

Synthesis and Characterization of Dendritic Nonlinear Optical Chromophore Containing Phenylene Attached with Bulky Alkyl Group

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Abstract: Star-shaped, nonlinear optical (NLO) material was synthesized and its optical, thermal, and electro-optic properties were investigated. Three NLO-active dipolar chromophores containing a phenylene ring substituted with a bulky alkyl chain as a conjugation bridge were chemically bonded to the core of 1,1,1-tris(4-hydroxyphenyl)ethane to form a dendritic architecture. The chemical structure and purity of the chromophore were verified by NMR spectroscopy. The chromophore exhibited a broad absorption band centered at around 608 nm tailing up to 760 nm in toluene solution and also showed a discernible solvatochromic shift in more polar solvent. The chloroform solution of the dendrimer produced an absorption band with a red-shifted maximum as large as 28 nm when compared to that of the toluene solution. It was thermally stable up to 275 °C in a nitrogen atmosphere and had a glass transition temperature of 76 °C. In a preliminary result, the polymer film containing the dendritic compound exhibited a shift of 19 pm/V taken at 1.55 μ .

Keywords: nonlinear optical chromophore, electro-optic, dendrimer, thermal stability.

Introduction

For the practical electro-optic (EO) devices, organic materials need to simultaneously optimize critical requirements such as large EO coefficient, high stability (thermal, chemical, photochemical, and mechanical), and low optical loss.¹⁻⁸ In the past decades a large number of highly active nonlinear optical (NLO) chromophores have been synthesized and some of these exhibited very large macroscopic optical nonlinearities in the poled polymers.^{9,10} To maintain a stable dipole alignment, it is a common practice to utilize either high glass-transition temperature (T_g) polymers attached with NLO chromophores as side chains or cross-linkable polymers with NLO chromophores that could be locked in the polymer network.^{11,12} However, it is difficult to achieve both large macroscopic nonlinearities and good dipole alignment stability. This is mainly due to strong intermolecular electrostatic interactions among high dipole moment chromophores and high-temperature aromatic-containing polymers, such as polyimides and polyquinolines that tend to form aggregates.

The large void-containing dendritic structures may provide an attractive solution to this critical issue because the dendrons can effectively decrease the interactions among chromophores due to the steric effect.¹³⁻¹⁷ Furthermore, these materials are mono-disperse, well defined, and easily purified

when compared to polymers that are made by the conventional synthetic approaches.

In this work, we report on a NLO material adopting dendritic architecture in which three branches of the NLO-active component were linked with the core. The NLO-active component contains a phenylene ring substituted with a bulky alkyl chain as a conjugation bridge. The NLO dendrimer was successfully synthesized and verified by NMR spectroscopy, thermal instruments and absorption spectroscopy. Optically quality thin films were prepared by spincoating a solution of the dendrimer and a polymer host. Macroscopic optical nonlinearities were also evaluated by a simple reflection method. A preliminary study showed as large as 19 pm/V electro-optic coefficient for the poled film.

Experimental

Materials. *N*-Methyl-*N*-(2-hydroxyethyl)-4-aminobenzaldehyde, methanesulfonyl chloride, methylhydroquinone, 2-ethylhexylbromide, triethylphosphite, sodium hydride (95%), *n*-butyllithium (2.5 M solution in hexane), and piperidine were purchased from Aldrich and used as received. Poly[bisphenol A carbonate-*co*-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol] (APC) was purchased from Aldrich and purified by reprecipitating the polymers in methanol. All solvents used in this work were freshly purified by a suitable distillation method. Diethyl-[2,5-bis(2-ethylhexyloxy)-4-bromophenyl]

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methylphosphonate (compound **3**) and 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) were prepared according to the literature.^{18,19}

Synthesis of NLO Compound with Dendritic Structure.

Synthesis of Methanesulfonic acid 2-[(4-formyl-phenyl)-methyl-amino]-ethyl ester (Compound **4):** Triethylamine (15.2 mL, 109 mmol) was added dropwise to a solution of *N*-methyl-*N*-(2-hydroxyethyl)-4-aminobenzaldehyde (15.0 g, 84 mmol) in 100 mL of dry methylene chloride at 0°C under nitrogen flow. Methanesulfonyl chloride (8.4 mL, 109 mmol) was then added and stirred at room temperature for 5 min. The residue was partitioned between the water and methylene chloride, and the aqueous layer was extracted with methylene chloride. The combined extract was dried over anhydrous magnesium sulfate. After removing the solvent by rotary evaporator, a dark green solid was obtained (21.5 g, yield: 99%): ¹H NMR (CDCl₃) δ 9.76 (s, 1H), 7.78-7.73 (d, *J*=9.0 Hz, 2H), 6.79-6.76 (d, *J*=9.0 Hz, 2H), 4.40 (t, *J*=6.0 Hz, 2H), 3.83 (t, *J*=6.0 Hz, 2H), 3.14 (s, 3H), 2.96 (s, 3H).

Synthesis of Compound **5:** The mixture of compound **4** (16.38 g, 64 mmol), 1,1,1-tris(4-hydroxyphenyl)ethane (5 g, 16 mmol), K₂CO₃ (10 g, 72 mmol), and 18-crown-ether (1.23 g, 4.8 mmol) was stirred in dry acetone at room temperature for 30 min. The reaction mixture was heated at 50°C for 4 days. After filtration, all the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using methylene chloride/ether (20:1 by volume) to afford compound **5** as a yellow solid (9.0 g, yield: 71%): ¹H NMR (CDCl₃) δ 9.74 (s, 3H), 7.74-7.72 (d, *J*=8.9 Hz, 6H), 6.94-6.92 (d, *J*=8.7 Hz, 6H), 6.77-6.71 (m, 12H), 4.13 (t, *J*=5.6 Hz, 6H), 3.84 (t, *J*=5.6 Hz, 6H), 3.16 (s, 9H), 2.05 (s, 3H).

Synthesis of Compound **6:** To a solution of compound **3** (2.12 g, 3.76 mmol) in dry THF was added 0.12 g (5.13 mmol) of NaH at 0°C for 15 min. A solution of compound **5** (0.9 g, 1.14 mmol) in dry THF was added, and the reaction mixture was allowed to reflux under nitrogen for 12 h. The cooled solution was neutralized by water. The solvent was then evaporated under reduced pressure. The residue was extracted by methylene chloride and dried over anhydrous magnesium sulfate. The crude product was purified by flash column chromatography with hexane/ethyl acetate (10:1 by volume) to afford compound **6** as a yellow solid (1.83 g, yield: 80%): ¹H NMR (CDCl₃) δ 7.41-7.38 (d, *J*=8.5 Hz, 6H), 7.22-7.17 (d, *J*=16.3 Hz, 3H), 7.09 (s, 3H), 7.05 (s, 3H), 7.05-7.00 (d, *J*=15.3 Hz, 3H), 6.96-6.96 (d, *J*=8.8 Hz, 6H), 6.76-6.71 (m, 12 H), 4.11 (t, *J*=5.6 Hz, 6H), 3.92-3.82 (dd, *J*=5.5 Hz, 12H), 3.76 (t, *J*=5.6 Hz, 6H), 3.07 (s, 9H), 2.07 (s, 3H), 1.77-1.74 (m, 6H), 1.60-1.32 (m, 48H), 0.98-0.90 (m, 36H).

Synthesis of Compound **7:** Compound **6** (1.83 g, 0.907 mmol) was dissolved in dry diethyl ether. The solution was cooled to -10°C, and 2.5 M *n*-butyllithium in hexane (1.7 mL, 4.35 mmol) was added slowly. After the mixture was stirred

for 10 min, the cooling bath was removed and dry DMF (*N,N*-dimethylformamide, 1.1 mL, 13.61 mmol) was added dropwise. The mixture was stirred for 10 min at 0°C. After addition of 6 M HCl, the organic layer was washed with water, a saturated NaHCO₃ solution, and again water. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. The product was obtained as orange oil. ¹H NMR (CDCl₃) δ 10.43 (s, 3H), 7.45-7.42 (d, *J*=8.8 Hz, 6H), 7.31 (s, 3H), 7.31-7.25 (d, *J*=15.8 Hz, 3H), 7.22-7.16 (d, *J*=16.3 Hz, 3H), 7.15 (s, 1H), 6.97-6.94 (d, *J*=8.8 Hz, 6H), 6.77-3.72 (m, 12H), 4.12 (t, 6H), 4.01-3.90 (dd, *J*=5.3 Hz, 12H), 3.78 (t, 6H), 3.09 (s, 9H), 2.07 (s, 9H), 1.81-1.75 (m, 48H), 1.58-1.25 (m, 36H).

Synthesis of Compound **8 (GITCF):** To a solution of TCF (0.83 g, 4.18 mmol) in dry THF was added dropwise 0.64 mL (6.43 mmol) of piperidine at 0°C for 20 min, and then a solution of compound **7** (2.0 g, 1.07 mmol) in dry THF was added. The reaction mixture was stirred at room temperature overnight. The residue was extracted by CH₂Cl₂ and dried over MgSO₄. The crude product was purified by flash column chromatography with hexane/ethyl acetate (1:1 by volume) to afford GITCF as a dark purple solid (1.4 g, yield: 54%): ¹H NMR (CDCl₃) δ 8.03-7.98 (d, *J*=16.2 Hz, 3H), 7.46-7.43 (d, *J*=8.9 Hz, 6H), 7.34-7.29 (d, *J*=16.4 Hz, 3H), 7.26-7.21 (d, *J*=16.2 Hz, 3H), 7.12 (s, 3H), 7.09-7.03 (d, *J*=16 Hz, 3H), 7.03 (s, 3H), 6.97-6.94 (d, *J*=8.9 Hz, 6H), 6.77-6.73 (m, 12 H), 4.11 (t, 6H), 4.03-3.94 (m, 12H), 3.79 (t, 6H), 3.11 (s, 9H), 2.07 (s, 3H), 1.76 (m, 24H), 1.58-1.34 (m, 48H), 1.01-0.85 (m, 36H).

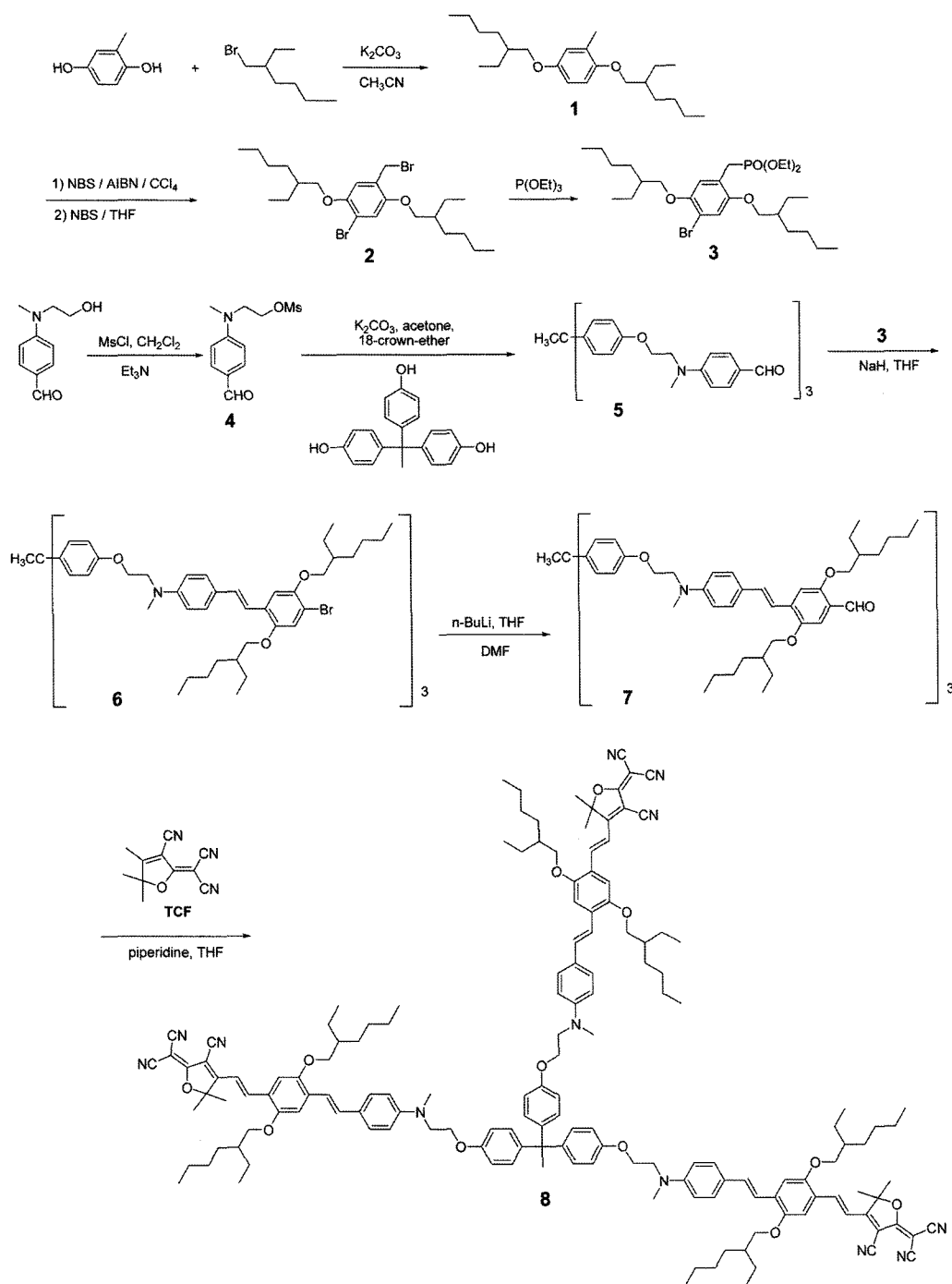
Instruments. NMR spectra were recorded on a Bruker AM-300 spectrometer at frequencies of 300 and 75 MHz for ¹H nuclei. TMS was used as the internal standard and CDCl₃ was used as a solvent unless specified otherwise. UV-visible absorption spectra were measured by Shimadzu UV-3100S. Differential scanning calorimetric (DSC) analysis and thermogravimetric analysis (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min with a TA Instruments DSC 2910.

Measurement of Electro-optic Coefficient. Thin films were prepared by spincoating the solution of NLO dendrimer GITCF and APC dissolved in cyclopentanone. The spincoated films on ITO glasses were thoroughly dried in the vacuum oven at 100°C for 2 h. The dark blue films were about 1 μm thick. 100 nm-thick gold electrodes were deposited on the top of the films in a thermal evaporator. Then we carried out a contact poling process in order to align the chromophore molecules in a noncentrosymmetric way. The samples were heated on a hot plate with a temperature controller to around the glass transition temperature of the polymer films, remained in the temperature for about 5-30 min, and cooled down to room temperature under the electric field. The amplitude of the modulated light was measured by the reflection method proposed by Teng and Man and then the electro-optic coefficient (*r*₃₃) was calculated from the amplitude.²⁰

Results and Discussion

While aminobenzene is commonly adopted as a donor, a variety of candidates have still competed for an acceptor of NLO molecules. One of the known efficient acceptors is 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) and its derivatives. Since aromatic groups are reported to possess much better stability than the polyene as a conju-

gation bridge, we have chosen the phenylene ring as a bridge for the NLO-active component of the dendrimer GITCF as shown in Scheme I. 2-Ethylhexyl group was attached to the bridge so as to keep the chromophore molecule from contacting closely its neighboring molecules and hence minimize its intermolecular electrostatic interaction. The alkyl chains may also play a major role in suppressing formation of cis-isomer as well as offering high solubility in solvents. The



Scheme I. Synthesis of NLO dendrimer GITCF.

alkyl chains were designed to connect to the phenyl ring through an ether linkage because direct coupling between the alkyl group and the ring results in benzylic carbon, which is vulnerable to a radical attack.

Synthetic procedure was started by attaching the electron donor, 4-aminobenzaldehyde to the core, 1,1,1-tris(4-hydroxyphenyl)ethane. Dialkoxy-substituted phenyl ring (compound **3**) was connected with the donor, and then the acceptor (TCF) was linked. *N*-methyl-*N*-(2-hydroxyethyl)-4-aminobenzaldehyde was mesylated to give compound **4**. The mesylated donor compound was attached with the core, providing the compound **5** with a high yield of more than 70%. Subsequently, the dialkoxy-substituted phenyl ring (compound **3**) was reacted with the compound **5**. The Wittig-Horner coupling reaction of the phosphonate with the aldehyde gave compound **6** in 80% yield. The terminal bromide was transformed into aldehyde by treatment with *n*-butyllithium and

DMF according to the Bouveault method, to afford compound **7**. The resulting compound **7** was reacted with TCF to give a dendritic electro-optical chromophore, GITCF as a dark purple solid.

Chemical structure of the dendritic chromophore was verified by ^1H NMR spectroscopy. In the ^1H NMR spectrum of GITCF (Figure 1) all the relevant proton peaks appear without any impurity peaks and their integration ratio is in good agreement with the calculated one. The peaks of protons in the double bond connecting the phenylene bridge and the acceptor are shown at 8.0 and 7.05 ppm. As large as 16 Hz coupling constant in the peaks indicates that the ethenyl moiety has a *trans*-conformation. Another ethenyl protons in the double bond connecting the donor and the phenylene bridge showed peaks centered around 7.26 ppm with a coupling constant of 16 Hz. The NMR data showed that we obtained the chromophore with a *trans*-conformation.

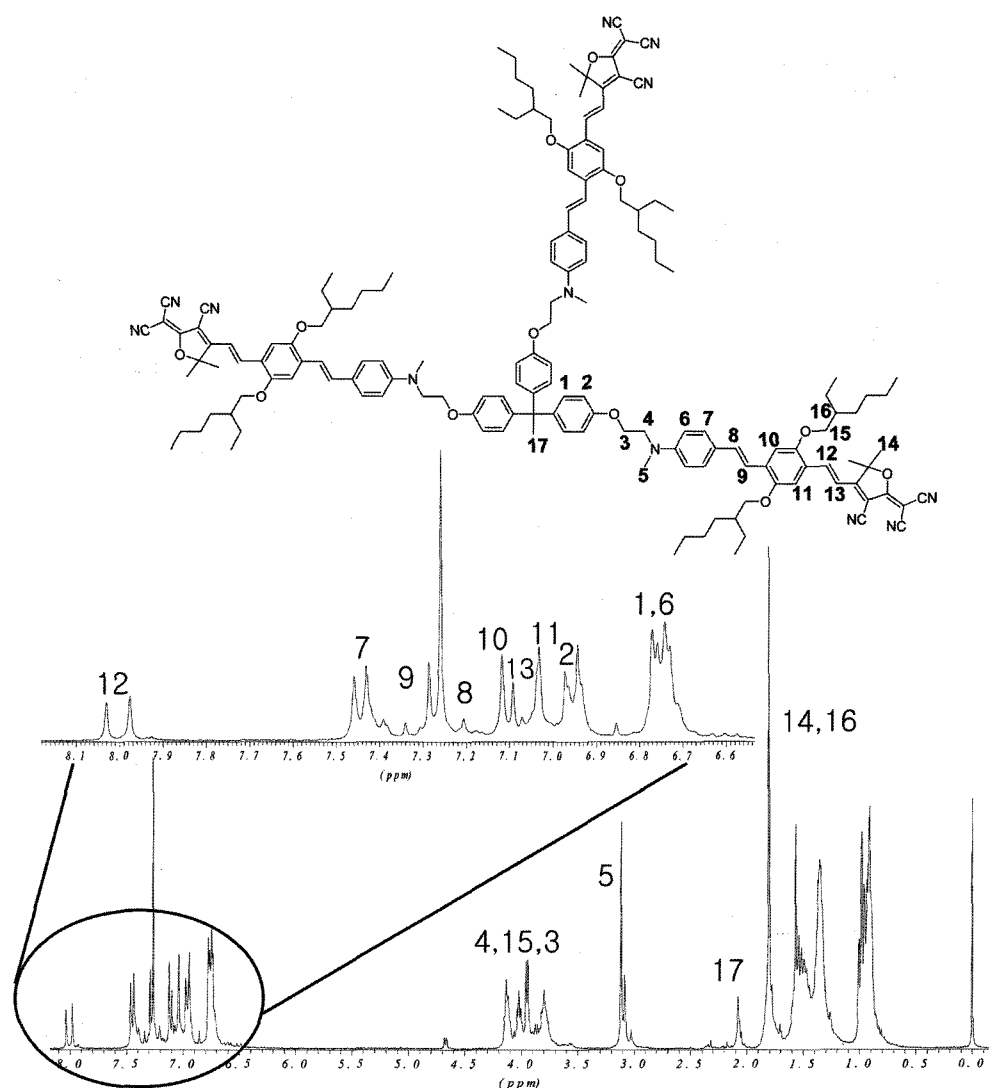


Figure 1. ^1H NMR spectrum of NLO dendrimer GITCF.

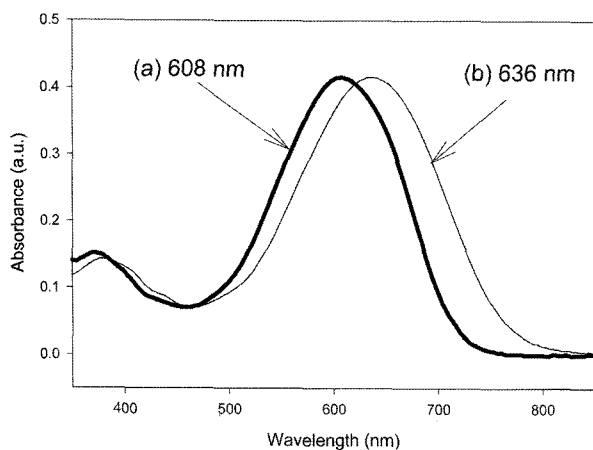


Figure 2. UV/Vis absorption spectra of GITCF in the solution of (a) toluene and (b) chloroform.

The absorption spectrum was taken from the solution of the dendrimer GITCF in toluene. Figure 2 shows that the broad absorption band centered at around 608 nm tails to 760 nm. The dendrimer showed discernible solvatochromic shift when it was dissolved in more polar solvent. The chloroform solution of the dendrimer gives absorption band with as large as 28 nm red-shifted maximum, when compared to that of the toluene solution.

The NLO dendrimer is well soluble in common solvents including chloroform, tetrahydrofuran, cyclopentanone, cyclohexanone, etc. The dendrimer was made into an optical quality thin film by spincoating the cyclopentanone solution. Then the film was dried thoroughly and the gold electrode was deposited on the top of the film. From the DSC analysis, we found that the film showed T_g at 76 °C. We carried out poling process on the film at around T_g under high electric field of 1 MV/cm. However the film was failed to endure the harsh poling condition. Hence, we used APC as a polymer matrix. The polymer is in amorphous state and optically transparent. Also it shows as high as 181 °C glass transition temperature and good thermal stability. The dendrimer and the polymer were dissolved in cyclopentanone and then the solution was made into about 1 μ m-thick, blue film by spincoating. The weight ratio of the dendrimer to the polymer was 55 to 45.

Thermal stability of the chromophore is considered one of the critical factors in determining processing condition of fabrication of the film and poling. When the spincoated films containing the NLO chromophore are dried, it should be kept in mind that the chromophore be thermally stable and all the residual solvent be removed. So we evaluated thermal stability through thermal scan of the dendrimer as a function of temperature. As shown in Figure 3, the dendrimer sustains almost its weight until about 275 °C, where it shows abrupt a weigh loss due to thermal degradation. We found that vacuum drying at 100 °C for 2 h was enough for all residual sol-

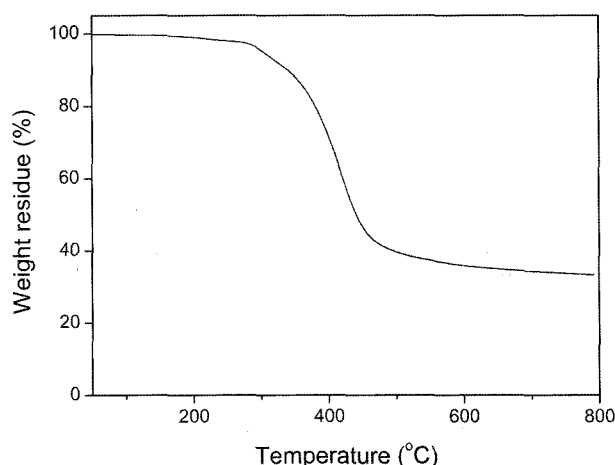


Figure 3. TGA thermogram of GITCF.

vent in the film to dry up. And also we checked out that the sample was intact during the process from the ^1H NMR measurement (the NMR spectrum is not included here).

After drying the APC/GITCF blend film, 100 nm-thick gold electrodes were deposited on the top of the films in a thermal evaporator. Then we carried out a contact poling process in order to align the chromophore molecules in a noncentrosymmetric way, which were randomly dispersed in the polymer host. In the poling process, the samples were heated on a hot plate with a temperature controller under the electric field. T_g of the film gives a clue in determining poling temperature, where the sample molecules should be relaxed freely enough to be rearranged by an external force such as electric field. The blend film exhibited T_g at 116 °C evidenced in the DSC scan. In a first trial, based on the DSC data, we heated the film at 116 °C for 1 h under 1 MV/cm of electric field. But, the film did not sustain such condition and then got damaged. In a second trial, we succeeded in poling the film at 100 °C and 1 MV/cm.

Macroscopic optical nonlinearity was evaluated by determining the electro-optic coefficient of the poled films. The reflection technique proposed by Teng is known a simple and efficient way among others. The amplitude of the modulated light is measured and then the electro-optic coefficient (r_{33}) is derived from a certain equation. We evaluated the r_{33} of the poled films according to the method. In this preliminary experiment, the film containing the NLO dendrimer exhibited 19 pm/V at 1.55 μ .

In conclusion, we designed and synthesized a NLO chromophore adopting dendritic architecture, in which three branches of the NLO-active component were linked with the core. The dendrimer exhibited that the broad absorption band centered at around 608 nm extends to 760 nm. It was thermally stable up to 275 °C in the nitrogen atmosphere and showed T_g at 76 °C. In a preliminary result, the film containing the NLO dendrimer exhibited 19 pm/V taken at 1.55 μ .

EO values are highly dependent upon the film quality such as smoothness of the surface, uniformity in the thickness, and any micropores and dusts in the films. We are trying to optimize the concentration of the solution and the speed and time of the spinning to assure best quality of the films. And poling temperature and electric field should be also adjusted to an optimum state. Now we are in preparing higher generation (*ex*: second generation) of such dendrimer in order to obtain higher molecular weight macromolecular dendrimer. Such dendrimer is expected to give good quality film with high T_g by itself so as to avoid the use of polymer matrix. The result will be published in elsewhere.

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