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Polymers Containing Rigid Benzodithiophene Repeating Unit with Extended Electron Delocalization

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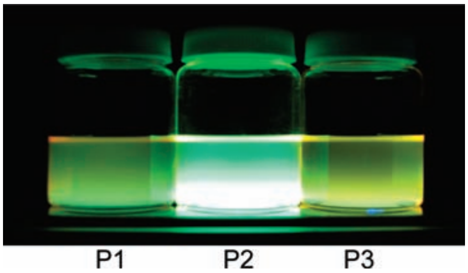
ABSTRACT



Polymers containing a fused benzodithiophene core with phenylethynyl substituents were prepared. The parent poly[4,8-bis(4-pentylphenylethynyl)benzo[1,2-*b*:4,5-*b′*]dithiophene] was prepared by a Stille coupling. Copolymers with the new core were also obtained by Stille coupling with dibrominated fluorene and carbazole monomers. The obtained polymers had a lower band gap as compared to the related benzodithiophene cores due to the extended electron conjugation. The polymers were also highly fluorescent as observed by high quantum yields.

Conjugated 3-alkyl-substituted polythiophenes have been extensively studied as a processable polymer with good electronic and photonic properties.[1] The regioregular poly(3-hexylthiophene) (P3HT) polymer, for example, has good solubility due to the hexyl substituents and also displays good conductivities due to the strong π overlap both in intra- and interchain delocalization as a result of the ordered lamellar packing that results from the minimization of steric interactions with the regioregular placement of the alkyl substituents.[2] These polymers have been studied as active components for sensors,[3] TFTs,[4] OLEDs,[5] and solar cells.[6] One limitation for these polymers, however, is the inability to control the molecular orbital energy levels for P3HT. With only one remaining aromatic substitution point available with P3HT, any substitution at this position will cause steric interactions with the adjacent alkyl substituent, thus limiting all of the benefits of the regioregular alkyl substituents for extended conjugation and interdigitation of the hexyl substituents.

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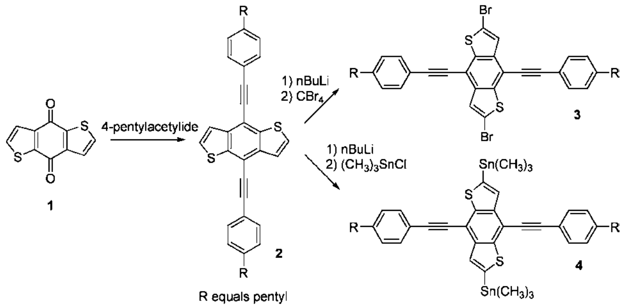
In order to maintain the electronic and photonic benefits of the regioregular P3HT, but still allow control of the molecular orbital levels for the polymer, the fused benzodithiophene monomer core has been studied.[7] The fused central ring allows the incorporation of substituents on the central benzene core, while also maintaining planarity of the two thiophene units. In addition, the symmetric nature of the benzodithiophene core eliminates the need to control the regioregularity during the polymerization process. Previously, groups have attached electron-donating alkyl and alkoxy substituents on the central benzene ring.[7] In order to create polymers with a better molecular orbital overlap for molecular electronic devices, however, we desired to create polymers with greater electron delocalization and thus a smaller band gap. The substitution of two phenylethynyl groups on the central fused benzene ring will allow extended electron delocalization.

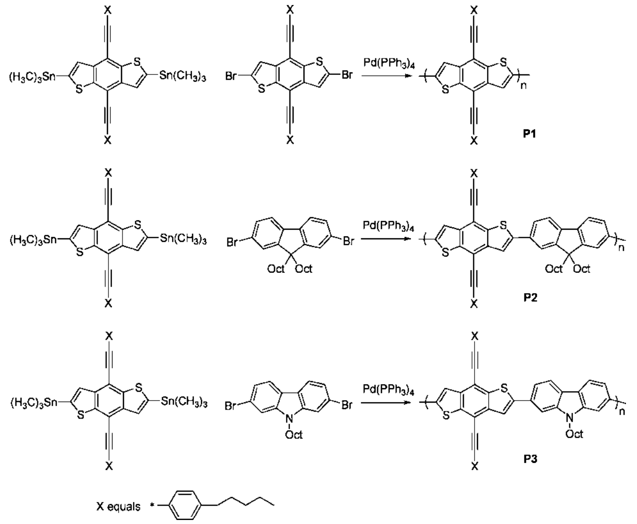
Scheme 1. Synthesis of Benzodithiophene Cores



As shown in Scheme 1, the previously prepared diketone **1**[8] was reacted with 4-pentylphenylacetylide, followed by aromatization with tin chloride to create compound **2**. Electropolymerization was attempted directly with compound **2**, but no polymer was obtained. The dibromo-substituted compound **3** was obtained by forming the dianion of **2** with 2 equiv of *n*-butyllithium, followed by reaction with carbon tetrabromide. Grignard metathesis (GRIM)[1] polymerization of compound **3** was attempted but gave low yields. The distannylated derivative of compound **2** was obtained by forming the dianion with 2 equiv of *n*-butyllithium, followed by reaction with trimethyltin chloride to obtain compound **4**. Stille coupling of compounds **3** and **4** proved successful as poly[4,8-bis(4-pentylphenylethynyl)benzo[1,2-*b*:4,5-*b*′]dithiophene] (**P1**) with an average number molecular weight of 3300 g/mol was obtained. Attempts are underway to attach longer alkyl groups than the pentyl group, which would presumably make the polymer more soluble during polymerization and thus allow the synthesis of high molecular weight polymer.

With the distannylated benzodithiophene monomer (**4**) in hand, copolymers could also be prepared with other conjugated cores through a Stille coupling with the corresponding dibromo monomers. Fluorene-based polymers have been shown to emit blue light with high quantum yields.[9] In addition, similar results have been obtained with poly(2,7-carbazole).[10] Due to the interest in fluorene and carbazole cores, the 2,7-dibromo-9,9-dioctylfluorene and the 2,7-dibromo-*N*-octylcarbazole monomers were polymerized with **4** to create polymers **P2** and **P3**, respectively (Scheme 2).

Scheme 2. Synthesis of Benzodithiophene-Containing Polymers



The number average molecular weight for both **P2** (26300 g/mol) and **P3** (40200 g/mol) were appreciably larger than the parent **P1**, presumably due to the higher solubilities during polymerization.

The UV−vis spectra for the monomer **2** and polymers **P1**, **P2**, and **P3** are shown in Figure 1. The phenylethynyl substituted monomer **2** displays a λ_{max} of 398 nm which is red-shifted by 62 nm compared to the previously reported benzo[1,2-*b*:4,5-*b*′]dithiophene monomer.[11]

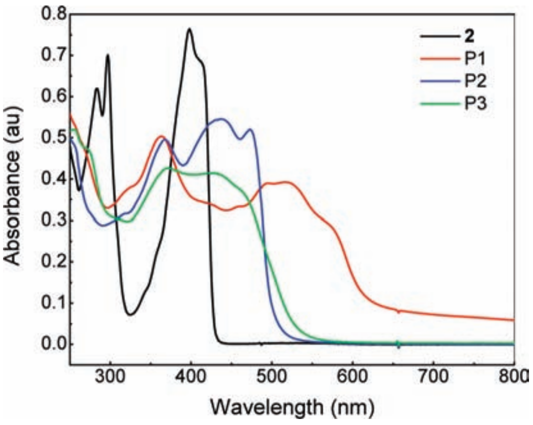


Figure 1. UV−vis absorbance of compounds in chloroform solution.

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The parent polymer **P1** is red-shifted by 84 nm compared to **P2** or **P3** (517 nm vs 433 nm). In addition, all three polymers display vibronic structure for the absorbance bands. Most surprising is the strong red shift for the **P1** benzodithiophene polymer in solution relative to regioregular P3HT (517 nm vs 450 nm) even though **P1** has a relatively low molecular weight of 3300 g/mol. This strong red shift, and vibronic structure in solution, indicates a long-range ordering of the **P1** polymer chains in solution that is not present for regioregular P3HT in solution. Films prepared by drop casting **P1** from chloroform solution also demonstrate vibronic structure with a red shift of 29 nm when the films were annealed at 120 °C for 5 min, thus indicating some long-range ordering for the polymer film. The annealed **P1** films have similar features to the films of regioregular P3HT. The films prepared from **P2** or **P3** show no shift in absorbance compared to solution either before or after annealing.

The band gap for the polymers was determined by electrochemical cyclic voltammetry. From the value of oxidation potential and reduction potential of the polymers, the HOMO and LUMO energy levels were determined as shown in table 1.[12] The band gap for **P1** was determined to be 2.04 eV. This value is smaller than the previously reported value of 2.49 eV for the alkoxy-substituted benzodithiophene polymer.[7b] More importantly, **P1** which has an extended electron delocalization displays a lower LUMO energy level than the previously reported alkoxy-substituted benzodithiophene analogue (−3.38 vs −2.67 eV).[7b] Presumably the band gap would lower further with a larger molecular weight of the polymer.

Table 1. Molecular Weight, Optical, and Electonic Energy Levels of Compounds

	M_w[a] (g/mol)	PDI	λ_{max}[b] (nm)	E_{ox}/V	Ered/V	HOMO[c] (eV)	LUMO[d] (eV)	band gap (eV)
2	530	N.A.	398	1.33	–1.23	–6.04	–3.48	n/a
P1	3300	1.9	517	0.708	–1.33	–5.42	–3.38	2.04
P2	26300	1.6	433	0.675	–1.17	–5.39	–3.54	1.85
P3	40200	2.6	433	0.718	–1.25	–5.43	–3.44	2.03

[a] Determined by SEC (THF eluent). [b] Absorptions in chloroform solution. [c] Estimated from peak average oxidation wave. [d] Estimated from peak average reduction wave.

The new polymers prepared in this study are fluorescent. **P1** displayed emission at 505 nm with a shoulder at 545 nm upon excitation at 400 nm. Both **P2** and **P3** also displayed a strong emission upon excitation. The quantum yields for the polymers are shown in Table 2. The parent **P1** polymer has a quantum yield of 48%. The fluorescence quantum yield of the copolymer **P2**, containing alternating fluorene and benzodithiophene cores, was 91%. This value is larger than those observed for polyfluorene (PFO) samples of 43%.[13] In addition, a copolymer containing alternating fluorene and two thiophene units, poly-9,9-dioctylfluorene-co-bithiophene (**F8T2**), has been previously prepared.[14] This polymer is similar to **P2**, which contains alternating fluorene with two fused thiophene rings. The reported quantum yield for F8T2 samples was 21%.[13] The **P2** sample with the two fused thiophene rings in a benzodithiophene structure has a greater than 4 times larger quantum yield. The **P3** copolymer containing the carbazole ring has a lower quantum yield of 22%.

Table 2. Fluorescence Data for Polymers[a]

	Ex (nm)	Em (nm)	quantum yield (%)
P1	400	505	48
P2	440	493	91
P3	430	488	22

[a] Fluorescence was measured in chloroform solution.

In conclusion, a benzodithiophene core with an extended conjugated phenylethynyl appendage has been synthesized. A Stille coupling of the respective dibromo and ditinylated derivatives generated homopolymer. A Stille coupling was also performed with the new core with both 2,7-dibromo-9,9-dioctylfluorene and 2,7-dibromo-*N*-octylcarbazole to create new conjugated copolymers. **P1** had a red-shifted absorption in solution (Figure 2). The electrochemical measurements also indicate a lower band gap for the polymer with extended conjugation. All new polymers had a strong fluorescence with high quantum yield. The quantum yield for the **P2** with alternating benzodithiophene and dioctylfluorene cores was 91%, significantly larger than observed for either parent polymer or for the analogous **F8T2** polymer that contains dioctylfluorene and two thiophene units in repetition. Presently the electrical mobilities of the new

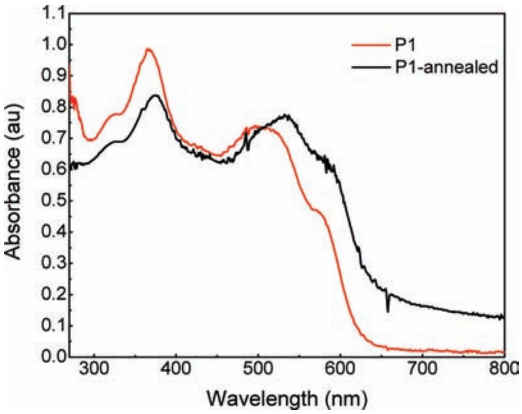

Figure 2. UV−vis absorbance of polymer films. **P1** and **P1** annealed at 120 °C for 5 min.

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polymers are being tested, and homologues of **P1** are being prepared with a longer alkyl tail appendage to increase the solubility and presumably the average molecular weight of the formed polymer.

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Supporting Information Available: Experimental procedures, spectroscopic data, and ^{1}H and ^{13}NMR spectra for all new compounds. CV, fluorescence, and quantum yield measurements for all polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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