

# Electronegative Oligothiophenes Based on Difluorodioxocyclopentene-Annulated Thiophenes: Synthesis, Properties, and n-Type FET Performances

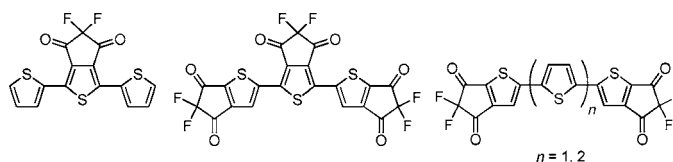
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## ABSTRACT



A series of oligothiophenes containing difluorodioxocyclopentene-annulated thiophene units was synthesized, and their electronic properties and structures were investigated by spectroscopic and electrochemical measurements and X-ray analyses. The oligothiophenes having the terminal difluorodioxocyclopentene annulations showed n-type semiconducting behavior on FET devices, and the quaterthiophene revealed field-effect electron mobility as high as  $1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

Organic field-effect transistors (OFETs) based on  $\pi$ -conjugated systems have received considerable interest in recent years as they are indispensable components in organic electronics.<sup>1</sup> Thiophene-based oligomers and polymers have been extensively investigated for this application,<sup>2</sup> and great

achievements for p-type organic semiconductors have been reported.<sup>1</sup> One of the most urgent aspects for the development of OFETs is the design and synthesis of new conjugated systems for electronically complementary n-type organic semiconductors.<sup>3</sup> Thus, the incorporation of electron-withdrawing groups such as fluorine<sup>4</sup> and perfluoroalkyl<sup>5–7</sup> substituents into oligothiophenes has been a part of ongoing efforts to lower and tune their LUMO energy levels, which leads to increasing electronegativity. In this context, we have recently revealed that the hexafluorocyclopenta[c]thiophene unit **1** (F) effectively contributes to increasing the electrone-

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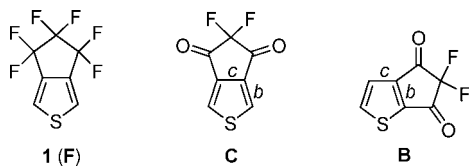
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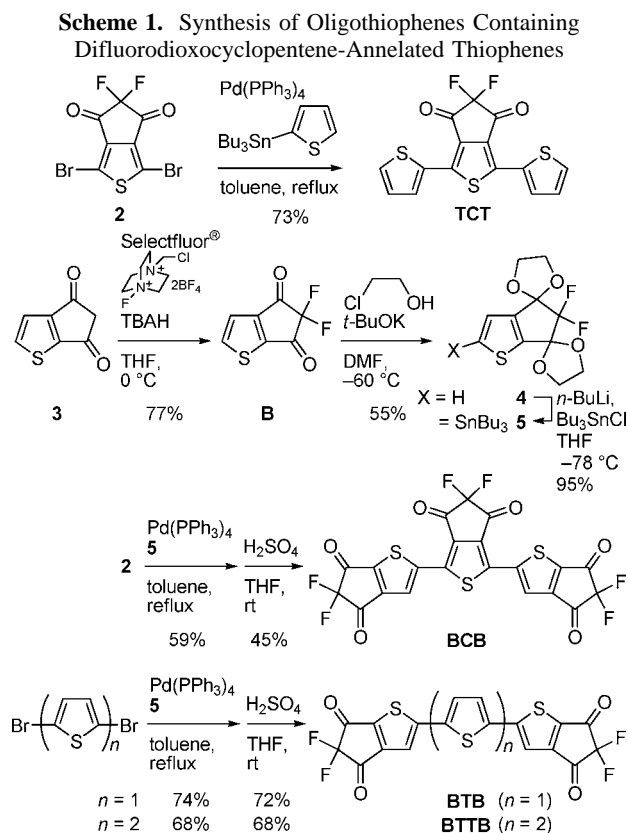
gative character of oligothiophenes without interrupting the effective conjugation (Figure 1).<sup>8</sup> On the basis of this finding



**Figure 1.** Structures of electronegative thiophene monomer units.

and the fact that only a few carbonyl-functionalized oligothiophenes are known to exhibit n-type OFET performance,<sup>9,10</sup> we have envisaged that difluorodioxocyclopenta[*c*]thiophene **C**, which is one of the key synthetic precursors of **1**,<sup>8</sup> also might be a valuable building unit for electronegative oligothiophenes because it has a cyclopentene-annulated structure as well as two strongly electron-withdrawing carbonyl groups conjugated with the thiophene  $\pi$ -system. In addition, as substituent groups on the terminal positions of conjugated oligomers are well-known to exert a strong influence on both the molecular orbital energies and the packing structures in film states,<sup>5e,6a,9,11</sup> we planned to utilize difluorodioxocyclopenta[*b*]thiophene **B** as a new electronegative terminal unit. Here, we report on the synthesis, properties, and n-type OFET performance of newly designed electronegative oligothiophenes containing the difluorodioxocyclopentene-annulated thiophenes.

The synthetic routes to carbonyl-functionalized oligothiophenes are outlined in Scheme 1. The terthiophene **TCT** was prepared by the palladium-catalyzed Stille coupling reaction between dibromide **2**<sup>8</sup> and 2-tributylstannylthiophene. Although 5,5-difluoro-4*H*-cyclopenta[*b*]thiophene-



4,6(5*H*)-dione (**B**) is a known compound, its reported synthetic procedures are difficult to reproduce because of the harsh reaction conditions and the use of volatile tetrafluoroethylene.<sup>12</sup> As the key chemical modification of the present work, we have established a new synthetic method for **B**. Thus, the electrophilic fluorination reaction of easily available 1,3-diketone **3**<sup>13</sup> with Selectfluor in the presence of tetrabutylammonium hydroxide (TBAH) took place smoothly under mild conditions to give **B** in 77% yield. After ketalization of the carbonyl groups under basic conditions,<sup>14</sup> lithiation of **4** with *n*-BuLi and subsequent reaction with tributylstannylchloride gave the counterpart monomer **5**. Oligothiophenes **BCB**, **BTB**, and **BTTB** were prepared via Stille coupling of **5** with the corresponding dibromothiophenes followed by acidic deprotection of the ketal groups. These oligomers were unambiguously characterized by spectroscopic measurements and elemental analyses.<sup>15</sup> To enable physical measurements and FET evaluation, purification was done by recrystallization for **TCT**, **BCB**, and **BTB** or by repeated sublimation under a high vacuum for **BTTB**.

Single crystals of **TCT** and **BCB** for X-ray crystallographic analyses were grown by slow evaporation from the  $\text{CHCl}_3$  solutions. Unfortunately, we were unable to obtain single crystals of **BTB** and **BTTB** despite numerous attempts.

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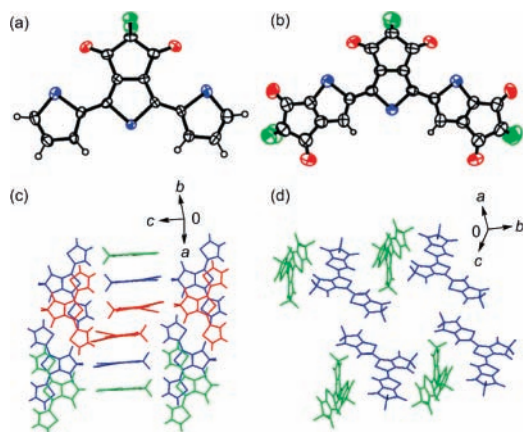
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There are three and two crystallographically independent molecules in the unit cells of **TCT**<sup>16</sup> and **BCB**,<sup>17</sup> respectively, and their conformations do not deviate much from each other. As representatively drawn in Figure 2, parts a and b, their



**Figure 2.** Molecular structures of **TCT** (a) and **BCB** (b) and packing diagrams of **TCT** (c) and **BCB** (d).

structures have transoid orientations between adjacent thiophene rings with expected coplanar geometries, which probably result from intramolecular interactions between the carbonyl oxygens on the central **C** units and the outerthiophene sulfur atoms; their nonbonding distances of 2.96–3.04 Å for **TCT** and 2.91–2.97 Å for **BCB** are shorter than the sum (3.32 Å) of the van der Waals radii. In the crystal, the **TCT** molecules are arranged in a slipped face-to-face stacking manner with interfacial distances of 3.48–3.50 Å (Figure 2c). In contrast, the crystal packing of **BCB** shows non-stacking behavior, resulting from the lack of strong intermolecular  $\pi$ – $\pi$  interactions (Figure 2d). This packing form of **BCB** might be disadvantageous to high charge-carrier transport.

The electronic absorption and photoluminescent maxima and the cyclic voltammetry (CV) data of the newly developed oligomers are summarized in Table 1 together with those of reference terthiophenes. The low solubility of **BTTB** did not allow measurement by CV. The absorption and fluorescence maxima of **TCT** are markedly red-shifted relative to those of **TFT**<sup>8</sup> and **TC'T**.<sup>15</sup> This indicates that the **C** unit not only contributes to keeping the effective conjugation but also has stronger electron-accepting ability than those of the **F** and **C'** units, leading to a unique donor–acceptor–donor con-

(16) Crystal data for **TCT**:  $C_{15}H_6O_2F_6S_3$ ,  $M = 352.39$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 15.6617(5)$  Å,  $b = 14.8817(5)$  Å,  $c = 17.7747(6)$  Å,  $\beta = 91.2299(10)^\circ$ ,  $V = 4141.8(2)$  Å<sup>3</sup>,  $Z = 12$ ,  $D_{\text{calc}} = 1.695$  g cm<sup>-3</sup>,  $F_{(000)} = 2136.00$ ,  $\mu = 5.618$  cm<sup>-1</sup> (Mo K $\alpha$ ;  $\lambda = 0.71075$  Å), 51159 reflections measured, 12597 unique,  $R = 0.0678$  for  $I > 2\sigma(I)$ ,  $wR = 0.1456$  for all data.

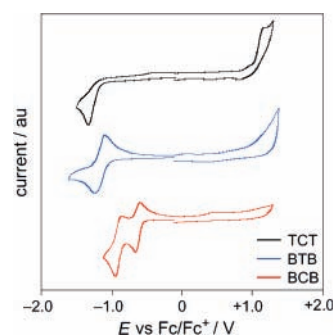
(17) Crystal data for **BCB**:  $C_{21}H_{10}O_6F_6S_3$ ,  $M = 560.41$ , monoclinic, space group  $C2/c$  (no. 15),  $a = 29.607(2)$  Å,  $b = 13.3040(10)$  Å,  $c = 17.5390(12)$  Å,  $\beta = 113.503(3)^\circ$ ,  $V = 6335.3(8)$  Å<sup>3</sup>,  $Z = 12$ ,  $D_{\text{calc}} = 1.763$  g cm<sup>-3</sup>,  $F_{(000)} = 3336.00$ ,  $\mu = 40.939$  cm<sup>-1</sup> (Cu K $\alpha$ ;  $\lambda = 1.54187$  Å), 34060 reflections measured, 5736 unique,  $R = 0.0795$  for  $I > 2\sigma(I)$ ,  $wR = 0.1713$  for all data.

**Table 1.** Spectroscopic and CV Data for the Oligomers

| compd       | abs <sub>max</sub> /nm <sup>a</sup> | flu <sub>max</sub> /nm <sup>a</sup> | $E_{p,a}/V^b$      | $E_{p,c}/V^b$      |
|-------------|-------------------------------------|-------------------------------------|--------------------|--------------------|
| <b>TCT</b>  | 467                                 | 535                                 | +1.13 <sup>c</sup> | –1.34 <sup>c</sup> |
| <b>BTB</b>  | 424                                 | 476                                 | not observed       | –1.24              |
| <b>BCB</b>  | 440                                 | 494                                 | not observed       | –0.66, –0.95       |
| <b>BTTB</b> | 463 <sup>d</sup>                    | 564 <sup>d</sup>                    | not measured       |                    |
| <b>TFT</b>  | 373                                 | 436, 452                            | +1.63 <sup>c</sup> | –1.72              |
| <b>TC'T</b> | 419                                 | 453                                 | +1.00 <sup>c</sup> | –1.63              |
| <b>3T</b>   | 354                                 | 406, 430                            | +1.15 <sup>c</sup> | nd (<–2.00)        |

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> In C<sub>6</sub>H<sub>5</sub>F, 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>, V vs Fc/Fc<sup>+</sup>. <sup>c</sup> Irreversible. <sup>d</sup> In THF.

figuration in **TCT**. Actually, solvent-dependent absorption shifts were observed for **TCT** ( $\lambda_{\text{max}} = 453$  nm in cyclohexane and 459 nm in THF). Thus, while the electrochemical oxidation peak of **TCT** is observed between those of **TFT** and **TC'T**, the reduction peak of **TCT** largely shifts to a positive potential compared with those of **TFT** and **TC'T**. DFT calculations are in agreement with these experimental results (Figure S2 and Table S1, see the Supporting Information). The absorption and fluorescence maxima of **BTB** and **BCB** are observed at longer wavelength than those of unsubstituted **3T**, and their oxidation potentials are not observed within the potential window of the measurement. These results indicate that the terminally annelated difluorodioxocyclopentene groups stabilize both the HOMO and LUMO levels with narrowing of the optical gap. Figure 3



**Figure 3.** Cyclic voltammograms of **TCT**, **BTB**, and **BCB** in C<sub>6</sub>H<sub>5</sub>F containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 100 mV s<sup>-1</sup>.

shows the cyclic voltammograms of **TCT**, **BTB**, and **BCB**. It is worth mentioning that, although an irreversible wave is observed for **TCT**, **BTB** displays a reversible reduction wave with the half-wave potential of  $E_{1/2} = -1.17$  V. This shows that the end-capping with the difluorodioxocyclopentene unit can stabilize the formation of radical anionic species.

Moreover, the introduction of a difluorodioxocyclopentene unit at all thiophenes causes two reversible reduction waves to arise and further positively shift the  $E_{1/2}$  values to  $-0.62$  and  $-0.91$  V for **BCB**. This reversibility of the reduction may contribute to forming a stable conductive channel in OFET devices.

The potential of **TCT**, **BCB**, **BTB**, and **BTTB** as n-type organic semiconductors has been examined by field-effect electron mobility. The source and drain Au electrodes of FET with bottom-contact geometry were pre-patterned on a  $\text{SiO}_2$  dielectric layer thermally grown on a p-doped silicon gate substrate, and films of these oligomers were deposited on the HMDS-modified  $\text{SiO}_2$  layer with a thickness of 300 nm under a high vacuum.<sup>18</sup> Neither **TCT** film nor **BCB** film deposited at room temperature showed FET behavior. On the other hand, as summarized in Table 2, the **BTB** and

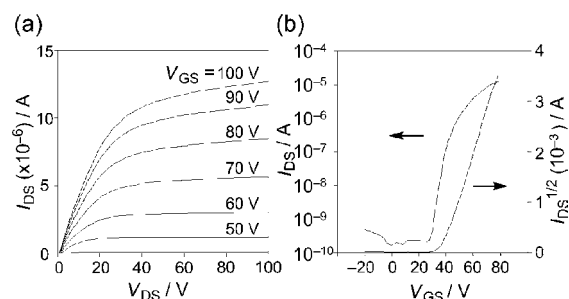
**Table 2.** Field-Effect Characteristics of **BTB** and **BTTB**

| compd       | geometry | $T_D/^\circ\text{C}^a$ | $\mu/\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ | $I_{\text{on}}/I_{\text{off}}$ | $V_{\text{th}}/\text{V}$ |
|-------------|----------|------------------------|---|--------------------------------|--------------------------|
| <b>BTB</b>  | bottom   | rt                     | $2.8 \times 10^{-5}$                          | $1.6 \times 10^3$              | 41                       |
| <b>BTTB</b> | bottom   | rt                     | $2.0 \times 10^{-4}$                          | $6.0 \times 10^3$              | 44                       |
| <b>BTTB</b> | bottom   | 90                     | $1.4 \times 10^{-3}$                          | $2.1 \times 10^3$              | 47                       |
| <b>BTTB</b> | bottom   | 110                    | $1.1 \times 10^{-3}$                          | $9.5 \times 10^4$              | 48                       |
| <b>BTTB</b> | top      | rt                     | $1.3 \times 10^{-2}$                          | $9.9 \times 10^4$              | 38                       |

<sup>a</sup> Deposition temperature.

**BTTB** films deposited at room temperature showed n-type FET behavior, and the field-effect electron mobility of **BTTB** is 1 order of magnitude higher than that obtained with **BTB**. When the substrate temperature during the deposition of **BTTB** was increased to  $90^\circ\text{C}$ , the electron mobility was improved and reached  $1.4 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ . Its output characteristics are depicted in Figure 4a. The FET performance was not further improved by thermal annealing of the device under a high vacuum, and the film did not show any peaks in the X-ray diffractogram. These results might correlate with the low crystallinity of **BTTB**. To further improve the performance, a top-contact OFET device was fabricated. The **BTTB** film was vacuum-deposited on a OTS-modified  $\text{SiO}_2/\text{Si}$  substrate.<sup>18</sup> The transfer characteristics of the device are shown in Figure 4b, and the field-effect electron mobility is found to be as high as  $1.3 \times 10^{-2} \text{ cm}^2$

(18) For details of bottom-contact and top-contact FET devices as well as the XRD chart and the AFM image of **BTTB** film, see the Supporting Information.



**Figure 4.** (a) Output characteristics of **BTTB** on bottom-contact geometry and (b) transfer characteristics of **BTTB** on top-contact geometry at 100 V of drain voltage.

$\text{V}^{-1} \text{s}^{-1}$  with the threshold voltage of 38 V and the on/off current ratio of  $9.9 \times 10^4$ , which is rather good performance among fluorinated oligothiophene systems.<sup>5c,7a</sup>

In summary, we have developed new oligothiophenes containing difluorodioxocyclopentene-annulated thiophene units. Spectroscopic and electrochemical measurements revealed that these oligomers have low-lying LUMO levels while maintaining effective conjugation. The quaterthiophene revealed good performance as an electron-transporting material on OFET devices. A major stimulus for further studies is the elucidation of the structure–FET-property relationship as well as the application to electron-transporting components of organic electronics such as photovoltaic devices.

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**Supporting Information Available:** Synthesis and characterization of all compounds and crystallographic CIF files of **TCT** and **BCB**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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