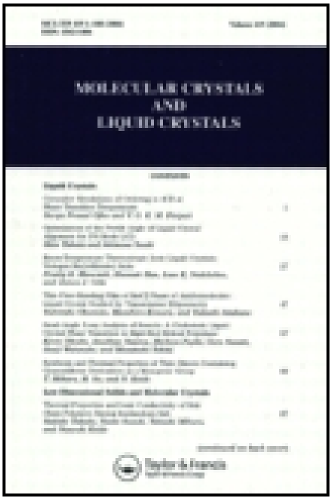

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Push-Pull Chromophore with Phenylene and Thiophene as Conjugation Bridge for Electro-Optic Applications

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Push-Pull Chromophore with Phenylene and Thiophene as Conjugation Bridge for Electro-Optic Applications

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We designed and synthesized a push-pull type chromophore (PT-TCF) containing phenylene and thiophene ring as a conjugation bridge. Bulky alkyl chain was substituted into the phenylene bridge to minimize the intermolecular interaction among the neighbor molecules and to enhance solubility of the chromophore in solvents and a polymer host. ^1H *NMR and* ^1H-^1H *COSY spectroscopy confirmed that the chromophore was in all trans-ethenyl conformation. The chromophore exhibited fairly high melting point of 188°C. The chromophore was thermally stable up to 220°C in the nitrogen atmosphere. The relatively high melting point and decomposition on-set may be attributable to the rigid bridge component. The chromophore was blended with an optically transparent polymer host to make a thin film and then its macroscopic optical nonlinearities were evaluated. In a preliminary result, the polymer films containing PT-TCF as a concentration of 50 wt% exhibited electro-optic coefficient as large as 22 pm/V taken at 1.55 μm.*

Keywords: bulky alkyl chain; electro-optic coefficient; nonlinear optical chromophore; thermal stability; trans-ethenyl conformation

INTRODUCTION

Since the first nonlinear optical (NLO) polymer was reported in 1982, a lot of researchers have concentrated their efforts on designing and preparing highly efficient NLO organic and polymeric materials. The NLO polymers inherit such superior properties as fast response time, small

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dispersion of the refractive index from dc to optical frequencies, and processability, when compared to the lithium niobate currently used in the commercial electro-optic modulators [1–7]. A recent work successfully demonstrated the electro-optic modulator based on a NLO polymer with drive voltage below 1 V as well as bandwidth over 150 GHz [8].

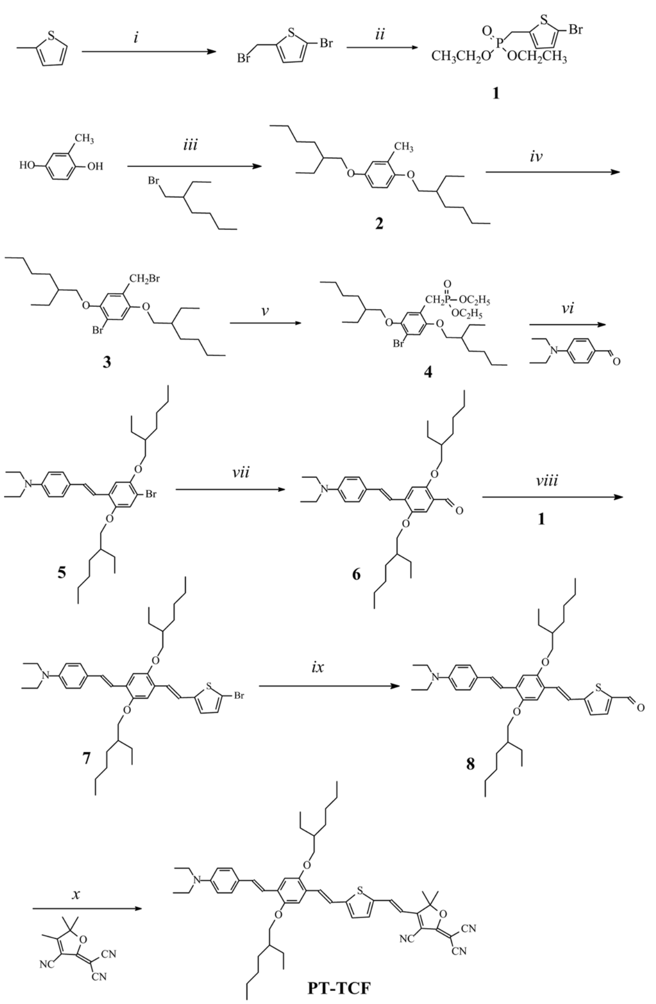
Experimental data and molecular simulation results in the past decades have suggested that NLO chromophores should have a push-pull structure, in which an electron donor in one end is connected with an electron acceptor in the other end through a conjugation bridge [1–2]. While aminobenzene is commonly adopted as a donor, a variety of candidates have still competed for an acceptor. One of the known efficient acceptors is 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) and its derivatives. A recent paper presented a highly efficient NLO chromophore, CLD which has aminobenzene and TCF connected with a polyene bridge [9]. It has some drawback in thermal and photo stability mainly because its polyene structure is susceptible to a radical attack, although the chromophore exhibits EO coefficient as large as 60 pm/V at 1.3 μm [10–11].

While there is certain trade-off between optical nonlinearity and stability of the chromophores, high NLO activity without stability is useless in the practical view. Since aromatic groups such as phenylene and thiophene rings are reported to possess much better stability than the polyene, we have chosen the aromatic rings as a bridge for our chromophore PT-TCF as shown in Scheme 1. 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 [9]. The alkyl chains may also play a major role in suppressing formation of cis-isomer as well as offering high solubility in solvents and polymer medium, which is critical in fabricating quality films. The alkyl chains were designed to connect to the phenylene ring through ether linkage because direct link between the alkyl group and the ring results in benzylic carbon, which is vulnerable to a radical attack. The resulting chromophore was blended with an optically transparent polymer host and was fabricated into thin films. Then its macroscopic electro-optic activity was evaluated by a simple reflection method proposed by Teng [12].

EXPERIMENTAL

Materials

Methylhydroquinone, 2-ethylhexylbromide, triethylphosphite, 4-(diethylamino)benzaldehyde, 2-methylthiophene, sodium hydride



SCHEME 1 Synthesis of the NLO chromophore PT-TCF. Reaction conditions: (i) NBS, BPO, CCl_4, 20 h, reflux; (ii) triethyl phosphite, 16 h, 160°C; (iii) acetonitrile, K_2CO_3, reflux, 3 days; (iv) (a) NBS, AIBN, CCl_4, 2 h, reflux and (b) NBS, THF, 1 h, reflux; (v) triethyl phosphite, 2 h, 160°C; (vi) NaH, THF, 0°C for 15 min and reflux for 11 h; (vii) butyl lithium, DMF, THF, 3 h, rt.; (viii) LDA, THF, 5 h, rt.; (ix) butyl lithium, DMF, THF, 16 h, rt.; (x) piperidine, THF, overnight, rt.

(95%), *n*-butyllithium (2.5 M solution in hexane), lithium diisopropylamide (LDA, 2.0 M solution in heptane/tetrahydrofuran/ethylbenzene) and piperidine were purchased from Aldrich and used as received.

N-bromosuccinimide (NBS), benzoyl peroxide (BPO) and 2,2′-azobis(2-methylpropionitrile) (AIBN) were obtained from Aldrich and used after purification by recrystallization. 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 several times. All solvents used in this work were freshly dried by distillation. 2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) was prepared according to the literature [13].

Synthesis of NLO Chromophore

Synthesis of Diethyl(5-bromothiophen-2-yl) Methylphosphonate (1)

Compound 1 was purified by flash column chromatography with hexane/ethyl acetate (1:5 by volume) to afford compound 1 as a yellow oil (yield: 24%): ^{1}H NMR ($CDCl_3$, ppm) δ 6.91–6.88 (d, $J = 3.6$ Hz, 1H), 6.74–6.72 (t, $J = 3.6$ Hz, 1H), 4.14–4.04 (m, 4H), 3.31–3.24 (d, $J = 20.7$ Hz, 2H), 1.30 (t, 6H).

Synthesis of 1,4-bis-(2-ethyl-hexyloxy)-2-methyl-benzene (2)

Compound 2 was purified by a column chromatography (ethylacetate/hexane = 1/10). Colorless liquid was obtained in 66% yield: ^{1}H-NMR ($CDCl_3$, ppm) δ 6.72 (3H), 3.77 (4H, d), 2.21 (3H, s), 1.68–0.9 (30H, m).

Synthesis of 1-bromo-4-bromomethyl-2,5-bis-(2-ethyl-hexyloxy)-benzene (3)

Compound 3 was purified by a column chromatography (methylene chloride/hexane = 1/5) to produce a colorless liquid in 51% yield: ^{1}H-NMR ($CDCl_3$, ppm) δ 7.06 (1H, s), 6.88 (1H, s), 4.49 (2H, s), 3.84 (4H, d), 1.68–0.9 (30H, m).

Synthesis of Diethyl-[2,5-bis(2-ethyl-hexyloxy)-4-bromophenyl] methylphosphonate (4)

Compound 4 was purified by column chromatography (ethylacetate/hexane = 1/3) to give a colorless liquid in 95% yield: ^{1}H-NMR ($CDCl_3$, ppm) δ 7.04 (1H, s), 6.98 (1H, s), 4.02 (4H, t) 3.84 (4H, d), 3.23 (2H, d) 1.72–0.93 (36H, m).

Synthesis of 4-[2,5-bis(2-ethyl-hexyloxy)-4-bromostyryl]-N,N-diethylbenzenamine (5)

Compound 5 was purified by a column chromatography (ethylacetate/hexane = 1/10) to produce a yellow liquid in 84% yield: ^{1}H-NMR ($CDCl_3$, ppm) δ 7.40 (2H, d), 7.15 (1H, d), 7.09 (1H, s), 7.05

(1H, s), 7.01 (1H, d), 6.67 (2H, d), 3.92 (2H, d), 3.84 (2H, d), 3.39 (4H, q), 1.77–0.95 (36H, m).

Synthesis of 2,5-bis(2-ethyl-hexyloxy)-4-[4-(diethylamino)styryl] benzaldehyde (6)

Compound 6 was purified by column chromatography (ethylacetate/hexane = 1/10) to produce an orange liquid in 87% yield: ^{1}H-NMR ($CDCl_3$, ppm) δ 10.43 (1H, s), 7.43 (2H, d), 7.31 (1H, s), 7.25 (1H, s), 7.21 (1H, s), 7.15 (1H, s), 6.68 (2H, d), 4.01 (2H, d), 3.92 (2H, d), 3.40 (4H, q), 1.79–0.97 (36H, m).

Synthesis of 4-{2,5-bis(2-ethylhexyloxy)-4-[(E)-2-(5-bromothiophen-2-yl)vinyl]styryl}-N,N-diethylbenzenamine (7)

Compound 7 was purified by flash column chromatography with hexane/ethyl acetate (20:1 by volume) to give compound 7 as yellow oil (yield: 83%): ^{1}H NMR ($CDCl_3$, ppm) δ 7.41–7.38 (d, $J = 8.7$ Hz, 2H), 7.29–7.24 (d, $J = 16.4$ Hz, 1H), 7.21–7.16 (d, $J = 15.4$ Hz, 1H), 7.16 (s, 1H), 7.09 (s, 1H), 7.09–7.03 (d, $J = 15.7$ Hz, 1H), 7.03–6.98 (d, $J = 16.7$ Hz, 1H), 6.93–6.91 (d, $J = 3.9$ Hz, 1H), 6.75–6.74 (d, $J = 3.8$ Hz, 1H), 6.67–6.64 (d, $J = 8.7$ Hz, 1H), 3.95–3.89 (m, 4H), 3.40–3.33 (m, 4H), 1.84–1.74 (m, 2H), 1.59–1.19 (m, 16H), 1.17–1.02 (t, 6H), 1.00–0.86 (m, 12H).

Synthesis of 5-{2,5-bis(2-ethylhexyloxy)-4-[4-(diethylamino)styryl]styryl}thiophene-2-carbaldehyde (8)

Compound 8 was purified by flash column chromatography with hexane/ethyl acetate (10:1 by volume) to afford compound 8 as an orange oil (yield: 38%): ^{1}H NMR ($CDCl_3$, ppm) δ 9.83 (s, 1H), 7.65–7.64 (d, $J = 3.9$ Hz, 1H), 7.55–7.49 (d, $J = 16.2$ Hz, 1H), 7.42–7.39 (d, $J = 8.7$ Hz, 2H), 7.29–7.24 (d, $J = 16.2$ Hz, 1H), 7.12–7.10 (d, $J = 5.1$ Hz, 1H), 7.10 (s, 1H), 7.11–7.07 (d, $J = 14.2$ Hz, 1H), 7.02 (s, 1H), 6.68–6.65 (d, $J = 8.7$ Hz, 2H), 3.98–3.91 (m, 4H), 3.42–3.35 (m, 4H), 1.83–1.74 (m, 2H), 1.60–1.35 (m, 16H), 1.21–1.16 (t, 6H), 1.02–0.87 (m, 12H).

Synthesis of 4-((1E)-2-(5-(2,5-bis(2-ethylhexyloxy)-4-(4-(diethylamino)styryl)styryl)thiophen-2-yl)vinyl)-2-(dicyanomethylene)-2,5-dihydro-5,5-dimethylfuran-3-carbonitrile (PT-TCF)

PT-TCF was purified by flash column chromatography with hexane/ethyl acetate (1:1 by volume) and recrystallization from dichloromethane/hexane mixture to afford PT-TCF as a dark purple crystal (yield: 39%): ^{1}H NMR ($CDCl_3$, ppm) δ 7.81–7.76 (d, $J = 15.7$ Hz, 1H), 7.50–7.44 (d, $J = 16.2$ Hz, 1H), 7.43–7.40 (d, $J = 8.2$ Hz, 2H), 7.40–7.39 (d, $J = 3.4$ Hz, 1H), 7.35–7.30 (d, $J = 16.2$ Hz, 1H), 7.29–7.24 (d, $J = 16.4$ Hz, 1H), 7.14–7.08 (d, $J = 16.9$ Hz, 1H), 7.11 (s, 1H), 7.10–7.08 (d, $J = 3.9$ Hz, 1H), 6.69–6.66 (d, $J = 9.0$ Hz, 2H), 6.62–6.57 (d, $J = 15.7$ Hz, 1H), 4.00–3.91 (m, 4H), 3.43–3.36 (m, 4H), 1.87–76 (m, 8H), 1.65–1.38 (m, 16H), 1.22–1.17 (t, 6H), 1.03–0.91 (m, 12H).

Instruments

^{1}H NMR spectra were recorded on Bruker DPX-300 spectrometer at 300 MHz. ^{1}H-^{1}H COSY and ^{13}C NMR spectra were obtained with Bruker AMX-500 spectrometer at 500 MHz and 125 MHz, respectively. Differential Scanning Calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on TA instruments DSC-2910 and TGA-2950 in a nitrogen atmosphere, respectively. UV/Vis absorption spectra of the chromophore solution and the thin film samples were taken by Shimadzu UV-2550 Spectrophotometer. Refractive Index of the polymer films was measured with a prism coupler (Sairon Co., SPA-4000) at 1550 nm. Thickness of the films was measured by using a surface profiler (Tencor Ins., Alpha-Step 500).

Measurement of Electro-Optic Coefficient

Host-guest films were prepared by spincoating the solution of PT-TCF and APC dissolved in cyclopentanone on ITO glasses. The chromophore was well blended up to 50 wt.% with the host polymer. The spin-coated films 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, which were randomly dispersed in the polymer host. 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 60 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 [12].

RESULTS AND DISCUSSION

Synthetic procedure of the NLO chromophore PT-TCF began with a build-up of conjugation bridge of dialkoxy-substituted phenylene and thiophene rings as shown in Scheme 1. Wittig-Horner reaction is an efficient coupling way between aldehyde and phosphonate. Knoevenagel condensation is a simple and high yield coupling method between aldehyde and activated methylene. So the phenylene and thiophene bridge was designed to have not only phosphonate functionality for coupling with the donor (aminobenzaldehyde), but also bromide terminal which was inert in the Wittig-Horner coupling but was able to easily transform to aldehyde for Knoevenagel condensation with the acceptor (TCF). 2-Ethylhexyl group was attached to the bridge to keep the chromophore molecule from interacting closely with its neighboring ones 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 and polymer medium, which is critical in fabricating quality films. The alkyl chains were designed to connect to the phenylene ring through ether linkage because direct coupling between the alkyl group and the ring results in benzylic carbon, which is vulnerable to a radical attack.

2-Methylthiophene was brominated by treatment of *N*-bromosuccinimide and then transformed to phosphonium salt (compound 1). A Williamson etherification of methylhydroquinone with 2-ethylhexylbromide gave 1,4-bis-(2-ethyl-hexyloxy)-2-methyl-benzene (compound 2). Subsequent bromination using *N*-bromosuccinimide and 2,2′-azobis(2-methylpropionitrile) in carbon tetrachloride produced 1-bromo-4-bromomethyl-2,5-bis-(2-ethyl-hexyloxy)-benzene (compound 3). Phosphonate (compound 4) was obtained from compound 3 by a Michalis-Arbuzov reaction. The phenylene bridge was coupled with 4-diethylamino-benzaldehyde via Wittig-Horner reaction. The terminal bromide of the compound 5 was transformed to aldehyde by treatment with *n*-butil-lithium and DMF according to the Bouveault method. The compound 6 was coupled with the thiophenephosphonate (compound 1) to give compound 7. After the terminal bromide was again changed to aldehyde, the compound 8 was reacted with the acceptor group of 2-(3-cano-4,5,5-trimethyl-5*H*-furan-2-ylidene)-malononitrile (TCF) to result in the NLO chromophore PT-TCF. The chromophore was thoroughly purified by column chromatography and recrystallization to yield a dark purple crystal.

The chemical structure and purity were confirmed by such instruments as ^{1}H NMR, ^{1}H-^{1}H COSY and ^{13}C NMR. ^{1}H NMR spectrum in Figure 1 shows that all the relevant proton peaks are appeared without any impurity peaks and the integration is in good accord with the calculated one. ^{1}H-^{1}H COSY is more helpful to identify the complicated molecular structure from the information about what protons

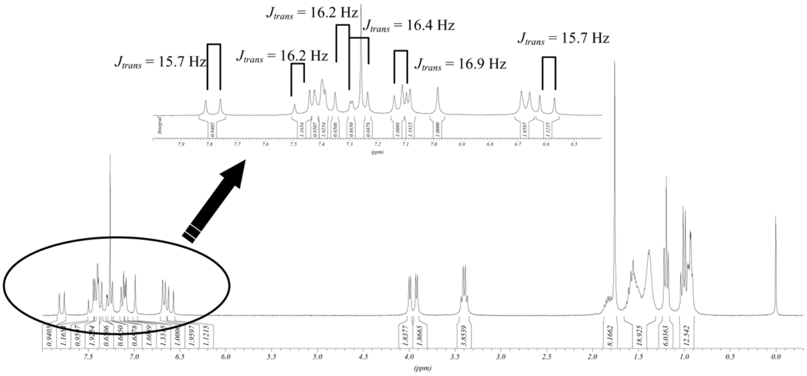


FIGURE 1 ^{1}H NMR spectrum of PT-TCF.

correlate to certain protons in the molecule. We could easily recognize the protons attached with the carbon-carbon double bond connecting the phenylene bridge and the aminobenzene donor in Figure 2, in which the proton at 7.81–7.76 ppm correlates to one at 6.62–6.57 ppm. As large as 15.7 Hz coupling constant indicates that the ethenyl moiety has a trans-conformation. The ethenyl protons in the double bond between the phenylene and the thiophene are observed at 7.29–7.24 ppm and 7.14–7.08 ppm with 16.4 Hz of coupling constant. The peaks of ethenyl protons in the double bond bridging the thiophene and the acceptor are appeared at 7.50–7.44 ppm and 7.35–7.30 ppm with 16.2 Hz. Such NMR data clearly suggested that we obtained the chromophore in all trans conformation. This is because the bulky alkyl chain may suppress the formation of a cis isomer.

Thermal behavior of the chromophore was traced by DSC and TGA. In spite of the bulky alkyl chains, PT-TCF exhibited fairly high melting point of 188°C. TGA thermogram in Figure 3 shows that there is no thermal decomposition up to 220°C in the nitrogen atmosphere. The high melting point and decomposition on-set may be attributable to the rigid bridge, phenylene and thiophene.

Overall procedures to evaluate the macroscopic optical nonlinearity of the chromophore are composed of spincoating, drying, poling and measurement of the amplitude of the modulated light. APC was used for a host polymer which was optically transparent and possessed a high T_g (181°C, determined by DSC). Such characteristics of the chromophore as solubility, thermal stability and purity have a significant influence on quality of the polymer film,

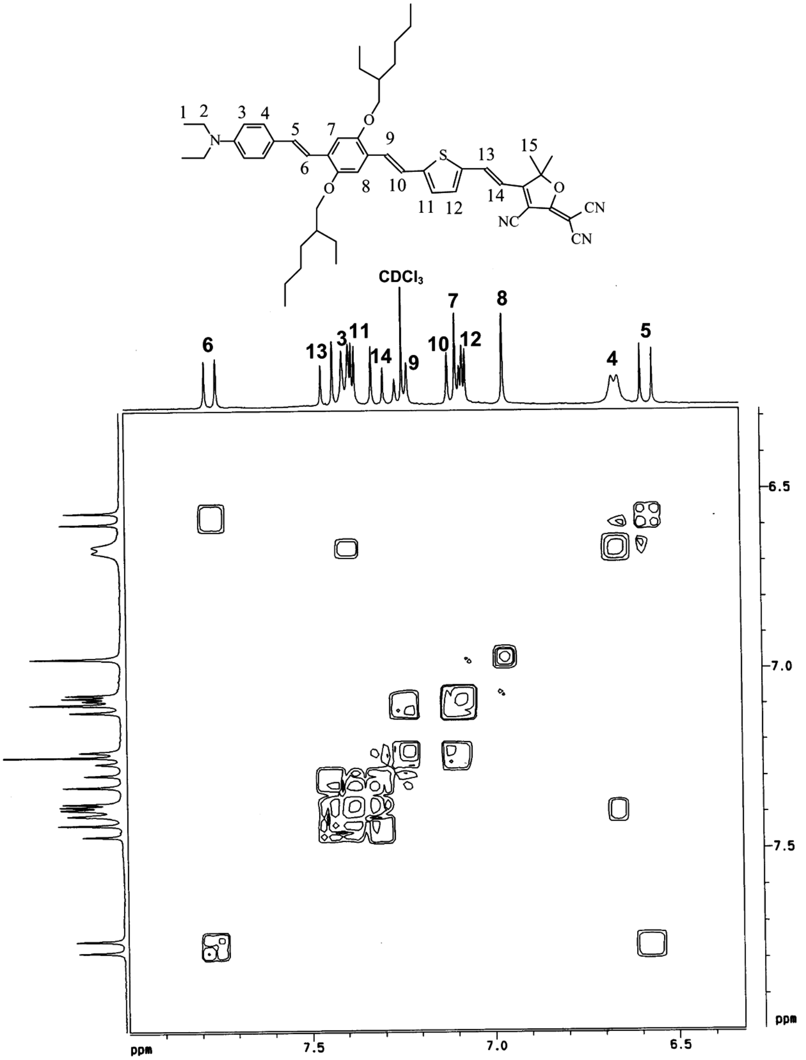


FIGURE 2 ^{1}H-^{1}H COSY NMR spectrum of PT-TCF at 500 MHz.

which subsequently determine the macroscopic optical nonlinearity. PT-TCF has a quite good solubility in solvents and is well blended with the polymer host. We could prepare optical quality polymer films containing up to 50 wt% of the chromophore. The spin-coated films were thoroughly dried in a vacuum oven at 100°C for 2 h.

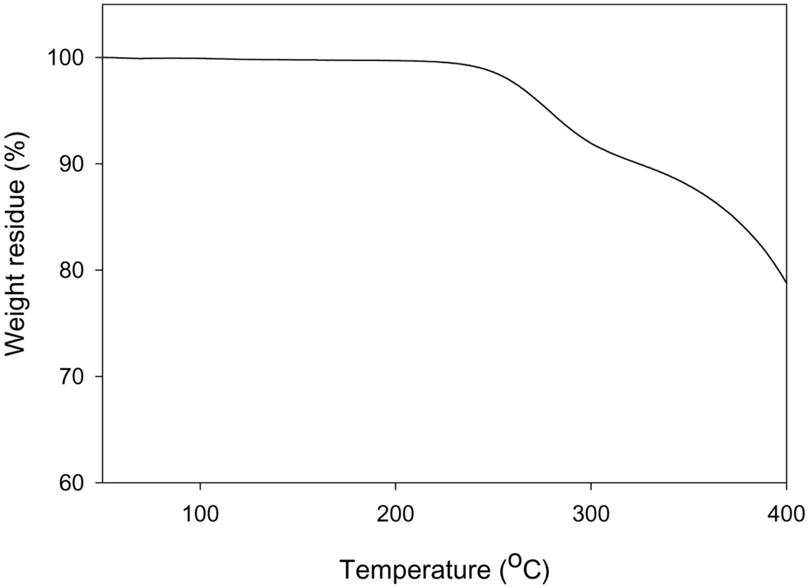


FIGURE 3 TGA thermogram of PT-TCF.

A 100 nm-thick gold was deposited on top of the film through a shadow mask in a thermal evaporator. The gold was utilized as an electrode. Then the film was contact poled under as high as 100 V/μm electric field at 95°C for 1 h. The reflection technique proposed by Teng is assumed a simple and efficient way to determine the electro-optic coefficient of the thin films containing NLO chromophores among others [12]. The amplitude of the modulated light was measured and then the electro-optic coefficient (r_{33}) was derived from a certain equation. In a preliminary result, the polymer films containing PT-TCF as a concentration of 50 wt% exhibited 22 pm/V taken at 1.55 μm.

In conclusion, we designed and synthesized a new NLO chromophore with thermal stability and relatively high EO coefficient. ^{1}H NMR and ^{1}H-^{1}H COSY clearly suggested that the chromophore was in all trans conformation. The chromophore exhibited fairly high melting point of 188°C and was thermally stable up to 220°C in the nitrogen atmosphere. The relatively high melting point and decomposition on-set may be attributable to the rigid phenylene and thiophene bridge. The polymer films containing PT-TCF as a concentration of 50 wt% exhibited electro-optic coefficient as large as 22 pm/V taken at 1.55 μm.

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