Temperature-independent carrier formation dynamics in bulk heterojunctions

Kouhei Yonezawa¹, Takeshi Yasuda², and Yutaka Moritomo¹,3*

¹Graduate School of Pure and Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan
²Photovoltaic Materials Unit, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan
³Center for Integrated Research in Fundamental Science and Engineering (CIRSE), University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan

E-mail: moritomo.yutaka.gf@u.tsukuba.ac.jp

Received August 27, 2015; accepted September 9, 2015; published online October 5, 2015

We investigated the effects of temperature on the carrier formation dynamics in a small-molecular blend film, 2,5-di-(2-ethylhexyl)-3,6-bis-[5′,5′′-n-hexy-[2,2′,5,2″]terthiophen-5-yl)-pyrrolo[3,4-c]pyrrolo-1,4-dione (SMDPPEH)/[6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM). We spectroscopically determined the absolute numbers of donor (nD) and acceptor (nA) excitons per absorbed photon as functions of the delay time (t), in addition to the relative number of donor carriers (nD,τ). We found that the carrier formation dynamics is independent of temperature at 300 and 80 K: the carrier formation time (τrise = 0.4 ps) is much faster than the decay time (τdecay ≈ 2.5 ps) of donor excitons. The temperature independence strongly suggests that only excitons created near the donor–acceptor interface contribute to the carrier formation.

© 2015 The Japan Society of Applied Physics

Optical solar cells (OSCs) with bulk heterojunctions (BHJs)¹⁻² are promising energy conversion devices with flexibility. They have a low-cost production process, e.g., the roll-to-roll process. The BHJ active layer, which is usually sandwiched between a transparent indium tin oxide (ITO) anode and an Al cathode, consists of phase-separated nano-scale domains of the donor (D) and acceptor (A) materials. In this layer, photo-irradiation creates donor (D⁺) and acceptor (A⁻) excitons within the respective nano domains. The photo-created excitons are considered to migrate to the D/A interface and separate into electrons and holes. Time-resolved spectroscopy is one of the most powerful tools for clarifying the carrier formation dynamics in BHJ layers.³⁻⁴ The analyses of photo-induced absorption (PIA) reveal the relative numbers of excitons (D⁺ and A⁻) and donor carriers (D⁺) and acceptor (A⁻) excitons as functions of the delay time (t). For example, the spectroscopy revealed that the carrier formation time (τrise ≈ 0.2 ps) is comparable to the decay time (τdecay ≈ 0.3 ps)⁵ of A⁻ in poly[[4,8-bis[(2-ethylhexyl)oxy]-benzo[1,2-b:4,5-b]thiophene-2,6-diyl][3-fluoro-2-(2-ethylhexyl)carbonil][thieno[3,4-b]thiophenediy]] (PTB7)/PC₇₁BM blend film.⁶⁻⁷

The nano-size domain structure of the BHJ layers is advantageous for efficient charge formation and, in turn, high power-conversion efficiency (PCE). The complex domain structure of the BHJ layer, however, impedes the microscopic observation of the charge formation process. For example, scanning transmission X-ray microscopy (STXM) has revealed significant fullerene mixing within donor-rich domains.⁸⁻¹⁰ In addition, Hedley et al.¹¹ reported substructures of ~10 nm within the ~100 nm domains in PTB7/PC₇₁BM blend film. Here, we emphasize that the temperature effect provides significant clues on the charge formation process. For example, Morimoto et al.¹² reported that the carrier formation efficiency (ΦCF), which is defined as the number of the photo-induced carriers per absorbed photon, is independent of temperature in regioregular poly(3-hexylthiophene) (rr-P3HT)/[6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) and PTB7/PC₇₁BM blend films. The independence of temperature strongly suggests that the exciton dissociation should be treated using the quantum-mechanical wave-packet picture, rather than the Marcus theory,²³ in which the charge separation is governed by the displacement of surrounding molecules.

Among the donor materials, the oligothiophene-diketo-pyropolyrole molecule with ethylhexyl substituents (SMDPPEH) is suitable for a detailed spectroscopic investigation on the charge formation dynamics because it shows intense and sharp PIA due to D⁺ and D⁻ in the infrared region.¹² In addition, the SMDPPEH/PC₇₁BM BHJ solar cell shows a high PCE of 3.0%, reflecting the intense absorption of SMDPPEH for relatively long wavelengths.²⁴⁻²⁶ In our previous paper,¹² we performed time-resolved spectroscopy in the SMDPPEH/PC₇₁BM blend film at 300 K and derived the relative numbers of D⁺, A⁻, and D⁻ as functions of t. However, the data points were too scattered to reveal the carrier formation dynamics in detail.

In this paper, we investigated the effects of temperature on the carrier formation dynamics in SMDPPEH/PC₇₁BM blend film. By comparing the absolute intensities of the PIA between the blend and neat films, we determined the absolute numbers of the donor (nD,τ) and acceptor (nA,τ) excitons per absorbed photon as functions of t. The improved data acquisition and analysis reveals that the carrier formation time (τrise = 0.4 ps) is less than the decay times (τdecay ≈ 2.5 ps) of D⁺, indicating that the late decay component (t ≥ τrise) does not contribute to the carrier formation process. The independence of temperature and the low value of τrise strongly suggest that only the excitons created near the D/A interface contribute to the carrier formation process.

The SMDPPEH/PC₇₁BM blend film was spin-coated on quartz substrates using a chlorobenzene solution of SMDPPEH:PC₇₁BM of 1:1 by weight. Then, the blend film was dried in an inert N₂ atmosphere. SMDPPEH was purchased from Sigma-Aldrich and used as received. For comparison, we prepared spin-coated SMDPPEH (PC₇₁BM) films on quartz substrates using chlorobenzene (chloroform) solution. The thicknesses of the SMDPPEH neat, PC₇₁BM neat, and SMDPPEH/PC₇₁BM blend films were 39, 50, and 96 nm, respectively.

Time-resolved spectroscopy was performed in a pump–probe configuration at 300 and 80 K, the details of which are
indicate the excitation wavelengths. The data were replotted from Ref. 12. The behavior of the decomposed PIA (ΔOD) spectra is observed at 80 K [Fig. 2(c)], together with the spectral decomposition into PIAs due to D⁺ (Cδ′, φD⁺), D⁻ (Cδ′, φD⁻), and A⁺ (CΔ, φA⁺). We regarded the ΔOD spectra of the SMDPPEH/PC71BM blend film (average between 8 to 10 ps), the SMDPPEH neat (at 1 ps) film, and PC71BM neat (at 1 ps) films as the basis functions φD⁺, φD⁻, and φA⁺, respectively. The spectral weights, i.e., Cδ′, Cδ′, and CΔ, of the respective components were determined so that they minimize the trial function: 

$$F = \sum [C\delta\prime, \phi\delta\prime, (\lambda_i)] + C\delta\prime, \phi\delta\prime, (\lambda_i) + C\Delta, \phi\Delta, (\lambda_i) - \phi_{\text{exp}}(\lambda_i)^2$$

where $\lambda_i$ denotes the respective wavenumbers. The unit of $\phi\delta\prime$, $\phi\delta\prime$, and $\phi\Delta$, is optical density. $C\delta\prime$, $C\delta\prime$, and $C\Delta$ are functions of $t$. We found that the average process of $\phi\delta\prime$ significantly improves the scattering of $C\delta\prime$, $C\delta\prime$, and $C\Delta$ against $t$, which enables us to discuss the difference in $t_{\text{rise}}$ of $D^+$ and $t_{\text{decay}}$ of $D^+$ and $A^+$. Figure 3(a) shows a prototypical example of the spectral decompositions at 300 K. We observed that the 400 nm excitation excites both $D^+$ and $A^+$.

To evaluate the absolute numbers of the donor (nD) and acceptor (nA) excitons per absorbed photon spectrscopically, we need the absolute intensities of the PIAs per unit density of D⁺ and A⁺. We assumed that one absorbed photon creates one $D^+$ ($A^+$) in the SMDPPEH (PC71BM) neat film. Then, the PIA intensity per unit density of $D^+$ ($A^+$) becomes $\alpha_{\text{exciton}} = 0.028$ (0.002) nm²/exciton on considering the absolute numbers of the donor and acceptor excitons per absorbed photon in the SMDPPEH neat film. We found that the average process of $\phi\delta\prime$ significantly improves the scattering of $C\delta\prime$, $C\delta\prime$, and $C\Delta$ against $t$, which enables us to discuss the difference in $t_{\text{rise}}$ of $D^+$ and $t_{\text{decay}}$ of $D^+$ and $A^+$. Figure 3(a) shows a prototypical example of the spectral decompositions at 300 K. We observed that the 400 nm excitation excites both $D^+$ and $A^+$.

To evaluate the absolute numbers of the donor (nD) and acceptor (nA) excitons per absorbed photon spectrscopically, we need the absolute intensities of the PIAs per unit density of D⁺ and A⁺. We assumed that one absorbed photon creates one $D^+$ ($A^+$) in the SMDPPEH (PC71BM) neat film. Then, the PIA intensity per unit density of $D^+$ ($A^+$) becomes $\alpha_{\text{exciton}} = 0.028$ (0.002) nm²/exciton on considering the absolute numbers of the donor and acceptor excitons per absorbed photon in the SMDPPEH neat film. We found that the average process of $\phi\delta\prime$ significantly improves the scattering of $C\delta\prime$, $C\delta\prime$, and $C\Delta$ against $t$, which enables us to discuss the difference in $t_{\text{rise}}$ of $D^+$ and $t_{\text{decay}}$ of $D^+$ and $A^+$. Figure 3(a) shows a prototypical example of the spectral decompositions at 300 K. We observed that the 400 nm excitation excites both $D^+$ and $A^+$.
Fig. 4. Absolute number of donor ($n_D$) and acceptor ($n_A$) excitons per absorbed photon and relative number of donor carriers ($n_{A^+}$) as functions of the delay time at (a) 300 K and (b) 80 K. Adjacent averages were plotted in $n_{A^+}$. The solid curves are results of least-squares fittings with exponential functions.

Table I. Characteristic times ($\tau_{\text{rise}}$ and $\tau_{\text{decay}}$) and amplitudes ($C$) of $n_D$, $n_{A^+}$, and $n_A$. The parameters were obtained through least-squares fittings with the exponential functions. The obtained $\tau_{\text{rise}}$, $\tau_{\text{decay}}$, and $C$ for $D^+$, $D^-$, and $A^+$ are listed in Table I. We emphasize that $\tau_{\text{rise}}$ shows no temperature dependence, even though $\tau_{\text{decay}}$ of $A^+$ significantly increased from 0.4 ps at 300 K to 1.0 ps at 80 K. The effect of temperature on $\tau_{\text{decay}}$ of $A^+$ is understood in terms of the thermally activated exciton diffusion. The fast $\tau_{\text{decay}}$ of $A^+$ at 300 K is ascribed to the fast exciton diffusion and resultant additional recombination process at the trap state. The temperature independence of $\tau_{\text{rise}}$ is well explained if only the excitons created near the interface contribute to the carrier formation process. In this case, $\tau_{\text{rise}}$ is hardly influenced by temperature because the process is free from activation-type exciton diffusion.

In summary, we spectroscopically clarified the effects of temperature on the carrier formation and exciton decay dynamics in SMDPPEH:PC$_{71}$BM blend film. We found that $\tau_{\text{rise}}$ of $D^+$ is independent of temperature. The temperature independence suggests that only the excitons created near the D/A boundary contribute to the carrier formation process.

**Acknowledgment** This work was supported by the Futaba Electronics Memorial Foundation.

1) M. Hiramoto, H. Fujiwara, and M. Yokoyama, Appl. Phys. Lett. 58, 1062 (1991).
2) N. S. Sariciftci, L. Smilowitz, A. H. Heeger, and F. Wudl, Science 258, 1474 (1992).
3) J-W. Hwang, D. Moses, and A. J. Heeger, J. Phys. Chem. C 112, 4350 (2008).
4) J. Guo, H. Okitaka, H. Benten, and S. Ito, J. Am. Chem. Soc. 131, 16869 (2009).
5) J. Guo, H. Okitaka, H. Benten, and S. Ito, J. Am. Chem. Soc. 132, 6154 (2010).
6) K. Yonezawa, M. Ito, H. Kamioka, T. Yasuda, L. Han, and Y. Moritomo, Adv. Opt. Technol. 1, 316045 (2012).
7) A. R. Marsh, J. M. Hodgkiss, S. Albert-Seifried, and R. H. Friend, Nano Lett. 10, 923 (2010).
8) J. M. Szalko, J.-C. Guo, B. S. Rolczynski, and L. X. Chen, J. Mater. Chem. 21, 7849 (2011).
9) B. S. Rolczynski, J. M. Szalko, H. J. Son, Y. Liang, L. Yu, and L. X. Chen, J. Am. Chem. Soc. 134, 4142 (2012).
10) K. Yonezawa, H. Kamioka, T. Yasuda, L. Han, and Y. Moritomo, Jpn. J. Appl. Phys. 52, 062405 (2013).
11) K. Yonezawa, H. Kamioka, T. Yasuda, L. Han, and Y. Moritomo, Appl. Phys. Lett. 103, 173901 (2013).
12) T. Akaba, K. Yonezawa, H. Kamioka, T. Yasuda, L. Han, and Y.
Moritomo, Appl. Phys. Lett. 102, 133901 (2013).
13) K. Yonezawa, H. Kamioka, T. Yasuda, L. Han, and Y. Moritomo, Appl. Phys. Express 5, 042302 (2012).
14) J. Guo, Y. Liang, J. Szarko, B. Lee, H.-J. Son, B. S. Rolczynski, L. Yu, and L. X. Chen, J. Phys. Chem. B 114, 742 (2010).
15) Y. Liang, Y. Wu, D. Feng, S.-T. Tsai, H.-J. Son, G. Li, and L. Yu, J. Am. Chem. Soc. 131, 56 (2009).
16) Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, and L. Yu, Adv. Energy Mater. 22, E135 (2010).
17) Z. He, C. Zhong, S. Su, M. Xu, H. Wu, and Y. Cao, Nat. Photonics 6, 593 (2012).
18) B. A. Collins, Z. Li, J. R. Tumbleston, R. Gunn, C. R. McNeill, and H. Ade, Adv. Energy Mater. 3, 65 (2013).
19) Y. Moritomo, T. Sakurai, T. Yasuda, Y. Takeichi, K. Yonezawa, H. Kamioka, H. Suga, Y. Takahashi, Y. Yoshida, N. Inami, K. Mase, and K. Ono, Appl. Phys. Express 7, 052302 (2014).
20) Y. Moritomo, T. Yasuda, K. Yonezawa, T. Sakurai, Y. Takeichi, H. Suga, Y. Takahashi, N. Inami, K. Mase, and K. Ono, Sci. Rep. 5, 9483 (2015).
21) G. J. Hedley, A. J. Ward, A. Alekseev, C. T. Howells, E. R. Martins, L. A. Serrano, G. Cooke, A. Ruseckas, and I. D. W. Samuel, Nat. Commun. 4, 2867 (2013).
22) Y. Moritomo, K. Yonezawa, and T. Yasuda, Appl. Phys. Lett. 105, 073902 (2014).
23) R. A. Marcus, Rev. Mod. Phys. 65, 599 (1993).
24) S. Qu and H. Tian, Chem. Commun. 48, 3039 (2012).
25) A. B. Tamayo, B. Walker, and T.-Q. Nguyen, J. Phys. Chem. C 112, 11545 (2008).
26) A. B. Tamayo, X.-D. Dang, B. Walker, J. Seo, T. Kent, and T.-Q. Nguyen, Appl. Phys. Lett. 94, 103301 (2009).
27) Y. Moritomo, K. Yonezawa, and T. Yasuda, Sci. Rep. 5, 13648 (2015).
28) S. D. Dimitrov, A. A. Bakulin, C. B. Nielsen, B. C. Schroder, J. Du, H. Brunstein, I. McCulloch, R. H. Friend, and J. R. Durrant, J. Am. Chem. Soc. 134, 18189 (2012).
29) H. Tamura and I. Burghardt, J. Am. Chem. Soc. 135, 16364 (2013).
30) M. Huix-Rotllant, H. Tamura, and I. Burghardt, J. Phys. Chem. Lett. 6, 1702 (2015).
31) O. V. Mikhnenko, F. Cordella, A. B. Sieval, J. C. Hummelen, P. W. M. Blom, and M. A. Loi, J. Phys. Chem. B 112, 11601 (2008).