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Supporting information for

A simple single-thiophene derivative assists efficient as-cast ternary organic solar cells through Förster resonance energy transfer

Xuyu Gao,[a] Xianwang Tao,[a] Yuanyuan Xu,[a] Xiaochen Song,[a] Huabin Wang,[a] Ruitao Yu,[a] Jian Ye[b] and Youtian Tao*[a]

[a] *Key Lab for Flexible Electronics and Institute of Advanced Materials, Nanjing Tech University, 30 South Puzhu Road, Nanjing, 211816, P. R. China*

[b] *Duolun Technology Corporation Ltd, 1555 Tianyin Avenue, Nanjing, 211100, P. R. China*

E-mail: iamyttao@njtech.edu.cn (Y. Tao)

Materials and characterizations

All solvents were commercially available and used without further purification. PTB7-Th was synthesized according to previous literature. IEICO-4F was purchased from Nanjing Zhiyan Technology Co., Ltd.

^{1}H NMR spectrum was measured on a BRUKER AVANCE spectrometer. Elemental analysis was performed on a Vario EL III microanalyzer. Ultraviolet–visible (UV–vis) absorption spectra of the solution in chloroform and thin film on a quartz substrate were measured using a Shimadzu UV-2500 recording spectrophotometer. Electrochemical cyclic voltammetry was conducted on a CHI voltammetric analyzer in a 0.1 mol L^{-1} acetonitrile solution of tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) at a potential scan rate of 100 mV s^{-1}. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl wire pseudo-reference electrode. The samples were coated on the platinum sheet of the working electrode. The reference electrode was checked versus ferrocenium-ferrocene (Fc^+/Fc) as an internal standard as recommended by IUPAC (vacuum energy level: 24.8 eV). All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements. HOMO energy levels were calculated from the equation E_{HOMO}=−(4.80+$E_{onset(ox)}$) eV, and LUMO was calculated from E_{LUMO}=−(4.80+$E_{onset(re)}$) eV. Photoluminescence spectra were obtained using an Edinburgh FLS980 spectrophotometer. *J-V* curves of OSCs were measured on a computer-controlled Keithley 2400 Source Measure Unit. An Oriel Sol3A Class Solar Simulator (model, Enlitech SS-F5-3A) with a 450 W xenon lamp and an air mass 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm^{-2} by a silicon reference cell. EQE spectra were measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology, Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The contact angle measurements were performed using a KRUSS DSA1005 contact angle analyzer. Distilled deionized water and diiodomethane were employed as probe liquids. Blend film morphologies were characterized via Bruker Dimension ICON atomic force microscopy.

Fabrication of organic solar cell devices

Devices with an inverted structure of ITO/ZnO/active layer/MoO_3/Ag were fabricated. ITO (patterned indium tin oxide) glass was cleaned in an ultrasonic bath with acetone and isopropanol solvents and treated in an ultraviolet-ozone chamber for 30 min. ZnO was deposited through spin-coating onto ITO glass at 4000 rpm followed by thermal treatment at 200°C for 1 h. The thickness of the ZnO layer was calculated as 40 nm. Afterwards, PTB7-Th:IEICO-4F (1:1.5, w/w) with a total concentration of 20 mg mL^{-1} premixed in chlorobenzene solution was spin-coated at 2000 rpm to form ~90 nm thick active layers. No solvent additive or thermal-annealing process was employed. Finally, a layer of ca. 8 nm MoO_3 and then a Ag layer of *ca.* 100 nm were evaporated subsequently under high vacuum (*approx*. 8×10^{-5} Pa). The fabrication of ternary devices maintained the same process as the corresponding binary controls. TTZD was added according to the different weight ratios to PTB7-Th.

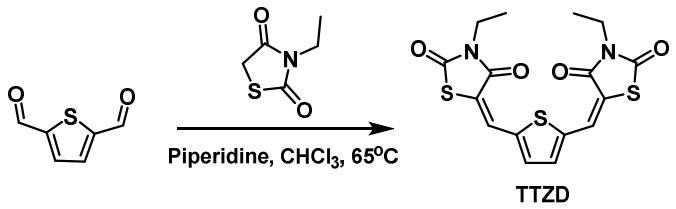
Fabrication of hole- and electron-only devices for SCLC measurements

Hole and electron mobility were measured using the space charge limited current (SCLC) method. Hole-only devices with the device structure of ITO/PEDOT:PSS/active layer/Au were used to measure the hole mobility, and electron-only devices were fabricated with the configuration of ITO/ZnO/active layer/PDINO/Al. The thicknesses of the active layers and buffer layers were measured with a stylus profiler (KLA Tencor P-7). The hole and electron mobilities were calculated by the Mott-Gurney equation.

Synthesis of TTZD

Scheme S1 depicts the synthetic route of TTZD. TTZD was synthesized through one-step Knoevenagel condensation by using thiophene-2,5-dicarbaldehyde and 3-ethylthiazolidine-2,4-dione as raw materials. In a two-neck bottle, thiophene-2,5-dicarbaldehyde (200 mg, 1.42 mmol), 3-ethylthiazolidine-2,4-dione (617 mg, 4.26 mmol) and piperidine (1 mL) were dissolved in 30 mL chloroform. The mixture was stirred at reflux for 10 hours under a nitrogen atmosphere. Then, the crude product was filtered and purified through Soxhlet extraction with methanol, hexene, ethyl acetate and chloroform as eluants. Finally, the extraction from chloroform was concentrated and precipitated with methanol again before drying under vacuum to

obtain yellow solid (524 mg). Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.01 (s, 2H), 7.41 (s, 1H), 3.84 (dd, *J* = 21.0, 6.0 Hz, 1H), 1.28 (t, *J* = 15.0 Hz, 12H). GC–MS (m/z): M^+ calculated at 394.48, found at 393.84; Anal. Calcd for $C_{16}H_{14}N_2O_4S_3$: C 48.72, H 3.58, N 7.10, S 24.38; found: C 48.46, H 3.69, N 7.25, S 24.44.



Scheme S1. Synthetic route of TTZD.

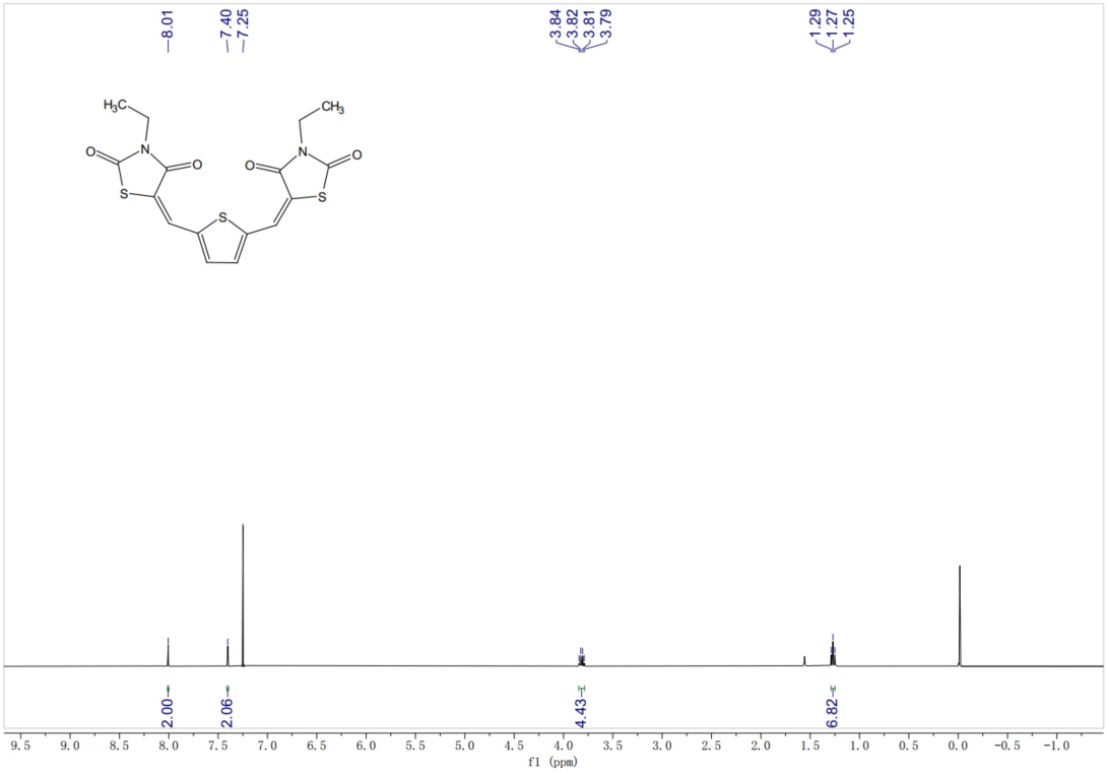


Figure S1. ^{1}H NMR spectrum of TTZD.

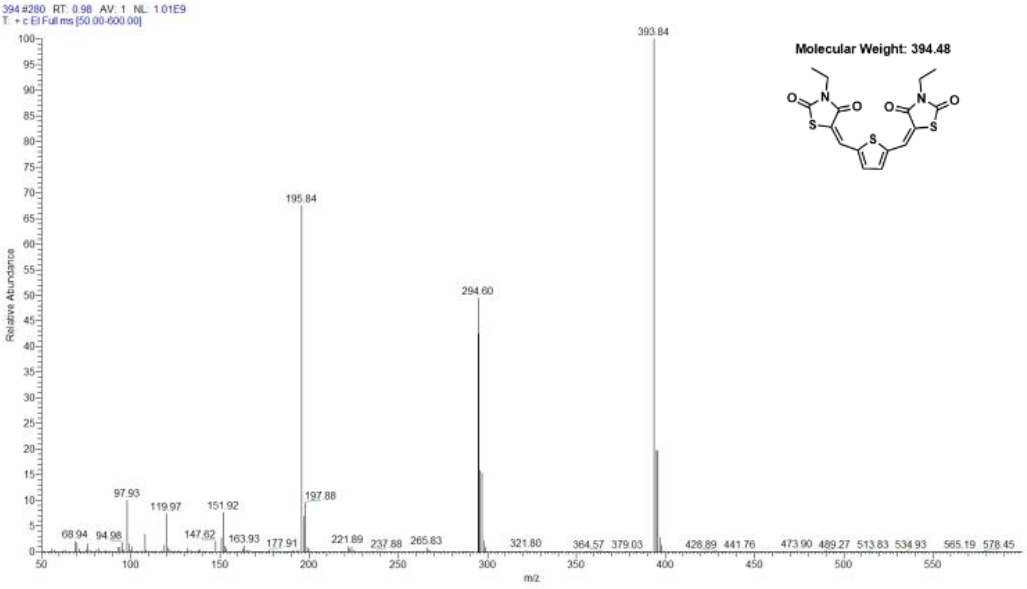


Figure S2. Mass spectrum of TTZD.

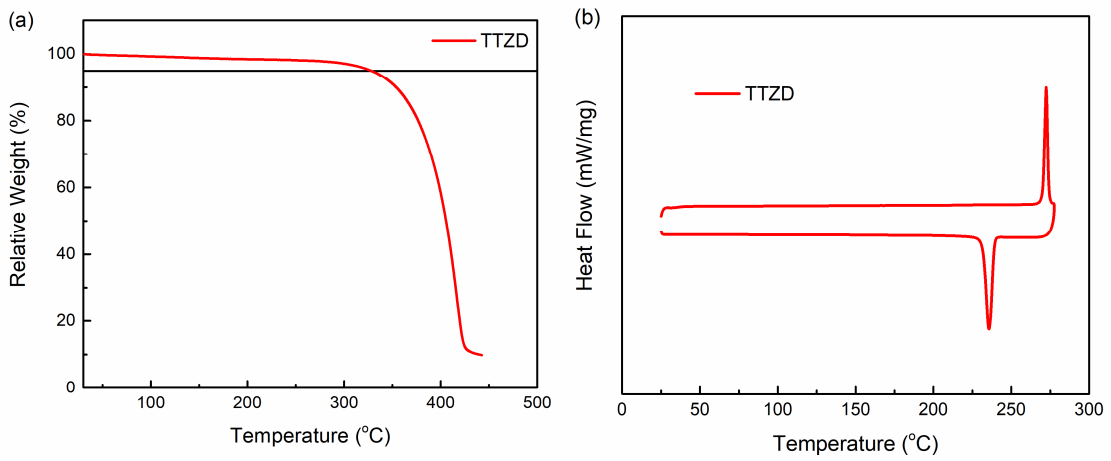


Figure S3. (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) curves of TTZD.

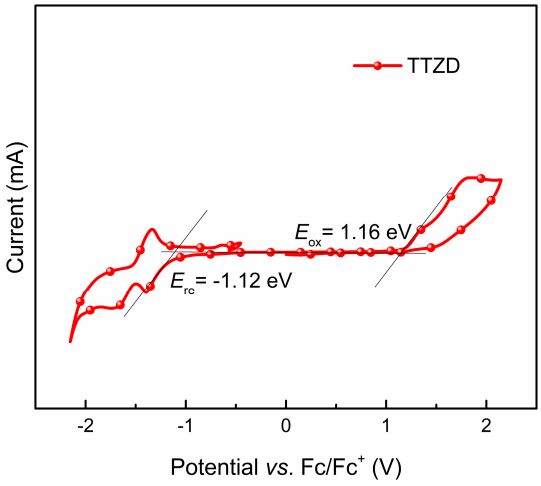


Figure S4. Cyclic voltammetry (CV) curves of TTZD.

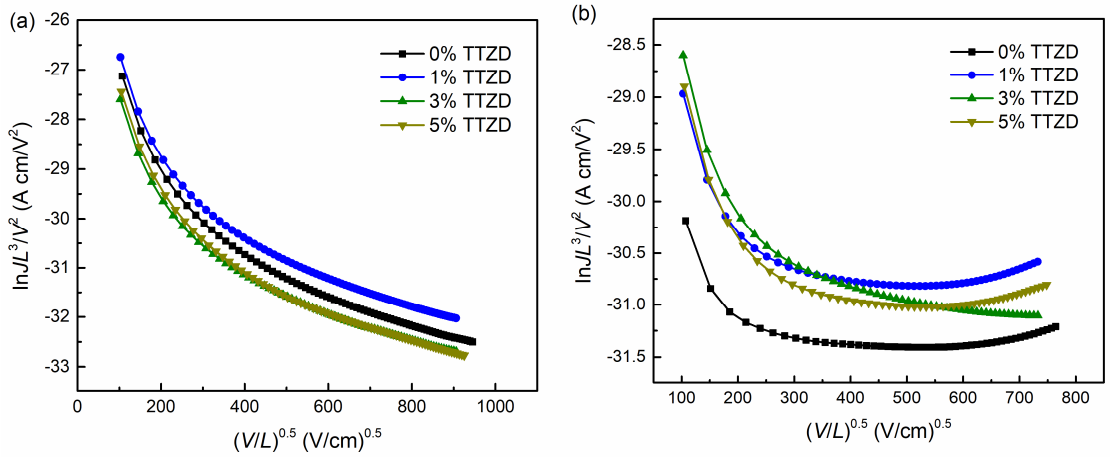


Figure S5. *J-V* curves fitted by the SCLC method for hole- (a) and electron-only (b) devices.

Table S1. Key parameters of the contact angel measurement of different neat films.

Film surface	ϑ_w [°]	ϑ_{oil} [°]	γ_d [mN m^{-1}]	γ_p [mN m^{-1}]	γ [mN m^{-1}]
PTB7-Th	99.6	51.3	33.55	0.21	33.76
IEICO-4F	100.7	39.1	40.06	1.58×10^{-4}	40.06
TTZD	77.3	32.5	43.16	3.70	46.86