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Novel Phenylene–Thiophene Oligomer Derivatives with Dibenzothiophene 5,5-Dioxide Core: Synthesis, Characterization, and Applications in Organic Solar Cells

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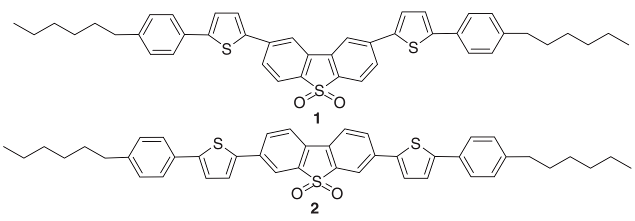
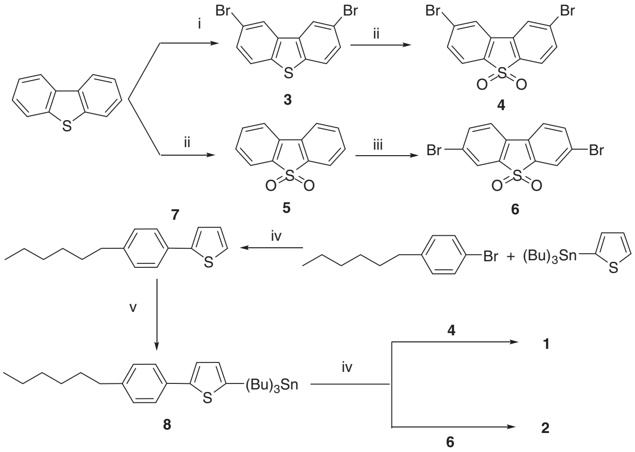
Donor–acceptor–donor oligomers with dibenzothiophene 5,5-dioxide core and end-cap phenylene–thiophene substitutes were newly synthesized. New oligomers were characterized by UV–vis absorption and photoluminescence spectroscopy, cyclic voltammetry, and applied as electron donor in bulk-heterojunction solar cells. The results indicate that phenylene–thiophene oligomer derivatives containing dibenzothiophene 5,5-dioxide moiety are appraised to be valuable electron donors.

Thiophene-containing oligomers with well-defined structures and monodispersed chain lengths, are easily modified by the introduction of a variety of functional groups into the aromatic backbone or through thienyl sulfur functionalization, and have been widely used in organic electronics including organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells (OSCs).[1,2] The selective dearomatization of the thienyl rings of oligothiophenes by the selective introduction of *S*,*S*-dioxides is a flexible and an efficient methodology to decrease energy band gaps and to improve electron affinities and stabilities of thiophene derivatives.[3] Recently, dibenzothiophene 5,5-dioxide moiety with electron-transporting character as a central core has been incorporated onto the backbone of electron donor units such as fluorene, carbazole, arylamine, quinoxaline, or pyrazine segments to afford highly efficient ambipolar charge-transporting light-emitting materials.[4,5] Phenylene–thiophene oligomers are promising electron-donor semiconducting materials with improved oxidation stability.[6,7] However, to our knowledge, there has been no paper reported on the synthesis of phenylene–thiophene oligomer derivatives containing dibenzothiophene 5,5-dioxide moiety and their applications in organic solar cells. Herein, dibenzothiophene 5,5-dioxide groups with electron-acceptor character were introduced into the framework of phenylene–thiophene oligomers via co-oligomerization, and two novel donor–acceptor–donor thiophene-containing oligomers **1** and **2** (Scheme 1) were obtained. Their characteristics and applications in solar cells were also investigated.

The strategy for preparation of the oligomers is outlined in Scheme 2. Starting from the commercially available dibenzothiophene, 2,8-dibromodibenzothiophene 5,5-dioxide (**4**) was obtained by bromination in glacial acetic acid with bromine and followed by oxidation with H_2O_2 according to the literature.[8] 3,7-Dibromodibenzothiophene 5,5-dioxide (**6**) could be attained by first oxidation of dibenzothiophene and then bromination with NBS.[4] The key precursor 2-(4-*n*-hexylphenyl)thiophene (**7**) was synthesized by the palladium-catalyzed Stille cross-coupling of 4-bromo-*n*-hexylbenzene with 2-tri-*n*-butylstannylthiophene. 2-(4-*n*-Hexylphenyl)thiophene was readily lithiated using butyllithium and then reacted with tributyltin chloride to give the stannyl compound **8**.[6] The target oligomers **1** and **2** have been systematically synthesized in good yields by Stille cross-coupling reactions of **8** with dibromodibenzothiophene 5,5-dioxides **4** and **6**, respectively, in DMF at 100 °C for 40 h.[9]



Scheme 1. Molecular structures of oligomers **1** and **2**.



Scheme 2. Reaction conditions; i) Br_2, CH_3COOH, 25 °C, 2 h, 115 °C, 5 h; ii) H_2O_2, CH_3COOH, 110 °C, 4 h; iii) NBS, H_2SO_4, 25 °C, 12 h; iv) DMF, $[Pd(PPh_3)_4]$, 100 °C, 40 h; v) *n*-BuLi, −78 °C, 1 h, then, $(Bu)_3SnCl$, 25 °C, 12 h.

The spectral (^1H, ^{13}C NMR and MS) and elemental analysis data for the newly synthesized oligomers are consistent with the proposed structures.[9] A single crystal of oligomer **2** was grown by slow evaporation from its benzene solution. Oligomer **2** crystallizes in a triclinic crystal system with a $P\bar{1}$ space group (Figure 1).[10] The selected averaged bond lengths and angles of **2** are listed in Table S1.[9] In the crystal structure, oligomer **2** is composed of one dithienyl dibenzothiophene 5,5-dioxide core,

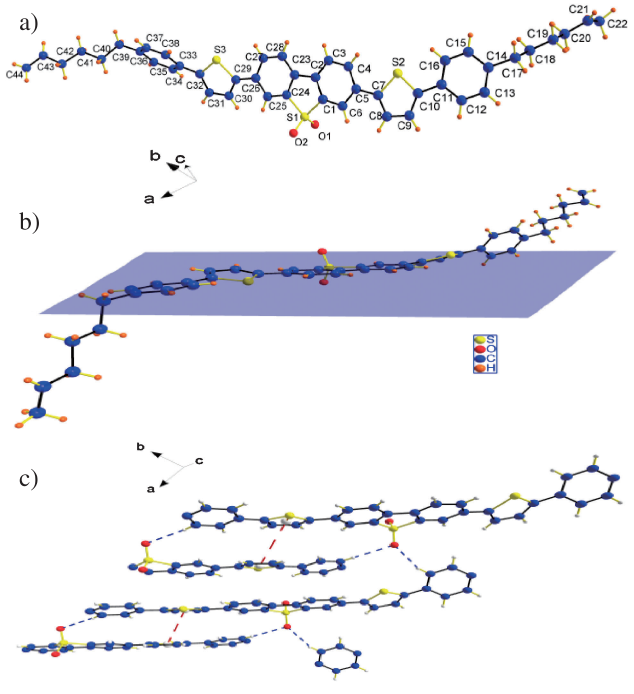


Figure 1. a) ORTEP drawing, b) model of "zigzag" shape, and c) view of the 1D supramolecular framework of **2**.

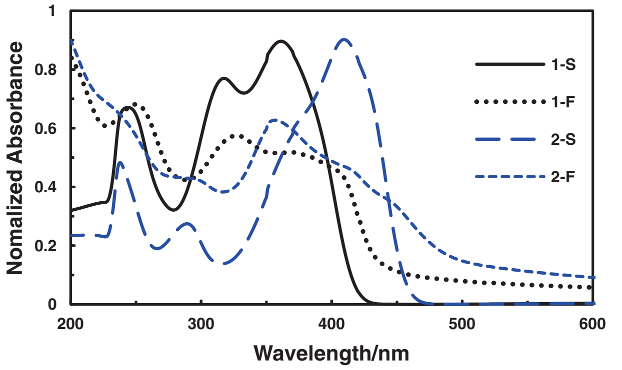


Figure 2. Normalized UV–vis absorption spectra: **1** in chloroform (**1**-S) and in film (**1**-F); **2** in chloroform (**2**-S) and in film (**2**-F).

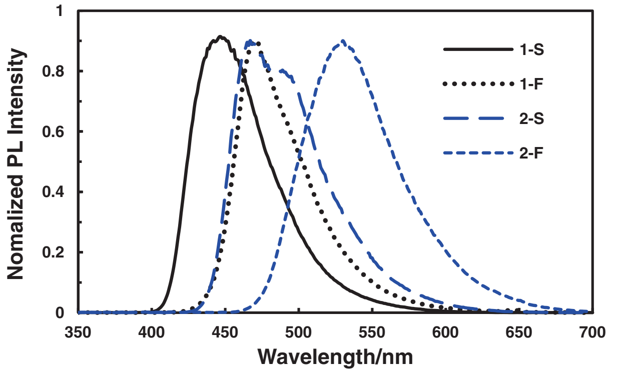


Figure 3. Normalized photoluminescence (PL) spectra: **1** in chloroform (**1**-S) and in film (**1**-F); **2** in chloroform (**2**-S) and in film (**2**-F).

and two end-cap *n*-hexylphenyl groups. The two end-cap *n*-hexylphenyl groups are situated in 2-positions of thiophene rings (C7–C10/*S*2, C29–C32/*S*3) of the dithienyl dibenzothiophene 5,5-dioxide core, respectively. The side view of the crystal structure reveals that molecule **2** does not have a flat conformation but a "zigzag" shape. The stacking structure of **2** along the α axis of the unit cell indicates that each molecule **2** has close contacts with the neighboring molecules by two types of weak interactions: (1) two adjacent molecules are packed into dimers through the π–π stacking interactions between the thiophene rings (C7–C10/*S*2), with a distance of 4.4745(5) Å; (2) C–H···O interactions between the C–H on benzene ring (C13, C38) with the O (O1, O2) atoms on the neighboring molecules with distances of 3.5574(6) and 3.4630(5) Å, respectively. All these weak interactions play important roles in the formation of the one-dimensional (1D) structure of **2**, and such 1D structure is desirable for fast charge transport along the stacking axis and thus **2** serves as a potential semiconductor material for photoelectronic applications.

Figure 2 shows the UV–vis absorption spectra of **1** and **2** in dilute $CHCl_3$ solution and in drop-cast films. The absorption maxima of **1** and **2** in solution peak at 362 and 409 nm (Table S2[9]), respectively, and there is a substantial red shift ($\Delta\lambda = 47$ nm) of the absorption maximum upon variation of substituted situations of 4-*n*-hexylphenyl-2-thienyl group at the aryl ring of dibenzothiophene, which is attributed to the asymmetric destabilization of the HOMO and the LUMO levels leading to a decrease in the energy band gap.[11] In thin films, the absorption bands become relatively broader and less structured. They are strongly blue-shifted with respect to the absorption spectra in solution. Such feature accounts for a very close packing in films of the oligomers as expected, Furthermore, the optical energy band gaps of **1** and **2** were determined from the absorption onset in film and were found to be 2.84 and 2.52 eV, respectively.[9,12]

Both oligomers are fluorescent in solution and in solid state (Figure 3). **1** shows strong sky-blue fluorescence in chloroform solution, which is red-shifted by 25 nm from 447 to 472 in thin film. The emission spectrum of **2** in solution shows a maximum emission peak at 465 nm with a broad shoulder peak in blue emission region. While in thin film, the emission spectrum of **2** is bathochromically shifted by 65 nm for maximum emission peak and only one broad peak in green emission region is observed. The pronounced changes in PL spectra are a result of the delocalization of the exciton within a cofacial stack induced by the π–π interactions.

The redox properties of oligomers were examined by cyclic voltammetry (CV) using a three-electrode cell in CH_2Cl_2 solution (Figure S1[9]) and showed quasi-reversible oxidation waves. Oligomers **1** and **2** exhibit onset oxidation potentials at 1.20 and 1.06 V vs. Ag/AgCl reference electrode, respectively. Considering the onset oxidation potential of ferrocene investigated at the beginning of the experiments is located at 260 mV relative to the Ag/AgCl reference electrode and assuming the energy level of the ferrocene/ferrocenium (Fc) reference is 4.8 eV below vacuum, the onset oxidation potentials can be used to determine the HOMO energy levels of oligomers.[12,13] The calculated HOMO energy levels of **1** and **2** are −5.74 and

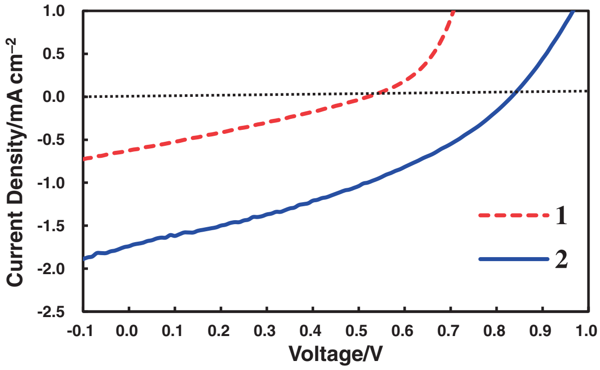


Figure 4. Current density–voltage (*J*–*V*) characteristic of solar cell devices under illumination.

−5.60 eV, respectively. It is noteworthy that such HOMO energy levels are lower than those of reported thiophene-containing oligomers.[1] These results indicate that the oligomers containing thiophene 1,1-dioxide moiety really have increased electron affinities and antioxidation stabilities. The CV analysis also includes the reduction waves. The LUMO energy levels of **1** and **2** determined from the onset reduction potentials are −3.04 and −3.12 eV, respectively (Table S2[9]). The LUMO energy levels calculated from the HOMO energy levels and optical energy band gaps are −2.90 and −3.08 eV, respectively. These values match quite well with each other. The HOMO and LUMO energy levels of oligomers **1** and **2** are well positioned appropriately with respect to those of the electron acceptor such as PCBM (phenyl-C61-butyric acid methyl ester), which clearly encourages the preparation of prototype organic solar cell devices based on these materials.[14]

Two oligomers can be dissolved in common organic solvents. It can hence be processed by spin-coating to fabricate bulk-heterojunction (BHJ) solar cell devices.[9,15] Figure 4 shows the current density–voltage curves of solar cell devices based on oligomer **1** and **2** under illumination of AM 1.5, 100 mW cm^{-2}. Due to the relatively large energy band gap, the maximum power conversion efficiency of solar cell device based on oligomer **1** is 0.09%. It is comparatively low, but verify the applicability of soluble phenylene–thiophene oligomer derivatives containing dibenzothiophene 5,5-dioxide moiety to BHJ solar cells.[16]

The BHJ solar cell device based on oligomer **2** shows an open circuit voltage of 0.83 V and a short-circuit current density of 1.74 mA cm^{-2}. Due to the lower HOMO level, the open circuit voltage of the solar cell based on **2** is higher than that of well-known poly(3-hexylthiophene) (about 0.65 V).[2,14] The fill factor, a measure of the squareness of the *J*–*V* characteristics, is equal to 36%. The evaluated power conversion efficiency is 0.52%, which is reasonably moderate, as compared to those previously reported using oligomers.[2] Optimizing of production parameters to obtain optimal device parameters is a task of future work.

In summary, the results indicate that phenylene–thiophene oligomer derivatives containing dibenzothiophene 5,5-dioxide moiety is a new kind of organic photoelectronic material with donor–acceptor–donor system, and oligomer **2** is a promising electron donor for organic solar cell.

These experiments were done at the Micro Functional Device Research Center of the College of Science and Technology, Nihon University.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

10 Selected data for **2**: Crystal system: Triclinic, Space group: $P\bar{1}$, $a = 10.4916(13)$ Å, $b = 10.9757(14)$ Å, $c = 16.4361(15)$ Å, $\alpha = 85.8190(10)°$, $\beta = 10.9757(14)°$, $\gamma = 82.6010(10)°$, $V = 1870.6(4)$ Å^3, $Z = 2$, $D = 1.245$ g cm^{-3}, $\mu = 0.235$ mm^{-1}, $T = 298$ K, $R_1 = 0.0855$, $wR_2 = 0.2621$, $S = 0.977$, Refl/Param. = 19082/442. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. 842675. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, U.K. (fax: +44 1223 336033); e-mail: deposit@ccdc.cam.ac.uk.

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15 Solar cell design: ITO-Glass/PEDOT:PSS/oligomer (**1** or **2**):PCBM/Al; solar cell area: 4 mm^2; oligomer (**1** or **2**):PCBM (1:1, w/w) layer spin-coated from chloroform solution.

16 Device parameters: An open circuit voltage (V_{OC}) of 0.52 V; a short circuit current density (J_{SC}) of 0.62 mA cm^{-2}; a fill factor (FF) of 0.28 and a power conversion efficiency (PCE) of 0.09%.