

# Electron-Transporting Oligothiophenes Containing Dicyanomethylene-Substituted Cyclopenta[*b*]thiophene: Chemical Tuning for Air Stability in OFETs

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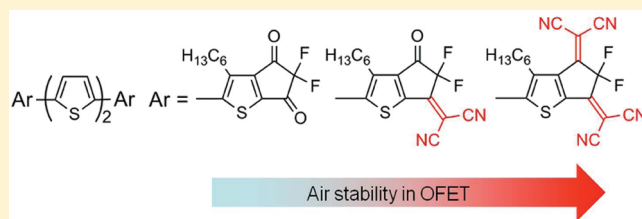
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**S** Supporting Information

**ABSTRACT:** We have synthesized new electron-transporting oligothiophenes containing dicyanomethylene-substituted cyclopenta[*b*]thiophene as an active material for the fabrication of solution-processable n-type organic field-effect transistors (OFETs). The influence of the number of dicyanomethylene groups as well as the position of hexyl groups was investigated in detail by performing photophysical and electrochemical measurements. Results revealed that the optical energy gaps and the lowest unoccupied molecular orbital (LUMO) energy levels can be controlled by changing the number of dicyanomethylene groups. In contrast, the position of hexyl groups has little influence on molecular electronic properties. X-ray diffraction and atomic force microscopy measurements revealed that spin-coated thin films of the new compounds had a crystalline structure. OFETs based on these compounds were evaluated in vacuum and air-exposed conditions, and the electron mobility of up to  $0.016 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was achieved. Furthermore, we demonstrated that the air stability of the OFETs depends on the LUMO energy level of the compounds.



## INTRODUCTION

Development of organic semiconducting materials based on  $\pi$ -conjugated systems for use in organic field-effect transistors (OFETs) has become an active area of research in recent years because of the potential applicability of these materials to large-area, lightweight, and flexible devices.<sup>1,2</sup> Another advantage of such organic materials is their diversity of molecular structures, which can be realized by versatile synthetic protocols in organic chemistry. For example, the introduction of electron-withdrawing groups such as fluorine,<sup>3</sup> perfluoroalkyl,<sup>4–7</sup> carbonyl,<sup>8–12</sup> and cyano<sup>13–15</sup> substituents into hole-transporting (p-type)  $\pi$ -conjugated systems lowers the lowest unoccupied molecular orbital (LUMO) energy level, which is effective for both the stabilization of anionic species of molecules and the injection of electrons to their films from metal electrodes, leading to the creation of electron-transporting (n-type) OFET semiconducting materials. This finding has accelerated the development of n-type materials.<sup>16</sup> n-Type materials can be made solution-processable also by the modification of chemical structures so as to apply the materials to a solution-processing technique.<sup>17–21</sup> In contrast, although compounds having a LUMO energy level less than  $-4.0 \text{ eV}$  have been proposed as possible air-stable n-type OFET materials,<sup>22–24</sup> the development of such n-type materials is still lacking because it is difficult to design molecules suitable for this proposal.

Recently, we reported the synthesis of new electron-transporting  $\pi$ -conjugated systems containing a dicyanomethylene-substituted cyclopenta[*b*]thiophene ( $\text{B}(\text{CN})_2$ ) unit (Figure 1).<sup>25</sup> Electrochemical measurements revealed that the compounds including the  $\text{B}(\text{CN})_2$  unit exhibited significantly lowered LUMO energy levels of  $-4.1$  to  $-4.2 \text{ eV}$ . As a result, OFETs based on these compounds were successfully demonstrated to have operating stability even in air-exposed conditions. However, the noncrystalline behavior of  $\text{B}(\text{CN})_2$ -functionalized oligothiophene  $\text{B}(\text{CN})_2\text{-2H}$  in the solid state resulted in moderate electron mobility of the order of  $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Thus, in order to improve electron mobility, it is desirable to tune crystalline film-forming properties while maintaining the low LUMO energy level.

Herein, we report the synthesis of a new electron-transporting  $\text{h-B}(\text{CN})_2$ -based oligothiophene  $\text{h-B}(\text{CN})_2\text{-2T}$  whose backbone is identical to that of  $\text{B}(\text{CN})_2\text{-2H}$  but whose structure differs in the position of solubilizing hexyl groups (Figure 1). Furthermore, since the new electronegative terminal group  $\text{h-B}(\text{CN})_2$  could be synthesized during the course of our study, we also report the synthesis of the new oligothiophene  $\text{h-B}(\text{CN})_2\text{-2T}$  (Figure 1). OFETs based on these compounds exhibited a

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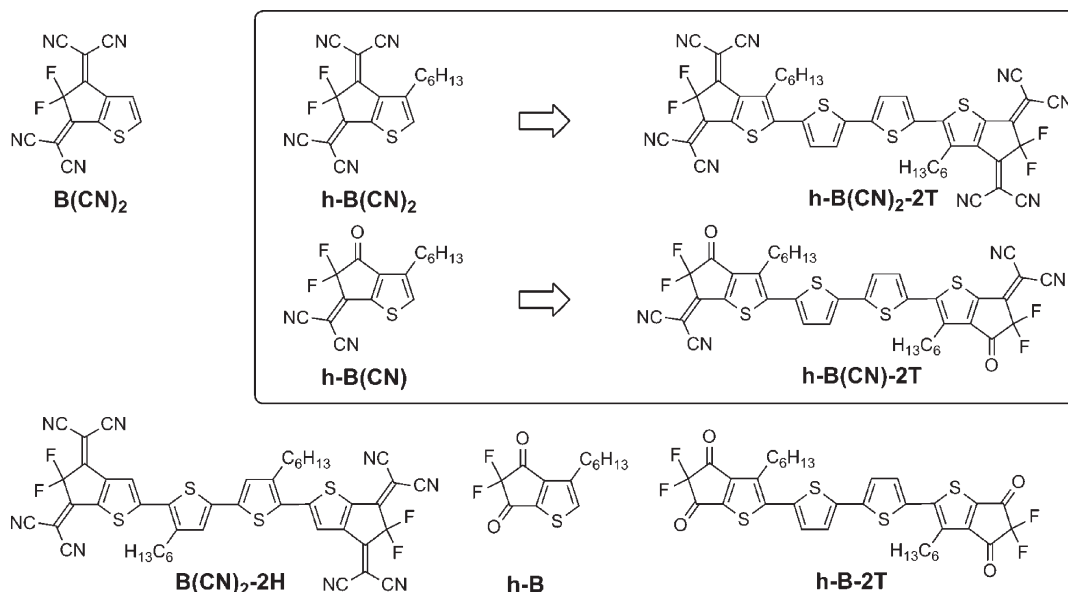


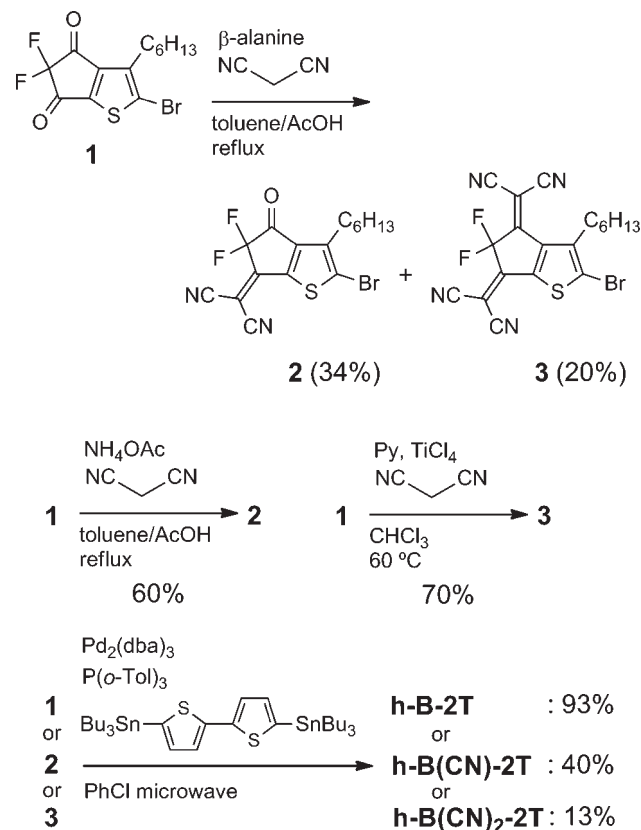
Figure 1. Chemical structures of compounds used in the present study.

considerable increase in electron mobility owing to the improvement in their crystalline film-forming properties. The photo-physical and electrochemical properties of the compounds and the performances of devices based on these materials were compared with those of **h-B-2T**, and the relationship between molecular electronic properties and air stability in OFETs was clarified.

## RESULTS AND DISCUSSION

The synthesis route of target oligothiophenes is shown in Scheme 1. Initially, the  $\beta$ -alanine-catalyzed Knoevenagel condensation method used for the synthesis of a **B(CN)<sub>2</sub>** derivative was applied to **1**.<sup>25</sup> However, this reaction gave a mixture of monosubstituted **2** (34%) and disubstituted **3** (20%), and the isolation of these compounds by chromatography was tedious. After screening the reaction conditions, we found that the application of  $\text{NH}_4\text{OAc}$  or pyridine/ $\text{TiCl}_4$  to the condensation of **1**<sup>26</sup> yielded **2** (60%) or **3** (70%) as a single product, respectively. It should be noted that the structure of **2** was unambiguously determined by measuring <sup>13</sup>C and heteronuclear multiple-bond correlation (HMBC) NMR spectra (Figures S1 and S2 in the Supporting Information). The following experimental results indicate that the steric influence rather than the electronic effect of the hexyl group might induce condition-dependent reactivity: (1) In the <sup>13</sup>C NMR spectra of **1** and the corresponding hexyl-unsubstituted compound (**1'**: structure is shown in Figure S3, Supporting Information), the chemical shifts of triplets assigned to the  $\text{C}_a$  position were similar (**1**:  $\delta = 176.4$  ppm, **1'**:  $\delta = 176.6$  ppm), indicating negligible electronic effect of the hexyl group (Figure S3, Supporting Information). (2) The condensation reaction of **1'** with malononitrile in the presence of  $\text{NH}_4\text{OAc}$  gave disubstituted product with 40% yield, with no monocondensation product being observed. Finally, the Pd-catalyzed Stille coupling reactions of **1–3** with 5,5'-bis-(tributylstannyl)-2,2'-bithiophene under microwave irradiation conditions gave oligothiophenes **h-B-2T**, **h-B(CN)-2T**, and **h-B(CN)<sub>2</sub>-2T**, respectively. Their structures and purity were fully characterized and verified by <sup>1</sup>H NMR spectroscopy, mass

Scheme 1. Synthetic Route to **h-B(CN)<sub>2</sub>-2T**, **h-B(CN)-2T**, and **h-B-2T**



spectrometry, and elemental analysis. All of the oligomers were found to be soluble in organic solvents: **h-B-2T** and **h-B(CN)-2T** are soluble in common organic solvents such as THF, chloroform, and chlorinated benzenes at room temperature, and **h-B(CN)<sub>2</sub>-2T** is soluble in hot chloroform and chlorinated

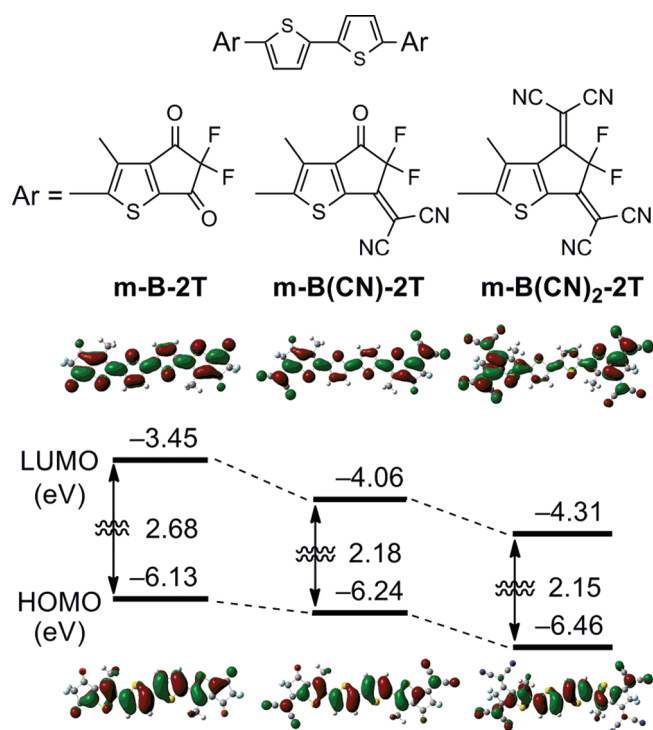


Figure 2. Calculated HOMOs and LUMOs and energy levels.

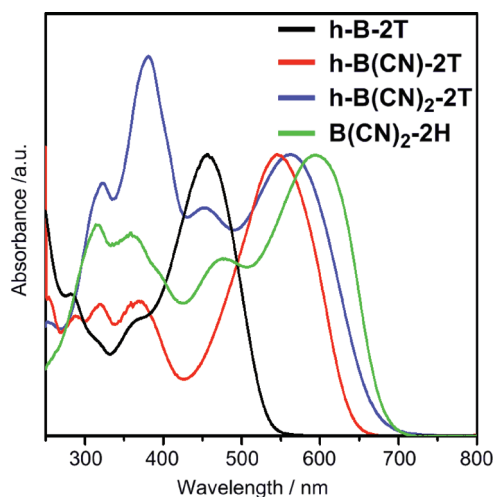


Figure 3. UV-vis absorption spectra measured in chloroform solution.

benzenes. The compound **h-B(CN)<sub>2</sub>-2T** is less soluble than **B(CN)<sub>2</sub>-2H** (soluble in chloroform and chlorinated benzenes at room temperature), indicating that the position of hexyl groups might have an influence on intermolecular interactions.

To estimate the molecular orbital of the newly synthesized oligothiophenes, theoretical calculations of **h-B(CN)<sub>2</sub>-2T**, **h-B(CN)-2T**, and **h-B-2T** were performed by the density functional theory (DFT) at the B3LYP/6-31G(d, p) level. We used methyl groups in place of the hexyl groups for easy calculation, and the calculated compounds are referred to as **m-B(CN)<sub>2</sub>-2T**, **m-B(CN)-2T**, and **m-B-2T**. Figure 2 shows the contours of the highest occupied molecular orbitals (HOMOs) and LUMOs and their energy levels. The LUMOs of **m-B(CN)-2T** and **m-B-2T** reside wholly at the conjugated backbones, while the LUMO of

Table 1. Photophysical and Electrochemical Properties of Oligomers

compd	$\lambda_{\max}$ / nm <sup>a</sup>	$E_g$ / eV	$E_{1/2}^{\text{red1}}$ / V <sup>b</sup>	$E_{1/2}^{\text{red2}}$ / V <sup>b</sup>	$E_{\text{LUMO}}$ / eV <sup>c</sup>
<b>h-B(CN)<sub>2</sub>-2T</b>	381, 555	1.77	-0.62	-1.09	-4.18
<b>h-B(CN)-2T</b>	546	1.83	-0.86	-1.57 <sup>d</sup>	-3.94
<b>h-B-2T</b>	456	2.23	-1.27	n.d.	-3.53
<b>B(CN)<sub>2</sub>-2H</b> <sup>e</sup>	591	1.81	-0.67	-1.15	-4.13

<sup>a</sup>In CHCl<sub>3</sub>. <sup>b</sup>In C<sub>6</sub>H<sub>5</sub>F, 0.1 M TBAPF<sub>6</sub>, V vs Fc/Fc<sup>+</sup>. <sup>c</sup> $E_{\text{LUMO}} = -(E_{1/2}^{\text{red1}} + 4.8)$ . <sup>d</sup>Irreversible. <sup>e</sup>Reference 25.

**m-B(CN)<sub>2</sub>-2T** is localized at the terminal units. The decrease in the LUMO energy level for **m-B(CN)<sub>2</sub>-2T** and **m-B(CN)-2T** can be explained by the contribution of the electron-withdrawing dicyanomethylene group to the LUMOs.

The UV-vis absorption spectra of **h-B(CN)<sub>2</sub>-2T**, **h-B(CN)-2T**, and **h-B-2T** in chloroform are shown in Figure 3. The photophysical data are summarized in Table 1. For comparison, the corresponding spectrum and data for **B(CN)<sub>2</sub>-2H** are included in Figure 3 and Table 1. The compounds **h-B(CN)-2T** and **h-B-2T** each show a distinct absorption band assigned to the HOMO-LUMO transition with a maximum at 546 and 456 nm, respectively. In contrast, the absorption spectrum of **h-B(CN)<sub>2</sub>-2T** covers a wide spectral range between 300 and 700 nm with absorption maxima at 381 and 555 nm. These two bands can be assigned to HOMO-LUMO+2 and HOMO-LUMO transitions, respectively, according to the time-dependent DFT calculations at the B3LYP/6-31G(d,p) level. The absorption maximum assigned to the HOMO-LUMO transition is red-shifted by the introduction of the dicyanomethylene groups, and the molar extinction coefficients show an increase (**h-B-2T** ( $3.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), **h-B(CN)-2T** ( $5.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), and **h-B(CN)<sub>2</sub>-2T** ( $6.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )). From the onset of the long-wavelength absorption, the optical energy gaps ( $E_g$ ) of **h-B(CN)<sub>2</sub>-2T**, **h-B(CN)-2T**, and **h-B-2T** are calculated to be 1.77, 1.83, and 2.23 eV, respectively. These results clearly show that the dicyanomethylene group significantly affects the electronic properties of these compounds. On the other hand, although the absorption maxima of **B(CN)<sub>2</sub>-2H** and **h-B(CN)<sub>2</sub>-2T** differ by 45 nm,  $E_g$  of **B(CN)<sub>2</sub>-2H** (1.81 eV) is almost equal to that of **h-B(CN)<sub>2</sub>-2T**, indicating that the position of the hexyl groups has little influence on the  $E_g$ s of the compounds.

The electrochemical properties of the oligothiophenes were studied by performing cyclic voltammetry (CV) measurements in fluorobenzene. The experiments were carried out using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte at a scan rate of 100 mV s<sup>-1</sup>, and the potentials are calibrated to ferrocene/ferrocenium (Fc/Fc<sup>+</sup>). Figure 4 shows CV curves for the oligomers, and their electrochemical data are listed in Table 1. In contrast to the observation of one reversible reduction wave for **h-B-2T** within the potential window, **h-B(CN)-2T** exhibits one reversible reduction wave with the half-wave reduction potential ( $E_{1/2}^{\text{red}}$ ) of -0.86 V and one irreversible reduction wave. Furthermore, **h-B(CN)<sub>2</sub>-2T** is found to be more electrochemically stable and shows two reversible reduction waves at  $E_{1/2}^{\text{red}} = -0.62$  and  $-1.09$  V. Notably, this behavior and these values coincide with those of **B(CN)<sub>2</sub>-2H**. According to the empirical equation  $E_{\text{LUMO}} = -(E_{1/2}^{\text{red1}} + 4.8)$ ,<sup>27</sup> the LUMO energy levels of **h-B(CN)<sub>2</sub>-2T**,

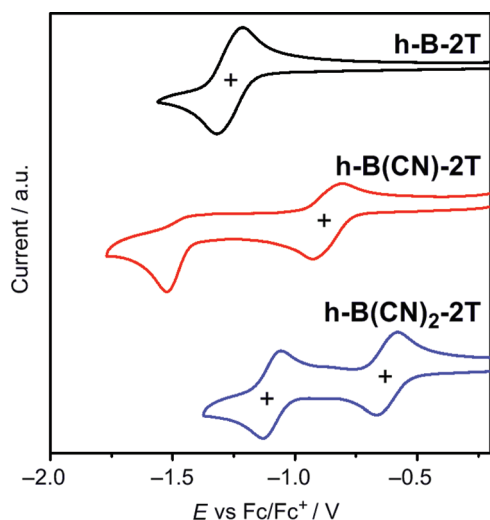


Figure 4. CV curves of oligothiophenes measured in fluorobenzene containing 0.1 M TBAPF<sub>6</sub>.

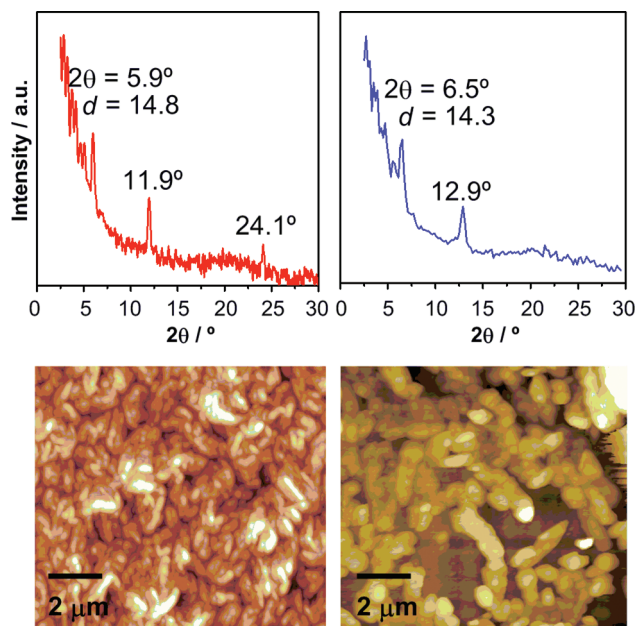


Figure 5. XRD patterns of (a) **h-B(CN)-2T** and (b) **h-B(CN)<sub>2</sub>-2T** films coated on ODTS-modified SiO<sub>2</sub> and AFM images of (c) **h-B(CN)-2T** and (d) **h-B(CN)<sub>2</sub>-2T** films.

**h-B(CN)-2T**, and **h-B-2T** were estimated as  $-4.18$ ,  $-3.94$ , and  $-3.53$  eV, respectively. This ordering indicates that the introduction of dicyanomethylene groups can considerably lower the LUMO energy level of the oligomers. These values and this overall trend are in good agreement with those of the calculation. It should be mentioned that the LUMO energy levels of these oligomers are potentially favorable for exhibiting n-channel OFET characteristics.

To investigate the properties of films in terms of structural ordering and surface morphology, thin films of **h-B(CN)<sub>2</sub>-2T**, **h-B(CN)-2T**, and **h-B-2T** were prepared by spin-coating from 1.0 wt % chloroform solutions on a SiO<sub>2</sub> dielectric that was treated

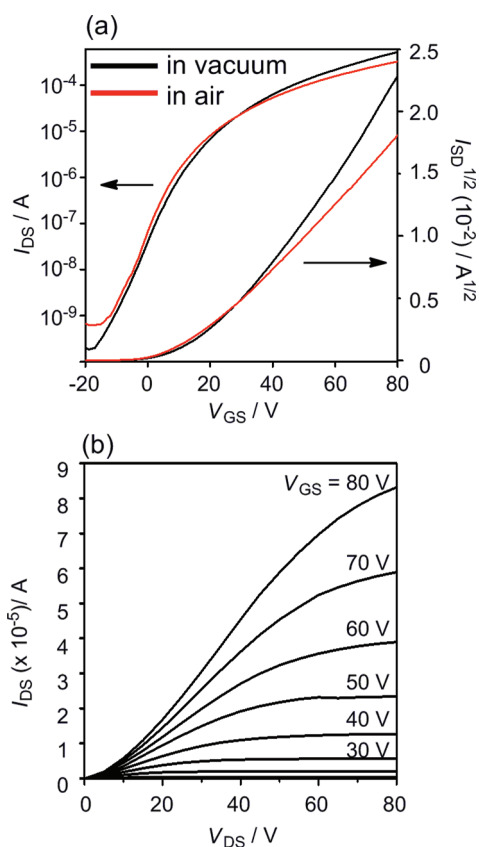
Table 2. Field-Effect Characteristics of Oligomers in Vacuum and in Air

compd	condition	electron mobility/ cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>	I <sub>on</sub> / I <sub>off</sub>	V <sub>th</sub> / V
<b>h-B(CN)<sub>2</sub>-2T</b>	in vacuum	$5.0 \times 10^{-3}$	10 <sup>6</sup>	25
<b>h-B(CN)<sub>2</sub>-2T</b>	in air	$2.4 \times 10^{-3}$	10 <sup>6</sup>	18
<b>h-B(CN)-2T</b>	in vacuum	$1.6 \times 10^{-2}$	10 <sup>5</sup>	11
<b>h-B(CN)-2T</b>	in air	$3.2 \times 10^{-7}$	10 <sup>2</sup>	10
<b>h-B-2T</b>	in vacuum	$2.5 \times 10^{-7}$	10 <sup>4</sup>	49
<b>h-B-2T</b>	in air	no FET <sup>a</sup>		
<b>B(CN)<sub>2</sub>-2H<sup>a</sup></b>	in vacuum	$5.4 \times 10^{-4}$	10 <sup>5</sup>	28
<b>B(CN)<sub>2</sub>-2H<sup>a</sup></b>	in air	$4.6 \times 10^{-4}$	10 <sup>5</sup>	30

<sup>a</sup> Reference 25.

with octadecyltrichlorosilane (ODTS). Thermal annealing was carried out at 150 °C for 30 min in a vacuum chamber (10<sup>-2</sup> Pa). X-ray diffraction (XRD) patterns (Figure 5 and Figure S4, Supporting Information) of these films show equidistant diffraction peaks, indicating an ordered orientation in the solid state. This result is different from what has been recently reported for compound **B(CN)<sub>2</sub>-2H**,<sup>25</sup> where no peak was observed for compound **B(CN)<sub>2</sub>-2H**, indicating that the crystalline properties of oligothiophenes containing a **B(CN)<sub>2</sub>** backbone can be improved by changing the position of hexyl groups. Atomic force microscopy (AFM) images of the films (Figure 5 and Figure S4, Supporting Information) show grains with a size of several micrometers; differences among the films are not significant. These results imply that these compounds are suitable for investigating the relationship between molecular electronic properties and OFET characteristics.

We fabricated bottom-contact OFETs to evaluate the field-effect electron mobility of newly developed oligothiophenes. The active layer of the thin films was prepared in the above-mentioned conditions. FET measurements were performed both under vacuum (10<sup>-2</sup> Pa) and air-exposed conditions, and the device performance data are summarized in Table 2. As expected from the estimated low LUMO energy level of the compounds, all the devices exhibited the typical n-type FET behaviors. In particular, **h-B(CN)-2T** and **h-B(CN)<sub>2</sub>-2T** showed a considerable improvement in electron mobility as compared to **B(CN)<sub>2</sub>-2H** under vacuum condition, and the device consisting of **h-B(CN)-2T** achieved an electron mobility of 0.016 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with an on/off current ratios of 10<sup>5</sup> and a threshold voltage of 11 V. On the other hand, the **h-B-2T**-based device exhibited a poor result. We recently reported that a compound composed of **h-B** as terminal units and carbonyl-bridged bithiazole as a central unit shows a good electron mobility of 0.011 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>;<sup>26</sup> thus, a combination of units with respect to tuning the LUMO energy level is crucial for obtaining good n-type characteristics. When the device was operated in air, **h-B-2T** did not show n-type characteristics at all. Surprisingly, the **h-B(CN)-2T**-based devices showed a significant decrease in electron mobility by a factor of 5. In contrast to **h-B-2T** ( $E_{\text{LUMO}} = -3.53$  eV) and **h-B(CN)-2T** ( $E_{\text{LUMO}} = -3.94$  eV), the electron mobility of **h-B(CN)<sub>2</sub>-2T** ( $E_{\text{LUMO}} = -4.18$  eV) in air-exposed conditions was retained as compared with that measured under vacuum conditions, as observed in the transfer characteristics shown in Figure 6. On the basis of the assumption that the film properties of these compounds are similar, the difference in the air stability of the OFETs stems from the LUMO energy level. Thus, our results



**Figure 6.** (a) Transfer characteristics of OFET based on **h-B(CN)<sub>2</sub>-2T** measured in vacuum (black) and in air (red) at drain voltage of 80 V. (b) Output characteristics of OFET based on **h-B(CN)<sub>2</sub>-2T**.  $I_{DS}$ ,  $V_{DS}$ , and  $V_{GS}$  denote the source–drain current, source–drain voltage, and gate voltage, respectively.

clearly support the previous finding that compounds having a LUMO energy level lower than  $-4.0$  eV are advantageous for acquiring air stability.<sup>22–24</sup>

## CONCLUSION

In conclusion, we synthesized new electron-transporting oligothiophenes having dicyanomethylene-substituted cyclopenta[*b*]-thiophene units (**h-B(CN)**, **h-B(CN)<sub>2</sub>**) as potential candidates for solution-processable n-type organic semiconductor materials. The photophysical and electrochemical measurements of these oligomers revealed that the optical energy gaps and LUMO energy levels can be modulated by changing the number of dicyanomethylene groups in the molecules. These measurements results of **h-B(CN)<sub>2</sub>-2T** and **B(CN)<sub>2</sub>-2H** also revealed that the position of the hexyl group has little influence on their molecular electronic properties. In addition, the introduction of hexyl groups at the terminal units improved the film-forming properties, thus enabling the fabrication of a thin film in the crystalline state. With **h-B(CN)<sub>2</sub>-2T** as an active layer, the electron mobility of the solution-processed OFETs increased up to  $0.016 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Furthermore, OFETs based on **h-B(CN)<sub>2</sub>-2T** showed an increase of 1 order of magnitude in electron mobility as compared to **B(CN)<sub>2</sub>-2H** while maintaining the air stability. The stability of OFETs in air-exposed conditions strongly depends on the LUMO energy level of the compounds.

These findings are of great importance to optimize and develop n-type OFETs.

## EXPERIMENTAL SECTION

**General Information.** Column chromatography was performed on silica gel. Thin-layer chromatography (TLC) plates were visualized with UV. Microwave irradiation was performed by a Biotage Initiator Ver. 2.5. The microwave power output was set at 400 W. The reaction temperature was kept at  $180$  °C, and internal temperature during the reaction was monitored by IR sensor.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  with tetramethylsilane as an internal standard.  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$ . Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet), coupling constant (Hz), and integration. Cyclic voltammetry was carried out using a platinum disk as the working electrode, platinum wire as the counter electrode, and  $\text{Ag}/\text{AgNO}_3$  as the reference electrode. The surface structure of the deposited organic film was observed by atomic force microscopy, and the film crystallinity was evaluated by X-ray diffractometer. X-ray diffraction patterns were obtained using Bragg–Brentano geometry with  $\text{CuK}\alpha$  radiation as an X-ray source with an acceleration voltage of 40 kV and a beam current of 40 mA.  $\theta$ – $2\theta$  scans were obtained between  $2.5^\circ$  and  $30^\circ$  a scanning step of  $0.01^\circ$ .

**Materials.** All reactions were carried out under a nitrogen atmosphere. Solvents of the highest purity grade were used as received. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification.

**2-(2-Bromo-5,5-difluoro-3-hexyl-4-oxo-4H-cyclopenta[*b*]thiophene-6(5H)-ylidene)propanedinitrile (2).** Compound **1** (1.09 g, 3.10 mmol) was placed in a 100 mL round-bottomed flask and dissolved with toluene (30 mL). To the mixture were added malononitrile (246 mg, 3.72 mmol), ammonium acetate (287 mg, 3.72 mmol), acetic acid (3 mL), and it was stirred at  $120$  °C for 4 h. The reaction was quenched by addition of satd  $\text{NaHCO}_3$  aqueous solution, and the organic layer was separated. The aqueous layer was washed with dichloromethane, and the combined organic layer was washed with satd  $\text{NaHCO}_3$  aqueous solution and water and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (10:1 hexane/ethyl acetate) to give **2** (738 mg, 60%): yellow solid; TLC  $R_f$  = 0.42 (10:1 hexane/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 2.89 (t, 2H,  $J$  = 7.6 Hz), 1.61 (m, 2H), 1.33 (m, 8H), 0.90 (t, 3H,  $J$  = 6.6 Hz);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) 176.7 (t,  $J$  = 25.6 Hz), 153.6, 151.1 (t,  $J$  = 23.5 Hz), 144.8, 141.7, 132.0, 111.7 (t,  $J$  = 265.9 Hz), 111.6, 108.9, 31.4, 29.0, 28.8, 27.3, 22.5, 14.0; MS (EI)  $m/z$  398 ( $M^+$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{13}\text{BrF}_2 \text{N}_2\text{OS}$ : C, 48.13; H, 3.28, N, 7.02. Found: C, 48.24; H, 3.48; N, 7.16.

**2,2'-(2-Bromo-5,5-difluoro-4H-cyclopenta[*b*]thiophene-4,6(5H)-diylidene)bispropanedinitrile (3).** Compound **1** (100 mg, 0.28 mmol) was placed in a 10 mL two-necked flask and dissolved with  $\text{CHCl}_3$  (3 mL). To the mixture were added malononitrile (56 mg, 0.85 mmol),  $\text{TiCl}_4$  (216 mg, 1.14 mmol), and pyridine (0.2 mL), and the mixture was stirred at  $60$  °C for 4 h. The reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was washed with dichloromethane, and the combined organic layer was washed with water dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (10:1 hexane/ethyl acetate) to give **3** (89 mg, 70%): yellow solid; TLC  $R_f$  = 0.31 (10:1 hexane/ethyl acetate);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 3.14 (t, 2H,  $J$  = 7.6 Hz), 1.56 (m, 2H), 1.44 (m, 2H), 1.32 (m, 2H), 0.90 (t, 3H,  $J$  = 6.6 Hz);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ) 150.4 (t,  $J$  = 24.2 Hz), 150. (t,  $J$  = 24.2 Hz), 147.2, 143.9, 141.9, 134.3, 119.9 (t,  $J$  = 263.2 Hz), 111.8, 111.5, 109.8, 108.8, 31.4, 30.6, 29.5, 28.0, 22.5, 14.0; MS (EI)  $m/z$  398 ( $M^+$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{13}\text{BrF}_2 \text{N}_2\text{OS}$ : C, 48.13; H, 3.28, N, 7.02. Found: C, 48.24; H, 3.48; N, 7.16.

2,2'-(2,2'-Bithiophene)-5,5'-diylbis[5,5-difluoro-3-hexyl-4H-cyclopenta[b]thiophene-4,6(5H)-dione] (**h-B-2T**). 5,5'-Tributylstannyl-2,2'-bithiophene (200 mg, 0.27 mmol), **1** (207 mg, 0.59 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (10 mg, 0.01 mmol), trio-tolylphosphine (14 mg, 0.04 mmol), and chlorobenzene (3 mL) were placed in a microwave proof walled glass vial equipped with a snap cap. The glass vial was purged with nitrogen, securely sealed, and heated in a microwave reactor, keeping the temperature at 180 °C for 5 min. After removal of the solvent under reduced pressure, the residue was first isolated by column chromatography on silica gel (chloroform), and then the fraction containing **h-B-2T** was further purified by preparative gel-permeation chromatography (GPC) (CHCl<sub>3</sub>) to give **h-B-2T** (176 mg, 93%): red solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 (d, 2H, J = 3.7 Hz), 7.35 (d, 2H, J = 3.7 Hz), 3.11 (t, 4H, J = 8.1 Hz), 1.71 (m, 4H), 1.46 (m, 4H), 1.35 (8H) 0.90 (t, 6H, J = 7.1 Hz); MS (MALDI-TOF) *m/z* 706.2 (M<sup>+</sup>, calcd 706.1). Anal. Calcd for C<sub>34</sub>H<sub>30</sub>F<sub>4</sub>O<sub>4</sub>S<sub>4</sub>: C, 57.77; H, 4.28. Found: C, 57.90; H, 4.33.

2,2',2'',2'''-[[2,2':5',2'':5'',2'''-Quaterthiophene]-5,5'''-diylbis(5,5-difluoro-3-hexyl-4-oxo-4H-cyclopenta[b]thiophene-2-yl-6(5H)-ylidene)]-bispropanedinitrile (**h-B(CN)-2T**). Compound **h-B(CN)-2T** was synthesized by following the procedure used for the preparation of **h-B-2T**, as a black solid (83 mg, 40%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 (d, 2H, J = 4.1 Hz), 7.39 (d, 2H, J = 4.1 Hz), 3.12 (t, 4H, J = 7.9 Hz), 1.68 (m, 4H), 1.46 (m, 4H), 1.35 (m, 8H) 0.90 (t, 6H, J = 7.1 Hz); MS (MALDI-TOF) *m/z* 802.1 (M<sup>+</sup>, calcd 802.1). Anal. Calcd for C<sub>40</sub>H<sub>30</sub>F<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub>: C, 59.83; H, 3.77; N, 6.98. Found: C, 59.73; H, 3.82; N, 6.97.

2,2',2'',2'''-[[2,2':5',2'':5'',2'''-Quaterthiophene]-5,5'''-diylbis(5,5-difluoro-3-hexyl-4H-cyclopenta[b]thiophene-2-yl-4,6(5H)-diylidene)]-tetrakispropanedinitrile (**h-B(CN)<sub>2</sub>-2T**). Compound **h-B(CN)<sub>2</sub>-2T** was synthesized by following the procedure used for the preparation of **h-B-2T**, as a black solid (32 mg, 13%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (d, 2H, J = 4.1 Hz), 7.40 (d, 2H, J = 4.1 Hz), 3.34 (t, 4H, J = 8.2 Hz), 1.63 (m, 4H), 1.45 (m, 4H), 1.31 (m, 8H) 0.88 (t, 6H, J = 6.9 Hz); MS (MALDI-TOF) *m/z* 898.2 (M<sup>+</sup>, calcd 898.1). Anal. Calcd for C<sub>46</sub>H<sub>30</sub>F<sub>4</sub>N<sub>8</sub>S<sub>4</sub>: C, 61.45; H, 3.76; N, 12.46. Found: C, 61.55; H, 3.84; N, 12.57.

**Device Fabrication.** The field-effect mobility 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 (SiO<sub>2</sub>) dielectric layer on the gate substrate has 300 nm thick and a capacitance of 10.0 nF cm<sup>-2</sup>. Interdigital source and drain electrodes were constructed with gold (30 nm) that were formed on the SiO<sub>2</sub> layer. The channel width (*W*) and channel length (*L*) are 38 mm and 5 μm, respectively. The silicon oxide surface was first washed with acetone and 2-propanol. It was then activated by UV-ozone treatment and pretreated with ODTs. The semiconductor layer was by spin-coating from 1.0 wt % chloroform solution at 1500 rpm for 1 min onto the substrate in air, followed by annealing for 30 min at 150 °C under a vacuum condition (10<sup>-2</sup> Pa). The characteristics of the OFETs were measured at room temperature under a pressure of 10<sup>-2</sup> Pa without exposure to air after fabricating the active layer or in air by using a semiconductor parameter analyzer. The field-effect electron mobility (*μ*) was calculated in the saturated region at the V<sub>DS</sub> of 80 V by the following equation.

$$I_{DS} = \frac{W}{2L} C_{it} \mu (V_{GS} - V_{th})^2$$

The current on/off ratio was determined from the I<sub>DS</sub> at V<sub>GS</sub> = 0 V (I<sub>off</sub>) and V<sub>GS</sub> = 80 V (I<sub>on</sub>).

## ■ ASSOCIATED CONTENT

Supporting Information. NMR spectra, computational details, XRD data, and AFM image of **h-B-2T**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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