



Synthesis and characterization of novel push-pull oligomer based on naphthodithiophene-benzothiodiazole for OFETs application

Kai Zhang^{a,b,*}, Ji Zhang^c, Xiaoqin Zhang^a, Gui Yu^{c,*}, Man Shing Wong^{b,*}

^a College of Preclinical Medicine, Southwest Medical University, Luzhou, People's Republic of China

^b Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, People's Republic of China

^c Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, People's Republic of China

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ABSTRACT

A novel push-pull oligomeric semiconductor, **ENBT** based on naphthodithiophene-benzothiodiazole was successfully designed and synthesized. **ENBT** was fully characterized by ¹H NMR, MS, thermogravimetric analysis (TGA), UV–vis spectra, and cyclic voltammetry (CV). Furthermore, **ENBT**-based OFETs were fabricated by solution-processed dip-coating technique and its charge transporting property was investigated. The film of **ENBT** exhibited a hole mobility as high as $1.4 \times 10^{-2} \text{ cm}^2/(\text{Vs})$ with a current on/off ratio of 10^6 – 10^7 after annealed at 160 °C. In order to give an insight to the transporting property of **ENBT** films, thin film morphologies after annealing at different temperatures were also studied by atomic force microscopy (AFM).

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Introduction

Solution-processed organic semiconductors have attracted extensive investigations, due to their advantages of low-cost, large-area, and flexibility, which would enable a wide potential applications in the next-generation electronics such as polymer solar cells (PSCs),¹ organic light-emitting diodes (OLEDs)² and organic field-effect transistors (OFETs).³ In recent years, intensive efforts have been made to develop OFETs with high device performance, including both investigations of new organic materials and device fabrication techniques.^{4,5}

Although many novel organic semiconductors with high charges transport and good stability have been developed,⁶ novel semiconductors with even better performance are greatly desirable to realize the commercialization of OFETs. Push-pull structure motif has been demonstrated as an efficient strategy to develop novel high-performance semiconductors for OFETs, due to their unique features including planar structure and facile structure modification. It is well-known that the charge transfer would be favorable with good π -delocalization and strong intramolecular charge transfer between donor-acceptor (D-A) units.^{7,8} Many push-pull polymer semiconductors with impressive performance

have been developed for OFET applications.^{9,10} On the contrary, relatively few small molecules with push-pull structure have been explored even though small molecules exhibit many advantages over their polymer counterparts, including the ease of functionalization, purification and reproducibility.¹¹

Naphthodithiophene and benzothiodiazole have been widely employed in previous research work to construct push-pull semiconductors for the applications of polymeric OPV, OFETs, and photosensitizers for DSSCs.^{12,13} In this article, a novel naphthodithiophene-benzothiodiazole based push-pull oligomer, namely **ENBT**, was designed and synthesized in which 2-ethylhexoxy group was grafted onto naphthodithiophene to ensure the solubility in organic solvents and processibility. Its charge mobility performance has also been investigated in OFETs fabricated by dip-coating technique.

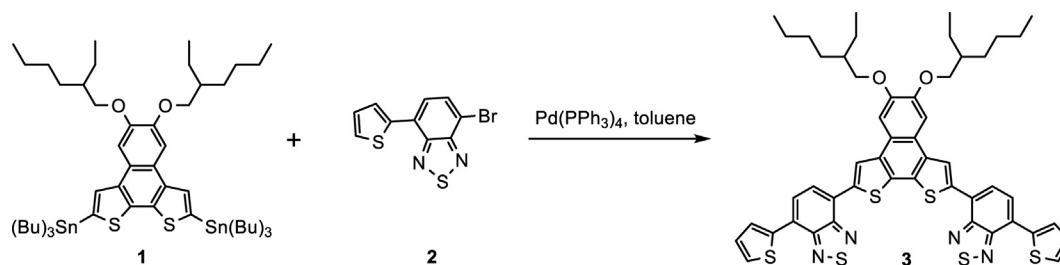
Experimental

Materials and synthesis

All reagents and starting materials were purchased from commercial sources. All the solvents were pretreated by standard methods wherever needed.¹⁴ **ENBT** was synthesized by palladium catalyzed Stille cross-coupling between **1** and **2** (Scheme 1). And the intermediates **1** and **2** were synthesized according to the literature procedures respectively.^{12,15}

* Corresponding authors at: College of Preclinical Medicine, Southwest Medical University, Luzhou, People's Republic of China (K. Zhang).

E-mail addresses: kzhang@swmu.edu.cn (K. Zhang), yugui@iccas.ac.cn (G. Yu), mshwong@hkbu.edu.hk (M.S. Wong).



Scheme 1. Synthetic route of ENBT.

Synthesis of 7,7'-(5,6-bis(2-ethylhexyl)oxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene-2,9-diylbis(4-(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole) (ENBT). To a solution of 4-bromo-7-(2-thiophenyl)-2,1,3-benzothiadiazole **2** (120 mg, 0.40 mmol) and 5,6-bis(2'-ethylhexyloxy)-2,5-bis(tri-*n*-butylstannyl)-naphtha-[2,1-*b*:3,4-*b'*]dithiophene **1** (215 mg, 0.20 mmol) in toluene (60 mL) was added Pd(PPh₃)₄ (20 mg). The resulting mixture was then stirred at 120 °C under N₂ for 40 h. After cooling to room temperature, the mixture was poured into methanol (100 mL) and filtered. The precipitated was washed by Soxhlet extraction with MeOH and hexane. The desired product was extracted with chloroform, recrystallized from methanol, collected and dried in vacuum for 12 h to afford the desired product as a black solid (135 mg, 72.6%). ¹H NMR (400 MHz, CDCl₃) δ: 8.89 (s, 2H), 8.14 (d, *J* = 3.17 Hz, 2H), 7.98 (d, *J* = 7.59 Hz, 2H), 7.88 (d, *J* = 8.09 Hz, 2H), 7.73 (s, 2H), 7.47 (d, *J* = 4.92 Hz, 2H), 7.23–7.21 (m, 2H), 4.18 (d, *J* = 5.25 Hz, 4H), 1.97–1.94 (m, 2H), 1.71–1.44 (m, 16H), 1.07 (t, *J* = 8.34 Hz, 6H), 0.97 (t, *J* = 6.89 Hz, 6H). ¹³C NMR measurement couldn't be performed due to low solubility. HRMS (MALDI-TOF) for C₅₀H₄₈N₄O₂S₆ (M)⁺ calcd 928.2096, found 928.2111. Anal. calc. for: C 64.62, H 5.21; found: C 63.88, H 5.21.

Device fabrication and characterization

The mobility performance of ENBT was measured by OFETs fabricated by dip-coating method. And the OFET devices were fabricated in a bottom-gate bottom-contact (BGBC) configuration (gold electrode on Si/SiO₂ substrates). Before the deposition of organic semiconductors, octadecyltrichlorosilane (OTS) treatment was performed on the gate dielectrics which were placed in a vacuum oven with OTS at a temperature of 120 °C for 3 h to form an OTS self-assembled monolayer. The semiconductor films were deposited onto the substrates by dip-coating solution in chlorobenzene (5 mg/mL, 2000–2500 rpm for 60 s). The semiconductor films were subsequently annealed at 80, 160 °C for 6 min in air, and measured after each annealing step at room temperature in air by using a Keithley 4200 Semiconductor Characterization System. As contrast, the characteristics of as-prepared

devices were also measured. The mobility of the devices was calculated in the saturation regime. The equation was listed as follows:

$$I_{DS} = (W/2L) C_i \mu (V_{GS} - V_{th})^2$$

where *W/L* was the channel width/length, *C_i* was the insulator capacitance per unit area, and *V_{GS}* and *V_{th}* were the gate voltage and threshold voltage, respectively.

The atomic force microscope (AFM) measurements were carried out using Veeco Nanoscope IV, tapping mode.

Results and discussion

Thermal, optical and electrochemical characterization

The thermal property of ENBT has been investigated by TGA measurement. As shown in Fig. 1a, ENBT exhibited good thermal stability with decomposition temperature (*T_d*) around 410 °C under a N₂ atmosphere at a heating rate of 10 °C/min, and such a *T_d* value is highly favorable for OFET device fabrication.

The optical characteristic of ENBT was investigated by UV–vis in both CH₂Cl₂ solution and solid film state. As shown in Fig. 1b, spectrum of ENBT exhibited two distinct absorption bands ranging from 300 to 650 nm in CH₂Cl₂ solution. The absorption band at high energy (308 nm) is attributed to the π–π* and the n–π* transitions of the extended conjugated oligomers. The intense and broad absorption band at 484 nm is due to the intramolecular charge transfer from donor to acceptor, corresponding to a bandgap of 2.23 eV. There is an obvious bathochromic-shift ranging from 300 to 750 nm found in the spectrum of solid film, which is attributed to the improved planarity of the π-conjugated backbone and π–π stacking in solid state.

Cyclic voltammetry (CV) was performed to estimate the electrochemical property of ENBT according to the reported method.¹⁶ The energy level of HOMO was evaluated from the onset of the oxidation wave, using ferrocene as an external standard. The LUMO energy level was then calculated from its HOMO level and bandgap. As shown in Fig. 1c, Table 1, the onset oxidation level of ENBT was estimated to be 0.70 eV, corresponding to a HOMO

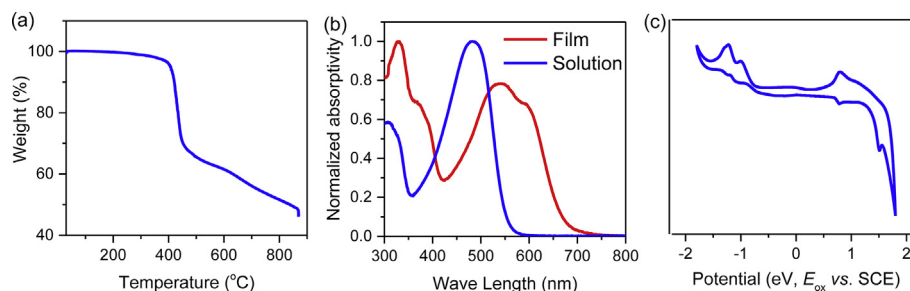


Fig. 1. TGA (a), UV-vis (b) and CV (c) curves of ENBT.

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