Phenyltetraene-Based Nonlinear Optical Chromophores with Enhanced Chemical Stability and Electrooptic Activity

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"Push-pull" phenyltetraene-based chromophores are too sensitive to be incorporated into Diels-Alder-type cross-linkable polymers due to the reactivity of its diene segment with maleimides. A facile synthetic route has been explored to incorporate a methoxy group into the R position of such chromophores, which reduces their diene reactivity during the poling and lattice hardening process. The poled polymers with one of such chromophores doped in a cross-linked polymer lattice showed ultrahigh electro-optic activities, up to 306 pm/V at 1310 nm.

Recently, the research of organic and polymeric electro-optic (EO) materials has made tremendous progress. EO coefficients (r_{33} values) of greater than 300 pm/V have been demonstrated through controlled molecular self-assembly and lattice hardening.¹ These material properties have been further translated into very low half-wave voltage (V_{π}) in Mach–Zehnder and phase modulators.² In addition to their applications in photonic devices, organic EO materials offer great potential for integrating with nanotechnologies for new generation of photonic systems with much smaller size and lower power consumption.³

To achieve ultrahigh EO activity, one of the key components in these newly developed organic EO materials is the conjugated (4-dialkylamino)phenyltetraene bridge with terminal substitueted CF_3 -TCF acceptors.⁴ This is a primary class of high- $\mu\beta$ chromophores with certain degree of synthetic efficacy. For general uses, it is very critical to improve chemical stability and maintain all-trans conformation of these phenyltetraene-based chromophores to optimize their nonlinear optical (NLO) properties.⁵

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As an example, we have recently developed a new scheme to synthesize 2-alkyl-isophorone-embeded phenyltetraene chromophores (**AJL24**-type, Chart 1).⁶ The alkylation sterically rigidified the polyenic bridge to ensure its all-trans conformation, and the end of the alkyl groups can be further

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R = H, AJL6-type; R = Alkyl, AJL24-type

 a The carbon atoms were labeled from C_{a} to C_{h} along the methine skeleton.

functionalized with dendrons to provide shape modification. In a guest—host polymer containing one such chromophore, a very large r_{33} value of 262 pm/V at 1.31 μ m has been demonstrated. However, this approach has its own design challenges. In an attempt to incorporate this type of chromophores into Diels—Alder (DA) cross-linkable polymers for better temporal stability, we observed a considerable decrease in EO activities.^{1a,6} Spectroscopic studies on these new systems revealed that these chromophores tend to react with dienophiles such as maleimides through cycloaddition, which lead to decomposition of chromophores and interference of DA lattice hardening.⁷

In general, diene can only react with dienophile in its s-cis conformation through the overlapped p-orbital.⁸ The above result revealed that a relatively high diene reactivity exist in these all-trans phenyltetraene-based compounds. This is not unusual since the s-trans conformers could rotate through their σ -bonds easily to form the s-cis conformers. In order to tackle this problem, it is essential to understand the conformational rigidity of the methine skeletons, and know how it can be adjusted by the substitution at the \mathbf{R} position. In this regard, we have introduced a methoxy group to the **R** position of typical phenyltetraene π -conjugates to make a new type of polyene chromophores. The methoxy group can be viewed as a good electron donor through its resonance structure, however, it also can be viewed as an inductive acceptor when compared to the H and sp³-C substituents at the **R** position of AJL6- and AJL24-type chromophores, respectively. Therefore, the methoxy group may create asymmetry of electron density and introduce energy perturbation to the rotational barrier of the polyene chains. This could be used to tune the physical properties of chromophores in an exquisite way which may not be easily achievable by steric modification. Here, we report the synthesis of this type of chromophores, and its chemical stability and EO property in poled polymers during DA lattice hardening.

As shown in Scheme 1, 4-bromoisophorone 1 could be converted to 2-methoxyisophorone 2 in quantitative yield by treating with excess amount of sodium methoxide through the allylic rearrangement.⁹ To the same reaction pot, dialkyl-

Scheme 1. Synthesis of the Methoxy-Substituted Phenyltetraene Chromophore AJL34



aminobenzaldehyde **3** was added and condensed with **2** after refluxing overnight to form the methoxy-substituted aminophenyldienone **4**. Then two hydroxyl groups on the donorend of **4** were protected by *tert*-butyldimethylsilyl group to afford compound **5**. The dienone **5** could be converted to the key intermediate, trienal **7**, in good yield by a three-step route in the sequence of nucleophilic addition, dehydration, and reduction. This route has been previously explored to synthesize the alkylated tienal analogues.⁶ Finally, compound **8**, a strong CF₃-TCF-type acceptor, was condensed with **7** to afford compound **AJL34** as a new phenyltetraene-based chromophore with the methoxy group substituted at the **R** position.

The chromophore **AJL34** was obtained as a highly amorphous organic solid with its glass transition temperature around 70 °C. It is soluble in common solvents such as methylene chloride, acetone, THF, hexane, and methanol. However, **AJLS102** and **YLD124** (Chart 2), which are





similar **AJL6**-type chromophores without the methoxy modification, are highly crystalline and could not be dissolved in hexane or methanol. These comparisons indicate

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that the modification of methoxy group on **AJL34** can prevent close packing of molecules, which in turn, may attenuate the strong dipole–dipole electrostatic interactions bewteen chromophores to improve poling efficiency of EO polymers.

The UV-vis-NIR absorption spectra of AJL34 are essentially the same as those for AJLS102 and YLD124 in organic solvents or in polymeric thin films. The λ_{max} of the $\pi - \pi^*$ charge-transfer bands all have similar absorption wavelengths. With the same donor/acceptor pair, AJL34 showed a slightly greater solvatochromic shift than that of YLD124. These linear absorption data suggest that the addition of methoxy group to the **R** position does not interfere the efficient charge-transfer property of phenyltetraene-based chromophores.

To study the poling and EO property of AJL34 in guesthost polymers, amorphous polycarbonate (APC) is selected as the host since it is commonly used in the literature, and the chromophore loading is 25 wt %. This standardized formulation has been also applied to another efficient chromophore, AJLS102, for the fabrication of low V_{π} and low optical loss EO modulators.¹⁰ By following the typical poling protocols for guest-host EO polymers,^{10,11} a relatively large r_{33} value of 137 pm/V was obtained at 1310 nm for AJL34/APC at a poling electric field of 1.0 MV/cm. This represents a 30% improvement over that obtained for AJLS102/APC. As we discussed earlier, this could be attributed to the reduced intermolecular electrostatic interactions by substituting the methoxy group on AJL34. Furthermore, the film of AJL34/APC poled at 163 °C (1.25 MV/ cm) has shown an r_{33} value of 166 pm/V at 1310 nm. The poled sample was isothermally annealed at 85 °C to study its temporal alignment stability. Under such testing conditions, 90% of its original r_{33} value could be retained over 500 h. With both large EO activity and good temporal stability, we believe that AJL34/APC EO polymer can be used as an excellent material candidate for device exploration.

Another critical study is to examine the reactivity of diene backbone on the AJL34 chromophore in the presence of maleimide dienophile. The accelerated testing was conducted as follows: To a small glass vial was added a few milligrams of recrystallized N-phenylmaleimide (NPM) and a polyene chromophore with the molar ratio of 25:1 together with methylene chloride as the solvent. After the mixture was completely dissolved, most of the solvent was evaporated, and the vial was put on top of a hot plate with its temperature set ~ 100 °C. A melt mixture was obtained, in which the polyene dye was dispersed homogeneously into a mixture with excessive NPM dienophile. The mixture was then annealed on top of the hot plate, and its composition change vs annealing time was analyzed by thin layer chromatography (TLC). This protocol is very convenient and only uses minimal amount of reagents. We have applied this testing

protocol to three phenyltetraene-based chromophores, namely AJL24, AJL28, and AJL34, respectively. After the samples were annealed for 1 h, both AJL24 and AJL28 chromophores were almost totally decomposed, while less than 20% decomposition was observed for AJL34. This result suggests significant difference in their diene reactivity toward NPM. Its reactivity can be ranked by the following order, AJL6-type \approx AJL24-type \gg AJL34.

The dienic reactivity of chromophores was further evaluated using the typical processing procedures for EO polymers. AJL28 and AJL34 were mixed with a maleimidecontaining copolymer $(\mathbf{PMI})^7$ in 1,1,2-trichloroethane. The resultant solutions were filtered, spin-coated onto glass substrates, and baked overnight at 50 °C in vacuum oven to afford thin films of AJL28/PMI and AJL34/PMI, respectively. After cured at 130 °C for 30 min, the intensity of the absorption spectra of AJL28/PMI decreased significantly $(\sim 35\%)$, which corresponds reasonably well with the percentage of dye decomposition. However, AJL34/PMI showed much improved stability under the same curing condition, with the intensity of its chromophoric absorption only dropped by 2%. This head-to-head comparison clearly showed that the diene reactivity of AJL34 chromophore was significantly reduced toward maleimido dienophiles.

Our previous analysis indicated that the chemical sensitivity of **AJL28** is mainly due to the butadiene segment next to the terminal of its strong dialkyaminophenyl donor. This diene structure has been labeled as the skeleton from C_a to C_d in Chart 1. The cycloaddition between such a inner-outerring diene and maleimido dienophile is determined by the rotational energy barrier (ΔE , Scheme 2) of the σ -bond



inbetween C_b and C_c (hereafter C_b-C_c). Although the s-trans conformation is energetically favored for these polyenic chromophores, the population distribution of different conformers still exists and follows the Boltzmann's law.^{8,12} At elevated temperatures, the equilibrium can be shifted to the formation of meta-stable s-cis conformers such as the one with respect to C_b-C_c . In the presence of dienophiles, this shift is irreversibly driven by DA cycloaddition and further amplified by severe decomposition of chromophores.

The reduced reactivity of diene segment on AJL34 indicates that the methoxy group does not significantly

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increase the electron density on diene through the electronic effect that is nomally observed in linear conjugated polyenes.⁸ Rather, the methoxy group acts as a polar substitution in the middle of the highly polarized phenyltetraene bridges with reduced bond order alternation (BOA).¹³

We have also observed that the two vinylic protons, H_b and H_f , have shown substantial long-range deshielding effect in their ¹H NMR spectra. In this series of methoxylated compounds, these two protons have all shown downfield shift around 0.4–0.5 ppm relative to those of nonsubstituted analogues (Table 1). Such a deshielding effect is due to the

Table 1.	Chemical Shift of Protons ^a H _b and H _f from the ¹ H
NMR Data	a of Methoxy-Substituted Molecules in CCDl ₃

	$\delta_{\mathrm{H}_{b}{}^{b}}\left(\mathrm{ppm} ight)$	$\delta_{\mathrm{H}_{\!f}}{}^b(\mathrm{ppm})$
dienone 5	7.28(+0.55)	
trienenitrile 6	7.14(+0.44)	5.50(+0.44)
trienal 7	7.24 (+0.48)	6.33(+0.46)
chromophore AJL34	7.27 (+0.49)	6.75(+0.38)

^{*a*} The H_b and H_f represent the vinylic protons attached to the C_b and C_f, respectively (Figure 1). ^b The values in parentheses are the shifted values relative to those from their analogues without the methoxy substitution, respectively; a positive value denotes a downfield shift.

fact that these two protons are in close vicinity with the polar methoxy group (Figure 1).¹⁴ While the real nature of such a



Figure 1. Illustration of the deshielding effect of the polar oxygen function on protons (H_b and H_f) in its vicinity.

deshielding effect is not yet well understood, the intramolecular interaction between these H and O atoms, probably the van der Waals interaction, could account for it. By using the MOPAC 7.0 (AM1) program in Chem3D Ultra package to perform a simple calculation of molecular conformation, the distance between H_b (or H_f) and the oxygen atoms was found to be around 2.37 to 2.42 Å, which is shorter than the sum of van der Waals radii of H and O atoms (2.72 Å). We suspect that such an interaction may rigidify the all-*trans* π -electron bridge of **AJL34** and elevate the rotational energy barrier (ΔE) of C_b-C_c, thereby reducing the diene reactivity of the chromophore.^{8,15}

Finally, poling and E-O properties of AJL34 in DA crosslinkable polymers were studied. The host polymer used is poly(methyl methacrylate-co-anthracen-9-ylmethyl methacrylate) (PMMA-AMA), in which the anthraceyl pendant groups can be thermally cross-linked with 1,6-bismaleimidohexane (BMI) through the DA cycloaddition reactions. By following the similar procedure used for AJ309,^{1a,2} 40 wt % of AJL34 was formulated into the mixture of PMMA-AMA/BMI. Thin films were poled and thermally cured at around 108 °C under a poling field of 1.12 MV/cm. An ultralarge r_{33} value of 306 pm/V can be achieved,¹¹ which represents a 25% improvement over that of AJ309 with the same loading of a AJL6-type chromophore. This result, again, is a great demonstration of the advantages offered by the methoxy substitution, which improves the poling efficiency and chemical stability of highly nonlinear phenyltetraene-based chromophores.

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Supporting Information Available: Experimental procedures and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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