Supplementary Information for

Blend Films of Amorphous Conjugated Polymer and Thermal Precursor Fullerene: Effects of Annealing Temperatures on Film Structures

and Photovoltaic Properties

Tomokazu Umeyama,*a Sho Shibata,a and Hiroshi Imahori*ab

^a Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto, 615-8510, Japan
^b Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
E-mail: umeyama@scl.kyoto-u.ac.jp, imahori@scl.kyoto-u.ac.jp;
Fax: +81-75-383-2571; Tel: +81-75-383-2568, +81-75-383-2566

Fullerene	E_1 (V) ^a	$E_2 (\mathbf{V})^a$	LUMO $(eV)^b$
C ₆₀ (9MA) ₂	-1.30	-1.70	-3.50
C ₆₀ (9MA)	-1.16	-1.55	-3.64
C ₆₀	-1.05	-1.44	-3.75
[60]PCBM	-1.12	-1.51	-3.68

 Table S1 Reduction potentials and LUMO energy levels

^{*a*} Values vs. Fc/Fc⁺. ^{*b*} LUMO / eV = $-(4.80 - E_1)$.



Fig. S1 Cyclic voltammograms (black) and differential pulse voltammograms (red) of (a) C_{60} –9MA-2, (b) C_{60} –9MA-1, (c) C_{60} , and (d) [60]PCBM measured in *o*-dichlorobenzene/acetonitrile mixture (v:v=5:1) containing 0.1 M Bu₄NPF₆. Sweep rate: 0.03 V s⁻¹; reference electrode: Ag/AgNO₃ (0.01 M AgNO₃, 0.09 M Bu₄PF₆ in acetonitrile).



Fig. S2 Optimized geometries, HOMO/LUMO electron density distributions, and energy levels of $C_{60}(9MA)_2$, $C_{60}(9MA)$, C_{60} , and [60]PCBM. As a representative example, the *trans*-1 type isomer of $C_{60}(9MA)_2$ was calculated.



Fig. S3 Tapping-mode atomic force micrograph of the PCDTBT:[60]PCBM film on a glass substrate without annealing. The color scale represents the height topography, with bright and dark representing the highest and lowest features, respectively. The rms surface roughness is 0.27 nm.



Fig. S4 Digital optical microscope images of the PCDTBT:C₆₀–9MA-2 films on glass substrates (a) without annealing, and annealed at (b) 120 °C, (c) 130 °C, (d) 140 °C, (e) 160 °C, and (f) 180 °C.



Fig. S5 Tapping-mode atomic force micrographs of the P3HT:C₆₀–9MA-2 (1:1, w/w) films on glass substrates (a) before and (b) after annealing at 140 °C for 20 min. The color scale represents the height topography, with bright and dark representing the highest and lowest features, respectively. The rms surface roughnesses are (a) 6.4 and (b) 10.5 nm, respectively.



Fig. S6 Current density-voltage curves under AM 1.5 solar illumination (solid line) and a dark condition (dotted line) for an OPV device based on PCDTBT:C₆₀–9MA-2 annealed at 140 °C. The nonzero slope near the y-intercept for the curve under illumination despite the flatness for the curve in dark suggests the occurrences of a shunt current loss and/or a geminate recombination at the polymer-fullerene interface under illumination.^{S1}



Fig. S7 Photocurrent action spectra of the OPV devices based on PCDTBT:C₆₀–9MA-2 annealed at various temperatures. The convolution of the spectral response with the photon flux of the AM 1.5G spectrum provided the estimated J_{SC} values of 2.04 mA cm⁻² (without annealing), and 6.18, 6.93, 7.65, 7.88, and 7.37 mA cm⁻² (annealed at 120, 130, 140, 160, and 180 °C), respectively.

References

[S1] J. D. Servaites, M. A. Ratner and T. J. Marks, *Energy Environ. Sci.*, 2011, 4, 4410.