} Consequently heavier atoms or higher density regions appear brighter than lower Z or lower density regions. The incoherent nature of the imaging means there are no contrast reversals with defocus or sample thickness, as can occur in phase contrast images.²¹

Electro-optic Characterization. A thin-film ellipsometric reflection technique^{14,22} was used to measure the linear electro-optic coefficient. Polymer blends were first spun-cast into 3–5 μm thick films on indium tin oxide coated glass substrates. After the films cured, gold electrodes (500 Å) were thermally evaporated onto the exposed surface, and the films were contact poled. A poling voltage of 150–200 V/ μm was applied. To measure the electro-optic coefficient, a linearly polarized laser beam illuminated the film at a 45° angle with respect to the substrate normal. The beam reflected from the gold electrode and was directed through a polarizer rotated 90° with respect to the incident laser polarization. A 29.0 kHz square wave voltage was applied to the film, which caused a phase shift between the s and p polarization components of the laser, and effectively changed the polarization state of the laser beam as it traversed the film. An amplified InGaAs photodiode and lock-in amplifier were used to detect the modulated light intensity transmitted through the polarizer. An optical compensator was used to bias the optical system so that the detected modulated intensity was proportional to the modulating voltage amplitude.

The electro-optic coefficient r_{33} is related to the modulated intensity I_m by

$$r_{33} = \frac{3\lambda}{2\pi V_m} \frac{(n^2 - \sin^2 \theta)^{1/2} I_m}{n^2 \sin^2 \theta I_{\text{max}}}$$

where I_{max} is the amplitude of the maximum transmitted intensity (with no voltage applied to the film), n is the refractive index, λ is the laser wavelength, and θ is the angle of incidence (in this case, $\theta = 45^\circ$). In a typical measurement, V_m is ramped from 0 to 10 V in 1 V increments. At each voltage step, multiple measurements of I_m were averaged over an appropriate time interval. The coefficient r_{33} is then obtained from the slope of I_m versus V_m . Electro-optic coefficients were measured at 1310 and 1550 nm using wavelength- and power-stabilized solid state lasers with an average output power of 3.0 mW. It should be noted that the expression for r_{33} assumes that $r_{33} = 3r_{13}$, the validity of which can vary according to the poling orientation distribution.¹⁴ Despite this, the ellipsometric reflection technique is an efficient way to compare r_{33} for different polymer blends and is used in a number of recent electro-optic studies.^{23,24}

Synthesis of *N*-(6-Bromohexyl)-*N*-butylaniline (1). To a 200 mL round-bottom flask fitted with a reflux condenser *N*-butylaniline (3.0 g, 0.02 mol) and 1,6-dibromohexane (38.0 g, 0.16 mol) were added. This mixture was refluxed for 36 h. The reaction mixture was cooled and extracted with dichloromethane and washed sequentially with a saturated solution of sodium bicarbonate, distilled water, and saturated sodium chloride solution. The dichloromethane extract was dried over MgSO_4 and concentrated by rotary evaporation. The crude product was purified by silica gel chromatography using 3:1 hexane/dichloromethane as eluent to obtain 5.0 g (80%) of product as pale yellow liquid. ¹H NMR (CDCl_3): δ 0.96 (t, 3H), 1.35–1.59 (m, 10H), 1.88 (m, 2H), 3.26 (t, 4H), 6.66 (d, 3H), 7.29 (t, 2H). ¹³C NMR (CDCl_3): δ 148.27, 129.21, 115.41, 111.99, 50.90, 33.69, 32.82, 33.67, 32.82, 29.51, 28.11, 27.19, 26.39, 20.41, 14.03. IR: γ C=O(s) 1717, C≡N 2211.

Potassium Salt of 1,1,1-Tris(4'-hydroxyphenyl)ethane (THPOK) (2). A 1 L three-necked round-bottom flask containing a stir bar was fitted with a Dean–Stark trap topped with a reflux condenser fitted with a guard tube. A mixture of 225 mL of DMSO, toluene (75 mL),

and 1,1,1-tris(4'-hydroxyphenyl)ethane (27.5 g, 0.09 mol) was added to the flask under nitrogen purge. After stirring for 15 min potassium hydroxide pellets (40.0 g, 0.60 mol) were slowly added to the flask. The mixture was refluxed for 48 h with azeotropic removal of water. The remaining solvent was distilled off, and the resulting light brown potassium salt was dried in a vacuum oven at 100 °C overnight to obtain a quantitative yield of the potassium salt. ¹H NMR ($\text{DMSO}-d_6$): δ 1.70 (s, 3H), 6.11 (d, 6H), 6.47 (s, 6H).

1,1,1-Tris(*N*-hexyloxyphenyl)-*N*-butylaniline (3). *N*-(6-Bromohexyl)-*N*-butylaniline (10.10 g, 0.0323 mol), THPOK (4.14 g, 9.58 mmol), and 50 mL of anhydrous DMSO were placed in a 100 mL round-bottom flask and reacted at 40 °C for 9 h. The reaction mixture was extracted with dichloromethane and the solvent removed under vacuum. The residue was column purified on neutral alumina using a 1:1 mixture of hexane/dichloromethane to obtain 6.90 g (72%) of viscous clear liquid as product. The excess starting aniline was quantitatively recovered and recycled. ¹H NMR (CDCl_3): δ 0.96 (t, 9H), 1.3–1.80 (m, 30H), 2.10 (s, 3H), 3.28 (t, 8H), 3.42 (t, 4H), 3.94 (m, 6H), 6.5–6.7 (br, 9H), 6.76 (d, 6H), 6.97 (d, 6H), 7.22 (m, 6H). ¹³C NMR (CDCl_3): δ 157.08, 148.24, 141.74, 129.57, 129.15, 115.25, 113.62, 111.87, 67.74, 50.95, 50.81, 50.60, 30.80, 29.45, 29.36, 27.22, 26.95, 26.04, 20.34, 13.95. IR: γ C–H str 3100, 2930, 2870 (m), C=C str 1590 (m), C–C str 1500 (s), C–N str 1360 (s), C–O str 1240, C–H def (s) 1470, 861. Anal. Calcd for $\text{C}_{68}\text{H}_{93}\text{N}_3\text{O}_3$: C, 81.63; H, 9.37; N, 4.20. Found: C, 81.20; H, 9.29; N, 4.05.

Synthesis of 2-Dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) (4). Under anhydrous conditions 5 g (0.05 mol) of 3-hydroxy-3-methyl-2-butanone and 6.63 g (0.10 mol) of malononitrile were dissolved in 125 mL of absolute ethanol in a 500 mL round-bottom flask equipped with a reflux condenser and Soxhlet extractor (containing 3 Å molecular sieves). Lithium shot (6 mg, 0.85 mmol) was added to the above mixture and refluxed for 8 h. Upon cooling to room temperature crystals of TCF (compound 4) separated out and were collected and dried in a vacuum oven. The final yield was 5.50 g (60%). ²⁵H NMR (CDCl_3): δ 1.6 (s, 6H), 2.3 (s, 3H). ¹³C NMR (CDCl_3): δ 182.21, 175.03, 110.88, 110.25, 108.84, 104.86, 99.58, 58.63, 24.31, 14.03. IR: γ C–H str 3100 (m), C=C str 1590 (m), C–O str 1150, C–H def (s) 861, C≡N 2230 (s).

Synthesis of 2-Dicyanomethylene-3-cyano-4,5-dimethyl-5-(*p*-methoxyphenyl)-2,5-dihydrofuran (5). This compound was synthesized following the general procedure outlined by the Corning group.¹⁷

4-Methoxyacetophenone. 4-Hydroxyacetophenone (5 g, 0.037 mol), methyl iodide (18.9 mL, 0.29 mol), and potassium carbonate (25.4 g, 0.18 mol) were dissolved in 150 mL of acetone and refluxed overnight. The reaction mixture was filtered to remove the potassium salt, and the filtrate was evaporated to dryness. The crude product was purified by a silica gel column using dichloromethane as solvent to obtain 5.51 g (98%) of light brown solid. ¹H NMR (CDCl_3): δ 2.49 (s, 3H), 3.8 (s, 3H), 6.88 (d, 2H), 7.86 (d, 2H).

1-Hydroxy-1-methyl-1-(4'-methoxyphenyl)-2-propanone. Ethyl vinyl ether (3.2 mL, 0.44 m) was dissolved in anhydrous THF (10 mL) in a round-bottom flask fitted with a reflux condenser. The solution was cooled to –78 °C, and *tert*-butyllithium (26 mL, 0.04 mol) solution in *n*-pentane was added gradually using a double-tipped needle under argon. The solution was allowed to warm to –10 °C. *p*-Methoxyacetophenone (3 g, 0.02 mol) was dissolved in 2 mL of THF and added dropwise to the above solution. The reaction mixture was stirred overnight at room temperature. A 20:60:20 mixture of HCl/MeOH/ H_2O was added to the solution to acidify to pH 5. The acidic solution was stirred for 2 h at room temperature followed by concentration under vacuum to remove THF. The ketol was extracted with ethyl ether, and the organic layer was washed with a saturated solution of NaHCO_3 , brine, and water followed by drying over MgSO_4 . The α -ketol obtained by evaporation of solvent was purified by a silica gel column using

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dichloromethane as solvent. The final yield was 3.97 g (50%). $^1\text{H NMR}$ (CDCl_3): δ 1.74 (s, 3H), 2.03 (s, 3H), 3.81 (s, 3H), 4.48 (s, 1H), 6.87 (d, 2H), 7.32 (d, 2H).

Synthesis of compound **5** was carried out by an identical procedure as TCF using 1.91 g (0.011 mol) of the above α -ketol, 1.45 g (0.02 mol) of malononitrile, and 0.6 mL of a 1 M solution of lithium in ethanol. The crude product was purified by a silica gel column using dichloromethane as solvent to obtain 1.8 g (80%) of a yellow solid. An analytical sample was triturated with methanol and dried under vacuum at 100 °C. $^1\text{H NMR}$ (CDCl_3): δ 1.92 (s, 3H), 2.19 (s, 3H), 3.81 (s, 3H), 6.94 (d, 2H), 7.11 (d, 2H). $^{13}\text{C NMR}$ (CDCl_3): δ 182.17, 175.46, 161.18, 126.71, 125.43, 114.98, 110.79, 110.28, 108.98, 104.70, 101.54, 58.88, 55.47, 22.27, 14.41. IR: γ C–H str 3100, 3030 (m), C \equiv N 2220(s), C=C str 1590, 1510 (m), C–O str 1250, 1190, C–H def (s) 832. Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2$: C, 70.09; H, 4.50; N, 14.42. Found: C, 69.98; H, 4.29; N, 14.17.

1,1,1-Tris[*N*-hexyloxy-*N*-butyl-4-(4-nitrophenylazo)phenylamino]ethane (Chromophore A). In a 100 mL flask 1 g (9.99 mmol) of **3** was dissolved in 40 mL of acetic acid at room temperature. This solution was cooled to 5 °C, and 0.75 g (3.19 mmol) of 4-nitrophenyldiazonium tetrafluoroborate was added followed by addition of 0.52 g (6.31 mmol) of sodium acetate in two portions. The reaction was allowed to proceed at room temperature overnight and diluted with dichloromethane. The crude product was obtained by washing the organic layer with a saturated solution of NaHCO_3 and water followed by removal of solvent under vacuum. The red residue was purified by silica gel column chromatography using a 1:1 mixture of dichloromethane/ethyl acetate to obtain 1.45 g (90%) of a red product. $^1\text{H NMR}$ (CDCl_3): δ 0.96 (m, 9H), 1.25–1.75 (br, 36H), 2.08 (s, 3H), 3.20–3.41 (br, 12H), 3.94 (m, 6H), 6.59 (d, 6H), 6.75 (d, 6H), 6.98 (d, 6H), 7.84 (m, 12H), 8.28 (d, 6H). $^{13}\text{C NMR}$ (CDCl_3): δ 157.03, 151.65, 147.26, 143.39, 141.76, 129.59, 126.31, 124.62, 122.48, 113.60, 111.25, 67.62, 58.89, 51.14, 50.60, 30.81, 29.49, 29.29, 27.32, 26.81, 26.01, 20.24, 13.88. IR: γ C–H str 3100, 2930, 2870 (m), C=C str 1590 (m), N=O str 1530, 1310 (s), C–C str 1500 (s), C–N str 1360 (s), C–O str 1240, C–H def (s) 1470, 861. Anal. Calcd for $\text{C}_{68}\text{H}_{66}\text{N}_{12}\text{O}_9$: C, 68.33; H, 5.57; N, 14.06. Found: C, 68.21; H, 5.44; N, 13.92.

Chromophore (B): 3-Cyano-2-dicyanomethylidene-4-{*trans-p*-aminostyryl}-5,5-dimethyl-2,5-dihydrofuran (6). In a round-bottom flask fitted with a reflux condenser, *p*-aminobenzaldehyde (1 g, 8.26 mmol) and TCF (compound **4**) (1.93 g, 9.9 mmol) were dissolved in 25 mL of absolute ethanol. NaOH (16.60 mg) was added to this mixture and refluxed for 14 h. The deep violet solution was extracted with dichloromethane from water, and the organic layer was dried with MgSO_4 . The yield of the crude product (**6**) was quantitative and used without further purification in the next step.

Compound **6** (0.5 g, 1.65 mmol) was dissolved in 5 mL of AcOH cooled to 10 °C. Concentrated HCl (0.46 mL) was added and stirred for 15 min. NaNO_2 (0.14 g, 2.02 mmol) dissolved in a minimum amount of water was added dropwise and stirred at room temperature for 30 min. NaPF_6 (0.20 g) was added slowly and stirred for an additional 30 min. The light yellow diazonium salt **7** was filtered from the solution and dried overnight in a vacuum oven at room temperature. $^1\text{H NMR}$ (CD_3CN): δ 1.80 (s, 3H), 7.3 (d, 1H), 7.7 (d, 1H), 8.2 (d, 2H), 8.5 (d, 2H). Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{N}_5\text{O}_6\text{PF}_6$: C, 47.07; H, 2.63; N, 15.24. Found: C, 47.86; H, 2.55; N, 14.82.

Compound **3** (0.23 g, 0.23 mmol) was dissolved in 5 mL of AcOH at room temperature, and 0.34 g (0.76 mmol) of the diazonium salt **7** was added to the above solution. A 0.13 g (1.52 mmol) sample of NaOAc was added in two portions and the mixture stirred overnight. The dark blue solution was extracted with dichloromethane and washed with NaHCO_3 solution and water. The organic layer was dried over

MgSO_4 and the solvent evaporated under vacuum. The crude solid was purified by a silica gel column using a 1:1 mixture of dichloromethane/ethyl acetate as solvent to obtain 0.42 g (93%) of chromophore B as a blue, tacky solid. The analytical sample was treated with an additional excess of diazonium salt and sodium acetate and purified using up to 5% ethyl acetate in dichloromethane as eluant on a silica gel column. $^1\text{H NMR}$ (CDCl_3): δ 0.96 (m, 9H), 1.25–1.75 (br, 36H), 1.87 (s, 18H), 2.08 (s, 3H), 3.20–3.30 (br, 8H), 3.3–3.5 (br, 8H), 3.94 (m, 6H), 6.59 (d, 6H), 6.64 (d, 4H), 6.75 (d, 6H), 6.98 (d, 6H), 7.08 (d, 3H), 7.16 (t, 6H), 7.64 (d, 3H), 7.73 (d, 4H), 7.86 (t, 6H). $^{13}\text{C NMR}$ (CDCl_3): δ 175.11, 173.24, 157.1, 148.24, 146.46, 143.47, 141.71, 133.83, 130.82, 130.06, 129.57, 126.18, 123.18, 115.25, 114.62, 113.62, 111.89, 111.45, 110.86, 110.19, 99.71, 97.46, 67.75, 57.72, 56.50, 50.93, 50.79, 50.60, 31.61, 30.79, 29.42, 29.34, 29.34, 27.36, 27.20, 26.93, 20.33, 13.95. IR: γ C–H str 3100, 2930, 2298 (m), C \equiv N 2220 (s), C=C str 1590 (m), C–C str 1510 (s), C–N str 1360 (s), C–O str 1240, 1180, 1130 C–H def (s), 1470, 834, 745. Anal. Calcd for $\text{C}_{122}\text{H}_{126}\text{N}_{18}\text{O}_6$: C, 75.51; H, 6.54; N, 12.99. Found: C, 75.27; H, 6.48; N, 12.77.

Chromophore C was synthesized by a procedure similar to that for chromophore B.

Synthesis of 3-Cyano-2-dicyanomethylidene-4-{*trans-p*-aminostyryl}-5-methyl-5-(*p*-methoxyphenyl)-2,5-dihydrofuran (8). This compound was synthesized by a procedure similar to that for **4**. Typically 2.0 g (6.86 mmol) of compound **5**, 0.80 g (6.60 mmol) of *p*-aminobenzaldehyde, and 30 mg of NaOH were dissolved in 40 mL of absolute ethanol and refluxed for 24 h. Workup was similar to compound **4** to obtain 1.68 g (65%) of crude product.

The diazonium salt was synthesized by following a procedure similar to that for compound **6** from 1.0 g (2.53 mmol) of **8**, 0.9 mL of concentrated HCl, 0.18 g (2.53 mmol) of NaNO_2 , and 0.42 g (2.49 mmol) of NaPF_6 . This gave 1.01 g (72%) of diazonium salt **9**. $^1\text{H NMR}$ (CD_3CN): δ 1.80 (s, 3H), 7.3 (d, 1H), 7.7 (d, 1H), 8.2 (d, 2H), 8.5 (d, 2H). Anal. Calcd for $\text{C}_{24}\text{H}_{16}\text{N}_5\text{O}_2\text{PF}_6$: C, 52.28; H, 2.92; N, 12.76. Found: C, 53.09; H, 2.89; N, 12.12.

Compound **3** (0.44 g, 0.44 mmol) was dissolved in 10 mL of AcOH at room temperature, and 0.80 g (1.45 mmol) of the diazonium salt **9** was added to the above solution. NaOAc (0.24 g, 2.90 mmol) was added in two portions and the mixture stirred overnight. The dark blue solution was extracted with dichloromethane and washed with saturated NaHCO_3 solution and water. The organic layer was dried over MgSO_4 and the solvent evaporated under vacuum. The crude solid was purified by a silica gel column using a 1:1 mixture of dichloromethane/ethyl acetate as solvent to obtain 0.60 g (62%) of chromophore C as a blue solid. $^1\text{H NMR}$ (CDCl_3): δ 0.96 (m, 9H), 1.25–1.75 (br, 36H), 1.97 (s, 9H), 2.07 (s, 3H), 2.19 (s, 9H), 3.23 (br, 6H), 3.36 (br, 6H), 3.82 (s, 9H), 3.90 (m, 6H), 6.55 (d, 4H), 6.65 (d, 4H), 6.75 (d, 6H), 6.95 (m, 10H), 7.03 (d, 3H), 7.11 (d, 6H), 7.18 (m, 6H), 7.28 (m, 6H), 7.51 (d, 3H), 7.91 (t, 6H). $^{13}\text{C NMR}$ (CDCl_3): δ 182.19, 175.48, 161.19, 157.07, 148.24, 141.68, 139.56, 130.08, 129.56, 129.17, 127.65, 126.71, 126.71, 126.10, 125.45, 123.03, 114.99, 113.61, 111.89, 111.33, 110.81, 110.29, 108.99, 104.71, 101.55, 99.33, 67.74, 58.87, 55.47, 51.02, 50.94, 50.60, 29.31, 26.90, 25.99, 24.55, 22.27, 20.29, 14.40, 13.92. IR: γ C–H str 2950, 2890, 2298 (br), C \equiv N 2230(s), C=C str 1600 (m), C–C str 1510 (s), C–N str 1370 (s), C–O str 1230, 1192, 1130 C–H def (s), 915, 849, 730. Anal. Calcd for $\text{C}_{140}\text{H}_{138}\text{N}_{18}\text{O}_6$: C, 75.86; H, 6.27; N, 11.37. Found: C, 74.59; H, 6.11; N, 10.80.

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