

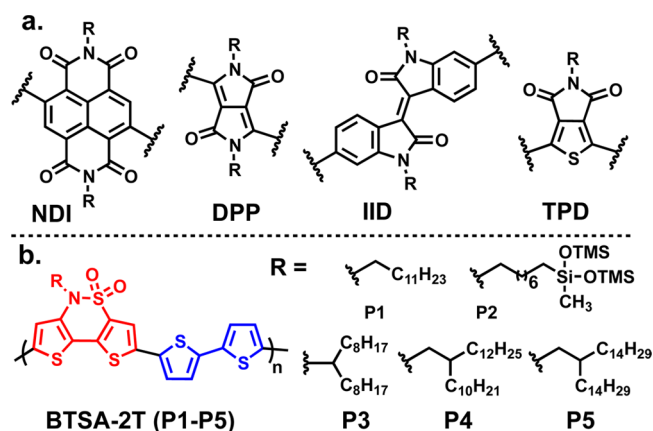
Bithiophenesulfonamide Building Block for  $\pi$ -Conjugated Donor–Acceptor SemiconductorsFerdinand S. Melkonyan,<sup>†</sup> Wei Zhao,<sup>‡</sup> Martin Drees,<sup>‡</sup> Nicholas D. Eastham,<sup>†</sup> Matthew J. Leonardi,<sup>†</sup> Melanie R. Butler,<sup>†</sup> Zhihua Chen,<sup>‡</sup> Xinge Yu,<sup>†</sup> Robert P. H. Chang,<sup>†,§</sup> Mark A. Ratner,<sup>†</sup> Antonio F. Facchetti,<sup>\*,†,‡</sup> and Tobin J. Marks<sup>\*,†,§</sup><sup>†</sup>Department of Chemistry and Materials Research Center, Argonne–Northwestern Solar Energy Research (ANSER) Center, and  
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## S Supporting Information

**ABSTRACT:** We report here  $\pi$ -conjugated small molecules and polymers based on the new  $\pi$ -acceptor building block, bithiophenesulfonamide (BTSA). Molecular orbital computations and optical, electrochemical, and crystal structure analyses illuminate the architecture and electronic structure of the BTSA unit versus other acceptor building blocks. Field-effect transistors and photovoltaic cells demonstrate that BTSA is a promising unit for the construction of  $\pi$ -conjugated semiconducting materials.

Organic semiconductors are among the most important components of new optoelectronic technologies.<sup>1</sup> Because of their low fabrication cost by solution processing, tunable optical and charge-transport properties, and compatibility with mechanically flexible plastic substrates, they are finding applications in organic light-emitting diode (OLED) displays,<sup>2</sup> organic photovoltaics (OPVs),<sup>3</sup> organic field-effect transistors (OFETs),<sup>4</sup> and circuitry.<sup>5</sup>  $\pi$ -Conjugated in-chain donor–acceptor (D–A) polymers are an enabling class of materials for many of these functions,<sup>6</sup> and selection of appropriate D and A building blocks and conjugation along the polymer backbone governs key polymer properties such as the frontier molecular orbital (FMO) energies ( $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ), the band gap ( $E_g$ ), and local dipole moments affecting intermolecular interactions, solid-state packing, and exciton dynamics.<sup>7</sup> Finally, existing efficient cross-coupling synthetic methodologies<sup>8</sup> facilitate access to libraries of new polymers by combining known units with newly developed building blocks.<sup>9</sup> Thus, new materials advances rely heavily on the discovery of novel elementary building blocks.<sup>10</sup>

Historically, oligothiophenes and related heterocycles dominated the organic semiconductor field as weak donor or  $\pi$ -bridging units.<sup>11</sup> Acceptor units include electron-poor heterocycles (benzo-fused azoles),<sup>12</sup> heterocycles with electron-withdrawing groups (EWGs),<sup>13</sup> and other aromatic amides and imides (Figure 1a).<sup>14</sup> Surprisingly, and in contrast to the carbon analogues, employing sulfonamide/imide acceptor functionalities in organic semiconducting materials has been underexplored. Here we report the design and realization of the first sulfonamide-based building block, bithiophenesulfonamide



**Figure 1.** (a) Imide-based in-chain acceptors widely used for constructing organic semiconductors. (b) BTSA-based D–A polymers.

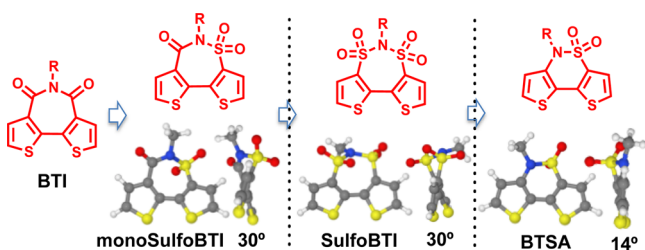
(BTSA). Moreover BTSA-based D–A polymers (Figure 1b) have been synthesized and characterized, with polymers BTSA-2T exhibiting promising OFET and OPV performance characteristics.

Earlier, this laboratory developed a bithiopheneimide (BTI) acceptor unit,<sup>10c</sup> which enabled the synthesis of high-performance p- and n-type OFET polymers (mobility  $>0.1$ – $1.0$   $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )<sup>15</sup> as well as highly efficient donors for bulk-heterojunction (BHJ) OPVs with power conversion efficiencies (PCEs) near 9%.<sup>16</sup> Thus, with BTI as the starting unit, we envisioned incorporating a dipolar  $\text{SO}_2$  group (Figures 2 and S1). According to density functional theory (DFT) computations, the resulting SulfoBTI structures exhibit relatively large dihedral angles between the thiophene rings ( $\sim 30^\circ$ ) whereas the BTSA unit is far more planar ( $14^\circ$ ). In addition, the six-membered BTSA ring is inherently less sterically congested than the seven-membered SulfoBTI core. Furthermore, recent work by Yu and co-workers indicates that strong electron-withdrawing functionalities connected to another EWG may create traps and decrease the charge-transport efficiency.<sup>17</sup> Thus, on the basis of the above-mentioned steric and electronic

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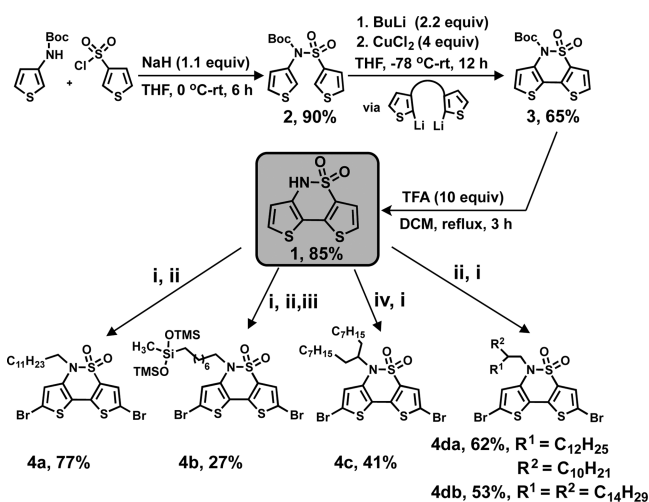


**Figure 2.** BTI-based design of sulfonamide-based building blocks and DFT models (B3LYP/6-31G\*\*).

considerations, the BTSA unit was selected as the synthetic target.

The optimized synthesis of unsubstituted BTSA (**1**) is an efficient three-step procedure (Scheme 1). Installing the

### Scheme 1. Synthesis and Functionalization of BTSA<sup>a</sup>

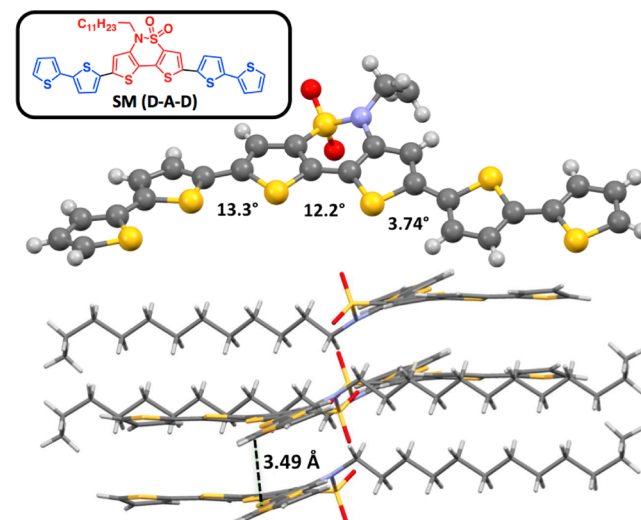


<sup>a</sup>Overall yields of monomers **4** from **1** are shown. Reagents and conditions: (i) Br<sub>2</sub> (2.5 equiv), DCM/AcOH (**4a**, **4b**) or DCM (**4c**, **4da**, **4db**), rt, 8 h; (ii) K<sub>2</sub>CO<sub>3</sub> (1 equiv), alkyl bromide (1.5 equiv), DMF, 80 °C, 12 h; (iii) Karstedt catalyst (0.5 mol %), (TMSO)<sub>2</sub>MeSiH (1.5 equiv), toluene, 80 °C, 12 h; (iv) DIAD (1.5 equiv), PPh<sub>3</sub> (1.5 equiv), heptadecan-9-ol (1.1 equiv), THF, 0 °C to rt, 36 h.

thiophene-3-sulfonyl group in *N*-Boc-3-aminothiophene affords sulfonamide **2** in high yield, which then undergoes the key anionic oxidative cyclization to produce **3**. Ultimately, protecting group removal yields **1**. The high overall yield, simplicity of this three-step sequence, and possibilities for BTSA scale-up represent one of the most concise and efficient building block syntheses to date for organic semiconductors.<sup>18</sup> Next, the BTSA core was functionalized with selected solubilizing alkyl and halogen substituents (Scheme 1).<sup>19</sup> It should be noted that the sulfonamide group's strong electron-withdrawing character not only imbues the BTSA unit with favorable FMO energies but also provides sufficient acidity for incorporating alkyl chains using a weak base (K<sub>2</sub>CO<sub>3</sub>). Thus, both linear (**4a**, **4b**) and  $\alpha$ -branched (**4da**, **4db**) primary alkyl substituents were introduced via simple alkylation (30–80% yield). Mitsunobu alkylation was used to introduce a secondary alkyl chain (**4c**).<sup>20</sup> Recently, Bao reported the use of a siloxy-terminated chain to modify the intermolecular interactions in isoindigo-based polymers to enhance OFET performance.<sup>21</sup> In

the BTSA system, siloxy-terminated alkyl substituents are readily introduced (**4b**).

Prior to polymer synthesis, a BTSA small molecule that models the target polymer backbone (SM) was prepared (Scheme S7) and characterized by single-crystal X-ray diffraction (Figure 3). The BTSA core architecture is in good



**Figure 3.** Molecular structure and packing of the model acceptor SM.

accord with the DFT results, having a nearly planar core and a dihedral angle of 12.2° between the thiophene rings. Interestingly, the bithiophene moiety on the SO<sub>2</sub> side of the molecule is twisted by 13.2° relative to the corresponding core thiophene with a syn-like thiophene conformation. The bithiophene moiety joined to the core N side is far less twisted (3.7°) and has an anti-like conformation. SM has a short  $\pi$ - $\pi$  stacking distance of 3.49 Å between the bithiophene planes, and the key BTSA sulfonamide (SO<sub>2</sub>N) functionality has seven short intermolecular S=O...H-C contacts, portending strong and unique intermolecular packing characteristics.<sup>22</sup>

Next, in-chain D-A polymers were synthesized using bithiophene as the D block to initially assess the macromolecular properties. All of the new polymers were prepared via Stille cross-coupling (Scheme 1 and Tables S1 and S2),<sup>23</sup> and Table 1 collects their relevant chemical and physical

**Table 1.** Physical Properties of Polymers P1–P5<sup>a</sup>

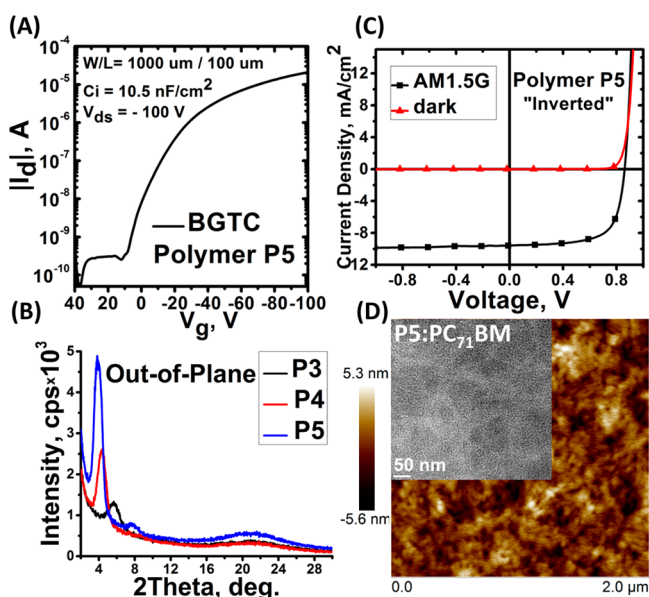
	$M_n$ /PDI	$E_g^{\text{opt}}$ solution/film	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\mu_h$
P1	3.3/1.51	1.85/1.83	−5.24	−3.41	—
P2	—	1.84/1.83	−5.21	−3.38	—
P3	6.3/1.7	1.90/1.89	−5.30	−3.41	$4.4 \times 10^{-4}$
P4	11.5/2.6	1.89/1.86	−5.34	−3.48	0.02
P5	14.4/4.6	1.89/1.84	−5.39	−3.55	0.06

<sup>a</sup> $M_n$ ,  $E$ , and  $\mu_h$  are given in kDa, eV, and cm<sup>2</sup> V<sup>−1</sup> s<sup>−1</sup>, respectively;  $E_{\text{HOMO}}$  was determined as the onset of the CV oxidation potential;  $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g(\text{film})$ ;  $\mu_h$  was measured in the saturation regime.

properties. P1 and P2 are marginally soluble, while polymers with secondary chain (P3) and long  $\alpha$ -branched (P4) substituents are more soluble and have  $M_n$  = 6.3 and 11.5 kDa, respectively, as determined by gel-permeation chromatography. P5 with the longest alkyl chain exhibits the best solubility and the highest  $M_n$  in the series (14.3 kDa).  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , and  $E_g$  were estimated by cyclic voltammetry (CV) and

optical absorption spectroscopy. P1 and P2 have identical solution-phase  $E_g$  values ( $\sim 1.85$  eV), whereas those of P3–P5 are slightly larger (Table 1), likely because the longer alkyl chains attenuate polymer aggregation.<sup>24</sup> The solid-state  $E_g$  values are similar to those in solution, suggesting similar degrees of aggregation (Figures S7–S11). For all of the polymers, the CV experiments reveal distinct quasi-reversible oxidation and irreversible reduction processes (Table 1 and Figures S12–S16). Thus,  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  were estimated from the oxidation onset and  $E_g$  and fall within similar ranges (5.2–5.4 and 3.4–3.5 eV, respectively). Thermogravimetric analysis and differential scanning calorimetry indicate appreciable thermal stability ( $T_d > 300$  °C) and no obvious thermal transitions (Figures S17–S20).

To characterize the polymer charge-transport properties, bottom gate top contact (BGTC) OFETs of structure Si/SiO<sub>2</sub>(300 nm)/OTS/polymer/Au(35 nm) were fabricated. Considering the poor solubility and film quality of P1 and P2, only P3–P5 were investigated. The BTSA-2T polymers exhibit OFET response with distinct p-type charge transport. All of the OFETs have high on/off current ratios and close to optimal turn-on voltages (Table S4). P3 exhibits a modest hole mobility ( $\mu_h = 4.4 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), whereas that of P4 is significantly greater (0.022 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). Importantly, BGTC transistors fabricated using P5 as a semiconductor layer exhibit  $\mu_h = 0.06$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, current modulation  $I_{\text{on}}/I_{\text{off}} = 10^5$ , and threshold voltage  $V_{\text{th}} = -9$  V (Figure 4A; details are shown in



**Figure 4.** (A) Transfer plot for a BGTC OFET using P5. (B)  $\theta$ - $2\theta$  thin-film XRD patterns. (C) Illuminated and dark  $J$ - $V$  response of an (ITO/ZnO/P5:PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag) inverted-architecture OPV device; (D) AFM height and (inset) TEM images of a P5:PC<sub>71</sub>BM (1:2 ratio) blend.

Figures S25–S28 and Table S4). Interestingly,  $\mu_h$  in the TGBC architecture is slightly smaller. Although these transport data are not groundbreaking, they suggest that the BTSA class includes promising semiconductors.

To probe the film morphology and understand the P3–P5 performance differences,  $2\theta$  X-ray diffraction (XRD) and atomic force microscopy (AFM) were used.<sup>25</sup> Interestingly, the carrier mobilities of these polymers correlate with the XRD-

derived film crystallinities. Thus, the polymer with the highest mobility, P5, exhibits the strongest Bragg reflections, and large, extended domains as observed by AFM (Figures 4B and S24). The secondary alkyl chains in P3 enhance the solubility and favor uniform film formation but strongly reduce the polymer backbone interactions and crystallinity. The film crystallinity and hole mobility of P4 lie between those of P3 and P5. Furthermore, the first Bragg reflection position corresponds to lamellar “edge-on” packing with  $d$ -spacings of 15.6, 19.9, and 22.4 Å for P3–P5, respectively, in agreement with the estimated N-chain lengths (Figures S21–23 and Table S3).<sup>26</sup>

Finally, BHJ OPVs were fabricated with P5 as the donor semiconductor in both conventional and inverted architectures (Figures S29 and S30 and Table S5). The highest PCE (5.5%) was measured for the device with the inverted architecture (Figure 4C). The high open-circuit voltage (0.85 V) and fill factor (FF) (68.2%) can be attributed to good HOMO energetic positioning and the pronounced P5 crystallinity, respectively. Transmission electron microscopy (TEM) and AFM images of the P5:PC<sub>71</sub>BM blend were obtained to probe the OPV internal morphology (Figure 4D) and clearly reveal polymer:fullerene nanoscale phase separation with 30–50 nm domains. Such phase segregation promotes bicontinuous network formation and hence facilitates charge extraction and enhances the FF. The blend-film AFM image shows the same nanoscale phase separation with surface features on a similar size scale extending in a continuous network across the film. These networks lessen the grain boundary densities and facilitate carrier migration. The AFM and XRD data for a pristine P5 film and one blended with PC<sub>71</sub>BM clearly indicate that P5 retains its crystallinity and “edge-on” orientation after fullerene blending (Figures S31–S33). The OPV performance of BTSA-based materials can doubtless be further enhanced by the optimizing the donor monomer, solubilizing substituents, and processing conditions.<sup>27</sup>

In summary, a conceptually new building block for organic semiconductors was designed and realized. Built on the previously unexplored BTSA unit, BTSA-2T polymers demonstrate promising preliminary results as p-type OFET materials and donor materials for OPVs. We believe that the future development of BTSA and other sulfonamide materials is appealing and can advance the field of organic semiconducting materials.

## ■ ASSOCIATED CONTENT

### § Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03498.

Experimental details and characterization data and images (PDF)

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### Notes

The authors declare no competing financial interest.

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