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# Iodine Effect in Ambipolar Organic Field-Effect Transistors Based on Indigo Derivatives

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5,5'-Diiodoindigo (4) exhibits excellent ambipolar transistor properties with the hole/electron mobilities of  $\mu_h/\mu_e = 0.42/0.85$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The halogen substituted indigos show systematically decreasing energy gaps from F to I due to the spreading highest occupied molecular orbitals, and decreasing tilt angles in the crystals. In addition, the iodine-iodine interaction provides extraordinarily large interchain interaction. However, the X-ray diffraction suggests that the indigo molecules are arranged approximately perpendicular to the substrate in the thin films, probably due to the extra iodine-iodine interaction. The remarkable performance is ascribed to this characteristic supramolecular interaction.

## Introduction

Ambipolar organic semiconductors, which exhibit both *p*-type and *n*-type transport, have attracted a great deal of attention due to the potential application to organic photovoltaic devices and organic light-emitting transistors.<sup>1-3</sup> In particular, diketopyrrolo pyrrole (DPP)-based polymers have afforded excellent ambipolar materials, which show hole and electron field-effect mobilities ( $\mu_h$  and  $\mu_e$ ) exceeding 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>2,3</sup> It has been recently reported that even the small-molecule DPP derivatives show ambipolar transport with  $\mu_h/\mu_e = 0.01 \sim 0.06$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>4</sup>

Similarly to the DPP derivatives, indigo shows high ambipolar performance.<sup>5-10</sup> Indigo is a plant-origin dye produced from Indigofera tinctoria and Isatis tintora, which have been cultivated for at least four thousand years for coloring textiles.<sup>6</sup> Because of the strong intermolecular interaction, indigo shows a very high melting point (390~392°C) and an extremely low solubility in common organic solvents together with the ambipolar transport with well-balanced mobilities  $\mu_h/\mu_e = 0.01/0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1.5}$  The amine (-NH) group is electron donating and an origin of the donor ability, and the carbonyl group (-C=O) is electron

withdrawing and an origin of the acceptor ability. However, it is surprising that such a minimal molecule shows ambipolar properties.<sup>11-13</sup> In addition, the intermolecular interaction mediated by the hydrogen bonding (-NH····O=C-) plays an important role in determining the molecular packing.<sup>11,13,14</sup> It has been reported that Tyrian purple (6,6'-dibromoindigo) shows improved ambipolar transport with  $\mu_{\rm b}/\mu_{\rm e} = 0.4/0.4 \ {\rm cm}^2$  $V^{-1}$  s<sup>-1.6,7</sup> We have reported that 5,5'-dibromoindigo (3, Scheme 1) and 5,5'-diphenylindigo exhibit excellent mobilities,  $\mu_{\rm h}/\mu_{\rm e} = 0.21/0.35$  and 0.56/0.95 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively.<sup>9</sup> Compound 3 has one-dimensional stacks basically similar to the parent indigo.<sup>14</sup> In contrast, the diphenyl derivative has a characteristic structure where the phenyl parts are not coplanar to the indigo core to form a herringbone packing, but the indigo core constructs a two-dimensional brickwork packing. Owing to this characteristic structure, the indigo cores are standing perpendicular to the substrate. We have previously reported in naphthalene diimide (NDI) series compounds that the charge mobility attains the maximum when the molecular long axis is perpendicular to the substrate.<sup>15</sup> In this respect, the diphenyl indigo has an ideal structure to realize high mobility, and this is considered to be the origin of the actually observed high



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#### performance.

Recently, several halogen-substituted indigo derivatives have been reported, where the introduction of the halogen atoms (F, Cl, and Br) to the 5-positions (1-3) induces the bathochromic shifts to reduce the energy gaps.<sup>10</sup> In the present work, we show that introduction of iodine atoms, namely 5,5'diiodoindigo (4), remarkably improves the transistor properties. The electrochemical properties, transistor characteristics, crystal structures, and thin-film properties are compared with other halogen-substituted compounds (1-3), and the characteristic role of the iodine atom is demonstrated. Polarizability of a halogen atom increases in the order of F < Cl< Br < I, and iodine shows particularly large polarizability among the halogen atoms. Accordingly, iodine atoms mediate halogen-halogen interactions and halogen bonds, and sometimes construct supramolecular architecture.<sup>16</sup> Halogen bonds have been extensively investigated in the conducting cation-radical salts based on tetrathiafulvalene (TTF) In the charge-transfer salts, a halogen atom derivatives.<sup>17</sup> substituted on the TTF skeleton makes a close contact with such an anion as Cl<sup>-</sup>, Br<sup>-</sup>, and CN<sup>-</sup> to form characteristic molecular packing. It has been also attempted to include the third component such as diiodoacethylene and p-bis(iodo ethynyl)benzene, where the iodine atom makes a contact with Cl<sup>-</sup> and Br<sup>-</sup> anions to construct supramolecular assembly.<sup>17f,g</sup> In the crystals of neutral TTF, it has been demonstrated that the halogen-halogen contact gives a significant effect on the molecular packing.<sup>17a</sup> In this analogy, here we show the iodine substitution produces remarkable supramolecular interaction that improves the transistor performance.

#### **Results and discussion**

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#### Preparation of the indigo derivatives

Although the preparation of **1** - **2** has been recently reported.<sup>10</sup> we have prepared these compounds following a different route (Scheme 1). Compound 4 has been also previously reported through another different route.<sup>18</sup> Compounds 1 - 4 were prepared by starting iodination of 5-halogenoindole (X = F, Cl, Br, and I),<sup>19,20</sup> followed by acetoxy substitution with silver acetate (AgOAc) in acetic acid (AcOH), to afford 5-halogenoacetoxyindole (Scheme 1). Subsequently, the standard coupling reaction in a basic condition gave the target compounds. All compounds were purified by repeated temperature gradient sublimation in the range of 270~350°C, to afford dark blue powders. The blue color came from the small energy gap, and the resulting long-wavelength absorption was closely related to the ambipolar transport.



Fig. 1. Energy levels of 1-4 estimated from the redox potentials and from the Gaussian 09 calculation at the B3LYP/CEP-31G level in the parentheses. The energy gaps are evaluated from the redox potentials  $(E_g^{\text{CV}})$  and the absorption edges  $(E_g^{\text{UV}})$ .



Fig. 2. Structure of an indigo field-effect transistor in bottomgate top-contact geometry, where length (L) and width (W) are 100 and 1000 µm, respectively. A 20 nm of TTC and a 45 nm of indigo derivatives are deposited by vacuum evaporation.

#### **Energy levels**

Fig. 1 lists the highest occupied molecular orbital (HOMO) levels and the lowest unoccupied molecule orbital (LUMO) levels estimated from the redox potentials (Supporting Information). The energy gaps  $(E_g)$  are estimated from the absorption edges of the ultraviolet-visible spectra (UV-Vis) measured in about 20 nm of thin films evaporated on a glass substrate (Fig. S2). HOMO and LUMO of 1-4 are calculated by Gaussian 09 package at B3LYP/CEP-31G level as shown in Fig. 1. In comparison with the parent indigo, the halogen substitution at the 5,5'-positions tends to induce slight bathchromic shifts of the absorption spectra (Table S1).<sup>10,12,21</sup> It has been reported that using gold (Au) source and drain electrodes, ambipolar transport is realized when the HOMO level is > -5.6 eV and the LUMO level is < -3.2 eV.<sup>22</sup> The LUMO levels of these compounds satisfy this condition, but the HOMO levels are located near the boarder of the range.

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Fig. 3. (a) Transfer characteristics, and (b) output characteristics at  $V_{DS} > 0$  of thin-film transistors based on 1. (c) Transfer characteristics, and (d) output characteristics at  $V_{DS} > 0$  of thin-film transistors based on 2. (e) Transfer characteristics, (f) output characteristics at  $V_{DS} < 0$ , and (g) output characteristics at  $V_{DS} > 0$  of thin-film transistors based on 4. All measurements are done under vacuum.

Table 1. Summary of transistor performance of 1-4.

Compound	Maximum mobilities under vacuum $[cm^2 V^{-1} s^{-1}]$		Average mobilities under vacuum $[cm^2 V^{-1} s^{-1}]$		Threshold Voltage [V]	
	Hole	Electron	Hole	Electron	Hole	Electron
<b>1</b> (F)	-	$1.7 \times 10^{-3}$	-	7.6×10 <sup>-4</sup>	-	19
<b>2</b> (Cl)	-	0.022	-	0.012	-	33
<b>3</b> (Br) <sup>9</sup>	0.07	0.04	0.02	0.03	-31	71
<b>4</b> (I)	0.42	0.85	0.16	0.48	-34	15
Indigo <sup>5</sup>	0.01	0.01	-	-	-	-

#### **Transistor characteristics**

The transistors were fabricated on a heavily doped *n*-type silicon substrate (300 nm of SiO<sub>2</sub> as a gate dielectric) with a 20 nm passivation layer of tetratetracontane (TTC,  $C_{44}H_{90}$ , Fig. 2). Long alkyl-chain molecules like TTC were advantageous in ambipolar transport due to the low dielectric constant, reduced polarlization effect, and the improved crystallinity of the semiconductor layer.<sup>23-26</sup> The indigo derivatives of about 45 nm thickness were deposited by vacuum evaporation, on which gold source and drain electrodes were formed to complete the bottom gate – top contact devices. The transfer and output characteristics were measured under vacuum (Fig. 3).

The transfer characteristics of **4** (Fig. 3e) shows clear ambipolar characteristics, which affords very high and wellbalanced mobilities of  $\mu_{\rm h}/\mu_{\rm e} = 0.42/0.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Table 1). The mobilities are extracted from the square root of the drain current ( $I_{\rm D}$ ) in the transfer characteristics. These mobilities are even larger than  $\mu_{\rm h}/\mu_{\rm e} = 0.21/0.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  of **3**, and amount to as large as those of the diphenyl compound ( $\mu_{\rm h}/\mu_{\rm e} =$   $0.56/0.95 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>9</sup> There have been recently reported a few donor-acceptor polymers in which both electron and hole mobilities exceeding 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>,<sup>3</sup> and a pentacene ambipolar transistor whose electron and hole mobilities are 3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>27</sup> However, mobilities of other small-molecule ambipolar transistors are still lower than 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, and the present values of **4** are one of the highest among the small-molecular ambipolar materials.<sup>3</sup> The electron and hole threshold voltages are estimated to be 15 V and -34 V, respectively (Table 1). These values are also consistent with the flat regions of the output characteristics (Fig. 3f and g).<sup>9,28</sup> Since the difference usually exceeds 100 V, the small difference (49 V) is characteristic of the present ambipolar transistor.

Compounds 1 and 2 show only *n*-type transport, where the maximum mobilities are  $\mu_e = 1.7 \times 10^{-3}$  and 0.022 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. This is in agreement with the electronegative nature of 1 and 2.<sup>10</sup>  $V_{\rm TH}$  of 1 and 2 are estimated to be 19 V and 33 V, respectively. The mobility decreases in the order of 4 (I) > 3 (Br) > 2 (Cl) > 1 (F), which is opposite to the electronegativity, but equal to the halogen size and the

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polarizing power. The order of mobility also coincides with the decreasing order of  $E_g$  (Fig. 1).

#### **Crystal structures**

Crystal structures of 1 and 3 have been recently reported.<sup>9,10</sup> Here, we show our data of crystal structures of 2 and 4 that are investigated by single-crystal X-ray structure analyses for comparison with the crystal structures of 1 and 3. Due to the poor solubility of these compounds in organic solvents, the crystals were grown by the sublimation method. Although all crystals belong to the same monoclinic space group  $P2_1/c$ (Table S2), only 2 and 3 are strictly isostructural, and 1 and 4 are different from these structures. In all cases, the stacking direction corresponds to the crystallographic b axis, and the molecular long axis is basically parallel to the *a* axis. However, the arrangements of the stacks are obviously different (Fig. 4). The interplanar spacing  $\Delta$  increases as the size of the halogen substituent increases (Table 2); the difference is very slight from 1 to 3, but 4 has a significantly large  $\Delta$ . The stacks are connected by hydrogen bonds with the N…O distance of 2.9 Å and the H…O distance of 2.1 Å in 4.14,29-32 For 1, hydrogen bonding F...H with the distance of 2.464 Å is found between the adjacent molecules along the molecular long axis (Fig. 4a).

By contrast, no interaction is found in 2 along the molecular long axis. However, short halogen-halogen contacts with the distances of 3.611 Å and 3.875 Å are observed in 3 and 4 along the molecular long axis (Fig. 4b). These values are 2.4% and 2. 2% shorter than the sum of the van der Waals radius (3.70 Å for Br…Br and 3.96 Å for I…I).<sup>17,33</sup> In comparison with **3** that shows one intermolecular Br ... Br contact, 4 has two intermolecular I...I contacts (Fig. 4d and 4e). These halogenhalogen contacts connect molecules of different conducting layers along the *a* axis. Along the *c* axis, the adjacent stacks are alternately tilted in the opposite directions (Fig. 4b). The dihedral angle between the adjacent molecules ( $\alpha$ ) and the tilt angle of the molecular long axis from the direction vertical to the stack direction ( $\beta$ , Fig. 4c) are summarized in Table 2. These angles monotonously decrease from 1 to 4. Since the molecules are slightly inclined from the stacking direction along the molecular short axis,  $\alpha = 2\beta$  does not hold except for 1. The molecular lengths l of 1-4 are estimated from the crystallographic *a* and the tilt angle  $\beta$  from  $l = a / \cos \beta$  (Table 2). The lattice constant b also decreases in the same order as  $\alpha$ and  $\beta$ , 6.0281 Å > 4.54025 Å > 4.462 Å > 4.38905 Å. This implies that the molecule in 4 is most close to perpendicular to the stacking direction. The lattice constants b of 2 to 4 are considerably smaller than the parent indigo, b = 5.77-5.88 Å



Fig. 4. Crystal structures of 1-4 viewed along the (a) *c* and (b) *b* axes. (c) Schematic illustration of the stacking structure. Halogen-halogen contacts of (d) 3 and (e) 4. The distances are 3.611 Å and 3.875 Å, respectively.

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(depending on the polymorphism),  $^{9,11,29\cdot32}$  indicating that the molecular long axis is less tilted from the stacking direction, and this is an origin of the enhanced mobility. However, the molecules of **4** are still by  $34^{\circ}$  tilted from the stacking direction, in contrast to the exactly perpendicular packing in the diphenyl indigo. Nonetheless, the mobilities are not much different from those of the diphenyl derivative. The high performance of **4** is not entirely attributable to the preferable crystal packing, and we have to assume a special effect of the iodine atoms.

The transfer integrals in the stacking (*b*) direction for HOMO and LUMO ( $t_{HOMO}/t_{LUMO}$ ) are estimated from the molecular orbital calculation as shown in Table 2. In **4**, the LUMO affords a large transfer, whereas the HOMO gives a small transfer. In addition, **4** has a particularly large transfer integral between halogen-halogen atoms,  $t_{X-X, HOMO} = 6.89$  meV along the molecular long axis (Fig. 4e). This is obviously due to the I···I interaction; the HOMO is most seriously influenced because the HOMO spread to the iodine atoms considerably (Fig. 1). Since this interstack interaction is comparable to the intrastack interaction in magnitude, there is a possibility that the charge transport of **4** is not confined in the stacking (*b*) direction.

#### Thin film properties

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Atomic force microscopy (AFM) images and X-ray diffraction (XRD) peaks of the thin films deposited on a TTC layer are shown in Fig. 5. The thin films of **1-4** consist of highly crystalline domains due to the strong intermolecular interactions, although the domain size is comparatively small. The crystalline nature is enhanced by the TTC passivation layer, because it has been reported in a wide variety of organic semiconductors that the crystallinity is improved on TTC. Accordingly, TTC plays a crucial role in the high mobility as well as the ambipolar charge transport. In particular, the thin film of **4** is densely and smoothly packed.

Fig. 5e shows X-ray diffraction (XRD) peaks. Several peaks coming from TTC appear below 5°, which prove highly crystalline and standing alignment of the TTC molecules.<sup>34</sup> The  $2\theta$  value coming from the indigo derivatives decreases systematically from 1 to 4, and the corresponding *d*-value increases as shown in Table 2. The *d*-values of 2 and 3 approximately coincide with the crystallographic *a* axis. Thus the thin-film molecular packing is considered to be the same as the crystal structure. However, the *d*-values of 1 and 4 are larger than the crystallographic axes (8.249 Å and 14.0666 Å), indicating the molecules are less tilted from the vertical direction in the thin films than in the crystals. In order to discuss this point more quantitatively, the molecular tilt angle in the

Compound	$1 (F)^{10}$	<b>2</b> (Cl)	<b>3</b> (Br) <sup>9</sup>	<b>4</b> (I)				
$\Delta$ (Å)	3.37	3.38	3.39	3.42				
α (°)	112	84	81	78				
Jable 2. Parameters extracted from the crystal and thin-film strugtures								
<i>l</i> (Å)	14.8	16.7	17.1	17.0				
$t_{\rm HOMO}/t_{\rm LUMO}~({\rm meV})$	11.8/39.2	12.2/12.6	12.4/21.0	2.96/35.3				
$t_{X-X, HOMO} \text{ (meV)}$	0.040	1.16	1.83	6.89				
2θ (°)	7.85	6.79	6.49	5.17				
d (Å)	11.2	13.0	13.6	17.1				
β'(°)	41	39	37	0				

thin film ( $\beta$ ', Fig. 5f) is calculated from  $l = d / \cos \beta$ ', where l is the molecule length estimated from the crystal structure (Table 2).  $\beta$ ' decreases in the same order as  $\alpha$  and  $\beta$ . The  $\beta$ ' values for 2 and 3 are not largely different from the  $\beta$  values in the crystals. However, the values for 1 and 4 are significantly smaller than those in the crystals. In particular, **4** shows nearly perpendicular arrangement ( $\beta' = 0^\circ$ ). Correlation of  $\beta$ ' and the maximum electron mobility (Table 1) is depicted in Fig. 5f.<sup>5,7,9</sup> Mobilities of not only the present compounds but also the parent indigo, 5,5'-diphenylindigo, and 6,6'dibromoindigo show satisfactory correlation with the tilt angle in the thin films. This reminds us the naphthalene diimide (NDI) series compounds, where the charge mobility attains the maximum when the molecular long axis is exactly perpendicular to the substrate.<sup>9,15</sup> It has been recently reported that the tilt angle of unsubstituted indigo is much reduced in a thin film on an inert layer.<sup>35</sup> Without assuming the thin-film structure different from the crystal structure, we have to attribute the high performance of 4 to the anomalous iodine-iodine electronic interaction coming from  $t_{X-X, HOMO}$ . It is, however, more plausible that the iodine-iodine interaction changes the thin-film structure, and the resulting perpendicular molecular arrangement realizes the high ambipolar performance comparable to the diphenyl derivative.



**Fig. 5.** AFM images of thin films of a) **1**, b) **2**, c) **3**, and d) **4**. e) XRD patterns of **1-4**. f) Correlation of the maximum electron mobility with the tilt angle of the molecule long axis to the substrate ( $\beta$ ') of **1-4**, indigo, 6,6'-dibromoindigo, and 5,5'-diphenylindigo.

#### Conclusion

In summary, we have investigated iodine introduction effect at the 5-position of indigo. The diiodo-indigo **4** shows excellent ambipolar transistor properties,  $\mu_h/\mu_e = 0.42/0.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which are comparable to those of the diphenyl derivative. The iodine-iodine interaction affords an extra interchain transfer integral as large as 6.89 meV in the crystal, which is comparable to the intrachain interaction. However, the systematic change of the thin-film *d*-value suggests a nearly perpendicular molecular arrangement achieved in the thin film. In this case, the iodine-iodine interaction is suspected to play an important role. Since iodine-iodine contacts are universally

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observed in organic crystals, such supramolecular assembling power is indispensable to achieve the exceptional packing pattern in the indigo derivative. The present finding demonstrates that supramolecular engineering mediated by halogen-halogen interaction has great possibilities in organic semiconductors.

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# Notes and references

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<sup>†</sup> Electronic supporting information (ESI) available: CCDC 1042518 contains the supplementary crystallographic information for **4**. Additional information of synthesis, redox properties, UV-vis spectra, single crystal structures, and device fabrication.

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#### The table of contents entry

## Title

Iodine effect in ambipolar organic field-effect transistors based on indigo derivatives

# Text

5,5'-Diiodoindigo exhibits excellent ambipolar transistor properties with the hole/electron mobilities of  $\mu_h/\mu_e = 0.42/0.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

Keywords

organic transistor, organic semiconductor, ambipolar

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ToC figure (maximum size 8 cm x 4 cm)



 $\mu_{\text{h}}/\mu_{\text{e}}$  : 0.42/0.85  $\text{cm}^2~\text{V}^{-1}~\text{s}^{-1}$