Chem. Mater. **2001,** *13,* 3043−3050

Low V_π Electrooptic Modulators from CLD-1: Chromophore Design and Synthesis, Material Processing, and Characterization

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Received May 9, 2001. Revised Manuscript Received June 20, 2001

A ring-locked, phenyltetraene-based, second-order nonlinear optical chromophore (CLD-1) was synthesized. It shows no drop in decomposition temperature compared to its phenyltriene analogue, while the molecular nonlinearity increases by a factor of 2.25 from 6252×10^{-48} to 14065×10^{-48} esu at 1.9 μm. Thin films and waveguide devices were prepared from CLD-1/PMMA and CLD-1/APC (an amorphous polycarbonate) composites to study its electrooptic (EO) activity, optical loss, and photostability. An average EO coefficient of 92 pm/V at 1.06 μm was achieved in a 25 wt % CLD-1/APC composite. Mach−Zender (MZ) modulators fabricated from CLD-1/APC showed good thermal stability, low optical loss, low modulation voltage, and high extinction ratio. The photochemical stability of the CLD-1/APC modulator can be dramatically improved by operating in an inert gas atmosphere. Evidence shows that the predominant photochemical degradation mechanism of the material in air at 1.55 μm is the reaction between oxygen and photoexcited polyene-based chromophores.

Introduction

Polymeric second-order nonlinear optical (NLO) materials have been intensively studied for more than 15 years due to their promising applications in information processing and fiber communications.[1] For use in practical devices, NLO chromophores, the active components in the NLO polymers, must possess large molecular nonlinearity as well as optical transparency at the telecommunication wavelengths, good processibility, and good thermal and chemical stability.[2] Highly active chromophores are characterized by large dipole moment (μ) and large first hyperpolarizability (β). The attenuation effect[3] of interchromophore electrostatic interaction on poling-induced alignment prevent us from obtaining r_{33} larger than 90 pm/V from a rather strong chromophore, FTC (Figure 1), which was reported earlier, by increasing chromophore loading density.[4] Chromophores with a larger molecular nonlinearity than that of FTC are needed for fabrication of low half-wave voltage (V_π) EO modulators.

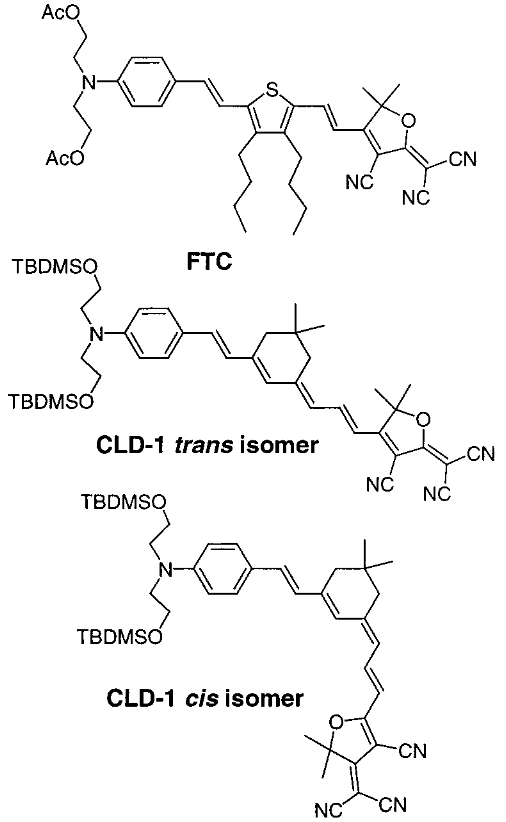

Figure 1. Chemical structures of FTC and CLD-1.

Polyenes have been widely adopted as the conjugate units in chromophore structures in place of aromatic

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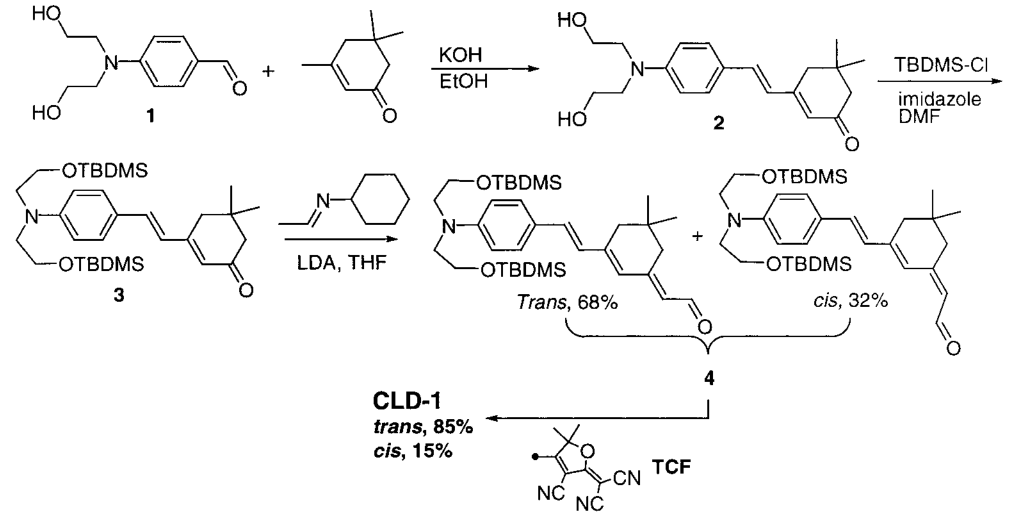
Scheme 1. Synthetic Scheme for CLD-1



rings to increase the $\mu\beta$ values of the chromophores,[5] and ring-locking of the polyenes is generally required to enhance the thermal stability of polyene-based chromophores.[6] Traditionally, the syntheses of ring-locked phenylpolyene chromophores involve the coupling of enones or aminophenylenones with acceptors.[6a−c] Due to the poor Knoevenagel reactivity of enones, only very reactive acceptors such as malononitrile and isoxazolone can be effectively coupled. In this article, we describe an efficient method to elongate the aminophenyldienone to obtain an aminophenyltrienal donor-bridge to circumvent the low-reactivity problem. The trienal is coupled with currently the best electron acceptor, TCF (tricyano-derivatized furan; 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran),[4,7] to form a aminophenyltetraene-bridge chromophore, CLD-1 (Figure 1). Structurally, the conjugate backbone of CLD-1 is obtained by substituting the thiophene unit in FTC with a diene. Such substitution is expected to have a dramatic enhancement of the $\mu\beta$ value based on the data of Marder et al. and Jen et al.[5d,8] Furthermore, the same level of optical transparency is expected for CLD-1 materials because the substitution does not red-shift the chromophore charge-transfer absorption.[5d,8]

TCF-based chromophores typically have a dipole moment of around 14 D because all the cyano groups pull electrons in approximately the same direction. Highly polar chromophores generally have poor solubility due to strong interchromophore electrostatic interaction. CLD-1 is designed with two bulky *tert*-butyldimethylsilyl (TBDMS) groups and is expected to have good solubility for use in guest−host systems.[3b] We report our investigation on the device-critical properties of CLD-1 composite materials, including their thermal stability, optical loss, electrical poling, and EO properties, and demonstrate that the common problems of guest−host systems, such as low loading density, chromophore phase separation, and poor solvent resistance, can be solved or avoided by optimizing the film spin-coating process and by using a novel waveguide fabrication technique.

Results and Discussions

Synthesis and Characterization. The ring-locked aminophenyltrienal donor-bridge was synthesized in four steps starting from *p*-*N*,*N*-bis(2-hydroxyethyl)-aminobenzaldehyde (**1**; Scheme 1).[9] Knoevenagel reaction of **1** and isophorone afforded the aminophenyldienone **2** in 42% yield. The hydroxyl groups of **2** were protected with TBDMS to facilitate the subsequent reaction and product purification and to increase the solubility of the final chromophore. The conjugate extension of the TBDMS-protected aminophenyldienone **3** to aminophenyltrienal **4** is the most critical step. We have previously reported a three-step procedure to extend the dienone to the trienal: conversion of the enone **3** to a tertiary alcohol using MgMeI, dehydration of the alcohol to an aminophenyltetraene, and formylation of the tetraene.[7b,10] The overall yield of the three steps is only $\sim$7%. A similar method was used to synthesize a ring-locked aminophenyldienal.[6e] In the

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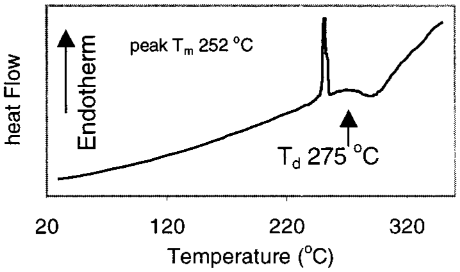

Figure 2. DSC curve of CLD-1.

new method reported here, the extension is effected in 41−70% yield by one-pot reaction of the enone **3** and *N*-cyclohexylacetimine/lithium diisopropylamide (LDA). The product **4** was a mixture of all-trans (68%) and trans−trans−trans−cis (32%) isomers, as shown in Scheme 1. The trans and cis isomers are distinguished by the ^{1}H NMR shift of the aldehydic proton, which is more to the low field for the cis isomer than for the trans isomer, since the trans conjugate linkage allows more efficient electron transfer from the amino group to the aldehyde group. The two isomers have slightly different retention times on a silica gel TLC plate. The difference is normally enough to allow for separation using a long silica gel column. However, we were not able to get any separation of the two isomers. Apparently, the trans−cis isomerization happened on the silica gel (Aldrich 28,-862-4) on a time scale of about 10 h. Since isomerization also happens in the subsequent Knoevenagel coupling of **4** and TCF, separation of two isomers is not very meaningful.

The donor-bridge **4** is very reactive to common acceptors such as malononitrile, isoxazolone, thiobabituric acid, and the Sandoz acceptor [3-(dicyanomethylidene)-2,3-dihydrobenzothiophen-2-ylidene-1,1-dioxide].[5a] In this paper we only discuss the most valuable chromophore CLD-1 derived from **4**. CLD-1 was obtained in 33% yield from the Knoevenagel reaction of **4** and TCF. Like its precursor **4**, ^{1}H NMR of CLD-1 in $CDCl_3$ showed that CLD-1 is also a mixture of trans and cis isomers. Interestingly, we found the percentage of trans isomer increased from 68% in **4** to 85% in CLD-1 and did not change from batch to batch. Compared to the aldehyde group in **4**, TCF is a much stronger electron acceptor, which favors the trans isomer even more, presumably due to the increased energy difference between the trans and cis isomers. The two isomers cannot be separated by chromatography, because they have no observable difference in retention time, or by crystallization. Therefore, an isomeric mixture of CLD-1 was used in the following studies. A differential scanning calorimetry (DSC) curve of CLD-1 (Figure 2) indicates an onset decomposition temperature (T_d) of 275 °C and a peak melting temperature (T_m) of 252 °C in N_2. The T_m agrees very well with the melting point of 249.5−251.4 °C measured in capillary tubes on a Mel-Temp II melting point apparatus. CLD-1 is soluble in common solvents, especially chlorinated solvents, thus allowing for a high-level doping in host polymers.

CLD-1 charge-transfer absorption peak wavelengths are 632 nm in dioxane, 648 nm in THF, and 692 nm in chloroform. The large solvatochromism is an indication of its large second-order nonlinearity. Its $\mu\beta$ value is 14065×10^{-48}esu in THF at 1.907 μm, determined by the electrical field-induced second-harmonic generation (EFISH) method using d_{11} of quartz = 0.4 pm/V as reference.[11] On the basis of the studies of Marder and Jen on polyene-based and thiophene-based chromophores,[5d,8] CLD-1 should have a $\mu\beta$ value much higher than its thiophene-based analogue FTC. The apparently higher $\mu\beta$ value of FTC (17600×10^{-48} esu at 1.9 μm)[4a,b] reported previously was determined indirectly in the following way: A β value of 2058×10^{-30} esu at 1.064 μm was obtained for FTC by hyper-Rayleigh scattering (HRS) in chloroform.[12] The β value was then extrapolated using the two-level model to obtain 1352×10^{-30} esu at 1.9 μm, which was multiplied with the AM1-calculated dipole moment (13 D) to obtain $17\,600 \times 10^{-48}$ esu. It has been pointed out that a great discrepancy exists between the HRS measurement at 1.06 μm and the EFISH measurement at 1.9 μm, due to the significant two-photo absorption induced fluorescence (TPF) at 1.06 μm and the inadequacy of the two-state model, both of which tend to give exaggerated results.[13]

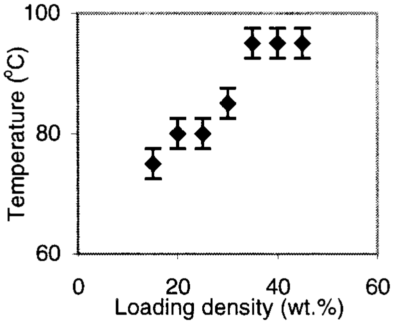

Figure 3. Optimal poling temperatures of CLD-1/PMMA material at different loading densities.

Material Processing and Device Fabrication. Electrooptic Study of CLD-1/PMMA Composite. CLD-1 was studied in PMMA (T_g 104 °C) composite thin films to get the relationship between the EO coefficient and loading density and to determine the optimal poling temperature. Selection of solvent is critical to the film quality of guest−host materials. CLD-1 is more soluble in chlorinated solvents than in ketones and DMF. Several chlorinated solvents were tested, including 1,2-dichloroethane (bp 83 °C), 1,2-dichloropropane (95 °C), 1,3-dichloropropane (120 °C), and 1,2,3-trichloropropane (156 °C). 1,2-Dichloroethane was chosen as the solvent because its low boiling point ensures fast solvent evaporation (typically in ~10 s), which is necessary for reducing the degree of chromophore phase separation but can hardly be avoided when high-boiling-point solvents are used. Films of loading densities ranging from 15 to 45 wt % were prepared and poled using a corona poling stage at various temperatures to determine the optimal poling temperatures for each loading level. We found that the optimal poling temperature (T_{opt}) increased with the loading density of the chromophore. As shown in Figure 3, the T_{opt} was 75 °C for 15 wt % film and became 95 °C when the loading density

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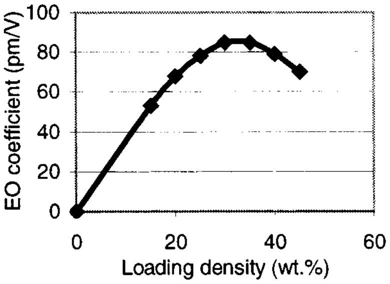

Figure 4. EO coefficient of poled CLD-1/PMMA as a function of loading density.

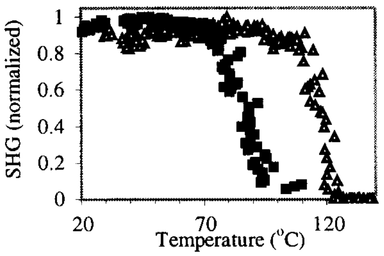

Figure 5. Dynamic thermal stability of poled CLD-1/PMMA (solid square) and CLD-1/PC (triangle) films.

was increased to 45 wt %. This phenomenon indicates that doping of a highly polar chromophore can increase lattice hardness of a soft polymer such as PMMA. EO coefficients of poled CLD-1/PMMA films are plotted in Figure 4 as a function of loading density. From the curve, the optimal loading density is determined to be 3.0×10^{-20} cm^{-3} or 32 wt % loading level. After passing the maximum point, the r_{33} dropped much faster than for weaker chromophores such as DR-19. This is in agreement with theoretic prediction for high $\mu\beta$ chromophores based on chromophore electrostatic interactions.[3]

Guest−Host Material for Device Fabrications: EO Coefficient, Optical Loss, and Thermal Stability. CLD-1/PMMA was able to give an r_{33} of 85 pm/V, but when it was incorporated in thermoset polyurethane, only 55 pm/V was obtained, even after alkyl derivatization to solve a solubility problem.[7b,d] To realize the highest EO coefficient from CLD chromophores, we focused on the guest−host approach to reduce the V_π of the polymeric EO modulator. We have shown that the 30 wt % CLD-1/PMMA material gave a V_π value as low as 0.8 V and an optical loss as low as 0.8 dB/cm at 1.31 μm.[14] However, its dynamic thermal stability of poling induced alignment was only 75 °C (see Figure 5). To solve the thermal stability problem, various high T_g polymers were tested to find one that possesses good compatibility with CLD-1, high thermal stability, and low optical loss. An Aldrich polycarbonate poly(bisphenol A carbonate-*co*-4,4′-(3,3,5-trimethylcyclohexylidene)-diphenol) (denoted APC) was chosen for detailed study due to its low crystallization tendency,[15] good solubility in halogenated solvents, and fairly high glass transition temperature (T_g = 202 °C from an Aldrich catalog). High quality thin films of CLD-1/APC are even more difficult to obtain than those of CLD-1/PMMA due to the formation of ripples on the surface during spin-coating of its dichloroethane solution. Ripples can be avoided by stopping the spin before the surface of the solution dries up. Therefore, we typically limit the spin time to just 2 s. Although higher-boiling-point solvents are easier to handle, low optical loss is not guaranteed due to phase separation, which is different from time to time. A 10 wt/v% solution of CLD-1 is usually used to spin films of 2−3 mm thickness at spin rates of 800−1100 rpm. The photothermal deflection spectrum (PDS)[16] and UV−vis absorption spectrum of 30 wt % CLD-1/polycarbonate thin film are shown in Figure 6. The PDS measures the absorption coefficient in the polymer thin film as a function of wavelength. It is very useful to identifying the mechanisms causing any possible high absorption at a wavelength of interest, such as 1.31 or 1.55 μm. There are two major absorption features in the spectrum, the C−H vibrational overtones at low energies,[17] with transmission windows near 1.55 and 1.31 μm, and the main absorption peak centered at 667 nm. Normally the absorption at 1.31 μm is lower than the absorption at 1.55 μm, but in the 30 wt % CLD1/APC film the absorption is higher at 1.31 μm than at 1.55 μm. This indicates that charge-transfer absorption of CLD-1 (667 nm in APC film) already contributes significantly to the optical loss at 1.31 μm. We also measured the light propagation loss of a TM mode laser in unpoled slab waveguides using the immersion technique[18] and obtained a smaller loss (1.0 dB/cm) at 1.31 μm and a larger loss (1.2 dB/cm) at 1.55 μm (see Figure 7). The discrepancy between the two methods is caused by the birefringence of the material, which has a higher TE mode refractive index (n_{TE}) in unpoled film (e.g., 1.635 at 1.06 μm for TE and 1.625 for TM by the attenuated total reflection method). The higher n_{TE} indicates that the chromophore is preferentially oriented in plane with the surface of the film. Such an orientation gave weaker absorption to the TM mode light used in the slab waveguide loss measurement than the absorption of the probe light in the PDS measurement in which the electrical field of the probe light is in plane with the film surface. When the film was corona poled, the induced alignment of the chromophore caused a significant increase in refractive index of TM light from 1.625

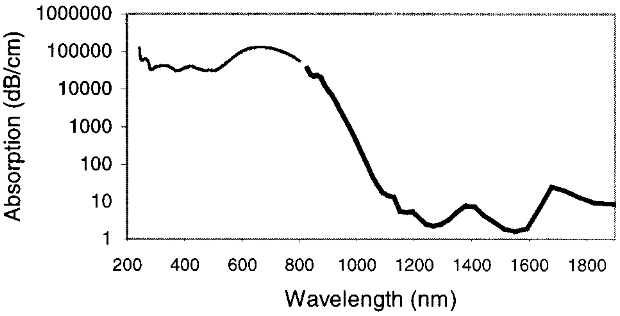

Figure 6. Photothermal deflection spectrum (PDS) and UV−vis absorption spectrum of 30 wt % CLD-1/APC thin film. Solid line, PDS; thin solid line, UV−vis.

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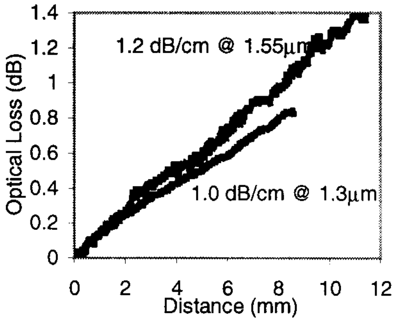

Figure 7. Optical loss of unpoled 25 wt % CLD-1/APC thin film at 1.33 and 1.5 μm by the immersion technique.

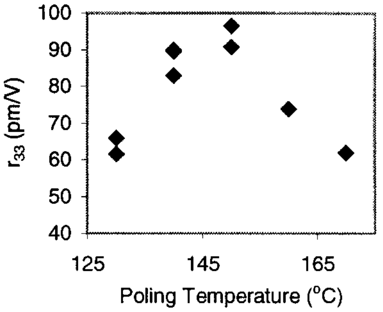

Figure 8. Electrooptic coefficients of 25 wt % CLD-1/APC films poled at different temperatures.

to 1.655 and a drop in refractive index of TE mode light from 1.637 to 1.626 at 1.06 μm. The chromophore alignment along the poling field direction led to an increase of TM mode optical loss at 1.31 μm to a level even slightly higher than the loss at 1.55 μm (see the next section).

The DSC scan of 25 wt % CLD-1/APC film, which was peeled off from silicon substrate, failed to show a glass transition, presumably due to the highly amorphous nature of the composite. The optimal poling temperature of 25 wt % CLD-1/APC was determined to be 150 °C by measuring the r_{33} of the films (Figure 8) poled under 8 kV corona discharge voltage for 30 min at different temperatures. The higher poling temperature of CLD-1/APC compared with that of CLD-1/PMMA did not cause any drop in r_{33} value, and a typical EO coefficient of 92 pm/V was routinely obtained. The dynamic thermal stability (Figure 5), measured by the second-harmonic generation (SHG)/ramping temperature method, was 40 °C higher than for the corresponding PMMA material.

EO Modulator Fabrication. We have demonstrated a low V_π of 0.8 V and a half-wave voltage-interaction length product of 2.2 V cm at 1.31 μm in optical push–pull electrooptic modulators made from 30% CLD-1/PMMA material.[14] These modulators had high propagation loss of light (which was mainly from the waveguide fabrication[14b]) and low thermal stability. Recently, we focused on 25 wt % CLD-1/APC material for better thermal stability and optical loss in addition to the low V_π. Like most guest–host materials, the CLD-1/APC material was difficult to process using the standard lithography, because the film could be dissolved easily during the photoresist coating. To protect the CLD-1/APC core layer from the attack of the photoresist, we coated an additional thin layer of UV-curable polymer UV-15 (from Masterbond Co.) on top of the core layer using methanol as solvent (methanol is a nonsolvent for APC and CLD-1). Figure 9 shows the fabrication steps of the CLD-1/APC polymer waveguide.[19] After coating with a UV-15 lower cladding layer and a CLD-1/APC core layer, the film was corona-poled at 150 °C for 30 min with 8 kV poling voltage. A dilute UV-15/methanol solution was then coated to make a thin protection layer of 0.6 μm thickness. The waveguide lines were patterned on the protection layer with photoresist AZ5214 (from Clariant International Ltd.) using standard photolithography. The UV-15 protection layer was etched by O_2 plasma to make a rib structure of 0.5-μm height. The photoresist was removed by a developer. Finally, the waveguide pattern in UV-15 layer was translated into the CLD-1/APC core layer by etching the whole area. Another UV-curable acrylic polymer, UFC-170 (from URAY Co., Korea), which does not attack the CLD-1/APC layer, was spin-coated and UV-cured to form the upper cladding layer.

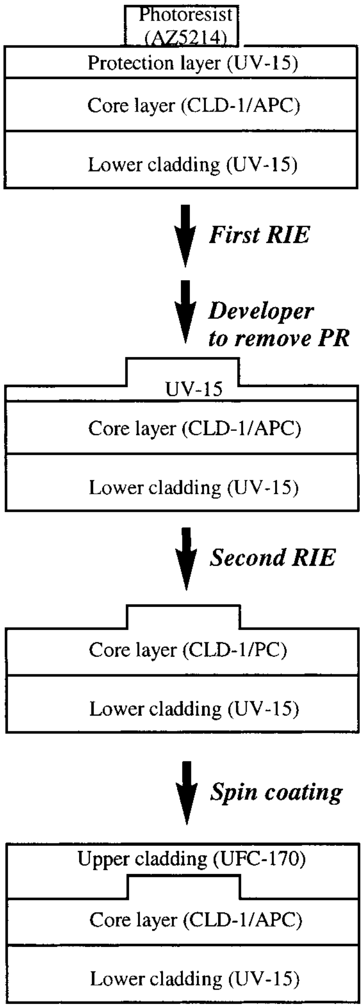

Figure 9. Two-step RIE of CLD-1/APC polymer waveguide fabrication with UV-15 thin protection layer.

The final device had a total length of 3 cm, a modulation length of 2 cm, and an overall thickness of 9.0 μm, including the core thickness of 2.4 μm. The V_π was measured to be 2.4 V at 1.31 μm, which is equivalent to the result reported earlier on the 3-cm

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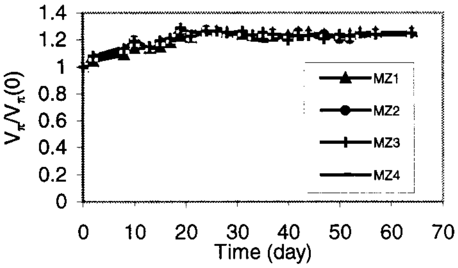

Figure 10. Long-term thermal stability of CLD-1/APC modulator at 60 °C in air. Four Mach−Zender modulators (MZ1−4) were tested.

push−pull CLD-1/PMMA modulators that were electrode-poled.[14] The V_π at 1.55 μm is 3.7 V and the extinction ratio was as high as 26 dB. The total insertion losses were 10 dB for both 1.31 and 1.55 μm, including the fiber coupling loss of 5 dB due to the significant mode mismatch. So the light propagation loss in CLD-1/APC waveguide was roughly 1.7 dB/cm for both 1.31 and 1.55 μm. The guided mode was 90% confined in the core layer; therefore, cladding layers also contribute a few tenths of dB/cm to the propagation loss. Both UV-15 and UFC-170 have higher optical loss at 1.55 μm than at 1.31 μm (UV-15, 4.2 dB/cm at 1.55 μm versus 1−2 dB/cm at 1.31 μm; UFC-170, 3.0 dB/cm at 1.55 μm versus 0.53 dB/cm at 1.31 μm). Therefore, the optical loss of CLD-1/APC material itself at 1.31 μm is estimated to be 1.4 dB/cm, slightly higher than the material-absorption-induced optical loss at 1.55 μm, which was estimated to be 1.3 dB/cm. After electrical poling, the loss at 1.31 μm increased from 1.0 dB/cm (see Figure 7) to 1.4 dB/cm. The reason for the higher loss of poled material at 1.31 μm was due to poling-enhanced chromophore absorption, as discussed earlier.

Thermal and Photostability of CLD-1/APC EO Modulator. To study the long-term thermal stability of chromophore alignment, a modulator chip was baked on a thermocouple-controlled 60 °C hot plate in air for 65 days. The hot plate was covered with a dish to maintain temperature uniformity across the surface. The V_π of the modulator was measured every 2−4 days, and the result is plotted in Figure 10. After a 25% increase in the first 20 days, V_π remained unchanged in the following 45 days. The photostability of the CLD-1/APC Mach−Zender (MZ) modulators have also been examined at the operation wavelength of 1.55 μm under the TM mode. The input fiber was butt-coupled to the MZ input end with a coupling loss of 3 dB. The output light of the modulator was collected by a lens that gives ~1 dB optical loss. First, one modulator was operated in air with a 10 mW output of the input fiber. The optical transmission was monitored for 73 h, and the result is shown in Figure 11. The transmission dropped very fast and only one-third of the initial output power was left after 24 h of operation. The loss of transmission was found due to the loss of TM mode confinement, which was caused by the photochemical degradation of CLD-1. We noticed that the channel waveguide still had good confinement on the TE mode light, which means that the TM refractive index of the core layer decreased faster than the TE refractive index. We will discuss in the next paragraph that illumination of a 1.55 μm laser does not cause relaxation of the CLD-1 dipole alignment. Therefore, the only explanation for the loss of the TM mode confinement is that the CLD-1 molecules aligned in the TM direction were bleached selectively. The selective bleaching behavior suggests that the photochemical reaction during device operation in air under 1.55 μm laser involves only or mostly CLD-1 molecules that have been excited via linear and/or nonlinear absorption of light.

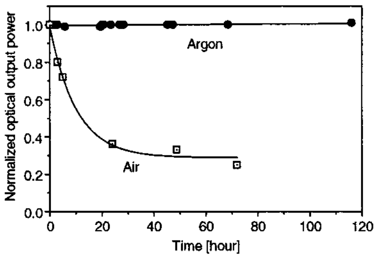

Figure 11. Photostability of the electrically poled CLD-1/APC ridge waveguide in air and in argon. (10 mW input, 1.55 μm)

In polymer host, reactions between multiple chromophores are rather unlikely at sub-T_g temperatures, due to very limited chromophore mobility. The fast photochemical reaction very likely involves oxygen. Similar observations have been reported for polymers containing lower $\mu\beta$ short chromophores.[20] To improve the photostability of the CLD-1/APC modulator, we sealed one device in argon and operated it at the same wavelength under TM mode for 116 h. Output power of 10 mW from the input fiber was again butt-coupled to the modulator. The output power of the modulator was monitored, and the result is shown in Figure 11. We were surprised to see that the transmission was very stable during the operation. It was also noticed that the V_π remained essentially unchanged during the operation, which indicates that chromophore excitation did not lead to chromophore bleaching or relaxation of poling-induced dipole alignment. This encouraging result proves that the predominant mechanism for device failure in air is the photoinduced oxidation of the polyene-based chromophore, and the photostability can be improved dramatically by excluding oxygen from the device environment.

Conclusions

An efficient method to extend ring-locked aminophenylpolyenone to aminophenylpolyenal has been developed. The resulting new donor-bridge leads to the synthesis of a highly active second-order nonlinear optical chromophore, CLD-1. The phenyltetraene chromophore shows no thermal stability decrease compared to its phenyltriene analog,[6e] while the molecular nonlinearity increases by a factor of 2.25 from 6252 × 10^{-48} esu to 14065 × 10^{-48} esu at 1.9 μm. CLD-1 has a fairly high decomposition temperature of 275 °C. Optical-quality films of CLD-1 composites are obtained by judicial selection of solvent and by optimization of spin-coating parameters. The intrinsic loss of CLD-1/APC is 1.2 dB/cm at 1.55 μm as measured in thin-film slab

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waveguides. An average electrooptic coefficient of 92 pm/V was achieved in corona-poled CLD-1/APC films. Chromophore alignment-induced loss is reported for the first time at a wavelength of 1.31 μm. CLD-1 charge-transfer absorption has already contributed significantly to optical loss. This finding implies that chromophores with λ_{max} values longer than that of CLD-1 (693 nm in chloroform) will not be very useful for 1.3 μm optical waveguide applications. A V_π of 0.8 V has been demonstrated in an EO modulator made from CLD-1/PMMA material. MZ modulators with 2.4-μm 25 wt % CLD-1/APC core and 2-cm long modulation electrodes show a long-term stability at ~45−50 °C, optical loss of 1.7 dB/cm, low modulation voltage of 3.7 V, and an extinction ratio of 26 at 1.55 μm. The photochemical stability of CLD-1/APC can be dramatically improved by removing oxygen from the device environment. Covalent incorporation of CLD chromophores into various low-loss polymer systems are under way to further increase long-term thermal stability and to reduce optical loss of CLD-based EO materials.

Experimental Section

General Methods of Material Characterization. All chemicals were purchased from Aldrich and were used as received. All reactions were carried out under argon. ^{1}H NMR and ^{13}C NMR were taken on a Bruker-250 FT NMR spectrometer, and tetramethylsilane was added to all NMR solvents as internal standard. UV−vis spectra were obtained from a Perkin-Elmer Lambda-4C UV/vis spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Inc. Thermal analyses were performed in N_2 on a Perkin-Elmer DSC-7 at a heating rate of 10 °C/min. Melting points were determined in capillary tubes on a Mel-Temp II melting point apparatus unless otherwise indicated. Melting points were not corrected.

3-[*p*-*N*,*N*-Bis(2-hydroxyethyl)aminostyryl]-5,5-dimethylcyclohex-2-enone (2). A solution of *p*-*N*,*N*-bis(2-hydroxyethyl)aminobenzaldehyde (**1**, 158 g, 0.755 mol), isophorone (125.4 g, 0.907 mol), potassium hydroxide (48 g), and water (50 mL) in 1.4 L of ethanol was stirred at room temperature for 137 h. After neutralization with acetic acid, the mixture was condensed under reduced pressure. The residue was extracted with hot ethyl acetate (EtOAc) three times (150 mL × 3). The combined EtOAc extract was condensed. The product precipitated out as orange yellow crystals (95% pure by ^{1}H NMR) to yield 110 g (42%). The product was used in the next step without further purification. ^{1}H NMR (DMSO-d_6): δ 7.42 (d, 8.41 Hz, 2H), 7.04 (d, 15.86 Hz, 1H), 6.83 (d, 15.84 Hz, 1H), 6.70 (d, 8.78 Hz, 2H), 5.94 (s, 1H), 4.82 (t, 5.46 Hz, 2H), 3.51 (m, 8H), 2.46 (s, 2H), 2.19 (s, 2H), 1.01 (s, 6H) ppm. ^{13}C NMR (DMSO-d_6): δ 180.17, 137.64, 130.46, 117.40, 110.56, 105.58, 105.40, 104.60, 92.99, 39.78, 34.80, 32.55, 19.78, 14.53, 9.67 ppm.

3-[*p*-*N*,*N*-Bis(2-tert-butyldimethylsiloxyethyl)aminostyryl]-5,5-dimethylcyclohex-2-enone (3). A mixture of **2** (28.0 g, 85.0 mmol), imidazole (29.6 g, 0.435 mol), *tert*-butyldimethylsilyl chloride (32.8 g, 0.217 mol), and DMF (65 mL) was stirred at 50 °C for 10 h. The resulting mixture was poured into water in a separation funnel and was extracted with hexane (200 mL × 2). The combined hexane extract was washed with water four times (200 mL × 4) to completely remove DMF and imidazole. The hexane extract was then dried over $MgSO_4$ and condensed via rotary evaporation. The crude product was purified by silica gel chromatography using 1/7 EtOAc/hexane as eluent to produce 45 g (95%) of yellow solid. Recrystallization from hexane gave yellow needles (mp 106.5−108 °C). ^{1}H NMR (CDCl$_3$): δ 7.35 (d, 8.97 Hz, 2H), 6.93 (d, 16.08 Hz, 1H), 6.71 (d, 16.08 Hz, 1H), 6.68 (d, 8.97 Hz, 2H), 6.00 (s, 1H), 3.77 (t, 6.29 Hz, 4H), 3.55 (t, 6.29 Hz, 4H), 2. 46 (s, 2H), 2.29 (s, 2H), 1.10 (s, 6H), 0.89 (s, 18H), 0.03 (s, 12H) ppm. ^{13}C NMR (CDCl$_3$): δ 199.99, 155.90, 148.75, 135.52, 128.88, 124.95, 124.49, 123.68, 111.67, 60.24, 53.49, 51.43, 39.07, 33.27, 28.56, 25.90, 18.24, −5.37 ppm. Anal. Calcd for $C_{32}H_{55}N_1O_3Si_2$: C, 68.88; H, 9.94; N, 2.51. Found: C, 69.04; H, 9.92; N, 2.48.

3-{3-[*p*-*N*,*N*-Bis(2-tert-butyldimethylsiloxyethyl)aminostyryl]-5,5-dimethylcyclohex-2-enylidene}-2-butenal (4). A solution of *N*-cyclohexylacetimine (110 mmol, 13.77 g) in 35 mL of THF was added to 77 mL of 1.5 M LDA/cyclohexane at −50 °C. After the addition, the mixture was warmed with an ice bath and then recooled to −78 °C. A solution of 61.35 g of the ketone **3** in 105 mL of THF was added. The mixture was then warmed in air and then acidified with dilute acetic acid solution and stirred at room temperature for 11 h. The resulting mixture was poured into water in a separation funnel and was extracted with hexane (200 mL × 2). The combined hexane extract was washed with water (200 mL × 2) and then with saturated $NaHCO_3$ solution (100 mL). The hexane extract was then dried over $MgSO_4$ and condensed via rotary evaporation. The crude product was purified by column chromatography using 1/10 EtOAc/hexane as eluent to give 26.56 g (41.6%) of pure product. ^{1}H NMR (CDCl$_3$) shows that the product is a mixture of trans and cis isomers. The two aldehydic proton doublets are well-separated: 10.04 ppm/J = 8.2 Hz, cis 10.12 ppm/J = 7.9 Hz. The peak at 10.04 ppm is assigned to the trans isomers because the trans linkage is a more efficient electron bridge and therefore facilitates charge transfer from the amino donor and makes the aldehydic proton a little more electron-rich. On the basis of their integration areas, the trans isomer is estimated to be 68% and the cis isomer 32%. All of the trans isomer ^{1}H NMR peaks can be identified: δ 10.04 (d, 8.2 Hz, 1H), 7.32 (d, 8.85 Hz, 2H), 6.73 (s, 2H), 6.66 (d, 8.90 Hz, 2H), 6.26 (s, 1H), 5.90 (d, 8.6 Hz, 1H), 3.77 (t, 6.17 Hz, 4H), 3.54 (t, 6.17 Hz, 4H), 2.67 (s, 2H), 2.34 (s, 2H), 1.05 (s, 6H), 0.89 (s, 18), 0.03 (s, 12H) ppm. ^{1}H NMR (CDCl$_3$) of cis isomer (32%): δ 10.12 (d, 7.78 Hz, 1H), 7.33 (d, 9.11 Hz, 2H), 7.18 (s, 1H), 6.76 (s, 2H), 6.66 (d, 8.90 Hz, 2), 5.70 (d, 8.03 Hz, 1H), 3.77 (t, 6.17 Hz, 4H), 3.54 (t, 6.17 Hz, 4H), 2.34 (s, 2H), 2.27 (s, 2H), 1.02 (s, 6H), 0.89 (s, 18 H), 0.03 (s, 12H) ppm. The cis isomer peaks cannot be fully identified due to their lower intensity and overlap with the trans isomer peaks. Anal. Calcd for $C_{34}H_{57}N_1O_3Si_2$: C, 69.93; H, 9.84; N, 2.40. Found: C, 69.64; H, 9.83; N, 2.45.

CLD-1 [3-Cyano-2-dicyanomethylidene-4-{*trans*,*trans*,*trans*-[3-(2-(*p*-*N*,*N*-bis(2-*tert*-butyldimethylsiloxyethyl)aminophenyl)vinyl)cyclohex-2-enylidene]-1-propenyl}-5,5-dimethyl-2,5-dihydrofuran]. A mixture of **4** (1.174 g, 2.01 mmol), 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF, 0.4 g, 2.01 mmol), triethylamine (40 mg, 0.4 mmol), and chloroform (5 mL) was refluxed for 12 h. Flash chromatography (1/1, ethyl acetate/hexane) and recrystallization from hexane/ethyl acetate gave 0.514 g (33%) of green needles: mp 249.5−251.4 °C. The NMR signal of the proton on the middle carbon between the cyclohexene ring and the acceptor ring is a double-doublet, due to its coupling with two neighboring protons. ^{1}H NMR (CDCl$_3$) of the product shows two well-separated sets of double-doublets, indicating that the product is a mixture of trans and cis isomers. The peak at 8.02 ppm with J_1 = 12.6 Hz, J_2 = 14.7 Hz is assigned to the trans isomer, and the one at 8.28 ppm with J_1 = 11.9 Hz, J_2 = 14.7 Hz is assigned to the cis isomer on the basis of the same judgment used for the donor-bridge **4**. On the basis of the integration areas of two double-doublets, the trans isomer is estimated to be 85% and the cis isomer 15%. ^{1}H NMR peaks of the trans isomer are identified: δ 8.02 (q, J_1 = 12.6 Hz, J_2 = 14.7 Hz, 1H), 7.37 (d, 8.99 Hz, 2H), 6.81 (m, 4H), 6.38 (s, 1H), 6.34 (d, 12.6 Hz, 1H), 6.26 (d, 14.7 Hz, 1H), 3.77 (t, 5.93 Hz, 4H), 3.57 (t, 5.93 Hz, 4H), 2.42 (s, 2H), 2.40 (s, 2H), 1.69 (s, 6H), 1.05 (s, 6H), 0.88 (s, 18H), 0.02 (s, 12H) ppm. ^{1}H NMR The cis isomer peaks cannot be fully identified due to their lower intensity. Anal. Calcd for $C_{45}H_{64}N_4O_3Si_2$: C, 70.63; H, 8.43; N, 7.32. Found: C, 70.66; H, 8.53; N, 7.36.

Guest−Host Materials. A mixture of CLD-1 and host polymer (PMMA or polycarbonate) was dissolved in 1,2-dichloroethane. The solution was spin-coated onto different substrates at 340−1200 rpm to obtain films of 1.7−2.6 μm thickness. Indium−tin-oxide (ITO)-coated glass substrates were used for EO coefficient measurement, where ITO served as the ground electrode. SiO_2-coated silicon wafers were used for optical loss measurement, where a low-loss SiO_2 layer serves to isolate the optical mode from the glossy silicon substrate. UV curable polymer coated SiO_2/silicon wafers were used for waveguide/EO modulator fabrication. Films were dried in a vacuum oven at room temperature overnight.

Optical and Electrooptical Characterization. The $\mu\beta$ value of CLD-1 was measured in THF at 1.9 μm using the EFISH technique and the d_{11} of quartz = 0.4 pm/V was used as reference.[11] Photothermal deflection spectroscopy and UV−vis of CLD-1/APC film were performed at Sandia National Laboratories. Optical losses of CLD-1/PMMA and CLD-1/APC films were measured using the immersion technique at the wavelengths of 1.31 and 1.55 μm.[18] Corona poling was employed to induce chromophore dipole alignment.[21] Dynamic thermal stability of poling-induced EO activity was measured in the SHG setup at a temperature ramping rate of 10 °C/min.[21] EO coefficient and refractive index measurements were performed on the ATR setup described earlier.[22] Procedures of CLD-1/APC EO modulator fabrication and testing have been described in a previous publication.[19]

Acknowledgment. This work was funded by the Air Force Office of Scientific Research and by the National Science Foundation. We gratefully acknowledge I. Liakatas, C. Cai, Ch. Bosshard, and P. Günter of the Swiss Federal Institute of Technology for the EFISH measurement and Timothy Van Eck, Doris Leung, Angie Moss, and Susan Ermer of Lockheed Martin Missiles & Space for the PDS data.

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