

Electronic Supplementary Information (ESI)

A Ternary Blend of Polymer, Fullerene, and Insulating Self-Assembling Triptycene Molecule for Organic Photovoltaics

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Experimental

Synthesis and characterization of TP-C₆ and TP-C₁₂'

Materials and Methods

Unless otherwise noted, all commercial reagents were used as received. 1,8,13-trihydroxytryptcene (TP-OH)^{S1} and 1,8-dihydroxytryptcene^{S2} was prepared according to previously reported procedures. Column chromatography was carried out using Wakogel silica C-200 (particle size: 75–150 μm). Infrared (IR) spectra were recorded at 25 °C on a JASCO FT/IR-660_{plus} Fourier transform IR spectrometer. Nuclear magnetic resonance (NMR) spectroscopy measurements were carried out on a Bruker AVANCE-400 spectrometer (¹H: 400.0 MHz and ¹³C: 100.6 MHz) or on a Bruker AVANCE III HD-500 spectrometer (¹H: 500.0 MHz and ¹³C: 125.7 MHz). Chemical shifts (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ¹H (CDCl₃: ¹H(δ) = 7.26 ppm) and the residual solvent for ¹³C (CDCl₃: ¹³C(δ) = 78.0 ppm). Absolute values of the coupling constants are given in Hertz (Hz), regardless of their sign. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). Mass spectrometry measurements were carried out on a Bruker micrOTOF II mass spectrometer equipped with an atmospheric pressure chemical ionization (APCI) probe.

Synthesis of 1,8,13-trihexyloxytryptcene (TP-C₆). 1-Bromohexane (2.18 g, 13.2 mmol) was added to a DMF suspension (10 mL) of a mixture of TP-OH^{S1} (500 mg, 1.65 mmol) and K₂CO₃ (1.37 g, 9.92 mmol) at 25 °C, and the resulting mixture was stirred at 80 °C for 12 h. The reaction mixture was allowed to cool to 25 °C, and then poured into water and extracted with Et₂O. A combined organic extract was washed successively with water and brine, and an organic phase separated was dried over anhydrous MgSO₄ and then evaporated to dryness under a reduced pressure. The residue was recrystallized from CHCl₃ to afford TP-C₆ as white solid (653 mg, 1.18 mmol) in 71% yield: FT-IR (KBr): ν (cm⁻¹) 3435, 2933, 2869, 1598, 1486, 1472, 1397, 1323, 1282, 1101, 1065, 787, 736. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.99 (d, *J* = 7.1 Hz, 3H), 6.91 (s, 1H), 6.87 (t, *J* = 7.8 Hz, 3H), 6.55 (d, *J* = 7.6 Hz, 3H), 5.37 (s, 1H), 3.96 (t, *J* = 6.5 Hz, 6H), 1.85 (m, 6H), 1.58 (m, 6H), 1.39–1.36 (m, 12H), 0.94 (t, *J* = 7.2 Hz, 9H). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 154.1, 148.5, 133.8, 125.5, 116.4, 110.1, 68.8, 54.6, 33.5, 31.8, 29.7, 25.8, 22.7, 14.2. APCI-TOF mass: calcd. for C₃₈H₅₀O₃ [M]⁺: *m/z* = 554.375, found: 554.375.

Synthesis of 1,8-didodecyloxytryptcene (TP-C₁₂'). 1-Bromododecane (3.93 g, 15.8 mmol) was added to a DMF suspension (30 mL) of a mixture of 1,8-dihydroxytryptcene^{S2} (1.10 mg, 3.84 mmol) and K₂CO₃ (1.65 g, 11.9 mmol) at 25 °C, and the resulting mixture was stirred at 80 °C for 12 h. The reaction mixture was allowed to cool to 25 °C, and then poured into water and extracted with Et₂O. A combined organic extract was washed successively with water and brine, and an organic phase separated was dried over anhydrous MgSO₄ and then evaporated to dryness under a reduced pressure. The residue was subjected to column chromatography (SiO₂, hexane/CHCl₃ 1/5 v/v) to allow isolation of TP-C₁₂' as white solid (2.00 g, 3.21 mmol) in 84% yield: FT-IR (KBr): ν (cm⁻¹) 3057, 3018, 2920, 2850, 2360, 1598, 1486, 1470, 1397, 1322, 1307, 1272, 1195, 1162, 1106, 1075, 959, 909, 867, 787, 759, 739, 720, 652, 624, 607. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.42–7.35 (m, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.97–6.95 (m, 2H), 6.90 (t, *J* = 7.8 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H), 5.39 (s, 1H), 4.00–3.95 (m, 4H), 1.86 (m, 4H), 1.60–1.53 (m, 4H), 1.45–1.30 (m, 32H), 0.90 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 155.0, 149.0, 147.3, 146.5, 134.6, 126.7, 125.9, 125.7, 124.8, 124.4, 117.3, 110.9, 69.7, 55.4, 41.1, 32.9, 30.8 (three peaks), 30.7, 30.6, 30.5, 30.4, 27.2, 23.7, 15.1. APCI-TOF mass: calcd. for C₄₄H₆₂O₂ [M]⁺: *m/z* = 622.474, found: 622.474.

Synchrotron X-ray Diffraction Analysis. Powder X-ray diffraction (PXRD) analysis of TP-C₆ and TP-C₁₂' were carried out at BL45XU in SPring-8 (Hyogo, Japan) with a R-Axis IV++ (Rigaku) model imaging plate area detector. The scattering vector, $q = 4\pi\sin\theta/\lambda$, and the position of incident X-ray on the detector were calibrated using several orders of layer reflections from silver behenate ($d = 58.380 \text{ \AA}$), where 2θ and λ are scattering angle and wavelength of X-ray (1.00 \AA), respectively. The sample-to-detector distance was 0.40 m, respectively. Using the FIT2D software^{S3}, the scattering/diffraction images recorded were integrated along the Debye-Scherrer ring to afford one-dimensional intensity data. The cell parameters were refined using the CellCalc ver. 2.10 software^{S4}. For the PXRD measurements, a powdery sample was placed into a 1.5 mm- ϕ glass capillary in a temperature-controlled heating block and was once heated for melting.

Supplementary References

- S1. N. Seiki, Y. Shoji, T. Kajitani, F. Ishiwari, A. Kosaka, T. Hikima, M. Takata, T. Someya and T. Fukushima, *Science*, 2015, **348**, 1122–1126.
- S2. Y. Li, R. Cao and S. J. Lippard, *Org. Lett.*, 2011, **13**, 5052–5055.
- S3. FIT2D: <http://www.esrf.eu/computing/scientific/FIT2D/>
- S4. CellCalc ver. 2.10: http://homepage2.nifty.com/~hsc/soft/cellcalc_e.html

Table S1. Series (R_s) and parallel (R_p) resistances of the best-performing P3HT:PCBM:TP-C₁₂ = 1:1:x devices.^a

| TP-C ₁₂ | FF | $R_s / \Omega \text{ cm}^2$ | $R_p / \text{k}\Omega \text{ cm}^2$ |
|--------------------|-------|-----------------------------|-------------------------------------|
| 0 | 0.704 | 1.30 | 1.99 |
| 0.05 | 0.661 | 1.47 | 3.35 |
| 0.10 | 0.675 | 1.45 | 1.43 |
| 0.15 | 0.646 | 1.87 | 1.41 |
| 0.20 | 0.613 | 1.90 | 1.42 |

^a Normal cell (ITO/PEDOT:PSS/BHJ/Ca/Al) under pseudo-sunlight at 100 mW cm⁻².

Table S2. Series (R_s) and parallel (R_p) resistances of the best-performing PffBT4T:PCBM:TP-C₆ = 1:1.2:x devices.^a

| TP-C ₆ | FF | $R_s / \Omega \text{ cm}^2$ | $R_p / \text{k}\Omega \text{ cm}^2$ |
|-------------------|-------|-----------------------------|-------------------------------------|
| 0 | 0.731 | 0.89 | 1.35 |
| 0.05 | 0.722 | 1.18 | 1.95 |
| 0.10 | 0.732 | 1.10 | 1.37 |

^a Inverted cell (ITO/ZnO/BHJ/MoO_x/Ag) under pseudo-sunlight at 100 mW cm⁻².

Table S3. Averaged SCLC hole and electron mobilities of PffBT4T:PCBM:TP-C₆ = 1:1.2:x devices.

| TP-C ₆ | Hole / cm ² V ⁻¹ s ⁻¹ | Electron / cm ² V ⁻¹ s ⁻¹ |
|-------------------|--|--|
| 0 | $(3.1 \pm 0.4) \times 10^{-3}$ | $(8.1 \pm 3.6) \times 10^{-4}$ |
| 0.05 | $(2.7 \pm 0.3) \times 10^{-3}$ | $(5.4 \pm 1.6) \times 10^{-4}$ |

Table S4. Summary of the OPV performance of P3HT:PCBM:TP-C₆ = 1:1:x.^a

| TP-C ₆ | J_{sc} (max) / mA cm ⁻² | V_{oc} (max) / V | FF (max) | PCE (max) /% |
|-------------------|--------------------------------------|--------------------------|--------------------------|-----------------------|
| 0 | 8.77 ± 0.08 (8.85) | 0.578 ± 0.008 (0.588) | 0.696 ± 0.012 (0.704) | 3.53 ± 0.12 (3.66) |
| 0.05 | 9.56 ± 0.17 (9.72) | 0.578 ± 0.004 (0.581) | 0.623 ± 0.020 (0.693) | 3.44 ± 0.13 (3.59) |
| 0.10 | 8.26 ± 0.30 (8.53) | 0.581 ± 0.001 (0.582) | 0.614 ± 0.006 (0.620) | 2.95 ± 0.10 (3.03) |

^a Normal cell (ITO/PEDOT:PSS/BHJ/Ca/Al) under pseudo-sunlight at 100 mW cm⁻².

Table S5. Degradation of OPV devices.^a

| Device | Time (min) | J_{sc} / mA cm ⁻² | V_{oc} / V | FF | PCE /% |
|-------------------------------------|------------|--------------------------------|--------------|-------|--------|
| PffBT4T:PCBM | 0 | 19.4 | 0.730 | 0.647 | 9.16 |
| (CB with DIO) ^b | 100 | 7.42 | 0.608 | 0.529 | 2.39 |
| PffBT4T:PCBM: | 0 | 16.5 | 0.732 | 0.595 | 7.20 |
| TP-C ₆ (CB) ^c | 100 | 14.7 | 0.735 | 0.570 | 6.15 |

^a Inverted structure (ITO/ZnO/active layer/MoO_x/Ag). Under AM1.5G at 100 mW cm⁻². The cells were placed in a N₂-filled chamber. The 0 min is the time when the PCE was stabilized (within a few min after starting a measurement). The cells were continued to be exposed to pseudo-sunlight. ^b PffBT4T:PCBM=1:1.2 processed from CB with 3 vol% DIO. The film thickness was ~520 nm. ^c PffBT4T:PCBM:TP-C₆=1:1.2:0.05 processed from CB. The film thickness was ~270 nm (about half of the optimal thickness).

Supplementary Figures.

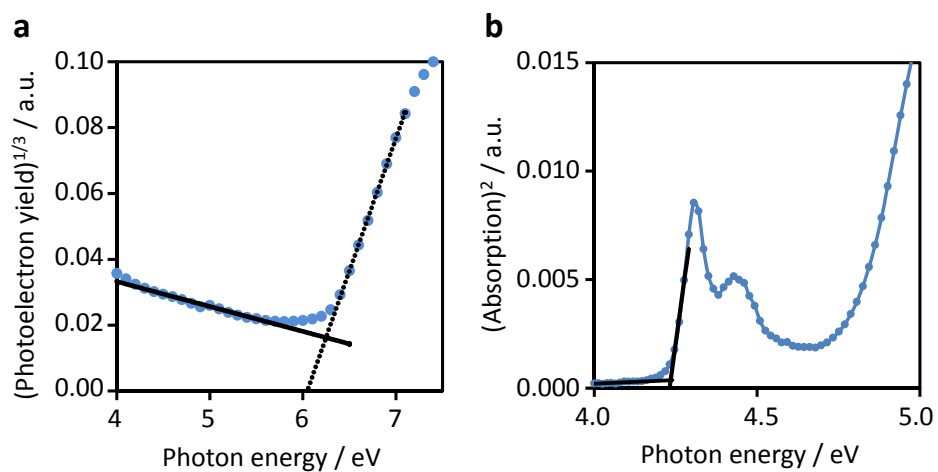


Fig. S1. Evaluation of HOMO and bandgap energy of TP-C₁₂ in the film state. (a) PYS spectrum. The least-mean-square fit of liner functions and their cross point yielded the HOMO of -6.25 eV from the vacuum level. (b) Square of photoabsorption vs. photon energy. The least-mean-square fit of liner functions and their cross point yielded the bandgap of 4.23 eV.

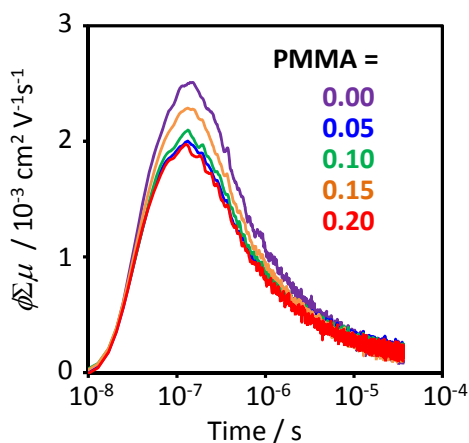


Fig. S2. TRMC transients of P3HT : PCBM : PMMA = 1 : 1 : x (x = 0–0.2) (w/w) excited at 355 nm.

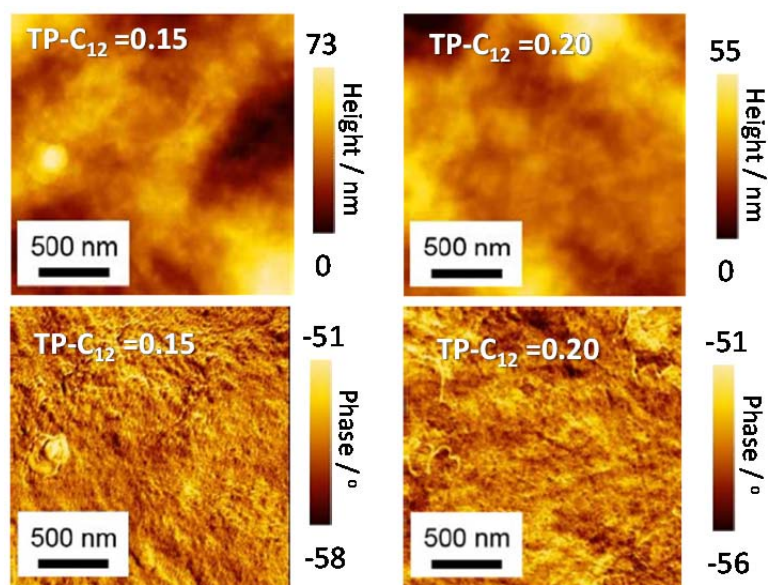


Fig. S3. AFM height (upper) and phase (lower) images of P3HT : PCBM : TP-C₁₂ = 1 : 1 : x (x = 0.15–0.2) (w/w).

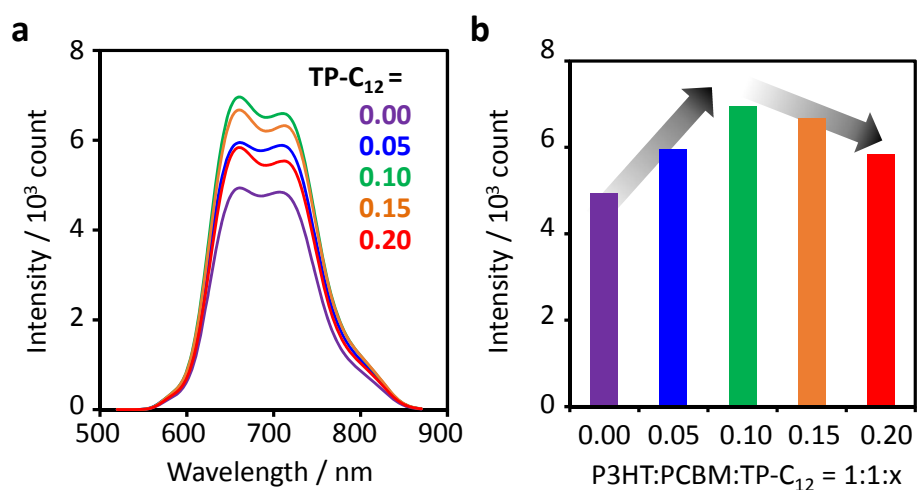


Fig. S4. (a) Fluorescence spectra of P3HT : PCBM : TP-C₁₂ = 1 : 1 : x (x = 0–0.2) (w/w) films (λ_{ex} = 500 nm). (b) Fluorescence maxima vs. TP-C₁₂ blend ratio.

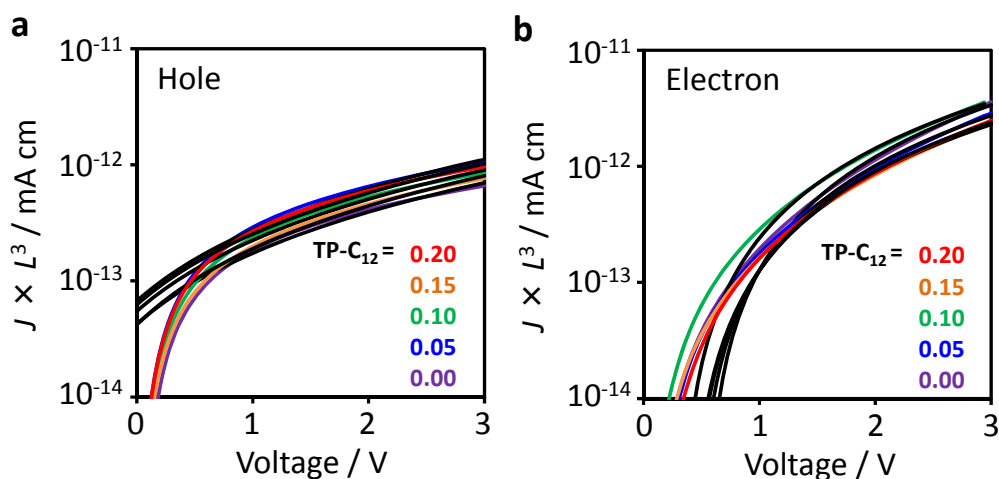


Fig. S5. SCLC J - V curves (typical ones) of P3HT : PCBM : TP- C_{12} = 1 : 1 : x ($x = 0$ – 0.2) (w/w). The black solid lines are fitting curve of Mott-Gurney law. (a) Hole only devices (ITO/PEDOT:PSS/active layer/Au). (b) Electron only devices (Al/active layer/LiF/Al).

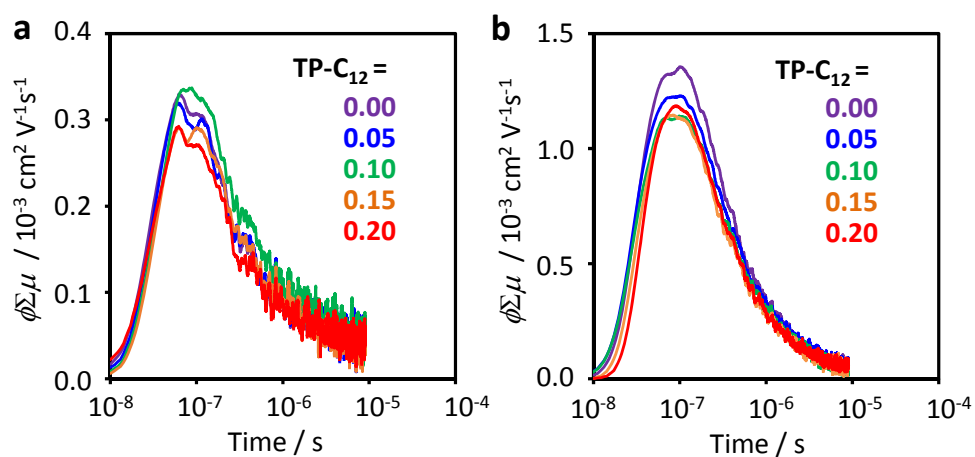


Fig. S6. TRMC transients of PTB7 : PCBM : TP- C_{12} = 1 : 1.5 : x ($x = 0$ – 0.2) (w/w) excited at 355 nm. Films were processed from (a) CB and (b) CB with 3 v/v% DIO.

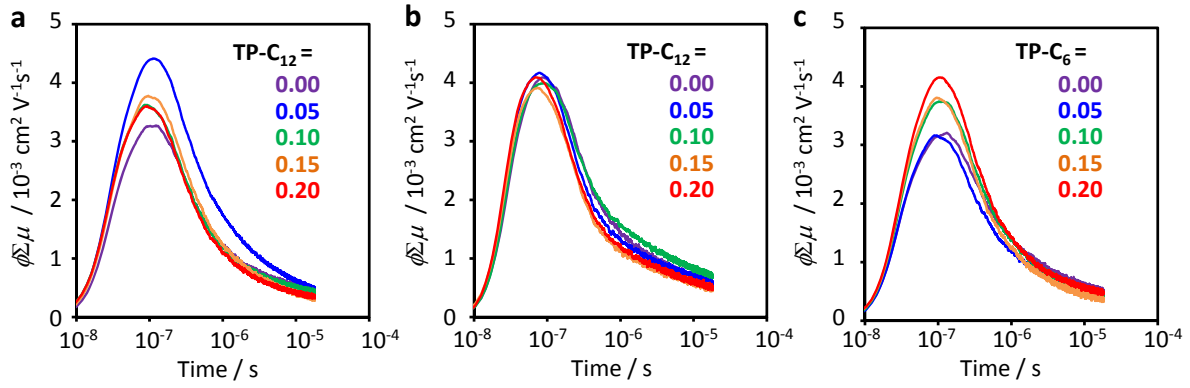


Fig. S7. TRMC transients of PffBT4T : PCBM : TP-C₁₂ (or TP-C₆) = 1 : 1.2 : x (x = 0–0.2) (w/w) excited at 355 nm. (a) Ternary blend with TP-C₁₂ processed from CB, (b) ternary blend with TP-C₁₂ processed from CB with 3 v/v% DIO, and (c) ternary blend with TP-C₆ processed from CB.

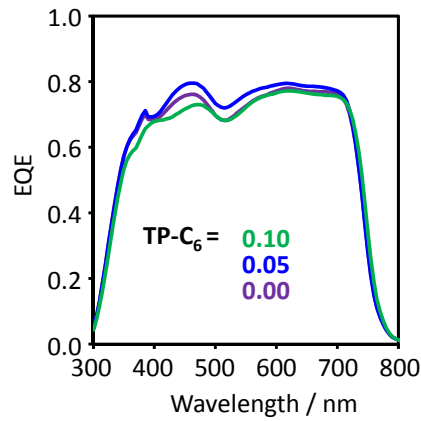


Fig. S8. EQE spectra of PffBT4T : PCBM : PT-C₆ = 1 : 1.2 : x (x = 0–0.1) (w/w) devices processed from CB. The J_{sc} calculated from the EQE spectra are 17.4, 17.9, and 17.3 mA cm⁻² for TP-C₆ = 0, 0.05, and 0.10, respectively. They are in excellent agreement with J_{sc} under pseudo sunlight (17.0, 18.4, and 17.5 mA cm⁻²), within only 3% difference.

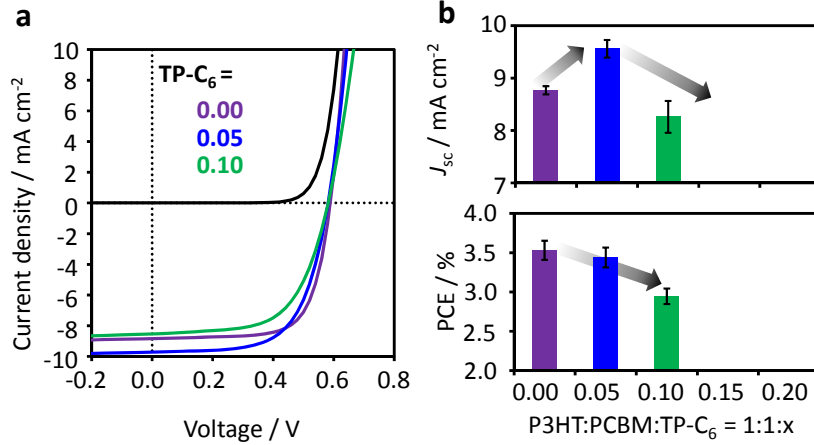


Fig. S9. OPV characterization of P3HT : PCBM : TP-C₆ = 1 : 1 : x (x=0-0.1). (a) J - V curves of the best-performing device. (b) Averaged J_{sc} (upper) and PCE (lower).

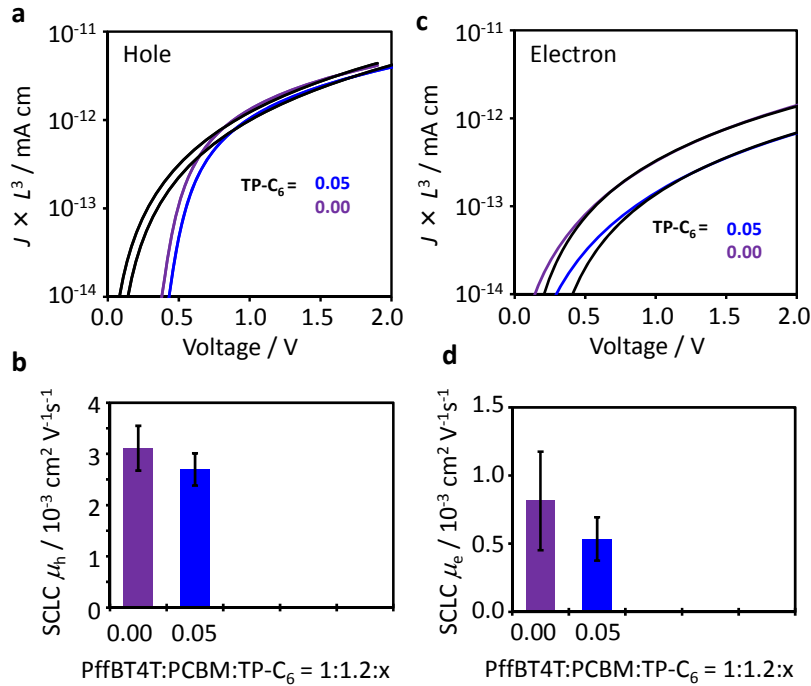
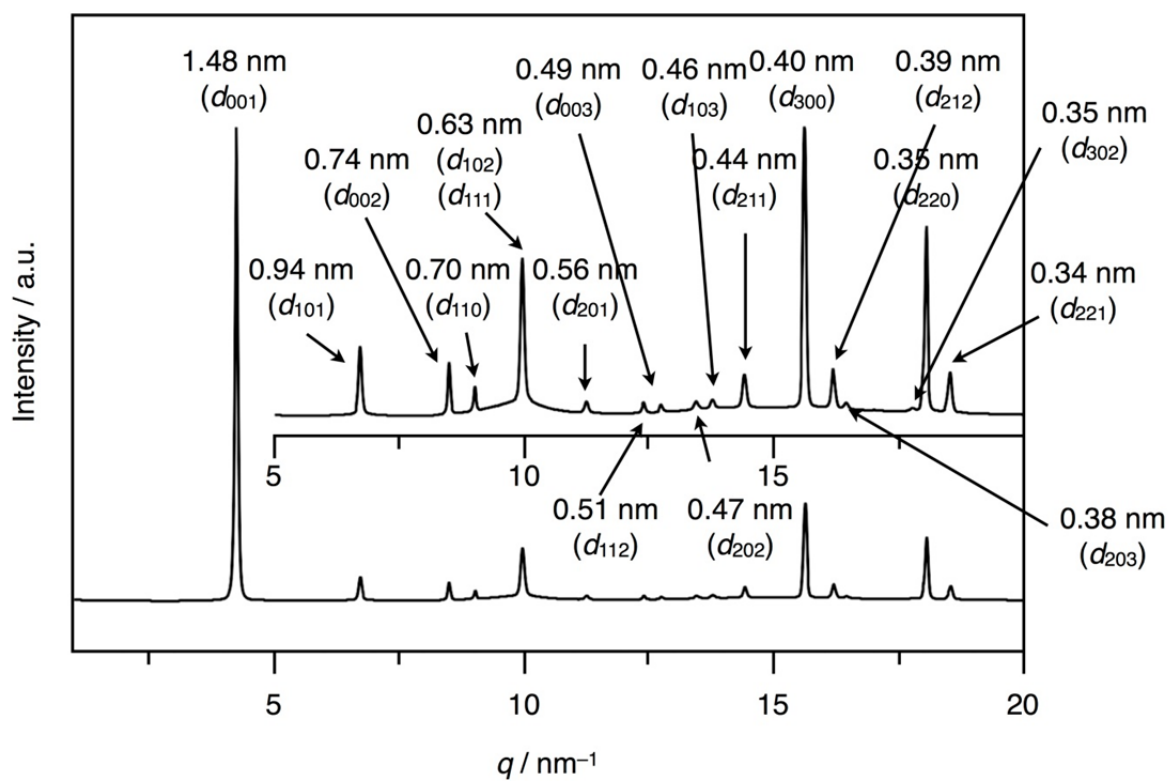


Fig. S10. SCLC hole (a, b) and electron (c, d) mobilities of PffBT4T : PCBM : TP-C₆ = 1 : 1.1 : x (x=0, 0.05). (a, c) The black solid lines are fitting curve of Mott-Gurney law. (b, d) The values were averaged over 4–8 devices.

(a) TP-C₆



(b) TP-C₁₂'

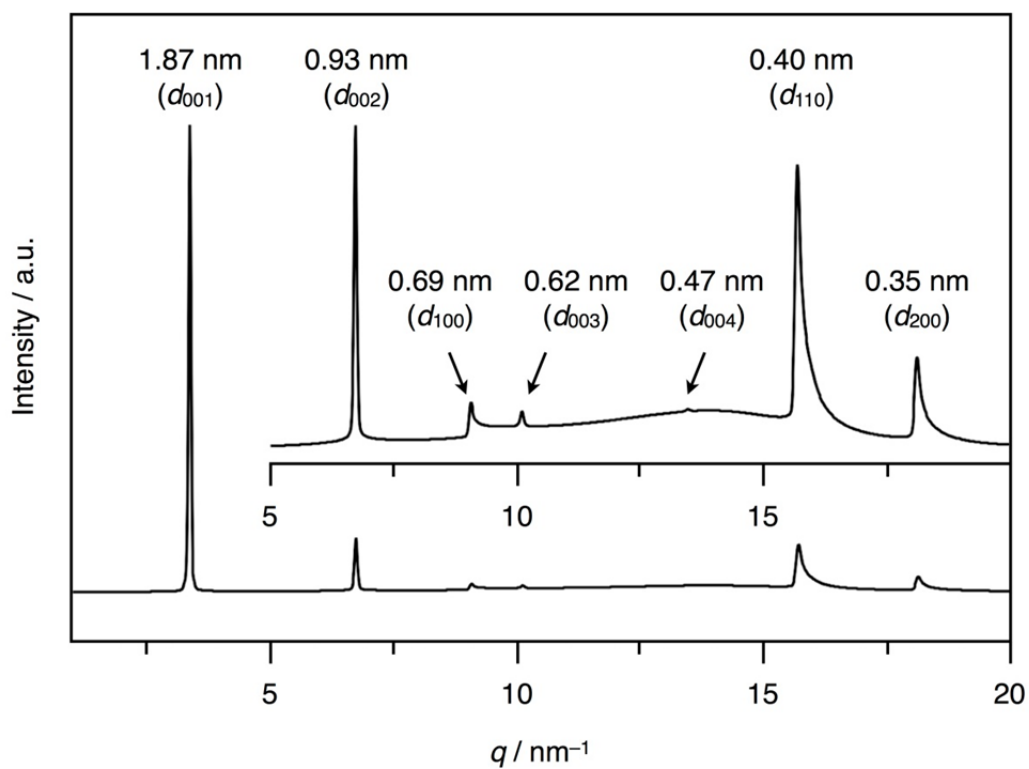


Fig. S11 Powder X-ray analysis using synchrotron radiation at SPring8, Japan. (a) TP-C₆ and (b) TP-C₁₂'.

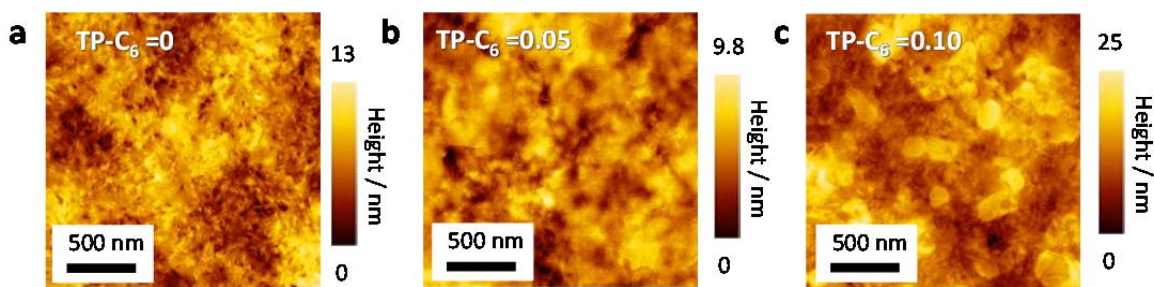


Fig. S12 AFM height images of PffBT4T : PCBM : TP-C₆ = 1 : 1.2 : x (x = 0–0.1) (w/w) devices processed from CB without DIO.

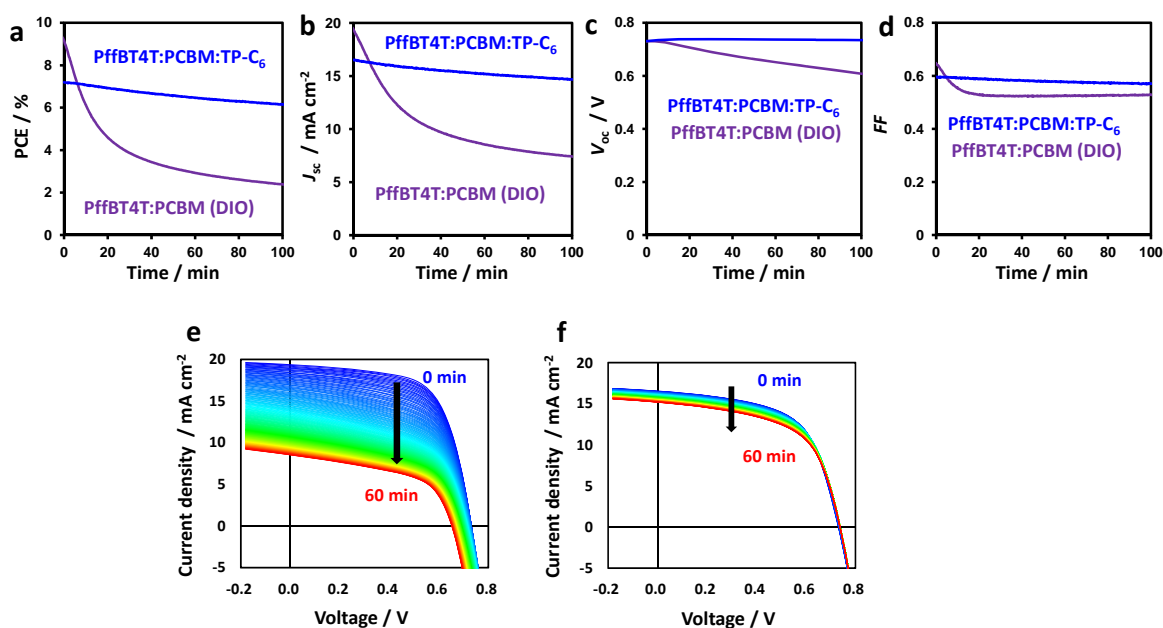


Fig. S13 Degradation of PffBT4T:PCBM = 1:1.2 devices (inverted structure, ITO/ZnO/active layer/MoO_x/Ag) sealed in a N₂-filled chamber under pseudo sunlight (100 mW cm⁻²). (a)-(d) Device parameters of PffBT4T:PCBM:TP-C₆ (0.05) processed from CB (blue) and PffBT4T:PCBM processed from CB with 3 v/v% DIO (purple). (e) *J-V* curves of PffBT4T:PCBM from 0 (blue) to 60 min (red). (f) *J-V* curves of PffBT4T:PCBM:TP-C₆ (0.05) from 0 (blue) to 60 min (red). The curves were measured for every 15 sec. See Table S5 for the values of *J*_{sc}, *V*_{oc}, FF, and PCE at 0 and 100 min.