Supporting Information:

Intramolecular Donor–Acceptor Regioregular Poly(3-hexylthiophene)s Presenting Octylphenanthrenyl-Imidazole Moieties Exhibit Enhanced Charge Transfer for Heterojunction Solar Cell Applications

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3,6-Dibromo-9,10-dihydrophenanthrene (1). NBS (9.88 g, 55.48 mmol) was added portionwise to a solution of 9,10-dihydrophenanthrene (5.0 g, 27.74 mmol) in THF (66 mL) and acetic acid (66 mL) and then the mixture was stirred for 20 min. The solution was washed with water (2 × 200 mL), saturated $NaHCO_3$ (1 × 200 mL), and then again with water (1 × 200mL). Follow extraction with ethyl acetate, the organic layer was dried ($MgSO_4$) and concentrated to yield **1** (8.0 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.60 (s, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.08 (s, 2H), 2.88 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 136.3, 134.0, 132.5, 131.5, 130.2, 120.4, 29.7.

HRMS-EI (*m*/*z*): [M$^+$] calcd. for $C_{14}H_{10}Br_2$, 335.9149; found, 335.9147.

3,6-Dibromophenanthrene-9,10-dione (2). 3,6-Dibromo-9,10-dihydrophenanthrene (7.0 g, 20.7 mmol) and chromic trioxide (4.84 g, 46.6 mmol) were dissolved in acetic anhydride (100 mL) and reacted for 3 h at room temperature. The solution was poured into 1 N HCl solution (300 mL) and extracted with ethyl acetate. The organic layer was dried ($MgSO_4$) and concentrated to yield **2** (6.8 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.88 (s, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.51 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 180.2, 136.3, 134.0, 132.5, 131.5, 130.2, 129.4. HRMS-EI (*m*/*z*): [M$^+$] calcd. for $C_{14}H_6Br_2O_2$, 363.8734; found, 363.8732.

6,9-Dibromo-1-phenyl-2-(thiophen-3-yl)-1*H*-phenanthro[9,10-d]imidazole (3). A mixture of aniline (7.95 g, 85.5 mmol), 3,6-dibromophenanthrene-9,10-dione (**2**, 6.63 g, 17.1 mmol), 3-thiophenecarboxaldehyde (1.92 g, 17.1 mmol), ammonium acetate (5.28 g, 68.57 mmol), and acetic acid (100 mL) was heated for 2 h under nitrogen in an oil bath maintained at a bath temperature of 120 °C. After cooling and filtering, the solid product was washed sequentially with an acetic acid/water mixture (1:1, 150 mL) and water, and then dried to yield **3** (8.22 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.84–8.87 (m, 1H), 8.75 (d, *J* = 8.4 Hz, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 7.45–7.78 (m, 7H), 7.22–7.27 (m, 2H), 7.14 (m, 1H), 7.08 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 149.2, 137.3, 134.0, 132.5, 131.5, 130.2, 128.4, 126.4, 125.7, 120.4. HRMS-EI (*m*/*z*):

[M^+] calcd. for $C_{25}H_{14}Br_2SN_2$, 531.9244; found, 531.9250.

6,9-Dioctyl-1-phenyl-2-(thiophen-3-yl)-1*H*-phenanthro[9,10-d]imidazole (**4**). A 100-mL round-bottom three-neck flask equipped with a stirrer bar, condenser, addition funnel, and N_2 inlet/outlet was charged with Mg (0.79 g, 32.7 mmol) and dry ether (10 mL). Bromooctane (2.89 g, 14.8 mmol) in dry ether (20 mL) was added dropwise to maintain a mild reflux. The mixture was heated under reflux for an additional 2.5 h. The Grignard reagent solution was then added dropwise to an ice-cooled 250-mL three-neck round-bottom flask containing 6,9-dibromo-1-phenyl-2-(thiophen-3-yl)-1*H*-phenanthro[9,10-d]imidazole (**3**, 4.00 g, 7.4 mmol), Ni(dppp)Cl_2 (0.04 g, 0.08 mmol), and dry ether (30 mL). The solution was then heated under reflux overnight. The cooled reaction mixture was quenched carefully with HCl (5%, 75 mL); the ether layer was separated, washed with H_2O (2 × 75 mL), and dried ($MgSO_4$). The crude product was purified by column chromatography (silica gel, 8% EtOAc/hexane) to yield **4** (4.0 g, 88%). ^1H NMR (300 MHz, $CDCl_3$, ppm): 8.84–8.87 (m, 1H), 8.75 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H), 7.45–7.78 (m, 7H), 7.22–7.27 (m, 2H), 7.14 (m, 1H), 7.08 (m, 1H). 1.00–1.80 (m, 30H), 2.66 (t, J = 7.2 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 149.2, 137.3, 134.0, 132.5, 131.5, 130.2, 128.4, 126.4, 125.7, 124.7, 31.9, 30.6, 29.6, 29.4, 29.3, 22.7, 14.1. HRMS-EI (*m*/*z*): [M^+] calcd. for $C_{41}H_{48}SN_2$, 600.3538; found, 600.3533.

2-(2,5-Dibromothiophen-3-yl)-6,9-dioctyl-1-phenyl-1*H*-phenanthro[9,10-d]imidazole (M2). NBS (2.07 g, 11.6 mmol) was added portionwise to a solution of 6,9-dioctyl-1-phenyl-2-(thiophen-3-yl)-1*H*-phenanthro[9,10-d]imidazole (**4**, 3.5 g, 5.82 mmol) in THF (33 mL) and acetic acid (33 mL) and then the mixture was stirred for 20 min. The solution was washed with water (2 × 200 mL), saturated $NaHCO_3$ (1 × 200 mL), and then again with water (1 × 200mL). Following extraction with ethyl acetate, the organic layer was dried ($MgSO_4$) and concentrated to yield **M2** (4.0 g, 90%). ^1H NMR (300 MHz, $CDCl_3$, ppm): 8.84–8.87 (m, 1H), 8.75 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H), 7.45–7.78 (m, 7H), 7.22–7.27 (m, 1H), 6.73 (s, 1H) 1.00–1.80 (m, 30H), 2.66 (t, J = 7.5 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 149.2, 137.3, 134.0, 132.5, 131.5, 130.2, 128.4, 126.4, 125.7, 124.7, 117.3, 99.2, 31.9, 30.6, 29.6, 29.4, 29.3, 22.7, 14.1. HRMS-FAB (*m*/*z*): [M^+ - H] calcd. for $C_{41}H_{47}SN_2Br_2$, 757.1826; found, 757.1817.

Preparation of Polythiophene Derivatives. All polymers were synthesized through Grignard metathesis polymerization in THF according to procedures similar to those described in the literature.[S1-S3] The Grignard metathesis polymerizations of 2,5-dibromo-3-hexylthiophene (**M1**) and 2-(2,5-dibromothiophen-3-yl)-6,9-dioctyl-1-phenyl-1*H*-phenanthro[9,10-d]imidazole (**M2**) are illustrated in Scheme 2.

Poly(3-hexylthiophene) (P3HT). CH_3MgBr (1.5 mL, 4.5 mmol) was added via syringe to a stirred solution of 2,5-dibromo-3-hexylthiophene (1.60 g, 4.5 mmol) and freshly distilled THF (80 mL) in a three-necked 100-mL round-bottom flask. The solution was heated under reflux for 2 h and then Ni(dppp)Cl_2 (12 mg, 0.02 mmol) was added. The mixture was stirred for 1 h before the reaction was quenched through the addition of methanol. The solid polymer was washed with methanol within a Soxhlet extractor. The polymer then was dissolved through Soxhlet extraction with chloroform; the solvent was evaporated and the residue dried under vacuum to yield poly(3-octylthiophene) (0.54 g, 61%; 99% coupled head-to-tail). ^1H NMR (300 MHz, $CDCl_3$): 6.98 (s, 1H), 2.78 (s, 2H); 0.86, 1.27, and 1.68 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): 139.9, 133.7, 130.5, 128.6, 31.9, 30.6, 29.6, 29.4, 22.7, 14.1. Anal. Calcd for $C_{10}H_{14}S$: H, 8.49; C, 72.27; S, 19.28. Found: H, 8.28; C, 72.58; S, 19.0.

P28. CH_3MgBr (1.5 mL, 4.5 mmol) was added via syringe to a stirred solution of 2,5-dibromo-3-octylthiophene (1.44 g, 4.05 mmol), 2-(2,5-dibromothiophen-3-yl)-1-phenyl-1*H*-phenanthro[9,10-d]imidazole (0.24 g, 0.45 mmol), and freshly distilled THF (80 mL) in a three-necked 100-mL round-bottom flask. The solution was heated under reflux for 2 h and then Ni(dppp)Cl_2 (12 mg, 0.02 mmol) was added. The mixture was stirred for 1 h and then the reaction was quenched through the addition of methanol. The solid polymer was washed with methanol within a Soxhlet extractor. The polymer then was dissolved through Soxhlet extraction with chloroform; the chloroform was evaporated and the residue dried under vacuum to yield **P28** (0.51 g, 60%; 99% coupled head-to-tail). ^{1}H NMR (300 MHz, $CDCl_3$): 8.4–8.9 (br, 2H), 7.3–7.9 (br, 13H), 6.98 (s, 1H), 2.75 (s, 9H); 0.85, 1.26, and 1.64 (m, 38H). ^{13}C NMR (75 MHz, $CDCl_3$): 149.2, 139.9, 137.4, 137.1, 133.2, 131.1, 130.4, 130.1, 129.6, 129.0, 128.4, 128.2, 127.5, 127.0, 126.5, 126.2, 125.5, 124.6, 123.4, 122.6, 122.0, 121.1, 120.0, 119.7, 31.9, 30.6, 29.6, 29.4, 29.3, 22.7, 14.1. Anal. Calcd for $C_{16.2}H_{21}SN_{0.4}$: C, 74.1; H, 8.4; N, 0.93; S, 16.57. Found: C, 72.78; H, 8.66; N, 0.87; S, 15.90.

Other polymer samples were synthesized using the method described for the preparation of **P28**, but with different amounts of 2-(2,5-dibromothiophen-3-yl)-1-phenyl-1*H*-phenanthro[9,10-d]imidazole (**M2**).

P46. ^{1}H NMR (300 MHz, $CDCl_3$): 8.4–8.9 (br, 2H), 7.3–7.9 (br, 13H), 6.98 (s, 1H), 2.75 (s, 9H); 0.85, 1.26, and 1.64 (m, 38H). ^{13}C NMR (75 MHz, $CDCl_3$): 149.2, 139.9, 137.4, 137.1, 133.2, 131.1, 130.4, 130.1, 129.6, 129.0, 128.4, 128.2, 127.5, 127.0, 126.5, 126.2, 125.5, 124.6, 123.4, 122.6, 122.0, 121.1, 120.0, 119.7, 31.9, 30.6, 29.6, 29.4, 29.3, 22.7, 14.1. Anal. Calcd for $C_{22.4}H_{28}SN_{0.8}$: C, 76.1; H, 8.38; N, 1.86; S, 13.66. Found: C, 74.78; H, 7.66; N, 1.69; S, 14.80.

P64. ^{1}H NMR (300 MHz, $CDCl_3$): 8.4–8.9 (br, 2H), 7.3–7.9 (br, 13H), 6.98 (s, 1H), 2.75 (s, 9H); 0.85, 1.26, and 1.64 (m, 38H). ^{13}C NMR (75 MHz, $CDCl_3$): 149.2, 139.9, 137.4, 137.1, 133.2, 131.1, 130.4, 130.1, 129.6, 129.0, 128.4, 128.2, 127.5, 127.0, 126.5, 126.2, 125.5, 124.6, 123.4, 122.6, 122.0, 121.1, 120.0, 119.7, 31.9, 30.6, 29.6, 29.4, 29.3, 22.7, 14.1. Anal. Calcd for $C_{28.6}H_{35}SN_{1.2}$: C, 77.98; H, 8.32; N, 2.79; S, 10.91. Found: C, 74.78; H, 7.66; N, 2.59; S, 10.80.

P82. ^{1}H NMR (300 MHz, $CDCl_3$): 8.4–8.9 (br, 2H), 7.3–7.9 (br, 13H), 6.98 (s, 1H), 2.75 (s, 9H); 0.85, 1.26, and 1.64 (m, 38H). ^{13}C NMR (75 MHz, $CDCl_3$): 149.2, , 139.9, 137.4, 137.1, 133.2, 131.1, 130.4, 130.1, 129.6, 129.0, 128.4, 128.2, 127.5, 127.0, 126.5, 126.2, 125.5, 124.6, 123.4, 122.6, 122.0, 121.1, 120.0, 119.7, 31.9, 30.6, 29.6, 29.4, 29.3, 22.7, 14.1. Anal. Calcd for $C_{33.2}H_{42}SN_{1.6}$: C, 79.9; H, 8.27; N, 3.72; S, 8.11. Found: C, 78.22; H, 8.72; N, 3.93; S, 7.83.

P91. ^{1}H NMR (300 MHz, $CDCl_3$): 8.4–8.9 (br, 2H), 7.3–7.9 (br, 13H), 6.98 (s, 1H), 2.75 (s, 9H); 0.85, 1.26, and 1.64 (m, 38H). ^{13}C NMR (75 MHz, $CDCl_3$): 149.2, 139.9, 137.4, 137.1, 133.2, 131.1, 130.4, 130.1, 129.6, 129.0, 128.4, 128.2, 127.5, 127.0, 126.5, 126.2, 125.5, 124.6, 123.4, 122.6, 122.0, 121.1, 120.0, 119.7, 31.9, 30.6, 29.6, 29.4, 29.3, 22.7, 14.1. Anal. Calcd for $C_{37.9}H_{45.5}SN_{1.8}$: C, 80.85; H, 8.24; N, 4.12; S, 6.79. Found: C, 81.22; H, 7.72; N, 3.93; S, 6.51.

Table S1 lists the redox data and HOMO and LUMO energy levels, as determined from onset potentials in cyclic voltammograms, for the synthesized polymers.[S4] We observe that the energy bandgap reduced upon increasing the content of incorporated octylphenanthrenyl-imidazole moieties in the copolymers, reconfirming that their effective conjugation lengths had increased.[S1] Moreover, the presence of the octylphenanthrenyl-imidazole moieties altered the HOMO and LUMO energy levels of the polythiophenes: the HOMO energy level increased to –4.65 eV for **P91** from –4.75 eV for **P3HT**, while the LUMO energy level reduced correspondingly to –2.75 from –3.05 eV; therefore, the bandgap decreased to 1.60 from 2.0 eV.

Table S1 Redox data, HOMO, LUMO energy levels, and band gap energies of our synthesized polymers.

	Reduction Onset Potential (eV)	Oxidation Onset Potential(eV)	HOMO (eV)	LUMO (eV)	Bandgap (eV)
P3HT	–1.75	0.35	–4.75	–2.75	2.0
P28	–1.70	0.30	–4.70	–2.80	1.90
P46	–1.63	0.30	–4.70	–2.87	1.83
P64	–1.55	0.25	–4.65	–2.95	1.70
P82	–1.48	0.25	–4.65	–3.02	1.63
P91	–1.35	0.25	–4.65	–3.05	1.60

Figure S1 presents the ^1H NMR spectra of **M2** and some of the synthesized polymers.[S1–S3]

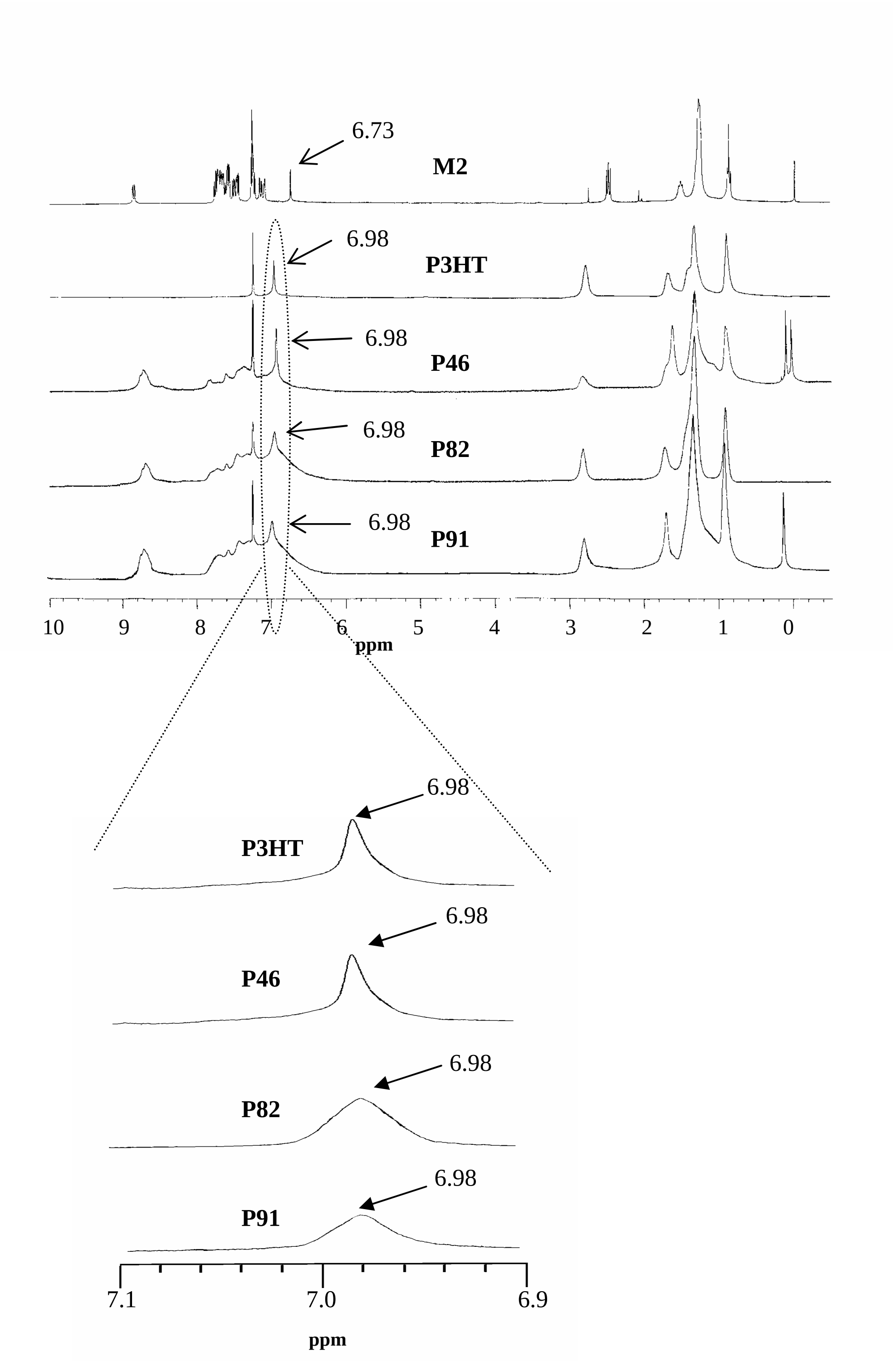

Figure S1. The ^1H NMR spectra of **M2**, **P3HT**, **P46**, **P82**, and **P91**.

Figure S2 shows the dihedral angel between the plane of thiophene and the plane of octylphenanthrenyl-imidazole simulated from the Chem. 3D software. The dihedral angel between the polymeric main chain and the octylphenanthrenyl-imidazole moiety is 82.13^{o}.

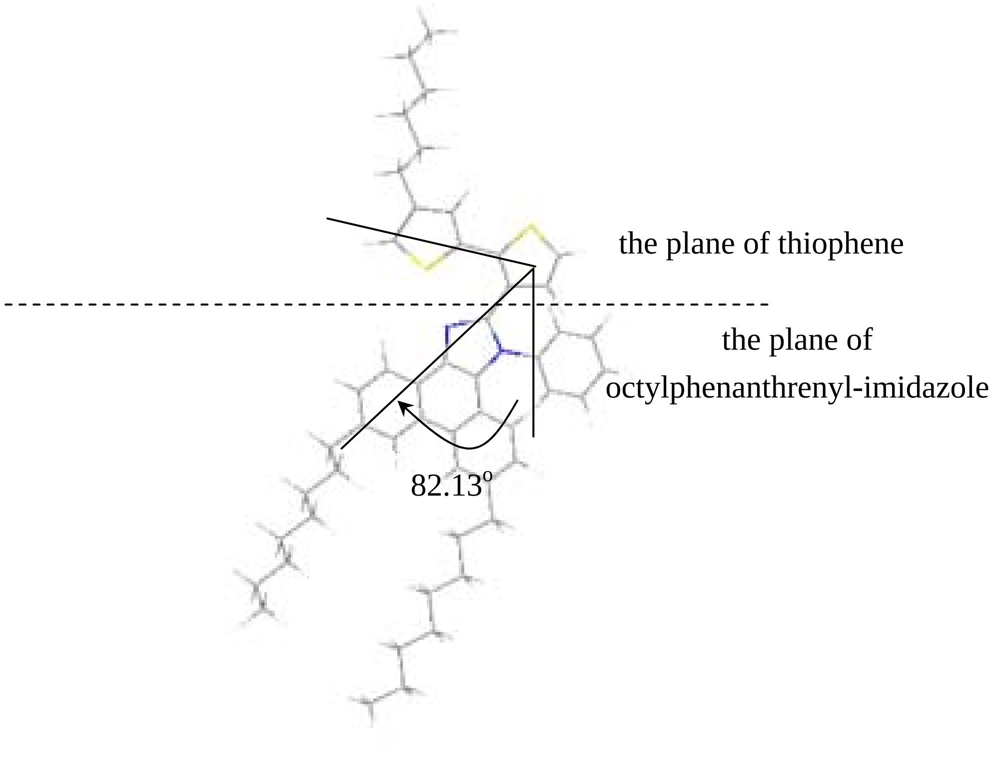

Figure S2. The chemical structure diagram of HT and octylphenanthrenyl-imidazole moiety.

Equation (1) is used to calculate the mismatch factor of our light source illumating at a standard AM 1.5G global spectrum (ASTM G173).

$$M = \frac{\int_{\lambda_1}^{\lambda_2} E_{\mathrm{Ref}}(\lambda) S_{\mathrm{R}}(\lambda)\mathrm{d}\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\mathrm{Ref}}(\lambda) S_{\mathrm{T}}(\lambda)\mathrm{d}\lambda} \; \frac{\int_{\lambda_1}^{\lambda_2} E_{\mathrm{S}}(\lambda) S_{\mathrm{T}}(\lambda)\mathrm{d}\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\mathrm{S}}(\lambda) S_{\mathrm{R}}(\lambda)\mathrm{d}\lambda} \qquad \textbf{(1)}$$

where $E_{\mathrm{Ref}}(\lambda)$ is the reference spectral irradiance, $E_{\mathrm{S}}(\lambda)$ is the source spectral irradiance, $S_{\mathrm{R}}(\lambda)$ is the spectral responsivity of the reference cell, and $S_{\mathrm{T}}(\lambda)$ is the spectral responsivity of the test cell, each as a function of wavelength (λ). The limits of integration λ_1 and λ_2 in the above equation should encompass the range of the reference cell and the test-device spectral responses, and the simulator and reference spectra should encompass λ_1 and λ_2 to avoid errors.

Figure S3 presents the current density at the wavelength from 400 nm to 720 nm converted from the output signal of the external quantum efficiencies. The calibrated current densities were calculated using the following equation:

$$I^{\mathrm{T,R}} = \frac{I^{\mathrm{R,R}} \; I^{\mathrm{T,S}}}{I^{\mathrm{R,S}} \; M} \qquad \textbf{(2)}$$

where $I^{\mathrm{R,R}}$ is the calibrated short-circuit current of the reference cell under the reference spectrum and total irradiance, $I^{\mathrm{T,S}}$ is the short-circuit current of a test cell measured under the source spectrum, and $I^{\mathrm{R,S}}$ is the short-circuit current of the reference cell under the source spectrum.[S5, S6] The current densities of our polymers/**PCBM** devices calculated from the integration of the area from 400 nm to 720 nm are 8.1, 11.4, 12.7 and 13.4 mA/cm^2, respectively.

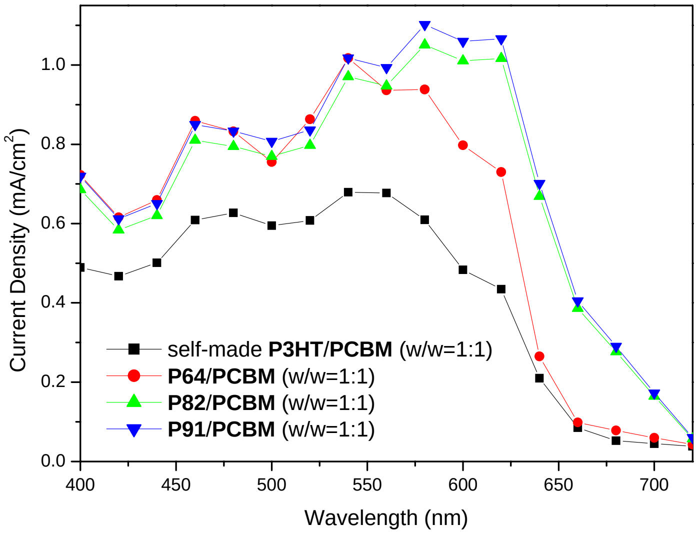

Figure S3. The current density vs. wavelength diagram of self-made **P3HT/PCBM**, **P64/PCBM**, **P82/PCBM**, and **P91/PCBM** devices.

The transients of the pure polymers and the blends with **PCBM** were found to be comprised of two time constants. For the sake of easy comparison, an amplitude-averaged rate constant of each transient was calculated. The averaged rate constants were calculated using the following equation:[S7]

$$\langle \tau \rangle_{\mathrm{a}} = \sum_{i=1}^{n} \mathrm{a}_i \tau_i \qquad \textbf{(3)}$$

where a_i are the fractional amplitudes where $\sum_{i=1}^{\mathrm{n}} \mathrm{a}_i = 1$ and τ_i are the individual rate constants, which are the reciprocals of the time constants.

Figures S4–S6 depict the time-resolved transient spectra of the individual polymers, **P3HT** and **P91**, and their blends with **PCBM** at values of λ_{em} of 600, 620, and 660 nm (λ_{ex} = 440 nm), along with the theoretical fit and the deconvoluted components.

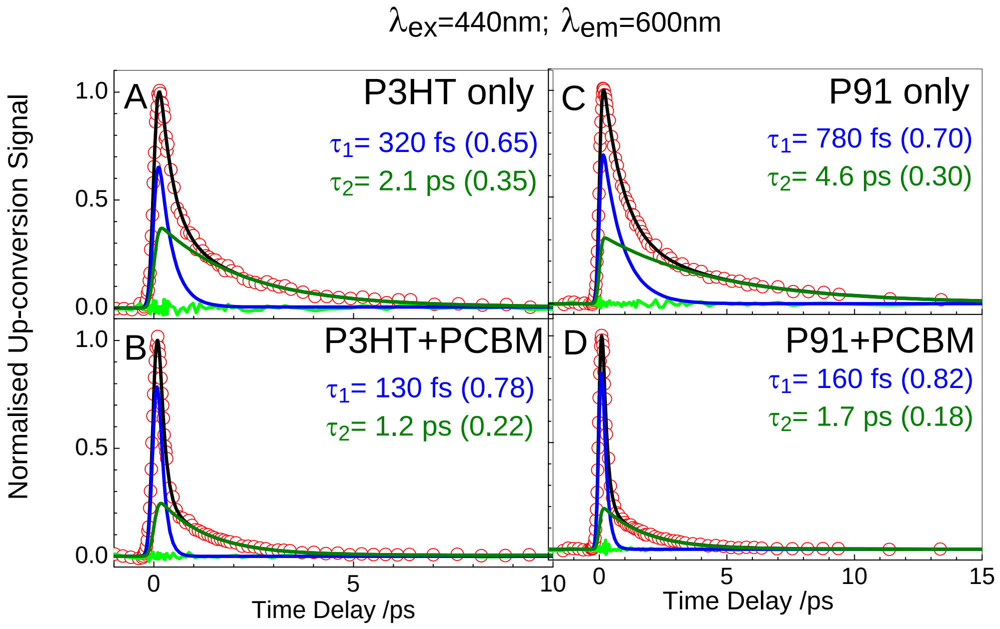

Figure S4. Time-resolved transients of (A) **P3HT**, (B) the blend of **P3HT** and

PCBM, (C) **P91**, and (D) the blend of **P91** and **PCBM** coated on quartz at values of λ_{ex} and λ_{em} of 440 and 600 nm, respectively. The red circles represent the standardized raw data; the black line is the theoretical fit. The blue and olive green lines represent the two deconvoluted components; the green line is the residual.

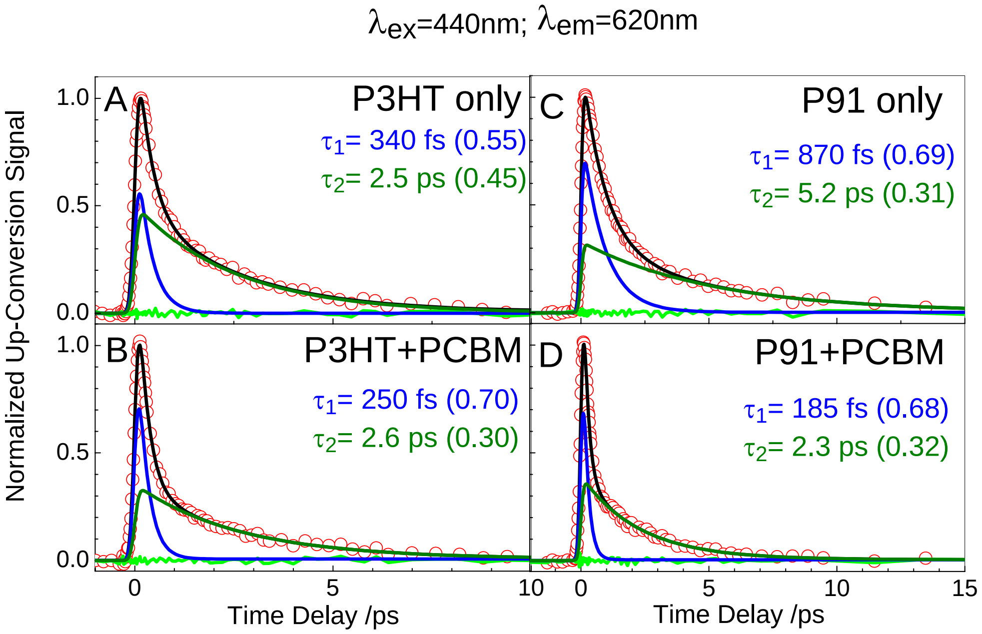

Figure S5. Time-resolved transients of (A) **P3HT**, (B) the blend of **P3HT** and **PCBM**, (C) **P91**, and (D) the blend of **P91** and **PCBM** coated on quartz at values of λ_{ex} and λ_{em} of 440 and 620 nm, respectively. The red circles represent the standardized raw data; the black line is the theoretical fit. The blue and olive green lines represent the two deconvoluted components; the green line is the residual.

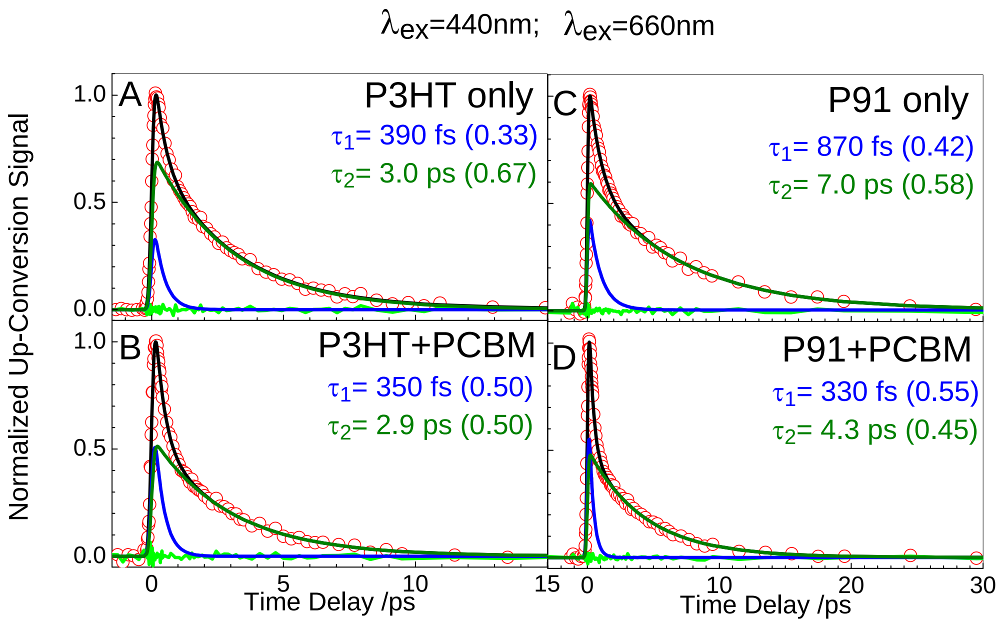

Figure S6. Time-resolved transients of (A) **P3HT**, (B) the blend of **P3HT** and **PCBM**, (C) **P91**, and (D) the blend of **P91** and **PCBM** coated on quartz at values of λ_{ex} and λ_{em} of 440 and 660 nm, respectively. The red circles represent the standardized raw data; the black line is the theoretical fit. The blue and olive green lines represent the two deconvoluted components; the green line is the residual.

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