Supporting Information

Can morphology tailoring based on functionalized fullerene nanostructures improve the performance of organic solar cells?

Lie Chen, Kai Yao, Yiwang Chen*

Institute of Polymers/Department of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

Experimental Section

Materials. All solvents are ACS grade unless otherwise noted. Anhydrous THF and toluene were obtained by distillation from sodium/benzophenone prior to use. chlorobenzene is dried in CaH_2. All reagents were purchased from Aldrich, TCI America, or Alfa Aesar, and were used without further purification.

Synthesis of **PCBA**. To a solution of PCBM (50 mg, 5.5×10^{-2} mmol) in chlorobenzene (20 mL) was refluxed under nitrogen atmosphere for 3 h. HCl (12 M, 2 mL) and acetic acid (5 mL) were introduced to the solution in one portion. The reaction mixture was refluxed for 24 h. The solvent was removed under reduced pressure to give a residue which was purified by precipitation from MeOH to obtain a brown solid PCBA. (79 mg, 81%).

Synthesis of PCBM derivates **PCBbP**: PCBA (54 mg, 0.060 mmol), 4-biphenylbutanol (16 mg, 0.070 mmol), and ODCB (7 mL) we re mixed in a 50 mL round-bottom Schlenk flask. The mixture was treated in room temperature for 2 h, then cooled down to 0 °C in an ice/water bath. Then, dimethlylaminopyridine (DMAP) (18 mg, 0.15 mmol) and dicyclohexylcarbodiimide (DCC) (32 mg, 0.15 mmol) were added quickly to the reaction flask under that atmosphere of N_2. The mixture was continuously stirred at 0 °C for 30 min, followed by warming up to room temperature and being continuously stirred overnight. After completion of the reaction and removal of the solvent under reduced pressure, the residue was purified by silica gel

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* Corresponding author. Tel.: +86 791 83969562; fax: +86 791 83969561. *E-mail address*: ywchen@ncu.edu.cn (Y. Chen); chenlienc@163.com (L. Chen).

chromatography using toluene then ethyl acetate/toluene (1:10, 1:8 to 1:6, v/v) as the eluent gradients to give a brown solid. Finally, the sediment was washed with MeOH and dried in vacuum at 70 °C for 2 days. Yield: 45 mg (68%). ^{1}H-NMR ($CDCl_3$, 400MHz): 7.98-7.91 (m, 3H), 7.77-7.69 (m, 4H), 7.61-7.51 (m, 7H), 4.22 (t, 2H), 3.02 (m, 2H), 2.83 (t, 2H), 2.35 (m, 2H), 2.01-1.84 (m, 6H). FDMS (m/z): 1105.2 (measured); 1105 (calculated).

PCBPy: The pyrene unit was introduced following the same procedure of PCBbP synthesis. Yield: 44 mg (65%). ^{1}H-NMR ($CDCl_3$, 400MHz): 7.97-7.90 (m, 5H), 7.71 (m, 1H), 7.61-7.51 (m, 7H), 4.23 (t, 2H), 2.92 (m, 2H), 2.66 (t, 2H), 2.23 (m, 2H), 2.03-1.81 (m, 6H). FDMS (m/z): 1153.2 (measured); 1153 (calculated).

Characterizations The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 600 NMR spectrometer with deuterated chloroform as the solvent and with tetramethylsilane (δ=0) as the internal standard. The ultraviolet–visible (UV) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. Fluorescence measurement for photoluminescence (PL) of the polymers was carried out on a Hitachi F-7000 PC spectrofluorophotometer with a xenon lamp as the light source. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target (λ =1.54 $\AA$) and at a scanning rate of 1°/min. The fluorescence lifetime was determined with an Edinburgh Instrument FLS920 fluorescence spectrophotometer using a H_2 gas lamp as the light source. TEM images were recorded using a JEOL-2100F transmission electron microscope and an internal charge-coupled device (CCD) camera. The morphology observations of active layer films were made by scanning electron microscopy (SEM; FEI, QuanTA-200F environmental scanning electron microscope) with gold vapor deposition.

Device Fabrication and Characterization

ITO-coated glasses were cleaned with acetone and isopropyl alcohol. After the substrates were dried with air, they were treated with UV ozone for 5 min. PEDOT:PSS (Baytron AI 4083) was spin-cast on the cleaned ITO as received and baked at 140 °C for 10 min. The blend solutions of the P3HT (purchased from Rieke Metals, used as received) and PCBM (purchased from Nano-C, used as received), blending as 1:1 wt %, 20 mg/mL in 1,2-dichlorobenzene (DCB), were prepared by stirring of the solution for 24 h in a glovebox and spin-cast at 650 rpm for 30 s. Alternatively, the functioned PCBM derivates are added as the acceptors in various ratio. All the activelayer films were measured with similar thicknesses by a Dektak profiler with an accuracy of ±1 nm. 0.8 nm of LiF and 100 nm of Al were deposited sequentially at 5×10^{-7} Torr. All devices were characterized under ambient conditions, and the typical illumination intensity was 100 $\mathrm{mW/cm^2}$ (AM 1.5G Oriel solar simulator). The spectral mismatch factor was calculated by comparison of the solar simulator spectrum and the AM 1.5 spectrum at room temperature. The IPCE spectra for the PSCs were measured on an IPCE measuring system. National Institute of Standards and Technology (NIST) calibrated UV-enhanced silicon, and germanium photodetectors were used to calibrate the measurements.

Solvent annealing: Spin-coating at 650 r.p.m. left the films wet for slow growth, which were then dried in covered glass petri dishes to control the growth of the activelayer films. And the solvent evaporation time is all about 60min, judging by visual inspection of the change in film color when it solidifies from the liquid phase.

Hole mobility measurement:

We used a device structure of ITO/PEDOT:PSS/polymer:$PC_{61}BM$/Au for the hole mobility measurement, based on the space-charge-limited current (SCLC) model. According to the following equation: $\mathrm{Ln}(JL^3/V^2) \square 0.89(1/E_0)^{0.5}(V/L)^{0.5} + \mathrm{Ln}(9\varepsilon\varepsilon_0\mu_0/8)$, Where μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, ε is the dielectric constant of the polymer, ε_0 is the permittivity of the vacuum, L is the thickness of the polymer layer, $V = V_{appl} - V_{bi}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential (in this device structure, $V_{bi} = 0.2$ V).

According to the equation, hole mobility can be calculated.

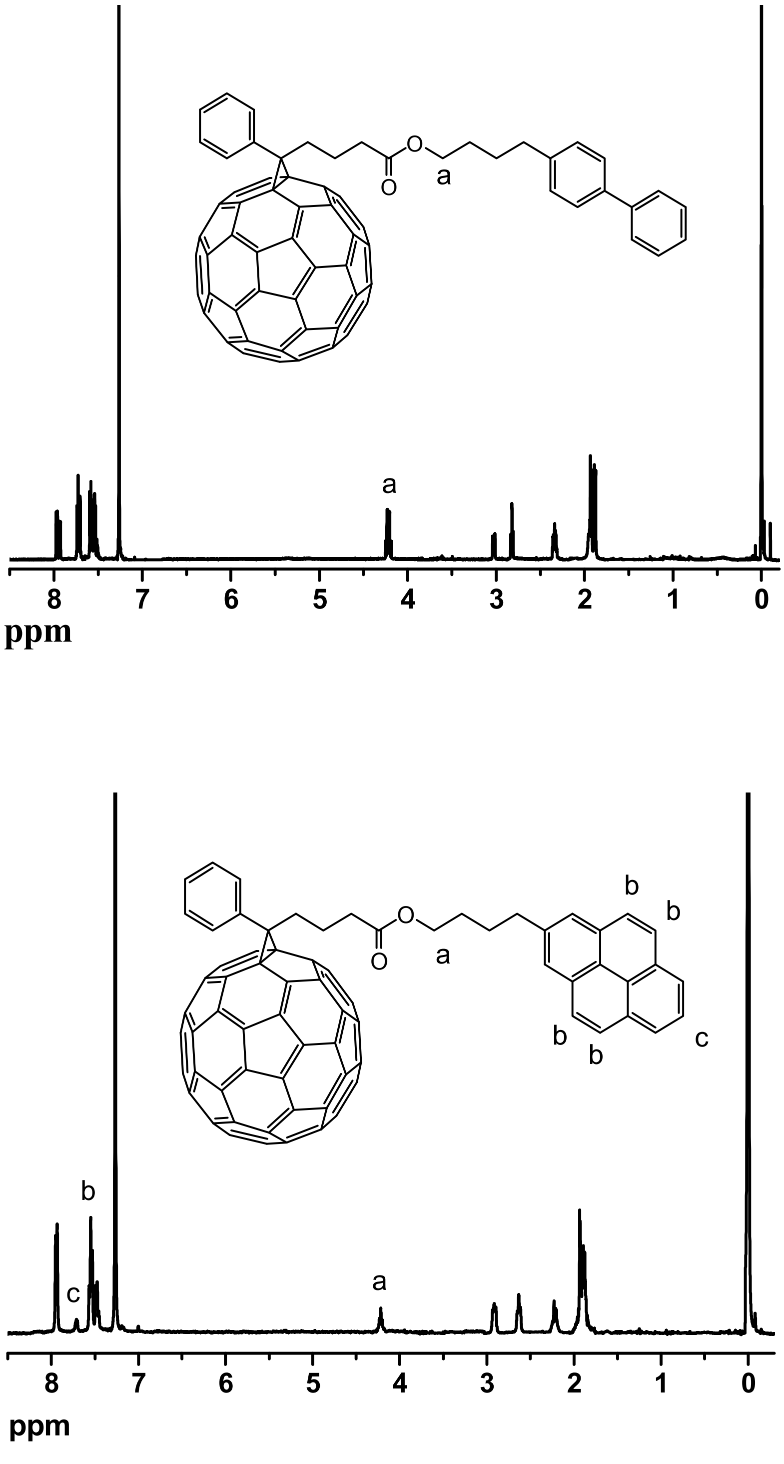

Figure S1. ^{1}H-NMR spectrum of compound PCBbP and PCBPy in $CDCl_3$.

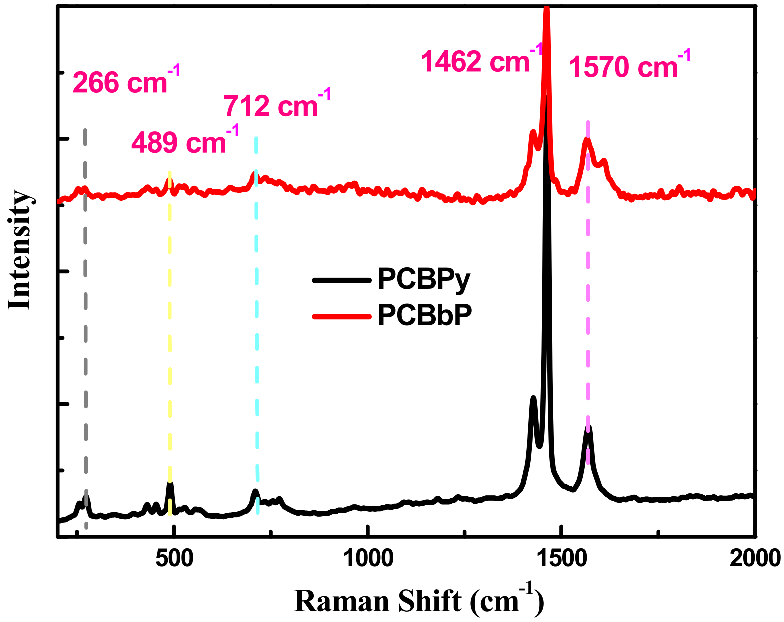

Figure S2. Raman spectra of PCBbP and PCBPy samples.

Table 1S Summary of the device performance of P3HT:PCBM based solar cells containing different PCBbP contain.

PCBbP content	J_{SC} *(mA cm^{-2})*	V_{OC} *(V)*	*FF (%)*	*η (%)*
10% PCBbP	*9.0*	*0.59*	*60*	*3.19*
20% PCBbP	*8.7*	*0.57*	*57*	*2.83*
40% PCBbP	*8.1*	*0.56*	*53*	*2.40*

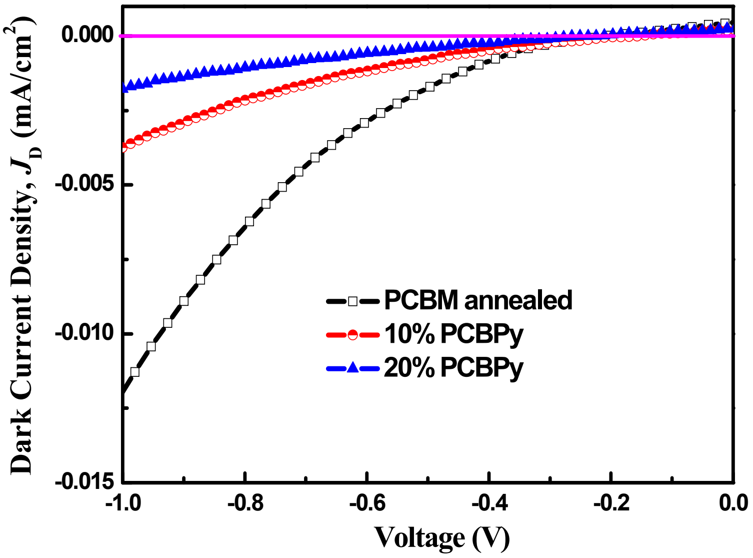

Figure S3. *J*–*V* curves in dark of the device under the various content of PCBPy.

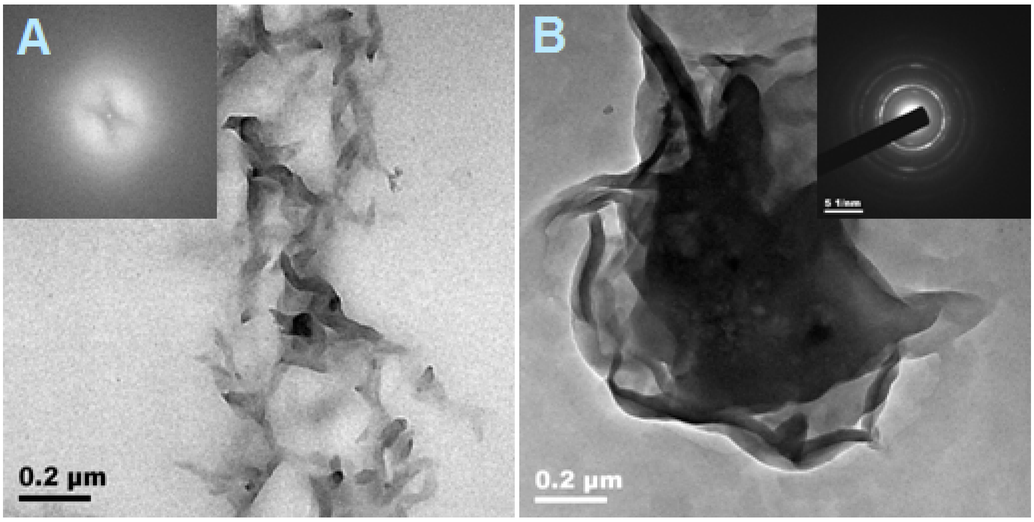

Figure S4. TEM images of PCBbP and PCBPy films annealed 30 min heating at 150°C. Insets are corresponding Fourier transform images.

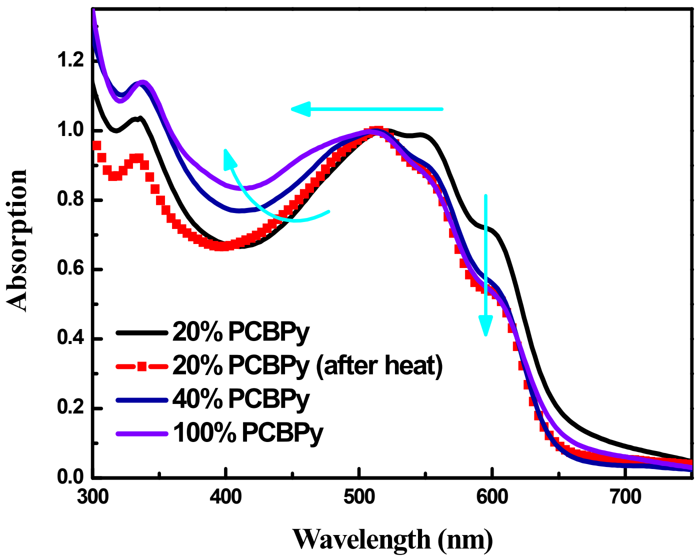

Figure S5. The absorption spectra of pristine P3HT/PCBM+PCBPy based on various content of PCBPy (20%, 40%, 100%); the annealed P3HT/PCBM+PCBPy (20%) are taking as to compare the thermal effect.

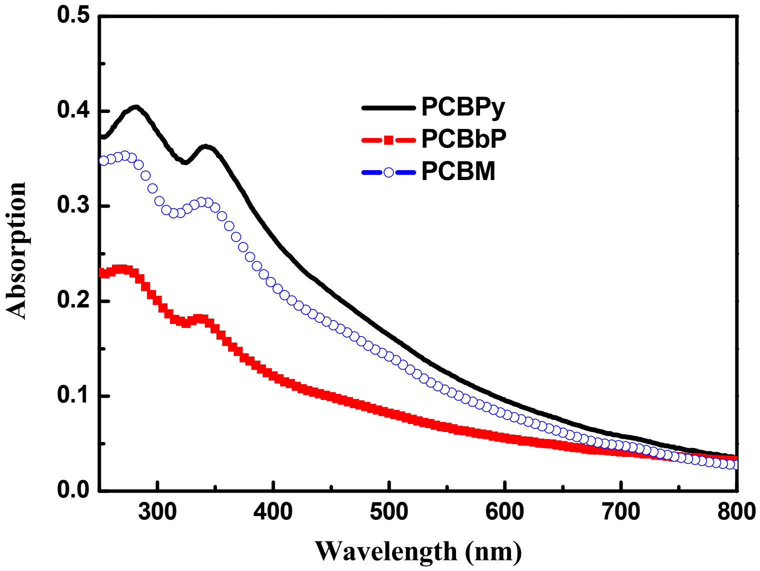

Figure S6. The absorption spectra of pure fullerene PCBM, PCBbP and PCBPy films.

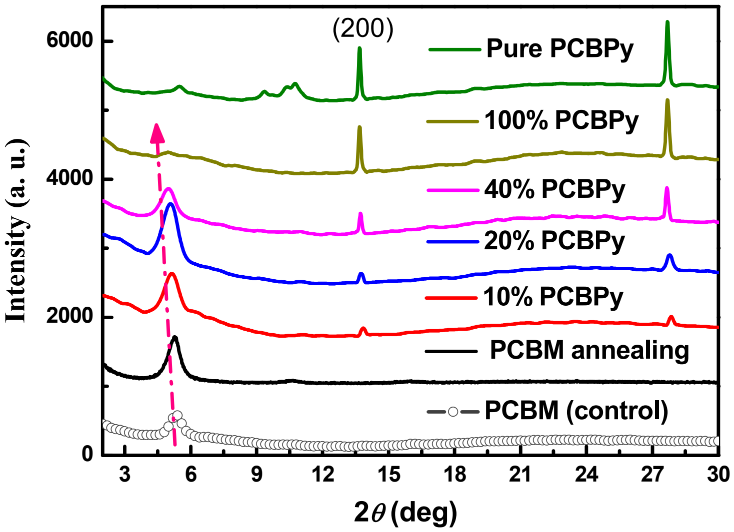

Figure S7. XRD patterns of P3HT:PCBM+PCBPy blending films with different acceptor composition (from 0 to 100%). The thermal annealed P3HT:PCBM and pure PCBPy fullerene samples are adding as reference.

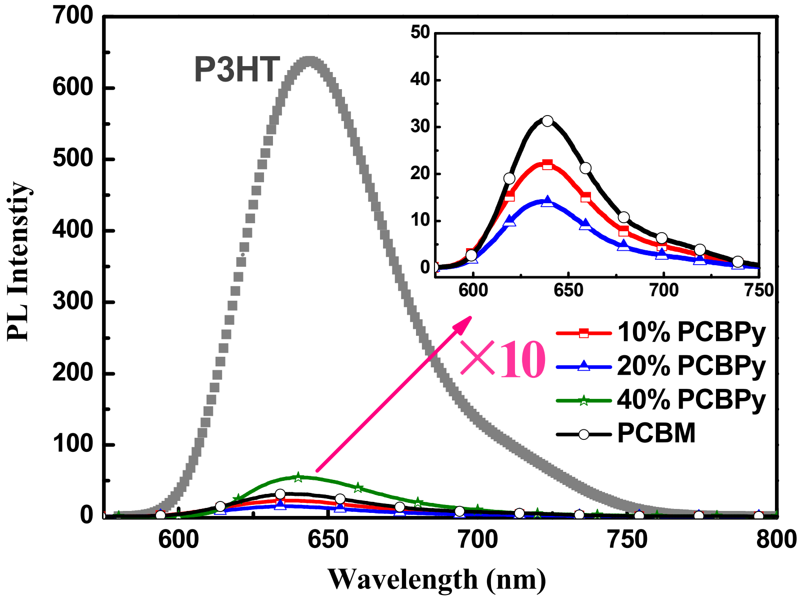

Figure S8. Photoluminescence (PL) spectra of P3HT:PCBM:PCBPy with various composites in solid films. The pure P3HT film is taking as reference.

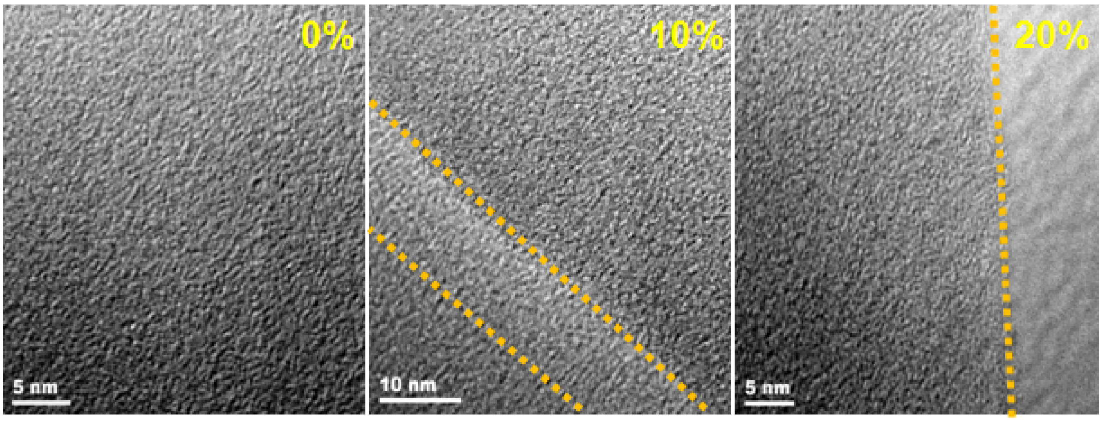

Figure S9. High-magnification TEM image of interface area between donor/acceptor (P3HT/PCBM+PCBPy) based on different content of PCBPy (0, 10%, 20%).