



A solution-processed and low threshold voltage p-type small molecule based on indolocarbazole- and benzothiophene-fused rings



Guiting Chen^{a,1}, Sheng Sun^{a,1}, Yong Yang^a, Linfeng Lan^{a,**}, Lei Ying^a, Wei Yang^a, Bin Zhang^{a,b,*}, Yong Cao^a

^a Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, China

^b College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou, 350002, China

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ABSTRACT

A novel planar heteroacene, 8,17-dihexadecyl-8,17-dihydrobenzo[4',5']thieno[2',3':5,6] indolo[3,2-b]benzo[4,5]thieno[2,3-h]carbazole (ICzDBT), was designed and synthesized. The thermal, optical, electrochemical and field-effect transistor properties were investigated systematically. The highest occupied molecular orbital energy levels (E_{HOMO}) measured by cyclic voltammetry and photoelectron yield spectra were -5.15 and -5.29 eV, respectively, which are close to the work function (WF) of Au (~ 5.2 eV). This suitable energy level alignment between the E_{HOMO} of ICzDBT and WF of Au is favorable for hole carrier injection from the Au electrode to the ICzDBT layer. The ICzDBT showed a hole mobility as high as $0.17 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a current on/off ratio of 1.2×10^6 , with a very low threshold voltage of -0.8 V. Moreover, the device displayed excellent stability with little roll-off of hole mobility in air. Hence, this kind of molecule is a promising candidate for p-type organic field-effect transistors (OFETs) with high mobility and air stability.

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1. Introduction

Organic semiconductors have attracted significant academic and industrial attention due to their potentially excellent applications in large-scale, flexible, portable and low-cost electronic devices, such as organic light-emitting diodes (OLEDs) [1,2], organic photovoltaics (OPVs) [3,4] and organic field-effect transistors (OFETs) [5–8]. In recent years, tremendous effort has been devoted to developing high-performance organic semiconducting materials, including small molecules and polymers. In particular, state-of-the-art achievements in OFETs have been obtained with very high mobility. For p-type OFETs, the hole mobility can exceed $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [9,10]. The n-type OFETs can achieve electron

mobilities over $8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [11]. These huge achievements make OFETs potentially applicable in real electronic devices.

In OFETs, solution-processed semiconducting small molecules and polymers have received particular interest. Among these materials, semiconducting polymers are widely studied as a result of their versatile merit: solution processing. Interestingly, remarkably high-efficacy polymer-based OFETs have been realized, including p- and n-type polymers. Although the use of conjugated polymers has resulted in many great achievements in OFETs, they also suffer from inevitable problems in materials purification and repeatable production [12,13]. Compared to polymers, solution-processable small molecules (SPSMs) have unique advantages, including high purity, massive and repeatable production, and feasible structure modification. Hence, they have played important roles in designing and developing high-performance OFETs [14–17].

Recently, many SPSMs have been developed for both p- and n-type OFETs, and they showed very impressive charge carrier mobilities [18,19]. Among them, a versatile strategy for acquiring high-performance SPSMs is synthesizing molecules with large planarity [20–22]. For instance, benzothiophene (BTh) [23,24] and dibenzothiophene (DBTh) [25,26] fused heterocyclic derivatives have

* Corresponding author. Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, China.

** Corresponding author.

E-mail addresses: lanlinfeng@scut.edu.cn (L. Lan), msbzhang@scut.edu.cn (B. Zhang).

¹ G. C. and S. S. contributed equally to this work.

been studied due to their high stability and hole mobility. Specifically, Lu et al. synthesized a series of ladder-type thienoacenes based on BTh, which showed versatile optical properties and p-type performance [27].

In parallel, indolocarbazole (ICz), a five ring-based aromatic compound, has been investigated in detail due to its large planarity, high hole mobility, high thermal and optical stability, and feasible structure modification. Due to these versatile merits, ICz-based small molecules and polymers are utilized widely in OLEDs, OPVs and OFETs [28,29]. Previously, we introduced the ICz unit into polymer main chains to synthesize narrow band-gap polymers for OPVs. These polymers showed high hole mobility and photovoltaic performance [30]. For OFETs, Leclerc et al. synthesized simple ICz-based derivatives by anchoring the phenyl as the end group, in which the best performance was acquired by vapor deposition of 3,9-diphenyl-5,11-dioctylindolo[3,2-*b*]carbazole [31] and 3,9-di(*p*-octylbenzene)-5,11-dihydroxyindolo[3,2-*b*]carbazole with a maximum hole mobility of $0.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [32]. Furthermore, they developed another series of ICz-based oligomers linked by phenyl or divinylbenzene groups, which displayed hole mobilities as high as $7.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [33]. Also, other versatile small molecules based on the ICz backbone have been investigated [34–36]. On the basis of these studies, ICz can be viewed as a potentially useful framework for designing and developing new p-type molecules and polymers.

However, the only solution-processed materials based on ICz are polymers. Therefore, the development of ICz-based SPSMs is becoming increasingly important for OFETs. Herein, we prepare a large planar heteroacene with nine rings, 8,17-dihexadecyl-8,17-dihydrobenzo[4',5']thieno[2',3':5,6]indolo[3,2-*b*]benzo[4,5]thieno[2,3-*h*]carbazole (ICzDBT), by combining the attractive merits of both BTh and ICz. Through an intramolecular cyclization, the ICzDBT displayed a large planarity. The introduction of two hexadecyl groups as side chains could increase the solubility of ICzDBT in common solvents to facilitate the solution processing. All the ICzDBT-based OFETs were fabricated from toluene solution in air. The ICzDBT showed a hole mobility of $0.17 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, with a very low threshold voltage (V_T) of -0.8 V and a high on/off ratio of 1.2×10^6 .

2. Experimental

2.1. Materials and characterization

All reagents were purchased from Sigma–Aldrich and Acros, and were used without further purification. All anhydrous organic solvents for the synthesis and device fabrication steps, including chloroform, toluene and *n*-butyl acetate, were purchased from Sigma–Aldrich. All reactions were performed with glassware that was oven-dried and then flamed under high vacuum and backfilled with nitrogen.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 600 spectrometer (operating at 600 MHz for ^1H NMR and 150 MHz for ^{13}C NMR) in deuterated *d*-chloroform solution with tetramethylsilane as a reference. Matrix-assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS) was measured on a Bruker autoflex III smartbeam. Cyclic voltammetry (CV) was carried out on a CHI600D electrochemical workstation with a standard three-electrode cell, with a Pt working electrode and a Pt wire counter electrode, against a saturated calomel electrode (SCE) as the reference electrode, at a scan rate of 50 mV s^{-1} in a nitrogen saturated anhydrous solution of 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile vs. ferrocene/ferrocenium (Fc/Fc^+) as the internal reference. Thermogravimetric analysis (TGA) was performed on a Netzsch TG

209 at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC) was carried out on a Netzsch DSC 204 under nitrogen flow at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. UV–vis absorption spectra were recorded with a SHIMADZU UV-2600 spectrophotometer. Photoluminescence (PL) spectra were recorded with a HORIBA Scientific Fluoromax-4 spectrofluorometer. Photoelectron yield spectroscopy (PYS) was measured at atmospheric ultraviolet photoelectron spectroscopy (Rikken Keiki AC-3).

2.2. Synthesis

2.2.1. 3,9-Dibromo-5,11-dihexadecylindolo[3,2-*b*]carbazole (2)

A freshly prepared 50% aq. KOH solution (1.4 mL) was added to a well-stirred mixture of 3,9-dibromoindolo[3,2-*b*]carbazole **1** (1.0 g, 2.4 mmol), tetrabutyl ammonium bromide (77 mg, 0.24 mmol), 1-bromohexadecane (2.2 g, 7.2 mmol), and DMSO (40 mL) in a 250-mL flask under an argon atmosphere. The mixture was stirred at room temperature for 1 h and then heated at $65 \text{ }^\circ\text{C}$ and maintained at this temperature for 4 h. Subsequently the reaction mixture was cooled down to room temperature and poured into 300 mL methanol with stirring. The precipitated yellow solid was filtered off and washed with water, and 3 times each with *N,N*-dimethylformamide, methanol, and acetone to afford Compound **2** as yellow powder (1.86 g, 90%). ^1H NMR (600 MHz, CDCl_3 , δ) 8.03 (d, 2H), 7.94 (s, 2H), 7.54 (s, 2H), 7.33 (d, 2H), 4.34 (t, 4H), 1.84 (m, 4H), 1.34 (m, 4H), 1.26 (m, 48H), 0.87 (t, 6H). ^{13}C NMR (150 MHz, CDCl_3 , δ): ^{13}C NMR experiment cannot be performed on this compound due to very low solubility in common deuterated solvent. Elemental analysis calcd (%) for $\text{C}_{50}\text{H}_{76}\text{N}_2$: C 85.11, H 10.78, N 3.97; found: C 85.13, H 11.22, N 3.97.

2.2.2. 3,9-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,11-dihexadecylindolo[3,2-*b*]carbazole (3)

Compound **2** (1.0 g, 1.1 mmol), potassium acetate (1.08 g, 11 mmol) and bis(pinacolato)diboron (0.9 g, 3.5 mmol) were dissolved in dioxane (50 mL) in a 100 mL flask under an argon atmosphere. The mixture was heated to $80 \text{ }^\circ\text{C}$ and then [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (40 mg, 0.055 mmol) was added quickly to the flask. The reaction was maintained at this temperature for 24 h. Subsequently the reaction mixture was cooled down to room temperature and filtered in vacuum. The residue was purified with column chromatography on silica gel with dichloromethane (DCM) as the eluent and the recrystallized to give Compound **3** as yellow needle crystals (0.8 g, 76%). ^1H NMR (600 MHz, CDCl_3 , δ) 8.22 (d, 2H), 8.03 (s, 2H), 7.88 (s, 2H), 7.69 (d, 2H), 4.44 (t, 4H), 1.96 (m, 4H), 1.41 (m, 4H), 1.26 (m, 48H), 0.87 (t, 6H). ^{13}C NMR (150 MHz, CDCl_3 , δ) 166.66, 140.50, 135.77, 131.70, 130.16, 128.09, 124.64, 123.62, 122.48, 118.74, 113.95, 98.31, 82.59, 42.35, 32.16, 31.23, 29.92, 29.00, 28.67, 28.20, 26.54, 25.20, 24.35, 21.98, 18.49, 13.46, 13.06. Elemental analysis calcd (%) for $\text{C}_{62}\text{H}_{98}\text{B}_2\text{N}_2\text{O}_4$: C 77.74, H 10.24, N 2.92; found: C 76.90, H 9.76, N 2.45.

2.2.3. 3,9-Bis(2-methylsulfinylphenyl)-5,11-dihexadecylindolo[3,2-*b*]carbazole (4)

K_2CO_3 solution (2 M, 10 mL) was added to a mixture of compound **3** (2.0 g, 2.1 mmol) and 2-bromo(methylsulfinyl)benzene (1.32 g, 6 mmol) in freshly distilled toluene (100 mL) under argon. $\text{Pd}(\text{PPh}_3)_4$ (100 mg) and tetrabutyl ammonium bromide (60 mg) was added in one portion to the reaction mixture, which was heated to reflux for 24 h. The mixture was cooled to room temperature and extracted with DCM. The organic layers were dried, evaporated in vacuum, and the residue was purified with column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) as the eluent to give **4** as yellow oil (1.25 g, 61%). ^1H NMR

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