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α,α′-*N*-Boc-Substituted Bi- and Terthiophenes: Fluorescent Precursors for Functional Materials

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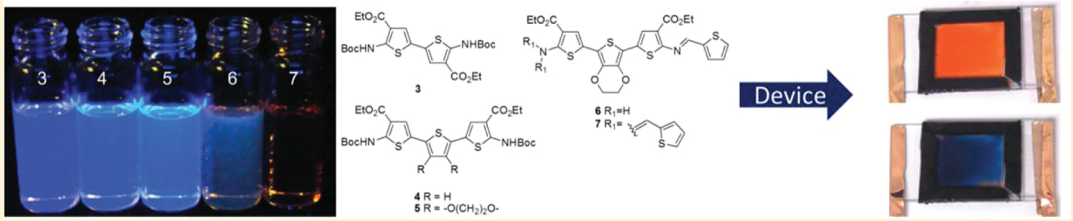
Supporting Information



ABSTRACT: Fluorescent α,α′-diamide substituted bi- and terthiophene derivatives were prepared by Stille and Suzuki couplings. Their one-pot deprotection and coupling with 2-thiophene carboxaldehyde led to stable conjugated azomethines. These exhibited electrochromic properties, and they were used to fabricate a working electrochromic device.

2-Aminothiophenes have successfully been used in a wide range of fields, including medicinal chemistry as pharmaceutically active compounds[1−4] and as precursors for conjugated azomethines for use in plastic electronics such as electrochromic devices and emitting applications.[5−8] The preparation of 4- and 5-substituted 2-aminothiophenes is typically done via the Gewald reaction involving α-methylene carbonyl thiophenes.[9,10] However, 2-aminobithiophenes and higher ordered oligomeric derivatives such as **3**−**5** are not possible with this strategy. This is a result of the instability of the required corresponding α-methylene carbonyl thiophenes for synthesizing such derivatives. As a consequence, there are no reports for the double Gewald reaction for the preparation of α,α′-diaminooligothiophenes. In fact, such stable compounds consisting of primary, secondary, or even Boc-protected amino derivatives have not been reported.

Alternate approaches to the Gewald reaction for preparing α,α′-diaminoterthiophenes are Suzuki and Stille couplings involving a 2-amino-5-bromothiophene derivative.[11,12] While Suzuki coupling has been applied to prepare a limited number of 2-amino-5-arylthiophene derivatives,[13−23] there is only one reported example of a 2-aminobithiophene derivative (**1**, Figure 1) prepared via this method.[24] Interestingly, neither Suzuki nor Stille couplings have been applied for obtaining α,α′-diamino bi- or terthiophenes derivatives. Such oligothiophene derivatives are interesting because they are expected to possess high fluorescence quantum yields (Φ_{fl}). This is because complementary electronic substituents incorporated in the α,α′-positions (**2x**) are known to suppress excited-state deactivation by intersystem crossing (ISC) in bithiophenes.[25,26] The additional advantage of 2-aminothiophene derivatives is that the primary amine can be further reacted. This provides the means to both tailor the fluorescence wavelength and prepare conjugated azomethines for use as functional materials by condensing with aryl aldehydes.[5,6,8,25]

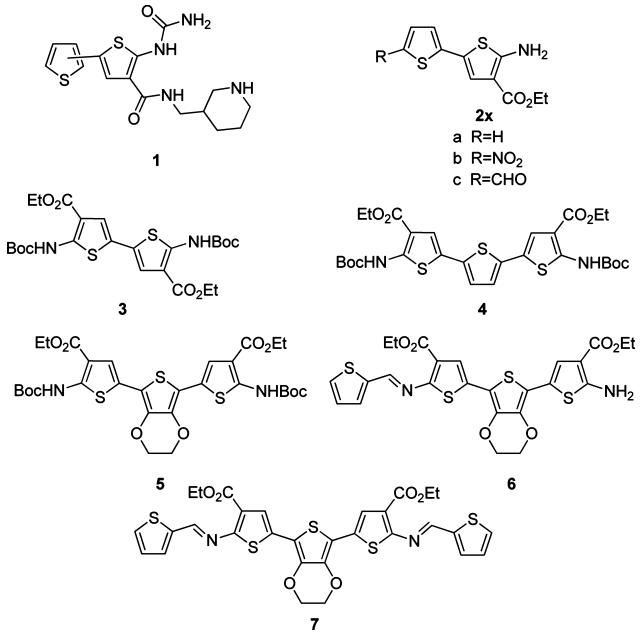


Figure 1. α,α′-*N*-Boc-substituted bi- and terthiophenes prepared and representative analogues.

Given the high Φ_{fl} expected from α,α′-diamino bi- and terthiophenes in addition to being desired precursors for functional materials synthesis, we were incited to prepare **3**−**5**.

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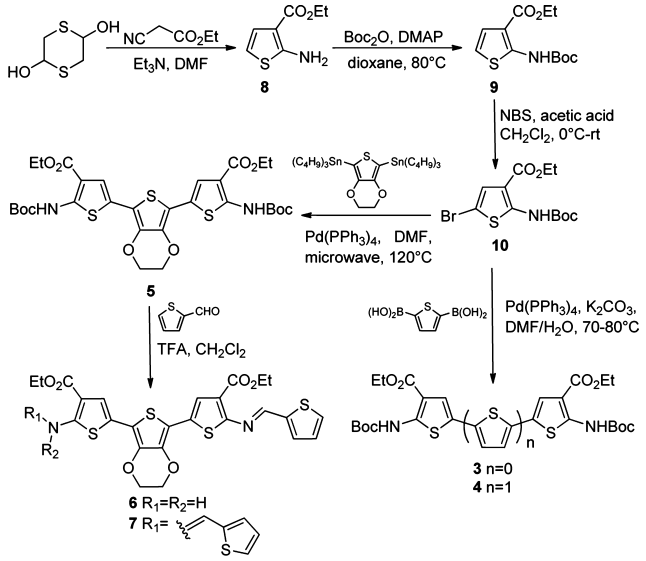
We were further motivated to prepare such derivatives to demonstrate that both Stille and Suzuki coupling protocols can be used for preparing amino end-capped bi- and terthiophenes. Such derivatives are of importance not only as fluorescence sensors, but also for pharmaceutical and plastic electronics applications. Therefore, the successful preparation of α,α'-diamino bi- and terthiophene derivatives provides an alternate means of preparing new materials that are otherwise not possible due to the limited stability of the precursors required for the Gewald reaction. The preparation of the conjugated thiophenes **3**−**5** are herein presented in addition to their fluorescence quantum yields. Their use as precursors for functional materials is further demonstrated by preparing azomethine conjugated materials. To confirm the use of the azomethines for use in plastic electronics, the optoelectronic characterization and electrochromic device fabricated from **7** are also presented.

The 2-amino-5-bromo derivative **10** is the required precursor for undertaking the targeted Stille and Suzuki couplings for preparing **3**−**5**. In turn, **10** was prepared from the 2-aminothiophene **9**. The starting synthon (**8**) was prepared in 64% yield by the base-catalyzed Gewald reaction with 1,4-dithiane-2,5-diol and ethylcyano acetate.[26] The resulting primary amine was subsequently protected with *tert*-butyl carbamate anhydride using standard conditions with catalytic DMAP to afford **9** in 65% yield (Scheme 1). N-Protection was

Scheme 1. Synthetic Scheme for the Preparation of 3−7



required for obtaining a stable 5-brominated derivative. Otherwise, the unprotected 2-bromo-5-aminothiophene derivative spontaneously polymerizes at room temperature. From the N-Boc-protected **9**, the bromo derivative **10** was obtained in 87%, which was stable under ambient conditions for extended periods of time. The heterocoupled product **4** was obtained in 57% yield by reacting **10** with 2,5-thiophene bisboronic acid via Suzuki coupling with tetrakis-(triphenylphosphine)palladium. The homocoupled product **3** was also obtained as a side product from the heterocoupling reaction, and it was isolated in 41% yield. Compound **5** was prepared in 59% yield via Stille coupling between **10** and bis(tributylstannyl)-EDOT with tetrakis(triphenylphosphine)-palladium.[27] Unlike with the Suzuki coupling, no homocoupled product was observed with the Stille coupling.

While cleavage of the Boc group is normally quantitative under acid conditions, **3**−**5** were found to resist weak acidic conditions (1−12 M HCl in ethanol) at both room temperature and elevated temperature. Meanwhile, strong acids (TFA and HBr in dichloromethane) resulted in their decomposition. Decomposition of **3**−**5** was also observed with other known deprotecting reagents such as $AlCl_3$, TsOH, and Bu_4NF. This was unexpected since removal of the of *N*-Boc protecting group of 2-aminothiophenes that are substituted with electron-withdrawing groups in the 3-position occurs with standard deprotecting conditions without decomposition. In fact, such 2-aminothiophene derivatives are extremely stable, and they can be handled under ambient conditions without special precautions.[26,28,29] The reactive intermediate could, however, immediately be trapped with 2-thiophenecarboxaldehyde leading to air-stable conjugated azomethine products. Product formation (**6** and **7**) was possible in one-pot by cleaving the Boc group with TFA at room temperature in the presence of an excess of 2-thiophenecarboxaldehyde (Scheme 1). Despite using an excess of the aldehyde, a mixture of both mono- (20%) and biscoupled (65%) products was obtained.

The fluorescence of **3**−**5** was investigated owing to their expected high fluorescence quantum yield. The fluorescence quantum yields of **3**−**7** were measured with an integrating sphere, which allowed the calculation of absolute Φ_{fl}. As seen in Table 1, **4**−**5** fluoresced with near-quantitative yields (Table 1,

Table 1. Photophysical and Electrochemical Data of 3−7

compd	λ_{abs}[a] (nm)	λ_{em}[a] (nm)	Φ_{fl}[b]	E_{pa}[c] (V)	E_{pc}[c] (V)
3	297	424	0.31	1.05	−1.14
4	387	451	0.93	0.86	−1.25
5	400	458	0.87	0.77, 1.03	−1.14
6	412, 485_{sh}	485	0.02	0.44, 0.64	−1.15
7	500	610	<0.01	0.89	−1.31

[a]Measured in deaerated dichloromethane. [b]Absolute quantum yield. [c]Relative to Ag/Ag^+ with ferrocene as an internal standard (E_{pa} = 453 mV).

inset Figure 2), compared to their unsubstituted terthiophene counterpart, whose Φ_{fl} = 0.06.[30] Meanwhile, the Φ_{fl} of **3** is less than **4** and **5**. However, it is exceptionally high compared to its unsubstituted counterparts such as bithiophene (Φ_{fl} = 0.018)[31] and **2a** (Φ_{fl} = 0.06).[26] The fluorescence data suggest that fluorescent bi- and terthiophenes are possible by incorporating electronic groups in the α,α'-positions, which suppress the otherwise efficient fluorescence quenching by intersystem crossing (ISC).

Cryofluorescence was further done to provide insight into the different Φ_{fl} of **3** relative to **4** and **5**. Variable-temperature fluorescence was also used to probe the quenched fluorescence of **6** and **7**. Given that ISC is an intrinsic property, it is temperature independent. Therefore, any temperature-dependent fluorescence changes would confirm fluorescence deactivation by molecular dynamics. As seen in Figure 2, the fluorescence of **3** increases with decreasing temperature. Correcting for the solvent refractive index change at different temperatures, the Φ_{fl} of **3** increased to 0.5 at 180 K. This provides evidence that deactivation of the singlet excited state occurs predominately by rotation around the aryl−aryl bond and not by ISC. This is further supported by extrapolating the

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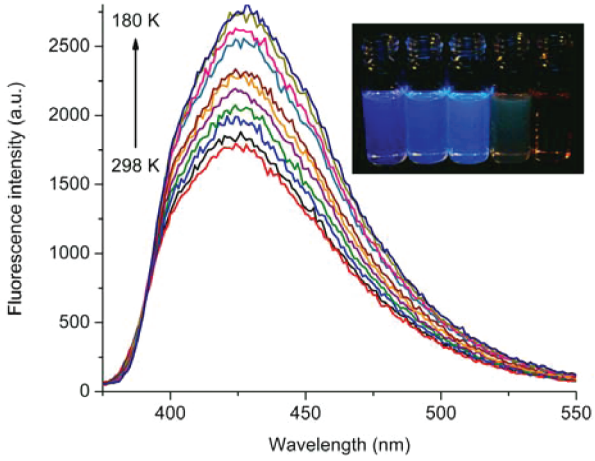

Figure 2. Cryofluorescence of **3** between 298 (red line) and 180 K (black line) in dichloromethane. Inset: photographs showing the fluorescence of **3**–**7** (from left to right) when excited with an UV lamp.

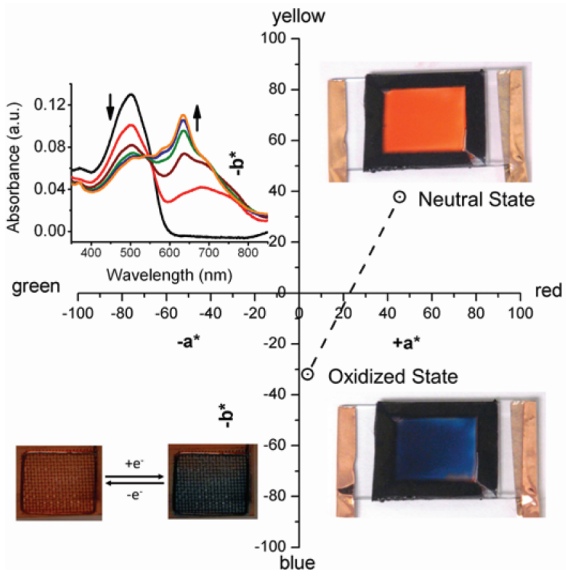

Figure 3. CIE $L^*a^*b^*$ color coordinates of the electrochromic device of **7** in the oxidized and neutral states. Photographs of the neutral (top right) and oxidized (lower right) states of the device. Top left: spectroelectrochemistry of **7** by applying a potential of 1 V for 0 (black line), 1 (red line), 2 (deep red line), 4 (green line), and 8 (blue line) and 10 min (orange line). Lower left: photographs showing the reversible color change of **7** at the platinum mesh electrode when oxidized (right) and neutralized (left).

cryofluorescence to reduced temperatures (Figure S24, Supporting Information), where $\Phi_{fl} \approx 1$ was calculated. The fluorescence measurements were done at low concentrations to ensure no bimolecular quenching. In contrast, the fluorescence of **6** and **7** is quenched at room temperature. This is a result of the azomethine linkage, which is a known efficient excited-state deactivator.[26,32−36] While the fluorescence of **7** increased by ca. 80 times at 77 K, the fluorescence of **6** increased to only 9% at reduced temperature. The fluorescence of **7** is therefore most likely quenched by molecular dynamics, while **6** is deactivated by other means.[33,34,37]

The oxidation potentials (E_{pa}) were measured by cyclic voltammetry. The effect of the degree of conjugation and the EDOT moiety on the E_{pa} is apparent from the cyclic voltammograms (Figure S25, Supporting Information). For example, **4** is shifted by 200 mV to less positive potentials relative to **3**, courtesy of its higher degree of conjugation. Similarly, **5** is shifted by 100 mV to less positive potential relative to **4**, owing to the strong electron donating EDOT moiety. The E_{pa} for **3**–**7** are all above 500 mV vs Ag/Ag^+, confirming their stability under ambient conditions. This is in part due to the electron withdrawing ester groups that increase the E_{pa}. This is evident when comparing the E_{pa} of α,α'-di(*N*,*N*-diphenyl)bi- and terthiophene whose E_{pa} is ca. 300 mV vs Ag/Ag^+.[38] The lowest E_{pa} of the series examined was of **6**, as a result of the electronic *push*−*pull* effect of the terminal donating amine and the withdrawing azomethine. Meanwhile, the two azomethine bonds of **7** increase the E_{pa} such that it is 450 mV more positive than **6**. Interestingly, the one-electron oxidation process for the diaminothiophenes was reversible only for **5** and **6**. This is in contrast to **3**, **4**, and **7**, whose oxidations are irreversible. This most likely is a result of radical cation coupling at the unsubstituted positions on the bithiophenes.

Conjugated azomethines such as **6** and **7** are interesting materials because of their strong absorbance in the visible region. In addition, their radical cations exhibit high color contrasts from the neutral state. These spectroscopic properties concomitant with their low oxidation potentials make them suitable candidates for electrochromic applications. The solution spectroelectrochemistry of the two azomethines were therefore investigated in 0.1 M $TBAPF_6/CH_2Cl_2$ electrolyte. As seen in the upper left panel of Figure 3, the absorbance of the neutral **7** decreases upon applying a potential of 1 V. A new absorbance occurs at 635 nm, corresponding to the radical cation. This simultaneously occurs with the disappearance of the absorbance at 500 nm. The resulting reversible color transitions between the neutral (orange) and oxidized states (blue) are shown in the lower left panel of Figure 3. Similarly, **6** could also be reversibly oxidized with the formation of a green color corresponding to an absorbance at 625 nm (see the Supporting Information).

To demonstrate the suitability and stability of the azomethines as functional materials, an electrochromic device was prepared using heteroconjugated materials as the electrochrome. Devices were prepared by spray-coating thin films of **7** onto ITO glass slides and sandwiching a UV curable gel electrolyte between ITO coated working and counter electrodes followed by UV curing.[39] The device was assembled by placing a counter ITO electrode on top of the spray-coated layers followed by UV curing. The devices were tested by continuous cycling between the oxidized and neutral states. Figure 3 shows the plot of the CIE $L^*a^*b^*$ color coordinates of the electrochromic device prepared from **7** and the digital photographs of the device in its neutral and oxidized states. In the neutral state, the device had a red-orange color (L^* = 73.15011, a^* = 45.45454, b^* = 37.84355), while in the oxidized state, a deep blue color (L^* = 53.69979, a^* = 3.787879, b^* = −31.92389) was observed. The device colors are consistent with those observed by spectroelectrochemistry, implying the same oxidized stated is produced in both cases. It should be noted that no color bleaching or color degradation, which would otherwise indicate the decomposition of **7**, were observed when cycling between the two states. This demonstrates the robustness of the materials and their resistance toward oxidative degradation, especially in the harsh redox environment of the electrochromic device.

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In summary, α,α′-diamino-protected bi- and terthiophenes were prepared by Stille and Suzuki coupling with 2-aminothiophene derivatives. Not only are the *N*-Boc-protected derivatives stable, but they fluoresce more than their unsubstituted counterparts. The high Φ_{fl} confirms that deactivation modes by intersystem crossing are negligible. While terthiophenes were prepared as a proof of concept, the Stille and Suzuki coupling with the 2-amino-5-bromothiophene derivative is amenable to any bis(boronic acid) or bis(stannylated) homo- or heterocycle. This offers the possibility of preparing diaminothiophene end-capped oligomers with central cores of varying electron density. In turn, this opens the possibility of tailoring both the oxidation potential and emission wavelength, while maintaining high fluorescence quantum yields. Meanwhile, the one-pot protecting group cleavage and azomethine formation affords the means to prepare colored conjugated materials with interesting optoelectronic properties that can successfully be used in electrochromic devices.

EXPERIMENTAL SECTION

Ethyl 2-Aminothiophene-3-carboxylate (8). The preparation was performed similarly to previous reports.[26,40] Triethylamine (3.6 g, 50 mmol) was added dropwise to a mixture of 1,4-dithiane-2,5-diol (7.6 g, 50 mmoL), ethyl cyanoacetate (11.3 g, 100 mmol), and DMF (20 mL) at 0 °C. The mixture was stirred at room temperature for 3 h, diluted with water (200 mL), extracted with dichloromethane (4 × 40 mL), washed with water (2 × 40 mL), and then dried with Na_2SO_4. After filtering and removal of the solvent, the residue was purified by silica gel chromatography. The collected eluents were evaporated under reduced pressure and diluted with hexane. The flask was cooled overnight, whereupon **8** crystallized to give a pale yellow solid (11 g, 64%): mp 47−48 °C; ^{1}H NMR (acetone-d_6) δ 6.95 (bs, 2H), 6.90 (J_2 = 5.6 Hz, 1H), 6.24 (J_2 = 5.6 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.29 (J_3 = 7.2 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 165.3, 164.3, 125.8, 106.6, 105.9, 59.4, 14.4.

Ethyl 2-((*tert*-Butoxycarbonyl)amino)thiophene-3-carboxylate (9). To a solution of **8** (3.42 g, 20 mmol) and Boc_2O (5.45 g, 25 mmol) in dioxane (50 mL) was added 4-dimethylaminopyridine (0.244 g, 2 mmol) at room temperature. The mixture was stirred overnight at 80 °C. Water was then added at 0 °C. The reaction mixture was extracted by ethyl acetate, dried over Na_2SO_4, and then filtered. The crude product was purified by silica gel chromatography to give **9** as a colorless oil (3.52 g, 65%): ^{1}H NMR ($CDCl_3$) δ 10.03 (bs, 1H), 7.05 (J_2 = 5.80 Hz, 1H), 6.55 (J_2 = 5.80 Hz, 1H), 4.22 (J_4 = 7.13 Hz, 2H), 1.47 (s, 9H), 1.29 (J_3 = 7.13 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 164.9, 151.7, 150.7, 123.8, 114.1, 111.0, 81.6, 60.1, 27.8, 14.020; HRMS (ESI, quadrupole, positive mode) calcd for $C_{12}H_{17}NO_4S$ $[M + H]^+$ 272.09511, found 272.09517.

Ethyl 5-bromo-2-((*tert*-butoxycarbonyl)amino)thiophene-3-carboxylate (10). To solution of **9** (35 mg, 1.3 mmol) in anhydrous dichloromethane (2 mL) and acetic acid (2 mL) was added NBS (278 mg, 1.56 mmol) at 0 °C. The mixture was stirred for 1.5 h at room temperature, and then it was diluted with H_2O, extracted with ethyl acetate, washed with $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and filtered. The crude product was purified by silica gel chromatography to give **10** as a colorless oil (39 mg, 87%): ^{1}H NMR ($CDCl_3$) δ 10.02 (bs, 1H), 7.04 (s, 1H), 4.25 (J_4 = 7.11 Hz, 2H), 1.49 (s, 9H), 1.31 (J_3 = 7.11 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 164.0, 151.8, 151.0, 125.8, 110.8, 102.2, 82.355, 77.3, 77.0, 76.7, 60.5, 27.9, 14.1; HRMS (ESI, quadrupole, positive mode) calcd for $C_{12}H_{16}BrNO_4S$ $[M + Na]^+$ 371.98756, found 371.98822.

Diethyl 5,5″-Bis((*tert*-butoxycarbonyl)amino)[2,2′:5′,2″-terthiophene]-4,4″-dicarboxylate (4). To the solution of **10** (175 mg, 0.5 mmol), 2,5-thiophene bisboronic acid (43 mg, 0.25 mmol), and $Pd(PPh_3)_4$ (57.75 mg, 0.05 mmol) in DMF (5 mL) was added K_2CO_3 (207 mg, 1.5 mmol) followed by H_2O (1 mL). The mixture was degassed for 30 min under N_2 and then stirred for 16 h at 70−80 °C. The reaction mixture was then diluted with H_2O, extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, and filtered. The crude product was purified by silica gel chromatography to give **4** as a pale yellow solid (90 mg, 57%): mp 212−214 °C; ^{1}H NMR (acetone-d_6) δ 10.11 (bs, 2H), 7.30 (s, 2H), 7.21 (s, 2H), 4.37 (J_4 = 7.12 Hz, 4H), 1.58 (s, 9H), 1.40 (J_3 = 7.12 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 165.1, 152.0, 150.0, 135.3, 125.7, 123.6, 119.9, 111.7, 82.6, 60.7, 28.2, 14.4; HRMS (ESI, quadrupole, positive mode) calcd for $C_{28}H_{34}N_2O_8S_3$ $[M + H]^+$ 622.14718, found 622.14679.

Diethyl 5,5′-Bis((*tert*-butoxycarbonyl)amino)[2,2′-bithiophene]-4,4′-dicarboxylate (3). The dimer **3** was obtained during the preparation of **4** and was isolated by silica gel column chromatography (hexane/ethyl acetate/dichloromethane 250:25:0.1 mL). The title compound was isolated as a yellow solid (23 mg, 41%): mp 216−218 °C; ^{1}H NMR ($CDCl_3$) δ 10.07 (bs, 2H), 7.17 (s, 2H), 4.32 (J_4 = 7.13 Hz, 4H), 1.56 (s, 18H), 1.40 (J_3 = 7.13 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 165.1, 152.1, 149.5, 125.5, 119.2, 111.6, 82.5, 60.6, 28.151, 14.3; HRMS (ESI, quadrupole, positive mode) calcd for $C_{24}H_{32}N_2O_8S_2$ $[M + H]^+$ 541.16728, found 541.16651.

Diethyl 5,5′-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxine-5,7-diyl)-bis(2-((*tert*-butoxycarbonyl)amino)thiophene-3-carboxylate) (5). Bis(tributylstannyl) EDOT (266 mg, 0.4 mmol) and **10** (349 mg, 1 mmol) were dissolved in DMF (6 mL) in a microwave reactor followed by $Pd(PPh_3)_4$ (116 mg, 0.1 mmol). The mixture was degassed for 30 min with N_2, and the reaction was run for 2 h at 120 °C in a microwave oven. The reaction mixture was quenched with H_2O, extracted with ethyl acetate, washed with satd NaCl, dried by Na_2SO_4, and filtered, and the solvent was evaporated under vacuum. The crude product was purified by silica gel chromatography to give **5** as a yellow solid (160 mg, 59%): mp 227−229 °C; ^{1}H NMR ($CDCl_3$) δ 10.09 (bs, 2H), 7.18 (s, 2H), 4.35 (s and q, 8H), 1.56 (s, 18H), 1.41 (J_3 = 7.06 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 165.2, 152.0, 150.1, 137.3, 123.6, 118.7, 111.1, 108.6, 82.2, 64.9, 60.6, 28.2, 14.3; HRMS (ESI, quadrupole, positive mode) calcd for $C_{30}H_{36}N_2O_{10}S_3$ $[M + Na]^+$ 703.14243, found 703.14124.

(*E*)-Ethyl 2-Amino-5-(7-(4-(ethoxycarbonyl)-5-((thiophene-2-ylmethylene)amino)thiophene-2-yl)-2,3-dihydrothieno[3,4-*b*]-[1,4]dioxin-5-yl)thiophene-3-carboxylate (6) and (*E*)-Diethyl 5,5′-(2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5,7-diyl)bis(2-((*E*)-(thiophene-2-ylmethylene)amino)thiophene-3-carboxylate) (7). TFA (0.1 mL) was added dropwise to the mixture of **5** (0.34 g, 0.5 mmol) and thiophene-2-carbaldehyde (0.56 g, 5 mmol) at room temperature. The reaction mixture was stirred neat for 1 h, and then it was diluted with dichloromethane. Silica gel was then added, and the resulting powder was applied to a silica gel column for purification.

(*E*)-Ethyl 2-Amino-5-(7-(4-(ethoxycarbonyl)-5-((thiophene-2-ylmethylene)amino)thiophene-2-yl)-2,3-dihydrothieno[3,4-*b*]-[1,4]dioxin-5-yl)thiophene-3-carboxylate (6). The title compound was obtained as a solid (69 mg, 20%): mp 118−120 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.60 (s, 1H), 7.59 (dt, J_1 = 5.0 Hz, J_2 = 1.0 Hz, 1H), 7.53 (dd, J_1 = 3.5 Hz, J_2 = 1.0 Hz, 1H), 7.46 (s, 1H), 7.16 (dd, J_1 = 5.0 Hz, J_2 = 4.0 Hz, 1H), 7.13 (s, 1H), 6.03 (bs, 2H), 4.39 (m, 6H), 4.33 (q, J = 7.0 Hz, 2H), 1.45 (t, J = 7.0 Hz, 3H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 128.5 MHz) *d* 165.2, 163.0, 162.1, 155.5, 151.8, 142.6, 138.4, 136.6, 132.9, 131.9, 128.1, 127.8, 125.2, 123.7, 121.6, 115.6, 110.6, 107.8, 107.1, 65.1, 64.9, 60.8, 59.9, 14.5, 14.4; HRMS (ESI, quadrupole, positive mode) calcd for $C_{25}H_{22}N_2O_6S_4$ $[M + H]^+$ 575.04335, found 575.04258.

(*E*)-Diethyl 5,5′-(2,3-Dihydrothieno[3,4-*b*][1,4]dioxine-5,7-diyl)bis(2-((*E*)-(thiophene-2-ylmethylene)amino)thiophene-3-carboxylate) (7). The title compound was obtained as a red solid (186 mg, 65%): mp 118−120 °C; ^{1}H NMR ($CDCl_3$, 128.5 MHz) δ 8.60 (s, 1H), 7.59 (dt, J_1 = 5.0 Hz, J_2 = 1.0 Hz, 1H), 7.53 (dd, J_1 = 3.5 Hz, J_2 = 1.0 Hz, 1H), 7.46 (s, 1H), 7.16 (dd, J_1 = 5.0 Hz, J_2 = 4.0 Hz, 1H), 7.13 (s, 1H), 6.03 (bs, 2H), 4.39 (m, 6H), 4.33 (q, J = 7.0 Hz, 2H), 1.45 (t, J = 7.0 Hz, 3H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 500 MHz) *d* 165.2, 163.0, 162.1, 155.5, 151.8, 142.6, 138.4, 136.6, 132.9, 131.9, 128.1, 127.8, 125.2, 123.7, 121.6, 115.6, 110.6, 107.8, 107.1, 65.1, 64.9, 60.8, 59.9, 14.5, 14.4; HRMS (ESI, quadrupole, positive mode) calcd for $C_{25}H_{22}N_2O_6S_4$ $[M + H]^+$ 575.04335, found 575.04258.

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■ ASSOCIATED CONTENT

Supporting Information

General experimental methods, characterization details, ^{1}H NMR and ^{13}C NMR spectra, absorbance and fluorescence spectra, cyclic voltammograms, spectroelectrochemistry spectra, and absorbance spectra of electrochromic device from **7**. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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