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Poly(thieno[3,4-*b*]thiophene)s from Three Symmetrical Thieno[3,4-*b*]thiophene Dimers

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ABSTRACT: Herein we report the synthesis of symmetrical bis(thieno[3,4-*b*]thiophene)s and their electrochemical polymerization. The 2,2'-bis(T34bT) has an oxidation peak at 0.73 V for electropolymerization whereas both 4,4'-bisT34bT and 6,6'-bisT34bT have peak oxidation potentials for polymerization at 0.49 and 0.53 V (0.44 V vs NHE), respectively. For comparison, thieno[3,4-*b*]thiophene (T34bT) polymerizes with an oxidation peak at 0.9 V. Conjugated T34bT polymers prepared from T34bT, 4,4'-bisT34bT, and 6,6'-bisT34bT exhibit similar redox behavior showing oxidation and reduction peaks located at ca. 0.1 V and ca. -0.3 V, respectively, and optical band gaps of ca. 0.9 eV (1377 nm), whereas the conjugated polymer from 2,2'-bisT34bT has redox peaks centered at 0.5 and 0.4 V. Like PT34bT prepared from T34bT, both PT34bTs prepared from 4,4'-bisT34bT and 6,6'-bisT34bT are pale blue to colorless in their oxidized states and sky blue in their neutral forms. PT34bT prepared from 2,2'-bisT34bT is brown in the oxidized state. The conductivities of the PT34bTs from both 4,4'- and 6,6'-bisT34bTs were found to be ca. 2×10^{-5} S/cm in the undoped state, increasing to 0.2 S/cm after iodine doping. The conductivity of PT34bT from 2,2'-bisT34bT was 2×10^{-5} and 0.007 S/cm in the neutral and oxidized forms, respectively.

Introduction

One of the significant goals in the field of conjugated and conductive polymers is the preparation of optically transparent conductors. Numerous potential applications for such materials exist for optically transparent conductive polymers exhibiting $<10^{-4}$ to very high conductivities. Low conductivities would have applicability in areas such as charge dissipation films,¹ as ion storage layers in dual polymer electrochromic devices,² and, with a proper work function, as hole injection layers for light-emitting diodes (LEDs).³ Optically transparent conductive polymers exhibiting high conductivities of >200 S/cm have the potential for indium-doped tin oxide (ITO) replacement in numerous device applications. All plastic electrochromic⁴ and photovoltaic devices⁵ have been fabricated from poly(3,4-ethylenedioxy)thiophene (PEDOT)–poly(styrenesulfonate) (PSS), a conducting polymer having a conductivity of ~ 200 S/cm when processed under the proper conditions.

When a conjugated polymer undergoes oxidation, typically the spectral absorbances shift to a lower energy. Hence, most studies focusing on the preparation of optically transparent conductive polymers have been focused on the synthesis of low-band-gap conjugated polymers. However, recently there was a report of a high-band-gap polymer exhibiting high optical transparency in the oxidized conductive state.⁶ Among several strategies to tune the band gap of conjugated polymers,⁷ polymerization of fused heterocyclic rings has long been known to yield polymers with very low band gaps. This is attributed to the stabilization effect of the fused ring on the quinoidal form

of the main-chain polymer. On the basis of this principle, poly-(isothianaphene) (PITN) is reported to exhibit a band gap of 1.0–1.2 eV.⁸ The oxidative chemical polymerization of 2-derivatized thieno[3,4-*b*]thiophenes has been reported to yield linear polymers with low band gaps ranging from 0.85 to 0.92 eV.^{9,10}

We reported the preparation of poly(thieno[3,4-*b*]thiophene) (PT34bT) from thieno[3,4-*b*]thiophene via oxidative electrochemical polymerization.¹¹ We have also demonstrated that PT34bT can be prepared via oxidative chemical polymerization and that the polymer can be reduced and then sulfonated to levels of 56–65% to yield variable gap water-processable PT34bT. Thin films were prepared via the layer-by-layer technique.¹² We have also reported the oxidative chemical polymerization of T34bT in water in the presence of poly(styrenesulfonic acid) (PSSA) to prepare water-dispersible PT34bT-PSS.¹³ This methodology permitted the formation of optically transparent and conductive films for potential use in low-conductivity applications. Oxidative polymerization of T34bT yields a conjugated polymer exhibiting a band gap of 0.85 eV.¹¹ We have reported the stability of PT34bT-PSS in water for almost a year. Hence, to our knowledge, this is the lowest band gap polymer to exhibit such stability in water and stored under ambient conditions. Films of PT34bT were found to be sky blue in the neutral form and highly transparent in the oxidized form.

PT34bT prepared by electrochemical oxidative polymerization was found to be capable of being both p- and n-doped at low positive and negative potentials, respectively, with excellent stability toward p-doping and moderate stability to n-doping.

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Toward this end, in an attempt to generate a more stable *n*-doper, a polymer consisting of T34bT and cyanovinylene units was prepared.¹⁴ In addition to band-gap tuning via this method and via the degree of sulfonation of PT34bT, we have reported the electrochemical copolymerization of T34bT with EDOT to produce conjugated polymers having band gaps ranging from 0.85 to 1.7 eV.¹⁵ Owing to its low band gap, its ability to easily change the band gap between 0.85 and 1.7 eV, and its stability in both air and water, PT34bT is a promising material for incorporation as an ion storage layer in electrochromics, as a hole injection layer for LED applications, and as transparent charge dissipation coatings. Further studies into this system could result in gaining insight into its potential for these applications and potentially for ITO replacement.

T34bT is more complicated than EDOT with its oxidative polymerization in that it has less symmetry and there are three positions alpha to a sulfur atom. Initial coupling of T34bT through alpha coupling could result in six different dimers, three of which exhibit symmetry. In an attempt to further understand the oxidative polymerization of T34bT, we report the synthesis of the three symmetrical T34bT dimers and their electrochemical polymerizations. The properties of these three dimers are compared with respect to oxidation potential, and the resulting PT34bTs prepared from them are compared with respect to their optical, electrooptical, and electrical properties. Comparisons of these PT34bTs are also made with PT34bT prepared from T34bT. The synthesis of the dimers is important in that they can serve as building blocks to more intricate conjugated structures. Furthermore, bisT34bTs could have the same effect on the synthesis of PT34bT as bis(ethylenedioxythiophene) (BiEDOT) has on the synthesis of PEDOT.¹⁶

Experimental Section

Chemicals. Thieno[3,4-*b*]thiophene (T34bT) was prepared in accordance to literature procedure from 3,4-dibromothiophene.¹⁷ Copper(II) chloride (99%), hydrazine hydrate (100%), anhydrous antimony(V) pentachloride (99%), and deuterated chloroform were purchased from ACROS Organics and used as received. Tetrahydrofuran (ACROS) was distilled over potassium before use. Nitrobenzene and acetonitrile were purchased from ACROS Organics and distilled over calcium hydride before use. Lithium trifluoromethanesulfonate (LITRIF) was purchased from Aldrich and used as received. Silica gel (catalog # 30930M-25) was purchased from Sorbent Technologies.

Instrumentation. Spectra were recorded using a Perkin-Elmer Lambda 900 UV-vis-NIR spectrometer. ¹H and ¹³C NMR spectra were obtained using a Bruker 400 FT-NMR spectrometer. ¹H and ¹³C chemical shifts are reported in ppm downfield with respect to tetramethylsilane (TMS) internal reference. Fourier transform infrared spectroscopy (FT-IR) was performed using a MAGNA-IR560. Polymer film thicknesses were measured using a Zygo New View 3-D surface profiler. ITO-coated glass (dimensions 7 mm × 50 mm × 0.7 mm, *R_s* = 15–25 Ω, unpolished float glass) was purchased from Delta Technologies.

Electrochemistry. All electrochemical experiments were performed in a three-electrode configuration and with a CHI 400 potentiostat. The reference electrode was a nonaqueous Ag/Ag⁺ reference electrode consisting of a silver wire immersed in a glass capillary body fitted with a Vycor tip and filled with a 10 mM silver nitrate, 0.1 M lithium triflate/ACN solution. The Ag/Ag⁺ reference electrode was calibrated to be 0.44 V vs the normal hydrogen electrode (NHE) using 10 mM ferrocene solution. Electrochemical quartz crystal microbalance (EQCM) studies were carried out using a CHI 400 potentiostat equipped with an oscillator circuit. Polished quartz crystals coated with a 0.201 in. diameter gold key electrode on both sides and operating at a resonance frequency of 7.995 MHz were purchased from International Crystal

Manufacturing. The key electrode consisted of a 1000 Å thick gold coating atop a 100 Å chromium coating and was soldered to electrical contact leads that were sealed away from the solution. A 1 cm² platinum flag was used as the counter electrode. All the electrochemical and EQCM studies were carried out using 0.1 M LITRIF/ACN/nitrobenzene (1:1 w/w).

Conductivity Measurements. Electrical conductivities were measured using a four-probe collinear array utilizing a Keithley Instruments 224 constant current source and a 2700 multimeter. Disks of the PT34bTs having 1.2 cm diameter were prepared by pressing 50 mg of the PT34bT under 57 kpsi. Current was applied across the outer leads on pressed conducting polymer pellet, and voltage was measured across the inner leads. To test whether the polymer films follow Ohm's law, a minimum of three different currents between 1 × 10⁻⁵ and 1 × 10⁻⁷ A was applied, and the resistance values were found to be the same at these different current levels within 1–2% error. During conductivity testing, the humidity was 65% with a room temperature of 25 ± 2 °C.

4,6-Bis(triisopropylsilyl)thieno[3,4-*b*]thiophene, 1. To a 100 mL vacuum-dried and nitrogen-purged three-neck round-bottomed flask, 50 mL of anhydrous THF and 1.045 g (7.5 mmol) of T34bT in 10 mL of anhydrous THF were added dropwise via syringe. The reaction mixture was cooled to -78 °C via dry ice/acetone and stirred for 15 min to equilibrate at this temperature. To this solution, 6.3 mL (15.7 mmol) of 2.5 M *n*-BuLi in *n*-hexane was added via a pressure-equalized addition funnel over a 5 min period, and the reaction mixture was stirred for a further 1.5 h. Then, 4.0 mL (18.7 mmol) of triisopropylsilyl chloride was added dropwise for 4 min at this temperature. The solution was stirred overnight at -78 °C. The reaction was completed by addition of 20 mL of deionized water, and the THF was evaporated in rotary evaporator. The organic components were twice extracted with 100 mL of diethyl ether. The organic layers were combined and dried over MgSO₄. The solution was filtered, and the diethyl ether was evaporated by rotary evaporator to yield a light green solid which was recrystallized from 2-propanol. 1.82 g (54%) of **1** was obtained as white crystals after filtration and room temperature vacuum-drying. ¹H NMR (CDCl₃): 6.97 (d, *J*(H,H) = 5.5 Hz, 1H; H-3), 7.37 (d, *J*(H,H) = 5.5 Hz, 1H; H-2), 1.52 (sept, *J*(H,H) = 7.6 Hz, 6H; CH), 1.33 (d, *J*(H, H) = 7.6 Hz, 36H; CH₃). ¹³C NMR: 133.6 ppm (C-2), 118.4 ppm (C-3), 127.3 ppm (C-4), 125.3 ppm (C-6), 148.4 ppm (C-7), 155.3 ppm (C-8), 18.7 ppm (CH₃), 12.4 ppm (CH). GC-MS: single peak with mass of molecular ion 452, FT-IR: 3095 and 3068 cm⁻¹ (aromatic C-H stretching), 2942 and 2864 cm⁻¹ (aliphatic C-H stretching), 1535 and 1460 cm⁻¹ (aromatic C=C stretching), 724 cm⁻¹ (Si-C stretching).

2-(4,6-Bis(triisopropylsilyl)thieno[3,4-*b*]thiophen-2-yl)-4,6-bis(triisopropylsilyl)thieno[3,4-*b*]thiophene, 2. To a 500 mL vacuum-dried and nitrogen-purged three-neck round-bottom flask was added 380 mL of anhydrous THF. Then, 2 g (4.4 mmol) of 4,6-bis(triisopropylsilyl)thieno[3,4-*b*]thiophene in 20 mL of anhydrous THF was added dropwise via syringe. The reaction mixture was cooled to -78 °C via dry ice/acetone and stirred for 15 min at this temperature. 2.0 mL (4.9 mmol) of 2.5 M *n*-BuLi in *n*-hexane was added dropwise for 3 min, and the reaction mixture was stirred for another 30 min. The dry ice/acetone bath was removed, and the reaction mixture was allowed to warm to room temperature during the course of 1 h. Then, 1.2 g (8.8 mmol) of copper(II) chloride was added in one portion. The solution was heated to 50 °C and stirred overnight. After reaction, 50 mL of deionized water was added and THF was removed. The organic components were extracted twice with 100 mL of diethyl ether. The organic layers were combined and dried over MgSO₄. The solution was filtered, and the diethyl ether was evaporated to yield a reddish-yellow crude solid. Purification was carried out by a silica column using petroleum ether to give 0.75 g of orange solid in 38% yield. ¹H NMR (CDCl₃): 7.07 (s, 2H; H-3), 1.55 (sept, *J*(H,H) = 7.6 Hz, 12H; CH), 1.18 (d, *J*(H,H) = 7.6 Hz, 72 H; CH₃). ¹³C NMR: 142.9 ppm (C-2), 115.7 ppm (C-3), 128.7 ppm (C-4), 125.3 ppm (C-6), 147.2 ppm (C-7), 155.0 ppm (C-8), 18.8 ppm (CH₃), 12.4 ppm (CH). FT-IR: 3105 and 3076 cm⁻¹ (aromatic C-H stretching),

2942 and 2864 cm^{-1} (aliphatic C–H stretching), 1530 and 1462 cm^{-1} (aromatic C=C stretching), 725 cm^{-1} (Si–C stretching).

2,2'-Bis(thieno[3,4-*b*]thiophene) (2,2'-bisT34bT), 3. To a 50 mL vacuum-dried and nitrogen-purged round-bottomed flask, 10 mL of anhydrous THF and 518 mg (0.57 mmol) of 2-(4,6-bis(triisopropylsilyl)thieno[3,4-*b*]thiophen-2-yl)-4,6-bis(triisopropylsilyl)thieno[3,4-*b*]thiophene were added and stirred for 10 min. The reaction mixture was cooled to -78°C via dry ice/acetone bath and stirred for 15 min at this temperature. To this solution, 2.9 mL (2.9 mmol) of 1 M tetrabutylammonium fluoride (TBAF) in THF was added using a syringe, and the reaction mixture was stirred for 5 h at -78°C . THF was then evaporated. To this flask, 25 mL of cold ethanol was added and shaken for 10 min. The filtered solid was washed twice with 25 mL of cold ethanol on the funnel. The yellow solid was dried under vacuum overnight to yield 138 mg of **3** as a yellow powder in 87% yield. There was no need for further purification. ^1H NMR (CDCl_3): 7.07 (s, 2H; H-3), 7.20 (d, $J(\text{H,H}) = 2.6$ Hz, 2H; H-4), 7.33 (d, $J(\text{H,H}) = 2.6$ Hz, 2H; H-6). ^{13}C NMR: 143.0 ppm (C-2), 110.8 ppm (C-3), 114.5 ppm (C-4), 113.0 ppm (C-6), 137.7 ppm (C-7), 147.1 ppm (C-8). GC-MS: single peak with mass of molecular ion 278, FT-IR: 3093 and 3055 cm^{-1} (aromatic C–H stretching), 1546 and 1463 cm^{-1} (aromatic C=C stretching). UV/vis (acetonitrile): λ_{max} (ϵ) = 248 nm (shoulder), 253 nm (2.5×10^4), 259 nm (2.6×10^4), 265 nm (2.1×10^4), 328 nm (3959), 345 nm (4204), 362 nm (3816).

6-Triisopropylsilylthieno[3,4-*b*]thiophene, 4. To a 250 mL vacuum-dried and nitrogen-purged round-bottom three-neck flask, 5.0 g (35.7 mmol) of T34bT in 150 mL of anhydrous THF was added and stirred for 10 min. The reaction mixture was cooled to -78°C via dry ice/acetone bath and stirred for 30 min. 14.3 mL (35.7 mmol) of 2.5 M *n*-BuLi in *n*-hexane was added by syringe, and the reaction mixture was stirred for 30 min at -78°C . 6.8 g of triisopropyl chloride was then added via syringe, and the solution was stirred for a further 2 h at -78°C . The solution was then poured into 500 mL of deionized water, and the organic components were extracted thrice with 200 mL of ethyl ether. The organic layers were combined and dried over MgSO_4 . The solution was filtered, and the ethyl ether was evaporated to yield a crude light brown liquid which solidified upon cooling. This solid was purified via silica column using petroleum ether to give 4.82 g (46%) of **4** as a yellow powder. ^1H NMR (CDCl_3): 6.94 (d, $J(\text{H,H}) = 5.5$ Hz, 1H; H-3), 7.34 (d, $J(\text{H,H}) = 5.5$ Hz, 1H; H-2), 7.62 (s, 1H; H-4), 1.54 (sept, $J(\text{H,H}) = 7.0$ Hz, CH, 3H), 1.15 (d, $J(\text{H,H}) = 7.0$ Hz, CH_3 , 18H). ^{13}C NMR: 132.1 ppm (C-2), 116.3 ppm (C-3), 117.6 ppm (C-4), 119.0 ppm (C-6), 132.0 ppm (C-7), 148.6 ppm (C-8), 18.6 ppm (CH_3), 12.3 ppm (CH). GC-MS: single peak with mass of molecular ion 296. FT-IR: 3090 and 3079 cm^{-1} (aromatic C–H stretching), 2944 and 2862 cm^{-1} (aliphatic C–H stretching), 1539 and 1466 cm^{-1} (aromatic C=C stretching), 752 cm^{-1} (Si–C stretching).

6,6'-Bis(triisopropylsilyl)-4,4'-bis(thieno[3,4-*b*]thiophene), 5. To a 250 mL vacuum-dried and nitrogen-purged round-bottomed flask, 2.5 g (8.4 mmol) of **4** and 150 mL of anhydrous THF were added and stirred for 10 min. The reaction mixture was cooled to -78°C via dry ice/acetone and stirred for 30 min. To this solution, 3.5 mL (8.8 mmol) of 2.5 M *n*-BuLi was added by syringe, and the reaction mixture was stirred for 30 min. 1.1 g (8.3 mmol) of CuCl_2 was added in one portion. The solution was stirred for a further 2 h at -78°C , after which 200 mL of deionized water was added, and the organic components were extracted thrice with 150 mL of chloroform. The organic layers were combined and dried over MgSO_4 , and the solution was filtered and chloroform evaporated to yield a crude light brown solid. Purification by silica column was carried out using CHCl_3 as the eluent. 1.65 g (33%) of **5** was isolated as a yellow solid. ^1H NMR (CDCl_3): 7.28 (d, $J(\text{H,H}) = 5.8$ Hz, 2H; H-3), 7.37 (d, $J(\text{H,H}) = 5.8$ Hz, 2H; H-2), 1.48 (sept, $J(\text{H,H}) = 7.2$ Hz, CH, 6H), 1.13 (d, $J(\text{H,H}) = 7.2$ Hz, CH_3 , 36H). ^{13}C NMR: 132.5 ppm (C-2), 117.4 ppm (C-3), 128.5 ppm (C-4), 118.6 ppm (C-6), 144.3 ppm (C-7), 148.4 ppm (C-8), 18.7 ppm (CH_3), 12.4 ppm (CH). FT-IR: 3095 and 3078 cm^{-1} (aromatic C–H stretching), 2941 and 2863 cm^{-1} (aliphatic C–H

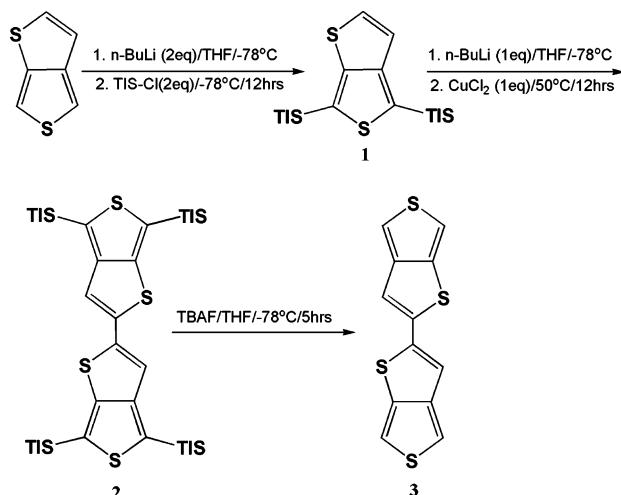
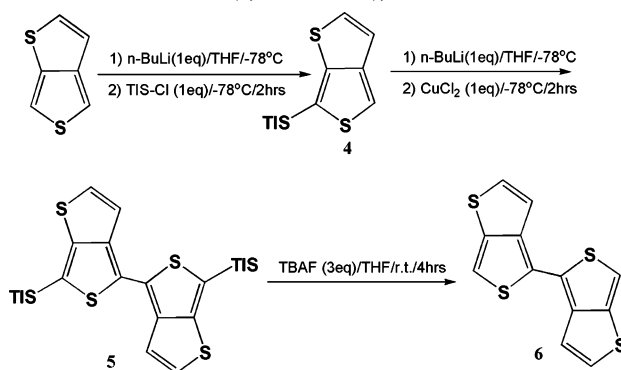
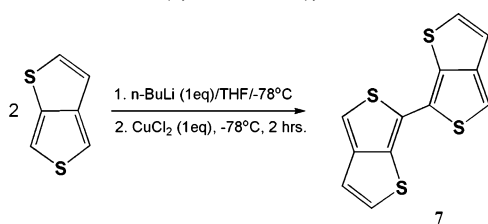
stretching), 1541 and 1463 cm^{-1} (aromatic C=C stretching), 752 cm^{-1} (Si–C stretching).

4,4'-Bis(thieno[3,4-*b*]thiophene) (4,4'-bisT34bT), 6. To a 500 mL vacuum-dried and nitrogen-purged round-bottom flask, 1.0 g (1.7 mmol) of **5** and 200 mL of anhydrous THF were added and stirred for 10 min. 5.4 mL (5.1 mmol) of 1 M tetrabutylammonium fluoride (TBAF) in THF was added by syringe, and the reaction mixture was stirred for 4 h at room temperature. Then, THF was evaporated to give dark brown sludge. 150 mL of ethanol was added, and the solution was agitated for 10 min and then sonicated for an additional 5 min before filtration. The filtered solid was washed twice with 50 mL of cold ethanol on the funnel. The yellow solid was dried under vacuum overnight to yield 0.45 g (94%) of **6** as a light green powder. ^1H NMR (CDCl_3): 6.95 (d, $J(\text{H,H}) = 5.5$ Hz, 2H; H-3), 7.36 (s, 2H; H-4), 7.43 (d, $J(\text{H,H}) = 5.5$ Hz, 2H; H-2). ^{13}C NMR: 133.1 ppm (C-2), 117.4 ppm (C-3), 122.8 ppm (C-4), 110.8 ppm (C-6), 134.7 ppm (C-7), 147.8 ppm (C-8). GC-MS: single peak with mass of molecular ion 278, FT-IR: 3105 and 3076 cm^{-1} (aromatic C–H stretching), 1541 and 1466 cm^{-1} (aromatic C=C stretching). UV/vis (acetonitrile): λ_{max} (ϵ) = 248 nm (shoulder), 253 nm (2.5×10^4), 259 nm (2.8×10^4), 265 nm (2.4×10^4), 405 nm (1540), 430 nm (shoulder).

Preparation of 6,6'-Bis(thieno[3,4-*b*]thiophene), 7. To a 100 mL vacuum-dried and nitrogen-purged round-bottom flask, 0.50 g (3.6 mmol) of T34bT and 50 mL of anhydrous THF were added and stirred for 10 min. The reaction mixture was cooled to -78°C via a dry ice/acetone bath and stirred for 30 min. 1.45 mL (3.6 mmol) of 2.5 M *n*-BuLi in *n*-hexane was added by syringe, and the reaction mixture was stirred for 30 min. 0.49 g (3.6 mmol) of CuCl_2 was added in one portion, and the solution was stirred for a further 2 h. The solution was then poured into 150 mL of deionized water, and the organic components were extracted twice with 150 mL of diethyl ether. The organic layers were combined, dried over MgSO_4 , and filtered, and the solvent was evaporated to yield a crude light brown solid. Silica column using CHCl_3 as the eluent was used for purification to yield 0.41 g (84%) of **7** as a yellow solid after 3 h of vacuum-drying. ^1H NMR (CDCl_3): 6.95 (d, $J(\text{H,H}) = 5.5$ Hz, 2H; H-3), 7.36 (s, 2H; H-4), 7.43 (d, $J(\text{H,H}) = 5.5$ Hz, 2H; H-2). ^{13}C NMR: 133.1 ppm (C-2), 117.4 ppm (C-3), 110.8 ppm (C-4), 122.8 ppm (C-6), 134.7 ppm (C-7), 147.8 ppm (C-8). GC-MS: single peak with mass of molecular ion 278, FT-IR: 3098 and 3071 cm^{-1} (aromatic C–H stretching), 1541 and 1466 cm^{-1} (aromatic C=C stretching). UV/vis (acetonitrile): λ_{max} (ϵ) = 243 nm (shoulder), 253 nm (3.6×10^4), 259 nm (3.8×10^4), 265 nm (3.4×10^4), 378 nm (1837), 393 nm (2040), 398 nm (shoulder).

Results and Discussion

Preparation of T34bT Dimers. It was necessary to prepare 2,2'-bisT34bT by Ullmann coupling^{18,19} from the 4,6-silyl-protected T34bT, **2**. 1 equiv of *n*-butyllithium was used to lithiate the 2-position of **2** followed by coupling mediated by copper(II) chloride. Deprotection of **3** by tetrabutylammonium fluoride gave an overall 17.8% purified yield of **3** from T34bT. 4,4'-bisT34bT, **6**, was prepared similar to 2,2'-bisT34bT (Scheme 2). Since it was determined that the 6-position of T34bT is deprotonated first using *n*-butyllithium, it was necessary to first silyl protect this position. The 4-position could then be lithiated coupling promoted using copper(II) chloride. Deprotection of the silyl groups using tetrabutylammonium fluoride afforded **6** in a 14.3% overall purified yield from T34bT. 6,6'-bisT34bT could be prepared directly by the Ullmann coupling reaction in a 84.0% yield, as shown in Scheme 3. The structures of the bisT34bTs were verified via nuclear magnetic resonance spectroscopy (NMR) in conjunction with gas chromatography–mass spectrometry. NOESY (nuclear Overhauser effect spectroscopy), HMQC (heteronuclear correlation through multiple quantum coherence), HMBC (heteronuclear multiple bond connectivities), and COSY (correlation spectroscopy) experi-

Scheme 1. Synthesis of 2,2'-Bis(thieno[3,4-*b*]thiophene) (2,2'-bisT34bT), 3**Scheme 2. Synthesis of 4,4'-Bis(thieno[3,4-*b*]thiophene) (4,4'-bisT34bT), 6****Scheme 3. Synthesis of 6,6'-Bis(thieno[3,4-*b*]thiophene) (6,6'-bisT34bT), 7**

ments confirm the connectivity between the 2- and 2', 4- and 4', and 6- and 6'-positions in the three symmetrical T34bT dimers.

Electrochemical Polymerization. 2,2'-bisT34bT (**3**), 4,4'-bisT34bT (**6**), and 6,6'-bisT34bT (**7**) were electrochemically polymerized using cyclic voltammetry with a potential window of -0.8 to 1.0 V for 2,2'-bisT34bT and -0.8 to 0.6 V for both 4,4'-bisT34bT and 6,6'-bisT34bT. The electrochemical polymerizations of T34bT and bisT34bTs were performed at scan rates of 50 mV/s from a 3 mM monomer/ 0.1 M LITRIF in acetonitrile/nitrobenzene ($1:1$ w/w). Figure 1 shows the cyclovoltammogram obtained from the polymerization of T34bT and dimers. The onset for the oxidation of T34bT was ca. 0.90 V with a peak at 1.06 V. The onset and peak for oxidation of 2,2'-bisT34bT are located at 0.73 and 0.89 V, respectively. Oxidation of 4,4'-bisT34bT and 6,6'-bisT34bT occurs with onset potentials of ca. 0.41 and 0.36 V with diffusion-limited peaks at 0.51 and 0.53 V, respectively. The peaks for 4,4'-bisT34bT and 6,6'-bisT34bT oxidation are 0.55 and 0.53 V lower than the corresponding values for T34bT and 0.38 and 0.36 V lower

than the corresponding values for 2,2'-T34bT. Both the 6,6' and 4,4' dimers are significantly more conjugated than the T34bT, leading to higher energy HOMOs and thereby a lower oxidation potential. The 2,2' dimer is only 0.17 V lower than the T34bT, indicating that the two T34bT rings are most likely torqued from planarity, resulting in only a slightly conjugated structure due to poor π -orbital overlap. This is also indicated by the higher peak oxidation potential of the 2,2' dimer in comparison to the 4,4' and 6,6' dimers (see Figure 2). Of further note is that at the same concentrations the 2,2' dimer exhibits approximately twice the peak current in comparison to the other two dimers, possibly indicating that polymerization ensues from both T34bT rings of the 2,2' dimer. This will be further elaborated on with the gravimetry studies.

For each of the electrochemical polymerizations, the reduction of the conductive polymer deposited on the electrode is observed upon scanning in the cathodic direction, and upon further cycling in the anodic direction, polymerization continues as observed by the increase in current response of the redox of the polymer, indicating an increase in this electroactive species on the electrode surface. The current response of the redox of the polymer from the electrochemical polymerization of the 2,2'-bisT34bT was found to remain constant after five cycles, which is an indication of the passivation of the electrode surface.

Polymer Electrochemistry. After electrochemical polymerization, the conjugated polymers obtained on the Pt electrodes were washed with acetonitrile, and the cyclovoltammograms were obtained in the 0.1 M LITRIF in ACN/nitrobenzene ($1:1$ w/w) solution. The polymers from 2,2'-bisT34bT (**3**), 4,4'-bisT34bT (**6**), and 6,6'-bisT34bT (**7**) will be referred to as PT34bT-3, PT34bT-6, and PT34bT-7, respectively. PT34bT is the polymer obtained from the electrochemical polymerization of T34bT. From Figure 3, PT34bT, PT34bT-6, and PT34bT-7 were found to have broad oxidation and reduction peaks located at ca. 0.1 V and ca. -0.3 V, respectively. There was no observable loss in electroactivity upon 30 repeated scans of each of these polymers. PT34bT-3, however, shows different redox behavior. Its oxidation and reduction peaks occur at ca. 0.5 V and ca. 0.4 V, respectively, which are ~ 0.4 V higher in potential compared to those of PT34bT-6 and PT34bT-7. Similarities of the PT34bT, PT34bT-6, and PT34bT-7 cyclovoltammograms indicate that these polymers are very similar in electronic structure. As eluded to above, monomer-3 could polymerize through both the 4- and 6-positions of both T34bTs, and the resulting PT34bT could be a highly cross-linked network. We postulate from our results that the polymerization of both 4,4'-bisT34bT and 6,6'-bisT34bT occurs mainly through the 4- and 6-positions.

Spectral Properties. Figure 4 shows the vis-NIR spectra of ca. 30 nm thick PT34bT films prepared by electrochemical polymerization of the T34bT dimers on ITO/glass substrate. These films were treated with 0.01 wt % SbCl_5 /acetonitrile solution to ensure the polymers were in their fully oxidized state, and the vis-NIR spectra were recorded. After recording the vis-NIR spectra of the oxidized PT34bTs, the films were then dipped into 0.02 wt % hydrazine hydrate/acetonitrile solution to produce the undoped, neutral polymer, and the vis-NIR spectra were obtained. The spectra of PT34bT-6 and PT34bT-7 in their oxidized state exhibit a maximum absorbance (λ_{max}) at 1065 and 1190 nm. After undoping of PT34bT-6 and PT34bT-7 was accomplished, peaks with λ_{max} values at 750 and 890 nm were apparent, and a complete loss of absorbance at 1065 and 1190 nm, respectively, was observed. The band gaps of PT34bT-6 and PT34bT-7 as determined from the onset of the

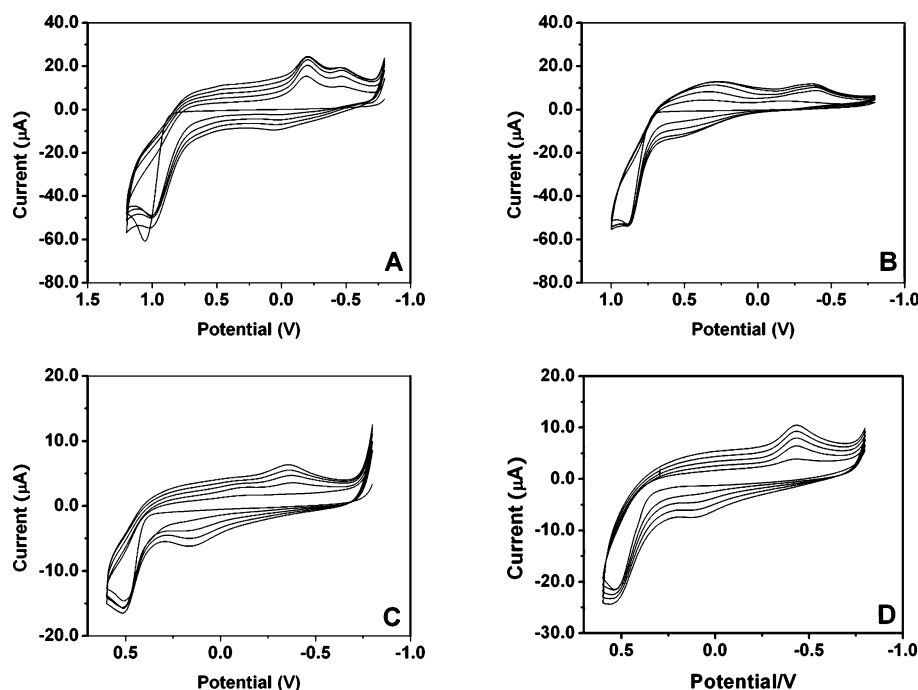


Figure 1. Electrochemical polymerization of (A) T34bT, (B) 2,2'-bisT34bT, **3**, (C) 4,4'-bisT34bT, **6**, and (D) 6,6'-bisT34bT, **7**, using a 3 mM monomer concentration. Scan rate is 50 mV/s using 0.1 M LITRIF in ACN/nitrobenzene (1:1 w/w).

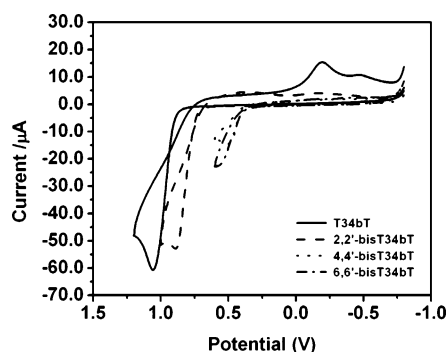


Figure 2. Overlay of the first cyclic voltammograms obtained for the electrochemical polymerizations of T34bT, **3**, **6**, and **7** of Figure 1.

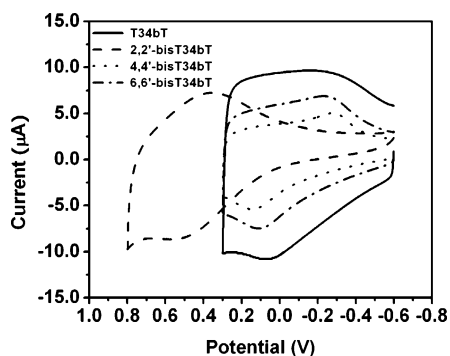


Figure 3. Overlay of the cyclic voltammograms of PT34bT, PT34bT-**3**, PT34bT-**6**, and PT34bT-**7** in 0.1 M LITRIF in ACN/nitrobenzene (1:1 w/w) at a scan rate of 50 mV/s.

π to π^* transition of the undoped polymer were both found to be ca. 0.90 eV, which is in very close agreement with the band gap and of λ_{max} values obtained for PT34bT prepared from T34bT of 0.85 eV (1459 nm) and 1.46 eV (846 nm), respectively.¹⁵ It was difficult to determine the band gap for PT34bT-**3** since the polymer was not completely undoped by either the electrochemical method or chemical methods. The PT34bTs prepared from T34bT, **6**, and **7** are transmissive blue in the

oxidized state and turn a deeper blue upon reduction to the neutral state, whereas PT34bT-**3** was brown and did not demonstrate the ability to be fully oxidized or fully reduced. The as-prepared PT34bTs from T34bT, **6**, and **7** were all found to be stable in both the oxidized and neutral states as indicated by the retention of spectral absorbance as a function of time spent in ambient conditions in each of their corresponding states. The as-prepared PT34bT-**3** was observed to shrink and peel off the electrode upon drying of the solvent, which could be a further indication of the cross-linked nature of the polymer.

Gravimetry. Figure 5 shows the chronogravimetry obtained during the constant potential oxidative electrochemical polymerization of T34bT and dimers. All constant potential polymerizations were performed at the peak oxidation potential of the monomers for a period of 10 s. During this time, the polymer deposited onto crystal as evidenced by a steady increase of mass corresponding to both the conductive polymer and charge balancing counterions. After 10 s, the potential was switched to -0.7 V, at which the polymer is reduced to the neutral form and a loss in mass occurs due to expulsion of primarily anions into the electrolyte solution. It was found that the mass of polymer deposited on gold-coated QCM crystals was 2.22×10^{-5} mmol for T34bT, 1.14×10^{-5} mmol for **3**, 5.54×10^{-6} mmol for **6**, and 4.86×10^{-6} mmol for **7**. The difference in mass deposited on the electrode could be explained by the different reactivities of the corresponding radical cations. As is shown in Figure 2, the oxidation potential of T34bT is 0.90 V, and those of **6** and **7** are ca. 0.4 and 0.5 V lower than that of T34bT. The oxidation potential of **3** is 0.73 V, which is located between T34bT and both **6** and **7**. The higher potential required to oxidize T34bT and **3** is an indication that their radical cations have a higher reactivity, being less conjugated as evidenced in electrochemical polymerization of 2,2'-bisthiophene and 2,2':5',2''-terthiophene compared to thiophene^{20–23} and 2,2'-bis(3,4-ethylenedioxythiophene) compared to 3,4-ethylenedioxythiophene.^{19,24} The higher reactivity of radical cations from T34bT and **3** results in faster polymerization rates as evidenced by increased mass being deposited on the electrode surface. All

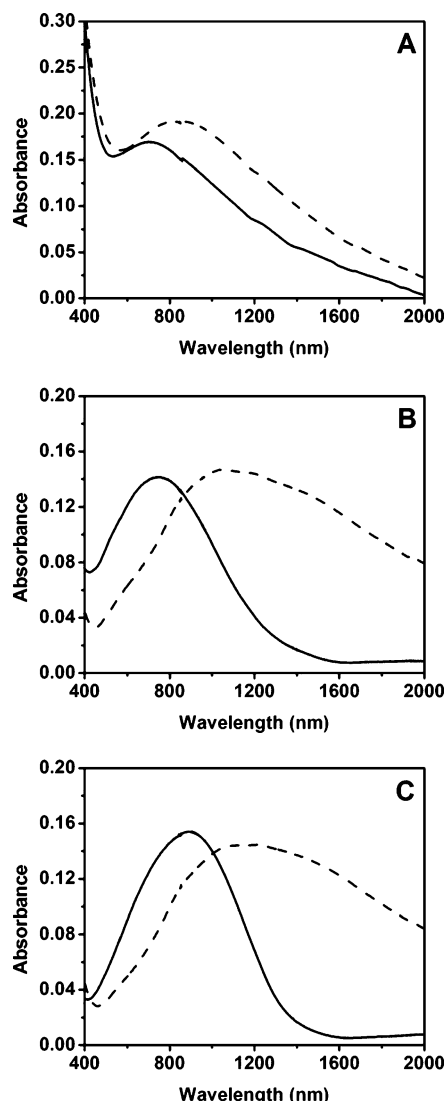


Figure 4. Vis-NIR spectra of (A) PT34bT-3, (B) PT34bT-6, and (C) PT34bT-7 (solid line, undoped state; dashed line, oxidized state).

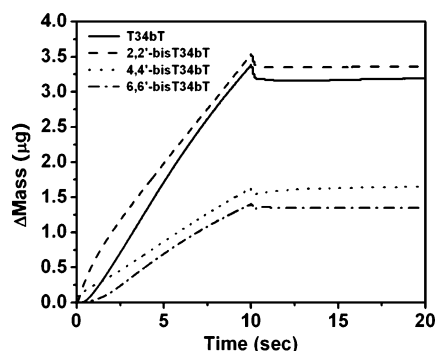


Figure 5. Gravimetry of polymerization and undoping of T34bT, 3, 6, and 7 in 0.1 M LITRIF in ACN/nitrobenzene (1:1 w/w).

three dimers should have the same diffusion in solution, since they are all isomers of each other, whereas diffusion of T34bT should be faster than all three dimers due to its smaller size. Nonetheless, the polymerization of the **3** is faster than T34bT even though its radical cation should have a lower reactivity than the radical cation of T34bT due to a lower oxidation potential. This is an indication that polymerization proceeds from both T34bTs, as if both T34bTs in the dimer behave as if they were individual polymerizable units.

Table 1. Conductivities of Pressed Pellets of PT34bTs Prepared by Electrochemical Polymerization of T34bT, 2,2'-bisT34bT (**3**), 4,4'-bisT34bT (**6**), and 6,6'-bisT34bT (**7**) ($\sigma = \text{S/cm}$)

polymer	neutral	after I ₂ doping
PT34bT	2.2×10^{-5}	1.9×10^{-1}
PT34bT-3	2.8×10^{-5}	7.4×10^{-3}
PT34bT-6	1.8×10^{-5}	2.3×10^{-1}
PT34bT-7	1.4×10^{-5}	2.5×10^{-1}

Electrical Conductivity Measurements. PT34bTs were prepared via the electrochemical polymerization of each dimer using 1 in.² ITO plates as working and counter electrodes. After polymerization at the oxidation peak potentials of each dimer for 500 s, the potential was stepped to -0.8 V in order that the polymer be in the neutral state. The resulting PT34bT was collected from the electrode as a powder, and this process was repeated until 50 mg of polymer was obtained for pellet preparation. The powder was treated with 0.5 M hydrazine hydrate/acetonitrile to ensure a completely undoped polymer, and the polymer was filtered and dried under vacuum for 24 h. 250 μm thick PT34bT pellets with a diameter of 1.2 cm were fabricated using a KBr mold and a press. The conductivities of undoped PT34bTs prepared from electrochemical polymerization of T34bT and its dimers were 10^{-4} – 10^{-5} S/cm . After exposing the pellets to I₂ vapor for 30 min, PT34bTs prepared from T34bT, **6**, and **7** had conductivities averaging ca. 0.2 S/cm, while PT34bT prepared from **3** had conductivity of 0.007 S/cm, as shown in Table 1.

The low conductivity of PT34bT-**3** after I₂ doping could be explained by the spectral response obtained for the doped polymer. The spectral response does not indicate behavior typical of a conductive polymer in that a strong absorption persists through the NIR region. Although electroactive, as indicated from the cyclic voltammetry, the polymer is not significantly conductive. This was also observed from the passivation of the electrode during the oxidative electrochemical polymerization of the 6,6'- dimer. All of these results, we believe, point toward a highly strained polymeric structure due to cross-linking. For comparative purposes conductivities of PEDOT-PSS films prepared from drop-casting commercially available Baytron-P (V 4071 grade) were averaged to 0.1 S/cm in our lab.

Conclusions

We successfully prepared three symmetrical dimers of T34bT via the Ullmann coupling reaction. These dimers were used to evaluate electrochemical production of PT34bT starting at the oligomeric stage. Polymers consisting of each of the dimers, namely **3**, **6**, and **7**, will contain exclusive coupling of the 2-, 4-, and 6-positions, respectively. From the results, having a conjugated PT34bT with 100% 2 coupled positions does not result in a low-band-gap polymer with the ability, in accordance to the vis-NIR spectrum and electrical conductivity results, to be easily transitioned from the neutral to oxidized states. Furthermore, PT34bT-**3** was shown only to exhibit very low conductivities. From the data, it is apparent that both T34bT rings of **3** behave in an independent manner as indicated by the high oxidation potential compared to **6** and **7**. Should coupling occur through the 6,6'- and 4,4'-positions of **6** and **7**, respectively, then the polymers should have the same repeat structure and thereby should be identical with respect to polymer properties. For the most part, we found this to be the case, and furthermore, we found the properties of these polymers, PT34bT-**6** and PT34bT-**7**, to be very similar to PT34bT prepared

from T34bT. Future studies will involve the preparation and study of the asymmetric dimers, 2,4'-bisT34bT, 2,6'-bisT34bT, and 4,6'-bisT34bT, and their comparison with the systems reported here. The synthesis of 2,4'-bisT34bT, 2,6'-bisT34bT, and 4,6'-bisT34bT is significantly more challenging and thereby was not able to be reported here and will be reserved for future publication. The dimers reported within this paper will be further utilized for the preparation of unique conjugated macrocycles and regioregular polymers.

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