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Facile Synthesis of Highly Efficient Phenyltetraene-Based Nonlinear Optical Chromophores for Electrooptics

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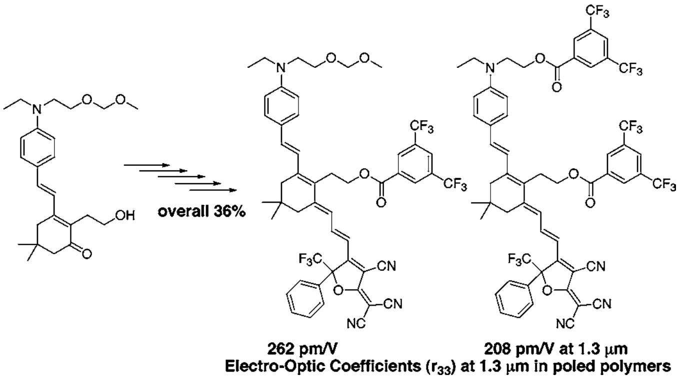
ABSTRACT



A facile synthetic route has been developed to convert an electron-rich, sterically hindered dialkylaminodienone into a conjugated dialkylaminotrienal with good yield. The derived dialkylaminotetraene-type nonlinear optical chromophores possess an all-trans conformation and can be functionalized with fluoro-dendron to provide proper shape modification for poling. Polymers doped with two examples of these chromophores in high concentrations have been poled to afford ultra-large electrooptic coefficients (r_{33}) of 208 and 262 pm/V, respectively, at the measuring wavelength of 1.31 μm.

Integrated optical devices based on organic nonlinear optical (NLO) polymers have emerged as one of the enabling elements for a new generation of optical telecommunications, which needs fast modulation and switching of optical signals at the speed of 100 Gbit/s or above to accommodate anticipated growth in data traffic.[1] The macroscopic NLO response of such materials arises from the poling-induced polar order of noncentrosymmetric NLO chromophores in polymers.[2] The dipolar NLO chromophores used in poled polymers are generally represented as D-π-A, where D is an electron donor, A is an electron acceptor, and π is a conjugating bridge connecting the D and A moieties. In such molecules, the donor and acceptor substituents provide the requisite ground-state charge asymmetry, whereas the π-conjugation bridge provides a pathway for the ultrafast redistribution of electric charges under an applied external electric field.

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(1) (a) Kim, S. K.; Hung, Y. C.; Seo, B.-J.; Geary, K.; Yuan, W.; Bortnik, B.; Fetterman, H. R.; Wang, C.; Steier, W. H.; Zhang, C. *Appl. Phys. Lett.* **2005**, *87*, 061112/1−061112/3. (b) Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science* **2000**, *288*, 119. (c) Song, H.-C.; Oh, M.-C.; Ahn, S.-W.; Steier, W. H.; Fetterman, H. R.; Zhang, C. *Appl. Phys. Lett.* **2003**, *82*, 4432. (d) Ahn, S.-W.; Steier, W. H.; Kuo, Y.-H.; Oh, M.-C.; Lee, H.-J.; Zhang, C.; Fetterman, H. R. *Opt. Lett.* **2002**, *27*, 2109. (e) Lee, M.; Katz, H. E.; Erben, C.; Gill, D. M.; Gopalan, P.; Heber, J. D.; McGee, D. J. *Science* **2002**, *298*, 1401.

(2) (a) *Molecular Nonlinear Optics: Materials, Physics and Devices*; Zyss, J., Ed.; Academic Press: New York, 1994. (b) *Advanced Functional Molecules and Polymers*; Nalwa, H. S., Ed.; Gordon and Breach Science Publishers: Los Angeles, 2001. (c) Marder, S. R.; Kippelen, B.; Jen, A. K-Y.; Peyghambarian, N. *Nature* **1997**, *388*, 845. (d) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155.

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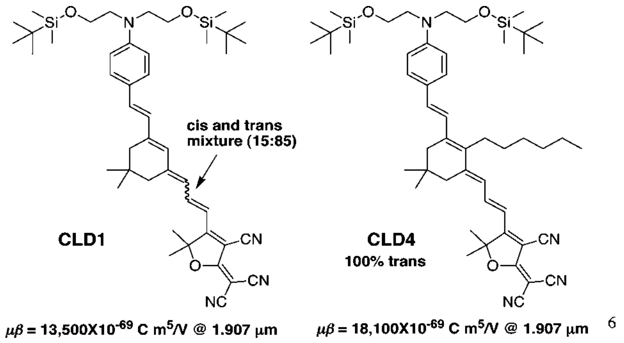
The polyene systems, with few or no aromatic rings, are the most effective π-conjugated bridges for achieving large molecular first hyperpolarizabilities (β).[3] The conformation of all-trans polyene bridges can be preserved by incorporating part or all of their methine skeletons into single or fused aliphatic rings.[4] This approach has been employed by numerous groups to effectively improve both thermal and photochemical stability of polyene-based chromophores without compromising their NLO properties. Typical examples are the ring-locked phenyltetraene-based "push−pull" compounds, known as the CLD type of chromophores (Chart 1).[5] The ring-locked structure of these compounds is based on an isophorone-derived six-membered ring to furnish the central core of D-π-A chromophores and to provide a nearly coplanar conjugation and prolate pseudo-ellipsoidal shape. To prevent close packing of such extended dipolar structures and improve their solubility, bulky *tert*-butyldimethylsilyl (TBDMS) groups and asymmetric substituents have been used to functionalize on either the donor or the acceptor end of the chromophores. As a result of these shape modifications, relatively high electrooptic (EO) coefficients (r_{33} around 40−70 pm/V measured at the wavelengths of 1.3 and 1.55 μm) have been achieved from poled polymeric composites using these polyenic chromophores as dopants.

Chart 1. Typical Examples of Alkylaminophenyltetraene-Based NLO Chromophores



Recently, the results of using a Monte Carlo simulation[6] and nanoscale tailoring of the size, shape, or conformation of NLO polymers and dendrimers[7] all show that the ideal shape of chromophores is spherical. For example, in a newly developed efficient side-chain dendronized polymer, the center of the phenylthiophene stilbene bridge can be functionalized with a dendron, through the process of Diels−Alder "click chemistry", to provide better site isolation for poling.[8] As a result, very large r_{33} values (up to 110 pm/V at 1.31 μm) can be achieved.

To improve the performance of these organic NLO materials further, the most efficient polyenic dyes are ideal because of their large nonlinearities. However, several parameters concerning synthesis and control of the molecular shape of these chromophores should be addressed before they can be applied for general use. A majority of the double bonds on the polyene chain, except the one embedded in the isophorone ring structure, are often kept as unlocked to avoid twisting of the conjugating backbone and to provide synthetic convenience. Accordingly, the dialkylaminophenyltrienal intermediates and the obtained CLD-type chromophores are often a mixture of trans and cis isomers. Attempts to purify these isomers through column chromatography for higher NLO activity are proven to be very difficult. In the best case reported, CLD-4, an all-trans *n*-hexyl-substituted analogue of CLD-1, can only be synthesized with an overall yield of <1% because of the low reactivity of the hexylated enones and aminophenylenone intermediates.[5d]

To solve this problem, we have developed a facile synthetic route to generate all-trans dialkylaminophenyltetraene chromophores. Both sides of the π-conjugated bridge of these chromophores can be protected through an isophorone ring and a fluoro-dendron. A very strong acceptor, 2-(3-cyano-4-methyl-5-phenyl-5-trifluoromethyl-5*H*-furan-2-ylidene)-malononitrile (CF_3−TCF), can also be functionalized on these bridges to significantly enhance the molecular nonlinearity of these chromophores.[9] The poled guest−host or cross-linked polymers using these chromophores showed exceptionally high r_{33} values (208 and 262 pm/V) at 1.31 μm.

To obtain the target aminophenyltrienal donor bridges (compound **6**), the main challenge is to improve the reactivity of the quite inert enones (such as compound **2** in Scheme 1) and aminophenylenones (compound **3**) which have an alkyl group substituted on the isophorone ring. We found that sodium ethoxide is quite effective in improving the Knoev-

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[3] (a) Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhoej, J. *Science* **1994**, *263*, 511. (b) Marder, S. R.; Perry, J. W.; Bourhill, G.; Gorman, C. B.; Tiemann, B. G.; Mansour, K. *Science* **1993**, *261*, 186.

[4] (a) Ermer, S.; Lovejoy, S. M.; Leung, D. S.; Warren, H.; Moylan, C. R.; Twieg, R. J. *Chem. Mater.* **1997**, *9*, 1437. (b) Staub, K.; Levina, G. A.; Barlow, S.; Kowalczyk, T. C.; Lackritz, H. S.; Barzoukas, M.; Fort, A.; Marder, S. R. *J. Mater. Chem.* **2003**, *13*, 825. (c) Shu, C.-F.; Tsai, W.-J.; Jen, A. K-Y. *Tetrahedron Lett.* **1996**, *37*, 7055.

[5] (a) Zhang, C.; Dalton, L. R.; Oh, M.-C.; Zhang, H.; Steier, W. H. *Chem. Mater.* **2001**, *13*, 3043. (b) Zhang, C.; Ren, A. S.; Wang, F.; Zhu, J.; Dalton, L. R.; Woodford, J. N.; Wang, C. H. *Chem. Mater.* **1999**, *11*, 1966. (c) Liakatas, I.; Cai, C.; Bosch, M.; Jager, M.; Bosshard, Ch.; Gunter, P.; Zhang, C.; Dalton, L. R. *Appl. Phys. Lett.* **2000**, *76*, 1368. (d) Zhang, C.; Wang, C.; Dalton, L. R.; Zhang, H.; Steier, W. H. *Macromolecules* **2001**, *34*, 235. (e) He, M.; Leslie, T.; Garner, S.; DeRosa, M.; Cites, J. *J. Phys. Chem. B* **2004**, *108*, 8731. (f) He, M.; Leslie, T. M.; Sinicropi, J. A.; Garner, S. M.; Reed, L. D. *Chem. Mater.* **2002**, *14*, 4669.

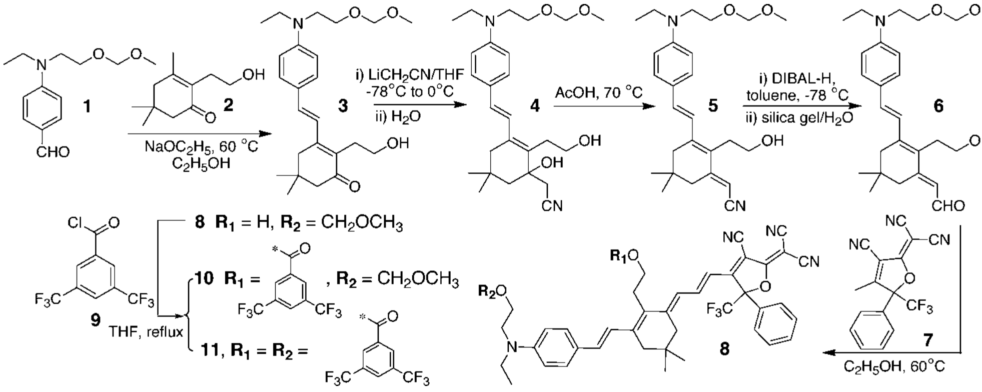
[6] (a) Robinson, B. H.; Dalton, L. R. *J. Phys. Chem. A* **2000**, *104*, 4785. (b) Dalton, L. R.; Steier, W. H.; Robinson, B. H.; Zhang, C.; Ren, A.; Garner, S.; Chen, A.; Londergan, T.; Irwin, L.; Carlson, B.; Fifield, L.; Phelan, G.; Kincaid, C.; Amend, J.; Jen, A. K-Y. *J. Mater. Chem.* **1999**, *9*, 19.

[7] (a) Ma, H.; Liu, S.; Luo, J.; Suresh, S.; Liu, L.; Kang, S. H.; Haller, M.; Sassa, T.; Dalton, L. R.; Jen, A. K-Y. *Adv. Funct. Mater.* **2002**, *12*, 565. (b) Luo, J.; Liu, S.; Haller, M.; Lu, L.; Ma, H.; Jen, A. K-Y. *Adv. Mater.* **2002**, *14*, 1763. (c) Luo, J.; Haller, M.; Li, H.; Tang, H. Z.; Jen, A. K-Y.; Jakka, K.; Chou, C. H.; Shu, C. F. *Macromolecules* **2004**, *37*, 248. (d) Luo, J.; Ma, H.; Haller, M.; Jen, A. K-Y.; Barto, R. R. *Chem. Commun.* **2002**, 888. (e) Ma, H.; Chen, B.; Sassa, T.; Dalton, L. R.; Jen, A. K-Y. *J. Am. Chem. Soc.* **2001**, *123*, 986. (f) Luo, J.; Haller, M.; Li, H.; Kim, T.-D.; Jen, A. K-Y. *Adv. Mater.* **2003**, *15*, 1635. (g) Luo, J.; Haller, M.; Ma, H.; Liu, S.; Kim, T.-D.; Tian, Y.; Chen, B.; Jang, S.-H.; Dalton, L. R.; Jen, A. K-Y. *J. Phys. Chem. B* **2004**, *108*, 8523.

[8] Kang, J.-W.; Kim, T.-D.; Luo, J.; Haller, M.; Jen, A. K-Y. *Appl. Phys. Lett.* **2005**, *87*, 071109/1−071109/3.

[9] Liu, S.; Haller, M. A.; Ma, H.; Dalton, L. R.; Jang, S.-H.; Jen, A. K-Y. *Adv. Mater.* **2003**, *15*, 603.

Scheme 1. Synthesis of All-Trans Dendronized Alkylaminophenyltetraene-Type NLO Chromophores **10** and **11**.



enagel condensation between dialkylaminobenzaldehyde **1** and 2-hydroxylethyl-substituted isophorone **2**. The yield of these reactions increased from 10−15% to ∼50% simply by replacing the commonly used potassium hydroxide or potassium *tert*-butoxide with sodium ethoxide,[4,5] possibly because of its proper combination of strong basicity and less steric hindrance. Three different pathways have been explored to extend the conjugation of aminophenyldienone **3** to aminophenyltrienal **6**. In the literature, the one-pot reaction to extend the alkyl-substituted enone to form the extended conjugated aldehyde using *N*-*tert*-butylacetimine/lithium diisopropylamide (LDA) as base has been reported to give only 12% yield because of the steric hindrance of the alkyl group.[5d] Another alternative route is to use the trienenitrile synthon in a Hornor−Emmons reaction sequence. Compound **3** is reacted first with the anion of diisopropyl cyanomethylphosphonate to, if applicable, generate the intermediate of aminophenyltrienenitrile, which can be reduced by DIBAL-H to afford the aminophenyltrienal bridge.[10] In the past, we have employed this efficient two-step synthetic scheme to synthesize extended aldehydes for donor-substituted conjugating bridges. However, this approach is difficult to apply to dienone **3** or its *tert*-butyldimethylsilyl-protected analogues because of their steric congestion or low reactivity toward the Hornor−Emmons reaction conditions.

Because lithioacetonitrile is a less bulky nucleophile compared to the anions generated from *N*-*tert*-butylacetimine or diisopropyl cyanomethylphosphonate,[11] it can be reacted with dienone **3** easily to produce the carbinol **4** in quantitative yield. After dehydration, the newly formed nitrile synthon **5** can be reduced with DIBAL-H to form the donor-substituted bridge aldehyde **6**. The total yield from **4** to **6** is 60%.

Trienenitrile **5**, trienal **6**, and the derived tetraene chromophores (**8**, **10**, and **11**) possess all-trans conformation, as shown in the ^{1}H NMR spectra (Figure 1). Compound **7**, one of the strongest acceptors, was condensed with the donor-substituted bridge **6** to afford chromophore **8** with a hydroxyl group. It should be noted that the conjugated skeleton of such a highly polarizable polyenic chromophore is very prone to the attack of nucleophiles such as pyridine or triethylamine. To functionalize the all-trans chromophores **10** and **11** with a dendron to modify their shape, a one-pot esterification was carried out in refluxing tetrahydrofuran (THF) with an excess amount of acid chloride **9**. Because no base catalysts are involved, the solution mixture remains acidic. It can in situ cleave the methoxymethyl (MOM) protecting group and generate the second hydroxyl group at the donor end of the chromophores to afford the didendronized product **11**. This procedure avoids the side reactions that often occur to cause chromophore decomposition during the typical reaction of MOM cleavage.[7b,g] The chromophores **10** and **11** can be obtained in excellent yield after being purified through flash chromatography. The relative ratio

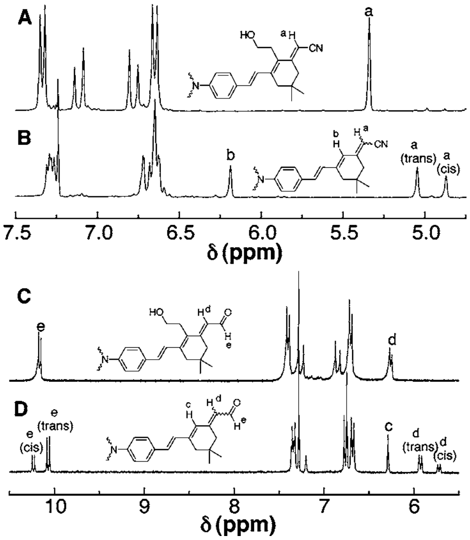


Figure 1. ^{1}H NMR spectra of all-trans trienenitrile **5** (**A**) and trienal **6** (**C**), in comparison with cis- and trans-isomer mixtures of isophorone-unsubstituted analogues **B** and **D**, respectively.

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(10) (a) Wada, A.; Fujioka, N.; Tanaka, Y.; Ito, M. *J. Org. Chem*. **2000**, *65*, 2438. (b) Durantini, E. N. *Synth. Commun.* **1999**, *29*, 4201.

(11) Guthrie, R. W.; Kaplan, G. L.; Mennona, F. A.; Tilley, J. W.; Kierstead, R. W.; Mullin, J. G.; LeMahieu, R. A.; Zawoiski, S.; O'Donnell, M.; Crowley, H.; Yaremko, B.; Weltont, A. F. *J. Med. Chem.* **1989**, *32*, 1820.

between **10** and **11** can be controlled easily by reaction time and monitored by thin-layer chromatography (TLC).

To study the EO property of polymers using these chromophores as dopant, 47 wt % of **10** was formulated into poly(methyl methacrylate) (PMMA) using 1,1,2-trichloroethane as solvent. The solution of this polymer (7 wt % concentration) was filtered through a 0.2-μm PTFE-syringe filter and spin-coated onto an indium tin oxide (ITO) glass substrate. The resulting films were baked in a vacuum oven at 60 °C overnight to ensure the removal of any residual solvent. Then, a thin layer of gold was sputtered onto the films as a top electrode for contact poling. The r_{33} values were measured using the Teng−Man simple reflection technique at the wavelength of 1.31 μm.[12] The ITO glass substrates were also examined at the near-infrared (NIR) wavelength of 1.31 μm to ensure their optical transparency (over 85% transmission). After we calibrated the poling results with a standardized AJL8/APC EO polymer,[13] the measurement accuracy of r_{33} values at 1.31 μm was very consistent with the results measured from other transparent electrodes such as ZnO or In_2O_3.[14]

The films of **10**/PMMA were poled at 90 °C with a DC electric field of 0.80 MV/cm. After cooling to room temperature and removing the electric field, the poled films showed an exceptionally large EO coefficient ($r_{33} = 262$ pm/V at 1.31 μm). This value is exceptionally large compared to those reported (70−110 pm/V at 1.31 μm) for guest−host EO polymers containing polyene-type chromophores.[15] Such a great increase is attributed to the purity and structural features of chromophore **10**. Its all-trans conformation could provide a better conjugation and increase the $\beta\mu$ value of the chromophores significantly.[5c] In addition, the central polyene bridge is spatially isolated by both the isophorone ring and the center-anchored perfluoro aromatic dendron. This spatial arrangement also greatly increases the solubility of **10** resulting in a higher number density of chromophores that can be incorporated into the polymer matrix. The dendron also provides effective site isolation to decrease the strong electrostatic interactions among chromophores.

Poling and EO properties of the double-dendron-functionalized chromophore **11** were also studied. The host polymer used was poly(methyl methacrylate-*co*-anthracen-9-ylmethyl methacrylate) (PMMA-AMA), in which the anthracenyl pendant groups can be thermally cross-linked with tris(2-maleimidoethyl)amine (TMI) through the Diels−Alder cycloaddition reactions.[16] By following the similar procedure used for **10**/PMMA, 45 wt % of **11** was formulated into the mixture of PMMA-AMA/TMI. The thin films were poled and cured at around 105 °C under a poling field of 90 V/μm. Again, a very large r_{33} value of 208 pm/V can be achieved. Through efficient lattice hardening by using the Diels−Alder reaction, over 70% of the original EO activity can be retained at 85 °C for several hundred hours.

In summary, we have developed a facile route to synthesize all-trans dendronized dialkylaminotetraene-based NLO chromophores in good overall yields. This new design provides an efficient way to modify the shape of high $\beta\mu$ extended polyenic chromophores. Two exemplary chromophores (**10** and **11**) were incorporated in polymers with high concentrations and efficiently poled to generate exceptionally large r_{33} values of 208 and 262 pm/V at 1.31 μm with good temporal stability.

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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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[12] Teng, C. C.; Man, H. T. *Appl. Phys. Lett.* **1990**, *56*, 1734−1736.

[13] (a) Paloczi, G. T.; Huang, Y.; Yariv, A.; Luo, J.; Jen, A. K-Y. *Appl. Phys. Lett*. **2004**, *85*, 1662. (b) Xu, G.; Liu, Z.; Ma, J.; Liu, B.; Ho, S.-T.; Wang, L.; Zhu, P.; Marks, T. J.; Luo, J.; Jen, A. K-Y. *Opt. Express* **2005**, *13*, 7380. (c) Sinyukov, A. M.; Leahy, M. R.; Hayden, L.; Haller, M.; Luo, J.; Jen, A. K-Y.; Dalton, L. R. *Appl. Phys. Lett.* **2004**, *85*, 5827.

[14] (a) Michelotti, F.; Belardini, A.; Larciprete, M. C.; Bertolotti, M.; Rousseau, A.; Ratsimihety, A.; Schoer, G.; Mueller, J. *Appl. Phys. Lett.* **2003**, *83*, 4477. (b) Michelotti, F.; Nicolao, G.; Tesi, F.; Bertolotti, M. *Chem. Phys.* **1999**, *245*, 311−326. (c) Wang, L.; Yang, Y.; Marks, T. J.; Liu, Z.; Ho, S.-T. *Appl. Phys. Lett*. **2005**, *87*, 161107/1−161107/3.

[15] Jen, A.; Luo, J.; Kim, T.-D.; Chen, B.; Jang, S.-H.; Kang, J.-W.; Tucker, N. M.; Hau, S.; Tian, Y.; Ka, J.-W.; Haller, M.; Liao, Y.; Robinson, Br.; Dalton, L.; Herman, W. Linear and Nonlinear Optics of Organic Materials V. *Proceedings of SPIE-The International Society for Optical Engineering*, 2005, *5935*, 49.

[16] (a) Haller, M.; Luo, J.; Li, H.; Kim, T.-D.; Liao, Y.; Robinson, B. H.; Dalton, L. R.; Jen, A. K-Y. *Macromolecules* **2004**, *37*, 688. (b) Luo, J.; Haller, M.; Li, H.; Kim, T.-D.; Jen, A. K-Y. *Adv. Mater.* **2003**, *15*, 1635.