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Spectroscopic Determination of Charge Formation Efficiency of Organic Photovoltaic Cells

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Abstract

The internal quantum efficiency (Φ_{IQ}) of an organic photovoltaic (OPV) cell is governed by plural processes, *i.e.*, the carrier formation process at the D/A interface and the carrier transfer process toward the collector electrode. Then, Φ_{IQ} can be decomposed into the carrier formation (Φ_{CF}) and carrier transfer efficiencies (Φ_{CT}). By combination of femtosecond time-resolved and electrochemical spectroscopies, we determined absolute values of Φ_{CF} of F8T2/PC₇₁BM, P3HT/PCBM, and PTB7/PC₇₁BM solar cells. We found that Φ_{CF} at 400 nm of the F8T2/PC₇₁BM cell is higher than those of the P3HT/PCBM, and PTB7/PC₇₁BM cells, although Φ_{IQ} at 400 nm is the lowest.

Keyword: Organic photovoltaic cell, carrier formation efficiency, ultrafast spectroscopy, electrochemical spectroscopy.

Introduction

OPV cells with a bulk heterojunction (BHJ)[1,2] are promising energy conversion devices, because they are flexible, environmental-friendly, and low-cost. The BHJ active layer is a nano-level mixture of a donor (D) polymer and acceptor (A) fullerenes. Extensive time-resolved spectroscopy studies have been carried out to reveal the carrier formation dynamics in a poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) [3-7] and poly-[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b⁰]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl] (PTB7)/ [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM) [8-13] blend films.

Careful analyses of time-dependence of photoinduced absorption (PIA) reveals relative numbers of excitons and carriers against the time (t). Thus, one can determine the lifetime of exciton and/or formation time of carrier, which clarifies the conversion process from exciton to carrier. For example, the exciton-carrier conversion process in PTB7/PC₇₁BM blend film takes place within ~ 0.3 ps.[11] However, interrelation between the carrier formation time/exciton decay time and the photovoltaic properties, *e.g.*, power conversion efficiency (PCE), is unclear.

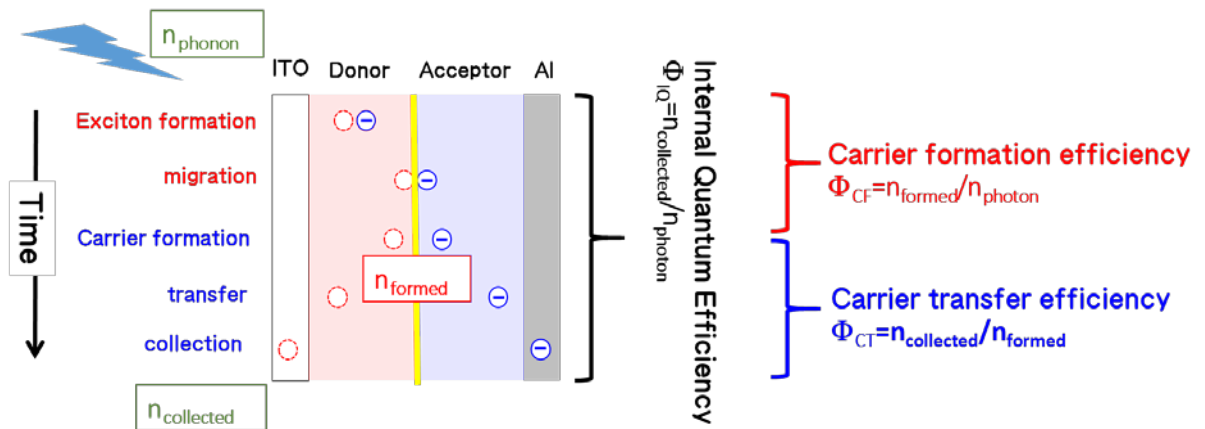


Fig.1: Schematic illustration of photovoltaic process in organic solar cell.

The energy conversion of an OPV cell is governed by plural processes (see Fig.1). In the former process, carriers are formed by the photo-irradiation: the photo irradiation creates a donor exciton (D^*) in the donor region, and D^* migrates to the D/A interface, and finally, D^* separates into acceptor electron (A^-) and donor hole (D^+) at the interface. In the latter process, the carriers transfer to the collector electrode, and then, collected as photocurrent. This process is in sharp contrast with that of an inorganic photovoltaic (IPV) cell, which consists of only the latter process. The internal quantum efficiency (Φ_{IQ}) is defined by $n_{collected} / n_{photon}$, where $n_{collected}$ is the number of the carriers collected as current and n_{photon} is the number of the photon absorbed by the device. If we can determine the number of carriers formed at the D/A interface (n_{formed}), we can calculate carrier formation efficiency ($\Phi_{CF} = n_{formed} / n_{photon}$) and carrier transfer efficiency ($\Phi_{CT} = n_{collected} / n_{formed}$). These efficiencies are important quantities to comprehend the device process, because Φ_{IQ} is expressed as $\Phi_{CF} \times \Phi_{CT}$. Significantly, the carrier formation process completes within several ps in prototypical OPV cells.[11] Then, the time-resolved spectroscopy can separate the process from the subsequent slow carrier transfer process.

In this paper, we proposed a spectroscopic method to determine Φ_{CF} and applied the method to poly-(9,9'-dioctylfluorene-co-bithiophene) (F8T2)/PC₇₁BM, P3HT/PCBM, and PTB7/PC₇₁BM solar cells. We found that Φ_{CF} at 400 nm of the F8T2/PC₇₁BM cell is higher than those of the P3HT/PCBM, and PTB7/PC₇₁BM cells, although Φ_{IQ} at 400 nm is the lowest.

Determination of Carrier Formation Efficiency

The magnitude of Φ_{CF} was determined by combination of the femtosecond time-resolved and electrochemical spectroscopies. The former spectroscopy tells us the coefficient (α_{photon}) between the PIA (ΔOD) due to carrier and n_{photon} , while the latter spectroscopy tells us the coefficient (α_{carrier}) between ΔOD and n_{formed} . Then, Φ_{CF} is calculated by $\alpha_{\text{photon}}/\alpha_{\text{carrier}}$. In TABLE I, we listed the magnitude of α_{photon} , which are cited from literatures.[12,14,15] We choose the data at 400 nm because we can gather reliable α_{photon} values including the temperature dependence. The 400 nm photon, however, excites both the donor and acceptor excitons. Then, D^+ is produced by two process, *i. e.*, $D^* \rightarrow D^+ + A^-$ and $A^* \rightarrow D^+ + A^-$. Then, Φ_{CF} and Φ_{IQ} are the sum of the efficiencies for the two processes. We used the PIA signal due to D^+ to evaluate Φ_{CF} , because the D^+ signal is much stronger than the A^- signal.

| OPV | T (K) | α_{photon} (nm ²) | I ($\mu\text{J}/\text{cm}^2$) | α_{carrier} (nm ²) | $\Phi_{CF@400\text{nm}}$ |
|--------------------------|---------|---|-----------------------------------|--|--------------------------|
| F8T2/PC ₇₁ BM | 300 | 0.0027[15] | 27 | 0.0041 | 0.66 |
| P3HT/PCBM | 300 | 0.0047[12] | 27 | 0.0086 | 0.55 |
| P3HT/PCBM | 80 | 0.0047[12] | 27 | 0.0086 | 0.55 |
| PTB7/PC ₇₁ BM | 300 | 0.0076[14] | 27 | 0.0130 | 0.58 |
| PTB7/PC ₇₁ BM | 80 | 0.0072[14] | 27 | 0.0130 | 0.55 |

TABLE I. α_{photon} , α_{carrier} , and Φ_{CF} at 400 nm for several OPV cells. α_{photon} , and α_{carrier} were estimated by femtosecond time-resolved and electrochemical spectroscopies, respectively. I is the excitation intensity.

Experimental Procedure

The electrochemical spectroscopy was performed for the F8T2, P3HT, and PTB7 neat films. The F8T2 neat film was spin-coated on an indium-tin-oxide (ITO) glass substrate from an *o*-dichlorobenzene (*o*-DCB) solution and annealed for 10 min at 80 °C in an inert N₂ atmosphere. The P3HT neat film was spin-coated from an *o*-DCB solution and

annealed for 10 min at 110 °C in an inert N₂ atmosphere. The PTB7 neat film was spin-coated on the substrate from an *o*-DCB solution and was dried in an inert N₂ atmosphere. The thicknesses of the F8T2, P3HT, and PTB7 films were 67, 86, and 96 nm, respectively. The electrochemical hole-doping was performed against Li in propylene carbonate (PC) solution containing 1 mol/l LiClO₄ in an optical cell with a pair of quartz windows. [16,17] The active area of the film was ~ 2 cm², and the current was 100 nA. The voltages in the hole-doping process were 3.8, 3.4, and 3.7 V against Li for the F8T2, P3HT, and PTB7 films, respectively. The electrochemical differential absorption (ΔOD_{EC}) spectrum is expressed as $-\log(I_{doped}/I_{non})$, where I_{doped} and I_{non} are the transmission spectra of the hole-doped and non-doped films, respectively.

We fabricated an BHJ solar cells with the structure of ITO / PEDOT:PSS (~40 nm)/active layer/LiF (~1 nm)/Al (~80 nm). Details of fabrication processes are described in the literature. [6, 17] In TABLE II, we listed the photovoltaic performances under AM 1.5 solar-simulated light irradiation of 100 mW/cm².

| OPV | J_{SC} (mA/cm ²) | V_{OC} (V) | FF | PCE (%) | $\Phi_{IQ@400nm}$ | $\Phi_{CF@400nm}$ |
|--------------------------|--------------------------------|--------------|------|---------|-------------------|-------------------|
| F8T2/PC ₇₁ BM | 4.28 | 1.00 | 0.43 | 2.28 | 0.35 | 0.66 |
| P3HT/PCBM | 9.9 | 0.60 | 0.64 | 3.80 | 0.60 | 0.55 |
| PTB7/PC ₇₁ BM | 14.21 | 0.72 | 0.61 | 6.24 | 0.61 | 0.58 |

TABLE II. Short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), PCE, Φ_{IQ} , and Φ_{CF} of BHJ solar cells.

Results

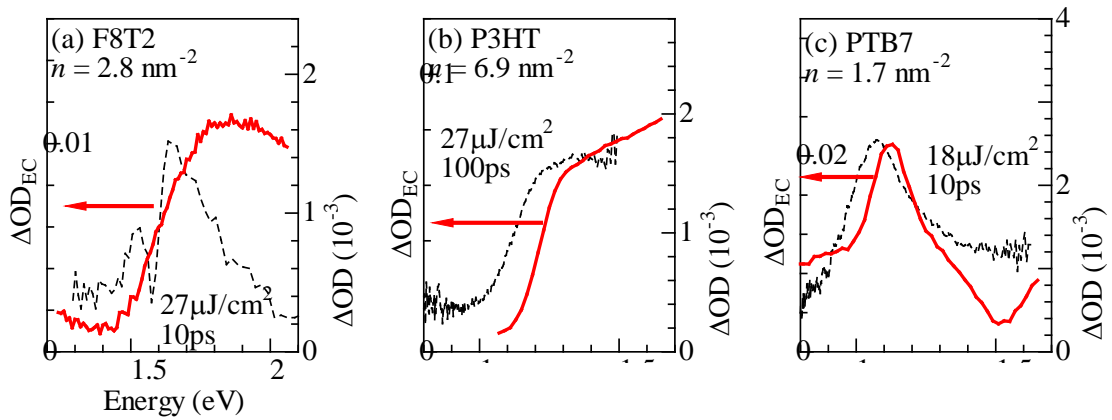


Fig.2: ΔOD_{EC} spectrum of (a) F8T2, (b) P3HT, and PTB7 neat films. n is the density of

the electrochemically-doped holes. Broken curves are ΔOD spectra cited from literatures: (a) F8T2/PC₇₁BM[15], (b) P3HT/PCBM,[12] and (c) PTB7/PC₇₁BM.[14]

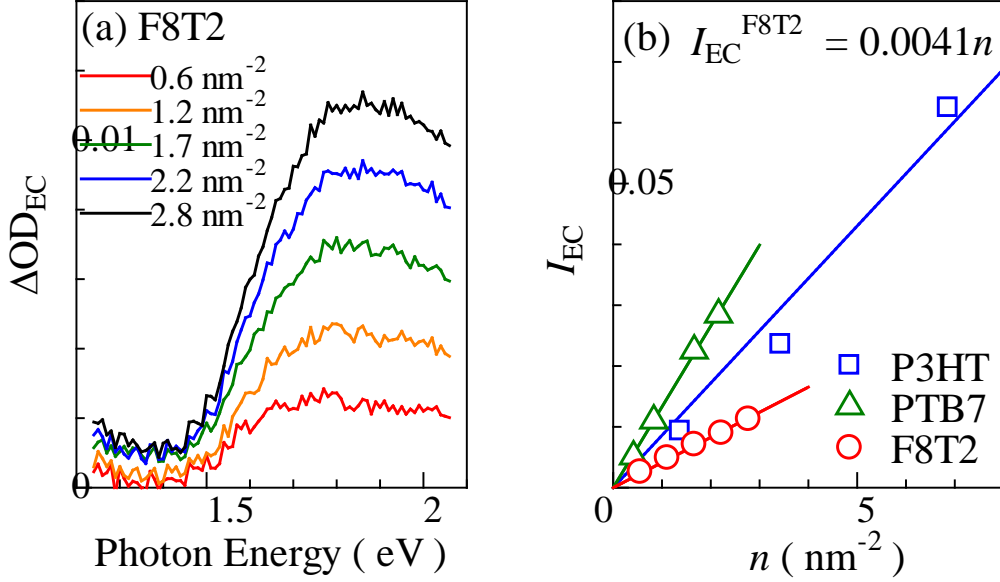


Fig.3: (a) ΔOD_{EC} spectrum of neat F8T2 film against carrier density (n). (b) Intensity (I_{EC}) of the ΔOD_{EC} spectra against n in the F8T2, P3HT, and PTB7 neat films. The straight lines are the results of least-squares fittings.

Figure 2 shows the ΔOD_{EC} spectra of (a) F8T2, (b) P3HT, and PTB7 neat films. In all the polymers, the profiles of the ΔOD_{EC} spectra are similar to those of the ΔOD spectra. This indicates that the absorption should be ascribed to D^+ . Figure 3 (a) shows the ΔOD_{EC} spectra of the neat F8T2 film against carrier density (n). Figure 3 (b) shows intensity (I_{EC} at 1.8 eV) of the ΔOD_{EC} spectra of F8T2 neat film against n . The magnitude of I_{EC} increases in proportional to n . $\alpha_{carrier}$ was determined by least-squares fitting, as indicated by straight line. With use of $\alpha_{carrier}$ and α_{photon} , we calculated Φ_{CF} and listed in TABLE I and TABLE II.

Discussion

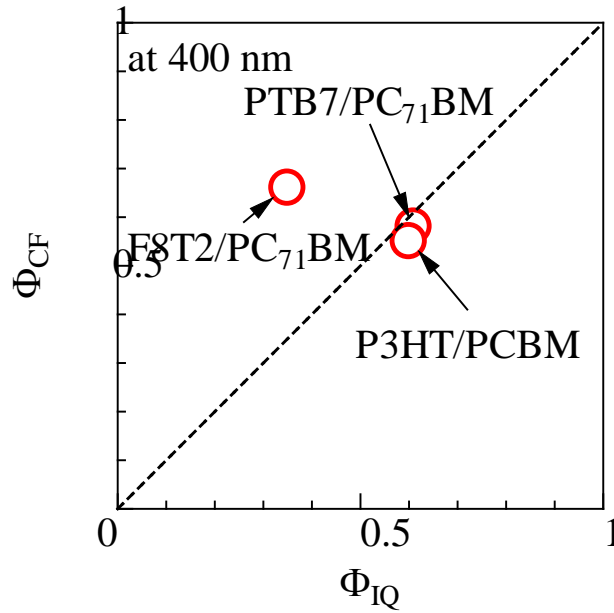


Fig.4: Interrelation between Φ_{CF} and Φ_{IQ} for F8T2/PC₇₁BM, P3HT/PCBM, and PTB7/PC₇₁BM solar cells.

We plotted in Fig.4 interrelation between Φ_{CF} and Φ_{IQ} for F8T2/PC₇₁BM, P3HT/PCBM, and PTB7/PC₇₁BM solar cells. As seen in TABLE II, PCE of the PTB7/PC₇₁BM cell is larger than that of the P3HT/PCBM cell. However, the Φ_{IQ} values at 400 nm are nearly the same between the two solar cells. Our spectral analysis revealed that the Φ_{CF} values at 400 nm are approximately the same between the two solar cells. Then, the larger PCE in the PTB7/PC₇₁BM cell should be ascribed to the low band-gap nature of the PTB7. Looking at Fig. 4, we found that Φ_{CF} of the F8T2/PC₇₁BM cell is higher than those of the P3HT/PCBM and PTB7/PC₇₁BM cells, although Φ_{IQ} at 400 nm is the lowest. We suspect that the high- Φ_{CF} is ascribed to the nano-level mixing of F8T2 and PC₇₁BM. Our spectral analysis revealed that the low- Φ_{IQ} of the F8T2/PC₇₁BM cell should be ascribed to the worse carrier transfer efficiency (Φ_{CF}).

Conclusion

We proposed a spectroscopic method to determine Φ_{CF} and applied the method to the F8T2/PC₇₁BM, P3HT/PCBM, and PTB7/PC₇₁BM solar cells. Our method is applicable to the fast screening of the photovoltaic materials, because the high- Φ_{CF} should be one necessary condition for a high-PCE solar cell. The spectroscopic determination of Φ_{CF} is a powerful tool to comprehend the complicated process of organic solar cells.

References

1. Hiramoto, M., Fujiwara, H., and Yokoyama, M. (1991). *Appl. Phys. Lett.*, 58, 1062 .
2. Sariciftci, N. S., Smilowitz, L., Heeger, A. J., and Wudl, F. (1992). *Science*, 285, 1474.
3. Hwang, I.-W., Moses, D., and Heeger, A. J. (2008). *J. Phys. Chem., C* 112, 4350.
4. Guo, J., Ohkita, H., Benten, H., and Ito, S. (2009). *J. Am. Chem. Soc.*, 131, 16869.
5. Guo, J., Ohkita, H., Benten, H., and Ito, S. (2010). *J. Am. Chem. Soc.*, 132, 6154.
6. Yonezawa, K., Ito, M., Kamioka, H., Yasuda, T., Han, L., and Moritomo, Y. (2012). *Adv. Opt. Technol.*, 2012, 316045.
7. Marsh, R. A., Hodgkiss, J. M., Albert-Seifried, S., and Friend, R. H. (2010). *Nano Lett.*, 10, 923.
8. Guo, J., Liang, Y., Szarko, J., Lee, B., Son, H.-J., Rolczynski, B. S., Yu, L., and Chen, L. X. (2010). *J. Phys. Chem., B* 114, 742.
9. Szarko, J. M., Guo, J.-C., Rolczynski, B. S., and Chen, L. X. (2011). *J. Mater. Chem.*, 21, 7849.
10. Rolczynski, B. S., Szarko, J. M., Son, H. J., Liang, Y., Yu, L., and Chen, L. X. (2012). *J. Am. Chem. Soc.*, 134, 4142.
11. Yonezawa, K., Kamioka, H., Yasuda, T., Han, L., and Moritomo, Y. (2013). *Jpn. J. Appl. Phys.*, (2013) 52, 062405.
12. Yonezawa, K., Kamioka, H., Yasuda, T., Han, L., and Moritomo, Y. (2013). *Appl. Phys. Lett.*, 103, 173901.
13. Akaba, T., Yonezawa, K., Kamioka, H., Yasuda, T., Han, L., and Moritomo, Y. (2013). *Appl. Phys. Lett.*, 102, 133901.
14. Moritomo, Y., Yonezawa, K., and Yasuda, T. (2014). *Appl. Phys. Lett.*, 105, 073902.
15. Yonezawa, K., Ito, M., Kamioka, H., Yasuda, T., Han, L., and Moritomo, Y. (2011). *Appl. Phys. Express*, 4 122601.
16. Harbeke, G., Baeriswyl, D., Kiess, H., and Kobel, W. (1986). *Phys. Scr.*, T13, 302.
17. Yasuda, T., Yonezawa, K., Ito, M., Kamioka, H., Han, L., and Moritomo, Y. (2012). *J. Photopolym. Sci. Technol.*, 25, 271.