

**Electronic Supplementary Information (ESI) for
New Push-Pull Polyene Chromophores Containing Michler's Base Donor and
Tricyanofuran Acceptor: Multicomponent Condensation, Allopolar Isomerism and Large
Optical Nonlinearity**

Jingdong Luo,^{*a} Francis Lin,^a Zhong'an Li,^a Ming Li,^a Tae-Dong Kim,^a Sei-Hum Jang^a
and Alex K-Y. Jen^{*a,b}

^aDepartment of Materials Science and Engineering, University of Washington, Seattle, WA 98195-2120

^bDepartment of Biology & Chemistry, City University of Hong Kong, Kowloon, HK.

Table of Content

Experimental section	ESI-2
Synthesis of Compound 4a and 4b	ESI-2
Cyclic Voltammograms of Compound 4a and 4b	ESI-3
¹ H-NMR and ¹³ C-NMR Spectra	ESI-4
DSC Curves of Chromophores 4a and 4b	ESI-8
References	ESI-9

Experimental section

General Methods. All chemicals were purchased from Aldrich and used as received. Compounds **1**, **2** and **3a-b** were prepared according to the literature procedures with modifications, respectively.^{1,2,3} The ¹H and ¹³C NMR spectra were recorded on a Bruker AV500 spectrometer using CDCl₃ as solvent in all cases. High-resolution mass spectrometry (HRMS) was performed on Bruker APEX III 47e Fourier Transform mass spectrometer. Thermal transitions were analyzed with a TA Instruments differential scanning calorimeter (DSC) Q20 under nitrogen at a heating rate of 10 °C/min. Cyclic voltammetric data were measured on a Model 600E Series Electrochemical Analyzer/Workstation using a conventional three-electrode cell with a glassy carbon working electrode, Pt wire counter-electrode, and Ag/AgCl reference electrode at a scan rate of 100 mV/s. The 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in CH₂Cl₂ is the electrolyte and referenced to the FeCp₂/FeCp₂⁺ redox couple. The UV-vis-NIR spectra were recorded on a Varian Cary 5000 UV-Vis-NIR Spectrophotometer.

Poling Conditions and r_{33} Measurement. For studying the E-O property derived from the chromophores, guest-host polymers were generated by formulating chromophores **4a** (10 wt%) into poly(styrene-*co*-methyl methacrylate) (PS-*co*-PMMA) using 1,1,2-trichloroethane (TCE) as the solvent, or **4b** (33 wt%) into poly(bisphenol-A carbonate) with dibromomethane as the solvent. The resulting solutions (with the solid content of 10 wt % for **4a**/PMMA, or 6 wt% for **4b**/polycarbonate) were filtered through a 0.2- μ m PTFE filter and spin-coated onto thin-film device (TFD) indium tin oxide (ITO) glass substrates. Films of doped polymers were baked in a vacuum oven at 60-70 °C overnight to ensure the removal of the residual solvent. Then, a thin layer of gold was sputtered onto the films as a top electrode for contact poling. The poling temperature was 115 °C for **4a**/PMMA samples and 140 °C for **4b**/polycarbonate, and the poling field was set at 100 V/ μ m. The r_{33} values were measured using Teng-Man simple reflection technique at the wavelength of 1.31 μ m, and we use a carefully selected thin ITO electrode with low reflectivity and good transparency in order to minimize the contribution from multiple reflections.⁴

Compound 4a. Compound **1** (100 mg, 0.31 mmol), bridge intermediate **2** (50 mg, 0.31 mmol) and acceptor **3a** (63 mg, 0.31 mmol) were mixed in 1.3 mL of anhydrous ethanol, followed by the addition of added 0.4 mL of acetic anhydride and one drop of pyridine. The reaction mixture was allowed to stir at 70 °C for 30 minutes and monitored by TLC. After removal of the solvents, the crude product was purified by flash chromatography eluting with methylene chloride. Further purification of the product by reprecipitation from methanol/dichloromethane afforded the desired product as bronze-colored crystalline solid (150 mg, yield: 75%). Melting Point (mp) by DSC: ~250 °C. ¹H NMR (CDCl₃, 500 MHz) δ 7.62 (d, J = 15 Hz, 1H), 7.28 (d, J = 10 Hz, 2H), 7.18 (d, J = 10 Hz, 2H), 7.05 (d, J = 15 Hz, 1H), 6.69 (d, J = 10 Hz, 2H), 6.62 (m, 3H), 6.36 (d, J = 15 Hz, 1H), 3.45 (m, 8H), 2.97 (s, 2H), 2.84 (s, 2H), 1.75 (s, 6H), 1.21 (m, 12H); ¹³C NMR (CDCl₃, 125 MHz) δ 175.7, 172.5, 152.4, 148.5, 148.2, 141.8, 139.1, 137.7, 132.9, 130.7, 130.6, 129.3, 125.8, 114.2, 111.0, 110.7, 96.7, 96.5, 55.3, 44.5, 44.3, 27.4, 26.9, 25.9, 12.7, 12.6; HRMS (m/z, ESI) Calcd for 644.3150, found 644.3137.

Compound 4b. Compound **1** (100 mg, 0.31 mmol), bridge intermediate **2** (50 mg, 0.31 mmol) and acceptor **3b** (104 mg, 0.31 mmol) were mixed in 1.3 mL of anhydrous ethanol, followed by the addition of added 0.4 mL of acetic anhydride and one drop of pyridine. The reaction mixture was allowed to stir at 65 °C for 30 minutes and monitored by TLC. After removal of the solvents, the crude product was purified by flash chromatography eluting with methylene chloride. Further purification of the product by reprecipitation from methanol/dichloromethane afforded the desired product as dark solid (160 mg, yield: 66%). ¹H NMR (CDCl₃, 500 MHz) δ 7.66 (d, J = 5 Hz, 2H), 7.59 (d, J = 5 Hz, 2H), 7.46 (t, J = 5 Hz, 2H), 7.40 (m, 3H), 7.28 (m, 3H), 7.13 (d, J = 10 Hz, 2H), 6.98 (d, J = 15 Hz, 2H), 6.66 (d, J = 10 Hz, 2H), 6.61 (d, J = 10 Hz, 2H), 6.57 (d, J = 15 Hz, 2H), 6.37 (d, J = 15 Hz, 2H), 3.41 (m, 8H), 2.88 (s, 2H), 2.74 (s, 2H), 2.16 (s, 6H), 1.22 (m, 12H); ¹³C NMR (CDCl₃, 125 MHz) δ 175.9, 172.0, 152.7, 148.6, 148.3, 148.0, 143.2, 141.8, 139.7, 139.3, 139.1, 135.1, 132.9, 130.7, 129.3, 128.9, 128.0, 127.2, 126.4, 125.9, 120.5, 114.3, 112.4, 111.7, 111.1, 110.8, 98.1, 96.6, 55.8, 44.5, 44.3, 27.2, 25.9, 24.8, 12.7; HRMS (m/z, ESI) Calcd for 781.3541,

found 781.3532.

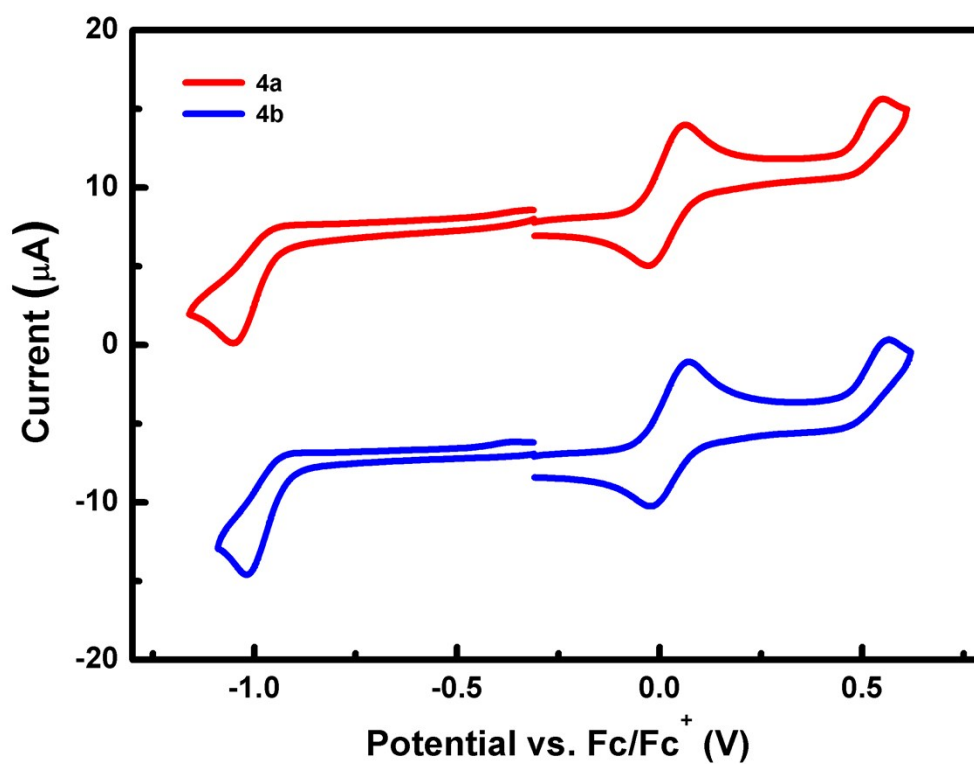
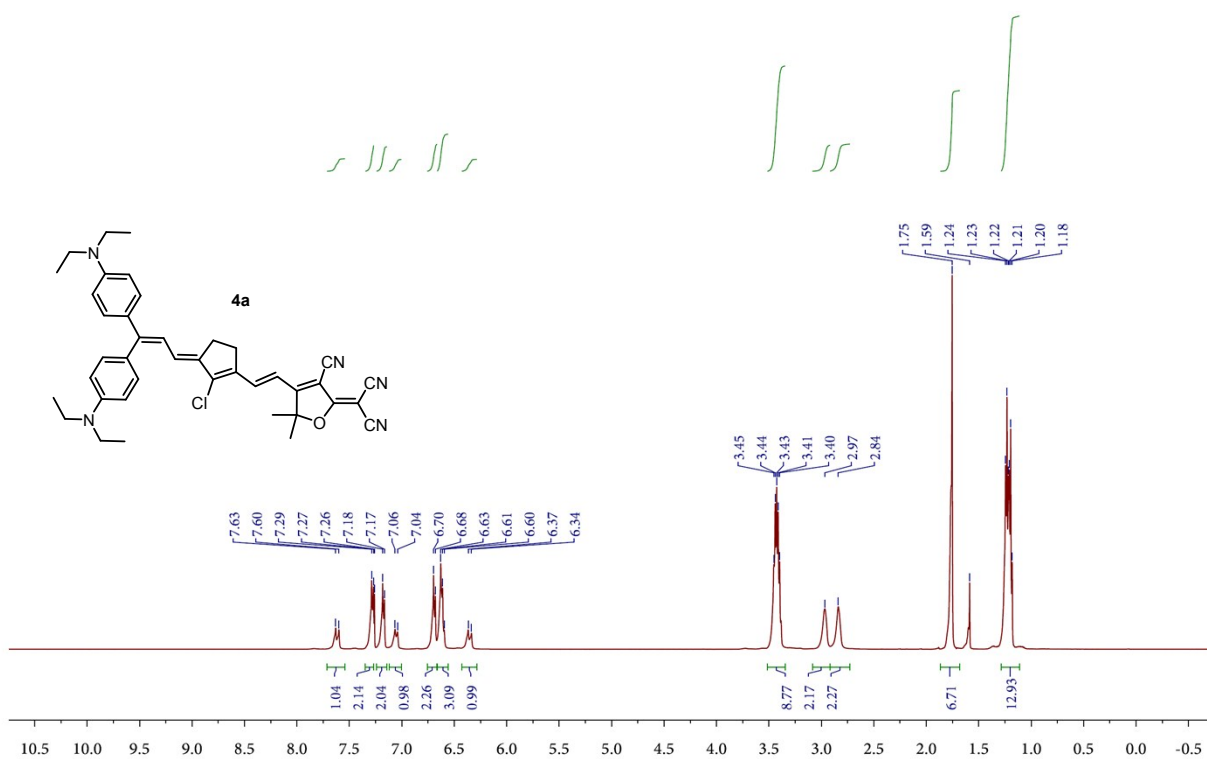
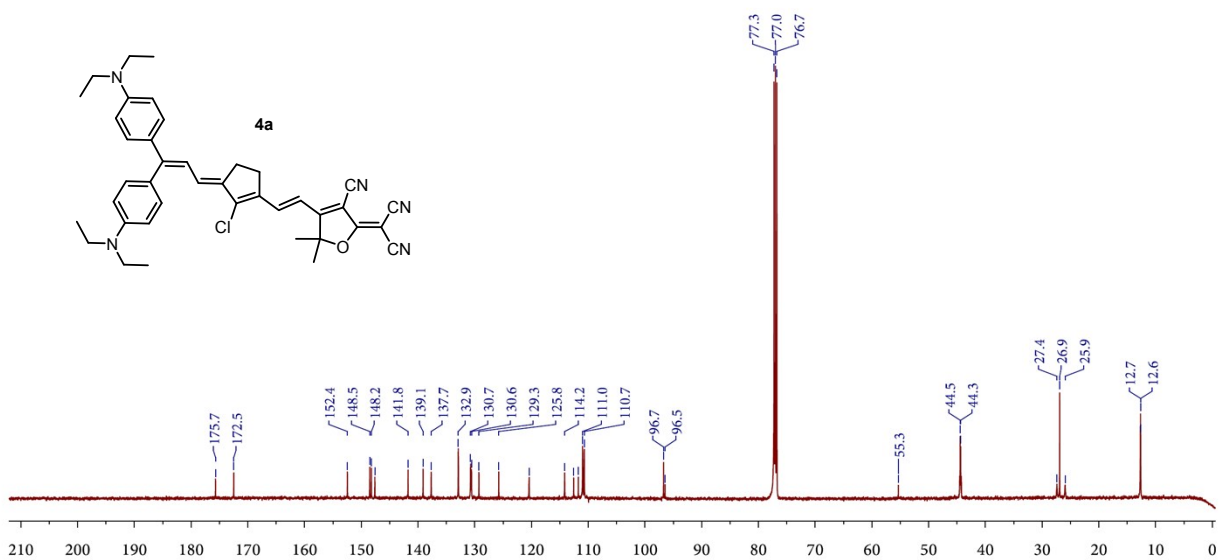
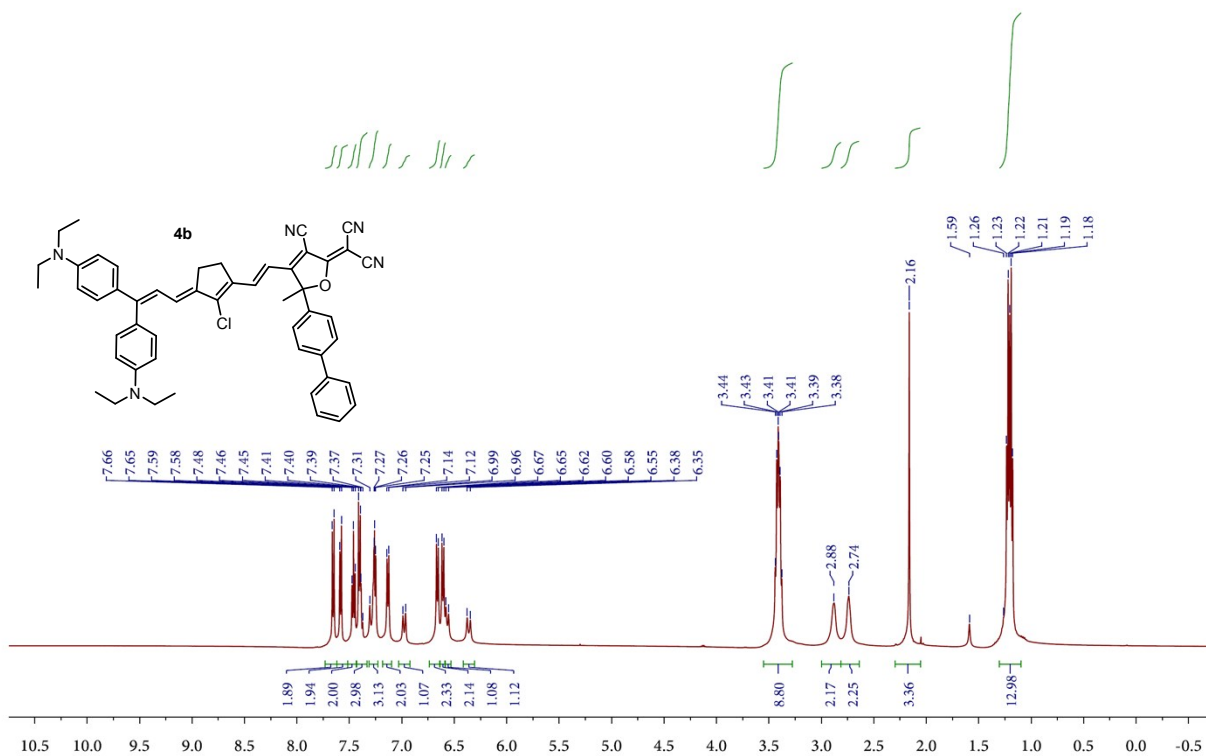


Figure ESI-1. Cyclic voltammograms of chromophores **4a** and **4b** recorded in CH₂Cl₂ solutions containing 0.1 M Bu₄NPF₆ supporting electrolyte at a scan rate of 100 mV/s.







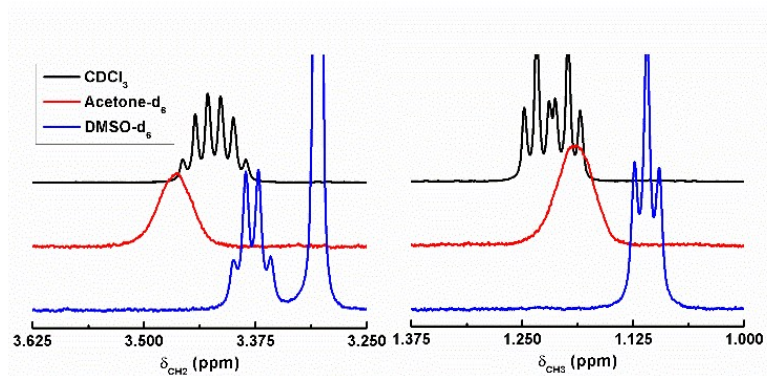
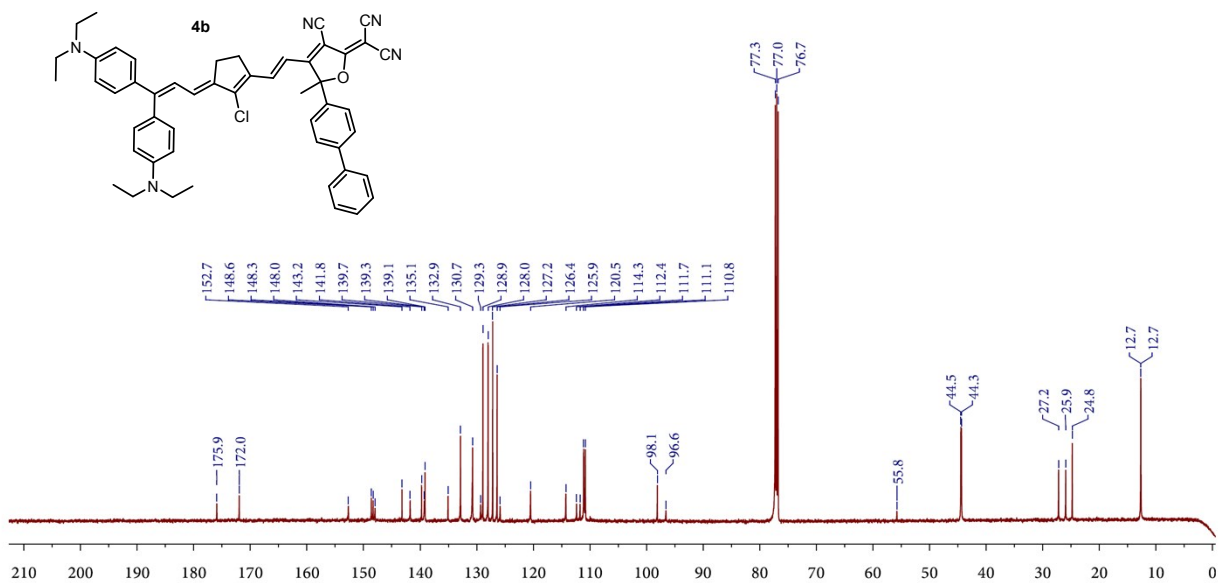


Figure ESI-2. The ^1H NMR spectra of the *N,N*-diethylamino group in compound 4a in deuterated solvents of CDCl_3 , Acetone- d_6 and DMSO- d_6 with different dielectric constant. Left, chemical shift for the methylene proton of NCH_2CH_3 ; Right, chemical shift for the methyl proton of NCH_2CH_3 .

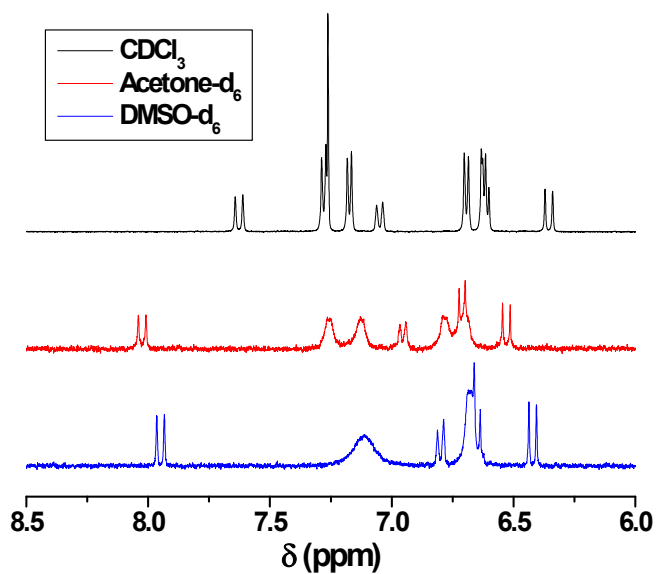


Figure ESI-3. The ^1H NMR spectra of compound **4a** with chemical shift ranged from ~ 6.3 ppm to ~ 8.0 ppm in deuterated solvents of CDCl_3 , Acetone-d_6 and DMSO-d_6 .

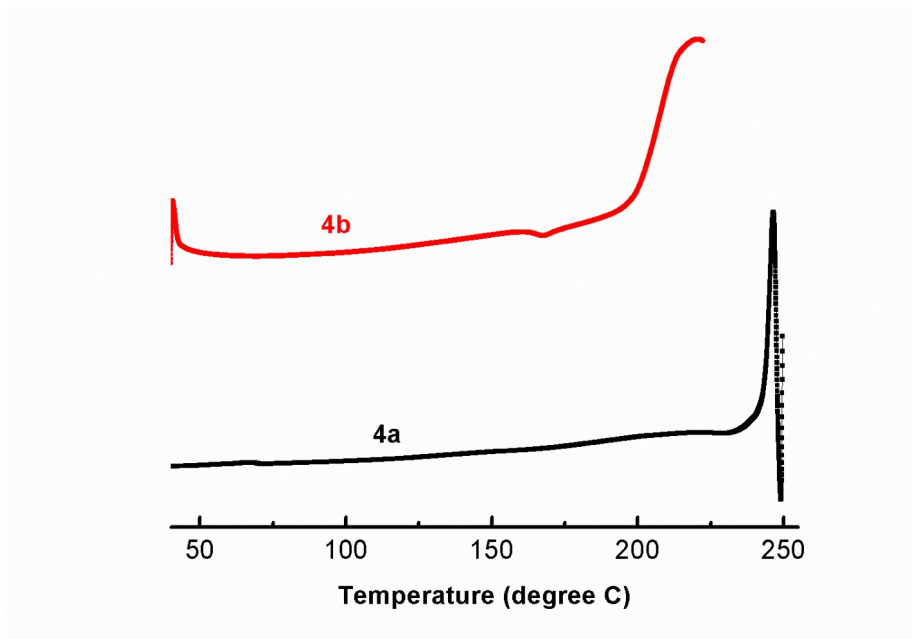


Figure ESI-4. DSC curves of chromophores **4a** and **4b** with a heating rate of $10\text{ }^\circ\text{C/min}$ in nitrogen.

References:

1. Yanagisawa, S., Adeka Corporation, 2010. Compound, optical filter and optical recording material using the same. US Patent 7,695,793.
2. Caputo, G. and Della Ciana, L., 2004. Symmetric, monofunctionalised polymethine dyes labelling reagents. US Patent 6,747,159.
3. a) He, Mingqian, Thomas M. Leslie, and John A. Sinicropi. "α-Hydroxy ketone precursors leading to a novel class of electro-optic acceptors." *Chemistry of Materials* 14, no. 5 (2002): 2393-2400. b) Liu, Sen, Marnie A. Haller, Hong Ma, Larry R. Dalton, Sei-Hum Jang, and Alex K-Y. Jen. "Focused Microwave-Assisted Synthesis of 2,5-Dihydrofuran Derivatives as Electron Acceptors for Highly Efficient Nonlinear Optical Chromophores." *Advanced Materials* 15, no. 7-8 (2003): 603-607.
4. (a) Teng, C. C., and H. T. Man. "Simple reflection technique for measuring the electro-optic coefficient of poled polymers." *Applied Physics Letters* 56, no. 18 (1990): 1734-1736. (b) Park, Dong H., Chi H. Lee, and Warren N. Herman. "Analysis of multiple reflection effects in reflective measurements of electro-optic coefficients of poled polymers in multilayer structures." *Optics Express* 14, no. 19 (2006): 8866-8884.