Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Charge-Carrier Generation in Organic Solar Cells using Crystalline Donor Polymers

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Details of Spectroscopic Measurements. The photoluminescence (PL) spectra were measured with a fluorescence spectrophotometer (Horiba Jobin Yvon, NanoLog) equipped with a photomultiplier tube (Hamamatsu, R928P) and a liquid-nitrogen-cooled InGaAs near-IR alloy detector (Horiba Jobin Yvon, Symphony II) under ambient atmosphere. Electroluminescence (EL) spectra from a photovoltaic cell consisting of a PSBTBT/PCBM blend film were measured with the same system under N_2 atmosphere. The photovoltaic cell employed consisted of an indium/tin oxide (ITO) anode (10 Ω per square), poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT:PSS, 40 nm), an active layer (~200 nm), and an Al cathode. The EL spectra were measured under a forward bias of 1.5 V.

The PL decay was measured by the time-correlated single-photon-counting (TCSPC) method (Horiba Jobin Yvon, FluoroCube). The excitation and detection wavelengths were 407 and 1150 nm, respectively. The total instrument response function is an fwhm of ca. 1.4 ns.

The ionisation potentials of PSBTBT pristine films with different crystallinity were measured with a photoelectron yield spectrometer (Riken Keiki, AC-3). All films were prepared onto ITO-coated glass substrates. The threshold energy for the photoelectron emission was estimated on the basis of the cubic root of the photoelectron yield plotted against the incident photon energy.

Femtosecond transient absorption data were collected with a pump and probe femtosecond transient spectroscopy system. This system consists of a transient absorption spectrometer (Ultrafast Systems, Helios) and a regenerative amplified Ti:sapphire laser (Spectra-Physics, Hurricane). The amplified Ti:sapphire laser provided 800 nm fundamental pulses at a repetition rate of 1 kHz with an energy of 0.8 mJ and a pulse width of 100 fs (fwhm), which were split into two optical beams with a beam splitter to generate pump and probe pulses. One fundamental beam was used as pump pulses at 800 nm, or at 600 nm after converted with an ultrafast optical parametric amplifier (Spectra-Physics, TOPAS). The other fundamental beam was converted into white light pulses employed as probe pulses in the wavelength region from 400 to 1700 nm. The pump pulses were modulated mechanically with a repetition rate of 500 Hz. The temporal evolution of the probe intensity was recorded with a CMOS linear sensor (Ultrafast Systems, SPEC-VIS) for the visible measurement and with an InGaAs linear diode array sensor (Ultrafast Systems, SPEC-NIR) for the near-IR measurement. Transient absorption spectra and decays were collected over the time range from −5 ps to 3 ns. Typically, 2500 laser shots were averaged at each delay time to obtain a detectable absorbance change as small as $\sim 10^{-4}$. In order to cancel out orientation effects on the dynamics, the polarization direction of the linearly polarized probe pulse was set at a magic angle of 54.7 ° with respect to that of the pump pulse.

Microsecond transient absorption data were collected with a highly sensitive microsecond transient absorption system. A dye laser (Photon Technology International Inc., GL-301) pumped by a nitrogen laser (Photon Technology International Inc., GL-3300) was used as an excitation source, which provides sub-nanoseconds pulses with various fluences from ~μJ to 0.1 mJ cm^{-2} at a repetition rate of 4 Hz. The excitation wavelength was 400 nm. A tungsten lamp (Thermo-Oriel, Model 66997) with an intensity controller (Thermo-Oriel, Model 66950) was used as a probe light source. The probe wavelength was selected by two monochromators (Ritsu, MC-10C) and appropriate optical cut-off filters equipped before and after the sample to reduce scattered light and emission. The temporal evolution of ΔOD was monitored with a high-gain Si photodiode (Hamamatsu Photonics, S1722-01). The signal from the photodiode was pre-amplified and sent to a main amplifier (Costronics Electronics) with an electronic band-pass filter to improve the signal-to-noise ratio. Finally, the amplified signal was collected with a digital oscilloscope (Tektronix, TDS2022), which was synchronized with a trigger signal of the laser pulse from Si photodiode (Thorlabs Inc., DET10A). The instrument response was in the order of 60 ns. Transient absorption decays were collected over the time range from sub-micro to milliseconds, averaging 1200 laser shots on each decay time scale, yielding a sensitivity of 10^{-6} to 10^{-4} depending on the measuring time domain.

The sample films were sealed in a quartz cuvette purged with N_2. Note that the transient absorption spectra and dynamics were highly reproducible even after the several times measurements. In other words, the laser irradiation had negligible effects on the sample degradation at least under this experimental condition.

PL and EL Spectra. Figure S1a shows the PL spectra of PSBTBT pristine (solid line) and PSBTBT/PCBM blend (50 : 50 wt%, broken line) films. The fluorescence quenching efficiency was calculated by

$$\Phi_f = 1 - {}^{I}\!/_{I_0} \qquad \text{(S1)}$$

where I_0 is the PL intensity of a PSBTBT pristine film, I is the PL intensity of a PSBTBT/PCBM blend film, after normalized by the absorption at an excitation wavelength of 670 nm. The quenching efficiency was estimated to be >98%. Figure S1b shows the EL spectrum of a PSBTBT/PCBM blend photovoltaic cell. The EL spectrum was red-shifted compared to the PL spectra of both PSBTBT and PCBM[S1] pristine films, suggesting that the EL spectrum was attributable to the emission from the CT state.

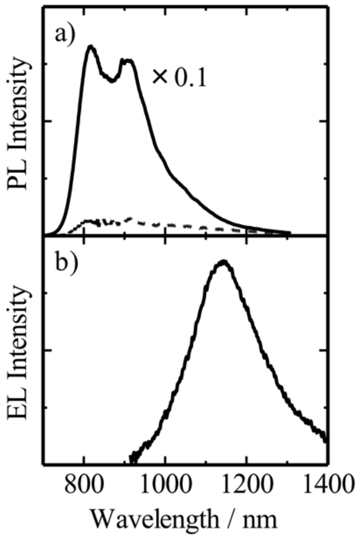

Figure S1. a) PL spectra of PSBTBT pristine (solid line) and PSBTBT/PCBM blend (broken line) films. b) EL spectrum of a PSBTBT/PCBM blend photovoltaic cell.

PL Decay. Figure S2 shows the PL decay curve of a PSBTBT/PCBM blend film measured by the time-correlated single-photon-counting (TCSPC) method at room temperature. The detection wavelength was 1150 nm so as to detect the CT emission as shown in Figure S1b. The PL decay curve was fitted with the sum of two exponential functions (solid line). The CT emission lifetime was evaluated to be 810 ps on average.

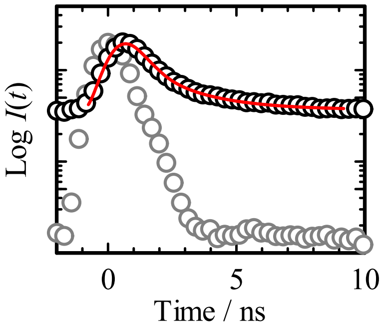

Figure S2. PL decay curve of a PSBTBT/PCBM blend film. The black circles represent the PL decays. The grey circles are the instrument response function for the TCSPC measurement. The solid line represents the best fitting curve with the sum of two exponential functions. The lifetimes (the fraction) of two exponentials were 510 ps (80%) and 2 ns (20%). The averaged lifetime was calculated as $<\tau> = \sum a_i \tau_i$ where τ_i and a_i are each lifetime and its fraction, respectively.

Ionisation Potential of PSBTBT. Figure S3 shows the photoelectron yield spectra of PSBTBT pristine films prepared from *o*-dichlorobenzene (open circles) and chloroform (open triangles). The ionisation potentials were estimated to be 4.89 eV (open circles) and 4.95 eV (open triangles).

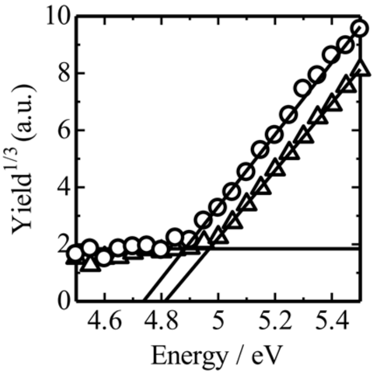

Figure S3. Photoelectron yield spectra of PSBTBT pristine films prepared from *o*-dichlorobenzene (open circles) and chloroform (open triangles). The threshold energy for the photoelectron emission was estimated on the basis of the cubic root of the photoelectron yield plotted against the incident photon energy.

Spectral Templates of Polarons. The spectral template of singlet excitons can be easily obtained from the transient absorption spectra of PSBTBT pristine films, and hence there is no need to provide further complement explanation. The spectral templates of polarons were obtained as follows. Figure S4a shows the femtosecond transient absorption spectra of PSBTBT in 1-chloronaphthalene (CN) solution after the laser excitation at 600 nm. A large absorption band was observed at 1350 nm, and then red-shifted to 1400 nm with time, which is attributable to the absorption band of the PSBTBT S_1–S_n absorption. Note that, as mentioned in the manuscript, the PSBTBT S_1–S_n absorption band in the solid state is red-shifted compared to that in CN solution, suggesting that singlet excitons generated in the PSBTBT film are delocalized over the crystalline phase. At 3 ns after the laser excitation, a small absorption band was observed at around 1100 nm, which is assigned to triplet excitons. Figure S4b shows the femtosecond transient absorption spectra of PSBTBT blended with PCBM in CN solution measured at 3 ns after the laser excitation (red line). A new broad absorption band from 800 to 1200 nm was observed, which we assign to polarons in the disorder phase because PSBTBT is well dissolved, and hence does not form crystalline phase at all in CN solution as mentioned in the manuscript.

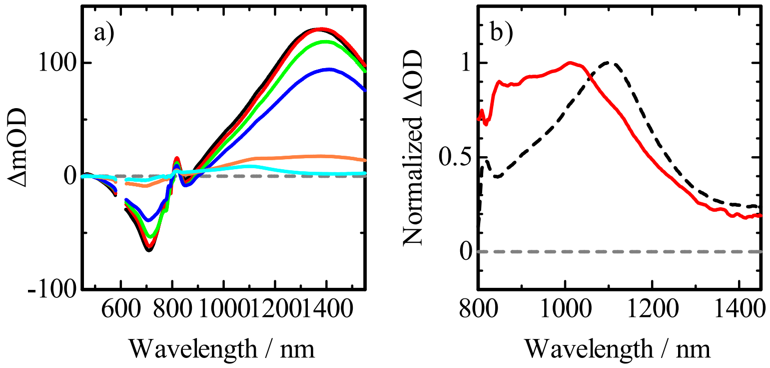

Figure S4. a) Transient absorption spectra of PSBTBT in CN solution excited at 600 nm (64 μJ cm^{-2}) measured at 0, 1, 10, 100, 1000, and 3000 ps after the laser excitation from top to bottom. b) Normalized transient absorption spectra of PSBTBT/PCBM (red line) and PSBTBT (broken line) in CN solution excited measured at 3000 ps after the laser excitation.

Figure S5 shows the wavelength dependence of transient absorption decays of a PSBTBT/PCBM blend film. As shown in Figure S5, the decay dynamics was dependent on the wavelength ranging from 1000 (green line) to 1200 nm (red line), indicating that the transient signals in this region consist of more than two species with different kinetics, which we have already assigned in the manuscript to polarons in the disorder and crystalline phases. On the other hand, the decay dynamics was independent of the wavelength ranging from 1000 (green line) to 850 nm (purple line), indicating that the transient signals in this region consisted mainly of one component, which we can safely assign to polarons in the disorder phase as shown in Figure S4. The spectral template of polarons in the crystalline phase, therefore, was obtained by subtracting the absorption of polarons in the disorder phase from the transient absorption of the blend film at 10 ps (the green line in Figure 5 in the manuscript) after the signal at 850 nm is normalized. Figure 5 in the manuscript shows the spectral templates of singlet excitons (broken line), polarons in the disorder phase (grey solid line), and polarons in the crystalline phase (black solid line) used in this study. As described in the next section, the molar absorption coefficient ratio of these transients was estimated to be 2.4 : 1 : 2 at each peak wavelength.

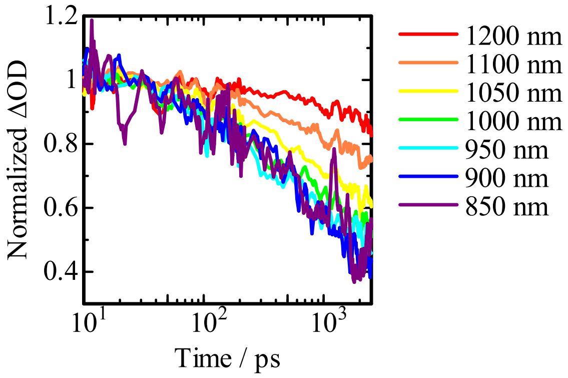

Figure S5. Normalized transient absorption decays of a PSBTBT/PCBM blend film excited at 800 nm (11 μJ cm^{-2}) measured at various wavelengths from 850 to 1200 nm from bottom to top.

Singular Value Decomposition (SVD) and Global Fitting.

In order to deconvolute the intricately overlapped transient absorption spectra, we performed singular value decomposition (SVD) and global fitting analysis for the transient absorption spectra.[S2,S3] Using SVD, the 3D matrix of the transient absorption data can be decomposed into its principal spectra and kinetic traces. The principal kinetic traces are then globally fitted to a multi-exponential function convoluted with the Gaussian instrument response function (~130 fs). The pre-exponential coefficients are obtained as a function of the wavelength from fitting of the 3D matrix to the exponentials. Although it has no physical meaning to use multi-exponential functions, this analysis provides us an excellent initial clue to obtain insights into the dynamics of transient species. Applying this procedure to the PSBTBT/PCBM blend film, we obtained four exponential components and a constant component. Figure S6 shows pre-exponential coefficient spectra of these components. As shown by the green lines, we can reproduce each spectrum by the sum of spectral templates as shown in Figure 5 in the manuscript. Note that the positive and negative signals correspond to decay and rise dynamics, respectively, of the transient signal at the wavelength. The fastest two components (panels a and b) consisted of the singlet exciton decay and charge rises, and hence can be unambiguously ascribed to charge transfer from PSBTBT to PCBM. The slowest component (panel d) consisted of the decay of polarons in the disorder phase, and coincident with a CT emission lifetime of ~810 ps evaluated by the TCSPC method. We thus attributed to the geminate recombination of polarons loosely bound to PCBM anions in the disorder phase. The constant fraction consisted of polarons in the disorder and crystalline phases, which can be assigned to dissociated charge carriers. We found an interesting phenomenon in the panel (c). This component consisted of the decay of polarons in the disorder phase and the rise of polarons in the crystalline phase, which we attribute to hole transfer from the disorder to crystalline phase as discussed in the manuscript. The molar absorption coefficient ratios of the spectral templates were estimated as follows. From the panel (c) in Figure S6, the molar absorption coefficient ratio between polarons in the disorder and crystalline phases is estimated to be 1 : 2. The molar absorption coefficient ratio between polarons in the crystalline phase and singlet excitons is then estimated to be 1 : 1.2 from the panels (a) and (b) because $\Phi_f = \sim 1$ as mentioned above.

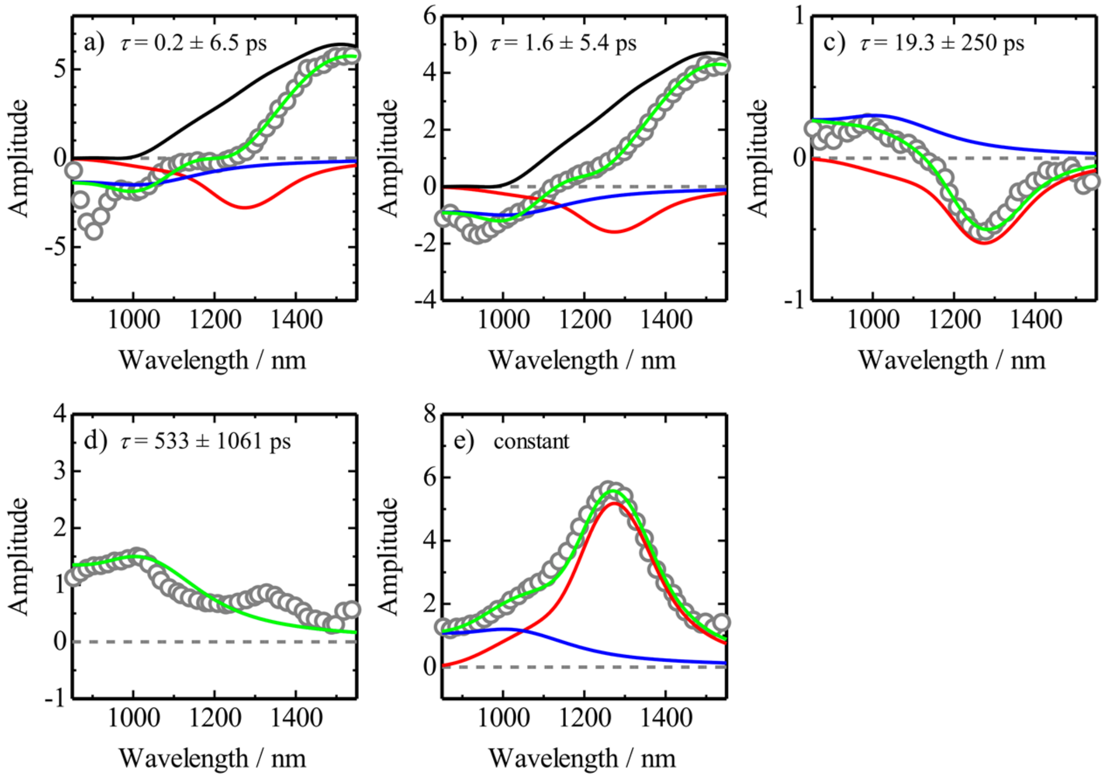

Figure S6. Pre-exponential coefficient spectra obtained by the SVD and global fitting analysis. The time constants were a) 0.2 ± 6.5 ps, b) 1.6 ± 5.4 ps, c) 19.3 ± 250 ps, and d) 553 ± 1061 ps. The solid lines in each panel represent the spectral templates of PSBTBT singlet exciton (black lines), PSBTBT polarons in the disorder (blue lines), and PSBTBT polarons in the crystalline (red lines) phases. The green lines in each panel represent the spectra simulated by the sum of these templates.

Spectral Simulation. Here we show some examples of spectral simulation of the transient absorption spectra of a PSBTBT/PCBM blend film. As shown in Figure S7, the transient absorption spectra measured at 0, 1, 10, and 1000 ps after the laser excitation can be well reproduced by the sum of the spectral templates shown in Figure 5 in the manuscript.

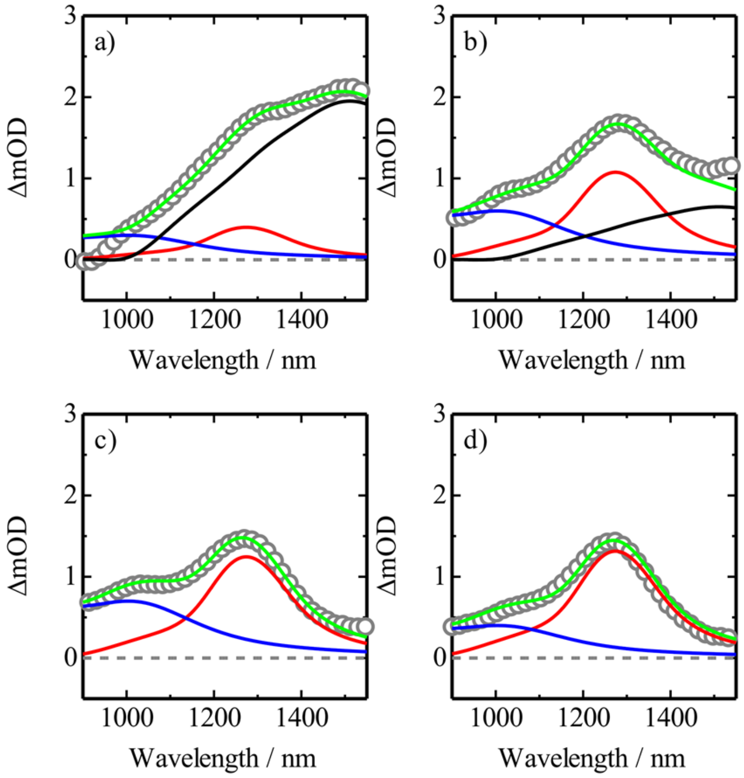

Figure S7. Transient absorption spectra of a PSBTBT/PCBM blend film (open circles) measured at a) 0, b) 1, c) 10, and d) 1000 ps after the laser excitation. The green lines represent spectra simulated by the sum of (black) singlet excitons, (blue) polarons in the disorder, (red) polarons in the crystalline phases.

References

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