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Effect of donor–acceptor molecular orientation on charge photogeneration in organic solar cells

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Abstract

The relative orientation of an electron donor and electron acceptor, which significantly affects charge photogeneration in an organic solar cell, is investigated here. The effects of the molecular orientations at the donor–acceptor heterojunction are examined using bilayer solar cells comprising a fixed acceptor layer and donor polymer layers that assume a variety of orientations. The orientation of the conjugated polymer is controlled during film formation using solvents with slow or fast drying rates. Although the donor polymer layers show similar light-harvesting and nongeminate recombination dynamics, photocurrent generation is more efficient at the face-on donor–acceptor interface than at the edge-on interface. Photophysical analysis reveals that the efficient charge generation at the face-on interface originates from enhanced exciton diffusion toward the donor–acceptor interface and reduced geminate recombination of charge pairs. These findings offer clear evidence that the separation efficiency of an interfacial charge pair is affected by the relative orientations of the donor and acceptor molecules. This orientation should be controlled to maximize the PCE of an organic solar cell.

Introduction

Single-junction organic solar cells (OSCs) have achieved power conversion efficiencies (PCEs) >12%¹. This remarkable progress stems from a deep understanding of the correlations between the morphology and photovoltaic properties of the photoactive layer as well as the development of new highly efficient materials². A variety of morphological factors can affect the photovoltaic properties. In particular, the molecular orientations in the photoactive layer can significantly influence the properties of some OSC systems^{3–12}. Conjugated organic molecules oriented parallel to the substrate plane provide good charge transport in vertically structured OSC devices⁸. Controlling the molecular orientations can affect the dipole interactions and energy levels of the molecules and

can therefore improve other properties, such as the light harvesting of the photoactive layer and the energetics of the device^{13–16}. The donor and acceptor molecular orientations can also affect photocurrent generation^{4–7,9–11}.

The effects of the relative orientations between donor and acceptor molecules on charge generation were initially studied theoretically and then explored experimentally^{3,17}. Most early investigations of the donor–acceptor orientation used bilayer devices that permitted control over the donor orientation because characterizing the orientations of donor molecules with respect to the commonly used spherical fullerene acceptor tends to be extremely difficult in bulk heterojunction (BHJ) structures. These experiments established the basic principles of the donor–acceptor orientation dependence of photocurrent generation and suggested that changes in the electronic coupling and molecular energy states with the orientation affected the charge transfer (CT) rate and therefore the photocurrent generation^{4,5}. Resonant soft X-ray scattering studies revealed the relationship between

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the donor–fullerene orientation and the photocurrent generation in BHJ devices⁷. Similar results have been reported for non-fullerene acceptor systems^{6,9,10}. The effect of the donor–acceptor orientation on non-fullerene OSC performance is still under investigation. Academic interest in non-fullerene acceptors has increased owing to the relative ease with which the acceptor orientation may be determined.

Although previous studies revealed the dependence of photocurrent generation on donor–acceptor molecular orientation, these studies have been limited. To isolate the effects of the donor–acceptor orientation, conditions that could affect the photocurrent generation must be held constant while the donor–acceptor molecular orientations are varied; however, the molecular orientations were often controlled in previous studies using rather complex experimental systems in which chemical or morphological factors changed significantly with the molecular orientations. For example, a series of polymers with different backbone structures, with different molecular weights, or with different blend domain structures were incorporated to change the donor–acceptor orientations within the active layer^{6,7,9,10,18}. Effective control of the orientations required these conditions but may also have led to variations in factors other than the orientation.

In addition, prior studies have rarely observed the orientation-dependent charge separation dynamics at the donor–acceptor interface. Instead, they relied on measurements of the device current–voltage characteristics to evaluate the orientation-dependent photocurrent generation. Although such observations are sufficient to outline the correlation between photocurrent generation and the donor–acceptor molecular orientation, the effect of the orientation on charge generation must be examined in the early stages before the generated carriers undergo non-geminate recombination. Otherwise, the observed orientation dependence of charge generation can be distorted by subsequent charge transport and collection processes, especially when morphological factors other than the donor–acceptor orientation are changed simultaneously with the orientation. Therefore, direct observation of the charge separation dynamics will lead to a better understanding of the effect of orientation on interfacial charge generation.

In this work, we used a well-controlled model system to systematically investigate how molecular orientation at the donor–acceptor interface affected photocurrent generation. Bilayer devices prepared using poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C71 butyric acid methyl ester (PCBM) had well-defined P3HT orientations and a sharp donor–acceptor interface without molecular intermixing. The P3HT orientation was varied between the face-on and edge-on orientations by changing the film drying kinetics, and a sharp and unmixed P3HT/PCBM

interface was fabricated using a nondestructive film transfer method. In these devices, other factors, such as light-harvesting ability and nongeminate recombination, were shown to be relatively similar despite the change in the molecular orientation. The changes in the photo-physical processes at the donor–acceptor interface could therefore be observed in isolation. Analyses revealed that the molecular orientations strongly affected the exciton diffusion behavior and the charge separation dynamics and that the face-on orientations improved photocurrent generation because this orientation facilitated exciton diffusion toward the interface and increased the free charge carrier yield by reducing the geminate recombination of charge pairs at the interface.

Materials and methods

Materials and device fabrication

Regioregular P3HT (weight-average molecular weight = 50,000–70,000 g mol^{−1}, regioregularity = 91–94%, 4002-E, Rieke Metals, Lincoln, NE, USA) and PCBM (purity > 99%, Solenne BV, Groningen, The Netherlands) were used as received. For device fabrication, glass and indium tin oxide (ITO)-coated glass substrates were cleaned sequentially with detergent, distilled water, acetone, and 2-propanol. After drying, the substrates were ultraviolet (UV)-ozone treated for 30 min. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS; Baytron P VP AI4083, Clevios) was spin-coated onto the glass substrates (30 nm) and baked in a convection oven for 40 min at 120 °C. A ZnO precursor solution was prepared by dissolving zinc acetate dehydrate (C₄H₆O₄Zn·2(H₂O), 99.5%, Sigma-Aldrich, 1 g) and monoethanolamine (HOCH₂CH₂NH₂, 98%, Acros, 0.252 g) in 2-methoxyethanol (10 mL) with stirring for 8 h to achieve hydrolysis and aging^{19,20}. The ZnO precursor was spin-coated onto the ITO-coated glass (40 nm) and then thermally annealed at 180 °C for 1 h in air. The PCBM solution was prepared using chloroform (CF) as a solvent (10 mg mL^{−1}) and was spin-coated onto the ZnO/ITO-coated glass substrates (30 nm). The P3HT solution was prepared using either CF or 1,2-dichlorobenzene (DCB) as a solvent, was spin-coated onto the PEDOT:PSS/glass substrates, and was transferred onto the PCBM/ZnO/ITO-coated substrates to fabricate the bilayer solar cell devices, as described in section “Device fabrication and *J*–*V* characterization”. The concentrations of the P3HT solutions were varied to change the P3HT film thickness. For MoO₃ (3 nm) and Au (60 nm) deposition, the samples were transferred into a vacuum chamber, and the MoO₃ and Au layers were thermally evaporated in sequence under a background pressure of ~1 × 10^{−6} Torr. For the hole-only device used in space-charge-limited current (SCLC) measurements, a P3HT layer (25 nm) was sandwiched between ITO/PEDOT:PSS(30 nm) and MoO₃(3 nm)/Au(60 nm) electrodes.

Characterizations

Grazing-incidence wide-angle X-ray scattering (GIWAXS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopic measurements were performed at the 3C, 4D, and 9A beamlines at the Pohang Accelerator Laboratory in Korea. For GIWAXS measurement, the angle between the film surface and the incident beam was fixed at 0.12° . The photon energy was 11.06 keV ($\lambda = 1.121 \text{ \AA}$). A Rayonix MAR165 detector was used for data collection. The samples were prepared on silicon wafer/PEDOT:PSS substrates and were deposited in the same way as described above. The J – V characteristics were measured using a Keithley 4200 power source. The light was simulated using an Oriel Sol³A class AAA solar simulator (1-kW Xenon lamp) and was referenced to a Newport Oriel 91150 V Si-based reference cell (KG5-filtered) calibrated at the US National Renewable Energy Laboratory. UV–vis absorption spectra were measured using a CARY-5000 spectrometer (Varian). Photoluminescence (PL) spectra were measured using a FP-6500 spectrofluorometer (Jasco). The thicknesses of the bathocuproine (BCP) and C_{60} layers used as the exciton blocking and quenching layers, respectively, in the PL measurements were $\sim 5 \text{ nm}$. Transient photovoltage (TPV) decay was measured using a digital oscilloscope (Tektronix TDC3054C) connected to SR560 and DHPCA-100 high-speed preamplifiers. The input impedance for TPV was $100 \text{ M}\Omega$ to ensure an open circuit. The samples were excited by a 3 ns pulse laser at $\lambda = 532 \text{ nm}$ (OBB, NL4300, and OD401) under 1 sun (AM1.5) illumination. Transient absorption (TA) measurements were conducted using a HELIOS ultrafast system–femtosecond TA spectrometer and a Libra 1 kHz femtosecond Ti:sapphire regenerative amplifier system with a 780 nm center wavelength and an 80 fs pulse duration. The laser beam was divided by a beam splitter. Approximately 95% of the laser beam was driven to a Coherent TOPAS Prime optical parametric amplifier to be used as a tunable pump beam with a pulse duration of 200 fs. The other $\sim 5\%$ was focused on a 5 mm sapphire

crystal to generate a white-light continuum for use as a probe beam.

Results and Discussion

Device fabrication and J – V characterization

OSCs with a bilayer structure were fabricated (Fig. 1) to investigate the effect of the molecular orientation at the donor–acceptor heterointerface. P3HT and PCBM were used as the donor and the acceptor materials of the OSCs, respectively. To obtain a sharp and unmixed donor–acceptor interface, the contact-film-transfer method was used to stack the donor layer on the acceptor layer^{21,22}. The P3HT layer was first spin-coated onto a PEDOT:PSS-coated glass substrate and then flipped and stacked onto a PCBM/ZnO/ITO substrate. The P3HT film was then detached from the glass substrate using drops of distilled water to dissolve the PEDOT:PSS layer, yielding the P3HT/PCBM/ZnO/ITO part of the device. The contact-film-transfer method enabled the formation of a neat P3HT/PCBM interface with negligible intermixing, which clearly revealed how the molecular orientations at the donor–acceptor interface affected the solar cell operation. After the transfer process, MoO_3 and Au were deposited in sequence on top of the P3HT layer to complete the device fabrication.

The relative orientations of the donor and acceptor molecules at the P3HT/PCBM interface were controlled by changing the molecular orientation of the P3HT layer through control of the evaporation rate of the solvent during the spin-coating process^{13,23}. Large differences in the solvent evaporation rate were achieved by carefully selecting the solvent volatility and spin speed. Slow evaporation was obtained by spin-coating a solution prepared using DCB at a low spin speed (500 rpm). Fast evaporation of the solvent was obtained by spin-coating a P3HT solution prepared using CF at a high spin speed (9000 rpm). The concentration of each solution was adjusted to give films with a thickness of 25 nm.

The molecular orientation distributions of the P3HT thin films were characterized using GIWAXS (Fig. 2).

Fig. 2 GIWAXS results of the P3HT films with controlled orientation. **a** 2D images of the fast-dried (top) and slow-dried (bottom) P3HT films. **b** Corresponding pole figure of the P3HT (100) peak

Two-dimensional GIWAXS images (Fig. 2a) of the slow-dried P3HT film (spun-cast from DCB solution) revealed a population of crystallites that were primarily oriented edge-on with respect to the substrate. The fast-dried film (spun-cast from the CF solution) included a significantly larger population of face-on-oriented crystallites. The pole figure of the P3HT (100) peak was constructed from the images to obtain a quantitative comparison of the molecular orientation distributions in the films (Fig. 2b). The (100) peak intensity was recorded as a function of the polar angle and corrected with a weighting factor $\sin(\omega)$, where ω is the polar angle measured from the q_z axis²⁴. The face-on orientation was dominant in the fast-dried P3HT film.

Angle-dependent NEXAFS spectroscopy was conducted in partial electron yield mode to collect the molecular orientation information from the uppermost (~ 10 nm) part of the P3HT films (Fig. 3a). Because the carbon $1s \rightarrow \pi^*$ transition of the conjugated polymer displayed a strong NEXAFS absorbance, the P3HT-conjugated plane orientations could be determined from the dependence of the $1s \rightarrow \pi^*$ transition intensity on the angle of X-ray incidence. The major carbon K -edge resonances of P3HT appeared at photon energies of 285.3, 287.8, and 293.0 eV, which corresponded to the carbon–carbon $1s \rightarrow \pi^*$,

carbon–hydrogen $1s \rightarrow \sigma^*$, and carbon–carbon $1s \rightarrow \sigma^*$ transitions, respectively²³. The $1s \rightarrow \pi^*$ transition intensity at low incidence angles was higher than that at high incidence angle in the fast-dried film. This difference indicated that the π^* orbitals were oriented vertically on the substrate and that the P3HT molecules were oriented face-on in the fast-dried film. By contrast, the $1s \rightarrow \pi^*$ intensity at high incidence angles was higher than that at low incidence angles in the slow-dried film. This difference indicated that the π^* orbitals were oriented parallel to the substrate and that the P3HT molecules were oriented edge-on in the slow-dried film. For a quantitative description of the molecular orientations, the dichroic ratio, R , was calculated for the π^* transition according to previous reports (Fig. 3b)²³. The R value, by definition, can vary from 1 to -1 depending on the orientation of the conjugated plane, and its positive and negative values represent preferential edge-on and face-on orientations, respectively. $R=0$ represents no preference for specific orientations. As expected, the slow-dried film, which was observed to have strong edge-on-dominant orientation in the GIWAXS measurements, showed a positive dichroic ratio of $R=0.22$. The fast-dried film showed a negative dichroic ratio of $R=-0.10$, which was also in accordance with the face-on-dominant orientation observed from the

GIWAXS data. From the R values, it seemed that the face-on orientation preference of the fast-dried film was relatively weak compared to the edge-on orientation preference of the slow-dried film. Nevertheless, this degree of molecular orientation change was sufficient to generate the orientation effects on charge generation, as shown below.

The J – V characteristics of OSC devices prepared with orientation-controlled P3HT layers were compared (Fig. 4a, Table 1). The fast-dried (‘face-on-rich’) and slow-dried (‘edge-on-rich’) P3HT films were both 25 nm thick, and the PCBM layer was 30 nm thick and was prepared in the same way for all devices. The photovoltaic parameter values were averaged from >15 devices. The device prepared with the fast-dried film (‘face-on-rich device’) had a PCE of 0.387% with a J_{sc} = 2.38 mA cm^{−2}, a V_{oc} = 0.32 V,

and an FF = 0.518. The device prepared with the slow-dried film (‘edge-on-rich device’) had a PCE = 0.240% with a J_{sc} = 1.65 mA cm^{−2}, a V_{oc} = 0.30 V, and an FF = 0.491. The PCEs were low due to the extremely small donor–acceptor interfacial area associated with the sharp and unmixed P3HT-PCBM interface; however, considering the molecular orientations of P3HT, photocurrent generation in the face-on-rich device was higher than that in the edge-on-rich device. V_{oc} was also slightly higher in the face-on-rich device than in the edge-on-rich device. The V_{oc} change due to molecular orientation has been well studied in previous papers and understood mainly as a result of the change in the highest occupied molecular orbital (HOMO) and CT state energy level of molecules as a consequence of its altered orientation^{11,13,16,25,26}. That is, the V_{oc} was higher when the P3HT molecules were oriented face-on than when they were oriented edge-on because the HOMO level of P3HT was deeper in the former case^{13,16}. For the thick P3HT layers (>25 nm), the PCE decreased as the P3HT layer thickness increased, possibly because the hole transit time through P3HT

Table 1 Photovoltaic parameters of orientation-controlled P3HT/PCBM bilayer devices and the devices with the common P3HT interfacial layer

	PCE [%]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF
P3HT (face-on-rich)/PCBM	0.387 (± 0.058)	2.38 (± 0.27)	0.32 (± 0.03)	0.518 (± 0.035)
P3HT (edge-on-rich)/PCBM	0.240 (± 0.026)	1.65 (± 0.19)	0.30 (± 0.02)	0.491 (± 0.021)
P3HT (face-on-rich)/P3HT (common)/PCBM	0.170 (± 0.014)	1.24 (± 0.10)	0.30 (± 0.01)	0.466 (± 0.006)
P3HT (edge-on-rich)/P3HT (common)/PCBM	0.160 (± 0.026)	1.25 (± 0.14)	0.29 (± 0.01)	0.437 (± 0.026)

increased, which increased bimolecular recombination (Figure S1, Table S1)²⁷. The face-on- and edge-on-dominant molecular orientation distributions of the fast- and slow-dried P3HT films remained unchanged at other thicknesses, although the width of the orientation distribution broadened slightly as the thickness increased (Figure S2). Devices prepared with very thin P3HT layers displayed a low reproducibility, and most devices suffered from severe leakage or short circuits in the anode and the cathode because the P3HT film was easily damaged during the transfer process. Therefore, most characterization was conducted using devices prepared with 25 nm thick films.

We postulated that the increased current generation in the face-on-rich device originated from an increase in the charge generation at the donor–acceptor interface. To test this idea, devices with a common interfacial layer (Fig. 4b, inset) were fabricated and compared. In these devices, a thin P3HT film (7 nm) was transferred onto the PCBM layer to form a common interfacial layer. This P3HT film was spin-coated from a P3HT solution dissolved in DCB (3 mg mL^{-1}) at a medium spin speed (2500 rpm) and had a preferentially edge-on molecular orientation distribution (Figure S3). The orientation-controlled P3HT films were then transferred onto the common P3HT layer. These devices featured fixed conditions near the donor–acceptor interface but retained the properties of the orientation-controlled P3HT layer throughout the donor layer. The J – V characteristics (Fig. 4b) of these devices were comparable. This result confirmed that the differences in the electrical characteristics of the devices (Fig. 4a) arose from the P3HT orientation at the donor–acceptor interface.

Optical properties of the orientation-controlled P3HT films

The high photocurrent generation in the face-on-rich device was explored as a function of several factors that could be affected by the molecular orientation of the P3HT layer. Changes in the molecular orientations of the donor material could conceivably change several factors, including the light absorption capability, exciton diffusion length, charge-carrier mobility, and charge-pair separation efficiency at the donor–acceptor interface. In this

study, we showed that the light absorption properties and charge-carrier transport were similar in both the face-on-rich and edge-on-rich P3HT films and could not account for the differences (Fig. 4a) between the devices in photocurrent levels.

The absorption spectra of the face-on-rich and edge-on-rich P3HT films in the UV–vis region were measured (Fig. 5a). The P3HT samples did not display new absorption peaks due to changes in the molecular orientations. The films showed only small differences in the vibronic shoulder peaks of P3HT at $\lambda = 550$ and 605 nm. Compared to the face-on-rich film, the edge-on-rich film had stronger vibronic peaks due to its higher crystallinity because the P3HT molecules were allowed to self-assemble over a longer period of time. The edge-on-rich film, therefore, had a slightly larger total absorption than the face-on-rich film, but the difference was not meaningful.

The PL quenching efficiency of each P3HT film was investigated to quantify the efficiency with which excitons diffusing through the P3HT film reached the P3HT/PCBM interface. PL spectral measurements were obtained from 25 nm thick P3HT films prepared on a quartz substrate. BCP and C_{60} were used as exciton blocking and quenching layers, respectively. The films were excited at $\lambda = 530$ nm, and steady-state PL spectra were recorded (Fig. 5b). As the blocking layer was replaced by the quenching layer, the PL intensities decreased to 37 and 47% of their initial values in the face-on-rich and edge-on-rich P3HT films, respectively. These results indicated that, compared to the edge-on-rich film, the face-on-rich P3HT film displayed improved exciton diffusion, so more excitons reached the donor–acceptor interface, giving a higher exciton quenching efficiency.

To understand why the exciton quenching efficiency was higher in the face-on-rich P3HT film, spectrally resolved PL quenching (SR-PLQ) experiments were conducted to directly extract the exciton diffusion length in the P3HT films. The SR-PLQ method is used to determine the relationship between the absorption coefficient α and the PL quenching ratio η , which is defined as the ratio between the PL intensities of the sample with an exciton blocking (PL_B) layer and an exciton quenching (PL_Q) layer

28,29;

$$\eta = \frac{PL_B}{PL_Q} = \alpha L_D + 1 \quad (1)$$

Here the exciton diffusion length L_D appears as the slope of η versus α . The P3HT films used in the measurement had a thickness of 130 nm, thick enough to satisfy the requirements for the application of Eq. 1. The edge-on-rich film yielded an $L_D = 5.8$ nm (Fig. 5c), and the face-on-rich film yielded $L_D = 11.1$ nm, in agreement with the values reported in previous reports³⁰. We hypothesized that this increase in L_D in the face-on-rich

film occurred because the face-on orientation featured a short π - π stacking distance that facilitated exciton diffusion in the vertical direction^{5,15}. Förster energy transfer, which describes singlet exciton diffusion in an organic semiconductor, defines L_D as inversely proportional to the square of the distance between chromophores³¹. GIWAXS data indicated that, in the direction perpendicular to the substrate, the lattice spacing of P3HT crystals in the face-on orientation was 3.81 Å ($q \sim 1.65$ Å⁻¹), which corresponded to the π - π stacking distance, and the lattice spacing of P3HT crystals in the edge-on orientation was 16.4 Å ($q \sim 0.384$ Å⁻¹), which corresponded to the lamellar stacking distance between side chains. This large difference in the chromophore distance may have increased the L_D in the face-on-rich P3HT film. The increased exciton diffusion, as a consequence, would have increased the photocurrent in the face-on-rich device.

Charge-carrier transport and nongeminate recombination in the orientation-controlled devices

Transport of free charge carriers in the orientation-controlled bilayer devices was investigated to determine how the molecular orientation and crystallinity of the P3HT films contribute to the photovoltaic performances by affecting the charge transport properties of the devices. If the molecular orientations and crystallinity affected the hole mobility (μ_h) of the P3HT film, the electron collection and hole collection efficiencies in the bilayer devices would change and affect the degree of nongeminate recombination and photocurrent generation. Therefore, we measured μ_h in the P3HT films and the nongeminate recombination dynamics in bilayer devices.

The values of μ_h in the P3HT films were quantified (Table S2) by measuring the SCLC of hole-only devices (ITO/PEDOT:PSS/P3HT/MoO₃/Au). SCLC measurement of charge mobility in the vertical direction revealed that the face-on-rich device had $\mu_h = 4.42 \times 10^{-6}$ cm² V⁻¹ s⁻¹ and that the edge-on-rich device had $\mu_h = 5.58 \times 10^{-6}$ cm² V⁻¹ s⁻¹ (Figure S4). The similarity in μ_h values despite the differences in crystallinity may have resulted from the face-on orientation of the P3HT molecules in the face-on-rich device, which facilitated vertical charge transport³².

The similar μ_h values measured in the two P3HT films suggested that nongeminate recombination losses were also similar in the face-on-rich and edge-on-rich devices. The degree of nongeminate recombination was measured by quantifying the effect of the light intensity on the photocurrent in the devices. The magnitude of the photocurrent in the OSCs as a function of the incident light power could be expressed as $J_{ph} \sim (P_{in})^\beta$, where J_{ph} is the photocurrent density, defined as the difference between the current densities under illumination and in darkness; P_{in} is the power of the incident light; and β is a scaling

exponent. $\beta \approx 1$ indicates negligible nongeminate recombination, whereas $\beta < 1$ indicates some extent of nongeminate recombination in the device. In the case of severe nongeminate recombination with space charge accumulation, β approaches 0.75, and J_{ph} varies as the square root of the effective applied voltage ($V_{eff} = V_0 - V$, where V_0 is the voltage at $J_{ph} = 0$ and V is the applied voltage) in the device operating voltage range^{33,34}. In the experiments, the face-on-rich device had a $\beta = 0.98$ under short-circuit conditions and $\beta = 0.93$ at $V_{eff} = 0.1$ V. The edge-on-rich device had a $\beta = 0.99$ under short-circuit conditions and $\beta = 0.95$ at $V_{eff} = 0.1$ V (Fig. 6a). The devices did not show space-charge-limited behavior. The similarities between the values indicated that the nongeminate recombination losses in the face-on-rich and edge-on-rich devices were similar.

Nongeminate recombination in the devices was further investigated using TPV decay measurements. The TPV decay signals were measured by perturbing the solar cell devices with a laser pulse ($\lambda = 532$ nm) under 1 sun (AM1.5) background illumination (Fig. 6b). The lifetime (τ_c) of the charge carriers generated by this small laser perturbation was calculated by fitting the photovoltage decay to a mono-exponential function. This lifetime represented the extent of nongeminate recombination among free charge carriers during device operation^{15,35–37}. The face-on-rich and edge-on-rich devices had very similar τ_c values (23.4 and 22.9 μs , respectively), i.e., they had nearly the same degree of nongeminate recombination.

We determined that the P3HT orientation minimally affected the light absorption and charge transport properties of our devices, although the orientation did affect exciton diffusion and therefore photocurrent generation in the devices. Another factor that could affect the orientation-dependent photocurrent generation was charge separation at the donor–acceptor interface.

Charge separation dynamics at the orientation-controlled donor–acceptor interfaces

Charge separation at the orientation-controlled P3HT-PCBM interface was investigated using TA analyses to observe the decay dynamics of the excited species. The samples were excited with a pump beam at $\lambda = 530$ nm and probed at $550 \leq \lambda \leq 810$ nm on a timescale of 1–1000 ps. Low excitation fluence ($\sim 2 \mu J cm^{-2}$) was chosen to avoid the emergence of unwanted processes such as exciton–exciton annihilation^{38,39}.

We assumed that free charge carriers were predominantly produced via a single pathway involving the lowest-lying CT state. The current consensus is that excitons that reach a donor–acceptor interface form interfacial CT states via electron transfer, in which the electrons and holes are partially separated but are still bound to one another by significant coulombic interactions⁴⁰. This CT state can be separated into free charge carriers that contribute to photocurrent generation or recombine to the ground state resulting in charge carrier loss. Recombination loss of the CT states is called geminate recombination loss. Some authors have proposed that some of the free charge carriers can be generated from “hot” CT states on the ultrafast timescale and are not affected by competition between separation and recombination on the picosecond–nanosecond timescales^{38,41–44}. The excess energy in the high-energy CT states appeared to overcome the coulombic interactions, enabling the immediate formation of free charges. More recent studies, however, have revealed that the excess energy is not necessary for efficient charge generation^{43–47}, i.e., the loss of the excess energy by thermal relaxation of the hot CT states is so fast that the excess

energy cannot increase the charge carrier yield. The most important state is, therefore, the lowest-lying CT state because all CT states with a higher energy pass through the lowest-lying state due to ultrafast relaxation^{45,46}. Therefore, in this study, we assumed that free charge carriers were generated from a single CT state, in competition with geminate recombination to the ground state.

The TA spectra (Fig. 7 and S5) were obtained from samples prepared using orientation-controlled single-layer P3HT films (70 nm thick) and P3HT/PCBM bilayers (25 nm/30 nm, the same as the device fabrication conditions) prepared on quartz substrates. The spectral shape was consistent with several previous reports of TA signals in P3HT–PCBM systems^{38,39,48–50}. In the literature, the negative signals at approximately $550 \leq \lambda \leq 600$ nm are well established to be attributable to photobleaching of the ground state of P3HT, indicating that excited species such as excitons and P3HT hole polarons were generated. The broad absorption bands at $700 \leq \lambda \leq 810$ nm corresponded to the photoinduced absorption (PIA) of the P3HT polarons. More specifically, the PIA of the P3HT hole polarons appeared over a broad wavelength range of $700 \leq \lambda \leq 1000$ nm, which includes the absorption bands at 700 and 1000 nm, corresponding to the PIAs of free hole polarons (i.e., free charges), and the band at ~ 800 nm, corresponding to the PIA of the hole polarons bound to PCBM anions (i.e., CT states). The instrumental detection limit allowed us to obtain only PIA signals up to ~ 810 nm. Finally, the pronounced peak at $\lambda \sim 650$ nm, which decayed rapidly over time, was attributed to the polaron pairs of the P3HT cation and anion formed within the P3HT films^{48,49}. Note that the photobleaching signal at $\lambda \sim 600$ nm was more pronounced in the edge-on-rich films than in the face-on-rich films. This result confirmed again that the edge-on-rich films had a higher crystallinity than the face-on-rich films. In the absence of a PCBM layer (Figure S5), the polaron PIA bands at $610 \leq \lambda \leq 810$ nm decayed completely within 1 ns, and we concluded that only a negligible amount of long-lived free charge carriers were generated without the PCBM. By contrast, in the bilayer samples (Fig. 7a, b), the polaron PIA bands persisted until 1 ns. These observations indicated that long-lived free charge carriers formed via the separation of CT states.

Charge separation was quantified by analyzing the decay kinetics of the polaron PIA bands (Fig. 7c). The decay profile was observed at $750 \leq \lambda \leq 810$ nm, where the broad PIAs of the CT states and of the free charges overlapped. In this wavelength range, the molar absorption coefficients of the CT states and the free charges were the same; therefore, the total PIA signal intensity was simply proportional to the sum of the concentrations of the CT

Fig. 7 TA analysis of P3HT/PCBM bilayer samples with controlled P3HT orientation. **a, b** TA spectra of P3HT/PCBM bilayer samples. **a**: sample with the face-on-rich P3HT film; **b**: sample with edge-on-rich P3HT film. **c** Decay profiles of the TA signal of P3HT/PCBM bilayer samples with face-on-rich or edge-on-rich P3HT films at $750 \leq \lambda \leq 810$ nm. Solid lines: experimental data; dot-dashed lines: curves fitted using Eq. 4

states and free charges^{38,51}. A simple model suggested by Massip et al. was then used to analyze the decay kinetics⁵². This model considered the situation in which the free charges were generated by separation of the CT states as the remaining nondissociated CT states recombined to the ground state. Nongeminate recombination of the free charges was neglected because the model considered the 1–1000 ps timescale, which was too short for nongeminate recombination to occur. This model considered exactly the same situation that we considered and therefore was applied in our analyses without modification. According to the kinetic model, the concentrations of the

Table 2 Extracted values of kinetic modeling parameters (Eq. 4) obtained by fitting the decay profiles in Fig. 7c

	k_s [10^9 s^{-1}]	k_r [10^9 s^{-1}]	$k_s/(k_s+k_r)$
P3HT (face-on-rich)/PCBM	6.62	5.33	0.554
P3HT (edge-on-rich)/PCBM	8.89	13.1	0.404

CT states and free charges could be written as follows:

$$\frac{d[CT]}{dt} = -(k_s + k_r)[CT] \quad (2)$$

$$\frac{d[FC]}{dt} = k_s[CT] \quad (3)$$

where [CT] is the concentration of the CT states, [FC] is the concentration of the free charges, k_s is the separation rate constant, and k_r is the geminate recombination rate constant. Solving these rate laws yields the total PIA intensity:

$$S(t) \sim e^{-(k_s+k_r)t} + \frac{k_s}{k_s+k_r} \left(1 - e^{-(k_s+k_r)t}\right) \quad (4)$$

where the first and second terms in the right-hand side correspond to [CT] and [FC], respectively. Equation 4 was used to fit the decay profile (Fig. 7c) and extract the separation and recombination rate constants (Table 2).

The remaining PIA signal at 1 ns was higher in the face-on-rich device than in the edge-on-rich device (Fig. 7c). This difference indicated that the face-on-rich device had more long-lived free charges than the edge-on-rich device and could be understood from the results of the kinetic model. That is, the larger quantity of free charges produced in the face-on-rich device arose from the strong decrease in the recombination rate of the CT states. As a result, the CT state separation efficiency, $k_s/(k_s+k_r)$, was higher in the face-on-rich device (0.554) than in the edge-on-rich device (0.404), and the yield of the long-lived free charges was higher in the former case than in the latter. These results indicated that free charge generation was more efficient among the face-on-oriented P3HT molecules at the donor–acceptor interface than among the edge-on-oriented P3HT molecules.

The physical origin of the increased charge separation at the face-on-oriented donor–acceptor interface is discussed in the literature. The most critical factor influencing the molecular orientation-dependent charge separation is the electronic coupling between the electronic states. Marcus theory, which is frequently used to evaluate the rates of charge separation and recombination, predicts that the rate of CT depends significantly on the strength of the electronic coupling between the involved

electronic states^{3,5,53}. Electronic coupling varies with the relative orientations of the donor and acceptor molecules and is improved in the face-on configuration due to the improved orbital overlap between the donor and acceptor^{3,5–7,9,10}. The electronic coupling calculated as a function of the angle between ZnPc and C₆₀ molecules has been reported⁵. Calculated electronic couplings of charge separation and recombination varied with the angle. As a result, the overall charge separation yields differed. Our experimental observation of an increased charge separation efficiency in the face-on donor–acceptor configuration may occur for a similar reason, i.e., as a result of changes in the electronic couplings of the charge separation and recombination via the molecular orientations.

Even though most of the studies on molecular orientation-dependent charge separation observed higher charge separation efficiency at the face-on-oriented donor–acceptor interface than at the edge-on-oriented interface, opposing results were also reported very recently¹¹. Interestingly, the results showed that the edge-on-oriented interface was more efficient at charge generation and had smaller activation energy for charge generation than the face-on-oriented interface. The small activation energy of the edge-on interface for charge generation was attributed to weak electronic coupling between the CT and ground states and the concomitant reduction in geminate recombination.

These opposing results (whether the face-on orientation is superior or not) look controversial. However, both of them are understandable considering that the efficiency of charge generation is determined by the relative magnitude of charge separation rate and geminate recombination rate. The electronic coupling between the CT state and charge-separated state affects the charge separation rate, and at the same time, the electronic coupling between the CT states and ground state affects the geminate recombination rate. Therefore, change in interfacial molecular orientation can lead to changes in both electronic couplings and consequently the ratio between charge separation and recombination rates. Whether this ratio is higher in face-on configuration or higher in edge-on configuration is expected to be dependent on the electronic nature of donor–acceptor material sets. Generalized explanations of why the face-on configurations typically exhibit improved charge generation in terms of electronic coupling is beyond the scope of this paper.

Calculations on the long-range electrostatic interactions across the donor–acceptor interface also support the enhanced charge separation at the face-on-oriented donor–acceptor interface²⁵. The calculations demonstrated that the electrostatic potential resulting from the superposition of quadrupolar fields across the donor–acceptor interface could assist or hinder charge

separation depending on the molecular orientation. The face-on donor–acceptor configuration yielded electrostatic force that pushed holes toward the donor and electrons toward the acceptor, which drove charge separation process. In contrast, the direction of the electrostatic force was reversed in the edge-on donor–acceptor configuration, and therefore, trapping and recombination of charge carriers became probable in the edge-on-oriented donor–acceptor interface.

Another viewpoint on the enhanced charge separation at the face-on-oriented donor–acceptor interface considers the stronger delocalization of charges at the face-on interface than that at the edge-on interface. Previous calculations suggested that the holes were more strongly delocalized at the donor in the face-on donor–acceptor configuration than in the edge-on orientation and that the center of the hole density was forced to migrate away from the donor–acceptor interface⁵⁴. This process led to a significant increase in the electron–hole separation distance, which reduced charge pair recombination at the face-on donor–acceptor interface.

The dependence of the CT state energy on the molecular orientation could also have affected the charge separation efficiency. The HOMO and CT state energy levels of an organic semiconducting material can vary with the molecular orientation^{4,11,13,25,26,54,55}. Marcus theory predicts that the energy difference between the electronic states can affect the CT rate. As a result, variations in the CT state energy level accompanied by changes in the molecular orientations could affect the charge separation efficiency; however, the contributions from the energy level of the CT state were considered to be small in our experiments because the change in CT state energy level was not expected to be large enough (~0.02 eV) to cause a meaningful change in the electron transfer rates. The estimate of the CT energy level difference was based on a rough approximation, that V_{oc} in a solar cell device is proportional to the CT state energy, as is generally accepted⁵⁶.

One might think that the charge separation at the donor–acceptor interface in our experiments would also be affected by the crystallinities of the face-on-rich and edge-on-rich P3HT films. Indeed, a high crystallinity in a material at a donor–acceptor interface is beneficial for charge separation and free charge generation due to its effects on the interfacial energetics, charge delocalization, and local charge-carrier mobility^{43,44,57–59}; however, our results revealed more efficient charge separation in the face-on-rich device, although it had a lower P3HT crystallinity than the edge-on-rich device. These results again emphasized the important influence of the optimal molecular orientation at the donor–acceptor interface on efficient charge separation and free charge generation.

Conclusion

The effects of the relative orientations of the donor and acceptor molecules on photocurrent generation were systematically investigated with a focus on the photo-physical processes at the donor–acceptor interface. The drying kinetics of the polymer thin film were controlled, and a nondestructive film transfer method was used to construct bilayer devices with well-controlled molecular orientation and sharp donor–acceptor interfaces. In the devices, the light absorption and charge transport properties were comparable despite differences in the molecular orientations; therefore, the processes involved in charge generation at the donor–acceptor interfaces could be studied in isolation. Our analysis revealed that photocurrent generation was significantly higher when the donor polymer was oriented face-on at the donor–acceptor interface than when it was oriented edge-on. This difference was primarily due to efficient exciton diffusion toward the interface and efficient charge separation to free charge carriers.

It should be noted that the findings from this study may be limited to a certain class of photovoltaic materials. For example, many highly performing donor polymers are quite different from P3HT in many aspects, such as molecular structure and morphology, and this difference may affect the orientation effects. Nevertheless, our systematic study clearly demonstrates that the molecular orientation at the donor–acceptor interface is an important morphological factor that should be controlled to achieve high-performance OSCs.

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Conflict of interest

The authors declare that they have no conflict of interest.

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