Electronic Supplementary Information

for

A Double B←N Bridged Bipyridine (BNBP)-Based Polymer Electron Acceptor: All-Polymer Solar Cells with High Donor:Acceptor Blend Ratio

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1. ^{1}H, ^{13}C and ^{11}B NMR spectra

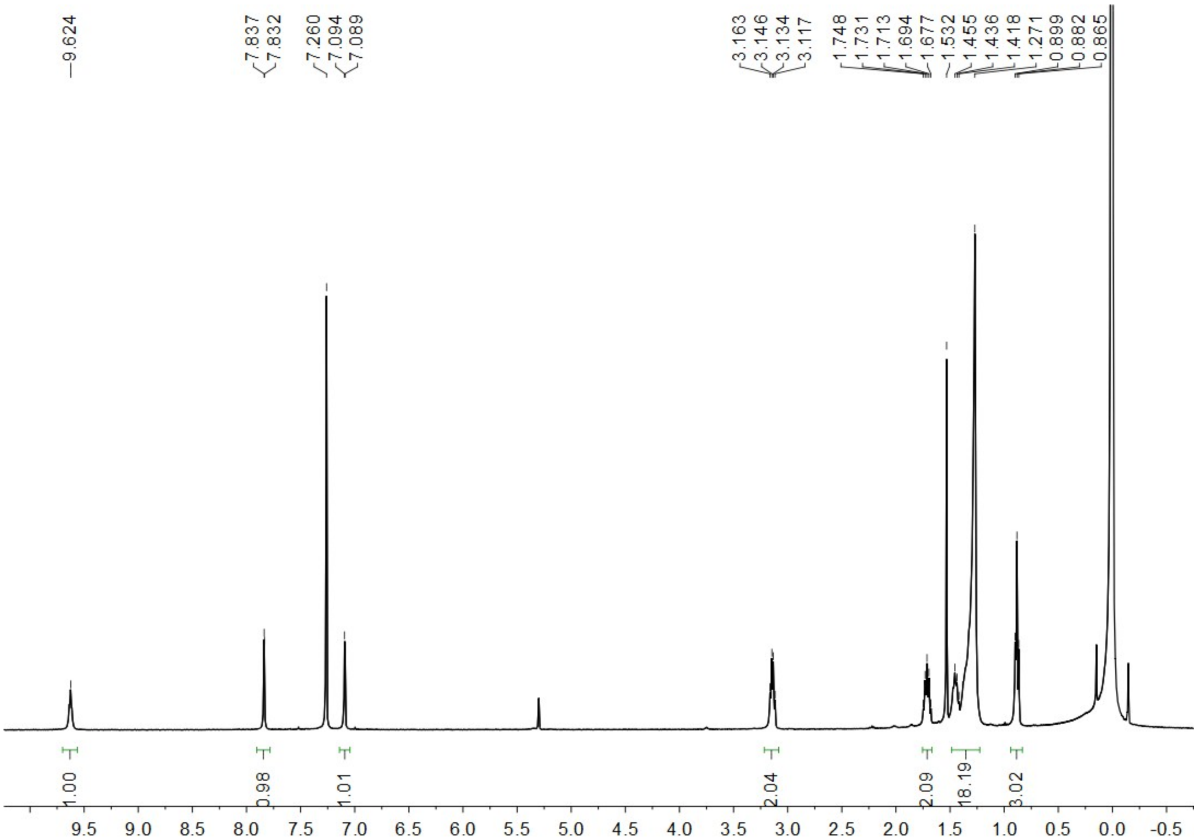

Figure S1. ^{1}H NMR spectrum of **2**.

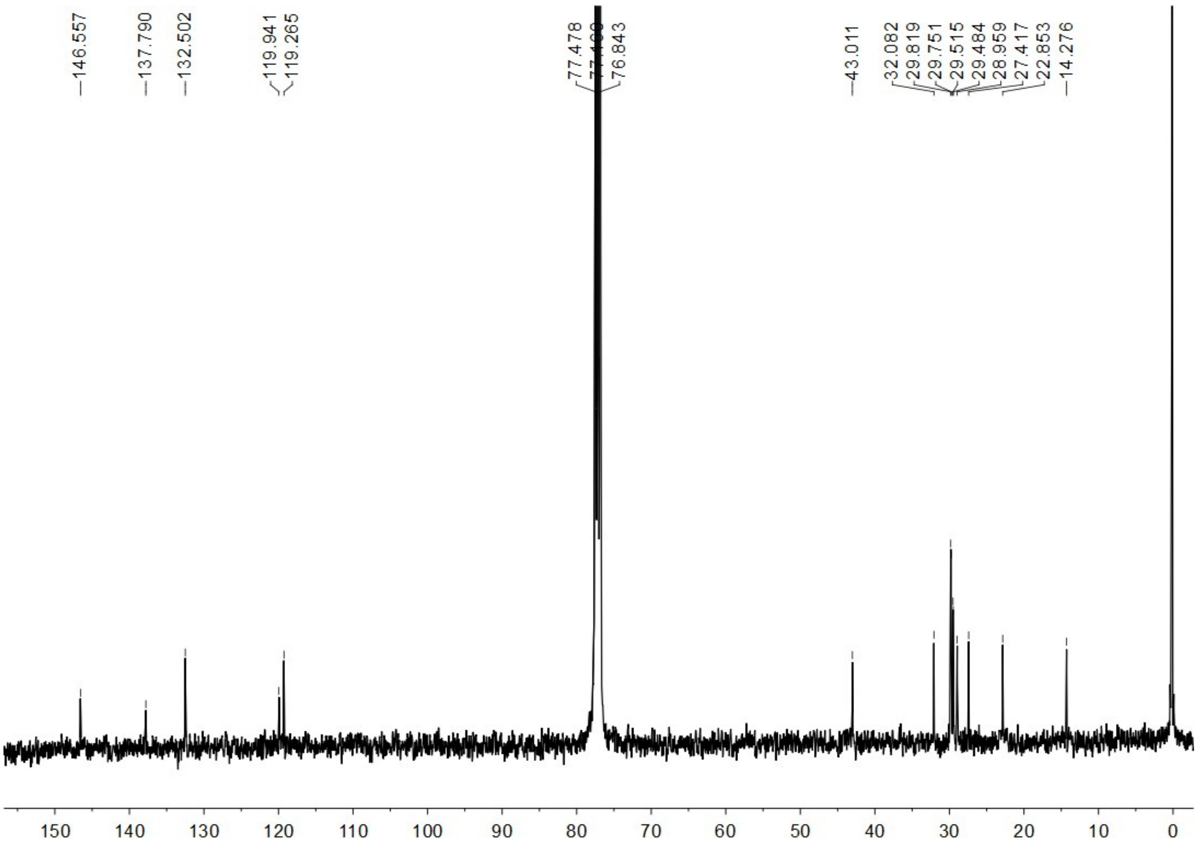

Figure S2. ^{13}C NMR spectrum of **2**.

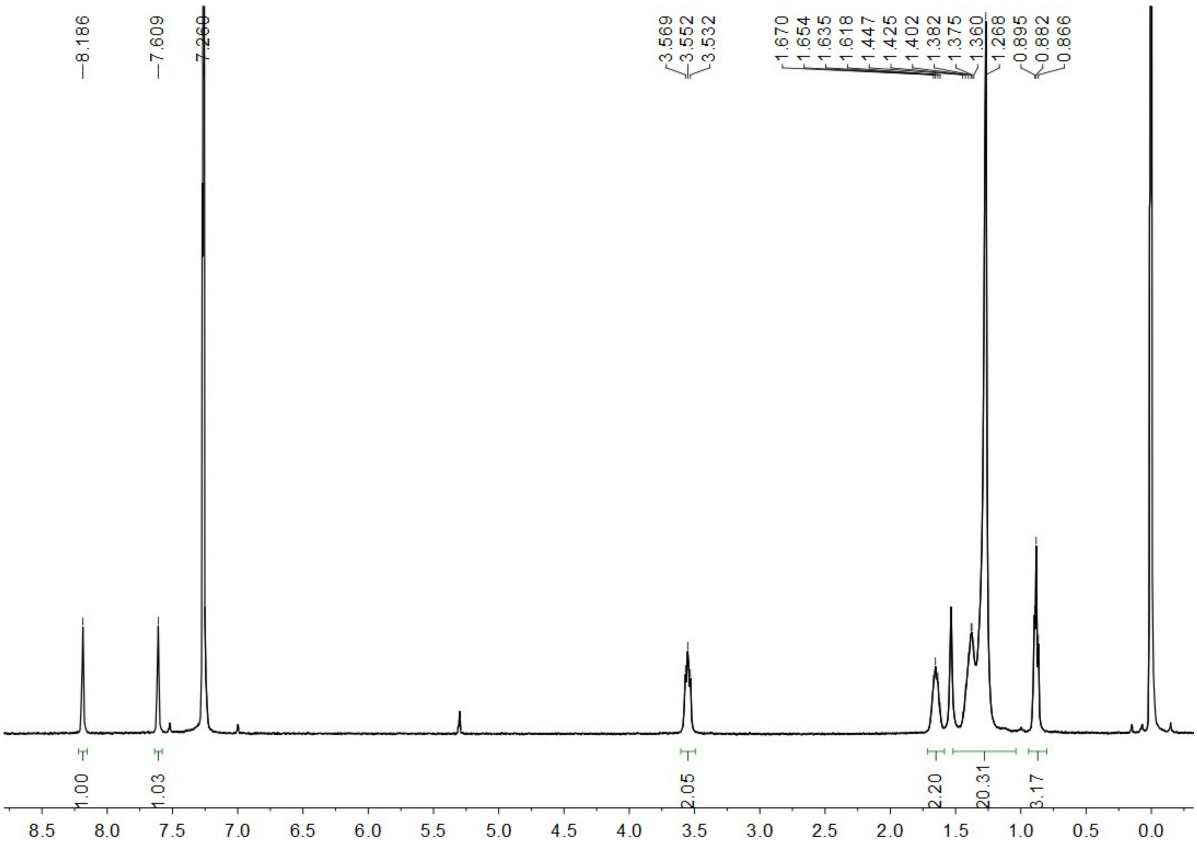

Figure S3. ^{1}H NMR spectrum of **3**.

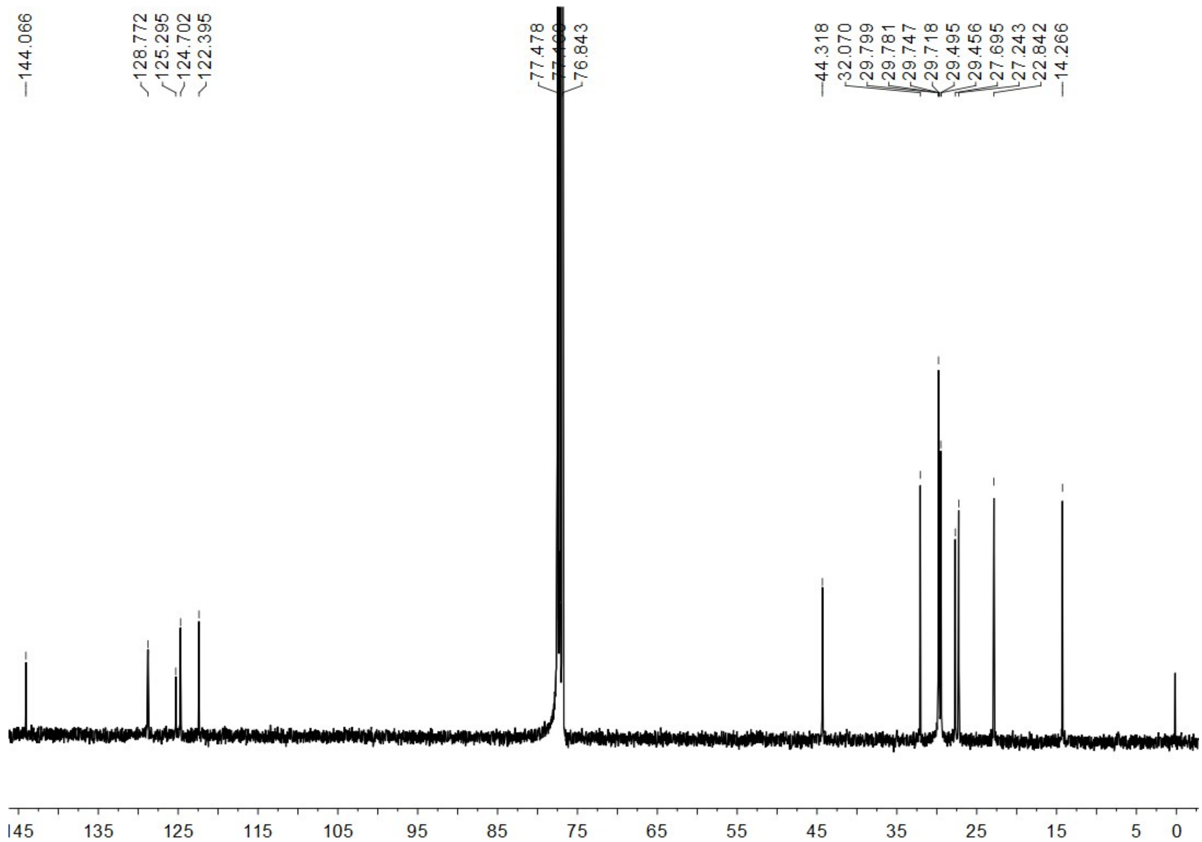

Figure S4. ^{13}C NMR spectrum of **3**.

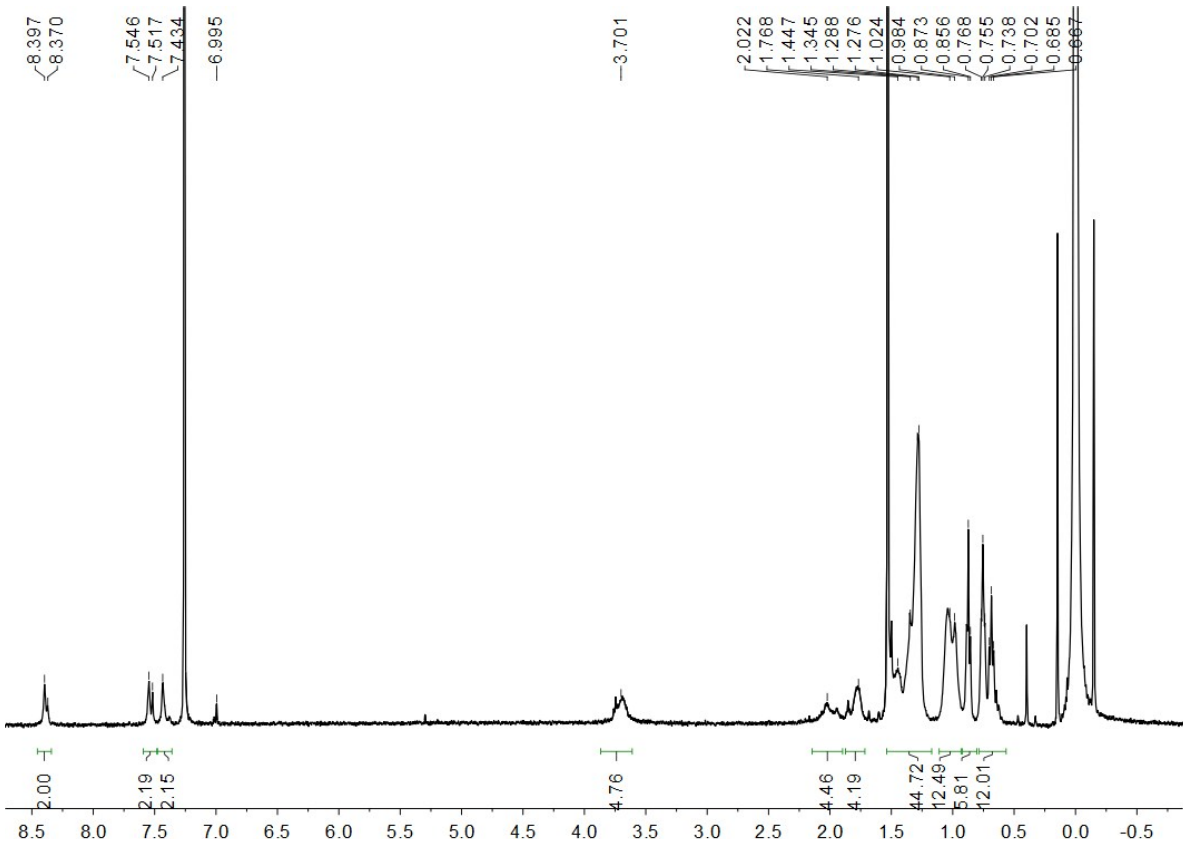

Figure S5. ^{1}H NMR spectrum of **P-BNBP-CDT**.

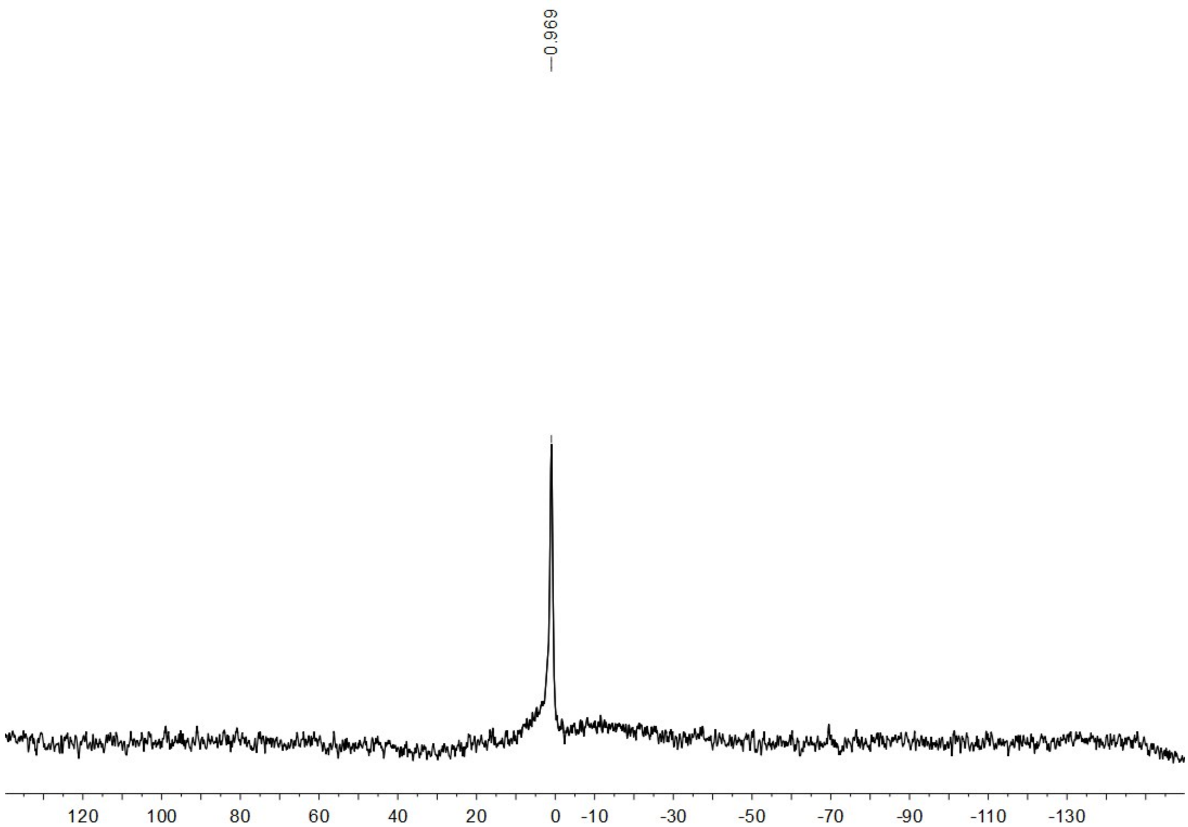

Figure S6. ^{11}B NMR spectrum of **P-BNBP-CDT**.

2. Thermal property

The thermal property of **P-BNBP-CDT** was studied by thermogravimetric analysis (TGA). TGA analysis shows that it has good thermal stability with decomposition temperature at 5% weight loss of 380 °C under N_2.

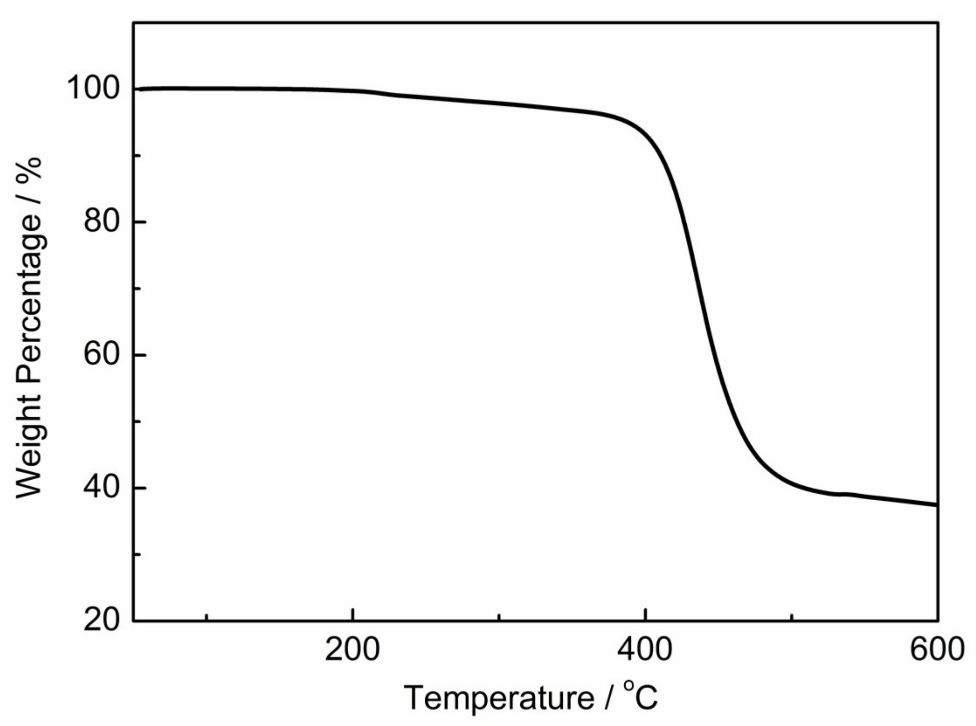

Figure S7. TGA curve of **P-BNBP-CDT**.

3. All-PSC device performance

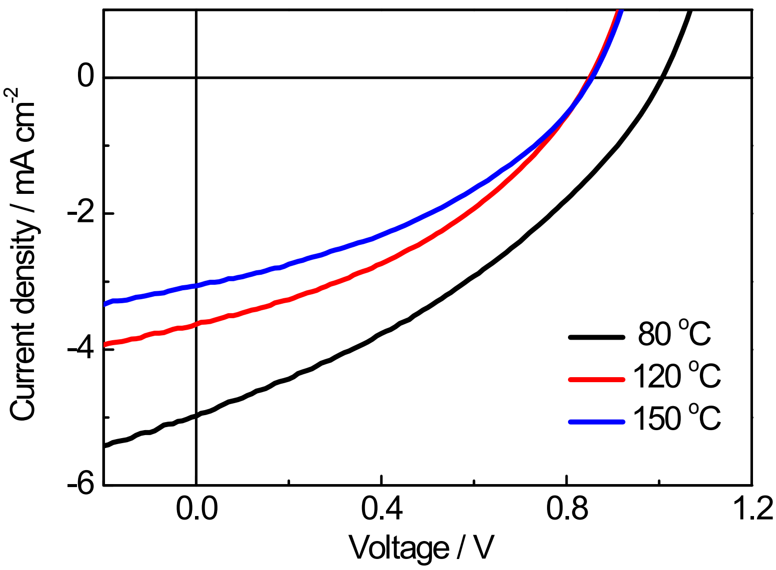

Figure S8. *J–V* curves of the all-PSC devices of the P3HT:**P-BNBP-CDT** (*w*:*w*, 5:1) devices with the blend films annealing at 80 °C, 120 °C and 150 °C, respectively.

Table S1. Summary of the P3HT:**P-BNBP-CDT** (*w*:*w*, 5:1) device performance with the blend films annealing at 80 °C, 120 °C and 150 °C, respectively.

T (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	$PCE_{max/ave}$[a] (%)
80	1.01	4.98	0.35	1.76 (1.67)
120	0.85	3.63	0.38	1.20 (1.10)
150	0.83	3.06	0.39	1.01 (0.92)

[a]The average PCE value is calculated from four devices.

4. Charge-transporting properties

The electron/hole mobilities of the films were measured using the space-charge-limited current (SCLC) method. The electron-only and hole-only device structures for devices are ITO/PEIE/Active layer/LiF/Al and ITO/PEDOT:PSS/Active layer/MoO_3/Al, respectively. The current-voltage curves in the range of 0–10 V were recorded using a computer-controlled Keithley 2400 source meter, and the results were fitted to a space-charge limited function:

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \exp\left(0.89\beta \frac{\sqrt{V}}{\sqrt{L}}\right)$$

where J is the current density, ε_0 is the permittivity of free space, ε_r is the relative permittivity (the ε_r is assumed to be 3 in our analysis for the polymers), μ is the zero-field mobility, V is the potential across the device ($V = V_{applied} - V_{bias} - V_{series}$), L is the thickness of active layer, and β is the field-activation factor. The series and contact resistance (V_{series}) of the device (10–15 Ω) were measured using blank devices of ITO/PEIE/LiF/Al or ITO/PEDOT:PSS/MoO_3/Al.

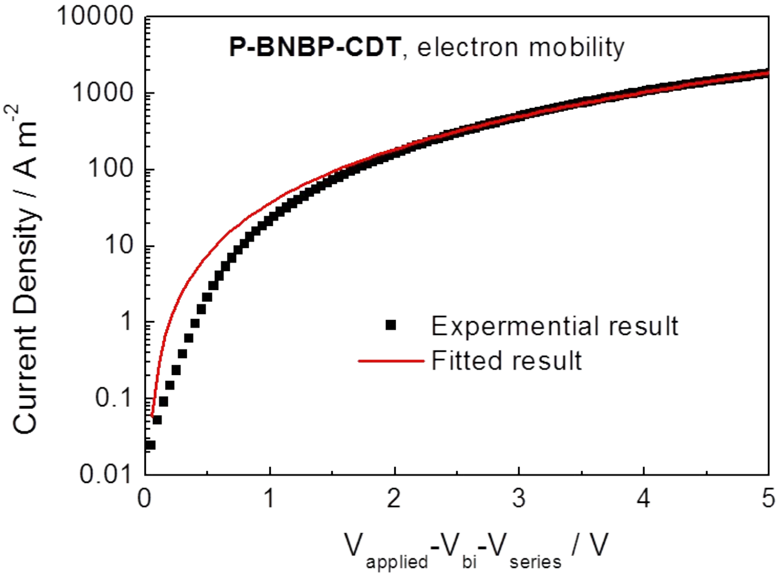

Figure S9. Space-charge-limited current (SCLC) fitting of the device based on the prime **P-BNBP-CDT** film. The μ_e value of **P-BNBP-CDT** is 5.20×10^{-5} cm^2 V^{-1} S^{-1}.

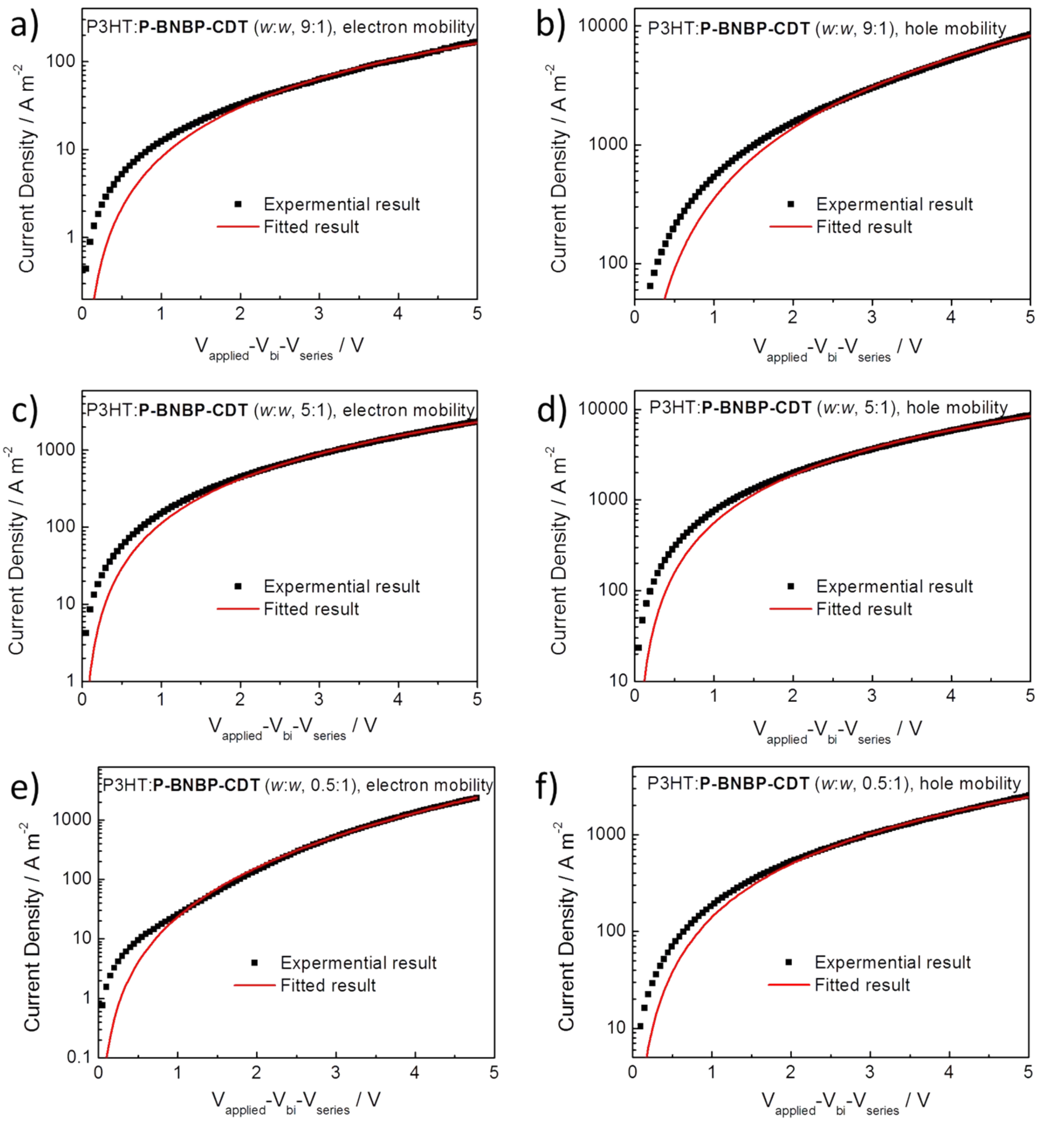

Figure S10. SCLC fittings of the devices based on the blend films.

Table S2. Summary of the charge-transporting properties of the P3HT:**P-BNBP-CDT** blends with the donor:acceptor ratios of 0.5:1, 5:1 and 9:1.

w:*w*	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
0.5:1	5.51×10^{-5}	8.89×10^{-6}	6/1
5:1	2.31×10^{-4}	3.0×10^{-5}	8/1
9:1	1.54×10^{-4}	3.32×10^{-6}	46/1

5. Reference

Gaussian 09 (Revision A.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian, Inc*., Wallingford CT, 2009.