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### Journal Name

## ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A series of low band-gap  $\pi$ -conjugated molecules comprising N,N-dihexyl-indolo[3,2-b]indole as an electron donor (D) and dicyanovinyl as an electron acceptor (A) with A-π-D-π-A architecture, are designed and synthesized to realize singlecomponent ambipolar organic field-effect transistor (OFET). Molecules with different  $\pi$ -bridging units (none, thiphene, bithiophene) are synthesized and characterized to explore the structure-property correlation. Through cooperative effects of intramolecular charge transfer (ICT) interaction and conjugation extension, band-gap of newly synthesized molecules is reduced down to 1.41 eV in solution state. Among others, 2H2TIDID-DCV (with thiophene π-spacer) exhibits highly balanced ambipolar charge transport with hole and electron mobilities of 0.08 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 0.09 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, from vacuum-deposited OFET device. The spin-coated OFET devices using OD2TIDID-DCV, for which hexyl side chains of 2H2TIDID-DCV are replaced by 2-octyldodecyl, also exhibits ambipolar charge transporting nature (mobility of 9.67  $\times$  10<sup>-2</sup>  $\text{cm}^2$  V<sup>-1</sup> s<sup>-1</sup> for hole, and 3.43 × 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for electron). Both 2H2TIDID-DCV and OD2TIDID-DCV exhibit favorable thinfilm morphology for charge transporting channel formation, and structure analyses of those films reveal the same molecular packing characteristics of three-dimensional lamellar π-stacking structure.

#### Introduction

Research interests in the ambipolar organic field-effect transistors (OFETs) have been significantly grown because of their potential application to the complementary circuits like inverters without complicated multi-step deposition process.<sup>1-2</sup> Especially, single-component ambipolar OFETs simply comprised of a single-layer active channel with symmetric source-drain electrodes, have attracted much attention owing to their expediency in practical device fabrication.<sup>2-4</sup> Theoretically, many of organic semiconductors are known to transport both types of charge carriers in their solid-state, if and only if charge carriers are efficiently injected.<sup>2,5</sup> However, majority of reported organic semiconductors exhibited unipolar characteristics, i.e., either hole- or electron-transport only depending on the work function of the electrodes, mainly due to the restriction of high injection barrier for one of the carriers.<sup>6-8</sup> Therefore, among various crucial issues in realizing single-component ambipolar OFETs, balanced energy level alignment of the highest occupied molecular orbital (HOMO)

and lowest unoccupied molecular orbital (LUMO) of the organic semiconductor relative to the work function of symmetric electrode is most essential for the favorable bipolar injection.<sup>2, 8-11</sup> In this regard, wide ranges of low band-gap organic materials have been extensively investigated, and some of  $\pi$ -conjugated structures, such as TIPS-pentacenes, <sup>12-14</sup> diketopyrrolopyrroles,<sup>15-18</sup> indigos,<sup>19</sup> isoindigos,<sup>20</sup> and quinoinal oligothiophenes,<sup>21-23</sup> have been reported as promising backbone structures for designing high performance ambipolar semiconductor, through appropriate molecular structure engineering.<sup>24</sup> In spite of such extensive materials research on ambipolar OSCs, molecular structural effect on the operating mechanism of ambipolar OFETs has seldom been explored. In this regard, exploring structure-property correlation based on the comprehensive photophysical, electrochemical, and quantum-chemical calculation studies is essential developing high performance in organic semiconductors.

Very recently, we have synthesized indolo[3,2-b]indole (IDID) derivatives as promising p-type organic semiconductors with remarkable hole mobility of 0.97 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and versatile processability.<sup>25</sup> Besides apparent advantages of pyrrole-fused structure such as facile solubility control and structural derivatization, IDID core is characterized by stronger electron donating nature than those of other reported pyrrole-fused heteroarene cores (e.g., carbazole and indolocarbazole), owing to the larger proportion of five-membered pyrrole units in the backbone. To examine the possible bipolar carrier injection

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Electronic Supplementary Information (ESI) available: [Additional synthetic procedures, AFM images, and OFET device data]. See DOI: 10.1039/x0xx00000x

and transport, we herein designed and synthesized intramolecular charge transfer (ICT)-type IDID derivatives (IDID-DCV derivatives), 2HIDID-DCV, 2H2TIDID-DCV, and 2H4TIDID-DCV, which comprise the IDID as an electron donor (D) and dicyanovinyl (DCV) as an electron acceptor (A) with A- $\pi$ -D- $\pi$ -A type architecture. Three different  $\pi$ -linking units (none, thiphene, bithiophene) were incorporated to explore different degrees of ICT interaction and  $\pi$ -conjugation, which enabled both molecular structure-property correlation and precise control of electronic characteristics. To elaborate indepth analysis of structure-property correlation, we also prepared p-type reference molecules, 2HIDID, 2H2TIDID, and 2H4TIDID, with which comprehensive studies were conducted in terms of their theoretical, photophysical, electrochemical, morphological, electrical, and structural characteristics. Among others, 2H2TIDID-DCV (with thiophene  $\pi$ -linker) exhibited dramatically reduced energy band-gap (1.62 eV in solution state) as well as excellent film morphology, which afforded highly balanced ambipolar charge transport with hole and electron mobilities of 0.08 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 0.09 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, in the vacuum-deposited (VD) OFET devices. Aiming at a solution processable IDID-DCV derivative, OD2TIDID-DCV was also synthesized for which hexyl side chains of 2H2TIDID-DCV was replaced by 2-octyldodecyl group. The spin-coated OFET device of OD2TIDID-DCV also exhibited ambipolar charge transport behavior (mobility of  $9.67 \times 10^{-2}$  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  for hole, and  $3.43 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for electron). To the best of our knowledge, this is the first report of singlecomponent ambipolar OFET based on pyrrole-fused heteroacene family even including the widely studied indolocarbazole derivatives.

#### **Result and Discussion**

To understand the effect of the ICT interaction and molecular structure alteration on electronic characteristics of IDID derivatives, and also to realize ambipolar OSC for practical application, we rationally designed molecular structure as follows. Using the DCV unit as a strong electronic acceptor, we constructed A- $\pi$ -D- $\pi$ -A type molecular architecture not only for manifesting strong ICT interaction but also for enabling efficient electron injection through lowering LUMO energy level, <sup>26,27</sup> for which their electronic and intermolecular interaction characteristics were delicately tuned by altering the  $\pi$ -linker (none, thiophene, bithiophene). Based on this idea, we have designed a series of three IDID-DCV derivatives, 2HIDID-DCV, 2H2TIDID-DCV, and 2H4TIDID-DCV (Scheme 1). Synthesis of 2,7-dibromo-N,N-dihexyl-IDID (compound 1) was according to our previous report; <sup>25</sup> from which IDID-DCV derivatives were successfully synthesized through lithiumexchange formylation, palladium-catalyzed borylation, Suzuki-Miyaura cross-coupling, and Knoevenagel-condensation reaction. All the three target compounds were carefully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis, and mass analysis. Detailed synthetic procedures are described in Scheme 1 and Experimental Section.

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Scheme 1 a) Synthesis route for IDID-DCV derivatives and their chemical structure ((I) bis(pinacolato)diborone, Pd<sub>2</sub>(dppf)<sub>2</sub>, KOAc, anhydrous dimethylformamide, (II) n-BuLi, tetrahydrofuran, (III) Pd(PPh<sub>3</sub>)<sub>4</sub>, 2N K<sub>2</sub>CO<sub>3</sub>, tetrahydrofuran, (IV) Al<sub>2</sub>O<sub>3</sub>, methylene chloride); b) Chemical structure of IDID reference derivatives.

For the comprehensive understanding of newly synthesized IDID-DCV derivatives in terms of their photophysical properties, we also prepared three IDID reference materials, 2HIDID, 2H2TIDID, and 2H4TIDID, which have exactly the same molecular structures with those of 2HIDID-DCV, 2H2TIDID-DCV, and 2H4TIDID-DCV but without acceptor unit (DCV), respectively (see Scheme 1, 2H2TIDID and 2H4TIDID were reported earlier,<sup>25</sup> but 2HIDID was newly synthesized in this work. Detailed synthetic procedure and characterization of 2HIDID is described in Electronic Supplementary Information). The electronic characteristics of IDID-DCV derivatives were evaluated through the molecular orbital calculation, UV-vis spectroscopy, and cyclic voltammetry (CV) measurement. Ground-state optimized geometries and electronic structures of IDID derivatives were calculated within the density functional theory (DFT) B3LYP method by using Gaussian 09 package with basis set of 6-31G d p. According to the calculated frontier orbital energies shown in Fig. 1, it is noted that the effect of different  $\pi$ -linking units (none, thiophene, bithiophene) in IDID-DCV derivatives is guite different from that in p-type IDID reference derivatives. Because IDID unit intrinsically holds very low ionization potential,  $\pi$ -conjugation extension with thiophene unit mostly resulted in the stabilization of LUMO energies without any HOMO variation in case of the p-type reference derivatives. While both the HOMO and LUMO energies of a given IDID-DCV derivative were strongly stabilized compared to those of respective IDID reference derivative, the actual degree of stabilization

DOI: 10.1039/C6TC02777F Journal Name

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Fig. 1 Plot of calculated energy levels for IDID-DCV derivatives and IDID reference derivatives, and their molecular orbital contour (DFT/B3LYP-6-31G d p, the alkyl chains were replaced by methyl in calculation).

increased in the order of different  $\pi$ -linking units (none > thiophene > bithiophene) as seen in Fig. 1. This can be rationally correlated with the increasing strength of ICT characteristics with decreasing D-A distance.

For the empirical exploration of electronic transitions, UV-vis absorption spectra of IDID derivatives were measured at a concentration of  $1 \times 10^{-5}$  M in tetrahydrofuran (THF) solutions and also for spin-coated films (see Fig. 2, detailed data listed in Table 1). In solution states, all the IDID-DCV derivatives exhibited broad absorption bands consisting of three absorption maxima. Interestingly, the location of lowest energy transition maxima corresponding to the ICT transition were virtually the same for all of them (544 nm for 2HIDID-DCV, and 555 nm for 2H2TIDID-DCV and 2H4TIDID-DCV), in spite of their different  $\pi$ -linker length from each other. This feature can be comprehended by comparing their absorption spectra with those of the reference derivatives. As shown in Fig. 2c, IDID-DCV derivatives show different degree of bathochromically shifted absorption spectra ( $\Delta \lambda_{max}$ s, see Table 1) which increases with decreasing D-A distance. The apparently similar ICT absorption wavelengths among IDID-DCV derivatives can thus be rationalized by compromised ICT strength and conjugation length effects. Strength of ICT interaction between IDID and DCV is getting weaker for the molecules with larger number of thiophene  $\pi$ -spacer, which at the same time is compensated by increased  $\pi$ -conjugation length to give comparable absorption  $\lambda$  maximum. In the solid states samples of IDID-DCV derivatives, further bathochromic shifts of 90-100 nm with distinct vibronic features are observed as shown in Fig. 2b and summarized in Table 1.

To investigate electrochemical properties of IDID-DCV derivatives, cyclic voltammetry (CV) measurements were made both in solution states and solid (film) states. The HOMO, LUMO, and electrochemical band-gap energies which were extracted from the first oxidation onset and the first reduction onset of CV curves are listed in Table 1. As shown in **Fig. 3**, IDID-DCV derivatives exhibited quasi-reversible multistage electrochemical oxidation and reduction behaviors in THF solvent. Consistent with the DFT calculation results in Fig. 1,



Fig. 2 Absorption spectra of IDID-DCV derivatives for solution state (a) and film state (b), and each solution state absorption spectra with correspondent reference (c).

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ible 1 Optical and electrochemical properties of IDID-DCV derivatives									
Compound	Abs. $\lambda_{max}$ [sol./film/ $\Delta \lambda_{max}$ , nm] <sup>a)</sup>	$\Delta \lambda_{max}$ s [nm] <sup>b)</sup>	HOMO [sol./film, eV] <sup>c)</sup>	LUMO [sol./film, eV] <sup>c)</sup>	Band-gap [sol./film, eV] <sup>d)</sup>				
2HIDID-DCV	544/636/89	179	-5.34/-5.42	-3.51/-3.71	1.81/1.71				
2H2TIDID-DCV	555/657/103	151	-5.08/-5.09	-3.46/-3.86	1.62/1.23				
2H4TIDID-DCV	555/641/89	118	-4.90/-4.99	-3.49/-3.74	1.41/1.25				

<sup>a)</sup>  $\lambda$  max is extracted from lowest spin-allowed transition maximum,  $\Delta \lambda_{max}$  presents  $\lambda_{max}$  difference between solution state and film state, solution absorption spectra were measured in THF (concentration of 1×10<sup>-5</sup>M), and film absorption spectra were measured with spin-coated sample (1500 RPM/60s, 0.3 wt% in chloroform); <sup>b)</sup>  $\Delta \lambda_{max}$  presents Abs.  $\lambda_{max}$  difference between IDID-DCV derivatives and correspondent IDID reference in solution state; <sup>cl</sup> HOMO and LUMO energy levels were determined by cyclic voltammetry. Solution sample was prepared 3 × 10<sup>-3</sup> M in THF and film sample was prepared on ITO patterned glass by drop-casting; <sup>dl</sup> band-gap = V<sub>oxidation</sub> - V<sub>reduction</sub>.



Fig. 3 Cyclic voltammograms of IDID-DCV derivatives in solution state (a) and film state (b) (Inset: ferrocene).

LUMO energies of IDID-DCV derivatives were strongly stabilized and located at similar level (around -3.5 eV) as seen in Fig. 3 and Table 1. Meanwhile, HOMO energies were gradually destabilized with increasing  $\pi$ -spacer length; i.e., -5.34, -5.08, and -4.90 eV. Consequently, we could achieve quite small band-gap (i.e., down to 1.41 eV) using compensated ICT interaction between IDID and DCV. In case of film states, HOMO and LUMO energies of IDID-DCV derivatives were even further stabilized with higher degree of stabilization for LUMO energies than HOMO energies to give smaller bandgap energies. Interestingly, largest solid state LUMO stabilization to give the smallest band-gap energy of 1.23 eV was observed for 2H2TIDID-DCV (see Table 1), which attests the most strong and efficient electronic interaction in the tightly packed solid state suggesting its excellent OFET mobility (vide infra).

Based on the photophysical and electrochemical properties (i.e., satisfactorily low band-gap with suitable HOMO and LUMO energy in the solid state for efficient bipolar injection from symmetric source-drain electrodes), two of the IDID-DCV derivatives, 2H2TIDID-DCV and 2H4TIDID-DCV, were selected for the evaluation of OFET characteristics. Before the OFET device fabrication, however, we have examined their VD thinfilm surface topography as a function of substrate temperature (T<sub>sub</sub>) alteration. As shown in Fig. S1, 2H2TIDID-DCV films showed dense and compact grain features suitable for OFET fabrication, whilst 2H4TIDID-DCV VD films showed coarse and unfilled topological characteristics unsuitable for device evaluation. Therefore, Charge transporting characteristics of 2H2TIDID-DCV was evaluated for its ambipolar mobility in the geometry of bottom-gate top-contact (BGTC) VD OFET devices. 2H2TIDID-DCV was thermally evaporated and deposited on octadecyltrichlorosilane (ODTS) treated SiO<sub>2</sub>/Si substrates at different Tsub from room temperature (RT) to 140 °C to optimize the device performance. As previous reported, 2H2TIDID OFET devices exhibited typical p-type OFET behavior.<sup>(25)</sup> In contrast, 2H2TIDID-DCV OFET devices showed ambipolar OFET behavior exhibiting typical V-shaped transfer curves and unique output curves with superlinear regime as seen in Fig. 4a to f. With the  $T_{sub}$  increase, hole and electron mobilities were increased simultaneously (see Fig. S2 and Table 2).

In particular, the electron mobility was much more dramatically enhanced by altering the deposition temperature (nearly four orders of magnitude increase, from  $1.5 \times 10^{-5}$  cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup> to 9.2 × 10<sup>-2</sup>) than that of hole mobility (from 1.8 × 10<sup>-3</sup>  $\text{cm}^2~\text{V}^{\text{-1}}~\text{s}^{\text{-1}}$  to  $8.2\times10^{\text{-2}}\text{)},$  and the devices which were deposited at high T<sub>sub</sub> (> 70 °C), showed well balanced hole and electron mobilities (hole mobility to electron mobility ratio is 0.63 at T<sub>sub</sub> of 140 °C). Such different tendency of electron and hole mobility modulation is most probably due to the higher sensitivity for the trap site of electron charge carrier than that of hole charge carrier.<sup>28</sup> The mobility increment could be attributed to the reduced density of trap sites originating from increased grain size, as was rationalized from surface topography study using atomic force microscopy (AFM) measurement. As shown in Fig 5a to f, surface topography of 2H2TIDID-DCV film was transformed from uniform film (rootmean-square roughness value of 0.7 nm) to highly ordered

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Fig. 4 OFET devices characteristics. (a to f) Representative OFET device characteristics of 2H2TIDID-DCV ((a and c) transfer curves of *T<sub>sub</sub>* 120 °C device, (b and d) output curves *T<sub>sub</sub>* 120 °C device, and (e and f) temperature dependent mobility for p- and n-channel operation, respectively. (white stars represent average value)); (g and j) Spin-coated OFET device characteristics of OD2TIDID-DCV (annealing temperature is 150 °C, (g and i) transfer curves and (h and j) output curves for p- and n-channel operation, respectively).



Fig. 5 AFM surface topologies (height images, 5  $\mu$ m × 5  $\mu$ m) of 2H2TIDID-DCV VD thin films under different  $T_{sub}$  ((a) RT; (b) 50 °C; (c) 70 °C; (d) 100°C; (e) 120 °C; (f) 140 °C), and OD2TIDID-DCV spin-coated film ((g), annealed at 150 °C).

crystalline films with terrace-structured grains along with increasing  $T_{sub}$ ; structured grains were developed from  $T_{sub}$  of 70 °C, and micron-sized grains were observed from  $T_{sub}$  of 120 °C. By correlating charge carrier mobility and surface topography, it was found that the terrace-structured and enlarged grains are responsible for the favorable intermolecular packing structure for both hole and electron charge carrier transport (*vide infra*).

To demonstrate a solution processable IDID-DCV derivative, we additionally synthesized OD2TIDID-DCV, for which linear hexyl side chains in 2H2TIDID-DCV were replaced by branched 2-octyldodecyl group (see Scheme 1 and **Scheme S2**, detailed

synthetic procedures and characterizations are described in Electronic Supplementary Information). Spin-coated OFET devices of OD2TIDID-DCV were fabricated and characterized for the same OFET structure and geometry as the VD ones, but with the semiconductor material (OD2TIDID-DCV) deposited by spin-coating method. As shown in Fig. 4g to j, optimized spincoated OFET device (post annealing temperature of 150 °C) exhibited ambipolar charge transport behavior with hole and electron mobilities of  $9.6 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $3.4 \times 10^{-3}$  cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup>, respectively. With respect to the charge carrier mobility values, solution processed OD2TIDID-DCV devices exhibited slightly higher hole mobility but relatively lower electron mobility values than those of 2H2TIDID-DCV. Such different mobility values are due to the somewhat different  $\pi$ - $\pi$ distance, vide infra, and rather smaller grain size compared to that of optimized VD device (see Fig. 5g). Anyway, experimentally evidenced ambipolarity in the 2H2TIDID-DCV and OD2TIDID-DCV devices suggest that 2TIDID-DCV is a promising  $\pi$ -conjugate backbone for the single-component ambipolar OFET.

To investigate the molecular packing structure in the organic semiconductor samples, out-of-plane X-ray diffraction (XRD), powder XRD, and 2D grazing incidence X-ray diffraction (2D-GIXD) analyses were carried out. Fig. 6a shows out-of-plane XRD patterns of 2H2TIDID-DCV thin films. While low  $T_{sub}$  (RT and 50 °C) samples exhibited quite dim diffraction peaks, samples which were deposited at high  $T_{sub}$  (over 70 °C) exhibited sharp and strong diffraction peaks up to the third (300) order, at 2 theta degrees of 8.37°, 16.78°, and 25.28°; this could be interpreted as lamellar diffraction with a dspacing of 10.58 Å. From the powder XRD, (Fig. 6b) identical lamellar diffraction peaks with those of out-of-plane XRD could be observed at almost same 2 theta degrees (8.36°, 16.67°, and 25.16°), and moreover, we could recognize diffraction peak at wide angle region (24.9°) which might be interpreted as  $\pi$ - $\pi$  distance with a *d*-spacing of 3.57 Å (inset of Fig. 6b). The

DOI: 10.1039/C6TC02777F Journal Name

Compound	T <sub>sub</sub> [°C] <sup>a)</sup>	p-channel operation		n-channel operation			p/n ratio	
		$\mu_h$ , max/average [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] <sup>b)</sup>	$V_{th}$ $[V]^{c)}$	I <sub>on</sub> /I <sub>off</sub>	$\mu_e$ , max/average [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] <sup>b)</sup>	$V_{th}$ $[V]^{c)}$	I <sub>on</sub> /I <sub>off</sub>	]
2H2TIDID-DCV	RT	$1.85 \times 10^{-3}/$ $1.43 \times 10^{-3}$	-42 (±8)	$3 \times 10^4$	$1.47 \times 10^{-5}/$ $8.79 \times 10^{-6}$	60 (±5)	$2 \times 10^{1}$	125.85
	50	$2.30 \times 10^{-2}/$ $1.39 \times 10^{-2}$	-22 (±12)	$1 \times 10^{5}$	$2.32 \times 10^{-4}/$ $1.23 \times 10^{-4}$	100 (±10)	$3 \times 10^2$	99.14
	70	$2.76 \times 10^{-2}/$ $1.69 \times 10^{-2}$	-9 (±9)	$4 \times 10^4$	$8.07 \times 10^{-3}/$ $5.39 \times 10^{-3}$	67 (±18)	$3 \times 10^3$	3.42
	100	$8.28 \times 10^{-2}/$ $4.30 \times 10^{-2}$	-7 (±3)	$1 \times 10^3$	$4.46 \times 10^{-2}/$ $2.09 \times 10^{-2}$	61 (±10)	$5 \times 10^2$	1.86
	120	$6.86 \times 10^{-2}$ / $3.30 \times 10^{-2}$	-13 (±4)	$4 \times 10^3$	$8.13 \times 10^{-2}/$ $5.45 \times 10^{-2}$	61 (±13)	$9 \times 10^2$	0.84
	140	$5.89 \times 10^{-2}$ / $4.41 \times 10^{-2}$	-15 (±3)	$1 \times 10^4$	$9.24 \times 10^{-2}/$ $6.21 \times 10^{-2}$	77 (±9)	$3 \times 10^3$	0.63
2H2TIDID <sup>e)</sup>	70	$3.20 \times 10^{-2}/$ $3.00 \times 10^{-2}$	-11 (±2)	$1 \times 10^4$	-	-	-	-
D2TIDID-DCV	150 <sup>d)</sup>	$9.67 \times 10^{-2}$ / 5.28 × 10^{-2}	-24 (+9)	$4 \times 10^4$	$3.42 \times 10^{-3}/$ 1.25 × 10^{-3}	50 (±11)	$1 \times 10^2$	28.27

<sup>a)</sup> Substrate temperature in vacuum deposition; <sup>b)</sup> The mobilities were extracted from the saturation regimes; <sup>c)</sup> Average threshold voltages. The values in parentheses represent one standard deviation; <sup>d)</sup> Post annealing temperature of spin-coated device (°C); <sup>e)</sup> from reference 25.



Fig. 6 (a) Out-of-plane XRD pattern of 2H2TIDID-DCV VD films under different *T*<sub>sub</sub>; (b) Powder XRD pattern of 2H2TIDID-DCV powder; (c) 2D-GIXD diffraction pattern image of 2H2TIDID-DCV VD films (*T*<sub>sub</sub> 140°C); (d and e) Horizontal and vertical line profile of (c), respectively; (f) 2D-GIXD diffraction pattern image of OD2TIDID-DCV film; (g and h) Horizontal and vertical line profile of (e), respectively; (i) Calculated molecular size of 2H2TIDID-DCV; (j) Schematic diagram of 2H2TIDID-DCV packing structure.

2D-GIXD result of 2H2TIDID-DCV thin film could further support our interpretation; we observed diffraction peaks corresponding to lamellar and  $\pi$ - $\pi$  *d*-spacing at  $q_z$  of 0.60 Å<sup>-1</sup> (10.47 Å) and  $q_{xy}$  of 1.76 Å<sup>-1</sup>(3.57 Å), respectively. Moreover, the 2D-GIXD patterns of OD2TIDID-DCV spin-coated film also exhibited similar result with that of 2H2TIDID-DCV; i.e., semiconductor molecules are oriented exactly same manner with that of 2H2TIDID-DCV VD film but with different values of *d*-spacing (the lamellar spacing and  $\pi$ - $\pi$  spacing values are 17.9 Å and 3.64 Å, respectively). Through the comprehensive

correlation between XRDs, DFT calculation, and AFM surface topographic results shown in Fig. 6, we could conclude that 2H2TIDID-DCV (and OD2TIDID-DCV) molecules are oriented on the substrate with edge-on manner, and their  $\pi$ -planes are stacked up toward surface parallel direction. On the other hand, van der Waals interactions of *N*-aliphatic chains enable 2H2TIDID-DCV and OD2TIDID-DCV to construct well-organized three-dimensional lamellar structure with lamellar spacing of 10.58 Å and 17.9 Å, respectively (see Fig. 6j).

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#### Conclusions

We have designed and successfully synthesized A- $\pi$ -D- $\pi$ -A type IDID-DCV derivatives with different  $\pi$ -spacer. It was found that the compensated ICT interaction between IDID and DCV of 2TIDID-DCV derivatives (with thiophene  $\pi$ -spacer) and their efficient electronic interaction in the three-dimensional lamellar  $\pi$ -stacking structure gave rise to the dramatically reduced energy band-gap as well as excellent film morphology. As a consequence, the VD OFET device using 2H2TIDID-DCV exhibited highly balanced ambipolar charge transport with hole and electron mobilities of 0.08 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and 0.09 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively, and the spin-coated OFET devices using OD2TIDID-DCV, also exhibited ambipolar charge transport behavior (mobility of 9.67 × 10<sup>-2</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for hole, and 3.43 × 10<sup>-3</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for electron).

#### **Experimental section**

#### Synthesis

The final products were synthesized according to the synthetic procedure shown in Scheme 1. 2,7-dibromo-5,10-dihexyl-5,10-dihydroinolo[3,2-b]indole (2-,7-dibromo-*N*,*N*-dihexyl-IDID) was synthesized according to our previous report.<sup>[25]</sup> Unless stated otherwise, all reagents were purchased at Sigma Aldrich, TCI, and Alfa Aeasar.

Synthesis of 5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole-2,7-dicarbaldehyde (2): A 100 mL round-bottom-flask, equipped with a magnetic stirrer bar, was baked under reduced pressure and backfilled with Ar for three times. A solution of compound 1 (200 mg, 0.375 mmol) in anhydrous tetrahydrofuran (THF) in baked reaction vessel was cooled down to -17 °C, afterwards, n-butyllithium (n-BuLi, 1.6 M solution, 0.36 mL, 0.902 mmol) was added slowly. One hour later, dimethylformamide (DMF, 69 µL, 0.902 mmol) was added to a reaction mixture, and then, reaction vessel was warmed to room temperature. After reaction finished, reaction mixture was guenched with distilled water (200 mL), and organic compounds were extracted with methylene chloride (DCM). Combined organic phase was separated and concentrated. Crude product was purified by column chromatography (ethyl acetate (EA)/n-hexane (n-hex.); 1:19, v/v) to afford **2** as yellow solid. (90 mg, 55.3 %) <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 10.14 (s, 2H), 8.04 (s, 2H), 7.98 (d, J = 8.22 Hz, 2H), 7.74 (d, J = 8.19 Hz, 2H), 4.58 (t, J = 7.14 Hz, 4H), 2.00 (m, J = 7.41 Hz, 4H), 1.44-1.25 (m, 12H), 0.87 (t, J = 7.02 Hz, 6H)

Synthesis of **2HIDID-DCV**: A mixed solution of **2** (200 mg, 0.462 mmol), malononitrile (67.9 mg, 1.017 mmol),  $AI_2O_3$  (377 mg, 3.698 mmol), and DCM (50 mL) was vigorously stirred during 2 hours at room temperature. After reaction finished, reaction mixture was filtered through celite plug to remove residual  $AI_2O_3$ , and filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography (THF) and subsequently by recrystallization (EA) to afford **2HIDID-DCV** as dark purple solid (220 mg, 90.3%). <sup>1</sup>H-NMR (500MHz, Tetrahydrofuran-d8,  $\delta$ ): 8.30 (s, 2H), 8.24 (s, 2H), 8.13 (d, *J* = 8.5Hz, 2H), 7.86 (d, *J* = 8.5Hz, 2H),

4.64 (t, J = 7.5Hz, 4H), 2.00 (q, J = 7.5Hz, 4H), 1.43 (q, J = 7.5Hz, 4H), 1.35-1.24 (m, 8H), 0.83 (t, J = 7.5Hz, 6H). 13C-NMR (500MHz, Tetrahydrofuran-d8,  $\delta$ ): 161.30, 142.50, 131.37, 127.80, 121.68, 120.41, 117.81, 115.66, 115.08, 115.04, 79.72, 46.40, 32.63, 31.28, 27.77, 23.54, 14.43. HRMS (FAB, m/z) Calcd. for  $C_{34}H_{34}N_6$ : 526.28; found: 526.2851. Elem. Anal. Calcd. for  $C_{34}H_{34}N_6$ : C 77.54, H 6.51, N 15.96; found: C 77.4905, H 6.5662, N 15.8965.

Synthesis of 5,10-dihexyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-5,10-dihydroindolo[3,2-b]indole (3): A 100 mL round-bottom-flask, equipped with a magnetic stirrer bar and reflux condenser, was baked under reduced pressure and backfilled with Ar for three times. Compound 1 (1.00 g, 1.878 mmol), bis(pinacolato)diboron (1.06 g, 4.133 mmol), [1,1'-Bis(diphenylphosphino)ferrocene]-dichloropalladium(II) (345 mg, 0.413 mmol), potassium acetate (1.10 g, 11.271 mmol), and anhydrous DMF (35mL) were added, then gently refluxed for 24 hours. After reaction finished, reaction mixture was guenched with brine (300 mL), and extracted with DCM. The combined organic phase was dried with MgSO4 and concentrated under reduced pressure. The crude product was purified by column chromatography (EA/n-hex.; 1:9, v/v) to afford **3** as yellow solid (350 mg, 41%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.93 (s, 2H), 7.84 (d, J = 7.86Hz, 2H), 7.62 (d, J = 7.86 Hz, 2H), 4.55 (t, J = 6.93 Hz, 4H), 1.98 (q, J = 6.57 Hz, 4H), 1.39 (s, 24H), 1.29 (m, 12H), 0.86 (t, J = 6.72 Hz, 6H)

5,5'-(5,10-dihexyl-5,10-dihydroindolo[3,2-Synthesis of b]indole-2,7-diyl)bis(thiophene-2-carbaldehyde) (4): 3 (205 mg, 0.223 mmol), 5-bromothiophene-2-carbaldehyde (131.3 mg, 0.469 mmol), tetrakis(triphenylhosphine)palladium(0) (37.38 mg, 0.032 mmol), 2N K<sub>2</sub>CO<sub>3</sub> aqueous solution (10 mL), and THF (20 mL) were added into a 100 mL round-bottom-flask, and the reaction vessel evacuated and backfilled with Ar. After then, reaction mixture was gently refluxed for 12 hours. After reaction finished, reaction mixture was guenched with 1N HCl aqueous solution (300 mL), and extracted with DCM. The combined organic phase was dried with MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by flash column chromatography (EA/n-hex.; 1:2, v/v) and recrystallization (EA) to afford 4 as red solid (190 mg, 94%) <sup>1</sup>H-NMR (300 MHz, DMSO-d6, δ): 9.91 (s, 2H), 8.13 (s, 2H), 8.07 (d, J = 4.05 Hz, 2H), 8.00 (d, J = 8.37 Hz, 2H), 7.78 (d, J = 3.96 Hz, 2H), 7.58 (d, J = 8.40 Hz, 2H), 4.68 (t, J = 6.48 Hz, 4H), 1.88 (q, J = 6.57 Hz, 4H), 1.23 (m, 12H), 0.81 (t, J = 6.57 Hz, 6H)

Synthesis of **2H2TIDID-DCV**: **2H2TIDID-DCV** was synthesized by the same synthetic procedure as that for **2HIDID-DCV** by using compound **4** (166 mg, 0.279 mmol), malononitrile (40.6 mg, 0.615 mmol),  $Al_2O_3$  (0.228 g, 2.535 mmol), and DCM (50 mL). The crude product was purified by flash column chromatography (THF) and subsequently by recrystallization (EA) to afford **2H2TIDID-DCV** as dark purple solid (0.189 g, 98%) <sup>1</sup>H-NMR (500MHz, Tetrahydrofuran-d8,  $\delta$ ): 8.23 (s, 2H), 8.01 (d, *J* = 1.5Hz, 2H), 7.98 (d, *J* = 8.5Hz, 2H), 7.86 (d, *J* = 4Hz, 2H), 7.73 (d, *J* = 4Hz, 2H), 7.61 (dd, *J* = 8.5Hz, 1.5Hz, 2H), 4.66 (t, *J* = 7Hz, 4H), 2.00 (q, *J* = 7.5Hz, 4H), 1.45 (q, *J* = 7.5Hz, 4H), 1.38-1.25 (m, 8H), 0.85 (t, *J* = 7.5Hz, 6H). 13C-NMR (500MHz, Tetrahydrofuran-d8,  $\delta$ ):158.93, 151.96, 142.73, 141.77,

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DOI: 10.1039/C6TC02777F Journal Name

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125.19, 119.90, 118.46, 116.19, 115.45, 114.78, 109.18, 45.98,32.70, 31.35, 27.73, 23.57, 14.46. HRMS (FAB, m/z) Calcd. for  $C_{42}H_{38}N_6S_2$ : 690.26; found: 690.2563. Elem. Anal. Calcd. for  $C_{42}H_{38}N_6S_2$ : C 73.01, H 5.54, N 12.16, S 9.28; found: C 73.0165, H 5.5255, N 12.1216, S 9.2924..

Synthesis of 5',5'''-(5,10-dihexyl-5,10-dihydroindolo[3,2b]indole-2,7-diyl)bis([2,2'-bithiophene]-5-carbaldehyde) (5): 5 was synthesized by the same synthetic procedure used for 4 with compound 3 (170 mg, 0.271 mmole), 5'-bromo-[2,2'bithiophene]-5-carbaldehyde (135 mg, 0.569 mmol), tetrakis(triphenylhosphine)palladium(0) (32 mg, 0.027 mmol), 2N K<sub>2</sub>CO<sub>3</sub> aqueous solution (10 mL), and THF (20 mL). The crude product was purified by column chromatography (CHCl3/EA/n-hex; 3:1:6, v/v) and subsequently by recrystallization (EA) to afford compound 4 as red solid (162 mg, 78%). <sup>1</sup>H-NMR (300 MHz, Tetrahydrofuran-d8,  $\delta$ ): 9.83 (s, 2H), 7.90 (d, J = 8.28 Hz, 2H), 7.83 (s, 2H), 7.79 (d, J = 3.9 Hz, 2H), 7.48-7.46 (m, 6H), 7.39 (d, J = 3.9 Hz, 2H), 4.61 (t, J = 6.9 Hz, 4H), 1.98 (q, J = 7.47 Hz, 4H), 1.46-1.25 (m, 12H), 0.49 (t, J = 7.08 Hz, 6H)

Synthesis of 2H4TIDID-DCV: 2H4TIDID-DCV was synthesized by the same synthetic procedure used for 2HIDID-DCV using compound 5 (162 mg, 0.213 mmol), malononitrile (43 mg, 0.640 mmol),  $AI_2O_3$  (0.228 g, 1.921 mmol), and DCM (60 mL). The crude product was purified by flash column chromatography (THF) and subsequently by recrystallization (THF) to afford **2H4TIDID-DCV** as black solid (0.110 g, 60%): <sup>1</sup>H-NMR (500MHz, Tetrahydrofuran-d8, δ): 8.14 (s, 2H), 7.90 (d, J = 8.5Hz, 2H), 7.84 (s, 2H), 7.78 (d, J = 4Hz, 2H), 7.56 (d, J = 3.5Hz, 2H), 7.49 (m, 4H), 7.44 (d, J = 4Hz, 2H), 4.61(t, J = 7Hz, 4H), 2.03 (m, 4H), 1.48 (q, J = 7Hz, 4H), 1.39-1.27 (m, 8H) 0.85 (t, J = 7Hz, 6H). HRMS (FAB, m/z) Calcd. for C<sub>50</sub>H<sub>42</sub>N<sub>6</sub>S<sub>4</sub>: 854.24; found: 854.2363. Elem. Anal. Calcd. for C<sub>50</sub>H<sub>42</sub>N<sub>6</sub>S<sub>4</sub>: C 70.23, H 4.95, N 9.83, S 15.0; found: C 69.8566, H 5.0406, N 9.8086, S 15.0143. (We could not obtain <sup>13</sup>C NMR date due to insufficient solubility of 2H4TIDID-DCV for common NMR solvents such as CDCl<sub>3</sub> or Tetrahydrofuran-d8.)

#### Characterization

Chemical structures of newly synthesized materials were fully identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, (Bruker. Advanced-300 and Advanced-500), GC-Mass (JEOL, JMS-700) and elemental analysis (CE Instrument, EA1110). UV-vis spectra were recorded on a SHIMADZU UV-1650PC. HOMO and LUMO energy levels of organic materials were obtained from the cyclic voltammetry (CV) measurements. CV measurements were performed using a 273A (Princeton Applied Research) with a one-compartment platinum working electrode, a platinum wire counter-electrode, and a quasi Ag+/Ag electrode as a reference electrode. Measurement was performed in a 0.5 mM tetrahydrofuran solution with 0.1M tetrabutylammonium tetrafluoroborate (TBATFB) as a supporting electrolyte, and acetonitrile with 0.1 M TBATFB for film as a supporting electrolyte, at a scan rate of 50 mV/s. Each oxidation and reduction potential was calibrated using ferrocene as a reference. Film surface topologies were obtained by a Bruker

Nanoscope III multimode SPM with tapping mode using TREST cantilever. Out-of-plane X-ray diffraction and powder X-ray diffraction measurement was performed using a Bruker D8-Advance X-ray diffractometer. Two-dimensional grazing incidence X-ray diffraction measurement was performed at the 3C beam-line of Pohang Acceleration Laboratory. Density functional theory (DFT) calculations were performed using Gaussian 09 package B3LYP method with the basis set of 6-31G d p. The *I-V* characteristics of all devices were measured using Keithley 4200 SCS.

#### **OFET device fabrication and measurement**

To prepare the substrates, SiO<sub>2</sub>/Si substrates (p-doped 300 nm) were rinsed with acetone and isopropyl alcohol, sequentially, for 10 minutes in an ultrasonicator, followed by 15 minutes UV (360 nm) O3 treatment. For the thermally evaporated vacuum deposited OFET device fabrication, octadecyltrichlorosilane (ODTS) was treated as self-assembled monolayer (SAM) on prepared substrate to reduce charge trap sites as well as to domain enlargements. ODTS was treated in vapor phase in a vacuum oven; then the substrates were passed into nitrogen filled glove box. 30 nm thick of organic semiconductor active layers were thermally deposited with deposition rate of 0.1 - 0.2 Å s<sup>-1</sup> and different substrate temperature (T<sub>sub</sub>: room temperature, 50, 70, 100, 120, and 140 °C), under a vacuum of  $7 \times 10^{-7}$  Torr. As source and drain electrode, 50 nm thick of gold (Au) was thermally deposited with deposition rate of 0.2 - 0.3 Å s<sup>-1</sup>. For the spin-coated OFET device fabrication, same substrate preparation procedure with VD device was performed. OD2TIDID-DCV were dissolved in chloroform (0.3 - 0.4 weight %), and spin-coated at 1500-3000 rpm for 1 minute in nitrogen filled glove box; then the substrates were annealed with different temperature from room temperature to 150 °C). Source and drain electrode were thermally deposited same condition with VD device fabrication. The I-V 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. For the charge carrier mobility calculations, we checked the channel width and length of the individual devices using an optical microscope.

#### Acknowledgements

This research was supported by the National Research Foundation of Korea (NRF) through a grant funded by the Korean government (MSIP; No. 2009-0081571[RIAM0417-20150013]).

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## Graphical and textual abstract

## Dicyanovinyl-Substituted Indolo[3,2-b]indole Derivatives: Low band-Gap $\pi$ -conjugated Molecules for Single-Component Ambipolar Organic Field-Effect Transistor

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A series of indolo[3,2-b]indole-dicyanovinyl derivatives are prepared to realize ambipolar organic semiconductor. Through cooperative effects of intramolecular charge transfer interaction and conjugation extension, low band-gap  $\pi$ -conjugated molecules are successfully prepared. Among others, 2H2TIDID-DCV and OD2TIDID-DCV exhibit ambipolar charge transport behavior (hole/electron mobilities of 0.08/0.09 and 0.09/0.003 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively) with same molecular packing motif of 3D lamellar  $\pi$ -stacking structure.

