Supporting Information

Epitaxially-Crystallized Oriented Naphthalene Bis(dicarboximide) Morphology for Significant Performance Improvement of Electron-Transporting Thin-Film Transistors

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Preparation and Characterization

Synthesis of F-NDI: F-NDI was synthesized according to the procedure published by Katz etc.[1] ^{1}H NMR (400 MHz, 298 K, $CDCl_3$, ppm) δ = 8.87 (s, 4H), 5.07-4.99 (t, *J* =15.3Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ =162.2, 131.8, 127.0, 126.4, 38.9, 38.6, 38.4. HRMS (MALDI, 100%) m/z calcd (%) for $C_{22}H_8F_{14}N_2O_4$: 630.0226, found 630.0266.

The preparation of oriented film and device: The epitaxial growth of F-NDI on oriented PE substrate was conducted in vapor phase. It was performed in a three-zone horizontal-tube furnace (**Figure S1**). The powder of F-NDI was placed in the high-temperature zone (115 °C) in a quartz boat with high-purity argon used as the carrier gas (100 mL min^{-1}). The PE-SiO_2/Si substrates were placed at the low-temperature zone (50 °C). The pressure in the quartz tube was 2 Pa. Thin film transistors based on the F-NDI/PE film were built to test the performance of the devices according to the same procedure as reported in Ref. [2]. Then Au of 60 nm in thickness was vacuum deposited on the films at a rate of 0.1 Å.s^{-1}. A copper grid was used as mask, which makes the channel length L = 25 μm and the channel width W = 200 μm. While, the F-NDI/OTS device has a different channel structure with W/L=50. *I-V* characteristics of OFETs were recorded by a Keithley 4200SCS with a Micromanipulator 6150 probe station in a clean and shielded box at room temperature in air. In this work, the PE film together with SiO_2 act as the dielectric layer, and the capacitance is 6.3 nF/cm^2, but 10 nF/cm^2 for the OTS modified SiO_2 dielectric layer.The optical microscopy images were obtained by using the Axioskop 40A Pol optical microscope (Carl Zeiss) under crossed polarizers.

AFM observations were performed by using an Agilent Technologies 5500 atomic force microscope (Agilent Technologies Co. Ltd., U.S.) at room temperature in air. The images were obtained by means of tapping mode (height and phase) with a silicon cantilever having a spring constant of 20-30 N/m and a resonating frequency of 320-350 kHz, and the scanning rates varied 10 μm/s.

UV-Vis absorption spectra were recorded on a Hitachi U-2900 recording spectrophotometer.

A JEOL JEM-2100F TEM operated at 200 kV was used in this study.

Polarized photoluminescence measurements (emission mode) were carried out using a 360 nm excitation wavelength with FLS980 (Edinburgh photonics) having a 450 W xenon lamp as the steady-state excitation source.

[1] H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y. Y. Lin, A. Dodabalapur, *Nature* 2000, **404**, 478.

[2] S. D. Jiang, H. L. Qian, W. Liu, C. R. Wang, Z. H. Wang, S. K. Yan, D. B. Zhu, *Macromolecules* 2009, **42**, 9321.

Supporting figures

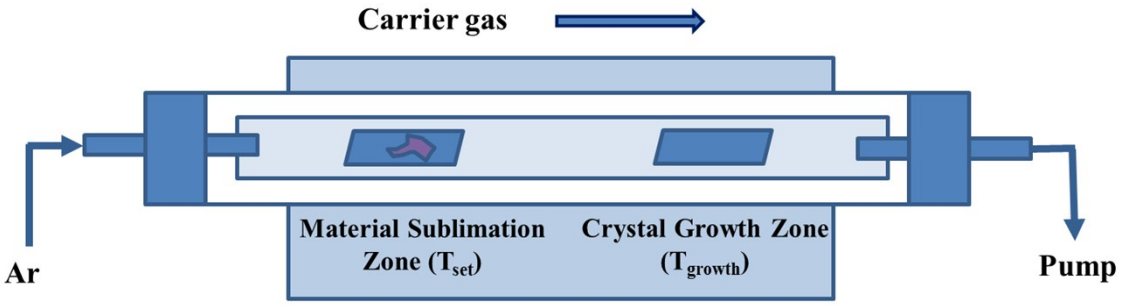

Figure S1. a sketch of the vacuum evaporation equipment.

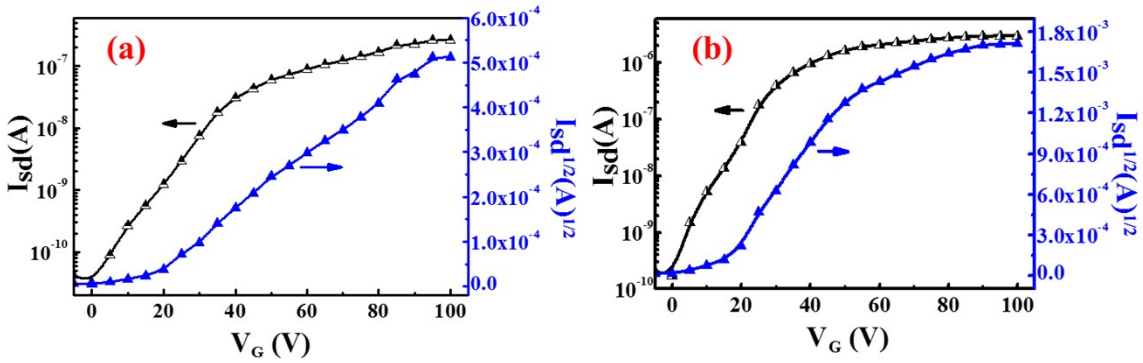

Figure S2. Transfer characteristics of the transistors based on the F-NDI film deposited on the OTS-Si/SiO_2 film with the substrate temperature 25 °C (a) and 50 °C (b).

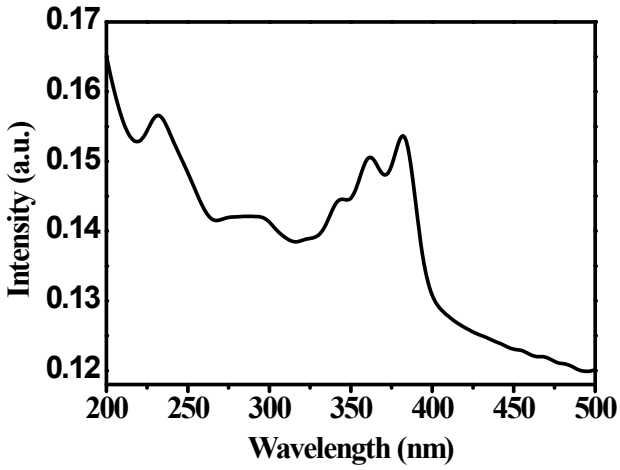

Figure S3. Uv spectrum of F-NDI on the oriented PE film.

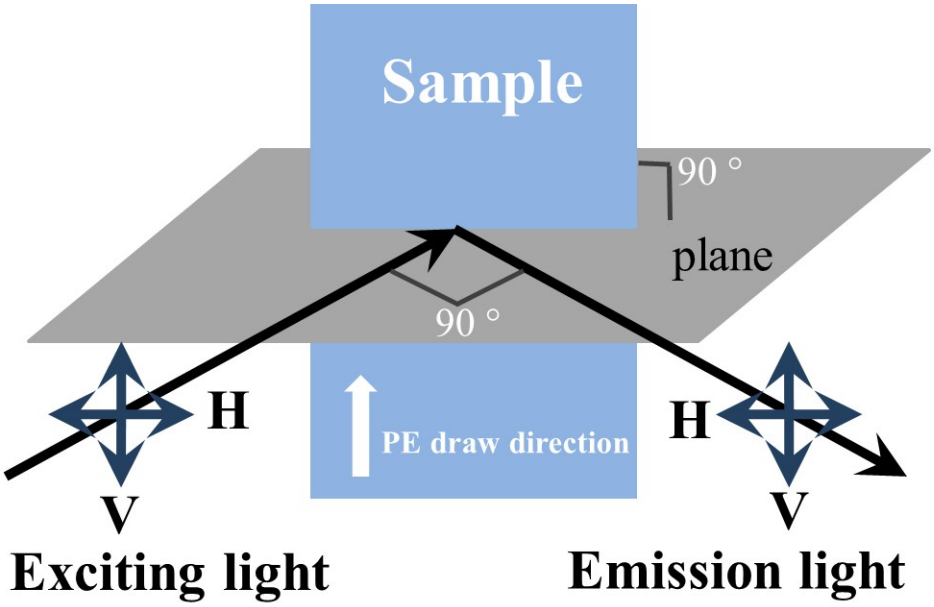

Figure S4. Set-up of Polarized Photoluminescence measurement.

The set-up of Polarized Photoluminescence measurement was shown in Figure S2. In this set-up, the polarized emission was collected at a perpendicular direction with respect to the excitation light. The plane defined by excitation and emission light was perpendicular to the sample plane. The different emission intensity results were defined with polarized light as I_{HH}, Exciting light and emission collected perpendicular to PE draw direction; I_{HV}, Exciting light is perpendicular to PE draw direction, emission collected parallel to PE draw direction and I_{VV}, Exciting light is parallel to PE draw direction, emission collected parallel to PE draw direction.

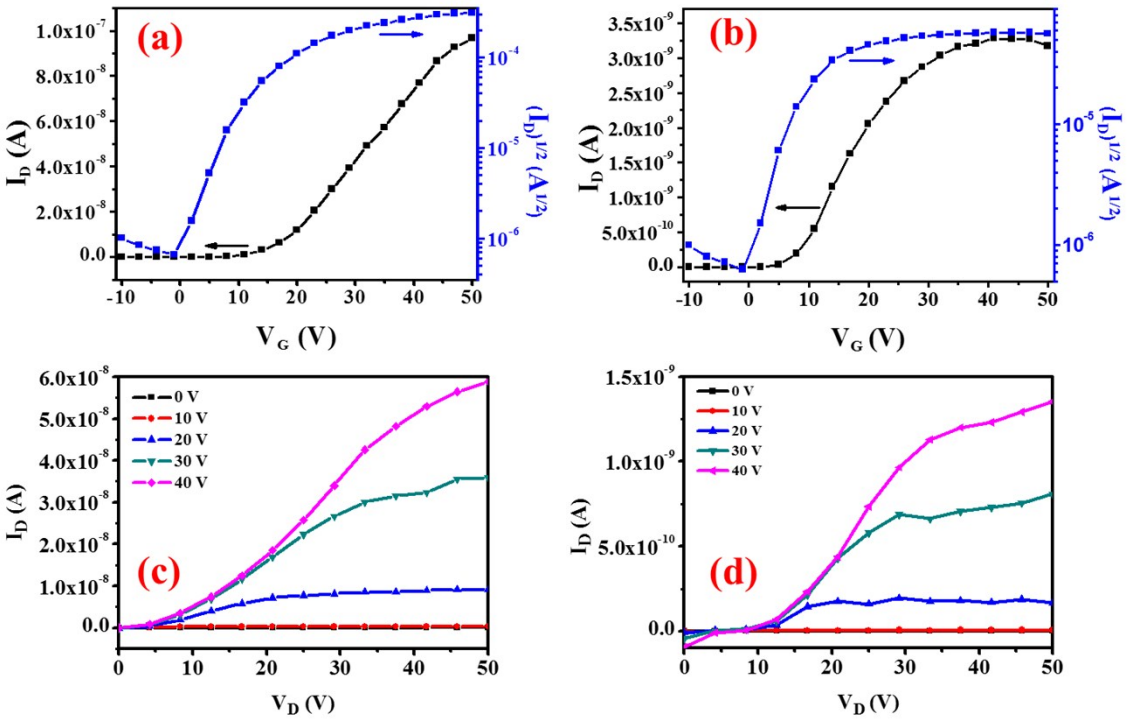

Figure S5. Transfer characteristics ((a) and (b)), and output characteristics ((c) and (d)) of the transistors based on the F-NDI film deposited on the melt-drawing PE film measured ((a) and (c) along (0°) and ((b) and (d)) perpendicular (90°) to the molecular chain direction of the PE substrate.

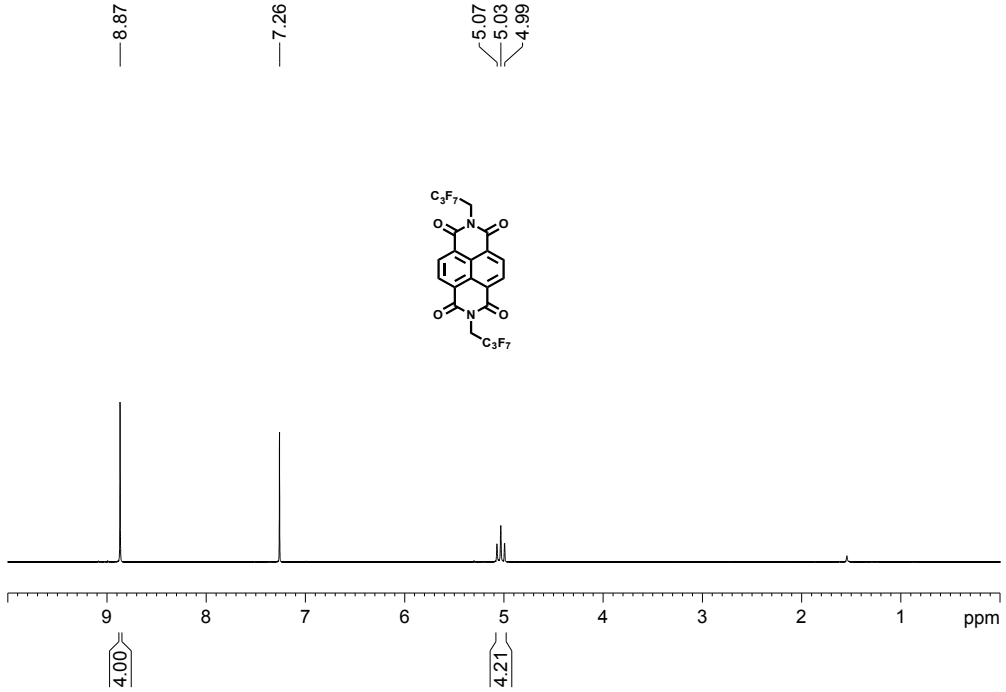

Figure S6. ^{1}H NMR spectrum of F-NDI in $CDCl_3$

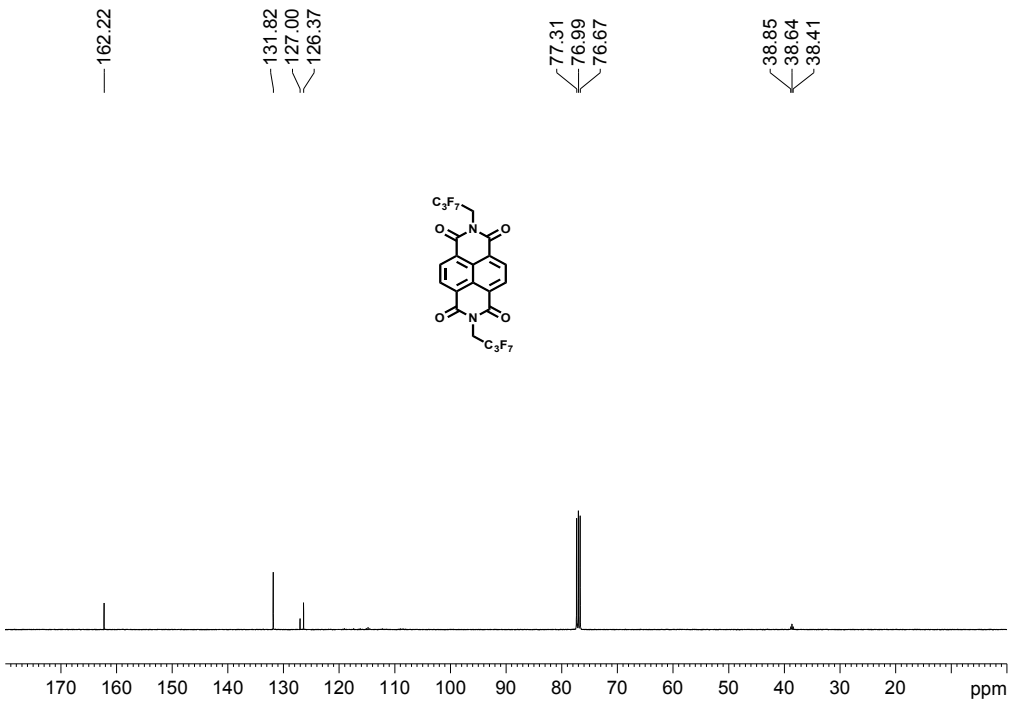

Figure S7. ^{13}C NMR spectrum of F-NDI in $CDCl_3$

Table S1 The charge mobility, threshold voltage and on/off ratio for six F-NDI/PE-0°-based transistors on different positions

	μ [$cm^2V^{-1}s^{-1}$]	V_T [V]	I_{on}/I_{off}
1	0.23	16.7	1.38×10^5
2	0.23	13.0	2.47×10^5
3	0.21	17.2	3.57×10^5
4	0.19	20.0	1.86×10^5
5	0.18	15.6	1.03×10^5
6	0.16	19.6	1.64×10^5

Table S2 The charge mobility, threshold voltage and on/off ratio for six F-NDI/PE-90°-based transistors on different positions

	μ [$cm^2V^{-1}s^{-1}$]	V_T [V]	I_{on}/I_{off}
1	1.5×10^{-2}	25.2	8.5×10^3
2	1.4×10^{-2}	17.9	7.5×10^3
3	1.4×10^{-2}	23.1	5.5×10^3
4	1.2×10^{-2}	12.5	1.6×10^4
5	1.1×10^{-2}	13.7	1.03×10^4
6	1.1×10^{-2}	12.5	5.5×10^3