



Synthesis, characterization, and field-effect performance of the halogenated indolone derivatives



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ABSTRACT

In this paper we present the design and synthesis of three π -extended indolone derivatives, namely (3Z,3'Z)-3,3'-((5,5'-((E)-ethene-1,2-diyl)bis(thiophene-2,5-diyl))bis(methanylylidene))bis(1-octylindolin-2-one) (**3a**), (3Z,3'Z)-3,3'-((5,5'-((E)-ethene-1,2-diyl)bis(thiophene-2,5-diyl))bis(methanylylidene))bis(5-fluoro-1-octylindolin-2-one) (**3b**) and (3Z,3'Z)-3,3'-((5,5'-((E)-ethene-1,2-diyl)bis(thiophene-2,5-diyl))bis(methanylylidene))bis(5-chloro-1-octylindolin-2-one) (**3c**), with (E)-1,2-di(thiophen-2-yl)ethene as the donor and indolin-2-ones as the acceptors. All of the three acceptor-donor-acceptor type molecules have high conjugations and planar energy-minimized conformations, which are beneficial to forming ordered molecular packing and facilitating charge transport in thin films. Additionally, to study the effect of halogenation, fluorine and chlorine atoms were introduced in terms of microscale and mesoscale molecular engineering. **3b** and **3c** show obviously different features of crystalline tendencies and morphologies compared with those of **3a**. Organic field-effect transistors based on the three small molecules display typical p-channel charge transport characteristics under ambient conditions. Fluorinated **3b** affords the highest mobility of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ among the three analogues, demonstrating that fluorination is a useful strategy to optimize the solid-state arrangement and device performances.

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1. Introduction

Organic semiconductors have been drawing extensive attention as promising candidates for flexible opto-electronics in recent years [1–3]. Development of novel semiconducting materials enable a new generation of low-cost, large-area applications in numerous electronic devices such as radio frequency identification tags, smart cards, electronic papers, displays, and sensors [4–6]. During the last decades, there has been considerable progress in small-molecular and polymeric semiconductors. A variety of both classes of π -

conjugated materials have been synthesized and applied in organic field-effect transistors (OFETs) with charge carrier mobilities higher than that of amorphous silicon ($1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [7,8]. Meanwhile, structure-property relationships pertaining to organic semiconductors have been put forward and reviewed, for example, heteroatom effect [9,10], molecular symmetry [11], and alkyl side chains [12–14]. Moreover, some design strategies beyond molecular formula have also been concluded such as molecular size/weight [15] and impurities [16,17]. However, they are still not enough in digging the structure-property relationships with the aim of developing high-performance organic semiconductors for large-scale applications.

For small molecular semiconductors, acenes and heteroacenes, especially thienoacenes, have been intensively studied in recent years [18–20]. These small molecule materials tend to afford high carrier mobilities, which are ascribed to suitable HOMO energy levels, reorganization energies and orderly molecular packing in solid states [21]. However, these fused heteroacenes pose daunting

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synthetic challenges, and cannot readily incorporate as building blocks into π -conjugated backbones of polymeric semiconductors. Thus, developing new building blocks that are readily synthesized are meaningful for both small molecular and polymeric semiconductors. At present, the third generation polymers, donor–acceptor (D–A) copolymers, have been largely investigated in OFETs [22]. One of the important reasons is that the optoelectronic properties of the polymer could be fine-tuned by modifying the chemical structures of either electron-rich or electron-deficient units. Moreover, this class of polymers often own weakly polarized state along their polymer backbones, which will promote the charge injection at the electrode/semiconductor interface and facilitate the charge transport in the corresponding OFET devices [23]. D–A type small molecules have also been developed as the prototype semiconductor for further rational design [24]. Among these molecules, symmetric small molecules have greater potential because not only could they intrinsically behave as high-performance semiconductors themselves as a result of the highly ordered molecular packing in thin films, but could be used as building blocks as well through slight modification in chemical structures.

To design such small molecules, backbone planarity is typical concern due to the enhancement of π -orbital overlaps promoting close stacking and charge transporting. Some weak noncovalent interactions have been purposefully introduced to obtain planar structure. A variety of potential interactions, including S...O, S...F, and H-bonds, etc. are named as “conformational locks” [25]. Meanwhile, intermolecular interactions have also been enhanced between neighbouring molecules and even act as charge transport channels [26]. Thus, these interactions are essential in constructing high-performance semiconducting materials. Halogenation proved to be an efficient strategy to lower frontier molecular orbital energy levels and induce face-to-face π -stacking, providing a powerful tool for molecular engineering [27,28]. The large dipole of carbon–halogen bonds depletes the electron density of π -frameworks, subsequently affecting the stacking interactions. Herein, we have designed and synthesized a series of A–D–A type small molecules with or without halogens, (3Z,3'Z)-3,3'-((5,5'-((E)-ethene-1,2-diyl)bis(thiophene-2,5-diyl))bis(methanylylidene))bis(1-octylindolin-2-one) (**3a**), (3Z,3'Z)-3,3'-((5,5'-((E)-ethene-1,2-diyl)bis(thiophene-2,5-diyl))bis(methanylylidene))bis(5-fluoro-1-octylindolin-2-one) (**3b**) and (3Z,3'Z)-3,3'-((5,5'-((E)-ethene-1,2-diyl)bis(thiophene-2,5-diyl))bis(methanylylidene))bis(5-chloro-1-octylindolin-2-one) (**3c**), in which indolin-2-ones and (E)-1,2-di(thiophen-2-yl)ethene (TVT) serves as the acceptor and donor unit, respectively. Compared with previously reported analogues containing thieno[3,2-*b*]thiophene (TT) or 2,2'-bithiophene (BT), TVT has planar energy-minimized conformation and excellent rigidity, allowing for the enhanced planarity of the molecular skeleton. Additionally, the introduction of TVT unit is in favour of the aggregation because the bulky alkyl chains are separated farther due to the longer conjugation length. This class of π -conjugated backbone could be utilized to further synthesize semiconducting copolymers through minor modifications. The presence of S...O conformational locks is in favour of maintaining planar structures. Theoretical calculation results show that these molecules own highly delocalized frontier orbitals. With the introduction of halogen atoms at the 5-position of indolin-2-one unit, the two halogenated small molecule semiconductors show different charge transport characteristics. Especially, the fluorine substituted **3b**, exhibited enhanced field-effect properties with the highest hole mobility of 0.10 cm² V⁻¹ s⁻¹, which is much higher than those of **3a** and **3c**. The results highlight the promising potentials of fluorinated building blocks in constructing small molecular and polymeric semiconductors.

2. Experimental section

2.1. Materials and methods

The chemicals and catalysts were purchased from ACROS, Sigma-Aldrich, and Sinopharm Chemical Reagent CO., Ltd. The solvents were freshly distilled according to standard methods under nitrogen atmosphere. The reactions were performed in Schlenk flask under nitrogen atmosphere.

Nuclear magnetic resonance (NMR) spectra were obtained in deuterated chloroform (CDCl₃) with a Bruker AVANCE 300 spectrometer. EI-MS and high-resolution EI-MS were recorded on a Shimadzu QP 2010 gas chromatograph mass spectrometer. MALDI-TOF mass spectrometric measurements were performed on Bruker Autoflex III type MALDI-TOF. HR-MALDI-TOF were acquired on Bruker Solarix type Fourier transform ion cyclotron resonance mass spectrometer. UV–vis absorption spectra were measured on a Jasco V-570 type spectrophotometer. Cyclic voltammetry (CV) experiments were conducted on an electrochemistry workstation (CHI660C, Chenhua Shanghai) using a three-electrode cell. Thermogravimetric analysis (TGA) were carried out on DTG-60 instrument under nitrogen flow, heating from room temperature (RT) to 550 °C, with a heating rate of 10 °C/min. The XRD were tested on Polycrystalline diffractometer (PANalytical).

All theoretical calculations were carried out with the Gaussian 09 package. The geometry structure for **3a**, **3b** and **3c** were optimized by performing density functional theory (DFT) calculations at the B3LYP level with a 6-31 + G (d) basis set.

2.2. Device fabrication and characterization

Bottom gate/bottom contact devices using n⁺⁺-Si/SiO₂ substrates (300 nm) were fabricated to investigate the charge transport properties. The Au was used as the source-drain electrodes, and they were prepared by the photolithography technique. The next processes are as follows: the SiO₂ substrates were washed in acetone, deionized water, and ethanol. Then, the substrates were dried in atmosphere at 60 °C. Octadecyltrichlorosilane (OTS) self-assembled layer was formed by using OTS in vacuum at 120 °C. The treated substrates were rinsed with hexane, ethanol and chloroform. After that, a layer of **3a** (**3b** or **3c**) thin film was deposited on the OTS-modified SiO₂ substrates by spin-coating a solution of the corresponding compound in chloroform (10 mg/mL) with a speed of 1400 rpm for 60 s. To optimize the FET performance, the devices were annealed at different temperature. The devices were heated in air directly on a hotplate and the FET characteristics of the devices were tested directly in air with a Keithley 4200 SCS semiconductor parameter analyser. The mobility was calculated in the saturated regime using the following equation:

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

in which W/L is the ratio of the channel width/length, C_i is the insulator capacitance per unit area, V_{GS} and V_{TH} corresponds to the gate voltage and threshold voltage, respectively.

2.3. Synthetic procedures

2.3.1. (3Z,3'Z)-3,3'-((5,5'-((E)-ethene-1,2-diyl)bis(thiophene-2,5-diyl))bis(methanylylidene))bis(indolin-2-one) (**2a**)

To a suspension of (E)-5,5'-((ethene-1,2-diyl)dithiophene-2-carbaldehyde (0.30 g, 1.21 mmol) and 1,3-dihydro-2H-indol-2-one (**1a**, 0.32 g, 2.42 mmol) in methanol (30 mL) was added catalytic piperidine under argon. The reaction mixture was heated to reflux and stirred overnight. The mixture was allowed to cool to room

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