Enhanced Performance of Benzothieno[3,2-b]thiophene (BTT)-Based Bottom-Contact Thin-Film Transistors

Peng-Yi Huang,^[a] Liang-Hsiang Chen,^[b] Yu-Yuan Chen,^[a] Wen-Jung Chang,^[a] Juin-Jie Wang,^[a] Kwang-Hwa Lii,^[a] Jing-Yi Yan,^[b] Jia-Chong Ho,^[b] Cheng-Chung Lee,^[b] Choongik Kim,^{*[c]} and Ming-Chou Chen^{*[a]}

Abstract: Three new benzothieno[3,2b]thiophene (**BTT**; 1) derivatives, which were end-functionalized with phenyl (**BTT-P**; 2), benzothiophenyl (**BTT-BT**; 3), and benzothieno[3,2b]thiophenyl groups (**BBTT**; 4; dimer of 1), were synthesized and characterized in organic thin-film transistors (OTFTs). A new and improved synthetic method for **BTT**s was developed, which enabled the efficient realization of new **BTT**-based semiconductors. The crystal structure of **BBTT** was determined by single-crystal X-ray diffraction. Within this family, **BBTT**, which had the largest conjugation of the **BTT** derivatives in this study, exhibited the

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highest p-channel characteristic, with a carrier mobility as high as $0.22 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and a current on/off ratio of 1×10^7 , as well as good ambient stability for bottom-contact/bottom-gate OTFT devices. The device characteristics were correlated with the film morphologies and microstructures of the corresponding compounds.

Introduction

Over the past decade, organic thin-film transistors (OTFTs) have received considerable interest for various applications in flexible electronics, such as flexible displays, RF-ID (radio-frequency identification) tags, and e-papers.^[1,2] Among the three essential components in OTFTs, that is, semiconductors, insulators, and conductors, there has been huge progress in the development of organic semiconductors with performance that is comparable to (or surpassing) that of amorphous silicon.^[3] Among organic semiconductors, pentacene and its derivatives are representative examples that exhibit high electrical performance with carrier mobilities of $> 0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.^[4] However, pentacene derivatives exhibit photoinduced oxidative instability in an ambient en-

National Central University, Chung-Li, Taiwan (Republic of China) E-mail: mcchen@ncu.edu.tw

[b] Dr. L.-H. Chen,⁺ Dr. J.-Y. Yan, Dr. J.-C. Ho, Dr. C.-C. Lee Process Technology Division, Display Technology Center Industrial Technology Research Institute Hsinchu, Taiwan (Republic of China)

[c] Prof. C. Kim Department of Chemical & Biomolecular Engineering Sogang University, 1 Shinsoo-Dong, Mapo-Gu Seoul 121-742 (Republic of Korea) E-mail: choongik@sogang.ac.kr

- [+] These authors contributed equally to this work.
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vironment, which limits their application in solution processes.^[5] Hence, the development of new heteroacenes with high electrical performance and ambient stability has been of great recent interest. To this end, fused-thiophene-based materials with extensive conjugation, high ambient stability, and strong intermolecular interactions are among the mostinteresting candidates. Recently, several fused-thiophene derivatives with good electrical performance have been reported (Figure 1).^[6-10] Among the available p-channel semiconductors, DP-DTT (A),^[7a] DP-TTA (B),^[7b] DBTDT (C),^[7c] and **BTDT** $(\mathbf{D})^{[8]}$ are representative examples with hole mobilities (μ_h) of up to 0.42, 0.14, 0.51, and >1.0 cm²V⁻¹s⁻¹, respectively. For n-channel semiconductors,^[9] we have developed **DFP-DTT** $(E)^{[9b]}$ and **DFP-TTA** $(F)^{[9c]}$ with electron mobilities (μ_e) as high as 0.07 and 0.3 cm²V⁻¹s⁻¹, respectively. Recently, a few benzo[d,d']thieno[3,2-b;4,5-b']dithiophene derivatives have been reported and, in particular, its phenylend-capped derivative (P-BTDT; G) exhibited excellent electrical performance, with a hole mobility of up to 0.70 cm²V⁻¹s⁻¹.^[7d] Furthermore, good electrical performance has been reported in optimized DTBTE (H)-based OTFTs, with which a carrier mobility of 0.50 cm²V⁻¹s⁻¹ was achieved, as compared to $< 0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with un-optimized **BBTT** (4).^[10] More recently, a **DBTDT** derivative (I) demonstrated excellent electrical performance with a hole mobility of up to 8.8 cm²V⁻¹s⁻¹.^[7f] In addition, good electrical performance, with a mobility of 0.15 cm²V⁻¹s⁻¹, was achieved for **DBTTA** (J)-based thin-film transistors.^[7g]

Herein, we explore new semiconductors that are based on the simple fused-thiophene, benzothieno[3,2-*b*]thiophene (**BTT**). Firstly, we explored a new, simple synthetic method for the preparation of the **BTT** core. Secondly, the molecu-

[[]a] Dr. P.-Y. Huang,⁺ Y.-Y. Chen, W.-J. Chang, J.-J. Wang, Dr. K.-H. Lii, Prof. M.-C. Chen Department of Chemistry

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 μ_h : 0.15 cm² V⁻¹ s⁻¹

Figure 1. Examples of fused-oligothiophene semiconductors that were employed in OTFTs.

lar-structure-property relationships were elucidated by introducing phenyl (**BTT-P**; **2**), benzothiophenyl (**BTT-BT**; **3**), or benzothieno[3,2-*b*]thiophenyl groups (**BBTT**; **4**; dimer of **BTT**) onto the **BTT** core (Figure 2). Thirdly, the crystal structure of **BBTT** was determined by single-crystal X-ray diffraction, which showed ideal molecular-stacking arrangements for charge transport. Finally, the film morphology and microstructure were investigated and correlated with the film-growth conditions as well as device performance. Our



Figure 2. Chemical structures of the benzothieno[3,2-*b*]thiophene (**BTT**; **2–4**) derivatives that were employed in this study.

results revealed that bottom-contact/bottom-gate TFTs that were based on **BBTT** films exhibited good electrical performance, with a carrier mobility as high as $0.22 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, a current on/off ratio of 1×10^7 , and good environmental stability.

Results and Discussion

Synthesis: The benzo[*b*]thieno[2,3-*d*]thiophene (**BTT**)^[11,16] moiety has been synthesized by using various synthetic procedures in various yields. To efficiently obtain the **BTT** core, we developed a new, practically simple synthetic procedure from commercially available benzothiophene in an overall yield of 36% over three steps. As shown in Figure 3, 2,3-dibromobenzothiophene, which was obtained from the bromination of benzothiophene with Br₂ in 90% yield, was alkynylated with trimethylsilylacetylene in a Sonogashira coupling reaction to give 1-(3-bromobenzo[*b*]thiophen-2-yl)-2-trimethylsilylacetylene (**5**) in 80% yield. Annulation and desilylation with Na₂S in *N*-methyl-2-pyrrolidone (NMP) at 190°C gave **BTT** (**1**) in 52% yield. Markedly, our new synthetic route is the fastest and shortest synthetic approach for the preparation of the asymmetric fused ring.



Figure 3. Synthetic route to the BTT core.

The synthesis of functionalized **BTTs** (2–4) was achieved as shown in Figure 4. Deprotonation of **BTT** with *n*BuLi and subsequent alkylstannylation afforded the corresponding 2- SnR_3 -**BTT** derivative in situ, which was coupled with the corresponding aryl bromide in Stille coupling reactions to



Figure 4. Synthetic routes to the new **BTT** derivatives.

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Compound	DSC	TGA	UV/Vis ^[a]	Reductive	Oxidative	ΔE_{gap} [eV]	
	$T_{\rm m} [^{\circ}{\rm C}]$	(5%) [°C]	λ_{\max} [nm]	potential [V] ^[b]	potential [V] ^[b]	UV ^[a]	DPV ^[b]
2	160	189	330	-1.95	1.61	3.32	3.56
3	230	253	366	-1.91	1.48	3.04	3.39
4	334	313	388	-1.89	1.27	2.91	3.16
2'	258	255	358	-1.93	1.33	3.17	3.26
3'	341	309	378	-1.86	1.30	2.99	3.16
4'	461	471	411	-1.75	1.14	2.74	2.89

Table 1. Thermal, optical absorption/emission, and electrochemical data for BTTs 2-4.

[a] In o-C₆H₄Cl₂. [b] By DPV in o-C₆H₄Cl₂ at 50 °C.

give compounds **2–4** in crude yields of 70, 75, and 72%, respectively. These **BTTs** were further purified by gradient sublimation at a pressure of about 1×10^{-5} Torr at 190–255 °C to give materials that were suitable for the fabrication of OTFT devices in a yield of about 50%.

Thermal and optical properties: For three new **BTT** derivatives, differential scanning calorimetry (DSC) exhibited sharp endotherms above 160°C, and thermogravimetric analysis plots only showed weight loss (about 5%) upon heating above 189°C (Table 1). Although the melting temperatures of these **BTT**s are lower than those of **BTDT**s (Figure 5),^[7d] both **BTT**s and **BTDT**s show excellent thermal stability among heteroacenes.



Figure 5. Chemical structures of the **BTDT** derivatives (2'-4'); see ref. [7d].

In particular, **BTT**-capped **BBTT** (4) exhibited the highest melting point (334 °C) and highest weight-loss temperature (313 °C) among the **BTT** series. The optical absorption spectra of compounds **BTT-P** (2; $\lambda_{max} \approx 330$ nm), **BTT-BT** (3; $\lambda_{max} \approx 366$ nm), and **BBTT** (4; $\lambda_{max} \approx 388$ nm) were significantly blue-shifted compared to those of their corresponding **BTDT** derivatives (2', 3', and 4'; $\lambda_{max} \approx 358$, 378, and 411 nm, respectively) in *o*-C₆H₄Cl₂ (Figure 6). Compared to the phenyl- or benzothiophenyl-capped **BTT**s, greater π -electron delocalization (between the two **BTT** moieties) was observed for the benzothieno[3,2-*b*]thiopheyl-substituted **BBTT** (4), which gave the latter compound the lowest HOMO–LUMO energy gap among the **BTT** derivatives (Table 1).

The HOMO-LUMO energy gaps that were calculated from the onset of the experimental optical absorption (2.91–3.32 eV) increased in the order: **BBTT** (4) < **BTT-BT** (3) < **BTT-P** (2), which was consistent with the electrochemically derived HOMO-LUMO gaps (see below). Notably, the



Figure 6. Optical spectra of the BTT (2–4) and BTDT derivatives (2'–4') in $\it o\text{-}C_6H_4Cl_2.$

BTTs exhibit much lower HOMOs (>5.47 eV) as well as significantly larger HOMO–LUMO gaps (>3.16 eV) in comparison with those of pentacene (about 5.0 eV; 1.70–2.09 eV) or anthradithiophene (**ADT**) derivatives (about 5.1 eV; 2.09–2.57 eV),^[12] which suggests that the **BTT** derivatives are not easily oxidized and may have better stability under ambient conditions compared to pentacene and **ADT** derivatives. Hence, the photo-oxidative stability of the **BTT** derivatives was investigated by monitoring the absorbance decay at the λ_{max} of solutions of **BTTs** in aerated *o*-C₆H₄Cl₂ that were exposed to the white light of a fluorescent lamp at room temperature. Under these conditions, no decomposition was observed for all of the **BTTs** after five days, thus demonstrating the good ambient stability of these materials.

Electrochemical characterization: Differential pulse voltammetry (DPVs) of the BTT derivatives was performed in dichlorobenzene at 50°C and the resulting oxidation and reduction potentials are summarized in Table 1. The DPVs of BTT-P and BTT-BT exhibited oxidation peaks at about +1.61 and +1.48 V, respectively (versus ferrocene/ferrocenium as an internal standard at +0.6 V). In comparison, the oxidation potential of the more-conjugated BBTT (4) was shifted to a less-positive value than those for compounds 2 and 3 ($E_{ox} = +1.27$ V). Similarly, the E_{ox} values of the **BTT** derivatives (+1.61 to +1.27 V) were shifted to more-positive values than those of their corresponding BTDTs (+1.33 to +1.14 V), which can be attributed to the lower degree of molecular conjugation of the BTT core. The electrochemically derived HOMO-LUMO energy gaps that were obtained from the DPV data were in the order: BBTT

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Figure 7. DPV-derived HOMO and LUMO energy levels of BTTs 2-4 and pentacene (Pen).

(3.16 eV) < BTT-BT (3.39 eV) < BTT-P $(3.56 \text{ eV}; \text{ assuming ferrocene/ferrocenium oxidation at 4.8 eV; Figure 7), which was consistent with the values that were obtained from optical spectroscopy, that is,$ **BBTT**<math>(2.91 eV) < BTT-BT (3.04 eV) < BTT-P (3.32 eV; Table 1). The significantly lower HOMO energy levels and the larger band-gaps of these three new **BTTs** compared to pentacene suggest that these newly developed fused thiophenes are environmentally very stable (see above).

Single-crystal X-ray diffraction: The diffraction-derived single-crystal structure of **BBTT** is shown in Figure 8 and the Supporting Information, Figure S1, and detailed crystal-lographic data are summarized in the Supporting Information, Table S1. As shown, **BBTT** crystallizes in monoclinic space group $P2_1/c$, with unit-cell parameters of a = 14.1293(6), b = 3.9653(2), c = 15.0241(6) Å; a = 90.00, $\beta = 111.527(2)$, $\gamma = 90.00^\circ$; Z = 2.



Figure 8. Crystal structure of **BBTT**: A), B) two orthogonal views; distance [Å] and the dihedral angle [°] of two **BTT** moieties are shown in (A). C) Molecular stacking of **BBTT** molecules, which adopted an edge-to-face packing with a herringbone angle of 54.2°. D)–F) Three orthogonal views of the space-filling model; selected S–S/C–C distances [Å] are indicated.

The fused-phenylene moiety is almost coplanar with the two fused thiophenes and the two **BTT** moieties in a single molecule are coupled in a completely flat geometry with a separation of 1.45 Å and a dihedral angle of 0° (Figure 8A and B). The intermolecular distance between adjacent **BBTT** planes is 3.53 Å (Figure 8C). Similar to other fused thiophenes,^[7] the unit cell of **BBTT** exhibits a commonly observed edge-to-face herringbone packing motif with an intermolecular packing angle of approximately 54.2° (Figure 8C). The molecular sheets are stacked along the *b* axis and the interactions are reinforced by close interplanar S–S and S–H contacts. The shortest intermolecular S–H distance be-

tween the edge-to-face **BBTT** molecules is approximately 3.17 Å (not shown), with a shortest intermolecular S–S distance of 3.97 Å (Figure 8G). The planar molecular structure and short stacking distance afford ideal conditions for extended π -orbital interactions of the corresponding molecules.

Thin-film transistors: Bottom-contact/bottom-gate OTFT devices were fabricated by the thermal evaporation of a gold source and drain contacts (channel length: $100 \,\mu\text{m}$, width: $500 \,\mu\text{m}$), followed by vacuum deposition (1.6×10^{-6} Torr) of each compound onto OTS-treated SiO₂/Ag ($100 \,\text{nm}/100 \,\text{nm}$) substrates at preset deposition temperatures (T_D). The TFT properties were tested under ambient conditions to explore the device performance. All TFT data, including carrier mobility, current on/off ratio, and threshold voltage, are summarized in Table 2 and representative transfer and output plots are shown in Figure 9 (for compound 4) and in the Supporting Information, Figure S2 (for compounds 2 and 3).

Devices that were fabricated from these **BTT** derivatives all exhibited TFT activity, thus performing as p-channel semiconductors. Of the compounds that were developed in this study, compound **4** (**BBTT**), which had the largest degree of conjugation, exhibited the highest device performance, with

Table 2. Carrier mobilities (μ), current on/off ratios (I_{on}/I_{off}), and threshold voltages (V_T) for OTFTs that were fabricated by the vacuum deposition of compounds **2–4** on OTS-treated substrates at the indicated deposition temperatures (T_D).

Compound	$T_{\rm D} \left[{}^{\circ} \mathrm{C} \right]$	$\mu [\mathrm{cm}^2 \mathrm{V}^{-1} \mathrm{s}^{-1}]$	$I_{\rm on}/I_{\rm off}$	$V_{\mathrm{T}}\left[\mathrm{V} ight]$
2	30	0.001	10^{6}	-5.4
	50	0.008	10^{7}	-6.5
	80	0.012	107	-9.5
3	30	0.01	10^{6}	-1.8
	50	0.05	10^{7}	-1.2
	80	0.10	10^{7}	-2.4
4	30	0.08	10^{6}	-5.4
	50	0.13	10^{7}	-2.5
	80	0.22	10^{7}	-4.2



Figure 9. Transfer ($V_{\rm DS} = -16$ V) and output plots of an OTFT device that was fabricated from **BBTT** (4) films that were grown on an OTS-coated SiO₂ substrate ($T_{\rm D} = 80$ °C, channel length: 100 µm, channel width: 500 µm). Inset: structure of the OTFT device.

hole mobilities of $0.08-0.22 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and current on/off ratios of $1 \times 10^6 - 1 \times 10^7$ (Figure 9). Compounds **2** and **3** showed poorer device performance than compound **4**, with carrier mobilities of $0.001-0.012 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and 0.01- $0.12 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. The current on/off ratios of compounds **2** and **3** were comparable to those of compound **4**. Furthermore, the derived carrier mobilities of the **BTT** derivatives strongly depended upon the deposition temperature (T_{D}). Within the range $T_{\text{D}}=30-80$ °C, enhanced device performance was observed at higher deposition temperatures. A clear correlation between μ and T_{D} was also evident in the XRD and AFM characterization data of the corresponding semiconductor films (see below).

Thin-film microstructure and morphology: Vacuum-deposited film crystallinity and surface morphology are often used to evaluate device performance. In general, high device performance, in particular in terms of carrier mobility, is obtained for films that show high crystallinity and large grain size with enhanced interconnectivity.^[1,7d] Thus, the thin-film microstructures and morphologies of this new class of materials were studied by wide-angle $\theta/2\theta$ XRD and AFM. Conventional $\theta/2\theta$ XRD scans were performed to obtain out-ofplane d-spacings in the vacuum-deposited thin films on OTS-coated SiO₂ substrates at various $T_{\rm D}$ values. The thicknesses of all of these films were determined to be about 50 nm by using profilometry. Representative XRD scans of thin films of these BTT derivatives are shown in Figure 10 (for compound 4) and in the Supporting Information (for compounds 2 and 3).



Figure 10. The $\theta/2\theta$ XRD scans of **BBTT** (4) films that were vapor-deposited at the indicated $T_{\rm D}$ values on OTS-coated SiO₂ substrates.

The $\theta/2\theta$ XRD scans of films of **BBTT** (4; Figure 10) indicated the formation of highly textured films with high peak intensities, which were consistent with good TFT performance (see above). The first reflection in the XRD spectrum was observed at $2\theta = 5.63^{\circ}$, which corresponded to a *d*-spacing of 15.7 Å, that is, slightly smaller than the molecular length of the corresponding molecule (16.6 Å). This result indicates that the films might be predominantly aligned such that their long molecular axes are along the substrate normal, with a certain degree of tilt angle. Films of **BTT-BT** (3), with good carrier mobility (slightly lower than that of **BBTT**), showed similar XRD patterns, with slightly lower peak intensities than those of **BBTT** (see the Supporting Information, Figure S3 A). Films of **BTT-P** (2), with poor TFT mobility, exhibited low XRD peak intensities, thus indicating low film texturing (see the Supporting Information, Figure S3B). This low film texturing is possibly due to compound 2 having the lowest degree of molecular conjugation among the **BTT** series considered in this study. The *d*-spacings of the **BTT-BT** and **BTT-P** films (at $2\theta = 6.36^{\circ}$ and 6.93° for the first reflections) were 13.9 and 12.7 Å, respectively, which were smaller than that of **BBTT**.

Because the TFT performance was quite sensitive to the deposition temperature (see above), $T_{\rm D}$ -dependent XRD patterns were also examined. There was a clear correlation between the mobility values and the XRD peak intensity. As $T_{\rm D}$ increased, the XRD peak intensities for the films of all of the compounds (with the same thickness, about 50 nm) increased and sharpened (Figure 10 and the Supporting Information), as did the TFT carrier mobility (see above).

It is challenging to characterize the dielectric/semiconductor interface, at which charge transport in the TFTs occurs, by using conventional experimental techniques. Hence, the surface morphologies of organic semiconductor thin films (50 nm), at which information about the underlying microstructure at the interface is conveyed, were characterized by AFM (Figure 11). Films of **BTT-P** and **BTT-BT** exhibited



Figure 11. A) AFM images $(5 \times 5 \ \mu m^2)$ of films of: A) **BTT-P** (2), B) **BTT-BT** (3), and C) **BBTT** (4) on OTS-coated SiO₂ substrates that were grown at the indicated T_D values. Scale bars: 1 μm .

small ball-shaped grains, whereas films of **BBTT** showed rod-like morphologies. Furthermore, similar to the XRD patterns, the surface morphologies of the films also showed a strong dependence on the $T_{\rm D}$ value and correlated with the device performance (see above). At high substrate temperatures, films of **BTT-P** and **BTT-BT** exhibited larger grain sizes (Figure 11 A and B) than at low $T_{\rm D}$ values.^[13] Similarly, films of **BBTT** also showed rod-like morphologies with larger lengths and diameters at higher $T_{\rm D}$. The large surface features of all of the thin films at the higher deposi-

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tion temperature correlated well with their enhanced TFT performance.

Conclusion

A new family of benzothieno[3,2-b]thiophene-based semiconductors was synthesized and characterized. Thin-film transistors that were fabricated from these molecules exhibited decent device performance and excellent air stability. Films that were deposited onto OTS-coated SiO₂ substrates under properly adjusted substrate temperatures achieved an efficacious compromise between high film crystallinity and good film-grain interconnectivity, thereby resulting in high OTFT performance, with mobilities as high as $0.22 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and current on/off ratios as high as 1×10^7 . In particular, our study with optimized device-fabrication conditions showed a 30-70-fold increase in carrier mobility for **BBTT** films, in comparison to the results (carrier mobilities of 0.003–0.007 $cm^2 V^{-1} s^{-1}$) in the literature.^[10]

Experimental Section

Materials and methods: All chemicals and solvents (Aldrich, Arco, or TCI Chemical Co.) were of reagent grade. The reaction solvents (toluene, diethyl ether, and THF) were distilled under a nitrogen atmosphere from sodium/benzophenone ketyl and halogenated solvents were distilled from CaH₂. ¹H and ¹³C NMR spectra were recorded on Bruker 300 or 500 instruments and were referenced to solvent signals. Differential scanning calorimetry (DSC) was performed on a Mettler DSC 822 instrument at a scan rate of 10 K min⁻¹. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 thermal analysis system by using dry nitrogen as the carrier gas at a flow rate of 10 mLmin⁻¹. UV/Vis absorption and fluorescence spectra were obtained in the indicated solvents at RT on JASCO V-530 and Hitachi F-4500 spectrometers, respectively. IR spectra were obtained on a JASCO FT/IR-4100 spectrometer. Differential pulse voltammetry (DPV) experiments were performed with a conventional three-electrode configuration (platinum-disk working electrode. an auxiliary platinum-wire electrode, and a non-aqueous silver reference electrode) with a supporting electrolyte of 0.1 m tetrabutylammonium hexafluorophosphate (TBAPF₆) in the specified dry solvent on a CHI621C Electrochemical Analyzer (CH Instruments). All electrochemical potentials were referenced to an Fc⁺/Fc internal standard (at +0.6 V). Elemental analysis was performed on a Heraeus CHN-O-Rapid elemental analyzer. Mass spectrometry was performed on a JMS-700 HRMS instrument. 3-Bromobenzo[b]thiophene^[14] and 2,3-dibromobenzo[b]thiophene^[15] were prepared according to literature procedures. Benzothieno-[3,2-*b*]thiophene^[16] was prepared according the following new routes:

New synthetic route to benzothieno[3,2-*b*]thiophene (BTT; 1): Under a nitrogen atmosphere and anhydrous conditions, a solution of 2,3-dibro-mobenzo[*b*]thiophene (1.0 g, 3.43 mmol) in triethylamine (50 mL), [Pd-(PPh₃)₂Cl₂] (120.2 mg, 0.171 mmol), CuI (65.2 mg, 0.343 mmol), and trimethylsilylacetylene (344 mg, 3.43 mmol) was heated at reflux for 19 h.^[17] Water was added to quench the reaction and the solvent was removed. The organic fraction was extracted with diethyl ether, filtered through a short column of celite, and then dried with anhydrous Na₂SO₄. The desired product was distilled at 80 °C under vacuum (10⁻³ Torr) to give 1:(3-bromobenzo[*b*]thiophen-2-yl)-2-trimethylsilylacetylene as a white solid (790 mg, 75 %). ¹H NMR (CDCl₃, 300 MHz): δ = 7.75 (m, 2H), 7.44 ppm (m, 2H); ¹³C NMR (CDCl₃, 75 MHz): 138.09, 137.26, 126.65, 125.45, 123.77, 122.22, 120.24, 114.35, 106.00, 96.06, -0.23 ppm; elemental analysis calcd for C₁₃H₁₃S₂BrSSi: HRMS (FAB): *m/z* calcd for C₁₃H₁₃S₂BrSSi: 307.9691 [*M*]⁺ (⁸¹Br).

Under a nitrogen atmosphere, a solution of 1-(3-bromobenzo[*b*]thiophen-2-yl)-2-trimethylsilylacetylene (112 mg, 0.363 mmol) and Na₂S·9H₂O (174.4 mg, 0.726 mmol) in NMP (15 mL) was stirred at 190°C for 12 h. A saturated aqueous solution of NH₄Cl was added to the reaction mixture and the organic fraction was extracted several times with hot hexanes, washed with a saturated aqueous solution of NaCl, and dried with anhydrous Na₂SO₄. The crude product was purified by column chromatography on silica gel (hexanes) to give the product as a white solid (36 mg, 52%). ¹H NMR (CDCl₃, 300 MHz): δ =7.87 (m, *J*=1.5 Hz, 1H), 7.84 (m, *J*=1.5 Hz, 1H), 7.51 (d, *J*=5.4 Hz, 1H), 7.4 (m, 2H), 7.32 (d, *J*=5.4 Hz, 1H).

Synthesis of 2-biphenylbenzothieno[3,2-b]thiophene (BTT-P; 2): Under a nitrogen atmosphere and anhydrous conditions at 0°C, nBuLi (0.75 mL, 2.5 M in hexanes, 1.86 mmol) was slowly added to a solution of BTT (354 mg, 1.86 mmol) in THF (30 mL) and the mixture was stirred for 40 min. Next, tri-n-butyltin chloride (0.67 g, 2.05 mmol) was added and the mixture was stirred at 0°C for 30 min, warmed to RT, and stirred for a further 8 h. After simple filtration under a nitrogen atmosphere, THF was removed under vacuum and toluene (40 mL) was added. This solution was transferred into a solution of 4-bromobenzene (292 mg, 1.86 mmol) and tetrakis(triphenylphosphine)palladium (129 mg, 0.11 mmol) in toluene (40 mL) and the mixture was heated at reflux (140°C) for 2 days. After cooling to RT, the mixture was filtered through a column of celite; toluene was used to extract the product from the celite pad. The combined toluene solution was evaporated and the desired product was recrystallized from hexanes to give the crude product in 75% yield. The product was further purified by gradient sublimation at a pressure of about $\times 10^{-5}$ Torr at 190°C, thus giving the product as a bright-yellow solid (336 mg, 68%). M.p. 160 °C; ¹H NMR (CDCl₃, 300 MHz): δ=7.85 (dd, J=7.5, 3.6 Hz, 2H), 7.69 (d, J=7.2 Hz, 2H), 7.54 (s, 1H), 7.46–7.32 ppm (m, 5H); ¹³C NMR (75 MHz; CDCl₃): 147.09, 142.20, 138.56, 134.48, 133.81, 132.77, 129.04, 128.03, 125.86, 124.73, 124.39, 123.80, 120.86, 116.11 ppm; elemental analysis calcd for C₁₆H₁₀S₂: C72.14, H 3.78; found: C 72.09, H 3.85; HRMS (EI): m/z calcd for C₁₆H₁₀S₂ 266.0224 [M]+; found: 266.0219.

Synthesis of 2-benzothiophenylbenzothieno[3,2-b]thiophene (BTT-BT; 3): The synthetic procedure was similar to that for BTT-P (2), except that 2-bromobenzothiophene (397 mg, 1.86 mmol) was used instead of 4-bromobenzene. After similar work-up steps, the desired product was purified by gradient sublimation at a pressure of about $\times 10^{-5}$ Torr at 240 °C, thus giving the product as a green–yellow solid (312 mg, 52%). M.p. 230 °C; ¹H NMR (CDCl₃, 300 MHz): δ =7.87–7.75 (m, 4H), 7.52 (s, 1H), 7.50 (s, 1H), 7.44–7.33 ppm (m, 4H); this material was insufficiently soluble to obtain a useful ¹³C NMR spectrum; elemental analysis calcd for C₁₈H₁₀S₃: C 67.04, H 3.13; found: C 67.09, H 3.08; HRMS (EI): *m*/*z* calcd for C₁₈H₁₀S₃: 321.9945 [*M*]⁺; found: 321.9940.

Synthesis of bisbenzothieno[3,2-*b*]thiophene (BBTT; 4): At 0 °C, a solution of BTT (5.30 g, 0.028 mol) and *N*-bromosuccinimide (NBS, 5.45 g, 0.031 mol) in THF (175 mL) was stirred for 30 min, then warmed to RT and stirred for a further 12 h. NaHSO₄ was added to the reaction mixture, followed by a saturated aqueous solution of NaCl. The organic fraction was extracted with diethyl ether and dried with anhydrous MgSO₄. 2-Bromobenzothieno[3,2-*b*]thiophene was obtained after column chromatography on silica gel (hexanes) as a white solid (7.24 g, 96%).^[18] The product was used in the next step without further purification. ¹H NMR (CDCl₃, 300 MHz): δ =7.84 (d, *J*=8.1 Hz, 1 H), 7.77 (d, *J*=6.3 Hz, 1 H), 7.44–7.33 (m, 2 H), 7.32 pm (s, 1 H).

The subsequent synthetic procedure was similar to that for **BTT-P**, except that 2-bromobenzothieno[3,2-*b*]thiophene was used instead of 4-bromobenzene. After similar work-up steps, the desired product (72% crude yield) was purified by gradient sublimation at a pressure of about $\times 10^{-5}$ Torr at 255°C, thus giving the product as a bright-yellow solid (254 mg, 51%). M.p. 334°C; this material was insufficiently soluble to obtain useful ¹H or ¹³C NMR spectra; elemental analysis calcd for C₂₀H₁₀S₄: C 63.46, H 2.66; found: C 63.40, H 2.73; HRMS (EI): *m/z* calcd for C₂₀H₁₀S₄: 377.9665 [*M*]⁺; found: 377.9655.

X-ray crystal-structure determination of BBTT: Yellow crystals that were suitable for X-ray diffraction were crystallized from a hot solution of

BBTT in toluene. The chosen crystals were mounted onto a glass fiber. Data collection for **BBTT** was performed on a Bruker Smart Apex2 CCD diffractometer with Cu_{Ka} radiation ($\lambda = 1.54178$ Å) at 293(2) K. After data collection, the frames were integrated and absorption corrections were applied. The initial crystal structure was solved by using direct methods, the structure solution was expanded through successive least-squares cycles, and the final solution was determined. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms that were attached onto carbon atoms were fixed at calculated positions and refined by using a riding mode. Crystal data, data collection, and refinement parameters are summarized in the Supporting Information, Table S1 (CCDC-911203 (**BBTT**) the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Device fabrication and characterization: For the fabrication of bottomcontact/bottom-gate OTFTs, silver (100 nm) was deposited by sputtering onto a glass substrate as a bottom-gate electrode, as patterned by a shadow mask. Then, a SiO₂ layer (100 nm) was thermally deposited as a gate dielectric onto the bottom-gate electrode. For treatment with OTS (octadecyltrichlorosilane), the SiO_2 surface was exposed to a solution of OTS in toluene in a self-assembly chamber for 10 h to give a hydrophobic surface with an advancing aqueous contact angle of about 105°. A gold layer (thickness: 100 nm) was thermally evaporated through a shadow mask to define the source and drain contacts with a channel length and width of 100 and 500 µm, respectively. Subsequently, an organic semiconductor layer (50 nm) was thermally evaporated through a shadow mask onto substrates that were held at a predetermined temperature of 30, 50, or 80 °C at a rate of 0.03 nm s⁻¹. All of the vacuum-deposition processes were performed at a pressure of about 1.6×10^{-6} Torr. The film thicknesses were measured on a Dektak 3030 profilometer. The capacitance of the gate insulators were measured on a HP 4284A Precision LCR meter. The I-V characteristics of the OTFTs were measured in the dark on a semiconductor parameter analyzer (HP 4155A) for at least 10 different devices. All of the films were examined by X-ray diffraction (XRD, Siemens D5000) with $Cu_{K\alpha}$ radiation. The surface morphology was characterized by using atomic force microscope (AFM, Digital Instruments Nanoscope III).

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