

## Low Optical Bandgap Polythiophenes by an Alternating Donor/Acceptor Repeat Unit Strategy

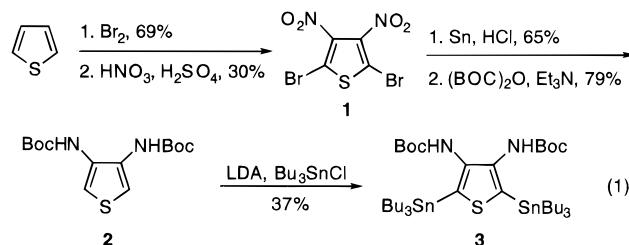
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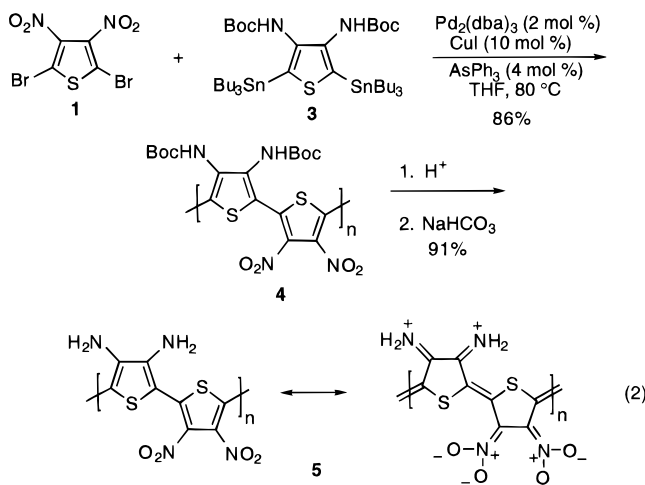
The synthesis of low optical bandgap polymers has been an area of intense interest due to their unique optoelectronic properties. The optical bandgaps of conjugated polymers have often been lowered by maximizing the extended  $\pi$ -conjugation through promotion of a near-planar conformation between the consecutive repeat units. Generally, irreversible ladder-type linkages between the consecutive repeat units of the polymers have been used to effect the coplanar arrangements.<sup>1</sup> More recently, reversible<sup>2</sup> or noncovalent linkages, specifically H-bonding,<sup>3</sup> have provided the desired twist inhibition. We report here a far less-exploited strategy to induce minimally twisted arrangements in conjugated polymers: constructing an alternating [AB] polymer where the A-unit has strong electron-donating moieties and the B-unit has strong electron-withdrawing moieties.<sup>4</sup> This results in a consecutive zwitterion-like interaction with high double bond character between the repeat units, stabilizing the low optical bandgap quinoidal forms of the polymers.<sup>5</sup>

Two required monomers for an [AB] polymerization were obtained from a common intermediate as shown in eq 1. Thiophene was selectively brominated at the 2,5-positions and then nitrated at the 3,4-positions to afford the electron deficient monomer **1**.<sup>6</sup> Reduction of the nitro moieties with concomitant dehalogenation followed by *tert*-butoxycarbonyl (Boc) protec-



tion afforded **2**.<sup>7</sup> Stannylation yielded the requisite electron rich thiophene monomer **3** which was ready for the modified Stille cross coupling<sup>8</sup> with monomer **1**.

After screening various coupling conditions, the optimal molecular weights (by size exclusion chromatography (SEC) relative to polystyrene (PS) standards)<sup>9</sup> of **4** ( $M_n = 7000$ ,  $M_w = 10,200$ ) were obtained using a mixed Pd(0)/CuI pre-catalyst system (eq 2).<sup>8c,10</sup> Triphenylarsine was used as the supporting



ligand of the catalyst, since triphenylphosphine is known to undergo aryl transfer acting as a chain terminator.<sup>8c,d</sup> Compound **4** was purified by dissolution in acetone and fractional precipitation with hexane. Deprotection of **4** with trifluoroacetic acid afforded **5** which, due to its solubility in water, was purified by dialysis (added to aqueous NaHCO<sub>3</sub> in a cellulose membrane tube with a pore size molecular weight cutoff of 3500 Da, suspension of the tube in deionized water, and changing the water three times per day for 7 days whereupon the resistivity of the water remained constant). There were no residual Boc moieties in **5** as determined by <sup>1</sup>H NMR and IR analyses.

There were several pieces of evidence which suggested that **5** had a high degree of zwitterionic and quinoidal character. First, unlike **4**, polymer **5** was only soluble in polar solvents such as MeOH, DMSO, and H<sub>2</sub>O. Second, the optical spectral shift on the conversion of **4** to **5** was profound; for **4**,  $\lambda_{max}$  (THF) = 407 nm and (MeOH) = 395 nm, while for **5**,  $\lambda_{max}$  (MeOH) = 662 nm (Figure 1). The optical bandgap decrease, evidenced by the strong bathochromic shift of 267 nm in the conversion of **4** to **5**, suggested that there was significant quinoidal character

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(9) Since SEC is a measure of the hydrodynamic volume and not the molecular weight, significant yet consistent errors in  $M_n$  and  $M_w$  usually result when comparing rigid rod polymers to the flexible coils of PS standards. Therefore, the values recorded here are given simply as a reference. For the degree of errors that could be generated, see: Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.

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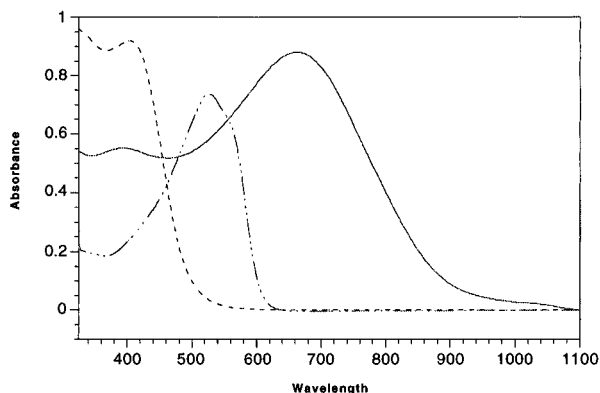
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**Figure 1.** Optical absorbance spectra of **4** (THF) (---), **5** (MeOH) (—), and **8** (THF) (— · — · —).

in **5**. This change was even more striking in view of the fact that highly regiochemically pure 3-substituted polythiophenes have  $\lambda_{\max}$  values of 450–460 nm in solution<sup>11</sup> while 3,4-disubstituted polythiophenes generally have  $\lambda_{\max} < 300$  nm due to the unavoidable 3–3' (head-to-head) interactions.<sup>11,12</sup> Here, we have a fully substituted polythiophene, albeit non-alkyl-substituted, with an unusually low bandgap by exploitation of the donor/acceptor repeat unit strategy.

We also prepared an analogous donor/acceptor system that had an imide rather than a dinitro acceptor unit. Tetrabromination of thiophene followed by selective 2,5-debromination afforded 3,4-dibromothiophene.<sup>13</sup> Cyano-substitution, hydrolysis,<sup>14</sup> and rebromination<sup>15</sup> at the 2,5-positions afforded **6**. Diacid chloride formation and treatment with *n*-butylamine afforded the desired imide monomer **7** which could be polymerized with **3** to afford the donor/acceptor polymer **8** ( $M_n = 5900$ ,  $M_w = 16\,800$ ) (eq 3). Remarkably, even in its sterically encumbered *N,N'*-di-Boc-protected form, **8** had an intensely bathochromically shifted optical absorbance:  $\lambda_{\max}$  (THF) = 526 nm and (MeOH) = 548 nm (Figure 1). Attempts to remove the Boc group yielded insoluble polymer. This may be due to ensuing amide formation and concomitant loss of *n*-butylamine, although we were successful in accomplishing the efficient deprotection (80%) in small oligomeric systems (*vide infra*).

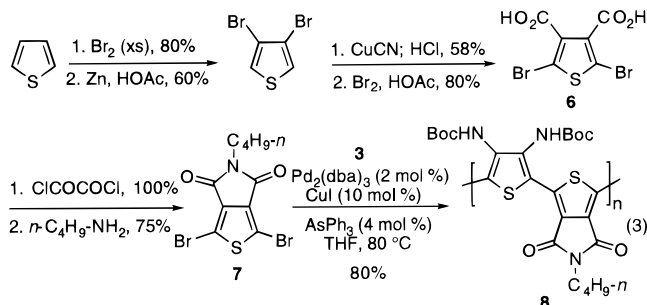
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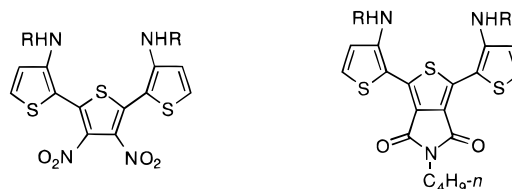
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In an effort to further confirm the need for the repeating donor/acceptor structure of the polymers for these unusually large wavelength absorptions, trimers **9–12** were prepared that had one electron-donating group per electron-withdrawing group, much like in the polymers **4**, **5**, and **8**.



**9**, R = Boc,  $\lambda_{\max}$  (MeOH) < 350 nm  
**10**, R = H,  $\lambda_{\max}$  (MeOH) = 447 nm

**11**, R = Boc,  $\lambda_{\max}$  (MeOH) = 375 nm  
**12**, R = H,  $\lambda_{\max}$  (MeOH) = 420 nm

In each case, the efficacy of the extended polymeric systems were verified since the polymers had much lower optical bandgaps. Even more striking is the fact that **8** is 128 nm bathochromically shifted relative to **12**, even though **8** had sterically larger and electronically poorer donors units than **12**.

In summary, we have prepared low optical bandgap conjugated polymers based on an [AB] polymer using alternating donor and acceptor moieties within the repeat unit to maximize extended  $\pi$ -conjugation. The polymers have significant quinoidal and/or zwitterionic character as evidenced by their optical absorbance spectra and solubility properties.

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**Supporting Information Available:** Synthetic and characterization details for the new compounds **3–8** (4 pages). See any current masthead page for ordering and Internet access instructions.

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