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## Ambipolar organic field-effect transistors based on *N*-Unsubstituted thienoisoindigo derivatives

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#### ABSTRACT

To investigate a hybrid of isoindigo and thienoisoindigo (TIIG), a new series of unsymmetrical TIIG analogs, in which one of the outer thiophene rings of TIIG is replaced by benzene (CS) or pyridine (NS) are prepared. In addition, the  $\pi$ -skeleton extension effects are studied by examining  $\alpha$ -substituted TIIG derivatives with thienyl (Dth-TIIG), furyl (Dfu-TIIG), and 1-phenyl-5-pyrazolyl groups (Bis(1-ph-5-py)-TIIG). These materials exhibit ambipolar transistor properties as expected from the energy levels. Dth-TIIG and Dfu-TIIG show hole mobilities exceeding 0.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, and electron mobilities about 0.04 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which are close to those of the diphenyl derivative. These molecules are arranged nearly perpendicularly to the substrates in the thin films, and Dth-TIIG has a brickwork-like structure, whereas Dfu-TIIG has uniform columns. CS and Bis(1-ph-5-py)-TIIG have uniform stacking structures, but NS has a dimerized stacking structure due to the slightly bent molecular plane that results from largely unbalanced electron density.

#### 1. Introduction

Ambipolar organic semiconductors (OSC) are capable of conducting both holes and electrons particularly in organic transistors [1,2]. In practice, however, unipolar transport dominates when OSCs are applied in organic transistors because of the charge traps and existence of the injection barriers between electrodes and molecular frontier orbitals [3–5]. Therefore, it is necessary that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have to fulfill relatively strict conditions to achieve ambipolar transport [6,7]. For more than a decade, OSCs showing ambipolar transport have been extensively investigated to identify their carrier-transport mechanism [8–10], and to develop applications to inverters and light-emitting field-effect transistors. In these semiconductors, p-type and n-type transporting properties are integrated into a single component [11,12]. Numerous OSCs have been designed and devised for ambipolar transport [13]; they include small energy-gap organic small molecules [9, 14–21], donor-acceptor (DA) polymers [22–28], mix-stacked DA-type charge-transfer complexes [29–35], and metal complexes [36–38]. Among them, organic small molecules are composed of a single component, but others consist of more than two components. In principle, organic small molecules that show ambipolar transport can be designed by engineering the energy levels and energy gaps, but this is a difficult task. To achieve appropriate energy levels with suitable HOMO levels and low-lying LUMO levels, it is necessary to introduce both electron-donating and electron-withdrawing groups. From this point of view, indigo and isoindigo, which is a structural isomer of indigo, are promising materials because the amino and carbonyl groups realize

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well-balanced ambipolar transport in organic field-effect transistors (OFET) [14,18,39,40]. Substituting thiophene for the benzene ring of isoindigo yields thienoisoindigo (TIIG), and this molecule has oxygen-sulfur (S···O) intramolecular interactions that stabilize the molecular planarity. In addition, because of the sulfur atom, the intermolecular sulfur-sulfur (S···S) interactions are expected to lead to efficient carrier transport [41]. Therefore, TIIG has been extensively investigated by varying the *N*-alkyl chains as OFET materials and as repeating units in conjugated polymers [42–50].

*N*-unsubstituted **TIIG**s with diphenyl groups (**Dph-TIIG**) exhibit ambipolar transport with hole and electron mobilities exceeding 0.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> [21]. Removal of *N*-alkyl chains allows S...S interactions and hydrogen bonds, which together tighten the molecular packing. Actually, **Dph-TIIG** forms a two-dimensional conduction path due to the combination of the core-part brickwork and the phenyl-part herringbone arrangements [21]; this configuration is advantageous for transistor properties [9].

Here, to further investigate substitution effects from isoindigo to TIIG in more detail, we have prepared unsymmetrically-substituted TIIG analogs in which one of the outer thiophene rings of TIIG is replaced by benzene (thieno-benzo-isoindigo, CS) or pyridine (thienopyridine-isoindigo, NS) (Scheme 1). We then quantified how the substitutions affected changes of the energy levels, crystal structures, and transistor properties. Although these are unsymmetrical molecules, CS with N-alkyl chains has been previously synthesized as a monomer unit of a DA copolymer that has fine backbone coplanarity [51]. This copolymer has a face-on orientation so it is favorable for use in organic photovoltaics, but CS without the N-alkyl substituent chain has not been investigated as a small-molecule OSC. Furthermore, Dph-TIIG has realized a favorable molecular packing, so other substituents are investigated: three  $\alpha$ -substituted TIIG derivatives, dithienyl-TIIG (Dth-TIIG), difuryl-TIIG (Dfu-TIIG), and bis(1-phenyl-5-pyrazolyl)-TIIG (Bis(1-ph-5-py)-TIIG) are designed for use in extending the  $\pi$ -skeleton. In this paper, we report the crystal structures and OFET properties of these five N-unsubstituted TIIG derivatives.



Scheme 1. Chemical structures of (a) TIIG [21], (b) CS, (c) NS, (d) Dph-TIIG [21], (e) Dth-TIIG, (f) Dfu-TIIG, and (g) Bis(1-ph-5-py)-TIIG.

#### 2. Experimental section

#### 2.1. Synthesis

*t*-Boc-thienoisatin and compound **2** were prepared according to the previous report [21,52]. **CS** and **NS** were prepared by cross coupling of *t*-boc-thienoisatin with oxindole or Compound **2** (Scheme 2). These reactions are kinds of aldol condensation, and hydrochloric acid was used as a catalyst. Therefore, the *t*-boc groups were removed concurrently during the coupling reactions.

*t*-Boc-**dBr-TIIG** was prepared according to the previous report [21], and **Dth-TIIG**, **Dfu-TIIG**, and **Bis(1-ph-5-py)-TIIG** were prepared by the Stille coupling reaction (Scheme 3), followed by removal of *t*-boc groups by using trifluoroacetic acid.

#### 2.2. Device fabrication

Thin-film transistors were fabricated onto n-doped Si substrates with a thermally-grown SiO<sub>2</sub> (300 nm,  $C = 11.5 \text{ nF/cm}^2$ ) dielectric layer. The SiO<sub>2</sub> surface was passivated with 20 nm thick layer of tetratetracontane (C<sub>44</sub>H<sub>90</sub>, **TTC**,  $\varepsilon = 2.5$ ), by thermal deposition under a vacuum of  $10^{-3}$ Pa [53–55]. The resulting overall capacitance of the gate dielectrics was 10.4 nF/cm<sup>2</sup> [56]. A 50 nm thick active layer was formed by thermal deposition under a vacuum of  $10^{-3}$  Pa. Then the top-contact electrodes were patterned by thermal deposition of Au through a shadow mask; the channel had width  $W = 1000 \ \mu m$  and length  $L = 100 \ \mu m$ . OFET properties were measured using a Keithley 4200 semiconductor parameter analyzer under a vacuum of  $10^{-3}$  Pa. The field-effect mobility  $\mu$  and threshold voltage  $V_{\rm T}$  were calculated in the saturation regime by using the equation,  $I_{\rm DS} = \mu (WC_{\rm i}/(2L))(V_{\rm G} - V_{\rm T})^2$ , where  $I_{\rm DS}$  is drain current and  $V_{\rm G}$  is gate voltage;  $\mu$  is extracted from the slope where the plot of  $\sqrt{I_{\rm DS}}$  vs.  $V_{\rm G}$  is straight. We attempted to make the single-crystal transistors, but the characteristics were not observed.

#### 2.3. DFT calculation

The density functional calculations such as geometry optimization, calculation of transfer integrals t, and calculation of reorganization energies were performed with the B3LYP\* functional and TZP basis set using ADF software [57].



Scheme 2. Synthetic scheme to CS and NS.



Scheme 3. Synthetic scheme of the α-substituted TIIG derivatives.

#### 3. Results and discussion

#### 3.1. Electronic properties

The HOMO and LUMO levels were estimated by using cyclic voltammetry and ultraviolet visible (UV-vis) absorption spectroscopy. Dth-TIIG and Bis(1-ph-5-py)-TIIG in DMF solutions exhibited reversible oxidation waves, whereas CS, NS, and Dfu-TIIG showed irreversible oxidative peaks (Fig. 1a and b). The HOMO levels were estimated from the oxidation onset potentials  $E_{onset}$ . The optical energy gaps  $E_{\sigma}^{opt}$  were estimated from onset wavelength  $\lambda_{onset}$  of the DMF solution absorption spectra (Fig. 1c and d), and the LUMO levels are estimated by adding  $E_{\alpha}^{opt}$ to the HOMO levels. The energy levels (Table 1 and Fig. 2) deepen in the order of **TIIG** < **CS** < **NS** according to the order of electron-withdrawing ability of thiophene < benzene < pyridine. The HOMO and LUMO levels of CS and NS are by about 0.1 eV deeper than those of TIIG. The optical energy gaps of the three  $\alpha$ -substituted TIIG derivatives are smaller than those of **CS** and **NS** because of the extended  $\pi$ -skeleton. The acceptor abilities of Dth-TIIG and Dfu-TIIG are comparable to those of CS and NS, whereas the donor abilities are obviously improved, even in comparison with **Dph-TIIG**. **Dth-TIIG** and **Dfu-TIIG** have identical  $E_{\sigma}^{\text{opt}}$ , but



Fig. 1. Cyclic voltammograms of (a) CS and NS, and (b)  $\alpha$ -substituted TIIG derivatives. UV–vis absorption spectra of (c) CS and NS, and (d)  $\alpha$ -substituted TIIG derivatives in DMF solutions.

**Bis(1-ph-5-py)-TIIG** has slightly larger  $E_g^{opt}$  than **Dth-TIIG** and **Dfu-TIIG** because of the torsion angle of the pyrazolyl planes against the central TIIG plane. When gold is used as electrodes, hole transport is expected when the HOMO level is higher than -5.6 eV, and electron transport appears when the LUMO level is lower than -3.15 eV [6,7]. The observed energy levels indicate that these compounds are expected to exhibit ambipolar OFET properties (Fig. 2). The absorption bands of the thin film undergo bathochromic shift due to the intermolecular interactions in the solid state (Fig. S1 and Table S1).

#### 3.2. Crystal structures

Detailed crystal data were obtained for all five compounds (Table 2). **CS** crystallizes in the space group  $P2_1/c$ , in which one molecule is crystallographically independent (Fig. 3), and **CS** has an intramolecular S…O interaction with the distance of 2.760(5) Å, which guarantees planar structure (Fig. 3a). **CS** forms a uniform stacking structure along the *b* axis with interplanar spacing of 3.34 Å, and with adjacent columns in the *c* axis direction tilted in opposite directions (88°) (Fig. 3b and c). An S…S short contact with the distance of 3.444(2) Å is observed along the *a* + *c* axis (Fig. 3d), and hydrogen bonds with length around 2.82 Å for N(H)…O are observed between adjacent columns along the *c* axis. Although intermolecular interactions occur, **CS** constructs a one-dimensional conduction path along the stacking direction, which is represented in the values of the transfer integrals in Fig. 3e and Table 3.

The crystal structure of NS (thieno-pyridine-isoindigo) is isostructural to benzo-pyridine-isoindigo [18]. NS crystallizes in a triclinic system (Fig. 4), in which two molecules (1 and 2) are crystallographically independent (Fig. 4a-d). Molecules 1 and 2 have intramolecular S...O interactions with the distance of 2.682(4) and 2.691(4) Å, respectively (Fig. 4a). Molecules 1 and 2 construct independent conducting layers (Fig. 4e-h). Within the layers, these molecules have hydrogen bonds with the adjacent molecules; N(H)...O: 2.869(6) Å and N(H)...N: 2.868(6) Å for Molecule 1, and N(H)...O: 2.867(6) Å and N (H)…N: 2.884(6) Å for Molecule 2 (Fig. 4c and d). Between these layers, the molecules are tilted in opposite directions with a mutual dihedral angle of 88°, between which intermolecular S…O interactions with the distance of 3.197(4) Å are formed (Fig. 4b). Despite the intramolecular S…O interaction, the NS molecules are considerably bent (Fig. 4e and f), possibly because of largely unbalanced electron density that results from the remarkably different electron-donating and electron-withdrawing abilities of the thiophene and pyridine rings. The twist angles are 9.3° for Molecule 1 and  $10.5^{\circ}$  for Molecule 2. Therefore, concave and convex molecules are alternately stacked in a column, so slight dimerization occurs. The transfer integrals (Fig. 4g and h and Table 4) indicate that within the intradimer pair ( $t_{a1}$  and  $t_{b1}$ ), the molecules are slightly slipped along the molecular short axis, whereas for the interdimer interactions

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#### Table 1

Summary of electrochemical and optical properties.

Compound	$E_{\text{onset}}$ (V)	$E_{\rm HOMO}$ (eV)	$\lambda_{\text{onset}}$ (nm)	$\lambda_{\max}$ (nm)	$E_{\rm g}^{\rm opt}$ (eV)	$E_{\rm LUMO}$ (eV)
CS	0.45	-5.25	613	381, 512	2.02	-3.23
NS	0.47	-5.27	614	368, 511	2.02	-3.25
Dph-TIIG [21]		-5.11			1.79	-3.32
Dth-TIIG	0.19	-4.99	716	370, 619, 659	1.73	-3.26
Dfu-TIIG	0.17	-4.97	715	328, 617, 662	1.73	-3.24
Bis(1-ph-5-py)-TIIG	0.36	-5.16	682	335, 593	1.82	-3.34



Fig. 2. Energy levels of CS, NS and α-substituted TIIG derivatives with TIIG and Dph-TIIG [21]. Values in the parentheses are obtained using ADF calculation.

Table 2					
Crystallographic	data	of the	five	compounds	tested

	CS	NS	Dth-TIIG	Dfu-TIIG	Bis(1-ph-5-py)-TIIG
Chemical formula	$C_{14}H_8N_2O_2S$	$C_{13}H_7N_3O_2S$	$C_{20}H_{10}N_2O_2S_4$	$C_{20}H_{10}N_2O_4S_2$	$C_{30}H_{18}N_6O_2S_2$
Formula weight	268.29	269.28	438.55	406.43	558.63
Crystal system	monoclinic	triclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	P-1	Сс	P-1	$Pna2_1$
a (Å)	15.7745(4)	7.45322(14)	11.2237(2)	4.69727(9)	32.9717(12)
b (Å)	4.72502(12)	7.57431(14)	11.0897(2)	14.6021(3)	4.6935(2)
c (Å)	15.5424(4)	20.1443(4)	30.5522(5)	15.1633(3)	16.1986(7)
α (°)	90	100.7500(11)	90	71.6590(9)	90
β (°)	94.2498(15)	95.8199(10)	96.6100(10)	83.8198(9)	90
γ (°)	90	90.6023(10)	90	89.0535(8)	90
V (Å <sup>3</sup> )	1155.26(5)	1110.98(4)	3777.48(11)	981.31(3)	2506.78(18)
Ζ	4	4	8	2	4
Total refls.	12212	13173	21225	11377	26882
Unique refls. (R <sub>int</sub> )	2025 (0.0985)	3982 (0.0529)	6699 (0.0557)	3519 (0.0421)	4589 (0.0885)
$D_{\rm calc}$ (g/cm <sup>3</sup> )	1.542	1.610	1.542	1.375	1.480
$R_1^a$	0.0994	0.0665	0.0952	0.0523	0.0777
$R_{\rm w}^{\rm b}$	0.3130	0.2382	0.2927	0.1653	0.2199
GOF	1.127	1.148	1.174	1.155	1.068
<i>T</i> (K)	104	171	275	104	171

<sup>a</sup>  $R_1[F^2 > 2\sigma(F^2)].$ 

<sup>b</sup>  $wR_2(F^2)$  for all observed reflections.

( $t_{a2}$  and  $t_{b2}$ ), the molecules are considerably slipped along the molecular long axis. Consequently, **NS** constructs a dimerized one-dimensional conduction path (Fig. 4e and f).

The **Dth-TIIG** molecules assume two disordered orientations that are connected by a two-fold axis along the molecular long axis (Fig. 5a).

Two crystallographically-independent Molecules 1 and 2 have the same kind of disorder, in which the ratio of the main and flipped molecules is 3:1. To avoid confusion, only the main molecules are depicted in the following description. Molecules 1 and 2 have intramolecular S…O interaction with the distance of about 2.8–2.9 Å, which result in a planar



Fig. 3. (a) Crystal structure of CS viewed along the b axis. (b) Molecular overlap mode. (c) Crystal structure viewed along the c axis. (d) Molecular network with intermolecular interactions. (e) Crystal structure viewed along the molecular short axis (Columns 2 and 4 are omitted for clarity). Distances in (a) and (d) are in angstroms.

Table 3 Transfer integrals of CS.

t (meV)	t <sub>b</sub>	t <sub>p</sub>	$t_{ m q}$	tr
HOMO LUMO	-44.2 53.6	2.56 18.5	$\begin{array}{c} 0.80 \\ -0.82 \end{array}$	$1.98 \\ -1.07$

TIIG skeleton (Fig. 5b). However, the  $\alpha$ -substituted thiophenes are twisted from the TIIG plane by about 12–14° for Molecule 1 and by about 8–11° for Molecule 2 (Fig. 5b and c); these observations agree with the results from ADF calculation (Supplementary data). The outer thiophene sulfur atom points to the opposite side relative to the inner thiophene sulfur atom. Hydrogen bonds are formed between the parallel molecules with the distance of about 2.77(2) ~ 2.87(2) Å for N(H)…O (Fig. 5d and e). The molecules in a column are considerably slipped along the molecular short axis, and constitute a brickwork structure (Fig. 5f), where the molecular layers are parallel to the *ab* plane (Fig. 5g). Within the same layer, Molecules 1 are aligned in the same horizontal level, and Molecules 2 construct the next level above and below the layer of Molecules 1 (Fig. 5f). The repetition of Molecules 1 is

associated with the *C*-centered lattice. These molecular layers are stacked along the *c* axis, in which the adjacent layers are alternately tilted in reverse directions, similarly to **Dph-TIIG** (Fig. 5g) [21]. Contrary to the ideal brickwork structure [21,58], the transfer integrals are not uniform (Table 5), because two kinds of Molecules are present.

Dfu-TIIG crystallizes in a triclinic system (Fig. 6), in which two units of half molecules are crystallographically independent. This molecule has similar intramolecular S…O interactions with the distance of 2.866 (2) Å for Molecule 1 and 2.802(2) Å for Molecule 2 (Fig. 6a and b), which yield a planar TIIG skeleton. The  $\alpha$ -substituted furans in **Dfu-TIIG** are arranged almost in the identical planes to the TIIG skeletons, where the furan oxygen atoms are located on the same side as the thiophene sulfur atoms (Fig. 6a and b); this arrangement is different from Dth-TIIG, and is a result of the intramolecular attractive force between the sulfur and oxygen atoms even though a short contact between these species is not observed. The stacked molecules are slipped along the molecular short axis as well as along the molecular long axis, and form a uniform stacking structure (Fig. 6c). Molecules 1 and 2 construct respectively independent columns. The adjacent columns along the c axis are tilted by about 85° (Fig. 6d), in which hydrogen bonds with the distance of about 2.725(3) ~ 3.015(3) Å are formed between N(H)...O of



Fig. 4. (a) Molecular structure of NS. (b) Molecular network with the intermolecular interactions. (c) Hydrogen bonds in the Molecule 1 and (d) Molecule 2 layers. Crystal structure viewed along the molecular short axis of (e) Molecule 1 and (f) Molecule 2. Crystal structure viewed along the molecular long axis of (g) Molecule 1 and (h) Molecule 2. All distances are in angstroms.

Molecules 1 and 2 (Fig. 6e). Consequently, **Dfu-TIIG** forms a relatively planar molecular structure, and these molecules construct a one-dimensional conduction path with interplanar spacing of 3.37 Å along the *a* axis (Fig. 6f and g). The calculated transfer integrals also indicate that the conducting path is one-dimensional (Table 6).

Bis(1-ph-5-py)-TIIG crystallizes in an orthorhombic system with the

space group *Pna*2<sub>1</sub>, in which one molecule is crystallographically independent (Fig. 7). This molecule has intramolecular S…O interactions with distances of 2.796(9) and 2.86(1) Å in the TIIG skeleton, like **Dth-TIIG** and **Dfu-TIIG** (Fig. 7a). The torsion angles of the pyrazolyl planes against the TIIG plane are 20.0° and 32.2°, respectively, and the phenyl groups are twisted by 55.4° and 50.5° (Fig. 7b). The bulky substituents

### Table 4

	t (meV)	t <sub>a1</sub>	t <sub>a2</sub>	t <sub>b</sub>	t <sub>r1</sub>	t <sub>r2</sub>
Molecule 1	HOMO	3.50	58.6	7.51	-8.75	-1.16
	LUMO	34.1	39.6	-11.4	5.71	2.47
	t (meV)	t <sub>b1</sub>	$t_{b2}$	ta	t <sub>q1</sub>	$t_{q2}$
Molecule 2	HOMO	8.46	55.3	7.50	-8.37	-1.16
	LUMO	22.8	38.9	-12.9	5.67	2.50

interrupt the intermolecular interactions, so **Bis(1-ph-5-py)-TIIG** forms a uniform stacking structure with interplanar spacing of 3.27 Å, in which the molecules are slipped along the molecular long axis and the short axis (Fig. 7c and d). A few hydrogen bonds form between the nitrogen of the pyrazole and the amino groups of the TIIG skeleton (Fig. 7e), but this molecule constructs a one-dimensional conduction path along the *b* axis in the crystal (Fig. 7 caption).

In summary, the brickwork structure of **Dph-TIIG** is maintained in **Dth-TIIG**, although with lowered symmetry. Although molecular flipping disorder is observed, the brickwork structure is analogous to **Dph**-

**TIIG.** The structure of **Dth-TIIG** is similar to the monomer unit in polymers composed of **TIIG** and thiophene, the present finding suggests the possibility that the  $\pi$ -stacking structure is maintained also in such polymers despite the disordered main chains. By contrast, **CS**, **Dfu-TIIG**, and **Bis(1-ph-5-py)-TIIG** have uniform stacks, whereas **NS** has a dimerized column due to the nonplanar molecule. In general, unsymmetrically pyridine-condensed isoindigo analogs adopt a nonplanar molecular structure owing to the unbalanced electron density, although symmetrically pyridine-condensed isoindigo forms a planar molecular structure [59].

Table 5		
Transfer	integrals	of Dth-TIIG.

<i>t</i> (meV)	t <sub>a1</sub>	t <sub>a2</sub>	t <sub>b1</sub>	t <sub>b2</sub>	t <sub>r1</sub>	t <sub>r2</sub>
HOMO	-25.6	-24.7	-24.5	-23.5	8.23	8.19
LUMO	24.1	22.6	25.7	20.6	8.18	5.51



**Fig. 5.** (a) Molecular structure of **Dth-TIIG**; the major molecules are bonded and the minor molecules are non-bonded. (b) Intermolecular hydrogen bonds in **Dth-TIIG**, and (c) a view along the molecular short axis. (d) Hydrogen bonds of Molecules 1 and (e) Molecules 2. Crystal structure viewed (f) along the molecular long axis and (g) along the *a* axis. For clarity, the minor molecules are omitted except in (a). Distances in (b) are in angstroms.



**Fig. 6.** Molecular structure of **Dfu-TIIG** for (a) Molecule 1 and (b) Molecule 2. (c) Molecular overlap mode. Crystal structure viewed (d) along the *c* axis and (e) along the *a* axis. Crystal structure viewed (f) along the molecular long axis of Molecule 1 and (g) along the molecular long axis of Molecule 2. Distances in (a), (b), and (e) are in angstroms.

Table 6
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Transfer integrals of Dfu-TIIG.

	8				
t (meV)	t <sub>a1</sub>	t <sub>a2</sub>	t <sub>c1</sub>	t <sub>c2</sub>	$t_{c3}$
HOMO	-27.1	-15.4	-0.92	0.84	10.4
LUMO	16.0	22.5	2.49	1.43	-5.18

#### 3.3. Thin film properties

To investigate the thin-film morphologies and the molecular orientation, X-ray diffraction (XRD), and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out (Fig. 8). All thin films except for **Bis(1-ph-5-py)-TIIG** show sharp XRD peaks (Fig. 8a and b), and the extracted *d* values are in good agreement with the out-ofplane *d*-spacings of GIWAXS. In the in-plane ( $q_z = 0$ ) GIWAXS, **NS** exhibits a single peak; the other thin films show only the in-plane peaks of TTC.

In **CS** thin films, XRD results estimate the *d*-spacing as 10.7 Å, which is close to  $q_z = 0.58$  Å<sup>-1</sup> (= 10.8 Å) in the GIWAXS pattern (Fig. 8c).

These values correspond to half of |a+c| (10.7 Å); this similarity indicates that the (101) plane is aligned parallel to the substrate (Fig. S6). Therefore, the molecules are oriented in the side-on arrangement, in which the molecular tilt angle is 25° from normal to the substrate.

In **NS** thin films, XRD results estimate the *d*-spacing as 10.1 Å, which corresponds to  $q_z = 0.62 \text{ Å}^{-1} (= 10.1 \text{ Å})$  in the GIWAXS pattern (Fig. 8d). This value is very close to  $(c/2) \cdot \sin(\alpha) \cdot \sin(\beta)$  (=9.8 Å) of the crystal lattice, and the peak observed in the in-plane GIWAXS pattern at  $q_{xy} = 0.84 \text{ Å}^{-1} (= 7.45 \text{ Å})$  corresponds to the crystallographic *a* axis (7.45 Å). These observations indicate that the crystallographic *ab* plane is aligned parallel to the substrate (Fig. S7). Therefore, the molecular tilt angle is 11° from the substrate normal in the edge-on orientation.

In **Dth-TIIG** thin films, the *d*-spacing extracted from XRD is 17.0 Å, which corresponds to  $q_z = 0.37$  Å<sup>-1</sup> (= 17.0 Å) in the GIWAXS pattern (Fig. 8e). However, this value is considerably larger than half (=15.3 Å) of the crystallographic *c* axis. This discrepancy suggests the molecules in the thin films are less tilted than the molecules in the single crystals. The thin-film tilt angle  $\beta'$  is calculated from  $l = d/\cos(\beta')$ , where l = 18.2 Å is the molecule length estimated from the crystal structure, and d = 17.0 Å



**Fig. 7.** (a) Molecular structure of **Bis(1-ph-5-py)-TIIG** and (b) a view along the molecular short axis. (c) Molecular overlap mode. Crystal structure viewed (d) along the molecular short axis and (e) along the *b* axis. Transfer integrals of the HOMO-HOMO interactions are  $t_b = -55.6$ ,  $t_{q1} = -6.45$ , and  $t_{q2} = -3.41$  meV. Transfer integrals of the LUMO-LUMO interactions are  $t_b = -29.9$ ,  $t_{q1} = -2.68$ , and  $t_{q2} = 0.16$  meV. Distances in (a) and (e) are in angstroms.

is the *d*-spacing in the XRD pattern. The result is  $\beta^{\circ} = 21^{\circ}$ , which is remarkably smaller than the single-crystal value, 35°. In the thin films, the molecules are packed more closely to the perpendicular direction than the single crystals are (Fig. S8).

From the XRD pattern of **Dfu-TIIG** thin films, the *d*-spacing is estimated as 14.6 Å, which is identical to  $q_z = 0.43 \text{ Å}^{-1}$  (= 14.6 Å) in the GIWAXS pattern (Fig. 8f). This *d*-spacing is close to  $c \cdot \sin(a) \cdot \sin(\beta)$  (=14.3 Å) of the crystal lattice; this similarity indicates that the *ab* plane is aligned parallel to the substrate (Fig. S9). Therefore, the molecules are arranged with a side-on orientation, and the molecular tilt angles are 4° for Molecule 1 and 17° for Molecule 2 from the substrate normal.

In **Bis(1-ph-5-py)-TIIG** thin films, XRD and GIWAXS show no distinct peaks except for the TTC peaks (Fig. S10). Therefore, the thin

film of **Bis(1-ph-5-py)-TIIG** is not crystalline, because the bulky phenyl substituents inhibit the crystallization during deposition on the substrate.

#### 3.4. Transistor properties

As expected, these molecules exhibit ambipolar transistor characteristics under vacuum (Fig. 9 and Table 7). **CS** and **NS** show comparable carrier mobilities to **TIIG** because they form one-dimensional stacking structures [21]. The comparatively large  $V_T$  is also in common with **TIIG**; large  $V_T$  difference for electron and hole more than 100 V is characteristic of single-component ambipolar molecules [9]. For **CS**, the transfer integrals of LUMO along the diagonal direction ( $t_p$  in Table 3) as



Fig. 8. XRD patterns of (a) CS and NS, and (b) Dth-TIIG and Dfu-TIIG. GIWAXS patterns of (c) CS, (d) NS, (e) Dth-TIIG, and (f) Dfu-TIIG.

well as the stacking direction ( $t_b$  in Table 3) are much larger than those of HOMO. For **NS**, the transfer integrals of HOMO between the dimerized molecules ( $t_{a1}$  and  $t_{b1}$  in Table 4) are considerably smaller than those of LUMO, but the transfer integrals of LUMO are well balanced along the stacking direction ( $t_{a1}$ ,  $t_{a2}$ ,  $t_{b1}$ , and  $t_{b2}$  in Table 4). These are the reasons that both **CS** and **NS** exhibit slightly n-dominant ambipolar transistor properties even though reorganization energies for electron are larger than those for hole (Table S2). **NS** shows higher carrier mobilities than **CS**. As shown in the thin-film properties, the **NS** molecules are arranged more closely than **CS** to the perpendicular direction to the substrate [58]. The side-on orientation is another factor of the low mobilities of **CS**.

Owing to the balanced transfer integrals (Tables 5 and 6), **Dth-TIIG** and **Dfu-TIIG** show well-balanced carrier mobilities, which are higher by one or two orders of magnitude than are those in **CS** and **NS**. The reduced reorganization energy due to the extended  $\pi$ -skeleton is another factor of the improved transistor properties (Table S2). In addition, the two-dimensional conduction path coming from the brickwork structure is also important for the increased mobilities. Compared to **Dph-TIIG** with a similar crystal structure [21], **Dth-TIIG** exhibits reduced transistor properties because of the flipping disorder and the reduced symmetry, but the carrier mobilities are comparable to those of isoindigo [18]. In case of **Dfu-TIIG**, the molecular orientation is very close to the perpendicular to the substrate; this orientation is favorable for the transistor properties [58]. However, the use of furyl instead of phenyl as a substituent, causes side-on orientation and reduced dimensionality of the conduction path; these changes are the causes of the reduced carrier

Table 7	
Summary of the trans	sistor properties

Summary of th	Summary of the transistor properties.									
	hole			electron						
Compound	$\mu_{\rm av}  [\mu_{\rm max}]$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	<i>V</i> <sub>T</sub> (V)	I <sub>on</sub> / I <sub>off</sub>	$\mu_{av} [\mu_{max}]$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	V <sub>T</sub> (V)	$I_{ m on}/I_{ m off}$				
TIIG [21]	$\frac{1.3\times 10^{-3}}{[1.6\times 10^{-3}]}$	-62.4	10 <sup>4</sup>	$\begin{array}{c} 2.5 \times 10^{-3} \\ [2.9 \times 10^{-3}] \end{array}$	55.8	10 <sup>6</sup>				
CS	$3.5 imes 10^{-4}\ [1.1 imes 10^{-3}]$	-97	$10^{4}$	$\frac{1.5\times 10^{-3}}{[2.8\times 10^{-3}]}$	61	10 <sup>5</sup>				
NS	$5.5 imes 10^{-4}\ [1.3 imes 10^{-3}]$	-79	10 <sup>4</sup>	$6.4 imes 10^{-3}\ [7.6 imes 10^{-3}]$	68	10 <sup>5</sup>				
Dph-TIIG [21]	0.084 [0.12]	-13.9	10 <sup>6</sup>	0.102 [0.13]	77.1	10 <sup>5</sup>				
Dth-TIIG	0.033 [0.055]	-17	$10^{5}$	0.029 [0.039]	70	10 <sup>5</sup>				
Dfu-TIIG	0.031 [0.056]	-31	10 <sup>6</sup>	0.029 [0.041]	80	10 <sup>5</sup>				
Bis(1-ph-5- py)-TIIG	$\begin{array}{l} 5.1 \times 10^{-5} \\ [6.4 \times 10^{-5}] \end{array}$	-28	10 <sup>3</sup>	$\begin{array}{c} 2.3 \times 10^{-6} \\ [3.1 \times 10^{-6}] \end{array}$	22	10 <sup>2</sup>				



Fig. 9. Transfer characteristics of (a) CS, (b) NS, (c) Dth-TIIG, (d) Dfu-TIIG, and (e) Bis(1-ph-5-py)-TIIG.

mobilities compared to **Dph-TIIG** [21]. **Bis(1-ph-5-py)-TIIG** shows slightly p-dominant ambipolar properties, and well-balanced threshold voltages in the hole and electron transport. However, thin films composed of this compound are rather amorphous even though the molecules form a uniform stacking structure in the single crystal, so OFETs that use the thin-films exhibit a reduced on/off current ratio and considerably reduced carrier mobilities.

#### 4. Conclusions

In this study, we prepared five compounds: two of them are Nunsubstituted TIIG analogs, which are unsymmetrically substituted thieno-benzo-isoindigo (CS) and thieno-pyridine-isoindigo (NS). Other three compounds are  $\alpha$ -substituted **TIIG** derivatives, which are dithienyl-TIIG (Dth-TIIG), difuryl-TIIG (Dfu-TIIG), and bis(1-phenyl-5pyrazolyl)-TIIG (Bis(1-ph-5-py)-TIIG). CS and NS show almost the same energy levels, which are slightly lower than that of TIIG. Dth-TIIG, Dfu-TIIG, and Bis(1-ph-5-py)-TIIG exhibit increased electron-donating ability and narrow energy gaps due to the extended  $\pi$ -skeleton. The HOMO and LUMO levels of these molecules are suitable for the ambipolar OFETs. Single crystals of CS. Dfu-TIIG, and Bis(1-ph-5-py)-TIIG construct uniform stacks of the planar molecular cores, but NS forms twisted molecular cores with the slight dimerization. Dth-TIIG shows higher dimensionality of the conduction path due to the brickwork structure, but this molecule has flipping disorder that impedes charge transport. CS and NS form many intra- and intermolecular interactions through S...S, S...O short contacts, and hydrogen bonds. Dth-TIIG and Dfu-TIIG also form hydrogen bonds with the adjacent molecules. Such interactions are favorable for the compact molecular packing and the effective charge transport.

Combined XRD and GIWAXS analyses of the crystal structures reveal the molecular arrangements in thin films of **CS**, **NS**, **Dth-TIIG**, **Dfu-TIIG**, and **Bis(1-ph-5-py)-TIIG**. **CS** molecules assume a relatively large tilt angle from the substrate normal, and this orientation causes lower OFET carrier mobilities in comparison with **NS**, in which the molecules are arranged more perpendicularly to the substrate. **Dth-TIIG** molecules are arranged more closely to the perpendicular direction to the substrate in the thin films than in the single crystals, and the **Dfu-TIIG** molecules are also arranged very closely to the vertical direction to the substrate. However, the thin film of **Bis(1-ph-5-py)-TIIG** is not crystalline.

These molecules exhibit ambipolar OFET properties that agree well with the energy levels. CS and NS show n-dominant moderate hole and electron mobilities, which are explained by the transfer integrals. Dth-TIIG and Dfu-TIIG show hole mobilities of about 0.02–0.056  $\text{cm}^2 \text{ V}^{-1}$  $s^{-1}$  and electron mobilities of about 0.02–0.041 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with wellbalanced ambipolar properties; these values are slightly smaller than those of **Dph-TIIG** but comparable to those of isoindigo [18,21]. These relatively high carrier mobilities are a result of the crystal structure with a two-dimensional conduction path in Dth-TIIG, and of the perpendicular molecular arrangements in **Dfu-TIIG**. In general,  $\pi$ -extended planar molecules are suitable for OFET, but the present work demonstrates that crystal structures preferable for the ambipolar OFET properties are considerably susceptible to the  $\alpha$ -substituents. The observation of molecular disorder in Dth-TIIG suggests possibility that the same kind of disorder exists in polymers which have similar chemical structures studied here.

#### Declaration of competing interest

The authors declare no conflicts of interest associated with this manuscript.

#### CRediT authorship contribution statement

Dongho Yoo: Conceptualization, Formal analysis, Resources, Writing - original draft, Visualization. Tsukasa Hasegawa: Formal

analysis. Akihiro Kohara: Formal analysis. Haruki Sugiyama: Software, Formal analysis. Minoru Ashizawa: Investigation, Data curation, Writing - review & editing, Supervision. Tadashi Kawamoto: Formal analysis, Validation, Writing - review & editing. Hiroyasu Masunaga: Formal analysis. Takaaki Hikima: Formal analysis. Noboru Ohta: Formal analysis. Hidehiro Uekusa: Supervision. Hidetoshi Matsumoto: Supervision. Takehiko Mori: Validation, Writing - review & editing, Supervision, Project administration.

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#### Appendix A. Supplementary data

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