Magnetoco nductance Study on Nongeminate Recombination in Solar Cell Using Poly(3-hexylthiophene) and [6,6]-Phenyl-C$_{61}$-butyric Acid Methyl Ester

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1. INTRODUCTION

Organic solar cells have many advantages because of being lightweight and form-flexible, as well as their low cost for fabrication.$^1$ Therefore, organic solar cells have attracted attention as next-generation solar cells and as the alternative to conventional silicon-based solar cells.$^2$ However, compared with inorganic solar cells, the power conversion efficiency ($\eta$) of organic solar cells is not yet sufficiently high$^1$ because of some loss mechanisms caused by intrinsic properties of the organic molecules, such as lower ability for absorption of solar spectrum in the near infrared region, short exciton diffusion distances, large binding energies between electrons (e) and holes (h), and slow drift mobility.$^3$ The dissociation of excitons, and the generation and recombination of charged carriers occur in the range of the interface between the electron-donor (D) and acceptor (A) in the active layer of a cell; therefore, some of the loss mechanisms are heavily dependent on the combination and junction architecture of the D and A.$^4,^5$ The electron spin in a molecule also plays an essential role in the exciton and carrier dynamics at the D/A-junction. For instance, mutual orientation of the spin angular momenta for two electrons in singly occupied molecular orbitals of the exciton significantly changes the exciton energy, which determines the ability of the electron transfer at the D/A-junction. The spin configuration of an e–h pair in the D/A-junction area affects the recombination efficiency because the e–h pair is a precursor in spin conservative recombination. Recombination at the D/A-junction is one of the main loss mechanisms that suppress the device performance. Therefore, an understanding of the recombination mechanism is critical for the development of organic solar cells with high $\eta$.

Received: July 23, 2018
Accepted: August 1, 2018
Published: August 17, 2018

DOI: 10.1021/acsomega.8b01746
ACS Omega 2018, 3, 9369−9377

Supporting Information

ABSTRACT: The magnetoconductance (MC) effect was investigated for two types of organic solar cells with single junction (SJ) and bulk junction (BJ) of poly(3-hexylthiophene) (P3HT) as donor (D) and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) as acceptor (A). Three components with different half-field-at-half-maximums ($B_{1/2}$) of $4 \pm 1, 20 \pm 15$ and $>400$ mT, hereafter referred to MC$_{M,B}$ in a sequence, were observed in the magnetic field dependence of the MC effects measured under dark and light conditions. The magnitude of the MC$_{M,B}$ components is sensitive to not only the junction structure of the cell but also the presence or absence of incident light. The bias voltage ($V$) dependence of the MC effect in the dark for the SJ-cell is maximized around the turn-on voltage ($V_{ON}$) of the dark current, where a flat band condition of the active layer is achieved. The $B_{1/2}$ for the MC$_M$ component of the SJ-cell increases with $V$ beyond $V_{ON}$. In light, the BJ-cell exhibits the MC effect, whereas no effect is detected for the SJ-cell. The MC$_{M,B}$ components for the BJ-cell in light increase with the incident light power. The transient MC$_{M,B}$ components for the BJ-cell measured using a nanosecond pulse laser increases with the delay time after the flash. By integrating these phenomena and the phase of the MC effect, it is concluded that all of the MC components arise from the magnetic field effect on the spin conversion of nongeminate electron (e)–hole (h) pairs with spin-dependent charge recombinations at the D/A-interface. The $B_{1/2}$ values for MC$_{M,B}$ are, respectively, understood by the spin conversion due to the hyperfine interaction, the spin relaxation, and the g-factor difference for e (PCBM$^+$) and h (P3HT$^+$). Kinetic simulations of the MC$_{M,B}$ components for the BJ-cell observed at the short-circuit condition in light yield an efficiency of ca. 40% for the nongeminate recombination, which is accompanied by the generation of triplet excitons as well as relaxation to a ground singlet state. The loss mechanism of moderate triplet recombination suggests an important possibility to improve the power conversion efficiency by harvesting of the triplet excitons.
Magnetococonductance (MC) in organic semiconductors, which is defined by a change of current density \( J \) induced by an external magnetic field \( B \): MC (\%) = \( \frac{\left| J(B) - J(0) \right|}{J(0)} \times 100 \), arises from the interplay between spin-dependent recombination and the magnetic field-dependent spin conversion of spin pairs. The MC effect can thus provide information regarding the carrier dynamics in organic solar cells under operating conditions without destruction of the device. The MC effect due to the hyperfine mechanism of \( e-h \) pairs in a single junction (SJ) solar cell with a simple D/A-junction of pentacene and \( C_{60} \) layers in the center of device has recently clarified a geminate recombination yield of 1\%\(^\text{a}\). In a bulk junction (BJ) solar cell that possess random orientation of the D/A-junction due to nanoscaled interpenetrating phase separation with fibrillar networks of regioregular poly(3-hexylthiophene) (P3HT) crystals as A and domains of 6,6-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) as A, a negative MC effect in dark\(^6\) and a positive MC effect in light\(^7,8\) because of the hyperfine mechanism is also observed in the magnetic field region lower than 20 mT. In addition, broad MC effects are detected due to the \( \Delta g \) mechanism of \( e-h \) pairs, which are, respectively, negative and positive below and above 1 T in light.\(^9\) From the abstruse magnetic field dependence of the MC effect, it is suggested that an inhomogeneous junction structure affects the MC effect; however, the relation between the MC effects and the D/A-junction architecture is not yet well understood. Therefore, here we comprehensively examine the MC effects observed for the BJ-cell estimates a substantial nongeminate recombination with the generation of triplet excitons at the short-circuit condition.

2. RESULTS

2.1. Device Performance and Multicomponent MC Effects. Figure 1 shows the bias voltage \( V \) dependence of \( J \) for the SJ- and BJ-cells. Both cells exhibited rectifying and photovoltaic effects in dark and light, respectively. The turn-on voltage in dark \( (V_{\text{ON}}) \) and the open-circuit voltage \( (V_{\text{OC}}) \) in light were around 0.4 V. The fill-factors (FF) for both cells were also almost the same, although the short-circuit current \( (J_{\text{SC}}) \) for the BJ-cell became much higher than that of the SJ-cell. The high \( J_{\text{SC}} \) of the BJ-cell stems from the larger area of the D/A-junction than that of the SJ-cell, which enhances the efficiency of exciton dissociation to geminate \( e-h \) pairs by electron transfer from P3HT to PCBM. The \( \eta \) of the BJ-cell was approximately five times as large as that of the SJ-cell (Table 1), mainly because of the large \( J_{\text{SC}} \) difference for the SJ- and BJ-cells. It was noted that the BJ-cell in this work exhibits \( \eta \) less than well-optimized BJ-cells \((2-5\%)\).\(^7,10\) \( J_{\text{SC}} \) for the BJ-cell was dependent on the incident light power \( (P_{\text{in}}) \), which obeyed the power law \( J_{\text{SC}} \propto P_{\text{in}}^{\alpha} \) with \( \alpha = 0.93 \), while in the case of the SJ-cell, \( \alpha \) was almost unity \((0.99)\). These results suggest the recombination of nongeminate \( e-h \) pairs in the BJ-cell in light. On the other hand, transient photocurrents for the SJ- and BJ-cells were observed in the microsecond region, as represented in Figure S1. In the time profile of the photocurrent for the SJ-cell, two shoulders were evident at 7.6 \( \times 10^{-8} \) and 5.2 \( \times 10^{-7} \) s, which correspond to the transit times \( (\tau) \) for \( e \) in the PCBM layer and for \( h \) in the P3HT layer, respectively. The photocurrent decay for the BJ-cell is a smooth and downwardly convex curve. Simulations for the observed decay indicate the presence of both pseudo-first and second-order recombinations during the carrier transport in the blend film of P3HT:PCBM.

Table 1. Device Parameters Determined from \( J-V \) Curves for the SJ- and BJ-Cells in Light

| cell type | \( J_{\text{SC}}/\text{mA cm}^{-2} \) | \( V_{\text{OC}}/\text{V} \) | FF/\% | \( \eta/\% \) |
|-----------|-----------------|----------------|------|------|
| SJ        | 1.3             | 0.45           | 36   | 0.21 |
| BJ        | 8.9             | 0.37           | 35   | 1.1  |

\( J_{\text{SC}} \): short-circuit photocurrent density; \( V_{\text{OC}} \): open-circuit voltage; FF: fill factor; \( \eta \): power conversion efficiency.

Figure 2 shows the typical magnetic field dependence of the MC effects observed for the SJ- and BJ-cells. The phase of the MC effect for the SJ-cell in dark is negative, and the magnitude symmetrically increases with |B| in the low magnetic field range within ±50 mT and gradually decreases with |B| in the magnetic field range of |B| > 50 mT. The magnitude of the negative MC effect for the BJ-cell in dark also indicates a symmetric increase in low magnetic fields but remains level in high magnetic fields. On the other hand, no reliable MC effect was detected for the SJ-cell in light. For the BJ-cell in light, the MC effect detected in low magnetic fields changed the phase to positive and the magnitude increased gradually in high

Figure 1. \( J-V \) characteristics for (a) the SJ- and (b) BJ-cells measured in dark (blue) and under light (red) of a solar simulator at 100 mW cm\(^{-2}\) (AM1.5 G).

Figure 2. Magnetic field dependence of the MC effect for (a) the SJ- and (b) the BJ-cells measured at \( V = 0.3 \) V in dark (blue) and at \( V = 0.0 \) V in light (red). The gray curves are fitting results obtained using the multi-Lorentzian function (eq 1).
The phases of the MC effects observed in dark and light were, respectively, interpreted in terms of the recombination and dissociation currents, as detailed in the Discussion section. To elucidate the individual components involved in the observed MC effects, they were fitted using the Lorentzian and Gaussian functions, assuming that all of the MC components were saturated at the high magnetic field limit. The fitting with the following multi-Lorentzian function reproduced the measured results slightly better than that with the multi-Gaussian function as described in Section S2 of the Supporting Information.

$$\sum \frac{C_i M_{C(i)}(B)}{B^2 + \left(\frac{B}{B_{1/2}}\right)^2}$$

As shown in Figure 2, the fitting results clarified the coexistence of at most three components with different $B_{1/2}$ (see Figure S3 for detail). Here, $B_{1/2}$ is the field at which the MC effect reaches half of $M_C$, the saturated value in extremely high fields. Hereafter, the three components, that is, the sharp ($B_{1/2} = 4 \pm 1$ mT), middle ($B_{1/2} = 20 \pm 15$ mT), and broad ($B_{1/2} > 400$ mT) MC components are denoted $MC_S$, $MC_M$, and $MC_B$, respectively, as listed in Table 2. The MC effect for the SJ-cell in dark consists of $MC_S$ with a negative phase, $MC_M$ with a negative phase, and $MC_B$ with a positive phase, whereas that for the BJ-cell in dark is comprised of negative $MC_S$ and $MC_M$ components. The light MC effect for the BJ-cell possesses a positive $MC_S$, a positive $MC_M$, and a negative $MC_B$. The phase of $MC$ is dependent not only on the D/A-junction architecture in the active layer of the solar cell but also on the condition of dark or light.

### 2.2. Dark MC Effect

The MC effects for the SJ- and BJ-cells changed with the variation of $V$, as shown in Figure S5. The observed magnetic field dependence of the MC effect could be fitted by the multi-Lorentzian function. The MC curves for the SJ-cell were analyzed with the $MC_S$, $MC_M$, and $MC_B$ components, whereas those for the BJ-cell were fitted using only the $MC_S$ and $MC_M$ components. Fitting of the observed $MC_B$ component for the SJ-cell could not provide a unique set of $B_{1/2}$ and $M_C$ because the magnetic field range measured was not sufficiently wide to detect the saturation behavior of the $MC_B$ component. As shown in Figure 3, $B_{1/2}$ of the $MC_S$ component for the SJ-cell (ca. 4 mT) did not change significantly with $V$, whereas the $MC_M$ component increased with $V$. In the BJ-cell, $B_{1/2}$ of the $MC_S$ component was almost the same as that of the SJ-cell, but one of the $MC_M$ components was approximately 30 mT at low voltages, which is larger than that of the SJ-cell and slightly increased.

### Table 2. Half Field ($B_{1/2}$), Phase of Saturated Value ($M_C$) and Spin Conversion Mechanism for the Three Components Involved in the MC Effects Due to Nongeminate e−h Pair Mechanisms Observed for the SJ- and BJ-Cells

| Component | $B_{1/2}$/mT | Phase for the SJ-cell | Phase for the BJ-cell | Spin Conversion Mechanism |
|-----------|-------------|----------------------|----------------------|---------------------------|
| $MC_S$    | 4 ± 1       | in dark: negative    | in dark: negative    | hyperfine                 |
| $MC_M$    | 20 ± 15     | in dark: negative    | in dark: negative    | relaxation                |
| $MC_B$    | >400        | in dark: positive    | in dark: negative    | $g$-difference            |

Figure 3. Logarithmic plot of $J$−$V$ curves for (a) the SJ-cell and (b) the BJ-cell in dark. Bias voltage dependence of $B_{1/2}$ (c,d) and $MC$ (e,f) of the $MC_S$ (red) and $MC_M$ (green) components involved in the dark MC effects for the SJ- and BJ-cells. Data corresponding to the $MC_B$ component (blue) shown in (e) are the values of the $MC_B$ component measured at 300 mT. Dotted lines are used to show the trend.
at high biases. The differences of not only the size but also the bias voltage dependence of $B_{1/2}$ between the MC$_S$ and MC$_M$ components implies a difference in the mechanism for the spin dynamics behind the MC effect.

The magnitude of MC$^\infty$ is significantly dependent on $V$. MC$^\infty$ for the SJ-cell has a large dispersion; therefore, the MC effect due to the MC$_B$ component at 300 mT is plotted in Figure 3e, which was extracted from the curve fitting, to observe the bias voltage variation of the MC$_B$ component. All of the components detected for the SJ-cell have a maximum amplitude around 0.3 V, which decreases with an increase of $V$. Comparison with the $J−V$ characteristics indicates that the voltage for the MC peak is in agreement with $V_{ON}$ where the nature of dark current switches from diffusion to drift. $V_{ON}$ of the $J−V$ curve in dark is very close to the built-in potential estimated from the transit times that appeared in transient photocurrent for the SJ-cell (see Section S1). The dependence of MC$^\infty$ with a peak was also observed for the SJ-cell that consisted of pentacene and fullerene in our previous report, and this is interpreted in terms of the balance between the dissociation and recombination rate constants ($k_{dis}$ and $k_{rec}$) of nongeminate e−h pairs formed at the D/A-interface. In the SJ-cell, the increase in the internal electric field in the D-to-A direction (forward bias) promotes drift motions of hole and electron toward the D/A-interface, which results in promotion of recombination and inhibition of dissociation of the e−h pair; namely, the ratio $k_{dis}/k_{rec}$ monotonically decreases. No large MC effect is expected in the case of extremely small $k_{dis}$ or $k_{rec}$ because the MC effect is caused by a change between the dissociation and recombination yields due to the external magnetic field. This is a basic reason for the peak dependence of MC$^\infty$ for the SJ-cell, as described in detail in the Discussion section. The flat band condition of the active layer achieved around $V_{ON}$ may allow $k_{dis}$ to be comparable with $k_{rec}$. The three MC effects observed for the SJ-cell of P3HT:PCBM are maximized around $V_{ON}$ which indicates that all of the components are attributed to the magnetic field-dependent spin dynamics of the same nongeminate e−h pair. The MC$_S$ and MC$_M$ components observed for the BJ-cell also show a similar bias voltage dependence to that for the SJ-cell, although their peaks are broad and obscure. The $J−V$ curve for the BJ-cell indicates a gradual transition from a diffusion current regime with a slope of one to a drift current regime with a slope larger than one. This broad transition in the BJ-cell suggests that the flat band condition cannot be uniformly realized in the entire active layer because of an inhomogeneous D/A-junction structure. The random orientation of the D/A-junction in the BJ-cell is probably also the reason for the lack of a clear peak in the voltage dependence of the MC effects.

2.3. Light MC Effect. No reliable MC effect was observed for the SJ-cell at the short-circuit condition under irradiation with the solar simulator at various light powers, whereas the BJ-cell showed a clear MC effect that increased in intensity with the light power as shown in Figure S6. Analysis of the MC effect observed for the BJ-cell using the multi-Lorentzian function confirmed the presence of all three components. As shown in Figure 4a, MC$^\infty_S$ and MC$^\infty_M$ increase with the light power, whereas their $B_{1/2}$ values are maintained almost constant. The observed dependence on the light power proves that both the MC$_S$ and MC$_B$ effects in light are caused by a multiphoton process. The MC effect due to the MC$_B$ component at 500 mT also increases with the light power, suggesting the same multiphoton process.

The time dependence of the MC effect obtained from transient photocurrents detected at the short-circuit condition by excitation with the pulse laser is depicted in Figure S7. No MC effect for the SJ-cell was observed, whereas the BJ-cell showed a clear MC effect that increased in intensity with the delay time ($t$). The magnetic field dependence of the transient MC effect for the BJ-cell was simulated by adopting positive MC$^\infty_P$ positive MC$_M$ and negative MC$_S$ components as with the light MC effect observed under continuous light (see Figure S3d). Figure 4c,d shows that $B_{1/2}$ does not change with $t$, but the three MC components simultaneously increase in intensity with $t$. The apparent increase rate constant for both components is ca. $6 \times 10^5$ s$^{-1}$, which is almost the same as that for charge recombination estimated by simulations of the transient photocurrents for the BJ-cell. Combined with the light power dependence and the time variation of the light MC effects, it is concluded that the three MC components arise from the charge recombination of nongeminate e−h pairs.
Scheme 1. Elementary Processes of the Nongeminate e−h Pairs Formed at the D/A-Junction

**3. DISCUSSION**

**3.1. Sharp MC Component.** As listed in Table 2, the MC$_S$ component with $B_{1/2}$ of ca. 4 mT due to nongeminate e−h pairs was detected for the SJ- and BJ-cells in dark. In light, the MC$_C$ component appears only for the BJ-cell. Although not only nongeminate pairs but also geminate pairs are generated in light, it is considered that the MC effect due to the recombination of geminate pairs could be undetectable because of the high dissociation yield at the interface between P3HT and PCBM. In addition, the SJ-cell has a D/A-junction only at the center of the active layer, which does not form nongeminate e−h pairs after separation of e and h because of the drift motion along the internal electric field. This is probably the reason for the lack of a clear MC effect with the SJ-cell. $B_{1/2}$ for the MC$_S$ component, which is comparable with the hyperfine coupling constant ($\omega_{\text{hf}}$) of organic radicals, indicates that coherent spin conversion ($\omega_{\text{hf}}$) of nongeminate e−h pairs is driven by the magnetic interaction between the electron and nuclear spins.

The phases of the dark and light MC$_S$ components for the BJ-cell can be qualitatively understood by the magnetic field-dependent spin conversion among the spin sublevels of the nongeminate e−h pairs, which has a rate constant of singlet recombination ($k_{\text{S}}$) to the ground singlet state (1$^\text{gr}$) that is different from that of triplet recombination ($k_T$) to a triplet exciton (3$^\text{ex}$), as illustrated in Scheme 1.

The spin conversion between the three triplet spin sublevels ($^T$) and the singlet state ($^S$) of the e−h pair efficiently occurs in the absence of an external magnetic field; however, the Zeeman interaction prohibits the $^T$ and $^S$ sublevels from spin conversion because the energy shift ($\pm \Delta E_Z$) is much larger than the splitting by hyperfine interaction. Therefore, dissociation of the $^T$ sublevels takes over recombination via the $^S$ state, so that the dissociation and recombination yields ($\phi_{\text{dis}}$ and $\phi_{\text{rec}}$) of the e−h pairs at the D/A-junction increase and decrease, respectively, under strong magnetic fields. The magnetic field effect on these yields of nongeminate e−h pairs results in negative MC in dark and positive MC in light because most of the dark current is terminated by the recombination of e and h, while the photocurrent originates from the dissociation of e−h pairs.

In the case of fast spin conversion and slow spin relaxation, the MC effect due to the e−h pair mechanism can be calculated using the equations as described at Section S5 of the Supporting Information.

$$MC_{\text{dark}}(k_{\text{dis}}, k_T) = \frac{\phi_{\text{rec}}(B) - \phi_{\text{rec}}(0)}{\phi_{\text{rec}}(0)} \times 100$$

$$= \frac{-k_{\text{dis}}(1 - k_T^4)}{(k_{\text{dis}} - k_T^4 + 2)(k_{\text{dis}} + k_T^4)} \leq 0$$

$$(2)$$

$$MC_{\text{light}}(k_{\text{dis}}, k_T) = \frac{\phi_{\text{dis}}(B) - \phi_{\text{dis}}(0)}{\phi_{\text{dis}}(0)} \times 100$$

$$= \frac{-k_{\text{dis}}(1 - k_T^4)}{(k_{\text{dis}} - k_T^4 + 2)(k_{\text{dis}} + k_T^4)} \geq 0$$

$$\therefore k_T^4 = \frac{k_{\text{dis}}}{k_{\text{rec}}}, \quad k_T^4 = \frac{k_T}{k_{\text{rec}}}, \quad k_{\text{rec}} = \frac{k_s + 3k_T}{4}$$

$$(3)$$

Here, $k_{\text{dis}}$ is the dissociation rate constant and $k_{\text{rec}}$ is the total recombination rate constant defined by taking the average of the recombination rate constants from the individual spin sublevels. Equations 2 and 3 indicate that the dark MC effect is negative and that the light MC effect is positive. Figure 5a shows a plot of $MC_{\text{dark}}$ against the reduced dissociation rate constant ($k_{\text{dis}}$) calculated with variation of the reduced triplet recombination rate constant ($k_T^4$), which reflects the spin-selectivity in recombination ($k_s/k_T$). The $k_{\text{dis}}$ of the SJ-cell is expected to monotonically increase with the bias voltage because the electrostatic potential for the e−h pair becomes dissociative with the bias voltage like the Onsager and Poole–Frenkel models. The calculated U-shaped tendency of $MC_{\text{dark}}$ of Figure 5a is the same as the peak behavior observed in the bias voltage dependence of the dark MC effect for the SJ-cell of Figure 3c, which appears in the flat band region where dissociation and recombination are sufficiently competitive. According to eq 2, the MC$_{\text{dark}}$ value reaches a maximum

$$MC_{\text{dark}}^{\text{max}}(k_T) = \frac{-k_T^4 \sqrt{k_T^2(2 - k_T^2)}}{2(k_T^4 - 2k_T^2 + \sqrt{k_T^4(2 - k_T^2)})}$$

$$(5)$$

at

$$k_{\text{dis}} = \sqrt{k_T^2(2 - k_T^2)}, \quad \left\{ k_T: 0 \leq k_T^4 \leq \frac{4}{3} \right\}$$

$$(6)$$
The incident light power dependence of the nongeminate recombination yield in the BJ-cell estimated by comparison of the calculated MC_light and the magnitude of the observed light MC_s and MC_M effects.

3.2. Middle and Broad MC Components. As summarized in Table 2, the observed bias voltage, light power, and time dependences of the MC_M and MC_B components, which are similar to those of the MC_S component, indicate that both MC_M and MC_B originate from the nongeminate e−h pairs. Compared with the MC_S component, B_1/2 for the MC_M is larger and that for the MC_B is even larger. The phase of MC_M is the same as the MC_S while that of MC_B is opposite. The same phase as MC_S (hyperfine mechanism) and the B_1/2 values of 30 ± 22 mT suggest that the spin conversion in nongeminate e−h pairs for the MC_B component is caused by the exchange of the local magnetic field (B_{loc}). The spin relaxation rate (k_{ds}) is written by

\[ k_{ds} = \frac{g \mu_B B_{loc}}{2h} \left( \frac{\tau}{1 + (\omega \tau)^2} \right) \]  

Here, g, \mu_B, and h are the g-factor, Bohr magneton, and Dirac constant, respectively. The dependence of k_{ds} determines the B_1/2 of MC effect because of the spin relaxation mechanism. \tau is the correlation time that characterizes the fluctuation. The fluctuation is affected by the drift motion of carriers; therefore, \tau should be shortened under high voltages. This voltage dependence of \tau is consistent with the observed steep increase of B_1/2 for the dark MC_M component above V_{ON}. For example, the k_{ds} for a hole in P3HT increases with the temperature and is expected to be larger than 10^{-7} s^{-1} because of the fast hole dynamics at room temperature in the absence of an internal electric field. Therefore, k_{ds} is accelerated above V_{ON} and becomes less sensitive to B, which results in broadening of the MC curve. On the other hand, the spin conversion for the anti-phase of MC_B with large B_1/2 is interpreted in terms of the \Delta g mechanism. The different Larmor precessions of the individual spins of e and h coherently modulates the spin.
character of the e−h pair between the S and T₀ states at a frequency \( \alpha_{Δg} \)

\[
\alpha_{Δg} = \frac{|g_e - g_h| \mu_e B}{\hbar} = \frac{Δg|\mu_e B}{\hbar}
\]

Here, \( g_e \) and \( g_h \) are g-factors for e and h, respectively. Equation 8 indicates that the spin conversion rate due to the Δg mechanism is typically negligible in the low magnetic field region. However, the g difference in the combination of P3HT and PCBM (\( Δg \approx 2.5 \times 10^{-5} \)) is relatively large; therefore, \( \alpha_{Δg} \) for the e−h pair can reach at 10⁳ s⁻¹ at 500 mT, which is almost in the same order as \( \alpha_{he} \). However, the lack of a MCB component detected for the BJ-cell in dark implies a mechanism other than the g-factor difference, which could be related with light irradiation, but this requires further investigation. It is concluded that the nongeminate e−h pair that yields the MCS effect due to the hyperfine mechanism could also be the origin for MCB because of the particularly large Δg.

4. CONCLUSION

SJ- and BJ-cells with standard materials of P3HT and PCBM were used to comprehensively measure the MC effects in dark and light. Multi-Lorentzian fitting of the observed magnetic field dependence of the MC effects indicated the presence of three components with different \( B_{1/2} \) values, named as \( MC_{S,M,B} \) in ascending order of \( B_{1/2} \). The bias voltage dependence of the dark MC effect and the light power and time dependences of the light MC effect clarified that all three components were attributed to nongeminate e−h pairs with spin-selective recombination. The \( MC_{S,M,B} \) components are, respectively, derived from the hyperfine, spin relaxation, and Δg mechanisms for spin conversion among the singlet and triplet states. The spin-selectivity in recombination was elucidated by kinetic simulation of the dark \( MC_{S,M} \) effects for the SJ-cell. The nongeminate recombination efficiency in the BJ-cell with \( q = 1.1\% \) was estimated to ca. 40% at the short-circuit condition by simulation of the magnitude of the light \( MC_{S,M} \) effects. The relatively high \( \phi_{he} \) and same magnitude in order of \( k_S \) and \( k_T \) indicate the effective generation of \( ^3e \), which still has an electronic energy with a long lifetime. The reuse of \( ^3e \) may be a key point to improve the power conversion efficiency of P3HT:PCBM-cells.

5. EXPERIMENTAL SECTION

The SJ- and BJ-cells were fabricated according to a standard procedure. Quartz glass substrates coated with a transparent indium tin oxide (ITO) electrode were successively cleaned by sonication in hexane, acetone, and 2-propanol for 20 min, followed by oxygen plasma treatment (PL16-110, Yodogawa Electric Blower). A hole buffer layer with a thickness of ca. 50 nm was deposited on the plasma-treated substrates by spin-coating poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS; AI4083, Clevous), which was filtrated with a filter (Millex-HV, Millipore) before use, at 5000 rpm for 40 s. The buffer layer was then annealed at 120 °C for 20 min. To deposit an active layer for the BJ-cell, an \( \sigma \)-dichlorobenzene solution of P3HT (Luminescence Technology) and PCBM (Luminescence Technology) was then spin-coated on the PEDOT:PSS layer at 800 rpm for 28 s. This \( \sigma \)-dichlorobenzene solution was prepared at 40 °C by overnight stirring of an anhydrous solution comprised of 1.2 wt % solutes of P3HT and PCBM in a weight ratio of 3:2 in \( \sigma \)-dichlorobenzene (Aldrich) solvent. The deposited active layer with a thickness of ca. 100 nm was annealed at 110 °C for 20 min. For the active layer for SJ-cell, an \( \sigma \)-dichlorobenzene solution with only P3HT was prepared in the same manner as the solution for the BJ-cell and was spin-coated on the PEDOT:PSS layer at 800 rpm for 10 s. After annealing at 120 °C for 20 min, a PCBM layer with a thickness of ca. 50 nm was deposited under 2.0 \( \times \) 10⁻³ Pa using a vacuum vapor deposition apparatus (VPC-260F, ULVAC). Deposition of Al as a cathode on the active layers was performed using another vacuum vapor deposition apparatus (VPC-260, ULVAC). Finally, to prevent degradation by air exposure, SJ- and BJ-cells were sealed under a N₂ atmosphere using a glovebox.

The steady-state \( J \) versus \( V \) characteristics of the device were observed using an in-house-built measurement system combined with a source meter (2611, Keithley) and a solar simulator (HAL-C100, Asahi Spectra). To detect the MC effect, \( B \) was applied parallel to the electric field (\( E \)) of the bias voltage on the device using an electromagnet (TM-YSV6609J-021.5, Tamagawa Factory). The strength of \( B \) was monitored by a gaussmeter (421, LakeShore) placed close to the device. The transient photocurrent (\( I \)) was measured using a nanosecond pulsed laser with a wavelength (\( λ \)) of 532 nm (FDSS 532-150-I, CryLas) to excite the main band of P3HT and a circuit comprised of the solar cell in an electromagnet (TM-YSV5410-061.5, Tamagawa Factory) and an external resistance of \( R = 50 \Omega \). The voltage change at the resistance (\( ΔV = IR \)) caused by irradiation was monitored as a function \( t \) with a digital oscilloscope (DPO7104, Tektronix). The incident photon flux was controlled in the range of \( 10^{12} \) to \( 10^{14} \) photons/(cm² pulse) by a glan laser prism located before the solar cell. \( V \) at the ITO electrode was changed using a variable DC power supply (PLE-160-0.45, Matsusada Precision). All measurements were conducted at room temperature.

associated content

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01746.

Transient Photocurrent (S1); line-shape analysis of magnetic field dependence of MC effect (S2); bias voltage dependence of dark MC effect (S3); light power and time dependences of light MC effect (S4); and kinetic model for the MC effects due to nongeminate e−h pair (S5) (PDF)

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Notes

The authors declare no competing financial interest.
T.I. thanks Hiroki Yokoyama-Miura, Ryosuke Kobayashi and Minami Sato (Niigata University) for their valuable contributions in many preliminary experiments and discussion. This work was supported by JSPS KAKENHI Grants (nos. 16KT0049, 17K14477 and 18H1951), the Cooperative Research Program of “Network Joint Research Center for Materials and Devices: Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials” (no. 20180202), and the Collaborative Research Program of the Institute for Chemical Research, Kyoto University (no. 2018-65).

**ACKNOWLEDGMENTS**

This research was supported by JSPS KAKENHI Grants (nos. 16KT0049, 17K14477 and 18H1951), the Cooperative Research Program of “Network Joint Research Center for Materials and Devices: Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials” (no. 20180202), and the Collaborative Research Program of the Institute for Chemical Research, Kyoto University (no. 2018-65)

**REFERENCES**

(1) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. Science 1995, 270, 1789–1791. (b) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. Plastic Solar Cells. Adv. Funct. Mater. 2001, 11, 15–26. (c) Brabec, C. J. Organic photovoltaics: technology and market. Sol. Energy Mater. Sol. Cells 2004, 83, 273–290.

(2) (a) Brabec, C. J.; Dyakonov, V.; Parisi, J.; Sariciftci, N. S. Organic Photovoltaics: Concepts and Realization; Springer: Berlin, 2003; p 300.

(3) (a) Sun, S.-S.; Dalton, L. R. Introduction to Organic Electronic and Optoelectronic Materials and Devices, 1st ed.; CRC Press, 2008; p 936.

(4) (a) You, J.; You, J.; Hong, Z.; Xu, Z.; Li, G.; Street, R. A.; Yang, Y. 25th Anniversary Article: A Decade of Organic/Polymeric Photovoltaic Research. Adv. Mater. 2013, 25, 6642–6671. (b) Sun, S.-S.; Dalton, L. R. Introduction to Organic Electronic and Optoelectronic Materials and Devices, 1st ed.; CRC Press, 2008; p 936.

(5) (a) Kippelen, B.; Brédas, J.-L. Organic photovoltaics. Energy Environ. Sci. 2009, 2, 251–261. (b) Zhang, J.; Zhu, L.; Wei, Z. Toward Over 15% Power Conversion Efficiency for Organic Solar Cells: Current Status and Perspectives. Small Methods 2017, 1, 1700025.

(6) (a) Blom, P. W. M.; Mhialetchi, V. D.; Koster, L. J. A.; Markov, D. E. Device Physics of Polymer:Fullerene Bulk Heterojunction Solar Cells. Adv. Mater. 2007, 19, 1551–1566. (b) Yeh, N.; Yeh, P. Organic solar cells: Their developments and potentials. Renewable Sustainable Energy Rev. 2013, 21, 421–431. (c) Ossloherova, Z. Organic Photovoltaics: Mechanisms and Applications. Chem. Rev. 2016, 116, 13279–13412. (d) Clarke, T. M.; Durrant, J. R. Charge Photogeneration in Organic Solar Cells. Chem. Rev. 2010, 110, 6736–6767.

(7) Heremans, P.; Cheyns, D.; Rand, B. P. Strategies for Increasing the Efficiency of Heterojunction Organic Solar Cells: Material Selection and Device Architecture. Acc. Chem. Res. 2009, 42, 1740–1747.

(8) Omori, T.; Wakikawa, Y.; Mura, T.; Yamaguchi, Y.; Nakayama, K.-i.; Ikoma, T. Carrier Dynamics in Pentacene|C60 Bilayer Solar Cell Investigated by the Magnetocconductance. J. Phys. Chem. C 2014, 118, 28418–28424.

(9) (a) Gebeheyu, D.; Brabec, C. J.; Padinger, F.; Fromherz, T.; Hummelen, J. C.; Badt, D.; Schindler, H.; Sariciftci, N. S. The interplay of efficiency and morphology in photovoltaic devices based on interpenetrating networks of conjugated polymers with fullerenes. Synth. Met. 2001, 118, 1–9. (b) Schulinsky, P.; Waldau, C.; Brabec, C. J. Recombination and Loss Analysis in Polymer Photodiodes. Appl. Phys. Lett. 2002, 81, 3885–3887. (c) Yang, X.; Loos, J.; Veenstra, S. C.; Verhees, W. J.; H.; Wienk, M. M.; Kroon, J. M.; Michels, M. A. J.; Janssen, R. A. J. Nanoscale Morphology of High-Performance Polymer Solar Cells. Nano Lett. 2013, 5, 579–583. (d) Ma, W.; Yang, C.; Heeger, A. J. Spatial Fourier-Transform Analysis of the Morphology of Bulk Heterojunction Materials Used in “Plastic” Solar Cells. Adv. Mater. 2007, 19, 1387–1390.

(10) (a) Kippen, G.; Brédas, J.-L. Organic photovoltaics. Energy Environ. Sci. 2009, 2, 251–261. (b) Zhang, J.; Zhu, L.; Wei, Z. Toward 15% Power Conversion Efficiency for Organic Solar Cells: Current Status and Perspectives. Small Methods 2017, 1, 1700025.
Recombination Coefficient as a Sensitive Testing Parameter for Low-Mobility Solar-Cell Materials. *Phys. Rev. Lett.* **2005**, *94*, 176806. (b) Pirvika, A.; Sariciftci, N. S.; Juška, G.; Osterbacka, R. A review of charge transport and recombination in polymer/fullerene organic solar cells. *Prog. Photovoltraiics* **2007**, *15*, 677–696.

(18) Cowan, S. R.; Street, R. A.; Cho, S.; Heeger, A. J. Transient photoconductivity in polymer bulk heterojunction solar cells: Competition between sweep-out and recombination. *Phys. Rev. B: Condens. Matter Mater.* **2011**, *83*, 035205.

(19) Li, Z.; Gao, F.; Greenham, N. C.; McNeill, C. R. Comparison of the Operation of Polymer/Fullerene, Polymer/Polymer, and Polymer/Nanocrystal Solar Cells: A Transient Photocurrent and Photo-voltage Study. *Adv. Funct. Mater.* **2011**, *21*, 1419–1431.

(20) (a) Shuttle, C. G.; O’Regan, B.; Ballantyne, A. M.; Nelson, J.; Bradley, D. D. C.; de Mello, J.; Durrant, J. R. Experimental determination of the rate law for charge carrier decay in a polythiophene: Fullerene solar cell. *Appl. Phys. Lett.* **2008**, *92*, 093311. (b) Shuttle, C. G.; O’Regan, B.; Ballantyne, A. M.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. Bimolecular Recombination Losses in Polythiophene/Fullerene Solar Cells. *Phys. Rev. B: Condens. Matter Mater.* **2008**, *78*, 113201.

(21) (a) Cowan, S. R.; Roy, A.; Heeger, A. J. Recombination in Polymer-Fullerene Bulk Heterojunction Solar Cells. *Phys. Rev. B: Condens. Matter Mater.* **2010**, *82*, 245207. (b) Meskers, S. C. J.; van Hal, P. A.; Spiering, A. J. H.; Hummelen, J. C.; van der Meer, A. F. G.; Janssen, R. A. J. Time-resolved infrared-absorption study of photoinduced charge transfer in a polythiophene-methanofullerene composite film. *Phys. Rev. B: Condens. Matter Mater.* **2000**, *61*, 9917–9920. (c) Hamilton, R.; Shuttle, C. G.; O’Regan, B.; Hammant, T. C.; Nelson, J.; Durrant, J. R. Recombination in Annealed and Nonannealed Polythiophene/Fullerene Solar Cells: Transient Photo-voltage Studies versus Numerical Modeling. *J. Phys. Chem. Lett.* **2010**, *1*, 1432–1436.

(22) Ikoma, T.; Ogiwara, T.; Takahashi, Y.; Akiyama, K.; Tero-Kubota, S.; Takahashi, Y.; Suzuki, T.; Wakikawa, Y. Giant Magnetoresistance due to Electron-hole Pair Mechanism in Poly(N-vinylcarbazole). *Synth. Met.* **2010**, *160*, 285–290.

(23) Atherton, N. M. *Principles of Electron Spin Resonance*; Ellis Horwood Ltd: West Sussex, 1993.

(24) (a) Krinichnyi, V. I.; Yudanova, E. I.; Spitsina, N. G. Light-Induced Electron Paramagnetic Resonance Study of Poly(3-alkylthiophene)/Fullerene Composites. *J. Phys. Chem. C* **2010**, *114*, 16756–16766. (b) Krinichnyi, V. I.; Yudanova, E. I. Light-Induced EPR Study of Charge Transfer in P3HT/PC 

(29) Wakikawa, Y.; Ikoma, T.; Yamamoto, Y.; Fukushima, T.; Aida, T.; Akiyama, K. Effect of Acceptor Lamination on Photocarrier Dynamics in Hole Transporting Hexabenzocoronene Nanotubular Self-assembly. *J. Phys. Chem. C* **2013**, *117*, 15295–15305.