

Effects of Substituted Alkyl Chain Length on Molecular Packing and Properties in Solution-Processable Organic Semiconductors

We report the stabilization and modulation of layered-herringbone (LHB) packing, which is known to afford high-performance organic thin-film transistors, based on crystal structure analyses for alkyl-substituted benzothieno[3,2-*b*][1]benzothiophenes (BTBTs). Substitutions with relatively long alkyl chains effectively stabilize LHB packing due to interchain ordering, whereas substitutions with short alkyl chains impede the LHB packing. The solubilities, thermal characteristics, and charge transport properties of the alkylated BTBTs closely correlate with the variation of the molecular packings depending on the alkyl chain length. The origin of the alkyl chain length dependences was investigated by theoretical calculations of the intermolecular interactions within each packing structure.

Solution-processable organic semiconductors (OSC) are key materials for flexible and printed electronics technologies. Various OSCs have been developed so far for tuning crystal structure and material properties by introducing substituents into the p-conjugated skeletons. One of the essential requirements for solution-processable OSCs is the formation of *layered-herringbone* (LHB) packing, which is unique and known to be the most suitable for realizing uniform thin film fabrication and efficient two-dimensional carrier transport in organic thin-film transistors (OTFTs). However, a systematic understanding of the chemical substitution effects on molecular packing structures of OSCs has not yet been obtained.

In order to clarify the effects of alkyl chain substitution, which is the most fundamental chemical modification for improving the solubility and solution-processability of OSCs, here we report a systematic investigation

of the alkyl chain-length (n) dependences of molecular packing and material properties based on the structural characterizations for three series of symmetrically and asymmetrically alkyl-substituted benzothieno[3,2-*b*][1]benzothiophene (BTBT) derivatives [1]: asymmetric monoalkylated BTBT (*mono-C_n*-BTBT), symmetric dialkylated BTBT (*di-C_n*-BTBT), and asymmetric phenyl-alkylated BTBT (Ph-BTBT-C_{*n*}) (Fig. 1a).

Full structural analyses were successfully conducted for *mono-C_n*-BTBT ($n = 2, 3, 4,$ and 9), for *di-C_n*-BTBT ($n = 2, 3, 4,$ and 5), and for Ph-BTBT-C_{*n*} ($n = 3, 4, 5, 6, 8, 10$) [2-5]. Single crystals for the measurements were obtained via recrystallization from toluene or 1,2-dichlorobenzene at room temperature. Powder X-ray diffraction experiments were also conducted for all the *mono-C_n*-BTBTs with long alkyl chains ($n = 4-16$). The unit cell molecular packing structures for *mono-C_n*-BTBTs and unsubstituted BTBT ($n = 0$) are shown in Fig. 1b. We

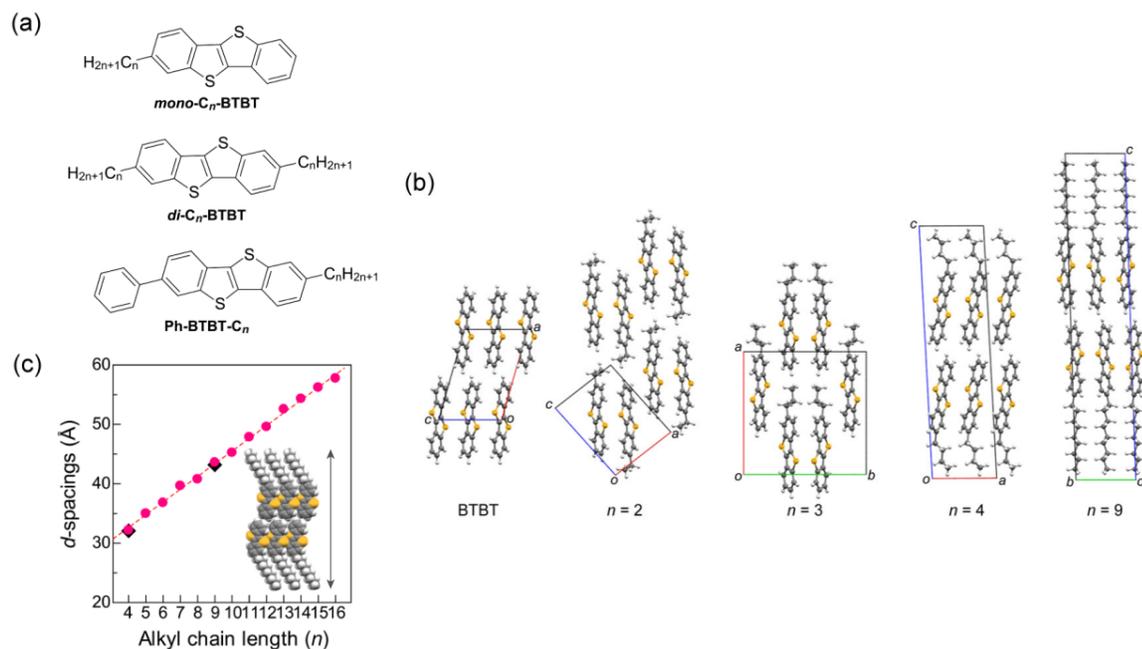


Figure 1: (a) Chemical structures of alkylated BTBTs, (b) Crystal packing structures of BTBT and *mono-C_n*-BTBTs, (c) Alkyl chain-length dependences of the d -spacing values calculated for the (001) reflections in the powder XRD patterns of *mono-C_n*-BTBT (red ●). The corresponding values derived from the unit cell parameters of single crystals are also plotted (black ◆).

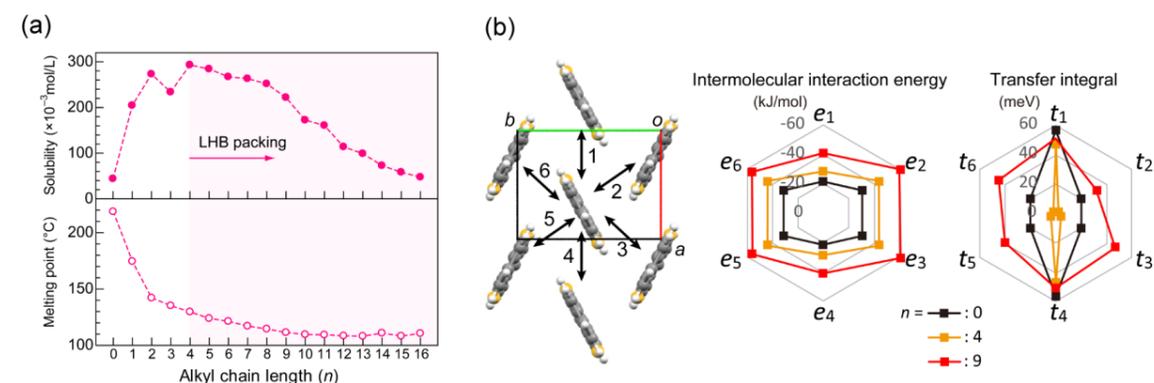


Figure 2: (a) Solvent solubilities at 25°C (left) and thermal characteristics (right) of *mono-C_n*-BTBTs and (b) Calculated intermolecular interaction energies and transfer integrals for LHB packing of BTBT, *mono-C₄*-BTBT, and *mono-C₉*-BTBT.

found that the compounds with $n = 4$ and 9 exhibited the LHB packing motif of the BTBT skeleton and isolated alkyl chain layers. The d -spacing values estimated from (001) reflections in the powder XRD patterns of *mono-C_n*-BTBTs systematically increase with increasing alkyl chain length and roughly correspond to the nominal length of two *mono-C_n*-BTBT molecules (Fig. 1c). These results clearly indicate that all the *mono-C_n*-BTBT compounds with long alkyl chains form isostructural LHB packing. On the other hand, the compounds with shorter alkyl chains do not form a layer-by-layer structure but adopt various molecular packing motifs depending on the different n . A similar trend was observed in the molecular packing motifs for the *di-C_n*-BTBT and Ph-BTBT-C_{*n*} compounds; LHB packings were observed for the compounds with $n \geq 6$ for dialkylated, and $n \geq 5$ for phenyl-alkylated BTBTs [2-4].

All three series of compounds show similar alkyl chain length dependence in solubility and thermal characteristics. Figure 2a shows the solubility and melting point of the *mono-C_n*-BTBT compounds plotted as a function of n . The rapid increase and decrease at relatively short alkyl chain length regions may correspond to the variation of molecular packing. The subsequent gradual decrease at longer n may be ascribed to the increased cohesive forces between the alkyl chains in the crystals. Melting points and phase transition temperatures, which relate to thermal durability of OTFTs, also exhibit similar alkyl chain length dependences. The results demonstrate that the structural features govern the solubilities and thermal characteristics of the three series of compounds, and this is associated with the cohesive forces between the alkyl chains, which increase with increasing n .

Intermolecular attractive forces within the LHB packing were evaluated by DFT calculations using single crystal structures (Fig. 2b). The attractive forces

between neighboring molecules are roughly isotropic within the herringbone-packed molecular layer, along the face-to-edge and π -stack directions. This should be the origin of the formation of highly two-dimensional molecular layers in the crystals. The intermolecular interactions between the alkyl chains within the layers increase with the increase of n , which help to increase the total cohesive energy and thus decrease solubility with n . In contrast, the calculated transfer integrals between HOMOs, which relate to the hole transport properties within the LHB, are highly anisotropic at shorter n , while they become larger and more isotropic at longer n . All the results clearly demonstrate how and why the alkyl chains play crucial roles in the formation of layer-by-layer and LHB packing motifs and determination of the material properties.

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BEAMLINES

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