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Synthesis and Physicochemical Properties of Dibenzo[2,3-*d*:2',3'*d*']anthra[1,2-*b*:5,6-*b*']dithiophene (DBADT) and Its Derivatives: Effect of Substituents on Their Molecular Orientation and Transistor Properties

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ABSTRACT. We have synthesized dibenzo[2,3-*d*:2',3'-*d*']anthra[1,2-*b*:5,6-*b*']dithiophene (DBADT) and several derivatives bearing alkyl and phenyl groups at various positions. The optical and electrochemical properties of the synthesized compounds were investigated. All the fabricated OFET devices exhibited typical p-type behavior under ambient conditions, and diphenyl-substituted analogue-based OFET devices showed excellent mobility, as high as $0.66 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The surface morphology and molecular orientation in thin films were also investigated using atomic force microscopy (AFM) and two-dimensional grazing incidence X-ray diffraction (2D-GIXD). It was found that the substituents and their positions affect the molecular orbitals, molecular orientation, and morphology of the thin films, producing different FET performance.

Introduction

Organic semiconducting materials with highly extended π -electron systems have been widely used in organic electronic devices, such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs).¹ In particular, integrated circuits based on OFETs have been recognized as important components that can play a key role in organic electronics, because they are needed to operate active-matrix displays, sensors, and RF-ID tags. Polycyclic aromatic hydrocarbons (PAHs) are one of the potential high-performance OFET materials.² For instance, linearly extended pentacene and picene derivatives are representative high-performance p-type semiconductors, which respectively showed high mobilities of up to 3 cm² V⁻¹ s⁻¹³ and 20.9 cm² V⁻¹ s⁻¹⁴. However, the former is unstable and easily deteriorates under ambient conditions due to its high HOMO energy level of -5.0 eV.⁵ The latter exhibited an extremely high threshold voltage owing to its deep HOMO energy level of -5.5 eV, ⁶ which often prevents smooth hole injection.⁷

Thienoacenes, which are sulfur-containing polycyclic aromatic compounds, are also promising candidates for high-performance materials for the following reasons. First, the Page 3 of 36

large atomic radius of sulfur atoms can enhance the extent of their interaction, leading to more effective π -orbital overlaps intermolecularly.⁸ Second, the thienoacenes can extend their π -conjugation and construct a pseudo-linear structure without significant elevation of their HOMO energy level, resulting in low-voltage device operation.⁹ Third, a thiophene ring is easier to construct than a benzene ring. Recent synthetic progress has yielded many types of ring-closing reactions for the preparation of thiophene rings, and it has become possible to synthesize highly extended thienoacenes.¹⁰ In these efforts, numerous thienoacenes involving [1]benzothieno[3,2-*b*]benzothiophene (BTBT) analogues,¹¹ dinaphtho[2,3-*b*:2',3'-*d*]thiophenes (DNT-Vs),¹² and dinaphtho[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophenes (DNBDTs)¹³ have been developed, with hole mobilities reaching over 5 cm² V⁻¹ s⁻¹.

Two strategies in the hunt for high-performance thienoacene-based OFETs are 1) expansion of π -electron systems and 2) introduction of alkyl or aromatic groups.^{10,14} For instance, C₁₀-DNBDT with seven fused aromatic rings showed excellent hole mobility of up to 16 cm² V⁻¹ s⁻¹,¹³ which is higher than that of the related five ring-fused molecules, C₆-DNT-VW ($\mu_{FET} = 9.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).¹² Such π -extension can enhance the intermolecular electronic coupling due to large π -planes, which lead to a dense packing structure in the solid state. Additionally, the introduction of long alkyl chains or aromatic rings has shown another promising way. In the study of dinaphtho[2,3-*b*:2',3'-*f*']thieno[3,2-*b*]thiophene (DNTT) derivatives, as reported by Takimiya and coworkers, DNTT-based OFET devices exhibited high mobility of up to 2.9 cm² V⁻¹ s⁻¹,^{15a} while dialkylated-DNTT-based devices displayed a further enhanced mobility of up to 8.0 cm² V⁻¹ s^{-1 15b} owing to the fastener effect, which can lead to a tight packing structure through van der Waals intermolecular interactions between alkyl chains.^{15c,15d} Moreover, diphenyl-bis[1]benzothieno[2,3-*d*;2',3'-*d*']naphtho[2,3-*b*;6,7-*b*']dithiophene (DPh-BBTNDT) also has higher hole transport ability ($\mu_{FET} = 7.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)

isotropic electronic structure.¹⁶ However, the position of substituents strongly affects the packing structure and thus the OFET performance, particularly along the molecules' long axis.¹⁷ Thus, the introduction of long alkyl chains or aromatic rings at the optimal position is highly important for the development of high-performance thienoacenes.

Previously, we have developed various phenacene-type molecules via Lewis acidcatalyzed cycloaromatization.^{18–21} In particular, 2,7-didodecyl-phenanthro[2,1-b:7,8b']dithiophene (C12-PDT-2) exhibited excellent mobility of up to 5.6 cm² V⁻¹ s⁻¹ with a PbZr_{0.52}Ti_{0.48}O₃ (PZT) gate dielectric with a high k value.²⁰ Although our developed materials displayed better mobilities, the absolute threshold voltages bear high values due to a large energy barrier between the work function of gold (~5.1 eV) as source and drain electrodes and the HOMO energy levels of the active layer ($-5.6 \sim -5.8$ eV). In order to solve this problem, we have recently developed a material with nine fused aromatic rings, bis[1]benzothieno[2,3-d:2',3'-d']anthra[1,2-b:5,6-b']dithiophene (BBTADT), incorporating an acene moiety in its molecular center, which increases its HOMO energy level, leading to smooth hole injection from the gold electrodes.²² Fabricated OFET devices showed the lowvoltage operation ($|V_{\text{th}}| = 9 \text{ V}$), although the highest mobility was only $2.7 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ due to its unfavorable solid state structure. One of the reasons for the low mobility is the unsuitable HOMO geometry, indicating that the sulfur atoms are completely in the nodal plane, which would reduce intermolecular orbital overlaps.¹⁰ To overcome these drawbacks, we newly designed dibenzo [2,3-d:2',3'-d'] anthra [1,2-b:5,6-b'] dithiophene (DBADT) and its alkyl and phenyl-substituted derivatives. From DFT calculations (Figure 1), DBADT's HOMO has a large electron density on the sulfur atoms, which can thus form efficient π orbital overlaps between neighboring molecules in the solid state. In addition, such effective intermolecular interaction may provide a dense packing structure, leading to highly ordered

 crystalline films. Herein, we report the synthesis and characterization of a series of DBADT derivatives, and discuss the effect of the substituents and their positions on FET performance.



Figure 1. Molecular structures and HOMO orbitals of BBTADT and DBADT derivatives.

Results and Discussion

Synthesis of DBADT and Its Derivatives. A subsequent synthetic route to DBADT derivatives **5a-5e** is summarized in Scheme 1. Palladium-catalyzed Suzuki-Miyaura coupling of commercially available 2-benzothienylboronic acid (**1a**) and **2** afforded dialdehyde **3a** in 96% yield. Accordingly, dialdehydes **3b-3e** bearing various substituents were synthesized with excellent yields through palladium-catalyzed Negishi coupling of **2** with 2.2 equiv of the corresponding zinc reagents, derived from deprotonation ²³ and the subsequent zincation of benzo[*b*]thiophene derivatives **1b-1e**. The subsequent epoxidation of **3a-3d** afforded the corresponding epoxides **4a-4d** in high yields. However, epoxidation of **3e** in acetonitrile did not afford the epoxide **4e** because of its low solubility. To our delight, we could successfully synthesize **4e** by epoxidation of **3e** in benzonitrile as the solvent. Finally, DBADT derivatives **5a-5e** were obtained in 78-91% yields through indium-catalyzed Friedel-Crafts-type intramolecular double cycloaromatization.²⁴ DBADT derivatives **5a-5e** showed quite low solubility in common organic solvents such as THF, toluene, chloroform, and even

chlorobenzene. Since our synthetic method does not yield any structural isomers of DBADT upon cycloaromatization, the purity of DBADT derivatives was confirmed by elemental analyses.



Scheme 1. A synthetic route to DBADT derivatives

Optical and Electrochemical Properties. To investigate the optical properties of DBADT derivatives **5a-5e**, we next measured UV-vis absorption spectra in CH₂Cl₂ solution and thin films, which are shown in Figure 2, and the corresponding optical data is summarized in Table 1. The thin films were prepared by vapor deposition at the rate of 0.1 Å/s on a quartz glass substrate. Molar absorption coefficients of all DBADT derivatives were not determined due to their low solubility. The maximum absorption wavelength of DBADT **5a** in solution was observed at 327 nm, which is ca. 20 nm red-shifted relative to that of anthra[1,2-*b*:5,6-*b*']dithiophene (ADT, $\lambda_{max} = 304$ nm),²⁵ due to its extended π -conjugation. Dialkylated

derivatives **5b** and **5c** showed similar absorption maxima of 331 nm and 333 nm, respectively. Accordingly, their HOMO-LUMO energy gaps (2.89 eV for **5b** and **5c**) were slightly smaller than that of 5a (2.92 eV), indicating that any substitution position effect on the electronic structure is negligible when alkylating DBADT. One possible reason for the slight alkylation effect on electronic structure may be the weak electron-donating nature of alkyl groups. The absorption maximum of diphenylated derivative 5d was also shifted bathochromically by 15 nm and the energy gap of 5d (2.86 eV) was smaller than that of 5a owing to the additional aromatic groups incorporated, which led to the extended π -conjugation. On the other hand, the absorption maximum of diphenyl-substituted DBADT 5e at 4,12-positions was blueshifted by about 7 nm compared with that of 5d. In addition, the optical energy gap of 5e (2.90 eV) is almost same as that of 5a, indicative of no extension of π -conjugation. This result might come from the coefficients of the highest occupied molecular orbitals (HOMO). DFT calculations indicate that the HOMO coefficients of 5d are delocalized over the entire molecule, including the introduced benzene rings. In contrast, the HOMO coefficients of 5e are completely localized on the DBADT framework, because the 4,12-positions of a DBADT core are nodal planes in HOMO geometry (Figure S1). These results indicate that the introduction of benzene rings at the 3,11-positions of the DBADT core affects the electronic structure of DBADT, whereas the installation of phenyl groups at 4,12-positions has little effect on the electronic state of DBADT. According to the absorption spectra in thin films, the absorption maxima of 5a-5e were bathochromically shifted at around 432-442 nm compared to their longest absorption wavelength in solution, indicating that they have a highly ordered packing structure in the solid state.

Furthermore, we used cyclic voltammetry (CV) to investigate the electrochemical properties of DBADT derivatives **5a-5e**. Figure S2 shows the cyclic voltammograms of **5a-5e**, and their electrochemical data are also listed in Table 1. Three DBADT derivatives, **5a-**

 5c, showed one oxidation wave with a clear reduction process, while **5d** showed no oxidation wave due to its low solubility in CH₂Cl₂, caused by the introduction of benzene rings onto the DBADT framework. In contrast, **5e** displayed a reversible oxidation process, which indicates that the substitution positions of benzene rings affect the solubility, likely due to different dihedral angles between phenyl rings and the DBADT core. The estimated HOMO energy levels of **5a-5e** were $-5.43 \sim -5.50$ eV below the vacuum level from the onset of oxidation peaks, which indicates that the introduction of alkyl or phenyl groups onto a DBADT framework elevates the HOMO energy levels slightly, but no significant trend was observed. These results suggest that the fabricated OFET devices based on DBADT derivatives **5a-5e** can be expected to have high air stability.



Figure 2. UV-vis absorption spectra of **5a-5e** in CH₂Cl₂ solution (solid line) and thin films (dashed line).

Compound	$\lambda_{ m max}^{ m abs, sol} \ ({ m nm})^a$	$\lambda_{ m max}^{ m abs, film} \ (nm)$	$E_{g}^{opt} (eV)^{b}$ / $\lambda_{edge} (nm)$	<i>Е</i> номо (eV) ^{<i>c</i>}	E LUMO $(eV)^d$
5a	327	432	2.97/417	-5.50	-2.53
5b	331	432	2.92/424	-5.45	-2.53
5c	333	433	2.91/426	-5.43	-2.52
5d	342	442	2.90/427	ND ^e	ND ^e
5e	335	442	2.96/419	-5.46	-2.50

Table 1.	Optical	and Electr	ochemical	l Data (of 5a-5e
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^{*a*}Absorption maxima in the CH₂Cl₂ solution $(1 \times 10^{-5} \text{ M})$. ^{*b*}Estimated from the absorption edge (λ_{edge}). ^{*c*}Estimated from: $E_{HOMO} = -4.80 - E_{onset}$. ^{*d*}Calculated according to the formula: $E_{LUMO} = E_{HOMO} + E_{g}^{opt}$. ^{*e*} E_{onset} was not determined by cyclic voltammetry due to the low solubility of 5a-5e.

FET Characteristics. To investigate the FET characteristics, we next fabricated bottomgate/top-contact OFET devices based on DBADT derivatives **5a-5e** with an Si/SiO₂ substrate. The surfaces of the Si/SiO₂ substrates were modified with *n*-octyltrichlorosilane (OTS) or *n*octadecyltrichlorosilane (ODTS) as a self-assembled monolayer (SAM). Active layers of **5a-5e** were prepared by vapor deposition at a rate of 0.1 Å/s, and sequential thermal annealing processes were performed at 100, 150, and 200 °C for 30 min under an inert atmosphere in order to form a highly ordered packing structure in the thin films. The gold source and drain electrodes were applied through a shadow mask by vacuum deposition, which gave a channel length (*L*) of 100 μ m and a width (*W*) of 2 mm. Measurement of FET characteristics was carried out under ambient conditions in the dark. The best hole mobilities for each compound under the optimized FET parameters are summarized in Table 2, and the corresponding transfer and output characteristics are shown in Figures 3 and S3, respectively. Hole mobilities were compensated by the ideal Shockley equations.²⁶ All the fabricated devices

exhibited typical p-channel characteristics, and DBADT **5a**-based OFET devices exhibited a high hole mobility of 0.37 cm² V⁻¹ s⁻¹ on OTS-treated Si/SiO₂ substrate. However, the mobilities of dialkyl-substituted DBADT **5b** and **5c** were lower than that of **5a**. These results indicated that the introduction of alkyl chains onto the DBADT core does not induce the higher mobility by a fastener effect. Although the highest mobility of **5d**-based OFET devices was 0.08 cm² V⁻¹ s⁻¹, which is about five times lower than that of **5a**, to our delight, **5e**-based OFET devices displayed the highest hole mobility of up to 0.66 cm² V⁻¹ s⁻¹, indicating that the introduction of phenyl groups at the 4,12-positions of the DBADT core could enable effective carrier transport in OFET devices due to the resulting surface morphology, high crystallinity and molecular orientation in thin films (*vide infra*).



Figure 3. Transfer characteristics of fabricated OFET devices based on DBADT derivatives 5a-5e.

Compound	SAM	Ta/°C	$\mu/cm^2 V^{-1} s^{-1 a, b}$	$V_{ m th}/{f V}^b$	$I_{ m on/off}$
5a	OTS	150	0.37 (0.26)	-38 (-30)	$10^6 \sim 10^7$
5b	OTS	100	0.32 (0.32)	-32 (-32)	$10^5 \sim 10^6$
5c	OTS	as depo.	0.31 (0.31)	-35 (-29)	$10^4 \sim 10^5$
5d	OTS	100	0.08 (0.08)	-38 (-33)	$10^{5} \sim 10^{6}$
5e	ODTS	200	0.66 (0.46)	-37 (-37)	$10^{6} \sim 10^{7}$

 Table 2. FET Characteristics of OFET Devices Based on 5a-5e

^aCalculated with saturated regime. ^bAverage values are shown in parentheses.

Surface Morphology of Fabricated Thin Films. We next examined atomic force microscopy (AFM) images of the fabricated thin films in order to determine their surface morphology, which must be correlated with their FET performance. Figure 4 shows $2 \mu m \times 2 \mu m$ AFM topographic images of **5a-5e**-based thin films on SAM-modified Si/SiO₂ substrate. The thin films of **5a** and **5e** showed relatively large crystalline grains with a bicontinuous network, which is often observed in high-performance materials. Indeed, the fabricated OFET devices obtained from **5a** and **5e** exhibited high mobilities. However, a few dark spots and clear grain boundaries were also observed in the thin film of **5a**, which resulted in its lower mobility in comparison with **5e**. Furthermore, the quality of thin films of **5b** and **5c** was poor. The thin film of **5b** revealed that these crystallized films had a large root mean square (RMS) roughness of 8.44 nm, and **5c**- and **5d**-based thin films showed numerous dark spots and a discontinuity, defects that lead to a low carrier transport ability.



Figure 4. AFM height images $(2 \ \mu m \times 2 \ \mu m)$ of the fabricated thin films based on **5a-5e** on SAM-modified Si/SiO₂ substrate, which afforded the best device characteristics.

Two-Dimensional Grazing Incidence X-ray Diffraction (2D-GIXD) Patterns of the Fabricated Thin Films. In order to investigate the molecular orientation in the thin films of DBADT derivatives **5a-5e**, two-dimensional grazing incidence X-ray diffraction (2D-GIXD) patterns were measured. Figure 5 shows the 2D-GIXD patterns and the corresponding 1D profiles of **5a-5e** thin films on SAM-modified Si/SiO₂ substrate. The calculated interlayer distances are summarized in Table S1. Thin films of **5a** exhibited fifth order (*001*) diffraction peaks as spots at the q_z direction. The interlayer distance was calculated to be 17.2 Å, which is consistent with computed longitudinal molecular length. In addition, three characteristic peaks in the q_{xy} direction were observed as spots, which are often assignable to a herringbone

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structure in the in-plane direction. This indicates that 5a formed a highly ordered 2D layerby-layer structure perpendicular to the substrate. It is well known that such a well-ordered edge-on orientation with herringbone arrangement is suitable for effective 2D carrier transport in OFET devices,¹⁰ and in fact 5a-based OFET devices exhibited high mobilities of up to $0.37 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Next, we examined the 2D-GIXD patterns of thin-films of **5b** and **5c**. In comparison with 5a and dialkylated DBADTs 5b and 5c, all compounds mainly formed edge-on orientation in the solid state, indicating no substantial impact of alkyl substitution and their positions on their main crystalline structures. On the other hand, their crystallinity and packing structures were different. The thin film based on 5b showed broad (00l) diffraction peaks and other diffraction peaks (indicated by asterisks) were observed at the q_z direction, indicating the small crystallite size and co-existence of an unsuitable crystallite in the solid state. The interlayer distance in **5b** is shorter than its molecular length calculated from an optimized geometry, implying that **5b** formed an interdigitated structure in each alkyl layer or a 33° tilted structure relative to the substrate, which may prevent effective intermolecular electronic coupling. Furthermore, **5b** film showed distinct structural disorder in the in-plane direction, because three diffraction peaks in the q_{xy} direction were observed as short arcs. Therefore, the mobility of **5b** was slightly lower than that of **5a**. Thin films of **5c** also showed a fourth order of (001) diffraction peaks in the q_z direction and three short arclike peaks in the q_{xy} direction, much like **5b**. On the other hand, the calculated *d*-spacing and molecular length of 5c are almost the same, indicating that 5c formed a completely edge-on orientation, which is suitable for high-performance OFETs. However, since 5c formed a poor surface morphology including the construction of many dark spots and a small grain size, it exhibited the almost same hole mobility as **5b**. In contrast to dialkylated DBADTs **5b** and **5c**, diphenyl DBADTs 5d and 5e showed quite different features in the solid state. The interlayer distances of 5d and 5e were estimated to be 24.7 and 23.7 Å, respectively. Their

corresponding tilt angles (θ) were almost the same, at 19 and 16°, respectively. Although all diffraction from **5d** film was obtained as spots, it showed fifth order ($\theta\theta l$) diffraction patterns in both q_z and q_{xy} directions, indicating that edge-on and face-on orientations coexisted in the thin films. In general, a face-on orientation is unsuitable for effective carrier transport in OFET devices, and in fact OFET devices based on **5d** showed the relatively low mobility of 0.08 cm² V⁻¹ s⁻¹. Although **5e**-based thin films also showed a component of face-on orientation to some extent, the face-on ratio of **5e** was significantly smaller than that of **5d** (*vide infra*). In addition, **5e** film also exhibited intense and spot-like diffraction in all diffraction patterns, indicating the formation of a highly crystalline and well-ordered structure in the thin film. Although the reason for the highest hole mobility of **5e** is still not understood at the current stage, a highly ordered crystalline film with the optimal morphology of **5e** may point the way to effective carrier transport in this system. We also reasoned that the incorporation of two phenyl rings at the optimal positions should enhance the intermolecular orbital overlap, leading to high hole mobility.



Figure 5. 2D-GIXD patterns and the corresponding 1D profiles of **5a-5e** thin films on a SAM-treated Si/SiO₂ substrate.

In order to further investigate the molecular orientation quantitatively, we calculated the face-on ratio of DBADT derivatives **5d** and **5e** by the pole figure analyses of (001) diffraction using the 2D-GIXD patterns, as shown in Figure 6.²⁷ The components of face-on and edge-on orientations were extracted from the integrated areas with pole angle χ ranges of 0-22.5° and 157.5-180° (face-on) and 67.5-112.5 (edge-on), respectively. As a result, the face-on ratio of **5d** was calculated to be 28%, which is considerably higher than that of **5e** (4%). According to these results, installation of phenyl groups can enhance π -orbitals overlaps, while the ratio of unsuitable face-on crystallites was increased in spite of their different substitution positions. This tendency of mis-oriented structure is similar as phenyl substituted BBTBDT and DNTT derivatives.^{17d,27b} Thus, we hypothesized that twisted phenyl substituents on π -cores may interact with neighboring moieties along the multi-direction, resulting in the increased face-on ratio in comparison with parent and dialkylated derivatives.

According to the 2D-GIXD results of DBADT derivatives, **5c** and **5e**, which possessed substituents at 4,12-positions formed more ordered packing structures as well as **5a** in comparison with **5b** and **5d**. This tendency has not been fully proved, but we presume that molecular orbitals were quite important (Figure 7). In the HOMO orbitals of **5a**, no HOMO coefficients existed on 4,12-positions, while 3,11-positions were electron rich sites. Hence, HOMO orbitals of **5c** and **5e** were similar as **5a**, suggesting no significant effect of alkyl and phenyl substitution on their electronic structures. On the other hand, in **5b** and **5d**, HOMO orbitals of outer benzothiophene units were slightly delocalized like a node, which is not suitable for effective π -orbital overlaps.^{17d,19} Therefore, we may think that functionalization of no electron rich sites is highly important for favorable packing motif as well as parent cores and enhancement of semiconducting properties.



Figure 6. (a) 2D-GIXD patterns and (b) Pole figure plots extracted from the (001) diffraction of **5d** and **5e** thin films.



Figure 7. HOMO orbitals of 5a, 5d, and 5e obtained from DFT calculation.

Conclusion

In summary, we have successfully synthesized an array of DBADT derivatives through sequential palladium-catalyzed Suzuki-Miyaura or Negishi coupling, epoxidation, and Lewis acid-catalyzed cycloaromatization without the formation of structural isomers. UV-vis

absorption spectra showed small differences regardless of the positions of the substituents on a DBADT framework. In addition, all DBADT derivatives showed almost the same HOMO energy levels around -5.5 eV, which is enough to ensure high air stability. The fabricated OFET devices based on DBADT derivatives exhibited typical p-type semiconducting behavior under ambient conditions in the dark. Specifically, the maximum hole mobility reached to 0.66 cm² V⁻¹ s⁻¹ in **5e**-based OFET devices. On the other hand, dialkyl-substituted DBADT derivatives 5b and 5c showed relatively low mobilities due to the formation of polymorphs, disordered structure in the in-plane direction, and small crystallite size for 5b, and also poor film quality for 5c. This indicates that the substitution position effect of alkylated DBADTs on the OFET performance is small. In sharp contrast, diphenylated DBADT's performance depended strongly on their substitution position. Intriguingly, the molecular orientation could be controlled by the substituents and their positions; diphenylsubstituted DBADT 5e showed a significantly lower component of face-on orientation (4%) in comparison with that of 5d (28%), leading to higher hole mobility. We conclude that installation of functional groups into non-electron-rich sites of the parent core is important for creating more suitable packing structure in the solid state. To achieve higher mobility as well as lower voltage operation, we are currently undertaking the design and synthesis of novel organic materials with extended π -electron systems, and incorporating extended or multiple acene moieties into molecular frameworks.

Experimental Section

General. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure prior to use. Dehydrated tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and toluene were purchased from Kanto Chemicals Co., Ltd. For thin layer chromatography

(TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 N (spherical, neutral, 40-100 μ m) from Kanto Chemicals Co., Ltd. NMR spectra (¹H and ¹³C{¹H}) were recorded on Varian INOVA-600 (600 MHz) spectrometer. Chemical shifts are in parts per million relative to CDCl₃ at 7.26 ppm for ¹H and at 77.0 ppm for ¹³C{¹H} NMR spectra. Infrared spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer and reported in wave numbers (cm⁻¹). HRMS were determined on a JEOL JMS-700 MStation (double-focusing mass spectrometer). Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at Okayama University.

5-Octylbenzo[*b*]thiophene (1c),²⁸ 6-phenylbenzo[*b*]thiophene (1d),¹⁶ 5phenylbenzo[*b*]thiophene (1e),²⁹ and 2,5-diiodo-1,4-benzendicarboxaldehyde (2)³⁰ were synthesized according to the reported procedures. All other chemicals were used without further purification.

Synthesis of 6-Octylbenzo[*b*]thiophene (1b). To a solution of 1-octene (1.17 mL, 7.5 mmol, 1.5 equiv) in anhydrous THF (100 mL) in a 200 mL 2-neck round-bottomed flask under argon was added 9-BBN dimer (915 mg, 3.75 mmol, 0.75 equiv) at room temperature. The reaction mixture was stirred at 60 °C for 1 h, then allowed to cool to room temperature, and Pd(dba)₂ (144 mg, 0.25 mmol, 5 mol %), [HP*t*-Bu₃]BF₄ (145 mg, 0.25 mmol, 10 mol %), powdered KOH (842 mg, 15 mmol, 6 equiv), and 6-bromobenzo[*b*]thiophene (1.07 g, 5 mmol, 1 equiv) were added at room temperature. The reaction mixture was stirred at 85 °C for 8 h, quenched with water (10 mL), and extracted with chloroform (100 mL × 2). The combined organic layers were washed with brine and dried over MgSO₄. Filtration and evaporation afforded a pale yellow liquid. Column chromatography on silica gel (eluent: hexane) gave the titled product **1b** (1.20 g, 4.85 mmol, 97%) as a colorless liquid. R_f = 0.56 (hexane). FT-IR (KBr, cm⁻¹): 3101 (s), 3073 (s), 3051 (s), 3022 (s), 2953 (w), 2924 (w),

 2853 (w), 1464 (m), 1396 (m), 1202 (s), 881 (m), 816 (m), 785 (s), 721 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 0.88 (t, J = 7.2 Hz, 3H), 1.25-1.38 (m, 10H), 1.67 (quintet, J = 7.2 Hz, 2H), 2.73 (t, J = 7.2 Hz, 2H), 7.19 (dd, J = 8.4, 1.6 Hz, 1H), 7.28 (dd, J = 5.4, 0.6 Hz, 1H), 7.35 (d, J = 5.4 Hz, 1H), 7.68 (d, J = 0.6 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt): δ 14.3, 22.8, 29.41, 29.47, 29.6, 31.9, 32.0, 36.2, 121.8, 123.3, 123.7, 125.3, 125.5, 137.7, 139.5, 140.1. Anal. Calcd for C₁₆H₂₂S: C, 77.99; H, 9.00%. Found: C, 77.64; H, 9.31%.

Synthesis of 2,5-Bis(benzo[*b***]thiophene-2-yl)-1,4-phthalaldehyde (3a).** To a solution of **2** (386 mg, 2.2 mmol, 1 equiv) in anhydrous THF (30 mL) in a 50 mL Schlenk tube under argon were added 2-benzothienylboronic acid (392 mg, 2.2 mmol, 2.2 equiv), Pd(dba)₂ (29 mg, 0.05 mmol, 5 mol %), Sphos (41 mg, 0.1 mmol, 10 mol %), potassium fluoride (267 mg, 4.6 mmol, 4.6 equiv), and H₂O (110 μ L, 6 mmol, 6 equiv) at room temperature. The reaction mixture was stirred at reflux for 4 h, quenched with water (10 mL) and poured into MeOH (100 mL), producing a yellow precipitate, which was filtered, and dried under vacuum to afford the titled product **3a** (381 mg, 0.96 mmol, 96%) as a yellow solid. Mp = 264-266 °C. FT-IR (KBr, cm⁻¹): 3096 (s), 3059 (w), 3048 (w), 3028 (w), 2891 (s), 1684 (w), 1531 (m), 1375 (m), 1152 (m), 908 (m), 862 (m), 810 (m), 737 (m), 721 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 7.38 (s, 2H), 7.44-7.46 (m, 4H), 7.87 (d, *J* = 6.6 Hz, 2H), 7.92 (d, *J* = 6.0 Hz, 2H), 8.28 (s, 2H), 10.35 (s, 2H). ¹³C{¹H} NMR (CDCl₃, 150 MHz, rt): δ 122.3, 124.2, 125.2, 125.5, 127.1, 131.1, 137.3, 137.5, 139.9, 140.9, 190.9. Anal. Calcd for C₂₄H₁₄O₂S₂: C, 72.34; H, 3.54%. Found: C, 72.16; H, 3.29.

A Typical Procedure for 3: Synthesis of 2,5-Bis(6-octylbenzo[b]thiophen-2-yl)-1,4phthalaldehyde (3b). To a solution of 6-octylbenzo[b]thiophene (1b) (542 mg, 2.2 mmol, 2.2 equiv) in anhydrous THF (20 mL) in a 50 mL Schlenk tube under an argon atmosphere was added *n*-butyllithium (1.6 M in hexane, 1.5 mL, 2.4 mmol, 2.4 equiv) at -78 °C. After

being stirred for 1 h at room temperature, the mixture was cooled to 0 °C, then zinc chloride (327 mg, 2.4 mmol, 2.4 equiv) was added to the reaction mixture, which was allowed to warm to room temperature, and stirred for 1 h. 2,5-Diiodo-1,4-benzendicarboxaldehyde (2) (386 mg, 1 mmol, 1 equiv), Pd(dba)₂ (29 mg, 0.05 mmol, 5 mol %), and tris(2furyl)phosphine (23 mg, 0.01 mmol, 10 mol %) were added at room temperature. The resulting reaction mixture was stirred at reflux for 3 h, guenched with water (10 mL), and then poured into MeOH (100 mL), producing a yellow precipitate, which was filtered, then dried under vacuum to afford the titled product **3b** (551 mg, 0.88 mmol, 88%) as a yellow solid. Mp = 121-122 °C. FT-IR (KBr, cm⁻¹): 3049 (s), 2955 (m), 2924 (w), 2853 (m), 1686 (w), 1468 (s), 1369 (m), 1150 (m), 907 (s), 847 (m), 795 (s), 721 (s). ¹H NMR (600 MHz, CDCl₃, rt): δ 0.89 (t, J = 7.2 Hz, 6H), 1.26-1.39 (m, 20H), 1.70 (quintet, J = 7.8 Hz, 4H), 2.77 (t, J = 7.8 Hz, 4H), 7.28 (dd, J = 7.8, 1.2 Hz, 2H), 7.31 (s, 2H), 7.70 (s, 2H), 7.76 (d, J = 8.4 Hz)Hz, 2H), 8.26 (s, 2H), 10.34 (s, 2H). ${}^{13}C{}^{1}H$ NMR (150 MHz, CDCl₃, rt): δ 14.1, 22.7, 29.26, 29.31, 29.5, 31.7, 31.9, 36.1, 121.4, 123.8, 126.3, 126.9, 131.0, 136.2, 137.0, 137.5, 137.9, 140.9, 141.2, 191.0. Anal. Calcd for C40H46O2S2: C, 77.12; H, 7.44%. Found: C, 76.90; H, 7.40%.

Dialdehydes **3c-3e** were synthesized according to the same procedure as **3b**.

2,5-Bis(5-octylbenzo[b]thiophen-2-yl)-1,4-phthalaldehyde (3c). Yellow solid. 96% yield (894 mg, 1.44 mmol). Mp = 115-117 °C. FT-IR (KBr, cm⁻¹): 2957 (m), 2922 (w), 2852 (m), 1686 (w), 1528 (m), 1458 (s), 1364 (m), 1252 (s), 962 (s), 887 (m), 816 (m), 723 (s). ¹H NMR (600 MHz, CDCl₃, rt): δ 0.89 (t, J = 7.2 Hz, 6H), 1.26-1.38 (m, 20H), 1.69 (quintet, J = 7.8 Hz, 4H), 2.76 (t, J = 7.8 Hz, 4H), 7.28 (d, J = 8.4, 1.2 Hz, 2H), 7.31 (s, 2H), 7.67 (s, 2H), 7.80 (d, J = 8.4 Hz, 2H), 8.26 (s, 2H), 10.34 (s, 2H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt): δ 14.1, 22.7, 29.26, 29.29, 29.5, 31.8, 31.9, 35.9, 121.9, 123.4, 126.7, 126.9, 130.9, 137.0,

137.3, 137.6, 138.3, 140.16, 140.22, 191.0. Anal. Calcd for C₄₀H₄₆O₂S₂: C, 77.12; H, 7.44%. Found: C, 77.10; H, 7.44%.

2,5-*Bis*(6-phenylbenzo[b]thiophen-2-yl)-1,4-phthalaldehyde (3d). Yellow solid. 98% yield (540 mg, 0.98 mmol). Mp > 270 °C. FT-IR (KBr, cm⁻¹): 3099 (s), 3080 (s), 3059 (s), 3024 (s), 2851 (m), 1636 (w), 1528 (m), 1476 (m), 1369 (w), 1298 (m), 1159 (m), 854 (w), 818 (w), 758 (w), 698 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 7.41 (t, *J* = 7.8 Hz, 4H), 7.50 (t, *J* = 7.8 Hz, 4H), 7.69-7.71 (m, 6H), 7.93 (d, *J* = 8.4 Hz, 2H), 8.12 (s, 2H), 8.31 (s, 2H), 10.34 (s, 2H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt) was not obtained due to poor solubility. Anal. Calcd for C₃₆H₂₂O₂S₂: C, 78.52; H, 4.03%. Found: C, 78.28; H, 4.03%.

2,5-Bis(5-phenylbenzo[b]thiophen-2-yl)-1,4-phthalaldehyde (3e). Yellow solid. Quant (825 mg, 1.50 mmol). Mp > 270 °C. FT-IR (KBr, cm⁻¹): 3078 (s), 3051 (s), 3030 (s), 2862 (s), 1683 (w), 1447 (m), 1362 (m), 1287 (m), 1150 (m), 901 (m), 820 (m), 758 (w), 689 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 7.40 (t, *J* = 7.8 Hz, 2H), 7.44 (s, 2H), 7.50 (t, *J* = 7.8 Hz, 4H), 7.68-7.69 (m, 4H), 7.70 (d, *J* = 1.8 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 1.8 Hz, 2H), 8.32 (s, 2H), 10.38 (s, 2H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt) was not obtained due to poor solubility. Anal. Calcd for C₃₆H₂₂O₂S₂: C, 78.52; H, 4.03%. Found: C, 78.17; H, 3.86%.

A Typical Procedure for 4: Synthesis of 2,2'-(2,5-Bis(benzo[b]thiophen-2-yl)-1,4phenylene)bis(oxirane) (4a). To a solution of 3a (40 mg, 0.1 mmol, 1 equiv) in anhydrous acetonitrile (3 mL) in a 20 mL Schlenk tube under an argon atmosphere, were added trimethylsulfonium iodide (49 mg, 0.24 mmol, 2.4 equiv) and powdered KOH (31 mg, 0.55 mmol, 5.5 equiv) at room temperature. The reaction mixture was vigorously stirred at 60 °C for 3 h, quenched with water (5 mL), and extracted with chloroform (30 mL × 2). The combined organic layers were washed with brine, then dried over MgSO₄. Filtration and evaporation afforded the titled product 4a (41.7 mg, 0.098 mmol, 98%) as a pale yellow solid. Mp = 197-198 °C. FT-IR (KBr, cm⁻¹): 3053 (s), 2986 (s), 2924 (s), 1437 (m), 1304 (s), 1248

 (m), 1157 (m), 880 (m), 862 (w), 833 (m), 750 (w), 727 (w). ¹H NMR (600 MHz, CDCl₃, rt): δ 2.86 (dd, J = 5.7, 2.4 Hz, 1H), 2.91 (dd, J = 5.7, 2.4 Hz, 1H), 3.22 (t, J = 6.0 Hz, 2H), 4.18 (dd, J = 3.9, 2.4 Hz, 2H), 7.37-7.42 (m, 6H), 7.57 (s, 2H), 7.83-7.88 (m, 4H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt): δ 50.82, (50.85), 51.7, (51.9), 122.3, 123.9, 124.20, 124.24, 124.8, 126.7, 134.3, 135.7, 140.1, 140.4, 140.8. Chemical shifts assigned to one of two diastereomers are shown in parentheses. HRMS (EI⁺) m/z: [M]⁺ Calcd for C₂₆H₁₈O₂S₂: 426.0748. Found: 426.0748.

Diepoxides 4b-4d were synthesized according to the same procedure as 4a.

2,2'-(2,5-Bis(6-octylbenzo[b]thiophen-2-yl)-1,4-phenylene)bis(oxirane) (4b). Pale yellow solid. Quant (326 mg, 0.50 mmol). Mp = 91-93 °C. FT-IR (KBr, cm⁻¹): 2955 (w), 2926 (w), 2853 (w), 1560 (w), 1406 (m), 1200 (s), 1146 (s), 883 (m), 808 (m), 727 (s). ¹H NMR (600 MHz, CDCl₃, rt): δ 0.88 (t, J = 7.2 Hz, 6H), 1.26-1.39 (m, 20H), 1.68 (quintet, J = 7.8 Hz, 4H), 2.74 (t, J = 7.2 Hz, 4H), 2.85 (dd, J = 3.0, 2.4 Hz, 1H), 2.94 (dd, J = 3.0, 3.0 Hz, 1H), 3.20-3.22 (m, 2H), 4.17 (dd, J = 2.4, 1.2 Hz, 2H), 7.22 (dd, J = 1.2, 6.6 Hz, 2H), 7.35 (s, 2H), 7.55 (d, J = 2.4 Hz, 2H), 7.63 (s, 2H), 7.76 (d, J = 7.8 Hz, 2H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt): δ 14.2, 22.6, 29.3, 29.4, 29.6, 31.9, 32.0, 36.0, 50.5, 51.5, (51.6), 121.5, 123.1, 123.9, 125.8, (126.5), 126.7, 134.2, 135.7, 137.7, 139.8, 140.7, 141.0. Chemical shifts assigned to one of two diastereomers are shown in parentheses. HRMS (EI⁺) *m/z*: [M]⁺ Calcd for C₄₂H₅₀O₂S₂: 650.3252. Found: 650.3222.

2,2'-(2,5-Bis(5-octylbenzo[b]thiophen-2-yl)-1,4-phenylene)bis(oxirane) (4c). Pale yellow solid. 86% yield (279 mg, 0.43 mmol). Mp = 87-88 °C. FT-IR (KBr, cm⁻¹): 2955 (w), 2926 (w), 2853 (w), 1560 (m), 1465 (m), 1406 (m), 1250 (s), 1159 (s), 883 (m), 808 (m), 727 (s). ¹H NMR (600 MHz, CDCl₃, rt): δ 0.89 (t, J = 6.9 Hz, 6H), 1.27-1.35 (m, 20H), 1.69 (quintet, J = 7.5 Hz, 4H), 2.74 (t, J = 6.9 Hz, 4H), 2.85 (dd, J = 5.6, 2.4 Hz, 1H), 2.91 (dd, J = 6.3, 2.7 Hz, 1H), 3.20-3.23 (m, 2H), 4.18 (dd, J = 3.1, 2.7 Hz, 2H), 7.22 (dd, J = 8.1, 1.5 Hz, 2H),

 7.36 (s, 2H), 7.56 (d, J = 2.4 Hz, 2H), 7.63 (s, 2H), 7.77 (d, J = 8.4 Hz, 2H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt): δ 14.4, 22.9, 29.5, 29.6, 29.8, 32.0, 32.1, 36.2, 51.0, 51.8, (52.0), 122.6, 123.4, 124.1, 126.1, 127.0, 134.5, 135.7, 137.9, 139.9, 140.6, 141.0. Chemical shifts assigned to one of two diastereomers are shown in parentheses. HRMS (EI⁺) *m/z*: [M]⁺ Calcd for C₄₂H₅₀O₂S₂: 650.3252. Found: 650.3223.

2,2'-(2,5-Bis(6-phenylbenzo[b]thiophen-2-yl)-1,4-phenylene)bis(oxirane) (4d). Pale yellow solid. 90% yield (443 mg, 0.77 mmol). Mp = 237-238 °C. FT-IR (KBr, cm⁻¹): 3053 (s), 3028 (s), 2988 (s), 2918 (s), 1462 (m), 1373 (m), 1298 (s), 1250 (s), 1163 (s), 955 (m), 851 (m), 760 (w), 729 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 2.89 (dd, J = 5.4, 3 Hz, 1H), 2.94 (dd, J = 5.4, 3 Hz, 1H), 3.24-3.26 (m 2H), 4.21 (t, J = 3 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.45 (s, 2H), 7.49 (t, J = 7.2 Hz, 4H), 7.61 (d, J = 1.8 Hz, 2H), 7.66 (dd, J = 8.4, 1.2 Hz, 2H), 7.69 (d, J = 7.8 Hz, 4H), 7.89 (d, J = 8.4 Hz, 2H) 8.08 (s, 2H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt): δ 50.7, (50.8), 51.6, (51.7), 120.4, 123.79, (123.83), 124.0, 124.4, 126.7, 126.9, 127.37, (127.39), 128.9, 134.2, 134.3, 135.57, (135.58), 138.1, 139.2, 140.9, (141.01), 141.03, (141.1). Chemical shifts assigned to one of two diastereomers are shown in parentheses. HRMS (EI⁺) *m/z*: [M]⁺ Calcd for C₃₈H₂₆O₂S₂: 578.1374. Found: 578.1363.

Synthesis of 2,2'-(2,5-Bis(5-phenylbenzo[*b*]thiophen-2-yl)-1,4-phenylene)bis(oxirane) (4e). To a solution of 3e (441 mg, 0.68 mmol, 1 equiv) in benzonitrile (30 mL) in a 50 mL Schlenk tube under an argon atmosphere, were added trimethylsulfonium iodide (333 mg, 1.63 mmol, 2.4 equiv) and powdered KOH (210 mg, 3.80 mmol, 5.5 equiv) at room temperature. The reaction mixture was vigorously stirred at 60 °C for 3 h, quenched with water (5 mL), and extracted with chloroform (30 mL \times 2). The combined organic layers were washed with brine and dried over MgSO4. Filtration and evaporation afforded the titled product 4e (278 mg, 0.48 mmol, 71%) as a pale yellow solid. Mp = 220-222 °C. FT-IR (KBr, cm⁻¹): 3082 (s), 3053 (m), 3032 (m), 2995 (m), 2911 (s), 1501 (m), 1445 (w), 1373 (m), 1244

 (m), 1157 (m), 870 (w), 818 (m), 758 (w), 725 (m). ¹H NMR (600 MHz, CDCl₃, rt): δ 2.89 (dd, J = 5.4, 1.5 Hz, 1H), 2.94 (dd, J = 5.4, 1.5 Hz, 1H), 3.24-3.26 (m 2H), 4.21 (dd, J = 3.6, 1.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.48-7.51 (m, 6H), 7.61 (d, J = 2.4 Hz, 2H), 7.63 (dd, J = 8.4, 1.8 Hz, 2H), 7.69 (d, J = 7.2 Hz, 4H), 7.93 (d, J = 8.4 Hz, 2H) 8.04 (d, J = 1.2 Hz, 2H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt): δ 50.70, (50.73), 51.6, (51.7), 122.1, 122.4, 124.27, (124.31), 124.4, 126.7, 126.9, 127.3, (127.4), 128.9, 134.2, (134.3), 135.61, (135.63), 138.2, 139.3, 140.60, (140.61), 141.1, 141.41, (141.45). Chemical shifts assigned to one of two diastereomers are shown in parentheses. HRMS (EI⁺) m/z: [M]⁺ Calcd for C₃₈H₂₆O₂S₂: 578.1374. Found: 578.1374.

A Typical Procedure for 5: Synthesis of Dibenzo[2,3-*d*:2',3'-*d*']anthra[1,2-*b*:5,6*b*']dithiophene (5a). To a solution of 4a (116 mg, 0.27 mmol, 1 equiv) in anhydrous 1,2dichloroethane (10 mL) in a 50 mL Schlenk tube under an argon atmosphere, was added indium chloride (12 mg, 0.054 mmol, 20 mol %) at room temperature. The reaction mixture was stirred at reflux for 48 h, quenched with water (10 mL), and then poured into MeOH (100 mL) and filtered. The filter cake was rinsed successively with water (50 mL), hexane (50 mL), acetone (50 mL), and hot chloroform (50 mL). Drying *in vacuo* afforded the titled product **5a** as a pale yellow solid, which was further purified by sublimation to give analytically pure samples (82 mg, 0.21 mmol, 78%) as a yellow solid. Mp > 270 °C. FT-IR (KBr, cm⁻¹): 3051 (s), 3015 (s), 1527 (s), 1429 (m), 1085 (m), 878 (w), 809 (m), 770 (w), 735 (w), 689 (m). ¹H NMR (600 MHz, CDCl₃, rt) was not obtained due to poor solubility; nor was ¹³C{¹H} NMR (CDCl₃, 150 MHz, rt). Anal. Calcd for C₂₆H₁₄S₂: C, 79.96; H, 3.61%. Found: C, 79.90; H, 3.35%.

DBADT derivatives **5b-5e** were synthesized according to the same procedure as **5a**.

3,11-Dioctyldibenzo[2,3-d:2',3'-d']anthra[1,2-b:5,6-b']dithiophene (5b). Yellow solid. 84% yield (75 mg, 0.12 mmol). Mp > 270 °C. FT-IR (KBr, cm⁻¹): 2957 (m), 2922 (w), 2872

(m), 2851 (w), 1466 (s), 1414 (s), 1257 (s), 878 (m), 806 (m), 721 (s), 691 (s). ¹H NMR (600 MHz, CDCl₃, rt) was not obtained due to poor solubility; nor was ¹³C{¹H} NMR (150 MHz, CDCl₃, rt). Anal. Calcd for C₄₂H₄₆S₂: C, 82.03; H, 7.54%. Found: C, 81.93; H, 7.54% *4,12-Dioctyldibenzo[2,3-d:2',3'-d']anthra[1,2-b:5,6-b']dithiophene (5c)*. Yellow solid. 78% yield (170 mg, 0.27 mmol). Mp = 265 °C. FT-IR (KBr, cm⁻¹): 3049 (s), 3034 (s), 3009 (s), 2956 (m), 2922 (w), 2872 (m), 2852 (w), 1541 (s), 1456 (m), 1252 (s), 988 (s), 878 (w), 806 (m), 723 (s), 623 (s). ¹H NMR (600 MHz, CDCl₃, rt) was not obtained due to poor solubility; nor was ¹³C{¹H} NMR (150 MHz, CDCl₃, rt). Anal. Calcd for C₄₆H₅₄S₂: C, 82.33; H, 8.11%. Found: C, 82.19; H, 8.11%.

3,11-Diphenyldibenzo[2,3-d:2',3'-d']anthra[1,2-b:5,6-b']dithiophene (5d). Yellow solid. 90% yield (97 mg, 0.18 mmol). Mp > 270 °C. FT-IR (KBr, cm⁻¹): 3057 (s), 3030 (s), 3005 (s), 1541 (s), 1466 (m), 1412 (m), 1244 (s), 1078 (s), 880 (w), 808 (w), 768 (m), 754 (w), 696 (m). ¹H NMR (600 MHz, CDCl₃, rt) was not obtained due to poor solubility; nor was ¹³C{¹H} NMR (150 MHz, CDCl₃, rt). Anal. Calcd for C₃₈H₂₂S₂: C, 84.10; H, 4.09%. Found: C, 83.97; H, 3.91%.

4,12-Diphenyldibenzo[*2,3-d:2',3'-d']anthra*[*1,2-b:5,6-b']dithiophene* (*5e*). Yellow solid. 91% yield (103 mg, 0.19 mmol). Mp > 270 °C. FT-IR (KBr, cm⁻¹): 3049 (s), 3030 (w), 3005 (m), 1541 (s), 1452 (m), 1250 (m), 1093 (s), 874 (w), 820 (m), 802 (m), 758 (w), 700 (m), 638 (m). ¹H NMR (600 MHz, CDCl₃, rt) was not obtained due to poor solubility; nor was ¹³C{¹H} NMR (150 MHz, CDCl₃, rt). Anal. Calcd for C₃₈H₂₂S₂: C, 84.10; H, 4.09%. Found: C, 84.18; H, 3.76%.

Instrumentation and Theoretical Calculations. UV-vis absorption spectra were measured using a Shimadzu UV-2450 UV-vis spectrometer. Cyclic voltammograms (CVs) were recorded on Electrochemical Analyzer CHI-600B in acetonitrile containing tetrabutylammonium hexafluorophosphate (TBAP, 0.1 M) as supporting electrolyte at a scan

rate of 100 mV/s. A Pt electrode (surface area: $A = 0.071 \text{ cm}^2$, BAS), a Ag/Ag⁺ (Ag wire in 0.01 M AgNO₃/0.1 M TBAP/CH₂Cl₂), and a Pt wire electrode were used as working, reference, and counter electrodes, respectively. Dynamic force-mode atomic force microscopy was carried out using an SPA 400-DFM (SII Nano Technologies). Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) analyses were carried out at SPring-8 on beamlines BL46XU. The samples were irradiated at a fixed angle on the order of 0.12° through a Huber diffractometer with an X-ray energy of 12.39 keV ($\lambda = 1$ Å), and the GIXD patterns were recorded on a 2D image detector (Pilatus 300K). DFT calculations were performed at the B3LYP/6-31G(d) level using the Gaussian 09, Revision A.02 program package.³¹

Fabrication of Vapor Deposited OFET Devices. Typical bottom-gate top-contact OFET devices were fabricated as follows. All processes except for substrate cleaning were performed under a nitrogen atmosphere. A heavily doped *n*-Si wafer with 200 nm thick thermally grown SiO₂ ($C_i = 17.3 \text{ nF cm}^{-2}$) as the dielectric layer was used as the substrate. The Si/SiO₂ substrates were carefully cleaned using ultrasonication with acetone and isopropanol for 10 min, respectively. After being dried, the substrates were irradiated by UV-O₃ for 20 min, and then treated with the solution of 0.1 M *n*-octyltrichlorosilane (OTS), *n*-octadecyltrichlorosilane (ODTS) in anhydrous toluene to form a self-assembled monolayer (SAM). The active layers were deposited on the treated substrate by vapor deposition at the rate of 0.1 Å/s. Thermal annealing was performed at 100, 150, and 200 °C for 30 min on a hotplate in a glove box. After treatment, gold electrodes (50 nm thick) were deposited through a shadow mask on the top of the active layer under reduced pressure (5×10^{-5} Pa). The current-voltage characteristics of the OFET devices were measured at room temperature in air on a Keithley 6430 Sub-Femtoamp Remote Sourcemeter combined with a Keithley 2400 SourceMeter Unit. Field-effect mobilities were calculated in the saturation regime of

the I_D using following equation,

$$I_{\rm D} = (WC_{\rm i}/2L) \,\mu \,(V_{\rm G}-V_{\rm th})^2$$

Where C_i is the capacitance of the SiO₂ insulator. I_D is the source-drain current, and V_D , V_G , and V_{th} are the source-drain, gate, and threshold voltages, respectively. Current on/off ratio ($I_{on/off}$) was determined from a minimum I_D at around $V_G = -60$ V.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI:. ¹H and ¹³C NMR spectra are available for all new compounds, as well as details of physicochemical properties, computational data, surface morphologies, and device characteristics.

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Notes

The authors declare no competing financial interests.

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