Electronic Supplementaly Information (ESI)

On the Role of Local Charge Carrier Mobility in the Charge Separation Mechanism of Organic Photovoltaics

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Supporting Tables S1-S4, Figures S1-S11

Supporting Table

Table S1. OPV device parameters and $\Sigma\mu$ measured by TRMC

Polymer [a]	PCE (%)	V_{oc} (V)	J_{sc} ($mAcm^{-2}$)	FF (%)	PCE/V_{oc} (% V^{-1})	Solvent [b]	$\Sigma\mu$ blend ($cm^2V^{-1}s^{-1}$)	$\Sigma\mu$ polymer ($cm^2V^{-1}s^{-1}$)	Ref [c]
PCPDTBT (1:3)	3.35	0.66	11.74	43	5.08	DCB	0.050	0.19	[S1]
PCPDTBT (1:3)	5.12	0.61	15.73	53	8.39	CB / DIO	0.099		[S1]
PCDTBT (1:4)	6.10	0.88	10.60	66	6.93	DCB	0.060	0.22	[S2]
PBDTTT-CF (1:1.5)	6.22	0.75	13.56	59	8.29	DCB	0.13	0.031	[S3]
PBDTTT-CF (1:1.5)	7.40	0.75	13.56	69	9.87	CB / DIO	0.089		[S3]
PSBTBT (1:1.5)	5.10	0.68	12.70	55	7.50	DCB	0.083		[S4]
P3HT (1:1)	4.37	0.61	10.6	67	7.16	DCB	0.26	0.30	[S5]
PBTTT-C_{14} (1:4)	2.34	0.53	9.37	48	4.42	DCB	0.16	2.3	[S6]
PQT-12 (1:4)	1.15	0.61	4.31	44	1.88	DCB	0.057	0.22	[S7]
PTzBT-BOHD (1:2)	6.65	0.89	11.35	65	7.47	CB	0.23	0.24	[S8]
PTzBT-14HD (1:2)	5.42	0.82	9.93	66	6.61	CB	0.19		[S8]
PTzBT-14OD (1:2)	5.12	0.82	9.77	64	6.24	CB	0.14		[S8]

[a] Polymer (p/n blend ratio with PCBM) [b] The solvent and additive. DCB: *o*-dichlorobenzene, CB: chlorobenzene, DIO: 1,8-diiodeoctane. [c] Reference number of the device performance.

Table S2. Summary of XRD measurements of polymer:PCBM blend.

Polymer [a]	Inter-lamellar peak intensity (counts)	2θ (°)	d (nm)[b]	$L_{(100)}$ (nm)[c]
P3HT (1:1)	3.8×10^3	5.44	1.62	18.5
PQT-12 (1:4)	1.6×10^3	3.44	2.57	35.7
PBTTT-C_{14} (1:4)	2.6×10^3	3.20	2.76	14.2
PTzBT-14HD (1:2)	1.5×10^4	4.06	2.18	10.9
PTzBT-14OD (1:2)	2.7×10^4	3.58	2.47	16.4
PTzBT-BOHD (1:2)	2.7×10^3	4.78	1.85	8.6
PCPDTBT (1:3)	1.3×10^2	6.46	1.37	2.9
PCPDTBT (1:3) DIO	-[d]	-[d]	-[d]	-[d]
PSBTBT (1:2)	4.9×10^2	5.24	1.69	7.9
PBDTTT-CF (1:1.5)	8.5×10^2	5.38	1.64	3.7
PBDTTT-CF (1:1.5) DIO	6.3×10^2	5.08	1.74	3.2
PCDTBT (1:4)	1.2×10^2	5.26	1.68	4.5

[a] Polymer (p/n blend ratio with PCBM) with/without DIO. [b] Inter-lamellar distance. [c] Correlation length in the inter-lamellar direction calculated using Scherrer equation. [d] Not obtained.

Table S3. Electrochemical properties of the polymers.

Polymer	HOMO /eV	LUMO /eV	bandgap /eV	Normalized η_{abs}	Ref [a]
PCPDTBT	-5.30	-3.55	1.75	1.00	[S9]
PBDTTT-CF	-5.22	-3.45	1.77	0.97	[S10]
PCDTBT	-5.50	-3.60	1.90	0.80	[S2]
PSBTBT	-5.05	-3.27	1.78	0.96	[S4]
P3HT	-5.10	-3.10	2.00	0.68	[S11]
PQT-12	-5.10	-3.10	2.00	0.68	[S7]
PBTTT-C_{14}	-5.10	-3.10	2.00	0.68	[S6]
PTzBT-BOHD	-5.23	-3.43	1.80	0.93	[S8]
PTzBT-14HD	-5.21	-3.41	1.80	0.93	[S8]
PTzBT-14OD	-5.21	-3.41	1.80	0.93	[S8]

[a] Reference number of the electrochemical properties.

Table S4. Charge collection efficiency calculated by Hecht equation.

Polymer [a]	$\tau_{1/2}$ (μs) [b]	SCLC hole mobility ($cm^2V^{-1}s^{-1}$)	V_{oc} (V)	Thickness (nm)	η_{CC} [c]	Ref [d]
PCPDTBT (1:3)	0.18	4.0×10^{-4}	0.66	100	0.62	[S12]
PBDTTT-CF (1:1)	0.22	7.0×10^{-4}	0.76	100	0.81	[S10]
PCDTBT (1:4)	0.20	1.5×10^{-4} (FET)	0.90	100	0.46	[S13]
PSBTBT	0.35	1.0×10^{-3} (FET)	0.68	100	0.90	[S14]
P3HT (1:1)	0.50	3.1×10^{-4}	0.61	220	0.36	[S15]
PQT-12 (1:4)	0.50	2.7×10^{-4}	0.61	220	0.32	[S16]
PBTTT (1:4)	0.089	3.8×10^{-4}	0.61	100	0.38	[S6]
PTzBT-BOHD (1:2)	0.22	4.8×10^{-4}	0.53	100	0.66	[S8]
PTzBT-14HD (1:2)	0.85	1.9×10^{-4}	0.89	200	0.54	[S8]
PTzBT-14OD (1:2)	0.95	3.6×10^{-4}	0.82	200	0.72	[S8]

[a] Polymer (p/n blend ratio with PCBM). [b] Half-lifetime of TRMC transient excited at 355 nm ($I_0 = 4.6\times10^{15}$ photons cm^{-2}). [c] η_{cc} was calculated by Hecht expression[S17,S18] given by

$$\eta_{CC} = \frac{\mu\tau V_b}{d \cdot d_C}\left\{1 - \exp\left(-\frac{d \cdot d_C}{\mu\tau V_b}\right)\right\}$$

, where μ is the mobility, τ is the lifetime, V_b is the internal bias voltage at the short circuit (= V_{oc}), d is the thickness of the active layer, and d_c is the average collection length (=d /2). [d] Reference number of the SCLC or FET mobilities.

Supporting Figures.

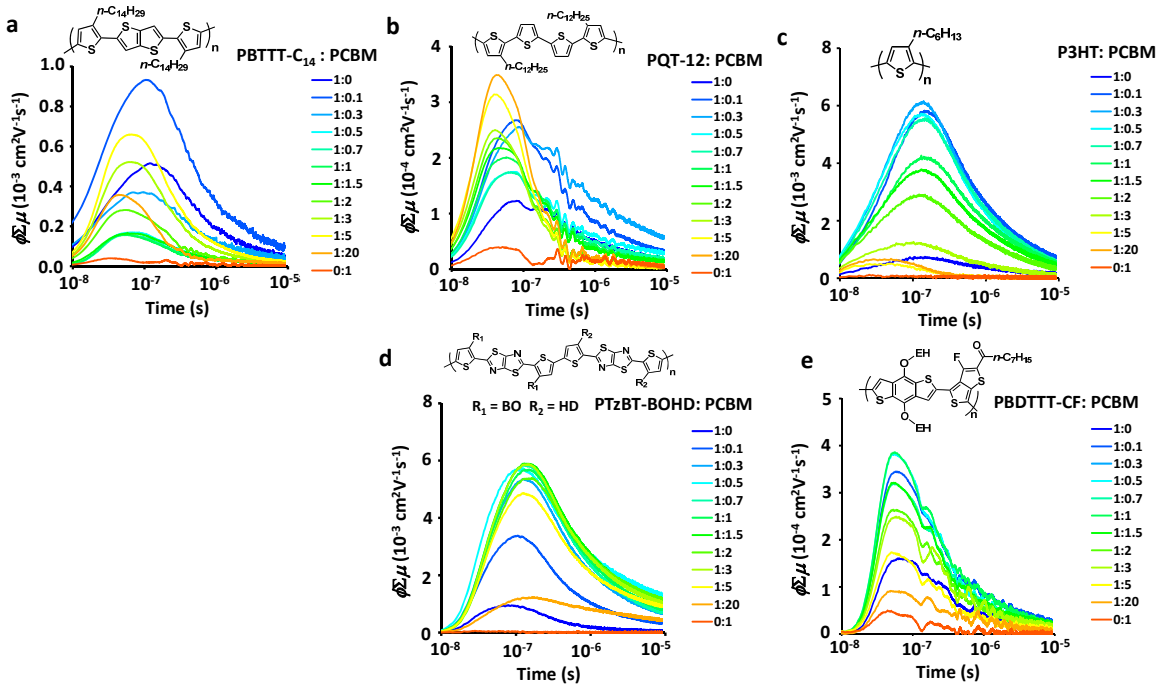

Figure S1. TRMC transients of a) PBTTT-C_{14}:PCBM, b) PQT-12:PCBM, c) P3HT:PCBM, d) PTzBT-BOHD:PCBM, and e) PBDTTT-CF:PCBM blend films under 355 nm excitation. Each color line corresponds to the blend ratio shown in the inset.

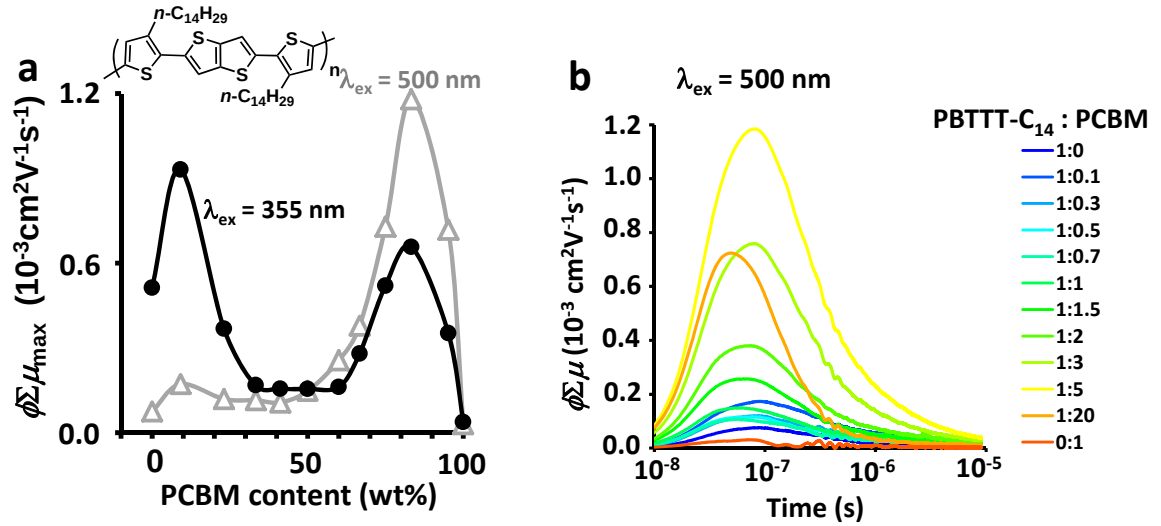

Figure S2. a) $\phi\Sigma\mu_{max}$ dependence of PBTTT-C_{14}:PCBM on PCBM under 355 (black circles) and 500 (gray triangles) nm. b) TRMC transients of a PBTTT-C_{14}:PCBM at 500 nm excitation. Each color line corresponds to the blend ratio shown in the inset.

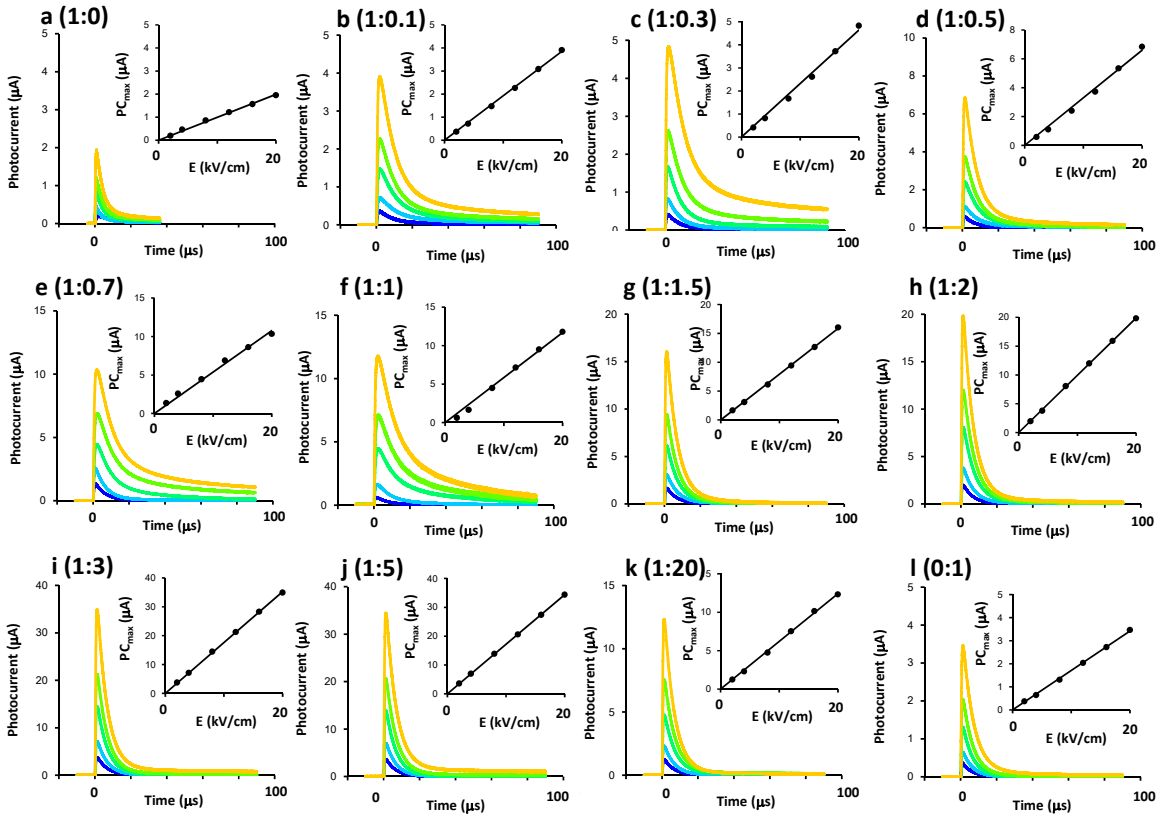

Figure S3. PC transients of BTTT-C_{14}:PCBM blend films excited at 355 nm. The applied direct-current voltages are increased from blue (2 kV cm^{-1}), green to orange (20 kV cm^{-1}). The blend ratio of polymer and PCBM is shown in the blankets.

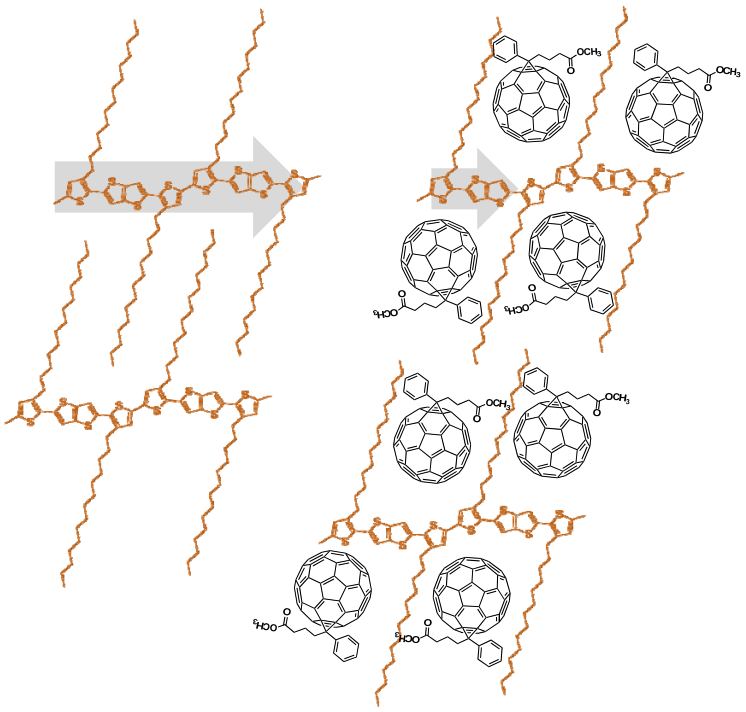

Figure S4. Schematic drawing of PCBM intercalation into PBTTT-C_{14}.[S19] The gray arrows represents the degree of intramolecular hole transport.

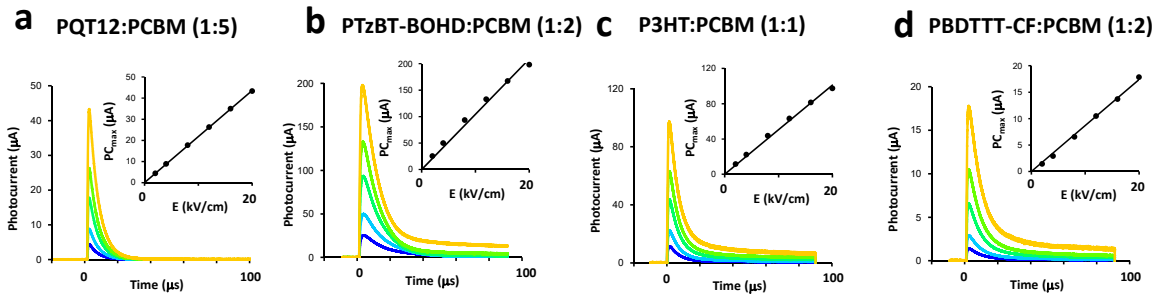

Figure S5. PC transients of a) PQT-12:PCBM (1:5 in wt%), b) PTzBT-BOHD:PCBM (1:2 in wt%), c) P3HT:PCBM (1:1 in wt%), and d) PBDTTT-CF:PCBM (1:2 in wt%) blend films excited at 355 nm. The applied direct-current voltages are increased from blue (2 kV cm^{-1}), green to orange (20 kV cm^{-1}).

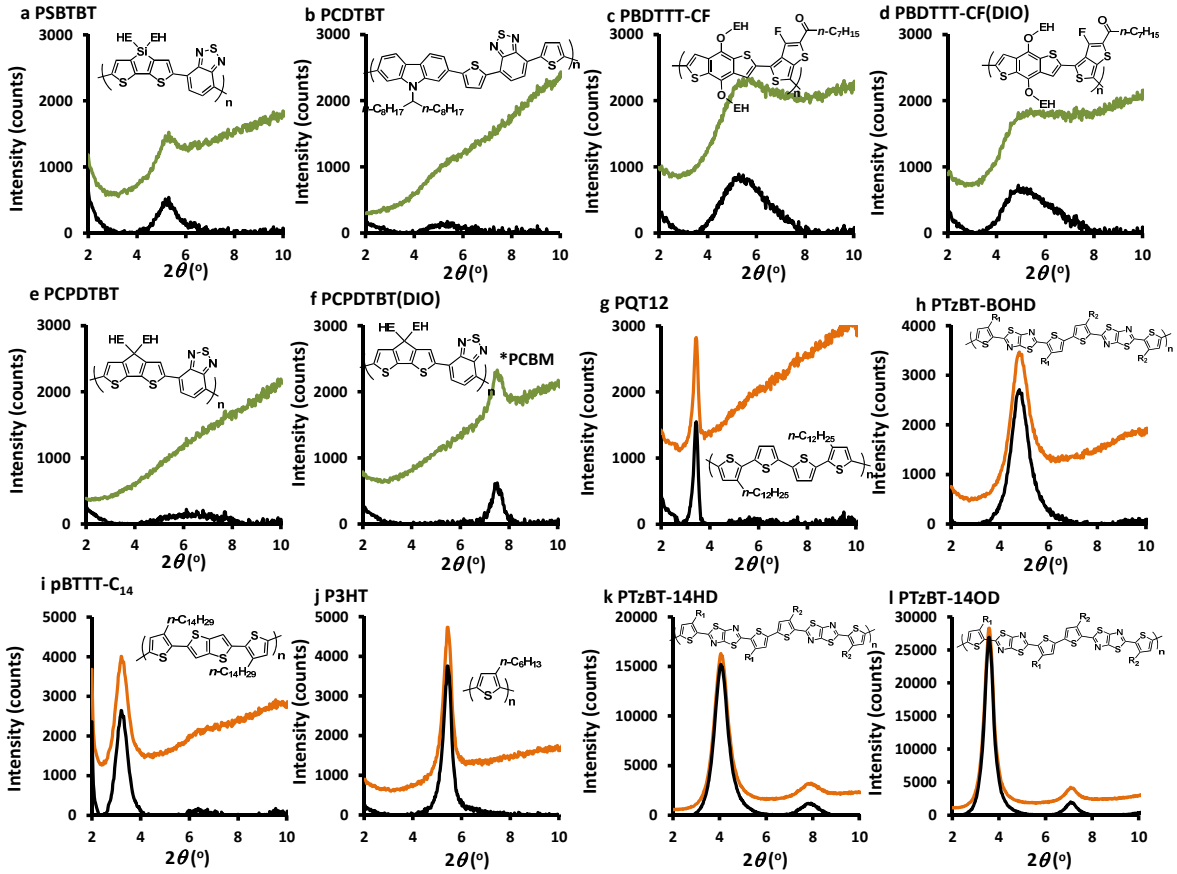

Figure S6. XRD spectra of polymer:PCBM films at device-optimal blend ratio in out-of-plane direction (Cu Kα: 1.5418 Å). The colorized and black lines are the raw data and baseline-subtracted data, respectively. The peak intensities in Table S2 are based on the latter. The peak of PCPDTBT(DIO) in the panel f is due to PCBM.[S20]

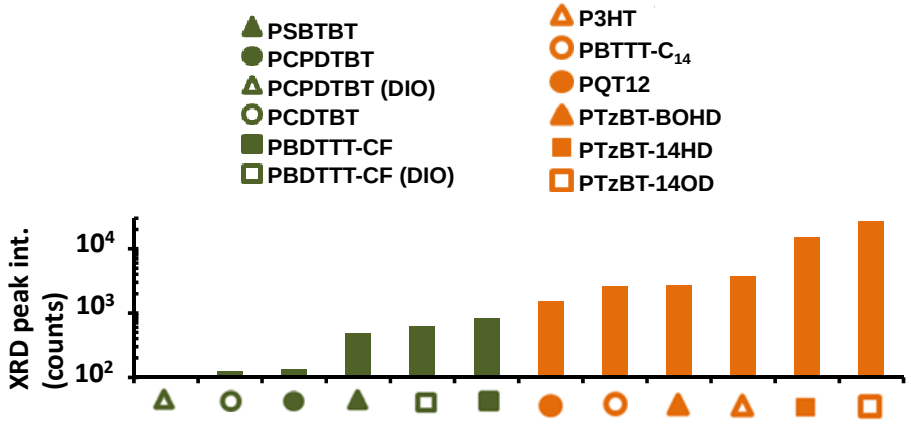

Figure S7. XRD peak intensities at the inter-lamellar diffraction peaks of device-optimal polymer:PCBM blends in the out-of-plane direction.

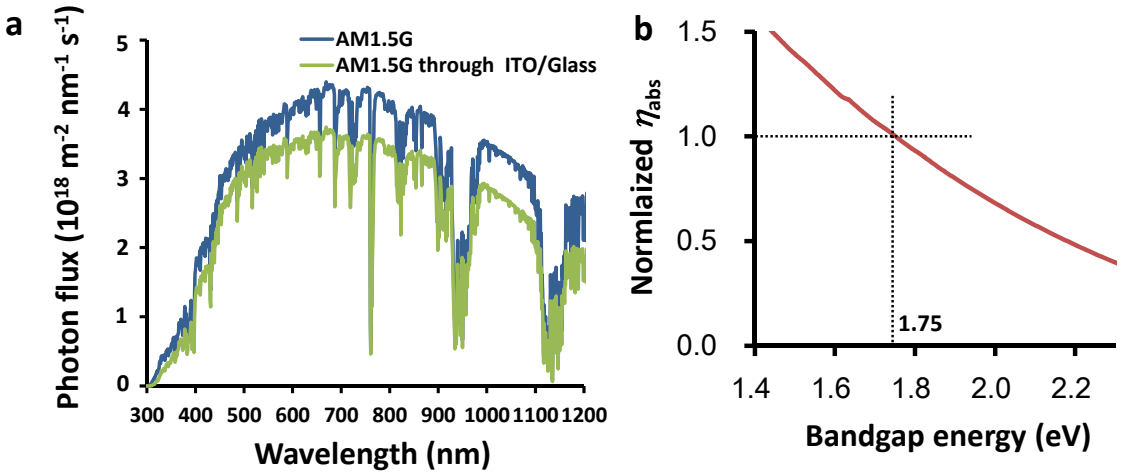

Figure S8. a) AM1.5G solar spectrum (blue line) and that through a glass/ITO substrate (green line). b) Photoabsorption efficiency normalized at the bandgap energy (E_g) of 1.75 eV (PCPDTBT). The curve was constructed by integrating the green line in a) and assuming 100% absorption of photon for > E_g.

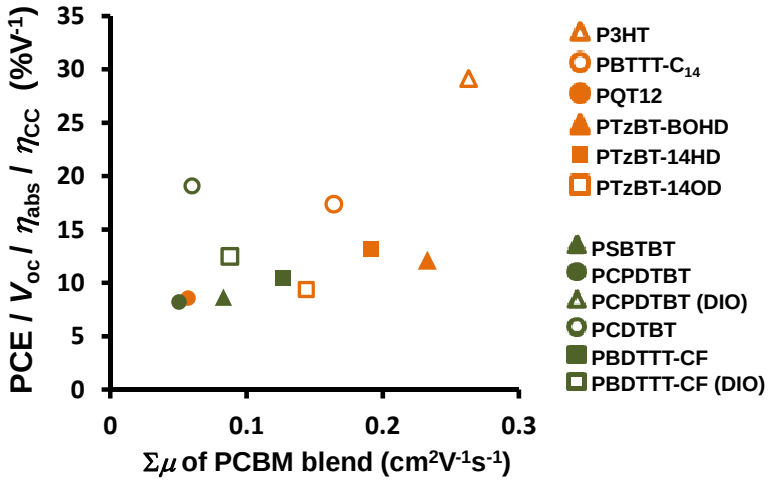

Figure S9. PCE/V_{oc}/η_{abs}/η_{CC} vs. TRMC mobilities of the polymer:PCBM blends. η_{CC} was calculated by Hecht equation with long range mobilities of SCLC or FET. See Table S4.

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