Synthesis and redox properties of racemic electroactive polymers containing axially chiral adamantyl segments

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ABSTRACT

A method of introducing chirality directly into a polymer backbone has been developed that employs the dissymmetry of an adamantane derivative with axial chirality. This new chiral adamantane building block was readily functionalized with electroactive thiophene rings using palladium-catalyzed cross-coupling methodology. The two resulting electroactive monomers were electropolymerized to create racemic electroactive polymers containing phenyl-capped oligothiophene segments alternating with chiral adamantyl segments. Synthesis, electrochemistry, and spectroelectrochemistry studies are reported.

1. Introduction

In recent years, introduction of chirality into conjugated polymers has become of synthetic interest because of the promise these polymers have as enantioselective sensors based on optical and electrochemical signal transduction.[1–4] Introducing axial chirality directly into the main chain of a polymer is highly desirable because of the potential for significant amplification of chiroptical properties, compared to when chiral groups are incorporated into pendant side chains.[5–7] To date, the quintessential molecular building block used to incorporate axial chirality into the main chain of a polymer is 1,1′-binaphthyl.[5,8–12] 1,1′-Binaphthyl and its derivatives are axially chiral by virtue of restricted rotation about the 1,1′-bond. Aside from 1,1′-binaphthyl derivatives, there are relatively few other examples of molecules that can be used to introduce axial chirality directly into a polymer backbone.[13–16] Those that do exist require several steps to synthesize and install appropriate functionalization for subsequent polymerization.

Appropriately substituted adamantanes, such as those illustrated in Figure 1, are chiral with respect to an axis because of the spatial arrangement of the substituents that are attached to the rigid adamantane skeleton.[17]
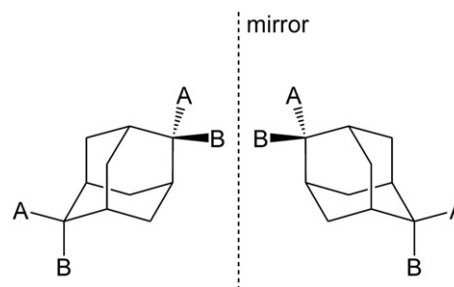
Figure 1. Non-superimposable mirror images of a generic tetrasubstituted ($A \neq B \neq H$ atom) adamantane.

By exploiting the dissymmetry of a tetrasubstituted adamantane derivative with versatile synthetic handles, we have discovered a new molecular building block for introducing axial chirality directly into a polymer backbone. Racemic dibromide **1** was synthesized from achiral 2,6-adamantanedione (Fig. 2).
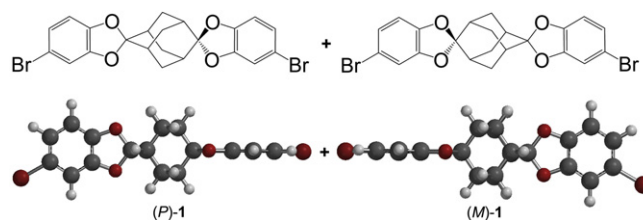
Figure 2. Structures of axially chiral dibromide **1** enantiomers, where the bottom structures were calculated at the AM1 level of theory.

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This new axially chiral molecular building block has the potential for a wide range of functionalization in few synthetic steps. Dibromide **1** features two aryl ketal groups that are fixed in a perpendicular orientation to one another based on how they are attached to opposite ends of the adamantane skeleton. The relative positioning of the bromine atoms on each aromatic ring breaks the symmetry of the overall molecule, creating a pair of enantiomers with axial chirality. The bromines serve as synthetic handles, allowing for the aromatic rings to be derivatized with a variety of groups using palladium–catalyzed coupling methodology.[18] Polymerization could be accomplished either by direct palladium–catalyzed polymerization with another appropriately functionalized monomer or by appending electroactive groups to **1** (e.g., thiophene or 3,4-(ethylenedioxy)thiophene) and electropolymerizing the resulting monomer.

The synthetic versatility of dibromide **1** makes it an attractive building block for incorporating axial chirality into a polymer backbone. Furthermore, an advantage of using chiral adamantane derivatives over 1,1′-binaphthyl derivatives is that the former molecules are configurationally stable under thermal conditions. Thus, polymer racemization would not be a concern. Enantioselective sensing capabilities could be optimized by appending groups to **1** that have built in molecular recognition sites, in addition to the ketal oxygens that offer hydrogen bonding opportunities. Whether signal transduction would occur optically or electrically in sensory applications could also be varied and controlled by choice of functionalization.

In the emerging field of organic electronics, the synthesis of electroactive polymers with novel molecular architectures is extremely important, and they have been the subject of vigorous investigation since their discovery in the 1970s,[19–22] particularly for sensory applications.[2,23] Herein we report the racemic synthesis of chiral dibromide **1** and the subsequent use of this building block to create racemic electroactive polymers containing either phenyl-capped bithiophene or quaterthiophene segments alternating with chiral adamantyl segments. Accordingly, the synthesis and electrochemical polymerization of two electroactive monomers derived from dibromide **1** have been accomplished. Cyclic voltammetry and spectroelectrochemistry were used to study the redox and optical properties of the resulting polymers.

## 2. Results and discussion

2.1. Synthesis

An acid-catalyzed ketalization reaction between two equivalents of 4-bromocatechol and 2,6-adamantanedione under Dean–Stark conditions led to a racemic mixture of dibromide **1** in 70% yield (Scheme 1).
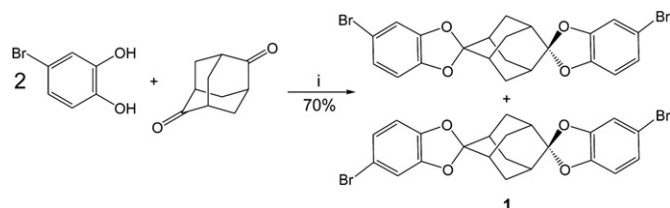
Scheme 1. Reagents and conditions: (i) Dean–Stark apparatus, TsOH, toluene, 9 h reflux.

Suzuki coupling methodology was used to generate racemic electroactive monomers **2** and **3**, as shown in the synthetic routes outlined in Schemes 2 and 3, respectively. The attachment of

thiophene and bithiophene rings to both sides of the adamantane catechol diketal by means of compound **1** was pursued because the resulting compounds, **2** and **3**, were expected to undergo oxidative polymerization to create electroactive polymers, poly(**2**) and poly(**3**) (Fig. 3).
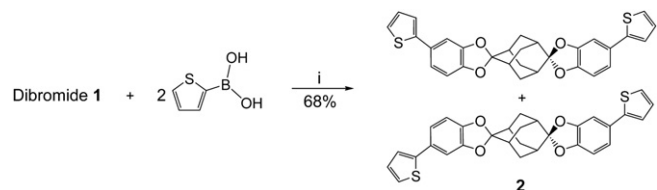
Scheme 2. Reagents and conditions: (i) Pd(PPh₃)₄, 2 M Na₂CO₃(aq), toluene/ethanol, 80 °C, 16 h.
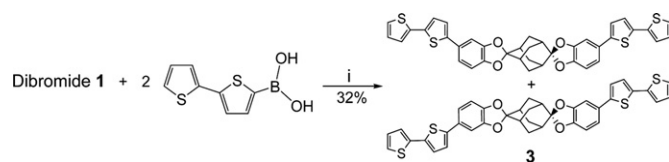
Scheme 3. Reagents and conditions: (i) Pd(PPh₃)₄, 2 M Na₂CO₃(aq), toluene/ethanol, microwave irradiation at 120 °C for 0.5 h.
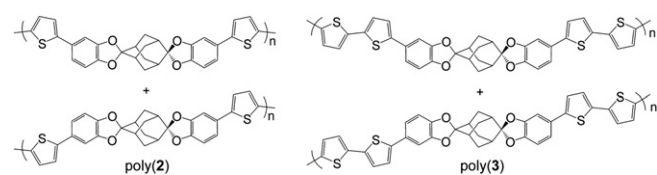
Figure 3. Structures of poly(**2**) and poly(**3**), segmented electroactive polymers containing axially chiral segments.

Thiophene rings were attached to dibromide **1** by reacting two equivalents of 2-thiopheneboronic acid with **1** in the presence of a catalytic amount of Pd(PPh₃)₄, producing bisthiophene monomer **2** in 68% yield (Scheme 2). Bithiophene rings were attached to each side of dibromide **1** by reacting two equivalents of 2,2′-bithiophene-5-boronic acid with **1** under similar conditions used to produce **2**, except microwave-assisted heating was used, producing electroactive bisbithiophene monomer **3** (Scheme 3).

Early attempts to purify compound **3** by chromatography on silica gel were unsuccessful as it became evident that the compound was decomposing to a large extent prior to elution. Thus, recrystallization was explored and subsequently led to the isolation of pure **3** in 32% yield. The success of these reactions, as demonstrated by ¹H and ¹³C NMR spectroscopy, confirmed the facility with which electroactive groups can be attached to **1** by means of palladium–catalyzed Suzuki cross-coupling reactions.

2.2. Electrochemical polymerization of monomers 2 and 3

Electrochemical oxidation of monomers **2** and **3** was carried out at a platinum button electrode to determine whether polymerization would result, giving poly(**2**) and poly(**3**), respectively. Cyclic voltammetry (CV) of bisthiophene monomer **2** in supporting electrolyte and of resulting poly(**2**) in a monomer-free electrolyte solution are displayed in Figure 4.
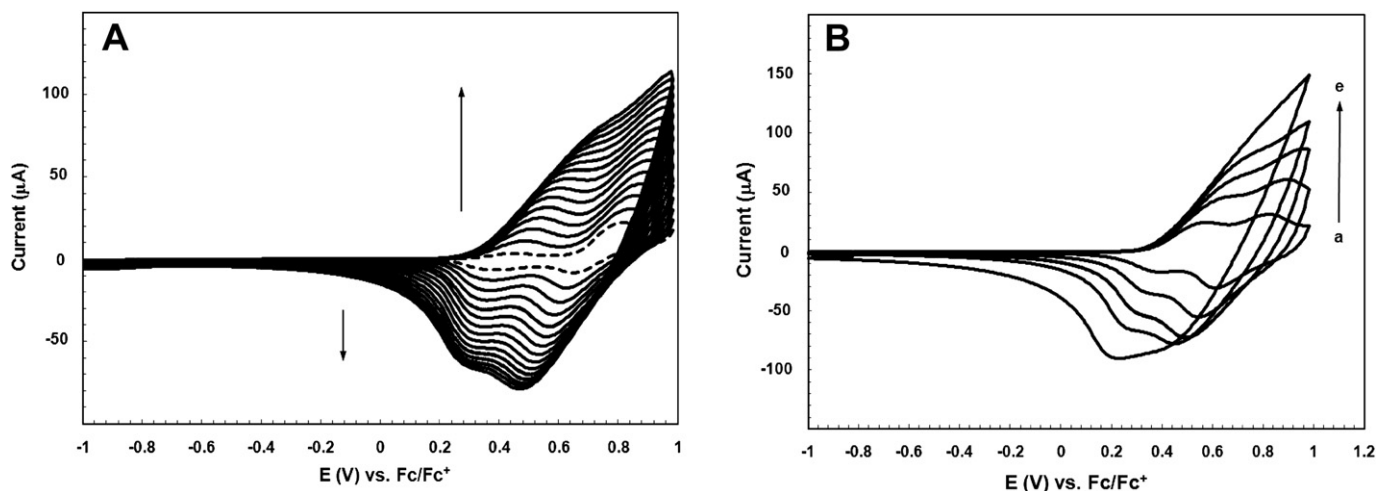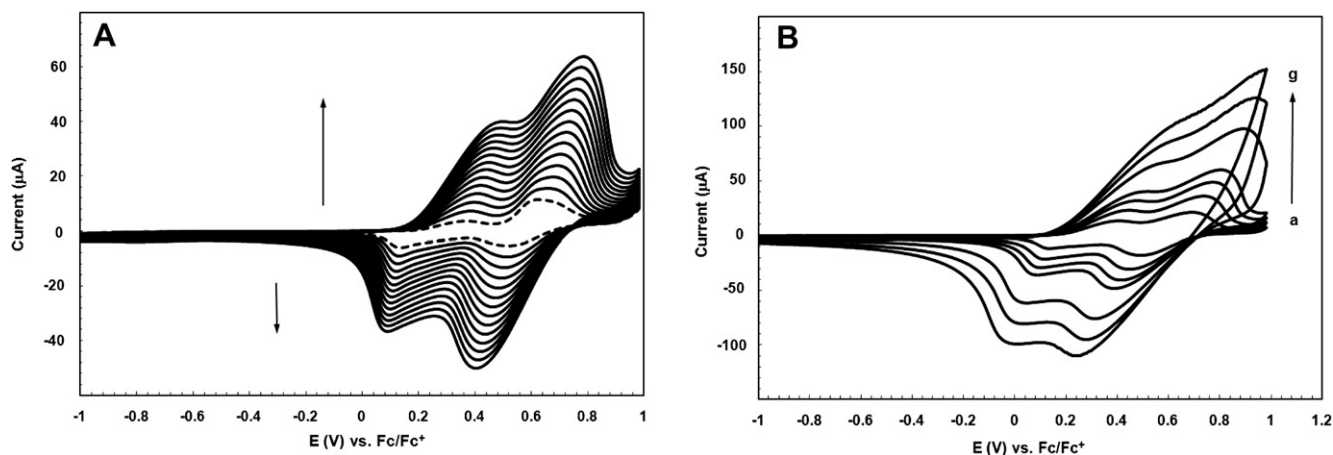
Figure 4. (A) CV of monomer **2** (~1 mM) in 0.1 M TBAPF$_6$ (CH$_2$Cl$_2$) cycled at 100 mV/s on a Pt button electrode, where the first scan is shown with a dashed line; (B) CV of resulting poly(**2**) in monomer-free electrolyte solution cycled at: (a) 25; (b) 50; (c) 75; (d) 100; (e) 200 mV/s.

Repeated cycling of monomer **2** from −1.0 to 1.0 V (V vs Fc/Fc$^+$) at a scan rate of 100 mV/s led to deposition of poly(**2**) on the working electrode, as demonstrated by the increase in current with each successive scan (Fig. 4A). The first polymerization scan of **2** (dashed line) showed an anodic peak current (E_{pa}) representing monomer oxidation at 0.8 V that appeared to be quasi-reversible, indicating that the radical cation may be stabilized to some extent by electron-donation from the phenolic oxygen that is *para* to the thiophene segment. Scan-rate dependence studies on the deposited poly(**2**) film show that oxidation and reduction of the polymer was reversible up to approximately 100 mV/s (Fig. 4B), but charge transport through the film at higher scan rates was more sluggish. Similarly, CV was utilized to oxidize monomer **3** to determine if polymerization would result. As shown in Figure 5A, with each successive scan from −1.0 to 1.0 V at 100 mV/s, the current increased, indicating that poly(**3**) was indeed growing on the electrode surface.

the redox potential of **3** compared to **2**. In contrast to the eventual film passivation during polymerization and sluggish film kinetics observed for poly(**2**), growth of poly(**3**) was more sustainable over extended scan periods and scan-rate dependence experimentation on poly(**3**) revealed that the redox kinetics of poly(**3**) were reversible up to around 300 mV/s (Fig. 5B). Both results suggest that poly(**3**) is more robust than poly(**2**), which can be attributed to the lower redox potential of **3** resulting in a more ordered growth of the polymer with better film characteristics.

### 2.3. Spectroelectrochemical studies of poly(2) and poly(3)

CV was used to deposit thin films of poly(**2**) and poly(**3**) onto indium–tin oxide (ITO)-coated glass for UV–vis spectroelectrochemistry studies. Spectroelectrochemistry is used to probe the evolution of charge carriers, polarons and bipolarons, in conducting polymers to assess the delocalization of charge as a function of

Figure 5. (A) CV of monomer **3** (~1 mM) in 0.1 M TBAPF$_6$ (CH$_2$Cl$_2$) cycled at 100 mV/s on a Pt button electrode, where the first scan is shown with a dashed line; (B) CV of resulting poly(**3**) in monomer-free electrolyte solution cycled at: (a) 25; (b) 50; (c) 75; (d) 100; (e) 200; (f) 300; (g) 400 mV/s.

The first polymerization scan of **3** (dashed line) showed an anodic peak current representing monomer oxidation at 0.6 V, which was lower than that of **2**. This is consistent with the additional thiophene ring increasing monomer conjugation, thereby lowering

applied potential. To this end, a UV–vis spectrum of each polymer film was obtained in 200 mV steps held between −0.8 and 1.0 V. The neutral, undoped form of poly(**2**) had an absorption band at 380 nm (Fig. 6A).
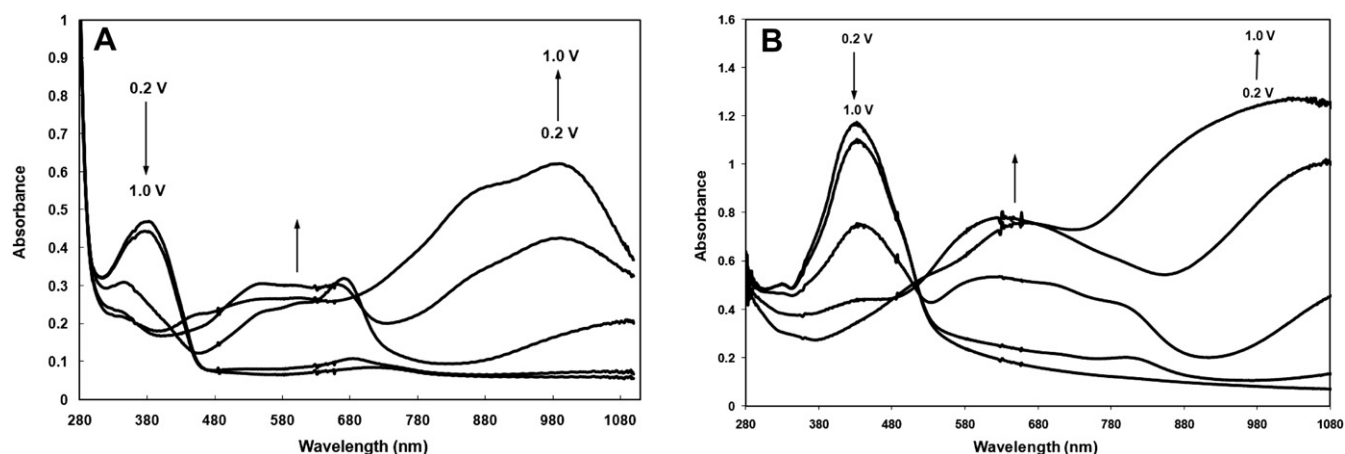
Figure 6. Spectroelectrochemistry data for thin polymer films of (A) poly(**2**) and (B) poly(**3**) grown on ITO-coated glass. The experiments were carried out in 0.1 M TBAPF$_6$ (CH$_2$Cl$_2$) and held at 200 mV steps (vs Fc/Fc$^+$).

As the polymer was subjected incrementally to higher potentials it became oxidized, the onset of which occurred at 0.4 V. Consequently, the band at 380 nm slowly diminished while an intermediate band centered at 600 nm grew in at moderate doping levels and eventually gave way to a broad absorbance band between 780 and 1080 nm at high doping levels. These results demonstrate that poly(**2**) is electrochromic, consistent with it being a light yellow color in its neutral form (<0.4 V) that switched to a deep purple color when the polymer film was highly oxidized (1.0 V). Neutral, undoped poly(**3**) had an absorbance band at 430 nm (Fig. 6B). As poly(**3**) became oxidized, which commenced around 0.4 V, the absorbance band at 430 nm slowly diminished concomitantly with the appearance of an intermediate band centered at ~640 nm at moderate doping levels. The intermediate band eventually diminished at higher potentials while a band centered around 980 nm grew in that extended into the near-IR region. Poly(**3**) is also electrochromic, as the film exhibited a yellow-green color in the neutral form (<0.4 V) that changed to a navy blue color when the film was highly oxidized (1.0 V).

The UV–vis absorption spectra of the two polymers are comparable at similar oxidation levels with the exception that the bands of poly(**3**) are all red-shifted compared to the corresponding bands observed for poly(**2**). Also, the amount of color change for poly(**2**) at 0.4 V appears to be less than that for poly(**3**). The noted differences between the polymers are consistent with the fact that, although they are structurally similar, the chromophore segment in poly(**3**) is extended in conjugation length by two thiophene rings leading to poly(**3**) having a lower oxidation potential than poly(**2**). The optical transitions of poly(**2**) and poly(**3**) corresponding to the intermediate and fully oxidized states, widely accepted as being polarons and bipolarons, respectively, are all of fairly well-defined structure.[24] This result is in contrast to the more broad, diffuse-looking nature of these bands for a fully conjugated conducting polymer, such as poly(thiophene). These observations are fully consistent with poly(**2**) and poly(**3**) being segmented electroactive polymers since they consist of electroactive phenyl-capped oligothiophene segments held between bridging adamantyl segments that are likely to be insulating.[25–27] Thus, charge carriers in these polymers appear to be localized between adamantyl segments and therefore charge-delocalization in these polymers may be limited to inter-chain charge hopping. Nonetheless, analogous studies on model compounds are needed to fully evaluate the nature of the charge carriers in these polymers.

3. Conclusions

Synthesis of the axially chiral dibromide **1** has been accomplished in relatively high yield (70%). This compound can be readily functionalized using palladium–catalyzed Suzuki coupling methodology, as demonstrated by the successful synthesis of electroactive monomers **2** and **3** (68% and 32% yield, respectively). Electroactive monomers **2** and **3** were electropolymerizable using cyclic voltammetry, with **3** having a lower oxidation potential than **2**, thereby producing segmented electroactive polymers, poly(**2**) and poly(**3**). Spectroelectrochemistry studies revealed that poly(**2**) and poly(**3**) are electrochromic, with the typical evolution of lower energy transitions in their UV–vis absorption spectra as a function of increasingly positive applied potential. The well-defined shapes of the polaronic and bipolaronic bands were suggestive of localized charge carriers between the bridging adamantyl segments.

4. Experimental

4.1. General methods and instrumentation

A Schlenk line was used to carry out all reactions under nitrogen. ^{1}H and ^{13}C NMR spectra were determined at 200 MHz using a Varian 200 MHz spectrometer and are referenced to TMS equals zero and residual CHCl$_3$ (Cambridge Isotope Laboratories, Inc.) at 77.23 ppm, respectively. Melting points were determined on a Barnstead International MEL-TEMP® apparatus and are uncorrected. AM1 calculations were performed by using the program Spartan '06 Essential (Wavefunction, Inc.). High-resolution mass spectrometry (HRMS) analysis on **2** was carried out at Brown University and HRMS analysis on **3** was carried out at the University of Illinois SCS Mass Spectrometry Laboratory. Elemental analysis was conducted at Quantitative Technologies, Inc. (Whitehouse, NJ). Pd(PPh$_3$)$_4$ was purchased from Strem Chemicals, Inc., 4-bromocatechol was from TCI America, and 2,2′-bithiophene-5-boronic acid was from Combi-Blocks. All other solvents and chemicals used for synthesis were reagent-grade, purchased from either Acros Organics or Sigma–Aldrich, and used without further purification. The microwave reactor was a CEM Discover BenchMate. All electrochemistry experiments were performed using an Eco Chemie AUTOLAB with PGSTAT302 potentiostat running GPES software (Version 4.9). Cyclic voltammetry was performed at a 2 mm^2 Pt button electrode in a three electrode, one chamber cell (VC-2 cell; Bioanalytical Systems, Inc., BASi) under a blanket of nitrogen. Prior to each new experiment, fresh electrolyte was purged with nitrogen. The reference

electrode was a quasi-internal Ag wire (BASi) submersed in 0.01 M AgNO$_3$ in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (Fluka, electrochemical grade) in anhydrous acetonitrile (Sigma–Aldrich). The supporting electrolyte in all experiments was 0.1 M TBAPF$_6$ in anhydrous CH$_2$Cl$_2$ (Sigma–Aldrich). Either a Pt rod or mesh flag was used as the counter electrode for all electrochemical studies. All potentials are externally referenced to the Fc/Fc$^+$ redox couple (Fluka). Spectroelectrochemistry studies were performed on polymer films grown on indium-tin oxide (ITO) coated glass (Delta Technologies, Ltd.), and absorption spectra were collected using an Agilent 8453 diode array spectrophotometer.

4.1.1. Synthesis of dibromide 1.

A 25 mL round bottom flask equipped with a stir bar was attached to a Dean–Stark apparatus that was fitted with a reflux condenser. The flask was charged with 2,6-adamantanedione (229 mg; 1.39 mmol), 4-bromocatechol (686 mg; 3.63 mmol), TsOH (35 mg; 0.184 mmol), and 10 mL of toluene. The Dean–Stark reservoir was filled with toluene, and the reaction was refluxed under nitrogen for 9 h (135 °C, oil bath). The solution was cooled to room temperature then poured into a separatory funnel containing aqueous 10% Na$_2$CO$_3$. After the layers were separated, the organic layer was washed with brine, dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure. The crude off-white solid was purified by column chromatography on silica gel (20% CH$_2$Cl$_2$ in hexanes) to give compound 1 as a white powder (494 mg; 70% yield). Compound 1 (mp 225–227 °C): ^{1}H NMR (200 MHz, CDCl$_3$) δ 2.13–2.18 (m, 12H), 6.63 (d, J=8.6 Hz, 2H), 6.88–6.93 (m, 4H). ^{13}C NMR (200 MHz, CDCl$_3$) δ 30.5, 35.1, 109.7, 112.4, 112.6, 120.7, 123.9, 147.0, 148.6. Elem. Anal. calcd for C$_{22}$H$_{18}$Br$_2$O$_4$: C, 52.20; H, 3.58. Found: C, 52.17; H, 3.60.

4.1.2. Synthesis of bisthiophene monomer 2.

A 50 mL Schlenk flask equipped with a stir bar was charged with compound 1 (200 mg; 0.395 mmol), 2-thiopheneboronic acid (135 mg; 1.06 mmol), aqueous 2 M Na$_2$CO$_3$ (2 mL), toluene (12 mL), and absolute ethanol (4 mL). After the solution was bubbled with nitrogen for 15 min, Pd(PPh$_3$)$_4$ (29 mg; 0.0251 mmol) was added, and the flask was sealed with a septum held on by copper wire. The reaction mixture was heated with stirring at 80 °C in an oil bath for 16 h. Upon cooling, 20 mL of water was added, and the reaction mixture was extracted three times with ethyl acetate. The organic layer was washed with brine, dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (30% CH$_2$Cl$_2$ in hexanes) to give compound 2 as a white powder (138 mg; 68% yield). Compound 2 (mp 229–231 °C dec): ^{1}H NMR (200 MHz, CDCl$_3$) δ 2.19–2.23 (m, 12H), 6.77 (d, J=8.6 Hz, 2H), 7.02–7.09 (m, 6H), 7.16 (d, J=3.8 Hz, 2H), 7.20 (d, J=4.8 Hz, 2H). ^{13}C NMR (200 MHz, CDCl$_3$) δ 30.7, 35.3, 106.8, 108.7, 119.4, 120.1, 122.4, 124.1, 128.1, 128.5, 144.9, 147.4, 148.2. HRMS (FAB+/NBA/NaI) calcd for C$_{30}$H$_{24}$O$_4$S$_2$ [M+] 512.1116, found 512.1126. Elem. Anal. calcd for C$_{30}$H$_{24}$O$_4$S$_2$: C, 70.29; H, 4.72. Found: C, 69.92; H, 4.45.

4.1.3. Synthesis of bisbithiophene monomer 3.

A 10 mL microwave vial containing a stir bar was charged with compound 1 (100 mg; 0.198 mmol), toluene (4 mL), and absolute ethanol (1 mL). After bubbling nitrogen through the solution for 5 min, 2,2′-bithiophene-5-boronic acid (166 mg; 0.790 mmol) and aqueous 2 M Na$_2$CO$_3$ (0.2 mL) were added. Then, Pd(PPh$_3$)$_4$ (23 mg; 0.0199 mmol) was added quickly, and the headspace was purged with nitrogen just prior to capping the vial. The reaction mixture was placed into the microwave reactor at 120 °C for 30 min. Upon cooling, the reaction mixture was extracted twice with dichloromethane. The organic extracts were combined, washed with brine, dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure. The crude light brown solid was dissolved in CH$_2$Cl$_2$ and passed through a short plug of neutral alumina. After concentration, the resulting green solid was recrystallized from ethyl acetate to give compound 3 as a light yellow powder (43 mg; 32% yield). Compound 3 (mp 241–242 °C dec): ^{1}H NMR (200 MHz, CDCl$_3$) δ 2.20–2.23 (m, 12H), 6.77 (d, J=8.2 Hz, 2H), 7.00–7.12 (m, 10H), 7.17 (d, J=3.6 Hz, 2H), 7.21 (d, J=5.0 Hz, 2H). ^{13}C NMR (200 MHz, CDCl$_3$) δ 30.7, 35.3, 106.4, 108.8, 119.2, 120.2, 123.0, 123.6, 124.4, 124.7, 128.0, 128.1, 135.9, 137.8, 143.7, 147.5, 148.2. HRMS (EI$^+$) calcd for C$_{38}$H$_{28}$O$_4$S$_4$ [M$^+$] 676.0870, found 676.0878.

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