

Supporting Information

An Asymmetric Naphthalimide Derivative for n-Channel Organic Field-Effect Transistors

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Experimental Section

Materials and general methods:

Naphthalene-1,4,5,8-tetracarboxylic Dianhydride, tetradecan-1-amine and benzene-1,2-diamine were purchased from Alfa Aesar company. All solvents were used without further purification. Fourier transform infrared (FTIR) spectra was conducted on TENSOR 27. The UV-*vis* spectrum was obtained on a JASCO V-570 UV-*vis* spectrometer in a CH₂Cl₂ solution. Thin film samples were prepared from the corresponding materials thermally evaporated on quartz plates. The optical band gap E_g^{opt} was derived from the onset of absorption spectra ($E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$). Cyclic Voltammograms (CVs) were recorded on a CHI660C electrochemical workstation at a scan rate of 100 mV s⁻¹, with glassy carbon discs or ITO evaporated the corresponding material as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) dissolved in CH₂Cl₂ (HPLC grade) was employed as the supporting electrolyte. The LUMO level was estimated according to $E_{\text{LUMO}} = -|eE_{\text{red}} + 4.4\text{eV}|$. The HOMO was obtained by $E_{\text{HOMO}} = E_{\text{LUMO}} - E_g^{\text{opt}}$. Thermogravimetric analysis (TGA) was run on a PERKIN ELMER TGA7 with the scanning rate of 10 °C min⁻¹ under nitrogen atmosphere. X-Ray diffraction (XRD) measurements were performed in reflection mode at 40 kV and 200 mA with Cu K α radiation using a 2 kW Rigaku X-ray diffractometer. Atomic force microscopy (AFM) images were carried out on a Nanoscope IIIa AFM (Digital Instruments) operating in tapping mode. SEM images were captured on a Hitachi S-4800 FESEM. TEM and SAED measurements were carried out using a JEOL Model JEM-2011 (Japan).

FET devices were fabricated in a top-contact bottom-gate geometry with n-doped Si as gate electrodes and SiO₂ (300 nm) as dielectric layer. Prior to deposition of the semiconductor thin films, the silanol groups on SiO₂ surface was passivated with *n*-octadecyltrichlorosilane (OTS), hexamethyldisilazane (HMDS), or octadecyltrimethoxysilane (OTMS) monolayer to reduce charge trapping and thus enhance n-type mobility. Then films were thermally evaporated on the SAMs-

modified and unmodified silicon oxide layer at a rate of 0.1 Å/s for the first ten nanometers and then increasing to 0.5 Å/s gradually to a final thickness of 50 nm at a base pressure of about $4 \sim 6 \times 10^{-4}$ Pa. The films with thickness of 10 nm were obtained by thermally evaporating at a rate of 0.1 Å/s at a base pressure of about $4 \sim 6 \times 10^{-4}$ Pa as well. Gold electrodes were deposited by using shadow masks with W/L of ca. 200/25. The ultra-high quality two-dimensionally polycrystalline film and single crystalline micro-ribbons of IZO were directly fabricated on the OTS-modified substrates through the physical vapor transport (PVT) technique. The quartz boat containing the powder of IZO material was placed at the high temperature zone (around 170 °C) of the tube furnace with the high-pure Ar as the carrier gas, and the low temperature zone placed the OTS-modified substrates. After ~3 hours, polycrystalline film and the ribbon-like crystals on the substrate were obtained. The shape, size and thickness of the crystals were depending on the crystal growth parameters such as growth temperature, growth time, gas flow speed, system vacuum and etc. Following the crystals deposition, the top-contact source-drain electrodes were fabricated using the “organic ribbon mask technique”. And the OFET devices based on ultra-highly crystalline films were fulfilled by vacuum-evaporating gold electrodes through shadow masks with W/L of ca. 200/25. OFET characteristics were characterized using a Keithley 4200 SCS semiconductor parameter analyzer and a Micromanipulator probe station in vacuum or in glove box filled with nitrogen gas at room temperature.

Synthesis of IZO :

The synthesis procedure of the compound were depicted in Scheme 1 based on the reported literature¹⁻² with simple modification. Tetradecan-1-amine (2 ml, 6.39 g, 30 mmol) was added to a suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (**1**, 2.68 g, 10 mmol) in a mixture of water (50 ml) and 2-propanol (50 ml) at room temperature under N₂. The resulting solution was heated at 50 °C for 24 h to give a white precipitate. The reaction mixture was cooled down to room temperature. The solid was filtered off and stirred in acetic acid (200 mL) at reflux for 5 h, producing

first a suspension and then a clear yellow solution. It was cooled to room temperature and the precipitate was collected by filtration, washed with ethanol and last dried in vacuum oven. The solid was confirmed to be the mixture of monoimide monoanhydride naphthalene (**2**, MMN) and bisimide naphthalene (~1:1). MALDI-TOF MS: calcd. 463.57 and 658.95; found: 463.28 and 660.82, respectively. The mixture was used directly for the next synthesis procedure: Mixture (0.93 g, containing MMN: 0.46 g, 0.1 mmol) and benzene-1,2-diamine (**3**, 0.16 g, 0.15 mmol) was added into pyridine (10 mL) and refluxed for 4h. The solution was cooled to room temperature and diluted with ethanol (100 mL) under strong agitation. The crude residue was washed in 50 mL methanol under strong agitation. After 1h, the solid was collected by vacuum filtration and purified using silica-gel column chromatography with methylene chloride: methanol (50:1) to afford IZ0 (0.22 g, ~40%) as a bright orange powder. ¹H NMR (CDCl₃, 400 MHz): δ=8.92-8.98(m, 2H), 8.79-8.84 (t, *J*=7.45 Hz, 2H), 8.52-8.55 (m, *J*=7.74 Hz, 1H), 7.91-7.94(m, 1H), 7.53-7.55 (m, 2H), 4.18-4.23(t, *J*=7.80 Hz, 2H), 1.76(m, 2H), 1.25(m, 22H), 0.87 ppm (t, 3H). MALDI-TOF MS exact mass (M + H⁺): 536.17; calcd. Mass: 535.68, HiRes Mass (M + H⁺): 536.2902.

Reference:

- 1 N. M. Shavaleev, H. Adams, J. Best and J. A. Weinstein, *J. Organomet. Chem.*, 2007, **692**, 921.
- 2 X. Li, Y. Xiao and X. Qian, *Org. Lett.*, 2008, **10**, 2885.

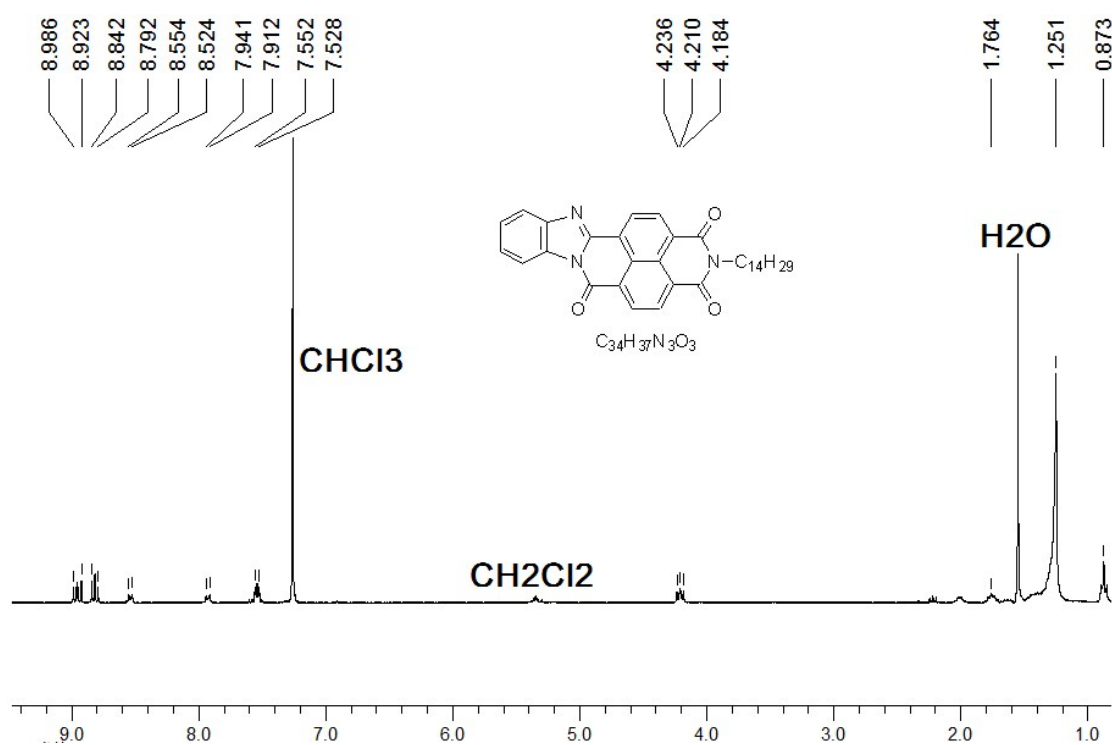


Fig. S1 ¹H NMR (CDCl₃, 400 MHz) of IZO (δ =8.92-8.98(m, 2H), 8.79-8.84 (t, J =7.45 Hz, 2H), 8.52-8.55 (m, J =7.74 Hz, 1H), 7.91-7.94(m, 1H), 7.53-7.55 (m, 2H), 4.18-4.23(t, J =7.80 Hz, 2H), 1.76(m, 2H), 1.25(m, 22H), 0.87 ppm (t, 3H)).

Data: <Untitled>.A5[c] 1 Mar 2012 16:51 Cal: 5 Nov 2007 18:55
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%Int. 19 mV[sum= 3718 mV] Profiles 1-200 Unsmoothed

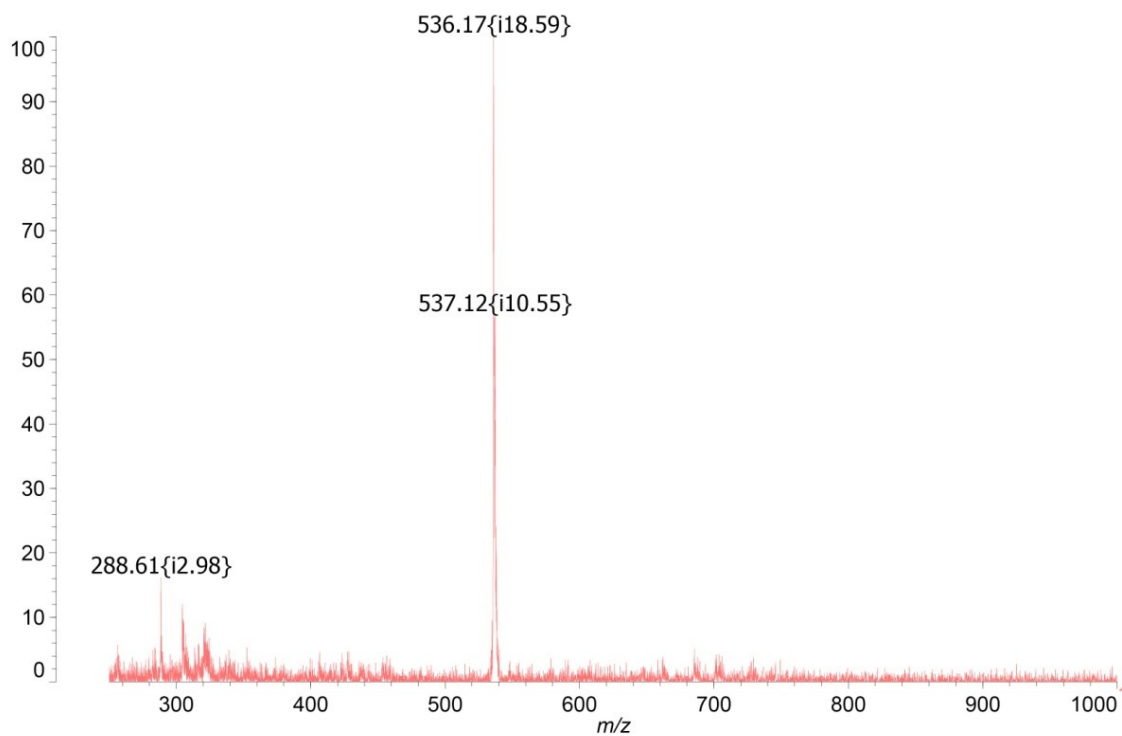


Fig. S2 MALDI-TOF of IZ0.

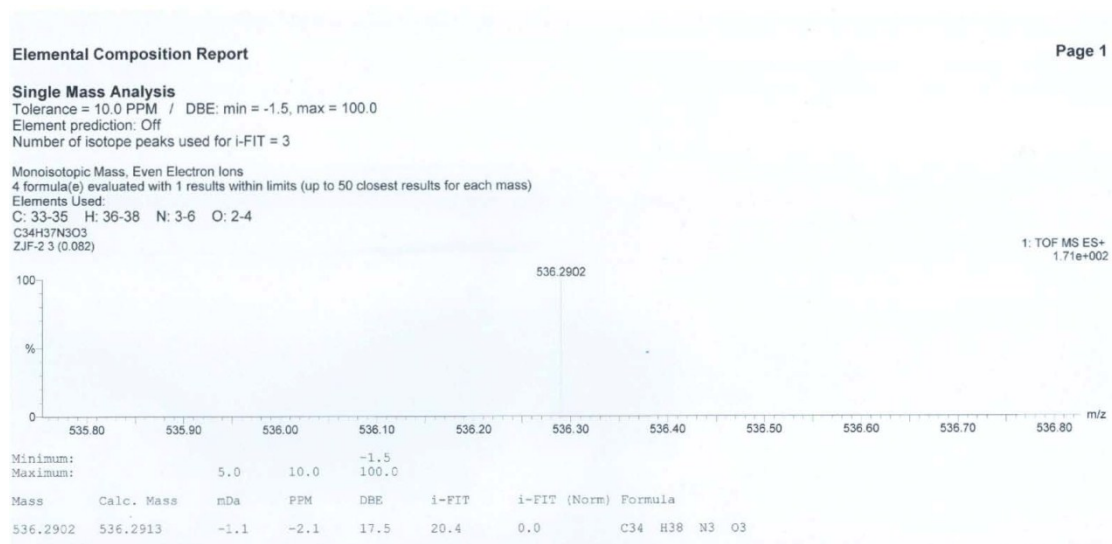


Fig. S3 HiRes MALDI-TOF of IZ0.

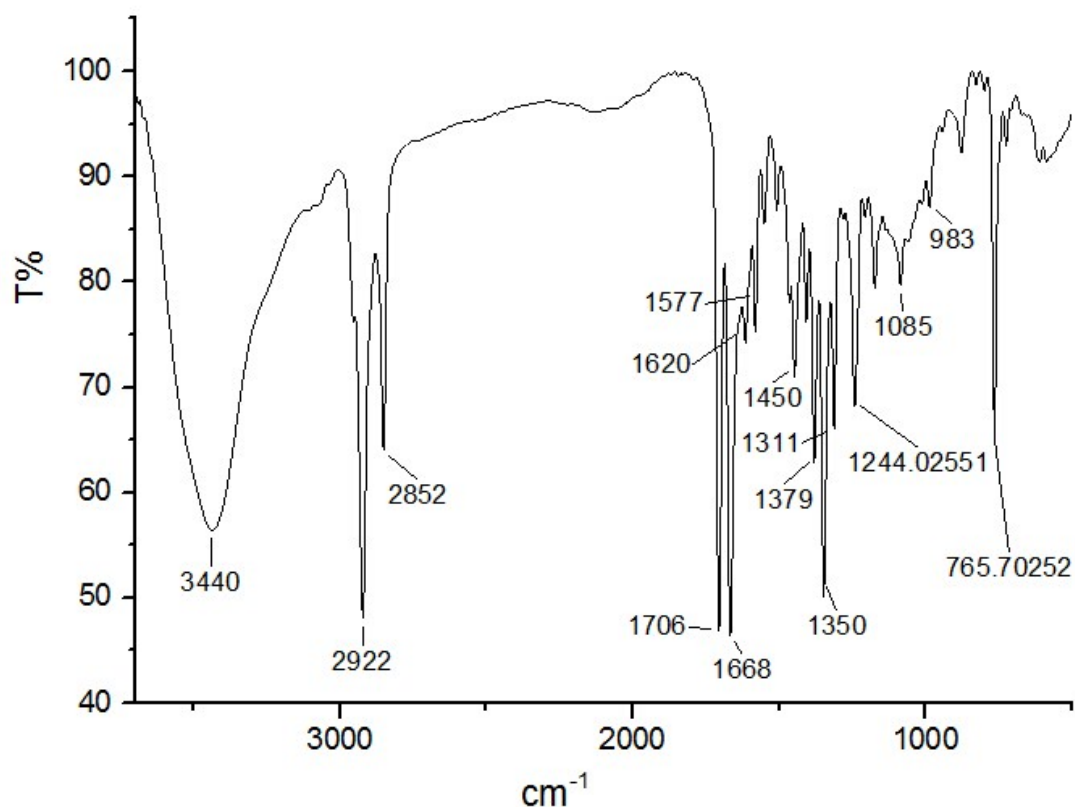


Fig. S4 FTIR spectrum of IZO ($\nu=3440, 2922, 2852, 1706, 1668, 1620, 1577, 1450, 1379, 1350, 1311, 1244, 1085, 983, 765 \text{ cm}^{-1}$).

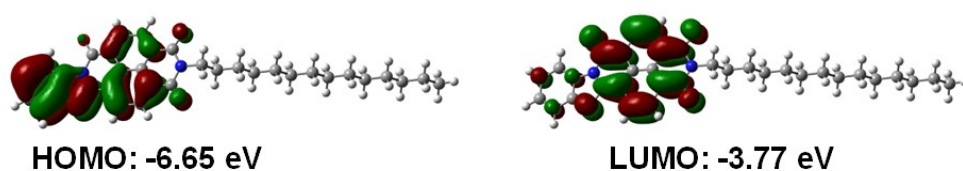


Fig. S5 HOMO and LUMO orbitals of IZO obtained by DFT calculations.

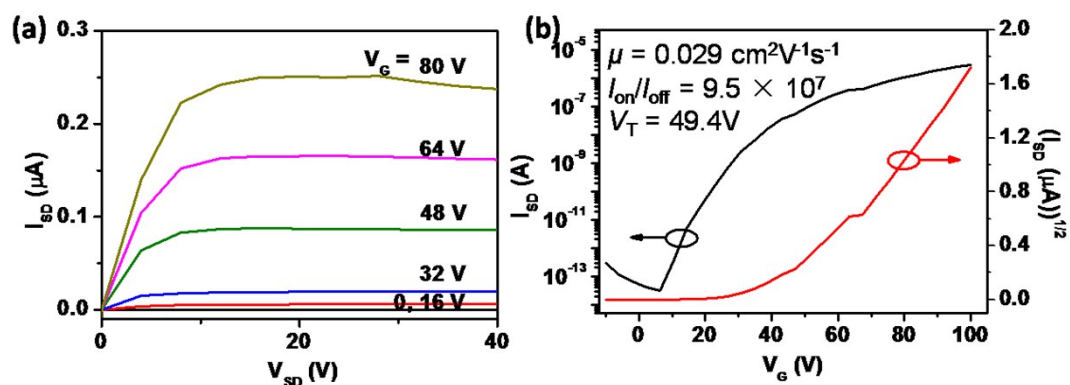


Fig. S6 Typical output (a) and transfer (b) characteristics of IZO film on the OTMS-

modified SiO₂/Si substrate at the deposition temperature of 90 °C (Film thickness: 50 nm).

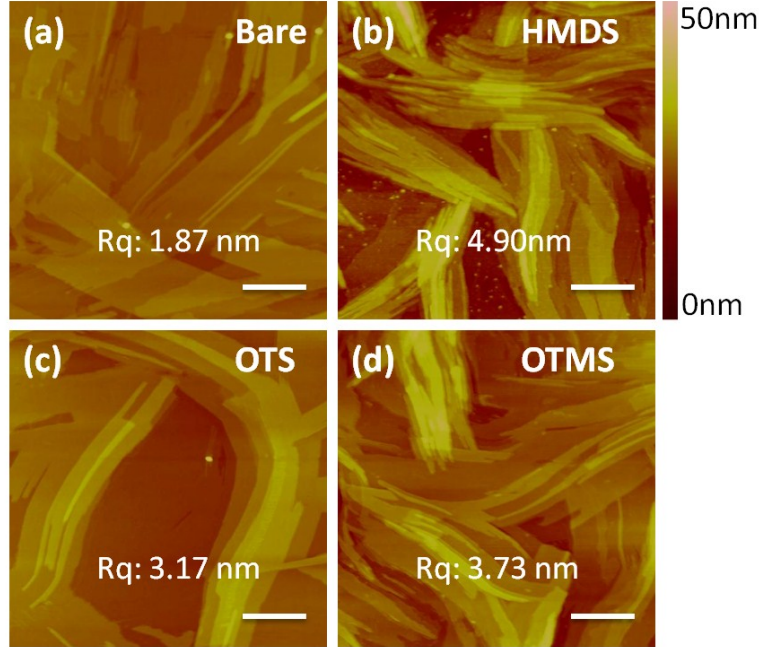


Fig. S7 AFM images of vacuum-deposited IZO thin films with the thickness of 10 nm on (a) unmodified bare SiO₂ substrate, (b) HMDS-modified substrate, (c) OTS-modified substrate, and (d) OTMS-modified substrates at the deposition temperatures of 90 °C. Inst: Rq refers to the root-mean-square roughness, scale bar: 1 μm.

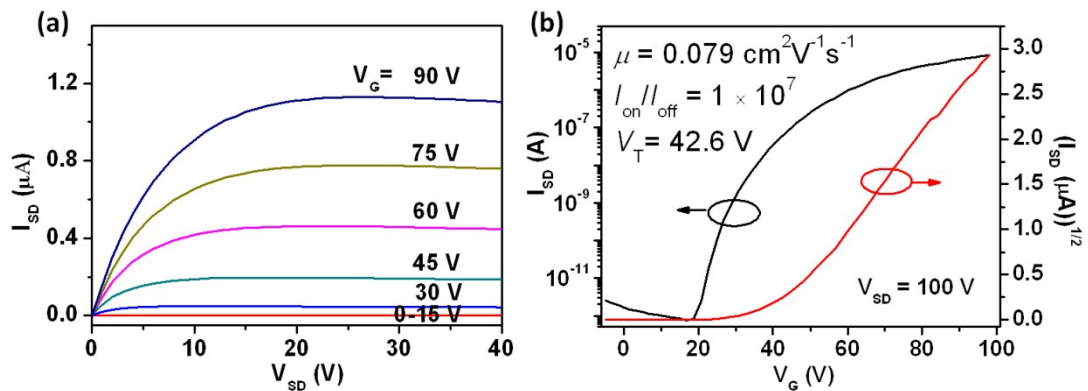


Fig. S8 Typical output (a) and transfer (b) characteristics of IZO film on the OTMS-modified SiO₂/Si substrate at the deposition temperature of 90 °C (Film thickness: 10 nm).

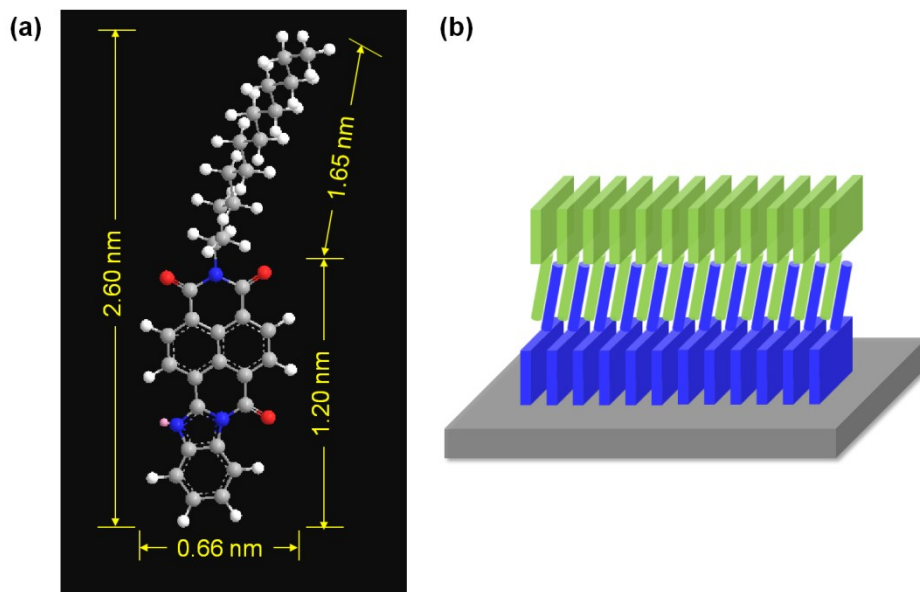


Fig. S9 (a) The molecule length calculated by Chem3D. (b) Schematic diagram of the speculated molecular packing in the thin film.

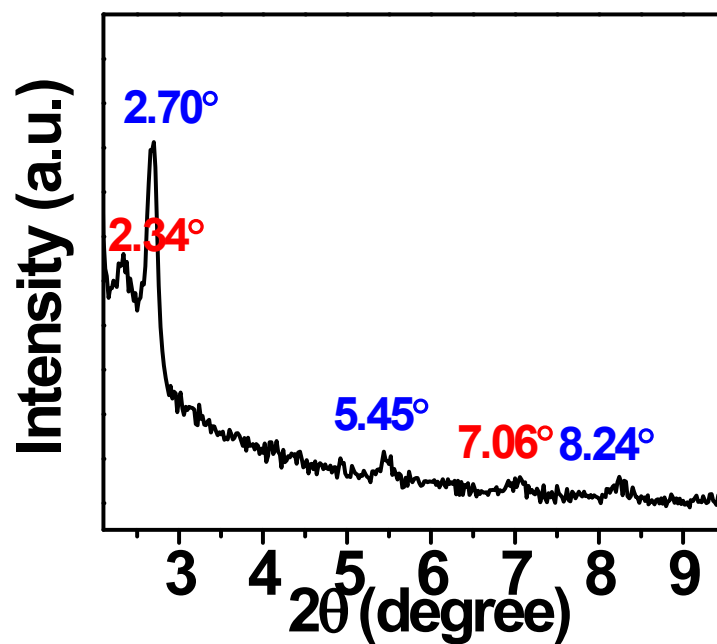


Fig. S10 XRD patterns of two-dimensional IZO crystalline film grown from PVT technique.

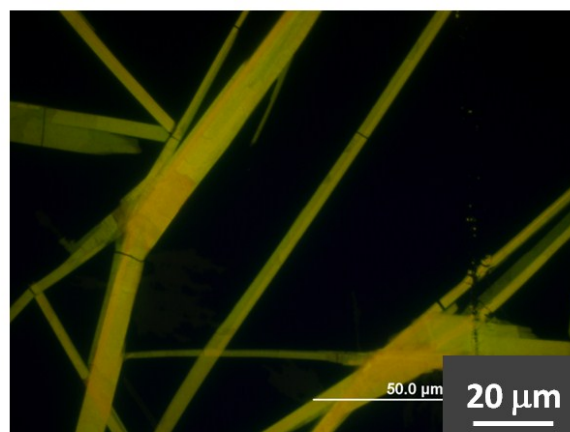


Fig. S11 Laser-scanning confocal microscopy image of the single-crystalline micro-ribbons grown from the PVT technique irritated by ultraviolet light.

Table S1. OFET characteristics of IZO vacuum-deposited thin films of 10 nm on different substrate conditions at the deposition temperatures of 90 °C.

T_{sub} (°C)	Substrate		μ (cm ² /Vs)	$I_{\text{on}}/I_{\text{off}}$	V_t (V)	Thickness (nm)
90	Bare	μ_{ave}	1.03×10^{-2}	1.70×10^6	46.4	10
		μ_{max}	1.35×10^{-2}	2.38×10^6	47.8	
	HMDS	μ_{ave}	1.26×10^{-2}	3.06×10^6	49.3	
		μ_{max}	1.39×10^{-2}	3.11×10^6	46.3	
	OTS	μ_{ave}	3.28×10^{-2}	9.78×10^6	51.7	
		μ_{max}	3.76×10^{-2}	9.37×10^6	51.0	
	OTMS	μ_{ave}	6.83×10^{-2}	1.37×10^7	38.1	
		μ_{max}	7.86×10^{-2}	1.12×10^7	42.6	