

Side chain engineering on a small molecular semiconductor: Balance between solubility and performance by choosing proper positions for alkyl side chains



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ABSTRACT

Small molecular (SM) semiconductors with sufficient solubility and high performance are highly desired in solution-processed organic electronics. In order to address the poor solubility that a reported high performance molecular semiconductor (**BDT(ThBTTh)₂**) with a benzodithiophene (BDT) core and two thiophene-benzothiadiazole-thiophene arms (ThBTTh) suffers from, two additional hexyl side chains have been designed into its scaffold and different attaching fashions yield two new SM semiconductors, **SM1** and **SM2**. The integration positions in **SM1** are terminal thiophene units, while that of **SM2** are located on the inner thiophene units neighbor to the central BDT unit. With expectation, the so-prepared **SM1** and **SM2** possess much better solubility than **BDT(ThBTTh)₂**. However, the integration of additional alkyl side chains sacrifices its optoelectronic performance and the sacrifice extent is highly dependent on their attaching fashions. The molecule **SM2** having new additional side chains in two inner thiophene units displayed much better performance (hole mobility: $1.80 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, solar cell efficiency: $(2.57 \pm 0.17)\%$) than **SM1** that integrates them at the two terminal thiophene units (hole mobility: $2.18 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, solar cell efficiency: $(0.87 \pm 0.11)\%$). For understanding the origination of such performance differences, detail characterizations including differential scanning calorimetry, ultraviolet–visible absorption spectroscopy, cyclic voltammetry, density function theoretical calculation, X-ray diffraction and atomic force microscopy have been carried out. Finally, benefiting from their enhanced good solubility in non-chlorinated solvents, toluene has been proved capable as a green processing solvent for organic solar cell fabrication. The so-obtained **SM2** devices displayed an optimized efficiency of $(2.35 \pm 0.19)\%$.

1. Introduction

As compared with inorganic counterparts, organic optoelectronics including organic solar cells (OSCs) [1–5], organic field-effect transistors (OFETs) [6–8], and organic light-emitting diodes (OLEDs) [9–11], have advantages in terms of flexibility, light-weight, solution-processability, and adaptability for large area device fabrication technologies, owing to the use of organic semiconductors as key component in their active layers. While light weight and flexibility are inherent for organic

materials, solution processability requires the materials have sufficient solubilizing side chains in their chemical structures to provide a good solubility. However, since most solubilizing side chains, such as alkyl substituents, are generally inactive and have disfavoured effect on material optoelectronic functions, special attention must be paid on the balance between material solution processability and their optoelectronic performance.

There are several ways to improve the solubility of a present-known material: (1) increasing the size of solubilizing side chains [12–14], (2)

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using branched side chains in place of linear ones [15,16]; and (3) adding one (or more) solubilizing side chain(s) [17]. For achieving balance between solution processability and material performance, the size and branch of solubilizing side chains should be optimized in the former two approaches [13]. While in the latter one, the position(s) for placing more side chain(s) have to take into consideration additionally. In literature, there are well documented that side chain position has significant impact on optical, molecular packing structure, crystalline, and optoelectronic properties of final materials [17–20]. For example, Jassen et al. studied three diketopyrrolopyrrole-centred oligothiophene isomers with different terminal hexyl side chains and found that the position of these side chains have significant impact on their photovoltaic performance [17]. Li and coworkers found that the right position for soluble side chains is a key to achieve high mobility for either small molecular or conjugated polymer semiconductors [19,20].

Recently, we were endeavored to develop small molecular (SM) organic semiconductors for both OSC and OFET applications. Compared with conjugated polymers, small molecular compounds have merits of defined chemical structures that can avoid any reproducibility issues in synthesis and performance [21–23]. In a previous work, we reported a SM optoelectronic compound based on benzodithiophene (BDT) and benzothiadiazole (BT) namely **BDT(ThBTTh)₂** (Fig. 1) with an OFET hole mobility (μ_h) of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an OSC power conversion efficiency (PCE) of 4.53% [24]. Despite the acceptable optoelectronic performance, the solubility of this compound is very poor. It was found that even in its good solvent (chlorobenzene), the solubility is only 1.90 mg mL^{-1} at room temperature. Since such low solubility would limit its further study and real application, we were motivated to improve its solubility by structural modification. This time, we adopted the last aforementioned strategy, i.e. adding more soluble side chains. After consideration on **BDT(ThBTTh)₂** structure and synthesis convenience, two potential positions have been chosen for placing the newly added hexyl side chains, as shown in Fig. 1, producing two new compounds, namely **SM1** and **SM2**. In **SM1**, these two additional hexyl side chains are attached to 3,3'-position of terminal thiophene units. Whereas in **SM2**, they are placed on the thiophene units neighbor to center BDT moiety. Since middle alkyl substitution generally brings a much twisted conjugated backbone, **SM2** is assumed to have

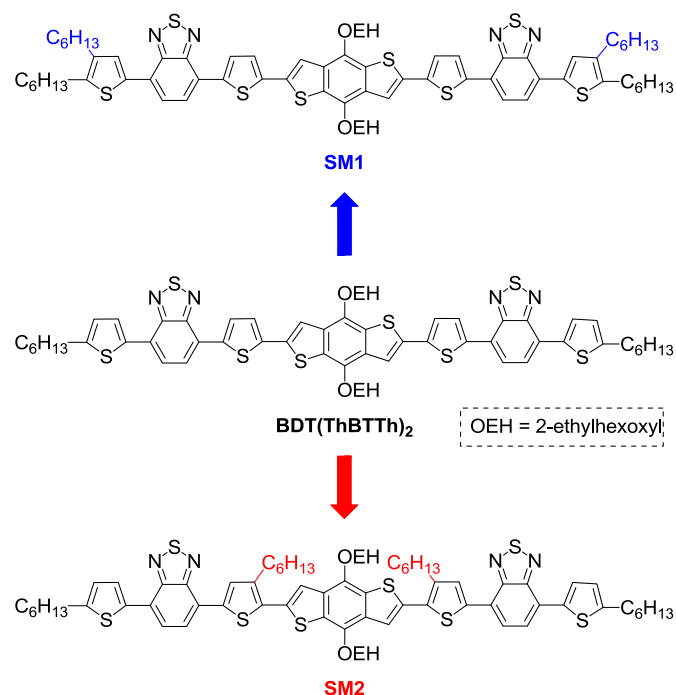


Fig. 1. Molecular Structure of the studied compounds.

optoelectronic properties inferior to **SM1**. However in reality, to our surprise, **SM2** displayed a μ_h of $1.80 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a PCE of $(2.57 \pm 0.17)\%$ for organic solar cells, much better than those for **SM1** ($\mu_h = 2.18 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, PCE = $(0.87 \pm 0.11)\%$). Studies found different side chain substitution fashions result in different molecular packing structures in film state, and thus accounting for such property discrepancy.

2. Results and discussion

The syntheses of compound **SM1** and **SM2** are outlined in Scheme 1. They were started from mono Stille-coupling of 4,7-dibromo-2,1,3-benzothiadiazole with the corresponding starting reagents, 4,5-dihexyl-2-tributylstannylthiophene and 5-hexyl-2-tributylstannylthiophene, producing intermediates **1** and **4**, respectively. After Suzuki coupling with thiopheneboronic acid or 4-hexylthiopheneboronic acid pinacol ester, these two intermediates were π -extended with one thienyl unit and converted into compound **2** and **5**, respectively. Then, compound **2** and **5** were brominated with *N*-bromosuccinimide (NBS) and further Stille coupling with 2,6-bis-trimethylstannylated benzodithiophene, affording the final products of **SM1** and **SM2**, respectively. To our delight, both **SM1** and **SM2** possess excellent solubility in common solvents at room temperature. The solubility in chlorobenzene (CB) was estimated to be 40.5 mg mL^{-1} for **SM1** and 32.6 mg mL^{-1} for **SM2**, which are much larger than that of **BDT(ThBTTh)₂** (1.90 mg mL^{-1}) and suggest them having a good solution-processability.

Thermogravimetric analysis (TGA) revealed a good thermal stability for both compounds with a 5%-weight-loss temperature (T_d) of 326°C for **SM1** and 338°C for **SM2** (Fig. 2a). Compared with that of **BDT(ThBTTh)₂** (335.2°C) [24], it is clear that the integration of two additional hexyl side chains irrespective of their functionalization positions does not influence material thermal stability. However, such functionalization was found to have significant impact on material phase transition behavior. As revealed by differential scanning calorimetry (DSC, Fig. 2b), **SM2** displayed a pair of melting and recrystallizing phase transitions during the second heating and cooling processes with a melting (T_m) and recrystallizing temperature (T_c) at 193 and 152°C , respectively. These phase transition temperatures are much lower than those of **BDT(ThBTTh)₂** (T_m : 202.5°C and T_c : 192.8°C) [24]. In the case of **SM1**, the melting temperature was found to further drop to 181°C , whereas its recrystallizing phase transition kept at 154°C . Moreover, the comparison on phase transition enthalpy found that these compounds obey the order of **BDT(ThBTTh)₂** > **SM2** > **SM1**. All these observations suggest that the integration of additional two alkyl chains into the molecule of **BDT(ThBTTh)₂** decreases intermolecular interactions and the reduce degree is closely associated with functionalization positions.

Fig. 3 displays UV-vis absorption spectra of **SM1** and **SM2** in solution and neat film state. Their data are summarized in Table 1. Similar to **BDT(ThBTTh)₂**, both **SM1** and **SM2** in solution showed a spectral feature with two absorption bands in the range of 350–800 nm. The band locating in longer wavelength region originates from intramolecular charge transfer (ICT) transition between electron-rich BDT/thiophene units and electron-deficient BT units, while that in shorter wavelength region is ascribed to local π - π^* transition of the conjugated backbone. Of interest, as referred to that of **BDT(ThBTTh)₂** (526 nm) [24], **SM1** ICT band (532 nm) was 6 nm red-shifted, whereas that of **SM2** (518 nm) was 8 nm blue-shifted. Considering alkyl functionalization generally causes bathochromic effect and terminal integration does not induce any additional steric hindrance among neighboring conjugated moieties of the conjugated backbone, the red shift observed in **SM1** ICT band is understandable. However, in contrast to conventionally observed red shift, alkyl functionalization on the inner thiophene units causes blue shift in **SM2** ICT band. This can be interpreted by the inner alkyl side chain integration brings considerable steric hindrance between thienyl and BDT units and forces them adopt a

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