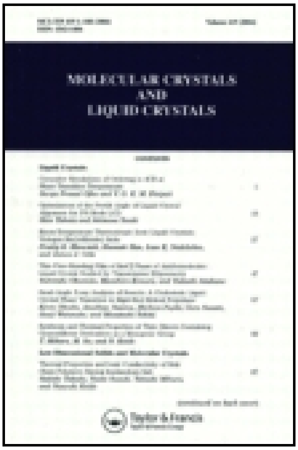


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Macroscopic Optical Nonlinearity of Heterocyclic Chromophores bearing 2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran

Min Ju Cho [a] , Sang Kyu Lee [a] , Jung-Il Jin [a] & Dong Hoon Choi [a]

[a] Department of Chemistry, Center for Electro- & Photo-responsive Molecules, Korea University, Seoul, Korea

Version of record first published: 22 Sep 2010

To cite this article: Min Ju Cho, Sang Kyu Lee, Jung-Il Jin & Dong Hoon Choi (2007): Macroscopic Optical Nonlinearity of Heterocyclic Chromophores bearing 2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, Molecular Crystals and Liquid Crystals, 471:1, 381-389

To link to this article: http://dx.doi.org/10.1080/15421400701549033

Mol. Cryst. Liq. Cryst., Vol. 471, pp. 381–389, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701549033

Macroscopic Optical Nonlinearity of Heterocyclic Chromophores bearing 2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran

Min Ju Cho
Sang Kyu Lee
Jung-Il Jin
Dong Hoon Choi
Department of Chemistry, Center for Electro- & Photo-responsive Molecules, Korea University, Seoul, Korea

We prepared the heterocyclic nonlinear optical chromophores that contain phenothiazine conjugative bridge between an electron donor and acceptor. Electrochemical analysis and absorption spectroscopic study were performed to investigate the molecular energy states of phenothiazine-based chromophores. Electro-optic properties of guest-host systems in amorphous polycarbonate (APC) were investigated by optimizing poling conditions. 52 pm/V of a maximum r_{33} *was obtained in the APC sample bearing 31 wt% of highly conjugated chromophore,* **6** *at 1.3* μ*m and it also displayed good thermal stability.*

Keywords: electro-optic; gradient donor moiety; nonlinear optical chromophore; phenothiazine; tricyanofuran

INTRODUCTION

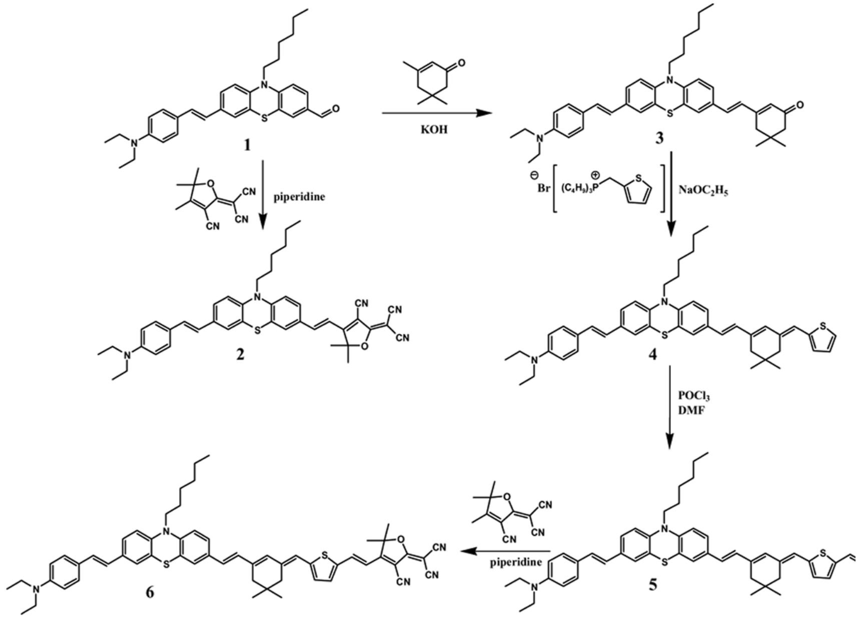
Organic nonlinear optical (NLO) materials provide strong potential advantages for second harmonic generation and electro-optic (EO) applications and are considered as most promising candidates for application in electro-optic and photonic devices [1–4].

This work was supported by the Korea Science and Engineering Foundation through CRM of Korea University. Particularly, Prof. D. H. Choi thanks the financial support by the Seoul R & BD Program (2005–2006).

Address correspondence to Dong Hoon Choi, Department of Chemistry, Center for Electro- & Photo-responsive Molecules, Korea University, Anam-dong, Sungbuk-ku Seoul 136-701, Korea. E-mail: dhchoi8803@korea.ac.kr

A NLO chromophore has to possess simultaneously high microscopic molecular nonlinearity ($\mu\beta(0)$), good thermal stability, good photostability, low absorption, and weak molecular electrostatic interaction in the polymer matrix. Some electron-deficient heterocyclic compounds have been known as strong acceptors for designing nonlinear optical chromophores. Particularly, 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) was often employed as a strong electron acceptor to induce significantly high dipole moment (μ), first-order molecular hyperpolarizability (β), and their product ($\mu\beta(0)$) [5–7].

In this article, we describe the synthesis and electro-optic properties of two heterocyclic chromophores with the conjugation length in the push-pull type NLO chromophores. Additional donor of diethylaminostyryl group was tethered to phenothaizine that plays as a conjugative donor bridge in DEA-PTZ-TCF (**2**) and DEA-PTZ-IT-TCF (**6**) (see Scheme 1). The chromophore, **2** was already reported and its EO property was compared with those of similar serial chromophores [8]. Particularly, chromophore **6** has much longer conjugative pathway from a donor to acceptor and exhibits unusual glass transition



SCHEME 1 Synthetic procedure for DEA-PTZ-TCF, **2** and DEA-PTZ-IT-TCF, **6**.

behavior at 121°C that can enhance the temporal stability of EO effect in a guest-host system.

We doped the chromophores with an identical concentration in amorphous polycarbonate (APC) and poled the sandwiched EO sample under different conditions to measure the EO coefficient at 1300 nm. Real time pole and probe technique permits us to measure EO signal during poling simultaneously.

EXPERIMENTALS

General

All chemicals were purchased from Aldrich and were used as received. The synthesis of 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran was synthesized following the known procedure [9]. Proton NMR was recorded with VARIAN AS 400 spectrometer. Deuterated chloroform ($CDCl_3$) was used as a solvent for recording the spectra. Absorption spectra were obtained from a HP 8453 UV/Vis spectrophotometer. The melting temperature of **2** and glass transition temperature of **6** were measured using Perkin Elmer 7 DSC under nitrogen (rate of temperature raise: 5°C/min).

Synthesis

Compound **3**, **4** were prepared by following the literature method [5].

3-(2-{7-[2-(4-Diethylamino-phenyl)-vinyl]-10-hexyl-10H-phenothiazin-3-yl}-vinyl)-5,5-dimethyl-cyclohex-2-enone (3)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, $J = 8.4$ Hz, 2H), 7.20 ~ 7.25 (m, 4H), 6.90 (d, $J = 16.4$ Hz, 1H), 6.86 (d, $J = 16.4$ Hz, 1H), 6.71 ~ 6.80 (m, 4H), 6.65 (d, $J = 8.4$ Hz, 2H), 6.04 (s, 1H), 3.82 (t, 2H), 3.37 (q, 4H), 2.44 (s, 2H), 2.30 (s, 2H), 1.74 ~ 1.84 (m, 2H), 1.37 ~ 1.48 (m, 2H), 1.27 ~ 1.36 (m, 4H), 1.17 (t, 6H), 1.10 (s, 6H), 0.89 (t, 3H)

[4-(2-{7-[2-(5,5-Dimethyl-3-thiophen-2-ylmethylene-cyclohex-1-enyl)-vinyl]-10-hexyl-10H-phenothiazin-3-yl}-vinyl)-phenyl]-diethyl-amine (4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, $J = 8.0$ Hz, 2H), 7.17 ~ 7.27 (m, 5H), 7.04 (d, $J = 4.0$ Hz, 2H), 6.80 (d, $J = 16.0$ Hz, 1H), 6.74 ~ 6.80 (m, 4H), 6.66 (d, $J = 8.0$ Hz, 2H), 6.63 (s, 1H), 6.47 (d, $J = 16.0$ Hz, 1H), 6.29 (s, 1H), 3.82 (t, 2H), 3.38 (q, 4H), 2.50 (s, 2H), 2.23 (s, 2H), 1.77 ~ 1.84 (m, 2H), 1.40 ~ 1.47 (m, 2H), 1.29 ~ 1.35 (m, 4H), 1.18 (t, 6H), 1.03 (s, 6H), 0.89 (t, 3H).

5-[3-(2-{7-[2-(4-Diethylamino-phenyl)-vinyl]-10-hexyl-10H-phenothiazin-3-yl}-vinyl)-5,5-dimethyl-cyclohex-2-enylidenemethyl]-thiophene-2-carbaldehyde (5)

Into a mixture of DMF (1.64 g, 0.021 mol) and 1,2-dichloroethane (20 mL), $POCl_3$ (1.61 g, 0.010 mol) was slowly added at 0°C over 30 min. Then, **4** (6.00 g, 0.088 mol) in 1,2-dichloroethane (20 mL) was added dropwise over 30 min. The mixture was allowed to stir for 12 h at 90°C. It was poured into ice-water (300 mL) and neutralized with an aqueous solution saturated with $NaHCO_3$. The aqueous solution was 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 (chloroform) to yield 4.62 g (74%) of red solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.65 (d, $J = 4.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.16 ~ 7.24 (m, 4H), 7.06 (d, $J = 4.0$ Hz, 1H), 6.89 (d, $J = 16.0$ Hz, 1H), 6.72 ~ 6.78 (m, 4H), 6.65 (d, $J = 8.0$ Hz, 2H), 6.61 (s, 1H), 6.55 (d, $J = 16.0$ Hz, 1H), 6.30 (s, 1H), 3.81 (t, 2H), 3.37 (q, 4H), 2.53 (s, 2H), 2.26 (s, 2H), 1.76 ~ 1.83 (m, 2H), 1.39 ~ 1.47 (m, 2H), 1.29 ~ 1.34 (m, 4H), 1.17 (t, 6H), 1.05 (s, 6H), 0.88 (t, 3H).

2-[3-Cyano-4-(2-{5-[3-(2-{7-[2-(4-diethylamino-phenyl)-vinyl]-10-hexyl-10H-phenothiazin-3-yl}-vinyl)-5,5-dimethyl-cyclohex-2-enylidenemethyl]-thiophen-2-yl}-vinyl)-5,5-dimethyl-5H-furan-2-ylidene]-malononitrile (DEA-PTZ-IT-TCF, 6)

5 (4.00 g, 5.61 mmol) and TCF (2.24 g, 11.22 mmol) 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. After 3 h reaction, the solvent was evaporated to obtain a dark solid. The resulting product was purified by silica gel column chromatography (ethylacetate: chloroform = 1:15, v/v%) to yield 2.56 g (45%) of dark black solid. $T_g = 121$°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, $J = 16.0$ Hz, 1H), 7.40 (d, $J = 4.0$ Hz, 1H), 7.34 (d, $J = 4.0$ Hz, 2H), 7.17 ~ 7.24 (m, 4H), 7.05 (d, $J = 4.0$ Hz, 1H), 6.90 (d, $J = 16.0$ Hz, 1H), 6.72 ~ 6.80 (m, 4H), 6.57 ~ 6.66 (m, 5H), 6.33 (s, 1H), 3.82 (t, 2H), 3.37 (q, 4H), 2.53 (s, 2H), 2.30 (s, 2H), 1.76 ~ 1.83 (m, 8H), 1.39 ~ 1.47 (m, 2H), 1.26 ~ 1.34 (m, 4H), 1.17 (t, 6H), 1.10 (s, 6H), 0.88 (t, 3H).

Electrochemical Analysis

The electrochemical experiments were carried out using on a EC-Epsilon (E2P) cyclic voltammetry 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.

Real Time Pole and Probe Measurement for EO Effect

For studying EO effect, thin films (thickness: 2.0–2.5 μm) were fabricated on indium tin oxide (ITO) pre-coated glass with a filtered solution (solvent: cyclopentanone/cyclohexanone (1:1)). For EO coefficient measurement, we deposited a gold electrode on the surface of the film (thickness: 100 nm) to fabricate sandwiched samples.

We measured the linear EO signal of chromophore doped APC sample by way of a modified reflection technique [10]. For *in situ* EO study, the sample was placed on the heater to apply the voltage ($V(t) = V_{d.c.} + V_o \sin\omega t$) combined with d.c. and a.c. components. An a.c. voltage ($V_o \sin\omega t$) was added to the poling d.c. voltage ($V_{d.c.}$) for probing the electro-optic signal simultaneously. EO signal could be monitored during poling with the sample temperature [11,12].

RESULTS AND DISCUSSION

1. Synthetic Consideration

The synthetic procedure for a highly conjugated NLO chromophore, **6** was illustrated in Scheme 1. The chromophore was synthesized based on the heterocyclic donor unit and contains a strong electron acceptor of TCF. We also synthesized the chromophore, **2** to compare its electro-optic property with that of chromophore **6**. Chromophore **2** was synthesized in our group and reported elsewhere [13]. **3** and **4** were prepared by following the literature method [5]. **4** was then formylated using phosphorous trichloride and dimethylformamide under Vilsmeier-Haack condition to give **5** in 74% yield. Knoevenagel coupling of a TCF acceptor to the aldehyde group in **5** was performed in ethanol/chloroform solvent in the presence of piperidene.Chromophore **6** was precipitated from the ethanol and collected by filtration to afford a dark solid in 45% yield.

2. Energy States of the NLO Chromophores

The highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) energy, and the bandgap energy (E_g) were determined by electrochemical analysis and absorption spectroscopic method.

The absorption spectra of both chromophores in a solution state were shown in Figure 1. The variation of conjugation length has a significant effect on the position of the charge transfer band. The wavelength of maximum absorbance (λ_{max}) and cut-off edge wavelength ($\lambda_{cut\text{-}off}$) were affected by the conjugation length. Chromophore **6** has much longer conjugation length than **2** so that their λ_{max} appeared much higher wavelength (674 nm). The cut-off wavelength provides us a lowest bandgap energy to evaluate the strength of donor and effect of conjugation length. Chromophore **6** has 1.52 eV of E_g which is smaller than that of chromophore **2**.

Cyclic voltammetry was employed for estimating the energy level of the synthesized NLO chromophores. They exhibit a single reversible oxidative wave in a positive energy mostly and an irreversible reductive peaks in a negative energy. Since 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 E_g in each chromophore after combining the two experimental results (see Table 1).

With the longer conjugation length, typically the reductive peak shifts anodically and the oxidative peak shifts cathodically to reduce

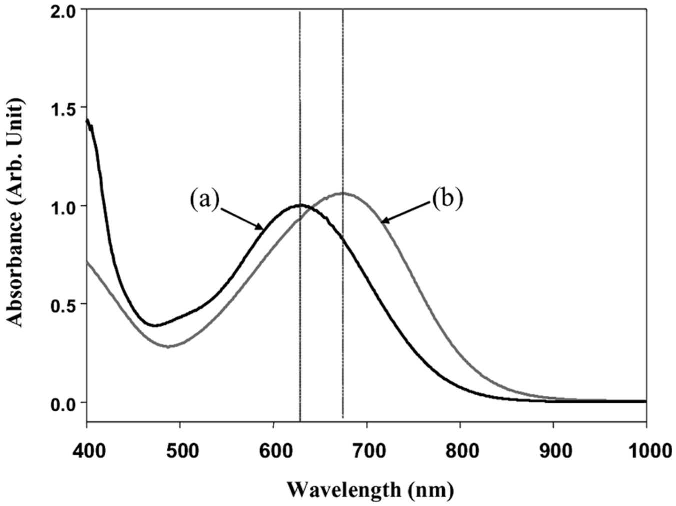


FIGURE 1 Absorption spectra of two chromophores in a solution state. (a) DEA-PTZ-TCF, **2**, (b) DEA-PTZ-IT-TCF, **6**. *solvent: chloroform.

TABLE 1 Measured and Calculated Parameters for Two Chromophores and their EO Samples

	λ (nm) ($CHCl_3$)	$E_{ox}^{1/2}$ (V)	HOMO[a] (eV)	LUMO[b] (eV)	E_g[c]	n (1300 nm)	$(r_{33})_{max}$ (pm/V (Ep = 70 V/μm)	Isothermal decay at 100°C (%)[d]
2	631	0.08	4.88	3.28	1.60	1.599	30	85.7
6	674	0.06	4.86	3.34	1.52	1.635	52	92.9

[a] HOMO level determined by cyclic voltammetry.
[b] LUMO level determined by using optical bandgap ($E_g^{opt.}$).
[c] $E_g^{opt.}$ determined by absorption edge (λ^{cutoff}).
[d] Annealing time = 2500 sec.

the E_g. The chromophore **6** showed well consistent behavior with general phenomena.

3. Electro-Optic Properties of the APC Samples

We investigated the EO property of APC sample doped with each chromophore. Although the conjugation length of **6** is quite long, it has excellent solubility in common organic solvent and good miscibility in APC. The doped film sample does not display phase separation and crystallization after long-term storage. Following the known procedure to evaluate EO polymers, chromophores were doped with an identical concentration (25–31 wt%) in APC. All samples have very little absorption at 1300 nm so that we did not consider the absorption induced resonance enhancement.

We performed real-time pole and probe method to observe the maximum EO effect from each sample. In this experiment, we applied a fairly low electric field (70 V/μm) to the sample in order to avoid dielectric breakdown.

In Figure 2, the increasing behavior of EO signal was demonstrated during poling. In APC sample doped either with **2** or **6**, the EO signal showed transition behavior, increasing abruptly around 135 ~ 140°C. Then, the signal increased continuously until the temperature reached to 143°C. Over this temperature, we observed the decrement of EO signal. We thought that it is due to decrease of the specific resistivity of EO sample at high temperature resulting in decrease of an applied electric field. We selected 140–143°C as an optimum temperature range for poling. From the saturated value of EO signal, we could calculate the EO coefficient of each sample. The EO coefficients of two samples poled under 70 V/μm were shown in Table 1. The APC

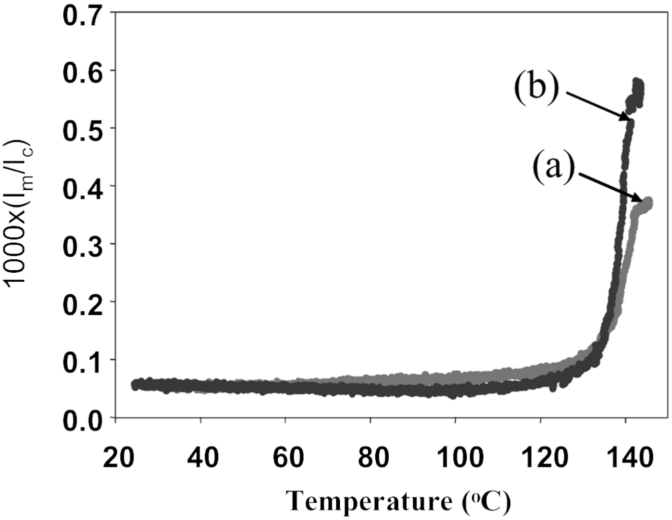


FIGURE 2 Increasing behavior of EO signal in the presence of a constant poling field. ($E_p = 70V/\mu m$). (a) APC sample with DEA-PTZ-TCF, **2**, (b) APC sample with DEA-PTZ-IT-TCF, **6**.

sample doped with **6** showed a higher maximum EO signal and a little higher onset temperature in an increasing behavior (see Figure 2).

In order to investigate the thermal stability of EO effect, dynamic and isothermal relaxation experiments were performed. After poling the sample, we raised the temperature to monitor the variation of

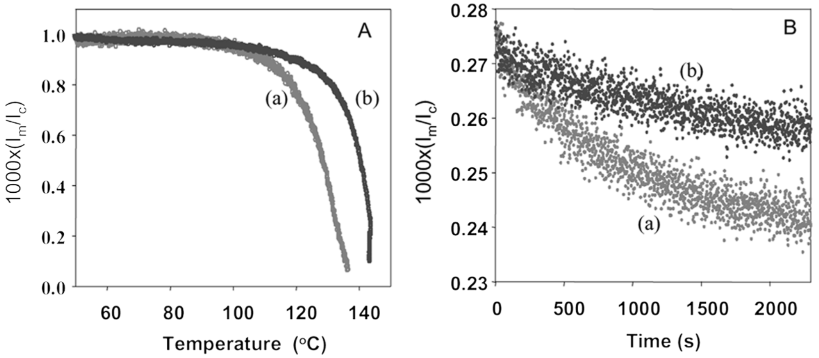


FIGURE 3 A: Dynamic decaying behaviors of two EO samples. B: Isothermal decaying behaviors of two EO samples at 100°C. (a) APC sample with DEA-PTZ-TCF, **2**, (b) APC sample with DEA-PTZ-IT-TCF, **6**.

EO signal (see Figure 3A). Additionally, we annealed the poled samples at 100°C for 40 min and monitored the EO signal simultaneously (see Figure 3B). The sample bearing a longer and rigid chromophore, **6** exhibited significantly better thermal stability than that with chromophore **2**. The chromophore **6** exhibits a glass transition temperature at 121°C, which is attributed to a high molar mass and molecular rigidity. The sample containing chromophore **2** was plasticized showing poor stability of poled order. The randomization of poled alignment in the sample doped with **6** is conjectured to require higher activation energy due to intrinsic molecular rigidity.

CONCLUSION

We successfully synthesized phenothiazine-based chromophores with the conjugation length and investigated their potential for electro-optic applications. A longer conjugation length and higher molar mass of chromophore **6** affect the electro-optic property of guest-host material significantly. APC doped with chromophore **6** exhibited a fairly high EO coefficient of 52 pm/V at 1.3 μm after the sample was poled under 70 V/μm. Due to high glass transition temperature of chromophore **6**, the sample containing them showed good thermal stability of EO effect.

REFERENCES

[1] Dalton, L. R., Harper, A. W., Ghosn, R., Steier, W. H., Ziari, M., Fetterman, H., Shi, Y., Mustacich, R. V., Jen, A. K-Y., & She, K. J. (1995). *Chem. Mater.*, *7*, 1060.

[2] Lee, M., Katz, H. E., Erben, C., Gill, D. M., Gopalan, P., Heber, J. D., & McGee, D. J. (2002). *Science*, *298*, 1401.

[3] Shi, Y., Zhang, C., Zhang, H., Betchel, J. H., Dalton, L. R., Robinson, B. H., & Steier, W. H. (2000). *Science*, *288*, 119.

[4] Samyn, C., Verbiest, T., & Persoons, A. (2000). *Macromol. Rapid Commun.*, *21*, 1.

[5] He, M. Q., Leslie, T. M., Sinicropi, J. A., Garner, S. M., & Reed, L. D. (2002). *Chem. Mater.*, *14*, 4669.

[6] Wu, X., Wu, J., & Jen, A. K-Y. (1999). *J. Am. Chem. Soc.*, *121*, 472.

[7] Wang, F., Ren, A. S., He, M., Harper, A. W., Dalton, L. R., Zhang, H., Garner, S. M., Chen, A., & Steier, W. H. (1998). *Polym. Prepr.*, *39*, 1065.

[8] Lee, S. K., Cho, M. J., Kim, G. W., Jun, W. G., Jin, J-I., Dalton, L. R., & Choi, D. H. (2007). *Optical Materials*, *29*, 451.

[9] He, M. Q., Leslie, T. M., & Sinicropi, J. A. (2002). *Chem. Mater.*, *14*, 2393.

[10] Teng, C. C. & Man, H. T. (1990). *Appl. Phys. Lett.*, *56*, 1734.

[11] Michelotti, F., Toussare, E., Levenson, R., Liang, J., & Zyss, J. (1995). *J. Appl. Phys.*, *80*, 1773.

[12] Choi, D. H., Park, J. H., Lee, J. H., & Lee, S-D. (2000). *Thin Solid Films*, *360*, 213.

[13] Cho, M. J., Kim, J. Y., Kim, J. H., Lee, S. H., Dalton, L. R., & Choi, D. H. (2004). *Bull. Kor. Chem. Soc.*, *12*, 484.