Supporting Information

High-performance n-Type Field-effect Transistor Based on Highly Crystalline Tricyanovinyldihydrofuran Derivative

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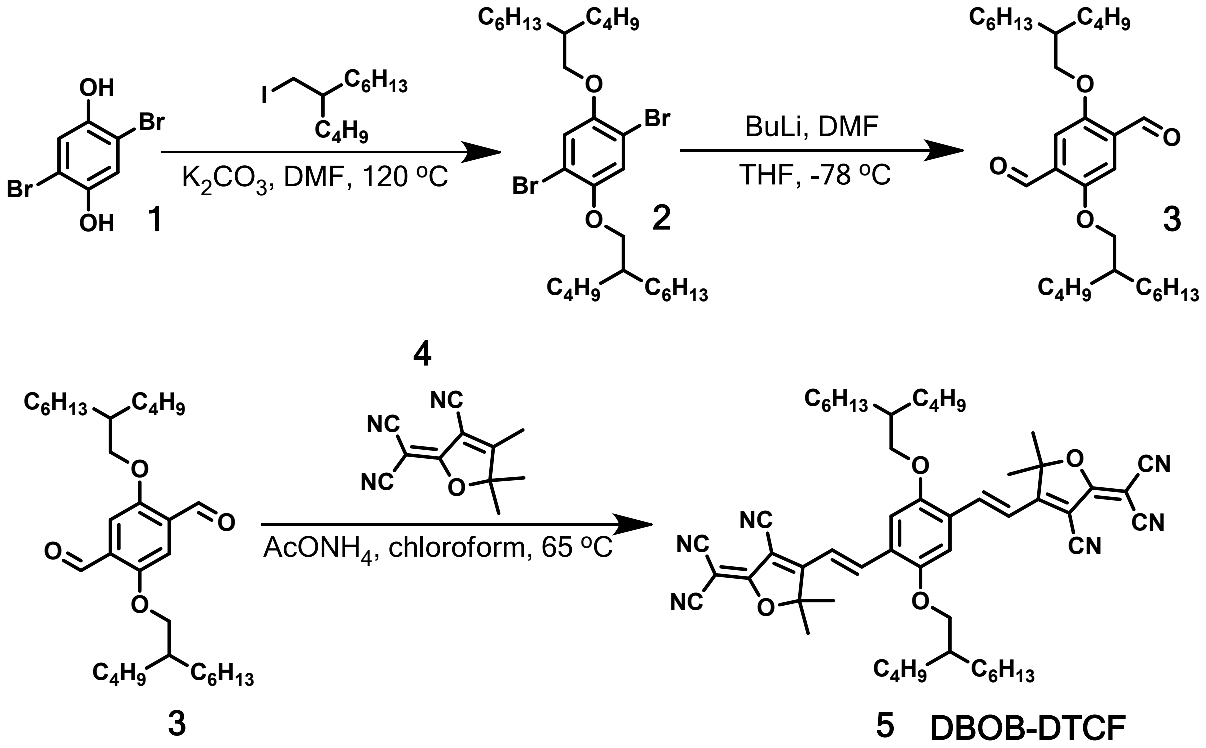
1. Experimental

All commercial reagents and solvents were purchased from Tokyo Chemical Industry (TCI), Alfa Aesar, Sigma-Aldrich, and Acros Organics. 2,5-Dibromohydroquinone (compound **1**) and 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF, compound **4**) were synthesized according to literatures.[1,2]

1.1 Synthesis



Scheme S1. Synthesis of the **DBOB-DTCF**.

Synthesis of 1,4-dibromo-2,5-bis((2-butyloctyl)oxy)benzene, 2

A suspension of K_2CO_3 (10 g, 186.6 mmol) in dimethylformamide (DMF, 150 mL) was degassed under stirring for 1 h. Compound **1** (5 g, 18.66 mmol) and 2-butyloctyliodide (12.16 g, 41.06 mmol) were added and stirred for 12 h at 120 °C. The solution was concentrated and the residue was purified by column chromatography on silica gel. The product was obtained as colorless liquid, compound **2** (6.21 g, 55%). ^{1}H NMR (500 MHz,

$CDCl_3$) δ (ppm) : 7.07 (s, 2H), 3.82 (d, *J* = 5 Hz, 4H), 1.77-1.82 (m, 2H), 1.45-1.52 (m, 8H), 1.29-1.33 (m, 24H), 0.87-0.92 (m, 12H).

Synthesis of 2,5-bis((2-butyloctyl)oxy)terephthalaldehyde, 3

Compound **2** (2 g, 3.31 mmol) was dissolved in 70mL of tetrahydrofuran (THF) and cooled to -78 °C. 2.5 M *n*-butyllithium (3.31 mL, 8.27 mmol) of was added dropwise. After addition was complete, DMF (1.93 g, 26.47 mmol) was added rapidly and the solution was stirred and warmed to room temperature overnight. The solution was then poured into water, which had been acidified with a few drops of HCl. The mixture was then extracted with dichloromethane and the organic layer was dried with Na_2SO_4. The mixture was purified by column chromatography on silica gel. The product was obtained as yellow viscous liquid, compound **3** (0.5 g, 30%). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) : 10.53 (s, 2H), 7.44 (s, 2H), 3.98 (d, *J* = 5 Hz, 4H), 1.77-1.82 (m, 2H), 1.45-1.52 (m, 8H), 1.29-1.33 (m, 24H), 0.87-0.92 (m, 12H).

Synthesis of DBOB-DTCF, 5

A mixture of compound **3** (0.5 g, 0.99 mmol), compound **4** (0.44 g, 2.18 mmol) and a catalytic amount of ammonium acetate ($AcONH_4$) in 50 mL of chloroform was stirred at 65 °C for 4 h. After the removal of the solvent, the residue was purified by column chromatography on silica gel. A dark purple solid was obtained. **DBOB-DTCF** (0.58 g, 67%). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) : 7.93-7.97 (d, *J* = 20 Hz, 2H), 7.20-7.23 (d, *J* = 15 Hz, 2H), 7.13 (s, 2H), 4.03 (d, *J* = 5 Hz, 4H), 1.83 (s, 12H), 1.45-1.50 (m, 8H), 1.25-1.40 (m, 24H), 0.85-0.95 (m, 12H). m/z = 865.16

1.2. Measurement

The structure of synthesized compounds w identified by ^1H NMR spectroscopy (Bruker 500 MHz spectrometer). The mass of compounds were examined by Matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry (LRF20, a Bruker

Daltonics). The thermal properties were studied under a nitrogen atmosphere on a Mettler differential scanning calorimetry (DSC) 821e instrument (Mettler, Greifensee, Switzerland).

The UV-vis absorption properties of the solution and film states (λ = 190-1100 nm) were measured by HP 8453 photodiode array UV-vis absorption spectrometer. The film sample was deposited on washed glass substrates using a chloroform solution (5 mg mL^{-1}) by a spin-coating method.

The electrochemical property of the small molecule was determined using cyclic voltammetry (CV, eDAQ EA161). The chloroform solution (5 mg mL^{-1}) was deposited on Pt plate and it was used as working electrode. Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The 0.1 M electrolyte solution was made by dissolving tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in dried acetonitrile.

The grazing incident X-ray diffraction (GI-XRD) measurements were performed at the 9A (U-SAXS) beamline at the Pohang Accelerator Laboratory (PAL). The energy, pixel size, wavelength, and scanning interval at the 9A beamline were 11.04 keV, 79.59 μm, 1.10 Å, and $2\theta = 0^\circ$–20°, respectively. The scattering vectors, q_{xy} and q_z were parallel and perpendicular to the substrate. The film samples used in the GI-XRD analysis were fabricated by spin coating a solution on *n*-octyltrichlorosilane (OTS)-treated SiO_2/Si substrates.

The surface morphologies of the films were measured by atomic force microscopy (AFM, XE-100 advanced scanning probe microscope, PSIA) with a silicon cantilever. The AFM measurements were performed for the samples fabricated by the same method as for thin film transistor (TFT) devices.

All images of scanning electron microscopy (SEM) were obtained by using JEOL JSM-7001F instrument at 15.0 kV using Pt-sputtered samples.

The transmission electron microscopy (TEM) images and the selected-area electron diffraction (SAED) patterns were recorded with a FEI Titan Cubed 60-300 transmission electron microscope (FEI Inc. Operating voltage = 300 V). The samples for TEM were prepared by putting crystals on carbon-coated copper grids.

1.3. Fabrication of Single Crystal Microplates (CMs)

The self-assembly method was adopt for preparing the **DBOB-DTCF** microcrystals. **DBOB-**

DTCF was dissolved in chlorobenzene with a concentration of 5 mg mL^{-1}. The solution was stirred and heated at 70 °C for 3 h, and then allowed to cool slowly to room temperature without stirring process under N_2 conditions. After the solution had been stored for 12 h under N_2 condition, formed crystalline microplates in solution were spin-coated on the OTS-treated SiO_2/Si substrates. Then, the resulting microcrystals were baked on a hot plate for 15 min at 50 °C to remove the residual solvent.

1.4. Fabrication of Thin Film Transistors (TFTs)

Bottom-gate bottom-contact device geometry was employed to evaluate the TFT performance of the **DBOB-DTCF**. Source and drain electrodes (80 nm) were thermally deposited on OTS-treated SiO_2/Si substrates through a shadow mask; the width and length of the channel were 1500 μm and 100 μm, respectively. Spin-coated films of **DBOB-DTCF** were then deposited on substrates using chloroform as the solvent (10 mg mL^{-1}). The saturated field-effect mobilities were measured in the saturation regime using the relationship: $\mu_{sat} = (2I_{DS}L)/(WC(V_G-V_{th})^2)$, where W is the channel width, L is the channel length, I_{DS} is the saturation drain current, C is the capacitance (~11.5 nF cm^{-2}) of the dielectric SiO_2 (300 nm) per unit area, V_G is the gate bias, and V_{th} is the threshold voltage. The device performances were evaluated in both ambient condition and vacuum condition using a 4200-SCS semiconductor characterization system.

1.5. Fabrication of Crystalline microplate (CM)-based Field-Effect Transistors

CMs of **DBOB-DTCF** were formed on OTS-treated SiO_2/Si substrates with n-doped Si gate electrode and SiO_2 (300 nm) gate insulator. Subsequently, shadow masks were placed on individual **DBOB-DTCF** CM. Next, 100-nm-thick source and drain Au electrodes were deposited on the CM by thermal evaporation using the shadow masks. The saturated field-effect mobilities of CM-based FETs were measured in the saturation regime using the relationship: $\mu_{sat} = (2I_{DS}L)/(WC(V_G-V_{th})^2)$, where W is the width of CM, L is the length of CM, I_{DS} is the saturation drain current, C is the capacitance of the dielectric SiO_2 (300 nm) per unit area, V_G is the gate bias, and V_{th} is the threshold voltage. The FET device performance was measured in air using a 4200-SCS semiconductor characterization system.

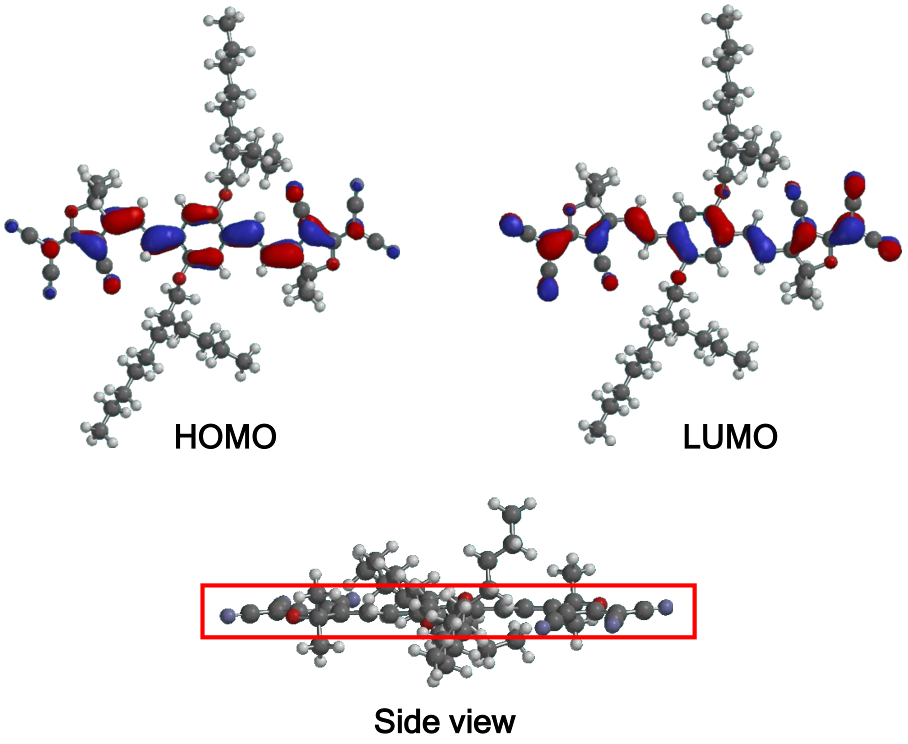


Fig. S1. The geometry of DBOB-DTCF in energy-minimized state. (DFT method, B3LYP/6-31G*).

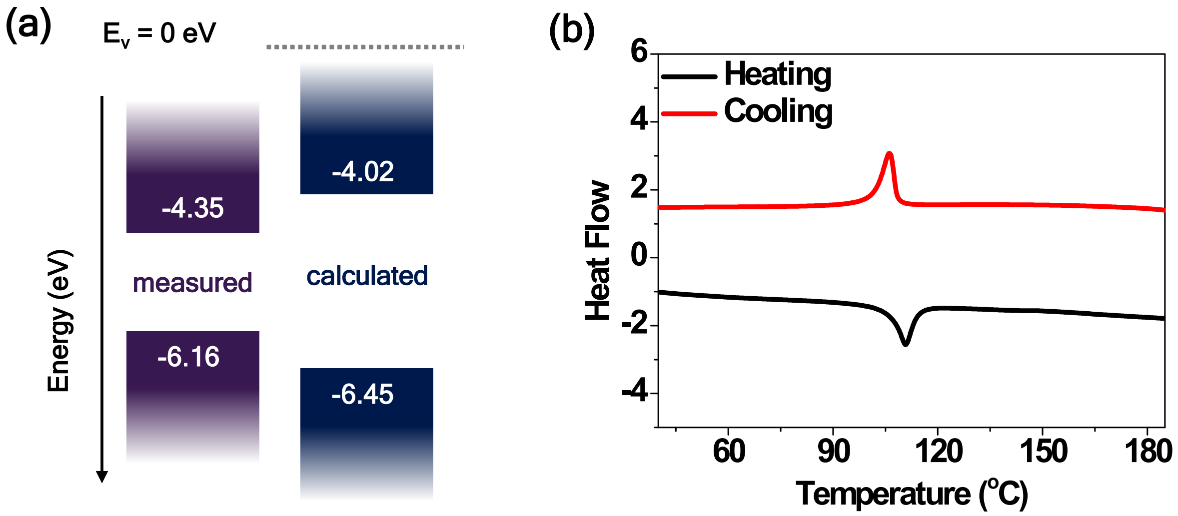


Fig. S2. (a) Energy diagrams of DBOB-DTCF having theoretically calculated and experimentally determined HOMO/LUMO energy levels. (b) DSC curves of DBOB-DTCF.

Table S1. Optical and electrochemical properties of DBOB-DTCF.

	Absorbance (nm)		**$\lambda_{\text{cut-off}}$ (nm)[a]**	**E_g^{opt} (eV)[a]**	**$E_{\text{red}}^{\text{onset}}$ (V)[a]**	**Energy levels**	
	solution	**film**				**HOMO (eV)[b]**	**LUMO (eV)[b]**
DBOB-DTCF	416, 550	437, 595, 652	684	1.81	-0.09	-6.16	-4.35

[a] Film, [b] The values were obtained from cyclic voltammetry. (Sample: film on Pt electrode)

[c] E_{HOMO} (eV) = E_{LUMO} (eV)-$E_g^{\text{opt,b}}$ (eV).

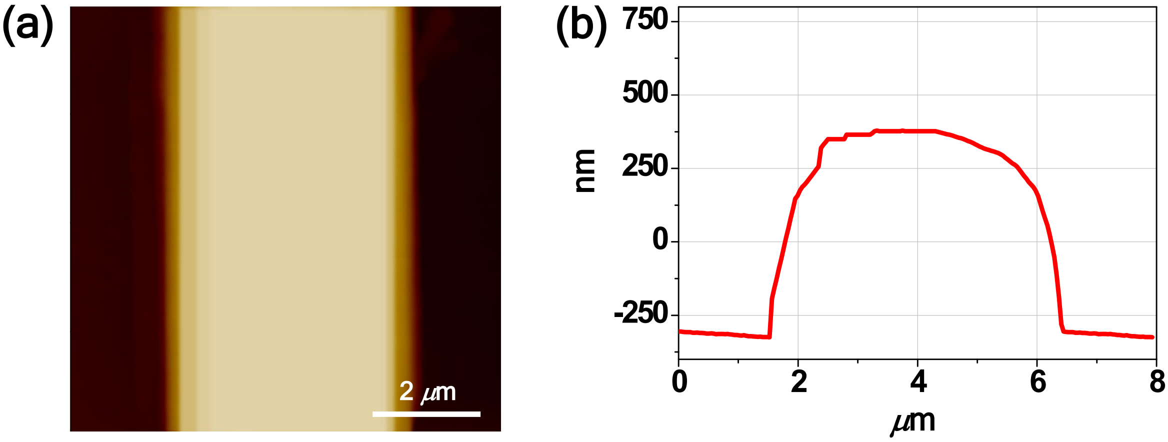


Fig. S3. AFM height image of DBOB-DTCF based CM (a) and the corresponding height profile (b).

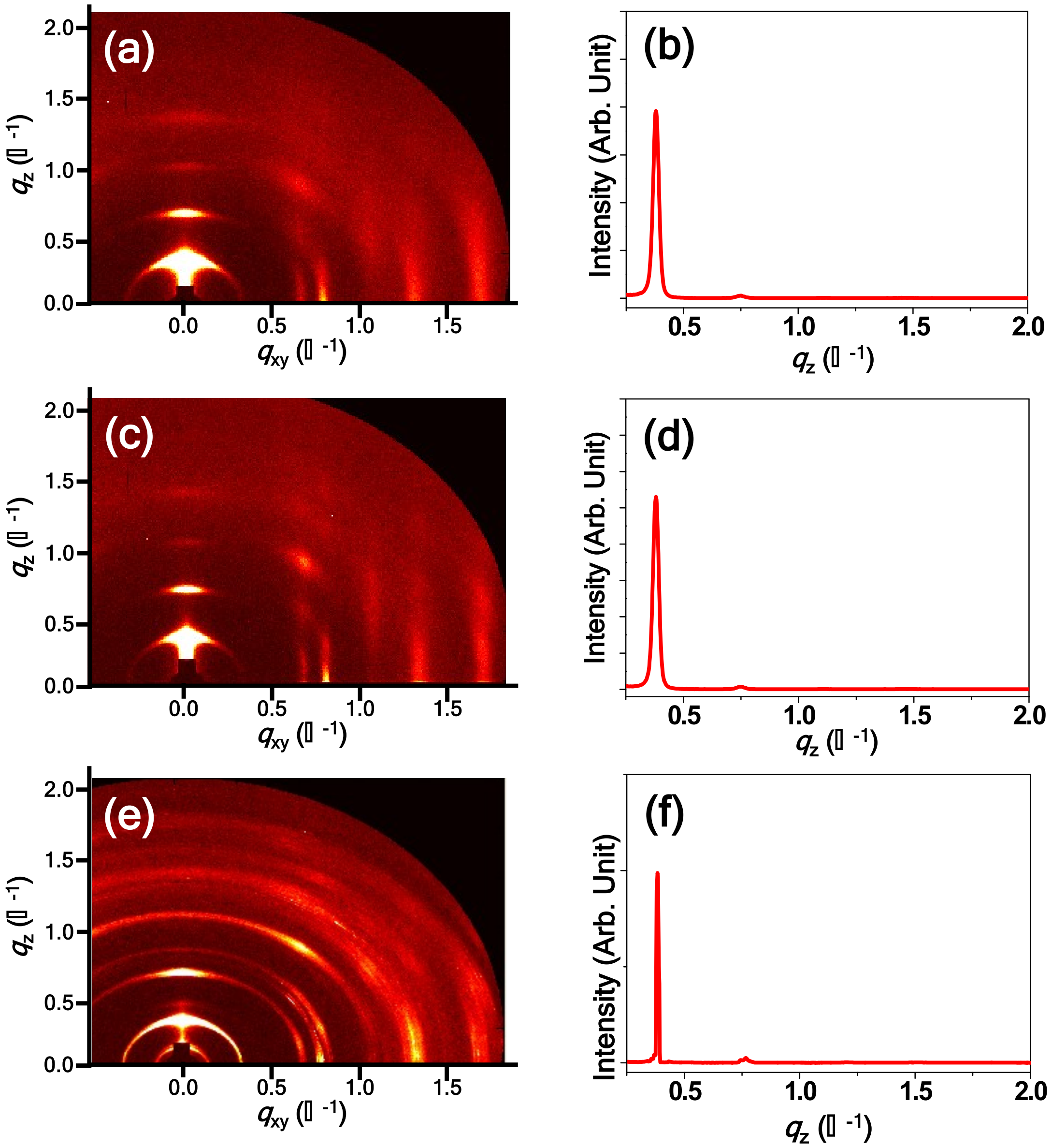


Fig. S4. 1D X-ray diffraction patterns (XRDs) in out-of-plane and 2D grazing incidence X-ray diffraction (GIXRD) patterns of DBOB-DTCF films and CMs. (a) and (b) Pristine film, (c) and (d) annealed film. (e) and (f) Scattered pile of CMs on octyltrichlorosilane-treated SiO_2/Si substrate. It is impossible to focus single CM due to large X-ray beam size (hundreds of micrometers).

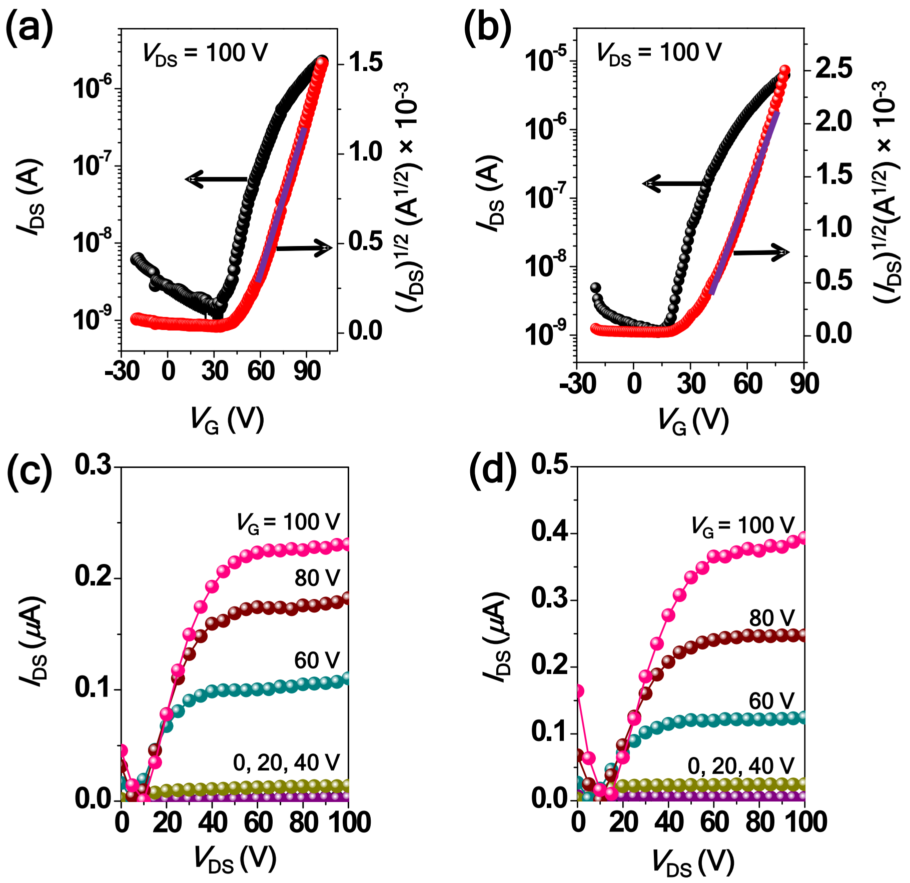


Fig. S5. Transfer curves of TFTs with thin film annealed at 90 °C made of DBOD-DTCF in (a) ambient condition and (b) in vacuum condition. Output curves of TFTs with thin film annealed at 90 °C made of DBOD-DTCF in (a) ambient condition and (b) in vacuum condition.

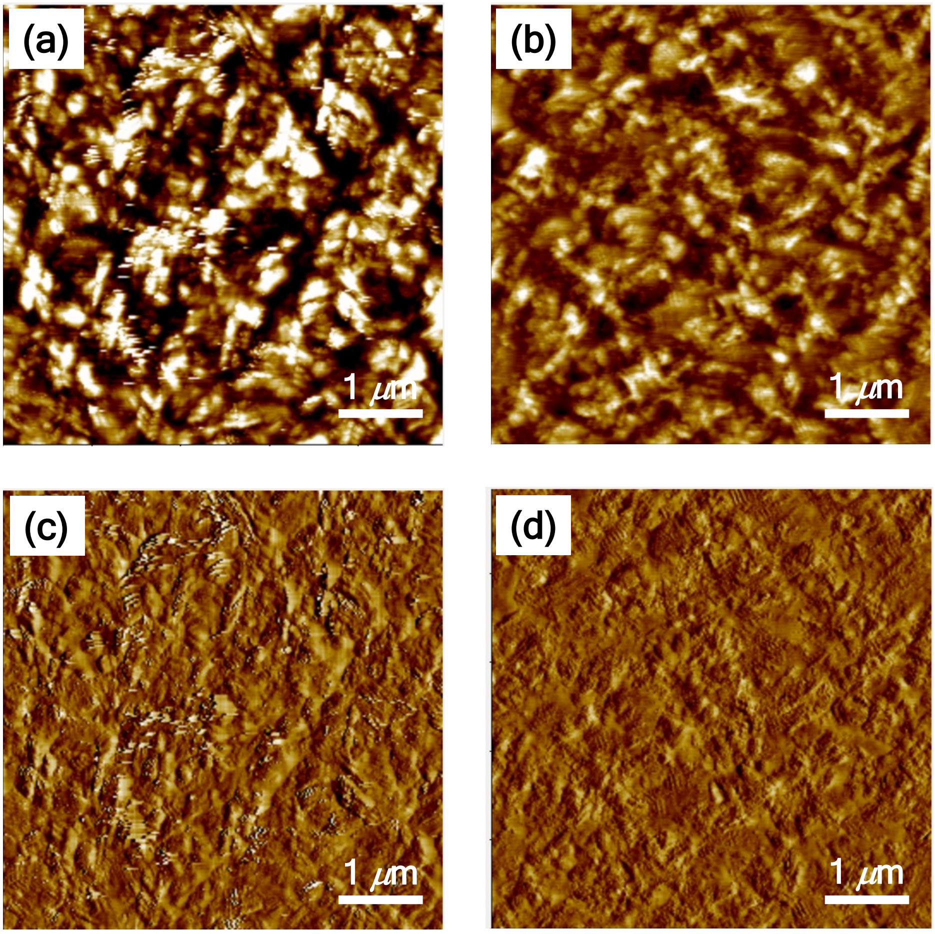


Fig. S6. AFM height (a, b) and phase (c, d) images of DBOB-DTCF films. Pristine film (a, c) and annealed film at 90 °C (b, d).

References

S1. S. Liu, Z. Jin, Y. C. Teo, and Y. Xia, *J. Am. Chem. Soc.* 2014, **136**, 17434.

S2. P. Gopalan, H. E. Katz, D. J. McGee, C. Erben, T. Zielinski, D. Bousquet, D. Muller, J. Grazul, and Y. Olsson, *J. Am. Chem. Soc.* 2004, **126**, 1741.