

Exciton Harvesting in Ternary Blend Polymer Solar Cells

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Chapter 1

General Introduction

1.1. Background and Motivation

The sun is a stable and inexhaustible source of renewable energy. The annual energy input of solar irradiation on the earth exceeds the world's yearly energy consumption by several thousand times, and thus harvesting energy directly from sunlight using photovoltaic (PV) technology is considered as one of the most important ways to address the growing world-wide energy crisis.^[1,2] Now, most commercialized solar cells are based on silicon and other inorganic semiconductor materials. However, the high cost and complex production processes of these inorganic solar cells have limited their widespread utilization. On the other hand, organic solar cells have recently been attracting more and more attention as a next generation solar cell because of their advantages of low cost, lightweight, and flexibility.^[3-5] The power conversion efficiency (PCE) of organic solar cells has been improved steadily and exceeded 10% very recently.^[6-11] Further improvements up to 15% or higher are desired as a potential alternative to inorganic solar cells.^[12]

1.1.1. Organic Solar Cells

Organic solar cells based on a conjugated polymer and a fullerene derivative have great potential as a sustainable energy source because of their unique advantages such as high-throughput and large-area production with low-cost printing techniques.^[13] Most organic solar cells typically employ a bulk heterojunction photoactive layer, where

phase-separated interpenetrating networks of electron donating and accepting materials are formed on a scale of tens of nanometers to provide large donor/acceptor interface enough for efficient exciton dissociation and continuous pathways for efficient charge transport. The fundamental processes of photovoltaic conversion in the photoactive layer of organic solar cells can be classified into the following five key steps as shown in Figure 1-1: 1) photon absorption in the active layer to generate an exciton (η_A), which mainly depends on the strength and width of the absorption bands of the photoactive materials, 2) exciton diffusion to a donor/acceptor interface (η_{ED}), 3) charge transfer at the donor/acceptor interface (η_{CT}), 4) charge dissociation into free charge carriers (η_{CD}), and 5) charge carrier collection to each electrode (η_{CC}). The product of these five step efficiencies corresponds to the external quantum efficiency (EQE), and integration of the EQE over the whole solar spectrum gives to a short-circuit current density (J_{SC}), which is one of three critical parameters for solar cells, along with an open-circuit voltage (V_{OC}) and a fill factor (FF). The product of the three parameters (J_{SC} , V_{OC} , and FF) gives power conversion efficiency (PCE), which is an important measure of the overall performance of organic solar cells.

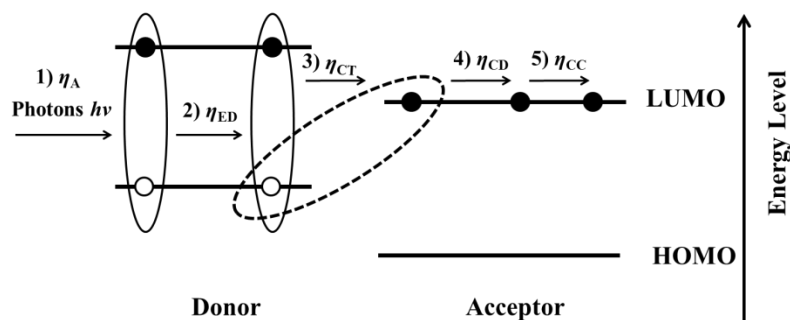


Figure 1-1. Schematic illustration of photovoltaic conversion processes in polymer solar cells: 1) photon absorption (η_A), 2) exciton diffusion (η_{ED}), 3) charge transfer (η_{CT}), 4) charge dissociation (η_{CD}), and 5) charge collection (η_{CC}).

In the past few years, the PCE of organic solar cells has been improved considerably, but it is still lower than that of inorganic solar cells. One of the most important reasons is the mismatch between absorption band of the photoactive layers and the terrestrial solar radiation. For example, poly(3-hexylthiophene) (P3HT) as a benchmark polymer exhibits a large absorption band in the visible region from 400 to 600 nm, but no absorption band in the near-infrared (IR) region. As a result, the J_{SC} of organic solar cells based on a blend of P3HT and a fullerene derivative (PCBM) is usually limited to 12 mA cm^{-2} , even though the EQE is as high as 80%.^[14–16] Subsequently, various low-bandgap polymers have been intensively designed and synthesized to harvest more photons in the near-IR region and hence to increase J_{SC} further.^[17–28] For example, a low-bandgap polymer, poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-*b*:2'3'-*d*]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT), shows a large absorption band in the near-IR range up to 800 nm and the J_{SC} of organic solar cells based on PSBTBT and PCBM is as high as 16.4 mA cm^{-2} .^[27] However, there is still significant room for improving the photovoltaic performances furthermore. It is noteworthy that although these low-bandgap polymers like PSBTBT exhibit a large absorption band in the near-IR range, at the same time, they also exhibit an absorption window in the visible range. In other words, it is difficult to harvest photons effectively from visible to near-IR range with a single conjugated polymer.

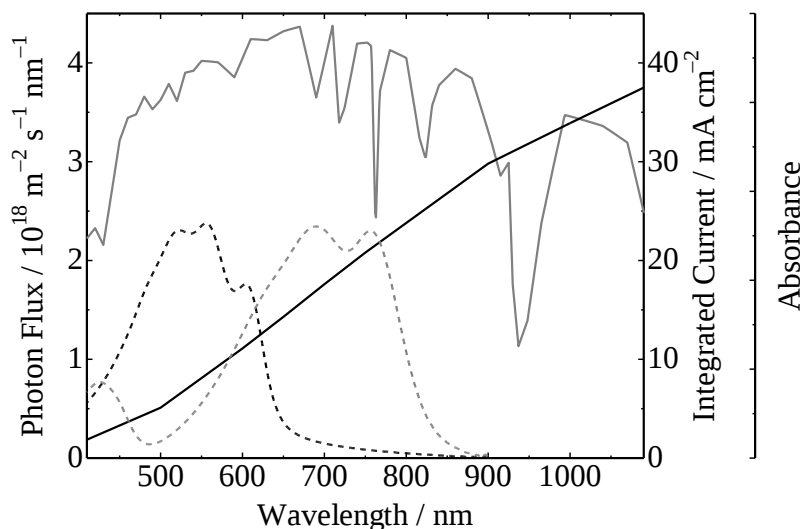


Figure 1-2. Photon flux of the sun light (AM1.5G) plotted against wavelength (gray line). The integrated current density is calculated from the number of absorbed photons (black line). The absorption spectra of P3HT (black broken line) and PSBTBT (gray broken line) neat films.

Organic tandem solar cells are an alternative way to harvest more photons in the solar light effectively, which consist of two or more single cells with complementary absorption bands, and therefore can harvest a greater part of the solar spectrum compared with single junction organic solar cells.^[29–31] Furthermore, this tandem structure has a reduced voltage loss during the photon-to-electron conversion processes. For a series connection of two cells, the V_{OC} in tandem cells is equal to the sum of the V_{OC} of the individual two subcells. Recently, Brabec et al. predicted that a PCE of 15% can be achieved for organic tandem solar cells, which is about 1.4 times the maximum efficiency ($\sim 11\%$) forecasted for single junction organic solar cells.^[32] However, organic tandem solar cells are still a challenging issue. Firstly, the photocurrent generated in the top cell should be the same as that in the bottom cell because the overall photocurrent is limited to that in the lower current cell in a series

connection. Recent studies have shown that optical simulation is useful for designing tandem device structures because it can predict the charge generation yield in the individual subcells by considering the optical interference effects.^[33] Note that it is still difficult to realize the current matching in the case of different charge transport in the individual subcells. Secondly, as shown in Figure 1-3, one must carefully design and optimize a charge recombination (interlayer) electrode in between the two subcells in addition to two charge-collecting electrodes.^[34,35] The interlayer should meet the following required conditions at the same time: 1) it should efficiently collect electrons from one subcell and holes from another subcell; and 2) it should serve as an efficient recombination zone free from potential loss for the collected electrons and holes. Unfortunately, inefficient interlayers often cause potential losses, resulting in smaller V_{OC} of the tandem solar cells than the sum of V_{OC} of each subcell.^[31] Thirdly, all solution-processed organic tandem solar cells are most desired in terms of production cost, but still technically challenging issue. This is mainly because layer-by-layer solution production might dissolve or damage underlying photoactive layers. Therefore, protective interlayers have been intensively developed. In summary, as mentioned above, enormous efforts have been devoted to developments of tandem solar cells, but there have been only a few successful reports on highly efficient organic tandem solar cells.^[9,36] Consequently, it would be desirable to develop alternative approach to harvest much more photons effectively in a simple way as described below.

Recently, organic ternary solar cells have been proposed as a more simple and versatile alternative approach in realizing a broad solar photon capture range by incorporation of near-IR sensitizers into the host system consisting of a wide-bandgap polymer blended with a fullerene derivative.^[37–53] Honda et al. reported efficient ternary solar cells incorporating a near-IR dye molecule silicon phthalocyanine derivative (SiPc) into P3HT/PCBM binary blends, the J_{SC} increased from 6.5 to 7.9 mA cm⁻², and the PCE was improved from 2.2 to 2.7%.^[41] Of particular interest is that with introduction of SiPc, the EQE is enhanced not only at the SiPc absorption band from 650 to 700 nm in the near-IR range but also at the P3HT absorption band from 400 to 600 nm in the visible range. This finding indicates that P3HT excitons can be dissociated into charge carriers more efficiently in the presence of SiPc molecules. This is because of long-range Förster energy transfer from P3HT to SiPc, which can collect P3HT excitons that could not reach the interface only by repetition of short-range excitation energy hoppings.^[47] In order to harvest more photons in the near-IR region, multi-colored dye sensitization has been demonstrated: two different dyes with complementary absorption bands in the near-IR region, SiPc and silicon naphthalocyanine bis(trihexylsilyl oxide) (SiNc) were incorporated into the P3HT/PCBM binary blends.^[44] The photocurrent increased by about 10% in the individual ternary blend solar cells and interestingly increased by about 20% in the quaternary blend solar cells, and the PCE was enhanced from 3.5 to 4.3%. Although the photovoltaic performances were improved obviously, it could be improved further by using light-harvesting materials with a wider absorption bandwidth like low-bandgap polymers.

Ternary blend solar cells with two donor polymers and a fullerene have been

reported by Koppe et al.^[43] They employed a wide-bandgap polymer P3HT, a low-bandgap polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), as a near-IR sensitizer, and PCBM. A photoinduced absorption (PIA) study has shown that charge transfer is the dominant sensitization mechanism in the ternary blend because of the appropriate energy levels in the HOMO and LUMO levels of P3HT, PCPDTBT, and PCBM while energy transfer from P3HT to PCPDTBT is negligible in spite of a large spectral overlap between the P3HT fluorescence and the PCPDTBT absorption. By addition of 10 wt% PCPDTBT into P3HT/PCBM blends, the PCE was improved from 2.5 to 2.8% because the low-bandgap polymer PCPDTBT contributed to photocurrent generation. However, when a weight ratio of PCPDTBT exceeded 10 wt%, a depressing drop in FF degraded the overall photovoltaic efficiency of the ternary solar cells. In the following study, they fabricated P3HT/PSBTBT/PCBM ternary solar cells by replacing the low-bandgap polymer PCPDTBT with PSBTBT.^[48] As a result, the J_{SC} linearly increased from 8.6 to 13 mA cm⁻², and hence the PCE increased from 3.1 to 4.0% with increasing fraction of PSBTBT up to 35 wt%. However, the PCE of the ternary blend solar cells was still lower than that of binary solar cells based on PSBTBT/PCBM. This is partly because with increasing fraction of PSBTBT, the photocurrent in the near-IR region increased but the photocurrent in the visible region decreased at the same time because P3HT fraction decreased obviously. In addition, FF also decreased at high fractions of PSBTBT, indicating that the charge transport would be degraded. In other words, there is still room for improvement of the photovoltaic performance of such ternary blend solar cells with two donor polymers and PCBM acceptor.

1.1.3. Exciton Harvesting by Exciton Diffusion and Transfer

Exciton diffusion is of great importance in the development of highly efficient polymer solar cells.^[54] Excitons are coulombically bound electron-hole pairs with a large binding energy that are generated mainly in conjugated polymers upon the photon absorption, and have to be dissociated into free charge carriers to generate photocurrent. Such charge dissociation is possible only at an interface with an electron-accepting material such as PCBM through charge transfer.^[55] Thus, excitons should reach the interface of polymer/fullerene to generate charge carriers. The exciton diffusion length (L_D) is considered to be the distance that excitons can diffuse before deactivating to the ground state, which is given by $L_D = \sqrt{D\tau}$ where D is the diffusion constant and τ is the exciton lifetime. Because of their short lifetime, the diffusion length of excitons in most conjugated polymers is typically less than 20 nm,^[56–60] which is much shorter than the optical absorption path length. On the other hand, phase-separated domain size should be comparable to the exciton diffusion length on a scale of tens of nanometers. However, such intimate mixing of donor and acceptor materials would be undesirable for efficient charge transport. Therefore, the key issue is to increase the exciton diffusion length for developing highly efficient polymer solar cells.

Energy transfer is long-range transport of excitation energy, which would be available for improving exciton harvesting efficiency in organic solar cells.^[61–64] This is because energy transfer has several advantages over exciton diffusion. First, exciton harvesting by energy transfer is long-range transport compared to exciton hoppings. Second, it is not random walk but vectorial transport to an energy-accepting site. Thus, excitons can be harvested to appropriate sites if energy-accepting materials are located there: for example excitons can be collected to heterojunction in blend films.

For efficient energy transfer from a donor to an acceptor, the following requirements should be satisfied: 1) the energy of donor excited state should be higher than that of the acceptor excited state and 2) the rate of energy transfer should be more rapid than the decay rate of the donor excited state. The rate of Förster transfer based on dipole–dipole interaction is given by

$$k_f(d) = \frac{1}{\tau} \left(\frac{R_0}{d} \right)^6 \quad (1-1)$$

where τ is the measured exciton lifetime, R_0 is the Förster radius of energy transfer, and d is the donor–acceptor separation distance. The Förster radius R_0 is given by

$$R_0^6 = \frac{9000\kappa^2(\ln 10)\eta_D}{128\pi^5 n^4 N_A} \int f_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4} \quad (1-2)$$

where κ is the orientation factor, c is the speed of light in vacuum, η_D is the fluorescence quantum yield of the donor in the absence of the acceptor, n is the refractive index of the medium, N_A is the Avogadro's number, f_D is the normalized donor fluorescence spectrum, ε_A is the molar absorption coefficient of the acceptor, and $\tilde{\nu}$ is the wavenumber. Consequently, there should be larger overlap between the fluorescence spectrum of the donor and the absorption spectrum of the acceptor to obtain the faster energy transfer rate.

Efficient long-range energy transfer has been demonstrated in bilayer films of a highly efficient red-emitting polymer, DOW Red, as an energy donor and a highly absorptive low-bandgap polymer, poly(*N*-hexadecan-2-yloxy carbonyl-2,5-bis(2'-thienyl)-pyrrole-2,1,3-benzothiadiazole) (PTPTB), as an energy acceptor.^[62] The exciton diffusion length in DOW Red is estimated to be as short as 3 nm. On the other hand, the effective diffusion length is increased from 3 to 27 nm because of the energy transfer from DOW Red to PTPTB. Although there are no reports on efficient

energy transfer in ternary blends based on two different bandgap polymers and PCBM at this moment, excitons in wide-bandgap donor polymers could be harvested much more efficiently by using the energy transfer from a wide-bandgap donor to low-bandgap donor polymer. In other words, the low-bandgap donor polymer would serve not only as a photosensitizer but also as an energy transport funnel in ternary blend solar cells.

1.2. Outline of This Thesis

The main aim of this thesis is to design ternary blend photoactive layers for organic solar cells and investigate their sensitization mechanism. This thesis consists of six chapters. The historical background and the motivation of this thesis are summarized in Chapter 1. In the other five chapters, the exciton harvesting in polymer solar cells is studied as follows.

In Chapter 2, a new cross-linkable fullerene derivative (bis-PCBVB) has been synthesized by functionalizing [6,6]-diphenyl- C_{60} -bis(butyric acid methyl ester) (bis-PCBM) with two styryl groups to obtain a smooth and solvent-resistant film (p-PCBVB). The p-PCBVB film was characterized by UV–visible absorption, atomic force microscopy, and photoelectron yield spectroscopy, which revealed that the p-PCBVB film can be used as a well-defined donor/acceptor bilayer model system for the accurate determination of exciton diffusion length. With the bilayer model system, the exciton diffusion length and diffusion coefficient of poly[2,7-(9,9-didodecylfluorene)-*alt*-5,5-(4',7'-bis(2-thienyl)-2',1',3'-benzothiadiazole)] (PF12TBT) were evaluated to be $L_D = 11$ nm and $D = 9.8 \times 10^{-4}$ cm² s⁻¹, respectively.

In Chapter 3, the effective diffusion length in P3HT has been evaluated by using donor/acceptor bilayers with two different exciton-quenching acceptors. One is an insoluble p-PCBVB, which is an efficient electron-accepting material with negligible absorption in the visible region. The other is a low-bandgap polymer PSBTBT. This polymer has a large absorption band in the near-IR region, which is well overlapped with the emission band of P3HT. The effective diffusion length of P3HT excitons was evaluated to be 15 nm for P3HT/p-PCBVB bilayers and improved to 30 nm for P3HT/PSBTBT bilayers. This improvement is ascribed to long-range energy transfer from P3HT to PSBTBT. This finding suggests that effective diffusion length of P3HT excitons can be increased through long-range energy transfer by incorporating PSBTBT to P3HT/PCBM blends.

In Chapter 4, highly efficient ternary blend solar cells have been fabricated with a wide-bandgap crystalline polymer P3HT, a low-bandgap polymer PSBTBT, and a fullerene derivative PCBM to obtain a good balance between charge generation and charge transport. By using highly crystalline P3HT, high FF was obtained even for ternary blend solar cells, suggesting efficient charge transport due to large P3HT crystalline domains. In such large crystalline domains, some P3HT excitons could not diffuse into the interface to PCBM but can be collected to PSBTBT domains by efficient energy transfer because of large spectral overlap between the P3HT fluorescence and the PSBTBT absorption. Consequently, all the P3HT excitons can contribute to the photocurrent generation at the P3HT/PCBM interface and/or PSBTBT domains mixed with PCBM in the ternary blends. As a result, P3HT/PSBTBT/PCBM ternary blend solar cells exhibited a power conversion efficiency of 5.6%, which is even higher than both individual binary devices of

P3HT/PCBM and PSBTBT/PCBM.

In Chapter 5, a low-bandgap small molecule 7,7'-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole), p-DTS(FBTTh₂)₂, has been incorporated into P3HT/PCBM to improve the charge generation in the near-IR range. With addition of a low concentration of p-DTS(FBTTh₂)₂, the J_{SC} raised significantly and hence the overall PCE increased by more than 20% compared with binary device P3HT/PCBM.

In Chapter 6, ternary blend solar cells have been designed by incorporating a wide-bandgap molecule, tris[4-(5-dicyanomethylidenemethyl-2-thienyl)phenyl]amine (TDCV-TPA), into a low-bandgap polymer, poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-*alt*-thiophene-2,5-diyl] (PTQ1), and a fullerene derivate PCBM binary blends to enhance exciton generation and hence charge generation in the visible region. The ternary blend solar cells exhibited large EQE in the visible range as well as in the near-IR range. As a result, the J_{SC} was improved by more than 20%. The sensitization mechanism of this ternary blend was discussed in terms of dye location.

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Chapter 2

Measurement of Exciton Diffusion in a Well- Defined Donor/Acceptor Heterojunction Based on a Conjugated Polymer and Cross-Linked Fullerene Derivative

2.1. Introduction

Conjugated polymers have great potential for application in organic solar cells because of their efficient light absorption and excellent charge transport properties, combined with simple solution-based processing and inherently low cost manufacturing.^[1,2] The most widely studied polymer-based solar cells have a bulk-heterojunction photovoltaic layer in which an electron donor polymer is mixed with a fullerene-based acceptor.^[2,3] For polymer-based organic solar cells, the diffusion of singlet excitons to the heterojunction is a very important step because excitons of polymers have to diffuse to the interface with the fullerenes only where they can be dissociated into free charge carriers by breaking the strong Coulombic binding energy between an electron-hole pair in them.^[4-6] However, in most conjugated polymers, singlet excitons can diffuse only a short distance during their short lifetimes.^[7] Therefore, the size of the phase-separated polymer domain size in bulk-heterojunction structures should be comparable to a diffusion length of the

excitons. Consequently, it is important to measure the exciton diffusion length accurately to guide optimization of both the structure and morphology of the photovoltaic layers.

To date, the exciton diffusion length L_D in conjugated polymers has been evaluated by several methods,^[7] including exciton-exciton annihilation,^[8–10] the photovoltaic response of solar cells,^[11–13] microwave conductivity,^[14] and steady-state or time-resolved photoluminescence (PL) quenching measurements.^[15–23] Among these, one of the most popular methods is the steady-state PL quenching measurements on a bilayer system consisting of a conjugated polymer as electron donor and an electron-accepting material. In particular, the steady-state PL quenching technique is simple and versatile method because it does not need the high temporal resolution and/or high excitation intensity required for time-resolved PL quenching and exciton-exciton annihilation measurements.^[15–17] In this method, the L_D can be directly evaluated from the dependence of the steady-state PL quenching efficiency on the polymer donor-layer thickness.

For the measurement of steady-state PL quenching in bilayer systems, the donor/acceptor interface forming the planar heterojunction should be flat and smooth, and efficient short-range quenching of excitons via interfacial electron transfer is desirable. Fullerene (C_{60}) and its derivatives such as [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) are suitable materials for use as an electron-accepting quenching layer, because of ultrafast electron transfer at the interface with the conjugated polymers and small absorption in the visible region.^[24–26] Therefore, a C_{60} has been employed as a quenching layer in a donor/acceptor bilayer to evaluate L_D of donor polymers. However, recent studies have shown that low-molecular-weight fullerenes are likely to

diffuse into the polymer layers even at room temperature, resulting in the loss of the defined donor/acceptor interface.^[27–31] Thus, L_D would be overestimated in such intermixing quasi-bilayer systems.^[19]

Such diffusion of small molecules can be effectively suppressed by cross-linking of the material. This is also beneficial for designing well-defined multilayer structures because it can make thin films solvent-resistant.^[32,33] In this chapter, a thermally cross-linkable fullerene derivative was synthesized by introducing two styryl groups (bis-PCBVB, Scheme 2-1). The advantage of the styryl group is that it can be easily polymerized in the solid state even at a low temperature.^[34–38] With a well-defined bilayer based on the cross-linked bis-PCBVB, the exciton diffusion length and exciton diffusion coefficient of poly[2,7-(9,9-didodecylfluorene)-*alt*-5,5-(4',7'-bis(2-thienyl)-2',1',3'-benzothiadiazole)] (PF12TBT, Figure 2-1) were evaluated.

2.2. Experimental

2.2.1 Materials

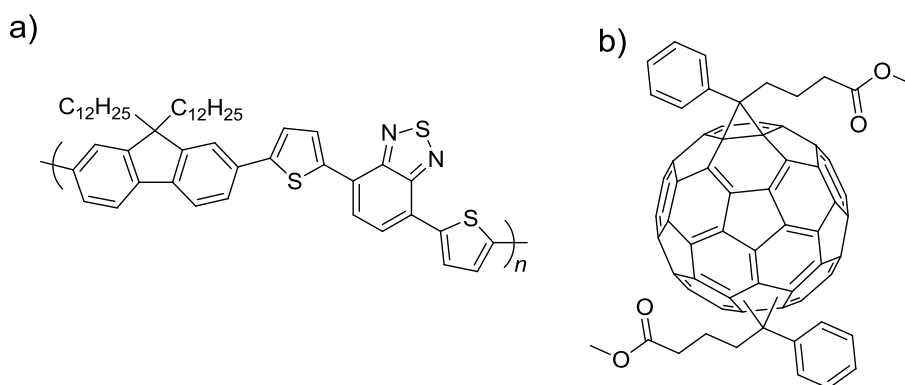
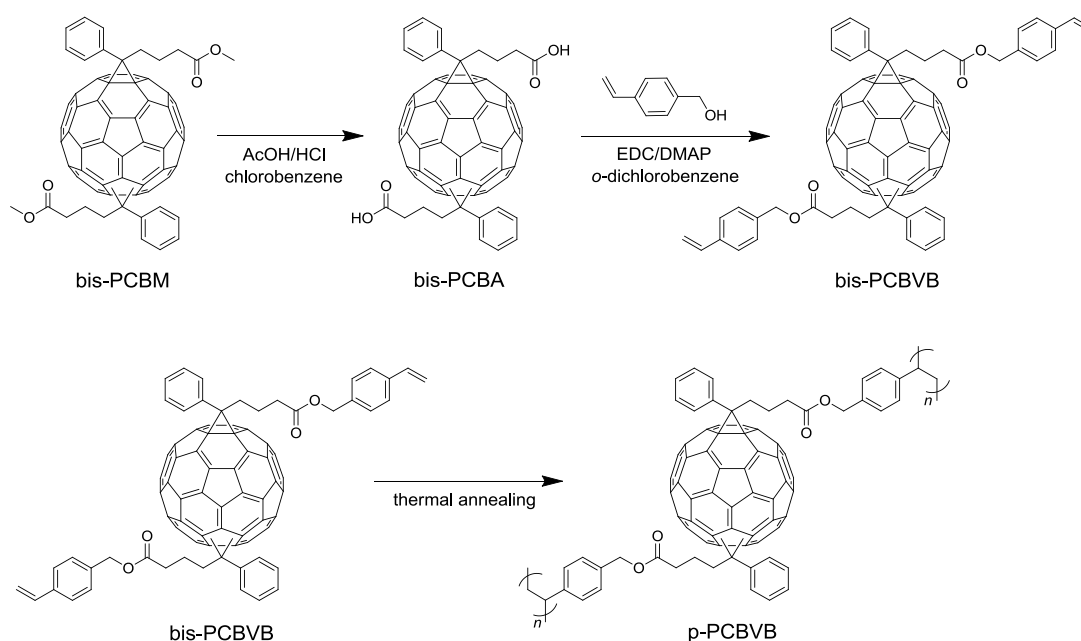


Figure 2-1. Chemical structure of materials used in this study: a) PF12TBT and b) bis-PCBM.

The starting reactants [6,6]-diphenyl-C₆₂-bis(butyric acid methyl ester) (bis-PCBM) and 4-vinylbenzyl chloride were purchased from Aldrich Chemical Co. 4-(Dimethylamino)pyridine (DMAP) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) were purchased from Tokyo Chemical Industry Co., Ltd., and Wako Pure Chemical Industries Ltd., respectively. The PF12TBT was synthesized and characterized at Sumitomo Chemical Co., Ltd. The weight-average molecular weight M_w , polydispersity index (PDI, given by M_w/M_n , where M_n is the number-average molecular weight), and glass transition temperature T_g were 26,900 g mol⁻¹, 3.4, and 81 °C, respectively. The other reagents and solvents were purchased from Nacalai Tesque and Wako, respectively, and used as received without any further purification.

2.2.2. Synthesis of Insoluble Fullerene Polymer



Scheme 2-1. Synthetic route for bis-PCBVB and p-PCBVB.

4-Vinylbenzyl acetate: A mixture of 4-vinylbenzyl chloride (10 mL, 0.071 mol) and potassium acetate (8 g, 0.0815 mol) in DMSO (30 mL) was stirred at 40 °C for 2 days under N₂ atmosphere. The reaction mixture was poured into water and extracted three times with ethyl acetate. The collected ethyl acetate layers were dried with anhydrous MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1 : 10, v/v) as eluent to afford the product (11.96 g, 96%) as yellow oil. ¹H-NMR (400 MHz, CDCl₃, δ): 2.09 (s, 3H), 5.08 (s, 2H), 5.24 (d, *J* = 10.8 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 6.67 (dd, *J* = 11.2, 11.2 Hz, 1H), 7.30 (d, *J* = 12 Hz, 2H), 7.39 (d, *J* = 8 Hz, 2H).

4-Vinylbenzyl alcohol: Sodium hydroxide (2.45 g, 0.061 mol) was added to a solution of 4-vinylbenzyl acetate (3.60 g, 0.024 mol) in ethanol (10 mL) and water (3 mL) under N₂ atmosphere. After stirring at room temperature for 20 min, the reaction mixture was heated to 80 °C slowly and stirred for a further 2 h. It was then poured into water and extracted three times with ethyl acetate, and then dried with anhydrous MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1 : 5, v/v) as eluent to afford the product (2.66 g, 96%) as dark brown oil. ¹H-NMR (400 MHz, CDCl₃, δ): 2.22 (s, 1H), 4.61 (s, 2H), 5.21 (d, *J* = 11.2 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 1H), 6.66 (dd, *J* = 10.8, 10.8 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H).

Bis-[6,6]-phenyl-C₆₂-butyric acid (bis-PCBA): To a solution of bis-PCBM (0.1 g, 0.09 mmol) in chlorobenzene (40 mL) was added acetic acid (12 mL) and concentrated

hydrochloric acid (8 mL). The mixture was stirred and refluxed overnight. The course of the reaction was monitored by TLC (ethyl acetate/hexane (1 : 10, v/v)), which showed an R_f change after complete conversion from 0.95 to 0.68. The solvent was removed in vacuo and the precipitate was collected by filtration. The crude product was washed with methanol and hexane several times to afford the product (0.082 g, 81.2%) as dark brown powder. FTIR (KBr pellet, cm^{-1}) ν : 1702, 1430, 1424, 1204, 1179, 1150, 719, 566, 525.

Bis-[6,6]-phenyl- C_{62} -butyric acid vinylbenzyl ester (bis-PCBVB): 4-Vinylbenzyl alcohol (50 mg, 0.373 mmol) was mixed with bis-PCBA (81.5 mg, 0.074 mmol) and DMAP (27.4 mg, 0.224 mmol) in *o*-dichlorobenzene (20 mL). The mixture was stirred for 1 h and then cooled to 0 °C in an ice/water bath. Finally, EDC (60 mg, 0.33 mmol) was added to the mixture quickly via syringe. The mixture was stirred at 0 °C for 5 h and then warmed to room temperature with continuous stirring for 12 h. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography using chloroform/methanol (20 : 1, v/v) as eluent to afford the product (61.7 mg, 62.6%) as a dark brown solid. ^1H -NMR (400 MHz, CDCl_3 , δ) 2.05–3.12 (m, 12H), 5.13–5.03 (m, 4H), 5.28–5.25 (m, 2H), 5.78–5.70 (m, 2H), 6.73–6.66 (m, 2H), 7.93–7.31 (m, 18H). FTIR (KBr pellet, cm^{-1}) ν : 1734, 1627, 1602, 1495, 1426, 1249, 1177, 1149, 910, 713, 572, 526.

2.2.3. General Measurement and Characterization

^1H -NMR spectra were recorded on a JEOL JNM-AL400 (400 MHz) in deuterated chloroform. FTIR spectra were recorded with a Jasco FT/IR-4200

spectrophotometer using the KBr pellet method for thin film study. Absorption spectra were measured with a Hitachi U-3500 spectrophotometer.

The steady-state PL spectra were measured with a calibrated fluorescence spectrophotometer (Hitachi, F-4500) equipped with a photomultiplier (Hamamatsu, R928F). For both PF12TBT/p-PCBVB bilayer and PF12TBT neat films, PF12TBT was selectively excited at 580 nm from the side of the PF12TBT/air interface. The PL quenching efficiency of PF12TBT in the bilayer films was evaluated from the ratio of the PL intensity for the PF12TBT/p-PCBVB bilayer film to that for a PF12TBT neat film. The PL decay curve was measured by the TCSPC technique with a photon counting system (HORIBA Jobin Yvon, FluoroCube), and the decay curve was analyzed with DAS6 decay analysis software (HORIBA). The PF12TBT film was excited at 640 nm with a pulsed laser diode (HORIBA Jobin Yvon, NanoLED-635L) and the emission was collected at 700 nm. The total instrument response function has a full-width at half maximum (FWHM) of ca. 260 ps for the PL decay measurement. The steady-state PL spectra and PL decay measurements were obtained under N₂ atmosphere.

The AFM surface images were collected in tapping mode (Shimadzu, SPM-9600) using silicon probes (Nanoworld, NCHR) with a tip radius of typically smaller than 8 nm. The film thickness was evaluated by contact-mode measurement as follows: a part of the film was scratched out with a sharp needle to expose the substrate, and the film thickness was evaluated from the height difference between the film and substrate surfaces.

The HOMO energy levels of the bis-PCBM and p-PCBVB neat films were estimated by photoelectron yield spectroscopy (Riken Keiki, AC-3).

The surface energy γ_X of the material X was examined by the contact angle measurement on a spin-coated film of material X using both water and ethylene glycol at room temperature. The surface energy γ_X was evaluated from the contact angle γ_X by the harmonic mean method.^[47,48]

2.3. Results and Discussion

2.3.1. Synthesis of Cross-Linkable Fullerene

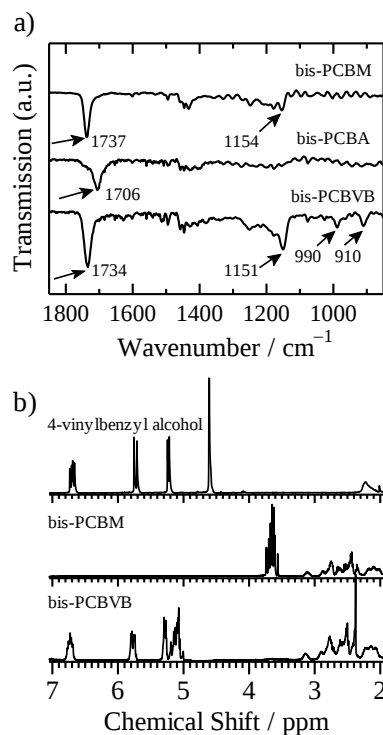


Figure 2-2. a) FT-IR spectra of bis-PCBM, bis-PCBA, and bis-PCBVB. b) ¹H-NMR spectra of 4-vinylbenzyl alcohol, bis-PCBM, and bis-PCBVB.

In order to design a well-defined polymer/fullerene bilayer heterojunction, a cross-linkable fullerene should satisfy the following requirements. First, the reactive units should be introduced without changing the electronic structure of the parent

fullerene molecules. Second, the cross-linkable fullerene should be sufficiently soluble to form a uniform thin film by spin-coating. Thirdly, the precursor film should be easily polymerized in the solid state and the resulting film should be insoluble in common organic solvents. Finally, the reactive units should be inactive both optically and electronically after the cross-linking. Markov et al. have reported a thermally cross-linkable fullerene bearing carefully designed diacetylene groups; they successfully fabricated a polymer/fullerene bilayer heterojunction by using the insoluble fullerene film.^[19] However, not all diacetylenes undergo polymerization in the solid state because they need a favorable stacking alignment for efficient polymerization.^[39,40] Moreover, polydiacetylenes have extended π -conjugation throughout the polymer chains,^[39,40] and might electronically interact with the fullerene and donor polymers. A styryl group was selected as a reactive unit to avoid these drawbacks because it is easily synthesized and can be polymerized in the solid state even at a low temperature.^[34–38] Furthermore, a polystyrene structure formed by the cross-linking of the styryl group is inactive both optically and electronically. A fullerene derivative [6,6]-phenyl-C₆₂-bis(butyric acid methyl ester), bis-PCBM, was selected^[41] as a parent fullerene molecule, because two cross-linkable units can be introduced without changing the core electronic structure of bis-PCBM, as will be discussed below.

As shown in Scheme 2-1, a thermally cross-linkable fullerene bearing two styryl groups (bis-PCBVB) was synthesized. Hydrolysis of bis-PCBM gave the corresponding diacid, bis-PCBA.^[43,44] 4-Vinylbenzyl alcohol was synthesized according to a reported method.^[42] The bis-styryl ester, bis-PCBVB, was synthesized by the esterification of bis-PCBA with 4-vinylbenzyl alcohol in the presence of EDC and DMAP. In the FT-IR spectra of the compounds, as shown in Figure 2-2a, the

carbonyl stretching vibration was shifted from 1737 to 1706 cm^{-1} after the hydrolysis of bis-PCBM, indicating formation of bis-PCBA by the ester-to-acid conversion. The carbonyl stretching vibration returned to 1734 cm^{-1} and vibrational stretches due to the vinyl groups appeared at 910 and 990 cm^{-1} after the esterification of bis-PCBA. Although the stretching band of the C–O bond of the ester group disappeared in the bis-PCBA spectrum, it was observed at 1154 cm^{-1} in bis-PCBM and 1151 cm^{-1} in bis-PCBVB. Moreover, as shown in Figure 2-2b, the ^1H -NMR spectra of the two esters revealed that the methyl group signal at 3.69 ppm in bis-PCBM was absent in the bis-PCBVB spectrum, and was replaced by signals of the styryl groups at 6.73–6.66, 5.78–5.70, and 5.28–5.25 ppm. These changes in the FT-IR and ^1H -NMR spectra support the successful modification of bis-PCBM to bis-PCBVB.

2.3.2. Cross-Linking of Fullerene

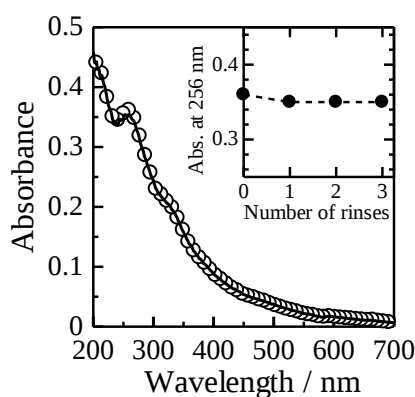


Figure 2-3. Absorption spectra of bis-PCBVB film annealed at 170 °C for 60 min (circles) and after rinsing with chlorobenzene (solid line). The inset shows absorbance at 256 nm of annealed bis-PCBVB film measured after spin-rinsing with chlorobenzene several times.

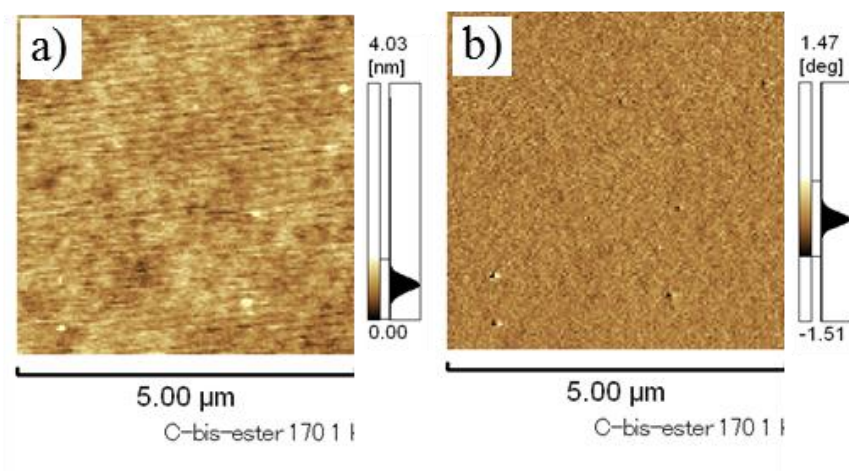


Figure 2-4. AFM tapping mode a) height and b) phase images of bis-PCBVB thin film after thermal annealing at 170 °C for 60 min and then spin-rinsing with chlorobenzene ($5\ \mu\text{m} \times 5\ \mu\text{m}$).

The styryl groups were cross-linked thermally by spin-coating a bis-PCBVB film from chlorobenzene solution onto a glass substrate and then heated under nitrogen atmosphere at selected temperatures for various lengths of time. The solvent resistance of the resulting cross-linked films (p-PCBVB) was studied by UV–visible absorption spectroscopy. The absorption of the bis-PCBVB film heated at 170 °C for 60 min, was not change after spin-rinsing with chlorobenzene, indicating both the full crosslinking of the bis-PCBVB monomers and the film’s insolubility (Figure 2-3). The annealing temperature of 170 °C is reasonably close to the temperature required for the thermal cross-linking reaction of styryl units.^[37,38,45] The film resulting from the thermal polymerization of a fullerene with a single styryl group exhibited a reduction in the absorbance by approximately 26% after washing with chlorobenzene.^[45] With a single styryl substituent, linear fullerene polymers may be formed dominantly, which

would not provide the needed solvent resistance.^[46] On the other hand, the bis-PCBVB monomer bearing two styryl groups can form cross-linked networks, which provide superior solvent resistance.

Figure 2-4 shows topographical and phase images of the p-PCBVB film after spin-rinsing with chlorobenzene: the surface is smooth and uniform with a root-mean-square roughness of 0.81 nm. The AFM images demonstrate that the surface of the p-PCBVB layer is not eroded by the subsequent spin-coating of a conjugated polymer layer from chlorobenzene solution. Further examined the wetting properties of the p-PCBVB surface was carried out by comparing with that of the bis-PCBM surface. From the contact angle measurement,^[47,48] the surface energy was evaluated to be 30.0 mJ m^{-2} for the p-PCBVB film, which was almost the same as that of the bis-PCBM spin-coated film (30.6 mJ m^{-2}). In summary, the in-situ cross-linked bis-PCBVB films are solvent resistant and exhibit a pinhole-free and smooth surface with a surface energy similar to that of bis-PCBM.

2.3.3. Optical and Electrical Properties

Figure 2-5a shows the absorption spectra of bis-PCBM (circles) and bis-PCBVB (solid line) measured in THF solution. Both fullerene derivatives exhibit essentially the same spectrum with the same molar absorption coefficients ϵ , indicating that the electronic structure of core fullerene in bis-PCBVB is the same as that of the parent bis-PCBM even after the styryl group functionalization. To confirm the electron-accepting ability of bis-PCBVB, PL quenching was measured for a conjugated polymer film blended with bis-PCBVB. Here, a fluorene-based copolymer was selected, PF12TBT, since fluorene-based copolymers are one of the most popular

conjugated polymers used for efficient polymer-based solar cells.^[49] The PL from PF12TBT was quenched completely in the film blended with 50 wt% bis-PCBVB. This efficient PL quenching ensures that bis-PCBVB acts as an effective electron acceptor.

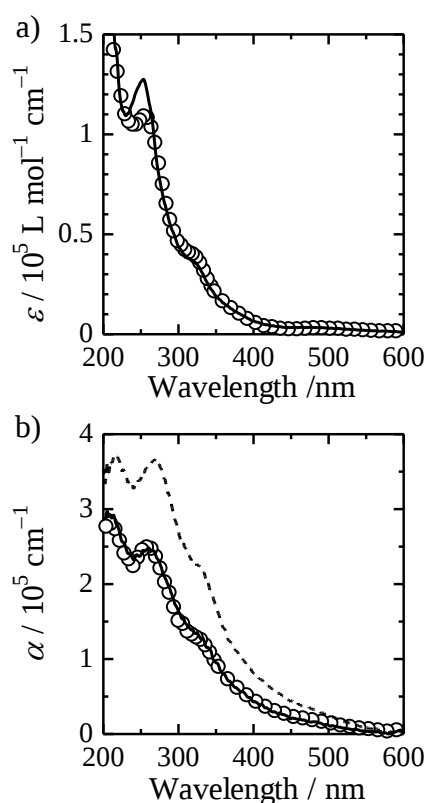


Figure 2-5. a) Molar absorption coefficients ϵ of bis-PCBM (circles) and bis-PCBVB (solid line) measured in THF. b) Absorption coefficients α of bis-PCBM (broken line), bis-PCBVB (circles), and p-PCBVB (solid line) films.

Next, the optical and electrical properties of the fullerene films were also investigated. Figure 2-5b shows the absorption coefficients α of thin films of bis-PCBM (broken line), bis-PCBVB (circles), and p-PCBVB (solid line) spin-coated on quartz substrates. The α value for the p-PCBVB film was the same as that of

bis-PCBVB, indicating that the electronic structure of core fullerene in bis-PCBVB is not damaged by the cross-linking reaction among the styryl groups. On the other hand, the α value of the p-PCBVB film was smaller than that of the bis-PCBM film. The reduction in α is attributable to an increase in the molecular volume due to the introduction of the two cross-linkable units, which would decrease the density of the C₆₀ core units in the bis-PCBVB film as compared with that of bis-PCBM.

Finally, the electron-accepting ability of the p-PCBVB film in terms of the energetics was examined. The highest occupied molecular orbital (HOMO) energy level of the p-PCBVB was evaluated to be 6.0 eV by photoelectron yield spectroscopy. The lowest unoccupied molecular orbital (LUMO) energy level was estimated to be 3.9 eV by adding the energy of the onset of the optical absorption (600 nm) to the HOMO energy. The HOMO and LUMO energy levels of the p-PCBVB film agreed well with them of the bis-PCBM film determined in the same manner. The deep LUMO energy level of the p-PCBVB film, equivalent to that of bis-PCBM, reveals that the p-PCBVB surface can act as an electron acceptor for typical conjugated polymer donors.

2.3.4. Thermal Stability of D/A Bilayer Structure

The thermal stability of the bilayer structure was examined by measuring the PL intensity of a PF12TBT/p-PCBVB bilayer sample before and after the sample was heated at 140 °C for 60 min in N₂ atmosphere. Note that the annealing temperature (140 °C) is far above the glass transition temperature T_g of PF12TBT ($T_g = 81$ °C). Figure 2-6 shows the PL spectra of a PF12TBT/p-PCBVB bilayer film before (circles) and after (solid line) heating, together with that of a PF12TBT reference film without a p-PCBVB layer (broken line). In both bilayer samples, the PL intensity was not

changed after heating: the PL intensity was quenched by the p-PCBVB layer to 70% relative to that of the reference film. If the thermal annealing induced interlayer mixing of p-PCBVB with PF12TBT and hence eroded the flat interfacial structure, the PL intensity would decrease because of an increase in the donor/acceptor interface available for exciton dissociation.^[19] However, this is not the case as shown in the figure. The same PL intensity before and after the heating is indicative of no intermixing between the PF12TBT and p-PCBVB layers under these experimental conditions. This stability is in contrast to the previous studies reported for bilayer samples prepared by evaporating fullerene onto a polymer film^[19,27,30] or by laminating a polymer layer onto a fullerene spin-coated film.^[28,31] The thermal stability of the p-PCBVB film is beneficial for designing a well-defined donor/acceptor bilayer to evaluate the exciton diffusion length precisely.

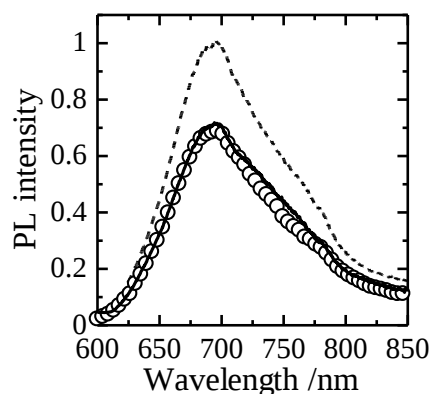


Figure 2-6. PL spectra of 30-nm-thick PF12TBT film spin-coated on quartz substrate (broken line), and on p-PCBVB surfaces before (circles) and after thermal annealing at 140 °C for 60 min (solid line). The PL intensities were normalized by the PL intensity of the PF12TBT film spin-coated on the quartz substrate.

2.3.5. Exciton Diffusion in PF12TBT Film

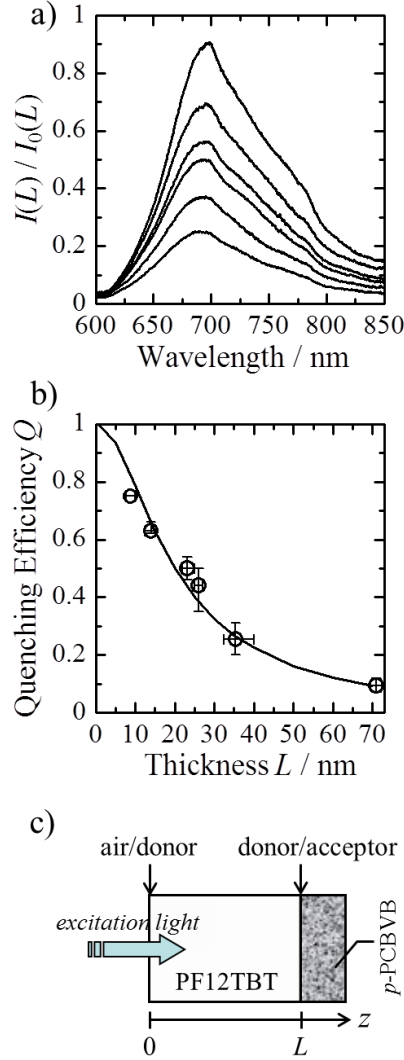


Figure 2-7. a) PL intensity $I(L)$ of PF12TBT/p-PCBVB bilayer films with different PF12TBT thicknesses. The intensity of each bilayer film is normalized against the intensity $I_0(L)$ of a PF12TBT reference film with a corresponding thickness. b) PL quenching efficiencies $Q(L)$ of PF12TBT/p-PCBVB bilayer films with different PF12TBT thicknesses: experimental (circles) and calculated (solid line) values. The calculations were performed using eq 2-1 with an exciton diffusion length L_D of 11 nm. c) Schematic of the bilayer structure used in the PL quenching measurements. The choice of coordinate z used in eq 2-1 is shown. PF12TBT was excited at 580 nm from the side of the PF12TBT/air interface.

Finally, the exciton diffusion in PF12TBT is investigated from the PL quenching efficiency in the PF12TBT/p-PCBVB bilayer samples. The thickness of the PF12TBT layer L was systematically varied from 9 to 71 nm while that of p-PCBVB layer was fixed to 20 nm. For comparison, PF12TBT neat films with the same thicknesses as the PF12TBT in the bilayers were prepared as references. For both bilayer and reference samples, PF12TBT was selectively excited at 580 nm from the side of the PF12TBT/air interface. Figure 2-7a shows the PL spectra of the bilayer samples. In this figure, the PL intensity of bilayer samples $I(L)$ was normalized by that of the corresponding PF12TBT reference film $I_0(L)$. The relative PL intensity $I(L)/I_0(L)$ decreased with decreasing thickness of PF12TBT, meaning that a larger portion of PF12TBT excitons reached the interface with the p-PCBVB acceptor in the thinner PF12TBT.

In order to evaluate the exciton diffusion length, the PL quenching data was analyzed on the basis of a one-dimensional diffusion model. Here, it is assumed that an infinite exciton quenching rate at the PF12TBT/p-PCBVB interface and no exciton quenching at the PF12TBT/air interface. Under these assumptions, the exciton quenching efficiency $Q(L)$ is given by eq 2-1^[19]

$$Q(L) = 1 - \frac{I(L)}{I_0(L)} = \frac{[\alpha^2 L_D^2 + \alpha L_D \tanh(L/L_D)] \exp(-\alpha L) - \alpha^2 L_D^2 [\cosh(L/L_D)]^{-1}}{(1 - \alpha^2 L_D^2) [1 - \exp(-\alpha L)]} \quad (2-1)$$

where α is the absorption coefficient at the excitation wavelength and L_D is the exciton diffusion length in the direction normal to the acceptor surface (the inset of Figure 2-7c). As shown in Figure 2-7b, the best fitting curve by eq 2-1 is obtained for an exciton diffusion length of 11 nm (solid line). The L_D and the diffusion coefficient D have been reported mostly within the range of 5–8 nm and $(3\text{--}30) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, respectively,

for amorphous conjugated polymers such as poly(*p*-phenylene vinylene) (PPV) and its derivatives.^[10,16,20,21,50] The diffusion length of 11 nm estimated for PF12TBT is slightly larger than that reported previously.

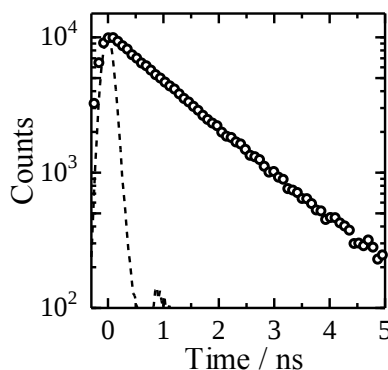


Figure 2-8. PL decay curve of a PF12TBT neat film spin-coated on quartz substrate. The excitation and monitor wavelengths were 640 and 700 nm, respectively. The broken line shows an instrumental response function.

D of a PF12TBT singlet exciton was evaluated to address the origin of the larger L_D in PF12TBT. Figure 2-8 shows the PL decay curve of a PF12TBT neat film obtained by time-correlated single photon counting (TCSPC) measurements. The PL decay $I(t)$ was well fitted by a single exponential function with a lifetime of $\tau_0 = 1.24$ ns. Consequently, the diffusion coefficient was evaluated to be $D = 9.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ from the relationship with $L_D = 11$ nm and $\tau_0 = 1.24$ ns. The diffusion constant is well consistent with those reported for various amorphous conjugated polymers ($(3\text{--}30) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$) as mentioned above.^[10,16,20,21,45] On the other hand, the exciton lifetime of PF12TBT is relatively longer: most conjugated polymers such as PPV derivatives exhibit PL lifetimes shorter than 1 ns.^[18,21,22] Thus, the large L_D in the PF12TBT is attributed to the relatively long singlet exciton lifetime of 1.24 ns. This is probably

because the PF12TBT excitons do not suffer from structural- and chemical-defect-related nonradiative quenching in the film.^[17,18,21]

2.4. Conclusions

A thermally cross-linkable fullerene derivative was designed and synthesized. In-situ cross-linking was carried out by annealing the bis-PCBVB thin film at 170 °C for 60 min, giving a solvent-resistant and thermally stable film with a flat and smooth surface. The LUMO energy level of the film was evaluated to be 3.9 eV, which is in agreement with that of the parent fullerene, indicating that the film can act as a good electron-accepting layer. On the basis of the PL quenching in the bilayer films, the exciton diffusion length and diffusion coefficient of PF12TBT were determined as $L_D = 11$ nm and $D = 9.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, respectively. Our donor/acceptor bilayer system is widely applicable to systematic studies of L_D in various conjugated polymers.

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Chapter 3

Efficient Exciton Harvesting through Long-Range Energy Transfer

3.1. Introduction

Polymer solar cells have attracted a great deal of attention because of their potential applications to flexible, light-weight, and large-area devices.^[1–3] The active layer of them is typically based on bulk heterojunction structures, which consist of donor and acceptor materials with interpenetrating nanoscale networks to maximize the donor/acceptor interfacial area. In polymer solar cells, excitons (coulombically bound electron–hole pairs) should be transferred to the donor/acceptor interface to be efficiently dissociated into free hole and electron carriers because of the strong binding energy.^[4–6] However, the exciton diffusion length in most conjugated polymers is as short as 5–20 nm,^[7–13] which is not always enough to make sure all the excitons generated reach the interface of polymer/fullerene before deactivating to the ground state. For example, it has been reported that about 10–20% excitons are lost before arriving at the interface even in a benchmark solar cell based on poly(3-hexylthiophene) (P3HT) and a fullerene derivative (PCBM).^[14] Therefore, efficient exciton harvesting is required for further improvement in polymer solar cells.

Energy transfer is long-range excitation transport and hence could collect excitation energy more efficiently to certain sites than random exciton diffusion if

energy donating and accepting materials are allocated appropriately.^[15–21] Indeed, it has been reported that P3HT excitons are collected more efficiently to a low-bandgap dye molecule silicon phthalocyanine derivative (SiPc) located at a donor/acceptor interface in P3HT/PCBM blends.^[14,18,22] As a result of such appropriate incorporation of SiPc, the external quantum efficiency (EQE) is improved not only at the dye absorption band in the near-IR region but also at the P3HT absorption band in the visible region. The former is ascribed to the additional light-harvesting by SiPc dye molecules. The latter is ascribed to long-range energy transfer from P3HT to SiPc at the heterojunction of P3HT/PCBM blends. Because of the spectral overlap between P3HT emission and SiPc absorption bands, the Förster radius is as long as 3.7 nm, which is enough long compared to a hopping length of excitons. In P3HT/PCBM/SiPc ternary blends, half of P3HT excitons that would be lost in the absence of SiPc are collected by energy transfer to SiPc molecules at the heterojunction. Consequently, this finding demonstrates that the energy transfer can increase the effective exciton diffusion length.

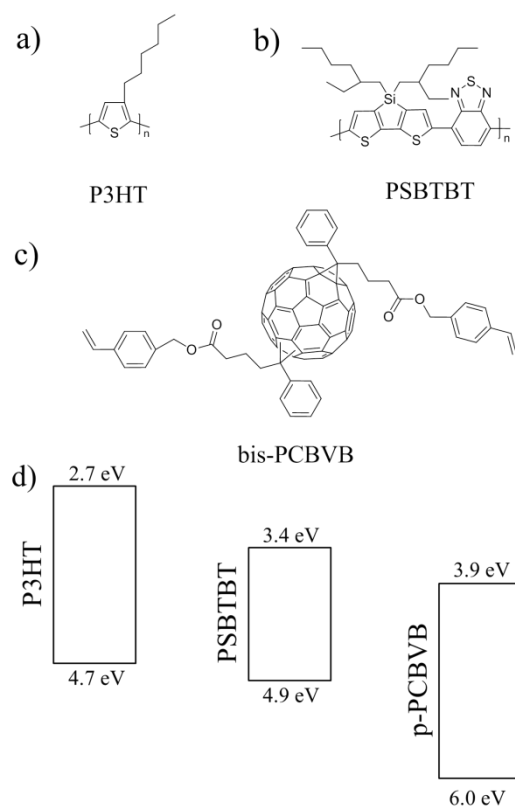
Recently, the photocurrent improvement has been reported for ternary blend solar cells based on P3HT, PCBM, and a low-bandgap polymer PSBTBT.^[23] This is primarily ascribed to the additional light harvesting in the near-IR region due to PSBTBT. It has been demonstrated that the energy transfer from P3HT to PSBTBT would improve the exciton harvesting and hence the device performance in this ternary blend solar cells because of the spectral overlap between P3HT emission and PSBTBT absorption bands. In this chapter, the effective diffusion length of P3HT excitons to PSBTBT domains is studied in order to address how energy transfer impacts on the diffusion length in P3HT/PSBTBT/PCBM ternary blends. To evaluate the exciton

diffusion length of P3HT excitons correctly, bilayer films based on P3HT and insoluble fullerene polymer (p-PCBVB) was employed. In this polymer/fullerene bilayers, P3HT excitons would be quenched dominantly by electron transfer at the interface. On the other hand, the effective diffusion length of P3HT excitons was evaluated for P3HT/PSBTBT bilayers in comparison with that in P3HT/p-PCBVB bilayers. In this polymer/polymer bilayers, P3HT excitons would be quenched dominantly by energy transfer to the interface.

3.2. Experimental

3.2.1. Materials

A cross-linkable bi-functionalized fullerene derivative (bis-PCBVB) was synthesized according to literatures.^[24,25] The insoluble fullerene polymer p-PCBVB was obtained by thermal cross-linking of bis-PCBVB at 170 °C for 1 h. The details have been described elsewhere.^[26] The other chemicals were used without any purification unless otherwise noted: P3HT (Sigma-Aldrich, regioregular, $M_n = 87,000 \text{ g mol}^{-1}$) and PSBTBT (Solarmer Materials Inc., $M_n = 11,900 \text{ g mol}^{-1}$). The chemical structures and energy levels of materials used in this study are summarized in Scheme 3-1.

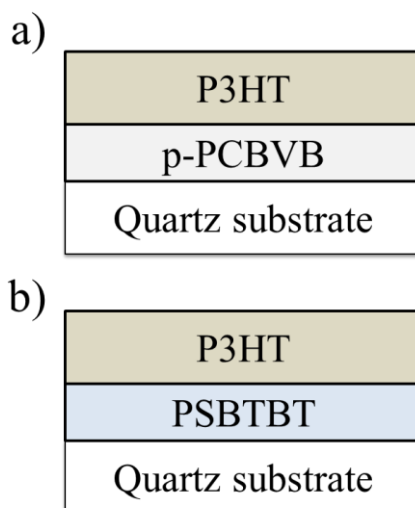


Scheme 3-1. Chemical structures of materials used in this study: a) P3HT, b) PSBTBT, and c) p-PCBVB. d) The HOMO (lower) and LUMO (upper) energy levels of these materials.

3.2.2. Fabrication of Bilayers

Bilayer films of P3HT/p-PCBVB were fabricated as follows. First, bis-PCBVB layer was spin-coated on quartz substrates from chlorobenzene solution (4 mg mL^{-1}) at a spin rate of 1000 rpm for 60 s. Prior to the spin-coating, the quartz substrates were washed by ultrasonication in toluene, acetone, and ethanol for 15 min in sequence, dried with nitrogen gas, and then cleaned with UV–ozone cleaner for 30 min. Subsequently, the bis-PCBVB film was thermally annealed at 170°C for 1 h under

nitrogen atmosphere to be converted to cross-linked and insoluble p-PCBVB film. The p-PCBVB film was rinsed with chlorobenzene twice and dried for next step. On the other hand, polymer layers were separately prepared on glass substrates by successive spin-coatings of poly(sodium 4-styrenesulfonate) (PSS: Sigma-Aldrich, $M_w = 70,000 \text{ g mol}^{-1}$) and P3HT, resulting in a layered structure with glass/PSS/P3HT. Here, PSS was employed as a sacrificial layer and prepared by spin-coating on pre-cleaned glass substrates from an aqueous solution of PSS (10 mg mL^{-1}) at a rate of at 400 rpm for 10 s and 4000 rpm for 30 s. By immersing the glass substrate coated with PSS/P3HT into water slowly, the P3HT layer was floated on the water because the PSS sacrificial layer was selectively dissolved. Finally, the quartz substrate coated with p-PCBVB was gently placed on the P3HT film to obtain a bilayer film of P3HT/p-PCBVB.



Scheme 3-2. Layer structures of a) P3HT/p-PCBVB and b) P3HT/PSBTBT bilayer films fabricated on quartz substrates. The thickness of each acceptor layer was 20 nm.

Bilayer films of P3HT/PSBTBT were fabricated in a similar fashion. First, PSBTBT layer was prepared by spin-coating on the cleaned quartz substrate from a chlorobenzene solution with a concentration of 4 mg mL^{-1} at a spin rate of 2000 rpm for 60 s. Subsequently, a P3HT layer was transferred from the water surface to the PSBTBT coated substrate as is the same with P3HT/p-PCBVB bilayers. The bilayer structures obtained are summarized in Scheme 3-2.

3.2.3. Measurements

Absorption and photoluminescence (PL) spectra were measured with a spectrophotometer (Hitachi, U-3500) and a spectrofluorometer (Horiba Jobin Yvon, NanoLog) equipped with a calibrated imaging detector (Horiba Jobin Yvon, iHR320), respectively. The optical bandgap of materials used in this study was evaluated from the wavelength of intersection between the absorption and PL spectra. The film thickness was evaluated with an atomic force microscope (Shimadzu, SPM-9500J) in the contact mode at room temperature. The ionization potential of P3HT, PSBTBT, and p-PCBVB was measured with a photoelectron yield spectrometer (Riken Keiki, AC-3). All the neat films (ca. 60 nm) were fabricated by spin-coating from each chlorobenzene solution on the ITO substrate. 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.

3.3. Theory

The continuity equation of the exciton density in one-dimensional diffusion is given by eq 3-1

$$\frac{\partial}{\partial t} n(x,t) = D \frac{\partial^2}{\partial x^2} n(x,t) - \frac{n(x,t)}{\tau} + G(x) \quad (3-1)$$

where $n(x,t)$ is the exciton density at a position x and time t , D is the exciton diffusion coefficient, τ is the exciton lifetime without quenching wall, and $G(x)$ is the exciton generation rate at a position x . Under steady state condition, this equation can be solved with two boundary conditions at the two interfaces eqs 3-2 and 3-3.

$$n(0,t) = 0 \quad (3-2)$$

$$-D \frac{\partial}{\partial x} n(L,t) = 0 \quad (3-3)$$

In eq 3-2, it is assumed that all the excitons arriving at the interface $x = 0$ are quenched with 100% efficiency. In eq 3-3, it is assumed that the excitons arriving at the air/polymer interface $x = L$ are not quenched at all and just reflected. In this manner, an analytical expression for the exciton quenching efficiency $Q(L)$ is given by eq 3-4 as a function of the polymer film thickness L

$$Q(L) = \frac{\left[\alpha^2 L_D^2 + \alpha L_D \tanh\left(\frac{L}{L_D}\right) \right] \exp(-\alpha L) - \alpha^2 L_D^2 \left[\cosh\left(\frac{L}{L_D}\right) \right]}{(1 - \alpha^2 L_D^2) [1 - \exp(-\alpha L)]} \quad (3-4)$$

where α as the absorption coefficient and the exciton diffusion length $L_D = \sqrt{D\tau}$.

When excitons are quenched not only by electron transfer at the interface but also by long-range energy transfer to the interface $x = 0$, an additional quenching term should be added to eq 3-1. This is true for low-bandgap acceptors such as PSBTBT. In this case, an additional quenching term is added as shown in eq 3-5.^[27]

$$\frac{\partial}{\partial t} n(x,t) = D \frac{\partial^2}{\partial x^2} n(x,t) - \frac{n(x,t)}{\tau} - k_F(x)n(x,t) + G(x) \quad (3-5)$$

Here, $k_F(x)$ is the energy transfer rate from position x to the interface $x = 0$, which is given by eq 3-6

$$k_F(x) = \frac{C_A}{\tau} \frac{\pi R_0^6}{6 x^3} \quad (3-6)$$

where C_A is the density of energy-accepting molecules, and R_0 is the Förster radius. McGehee reported that the exciton diffusion length effectively increases in the presence of the energy transfer mechanism. Interestingly, they also found that the exciton quenching data in the presence of the energy transfer can be still well reproduced by eq 3-4 even though only exciton diffusion is considered.^[20] For comparison, therefore the effective diffusion length was evaluated by eq 3-4 for the exciton quenching in the absence and presence of long-range energy transfer.

3.4. Results and Discussion

3.4.1. Optoelectronic Properties

The highest occupied molecular orbital (HOMO) level was estimated to be 4.7 eV for P3HT, 4.9 eV for PSBTBT, and 6.0 eV for p-PCBVB in the solid state by photoemission yield spectroscopy. The lowest unoccupied molecular orbital (LUMO) level was evaluated to be 2.7 eV for P3HT, 3.4 eV for PSBTBT, and 3.9 eV for p-PCBVB from the HOMO level and the optical bandgap estimated from the absorption and emission spectra. As shown in Scheme 3-1d, these energy structures make sure efficient charge separation between P3HT and p-PCBVB and between P3HT and PSBTBT. As shown in Figure 3-1, the fullerene polymer p-PCBVB exhibits large absorption in the ultraviolet region but negligible absorption in the visible region and

the low-bandgap PSBTBT exhibits a large absorption band at around 700 nm with a absorption coefficient of $145\ 000\ \text{cm}^{-1}$. On the other hand, as shown in the figure, P3HT exhibits an emission band at around 700 nm, which negligibly overlapped with the absorption of p-PCBVB but well overlapped with the absorption band of PSBTBT. From the spectral overlap between the absorption and emission band, the Förster radius is estimated to be as short as 1.6 nm for the energy transfer from P3HT to p-PCBVB but as long as 3.5 nm for the energy transfer from P3HT to PSBTBT. These optoelectronic properties indicate that P3HT excitons are quenched by electron transfer at the interface with p-PCBVB or PSBTBT and also quenched by long-range energy transfer to the interface of PSBTBT.

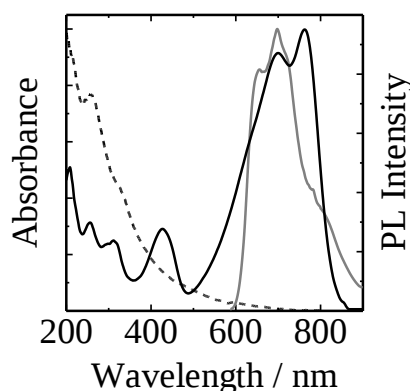


Figure 3-1. Absorption spectra of PSBTBT (black solid line) and p-PCBVB (black broken line) and PL spectrum of P3HT (gray line) neat films.

3.4.2. Exciton Diffusion Length

In order to accurately evaluate the exciton diffusion length, an insoluble fullerene polymer p-PCBVB as an electron-accepting layer is employed in donor/acceptor bilayers instead of small molecule acceptors such as a fullerene derivative PCBM. As reported recently, PCBM molecules are likely to diffuse into the

other layer in bilayers even at room temperature.^[28] On the other hand, as described in chapter 2, p-PCBVB insoluble films exhibit flat and smooth surface, which can serve as a suitable quenching wall in donor/acceptor bilayers for evaluating the exciton diffusion length.^[29] The thickness of P3HT layers was varied from 10 to 70 nm, which was precisely evaluated with an absorption coefficient of P3HT. For all the films employed in this study, P3HT was selectively excited in nitrogen atmosphere to prevent PL quenching at the P3HT/air surface.

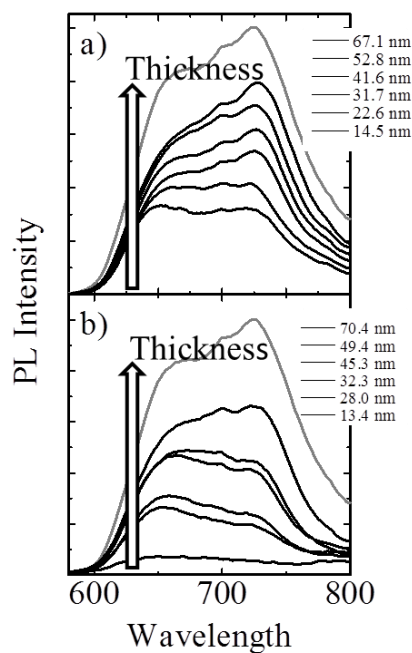


Figure 3-2. PL spectra of a) P3HT/p-PCBVB and b) P3HT/PSBTBT bilayer films with different P3HT thickness. The gray lines represent the PL spectra of P3HT neat films. The PL intensity of each bilayer film was normalized by the intensity of P3HT neat films with the same thickness.

For P3HT/p-PCBVB bilayers, as shown in Figure 3-2a, the normalized PL intensity of P3HT decreased with decreasing P3HT thickness. This is because most

P3HT excitons can diffuse to the P3HT/p-PCBVB interface in the thinner P3HT layer and hence quenched efficiently. For P3HT/PSBTBT bilayers, as shown in Figure 3-2b, the normalized PL intensity of P3HT more steeply decreased with decreasing P3HT thickness than that for P3HT/p-PCBVB. Instead, as shown in Figure 3-3, the PL band of PSBTBT was observed even though P3HT was selectively excited at 485 nm. The PL intensity due to direct excitation of PSBTBT was negligibly small as shown in the figure: it was as small as 5% at most because the PSBTBT absorption is the smallest at 485 nm. Thus, the PSBTBT emission observed is indicative of energy transfer from P3HT to PSBTBT.

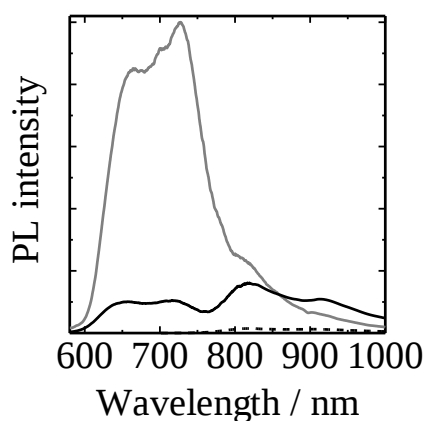


Figure 3-3. PL spectra of P3HT/PSBTBT bilayer (black line), P3HT neat (gray line), and PSBTBT neat (broken line) films excited at 485 nm. The thickness of each layer was 13.5 nm (P3HT) and 20 nm (PSBTBT).

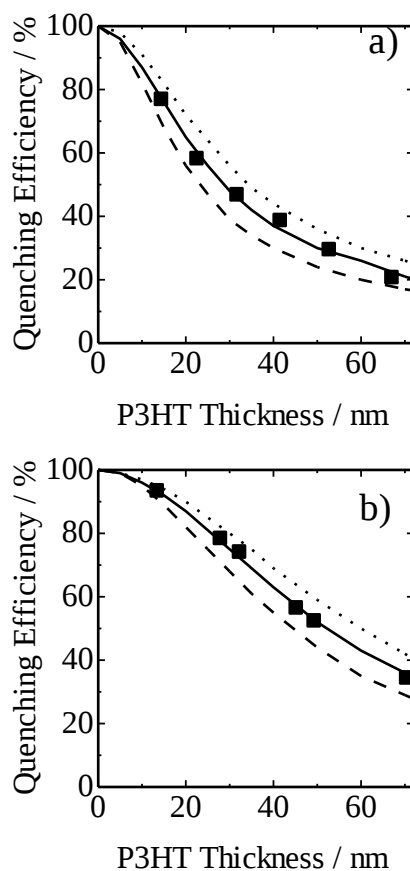


Figure 3-4. PL quenching efficiency of a) P3HT/p-PCBVB and b) P3HT/PSBTBT bilayer films plotted against P3HT thickness. The broken, solid, and dotted lines represent the PL quenching efficiency calculated by eq 3-4 with an exciton diffusion length of 12, 15, and 18 nm (panel a) and 25, 30, and 35 nm (panel b).

Figure 3-4 shows the quenching efficiency of P3HT in the two bilayer models plotted against the P3HT thickness. The solid lines represent theoretical curves calculated by eq 3-4 with various diffusion lengths. For P3HT/p-PCBVB bilayers, as shown in Figure 3-4a, the quenching efficiency is well fitted with a diffusion length of 15 nm, which is slightly shorter than that in P3HT crystalline domains recently reported (20 nm).^[9] This is probably because the diffusion length evaluated for the bilayer is average of exciton diffusions in amorphous and crystalline domains. For

P3HT/PSBTBT bilayers, as shown in Figure 3-4b, the quenching efficiency is well fitted with an effective diffusion length of 30 nm, which is two times longer than that for P3HT/p-PCBVB bilayers. This is because P3HT excitons are more effectively collected to the PSBTBT quenching wall by efficient energy transfer.

Finally, the relevance of the effective diffusion length to photovoltaic performance of ternary blend solar cells is discussed. More specifically, ternary solar cells based on P3HT, PSBTBT, and PCBM is researched. In this blend, P3HT is the most crystalline material and hence would form large crystalline domains under appropriate fabrication conditions such as thermal or solvent annealing. Consequently, PSBTBT also would form phase-separated domains, which are probably mixed with PCBM as reported previously. Typically, phase-separated domain size would be of the order of tens of nanometers,^[29,30] which is consistent with the acceptor thickness employed in this study. Therefore it is proposed that energy transfer from P3HT to PSBTBT would be efficient in ternary blends with large P3HT crystalline domains. In other words, the energy transfer can harvest more efficiently P3HT excitons that would be lost in such large crystalline domains in the absence of PSBTBT. The large P3HT crystalline domains would be beneficial for the efficient charge transport and hence improve photovoltaic performance.

3.5. Conclusions

In summary, the effective diffusion length of singlet excitons was demonstrated to be increased by long-range energy transfer. In P3HT/p-PCBVB bilayer films, the diffusion length of P3HT excitons is evaluated to be 15 nm, which is slightly shorter than that evaluated for P3HT crystalline domains by singlet exciton-exciton

annihilation. In other words, this exciton diffusion length is an average value for P3HT amorphous and crystalline domains. In P3HT/PSBTBT bilayer films, on the other hand, the effective diffusion length of P3HT excitons is evaluated to be 30 nm. This is most probably because P3HT excitons are more efficiently collected to the PSBTBT quenching wall in the bilayer film. The Förster radius is estimated to be 3.5 nm for the energy transfer from P3HT to PSBTBT on the basis of the spectral overlap. In ternary blends of P3HT, PSBTBT, and PCBM, the energy transfer would enhance the effective diffusion length as is the case with the bilayer system employed in this study. Therefore, it is suggested that growing large P3HT crystalline domains would be the key to the improvement in photovoltaic performance of P3HT/PSBTBT/PCBM ternary solar cells.

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Chapter 4

Highly Efficient Exciton Harvesting and Charge Transport in Ternary Blend Solar Cells Based on Wide- and Low-Bandgap Polymers

4.1. Introduction

Polymer solar cells based on binary blends of polymeric donor and fullerene acceptor materials have been extensively investigated in the past decade.^[1–3] The power conversion efficiency (PCE) has been improved every year and very recently exceeded 10% by several groups.^[4–6] However, it is still not high enough to compete with commercialized inorganic solar cells. One of the most important reasons is the mismatch of spectra between an absorption band of the photoactive layer and the terrestrial solar radiation.^[7] For example, poly(3-hexylthiophene) (P3HT) exhibits a large absorption band in the visible region from 400 to 600 nm but no absorption band in the near-IR region. As a result, the PCE of polymer solar cells based on a blend of P3HT and a fullerene derivative (PCBM) is limited to less than 5%, even though the external quantum efficiency (EQE) is as high as 80%.^[8,9] Therefore, much more photons not only in the visible region but also in the near-IR region should be absorbed to improve the efficiency furthermore.

Ternary blend solar cells have been proposed as a simple and versatile alternative approach to extending the light-harvesting range up to the near-IR region.^{[10–}

^{12]} More specifically, ternary blend solar cells are classified into two types. One is dye-sensitized polymer/fullerene solar cells, which are incorporated with dye molecules with complementary absorption bands.^[13–20] The other is ternary blends based on an acceptor fullerene and two donor polymers with complementary absorption bands.^[21–30] For dye-sensitized ternary blend polymer solar cells, the device performance is higher than that of the original binary solar cells because of the additional dye absorption and the improved exciton harvesting. For two-donor ternary blend polymer solar cells, the device performance is higher than that of the original binary solar cells with a wide-bandgap polymer. However, it is still lower than that of the original binary solar cells with a low-bandgap polymer after appropriate optimizations, suggesting that there are some limitations for this ternary solar cell. This is partly because the light absorption is enhanced in the near-IR region but reduced in the visible region with increasing fraction of the low-bandgap polymer^[23,24,29] and partly because a fill factor (FF) is degraded with increasing fraction of the low-bandgap polymer.

In this chapter, ternary blend solar cells based on wide- and low-bandgap polymers and PCBM have been fabricated. To overcome the limitations mentioned above, highly crystalline P3HT as a wide-bandgap polymer and poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-*b*:2'3'-*d*]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT) as a low-bandgap polymer are employed, which have complementary absorption bands in the visible and in the near-IR region, respectively. Highly crystalline P3HT is likely to form large crystalline domains, which would improve charge transport even in ternary blends. The complementary absorption bands can extend the light-harvesting range from visible to near-IR region and also give large spectral overlap between the P3HT fluorescence and the PSBTBT absorption,

which would improve exciton harvesting by efficient energy transfer from P3HT to PSBTBT even in large P3HT crystalline domains. On the basis of these strategies, high short-circuit current density (J_{SC}) and high fill factor were obtained at the same time, resulting in an improved PCE of 5.6%, which is even higher than that of both individual binary solar cells based on P3HT/PCBM and PSBTBT/PCBM reported so far.^[32–34] In order to discuss how P3HT crystallization impacts on the photovoltaic performance of ternary blend solar cells, two different P3HT with a regioregularity of >98% (P3HT-H) and 85%, P3HT-L) are employed.

4.2. Experiment

4.2.1 Materials

Three kinds of materials were employed for ternary blend films: P3HT (Plextronics OS2000, regioregularity >98%, number-averaged molecular weight, $M_n \approx 54,000 \text{ g mol}^{-1}$ P3HT-H; Aldrich, regioregularity $\approx 80\%$, $M_n \approx 75\,000$ P3HT-L), PCBM (Frontier Carbon, E100H), and PSBTBT (Solarmer Materials Inc., $M_n \approx 11\,900$). These materials were used without further purification.

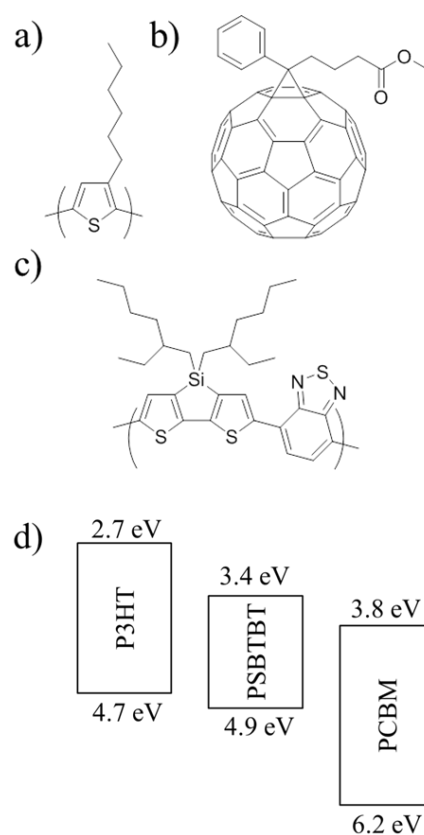


Figure 4-1. Chemical structures of materials employed in this study: a) P3HT, b) PCBM, and c) PSBTBT. d) Energy levels of these three materials. The figures represent the HOMO (upper) and LUMO (lower) energy levels in electron volts.

4.2.2. Device Fabrication

All devices were fabricated as follows: Indium–tin–oxide (ITO, 10 Ω per square) coated glass substrates were cleaned by ultrasonication in toluene, acetone, and ethanol for 15 min, dried with N_2 , and then cleaned with a UV– O_3 cleaner for 30 min. A hole-transporting layer of poly(3,4-ethylenedioxythiophene) with poly(4-styrenesulfonate) (PEDOT:PSS, Celvios PH500) was spin-coated onto the cleaned substrates, and then dried at 140 $^{\circ}C$ for 10 min in air. Subsequently, the active

layer was fabricated from a dichlorobenzene solution of P3HT (Plextronics, OS2000), PSBTBT, and PCBM with different compositions. The solution was prepared with a blend ratio of P3HT : PSBTBT : PCBM = $5 - x : x : 5 \text{ mg mL}^{-1}$ ($0 \leq x \leq 5$). For P3HT-H, the active layer was spin-coated at a spin rate of 600 rpm for 60 s and left in a Petri dish with a cover plate to evaporate the solvent slowly. Finally, a metal electrode of calcium (20 nm) and aluminum (100 nm) was thermally deposited in a vacuum ($2.5 \times 10^{-4} \text{ Pa}$) sequentially. For P3HT-L, the active layer was spin-coated at 1200 rpm for 60 s, and thermally annealed at 140 °C for 5 min in a glove box ($\text{O}_2 < 10 \text{ ppm}$, $\text{H}_2\text{O} < 10 \text{ ppm}$).

4.2.3. Measurements

The J - V characteristics were measured in an N_2 atmosphere with a direct-current voltage/current source monitor (Advantest, R6243) in the dark and under illumination with AM1.5G simulated solar light at 100 mW cm^{-2} . The light intensity was corrected with a calibrated silicon photodiode reference cell (Bunkoh-Keiki, BS-520). The active area of the device was 0.07 cm^2 . Absorption and PL spectra were measured with a spectrophotometer (Hitachi, U-3500) and a spectrofluorometer (Horiba Jobin Yvon, NanoLog) equipped with a calibrated imaging detector (Horiba Jobin Yvon, iHR320), respectively.

4.3. Results

4.3.1 Absorption Spectra

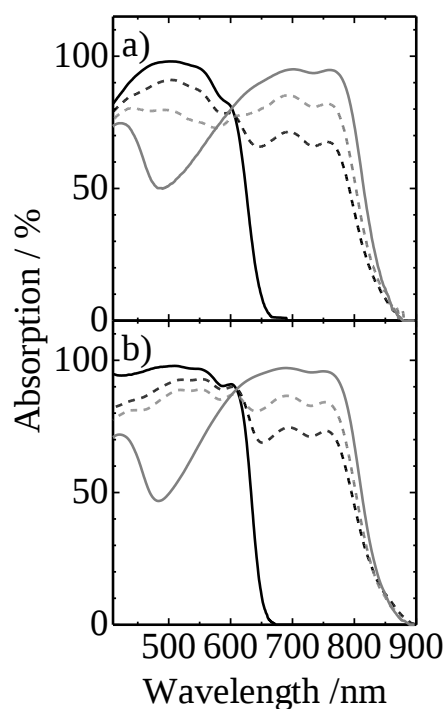


Figure 4-2. Absorption spectra of ternary blend films covered with Al metal electrode, which was measured in the reflection mode. a) P3HT-L/PSBTBT/PCBM and b) P3HT-H/PSBTBT/PCBM with different blend ratios: P3HT : PSBTBT : PCBM = 50 : 0 : 50 (black solid lines), 30 : 20 : 50 (black broken lines), 20 : 30 : 50 (gray broken lines), and 0 : 50 : 50 (gray solid lines).

Figure 4-2 shows the absorption spectra of P3HT/PSBTBT/PCBM ternary blends with different blend compositions. As shown in the figure, two distinct absorption bands were observed at around 400–600 nm and 650–800 nm, which are ascribable to P3HT and PSBTBT, respectively. Because of complementary absorption bands, the ternary blends exhibit broad absorption bands ranging from 400 to 800 nm, which is desirable for the wide-band light harvesting in polymer solar cells. With increasing fraction of PSBTBT from 0 to 50 wt%, the PSBTBT absorption from 650 to 800 nm increased while the P3HT absorption from 400 to 600 nm decreased. For P3HT-H/PSBTBT/PCBM blends, vibronic absorption bands were clearly observed at around 600 nm, which are ascribed to P3HT crystallization. On the basis of weakly

interacting H-aggregated model,^[35-38] the P3HT crystallinity is evaluated to be 50% for P3HT-L and 65% for P3HT-H. It has been confirmed that these spectral changes can be reproduced by the sum of absorption spectra of P3HT and PSBTBT neat films. In other words, the P3HT crystallinity remained the same independently of the blend ratios.

4.3.2. Photoluminescence (PL) Quenching

Figure 4-3 shows the photoluminescence (PL) spectra of neat or blend films with different blend compositions. For P3HT-L/PSBTBT/PCBM ternary blend films, as shown in Figure 4-3a, the PL from P3HT-L was strongly quenched with almost 100% quenching efficiency. For P3HT-L/PSBTBT binary blend films, the PL from P3HT was strongly quenched and instead the PL from PSBTBT was clearly observed, suggesting efficient energy transfer from P3HT to PSBTBT. From the spectral overlap, the Förster radius from P3HT to PSBTBT was estimated to be 3.5 nm assuming point-dipoles, which is long enough for the efficient energy transfer. The PL from P3HT was completely quenched not only for P3HT-L/PSBTBT/PCBM ternary blends but also for P3HT-L/PCBM binary blends. In other words, almost 100% P3HT excitons are efficiently quenched mainly by PCBM in the presence or absence of PSBTBT. This is probably because PCBM molecules are well mixed with P3HT-L and hence can quench P3HT excitons efficiently in blend films. On the other hand, for P3HT-H/PSBTBT binary blend films, the PL from P3HT was strongly quenched and instead the PL from PSBTBT was clearly observed, again suggesting efficient energy transfer from P3HT to PSBTBT. For P3HT-H/PCBM binary blends, the PL from P3HT was quenched but still observed with 20% efficiency, indicating that 20% of

P3HT excitons are radiatively deactivated to the ground state before arriving at the donor/acceptor interface. For P3HT-H/PSBTBT/PCBM ternary blends, the PL from P3HT was completely quenched. This is probably because the 20% P3HT excitons that would be lost in the absence of PSBTBT are collected to PSBTBT domains by energy transfer and then quenched by PCBM. These findings indicate that the charge generation efficiency is dependent upon the crystallinity of P3HT in ternary blend films.

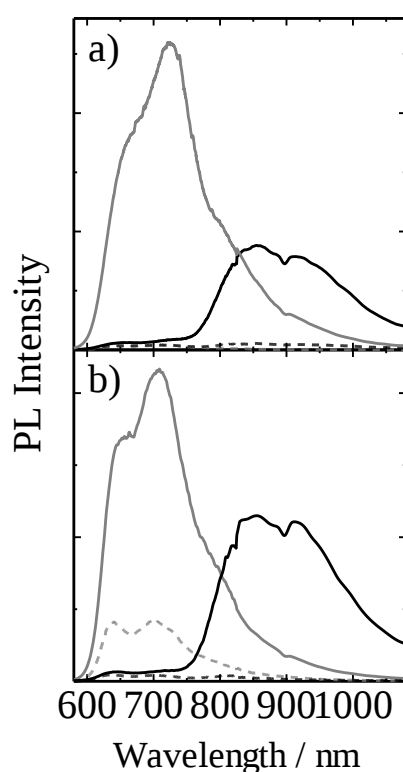


Figure 4-3. Photoluminescence spectra of a) P3HT-L and b) P3HT-H neat or blend films with different compositions: P3HT neat films (gray lines), P3HT/PCBM (50 : 50 w/w) (gray broken lines), P3HT/PSBTBT/PCBM (20 : 30 : 50 w/w) (broken lines), and P3HT/PSBTBT (40 : 60 w/w) (solid lines) blend films. The PL intensity of P3HT was corrected for variation in the absorption at an excitation wavelength of 550 nm. The PL intensity of PSBTBT was corrected by subtracting the PL intensity due to the direct excitation of PSBTBT at 550 nm.

4.3.3. J - V Characteristics

Figure 4-4 shows the J - V characteristics of P3HT/PSBTBT/PCBM ternary blend solar cells with different blend compositions. For P3HT-L/PSBTBT/PCBM blends, as shown in Figure 4-4a, J_{SC} and V_{OC} increased only slightly and FF clearly decreased from 0.57 to 0.45 with increasing fraction of PSBTBT from 0 to 30 wt%, resulting in degraded PCE from 2.4 to 2.2%. At 50 wt% PSBTBT (PSBTBT/PCBM binary solar cell), J_{SC} jumped up to 13.4 mA cm^{-2} and FF recovered to 0.56, leading to the best PCE of 4.9%. A similar dependence has been reported previously for the same ternary blend solar cells.²³ In other words, the PCE of P3HT-L/PSBTBT/PCBM ternary blend solar cells is lower than that of PSBTBT/PCBM binary blend solar cells.

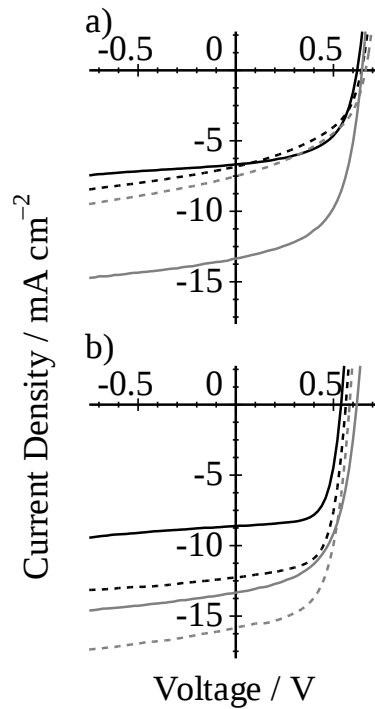


Figure 4-4. J - V characteristics of a) P3HT-L/PSBTBT/PCBM and b) P3HT-H/PSBTBT/PCBM ternary solar cells with different blend compositions: P3HT : PSBTBT : PCBM = 50 : 0 : 50 (solid lines), 30 : 20 : 50 (broken lines), 20 : 30 : 50 (gray broken lines), and 0 : 50 : 50 (gray solid lines).

For P3HT-H/PSBTBT/PCBM blends, as shown in Figure 4-4b, J_{SC} significantly increased from 8.6 to 15.8 mA cm⁻² with increasing fraction of PSBTBT from 0 to 30 wt% and then decreased to 13.3 mA cm⁻² at 50 wt% PSBTBT (PSBTBT/PCBM binary solar cell). On the other hand, no distinct changes in V_{OC} and FF were observed for any blend composition. Interestingly, the FF of ternary devices is even higher than that of the PSBTBT/PCBM binary reference device (0.57), suggesting that charge transport is better in ternary blends rather than in PSBTBT/PCBM binary blends. As a result, the best PCE of 5.6% was obtained for P3HT/PSBTBT/PCBM ternary blend solar cells (30 wt% PSBTBT). In other words, P3HT/PSBTBT/PCBM ternary blend solar cells exhibit higher PCE than either P3HT/PCBM or PSBTBT/PCBM binary blend solar cell.

4.3.4. External Quantum Efficiency (EQE)

Figure 4-5 shows the EQE spectra of P3HT/PSBTBT/PCBM ternary blend solar cells with different blend compositions. For P3HT-L/PSBTBT/PCBM blends, as shown in Figure 4-5a, the EQE signals at around 750 nm increased monotonically up to >60% while the EQE signals at around 500 nm decreased monotonically from ~50 to ~25% with increasing fraction of PSBTBT. This is consistent with the spectral change shown in Figure 4-2a.

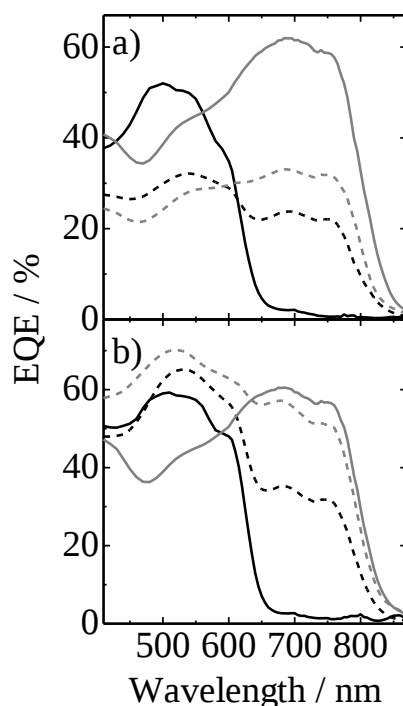


Figure 4-5. EQE spectra of a) P3HT-L/PSBTBT/PCBM and b) P3HT-H/PSBTBT/PCBM ternary solar cells with different blend compositions: P3HT : PSBTBT : PCBM = 50 : 0 : 50 (solid lines), 30 : 20 : 50 (broken lines), 20 : 30 : 50 (gray broken lines), and 0 : 50 : 50 (gray solid lines).

For P3HT-H/PSBTBT/PCBM blends, on the other hand, the EQE signals at around 750 nm increased monotonically up to ~60% with increasing fraction of PSBTBT. As shown in Figure 4-5, this increase is much steeper than that observed for P3HT-L/PSBTBT/PCBM blends. Interestingly, the EQE signals at around 500 nm also increased from ~60 up to ~70% at 30 wt% PSBTBT even though the P3HT absorption decreased as shown in Figure 4-2b, and then decreased to ~40% at 50 wt% PSBTBT (no P3HT). Rather, such energy transfer has been reported for dye-sensitized ternary blend polymer solar cells.^[13,18,19,40] These findings suggest that the charge generation and transport mechanisms are dependent upon the crystallinity of P3HT in ternary blends.

4.4. Discussion

In order to address the origin of the difference in the photovoltaic performance between P3HT-L/PSBTBT/PCBM and P3HT-H/PSBTBT/PCBM ternary solar cells, the dependence of each photovoltaic parameter on the blend compositions is researched. As shown in Figure 4-6, remarkable differences were found in J_{SC} and PCE while no distinct difference was seen in V_{OC} . In particular, the composition dependence of PCE primarily follows that of J_{SC} for both ternary solar cells. In other words, the difference in the photovoltaic performance is primarily due to the difference in the J_{SC} . For P3HT-L/PSBTBT/PCBM, J_{SC} remains almost the same up to 30 wt% PSBTBT and jumps up at 50 wt% PSBTBT, resulting in almost the same PCE (~2%) up to 40 wt% PSBTBT and jumps to ~5% at 50 wt% PSBTBT. For P3HT-H/PSBTBT/PCBM, on the other hand, J_{SC} substantially increases up to 30 wt% PSBTBT and then slightly decreases above 40 wt% PSBTBT, resulting in the most improved PCE (5.6%) at 30 wt% PSBTBT, which is higher than that of either P3HT/PCBM or PSBTBT/PCBM binary blend solar cell.

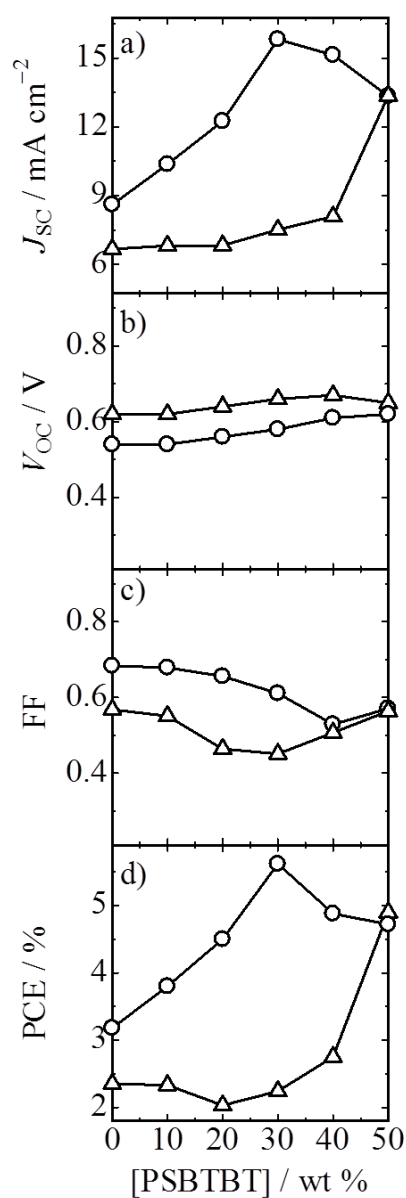


Figure 4-6. Photovoltaic parameters plotted against the weight fraction of PSBTBT in ternary blend films: a) J_{SC} , b) V_{OC} , c) FF, and d) PCE. The open circles and triangles represent the photovoltaic parameters for ternary blends of P3HT-H/PSBTBT/PCBM and P3HT-L/PSBTBT/PCBM, respectively.

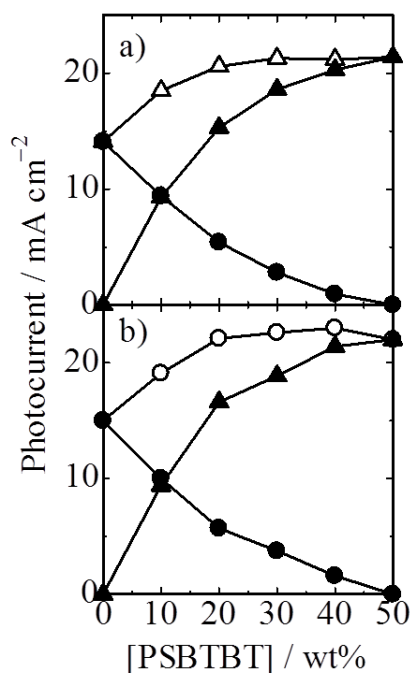


Figure 4-7. Integrated photocurrent of a) P3HT-L/PSBTBT/PCBM and b) P3HT-H/PSBTBT/PCBM ternary solar cells with different blend compositions, which is calculated from the absorption spectra. The closed circles represent photocurrent from P3HT, and the closed triangles represent photocurrent from PSBTBT, the open triangles and open circle represent the sum of the photocurrent from P3HT (closed circles) and from PSBTBT (triangles), which correspond to the maximum photocurrent $J_{\max}$ with IQE = 100%.

First, the slight difference in the absorption spectra is investigated as shown in Figure 4-2, which would cause the different dependence of J_{SC} . Here, the maximum contribution of each donor material to the photocurrent is estimated by integrating the product of their corresponding absorption spectra in the ternary blend, the sum of which corresponds to the maximum photocurrent. With increasing fraction of PSBTBT, as shown in Figure 4-7, the increase in the photocurrent from PSBTBT exceeds the decrease in the photocurrent from P3HT, resulting in the increase in the maximum photocurrent up to more than 20 mA cm^{-2} for both ternary blend solar cells. Thus, the

different dependence of J_{SC} cannot be ascribed to the slight difference in the photon absorption efficiency.

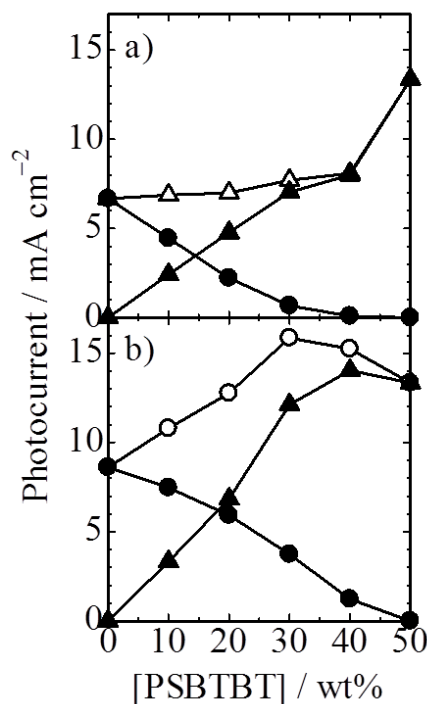
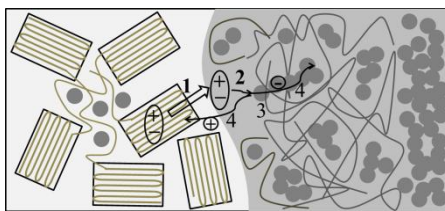


Figure 4-8. Integrated photocurrent of a) P3HT-L/PSBTBT/PCBM and b) P3HT-H/PSBTBT/PCBM ternary solar cells with different blend compositions, which is calculated from the EQE spectra. The closed circles represent photocurrent from P3HT, the closed triangles represent photocurrent from PSBTBT, the open triangles and the open circle represent the sum of the photocurrent from P3HT (closed circles) and from PSBTBT (triangles), which correspond to the total photocurrent J_{SC} .

The contribution of each donor material to the photocurrent by integrating the product of their corresponding EQE spectra was estimated to discuss the different dependence of J_{SC} in more details. For P3HT-L/PSBTBT/PCBM, as shown in Figure 4-8a, the increase in the photocurrent from PSBTBT cancels out the decrease in the photocurrent from P3HT with increasing fraction of PSBTBT in the ternary blends,

resulting in the almost constant total photocurrent (J_{SC}) up to 40 wt% PSBTBT. For P3HT-H/PSBTBT/PCBM, as shown in Figure 4-8b, the photocurrent from PSBTBT increases more steeply and the photocurrent from P3HT decreases more gradually with increasing fraction of PSBTBT. As a result, the total photocurrent (J_{SC}) shows the maximum at 30 wt% PSBTBT. As mentioned above, this improvement in J_{SC} cannot be ascribed to the photon absorption efficiency but rather should be ascribed to the charge generation or charge collection efficiency. The enhanced photocurrent from P3HT in P3HT-H/PSBTBT/PCBM is partly ascribed to the improved charge generation due to energy transfer from P3HT to PSBTBT as described before, which can harvest P3HT excitons that would be lost in the absence of PSBTBT. On the other hand, the enhanced photocurrent from PSBTBT is most probably due to the improved charge collection in the presence of P3HT because FF remains as high as >0.6 up to 30 wt% PSBTBT as shown in Figure 4-6.



Scheme 4-1. Schematic illustration of charge generation and transport in P3HT-H/PSBTBT/PCBM ternary blend solar cells. 1) energy transfer from P3HT to PSBTBT, 2) exciton diffusion, 3) exciton dissociation, and 4) free charge transport.

Finally, the photovoltaic conversion mechanism in P3HT-H/PSBTBT/PCBM ternary solar cells is proposed as shown in Scheme 4-1. Because of the high crystallinity of P3HT-H, there are at least four phases in ternary blends: P3HT

crystalline phase, P3HT amorphous phase mixed with PCBM, PSBTBT phase mixed with PCBM, and PCBM rich phase. Although PSBTBT is also a crystalline polymer, it is considered to be one phase because PSBTBT crystallites are so small that the exciton diffusion is negligible as reported previously.^[31] Upon the photoexcitation of P3HT, P3HT excitons generated near the interface or in the amorphous domains are promptly converted to P3HT polarons and P3HT excitons generated in the large crystalline domains are collected to PSBTBT domains by energy transfer, which would be lost in the absence of PSBTBT. As reported previously, some P3HT polarons are transferred to more stable crystalline domains because of smaller ionization potential. Upon the photoexcitation of PSBTBT, PSBTBT excitons are promptly converted to PSBTBT polarons, some of which would be transferred to more stable P3HT crystalline domains. Indeed, it has been observed shown that PSBTBT polarons are transferred from disordered to crystalline domains in PSBTBT/PCBM blends.^[41] In summary, the improved PCE is most probably because of the energy transfer from P3HT to PSBTBT and the efficient charge transport due to crystalline P3HT. In other words, crystalline wide-bandgap polymer and amorphous low-bandgap polymer would be suitable combination for ternary blend solar cells.

4.5. Conclusions

In summary, the photovoltaic performance of P3HT/PSBTBT/PCBM ternary solar cells was demonstrated to be effectively improved by using highly crystalline P3HT. This is because highly crystalline P3HT forms large crystalline domains and hence would improve charge transport even in ternary blends. Even in such large P3HT crystalline domains, P3HT excitons are effectively collected by energy transfer to

PSBTBT domains mixed with PCBM where charge carriers are efficiently generated. This is because of the large spectral overlap between the P3HT fluorescence and the PSBTBT absorption. As a result, J_{SC} was improved to 15.8 mA cm^{-2} with a high fill factor of 0.61 at a weight ratio of P3HT : PSBTBT : PCBM = 20 : 30 : 50, and hence PCE reached 5.6% , which is even higher than that of both individual binary solar cells based on P3HT/PCBM and PSBTBT/PCBM reported so far. It is worthy to note that this finding is generally applicable to other ternary blend polymer solar cells. It is suggested wide-bandgap crystalline polymer and a low-bandgap amorphous polymer would be good combination for highly efficient ternary solar cells. Because of large spectral overlap between the wide-bandgap polymer fluorescence and the low-bandgap polymer absorption, excitons even in large crystalline domains of the wide-bandgap polymer are efficiently harvested by energy transfer to the low-bandgap polymer domains mixed with PCBM followed by prompt charge generation. Most of the charge carriers are likely to be transferred to more stable crystalline domains of the wide-bandgap polymer where charge transport would be efficient.

4.6. Appendix

Table 4-A1. Photovoltaic parameters of P3HT-L/PSBTBT/PCBM ternary solar cells with different blend compositions.

P3HT : PSBTBT : PCBM	$J_{SC} / \text{mA cm}^{-2}$	V_{OC} / V	FF	PCE / %
50 : 0 : 50	6.67	0.62	0.57	2.4
40 : 10 : 50	6.82	0.62	0.55	2.3
30 : 20 : 50	6.83	0.64	0.46	2.0
20 : 30 : 50	7.52	0.66	0.45	2.2
10 : 40 : 50	8.09	0.67	0.51	2.8
0 : 50 : 50	13.4	0.65	0.56	4.9

Table 4-A2. Photovoltaic parameters of P3HT-H/PSBTBT/PCBM ternary solar cells with different blend compositions.

P3HT : PSBTBT : PCBM	$J_{SC} / \text{mA cm}^{-2}$	V_{OC} / V	FF	PCE / %
50 : 0 : 50	8.61	0.54	0.68	3.2
40 : 10 : 50	10.4	0.54	0.68	3.8
30 : 20 : 50	12.3	0.56	0.66	4.5
20 : 30 : 50	15.8	0.58	0.61	5.6
10 : 40 : 50	15.1	0.61	0.53	4.9
0 : 50 : 50	13.3	0.62	0.57	4.7

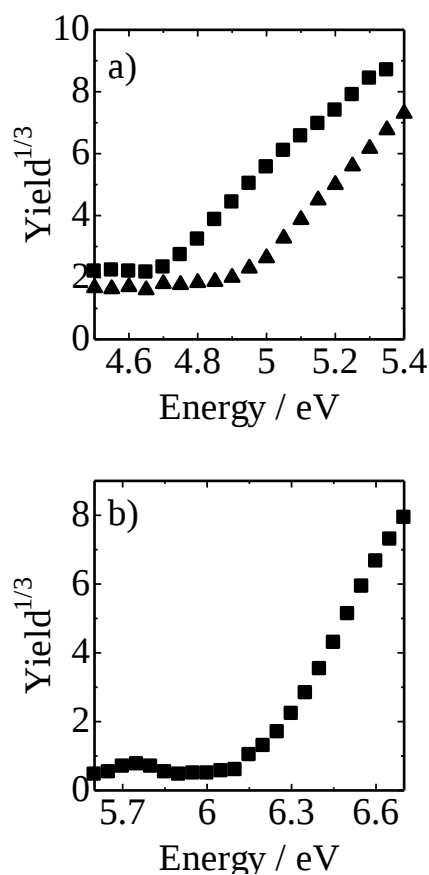


Figure 4-A1. Photoemission yield spectra of a) P3HT (squares) and PSBTBT (triangles), and b) PCBM (squares). The cut-off energy was estimated by a threshold energy of the cubic root of the photoelectron yield.

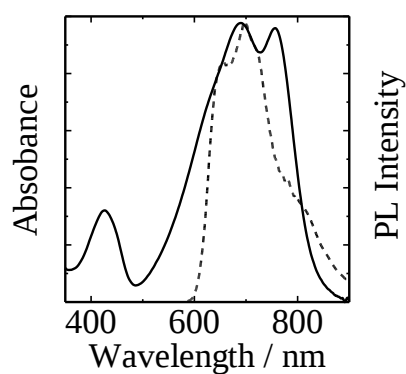


Figure 4-A2. Absorption and PL spectra of PSBTBT (solid line) and P3HT (broken line) films, respectively. The excitation wavelength was 550 nm.

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Chapter 5

Near-IR Sensitization of Polymer Solar Cells Incorporating Low-Bandgap Small Molecule

5.1. Introduction

Polymer solar cells based on a binary blend of a donor polymer and an acceptor fullerene have attracted more and more attention. The power conversion efficiency (PCE) exceeding 10% has been reported by several groups.^[1–3] However, it is still not high enough compared with that of inorganic solar cells. This is mainly because of spectral mismatch between the absorption spectrum of the photoactive layer and the terrestrial solar radiation. To overcome this limitation, extensive research efforts have been devoted to developments of various low-bandgap polymers and tandem solar cells with different bandgap materials.^[4–8] On the other hand, ternary blend solar cells have been recently proposed as an alternative approach to extending the light-harvesting range to near-IR region.^[9–21]

In this chapter, ternary blend solar cells based on P3HT, a fullerene derivative (PCBM), and a small low-bandgap molecule p-DTS(FBTTh₂)₂ has been fabricated as shown in Figure 5-1. Because of the absorption band of p-DTS(FBTTh₂)₂ in the near-IR region, the external quantum efficiency (EQE) signal was additionally observed in the near-IR range, resulting in the increase in the short-circuit current density (J_{SC}).

Interestingly, the EQE of the ternary blend solar cells also increased significantly at the P3HT absorption band in the visible region. As a result, the J_{SC} of the ternary blend solar cells was improved by 32% compared with that of the control solar cell of P3HT/PCBM binary blend. The origin of the improvements in terms of the dye-sensitization mechanism and the location of the dye molecules in ternary blend films are investigated.

5.2 Experiment

5.2.1. Materials

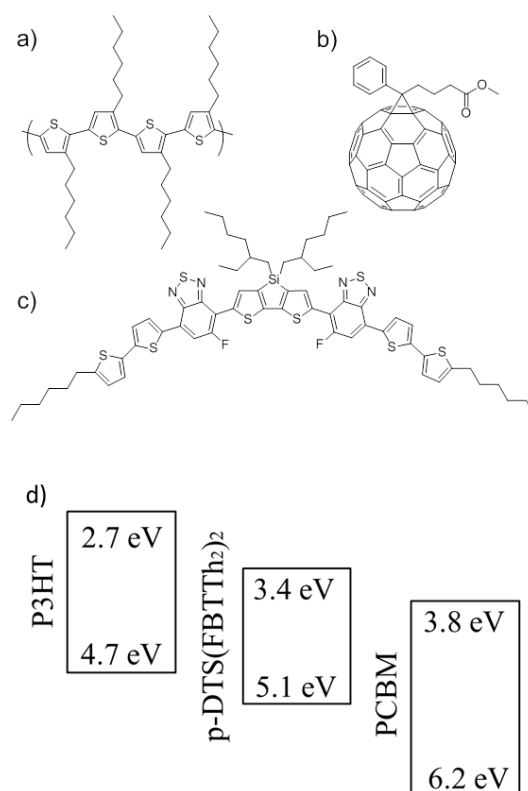


Figure 5-1. Chemical structures of the materials employed in this study: a) P3HT, b) PCBM, and c) p-DTS(FBTTh₂)₂. d) Energy diagram for these three materials. The figures represent HOMO (lower) and LUMO (upper) levels.

Three kinds of materials were employed for ternary blend films: P3HT (Plextronics, regioregularity >98%, number-averaged molecular weight, $M_n \approx 54,000 \text{ g mol}^{-1}$), PCBM (Frontier Carbon, E100H), and p-DTS(FBTTh₂)₂ (1-Material). These materials were used without further purification.

5.2.2 Device Fabrication

Ternary blend solar cells were fabricated as follows. First, indium/tin oxide (ITO)-coated glass substrates (10 Ω per square) were washed by ultrasonication in toluene, acetone, and ethanol for 15 min, dried with nitrogen gas, and then cleaned with a UV-O₃ cleaner (Nippon Laser & Electronics, NL-UV253S) for 30 min. A thin layer (~40 nm) of poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate) (PEDOT:PSS) (H.C. Starck, PH500) was spin-coated onto the cleaned substrates at a spin rate of 3000 rpm, and was dried at 140 °C for 10 min in air. Prior to the spin-coating, the solution of PEDOT:PSS was filtered with a PTFE syringe filter (pore size: 0.45 μm). Subsequently, a ternary blend active layer of P3HT/PCBM/p-DTS(FBTTh₂)₂ was spin-coated at a spin rate of 600 rpm for 60 s. The ternary blend solution was prepared as follows: P3HT, PCBM, and p-DTS(FBTTh₂)₂ were dissolved in *o*-dichlorobenzene at a concentration ratio of 10 : 10 : 0.7 mg mL⁻¹ ([p-DTS(FBTTh₂)₂] = 3.4 wt%) and then the mixed solution was stirred at 40 °C overnight. An electrode of Ca/Al layer (15/70 nm) was deposited in sequence on top of the active layer at 2.5×10^{-4} Pa. The effective device area was 0.07 cm².

5.2.3 Measurements

The J - V characteristics were measured in a nitrogen atmosphere with a direct-current voltage and current source/monitor (Advantest, R6243) in the dark and under illumination with AM1.5G simulated solar light at 100 mW cm^{-2} . The light intensity was corrected with a calibrated silicon photodiode reference cell (Bunkoh-Keiki, BS-520). The active area of the device was 0.07 cm^2 . The EQE spectra were measured with a digital electrometer (Advantest, R8252) under monochromatic light illumination from a 500-W xenon lamp (Thermo Oriel, 66921) with optical cut filters and a monochromator (Thermo Oriel, Cornerstone). The illumination was carried out from the ITO side under nitrogen atmosphere at room temperature. Absorption and photoluminescence (PL) spectra were measured with a spectrophotometer (Hitachi, U-3500) and a spectrofluorometer (Horiba Jobin Yvon, NanoLog) equipped with a calibrated imaging detector (Horiba Jobin Yvon, iHR320), respectively. The contact angles θ_X of ultrapure water droplets were measured on a spin-coated film of material X at room temperature. The surface energy γ_X of the material X was evaluated from θ_X by the Neumann's equation combined with Young's equation. The interfacial energy γ_{AB} between materials A and B was evaluated from γ_A and γ_B by the Neumann's equation. The wetting coefficient ω_C of material C in a blend of materials A and B was evaluated from the interfacial energies.

5.3. Results and Discussion

Figure 5-2 shows the absorption spectra of P3HT/PCBM/p-DTS(FBTTh₂)₂ ternary and P3HT/PCBM binary blend films. The ternary blend film exhibited an

additional absorption band at around 700 nm, which is ascribable to p-DTS(FBTTh₂)₂. On the other hand, the absorption at around 400–600 nm is ascribed to P3HT. The vibrational bands at around 600 nm are indicative of the crystallization of P3HT, suggesting that the crystallization of P3HT is not disturbed even in the presence of p-DTS(FBTTh₂)₂.

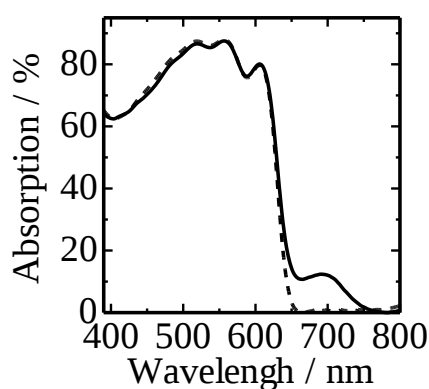


Figure 5-2. Absorption spectra of P3HT/PCBM/p-DTS(FBTTh₂)₂ ternary blend (solid line) and P3HT/PCBM binary blend (broken line) films.

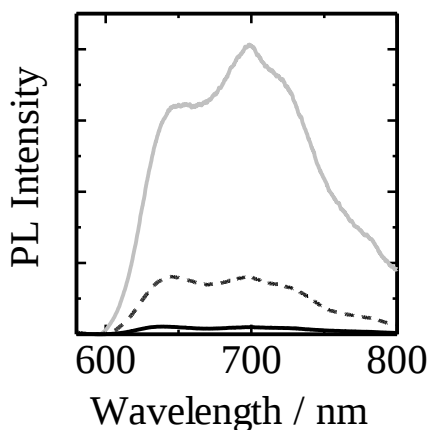


Figure 5-3. PL spectra of P3HT/PCBM/p-DTS(FBTTh₂)₂ ternary blend (solid line), P3HT/PCBM binary blend (broken line), and P3HT (gray line) neat films.

Figure 5-3 shows the PL spectra of P3HT/PCBM/p-DTS(FBTTh₂)₂ ternary blend, P3HT/PCBM binary blend, and P3HT neat films. For the evaluation of PL quenching efficiency, the PL intensity was corrected by variation of the absorption at an excitation wavelength of 550 nm. As shown in the figure, the PL quenching efficiency of P3HT was about 80% for the P3HT/PCBM binary blend, suggesting that 20% P3HT excitons radiatively deactivate before arriving at the P3HT/PCBM interface. On the other hand, the PL quenching efficiency of P3HT was as high as 100% for the P3HT/PCBM/p-DTS(FBTTh₂)₂ ternary blend, suggesting that almost all the P3HT excitons are effectively quenched in the presence of p-DTS(FBTTh₂)₂ in the ternary blend film. As shown in Figures 5-2 and 5-3, the PL band of P3HT is well overlapped with the absorption band of p-DTS(FBTTh₂)₂, suggesting efficient energy transfer. Indeed, the Förster radius is estimated to be 2.6 nm assuming point-dipoles.

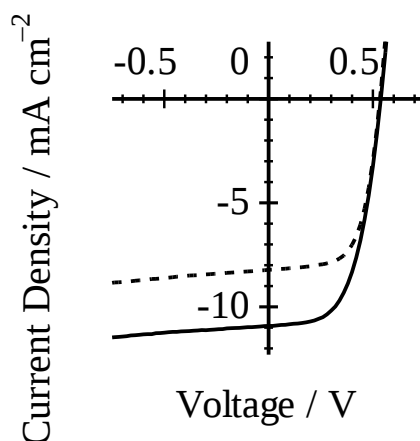


Figure 5-4. *J*-*V* characteristics of P3HT/PCBM/ p-DTS(FBTTh₂)₂ ternary blend (solid line) and P3HT/PCBM binary blend (broken line) solar cells.

Figure 5-4 shows the J - V characteristics of P3HT/PCBM/p-DTS(FBTTh₂)₂ ternary and P3HT/PCBM binary blend solar cells under simulated AM1.5G illumination with an intensity of 100 mW cm⁻². With addition of only 3.4 wt% of p-DTS(FBTTh₂)₂, as shown in the figure, the J_{SC} was remarkably improved from 8.2 to 10.9 mA cm⁻². On the other hand, no change was observed for the open-circuit voltage (V_{OC}), indicating that the charge recombination between P3HT polarons and PCBM anions is still dominant in the ternary blend because of the small fraction of p-DTS(FBTTh₂)₂. The fill factor (FF) slightly decreased. As a result, the overall PCE was improved by 21%: ternary blend (3.4%) and binary blend (2.8%).

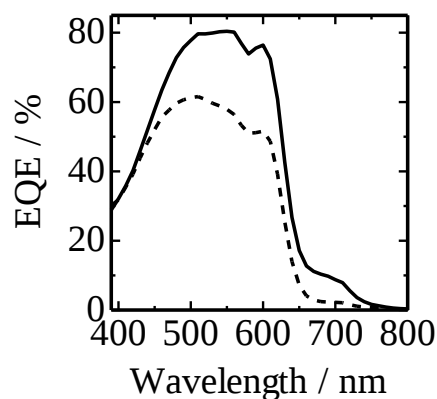


Figure 5-5. EQE spectra of P3HT/PCBM/ p-DTS(FBTTh₂)₂ ternary blend (solid lines) and P3HT/PCBM binary blend (broken lines) films.

The EQE spectra of P3HT/PCBM/p-DTS(FBTTh₂)₂ ternary and P3HT/PCBM binary blend solar cells were measured to address the origin of the increase in J_{SC} . As shown in Figure 5-5, an additional EQE signal was observed at around 700 nm for ternary blend solar cells, indicating that p-DTS(FBTTh₂)₂ molecules do contribute to the photocurrent generation. Furthermore, the EQE at around 500 nm due to the P3HT

absorption increased from 63 to 80%, although no difference in the absorption was observed for the ternary and binary blend films as shown in Figure 5-2. This is probably because P3HT excitons are more efficiently collected to the P3HT/PCBM interface by long-range energy transfer from P3HT to p-DTS(FBTTh₂)₂ and subsequently are dissociated into free carriers. This is consistent with higher PL quenching efficiency in the ternary blend as mentioned before. Previously, it was reported a similar energy transfer in analogous ternary blend solar cells by transient absorption spectroscopy.^[9,11,19,21] In other words, there are two origins for the increase in J_{SC} : one is the photocurrent due to additional light harvesting by the direct photoexcitation of p-DTS(FBTTh₂)₂, and the other is the photocurrent due to efficient exciton harvesting by long-range energy transfer from P3HT to p-DTS(FBTTh₂)₂ at the interface. From the EQE spectra, the contribution of each mechanism to the increase in the J_{SC} was estimated to be 0.4 mA cm⁻² for the additional light harvesting and 2.3 mA cm⁻² for the exciton harvesting. In other words, the increase in J_{SC} is mainly due to the improvement in the P3HT exciton harvesting by the energy transfer from P3HT to p-DTS(FBTTh₂)₂. If the majority of p-DTS(FBTTh₂)₂ were not located at the P3HT/PCBM interface, P3HT excitons transferred to the dye could not contribute to the photocurrent generation because of the cascaded energy structures both in HOMO and LUMO levels as shown in Figure 5-1.^[9] Thus, these findings show that the majority of p-DTS(FBTTh₂)₂ are spontaneously segregated to the P3HT/PCBM interface.

Table 5-1. Surface energy of materials used in this study.

	P3HT	p-DTS(FBTTh ₂) ₂	PCBM
$\gamma / \text{mJ m}^{-2}$	18.9	21.1	30.6

Finally, the origin of such spontaneous segregation of p-DTS(FBTTh₂)₂ molecules in ternary blend films is discussed in terms of surface energy (γ). The surface energy of each material employed in this study was evaluated by the contact angle method. Sumita et al. have studied the location of the third material in polymer/polymer blends in terms of the surface energy.^[22] They introduced a key parameter of the wetting coefficient (ω), which is evaluated from the surface energy of each component material, to predict the location of the third material fillers in polymer/polymer binary blends. It is suggested that the location of dye molecules in P3HT/PCBM blends can be predicted on the basis of the wetting coefficient.^[12] The surface energy of materials used in this study is summarized in Table 5-1. The wetting coefficient of p-DTS(FBTTh₂)₂ for P3HT/PCBM blends is evaluated to be 0.62, suggesting that the p-DTS(FBTTh₂)₂ are likely to be located at the interface of P3HT and PCBM. Therefore it is concluded that dye location is the key to success for efficient sensitization in ternary blends.

5.4. Conclusions

The efficient ternary blend solar cells consisting of P3HT, PCBM, and a small low-bandgap molecule p-DTS(FBTTh₂)₂ were demonstrated. Because of the

complementary absorption of P3HT and p-DTS(FBTTh₂)₂, the photocurrent response range was extended to the near-IR range. Furthermore, the photocurrent due to the P3HT absorption was also significantly improved. This is because of efficient energy transfer from P3HT excitons to p-DTS(FBTTh₂)₂ molecules located at the P3HT/PCBM interface. Interestingly, the dye molecules are spontaneously segregated to the interface. This is partly because p-DTS(FBTTh₂)₂ has intermediate surface energy between P3HT and PCBM. As a result, the PCE of P3HT/PCBM/p-DTS(FBTTh₂)₂ ternary blend solar cells was improved by more than 20% compared with that of the P3HT/PCBM binary blend solar cell.

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Chapter 6

Dye Sensitization in the Visible Region for Low-Bandgap Polymer Solar Cells

6.1. Introduction

Polymer solar cells have attracted increasing attention because of their unique advantages such as light weight, flexible, and low-cost and high-throughput processing for large-area devices.^[1-3] Currently, a power conversion efficiency of more than 10% has been reported.^[4,5] This remarkable progress is mainly due to intensive developments of various low-bandgap polymers that can harvest the solar light in the near-IR region.^[6-10] Low-bandgap polymers have an absorption band in the near-IR region but an absorption window in the visible region at the same time because of their narrow absorption bandwidth. In other words, it would be difficult to harvest the solar light over a wide wavelength range by using low-bandgap polymers alone. For further improvements, it is necessary to harvest much more photons not only in the visible but also in the near-IR region. In order to overcome this limitation, ternary blend solar cells have been proposed in recent years.^[11-25] Previously, it has been demonstrated near-IR dye sensitization of polymer/fullerene solar cells, in which the light-harvesting efficiency in the near-IR region can be improved by incorporating a near-IR dye into binary blend solar cells based on a wide-bandgap polymer and a fullerene derivative.^[11]

In this chapter, dye sensitization in the visible region for low-bandgap polymer solar cells is studied based on poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-*alt*-thiophene-2,5-diyl] (PTQ1) and phenyl-C₆₁-butyric acid methyl ester (PCBM). For dye sensitization in the visible region, a wide-bandgap molecule tris[4-(5-dicyanomethylidenemethyl-2-thienyl)phenyl]amine (TDCV-TPA) was incorporated into low-bandgap binary blends of PTQ1/PCBM. As a result, the light-harvesting efficiency was improved in the visible region and hence the short-circuit current density J_{SC} of ternary blend solar cells was increased by 24% compared to that of control solar cells based on PTQ1/PCBM binary blends. The sensitization mechanism in PTQ1/PCBM/TDCV-TPA solar cells is discussed in terms of dye location in the ternary blend films.

6.2. Experimental

6.2.1 Materials

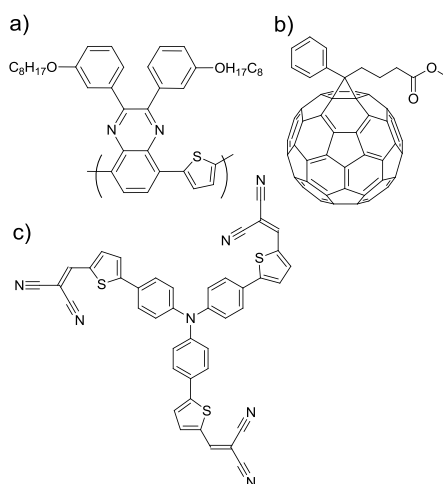


Figure 6-1. Chemical structures of materials employed in this study: a) PTQ1, b) PCBM, and c) TDCV-TPA.

Three kinds of materials were employed for ternary blend films: PTQ1 (Solarmer, number-averaged molecular weight, $M_n \approx 28,000 \text{ g mol}^{-1}$), PCBM (Frontier Carbon, E100H), and TDCV-TPA (Aldrich).

6.2.2. Device Fabrication

Ternary blend solar cells were fabricated as follows. First, indium/tin oxide (ITO)-coated glass substrates ($10 \text{ } \Omega \text{ per square}$) were washed by ultrasonication in toluene, acetone, ethanol for 15 min, dried with nitrogen gas, and then cleaned with a UV- O_3 cleaner (Nippon Laser & Electronics NL-UV253S) for 30 min. A thin layer ($\sim 40 \text{ nm}$) of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS; H. C. Starck PH500) was spin-coated onto the cleaned substrates at a spin rate of 3000 rpm, and the layer was dried at $140 \text{ }^\circ\text{C}$ for 10 min in air. The solution of PEDOT:PSS was filtered by using a $0.45 \text{ } \mu\text{m}$ PTFE syringe filter prior to the spin-coating. A ternary blend active layer of PTQ1/PCBM/TDCV-TPA was prepared by spin-coating on the PEDOT:PSS-coated ITO substrate at a spin rate of 1000 rpm for 60 s. The ternary blend solution was prepared as follows: PTQ1, PCBM, and TDCV-TPA were dissolved in *o*-dichlorobenzene at a concentration ratio of 20 : 40 : 2 mg mL^{-1} ([TDCV-TPA] = 3.2 wt%) and then the mixed solution was stirred at $40 \text{ }^\circ\text{C}$ overnight. Note that the dye composition was optimized in the range from 1.6 to 4.8 wt% and the best performance was obtained at 3.2 wt%. An electrode of Ca/Al layer (15/70 nm) was deposited in sequence on top of the active layer at $2.5 \times 10^{-4} \text{ Pa}$. The effective device area was 0.07 cm^2 .

6.2.3. Measurements

Electrochemical properties were examined by cyclic voltammetry. The cyclic voltammograms were performed with a potentiostat/galvanostat (Princeton Applied Research, 273A) in an Ar-bubbled o-dichlorobenzene/acetonitrile = 4 : 1 (v/v) solution containing 0.1 M of tetrabutylammonium tetrafluoroborate as a supporting electrolyte with an Ag/Ag⁺ (0.01 M AgNO₃) as a reference electrode, a Pt wire as a counter electrode, and Pt as a working electrode with an area of 2.0 mm². The scan rate was set to 50 mV s⁻¹.

The ionization potential of PTQ1 and PCBM was measured with a photoelectron yield spectrometer (Riken Keiki, AC-3). All the neat films (ca. 60 nm) were fabricated by spin-coating from each chlorobenzene solution on the PEDOT:PSS-coated ITO substrate. 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 as reported previously.^[28]

The *J*-*V* characteristics were measured in a nitrogen atmosphere with a direct current/voltage and a current source/monitor (Advantest, R6243) in the dark and under illumination with AM1.5G simulated solar light at 100 mW cm⁻². The light intensity was corrected with a calibrated silicon photodiode reference cell (Bunkoh-Keiki, BS-520). The active area of the device was 0.07 cm². The EQE spectra were measured with a digital electrometer (Advantest, R8252) under monochromatic light illumination from a 500-W xenon lamp (Thermo Oriel, 66921) with optical cut filters and a monochromator (Thermo Oriel, Cornerstone). The illumination was carried out from the ITO side under nitrogen atmosphere at room temperature.

Absorption and photoluminescence (PL) spectra were measured with a spectrophotometer (Hitachi, U-3500) and a spectrofluorometer (Horiba Jobin Yvon, FluororLog-3) equipped with a calibrated iHR320 imaging detector respectively.

Contact angles θ_X of ultrapure water droplets were measured on a spin-coated film of material X at room temperature. The surface energy γ_X of the material X was evaluated from θ_X by the Neumann's equation combined with Young's equation. The interfacial energy γ_{A-B} between materials A and B was evaluated from γ_A and γ_B by the Neumann's equation. The wetting coefficient ω_C of material C in a blend of materials A and B was evaluated from the interfacial energies. The details are described elsewhere.^[15,26]

6.3. Results and Discussion

6.3.1. Optoelectronic Properties

As shown in Figure 6-2a, PTQ1 has an absorption band at around 640 nm and an absorption window at around 500 nm, and TDCV-TPA has an absorption band at around 550 nm. In the PL spectra, PTQ1 and TDCV-TPA have an emission peak at around 730 and 700 nm, respectively. The optical bandgap of PTQ1 was evaluated to be 1.8 eV from the wavelength of intersection between the absorption and PL spectra. On the other hand, the HOMO level was estimated to be 5.1 eV for PTQ1 and 6.2 eV for PCBM by photoemission yield spectroscopy in the solid state and to be 5.5 eV for TDCV-TPA by the cyclic voltammetry. The LUMO level was evaluated to be 3.8 eV for PCBM and 3.4 eV for TDCV-TPA by the cyclic voltammetry and to be 3.3 eV for

PTQ1 from the optical bandgap and HOMO level. The energy diagrams of these materials are summarized in Figure 6-2b.

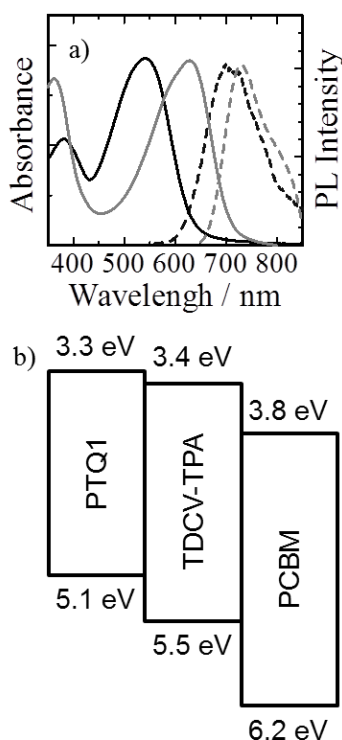


Figure 6-2. a) Absorption (solid lines) and photoluminescence (broken lines) spectra of PTQ1 (gray lines) and TDCV-TPA (black lines). b) Energy diagram of materials employed in this study. The figures represent the HOMO (lower) and LUMO (upper) energy in electron volts.

Figure 6-3 shows the absorption spectra of PTQ1/PCBM (1:2 w/w) binary and PTQ1/PCBM/TDCV-TPA (1:2:0.1 w/w) ternary blend films. As shown in the figure, the absorption bandwidth (full width at half maximum) is effectively increased from 450 to 600 nm by a small addition of TDCV-TPA at only one tenth the weight ratio. This is because TDCV-TPA has a large absorption coefficient of $2.5 \times 10^5 \text{ cm}^{-1}$ at 550 nm.^[27] Furthermore, it is noteworthy that there is a large spectral overlap between the

PL band of TDCV-TPA and the absorption band of PTQ1. Assuming point dipoles, the Förster radius is estimated to be 3.1 nm from the spectral overlap with a PL quantum efficiency of 14% for TDCV-TPA and a molar absorption coefficient of $2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 600 nm of PTQ1. Thus, the energy transfer from TDCV-TPA to PTQ1 would be efficient in the blend film as described later. In summary, these two materials are a suitable combination for extending the light-harvesting range because of the complementary absorption bands and for the efficient energy transfer from TDCV-TPA to PTQ1.

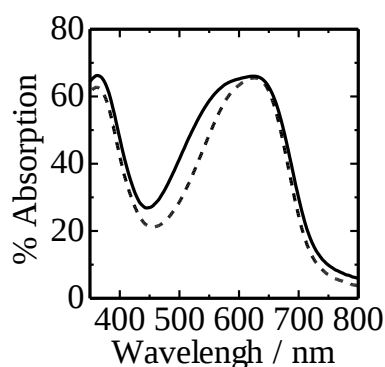


Figure 6-3. Absorption spectra of PTQ1/PCBM binary (broken line) and PTQ1/PCBM/TDCV-TPA ternary (solid line) blend films.

6.3.2. Energy and Charge Transfer

The efficiency of the energy transfer from TDCV-TPA to PTQ1 was investigated by measuring the PL spectrum of PTQ1/TDCV-TPA binary blend films excited at 500 nm where TDCV-TPA has an absorption band as mentioned above. Figure 6-4a shows the PL spectra of PTQ1/TDCV-TPA binary blend and TDCV-TPA neat films. As shown in the figure, no emission from TDCV-TPA was observed and

instead emission from PTQ1 was clearly observed for the PTQ1/TDCV-TPA binary blends even though TDCV-TPA was excited at 500 nm. This result is indicative of quantitative energy transfer from TDCV-TPA to PTQ1: all the TDCV-TPA excitons are efficiently transferred to PTQ1 domains in the blend.

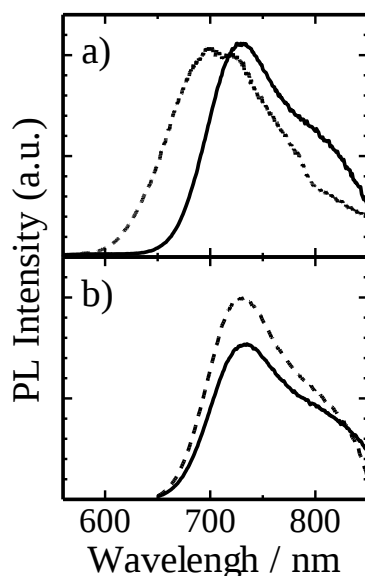


Figure 6-4. PL spectra of a) PTQ1/TDCV-TPA blend (solid line) and TDCV-TPA neat (broken line) films excited at 500 nm, and b) PTQ1/TDCV-TPA blend (solid line) and PTQ1 neat (broken line) films excited at 630 nm.

Next, the possibility of charge transfer from PTQ1 excitons to TDCV-TPA is studied. Figure 6-4b shows the PL spectra of PTQ1/TDCV-TPA binary blend and PTQ1 neat films upon the selective excitation of PTQ1 at 630 nm. As shown in the figure, the PTQ1 emission from PTQ1/TDCV-TPA binary blend was comparable to that from the PTQ1 neat film, indicating negligible charge transfer from PTQ1 excitons to TDCV-TPA. This is probably because offset energy in the LUMO levels between PTQ1 and TDCV-TPA is as small as 0.1 eV, which would not be enough to break the

Coulomb attraction in PTQ1 excitons. In other words, TDCV-TPA does not serve as a quencher for PTQ1 excitons.

6.3.3. Photovoltaic Properties

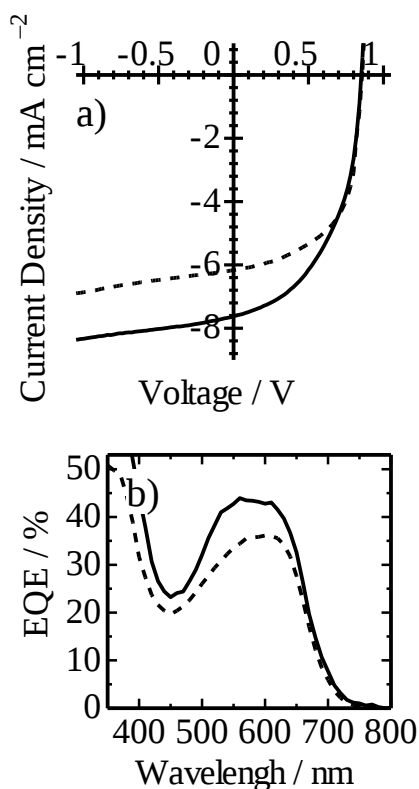


Figure 6-5. a) J - V characteristics and b) EQE spectra of PTQ1/PCBM binary blend (broken lines) and PTQ1/PCBM/TDCV-TPA ternary blend (solid lines) solar cells.

Figure 6-5a shows J - V characteristics of PTQ1/PCBM/TDCV-TPA ternary blend and PTQ1/PCBM binary blend solar cells under the simulated solar illumination at 100 mW cm^{-2} . The device parameters are summarized in Table 6-1. As shown in the figure, the J_{SC} is significantly improved by more than 20% from 6.2 to 7.6 mA cm^{-2}

even though the amount of TDCV-TPA is added as small as 3.2 wt%. This improvement in J_{SC} is ascribed to the increase in the EQE signals over 500 – 600 nm as shown in Figure 6-5b. The bandwidth of the EQE spectrum was larger for the PTQ1/PCBM/TDCV-TPA ternary cell than for the PTQ1/PCBM binary blend cell. This is because the absorption bandwidth is extended by addition of TDCV-TPA as mentioned above. It should be noted that there is no change in the open-circuit voltage (V_{OC}) between ternary and binary blend solar cells. This finding suggests that TDCV-TPA molecules are not involved in the charge recombination at the heterojunction. Rather, TDCV-TPA molecules are possibly located in PTQ1 or PCBM domains as discussed below.

Table 6-1. Photovoltaic parameters of PTQ1/PCBM/TDCV-TPA ternary and PTQ1/PCBM binary blend solar cells.

	$J_{SC} / \text{mA cm}^{-2}$	V_{OC} / V	FF	PCE / %
Ternary	7.6	0.86	0.50	3.3
Binary	6.2	0.86	0.59	3.1

6.3.4. Dye Location

Table 6-2. Surface energy of materials employed in this study.

	TDCV-TPA	PTQ1	PCBM
$\gamma / \text{mJ m}^{-2}$	23.5	26.6	30.6

Finally, the location of dye molecules in ternary blend films is discussed in terms of surface energy (γ). Table 6-2 summarizes the surface energy of each material evaluated by the contact angle method.

Sumita et al. have studied the location of the third material in polymer/polymer blends in terms of surface energy.^[26] They introduced a key parameter of the wetting coefficient (ω), which is evaluated from the surface energy of each component material, to predict the location of the third material fillers in polymer/polymer binary blends. It was also reported that the location of dye molecules in polymer/PCBM blends can be predicted on the basis of the wetting coefficient.^[15] The wetting coefficient of TDCV-TPA for PTQ1/PCBM blends is evaluated to be 2.5, suggesting that TDCV-TPA molecules are likely to be located in PTQ1 domains with a lower surface energy. This is consistent with no change in the V_{OC} between ternary and binary blend solar cells mentioned above. Therefore, it is concluded that TDCV-TPA molecules are primarily located in PTQ1 domains. In this case, PTQ1 excitons are efficiently generated from TDCV-TPA excitons by energy transfer even upon the photoexcitation of TDCV-TPA in the shorter wavelength region, and hence migrate to a PTQ1/PCBM interface to generate charge carriers. Thus, the dye location in low-bandgap polymer domains is the key to success for efficient dye sensitization in the visible region.

6.4. Conclusions

In summary, it has been demonstrated a novel approach to improving the photovoltaic performances of binary solar cells based on a low-bandgap polymer PTQ1 and PCBM by incorporating a wide-bandgap molecule TDCV-TPA. As a result, the J_{SC} is improved by more than 20% from 6.2 to 7.6 mA cm⁻² compared to that of the

control binary cell. This is because the incorporation of TDCV-TPA can extend the absorption bandwidth to collect much more photons in the visible as well as in the near-IR region. The keys to the improvement are as follows: 1) dye molecules should be located in low-bandgap polymer domains, 2) the PL band of wide-bandgap dye molecules should be well overlapped with the absorption band of low-bandgap polymers to make sure efficient energy transfer from the dye to the matrix polymer, and 3) polymer excitons should not be quenched by incorporating dye molecules. For the selective dye loading to low-bandgap polymer domains, the surface energy of wide-bandgap molecules should be lower than that of low-bandgap polymer and PCBM. This requirement is different from that for near-IR dye molecules into the heterojunction. Thus, this approach is compatible with near-IR dye sensitization. Therefore, it is proposed that it would be useful for further improvements to employ wide-bandgap and near-IR dye molecules at the same time in low-bandgap polymer solar cells in order to extend the light-harvesting range from visible to near-IR region.

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Summary

In this thesis, the author designed a series of ternary blend solar cells to improve the light-harvesting efficiency. The photovoltaic performances and sensitization mechanism of these ternary blend solar cells were studied.

In Chapter 1, the historical background and motivation of this thesis have been summarized in terms of organic solar cells, ternary blend solar cells, and exciton harvesting by energy transfer and exciton diffusion.

In Chapter 2, a new class of cross-linkable fullerene derivative (bis-PCBVB) has been synthesized by functionalizing the [6,6]-diphenyl-C₆₂-bis(butyric acid methyl ester) with two styryl groups to measure the exciton diffusion length through bilayer model. In-situ cross-linking of the bis-PCBVB spin-coated film was carried out by heating at 170 °C for 60 min to obtain a smooth and solvent-resistant film (p-PCBVB). The HOMO level was estimated to be 6.0 eV by photoemission yield spectroscopy, and the LUMO energy level was estimated to be 3.8 eV from the optical bandgap and HOMO level. These HOMO–LUMO energy levels were the same as those of its parent material bis-PCBM, showing that p-PCBVB film acts as an electron acceptor for typical conjugated polymers. The PL intensity of PF12TBT/p-PCBVB bilayer sample before and after the sample was thermal annealed at 140 °C for 60 min to examine the thermal stability of the bilayer structure. The unchanged PL intensity before and after thermal anneal indicated there is no interdiffusion between PF12TBT and p-PCBVB, which provided a well-defined planar heterojunction for studying exciton diffusion at organic interfaces. With this bilayer model system, both the exciton diffusion length

and diffusion coefficient of a conjugated polymer PF12TBT were evaluated to be 11 nm and $9.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, respectively. It is believed that this fullerene polymer p-PCBVB is widely applicable to systematic studies of the exciton diffusion length in various conjugated polymers through the bilayer model.

In Chapter 3, the effective diffusion length of P3HT excitons has been evaluated by using donor/acceptor bilayers with two different exciton-quenching acceptors. In P3HT/p-PCBVB bilayers, the exciton diffusion length was evaluated to be 15 nm, which is slightly shorter than that evaluated for P3HT crystalline domains by singlet exciton–exciton annihilation. In other words, this exciton diffusion length is an average value for P3HT amorphous and crystalline domains. In P3HT/PSBTBT bilayers, on the other hand, the effective diffusion length of P3HT excitons was evaluated to be 30 nm. This is most probably because P3HT excitons are more efficiently collected to the PSBTBT quenching wall in the bilayer film. The Förster radius was estimated to be 3.5 nm for the energy transfer from P3HT to PSBTBT on the basis of the spectral overlap. This finding suggest that in ternary blends of P3HT, PSBTBT, and PCBM, the energy transfer would enhance the effective diffusion length as is the case with the bilayer system employed in this study.

In Chapter 4, highly efficient ternary blend solar cells have been fabricated with a highly crystalline wide-bandgap polymer P3HT, a low-bandgap polymer PSBTBT, and PCBM. This is because highly crystalline P3HT forms large crystalline domains and hence would improve charge transport even in ternary blends. Even in such large P3HT crystalline domains, P3HT excitons are effectively collected by energy transfer to PSBTBT domains mixed with PCBM where charge carriers are efficiently generated. This is because of the large spectral overlap between the P3HT fluorescence and the

PSBTBT absorption. As a result, J_{SC} was improved to 15.8 mA cm^{-2} with a high FF of 0.61 at a weight ratio of P3HT : PSBTBT : PCBM = 20 : 30 : 50, and hence PCE reached 5.6% , which is even higher than that of both individual binary solar cells based on P3HT/PCBM and PSBTBT/PCBM reported so far. This finding is generally applicable to other ternary blend polymer solar cells. Therefore, it can be said that a wide-bandgap crystalline polymer and a low-bandgap amorphous polymer would be good combination for highly efficient ternary solar cells. Because of large spectral overlap between the wide-bandgap polymer fluorescence and the low-bandgap polymer absorption, excitons even in large crystalline domains of the wide-bandgap polymer are efficiently harvested by energy transfer to the low-bandgap polymer domains mixed with PCBM followed by prompt charge generation. Most of charge carriers are likely to be transferred to more stable crystalline domains of the wide-bandgap polymer where charge transport would be efficient.

In Chapter 5, a low-bandgap small molecule p-DTS(FBTTh₂)₂ has been incorporated into polymer solar cells based on blends of P3HT and PCBM to improve the light-harvesting efficiency in the near-IR range. With addition of 3.4 wt% p-DTS(FBTTh₂)₂, J_{SC} was raised significantly from 8.2 to 10.9 mA cm^{-2} and hence the PCE was increased by more than 20% compared to that of P3HT/PCBM binary cells. Interestingly, the EQE was enhanced not only at the absorption band of p-DTS(FBTTh₂)₂ in the near-IR range but also at the P3HT absorption band in the visible range. This is because of efficient energy transfer from P3HT excitons to p-DTS(FBTTh₂)₂ molecules located at the P3HT/PCBM interface. This finding indicates that the dye molecules are spontaneously segregated to the interface. This is partly because p-DTS(FBTTh₂)₂ has intermediate surface energy between P3HT and

PCBM.

In Chapter 6, ternary blend solar cells have been fabricated by incorporating a wide-bandgap molecule TDCV-TPA into a binary blend of a low-bandgap polymer PTQ1 and PCBM in order to enhance exciton generation and hence charge generation in the visible region. As a result, the J_{SC} was improved by more than 20% from 6.2 to 7.6 mA cm^{-2} compared to that of the control binary cell. This is because the incorporation of TDCV-TPA can extend the absorption bandwidth to collect much more photons in the visible as well as in the near-IR region. The keys to the improvement are as follows: 1) dye molecules should be located in low-bandgap polymer domains, 2) the PL band of wide-bandgap dye molecules should be well overlapped with the absorption band of low-bandgap polymers to make sure efficient energy transfer from the dye to the matrix polymer, and 3) polymer excitons should not be quenched by incorporating dye molecules. For the selective dye loading to low-bandgap polymer domains, the surface energy of wide-bandgap molecules should be lower than that of low-bandgap polymer and PCBM.

List of Publications

Chapter 2.

“Measurement of Exciton Diffusion in a Well-defined Donor/Acceptor Heterojunction Based on a Conjugated Polymer and Cross-linked Fullerene Derivative”

Yanbin Wang, Hiroaki Bente, Shunji Ohara, Daichi Kawamura, Hideo Ohkita, Shinzaburo Ito

ACS Appl. Mater. Interfaces, DOI: 10.1021/am503434p.

Chapter 3.

“Efficient Exciton Harvesting through Long-Range Energy Transfer”

Yanbin Wang, Hideo Ohkita, Hiroaki Bente, Shinzaburo Ito

To be Submitted.

Chapter 4.

“Highly Efficient Exciton Harvesting and Charge Transport in Ternary Blend Solar Cells Based on Wide- and Low-Bandgap Polymers”

Yanbin Wang, Hideo Ohkita, Hiroaki Bente, Shinzaburo Ito

To be Submitted.

Chapter 5.

“Near-IR Sensitization of Polymer Solar Cells Incorporating Low-Bandgap Small Molecule”

Yanbin Wang, Hideo Ohkita, Hiroaki Bente, and Shinzaburo Ito

Submitted to Trans. Mater. Res. Soc. Jpn.

Chapter 6.

“Dye Sensitization in the Visible Region for Low-Bandgap Polymer Solar Cells”

Yanbin Wang, Bo Zheng, Yasunari Tamai, Hideo Ohkita, Hiroaki Bente, and Shinzaburo Ito

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