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A Steady Operation of *n*-Type Organic Thin-Film Transistors with Cyano-Substituted Distyrylbenzene Derivative

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ABSTRACT

A novel *n*-type organic semiconductor, cyano-substituted distyrylbenzene derivative, 1,4-bis(2-(4-(trifluoromethyl)phenyl)acrylonitorile)benzene, was synthesized by Knoevenagel condensation with aldehyde and acetonitrile derivatives. Fabricated thin-film transistors (TFTs) exhibited high electron field-effect mobility of 10^{-2} - 10^{-1} $cm^2V^{-1}s^{-1}$, on/off current ratio of 6×10^5. Hysteresis-free *n*-type transport characteristics observed in this device promises a steady operation of organic logic circuit. Almost same TFT characteristic was observed even after 1 month storage in ambient condition. The findings indicate that the material has a good resistance to atmospheric oxidants.

Organic semiconductors have been attracted much attention to offer low-cost, flexible, and throwaway electronic applications, such as organic thin-film transistors (OTFT), organic solar cells, or radio frequency identification (RFID) tags. Since thin-film transistor (TFT) is the most fundamental electronic device in electronic circuit, improvements of OTFT performance is strongly desired. In particular, field-effect mobility is the most important factor or TFT, which identified the switching speed with cut-off frequency.[1-3] Besides this, the stability of channel conductance at on-state is also another important subject for steady operation of logic circuit. Development of new organic semiconductor is the most fundamental and important approach for providing intrinsic and potentially high-performance electronic devices. Although there are many reports of new candidate organic semiconductor having high carrier mobility, only few reports mentioned drifting characteristics of on-current in OTFTs at on-state.[4,5] Generally, the static operation in particular in the output characteristics tend to show a hysteresis characteristic in the drain current (I_D) with stepwise gate voltage (V_G) application.

n-type organic semiconductor with high performance transport characteristics is also strongly desired in organic electronics. Quite a small number of *n*-type semiconductor limits to research and develop the optimizing device configuration for organic logic circuit. Providing new candidate materials having *n*-type transport characteristics is therefore required in this field. *n*-type transport characteristics easily vanished by exposure to atmospheric air because of the electron trapping and/or redox reaction by adsorbing atmospheric oxidants. It was reported that two main factors, deep energy level of lowest unoccupied molecular orbital (LUMO) and dense molecular packing with large van-der Waals radius atom moieties, were possibly preventing degradation of *n*-type transports characteristics.[6-12] B. A. Jones and co-workers have succeeded in achieving the air stability to perylenediimide derivatives by cyano (CN) and fluorine substituent.[9,10] Providing *n*-type organic semiconductors having air stability is strongly required.

Cyano substituted poly(p-phenylenevinylene) (CN-PPV) is one well-known polymer to show *n*-type transport characteristics.[13, 14] Side-chain is generally substituted on PPV backbones in order to incorporate the solubility due to its strong π-π stacking characteristics. Yasuda and co-workers reported good *p*-type transport characteristics in PPV-type oligomer, which represents the intrinsic stacking functionality by the PPV structure as distyrylbenzene (DSB) derivatives. Even in terms of *n*-type transport simple DSB derivatives end-capped with an electron-withdrawing substituent of trifluoromethane (CF_3DSB) are not reported so far. [15] For more strong electron-withdrawing functionality, CN substituted vinyl should be a good candidate of elemental structure for *n*-type transport as a sort of CN-PPV oligomer.

We report excellent *n*-type transport characteristics in CN-PPV oligomer, namely, CF_3DSB derivative having CN substituent of 1,4-bis(2-(4-(trifluoromethyl)phenyl)acrylonitorile)benzene (CN-CF_3DSB). Fabricated OTFTs were found to show relative high electron mobility of 10^{-2} - 10^{-1} cm^2 V^{-1} s^{-1} with extremely stable, hysteresis-free *n*-type OTFT characteristics. Furthermore, the material has large advantages in terms of the simple procedure via one step synthesis by using general chemicals of aldehyde compound and acetonitrile derivative. This should be one good candidate material for *n*-type organic semiconductor.

CN-CF_3DSB was synthesized by Knoevenagel condensation of the 4-(trifluoromethyl)phenylacetonitrile (TCI) and terephthalaldehyde (TCI) in anhydrous ethanol with catalytic sodium ethoxide (Wako) along with Fig. 1, then purified by recrystallization in anhydrous chloroform solution. Top contact type OTFTs were constructed on highly doped *n*-type silicon wafers covered with 300-nm-thick silicon dioxide, providing a capacitance per unit area (C_{ins}) of 10 nF cm^{-2}. CN-CF_3DSB was deposited on bare silicon dioxide surface without controlling substrates temperature. 40-nm-thick gold source-drain electrodes were evaporated on top of the CN-CF_3DSB films though a shadow mask, defining with channel length (L) of 20 µm, and channel width (W) of 2 mm. TFT characteristics were measured with a computer-controlled source-measure unit (Keithley2612 sourcemeter) under vacuum (< 10^{-5} Torr). The device characteristics were analyzed with the standard formalism for field-effect transistors. On-current hysteresis as well as device stability was also investigated.

A highest occupied molecular orbital (HOMO) level of CN-CF_3DSB determined from photoelectron yield spectroscopy was 6.7 eV. An energy bandgap (E_g) was estimated to be 2.6 eV from an absorption spectra edge of CN-CF_3DSB thin film. LUMO energy level was calculated to be 4.1 eV by subtracting the E_g from the HOMO energy level. Relative deep LUMO level of CN-CF_3DSB compared with CF_3DSB (3.4 eV) was achieved by CN substituent.

Molecular orientation in the deposited thin film was investigated by the synchrotron-sourced X-ray diffraction (XRD) performed at BL46XU beamline of SPring-8 (JASRI) equipped with ATX-GSOR.[16] The out-of-plane profile presents a typical periodicity with *d*-spacing value of 2.21 nm. The observed *d*-spacing value was larger than the corresponding to long molecular length of CN-CF_3DSB (2.04 nm by B3LYP/6-31G* calculations), which denotes a well-ordered film structure with the molecular long axis standing perpendicularly on a substrate. Beside this, the corresponding periodicity was not well displayed in the in-plane profile. These findings indicate that the π-π stacking direction is almost parallel to the substrate surface, suitable for in-plane charge carrier transports.

Fig. 2 displays the (a) output and (b) transfer characteristics of CN-CF_3DSB OTFT, where I_D, V_D, and V_G represent source-drain current, source-drain voltage, and gate voltage, respectively. I_D increases with positive biasing of V_G, representing clear electron-transport characteristics. The electron mobility (μ) of 0.068 $cm^2\ V^{-1}\ s^{-1}$ and the threshold voltage (V_T) of 38 V were estimated at the saturation regime at V_D of 80 V. The on/off current ratio exceeds 6.0×10^5 and the turn-on voltage (V_{ON}) is 7 V. Several measurements with individual OTFTs provide a highest μ of 0.127 $cm^2\ V^{-1}\ s^{-1}$ at V_D of 100 V. CN-CF_3DSB OTFT shows fine *n*-type transfer characteristics with hysteresis-free traces between forwarding and backwarding sweep of V_G even fabricated on bare silicon dioxide. This feature reduces the silanization procedure, which is generally required for OTFT fabrication. Hysteresis in on-current was generally reported in OTFT with bare silicon dioxide as gate dielectric, possibly due to an existence of carrier trapping sites at the interface and/or sensitive transport characteristics of organic semiconductor. The hysteresis-free characteristics revealed above represent an excellent steady electron transport in this material. A simple resistor load inverter using CN-CF_3DSB OTFT was constructed with a load resistor (R_L) of 50 MΩ, and provides a hysteresis-free inverter characteristic with good signal gain of 6 at V_{DD} = -100 V as shown in Fig. 3. The input voltage difference at the half output voltage of full swing was designated as the amount of hysteresis (V_{hys}). There was no significant hysteresis behavior effect, V_{hys} of 0.1 V. This represents that the device promises to operate with quite reversal as well as stable switching operation desired for logic circuit.

In case to use CF_3DSB, OTFT with polymer dielectric layer have μ of 0.013 cm^2 V^{-1} s^{-1} and on/off current ratio of 10^4 in order without air exposure during device fabrication and characteristics measurements.[15] After exposure to air for 10 min, a degrade performance was reported even again measured under inert atmosphere. Both of the μ and the on/off current ratio drastically decreased 2 orders of magnitude, corresponding to 99% degradation as the percentage drop of mobility ($\Delta\mu$). Generally the degradation of *n*-type transport is very common for *n*-type organic semiconductors such as fullerene and perylenediimide derivatives due to absorbing atmospheric oxidants. [6, 7, 12] In the case to use CN-CF_3DSB, despite of several times exposure to atmospheric air, OTFTs persist with their relative high device performance as *n*-type. This indicates that the CN-CF_3DSB essentially possesses stable electron transport characteristics against the atmospheric oxidants.

To confirm the stability of CN-CF_3DSB OTFTs, the *n*-type transport characteristics were also investigated by comparing the transfer characteristics in the same device stored under an ambient and dark condition. Fig. 4 shows the comparison of transfer characteristics of a CN-CF_3DSB OTFT. Quite a small change in transfer characteristics was found even after 1 month storage. The device properties with exposure time were summarized in Table I. $\Delta\mu$ is 4.4% and V_{ON} shift (ΔV_{ON}) is 5 V after 1 month storage. In contrast, the transfer characteristic measured under atmospheric air shows as hysteresis and degradation, $\Delta\mu$ of 41.0% and ΔV_{ON} of 5 V as air exposing, $\Delta\mu$ of 76.2% and ΔV_{ON} of 31 V after 24 h air exposing. The degradation in CN-CF_3DSB OTFT is relative mild even operated under atmospheric air condition. Furthermore, after 24 h air exposing, the CN-CF_3DSB OTFT measured again under vacuum showed the revived characteristics with a hysteresis-free characteristic, $\Delta\mu$ of 14.1% and ΔV_{ON} of 14

V. A simple encapsulation possibly extends the operation lifetime with CN-CF_3DSB, which represents the ready for practical use.

Deep energy level of LUMO for preventing the redox reaction against atmospheric oxidants and strong molecular packing for preventing atmospheric oxidants from penetrating into a channel region are possibly main factors for realizing air stability of *n*-type organic semiconductor.[8-12] Relative deep LUMO level will assist the air stability as compared to that of CF_3DSB by CN substituent. CN-CF_3DSB also has a strong molecular interaction due to the presence of electron-withdrawing CN substituent with its in-plane structure.[14] Both of the strong interaction due to the CN substituent and the large van-der Waals radius of a fluorine atom in CF_3 may provide a kinetic barrier to an atmospheric oxidants penetration.[10] The absorbed oxidants on a surface region might be able to remove easily by only vacuum exhaust.

In summary, we have synthesized *n*-type organic semiconductor, CN-CF_3DSB, via one step procedure of Knoevenagel condensation with commercially available aldehyde and acetonitrile derivatives. CN-CF_3DSB OTFT exhibited high electron mobility even after 1 month air exposure and hysteresis-free TFT characteristics toward a steady operation of organic logic circuit. CN-CF_3DSB has a good resistance to atmospheric oxidants probably by a dense molecular packing due to CF_3 and CN substituent. CN-CF_3DSB is one model *n*-type organic semiconductor proposed in this study, beneficial for many analogue compounds easily replaced the central unit into other general aromatics such as thiophene derivatives.

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Figure Captions

Figure 1. Synthetic route and molecular structure of CN-CF_3DSB.

Figure 2. Output (a) and transfer (b) characteristics of CN-CF_3DSB OTFT.

Figure 3. Static characteristics of a resistor load (R_L = 50 MΩ) inverter and corresponding circuit diagram (insert).

Figure 4. Transfer characteristics of the same CN-CF_3DSB OTFT by forward operation after exposure to atmospheric air with different time. All the measurements were conducted after 1 h vacuuming.

Table I. Field-effect electron mobilities, threshold voltages and on/off current ratios in CN-CF_3DSB OTFT with different times of exposure to atmospheric air.

Exposure time	μ ($cm^2 V^{-1} s^{-1}$)	V_T (V)	On/off ratio	$\Delta\mu$ (%)	ΔV_{ON} (V)
Initial	0.068	38	6.0×10^5	-	-
1 day	0.066	38	5.8×10^5	2.9	2
1 week	0.067	41	4.5×10^5	1.5	5
1 month	0.065	42	4.7×10^5	4.4	5

Device was kept in atmospheric air without light expose.
Measurement was carried out under vacuum.

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Figure 1

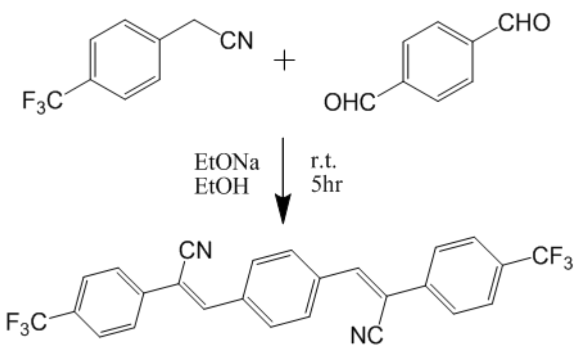

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Figure 2

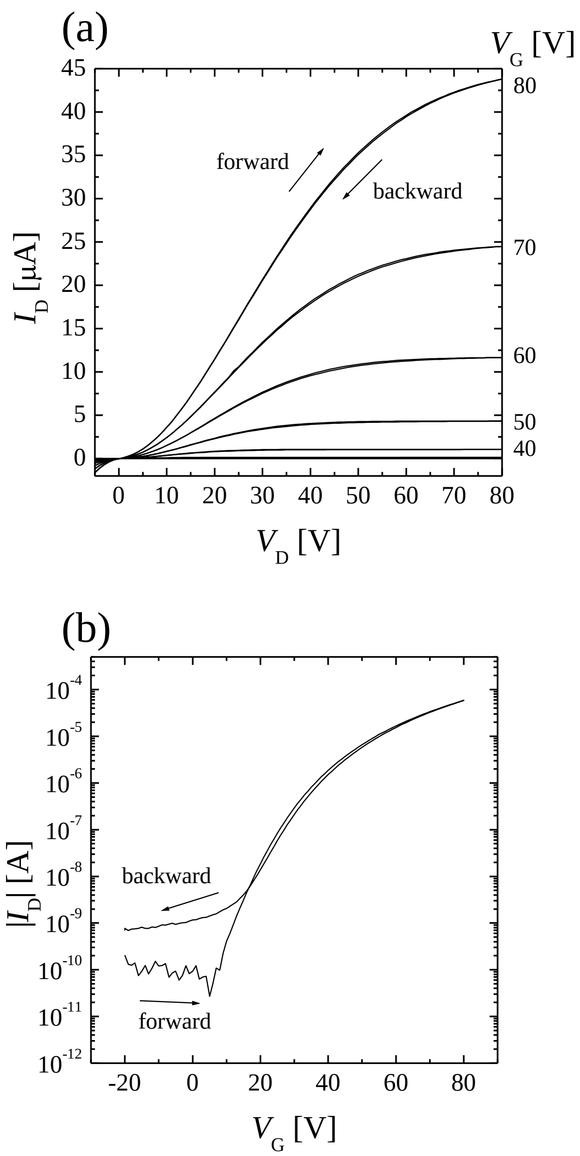

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Figure 3

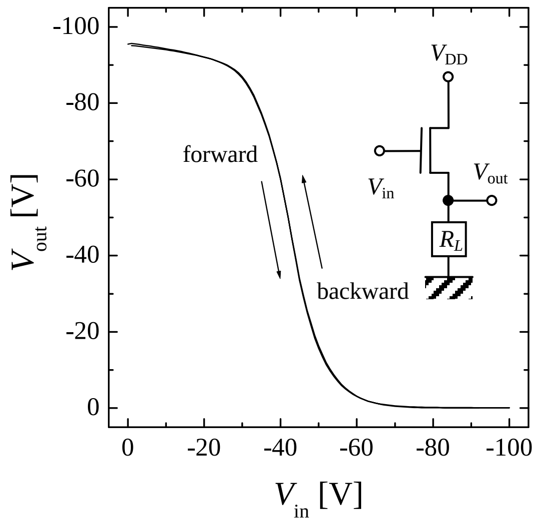

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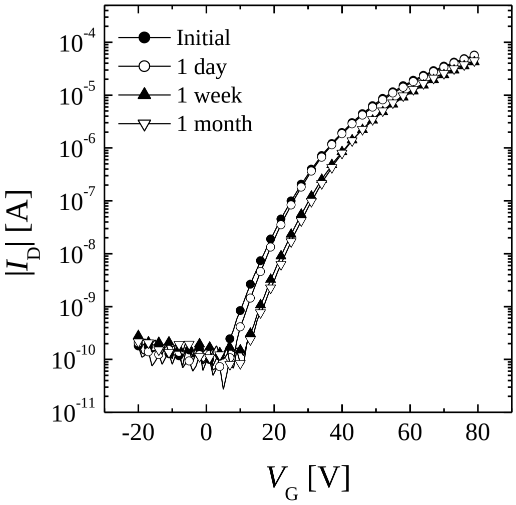
Figure 4



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