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Formation of Methanofullerene Cation in Bulk Heterojunction Polymer Solar Cells Studied by Transient Absorption Spectroscopy**

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Photogenerated charge carriers for blend films of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) have been investigated by transient absorption spectroscopy. The blend film with a low PCBM fraction (<10 wt %) exhibits a wide absorption that ranges from 900 to 1000 nm, which is characteristic of the MDMO-PPV hole polaron and PCBM radical anion. On the other hand, the blend film with a higher PCBM fraction (> 30 wt %) exhibits a major absorption band at ~900 nm, which is characteristic of the PCBM radical cation. For identification of charge carriers, the absorption spectrum and molar absorption coefficient of each charged species have been evaluated separately using various combinations of electron donor and acceptor materials. Consequently, the MDMO-PPV hole polaron has been found to have a broad absorption at ~950 nm and the PCBM radical anion and cation show a distinct absorption at 1020 and 890 nm, respectively. On the basis of these absorption spectra, the transient spectra observed for the blend films have been simulated. The spectrum for a low PCBM fraction is well reproduced by superposition of the absorption spectra of the MDMO-PPV hole polaron and PCBM radical anion. On the other hand, the spectrum for a high PCBM fraction is well reproduced by superposition of the absorption spectra of the MDMO-PPV hole polaron, PCBM radical anion, and PCBM radical cation, which indicates that the PCBM radical cation is formed in the blend films with PCBM at a high concentration. Possible mechanisms for the formation of the PCBM radical cation in the blend are also discussed.

1. Introduction

Since the discovery of efficient electron transfer in blend films of conjugated polymers with fullerene,^[1,2] such blend systems have attracted increasing interest in photophysical studies and application to organic devices. For blend films of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), ultrafast charge separation has been reported.^[3] Furthermore, the intermixing of the polymer electron donor and the fullerene electron acceptor can provide a significantly enlarged interfacial area of donor and acceptor 'bulk heterojunction', which results in a high charge separation efficiency. This blend system is one of the most thoroughly

studied donor-acceptor pairs for bulk heterojunction organic solar cells, and exhibits power conversion efficiencies of about 3% with a 1:4 weight ratio of polymer to fullerene.^[4-6] In other words, the most efficient solar cells that consist of MDMO-PPV and PCBM require a high content of PCBM (80 wt %). This is unfavorable for light absorption, because fullerene derivatives such as PCBM have a low absorption in the visible region compared with conjugated polymers such as MDMO-PPV. Moreover, this biased ratio seems to have a disadvantage for charge transport, because charge-carrier mobility for electrons in PCBM ($2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[7] is more than three orders of magnitude larger than that for holes in a MDMO-PPV pristine film ($3 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[8]

Recent studies have shown that the hole mobility of the MDMO-PPV/PCBM blend is larger than that of pristine MDMO-PPV by more than two orders of magnitude at 80 wt % PCBM,^[8,9] which suggests that the charge transport in the blend is much more balanced than previously assumed. This finding seems contradictory to the prevailing view that conjugated polymers such as MDMO-PPV act as a hole-transporting material and that fullerene derivatives such as PCBM act as an electron-transporting material. Blom et al. proposed that a ring-like molecular conformation of MDMO-PPV might be the origin of the poor transport properties in the pristine film, which would be hindered in the blend to improve the hole mobility.^[8] On the other hand, Nelson and coworkers

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demonstrated that adding PCBM to the blend increases the mobility of both the electron and hole compared with the pristine MDMO-PPV.^[9] They also found that electron and hole mobilities are of similar magnitude for PCBM dispersed in a polystyrene (PS) matrix. Indeed, ambipolar charge transport has already been reported for fullerene-based field-effect transistors (FET) that include PCBM.^[10,11] However, it is still not clear whether the PCBM radical cation is formed as a hole carrier in the blend films or not.

Herein, we report a detailed spectroscopic study of charged carriers formed in MDMO-PPV/PCBM blend films at a PCBM concentration that ranges from 0 to 80 wt % by transient absorption spectroscopy. For identification of charge carriers formed in the blend, the absorption spectrum and the molar absorption coefficient of each charge carrier, MDMO-PPV hole polaron, PCBM radical anion, and PCBM radical cation, were measured by using various combinations of electron donor and acceptor materials shown in Figure 1. The transient absorption spectra of the blend (<10 wt % PCBM) were reproduced by a simple summation of that of the MDMO-PPV hole polaron and PCBM radical anion. On the other hand, the transient spectra (>30 wt % PCBM) were not reproduced by a simple summation but were well reconstructed by a summation of that of the MDMO-PPV hole polaron, PCBM radical anion, and PCBM radical cation. This finding provides spectroscopic evidence of the formation of the PCBM radical cation in blend films with PCBM at a high concentration, and suggests that PCBM serves not only as an electron-transporting material but also a hole-transporting material in bulk heterojunction solar cells with high PCBM fractions.

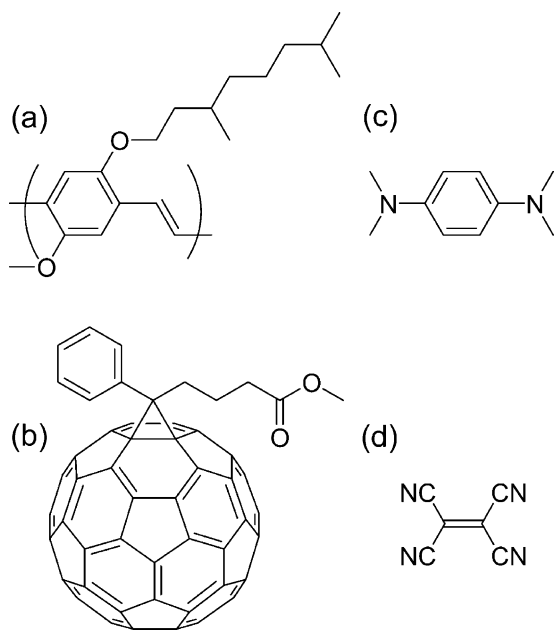


Figure 1. Chemical structures used in this study: a) MDMO-PPV, b) PCBM, c) TMPD, and d) TCNE.

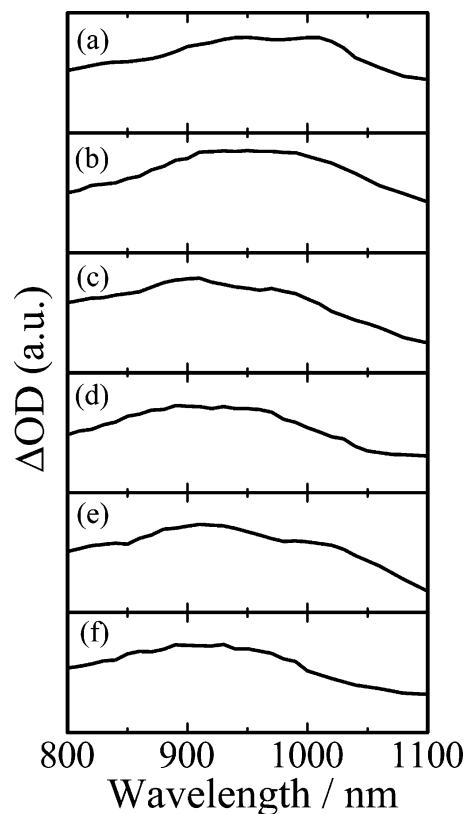


Figure 2. Transient absorption spectra of MDMO-PPV/PCBM blend films at 1 μs after the laser excitation at 500 nm with a fluence of 30 μJ cm⁻² pulse⁻¹. The PCBM concentration is as follows: a) 5, b) 10, c) 30, d) 50, e) 68, and f) 80 wt %.

2. Results

2.1. Transient Absorption Spectra

Figure 2 shows the transient absorption spectra of MDMO-PPV/PCBM blend films with various concentrations of PCBM ranging from 5 to 80 wt %. The blend films with PCBM at a low concentration (<10 wt %) exhibit broad absorption bands from 900 to 1000 nm. The absorption peak at ~1000 nm is characteristic of fullerene radical anions.^[12] The remaining broad absorption around 950 nm is indicative of the formation of MDMO-PPV hole polarons as reported previously.^[13] Therefore, the broad absorption from 900 to 1000 nm is tentatively assigned to the formation of an MDMO-PPV hole polaron and a PCBM radical anion as charge carriers in the blend films at low PCBM concentrations. On the other hand, the transient absorption spectra changed at higher PCBM concentrations (>30 wt %) where a new absorption band appeared at ~900 nm. One possible explanation for this spectroscopic change is that another charge carrier is newly formed in the blend films with PCBM at a high concentration, as is discussed later. Another explanation is that the absorption spectra of charge carriers vary with the PCBM concentration. Fullerene C₆₀ anions in films have essentially the same

absorption spectra as in solution.^[14] More probably, therefore, the absorption spectrum of MDMO-PPV polarons may be dependent upon the PCBM concentration. Blom et al. proposed the conformational change of MDMO-PPV because of interactions between MDMO-PPV and PCBM to explain the high hole mobility in the blend films with PCBM at a high concentration.^[7] The conformational change would cause a spectroscopic change in transient absorption of the blend films heavily doped with PCBM.

To examine the dependence of the absorption spectrum of MDMO-PPV polarons on dopant concentrations, we fabricated blend films with tetracyanoethylene (TCNE) instead of PCBM because the TCNE radical anion has no absorption band from 900 to 1000 nm. Furthermore, TCNE is a strong electron acceptor ($E_{1/2}(\text{TCNE}^-/\text{TCNE}) = 0.24 \text{ V}$ versus saturated calomel electrode (SCE))^[15] compared with C_{60} ($E_{1/2}(\text{C}_{60}^-/\text{C}_{60}) = -0.3\text{--}0.4 \text{ V}$ versus SCE).^[12] Figure 3 shows the transient absorption spectra of MDMO-PPV/TCNE blend films with 5 and 50 wt % TCNE. For the blend film with 5 wt % TCNE, a broad absorption is observed at $\sim 950 \text{ nm}$. A similar absorption is observed at $\sim 960 \text{ nm}$ for the blend film with 50 wt % TCNE. As mentioned before, both spectra can be safely assigned to the MDMO-PPV hole polaron. It should be noted that there is no distinct absorption peak at $\sim 900 \text{ nm}$ where a new absorption band was observed for MDMO-PPV/PCBM blend films with PCBM at a high concentration ($> 30 \text{ wt } \%$). Rather, the 900 nm band is more likely a result of the formation of charge carriers related to PCBM. To study charge carriers formed in the blend films, we will assign the absorption spectrum for possible charge carriers in the following section.

2.2. Assignment of Charge Carriers

For the quantitative discussion, we will not only assign the absorption spectrum but also evaluate the molar absorption

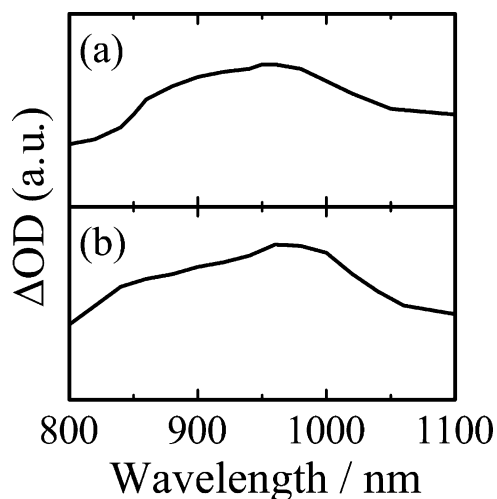


Figure 3. Transient absorption spectra of MDMO-PPV/TCNE blend films at $10 \mu\text{s}$ after the laser excitation at 500 nm with a fluence of $30 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$. The TCNE concentration is: a) 5 and b) 50 wt %.

coefficient of each charge carrier by using various combinations of electron donor and acceptor materials.

First, we measured the transient absorption spectra of an MDMO-PPV pristine film to confirm the absorption of the MDMO-PPV hole polaron. Figure 4a shows transient absorption spectra of the MDMO-PPV pristine film from 2 to $10 \mu\text{s}$ after the laser excitation. The absorption peak shifted from 860 nm at $< 2 \mu\text{s}$ to $\sim 950 \text{ nm}$ with a time delay of $> 5 \mu\text{s}$, which demonstrates the formation of two independent transient species in the pristine film. Figure 4b shows the time evolution of the transient signals at 850 nm (solid line) and 940 nm (broken line). The decay at 850 nm was fitted with a sum of a single-exponential function and a power equation, $\Delta\text{OD} = A \exp(-t/\tau) + B \cdot t^{-\alpha}$, while the decay at 940 nm was well fitted with only a power equation. The mono-exponential phase decayed with a lifetime of $\tau \sim 0.5 \mu\text{s}$ in an Ar atmosphere and disappeared in an O_2 atmosphere. The absorption peak and the lifetime in the earlier time domain were in agreement with those reported for the triplet-triplet (T-T) absorption of PPV derivatives.^[16,17] This fast decay is, therefore, assigned to MDMO-PPV triplet excitons. For a time delay of $> 5 \mu\text{s}$, on the other hand, the decay at both 850 nm and 940 nm is well fitted by the power equation with the same exponent $\alpha = 0.27$, which suggests that there is one decay pathway. The power-law decay is characteristic of the

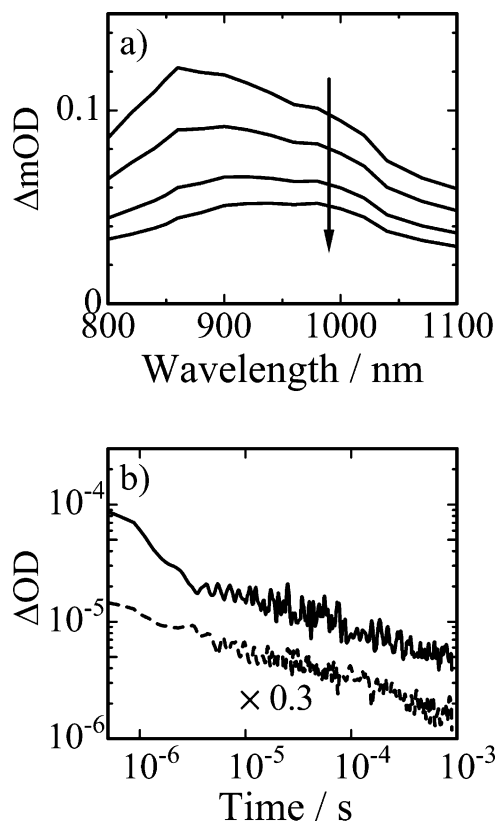


Figure 4. a) Transient absorption spectra of an MDMO-PPV pristine film (solid lines) at 1, 2, 5, and $10 \mu\text{s}$ after the laser excitation at 500 nm with a fluence of $30 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$. b) The transient decay at 850 nm (solid line) and 940 nm (broken line). The decay at 940 nm is multiplied by a factor of 0.3.

bimolecular recombination of charged species in the presence of energetic disorder.^[18] Furthermore, the transient absorption spectra at $>5 \mu\text{s}$ of the MDMO-PPV pristine film were similar to that assigned to the MDMO-PPV hole polaron in MDMO-PPV/TCNE blend films shown in Figure 3, which suggests that there is little contribution of the MDMO-PPV electron polaron to the absorption band. Thus, the absorption band at $\sim 950 \text{ nm}$ is safely attributable to the MDMO-PPV hole polaron. The molar absorption coefficient will be evaluated later by using the absorption spectrum at $10 \mu\text{s}$ as the MDMO-PPV hole polaron.

Next, we measured the transient absorption spectra of PS films doped with N,N,N',N' -tetramethyl-*p*-phenylenediamine (TMPD) as an electron donor and PCBM as an electron acceptor to assign the absorption of the PCBM radical anion. The weight ratio of each component in the film was PS/TMPD/PCBM = 5: 2: 3. As shown in Figure 5, two absorption bands were observed at 570 and 1020 nm. The absorption band at 570 nm is in good agreement with that reported for the oxidation product of TMPD called Wurster's Blue,^[19] and is, therefore, assigned to the TMPD radical cation. The absorption band at 1020 nm is assigned to the PCBM radical anion because, as mentioned before, various radical anions of fullerene derivatives have a characteristic absorption band around 1000 nm: a C_{60} radical anion (1080 nm), a methanofullerene radical anion (1040 nm), and a fulleropyrrolidine radical anion (1010 nm).^[12] In a time domain longer than 10 ps, as shown in the inset to Figure 5, both bands obeyed the power-law decay dynamics with the same exponent $\alpha \sim 0.25$. Thus, the same decay dynamics observed at 570 and 1020 nm is ascribable to the bimolecular recombination of the TMPD radical cation and PCBM radical anion without other decay pathways, which suggests that no other transient species such as singlet and triplet excitons contribute to the transient absorption spectra on the longer time scales ($>10 \text{ ps}$). Therefore, the molar absorption coefficient of the PCBM radical anion can be evaluated from the transient absorption

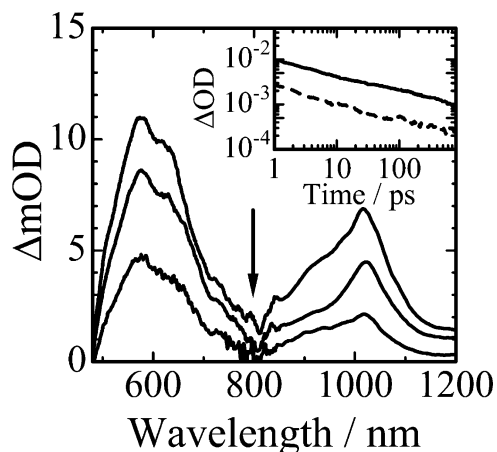


Figure 5. Transient absorption spectra of PS/TMPD/PCBM (5: 2: 3, w/w) blend films at 1, 2, and 10 ps after the laser excitation at 400 nm with a fluence of $65 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$. The inset shows the transient decay at 600 nm (solid line) and 1050 nm (broken line).

spectra at 10 ps. On the basis of the molar absorption coefficient of the TMPD radical cation ($\epsilon = 12\,000 \text{ M}^{-1} \text{ cm}^{-1}$),^[19,20] that of the PCBM radical anion was evaluated to be $\epsilon = 6000 \text{ M}^{-1} \text{ cm}^{-1}$ at 1020 nm. This value is smaller than that reported for the C_{60} radical anion ($\epsilon = 15\,000 \text{ M}^{-1} \text{ cm}^{-1}$) but rather comparable to that of fullerene derivatives: a fulleropyrrolidine radical anion ($\epsilon = 8000 \text{ M}^{-1} \text{ cm}^{-1}$) and a methanofullerene radical anion ($\epsilon = 10\,000 \text{ M}^{-1} \text{ cm}^{-1}$).^[12] Note that essentially the same transient absorption spectra were obtained for PS/TMPD/PCBM (2: 2: 6, w/w) blend films (data not shown). In other words, the PCBM radical anion has a characteristic absorption around 1020 nm, independent of the PCBM concentration. This trend is consistent with a previous report for C_{60} .^[14]

Finally, we measured the transient absorption spectra of a benzonitrile solution dissolved with PCBM as an electron donor and TCNE as an electron acceptor to assign the absorption of the PCBM radical cation. Note that this measurement was performed in solution because PCBM/TCNE blend films were not uniform at high TCNE concentrations owing to the poor solubility of TCNE. Photoexcitation of this blend solution will give a PCBM radical cation and a TCNE radical anion, because photo-induced electron transfer from the C_{60} triplet to TCNE has been reported.^[21] Figure 6 shows the transient absorption spectra of a mixture of PCBM and TCNE in benzonitrile. Two distinct absorption peaks were observed at 450 and 890 nm. The absorption band at 450 nm is indistinguishable from the spectrum of the TCNE radical anion previously reported^[22] and the other band at 890 nm is slightly blue-shifted compared with that of the C_{60} radical cation (980 nm)^[23,24] but is rather similar to that of a fullerene derivative (960 nm).^[25] These two bands are, therefore, assigned to the formation of the PCBM

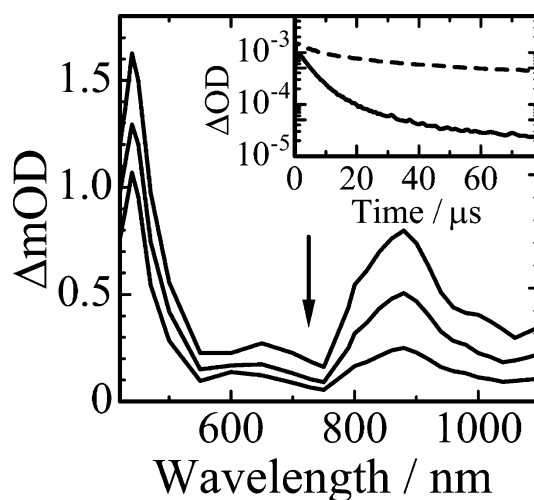


Figure 6. Transient absorption spectra of a PCBM/TCNE solution in benzonitrile at 2, 5, and 10 μs after the laser excitation at 400 nm with a fluence of $30 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$. The molar concentration is $[\text{PCBM}] = 1.3 \times 10^{-3} \text{ M}$ and $[\text{TCNE}] = 6.6 \times 10^{-3} \text{ M}$. The inset shows the transient decay at 900 nm (solid line) and 450 nm (broken line).

radical cation and TCNE radical anion. As shown in the inset to the figure, the transient signal at 890 nm decayed much faster than that at 450 nm, while both decay dynamics were finally similar at the longer time stage. The decay at 450 nm was well fitted with the sum of the first- and second-order equations: $\Delta OD = A \cdot t^{-1} + B \exp(-t/\tau)$ while the band at 890 nm obeyed the second order kinetics: $\Delta OD = A \cdot t^{-1}$. The mono-exponential lifetime of the transient signal at 450 nm was $\sim 80 \mu\text{s}$ and significantly shortened in an O_2 atmosphere. In a reference experiment, a similar transient absorption was observed at 450 nm with the same lifetime for a benzonitrile solution with TCNE alone. Thus, the first-order decay component of the blend solution is attributable to TCNE in the excited triplet state. The second-order decay is, therefore, assigned to bimolecular recombination of the PCBM radical cation and TCNE radical anion. On the basis of the molar absorption coefficient of the TCNE radical anion $\epsilon = 5670 \text{ M}^{-1} \text{ cm}^{-1}$ at 457 nm,^[22] that of the PCBM radical cation is evaluated to be $\epsilon = 9000 \text{ M}^{-1} \text{ cm}^{-1}$ at 890 nm, which is comparable to that of the C_{60} radical cation ($\epsilon = 11\,000 \text{ M}^{-1} \text{ cm}^{-1}$).^[23]

3. Discussion

3.1. Charge Carriers Formed in MDMO-PPV/PCBM Blends

We start off our discussion by considering charge carriers formed in MDMO-PPV/PCBM blend films. For blend films with PCBM at a low concentration, as mentioned above, the transient spectra observed were tentatively assigned to the formation of the MDMO-PPV hole polaron and PCBM radical anion. For confirmation of this assignment, the spectra for the film with 5 wt % PCBM were compared with a summation of each spectrum of the MDMO-PPV hole polaron and PCBM radical anion obtained in the previous section. As shown in Figure 7a, the reproduced spectrum was in good agreement with that observed for the blend film with 5 wt % PCBM. Therefore, we conclude that an MDMO-PPV hole polaron and a PCBM radical anion are formed as charge carriers in the blend films with PCBM at a low concentration ($< 10 \text{ wt } \%$). From the spectroscopic simulation, the molar absorption coefficient of the MDMO-PPV hole polaron is evaluated to be $\epsilon_{\text{MDMO-PPV}^+} = 15\,000 \text{ M}^{-1} \text{ cm}^{-1}$ on the basis of that of the PCBM radical anion $\epsilon_{\text{PCBM}^-} = 6000 \text{ M}^{-1} \text{ cm}^{-1}$. This value is comparable to an absorption cross section of polarons reported for a PPV derivative.^[26]

On the other hand, we considered earlier two possible explanations for the different transient spectra observed for blend films with PCBM at a high concentration. As shown in Figure 3, the absorption spectrum of the MDMO-PPV hole polaron at $\sim 950 \text{ nm}$ is essentially independent of TCNE dopant concentrations up to 50 wt % (which corresponds to $\sim 40\%$ by volume).^[27] This TCNE concentration is much higher than the 30 wt % PCBM concentration (which corresponds to $\sim 20\%$ by volume)^[30] above which spectroscopic changes were observed in the transient measurements for MDMO-PPV/PCBM blend films. Assuming that the heavy

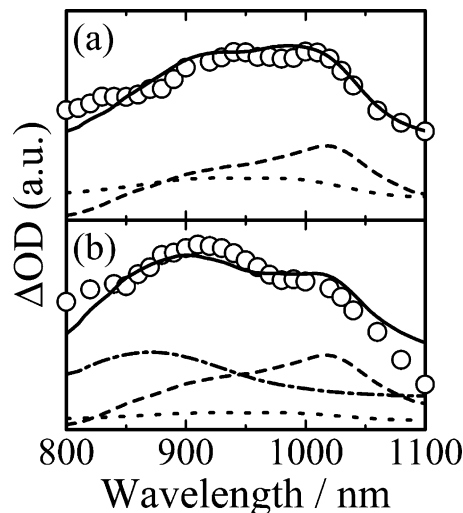


Figure 7. Transient absorption spectra of MDMO-PPV/PCBM blend films (open circles) at 1 μs after the laser excitation at 500 nm with a fluence of $30 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$. The PCBM concentration is a) 5 and b) 68 wt %. The solid lines represent absorption spectra simulated by a sum of each absorption spectrum of charge carriers: MDMO-PPV⁺ (dotted lines), PCBM⁻ (broken lines), and PCBM⁺ (dashed-dotted lines). The mole fraction of each spectrum is MDMO-PPV⁺/PCBM⁺/PCBM⁻ = a) 0.5: 0.5: 0.5 and b) 0.15: 0.35: 0.5.

doping, independently of acceptor materials, induces some conformational changes of MDMO-PPV that are related to the spectroscopic change, these results suggest that the absorption spectrum of the MDMO-PPV hole polaron is not affected by an acceptor concentration. Furthermore, no spectroscopic change was observed for PS/TMPD/PCBM blend films with PCBM concentrations up to 60 wt %, which suggests that the absorption spectrum of the PCBM radical anion is also essentially independent of the PCBM concentration as reported previously.^[14] We, therefore, conclude that neither the MDMO-PPV polaron nor the PCBM radical anion is related to the spectroscopic change observed for blend films with PCBM at a high concentration ($> 30 \text{ wt } \%$). Instead we conclude that another charge carrier is formed in blend films at the high PCBM concentrations. We consider the PCBM radical cation to be the most possible carrier formed at the high PCBM concentrations because, as mentioned before, the MDMO-PPV electron polaron has negligible absorption in the wavelength region from 800 to 1000 nm.

To verify our assumption that the PCBM radical cation is formed in the blend films, we reproduced transient spectra observed for blend films with PCBM at a high concentration. In contrast to the spectrum at a low PCBM concentration, the spectrum at 68 wt % PCBM was irreproducible by a simple summation of each spectrum of the MDMO-PPV hole polaron and PCBM radical anion. However, as shown in Figure 7b, it was well reproduced by a summation of each spectrum of the MDMO-PPV hole polaron, PCBM radical anion, and PCBM radical cation. We, therefore, conclude that the PCBM radical cation is formed as a new charge carrier at the high PCBM concentrations. Furthermore, the mole fraction of the PCBM

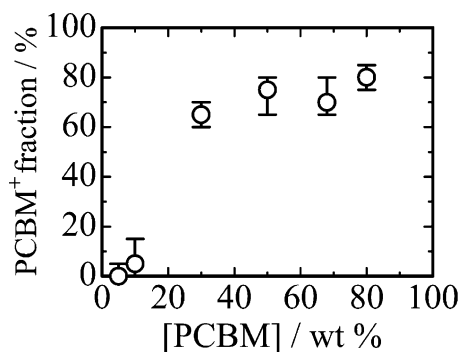


Figure 8. The mole fraction of PCBM⁺ in hole carriers plotted against the weight concentration of PCBM in MDMO-PPV/PCBM blend films. The fraction is evaluated from the spectroscopic simulation shown in Figure 7.

radical cation formed in the blend films can be quantitatively evaluated on the basis of each molar absorption coefficient obtained in the previous section. Figure 8 shows the dependence of the evaluated mole fraction of the PCBM radical cation in hole carriers on the PCBM concentration in blend films. At low PCBM concentrations (<10 wt %), the mole fraction of the PCBM radical cation was negligible, which is indicative of the formation of the MDMO-PPV hole polaron and PCBM radical anion pairs alone. Above 30 wt % of PCBM, on the other hand, it drastically increased to 60 mol %, and gradually up to 80 mol % at 80 wt % PCBM. In other words, most holes formed in blend films are located on PCBM molecules rather than MDMO-PPV chains. This finding seems contradictory to the prevailing view that MDMO-PPV serves as a hole-transporting material and PCBM as an electron-transporting material in blend films. However, this is consistent with the ambipolar transport reported for fullerene derivatives including PCBM.^[9–11] The field-effect hole mobility of PCBM is reported to be $8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^[11] which is much higher than the hole mobility of pristine MDMO-PPV ($\sim 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[8,9] but rather comparable to that of MDMO-PPV/PCBM blend films ($\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[8,9] Thus, our finding can explain previous reports^[9] that the hole mobility in MDMO-PPV/PCBM blend films increased at higher PCBM concentrations (> 50 wt %).

3.2. Mechanisms of PCBM Radical Cation Generation

We now consider the formation mechanism of the PCBM radical cation in MDMO-PPV/PCBM blend films with PCBM at a high concentration (>30 wt %). As shown in Figure 8, the mole fraction of the PCBM radical cation sharply increased between 10 and 30 wt %. This turning point is in agreement with the theoretical percolation threshold of $\sim 17\%$ by volume (which corresponds to $\sim 25 \text{ wt } \% \text{ PCBM}$) for a three-dimensional random network.^[6] Furthermore, the abrupt increase is characteristic of the percolation probability. These results suggest that the formation of the PCBM radical cation is closely correlated with the formation of the PCBM domain in the blend films. In other words, the PCBM radical cation is likely to be formed from the dissociation of excited states in the

PCBM domain, as long-lived charge carriers identified as spin 1/2 polarons (C_{60}^{\pm}) in photoexcited C_{60} solid films.^[31] Previous studies of C_{60} ^[32,33] and PCBM solid films^[34] have revealed enhanced absorption in the visible region assigned to intermolecular charge transfer (CT) transitions, which are closely correlated with photocurrent generation.^[32] For the PCBM pristine film, significantly greater absorption is observed in the visible region compared with 12 wt % PCBM dispersed in a PS film where PCBM is likely to be more isolated.^[34] In other words, the absorption of PCBM is more enhanced in the visible region than expected from the PCBM fraction because intermolecular CT transitions appear along with the formation of the PCBM domain. Furthermore, the spectroscopic overlap between the MDMO-PPV fluorescence with the intermolecular CT absorption of PCBM is small but not negligible. Thus, the excited CT states of PCBM may be formed through energy transfer from MDMO-PPV. Therefore, we conclude that the direct or indirect photoexcitation of PCBM is substantial for MDMO-PPV/PCBM blend films at higher PCBM concentrations, which results in the formation of the PCBM radical cation and anion pairs.

Another mechanism for the formation of the PCBM radical cation is hole transfer from MDMO-PPV to the PCBM domain. On the basis of the reported ionization potentials (IPs) for the two materials (IP = 5.1 eV for MDMO-PPV and IP = 6.1 eV for PCBM),^[9] the hole transfer from MDMO-PPV to PCBM should be energetically forbidden because of an energy difference as large as 1 eV, which is consistent with the prevailing view that MDMO-PPV and PCBM serve as a hole-transporting material and an electron-transporting material, respectively, in the blend. Nelson and coworkers estimated the Gibbs free energy for the hole transfer to be $\Delta G \sim 0.5\text{--}0.7 \text{ eV}$ considering interfacial dipole and higher polarizability and larger density of states of PCBM in addition to the simple energy difference of IPs.^[9] They concluded that the hole transfer from MDMO-PPV to PCBM through a single CT step was unlikely because their simulation of time-of-flight measurements suggested that hole transport through PCBM can dominate only for values of ΔG less than $\sim 0.2 \text{ eV}$ at room temperature. Instead they tentatively explained the hole transport in the blend films as hopping between CT states at the polymer/fullerene interface into which hole polarons generated in the MDMO-PPV phase may be transferred. Indeed, Goris et al. found optical sub-gap transitions in MDMO-PPV/PCBM blend films by photothermal deflection spectroscopy.^[35] They assigned the broad absorption that ranged from 1.1 to 1.68 eV to the CT transition because of the ground-state interaction between MDMO-PPV and PCBM. However, our transient results demonstrate the formation of a PCBM radical cation rather than such a new CT state, because the absorption spectrum of the interfacial CT state ($\text{MDMO-PPV}^{\delta+}/\text{PCBM}^{\delta-}$) is expected to be similar to that of the MDMO-PPV hole polaron or PCBM radical anion rather than the PCBM radical cation. Furthermore, no absorption ascribable to the CT state was observed for MDMO-PPV/TCNE blend films. Therefore, we conclude that hole carriers in

MDMO-PPV/PCBM blend films are the MDMO-PPV polaron and PCBM radical cation rather than the interfacial CT states. Rather, the interfacial CT states may be associated with the formation of the PCBM radical cation to reduce the energy barrier for the hole transfer from MDMO-PPV to PCBM. Furthermore, the effective energy difference may be smaller considering the relatively wide bandwidth reported for C_{60} solid ($\sim 0.4\text{--}0.6\text{ eV}$).^[36,37] However, we have no clear evidence for such an unusual hole transfer. Further studies are needed to address the formation mechanism of the PCBM radical cation in the MDMO-PPV/PCBM blend films.

4. Conclusions

We have studied by transient absorption spectroscopy, photogenerated charge carriers in MDMO-PPV/PCBM blend films with a PCBM concentration that ranges from 0 to 80 wt %. To identify the charge carriers, we measured the transient absorption of each charge carrier separately using various combinations of electron donor and acceptor materials. The MDMO-PPV hole polaron has a broad absorption at $\sim 950\text{ nm}$ ($15\,000\text{ M}^{-1}\text{ cm}^{-1}$), PCBM radical anion at 1020 nm ($6000\text{ M}^{-1}\text{ cm}^{-1}$), and PCBM radical cation at 890 nm ($9000\text{ M}^{-1}\text{ cm}^{-1}$). The transient absorption spectrum of the blend film ($<10\text{ wt } \% \text{ PCBM}$) was reproduced by a simple summation of the spectrum of the MDMO-PPV hole polaron and PCBM radical anion, which suggests that the charge carriers in the blend are the MDMO-PPV hole polaron and PCBM radical anion alone. On the other hand, the transient absorption spectrum ($>30\text{ wt } \% \text{ PCBM}$) was reproduced by a summation of each spectrum of the MDMO-PPV hole polaron, PCBM radical anion, and PCBM radical cation, which suggests that charge carriers in the blend are not only the MDMO-PPV hole polaron and PCBM radical anion but also the PCBM radical cation. Furthermore, we confirm that the transient absorption of the MDMO-PPV hole polaron and PCBM radical anion is independent of the dopant concentration. Thus, we conclude that the PCBM radical cation is formed as a hole carrier in the blend films with PCBM at a high concentration. Possible mechanisms of the formation of the PCBM radical cation in the blend include the following: i) direct or indirect photoexcitation of intermolecular CT transitions of PCBM is pronounced at higher PCBM concentrations, which results in the formation of the PCBM radical cation and anion pairs at the PCBM domain in the blend, and ii) hole transfer from MDMO-PPV to the PCBM domain via interfacial CT states. Further studies are required to resolve which mechanism is dominant. Our study provides spectroscopic evidence for ambipolar transport of PCBM in polymer–fullerene blend films and proposes a new strategy to design bulk heterojunction solar cells.

5. Experimental

Preparation: Polymer/fullerene blend films were prepared on glass substrates by spin-coating from a chlorobenzene solution of MDMO-

PPV (Aldrich, $M_n = 95\,000\text{ g mol}^{-1}$) and PCBM (Frontier Carbon, $>99\%$) at a spin rate of 1000 rpm under ambient conditions. The film thickness was typically $150\text{--}200\text{ nm}$. The weight fraction of PCBM was varied from 5 to 80 wt %. The blend solution was stirred at $35\text{ }^\circ\text{C}$ overnight to be dissolved homogeneously. Before spin-coating, the glass substrates were cleaned by ultrasonic treatment in toluene, acetone, and ethanol sequentially for 15 min each, and then with a UV-ozone cleaner (Nippon Laser & Electronics Lab., UV253) for 1 h. For blend films of MDMO-PPV and TCNE (Aldrich, $>98\%$), cyclohexanone was used as a solvent instead of chlorobenzene. The blend solution was stirred at $50\text{ }^\circ\text{C}$ for 5 h. The weight fraction of TCNE was adjusted to 5 and 50 wt % in the final films. For blend films of PS (Aldrich, $M_n = 280\,000\text{ g mol}^{-1}$) doped with PCBM and TMPD (Wako, $>98\%$), chlorobenzene was used as a solvent. The PS was purified by reprecipitation from toluene solution into methanol three times. The blend solution was stirred at room temperature overnight. The weight ratio in the blend films was adjusted to PS/PCBM/TMPD = 5: 3: 2 (30 wt % PCBM) or 2: 6: 2 (60 wt % PCBM). For the blend solution of PCBM and TCNE, benzonitrile was used as a solvent. The molar concentration of PCBM and TCNE was 1.3×10^{-3} and $6.6 \times 10^{-3}\text{ M}$, respectively.

Measurements: Transient absorption data were collected in an Ar atmosphere with a highly sensitive microsecond transient absorption system and with a femtosecond transient absorption system as described below. The sample films were sealed in a quartz cuvette purged with Ar for 30 min. The sample solution in a quartz cell was deaerated by Ar bubbling for 30 min.

For the microsecond transient absorption measurement, the sample was excited with a light pulse (500 nm , $30\text{ }\mu\text{J cm}^{-2}\text{ pulse}^{-1}$, 4 Hz) from a dye laser (Photon Technology International, GL-301) that was pumped with a nitrogen laser (Photon Technology International, GL-3300), and probed with a monochromatic light from a 50 W quartz tungsten halogen lamp (Thermo-ORIEL, Model 66997) with a light intensity controller (Thermo-ORIEL, Model 66950), which was equipped with appropriate optical cut-filters and two monochromators (Ritsu, MC-10N) before and after the sample to reduce stray light, scattered light, and emission from the sample. The probe light was detected with a pre-amplified Si photodiode (Costronics Electronics). The detected signal was sent to the main amplification system with an electronic band-pass filter (Costronics Electronics) to improve the noise-to-signal ratio. The amplified signal was collected with a digital oscilloscope (Tektronix, TDS2022), which was synchronized with a trigger signal of the laser pulse from a photodiode (Thorlabs, DET10A). The detectable absorbance change ΔOD was as small as $\sim 10^{-5}\text{--}10^{-6}$ depending on the measuring time domain.

The femtosecond transient absorption data were collected with a pump and probe transient absorption spectroscopy system (Ultrafast Systems, Helios). The pump light was second harmonic pulses (400 nm , $65\text{ }\mu\text{J cm}^{-2}\text{ pulse}^{-1}$, fwhm 100 fs , 500 Hz) from a regeneratively amplified Ti-sapphire laser (Spectra-Physics, Hurricane). The probe beam was detected with a linear CCD array (Ocean Optics, S2000) for the visible wavelength range from 400 to 900 nm and with a digital line scan InGaAs camera (Sensors, SU-LDV) for the near-IR wavelength range from 850 to 1600 nm . The typical noise level of this system is lower than 2×10^{-4} .

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