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Quinoidal Oligothiophenes with (Acyl)cyanomethylene Termini: Synthesis, Characterization, Properties, and Solution Processed n-Channel Organic Field-Effect Transistors†

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A new class of oligothienoquinoidal derivatives with newly employed (acyl)cyanomethylene termini are reported. For the synthesis of (acyl)cyanomethylene-substituted thienoquinoidals, similar methods successfully employed for the synthesis of related dicyanomethylene- or ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidals were not applicable, and thus a new synthetic route was developed. The introduced (acyl)cyanomethylene terminal groups act both as a solublizing group to facilitate solution processability and an electron-withdrawing group to keep the LUMO energy levels sufficiently low for n-channel organic semiconductors. The LUMO energy levels estimated from their reduction potential are ∼4.2 eV below the vacuum level, which just falls in between those for the corresponding dicyanomethylene- and ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidals. This qualitatively agrees with the electron-withdrawing nature of the terminal groups; the order of the electron withdrawing nature is cyano- > acyl- > (alkyloxy)carbonyl- groups. Spin-coating chloroform solutions of (acyl)cyanomethylene-substituted thienoquinoidals gave homogeneous thin films on the Si/SiO_2 substrates, and the thin films based on the terthienoquinoidal derivatives became highly crystalline upon thermal annealing. The annealed film acted as the active semiconducting channel in the FET devices under ambient conditions, and the electron mobilities extracted from the saturation regime were ∼0.06 cm^2 V^{-1} s^{-1}. These n-channel FET characteristics are nearly the same or slightly better than those of the FETs based on the related ((alkyloxy)carbonyl)cyanomethylene-terminated terthienoquinoidal, indicating that the (acyl)cyanomethylene moiety is a useful terminal group on the thienoquinoidals for the development of soluble n-channel organic semiconductors.

Introduction

7,7,8,8-Tetracyanoquinodimethane (TCNQ, Figure 1), the archetypical electron-accepting molecule, has played important roles in the field of conducting charge-transfer (CT) complexes since the discovery of the first metallic organic material, terathiafulvalene-TCNQ CT salt, reported by Cowan et al. in 1970s.[1] Since then, a variety of TCNQ derivatives[2] as well as its related quinoidal compounds[3] have been developed. Dicyanomethylene-terminated quinoidal-thiophenes or thiophene TCNQs are among such compounds[4] and were intensively studied by Ogura et al. in the 1980s as a promising electron accepting molecules for conducting CT salts.[5]

Recent rising interests in the field of organic electronics has renewed the interests in the TCNQ-type compounds as n-channel organic semiconductors.[6] In fact, the parent TCNQ[7] and its π-extended analogue, 9,9,10,10-tetracyanonaphtho-2,6-quinodimethane (TNAP) (Figure 1),[8] were examined as an active material in the field-effect transistors (FETs) showing relatively good field-effect electron mobility. Several dicyanomethylene-terminated thienoquinoidals have also been examined as active n-channel materials in OFET devices.[9] However, the parent bithienoquinoidal- (**1a**) or terthienoquinoidal (**1b**)-based FETs showed poor device characteristics with low mobility

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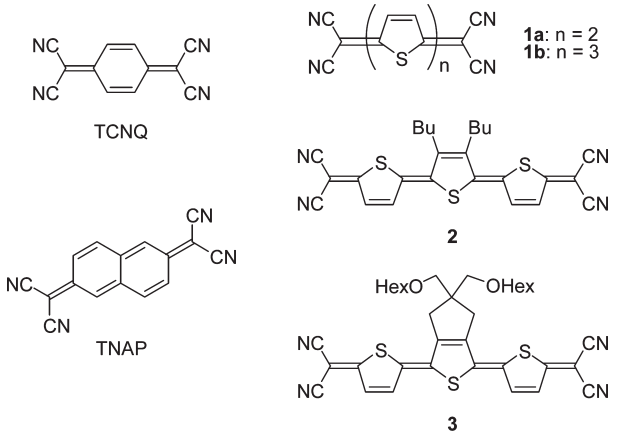

Figure 1. Structures of representative dicyanomethylene-substituted benzoquinoidal and thienoquinoidal compounds.

($\sim 1 \times 10^{-4}$ cm^2 V^{-1} s^{-1}) because of their poor molecular ordering in the thin film state.[9c,10] In sharp contrast, the derivatives of **1b** with substituents on the thienoquinoidal core (**2**) act as superior n-channel organic semiconductors showing mobility up to 0.2 cm^2 V^{-1} s^{-1}.[9a,b] Furthermore, a proper modification with a solubilizing group affords a solution processable derivative (**3**) with retaining high mobility.[9d,e] These fruitful results on **2** and **3** imply that the molecular modification on the thienoquinoidal core would be a key not only for solubilizing the materials but also enabling molecular ordering in the thin-film state. However, the core substitution often requires elaborated synthesis,[9d] which makes the material less practical, even though the given material provides superior semiconductor characteristics.

On the other hand, we have pursued another approach for developing superior new n-channel organic semiconductors based on the quinoidal thiophene structure rather than the molecular modification on the quinoidal core. Actually, we have recently found that a newly employed terminal group containing solublizing long alkyl group, namely the ((alkyloxy)carbonyl)cyanomethylene terminus instead of the conventional dicyanomethylene terminus is quite effective to develop a series of new thienoquinoidals. Thus developed ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidals (Figure 2, **4**) can act as soluble n-channel organic semiconductors that afford solution-processed OTFTs with electron mobility up to 0.015 cm^2 V^{-1} s^{-1}.[10] The devices based on **4** can operate under ambient conditions, indicating

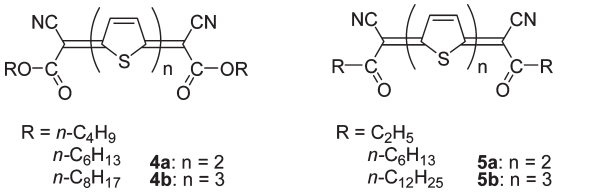

Figure 2. Thienoqunioidal derivatives with soluble terminal groups.

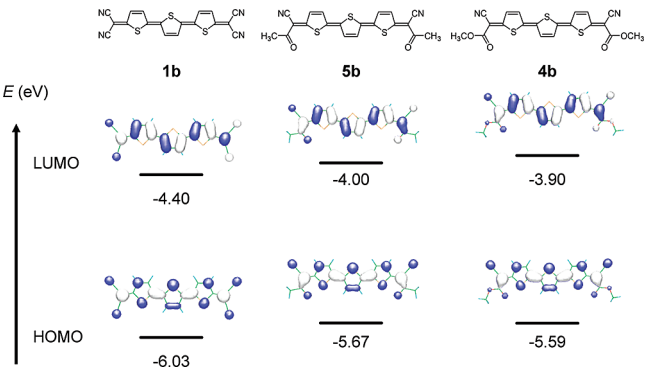

Figure 3. Calculated HOMO and LUMO of terthienoquinoidal derivatives with different terminal groups (**1b**, **4b**, and **5b**).

good air stability due to their low-lying LUMO energy level (<4.0 eV below the vacuum level).[11] In these new thienoquinoidals, the ((alkyloxy)carbonyl)cyanomethylene termini serves both as a solubilizing and an electron-withdrawing group: in other words, this chemical structure satisfies simultaneously the criteria requested for developing soluble, air-stable n-channel organic semiconductors.

Theses results impelled us to explore related thienoquinoidals terminated with (acyl)cyanomethylene groups (Figure 2, **5**) as new potential n-channel organic semiconductors. In fact, theoretical calculations predict that the (acyl)cyanomethylene-substituted thienoquinoidals have slightly lower LUMO energy levels than those of ((alkyloxy)carbonyl)cyanomethylene-substituted ones, reflecting the enhanced electron-withdrawing nature of the acyl group compared to that of alkyloxycarbonyl group (Figure 3).[12] We report herein the synthetic approaches to new soluble oligothienoquinoidals terminated with (acyl)-cyanomethylene groups (**5**) that provides a new class of soluble n-channel organic semiconductors for solution-processed OFETs with mobility up to 0.06 cm^2 V^{-1} s^{-1}.

Results and Discussions

Synthesis. The synthesis of the target thienoqunioidals (**5**) was thought to be deceptively simple by employing the

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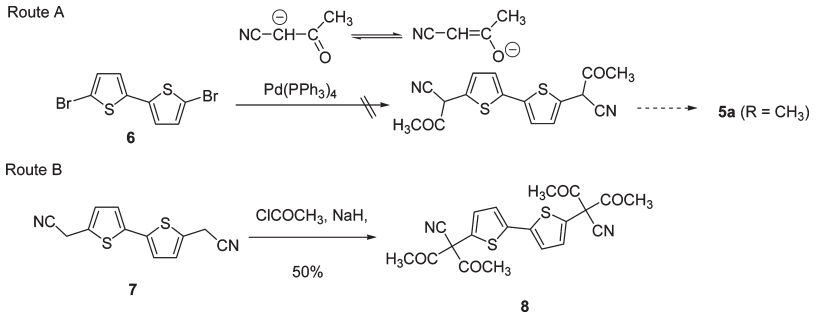
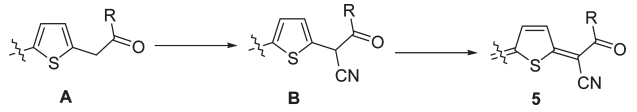
Scheme 1. Attempted Synthesis of 3a



Scheme 2. Synthetic Strategy for (Acyl)Cyanomethylene-Substituted Thienoquinoidals



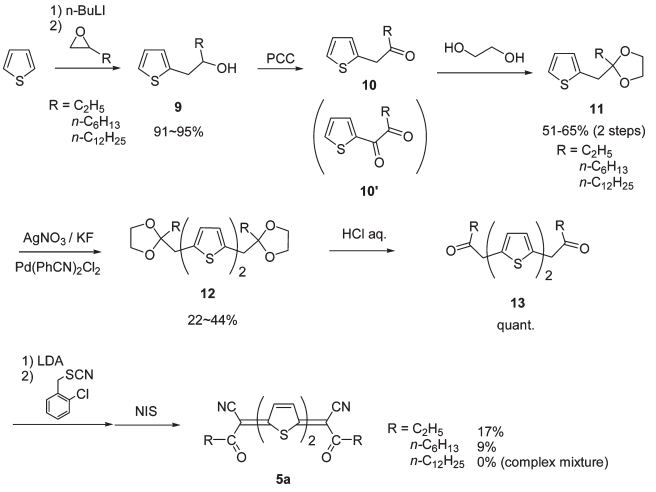
successful synthetic methods for the related ((alkyloxy)-carbonyl)cyanomethylene-substituted thienoqunioidals (**4**). However, initial attempts to synthesize **5a** (R = CH_3) as a model compound were failed: the first attempted route (route A in Scheme 1) consisting of the direct substitution reaction of acetylcyanomethanoide anion[13] with 5,5′-dibromo-2,2′-bithiophene (**6**) gave an ill-characterized complex mixture. This is due to poor reactivity of (acetyl)cyanomethanoide anion in situ generated from cyanoacetone and sodium hydride compared with the ((alkyloxy)carbonyl)cyanomethanoide anion, because the (acetyl)cyanomethanoide anion is stabilized by the enolate form (Scheme 1).

As the next attempt, we tried to introduce acetyl groups on the benzyl carbon atoms of the 5,5′-bis(cyanomethyl)-2,2′-bithiophene[10] (**7**, Scheme 1, route B). However, the isolated product was an overreacted one, 5,5′-bis-(diacetylcyanomethyl)-2,2′-bithiophene (**8**).

These results sharply contrast to the easy accessibility of **4** and related ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidals.[10] We then examined several different synthetic trials for **5** and finally found a reproducible synthetic method for the target oligothienoquinoidals. Key features in the newly developed synthesis are to construct the α-thienylketone moiety (A) and subsequent introduction of a cyano group to give the (acyl)cyanomethyl-substituted thiophene (B), which is supposed to be oxidized to the target thienoquinoidal (Scheme 2).

Actual synthesis of **5a** is shown in Scheme 3. Thienyl ketones (**10**) were first synthesized via a ring-opening reaction of epoxides with 2-thienyl lithium to form the alcohol intermediates (**9**) followed by oxidation.[14] In the oxidation reaction, careful control of the oxidant was crucial, otherwise an overreacted thienyl dione (**10′**, Scheme 3) was easily formed. Because monoketo thiophenes (**10**) were labile and decomposed rapidly, **10** were isolated and purified as the

Scheme 3. Synthesis of Bithienoquinoidal Compounds (5a)



corresponding acetals (**11**). Functionalization of the vacant 5-position of **11** was easily done as the ordinary thiophene derivatives, and dimerization of **11** via $AgNO_3$/KF-mediated coupling gave **12**.[15] After deprotection of the acetal moieties (**13**), treatment of **13** with LDA and 2-chlorobenzylthiocyanate[16] followed by oxidation with *N*-iodosuccinimide finally gave desired **5a** compounds (R = C_2H_5, *n*-C_6H_{13}). In the case of the synthesis of the dodecyl derivative (**5a**, R = *n*-$C_{12}H_{15}$), only a complex mixture was obtained, and the desired **5a** could not be isolated.

Although the desired **5a** compounds were obtained, their isolated yields were very low even after careful optimizations of the reaction conditions and the subsequent workup processes. One of the reasons for such low yields is the formation of byproducts: from the reaction mixture, a crystalline byproduct (**14**) was isolated and characterized by means of single-crystal X-ray analysis (Figure 4). As depicted in Figure 4, **14** may form via a reaction of the carbanion intermediate (**A′**) with 2-chlorobenzylthiocyanate at the benzyl carbon atom (blue arrows) instead of the desired nitrile carbon atom (red arrows).

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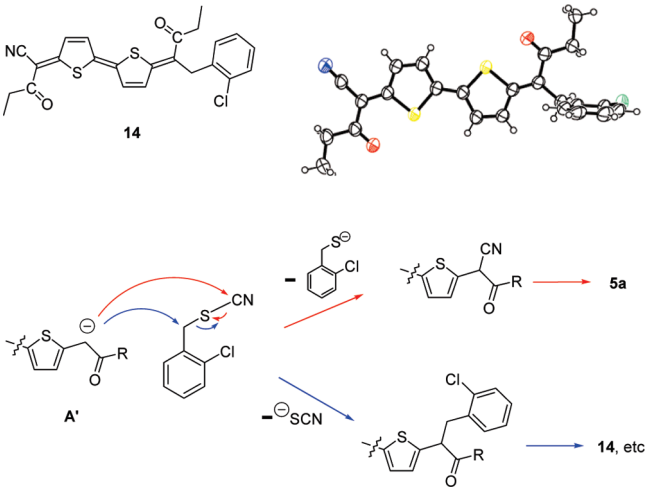
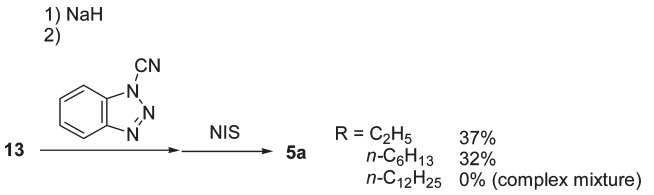


Figure 4. Structure of **14** and the plausible reaction path to **14**.

Scheme 4. Improved Synthesis of 5a (R = C_2H_5, *n*-C_6H_{13}) with 1-Cyano-1*H*-1,2,3-bezotriazole



It is also interesting to note that the molecular structure of **14** at the (acyl)cyanomethane terminus has the *Z*-isomer form as observed for the molecular structure of ((alkyloxy)carbonyl)cyanomethylene-substituted thienoquinoidals as previously reported.[10] This is probably due to the intramolecular interaction between the sulfur atom in the thiophene ring and the carbonyl oxygen atom (2.65 Å) shorter than the sum of van der Waals radii.[17] In addition, a similar short intramolecular nonbonded contact exists in the other terminus (2.59 Å) between the sulfur atom in the thiophene ring and the carbonyl oxygen atom. These structural features, in combination with a similar intramolecular nonbonded contact in the ((alkyloxy)-carbonyl)cyanomethylene-substituted thienoquinoidals,[10] indicate that this type of intramolecular attractive interaction is common for theses classes of thienoquinoidal compounds with carbonyl groups at the exomethylene moiety and may define the terminal structure as the *Z*-form.

The formation of **14** and other structurally related by-products should be avoided to improve the yield of **5** in the cyanation reaction, and thus we tried to use another cycano source, 1-cyano-1*H*-1,2,3-bezotriazole, instead of 2-chlorobenzylthiocyanate (Scheme 4).[18] In this case, the isolated yields of **5a** were improved to 37% (R = C_2H_5) and 32% (*n*-C_6H_{13}), respectively, although the decyl derivative (**5a**, *n*-$C_{12}H_{25}$) could not be synthesized, perhaps because of the poor solubility of the precursor, **13** (*n*-$C_{12}H_{25}$).

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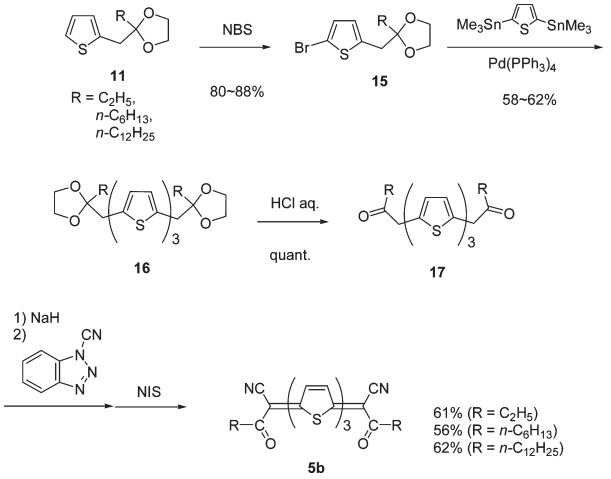
Scheme 5. Synthesis of Terthienoquinoidal Compounds (5b)



The terthienoquinoidal derivatives (**5b**) were also synthesized in a similar manner to that of **5a**. Bromination at the 5-position of the protected thienyl ketone (**11**) with NBS smoothly gave **15**, which was then utilized to the Stille coupling with 2,5-bis(trimethylstannyl)thiophene[19] to give terthiophene intermediate (**16**). After deprotection of the acetal moieties, introduction of the cyano groups on the benzylic carbon atoms followed by oxidation gave **5b** in good yields (Scheme 5). All these new thienoquinoidal compounds were well-characterized by means of spectroscopic and combustion elemental analysis (see Experimental Section).

Physicochemical Evaluation. Cyclic voltammetry of **5a** and **5b** showed similar redox behaviors to those of corresponding **1** and **4** (Figure 5, Table 1). As expected from the extent of electron-withdrawing nature of the cyano, ester, and acyl groups[20] and the DFT calculation results described above (Figure 3), the empirical reduction potentials of **5** are in between those of **1** and **4** (Figure 5). The LUMO energy levels of **5a** and **5b** estimated from the onset of the redox wave are around 4.2−4.3 eV below the vacuum level, which meets the criteria for air-stable n-channel OFET materials.[11] Similar to the voltamograms of **1b** and **4b**, the terthienoquinoidal derivatives **5b** also show oxidation peaks, indicating that the HOMO energy levels of **5b** are relatively high compared to those of **5a** as in the cases for **1b** and **4b**. Judging from the HOMO energy levels of **5b** (5.5 eV below the vacuum level), the hole injection from the gold electrode to the **5b** thin film might take place,[9b,e,f,h] which brings about the p-channel transistor behavior. However, we could not observe any p-channel response in the **5b**-FET devices (vide infra), although the actual reasons for the lack of ambipolar behavior are not clear.

Absorption spectra of **5a** and **5b** depicted in Figure 6 show a slight bathochromic shift compared to the corresponding **1** and **4**. This is provably due to more effective conjugation of the carbonyl group with the thienoquinoidal core than those of the cyano or ester group in **1** and **4**.

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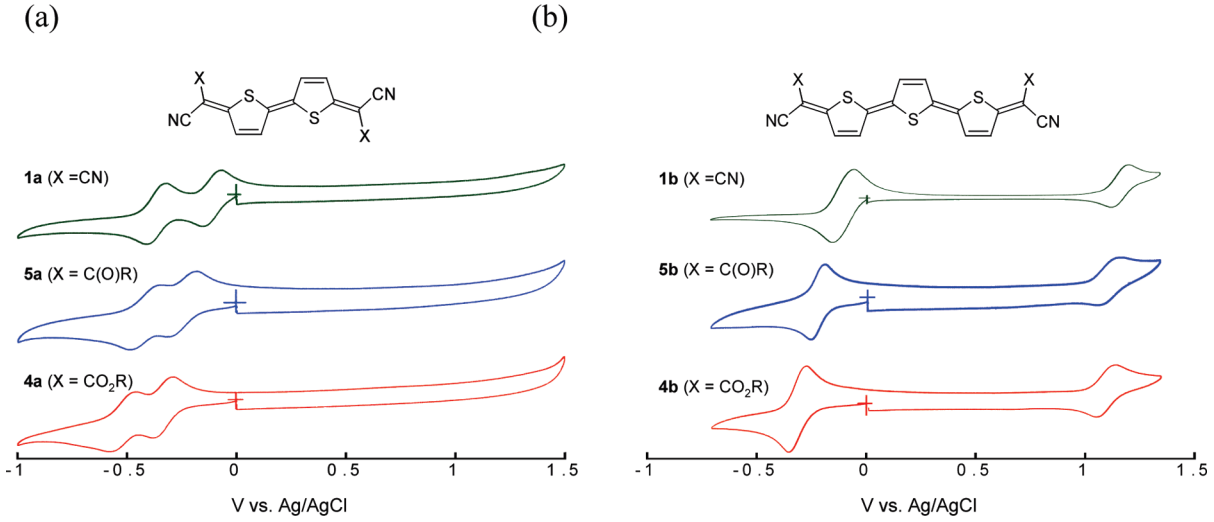

Figure 5. Cyclic volatmmogram of **5** (R = n-C_6H_{13}) in comparison with **1** and **4** (R = n-C_6H_{13}): (a) bithienoquinoidals, **1a**, **4a**, and **5a**; (b) terthienoquinoidals, **1b**, **4b**, and **5b**.

Table 1. Comparison of Bithienoquinoidal (1a, 4a, and 5a) and Terthienoquinoidal Compounds (1b, 4b, and 5b) with Different Terminal Groups

	$E^{1/2}_{red}$ (V)[a]	E^{onset}_{red} (V)[a]	LUMO (eV)[b]	$E^{1/2}_{ox}$/V	λ_{max} (log ε) (nm)	λ_{onset} (nm)	E_g (eV)[c]	HOMO (eV)[b,d]
5a[e]	−0.23 (1e), −0.35 (1e)	−0.16	−4.24		575 (4.87)	647	1.9	−6.1[d]
4a[e]	−0.34 (1e), −0.48 (1e)	−0.26	−4.14		556 (4.92)	610	2.0	−6.1[d]
1a	−0.10 (1e), −0.32 (1e)	−0.03	−4.37		550 (4.86)	612	2.0	−6.4[d]
5b[e]	−0.22 (2e)	−0.16	−4.24	+1.10	668 (5.06)	797	1.5	−5.5[b]
4b[e]	−0.32 (2e)	−0.23	−4.17	+1.10	649 (5.04)	785	1.5	−5.5[b]
1b	−0.12 (2e)	−0.04	−4.36	+1.35	643 (5.02)	811	1.5	−5.7[b]

[a] V vs Ag/AgCl. All the potentials were calibrated with the Fc/Fc^+ ($E^{1/2}$ = +0.43 V measured under identical conditions). [b] Estimated with a following equation: E (eV) = −4.4 − E_{onset}. [c] Calculated from λ_{onset}. [d] Estimated from the LUMO energy level and E_g. [e] Compounds with R = n-C_6H_{13} were used.

However, overall similarity of the absorption spectra for **1**, **4**, and **5** again confirms that the electronic perturbation from the acyl groups are not significant, and **5a** and **5b** would be potential n-channel organic semiconductors as **1** and **4**.

Thin Film Deposition. Spin-coating chloroform solutions of **5a** (R = n-C_6H_{13}) and **5b** (R = n-C_6H_{13}, n-$C_{12}H_{25}$) gave homogeneous thin films on Si/SiO_2 and quartz glass substrates. As-spun films were amorphous-like in all three cases, whereas annealing (~120 °C) clearly improved the molecular ordering in the thin film state of **5b** (R = n-C_6H_{13}, n-$C_{12}H_{25}$), as evident from the X-ray diffraction (XRD) patterns (Figure 7b). In case of the **5a** (R = n-C_6H_{13}) thin film, no noticeable change in XRD pattern on annealing was observed (Figure 7a), which reflects its poor crystallinity, or in other words inherent amorphous nature of **5a** in the thin film state. This contrasts to **4a**, the bithienoquinoidal counterpart with the ((alkyloxy)carbonyl)cyanomethylene termini, that gives well-ordered crystalline thin films by spin-coating and subsequent annealing.

Improved molecular ordering in the thin film of **5b** (R = n-C_6H_{13}, n-$C_{12}H_{25}$) on annealing was concomitant with hypsochromic shifts in the UV−vis spectra of thin films as shown in Figure 8b, which is reminiscent of similar hypsochromic shifts for **4a** and **4b**.[10] In sharp contrast, the **5a** (R = n-C_6H_{13}) thin film does not show such hypsochromic shifts (Figure 8a); rather, bathochromic shift was observed in the thin film state compared with that in the solution. This spectroscopic behavior in the thin film state and the aforementioned thin film XRD indicates that the molecular ordering nature of **5a** is quite different from those of analogous **4a** and **5b**.[21]

Thin Film FET Devices. OFET devices using the spin-coated thin films of **5a** (R = n-C_6H_{13}) and **5b** (R = n-C_6H_{13}, n-$C_{12}H_{25}$) as the active semiconducting channel were evaluated with a top-contact, bottom gate device configuration on the Si/SiO_2 substrate modified with octadecyltrichlorosilane. As expected from the poor molecular ordering in the thin film state, **5a**-based OFETs did not show decent n-channel FET responses. On the other hand, **5b**-based ones showed typical n-channel FET behaviors under ambient conditions: without thermal annealing of the thin films, the mobilities were on the order of 1×10^{-5} cm^2 V^{-1} s^{-1}, whereas the mobilities for the devices with annealed thin films extracted from the saturated regime are 0.007 cm^2 V^{-1} s^{-1} for **5b** (R = n-C_6H_{13}) and 0.06 cm^2 V^{-1} s^{-1} for **5b** (R = n-$C_{12}H_{25}$), respectively (Figure 9).

These mobilities are nearly the same as or slightly higher than those reported for ((alkyloxy)carbonyl)cyanomethylene-substituted terthienoquinoidals (**4b**, $\mu \approx 0.015$ cm^2 V^{-1} s^{-1}), indicating that the (acyl)cyanomethylene moiety is a

(21) As in the cases for the thin films of **4a** and **4b**, the large hypsochromic shift for thin films of **5b** would be ascribed to the H-type molecular aggregation in the thin film state (see ref 10). In contrast, the bathochromic shift observed for the thin film of **5a** should be related to J-type aggregation. These totally different behaviors in the thin film state of **5a** and **5b** are in contrast to those for **4a** and **4b**, although the cause for such differences can not be well explained.

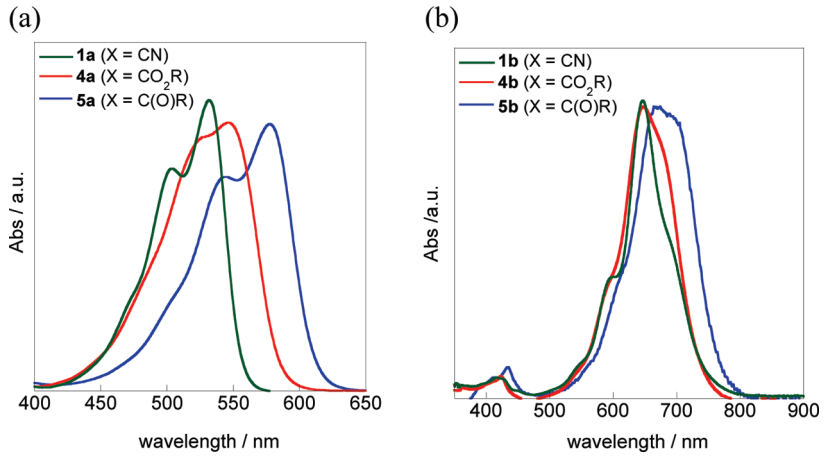

Figure 6. Absorption spectra of (a) **1a**, **4a**, and **5a**; (b) **1b**, **4b**, and **5b**. **1**, green lines; **4** (R = *n*-C_6H_{13}), red lines' and **5** (R = *n*-C_6H_{13}), blue lines.

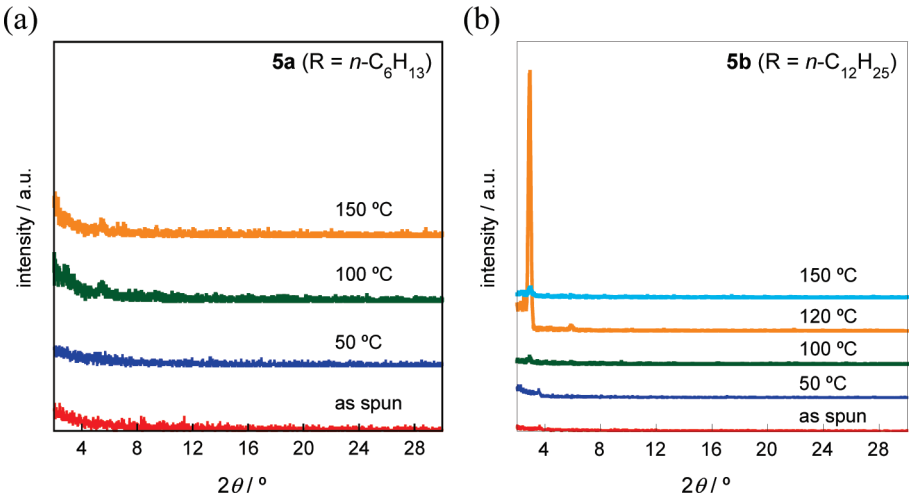

Figure 7. XRD patterns of spin-coated thin films: (a) **5a** (R = *n*-C_6H_{13}), (b) **5b** (R = *n*-$C_{12}H_{25}$).

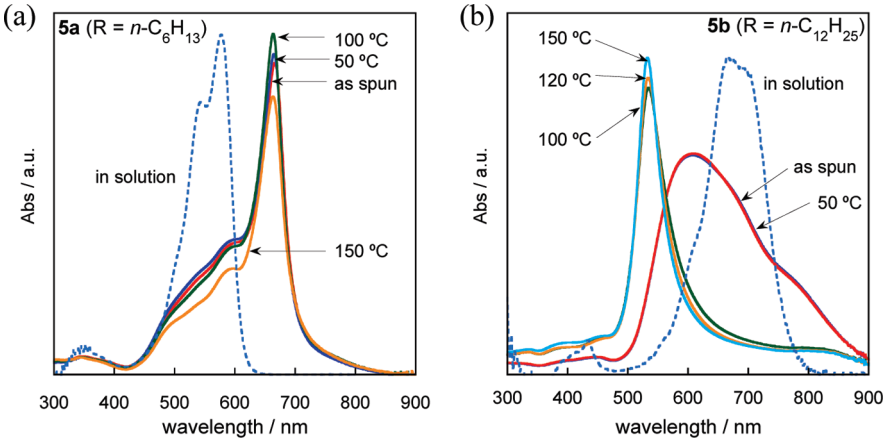

Figure 8. Absorption spectra of spin-coated thin films upon annealing: (a) **5a** (R = *n*-C_6H_{13}), (b) **5b** (R = *n*-$C_{12}H_{25}$).

useful terminal group on the thienoquinoidals for the development of soluble n-channel organic semiconductors. One notable characteristic is that the derivatives with longer *n*-$C_{12}H_{25}$ groups gave higher mobility by ca. 1 order of magnitude than that with the shorter *n*-C_6H_{13} groups. Such alkyl chain dependence was not observed for **4b**,[10] implying that molecular ordering nature could be affected by the presence/absence of oxygen atom in the long alkyl groups.

Conclusion

We have successfully developed a new class of oligothienoquinoidal derivatives (**5**) with a newly employed (acyl)cyanomethylene terminal group. Although their synthesis were seemingly easy, it turned out that the analogous methods successfully applied to the syntheses of dicyanomethylene- (**1**) and ((alkyloxy)carbonyl)cyanomethylene-substituted

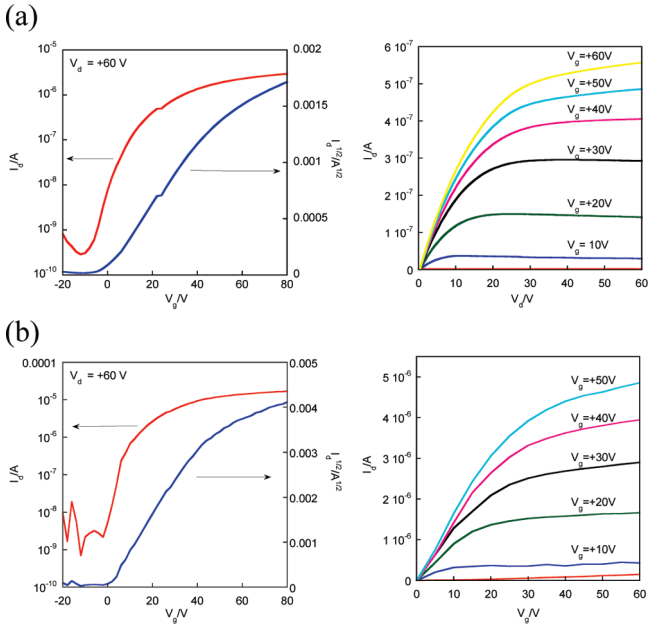

Figure 9. Transfer and output curves of FETs using annealed thin films. (a) **5b** (R = n-C_6H_{13}), (b) **5b** (R = n-$C_{12}H_{25}$).

thienoquinoidals (**4**) were not applicable. Thus, we examined several potential methods, and finally established a new synthetic route to the desired oligothienoquinoidals. The introduced (acyl)cyanomethylene terminal groups act both as a solublizing group to facilitate solution processability and an electron-withdrawing group to keep the LUMO energy levels sufficiently low for n-channel organic semiconductors. The LUMO energy levels estimated from their reduction potential are ~4.2 eV below the vacuum level, which just falls in between those for the corresponding dicyanomethylene- (**1**) and ((alkyloxy)-carbonyl)cyanomethylene-substituted thienoquinoidals (**4**). This qualitatively agrees with the electron-withdrawing nature of the terminal groups: the order of the electron withdrawing nature is cyano- > acyl- > (alkyloxy)carbonyl groups. The present (acyl)cyanomethylene-substituted thienoquinoidals (**5**) gave homogeneous thin films on the Si/SiO_2 substrates by spin coating, and the thin films based on the terthienoquinoidal derivatives (**5b**) became highly crystalline upon thermal annealing. The annealed film acted as the active semiconducting channel in the FET devices, and the mobilities extracted from the saturation regime are ~0.06 $cm^2\ V^{-1}\ s^{-1}$. These n-channel FET characteristics are nearly the same as or slightly higher than those of **4**-based FETs. These results indicate that the (acyl)cyanomethylene moiety is a useful terminal group on the thienoquinoidals for the development of soluble n-channel organic semiconductors. Further optimization of the molecular structure of the present thienoquinoidal series is now underway in our group. In this relation, although the present synthetic method is useful for the synthesis of oligothienoquinoidals, the method can not be applicable to the synthesis of the fused thienoquinoidals. Thus, new versatile and efficient methods for the synthesis of this class of thienoquinoidals are also intensively investigated.

Experimental Section

Synthesis. *General.* All chemicals and solvents are of reagent grade unless otherwise indicated. THF was purified with a standard distillation procedure prior to use. Melting points were uncorrected. All reactions were carried out under a nitrogen atmosphere. Nuclear magnetic resonance spectra were obtained in deuterated chloroform ($CDCl_3$) with TMS as internal reference; chemical shifts (δ) are reported in parts per million. IR spectra were recorded as a neat spectrum for oil samples or using a KBr pellet for solid samples. EI-MS spectra were obtained using an electron impact ionization procedure (70 eV). MALDI-TOF spectra were obtained using dithranol matrix. FAB-MS spectra were recorded using 3-nitrobenzyl alcohol as a matrix. Solubilities of **5a** and **5b** in chloroform were determined as the saturated concentration (g L^{-1}) at room temperature.

Synthesis of 2-Thienylethanol Derivative (General Procedure)[14]**.** *1-(2-Thienyl)butane-2-ol* (***9***, *R = C_2H_5*). To a solution of thiophene (5 mL, 63 mmol) in THF (100 mL) was slowly added n-butyllithium (1.59 M solution in hexane, 45 mL, 69 mmol) at −78 °C. After stirring for 1 h at room temperature, 1,2-epoxybutane (11 mL, 126 mmol) was slowly added at −78 °C, and the mixture was stirred overnight at room temperature. To the mixture was added hydrochloric acid (1 M, 100 mL), and the resulting mixture was extracted with ethyl acetate (100 mL × 3). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over magnesium sulfate (anhydrous), and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluted with dichloromethane (R_f = 0.45) to give **9** (R = C_2H_5) as a pale yellow oil (9.0 g, 91%). ^{1}H NMR (270 MHz) δ 7.18 (d, J = 4.0 Hz, 1H), 6.96 (dd, J = 4.0 Hz, J = 3.3 Hz, 1H), 6.87 (d, J = 3.3 Hz, 1H), 3.74 (m, 1H), 3.00 (m, 2H), 1.56 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 10.1, 29.4, 37.5, 73.9, 124.3, 126.1, 127.1, 140.8. MS (EI) m/z = 156 (M^+). IR (neat) ν = 3381 cm^{-1} (OH). Anal. Calcd for $C_8H_{12}OS$: C, 61.50; H, 7.74%. Found: C, 61.16; H, 7.54%.

1-(2-Thienyl)octan-2-ol (***9***, *R = n-C_6H_{13}*). Yellow oil, 93% isolated yield. ^{1}H NMR (400 MHz) δ 7.18 (d, J = 5.2 Hz, 1H), 6.96 (dd, J = 5.2 Hz, J = 3.3 Hz, 1H), 6.86 (d, J = 3.3 Hz, 1H), 3.80 (m, 1H), 3.01 (m, 2H), 1.55−1.29 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 14.2, 22.7, 25.8, 29.4, 31.9, 36.6, 38.0, 72.5, 124.3, 126.1, 127.1, 140.8. MS (EI) m/z = 212 (M^+). IR (neat) ν = 3381 cm^{-1} (OH). Anal. Calcd for $C_{14}H_{24}OS$: C, 67.87; H, 9.49%. Found: C, 67.78; H, 9.64%.

1-(2-Thienyl)tetradecan-2-ol (***9***, *R = n-$C_{12}H_{25}$*). Waxy white solid (mp < 30 °C), 95% isolated yield. ^{1}H NMR (270 MHz) δ 7.18 (dd, J = 5.2 Hz, J = 1.2 Hz, 1H), 6.96 (dd, J = 5.2 Hz, J = 3.3 Hz, 1H), 6.86 (d, J = 3.3 Hz, J = 1.2 Hz, 1H), 3.81 (m, 1H), 3.01 (m, 2H), 1.55−1.29 (m, 22H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 14.5, 23.0, 26.0, 29.7, 29.9, 30.0, 32.3, 36.9, 38.3, 72.7, 124.4, 126.3, 127.2, 141.0. MS (EI) m/z = 296 (M^+). IR (neat) ν = 3375 cm^{-1} (OH). Anal. Calcd for $C_{18}H_{32}OS$: C, 72.91; H, 10.88%. Found: C, 72.77; H, 10.73%.

Synthesis of α-Thienylmethylketone Derivative (General Procedure). *1-(2-Thienyl)butan-2-one* (***10***, *R = C_2H_5*). To a solution of **9** (R = C_2H_5, 20.0 g, 128 mmol) in dichloromethane (800 mL) was portionwise added pyridinium chlorochromate (30.4 g, 141 mmol) at 0 °C. After stirring overnight at room temperature, the mixture was filtered through a silica gel pad, and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel eluted with hexane-ethyl acetate (v/v = 9:1, R_f = 0.3) to give **10** (*R* = C_2H_5) as yellow oil (13.0 g, 66%). Because of its instability, the title

compound was immediately used in the next step without further purification. ^{1}H NMR (270 MHz) δ 7.22 (d, J = 5.1 Hz, 1H), 6.98 (dd, J = 5.1 Hz, J = 3.2 Hz, 1H), 6.89 (d, J = 3.2 Hz, 1H), 3.89 (s, 2H), 2.54 (q, J = 7.3 Hz, 2H), 1.06 (t, J = 7.3 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 8.0, 35.3, 43.5, 53.9, 125.3, 127.0, 127.3, 135.7, 207.8. MS (EI) m/z = 154 (M^+). IR (neat) ν = 1716 cm^{-1} (C=O).

1-(2-Thienyl)octan-2-one (***10***, R = *n*-C_6H_{13}). Pale yellow oil, 64% isolated yield. ^{1}H NMR (400 MHz) δ 7.22 (d, J = 5.0 Hz, 1H), 6.98 (dd, J = 5.0 Hz, J = 3.1 Hz, 1H), 6.89 (d, J = 3.1 Hz, 1H), 3.88 (s, 2H), 2.49 (t, J = 5.9 Hz, 2H), 1.30−1.24 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 14.1, 22.5, 23.7, 28.8, 31.6, 41.8, 43.6, 53.2, 125.0, 126.8, 127.7, 135.5, 207.2. MS (EI) m/z = 210 (M^+). IR (neat) ν = 1716 cm^{-1} (C=O).

1-(2-Thienyl)tetradecan-2-one (***10***, R = *n*-$C_{12}H_{25}$). Pale yellow solid, 86% isolated yield. Mp 29−30 °C, ^{1}H NMR (270 MHz) δ 7.22 (dd, J = 5.1 Hz, J = 1.1 Hz, 1H), 6.98 (dd, J = 5.2 Hz, J = 5.1 Hz, 1H), 6.88 (dd, J = 5.2 Hz, J = 1.1, 1H), 3.88 (s, 2H), 2.49 (t, J = 7.5 Hz, 2H), 1.30−1.24 (m, 20H), 0.88 (t, J = 6.5 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 14.5, 23.1, 24.1, 29.4, 29.7, 29.8, 30.0, 42.1, 47.5, 52.8, 125.3, 127.0, 127.3, 1235.7, 207.4. MS (EI) m/z = 294 (M^+). IR (neat) ν = 1710 cm^{-1} (C=O).

Synthesis of α-Thienylmethylketone Acetals (General Procedure). *1-(2-Thienyl)butan-2-one Ethylene Acetal* (***11***, R = C_2H_5). A solution of ethylene glycol (8.09 g, 129 mmol) and *p*-toluene sulfonic acid monohydrate (60 mg, 0.324 mmol) in benzene (50 mL) was refluxed for 1 h to remove water with a Dean−Stark condenser. Then, **10** (R = C_2H_5, 1.0 g, 6.49 mmol) was added to the solution, and the resulting mixture was refluxed overnight. After cooling, the mixture was poured into an ice-cooled saturated $NaHCO_3$ aqueous solution (50 mL) and extracted with dichloromethane (30 mL × 3). The combined extracts were washed with water (10 mL) and brine (10 mL) and dried over magnesium sulfate (anhydrous). Concentration in vacuo gave practically pure **11** (R = C_2H_5) as yellow oil (1.20 g, 93%). ^{1}H NMR (270 MHz) δ 7.17 (dd, J = 1.2 Hz, 5.1 Hz, 1H), 6.93 (dd, J = 3.5 Hz, 5.1 Hz, 1H), 6.88 (m, 1H), 3.12 (s, 2H), 3.80−3.96 (m, 4H), 1.67 (q, J = 7.5 Hz, 2H), 0.94 (t, J = 7.5 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 8.1, 30.4, 38.2, 65.6, 111.1, 122.5, 127.7, 137.3, 137.4. MS (FAB) m/z = 177 ([M−H]$^+$). Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12%. Found: C, 60.45; H, 7.12%.

1-(2-Thienyl)octan-2-one Ethylene Acetal (***11***, R = *n*-C_6H_{13}). Colorless oil, quantitative yield. ^{1}H NMR (270 MHz) δ 7.17 (dd, J = 1.2 Hz, 5.1 Hz, 1H), 6.93 (dd, J = 3.5 Hz, 5.1 Hz, 1H), 6.88 (m, 1H), 3.11 (s, 2H), 3.79−3.95 (m, 4H), 1.26−1.66 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR (67.8 MHz) δ 14.4, 22.9, 23.9, 29.8, 32.1, 37.9, 38.4, 65.7, 111.1, 125.0, 126.7, 127.3, 138.8. MS (FAB) m/z = 253 ([M−H]$^+$). Anal. Calcd for $C_{14}H_{22}O_2S$: C, 66.10; H, 8.72%. Found: C, 65.95; H, 9.05%.

1-(2-Thienyl)tetradecan-2-one Ethylene Acetal (***11***, R = *n*-$C_{12}H_{25}$). Waxy white solid, 59% isolated yield. Mp < 30 °C. ^{1}H NMR (270 MHz) δ 7.17 (dd, J = 1.2 Hz, 5.1 Hz, 1H), 6.93 (dd, J = 3.5 Hz, 5.1 Hz, 1H), 6.88 (m, 1H), 3.11 (s, 2H), 3.79−3.95 (m, 4H), 1.26−1.66 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 14.5, 23.0, 24.0, 29.7, 29.9, 30.0, 30.1, 32.2, 37.8, 38.4, 65.6, 111.0, 124.9, 126.7, 127.3, 138.8. MS (EI) m/z = 336 (M^+). Anal. Calcd for $C_{20}H_{34}O_2S$: C, 70.95%; H, 10.12. Found: C, 71.02; H, 9.87%.

5,5′-Bis(2-oxobutyl)-2,2′-bithiophene Ethylene Acetal (12, R = C_2H_5)[15] **(General Procedure).** To a degassed solution of **11** (R = C_2H_5, 500 mg, 2.53 mmol) in DMSO (12.5 mL) was added $AgNO_3$ (859 mg, 5.05 mmol), potassium fluoride (293 mg, 5.05 mmol), and $Pd(PhCN)_2Cl_2$ (10 mg, 0.025 mmol). After being stirred overnight at 60 °C, $AgNO_3$ (859 mg, 5.05 mmol) and potassium fluoride (293 mg, 5.05 mmol) were again added and the resulting mixture was further stirred overnight. The mixture was diluted with ethyl acetate (100 mL) and filtered through a Celite-pad. The filtrate was diluted with water (100 mL), and the organic layer was separated. The aqueous layer was then extracted with ethyl acetate (50 mL × 3), and the combined organic layer was washed with water (100 mL) and brine (100 mL), dried over magnesium sulfate (anhydrous), and concentrated in vacuo. The residue was purified by column chromatography on alumina eluted with hexane-ethyl acetate (v/v = 9:1, R_f = 0.3) to give **12** (R = C_2H_5) as a pale yellow solid (220 mg, 44%). Mp 87−88 °C. ^{1}H NMR (270 MHz) δ 6.95 (d, J = 3.6 Hz, 2H), 6.74 (d, J = 3.6 Hz, 2H), 3.84−3.95 (m, 8H), 3.07 (s, 4H), 1.69 (q, J = 7.3 Hz, 4H), 0.95 (t, J = 7.3 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 8.06, 30.4, 38.2, 65.6, 111.1, 122.5, 127.7, 137.3, 137.4. MS (EI) m/z = 394 (M^+). Anal. Calcd for $C_{20}H_{26}O_4S_2$: C, 60.88; H, 6.64%. Found: C, 60.95; H, 6.61%.

5,5′-Bis(2-oxooctyl)-2,2′-bithiophene Ethylene Acetal (***12***, R = *n*-C_6H_{13}). The title compound was obtained from **11** (R = C_6H_{13}) with the same manner as **12** (R = C_2H_5). Pale yellow solid, 44% isolated yield. Mp 74−75 °C. ^{1}H NMR (400 MHz) δ 6.94 (d, J = 3.8 Hz, 2H), 6.73 (d, J = 3.8 Hz, 2H), 3.84−3.95 (m, 8H), 3.06 (s, 2H), 1.64 (t, J = 7.7 Hz, 4H), 1.27−1.54 (m, 16H), 0.87 (t, J = 6.6 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 14.2, 22.7, 23.7, 29.6, 31.9, 37.6, 38.5, 65.5, 110.9, 122.5, 128.5, 137.3, 137.4. MS (EI) m/z = 506 (M^+). Anal. Calcd for $C_{28}H_{42}O_4S_2$: C, 66.36 H, 8.35%. Found: C, 66.38; H, 8.35%.

5,5′-Bis(2-oxotetradecyl)-2,2′-bithiophene Ethylene Acetal (***12***, R = *n*-$C_{12}H_{25}$). The title compound was obtained from **11** (R = *n*-$C_{12}H_{25}$) with the same manner as **12** (R = C_2H_5). Pale yellow solid, 22% isolated yield. Mp 58−59 °C. ^{1}H NMR (400 MHz) δ 6.94 (d, J = 3.6 Hz, 2H), 6.74 (d, J = 3.6 Hz, 2H), 3.84−3.95 (m, 8H), 3.06 (s, 4H), 1.24−1.66 (m, 44H), 0.95 (t, J = 7.5 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 14.3, 22.8, 23.8, 29.5, 29.7, 29.8, 29.9, 32.1, 37.6, 38.5, 65.5, 110.9, 122.5, 127.3, 137.3, 137.4. EI MS (70 eV) m/z = 674 (M^+). Anal. Calcd for $C_{40}H_{66}O_4S_2$: C, 71.17 H, 9.85%. Found: C, 70.97; H, 10.08%.

5,5′-Bis(2-oxobutyl)-2,2′-bithiophene (13, R = C_2H_5). A solution of **12** (R = C_2H_5, 1.06 g, 2.69 mmol) in THF (12 mL) and hydrochloric acid (2 M, 1 mL) was refluxed overnight. The resulting mixture was extracted with dichloromethane (20 mL × 3). The combined extracts were washed with water (10 mL) and brine (10 mL), dried over magnesium sulfate (anhydrous), and concentrated in vacuo to give **13** (R = C_2H_5) as a pale yellow solid (813 mg, quantitative). Mp 77−79 °C. NMR (270 MHz) δ 6.99 (d, J = 3.9 Hz, 2H), 6.77 (d, J = 3.9 Hz, 2H), 3.85 (s, 4H), 2.59 (q, J = 7.2 Hz, 4H), 0.75 (t, J = 7.2 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 7.9, 35.2, 43.5, 123.4, 127.5, 134.6, 137.1, 207.3. MS (EI) m/z = 506 (M^+). IR (KBr) ν = 1707 cm^{-1} (C=O); Anal. Calcd for $C_{16}H_{18}O_2S_2$: C, 62.71; H, 5.92%. Found: C, 62.73; H, 5.86%.

5,5′-Bis(2-oxooctyl)-2,2′-bithiophene (***13***, R = *n*-C_6H_{13}). The title compound was obtained from **12** (R = *n*-C_6H_{13}). Pale yellow solid, quantitative yield. Mp 84−85 °C. ^{1}H NMR (400 MHz) δ 6.99 (d, J = 3.7 Hz, 2H), 6.77 (d, J = 3.7 Hz, 2H), 3.84 (s, 4H), 2.51 (q, J = 7.5 Hz, 4H), 1.03−1.76 (m, 20H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 14.4, 22.8, 24.0, 29.1, 21.9, 42.2, 44.1, 123.7, 127.7, 134.8, 137.4, 207.2. MS (EI) m/z = 418 (M^+). IR (KBr) ν = 1707 cm^{-1} (C=O); Anal. Calcd for $C_{26}H_{24}N_2O_4S_3$: C, 61.82; H, 5.19%. Found: C, 61.91; H, 5.15%.

5,5′-Bis(2-oxotetradecyl)-2,2′-bithiophene (***13***, R = *n*-$C_{12}H_{25}$). The title compound was obtained from **12** (R = *n*-$C_{12}H_{25}$).

Pale yellow solid, 85% isolated yield. Mp 110−111 °C. ^{1}H NMR (270 MHz) δ 6.98 (d, J = 3.2 Hz, 2H), 6.76 (d, J = 3.2 Hz, 2H), 3.84 (s, 4H), 2.51 (q, J = 7.6 Hz, 4H), 1.16−1.34 (m, 36H), 0.88 (t, J = 7.3 Hz, 6H); ^{13}C NMR (67.8 MHz) δ 14.3, 22.8, 23.9, 29.2, 29.4, 29.5, 29.6, 29.7, 29.8, 32.1, 42.0, 43.9, 123.4, 127.5, 134.5, 137.2, 207.0. EIMS (70 eV) m/z = 586 (M^+). IR (KBr) ν 1710 cm^{-1} (C═O). Anal. Calcd for $C_{36}H_{58}O_2S_2$: C, 73.66; H, 9.96%. Found: C, 73.90; H, 9.90%.

(*Z,Z*)-5,5′-Bis(α-cyano-α-propionylmethylene)-5,5′-dihydro-Δ$^{2,2'}$-bithiophene (5a, R = C$_2$H$_5$)[16]**.** To a solution of **13** (R = C_2H_5, 100 mg, 0.33 mmol) in THF (6 mL) was added LDA (1 M solution in THF, 0.72 mL, 0.72 mmol) at 0 °C. After the solution was stirred for 30 min at the same temperature, a solution of *o*-chlorobenzylthiocyanate (239 mg, 1.31 mmol) in THF (3 mL) was slowly added, and stirred overnight at room temperature. To the mixture was then added hydrochloric acid (1 M, 10 mL), and the resulting mixture was extracted with dichloromethane (30 mL × 3). The combined extracts were washed with water (10 mL) and brine (10 mL), dried over magnesium sulfate (anhydrous), and concentrated in vacuo. The residue was suspended in a mixed solution of acetonitrile (5 mL) and water (5 mL), and then NIS (174 mg, 0.65 mmol) was added to the suspension at 0 °C. After being stirred for 30 min at the same temperature, the resulting precipitate was collected by filtration. The solid product was purified with column chromatography on silica gel eluted with dichloromethane (R_f = 0.15) and recrystallized from chloroform-acetonitrile to give **5a** (R = C_2H_5) as a purple solid (18 mg, 17%). Mp >300 °C. ^{1}H NMR (400 MHz) δ 7.66 (d, J = 4.0 Hz, 2H), 7.59 (d, J = 4.0 Hz, 2H), 2.95 (m, 4H), 1.23 (m, 6H). MS (EI) m/z = 354 (M^+). IR (KBr) ν = 2298 (CN), 1654 cm^{-1} (C═O). MS (HRMS) m/z = 354.0497 (M^+, calcd for $C_{18}H_{14}N_2O_2S_2$, 354.0497). Solubility: <0.5 g L^{-1}. From ^{1}H NMR spectra, **5a** exists as a mixture of *E*- and *Z*-isomers at the bithienoquinoidal part as in the case for **4a** (see Figure S1 in the Supporting Information).[10]

Alternatively, the same compound was obtained as follows: To a mixture of **13** (R = C_2H_5, 100 mg, 0.33 mmol) and NaH (31 mg, 60% oily, 0.72 mmol) in THF (6 mL) was added 1-cyano-1*H*-1,2,3-bezotriazole[18] (123 mg, 0.72 mmol) at −30 °C. After the mixture was stirred overnight at the same temperature, a similar workup and purification procedure described above gave the desired compound (43 mg, 37%).

(Z,Z)-5,5′-Bis(α-cyano-α-heptanoylmethylene)-5,5′-dihydro-Δ$^{2,2'}$-bithiophene (***5a**, R = n-C$_6$H$_{13}$*). Purple solid from hexane, 9% isolated yield (the LDA−*o*-chlorobenzylthiocyanate method) or 32% isolated yield (the NaH−1-cyano-1*H*-1,2,3-bezotriazole method). Mp 194−195 °C (melt with decomposition). ^{1}H NMR (270 MHz) δ 7.47−7.67 (m, 4H), 2.90 (m, 4H), 1.33−1.76 (m, 16H), 0.89 (m, 6H), 0.88 (t, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz) δ 14.0, 22.5, 24.2, 28.8, 31.5, 41.1, 99.5, 100.0, 116.7, 116.8, 135.5, 136.4, 146.5, 147.5, 165.2, 165.3. MS (EI) m/z = 466 (M^+). IR (KBr) ν = 2298 (CN), 1654 cm^{-1} (C═O). MS (HRMS) m/z = 489.16411 ([M + Na]$^+$, calcd for $C_{26}H_{30}N_2NaO_2S_2$, 489.16409). Solubility: 5.0 g L^{-1}.

Bromination of 11 (General Procedure). *1-(5-Bromo-2-thienyl)-butan-2-one Ethylene Acetal* (***15**, R = C$_2$H$_5$*). To a solution of **11** (*R* = C_2H_5, 3.0 g, 15.2 mmol) in DMF (150 mL) was portionwise added NBS (2.72 g, 15.2 mmol). After being stirred overnight, an aqueous $NaHCO_3$ solution (saturated, 100 mL) was added to the mixture, and the resulting mixture was then extracted with hexane (50 mL × 3). The combined extracts were washed with water (50 mL) and brine (50 mL) and dried over magnesium sulfate (anhydrous). Concentration of the extract in vacuo gave practically pure **15** (R = C_2H_5) as yellow oil (3.68 g, 88%). ^{1}H NMR (270 MHz) δ 6.86 (d, J = 3.7 Hz, 1H), 6.62 (dd, J = 3.7 Hz, 1H), 3.84−3.94 (m, 4H), 3.04 (s, 2H), 1.65 (q, J = 7.5, 2H), 0.93 (t, J = 7.5 Hz, 3H), ^{13}C NMR (67.8 MHz) δ 8.0, 30.3, 38.4, 65.5, 110.72, 110.83, 127.3, 129.1, 140.4, MS (FAB) m/z = 275 ([M−H]$^+$), Anal. Calcd for $C_{10}H_{13}O_2SBr$: C, 43.33; H, 4.73%, Found: C, 43.43; H, 4.74%.

1-(5-Bromo-2-thienyl)octan-2-one Ethylene Acetal (***15**, R = n-C$_6$H$_{13}$*). Yellow oil, 86% isolated yield. ^{1}H NMR (400 MHz) δ 6.87 (d, J = 3.8 Hz, 1H), 6.62 (d, J = 3.8 Hz, 1H), 3.82−3.95 (m, 4H), 3.04 (s, 2H), 1.26−1.63 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 14.4, 22.9, 23.9, 29.8, 32.1, 37.8, 39.0, 65.7, 110.8, 111.1, 127.6, 129.4, 140.7. MS (FAB) m/z = 331 ([M−H]$^+$). Anal. Calcd for $C_{14}H_{21}BrO_2S$: C, 50.45; H, 6.35%. Found: C, 50.55; H, 6.39%.

1-(5-Bromo-2-thienyl)tetradecan-2-one Ethylene Acetal (***15**, R = n-C$_{12}$H$_{25}$*). Colorless oil, 80% isolated yield. ^{1}H NMR (400 MHz) δ 6.86 (d, J = 3.7 Hz, 1H), 6.61 (d, J = 3.7 Hz, 1H), 3.82−3.95 (m, 4H), 3.04 (s, 2H), 1.26−1.58 (m, 22H), 0.88 (t, J = 6.5 Hz, 3H). ^{13}C NMR (67.8 MHz) δ 14.5, 23.0, 24.0, 29.7, 29.8, 30.0, 30.1, 32.3, 37.8, 39.0, 110.7, 111.1, 127.6, 129.3, 140.7. MS (FAB) m/z = 415 ([M−H]$^+$). Anal. Calcd for $C_{20}H_{33}BrO_2S$: C, 57.54; H, 7.97%. Found: C, 57.24; H, 8.10%.

Stille Coupling Reaction of 15 with 2,5-Bis(trimethylstannyl)-thiophene (General Procedure)[19]**.** *5,5″-Bis(2-oxobutyl)-2,2′;5′,2″-terthiophene Ethylene Acetal* (***16**, R = C$_2$H$_5$*). To a degassed solution of **15** (*R* = C_2H_5, 1.35 g, 4.88 mmol) and 2,5-bis(trimethylstannyl)thiophene[19] (1.0 g, 2.44 mmol) in DMF (25 mL) was added $Pd(PPh_3)_4$, and the mixture was heated at 80 °C overnight. The resulting mixture was diluted with water (100 mL) and extracted with dichloromethane (50 mL × 3). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over magnesium sulfate (anhydrous), and concentrated in vacuo. The residue was purified by column chromatography on alumina eluted with hexane-dichloromethane (v/v = 2:1, R_f = 0.3) and recrystallized from hexane to give **16** (R = C_2H_5) as a yellow solid (734 mg, 63%). Mp 54−55 °C. ^{1}H NMR (270 MHz) δ 7.00 (s, 2H), 6.98 (d, J = 3.5 Hz, 2H), 6.77 (d, J = 3.5 Hz, 2H), 3.88−3.95 (m, 8H), 3.08 (s, 4H), 1.70 (q, J = 7.5 Hz, 4H), 0.95 (t, J = 7.5 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 8.1, 30.4, 38.2, 65.6, 111.0, 123.0, 123.7, 127.9, 136.2, 136.7, 138.0. MS (EI) m/z = 476 (M^+). Anal. Calcd for $C_{24}H_{28}O_4S_3$: C, 60.47; H, 5.92%. Found: C, 60.38; H, 5.66%.

5,5″-Bis(2-oxooctyl)-2,2′;5′,2″-terthiophene Ethylene Acetal (***16**, R = n-C$_6$H$_{13}$*). Yellow solid, 58% isolated yield. Mp 74−75 °C. ^{1}H NMR (400 MHz) δ 7.00 (s, 2H), 6.98 (d, J = 3.5 Hz, 2H), 6.76 (d, J = 3.5 Hz, 2H), 3.86−3.97 (m, 4H), 3.08 (s, 4H), 1.65 (q, J = 7.5 Hz, 4H), 1.03−1.50 (m, 20H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 14.2, 22.7, 23.7, 29.6, 31.9, 37.6, 38.5, 65.6, 110.8, 123.0, 123.7, 127.9, 136.2, 136.7, 138.0. MS (EI) m/z = 588 (M^+). Anal. Calcd for $C_{32}H_{44}O_4S_3$: C, 65.27; H, 7.53%. Found: C, 65.37; H, 7.61%.

5,5″-Bis(2-oxotetradecyl)-2,2′;5′,2″-terthiophene Ethylene Acetal (***16**, R = n-C$_{12}$H$_{25}$*). Yellow solid, 62% isolated yield. Mp 66−67 °C. ^{1}H NMR (400 MHz) δ 7.00 (s, 2H), 6.98 (d, J = 3.5 Hz, 2H), 6.76 (d, J = 3.5 Hz, 2H), 3.86−3.97 (m, 4H), 3.08 (s, 4H), 1.23−1.65 (m, 44H), 0.88 (t, J = 6.3 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 14.3, 22.8, 23.8, 29.5, 29.6, 29.7, 29.8, 29.9, 32.1, 37.6, 38.5, 65.5, 110.8, 122.9, 123.7, 127.9, 136.2, 136.7, 138.0. MS (EI) m/z = 756 (M^+); Anal. Calcd for $C_{44}H_{68}O_4S_3$: C, 69.79; H, 9.05%. Found: C, 69.61; H, 8.92%.

Deprotection of the Acetal Moiety (General Procedure). *5,5″-Bis(2-oxobutyl)-2,2′;5′,2″-terthiophene* (***17**, R = C$_2$H$_5$*). A solution of **16** (*R* = C_2H_5, 20 mg, 0.042 mmol) in THF (3 mL) and hydrochloric acid (2 M, 1 mL) was refluxed overnight. The resulting mixture was extracted with dichloromethane (20 mL × 3). The combined extracts were washed with water (10 mL) and brine

(10 mL), dried over magnesium sulfate (anhydrous), and concentrated in vacuo to give **17** (R = C_2H_5) as a pale yellow solid (18 mg, quantitative). Mp 107−109 °C; ^{1}H NMR (270 MHz) δ 7.03 (s, 2H), 7.02 (d, J = 3.7 Hz, 2H), 6.78 (d, J = 3.7 Hz, 2H), 3.87 (s, 2H), 2.56 (q, J = 7.3 Hz, 4H), 1.09 (t, J = 7.3 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 7.8, 35.2, 43.5, 123.5, 124.1, 127.6, 134.8, 136.0, 136.8, 207.2. MS (EI) m/z = 388 (M^+). IR (KBr) ν = 1712 cm^{-1} (C═O). Anal. Calcd for $C_{20}H_{20}O_2S_3$: C, 61.82; H, 5.19%. Found: C, 61.19; H, 5.15%.

5,5″-Bis(*2-oxooctyl*)*-2,2′;5′,2″-terthiophene* (***17***, *R = n-C_6H_{13}*). Orange solid, quantitative yield. Mp 125−127 °C. ^{1}H NMR (270 MHz) δ 7.01 (s, 2H), 7.01 (d, J = 3.6 Hz, 2H), 6.78 (d, J = 3.6 Hz, 2H), 3.85 (s, 2H), 1.58 (q, J = 7.2 Hz, 4H), 1.25−1.30 (m, 16H), 0.87 (t, J = 6.5 Hz, 6H). ^{13}C NMR (67.8 MHz) δ 14.3, 22.8, 24.0, 29.1, 31.9, 42.2, 42.3, 44.1, 123.8, 124.4, 127.9, 135.0, 136.3, 137.2, 207.1. MS (EI) m/z = 500 (M^+). IR (KBr) ν = 1710 cm^{-1} (C═O); Anal. Calcd for $C_{28}H_{36}O_2S_3$: C, 67.15; H, 7.25%. Found: C, 67.41; H, 7.16%.

5,5″-Bis(*2-oxotetradecyl*)*-2,2′;5′,2″-terthiophene* (***17***, *R = n-$C_{12}H_{25}$*). Orange solid, 83% yield. Mp 117−120 °C. ^{1}H NMR (270 MHz) δ 7.01 (s, 2H), 7.01 (d, J = 3.6 Hz, 2H), 6.78 (d, J = 3.6 Hz, 2H), 3.86 (s, 2H), 2.52 (q, J = 7.3 Hz, 4H), 1.24−1.30 (m, 40H), 0.88 (t, J = 6.5 Hz, 6H). ^{13}C NMR (100 MHz) δ 14.3, 22.8, 23.7, 29.2, 29.5, 29.6, 29.7, 29.8, 32.1, 42.1, 43.9, 123.5, 124.2, 127.6, 134.8, 136.1, 136.9. MS (EI) m/z = 668 (M^+). IR (KBr) ν = 1716 cm^{-1} (C═O). Anal. Calcd for $C_{40}H_{60}O_2S_3$: C, 71.80; H, 9.04%. Found: C, 71.84; H, 9.15%.

(Z,Z)-5,5″-Bis(α-cyano-α-propionylmethylene)-5,5′-dihydro-$\Delta^{2,2':5',2''}$-terthiophene (5b, R = C_2H_5). To a solution of **17** (R = C_2H_5, 100 mg, 0.26 mmol) in THF (5 mL) was added NaH (25 mg, 60% oily, 0.57 mmol) at 0 °C. After this solution was stirred for 30 min at the same temperature, a solution of 1-cyano-1*H*-1,2,3-benzotriazole (82 mg, 0.57 mmol) in THF (3 mL) was slowly added to the mixture, and the resulting mixture was stirred overnight at 0 °C. To the mixture was added hydrochloric acid (1 M, 10 mL), and the resulting mixture was extracted with dichloromethane (30 mL × 3). The combined extracts were washed with water (10 mL) and brine (10 mL), dried over magnesium sulfate (anhydrous), and concentrated in vacuo. The residue was suspended in a mixed solvent of acetonitrile (5 mL) and water (5 mL), and then NIS (116 mg, 0.52 mol) was added to the suspension at 0 °C. After being stirred for 30 min at the same temperature, the precipitate was collected by filtration. The solid collected was purified by column chromatography on silica gel eluted with dichloromethane (R_f = 0.1) to give **5b** (R = C_2H_5) as a purple solid (76 mg, 61%). Mp >300 °C. MS (MALDI-TOF) m/z = 436 (M^-). IR (KBr) ν = 2294 (CN), 1653 cm^{-1} (C═O). Anal. Calcd for $C_{26}H_{24}N_2O_4S_3$: C, 60.52; H, 3.69; N, 6.42%. Found: C, 60.27; H, 3.69; N, 6.11%. Solubility: ~1 × 10^{-3} g L^{-1}. From ^{1}H NMR spectra, **5b** exists as a mixture of *E,E*-, *Z,Z*-, and *E,Z*-isomers at the terthienoquinoidal part as in the case for **4b** (see Figure S1 in the Supporting Information).[10]

(Z,Z)-5,5″-Bis(*α-cyano-α-heptanoylmethylene*)*-5,5′-dihydro-$\Delta^{2,2':5',2''}$-terthiophene* (***5b***, *R = n-C_6H_{13}*). The title compound was obtained from **17** (R = *n*-C_6H_{13}) as a purple solid (dichloromethane) in 56% isolated yield. Mp 180−182 °C (melt with decomposition). ^{1}H NMR (400 MHz) δ 7.38−7.64 (m, 6H), 2.88 (m, 4H), 1.33−1.72 (m, 16H), 0.88 (m, 6H). MS (MALDI-TOF) m/z = 548 (M^-). IR (KBr) ν = 2291 (CN), 1647 cm^{-1} (C═O). Anal. Calcd for $C_{30}H_{32}N_2O_2S_3$: C, 65.66; H, 5.88; N, 5.10%. Found: C, 65.59; H, 5.88; N, 4.96%. Solubility: 4.1 g L^{-1}.

(Z,Z)-5,5″-Bis(*α-cyano-α-tridecanoylmethylene*)*-5,5′-dihydro-$\Delta^{2,2':5',2''}$-terthiophene* (***5b***, *R = n-$C_{12}H_{25}$*). The title compound was obtained from **17** (R = *n*-$C_{12}H_{25}$) as a purple solid (dichloromethane) in 62% isolated yield. Mp 185−186 °C (melt with decomposition). ^{1}H NMR (270 MHz) δ 7.38−7.64 (m, 6H), 2.88 (t, J = 8.6 Hz, 4H), 1.33−1.72 (m, 36H), 0.88 (t, J = 6.0 Hz, 6H). MS (MALDI-TOF) m/z = 716 (M^-). IR (KBr) ν = 2291 (CN), 1647 cm^{-1} (C═O). Anal. Calcd for $C_{42}H_{56}N_2O_2S_3$: C, 70.35; H, 7.87; N, 3.91%. Found: C, 70.62; H, 7.95; N, 3.97%. Solubility: 0.6 g L^{-1}.

Single-Crystal X-ray Analysis. Single crystals of **14** suitable for X-ray structural analysis were obtained by careful recrystallization from chloroform. The X-ray crystal structure analysis of **14** was made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer (Mo Kα radiation, λ = 0.71069 Å, graphite monochromator, T = 150 K, $2\theta_{max}$ = 54.9°). The structure was solved by the direct methods.[22] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the calculations but not refined. All calculations were performed using the crystallographic software package TeXsan 1.2.[22] Crystallographic data: $C_{24}H_{20}ClNO_2S_2$ (453.06), violet block, 0.70 × 0.25 × 0.10 mm^3, triclinic, space group, $P\bar{1}$ (#2), a = 9.198(1) Å, b = 9.549(1) Å, c = 13.271(2) Å, α = 75.930(3)°, β = 75.466(3)°, γ = 82.159(3)°, V = 1091.0(2) Å^3, Z = 2, R = 0.0912 for 2502 observed reflections ($I > 2\sigma(I)$) and 271 variable parameters, wR^2 = 0.290 for all data.

Fabrication and Evaluation of FET Devices. Si/SiO_2 substrates were treated with octadecyltrichlorosilane (ODTS) by immersing the silicon wafers to ODTS solution in dry toluene at room temperature under nitrogen for 12 h.[23] OFETs were fabricated in a "top-contact" configuration on a heavily doped n^+-Si (100) wafer with a 200 nm thermally grown SiO_2 (C_i = 17.3 nF cm^{-2}). Thin film of **5a** or **5b** as an active layer was spin-coated on the Si/SiO_2 substrate. On top of the organic thin film, gold films (80 nm) as drain and source electrodes were deposited through a shadow mask. For a typical device, the drain-source channel length (L) and width (W) are 50 μm and 1.5 mm, respectively. Characteristics of the OFET devices were measured at room temperature under ambient conditions with a Keithley 4200 semiconducting parameter analyzer. Field-effect mobility (μ_{FET}) was calculated in the saturation regime (V_d = 60 V) of the I_d using the following equation,

$$I_d = (WC_i/2L)\mu_{FET}(V_g - V_{th})^2$$

where C_i is the capacitance of the SiO_2 insulator, and V_g and V_{th} are the gate and threshold voltages, respectively. Current on/off ratio (I_{on}/I_{off}) was determined from the I_d at V_g = 0 V (I_{off}) and V_g = 60 V (I_{on}). The μ_{FET} data reported are typical values from more than five different devices.

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Supporting Information Available: Instrumentation for the characterization of compounds and physicochemical evaluation, crystallographic information file (CIF) for **14**, complete entry for ref 12, NMR spectra of compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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