Electronic Supplementary Information (ESI) for

Improving the exciton dissociation of polymer/fullerene interface with a minimal loading amount of energy cascading molecular dopant

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General Details.

Device Fabrication and Characterization. The glass/ITO substrates were pre-cleaned with a special detergent (Alconox Inc.), acetone, isopropanol, and dried under a flow of dry nitrogen. Before deposition of the electron-collecting interlayer, ITO substrates were cleaned in UV azone for 5 min. Inverted devices were fabricated with the structure of ITO/ZnO/active layer/MoO_3/Ag. The sol-gel derived ZnO films were prepared according to the literature.[1] The prepared precursor was spin-cast on ITO substrates at 4000 rpm, and subseuqently annealed in ambient at 130°C for 30 min. The ZnO deposited substrates were then transferred into a nitrogen-filled glove box (< 0.1 ppm O_2 and H_2O).

The binary active layer was prepared by spin-coating a mixture of PTB7-Th: $PC_{71}BM$ in chlorobenzene (9 mg/mL for PTB7-Th, 13.5 mg/mL for $PC_{71}BM$) solution with 3% (v/v) 1, 8-diiodooctane (DIO) at 2000 rpm to form a film around 100 nm. For the ternary blend based devices, additional amounts of BTTCN with various ratios were added into PTB7-Th: $PC_{71}BM$ (1:1.5) solution. After spin-casting, the as-prepared films were put in vacuum for 30 min to remove DIO residue. The PTB7-Th: BTTCN binary devices were prepared by spin-casting their chloroform solution (1:1.5, w/w) at 5000 rpm for 30 s to form a film with the thickness around 90 nm. Top electrodes were thermally evaporated through a shadow mask onto the active layer. Specifically, the 8.0 nm MoO_3 followed by 80 nm Ag top electrodes were thermally deposited in vacuum at a base pressure of 3×10^{-6} Torr. The active area of the pixels as defined by the overlap of anode and cathode area was 0.075 cm^2. Four individual devices were simultaneously prepared on each substrate. All the devices were encapsulated in the glove box with the mixture of epoxy and hardener (1:1 in volume) and then covered with a glass slide.

The current density-voltage (*J-V*) characteristics were measured using a Keithley 2400 source measure unit. The photocurrent was measured under AM 1.5G illumination (through the glass substrate) at 100 mW/cm^2 using a Newport Thermo Oriel 91192 1000W Solar Simulator. Light intensity of the measurement was calibrated with an NREL-certified monocrystaline silicon reference cell. Incident photon conversion efficiency (IPCE) spectra were recorded using the monochromated (Bentham) output from a tungsten halogen lamp calibrated with a Newport UV-181 photodiode; phase sensitive detection with a lock-in amplifier was used to increase signal to noise.

Other Characterizations. NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz NMR (^{1}H: 400 MHz, ^{13}C: 100 MHz). The molecular weight of intermediates was measured by a Bruker matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) without using any matrix. UV-Vis spectra were measured with Shimadzu UV-Vis-NIR spectrophotometer. Atom force microscopy (AFM) measurements for surface morphology were conducted on Bruker ScanAsyst AFM in tapping mode. Transmission electron microscopy (TEM) images were recorded on a JEOL 2010 transmission electron microscope at an accelerating voltage of 100 kV. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at beamline 7.3.3 at the Advanced Light Source, the National Center for Nanoscience and Technology, Beijing, China. GIWAXS samples were prepared on glass/ITO substrates coated with ZnO layer using identical blend solutions as those used in devices. Impedance spectra of the devices were measured using WAYNE KERR 6500B. The electrochemical behaviors of BTTCN were investigated by cyclic voltammetry (CV) with a standard three electrodes electrochemical cell in a 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution at room temperature under nitrogen with a scanning rate of 100 mV/s. A platinum working electrode, a platinum wire counter electrode and a reference electrode of $Ag/AgNO_3$ (0.1 M) were used. The BTTCN films for electrochemical measurements were coated from its dilute solution. The energy levels were determined by oxidation and reduction onset. Ferrocene was utilized as the reference.

Materials

All reagents and solvents for synthesis, unless otherwise specified, were obtained from Aldrich and TCI Chemical Co and used as received. All manipulations involving air sensitive reagents were performed under an atmosphere of dry argon. PTB7-Th and $PC_{71}BM$ were purchased from Lumtec co. and Solenne, respectively. Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 99.95%) was purchased from Aldrich. All the materials for polymer solar cells fabrication were used as received.

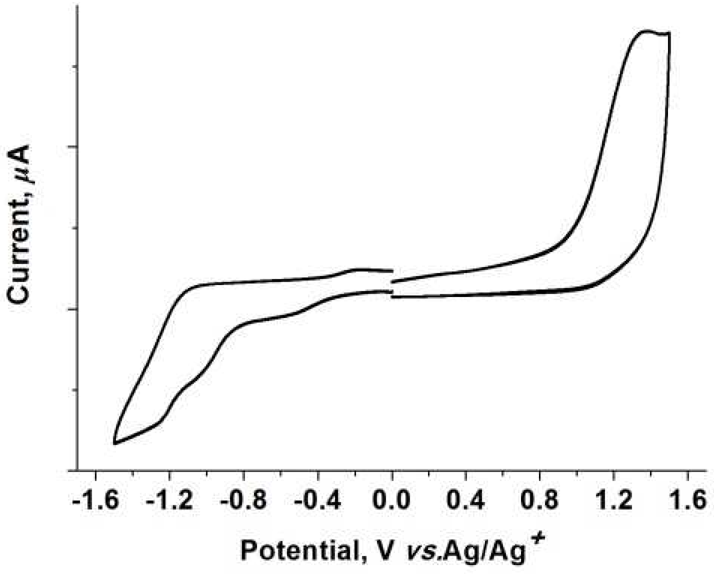


Fig. S1. Oxidative and reductive cyclic voltammetry plots of BTTCN measured in film states.

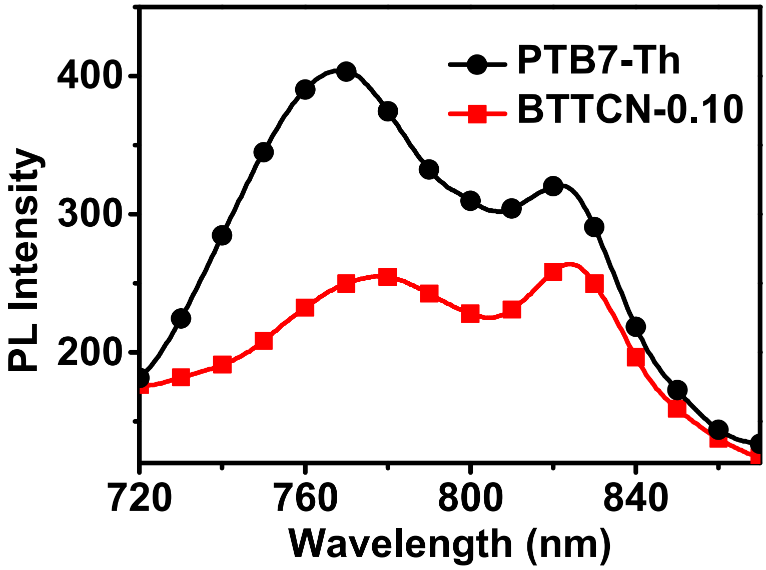


Fig. S2. The PL spectra for pure PTB7-Th film and the ternary film with 10 wt% BTTCN doping.

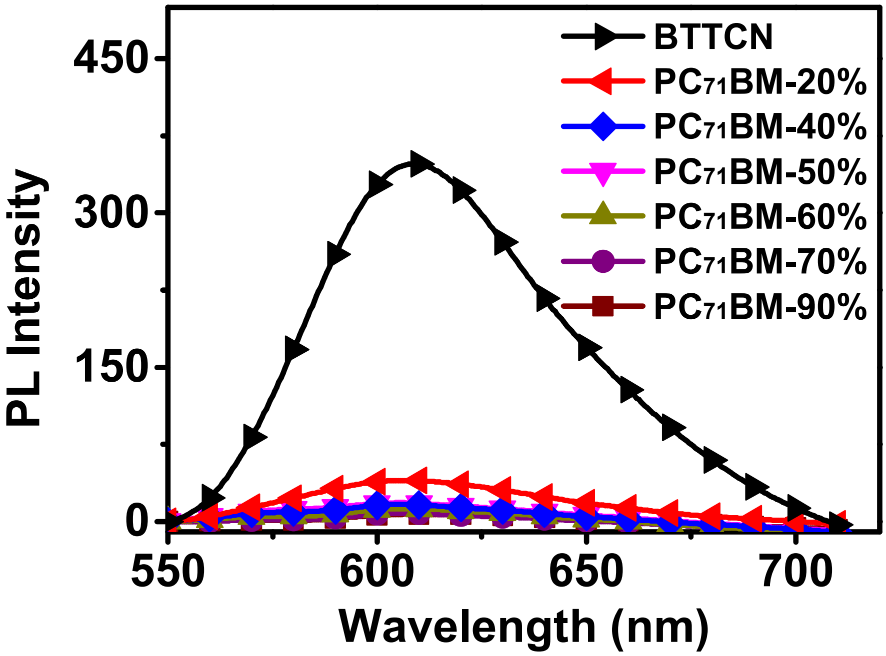


Fig. S3. The PL spectra for pure BTTCN film and the corresponding blending films with various amount of $PC_{71}BM$.

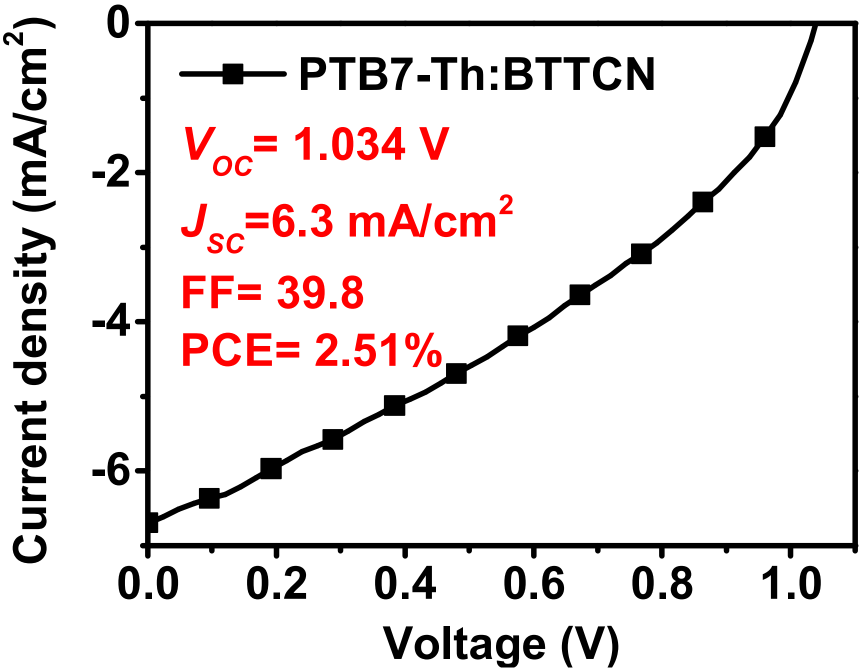


Fig. S4. *J*-*V* characteristics of the device based on PTB7-Th/BTTCN under AM 1.5 G irradiation at 100 mW/cm^2.

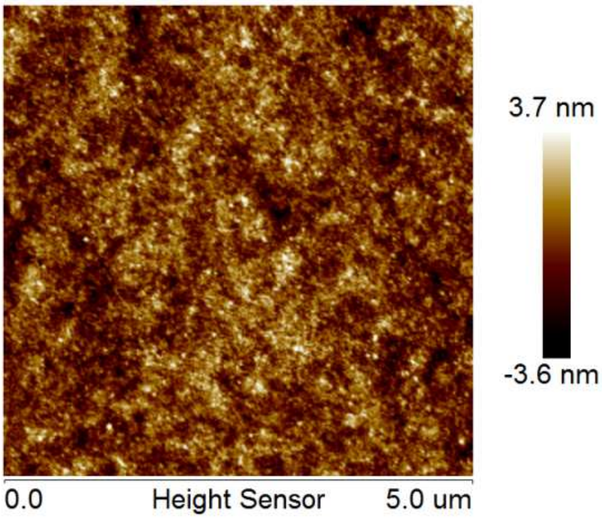


Fig. S5. Atomic force microscopy (AFM) images of PTB7-Th:BTTCN (1:1.5) binary blend films coated from chloroform solution.[2]

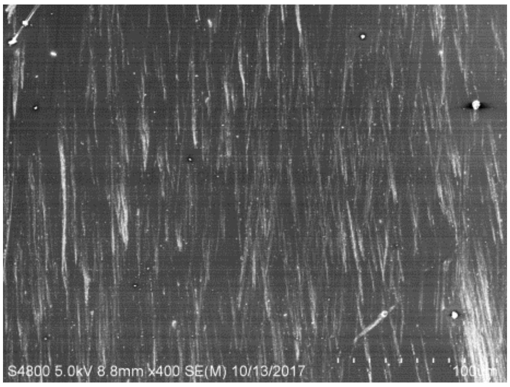


Fig. S6. SEM images for the film of ITO/ZnO/BTTCN:$PC_{71}BM$ coated from chlorobenzene solution. The bar was set at 100 μm.

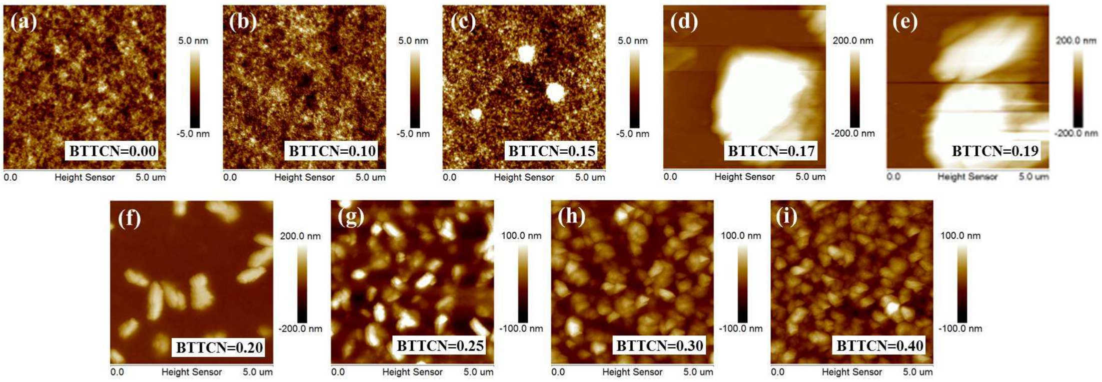


Fig. S7. AFM images of ITO/ZnO/PTB7-Th:$PC_{71}BM$ blend films and with varioius BTTCN contents coated from their chlorobenzene solution. The all bars were set at 5 μm.

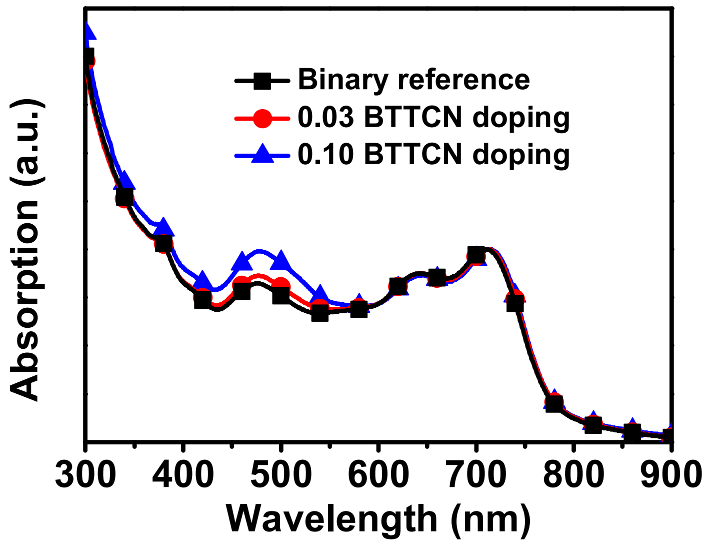
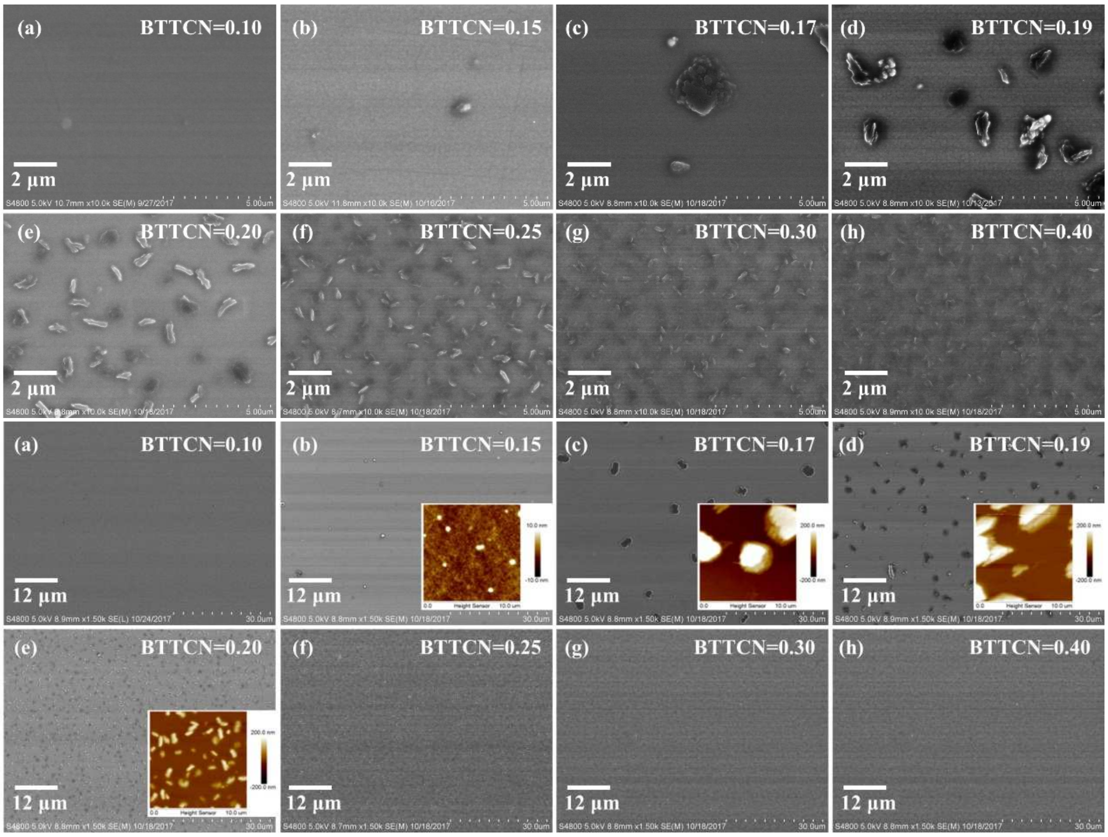


Fig. S8. Normalized UV–vis absorption spectra of the active layer without and with various BTTCN contents in films.



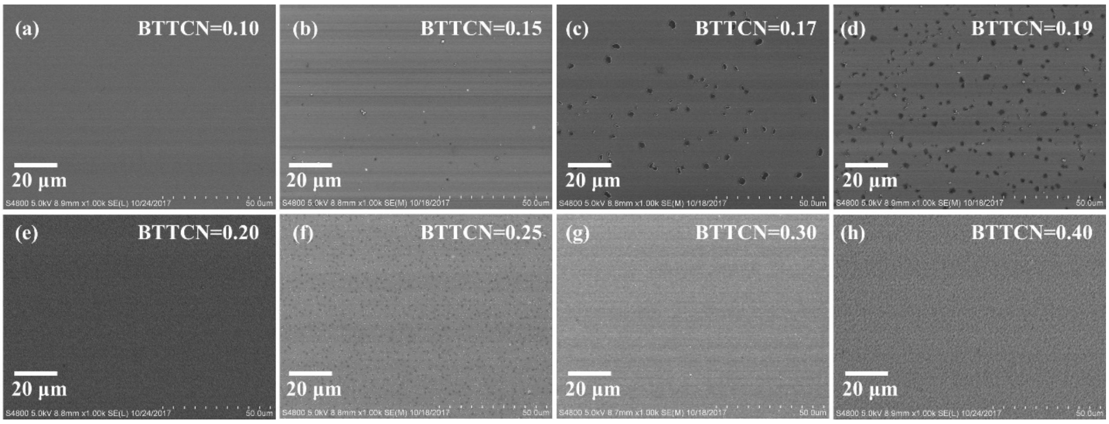


Fig. S9. SEM images for the films of ITO/ZnO/PTB7-Th: PC$_{71}$BM: BTTCN with different sizes coated from their chlorobenzene solution. The all bars were set at 5 μm, 30 μm and 50 μm. AFM images of ITO/ZnO/PTB7-Th: PC$_{71}$BM blend films and with various BTTCN contents coated from their chlorobenzene solution. The all bars were set at 10 μm.

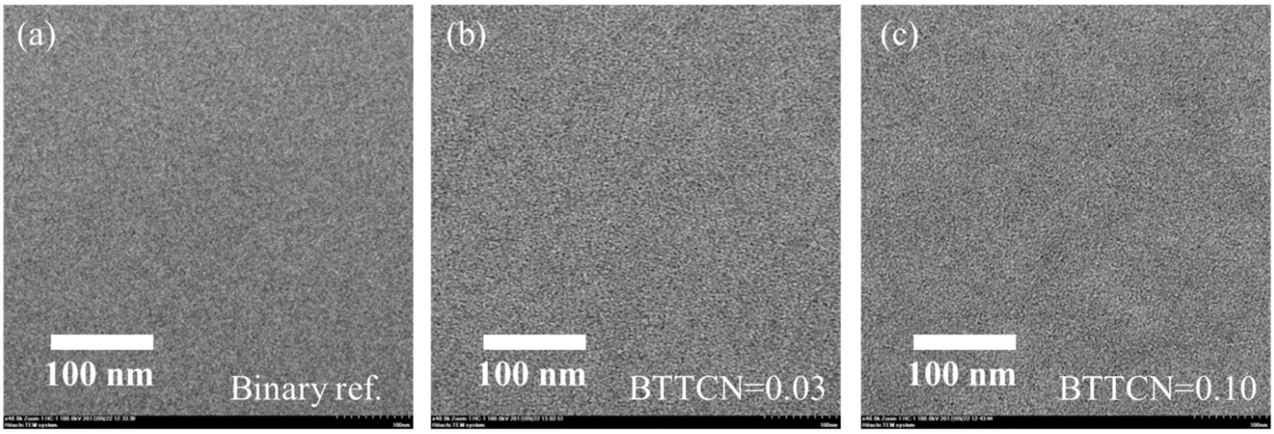


Fig. S10. TEM images of PTB7-Th:PC71BM blend films with various BTTCN contents spincoated from their chlorobenzene solution.

The mobility was measured in the hole-only devices with the structure of ITO/PEDOT:PSS/ active layer/MoO$_3$/Au, and the electron mobility was measured in the electron-only devices with structure of ITO/ZnO/active layer/LiF/Al, and determined in the space charge limited current (SCLC) regime by Mott-Gurney law. The used fitting equation is described as following:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_0 e^{0.89\gamma\sqrt{E}}\frac{V^2}{L^3}$$

Where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, V is the voltage drop across the device, and L is the active layer thickness, E is the electric field, μ_0 the zero-field mobilility, and γ the field dependence prefactor. The value of ε_r is assumed to be 3, which is a typical value for a conjugated polymer.

The utilized work function values of the electrodes are -5.2 eV to ITO/PEDOT:PSS, -5.1 eV for Au, -4.4 eV for ITO/ZnO and -2.9 eV for LiF/Al.[3-4]

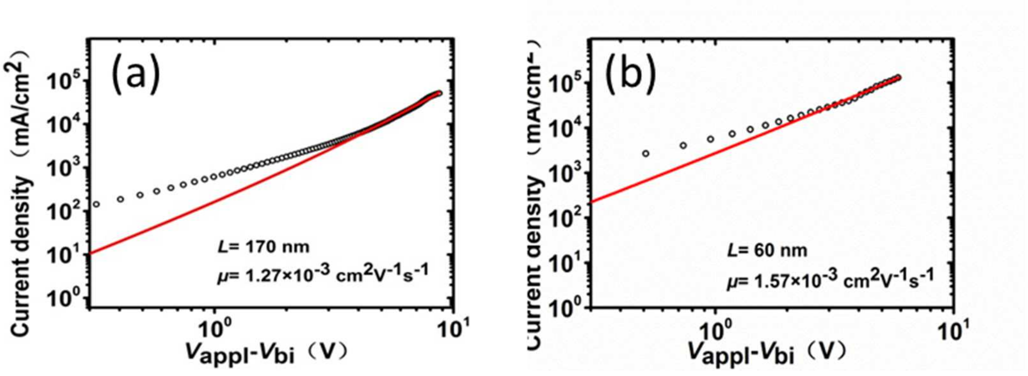


Fig. S11. Representative *J-V* curves for the hole-only diodes for estimation of hole mobilities using an SCLC model. (a) PTB7-Th: $PC_{71}BM$ = 1:1.5; (b) PTB7-Th:$PC_{71}BM$: BTTCN = 1:1.5:0.03.

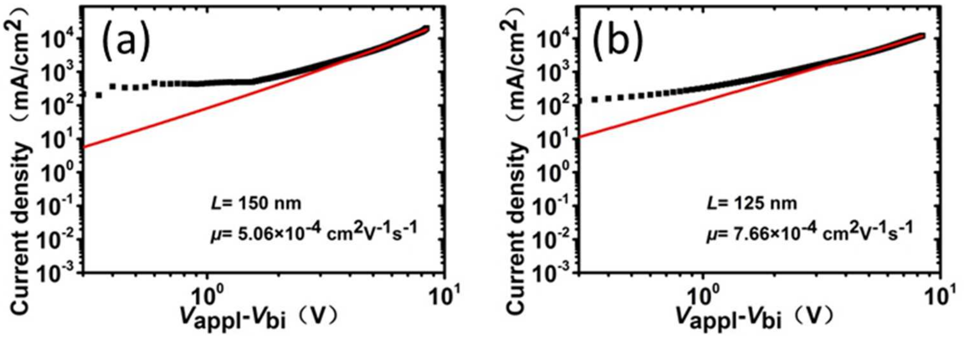


Fig. S12. Representative *J-V* curves for the electron-only diodes for estimation of electron mobilities using an SCLC model. (a) PTB7-Th:$PC_{71}BM$ = 1:1.50; (b) PTB7-Th:$PC_{71}BM$:BTTCN = 1:1.50:0.03.

Synthetic procedures

BrRTCN: Malononitrile (47.9 mg, 1.1 mmol) and 5-bromo-3-(2-ethylhexyl)thiophene-2-carbaldehyde (200 mg, 1 mmol) were dissolved in 20 ml of $CHCl_3$, and then 0.1 mL of triethylamine was added. The solution was stirred at room temperature for 1 h. The mixture was then diluted with chloroform and washed by brine for three times. The organic phase was combined and dried over $MgSO_4$. After the solvent was removed, the resulting residue was purified by column chromatography using hexane as the eluent to give **BrRTCN** as a yellow solid (211.5 mg, 91.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.38(s, 1H), 2.54-2.53 (d, 2H), 1.61-1.58 (m, 1H), 1.32-1.24 (m, 8H), 0.90-0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.17, 143.93, 139.56, 134.75, 124.64, 113.78, 113.03, 39.85, 33.37, 32.38, 28.71, 25.58, 22.98, 14.10, 10.75, 0.97. MALDI-TOF-MS (m/z): Calcd for $C_{32}H_{32}N_4S_3$, Exact Mass: M^+ 568.18; Found: 567.97 (M^+).

BTTCN: BrRTCN (430.3 mg, 4.5 mmol) and 2,5,8-tris(trimethylstannyl)benzo[1,2-b:3,4-b':5,6-b'']trithiophene (200 mg, 1 mmol), $Pd(PPh_3)_4$ (25 mg, 0.02 mmol) were dissolved in toluene (10 mL) in a degassed vessel. The mixture was heated at 110°C for 24 h. After cooling down, the mixture was diluted with chloroform and washed by brine for three times. The organic phase was combined and dried over $MgSO_4$. After the solvent was removed, the residue was purified by silica gel column using hexane/dichloromethane (1:1) as the eluent to give **BTTCN** as a dark red solid (230.9 mg, 80.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 3H), 7.80 (s, 3H), 7.58 (s, 3H), 2.93-2.91 (d, 6H), 1.75-1.69 (m, 3H), 1.40-1.28 (m, 24H), 0.90-0.85 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.09, 142.55, 142.16, 141.62, 134.23, 133.73, 133.57, 131.33, 122.99, 113.96, 113.17, 40.25, 33.47, 32.57, 28.76, 25.78, 23.00, 14.09, 10.76, 1.02. MALDI-TOF-MS (m/z): Calcd for $C_{32}H_{32}N_4S_3$, Exact Mass: M^+ 568.18; Found: 567.97 (M^+).

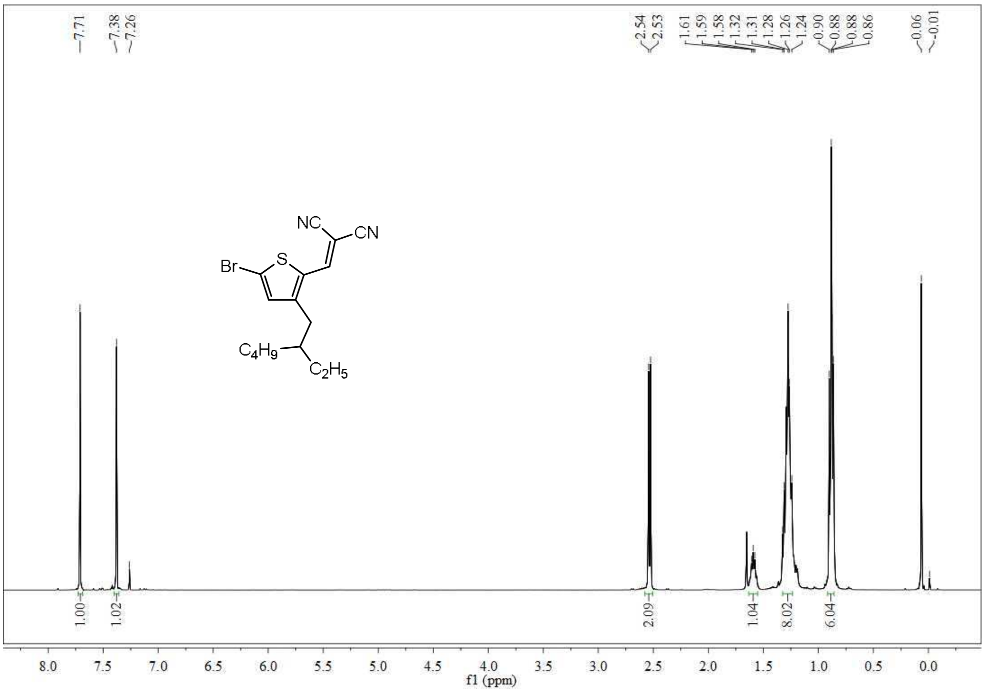


Fig. S13. ^{1}H NMR spectra for BrRTCN.

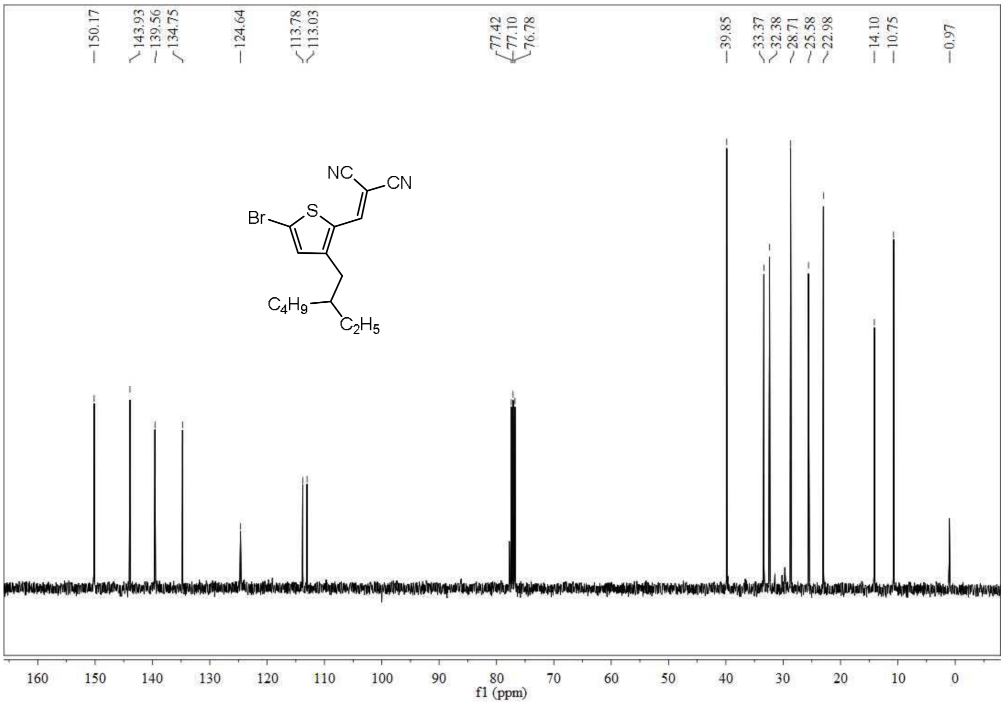


Fig. S14. ^{13}C NMR spectra for BrRTCN.

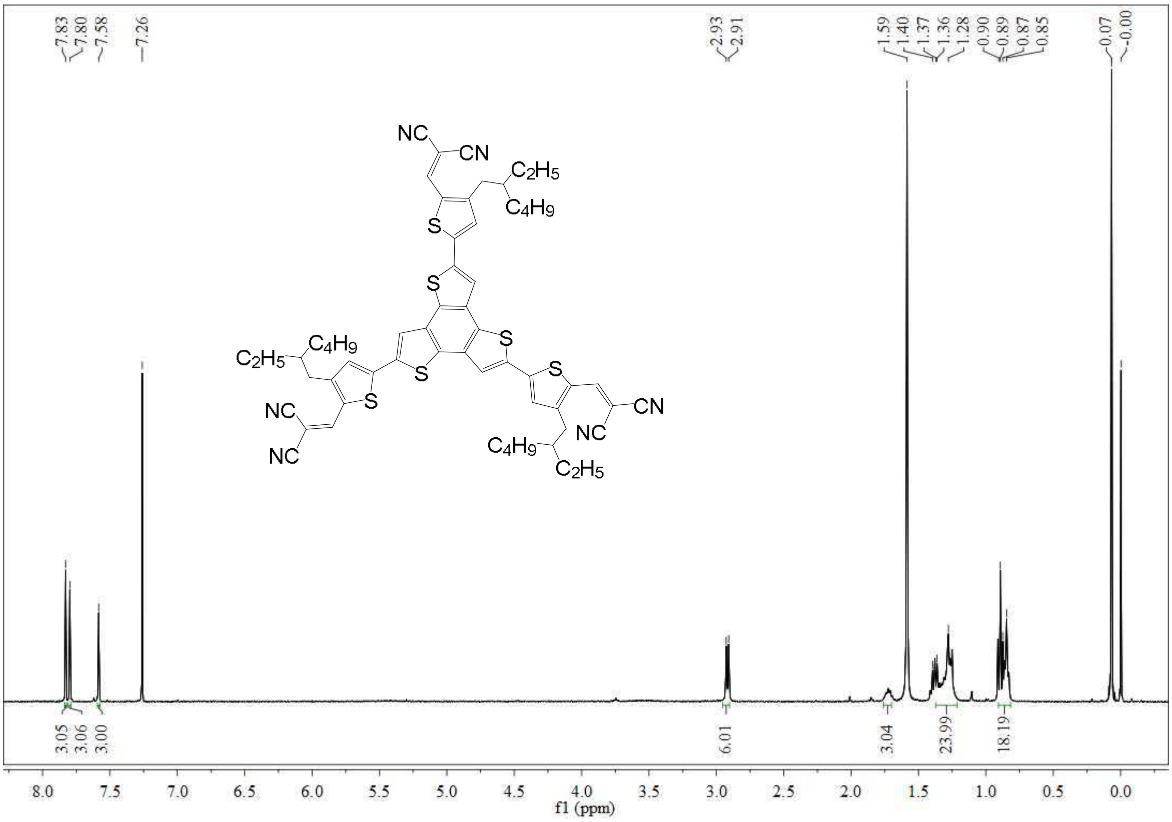


Fig. S15. ^{1}H NMR spectra for BTTCN.

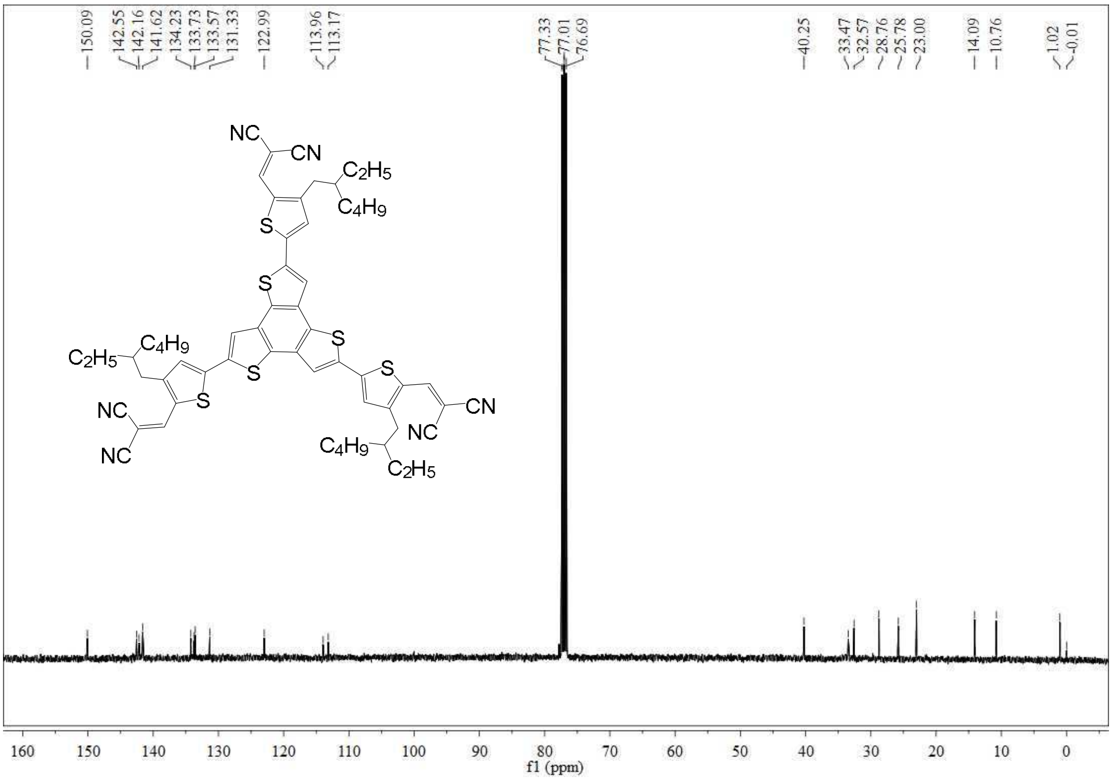


Fig. S16. ^{13}C NMR spectra for BTTCN.

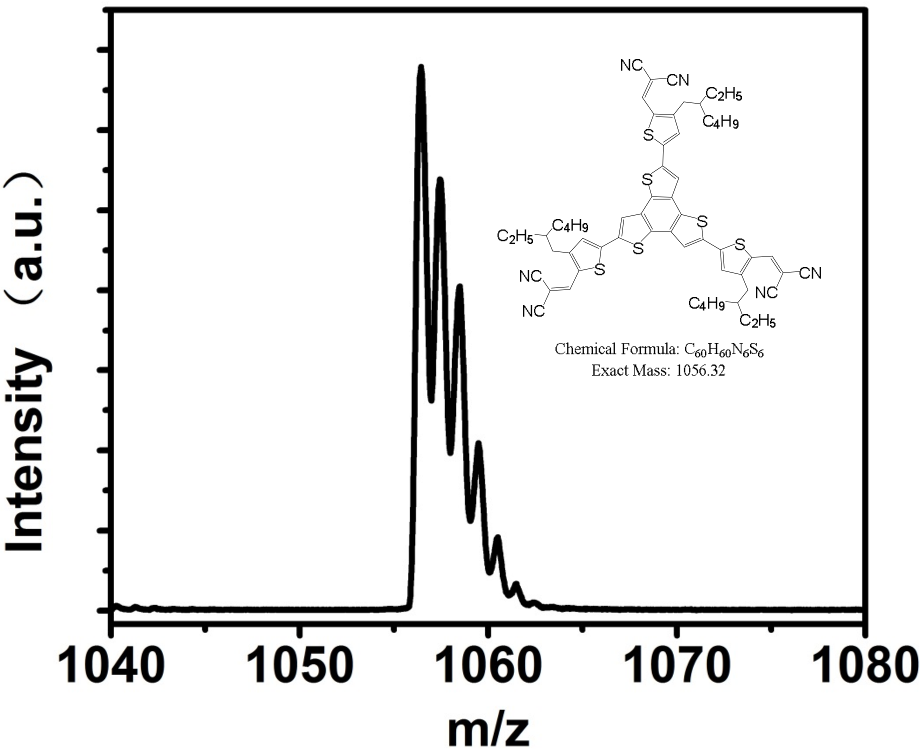


Fig. S17. MALDI-TOF-MS spectra for BTTCN.

References

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