

**SUPPLEMENTARY INFORMATION FOR:**

**Trends in Optical Nonlinearity and Thermal Stability in Electro-optic Chromophores based upon the 3-(Dicyanomethylene)-2,3-dihydrobenzothiophene-1,1-dioxide Acceptor**

Zhongying Hu, Alain Fort, Marguerite Barzoukas, Alex K.-Y. Jen, Stephen Barlow, and Seth R. Marder

**Experimental Details**

**General Procedures.** NMR spectra were obtained at a General Electric QE300 NMR spectrometer (300 MHz for  $^1\text{H}$ ) or a Bruker AM500 NMR spectrometer (500 MHz for  $^1\text{H}$ ). Chemical shifts are reported relative to tetramethylsilane (TMS) and were referenced using internal TMS for  $^1\text{H}$  spectra and using the solvent peaks for  $^{13}\text{C}$  spectra. UV-visible spectra were recorded on an HP 8452A Diode-Array Spectrophotometer. Elemental analyses were performed by the analytical faculty at the California Institute of Technology. Differential scanning calorimetry data were obtained on a Perkin Elmer DSC-7. Mass spectra were acquired by the University of California, Riverside Mass Spectrometry Center or by the Caltech Biology/Chemistry Mass Spectrometry Facility. Values of  $\mu\beta$  were determined by EFISH (electric field induced second harmonic generation) using 1.9  $\mu\text{m}$  fundamental radiation in

dichloromethane, using a set-up similar to that previously described.<sup>1</sup> Synthetic procedures requiring anhydrous conditions were performed in an atmosphere of dry nitrogen. Where necessary THF was distilled from sodium/benzophenone ketyl. Commercial reagent grade solvents and chemicals were used as obtained.

**2-[4-(Di-*n*-butylamino)styryl]thiophene (9).** To a solution of 3.75 g 4-(di-*n*-butylamino)benzaldehyde and 6.36 g of 2-thienylmethyl triphenylphosphonium chloride in 150 mL absolute ethanol, EtOH, was added a freshly prepared sodium ethoxide solution in ethanol (0.54 g sodium dissolved in 60 mL EtOH) dropwise under nitrogen. The reaction mixture was refluxed for 3 hr, and then cooled to room temperature. A oily liquid was obtained by adding 125 mL water and separating it from the upper, clear solution. The viscous liquid was extracted with dichloromethane, and the extract was dried over magnesium sulfate. Evaporation of solvent gave a yellow liquid, which was subjected to column chromatography (silica, dichloromethane) to give 4.48 g of *E* and *Z* isomers of **9**, in a total yield of 88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) *E*-isomer, δ 7.31 (d, *J* = 8.7 Hz, 2 H), 6.94 (d, *J* = 3.1 Hz, 2 H), 6.92 (d, *J* = 16.0 Hz, 1 H), 6.90 (m, 1H), 6.82 (d, *J* = 15.9 Hz, 1 H), 6.59 (d, *J* = 8.6 Hz, 2 H), 3.26 (t, *J* = 7.7 Hz, 4 H), 1.56 (p, *J* = 7.5 Hz, 4 H), 1.34 (sext, *J* = 7.3 Hz, 4 H), 0.96 (t, *J* = 7.4 Hz, 6H). HRMS(FAB); Calcd for C<sub>20</sub>H<sub>27</sub>NS: 313.1864. Found 313.1872. *Z*-isomer, 7.22 (d, *J* = 8.65 Hz, 2 H), 7.09(d, *J* = 4.6 Hz, 1 H), 7.07(d, *J* = 4.6 Hz, 1 H), 7.01(m, 1H), 6.55(d, *J* = 8.65 Hz, 2 H), 6.46(d, *J* = 12.85 Hz, 1 H),

6.42(d,  $J = 12.85$  Hz, 1 H), 3.28 (t,  $J = 7.65$  Hz, 4 H), 1.56 (p,  $J = 7.49$  Hz, 4 H), 1.35 (sext,  $J = 7.34$  Hz, 4 H), 0.94 (t,  $J = 7.35$  Hz, 6H).

**2-[4-(Di-n-butylamino)styryl]thiophene-5-carboxaldehyde (12).** To a solution of 2.5 g (8.0 mmol) of **9** in 100 mL THF under nitrogen, was added 3.5 mL of 2.5 M n-butyl lithium in hexane at  $-78$  °C. The reaction mixture was stirred at  $-78$  °C for 30 min.; the cooling bath was then removed, the reaction mixture was stirred for another 30 min. allowing the temperature to rise to 0 °C. Then the reaction mixture was cooled to  $-78$  °C again and 0.68 mL (0.64 g, 8.75 mmol) of DMF was added. The reaction mixture was stirred for 2 hr after removing the cooling bath, poured into 100 mL of 10% HCl and extracted with dichloromethane. The extract was washed with water ( $2 \times 50$  mL) and dried over anhydrous magnesium sulfate. Evaporation of solvent gave a brown thick liquid, which was subjected to flash column chromatography to give **12**, 2.1 g, yield 77%. From the *E* isomer of **9**, *E*-**12** was obtained.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  9.79 (s, 1 H), 7.60 (d,  $J = 3.54$  Hz, 1 H), 7.34 (d,  $J = 8.65$  Hz, 2 H), 7.06 (d,  $J = 15.8$  Hz, 1 H), 7.01 (d,  $J = 3.7$  Hz, 1 H), 6.94 (d,  $J = 15.9$  Hz, 1 H), 6.59 (d,  $J = 8.9$  Hz, 2 H), 3.28 (t,  $J = 7.7$  Hz, 4 H), 1.56 (quint,  $J = 7.5$  Hz, 4 H), 1.35 (sext,  $J = 7.3$  Hz, 4 H), 0.94 (t,  $J = 7.35$  Hz, 6H). HRMS(FAB); Calcd for  $\text{C}_{20}\text{H}_{27}\text{NOS}$ : 341.1813. Found 341.1822. From the *Z*-**9**, *Z*-**12** was obtained.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) 9.79 (s, 1 H), 7.56 (d,  $J = 4.11$  Hz, 1 H), 7.34 (d,  $J = 8.65$  Hz, 2 H), 7.10 (d,  $J = 4.1$  Hz, 1 H), 6.63 (d,  $J = 12.85$  Hz, 1 H), 6.54 (d,  $J = 8.51$  Hz, 2 H), 6.42 (d,  $J = 12.26$  Hz, 1 H),

3.28 (t,  $J = 7.65$  Hz, 4 H), 1.56 (p,  $J = 7.49$  Hz, 4 H), 1.35 (h,  $J = 7.34$  Hz, 4 H), 0.94 (t,  $J = 7.35$  Hz, 6H).

**Chromophore 15.** A mixture of 300 mg (0.88 mmol) **12** and 285 mg (0.89 mmol) **2** in 50 mL acetic anhydride was refluxed under nitrogen for 20 min. and cooled to room temperature. The reaction mixture was poured into 100 mL and stirred for 10 min., then extracted with dichloromethane. The extract was washed with water, saturated sodium bicarbonate and brine, dried over anhydrous magnesium sulfate. Evaporation of solvent gave a dark green crystalline compound that was further washed with ethanol and dried to give 350 mg **15**, yield 72%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 8.83 (d,  $J = 7.76$  Hz, 1 H), 8.71 (s, 1 H), 7.97 (d,  $J = 7.23$  Hz, 1 H), 7.87 (d,  $J = 3.90$  Hz, 1 H), 7.82 (m, 2 H), 7.41 (d,  $J = 8.53$  Hz, 2 H), 7.28 (d,  $J = 15.75$  Hz, 1 H), 7.15 (d,  $J = 4.29$  Hz, 1 H), 7.02 (d,  $J = 15.77$  Hz, 1 H), 6.61 (d,  $J = 8.92$  Hz, 2 H), 3.31 (t,  $J = 7.65$  Hz, 4 H), 1.58 (p,  $J = 7.49$  Hz, 4 H), 1.36 (sext,  $J = 7.34$  Hz, 4 H), 0.96 (t,  $J = 7.35$  Hz, 6H). UV-Vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  744 nm. HRMS(FAB); Calcd for  $\text{C}_{32}\text{H}_{31}\text{N}_3\text{O}_2\text{S}_2$ : 553.1857. Found 553.1816. Analysis calcd for  $\text{C}_{32}\text{H}_{31}\text{N}_3\text{O}_2\text{S}_2$ : C, 69.41; H, 5.64; N, 7.59. Found, C, 69.29; H, 5.93; N, 7.48.

**4-(Diphenylamino)benzaldehyde (7).** In a three-necked round-bottomed flask, equipped with reflux condenser, dropping funnel, magnetic stirring and nitrogen, was placed 36 mL DMF. While the flask was cooled in an ice-bath, 12.1 mL phosphorus oxytrichloride was added

dropwise, followed by 25 g (0.1 mol) solid triphenylamine. The reaction mixture was refluxed for 3 hr, then cooled and poured over crushed ice (about 150 g) in a beaker. The precipitate remained in the flask was washed with 100 mL cold water and added to the beaker. The solution was neutralized to pH 6 – 8 by adding saturated aqueous sodium acetate. The product began to precipitate while aqueous sodium acetate was added. The neutral mixture was stored in refrigerator overnight. The precipitate was filtered off and washed with water, and dissolved in minimum amount of dichloromethane for column chromatography. The first fraction gave 20 g of **7**, yield 72%.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ) 9.78 (s, 1 H), 7.65 (d,  $J = 8.7$  Hz, 2 H), 7.31 – 7.35 (m, 4 H), 7.12 – 7.17 (m, 6 H), 6.99 (d,  $J = 8.7$  Hz). The second fraction gave 2 g of 4,4'-diformylated product:  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ), 9.87 (s, 2 H), 7.75 (d,  $J = 8.7$  Hz, 4 H), 7.38 (m, 2 H), 7.27 (m, 3 H), 7.16 (d,  $J = 8.7$  Hz, 4 H).

**2-[4-(Diphenylamino)styryl]thiophene (10).**<sup>2</sup> This compound was synthesized in the same way as **9** and used without further characterization in the synthesis of **13**.

**2-[4-(Diphenylamino)styryl]thiophene-5-carboxaldehyde (13).** The same procedure as for **12** was used. Yield 90 %.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ),  $\delta$  9.88 (s, 1 H), 7.86 (d,  $J = 3.89$  Hz, 1 H), 7.54 (d,  $J = 8.61$  Hz, 2 H), 7.37 (d,  $J = 16.42$  Hz, 1 H), 7.35-7.31 (m, 5 H), 7.25 (d,  $J = 16.15$  Hz, 1 H), 7.12 – 7.09 (m, 6H), 7.00 (d,  $J = 8.55$  Hz, 2 H). HRMS(FAB); Calcd for  $\text{C}_{15}\text{H}_{19}\text{NOS}$ : 381.1187.

Found 381.1187.

**Chromophore 16.** A mixture of 500 mg (1.31 mmol) of **13** and 420 mg (1.31 mmol) of 3-dicyanomethylene-2,3-dihydrobenzothiophene-1,1-oxide in 60 mL acetic anhydride was refluxed under nitrogen for 30 min. and cooled down to room temperature. The precipitated product was filtered and washed with additional 20 mL acetic anhydride and dried to give 500 mg of **16**. Yield 64%. It was further recrystallized in acetonitrile for elemental analysis.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.83 (dd,  $J = 8.02$  Hz,  $J = 1.25$  Hz, 1 H), 8.69 (s, 1 H), 7.99 (dd,  $J = 7.0$  Hz,  $J = 1.5$  Hz, 1 H), 7.93 (d,  $J = 4.2$  Hz, 1 H), 7.88 (m, 2 H), 7.43 (d,  $J = 8.8$  Hz, 2 H), 7.33 – 7.27 (m, 6 H), 7.20 (d,  $J = 16.01$  Hz, 1 H), 7.15 – 7.10 (m, 6 H), 7.01 (d,  $J = 8.6$  Hz, 2 H). UV-Vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  670 nm ( $\log \epsilon_{\text{max}} = 4.63$ ). HRMS(FAB); Calcd for  $\text{C}_{36}\text{H}_{23}\text{N}_3\text{O}_2\text{S}_2$ : 593.1231. Found 593.1237. Analysis calcd for  $\text{C}_{36}\text{H}_{23}\text{N}_3\text{O}_2\text{S}_2$ : C, 72.83; H, 3.90; N, 7.08. Found, C, 72.46; H, 3.91; N, 6.68.

**2-[4-(Dimethylamino)styryl]thiophene (11)**<sup>3,4</sup> and **2-[4-(Dimethylamino)styryl]thiophene-5-carboxaldehyde (14)**.<sup>5,6</sup> These compounds were synthesized in analogy with **9** and **12** and used without further characterization in the synthesis of **17**.

**Chromophore 17.** A mixture of 500 mg (1.78 mmol) **2** and 460 mg (1.79 mmol) 2-(4-N, N-dimethylamino) styrenylthiophene-5-carboxaldehyde and 0.5 mL piperidine in 150 mL methanol

was refluxed under nitrogen for 6 hr. The reaction mixture was cooled to room temperature. The precipitate was filtered off and washed with additional ethanol then dried to give 200 mg of 17, yield 24%. mp 240 – 241 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 8.83 (d, *J* = 7.7 Hz, 1 H), 8.71 (s, 1 H), 7.97 (d, *J* = 6.9 Hz, 1 H), 7.88 (d, *J* = 3.92 Hz, 1 H), 7.82 (m, 2 H), 7.43 (d, *J* = 8.75 Hz, 2 H), 7.30 (d, *J* = 15.9 Hz, 1 H), 7.07 (d, *J* = 15.8 Hz, 1 H), 6.70 (d, *J* = 7.92 Hz, 2 H), 3.04 (s, 6 H). HRMS(FAB); Calcd for C<sub>26</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: 469.0918. Found 469.0956. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{\max}$  704 nm (log  $\epsilon$  = 4.54).

**4-Tri-*n*-butylstannyl-*N,N*-di-*n*-butylaniline (18).** To a solution of 10 g (35 mmol) 4-bromo-*N,N*-di-*n*-butylaniline in 150 mL THF at -78 °C, was added dropwise under nitrogen 16.9 mL (2.5 M in hexane, 42.25 mmol) of *n*-butyl lithium. The reaction mixture was stirred at -78°C for 30 min., then 12.59 mL (15.10 g, 46.5 mmol) of tri-*n*-butyltin chloride was added dropwise. The ice-bath was removed and the temperature was allowed to ambient temperature while being stirred for 1hr. The reaction mixture was poured into 200 mL brine. The organic layer was washed with brine twice and dried over anhydrous sodium sulfate. 23 g of 4-tributylstannyl-*N,N*-dibutylaniline was obtained as a liquid upon evaporation of solvent, and was used directly in next step without further purification.

**2-[4-(Di-*n*-butylamino)phenyl]thiophene-5-carboxaldehyde (19).** A degassed solution of 23 g

(46.5 mmol) **18**, 8.9 g (46.5 mmol) 5-bromo-2-thiophenecarboxaldehyde and 1.12 g (1.7 mmol)  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  in 150 mL DMF was heated under nitrogen at 80 °C for 10 min, then cooled to 25 °C and stirred at 25 °C overnight. A crystalline solid precipitated from the solution. The reaction mixture was cooled to 0 °C and the precipitate was filtered off and washed with hexane. The precipitate was identified as 2,2'-bithiophene-5,5'-dicarboxaldehyde (3.5 g, 68% from 5-bromo-2-thiophenecarboxaldehyde). The filtrate was poured into 200 mL water and extracted with hexane. The extract was washed with water and dried over anhydrous sodium sulfate. Evaporation of solvent gave a brown liquid (20 g) that was further purified to give 1.5 g of **19**, yield 10% (from **18**).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) 9.83 (s, 1H), 7.73 (d,  $J = 3.6$  Hz, 1H), 7.58 (d,  $J = 9.0$  Hz, 2H), 7.27 (d,  $J = 3.6$  Hz, 1H), 6.67 (d,  $J = 9.0$  Hz, 2H), 3.34 (t,  $J = 7.66$  Hz, 4 H), 1.65 (p,  $J = 7.51$  Hz, 4 H), 1.37 (sext,  $J = 7.51$  Hz, 4 H), 0.96 (t,  $J = 7.32$  Hz, 6 H). HRMS(FAB); Calcd for  $\text{C}_{19}\text{H}_{25}\text{NOS}$ : 315.1657. Found 315.1680.

**Chromophore 20.** A mixture of 1.5 g (4.7 mmol) **19** and 1 g (3.6 mmol) **2** in 100 mL acetic anhydride was heated at 120 °C for 30 min, then cooled to room temperature and poured into 150 mL water. The precipitate was filtered off and washed with hexane and air dried to give 1.0 g crude product, which was further recrystallized from ethanol to give green crystals of **20**, 500 mg, yield 26%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) 8.83 (d,  $J = 7.75$  Hz, 1 H), 8.69 (s, 1 H), 7.98 (d,  $J = 3.99$  Hz, 1 H), 7.96 (d,  $J = 7.09$  Hz, 1 H), 7.80 (m, 2H), 7.61 (d,  $J = 8.83$  Hz, 2 H), 7.38 (d,  $J = 4.33$



Hz, 1 H), 6.62 (d,  $J = 8.83$  Hz, 2 H), 3.34 (t,  $J = 7.66$  Hz, 4 H), 1.59 (p,  $J = 7.51$  Hz, 4 H), 1.37 (sext,  $J = 7.51$  Hz, 4 H), 0.96 (t,  $J = 7.32$  Hz, 6 H). UV-Vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  702 nm (log  $\epsilon = 4.62$ ). HRMS(FAB); Calcd for  $\text{C}_{30}\text{H}_{29}\text{N}_3\text{O}_2\text{S}_2$ : 527.1701. Found 527.1699. Analysis calcd for  $\text{C}_{30}\text{H}_{29}\text{N}_3\text{S}_2\text{O}_2$ : C, 68.28; H, 5.54; N, 7.96. Found, C, 68.10; H, 5.73; N, 7.77.

**2-[2-[5-(Diphenylamino)thien-2-yl]vinyl]thiophene-5-carboxaldehyde (22).** The same procedure as for **12** was used. Yield 95%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), 9.79 (s, 1 H), 7.58 (d,  $J = 3.71$  Hz, 1 H), 7.26 – 7.30 (m, 4 H), 7.06 – 7.18 (m, 7 H), 6.97 (d,  $J = 3.9$  Hz, 1 H), 6.86 (d,  $J = 3.86$  Hz, 1 H), 6.70 (d,  $J = 15.6$  Hz, 1 H), 6.46 (d,  $J = 3.9$  Hz, 1 H). HRMS(FAB); Calcd for  $\text{C}_{23}\text{H}_{17}\text{NOS}_2$ : 387.0751. Found 387.0752.

**Chromophore 23.** The same procedure as for **16** was used. Yield 76%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ), 8.83 (d,  $J = 7.78$  Hz, 1 H), 8.67 (s, 1 H), 7.96 (d,  $J = 7.0$  Hz, 1 H), 7.78 – 7.84 (m, 3 H), 7.10 – 7.30 (m, 11 H (10 phenyl-H, and 1H on C=C bridge)), 7.07 (d,  $J = 4.25$  Hz, 1 H), 6.97 (d,  $J = 3.98$  Hz, 1 H), 6.69 (d,  $J = 15.50$  Hz, 1 H), 6.42 (d,  $J = 4.0$  Hz, 1 H). UV-Vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  738 nm (log  $\epsilon = 4.62$ ). HRMS(FAB); Calcd for  $\text{C}_{34}\text{H}_{21}\text{N}_3\text{O}_2\text{S}_3$ : 599.0796. Found 599.0797. Analysis calcd for  $\text{C}_{34}\text{H}_{21}\text{N}_3\text{O}_2\text{S}_3$ : C, 68.09; H, 3.53; N, 7.01. Found, C, 68.23; H, 3.44; N, 6.87.

**2-[4-(Ethyl-2-hydroxyethylamino)styryl]thiophene (26).** A similar procedure as for **10** was

used. Upon adding water, the product was crystallized out and collected. Yield 79%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) 7.32 (d,  $J = 8.70$  Hz, 2 H), 7.10 (dd,  $J = 4.2$  Hz,  $J = 1.8$  Hz, 1 H), 7.02 (d,  $J = 15.90$  Hz, 1 H), 6.96 (m, 2 H), 6.83 (d,  $J = 16.2$  Hz, 1 H), 6.72 (d,  $J = 8.7$  Hz, 2 H), 3.80 (q  $J = 5.0$  Hz, 2 H), 3.50 (t,  $J = 5.74$  Hz, 2 H), 3.43 (q,  $J = 7.10$  Hz, 2 H), 1.15 (t,  $J = 7.00$  Hz, 3 H). HRMS(FAB); Calcd for  $\text{C}_{16}\text{H}_{19}\text{NOS}$ : 273.1187. Found 273.1191.

**2-[4-(Ethyl-2-hydroxyethylamino)styryl]thiophene-5-carboxaldehyde (28).** The same procedure as for **12** was used starting from 2 g (7.3 mmol) of **26**, 8.8 mL *n*-butyl lithium (2.5 M in hexane, 22 mmol) and 1.5 mL of DMF. Yield 90%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) 9.79 (s, 1 H), 7.61 (d,  $J = 3.9$  Hz, 1 H), 7.36 (d,  $J = 9.0$  Hz, 2 H), 7.06 (d,  $J = 15.90$  Hz, 1 H), 7.03 (d,  $J = 3.6$  Hz, 1 H), 6.97 (d,  $J = 16.2$  Hz, 1 H), 6.72 (d,  $J = 9.0$  Hz, 2 H), 3.81 (q  $J = 4.5$  Hz, 2 H), 3.50 (t,  $J = 5.70$  Hz, 2 H), 3.45 (q,  $J = 7.20$  Hz, 2 H), 1.17 (t,  $J = 6.9$  Hz, 3 H). HRMS(FAB); Calcd for  $\text{C}_{17}\text{H}_{19}\text{NO}_2\text{S}$ : 301.1136. Found 301.1142.

**Chromophore 30.** A mixture of 2 g (6.6 mmol) of **28**, 1.5 g (1.31 mmol) **2** and 0.5 mL pyridine in 60 mL *n*-pentanol was refluxed under nitrogen for 30 min. and cooled to room temperature. The precipitated product was filtered and washed with additional 25 mL *n*-pentanol and dried to give 1.5 g of **30**. Yield 44%. It was further recrystallized in acetonitrile for elemental analysis.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J = 7.8$  Hz, 1 H), 8.71 (s, 1 H), 7.97 (d,  $J = 7.2$  Hz, 1 H), 7.88 (d,  $J =$

4.4 Hz, 1 H), 7.80 (m, 2 H), 7.41 (d,  $J = 8.9$  Hz, 2 H), 7.28 (d,  $J = 15.8$  Hz, 1 H), 7.17 (d,  $J = 4.0$  Hz, 1 H), 7.05 (d,  $J = 15.9$  Hz, 1 H), 6.73 (d,  $J = 8.9$  Hz, 2 H), 3.84 (q,  $J = 5.5$  Hz, 2 H), 3.54 (t,  $J = 5.7$  Hz, 2 H), 3.49 (q,  $J = 7.1$  Hz, 2 H), 1.50 (t,  $J = 5.6$  Hz, 1H), 1.20 (t,  $J = 7.0$  Hz, 3 H). UV-Vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  710 nm ( $\log \epsilon_{\text{max}} = 4.66$ ). HRMS(FAB); Calcd for  $\text{C}_{28}\text{H}_{23}\text{N}_3\text{O}_3\text{S}_2$ : 513.1180. Found 513.1164. Analysis calcd for  $\text{C}_{28}\text{H}_{23}\text{N}_3\text{O}_3\text{S}_2$ : C, 65.48; H, 4.51; N, 8.18. Found, C, 65.15; H, 4.64; N, 7.88.

**2-{4-[Bis(2-hydroxyethyl)amino]styryl}thiophene (27)**. The same procedure as for **26** was used. Yield 60%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 8.1$  Hz, 2H), 7.10 (d,  $J = 3.9$  Hz, 1H), 7.02 (d,  $J = 16.0$  Hz, 1H), 6.97 (m, 2 H), 6.83 (d,  $J = 16.01$  Hz, 1H), 6.67 (d,  $J = 8.1$  Hz, 2H), 3.87 (t,  $J = 3.8$  Hz, 4H), 3.60 (t,  $J = 3.8$  Hz, 4 H).

**2-{4-[Bis(2-hydroxyethyl)amino]styryl}thiophene-5-carboxaldehyde (29)**. The same procedure as for **28** was used. Yield 60%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  9.80 (s, 1 H), 7.62 (d,  $J = 3.9$  Hz, 1 H), 7.37 (d,  $J = 8.7$  Hz, 2 H), 7.07 (d,  $J = 15.9$  Hz, 1 H), 7.05 (d,  $J = 3.9$  Hz, 1 H), 6.98 (d,  $J = 15.9$  Hz, 1 H), 6.68 (d,  $J = 8.7$  Hz, 2 H), 3.90 (t,  $J = 4.8$  Hz, 4 H), 3.64 (t,  $J = 4.8$  Hz, 4 H), 2.8 (s, broad, 2 H). HRMS(FAB); Calcd for  $\text{C}_{17}\text{H}_{19}\text{NO}_3\text{S}$ : 317.1085. Found 317.1075.

**Chromophore 31**. The same procedure as for **30** was used. Yield 58%.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )

8.68 (s, 1H), 8.65 (d,  $J = 7.2$  Hz, 1H), 8.19 (dd,  $J = 6.0$  Hz,  $J = 1.5$  Hz, 1H), 8.05-7.99 (m, 3H), 7.54 (d,  $J = 9.0$  Hz, 2 H), 7.51 (d,  $J = 4.3$  Hz, 1H), 7.38 (s, 2H, vinyl protons on *E* C=C), 6.76 (d,  $J = 9.0$  Hz, 2H), 4.75 (s, broad, 2 H), 3.56 (q  $J = 6.0$  Hz, 4H), 3.49 (t,  $J = 5.9$  Hz, 4H). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{\max}$  688 nm (log  $\epsilon_{\max} = 4.62$ ). HRMS(FAB); Calcd for C<sub>28</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>: 529.1130. Found 529.1142. Analysis calcd for C<sub>28</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>: C, 63.50; H, 4.38; N, 7.93. Found, C, 63.35; H, 4.76; N, 7.81.

**Chromophore 32.** The same procedure as for **16** was used. Yield 40 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 8.83 (d,  $J = 8.0$  Hz, 1H), 8.7 (s, 1H), 7.96 (d,  $J = 7.26$  Hz, 1H), 7.86 (d,  $J = 4.2$  Hz, 1H), 7.81 (m, 2 H), 7.39 (d,  $J = 8.9$  Hz, 2H), 7.27 (d,  $J = 15.94$  Hz, 1H), 7.17 (d,  $J = 4.1$  Hz, 1H), 7.05 (d,  $J = 15.81$  Hz, 1H), 6.71 (d,  $J = 8.50$  Hz, 2H), 4.24 (t,  $J = 6.15$  Hz, 2H), 3.60 (t,  $J = 6.12$  Hz), 3.46 (q,  $J = 6.8$  Hz, 2H), 2.04 (s, 3H), 1.20 (t,  $J = 6.9$  Hz, 3H). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{\max}$  704 nm (log  $\epsilon_{\max} = 4.74$ ). HRMS(FAB); Calcd for C<sub>30</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>: 555.1286. Found 555.1287.

**3-Dicyanomethylene-4,4-dimethyl-2,3,4,5-tetrahydrothiophene-1,1-dioxide (3).** A suspension of 1.0 g (6.2 mmol) of **5**,<sup>7,8</sup> 1.0 g of malononitrile and 0.5 g of anhydrous sodium acetate in 100 mL absolute ethanol was refluxed under nitrogen overnight. Upon cooling to room temperature, 100 mL water was added. The resulting solution was acidified with 5% HCl and extracted twice each with 100 mL dichloromethane. The combined extract was washed with 50 mL water and

dried over sodium sulfate. Evaporation of solvent gave a yellow oil, that solidified upon treatment with petroleum ether. Further recrystallization from EtOH/petroleum ether gave white crystals of **32**, 1.0 g, yield 77%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) 4.30 (s, 2H), 3.27 (s, 2H), 1.74 (s, 6H). HRMS(FAB); Calcd for  $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ : 210.0463. Found 210.0454.

**Chromophore 33.** The same procedure as for **15** was used, using **3** in place of **2**. The product was purified by column chromatography (silica, 25% ethyl acetate in petroleum ether). Yield 38%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.42 (s, 1H), 7.78 (d,  $J = 3.80$  Hz, 1H), 7.40 (d,  $J = 8.7$  Hz, 2H), 7.30 (d,  $J = 15.9$  Hz, 1H), 7.13 (d,  $J = 4.2$  Hz, 1H), 7.01 (d,  $J = 15.8$  Hz, 1H), 6.62 (d,  $J = 8.7$  Hz, 2H), 3.32 (t,  $J = 7.68$  Hz, 4H), 3.24 (s, 2 H), 1.74 (s, 6H), 1.59 (sext,  $J = 6.0$  Hz, 4H), 1.37 (sext,  $J = 7.4$  Hz, 4H), 0.97 (t,  $J = 7.2$  Hz, 6H). UV-Vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  724 nm ( $\log \epsilon_{\text{max}} = 4.52$ ). HRMS(FAB); Calcd for  $\text{C}_{30}\text{H}_{35}\text{N}_3\text{O}_2\text{S}$ : 533.2170. Found 533.2078. Analysis calcd for  $\text{C}_{30}\text{H}_{35}\text{N}_3\text{O}_2\text{S}$ : C, 67.51; H, 6.61; N, 7.87. Found, C, 67.33; H, 6.68; N, 7.70.

## References

- (1) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631-10643.
- (2) Jen, A. K.-Y.; Ma, H.; Wu, X.; Wu, J.; Liu, S.; Herguth, P.; Marder, S. R.; Shu, C.-F.; Dalton, L. R. *Nonlinear Optics* **1999**, *22*, 9-15.
- (3) Lee, I. S.; Seo, H.; Chung, Y. K. *Organometallics* **1999**, *18*, 1091-1096.
- (4) Jeffery, T.; Ferber, B. *Tetrahedron Lett.* **2002**, *44*, 193-197.
- (5) Chen, C. T.; Marder, S. R. *Adv. Mater.* **1995**, *7*, 1030-1033.
- (6) Farrell, T.; Meyer-Friedrichsen, T.; Heck, J.; Manning, A. R. *Organometallics* **2000**, *19*, 3410-3419.
- (7) Truce, W. E.; Knospe, R. H. *J. Am. Chem. Soc.* **1955**, *77*, 5063-5067.
- (8) Truce, W. E.; Babbister, W. W.; Knospe, R. H. *J. Am. Chem. Soc.* **1962**, *27*, 2821.