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# 2-Thiopene[1]benzothieno[3,2-*b*]benzothiophene derivatives as solution-processable organic semiconductors for organic thin-film transistors

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ABSTRACT

Novel [1]benzothieno[3,2-*b*]benzo-thiophene (BTBT) derivatives were synthesized and characterized as solution-processable organic semiconductors for top-contact/bottom-gate organic filed-effect transistors (OFETs). Physicochemical properties of the new compounds were characterized by UV–vis absorption spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), cyclic voltammetry (CV), and density functional theory (DFT) calculation. The electrical properties of the corresponding compounds were investigated through the fabrication and characterization of field-effect transistors via solution-shearing. Both compounds were FET active and exhibited decent p-channel activity with carrier mobilities up to 0.10 $cm^2 V^{-1} s^{-1}$ and current on/off ratio > $10^8$. Film morphology and microstructure, as characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD) were correlated with the device performance.

## 1. Introduction

Semiconductor is an indispensable element for all electronic devices in modern society and is applied to a wide range of fields, such as memory devices, displays, solar cells, and sensors [1–8]. Recently, organic semiconductors with high carrier mobility have attracted attention due to their unique properties such as solution-processability, simple fabrication process, low cost, and applicability on flexible substrates [9–16]. Therefore, organic semiconductors have widely been pursued as active layers in many applications such as organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and organic light-emitting diodes (OLEDs) [17–19]. Of these, organic field-effect transistors have achieved great improvements in electrical performance since their first reports in the 1980s [20,21]. Among organic semiconducting materials, π-conjugated small molecules have received considerable attention in the emerging organic electronics field because they provide significant advantages due to their limited π-extended core that can be easily modified into a variety of functional groups to finely adjust their optoelectronic and physicochemical properties [22,23]. In addition, simple synthesis, synthetic reproducibility, easy purification, high purity levels, and high solubility are superior properties of organic small molecules to those of polymeric counterparts [24–27]. Among various chemical moieties for organic semiconductors, [1]benzothieno[3,2-b]benzo-thiophene (BTBT) is a promising core structure for high-performance OFETs [28–41]. The BTBT core contains four consecutive aromatic rings in fused-manner. Despite the highly extended π-electron system, highest-occupied molecular orbital (HOMO) of BTBT can be stabilized because sulfur atoms supply two π-electrons in five-membered aromatic ring system to complete the aromatic sextet. Such stabilization of low-lying HOMO level can qualitatively explain the stability of FET devices containing BTBT moiety under ambient conditions.

The application and synthesis of BTBT derivatives have attracted much research interest. Some recent studies on BTBT-based small molecules as semiconductor materials are summarized in Fig. 1 [31–41]. **Cn-BTBT** (**I**) and **BTBT-Cn** (**II**) are BTBTs with alkyl substituents. **Cn-BTBTs** with alkyl substituents on both sides of BTBT core have been reported to be highly soluble and films based on these compounds exhibited high hole mobilities [31–34]. Among them, Yuan et al. reported record-breaking high field-effect mobility up to 43 $cm^2 V^{-1} s^{-1}$ for 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C8-BTBT) [32]. **BTBT-Cns** with mono-substituted alkyl chains showed relatively low solubility [35] and showed mobility up to 17.2 $cm^2 V^{-1} s^{-1}$ via vacuum deposition method [36]. Although **Ph-BTBT** (**III**) exhibited relatively low hole mobility of 0.034 $cm^2 V^{-1} s^{-1}$ via vacuum process [37], **C12-Ph-BTBT** (**IV**) showed ordered liquid-crystalline phases with high hole mobility of 8.7 $cm^2 V^{-1} s^{-1}$ via vacuum process [38]. **Ph-BTBT-C10** (**V**) single crystal films were prepared by blade coating method and

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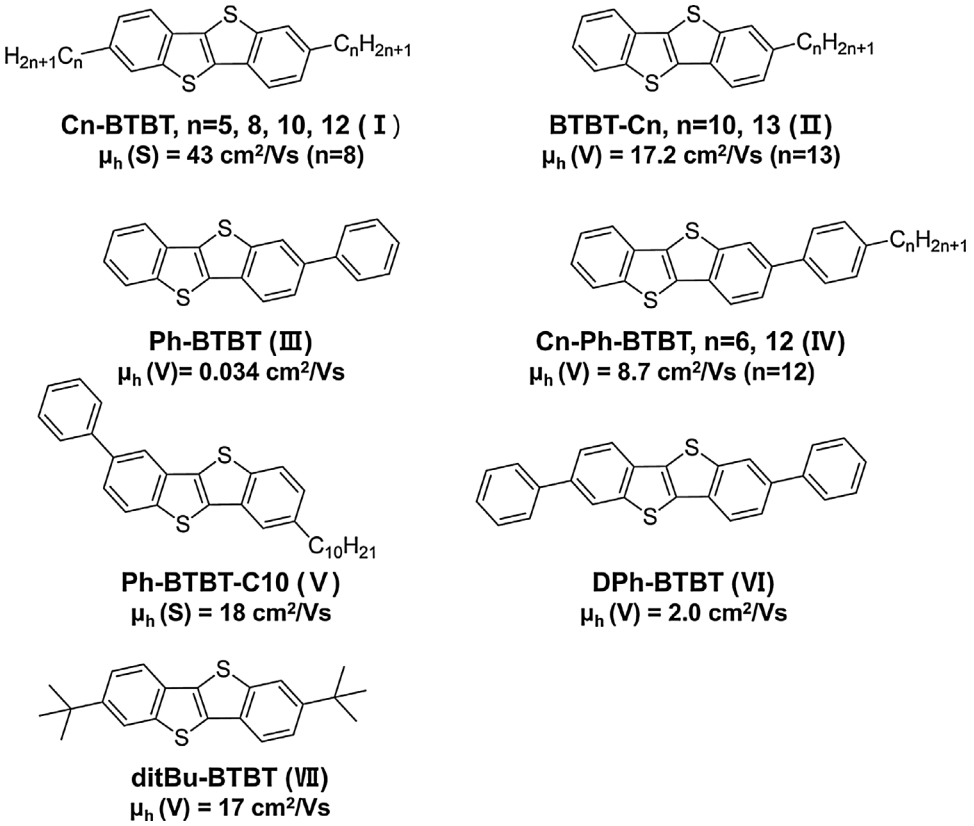


**Fig. 1.** Chemical structures and charge carrier mobilities of the reported BTBT-based small molecules. The symbols (S), (V) denote films formed by solution-process and vacuum-process, respectively.

showed mobility of 18 $cm^2 V^{-1} s^{-1}$ [39]. **DPh-BTBT** (**VI**) and **ditBu-BTBT** (**VII**) with phenyl and *tert*-butyl substitutions on both sides of BTBT core showed mobility of 2.0 and 17 $cm^2 V^{-1} s^{-1}$, respectively, using vacuum deposition methods [40,41]. As shown, BTBT-based small molecules showed high carrier mobilities, although they were mostly processed via vacuum deposition or were single crystals grown from solution, with a few exceptions [42]. Hence, it is desirable to explore novel BTBT-based semiconductors with high electrical performance via solution process.

To this end, we report the synthesis and characterization of BTBT-based small molecular semiconductors, 2-thiopene[1]benzothieno[3,2-*b*]benzothiophene (**3**) and 2-thiophene-7-octyl-[1]benzothieno[3,2-*b*][1]benzothiophene (**4**) (Fig. 2), as well as their implementation as active semiconducting channels in OFETs via solution process to further explore and elucidate architecture-device response relationships. New compounds were characterized by cyclic voltammetry (CV), UV–vis spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) to determine the electrochemical, optical, and thermal properties of the corresponding materials. Density functional theory (DFT) calculations were carried out to obtain HOMO/LUMO energy levels as well as molecular geometries of each compound. Our results revealed that new compounds were FET active and exhibited decent p-type activity with carrier mobilities up to 0.10 $cm^2 V^{-1} s^{-1}$ and current on/off ratio $> 10^8$. Film morphology and microstructure, as characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD) were correlated with the device performance.

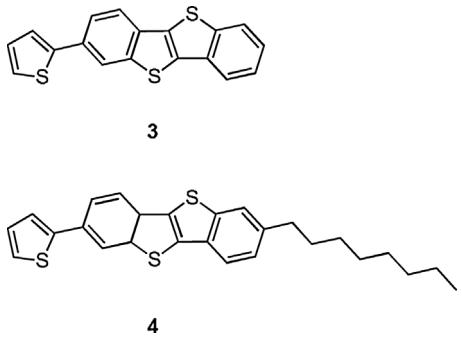


**Fig. 2.** Chemical structure of compounds **3** and **4**, developed in this study.

## 2. Experiment details

### 2.1. General methods

Air and/or moisture sensitive reactions were carried out under an argon atmosphere in oven-dried glassware and with anhydrous solvents. Unless otherwise noted, all compounds were purchased from commercial sources and used without further purification. 2-Iodo[1]benzothieno[3,2-*b*]benzothiophene (**1**) [43,44] and 2-bromo-7-octyl-[1]benzothieno[3,2-*b*][1]benzothiophene (**2**) were synthesized according to reference methods [45,46]. Solvents were freshly distilled or dried by passing through an alumina column. General analysis method of the synthesized compounds was already described in previous work [47].

### 2.2. Synthesis

#### 2.2.1. Synthesis of 2-iodo[1]benzothieno[3,2-b]benzothiophene (1)

Compound **1** was synthesized employing a published procedure [43,44]. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.23 (d, 1.1 Hz, 1H), 7.93–7.85 (m, 2H), 7.73–7.70 (dd, 1.5, 8.4 Hz, 1H), 7.61–7.59 (m, 1H), 746–7.39 (m, 2H).

#### 2.2.2. Synthesis of 2-bromo-7-octyl-[1]benzothieno[3,2-b][1]benzothiophene (2)

Compound **2** was synthesized employing a published procedure [45,46]. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.01 (d, 1.8 Hz, 1H), 7.75 (d, 8.0 Hz, 1H), 7.69–7.67 (m, 2H), 7.53–7.49 (dd, 1.4, 8.4 Hz, 1H), 7.27-