Supplementary Information for

Unique cohesive nature of β_1-isomer of [70]PCBM fullerene on structures and photovoltaic performances of bulk heterojunction films with PffBT4T-2OD polymer

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Experimental

Instruments. Regioisomer and diastereomer separations of [70]PCBM were conducted by Shimadzu Prominence Modular HPLC with Nacalai Tesque Cosmosil 5PBB (20 × 250 mm); eluent, toluene; flow rate, 10 mL min^{-1}; temperature, 40 °C; detection, 330 nm. ^{1}H NMR spectra were measured with a JEOL JNM-EX400 NMR spectrometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using an ALS 630A electrochemical analyzer in *o*-dichlorobenzene/acetonitrile mixture (v:v=5:1) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4PF_6) as a supporting electrolyte. UV-visible absorption spectra were obtained on a Perkin Elmer Lambda 900UV/vis/NIR spectrometer. Optical micrographs were recorded using KH-7700 (Hirox). Atomic force microscopy (AFM) analyses were carried out with an Asylum Technology MFP-3D-SA in the AC mode. XRD analyses of film samples were carried out with a Rigaku SmartLab 9 kW using Cu Kα radiation. Steady-state fluorescence spectra were recorded on a HORIBA SPEX Fluoromax-3 spectrofluorometer.

Photocurrent-voltage characteristics were measured by Keithley 2400 SourceMeter under a nitrogen atmosphere and simulated solar light (100 mW cm^{-2}, AM1.5) with OTENTO-SUN III solar simulator (Bunkoukeiki). Photocurrent action spectra were recorded with CEP-2000RR (Bunkoukeiki). Current–voltage characteristics of the electron- and hole-only devices for space-charge-limited current (SCLC) measurements were conducted using Keithley 2400 SourceMeter under an argon atmosphere.

Materials. [70]PCBM (>99.0%) and PffBT4T-2OD (PCE-11) were purchased from American Dye Source, Inc. and 1-Material, respectively. All other solvents and chemicals were of reagent-grade quality, purchased commercially, and used without further purification unless otherwise noted.

Solubility tests. The solubilities of fullerene samples in chlorobenzene (CB) and *o*-dichlorobenzene (ODCB) were estimated as follows.[S1] Saturated solutions of the fullerene materials were prepared by adding an excess amount of the fullerenes to solvents, followed by sonication at room temperature for 1 min. Then, the saturated solutions were filtered through a membrane filter (Cosmonice Filter S, COSMOSIL, pore size: 0.45 μm) to remove the aggregates. The amounts of the fullerene materials dissolved in the filtrates were determined by weighing the solid contents that remained after evaporation of the solvent and thorough drying under vacuum.

Time-resolved microwave conductivity (TRMC) measurements. The nanosecond laser pulses from an Nd:YAG laser (third harmonic generation, THG (355 nm) from Spectra Physics, INDI-HG, FWHM 4 ns) was used as excitation source. The excitation density was 4.6×10^{15} photons cm^{-2}. The resonant frequency and the microwave power were set at ~9.1 GHz and 5 mW, respectively. The TRMC signal from a diode was recorded on a digital oscilloscope (Tektronix, TDS 3032B). The transient photoconductivity ($\Delta\sigma$) of the samples is related to the reflected microwave power ($\Delta P_r/P_r$) and sum of the mobilities of charge carriers via:

$$\langle \Delta\sigma \rangle = \frac{1}{A}\frac{\Delta P_r}{P_r} \qquad (1)$$

$$\Delta\sigma = e\phi N \sum \mu \qquad (2)$$

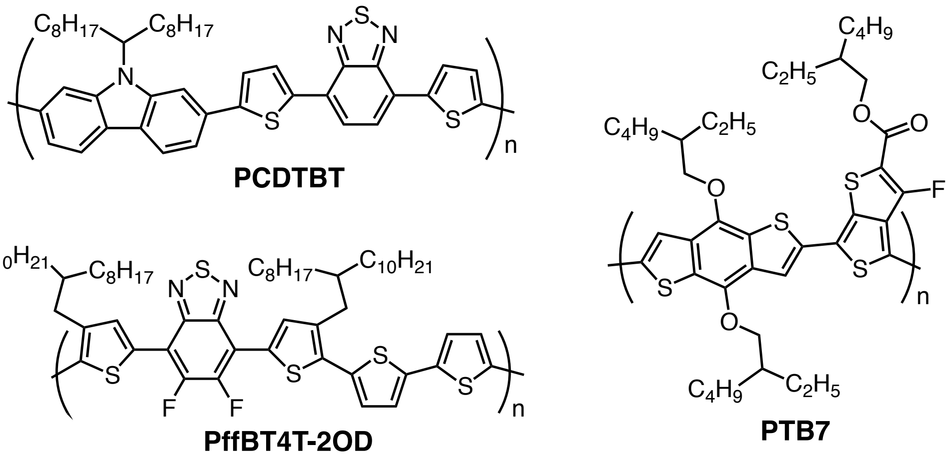
where A is the sensitivity factor, e is the elementary charge of electron, ϕ is the photo-carrier generation yield (quantum efficiency), N is the number of absorbed photons per unit volume, and $\Sigma\mu$ is the sum of mobility for the negative and positive carriers. For the sample preparations, fullerene single component films were formed on quartz substrates.

OPV device fabrications. Indium tin oxide (ITO) on a glass substrate with a sheet resistance of 5 Ω/sq (Geomatec) was used. The substrates were cleaned by ultra-sonication in deionized water, chloroform, acetone, and tetramethyl-ammonium hydroxide aqueous solution for 15 min each, and then deionized water for 25 min, followed by 2-propanol and ethanol for 15 min each. They were subsequently dried under nitrogen flow and treated in a UV-ozone cleaner for 25 min. A solution containing $Zn(CH_3COO)_2 \cdot 2H_2O$ (44.44 mg), 2-methoxyethanol (1 mL) and ethanolamine (12.25 μL) was stirred at room temperature overnight, and was spin-coated on the ITO substrates at 5000 rpm for 20 sec. The ZnO layer was dried at 175 ºC for 10 min, and then transferred into a glove box filled with dried N_2 gas to coat the active layer. A blended solution of PffBT4T-2OD (10 mg mL^{-1}) and [70]PCBM in organic solvents with an additive, 1,8-diiodooctane (DIO), was prepared and stirred on a hotplate at 80 ˚C overnight. Before spin coating, both the blended solution and ITO substrates were preheated on a hotplate at 130 ºC for 1 hour. The active layer was spin-coated from the warm blended solution on the preheated substrate at 800 rpm for 20 sec. Then, the thermal annealing was conducted at 80 °C for 5 min. The film thicknesses of the active layers were ca. 200 nm except for PffBT4T-2OD:β_1-[70]PCBM (100 nm). The samples were finally transferred to an evaporation chamber for MoO_3 deposition (20 nm) at a rate of 0.5–1 Å s^{-1} and Al deposition (100 nm) at a rate of 6–10 Å s^{-1} to obtain the OPV devices denoted as ITO/ZnO/PffBT4T-2OD:fullerene/MoO_3/Al. The optimized conditions for the active layer formations are as follows. mix-[70]PCBM; 12 mg mL^{-1}, *o*-dichlorobenzene (ODCB) : chlorobenzene (CB) = 1 : 1, 3.0% DIO. α-[70]PCBM; 15 mg mL^{-1}, ODCB : CB = 1 : 1, 3.0% DIO. mix-β-[70]PCBM; 16 mg mL^{-1}, ODCB : CB = 1 : 1, 3.0% DIO. β_1-[70]PCBM; 12 mg mL^{-1}, ODCB : CB = 1 : 0, 3.0% DIO. β_2-[70]PCBM; 14 mg mL^{-1}, ODCB : CB = 1 : 1, 1.5% DIO.

SCLC measurements. The hole and electron mobilities were measured using the SCLC method by using devices with the configurations of glass/ITO/PEDOT:PSS/PffBT4T–2OD:fullerene/MoO_3/Au and glass/Al/PffBT4T-2OD:fullerene/Al by taking current–voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, μ is the charge mobility, V is the voltage drop across the device and L is the thickness of the blend film. The dielectric constant ε_r is assumed to be 3, which is a typical value for conjugated polymers.

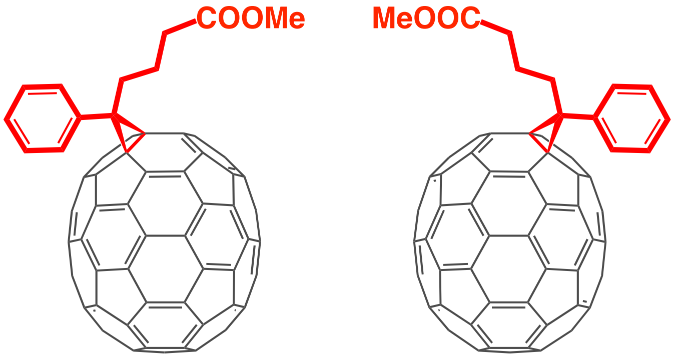


PCDTBT

PffBT4T-2OD

PTB7

Fig. S1 Structures of conjugated polymers.



(R)-α-[70]PCBM (S)-α-[70]PCBM

Fig. S2 Structures of (R)-α-[70]PCBM and (S)-α-[70]PCBM.

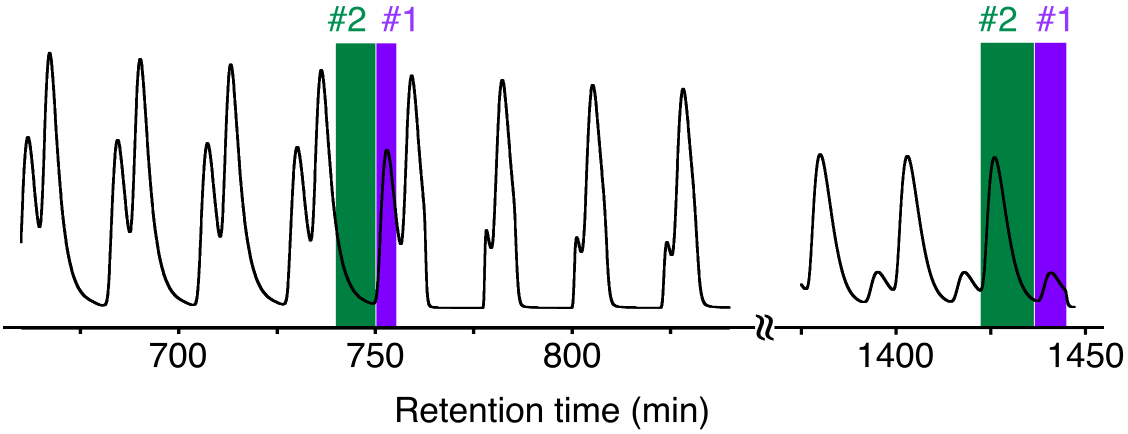


Fig. S3 HPLC profile of mix-β-[70]PCBM. The first and second fractions were collected during the retention time regions denoted as #1 and #2, respectively, in the figure. The first and second fractions were assigned to β_1-[70]PCBM and β_2-[70]PCBM, respectively.

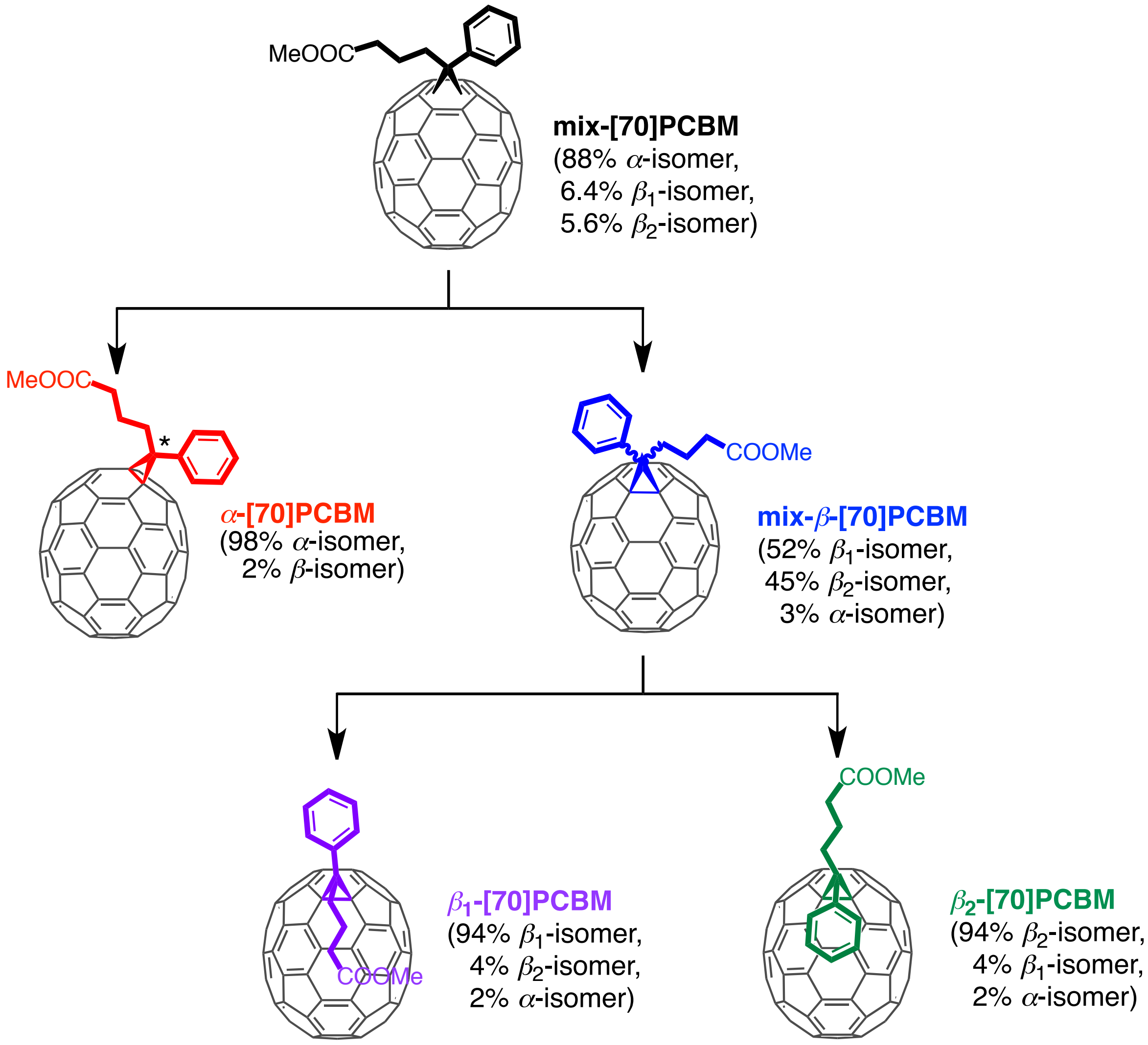


Fig. S4 Flow chart of the separation of [70]PCBM isomers. The isomer composition ratios are calculated from the ^{1}H NMR data.

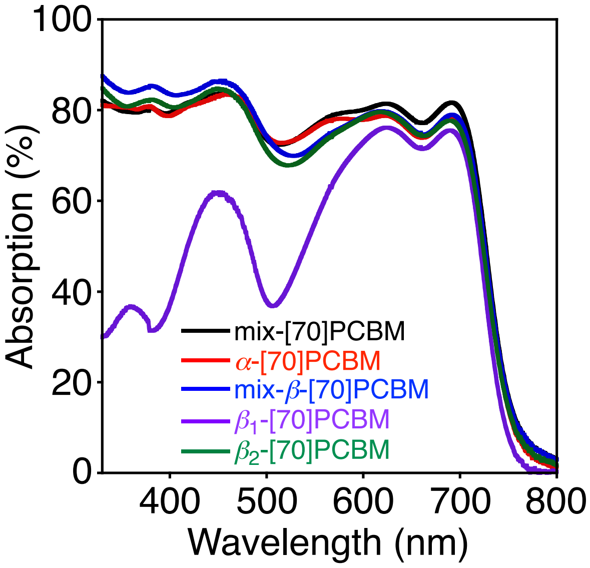


Fig. S5 UV-visible absorption spectra of blend films of PffBT4T-2OD with mix-[70]PCBM (black), α-[70]PCBM (red), mix-β-[70]PCBM (blue), β_1-[70]PCBM (purple), and β_2-[70]PCBM (green) on ITO/ZnO substrates.

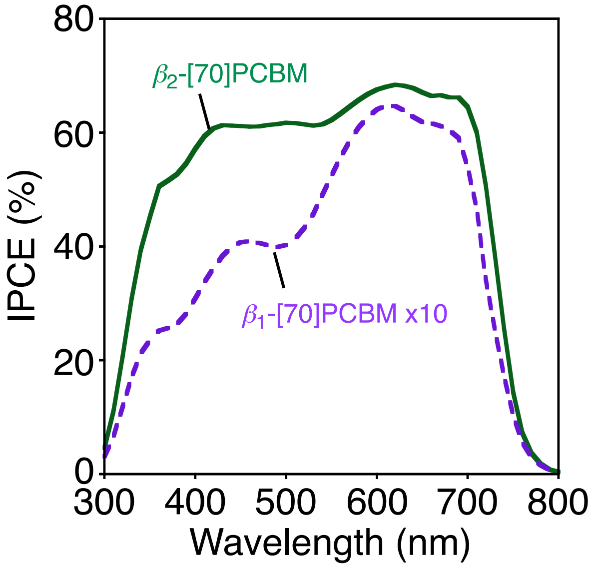


Fig. S6 Photocurrent action spectra of OPV devices based on PffBT4T-2OD:β_1-[70]PCBM (purple dotted) and PffBT4T-2OD:β_2-[70]PCBM (green). The spectrum of PffBT4T-2OD:β_1-[70]PCBM is enlarged by a factor of ten to clearly show the spectral shape.

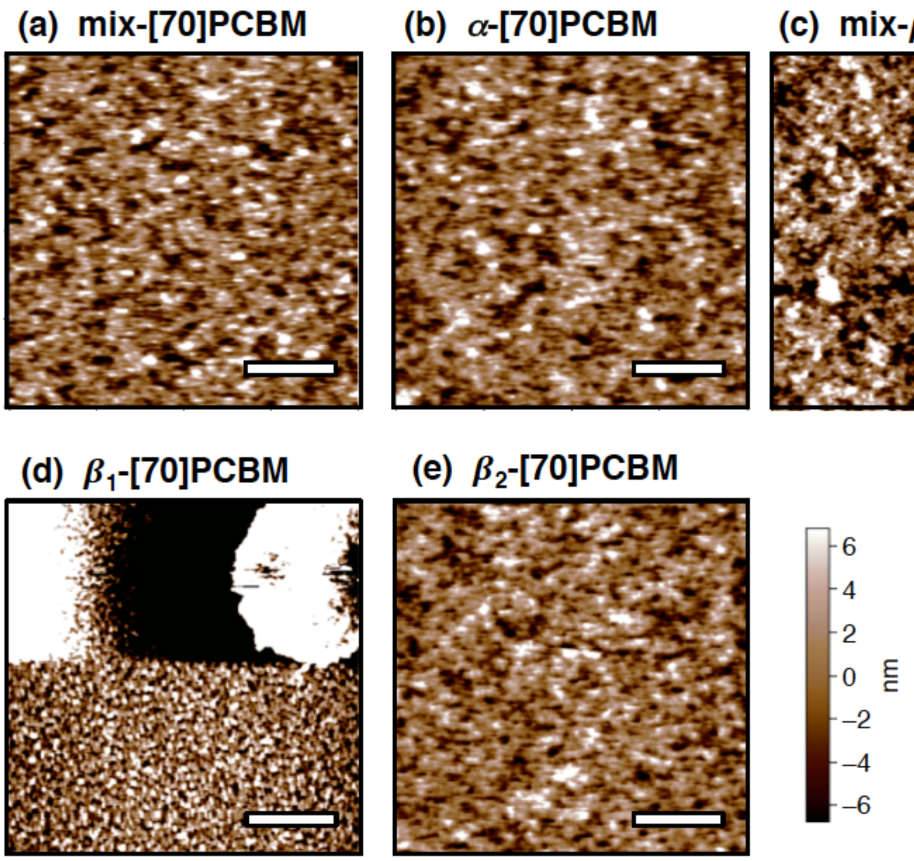


Fig. S7 AFM images of the blend films of PffBT4T-2OD with (a) mix-[70]PCBM, (b) *α*-[70]PCBM, (c) mix-*β*-[70]PCBM, (d) β_1-[70]PCBM, and (e) β_2-[70]PCBM on ITO/ZnO substrates. Scale bars represent 5 μm. The color scale represents the height topography, with bright and dark representing the highest and lowest features, respectively.

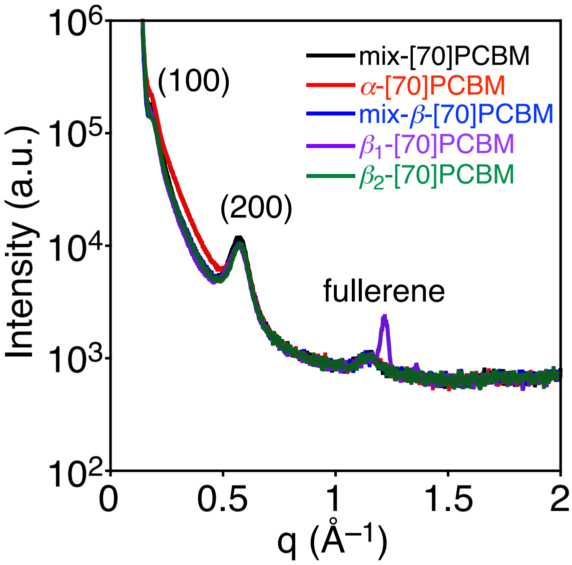


Fig. S8 XRD patterns of blend films of PffBT4T-2OD with mix-[70]PCBM (black), α-[70]PCBM (red), mix-β-[70]PCBM (blue), β_1-[70]PCBM (purple), and β_2-[70]PCBM (green).

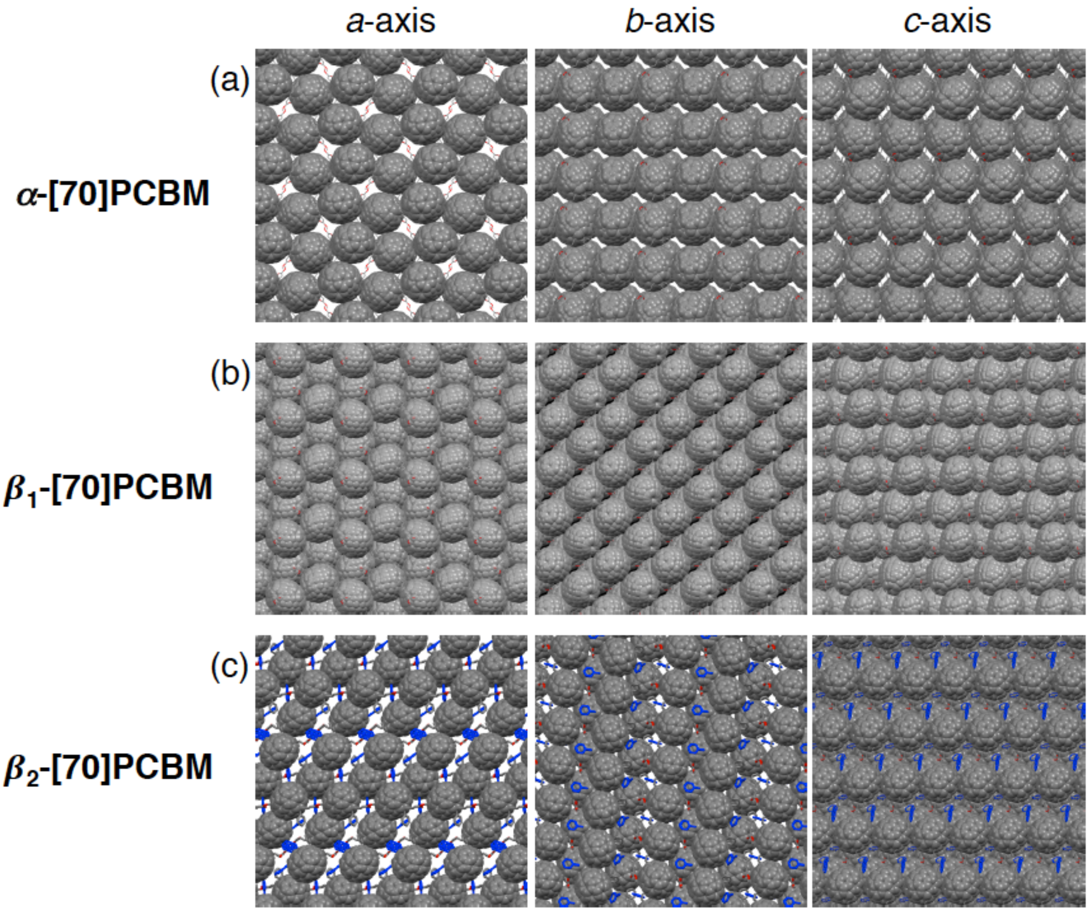


Fig. S9 X-ray crystal packing structures of (a) α-[70]PCBM, (b) β_1-[70]PCBM, and (c) β_2-[70]PCBM along with *a*-, *b*-, and *c*-axes. Solvent molecules are contained in (c). The crystal data were taken from literatures.[S2]

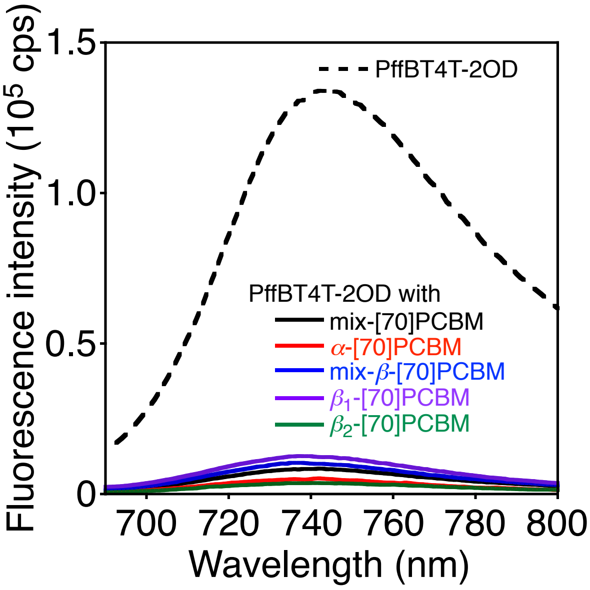


Fig. S10 Photoluminescence spectra of PffBT4T-2OD single component film (black dotted) and blend films of PffBT4T-2OD with mix-[70]PCBM (black), *α*-[70]PCBM (red), mix-*β*-[70]PCBM (blue), β_1-[70]PCBM (purple), and β_2-[70]PCBM (green). The excitation wavelengths are 671 nm. The emission intensities were normalized by that of the PffBT4T-2OD film considering the difference in the absorbances of the PffBT4T-2OD:fullerene films at the excitation wavelength. The emissions of PffBT4T-2OD were quenched efficiently (90–97%) in all the blend films.

References

[S1] T. Umeyama, S. Shibata, T. Miyata, K. Igarashi, T. Koganezawa and H. Imahori, *RSC Adv.*, 2017, **7**, 45697.

[S2] (*a*) T. Umeyama, T. Miyata, A. C. Jakowetz, S. Shibata, K. Kurotobi, T. Higashino, T. Koganezawa, M. Tsujimoto, S. Gélinas, W. Matsuda, S. Seki, R. H. Friend and H. Imahori, *Chem. Sci.*, 2017, **8**, 181; (*b*) X.-X. Zhan, X. Zhang, S.-M. Dai, S.-H. Li, X.-Z. Lu, L.-L. Deng, S.-Y. Xie, R.-B. Huang and L.-S. Zheng, *Chem. Eur. J.*, 2016, **22**, 18709.