Alkylated 2,6-Bis(dicyanomethylene)-2,6-dihydrobenzo[1,2-*b*:4,5-*b*′]dithiophenes: New Soluble n-Channel Organic Semiconductors for Air-stable OFETs

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New solution-prosessable n-channel organic semiconductors were developed based on a 2,6-bis(dicyanomethylene)-2,6-dihydrobenzo[1,2-*b*:4,5-*b*′]dithiophene core. The OFETs showed n-channel transistor characteristics under ambient conditions with electron field-effect mobility up to $6.3 \times 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$.

Recent intensive research efforts in material development and device optimization have improved the performance of solution-processed organic field-effect transistors (OFETs).[1] In particular, p-channel OFETs have attained both high field-effect mobility comparable with or superior to amorphous silicon-based FETs and stability under ambient conditions.[1,2] In contrast, solution-processed n-channel OFETs suffered from both poor performances and lack of air-stability. Very recently, however, Facchetti and co-workers have reported several air-stable solution-processed n-channel OFETs with electron field-effect mobility ($\mu^{\mathrm{e}}_{\mathrm{FET}}$) higher than $0.1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$.[3]

We also recently reported a new n-channel organic semiconductor, dicyanomethylene-substituted terthienoquinoid derivative **1**, which afforded solution-processed n-channel OFETs with $\mu^{\mathrm{e}}_{\mathrm{FET}}$ of $0.16\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ under ambient conditions.[4] This result indicates that π-extended thienoquinoidal compounds modified with dicyanomethylene moieties are promising for air-stable n-channel organic semiconductors and even for soluble ones, provided that appropriate solubilizing modifications are made. From this viewpoint, 2,6-bis(dicyanomethylene)-2,6-dihydrobenzo-[1,2-*b*:4,5-*b*′]dithiophene (CNBDT, Figure 1)[5,6] is an interesting core structure, because of its linearly extended rigid benzodithienoquinoidal structure and low-lying LUMO level comparable with that of TCNQ.[7,8] In this communication, we report the synthesis and characterization of 4,8-dialkyl-CNBDT (C_n-CNBDT, n = 8, 10, and 12, Figure 1) as a soluble n-channel organic semiconductor, together with evaluation of the parent CNBDT as a vapor processable n-channel organic semiconductor.

Because of its poor solubility and difficulty in purification, the reported yield of CNBDT was very low (10% isolated yield).[7] In contrast, the synthesis and purification of C_n-CNBDTs proceeded straightforward: the conventional Takahashi reaction[9] using the corresponding 2,6-dibromo-4,8-dialkyl-BDTs **2**[6] with sodium dicyanomethanide in the presence of catalytic tetrakis(triphenylphosphine)palladium in refluxing tetrahydrofuran followed by spontaneous air oxidation gave C_n-CNBDTs in reasonable yields (ca. 60%).[10] Thanks to their improved solubility (up to $1.31\,\mathrm{g\,L^{-1}}$ in chloroform at rt for C_{12}-CNBDT), C_n-CNBDTs were fully characterized by spectroscopy and combustion elemental analyses.[9] C_n-CNBDTs showed a quasi-reversible, two-stage reduction wave (Figure S1),[10] and estimated LUMO energy level from the onset of the first reduction is ca. 4.6 eV below the vacuum level, which agrees well with their LUMO level theoretically calculated at the DFT B3LYP-6-31G(d) level.[10]

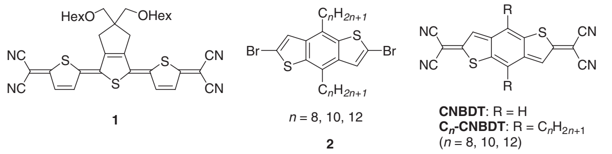

Figure 1. Molecular structures of **1**, **2**, and CNBDT derivatives.

Thin film deposition of the parent CNBDT was done by vapor deposition, whereas thin films of C_n-CNBDTs were readily obtained by spin-coating with 0.2 wt% chloroform solution at 4000 rpm for 30 s on $\mathrm{Si/SiO_2}$ substrates. On top of the thin films, vapor deposition of gold source and drain electrodes completed fabrication of OFETs with a top-contact configuration. Figure 2a shows the output characteristics of the CNBDT-based device evaluated under ambient conditions, where enhancement of the drain current (I_{d}) by application of the gate voltage (V_{g}) was observed. However, I_{d} at $V_{\mathrm{g}} = 0\,\mathrm{V}$ was fairly large. Although the reasons for such large off-current are not clear, we speculate that the face-on molecular orientation on the substrate estimated from the XRD pattern suggesting the inter-layer spacing of ca. 3.3 Å (Figure 2b), is related to such poor FET characteristics.

In sharp contrast, solution-processed OFETs using C_n-CNBDTs as an active semiconducting material showed typical n-channel FET responses (Figure 3): not only clear off-state but also enhancement of I_{d} by application of V_{g} as well as the saturation of I_{d} in the high drain voltage (V_{d}) regime were observed. The $\mu^{\mathrm{e}}_{\mathrm{FET}}$ extracted from the saturation regime are in the order of $10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ with $I_{\mathrm{on}}/I_{\mathrm{off}}$ of 10^4, and no large difference between the derivatives with different alkyl chain lengths was observed (Table 1 and Figures S3 and S4). These FET performances are not the best among recently reported solution-processed n-channel OFETs based on the state of the art air-stable n-channel semiconductors. To understand the relatively low mobility, we investigated the thin films by AFM and XRD measurements.

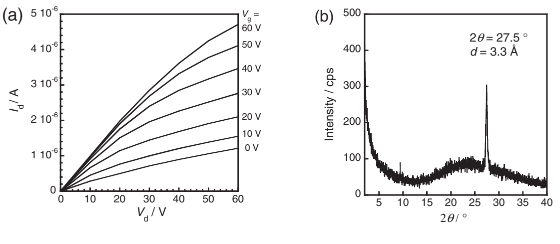

Figure 2. (a) Output characteristics of CNBDT-based OFET. Note that no clear off state was observed. (b) XRD pattern of evaporated thin film of CNBDT.

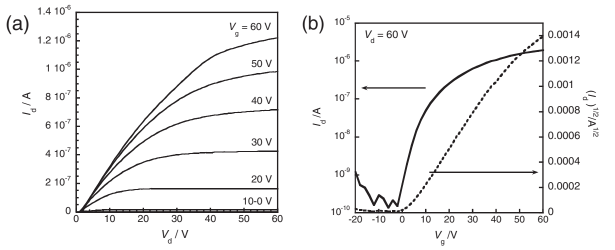

Figure 3. FET characteristics of C_8-CNBDT evaluated under ambient conditions: (a) output and (b) transfer characteristics.

Table 1. FET characteristics[a] of C_n-CNBDTs using spin-coated thin films and interlayer spacings estimated from XRD measurement

n	μ^{e}_{FET} /cm^2 V^{-1} s^{-1}	I_{on}/I_{off}	V_{th}/V	d-spacing[b] /Å
8	3.7×10^{-3}	10^4	+2.0	14.1
10	1.0×10^{-3}	5×10^3	+2.6	16.0
12	1.1×10^{-3}	5×10^3	+8.0	17.6

[a] "top-contact" configuration with 50 µm and 1.5 mm of channel length and width, respectively, was used. [b] Estimated from the first diffraction peak in XRDs shown in Figure 4 and Figure S5.[10]

Figure 4a shows an AFM image of the spin-coated thin film of C_8-CNBDT as a representative, where continuous thin film surface without clear grain boundaries is observed. In the XRD pattern (Figure 4b), a broad peak at around $2\theta = 6.2°$ was observed, which corresponds to interlayer spacing of 14.1 Å. Similar XRD patterns were obtained for other derivatives with longer d-spacings depending on the alkyl chain lengths (Table 1), implying that the molecular short-axis direction parallel to the two alkyl chains tends to orient upright to the substrate with relatively large inclination of the molecules from the substrate normal. However, the peaks in the XRDs were very weak, indicative of the poor crystalline order, which is thought to be a major cause for the low mobility of C_n-CNBDT-based OFETs.

In order to improve the crystallinity, we examined thermal annealing of the thin films. The annealed films afforded enhanced peaks in the XRDs, in particular at 150 °C, not only the first peak with high intensity but also the second and third peaks were observed (Figure 5a). With the thin film annealed at 50 °C, the FET performances were slightly improved with μ^{e}_{FET} of 6.3×10^{-3} cm^2 V^{-1} s^{-1} for C_8-CNBDT. In contrast, annealing at higher temperatures deteriorated the FET responses, which was apparently related to the morphological changes of the thin film, since the films became clouded on the surface by annealing at 100 °C or higher temperature. In the AFM image of the annealed thin film at 150 °C (Figure 5b), large crystal grains sub-µm in size were observed. The crystal grains do not connect to each other, indicating that continuous active channels for the transistor are destroyed by thermal aggregation concomitant with crystallization.

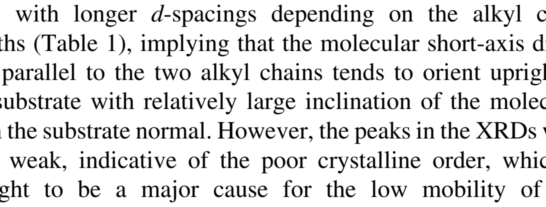

Figure 4. AFM image (a) and XRD pattern (b) of spin-coated thin film of C_8-CNBDT.

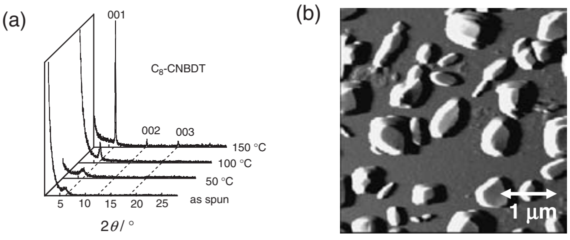

Figure 5. XRD patterns of C_8-CNBDT thin films depending on the annealing temperature (a) and AFM image of C_8-CNBDT thin film annealed at 150 °C.

In summary, we have synthesized and evaluated C_n-CNBDTs as soluble n-channel organic semiconductors. Different from the parent CNBDT, C_n-CNBDTs are soluble n-channel semiconductors that afford solution-processed OFETs with μ^{e}_{FET} of the order of 10^{-3} cm^2 V^{-1} s^{-1}. Although attempts to further enhance the FET characteristics by thermal annealing of the thin films failed, the present results show that the quinoidal heteroarene structure is promising as new air-stable n-channel organic semiconductors. Further trial to develop related soluble n-channel organic semiconductors is now underway.

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