

# Tetracyanodibenzotetrathiafulvalene Diimides: Design, Synthesis, and Property Study

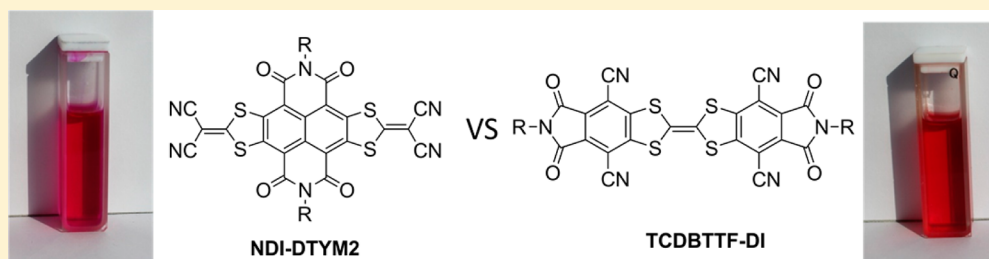
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## Supporting Information



**ABSTRACT:** Tetracyanodibenzotetrathiafulvalene diimide (TCDBTTF-DI), an isomer of core-expanded naphthalene diimides bearing two 2-(1,3-dithiol-2-ylidene)malononitrile moieties (NDI-DTYM2), has been designed and synthesized to explore the effect of its isomeric structure on the optical and electrochemical properties of the materials. UV-vis spectra show that TCDBTTF-DI exhibits variation in its absorption peaks while maintaining a similar optical band gap to NDI-DTYM2. Electrochemical studies indicate that TCDBTTF-DI can not only accept but also lose electrons, in contrast to the solely electron-accepting behavior of NDI-DTYM2.

Variations in properties observed for different isomers have been investigated for  $\pi$ -functional materials, for example, the isomeric organic heteroarenes<sup>1</sup> and polycyclic aromatic hydrocarbons (Figure 1).<sup>2</sup> These differences in properties observed for isomers generally arise from the varied positions of heteroatoms or functional groups on the  $\pi$ -system or from the different modes of combining the molecular units. It is well-known that the structure of organic semiconducting materials affects their molecular self-assembling behaviors, solid-state molecular packing, and charge-transport properties. However, it is challenging to achieve the performance desired by traditional molecular design.<sup>3</sup> Structural (or constitutional) isomers provide unique opportunities to study the effect of molecular structure on the charge transport behaviors of organic semiconducting materials.<sup>4</sup> For example, as an isomer of pentacene, picene (Figure 1) has superior chemical stability, and organic thin film transistors (OTFTs) employing picene show a high hole mobility of  $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  under  $\text{O}_2$  atmosphere.<sup>2</sup> It has been found that the *anti/syn* isomers of fused-ring thienoacene derivatives (Figure 1) exhibit distinct solution self-assembling behaviors under the same experimental conditions, the *syn* isomer formed one-dimensional (1D) micro- and nanoribbons while the *anti* isomer exhibited two-dimensional (2D) nanoplates, leading to different field-effect

mobilities.<sup>4a</sup> In addition, the positions of the heteroatoms of heteroarenes (Figure 1) could greatly influence the charge mobility observed in OTFT devices. For example, a silylthynylated *N*-heteropentacenes with pyrazines on the terminal positions of the backbone (Figure 1) shows ambipolar charge transport ( $\mu_{\text{h}} = 0.05\text{--}0.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $\mu_{\text{e}} = 0.3\text{--}1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), while the isomer employing pyrazines within the backbone (Figure 1) exhibits n-channel charge transport with electron mobilities of  $1.0\text{--}3.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>4b</sup> These results demonstrate that examining property variation between isomers may be an effective route to explore new semiconductors.

Naphthalene diimide (NDI) is one of the most popular building blocks for constructing n-type semiconductors for OTFTs.<sup>5</sup> The development of new NDI-based materials mainly depends on the modification of the NDI core and/or *N*-substituent to tune the molecular electronic structure, solubility, and charge-transport properties.<sup>5,6</sup> Among the newly developed NDI-based materials, a class of NDIs fused with two 2-(1,3-dithiol-2-ylidene)malononitrile moieties (NDI-DTYM2) have been designed and synthesized by Gao and co-

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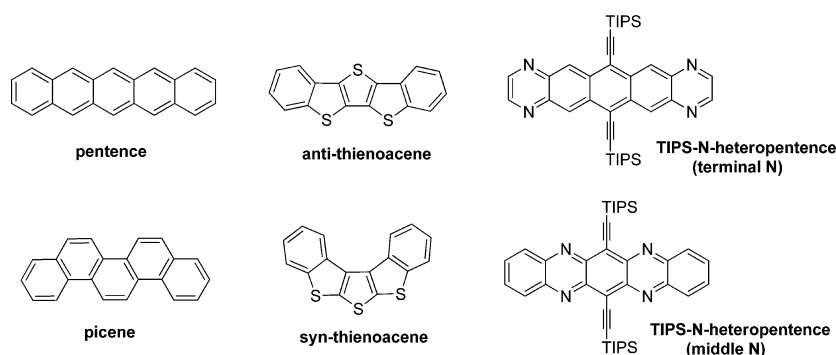


Figure 1. Representative  $\pi$ -conjugated materials with isomeric structures.

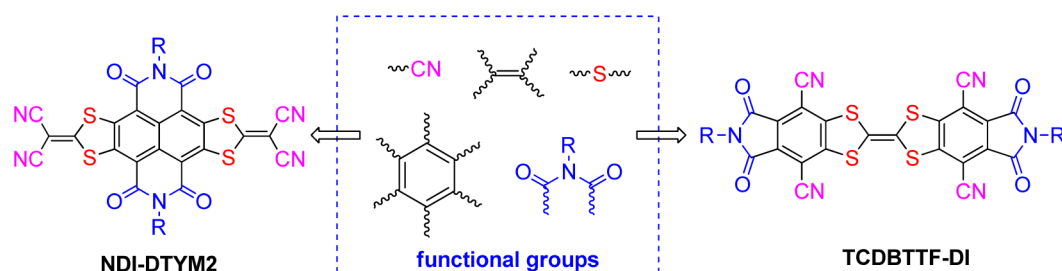
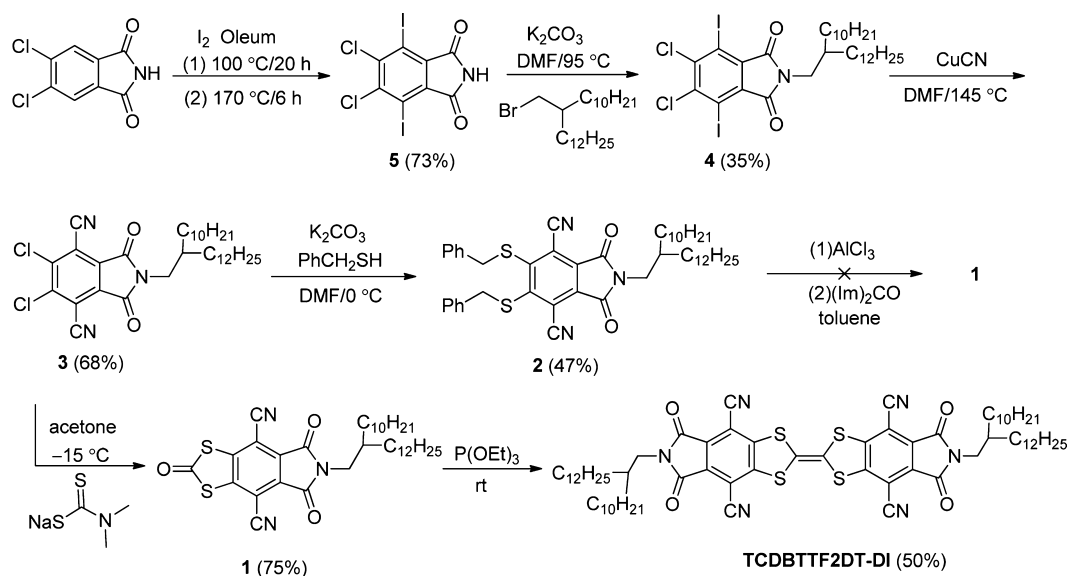


Figure 2. Different constructions of the NDI-DTYM2 and TCDBTTF-DI derivatives.

### Scheme 1. Synthesis of TCDBTTF2DT-DI



workers.<sup>6a,b,d</sup> OTFTs based on NDI-DTYM2 derivatives showed excellent device performance with electron mobilities of  $0.1\text{--}3.5\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  and good air stability, demonstrating that the  $\pi$ -core of NDI-DTYM2 derivatives is a perfect building block for n-type organic semiconductors.<sup>6</sup>

Inspired by the excellent device performance of NDI-DTYM2 derivatives in n-channel OTFTs<sup>6</sup> and by curiosity about the effect of molecular structure on chemical and physical properties of semiconducting materials,<sup>1,2,4</sup> we chose to synthesize the structural isomers of NDI-DTYM2. Investigation of these isomers can not only provide understanding of the structure–property relationship of the isomers but could also provide important clues for designing new  $\pi$ -functional materials. Herein, we synthesized a tetracyanodibenzotetrathiafulvalene diimide (TCDBTTF2DT-DI) that bears long

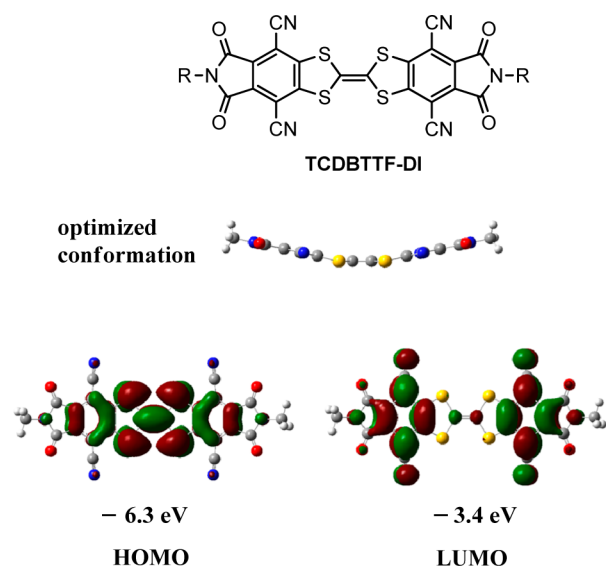
branched alkyl chains (Figure 2, R = 2-decyltetradecyl), a structural isomer of NDI2DT-DTYM2.<sup>6a,b</sup> As shown in Figure 2, TCDBTTF2DT-DI shares the same chemical building blocks as NDI2DT-DTYM2 (e.g., four cyano groups, two benzene units, two imide moieties, and two 1,3-dithiol rings) but has a new method of linking these functional groups. In addition, TCDBTTF2DT-DI contains a tetrathiafulvalene (TTF) moiety, which is known as a strong electron-donating unit.<sup>7</sup> Therefore, the optical and electrochemical properties of TCDBTTF2DT-DI should be quite different from those of NDI2DT-DTYM2.

The synthetic route for TCDBTTF2DT-DI is shown in Scheme 1. The iodination of 4,5-dichlorophthalimide was carried out in 50% oleum,<sup>8</sup> affording 5,6-dichloro-4,7-diiodoisindoline-1,3-dione (5) in a moderate yield of 73%.

An alkyl chain was introduced to the nitrogen atom of the imide of **5** by using a  $S_N2$  nucleophilic substitution reaction, giving 5,6-dichloro-2-(2-decyltetradecyl)-4,7-diiodoisindoline-1,3-dione (**4**) in 35% yield. 5,6-Dichloro-2-(2-decyltetradecyl)-1,3-dioxoisindoline-4,7-dicarbonitrile (**3**) was achieved in 68% yield by a selective cyanation of the iodine positions of **4**. We attempted to synthesize the key precursor 6-(2-decyltetradecyl)-2,5,7-trioxo-6,7-dihydro-5H-[1,3]dithiolo[4,5-f]isindole-4,8-dicarbonitrile (**1**) by using a literature method,<sup>9</sup> where **3** was converted to 5,6-bis(benzylthio)-2-(2-decyltetradecyl)-1,3-dioxoisindoline-4,7-dicarbonitrile (**2**) by a nucleophilic aromatic substitution reaction ( $S_NAr$ ) with benzyl mercaptan in the presence of  $K_2CO_3$ . However, this debenylation of **2** failed, preventing us from using this route to obtain **1**. After some explorations, we found that **3** could efficiently react with sodium dimethyldithiocarbamate in acetone at  $-15\text{ }^\circ\text{C}$ , affording the desired thioketone **1** in 75% yield.<sup>10</sup> The self-coupling reaction of **1** in triethyl phosphite produced the final product TCDBTTF2DT-DI in 50% yield. It is worth noting that the phosphite-induced self-coupling reaction of **1** occurred at room temperature. This is uncommon for the synthesis of TTF derivatives, where high temperature is required, sometimes even larger than  $120\text{ }^\circ\text{C}$ .<sup>11</sup>

Thermal properties of TCDBTTF2DT-DI have been investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA study (Figure S1, Supporting Information) shows that TCDBTTF2DT-DI has good thermal stability with a thermolysis onset temperature of  $366\text{ }^\circ\text{C}$ , which is slightly lower than that of NDI2DT-DTYM2 ( $388\text{ }^\circ\text{C}$ ).<sup>6a,b</sup> DSC analysis (Figure S2, Supporting Information) gives the melting point of TCDBTTF2DT-DI as  $261\text{ }^\circ\text{C}$ , which is higher than that of NDI2DT-DTYM2 ( $242\text{ }^\circ\text{C}$ ).<sup>6a,b</sup>

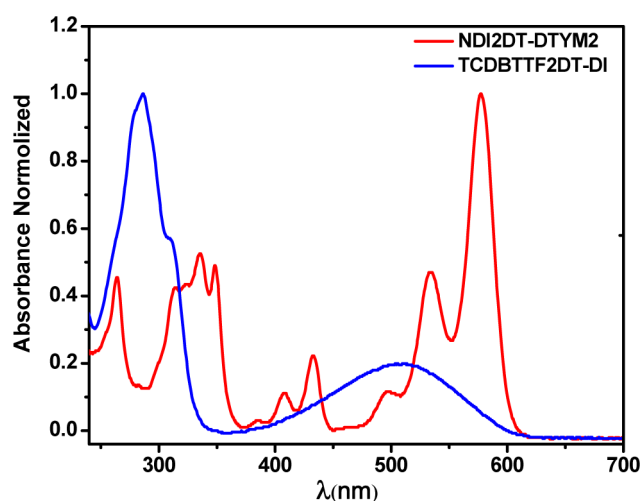
To gain an insight into the electronic structure of the TCDBTTF-DI derivative, DFT calculations were performed at the B3LYP/6-31G(d) level using Gaussian 09, and the minimum-energy conformation and frontier orbitals of a model molecule of TCDBTTF-DI with *N*-methyl groups were obtained (Figure 3). In comparison with the coplanar and rigid  $\pi$ -backbone of NDI-DTYM2,<sup>6</sup> TCDBTTF-DI exhibits a



**Figure 3.** M structure, geometry, frontier orbitals, and energies of a model TCDBTTF-DI derivative molecule, obtained by DFT calculations.

bent molecular backbone with a dihedral angle of about  $170^\circ$ . As mentioned in previously studies, the largest coefficients in the HOMO orbital of NDI-DTYM2 are delocalized along the long axis of the  $\pi$ -system, and the electron density distribution of the LUMO orbital is mainly positioned on the central NDI core, with low HOMO and LUMO energies of  $-6.8$  and  $-4.5$  eV, respectively.<sup>6a,b</sup> The electron density distribution of the HOMO orbital of TCDBTTF-DI is mainly located on the TTF unit, while the LUMO energy distribution is interrupted by the TTF segment and is located on the two electron-deficient phthalimide units. This indicates that there would be intramolecular charge transfer between the TTF unit and the two phthalimide moieties. The HOMO and LUMO energies of TCDBTTF-DI estimated by DFT calculations are  $-6.3$  and  $-3.4$  eV, respectively, where the LUMO level is approximately 1.1 eV higher than that of NDI-DTYM2. The significantly higher LUMO energy of TCDBTTF-DI might be explained by the weaker electron-withdrawing ability of the five-membered imide ring and the interrupted electron density distribution of its LUMO by the TTF unit.

The absorption spectra of TCDBTTF2DT-DI and NDI2DT-DTYM2<sup>6a,b</sup> in dichloromethane are shown in Figure 4. The data are summarized in Table 1. The absorption of



**Figure 4.** UV-vis spectra of TCDBTTF2DT-DI and NDI2DT-DTYM2 in dichloromethane solution.

NDI2DT-DTYM2 shows fine vibrational features, indicating a strong rigidity and planarity of its molecular backbone.<sup>12</sup> In contrast, TCDBTTF2DT-DI exhibits two broad absorption bands: one at a higher energy that originates from the  $\pi$ - $\pi^*$  transition of the conjugated backbone and the other at a lower energy that is attributed to the internal charge transfer (ICT) between TTF and phthalimide moieties.<sup>13</sup> In addition, the absorption spectra of TCDBTTF2DT-DI and NDI2DT-DTYM2 exhibit distinct behaviors in solution versus in the solid state (Figure S3, Supporting Information). TCDBTTF2DT-DI shows a blue shift, indicating H-type molecular aggregation, while NDI2DT-DTYM2 exhibits a red shift, a feature of J-type molecular aggregation.<sup>14</sup> Interestingly, in spite of the large difference in absorption spectral features, NDI2DT-DTYM2 and TCDBTTF2DT-DI show similar solution absorption onsets of 614 and 608 nm, respectively, with almost the same optical band gap of approximately 2.0 eV and similar colors in either the solution or solid state.

Table 1. Optical and Electrochemical Properties of NDI2DT-DTYM2 and TCDBTTF2DT-DI

compd	$\lambda_{\max}$ (nm)		HOMO (eV)	LUMO <sup>a</sup> (eV)	$E_g^{\text{opt}}$ (eV)
	solution	film			
NDI2DT-DTYM2 <sup>ref:6a,b</sup>	335, 348, 534, 576	342, 355, 539, 595	-6.3 <sup>b</sup>	-4.3	2.02 (1.92)
TCDBTTF2DT-DI	286, 508	275, 486	-5.8 <sup>c</sup>	-3.6	2.04 (2.13)

<sup>a</sup>Estimated from the equation  $\text{LUMO} = -4.4 - E_{\text{red1}}^{1/2}$ . <sup>b</sup>Estimated from the equation  $\text{HOMO} = \text{LUMO} - E_g^{\text{opt}}$ . <sup>c</sup>Estimated from the equation  $\text{HOMO} = -4.4 - E_{\text{ox1}}^{1/2}$ .

As shown in Figure 5, cyclic voltammetry (CV) for NDI2DT-DTYM2<sup>6a,b</sup> shows two reversible reduction waves

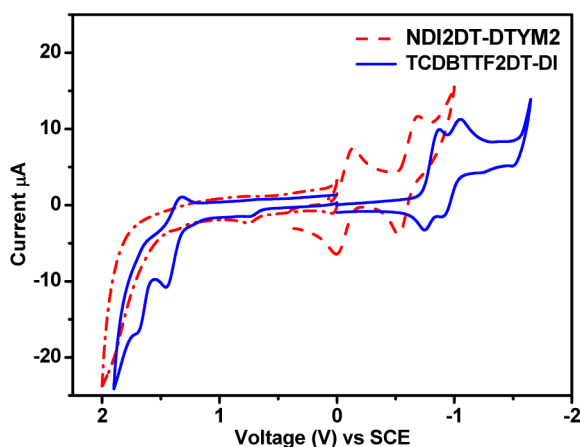


Figure 5. Cyclic voltammograms of NDI2DT-DTYM2 and TCDBTTF2DT-DI with 0.1 M  $\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_2\text{Cl}_2$  solution under scan rate of 100 mV/s.

with half-wave reductive potentials of  $E_{\text{red1}}^{1/2} = -0.07$  and  $E_{\text{red2}}^{1/2} = -0.65$  V. In comparison with NDI2DT-DTYM2, TCDBTTF2DT-DI is more difficult to be reduced and showed more negative reduction potentials with half-wave reduction potentials at  $E_{\text{red1}}^{1/2} = -0.80$  and  $E_{\text{red2}}^{1/2} = -0.97$  V. The more negative reduction potentials of TCDBTTF2DT-DI may be explained by the weaker electron-withdrawing ability of the five-membered imide ring and by the interruption of the electron density distribution of molecular LUMO orbital by the electron-donating TTF unit. Additionally, TCDBTTF2DT-DI exhibits a quasi-reversible oxidation wave with  $E_{\text{ox1}}^{1/2} = 1.38$  V, which could be ascribed to the electron-donating TTF unit. The CV results indicate that TCDBTTF2DT-DI has HOMO and LUMO energies of  $-5.8$  and  $-3.6$  eV, respectively, and act both as an electron donor and an electron acceptor. This makes TCDBTTF-DI derivatives potential ambipolar semiconducting materials. It is worth noting that the HOMO/LUMO energy levels of TCDBTTF2DT-DI are very close to those of some representative ambipolar organic semiconductors,<sup>4b,15</sup> demonstrating the possibility of TCDBTTF-DI derivatives for ambipolar semiconducting materials.<sup>16</sup>

In summary, TCDBTTF2DT-DI, an isomer of the high performance n-type NDI2DT-DTYM2, has been successfully synthesized by a phosphate-induced self-coupling reaction at room temperature. Optical and electrochemical behaviors of TCDBTTF2DT-DI have been investigated and compared with those of NDI2DT-DTYM2 to understand the influence of molecular structure on the properties of  $\pi$ -conjugated materials. TCDBTTF2DT-DI adopts H-type molecular aggregation in the solid state, which differs from the J-type molecular aggregation of NDI2DT-DTYM2. In comparison with the

electron-accepting properties of NDI2DT-DTYM2, TCDBTTF2DT-DI can act as an electron donor and an electron acceptor and could be a potential ambipolar semiconducting material. Our results confirm that the isomeric structural variation of  $\pi$ -systems can be an effective strategy for exploring new  $\pi$ -functional materials.

## EXPERIMENTAL SECTION

**Synthesis.** 4,5-Dichlorophthalimide<sup>17</sup> and 11-(bromomethyl)tricosane<sup>18</sup> were synthesized according to the literature procedures.

**5,6-Dichloro-4,7-diiodoisindoline-1,3-dione (5).** 4,5-Dichlorophthalimide (2 g, 9.26 mmol) and iodine (2.35 g, 9.26 mmol) were dissolved in 10 mL of fuming sulfuric acid (50%) and heated at 100 °C for 20 h. The temperature was gradually raised to 170 °C and left at this temperature for 6 h. The mixture was then cooled to room temperature and poured into ice-water to yield a brown solid. The solid was washed with water and dichloromethane several times to remove the residual acid and iodine, and then the product was recrystallized in DMF, affording 3.18 g of a white solid (yield 73%). <sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  11.86 (s, NH); <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  96.9, 134.7, 142.2, 165.4 (C=O); MS (EI)  $m/z$  467 M<sup>+</sup>. Anal. Calcd for  $\text{C}_8\text{HCl}_2\text{I}_2\text{NO}_2$ : C, 20.54; H, 0.22; N, 2.99. Found: C, 20.63; H, (<0.3); N, 3.01.

**5,6-Dichloro-2-(2-decyltetradecyl)-4,7-diiodoisindoline-1,3-dione (4).** Compound 5 (1.36 g, 2.91 mmol) was reacted with 11-(bromomethyl)tricosane (1.40 g, 3.20 mmol) in the presence of an excess of potassium carbonate (0.8 g, 5.82 mmol) in 10 mL of DMF at 95 °C for 8 h. The reaction mixture was then cooled to room temperature and washed with water. The crude product was purified by column chromatography using a mixture of petroleum ether and dichloromethane (3:1) as the eluent. Product (800 mg) was obtained as a solid (yield 35%): <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 0.85–0.90 (m, 6H), 1.17–1.32 (m, 40H), 1.87 (br, 1H), 3.58–3.61 (m, 2H); <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 26.2, 29.3, 29.4, 29.55, 29.62, 29.65, 29.67, 29.68, 29.9, 31.5, 31.9, 36.8, 43.7, 94.7, 133.2, 143.8, 164.2; MS (MALDI-TOF)  $m/z$  804.1 M<sup>+</sup>. Anal. Calcd for  $\text{C}_{32}\text{H}_{49}\text{Cl}_2\text{I}_2\text{NO}_2$ : C, 47.78; H, 6.14; N, 1.74. Found: C, 47.72; H, 6.10; N, 1.61.

**5,6-Dichloro-2-(2-decyltetradecyl)-1,3-dioxoisindoline-4,7-dicarbonitrile (3).** To a mixture of 4 (2.2 g, 2.73 mmol) and 15 mL of DMF was added cuprous cyanide (0.98 g, 10.9 mmol), and the mixture was refluxed for 6 h. The resulting mixture was diluted with dichloromethane and washed with brine several times. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography using a mixture of petroleum ether and dichloromethane (1:1) as the eluent to afford 1.1 g of white product (yield 68%): <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 0.85–0.90 (m, 6H), 1.17 (m, 40H), 1.80 (br, 1H), 3.56–3.58 (m, 2H); <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.6, 26.1, 29.3, 29.49, 29.53, 29.6, 29.7, 29.8, 31.3, 31.8, 36.9, 43.7, 112.6, 110.1, 132.5, 142.9, 162.7; MS (MALDI-TOF)  $m/z$  633.4 (M + K)<sup>+</sup>. Anal. Calcd for  $\text{C}_{34}\text{H}_{49}\text{Cl}_2\text{N}_3\text{O}_2$ : C, 67.76; H, 8.19; N, 6.97. Found: C, 67.99; H, 8.23; N, 7.06.

**5,6-Bis(benzylthio)-2-(2-decyltetradecyl)-1,3-dioxoisindoline-4,7-dicarbonitrile (2).** Compound 3 (200 mg, 0.332 mmol) and  $\text{K}_2\text{CO}_3$  (229 mg, 1.66 mmol) were dissolved in DMF (8 mL), and the mixture was stirred under a nitrogen atmosphere at room temperature for 30 min. Benzyl mercaptan (86.5 mg, 0.697 mmol) was then added to the mixture at 0 °C under a nitrogen atmosphere, and the mixture was stirred at 0 °C for 3 h. The reaction mixture was poured into ice-

water and filtered. The red solid obtained was purified by flash chromatography using the mixture of petroleum ether and dichloromethane (1:2) as the eluent to afford 122 mg of a yellow solid (yield 47%):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 0.84–0.88 (m, 6H), 1.2 (m, 40H), 1.83 (br, 1H), 3.54–3.57 (m, 2H), 4.40 (s, 4H), 7.18–7.24 (br, 10H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 26.3, 29.4, 29.6, 29.9, 31.4, 31.9, 41.4, 43.4, 112.1, 115.7, 128.2, 128.9, 129.2, 132.7, 134.9, 152.2, 163.2; MS (MALDI-TOF)  $m/z$  778.4  $\text{M}^+$ . Anal. Calcd for  $\text{C}_{48}\text{H}_{63}\text{N}_3\text{O}_2\text{S}_2$ : C, 74.09; H, 8.16; N, 5.40. Found: C, 74.29; H, 8.13; N, 5.42.

**6-(2-Decyltetradecyl)-2,5,7-trioxo-6,7-dihydro-5H-[1,3]-dithiolo[4,5-f]isoindole-4,8-dicarbonitrile (1).** Sodium dimethyl-dithiocarbamate (53.4 mg, 0.249 mmol) was dissolved in 10 mL of acetone and dropped into a mixture of 3 (150 mg, 0.167 mmol) and 10 mL acetone under a nitrogen atmosphere at  $-15^\circ\text{C}$ . The mixture was maintained at  $-15^\circ\text{C}$  for 1 h and then exposed to air at room temperature for another 1 h. The solvent was removed under reduced pressure. Chromatography of the residue on a silica gel column with petroleum ether and dichloromethane (2:3) as eluent afforded 117 mg of white product (yield 75%):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.85–0.90 (m, 6H), 1.25 (m, 40H), 1.87 (br, 1H, CH), 3.64–3.67 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 22.7, 26.2, 29.3, 29.57, 29.61, 29.64, 30.0, 31.9, 37.0, 43.6, 104.7, 111.3, 131.4, 143.9, 162.8, 181.2; MS (MALDI-TOF)  $m/z$  646.3 ( $\text{M} + \text{Na}$ ) $^+$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{49}\text{N}_3\text{O}_3\text{S}_2$ : C, 67.38; H, 7.92; N, 6.73. Found: C, 67.28; H, 7.92; N, 6.73.

**TCDBTTF2DT-DI.** At room temperature, compound 1 (100 mg, 0.16 mmol) was dissolved in  $\text{P}(\text{OEt})_3$  (5 mL) and stirred for 3 h. A purplish red solid precipitated out of solution and was washed with methanol and then purified by column chromatography using petroleum ether and dichloromethane (1:2) as the eluent. 50 mg of pure product was obtained (yield 50%): mp 261–263  $^\circ\text{C}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 0.85–0.90 (m, 6H), 1.25 (m, 40H), 1.85 (br, 1H), 3.60–3.62 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 26.2, 29.3, 29.4, 29.57, 29.61, 29.65, 29.66, 29.7, 29.9, 31.4, 31.9, 31.91, 102.8, 111.2, 131.7, 149.3, 162.8; MS (MALDI-TOF)  $m/z$  1216  $\text{M}^+$ . Anal. Calcd for  $\text{C}_{70}\text{H}_{98}\text{N}_6\text{O}_4\text{S}_4$ : C, 69.15; H, 8.12; N, 6.91. Found: C, 69.10; H, 8.10; N, 6.89.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

General methods, thin film UV–vis spectra of NDI2DT-DTYM2 and TCDBTTF2DT-DI, TGA and DSC plots of TCDBTTF2DT-DI, AFM and XRD images of thin films of TCDBTTF2DT-DI, MS and NMR spectra of compounds 1–5 and TCDBTTF2DT-DI, and tables of atom coordinates and absolute energies for TCDBTTF2DT-DI. 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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## ■ REFERENCES

- (1) (a) Shinamura, S.; Osaka, I.; Miyazaki, E.; Nakao, A.; Yamagishi, M.; Takeya, J.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 5024. (b) Mas-Montoya, M.; Ortiz, R. P.; Curriel, D.; Espinosa, A.; Allain, M.; Facchetti, A.; Marks, T. J. *J. Mater. Chem. C* **2013**, *1*, 1959.
- (2) Okamoto, H.; Kawasaki, N.; Kaji, Y.; Kubozono, Y.; Fujiwara, A.; Yamaji, M. *J. Am. Chem. Soc.* **2008**, *130*, 10470.
- (3) Newman, C. R.; Frisbie, C. D.; da Silva, D. A.; Bredas, J. L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436.
- (4) (a) Li, R.; Dong, H.; Zhan, X.; Li, H.; Wen, S.; Deng, W.; Han, K.; Hu, W. *J. Mater. Chem.* **2011**, 11335. (b) Liang, Z.; Tang, Q.; Mao, R.; Liu, D.; Xu, J.; Miao, Q. *Adv. Mater.* **2011**, *23*, 5514. (c) Zhao, Z.; Zhang, F.; Zhang, X.; Yang, X.; Li, H.; Gao, X.; Di, C.; Zhu, D. *Macromolecules* **2013**, *46*, 7705.
- (5) (a) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Adv. Mater.* **2011**, *23*, 268. (b) Meng, Q.; Hu, W. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14152.
- (6) (a) Gao, X.; Di, C.; Hu, Y.; Yang, X.; Fan, H.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *J. Am. Chem. Soc.* **2010**, *132*, 3697. (b) Hu, Y.; Gao, X.; Di, C.; Yang, X.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *Chem. Mater.* **2011**, *23*, 1204. (c) Zhao, Y.; Di, C.; Gao, X.; Hu, Y.; Guo, Y.; Zhang, L.; Liu, Y.; Wang, J.; Hu, W.; Zhu, D. *Adv. Mater.* **2011**, *23*, 2448. (d) Hu, Y.; Qin, Y.; Gao, X.; Zhang, F.; Di, C.; Zhao, Z.; Li, H.; Zhu, D. *Org. Lett.* **2012**, *14*, 292. (e) Zhang, F.; Hu, Y.; Schuettfort, T.; Di, C.; Gao, X.; McNeill, C. R.; Thomsen, L.; Mannsfeld, S. C. B.; Yuan, W.; Sirringhaus, H.; Zhu, D. *J. Am. Chem. Soc.* **2013**, *135*, 2338.
- (7) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891.
- (8) Pratt, D. S.; Perkins, G. A. *J. Am. Chem. Soc.* **1918**, *40*, 219.
- (9) Gao, X.; Wang, Y.; Yang, X.; Liu, Y.; Qiu, W.; Wu, W.; Zhang, H.; Qi, T.; Liu, Y.; Lu, K.; Du, C.; Shuai, Z.; Yu, G.; Zhu, D. *Adv. Mater.* **2007**, *19*, 3037.
- (10) Sipyagin, A. M.; Aliev, Z. G. *Chem. Heterocycl. Compd.* **1993**, *29*, 1030.
- (11) (a) Miles, M. G.; Wilson, J. D.; Dahm, D. J.; Wagenknecht, J. H. *J. Chem. Soc., Chem. Commun.* **1974**, 751. (b) Miles, M. G.; Wager, J. S.; Wilson, J. D. *J. Org. Chem.* **1975**, *40*, 2577. (c) Gautier, N.; Dumur, F.; Lloveras, V.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C.; Hudhomme, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 2765. (d) Baffreau, J.; Dumur, F.; Hudhomme, P. *Org. Lett.* **2006**, *8*, 1307. (e) Oton, F.; Lloveras, V.; Mas-Torrent, M.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 10902.
- (12) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Sausalito, CA, 2006; p 942.
- (13) Roquet, S.; Cravino, A.; Leriche, P.; Alevque, O.; Frere, P.; Roncali, J. *J. Am. Chem. Soc.* **2006**, *128*, 3459.
- (14) Mishra, A.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. B. *Chem. Rev.* **2000**, *100*, 1973.
- (15) (a) Tang, M.; Reichardt, A. D.; Miyaki, N.; Stoltenberg, R. M.; Bao, Z. *J. Am. Chem. Soc.* **2008**, *130*, 6064. (b) Liu, Y.; Song, C.; Zeng, W.; Zhou, K.; Shi, Z.; Ma, C.; Yang, F.; Zhang, H.; Gong, X. *J. Am. Chem. Soc.* **2010**, *132*, 16349. (c) Suraru, S. L.; Zschieschang, U.; Klauk, H.; Wurthner, F. *Chem. Commun.* **2011**, *47*, 11504. (d) Irimia-Vladu, M.; Glowacki, E. D.; Troshin, P. A.; Schwabegger, G.; Leonat, L.; Susarova, D. K.; Krystal, O.; Ullah, M.; Kanbur, Y.; Bodea, M. A.; Razumov, V. F.; Sitter, H.; Bauer, S.; Sariciftci, N. S. *Adv. Mater.* **2012**, *24*, 375.
- (16) Bottom-gate top-contact OTFTs based on TCDBTTF2DT-DI were fabricated by spin-coating its chloroform or dichlorobenzene solution on octadecyltrichlorosilane (OTS)-modified  $\text{SiO}_2/\text{Si}$  wafers to investigate the charge-transport properties of TCDBTTF2DT-DI. Unfortunately, TCDBTTF2DT-DI did not show any FET characteristics although the thin-film morphology is generally good, as shown in atomic force microscopy (AFM) images (Figure S4, Supporting Information). X-ray diffraction (XRD) measurements showed few crystallization features of thin films of TCDBTTF2DT-DI (Figure S5, Supporting Information). The inactivity of TCDBTTF2DT-DI in transistors was probably ascribed to its unfavorable molecular packing

in solid state. Further device work and *N*-substituent modulation of TCDBTTF-DI derivatives are currently underway.

(17) Crockett, G. C.; Swanson, B. J.; Anderson, D. R.; Koch, T. H. *Synth. Commun.* **1981**, *11*, 447.

(18) Guo, X.; Watson, M. D. *Org. Lett.* **2008**, *10*, 5333.