Synthesis and Relative Thermal Stabilities of Diphenylamino- vs Piperidinyl-Substituted Bithiophene Chromophores for Nonlinear Optical Materials

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Electrooptic poled polymers can be used in a variety of photonic applications involving the switching or modulation of light. These polymers contain second-order nonlinear optical chromophores that have been aligned by electric-field poling near the glass transition temperature of the polymer host. Loss of poling-induced alignment of the chromophores results in a decay of the macroscopic nonlinearity and presents an important issue that must be addressed if these materials are to have a commercial impact. Accordingly, researchers have attempted to incorporate chromophores into polymers with glass transition temperatures far in excess of the anticipated operating temperatures, such that over the lifetime of the devices the decay of chromophore alignment is minimized. This has created a need for chromophores that not only are very nonlinear but also have adequate thermal stability to survive the poling process which may occur at temperatures exceeding 200 °C. Accordingly, as part of our ongoing effort to develop chromophores for nonlinear optical applications we synthesized a series bithiophene-based chromophores (Figure 1) with the hope that they may have both high optical nonlinearity and good thermal stability. The donor−acceptor bithiophene chromophores have the advantage of having moderate aromatic stabilization in the ground state, making them more oxidatively stable than the analogous polyene chromophores and more polarizable than the analogous biphenyl chromophores.[4] In addition, several reports in the literature demonstrated that protons α to the amine donor attenuate the thermal stability of other nonlinear optical chromophores.[5] Therefore we examined the relative stability of compounds substituted with either piperidinyl or diphenylamino donors.

Results and Discussion

Synthesis of the Chromophores. As noted above, a series of chromophores was synthesized with either

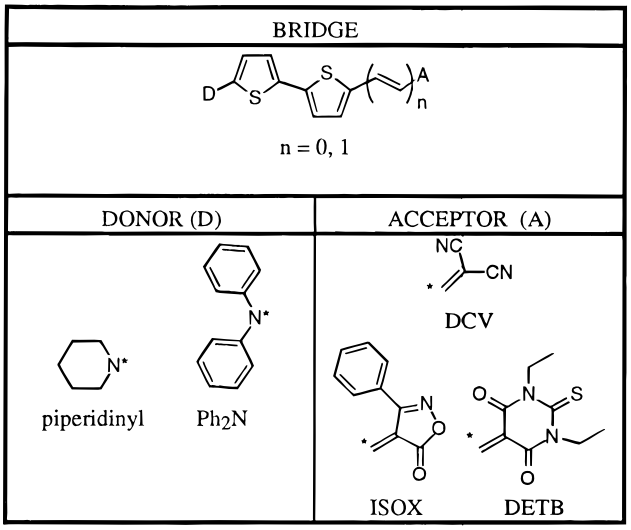

Figure 1. Bithiophene bridges, donors, and acceptors used in the study. (* indicates point of attachment).

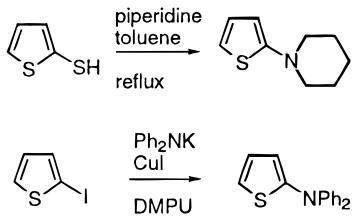

Figure 2. Synthesis of (top) 2-piperidinylthiophene and (bottom) 2-(diphenylamino)thiophene.

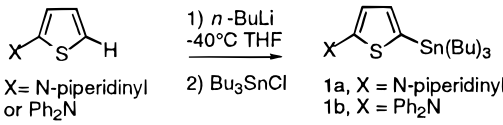

Figure 3. Synthesis of the aminothiophene stannanes.

N-piperidinyl or *N*,*N*-diphenylamino donors and 1,1-dicyanovinyl (DCV), 4-methylidene-3-phenylisoxazolone (ISOX), or 4-methylidenediethylthiobarbituric acid (DETB) acceptors across a conjugated π-bridge containing a bithiophene moiety (Figure 1). The chromophores were assembled in a convergent manner as outlined below. The donor sides of the chromophores, 2-(*N*-piperidinyl)thiophene[6] and 2-(*N*,*N*-diphenylamino)thiophene, were prepared from 2-thiophenethiol[7] and 2-iodothiophene, respectively (Figure 2). The modified Ullman coupling[8] to form 2-(*N*,*N*-diphenylamino)thiophene required the use of stochiometric copper iodide and a polar aprotic solvent such as hexamethylphosphoramide or dimethylpropyleneurea. The use of catalytic copper salts and less polar aprotic solvents yielded either an intractable polymeric mixture from which no appreciable amount of the desired product could be obtained or, under less forcing conditions, no evidence of reaction. The aminothiophenes were then lithiated with *n*-butyllithium and converted to 5-(tri-*n*-butylstannyl)-2-aminothiophenes (Figure 3).

The acceptor sides of the chromophores were prepared from 2-bromothiophene which was treated with lithium

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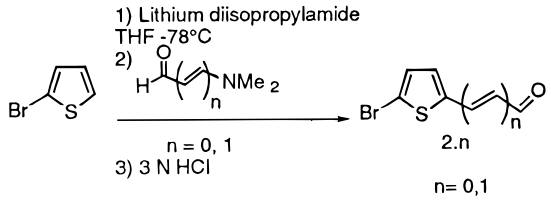


Figure 4. Synthesis of the bromothiophene aldehydes.

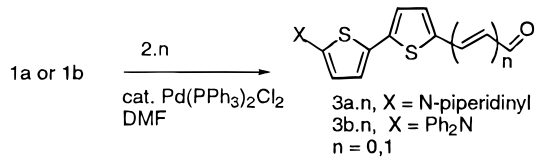


Figure 5. Synthesis of the aminobithiophene aldehydes.

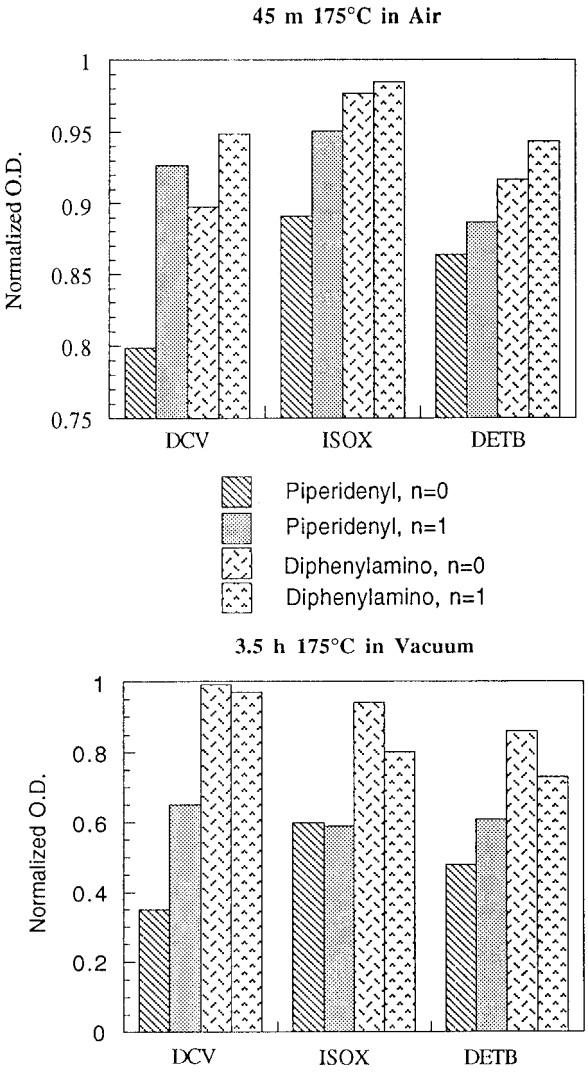
Table 1. Absorption Maxima (λ_{max}) and $\mu\beta$ Values Determined by EFISH in Chloroform at 1.9 μm for the Chromophores(Estimated Error in the $\mu\beta$ Values is ±20%)

compd	λ_{max} (nm) (ligroin), ($CHCl_3$), (NMP)	$\mu\beta/10^{-48}$ (esu)
4a.0	414, 566, 572	1150
4b.0	516, 542, 552	550
4a.1	534, 582, 584	
4b.1	522, 534, 558	740
5a.0	574, 608, 650	960
5b.0	574, 588, 606	725 (dioxane)
5a.1	insol, 632, 642	1780
5b.1	568, 580, 584	1420 (dioxane)
6a.0	574, 632, 650	1170
6b.0	532, 580, 616	1780
6a.1	578, 676, 700	3840
6b.1	534, 578, 610	2200

diisopropylamide to give 2-bromo-5-lithiothiophene, *in situ*. Addition of either dimethylformamide or (dimethylamino)acrolien[9] to the solution of 2-bromo-5-lithiothiophene gave, after aqueous acidic workup, 2-bromothiophene-5-carboxaldehyde and 3-(2-bromothiophene-5-yl)acrolein (Figure 4). The donor and acceptor precursors were coupled using a Stille palladium-catalyzed cross-coupling to give the precursor aldehydes (Figure 5),[10] in yields ranging from 70% to 90%. These precursor aldehydes were then converted to the desired chromophores by Knoevenagel condensation[11] (Figure 6) to give the desired product in high yield. Typically it was necessary to purify the product by recrystallization from ethanol in order to obtain analytically pure materials.

Thermal and Optical Properties of the Chromophores. All of the chromophores in this study have a strong charge-transfer band in the visible region of the spectrum. With increasing solvent polarity the position of the absorption maximum shifts to lower energy, indicative of an increase in the dipole moments upon excitation. While designing the chromophores, one problem we envisioned was the attenuated donor strength of the diphenylamino donor relative to the piperidinyl donor. Synthetically, the reduced donor strength (related to nucleophilicity) of diphenylamine manifested itself in the difficulty of the synthesis of the structurally simple (diphenylamino)thiophene, as noted above. We reasoned that the reduced donor strength would result in attenuated $\mu\beta$ (the dot product of the first hyperpolarizability along the dipole axis and the dipole moment) values compared to those of the dialkylamino chromophores. Consistent with this speculation, in most cases the diphenylamino donor yielded dyes whose absorption maxima were blue shifted and had $\mu\beta$ values of about half those of the analogous piperidinyl dyes. Nonetheless the $\mu\beta$ values are still comparable to or larger than commonly used chromophores, such as Disperse Red 1.[4]

Chart 1. Fraction of Chromophore That Survives heating (bottom) for 3.5 h at 175 °C in Vacuum and (top) 45 min at 175 °C in Air



In an effort to determine the thermal stability of the chromophores, we initially used closed pan differential scanning calorimetry (DSC) measurements.[5] Unfortunately, the T_d (onset of decomposition) was close to T_m (onset of melt) in all cases. We felt that in this case the values obtained from DSC did not give a useful measure of relative thermal stability for the ultimate host−guest polymer system. Accordingly, we examined the chromophore within a poly(methyl methacrylate) film. To do this we fabricated 2% weight to weight dye in poly(methyl methacrylate) solid solution films on glass substrates by spin coating. The films were then heated in air or vacuum in the dark. The change in optical density at the absorption maximum of the visible spectrum (λ_{max}), as a function of time, at various temperatures was determined, and the results are shown in Chart 1. In all cases the diphenylamino chromophores were more

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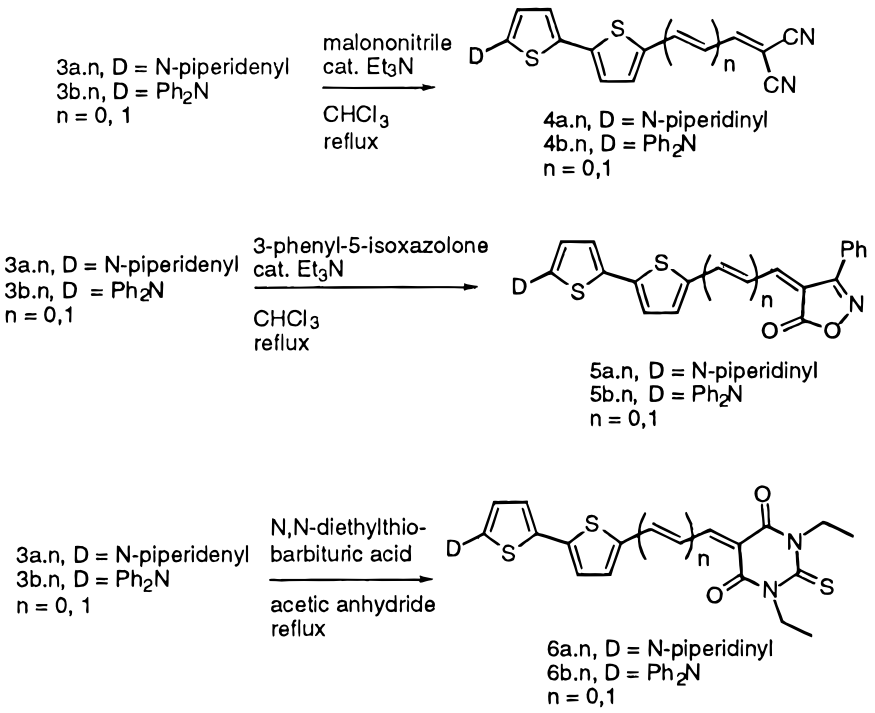

Figure 6. Synthesis of the donor−acceptor bithiophene by Knoevenagel condesation of aminobithiophene aldehydes with (top) malononitrile, (midde) 3-phenyl-5-isoxazolone, and (bottom) 1,3-diethylthiobarbituric acid.

thermally stable than their piperidinyl analogs. We also found that aerobic conditions drastically reduced the life of the chromophores. Surprisingly, the data also suggests that under aerobic conditions the $n = 1$ chromophores are more thermally stable than the $n = 0$ chromophores.

In summary, the results obtained here suggest that in agreement with previous findings for systems in which the thermal stability of (diarylamino)phenyl chromophores were compared to the analogous (dialkylamino)phenyl chromophores,[5] the (diphenylamino)thiophenes are more stable than the piperidinyl chromophores. In addition in several cases optical nonlinearities significantly larger than that of Disperse Red 1 were observed, suggesting that these compounds may be attractive candidates for poled polymer applications.

Experimental Section

Ultraviolet−visible electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array detector or a Perkin-Elmer Lambda 9 spectrophotometer. ^{1}H NMR spectra were recorded at 300 MHz using a General Electric QE-300 or at 500 MHz using a Bruker AM-500. Elemental analyses were performed by Atlantic Microlabs. Chemical shifts were referenced to the chemical shift of the residual protons of the solvent relative to tetramethylsilane. All reactions were performed under nitrogen. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. Dimethylformamide and dimethylpropyleneurea were distilled from calcium hydride under reduced pressure. Copper iodide was prepared using the method of Kauffman[12] and then dried overnight at 100 °C under vacuum. 2-(*N*-Piperidinyl)thiophene was prepared by the method of Hartmann.[6] Bis(triphenylphosphine)palladium(II) chloride, butyllithium, chlorobenzene, (dimethylamino)acrolein, diethylthiobarbituric acid, diphenylamine, malononitrile, 3-phenyl-5-isoxazolone, poly(methyl methacrylate) (PMMA), and tributylchlorostannane were purchased from Aldrich and used as received. 2-Iodothiophene was purchased from Lancaster and used as received. $\mu\beta$ was determined by EFISH (electric field induced second harmonic generation)[13] using 1.9 μm fundamental radiation in chloroform or dioxane. Thin films of dyes in PMMA were prepared by dissolving 20 mg of dye in 10 mL of 10%w/v PMMA in chlorobenzene. Thus an excess of the solution was then applied to square microscope cover slides on a spincoater and spun at 1600 rpm for 90 s. These slides were dried overnight in vacuum, in the dark, before thermal testing. The absorbances were recorded using a glass slide as reference.

2-(*N*,*N*-Diphenylamino)thiophene. To a slurry of hexane washed potassium hydride (31 g, 35% in mineral oil, 275 mmol) in dimethylpropyleneurea (50 mL) was added a solution of *N*,*N*-diphenylamine (46 g, 275 mmol) dropwise over 1 h under nitrogen. The resulting yellow slurry was stirred an additional hour. To the yellow slurry was added freshly prepared anhydrous copper(I) iodide (52 g, 275 mmol), and the mixture was stirred for 1 h by which time all the copper(I) iodide had dissolved giving a dark green turbid solution. The solution was then heated to 80 °C, and a solution of 2-iodothiophene (46 mL, 412 mmol) in dimethylpropyleneurea (75 to 125 mL) was added dropwise over 3 h. The dark mixture was heated until most of the diphenylamine was consumed (10% remained) as determined by gas chromatography. The mixture was then cooled and poured into ethyl acetate (1000 mL) and filtered, concentrated ammonium hydroxide (100 mL), was added and the organic layer was washed with 10% ammonium hydroxide until no blue color was observed. The organic layer was dried over magnesium sulfate and filtered and the solvent removed *in vacuo* to give a thick brown oil. The oil was subsequently subjected to molecular path distillation with the major fraction distilling at 135 °C, 0.005 mmHg. This material was then recrystallized from ethanol to give 27 g (40%) of the title compound: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (ddd, J = 10.82, 7.33, 1.14 Hz, 4 H), 7.26 (ddd, J = 10.82, 1.35, 1.14 Hz, 4 H), 7.14 (tt, J = 7.36, 1.14 Hz, 2 H), 7.13 (dd, J = 5.67, 1.35 Hz, 1 H), 7.01 (dd, J = 5.67, 3.74 Hz, 1 H), 6.86 (dd, J = 3.67, 1.30 Hz, 1 H). Anal. Calcd: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.88; H, 5.84; N, 5.11.

5-(*N*-Piperidinyl)-2-(tri-*n*-butylstannyl)thiophene. To a solution of 2-(*N*-piperidinyl)thiophene (18 g, 100 mmol) in tetrahydrofuran (300 mL) at −78 °C under nitrogen was added *n*-butyllithium (82 mL, 130 mmol, 1.6 M in hexanes). The solution was stirred for 5 min. then warmed to ambient

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temperature. The solution was then cooled with an ice/water bath, tri-n-butylchlorostannane (35 mL, 130 mmol) was added, and the reaction was stirred overnight. The mixture was then added to brine (200 mL). The aqueous layer was extracted with methylene chloride (3 × 50 mL). The combined organic layers were dried with magnesium sulfate, and the solvent was removed *in vacuo* to give the product in quantitative yield contaminated with tri-n-butylchlorostannane residue (about 5%). The product was used without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (d, J = 3.3 Hz, 1 H), 6.25 (d, J = 3.3 Hz, 1 H), 3.2 (t, 7 Hz, 4 H), 2.0−1.0 (5 overlapping m, 33 H).

5-(*N*,*N*-Diphenylsmino)-2-(tri-*n*-butylstannyl)thiophene was prepared by the above method with nearly quantitative yield and used without further purification: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dt, J = 10, 2 Hz, 4 H), 7.1 (dm, J = 10 Hz, 4 H) , 6.97 (tt, J = 7.32, 1.1 Hz, 2 H), 6.91 (d, J = 3.45 Hz, 1 H), 6.77 (d, J = 3.45 Hz, 1 H), 1.6−1.4 (m, 6 H), 1.4−1.2 (m, 12 H), 0.87 (t, J = 5.8 Hz, 9 H).

3-(5-Bromothiophene-2-yl)acrolein. To a solution of diisopropylamine (21.5 mL, 148 mmol) in tetrahydrofuran (200 mL) at −78 C under nitrogen was added *n*-butyllithium (59.2 mL, 148 mmol, 2.5 M in hexanes). The solution was warmed to 0 °C using an ice/water bath and then cooled to −78 °C. To the solution was added 2-bromothiophene (14.2 mL, 148 mmol). The solution was stirred for 1 h at −78 °C, then 3-(dimethylamino)-acrolein (15 mL, 150 mmol) was added, and the solution was allowed to warm to ambient temperature. The mixture was added to 3 N hydrochloric acid (1000 mL) and extracted with methylene chloride (3 × 100 mL). The combined organic layers were dried over magnesium sulfate, and the solvent was removed *in vacuo*. The crude material was distilled (2 mmHg, 110−120 °C) to give 25 g (80% yield) of the title product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (d, J = 7.59 Hz, 1 H), 7.5 (d, J = 15.7 Hz, 1 H), 7.08 (ABq, $\Delta\nu$ = 0.03 ppm, J = 4.4 Hz, 2 H), 6.38 (dd, J = 15.7, 7.6 Hz, 1 H); HRMS calcd m/z = 215.9231, found m/z = 215.9244.

5′-*N*-Piperidinyl-2′,5-bithiophene-2-carboxaldehyde. To a degassed solution of 5-bromo-2-thiophenecarboxaldehyde (10.5 g, 55 mmol) and 2-(tri-*n*-butylstannyl)-5-*N*-piperidinylthiophene (22.3 g, 55 mmol) in dimethylformamide (100 mL) was added bis(triphenylphosphine)palladium(II) chloride (1.4 g, 2 mmol). The mixture was heated to 80 °C for 10 min, then cooled to 40 °C, and stirred under nitrogen for 5 h. The solution was cooled to 0 °C for 10 h and then filtered and washed with cold dimethylformamide to give 10.44 g (80% yield) of the title compound: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1 H), 7.56 (d, J = 4.0 Hz, 1 H), 7.09 (d, J = 4.05 Hz, 1 H), 6.95 (d, J = 3.96, 1 H), 5.99 (d, J = 4.07, 1 H), 3.19 (t, J = 5.65 Hz, 4 H), 1.71 (pent, J = 5.59 Hz, 4 H), 1.59 (pent, J = 5.43 Hz, 2 H): ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.36, 137.91, 126.99, 120.98, 104.76, 51.83, 25.02, 23.61; UV−vis (CH_2Cl_2) λ_{max} 444 nm; (CCl_4) λ_{max} 430 nm; (EtOH) λ_{max} 548 nm; (DMSO) λ_{max} 450 nm; mp 143−145 °C; HRMS calcd m/z = 277.0596, found m/z = 277.0595. Anal. Calcd: C, 60.604; H, 5.461; N, 5.050; O 5.767; S, 23.119. Found: C, 60.66; H, 5.53; N, 5.11; S, 23.05.

(5′-*N*-Piperidinyl-2′,5-bithiophene-2-yl)acrolein was prepared using the above method (90% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (d, J = 7.74 Hz, 1 H), 7.76 (d, J = 15.42 Hz, 1 H), 7.17 (d, J = 4.02 Hz, 1 H), 6.99 (d, J = 4.07 Hz, 1 H), 6.87 (d, J = 4.02, 1 H), 6.33 (dd, J = 15.41, 7.74 Hz, 1 H), 5.95 (d, J = 4.07 Hz, 1 H), 3.17 (dd, J = 5.69, 5.69 Hz, 4 H), 1.70 (pent, J = 5.74 Hz, 4 H), 1.57 (pent, J = 5.38 Hz, 2 H); HRMS calcd m/z = 303.0750, found m/z = 303.0752.

5′-(*N*,*N*-Diphenylamino)-2′,5-bithiophene-2-carboxaldehyde was prepared using the above method (80% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1 H), 7.58 (d, J = 4.1 Hz, 1 H), 7.28 (t, J = 7.9 Hz, 4 H), 7.18 (d, J = 7.63 Hz, 4 H), 7.12 (d, J = 4.01 Hz, 1 H), 7.09 (t, J = 7.39 Hz, 2 H), 7.03 (d, J = 4.01 Hz, 1 H), 6.53 (d, J = 6.53 Hz, 1 H).

(5′-(*N*,*N*-Diphenyl amino)-2′,5-bithiophene-2-yl)acrolein was prepared using the above method (80% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.63 (d, J = 7.8 Hz, 1 H), 7.53 (d, J = 15.6 Hz, 1 H), 7.4−7.3 (m, 4 H), 7.3−7.2 (m, 4 H), 7.2−7.1 (m, 4 H), 7.01 (d, J = 3.9 Hz, 1 H), 6.59 (d, J = 3.9 Hz, 1 H), 6.44 (dd, J = 15.6, 7.8 Hz, 1 H); HRMS calcd m/z = 387.0752, found m/z = 387.0742.

5′-*N*-Piperidinyl-2-(1,1-dicyanovinyl)-2′,5-bithiophene. To a solution of malononitrile (0.8 g, 12 mmol) and 5′-*N*-piperidinyl-2′,5-bithiophene-2-carboxaldehyde (2.61 g, 10 mmol) in chloroform (10 mL) was added triethylamine (1 drop). The solution was heated to reflux for 1 h, then cooled, and dried over magnesium sulfate, and filtered and the solvent removed *in vacuo*. The resulting purple solid was recrystallized from ethanol to give 1.8 g (70 %) of the title product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1 H), 7.45 (d, J = 4.14 Hz, 1 H), 7.20 (d, J = 4.25 Hz, 1 H), 6.92 (d, J = 4.20 Hz, 1 H), 5.99 (d, J = 4.30 Hz, 1 H), 3.25 (t, J = 5.47, 4 H), 1.71 (pent, J = 5.46, 4 H), 1.61 (pent, J = 5.57 Hz, 2 H); ^{13}C NMR (125 MHz**,** $CDCl_3$) δ 163.27, 152.35, 149.05, 149.02, 141.04, 130.53, 129.53, 120.97, 118.90, 115.36, 114.46, 104.89, 71.34, 51.41, 24.93, 23.51; UV−vis (CH_2Cl_2) λ_{max} 560 nm; (CCl_4) λ_{max} 536 nm; (petroleum ether) λ_{max} 414 nm; (NMP) λ_{max} 572 nm; (AcCN) λ_{max} 440 nm; (NMP) λ_{max} 448 nm; mp 169−172 °C; HRMS calcd m/z = 325.0698, found m/z = 325.0707. Anal. Calcd: C, 62.727; H, 4.655; N, 12.913; S, 19.706. Found: C, 62.67; H, 4.59; N, 12.94; S, 19.60.

2-*N*-Piperidinyl-5′-(1,1-dicyano-1,3-butadien-4-yl)-2′,5-bithiophene. The above method was used (70% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 11.8 Hz, 1 H), 7.25 (d, J = 14.6 Hz, 1 H), 7.20 (d, J = 4.1 Hz, 1 H), 7.07 (d, J = 4.2 Hz, 1 H), 6.89 (d, J = 4.0 Hz, 1 H), 6.77 (dd, J = 14.5, 11.8 Hz, 1 H), 5.98 (d, J = 4.1 Hz, 1 H), 3.21 (3 line m, 4 H), 1.76−1.65 (m, 4 H), 1.64−1.57 (m, 2 H); UV−vis (ligroin) λ_{max} 534 nm; ($CHCl_3$) λ_{max} 582 nm; (NMP) λ_{max} 584 nm; HRMS calcd m/z = 351.0858, found m/z = 351.0864. Anal. Calcd: C, 64.93; H, 4.87; N, 9.11.96; S, 18.24. Found: C, 64.78; H, 4.97; N, 11.83; S, 18.93.

5′-(1,1-Dicyanovinyl)-2-(*N*,*N*-diphenylamino-2′,5-bithiophene. The above method was used (75% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1 H), 7.52 (d, J = 4.19, 1 H), 7.32 (t, J = 7.9 Hz, 4 H), 7.2 (d, J = 8.6 Hz, 4 H), 7.21 (d, J = 4.19 Hz, 1 H), 7.14 (t, J = 7.36 Hz, 2 H), 7.01 (d, J = 4.17 Hz, 1 H), 6.48 (d, J = 4.13 Hz, 1 H); UV−vis (ligroin) λ_{max} 516 nm; ($CHCl_3$) λ_{max} 552 nm; (NMP) λ_{max} 542 nm. Anal. Calcd: C, 70.39; H, 3.69; N, 10.26; S, 15.66. Found: C, 70.10; H, 3.76; N, 10.03; S, 15.44.

5′-(1,1-Dicyano-1,3-butadien-4-yl))-2-(*N*,*N*-diphenylamino)-2′,5-bithiophene. The above method was used (70% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 11.7 Hz, 1 H), 7.4−7.1 (m, 13 H), 6.98 (d, J = 4.2 Hz, 1 H), 6.86 (dd, J = 14.7, 11.7 Hz, 1 H), 6.53 (d, J = 4.2 Hz, 1 H); UV−vis (ligroin) λ_{max} 522 nm; ($CHCl_3$) λ_{max} 558 nm; (NMP) λ_{max} 554 nm. Anal. Calcd: C, 71.70; H, 3.93; N, 9.65; S, 14.72. Found: C, 71.61; H, 3.85; N, 9.58; S, 14.62.

5′-*N*-Piperidinyl-2-(3-phenyl-5-oxo-4-isoxazolyl)methylidene)-2′,5-bithiophene. To a solution of 3-phenyl-5-isoxazolone (1 g, 6 mmol) and 5′-*N*-piperidinyl-2′,5-bithiophene-2-carboxaldehyde (1.3 g, 5 mmol) in chloroform (10 mL) was added triethylamine (1 drop), and the solution was heated to reflux for 1 h, then cooled, dried over magnesium sulfate, and filtered and the solvent removed *in vacuo*. The resulting purple solid was recrystallized from ethanol to give 1.5 g (75 %) of the title product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (br s, 1 H), 7.62−7.58 (m, 2 H), 7.55−7.80 (m, 4 H), 7.31 (d, J = 4.22 Hz, 1 H), 7.02 (d, J = 4.24 Hz, 1 H), 6.04 (d, J = 4.28 Hz, 1 H), 3.26 (br t, J = 5.62 Hz, 4 H), 1.71 (br pent, J = 5.34 Hz, 4 H), 1.62 (br sext, J = 5.2 Hz, 2 H); UV−vis (ligroin) λ_{max} 574 nm; ($CHCl_3$) λ_{max} 608 nm; (NMP) λ_{max} 650 nm; HRMS calcd m/z = 420.0978, found m/z = 420.0966. Anal. Calcd: C, 65.69; H, 4.79; N, 6.66; S, 15.25. Found: C, 65.79; H, 4.77; N, 6.7 ; S, 15.27.

5′-*N*-Piperidinyl-2-(3-(3-phenyl-5-oxo-4-isoxazolylidene)-propenyl)-2′,5-bithiophene. The above method was used (75% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, J = 14.02, 12.11 Hz, 1 H), 7.60−7.55 (m, 2 H), 7.55−7.45 (m, 3 H), 7.33 (d, J = 12.10 Hz, 1 H), 7.25 (d, J = 14.57 Hz, 1 H), 7.19 (d, J = 4.06 Hz, 1 H), 7.07 (d, J = 4.15 Hz, 1 H), 6.88 (d, J = 4.00 Hz, 1 H), 5.99 (d, J = 4.12 Hz, 1 H), 3.21 (br t, J = 5.54 Hz, 4 H), 1.70 (br pent, J = 5.45 Hz, 4 H), 1.65−1.55 (m, 2 H); UV−vis ($CHCl_3$) λ_{max} 632 nm; (NMP) λ_{max} 542 nm; HRMS calcd m/z = 446.1108, found m/z = 446.1123. Anal. Calcd: C, 67.24; H, 4.97; N, 6.24; S, 14.29. Found: C, 67.14; H, 5.07; N, 6.19; S, 14.29.

2-((3-Phenyl-5-oxo-4-isoxazolyl)methylidene)-5′-(N,N-diphenylamino)-2′,5-bithiophene. The above method was used (70% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (bd, J = 3 Hz, 1 H), 7.7−7.5 (m, 5 H), 7.4−7.2 (m, 10 H), 7.16 (t, J = 7.2 Hz, 2 H), 7.09 (d, J = 4.2 Hz, 1 H), 6.51 (d, J = 4.2 Hz, 1 H); UV−vis (ligroin) λ_{max} 574 nm; ($CHCl_3$) λ_{max} 588 nm; (NMP) λ_{max} 606 nm; HRMS calcd m/z = 504.0959, found m/z = 504.0959.

2-(3-(3-Phenyl-5-oxo-4-isoxazolylidene)propenyl)-5′-(*N*,*N*-diphenylamino)-2′,5-bithiophene. The above method was used (70% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, J = 15, 12.3 Hz, 1 H), 7.7−7.5 (m, 5 H), 7.4−7.1 (m, 14 H), 6.97 (d, J = 3.9 Hz, 1 H), 6.54 (d, J = 3.9 Hz, 1 H); UV−vis (ligroin) λ_{max} 568 nm; ($CHCl_3$) λ_{max} 580 nm; (NMP) λ_{max} 584 nm; HRMS calcd m/z = 530.1122, found m/z = 530.1099.

5′-*N*-Piperidinyl-2-((*N*,*N*-diethylthiobarbituryl)methylidene)-2′,5-bithiophene. A solution of 5′-*N*-piperidinyl-2′,5-bithiophene-2-carboxaldehyde (1.3 g, 5 mmol) and *N*,*N*-diethylthiobarbituric acid (1.2 g, 6 mmol) in acetic anhydride (5 mL) was heated to reflux for 30 min and then cooled to ambient temperature. The resulting mixture was poured into chloroform and washed with 5% ammonium chloride solution. The organic layer was dried over magnesium sulfate and the solvent removed *in vacuo*. The resulting purple solid was recrystallized from ethanol to give 1.4 g (65%) of the title product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1 H), 7.66 (d, J = 4.2 Hz, 1 H), 7.38 (d, J = 4.4 Hz, 1 H), 7.06 (d, J = 4.4 Hz, 1 H), 6.03 (d, J = 4.3 Hz, 1 H), 4.6−4.5 (m, 4 H), 3.28 (t, J = 5.3 Hz, 4 H), 1.70 (br pent, J = 5.7 Hz, 4 H), 1.68−1.58 (m, 2 H), 1.32 (t, J = 6.7 Hz, 3 H), 1.29 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 164.12, 161.5, 160.2, 158.6, 148.7, 147.7, 133.7, 130.7, 122.2, 119.8, 106.2, 105.3, 51.4, 43.8, 42.9, 24.9, 23.5, 15.5, 12.4; UV−vis (CCl_4) λ_{max} 598 nm; (DMSO) λ_{max} 598 nm; (NMP) λ_{max} 650 nm; (petroleum ether) λ_{max} 574 nm; 192−210 °C dec; HRMS calcd m/z = 459.1101, found m/z = 459.1109. Anal. Calcd: C, 57.48; H, 5.49; N, 9.14; Found: C, 57.21; H, 5.51; N, 9.24.

(5′-*N*-Piperidinyl-2′,5-bithiophene-2-yl)acrolein−*N*,*N*-Diethylthiobarbituric Acid Condensation Product. The above method was used (75% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, J = 14.34, 12.41 Hz, 1 H), 8.08 (d, J = 12.49 Hz, 1 H), 7.48 (d, J = 14.35, 1 H), 7.27 (d, J = 4.14 Hz, 1 H), 7.10 (d, J = 6.14 Hz, 1 H), 6.91 (d, J = 4.07 Hz, 1 H), 5.99 (d, J = 4.13 Hz, 1 H), 4.53 (pent, J = 7.63 Hz, 4 H), 3.22 (dd, J = 5.5, 5.5 Hz, 4 H), 1.71 (pent, J = 5.5 Hz, 4 H), 1.65−1.50 (m, 4 H), 1.31 (t, J =5.2 Hz, 3 H), 1.28 (t, J = 6.96 Hz, 3 H); UV−vis (ligroin) λ_{max} 578 nm; ($CHCl_3$) λ_{max} 676 nm; (NMP) λ_{max} 700 nm; HRMS calcd m/z = 485.1286, found m/z = 485.1265.

Diethylthiobarbituric Acid Adduct of 5′-(*N*,*N*-Diphenylamino)-2′,5-bithiophene-2-carboxaldehyde. The above method was used (75% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1 H), 7.71 (d, J = 4.26 Hz, 1 H), 7.36 (d, J = 4.14 Hz, 1 H), 7.32 (t, J = 7.82 Hz, 4 H), 7.24 (d, J = 4.13 Hz, 1H), 7.23 (d, J = 8.3 Hz, 4 H), 7.14 (t, J = 8.1 Hz, 2 H), 6.49 (d, J = 4.15 Hz, 1 H), 4.58 and 4.56 (overlapping q, J = 7.06 and 7.03 Hz, 4 H), 1.32 and 1.28 (overlapping t, J = 6.92 and 6.97 Hz, 6 H); UV−vis (ligroin) λ_{max} 532 nm; ($CHCl_3$) λ_{max} 580 nm; (NMP) λ_{max} 616 nm. Anal. Calcd: C, 64.06; H, 4.63; N, 7.73; S, 17.69. Found: C, 64.27; H, 4.64; N, 7.60; S, 17.54.

3-(5′-(*N*,*N*-Diphenylamino)2′,5-bithiophene-2-yl)acrolein−*N*,*N*-Diethyltiobarbituric Acid Condensation Product. The above method was used (80% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (dd, J = 14.4, 12.3 Hz, 1 H), 8.13 (d, J = 12.3 Hz, 1 H), 7.51 (d, J = 14.4 Hz, 1 H), 7.40−7.05 (m, 12 H), 6.70 (d, J = 3.9 Hz, 1 H), 6.53 (d, J = 3.9 Hz, 1 H), 4.6−4.5 (m, 4 H), 1.3−1.4 (m, 6 H); UV−vis (ligroin) λ_{max} 534 nm; ($CHCl_3$) λ_{max} 578 nm; (NMP) λ_{max} 610 nm. Anal. Calcd: C, 65.35; H, 4.78; N, 7.38; S, 16.88. Found: C, 64.88; H, 4.90; N, 7.22.

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