

# Supporting Information

## A Simple and Effective Way of Achieving Highly Efficient and Thermally Stable Bulk-Heterojunction Polymer Solar Cells Using Amorphous Fullerene Derivatives as Electron Acceptor

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### Experimental

#### Materials synthesis

All chemicals, unless otherwise specified, were purchased from Aldrich and used as received. Regioregular poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals, Inc. and was used as received without further purification. 9,9-Dimethylfluorene and PCBM were synthesized according to literature methods.<sup>1-2</sup>

#### *Methyl 4-(N,N-diphenyl)phenyl butyrate (1)*

Triphenylamine (5.1 g, 21 mmol) and AlCl<sub>3</sub> (6.0 g, 45 mmol) were dissolved into dry dichloromethane (50 mL) and cooled to 0 °C. The glutaric anhydride (2.8 g, 24 mmol) in dry dichloromethane (10 mL) was added slowly into the mixture solution. The mixture was stirred at room temperature for overnight and poured into ice/water, and then, extracted with

dichloromethane twice. The combined organic phase was dried over anhydrous  $\text{MgSO}_4$ , and the solvent was removed under vacuum. The crude triphenylamine-based acid was directed used in next step. The acid crude was dissolved into methanol solution. After adding several drops of concentration  $\text{H}_2\text{SO}_4$ , the methanol solution was heated to reflux for overnight. Then, the mixture was cooled to room temperature and poured into water and extracted with dichloromethane. The organic phase was washed using water for several times and dried over anhydrous  $\text{MgSO}_4$ . After removing the solvent, the title compound was gotten in the yield of 30% after purifying by silica column.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.71 (d,  $J=9.3$  Hz, 2H), 7.24 (m, 4H), 7.06 (m, 6H), 6.89 (d,  $J=9.0$ , 2H), 3.60 (s, 3H), 2.86 (t, 2H), 2.33 (t, 2H), 1.96 (t, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 197.91, 174.00, 173.56, 152.33, 146.66, 129.79, 126.14, 124.81, 119.89, 51.80, 37.19, 33.43, 33.23, 20.28, 19.87. HRMS (ESI) ( $\text{M}^+$ ,  $\text{C}_{24}\text{H}_{23}\text{NO}_3$ ): calcd, 373.1678; found, 373.1662.

*Methyl 4-(N,N-diphenyl)phenyl butyrate p-tosylhydrazone (2)*

The compound **1** (0.7 g, 1.9 mmol) and *p*-toluenesulfonyl hydrazide (0.5 g, 2.7 mmol) were dissolved into methanol with addition of several drops of concentration HCl as catalyst. Then, the mixture solution was reflux for 10 hours. After cooling to room temperature, a white precipitate was collected by filtration and washed using cool methanol twice. The methanol solution was concentrated to around 10 mL and cooled at  $-4^\circ\text{C}$  for overnight. The resulted white precipitate was collected by filtration and washed with cool methanol. The combined white solid was dried overnight under vacuum to give the title compound with 74% yield. Yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 8.99 (s, 1H), 7.91 (d,  $J=8.4$  Hz, 2H), 7.49 (d,  $J=8.7$  Hz, 2H), 7.27 (m, 6H), 7.10 (m, 6H), 6.90 (d,  $J=8.8$  Hz, 2H), 3.82 (s, 3H), 2.59 (t, 2H), 2.42 (s, 3H), 2.32 (t, 2H), 1.67 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 174.92, 153.78, 149.31, 147.35, 143.82, 136.24, 129.63, 129.55,

128.17, 127.32, 125.18, 123.75, 122.20, 52.59, 32.31, 25.85, 21.78, 21.22. HRMS (ESI) ( $M^+$ ,  $C_{31}H_{31}N_3O_4S$ ): calcd, 541.2035; found, 541.2022.

*Methyl 2-(9,9-dimethylfluorenyl)butyrate (3)*

To a solution of 9,9-dimethylfluorene (3.5 g, 18 mmol) and  $AlCl_3$  (2.8 g, 21 mmol) in dry dichloromethane was added glutaric acid monomethyl ester chloride (3.0 g, 18 mmol) at 0 °C. The mixture was stirred at room temperature for overnight. Then, the resulted solution was poured into ice/water, and extracted with dichloromethane. The combined organic phase was dried over anhydrous  $MgSO_4$ , and then the solvent was removed under vacuum. The crude product was purified by silica column to give the title compound with 42% yield.  $^1H$  NMR ( $CDCl_3$ , ppm): 8.07 (s, 1H), 7.98 (dd, 1H), 7.78 (m, 2H), 7.48 (m, 1H), 7.39 (m, 2H), 3.72 (s, 3H), 3.11 (t, 2H), 2.48 (t, 2H), 2.11 (t, 2H), 1.54 (s, 6H).  $^{13}C$  NMR ( $CDCl_3$ , ppm): 199.34, 173.98, 154.99, 154.04, 144.28, 138.05, 135.90, 128.75, 127.97, 127.41, 123.00, 122.40, 121.14, 119.98, 51.77, 47.20, 37.75, 33.37, 27.12, 19.73. HRMS (ESI) ( $M^+$ ,  $C_{21}H_{22}O_3$ ): calcd, 322.1569; found, 322.1558.

*Methyl 2-(9,9-dimethylfluorenyl)butyrate p-tosylhydrazone (4)*

Compound **3** (1.3 g, 4 mmol) and p-toluenesulfonyl hydrazide (1.5 g, 8 mmol) were dissolved into methanol (15 mL) with addition of several drops of concentration HCl as catalyst. Then, the mixture solution was reflux for 10 hours. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane. The combined organic phase was dried over  $MgSO_4$ . After removing the solvent, the crude product was purified by silica column to give the title compound with 71% yield. Yield.  $^1H$  NMR ( $CDCl_3$ , ppm): 9.22 (s, 1H), 7.96 (d, J=8.3

Hz, 2H), 7.67-7.45 (m, 5H), 7.32 (m, 4H), 3.84 (s, 3H), 2.67 (t, 2H), 2.43 (s, 3H), 2.37 (m, 2H), 1.75 (m, 2H), 1.50 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 174.99, 154.32, 154.16, 153.91, 143.93, 140.89, 138.56, 136.23, 135.32, 129.61, 128.28, 127.94, 127.27, 125.56, 122.86, 120.62, 120.53, 119.96, 52.62, 47.03, 32.29, 27.28, 26.24, 21.78, 21.24. HRMS (ESI) ( $\text{M}^+$ ,  $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4\text{S}$ ): calcd, 490.1926; found, 490.1911.

*[6,6]-[(4-N,N-diphenyl)phenyl] C<sub>61</sub>-butyric acid methyl ester (TPA-PCBM)*

Compound **3** (360 mg, 0.66 mmol) was dissolved into dry pyridine (10 mL) under nitrogen. Then, the sodium methoxide (45 mg) was added quickly under nitrogen, the solution was stirred at room temperature for 20 min.  $\text{C}_{60}$  (400 mg, 0.56 mmol) in dichlorobenzene (30 mL) was added in one portion. The resulted purple solution was heated to 70-80 °C and stirred for 48 hours. Then, the solution was heated to reflux and stirred for 24 hours. After cooling to room temperature, the solution was loaded into silica column and pre-eluted with chlorobenzene, then by toluene. The fraction containing TPA-PCBM was collected and concentrated. The concentration solution was poured into methanol solution to give TPA-PCBM with 35% yield. Yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.74 (d, 2H), 7.33 (t, 4H), 7.20 (m, 6H), 7.10 (t, 2H), 3.74 (s, 3H), 2.91 (t, 2H), 2.58 (t, 2H), 2.24 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 173.78, 149.19, 148.16, 147.74, 147.61, 146.09, 145.40, 145.36, 145.33, 145.24, 144.99, 144.96, 144.84, 144.68, 144.59, 144.22, 143.98, 143.31, 143.22, 143.18, 143.11, 142.43, 142.31, 141.13, 140.92, 138.17, 137.84, 132.92, 129.62, 125.30, 123.68, 122.01, 80.38, 51.90, 51.69, 34.14, 33.81, 22.66. MALDI-TOF ( $\text{C}_{84}\text{H}_{23}\text{NO}_2$ ) calcd, 1077.173; found, 1077.136.

*[6,6]-[9,9-dimethylfluorenyl] C<sub>61</sub>-butyric acid methyl ester (MF-PCBM)*

Compound **4** (230 mg, 0.47 mmol) was dissolved into dry pyridine (9 mL) under nitrogen. Then, the sodium methoxide (35 mg) was added quickly under nitrogen, the solution was stirred at room temperature for 20 min. The C60 (281 mg, 0.39 mmol) in dichlorobenzene (33 mL) was added in one portion. The resulted purple solution was heated to 70-80 °C and stirred for 48 hours. Then, the solution was heated to reflux and stirred for 24 hours. After cooling to room temperature, the solution was loaded into silica column and pre-eluted with chlorobenzene, then by toluene. The fraction containing MF-PCBM was collected and concentrated. The concentration solution was poured into methanol solution to give MF-PCBM with 33% yield. Yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.96 (s, 1H), 7.89 (m, 2H), 7.80 (d, 1H), 7.49 (d, 2H), 7.36 (m, 2H), 3.69 (s, 3H), 2.97 (t, 2H), 2.56 (t, 2H), 2.25 (m, 2H), 1.57 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 173.67, 154.09, 153.75, 149.17, 148.09, 146.12, 145.38, 145.35, 145.24, 145.19, 144.99, 144.90, 144.84, 144.69, 144.64, 144.20, 143.97, 143.94, 143.19, 143.12, 142.46, 142.33, 142.30, 141.18, 140.91, 139.43, 138.83, 138.26, 137.75, 135.83, 131.27, 129.23, 127.82, 127.34, 126.79, 122.93, 120.45, 120.06, 80.31, 52.55, 51.87, 47.18, 34.13, 33.81, 27.22, 22.71. MALDI-TOF ( $\text{C}_{81}\text{H}_{22}\text{O}_2$ ) calcd, 1026.162; found, 1026.154.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were collected on a Bruker AV 500 spectrometer operating at 500 MHz and 125 MHz in deuterated chloroform solution with tetramethylsilane as reference.

## General characterization method

UV-Vis spectra were studied using a Perkin-Elmer Lambda-9 spectrophotometer. Cyclic voltammetry of different fullerenes was conducted in nitrogen-saturated dichlorobenzene with 0.1 M of tetrabutylammonium hexafluorophosphate using a scan rate of  $50 \text{ mV s}^{-1}$ . Gold micro-disc, Ag/AgCl and Pt mesh were used as working electrode, reference electrode and counter

electrode, respectively. The differential scanning calorimetry (DSC) was performed using DSC2010 (TA instruments) under a heating rate of 20 °C min<sup>-1</sup> and a nitrogen flow of 50 mL min<sup>-1</sup>. AFM images under tapping mode were taken on a Veeco multimode AFM with a Nanoscope III controller.

## **Device fabrication and characterization**

### **Organic solar cells**

To fabricate the inverted solar cells, ITO-coated glass substrates (15 Ω/□) were cleaned with detergent, de-ionized water, acetone, and isopropyl alcohol. Substrates were then treated with oxygen plasma for 5 min. A thin layer of ZnO nanoparticles (~50 nm), synthesized using the method described by Beek *et. al.*<sup>3</sup>, was spin-coated onto ITO-coated glass. The C<sub>60</sub>-SAM was then deposited on the ZnO surface using a two-step spin-coating process. First, a 1 mM solution of the molecules in tetrahydrofuran (THF)/chlorobenzene (CB) (1:1 v/v) was spin-coated on the ZnO film. To remove physically absorbed molecules, a second spin-coating using pure THF was applied. Afterward, a CB solution of P3HT (Rieke Metals) and different PCBMs (40 mg/ml) with a weight ratio of (1:0.7) was transferred and spin-coated on the ZnO modified layer to achieve a thickness of (~200 nm) in a glove box and annealed at 150 °C for different time. After the annealing process, a PEDOT:PSS solution (50 nm) was spin-coated onto the active layer and annealed for 10 min at 120 °C as previously reported.<sup>4</sup> A silver electrode (100 nm) was then vacuum deposited on top to complete the device structure.

The *J–V* characteristics of the solar cells were tested in air using a Keithley 2400 source measurement unit and an Oriel xenon lamp (450 W) coupled with an AM1.5 filter was used as

the light source. The light intensity was calibrated with a calibrated standard silicon solar cell with a KG5 filter which is traced to the National Renewable Energy Laboratory and a light intensity of a  $100 \text{ mW cm}^{-2}$  was used in all the measurements in this study. A physical mask was used to define the device illumination area of  $0.0314 \text{ cm}^2$  to minimize photocurrent generation from the edge of the electrodes. The performance of the OPV was averaged over at least 10 devices for each processed condition. The series resistance ( $R_s$ ) and shunt resistance ( $R_{sh}$ ) were calculated from the inverse gradient of the  $J$ - $V$  curve at 1 V and 0V, respectively.

### **Organic field-effect transistors**

Top contact OFETs were fabricated on heavily n-doped silicon substrates with a 300 nm thick thermally grown  $\text{SiO}_2$  dielectric (from Montco Silicon Technologies, Inc.). Before the PCBM deposition, the substrates were treated with HMDS by vapor phase deposition in a vacuum oven (200 mTorr,  $80^\circ\text{C}$ , 5 hrs). The different PCBM films were spin-coated at in a dry argon environment from a 1 wt% chloroform solution to obtain a film thickness of 50 nm. Interdigitated source and drain electrodes ( $W=9000 \text{ }\mu\text{m}$ ,  $L=90 \text{ }\mu\text{m}$ ,  $W/L=100$ ) were defined by evaporating a 10 nm Ca followed by 100 nm Al film through a shadow mask from the resistively heated Mo boat at  $10^{-6}$  Torr. OFET characterization was carried out in a  $\text{N}_2$ -filled glovebox using an Agilent 4155B semiconductor parameter S6 analyzer. The field-effect mobility was calculated in the saturation regime from the linear fit of  $(I_{ds})_{1/2}$  vs  $V_{gs}$ . The threshold voltage ( $V_t$ ) was estimated as the x intercept of the linear section of the plot of  $(I_{ds})_{1/2}$  vs  $V_{gs}$ . The subthreshold swing was calculated by taking the inverse of the slope of  $I_{ds}$  vs  $V_{gs}$  in the region of exponential current increase.

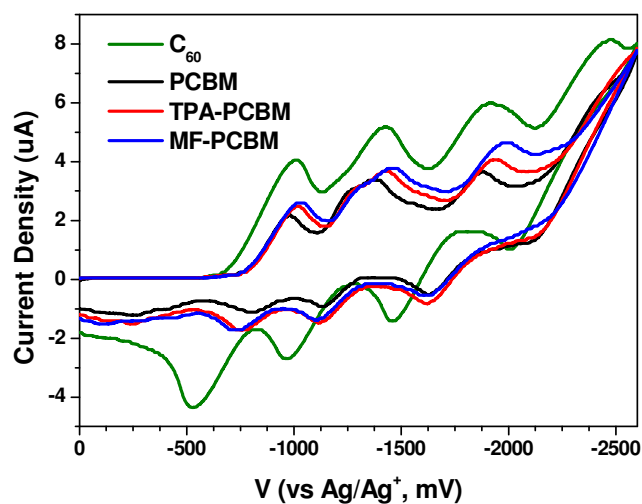


Figure S1. Cyclic voltammograms of  $C_{60}$ , PCBM, TPA-PCBM and MF-PCBM in dichlorobenzene solution.

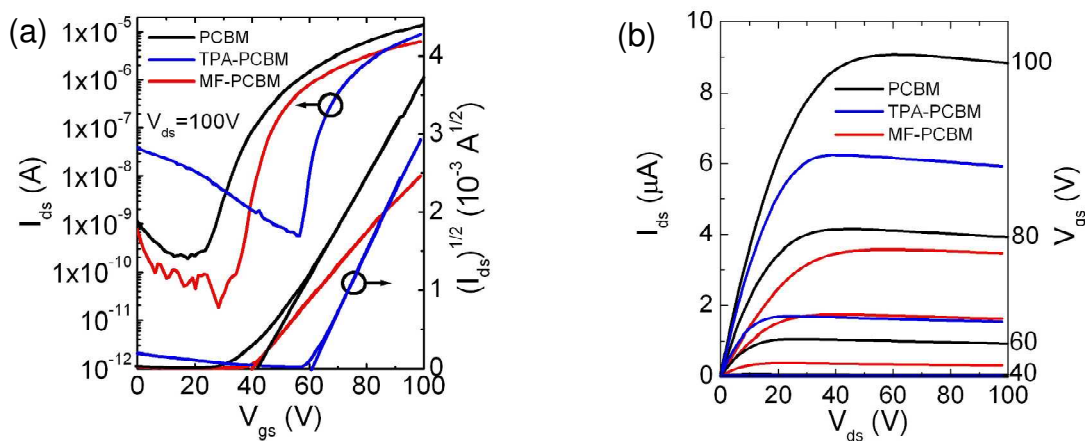
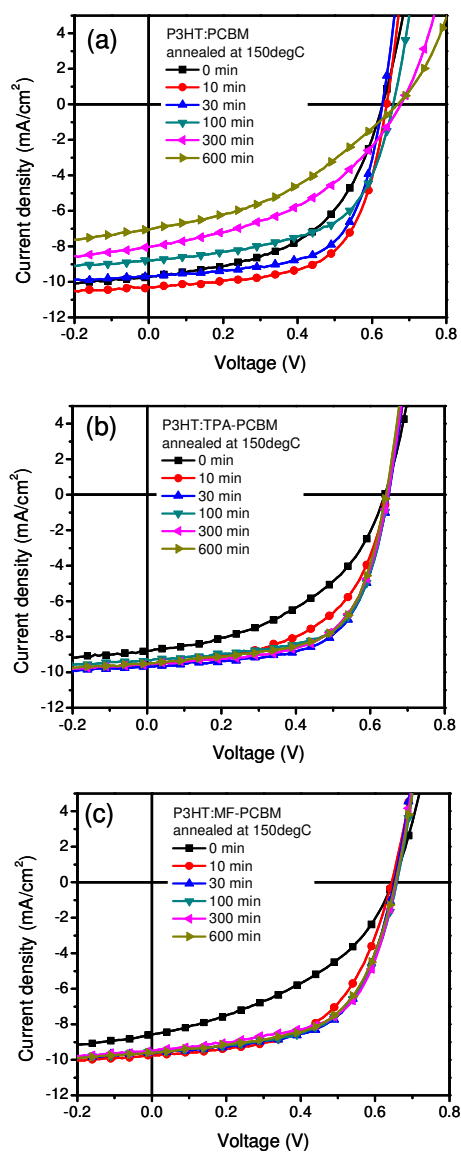


Figure S2. (a) Transfer characteristics and (b) Output current-voltage characteristics of PCBM, TPA-PCBM and MF-PCBM.





(d)

	$V_{oc}$	$J_{sc}$		PCE	$R_{sh}$	$R_s$
	(V)	(mA/cm <sup>2</sup> )	FF	(%)	( $\Omega$ cm <sup>2</sup> )	( $\Omega$ cm <sup>2</sup> )
PCBM	0.63	10.4	0.64	4.2	797	1.4
TPA-PCBM	0.65	9.9	0.62	4.0	911	2.0
MF-PCBM	0.65	9.8	0.59	3.8	738	2.6

Figure S3. The  $J$ - $V$  characteristics of (a) PCBM, (b)TPA-PCBM, (c) MF-PCBM based OPVs with different annealing times at 150 °C. (d) Performance table of PCBM, TPA-PCBM and MF-PCBM based OPV at optimum processed condition.

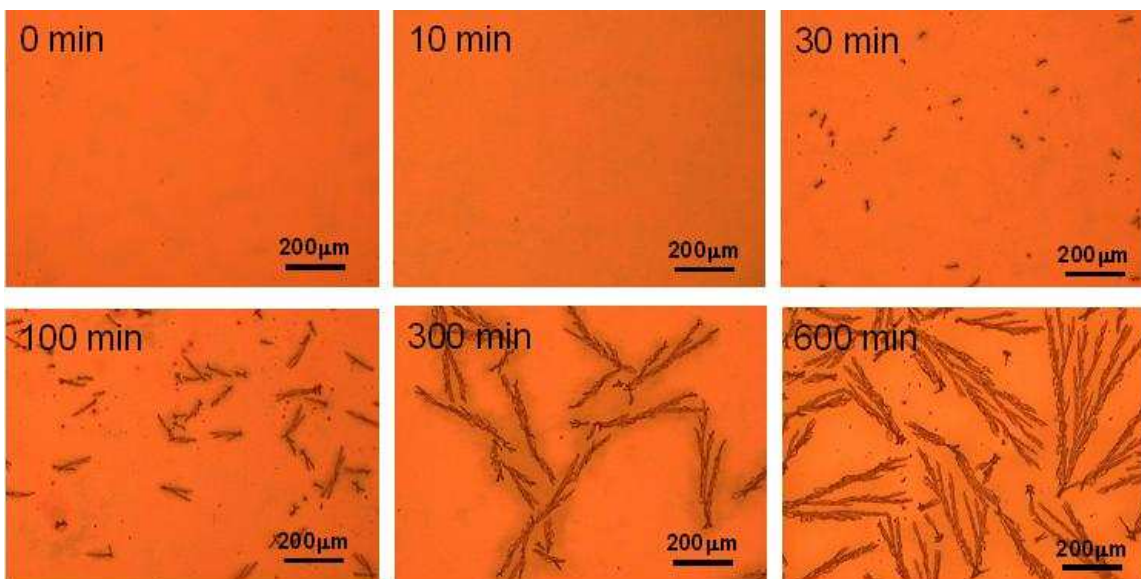


Figure S4. The annealing time-dependent optical images of PCBM:P3HT blend films annealed at 150 °C.

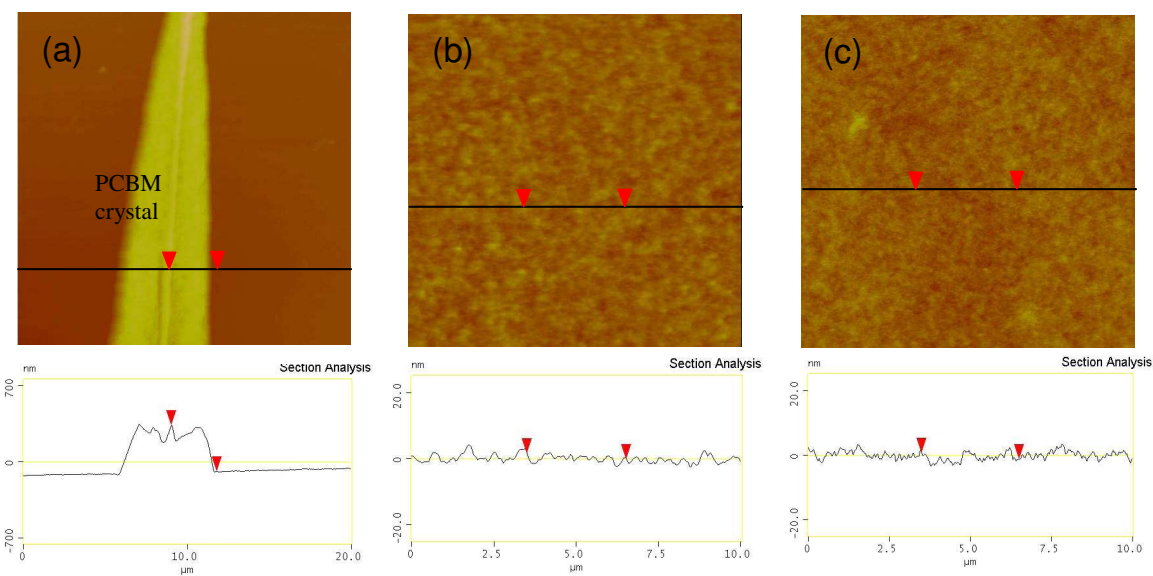


Figure S5. AFM images of (a) P3HT:PCBM, (b) P3HT:TPA-PCBM and (c) P3HT:MF-PCBM film annealed at 150°C for 600 min.

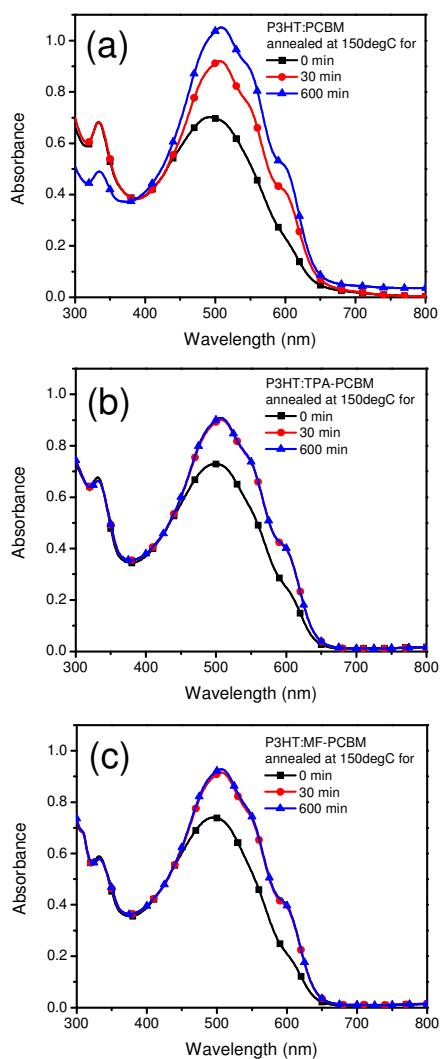


Figure S6. UV-Vis absorption spectra of (a) P3HT:PCBM, (b) P3HT:TPA-PCBM and (c) P3HT:MF-PCBM film annealed at 150°C for 0 min, 30 min and 600 min.

#### Reference:

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