

Supporting Information

An effective way to reduce energy loss and enhance open-circuit voltage in polymer solar cells based on a diketopyrrolopyrrole polymer containing regular alternating ternary units

Yahui Liu,^a Guangwu Li,^a Zhe Zhang,^a Liangliang Wu,^a Jianya Chen,^b Xinjun Xu,^{*a} Xuebo Chen,^a Wei Ma,^b Zhishan Bo^{*a}

^aBeijing Key Laboratory of Energy Conversion and Storage Materials,
College of Chemistry, Beijing Normal University, Beijing 100875, China.

E-mail: xuxj@bnu.edu.cn, zsbo@bnu.edu.cn. Tel: +86-10-62206891.

^bState Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China.

Keywords: conjugated polymers, polymer solar cells, DPP based polymer, ternary copolymerization.

Experiment Part

1.1 Material and Instruments.

Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature and stored in a Schlenk tube under nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from Na under nitrogen atmosphere. N,N-Dimethylformamide (DMF) was distilled from CaH₂ under reduced pressure. Unless otherwise noted, all reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel. Column chromatography was carried out on silica gel (200-300 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) were performed on TA2100 under a nitrogen atmosphere at a heating rate of 10 °C/min to record TGA curves. The gel permeation chromatography (GPC) measurements were performed at 80 °C on a PL-220 (Polymer Laboratories) chromatography connected to a differential refractometer with chlorobenzene as an eluent. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. The powder X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO MPD diffractometer with Cu KR radiation. The electrochemical behavior of the polymers was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu₄NPF₆ solution in CH₃CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO₃ (0.01 M in CH₃CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (F_c) redox system and assumption that the energy level of F_c is 4.8 eV below vacuum.

1.2 Polymer Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/PEDOT:PSS (30 nm)/polymer:PC₇₁BM/LiF/Al (100 nm). The conductivity of ITO is 20 Ω. PEDOT:PSS (Baytron AL 4083 from H.C. Starck) was filtered with a 0.45 μm polyvinylidene difluoride (PVDF) film before

use. A PEDOT:PSS thin layer was spin-coated on top of the cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 °C for 20 min on a hotplate. The thickness of the PEDOT:PSS layer is about 30 nm. A mixture of polymer and PC₇₁BM in chlorobenzene (CB with different additive ratios) was stirred at dissolving temperature (110 °C) more than two hours to ensure sufficient dissolution and then the blend solution (cooled to 90 °C) was spin-coated onto PEDOT:PSS layer to form active layer. On one substrate five cells with an effective area of 0.04 cm² for each were fabricated. Current-voltage (I-V) and external quantum efficiency (EQE) measurements were conducted in air without encapsulation. I-V characteristics were recorded at room temperature using an Agilent B2902A Source Meter under the illumination of an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mW cm⁻² and the white light intensity was calibrated with a standard single-crystal Si solar cell

1.3 Space-Charge Limited Current Measurement

Hole devices with a structure of ITO/PEDOT:PSS (30 nm)/polymer:PC₇₁BM /Au were fabricated. The blend solution of **PCDPP** and PC₇₁BM in CB (1% DIO) was spin-coated onto PEDOT:PSS layer to form active layer like PSC devices, and Au was thermally evaporated at a pressure of 10⁻⁴ Pa through a shadow mask. Dark J-V curves of the hole/electron devices were measured by the space-charge limited current (SCLC) method.

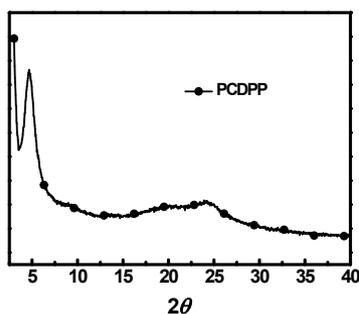


Figure S1. X-ray diffraction of PCDPP powdery sample.

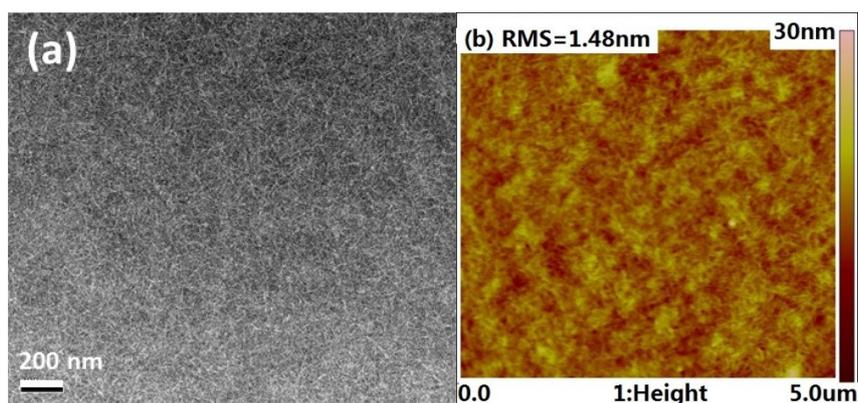


Figure S2. AFM (a) and TEM (b) images of PCDPP:PC₇₁BM (1:2 by weight) blend.

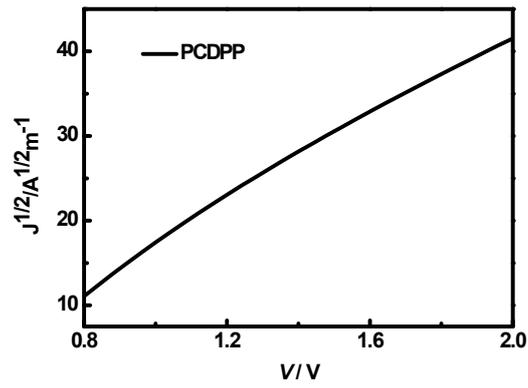


Figure S3. The hole mobility of blend film based on PCDPP.

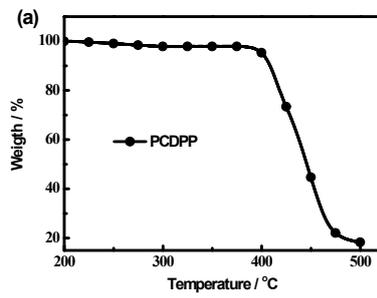


Figure S4. TGA curves of PCDPP.

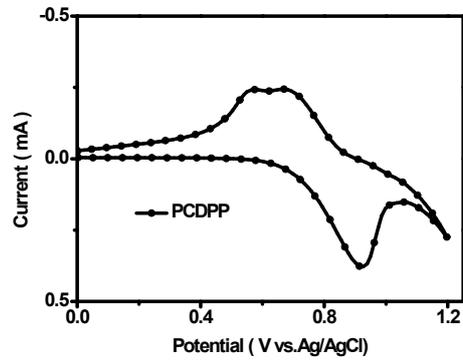


Figure S5. Cyclic voltammogram of polymers in films on Pt electrode measure in 0.1 M Bu_4NPF_6 acetonitrile solutions for oxidation at a scan rate of 100 mV/s.

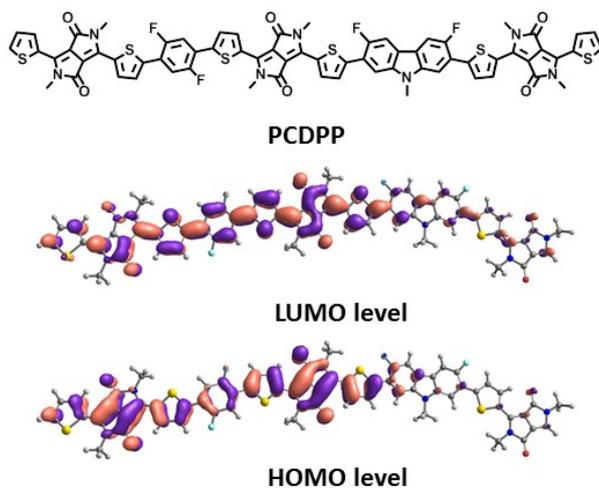


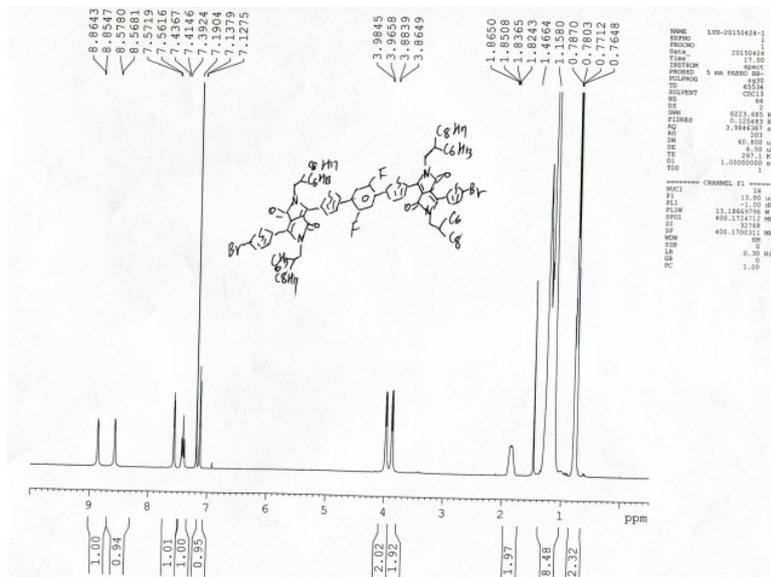
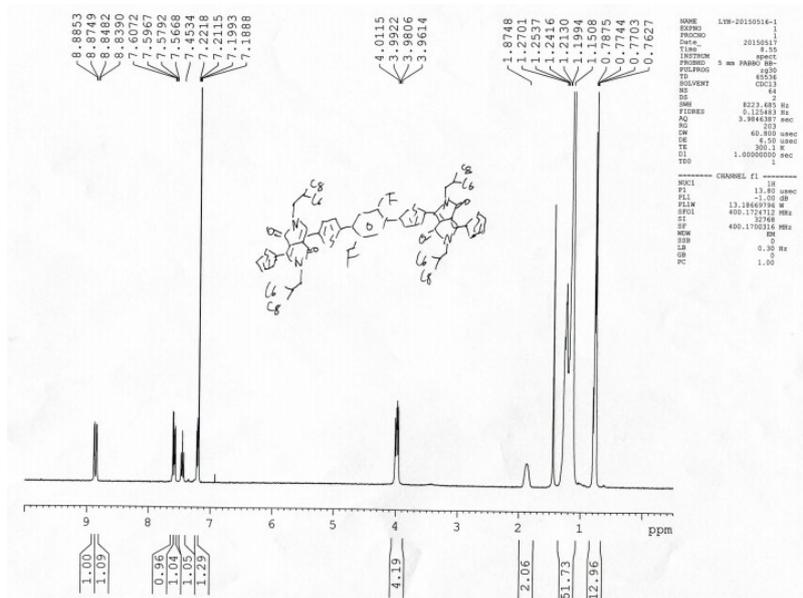
Figure S6. Optimized frontier molecular orbitals using DFT evaluated at the B3LYP/6-31G(d) level of theory.

Table S1. Photovoltaic Parameter of PCDPP-based device with different additive ratios and spin-coating rates.

Solvent (additives)	Spin-coating rate (r/min)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF(%)	PCE (%) _{max}
CB (0.5% DIO)	750	0.87	14.1	0.68	8.25
	500	0.86	16.00	0.63	8.72
CB (1% DIO)	750	0.86	16.00	0.65	9.02
	1000	0.86	14.90	0.67	8.60
CB (1.5% DIO)	750	0.87	15.6	0.63	8.55
CB (2% DIO)	750	0.87	15.4	0.62	8.29

Table S2. Device Performance of DPP polymer solar cells over 8%.

Polymer	V_{oc} (V)	J_{sc} (mA/cm ⁻²)	FF	PCE (%)	E_g (eV)	E_{loss} (eV)	EQE _{max}	Reference
PDPP3T<i>alt</i>TP T	0.75	15.9	0.67	8.0	1.43	0.69	0.59	S1
PDPP2T-TT	0.67	20.1	0.70	9.4	1.35	0.68	0.51	S2
C3-DPPTT-T	0.57	23.5	0.66	8.8	1.39	0.82	0.51	S3
PCDPP	0.86	16.0	0.65	9.0	1.55	0.69	0.68	this work



Reference

[S1] K. H. Hendriks, G. H. L. Heintges, V. S. Gevaerts, M. M. Wienk and R. A. J. Janssen, *Angew. Chem. Int. Ed.*, 2013, **52**, 8499-8502.

[S2] H. Choi, S. J. Ko, T. Kim, P. O. Morin, B. Walker, B. H. Lee, M. Leclerc, J. Y. Kim and A. J.

Heeger, *Adv. Mater.*, 2015, **27**, 3318-3324.

[S3] R. S. Ashraf, I. Meager, M. Nikolka, M. Kirkus, M. Planells, B. C. Schroeder, S. Holliday, M. Hurhangee, C. B. Nielsen and H. Sirringhaus, *J. Am. Chem. Soc.*, 2015, **137**, 1314-1321.