

Supporting Information for

A Thieno[3,4-b]pyrazine-based A₂-A₁-D-A₁-A₂ Type Low Bandgap Non-fullerene Acceptor with 1,1-dicyanomethylene-3-indanone (IC) as the Terminal Groups

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1: Materials and Methods

Materials. All Chemicals and solvents were reagent grades and purchased from Alfa, Aldrich, TCI, Innochem, Beijing Chemical Plant or other chemical companies and used without further purification. The compounds 3 were synthesized according to the procedures in the literatures¹.

Synthetic Procedure. Compound 3 (400 mg, 0.26 mmol), 1,1-dicyanomethylene-3-indanone (IC) (301 mg, 1.56 mmol), chloroform (30 mL) and pyridine (1 mL) were added to a two-necked round-bottom flask. The mixture was deoxygenated with nitrogen for 10 minutes, and then refluxed for 30 minutes. After cooling to room temperature, the mixture

was poured into methanol (100 mL) and stirred for 10 minutes, then filtered. The residue was purified by column chromatography on silica gel with CHCl_3 as an eluent yielding a dark solid (280mg, 52% yield). $^1\text{H NMR}$ (400 M, CDCl_3): δ (ppm) 10.31(s, 2H), 8.82(s, 2H), 8.77 (d, 2H), 8.60(d, 2H), 8.00(d, 2H), 7.94(d, 2H), 7.79(m,12H), 7.46(ddd, 12H), 2.23(d, 4H), 1.11(m, 18H), 0.84(s, 6H), 0.73(t, 6H). MALDI-TOF MS (m/z) calcd:1370.5, found:1371.1 (M+H)⁺

Methods. $^1\text{H NMR}$ spectra were obtained using an Avance III 400 (Bruker, Billerica, MA; 400 MHz) NMR spectrometer. UV-vis absorption spectra were acquired on a Lambda 950 spectrophotometer (PerkinElmer, Waltham, MA). Thermogravimetric analysis (TGA) was recorded on Diamond TG/DTA under the protection of nitrogen at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$. Cyclic voltammetry (CV) was performed on a CHI-600E electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., Shanghai, China) using a platinum plate coated with a thin blend film, a platinum wire, and an Ag/AgCl electrode as the working electrode, counter electrode, and reference electrode, respectively. The CV system was calibrated using the ferrocene–ferrocenium (Fc/Fc⁺) redox couple in a 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in acetonitrile. Photoluminescence spectra was tested on Perkin Elmer Instruments (shanghai) Co. Ltd, USA. Atomic force microscopy (AFM) images of the blend films were obtained on a MultiMode 8 scanning probe microscope (Bruker).

2: Fabrication and characterization of photovoltaic cells

A patterned ITO was pre-cleaned by detergent, deionized water, acetone and 2-propanol for 15 min, respectively, under ultrasonic condition. The cleaned ITO was then treated by ultraviolet ozone cleaner (Jelight Company, USA) to form the hydrophilic surface. The PEDOT:PSS solution was spin-coated on the ITO at 3500 rpm for 30s and dried over 150°C for 15 min under air. The **PBDB-T: TP28** solution (optimized weight ratio of 1:1) in

chlorobenzene was then spin-coated above PEDOT:PSS layer at a total concentration of 20 mg/mL within a nitrogen-filled glove box. Then the active layer was used CB as solvent and spin speed of 3000 rpm for the active layer, the D/A weight ratio of 1:1 and annealing temperature of 140 °C for 10 min. The Ca (20 nm) and Al (80 nm) cathode were evaporated onto the active layer under a pressure of below 3×10^{-6} mbar with an active area of 4 mm². The current density-voltage curves were collected by a Keithley 2420 under Oriel Newport 150W solar simulator (AM 1.5G). The thicknesses of the active layer were detected by Alpha-atopD-120stylus profilometer, Kla-Tencor.

The EQEs were measured by an Oriel Newport System. All above measurements were done at room temperature in air. The mobility of hole-only or electron-only of the PSCs device was achieved by fabricated the architecture ITO/PEDOT:PSS/active layer/Au for holes or ITO/TiOx/active layer/Al for electrons, where TiOx layer was fabricated by sol-gel method from titanium (diisopropoxide) bis (2,4-pentanedionate), 75% in isopropanol liquid (TIPD).

3: ¹H NMR Spectra and MALDI-TOF MS of the Monomers

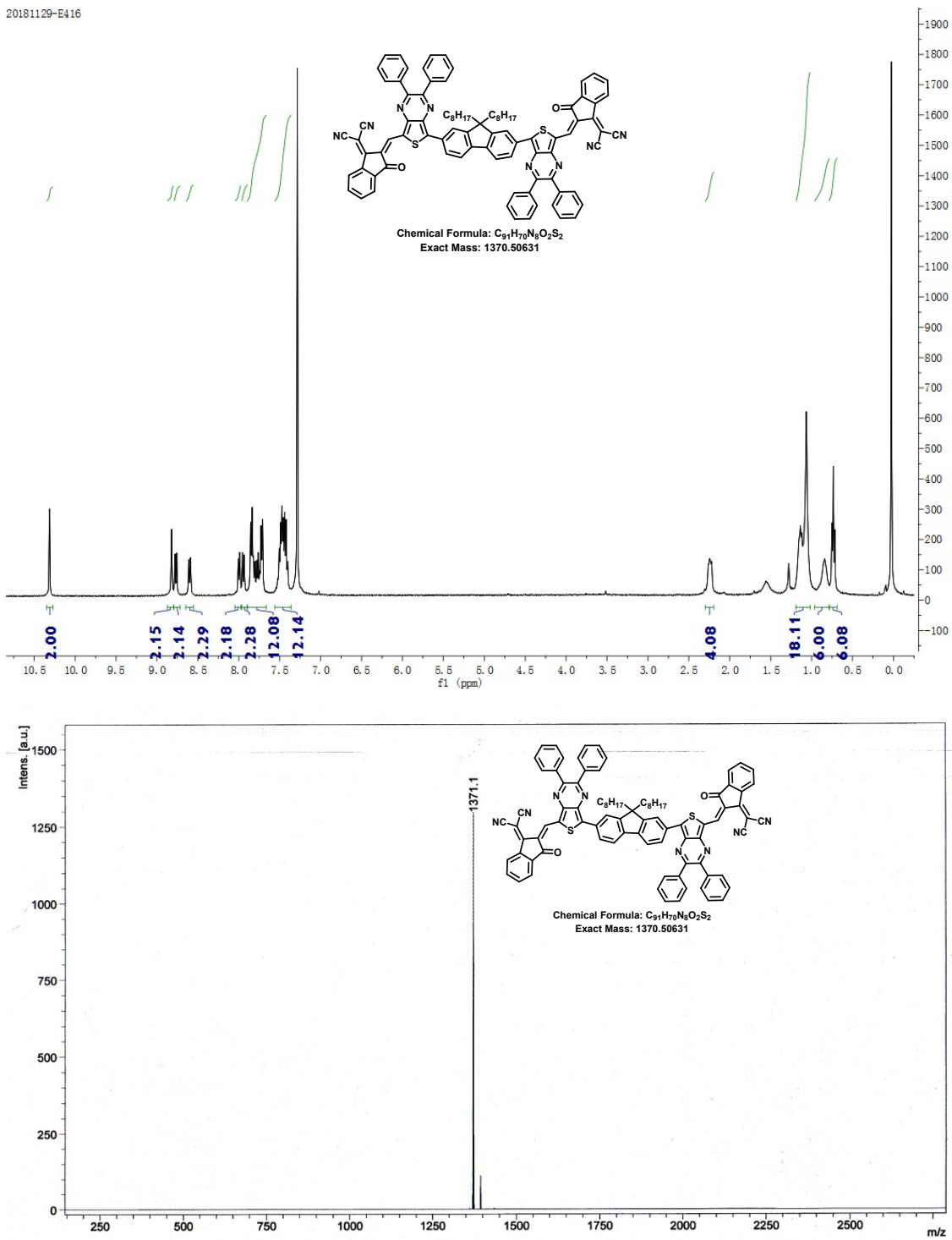


Figure S1. ^1H NMR and MALDI-TOF MS of TP28.

4: Thermogravimetric analysis, Cyclic voltammogram, Gaussian calculate result, The J - V curves of the electron-only devices and PL spectra

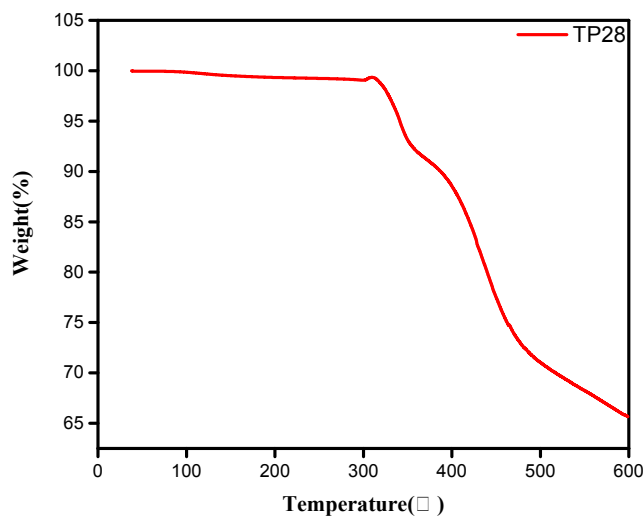


Figure S2. Thermogravimetric analysis ($10^{\circ}\text{C min}^{-1}$ at N_2 atmosphere) of **TP28**.

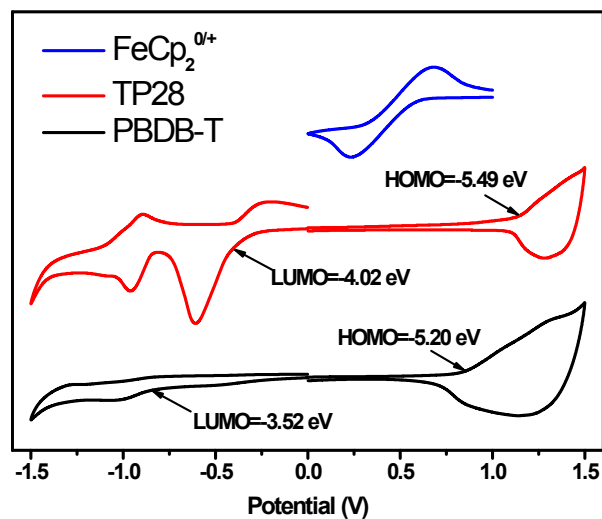


Figure S3. Cyclic voltammogram of **TP28** films on a platinum plate in acetonitrile solution of $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ (Bu = butyl) at scan rate of 50 mV s^{-1} .

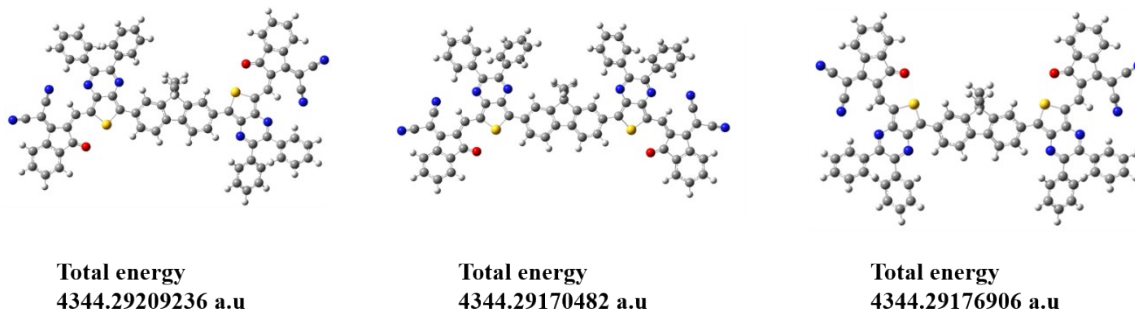


Figure S4. The total energy of three isomers of TP28.

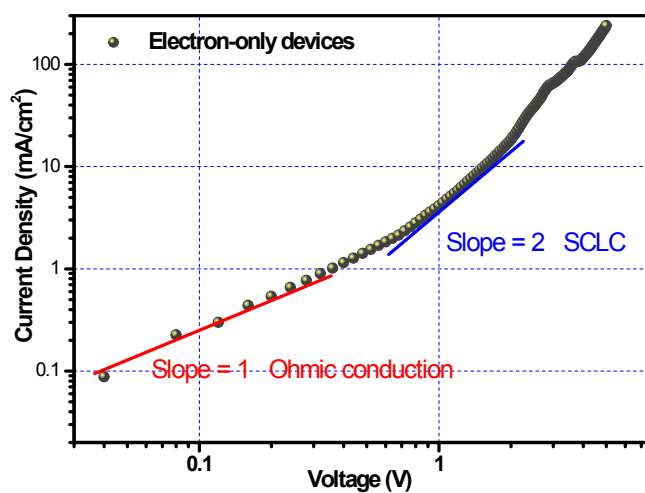


Figure S5. the electron-only devices of ITO/TiOx/active layer/Al for electrons.

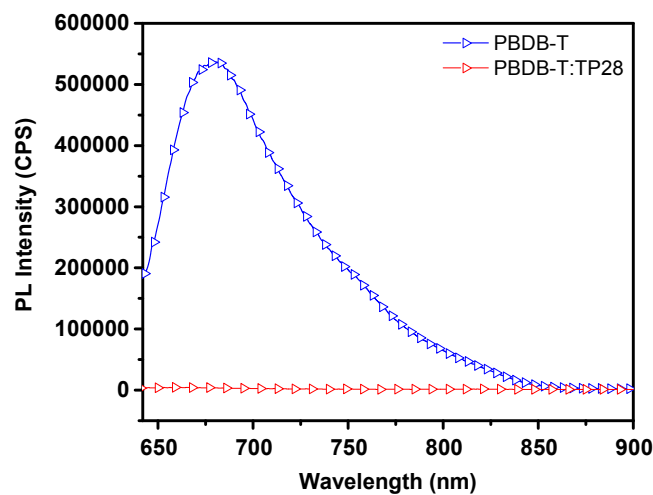


Figure S6. PL spectra of PBDB-T:TP28 blend film, together with donor film.

5: Photovoltaic results

Table S1. Photovoltaic performance parameters of the PSCs based on PBDB-T: TP28 with various blend weight ratios.

D/A	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF	PCE (%)
1.5:1	0.77	8.70	54.89	3.68
1:1	0.76	10.04	59.89	4.57
1:1.5	0.75	8.89	61.21	4.08

Table S2. Photovoltaic performance parameters of the PSCs based on PBDB-T: TP28 with different additives and the annealing temperatures.

Additive	TA(°C)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF	PCE (%)
NO	120	0.76	10.36	61.11	4.81
	140	0.76	11.03	61.31	5.14
1%DPE	120	0.77	11.79	57.72	5.24
	140	0.77	11.62	59.46	5.32
1%CN	120	0.77	10.11	62.57	4.87
	140	0.76	10.58	62.92	5.06
1%DIO	120	0.76	0.73	45.20	0.25
	140	0.77	0.79	44.10	0.27

Table S3. Photovoltaic performance parameters of the PSCs based on PBDB-T: TP28 with different proportion of additives.

	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF	PCE (%)
NO	0.76	11.03	61.31	5.14
1%DPE	0.77	11.62	59.46	5.32
3%DPE	0.77	7.67	50.29	2.97
5%DPE	0.76	2.65	33.78	0.68

References

1. Li, J.; Yang, J.; Hu, J.; Chen, Y.; Xiao, B.; Zhou, E., The first thieno[3,4-b]pyrazine based small molecular acceptor with a linear A2–A1–D–A1–A2 skeleton for fullerene-free organic solar cells with a high Voc of 1.05 V. *Chem. Commun.* **2018**, *54*, 10770-10773.