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Consecutive Thiophene-Annulation Approach to π-Extended Thienoacene-Based Organic Semiconductors with [1]Benzothieno[3,2-*b*][1]benzothiophene (BTBT) Substructure

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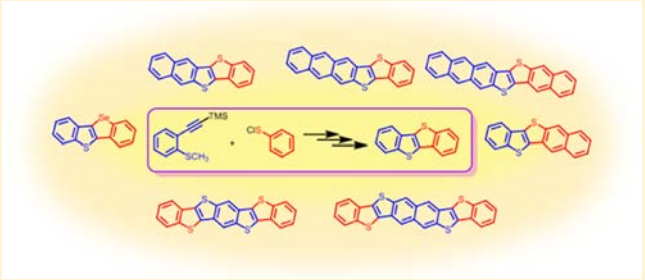
Supporting Information

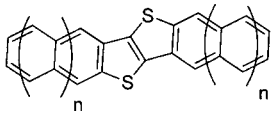
ABSTRACT: We describe a new synthetic route to the [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT) substructure featuring two consecutive thiophene-annulation reactions from *o*-ethynyl-thioanisole substrates and arylsulfenyl chloride reagents that can be easily derived from arylthiols. The method is particularly suitable for the synthesis of unsymmetrical derivatives, e.g., [1]benzothieno[3,2-*b*]naphtho[2,3-*b*]-thiophene, [1]benzothieno[3,2-*b*]anthra[2,3-*b*]thiophene, and naphtho[3,2-*b*]thieno[3,2-*b*]anthra[2,3-*b*]thiophene, a selenium-containing derivative, [1]benzothieno[3,2-*b*][1]-benzoselenophene. It also allows us to access largely π-extended derivatives with two BTBT substructures, e.g., bis[1]benzothieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene and bis[1]benzothieno[2,3-*d*:2′,3′-*d*′]naphtho[2,3-*b*:6,7-*b*′]dithiophene (BBTNDT). It should be emphasized that these new BTBT derivatives are otherwise difficult to be synthesized. In addition, since various substrates and reagents, *o*-ethynyl-thioanisoles and arylthiols, respectively, can be combined, the method can be regarded as a versatile tool for the development of thienoacene-based organic semiconductors in this class. Among the newly synthesized materials, highly π-extended BBTNDT afforded very high mobility (>5 $cm^2\ V^{-1}\ s^{-1}$) in its vapor-deposited organic field-effect transistors (OFETs), which is among the highest for unsubstituted acene- or thienoacenes-based organic semiconductors. In fact, the structural analyses of BBTNDT both in the single crystal and thin-film state indicated that an interactive two-dimensional molecular array is realized in the solid state, which rationalize the higher carrier mobility in the BBTNDT-based OFETs.



INTRODUCTION

Highly extended polyacenes, such as pentacene[1] and naphthacene,[2] have been prototypical organic semiconductors applicable to the high-performance organic field-effect transistors (OFETs). In fact, they have driven the field of organic electronics in the past decade.[3] Although the carrier mobility of such polyacenes-based OFETs is generally enhanced by increasing the number of fused aromatic rings, too large polyacenes,[4] e.g., hexacene[5,6] and heptacene,[7] are not chemically stable,[7] unless bulky groups that kinetically protect them from possible reactions are substituted, which makes their devices less stable under ambient conditions, preventing the practical use of the larger polyacenes-based OFETs.[6] In order to avoid such instability of simple hydrocarbon-based large acenes, heteroaromatics, thiophene among others, are incorporated into the acene structures, affording thienoacens,[8] which in many cases realizes good stability and enables high carrier mobility simultaneously.

Among a vast numbers of the thienoacene-based organic semiconductors,[9] diacene-fused thieno[3,2-*b*]thiophenes (DAcTTs) represented by [1]benzothieno[3,2-*b*][1]-benzothiophene (BTBT)[10] and dinaphtho[2,3-*b*:2′,3′-*f*]thieno-[3,2-*b*]thiophene (DNTT) derivatives[11] are one of the most promising organic semiconductors owing to their excellent stability and high mobility (>1.0 $cm^2\ V^{-1}\ s^{-1}$) in various transistor architectures (Figure 1).[12,13] Such superior properties can be rationalized by their low-lying HOMO energy levels (stability)[14] and interactive solid-state structure enabling intermolecular large orbital overlap (high mobility). For



n = 0: BTBT
n = 1: DNTT
n = 2: DATT

Figure 1. Molecular structures of diacene-fused thieno[3,2-*b*]-thiophenes.

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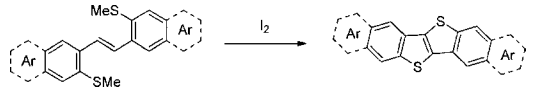
Scheme 1. Conventional Synthesis of BTBT and Its Related Compounds



realizing these, the thieno[3,2-*b*]thiophene substructure incorporated into the acene framework plays important roles,[8] and thus, to develop related DAcTTs is a promising approach to create new superior materials for OFETs.

The synthesis of DAcTTs are generally attained by the iodine-promoted cyclization of *o*-bis(methylthio)stilbene precursors (Scheme 1) to form the BTBT substructure,[15] the merit of which is in fact manifold: a straightforward synthesis with good reproducibility, applicability to selenium analogues,[11a,16] and amenability to two-fold reactions affording largely π-extended thienoacenes, such as bis[1]benzothieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (BBTBDT) and bis(naphtho[2,3-*b*]thieno)[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (BNTBDT).[17] On the other hand, a drawback of the method associated with relatively poor accessibility of the *o*-bis(methylthio)stilbene precursors limits the material diversity. The low synthetic yields in the two-fold reactions[17] also prevent the practical access to the largely extended derivatives with plural thienothiophene moieties. In addition, although unsymmetrical BTBT derivatives have recently been revealed as promising organic semiconductors showing very high mobility and good thermal stability,[11c,d] the conventional method based on the iodine-promoted cyclization illustrated in Scheme 1 may not be amenable to the synthesis of unsymmeterical derivatives. It is thus very important to devise new synthetic approaches to the BTBT substructure, the most basic structure of DAcTTs, for further material developments in this class.

With these motivations, we first describe a new synthetic approach to parent BTBT and then its application to the synthesis of various BTBT-based compounds including unsymmetrical, selenium-containing, or largely π-extended ones with two-fold thieno[3,2-*b*]thiophene moieties (Figure 2). In addition to the synthetic works, we have characterized new BTBT-based materials and found that among the newly developed materials, bis[1]benzothieno[2,3-*d*:2′,3′-*d*′]naphtho[2,3-*b*:6,7-*b*′]dithiophene (BBTNDT) with eight aromatic rings is a superior organic semiconductor that affords excellent thin-film transistors showing very high field-effect mobility (>5 $cm^2 V^{-1} s^{-1}$).

RESULTS AND DISCUSSIONS

Synthesis. *Synthesis of Parent BTBT As a Model Synthesis.* For the development of a new method for the synthesis of the BTBT framework, we designed a strategy

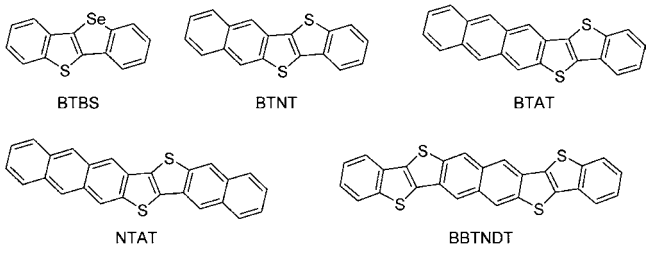
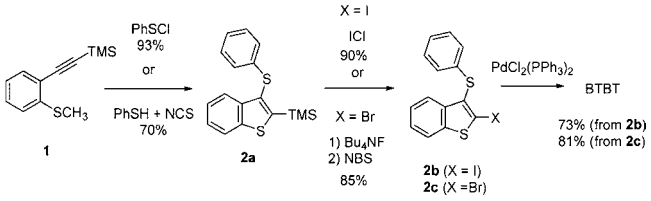


Figure 2. New BTBT derivatives targeted in the present work.

Scheme 2. New BTBT Synthesis via the Consecutive Thiophene-Annulation Reactions



consisting of two consecutive thiophene-annulation (thienannulation) reactions (Scheme 2). The initial one is the Larock reaction from readily available *o*-ethynylthioanisoles with an electrophile:[18] When the reaction is carried out with phenylsulfenyl chloride as the electrophile, the product, 3-phenylthiobenzo[*b*]thiophene, contains all the carbon and sulfur atoms needed for constructing the BTBT framework. The intermediate is then supposed to be further cyclized into the BTBT framework via an intramolecular aryl−aryl coupling.[19]

According to the strategy, we first examined the synthesis of parent BTBT from *o*-[2-(trimethylsilyl)ethynyl]thioanisole (**1**).[18] The first cyclization with phenylsulfenyl chloride (PhSCl) proceeded smoothly to afford corresponding 2,3-disubstituted benzo[*b*]thiophenes (**2a**) in an excellent yield.[18] Since PhSCl is not commercially available, we also carried out the reaction with in situ generated PhSCl from benzenethiol and *N*-chlorosuccinimide (NCS).[20] Although the isolated yield was slightly reduced, **2a** was obtained in an acceptable yield (70%). Then the α-TMS group in **2a** can be converted into the iodine (**2b**) by an action of iodine monochloride (ICl)[21] or bromide group (**2c**) by deprotection of the TMS group followed by a reaction with *N*-bromosuccinimide. The final palladium catalyzed intramolecular aryl−aryl coupling to build the second benzo[*b*]thiophene moiety also proceeded smoothly to afford BTBT in 73% (from **2b**) or 81% yield (from **2c**). Note that the final step is a relatively rare example of intramolecular aryl−aryl coupling to construct a thiophene ring (Scheme 2).[19]

With the successful synthesis of BTBT, we confirmed that the new synthetic strategy is useful. At the same time, we also recognized that the method inherently includes "synthetic flexibility", as various substrates and reagents can be chosen and combined. We thus applied the method to the synthesis of: (i) [1]benzothieno[3,2-*b*][1]benzoselenophene (BTBS) by using commercial phenyl selenenyl chloride; (ii) unsymmetrical BTBT derivatives with five-, six-, or seven-fused aromatic ring systems by employing naphthalene- and/or anthracene-based substrate and reagent; and (iii) largely extended derivatives with two thieno[3,2-*b*]thiophene moieties by using substrates with two-fold cyclization sites.

Synthesis of BTBS. For the synthesis of BTBS, in which one of two thiophene rings in BTBT is substituted by selenophene, the reagent in the first step was changed from PhSCl to phenylselenenyl chloride (Scheme 3). The first cyclization afforded corresponding 2,3-disubstituted benzo[*b*]thiophenes (**3a**) in a very high yield.[18] Conversion of **3a** to the corresponding idodide (**3b**) by an action of ICl,[21] however, gave 2,3-diiodebenzo[*b*]thiophene as a byproduct, which reduces the yield of desired **3b** to 54% yield. Instead, a reaction of iodine with in situ generated α-lithium intermediate after the desilylation with tetrabutylammonium fluoride gave

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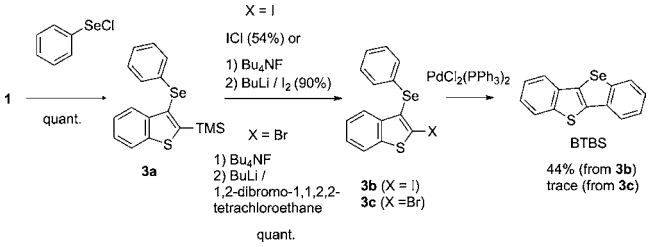
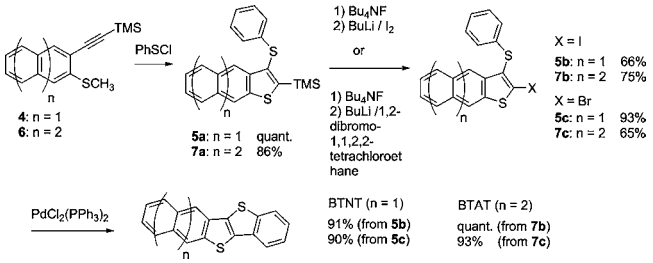
Scheme 3. Synthesis of BTBS



the desired **3b** in 90% isolated yield. The corresponding bromide (**3c**) can be also synthesized by the same sequence. The selenophene ring annulation via the palladium catalyzed intramolecular coupling was found to be less effective compared to the thiophene ring formation. In the case of the iodide precursor (**3b**), BTBS can be obtained in a moderate yield (44%), whereas the selenophene-annulation reaction from the bromide precursor (**3c**) proceeded very slowly, and virtually only a trace amount of BTBS was detected from the reaction mixture.

Synthesis of Unsymmetrical BTBT Derivatives. To develop new π-extended derivatives with unsymmeterical structures, [1]benzothieno[3,2-*b*]naphtho[2,3-*b*]thiophene (BTNT)[22] and -anthra[2,3-*b*]thiophene (BTAT), we employed 2-methylthio-3-(trimethylsilyl)ethynyl-naphthalene (**4**) and -anthracene (**6**), respectively, as the substrates combined with the PhSCl reagent (Scheme 4). Different from the above BTBT synthesis in Scheme 2, the direct iodination of **5a** and **7a** using ICl did not afford the desired 2-iodo intermediates (**5b** and **7b**), owing to the preferential chlorination on the naphthalene or anthracene part as the major reaction.[23] Alternatively, two-step iodination and bromination consisting of the initial desilylation followed by lithiation and electrophilic halogenation was carried out to obtain **5b**, **7b** (iodides) and **5c**, **7c** (bromides), and the second cyclization gave the corresponding thienoacenes (BTNT and BTAT) in good yields regardless of the halogen functionality.

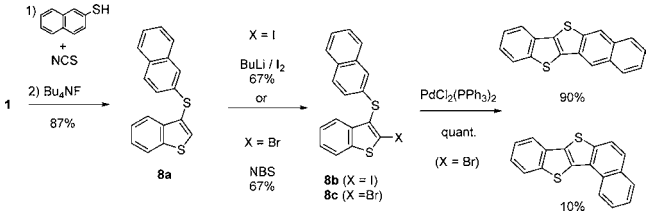
Scheme 4. Synthesis of Unsymmetrical Thienoacenes



From these results, it is obvious that the present approach is quite suitable for the synthesis of unsymmetrical BTBT derivatives. On the other hand, compared to versatility of the substrate, i.e., *o*-[(trimethylsilyl)ethynyl]thioanisole derivatives, the reagent, arylsulfenyl chloride, is rather limited, especially for one with π-extended structure. Thus, to extend the utility of the present method, we examined 2-naphthylsulfenylchloride in situ generated from 2-naphthalenethiol and NCS, where *o*-[2-(trimethylsilyl)ethynyl]thioanisole (**1**) was employed as the substrate (Scheme 5).

As shown in Scheme 5, the initial benzo[*b*]thiophene formation gives **8a**, and the following halogenation proceeded

Scheme 5. BTNT Synthesis via a "Reverse" Combination of the Substrate and Reagent



smoothly to give the precursors (**8b** and **8c**) for the second thienannulation reaction. The precursors, however, have two possible reaction sites, i.e., 1- or 3- position on the naphthalene, likely producing an isomeric mixture. We first examined the reaction from **8b**, but to our surprise, the reaction proceeded very slowly, and during prolonged reaction time, the iodine atom was cleaved off to afford **8a** as the major product. On the contrary, with the bromide (**8c**) as the precursor, the annulation reaction proceeded smoothly, and almost a quantitative amount of the cyclized product was obtained. Its ^{1}H NMR spectrum (Figure 3a) clearly shows that the product consists of two isomers including BTNT, which can be readily assignable by the comparison with the spectrum of the authentic BTNT sample obtained from the route demonstrated in Scheme 4. The diagnostic peaks for the linear-shaped BTNT are two singlets assignable to the 6- and 11-positions (Figure 3a, top), whereas that for the angular isomer is a doublet at the lowest magnetic field region (~ 8.5 ppm) assignable to the 1-hydrogen at the bay position (Figure 3a bottom, see also Table S1 for calculated and observed chemical shifts of BTNT and the isomer). From the integrals of these diagnostic hydrogen peaks, the product ratio of the linear BTNT to the angular isomer is ca. 9:1, which is quite fortunate because the linear-

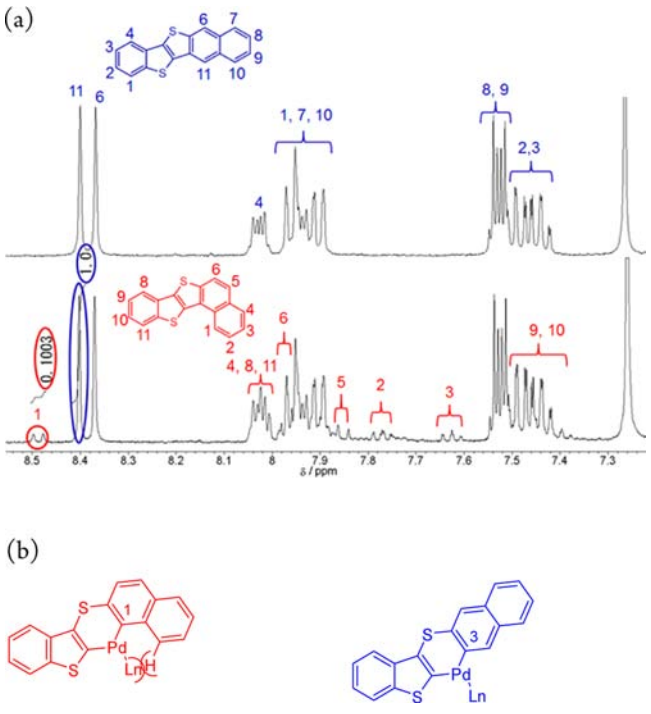


Figure 3. (a) ^{1}H NMR spectra of the products (bottom) and authentic BTNT (top), and (b) proposed palladacycle intermediates for both isomers.

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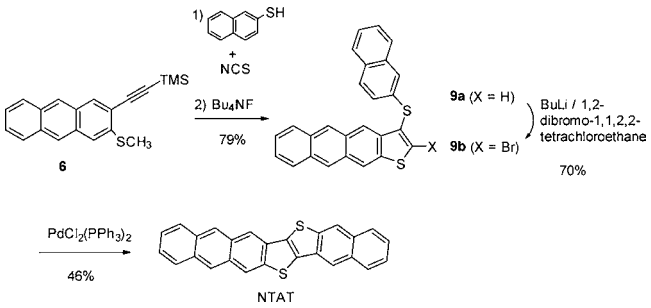
shaped isomer, BTNT, is more desirable as an organic semiconductor.[24] Since the angular-shaped isomer has higher solubility in common organic solvents than that of the linear isomer, the former can be easily removed from the mixture by washing with ethanol, and the isomerically pure BTNT was isolated in 80% yield.

The preferential formation of the linear isomer can be interpreted by the steric issue in the intramolecular coupling reaction, where six-membered palladacycles are supposed to have intermediacy (Figure 3b). One of the intermediates having the palladacycle with the naphthalene 1-position seems to be a less favorable structure owing to the steric hindrance between the ligands on the palladium atom and the 8-hydgogen on the naphthalene ring (Figure 3b, left). On the other hand, such steric problem does not occur in the linear intermediate (Figure 3b, right), and therefore the naphthalene 3-position preferentially undergoes the oxidative addition to afford linear BTNT as the major product.

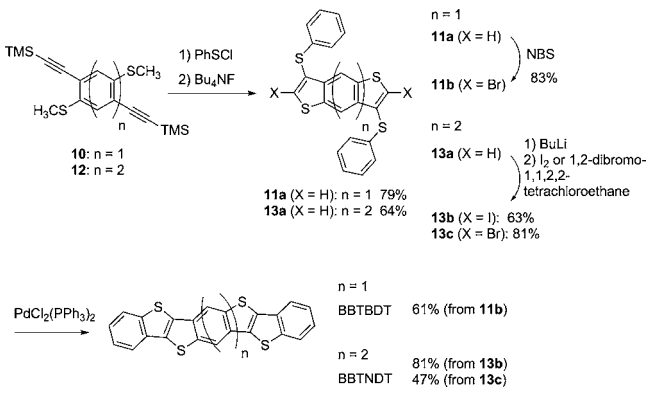
With this successful use of in situ generated 2-naphthylsulfenyl chloride, we also examined another π-extended unsymmetrical BTBT derivative, i.e., NTAT (Scheme 6), by using **6** as the substrate. As expected, NTAT can be obtained, though the isolated yield was moderate owing to difficulty in the separation from the isomer having rather little solubility difference.

Scheme 6. Synthesis of NTAT



Synthesis of Larger BTBT Derivatives with Two Thieno[3,2-b]thiophene Moieties. Further utility of the present method was examined by applying the synthesis of larger BTBT derivatives with two thieno[3,2-*b*]thiophene moieties. As the first trial, we chose BBTBDT[17] as the target (Scheme 7), and thus 1,4-bis(methylthio)-2,5-bis[2-(trimethylsilyl)ethynyl]-benzene (**10**)[21] was reacted with two-fold PhSCl to afford the corresponding benzo[1,2-*b*:4,5-*b*′]dithiophene derivative (**11a**) in 79% yield. After bromination of the thiophene α-positions to give **11b**, the palladium-catalyzed double thienannulation reaction afforded BBTBDT. It should be noted that even for the two-fold reaction in each step the yield is high, and the total yield of BBTBDT is better than the former synthesis.[17]

Scheme 7. Synthesis of BBTBDT and BBTNDT



With the successful application to the synthesis of BBTBDT, we further exploited the versatility of the method to synthesize BBTNDT, a BTBT-fused dimer (Scheme 7), which is otherwise very difficult to be synthesized. Starting from 2,6-bis(methylthio)-3,7-bis[(trimethylsilyl)ethynyl]naphthalene (**12**),[25] the first thienannulation reaction afforded naphtho[2,3-*b*:6,7-*b*′]dithiophene derivative (**13a**) with phenylthio substituents at the appropriate 3- and 8-positions (64%). Although the second thienannulation gave the desired BBTNDT, the reaction was affected by the halogen substituents. When the dibromide (**13c**) was used, the isolated yield of BBTNDT is rather lower (47%) than that from the corresponding iodide (**13b**, 81%). We speculate that the limited reactivity of the bromide (**13c**) and poor solubility of a monocyclized intermediate could be related: Even after the monocyclization the intermediate has a six-ring-fused structure, which should not be quite soluble, and thus, before the second reaction, the monocyclized intermediate may precipitate out ending up in producing monocyclized byproducts. On the contrary, rather smooth cyclization reaction at the both reaction sites can take place for the iodide (**13b**) case with better reactivity, resulting in higher yield than the bromide case.

Compared to the previous synthesis of the extended BTBT derivatives with two thieno[3,2-*b*]thioiphene moieties via double iodine-promoted cyclization,[17] the present synthesis of BBTBDT and BBTNDT has many advantages: better yields and good reproducibility at the final step and, more importantly, better accessibility to the substrates and reagent, particularly, for the synthesis of BBTNDT, where virtually inaccessible multi and selective functionalized naphthalene intermediates, i.e., 3,7-bis(methylthio)naphthalene-2,6-dialdehyde is required for the preparation of potential precursor for BBTNDT in the double iodine-promoted cyclization (Figure 4).

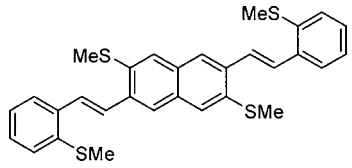


Figure 4. Potential precursor for BBTNDT via the double iodine-promoted cyclization.

Characterization of New BTBT Derivatives. *Electronic Structures.* Electronic structures of the BTBT derivatives newly synthesized were evaluated by cyclic voltammetry (CV), photoemission yield spectroscopy in air (PESA, Figure S1) and UV−vis absorption spectra (Figure 5). Figure 5a shows the absorption spectra of BTBT, BTBS, and [1]benzoselenopheno[3,2-*b*][1]benzoselenophene (BSBS) in chloroform, clearly indicating the gradual bathochromic shift caused by substituting the sulfur atom by selenium atom. On the other hand, the HOMO energy level estimated from their oxidation onsets in CV indicates that the first substation of the sulfur by selenium atom is effective to raise the HOMO, and the effect from the second substitution is rather marginal.

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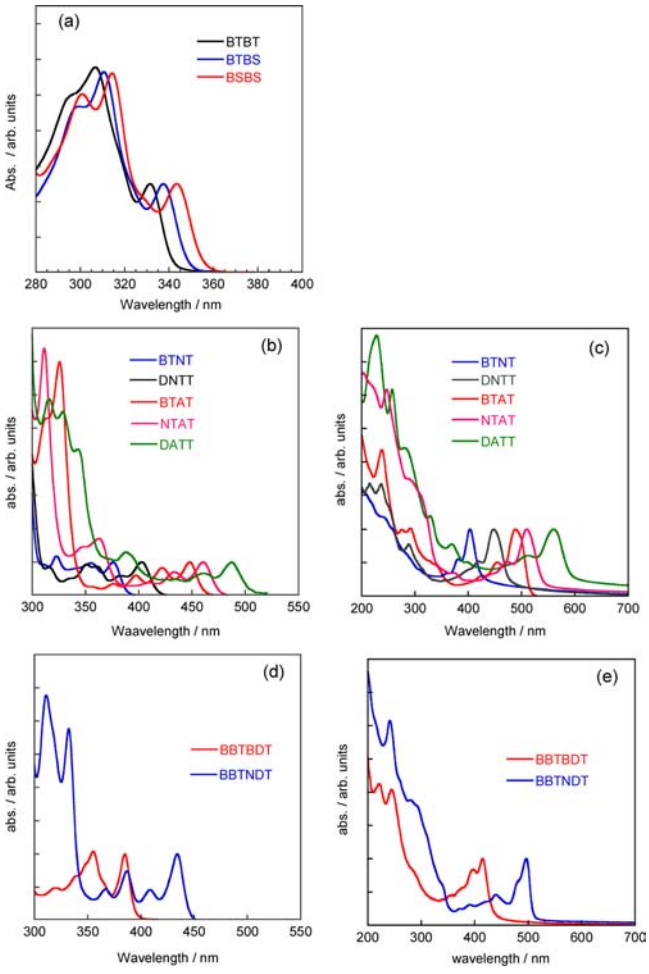

Figure 5. Absorption spectra of new BTBT derivatives with related compounds: BTBT, BTBS, and BSBS in chloroform solution (a); a series of compounds with one thieno[3,2-*b*]thiophene moiety in chlorobenzene solution (100 °C) (b) and in the evaporated thin film (c); and BBTBDT and BDTNDT with two thieno[3,2-*b*]thiophene moieties in chlorobenzene solution (100 °C) (d) and in the evaporated thin film (e).

Being different from highly soluble BTBT-BSBS series, the other derivatives were evaluated by using chlorobenzene solution at 100 °C or evaporated thin films. Figure 5b,c shows the absorption spectra of a series of extended BTBT derivatives with one thieno[3,2-*b*]thiophene moiety. With increasing the number of aromatic rings, the absorption bands shift bathochromically, which can be reasonably understood by the fact that the HOMO−LUMO energy gap (E_g) reduces with extension of the conjugation system (Table 1).[11a,17,26] However, comparing the absorption spectra of DNTT and BTAT, which are structural isomers to each other with six-fused aromatic rings, the latter with the unsymmetrical structure definitely has red-shifted absorption bands, e.g., smaller E_g. This can be explained by different contribution of local substructures in both compounds to their frontier orbitals. In DNTT, the two naphtho[2,3-*b*]thiophene substructures contribute equally to its frontier orbitals, whereas the anthra[2,3-*b*]thiophene substructure may dominate the electronic structures of the BTAT's HOMO and LUMO, resulting in smaller of E_g by ca. 0.2 eV. This qualitative explanation is supported by the theoretical calculations using the DFT methods, where the anthra[2,3-*b*]thiophene-dominant frontier orbitals and elevated E_{HOMO} are characteristic for BTAT (Figure S2). Consideration of the anthra[2,3-*b*]thiophene-dominant frontier orbitals also well explain similar HOMO energy levels (E_{HOMO}s, −5.1 eV for both) and E_gs (2.6 and 2.5 eV in solution and 2.4 and 2.3 eV in the thin film, respectively) of BTAT and NTAT. A similar interpretation is also possible for almost the same E_{HOMO}s of BTNT and DNTT; the E_{HOMO} of BTNT should be governed by the naphtho[2,3-*b*]thiophene substructure.

Table 1. Electronic Properties of BTBT Derivatives

compd	E_{HOMO}, eV	λ_{max}, nm[a]	λ_{edge}, nm[a]	E_g, eV[a,b]
BTBT[e]	−5.8[c]	332	340	3.6
BTBS	−5.6[c]	338	350	3.5
BSBS[f]	−5.6[c]	344	357	3.5
BTNT	−5.4[d]	376 (403)	404 (431)	3.1 (2.9)
DNTT[g]	−5.4[d]	403 (447)	431 (475)	2.9 (2.6)
BTAT	−5.1[d]	448 (488)	474 (514)	2.6 (2.4)
NTAT	−5.1[d]	461 (510)	487 (539)	2.5 (2.3)
DATT[h]	−5.1[d]	487 (565)	509 (602)	2.4 (2.1)
BBTBDT[i]	−5.2[d]	385 (415)	406 (435)	3.1 (2.8)
BBTNDT	−5.1[d]	434 (494)	453 (515)	2.7 (2.4)

[a]From absorption spectra in solution and evaporated thin film on a quarts substrate (in parentheses). [b]Calculated from λ_{edge}. [c]Determined from the onset potential in cyclic valtammogram (CV, Figure S1) [d]Determined by photoemission yield spectroscopy in air (PESA, Figure S1). [e]Ref 29. [f]Ref 16 [g]Ref 11a. [h]Ref 26. [i]Ref 17.

Depicted in Figure 5d,e is the absorption spectra of BBTBDT and BBTNDT with two thieno[3,2-*b*]thiophene moieties and seven- or eight-fused aromatic rings, respectively. It is interesting to note that their absorption bands are rather blue-shifted, in other words, larger E_gs, compared to the monothieno[3,2-*b*]thiophene counterparts with the same number of aromatic rings, i.e., NTAT and DATT. This can be understood by the effect of thieno[3,2-*b*]thiophene inserted into oligoacene framework, which effectively adds the phene-like electronic structure in the resulting system.[14a] On the other hand, the E_{HOMO}s of BBTBDT and BBTNDT are almost the same with NTAT and DATT, respectively (Table 1). The DFT calculations imply that the electronic structures of their HOMOs are mainly contributed by the central part, dithieno-[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene[27] and naphtho-[2,3-*b*:6,7-*b*′]dithiophene,[28] respectively (Figure S2); in other words, the E_{HOMO} could be scaled to some extent by these acenedithiophene substructures. In addition, their strongly interactive structures in the solid state may also play an important role in the present evaluation of HOMO by PESA using evaporated thin films. In particular, a π-stacking structure with a close face-to-face interaction (3.58 Å) in BBTBDT as previously mentioned could significantly affect its E_{HOMO} in the thin-film state.[17] In summary, although the extent of π-extension and the incorporation manner of the thieno[3,2-*b*]thiophene moiety alters the E_{HOMO}s and E_gs, all the present BTBT derivatives keep a relatively low-lying E_{HOMO} sufficient for stable operation of their p-channel OFETs under ambient conditions.[14]

Molecular and Crystal Structures of BTAT and BBTNDT. Molecular and packing structures in the solid state are one of the most important materials factors for organic electronics application. In the present work, the structural analyses are thought to be very important, since the molecular structures of the BTBT derivatives discussed here are rather "unconven-

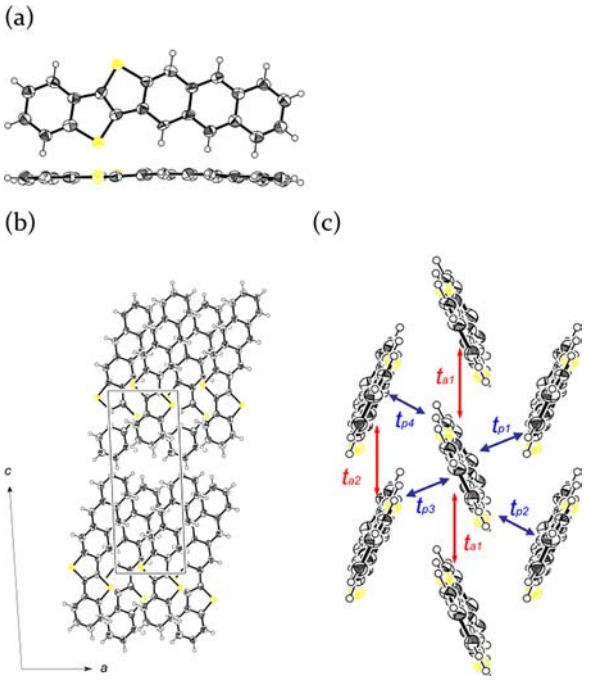

Figure 6. Crystal structure of BTAT: (a) molecular structure, (b) packing structure projected along the crystallographic *a*-axis, and (c) herringbone packing structure in the crystallographic *ab*-cell. Calculated intermolecular transfer integrals of HOMOs (t_{HOMO}s) are t_{a1} = 62, t_{a2} = 53, t_{p1} = 32, t_{p2} = 35, t_{p3} = 73, and t_{p4} = 89 meV, respectively.

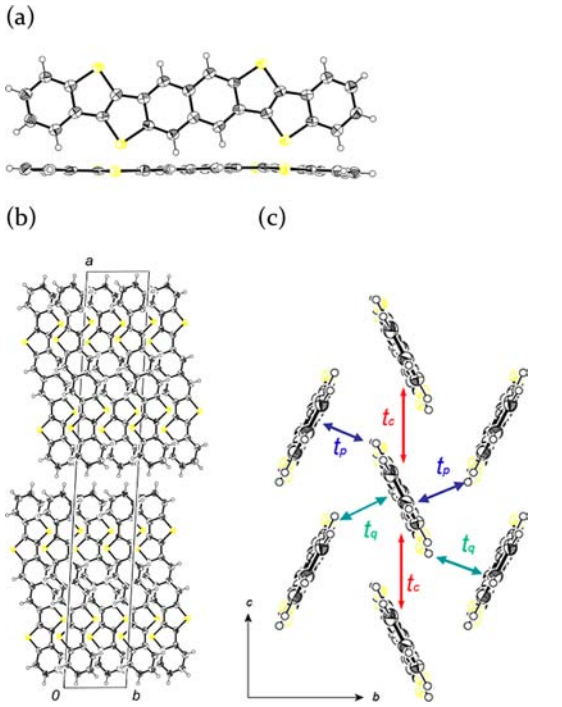

Figure 7. Crystal structure of BBTNDT: (a) molecular structure, (b) packing structure projected along the crystallographic *a*-axis representing a molecular lamella structure, and (c) herringbone packing structure in the crystallographic *bc*-cell and calculated transfer integrals. Calculated intermolecular transfer integrals of HOMOs (t_{HOMO}s) are t_c = 75, t_p = 32, and t_q = 41 meV, respectively.

tional"; we should elucidate how the unsymmetrical structure affects the packing, or how two thieno[3,2-*b*]thiophene moieties in the largely extended molecule, e.g., BBTNDT, can contribute to intermolecular interaction in the solid state. With these motivations, we carefully prepared single crystals of BTAT and BBTNDT suitable for X-ray analyses by the physical vapor transport method.[30] Depicted in Figures 6 and 7 are molecular and packing structures of these molecules.

The BTAT crystal was found to have a triclinic *P*1 space group with two crystallographically independent molecules in the unit cell. Both the BTAT molecules having almost planar structures are virtually identical. Unsymmetrical molecules often form dimers with the inversion center to diminish asymmetric nature, but in the present case, as expected from the *P*1 space group, such dimeric structure is not formed, and all the molecules in the crystal structure can be thus expressed by the translation symmetry operation of the molecules in the asymmetric unit, indicating that all the molecules point the same direction (Figure 6b). The packing structure of BTAT can be described as a layer-by-layer structure with the herringbone motif, which is quite typical for BTBT and DNTT-based molecules so far reported (Figure 6b,c).[8] Owing to its unsymmetrical unit cell, the thieno[3,2-*b*]thiophene moieties are nicely aligned in the crystallographic *ab* plane direction, which results in effective intermolecular interactions via the sulfur atoms with nonbonded distances shorter than or close to the sum of van der Waals radius of sulfur atom (3.6 Å). As a result, calculated orbital overlaps of HOMO (transfer integrals, t_{HOMO}) in the two-dimensional BTAT layer are similar to what was observed for other π-extended BTBT derivatives, such as DNTT and DATT (Figure 6c), implying the BTAT can be another candidate for high-performance organic semiconductor for OFET application.[31]

Being different from the structure of BTAT, BBTNDT crystallizes into a monoclinic $P2_1/n$ space group (Figure 7a). Its packing structure is, however, similar to that of BTAT, representing the typical layer-by-layer structure with herringbone parking motif (Figure 7b). It should be emphasized that BBTBDT crystallizes into the π-stacking structure,[17] which is strikingly different from the present BBTNDT, despite their structural similarity, i.e., the linearly π-extended thienoacene structure with two thieno[3,2-*b*]thiophene moieties. This marked difference in molecular arrangements in the solid state could be explained by the presence/absence of the CH$-\pi$, hydrogen bond-like intermolecular interaction, which facilitates the face-to-edge bimolecular interaction, resulting in herringbone structures.[32] The increased number of *peri*-hydrogen atoms at the central part of BBTNDT compared to BBTBDT may play a crucial role for the face-to-edge bimolecular interaction. The electronic structure in the herringbone cell of BBTNDT estimated by the calculation of t_{HOMO}s (Figure 7c) is mostly two-dimensional with well-balanced large orbital overlaps in each direction, implying again its potential as high-performance organic semiconductor (vide infra).[31]

Thin-Film FET Devices of New BTBT Derivatives. *Device Characteristics for Monothieno[3,2-b]thiophene Series.* To evaluate the utility of the new BTBT derivatives for organic semiconductors, we fabricated FET devices using their vapor deposited thin films with a bottom gate, top-contact configuration on Si/SiO_2 substrates. Depicted in Figure 8 are the output- and transfer- characteristics of the FETs evaluated under ambient conditions, and their field-effect mobilities (μ_{FET}) extracted from the saturation regime are summarized in Table 2.

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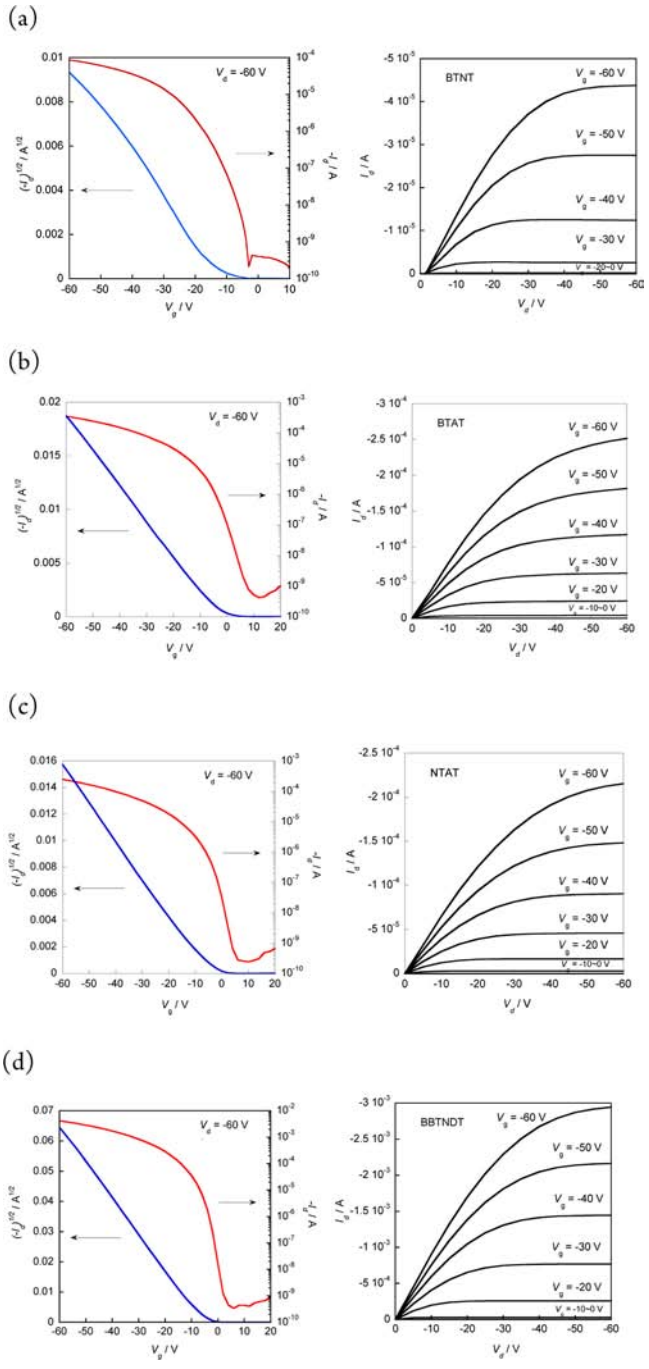

Figure 8. Transfer and output characteristics of top contact, bottom gate OFET devices fabricated on the OTS-treated substrate by using vapor deposited thin films. (a) BTNT (T_{sub} = rt), (b) BTAT (T_{sub} = 60 °C), (c) NTAT (T_{sub} = 60 °C), and (d) BBTNDT (T_{sub} = 150 °C).

Owing to the relatively low molecular weight, the BTNT thin film can be deposited only on the substrate kept at rt (T_{sub} = rt). On the other hand, thin films of other compounds can be deposited on the substrates at higher T_{sub}s. Field-effect mobilities extracted from the saturation regime for the BTNT, BTAT, and NTAT-based transistors, however, were in the range of 0.1−0.5 cm^2 V^{-1} s^{-1} (Table 2). Compared to the reported mobility for the DNTT-[11a] and DATT-based semiconductors, up to 3.0 cm^2 V^{-1} s^{-1},[26] the mobilities obtained from unsymmetrical derivatives appear to be quite low. In particular, considering the relatively large t_{HOMO}s

Table 2. FET Characteristics

compd	SAM	T_{sub}, °C	μ_{FET}[b], cm^2 V^{-1} s^{-1}	I_{on}/I_{off}	V_{th}, V
BTNT	OTS[c]	rt	0.15 (0.14)	10^5	−11
	ODTS[c]	rt	0.25 (0.23)	10^5	−6.0
BTAT	OTS[c]	rt	0.30 (0.28)	10^5	−7.3
		60	0.55 (0.42)	10^5	−1.0
		100	0.36 (0.27)	10^5	−5.6
	ODTS[c]	rt	0.11 (0.08)	10^4	−3.7
		60	0.12 (0.11)	10^5	+3.6
		100	0.29 (0.19)	10^5	−1.5
NTAT	OTS[c]	rt	0.33 (0.25)	10^6	−7.8
		60	0.41 (0.37)	10^5	−3.1
		100	0.38 (0.28)	10^5	−4.2
	ODTS[c]	rt	0.07 (0.05)	10^5	+0.50
		60	0.14 (0.10)	10^5	−7.6
		100	0.21 (0.16)	10^5	−3.1
BBTNDT	OTS[c]	rt	0.19 (0.17)	10^4	−2.0
		60	0.48 (0.39)	10^5	+1.0
		100	2.2 (1.8)	10^6	−4.0
		150	5.1 (3.4)	10^7	−3.0
	ODTS[c]	rt	0.15 (0.11)	10^5	−3.8
		60	0.40 (0.38)	10^5	−8.0
		100	5.6 (4.7)	10^7	−6.0
		150	4.4 (3.3)	10^7	−6.0

[a]Substrate temperature during deposition of the thin film. [b]Typical and averaged values (in parentheses) obtained from>10 devices with L = 50 μm and W = 1500 μm. [c]OTS: octyltrichlorosilane, ODTS: octadecyltrichlorosilane.

calculated for the herringbone cell of BTAT (Figure 6c), which are almost comparable to those for DNTT and DATT, the results on the present OFETs showing lower mobility by 1 order of magnitude are rather puzzling.

To understand these unexpected results, we first examined the crystallinity and molecular orientation in the evaporated thin films by XRD measurements. As clearly seen in the out-of-plan XRDs (Figure 9a−c), all these molecules tend to stand perpendicular to the substrate surfaces, which is a common feature for the BTBT-based organic semiconductors. Also in the in-plan XRDs, three characteristic peaks for the herringbone *ab*-cell are observed, indicating that the molecular orientation and crystallinity of the thin films are not significantly different from what was observed for other BTBT-based organic semiconductors.[10,11] On the other hand, one possible explanation of low mobility for the unsymmetrical derivatives could be the localized HOMO on one side of the molecule; in the case of BTAT, its HOMO is localized on the anthra[2,3-*b*]thiophene moiety, which affords nonuniform HOMO distribution in the solid state as depicted in the schematic picture for HOMO distribution of the crystallographic *ac*-cell (Figure 10), where the dense parts (anthra[2,3-*b*]thiophene moiety) and dilute parts (benzo[*b*]thiophene moiety) of HOMO alternately exist along the *c*-axis direction. In the actual thin films consisting of many crystalline domains/grains, it is natural to consider that, although the crystallites orient along the *c*-axis (as evidenced by the XRDs), the direction of the domains/grains should not be always the same, in other words, the crystallites could orient either along the 001 or 00$\bar{1}$ directions randomly. In such circumstance, the electronic coupling between the crystallites with the reverse orientation should be poor. From these experimental results and also the theoretical considerations, the BTBT derivatives with unsym-

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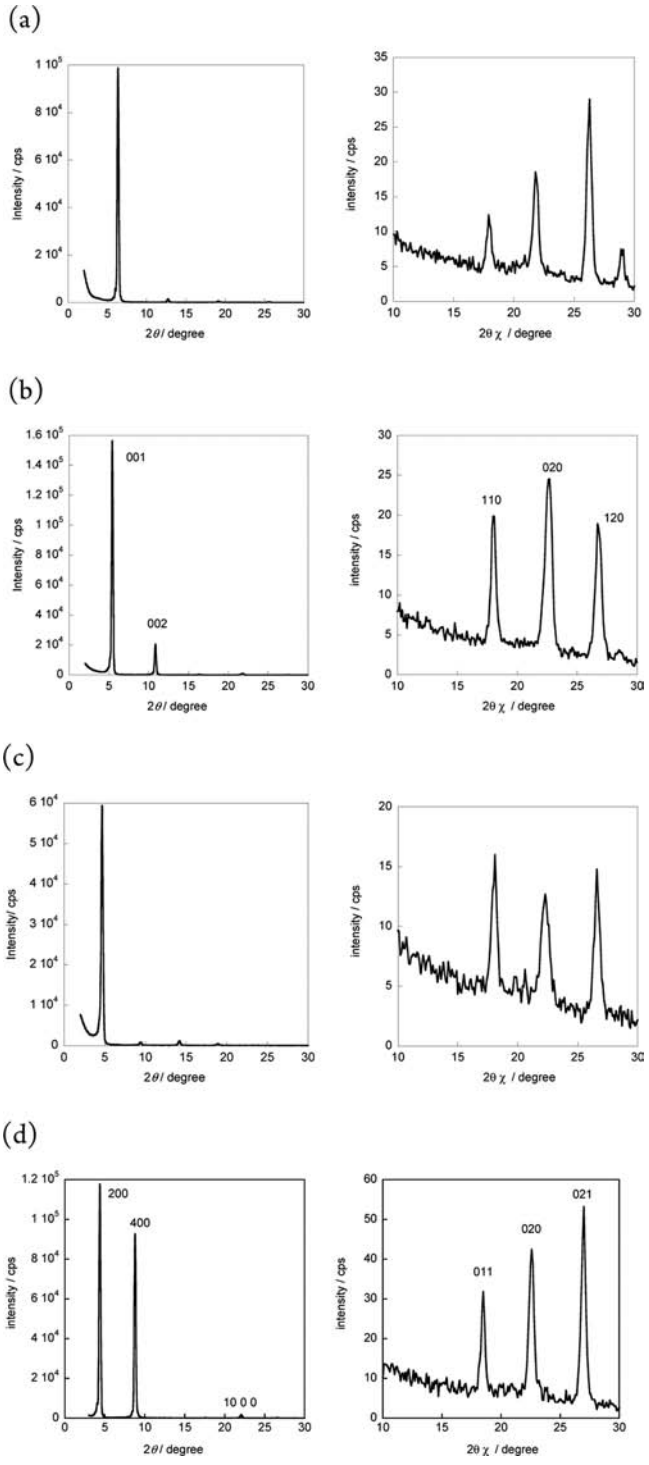

Figure 9. Out-of-plane (left) and in-plan XRD patterns (right) of evaporated thin film on the Si/SiO_2 substrate: (a) BTNT (T_{sub} = rt), (b) BTAT (T_{sub} = 60 °C), (c) NTAT (T_{sub} = 60 °C), and (d) BBTNDT (T_{sub} = 100 °C).

metrical core structures seem to be less favorable for the development of high-performance organic semiconductors.

Device Characteristics for BBTNDT. In sharp contrast, the BBTNDT-based devices showed quite high mobilities (Table 2, Figure 8d). As summarized in Table 2, although the mobility largely depended on T_{sub}s, the devices showed excellent FET characteristics with the mobility higher than 2 $cm^2\ V^{-1}\ s^{-1}$ at higher T_{sub}s than 100 °C. In particular, the best mobilities

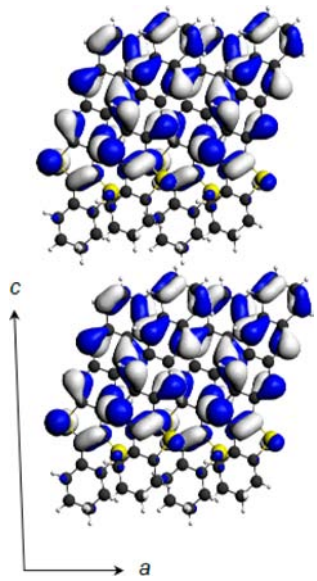

Figure 10. Schematic picture of HOMO distribution in the *ac*-cell of BTAT: HOMO coefficients are superimposed on the packing structure of BTAT.

exceed 5 $cm^2\ V^{-1}\ s^{-1}$, which is comparable to the highest mobility so far reported for small-molecule-based OFETs with multigrain thin films as the active semiconducting channel. It should be noted that the HOMO energy level of BBTNDT (5.1 eV below the vacuum level, Table 1) can realize a relatively small injection barrier from the gold source electrode to the semiconducting layer (Figure 8d, output). Furthermore, BBTNDT with the largely π-extended structure ensures thermal stability in thin-film state on the substrate, and in fact the OFET devices resisted thermal treatments up to 200 °C for 15 min (Figure S3).[33] These excellent semiconducting behaviors can be rationalized by its packing structure in the thin film state; all the peaks observed in both the out-of-plane and in-plane XRDs (Figure 9d) are well indexed by the single crystal cell, indicating that a highly intermolecularly interactive structure with the edge-on molecular orientation and herringbone arrangement (Figure 7b,c) is also realized in the thin-film state, as observed in many related high-performance thinenoacene-based organic semiconductors.

Discussion on Largely π-Extended Thienoacens As High-Performance Organic Semiconductors. Recent intensive efforts in the material development have produce many high-performance organic semiconductors showing mobility higher than 5 $cm^2\ V^{-1}\ s^{-1}$, but most of them have substituents such as long alkyl[10b,d,11c,d] or (trialkylsilyl)ethynyl group[4b,34] that promotes self-assembling of the π-conjugated cores, facilitating the efficient intermolecular interaction in the active semiconducting layer. In this relation, it has been recently pointed out that the substituents (e.g., long alkyl groups) may also act as "screen" from possible charge trapping effect caused by the coupling between the charge carriers in the channel and the electrical polarization in the gate dielectric.[35] Both of these two effects from the substituents can facilitate effective charge transport. In fact, FET mobilities reported for thin film transistors based on "naked" thienoacenes without the substituents are relatively limited: e.g., ~0.30 $cm^2\ V^{-1}\ s^{-1}$ for ADT,[36] ~0.15 $cm^2\ V^{-1}\ s^{-1}$ for DBTBT,[37] ~0.57 $cm^2\ V^{-1}\ s^{-1}$ for PT,[38] ~0.94 $cm^2\ V^{-1}\ s^{-1}$ for BNTBDT (Figure 11),[17] ~0.14 $cm^2\ V^{-1}\ s^{-1}$ for BBTBDT (Scheme 7),[17] ~3.0 $cm^2\ V^{-1}\ s^{-1}$ for

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DNTT[11a] and DATT[26] (Figure 1). From the viewpoint of the structure−property relationship, BBTNDT can be regarded as a very promising and interesting new thienoacene core structure for further investigations both for device applications and theoretical investigation.

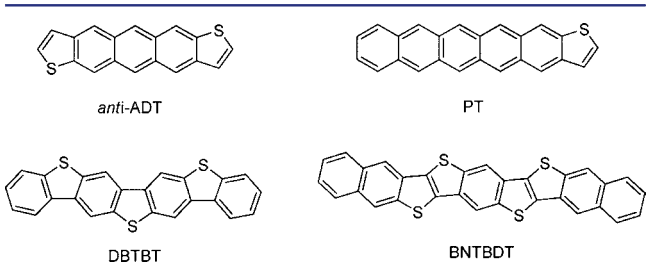

Figure 11. Molecular structures of π-extended thienoacenes.

CONCLUSION

In summary, we have established new synthetic route to the BTBT substructure featuring two consecutive thienannulation reactions from *o*-ethynyl-thioanisole substrates and arylsulfenyl chloride reagents. The method is suitable to the synthesis of unsymmetrical derivatives, a selenium-containing derivative and also largely π-extended derivatives with two BTBT substructures. It should be emphasized that these new derivatives are otherwise difficult to be synthesized, and thus the present method is quite useful for the development of materials in this class. In fact, the merits of the present method for the synthesis of the BTBT-based materials are summarized as follows: (1) the various substrates and reagents are readily accessible and can be combined, which can lead to a wide range of materials; (2) each reaction in the method proceeds in a good yield; and (3) the present method is suitable to the synthesis of unsymmetrical derivatives and two-BTBT incorporated derivatives. In fact, BBTNDT, a newly developed π-extended thienoacene by using this method, behaves as an excellent p-channel organic semiconductor showing mobility as high as 5 $cm^2 V^{-1} s^{-1}$ in thin-film transistor settings, which indicates that such π-extended heteroacenes with an appropriate molecular design are potential materials for high-performance organic semiconductors. We believe that the present method can accelerate the design and synthesis of new π-extended heteroacenes to develop superior organic semiconductors, and the new high-performance organic semiconductor, BBTNDT, will be utilized into sophisticated applications in future.

EXPERIMENTAL SECTION

General. All chemicals and solvents are of reagent grade unless otherwise indicated. Tetrahydrofuran (THF), triethylamine, *N*,*N*-dimethylformamide, (DMF), and dichloromethane were purified with standard distillation procedures prior to use. 2-Iodothioanisole was purchased from Tokyo Chemical Industry Co., Ltd. 2-[2-(Trimethylsilyl)ethynyl]thioanisole (**1**),[18] 3-(methylthio)naphthalen-2-yl-trifluoromethanesulfonate,[11] 3-(methylthio)anthracen-2-yl-trifluoromethanesulfonate,[26] 2,6-dimethoxy-3,7-bis(methylthio)-naphthalene,[39] 1,4-bis(methylthio)-2,5-bis[2-(trimethylsilyl)ethynyl]-benzene,[21] and phenylsulfenyl chloride[40] were prepared according to reported procedures. All reactions were carried out under nitrogen atmosphere unless otherwise mentioned. Melting points were uncorrected. NMR spectra were obtained in deuterated chloroform with TMS as internal reference; chemical shifts (δ) are reported in parts per million. EI-MS spectra were obtained using an electron impact ionization procedure (70 eV). The molecular ion peaks of the chlorine, bromine, sulfur, or selenium containing compounds showed a typical isotopic pattern, and all the mass peaks are reported based on ^{35}Cl, ^{79}Br, ^{32}S, ^{80}Se, respectively.

3-Phenylthio-2-(trimethylsilyl)benzo[*b*]thiophene (2a). A solution of phenylsulfenyl chloride (0.7 mL, 7.5 mmol) in dichloromethane (50 mL) was added to a solution of **1** (1.1 g, 5 mmol) in dichloromethane (70 mL) at 0 °C. The reaction mixture was stirred at rt for 4 h. The mixture was diluted with dichloromethane (10 mL) and washed with water (50 mL × 3) and brine (50 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate−hexane, 1:10 v/v, R_f = 0.8) to give 3-(phenylthio)-2-trimethylsilylbenzo[*b*]thiophene (**2a**, 1.4 g, 93%) as a white solid. Mp. 82−84 °C; ^1H NMR (400 MHz) δ 0.41 (s, 9H), 6.97 (td, *J* = 1.4, 7.2 Hz, 2H), 7.05 (tt, *J* = 1.4, 7.2 Hz, 1H), 7.15 (dt, *J* = 1.1, 7.2 Hz, 2H), 7.30 (dt, *J* = 1.1, 7.0 Hz, 1H), 7.35 (dt, *J* = 1.3, 7.2 Hz, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.89 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz) δ 0.1, 122.7, 123.4, 125.0, 125.1, 125.3, 126.3, 129.2, 129.5, 138.4, 142.0, 143.0, 149.7; EI-MS (70 eV) *m*/*z* = 314 (M^+); Anal. calcd for $C_{17}H_{18}S_2Si$: C, 64.91; H, 5.77%. Found: C, 64.86; H, 5.57%.

2-Iodo-3-(phenylthio)benzo[*b*]thiophene (2b). A solution of ICl in dichloromethane (1 M, 0.6 mL, 0.6 mmol) was added to a solution of **2a** (157 mg, 0.5 mmol) in dichloromethane (5 mL) at −40 °C. The mixture was stirred for 3 h at the same temperature and then poured into a saturated aqueous solution of $Na_2S_2O_5$ (3 mL). The resulting mixture was extracted with dichloromethane (10 mL × 3), and the combined extracts were washed with brine (15 mL × 3), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (chloroform, R_f = 0.9) to give 2-iodo-3-(phenylthio)benzo[*b*]thiophene as a white solid (**2b**, 167 mg, 90%). Mp. 97−98 °C; ^1H NMR (400 MHz) δ 7.08−7.14 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.28−7.35 (m, 2H), 7.79 (dd, *J* = 2.3, 6.9 Hz, 2H); ^{13}C NMR (100 MHz) δ 95.7, 122.1, 124.0, 125.4, 125.5, 126.1, 127.4, 129.3, 131.6, 136.0, 139.0, 143.9; EI-MS (70 eV) *m*/*z* = 368 (M^+); Anal. calcd for $C_{14}H_9IS_2$: C, 45.66; H, 2.46%. Found: C, 46.04; H, 2.08%.

2-Bromo-3-phenylthiobenzo[*b*]thiophene (2c). To a solution of **2a** (150 mg, 0.5 mmol) in THF (5 mL) and water (0.1 mL) was added a solution of tetrabutylammonium fluoride (1 M, 1 mL, 1.0 mmol). The mixture was stirred for 4 h at rt, then poured into water (10 mL), and extracted with ethyl acetate (10 mL × 3). The combined extracts were washed with brine (20 mL × 3), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (chloroform, R_f = 0.9) to give 3-phenylthiobenzo[*b*]thiophene (115 mg, quantitative) as colorless oil. ^1H NMR (400 MHz) δ 7.10−7.23 (m, 5H), 7.36 (dt, *J* = 1.6, 7.1 Hz, 1H), 7.40 (dt, *J* = 1.6, 7.1 Hz, 1H), 7.72 (s, 1H), 7.80 (dd, *J* = 2.1, 6.6 Hz, 1H), 7.90 (dd, *J* = 2.4, 7.6 Hz, 1H), ^{13}C NMR (100 MHz) δ 123.3, 123.4, 124.3, 125.1, 125.3, 126.2, 127.8, 129.3, 132.5, 136.9, 139.2, 140.3; EI-MS (70 eV) *m*/*z* = 242 (M^+); HRMS (APCI) *m*/*z* calcd for $C_{14}H_{11}S_2$ $[M + H]^+$: 243.02967. Found: 243.02963.

To a solution of 3-phenylthiobenzo[*b*]thiophene (115 mg, 0.48 mmol) in chloroform (3 mL) was added *N*-bromosuccinimide (89 mg, 0.5 mmol), and the resulting mixture was stirred at rt for 12 h. The mixture was poured into water (10 mL) and was extracted with chloroform (5 mL × 3). The combined extracts were washed with brine (10 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (chloroform, R_f = 0.9) to give 2-bromo-3-phenylthiobenzo[*b*]-thiophene (**2c**, 129 mg, 85%) as a white solid. Mp. 86−87 °C; ^1H NMR (400 MHz) δ 7.11−7.22 (m, 5H), 7.33 (dt, *J* = 1.6, 7.1 Hz, 1H), 7.37 (dt, *J* = 1.6, 7.1 Hz, 1H), 7.74−7.79 (m, 2H); ^{13}C NMR (100 MHz) δ 122.3, 123.9, 125.5, 125.72, 125.73, 125.76, 126.3, 127.6, 129.4, 135.8, 139.3, 139.9; EI-MS (70 eV) *m*/*z* = 320 (M^+); HRMS (APCI) *m*/*z* calcd for $C_{14}H_9BrS$ $[M]^+$: 319.93236. Found: 319.93259.

[1]Benzothieno[3,2-*b*][1]benzothiophene (BTBT). To a deaerated solution of **2b** (150 mg, 0.4 mmol), sodium acetate (67 mg, 0.8 mmol), in *N*,*N*-dimethylacetamide (8 mL) was added $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol). The mixture was stirred for 12 h at 140 °C and

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then quenched by adding hydrochloric acid (1 M, 20 mL). The resulting mixture was extracted with ethyl acetate-hexane (1:1 v/v, 50 mL), and the extract was washed with brine (50 mL × 3), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane, R_f = 0.3) to give BTBT as a white solid (72 mg, 73%). Mp. 213−215 °C (ref 41 216−218 °C); ^{1}H NMR (400 MHz,) δ 7.41 (dt, J = 1.4, 7.6 Hz, 2H), 7.47 (dt, J = 1.4, 7.6 Hz, 2H), 7.90 (dd, J = 1.4, 7.6 Hz, 2H), 7.93 (dd, J = 1.4, 7.6 Hz, 2H); ^{13}C NMR (100 MHz) δ 122.0, 124.4, 125.3, 125.4, 133.6, 133.9, 142.8; EI-MS (70 eV) m/z =240 (M^+). BTBT was also obtained from **2c** in the same manner as described above. 81% isolated yield.

3-Phenylseleno-2-(trimethylsilyl)benzo[*b*]thiophene (3a). The title compound was obtained in the same manner as described in ref 18a (quantitative yield). Yellow oil. ^{1}H NMR (400 MHz) δ 0.43 (s, 9H), 7.05−7.14 (m, 5H), 7.25−7.3 (m, 2H), 7.82 (dd, J = 1.4, 7.1 Hz, 1H), 7.90 (dd, J = 1.4, 7.1 Hz, 1H); ^{13}C NMR (100 MHz) δ 0.33, 122.4, 124.5, 125.0, 125.1, 125.6, 126.0, 128.8, 129.4, 133.7, 142.9, 143.3, 149.4; EI-MS (70 eV) m/z = 362 (M^+).

2-Iodo-3-(phenylseleno)benzo[*b*]thiophene (3b). The title compound was obtained in the same manner for the synthesis of **2b** (54% isolated yield). White solid; Mp. 86−87 °C; ^{1}H NMR (400 MHz) δ 7.15−7.25 (m, 5H), 7.29 (dt, J = 1.9, 5.0 Hz, 1H), 7.31(dt, J = 1.9, 5.0 Hz, 1H), 7.77−7.79 (m, 1H), 7.82−7.85 (m, 1H); ^{13}C NMR (100 MHz) δ 96.0, 121.9, 125.4, 125.6, 125.7, 127.0, 129.7, 130.3, 131.7, 132.7, 140.6, 144.5; EI-MS (70 eV) m/z = 416 (M^+); HRMS (APCI) m/z Calcd for $C_{14}H_9ISSe$ $[M]^+$: 415.86294. Found: 415.86227.

3b was also synthesized via desilylation and following lithiation/electrophilic iodination: treatment of **3a** with a solution of tetrabutylammonium fluoride gave 3-(phenylseleno)benzo[*b*]-thiophene as colorless oil (quantitative): ^{1}H NMR (400 MHz) δ 7.14−7.18 (m, 3H), 7.27−7.29 (m, 2H), 7.36 (t, J = 6.0 Hz, 1H), 7.38 (t, J = 6.0 Hz, 1H), 7.72 (s, 1H), 7.82−7.86 (m, 1H), 7.88−7.91 (m, 1H); ^{13}C NMR (100 MHz) δ 119.6, 123.0, 124.4, 125.15, 125.20, 126.8, 129.6, 130.5, 132.0, 132.8, 140.3, 140.4; EI-MS (70 eV) m/z = 290 (M^+); HRMS (EI) m/z calcd for $C_{14}H_{10}SSe$ $[M]^+$: 289.9667. Found: 289.9663.

To a solution of 3-(phenylseleno)benzo[*b*]thiophene (211 mg, 0.73 mmol) in THF (5 mL) was added *n*-butyllithium (1.63 M in hexane, 0.53 mL, 0.87 mmol) at 0 °C. The mixture was warmed to rt and then stirred for 1 h. Iodine (221 mg, 0.87 mmol) was added to the mixture at 0 °C, and the resulting mixture was stirred for 10 h at rt, and then poured into hydrochloric acid (1 M, 10 mL). The resulting mixture was extracted with dichloromethane (10 mL × 3), and the combined extracts were washed with brine (15 mL × 3), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (chloroform, R_f = 0.9) to give **3b** as a white solid (274 mg, 90%).

2-Bromo-3-(phenylseleno)benzo[*b*]thiophene (3c). A similar procedure using 1,2-dibromo-1,1,2,2-tetrachloroethane instead of iodine gave **3c** in quantitative yield. White solid; Mp. 60−63 °C; ^{1}H NMR (400 MHz) δ 7.15−7.19 (m, 3H), 7.25−7.28 (m, 2H), 7.31−7.37 (m, 2H), 7.72−7.84 (m, 2H); ^{13}C NMR (100 MHz) δ 122.0, 123.1, 125.13, 125.15, 125.6, 125.7, 127.0, 129.6, 130.5, 131.2, 140.5, 140.7; EI-MS (70 eV) m/z = 368 (M^+); HRMS (EI) m/z calcd for $C_{14}H_9BrSSe$ $[M]^+$: 367.8768, Found: 367.8768.

[1]Benzothieno[3,2-*b*][1]benzoselenophene (BTBS). The title compound was obtained in the same manner as for the synthesis of BTBT. BTBS was purified by column chromatography on silica gel (hexane-chloroform, 5:1 v/v, R_f = 0.6) as a white solid (44%). Mp. 208−209 °C; ^{1}H NMR (400 MHz) δ 7.33 (dt, J = 1.3, 7.6 Hz, 1H), 7.38−7.48 (m, 3H), 7.82 (dd, J = 1.3, 7.6 Hz, 1H), 7.87−7.97 (m, 3H); ^{13}C NMR (100 MHz) δ 122.7, 123.6, 124.3, 125.3, 125.4, 125.7, 125.8, 127.5, 132.2, 135.7, 136.1, 136.2, 141.7, 142.6; EI-MS (70 eV) m/z = 288 (M^+); HRMS (APCI) m/z calcd for $C_{14}H_8SSe$ $[M]^+$: 287.95064, Found: 287.95059.

2-Methylthio-3-[2-(trimethylsilyl)ethynyl]naphthalene (4). To a deaerated solution of 3-(methylthio)naphthalen-2-yl-trifluoromethanesulfonate (5 g, 15.5 mmol), tributyl(trimethylsilylethynyl)tin (6.6 g, 17.1 mmol) in DMF (150 mL) was added $Pd(PPh_3)_4$ (537 mg, 0.5 mmol), and the mixture was stirred for 10 h at 90 °C. The mixture was poured into water (150 mL) and was extracted with ethyl acetate-hexane (1:1 v/v, 100 mL × 3). The combined extracts were washed with brine (50 mL × 3), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane, R_f = 0.2) to give 2-methylthio-3-[(2-trimethylsilyl)ethynyl)]-naphthalene (4.1 g, quantitative) as yellow oil. ^{1}H NMR (400 MHz) δ 0.31 (s, 9H), 2.58 (s, 3H), 7.39 (dt, J = 1.3, 6.9 Hz, 1H), 7.45 (s, 1H), 7.46 (dt, J = 1.3, 6.9 Hz, 1H), 7.72 (m, 2H), 7.96 (s, 1H); ^{13}C NMR (100 MHz) δ 0.3, 15.5, 101.1, 102.5, 120.0, 121.9, 125.7, 126.9, 127.2, 127.8, 130.6, 133.0, 133.7, 138.6; EI-MS (70 eV) m/z = 270 (M^+); Anal. calcd. for $C_{16}H_{18}SSi$: C, 71.05; H, 6.71%. Found: C, 70.83; H, 6.99%.

3-Phenylthio-2-(trimethylsilyl)naphtho[2,3-*b*]thiophene (5a). A similar procedure to the synthesis of **2a** gave title compound from **4** and phenylsulfenyl chloride (quantitative). White solid; Mp. 170−172 °C ;^{1}H NMR (400 MHz) δ 0.44 (s, 9H), 7.00−7.07 (m, 3H), 7.15 (t, J = 7.6 Hz, 2H), 7.41 (dt, J = 1.2, 7.3 Hz, 1H), 7.47 (dt, J = 1.2, 7.3 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 8.25 (s, 1H), 8.38 (s, 1H); ^{13}C NMR (100 MHz) δ 0.0, 120.9, 121.8, 125.4, 126.1, 126.3, 127.5, 125.6, 129.0, 129.1, 129.2, 131.3, 131.5, 138.3, 140.6, 140.8, 152.9; EI-MS (70 eV) m/z = 364 (M^+); Anal. calcd for $C_{21}H_{20}S_2Si$: C, 69.18; H, 5.53%. Found: C, 69.56; H, 5.29%.

2-Iodo-3-(phenylthio)naphtho[2,3-*b*]thiophene (5b). To a solution of **5a** (1.0 g, 2.7 mmol) in THF (100 mL) and water (1 mL) was added a solution of tetrabutylammonium fluoride (1 M, 4.1 mL, 4.1 mmol) at rt. The mixture was stirred for 4 h at the same temperature and then poured into water (100 mL), and the resulting precipitate was collected by filtration and washed with ethanol and hexane. The crude product was purified by column chromatography on silica gel (chloroform, R_f = 0.9) to give 3-(phenylthio)naphtho[2,3-*b*]thiophene as a white solid (quantitative). Mp. 136−138 °C; ^{1}H NMR (400 MHz) δ 7.11−7.21 (m, 5H), 7.45 (dt, J = 1.4, 7.9 Hz, 1H), 7.50 (dt, J = 1.4, 7.9 Hz, 1H), 7.78 (s, 1H), 7.93 (d, J = 7.9 Hz, 2H), 8.31 (s, 1H), 8.39 (s, 1H); ^{13}C NMR (100 MHz) δ 121.7, 121.9, 123.9, 125.5, 126.1, 127.5, 128.0, 128.9, 129.3, 131.2, 131.4, 134.3, 134.4, 136.7, 137.9, 138.3; EI-MS (70 eV) m/z = 292 (M^+); Anal. calcd for $C_{18}H_{12}S_2$: C, 73.93; H, 4.14%. Found: C, 73.83; H, 3.90%.

To a solution of 3-(phenylthio)naphtho[2,3-*b*]thiophene (146 mg, 0.5 mmol) in THF (5 mL) was added *n*-butyllithium (1.63 M in hexane, 0.46 mL, 0.75 mmol) at 0 °C. The mixture was warmed to rt and then stirred for 1 h, and iodine (190 mg, 0.75 mmol) was added to the mixture at 0 °C. The resulting mixture was stirred for 6 h at rt, poured into an aqueous solution of $Na_2S_2O_5$ (saturated, 5 mL), and extracted with dichloromethane (50 mL × 3). The combined extracts were washed with brine (50 mL × 3), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (chloroform, R_f = 0.9) to give **5b** (138 mg, 66%) as a pale yellow solid. Mp. 194−196 °C; ^{1}H NMR (400 MHz) δ 7.10−7.22 (m, 5H), 7.46 (dt, J = 1.4, 7.5 Hz, 1H), 7.51 (dt, J = 1.4, 7.5 Hz, 1H), 7.90 (t, J = 7.5 Hz, 2H), 8.28 (s, 1H), 8.30 (s, 1H); ^{13}C NMR (100 MHz) δ 99.0, 120.4, 122.6, 126.0, 126.5, 126.6, 127.4, 127.5, 129.0, 129.5, 131.2, 131.4, 131.4, 135.9, 137.4, 141.3; EI-MS (70 eV) m/z = 418 (M^+); HRMS (APCI) m/z calcd for $C_{18}H_{11}IS_2$ $[M]^+$: 417.93414, Found: 417.93405.

2-Bromo-3-(phenylthio)naphtho[2,3-*b*]thiophene (5c). A similar procedure using 1,2-dibromo-1,1,2,2-tetrachloroethane instead of iodine gave **5c** in 93% yield. Pale-yellow solid; Mp. 181−183 °C; ^{1}H NMR (400 MHz) δ 7.10−7.23 (m, 5H), 7.46 (dt, J = 1.3, 6.8 Hz, 1H), 7.51 (dt, J = 1.3, 7.9 Hz, 1H), 7.91(t, J = 7.9 Hz, 2H), 8.26 (s, 1H), 8.28 (s, 1H); ^{13}C NMR (100 MHz) δ 120.7, 122.4, 125.3, 126.0, 126.3, 126.5, 127.51, 127.53, 127.9, 128.9, 129.5, 131.5, 131.7, 135.7, 137.6, 137.8; EI-MS (70 eV) m/z = 370 (M^+); HRMS (APCI) m/z calcd for $C_{18}H_{11}BrS_2$ $[M]^+$: 369.94801. Found: 369.94739.

[1]Benzothieno[3,2-*b*]naphtho[2,3-*b*]thiophene (BTNT). The title compound was obtained in the same manner as for the synthesis of BTBT: 91% isolated yield from **5b** and 90% yield from **5c**. Yellow solids; Mp. 289−291 °C; ^{1}H NMR (400 MHz) δ 7.43 (dt, J = 1.3, 7.2 Hz, 1H), 7.48 (dt, J = 1.3, 7.2 Hz, 1H), 7.52 (t, J = 6.5 Hz, 1H), 7.53 (t, J = 6.5 Hz, 1H), 7.89−7.96 (m, 3H), 8.02 (dd, J = 3.5, 6.5 Hz, 1H),

8.36 (s, 1H), 8.39 (s, 1H); ^{13}C NMR (100 MHz) δ 120.1, 122.3, 122.8, 124.4, 125.4, 125.7, 126.0, 126.1, 127.7, 127.8, 128.6, 131.7, 131.8, 132.8, 133.7, 134.9, 141.1, 143.2; EI-MS (70 eV) m/z = 290 (M^+); HRMS (APCI) m/z calcd for $C_{18}H_{11}S_2$ $[M + H]^+$: 291.02967, Found: 291.02997.

2-Methylthio-3-[2-(trimethylsilyl)ethynyl]anthracene (6). The title compound was obtained as a yellow solid from 3-(methylthio)anthracen-2-yl-trifluoromethanesulfonate in the same manner as for the synthesis of **4**. 84% isolated yield. Mp. 161−164 °C; ^{1}H NMR (400 MHz) δ 0.33 (s, 9H), 2.62 (s, 3H), 7.41−7.48 (m, 2H), 7.56 (s, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 8.14 (s, 1H), 8.25 (s, 1H), 8.29 (s, 1H); ^{13}C NMR (100 MHz) δ 0.3, 15.6, 101.4, 102.6, 119.9, 121.1, 124.7, 125.7, 126.4, 126.6, 128.3, 128.7, 129.2, 131.6, 131.7, 133.0, 133.6, 137.6; EI-MS (70 eV) m/z = 320 (M^+); HRMS (APCI) m/z calcd for $C_{20}H_{20}SSi$ $[M]^+$: 320.10495. Found: 320.10550.

3-Phenylthio-2-(trimethylsilyl)anthra[2,3-*b*]thiophene (7a). The title compound was synthesized from **6** and phenylsulfenyl chloride. Yellow solid (86%). Mp. 193−196 °C ; ^{1}H NMR (400 MHz) δ 0.46 (s, 9H), 7.05−7.18 (m, 5H), 7.38 (dt, J = 1.6, 6.6 Hz, 1H), 7.42 (dt, J = 1.6, 6.6 Hz, 1H), 7.94 (dd, J = 1.6, 7.9 Hz, 1H), 7.98 (dd, J = 1.6, 7.9 Hz, 1H), 8.44 (s, 1H), 8.52 (s, 2H), 8.55 (s, 1H); ^{13}C NMR (100 MHz) δ 0.0, 120.7, 121.9, 125.3, 125.4, 125.5, 125.6, 126.3, 127.6, 128.4, 128.5, 129.0, 129.3, 129.8, 120.0, 131.5, 132.0, 138.2, 140.0, 140.7, 153.8; EI-MS (70 eV) m/z = 414 (M^+). HRMS (APCI) m/z calcd for $C_{25}H_{22}S_2Si$ $[M]^+$: 414.09267. Found: 414.09299.

2-Iodo-3-(phenylthio)anthra[2,3-*b*]thiophene (7b). 3-(Phenylthio)anthra[2,3-*b*]thiophene was synthesized from **7a** in the same as for the synthesis of 3-(phenylthio)naphtho[2,3-*b*]thiophene (quantitative). Yellow solid; Mp. 240−242 °C; ^{1}H NMR (400 MHz) δ 7.15−7.29 (m, 5H), 7.42 (dt, J = 2.2, 6.8 Hz, 1H), 7.44 (dt, J = 2.2, 6.8 Hz, 1H), 7.76 (s, 1H), 7.98 (d, J = 9.1 Hz, 1H), 8.01 (d, J = 9.1 Hz, 1H), 8.49 (s, 1H), 8.53 (s, 1H), 8.56 (s, 2H); ^{13}C NMR (100 MHz) δ 120.4, 121.7, 122.3, 125.5, 125.6, 125.8, 126.6, 127.5, 128.4 128.5, 128.6, 129.5, 129.8, 129.9, 130.2, 131.8, 132.2, 134.5, 136.6, 138.1; EI-MS (70 eV) m/z = 342 (M^+); HRMS (APCI) m/z calcd for $C_{22}H_{14}S_2$ $[M]^+$: 342.05314. Found: 342.05371.

To a solution of 3-(phenylthio)anthra[2,3-*b*]thiophene (200 mg, 0.58 mmol) in THF (40 mL) was added *n*-butyllithium (1.63 M in hexane, 0.7 mL, 1.17 mmol) at 0 °C. The mixture was warmed to rt and stirred for 1 h. Iodine (297 mg, 1.17 mmol) was added to the mixture at 0 °C, and the resulting mixture was stirred for 6 h at rt and then poured into an aqueous solution of $Na_2S_2O_5$ (saturated, 10 mL). The resulting precipitate was collected by filtration and washed with ethanol and hexane. The crude product was purified by recrystallization from chlorofrom to give 2-iodo-3-(phenylthio)anthra[2,3-*b*]-thiophene as a yellow solid (204 mg, 75%). Mp. 266−268 °C; ^{1}H NMR (400 MHz) δ 7.12−7.22 (m, 5H), 7.42 (dt, J = 1.6, 6.4 Hz, 1H), 7.46 (dt, J = 1.6, 6.4 Hz, 1H), 7.99 (t, J = 9.0 Hz, 2H), 8.44 (s, 1H), 8.49 (s, 1H), 8.50 (s, 1H), 8.55 (s, 1H); EI-MS (70 eV) m/z = 468 (M^+); HRMS (APCI) m/z calcd for $C_{22}H_{13}IS_2$ $[M]^+$: 467.94979. Found: 467.95032.

2-Bromo-3-(phenylthio)anthra[2,3-*b*]thiophene (7c). The title compound was obtained as the same manner described above by using 1,2-dibromo-1,1,2,2-tetrachloroethane as the electrophile (65%). Yellow solid; Mp. 245−246 °C; ^{1}H NMR (400 MHz) δ 7.13−7.23 (m, 5H), 7.43 (dt, J = 1.6, 6.6 Hz, 1H), 7.46 (dt, J = 1.6, 6.6 Hz, 1H), 7.99 (t, J = 8.6 Hz, 2H), 8.42 (s, 1H), 8.47 (s, 1H), 8.50 (s, 1H), 8.55 (s, 1H); EI-MS (70 eV) m/z = 420 (M^+); HRMS (APCI) m/z calcd for $C_{22}H_{14}BrS_2$ $[M + H]^+$: 420.97148. Found: 420.97165.

[1]Benzothieno[3,2-*b*]anthra[2,3-*b*]thiophene (BTAT). The palladium catalyzed cyclization reaction on **7b** and **7c** gave the desired BTAT in quantitative and 93% isolated yield. Yellow solid. For the device fabrication, BTAT was further purified by vacuum sublimation (source temperature, 220 °C under 10^{-3} Pa). Mp. >300 °C; ^{1}H NMR (400 MHz) δ 7.46 (m, 4H), 4.88 (d, J = 7.7 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H), 8.03 (d, J = 7.9 Hz, 2H), 8.52 (s, 2H), 8.54 (s, 1H), 8.63 (s, 1H); EI-MS (70 eV) m/z = 340 (M^+); HRMS (APCI) m/z Calcd for $C_{22}H_{12}S_2$ $[M]^+$: 340.03749, Found 340.03787; Anal. calcd for $C_{22}H_{12}S_2$: C, 77.61; H, 3.55%. Found: C, 77.50; H, 3.16%.

3-(2-Naphthylthio)benzo[*b*]thiophene (8a). To a solution of 2-naphthalenethiol (147 mg, 0.92 mmol) in dichloromethane (5 mL) was added *N*-chlorosuccinimide (123 mg, 0.92 mmol) at 0 °C. After the mixture was stirred for 20 min at rt, the resulting dichloromethane solution of 2-naphthylsulfenyl chloride was added to a solution of **1** (135 mg, 0.61 mmol) in dichloromethane (5 mL) at 0 °C. After stirring at rt for 2 h, a solution of tetrabutylammonium fluoride (1 M, 1.2 mL, 1.2 mmol) was added to the mixture, and the resulting mixture was stirred for 3 h, and the poured into saturated aqueous K_2CO_3 solution (50 mL). The mixture was extracted with dichloromethane (10 mL × 3), and the combined extracts were washed with brine (15 mL × 3), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (chloroform-hexane, 1:2 v/v, R_f = 0.6) to give 3-(2-naphthylthio)benzo[*b*]thiophene as a white solid (115 mg, 87%). Mp. 61−62 °C; ^{1}H NMR (400 MHz) δ 7.28 (dd, J = 1.9, 8.7 Hz, 1H), 7.34 (dt, J = 1.1, 7.0 Hz, 1H), 7.37−7.44 (m, 3H), 7.60−7.64 (m, 2H), 7.68 (d, J = 8.5 Hz, 1H), 7.73 (dd, J = 2.4, 7.0 Hz, 1H), 7.76 (s, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz) δ 123.3, 123.4, 124.3, 125.2, 125.4, 126.0, 126.2, 126.9, 127.5, 128.1, 129.0, 129.3, 132.1, 132.4, 134.0, 134.3, 139.2, 140.4; EI-MS (70 eV) m/z = 292 (M^+); HRMS (APCI) m/z calcd for $C_{18}H_{13}S_2$ $[M + H]^+$: 293.04532. Found: 293.04523.

2-Iodo-3-(2-naphthylthio)benzo[*b*]thiophene (8b). The title compound was obtained in the same manner as for the synthesis of **5b** (67%). White solid; Mp. 155−158 °C; ^{1}H NMR (400 MHz) δ 7.18 (dd, J = 2.1, 8.9 Hz, 1H), 7.25−7.33 (m, 2H), 7.38 (dt, J = 1.4, 6.8 Hz, 1H), 7.41 (dt, J = 1.4, 6.8 Hz, 1H), 7.52 (s, 1H), 7.62 (d, J = 7.4 Hz, 1H), 7.66 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.4 Hz, 1H), 7.80 (td, J = 2.1, 7.6 Hz, 2H); ^{13}C NMR (100 MHz) δ 95.6, 122.2, 124.1, 125.5, 125.62, 125.64, 125.65, 126.0, 126.9, 127.4, 128.1, 129.1, 131.5, 132.0, 133.5, 134.0, 139.1, 144.0; EI-MS (70 eV) m/z = 418 (M^+); HRMS (ESI) m/z calcd for $C_{18}H_{11}IS_2$ $[M + H]^+$: 418.9425. Found: 418.9420.

2-Bromo-3-(2-naphthylthio)benzo[*b*]thiophene (8c). The title compound was obtained in the same manner as for the synthesis of **2c** (67%). White solid; Mp. 121−123 °C; ^{1}H NMR (400 MHz) δ 7.22 (dd, J = 1.9, 8.7 Hz, 1H), 7.31 (dt, J = 1.1, 7.6 Hz, 1H), 7.36−7.44 (m, 3H), 7.56 (d, J = 1.9 Hz, 1H), 7.63 (dd, J = 1.9, 7.4 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.74 (dd, J = 1.9, 7.4 Hz, 1H), 7.77−7.81 (m, 2H); ^{13}C NMR (100 MHz) δ 122.3, 123.8, 125.5, 125.70, 127.72, 125.75, 125.79, 125.9, 126.0, 126.9, 127.4, 128.0, 129.1, 132.0, 133.2, 134.0, 139.4, 139.9; EI-MS (70 eV) m/z = 370 (M^+); HRMS (APCI) m/z calcd for $C_{18}H_{11}BrS_2$ $[M]^+$: 369.94801. Found: 369.94739.

[1]Benzothieno[3,2-*b*]naphtho[2,3-*b*]thiophene (BTNT). The palladium catalyzed cyclization reaction on **8b** proceeded very slowly, and only a trace amount of BTNT was detected by MS spectra. On the other hand, the reaction of **8c** gave an isomeric mixture of cyclized compounds (see main text) in quantitative yield. The ratio of the BTNT and its isomer, [1]benzothieno[2,3-*a*]naphtho[2,1-*b*]-thiophene, was ca. 9:1 judged from the ratio of the diagnostic protons (see Figure 3a). The latter isomer with better solubility can be removed by washing with ethanol, and isomerically pure BTNT can be isolated in 80% yield. To confirm the structures of BTNT and [1]benzothieno[2,3-*a*]naphtho[2,1-*b*]thiophene, their chemical shifts on ^{1}H NMR spectra were simulated by using Gaussian 03 program. The calculated and observed chemical shifts are listed in Table S1, which clearly states that the present characterization of each compound by ^{1}H NMR spectra is decent.

3-(2-Naphthylthio)anthra[2,3-*b*]thiophene (9a). As described in the synthesis of **8a**, a reaction of **6** (962 mg, 3 mmol) with in situ generated 2-naphthylsulfenyl chloride (4.5 mmol) gave **9a** (925 mg, 79%) as a yellow solid. Mp. 227−229 °C; ^{1}H NMR (400 MHz) δ 7.25−7.45 (m, 5H), 7.64 (dd, J = 2.5, 6.8 Hz, 1H), 7.69−7.76 (m, 3H), 7.81 (s, 1H), 7.92 (dd, J = 1.5, 7.5 Hz, 1H), 7.90 (dd, J = 1.5, 7.5 Hz, 1H), 8.50 (s, 1H), 8.51 (d, J = 1.6 Hz, 1H), 8.52 (s, 1H), 8.56 (s, 1H); ^{13}C NMR (100 MHz) δ 121.7, 122.25, 122.27, 124.5, 125.5, 125.6, 125.8, 126.2, 126.6, 126.9, 127.0, 127.5, 127.6, 128.1, 128.5, 128.5, 128.6, 129.2, 130.0, 130.2, 131.8, 132.2, 134.0, 134.2, 134.5,

138.1; EI-MS (70 eV) m/z = 392 (M^+); HRMS (APCI) m/z calcd for $C_{26}H_{17}S_2$ $[M + H]^+$: 393.07662. Found: 393.07578.

2-Bromo-3-(2-naphthylthio)anthra[2,3-*b*]thiophene (9b). To a solution of **9a** (500 mg, 1.5 mmol) in THF (50 mL) was added *n*-butyllithium (1.63 M in hexane, 1.2 mL, 2.0 mmol) at 0 °C. The mixture was warmed to rt and then stirred for 1 h. 1,2-Dibromo-1,1,2,2-tetrachloroethane (645 mg, 2.0 mmol) was then added to the mixture at 0 °C, and the resulting mixture was stirred for 10 h at rt, and poured into a mixture of hydrochloric acid (1 M, 10 mL) and ethanol (50 mL), and a precipitate solid was collected by filtration and washed with ethanol and hexane. The crude product was purified by recrystallization from chlorofrom to give **9b** as a yellow solid (502 mg, 70%). Mp. 245−246 °C; ^{1}H NMR (400 MHz) δ 7.31 (dd, J = 1.9, 8.6 Hz, 1H), 7.37−7.46 (m, 4H), 7.64−7.68 (m, 2H), 7,69 (d, J = 8.7, 1H), 7.74 (dd, J = 1.7, 7.1, 1H), 7.95 (d, J = 7.9 Hz, 1H), 8.00 (d, 7.9 Hz, 1H), 8.44 (s, 1H), 8.50 (s, 2H), 8.52 (s, 1H); EI-MS (70 eV) m/z = 470 (M^+); HRMS (APCI) m/z calcd for $C_{26}H_{16}BrS_2$ $[M + H]^+$: 470.98713 Found: 470.98724.

Naphtho[3,2-*b*]thieno[3,2-*b*]anthra[2,3-*b*]thiophene (NTAT). The palladium catalyzed cyclization reaction on **9b** gave a dark-red solid, which was extracted thoroughly with chloroform by using the Soxhlet apparatus. From the insoluble portion (residual solid), NTAT was obtained in 46% yield as a red solid. Although the extract contained NTAT, no attempt was made for isolating NTAT. For the device fabrication, NTAT was further purified by vacuum sublimation (source temperature, 300 °C under 10^{-3} Pa). HRMS (APCI) m/z calcd for $C_{26}H_{14}S_2$ $[M]^+$: 390.05314, Found 390.05215; Anal. calcd for $C_{26}H_{14}S_2$: C, 79.96; H, 3.61%. Found: C, 80.03; H, 3.26%.

3,7-Bis(phenylthio)benzo[1,2-*b*:4,5-*b*′]dithiophene (11a). As described for the synthesis of **2a**, treatment of 1,4-bis(methylthio)-2,5-bis[2-(trimethylsilyl)ethynyl]benzene with phenylsulfenyl chloride gave corresponding bis(trimethylsilyl) derivative of **11a**, which was then desilylated by an action of tetrabutylammonium fluoride to give the title compound as a white solid. The crude product was purified by column chromatography on silica gel eluted with chloroform to give **11a** as a white solid (79%). Mp. 251−253 °C; ^{1}H NMR (400 MHz) δ 7.12−7.24 (m, 10H), 7.78 (s, 2H), 8.31 (s, 2H); ^{13}C NMR (100 MHz) δ 117.5, 123.1, 126.3, 127.7, 129.5, 134.4, 136.7, 137.6, 138.2; EI-MS (70 eV) m/z = 406 (M^+); HRMS (APCI) m/z calcd for $C_{22}H_{15}S_4$ $[M + H]^+$: 407.00511. Found: 407.00482.

2,6-Dibromo-3,7-bis(phenylthio)benzo[1,2-*b*:4,5-*b*′]dithiophene (11b). The title compound was synthesized from **11a** with the same procedure for the synthesis of **2c**, and the product purified by column chromatography on silica gel (hexane-chloroform, 5:1 v/v, R_f = 0.5) (83% yield). White solid; Mp. 247−249 °C; ^{1}H NMR (400 MHz) δ 7.11−7.26 (m, 10H), 8.18 (s, 2H); ^{13}C NMR (100 MHz) δ 116.9, 124.8, 126.5, 127.2, 127.5, 129.6, 135.4, 137.5, 137.8; EI-MS (70 eV) m/z = 562 (M^+); HRMS (APCI) m/z calcd for $C_{22}H_{13}Br_2S_4$ $[M + H]^+$:562.82613. Found: 562.82581.

Bis[1]benzothieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene (BBTBDT). The palladium catalyzed cyclization reaction on **11b** gave BBTNDT; the crude product was washed thoroughly with acetone (12 h) and chloroform (12 h) by using the Soxhlet apparatus to give BBTBDT (310 mg, 61%) as a yellow solid. EI-MS (70 eV) m/z = 402 (M^+).

2,6-Bis(methylthio)-3,7-bis[2-(trimethylsilyl)ethynyl]-naphthalene (12). To a solution of 2,6-dimethoxy-3,7-bis-(methylthio)naphthalene (841 mg, 3 mmol) in dichloromethane (30 mL) was added boron tribromide (BBr_3, 12 mL, 12 mmol, 1 M in dichloromethane). The solution was stirred for 20 h at rt, and the resulting precipitate was collected by filtration and washed with water to give 2,6-dihydroxy-3,7- bis(methylthio)naphthalene as a white solid (760 mg, quantitative). Mp. 224−225 °C; ^{1}H NMR (400 MHz) δ 2.43 (s, 6H), 6.40 (s, 2H), 7.20 (s, 2H), 7.82 (s, 2H); ^{13}C NMR (100 MHz, DMSO) δ 14.5, 108.1, 121.5, 127.9, 128.6, 151.1; EI-MS (70 eV) m/z = 252 (M^+); HRMS (APCI) m/z calcd for $C_{12}H_{12}O_2S_2$ $[M]^+$: 252.02732. Found: 252.02768.

To a suspension of 2,6-dihydroxy-3,7-bis(methylthio)naphthalene (757 mg, 3 mmol) and triethylamine (3.2 mL, 23 mmol) in dichloromethane (30 mL) was slowly added trifluoromethanesulfonic anhydride (1.5 mL, 9 mmol) at 0 °C. After the mixture was stirred for 5 h, water (10 mL) and hydrochloric acid (1 M, 10 mL) were added. The resulting mixture was extracted with chloroform, and the residue was purified by column chromatography on silica gel eluted with chloroform (R_f = 0.9) to give 3,7-bis(methylthio)-2,6-bis-(trifluoromethanesulfonyloxy)naphthalene as a white solid (1.14 g, 74%). Mp. 171−174 °C; ^{1}H NMR (500 MHz) δ 2.61 (s, 6H) 7.60 (s, 2H), 7.69 (s, 2H); ^{13}C NMR (125 MHz) δ 15.8, 118.5, 119.1 (q, J = 319.7 Hz), 126.3, 130.7, 133.1, 146.7; EI-MS (70 eV) m/z 516 (M^+); HRMS (APCI) m/z calcd for $C_{14}H_{10}F_6O_6S_4$ $[M]^+$: 515.92589. Found: 515.92560.

The title compound was obtained from 3,7-bis(methylthio)-2,6-bis(trifluoromethanesulfonyloxy)naphthalene in the same manner as the synthesis of **4** (84%). Yellow solid from chloroform-ethanol; Mp.179−180 °C; ^{1}H NMR (400 MHz) δ 0.30 (s, 18H) 2.55 (s, 6H), 7.33 (s, 2H), 7.83 (s, 2H); ^{13}C NMR (100 MHz) δ 0.2, 15.4, 102.1, 102.3, 121.2, 121.4, 130.6, 131.5, 138.3; EI-MS (70 eV) m/z = 412 (M^+); Anal. calcd for $C_{22}H_{28}S_2Si_2$: C, 64.02; H, 6.84%. Found: C, 64.31; H, 6.77%.

3,8-Bis(phenylthio)naphtho[2,3-*b*:6,7-*b*′]dithiophene (13a). The title compound was synthesized from **12** and phenylsulfenyl chloride, and purified by recrystallization from chloroform as a yellow solid (64%). Mp. 251−253 °C; ^{1}H NMR (400 MHz) δ 7.12−7.24 (m, 10H), 7.78 (s, 2H), 8.37(s, 2H), 8.47 (s, 2H); ^{13}C NMR (100 MHz) δ 121.2, 122.4, 124.5, 126.5, 128.4, 129.4, 129.5, 134.6, 136.6, 138.0, 138.3; EI-MS (70 eV) m/z = 456 (M^+); Anal. calcd for $C_{26}H_{16}S_4$: C, 68.38; H, 3.53%. Found: C, 68.30; H, 3.32%.

2,7-Diiodo-3,8-bis(phenylthio)naphtho[2,3-*b*:6,7-*b*′]-dithiophene (13b). To a solution of 3,7-(phenylthio)naphtho[2,3-*b*:6,7-*b*′]dithiophene (758 mg, 1.7 mmol) in THF (100 mL) was added *n*-butyllithium (1.63 M in hexane, 3.1 mL, 5 mmol) at 0 °C. The mixture was warmed to rt and then stirred for 1 h. Iodine (1.27 g, 5 mmol) was added to the mixture at 0 °C, and the resulting mixture was stirred for 6 h at rt and then poured into an aqueous solution of $Na_2S_2O_5$ (saturated, 100 mL). The resulting precipitate was collected by filtration and washed with ethanol and hexane. The crude product was purified by recrystallization from toluene to give **13b** as a yellow solid (738 mg, 63%). Mp. 290−291 °C; ^{1}H NMR (400 MHz) δ 7.11−7.25 (m, 10H), 8.33 (s, 2H), 8.34 (s, 2H); EI-MS (70 eV) m/z = 708 (M^+); HRMS (APCI) m/z calcd for $C_{26}H_{15}I_2S_4$ $[M + H]^+$: 708.81405. Found: 708.81384.

2,7-Dibromo-3,8-bis(phenylthio)naphtho[2,3-*b*:6,7-*b*′]-dithiophene (13c). A similar procedure for the synthesis of **13b** using 1,2-dibromo-1,1,2,2-tetrachloroethane gave **13c** as a yellow solid (81%). Mp. 289−291 °C; ^{1}H NMR (400 MHz) δ 7.13−7.23 (m, 10H), 8.316 (s, 2H), 8.323 (s, 2H); EI-MS (70 eV) m/z = 612 (M^+); HRMS (APCI) m/z calcd for $C_{26}H_{15}Br_2S_4$ $[M + H]^+$: 612.84179. Found: 612.84229.

Bis[1]benzothieno[2,3-*d*:2′,3′-*d*′]naphtho[2,3-*b*:6,7-*b*′]-dithiophene (BBTNDT). The title compound was obtained in the same manner for the synthesis of BBTBDT. The crude product was washed thoroughly with acetone (12 h) and chloroform (12 h) by using the Soxhlet apparatus to give BBTNDT (310 mg, 81%) as an orange solid. For the device fabrication, BBTNDT was further purified by vacuum sublimation (source temperature, 360 °C under 10^{-3} Pa). HRMS (APCI) m/z calcd for $C_{26}H_{12}S_4$ $[M]^+$: 451.98163. Found 451.98148; Anal. calcd for $C_{26}H_{12}S_4$: C, 68.99; H, 2.67%. Found: C, 68.66; H, 2.34%.

Device Fabrication and Characterization. OFETs were fabricated in a "top-contact" configuration on a heavily doped n^+-Si (100) wafer with a 200 nm thermally grown SiO_2 (C_i = 17.3 nF cm^{-2}). The substrate surfaces were treated with OTS, or ODTS as reported previously.[10a] A thin film of the organic semiconductors as the active layer was vacuum deposited on the Si/SiO_2 substrates maintained at various temperatures (T_{sub}) at a rate of 1 Å s^{-1} under a pressure of ~10^{-3} Pa. On top of the organic thin film, gold films (80 nm) as drain and source electrodes were deposited through a shadow mask. For a typical device, the drain-source channel length (L) and width (W) are 50 μm and 1.5 mm, respectively. Characteristics of the OFET devices were measured at rt under ambient conditions with a Keithley 4200

semiconducting parameter analyzer. Field-effect mobility (μ_{FET}) was calculated in the saturation (V_d = −60 V) of the I_d using the following equation,

$$I_d = C_i\mu_{FET}(W/2L)(V_g - V_{th})^2$$

where C_i is the capacitance of the SiO_2 insulator, and V_g and V_{th} are the gate and threshold voltages, respectively. Current on/off ratio (I_{on}/I_{off}) was determined from the I_d at V_g = 0 V (I_{off}) and V_g = −60 V (I_{on}). The μ_{FET} data reported are typical values from more than 10 different devices.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra, calculated and observed ^{1}H NMR chemical shifts of BTNT and [1]benzothieno[2,3-*a*]naphtho[2,1-*b*]thiophene, CIF for BTAT and BBTNDT, CVs, PESA, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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