Molecular Ordering of Dithieno[2,3-d;2′,3′-d′]benzo[2,1-b:3,4-b′]dithiophenes for Field-Effect Transistors

Ashok Keerthi, §, †, © Witold Waliszewski, § Cunbin An, †, || Abdullah Jaber, †, ¶ Debin Xia, †, ‡ and Martin Baumgarten*, †, ©

1 Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
2 School of Physics and Astronomy Condensed Matter Physics Group, The University of Manchester, M13 9PL Manchester, U.K.
3 Department of Molecular Physics, Faculty of Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland
4 State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
5 Petrochemical Research Institute, King Abdulaziz City of Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia
6 MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, 150001 Harbin, P. R. China

Supporting Information

ABSTRACT: Four derivatives of dithieno[2,3-d;2′,3′-d′]benzo[1,2-b:3,4-b′]dithiophene (DTmBDT) have been synthesized to investigate the correlation between molecular structure, thin-film organization, and charge-carrier transport. Phenyl or thiophene end-capped derivatives at alpha positions of the outer thiophenes of DTmBDT present vastly different optoelectronic properties in comparison with bay-position alkyl-chain-substituted DTmBDT, which was additionally confirmed by density functional theory simulations. The film morphology of the derivatives strongly depends on alkyl substituents, aromatic end-caps, and substrate temperature. Field-effect transistors based on DTmBDT derivatives with bay-substituted alkyl chains show the best performance within this studied series with a hole mobility up to 0.75 cm²/V s. Attachment of aromatic end-caps disturbs the ordering, limiting the charge-carrier transport. Higher substrate temperature during deposition of the DTmBDT derivatives with aromatic end-caps results in larger domains and improved the transistor mobilities but not beyond the alkylated DTmBDT.

1. INTRODUCTION

Acenes and heteroacenes have been studied intensively over the recent years for their unique optoelectronic and semiconducting properties, which are used in electronic applications such as organic field-effect transistors (OFETs), organic light-emitting diodes, organic photovoltaics, and nonlinear optics. A remarkable progress in the development of highly stable and solution-processable acenes has been made by introducing heteroatoms into the acene core and solubilizing groups on the acene backbone, respectively. However, new acene core structures require thorough understanding of the molecular alignment with respect to substituted or functionalized pristine core to achieve a promising device performance. Therefore, the systematic investigation of novel and potential molecular model compounds that show robust performance under simple processing techniques still remains an important task. Among the class of heteroacenes, bridged thieno[3,2-b]thiophene (TT) units have attracted considerable interest. Bridging the bithieno[3,2-b]thiophene drives the two units into coplanarity, giving rise to good electron density delocalization, and reduces reorganization energy. The bridging moieties are also known to have a substantial impact on the solubility, molecular packing, and optoelectronic as well as thermal properties. We have developed heteroatom-containing pentacene analog molecules, namely, benzo[1,2-b:4,5-b′]bis[b]benzothiophene (BBBT), dithieno[2,3-d;2′,3′-d′]benzo[1,2-b:4,5-b′]dithiophene (DBTD), and very recently, 5,10-didodecyl-dithieno[2,3-d;2′,3′-d′]benzo[1,2-b;3,4-b′]dithiophene (DTmBDT). We demonstrated the potential of the later novel building block (DTmBDT) by alternating copolymerization with an acceptor unit, specifically, 2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)-2,5-dihydroppyrole[3,4-c]pyrrole-1,4-dione (DPP) to obtain a high-performance p-type polymer semiconductor.

Received: April 27, 2018
Accepted: May 24, 2018
Published: June 18, 2018

DOI: 10.1021/acsomega.8b00836
ACS Omega 2018, 3, 6513–6522
© 2018 American Chemical Society
versatile building block DTmBDT can be easily turned soluble by attaching suitable substituents at the bay positions or can be functionalized in the alpha positions of the outer thiophenes. Here, we have synthesized four DTmBDT core-based derivatives with either alkyl chains at bay positions or aromatic moieties as end-caps at alpha positions of the outer thiophenes namely, DTmBDT-C3, DTmBDT-C12, TH-DTmBDT-C12, and PH-DTmBDT-C12 (Figures 1 and S1). The electro-

![Chemical structures of synthesized DTmBDT derivatives.](image)

chemical, thermal, film morphologies, and charge-transport properties of these four compounds have been systematically investigated and discussed in terms of structure–property relations. It is observed that the aromatic end-caps disturb the morphology formation in vacuum-sublimated films of TH-DTmBDT-C12 and PH-DTmBDT-C12, limiting the charge-carrier transport in transistors. However, a higher substrate temperature of these two compounds results in large domains with improved transistor performance.

2. RESULTS AND DISCUSSION

Compound 3,3′-dibromo-2,2′-bithieno[3,2-b]thiophene (1) was coupled with 1,2-dodecyl or propyl ethenyl diboronic ester (2a,b) via Suzuki–Miyaura reaction (Scheme 1), followed by the removal of trimethylsilane moieties by excess addition of K2CO3 to the reaction mixture to yield respective products, 5,10-didodecyl-substituted DTmBDT-C12 and 5,10-dipropyl DTmBDT-C3. This one-pot synthesis is convenient with high yields of the desired products, 70% for DTmBDT-C12 and 77% for DTmBDT-C3. The 3,8-bisphenyl-5,10-didodecyl-dithieno[2,3-d;2′,3′-d′]-benzo[1,2-b;3,4-b′]-dithiophene (PH-DTmBDT-C12) and 3,8-bisthiophene-5,10-didodecyl-dithieno[2,3-d;2′,3′-d′]benzo[1,2-b;3,4-b′]-dithiophene (TH-DTmBDT-C12) were synthesized via Migita–Kosugi–Stille coupling reactions between 3,8-dibromo-5,10-didodecyl-dithieno[2,3-d;2′,3′-d′]benzo[1,2-b;3,4-b′]-dithiophene (Br3-DTmBDT) and corresponding tributyryl(aryl)stannane reagents, as shown in Scheme 1.

The crystallization of DTmBDT-C3 in tetrahydrofuran (THF) via slow diffusion of methanol led to colorless rod-shaped single crystals. However, attempts to obtain single crystals of DTmBDT-C12, PH-DTmBDT-C12, and TH-DTmBDT-C12 were not successful. Single-crystal X-ray diffraction analysis of DTmBDT-C3 revealed a packing in a P21/c (monoclinic) space group with a complete planar structure (Figure 2). Unlike Br3-DTmBDT, DTmBDT-C3 did not form dyads between two molecular planes in a face-to-face manner, but the edge overlapped with propyl chains at the same side. The packing pattern of the molecules in single crystals followed a “herringbone” arrangement with a π–π distance of 3.69 Å (Supporting Information).

The UV–vis absorption and emission spectra in 10−5 M solutions of the DTmBDT derivatives in DCM are depicted in Figure 3. The absorption spectra of DTmBDT-C12 and DTmBDT-C3 are identical with two bands around 342 and 275 nm, which are arising from the π→π* transition of conjugated backbone (see Supporting Information Figure S2). The phenyl and thiophene end-capped PH-DTmBDT-C12 and TH-DTmBDT-C12 showed red-shifted bands because of enhanced conjugation lengths (Table 1). The absorption maximum (λmax) of TH-DTmBDT-C12 was further red-shifted by 15 nm compared to PH-DTmBDT-C12. Their emission spectra showed a similar trend as the absorption spectra with bathochromic-shifted emission maximum (λem = 436 nm) for TH-DTmBDT-C12 compared to PH-DTmBDT-C12 (420 nm) and DTmBDT-C12 (357 nm). Besides the maxima of emission peaks, clearly resolved shoulder peaks were observed because of vibronic coupling of the nearly planar structures (Figure 3b).

Scheme 1. Synthesis of Alkylated and End-Capped DTmBDT Derivatives
Electrochemical properties of the DTmBDT molecules were investigated in a 0.1 M DCM solution using Bu4NPF6 as the electrolyte. DTmBDT-C12, TH-DTmBDT-C12, and PH-DTmBDT-C12 showed clearly visible two oxidation waves (Figure 4). The first oxidation of PH-DTmBDT-C12 occurred at 0.66 V and second oxidation at 0.8 V, whereas TH-DTmBDT-C12 showed first and second oxidations at 0.25 and 0.51 V, respectively. In contrast, DTmBDT-C12 exhibited the first oxidation at 0.53 V. It should be noted that DTmBDT-C3 and DTmBDT-C12 have same oxidation−reduction potentials similar to their optical properties. It was clearly evident that the substituents phenyl and thiophene have significantly influenced the highest occupied molecular orbital (HOMO) energy levels of the DTmBDT-based compounds (Table 1). The lowest

Table 1. Photophysical and Electrochemical Properties of the DTmBDT Derivatives

| compound      | λ_{max} (nm) | λ_{em} (nm) | η1 (V) | η2 (V) | HOMO<sup>a</sup> (eV) | LUMO<sup>a</sup> (eV) | E<sub>optical</sub> (eV) | HOMO<sup>c</sup> (eV) | LUMO<sup>c</sup> (eV) | dihedral angle (°)<sup>c</sup> |
|---------------|-------------|-------------|--------|--------|----------------------|----------------------|---------------------|----------------------|----------------------|------------------------|
| DTmBDT-C12    | 342, 325, 284 | 357         | 0.53   | 0.90   | −5.30                | −1.87                | 3.43                | −5.38                | −1.31                | NA                     |
| PH-DTmBDT-C12 | 385, 378, 260 | 420         | 0.66   | 0.80   | −5.34                | −2.39                | 2.95                | −5.12                | −1.66                | 27.5                   |
| TH-DTmBDT-C12 | 411, 394, 261 | 436         | 0.25   | 0.51   | −4.91                | −2.1                 | 2.81                | −5.05                | −1.82                | 20.5                   |

<sup>a</sup>=[E<sub>ox onset</sub> + 4.8]. <sup>b</sup>=[E<sub>HOMO</sub> + E<sub>optical</sub>]. <sup>c</sup>DFT calculations using B3LYP/6-31G(d); ox = oxidation potential. 
unoccupied molecular orbital (LUMO) energy levels were calculated from optical band gap ($E_{\text{optical}}$) and HOMO energy levels.

The geometric and electronic structures of the DTmBDT derivatives were calculated using Gaussian 09 with density functional theory (DFT) and B3LYP/6-31G(d) as the basis set. The optimized geometries of DTmBDT-C12, PH-DTmBDT-C12, and TH-DTmBDT-C12 were provided in Figure S1, and calculated dihedral angles ($\theta_{\text{dih}}$) between the DTmBDT core unit and end-capped moieties were listed in Table 1. Phenyl-capped PH-DTmBDT-C12 showed a bigger $\theta_{\text{dih}}$ than the thiophene-substituted molecule. As expected, the frontier orbitals and electronic structures of the three molecules. The calculated values of the HOMO levels agreed with the experimental oxidation levels. However, the energy gaps from time-dependent DFT calculation are much larger than the experimental oxidation levels. However, the energy gaps from time-dependent DFT calculation are much larger than the experimental oxidation levels. However, the energy gaps from time-dependent DFT calculation are much larger than the experimental oxidation levels. However, the energy gaps from time-dependent DFT calculation are much larger than the experimental oxidation levels. However, the energy gaps from time-dependent DFT calculation are much larger than the experimental oxidation levels.

The geometric and electronic structures of the DTmBDT derivatives were calculated using Gaussian 09 with density functional theory (DFT) and B3LYP/6-31G(d) as the basis set. The optimized geometries of DTmBDT-C12, PH-DTmBDT-C12, and TH-DTmBDT-C12 were provided in Figure S1, and calculated dihedral angles ($\theta_{\text{dih}}$) between the DTmBDT core unit and end-capped moieties were listed in Table 1. Phenyl-capped PH-DTmBDT-C12 showed a bigger $\theta_{\text{dih}}$ than the thiophene-substituted molecule. As expected, the frontier orbitals and electronic structures of the three molecules. The calculated values of the HOMO levels agreed with the experimental oxidation levels. However, the energy gaps from time-dependent DFT calculation are much larger than the optical gaps but that may be because of the neglect of full configuration in the simulation method (Table 1 and Figure S5).

Figure 5. Calculated HOMOs and LUMOs of DTmBDT, PH-DTmBDT, and TH-DTmBDT using DFT, B3LYP/6-31G(d).

Differential scanning calorimetry (DSC) was carried out to determine thermal properties during heating of DTmBDT-C12, PH-DTmBDT-C12, and TH-DTmBDT-C12. Information about these thermal transitions is necessary for the selection of the substrate temperature, which has a significant impact on the microstructure and surface morphology of organic semiconductors. During heating of DTmBDT-C12, a sharp endothermic peak appeared at 105 °C (Figure 6), which was attributed to the melting of the compound. TH-DTmBDT-C12 and PH-DTmBDT-C12 exhibited a more complex thermal behavior, with three and four endothermic transitions, respectively, during heating. TH-DTmBDT-C12 revealed two strong, sharp endothermic peaks, at 65 and 125 °C, related to transitions between crystalline phases and a small one at 144 °C because of the melting of the compound into the isotropic phase. The exothermic peak at 84 °C was probably caused by cold crystallization. The four endothermic peaks observed for PH-DTmBDT-C12 appeared at 25, 125, 140, and 177 °C, suggesting the presence of three phase transitions, and thus presence of different crystalline phases. The melting peak was located at the highest temperature. All compounds showed good thermal stabilities, and their decomposition temperature was about 390 °C for DTmBDT-C12 and about 430 °C for TH-DTmBDT-C12 and PH-DTmBDT-C12 (Figure S3). On the basis of these results, the substrate temperatures during sublimation were chosen. Apart from deposition of all compounds at 25 °C, the sublimation of TH-DTmBDT-C12 and PH-DTmBDT-C12 was performed onto hot substrates with temperatures of 100 and 150 °C, respectively, to investigate the character of different crystalline phases on the film morphology.

Atomic force microscopy (AFM) was used to investigate the influence of the alkyl chain length and the role of the thiophene and phenyl end-capping units on the film morphologies of the sublimed compounds. The compounds were deposited on silicone substrates equipped with a bis(trimethylsilyl)amine (HMDS)-treated SiO$_2$ dielectric. The AFM images in Figure 7 showed differences in the film microstructure between DTmBDT-C3 and DTmBDT-C12. Compound DTmBDT-C3 revealed a film topography consisting of crystals immersed in a featureless or amorphous fraction (Figure 7a). The crystals were distributed randomly without any distinct surface orientation, leading to a high film roughness of 2.9 nm. Compound DTmBDT-C12 exhibited relatively flat islands with a slightly lower surface roughness of 1.46 nm, suggesting a gradual film growth (Figure 7b). The height profiles of the DTmBDT-C12 film disclosed a step-terrace structure with step heights of 3.7–4.0 nm, which was characteristic for a layer-plus-island Stranski–Krastanov (SK) growth. This was a similar initial growth pattern, as reported for pentacene. In this growth model, the molecules approaching the substrate are more bound to the substrate than to each other. This condenses the first molecules as highly ordered monolayer on the surface. On the initial layer, flat islands are then formed with a height corresponding to the interplanar spacing of DTmBDT-C12 (Figure S4). During the SK growth, the flat islands grow laterally with the additional material deposited to eventually merge into a continuous layer, which can be partially observed in Figure 7b. The subsequent layers start to form before the previous layer is complete. This is consistent with the aforementioned SK growth mechanism. Summarizing the morphology study, longer alkyl chains improved the film formation process into homogenous and well-defined layers. Decrease of the domain surface roughness is connected to the type of the grown structure (crystal or island) and is induced by the longer dodecyl chains.

The AFM images of PH-DTmBDT-C12 and TH-DTmBDT-C12 showed sharp, fibrous grains of small-size and random orientation, with larger features for TH-DTmBDT-C12 (Figure 8a,c). Both surfaces were more familiar to each other than to the DTmBDT-C12 morphology. This suggested that the phenyl or thiophene end-caps significantly altered the film formation from SK growth for DTmBDT-C12 to a less-defined structure of PH-DTmBDT-C12 and TH-DTmBDT-C12.
An average grain size of 73 and 121 nm (detailed information about the grain size can be found in Figure S5) was determined for PH-DTmBDT-C12 and TH-DTmBDT-C12, respectively. TH-DTmBDT-C12 created almost two times larger grains than PH-DTmBDT-C12.

Figure 7. AFM height images of (a) DTmBDT-C3 and (b) DTmBDT-C12 sublimed at 25 °C substrate temperature.

Figure 8. AFM topography images of vacuum-deposited films at various substrate temperatures. PH-DTmBDT-C12 deposited onto (a) 25 and (b) 150 °C; TH-DTmBDT-C12 deposited onto (c) 25 and (d) 100 °C heated substrates.

Figure 9. GIWAXS patterns of (a) DTmBDT-C3, (b) DTmBDT-C12 (both deposited at 25 °C), (c) TH-DTmBDT-C12 deposited at 100 °C and PH-DTmBDT-C12 deposited at 150 °C substrate temperature.
larger crystal domains compared to PH-DTmBDT-C12 probably because of the smaller dihedral angle (θ) of 20.5° of the thiophene to the DTmBDT core, which less disturbed the molecular interactions with respect to PH-DTmBDT-C12 with θ = 27.5°. Significant changes in the surface morphology were found when the compounds were evaporated onto substrates with temperatures of 150 °C for PH-DTmBDT-C12 and 100 °C for TH-DTmBDT-C12 close to their melting points. Both compounds exhibited large elongated, interdigitated structures with reduced grain boundaries (Figure 8b, d). The average grain size dramatically increased to 9.9 and 2.2 μm for PH-DTmBDT-C12 and TH-DTmBDT-C12, respectively, which was 2 and 3 orders of magnitude larger than for films deposited at 25 °C. However, the film deposited at a high substrate temperature displayed clear deep cracks (Figure 8b, d). Height profiles of the AFM images for PH-DTmBDT-C12 revealed a crack depth of 46 nm through the entire 50 nm thick film.

To better understand the influence of the alkyl substituents (C3 and C12) on the self-organization of the molecules, grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed. The patterns indicate a highly crystalline structure for both compounds (Figure 9a, b). The interlayer distance of 1.79 nm for DTmBDT-C3 was determined from the main out-of-plane 100 reflections observed at qz = 0.0 Å⁻¹ and qx = 0.35 Å⁻¹. Second- and third-order reflections localized at qx = 0.69 Å⁻¹ and qx = 1.05 Å⁻¹ for qz = 0.0 Å⁻¹ implied a long-range organization of the molecules in the out-of-plane direction of the film. The increase of the interlayer distance from 1.79 nm for DTmBDT-C3 to 3.75 nm for DTmBDT-C12 was caused by the longer linear substituents implying no interdigitation of the side chains (Figure S6a). The interlayer distance of DTmBDT-C12 is in good agreement with the step height of the terrace structure observed in the AFM image. Additionally, in both cases, in-plane reflections at the same positions at qx = 0.77 Å⁻¹ and qx = 0 Å⁻¹ (d spacing of 0.82 nm) were found implying identical packing of the molecules in stacks with a herringbone structure and an edge-on arrangement on the surface (Figure S6a). A π-stacking distance of 0.38 nm was derived for DTmBDT-C3 from off-equatorial reflections located at qxy = 1.56 Å⁻¹ and qxz = 0.63 Å⁻¹ corresponding to the value found for the single crystal (0.37 nm). The high reflection intensity and small π-stacking distance were characteristic for well-ordered molecules within the layers. It was not possible to determine the π-stacking distance for DTmBDT-C12 because the corresponding reflection was broader suggesting a lower order because of the longer side chains. In contrast to the solely alkyl-substituted DTmBDT derivatives, the crystallinity of TH-DTmBDT-C12 and PH-DTmBDT-C12 deposited at 25 °C was poor as evident from the low intensity and small number of reflections in the corresponding GIWAXS patterns (Figure S7). This corresponds well to the disordered film morphology displayed in the AFM image in Figure 8a, c. Deposition of the compounds onto higher temperature substrate significantly improved the molecular order (Figure 9c, d). Interestingly, the interlayer distance for TH-DTmBDT-C12 decreased to 2.79 nm in comparison with 3.70 nm for DTmBDT-C12, as derived from the main interlayer reflection at qxz = 0 Å⁻¹ and qxz = 0.23 Å⁻¹ (Figure 9c). This decrease could originate from tilting of the molecules with respect to the substrate (Figure S6b). The off-equatorial position of the π-stacking reflection at qxz = 1.60 Å⁻¹ and qxz = 1.35 Å⁻¹ verified a 40° tilting of the molecules with respect to the out-of-plane direction. Assuming an interlayer distance of 3.70 nm for nontilted molecules, the cosine trigonometric function provided a theoretical interlayer distance of 2.83 nm for molecules tilted by 40° being in good agreement with the experimental data (Figure S6b). These calculations imply that interdigitation of the side chains did not occur also for TH-DTmBDT-C12. The long-range organization of TH-DTmBDT-C12 and PH-DTmBDT-C12 deposited at high temperature confirmed the higher order out-of-plane reflections. The in-plane reflection at qxz = 0.4 Å⁻¹ and qxz = 0 Å⁻¹ was assigned to a d spacing of 1.57 nm corresponding between the stacks in which the molecules were packed in the herringbone fashion (Figures S6b and S8). The increased distance in comparison with DTmBDT-C12 is related to the two additional thiophene units terminating the

Table 2. OFET Characteristics of the DTmBDT Derivatives

| compound             | substrate temperature (°C) | μ_{max} (cm²/V s) | μ_{average} (cm²/V s) | I_on/I_off (−) | V_TH (V) |
|----------------------|---------------------------|-----------------|----------------------|----------------|----------|
| DTmBDT-C3            | 25                        | 0.25            | 0.20                 | 10⁶            | −17      |
| DTmBDT-C12           | 25                        | 0.75            | 0.32                 | 10⁷            | −18      |
| TH-DTmBDT-C12        | 25                        | 0.026           | 0.022                | 10⁶            | −7       |
| TH-DTmBDT-C12        | 100                       | 0.055           | 0.043                | 10⁶            | −6       |
| PH-DTmBDT-C12        | 25                        | 0.0007          | 0.0006               | 10⁴            | −12      |
| PH-DTmBDT-C12        | 150                       | 0.17            | 0.15                 | 10⁶            | −6       |

Figure 10. Transfer characteristics of transistors based on (a) TH-DTmBDT-C12 and (b) PH-DTmBDT-C12 thin films deposited at 25, 100, and 150 °C substrate temperatures.
DTmBDT core. Only small changes in organization were observed for PH-DTmBDT-C12 with respect to TH-DTmBDT-C12 (for PH-DTmBDT-C12, the interlayer and stack distances are 2.75 and 1.60 nm, respectively).

The charge-carrier transport of the DTmBDT derivatives was investigated by field-effect transistors (OFETs) in bottom-gate bottom-contact (BGBC) configuration. The active layer of the DTmBDT-based OFETs was fabricated by thermal deposition on silicon substrates equipped with a HMDS- treated SiO2 dielectric. All compounds showed typical p-type behavior, as confirmed by the transfer and output characteristics. From the transfer characteristics in Figure S9, charge-carrier mobilities of 0.25 cm2/V s for DTmBDT-C3 and 0.75 cm2/V s for DTmBDT-C12 with an on/off ratio exceeding 105 were derived (Table 2). These mobilities were in the same order of magnitude as for dialkoxyated DTmBDT, as reported in the literature.35 However, the threshold voltage for DTmBDT-C3 and DTmBDT-C12 was lower in comparison with the literature values and was not dependent on the film morphology of the compounds.

In comparison with DTmBDT-C3 and DTmBDT-C12, a significant decrease of the charge-carrier mobility was observed to be 0.0007 cm2/V s for TH-DTmBDT-C12 and 0.026 cm2/V s for PH-DTmBDT-C12 when both were deposited at 25 °C (Figures 10 and S10). This decline in performance is caused by the molecular disorder, as confirmed by the low-intensity reflections in the GIWAXS patterns. The transistor performance improved for TH-DTmBDT-C12 and PH-DTmBDT-C12 films deposited onto higher temperature substrates because of changes in the morphology. Compound TH-DTmBDT-C12 sublimed onto 100 °C heated Si/SiO2 substrate exhibited a charge-carrier mobility of 0.06 cm2/V s with an unchanged on/off ratio of 106 (Figures 10 and S10). A larger increase in mobility to 0.17 cm2/V s and an on/off ratio of 108 was found for PH-DTmBDT-C12 after sublimation onto 150 °C substrate (Figures 10 and S10). At the same time, the threshold voltage for PH-DTmBDT-C12 was reduced by nearly half. This enhanced transistor performance of PH-DTmBDT-C12 and TH-DTmBDT-C12 is attributed to the significant increase in crystallinity and molecular order as well as formation of large domains in films obtained at higher temperatures, as evident in the AFM images (Figure 8b,d) and GIWAXS patterns (Figure 9c,d).

3. CONCLUSIONS

In summary, we have synthesized and studied the structure–property relations of four DTmBDT derivatives. Optoelectronic and electrochemical properties were significantly influenced by nature of end-capped moieties of the DTmBDT core. The 5,10-dipropyl DTmBDT-C3 single crystals were packed in a herringbone structure, demonstrating complete planarity of the core and complementing to the interdigitating of long alkyl chain in case of Br2-DTmBDT. Thermogravimetric analysis of these heteroacene derivatives exhibited high thermal stability with decomposition temperatures above 390 °C. The morphology of vacuum sublimated films was controlled by the substrate temperature and chemical structure of the derivatives such as alkyl chain length or aromatic endcaps. Because of the well-defined morphology, DTmBDT-C12 showed the highest charge-carrier mobilities of 0.75 cm2/V s in field-effect transistors within this series. Aromatic end-caps at the DTmBDT core disturbed the growth into a homogenous film morphology that limited the charge-carrier transport. Large domains could be obtained for these derivatives with a higher substrate temperature leading to improved transistor mobilities.

The dramatic increase of mobility associated with the change of the substrate temperature underlines the necessity of thermal investigation in case of novel organic semiconductors.

4. EXPERIMENTAL SECTION

4.1. General Methods. All reagents were purchased from commercial sources and used without further purification unless otherwise stated. Column chromatography was performed using Merck silica gel 60, 40–63 μm (230–400 mesh). Thin-layer chromatography (TLC) was carried out using precoated aluminum sheets with silica gel 60 F254 (Merck), visualization by UV light. 1H NMR and 13C NMR spectra were recorded in the listed deuterated solvents on a Bruker AVANCE 300 and 250 MHz spectrometer. Mass spectra were obtained using field desorption on a VG Instruments ZAB 2-SE-FPD spectrometer. Elemental analysis was carried out using a Foss Heraeus Vario EL in the Institute of Organic Chemistry at the Johannes Gutenberg-University, Mainz. The UV–vis spectra were recorded at 298 K on a PerkinElmer Lambda 900 spectrophotometer. Cyclic voltammetry measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell in a DCM solution of Bu4NPF6 (0.1 M) with a scan rate of 100 mV/s at room temperature, using Pt disc as the working electrode, Pt wire as the counter electrode, and Ag electrode as the reference electrode. HOMO energy levels were calculated from the onsets of the first oxidation peak by empirical formulas $E_{\text{HOMO}} = -(E_{\text{onset}} + 4.8) \text{ eV}$, whereas the potentials were determined using ferrocene (Fc) as a standard. DFT calculations were carried out at the B3LYP/6-31G(d) level using Gaussian 09,37 and molecular structures were generated using GaussView 5.0.9.38 The X-ray crystallographic data for the molecules were collected on a SMART charge-coupled device diffractometer using a Mo Kα graphite monochromator radiation source. Thermogravimetry analysis (TGA) was carried out on a METTLER 500 thermogravimetry analyzer with heating rates of 10 K/min. DSC were measured on a METTLER DSC 30 with heating and cooling rates of 10 K/min. AFM was performed with ScanAsyst-Fluid+ probes in peak force nanomechanical mapping mode with a Bruker FastScan instrument.

4.2. Synthesis. Compounds (3,3′-dibromo-2,2′-bithieno[3,2-b:3,2-b′]thiene-5,5′-dipyridine)[trimethylsilane] (1), (Z)-2,2′- (hexacos-13-ene-13,14-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2a), and (Z)-2,2′-(oct-4-ene-4,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2b) were synthetically followed by the reported procedures. Other stannyl compounds, tributyl(phenyl)stannane (3a) and tributyl(2-phenyl-2-yl)stannane (3b), were commercially available.

4.2.1. 5,10-Diododecyl-dithieno[2,3-d:2′,3′-d′]dithiophene (DTmBDT-C12). To a 50 mL Schlenk tube, (3,3′-dibromo-2,2′-bithieno[3,2-b:3,2-b′]thiene-5,5′-dipyridine)[trimethylsilane] (0.5 g, 0.86 mmol), (Z)-2,2′-(hexacos-13-ene-13,14-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.6 g, 0.97 mmol), 2 M K2CO3 aq solution (5 mL, 10 mmol), and dry toluene (15 mL) were added and then degassed by bubbling argon for 20 min at room temperature. The catalyst, Pd(PPh3)4 (100 mg, 0.09 mmol), was added, the reaction mixture was refluxed at 80 °C for 12 h, and the reaction progress was monitored by TLC. After the starting materials were consumed, the reaction mixture was cooled to room
temperature and 5 g of K₂CO₃ was added to it. The reaction mixture was refluxed at 80 °C for 1 h and its progress was monitored by TLC. The reaction mixture was cooled to room temperature, extracted with DCM, and washed with brine. The organic fraction was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude compound was purified by column chromatography on silica gel using hexane as an eluent to give a white solid (497 mg, yield 70%). ¹H NMR (250 MHz, CD₂Cl₂, ppm): δ 7.59 (d, J = 5 Hz, 2H), 7.41 (d, J = 5 Hz, 2H), 3.20 (t, J = 7.5 Hz, 4H), 1.76–1.63 (m, 8H), 1.51–1.28 (m, 32H), 0.91–0.86 (t, J = 5.7 Hz, 6H). ¹³C NMR (63 MHz, CD₂Cl₂, ppm): δ 136.57, 135.54, 135.00, 132.10, 131.18, 128.90, 120.56, 32.52, 31.69, 31.48, 30.77, 30.30, 30.28, 30.26, 30.23, 30.07, 29.96, 23.28, 14.47. FD-Mass: calcd, 638.31; found, 638.23.

4.2.2. 5,10-Dipropyl-dithieno[2,3-d;2',3'-d']benzo[1,2-b;3,4-b']dithiophene (DTmBDT-C3). The DTmBDT-C3 was synthesized by following the similar procedure used for the molecule DTMBDT. The starting materials, (3,3'-dibromo-2,2'-bithieno[3,2-b;3',2'-d']thienyl-S,S'-dial)bis(trimethylsilane) (0.5 g, 0.86 mmol) and (Z)-2,2'-oct-4-ene-4,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.36 g, 0.97 mmol) were reacted to give a final product white solid (255 mg, yield 77%) after the column chromatography on silica gel using hexane as an eluent. ¹H NMR (300 MHz, CD₂Cl₂, ppm): δ 7.59 (d, J = 5 Hz, 2H), 7.41 (d, J = 5 Hz, 2H), 3.19 (t, J = 5 Hz, 4H), 1.79–1.74 (m, 4H), 1.22 (t, J = 5 Hz, 6H). ¹³C NMR (75 MHz, CD₂Cl₂, ppm): δ 136.59, 135.57, 131.98, 130.20, 128.91, 125.83, 120.58, 33.43, 25.06, 14.89. FD-Mass: calcd, 386.03; found, 385.88.

4.2.3. 3,8-Bisphenyl-5,10-diodocetyl-dithieno[2,3-d;2',3'-d']benzo[1,2-b;3,4-b']dithiophene (PH-DMTBDT-C12). To a solution of 3,8-dibromo-5,10-diodocetyl-dithieno[2,3-d;2',3'-d']benzo[1,2-b;3,4-b']dithiophene (Br₂-DTMBDT, 100 mg 0.125 mmol), tributyl(chlorophenyl)stannane (3a, 100 mg, 0.272 mmol) and bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh₃)₂Cl₂), 7.65 mg, 0.0084 mmol) in 10 mL of THF were added. The mixture was vigorously stirred at 70 °C for 12 h, and the reaction progress was monitored by TLC. After the starting materials were consumed, reaction mixture was cooled to room temperature, extracted with DCM, and washed with brine. The organic fraction was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude compound was purified by column chromatography on silica gel using hexane as an eluent to give a yellow solid (63 mg, yield 70%). ¹H NMR (250 MHz, CD₂Cl₂, ppm): δ 7.72 (d, J = 7.5 Hz, 4H), 7.62 (s, 2H), 7.48–7.42 (m, 4H), 7.38–7.31 (m, 2H), 3.23 (t, J = 7.5 Hz, 4H), 1.71 (m, 8H), 1.34–1.27 (m, 32H), 0.88 (m, 6H). ¹³C NMR (63 MHz, CD₂Cl₂, ppm): δ 147.64, 137.28, 134.91, 134.53, 132.18, 131.44, 129.65, 128.62, 126.25, 116.43, 32.51, 31.74, 31.53, 30.75, 30.31, 30.28, 30.22, 30.06, 29.96, 23.28, 14.46. FD-Mass: calcd, 790.37; found, 790.11.

4.2.4. 3,8-Bis(thiophene-2-yl)-5,10-diodocetyl-dithieno[2,3-d;2',3'-d']benzo[1,2-b;3,4-b']dithiophene (TH-DMTBDT-C12). To synthesize TH-DMTBDT-C12, similar procedure as PH-DMTBDT-C12 was implemented. The starting compounds, Br₂-DTMBDT (100 mg 0.125 mmol) and tributyl(thiophen-2-yl)stannane (3b, 100 mg, 0.267 mmol), were reacted to give TH-DMTBDT-C12 as greenish yellow powder (96 mg, yield 90%) upon purification by column chromatography on silica gel using ethyl acetate and hexane mixture as an eluent to give a yellow solid. ¹H NMR (250 MHz, THF, ppm): δ 7.56 (s, 2H), 7.39 (d, J = 7.5 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.08–7.04 (m, 2H), 3.18 (t, J = 7.5 Hz, 4H), 1.72 (m, 8H), 1.46–1.28 (m, 32H), 0.88 (t, J = 5.25, 6H). ¹³C NMR (63 MHz, THF, ppm): δ 141.29, 138.22, 137.82, 135.21, 134.00, 132.29, 131.78, 128.96, 126.29, 125.12, 117.49, 33.07, 32.28, 31.94, 31.25, 30.89, 30.84, 30.81, 30.64, 30.53, 23.76, 14.64. FD-Mass: calcd, 802.29; found, 802.37.

4.3. AFM Analysis. Veeco Dimension 3100 atomic force microscope was used to inspect the microstructure and the thickness of the sublimated films. All images were obtained in the tapping mode with Olympus silicon cantilevers at 320 kHz resonance frequency. Grain-size analysis was performed by marking grains above a specified threshold height in Gwyddion 2.47 software. Root-mean-square roughness parameters were obtained using the same software package.

4.4. Grazing Incidence Wide-Angle X-ray Scattering. To investigate the molecular ordering in the sublimed films, GIWAXS measurements were performed at the DELTA Synchrotron using beamline BL09 with a photon energy of 10 keV (λ = 1.239 Å). The beam size was 1.0 mm × 0.2 mm (width × height), and samples were irradiated just below the critical angle for total reflection with respect to the incoming X-ray beam (∼0.1°). The scattering intensity was detected on a 2-D image plate (MAR-345) with a pixel size of 150 μm (2300 × 2300 pixels), and the detector was placed 381 mm from the sample center. The raw detector image needs to be converted into a reciprocal space. This was carried out by using a calibration standard (silver behenate), which has rings at known 2θ positions. Scattering data are expressed as a function of the scattering vector: q = 4π/λ sin(Θ), where Θ is a half of the scattering angle and λ = 1.239 Å is the wavelength of the incident radiation. Here, qₓ or (qᵧ) is a component of the scattering vector in-plane (out-of-plane) to the sample surface. All X-ray scattering measurements were performed under vacuum (~1 mbar) to reduce air scattering and beam damage to the sample. All GIWAXS data processing and analysis were performed by using the software package Datasqueeze (http://www.datasqueezesoftware.com).

4.5. Fabrication and Measurement of OFET Devices. OFET devices were fabricated in a BGBC configuration on Si/SiO₂ substrates with 50 nm thick gold electrodes. The SiO₂ dielectric layer was 300 nm thick with a dielectric constant of 3.9. The source–drain electrodes were interdigitated with channel length varying from 2.5 to 40 μm and channel width varying from 0.1 to 1 mm. Substrates were cleaned softly with IPA and acetone, making sure that the prefabricated electrodes are not damaged. Then, HMDS treatment was performed on the substrates that were placed in an oven with HMDS at a temperature of 120 °C for 5 h to form a HMDS self-assembled monolayer. Before evaporation, the glass crucibles were cleaned thoroughly in piranha solution (3:1 solution of sulfuric acid and hydrogen peroxide) to remove all organic residues and then washed with isopropyl alcohol and acetone. The organic semiconductor layers were deposited by vacuum-evaporation at a rate of 0.6 Å/min using Tectra mini-coater high-vacuum coating system. The film thickness was about 40 nm controlled using quartz crystal microbalance monitor and adjusted by AFM. Transistors were measured by using a Keithley 2634B source meter. Mobilities were calculated from the transfer characteristics in the saturation regime, using the following formula

\[ I_D = \frac{W}{2L} C \mu (V_G - V_T)^2 \]
where $I_d$ is the drain current, $W$ is the channel width, $L$ is the channel length, $C_i$ is the capacitance of gate dielectric, $V_g$ is the gate voltage, and $V_{th}$ is the threshold voltage.

This formula was further modified to extract $\mu_{sat}$ with respect to the slope of a straight line fitted to the square root of the transfer characteristic

$$\mu_{sat} = \frac{2aL}{W \sqrt{g}}$$

where $a$ is the slope of the fitted straight line.

Threshold voltage is estimated as a cross-point of the fitted line and OX axis. The ON/OFF ratio is calculated as a division of $I_d$ current in the highest $V_g$ and $V_{gs}$ voltages by $I_d$ current for the same $V_d$ and $V_{gs} = 0$ V.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00836.

Geometry-optimized structures and DFT calculations; TGA curves; AFM analysis, GIWAXS data, single crystal data, and NMR spectra; and X-ray CCD 1548551 (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

*E-mail: ashok.kee thi@man chester.ac.uk* (A.K.)

*E-mail: marsza lek@mpip-mainz.mpg.de* (T.M.)

*E-mail: martin.baumgarten@mpip-mainz.mpg.de* (M.B.)

ORCID

Ashok Kee thi: 0000-0002-8479-4762

Debin Xia: 0000-0002-2658-2577

Klaus Mü llen: 0000-0001-6630-8786

Wojciech Pisula: 0000-0002-5853-1889

Martin Baumgarten: 0000-0002-9564-4559

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We acknowledge Dr. Dieter Schollmeyer at Johannes Gutenberg University for the single-crystal structure analysis and Jutta Schnee for helping in the synthesis of thiene[3,2-b]thiophene derivatives. This work was financially supported by Transregio TR49 and the King Abdulaziz City of Science and Technology (KACST), W.W., T.M., and W.P. acknowledge for financially supported by the National Science Centre, Poland, through the grant UMO-2015/18/E/ST3/00322. The authors also acknowledge Beamline 9 of the DELTA electron storage ring in Dortmund for providing synchrotron radiation and technical support for GIWAXS measurements.

**REFERENCES**

(1) Takimiya, K.; Shinamura, S.; Osaka, I.; Miyazaki, E. Thienoacene-Based Organic Semiconductors. *Adv. Mater.* 2011, 23, 4347−4370.

(2) Holliday, S.; Donaghy, J. E.; McClurk, I. Advances in Charge Carrier Mobilities of Semiconducting Polymers Used in Organic Transistors. *Chem. Mater.* 2014, 26, 647−663.

(3) Zhao, Y.; Guo, Y.; Liu, Y. 25th Anniversary Article: Recent Advances in n-Type and Ambipolar Organic Field-Effect Transistors. *Adv. Mater.* 2013, 25, 5372−5391.

(4) Bujak, P.; Kulszewicz-Bajer, I.; Zagorska, M.; Maurel, V.; Wielgus, I.; Pron, A. Polymers for electronics and spintronics. *Chem. Soc. Rev.* 2013, 42, 8895−8899.

(5) Kang, I.; Yun, H.-J.; Chung, D. S.; Kwon, S.-K.; Kim, Y.-H. Record High Hole Mobility in Polymer Semiconductors via Side-Chain Engineering. *J. Am. Chem. Soc.* 2013, 135, 14896−14899.

(6) Kim, G.; Kang, S.-J.; Dutta, G. K.; Han, Y.-K.; Shin, T. J.; Noh, Y.-Y.; Yang, G. A Thieneoindigo-Naphthalene Polymer with Ultrahigh Mobility of 14.4 cm²/Vs That Substantially Exceeds Benchmark Values for Amorphous Silicon Semiconductors. *J. Am. Chem. Soc.* 2014, 136, 9477−9483.

(7) Sun, B.; Hong, W.; Yan, Z.; Aziz, H.; Li, Y. Record High Electron Mobility of 6.3 cm²V−1s−1 Achieved for Polymer Semiconductors Using a New Building Block. *Adv. Mater.* 2014, 26, 2636−2642.

(8) Tseng, H.-R.; Phan, H.; Luo, C.; Wang, M.; Perez, L. A.; Patel, S. N.; Ying, L.; Kramer, E. J.; Nguyen, T. Q.; Bazan, G. C.; Heeger, A. J. High-Mobility Field-Effect Transistors Fabricated with Macroscopic Aligned Semiconducting Polymers. *Adv. Mater.* 2014, 26, 2993−2998.

(9) Luo, C.; Kyaw, A. K. K.; Perez, L. A.; Patel, S.; Wang, M.; Grimm, B.; Bazan, G. C.; Kramer, E. J.; Heeger, A. J. General Strategy for Self-Assembly of Highly Oriented Nanocrystalline Semiconducting Polymers with High Mobility. *Nano Lett.* 2014, 14, 2764−2771.

(10) Sirringhaus, H. 25th Anniversary Article: Organic Field-Effect Transistors: The Path Beyond Amorphous Silicon. *Adv. Mater.* 2014, 26, 1319−1335.

(11) Minami, S.; Hirano, K.; Satoh, T.; Miura, M. Synthesis of [1]benzo[5,6]thiophene[3,2-b][1]benzothiophene (BTBT) and its higher homologues through palladium-catalyzed intramolecular decarboxylative arylation. *Tetrahedron Lett.* 2014, 55, 4175−4177.

(12) Zhang, X.; Coté, A. P.; Matzger, A. J. Synthesis and Structure of Fused α-Oligothiophenes with up to Seven Rings. *J. Am. Chem. Soc.* 2005, 127, 10502−10503.

(13) Wetzel, C.; Brier, E.; Vogt, A.; Mishra, A.; Mena-Osteritz, E.; Bäuerle, P. Fused Thiophene-Pyrrrole-Containing Ring Systems up to a Heterocenedacene. *Angew. Chem., Int. Ed.* 2015, 54, 12334−12338.

(14) Zhong, H.; Li, Z.; Deledalle, F.; Fregoso, E. C.; Shahid, M.; Fei, Z.; Nielsen, C. B.; Yaacobi-Gross, N.; Rossbauer, S.; Anthopoulos, T. D.; Durrant, J. R.; Heeney, M. Fused Dithienogermolodithiophene Low Band Gap Polymers for High-Performance Organic Solar Cells without Processing Additives. *J. Am. Chem. Soc.* 2013, 135, 2040−2043.

(15) Tsutsui, Y.; Sakurai, T.; Minami, S.; Hirano, K.; Satoh, T.; Matsuda, W.; Kato, K.; Takata, M.; Miura, M.; Seki, S. Evaluation of the intrinsic charge carrier transporting properties of linear- and bent-shaped [small pi]-extended benzo-fused thiieno[3,2-b]thiophenes. *Phys. Chem. Chem. Phys.* 2015, 17, 9624−9628.

(16) Xia, Y.; Li, Y.; Zhu, Y.; Li, J.; Zhang, P.; Tong, J.; Yang, C.; Li, H.; Fan, D. Dithieno[2,3-d:2′,3′-d′]naptho[1,2-b,3′-b]-thiophene – a novel electron-rich building block for low band gap conjugated polymers. *J. Mater. Chem. B* 2014, 2, 1601.

(17) Shaw, J.; Zhong, H.; Yau, C. P.; Casey, A.; Buchaca-Domingo, E.; Stingelin, N.; Sparrowe, D.; Mitchell, W.; Heeney, M. Alternating Copolymers: Incorporating Dithienogermolodithiophene for Field-Effect Transistor Applications. *Macromolecules* 2014, 47, 8602−8610.

(18) Rieger, R.; Beckmann, D.; Mavrinskyy, A.; Kastler, M.; Mü llen, K. Backbone Curvature in Poliythiophenes. *Chem. Mater.* 2010, 22, 5314−5318.

(19) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X.; Enkelmann, V.; Baumgarten, M.; Pisula, W.; Mü llen, K. Dithieno[2,3-d:2′,3′-d′]-benzo-[1,2-b,4,5-b′]thiophene (DTDBT) as Semiconductor for High-Performance, Solution-Processed Organic Field-Effect Transistors. *Adv. Mater.* 2009, 21, 213−216.

(20) Fei, Z.; Kim, Y.; Smith, J.; Domingo, E. B.; Stingelin, N.; McLachlan, M. A.; Song, K.; Anthopoulos, T. D.; Heeney, M. Comparative Optoelectronic Study between Copolymers of Peripherally Alkylated Dithienosilole and Dithienogermole. *Macromolecules* 2012, 45, 735−742.

(21) Schärer, M. C.; Koppe, M.; Gao, J.; Cordella, F.; Loi, M. A.; Denk, P.; Morana, M.; Egelhaaf, H.-J.; Forberich, K.; Dennler, G.
Gaudiana, R.; Waller, D.; Zhu, Z.; Shi, X.; Brabc, C. J. Influence of the Bridging Atom on the Performance of a Low-Bandgap Bulk Heterojunction Solar Cell. *Adv. Mater.* 2010, 22, 367–370.

(22) Zhang, Y.; Zou, J.; Yip, H.-L.; Sun, Y.; Davies, J. A.; Chen, K.-S.; Acton, O.; Jen, A. K.-Y. Conjugated polymers based on C, Si and N-bridged dithiophene and thiienopyrrole-dione units: synthesis, field-effect transistors and bulk heterojunction polymer solar cells. *J. Mater. Chem. B* 2011, 1, 3895–3902.

(23) Coppo, P.; Turner, M. L. Cyclopentadithiophene based electroactive materials. *J. Mater. Chem. 2005, IS, 1123–1133.*

(24) Zhong, H.; Han, Y.; Shaw, J.; Anthopoulos, T. D.; Heeney, M. Fused Ring Cyclopentadithiophenothiophenes as Novel Building Blocks for High Field Effect Mobility Conjugated Polymers. *Macromolecules* 2015, 48, 5605–5613.

(25) Liang, C.; Wang, H. Indacenodithiophene-based D-A conjugated polymers for application in polymer solar cells. *Org. Electron.* 2017, 50, 443–457.

(26) Guo, P.; Beckmann, D.; Tsoa, H. N.; Feng, X.; Enkolmann, V.; Psula, W.; Müllen, K. Benzo[1,2-b:4,5-b]bis[b]benzothiophene as solution processible organic semiconductor for field-effect transistors. *Chem. Commun.* 2008, 1548–1550.

(27) Guo, X.; Tsoa, H. N.; Gao, P.; Xia, D.; An, C.; Nazeeruddin, M. K.; Baumgarten, M.; Grätzel, M.; Müllen, K. Dithieno[2,3-d,2,3-d]:[1,2-b,4,5-b]-dithiophene based organic sensitizers for dye-sensitized solar cells. *RSC Adv.* 2014, 4, 54130–54133.

(28) Keerthi, A.; An, C.; Li, M.; Marszalek, T.; Ricciardulli, A. G.; Radha, B.; Alsewailm, F. D.; Müllen, K.; Baumgarten, M. Dithieno[2,3-d,2,3-d]:[1,2-b,3,4-b]-dithiophene: a novel building-block for a planar copolymer. *Polym. Chem.* 2016, 7, 1545–1548.

(29) Xia, D.; Keerthi, A.; An, C.; Baumgarten, M. Synthesis of a quinoidal dithieno[2,3-d,2,3-d]:[1,2-b,3,4-b]-dithiophene based open-shell singlet biradicaloid. *Org. Chem. Front.* 2017, 4, 18–21.

(30) McCulloch, I.; Heeney, M.; Bailey, C.; Genevics, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tienry, S.; Wagner, R.; Zhang, W.; Chabinc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. Liquid-crystalline semiconducting polymers with high charge-carrier mobility. *Nat. Mater.* 2006, 5, 328.

(31) Ino, H.; Usui, T.; Hanna, J.-i. Liquid crystals for organic thin-film transistors. *Nat. Commun.* 2015, 6, 6828.

(32) Baskaran, A.; Smereka, P. Mechanisms of Stranski-Krastanov growth. *J. Appl. Phys.* 2012, 111, 044321.

(33) Guo, D.; Ikeda, S.; Saiki, K. Modified bimodal growth mechanism of pentacene thin films at elevated substrate temperatures. *J. Phys.: Condens. Matter* 2010, 22, 262001.

(34) Liu, S.-W.; Lee, C.-C.; Tai, H.-L.; Wen, J.-M.; Lee, J.-H.; Chen, C.-T. In situ Electrical Characterization of the Thickness Dependence of Organic Field-Effect Transistors with 1–20 Molecular Monolayer of Pentacene. *ACS Appl. Mater. Interfaces* 2010, 2, 2282–2288.

(35) Yang, S. Y.; Shin, K.; Park, C. E. The Effect of Gate-Dielectric Surface Energy on Pentacene Morphology and Organic Field-Effect Transistor Characteristics. *Adv. Funct. Mater.* 2005, 15, 1806–1814.

(36) Zhang, J.; Zhang, K.; Zhang, W.; Mao, Z.; Wong, M. S.; Yu, G. Novel dialkoxy-substituted benzodithienothiophenes for high-performance organic field-effect transistors. *J. Mater. Chem. B* 2015, 3, 10892–10897.

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, USA, 2009.

(38) Roy Dennington, T. K.; Millam, J. Gaussian View 5; Semichem Inc., 2009.

(39) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. Platinum(0)-catalyzed diboration of alkenes. *J. Am. Chem. Soc.* 1993, 115, 11018–11019.

(40) Biniek, L.; Schroeder, B. C.; Donaghey, J. E.; Yaacobi-Gross, N.; Ashraf, R. S.; Soon, Y. W.; Nielsen, C. B.; Durrant, J. R.; Anthopoulos, T. D.; McCulloch, I. New Fused Bis-Thienobenzothienothiophene Copolymers and Their Use in Organic Solar Cells and Transistors. *Macromolecules* 2015, 46, 727–735.

(41) Yavari, K.; Moussa, S.; Ben Hassine, B.; Retailleau, P.; Voituriez, A.; Marinetti, A. 1H-Phosphindoles as Structural Units in the Synthesis of Chiral Helicenes. *Angew. Chem., Int. Ed.* 2012, 51, 6748–6752.