

### Article

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# Benzo[d][1,2,3]thiadiazole (isoBT). Synthesis, Structural Analysis, and Implementation in New Semiconducting Polymers

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Supporting Information Placeholder

**ABSTRACT:** Benzo[d][2,1,3]thiadiazole (BT) is a markedly electron-deficient heterocycle widely employed in the realization of organic semiconductors for applications spanning transistors, solar cells, photodetectors, and thermoelectrics. In this contribution we implement the corresponding isomer, benzo[d][1,2,3]thiadiazole (isoBT), along with new 6-fluoro-isoBT and 5,6-difluoro-isoBT units as synthons for constructing alternating co-polymers with tetrathiophene (**P1-P3**). New isoBT-based small molecules as well as the corresponding BT-quaterthiophene based polymers (**P4-P6**) are synthesized and characterized to probe architectural, electronic structural, and device performance differences between the two families. The results demonstrate that isoBT complements BT in enabling high-performance opto-electronic semiconductors with **P3** exhibiting hole mobilities surpassing 0.7 cm<sup>2</sup>/Vs in field-effect transistors and power conversion efficiencies of 9% in bulk-heterojunction solar cells.

### INTRODUCTION

 $\pi$ -Conjugated molecules and polymers comprising electron-accepting (A) and electron-donating (D) units in the core or main chain are among the most performing semiconductor families spanning applications from electronic circuits and sensors based on organic thin-film transistors (OTFTs),<sup>1-11</sup> photovoltaic cells such as the bulk-heterojunction (BHJ-OSC)<sup>12-26</sup> and dye-sensitized (DSSC) devices, 27-32 photodetectors,<sup>33-37</sup> and thermoelectrics.<sup>38-40</sup> Among the electron accepting functionalities, benzo[d][2,1,3]thiadiazole (BT) and its halogenated derivatives, have realized several D-A polymers with remarkable performance (Figure 1).41-53 For instance, BT-based small-molecules and polymers have shown maximum OTFT hole mobilities of 0.20 and 1.92 cm<sup>2</sup>/Vs,<sup>41,51</sup> respectively, as well as BHJ-OSC and DSSC with power conversion efficiencies as large as 11.7 and 7.1 %, respectively.<sup>42,53</sup> Photodetectors with detectivity of ~10<sup>12</sup> Jones<sup>54-55</sup> and thermoelectric devices with a Seebeck coefficient (Z) of  $230 \mu$ V/K have also been demonstrated.<sup>56-57</sup>



**Figure 1.** Chemical structure of representative BT-based small molecules and polymers used in organic electronics.

The commercial availability of BT, synthetic access to the halogenated precursors, and facile bromination at the 4,7 BT positions have greatly facilitated the availability of this core. Furthermore, the electron-poor nature of BT, further tunable via substitution/halogenation at the 5,6 positions, has been instrumental in controlling the frontier molecular orbitals (FMOs) of the resulting systems.<sup>17,58-59</sup> Finally, the low steric demands at the BT 4,7 *para*-positions promotes structural planarization and enhances intramolecular charge transfer and the extent of  $\pi$ conjugation in BT-based (macro)molecules.<sup>17</sup> Recent important studies have also addressed why BT (or F<sub>o</sub>BT, see Figure 2), and its mono- and di-fluoro (F<sub>1</sub>BT and F<sub>2</sub>BT) based polymers are highly crystalline and the origin of the intermolecular interactions that promote film texturing.<sup>42,44,60-65</sup>



**Figure 2.** Chemical structures of BT and isoBT units and polymers investigated in this study.

The BT isomer, benzo[1,2,3]thiadiazole (isoBT), is a known heterocycle which finds applications in several science.66-69 fields of chemical All of the abovementioned properties of BT combined with the greater steric demands of S vs. N at the benzothiadiazole 1 position rise interesting questions of whether isoBT is a suitable building block for organic electronics, whether halogen-functionalized derivatives can be synthesized and integrated into semiconducting materials, the nature of the electronic structure, molecular structure, physico-chemical properties, and device performance differences in BTversus isoBT-based molecules and the corresponding (macro)molecules.

Here we report the synthesis of the new 5-fluorobenzo[1,2,3]thiadiazole ( $F_1$ isoBT) and 5,6-difluorobenzo[1,2,3]thiadiazole ( $F_2$ isoBT) structures and their use, in conjunction with isoBT (or  $F_0$ isoBT), in synthesizing the alternating quaterthiophene-based co-polymers **P1-P3** (Figure 2). Structural analysis is carried out for isoBT molecules, rapresentative iso-BT building blocks [ $F_x$ isoBT-T2], and polymers, as well as the corresponding BT molecular [FxBT-T2] and polymeric systems (**P4-P6**), using single crystal and thin-film XRD techniques, respectively. Finally, all polymers are incorporated into OTFT and BHJ-OSC devices and the device performance compared and contrasted.

### EXPERIMENTAL SECTION

#### Synthesis

Materials and general characterization methods, synthesis of  $F_x$ -isoBT-T2, and synthesis of polymer **P4-P6** and their corresponding monomers are reported in the Supporting Information (SI).

#### Synthesis of Polymer P1

#### Synthesis of Compound 2:

Compound benzo[1,2,3]thiadiazole (1, 193 mg, 1.4 mmol) was dissolved in concentrated sulfuric acid (95-98%, 20 mL) and *N*-bromosuccinimide (NBS) (556 mg, 3.1 mmol) was then added in one portion. The resulting solution was heated to 50 °C and maintained at this temperature overnight. Upon cooling to rt, the reaction mixture was poured onto ice water (about 100 mL). This mixture was extracted with chloroform (100 mL), and the organic layer was washed with additional water (3 x 100 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo, leading to a beige solid as the product (2, 370 mg, 89.8%). 'H NMR (CDCl<sub>3</sub>, 400 MHz): 7.69-7.71 (d, *J* = 8.0 Hz, 1H), 7.65-7.67 (d, *J* = 8.0 Hz, 1H). Elemental Analysis: (Calcd: C: 24.52, H: 0.69, N: 9.53); Found: C: 23.47, H: 0.75, N: 8.55

### Synthesis of Compound 3:

Under Ar, compound **3S** (1.61 g, 1.6 mmol) was mixed with anhydrous tetrahydrofuran (THF) (70 mL), and the resulting solution was cooled by an isopropyl alcohol (IPA)/dry ice batch. A solution of n-BuLi (2.5 M in hexane, 1.3 mL, 3.3 mmol) was then added slowly over a course of about 5 mins. The reaction mixture was allowed to be stirred at this temperature for 1 h, before the cooling bath was removed and the reaction was allowed to warm to rt. After stirring for 1.5 h, the reaction mixture was cooled by IPA/dry ice bath again. A solution of Me<sub>2</sub>SnCl solution (1 M, 3.5 mL, 3.5 mmol) was then added in one portion. The reaction was stirred at this temperature for additional 30 mins, before the cooling bath was removed and the reaction was stirred at rt overnight. Most of the solvent was removed in vacuo, and the residue was treated with pentane (about 15 mL). This solution was filtered through a 0.45 µm PTFE syringe filter, and the filtrate was concentrated in vacuo, dried in vacuum, leading to a slightly orange oil, which solidified after cooling at refrigerator (1.86 g, 87.3%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): 7.12 (d, J = 3.6 Hz, 2H), 7.01 (d, J = 3.6 Hz, 2H), 6.99 (s, 2H), 2.74 (d, J = 7.2 Hz, 4H), 1.72 (s, br, 2H), 1.16-1.34 (m, br, 80H), 0.84-0.91 (m, br, 12H), 0.38 (s, 18H).

#### Synthesis of Polymer P1:

Compounds 2 (34.3 mg, 0.12 mmol) and tin reagent 3 (155.6 mg, 0.12 mmol) were added to a Schlenk flask with tris(dibenzylideneacetone) dipalladium(o) ( $Pd_2dba_3$ ) (2.2 mg, 0.0024 mmol) and tri(o-tolyl)phosphine (tol\_3P) (5.7 mg, 0.018 mmol). The flask was subject to vacuum and then backfilled with Ar, and this cycle was repeated four times. Under Ar, anhydrous toluene (15 mL) was added, and the resulting mixture was heated to 90 °C and maintained at this temperature for about 20 h. Bromobenzene (0.5 mL) was added to the reaction mixture and it was maintained at 90 °C for an additional 4 h. Upon cooling to rt, the reaction mixture was precipitated in methanol (about 200 mL), and the precipitate was collected by filtration and washed with methanol. This crude product was

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59 60 then subject to Soxhlet extraction with methanol (21 h), ethyl acetate (20 h), and finally extracted with chloroform. Upon cooling to rt, the chloroform extract was concentrated to about 5 mL, which was precipitated in methanol (about 100 mL). The precipitate was collected by filtration, washed with methanol, and dried in vacuum, leading to a dark red/brown solid as the polymer product **P1** (87.8 mg, 66.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>2</sub>CDCl<sub>2</sub>, 100 °C): 8.13 (m, br, 1H), 7.90-7.97 (m, br, 2H), 7.39 (s, br, 1H), 7.22-7.40 (m, br, 4H), 2.91 (m, br, 4H), 1.91 (m, br, 2H), 1.28-1.51 (m, br, 80H), 0.93 (m, br, 12H). GPC: Mn = 14.1K, PDI = 1.9. Elemental Analysis: (Calcd: C: 74.02, H: 9.41, N: 2.47); Found: C: 74.01, H: 9.01, N: 2.51.

### Synthesis of Polymer P<sub>2</sub>

### Synthesis of Compound 5:

To a mixture of compound 4 (875 mg, 5.98 mmol) in water (6 mL) was added 12M HCl (1.5 mL) slowly at rt. Sodium nitrite (620 mg, 8.98 mmol) was then added slowly at rt. THF (3 mL) was added to aid solubility and the reaction was stirred at rt overnight. To the above solution was added potassium carbonate aqueous solution (10%, ~7 mL) until the pH was ~9. The material was extracted with dichloromethane (DCM) and washed with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to a tan powder (720 mg, 78%). <sup>1</sup>H NMR, (400 MHz, CDCl<sub>3</sub>): 7.41 (m, br, 1H), 7.78 (dd, *J* = 7.6 Hz, *J* = 2.4 Hz, 1H), 8.61 (dd, *J* = 9.2 Hz, *J* = 4.4 Hz, 1H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -109.2 (m, 1F).

### Synthesis of Compound 6:

Compound 5 (600 mg, 3.9 mmol) was dissolved in oleum (60 mL). NBS (1.5 g, 8.6 mmol) was added in one portion and the reaction mixture was heated to 60 °C overnight. The solution was then cooled to rt and poured over 500 mL ice water. The product was extracted with DCM and washed with  $H_2O$  until the  $H_2O$  layer was neutral. The organic layer was dried over  $Na_2SO_4$ , filtered, and concentrated to yield a tan powder as the compound 3 (950 mg, 80%), which was directly used for next step without further purification. 'H NMR, (400 MHz, CDCl<sub>3</sub>): 7.67 (d, *J* = 8Hz, 1H). Elemental Analysis: (Calcd: C: 23.10, H: 0.32, N: 8.98); Found: C: 22.79, H: 0.34, N: 8.59

### Synthesis of Compound 8:

Compound **6** (600 mg, 1.92 mmol), 4-(2-decyltetradecyl)-2-trimethylstannyl thiophene (7) (2.47 g, 4.23 mmol), Pd<sub>2</sub>dba<sub>3</sub> (70 mg, 0.08 mmol), and tri(2-furyl)phosphine (70 mg, 0.31 mmol) were added to an air free flask which was then purged and backfilled 4 cycles with vacuum/Ar. Under Ar, anhydrous THF (50 mL) was added via syringe and the solution was stirred at 80 °C for 16 h. Upon cooling to rt, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexanes), yielding a yellow solid as compound **8** (650 mg, 34%). <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): 7.99 (s, 1H), 7.73 (d, *J* = 12 Hz), 7.43 (s, 1H), 7.16 (d, *J* = 11.6 Hz, 2H), 2.64 (d, J=6.4 Hz, 4H), 1.69 (m, br, 2H), 1.25 (m, br, 8oH), o.88 (t, J=6.8 Hz, 12H).

### Synthesis of Compound 9:

Compound **8** (400 mg, 0.40 mmol) was dissolved in a mixture of THF (10 mL) and acetic acid (1 mL) under nitrogen at rt. NBS (160 mg, 0.89 mmol) was added in one portion. The resulting mixture was stirred overnight and the product was precipitated with methanol/water (1:1, 20 mL). The precipitate was washed with methanol and this crude product was recrystallized from ethyl acetate (about 5 mL) in the fridge, yielding a yellow solid as the product (430 mg, 86%). 'H NMR (400 MHz, CDCl<sub>3</sub>): 7.82 (1H, s), 7.63 (d, *J* = 12 Hz, 1H), 7.25 (d, *J* = 8 Hz, 1H), 2.57 (d, *J* = 8.8 Hz. 4H), 1.74 (m, br, 2H), 1.24-1.40 (m, br, 80H), 0.87 (t, *J* = 6.8 Hz. 12H). Elemental Analysis: (Calcd: C: 64.78, H: 8.86, N: 2.44); Found: C: 64.35, H: 9.04, N: 2.48.

### Synthesis of Polymer P2:

Compound 9 (100.0 mg, 0.079 mmol), 5,5'bis(trimethylstannyl)-2,2'-bithiophene (10) (39.4 mg. 0.079 mmol), Pd2dba3 (3.0 mg, 0.003 mmol), tol3P (3.1 mg, o.o1 mmol) were placed in a Schlenk flask. The system was vacuumed and backfilled with argon four times, before anhydrous chlorobenzene (10 mL) was added via syringe. The resulting mixture was warmed and stirred at 90 °C for 18 h. The reaction was cooled to rt and precipitated in methanol (50 mL). The crude product was collected by filtration, washed with methanol, and subject to Soxhlet extraction under nitrogen with methanol (16 h), ethyl acetate (16 h), and hexanes (16 h). The polymer product was extracted into chlorobenzene (100 mL), and the extract was precipitated in methanol (100 mL). The precipitate was collected by filtration, washed with methanol, and dried under vacuum to afford a brown solid as the final product P2 (75.3 mg, 82.7%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>2</sub>CDCl<sub>2</sub>, 100 °C): 8.12 (s, br, 1H), 7.76-7.79 (m, br, 1H), 7.52 (s, br, 1H), 7.23-7.32 (m, br, 4H), 2.92 (m, br, 4H), 1.91 (m, br, 2H), 1.28-1.52 (m, br, 80H), 0.94 (m, br, 12H). GPC: Mn = 25.7 K, PDI = 1.4. Elemental Analysis: (Calcd: C: 73.04, H: 9.45, N: 2.37); Found: C: 72.40, H: 9.48, N: 2.43.

### Synthesis of Polymer P<sub>3</sub>

### Synthesis of Compound 12:

A solution of 2,4,5-trifluoroaniline (11) (25 g, 170 mmol) in anhydrous pyridine (14.4 mL, 178 mmol) was treated with acetic anhydride (16.9 mL, 178 mmol) and heated to 120 °C for 2 hours. After cooling to room temperature, the solution was poured into ice-cold water (150 mL). The resulting precipitate was filtered, dissolved in ethyl acetate, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The residue was dried to give 2,4,5-trifluoroacetanilide (12) (29.63 g, 92%) as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): 8.35-8.26 (m, 1H), 7.24 (s, br, 1H), 7.01-6.93 (m, 1 H), 2.22 (s, 3H); <sup>19</sup>F NMR (CDCl<sub>3</sub>): -133.5 (m, 1F), -139.6 – -139.7 (m, 1F), -140.1 – -140.3 (m, 1F). Synthesis of Compound 13:

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A dried 3-neck, 1L round-bottom flask was charged with phosphorus pentasulfide  $(P_2S_5)$  (34.08 g, 153 mmol) and diluted with anhydrous toluene (500 mL). Compound 2,4,5-trifluoroacetanilide (12) (29 g, 153 mmol) was added in one portion and the bright yellow suspension was heated to 90 °C for 15 hours. After cooling to room temperature, the reaction was washed with aqueous NaOH (15%, 250 mL). The aqueous phase was extracted with ethyl acetate (200 mL). The organic phases were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude product was passed through a silica gel column prepared with chloroform and concentrated to give 2,4,5-trifluorothioacetanilide (13) (23.23 g, 74%) as a vellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.69-8.62 (m, 1H), 8.47 (s, 1H), 7.08-7.01 (m, 1H), 2.76 (s, 3H). <sup>19</sup>F NMR (CDCl3): -128.5 (m, 1F), -134.3 - -134.5 (m, 1F), -139.4 - -139.5 (m, 1F).

### Synthesis of Compound 14:

A flame-dried, 1 L round-bottom flask with a condenser was charged with sodium hydride (5.15 g, 129 mmol, 60% by wt) and diluted with anhydrous toluene (500 mL). The suspension was treated with 2,4,5-trifluorothioacetanilide (13) (22 g, 107 mmol) in one portion and stirred at room temperature for 2 hours. Dimethylformamide (100 mL) was added and the reaction was refluxed at 110 °C for 3 hours. The solution was cooled to room temperature and washed with brine (500 mL). The aqueous phase was extracted with ethyl acetate (300 mL). The organic phases were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude product was passed through a silica gel column prepared with chloroform and concentrated to give 5,6-difluoro-2-methylbenzothiazole (14) (16.54 g, 83%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.73 (dd, *J* = 7.08 Hz, *J* = 10.48 Hz, 1H), 7.59 (dd, *J* = 7.52 Hz, J = 8.96 Hz, 1H), 2.83 (s, 3H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -138.4 - -138.5 (m, 1F), -139.4 - -139.5 (m, 1F).

### Synthesis of Compound 16:

A solution of 5, 6-difluoro-2-methylbenzothiazole (14) (10 g, 54 mmol) and hydrazine monohydrate (40 mL, 820 mmol) was stirred for 2 days at 115 °C. The reaction was cooled to room temperature, neutralized to pH = -7 with concentrated HCl solution, and extracted with dichloromethane (4 x 250 mL). The organic phases were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The yellow oil crystallized overnight to give 4,5-difluoro-2-aminothiophenol (15) (7.52 g), which was mixed with water (100 mL). A solution of 12M HCl (26 mL) was added slowly at room temperature, followed by addition of sodium nitrite (4.82 g, 70 mmol). THF (50 mL) was added to facilitate the dissolution of solids and the reaction was stirred at room temperature overnight. The reaction mixture was neutralized with saturated aqueous K<sub>2</sub>CO<sub>3</sub> (200 mL) and extracted with DCM (2 x 300 mL). The organic phases were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and

concentrated to give the product (**16**) (6.59 g, 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.40 (dd, J = 6.92 Hz, J = 9.12 Hz, 1H), 7.88 (dd, J = 7.16 Hz, J = 8.08 Hz, 1H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -129.6 - -129.7 (m, 1F), -134.1 - -134.2 (m, 1F).

### Synthesis of Compound 17:

Compound **16** (550 mg, 3.2 mmol) was dissolved in oleum (40 mL). NBS (1.2 g, 7.0 mmol) was added in one portion and the reaction mixture was heated to 50 °C overnight. The solution was then cooled to rt and poured over ice water (200 mL). Precipitation observed and suspension was filtered. The brown precipitate was then dissolved in DCM and flushed through a short pad of silica gel. The solvent was evaporated and the product was dried to a light tan powder as the product (**17**) (0.38 g, 36%), which was directly used for next step without further purifications. <sup>19</sup>F NMR (CDCl<sub>3</sub>): -120.7 (d, *J* = 17.6 Hz, 1F), -124.1 (d, *J* = 21.5 Hz, 1F).

### Synthesis of Compound 18:

Compound 17 (370 mg, 1.12 mmol), tin reagent 7 (1.43 mg, 2.45 mmol), Pd2dba3 (41 mg, 0.04 mmol), and tri(2furyl)phosphine (41 mg, 0.18 mmol) were added to an air free flask which was then purged and backfilled with vacuum/Ar 4 times. Under Ar, anhydrous THF (40 mL) was added via syringe and the solution was stirred at 85 °C for 16 h. Upon cooling to rt, the reaction mixture was flushed through a pad of silica gel with the aid of DCM and then concentrated in vacuo. The concentrated solid was then recrystallized in 10 mL heptane in the freezer, leading to a yellow solid as the product (18) (407.6 mg, 36%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): 8.15 (s, 1H), 7.48 (d, J = 6 Hz, 1H), 7.28 (s, 1H), 7.20 (s, 1H), 2.67 (dd, J = 10.4 Hz, J = 6.8 Hz, 2H), 1.71 (m, br, 2H), 1.32 (m, br, 2H), 1.26 (m, br, 80H), 0.87 (t, J = 6.0 Hz, 12H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): -131.9 (d, J = 17.3 Hz, 1F), -134.3 (d, *J* = 17.3 Hz, 1F).

### Synthesis of Compound 19:

Compound **18** (400 mg, 0.40 mmol) was dissolved in a mixture of THF (10 mL) and acetic acid (1 mL) at rt. NBS (155 mg, 0.87 mmol) was added in one portion. The resulting mixture was stirred overnight and the product was extracted with DCM and washed with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was then subjected to a short silica gel column with hexane as eluent to yield a yellow solid as the product (**19**) (0.32 g, 70%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): 8.03 (s, 1H,). 7.33 (s, 1H), 2.62 (dd, *J* = 8.8 Hz, *J* = 7.2 Hz, 4H), 1.26 (m, br, 82H), 0.87 (t, *J* = 6.0 Hz, 12H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): -131.4 (d, *J* = 16.9 Hz, 1F), -133.9 (d, *J* = 9.4 Hz, 1F). Elemental Analysis: (Calcd: C: 63.79, H: 8.63, N: 2.40); Found: C: 63.74, H: 8.64, N: 2.40.

### Synthesis of Polymer P3:

Compound 19 (150 mg, 0.13 mmol), compound 10 (63.2 mg, 0.13 mmol),  $Pd_2dba_3$  (4.6 mg, 0.005 mmol),  $tol_3P$  (6.2 mg, 0.02 mmol) were placed in a Schlenk flask. The sys-

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tem was vacuumed and backfilled with argon four times, before anhydrous chlorobenzene (12 mL) was added via syringe. The resulting mixture was warmed and stirred at 90 °C for 18 h. The reaction was cooled to rt and precipitated in methanol (100 mL). The crude product was collected by filtration, washed with methanol, and subject to Soxhlet extraction under nitrogen with methanol (10 h), ethyl acetate (13 h), and hexanes (9 h). Finally, the polymer product was extracted into chloroform (120 mL), and the extract was precipitated in methanol (200 mL). The precipitate was collected by filtration, washed with methanol, and dried under vacuum to afford a dark-blue solid as the final product P3 (135 mg, 88.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>2</sub>CDCl<sub>2</sub>, 100 °C): 8.26 (s, br, 1H), 7.56 (s, br, 1H), 7.23-7.34 (m, br, 4H), 2.93 (m, br, 4H), 1.90 (m, br, 2H), 1.28-1.51 (m, br, 80H), 0.93 (m, br, 12H). GPC: Mn = 23.6 K, PDI: 1.5. Elemental Analysis: (Calcd: C: 71.95, H: 9.22, N: 2.33); Found: C: 71.87, H: 9.34, N: 2.40.

### OTFT Device Fabrication

Top-qate Bottom Contact TFTs with Unpatterend Semiconductor/Gate Layers: Top-gate bottom contact TFTs were fabricated using P1-P6 as the semiconductor layer. Eagle 100 glasses (Corning Inc.) were used as device substrates. Prior to the semiconductor deposition, 500 Å gold source and drain electrode were thermally evaporated through a stencil mask to define the transistor channel (W/L =1000/60 µm), followed by a 3,4-difluorothiophenol (Sigma-Aldrich) contact treatment (spin dray of a 5 % solution in anisole). Polymers P1-P6 were dissolved in 1,2dichlorobenzene at a concentration of ~6 mg/ml. The formulations were spin coated on to the substrates at 1000 rpm for 60 sec, and baked at 100 °C on a hotplate for 5 mins in ambient to form the semiconductor films approximately 30-100 nm in thickness. The TFTs were completed by spin-coat a 500-700nm thick CYTOP (809M, AGC) layer as the gate dielectric (Ci = 3.0 nF/cm<sup>2</sup>), followed with thermal evaporation of a 500 Å thick gold gate electrode. All TFTs were tested under dark in a probe station (Signatone) in ambient environment using a Keithley 4200 two source electrometer.

Top-gate Bottom Contact TFTs with Patterned Semiconductor/Gate Layers: Top-gate bottom contact TFTs were fabricated using P3 or P6 as the semiconductor layer. PET substrates coated with a thin layer of a photocurable polymer (Polyera B3000) were used as device substrates. Prior to the semiconductor deposition, a 500 Å silver film was sputtered and the source/drain electrodes were defined with standard photolithography (W/L =  $100/13 \mu$ m), followed by a 3,4-difluorothiophenol (Sigma-Aldrich) contact treatment (spin dray of a 5 % solution in anisole). Polymers P1 and P6 were dissolved in 1,2,3,4tetrahydronaphthalene at a concentration of ~3 mg/ml. The formulations were spin coated on to the substrates at 1000 rpm for 60 sec, and baked at 100 °C on a hotplate for 5 mins in ambient to form semiconductor films approximately 30-50 nm in thickness. Next, D2200 (Polyera Corporation) was spin-coated and photopatterned to define the patterned semiconductor island between source and drain followed by a second D2200 layer. The resulting gate dielectric capacitance was 3.5-4.2 nF/cm<sup>2</sup>. Finally, the device was completed by sputtering/photolithography of a 500 Å Ag gate electrode. All TFTs were tested in the dark in a probe station (Signatone) in ambient environment using Keithley 4200 two source electrometer.

Gravure Printed Top-gate Bottom Contact TFTs: For gravure printing, the P<sub>3</sub> formulation (10 mg/mL in a mixture of 1,2,3,4-tetrahydronaphthalene-based solution) was printed on PEN substrates with Ag source-drain electrodes (W/L = 1000/60 um) using a Norbert Schlafli Labratester gravure printer, at the speed of around 5 m/min and the impact factor of 5. After printing, the substrate was transferred to a hotplate to bake at 110 °C for 5 mins in ambient to form the semiconductor films approximately 50-100 nm in thickness. The TFTs were completed by spin-coat a 500-700 nm thick CYTOP (809M, AGC) layer as the gate dielectric (Ci =  $3.0 \text{ nF/cm}^2$ ), followed with thermal evaporation of a 500 Å thick Ag gate electrode. All TFTs were tested under dark in a probe station (Signatone) in ambient environment using a Keithley 4200 two source electrometer.

#### **BHJ-OSC** Device Fabrication and test procedure

Conventional OSC devices: These devices were fabricated by first spin casting a thin layer of PEDOT (about 35 nm, Clevios PVP AI 4083) onto precleaned ITO substrates. Polymers P1-P6 (6-8 mg/mL) and PC70BM (1:1.5 weight ratio) were dissolved in chlorobenzene. 1-2% (by volume) diiodooctane were added to the solution before spin casting the active layers (film thickness ~ 100-270 nm). Finally, 0.6 nm of LiF and 100 nm of Al were evaporated as the top electrode. Device were encapsulated using a blanket of EPOTEK OG116-31 UV-curable epoxy (Epoxy Technologies) and a cover slip. The active area of the device defined by the mask aperture was 0.096 mm<sup>2</sup>. The photovoltaic characteristics of devices were tested in air. The currentvoltage (I-V) curves were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under simulated AM1.5G irradiation (100 mW cm<sup>-2</sup>) using a xenon-lamp-based solar simulator (Newport 91160A 300W Class-A Solar Simulator, 2 inch by 2 inch uniform beam). The light intensity was set using a NREL calibrated silicon photodiode with a color filter. External quantum efficiency was measured using Newport's QE setup. Incident light from a xenon lamp (300 W) passing through a monochromator (Newport, Cornerstone 260) was focused on the active area of the cell. The output current was measured using a current pre-amplifier (Newport, 70710QE) and a lock-in amplifier (Newport, 70105 Dual channel Merlin). A calibrated silicon diode (Newport 70356) was used as a reference.

*Blade-coated conventional OSC devices:* These devices were fabricated by spin-coating a layer of PEDOT:PSS (about 40

nm, Clevios AI 4083) on a pre-cleaned ITO glass which was dried at 120 °C for 10 min in air. Polymer P3 (14 mg mL<sup>-</sup> <sup>1</sup>) and [70]PCBM (21 mg mL<sup>-1</sup>) were dissolved in 1 mL of chlorobenzene with 2% 1-chloronaphthalene. Then the active ink was blade-coated on top of the PEDOT:PSS layer at 70 °C in ambient under an relative humidity of 50% (both ink and substrate were heated at 70 °C in air), to form a ~265 nm-thick film. Subsequently, a 0.6 nm-thick LiF and a 100-nm-thick Al electrode were deposited by thermal evaporation at a pressure of approximately 10<sup>-6</sup> Torr. The active area of the device defined by the mask aperture was 4 mm<sup>2</sup>. The photovoltaic characteristics of devices were tested in air, after the devices were encapsulated in nitrogen-filled glove box by lamination with a glass slide using a UV-curable epoxy glue before measurement. J-V characteristics of photovoltaic devices were taken using a Keithley 2400 source measurement unit under a simulated AM1.5G spectrum with a solar simulator (SAN-EI XES-40S2-CE), and the 100 mW/cm<sup>2</sup> light intensity was calibrated using a Si-based reference cell with a KG5 color filter (PV Measurements, Inc.).

### **RESULTS AND DISCUSSION**

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#### Molecular Design and Synthetic Strategies

Before synthetic efforts, molecular orbital computations were carried out to compare the structural and electronic properties of the isomeric BTs ( $F_x$ isoBT; x = o-2) and of the 4,6-dithienyl derivatives (F<sub>x</sub>isoBT-T<sub>2</sub>) to those of the known BT units F<sub>x</sub>BT and F<sub>x</sub>BT-T<sub>2</sub>. Details are reported in the Supplementary Information (Table S1). From these computations three important conclusions can be drawn: 1. The FMO energies indicate that the isomeric BT unit is also a strong electron-accepting functionality. 2. All isoBT-based systems have lower HOMO energies by ~ 0.1-0.4 eV, which should enhance BHJ-OSC  $V_{oc}$ 's. 3. The greater steric demands of S vs. N in the 1 position of the thiadiazole ring result in a far larger equilibrium torsional angle in  $F_x$  isoBT-T<sub>2</sub> (~ 30°) vs.  $F_xBT-T_2$  (~ 1-2°). Note that these torsional results are independent on the number of fluorine atoms.

The synthesis of benzo[d][1,2,3]thiadiazole building blocks and of the corresponding polymers is shown in Scheme 1 and some details are collected in the SI. isoBT (1) is commercially available and bromination with NBS in fuming  $H_2SO_4$  affords 4,7-dibromo-isoBT (2, 90%) yield), which is reacted with the bis(trimethystannyl)tetrathiophene 3 under Stille conditions to afford polymer P1 in 66% yield. 6-FluoroisoBT (5) was synthesized in 78% yields by diazotation/annelation of 2-amino-5-fluorothiophenole (4) with NaNO<sub>2</sub>/HCl.<sup>70</sup> Bromination of 5 with NBS in oleum affords 4,7-dibromo-F<sub>1</sub>isoBT (6) in 80% yields. Although 6 could be used to synthesize P2 following the same procedure as for P1, the reaction was not optimal (yield<40%, low M<sub>w</sub>), thus the most efficient route involves first the synthesis of bisthienyl derivative 8 (F<sub>1</sub>BT-T<sub>2</sub>), which was brominated in excellent yields



**Scheme 1.** Synthesis of isoBT building blocks and polymers **P1-P3**.

(86%) to 9 and then reacted with bis(trimethylstannyl)dithiophene (10) to produce polymer P2 in 83% yield. Finally, attempts to synthesize 5,6- difluorobenzo[d][1,2,3]-thiadiazole (16) by isolating 2-amino-4,5-difluorothiophenole (see SI) failed. Thus, the most efficient route begins by acylating 2,4,5-trifluoroaniline (11) with  $Ac_2O$  in pyridine to afford 12, which was then reacted with  $P_2S_5$  to yield thioacetanilide 13 in 74% compound affords 5,6-difluoro-2yields. This methylbenzothiazole (14) in 83% yields by subsequent deprotonation with NaH followed by intra-molecular nuclephilic substitution.<sup>71</sup> Next, the thiazole moiety of 14 was ring-opened by hydrolysis with hydrazinehydrate to afford 15,72 which was directly reacted with  $NaNO_2$  under acidic conditions to provide 16 (82%). Bromination of highly electron-deficient F2isoBT to compound 17 was accomplished with NBS/oleum at 50 °C,<sup>73</sup> and 17 was then converted to the dithienyl derivative 18, the latter brominated to 19, and 19 reacted with **10** to produce polymer **P3** in excellent yield (89%). The success of this polymerization reaction was verified by the synthesis of three polymer P3 batches with comparable  $M_n$  and PDI values (see details in the SI). Note that polymers P1-P3 are regioirregular due to the symmetry breaking of the isoBT building blocks. To compare the properties of the new isoBT polymers P1-P3 vis-à-vis the BT analogues, the new BT-based polymers P4 and P5 as well as the known polymer P6 were

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### **Chemistry of Materials**

also synthesized (see SI). All intermediates, key building blocks, and polymers were characterized by conventional chemical/physical methods.



**Figure 3.** Crystal structure and packing diagram of isoBT (a), BT (b), several 4,7-dithyenyl isoBTs (c-f) and -BT (g-h) derivatives. For unit cell, *a* axis (red), *b* axis (green), *c* axis (blue).

#### **Crystal Structure Determination**

Figure 3 shows the crystal structures of the isoBT/BT cores and of several thienyl-substituted derivatives, along with relevant intra/intermolecular distances (black and red), angles (blue), and torsions (green). From Figures 3a/b the greater skeletal asymmetry of isoBT vs. BT arises from the different atomic connectivity. Benzofusion at the thiophene-*b*-bond in isoBT vs. the thiophene-*c*-bond in BT results in a larger distortion of the pentatomic ring (larger variations in angles and distances) whereas, in contrast, the benzene

fragment exhibits a reduced bond length alternation signature of an enhanced aromatic character. When comparing the crystal structures of the new thienylsubstituted isoBT derivatives (Figure 3c-f) to the known BT-based ones (Figure 3g-h), similarities and differences appear. Thus, by analyzing  $F_0$  isoBT-T2 (Figure 3c) and  $F_2$  isoBT-T2 (Figure 3e), both units are essentially planar featuring maximum torsions of 5.2 and 3.8°, respectively, which are even smaller than the maximum torsional values observed in the corresponding  $F_0$ BT-T2 (4.3°, Figure 3g) and  $F_2$ BT-T2 (11.3°, Figure 3h).<sup>74</sup> Therefore, the more severely twisted core observed in F<sub>1</sub>isoBT-T<sub>2</sub> (12-17°, Figure 2d) is not the result of larger steric requirements of the isoBT ring and/or the presence of the F atom, but likely due to structural relaxation minimizing packing energy. Furthermore, the exocyclic C-C distances within the isoBT series (1.45-1.47 Å) are similar to those measured for the BT (1.42-1.47 Å), suggesting comparable ones πconjugation. Finally, all units pack in columnar structures where, within each column, the molecules are arranged into a slipped co-facial fashion with an interplanar distance of 3.4-3.6 Å. From this structural analysis it is clear that isoBT can produce planar, highlyconjugated units capable of strong intermolecular interactions.

#### **Polymer Characterization**

Before electrical measurements, the isoBT (P1-P3) and BT (P4-P6) based polymers were characterized and relevant data are collected in Table 1. Molecular masses of the polymers were obtained by GPC at 150 °C with 1,2,4trichlorobenzene as eluent. The M<sub>n</sub>s of P2, P3, and P5 are similar (24-26 KDa; PDI 1.4-1.8) whereas those of P1 and P4/P6 are slightly lower (14 KDa) and larger (29/31 KDa), respectively. Optical absorption and cyclic voltammetry (CV) measurements were carried out on thin films deposited on glass, with the latter using a Pt disk working electrode (see SI). The UV-Vis spectra of Figure 4a indicate that the absorption profiles of the nonfluorinated polymers of both polymer families (P1 and P4) are considerably broader and blue-shifted versus the corresponding mono- (P2 and P5) and difluorinated (P3 and P6) systems, clearly suggesting that fluorine

Table 1. Physical properties of the indicated polymers.

Poly.	Mn (KDa)	PDI	λ <sub>max</sub> (nm)	$\mathop{E_{g}}\limits^{\left[a ight]}\left(eV ight)$	E <sub>ox</sub> <sup>[b]</sup> (V)	$\frac{E_{\rm HOMO}/E_{\rm LUMO}{}^{[c]}}{(eV)}$	T <sub>m</sub> (°C)
Pı	14.1	1.9	562	1.87	1.18	-5.6/-3.7	183
P2	25.7	1.4	624	1.75	1.16	-5.6/-3.7	219
P <sub>3</sub>	23.6	1.5	637	1.80	1.30	-5.7/-3.8	255
P4	29.4	2.9	656	1.68	1.12	-5.6/-3.9	170
P5	24.6	1.8	707	1.61	1.04	-5.5/-3.9	215
P6	31.2	1.7	700	1.66	1.09	-5.5/-3.9	252

[a] Calculated from the absorption onset. [b] From the onset of first oxidation peak. [c] From the equation  $E_{HOMO} = -4.44 - E_{Ox}$  and  $E_{LUMO} = E_g + E_{HOMO}$ , respectively.

functionalization of isoBT/BT enhances intermolecular interactions. The optical data also demonstrate that the  $\lambda_{max}$  of the iso-BT polymers [562 nm (P1); 624 nm (P2); 637 (P3)] are blue shifted by ~70-90 nm versus the corresponding BT ones [656 nm (P4); 707 nm (P5); 700 (P6)]. Thus, the optical gaps of P1-P3 (1.75-1.87 eV) are larger than those of P4-P6 (1.61-1.68 eV), in agree-

ment with the MO computations on small molecules (Table S<sub>2</sub>, SI).

CV scans only reveal irreversible oxidations with onsets at 1.2-1.3 V (P1-P3) and 1.0-1.1 V (P4-P6) (Figure 4b). The HOMO and LUMO energies can be next estimated by combining the CV/optical data, (Table 1). Despite the approximate nature of CV-derived orbital energetics, the experimental results are in accord with the DFT computations, with the HOMO/LUMO energies of the isoBT polymers lower/higher by ~0.1-0.2 eV than those of the BT polymers. Interestingly, in sharp contrast to other polymer families, it appears that arene fluorination has negligible influence on the positioning of the CV/optical-derived FMOs. Finally, differential scanning calorimetry (DSC)-derived melting temperatures (T<sub>m</sub>s) indicate that the T<sub>m</sub>s for the isoBT polymers are greater by 3-10 °C than those of the corresponding BT polymers (Figure S1). Note, the reversibility of the DSC scans indicates that all polymers are thermally stable up their melting temperature, thus the presence of an azo (-N=N-) bond does not compromise iso-BT structural robustness.75 Furthermore, fluorine introduction enhances Tm by 72 and 82 °C on going from fluorinefree to the difluorinated polymers within the isoBT (P1-P<sub>3</sub>) and BT (P<sub>4</sub>-P<sub>6</sub>) series, respectively. Overall, the solid-state characterization data indicate that benzothiadiazole regiochemistry in polymers should affect charge transport by deepening the HOMO energies, influence photovoltaic response by reducing absorption and enhancing Voc, and minimally affect film microstructure. In contrast, while fluorination has little impact on MO energetics, it strongly affects macromolecule aggregation and intermolecular interactions. Finally, since the mono-fluoro substituted BT polymer **P5** is regioirregular as the corresponding iso-BT **P2**, and considering that within their respective families (all regioirregular for iso-BT and mixed for BT) thermal/optical/electronic trends holds, to a first approximation polymer regioregularity has small influence on the electronic structure and solid state characteristics. However, it is a further development of this study investigate and address the effect of iso-BT polymer backbone regioregularity considering that it usually improves opto-electronic device performance.52

### **Electronic Device Fabrication and Characterization**

OTFT and BHJ-OSC devices were fabricated (see insets of Figure 5 and SI) with all polymers/polymer blends processed under identical conditions to provide a direct performance comparison (Table 2). Thus, extensive device optimization has not been carried out at this point. The OTFT structure used is glass or PET(substrate)/Au or Ag(source-drain)/P1-P6/CYTOP



**Figure 4.** UV-Vis spectra of cast film of **P1-P6** (a) and CV plots of cast polymer **P1-P6** films measured in anhydrous acetonitrile containing 0.1 M  $Bu_4N^+PF_6^-$  as an electrolyte at a scan rate of 50 mV/s (b).

or D2200(dielectric)/Au or Ag(gate). Note, the maximum processing/annealing temperature of P1-P6 films is 100 °C for 5 min in air. Measurements were carried out in ambient and Figures 5a,b show representative transfer and output plots. From the TFT measurements note that all polymers are p-channel semiconductors with the hole mobility  $(\mu_h)$  increasing as the number of fluorine substituents is increased ( $P_1 \rightarrow P_3$ ,  $P_4 \rightarrow P_6$ ). When comparing the two polymer families, the isoBT unit is as effective as BT in promoting hole transport. Thus,  $\mu_{\rm h}$ s of the nonfluorinated polymers (P1 $\leftrightarrow$ P4) with CYTOP as gate dielectric are low and statistically identical (0.03-0.05 cm<sup>2</sup>/Vs) despite the  $M_n$  of P1 (~14 kDa) being substantially lower than that of  $P_4$  (~29) kDa). For the monofluorinated polymers, which have identical  $M_n$  values (~ 25 kDa),  $\mu_h$  of the isoBT polymer P2 (0.20-0.24  $\text{cm}^2/\text{Vs}$ ) is larger than that of the BT polymer P5 (0.06-0.08 cm<sup>2</sup>/Vs). Finally, the difluorinated polymers outperform the others, with  $\mu_h$  of isoBT P<sub>3</sub> (0.36-0.51 cm<sup>2</sup>/Vs,  $M_n \sim 23$  kDa) lower than that of the corresponding high- $M_n$  P6 (0.65-0.79 cm<sup>2</sup>/Vs,  $M_n \sim 31$ 

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**Figure 5.** Representative transfer (a) and output (b) plots for TFTs with structure Glass/Au/**P1-P6**/CYTOP/Au and BHJ-OSC J-V (c) and EQE- $\lambda$  (d) plots for the indicated polymers and polymer blended with PC<sub>71</sub>BM. Insets indicate schematics of OTFT (a) and OSC (c) architectures and materials.

kDa) but comparable to that of the lower-M<sub>n</sub> P6 batch (0.49-0.56,  $\text{cm}^2/\text{Vs}$ ,  $M_n \sim 18$  kDa). For all CYTOP-based devices the  $I_{on}$ :  $I_{off}$  ratios are ~ 10<sup>3</sup>-10<sup>5</sup>, however, these are underestimated values considering that the semiconductor/gate layers are unpatterned. Indeed rigorous patterning via photolithography by using the dielectric D2200, as exemplified for P3 and P6 (Figure S2 and Table 2), produces similar  $\mu_h$  for P6 (0.74-0.76 cm<sup>2</sup>/Vs) and slightly larger performance for P3 (0.65-0.72 cm<sup>2</sup>/Vs, probably because of the low trapping characteristics of D2200) and outstanding  $I_{on}$ :  $I_{off}$  of ~10<sup>8</sup>. Note that BT-quaterthiophene polymer P6 is the only known polymer of this series and was reported with a  $M_n \sim 46$  kDa having an average mobility in bottomgate top-contact TFTs of 1.03 cm<sup>2</sup>/Vs for films annealed in ambient. Considering the difference in TFT architecture, processing parameters, and Mn values, P6 results are in line with previous studies.41,76-78

Conventional photovoltaic cells of structure ITO/PEDOT/**P1-P6**~PC<sub>71</sub>BM/LiF-Al were also fabricat-

ed. The OSC performances (Figures 5c-d, S<sub>3</sub>, S<sub>4</sub>) track those of the FET mobility, with the PCE values steadily

**Table 2.** Transistor<sup>[a]</sup> and photovoltaic<sup>[b]</sup> performance of polymers **P1-P6**.

Pol.	μ (cm²/Vs)	$I_{\rm on}/I_{\rm off}$	PCE (%)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)
P1	0.03-0.05	~10 <sup>3</sup>	2.8-2.9	0.89-0,90	5.0-5.1	63-64
P2	0.20-0.24	<b>~</b> 10 <sup>4</sup>	7.1-7.2	0.91-0.92	10.4-10.5	70-71
P3	0.36-0.51 [0.65-0.72]	~10 <sup>5</sup> [6-8x10 <sup>7</sup> ]	8.7-9.0	0.92-0.93	12.7-13.1	73-74
P4	0.03-0.05	<b>~10</b> <sup>4</sup>	1.6-1.7	0.78-0.79	3.4-3.6	62-63
P5	0.06-0.08	~10 <sup>3</sup>	6.2-6.4	0.72-0.73	12.4-12.6	70-71
P6 <sup>[c]</sup> H	0.65-0.79 [0.74-0.76]	~10 <sup>5</sup> [8-9x10 <sup>7</sup> ]	8.5-8.8	0.75-0.76	16.2-16.5	70-71
L	0.49-0.56	~10 <sup>3</sup>	7.1-7.3	0.75-0.76	14.1-14.3	68-69

[a] Values are for TFTs with CYTOP and Au contacts with unpatterned semiconductor/gate layers. Thus,  $I_{on}/I_{off}$  are underestimated. Values in brackets refer to TFTs with photocrosslinkable ActivInk D2200 as gate dielectric and Ag contacts with photolithographically patterned semiconductor/gate layers.  $I_{on}/I_{off}$  are accurate. At least 10 TFTs were tested. All TFT measurements are carried out in ambient. [b] At least 5 BHJ-OPV devices were tested. [c] H corresponds to the P6 batch of Table 1 ( $M_n \sim 31$  kDa) whereas L corresponds to a P6 batch with a lower  $M_n = 18.3$  kDa and PDI = 2.0.

increasing upon heterocycle fluorination. Furthermore, the maximum PCEs of the isoBT family [**P1** (2.9 %), **P2** (7.2 %), **P3** (9.0 %)] are slightly larger than those of the corresponding BT polymers [**P4** (~ 1.7 %), **P5** (6.4%), **P6** (P6-H, 8.8%)], despite the blue-shifted absorption and, except when comparing **P2** $\leftrightarrow$ **P5**, the substantially lower M<sub>n</sub>. Note, as for TFTs, polymer **P6** with a lower M<sub>n</sub> (**P6-L**) affords a substantially lower PCE of 7.3%. This result agrees with the literature PCE for **P6** (7.6%).<sup>41</sup>

Finally, to further demonstrate the potential of the new isoBT family, **P3** was employed to fabricate in ambient the first gravure-printed TFT and blade-coated BHJ-OSC devices (see SI, Figures S6 and S7). The TFTs exhibit excellent performance with near-zero turn-on voltage,  $\mu_h = 0.20-0.35$  cm<sup>2</sup>/Vs,  $I_{on}/I_{off} > 10^7$  and negligible hysteresis, while the OPV cell achieve a respectable PCE of 4.1-4.2%. These results are possible because of the good processability and performance of low molecular weights polymer **P3** vs. the corresponding BT-based **P6** polymer.



**Figure 6.** WAXRD for the indicated polymers and polymer blends.

### **Polymer and Polymer Blend Morphology**

Wide-angle x-ray diffraction (WAXRD) of the pristine polymers and the corresponding polymer:PC71BM blends was carried out to better understand device performance. As shown in Figure 6a, distinct (hoo) specular reflections indicate that all polymers are polycrystalline, with the intensity increasing upon increasing isoBT/BT fluorination level. The first reflection located at  $2\theta = 3.97$ -4.00° indicates that all polymers adopt a bulk edge-on growth orientation characterized by a d-spacing ( $d_{lam}$ ) of 22.25-22.09 Å. These results further demonstrate that fluorination promotes better organization of the polymer long-range-ordered lamellar structures, in agreement with the optical data, and corroborating the in-plane charge transport measurements.<sup>79</sup> Interestingly, when going from the pristine polymers to the corresponding OSC blends, the XRD spectra evolve differently for the different polymers (Figure 6b). Thus, all blends exhibit the (hoo) reflection(s) at  $3.95-4.09^{\circ}$  (d<sub>lam</sub> = 22.37-21.60 Å), however those based on P1/P2 and P4/P5 exhibit comparable intensity whereas those based on P3 and P6 are substantially decreased. Furthermore, the P3 and P6 polymer blend spectra, as well as to a lesser degree blends based on P2, exhibit a (010) reflection at 25.10, 24.91, and 24.97°, signatures of  $\pi$ -face-on oriented polymer domains having stacking at a distance,  $d_{\pi}$ , of ~ 3.5 Å. These characteristics, in combination with the favorable fibrillary film morphology established by AFM (Figure S<sub>5</sub>),<sup>80</sup> enable the

large OSC efficiencies and FFs for the new isoBT **P2/P3** and BT **P6** versus those of the other polymers.

### Conclusions

In conclusion, a new polymer semiconductor family comprising isomeric benzothiadiazole building blocks is synthesized and characterized. To gain further insights, polymers based on the well-investigated BT units were also synthesized and analyzed. Single crystal analysis suggests that the new iso-BT units can enable a planar polymer backbone whereas thin-film XRD demonstrate considerable texturing of the polymer films. Overall, our data suggest interesting similarities and differences between the two families, highlighting the potential of the isoBT unit and isoBT-based polymers for organic opto-electronic devices.

The wider bandgap and considerable efficiencies of the isoBT polymers, and particularly **P3** vs. **P6**, may be more suitable for tandem cells and combination with molecular/polymer acceptors. The greater transistor performance at lower molecular weights for the isoBT polymers may be important for enabling more stable rheology of formulations. We believe that this work will promote the use of isoBT for different optoelectronic applications to complement the current generation high-performance BT-based semiconductors. Further investigations and optimization of the isoBT family performance will include synthesis of molecular systems,<sup>32,48-53,81-88</sup> the effect of the isoBT regio-chemistry,<sup>52,89-92</sup> and polymer side-chain engineering,<sup>56,93-97</sup> as widely demonstrated for (hetero)BT-based semiconductors.

### ASSOCIATED CONTENT

#### SUPPORTING INFORMATION

\*S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Synthetic procedures and characterization data of the monomers and polymers; DSC plots; AFM images; DFT computation Data; Single Crystal X-ray diffraction data; Selected NMR spectra; and details for all device characterizations.

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#### Notes

The authors declare no competing financial interest.

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