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((Alkyloxy)carbonyl)cyanomethylene-Substituted Thienoquinoidal Compounds: a New Class of Soluble n-Channel Organic Semiconductors for Air-Stable Organic Field-Effect Transistors

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Abstract: A new n-channel semiconductor class for organic field-effect transistors (OFETs) based on thienoquinoidal structures is reported. A newly employed terminal group, the ((alkyloxy)carbonyl)cyanomethylene moiety, plays two important roles in the thienoquinoidal compounds: i.e., as an electron-withdrawing group to keep the LUMO energy level sufficiently low for acting as an n-channel organic semiconductor and as a solubilizing group to facilitate solution processability. For the construction of this class of compounds, a new, straightforward synthetic method was established and applied to oligothienoquinoidal and fused thienoquinoidal systems. When both core and alkyl groups in the ester moiety were tuned, the thienoquinoidals exhibited good solubility, stability in the atmosphere, and electron-accepting properties, as well as solution processability. Solution-processed FETs based on the terthienoquinoid derivative with ((*n*-alkyloxy)carbonyl)cyanomethylene moieties exhibit good electron mobilities ($\mu \sim 0.015$ cm^2 V^{-1} s^{-1}) and $I_{on}/I_{off} \approx 10^5$ under ambient conditions. Vapor-processed FETs using the benzodithienoquinoidal derivative showed similar n-channel FET characteristics.

Introduction

Recent intensive effort in materials development and device optimization has improved the device performance of organic field-effect transistors (OFETs).[1] In particular, p-channel OFETs have attained both high performance comparable or superior to that of amorphous Si-based FETs and stability under ambient conditions.[2] In contrast, n-channel OFETs have suffered from both low performance and rather low air stability compared with p-channel OFETs.[3] Very recently, however, research on n-channel OFETs has made substantial progress: not only high-performance OFETs[4] but also solution-processed OFETs based on newly developed materials have been reported.[5] Accompanying these material developments, a reliable criterion for air-stable n-channel organic semiconductors was proposed: materials with high reduction potential ($E_{red} > -0.4$ V vs SCE), in other words, low-lying LUMO energy levels (<3.9 eV below the vacuum level), are promising as air-stable n-channel organic semiconductors.[6] However, few materials meet this criterion and only limited materials have such low-lying LUMO energy levels, e.g., BBL,[5a] F_{16}CuPC,[7] NDI,[8] and PDI[9] derivatives, as well as recently developed oligomers[5l] and polymers[5o] with rational molecular design strategy (Figure 1).

7,7,8,8-Tetracyanoquinodimethane (TCNQ; Figure 2) and its related compounds have long been known to be superior electron-accepting molecules and widely studied in the field of

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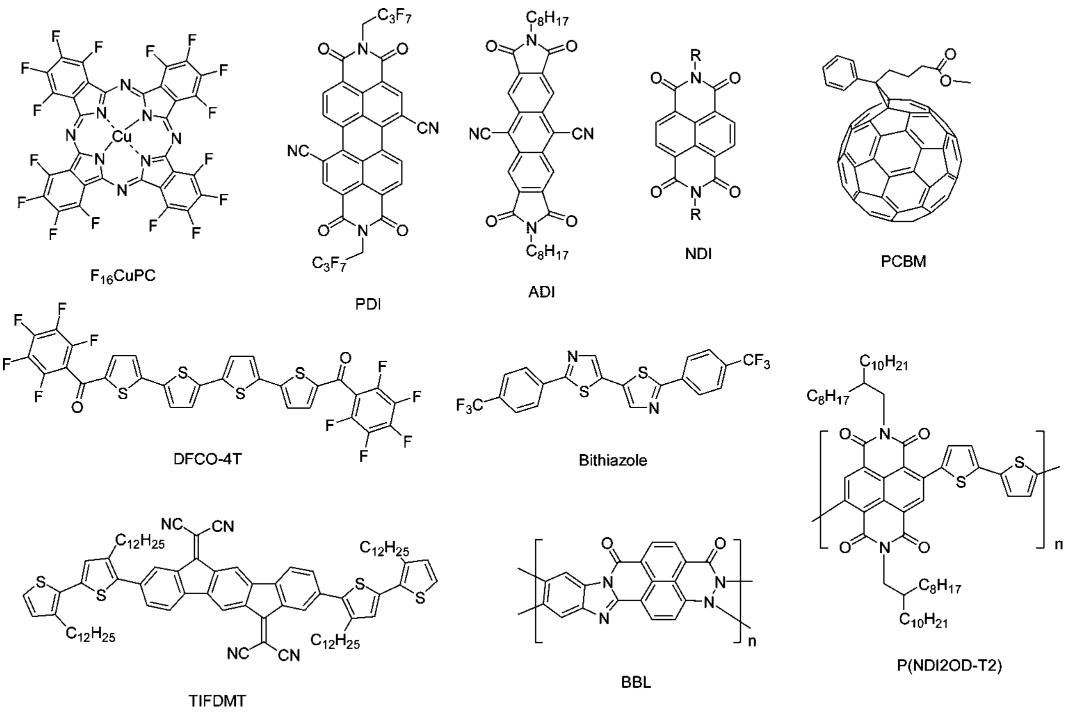

Figure 1. Some representative n-channel organic semiconductors.

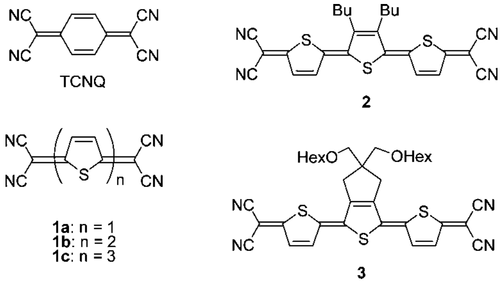

Figure 2. Structures of TCNQ and some dicyanomethylene-substituted thienoquinoidal compounds.

organic charge-transfer complexes.[10] Because of their low-lying LUMO energy level ($\sim$4.6 eV, depending on the molecular structure and the substituent attached), TCNQ-type materials have recently been investigated as n-channel organic semiconductors.[3,11] Dicyanomethylene-substituted thienoquinoidal derivatives (**1a**−**c**), which are the thiophene counterparts of the TCNQ series (Figure 2), were also studied in the late 1980s.[12] From the viewpoint of materials chemistry, the thienoquinoidals feature several advantages over the benzoquinoidals. First, the quinoidal core can be extended readily for the thienoquinoidals, not only in fused systems[12b,d,13] but also in oligomeric systems up to the hexamer.[14] In contrast, for the benzoquinoidals, even the biphenoquinoidal analogue cannot be synthesized[15] and, thus, π-extended derivatives are limited in fused systems, such as 9,9,10,10-tetracyanonaphtho-2,6-quinodimethane (TNAP)[15a,16] and 11,11,12,12-tetracyanoanthra-2,6-quinodimethane (TNAT).[17] Second, because of the ease of selective functionalization on thiophene, various solubilizing modifications are possible for the thienoquinoidals.

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Taking advantage of these merits, terthienoquinoidal derivatives (**2** and **3**) were developed and reported to be vapor- or solution-processable n-channel semiconductors with field-effect mobilities higher than 0.1 cm^2 V^{-1} s^{-1}.[18]

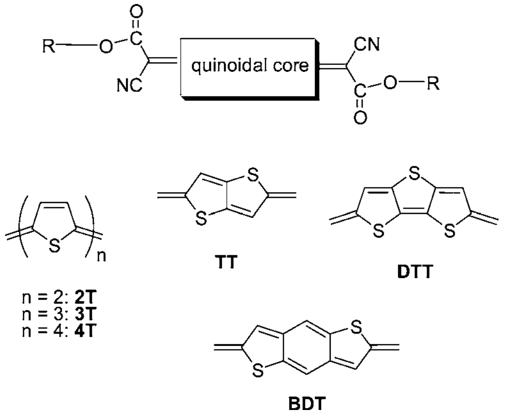

Figure 3. ((Alkyloxy)carbonyl)cyanomethylene-substituted oligothienoquinoidals.

In sharp contrast to the superior n-channel semiconducting characteristics and the improved solubility of **2** and **3**, the parent terthienoquinoidal compound (**1c**) acts as a poor n-channel organic semiconductor. The mobility of vapor-processed **1c**-based FET was on the order of 10^{-4} cm^2 V^{-1} s^{-1}, probably owing to the amorphous nature of its thin film (Figures S1 and S2, Supporting Information). The experimental results of **1c**-based FETs, in comparison with those of **2** and **3**, imply that the terthienoquinoidal core requires modification with substituents not only to improve solubility but also to achieve better molecular ordering in the thin film state. Similar solubility enhancement and control of molecular ordering in the thin film state by the introduction of substituents were also reported in the development of soluble p-channel molecular semiconductors and their solution-processed OFETs.[19]

As a new approach to modify thienoquinoidal compounds with solubilizing groups, we have focused on an ((alkyloxy)-carbonyl)cyanomethylene moiety, instead of the conventional dicyanomethylene moiety, as the terminal group of the thienoquinoidals, where the electron-withdrawing cyano group ensures electron affinity and the (alkyloxy)carbonyl moiety acts as a solubilizing group (Figure 3). Furthermore, the long alkyl groups in the ester moieties will be directed along the molecular long axis, thus facilitating molecular ordering in the thin film state.

The most fundamental compounds of this class, 7,8-bis((alkyloxy)carbonyl)-7,8-dicyanoquinodimethanes (**4**), have long been known since the 1980s,[20] and their electron-accepting properties were investigated in detail together with those of their related

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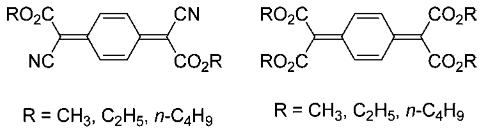
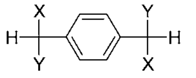


4 TACQ

Figure 4. Structures of benzoquinoidal compounds.



X = Cl, Y = H **5**
X = CN, Y = H **6**
X = CN, Y = CO_2R **7**

Figure 5. Chemical structures of **5**−**7**.

compounds TCNQ and 7,7,8,8-tetrakis((alkyloxy)carbonyl)quinodimethanes (TACQ; Figure 4). However, the application of **4** as electronic materials has not been examined at all. This is mainly due to their chemical lability to form homopolymers in the presence of various initiators, such as radicals and bases.[20]

In this paper, we report a series of ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidal compounds (Figure 3), including oligo and fused thienoquinoidals, in terms of syntheses, stability, solubility, physicochemical properties, and FET properties of their thin-film transistors.

Results and Discussion

Synthesis. Synthesis of Bithienoquinoidal Compounds. The reported synthesis of 7,8-bis((alkyloxy)carbonyl)-7,8-dicyanoquinodimethanes (**4**) started with the conversion of 1,4-bis(chloromethyl)benzene (**5**; Figure 5) into 1,4-bis(cyanomethyl)benzene (**6**) using sodium cyanide.[20] Then, **6** was reacted with sodium hydride in the presence of dialkylchlorocarbonate to give 1,4-bis(cyano((alkyloxy)carbonyl)methyl)benzene (**7**), which was finally oxidized to give **4**.

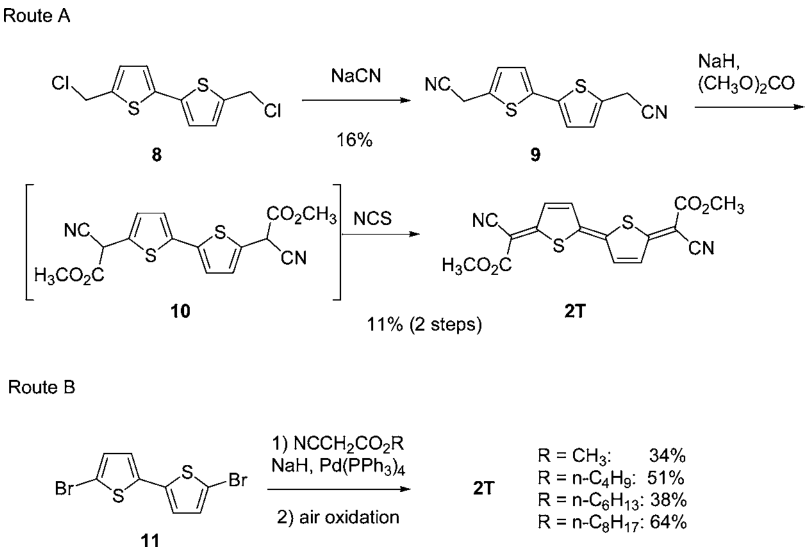
Applying the same synthetic strategy as that for **4**, we first examined the synthesis of a bithienoquinoidal compound, 2,2′-bis(α-cyano-α-(methoxycarbonyl)methylene)-5,5′-dihydrobithiophene (**2T**, R = CH_3) using 5,5′-bis(chloromethyl)-2,2′-bithiophene[21] (**8**) as the starting material (Scheme 1, route A). The first cyanation reaction gave bis(cyanomethyl)bithiophene (**9**) in 16% isolated yield, and the subsequent introduction of an ester moiety on each benzylic carbon atom of **9** followed by oxidation gave the desired **2T** (R = CH_3) in 11% yield without isolation of the intermediate (**10**). Although the desired **2T** could be synthesized successfully, the procedure required poorly accessible and unstable **8** having chloromethyl substituents as the starting material, and the yield in each step was quite low.

Alternatively, we examined a palladium-catalyzed nucleophilic substitution reaction of 5,5′-dibromo-2,2′-bithiophene (**11**) with cyano(methoxycarbonyl)methanide anion generated in situ from commercially available methyl cyanoacetate (Scheme 1, route B).[22] The reaction proceeded very smoothly to give **2T** (R = CH_3) in 34% isolated yield. It should be emphasized that, during the workup of the initial substitution reaction, spontaneous air-mediated oxidation took place to give the quinoidal structure reproducibly, and no intentional oxidation with an oxidizing agent was required to obtain the desired thienoquinoidal compound. This result prompted us to apply the same reaction to other cyanoacetates with long alkyl groups. *n*-Butyl, *n*-hexyl,[23] and *n*-octyl cyanoacetates were employed to synthesize the corresponding thienoquinoidal compounds with long alkyl groups in the ester moiety. Regardless of the alkyl group, the synthesis proceeded very smoothly to give the corresponding **2T** in reasonable yields.

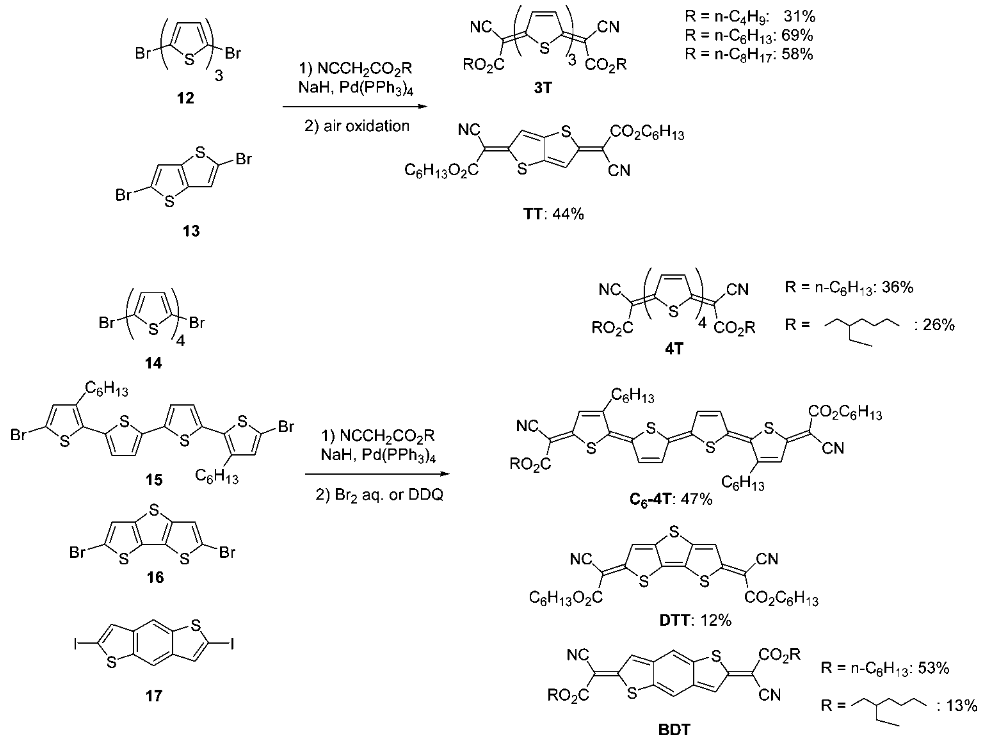
Comparing these two successful methods for the synthesis of **2T**, we found that the latter (route B in Scheme 1) has obvious advantages: few synthetic steps, easy experimental operation, and stability of the key intermediate (i.e., bromothiophene derivatives are more stable than the corresponding chloromethyl-substituted species). In addition, the ready availability of bromothiophenes and various cyanoacetates is also beneficial for the development of a series of compounds in this class. For these reasons, we employed route B to synthesize various thienoquinoidal compounds, including terthiophene (**3T**), quaterthiophenes (**4T** and **C_6-4T**), thieno[2,3-*b*]thiophene (**TT**), dithieno[2,3-*b*:4,5-*b*′]thiophene (**DTT**), and benzo[1,2-*b*:4,5-*b*′]dithiophene (**BDT**) (Scheme 2).

Synthesis of Various Derivatives. As shown in Scheme 2, a series of ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidal derivatives were synthesized from the corresponding

Scheme 1. Synthesis of 2,2′-Bis(α-cyano-α-((alkyloxy)carbonyl)methylene)-5,5′-dihydrobithiophenes (**2T**)



Scheme 2. Synthesis of Various Thienoquinoidal Compounds



α-bromo- or α-iodothiophene derivatives (**12**−**17**). The syntheses of **3T** and **TT** proceeded smoothly in moderate yields, as was observed for the syntheses of **2T**s. On the other hand, in highly π-extended thienoquinoidal compounds, e.g., **4T**, **C_6-4T**, **DTT**, and **BDT**, spontaneous air oxidation of the dihydro intermediates did not take place and, thus, intentional oxidation with aqueous bromine or DDQ was necessary to obtain the desired quinoidal compounds (Scheme 2). As described in Solubility, the ((*n*-alkyloxy)carbonyl)cyanomethylene moiety, except for the methyl ester, could afford good solubility for **2T**, **3T**, **C_6-4T**, **TT**, and **DTT** cores. However, the solubilities of **4T** and **BDT** (R = *n*-hexyl) were very low. Thus, the "dovetail" 2-ethylhexyl ester moiety was introduced to improve the solubility of these cores. The isolated yields of the thienoquinoidal compounds thus obtained were moderate except for **DTT** (R = *n*-hexyl) and **BDT** (R = 2-ethylhexyl), and all the derivatives were fully characterized by spectroscopic and combustion elemental analyses (see the Supporting Information).

Solubility. Thanks to the ((alkyloxy)carbonyl)cyanomethylene moieties with long alkyl groups, the solubilities of the present thienoquinoidal compounds are generally higher than those of the corresponding dicyanomethylene compounds (Table 1). The solubility mainly depends on the central cores rather than the length of the alkyl chain in the ester group attached, except for the methyl derivative of **2T**. As summarized in Table 1, the extension of the thienoquinoidal core reduces the solubility; **4T,** in particular, is hardly soluble, whereas **2T** and **3T** are sufficiently soluble for the fabrication of solution-processed OFETs (vide infra). On the other hand, the 2-ethylhexyl ester moiety makes **4T** sufficiently soluble for the solution process. The fused thienoquinoidals also show a similar tendency: **TT** with two thiophene rings shows higher solubility than **DTT** with three thiophene rings. The solubility of **BDT**, consisting of two thiophene rings and one benzene ring, is less than one-tenth of that of **DTT**. This is probably due to the difference in symmetry: **BDT** has C_{2h} symmetry with an inversion center, which brings about no dipole moment of the molecule, whereas **DTT** having C_{2v} with mirror symmetry has a non-negligible dipole moment that may enhance the solvation effect. The 2-ethylhexyl ester moiety also effectively enhances the solubility of **BDT,** as in the case of **4T**.

Table 1. Solubilities of ((Alkyloxy)carbonyl)cyanomethylene-Substituted Thienoquinoidals

compd	R	solubility[a]/g L^{-1}
2T[b]	R = *n*-butyl	1.2
	R = *n*-hexyl	8.3
	R = *n*-octyl	4.9
3T [b]	R = *n*-butyl	5.8
	R = *n*-hexyl	8.1
	R = *n*-octyl	9.4
4T	R = *n*-hexyl	0.028
	R = 2-ethylhexyl	1.7
C_6-4T	R = *n*-hexyl	5.0
TT	R = *n*-hexyl	11
DTT	R = *n*-hexyl	3.1
BDT [b]	R = *n*-hexyl	0.23
	R = 2-ethylhexyl	3.9

[a] Solubility was determined as the concentration of the saturated solution in chloroform at room temperature. [b] Solubilities of the corresponding dicyanomethylene compounds are 0.21 for **2T**, 9×10^{-3} for **3T**, and $<10^{-3}$ g L^{-1} for **BDT**.

Stability. 7,8-Bis((alkyloxy)carbonyl)-7,8-dicyanoquinodimethanes (**4**; Figure 4), the most basic compounds in this class, were reported to be labile and to homopolymerize in the presence of amine or other initiators.[20] To check the stability of the thienoquinoidal compounds, the solution UV−vis spectra of **2T** and **3T** (R = *n*-hexyl) in the presence of triethylamine were measured together with that of **4** for comparison (Figure 6). An absorption band of **4** centered at 400 nm weakened rapidly, reflecting homopolymerizability even in dilute solution (∼10^{-5} M). As materials related to **4**, TCNQ and TACQ (Figure 4), do not polymerize with any initiators, the lability of **4** was rationalized by its structural characteristics: i.e., **4** has two

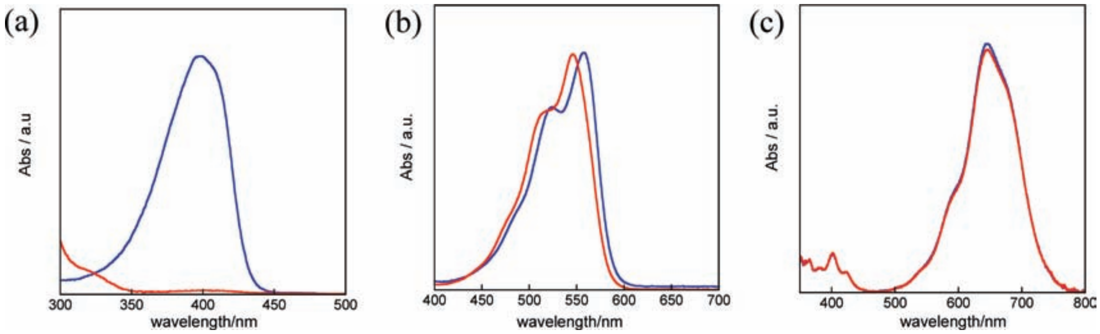


Figure 6. UV−vis spectra of (a) **4**, (b) **2T** (R = *n*-hexyl), and (c) **3T** (R = *n*-hexyl): (blue traces) spectra in pure chloroform; (red traces) spectra measured 24 h after the addition of triethylamine.

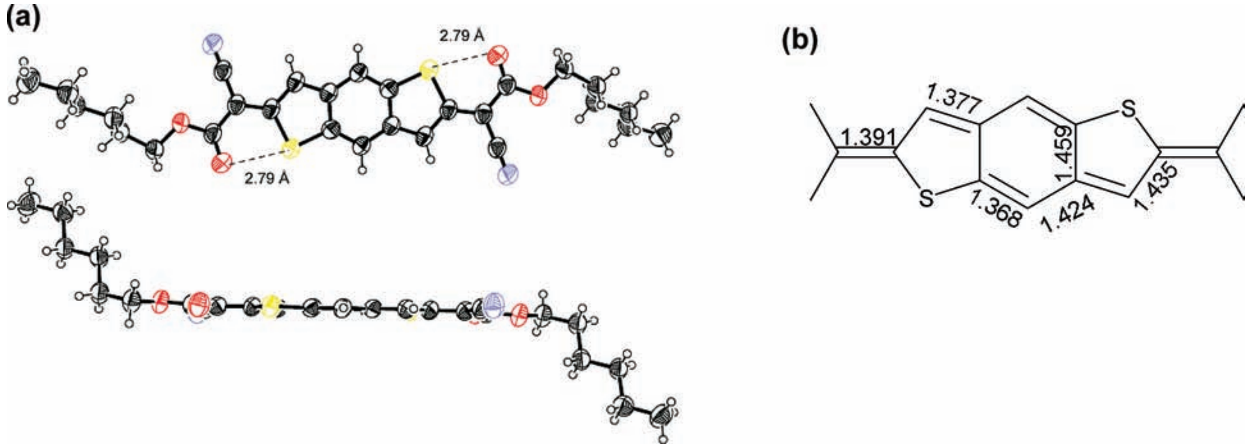


Figure 7. (a) Molecular structure of **BDT** (R = *n*-hexyl). (b) Selected C−C bond lengths (Å) in the benzodithienoquinoidal core.

different substituents at the 7- and 8-positions.[20] In contrast, the UV−vis spectra of **2T** and **3T** did not change even after 24 h, indicating that **2T** and **3T** are quite stable. These experimental results show that the ((alkyloxy)carbonyl)cyanomethylene moiety is not solely responsible for the homopolymerizability of this class of compounds.

Structure Characterization. Structure Determination of Fused Thienoquinoidals. There are two possible connectivities for the ((alkyloxy)carbonyl)cyanomethylene moiety at the thienoquinoidal terminus, i.e., *E* and *Z* isomers, which will give multiple peaks in the aromatic region of ^{1}H NMR spectra. However, only one peak (δ 7.2−7.3) assignable to β-hydrogen in the terminal thiophene ring was observed for **TT**, **BTT**, and **DTT**, indicating that there is only one isomer and no *E*/*Z* isomerism at the termini of these compounds. To determine the molecular structure clearly, single-crystal X-ray analysis of **BDT** (R = *n*-hexyl) was carried out.

The molecular structure of **BDT** depicted in Figure 7a is unambiguously defined as the *Z* isomer form at the cyano((*n*-hexyloxy)carbonyl)methylene termini. There are two notable features in the molecular structure. One is the existence of an intramolecular nonbonded contact (2.79 Å) between the sulfur atom in the thiophene ring and the carbonyl oxygen atom in the ester moiety, which is shorter than the sum of the van der Waals radii of sulfur and oxygen (3.32 Å).[24] The other is the high planarity of the molecule: the cyano((*n*-hexyloxy)carbonyl)methylene moieties, except for the hexyl groups, lie on almost the same plane defined by the central quinoidal core part with a maximum deviation of 0.187 Å. From these structural features, we speculate that the intramolecular interactive short contacts between the sulfur and oxygen atoms facilitate the high planarity and also stabilize the *Z* isomer form at the terminal cyano((*n*-hexyloxy)carbonyl)methylene moiety. In addition to these structural characteristics, the C−C bond lengths in the molecular structure of **BDT** (Figure 7b) clearly show that the bond alternation that represents the quinoidal structure rather than the aromatic structure is dominant in the present molecule.

Structural Isomers of Oligothienoquinoidals. For oligothienoquinoidal compounds, the *E*/*Z* isomerism can exist in the thienoquinoidal core parts in addition to the isomerism at the terminal moieties. However, the very simple ^{1}H NMR spectra for **2T**s strongly imply no *E*/*Z* isomerism at the termini also for oligothienoquinoidals. Figure 8a shows the ^{1}H NMR spectrum of a recrystallized sample of **2T** (R = *n*-hexyl) in freshly prepared $CDCl_3$ solution. The spectrum shows a pseudo-singlet peak in the aromatic region, which is assigned to

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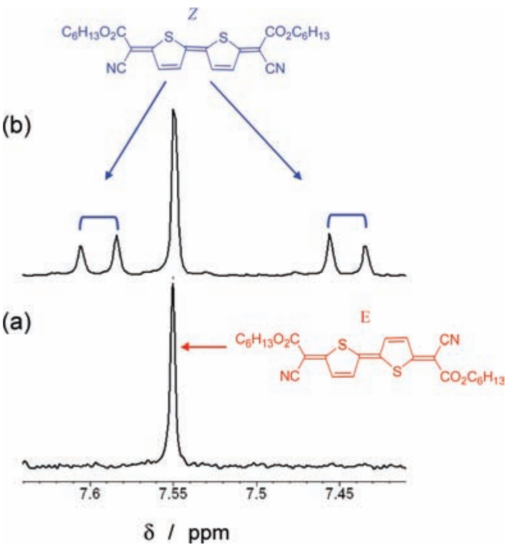

Figure 8. ^{1}H NMR spectra (aromatic region) of **2T** (R = *n*-hexyl): (a) freshly prepared $CDCl_3$ solution of a recrystallized sample; (b) $CDCl_3$ solution after standing overnight.

nonequivalent β protons on the thiophene rings appearing as an AB spin system with almost the same chemical shifts. Interestingly, the spectrum of the same solution after standing overnight shows two sets of aromatic peaks: one is the pseudo-singlet, and the other is a set of AB doublets with $J = 5.8$ Hz, indicating the coexistence of two isomers. The ratio of the isomers is almost 1:1, regardless of the alkyl group in the ester moiety. Simulation of the shielding constants of the β protons in each isomer using DFT calculations[25] strongly suggests that the pseudo-singlet can be assigned to the *E* isomers and the AB doublets to the *Z* isomers in the oligothienoquinoidal core (Figure S4, Supporting Information) and that there is no isomerism at the connectivity of the terminal groups, as in the case of the fused system. It should also be noted that ready isomerization takes place in solution for the oligothienoquinoidal core part.

The aromatic part in the ^{1}H NMR spectra of **3T**s is rather complicated, as shown in Figure 9, which indicates the coexistence of three possible isomers: i.e., *E*,*E*, *E*,*Z*, and *Z*,*Z* in the terthienoquinoidal core. With the aid of computations of the shielding constants of β protons in each isomer using DFT methods[25] under the premise that no *E*/*Z* isomerism at the termini exists, the spectra can be analyzed to be a mixture of all the three isomers, as shown in Figure 9 (see also Figure S5, Supporting Information). From the inspection of the ^{1}H NMR spectra, it is rational to conclude that *E*/*Z* isomerism exists in the oligothienoquinoidal parts, although there is no isomerism at the terminal ((alkyloxy)carbonyl)cyanomethylene moieties. Such isomerism was previously observed for **3**, which acted as a solution-processable n-channel organic semiconductor with FET mobility of up to 0.16 cm^2/(V s). Thus, the isomerism in the oligothienoquinoidal core is not a vital structural defect in the thin film state, although its actual effects on the transistor characteristics are not clear.

Physicochemical Properties. Cyclic Voltammetry. All the ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidals showed reversible reduction couples (Figure 10, Table 2). Among them, **3T** and **4T** also showed oxidation peaks within the present electrochemical window (−1.0 to +1.5 V vs Ag/AgCl), indicating that these materials have narrow HOMO−LUMO gaps. Similar redox behaviors were observed for dicyanomethylene-substituted thienoquinoidals.[14,18,26] Comparison of the reduction potentials of the present ((alkyloxy)carbonyl)cyanomethylene-substituted compounds with those of the corresponding dicyanomethylene species (Table S1, Supporting Information) clearly shows that the former have greater cathodic reduction potentials than the latter by ca. 0.2−0.4 V, indicating that the ((alkyloxy)carbonyl)cyanomethylene derivatives have lower electron-accepting properties, in other words, higher LUMO energy levels, than the dicyanomethylene-substituted species, which qualitatively agrees with the weaker electron-withdrawing nature of the ester group as compared to that of the cyano group.[27] Nevertheless, the LUMO energy levels of the ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidals expected from the onset of the first reduction wave fall into ca. 4.0−4.2 eV below the vacuum level (Table 2), thereby meeting the criteria for air-stable n-channel carrier transport in OFETs.[6]

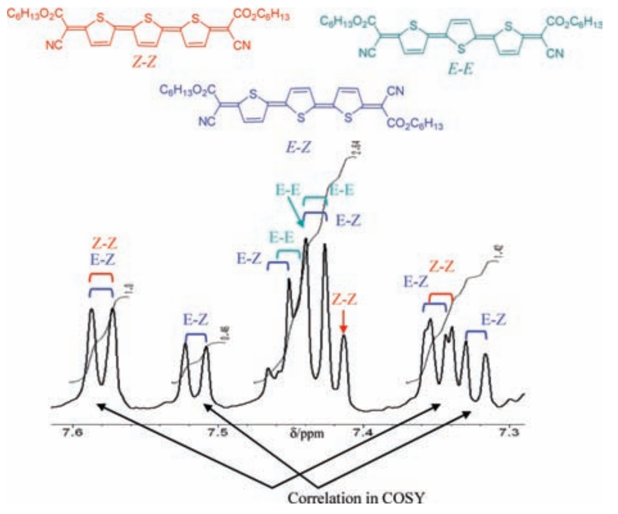

Figure 9. ^{1}H NMR spectra (aromatic region) of **3T** (R = *n*-hexyl).

Absorption Spectra. The UV−vis spectra of the ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidals in dichloromethane solution show characteristic strong absorption in the visible to near-infrared range, depending on the thienoquinoidal core (Figure 11). These spectra resemble those of the corresponding dicyanomethylene counterparts in the absorption range, again indicating that the electronic structures of both thienoquinoidal systems are similar to each other. Furthermore, the optical energy gaps estimated from the absorption onset are almost the same for the ((alkyloxy)carbonyl)cyanomethylene and dicyanomethylene derivatives (Table S1). This qualitatively corresponds to the fact that both HOMO and LUMO energy levels shift upward simultaneously by changing from the

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[25] MO calculations were carried out with the DFT method at the B3LYP/6-31g(d) level using the Gaussian 03 program package. Frisch, M. J. Gaussian 03, revision C.02; Gaussian, Inc., Wallingford, CT, 2004.

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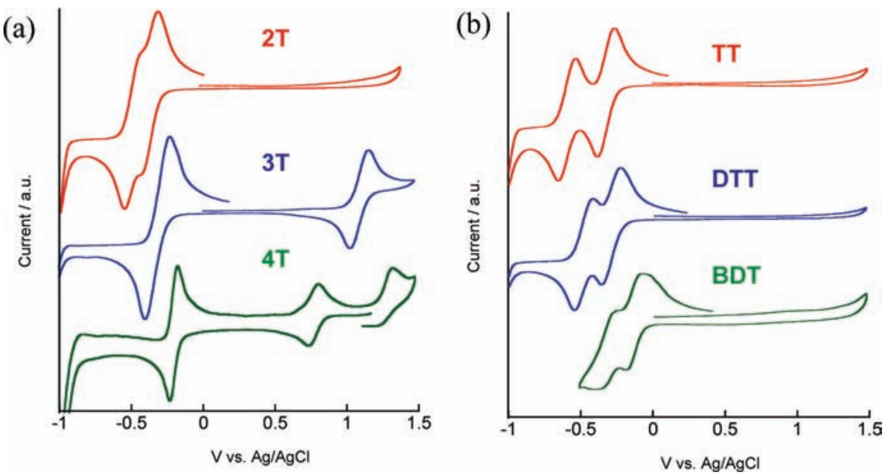

Figure 10. Cyclic voltammograms of (a) **2T**, **3T**, and **4T** and (b) **TT**, **DTT**, and **BDT** (R = *n*-hexyl).

Table 2. Physicochemical Properties of ((*n*-Hexyloxy)carbonyl)cyanomethylene-Substituted Oligothienoquinoidals (R = *n*-Hexyl)

	$E^{1/2}_{red}$/V[a]	E^{onset}_{red}/V[a]	LUMO/eV[b]	$E^{1/2}_{ox}$/V	λ_{max}/nm (log ϵ)	λ_{onset}/nm	E_g/eV[c]	HOMO/eV[d]
2T	−0.34 (1e), −0.48 (1e)	−0.26	−4.1		556 (4.92)	610	2.0	−6.1
3T	−0.32 (2e)	−0.23	−4.2	+1.10	649 (5.04)	785	1.5	−5.7
4T	−0.22 (2e)	−0.14	−4.3	+0.77	764 (5.28)	1074	1.2	−5.5
C_6-4T	−0.25 (2e)	−0.21	−4.2	+0.77	764 (5.18)	1028	1.2	−5.4
TT	−0.33 (1e), −0.60 (1e)	−0.22	−4.2		473 (4.88)	536	2.3	−6.5
DTT	−0.30 (1e), −0.49 (1e)	−0.19	−4.2		558 (4.86)	662	1.9	−6.1
BDT	−0.14 (1e), −0.32 (1e)	−0.05	−4.4		546 (4.99)	685	1.8	−6.2

[a] In V vs Ag/AgCl. All the potentials were calibrated with Fc/Fc$^+$ ($E^{1/2}$ = +0.43 V measured under identical conditions). [b] Estimated with the following equation: E^{LUMO} (eV) = −4.4 − E_{onset}. [c] Calculated from λ_{onset}. [d] Estimated from the LUMO energy level and E_g.

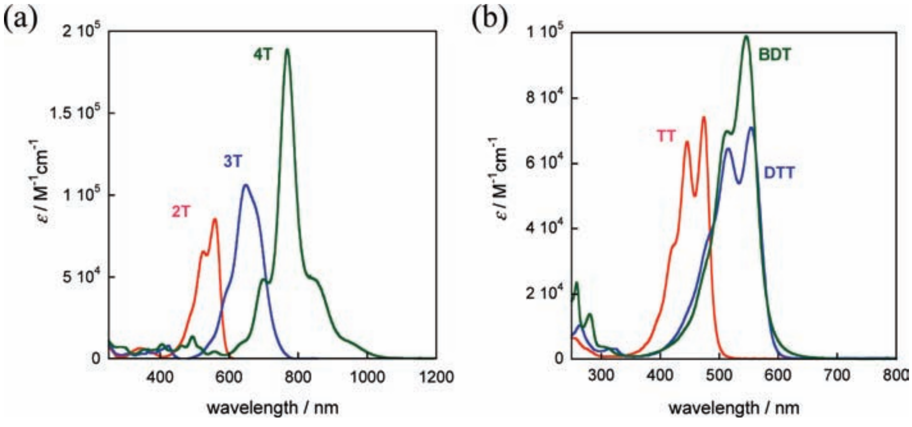

Figure 11. UV−vis spectra of (a) **2T**, **3T**, and **4T** and (b) **TT**, **DTT**, and **BDT**.

dicyanomethylene to the ((alkyloxy)carbonyl)cyanomethylene termini on the thienoquinoidal cores.

DFT MO Calculations. To confirm the energy levels of the frontier molecular orbitals experimentally estimated, we carried out DFT MO calculations at the B3LYP-6-31 g(d) level. Figure 12 shows the calculated HOMO and LUMO of the corresponding methyl esters as model compounds. The calculations reproduced the energy levels of the empirical HOMO and LUMO: in other words, the dependence of the energy levels of the frontier molecular orbitals on the thienoquinoidal cores. In the oligothienoquinoidal series, extension of the core from **2T** to **4T** slightly reduced the LUMO energy levels and at the same time notably raised the HOMO energy levels. Similar reduction of the LUMO and increase of the HOMO energy levels were observed for the fused systems **TT** and **DTT**. However, the fused systems tended to have lower HOMO energy levels than the oligothienoquinoidals. This is in good agreement with the experimental results; only reduction waves were observed for the fused thienoquinoidals in the electrochemical window employed for the present measurements (−1.0 to +1.5 V vs Ag/AgCl), whereas **3T** and **4T**s showed oxidation waves under identical conditions. The electron density distribution on the frontier molecular orbitals shown in Figure 12 is basically the same as that of the corresponding thienoquinoidal compounds with the dicyanomethylene termini (Figure S3, Supporting Information), which means that the substitution effect of the terminal group is minimal.

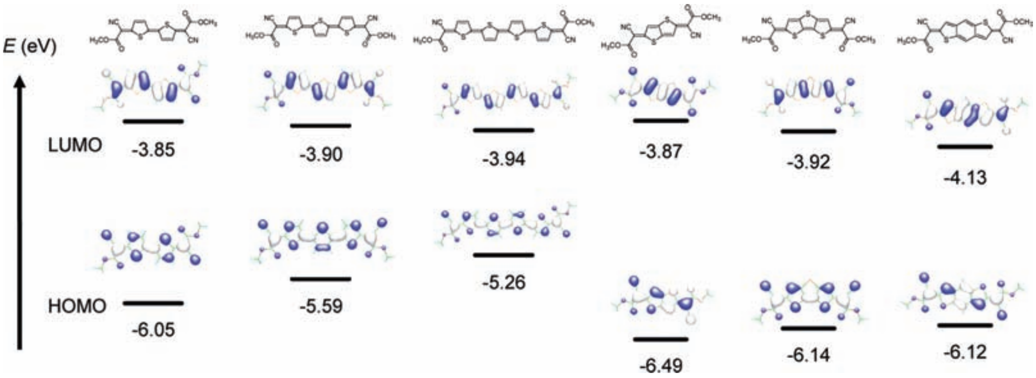

Figure 12. Calculated HOMO and LUMO of thienoquinoidal compounds.

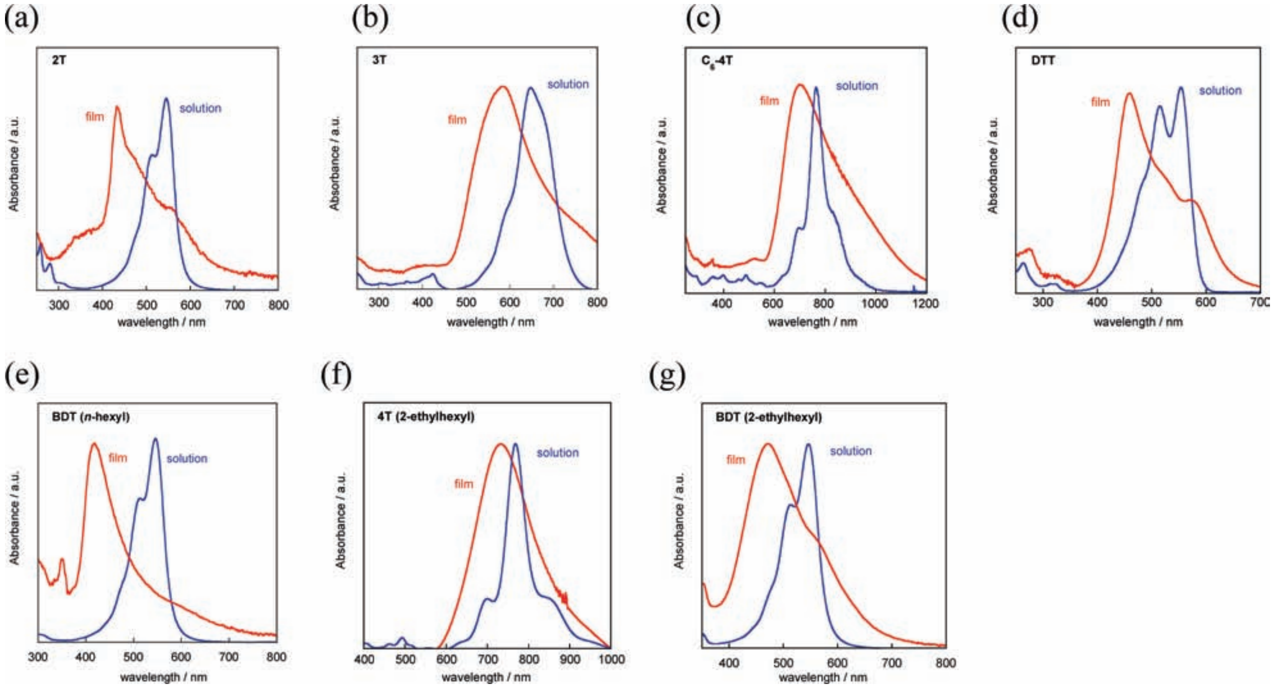

Figure 13. UV−vis spectra of thin films (as deposited) of the *n*-hexyl esters of (a) **2T**, (b) **3T**, (c) **C$_6$-4T**, (d) **DTT**, and (e) **BDT** (e) and the 2-ethylhexyl esters of (f) **4T** and (g) **BDT**.

We summarize the physicochemical characterization of the present thienoquinoidal system as follows: they have electronic structures similar to those of their dicyanomethylene-substituted counterparts, but both HOMO and LUMO energetically shift upward, owing to the electron-withdrawing nature of the ((alkyloxy)carbonyl)cyanomethylene terminal group being weaker than that of the dicyanomethylene group. This indicates that the present materials are potential candidates for a new class of n-channel organic semiconducting materials.

Thin-Film Deposition. Film-Forming Properties. All the present ((*n*-alkyloxy)carbonyl)cyanomethylene-substituted oligothienoquinoidals except for **2T** (R = CH$_3$), **4T** (R = *n*-hexyl), and **BDT** (R = *n*-hexyl) are sufficiently soluble for thin-film deposition by spin coating. Among the soluble derivatives, **2T**, **3T**, **C$_6$-4T,** and **DTT** gave homogeneous thin films on octyltrichlorosilane (OTS)-treated Si/SiO$_2$ or quartz glass substrates upon spin coating 0.2−0.5 wt % chloroform solution at 3000 rpm for 30 s. In contrast, the spin-coated thin film of **TT** had a clouded surface that could be ascribed to crystallization. Because of the poor uniformity of the films, **TT**-based OFETs did not show any transistor responses. On the other hand, vapor deposition of poorly soluble **BDT** (R = *n*-hexyl) gave thin films with good uniformity, whereas that of **4T** (R = *n*-hexyl) did not, owing to thermal decomposition during vapor deposition. The 2-ethylhexyl esters of **4T** and **BDT**, with improved solubility, also gave uniform thin films by spin coating.

Absorption Spectra. The UV−vis spectra of the thin films of ((*n*-hexyloxy)carbonyl)cyanomethylene and (((2-ethylhexyl)oxy)carbonyl)cyanomethylene derivatives are shown in Figure 13. Interestingly, all the spectra feature a *hypsochromic* (blue) shift as compared to the corresponding solution spectra, and the extent of the blue shift depends on the thienoquinoidal core. In contrast, the usual thin-film absorption spectra of organic semiconductors, including the related dicyanomethylene-substituted terthienoquinoidal **3**, show bathochromic (red) shifts relative to their solution spectra,[18d,e] because of strong intermolecular interaction via the formation of π-stacking and/or J-type molecular aggregation. Although the reasons for such a large blue shift for the present system are not clear, we speculate that some kind of H-type molecular aggregation could be one

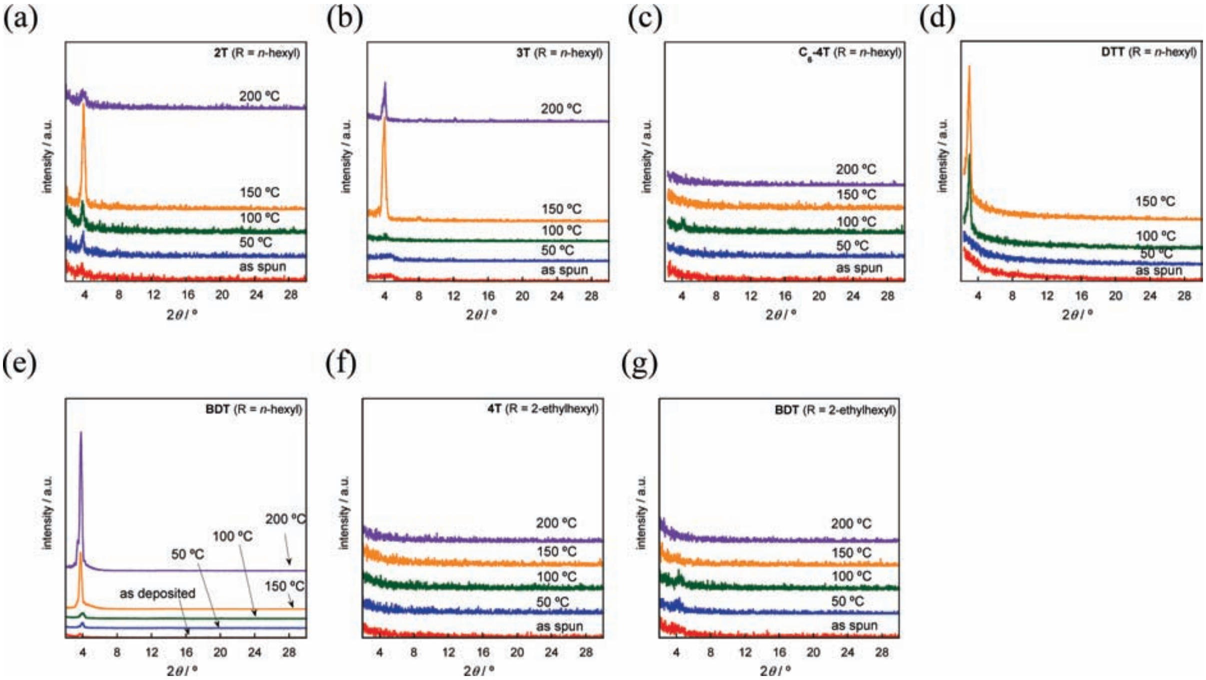

Figure 14. XRD patterns of thin films of the *n*-hexyl esters of (a) **2T**, (b) **3T**, (c) **C$_6$-4T**, (d) **DTT**, and (e) **BDT** and the 2-ethylhexyl esters of (f) **4T** and (g) **BDT**.

reason. To confirm this speculation, the solid-state structure of **BDT** elucidated by X-ray analysis was inspected in detail, and it was found that the **BDT** molecules form a π-stacking structure (see Figure 19b) with a slip angle of ~55° (Figure S6, Supporting Information), which falls into the structural criteria for H-aggregates.[28] To further understand the present electronic absorption behavior, we also carried out TD-DFT calculations[25] of the π-stacked dimer extracted from the X-ray structure. The results suggest that the π-stacked dimer tends to show a blue shift as compared to the **BDT** monomer (see Table S3, Supporting Information).

Thermal Annealing of Thin Films. As-deposited thin films of organic semiconductors from solution are often amorphous-like and have poor molecular ordering, and the molecular ordering can be improved by thermal annealing. This was also the case for thin films of soluble terthienoquinoidal compounds with dicyanomethylene moieties.[18d,e]

Figure 14 shows the XRD patterns of spin-coated thin films of **2T** (R = *n*-hexyl), **3T** (R = *n*-hexyl), **C$_6$-4T**, **DTT**, **4T** (R = 2-ethylhexyl), and **BDT** (R = 2-ethylhexyl) and the vapor-deposited film of **BDT** (R = *n*-hexyl) annealed at various temperatures. It is clear that the as-deposited films are amorphous-like or are weakly ordered, and thin films of **2T**, **3T, DTT**, and **BDT** (R = *n*-hexyl) show clear and intense peaks on annealing, indicative of improved molecular ordering. In those thin films, a high annealing temperature (150 °C) tended to give more intense peaks than did a low temperature. However, much higher temperatures weakened the peak intensity for the **2T** and **3T** thin films, indicating that thermal decomposition took place.

Interestingly, further blue shifts in the thin-film UV−vis spectra were observed on annealing the **2T** and **3T** thin films (Figure 15a,b). This demonstrates that improved molecular ordering causes a further shift in the spectra. This is additional evidence of the H-type molecular aggregation in the thin-film state. On the other hand, a significant decrease in absorbance was observed for the **DTT** thin film on annealing (Figure 15d). This is due to the formation of crystalline domains and thus the noncontinuous thin film morphology of **DTT** on annealing and is consistent with the clouded thin-film surface visually observed.

The XRD patterns of the thin films of **C$_6$-4T**, **4T** (R = 2-ethylhexyl), and **BDT** (R = 2-ethylhexyl) show no peaks even after annealing at 150 °C, indicating an amorphous nature. The poor molecular ordering for these compounds is rationalized by the steric bulk caused by the side alkyl groups (**C$_6$-4T**) or the branched ester moiety (**4T** and **BDT**). In accordance with the poor molecular ordering, the blue shift in the thin-film absorption spectra on annealing is very small. It is interesting to note that compounds that form well-ordered crystalline thin films: e.g., **2T**, **3T**, and **BDT** (*n*-hexyl) show large blue shifts from the solution spectra to the thin-film spectra, as tabulated in Table 3. This also indicates that the blue shift is closely related to the extent of molecular ordering and the intermolecular interaction thus induced.

Judging from the XRD patterns of the annealed thin films, **2T**, **3T**, and **BDT** (R = *n*-hexyl) molecules assume a lamella-like structure on the substrate with interlayer spacings (*d* spacings) of 22.4, 22.0, and 22.4 Å, respectively (Table 3). A comparison of the *d* spacings with the molecular lengths estimated from MOPAC-PM3-optimized molecular models indicates relatively large inclinations (36−40°) of the molecular long axes from the substrate normal. To achieve effective carrier transport in the thin-film state, a large intermolecular overlap is desired, and thus the molecular lamella structure consisting of perpendicularly standing molecules generally realizes high performance in OFET devices. Thus, the relatively large inclination of the molecules of **2T**, **3T**, and **BDT** (R = *n*-hexyl)

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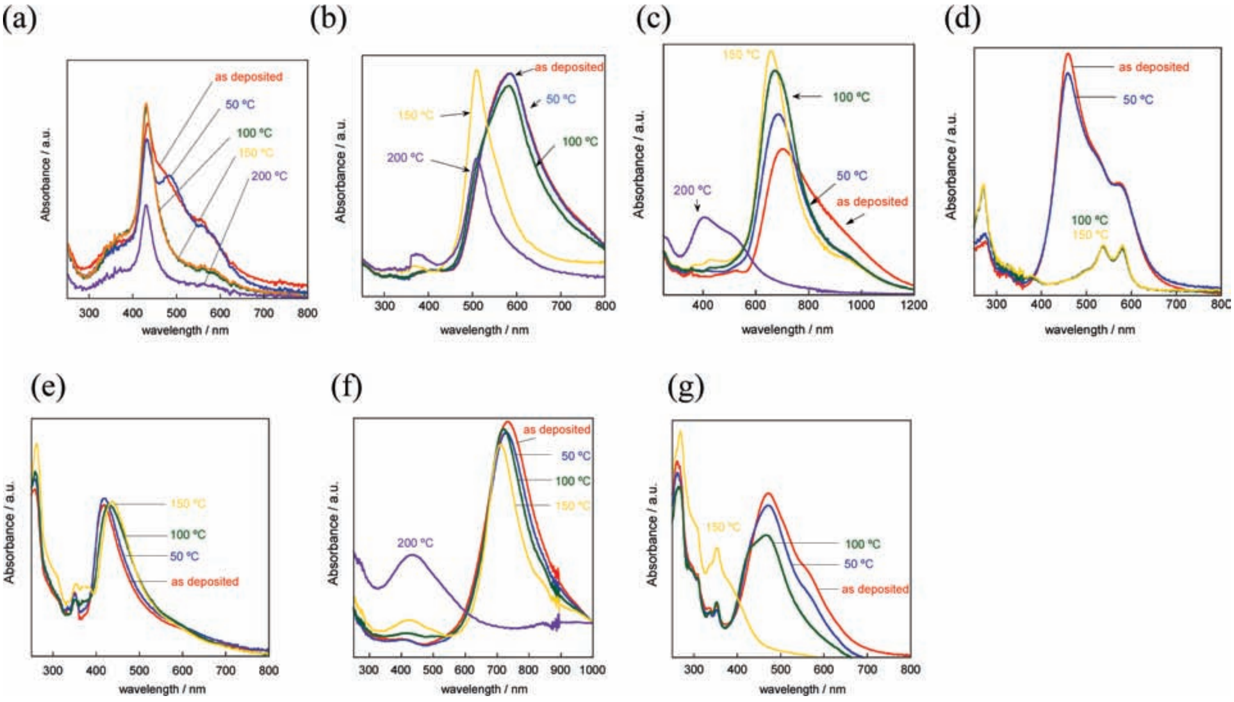


Figure 15. UV−vis spectra of thin films of the *n*-hexyl esters of (a) **2T**, (b) **3T**, (c) **C$_6$-4T**, (d), **DTT**, and (e) **BDT** and the 2-ethylhexyl esters of (f) **4T** and (g) **BDT**.

Table 3. Characterization of Thin Films of Thienoquinoidal Compounds

compd[a]	λ_{max} (as deposited)/nm (eV)	λ_{max} (annealed)/nm (eV)	ΔE^b/eV	$2\theta^c$/deg	*d* spacing/Å	molecular length[d]/Å
2T (*n*-hexyl)	429 (2.89)	431 (2.88)	0.65	3.94	22.4	27.8
3T (*n*-hexyl)	583 (2.13)	504 (2.46)	0.55	4.02	22.0	29.1 (*E*,*Z*), 30.2 (*E*,*E*)
C$_6$-4T (*n*-hexyl)	702 (1.77)	660 (1.88)	0.26	no peak		
BDT (*n*-hexyl)	433 (2.86)	437 (2.84)	0.57	3.94	22.4	27.2
4T (2-ethylhexyl)	730 (1.70)	712 (1.74)	0.13	no peak		
BDT (2-ethylhexyl)	471 (2.63)	468 (2.65)	0.38	no peak		

[a] DTT was omitted because of crystallization on annealing. [b] Degree of blue shift from solution spectra to thin-film spectra after annealing. [c] The first peak in the annealed thin films. [d] Estimated from MOPAC-PM3-optimized molecular models with *n*-hexyl groups having stretched, all-anti conformations.

in the thin films is one of the reasons for the moderate field-effect mobilities (~10^{-2} cm^2 V^{-1} s^{-1}) of their FET devices (vide infra).

Evaluation of Thin Film Transistors. FET characteristics were evaluated with top-contact-type FET devices using spin-coated or vapor-deposited thin films under ambient conditions. An evaluation of the same devices under vacuum showed no significant difference, indicating the stability in air of ((alkyloxy)carbonyl)cyanomethylene-substituted oligothienoquinoidals, as expected from the low-lying LUMO energy level.

Depicted in Figure 16a−c are the output and transfer curves of optimized devices using the spin-coated thin films of **2T** (R = *n*-hexyl), **3T** (R = *n*-hexyl), and **3T** (R = *n*-octyl) after thermal annealing. For all the devices, typical n-channel transistor responses were observed and the electron mobilities extracted from the saturated regime were 1.2×10^{-3}, 1.5×10^{-2}, and 1.4×10^{-2} cm^2 V^{-1} s^{-1}, respectively (Table 4). These FET mobilities are almost the same as or slightly lower than those reported for dicyanomethylene-substituted thienoquinoidals (**2** and **3**),[18] indicating that the ((alkyloxy)carbonyl)cyanomethylene moiety is a useful terminal group on the thienoquinoidals for the development of soluble n-channel organic semiconductors. The FET characteristics of those devices were improved by thermal annealing at 100−150 °C (Table 4), consistent with the improved molecular ordering in the thin film (vide supra), as confirmed by XRD measurements.

Vapor-processed **BDT** (R = *n*-hexyl) devices also acted as typical n-channel transistors (Figure 16d), and the FET mobility of the optimized device with the annealed thin film was 1.2×10^{-2} cm^2 V^{-1} s^{-1}. It should be noted that vapor-processed FET devices of dicyanomethylene-substituted BDT (CNBDT; Figure 17) showed miserable FET characteristics, owing to the poor molecular ordering in the thin film state,[13b] indicating that the ((*n*-hexyloxy)carbonyl)cyanomethylene moiety can serve as the molecular ordering group also for vapor-processable materials.

The solution-processed FETs based on **BDT** (R = 2-ethylhexyl) also showed typical n-channel transistor characteristics. However, their mobility (4.2×10^{-3} cm^2 V^{-1} s^{-1}) is lower than that of the vapor-processed **BDT** (R = *n*-hexyl) devices, which can be ascribed to the amorphous nature of its thin film (Figure 14g). Thermal annealing did not effectively improve the characteristics of the **BDT** (R = 2-ethylhexyl)-based FET: this is consistent with the amorphous nature of the thin film even after annealing at 100 °C.

In contrast to the unipolar n-channel FET characteristics of **2T**-, **3T**-, and **BDT**-based OFETs, solution-processed **4T** (R = 2-ethylhexyl)- and **C$_6$-4T**-based devices displayed ambipolar FET characteristics, as shown in Figure 18, reminiscent of the

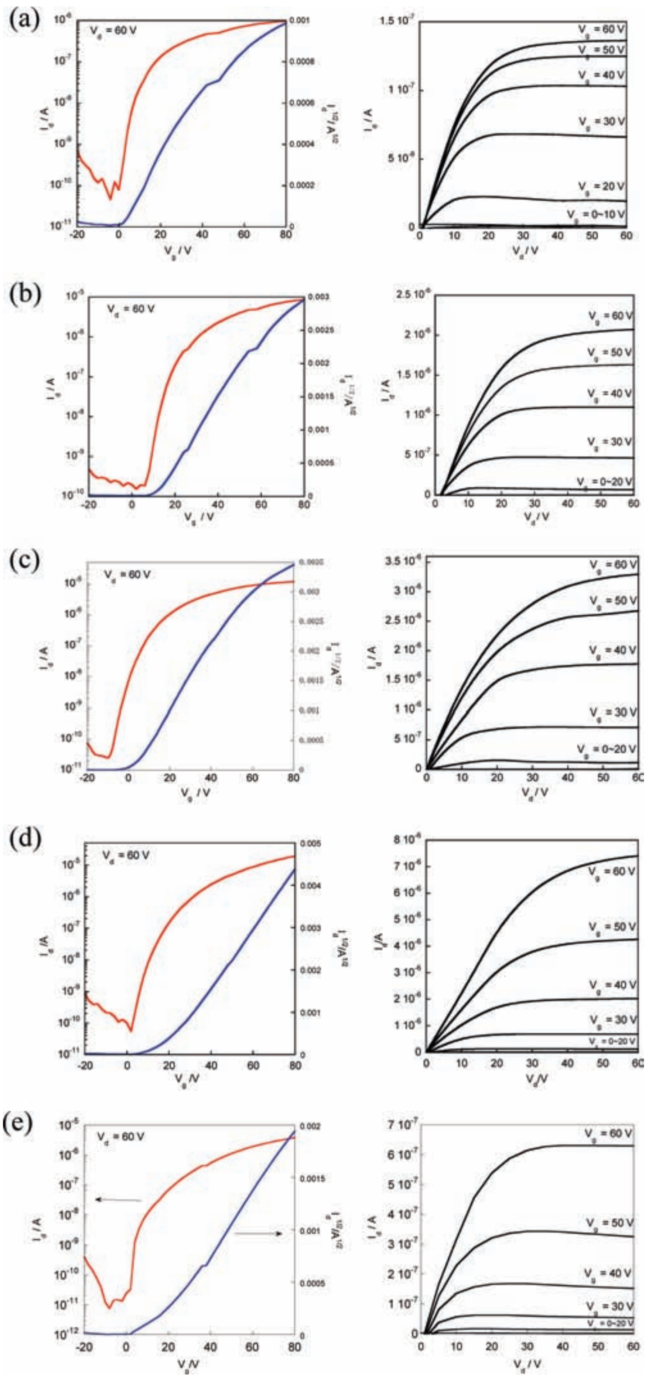
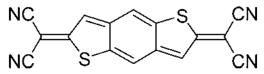


Figure 16. Transfer and output curves of TFTs using annealed thin films: (a) **2T** (R = *n*-hexyl); (b) **3T** (R = *n*-hexyl); (c) **3T** (R = *n*-octyl); (d) **BDT** (R = *n*-hexyl); (e) **BDT** (R = 2-ethylhexyl).

Table 4. FET Characteristics of Solution-Processed OFETs Based on **2T**, **3T**, and **BDT** Fabricated on OTS-Treated Si/SiO$_2$ Substrates

compd	T_{anneal}[a]/°C	μ[b]/cm^2 V^{-1} s^{-1}	$I_{on/off}$	V_{th}/V
2T (*n*-hexyl)	as spun	3.2×10^{-5}	10^2	−1.6
	100	1.2×10^{-3}	10^4	+2.0
3T (*n*-butyl)	as spun	2.6×10^{-5}	10	−24
	150	2.7×10^{-3}	10^4	+14
3T (*n*-hexyl)	as spun	2.2×10^{-5}	10	−8.6
	150	1.5×10^{-2}	10^5	+5.1
3T (*n*-octyl)	as spun	7.5×10^{-5}	10^2	+4.9
	150	1.4×10^{-2}[d]	10^5	+7.0
BDT (*n*-hexyl)[c]	as deposited	1.2×10^{-4}	10^2	+10
	150	1.2×10^{-2}	10^5	+15
BDT (2-ethylhexyl)	as spun	1.3×10^{-3}	10^4	+20
	100	4.2×10^{-3}	10^5	+11.4

[a] Annealing temperatures given in this column were those that gave the best device performance. [b] Extracted from the saturation regime. [c] Vapor deposited onto the substrate at room temperature. [d] Almost the same mobility was maintained after storage for 8 months under ordinary laboratory conditions.



CNBDT

Figure 17. Molecular structure of CNBDT.

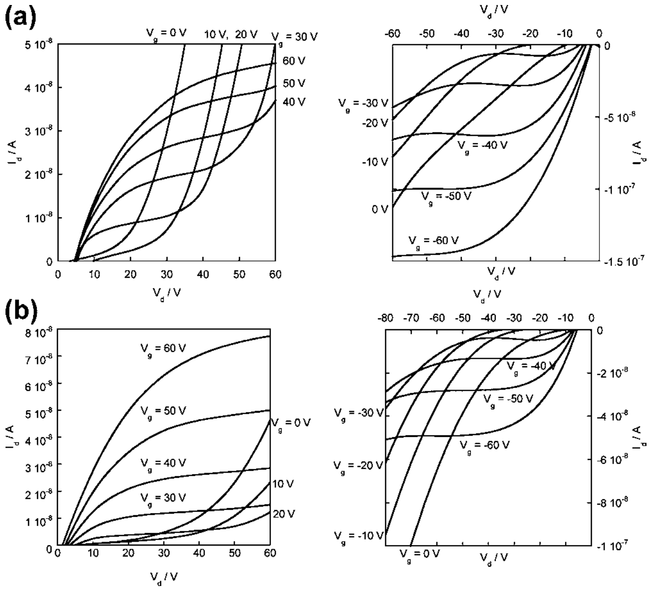


Figure 18. Ambipolar FET characteristics of (a) **4T** (R = 2-ethylhexyl)- and (b) **C$_6$-4T** (R = *n*-hexyl)-based devices.

related dicyanomethylene-substituted quaterthienoquinoidal compound.[26b] The extracted mobilities of electron (μ_e) and hole (μ_h) are 2.0×10^{-4} and 5.0×10^{-4} cm^2 V^{-1} s^{-1}, respectively, for **4T**, and 2.5×10^{-4} and 1.3×10^{-4} cm^2 V^{-1} s^{-1}, respectively, for **C$_6$-4T**. These carrier mobilities are lower than μ_e of **2T** and **3T**, consistent with the poor molecular ordering in the thin-film state (Figure 14c,f).

Molecular Packing Structure of BDT (R = *n*-Hexyl). Among the present thienoquinoidal compounds, only the crystal structure of **BDT** (R = *n*-hexyl), which gives high-quality single crystals, was fully elucidated by single-crystal X-ray analysis (Figure 19). Despite using the crystallographic parameters of the **BDT** single crystal, the peak in the thin-film XRD pattern of **BDT** (Figure 14e) cannot be indexed, indicating that the molecular ordering structure in the bulk single crystal and that in the thin film state are apparently different (Figure S7, Supporting Information). For this reason, it is not possible to discuss a direct correlation between the packing structure in the bulk single crystal and the electronic properties of the thin-film devices. Nevertheless, careful inspection of the packing structure in the single crystal would be beneficial to understand the structural features of the thienoquinoidals with the ((alkyloxy)carbonyl)-cyanomethylene termini.

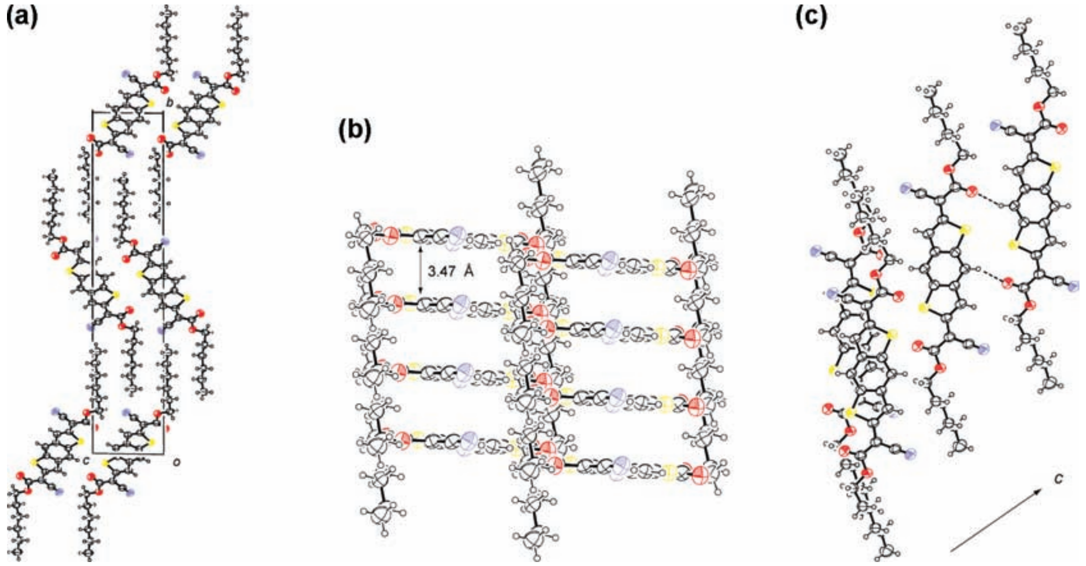


Figure 19. Packing structure of **BDT** (R = *n*-hexyl): (a) *a* axis projection representing lamella-like molecular packing; (b) π-stacking structure along the crystallographic *a* axis direction; (c) molecular ribbon structure along the crystallographic *c* axis direction.

Depicted in Figure 19 is the packing structure of **BDT**, where a lamella-like layered structure along the crystallographic *b* axis direction could be observed (Figure 19a). The characteristic feature of this layered structure is the interdigitation of the *n*-hexyl groups: the alkyl layers are composed of *n*-hexyl groups from two adjacent layers alternately, reminiscent of the lamella structure with interdigitated alkyl side chains observed for the thin film of poly(quaterthiophene)s (PQTs)[29] and their related conjugated polymers.[30] The molecular packing structure in each layer is primarily characterized by a π-stacking columnar structure with a short interfacial distance (3.47 Å),[31] indicating strong intermolecular orbital overlap in the stacking columns (Figure 19b). In addition, the side-by-side intermolecular interaction between the aromatic hydrogen atoms and the carbonyl oxygen atoms is observed, which brings about a molecular ribbon structure in an almost perpendicular direction to the stacking columns and results in a two-dimensional interactive structure (Figure 19c). Another feature of the present packing structure is the relatively large slippage of molecules along the molecular long axis direction in both columns and ribbons. This is probably due to the intermolecular donor−acceptor interaction that would bring about the large blue shift in the UV−vis spectra of the solid state of the present thienoquinoidals (Figure 19c).

These structural characteristics observed in the **BDT** crystal, i.e., strong π-stacking and side-by-side molecular interactions, indicate that the present thienoquinoidals are promising as high-performance n-channel semiconductors. Thus, the control of molecular ordering as well as the structural phase in the thin film state will be vital to further improving the electrical properties in the thin-film-based devices of the present thienoquinoidals.

Conclusion

A series of ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidal compounds have been synthesized with a straightforward method from readily available corresponding α-halo-substituted thiophene derivatives. The newly employed ((alkyloxy)carbonyl)cyanomethylene terminal groups play two important roles in those compounds: as a solubilizing group for solution processability and as an electron-withdrawing group to keep LUMO energy levels sufficiently low to ensure n-channel character. The new thienoquinoidal compounds are more soluble than the corresponding dicyanomethylene compounds, and their LUMO energy levels are ca. 4.0−4.2 eV below the vacuum level, which meet the criteria for air-stable n-channel organic semiconductors. We also confirmed that the present thienoquinoidal compounds are very stable, in contrast with the chemical instability of the related benzoquinoidal compounds.

An X-ray single-crystal structure analysis of **BDT** unambiguously determined its molecular structure, in which the terminal ((alkyloxy)carbonyl)cyanomethylene moieties have the *Z* isomeric form while retaining intramolecular interactions between the sulfur atom in the thiophene ring and the carbonyl oxygen atom in the ester moiety. Such structural characteristics can lead to the high planarity of the molecules and improve stability in solution. The packing structure of **BDT** represents an interactive 2D structure, indicating its potential for use as a high-performance n-channel semiconducting material, although the same structure is not preserved in the thin film state. In the thin film state, molecular inclination is relatively large not only for **BDT** but also for **2T** and **3T**, indicating that the intermolecular overlap in the thin-film state would not be very effective.

Thanks to the improved solubility, solution-processed OFETs were easily fabricated; of these, the terthienoquinoidal ones (**3T**) showed good n-channel FET characteristics with mobilities of up to 0.015 cm^2 V^{-1} s^{-1} and I_{on}/I_{off} values of ∼10^5 under ambient

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conditions. This mobility value is fairly good for solution-processed n-channel devices operated in air, although it is lower by 1 order of magnitude than those of state-of-the-art soluble n-channel materials. For the further enhancement of device performance, the improvement of molecular ordering in the thin film state will be a key issue and thus various printing techniques, such as dip coating and ink jetting, should be examined. In addition to FET application, solution-processed organic photovoltaics based on the present thienoquinoidals as n-channel materials are also very interesting. Relevant experiments are underway in our group.

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Supporting Information Available: Text giving synthetic procedures for the new thienoquinoidal compounds, a CIF file giving crystallographic data for **BDT** (R = *n*-hexyl), text giving the complete entries of refs 25 and 30c, and text, figures, and tables giving results of MO calculations and physicochemical properties of the corresponding dicyanomethylene-substituted oligothienoquinoidals. This material is available free of charge via the Internet at http://pubs.acs.org.

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