**Organic Semiconductors** 

# Boosting the Charge Transport Property of Indeno[1,2-b]fluorene-6,12-dione though Incorporation of Sulfur- or Nitrogen-Linked Side Chains

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Alkyl chains are basic units in the design of organic semiconductors for purposes of enhancing solubility, tuning electronic energy levels, and tailoring molecular packing. This work demonstrates that the carrier mobilities of indeno[1,2-b]fluorene-6,12-dione (IFD)-based semiconductors can be dramatically enhanced by the incorporation of sulfur- or nitrogen-linked side chains. Three IFD derivatives possessing butyl, butylthio, and dibutylamino substituents are synthesized, and their organic field-effect transistors (OFET) are fabricated and characterized. The IFD possessing butyl substituents exhibits a very poor charge transport property with mobility lower than  $10^{-7}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. In contrast, the hole mobility is dramatically increased to 1.03 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> by replacing the butyl units with dibutylamino groups (DBA-IFD), while the butylthio-modified IFD (BT-IFD) derivative exhibits a high and balanced ambipolar charge transport property with the maximum hole and electron mobilities up to 0.71 and 0.65 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. Moreover, the complementary metal-oxide-semiconductor-like inverters incorporated with the ambipolar OFETs shows sharp inversions with a maximum gain value up to 173. This work reveals that modification of the aromatic core with heteroatom-linked side chains, such as alkylthio or dialkylamino, can be an efficient strategy for the design of high-performance organic semiconductors.

# 1. Introduction

Organic filed-effect transistors (OFETs)<sup>[1]</sup> are key elements to the organic electronic devices and have received significant attention in recent years due to potential applications in various electronic devices such as display and electronic skin,<sup>[2]</sup> by virtue

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of large area and low-cost fabrication, and good flexibility.<sup>[3]</sup> To design organic semiconductors for high-performance OFETs, fine adjustment to their band gaps and energy level positions are very important. A large number of aromatic frameworks with different band structures have been developed to meet different carrier injection requirements.<sup>[4]</sup> In many cases, the selected aromatic frameworks need to be modified by electron-donating or -withdrawing substitutions in order to fine tune their energy levels to achieve ideal properties. For examples, Bao and co-workers have reported that chlorination is an efficient method to obtain high-performance organic semiconductors.<sup>[5]</sup> Dou et al. have reported that fluorination can effectively decrease energy level of the lowest unoccupied molecular orbital (LUMO) level to achieve high electron mobility.<sup>[6]</sup> Besides, Bunz and co-workers,<sup>[7]</sup> Miao and coworkers,<sup>[8]</sup> and our group<sup>[9]</sup> have studied how to modulate the charge carrier mobilities of through fusing heteroatom, like

nitrogen and sulfur, into pentacene frameworks.

To achieve high-performance solution-processable organic semiconductors, various alkyl chains are widely utilized as side groups to the aromatic cores. Through varying the structures of alkyl chains (such as the length, shape, and branching structures), a variety of physical properties related directly to the device performance can be tailored, including solubility, molecular packing in solid, and thin-film morphology.<sup>[10]</sup> For instance, Pei and co-workers reported that the branching point of alkyl chain has a significant effect on the charge transport properties of isoindigo-based conjugated polymers.<sup>[10c]</sup> With variation of side-chain branching position, Zhang et al. further utilized the branched alkyl chains to boost the mobility of NDI-DTYM2-based semiconductors.<sup>[11]</sup> We have reported that the variation of alkyl side-chain length can tune the carrier polarity of dithiophene-4,9-dione-based ambipolar semiconductors.<sup>[12]</sup>

Although playing a crucial role in the rational design of highperformance organic semiconductors, alkyl chain is considered to be an inefficient substitution for energy level adjustment, due to its limited electron-donating ability. However, recent researches in organic solar cell materials have shed new light on the role of alkyl chain substitutions. Li and co-workers and

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Scheme 1. Chemical structures of the IFD derivatives.

Hou and co-workers have reported the use of alkylthio side chains to improve the power conversion efficiency of polymerbased photovoltaics.<sup>[13]</sup> In their works, the alkylthio side chains play two roles simultaneously, i.e., tailoring the thin-film morphology and modulating the frontier orbital energies. However, whether such strategy is applicable to design new semiconductors for OFETs is unknown. To address this issue, we have designed indeno[1,2-b]fluorene-6,12-dione (**IFD**)-based molecules modified by different side chains, and investigated the impact of different heteroatom linkage in the side chains on their OFET performance.

IFD is selected as the core mainly because of its simple structure and easy synthesis. Unmodified IFD is commercially available, making it an ideal candidate as starting materials for low-cost organic electronics. However, unmodified IFD and IFD modified by simple alkyl substituents show barely observable filed-effect phenomenon in OFETs, which may be attributed to their lowlying highest occupied molecular orbital (HOMO) energy levels and relatively large band gaps.<sup>[14]</sup> Yamashita and co-workers and Park et al. have designed fluorinated IFD derivatives to decrease the LUMO energy level and obtained appreciable electron mobility up to 0.17 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>[14b,15]</sup> The indeno[2,1-b]fluorene derivative, a regioisomer of the IFD, has also been found efficient in electron transport.<sup>[16]</sup> Besides, the IFD unit was utilized to construct donor-acceptor (D-A) type of small molecules and polymers, and achieved ambipolar charge transport with maximum hole and electron mobilities of 0.02 and 0.12 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively.<sup>[17]</sup>

To study the effects of heteroatom linkage, we have designed and synthesized three IFD molecules containing butyl, butylthio, and dibutylamino side chains (B-IFD, BT-IFT, and DBA-IFD) as shown in Scheme 1. The lengths of the carbon chains are kept identical in order to unveil the effects of the heteroatom linkages. Thin-film transistors of the three molecules were fabricated and their electron and hole transport properties were carefully compared. We found that the butylthio and dibutylamino side chains can significantly change the energy levels and molecular packing, resulting in seven orders of enhancements to the hole and electron mobilities. The butylthio-modified IFD molecule exhibited high and balanced

ambipolar carrier transport properties, which have been successfully used in the fabrication of high-performance complementary metal–oxide–semiconductor (CMOS)-like inverters.

# 2. Result and Discussion

## 2.1. Design and Synthesis

The structures of the three IFD derivatives are shown in Scheme 1. B-IFD contains two butyl chains on the 2- and 8-positions of IFD framework and was designed as a reference. BT-IFD and DBA-IFD possess butylthio and dibutylamino units, respectively, at the 2- and 8-positions of the IFD framework. The synthetic route of the three IFD derivatives is depicted in Scheme 2, and the detailed synthetic procedures are described in Scheme S1 of the Supporting Information. Briefly, compound 1 was treated with n-BuLi and trimethylborate to give the intermediate boronic acid, which was used for the coupling reaction with compound 2 to produce compound 3. Compound 3 was subsequently hydrolyzed to the corresponding dicarboxylic acid, and then the dicarboxylic acid was reacted in polyphosphoric acid to obtain the desired IFD derivative. These newly synthesized IFD molecules were carefully characterized by NMR (<sup>1</sup>H, <sup>13</sup>C, and distortionless enhancement by polarization transfer (DEPT); Figures S1-S6, Supporting Information), mass spectra, and melting point measurement, as shown in the Supporting Information.

## 2.2. Optical and Electrochemical Properties

The UV–vis absorption spectra of the three **IFD** derivatives were measured in both solutions and thin films (**Figure 1a**,b). In solution, **B-IFD** shows a strong peak at 294 nm and a broad absorption band at 511 nm. In comparison, the unmodified **IFD** and **IFD** derivative with dodecyl chains substituted on the central phenyl ring were reported to show a broad absorption band at about 484 nm.<sup>[17a,18]</sup> However, the broad absorption band was not observed for the diffuoro-, dichloro-, or



Scheme 2. Synthetic route of the IFD derivatives.





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Figure 1. The optical and electrochemical characteristics of the IFD derivatives. a) Solution absorption spectra, b) film absorption spectra, c) cyclic voltammograms (CVs), and d) the calculated molecular orbitals and the diagram of energy levels for the IFD derivatives.

dibromo-substituted IFD derivatives.<sup>[14b,17a]</sup> For BT-IFD and DBA-IFD, the broad absorption bands are redshifted to 554 and 721 nm, respectively, along with increased absorption strength, especially for DBA-IFD. The UV-vis spectra indicate that sulfur and nitrogen linkages can significantly lower the band gap of the IFD framework. In thin film, all the three compounds show enhanced absorption strength in the visible region, indicating strong intermolecular  $\pi$ - $\pi$  interaction in the thin films. The electrochemical properties of the three compounds were investigated by cyclic voltammetry (Figure 1c), which enables a rough estimation of the energy levels of the HOMO and the LUMO. The molecular orbitals for the three IFD derivatives were calculated by the density functional theory (DFT) using Gaussian 09 package with basis set of B3LYP 6-311G++(2d,2p) (Figure 1d). Table 1 shows that the theoretical energy levels are in good agreement with that obtained from the experiment. B-IFD shows a LUMO energy of -3.6 eV and a HOMO energy of -6.0 eV. When the butyl chains are replaced by the butylthio groups, the LUMO energy of **BT-IFD** is lowered to -3.7 eV and the HOMO energy is raised to 5.6 eV. The effect of the sulfur linkage can be understood as that the sulfur group is a weak

electron-donating unit. Meanwhile, the sulfur atom has some  $\pi$ -acceptor capability due to the formation of  $p_{\pi}(C)$ – $d_{\pi}(S)$  orbital overlap.<sup>[19]</sup> Therefore, the sulfur linkage lowers the LUMO and raises the HOMO energy levels of **BT-IFD**. For **DBA-IFD**, the introduction of dibutylamino groups results in a rise of the HOMO energies to –5.0 eV, along with a small rise of the LUMO energy to about –3.4 eV (Table 1). The dramatic rise to the HOMO level can be attributed to the strong electron-donating effect of the nitrogen atoms.

Neutral bond orbital (NBO) analysis is a useful tool to analyze the formation of molecular orbitals from bond orbitals. As shown above, the sulfur and nitrogen linkages can dramatically change the molecular orbitals of the **IFD** derivatives. To gain further insights into effects of sulfur and nitrogen linkages on the frontier molecular orbitals' (FMOs) energy levels, the NBOs and their contributions to FMOs were analyzed by the DFT using Gaussian 09 package, as shown in Figure S7 and Tables S1–S2 in the Supporting Information. Tables S1 and S2 (Supporting Information) break down the FMOs of the three **IFD** derivatives into contributions of bonding (BD)-type, antibonding (BD\*)-type, and nonbonding (LP)-type NBOs,

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Compound	Abs. <sub>Sol.</sub> <sup>a)</sup>	Abs. <sub>Film</sub> b)	HOMO <sub>Cal./CV</sub> <sup>c)</sup>	LUMO <sub>Cal./CV</sub> <sup>c)</sup>	Eg Cal./CV/Abs. <sup>d)</sup>	
B-IFD	294 337 511	271 341 517	-6.0/-6.0	-3.4/-3.5	2.6/2.5/2.2	
BT-IFD	313 349 554	298 364 568	-5.7/-5.6	-3.5/-3.7	2.2/2.1/1.9	
DBA-IFD	326 394 721	564 714 776	-4.8/-5.0	-2.9/-3.4	1.9/1.6/1.4	

Table 1. Optical, electrochemical, and theoretical properties of the IFD derivatives.

<sup>a)</sup>Solution absorption measured in chloroform with concentration of  $1 \times 10^{-5}$  m; <sup>b)</sup>Film absorption measured with the sample prepared by using the physical vapordeposited method; <sup>c)</sup>The HOMO and LUMO energy levels were calculated by the density functional theory (DFT) using Gaussian 09 package with basis set of B3LYP 6-311G++(2d,2p), while that of the experimental values were determined by CV measured in 1 × 10<sup>-3</sup> M chloroform solution. Potential values are reported in voltage versus saturated calomel electrode (SCE) using the  $Fc^+/Fc$  couple as an internal standard. HOMO and LUMO energy levels were approximated using SCE = -4.68 eV versus vacuum<sup>[27]</sup> and the half-wave potential ( $E_{1/2}$ ) values, where  $E_{HOMO} = -4.68 - E_{1/2}^{oxidation}$  and  $E_{LUMO} = -4.68 - E_{1/2}^{reduction}$ , <sup>d)</sup>Band gap for calculation or CV was calculated with  $E_{\sigma}$  = HOMO – LUMO, while the absorption band gap was estimated with  $E_{\sigma} = 1240/\lambda_{onset}$ .

showing how contributions of each type are generally found mixed into FMOs, whether occupied or virtual. The NBO analysis reveals that the HOMO of **B-IFD** mainly comes from the CC  $\pi$ -bonds, while the LUMO is composed primarily of the carbonyl (CO) groups (38.6%) and the centered benzene ring (20.45%). For BT-IFD, the presence of the sulfur atoms changed the contributions of NBOs to HOMO. As shown in Table S1 (Supporting Information), the LP (2) S21 and LP (2) S22 of BT-IFD contribute about 35% of HOMO, which occur at much higher energy than the CC  $\pi$ -bonds and therefore elevate the HOMO energy level. Meanwhile, the linkage of sulfur atoms changes a little on the distributions of LUMO, but lowers the energy levels of the CO  $\pi^*$ -orbitals with main contributions, as well as the other NBOs with substantial contributions (Table S2, Supporting Information). For the DBA-IFD molecule, the LPs of the nitrogen atom compose about 21% of the HOMO orbital and obviously raise the energy levels of the CC  $\pi$ -bonds (Table S1, Supporting Information). Consequently, the effect of the nitrogen linkage in DBA-IFD on the promotion of HOMO energy level is stronger than that of the sulfur atom in BT-IFD. However, the linkage of nitrogen atoms raises the energy levels of the NBOs that have substantial contributions to LUMO of DBA-IFD, which explains the higher LUMO energy level of DBA-IFD than that of B-IFD and BT-IFD.

The energy levels of organic semiconductors play a key role in the charge carrier injection at the electrode/organic semiconductor interface and greatly influence device performance.<sup>[9c,20]</sup> To the three IFD derivatives, their relative hole and electron injection barriers can be estimated from Figure 1d. It is known that the work function of clean gold electrode is -5.1 eV. However, most literatures reported that the work functions of gold electrode in OFET devices were found in the range of -4.3 to -4.7 eV, due to either contamination or interface dipole.<sup>[21]</sup> Therefore, it is expected that either hole and electron injection to B-IFD would be difficult due to large injection barriers (around 1.2 eV), which explains the poor charge transport properties of most IFD analogs in literature reports.<sup>[14]</sup> As for BT-IFD, the energy barriers for either hole or electron injection are estimated to be around 1 eV, which is likely to show ambipolar charge transport according to our previous research. Furthermore, it can be seen that the HOMO of DBA-IFD matches well with the gold work function, implying small hole injection barrier.

## 2.3. Single Crystal and Thin-Film Structure Analyses

Single crystals of the three IFD derivatives were obtained in solutions, and their crystal structures were determined by singlecrystal X-ray analysis, which are shown in Figure 2. It is found that the different side chains induce significantly different molecular packing in the crystals. B-IFD formed needle-like crystal, which exhibits one dimensional (1D) column stacking with a  $\pi$ - $\pi$ distance of 3.447 Å between the IFD planes (Figure 2a). When the butylthio substituents are used as side chains, the crystal structure of BT-IFD is changed to two dimensional (2D) brickwall stacking with a shortest  $\pi$ - $\pi$  distance of 3.217 Å between the IFD planes (Figure 2b). In the crystal of DBA-IFD, the molecules adopt 2D crossed stacking with a  $\pi$ - $\pi$  distance of 3.387 Å between the IFD planes (Figure 2c). As discussed above, the sulfur and nitrogen linkages in the BT-IFD and DBA-IFD molecules exhibit electron-donating effect, hence increase the local polarity. Therefore, the BT-IFD and DBA-IFD molecules prefer 2D molecular packing motif, which can be stabilized by the dipolar interaction between the adjacent molecules.<sup>[22]</sup>

The 2D grazing-incidence X-ray diffraction (2D-GIXD) analysis was utilized to investigate the crystallinity and packing motif of the physical vapor-deposited (PVD) thin film.<sup>[23]</sup> Polycrystalline films were fabricated in vacuum tube furnace at 5  $\times$  10<sup>-4</sup> Pa with an evaporate temperature below 230 °C. Thermal gravimetric analysis confirmed that the IFD derivatives are stable at this temperature (Figure S8, Supporting Information). Figure 2d-f shows the 2D-GIXD patterns of the thin films; the corresponding out-of-plane ( $q_z$ -axis) and in-plane ( $q_{xy}$ -axis) line-cut profiles are shown in Figures S9–S11 in the Supporting Information. The 2D-GIXD patterns of the three IFD derivatives exhibit clear Bragg reflection points along the  $q_{z}$ - and  $q_{xy}$ -directions, revealing the good crystallinity of the thin films (Figure 2d-f). Generally, the reflections of (00l) and  $\{h,k\}$  planes are contained along the  $q_z$  and  $q_{xy}$ -axes, respectively. Therefore, the *d*-spacing can be calculated from the reflection of (001) plane, while the unit cell parameters can be determined by the  $\{h,k\}$  plane reflections.<sup>[23b]</sup> B-IFD clearly shows two Bragg reflections along the  $q_z$ -direction at 4.411 and 13.208 nm<sup>-1</sup> (Figure 2d; Figure S9, Supporting Information), corresponding to the reflections of the (001) and (003) planes. The *d*-spacing was calculated from the reflection of (001) plane to give the value of 14.24 Å. Along the  $q_{xy}$ -direction, four columns of reflections at 8.13, 13.26, 14.01, and 16.29  $\text{nm}^{-1}$  were

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Figure 2. The single-crystal structures for a) B-IFD, b) DBA-IFD, and c) BT-IFD molecules; and 2D-GIXD patterns of vacuum deposited d) B-IFD, e) BT-IFD, and f) DBA-IFD films.

observed, which were identified as  $\{0,1\}$ ,  $\{1,0\}$ ,  $\{1,1\}$ , and  $\{0,2\}$ planes, respectively. Then from the reflections along the  $q_{xy}$ direction, the crystal parameters of the B-IFD thin film were deduced to give a unit cell with a = 4.85 Å, b = 7.91 Å, and  $\gamma = 102.22^{\circ}$ . **BT-IFD** has only (001) reflection along the  $q_z$  direction with a value of 3.13  $\text{nm}^{-1}$ , giving the *d*-spacing of 20.06 (Figure 2e; Figure S10, Supporting Information). Along the  $q_{xy}$ -direction, the reflections of {0,1}, {1,0}, and {1,1} planes were observed at 11.10, 12.06, and 18.52 nm<sup>-1</sup>, from which the crystal parameters were calculated with a = 5.23 Å, b = 5.60 Å, and  $\gamma = 94.64^{\circ}$ . As for **DBA-IFD**, the *d*-spacing was calculated from the (001) reflection with a value of 17.13 Å (Figure 2f; Figure S11, Supporting Information). Along the  $q_{xy}$ -direction, the reflections of {1,0}, {1,1}, {0,2}, {2,0}, and {2,1} planes were found at 7.28, 9.52, 12.28, 14.56, and 15.79 nm<sup>-1</sup>. Therefore, the crystal parameters were determined with the values of a = 8.63Å, b = 10.23 Å, and  $\gamma = 90.04^{\circ}$ . The calculated crystal parameters of the films for the three **IFD** derivatives are summarized in **Table 2**, which reveals that the molecular packing motif of the three **IFD** derivatives in the thin film is same as that in their single crystal structures.

Whether charge transport occurs through a band-like or hopping mechanism, the transfer integral (*t*) plays a vital role in determining the carrier mobility.<sup>[24]</sup> As shown in Table 2, **B-IFD** shows a large transfer integral of -76.7 meV along the  $\pi$ - $\pi$  interaction direction, and therefore the poor performance is mainly attributed to large injection barrier. For **BT-IFD**, the 2D brick-wall structure allows the strong 2D electron coupling for both hole and electron transport. The transfer integrals for hole transport are -48.4 and -21 meV, while that of electron transport are 52.8 and 34.4 meV. The similar injection barrier and transfer integrals for both hole and electron transport indicate that the **BT-IFD** material may exhibit balanced ambipolar performance, according to our previous investigations.<sup>[9]</sup>

Compound	Crystallographic packing data				Transfer integral				
		A [Å]	B [Å]	d-spacing [Å]	γ[°]		tl [meV]	t2[meV]	t3[meV]
B-IFD	Crystal	4.84	7.90	14.26	102.28	Hole	-76.7	0.1	0.3
	Thin film	4.85	7.91	14.24	102.22	Electron	-23.1	-2.3	-8.3
BT-IFD	Crystal	5.23	5.59	20.08	94.79	Hole	-48.7	-21.0	-1.3
	Thin film	5.23	5.60	20.06	94.64	Electron	52.8	34.3	21.2
DBA-IFD	Crystal	8.60	10.26	17.11	90	Hole	-4.4	-4.3	0.1
	Thin film	8.63	10.23	17.13	90.04	Electron	-48.9	-48.7	11.7

Table 2. Crystallographic packing and transfer integral data for the IFD derivatives.

**DBA-IFD** exhibits that 2D crossed stacking with the transfer integrals for hole transport along the  $t_1$  and  $t_2$  directions is about -4.4 and -4.3 meV, respectively (Table 2). According to Bao and co-workers, the essentially equivalent transfer integral in two directions of a 2D electron coupling structure may facilitate charge transport.<sup>[25]</sup> The HOMO energy level of **DBA-IFD** exhibited similar transfer integral along the  $t_1$  and  $t_2$  directions, suggesting good hole transport property.

## 2.4. Film Morphology Analysis

The film morphology is one of the important factors that

determine charge transport property of thin-film OFETs. The morphology of the films was optimized by altering substrate temperature, and then was investigated by atomic force microscopy (AFM) technology. Figure 3 shows the AFM images of the polycrystalline films for the three molecules fabricated under substrate temperature of room temperature (RT), 60, and 100 °C, respectively. The B-IFD films show a minimum roughness of 4.655 nm at RT, while the films have increased roughness of 10.70 and 15.67 nm at 60 and 100 °C, respectively (Figure 3a-c). For the BT-IFD films, layer-bylayer terrace-like grains were formed with roughness of 3.635, 3.133, and 3.325 nm at RT, 60, and 100 °C, respectively (Figure 3d–f). As shown in Figure 3g-i, DBA-IFD formed terrace-like grains at 60 °C with a roughness of 3.353 nm, which are smaller than that of the films deposited at RT and 100 °C (8.37 and 5.605 nm at RT and 100 °C, respectively). The smaller roughness of DBA-IFD and BT-IFD than B-IFD suggests that the incorporation of sulfur- or nitrogen-linked side chains may help to increase carrier mobility.

2.5. Thin-Film OFET Characteristics

To evaluate the charge transport characteristics of the films for the three **IFD** derivatives, the bottom-gate top-contact OFETs devices were fabricated and examined in a glove box. The representative characteristics for the **IFD** derivatives are shown in **Figure 4** and Figure S12 (Supporting Information), and OFET properties obtained at different substrate temperatures are summarized in **Table 3**. As shown in Figure S12 (Supporting Information), the source–drain currents ( $I_{SD}$ ) of **B-IFD** devices are at only detectable current level (<10<sup>-12</sup> A), which can be considered as no field effect (mobility lower than 10<sup>-7</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and is consistent with literature reports.<sup>[14]</sup> As expected, the butylthio and dibutylamino substituents significantly increase the charge transport mobility. **BT-IFD** exhibits high and balanced ambipolar charge transport with maximum hole and electron mobilities of 0.71 and 0.65 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, as well as the balanced average



**Figure 3.** Atomic force microscopy images of the films for the IFD derivatives: for **B-IFD** at a) RT, b) 60 °C, c) and 100 °C, respectively; for **BT-IFD** at d) RT, e) 60 °C, and f) 100 °C, respectively; for **DBA-IFD** at g) RT, h) 60 °C, and i) 100 °C, respectively.

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Figure 4. Transfer curves and output curves of PVD OFETs bases on IFD derivatives, respectively. a,b) for DBA-IFD; c-f) for BT-IFD.

threshold voltage of -48 V (p-type) and 41 V (n-type), respectively. Moreover, DBA-IFD exhibits p-type charge transport with a maximum hole mobility of 1.03  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  (Figure 4a,b).

The results of OFET performance of the three IFD derivatives illustrate that both molecular packing and energy level are essential for charge carrier transport. The extremely low carrier mobilities of the thin-film OFET based on B-IFD are attributed to large injection barrier and 1D molecular packing. In contrast, BT-IFD has appropriate energy level due to the sulfur linkage, which allows both electron and hole injection from the gold Fermi level. In addition, the 2D stacking provides favorable charge transport channels for both types of carriers. As a result, **BT-IFD** exhibits high and balanced ambipolar transport behavior. DBA-IFD possesses 2D stacking structures that

Table 3. O	FET c	haracteristics	of the	IFD	derivatives.
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Compound	T <sub>sub</sub> [°C]	$\mu_{\rm h}  [{\rm cm}^2  {\rm V}^{-1}  {\rm s}^{-1}]  {\rm Max}  ({\rm Avg})$	V <sub>T</sub> [V] Min (Avg)	I <sub>on</sub> /I <sub>off</sub> Max (Avg)	$\mu_{\rm e}  [{\rm cm}^2  {\rm V}^{-1}  {\rm s}^{-1}]  { m Max}  ({ m Avg})$	V <sub>T</sub> [V] Min (Avg)	I <sub>on</sub> /I <sub>off</sub> Max (Avg)
B-IFD <sup>a)</sup>	RT	N.O.	_	_	N.O.	-	_
	60	N.O.	-	-	N.O.	-	-
	100	N.O.	-	-	N.O.	-	-
BT-IFD	RT	0.14 (0.09)	-36 (-31)	10 <sup>6</sup> (10 <sup>5</sup> )	0.05 (0.03)	62(66)	10 <sup>4</sup> (10 <sup>3</sup> )
	60	0.71 (0.38)	-48 (-32)	10 <sup>5</sup> (10 <sup>4</sup> )	0.65 (0.32)	41(53)	10 <sup>4</sup> (10 <sup>3</sup> )
	100	0.24(0.19)	-32 (-22)	10 <sup>4</sup> (10 <sup>3</sup> )	0.14 (0.12)	60(64)	10 <sup>5</sup> (10 <sup>4</sup> )
DBA-IFD	RT	0.19 (0.13)	-19 (-12)	10 <sup>6</sup> (10 <sup>5</sup> )	N.O.	_	-
	60	1.03 (0.41)	-27 (-11)	10 <sup>5</sup> (10 <sup>4</sup> )	N.O.	_	-
	100	0.22 (0.19)	-14 (-6.7)	10 <sup>6</sup> (10 <sup>5</sup> )	N.O.	_	-

a) The OFETs based on **B-IFD** exhibited only detectable filed-effect mobility (<10<sup>-7</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), which were considered with no mobility. The term N.O. stands for "not observed".

are favorable for charge transport. The nitrogen linkages significantly raise the HOMO level to allow efficient hole injection, but the LUMO level remains too high for electron injection. Therefore, the transistors from **DBA-IFD** exhibits high hole mobility but no electron transport property.

#### 2.6. Inverter Property

CMOS-like inverter is an important application for ambipolar OFETs. The ambipolar OFETs can transport both hole and electron carriers so that one active layer is enough to construct inverters, which avoid patterning n- and p-type materials into specific areas. The inverter circuits were constructed by the BT-IFD-based ambipolar OFETs, which possess excellent ambipolar charge transport property and balanced threshold voltage. As shown in Figure 5, each inverter circuit is composed of two adjacent OFETs with a common gate as the input voltage  $(V_{\rm IN})$  and a common drain as the output voltage  $(V_{\rm OUT})$ . In Figure 5a, a typical input/output characteristic curve is shown for an inverter based on two adjacent transistors with channel length L = 150 mm and channel width W = 3000 mm. In contrast to the conventional inverters based on unipolar materials, the inverters consisting of ambipolar transistors can work in both negative and positive supply biases  $(V_{DD})$ . The ambipolar OFETs based on **BT-IFD** exhibited an averaged threshold voltage of -48 V for the p-channel and 41 V for the n-channel. A  $V_{DD}$  of 100 V or -100 V was selected to ensure that both the n-channel and p-channel OFETs were operated in the saturation region (Figure 5a,b). For an ideal CMOS-like inverter consisting of equivalent n and p-type transistors, the ideal inversion voltage ( $V_{\rm INS}$ ) is located at  $V_{\rm DD}/2$ .<sup>[26]</sup> The gain, which is defined as the slope of the voltage transfer characteristics curve, is an important parameter to evaluate the performance of an inverter. For  $V_{\rm DD} = -100$  V, the maximum gain is up to 80 with a  $V_{\rm INS}$  of -49 V (Figure 5a); while under positive bias with  $V_{\rm DD} = 100$  V, the highest gain is up to 173 with a  $V_{\rm INS}$  of 40 V (Figure 5b). These results also confirm that **BT-IFD** is indeed a balanced ambipolar organic semiconductor.

## 3. Conclusion

We have demonstrated that by replacing the butyl chains with butylthio or dibutylamino substituents, the carrier mobilities of a classic organic semiconductor IFD can be boosted for several orders of magnitudes. The sulfur and nitrogen linkages have significant impact on the electronic energy levels of the IFD core, hence, could optimize the charge carrier injection. The OFETs of the butyl group terminated B-IFD exhibited a very poor charge transport property with a mobility lower than  $10^{-7}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Interestingly, the butylthio-modified BT-IFD derivative exhibited a high and balanced ambipolar charge transport property with maximum hole and electron mobilities up to 0.71 and 0.65 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. Highperformance CMOS-like inverters incorporated with the BT-IFD-based ambipolar OFETs showed sharp inversions with a maximum gain value up to 173. The dibutylamino groups containing DBA-IFD significantly boosted hole mobility up to 1.03 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, with no observable electron mobility. This



Figure 5. Devices structure and input/output characteristic for the CMOS-like inverters work at a) negative and b) positive supply biases.

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work reveals that incorporation of sulfur or nitrogen linkages between the alkyl chains and the aromatic cores could be a concise and efficient strategy for the design of highperformance organic semiconductors.

## 4. Experimental Section

*Synthesis*: The detailed synthetic procedures of the **IFD** derivatives were described in the Supporting Information.

Characterization: Chemical structures were fully identified by <sup>1</sup>H NMR and <sup>13</sup>C NMR (Bruker, AVANCE-III-400; INOVA) and GC-Mass (LTQ-Obitrap-ETD). UV-vis spectra were recorded on a T6 UV-Vis spectrometer. HOMO levels of organic materials were obtained from the cyclic voltammetry measurements. Cyclic voltammetry measurements were performed using a CHI660C electrochemistry station (CHI, USA) with one-compartment platinum working electrode, a platinum wire counterelectrode, and a quasi Ag<sup>+</sup>/Ag electrode as the reference. Measurements were performed in a  $1\times10^{-3}$   ${\rm M}$  dichloromethane solution with 0.1  ${\mbox{ M}}$  N(Bu)\_4^+BF\_4^- as the supporting electrolyte, at a scan rate of 100 mV s<sup>-1</sup>. Potential values are reported in voltage versus saturated calomel electrode (SCE) using the Fc<sup>+</sup>/Fc couple as an internal standard. HOMO and LUMO energy levels were approximated using SCE = -4.68 eVversus vacuum<sup>[27]</sup> and the half-wave potential  $(E_{1/2})$  values. Single-crystal structure analysis was carried out with a Bruker X8 APEX diffractometer with graphite monochromated Mo K $\alpha$  radiation. The 2D-GIXD experiments were performed on various semiconductor films at beam line BL14B1 of the Shanghai Synchrotron Radiation Facility. Film surface topologies were obtained by an Agilent 5500 with tapping mode. DFT calculations were performed using Gaussian 09 package with the basis set of B3LYP, 6-311G ++(2d, 2p). The transfer and output characteristics of all OFET devices were measured using a Keithley 4200 SCS.

Device Fabrication and Measurement: To prepare the substrates, SiO<sub>2</sub>/Si substrates (p-doped 300 nm) were treated with piranha solution  $(V(H_2O_2):V(H_2SO_4) = 3:7)$  for 30 min, and then rinsed with deionized water, acetone, and isopropyl alcohol, respectively, for 10 min in an ultrasonicator, followed by 10 min  $\rm O_2$  plasma treatment. For the physical vapor-deposited polycrystalline OFET device fabrication, octadecyltrimethoxy silane (OTMS) was treated as a self-assembled monolayer on prepared substrate by the spin-coating method, to reduce charge trap sites. Polycrystalline films were fabricated in vacuum tube furnace (self-made) at  $5 \times 10^{-4}$  Pa. About 1 mg of organic semiconductor powders was put on the high-temperature zone, and the substrates were put on the low-temperature zone. The temperature was set of hightemperature zone; the temperature was rose to  $T_1$  in 10 min form 25 °C, and then rose to  $T_2$  in 5 min, keeping  $T_2$  for 20 min (**B-IFD**:  $T_1 = 170$  °C,  $T_2 = 190 \text{ °C}$ ; **BT-IFD**:  $T_1 = 200 \text{ °C}$ ,  $T_2 = 210 \text{ °C}$ ; **DBA-IFD**:  $T_1 = 210 \text{ °C}$ ,  $T_2 = 230$  °C). The low-temperature zone was set to control substrate temperature ( $T_{sub}$ ; room temperature, 60, and 100 °C). As both source and drain electrodes, 50 nm thick Au was thermally deposited with a deposition rate of 0.2–0.3 Å s<sup>-1</sup>, with a channel length (L) of 150  $\mu$ m and width (W) of 3 mm. The transfer and output characteristics of all the OFETs were measured in a nitrogen filled glove box, using a Keithley 4200 SCS instrument connected to a probe station. All OFET characteristics were obtained from the transfer curve in the saturated regime.

[Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1536572 for **B-IFD**, CCDC 1536573 for **BT-IFD** and CCDC 1536578 for **DBA-IFD**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.]

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# Keywords

ambipolar materials, inverters, organic field-effect transistors, side-chain engineering

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