

Supporting Information

Donor-Acceptor Copolymers Based on Thermally Cleavable Indigo, Isoindigo and DPP Units: Synthesis, Field Effect Transistors, and Polymer Solar Cells

Chunchen Liu,[†] Sheng Dong,[†] Ping Cai,[†] Peng Liu,[†] Shengjian Liu,[†] Junwu Chen,[†] Feng Liu,[‡] Lei Ying,^{*,†} Thomas P. Russell,^{*,‡} Fei Huang,^{*,†} and Yong Cao[†]

[†]*Institute of Polymer Optoelectronic Materials & Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China*

[‡]*Department of Polymer Science and Engineering, University of Massachusetts Amherst, Massachusetts 01003, United States*

E-mail: msfhuang@scut.edu.cn; msleiyiing@scut.edu.cn; russell@mail.pse.umass.edu

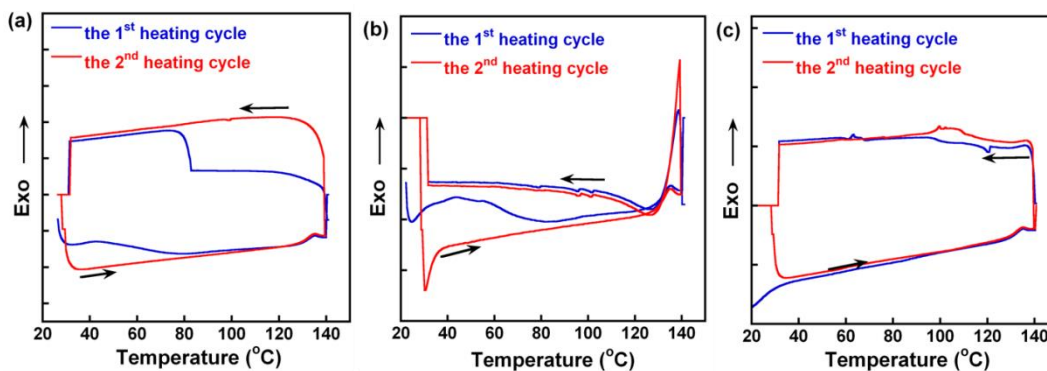


Figure S1. DSC characteristics of Boc-PBDT-I (a), PBDT-II (b), and PBDT-DPP (c) within the temperature range from 25 °C to 140 °C.

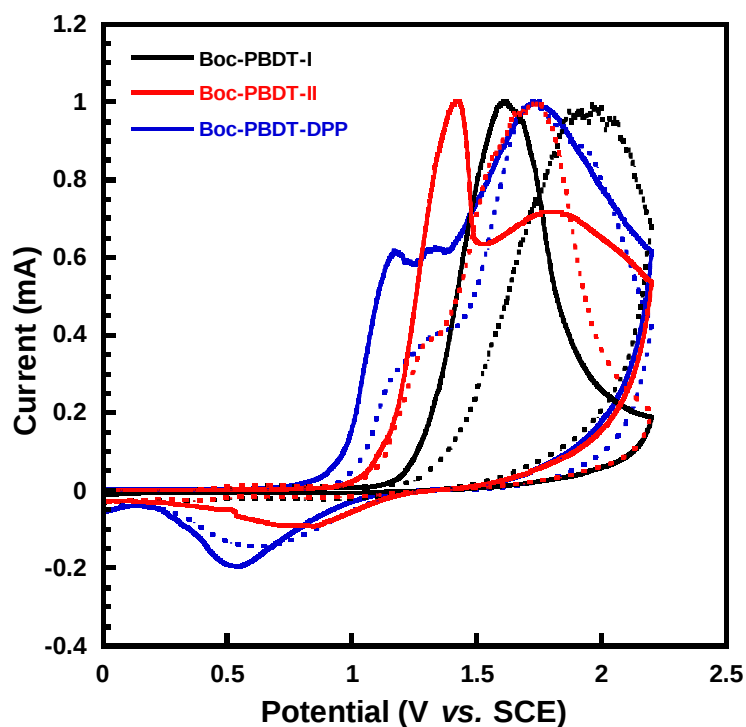
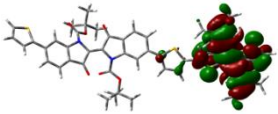
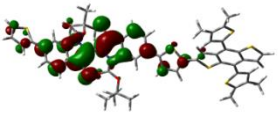
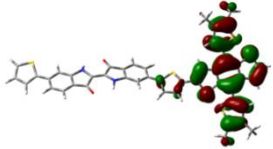
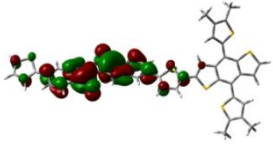
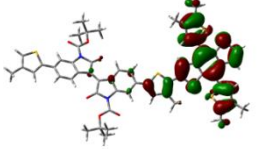
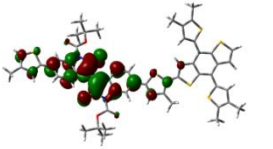
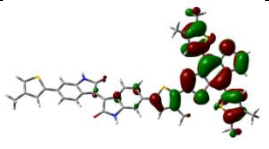
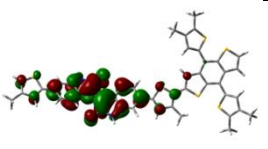
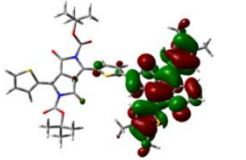
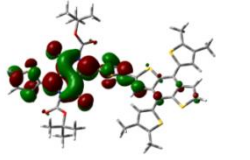
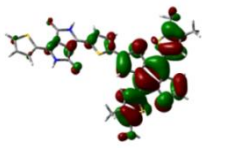
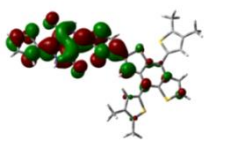


Figure S2. Cyclic voltammograms of copolymer thin films on ITO-coated glass electrode: the dotted lines represent the copolymer thin films after thermal cleavage at 200 °C for 10 min.

Table S1. Optimized geometries and charge-density surfaces for the HOMO and LUMO energy levels of copolymer units based on DFT calculation at B3LYP/6-31 G(d) basis with the Gaussian 09 package.

	HOMO	LUMO	HOMO LUMO →
Boc-BDT-I	 HOMO = -4.81 eV	 LUMO = -2.87 eV	1.94 eV
BDT-I	 HOMO = -4.77 eV	 LUMO = -2.75 eV	2.02 eV
Boc-BDT-II	 HOMO = -4.69 eV	 LUMO = -3.08 eV	1.61 eV
BDT-II	 HOMO = -4.66 eV	 LUMO = -2.80 eV	1.86 eV
Boc-BDT-DPP	 HOMO = -4.77 eV	 LUMO = -2.67 eV	2.10 eV
BDT-DPP	 HOMO = -4.77 eV	 LUMO = -2.55 eV	2.22 eV

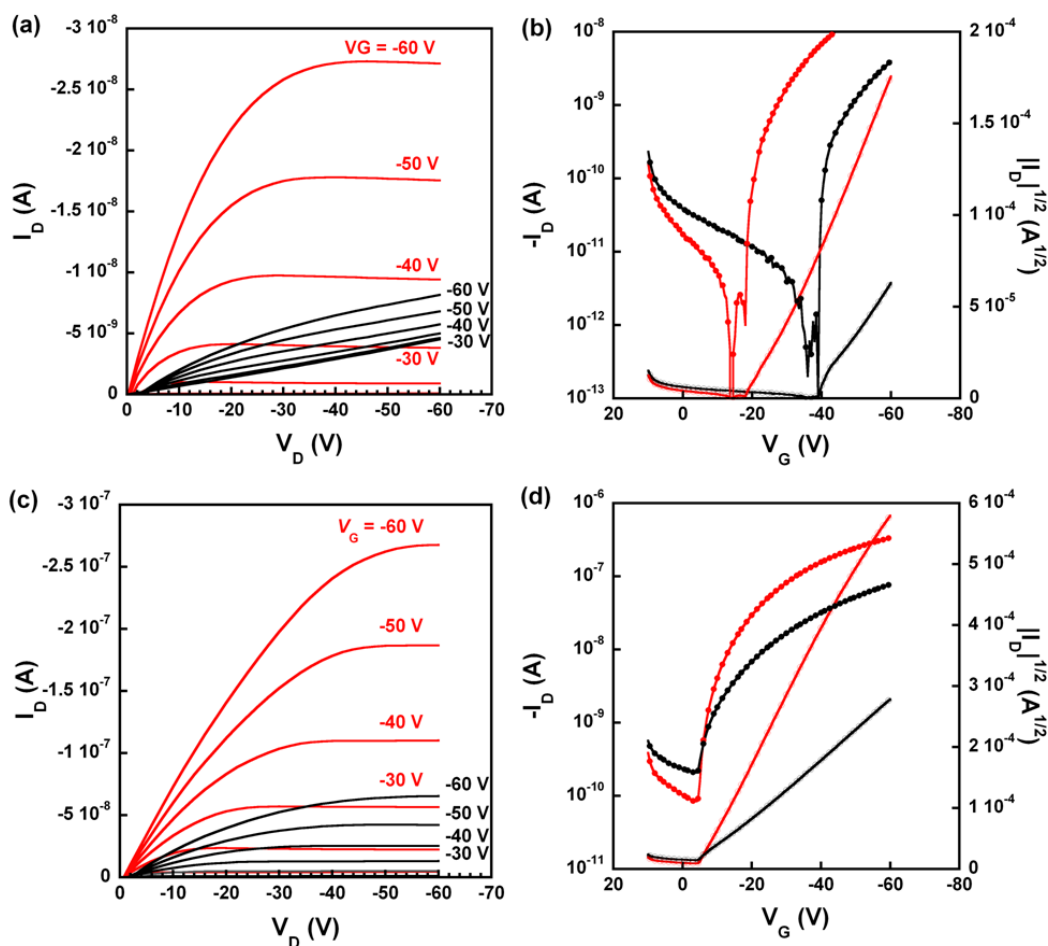


Figure S3. The OFET output and transfer characteristics of copolymers Boc-PBDT-I (a, b) and Boc-PBDT-II (c, d) with (red curves) or without (black curves) thermal cleavage at 200 °C for 10 min.

Table S2. Hole mobilities of copolymers with or without cleavage of *t*-Boc group measured by OFET

copolymer	Boc-PBDT-I	Boc-PBDT-II	Boc-PBDT-DPP
Pristine film (cm ² V ⁻¹ s ¹)	4.06×10 ⁻⁶	1.91×10 ⁻⁵	1.30×10 ⁻⁴
Annealed film (cm ² V ⁻¹ s ⁻¹)	3.24×10 ⁻⁵	9.05×10 ⁻⁵	7.89×10 ⁻⁴

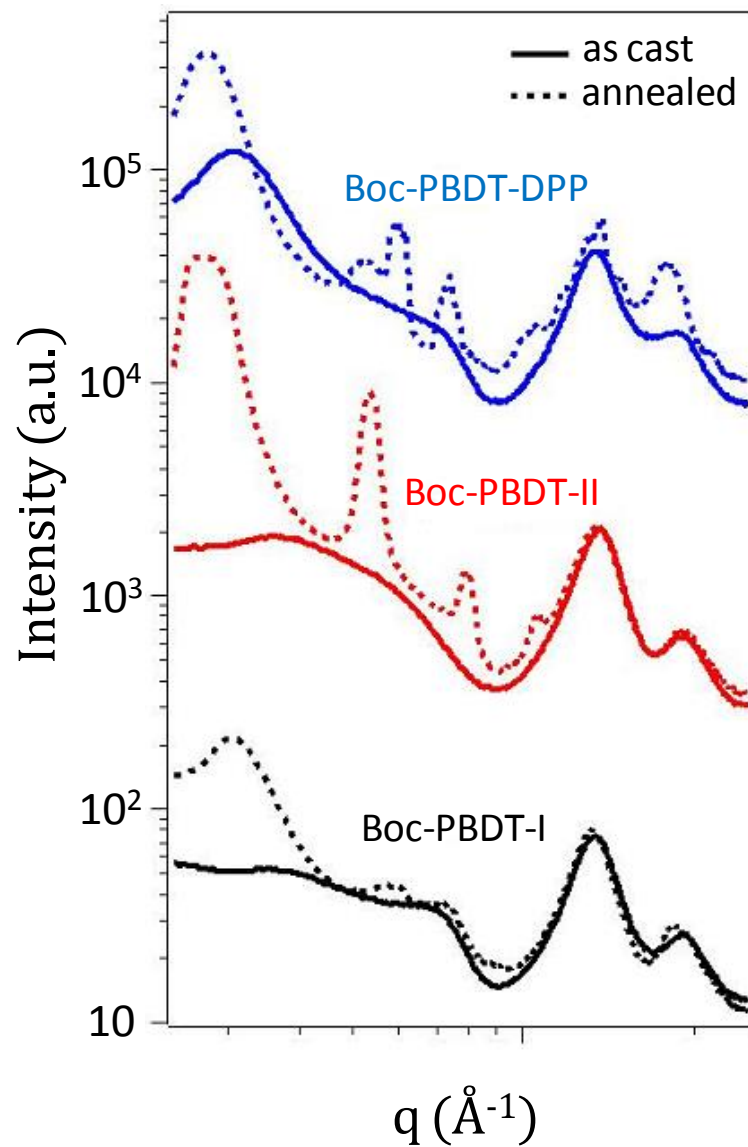


Figure S4. Out-of-plane line cut profiles of polymer:PC₇₁BM blends in GIXD. Boc-PBDT-I blend (black lines); Boc-PBDT-II blend (red lines); Boc-PBDT-DPP blend (blue lines).

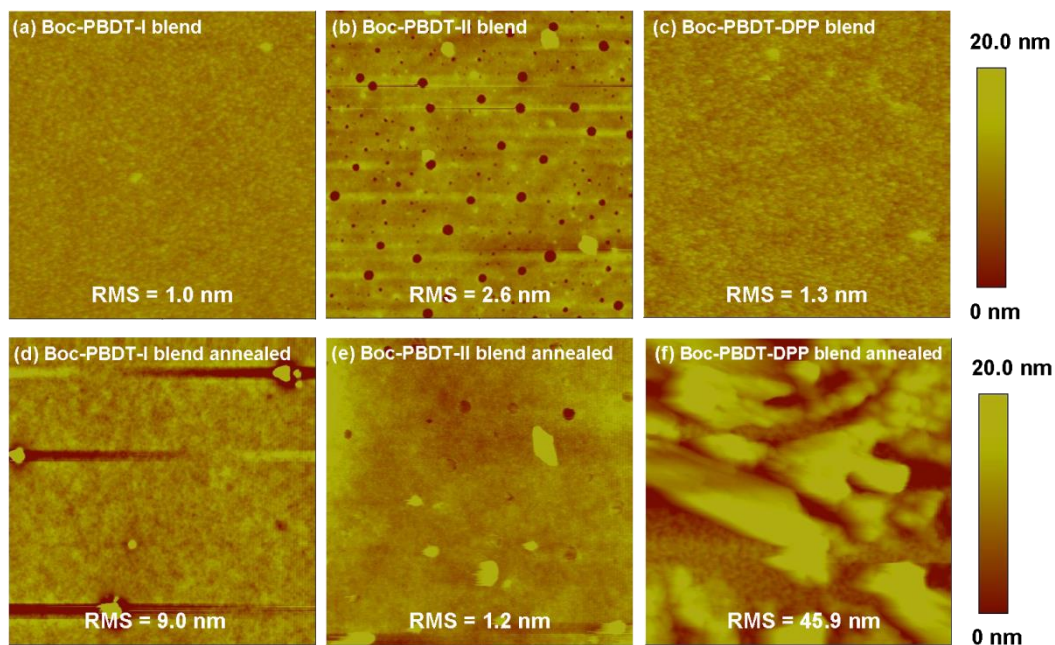


Figure S5. Tapping mode AFM images (5 $\mu\text{m} \times 5 \mu\text{m}$) of polymer: PC₇₁BM thin films. (a), (b), (c) as coated and (d), (e), (f) with thermal cleavage treatment, (a), (d) for Boc-PBDT-I; (b), (e) for Boc-PBDT-II; (c), (f) for Boc-PBDT-DPP.

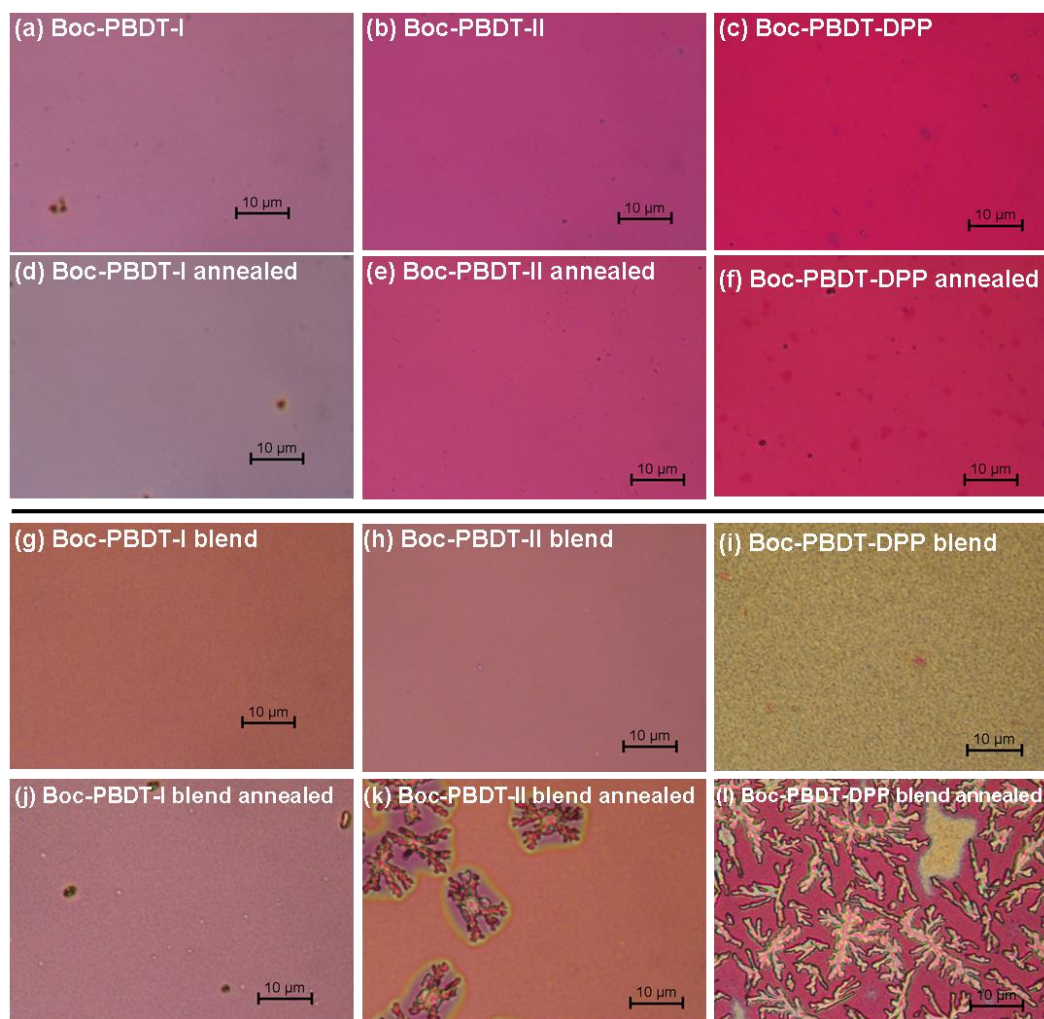


Figure S6. Polarized optical microscopy (POM) pictures of pristine polymers and blend films (copolymer: PC₇₁BM) before or after thermal cleavage of *t*-Boc groups. (a) Boc-PBDT-I pristine film; (b) Boc-PBDT-II pristine film; (c) Boc-PBDT-DPP pristine film; (d) Boc-PBDT-I annealed film; (e) Boc-PBDT-II annealed film; (f) Boc-PBDT-DPP annealed film; (g) Boc-PBDT-I: PC₇₁BM pristine film; (h) Boc-PBDT-II: PC₇₁BM pristine film; (i) Boc-PBDT-DPP: PC₇₁BM pristine film; (j) Boc-PBDT-I: PC₇₁BM annealed film; (k) Boc-PBDT-II: PC₇₁BM annealed film; (l) Boc-PBDT-DPP: PC₇₁BM annealed film

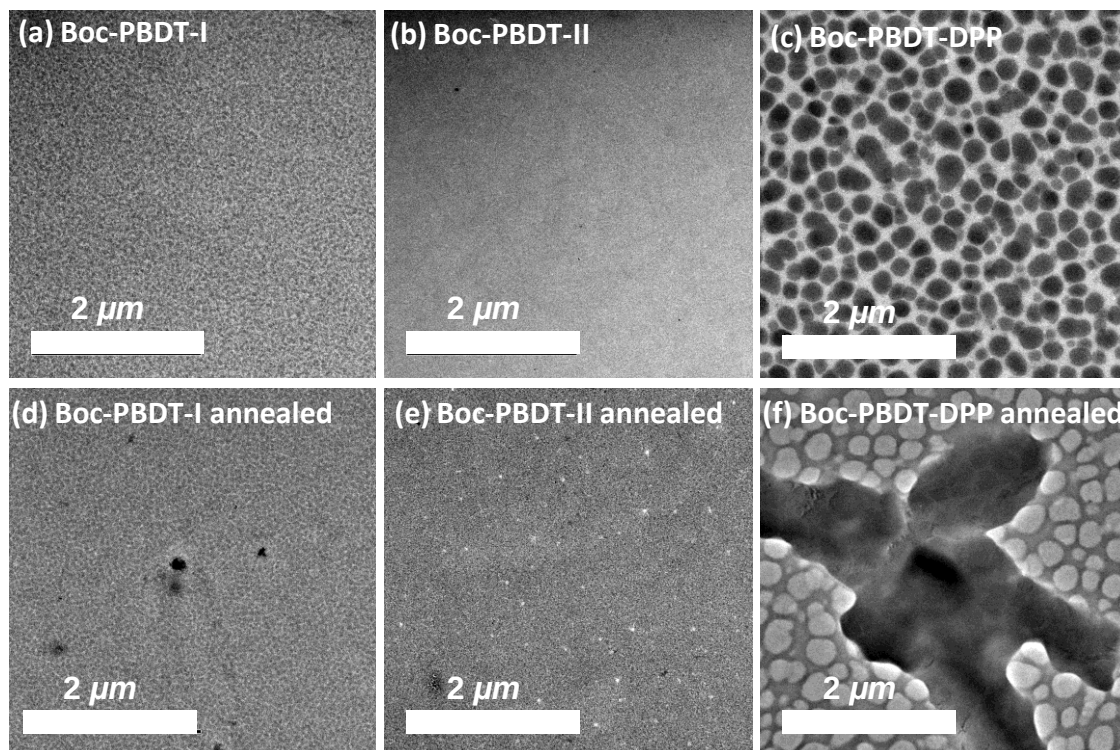


Figure S7. TEM images (the inset size of 2 μm) of polymer: PC₇₁BM blend films as coated (a, b, c) and with thermal cleavage treatment by annealing at 200 °C for 10 min (d, e, f). (a) Boc-PBDT-I pristine blend film; (b) Boc-PBDT-II pristine blend film; (c) Boc-PBDT-DPP pristine blend film; (d) Boc-PBDT-I annealed blend film; (e) Boc-PBDT-II annealed blend film; (f) Boc-PBDT-DPP annealed blend film.