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# Model compounds based on poly(p-phenylenevinyleneborane) and terthiophene: Investigating the p-n junction in diblock copolymers

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#### ABSTRACT

Conjugated block copolymers represent a class of materials with potential applications in electronics and optoelectronics. Three block copolymer model compounds were made by first synthesizing 5-ethynyl-2,2':5',2"-terthiophene, 5-(2-propynyl)-2,2':5',2"-terthiophene and 5-(3-butynyl)-2,2':5',2"-terthiophene and then performing hydroboration polymerization from the alkyne of the terthiophene. The impact of the connectivity between the polymer blocks of these compounds was investigated. Theoretical and experimental studies indicated that charge transfer was occurring within the all-conjugated copolymer model compound, and that electronic coupling decreased with increasing length of the linking bridge between the n-type and p-type materials. Preliminary efforts to synthesize the related regioregular poly(3-hexylthiophene) all-conjugated diblock copolymer and use this material as the active layer in photovoltaic cells are discussed.

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#### 1. Introduction

Conjugated block copolymers (BCPs) are of great interest because of their potential use in electronic and optoelectronic technologies such as light emitting diodes and organic photovoltaics (OPVs) [1,2]. The development of BCPs is an intriguing strategy to explore the interplay of structure and function because of their inherent ability to self-assemble into ordered morphologies. For example, BCPs can limit the phase separation between the donor and acceptor domains to be comparable to the exciton diffusion length while maintaining ordered and continuous pathways for charge transport. For these reasons, fundamental studies using block copolymers could provide valuable knowledge toward understanding the mechanisms of charge transfer, exciton diffusion and other properties in organic electronics. The subject of block copolymers for optoelectronics has been reviewed in the literature [1-3], and only a brief summary is provided here.

Since first reports of the synthesis and characterization of P3HTpolyacrylate and P3HT-polystyrene block copolymers [4], other P3HT-containing block copolymers have been developed for use in electronic applications. Boudouris et al. developed a P3HTpolylactide diblock copolymer that formed microphase separated domains with a high degree of ordering [5]. Botiz and Darling subsequently created self-assembled films of a similar polymer and then selectively removed the polylactide polymer, thereby forming a nanostructured vessel for  $C_{60}$  acceptor material [6,7]. Wu et al. used ethynyl-terminated P3HT to synthesize polythiophene-polypeptide copolymers and demonstrated their ability to self-assemble [8]. Sommer et al. and Zhang et al. reported donor-acceptor diblock copolymers with poly(perylene bisimide acrylate) as the acceptor block [9,10]. Zhang also included solar cell fabrication, obtaining 0.5% power conversion efficiency (PCE) in the annealed copolymer devices when thermal annealing was performed after fabrication of the





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Abbreviations: TipB-ter0, 5-{2-[[2-(4-{2-[propenyl-(2,4,6-triisopropyl-phenyl)-boranyl]-vinyl}-phenyl)-vinyl]-(2,4,6-triisopropyl-phenyl)-boranyl]-vinyl}-

<sup>[2,2&#</sup>x27;;5',2"]terthiophene; TipB-ter1, 5-[3-[[2-(4-[2-[propenyl-(2,4,6-triisopropyl-phenyl]-boranyl]-vinyl]-vinyl]-(2,4,6-triisopropyl-phenyl)-boranyl]-allyl]-[2,2';5',2"]terthiophene; TipB-ter2, 5-[3-[[2-(4-[2-[propenyl-(2,4,6-triisopropyl-phenyl]-boranyl]-vinyl]-vinyl]-(2,4,6-triisopropyl-phenyl)-boranyl]butenyl]-[2,2';5',2"]terthiophene.

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device, representing an improvement over the 0.4% PCE of the related mixture. In the annealed BCPs, they found increased short-circuit current, which could result from reorientation and enhanced ordering of the copolymer, thereby facilitating charge transport [10]. These are among highest reported efficiencies to date in a diblock copolymer system.

All-conjugated block copolymers may be even more interesting for their direct use as active layer materials. The first all-conjugated BCP was reported by Jenekhe [11], and several other reports have followed [12–16]. Recently, all-conjugated diblock and triblock copolymers have emerged that were also donor–acceptor systems and were shown to assemble into nanostructured domains [14,17–24].

Although most  $\pi$ -conjugated polymers are p-type (electrondonor) semiconductors, when a borane is incorporated regularly in the polymer backbone, the polymers are inherently electron deficient. Chujo first synthesized polymers with boron in the main chain and showed that the  $\pi$ -conjugation length was extended via the vacant p-orbital of the boron atom [25,26], demonstrating their potential to function as electron acceptors (n-type materials) [27– 30]. There has been increasing interest in the use of organoborane polymers for electronic applications, including the use of organoboranes as pendant groups [31–36].

Since the junction between the donor and acceptor polymer blocks (p-n junction) is the most likely location for intramolecular exciton splitting, studying the p-n junction could provide insight into the problems of recombination, exciton diffusion and charge generation in OPVs. Sun designed a block copolymer with a flexible bridge (spacer) between the donor and acceptor molecules, and found a much improved solar cell performance when compared with the corresponding polymer blends [37]. The spacer was originally proposed by Aviram and Ratner as a non-conjugated component between the donor and acceptor, which played the role of tunneling barrier, preventing recombination [38]. Ng and Yu designed a diblock oligomer that incorporated two different conjugated blocks with opposite electronic demands and showed a diode rectifying effect, even with the two molecules directly coupled (no spacer) [39].

Here, three terthiophene compounds with different alkynyl end groups were synthesized (Scheme 1). Then hydroboration polymerization was performed from the alkyne of the terthiophene compounds, yielding copolymer model compounds with three different p-n junctions (Scheme 2). UV–Vis absorption, cyclic voltammetry, and transient absorption measurements of these model compounds were obtained; supporting DFT calculations were also performed.

Using poly(phenylenevinyleneborane) as the n-type polymer [40] and P3HT as the p-type polymer, initial attempts were made to synthesize an all-conjugated donor—acceptor diblock copolymer (Scheme 3) and use it as the active material in OPVs.

#### 2. Experimental

Starting materials and reagents were purchased from Aldrich or Acros Organics; Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and Pd(PPh<sub>3</sub>)<sub>4</sub> were purchased from Strem Chemicals. An Innovative Technologies solvent purification system was used to obtain dry solvents (toluene, THF and diethyl ether). All reactions were run under an inert atmosphere of



Scheme 1. Synthesis of alkynyl terthiophenes.



Scheme 2. Synthesis of tipB-ter model compounds.

nitrogen or argon. NMR spectra were recorded on a Varian 300 or 400 MHz spectrometer. Chemical shifts are expressed in parts per million ( $\delta$ ) using residual solvent resonances for calibration.

Tripylborane **1** [41–43], ethynyl-P3HT [44], 2,2'-bithiophene [45,46], 2-tributyltin-2'-bithiophene [47,48], 2,2':5',2"-terthiophene [49,50] and 5-bromo-2,2':5',2"-terthiophene [45,50–52] were synthesized according to literature procedures.

5-(trimethylsilylethynyl)-2,2':5',2"-terthiophene **2** [52]: A solution of 5-bromo-2,2':5',2"-terthiophene (1.58 g, 4.8 mmol), trimethylsilylacetylene (TMSA) (0.90 mL, 5.8 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.144 mmol, 101 mg, 3 mol%), and CuI (0.288 mmol, 55 mg, 6 mol%) in a mixture of THF/Et<sub>3</sub>N ( $\nu/\nu$  = 32/8) was degassed for 15 min and then heated at 65 °C for 12 h. The solvent was removed, affording a brownish residue. The crude product was heated in hot hexane and filtered two times and then recrystallized from hexane to afford 1.36 g (82%) of a dark yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.23 (dd, J = 4.9, 0.7 Hz, 1H), 7.18 (dd, J = 3.8, 0.7 Hz, 1H), 7.00 (d, J = 3.8 Hz, 1H), 0.254 (s, 9H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  138.48,

136.98, 136.73, 135.16, 133.60, 128.01, 125.01, 124.89, 124.41, 124.01, 123.32, 121.82, 100.32, 97.07, -0.24.

5-ethynyl-2,2':5',2'-terthiophene **3** [52]: To a solution of **2** (103.4 mg, 0.300 mmol) in THF/MeOH (v/v = 3/1) was added 45.6 mg (0.33 mmol) of K<sub>2</sub>CO<sub>3</sub>. The mixture was stirred at room temperature for 1 h. After removal of the solvent, the crude product was loaded on a short plug of silica gel (~5 cm) and flushed with a large amount of hexane. The pure product was obtained as yellow-orange solid upon the evaporation of hexane (75.5 mg, 88%). The product turned dark brown within a few hours and thus the deprotection reaction was done immediately prior to use. <sup>1</sup>H NMR (400 MHz, CDCl3):  $\delta$  7.23 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.18 (dd, *J* = 3.8, 1.5 Hz, 1H), 7.13 (d, *J* = 3.8 Hz, 1H), 7.08 (s, 2H), 7.03 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.01(d, *J* = 3.8 Hz, 1H), 3.42 (s, 1H).

5-bromo-2-bromomethylthiophene **4** [53,54]: CCl<sub>4</sub> (80 mL) was added to NBS (28.5 g, 164 mmol). Methylthiophene (8.06 g, 82 mmol) was added slowly and the mixture was refluxed overnight. The CCl<sub>4</sub> was removed by reduced pressure, hexane was added and the mixture was filtered through Celite. After removal of



P3HT-tipBPh

Scheme 3. Synthesis of P3HT-tipBPh.

the hexane, the pure product (12.76 g, 60.8%) was collected by vacuum distillation (65 °C/0.5 Torr). It should be noted that 5-bromo-2-bromomethylthiophene **4** has a distinct smell and is a lachrymator. <sup>1</sup>H NMR (400 MHz, CDCl3):  $\delta$  6.86 (d, *J* = 3.9 Hz, 1H), 6.88 (d, *J* = 3.8 Hz, 1H), 2.44 (s, 2H). <sup>13</sup>C NMR (400 MHz, CDCl3):  $\delta$  142.21, 130.02, 128.49, 114.05, 26.42.

5-bromo-2-[3-(trimethylsilyl)-2-propynyl]-thiophene **5** [55]: A 1.5 M THF solution of 1-trimethylsilylethynylmagnesium bromide (10 mmol) (which was prepared by reacting TMSA (10.0 mmol, 1.42 mL) in 3.6 mL of THF with 10.0 mL of 1M ethylmagmesium bromide) was added to a stirred suspension of copper(I) bromide (71.7 mg, 0.500 mmol) in THF (2 mL). A solution of **4** (2.56 g, 10.0 mmol) in THF (3 mL) was then added and the mixture was refluxed for 2 h. The reaction mixture was poured into a cold saturated NH<sub>4</sub>Cl aqueous solution, stirred for 0.5 h, and extracted with Et<sub>2</sub>O. The organic extract was washed with water, dried, concentrated in vacuo and distilled (85 °C/0.5 Torr) to give 1.96 g (71.7%) of a clear liquid. MS: 272 (M+), 274 (M+2), 257, 259, 229, 231, 193, 89, 73. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.70 (dt, *J* = 3.7, 1.2 Hz, 1H), 6.87 (d, *J* = 3.7 Hz, 1H), 3.71 (d, *J* = 1.2 Hz, 2H), 0.19 (9H, s). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  141.01, 129.78, 125.52, 110.42, 102.38, 87.78, 21.60, 0.133.

5-[3-(trimethylsilyl)-2-propynyl]-2,2':5',2"-terthiophene **6** [48]: To a 40 mL solution of toluene containing 0.462 g (0.400 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> was added **5** (2.05 g, 7.05 mmol) and 2-(tributyl-stannyl)bithiophene (3.21 g, 7.05 mmol). After degassing for 15 min, the mixture was refluxed overnight. After evaporation of toluene, the residue was chromatographed on silica gel with 5% ether/hexane and recrystallized from hexane to give 0.401 g (14.2%) of a yellow brown crystalline solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.21 (dd, J = 5.1, 1.2 Hz, 1H), 7.16 (dd, J = 3.6, 1.1 Hz, 1H), 7.06 (d, J = 3.8 Hz, 1H), 7.04–7.01(m, 2H), 7.00(d, J = 3.8 Hz, 1H), 6.86 (dt, J = 3.6, 1.1 Hz, 1H), 3.78 (d, J = 1.0 Hz, 2H), 0.17 (s, 9H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  138.81, 137.38, 136.56, 136.19, 136.07, 128.07, 126.04, 124.63, 124.49, 124.18, 123.85, 123.60, 102.87, 87.48, 21.54, 0.196.

5-(2-propynyl)-2,2':5',2"-terthiophene **7** [55,56]: Trimethylsilylpropargylterthiophene **6** (72 mg, 0.20 mmol) was dissolved in 5 mL DMF. Then 1.5 equiv of KF2H<sub>2</sub>O (28 mg) and 1.5 equiv of acetic acid (17 µL) was added and it was stirred for 24 h at room temperature, then treated with an excess of 3N HCl and extracted with hexane. The hexane extract was washed with 3N HCl and then washed with saturated NaHCO<sub>3</sub>, water and dried with MgSO<sub>4</sub>. The hexane was removed by reduced pressure and the residue was recrystallized from hexane to give 51 mg (89%) of a brownish yellow crystalline solid. MS: 286(M+), 287(M+1), 253, 127. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.22 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.17 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.06 (d, *J* = 3.8 Hz, 1H), 7.04–6.99(m, 3H), 6.88 (dd, *J* = 3.6, 1.1 Hz, 1H), 3.75 (dd, *J* = 2.6, 1.1 Hz, 2H), 2.24 (t, *J* = 2.7 Hz, 1H).

2-bromo-5-(2-hydroxyethyl)thiophene **8** [56]: To a solution of 5.21 g (0.041 mol) of 2-(2-thienyl)ethanol in 50 mL of toluene was added stepwise 7.23 g (0.041 mol) of NBS at -20 °C. The mixture was stirred at room temperature overnight and then treated with 10% KOH and washed with brine. The toluene phase was dried with MgSO<sub>4</sub>, then filtered and the solvent was removed with reduced pressure. The crude product was chromatographed on silica gel (ethyl acetate/petroleum ether 7:3) and isolated as a colorless liquid (6.58 g, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.90 (d, *J* = 3.7 Hz, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 3.83 (t, *J* = 6.2 Hz, 2H), 3.00 (t, *J* = 6.2 Hz, 2H), 1.70 (s, 1H, OH); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  142.7, 129.5, 125.9, 109.7, 62.8, 33.5.

5-(2-Hydroxyethyl)-2,2':5',2"-terthiophene **9** [46,56]: To a 50 mL solution of toluene containing 0.578 g (0.500 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> was added **8** (2.06 g, 10 mmol) and 2-(tributylstannyl) bithiophene (4.55 g, 10 mmol). After degassing for 15 min, the mixture was refluxed overnight. After evaporation of toluene, the residue was chromatographed on silica gel with petroleum ether/

ethyl acetate 7:3 to give 0.95 g (31%) of a yellow brown crystalline solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.21 (dd, J = 5.1 Hz, J = 1.1 Hz, 1H), 7.16 (dd, J = 3.7 Hz, J = 1.1 Hz, 1H), 7.07 (d, J = 3.8 Hz, 1H) 7.04–7.01 (m, 3H), 6.79 (d, J = 3.6 Hz, 1H), 3.89 (q, J = 6.1 Hz, 2H), 3.06 (t, J = 6.2 Hz, 2H), 1.62 (t, J = 6.0 Hz, 1H, OH). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  140.56, 137.38, 136.58, 136.12, 136.01, 128.08, 126.69, 124.63, 124.50, 124.09, 123.84, 123.78, 63.54, 33.80.

5-(2-Bromoethyl)-2,2':5',2"-terthiophene 10 PPh<sub>2</sub> [57]: (674 mg, 2.57 mmol) was dissolved in 5 mL CH<sub>2</sub>Cl<sub>2</sub>, and bromine (411 mg, 2.57 mmol) in 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise, forming a colorless solution. Hydroxyethylterthiophene 9 (751.6 mg, 2.57 mmol) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was then added dropwise and the mixture stirred overnight at room temperature. The mixture was quenched with water (15 mL), separated, and the aqueous phase was extracted with  $2 \times 15$  mL CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phase was dried with MgSO<sub>4</sub>, filtered, and concentrated. The crude product was purified by chromatography on silica gel using 5% Et<sub>2</sub>O/hexanes) to afford 730 mg (78%) of a dark yellow solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.22 (dd, J = 5.1, 1.1 Hz, 1H), 7.17 (dd, J = 3.7, 1.1 Hz, 1H), 7.06 (d, J = 3.8 Hz, 1H), 7.02 (t, J = 4.1 Hz, 3H), 6.80 (d, J = 3.5, 1H), 3.59 (t, J = 7.4 Hz, 2H), 3.35 (t, J = 7.4 Hz, 2H).

5-[4-(trimethylsilyl)-3-butyn-1-yl]-2,2':5',2"-terthiophene 11 [58] A THF solution of 1-trimethylsilylethynylmagnesium bromide (0.8 mmol) was prepared by reacting TMSA (0.12 mL, 0.84 mmol) with a THF solution of ethylmagnesium bromide (0.8 mL, 0.8 mmol). The THF was evaporated under reduced pressure for 5 min to give a solid. Immediately, TMEDA (0.6 mL) was added to the flask to furnish a suspension. Cobalt(III) acetylacetonate (28.5 mg, 0.080 mmol) was placed in a 25-mL flask and was heated under vacuum for 5 min. Anhydrous TMEDA (0.4 mL) was added and the mixture was stirred for 3 min at room temperature. It was then added to bromoterthiophene (71.1 mg, 0.22 mmol) via a syringe. The suspension of 1-trimethylsilylethynylmagnesium bromide was next added to the mixture at room temperature with a syringe with stirring for 15 min after which the mixture turned brown. The mixture was poured into a saturated NH<sub>4</sub>Cl solution, extracted with hexane and ether (50 mL  $\times$  2) and dried over MgSO<sub>4</sub>, filtered and concentrated to give 115 mg of yellow crystals (38.6%). MS: 372 (M+), 261, 207, 73. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.22 (dd, J = 5.1, 1.1 Hz, 1H), 7.16 (dd, J = 3.6, 1.1 Hz, 1H), 7.06 (d, J = 3.8 Hz, 1H), 7.03-6.98 (m, 3H), 6.76 (d, J = 3.6, 1H), 3.02 (t, J = 7.4 Hz, 2H), 2.57 (t, J = 7.4 Hz, 2H), 0.168 (s, 9H).

5-(3-butynyl)-2,2':5',2"-terthiophene **12** [55]: The trimethylsilylbutynylterthiophene **11** (74.5 mg, 0.20 mmol) was dissolved in 5.0 mL of DMF and KF  $\cdot$  2H<sub>2</sub>O (28.2 mg, 0.30 mmol) was added. The mixture was stirred and the reaction was monitored by GCMS for quantitative removal of the TMS group. After 3 h at room temperature, the reaction was complete and the mixture was treated with an excess of 3N HCl and extracted with hexane. The hexane extract was washed with 3N HCl and then washed with saturated NaHCO<sub>3</sub>, water and dried with MgSO<sub>4</sub>. The hexane was removed by reduced pressure and the residue was recrystallized from hexane to give 54 mg (90%) of a dark yellow solid. MS: 300(M+), 301(M+1), 261, 131.

General procedure for the hydroboration polymerization of alkynyl terthiophene: The procedure with ethynylterthiophene, giving **tipB-ter0** is representative. Tripylborane **1** (1.0 mmol, 217 mg) was dissolved in 1 mL THF. Ethynylterthiophene **3** (0.10 mmol, 28.0 mg) in 1 mL THF was added with stirring for ½ hour. Then diethynylbenzene (0.80 mmol, 101 mg) in 2 mL THF was added with stirring for ½ hour and stirring continued overnight. After removal of the solvent, dry methanol was added to the dark orange residue, it was filtered and washed with methanol, then reprecipitated with THF/methanol. The precipitate was dissolved in toluene and was run quickly through a small silica gel column. The orange fraction was collected and 217 mg of a bright orange shiny

solid was collected after evaporation of the solvent. GPC:  $M_{\rm w}$  5419/ M<sub>n</sub> 3,656, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.13–7.71 (8H, Ar–H and B– CH = CH; 2H, thiophene), 6.92–7.06 (2H, Ar–H, (tripyl) and 5H, thiophene), 6.77 (d, *J* = 18.0 Hz, 1H, vinyl, thiophene), 3.70 (–OMe end group), 3.02–2.81 (m, 2H, CH(tripyl)), 2.41–2.55 (m, 1H, CH(tripyl)), 1.18–1.36 (18H, CH<sub>3</sub>(tripyl)); <sup>11</sup>B NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  45.8 (br).

**tipB-ter1**: shiny yellow solid, 455 mg. GPC:  $M_w$  4270/ $M_n$  2700. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.13–7.71 (8H, Ar–H and B–CH=CH; 2H, thiophene), 6.92–7.06 (2H, Ar–H, (tripyl); 5H, thiophene), 5.54 (B–CH=CH), 3.78-3.58 (CH<sub>2</sub>, propargyl, and –OMe end groups), 2.42–2.98 (3H, CH(tripyl)), 1.11–1.32 (18H, CH<sub>3</sub>(tripyl)).

**tipB-ter2**: dark yellow solid, 78 mg. GPC:  $M_w$  5750/ $M_n$  2630. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.15–7.64 (8H, Ar–H and B–CH=CH; 2H, thiophene), 6.85–7.13 (2H, Ar–H, (tripyl); 5H, thiophene), 5.90–6.34 (B–CH=CH), 3.78–3.45 (–OMe end groups), 2.72–2.98 (m, 1H, CH(tripyl)) and 4H, CH<sub>2</sub>(ethyl)), 2.39–2.52(m, 2H, CH(tripyl)), 1.11–1.32 (18H, CH<sub>3</sub>(tripyl)).

Polythiophene-*b*-poly(phenylenevinyleneborane) **P3HT**tipBPh: Ethynyl-P3HT [44] (50 mg, 0.013 mmol, M<sub>n</sub> 3900, MALDI-TOF MS) was dissolved in THF (50 mL). Tripylborane (154.6 mg, 0.715 mmol) was weighed in the glove box, dissolved in 3 mL THF, and from a gas-tight syringe, 0.1 mL was slowly added to the P3HT and stirred for 10 min. This was to ensure that all the ethynyl groups from the P3HT were reacted. Diethynylbenzene (81.2 mg, 0.64 mmol) was dissolved in 2.9 mL of THF and taken up into a syringe. A large excess  $(5\times)$  of the tripylborane and diethvnvlbenzene were then added to the mixture at the same rate over a 2-h period. The mixture was stirred overnight. Most of the THF was removed, and the thick solution was precipitated with dry methanol and filtered, then washed several times with dry methanol to obtain a dark purple residue. The residue was dissolved in toluene and run through a silica gel column, and the red fraction (75 mg), which contained the polymer, was collected. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.02–7.64 (8H, Ar–H and B–CH=CH), 6.95– 7.03 (2H, Ar–H, tripyl) 6.93 (s, CH, thiophene), 5.91–6.78 (B–CH= CH), 3.83–3.46 (–OMe end groups), 2.76–3.01 (m, 1H, CH(tripyl)), 2.86–2.74 (br, 2H CH<sub>2</sub>), 2.41–2.53(m, 2H, CH(tripyl)), 1.74–1.67 (br, 2H, CH<sub>2</sub>), 1.48–1.39 (br, 2H, CH<sub>2</sub>) 1.19–1.23 (br, 2H, CH<sub>2</sub>), 1.04–1.38 (18H and 4H, CH<sub>3</sub>(tripyl) and CH<sub>2</sub>), 0.95-0.87 (br, CH<sub>3</sub>).

UV–Vis measurements were performed in THF with a Varian/ Cary Eclipse UV–VIS Spectrometer or an Agilent 8352 UV–visible spectrophotometer. A Varian/Cary Eclipse fluorescence spectrophotometer and a Perkin–Elmer LS-55 fluorimeter were used for fluorescence measurements.

For cyclic voltammetry (CV) measurements, the three electrode system consisted of a glass-carbon electrode coated with polymer film as the working electrode, platinum wire as the counter electrode and Ag/Ag+ as the reference electrode. The voltammograms were recorded at 100 mV s<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub> containing Bu<sub>4</sub>N[PF<sub>6</sub>] (0.1M) as the supporting electrolyte. The scans were referenced after the addition of a small amount of ferrocene as internal standard and are reported relative to the Fc/Fc+ couple. HOMO energy levels were calculated by the equation HOMO =  $-[E_{ox} - E1/2(Fc/Fc+) + 4.8]eV$ , where  $E_{ox}$  was the onset oxidation potential versus SCE [59]. LUMO levels were calculated similarly.

Gel permeation chromatography (GPC) was performed in THF (35 °C) at a flow rate of 1.0 mL/min) using a Waters system comprised of a Waters HPLC 515 pump, a Waters 2410 RI detector and two 10 mm by 250 mm columns. The first column was a DuPont Instruments Zorbax S-06 and the second was a Jordi-Gel DVB mixed bed column. GPC for tipB-ter0 was performed using a Viscotek GPCmax with VE 2001 GPC solvent/sample module, a 2600 UV detector, a TDA 305 triple detector array and three columns, including one PLgel 5  $\mu$ m mixed-D and two PLgel 5  $\mu$ m mixed-C columns. Both

systems were calibrated with polystyrene standards having a molecular weight range of 3000 to 600,000 g/mol.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Reflex III spectrometer. MALDI-TOF samples were prepared by dropcasting a THF solution of polymer with terthiophene as a matrix.

Pump-probe ultrafast TA spectroscopy experiments were carried out at the Center for Nanoscale Materials (CNM) at Argonne National Laboratory using an amplified Ti:sapphire laser system (Spectra Physics, Spitfire-Pro) and an automated data acquisition system (Ultrafast Systems, Helios). The amplifier was seeded with the 120 fs output from the oscillator (Spectra Physics, Tsunami) and was operated at 1.66 kHz. The output from the amplifier was split with 90% used to pump an optical parametric amplifier (Topas, Light Conversion) and the 10% used to generate a visible continuum (440– 780 nm) probe by focusing into a thin sapphire plate. The excitation (pump) wavelength was 350 nm and the pump pulse energy was 1 µJ.

Molecular modeling of the three model compounds was performed using hybrid density functional theory (DFT). The calculations were done on terthiophene connected to a tetramer of the phenyleneborane and were carried out using Gaussian'09 [60] on a 28 TFlop computer cluster at Argonne National Laboratory; GaussView 5 was used for visualization. For ground state optimizations, the B3LYP/3-21G\* level was used. Molecular orbitals were calculated as a single point ground state energy B3LYP/6-311G(d,p) with tight convergence, and UV–Vis calculations were based on single point energy TD-SCF/PBE1PBE/6-31G+(d,p) gas phase calculations with tight convergence.

For photovoltaic cell fabrication, indium tin oxide (ITO)-coated glass slides of  $1.5 \times 1.5 \text{ cm}^2$  were used as the conducting positive electrode. The ITO layer was partially etched and the glass substrates (Delta Technologies Ltd. with resistivity 8–12  $\Omega$  per square) were cleaned with detergent and sonicated in deionized water, acetone, and isopropanol. The substrates were dried under N<sub>2</sub> flux and finally were treated for 20 min in a plasma surface decontamination system (Harrick Plasma) connected to an O<sub>2</sub> gas source. An aqueous PEDOT:PSS (0.5 w/v%, Baytron PH 500, HC Starck Inc.) solution was passed through a 0.45  $\mu$ m filter and then spin-coated from aqueous solution at 5000 rpm. The substrate was dried for 20 min at 120 °C on a hot plate.

In the glove box, a layer of copolymer P3HT-tipBPh was deposited on top of the PEDOT:PSS layer by spin-coating (1200 rpm) from anhydrous DCB (30 mg/mL) or a 1:1 mixture of P3HT and tipBPh, 20 mg/mL in DCB. A calcium layer (20 nm), which facilitates electron collection at the organic/metal electrode, and an aluminum layer (85 nm) were deposited on the polymer films by thermal evaporation at 2  $\times$   $10^{-6}$  mbar. The active area of the devices was ~ 0.16 cm<sup>2</sup>. All current voltage (I-V) characteristics of the devices were measured using a Keithley 2400 source meter under A.M. 1.5 illumination (100 mW/cm<sup>2</sup>) from a Xenon light source. Measurements were calibrated using an NREL-measured mono-Si photodetector (Hamamatsu S1133-14), which produces 1.638 mA of current at A.M. 1.5 illumination. Short circuit current density (J<sub>SC</sub>), open circuit voltage ( $V_{OC}$ ), and fill factor (FF) were obtained from the current density–voltage (I-V) curves. The conversion efficiency was calculated by  $\eta = J_{SC} \times V_{OC} \times FF/P_{in}$ , where  $P_{in}$  is the incident power density; and FF is given by FF =  $J_{max} \times V_{max} / J_{SC} \times V_{OC}$ , where  $J_{\text{max}} \times V_{\text{max}}$  is the maximum output power density of the solar cell.

#### 3. Results and discussion

#### 3.1. Synthesis of the model compounds

Terthiophene was made by reacting dibromothiophene with tributylstannylthiophene in the presence of  $Pd(PPh_3)_4$  in DMF

(Stille coupling) [49,50]. A Sonagashira coupling reaction with 5bromo-2,2':5',2'-terthiophene and TMSA provided good yields of the TMS-protected ethynylterthiophene **2** (Scheme 1) [52]. The TMS group was removed with standard deprotecting conditions and the product was used immediately [61].

Synthesis of propargylterthiophene was difficult due to the acidity of the non-conjugated carbon between the alkyne and terthiophene. The final synthesis started with 2-methylthiophene, which was dibrominated with NBS in CCl<sub>4</sub> and the product was purified by distillation [53,54]. The TMS-protected ethynyl Grignard was then used in the presence of copper bromide to give the protected propargylthiophene **5** [55]. Tributylstannyl-2,2'bithiophene [47,62] was coupled to the propargylthiophene using Stille conditions to give **6** [46,62]. When KF was used under neutral conditions to remove the TMS group the allene was obtained, but when acetic acid was added as a buffer, propargylterthiophene **7** was obtained [63].

For 3-butynylterthiophene, 2-(2-hydroxyethyl)thiophene was brominated with NBS [56]. Stille conditions were then used to couple tributylstannylbithiophene to the hydroxyethylthiophene to give **9**. The hydroxy group was transformed to a bromide using bromine and triphenylphosphine [57]. Finally a cobalt coupling method was used to add TMSA to the 2-(2-bromoethyl)terthiophene **10** to give the TMS-protected butynylterthiophene **11** [58]. The TMS group was efficiently removed with KF under standard conditions.

The deprotected terthiophene was dissolved in THF and tripylborane was added, the mixture was stirred for ½ hour, and then the dialkyne was added slowly with stirring continued overnight (Scheme 2). After repeated precipitation with methanol from THF, the product was dissolved in toluene and run quickly through a small silica gel column with toluene. Following precipitation with methanol, it was expected that most endgroups were methoxy-, although other possibilities exist (see Scheme 2).

#### 3.2. UV–Vis and fluorescence measurements of the model compounds

The UV–Vis and fluorescence spectra of the three copolymer model compounds were similar, except tipB-ter0 showed an additional absorption band at 470 nm and an additional fluorescence band at 525 nm (Fig. 1). That the extra absorbance and fluorescence was not present in either of the compounds with a non-conjugated link could signify that the alkyl groups prevent charge transfer from the terthiophene to the borane moieties.

It has been established that organoborane polymers show a strong bathochromic shift relative to the monomer, suggesting effective p- $\pi$  overlap [40]. This red shift of absorption represents the extension of the  $\pi$ -conjugated system containing the boron atom and is accompanied by a lowering of the LUMO [28,64]. A bathochromic effect was also observed in anthracene derivatives when more boryl anthracene moieties were added, indicating effective  $\pi$ -conjugation to the external moieties [65]. Unusually large Stokes shifts were found for organoborane heteroaromatic polymers containing thiophene and furan units in the main chain, which was likely due to increasingly pronounced charge transfer character [31,66]

The observed additional absorption peak at 470 nm in tipB-ter0 could be a marker of charge transfer, or the result of crossconjugation between the terthiophene and the boron polymer because it is in addition to the effects of extension of conjugation in the borane polymer itself (absorption of the borane homopolymer is observed at around 400 nm) [40]. In related work, Pammer, et al. observed bands at 330 and 470 nm in polythiophene with dimesitylvinylborane side groups [67]. In this system, the band at 470 nm represented extended conjugation with expansion of the molecular system, while the band at 330 nm was assigned to charge transfer as confirmed by its suppression upon addition of CN<sup>-</sup> or F<sup>-</sup>. Similarly, a polythiophene system with directly attached boryl groups showed a strong absorption at 412 nm with an additional peak at 340 nm, which resulted from excitation to a crossconjugated state of bithiophene with two mesitylborane mojeties [68]. Looking back at the UV–Vis of tipB-ter0, there is evidence of another band at  $\sim$  335 nm that would corroborate the findings of Jäkle and coworkers discussed above, but it overlaps with the broad absorption from the organoborane polymer.

Consequently, the additional absorption band at 470 nm is likely the result of extended conjugation between the terthiophene  $\pi$ system and the organoborane polymer as well as a marker of direct connectivity between the boron and the terthiophene systems. GPC measurements of tipB-ter0 with a UV–Vis PDA detector demonstrate this connectivity because the same GPC peak profile was observed at 378 nm and 470 nm (Fig S1 and Fig S2). Solid state UV– Vis measurements were also completed by spin coating a solution of tipB-ter0 onto a glass slide. The solid state spectra are similar to the solution UV–Vis, demonstrating that the solution data are likely representative of the solid state properties (Fig S3).



Fig. 1. UV-Visible absorption (left) and fluorescence emission (350 nm excitation) spectra of copolymer model compounds, terthiophene and tripylborane polymer. The spectra have been normalized.

#### 3.3. DFT calculations of the model compounds

The molecular orbitals and electronic states involved in the optical transitions were investigated with DFT calculations. The structures of the calculated compounds were the same as the synthesized compounds, except that the calculated compounds had four boron monomers, and based on GPC analysis, the synthesized compounds had an average of about ten boron monomers. In all three copolymer model compounds, the highest occupied molecular orbitals (HOMO)s resided on the terthiophene  $\pi$ -system, with similar orbital energies: -5.43 eV, -5.30 eV, -5.29 eV for tipB-ter0, tipB-ter1 and tipB-ter2, respectively (Fig. 2, Table 1). For tipB-ter0, there is spillover from the terthiophene onto the boron atom. This would be stabilizing and could therefore account for the slightly lower HOMO energy of tipB-ter0. In the other two model compounds, this spillover was blocked by the alkyl group(s).

In the LUMOs of all three model compounds, the electron density was spread across both the terthiophene and the organoborane moiety (except for the perpendicular tip group), and not on the alkyl groups (See Fig. 2). The next higher orbital (LUMO+1) is where the differences between tipB-ter0 and the other two model compounds become most significant. In tipB-ter0, the LUMO+1 shows cross conjugation from the terthiophene to the empty porbital on boron, whereas in the other two model compounds, all the electron density in the LUMO+1 resides only on the organoborane moiety.

To summarize the energy differences, while the orbital energies of tipB-ter1 and tipB-ter2 are nearly the same, for tipB-ter0, the HOMO is 0.13 eV lower, the LUMO is 0.05 eV higher and the LUMO+1 is 0.06 eV lower (see Table 1). The calculated HOMO–LUMO gap is 2.5 eV, about 0.2 eV larger than tipB-ter1 and tipB-

#### Table 1

Calculated energy levels (DFT) and transitions (TD-SCF), and experimental absorption data of model compounds. All energies are given in electron Volts (eV).

	НОМО	LUMO	LUMO+1	Transitions (Calcd) <sup>a</sup>	Transitions (Exp) <sup>b</sup>
tipB-ter0	-5.43	-2.96	-2.71	2.75, 2.67, 2.42	3.1, 2.79
tipB-ter1	-5.30	-3.01	-2.66	2.70	3.1
tipB-ter2	-5.29	-3.00	-2.65	2.70	3.1

<sup>a</sup> Electronic transitions with significant oscillator strengths (f > 0.11) based on TD-SCF calculations. Other orbitals involved in these transitions are detailed in Figure S2 and Figure S3.

<sup>b</sup> Based on the estimated absorption maxima from Fig. 1.

ter2. The larger HOMO–LUMO energy gap for tipB-ter0 is an unexpected result because the longest wavelength absorption of tipBter0 is significantly lower in energy than for the other two model compounds.

TD-SCF calculations reveal the reason for this result. The electronic transition to the first excited state of tipB-ter0 is primarily based on excitation from the HOMO to the LUMO with an additional smaller component from the HOMO to the LUMO+1 (Figure S4), both of which involve some charge transfer from the terthiophene to the borane polymer chain. For the other two model compounds only the  $S_0 \rightarrow S_2$  electronic transition shows significant intensity. This transition occurs primarily from the HOMO-1 to the LUMO (Figure S5), so the reason that these compounds absorb at higher energy is because the absorption is to the second excited state, a higher energy transition [32]. This HOMO-1 to LUMO excitation is also present in tipB-ter0 and corresponds to the  $S_0 \rightarrow S_3$  transition. In conclusion, while the higher HOMO-LUMO gap is seemingly inconsistent with the longer wavelength



Fig. 2. HOMO, LUMO and LUMO+1 of tipB-ter model compounds. Generated with Gaussview (scaling radii 75%, isovalue 0.02).

absorption of tipB-ter0, the TD-SCF calculations show that for tipB-ter1 and tipB-ter2, the lowest energy transition involves HOMO-1 to LUMO (not HOMO to LUMO) excitation. The calculations predict a  $\lambda_{max}$  at 458 nm (Figure S6). In comparison, for the experimental UV–Vis results, the  $\lambda_{max}$  is at 400 nm, and this consistent difference could be due to intermolecular charge transfer phenomena not captured by modeling individual molecules in the gas phase or to inherent problems associated in modeling charge transfer processes using TDDFT methods.

## 3.4. Cyclic voltammetry and transient absorption measurements of the model compounds

The experimental HOMO–LUMO gaps were determined using oxidation and reduction curves that were obtained from cyclic voltammetry measurements (Table 2), and match the values from calculations quite well. The gaps are similar to those found by Li et al., where in polythiophene with side group borylation the optical gap was lowered from 2.70 with silicon groups to 2.36 with boron groups [68].

In order to better understand the complex exciton dissociation processes at the donor-acceptor interface that affect photovoltaic performance, the photophysical and electronic properties of these materials needed to be further studied. Transient absorption measurements were performed on the three linker compounds (Fig. 3), as well as on the constituent parts: terthiophene and the organoborane polymer. The transient data show complex spectral evolution over time due to the competing interconversion between excited singlet and triplet states, and charge transfer and recombination. A complete analysis of the transient data is beyond the scope of this paper but a qualitative examination clearly supports the idea that photoinduced charge transfer occurs in some of the copolymer model compounds. As reported by Paa et al. [69], the transient absorption measurements of terthiophene excited at 350 nm exhibited strong singlet excited state absorption at 600 nm, which evolved into triplet state absorption at 470 nm with a time constant of ca. 175 ps. However, in analogous measurements of the compounds having either direct linkage or a onecarbon non-conjugated spacer (tipB-ter0 and tipB-ter1, respectively), neither the singlet nor the triplet state absorption signatures were detected. The terthiophene singlet and triplet peaks were observed in tipB-ter2, which has the longer, two-carbon bridge. These results are consistent with charge transfer occurring in the direct and one-carbon linked compounds and not in the two-carbon bridged compound (Fig. 3). These data are in agreement with a theoretical study of electron transport through a conjugated-saturated hydrocarbon molecular wire showing that the rectification performance was correlated to the length of the saturated barrier [70].

The transient absorption spectrum of the all-conjugated tipBter0 showed a new peak centered at  $\sim$  540 nm, which may be a signature of a state resulting from charge transfer. This possibility will require further study through spectroelectrochemical and other measurements for firm assignment [18].

#### Table 2

HOMO–LUMO gaps of model compounds calculated from cyclic voltammetry measurements and compared to the calculated  $E_{HOMO-LUMO}$ . All energies are given in electron Volts (eV).

	Е <sub>НОМО</sub>	E <sub>LUMO</sub>	E <sub>HOMO-LUMO</sub> (experimental) <sup>a</sup>	Е <sub>НОМО-LUMO</sub> (calculated)
TipB-ter0	-5.4	-3.0	2.4	2.47
TipB-ter1	-5.2	3.0	2.2	2.29
TipB-ter2	-5.2	-3.1	2.1	2.29

<sup>a</sup> Calculated from cyclic voltammetry measurements.



**Fig. 3.** Transient absorption spectroscopy data. a) TipB-ter2 and terthiophene spectra both exhibit peaks for the singlet (at 2 ps) and triplet (at 2 ns) excited state, demonstrating the electronic isolation in the former. b) Spectra for TipB-ter1 are similar to those for tipBPh and exhibit no evidence for terthiophene triplet character. c) Transient absorption measurements taken at excitation 350 nm show a new peak forming in tipB-ter0 that might be a charge transfer state.

Transient absorption measurements of the organoborane homopolymer (tipBPh) showed slow decay for the first excited state (exciton) of the polymer, which is desirable, because a long-lived excited state provides more time for charge separation to occur. The fluorescence lifetime of this tripylorganoborane polymer was measured to be  $\Gamma = 0.39$  ns + 0.85 ns,  $\chi^2 = 0.964$  (THF 1 mg/mL, Figure S7).



Fig. 4. UV-Vis (left) and fluorescence (excitation at 350) of the copolymer P3HT-tipBPh in THF.

#### 3.5. Synthesis and studies of the P3HT-tipBPh diblock copolymer

Attempts were then made to synthesize the all-conjugated diblock copolymer related to tipB-ter0, which was of interest because of the charge transfer band it exhibited (Scheme 3). P3HT was synthesized and endcapped with ethyne [44], and was subsequently characterized using GPC, NMR and MALDI-TOF MS. This compound was then dissolved in THF, and tripylborane was added to react with the alkyne groups. This was followed by a large excess of diethynylbenzene and tripylborane (1M in THF) added at the same rate over a 2-h period. The mixture was stirred overnight and precipitated with methanol. The filtered copolymer was dissolved in toluene and run through a silica gel column, and the red fraction containing the copolymer was collected. UV-Vis measurements showed the same band of absorbance at 470 nm that was found in tipB-ter0, (Fig. 4) indicating the presence of the diblock copolymer. The homopolymers P3HT and tipBPh absorb at 450 nm and 375-425 nm, respectively, so the absorbance at 470 nm in the P3HTtipBPh mixture must be indicative of the presence of the diblock copolymer. As was discussed with tipB-ter0, the additional band of absorption is the result of extended conjugation resulting from the direct connection of the terthiophene to the organoborane polymer, possibly indicating charge transfer at the p-n junction.



**Fig. 6.** NMR of P3HT-tipBPh copolymer (lower), tipBPh (middle) and P3HT (top) with integration of two peaks (1.0:1.2), each representing 2 protons in tipBPh and P3HT.

Oxidation and reduction peaks were obtained from cyclic voltammetry measurements (Fig. 5), and the HOMO and LUMO were calculated ( $E_{\text{HOMO}} = -5.1 \text{ eV}$ ;  $E_{\text{LUMO}} = -3.0 \text{ eV}$ ; HOMO–LUMO gap = 2.1 eV). The very small wave near 0.6 V is P3HT, showing a trace amount of P3HT impurity. The starting MW of the P3HT was 3900 by MALDI-MS. GPC of P3HT was 9360  $M_{\rm n}/14,000 M_{\rm w}$  (1.5) and of the copolymer was 13,809  $M_{\rm n}/44,905 M_{\rm w}$  (3.2) (Fig S8). Due to difficulties in obtaining MALDI mass spectra, representative spectra of the copolymer were not obtained. The NMR is shown in Fig. 6 and two isolated peaks ( $\delta$  2.47 tripyl, 2H, CH and 1.70 hexyl, 2H, CH<sub>2</sub>) were integrated to give a ratio of 1:1.2. The aryl region (7.2-7.4 ppm) demonstrates the presence of the organoborane polymer, but some of these resonances could be due to homopolymer. The MS weight of 3900 for P3HT represents 23 thiophene monomers and this was used with the ratio from the NMR to give another MW estimate of ~10,000 for the diblock copolymer (18 monomers (344 g/monomer) of the borane). From the UV data (peak at 470 nm), the presence of the diblock copolymer in this hybrid mixture was confirmed, but the presence of small amounts of triblock copolymer or the possibility of organoborane homopolymer and P3HT fragments cannot be excluded.

In order to further evaluate the optoelectronic properties of these novel materials, the diblock copolymer hybrid mixture was fabricated as the active layer in solar cells via spin casting from a 30 mg/mL solution in dichlorobenzene (DCB). As has been observed with organoborane acceptor OPV systems previously [71], the open



Fig. 5. Cyclic voltammograms of P3HT-tipBPh;  $CH_2CI_2/0.1M$  Bu<sub>4</sub>N[PF<sub>6</sub>], 100 mV s<sup>-1</sup>; reported relative to the Fc/Fc+ couple.

circuit voltage was quite high (1.1 V), but the short circuit current was low. The blend solar cells were also fabricated and the results for six cells each of the diblock copolymer mixture and the blend are given in Table S1, Table S2. J-V curves are given in Figure S9. The results from these preliminary studies gave power conversion efficiencies (PCE) of 0.053  $\pm$  0.007 for the diblock copolymer and  $0.0031 \pm 0.0009$  for the blend. The very low current, which was not seen in Cataldo's measurements, may be due to degradation of the polymer during the fabrication process. Lower than expected currents can also be attributed to severe photon loss due to a poor intrinsic energy gap of the materials as well as other causes [72]. Although no device optimization was performed at this time, the initial performance was relatively higher than that of the related blend bulk heterojunction cells, suggesting the forced proximity of donor and acceptor species improves device properties. The fill factor was  $\sim 23\%$  for the copolymer and  $\sim 28\%$  for the blend, which could be increased by changing the aryl group in the organoborane polymer; the extended absorption of the aryl group is reflected in the extended absorption of the polymer and could be selected to fit more closely with the solar spectrum [40]. Although the performance of these cells are far below that of good bulk heterojunction systems, their study may provide pertinent contributory knowledge in this field that can be applied to higher performance material systems [10].

#### 4. Conclusion

Starting with terthiophene, we have developed syntheses for three copolymer model compounds that could continue to be used for fundamental studies of the linking chemistry between donor and acceptor polymer blocks. Preliminary results from both computational and experimental studies show that charge transfer may be occurring in the all-conjugated copolymer and copolymer model compound, with electronic coupling—and hence the likelihood of charge transfer—decreasing with increasing length of the linking bridge. Unoptimized solar cell fabrication using the block copolymer hybrid mixture gave PCEs that were substantially higher than those for the related blend. Ongoing studies include extending these measurements to the solid state, and comparing transient absorption measurements of model compounds with the blend.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.05.008.

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