Packaging structures of (trialkylsilyl)ethynyl-substituted dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophenes (DNTTs): effects of substituents on crystal structures and transport properties‡

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The electronic structure of an organic semiconductor that is governed by its packing structure in the solid state is critically important for the transport properties of the organic-semiconductor solid. Dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophenes (DNTTs), which have been utilized as active semiconducting materials in high-performance organic field-effect transistors (OFETs), crystalized into a herringbone packing structure that affords a two-dimensional (2D) electronic structure. Here, we have investigated the effects of substituents on the packing structure of a series of DNTT derivatives modified with (trialkylsilyl)ethynyl substituents. The packing structures of the derivatives with small (trialkylsilyl)ethynyl substituents, such as (trimethylsilyl)ethynyl (TMSE) (1) and (triethylsilyl)ethynyl (TESE) (2) groups, were revealed to be the herringbone packing, whereas (trisopropylsilyl)ethynyl (TIPSE)-substituted DNTT (3) crystalized into a sandwich herringbone structure, in which face-to-face dimers of molecules are packed into a herringbone array. In-depth analyses of the packing structures by means of the functional-group symmetry-adapted perturbation theory (F-SAPT) calculations showed that the size of the TESE groups is critical to determine the packing structure; an intermolecular interaction between the sterically demanding TIPSE groups does not allow 3 to crystalize into the herringbone structure that is favorable for most of the DNTT derivatives including 1 and 2. Although the sandwich herringbone structure has not been regarded as a potential one for efficient carrier transport in the solid state, OFETs based on 1–3 showed a comparable high mobility of 0.19 to 0.87 cm² V⁻¹ s⁻¹, indicating that the sandwich herringbone structure is not necessarily quite unsuitable for carrier transport, which was also endorsed by the transfer integrals calculated based on the packing structure elucidated by single-crystal X-ray analysis. These results imply that versatile modifications on the molecular and packing structures can be applied to the DNTT core for the development of superior organic semiconductors.

Introduction

Organic field-effect transistors (OFETs) are expected to be an enabling technology for flexible and printed electronics.¹⁻³ For achieving high-performance OFETs, several requirements have been discussed, e.g., small contact resistance, low voltage operation, and so on, and among others, high mobility is the most important factor that largely affects the overall performances of the resulting electronic devices and thereby the utilization scope of OFETs.⁴ As high-mobility organic semiconductors for OFET applications, acenes, e.g., pentacene,⁵ and heteroacenes,⁶⁻⁸ e.g., dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophenes (DNTTs),⁹ have been employed, and these rectangular-shaped, linearly extended π-conjugated molecules are known to crystallize into a herringbone structure,¹⁰ which in general affords a two-dimensional (2D) and efficient orbital overlap that facilitates carrier transport in OFETs. In addition, acenes and heteroacenes can be chemically modified with various substituents to alter the molecular properties¹¹ and the packing structure in the solid state.¹² Among various packing structures so far reported, the brickwork structure (or the 2D π-stacking structure)¹³ and the pitched π-stacking structure¹⁴ have been

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known to be promising as active materials for high-performance OFETs.

For such structural modifications aiming at the packing structure control, it is crucial to rationally design molecules by combining the semiconducting cores and substituents. However, successful examples of such approaches have been limited, and thus it is important to widen the structural diversity of organic semiconductors modified with various substituents and thus to understand the relationship between the molecular structure and packing structure in the solid state. It is also crucial to find a new type of packing structure that can afford superior transport properties in addition to the three packing structures mentioned above. In this context, we have recently reported a versatile method for the synthesis of mono-functionalized DNTTs via the cross-coupling reactions of 2-bromodinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (Br-DNTT) and various organometallic reagents, and some of the resulting DNTT derivatives were evaluated by solution-processed OFETs. Using this method, (trialkylsilyl)ethynyl (TASE) derivatives of DNTT (1–3, Fig. 1) were also synthesized, since the TASE groups have been often employed to increase the solubility of largely π-extended organic semiconductor cores. However, the solubility of 1 with (trimethylsilyl)ethynyl (TMSE) groups was not that high, and only 3 with a (trisopropylsilyl)ethynyl (TIPSE) group could be evaluated by solution-processed OFETs. On the other hand, modification by TASE groups to the packing structures in mind, in this work we reevaluated 1–3 by fabricating/evaluating their OFETs via vapor deposition and by elucidating packing structures both in thin-film and single-crystal states.

Interestingly, 1 and 2 with a relatively small TASE group crystallized into the herringbone structure as in the case for many other DNTT derivatives, while 3 with a TIPSE group crystallized into a sandwich herringbone structure consisting of a face-to-face dimer of 3, being reminiscent of the packing structure of pyrene and its derivatives. Despite the marked difference in the packing structures, the OFET devices of 1–3 showed comparable field-effect mobilities of 0.19 to 0.87 cm² V⁻¹ s⁻¹, indicating that the sandwich herringbone structure is not necessarily detrimental for carrier transport in organic semiconductors.

**Experimental**

**Device fabrication and characterization**

TASE–DNTTs (1–3) were synthesized according to the reported procedure. For device fabrication, 1–3 were purified by train sublimation at 230–260 °C under vacuum (0.3 Pa). Bottom-gate-top-contact OFET devices were fabricated on a heavily doped n⁺Si(100) wafer with 200 nm-thick thermally grown SiO₂ (C₁ = 17.3 nF cm⁻²). The Si/SiO₂ substrates (10 × 7 mm) were ultrasonicated with water for 3 min thrice and with acetone and isopropanol for 10 min, respectively, were rinsed in boiling isopropanol for 10 min, and then were subjected to UV-ozone treatment for 30 min. The cleaned substrates were placed in a closed container in the presence of several drops of octyltri-methoxysilane (OTS) and kept in an oven at 80 °C overnight, and then the substrates were rinsed with boiling isopropanol. Thin films (thickness: 30 nm) of 1–3 as the active layers were vacuum-deposited on the Si/SiO₂ substrates maintained at rt at a rate of 0.2–0.3 Å s⁻¹ under a pressure of 2 × 10⁻³ Pa. On the top of the thin films, gold (thickness: 40 nm, Fig. S5, ESI†) or gold/MoO₃ (30 nm/5 nm, Fig. 2 and Fig S4, ESI†) as drain and source contact electrodes with a channel length and width of 100 and 1500 μm, respectively, were vacuum-deposited through shadow masks.

The current-voltage characteristics of the OFET devices were measured at rt under ambient conditions using a Keithley 4200-SCS semiconductor parameter analyzer. Field-effect hole mobilities were extracted from the square root of the drain current by using the following equation and averaging over the range of Vₕ from −30 to −60 V.

\[
\mu = \frac{2L}{WC_i} \left( \frac{dI}{dV_C} \right) \frac{1}{C_i} \left( \frac{dV_D}{dI} \right)^2
\]

where \( L \) and \( W \) are the channel length and width, respectively, and \( C_i \) is the capacitance of the gate insulator. The average hole mobility was obtained from more than eight devices.

**Single-crystal X-ray structural analysis and thin-film X-ray diffraction (XRD)**

Single crystals of 2 and 3 suitable for X-ray analysis were prepared by slow vapor-diffusion of methanol into the chloroform solutions of 2 and 3. Single-crystal X-ray analyses were carried out using a Rigaku Oxford Diffraction XtaLAB Synergy Custom DW system with a HyPix-6000HE detector (CuKα radiation, wavelength: 1.5418 Å, multilayer confocal optics). The structures were solved using the SHELXT program. Non-hydrogen atoms were refined anisotropically. All calculations were performed using the crystallographic software package Olex2 (ver. 1.3.0). Crystal data of 2: Ca₄H₃₂S₆Si (478.72), yellow plate, monoclinic, P2₁/c, \( a = 6.1861(6) \), \( b = 7.5626(12) \),

![Fig. 1](image-url)
\[ c = 51.696(11) \text{ Å}, \quad \beta = 89.772(14) \text{ Å}, \quad V = 2418.5(7) \text{ Å}^3, \quad Z = 4, \quad T = 100(2) \text{ K}, \quad R = 0.1422, \quad wR_2 = 0.4302, \quad \text{GOF} = 1.268. \]

Crystal data of 3: \[ \text{C}_{33}\text{H}_{32}\text{S}_{2}\text{Si} (520.79), \text{yellow plate, monoclinic, P2}_1/\text{c}, \quad a = 29.6315(6), \quad b = 11.8026(3), \quad c = 7.77030(12) \text{ Å}, \quad \beta = 95.9847(17)^\circ, \quad V = 2702.69(10) \text{ Å}^3, \quad Z = 4, \quad T = 100(2) \text{ K}, \quad R = 0.0537, \quad wR_2 = 0.1411, \quad \text{GOF} = 1.080. \]

The crystallographic data of 2 and 3 are deposited as CCDC 2108473 and 2108474, respectively.

X-ray diffraction patterns of the vapor-deposited thin-films of 1–3 on Si/SiO$_2$ substrates were recorded using a Rigaku Ultima IV diffractometer with CuK$_\alpha$ radiation (wavelength: 1.54184 Å).

**Theoretical calculations**

The geometries of isolated molecules in the neutral and cationic states were optimized using the B3LYP/6-31G(d) level with the Gaussian 16 program package.\textsuperscript{25} Intermolecular electronic coupling (transfer integral, \( t \)) in different molecular dimers extracted from the crystal structures of 2 and 3 was calculated using the Amsterdam Density Functional (ADF) program.\textsuperscript{26} Intermolecular interaction energies for dimers of 2 and 3 extracted from the crystal structures were obtained by symmetry-adapted perturbation theory (SAPT) calculations with the jun-cc-pvdz level using the PSI4 program package.\textsuperscript{27,28}

**Results and discussion**

**Fabrication of thin-film and field-effect transistors**

Thin-films of 1–3 were fabricated by vacuum deposition on an OTS-treated SiO$_2$/Si substrate, and OFETs with a bottom-gate-top-contact configuration were fabricated by defining the gold...
Crystallographic long-axes are almost along the crystallographic a-axis direction, and between the layers, the (triethylsilyl)ethynyl (TESE) groups reside so as to separate the DNTT molecules in the neighboring stacks are related by a 2-fold screw axis on the crystallographic b-axis, and thus the TESE groups alternately orient along the crystallographic b-axis direction. This packing motif can rationally minimize the steric bulk caused by the sterically demanding TESE groups (Fig. 4b, vide infra).

Single crystals of 3 suitable for X-ray analysis were also grown by slow vapor-diffusion of methanol into a chloroform solution of 3 as thin plate-like crystals. Similar to the packing structure of 2, 3 also forms a lamella structure along the molecular long-axis direction, which, in this case, corresponds to the crystallographic a-axis direction (Fig. 4c). Intriguingly, the packing motif in the lamella layer of 3 can be classified into a sandwich herringbone structure, in which pairs of molecules (i.e., dimers) of 3 with a face-to-face distance of 3.49 Å pack into a herringbone-like pattern (Fig. 4d). A simulated powder pattern from the crystal structure of 3 reproduces the four peaks assignable to 011, 021, 012, and 022 diffractions (Fig. S2, ESI†), which corresponds to the in-plane peaks observed in the thin film of 3 (Fig. 3b), indicating that the crystallites in vapor-deposited thin-films have basically the same packing structure as that in single crystals (vide supra).

**Differences in the crystal structures of 2 and 3**

It has been well known that similar sandwich herringbone structures to 3 are observed in the packing structures of small peri-condensed polyaromatic hydrocarbons (PAHs), such as pyrene\(^{20}\) and perylene,\(^{36}\) which is in stark contrast to the herringbone structures of linear cata-condensed PAHs, i.e., acenes such as anthracene,\(^{37}\) tetracene,\(^{38}\) and pentacene.\(^{39}\) The structural difference in the two systems was explained by the relative contribution of intermolecular C–C and C–H interactions and therefore by the number and position of carbon and hydrogen atoms in the molecule.\(^{10}\) This also means that the herringbone structure allows acenes to be packed densely while we could obtain a reasonable structure model of 2 with the P2\(_1\)/c space group. The unit cell of 2 contains two lamella layers consisting of the DNTT cores along the crystallographic c-axis direction, and between the layers, the (triethylsilyl)ethyl (TESE) groups reside so as to separate the DNTT layers, which is similar to the crystal structures of the alkylated BTBT and DNTT derivatives (Fig. 4a).\(^{36,35}\) As the molecular long-axes are almost along the crystallographic c-axis, the crystallographic ab-plane corresponds to the DNTT core array in the lamella layer. The packing structure in the DNTT core array is obviously classified into the herringbone structure as expected from in-plane XRD (Fig. 3b), and in fact, the simulated powder pattern from the single crystal structure can agree well with the three peaks, i.e., 110, 020, and 120 diffractions in the in-plane thin-film XRD pattern (see Fig. S2, ESI†).

In the herringbone structure, the molecules of 2 stack along the crystallographic a-axis direction, where all the molecules are related by the translation operation, which means that the TESE groups are in the same side of the molecular stacks along the crystallographic a-axis (Fig. 4b). On the other hand, the molecules in the neighboring stacks are related by a 2-fold screw axis on the crystallographic b-axis, and thus the TESE groups alternately orient along the crystallographic b-axis direction. This packing motif can rationally minimize the steric bulk caused by the sterically demanding TESE groups (Fig. 4b, vide infra).

**Single-crystal X-ray structural analyses of 2 and 3**

In order to gain further insights into the structural characteristics of 1–3 in the solid state, single-crystal X-ray structural analyses of 2 and 3 were carried out. Owing to the poor crystallinity, single crystals of 1 suitable for X-ray analysis were not obtained. Similarly, 2 also afforded very thin plate-like crystals, and thus the quality of the diffraction data was not high, yet we could obtain a reasonable structure model of 2 with the P2\(_1\)/c space group. The unit cell of 2 contains two lamella layers consisting of the DNTT cores along the crystallographic c-axis direction, and between the layers, the (triethylsilyl)ethyl (TESE) groups reside so as to separate the DNTT layers, which is similar to the crystal structures of the alkylated BTBT and DNTT derivatives (Fig. 4a).\(^{36,35}\) As the molecular long-axes are almost along the crystallographic c-axis, the crystallographic ab-plane corresponds to the DNTT core array in the lamella layer. The packing structure in the DNTT core array is obviously classified into the herringbone structure as expected from in-plane XRD (Fig. 3b), and in fact, the simulated powder pattern from the single crystal structure can agree well with the three peaks, i.e., 110, 020, and 120 diffractions in the in-plane thin-film XRD pattern (see Fig. S2, ESI†).

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and efficiently in the solid state. In this context, the herringbone structure should be favorable for 1–3 with the same acene-like DNTT-core. In addition, the number/position of the atoms in the DNTT core is the same for 1–3, and thus it is natural to consider that the present structural change should be related to the TASE substituents. We thus speculate that the TIPSE group in 3 is too large to be accommodated in the space created by the herringbone framework of the DNTT-core, whereas the TESE groups of 2 can reside in the DNTT herringbone framework.

Fig. 5 shows the packing structures of 2 and 3 projected along the molecular long-axis direction, similar to Fig. 4b and d, respectively, and here the molecules in the space-filling representation are colored by the symmetry operation. In the herringbone structure of 2, the TESE groups relatively loosely pack in the crystallographic ab-plane, where the molecules in white color direct the TESE groups in the front side, whereas the ones in green direct those in the back side (Fig. 5a). The TESE groups of the white molecules related by the translation operation are not densely packed in the crystallographic ab-plane, which can be visually understood by the fact that the molecules in green color can be seen in the c-axis projection through the TESE layer of the white molecules, indicating that the TESE layer does not fully cover the ab-plane. Further quantitative analysis of the effect of TESE groups in the crystal structure was carried out by functional-group SAPT (F-SAPT), through which the intermolecular interaction energy ($E_{int}$) can be calculated by considering the effective two-body partition of the various SAPT
terms to the localized chemical functional groups, the TESE group and the DNTT cores in the present case. As shown in Table 1, the $E_{\text{int}}$ between the TESE groups are generally negligible except for the pair of A–A100, that is, a pair of molecules in the crystallographic $c$-axis direction. The $E_{\text{int}}$ between the TESE–TESE groups in this pair is, as a whole, attractive; the dispersion term ($-4.04$ kcal mol$^{-1}$) mainly contributes to stabilization, whereas the exchange repulsion is also large (3.59 kcal mol$^{-1}$) that cancels out the stabilization effect by the dispersion term, resulting in a marginal effect of the $E_{\text{int}}$ between the TESE–TESE groups on the total $E_{\text{int}}$ compared to the large stabilization effects caused by the intermolecular interaction between the DNTT cores (Table 1, see also the ESIF). This means that the TESE–TESE contact is present in this pair, but the perturbation to the packing structure is rather limited, and as a result, the DNTT core mostly dictates the whole packing structure.

In contrast to the packing structure of 2, the effects of the TIPSE group on the packing structure of 3 are substantial (Fig. 5b). The molecules in white and pink, which are related by a glide plane, have the TIPSE groups in the front side that fully cover the $bc$-plane, indicating that the TIPSE groups closely pack to form a herringbone-like array in the $bc$-plane (Fig. 5b, left). The same is true for the back side of the packing structure, where the molecules in yellow and green direct the TIPSE groups in the front side (Fig. 5b right). Table 2 shows the partitioned $E_{\text{int}}$ to the TIPSE group and DNTT core by the F-SAPT method. The results of the F-SAPT calculations clearly indicate that the TIPSE–TIPSE interaction is present in the crystal structure of 3; for example, the $E_{\text{int}}$ of the molecular pairs of A–A001 and A–B show moderately large stabilization ($-4.15$ and $-3.78$ kcal mol$^{-1}$, respectively), where the TIPSE–TIPSE interactions largely contribute to the stabilization (Table 2). The F-SAPT calculations also tell us that the dispersion term is responsible for this stabilization, indicating that the bulky TIPSE groups can dictate the molecular arrangement in the crystal structure of 3. For this reason, the DNTT cores cannot keep their own herringbone packing, and instead, the DNTT cores are forced to form face-to-face dimers and edge-to-edge molecular contacts to adapt to the herringbone-like array of TIPSE groups. In fact, two herringbone-like arrays of TIPSE groups, where one consists of white/pink molecules and the other yellow/green molecules, are combined together as if the gears fold together.

**Relationship between the solid-state structure and transport properties**

The herringbone structure of 2 both in thin-film and single-crystal states can rationalize the comparable performances of 2-based OFETs with those of parent DNTT. The distribution of electronic couplings (transfer integrals, $t$s) in the packing structure of 2 calculated using the Amsterdam Density Functional (ADF) program$^{26}$ (Fig. 4b) is similar to that of the parent DNTT (Fig. S6, ESIF), indicating that the solid state of 2 has a 2D electronic structure and a relatively large $t$ of up to 91 meV. On the other hand, the asymmetric structure of 2 induces a less symmetrical distribution of $t$s in the transverse direction (crystallographic $b$-axis direction), which is in contrast to the symmetric distribution of $t$s observed in 2,9-didecy1- and 2,9-diphenyl-DNTTs showing much higher mobilities of $10^4$ and $5.6$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively, in their OFET devices. Although the exact packing structure of 1 is not elucidated, its thin-film XRD patterns (Fig. 3) rationality support that 1 also has mostly the same packing structure as that of 2. The slightly lower mobility of 1-based OFETs than those of 2 could be explained by the lower crystallinity of 1 than 2 in the thin film state, judging from the out-of-plane XRD patterns (Fig. 3a) and AFM images (Fig. S7, ESIF).

As clearly demonstrated by single crystal X-ray analysis, the electronic structure of 3 with a sandwich herringbone structure should be different from that of 2. Using the ADF program, a relatively large $t$ (61 meV) is calculated in the face-to-face dimer, whereas between the dimers $t$s are generally small ($5.5$ and $13$ meV), except the one with an edge-to-edge intermolecular interaction along the crystallographic c-axis (80 meV). This effective inter-dimer orbital overlap may facilitate the carrier transport in the bulk and could be a characteristic feature of 3. In the sandwich herringbone structure of a related molecule, dinaphtho[1,2-b:1′,2′-f]thieno[3,2-b]thiophene, a structural isomer of DNTT, the face-to-face dimer shows a very large $t$ (172 meV), whereas $t$s between the dimers are far smaller than that for the dimer (<10 meV), resulting in a low mobility of up to $2.6 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$, more than one order of magnitude lower than that of 3. To the best of our knowledge, the experimental mobility of 3-based OFETs (0.19 cm$^2$ V$^{-1}$ s$^{-1}$) is
among the highest reported for thin-film OFETs with a sandwich herringbone structure.44–47

Conclusion

In this work, a series of TASE-substituted DNTT derivatives 1–3 were evaluated by structural analysis both in thin-film and single-crystal states and then by OFETs with vapor-deposited thin-films. From the single-crystal X-ray analysis, the crystal structure of 2 with a TESE group was determined to be a herringbone structure. Similar to other DNTT derivatives with a herringbone structure, the electronic structure of 2 in the solid state is characterized as a 2D electronic structure with a large intermolecular electronic coupling of HOMOs. This corroborates the comparable high mobility of 2-based OFETs (0.89 cm² V⁻¹ s⁻¹) with those of other DNTT derivatives. In contrast, 3 with a TIPSE group was found to crystallize into a sandwich herringbone structure, where the face-to-face dimers of 3 are packed into a herringbone pattern, which is reminiscent of the packing structures of peri-condensed PAHs, such as pyrene and perylene. Although the crystal structure in the thin-film state of 3 may not be identical to that in single crystals, the out-of-plane and in-plane XRD patterns of the vapor deposited thin-film of 3 imply that the packing structure of 3 in the thin-film state is also a sandwich herringbone structure. The electronic structure of 3 in the solid state estimated from the crystal structure in the crystal state indicated that, together with the large intermolecular electronic coupling in the dimer, there exist relatively large inter-dimer electronic couplings, suggesting that the electronic structure of 3 in the solid state can be quasi 2D, which is consistent with the fact that the thin-film OFETs of 3 showed decent FET characteristics with a mobility of 0.19 cm² V⁻¹ s⁻¹. To the best of our knowledge, this mobility is the highest among thin-film OFETs with sandwich herringbone structures. With the present results on the decent performances of 3-based OFETs, we can say that the sandwich herringbone structure itself is not necessarily detrimental for carrier transport in organic semiconductors.

The structural change from the herringbone to sandwich herringbone structure in the present series was unexpected, but it can be rationally explained by the size of TASE groups, which plays a critical role in determining the packing structure of DNTT derivatives. TMSE and TESE allow the DNTT cores to crystallize into the herringbone pattern, whereas the sterically demanding TIPSE group did not allow the DNTT core to pack into the herringbone structure and does allow the crystal structure to pack into the sandwich herringbone structure. These results suggest that bulky substituents that can often enhance solubility could be introduced into the DNTT core without detrimental effects to the transport properties, even the herringbone structure could not be retained. In this relation, the introduction of two TASE groups at 2- and 9-positions could be an interesting approach, although such modifications with branched alkyl groups, e.g., 2-ethylhexyl, 3-ethylheptyl and 4-ethyl octyl groups, cannot retain the herringbone structure.12

Further molecular design and synthesis along this line is now underway in our group.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

26 ADF: powerful DFT code for modeling molecules; Scientific Computing and Modeling: Amsterdam; (http://www.scm.com/ADF/).