Heterocyclic Nonlinear Optical Chromophores Composed of Phenothiazine or Carbazole Donor and 2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran Acceptor

Min Ju Cho, Ja Youn Kim, Jae Hong Kim, Seung Hwan Lee, Larry R. Dalton,† and Dong Hoon Choi*

*College of Environment & Applied Chemistry, Institute of Natural Sciences, Kyung Hee University, Yongin, Gyeonggi-do 449-701, Korea. *E-mail: dhchoi@khu.ac.kr*
†Department of Chemistry, University of Washington, Seattle, WA 98195, U.S.A
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We prepared the new nonlinear optical chromophores that show fairly high microscopic nonlinearity through intramolecular charge transfer. Phenothiazine and carbazole units played an important role to contribute high electron donability and connect the resonance pathway *via* conjugative effect in the cyclized ring beside the aromatic ring. Theoretical calculation, electrochemical analysis, and absorption spectroscopic study gave us useful information about the energy states and microscopic nonlinearities of two serial chromophores. We compared the microscopic nonlinearities of four chromophores with the conjugation length and electron donability in the push-pull type NLO chromophores. The effect of gradient donability and lengthening the conjugation were investigated on the electronic state and microscopic nonlinearity.

Key Words : Phenothiazine, Carbazole, Nonlinear optical chromophore, Gradient donor moiety

Introduction

Organic nonlinear optical (NLO) materials provide strong potential advantages for second harmonic generation and electro-optic applications and are considered as most promising candidates for application in electro-optic and photonic devices.[1-6]

Factors such as high NLO susceptibility, fast response time, low dielectric constant, small dispersion in the refractive index, structural flexibility, and ease of material processing are advantageous in organic NLO materials systems. Taking advantage of these factors can lead to the application of the organic NLO materials systems to various photonic devices such as high speed EO modulators and switches. To achieve good device functionality, the NLO chromophore has to simultaneously possess the following criterion: high microscopic molecular nonlinearity ($\mu\beta$), good thermal stability and photostability, low absorption, and weak molecular electrostatic interaction in the polymer matrix.

Much effort was made to develop the highly functional chromophore with high molecular hyperpolarizability, β, and to improve the thermal/photo-stability. Recently, very large nonlinearities were achieved by employing heterocyclic rings such as thiophene and thiazole as a conjugative unit since they have lower resonance stabilization energy upon charge delocalization than benzene ring does.

Phenothiazine and carbazole used in this study are electron donating groups which can facilitate the charge transport of the carrier. Those moieties were often employed to photorefractive materials due to the property of charge carrier generation under light irradiation. In order to improve the figure of merit for photorefractivity, we designed four chromophores and synthesized them. These two building blocks exhibited different geometry each other. Carbazole units place perfectly in a plane-like geometry to stack themselves much more easily than the phenothiazine units since the center six membered ring in phenothiazine showed bent form arising from the dihedral angle in C-N-C (140.0°) and C-S-C (141.9°).[7] Therefore, the electrostatic interaction can be reduced between the chromophores that are even in high concentration of the phenothiazine-based chromophore. Accordingly, the phenothiazine chromophores can be expected to improve the macroscopic nonlinearity and its stability.

Some electron-deficient heterocyclic compounds have been known as strong acceptors for nonlinear optical materials. Particularly, 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) was well adopted as a strong electron acceptor that induces significantly high dipole moment (μ), first-order molecular hyperpolarizability (β), and their product ($\mu\beta$).[8-13]

In this report, we describe the synthesis and the microscopic nonlinear optical properties of two different types of the heterocyclic chromophores. Additional donor of diethylaminostyryl group was tethered to phenothaizine or carbazole that plays as conjugative donor bridge in DEA-PTZ-TCF and DEA-CBZ-TCF (see Figure 1). 2-Cyano-methylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) was commonly employed as a strong electron acceptor to induce strong charge transfer complex.[8-13]

Energy state diagram to describe the highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) energy, and the bandgap were determined by electrochemical analysis and absorption spectroscopic method. The molecular 1st-order hyperpolarizabilities and the dipole moments of the chromophores were

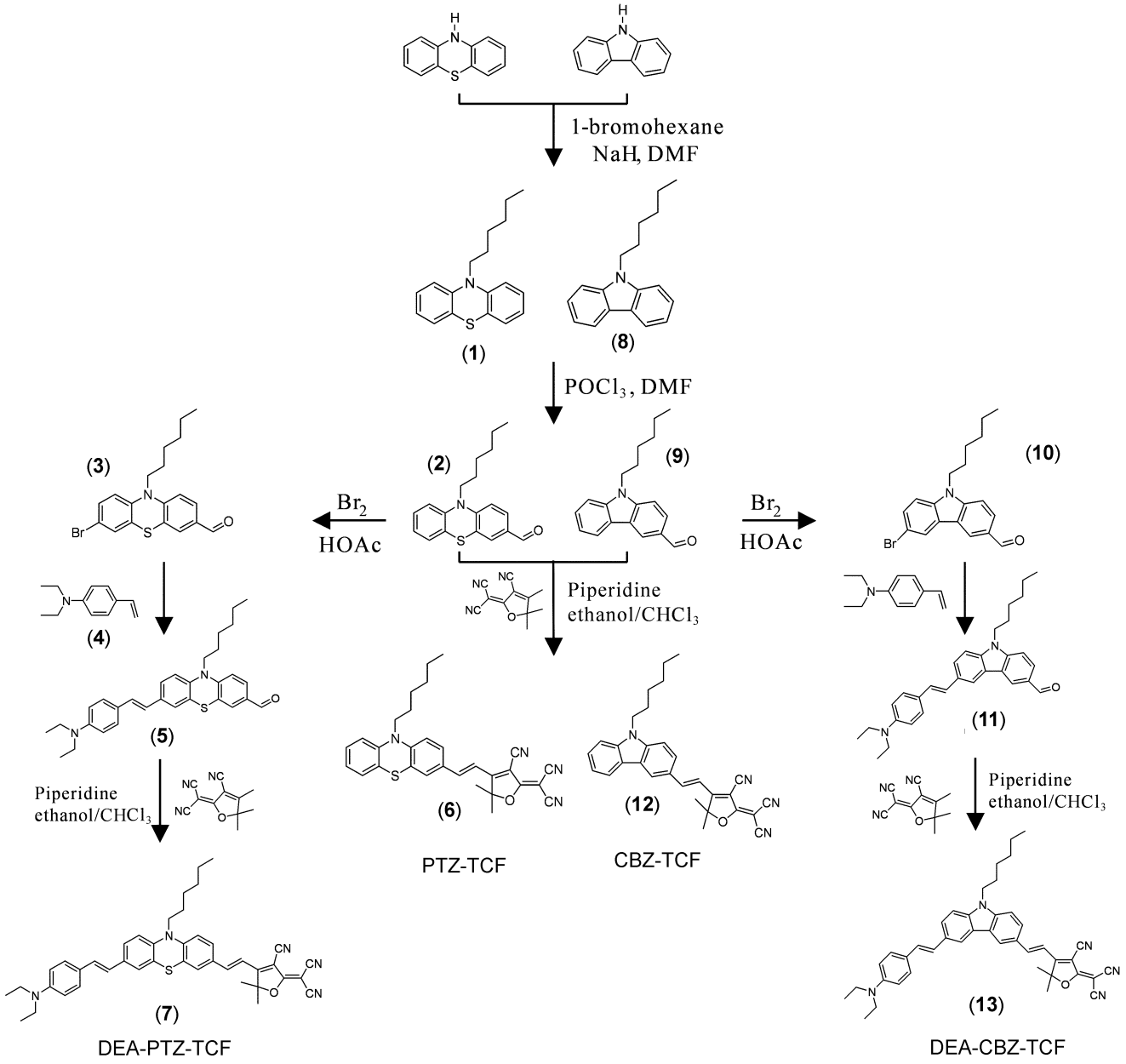


Figure 1. Synthetic procedure for phenothiazine and carbazole-based nonlinear optical chromophores.

calculated using semiempirical method. The effect of conjugation length and gradient donor system was investigated on the microscopic nonlinear optical properties and the energy states.

Experimentals

Materials. Phenothiazine, carbazole, 1-bromohexane, 4-(diethylamino) benzaldehyde, potassium *tert*-butoxide were purchased from ACROS Co. and used after purification. Phosphorous oxychloride ($POCl_3$) and bromine (Br_2) were purchased from Junsei Chem. Co. All solvents used in this study were freshly dried under distillation method. The synthesis of 2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) was synthesized following the known procedure.[13]

***Synthesis of 10-Hexyl-10H-phenothiazine (1)*:** Sodium hydride (14.4 g, 0.360 mol) was dissolved in dried dimethylformamide (DMF, 200 mL) at 0 °C. Phenothiazine (59.8 g, 0.300 mol) in DMF (100 mL) was added dropwise into the mother solution and stirred for one hour. Then, 1-bromohexane (59.5 g, 0.360 mol) in DMF (50 mL) was also added dropwise over a 30 min. period and the reaction mixture was kept stirring at room temperature for 12 hours. After completion of the reaction, the solution was neutralized with dilute HCl aqueous solution. The mixture was extracted with ethylacetate/water and its organic layer was dried under $MgSO_4$. The dried solution was concentrated. The resulting crude oily product was purified by silica gel column chromatography (ethylacetate : hexane = 1 : 15) to

yield 59.5 g (70%) of colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.90 (t, J = 7.6 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 3.85 (t, 2H, -CH_2-N), 1.83-1.78 (m, 2H), 1.46-1.41 (m, 2H), 1.33-1.29 (m, 4H), 0.87 (t, 3H).

***Synthesis of 10-Hexyl-10H-phenothiazine-3-carbaldehyde (2)*:** An oven dried 500 mL, round bottom flask was charged with a solution of DMF (29.3 g, 0.401 mol) and 1,2-dichloroethane (50 mL) at 0 °C. $POCl_3$ (38.3 g, 0.250 mol) was slowly added to the mixture for 30 min. Then, 10-hexyl-10H-phenothiaizne (56.7 g, 0.200 mol) in 1,2-dichloroethane (50 mL) was added dropwise for a 30 min. period. The mixture was stirred for 12 hours at 90 °C. Next, it was poured into ice-water, 300 mL and neutralized with $NaHCO_3$ aqueous solution. The solution was then extracted with chloroform. The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo* after filtration. The resulting product was purified by silica gel column chromatography (ethylacetate : hexane = 1 : 5) to yield 46 g (74%) of yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 1H, -CHO), 7.61 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.55 (d, J = 1.6 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 3.85 (t, 2H, -CH_2-N), 1.82-1.76 (m, 2H), 1.43-1.40 (m, 2H), 1.30-1.28 (m, 4H), 0.86 (t, 3H).

***Synthesis of 7-Bromo-10-hexyl-10H-phenothiazine-3-carbaldehyde (3)*:** An oven dried 500 mL, round bottom flask was charged with a solution of bromine (6.5 mL, 0.130 mol) and 50 mL, glacial acetic acid solution with 10-hexyl-10H-phenothiazine-3-carbaldehyde (40.48 g, 0.130 mol). The mixture was stirred for 48 hours at 25 °C. Next, the resulting mixture was poured into water, 600 mL and the aqueous layer was then extracted with ether. The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The resulting product was purified by silica gel column chromatography (chloroform : hexane = 1 : 1) to yield 38.5 g (77%) of greenish yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1H, -CHO), 7.63 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.23 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.18 (d, J = 2.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 3.82 (t, 2H, -CH_2-N), 1.80-1.72 (m, 2H), 1.43-1.37 (m, 2H), 1.30-1.23 (m, 4H), 0.86 (t, 3H).

***Synthesis of Diethyl-(4-vinyl-phenyl)-amine (4)*:** Methyltriphenylphosphonium bromide (35.7 g, 0.100 mol) and potassium *tert*-butoxide (13.5 g, 0.120 mol) were mixed in freshly dried tetrahydrofuran (THF, 300 mL). The yellow suspension was kept stirring for 30 min. Then, diethylaminobenzaldehyde (21.3 g, 0.120 mol) in THF (100 mL) was added dropwise into the mixture. After 1hr, methanol was added and the solution was filtered. The filtrate solution was evaporated under vacuum. The resulting product was purified by silica gel column chromatography (ethylacetate : hexane = 1 : 20) to yield 9.75 g (63%) of yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, J = 8.4 Hz, 2H), 6.61 (dd, J_1 = 17.4 Hz, J_2 = 11.1 Hz, 1H, -CH=CH_2), 6.60 (d, J = 8.4 Hz, 2H), 5.49 (d, J = 17.4 Hz, 1H, -CH=CH_2), 4.96 (d, J = 10.8 Hz, 1H, -CH=CH_2), 3.36 (q, 4H, -CH_2-N-CH_2-), 1.14 (t, 6H).

***Synthesis of 7-[2-(4-Diethylamino-phenyl)-vinyl]-10-hexyl-10H-phenothiazine-3-carbaldehyde (5)*:** An oven dried 500 mL, round bottom flask was charged with 7-bromo-10-hexyl-10H-phenothiazine-3-carbaldehyde (7.80 g, 0.020 mol), diethyl-(4-vinyl-phenyl)-amine (3.50 g, 0.200 mol), tri-*o*-tolylphosphine (0.610 g, 0.002 mol), palladium(II) acetate (0.220 g, 0.001 mol) and triethylamine (5.05 g, 0.050 mol) in DMF (20 mL). The solution was stirred for 3 days at 100 °C. After completion of the reaction, the resulting mixture was poured into water and the aqueous layer was then extracted with chloroform. The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The resulting product was purified by silica gel column chromatography (chloroform : hexane = 1 : 4) to yield 6.58 g (68%) of dark orange liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 1H, -CHO), 7.60 (dd, J_1 = 8.8 Hz, J_2 = 2.0Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.34 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.4 Hz, 1H), 7.19(s, 1H), 6.99 (d, J = 16.4 Hz, 1H, -CH=CH-), 6.83 (d, J = 8.4 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 6.72 (d, J = 16.4 Hz, 1H, -CH=CH-), 6.64 (d, J = 9.2 Hz, 2H), 3.82 (t, 2H, -CH_2-N), 3.36 (q, 4H, -CH_2-N-CH_2-), 1.82-1.74 (m, 2H), 1.44-1.38 (m, 2H), 1.33-1.27 (m, 4H), 1.16 (t, 6H), 0.86 (t, 3H).

***Synthesis of 2-{3-Cyano-4-[2-(10-henyl-10H-phenothiazin-3-yl)-vinyl]-5,5-dimethyl-5H-furan-2-ylidene}-malononitrile (6)*:** In a dried 250 mL, round bottom flask, 10-henyl-10H-phenothiazine-3-carbaldehyde (3.11 g, 0.010 mol) and TCF (1.99 g, 0.010mol) were dissolved in ethanol/chloroform (4 : 1, 50 mL) under argon. After heating the solution at 70 °C, a trace amount of piperidine was added dropwise. After 3 hours reaction, the solvent was evaporated to obtain a dark solid. The resulting product was purified by silica gel column chromatography (ethylacetate : chloroform = 1 : 20) to yield 2.31 g (47%) of dark violet solid, m.p. 165 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 16.0 Hz, 1H, -CH=CH-), 7.41 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.34 (d, J = 2.0 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 16.0 Hz, 1H, -CH=CH-), 3.88 (t, 2H, -CH_2-N), 1.85-1.78 (m, 2H), 1.76 (s, 6H, Me), 1.46-1.41 (m, 2H), 1.33-1.29 (m, 4H), 0.88 (t, 3H). FT-IR (KBr pellet, cm^{-1}): 2962 (-CH_3), 2925 (-CH_2-), 2228 (-C≡N), 1250 (-C-S-C-). Anal.: $C_{30}H_{28}N_4OS$ (492.20) Calcd. C 73.14, H 5.73, N 11.37; Found C 73.10, H 5.56, N 10.75.

***Synthesis of 2-[3-Cyano-4-(2-{7-[2-(4-diethylamino-phenyl)-vinyl]-10-hexyl-10H-phenothiazin-3-yl}-vinyl)-5,5-dimethyl-5H-furan-2-ylidene]-malononitrile (7)*:** In a dried 250 mL, round bottom flask, 7-[2-(4-diethylamino-phenyl)-vinyl]-10-hexyl-10H-phenothiazine-3-carbaldehyde (2.42 g, 0.005 mol) and TCF (1.99 g, 0.010 mol) were dissolved in ethanol/chloroform (4 : 1, 50 mL) under argon. After heating the solution at 70 °C, a trace amount of piperidine was added dropwise. After 3 hours reaction, the solvent was evaporated

to obtain a dark solid. The resulting product was purified by silica gel column chromatography (ethylacetate : chloroform = 1 : 15) to yield 1.50 g (45%) of dark black solid. m.p. 180 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 16.0 Hz, 1H, -CH=CH-), 7.39 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.35 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 2.0 Hz, 1H), 7.22 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.19 (d, J = 2.0 Hz, 1H), 6.92 (d, J = 16.4 Hz 1H, -CH=CH-), 6.81 (d, J = 16.4 Hz, 1H, -CH=CH-), 6.80 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.73 (d, J = 16.4 Hz, 1H, -CH=CH-), 6.65 (d, J = 9.2 Hz, 2H), 3.87 (t, 2H, -CH_2-N), 3.38 (q, 4H, -CH_2-N-CH_2-), 1.85-1.77 (m, 2H), 1.76 (s, 6H, Me), 1.49-142 (m, 2H), 1.36-1.30 (m, 4H), 1.18 (t, 6H), 0.89 (t, 3H). FT-IR (KBr pellet, cm^{-1}): 2963 (-CH_3), 2926 (-CH_2-), 2226 (-C≡N), 1605, 1595 (-$C_{arom.}$-N=), 1250 (-C-S-C-). Anal.: $C_{42}H_{43}N_5OS$ (665.32) Calcd. C 75.76, H 6.51, N 10.52; Found C 75.43, H 6.36, N 9.38

***Synthesis of 9-Hexyl-9H-carbazole (8)*:** The synthesis of this compound is much similar to that of the compound (1). The resulting crude oily product was purified by recrystallization in ethanol to yield 37.7 g (75%) of white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.2 Hz, 2H), 4.26 (t, 2H), 1.89-1.82 (m, 2H), 1.34-1.42 (m, 2H), 1.25-1.42 (m, 4H), 0.85 (t, 3H).

***Synthesis of 9-Hexyl-9H-carbazole-3-carbaldehyde (9)*:** The synthesis of this compound is much similar to that of the compound (2). The resulting crude oily product was purified by recrystallization in ethanol to yield 17 g (61%) of white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 1H, -CHO), 8.61 (s, 1H), 8.16 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 4.33 (t, 2H, -CH_2-N), 1.85-1.92 (m, 2H), 1.37-1.43 (m, 2H), 1.27-1.33 (m, 4H), 0.86 (t, 3H).

***Synthesis of 6-Bromo-9-hexyl-9H-carbazole-3-carbaldehyde (10)*:** The synthesis of this compound is much similar to that of the compound (3). The resulting crude oily product was purified by recrystallization in ethanol to yield 6 g (65%) of white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.08 (s, 1H, -CHO), 8.53 (s, 1H), 8.24 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 7.33 (d, J = 8.7 Hz, 1H), 4.29 (t, 2H, -CH_2-N), 1.81-1.90 (m, 2H), 1.23-1.38 (m, 2H), 1.23-1.38 (m, 4H), 0.85 (t, 3H).

***Synthesis of 6-[2-(4-Diethylamino-phenyl)-vinyl]-9-hexyl-9H-carbazole-3-carbaldehyde (11)*:** The synthesis of this compound is much similar to that of the compound (5). The resulting product was purified by silica gel column chromatography (ethylacetate : chloroform = 1 : 25) to yield 1.5 g (57%) of viscous orange liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.05 (s, 1H, -CHO), 8.60 (s, 1H), 8.21 (s, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.16-7.28 (m, 2H, -CH=CH-), 6.69 (d, J = 8.7 Hz, 2H), 4.27 (t, 2H, -CH_2-N), 3.37 (q, 4H, -CH_2-N-CH_2-), 1.81-1.90 (m, 2H), 1.16-1.38 (m, 12H), 0.86 (t, 3H).

***Synthesis of 2-{3-Cyano-4-[2-(9-hexyl-9H-carbazol-3-yl)-vinyl]-5,5-dimethyl-5H-furan-2-ylidene}-malononitrile (12)*:** The synthesis of this compound is much similar to that of the compound (6). The resulting product was purified by silica gel column chromatography (ethylacetate : chloroform = 1 : 20) to yield 2.07 g (45%) of dark red solid. m.p. 167 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 8.4 Hz, 16.0, 1H, -CH=CH-), 7.78 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.35 (t, J = 7.24 Hz, 1H), 7.07 (d, J = 16.0 Hz, 1H, -CH=CH-), 4.34 (t, 2H, -CH_2-N), 1.85-1.91 (m, 2H), 1.84 (s, 6H, Me), 1.27-1.40 (m, 6H), 0.86 (t, 3H). FT-IR (KBr pellet, cm^{-1}): 2964 (-CH_3), 2925 (-CH_2-), 2227 (-C≡N). Anal.: $C_{30}H_{28}N_4O$ (460.23) Calcd. C 78.24, H 6.13, N 12.16; Found C 78.37, H 6.11, N 12.21.

***Synthesis of 2-[3-Cyano-4-(2-{6-[2-(4-diethylamino-phenyl)-vinyl]-9-hexyl-9H-carbazol-3-yl}-vinyl)-5,5-dimethyl-5H-furan-2-ylidene]-malononitrile (13)*:** The synthesis of this compound is much similar to that of the compound (7). The resulting product was purified by silica gel column chromatography (ethylacetate : chloroform = 1 : 15) to yield 0.5 g (48%) of dark black solid. m.p. 192 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.23 (s, 1H), 7.86 (d, J = 15.9 Hz, 1H, -CH=CH-), 7.73 (d, J = 8.7 Hz, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.45 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.7 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 15.9 Hz, 1H, -CH=CH-), 7.08 (d, J = 16.2 Hz, 1H, -CH=CH-), 7.06 (d, J = 15.9 Hz, 1H, -CH=CH-), 6.70 (d, J = 8.7 Hz, 2H), 4.29 (t, 2H, -CH_2-N), 3.40 (q, 4H, -CH_2-N-CH_2-), 1.86-1.93 (m, 2H), 1.84 (s, 6H, Me), 1.19-1.41 (m, 6H), 1.18 (t, 6H), 0.86 (t, 3H). FT-IR (KBr pellet, cm^{-1}): 2964 (-CH_3), 2925 (-CH_2-), 2227 (-C≡N), 1600 (-C_{arom}-N=). Anal.: $C_{42}H_{43}N_5O$ (633.35) Calcd. C 79.59, H 6.84, N 11.05; Found C 76.72, H 6.33, N 11.30.

***Synthesis of 2-{3-Cyano-4-[2-(4-diethylamino-phenyl)-vinyl]-5,5-dimethyl-5H-furan-2-ylidene}-malononitrile (14)*:** The synthesis of this compound is much similar to that of the compound (7). The resulting product was purified by silica gel column chromatography (ethylacetate : chloroform = 1 : 20) to yield 2.4 g (67%) of green solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, J = 15.6 Hz, 1H, -CH=CH-), 7.52 (d, J = 8.7 Hz, 2H), 6.68 (d, J = 15.6 Hz, 1H, -CH=CH-), 6.67 (d, J = 9.0 Hz, 1H), 3.46 (q, 4H), 1.72 (s, 6H), 1.22 (t, 6H). λ_{max}: 585 nm (chloroform), m.p.: 239 °C.

***Spectroscopy*:** Proton NMR was recorded with VARIAN AS 400 and JEOL 300 NMR spectrometer. Deuterated chloroform ($CDCl_3$) was used as a solvent for recording the spectra. The UV-VIS absorption spectra of the chromophore solutions (solvent: chloroform, conc. 1×10^{-4} mole/L) were recorded with an UV-VIS spectrophotometer (HP 8453, photodiode array type 190-1100 nm).

Melting temperatures were measured using Perkin Elmer 7 DSC under nitrogen (rate of temperature: 5 °C). Infrared

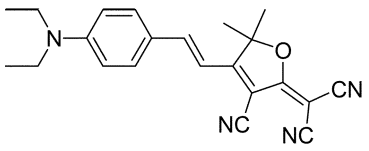
spectrum was recorded with Perkin Elmer FT-IR spectrophotometer. Elemental Analysis was performed with Flash F.A1112 (Automatic Elemental Analyzer, CE. Instruments, Italy).

***Electrochemical Analysis*:** The electrochemical experiments were carried out using on a EC-Epsilon (E2P) cyclic voltametry device. The voltamograms were obtained at 25 °C in anhydrous acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) at a scan rate of 100 mV/s under argon atmosphere. The working electrode was platinum (Pt). The counter electrode and the reference electrode were platinum wire and Ag/AgCl electrode respectively. The ionization potential values were internally calibrated against the ferrocene/ferricinium couple (E_o = 0.459 V *vs* Ag/AgCl) for each experiment.

Results and Discussion

Synthetic Consideration. The synthetic procedures for four NLO chromophores were illustrated in Figure 1. All chromophores were synthesized based on the heterocyclic donor unit and contains a strong electron acceptor of TCF. 1-Bromohexane was reacted with phenothiazine under potassium carbonate to give *N*-hexylphenothiazine. Under Vilsmeier-Haack condition, aldehyde group was introduced at 3-position with a good yield (> 60%). Then, in order to prepare the chromophore **6**, we dissolved the compound **2** in absolute ethanol/chloroform in the presence of piperidine as a base. The dark red or violet crystals were collected after purification of the reaction mixture. When we synthesized the chromophore **7**, using the compound **2**, bromination was performed in the presence of bromine and acetic acid. In order to add another donor moiety of diethylaminostyryl group at 7-position of phenothiazine, we employed Heck coupling method by use of Palladium (II) catalyst and tri-*o*-tolylphosphine as a relatively large ligand with a trace amount of weak amine base. The *N,N*-diethylamino-benzaldehdye was converted to *N,N*-diethylaminostyrene reacting with tetraphenylphosphonium bromide that is Wittig salt. Then, we reacted the styrene compound to 7-bromophenothiazine compound **3** under Heck conditions. 50% reaction yield was achieved as a reddish viscous oily product. TCF was reacted following the same way to synthesize the chromophore **7**. Based on the synthetic procedure for the phenothiazine chromophores, we performed the almost similar way to synthesize the carbazole-based chromophores. Finally, molecules for chromophore forming Donor-Acceptor (D-A) and Donor-donor bridge-acceptor (D-*D*-A) type were obtained and those structures result in the requisite ground-state charge symmetry, whereas π-conjugation or conjugative effect through the heterocyclic center bridge provides a pathway for the redistribution of electric charges under influence of electric field.

In order to compare the molecular properties between the chromophores, we simply synthesized the following chromophore (2-{3-cyano-4-[2-(4-diethylamino-phenyl)-vinyl]-5,5-diemthyl-5H-furan-2-ylidene}-malononitrile, **14**) with *N,N*-diethylamino benzaldehyde and TCF.



(14)

Thermal stability is an important requirement for the incorporation of the chromophores in poled-polymer systems. All chromophores synthesized in this study showed very good thermal stability as confirmed by the decomposition temperatures (T_d) shown in Table 1.

Energy States of the NLO Chromophores.

***Absorption Spectral Analysis*:** The absorption spectra of the chromophores both in solution state and film state were shown in Figure 2. The film sample was made in amorphous polycarbonate after doping the chromophore. The spectrum of chloroform solution was taken from 420 to 850 nm range at room temperature. The spectra were influenced by the structure of the donor or donor bridge moiety as to the same acceptor. The wavelength of maximum absorbance (λ_{max}) and cut-off edge wavelength ($\lambda_{cut\text{-}off}$) were affected by the conjugation length and donor strength.

Chromophore 7 and chromophore **13** have additional diethylamino donor and longer conjugation pathway than the chromophore **6** and **12** so that their λ_{max}s appeared higher wavelength ranges, respectively. The phenothiazine chromophores, **6** and **7** showed higher λ_{max} than the corresponding carbazole chromophores **12** and **13** even having the similar conjugation length.

Phenothiazine heterocyclic ring system has received a little attention as an electron donor or bridge component in nonlinear optical chromophores. However, relatively intense charge transfer (CT) band in the visible range of their electronic absorption spectra was observed that is attributed

Table 1. Measured absorption spectral data and calculated microscopic nonlinear optical parameters of the chromophores

	λ_{max} (nm), ε ($M^{-1}cm^{-1}$)		T_d (°C)	Theoretical data		
	$CHCl_3$	Film in APC		μ ($\times 10^{-18}$ esu)	$\beta(0)$ ($\times 10^{-30}$ esu)	$\mu\beta(0)$ ($\times 10^{-48}$ esu)
CBZ-TCF(**12**)	516 (2.9×10^4)	509	347	11.16	65.4	729.6
DEA-CBZ-TCF(**13**)	504 (3.9×10^4)	505	233 (372)	11.03	75.4	830.1
PTZ-TCF(**6**)	578 (3.0×10^4)	570	321	10.20	58.1	592.6
DEA-PTZ-TCF(**7**)	633 (2.9×10^4)	616	263 (371)	11.85	86.6	102.6

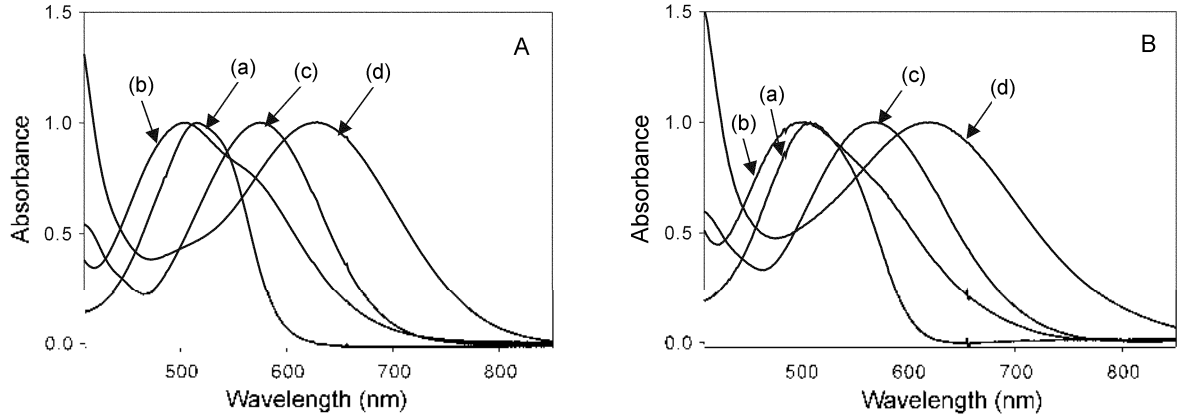


Figure 2. UV-Vis absorption spectra of the chromophores. A: solution in Chloroform. B: APC film. (a) CBZ-TCF (12), (b) DEA-CBZ-TCF (13), (c) PTZ-TCF (6), (d) DEA-PTZ-TCF (7).

to the fact that the two electron donating atoms (N,S) are placed in the phenothiazine central ring.

In the chromophore **6** and **12**, the absorption spectral difference is clearly due to the difference in electron donating power of phenothiaizine and carbazole. Phenothiazine can behave as a highly strong electron donating group as well as a bridge unit. The variation of donor substitution has a significant effect on the position of the charge transfer band that was shift bathochromically by 40-50 nm. Donor group's efficacy in phenothiazine chromophore was thought to be higher than that in carbazole-based chromophore. The chromophore **14** shows the λ_{max} around 585 nm which is red shifted compared to those of the chromophores **6** and **12**. From the λ_{max} and the cutoff wavelength ($\lambda_{cut-off}$) of the chromophore **6**, **12** and **14**, we could account the order of electron donor strength under the same accepting strength from TCF as follows. Carbazole < Phenothiazine < Diethylamino group.

Carbazole chromophore **13** exhibited slightly different absorption behavior compared to the other chromophores. In comparison, the chromophore **7** showed absorption maximum at 633 nm. However, the carbazole chromophore **13** showed two absorption bands around 504 and 563 nm. Particularly, the band around 563 nm appeared as a shoulder having relatively smaller absorption. This indicates that the absorption band at 504 nm is thought to be closely related to the effective conjugation between carbazole ring and the TCF acceptor unit. It can be thought that the chromophore bearing two donors through the molecular backbone can have two charge transfer states lying away to each other in energy. The chromophore **13** has the lowest transition at 563 nm, with a second excited state absorption appearing at 504 nm. The peak separation of 59 nm is significantly large. In the first excited state of the chromophore **13**, the diethylaminostyryl moiety acts as a net donating group. In this case, the energy difference of two charge transfer states is conjectured to be larger than that of the chromophore **7** because of a large difference of the electron donability of carbazole and diethylamino group. To be concise, the donor strength of the phenothiazine bridge is much higher than that of carbazole bridge unit and it is comparable to that of diethylaminostyryl group so that they may interact much less.

***Electrochemical Analysis of the NLO Chromophores*:** We performed electrochemical analysis to determine the redox ionization potentials of the chromophores. Cyclic voltametry is employed for estimating the energy level of organic NLO chromophores. The oxidation process corresponds to the removal of electrons from the highest occupied molecular orbital (HOMO), whereas the reduction cycle corresponds to fill the lowest unoccupied molecular orbital (LUMO) by electrons. Therefore, the oxidation and reduction potentials are closely related to the energies of the HOMO and LUMO levels of an organic NLO chromophore and thus can provide important information regarding the magnitude of the energy gap. They exhibit a single reversible oxidative wave in a positive energy mostly and an irreversible reductive peaks in a negative energy. (See Figure 3) HOMO-LUMO gaps can be estimated from the oxidation and reduction potentials. However, the reduction peaks are not clear enough to assign the accurate ionization potential. We have to employ the optical energy gap from the absorption edge of the electronic spectrum. We could obtain the experimental HOMO, LUMO, and energy band gap in each chromophore after combining the two experimental results. The electrochemical analysis results are collated in Table 2 including the data from spectroscopic measurement.

Within two series of the chromophore systems, a small cathodic shift of both the oxidation and the reduction peaks were observed with increasing donor strength. With the conjugation length, typically the reductive peak shifts anodically and the oxidative peak shifts cathodically to reduce the band gap energy. In this case, the effect of increasing donor strength is dominant over that of lengthening the conjugation. The HOMO and LUMO energy diagram can provide to compare donating strength and accepting strength in each chromophore. As can be seen in Figure 3 and Table 2, the cathodic shift of the oxidative wave was commonly observed when the donor strength and the conjugation length increased. In the energy diagram of

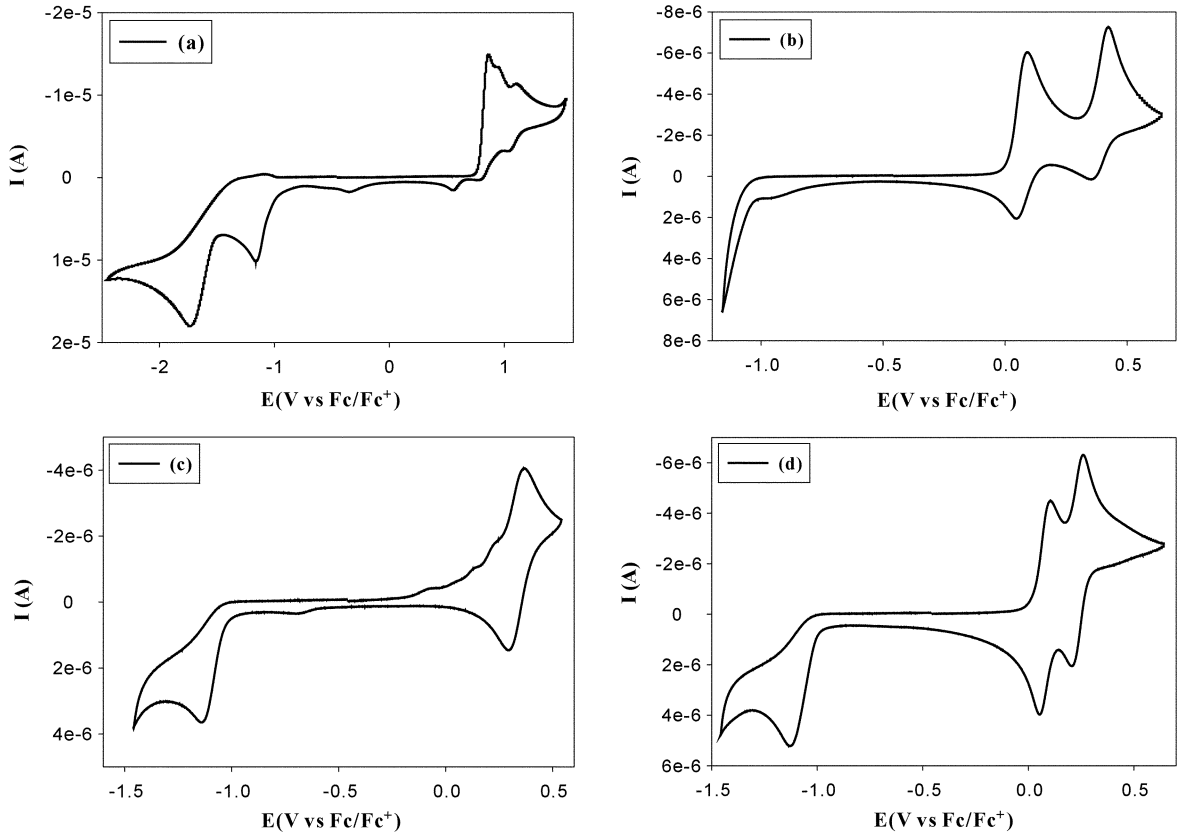


Figure 3. Cyclic voltammograms of the chromophores. (a) CBZ-TCF (12), (b) DEA-CBZ-TCF (13), (c) PTZ-TCF (6), (d) DEA-PTZ-TCF (7).

Table 2. Electrochemical and spectroscopic analysis data of the chromophores

	Cyclic Voltametry		Absorption Spectroscopic Data		
	$E^{1/2}_{ox}$	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E_{spect.}$	$\lambda_{cut\text{-}off}$ (nm)
CBZ-TCF(**12**)	0.709	−5.509	−3.408	2.101	590
DEA-CBZ-TCF(**13**)	0.068	−4.868	−3.001	1.867	664
PTZ-TCF(**6**)	0.331	−5.131	−3.316	1.815	683
DEA-PTZ-TCF(7)	0.079	−4.879	−3.277	1.602	774

Figure 4, the chromophores show strong electron donability and smallest bandgap energy, which can be used for NLO applications. In comparison of the energy bandgap, the chromophore containing the phenothiazine unit showed lower value than that of the chromophore with carbazole donor. Increasing the length of conjugation and introduction of additional donor results in a significant reduction of the HOMO-LUMO gap as is shown in Figure 4.

The absorption spectroscopic data and CV data are entirely consistent with an increase in electron delocalization with increasing conjugated chain length and addition of one more donor group such as diethylaminostyryl group. When we compare the HOMO levels of the chromophore **6** and **12**, donor strength of phenothiazine group was proven to be larger than that of carbazole. LUMO levels did not show large difference because we use the same TCF acceptor.

Microscopic Nonlinearities of the Chromophores. In order to study the microscopic nonlinear optical properties of the chromophores, we did molecular orbital calculation to determine quantum mechanical parameters. The geometry of the chromophore was optimized for compound (**6**, **7**, **12**, and **13**) by means of the MOPAC 2002 (CAChe version 5.04, PM3-Hamiltonian). The PM3 program was used for calculating the dipole moment, polarizability, and molecular hyperpolarizability in the ground state under the method of time-dependent Hartree-Fock (TDHF).

In Table 1, the calculated dipole moments (μ), polarizabilities (α), and molecular hyperpolarizabilities (β) of four chromophores were well tabulated. By using phenothiazine donor unit instead of carbazole donor as a bridge, we have obtained enhanced first-order molecular hyperpolarizabilities (β). The chromophore **7** showed highest microscopic nonlinearity ($\mu\beta(0)$) that is well explained by long conjugation and lowest transition state. Since the crystallographic structure of phenothiazine is likely to be butterfly shaped to interfere the coplanarity of all moieties in one chromophore, molecular hyperpolarizability of the chromophore **6** is lower than that of the chromophore **12**. By varying the conjugation length and donor strength with diethylaminostyrene through the phenothiazine or carbazole bridge, the microscopic nonlinearity was increased as we expected. The $\mu\beta(0)$ value of the chromophore **14** was calculated to be 877.5×10^{-48} esu that is higher than those of the chromophore **6** and **12**. This is well consistent with the

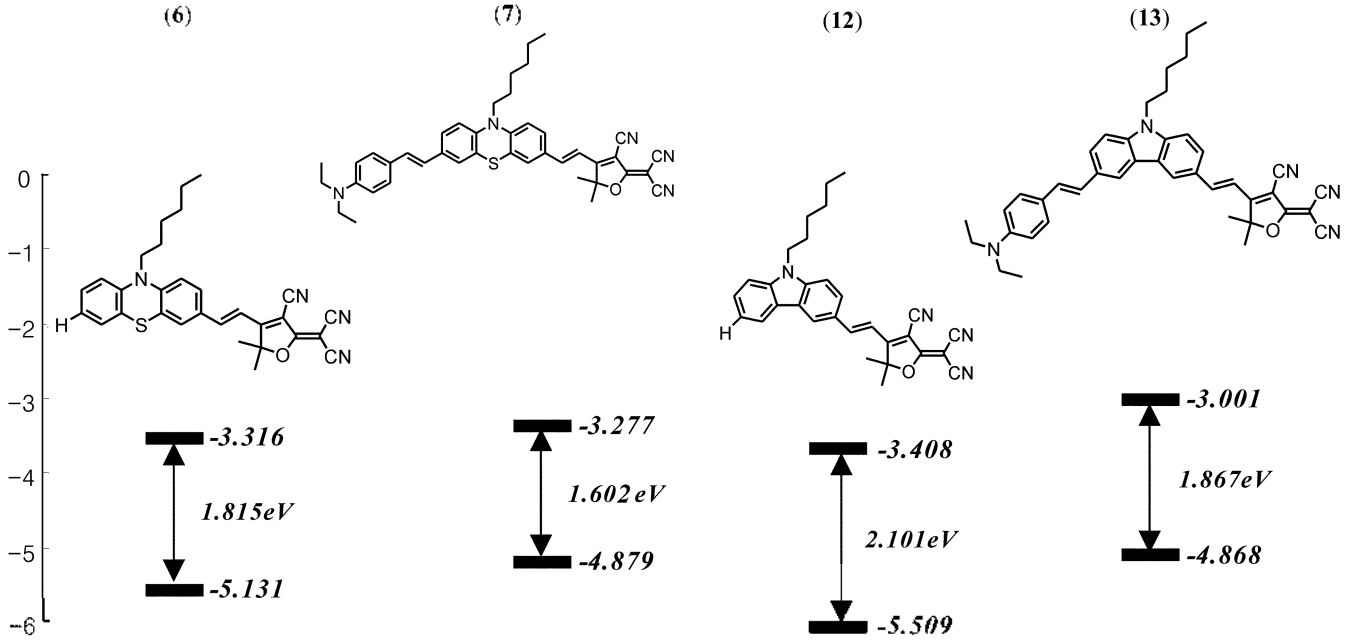


Figure 4. Energy diagram of the NLO chromophores.

results of the absorption spectral analysis. Diethylamino group has strongest electron donating property among three donors.

We are making much effort to investigate the macroscopic nonlinear optical properties using the guest-host system and covalently bonded NLO polymer bearing the phenothiazine-based chromophores. The properties of the infrared sensitive photorefractive composites are also being investigated using the chromophores synthesized in this study.

Conclusion

We successfully synthesized phenothiazine-based and carbazole-based chromophores and investigated their potential for NLO applications. Phenothiazine donor was confirmed to be a strong donor resulting from absorption spectroscopy and electrochemical analysis. The chromophore 7 and **13** contains two donors through the molecular backbone. The additional donor in DEA-PTZ-TCF(7) enhanced microscopic nonlinearity compared in DEA-CBZ-TCF(**13**), which was supported by the results of HOMO-LUMO bandgap energy.

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