Macromolecules

Concise Syntheses, Polymers, and Properties of 3-Arylthieno[3,2-b]thiophenes

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Supporting Information

ABSTRACT: Thieno[3,2-*b*]thiophenes (TT), having *para*-substituted phenyl groups at C-3, have been synthesized through a ring closure reaction, using P_4S_{10} , in moderate to high yields. Their absorbance studies displayed that the TT, having nitrophenyl group had the most red shift absorbance at 365 nm, which also showed the lowest optical band gap of 2.92 eV; the rest of the TTs had the absorbance between 300 and 302 nm. Cyclic voltammetry studies indicated that while all the TTs had the oxidation potentials above 1.0 V, the TT with dimethylaminophenyl



group had the lowest oxidation potential of 1.33 V. The rest had the oxidation potentials between 1.6 and 1.99 V. The TTs were both electropolymerized and copolymerized with thiophene through Suzuki coupling reaction. Electropolymerized polymers indicated that while the polymer having strong electron donating dimethylaminophenyl group had the lowest oxidation potential of 0.97 V, the rest of the polymers displayed the potentials between 1.09 and 1.39 V. Their electronic band gaps varied between 1.86 and 2.46 eV. The CV–UV studies of the polymers, electro-deposited on ITO, showed absorbance maxima between 431 and 468 nm, and the lowest optical band gap was observed with the polymer having methoxyphenyl group (1.99 eV). The rest of the polymers had the optical band gaps between 2.05 and 2.19 eV. Regarding the copolymers, the one with methoxyphenyl group had the lowest oxidation potential of 0.75 V. They displayed absorption and emission maxima between 325 and 445 and 454– 564 nm, respectively. Their optical and electronic band gaps varied between 2.0 and 2.5 eV. As the copolymer having strong electron donating methoxyphenyl group had the highest quantum yield, 0.64 eV, the one with strong electron withdrawing nitrophenyl group had the lowest quantum yield of 0.003 eV.

INTRODUCTION

Organic electronic materials have been the focus of an increasing attention particularly in chemistry and physics.¹⁻⁴ This is due to their possible applications in electronics and optoelectronics, such as organic light-emitting diodes (OLED),⁵ field-effect transistors (FET),^{4,6} lasers,⁷ photodiodes,⁸ and solar cells.⁹ Among them, thiophene-based π conjugated materials have been holding a particular interest, owing to their environmental stability, high charge carrier mobility, low cost and flexibility.¹⁰ One of the important advantages of using thiophene in designing organic materials is easy modification for tuning the electronic properties of the materials such as electron affinity, ionization potential, absorption and emission.¹¹ Such tuning could also be performed by fusing thiophene rings,¹² among which thienothiophenes (TT) play an important role as their core skeleton consists of two fused rigid thiophene rings to limit the rotational disorder between the rings and create a better π conjugation.^{12b,13} Recently various applications incorporating TT into conjugated oligomers or polymers to improve their electronic and optoelectronic properties have appeared in the literature.¹⁴

As two fused thiophenes, thienothiophenes have four isomers, thieno[3,2-b]thiophene (1), thieno[2,3-b]thiophene

(2), thieno[3,4-*b*]thiophene (3), and thieno[3,4-*c*]thiophene (4), among which the TT (1) has the lowest band gap and ionization potential.^{14e} This is due to the orientation of the fused rings, which lead to a better conjugation in TT. Moreover, when (1) was copolymerized with thiophene, a lower HOMO energy level was observed compared with poly(3-hexylthiophene).^{14e,7} This was explained that the flow of electrons from the TT is less favorable than a thiophene ring as TT has a larger resonance stabilization energy. One of the reasons for polythiophenes being susceptible to various oxidation mechanisms is having a very rich electron system.¹⁵



Reports on the syntheses of TTs have been concentrated on thieno [3,2-b] thiophene (1), as it has the most attractive chemical structure.^{12b} Leriche and co-workers achieved the

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synthesis in five steps through the ring closure of 3-(carboxymethylsulfanyl)thiophene.¹⁶ Henssler and Matzger reported that the reaction of 3-(2.2-diethoxy-ethylsulfanyl)thiophene in the presence of sulfonic acid resin gave (1) in high yield.¹⁷ Thermal decomposition of thieno[3,2-b]thiophene-2carboxylic acid by Fuller and co-workers, which was synthesized in three steps, in the presence of Cu in quinoline at 260 °C, produced TT (1).¹⁸ Various substituted TTs and analogues of TT, such as 2,3,5,6-tetrabromothieno[3,2-b]thiophene, 3,6dibromothieno [3,2-b] thiophene, 3-bromothieno [3,2-b]thiophene,¹⁸ 3,6-dialkylthieno[3,2-*b*]thiophene,^{14b,17} 5-bromo-3-chlorothieno[3,2-b]thiophene-2-carbonyl chloride, 6-bromo-3,5-dichlorothieno[3,2-b]thiophene-2-carbonyl chloride,¹⁹ 2-(6-bromo-5-methyl-3-(trifluoromethyl)thieno[3,2-b]thiophen-2-yl)benzo[d]thiazole, 3-chloro-6-methoxy-carbonylnaphtho-[2',1':2,3-b]thieno[4,5-d]thiophene-2-carboxylic acid chloride, benzo[b]thieno[3.2-b]thiophene-2-carboxylic acid. 3a.5-dimethyl-3aH-6,7,8,9-tetrahydrobenzo[*c*]thieno[3,2-*b*]thiophene, 2,3:5,6-bis(ethylenedithio)thieno[3,2-b]thiophene, thieno-[2',3':4,5]thieno[2,3-c]quinoline, and 2,5-bis(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-2-ylidene)-2,5-dihydro-1,4-dithiapentalene were reported.²⁰

As a continuation of our research on the synthesis of fused thiophene derivatives, 12a,21 we report here a concise syntheses of thieno[3,2-b]thiophenes, having phenyl moiety (PhTT) (5) at C-3, substituted with various groups such as methoxy (MPhTT) (6), nitro (NPhTT) (7), bromine (BrPhTT) (8), amine (APhTT) (9), and dimethylamine (DMAPhTT) (10). Their electropolymerizations and polymerizations with thiophene through Suzuki coupling were conducted and their properties were investigated.



7 R=NO₂, 8 R=Br 9 R=NH₂, 10 R=N(CH₃)₂

EXPERIMENTAL DETAILS

Materials. 3-bromothiophene, 97%, (Across), phosphorus decasulfide, 2-bromoacetophenone, 2-bromo-4'-methoxyacetophenone, 2bromo-4'-nitroacetophenone, 2,4'-dibromoacetophenone, *n*-butyllithium, dichloromethane (Aldrich), diethyl ether, toluene, and sodium bicarbonate (Merck) were used without further purification except for diethyl ether and THF, which was dried over metallic sodium.

Methods. CH-Instruments Model 400A was used as a potentiostat for the CV studies. FTIR spectra were recorded on a Thermo Nicolet 6700 FT-IR spectrometer. UV measurements were studied on HITACHI U-0080D. ¹H and ¹³C NMR spectra were recorded on a Varian model NMR (500 and 600 MHz). Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Mass spectra were recorded on Bruker MICROTOFQ and Thermo LCQ-Deca ion trap mass instruments. Thermal analyses (TA) of the polymers were conducted by PerkineElmer Thermal Analyzer System equipped with Pyris 6 model thermogravimetry and Jude Differential Scanning calorimetry (DSC) systems. A triple detection GPC (TD-GPC) setup with an Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR SE, HR 4, HR 3, and HR 2) and a Viscotek TDA 302 triple detector, including RI, dual laser light scattering ($\lambda = 670$ nm, at 90° and 7°) and a differential pressure viscometer, was conducted to measure the absolute molecular weights $(M_{n,\text{TDGPC}} \text{ and } M_{w,\text{TDGPC}})$ in THF with a flow rate of 0.5 mL/min at 35 °C. Three detectors were calibrated with a PS standard having a narrow molecular weight distribution $(M_n = 115\ 000\ \text{g/mol}, M_w/M_n = 1.02, [\eta] = 0.519\ \text{dL/g}$ at 35 °C in THF, $dn/dc = 0.185\ \text{mL/g})$, provided by Viscotek company.

1-Phenyl-2-(thiophen-3-ylthio)ethanone (13). To a solution of 3-bromothiophene (11) (11.83 mmol, 1.15 mL, 97%) dissolved in dry diethyl ether (50 mL) was added n- butyllithium (11.83 mmol, 7.4 mL, 1.6 M) at -78 °C under nitrogen atmosphere and the mixture was stirred for 1 h at the same temperature. Than, S_8 (11.83 mmol, 0.38 g) was added and the mixture was stirred for 1 h, after which it was placed into an ice bath and 2-bromoacetophenone (12) (14.2 mmol, 2.83 g) was introduced into the mixture portion wise. Stirring was continued for 3 h and the reaction was quenched with water (10 mL). The solution was extracted with diethyl ether and the organic layer was washed with NaHCO₃ (10%) and water. Organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The residue which remained in the reaction flask was washed with dichloromethane, and the organic layer was extracted with NaHCO₃ (10%) and water. The organic layer was dried over Na₂SO₄ and filtered, and the solvent was evaporated under reduced pressure. The crude products were combined and the residue was separated by column chromatography eluting with hexane/CH₂Cl₂ (3/1) to give the title compound (13) (1.13 g, 41%) as light yellow powder, mp 38–40 °C. IR (ATR, diamond) 3096, 2898, 1672, 1580, 1592, 772, 682 cm⁻¹; ¹H NMR (600 MHz, acetone- d_6) δ (ppm) 8.02 (d, J = 8.2 Hz, 2H), 7.63 (t, J = 8.2 Hz, 1H), 7.52 (t, J = 8.2 Hz, 2H), 7.49 (dd, J = 5.3, 2.9 Hz, 1H), 7.36 (dd, J = 2.9, 1.2 Hz, 1H), 7.08 (dd, J = 5.3, 1.2 Hz, 1H), 4.43 (s, 2H); ¹³C NMR (150 MHz, CDCl₂) δ (ppm) 194.2, 135.4, 133.5, 130.3, 129.8, 128.7, 126.5, 126.4, 42.1; HRMS m/z calcd for C₁₂H₁₀OS₂+Na 257.0065, found 257.007.

The following were similarly prepared.

1-(4-Methoxyphenyl)-2-(thiophen-3-ylthio)ethanone (14). The crude product was separated by column chromatography eluting with hexane/CH₂Cl₂ (3/1) to give the title compound (14) (1.6 g, 53%) as white powder, mp 69–71 °C. IR (ATR, diamond) 3099, 2976, 1660, 1600, 1572, 1508, 856, 833, 818, 632 cm⁻¹; ¹H NMR (600 MHz, acetone- d_6) δ (ppm) 8.00 (d, J = 8.78 Hz, 2H), 7.50 (dd, J = 4.9 Hz, 3.0 Hz, 1H), 7.36 (dd, J = 3.0 Hz, 1.2 Hz, 1H), 7.08 (dd, J = 4.9 Hz, 1,2 Hz, 1H), 7.03 (d, J = 8.78, 2H), 4.38 (s, 2H), 3.89 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 192.9, 163.8, 131.0, 130.3, 130.0, 128.4, 126.3, 126.2, 113.8, 55.5, 41.9; HRMS m/z calcd for C₁₃H₁₃O₂S₂ 265.0357, found 2265.035.

1-(4-Nitrophenyl)-2-(thiophen-3-ylthio)ethanone (15). The crude product was separated by column chromatography eluting with hexane/CH₂Cl₂ (3/1) to give the title compound (**15**) (2.76 g, 84%) as yellow powder, mp 99–100 °C. IR (ATR, diamond) 3100, 2889, 1680, 1519, 1345, 854, 842, 741, 684 cm⁻¹; ¹H NMR (600 MHz, acetone- d_6) δ (ppm) 8.35 (d, J = 8.8 Hz, 2H), 8.24 (d, J = 8.8 Hz, 2H), 7.51 (dd, J = 4.7 Hz, 3.0 Hz, 1H), 7.38 (dd, J = 3.0 Hz, 1.1 Hz, 1H), 7.09 (dd, J = 4.7 Hz, 1.1 Hz, 1H), 4.49 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 192.5, 150.4, 139.9, 130.4, 129.8, 128.6, 127.8, 126.9, 123.9, 42.1; HRMS m/z calcd for C₁₂H₈N₁O₃S₂ 277.9951, found 277.9940.

1-(4-Bromophenyl)-2-(thiophen-3-ylthio)ethanone (16). The crude product was separated by column chromatography eluting with hexane/CH₂Cl₂ (3/1) to give the title compound (**16**) (2.1 g, 57%) as yellow powder, mp 79–82 °C. IR (ATR, diamond) 3096, 2888, 1672, 1581, 1395, 1193, 856, 812 cm⁻¹; ¹H NMR (600 MHz, acetone- d_6) δ (ppm) 7.94 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.50 (dd, *J* = 5.3 Hz, 3.0 Hz, 1H), 7.37 (dd, *J* = 3.0 Hz, 1.2 Hz, 1H), 7.09 (dd, *J* = 5.3 Hz, 1.2 Hz, 1H), 4.41 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 193.2, 134.1, 132.0, 130.4, 130.2, 129.3, 128.7, 127.0, 126.6, 41.9; MS *m*/*z* = 314.87 (M + 1). Anal. Calcd fof C₁₂H₉BrOS₂: C, 46.0; H, 2.90. Found: C, 46.20; H, 2.82.

3-Phenylthieno[3,2-b]thiophene (5). A mixture of **13** (0.5 g, 2.1 mmol), P_4S_{10} (1.83 g, 4.1 mmol), and *p*-toluenesulfonic acid (1.9 g, 10.3 mmol) dissolved in toluene (80 mL) was refluxed for 3 h. The mixture was then extracted with dichloromethane and the organic layer

was washed with NaHCO₃ (10%), brine, water and the organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The crude product was separated by column chromatography eluting with hexane/CH₂Cl₂ (7/1) to give the title compound (**5**) (0.43 g, 94%) as white powder, mp 47–49 °C. IR (ATR, diamond) 3095, 3028, 1601, 1509, 1446, 1355, 840, 753, 688, 654 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.76 (d, *J* = 7.3 Hz, 2H), 7.5 (s, 1H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 5.3 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 5.3 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 139.6, 137.9, 134.8, 134.4, 128.9, 127.6, 127.2, 126.4, 122.6, 119.8; HRMS *m*/*z* calcd for C₁₂H₈N₁O₃S₂ 217.0146, found 217.015.

The following were similarly prepared.

3-(4-Methoxyphenyl)thieno[3,2-*b***]thiophene (6).** The crude product was separated by column chromatography eluting with hexane/CH₂Cl₂ (7/1) to give the title compound (6) (0.34 g, 80%) as yellow powder, mp 85–88 °C. IR (ATR, diamond) 3096, 1605, 1523, 1245, 1029, 829, 706, 655 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.70 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 5.3, 1H), 7.4 (s, 1H), 7.30 (d, *J* = 5.3 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 159.2, 139.5, 137.9, 135.1, 127.6, 127.6, 127.1, 121.2, 119.9, 114.3, 55.4; MS *m*/*z* = 247.27 (*M* + 1). Anal. Calcd for C₁₃H₁₀OS₂: C, 63.32; H, 4.10. Found: C, 63.46; H, 3.97.

3-(4-Nitrophenyi)thieno[3,2-b]thiophene (7). The crude product was separated by column chromatography eluting with hexane/ CH₂Cl₂ (7/1) to give the title compound (7) (0.37 g, 91%) as yellow powder, mp 128–130 °C. IR (ATR, diamond) 3114, 1591, 1503, 1322, 1109, 844, 704, 643 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.34 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.70 (s, 1H), 7.50 (d, *J* = 5.3 Hz, 1H), 7.35 (d, *J* = 5.3 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 146.8, 140.9, 140.2, 137.4, 132,2, 127.8, 126.8, 125.6, 124.5, 119.9; MS *m*/*z* = 261.20 (*M* + 1). Anal. Calcd for C₁₂H₇NO₂S₂: C, 55.10; H, 2.68. Found: C, 55.22; H, 2.58.

3-(4-Bromophenyl)thieno[3,2-b]thiophene (8). The crude product was separated by column chromatography eluting with hexane/CH₂Cl₂ (7/1) to give the title compound (8) (0.39 g, 85%) as white powder, mp 101–103 °C. IR (ATR, diamond) 3096, 1508, 1480, 1345, 1218, 1075, 1006, 845, 824, 721, 653 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.62 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.49 (s, 1H), 7.45 (d, *J* = 5.3 Hz, 1H), 7.31 (d, *J* = 5.3 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 139.8, 133.7, 133.3, 132.1, 129.8, 127.9, 127.4, 122.9, 121.5, 119.9; MS *m*/*z* = 295.07 (*M* + 1). Anal. Calcd for C₁₂H₇BrS₂: C, 48.79; H, 2.35. Found: C, 48.66; H, 2.29.

3-(4-Aminophenyl)thieno[3,2-b]thiophene (9). A mixture of 7 (0.1 g, 0.38 mmol), Fe powder (1 g, 17.8 mmol), and HCl (0.5 mL) was refluxed in ethanol (50 mL, 79%) for 2 h. The mixture was then extracted with dichloromethane, washed with NaHCO₃ (10%) and water. Organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The crude product was separated by column chromatography eluting with hexane/CH₂Cl₂ (3/1) to give the title compound (9) (84 mg, 83%) as brownish viscous liquid. IR (ATR, diamond) 3447, 3369, 3096, 1619, 1532, 1488, 1350, 1282, 1184, 1085, 945, 823, 729, 653 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.57 (d, *J* = 8.2 Hz, 2H), 7.42 (dd, *J* = 5.3, *J* = 1.8 Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 1H) 7.29 (d, *J* = 5.3 Hz, 1H) 6.77 (d, 2H, *J* = 8.2). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 145.9, 139.2, 137.8, 129.4, 127.4, 127.0, 120.2, 119.8, 115.3, 115.0. *m*/*z* = 233.02 (*M* + 1).

3-(4-*N*,*N*-**Dimethylaminophenyl)thieno[3,2-***b***]thiophene (10). To a mixture of 9 (74 mg, 0.319 mmol) and K_2CO_3 (44 mg, 0.319 mmol) in DMF (50 mL) was added iodomethane (99 mg, 0.7 mmol) by syringe and the mixture was stirred at 100 °C for 3 h. DMF was evaporated under reduced pressure. Water was added and the mixture was extracted with dichloromethane. Organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The crude product was separated by column chromatography eluting with hexane/CH₂Cl₂ (3:1) to give the title compound (10) (54 mg, 65%) as a white powder, mp 120–123 °C. IR (ATR, diamond) 3093, 2920, 1609, 1533, 1489, 1357, 1224, 1061, 946, 813**, 757, 699 cm⁻¹; ¹H NMR (600 MHz, acetone- d_6) δ (ppm) 7.69 (d, J = 8.8 Hz, 2H), 7.65 (dd, J = 5.3 Hz, 1.5 Hz, 1H), 7.61 (d, J = 1.5 Hz, 1H), 7.45 (d, J = 5.3 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 3.01 (s, 6H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 139.3, 137.9, 134.5, 128.0, 127.9, 127.2, 127.0, 120.0, 119.8, 113.0, 40.8; MS m/z = 260.13 (M + 1). Anal. Calcd for C₁₄H₁₃NS₂: C, 64.80; H, 5.03. Found: C, 64.99; H, 4.86.

2,5-Dibromo-3-phenylthieno[**3,2**-*b*]**thiophene (17).** To a solution of 3-phenylthieno[**3,2**-*b*]**thiophene (5)** (0.558 g, 2.58 mmol), dissolved in DMF (100 mL), was added N-bromosuccinimide (1.01 g, 5.67 mmol) in DMF (50 mL) by syringe at -10 °C in dark. After stirring for 3 h at the same temperature, the reaction mixture was poured into water (100 mL). The precipitated solid was filtrated and purified by column chromatography eluting with hexane to give the title compound (17) (0.59 g, 61%) as a white solid, mp 104–106 °C. IR (ATR, diamond) 3093, 3043, 2919, 2874, 1597, 1575, 1518, 1485, 1461, 1439, 1339, 1308, 1260, 1182, 1074, 1005, 871, 802, 759, 695, 575, 520, 466 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.64 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.4 Hz. 1H), 7.21 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 136.1, 133.3, 128.9, 128.8, 128.6. 128.5, 128.3, 128.2, 122.1, 113.7; MS *m/z* =374.87 (*M* + 1).

The following were similarly prepared.

2,5-Dibromo-3-(4-methoxyphenyl)thieno[3,2-*b***]thiophene (18). 18 was obtained (0.41 g, 65%) as a yellow solid, mp 102–103 °C. IR (ATR, diamond) 3076, 2933, 2833, 1604, 1528, 1487, 1463, 1339, 1287, 1244, 1177, 1110, 1031, 905, 828, 776, 695, 623, 580, 523, 450 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) \delta (ppm) 7.58 (d,** *J* **= 8.4 Hz, 2H), 7.21 (s, 1H), 7.02 (d,** *J* **= 8.4 Hz, 2H), 3.87 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) \delta (ppm) 156.6, 139.2, 135.8, 133.13, 133.11, 129.6, 125.6, 122.2, 114.2, 109.1, 103.2, 55.3; MS** *m***/***z* **= 404.98 (***M* **+ 1).**

2,5-Dibromo-3-(4-nitrophenyl)thieno[3,2-b]thiophene (19). 19 was obtained (0.41 g, 68%) as a white solid, mp. 121–123 °C. IR (ATR, diamond) 3090, 2923, 2848, 1592, 1512, 1342, 1184, 1104, 1008, 902, 843, 706, 574 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.36 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H) 7.25 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 147.3, 140.3, 138.1, 137.6, 131.4, 129.4, 126.9, 124.1, 119.6, 111.9; MS *m*/*z* = 419.87 (*M* + 1).

2,5-Dibromo-3-(4-aminophenyl)thieno[3,2-b]thiophene (20). A mixture of **19** (0.31 g, 0.74 mmol), Fe powder (0.165 g, 2.96 mmol), and HCl (0.1 mL) was refluxed in ethanol (50 mL, 79%) for 3 h. The mixture was then extracted with dichloromethane, washed with NaHCO₃ (10%) and water. The organic layer was dried over Na₂SO₄ and filtered, and the solvent was evaporated under reduced pressure. The crude product was separated by column chromatography eluting with hexane/CH₂Cl₂ (2/1) to give the title compound (**20**) (0.185 g, 43%) as white solid, mp 170–172 °C. IR (ATR, diamond) 3430, 3324, 3194, 2920, 2851, 1619, 1533, 1490, 1464, 1337, 1282, 1177, 1082, 1018, 806, 736, 574, 525, 459 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.45 (d, *J* = 8.5 Hz, 2H), 7.19 (s, 1H), 6.78 (d, *J* = 8.5 Hz, 2H) 3.85 (bs, 2H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 149.3, 136.1, 132.1, 125.9, 124.8, 124.2, 122.8, 117.6, 116.0, 111.2; MS *m*/*z* = 389.87 (*M* + 1).

2,5-Dibromo-3-(4-*N*,*N*-dimethylaminophenyl)thieno[3,2-*b*]thiophene (21). To a mixture of (20) (129 mg, 0.331 mmol) and K_2CO_3 (95 mg, 0.69 mmol) in DMF (20 mL) was added iodomethane (62 μ L, 0.99 mmol) by syringe, and the mixture was stirred at 100 °C for 3 h. The solvent was evaporated under reduced pressure, and the mixture was extracted with dichloromethane. Organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The crude product was separated by column chromatography, eluting with hexane to give the title compound (21) (50 mg, 36%) as yellow solid, mp 95–98 °C. IR (ATR, diamond) 3093, 3020, 2919, 2850, 1734, 1609, 1536, 1493, 1355, 1205, 1153, 1016, 946, 814, 734, 579, 463 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.55 (d, *J* = 8.2 Hz, 2H), 7.19 (s, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 3.03 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ (ppm) 138.2, 134.6, 132.4, 128.1, 125.1, 121.1, 118.3, 112.3, 111.3, 107.0, 28.6; MS *m*/*z* = 417.87 (*M* + 1).

4,4,5,5-Tetramethyl-2-(thiophene-2-yl)-1,3,2-dioxaborolane (22). A 1.223 g (14.53 mmol) sample of thiophene dissolved in 50 mL dry THF. At -78 °C and under nitrogen atmosphere 6.4 mL (15.9 mmol) 2.5 M n-butyllithium was added. After stirring 20 min, 3.26 mL (15.9 mmol) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. It was stirred at room temperature and under nitrogen atmosphere overnight. The solvent was removed under vacuum and the crude product was dissolved in dichloromethane and washed with HCl solution (5 N). The organic layer was dried over Na₂SO₄ and filtered, and the solvent was evaporated under reduced pressure. The crude product was separated by column chromatography eluting with hexane/dichloromethane (3/1) to give the title compound (22) (2.44 mg, 81%) as a white solid, mp. 64-67 °C. IR (ATR, diamond) 3098, 2976, 2926, 1519, 1422, 1360, 1328, 1295, 1267, 1209, 1133, 1055, 1017, 1001, 956, 848, 777, 722, 686, 663, 576, 518, 429 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.66 (dd, J = 3.9 Hz, J = 1.1 Hz, 1H), 7.64 (dd, J = 4.8 Hz, J = 1.1 Hz, 1H), 7.19 (dd, J = 4.8 Hz, J = 3.9 Hz, 1H), 1.35 (s, 12H) ; ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 137.1, 132.3, 128.2, 84.1, 24.7 (the signal of the carbon next to tetravalent boron was not observed due to quadrupolar broadening); MS m/z = 211.07 (M + 1).

2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)thiophene (23). To a solution of 2,5-dibromothiophene (0.95 g, 3.95 mmol), dissolved in dry THF (50 mL), was added n-butyllithium (5.18 mL, 8.3 mmol, 1.6 M) at -78 °C under nitrogen atmosphere. After stirring for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.03 mL, 19.75 mmol) was added by syringe, and the stirring was continued for further 1 h at -78 °C, after which the mixture was left stirring at room temperature overnight. The crude product was poured into water, extracted with ethyl acetate and washed with brine. The organic layer was dried over Na₂SO₄ and filtered, and the solvent was evaporated under reduced pressure. The crude product was dissolved in minimum amount of dichloromethane and precipitated in hexane to give the title compound (23) (1.245 mg, 93%) as a white solid, mp 210-212 °C. IR (ATR, diamond) 2973, 2924, 2849, 1521, 1369, 1320, 1259, 1134, 1040, 957, 851, 666, 578, 518, 423 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.66 (s, 2H), 1.34 (s, 24H) ; ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 137.6, 84.1, 24.7 (The signal of the carbon next to tetravalent boron was not observed due to quadrupolar broadening);²² MS m/z = 337.5 (M + 1).

Poly(3-phenyl-2-(thiophen-2-yl)thieno[3,2-b]thiophene) (24). In a Schlenk tube, bis(triphenylphosphine)palladium(II)chloride (14 mg, 0.021 mmol) was degassed under high vacuum. A mixture of 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)thiophene (23) (0.143 g, 0.427 mmol) and 2,5-dibromo-3-phenylthieno[3,2-b]thiophene (17) (0.160 g, 0.427 mmol), dissolved in THF (50 mL) and degassed with nitrogen, and a solution of K₂CO₃ (1.5 mL, 2 M), degassed with nitrogen, were added to the Schlenk tube under nitrogen atmosphere. The mixture was stirred at 70 °C for 3 days. Then, a solution of 2-bromothiophene (12 μ L, 0.125 mmol) dissolved in THF (1 mL) and degassed with nitrogen was added and the mixture was left stirring for 1 day. A solution of 4,4,5,5-tetramethyl-2-(thiophene-2-yl)-1,3,2-dioxaborolane (22) (32.6 mg, 0.137 mmol) dissolved in THF (1 mL) and degassed with nitrogen was added and stirred for overnight. After the mixture was filtrated through Celite, the solution was concentrated under vacuum and the polymer was precipitated in cold methanol: $M_{\rm w}$ 55213, $M_{\rm n}$ 47926, $M_{\rm w}/M_{\rm n}$ 1.15, and dn/dc 0.25 mL/g (THF, 35 °C).

The following were similarly prepared.

Poly(3-(4-methoxyphenyl)-2-(thiophen-2-yl)thieno[3,2-*b*]-thiophene) (**25**) $[M_w$ 262751, M_n 68470, M_w/M_n 3.83, and dn/dc 0.178 mL/g (THF, 35 °C)], poly(3-(4-nitrophenyl)-2-(thiophen-2-yl)thieno[3,2-*b*]thiophene) (**26**) $[M_w$ 264163, M_n 62726, M_w/M_n 4.21, and dn/dc: 0.09 mL/g (THF, 35 °C)], and poly(3-(4-*N*,*N*-dimethylaminophenyl)-2-(thiophen-2-yl)thieno[3,2-*b*]thiophene) (**27**) $[M_w$ 14360, M_n 6051, M_w/M_n 2.37, and dn/dc: 0.10 mL/g (THF, 35 °C)].

Cyclic Voltammetry (CV) Mesurements. Electropolymerizations of the monomers were studied by CV. Ag wire as the reference electrode and Pt wires as both counter and working electrodes were

placed into a three-component CV cell filled with TBABF_4 or $\text{NaClO}_4/\text{LiClO}_4$ (1:1) solutions in ACN, as a supporting electrolyte. Measurements were performed at room temperature.

RESULTS AND DISCUSSIONS

Syntheses of thienothiophenes (TT), PhTT (5), MPhTT (6), NPhTT (7), and BrPhTT (8), having substituted phenyl moiety at C-3 were achieved in two steps by applying the method developed for the syntheses of dithienothiophenes.²¹ Lithiation of 3-bromothiophene (11) with *n*-butyllithium at -78 °C was followed by addition of elemental sulfur and then α -bromoketones (12), which led to the production of the corresponding α -thioketones (13–16) in 41–84% yields (Scheme 1). Ring closure reaction of the ketones in the





presence of P_4S_{10} in refluxing toluene gave the corresponding thienothiophenes (5–8) in 80–94% yields.²³ It is important to note that the purity of P_4S_{10} is crucial to have higher yields of the products. Pure P_4S_{10} does not have any or has very low smell and its color is very light yellow. The nitro group on the phenyl moiety of the NPhTT (7) was reduced to amine with Fe/HCl to yield the APhTT (9) in 83%, which was noticed not to be stable enough for long-standing. It was then methylated with methyl iodide to obtain the DMAPhTT (10), having dimetylaminophenyl group in 65% yield.

The TTs, 5-8 and 10, were both electropolymerized and polymerized via Suzuki coupling with 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)thiophene 23 to obtain the polymers 24-27 (Scheme 2). For the Suzuki coupling polymerizations, initially, the TTs 5-7 were dibrominated with NBS to obtain the 2,5-dibromoTTs 17-19 in 61-68% yields. Reduction of the nitro group of the 2,5-dibromoTT 19 to amino 20 was achieved using Fe/HCl in 43% yield. Use of excess Fe powder, like in the reduction of the nitro group of 7 to the amino 9, caused the loss of one of the bromines on the ring; around 1:2 mol ratio of nitro 19/Fe was found to be the ideal. As it was noticed that the aminoTT 20 is not stable enough, which goes brownish in couple of hours, it was methylated with methyl iodide to obtain the dimethylaminoTT 21 in 36%. Four dibromoTTs, 17-19 and 21, were then subjected to polymerizations with 2,5-diborolaneylthiophene 23, reactions of which were terminated by using 2bromothiophene and 2-borolaneylthiophene 22 to give the polymers 24-27.

Electronic absorption spectra of the TTs were examined in dichloromethane (DCM) (Figure 1). While the TTs having Ph (5), 4-MeOPh (6), 4-BrPh (8), and 4-(CH₃)₂N groups showed absorption maxima between 300 and 302 nm, the TT with 4-



Scheme 2. Syntheses of TT-Thiophene Polymers

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NO₂Ph displayed a red shift up to 365 nm, which is not surprising as nitrobenzene has a strong absorption at 270 nm compare with the strong absorption peak of aniline at 229 nm (Figure 1, Table 1).²⁴ In parallel, optical band gap calculations of the TTs (5), (6), (8) and (10) had a comparable manner between 3.54 and 3.75 eV, except the TT having nitro group (7), which had the lowest band gap of 2.92 eV. It could be concluded that the groups on the phenyl moiety can make some effects on the TT ring, such as red shift on absorption and lowering the band gap when they provide π -extension to the ring.

Electrochemistry of the TTs **5–8** and **10** were conducted in a cyclic voltammetry (CV), using Pt wires as working and counter electrodes and Ag wire as a reference electrode. Electrolytes (TBA)PF₆ (0.1 M) for **5**, 7, and **8**, (TBA)BF₄ (0.1 M) for **6**, and NaClO₄ (0.1 M)/LiClO₄ (0.1 M) for **10** were employed. The TT concentrations were 1×10^{-3} M and the scan rate for the measurements was kept as 100 mV/s. As the compounds PhTT (**5**), MPhTT (**6**), NPhTT (7), and BrPhTT (**8**) displayed one semireversible oxidation potential above 1 V, i.e., 1.68, 1.60, 1.99, and 1.85, respectively, DMAPhTT (**10**) had two oxidation potentials of 0.74 and 1.33 V, irreversible and semireversible, respectively (Figure 2). The lowest



Figure 2. Cyclic voltammograms of the TTs. Conditions: 1×10^{-3} M solutions of 5, 7, and 8 in acetonitrile, 0.1 M Bu₄NPF₆; 6 in acetonitrile, 0.1 M Bu₄NBF₄; 10 in acetonitrile, NaClO₄/LiClO₄ (0.1 M) (1/1). 100 mV/s scan rate, Pt wires as working and counter electrodes, and Ag wire as a reference electrode.

| Table 1. Electrochemica | l, Optica | l and | Electronic | Properties | of the | TTs and | the P | olymers |
|-------------------------|-----------|-------|------------|------------|--------|---------|-------|---------|
|-------------------------|-----------|-------|------------|------------|--------|---------|-------|---------|

| | TT E_{ox} (V) | polymer E_{ox} (V) | polymer $E_{\rm red}$ (V) | polymer E_g^c (eV) | TT λ (nm) | polymer λ (nm) | TT $E_{g}^{opt h}$ (eV) | polymer $E_{g}^{opt h}$ (eV) |
|----|-----------------|----------------------|---------------------------|----------------------|------------------------------------|--|-------------------------|------------------------------|
| 5 | 1.68 | $1.39^{a}/1.04^{b}$ | $-1.54^{a}/-1.42^{b}$ | 2.46 | 300 ^d /329 ^e | 328 ^f /460 ^f /600 ^g | 3.75 | 2.05 |
| 6 | 1.60 | $1.36^{a}/0.89^{b}$ | $-1.27^{a}/-0.97^{b}$ | 1.86 | $302^{d}/334^{e}$ | 318 ^f /439 ^f /619 ^g | 3.70 | 1.99 |
| 7 | 1.99 | $1.09^{a}/1.04^{b}$ | $-1.22^{a}/-0.94^{b}$ | 1.98 | 365 ^d /424 ^e | $331^{f}/442^{f}/572^{g}$ | 2.92 | 2.16 |
| 8 | 1.85 | $1.12/0.92^{b}$ | $-1.67^{a}/-1.43^{b}$ | 2.35 | $302^{d}/336^{e}$ | 324 ^f /431 ^f /563 ^g | 3.68 | 2.19 |
| 10 | 0.74/1.33 | $0.97^{a}/0.73^{b}$ | $-1.77^{a}/-1.54^{b}$ | 2.27 | $302^{d}/349^{e}$ | 317 ^f /468 ^f /615 ^g | 3.54 | 2.01 |

^{*a*}Oxidation and reduction maxima. ^{*b*}Onsets of oxidation and reduction. ^{*c*}From the difference between the onsets of the oxidation and the reduction processes. ^{*d*}Absorption maxima in DCM. ^{*e*}Onset of the absorption in DCM. ^{*f*}Absorption maxima of the polymer films coated on ITO. ^{*g*}Onset of the absorption.



Figure 3. Electropolymerization of the TTs. One $\times 10^{-3}$ M solutions of (5), (7) and (8) in acetonitrile, 0.1 M Bu₄NPF₆; (6) in acetonitrile, 0.1 M Bu₄NBF₄, (10) in acetonitrile, NaClO₄/LiClO₄ (0.1 M) (1/1). 100 mV/s scan rate, Pt wires as working and counter electrodes and Ag wire as a reference electrode.

oxidation peak at 0.74 might be due to the dimethylaniline moiety of the molecule. The highest oxidation/reduction peaks were observed with the NPhTT (7), having strong electron withdrawing nitrophenyl group. The general trend indicated that the nature of the substituted groups has some effects on the oxidation/reduction potentials of the TTs. Electron donating groups, like dimethylamino and methoxy, make the TT rings electron rich and then reduce their oxidation/ reduction potentials. On the other hand, electron withdrawing groups, like nitro and bromine make the TT rings electron poor and increase their oxidation/reduction potentials.

The TTs were electropolymerized by repetitive-cycling over their redox-active peaks, using Pt wires as working and counter electrodes and Ag wire as a reference electrode in CH_3CN . Bu_4NPF_6 for **5**, **7**, and **8**, Bu_4NPF_4 for **6**, and the mixture of $NaClO_4/LiClO_4$ for **10** were applied as electrolytes. Their polymerizations were observed by means of deposition of the polymers on Pt electrode surface and as an increase of oxidation and reduction peaks (Figure 3).

Electrochemistries of the poly-TTs, i.e. p(PhTT), p-(MPhTT), p(NPhTT), p(BrPhTT), and p(DMAPhTT), were investigated with their films on Pt disk electrode in a monomer-free CH₃CN solution, containing Bu₄NPF₆ as a supporting electrolyte (Figure 4). Before the experiments, each polymer was dedoped to its neutral state by repetitive cycling in a region of no electroactivity. While the p(PhTT) and p(MPhTT) featured reversible and quasi-reversible oxidation waves, respectively, the rest of the polymers, p(NPhTT), p(BrPhTT) and p(DMAPhTT) displayed irreversible oxidation waves. Although the lowest oxidation peak was observed with the polymer p(DMAPhTT) with 0.97 V, having strong electron donating dimethylamino groups, there is no clear conclusion for the effect of the substituted groups on the TT polymer chains for the rest of the polymers, oxidation peaks of which varied between 1.09 and 1.39 V, i.e., 1.09 V for p(NPhTT), 1.12 V for p(BrPhTT), 1.36 V for p(MPhTT), and 1.39 V for p(PhTT). Such a result could be attributed to the factor of the morphology of the polymer films and interchain interactions. Regarding the reduction of the polymers, while the polymer, p(DMATT), had the most negative potential (-1.77 V), the polymer p(NPhTT), having the most electron withdrawing nitro group had the least negative potential (-1.22 V).



Figure 4. Cyclic voltammograms of the polymer films on Pt disk electrode in acetonitrile, 0.1 M Bu_4NPF_{6r} 100 mV/s scan rate.

Electronic band gaps of the polymers varied between 1.86 and 2.46 V (Table 1).

Optical behaviors of the polymers were examined by UV measurements. The TTs were electrochemically polymerized on indium-tin-oxide (ITO) coated glass electrodes (20 mC) and washed with a monomer free solution to remove the



Figure 5. CV–UV measurments of the polymers coated on ITO, 0-1.8 V. Conditions: 5, 7, and 8 in acetonitrile, 0.1 M Bu₄NPF₆; 6 in acetonitrile, 0.1 M Bu₄NPF₄; 10 in acetonitrile, NaClO₄/LiClO₄ (0.1 M) (1/1), 5 mV/s scan rate, Pt wire as counter electrode, and Ag wire as a reference electrode.

unreacted monomers. Absorbance measurements of the polymers on ITO indicated that all the polymers had two general absorbance maxima between 317 and 331 nm and at 431-468 nm, possibly due to the phenyl moieties and the TT backbones, respectively. Interestingly, contrary to the absorptions of the monomers, among which the monomer NPhTT (7) showed the longest absorption maximum (365 nm) and the longest onset of absorption (424 nm), the polymers displayed a regular trend of onsets of absorptions. As the polymers having electron donating groups had the longest onsets, the polymers having electron withdrawing groups had the shortest onsets. Then, their absorption onsets and, in connection, their optical band gaps could be summarized in the order of p(MPhTT)(619 nm) > p(DMAPhTT) (615 nm) > p(PhTT) (600 nm) >p(NPhTT) (572 nm) > p(BrPhTT) (563 nm) and p(MPhTT)(1.99 eV) < p(DMAPhTT) (2.01 eV) < p(PhTT) (2.05 eV) <p(NPhTT) (2.16 eV) < p(BrPhTT) (2.19 eV), respectively (Table 1). It looks like the effect of the conjugation of the nitro group with the TT ring was suppressed by long conjugation in the polymer chain.

Spectroelectrochemistry of the polymers was investigated (Figure 5). The polymer coated glasses were introduced into UV cuvettes as working electrodes, filled with monomer free electrolyte solution. Pt and Ag wires were used as counter and reference electrodes, respectively. For all the polymers p(PhTT), p(MPhTT), p(NPhTT), p(BPhTT), and p-(DMAPhTT), the changes in their absorbance were measured in situ as a function of potential change starting from 0 V, which was gradually increased up to 2.2 V. The alterations of the absorbances were observed through stepwise UV measurements. In overall appearance of the five polymers, as a result of the electrochemical doping, their absorption peaks at neutral states, decreased in intensity, while new polaron and bipolaron peaks were formed around 700 and 1000 nm (Figure 5).

The polymers 24–27, obtained by Suzuki coupling of the dibromoTTs 17–19 and 21 with 2,5-diborolaneylthiophene 23 (Scheme 2) displayed absorbance and emission bands between 413 and 445 and at 454–564 nm, respectively (Figure 6, Table 2). Their quantum yields indicated that as the polymer having



Figure 6. Absorbance and emission spectra of the polymers 24-27.

nitro group **26** had the lowest quantum yield (0.003), the one with methoxy group **25** had the highest yield (0.64) (Table 2), which are expected results as the strong electron withdrawing nitrobenzene group decreases the quantum yield.²⁵ Optical band gaps of the polymers were calculated to be between 2.28 and 2.57 eV from their absorption onsets.

Cyclic voltammetry behaviors of the polymers 24-27 were investigated in dry and degassed acetonitrile, having Bu_4NPF_6 as electrolyte, under nitrogen atmosphere, by drop-coating onto Pt disk electrode from their dichloromethane solutions (Figure 7, Table 2). Pt and Ag wires were applied as counter and reference electrodes. The polymers were scanned between -2and +2 V and their electronic bandgaps were calculated to be between 2.07 and 2.43 eV from the differences between the onsets of oxidation and reduction peaks.

Thermal gravity analyses of the polymers 24-27 displayed the start of exothermic weight lose at 248, 261, 255, and 301 °C, respectively, which was supported by decomposition peaks obtained from DSC measurements at the same temperatures (see Supporting Information).

CONCLUSIONS

In this work, a concise synthesis of thieno[3,2-b]thiophene (TT) derivatives, having substituted phenyl groups at C-3, have been reported, which involved two steps with overall moderate

| Tab | le 2. | Electroc | hemical, | 0 | ptical | and | Electronic | Pro | perties | of | the | Copol | lymers | 24 - 27 | 7 |
|-----|-------|----------|----------|---|--------|-----|------------|-----|---------|----|-----|-------|--------|---------|---|
|-----|-------|----------|----------|---|--------|-----|------------|-----|---------|----|-----|-------|--------|---------|---|

| | $E_{\rm ox}$ (V) | $E_{\rm red}$ (V) | E_{g}^{c} (eV) | $\mathrm{UV}_{\mathrm{max}}\lambda(\mathrm{nm})$ | $UV_{onset} \lambda (nm)$ | $E_{g}^{opt d}$ (eV) | $E_{\rm m}$, max λ (nm) | $\Phi_{\rm F}$ |
|----|---------------------|-----------------------|------------------|--|---------------------------|----------------------|----------------------------------|--------------------|
| 24 | $1.31^{a}/0.82^{b}$ | $-1.73^{a}/-1.61^{b}$ | 2.43 | 445 | 541 | 2.28 | 561 | 0.47 ^e |
| 25 | $0.93^a / 0.75^b$ | $-1.78^{a}/-1.56^{b}$ | 2.31 | 413 | 509 | 2.42 | 537 | 0.64 ^e |
| 26 | $1.27^{a}/0.88^{b}$ | $-1.51^{a}/-1.41^{b}$ | 2.29 | 325 | 481 | 2.57 | 454 | 0.003 ^f |
| 27 | $1.2^{a}/1.02^{b}$ | $-1.15^{a}/-1.05^{b}$ | 2.07 | 445 | 538 | 2.29 | 564 | 0.41 ^e |

^aOxidation and reduction maxima. ^bOxidation and reduction onsets. ^cFrom the difference between the onsets of the oxidation and the reduction processes. ^dFrom the onsets of the absorptions. ^eFluorescein was used as a reference. ^f9,10-Diphenylanthracene was used as a reference.



Figure 7. Cyclic voltammograms of the polymers 24-27 on Pt disk electrode in acetonitrile, 0.1 M Bu₄NPF₆, and 100 mV/s scan rate.

to high yields. As the syntheses of TTs, having functional groups at C-3, is a difficult task, the method reported here is a convenient one. Their polymers were prepared by both electrochemistry and Suzuki coupling with thiophene. Properties of the TTs and their polymers were characterized by absorption and fluorescence spectroscopies, CV and CV-UVvis spectroelectrochemistry. The longest absorption band and the lowest band gap were displayed by the TT having 4nitrophenyl group at 365 nm and as 2.92 eV, respectively. Regarding the polymers coated on ITO, the polymer with 4methoxyphenyl had the longest red edge and the lowest band gap of 1.99 eV. The copolymers of the TTs with thiophene displayed band gaps and emissions between 2.0 and 2.50 eV and 454-564 nm, respectively. The highest quantum yield was obtained as 0.64 with TT, having a methoxy group on the phenyl moiety. The most important part of the resultant TTs is that their functional groups such as nitrophenyl, aniline, bromophenyl and methoxyphenyl, could easily be further functionalized to synthesize new building blocks for new organic materials. Currently, our investigation has been focused on the syntheses of such materials, incorporating the TTs presented in this study.

ASSOCIATED CONTENT

Supporting Information

¹H and ¹³C NMR spectra, HRMS and MS of the new compounds, and TGA curves of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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