

Supporting Information

Narrow Band-gap Materials with Overlapping Absorption Simultaneously Increase the Open Circuit Voltage and Average Visible Transmittance of Semitransparent Organic Solar Cells

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Materials and synthesis

Compounds 1, compounds 4 and IT-4F were purchased from Solarmer Materials Inc., compounds 2 and 3 and Pd (PPH₃)₄ were purchased from SunaTech Inc. All reagents and commercially available compounds are used upon receipt. The synthetic processes of polymer PCE10-2Cl, PCE10-SF and PCE10-2F are provided in **Figure S1**.

The synthesis of PCE10-2Cl

Compounds 1 (194.6 mg, 0.2 mmol), Compounds 2 (94.4 mg, 0.2 mmol) and Pd (PPH₃)

4 (18.5 mg, 0.016 mmol) were dissolved in mixed solvents (toluene (8 ml) and DMF (2 ml) in nitrogen atmosphere in a 50 ml double-necked flask with condenser. Mix the mixture for 32 hours at 110 C. After cooling the solution to room temperature, it is poured into methanol (300 ml). The precipitation was collected by filtration, and then the product was further purified by Soxhlet extraction. The product was extracted with n-hexane, acetone and CHCl₃ for one day in turn. PCE10-2Cl were dissolved in CHCl₃ and precipitated with methanol. Finally, it is collected by filtration and dried in a vacuum oven at 80 C for more than 20 hours. PCE10-2Cl were obtained in the form of dark blue solids. (138.7 mg, yield 48%). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 1H), 7.26 (s, 11H), 7.00 (s, 1H), 2.04 (s, 1H), 1.75 (d, *J* = 89.8 Hz, 16H), 1.51 (d, *J* = 64.6 Hz, 45H), 1.25 (s, 26H), 1.01 (d, *J* = 20.8 Hz, 41H), 0.59 – 0.24 (m, 6H), 0.15 (s, 1H), 0.07 (s, 1H), -0.00 (s, 9H), -0.16 (s, 1H).

The synthesis of PCE10-SF

Compounds 3 (195.3 mg, 0.2 mmol), Compounds 2 (94.4 mg, 0.2 mmol) and Pd (PPh₃)**4** (18.5 mg, 0.016 mmol) were dissolved in mixed solvents (toluene (8 ml) and DMF (2 ml) in nitrogen atmosphere in a 50 ml double-necked flask with condenser. Mix the mixture for 16 hours at 110 C. After cooling the solution to room temperature, it is poured into methanol (300 ml). The precipitation was collected by filtration, and then the product was further purified by Soxhlet extraction. The product was extracted with n-hexane, acetone and CHCl₃ for one day in turn. PCE10-2Cl were dissolved in CHCl₃ and precipitated with methanol. Finally, it is collected by filtration and dried in a vacuum oven at 80 C for more than 20 hours. PCE10-2Cl were obtained in the form of dark blue solids. (214.4 mg, yield 74%). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 2H), 7.26 (s, 19H), 7.00 (s, 2H), 2.45 (d, *J* = 308.7 Hz, 56H), 2.04 (s, 104H), 1.59 (s, 18H), 1.13 (dd, *J* = 162.5, 52.0 Hz, 134H), 0.14 (s, 31H), 0.03 (d, *J* = 28.5 Hz, 19H), -0.00 (s, 16H), -0.00 (s, 14H).

The synthesis of PCE10-2F

Compounds 4 (188.1 mg, 0.2 mmol), Compounds 2 (94.4 mg, 0.2 mmol) and Pd (PPh₃)

PCE10-2Cl (18.5 mg, 0.016 mmol) were dissolved in mixed solvents (toluene (8 ml) and DMF (2 ml) in nitrogen atmosphere in a 50 ml double-necked flask with condenser. Mix the mixture for 18 hours at 110 C. After cooling the solution to room temperature, it is poured into methanol (300 ml). The precipitation was collected by filtration, and then the product was further purified by Soxhlet extraction. The product was extracted with n-hexane, acetone and CHCl_3 for one day in turn. PCE10-2Cl were dissolved in CHCl_3 and precipitated with methanol. Finally, it is collected by filtration and dried in a vacuum oven at 80 C for more than 20 hours. PCE10-2Cl were obtained in the form of dark blue solids. (180.8 mg, yield 64%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (s, 1H), 7.26 (s, 11H), 7.00 (s, 1H), 2.04 (s, 1H), 1.75 (d, J = 89.8 Hz, 16H), 1.51 (d, J = 64.6 Hz, 45H), 1.25 (s, 26H), 1.01 (d, J = 20.8 Hz, 41H), 0.59 – 0.24 (m, 6H), 0.15 (s, 1H), 0.07 (s, 1H), -0.00 (s, 9H), -0.16 (s, 1H).

Measurements

Optical absorption spectra of the polymers were measured on a PerkinElmer model Lambda 900 UV-vis/near-IR spectrophotometer. Solution and solid-state absorption spectra were obtained from dilute (10^{-6} M) polymer solution in chloroform and from thin films on glass substrate, respectively. Thin films were spin coated from 20 mg/mL solutions in chlorobenzene. Cyclic voltammetry (CV) experiments were done on an EG&G Princeton Applied Research potentiostat/galvanostat (model 273A). A three-electrode cell was used, using platinum wire electrodes as both counter and working electrode. Silver/silver ion (Ag in 0.1 M AgNO_3 solution) was used as a reference electrode. Films of the random copolymers were coated onto the S6 Pt wires by dipping the wires into the copolymer solutions in chloroform then drying the coated films at 25 °C. All the CV measurements were carried out in 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) electrolyte solution in acetonitrile at a scan rate of 50 mV/s. The reduction and oxidation potentials were referenced to the Fc/Fc^+ couple by using ferrocene as an internal standard. LUMO energy levels were estimated using ferrocene value of -4.8 eV with respect to vacuum level. The LUMO and HOMO levels were determined by using equation $E_{\text{LUMO}} = -(E_{\text{redonset}} + 4.8)$ and $E_{\text{HOMO}} = -$

(eEoxonset+4.8), respectively. The scan rate was 0.05 V s^{-1} . Steady-state photoluminescence (PL) spectra were taken with a Shamrock sr-303i-B spectrograph from Andor Tech. Time-resolved photoluminescence (TRPL) were measured by an Edinburgh Instruments FLS920 spectrometer.

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

Typically, in the process of biexponential decay, the fast part of decay (first exponent, τ_1) is referred the early event of exciton diffusion; the slow part of decay (second exponent, τ_2) has association with exciton lifetime to an interface of Bulk Heterojunction (BHJ). The specimen for atomic force microscopy (AFM) measurements was prepared using the same procedures those for fabricating devices but without PDINO/Al on top of the active layer. Transmission electron microscope (TEM) images were taken on a JEOL-2100F transmission electron microscope and an internal charge-coupled device (CCD) camera. The specimen for TEM measurement was prepared by spin casting the blend solution on ITO/PEDOT: PSS substrate, then floating the film on a water surface, and transferring to TEM grids. All the photographs are taken by Apple iPhone11.

GIWAXS measurement

The GIWAXS measurement was carried out at the PLS-II 6A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. The X-rays coming from the in-vacuum undulator (IVU) were monochromated (wavelength $\lambda = 1.10994 \text{ \AA}$) using a double crystal monochromator and focused both horizontally and vertically ($450 \text{ (H)} \times 60 \text{ (V)} \mu\text{m}^2$ in FWHM @ the sample position) using K-B type mirrors. The grazing incidence wide-angle X-ray scattering (GIWAXS) sample stage was equipped with a 7-axis motorized stage for the fine alignment of the sample, and the incidence angles of the X-ray beam were set to be 0.11° - 0.13° for the neat and blend films. The GIWAXS patterns were recorded with a 2D CCD detector (Rayonix SX165) and an X-ray irradiation time within 100 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (monoclinic, P21, $a=10.8631 \text{ \AA}$, $b=8.7044 \text{ \AA}$, $c=7.7624 \text{ \AA}$, and $\beta=102.938^\circ$) and the sample-to-detector distance was $\sim 231 \text{ mm}$.

Device fabrication

The device is fabricated with ITO/ZnO/active layer/MoO₃/Ag inverted structure. The ITO coated glass substrates were cleaned by ultrasound for 15 minutes in sequence in water/detergent, water, acetone and isopropanol, and then treated in ultraviolet-ozone for 1400 seconds. The sol-gel Zinc Oxide spin was applied to the substrate and annealed in air for 50 minutes at 200 °C. PCE10-2Cl/ PCE10-SF / PCE10-2F:IT-4F (1:1, w/w) mixture was dissolved in chlorobenzene (CB) with a concentration of 20 mg/ml, and 1,8-diiiodooctane (DIO) was added (volume ratio 0.5%). The solution is stirred at 70 °C for 10 hours and then spin-coated on the surface of zinc oxide layer in a glove box in nitrogen-based atmosphere. Finally, 10-nanometer thick MoO₃ and 90-nanometer thick Ag layers were deposited on the active layer under high vacuum of $\sim 3 \times 10^{-4}$ Pa. The overlapping area of cathode and anode was 4 square millimeters. J-V curves of devices based on PCE10-2Cl:IT-4F, PCE10-SF:IT-4F and PCE10-2F:IT-4F were measured under the standard AM 1.5G spectrum of 100 MW cm⁻².

Semitransparent device fabrication

The devices were fabricated with ITO/ZnO/active layer/MoO₃/Ag inverted structure. The ITO coated glass substrates were cleaned by ultrasound for 15 minutes in sequence in water/detergent, water, acetone and isopropanol, and then treated in ultraviolet-ozone for 1400 seconds. The sol-gel Zinc Oxide spin was applied to the substrate and annealed in air for 50 minutes at 200 °C. PCE10-2Cl:IT-4F (1:1, w/w) mixture was dissolved in chlorobenzene (CB) with a concentration of 20 mg/ml, and 1,8-diiiodooctane (DIO) was added (volume ratio 0.5%). The solution is stirred at 70 °C for 10 hours and then spin-coated on the surface of zinc oxide layer in a glove box in nitrogen-based atmosphere. Finally, 3-nanometer thick MoO₃ and 5/10/15-nanometer thick Ag layers were deposited on the active layer under high vacuum of $\sim 3 \times 10^{-4}$ Pa. The overlapping area of cathode and anode was 4 square millimeters. J-V curves of devices were measured under the standard AM 1.5G spectrum of 100 MW cm⁻².

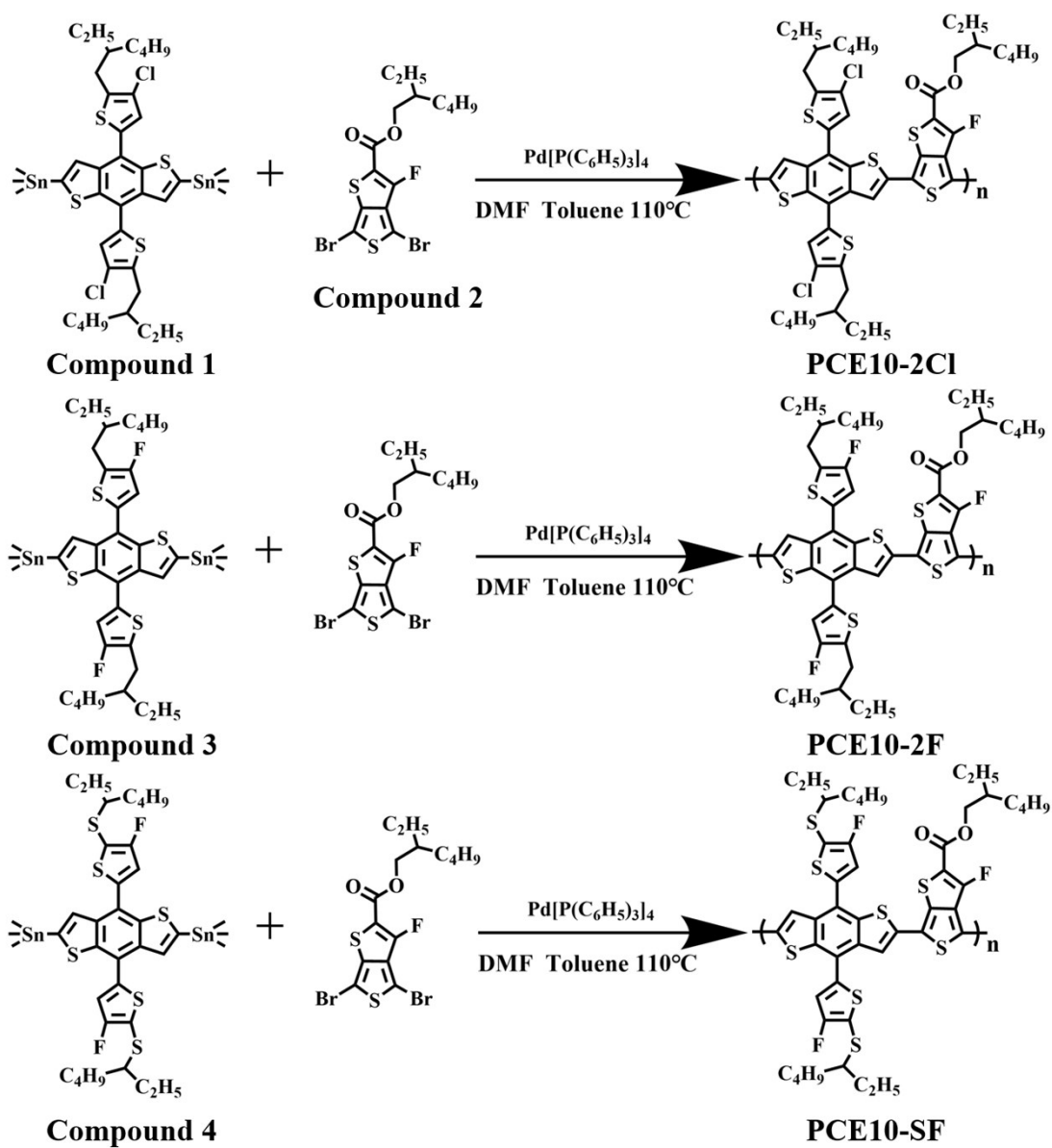
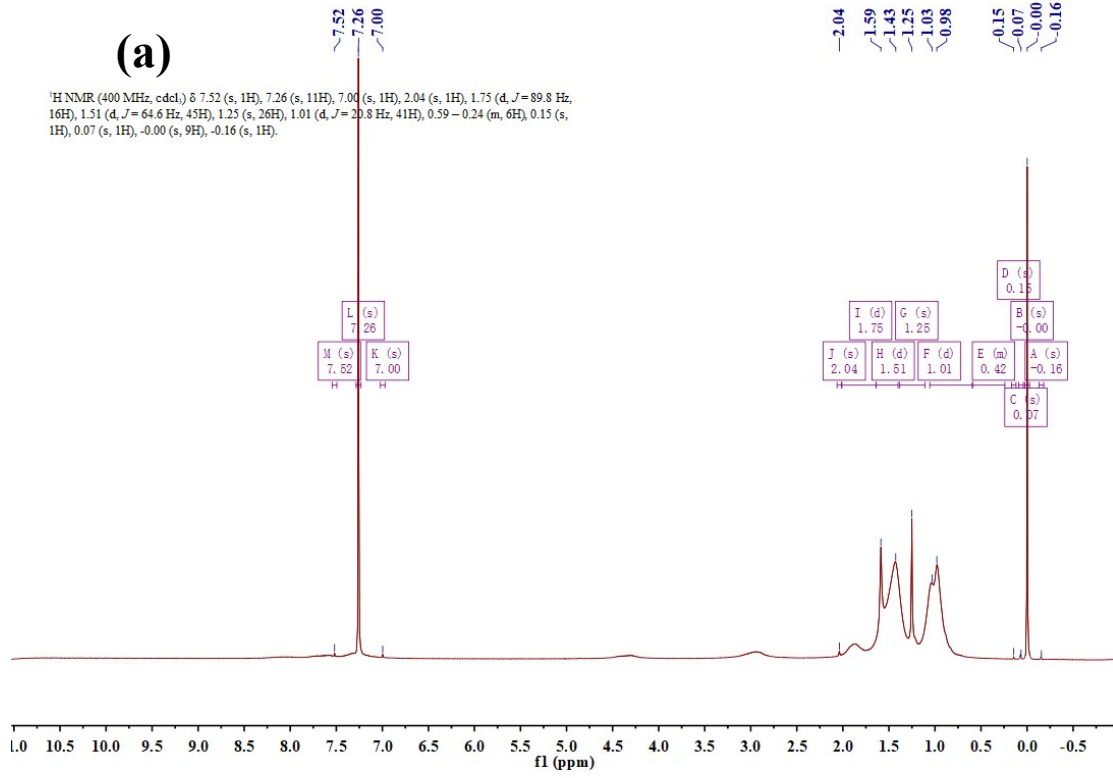


Figure S1. The synthetic routes of PCE10-2Cl, PCE10-SF, PCE10-2F.

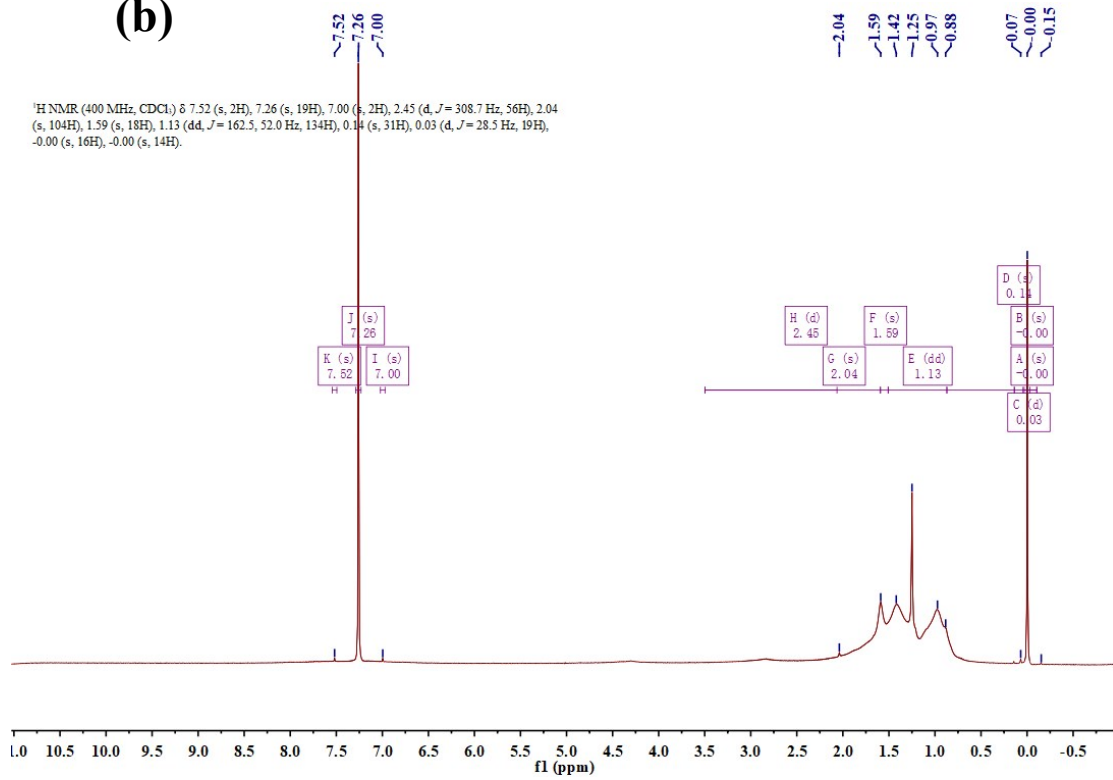
(a)

¹H NMR (400 MHz, cdcl₃) δ 7.52 (s, 1H), 7.26 (s, 11H), 7.00 (s, 1H), 2.04 (s, 1H), 1.75 (d, *J* = 89.8 Hz, 16H), 1.51 (d, *J* = 64.6 Hz, 45H), 1.25 (s, 26H), 1.01 (d, *J* = 20.8 Hz, 41H), 0.59 – 0.24 (m, 6H), 0.15 (s, 1H), 0.07 (s, 1H), -0.00 (s, 9H), -0.16 (s, 1H).



(b)

¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 2H), 7.26 (s, 19H), 7.00 (s, 2H), 2.45 (d, *J* = 308.7 Hz, 56H), 2.04 (s, 104H), 1.59 (s, 18H), 1.13 (dd, *J* = 162.5, 52.0 Hz, 134H), 0.14 (s, 31H), 0.03 (d, *J* = 28.5 Hz, 19H), -0.00 (s, 16H), -0.00 (s, 14H).



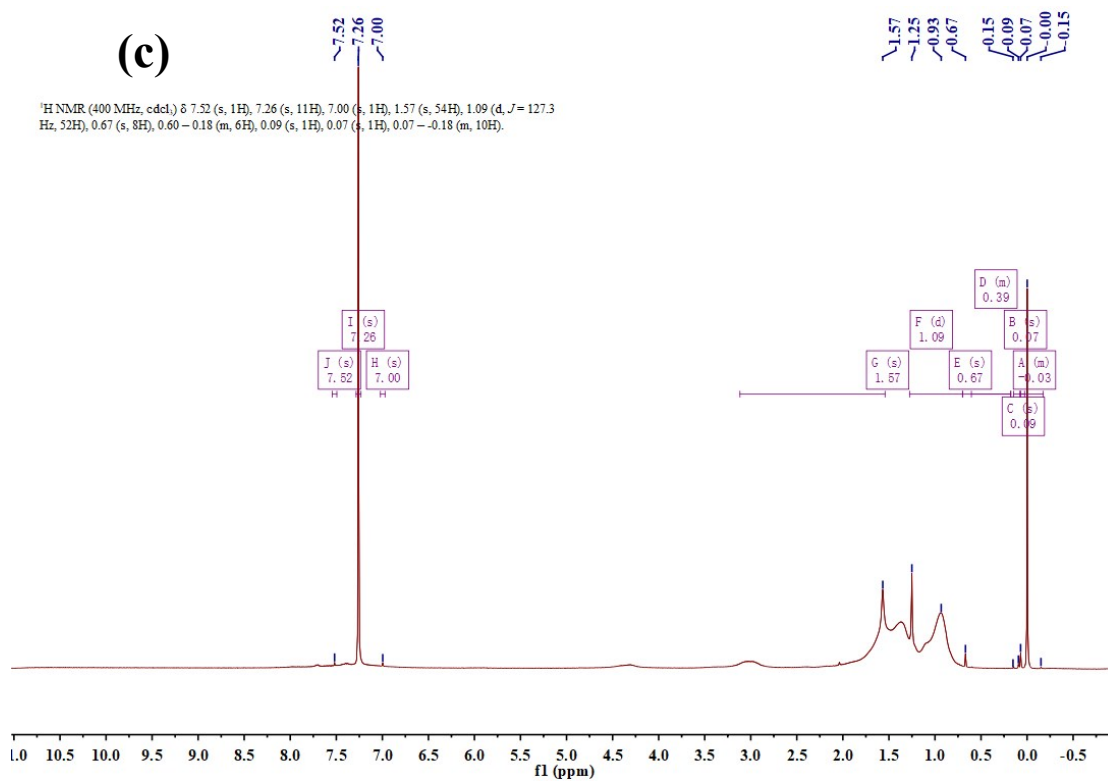
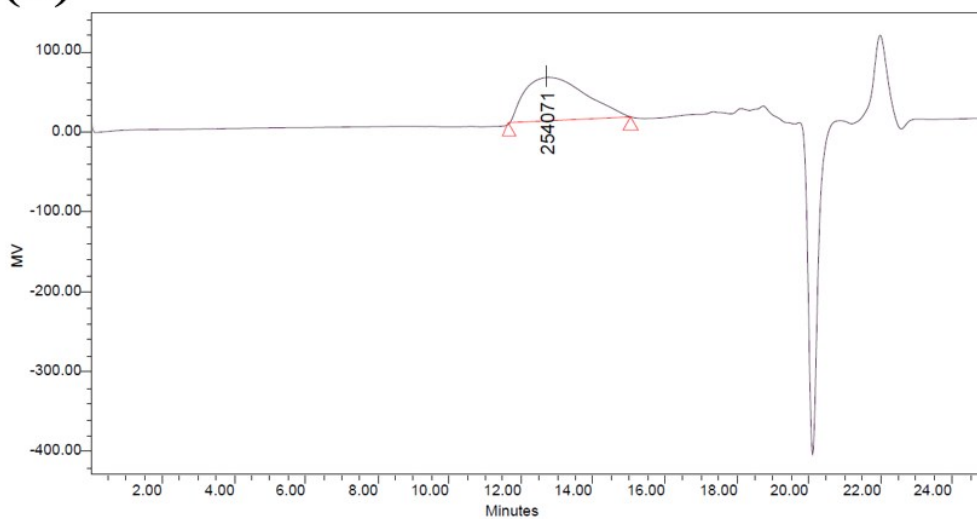


Figure S2. ¹H NMR spectra of (a) PCE10-2Cl (b) PCE10-2F and (c) PCE10-SF in CDCl₃

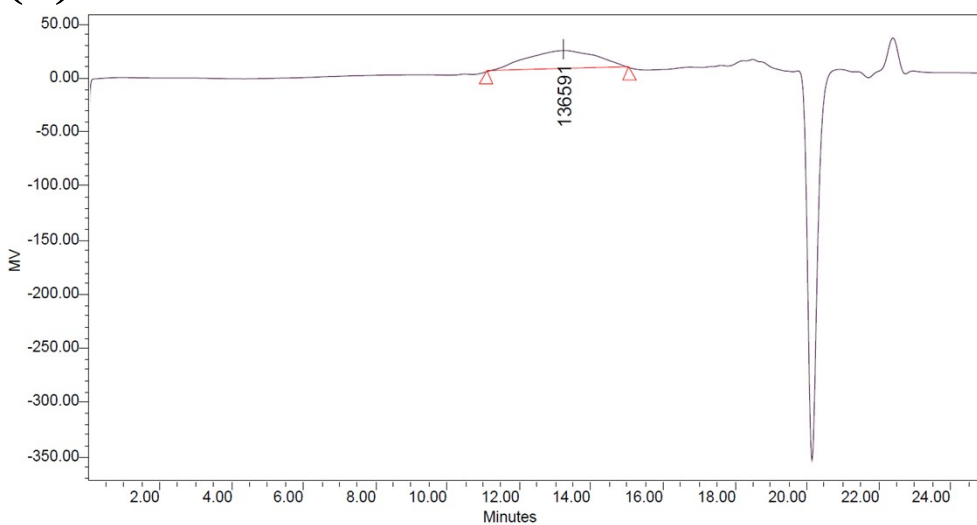
(a)



GPC Results

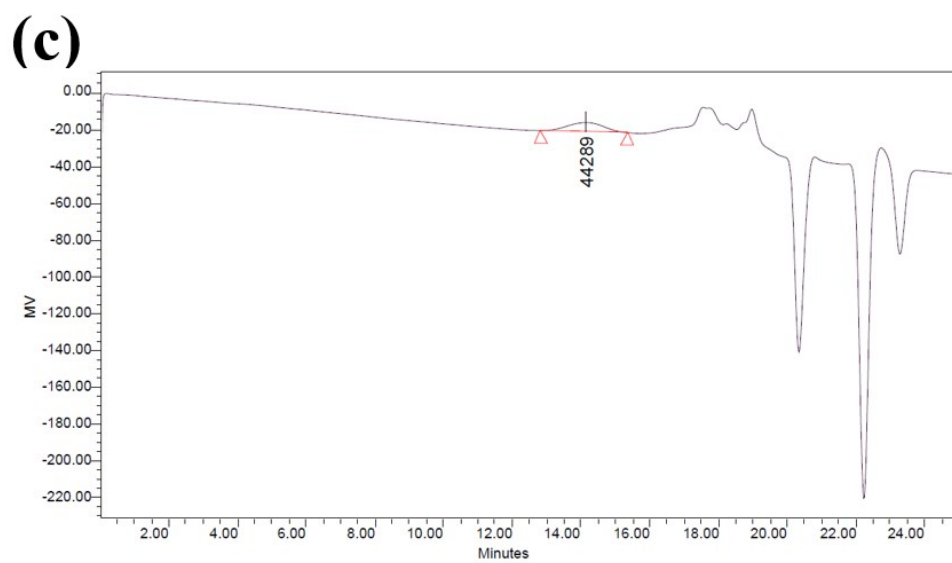
Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1	12.683	12.683	12.683	110869	227768	254071	349753	439629	1.535568

(b)



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1	13.213	13.213	13.213	90717	233832	136591	477163	714307	2.040622



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1	14.120	14.120	14.120	38287	52172	44289	69590	88020	1.333839

Figure S3. GPC spectra of **(a)** PCE10-2Cl **(b)** PCE10-2F and **(c)** PCE10-SF in THF

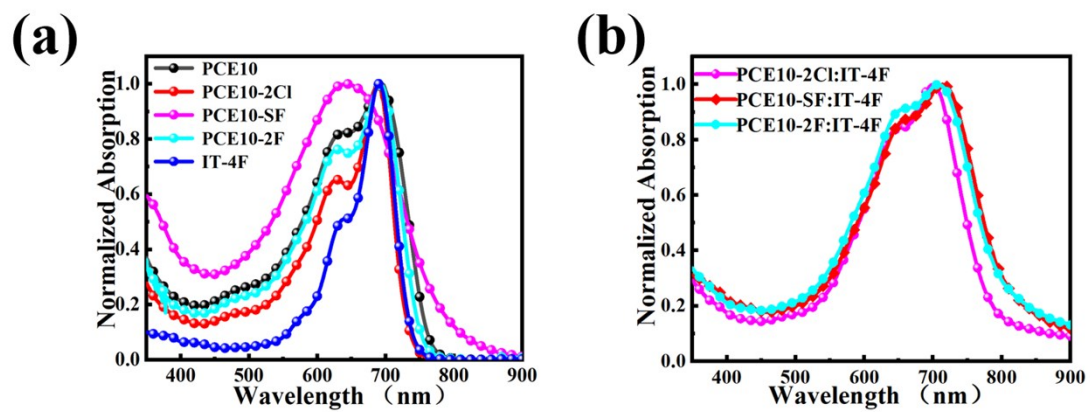


Figure S4. (a) Normalized absorption spectra of the PCE10, PCE10-2Cl, PCE10-2F and PCE10-SF in solutions. (b) Normalized absorption spectra of the PCE10-2Cl:IT-4F PCE10-2F:IT-4F and PCE10-SF:IT-4F blend films.

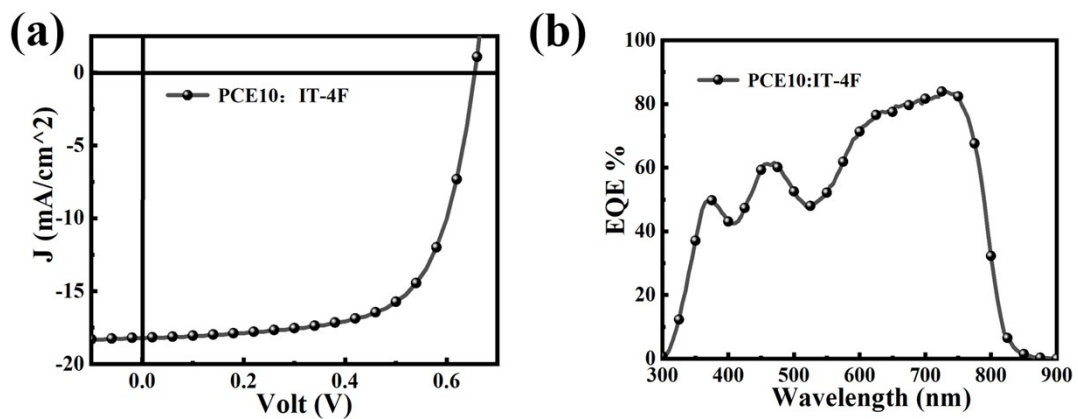


Figure S5. (a) Optimize the J-V curve of the equipment (PCE10:IT-4F) and (b) the corresponding EQE spectrum.

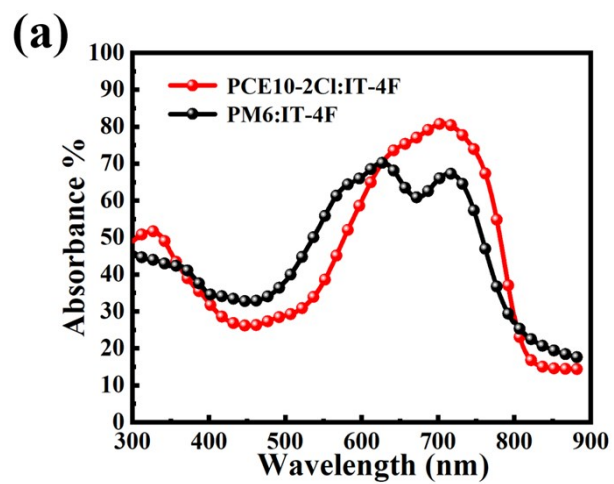


Figure S6. Absorbance of the active layer(110nm) PM6: IT-4F and PCE10-2Cl: IT-4F

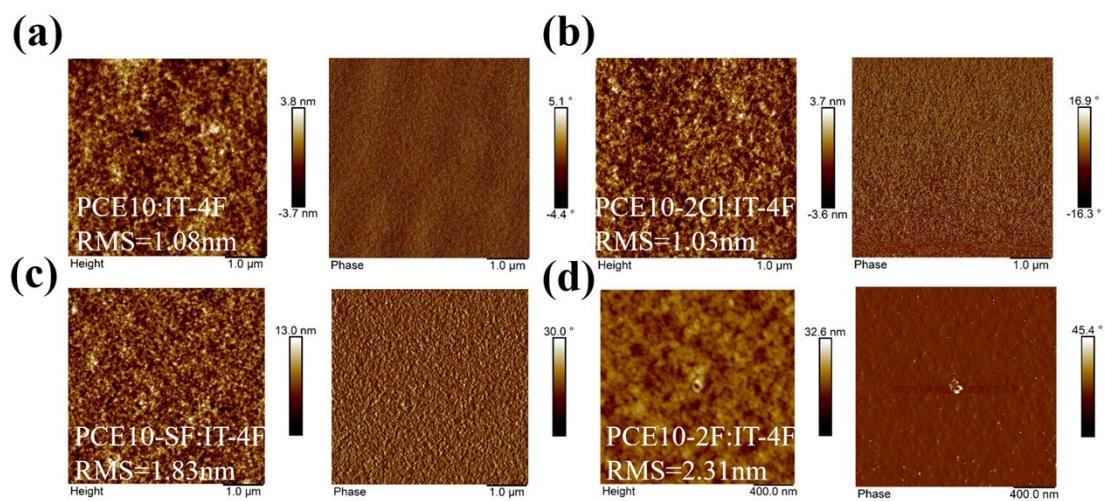


Figure S7. AFM images of different optimized blend films. **(a)** PCE10:IT-4F **(b)** PCE10-2Cl:IT-4F **(c)** PCE10-SF:IT-4F and **(d)** PCE10-2F:IT-4F.

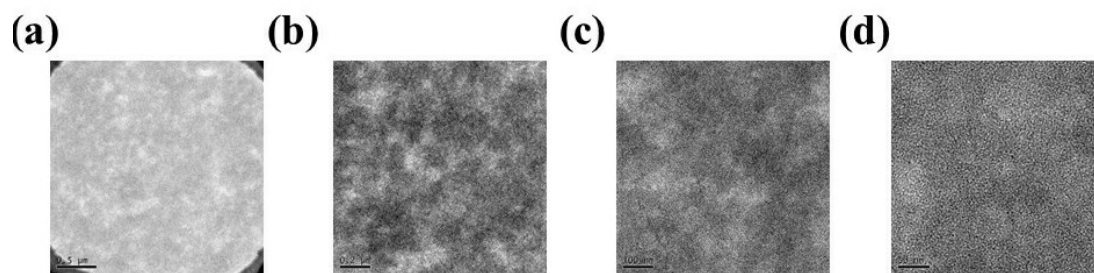


Figure S8. TEM image of PCE10-2Cl:IT-4F optimized blend films with different magnification. **(a)** 0.5 μm **(b)** 0.2 μm **(c)** 100 nm and **(d)** 50 nm.

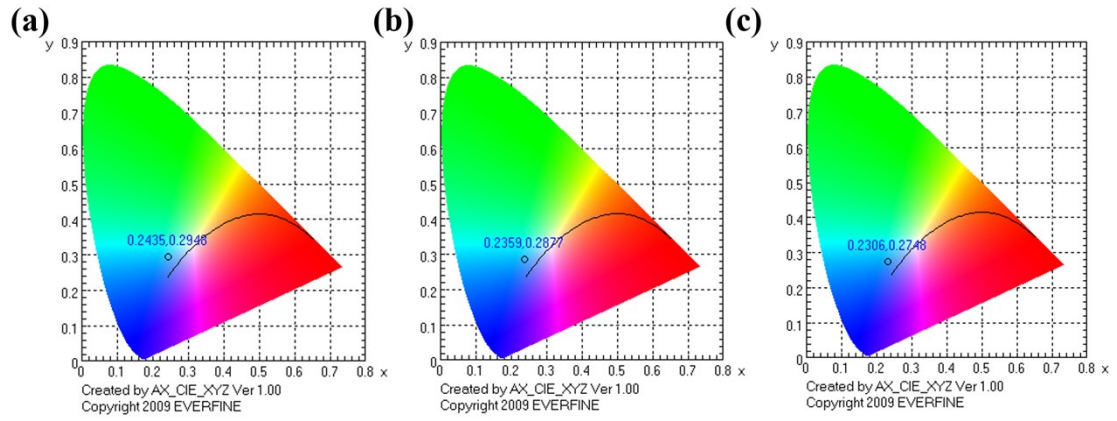


Figure S9. The CIE chromaticity diagram color coordinates of a semi-transparent device with a thickness of **(a)** 5 nm **(b)** 10 nm and **(c)** 15 nm Ag layer under AM 1.5G irradiation.

Table S1. Operating characteristics of OPVs under simulated AM 1.5G, 100 mW cm⁻² illumination.

Active layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE ^[a] (%)
PCE10:IT-4F	18.21±0.13	0.655±0.01	66.27±0.10	7.92 (7.72)

Table S2. Coherence length, *d*-spacing and integration of peak intensity for neat PCE10-2Cl, IT-4F and PCE10-2Cl:IT-4F blend films.

Materials	(100)Coherence length (Å)	(100)d-spacing (Å)	(010)Coherence length (Å)	(010)d-spacing (Å)
PCE10-2Cl	40.249	24.407	13.231	4.045
IT-4F	21.531	16.390	6.888	4.223
PCE10-2Cl: IT-4F	322.888	20.204	35.050	3.539