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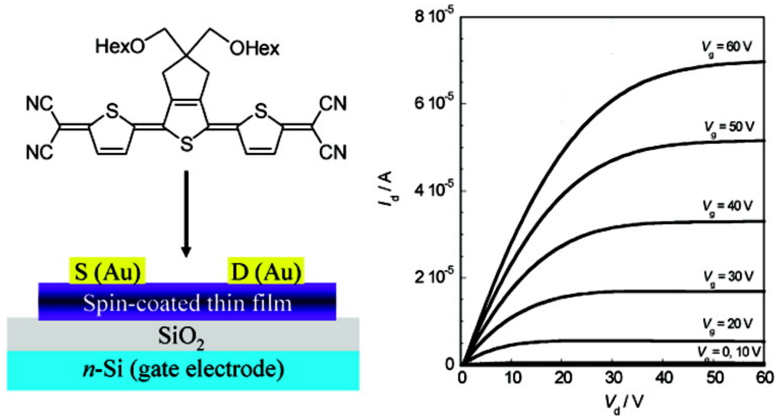

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Solution-Processible n-Channel Organic Field-Effect Transistors Based on Dicyanomethylene-Substituted Terthienoquinoid Derivative

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Organic field-effect transistors (OFETs) have been attracting much interest because of their potential use as low-cost alternatives to the present silicon-based transistors. Compared to the high performance of p-channel OFETs, which is comparable to those of amorphous silicon transistors, the device performance of n-channel OFETs is generally low.[1] With recent rapid progress in the development of novel n-channel organic semiconductors, however, high-performance n-channel OFETs showing electron mobilities as high as hole mobilities in p-channel OFETs have become available. Such high-performance n-channel semiconductors are naphthalene or perylene tetracarboximides[2] and extended aromatic compounds modified with strong electron-withdrawing groups.[3] However, devices based on these materials are generally fabricated by the vacuum process, and solution-processible n-channel materials that allow for cost-effective device fabrication are still limited. Furthermore, almost all of the n-channel OFETs so far reported can operate only in vacuum or under inert atmosphere and show greatly reduced performance in air, limiting their practical application. Therefore, the development of air-stable, solution-processible n-channel OFETs is one of the key issues for the further development of OFETs.[4]

Dicyanomethylene-substituted quinoidal oligothiophenes (**1**) are one of the representative classes of n-channel organic semiconductors, and vacuum-deposited thin film of the terthiophene derivative with two butyl substituents showed superior n-channel OFET characteristics (Figure 1).[5] However, the solubility of these compounds is rapidly reduced when the oligothiophene chain is extended: for example, the solubility of an unsubstituted terthiophene analogue (**1**, $n = 3$, R = H) in chloroform at room temperature is $\sim 6 \times 10^{-4}$ mol/L. On the other hand, we recently reported a series of highly soluble analogues (**2**) up to the hexamer, employing a soluble thiophene unit modified with a bis(butoxymethyl)cyclopentane ring.[6] However, these compounds are not suitable as organic semiconductors because of the steric bulkiness of the solubilizing units, which reduces intermolecular interactions in the solid state. To retain such properties as high solubility and intermolecular interaction in the solid state, we designed a new hybrid-type terthiophene derivative, 5,5″-bis(dicyanomethylene)-5,5″-dihydro-$\Delta^{2,1';3',2''}$-dithienyl-5′,5′-bis(hexyloxymethyl)cyclopenta[*c*]thiophene (**3**), in which only the central thiophene ring possesses the solubilizing bis(hexyloxymethyl)cyclopentane unit. We report here the synthesis and properties of **3** together with the FET characteristics of its solution-processed n-channel OFETs.

Hybrid compound **3** was synthesized from a corresponding dibromoterthiophene precursor (**5**) using the palladium-catalyzed Takahashi reaction[7] followed by air oxidation and was isolated as a stable deep green solid (Scheme 1; see Supporting Information for details).[8] The solubility of **3** was quite high as expected (2×10^{-2} mol/L in chloroform at rt).

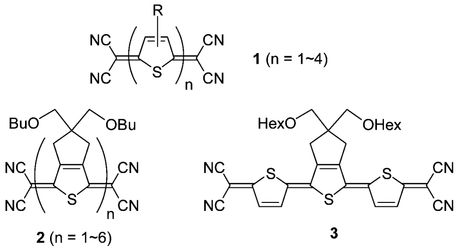
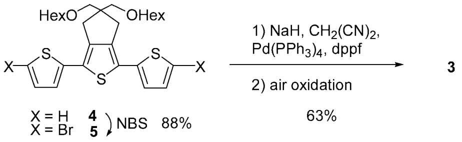


Figure 1. Dicyanomethylene-substituted thienoquinoid oligomers.

Scheme 1. Synthesis of **3**



Owing to the high solubility, thin-film fabrication of **3** was easily achieved by the spin-coating method using 0.4 wt % chloroform solution (2000 rpm, 30 s) on quartz glass or a Si/SiO_2 substrate. The UV−vis spectrum of the spin-coated film of **3** on the glass substrate showed a structureless broad peak centered at around 650 nm (Figure 2), which is almost the same as that observed in chloroform solution (Figure S3), implying no strong intermolecular interaction in the film state. Interestingly, the spectra of the film on the substrate drastically changed on annealing: at 100 °C, a shoulder appeared at around 1000 nm, and at 150 °C, the intensity of the shoulder was fairly enhanced. This indicates that the change of molecular packing is thermally induced, and a highly interactive molecular arrangement is realized in the annealed film of **3**.

In agreement with the spectral changes, thin-film X-ray diffraction (XRD) patterns also changed upon annealing (Figure 3). No peak was observed in the XRD pattern of the as-spun film, indicating that the film was amorphous. On the other hand, the XRD patterns of the annealed films showed a series of peaks indicating formation of crystalline domains in the film. At the annealing temperature of 150 °C, the intensity of the first peak (001) was fairly enhanced; at the same time, the emergence of peaks assignable to higher order up to the fifth order (005) was noted. From these results, we concluded that thermal annealing induced the transformation into crystalline film with intermolecular interactions in the solid state, although the as-spun film was amorphous and showed no intermolecular interaction.

Top contact OFET devices were fabricated on the spin-coated thin films on octyltrichlorosilane (OTS)-treated Si/SiO_2 substrates, and their characteristics in air were evaluated. In accordance with the UV−vis spectra and the XRD patterns discussed above, the FET characteristics of the devices strongly depended on the

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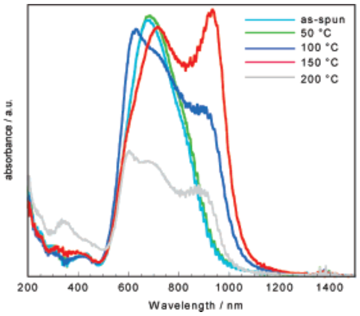

Figure 2. UV−vis spectra of spin-coated thin film of **3**: annealing at 150 °C produced a characteristic shoulder at ca. 1000 nm.

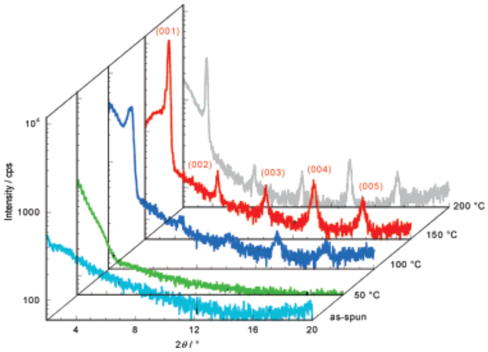

Figure 3. XRD patterns of spin-coated thin film of **3**: annealing led to the formation of crystalline film.

Table 1. Dependence of FET Characteristics on Annealing Temperature of **3** Thin Film

T_{anneal}/°C	μ_{FET}/cm^2 V^{-1} s^{-1}	I_{on}/I_{off}^{a}	V_{th}/V
−	1.4×10^{-4}	10^2 (10^3)	4.5
50	1.7×10^{-4}	10^2 (10^3)	−3.3
100	2.5×10^{-2}	10^3 (10^4)	−5.0
150	0.16	10^3 (10^4)	−1.2
200	5.2×10^{-3}	10^3 (10^4)	−2.5

[a] 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 values in parentheses are the maximum I_{on}/I_{off}, where I_{off} was the minimum in the transfer plots.

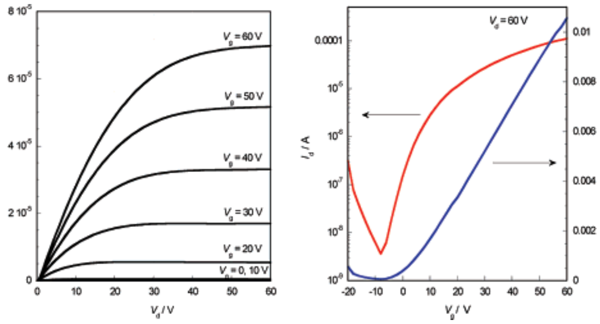

Figure 4. FET characteristics of **3**-based OFET on OTS-treated substrate (annealed at 150 °C): output characteristics (left) and transfer characteristics at $V_d = 60$ V (right).

annealing temperature of the films (Table 1). OFETs fabricated on the as-spun film showed poor FET characteristics with electron mobility (μ_{FET}) of 1.4×10^{-4} cm^2 V^{-1} s^{-1} ($I_{on}/I_{off} \sim 10^3$). In contrast, annealing at higher temperature improved FET characteristics: at 100 °C, μ_{FET} was 2.5×10^{-2} cm^2 V^{-1} s^{-1} with $I_{on}/I_{off} \sim 10^3$, and at 150 °C, μ_{FET} was increased to 0.16 cm^2 V^{-1} s^{-1} with $I_{on}/I_{off} \sim 10^3$ (Figure 4). The present n-channel FET performance is one of the best among solution-processed n-channel OFET devices so far reported. Considering the fact that the fabrication of thin films as well as the evaluation of FET characteristics was carried out under ambient conditions, **3** can be classified as a characteristic material that gives air-stable, solution-processible n-channel OFETs.

In conclusion, we have developed a new hybrid-type dicyanomethylene-substituted terthienoquinoid compound (**3**) for use as a highly soluble n-channel organic semiconductor. The as-spun film of **3** was amorphous, and the molecules in the film were not interactive. Thermal annealing induced the formation of a highly crystalline film that shows intermolecular interaction in the solid state. This film is a superior n-type semiconducting channel, showing electron mobilities of up to 0.16 cm^2 V^{-1} s^{-1} with $I_{on}/I_{off} \sim 10^3$. Although the present performance and air stability of **3**-based OFETs are remarkable, the reasons for these characteristics are not known. Detailed studies of the structure−property relationship are underway.

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Supporting Information Available: Experimental details of the synthesis and characterization of **3**, device fabrication, UV−vis spectra, and XRDs of thin films. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Compound **3** was fully characterized by the spectroscopic and combustion elemental analyses. Reduction potential ($E_{1/2}^{red}$) of **3** was −0.14 V (vs Ag/AgCl). From the electrochemical data, the LUMO energy level of **3** was estimated to be 4.2 eV below the vacuum level.

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