

Dithienobenzimidazole-Containing Conjugated Donor–Acceptor Polymers: Synthesis and Characterization

Jared D. Harris ⁽⁾,¹ Markus Stihl,^{1,2} Hans-Werner Schmidt ⁽⁾,² Kenneth R. Carter ⁽⁾

¹Department of Polymer Science and Engineering, University of Massachusetts Amherst, Conte Center for Polymer Research, 120 Governors Drive, Amherst, Massachusetts 01003

²Macromolecular Chemistry I and Bavarian Polymer Institute, University of Bayreuth, Universitätsstrasse 30, 95447, Bayreuth, Germany

Correspondence to: K. R. Carter (E-mail: krcarter@polysci.umass.edu)

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ABSTRACT: The synthesis of two new conjugated polymers based on the relatively under-exploited monomer, 5,8-dibromo-2-[5-(2-hexyldecyl)-2-thienyl]-1*H*-dithieno[3,2-*e*:2',3'-*g*]benzimidazole (dithienobenzimidazole, **DTBI**), and either 4,7-bis[4-hexyl-5-(trimethylstannyl)-2-thienyl]-2,1,3-benzothiadiazole (**BTD**) or 2,6-bis (trimethylstannyl)-4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo [1,2-*b*:4,5-*b*']dithiophene (**BDT**) is described. The polymers were synthesized via Stille polycondensation and characterized by traditional methods (¹H NMR, gel-permeation chromatography, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, thermal gravimetric analysis, differential scanning calorimetry, ultraviolet–visible spectroscopy, photoluminescence, and cyclic voltammetry). Prior to their synthesis,

INTRODUCTION Conjugated polymers continue to enjoy considerable interest owing to their marriage of semiconducting properties with inherent polymeric qualities (solution processability, mechanical flexibility, lightweight, etc.). Due to their semiconducting nature, these materials find applications in numerous electronic devices (light-emitting diodes, photovoltaic cells, thin-film transistors, electrochromic cells, etc.).^{1–3} However, conjugated polymers suffer from numerous drawbacks, limiting their commercial scalability, namely ill-defined morphologies obfuscating charge-transport mechanisms, high batch-to-batch variability, and low oxidative stability. Additionally, unlike inorganic systems, manipulating charge-carrier type and mobility after polymerization remains a major challenge for these materials. Our, and others', work with imidazole-containing conjugated polymers suggest a route to tune frontier molecular orbitals post-polymerization through controlling the charge state of the polymer backbone.^{4–13}

Our initial publications explored 2-alkylbenzimidazoles polymerized from the 4 and 7 positions with various fluorenebased co-monomers.^{4,5} This paper strives to incorporate trimer structures were modeled by DFT calculations facilitating a further understanding of the systems' electronic and geometric structure. Polymers were titrated with acid and base to take advantage of their amphiprotic imidazole moiety and their optical response monitored with ultraviolet–visible spectroscopy. Finally, pristine polymer thin-films were treated with acid and base to evaluate (de)protonation's effect on system electronics, but thin-film degradation was encountered. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**, *57*, 60–69

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lessons from earlier publications describing imidazolecontaining conjugated polymers and the vast body of literature studying conjugated polymer materials. Thus, a new imidazole-containing monomer was conceived and synthesized with the ideals of geometric imidazole isolation, planar fused polycyclic aromatics, and high solubility.^{5,14-16} We previously detailed the sterically favorable motivations for geometrically isolating imidazole.⁵ Innumerable reports discuss planarity's importance in the context of developing relevant materials for device applications. Meanwhile, conjugated polymers are notoriously difficult to solubilize, encouraging our use of relatively long side-chains. This work focuses on the synthesis and polymerization of 5,8-dibromo-2-[5-(2-hexyldecyl)-2-thienyl]-1*H*-dithieno[3,2-*e*:2',3'-*g*]benzimidazole DTBI) with 4,7-bis[4-hexyl-5-(trimethylstannyl)-2-thienyl]-2,1,3-benzothiadiazole (10, BTD) and 2,6-bis(trimethylstannyl)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*'] dithiophene (11, BDT) as well as the resulting polymers' (PDTBI-BTD and PDTBI-BDT, respectively) characteristics. BTD and BDT were chosen as classic acceptor and donor comonomers, respectively, to examine the hybridization

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interactions between the variously charged states of the DTBI moiety. We expected the relative inductive donicity to vary between the comonomers based on the DTBI's charged state—the cationic form acting as an acceptor while the anionic form acting as a donor—hence our general description of these materials as "donor-acceptor" copolymers.

To contextualize this work, a brief review of previously synthesized DTBI-containing polymers follows. A structural isomer, (5,8-dibromo-2-[4-[(2-ethylhexyl)oxy]phenyl]-1-hexyl-1*H*-dithieno[2,3-*e*:3',2'-*g*]benzimidazole), of this monomer core was initially synthesized and homopolymerized by Satapathy et al.¹⁷ with differing solubilizing side chains. By placing the fused thiophenes' sulfur atoms at the 4 and 9 positions, this monomer demonstrated an affinity for both Zn^{2+} and Hg^{2+} . Takagi et al. have also explored homo- and co-polymers (using bithiophene and fluorene co-monomers) from this monomer in addition to the structural isomer presented here.^{11,12} This work focused on the synthesis and general characterization of these materials, including optical spectroscopies and theoretical modeling. Of particular note, the authors demonstrate small decreases in the bithiophene-based co-polymers' E_{g} upon methylation¹¹ or protonation¹² of imidazole. The investigators suggest the positive charge acts as an inductively withdrawing group facilitating intramolecular charge transfer. Density Functional Theory (DFT) and TD-DFT calculations also support this claim as the frontier molecular orbitals were deepened considerably for model compounds as one would expect upon installing electron-withdrawing groups.

The only other known publications involving the polymerization of these monomers come from Keshtov et al.^{18,19} Their work involved the copolymerization of the DTBI structural isomer presented herein, however they employed differing solubilizing side chains; namely, 4-[(2-ethylhexyl)oxy]phenyl, 5-(2-ethylhexyl)thiophene-2-yl, and octafluorobutyl. These dibromo monomers were then polymerized with either benzodithiophene (BDT)¹⁸ or dithienyl-2,1,3-benzothiadiazole (BTD)¹⁹ monomers via Stille coupling. The BTD-containing polymers exhibited low E_g and spectral features typically associated with D-A polymers leading to photovoltaic powerconversion efficiencies (PCEs) in the range of 4.55–6.76%. The BDT-containing material showed very little photocurrent with PCEs <1%.

The polymers synthesized in this report bear strong resemblance to those reported by Keshtov et al. in terms of conjugated monomer cores. However, each of the monomers described herein differ in solubilizing side chains. Preliminary syntheses suggested these materials aggregate strongly, prompting the use of extended, branched 5-(2-hexyldecyl) thiophene-2-yl solubilizing chains on DTBI. Meanwhile, *n*hexyl chains were added to the BTD's flanking thiophenes and 5-(2-ethylhexyl)thiophene-2-yl groups were appended to BDT.

PDTBI-BTD and **PDTBI-BDT** were characterized by standard techniques, including: ¹H NMR, GPC, MALDI-ToF MS, TGA, DSC, UV-vis, PL, and CV. Additionally, trimers of each product



were modeled using DFT methods to gain an understanding of the materials' lowest energy confirmations and relative band structure. Polymer (de)protonation was monitored by UV-vis and PL. Finally, polymer thin films were treated with acid and base solutions in attempt to gain solid (de)protonated films.

EXPERIMENTAL

Materials

All chemicals, solvents, and reagents were used as received without further purification unless otherwise noted. All materials were purchased from typical commercial suppliers.

Instrumentation

NMR spectra were recorded on either a Bruker AvanceIII 500 (500 MHz) or a Bruker AvanceIII 400 (400 MHz). Chemical shifts were determined relative to residual peaks in the deuterated solvent.²⁰ NMR spectra are given in the Supporting Information (Figs. S1-S14). GPC was performed at 40 °C at a flow rate of 1.0 mL min⁻¹ using an Agilent 1260 series system equipped with a refractive index detector, PL Gel 5 µm guard column, two 5 µm analytical Mixed-C columns, and a 5 µm analytical Mixed-D column (Agilent) with THF as the eluent. MALDI-ToF mass spectra were obtained with a Bruker MicroFlex using a 3 kV accelerating potential. MALDI-ToF samples were prepared in THF at a volume ratio of 1:15 sample (5 mg mL⁻¹) to *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix (50 mg mL^{-1}) and drop cast on a ground steel plate. UV-vis absorption in solution, and solid-state were performed on a Cary 50 UV-vis absorption spectrometer with 1 cm path-length quartz cuvettes or quartz plates. Polymer thinfilms were prepared by drop-casting 1.5 mg mL⁻¹ product solutions in 3:1 (v:v) 1,2,4-trichlorobenzene:THF onto plasma treated, octadecyltriethoxysilane-functionalized quartz substrates at 60 °C under a N₂-rich dome. Photoluminescence from solutions was measured with a Cary Eclipse. Cyclic Voltammetry was carried out with a Bioanalytical Systems Inc. EC Epsilon potentiostat in an electrolyte solution of 0.1 M TBAPF₆ in dry acetonitrile. A 3 mm diameter glassy carbon work electrode (Bioanalytical Systems Inc.) was employed alongside a platinum wire counter electrode (Bioanalytical Systems Inc.) and an Ag/Ag⁺ reference electrode (Ag in 0.01 M AgNO₃ solution, Bioanalytical Systems Inc.). All sweeps were done at 200 mV s $^{-1}$ with a 2000 mV switching potential. Molecular modeling and quantum chemical calculations were performed using the Gaussian 09[™] program suite at the B3LYP level of DFT and the 6-31G (d,p) basis set.²¹

Synthesis

2-Hexyldecyl bromide $(1)^{22}$, 1,2-di(thiophen-3-yl)ethane-1,2-dione (4), benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (5), and 2,7-dibromo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (6)²³ were synthesized in accordance with the literature. 4,8-Bis[5-(2-ethylhexyl)-2-thienyl]-benzo[1,2-*b*:4,5-*b'*]dithiophene remained from previous studies.^{24,25}

2-(2-Hexvldecvl)Thiophene (2)

Thiophene (13.20 g, 156.9 mmol, 1.50 eq.) was weighed into an oven dried 1 L round-bottomed flask (A) containing a stir bar. The flask was then cooled in an isopropanol/ $CO_{2(s)}$ bath, evacuated and backfilled with Ar 5×. Anhydrous, deoxygenated THF (~400 mL) was cannulated into A under Ar. Anhydrous, deoxygenated THF (~100 mL) was cannulated into an oven dried 500 mL round-bottomed flask (B) containing a stir bar under Ar. A solution of *n*-BuLi (2.5 M in hexanes, 50 mL) was cannulated into a 100 mL graduated cylinder under Ar. n-BuLi solution (49 mL, 122.5 mmol, 1.17 eq.) was then cannulated into B under Ar, stirred. B was cooled in an isopropanol/CO_{2(s)} bath. B was cannulated into A dropwise under Ar over 50 min, maintaining the temperature of both flasks at -78 °C. A was stirred for 1 h at -78 °C, the pale-yellow solution was then allowed to warm to room temperature over the course of 1 h. Meanwhile, 2-hexyldecyl bromide (1) was added to an oven dried 150 mL round-bottomed flask (C), sealed with a septum and put under vacuum for 1+ h. C was then backfilled with Ar and ~50 mL anhydrous THF was cannulated into it under Ar. After A had warmed to room temperature, C was cannulated into A dropwise over the course of 50 min under Ar. A became orange, but remained clear. After 1.5 h at room temperature, A was warmed to 50 °C and stirred overnight. After 17 h, the dark orange reaction solution was cooled to room temperature and guenched with 250 mL water. THF was removed via rotary evaporation. The hazy aqueous mixture was then extracted with hexanes. The extracts were washed with brine, dried over MgSO₄, gravity filtered, and solvent removed via rotary evaporation to yield a dark orange/brown oil. The oil was dissolved in hexanes and purified by flash column chromatography on SiO₂ packed in hexanes. The unreacted 1 was recovered via Kugelrohr distillation at reduced pressure. The resulting oil (26.51 g) included product as well as bifunctional (2,5-bis(2-hexyldecyl) thiophene). The faintly orange oil was used without further purification. ¹H NMR (500.13 MHz, CDCl₃, δ , ppm, Supporting Information Figure S1) 7.11 (d, / = 5.2 Hz, 2H), 6.91 (t, / = 4.1 Hz, 2H), 6.75 (d, / = 2.7 Hz, 2H), 2.75 (d, / = 6.7 Hz, 2H), 1.99 (t, J = 7.7 Hz, 1H), 1.35-1.20 (m, 24H), 0.88 (t, J = 6.6 Hz, 6H).

5-(2-Hexyldecyl)-2-Thiophenecarboxaldehyde (3)

Anhydrous DMF (14.6 mL, 188.6 mmol, 2.20 eq.) was added to an oven dried, septum sealed, 100 mL round-bottomed flask containing a stir bar under N2 via syringe. The flask was then cooled to 0 °C. Phosphoryl chloride (8.0 mL, 86.1 mmol, 1.00 eq.) was added to the flask dropwise over 10 min via syringe. The mixture was stirred for 20 min before deoxygenated 2-(hexyldecyl)thiophene (2, 26.51 g, 85.9 mmol, 1.00 eq.) was added to the flask dropwise via cannula under N2. The flask was then heated at 100 °C for 3 h. After cooling to room temperature, the flask's contents were poured onto ice in a separatory funnel. The mixture was extracted with diethyl ether. The extracts were washed with water and brine, dried over MgSO₄, gravity filtered, and solvent removed via rotary evaporation. The brown residue was then dissolved in hexanes and purified via flash column chromatography on SiO₂

packed in hexanes using gradient elution up to 9:1 hexanes: EtOAc. The product was recovered as 18.95 g (53.9% over two steps) pale orange/yellow oil. ¹H NMR (500.13 MHz, $CDCl_3$, δ , ppm, Supporting Information Figure S2) 9.82 (bs, 1H), 7.61 (d, J = 4.0 Hz, 2H), 6.87 (d, J = 3.5 Hz, 2H), 2.80 (d, I = 7.0 Hz, 2H), 1.67 (m, 1H), 1.31–1.22 (m, 24H), 0.87₇ (t, J = 6.8 Hz, 3H), 0.87_5 (t, J = 6.8 Hz, 3H). ¹³C NMR (125.76 MHz, $CDCl_3$, δ , ppm, Supporting Information Figure S3) 182.82, 156.78, 141.92, 137.12, 126.95, 40.18, 35.38, 33.30, 33.28, 32.03, 31.97, 30.02, 29.71, 29.69, 29.44, 26.67, 26.65, 22.82, 22.79, 14.27, and 14.25.

5,8-Dibromo-2-[5-(2-Hexyldecyl)-2-Thienyl]-1H-Dithieno [3,2-e:2',3'-g]Benzimidazole (7)

2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**6**, 1.61 g, 4.01 mmol, 1 eq.), 5-(2-hexyldecyl)-2-thiophenecarboxaldehyde (3, 1.46 g, 4.34 mmol, 1.08 eq.), ammonium acetate (7.41 g, 96.1 mmol, 24.0 eq.), and stir bar were added to a 250 mL round-bottomed flask under N2. Glacial acetic acid (40 mL) was added to the mixture. The flask was fitted with a condenser, heated to 110 $^{\circ}$ C, and vigorously stirred under N₂. The reaction mixture was cooled to room temperature after 16 h and then quenched with 40 mL water. The mixture was extracted with toluene. The combined extracts were washed with brine and water then dried over MgSO₄. The mixture was filtered through a thin silica layer prepared atop a Celite pad and the toluene was removed via rotary evaporation. The yellow/brown residue was purified on a silica column packed in 17:2 v:v CHCl₃:hexanes. The product was then recrystallized from methanol once and hexanes once to yield 1.30 g off-white solids (46.8%). ¹H NMR (400.13 MHz, DMSO-d6, δ , ppm, Supporting Information Fig. S4) 13.40 (bs, 1H), 7.92 (s, 2H), 7.62 (d, 1H, J = 3.60 Hz), 6.94 (d, 1H, J = 3.60 Hz), 2.79 (d, 2H, J = 6.40 Hz), 1.65 (m, 1H), 1.32-1.20 (m, 24H), 0.85 (t, 3H, I = 6.75 Hz), 0.82 (t, 3H, 6.91 Hz). ¹³C NMR (100.62 MHz, DMSO-d6, δ , ppm, Supporting Information Fig. S5): δ 146.98, 145.86, 131.38, 127.61, 127.17, 126.62, 125.07, 112.97, 34.33, 33.12, 33.01, 31.77, 31.72, 29.74, 29.47, 29.38, 29.14, 26.40, 26.35, 22.56, 14.42, and 14.40.

Poly(2-[5-(2-Hexyldecyl)-2-Thienyl]-1H-Dithieno[3,2-e:2',3'g]Benzimidazole-2,5-Diyl-Alt-4,7-Bis[4-Hexyl-2-Thienyl]-2,1,3-Benzothiadiazole) (PDTBI-BTD)

7 (66.5 mg, 0.0957 mmol, 0.957 eq.) and 10 (81.8 mg, 0.103 mmol, 1 eq. (adjusted for impurity)) were carefully weighed and added to a 10 mL heavy-walled microwave vial along with a stir bar. The vial was loaded into an Ar-filled dry glovebox where Pd₂(dba)₃ (3.0 mg, 0.003 mmol, 0.03 eq.) and P(o-tol)₃ (4.2 mg, 0.014 mmol, 0.14 eq.) were carefully weighed and added to the vial. Distilled toluene (3.0 mL) was then added to the vial via syringe. The vial was sealed with a septum, removed from the glovebox, and reacted in a CEM Discover SP for 30 s at 110 °C (250 W max) and 45 min at 150 °C (300 W max). By holding the temperature at 110 °C for 30 s before heating to 150 $^\circ\text{C}$, the vial did not pressurize at a rate which could trigger the microwave's rapid pressurization safety feature. Following polymerization, the black mixture was diluted with toluene and dripped into 0 °C stirred, acidic methanol. The fine black solids were filtered through a

Soxhlet thimble and extraction began with MeOH followed by acetone, hexanes, and THF. THF was removed from the final fraction via rotary evaporation and the remnant black residue dissolved in minimal toluene before dripping into 0 $^{\circ}$ C stirred MeOH. The fine black flakes were vacuum filtered and washed with MeOH (59.3 mg, 59.5%).

Poly(2-[5-(2-Hexyldecyl)-2-Thienyl]-1H-Dithieno[3,2-e:2',3'g]Benzimidazole-2,5-Diyl-Alt-4,8-Bis(5-(2-Ethylhexyl) Thiophen-2-yl)Benzo[1,2-b:4,5-b']Dithiophen-2,6-Diyl) (PDTBI-BDT)

PDTBI-BDT was synthesized and purified analogously to **PDTBI-BTD** except **11** (90.5 mg, 0.100 mmol, 1 eq.) was used in place of **10** to gain a dark maroon solid (81.5 mg, 74.6%).

RESULTS AND DISCUSSION

Synthesis

The 5,8-dibromo-2-[5-(2-hexyldecyl)-2-thienyl]-1*H*-dithieno [3,2-e:2',3'-g]benzimidazole monomer (7) was synthesized in two parts (Scheme 1). The aromatic substrate (6) was synthesized in accordance with Arroyave et al. in reasonable yields.²³ First, 3-bromothiophene was lithiated under cryogenic conditions and then reacted with oxalyl chloride to yield **4.** Then **4** underwent an oxidative ring closure with FeCl₃ in high yield to form **5**. This substrate was easily brominated with the electrophilic brominating reagent, *N*-bromosuccinimide, to generate **6**. Attempts to condense **6** with alkyl aldehydes in the spirit of Satapathy et al.¹⁷ were unsuccessful, likely due to the relatively weak electrophilic nature of these aldehydes. Thus, we devised a synthetic route toward a more



SCHEME 1 Synthetic route to gain Br₂DTBI. *i*. PPh₃, CBr₄; *ii*. *n*-BuLi, **1**; *iii*. POCl₃, DMF; *iv*. *n*-BuLi, CuBr, LiBr, oxalyl chloride; *v*. FeCl₃; *vi*. NBS; *vii*. NH₄OAc, acetic acid, **3**. Isolated yields reported; *yield over two steps.

electrophilic side chain (3). Through an Appel reaction, 2-hexyldecyl bromide (1) was easily synthesized from the corresponding alcohol. 1 was then used as an electrophilic alkylating reagent for α -lithiated thiophene. The reaction generated a considerable quantity of bis-alkylated side product when thiophene:alkyl bromide ratios were ~1.1. As a result, we used excess thiophene (1.5 eq.) and found a reduction in bis-alkylated side product. We rigorously removed residual unreacted alkyl bromide from the product mixture. but deferred removal of bis-alkylated thiophene until the following carboxylation. Finally, 2 was carboxylated using Vilsmeier-Haack conditions and purified via column chromatography using gradient elution in hexanes/ethyl acetate. The column was first packed, loaded, and eluted in hexanes until unreacted starting materials and bis-alkylated thiophene were removed. Up to 9:1 hexanes:ethyl acetate was then used to elute the product.

The monomer, **7**, was then synthesized using an adopted procedure from Satapathy et al.¹⁷ We found this monomer somewhat challenging to purify owing to its tendency to drag and precipitate on the column, however, we were still able to obtain it in modest yields.

The bis-stannylated comonomers, 4,7-bis[4-hexyl-5-(trimethylstannyl)-2-thienyl]-2,1,3-benzothiadiazole (**10**) and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo [1,2-b:4,5-b']dithiophene (**11**), were synthesized through fairly

traditional methods (Supporting Information Scheme S1). To begin, 3-hexylthiophene was selectively stannylated in the 5-position through lithiation via sterically hindered LDA followed by Me₃SnCl to synthesize 2-(trimethylstannyl)-4-hexylthiophene (8). 8 was then Stille coupled to 4,7-dibromo-2,1,3-benzothiadiazole employing a Pd⁰ catalyst generated from the in situ reduction of Pd(PPh₃)₂Cl₂. The resulting product, 4,7-bis[4-hexyl-2-thienyl]-2,1,3-benzothiadiazole (9), was readily purified by column chromatography followed by recrystallization. Finally, this substrate was bis-lithiated and stannylated by LDA and Me₃SnCl, respectively. ¹H NMR indicated reasonable yields for this transformation (65-70%); however, purification proved difficult by column chromatography owing to the sensitivity of organostannes to Lewis Acids (silica). This necessitated the use of 5 vol % TEA in hexanes, which hampered efficient separation due to the increased polarity. The purified orange solid was then recrystallized from ethanol three times.

Much of the synthetic load required for the generation of **11** was mitigated owing to material remaining from the studies of Homyak et al.^{24,25} 4,8-Bis[5-(2-ethylhexyl)-2-thienyl]-benzo [1,2-*b*:4,5-*b'*]dithiophene was lithiated with *n*-BuLi and subsequently quenched with Me₃SnCl to yield **11**. **11** was purified by recrystallization from ethanol three times.

The polymers, poly(2-[5-(2-hexyldecyl)-2-thienyl]-1*H*-dithieno [3,2-*e*:2',3'-*g*]benzimidazole-*alt*-4,7-bis[4-hexyl-2-thienyl]-2,1, 3-benzothiadiazole) (**PDTBI-BTD**) poly(2-[5-(2-hexyldecyl)-2-thienyl]-1*H*-dithieno[3,2-*e*:2',3'-*g*]benzimidazole-*alt*-4,8-bis (5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene)





SCHEME 2 Synthesis of PDTBI derivatives. *i*. Pd₂(dba)₃, P(*o*-tolyl)₃, toluene, microwave heating.

(PDTBI-BDT) were synthesized via Stille polycondensation (Scheme 2). We also attempted Stille polycondensations with our **DTBI** monomer and thiophene, thieno[3,2:b]thiophene, or vinylene; however, these co-monomers led to sparingly soluble oligomeric dark solids. They were not characterized beyond GPC (Supporting Information Fig. S15). The bis(stannyl) monomers were used in excess (1.00:0.95) to limit product molecular weight as initial reactions run with equal stoichiometry generated insoluble, presumably high-molecular-weight materials. Assuming the extent of reaction, p, to be 0.985, this imbalance should yield polymers with $X_n = 20$. The materials were synthesized using microwave heating which not only accelerated the polymerization time (45 min), but enabled the use of temperatures (150 °C) exceeding the solvent's (toluene) boiling point. The crude reaction mixture was then diluted with toluene and dripped into cold, stirred acidic methanol to precipitate the polymer and cleave remaining trimethyl(stannyl) end-groups. The crude precipitate was then filtered directly in a Soxhlet thimble and sequentially extracted with methanol, acetone, hexanes, and tetrahydrofuran for at least 24 h per solvent. Following Soxhlet extraction, the THF-soluble fraction was reprecipitated into cold, stirred methanol, filtered and

dried in vacuum for 1 h. Consistent with earlier reports on similar polymers,¹⁸ we found that extended drying made the product largely intractable. **PDTBI-BDT** product yields outstripped those of **PDTBI-BTD** (74.6 vs. 59.5%, respectively) likely due to the latter's lower molecular weight, which enabled premature extraction of more oligomeric material during Soxhlet purification with hexanes.

The polymers enjoyed reasonable solubility in chlorinated benzene derivatives, THF, warm toluene, chloroform, and 2-methyltetrahydrofuran. Polymer molecular weight was estimated via GPC using THF eluent against poly(styrene) standards (Table 1, Supporting Information Fig. S15). As referenced earlier, the employed stoichiometric imbalance should produce polymers where $X_n = 20$. For **PDTBI-BTD** and **PDTBI-BDT** this would lead to polymers with $M_n = 10.5$ and 11.7 kg mol⁻¹, respectively. At first glance, the GPC results for **PDTBI-BTD** seem to reflect this prediction well. However, several reports document that the comparisons between the hydrodynamic volume of a random coil poly(styrene) to rigid-rod polymers tend to exaggerate molecular weights.²⁶⁻²⁸ In light of this, **PDTBI-BTD**'s theoretical molecular weight likely exceeds its

TABLE 1 Synthetic Data for **PDTBI-BTD** and **PDTBI-BDT**

	$M_{ m n}/M_{ m w}$ (kg mol ⁻¹) ^a	$X_{\rm n}/X_{\rm w}^{\rm a}$	Đ ^a	Yield (%) ^b	<i>T</i> g (°C) ^c	<i>T</i> _d (°C) ^d
PDTBI-BTD	9.88/22.3	20/45	2.30	59.5	_	388
PDTBI-BDT	15.3/38.1	28/69	2.49	74.6	-	406

^a Estimated by GPC in THF against PS standards.

^b Calculated based on quantity obtained from THF fraction of Soxhlet extraction

as-synthesized weight while **PDTBI-BDT**'s as-synthesized molecular weight is probably on-par with or less than its theoretical.

Analysis of the polymers by ¹H NMR was limited by the materials' aggregative tendencies and insolubility leading to broad, largely featureless spectra (Supporting Information Figs. S13 and S14). Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-ToF MS) proved to be a more useful tool in evaluating polymer structure. While MALDI-ToF MS often provides poor representations of molecular weight distributions for disperse samples, it may be used to differentiate chain-end populations for lower molecular weight chains.²⁹

MALDI-ToF MS was used to determine relative stoichiometries of **A** (**BTD** or **BDT**) and **B** (**DTBI**) units as well as end-group composition (Fig. 1 and Supporting Information Fig. S16). While the expected stoichiometry was (n + 1)**A**: (n)**B**, we found significant evidence of aryl stannane homocoupling leading to **A** rich polymers. This side reaction is believed to occur through an errant transmetalation that results in stannylation and elimination of **DTBI** in place of Br.^{30,31} This results in a L_nPd(**A**)(Br) species amenable to appropriate



FIGURE 1 Reflected path MALDI-ToF MS of **PDTBI-BTD** (top, black) and **PDTBI-BDT** (bottom, red). "A" represents **BTD** or **BDT** and "B" indicates **DTBI**. Samples were prepared by drop-casting 1:15 (v:v) solutions of 5 mg mL⁻¹ product and 50 mg mL⁻¹ *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) in THF onto a ground steel target. [Color figure can be viewed at wileyonlinelibrary.com]

 $^{\rm c}$ No transitions were visible by DSC at a heating rate of 10 $^{\circ}{\rm C}$ min $^{-1}.$

 $^{\rm d}$ Based on temperature at 5% mass loss under N_2

transmetalation of Me₃Sn(**A**)Z (where Z is any group) and subsequent reductive elimination of the homocoupled defect. MALDI-ToF also revealed a large percentage of peaks with a H**B**(**A-B**)_nH architecture despite (intentionally) favoring Me₃Sn**A**SnMe₃ monomers. These observations imply relatively poor control over the polymerization mechanism which may be alleviated through less extreme reaction conditions and increased monomer purity.

The thermal characteristics of each polymer were evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal decomposition was first evaluated via TGA under N₂ at a 10 °C min⁻¹ heating rate (Supporting Information Figs. S18 and S19). Both polymers demonstrated relatively robust thermal stabilities, having 5% mass losses at 388 and 406 °C for **PDTBI-BTD** and **PDTBI-BDT**, respectively. DSC samples were prepared by weighing dry samples into aluminum DSC pans and then adding ~30 µL THF to wet the solids. The resulting slurry was then lightly compressed with a DSC lid in attempt to flatten sample along the pans' bottom. Samples were then dried in vacuum and fully crimped. No observable transitions occurred in heat/ cool/heat cycles spanning from -80 to 350 °C for either product (Supporting Information Figs. S20 and S21).

Molecular Modeling

DFT was used to calculate an energetically minimized geometry for trimers (n = 3) of both polymer systems—labeled **(DTBI-BTD)**₃ and **(DTBI-BDT)**₃. The model shortened the solubilizing side chains to methyl groups, reducing the computational load. Table 2 documents the torsion angle between each pair of adjacent rings (Labeled in Fig. 2). Importantly, little disparity exists between the protonated and Schiff base sides of **DTBI**, suggesting that the fusion of flanking thiophenes sufficiently minimizes the steric effects of (de)protonation. The interannular rotations appear to be quite low with the largest contributor to torsion being the methyl groups at the β -positions of the thiophene units appended to 2,1,3-benzothiadiazole (angles *a*, *d*, *e*, *h*, and *i*).

The predicted frontier molecular orbitals indicate localization of the LUMO on the electron accepting 2,1,3-benzothiadiazole unit, and a delocalized HOMO spread over the conjugated backbone in **(DTBI-BTD)**₃ (Supporting Information Fig. S22). These results are consistent with classical donor–acceptor type systems wherein the LUMO is controlled by the accepting unit. However, both LUMO and HOMO are delocalized across the entire **(DTBI-BDT)**₃ backbone, indicating a general lack of



TABLE 2 Calculated Torsion Angles of (DTBI-BTD)₃ and (DTBI-BDT)₃

	(DTBI-BTD) ₃		(DTBI-BDT) ₃
Angle		arPhi (°)	
а	21.66		9.04
b	1.47		9.43
с	2.27		10.87
d	18.83		1.01
е	18.34		3.77
f	1.92		-
g	1.68		-
h	18.81		-
i	19.84		-
j	4.22		-
k	10.83		-



FIGURE 3 UV-vis spectra of **PDTBI-BDT** (red) and **PDTBI-BTD** (black) in THF (dot dash) and thin-films (solid). [Color figure can be viewed at wileyonlinelibrary.com]

Bond angles are determined by energy minimization calculations employing DFT/B3LYP/6-31G(d,p).

donor–acceptor character. Not surprisingly, the calculations predict a narrower $E_{\rm g}$ ($E_{\rm LUMO} - E_{\rm HOMO}$) for (**DTBI-BTD**)₃ compared to (**DTBI-BDT**)₃ (1.84 vs. 2.53 eV, respectively) (Table 3). Again, consistent with donor–acceptor theory, BTD considerably deepens the $E_{\rm LUMO}$ in comparison to the BDT-containing trimer (–2.80 vs. –2.23 eV, respectively).

Optical Spectroscopy

The polymers were characterized by UV-vis spectroscopy both in solution and in the solid state. Sample solutions prepared in THF had λ_{max} (the wavelength at which the absorptivity is highest) values of 329 and 552 nm, for **PDTBI-BTD** and **PDTBI-BDT**, respectively (Fig. 3). However, both products exhibited multiple absorbances. Two principle absorbances exist for **PDTBI-BTD**, a featureless, broad low energy peak centered at 535 nm and the aforementioned λ_{max} at 329 nm which contained subtle shoulders at 364 and 410 nm. The lower energy broad absorbance is typical of donor-acceptor polymer systems owing to intramolecular charge transfer events. Interestingly, these spectra differ considerably



FIGURE 2 Trimers depicting the modeled structures (DTBI-BTD)₃ and (DTBI-BDT)₃.

TABLE 3 Summary of Band Structure Data

	Optical <i>E</i> g (eV) ^a	$E_{\rm ox,onset}$ (–V) ^b	$E_{\rm HOMO} (-{\rm eV})^{\rm b}$	$E_{\rm LUMO} (-eV)^{\rm c}$	$E_{\rm HOMO} (-{\rm eV})^{\rm d}$	$E_{\rm LUMO} (-eV)^{\rm d}$	E _g (eV) ^d
PDTBI-BTD	1.78	0.52	5.21	3.43	4.64	2.80	1.84
PDTBI-BDT	2.08	0.72	5.43	3.35	4.76	2.23	2.53

^a Calculated from the absorption onset of thin films prepared by drop-casting on quartz plates.

 $^{\rm b}$ An average of at least three films drop-cast onto a glassy carbon electrode against a Ag/AgNO_3 reference electrode.

from those reported by Keshtov et al. for similar polymers.¹⁹ **PDTBI-BDT** displays highly structured absorbance in solution (and thin films) with notable peaks (552, 510, 418, and 347 nm) and a shoulder (475 nm) more in line with Keshtov et al.'s previously reported system.¹⁸ The high degree of vibronic structure visible in the spectra indicates localized excited states.³²

The optical E_{g} was determined from the solid-state spectra to be 1.78 and 2.08 eV for PDTBI-BTD and PDTBI-BDT, respectively. Samples were prepared from 1.5 mg mL^{-1} product solutions in 3:1 1,2,4-trichlorobenzene:THF drop-cast onto substrates at 60 °C. The observed relative magnitudes are consistent with the DFT predictions, but as expected the calculations overestimated the E_{g} , likely due to the limits of a single-chain trimer model. However, it is interesting to note the scalar difference between theory and observation; the observed BDT-containing system E_g is ~18% smaller than theory, while the same metric in the BTD case is 3%. The trimer model more accurately describes PDTBI-BTD's band structure due to its relatively low molecular weight. Homocoupling in PDTBI-BTD, mitigating the expected donor-acceptor hybridization may also explain the smaller overestimate in the BTD case.

Interestingly, the band-edge of **PDTBI-BDT**'s solution and solid-state spectra occur at nearly identical energies. Also, its lowest energy absorbance decreases in relative intensity when cast as a film. These features imply a fairly rigid system that does not gain planarization upon film deposition.

Photoluminescence of **PDTBI-BTD** and **PDTBI-BDT** solutions in THF (Supporting Information Fig. S17) indicated λ_{em} of 715 and 597 nm, respectively (Stokes shifts of 180 and

TABLE 4 Summai	y of (De)p	protonation's	s Effect on E _a
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	E _g (eV) ^a
PDTBI-BTD	1.55
PDTBI-BTD(+)	1.57
PDTBI-BTD(–)	2.06
PDTBI-BDT	2.06
PDTBI-BDT(+)	2.06
PDTBI-BDT(-)	2.05

^a E_{α} estimated by UV-vis absorbance in solution



^c Estimated by adding the optical E_{g} to E_{HOMO} .

^d Calculated using the Gaussian[™] 09 suite with DFT at the B3LYP level of theory and 6-31G (d.p) basis set.

45 nm). **PDTBI-BTD** displayed very broad photoluminescence (FWHM = 135 nm) with a single vibronic shoulder on the spectrum's high-energy side (687 nm). By contrast, **PDTBI-BDT**'s spectrum is relatively well-defined with the 0-0, 0-1, and 0-2 transitions evident at 597, 637, and 716 nm, respectively. Thin-film photoluminescence was immeasurably low for both materials.

Cyclic Voltammetry

The polymers' ionization potential was measured using cyclic voltammetry as an approximation of E_{HOMO} . Attempts to measure the reduction potential for the approximation of E_{LUMO} were unsuccessful in N2 sparged electrolyte solution. Thinfilms were drop-cast from THF solution onto a glassy carbon work electrode which was employed alongside Pt wire and Ag/AgNO₃ counter and reference electrodes, respectively. Sweeps were performed in ambient conditions using TBAPF₆ as the carrier electrolyte in acetonitrile (Supporting Information Fig. S23). E_{HOMO} was approximated from the oxidation onset after external calibration against the ferrocene/ferrocenium redox couple. As predicted by DFT modeling, PDTBI-BTD (-5.21 eV) had a relatively shallow E_{HOMO} relative to PDTBI-BDT (-5.43 eV). The E_{LUMO} level was approximated by adding the optical $E_{\rm g}$ to $E_{\rm HOMO}$. This estimation agrees with the prediction and rationale put forth above.

Solution (De)Protonation

The polymers were (de)protonated through the addition of 2 M TFA_(DMF) or 0.2 M NaOEt_(EtOH). Pristine product insolubility in anhydrous DMF or DMAc forced the use of a mixed solvent system wherein the material was first dissolved in THF and then diluted with DMF such that the final composition was 99% DMF by volume (7–15 μ g mL⁻¹).

Beginning with the acid treatment of **PDTBI-BTD** and **PDTBI-BDT**, little change is evident in the UV–vis spectra (Fig. 4, for incremental spectra see Supporting Information Figures S24 and S25). In keeping with our previous discussions^{4,5} we believe deprotonation should lead to an increase in the system's electron affinity if the LUMO is localized in the imidazole-containing unit. Thus, one should not expect significant band structure changes for **PDTBI-BTD**, considering its LUMO is predicted to be confined to **BTD**. It is unclear why **PDTBI-BDT** does not demonstrate E_g narrowing considering its well dispersed LUMO and the results of Takagi et al.¹² who note bathochromic shifts upon protonation of PDTBI-BT (bithiophene) copolymers (Table 4). They suggest the shift



FIGURE 4 Spectroscopy of PDTBI-BTD and PDTBI-BDT and their (de)protonated forms. Solution UV-vis spectra of neutral (solid), acid-doped (A., dashed), and base-doped (B., dashed) PDTBI-BTD (black) and PDTBI-BDT (red). [Color figure can be viewed at wileyonlinelibrary.com]

originates from an enhanced intramolecular charge transfer (ICT) between electron-rich bithiophene and cationic DTBI and we expected a similar observation here. However, the predicted electron densities shown in Supporting Information Figure S22 do not show wavefunction localization on the imidazole's N atoms; thus, protonation's impacts are minimized.

Mirroring observations from earlier work, spectral changes upon deprotonation were more dramatic for both polymers.^{4–8} Notably the ε increases for both systems, we suspect poly(anion) solubility improves in 99:1 DMF:THF compared to the neutral parent material. **PDTBI-BTD(–)** absorbs at considerably lower wavelengths (band-edge $1.55 \rightarrow 2.06 \text{ eV}$) suggesting significant disruption in conjugation length, potentially due to polymer degradation. Meanwhile, **PDTBI-BDT(–)** maintains its vibronic structure with a minor shift in band-edge $(2.06 \rightarrow 2.05 \text{ eV})$. Again, we rationalize the apparent lack of D-A, charge transfer activity upon deprotonation by turning to the modeling results which indicate minimal wavefunction density on the imidazole's N atoms.

Thin-Film (De)Protonation

The poor solubility of the poly(ionomer) prevented film formation by direct solution casting. Accordingly, thin-films of the pristine material were treated with acid/base in attempt to gain thin-films of (de)protonated product. Films were prepared by dropcasting filtered solutions of **PDTBI-BTD** or **PDTBI-BDT** onto octadecyltriethoxysilane-treated glass slides from 1.5 mg mL⁻¹ solutions in 3:1 (v:v) 1,2,4-trichlorobenzene:THF at 60 °C under a N₂-rich dome. After 4 h at 60 °C, smooth continuous films were obtained. Films were then overcoated with 0.15 mL of TFA or 0.5 M NaOEt_(EtOH) under a N₂-rich dome at room temperature. After 1 h, remnant TFA was blown off with a N_2 jet and excess NaOEt solution rinsed away with 2-propanol followed by drying with a N_2 jet. During this drying process, films consistently cracked, preventing an assessment of their conductivity (Supporting Information Fig. S26). The products' low molecular weight may contribute to cracking; thus, synthesis of higher molecular weight products would likely increase film robustness. Additionally, crosslinking the films would augment their mechanical strength to mitigate cracking for further study of poly(ionomer) thin films.

CONCLUSIONS

Through the synthesis and characterization of PDTBI-BTD and PDTBI-BDT, this report demonstrates the potential to incorporate imidazoles into complex D-A type copolymers. The polymers were synthesized in reasonable yields. MALDI-ToF MS revealed structural abnormalities in both products which probably arose from the extreme polymerization conditions-this appears to be a severely understudied issue ripe for optimization. DFT calculations, in conjunction with spectroscopic evidence, suggest BTD hybridizes with DTBI more effectively to lower the polymer's E_{g} . Solution (de)protonation led to less dramatic band-edge shifts than those observed for our earlier poly(2-alkylbenzimidazole-alt-fluorene) derivatives. However, we note that the characterization methods deployed herein provide no information positioning the E_{HOMO} and E_{LUMO} of **PDTBI-BTD/BDT (+/-)**. Thus, the relative energies may still deepen(shallow) upon (de)protonation. Finally, pristine thin-films lacked the mechanical robustness necessary for direct exposure to acid or base. Future work needs to resolve this issue in order for practical measurement of poly(ionomer) conductivities and electro-optical characteristics.

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