Thieno[3,2-b]pyrrole and Benzo[c][1,2,5]thiadiazole Donor–Acceptor Semiconductors for Organic Field-Effect Transistors

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Supporting Information

ABSTRACT: Two p-type donor–acceptor (D–A) semiconductor small molecules were synthesized to investigate the effect of the backbone curvature on the organic field-effect transistor performance. The backbone curvature of the donor–acceptor small molecules was modified by changing the spacer group from bithiophene to thienothiophene. Bithiophene to thienothiophene spacer groups were placed between 4H-thieno[3,2-b]pyrrole (donor) and benzo[c]-[1,2,5]thiadiazole (acceptor) to generate TP-BT4T-TP and TP-BT2TT-TP donor–acceptor molecules. A good charge carrier mobility of 2.59 × 10⁻² cm² V⁻¹ s⁻¹ was measured for the curved molecule (TP-BT4T-TP), while the linear molecule analog (TP-BT2TT-TP) only gave a low mobility of 5.41 × 10⁻⁵ cm² V⁻¹ s⁻¹ after annealing at 120 °C in bottom-contact bottom-gate devices. Out-of-plane grazing-incidence X-ray diffraction analysis revealed more drastic thermally induced crystallinity for TP-BT4T-TP as compared to TP-BT2TT-TP, explaining the difference observed in the performance of devices fabricated from each molecule.

INTRODUCTION

Organic semiconductors (OSCs) for organic field-effect transistors (OFETs) are technologically promising because of their lightweight, low cost, flexibility, large-area fabrication, and solution processability.1−7 The performance of OSCs used in OFETs has already surpassed the performance of both amorphous silicon (0.1−1 cm² V⁻¹ s⁻¹) and polycrystalline silicon (0.1−1 cm² V⁻¹ s⁻¹) with an on/off ratio from 10⁸ to 10³.8,9 The incorporation of acenes, such as pentacene and its derivatives, achieved impressive charge carrier mobilities in the range of 10−40 cm² V⁻¹ s⁻¹.8,9 The major drawback of these OSCs is the instability in air for prolonged durations and the necessity of vacuum deposition.10,11 These processing conditions and methods needed for the small molecules OSCs significantly curtail their use in real-world applications. To impart solution processability, solubilizing alkyl chains are employed to generate solution-processable small molecules and polymers. Compared to solution-processable polymers, small molecules are more attractive candidates for OFETs, as OSCs based on small molecules possess well-defined structures, high purity, less batch to batch variations, better crystallinity, and higher reproducibility.13,14

Currently, OFETs fabricated from small-molecule semiconductors have reported charge carrier mobilities exceeding 5 cm² V⁻¹ s⁻¹.15 However, multistep synthesis and low overall yields prevent commercialization of these materials encouraging chemists to pursue easy-to-synthesize high-performing materials with good overall yields. To further improve the performance, it is critical to understand the fundamental aspects of these small molecules such as planarity,16,17 heteroatom effect, and backbone curvature. Out of many variations, the backbone curvature has not been studied extensively in OFETs as other parameters. Design of novel OSCs with improved performance in devices is a demanding challenge. Design strategies include the use of fused rings,15,18 side-chain engineering,19−21 positioning of donor and acceptor (D–A) units,22,23 and heteroatom replacement in the conjugated backbone.8,13 Among them, the inclusion of fused rings in the backbone and D–A structural designs are widely studied to tailor their optoelectronic properties. Fused rings systems permit the formation of more rigid and planer assemblies, forming more favorable π–π intermolecular interactions with the deep-lying HOMO energy level through larger resonance stabilization energy, resulting in better charge carrier transport characteristics.15,18,24 Thieno[3,2-b]thiophene,25,26 4H-dithieno[3,2-b:2',3'-d]pyrrole,27,28 benzo[1,2-b:4,5-b']dithiophene,29,30 and benzo[1,2-b:4,5-b'-]dithiophene30,31 are some of the fused rings extensively explored to generate OSC constructs. Similarly, designing small molecules with D–A architecture increases the

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intermolecular interactions originated from donor and acceptor moieties, aiding in the production of high-performing OSC devices.\textsuperscript{32,33} On the other hand, heteroatom inclusions are not straightforward and require more research on the topic.\textsuperscript{8} Though not extensively investigated in OSCs as thiophene, pyrrole-containing OSCs are shown to be excellent electronic materials for organic electronic applications.\textsuperscript{14–16} High electron density, challenging synthesis, and less air stability of the pyrrole-unit limit their use as OSCs. Fusing thiophene with pyrrole generates a relatively stable TP unit with strong donor character, and more importantly, solubilizing groups can be easily added via the pyrrolic nitrogen atom. Thiieno[3,2-b]thiophene (TT) with TP as the donor and BT as acceptor small molecules reported here were synthesized by Stille coupling of ethyl 2-bromo-4-dodecyl-4H-thieno[3,2-b]pyrrole-5-carboxylate with 4,7-bis(5-(trimethylstannyl)-[1,2,5]-thiadiazole and 4,7-bis(5-(trimethylstannyl)-[2,2′-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole, respectively. The synthesis of ethyl 2-bromo-4-dodecyl-4H-thieno[3,2-b]pyrrole-5-carboxylate was carried out according to a literature reported procedure.\textsuperscript{37,38} The final products were precipitated out of solution in methanol as pure compounds without time-consuming column purification. All of the intermediates and final molecules were characterized with \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy and MALDI-TOF mass spectrometry. The detailed synthetic procedures for intermediates and final products can be found in Supporting Information.

### Optical and Electrochemical Properties

Optical properties of the small molecules were obtained in both solution and thin film using chloroform as the solvent. The absorption spectra of the molecules are shown in Figure 2, and their optical and electrochemical properties are summarized in Table 1. Both molecules show similar absorption behavior, having two peaks. The peaks centered at 400 nm (for TP-BT2TT-TP) and 412 nm (for TP-BT4T-TP) arise from the intramolecular π−π* transition along the conjugated backbone. On the other hand, the peaks appearing at 546 nm (for TP-BT2TT-TP) and 542 nm (for TP-BT2T-TP) come from the intramolecular charge transfer between delocalized HOMO to LUMO energy levels.\textsuperscript{43} In the solid state, both semiconductors exhibited a slight red shift (14–16 nm) in their absorption profile. Annealing of the thin film of TP-BT4T-TP at 120 °C did not result in a red shift (Figure S5, Supporting Information). However, annealing of the thin film of TP-BT2TT-TP gave a small red shift of ∼18 nm for both peaks (Figure S5, Supporting Information). The onset of the thin film absorption profiles was used to estimate the optical band gap of molecules. To calculate the HOMO/LUMO energy level and electrochemical band gap of molecules, cyclic voltammetry (CV) was used on thin films of the molecules deposited on the carbon electrode. The onset of oxidation and reduction peaks was used to estimate the HOMO and LUMO energy respectively using following equations: $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4) \text{ eV}$ and $E_{\text{LUMO}} = -(E_{\text{red}} + 4.4) \text{ eV}$. The corresponding HOMO/LUMO energies of TP-BT4T-TP and TP-BT2TT-TP are 2.99 eV/4.97 eV and 2.93 eV/4.78 eV, respectively. TP-BT4T-TP possesses a band gap of 1.98 eV, which is slightly higher than the band gap of TP-BT2TT-TP at 1.85 eV.

### Theoretical Calculations

The frontier molecular orbital and energy levels of TP-BT4T-TP and TP-BT2TT-TP were examined by theoretical calculations with Spartan’16 software at the B3LYP level of theory and with the 6-31G* basis set. The dodecyl alkyl chains were replaced with methyl groups for the ease of calculations. The optimized geometries, frontier molecular orbitals, and energies are depicted in Figure 3. TP-BT2TT-TP adopted a more planar backbone conformation compared to TP-BT4T-TP, with minimal dihedral angles between the TP unit and the backbone. The electron density of the LUMO energy level of both molecules is predominantly concentrated over the benzothiadiazole moiety; however, the electron density of the HOMO energy level of both molecules is distributed along the conjugated backbone. The calculated HOMO and LUMO energy levels for both TP-BT4T-TP and TP-BT2TT-TP are comparable with experimental obtained values.
Thermal Stability. Thermal properties of semiconductors were studied with thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The corresponding TGA curves and DSC thermograms are shown in Figure S1. All of the molecules were thermally stable having decomposition temperatures ($T_d$ at 95% weight loss) more than 250 °C. The corresponding decomposition temperatures of TP-BT4T-TP and TP-BT2TT-TP are 265 and 306 °C, respectively. Both TP-BT4T-TP and TP-BT2TT-TP showed melting peaks in the heating cycle at 177.6 and 262.2 °C.

**Table 1. Optical and Electrochemical Properties of TP-BT4T-TP and TP-BT2TT-TP**

| small molecule       | HOMO $^a$ (eV) | LUMO $^b$ (eV) | $E_g$ (ec)/$E_g$ (opt) $^c$ (eV) | $\lambda_{\text{max}}$ sol (nm) | $\lambda_{\text{max}}$ film (nm) | $\lambda_{\text{onset}}$ (nm) |
|----------------------|----------------|----------------|----------------------------------|---------------------------------|----------------------------------|-------------------------------|
| TP-BT2TT-TP          | −4.78          | −2.93          | 1.85/1.64                        | 400, 546                        | 415, 562                         | 756                           |
| TP-BT4T-TP           | −4.97          | −2.99          | 1.98/1.67                        | 412, 542                        | 426, 566                         | 741                           |

$^a$Estimated from the oxidation potential in CV.

$^b$Estimated from the reduction potential in CV.

$^c$Calculated from LUMO−HOMO.

$^d$Calculated from the onset of thin film absorption in UV−vis.

**Figure 2.** UV−vis spectra of (a) TP-BT4T-TP, (b) TP-BT2TT-TP, and (c) cyclic voltammogram of (c) TP-BT4T-TP, and (d) TP-BT2TT-TP.
respectively, which reflects the crystalline nature of the molecules. However, in their cooling traces, only TP-BT2TT-TP exhibited an intense cold crystallization peak at 253.6 °C.

**OFET Performance.** A summary of OFETs performance and corresponding transfer curves are given in Tables S1 and S2, and Figure S2. Although there was no initial OFET activity, upon annealing p-type FET characteristics were observed for both molecules. For TP-BT4T-TP, hole mobility of $1.87 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ was achieved along with an $I_{on}/I_{off}$ ratio exceeding $10^3$ after annealing at 60 °C for 5 min. Further increase of annealing temperature to 120 °C improved the OFET performance to obtain maximum hole mobility to $2.59 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ with an $I_{on}/I_{off}$ ratio greater than $10^4$. Beyond the annealing temperature of 120 °C, a decrease in carrier mobility was observed. This change can be attributed to
the deformation of thin films upon annealing. The maximum hole mobility of $5.41 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ was observed for TP-BT2TT-TP after annealing devices at 120 °C. The annealing temperature did not improve the performances of TP-BT2TT-TP significantly as in TP-BT4T-TP (Figure 4).

Grazing-Incidence X-ray Diffraction Analysis. Grazing-incidence X-ray diffraction (GIXRD) analysis was performed for both annealed and non-annealed films to analyze possible thermally induced crystallinity. The corresponding out-of-plane GIXRD patterns are shown in Figure 5. Thin films of TP-BT4T-TP and TP-BT2TT-TP were annealed at 120 °C for 5 min prior to GIXRD analysis. Before annealing the TP-BT4T-TP film, it exhibited only one diffraction peak at 28.5° arising because of π−π stacking. However, upon annealing at 120 °C, an additional diffraction peak at 2.60° was observed, and the intensity of π−π stacking diffraction also slightly increased. Consequently, the annealing process improved the ordering of TP-BT4T-TP films, reflected by devices possessing enhanced charge carrier mobilities. However, only a weak diffraction peak at 2.30° is seen in the GIXRD pattern for both annealed and non-annealed films of TP-BT2TT-TP. This observation aligns with the poor performance of TP-BT2TT-TP in devices. The respective d-spacing values for diffraction peaks in the pattern of both molecules are demonstrated in Table 2. The in-plane GIXRD showed no diffraction peaks (Figure S5, Supporting Information).

Table 2. GIXRD Analysis of Molecules

| molecule | peaks | 2θ (deg) | d-spacing (Å) |
|----------|-------|----------|---------------|
| TP-BT4T-TP | (100) | 2.60 | 33.9 |
| TP-BT4T-TP | (101) | 2.90 | 28.5 |

Thin-Film Morphology. Tapping mode atomic force microscopy (TMAFM) images were recorded for the devices in their channel regions to probe the morphology of the thin organic films. The height and phase images of thin films of TP-BT4T-TP and TP-BT2TT-TP are shown in Figures S5 and S4. Examining the images, the annealing of TP-BT4T-TP thin films at 120 °C for 5 min caused the formation of large domains compared to those present in non-annealed thin films. This indicates that TP-BT4T-TP possesses strong intermolecular interactions upon annealing, and this behavior is further confirmed by enhanced lamellar packing diffraction in the GIXRD analysis. On the other hand, the microstructure of TP-BT2TT-TP did not change with the annealing process, and it has more dense aggregates.

CONCLUSIONS

In summary, two novel small p-type molecules, TP-BT4T-TP and TP-BT2TT-TP, were synthesized from thieno[2,3-b]-pyrrole and benzothiadiazole spaced by two thiophene units and thiienothiophene, respectively, to generate two backbone curvatures. The OFET parameters of TP-BT4T-TP and TP-BT2TT-TP were evaluated with BG/BC device configuration. TP-BT4T-TP exhibited charge carrier mobility of 0.0259 cm$^2$ V$^{-1}$ s$^{-1}$ upon annealing at 120 °C, whereas the TP-BT2TT-TP molecule showed charge carrier mobility of 5.41 $\times$ 10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$. The drastic difference can be rationalized by thermally enhanced crystallinity and strong intermolecular interactions of TP-BT4T-TP as shown by GIXRD and TMAFM analysis.

EXPERIMENTAL SECTION

General Materials and Methods. All the chemicals were purchased from Fisher Scientific or Sigma-Aldrich and used without further purification unless otherwise mentioned. All the reactions were carried out in a nitrogen atmosphere. Ethyl 2-bromo-4-dodecyl-4H-thieno[3,2-b]pyrrole-5-carboxylate, 18 [2,2′-bithiophen]-5-yltrimethylstannane,44 4,7-dibromobenzo[c][1,2,5]thiadiazole,45 and trimethyl(thieno[3,2-b]thiophen-2-yl)stannane46 were synthesized according to previously published procedures. All the proton and carbon NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. The MALDI-TOF experiments were performed with a Shimadzu Biotech AXIMA Confidence in reflectron-HiRes mode by depositing chloroform solutions of the matrix (2,2′:7′,2′-terthiophene as the matrix, 1.0 μL) followed by depositing the analyte (1.0 μL) dissolved in chloroform. TGA and DSC were performed with a Mettler Toledo TGA/DSC-1 system by applying a heating rate of 10 °C/min and a cooling rate of −10 °C/min under a nitrogen flow. The UV–vis
spectra were obtained from an Agilent 8453 UV–vis spectrometer. The UV–vis spectra of final molecules in solution (chloroform) and thin films (after drop-casting on cleaned glass substrates) were obtained with an Agilent 8453 UV–vis spectrometer. The BAS CV-50W voltammetric analyzer was used for CV measurements by employing three electrodes (Pt inert working electrode, Pt wire auxiliary electrode, and Ag/Ag+ reference electrode) and 0.1 M tetrabutylammonium hexafluoropropionate solution as the electrolyte. GIXRD measurements of samples were carried out with a Rigaku III SmartLab XRD instrument by spin-coating of TP-BT4T-TP (in chloroform 5 mg/mL) and drop-casting of TP-BT2TT-TP (in chloroform 1.5 mg/mL) on a cleaned octadecyltrimethoxysilane (OTMS) treated Si substrate. TMAFM images were obtained with a Nanoscope IV Multimode Veeco instrument by scanning inside the channel region. The size of the scan area for recording images was 2 × 2 μm with a frequency of 1 Hz.

Fabrication of Solution-Processed OFET Devices. The small molecules were used to fabricate a bottom-gate/bottom-contact (BGBC) device configuration to test the OFET performance. Highly n-doped Si wafers with a thermally grown 200 nm SiO2 dielectric layer were used as substrates. A 5 nm thick layer of chromium and a 100 nm thick layer of Au were deposited on the Si/SiO2 surface using a Temescal E-beam evaporator. Source and drain contacts (Cr/Au) with different channel lengths were patterned by photolithography. The contacts were then covered with a photoresist, and the backside was etched with 7:1 BOE solution. Using the Temescal E-beam evaporator, 100 nm of gold gate electrode was deposited. The devices were washed with water, acetone, toluene, and 2-propanol. Before fabricating devices with small molecules, the surface of each device was modified with 6 μM OTMS solution to obtain a self-assembled monolayer, carried out via a previously published procedure. Small donor–acceptor molecule TP-BT4T-TP was dissolved in chloroform (5 mg/mL) and filtered through a 0.25 μm PTFE filter to remove any undissolved particles. The solution was spin-coated onto the device at 500 rpm for 45 s in a nitrogen-filled glove box.

Similarly, the small donor–acceptor molecule TP-BT2TT-TP was dissolved in chloroform (1.5 mg/mL) and filtered. It was drop-cast onto the devices to obtain a thin layer of semiconductor. All devices were kept in a nitrogen-filled glovebox until they were measured with a Keithly 4200 Parameter Analyzer.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02274.

Synthetic procedures for all the molecules, TGA, DSC, NMR spectra (1H and 13C), OFET performance, MALDI-TOF spectra, and TMAFM images (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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