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Air-Stable n-Type Organic Field-Effect Transistors Based on 4,9-Dihydro-s-indaceno[1,2-b:5,6-b']dithiazole-4,9-dione Unit

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Supporting Information

ABSTRACT: 4,9-Dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiazole-4,9-dione (**IDD**) was designed as a novel electronegative unit, and the π -conjugated compound (**2C-TzPhTz**) containing it was synthesized as a candidate for air-stable n-type organic fieldeffect transistor (OFET) materials. Cyclic voltammetry measurements revealed that the **IDD** unit contributes to lowering the lowest unoccupied molecular orbital (LUMO) energy level. X-ray crystallographic analysis of **2C-TzPhTz** showed an almost planar molecular geometry and dense molecular packing, which is advantageous to electron transport. OFETs based on **2C-TzPhTz** showed high electron mobility of up to 0.39 cm² V⁻¹ s⁻¹, which is one of the highest electron mobilities observed among pentacyclic dione-based materials.



Top-contact OFET devices showed operating stability and long-term stability under ambient conditions, attributed to the lowlying LUMO energy level and dense packing in the solid state. Furthermore, bottom-contact OFETs also maintained good electron mobility beyond 0.1 cm² V⁻¹ s⁻¹ under air-exposed conditions. We demonstrated that n-type OFETs are more sensitive to H₂O than O₂ and found that the acquirement of air stability for the **2C-TzPhTz**-based OFET is due to the increased stability against not only O₂ but also H₂O. All of these results indicate that **IDD** is a potentially useful building unit for high-performance air-stable n-type semiconducting materials.

KEYWORDS: organic field-effect transistor, electron-transporting material, organic electronics, structure-property relationships

INTRODUCTION

 π -Conjugated systems have tremendous potential as semiconducting materials for organic electronics such as organic light-emitting diodes, organic field-effect transistors (OFETs), and organic photovoltaic cells, since they can be applicable to low-cost, large-area, and flexible electronic devices.¹ OFETs are one of the most actively investigated applications within this field. Recent significant progress has shown that holetransporting (p-type) OFET materials have achieved high hole mobilities beyond the value of amorphous silicon.^{2,3} In contrast, there remain major challenges concerning the development of electron-transporting (n-type) OFET materials.⁴ This lag in development is predominately due to the difficulty in determining a molecular design suitable for existing guidelines: (1) lowering the lowest unoccupied molecular orbital (LUMO) energy level for efficient electron injection from metal electrodes and (2) invoking strong intermolecular interactions for efficient electron transport in the solid state.

Moreover, stable device operation under ambient conditions has been pursued for practical applications of n-type OFETs, which has consequently brought a more difficult hurdle to the development of suitable new materials. Several research works have proposed that the acquirement of both the low-lying LUMO energy level to overcome the oxidation of anionic carriers with ambient oxidants (O₂ and H₂O) and the dense packing in the solid state to reduce the permeation of ambient oxidants are highly desirable.^{5a,6a} In this context, the design of new electron-accepting units is still of significance for the development of n-type semiconducting materials since thin-film OFET materials producing both air-stable device operation and high electron mobility beyond 0.1 cm² V⁻¹ s⁻¹ are limited to only a few π -conjugated systems such as acene carboxylic

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Figure 1. Chemical structures and HOMO and LUMO energies calculated with DFT at the B3LYP/6-31G(d,p) level.





diimide compounds,^{5–10} dicyanomethylene-substituted conjugated compounds,^{10–14} metal phthalocyanine,¹⁵ azapentacene compounds,¹⁶ and benzobis(thiadiazole) compounds.¹⁷

Recently, we reported on carbonyl-bridged bithiazole (CBB) as a new electronegative unit (Figure 1),¹⁸ in which the combination of an electron-withdrawing thiazole ring with carbonyl bridging contributes to enhancing both the electronaccepting characteristics and the intermolecular interactions.^{18a} OFETs made from C-BTz, which is composed of the central CBB unit and trifluoroacetylphenyl groups¹⁹ as an electronegative terminal unit, have achieved good electron mobility, up to 0.06 cm² V⁻¹s⁻¹, and moderate air stability.^{18a} With this result in mind, we anticipated that expansion of the π conjugation from the tricyclic mono-one system to a pentacyclic dione system could further enhance both the electron-accepting characteristics and the intermolecular overlapping of the π -systems, resulting in higher electron mobility as well as air stability for the OFETs.²⁰⁻²² Therefore, in this study, we designed 4,9-dihydro-s-indaceno[1,2-b:5,6-b']-

dithiazole-4,9-dione (IDD) as a new electronegative unit after first calculating the molecular orbitals of IDD together with those of CBB by density functional theory (DFT) at the B3LYP/6-31G(d,p) level. As shown in Figure 1, in both cases, the HOMOs and LUMOs are spread over the entire π frameworks and the carbonyl groups strongly partcipate in the LUMOs. In reflection of the different number of carbonyl groups, IDD possesses a notably lower LUMO energy level than does CBB. These results encouraged us to develop the π conjugated compound 2C-TzPhTz that consists of IDD and trifluoroacetylphenyl groups. In this study, we report on the synthesis, properties, and structures of 2C-TzPhTz and its performance as an active layer of n-type OFETs. We successfully obtained high field-effect performances with electron mobility of up to 0.39 cm² V⁻¹ s⁻¹, and the OFET devices showed good stability under ambient conditions because of the concurrent features of a low-lying LUMO energy level and dense packing in the solid state. We will also report on the investigation of the influence of O₂ and H₂O,

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independently, on n-type OFET performance in order to clarify the origin of such air stability.

RESULTS AND DISCUSSION

Synthesis, Properties, and Structures. In general, an intramolecular Friedel-Crafts acylation reaction is utilized for the synthesis of pentacyclic dione compounds such as indenofluore-4,9-dione²³ and 4,9-dihydro-*s*-indaceno[1,2-b:5,6-b'] dithiophene-4,9-dione²⁴ derivatives. However, this method is not applicable to the synthesis of the title dione compound due to the considerable electron-deficient character of thiazole compared to benzene and thiophene. Furthermore, although we have previously established the synthesis of a carbonylbridged bithiazole derivative through double lithiation of 2,2'bis(triisopropylsilyl)-5,5'-bithiazole and subsequent treatment with ethyl 1-piperidine carboxylate, 18a a similar one-pot reaction failed to afford key intermediate 4. Thus, we synthesized bisamide compound 3 and then applied an intramolecular acylation reaction via double lithiation of 3 to give 4 in a good yield (Scheme 1). After acetal protection of the carbonyl groups and concomitant removal of the triisopropylsilyl groups under acidic conditions, we converted 5 into a stannylated derivative 6. Finally, the 2C-TzPhTz target compound was prepared by the Stille coupling reaction of 6 with 4'-bromo-2,2,2-trifluoroacetophenone followed by acidic acetal deprotection. The solubility of 2C-TzPhTz toward common organic solvents such as CHCl₃, chlorobenzene, and o-dichlorobenzene is very low. Thus, the 2C-TzPhTz compound was purified by gradient sublimation in a high vacuum and unambiguously characterized by MS, solid-state NMR spectroscopy, and elemental analysis (see the Supporting Information). As shown in Figure S1(a) (Supporting Information), thermogravimetric analysis (TGA) of 2C-TzPhTz showed a high thermal stability with 5% weight loss at 438 °C in a nitrogen atmosphere. As shown in Figure S1(b) (Supporting Information), the UV-vis absorption spectrum of 2C-TzPhTz in THF exhibits an intense absorption band at 408 nm, accompanied with a shoulder between 450 and 650 nm. According to time-dependent DFT calculations at the B3LYP/ 6-31G(d,p) level, this absorption band and shoulder can be mainly ascribed to the HOMO-LUMO+1 (433 nm) and HOMO-LUMO (642 nm) transitions with oscillator strengths (f) of 1.48 and 0.16, respectively.

To investigate the electrochemical properties of 2C-TzPhTz, cyclic voltammetry (CV) measurements were attempted. However, CV measurement of 2C-TzPhTz was restricted due to the lack of sufficient solubility. Thus, to directly compare the electrochemical properties of IDD and CBB units, CV measurements of pentacyclic unit 4 and carbonyl-bridged bithiazole derivative 7 (structure shown in Figure 2) were performed in fluorobenzene containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAP F_6) as the supporting electrolyte at a scan rate of 100 mV s⁻¹. A platinum disk, a platinum wire, and Ag/AgNO3 were used as the working electrode, counter electrode, and reference electrode, respectively. All potentials were calibrated against a ferrocene/ ferrocenium (Fc/Fc⁺) couple as the internal standard. As shown in Figure 2a, 4 gave two reversible reduction waves with half-wave potentials $E^{\text{red}}_{1/2} = -1.17$ and -1.58 V, whose values are positively shifted compared to those of 7 ($E^{\text{red}}_{1/2} = -1.47$ and -2.14 V).²⁵ This result clearly indicates that the pentacyclic dione unit contributes to an increase in the electron-accepting nature compared to the tricyclic system, in



Figure 2. (a) Cyclic voltammograms of 4 (blue) and 7 (black) in fluorobenzene at room temperature containing 0.1 M TBAPF₆. (b) Cyclic voltammogram of **2C-TzPhTz** in benzonitrile at 180 °C containing 0.1 M TBAPF₆. (c) Differential pulse voltammogram of **2C-TzPhTz** in benzonitrile at 180 °C containing 0.1 M TBAPF₆.

good agreement with the above-mentioned theoretical results. The cyclic voltammogram of **2C-TzPhTz** in benzonitrile at the high temperature of 180 °C shows one reversible reduction wave within a potential window of benzonitrile (Figure 2b), and the $E^{\text{red}}_{1/2}$ of -1.01 V was determined by a differential pulse voltammetry measurement (Figure 2c). On the basis of this $E^{\text{red}}_{1/2}$ value and on the premise that the energy level of Fc/Fc⁺ is -4.8 eV below the vacuum level,²⁶ the LUMO energy level of **2C-TzPhTz** is estimated to be -3.79 eV, which is lower than that of **C-BTz** (-3.64 eV).^{18a}

In order to investigate the molecular structure and packing in the solid state, X-ray crystallographic analysis of 2C-TzPhTz was carried out. Suitable single crystals were obtained by recrystallization from an iodobenzene solution. The 2C-TzPhTz molecules form a monoclinic primitive lattice with a space group of $P2_1/a$ and unit cell parameters of a =13.4677(11) Å, b = 4.7775(3) Å, c = 18.764(2) Å, and $\beta =$ 94.002(5)°. The molecular structure of 2C-TzPhTz reveals an almost planar geometry with inter-ring dihedral angles less than 2° (Figure 3a). As shown in Figure 3b, in contrast to the dense side-by-side packing of C-BTz,^{18a} the C_2 -symmetric molecular structure and two carbonyl groups on the pentacyclic unit in 2C-TzPhTz induce several short contacts between neighboring units, resulting in the formation of a cross-oriented layer-bylayer packing. In each layer, intermolecular $\pi - \pi$ interactions are observed with an interplanar distance of 3.38 Å, revealing a more dense π -stacking configuration than that of C-BTz (3.40 and 3.52 Å).^{18a} On the basis of this packing diagram, the intermolecular transfer integrals (t) between LUMOs of neighboring molecules were calculated using PW91/TZP, as implemented in the Amsterdam Density Functional (ADF) program.²⁷ As shown in Figure 4, large overlaps are observed

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Figure 3. (a) Molecular structure and (b) packing diagram of 2C-TzPhTz.



Figure 4. Estimated transfer integrals of LUMOs for (a) 2C-TzPhTz and (b) C-BTz between neighboring molecules.

along the π -stacked direction, and the transfer integral for 2C-TzPhTz is larger than that for the π -stacking of C-BTz (71.7 meV) under the same calculation method. This result supports that 2C-TzPhTz displays an efficient electron-transport character along the π -stacking direction.

Morphologies of the Thin Films and Field-Effect Properties. The morphology and structural order of 2C-TzPhTz in the solid state were investigated by atomic force microscopy (AFM) and X-ray diffraction (XRD). The 2C-TzPhTz thin films were prepared on octadecyltrichlorosilane (ODTS)-modified SiO₂/Si substrates by vacuum deposition at a substrate temperature of 170 °C and subsequent annealing at 300 °C for 1 h in a vacuum. As shown in Figure 5a, the AFM image of the 2C-TzPhTz film shows crystal-shaped submicrometer-sized grains with no observable grain boundaries. The Article



Figure 5. (a) AFM image and (b) XRD data of 2C-TzPhTz film on ODTS-modified SiO₂.

XRD measurement of the film exhibits regular-interval peaks up to the fifth order (Figure 5b), indicating that **2C-TzPhTz** forms a crystalline structure in the thin films. The first peak at $2\theta = 4.7^{\circ}$ corresponds to a *d*-spacing of 18.8 Å, which is almost equal to the length of the crystallographic *c*-axis. Thus, **2C-TzPhTz** molecules are positioned on a stacking orientation parallel to the SiO₂ surface with their long axes inclined at an angle of 46.2°. Notably, this orientation is advantageous for charge transport in the OFET geometry.

To evaluate the transistor characteristics of **2C-TzPhTz**, OFET devices with bottom-gate top-contact geometry were fabricated by patterning gold electrodes over the organic thin films using a shadow mask to define a channel width (W) of 5 mm and a channel length (L) 20 μ m. FET parameters obtained from the measurements are summarized in Table 1. Under a

Table 1. Field-Effect Characteristics of 2C-TzPhTz and C-BTz in a Vacuum and Air

run	compound	geometry	measurement conditions	${\rm cm}^2 \stackrel{\mu_{e'}}{{\rm V}^{-1}} {\rm s}^{-1}$	$\stackrel{I_{\rm on}/}{I_{\rm off}}$	$V_{ m th\nu}~{ m V}$
1	2C- TzPhTz	top- contact	under vacuum	0.13	10 ²	-51
2	2C- TzPhTz	top- contact	in air	0.11	10 ²	-39
3	2C- TzPhTz	bottom- contact	under vacuum	0.39	10 ⁶	23
4	2C- TzPhTz	bottom- contact	in air	0.14	107	24
5	C-BTz ^a	top- contact	under vacuum	0.03	10 ³	33
^a Reference 18a.						

vacuum, the OFET device using **2C-TzPhTz** showed typical nchannel responses with an electron mobility (μ_e) of 0.13 cm² V⁻¹ s⁻¹ (Figure S2, Supporting Information), which is almost four times higher than that of **C-BTz** under the same device conditions (runs 1 and 5 in Table 1). This higher electron mobility is consistent with the above-described estimation that the stacking of **2C-TzPhTz** has larger transfer integrals between the LUMOs than does **C-BTz**. Moreover, on the basis of calculated energies for neutral and radical-anionic states,²⁸ the reorganization energy of **2C-TzPhTz** is estimated to be 311 meV, which is smaller than that of **C-BTz** (356 meV). This result also supports that the introduction of the **IDD** unit gives rise to the potential for increased electron transport characteristics. As expected from the low-lying LUMO energy level and dense packing in the solid state, these **2C-TzPhTz**-based OFET devices are found to be stable under air-exposed conditions, maintaining a μ_e of 0.11 cm² V⁻¹ s⁻¹ (run 2). To examine their operational stability in air, the device was repeatedly biased by a gate-voltage (V_{GS}) sweep from -20 to 80 V under a fixed source-drain voltage (V_{DS}) at 80 V, and its source-drain currents (I_{DS}) were collected. As can be seen in Figure 6a, the observed transfer characteristics show



Figure 6. (a) Transfer characteristics of a top-contact OFET using 2C-TzPhTz with repeated biases up to 10 cycles under air-exposed conditions at source-drain voltage of 80 V. I_{DS} and V_{GS} denote source-drain current and gate voltage, respectively. (b) Electron mobility of a top-contact OFET using 2C-TzPhTz versus storage period under air-exposed conditions.

little hysteresis under the repeatedly biased conditions, tracing almost overlapped curves even after 10 cycles. Furthermore, on monitoring the long-term stability under air-exposed conditions, the **2C-TzPhTz**-based OFET only showed slight changes in the mobility even after 3 months, as shown in Figure 6b. These results demonstrate that **2C-TzPhTz** is a promising electron-transporting semiconducting material for practical OFET application.

To obtain further insight into intrinsic device performances, OFETs with bottom-gate bottom-contact geometry were fabricated. This device configuration is also desirable for practical transistor applications.^{8a,29} Since, on our fabricationmeasurement equipment for bottom-gate bottom-contact OFETs, the performances can be evaluated in a high vacuum without exposing the device to air after preparing the thin-films, the influence of atmospheric contaminants is minimized during device processing. For this measurement, source and drain gold electrodes with a W/L of 294 mm/25 μ m were prepatterned on a 300 nm layer of SiO₂ dielectric and thin-films of 2C-TzPhTz were vacuum-deposited by the above-mentioned conditions onto the ODTS-modified SiO₂/Si substrates. Figure 7 shows the transfer and output characteristics of the devices that exhibit a high electron mobility of 0.39 cm² V⁻¹ s⁻¹, an on/off current ratio (I_{on}/I_{off}) of 10⁶, and a threshold voltage (V_{th}) of 23 V (run 4 in Table 1). Compared to the top-contact OFETs with a similar channel length, the improved electron mobility is mainly



Figure 7. (a) Transfer characteristics of a bottom-contact OFET using **2C-TzPhTz**. (b) Output characteristics of the same device at source–drain voltage of 120 V. $V_{\rm DS}$ denotes source–drain voltage.

attributed to the complete exclusion of atmospheric contaminants, and the improved on/off current ratio and positive shift of the threshold voltage are probably due to the small area of gold electrode—organic layer contacts that restrains the surplus currents.³⁰

Surprisingly, after exposure to air, the bottom-contact OFETs still maintained a high electron mobility of 0.14 cm² V^{-1} s⁻¹ (run 4 in Table 1). Although the electron mobility deteriorates slightly compared to that in a vacuum, the value is an identical level with those observed in the top-contact devices. At present, bottom-gate bottom-contact OFETs with both air-stable device operation and high electron mobility exceeding 0.1 cm² V⁻¹ s⁻¹ have been limited to only a few precedents.^{8a,10b} Since we could not observe significant differences in the morphology and crystallinity between the thin-films of the top-contact and bottom-contact OFETs, we can speculate that, for the bottom-contact OFETs, the organic thin-films are not well-organized at the interface with the gold electrodes,³¹ resulting in them being susceptible to the intrusion of atmospheric contaminants.³² It is well-known that the performance deterioration of n-type OFETs in air is caused by O₂ and H₂O as the main ambient oxidants. On the basis of the reduction potentials of O2 (+0.57 V vs SCE, corresponding to +0.19 V vs Fc/Fc⁺) and H₂O (-0.66 V vs SCE, corresponding to -1.04 V vs Fc/Fc⁺) in aqueous media,^{33,34} it has been proposed that the O₂-oxidation process against anionic carriers has more serious influence on the thermodynamic stability of n-type OFETs than the H2Ooxidation process.^{6c,33} In fact, several researches revealed the influence of O_2 on n-type OFET performances.^{5a,35,36} In terms of a kinetic barrier of closely stacked conjugated polymers against the penetration of O₂, the OFET performances in a wide range of O2 pressures were also investigated.³⁷ In contrast, the influence of H₂O on n-type OFET performances has not been fully clarified.^{8a,38} Under these circumstances, to reveal the charge-trapping ability of O₂ and H₂O individually, we compared the characteristics of the bottom-contact OFETs under dry air (O₂: 20–22%, H₂O < 0.5 ppm) and under humid N₂ (O₂ < 0.1 ppm, around 80% of humidity). For the investigation of the relationship between molecular structures and the device stability, we measured the OFET performances of **2C-TzPhTz** as an air-stable material, **C-BTz** as a moderate air-stable material, and our previously reported **8**^{19b} as an airunstable reference material (structure shown in Figure 8). Note



Figure 8. Transfer characteristics of bottom-contact OFETs using (a) 2C-TzPhTz, (b) C-BTz, and (c) 8 at a source-drain voltage of 80 V.

that 8 possesses an electrochemically estimated LUMO energy level of -3.20 eV. To equalize the kinetic penetration of O₂ or H₂O into organic thin films, the thicknesses of the films were defined to be 10 nm for all the devices. It should be mentioned that 2C-TzPhTz, C-BTz, and 8 take a π -stacked crystalline structure in the solid state, and their interplanar distances of 3.38, 3.40, 3.52, and 3.45 Å, respectively, are comparable to the kinetic diameter of O₂ (3.46 Å) and longer than that of H₂O (2.65 Å).³⁶ We first measured the OFET characteristics in a vacuum chamber. Then, the measurements were performed after introducing the dry air or humid N2 to the chamber and keeping the conditions for 1 h at room temperature. All the devices were biased by a V_{GS} sweep from -20 to 60 V under a fixed $V_{\rm DS}$ of 80 V, and their $I_{\rm DS}$ values were collected. As shown in Figure 8a,b, both 2C-TzPhTz and C-BTz almost maintained their OFET characteristics in dry air. On the other hand, in humid N2, 2C-TzPhTz showed one order of decrease in electron mobility against that in a vacuum, and, furthermore, a decrease in two orders was observed for C-BTz. The pronounced decrease of the electron mobility for 2C-TzPhTz compared to that above-mentioned under air-exposed conditions comes from the increased humidity from around 50% for the ambient air to 80% for the humid N_2 . In contrast to 2C-TzPhTz and C-BTz, 8 showed an apparent deterioration even under dry air, and the n-type characteristics were completely quenched under humid N₂ (Figure 8c). Note that, in all the cases, the degraded performances can be recovered to the initial

levels after re-evacuating the devices, indicating that the airinstability is not due to irreversible chemical instability. These results clearly indicate that H₂O has more influence on the charge trapping of n-type OFETs than does O₂. By assuming the reduction potential of O₂ (-1.25 V vs Fc/Fc⁺) in aprotic media,³⁹ the electron affinities of O₂ and H₂O and the LUMO energy levels of the molecules are diagrammed in Figure 9. In



Figure 9. Energy diagram. LUMO energy levels of 2C-TzPhTz, C-BTz, and 8 were estimated from CV.

spite of the energetically mismatched relationship, as described above, **8** and **C-BTz** barely showed the n-type OFET characteristics under dry air and humid N₂, respectively, which might be brought by compensation with the kinetic barrier of the stacked hydrophobic molecules. On the other hand, **2C-TzPhTz** is superior to **C-BTz** in terms of the energetically matched LUMO energy level. In addition, the kinetic barrier of **2C-TzPhTz** derived from the dense packing is expected. Therefore, these combined effects contribute to accomplishing the high device stability toward not only O₂ but also H₂O. In other words, the expansion of π -conjugation from **BCC** to **IDD** is advantageous to an increase in both the thermodynamic and the kinetic stabilities of n-type OFETs.

CONCLUSION

In summary, we have successfully demonstrated that 4,9dihydro-*s*-indaceno[1,2-b:5,6-b']dithiazole-4,9-dione (IDD) is a promising electronegative unit for constructing π -conjugated systems for n-type OFET materials. The derivative of IDD combined with trifluoroacetylphenyl groups, 2C-TzPhTz, shows high electron mobility of up to $0.39 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ on OFETs, which is one of the highest values reported for pentacyclic dione-based materials. The high OFET performance is considered to originate from its low-lying LUMO energy level and an appropriate molecular arrangement in the solid state for charge-carrier transport, which were unambiguously investigated by electrochemistry and X-ray analysis. Besides the good OFET performances, it is notable that topcontact OFET devices show operating stability and long-term stability under air-exposed conditions. Furthermore, bottomcontact OFETs also maintained high n-type characteristics under air-exposed conditions, and electron mobility beyond 0.1

 $\rm cm^2~V^{-1}~s^{-1}$ was observed. We investigated the influence of $\rm O_2$ and H₂O, independently, on n-type OFET performance in order to clarify the origin of such air stability. We successfully demonstrated that n-type OFETs are more sensitive to H₂O than O₂ for our investigated compounds and found that the acquirement of air stability for 2C-TzPhTz-based OFET is due to the increased stability against not only O₂ but also H₂O. This feature is accomplished by the introduction of the IDD unit, which is advantageous to increase both thermodynamic and kinetic stabilities for the n-type OFET operation. Further improvements in device performance for 2C-TzPhTz through optimization of the device structure are anticipated. The present results indicate that, for the novel electron-transporting materials based on IDD, further improvement in transport properties and/or solution processability can be achieved by fine-modification of the constituent molecules.

EXPERIMENTAL SECTION

General Information. Column chromatography was performed on silica gel (KANTO Chemical silica gel 60 N, 40–50 μ m) or neutral alumina (Merck Aluminum oxide 90 standardized). Thin-layer chromatography (TLC) plates were visualized with UV. Preparative gel-permeation chromatography (GPC) was performed using a Japan Analytical Industry LC-908 equipped with a JAI-GEL 1H/2H column. Melting points were uncorrected. ¹H NMR and ¹³C NMR spectra were recorded using a JEOL JMM-ECS400 and JCM-ECA600 in CDCl₃ with tetramethylsilane as an internal standard. Solid-state ¹H NMR and ¹³C NMR spectra were recorded using a Bruker AVANCE III600WB. The NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, hept = heptet, m = multiplet), coupling constant (Hz), and integration. Mass spectra were obtained on a Shimadzu GCMS-QP-5050. UV-visible spectra were recorded using a Shimadzu UV-3100PC. All spectra were obtained in spectrograde solvents. Cyclic voltammetry and differential pulse voltammetry were carried out using a BAS CV-620C voltammetric analyzer. Elemental analyses were performed on PerkinElmer LS-50B by the Elemental Analysis Section of the Comprehensive Analysis Center (CAC) of ISIR, Osaka University. The surface structures of the deposited organic film were observed by atomic force microscopy (Shimadzu, SPM9600), and the film crystallinity was evaluated by an X-ray diffractometer (Rigaku, RINT2500). X-ray diffraction patterns were obtained using Bragg-Brentano geometry with Cu K α radiation as an X-ray source with an acceleration voltage of 40 kV and a beam current of 40 mA. The scanning mode was set to θ -2 θ scans between 2.5 and 30° with scanning steps of 0.01°.

Materials. All reactions were carried out under a nitrogen atmosphere. Especially, the reactions using lithium diisopropylamide or *n*-BuLi were carried out under complete exclusion of water and oxygen. The reaction using thionyl chloride was performed under a fume food. The removed thionyl chloride was disposed after neutralization with sodium carbonate. Solvents of the highest purity grade were used as received. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. 1,4-Dibromo-2,5-benzenedicarboxylic acid was prepared by the previously reported procedure.⁴⁰

Synthesis of 1. 1,4-Dibromo-2,5-benzenedicarboxylic acid (10 g, 30.9 mmol), dimethylformamide (a few drops), and thionyl chloride (50 mL) were placed in a 100 mL round-bottomed flask. The reaction mixture was stirred at 80 °C for 1 h. After removal of thionyl chloride under reduced pressure, the residue was dissolved in dichloromethane (300 mL) at 0 °C. Triethylamine (25.9 mL, 185 mmol) and piperidine (18.4 mL, 185 mmol) were added to the mixture, and the resulting mixture was allowed to warm to room temperature. After stirring for 2 h, the solution was poured into water and extracted with dichloromethane. The extract was dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was washed with methanol and diethyl ether to give compound 1 (12 g, 83%). White solid; mp

236–242 °C; ¹H NMR (400 MHz, CDCl₃, δ) 7.44 (s, 2H), 3.76–3.70 (m, 4H), 3.26–3.13 (m, 4H), 1.77–1.39 (m, 12H); ¹³C NMR (150 MHz, CDCl₃, δ) 165.9, 140.6, 131.9, 118.9, 48.3, 43.1, 26.6, 25.8, 24.7; MS (EI) m/z 457 [M⁺]. Anal. Calcd for C₁₈H₂₂Br₂N₂O₂: C, 47.18; H, 4.84; N, 6.11. Found: C, 47.18; H, 4.97; N, 5.96.

Synthesis of **3**. **1** (11.4 g, 24.8 mmol), **2** (31.6 g, 59.6 mmol), and tetrakis(triphenylphosphine)palladium(0) (2.90 g, 2.48 mmol) were placed in a pressure vessel and dissolved in toluene (100 mL). The reaction mixture was stirred at 120 °C for 10 h. After removal of the solvent under reduced pressure, the residue was washed with methanol and ethyl acetate to give compound **3** (16.7 g, 86%). White solid; mp 255–259 °C; ¹H NMR (400 MHz, CDCl₃, δ) 8.28 (s, 2H), 7.52 (s, 2H), 3.95–3.84 (m, 2H), 3.41–3.28 (m, 2H), 3.00–2.88 (m, 4H), 1.53–1.34 (m, 10H), 1.29–1.19 (m, 2H), 1.18–1.12 (m, 36H), 0.70–0.58 (m, 2H); ¹³C NMR (150 MHz, CDCl₃, δ) 172.4, 168.1, 144.9, 137.3, 136.9, 128.9, 48.1, 42.9, 26.1, 25.3, 24.5, 18.8, 12.0; MS (EI) *m*/*z* 779 [M⁺]. Anal. Calcd for C₄₂H₆₆N₄O₂S₂Si₂: C, 64.73; H, 8.54; N, 7.19. Found: C, 64.79; H, 8.57; N, 7.28.

Synthesis of 4. 3 (500 mg, 0.64 mmol) in THF (45 mL) was added to lithium diisopropylamide (1.0 M, 14 mL) in THF at -40 °C. After stirring for 1 h, the reaction was quenched by the addition of H₂O. The aqueous layer was extracted with CHCl₃, and the combined organic layer was washed with water and dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/CHCl₃ = 2.5/1) to yield 4 (343 mg, 89%). Purple solid; mp 255-260 °C; TLC $R_f = 0.29$ (2.5:1 hexane/CHCl₃); ¹H NMR (400 MHz, CDCl₃, δ) 7.37 (s, 2H), 1.53 (hept, 6H, J = 7.6 Hz), 1.18 (d, 36H, J = 7.6 Hz); ¹³C NMR (150 MHz, CDCl₃, δ) 183.6, 178.0, 159.8, 157.3, 140.5, 138.4, 117.0, 18.8, 12.0; MS (EI) m/z 609 [M⁺]. Anal. Calcd for C₃₂H₄₄N₂O₂S₂Si₂: C, 63.11; H, 7.28; N, 4.60. Found: C, 62.82; H, 7.33; N, 4.32.

Synthesis of 5. 4 (47 mg, 0.077 mmol), *p*-toluenesulfonic acid (133 mg, 0.77 mmol), and 2,2-dibutyl-1,3-propanediol (58 mg, 0.031 mmol) were placed in a three-necked round-bottomed flask and dissolved with benzene (30 mL). The reaction mixture was stirred at 110 °C for 8 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate =20/1) to yield 5 (42 mg, 85%). White solid; mp 268–275 °C; TLC $R_f = 0.27$ (20:1 hexane/ethyl acetate); ¹H NMR (400 MHz, CDCl₃, δ) 8.68 (s, 2H), 7.46 (s, 2H), 4.60 (s, 2H), 4.57 (s, 2H), 3.82 (s, 2H), 3.79 (s, 2H); ¹³C NMR (150 MHz, CDCl₃, δ) 163.8, 153.6, 149.2, 137.4, 132.9, 116.5, 100.1, 71.8, 35.7, 32.9, 31.1, 26.0, 24.7, 24.0, 23.9, 14.6, 14.4; MS (EI) *m*/*z* 636 [M⁺]. Anal. Calcd for C₃₆H₄₈N₂O₄S₂: C, 67.89; H, 7.60; N, 4.40. Found: C, 67.66; H, 7.58; N, 4.35.

Synthesis of 6. 5 (237 mg, 0.37 mmol) was placed in a threenecked round-bottomed flask and dissolved with THF (5 mL). *n*-BuLi (1.57 M, 0.7 mL) was added dropwise to the mixture at -40 °C. After stirring for 1 h, SnBu₃Cl (0.33 mL, 1.23 mmol) was added. After stirring for 0.5 h at room temperature, the reaction was quenched by the addition of H₂O (2 mL). The aqueous layer was extracted with ethyl acetate, and the combined organic layers were washed with water and dried over MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina (hexane/CHCl₃ = 10/1) followed by further purification with GPC (CHCl₃) to give 6 (396 mg, 88%) as a yellow solid: ¹H NMR (400 MHz, CDCl₃, δ) 7.41 (s, 2H), 4.76 (s, 2H), 4.73 (s, 2H), 3.77 (s, 2H), 3.74 (s, 2H).

Synthesis of 2C-TzPhTz. 6 (322 mg, 0.27 mmol), 4'-bromo-2,2,2-trifluoroacetophenone (201 mg, 0.80 mmol), and tetrakis-(triphenylphosphine)palladium(0) (31 mg, 0.027 mmol) were placed in a pressure vessel and dissolved with toluene (3 mL). The reaction mixture was stirred at 120 °C for 13 h. After removal of the solvent under reduced pressure, the residue was washed with methanol and diethyl ether. This compound was placed in a 100 mL round-bottomed flask and dissolved with AcOH (50 mL). Aq. HCl (12 M, 3 mL) was added to the mixture at 100 °C. The reaction mixture was stirred for 2 h. After being cooled to room temperature, the reaction was quenched by the addition of H₂O. The solid was collected and

washed with H₂O, methanol, and diethyl ether followed by purification under gradient sublimation under a high vacuum (10⁻⁶ Pa) to give pure **2C-TzPhTz** (77 mg, 45%) as a green solid; mp >300 °C; ¹H NMR (600 MHz, solid, δ) 5.72 (br); ¹³C NMR (150 MHz, solid, δ) 183.2, 175.4, 171.4, 154.5, 137.8, 135.7, 130.5, 128.2, 125.9, 124.0, 115.6; MS (EI) *m*/*z* 640 [M⁺]. Anal. Calcd for C₃₀H₁₀F₆N₂O₄S₂: C, 56.25; H, 1.57; N, 4.37. Found: C, 56.17; H, 1.65; N, 4.37.

X-ray Information. Single crystal diffraction: Diffraction data for **2C-TzPhTz** were collected using synchrotron radiation ($\lambda = 0.8000$ Å) at the BL38B1 in the SPring-8, with approval of JASRI (2010A1266). The cell refinements were performed with the HKL2000 software.⁴¹ Direct method (SIR-2004) was used for the structure solution.⁴² Calculation was performed with the observed reflections [$I > 2\sigma(I)$] using the CrystalStructure crystallographic software packages,⁴³ except for refinement, which was performed using SHELXL-97.⁴⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters.

 $C_{15}H_5F_3NO_2S: M_w = 320.27, a = 13.4677(11) Å, b = 4.7775(3) Å, c = 18.764(2) Å, <math>\alpha = 90^\circ$, $\beta = 94.002(5)^\circ$, $\gamma = 90^\circ$, $V = 1204.4(2) Å^3$, T = 93 K, monoclinic, space group $P2_1/a$ (No. 14), Z = 4, $\rho_{calcd} = 1.766$ g cm⁻³, 2455 unique reflections, final R1 and wR2 values 0.0784 ($I > 2.0\sigma(I)$) and 0.2401 (all data), respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-866114.

Top-Contact Device. The field-effect mobility of 2C-TzPhTz was measured using top-contact thin-film field-effect transistor (FET) geometry. The n-doped silicon substrate functions as the gate electrode. A thermally grown silicon oxide dielectric layer on the gate substrate was 300 nm thick with a capacitance (Ci) of 10.0 nF cm⁻². The silicon oxide surface was washed with toluene, acetone, water, and 2-propanol and then activated by ozone treatment and pretreated with ODTS.45 The semiconductor layer was vacuumdeposited on the Si/SiO₂ at a rate of 0.1 Å s⁻¹ under a pressure of 10^{-6} Pa to a thickness of 10 nm determined by a quartz crystal monitor. On the top of the semiconductor layer, gold source and drain electrodes (20 nm) were deposited using shadow masks with a channel width (5 mm) and channel length (20 μ m). The characteristics of the OFET devices were measured at room temperature under a pressure of 10⁻² Pa or in air. The field-effect mobility was calculated in the saturated region at the $V_{\rm DS}$ of 120 V by the equation of $I_{\rm DS} = W/(2L) \cdot Ci\mu_{\rm e} (V_{\rm GS})$ $-V_{\rm th}$)². The current on/off ratio was determined from the $I_{\rm DS}$ at $V_{\rm GS}$ = $-40 \text{ V} (I_{\text{off}}) \text{ and } V_{\text{GS}} = 80 \text{ V} (I_{\text{on}}).$

Bottom-Contact Device. The field-effect mobility of 2C-TzPhTz was measured using bottom-contact thin-film field-effect transistor (FET) geometry. The p-doped silicon substrate functions as the gate electrode. A thermally grown silicon oxide dielectric layer on the gate substrate was 300 nm thick with a capacitance of 10.0 nF cm $^{-2}$. Interdigital source and drain electrodes were constructed with gold (30 nm) that were formed on the SiO_2 layer. The channel width (W) and channel length (L) were 294 mm and 25 μ m, respectively. The silicon oxide surface was washed with toluene, acetone, water, and 2-propanol. The silicon oxide surface was then activated by ozone treatment and pretreated with octadecyltrichlorosilane (ODTS). (In case of 8, the surface was pretreated with hexamethyldisilazane (HMDS).) The semiconductor layer was vacuum-deposited on the Si/SiO2 substrate at a rate of 0.1 Å s⁻¹ under a pressure of 10⁻⁶ Pa to a thickness of 10 nm determined by a quartz crystal monitor. The characteristics of the OFET devices were measured at room temperature under a pressure of 10^{-6} Pa without exposure to air after fabricating the active layer. The field-effect electron mobility (μ_e) was calculated in the saturated region at the $V_{\rm DS}$ of 120 V, and the current on/off ratio was determined from the I_{DS} at $V_{GS} = -40 \text{ V} (I_{off})$ and $V_{GS} = 80 \text{ V} (I_{on})$.

ASSOCIATED CONTENT

S Supporting Information

NMR spectra, TGA curve, UV-vis absorption spectrum, computational details, and OFET characteristics. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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