Exploring Photovoltaic Feasibility of Pentaaryl [60]Fullerene in Bulk Heterojunction Architecture

Tsubasa Mikie, Akinori Saeki*, Naohiko Ikuma, Ken Kokubo, and Shu Seki*

*Department of Applied Chemistry, Graduate School of Engineering,
Osaka University, Osaka 565-0871, Japan.*

The photochemical process of pentaaryl [60]fullerenes (PAC₆₀) has been investigated by fluorescence and transient absorption spectroscopies, aiming at their use in bulk heterojunction organic photovoltaic (OPV). Fluorescence quenching was observed by adding C₆₀ into PAC₆₀, where the intensity was decreased in an exponential manner. The photo-generated radical cation of PAC₆₀ was identified at 925 nm in the presence of electron acceptor. Motivated from the observed shallow molecular orbital levels of PAC₆₀, we performed conceptual study of all-fullerene OPV, where PAC₆₀ and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) were presumably used as a p-type and n-type semiconductor, respectively. The power conversion efficiency was 0.007%, much smaller than 0.05% found for the conventional combination of P3HT (p-type) and PAC₆₀ (n-type). The mechanism is discussed on the basis of photoconductive and spectroscopic results.

keywords: organic solar cell, transient absorption spectroscopy, time-resolved microwave conductivity

1. Introduction

Organic photovoltaic cells (OPV) have attracted a great deal of attentions due to their low-cost and wide-area fabrication on a light-weight flexible substrate.^{1,2)} P-type conjugated polymers and n-type fullerenes are the key materials in this regard.^{3,4)} The nano-scale p/n bicontinuous network, termed bulk heterojunction, leads to the dramatic improvement of charge separation efficiency. Currently the power conversion efficiency (PCE) of single layer OPV exceeds 11 %, approaching the criteria of commercialization.^{5,6)}

As a counterpart of the conventional framework of p-type polymer and n-type fullerene, all-polymer OPV (p-type and n-type polymers)⁷⁻⁹⁾ and non-fullerene OPV (p-type polymer and n-type molecule)^{10,11)} have been investigated to explore the potential diversity of organic semiconductors. The PCEs are, however, still much lower than the polymer-fullerene OPV. The reason is likely linked to the delocalization of hole along the backbone,¹²⁾ crystallite of fullerene,¹³⁾ energy gradient in the mixed phase of polymer and fullerene,¹⁴⁾ and entropy of isotropic fullerenes domains,¹⁵⁾ all of which facilitate efficient charge separation in polymer-fullerene

OPV to escape from the strong Coulomb potential.

Interestingly, p-type nature of fullerene derivatives has been reported in the last decade. Anthopoulos *et al.* have demonstrated the ambipolar carrier transport in field-effect transistor of PCBM.^{16,17)} Nelson *et al.* have found a pronounced hole mobility in poly(para-phenylenevinylene):MDMO-PPV and PCBM blend films greater than the pristine polymer film, indicative of the hole transport in PCBM aggregates,¹⁸⁾ which was later supported by ultrafast spectroscopy.¹⁹⁾ Recently, unconventional use of C₆₀ or PCBM as a p-type semiconductor in OPV has been reported by some groups, where fluorinated-phthalocyanine (F₁₆-ZnPc)^{20,21)} or oligo-thiophene end-capped by strong electron withdrawing unit²²⁾ act as a n-type material. Furthermore, controlling the Fermi energy of C₆₀ was realized by precise doping of MoO₃ or Ca into the ultrapure C₆₀ film.^{23,24)} Synthetic chemistry also provides an attractive route toward precise tuning of the energy level by functionalizing the fullerene cage.²⁵⁻²⁷⁾

Herein, we focused on the multi-addition of fullerene which is known as a versatile approach to raise the lowest unoccupied molecular orbital (LUMO) level. To this end, pentaaryl

[60]fullerenes (PAC₆₀) developed by Nakamura *et al.*²⁸⁻³⁰⁾ are appropriate motifs, due to their facile synthetic procedure with a good yield. We have also investigated photochemical properties of PAC₆₀ in solution by transient absorption spectroscopy (TAS) and photoelectric conversion in film state by time-resolved microwave conductivity (TRMC). Finally we examined the OPV performance of PCBM:PAC₆₀ and P3HT:PAC₆₀ systems.

2. Experimental

PAC₆₀s (**1a–d**) were synthesized in the same way with Nakamura *et al.*²⁸⁻³⁰⁾ The chemical structures are drawn in Figure 1. They were identified by ¹H-NMR, ¹³C-NMR, and MALDI-TOF-MASS. The highest occupied molecular orbital (HOMO) levels were measured by photoelectron yield spectroscopy (PYS). The LUMO levels in the film state were obtained by adding the optical bandgap (absorption edge) to the HOMO levels. Fluorescence quenching was measured in *o*-dichlorobenzene (*o*-DCB) solutions by a fluorescence spectrometer ($\lambda_{\text{ex}} = 300$ nm). TAS experiments were performed by a streak camera or a Si-PIN photodetector upon 355 nm excitation from a nanosecond Nd:YAG laser. The details of TRMC measurements (9.1 GHz, $\lambda_{\text{ex}} = 355$ nm) have been reported previously.³¹⁾

OPV devices were fabricated according to our previous report.³²⁾ The device configuration is ITO/PEDOT:PSS/Active layer/Ca(20nm)/Al(100 nm). *o*-DCB without any additives was used as a solvent. Current-voltage (*J*-*V*) curves were measured using a source-measure unit under AM 1.5G solar illumination at 100 mWcm⁻² (1 sun) using a 300 W solar simulator.

3. Results and discussion

The energy diagram of PAC₆₀s along with C₆₀ and PCBM is shown in Figure 1. The penta-phenyl adduct (**1a**) revealed a significant raise of LUMO by 0.6 eV compared with the bare

Figure 1. Energy diagram of fullerene derivatives in film states determined from PYS and optical bandgap.

C₆₀. By substituting proton for electron-donating methoxy (**1b**) and *t*-butyl (**1c**) at the para-position of the phenyls, the LUMOs are further elevated from -3.82 eV (**1a**) to -3.70 eV (**1b**) and -3.63 eV (**1c**). Simultaneously, the HOMOs of these three PAC₆₀s were lowered with keeping the identical bandgap energy (ca. 2.3 eV). Inversely, the electron-withdrawing trifluoromethyl substitution deepened the LUMO level to -3.88 eV (**1d**). Notably, the HOMO (-6.25 eV) was deeper than those of PCBM and C₆₀. These substitutions allowed the control of the energy level by inductive effect of substituents.

In order to examine the electronic interaction between PAC₆₀ and fullerene, fluorescence quenching was measured in *o*-DCB solution. The C₆₀ was selected as the counterpart, because it has the lowest-lying LUMO. The most basic PAC₆₀ structure, **1a**, exhibited an intense orange fluorescence at 595 nm (Figure 2a). Upon addition of C₆₀, the fluorescence was progressively quenched in the exponential manner (Figure 2b). C₆₀ has a very weak fluorescence at ca. 700 nm,³²⁾ as a result of symmetrically forbidden transition from the excited singlet state to ground state.³⁴⁾ The observed nonlinear dependence of the intensity on C₆₀ content suggests that the electron or energy transfer is involved in the fluorescence quenching. More distinguished quenching was observed in the blend film, where only the presence of 0.11 wt% C₆₀ quenched about 90 % of fluorescence from **1a**, due to the efficient exciton migration in the film (Figure 2b).

To gain access to spectroscopic information of the short-lived species of **1a**, we carried out TAS in N₂-purged *o*-DCB solution. Figure 3a shows the TAS spectra at the pulse end observed for the single component of **1a** or C₆₀. The characteristic spectrum of C₆₀ solution centered at 740 nm is readily ascribed to the triplet excited state, in accordance with the literatures.^{35,36)} Similarly, we can safely attribute the **1a** spectrum

Figure 2. (a) Fluorescence spectra of **1a** (0.25wt% in *o*-DCB) upon addition of C₆₀. [C₆₀] is the weight fraction of C₆₀ given by C₆₀/(C₆₀+**1a**). $\lambda_{\text{ex}} = 300$ nm. (b) Dependence of intensity integrated over the photon energy on [C₆₀] in solution (triangles) and film (square).

centered at 660 nm to its triplet excited state ($^3\mathbf{1a}^*$). The time profiles at their maxima followed a single exponential decay with the lifetimes of 9.3 and 4.7 μs for $^3\mathbf{1a}^*$ and $^3\text{C}_{60}^*$, respectively (Figure 3b).

In sharp contrast, the TAS spectrum of $\mathbf{1a}$ was drastically changed to the broad feature with the maximum at 925 nm in the presence of excess amount of strong electron acceptor: tetracyanoethylene (TCNE, 1:20 in wt fraction) (Figure 3c). Ohkita *et al.* has investigated the photo-induced electron transfer from TCNE to PCBM and assigned the absorption peak at 890 nm to the PCBM radical cation.³⁷⁾ Accordingly, $\mathbf{1a}$ radical cation is the intermediate that gives the absorption in $\mathbf{1a}$:TCNE solution.

Having all that in mind, the TAS experiment was conducted for the *o*-DCB solution of $\mathbf{1a}$ and C_{60} mixture (1:1 in w/w%), which exhibited approximately 80% quenching of fluorescence from $\mathbf{1a}$ (Figure 2). The TAS spectra in Figure 3d, however, indicate a single dominant peak at ca. 750 nm arisen from C_{60} triplet excited state. Neither radical cation nor triplet of $\mathbf{1a}$ appeared at all even after 10 μs delay. Therefore, we can conclude that energy transfer from $\mathbf{1a}$ to C_{60} , eventually giving rise to the triplet excited state of the latter, is the primary process in the fluorescence quenching rather than electron transfer.

Photocarrier generation processes were also traced in the blend films of PAC_{60} with P3HT or

Figure 3. (a) End-of-pulse transient absorption spectra of triplet excited states of $\mathbf{1a}$ ($^3\mathbf{1a}^*$, black line) and C_{60} ($^3\text{C}_{60}^*$, gray line) observed in N_2 -bubbled *o*-DCB solutions excited at 355 nm. (b) Semi-logarithmic decay plots of $^3\mathbf{1a}^*$ (black triangles) and $^3\text{C}_{60}^*$ (gray squares) at their maxima. (c) End-of-pulse transient absorption spectrum of *o*-DCB solution of 0.5 wt% $\mathbf{1a}$ with 10 wt% TCNE. (d) Time evolution of transient absorption spectra in *o*-DCB solution of $\mathbf{1a} : \text{C}_{60} = 1:1$ (w/w%).

Figure 4. TRMC transient maxima ($\phi\Sigma\mu_{\text{max}}$) of (a) P3HT: $\mathbf{1b}$ and (b) $\mathbf{1b}$:PCBM blend films ($\lambda_{\text{ex}} = 355$ nm).

PCBM by TRMC. Hereafter $\mathbf{1b}$ was used instead of $\mathbf{1a}$, because of its superior film quality. The transient maxima, $\phi\Sigma\mu_{\text{max}}$ (ϕ : charge carrier generation efficiency, $\Sigma\mu$: the sum of hole and electron mobilities), display a marginal increase for the mixture of P3HT and $\mathbf{1b}$ (Figure 4a), but the largest $\phi\Sigma\mu_{\text{max}}$ is two orders of magnitude smaller than P3HT:PCBM.³²⁾ $\mathbf{1b}$:PCBM presented a further suppressed and straight dependence of $\phi\Sigma\mu_{\text{max}}$, indicating the absence of charge separation through electron transfer from PCBM to $\mathbf{1b}$. This TRMC result is consistent with the conclusion of inefficient charge separation upon excitation deduced from the fluorescence quenching and TAS experiments.

Finally, we evaluated OPV of P3HT: $\mathbf{1b}$ and $\mathbf{1b}$:PCBM (Figure 5). After the optimization of blend ratio and processes, the maximized PCEs were 0.049% for P3HT: $\mathbf{1b} = 1:1$ ($J_{\text{sc}} = 0.17$ mA cm^{-2} , $V_{\text{oc}} = 0.62$ V, FF = 0.47) and 0.0071% for $\mathbf{1b}$:PCBM ($J_{\text{sc}} = 0.044$ mA cm^{-2} , $V_{\text{oc}} = 0.28$ V, FF = 0.28). This fairly poor performance of all-fullerene OPV suffers strongly from the insufficient charge separation revealed by TAS and TRMC. Narrowing the bandgap of p-type fullerene to prevent the energy transfer is necessary for further improvement, with preserving the shallow LUMO levels.

Figure 5. J - V curves of P3HT: $\mathbf{1b}$ (1:3 w/w, gray line) and $\mathbf{1b}$:PCBM (1:1 w/w, black line) processed from *o*-DCB without thermal annealing under AM 1.5G (100 mWcm^{-2}).

4. Conclusion

We demonstrated that HOMO and LUMO of PAC₆₀s are significantly raised in comparison with PCBM and C₆₀ by rational tailoring of inductive effect at the para position. The radical cation and triplet excited state of **1a** has been characterized by TAS, the absorption maxima of which are 925 and 660 nm, respectively. The fluorescence quenching of PAC₆₀ by addition of C₆₀ was ascribed to the energy transfer rather than electron transfer, as unveiled by TAS and TRMC. The optimized PCEs of 0.05% were found for polymer-fullerene OPV and 0.007% for all-fullerene OPV.

Acknowledgements

This work was supported by JSPS Funding Program for NEXT Program, the PRESTO program of JST, and KAKENHI from MEXT, Japan. T. Mikie thanks the financial support of JSPS scholarship.

References

1. A. C. Arias, J. D. Mackenzie, I. McCulloch, J. Rivnay, A. Salleo, *Chem. Rev.* **110** (2010) 3.
2. G. Li, R. Zhu, Y. Yang, *Nature Photo.* **6** (2012) 153.
3. Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. C. Bradley, M. Giles, I. McCulloch, C. S. Ha, M. Ree, *Nature Mater.* **5** (2006) 107.
4. G. Demmler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* **21** (2009) 1323.
5. R. F. Service, *Science*, **332** (2011) 293.
6. M. A. Green, K. Emery, Y. Hishikawa, W. Warta, E. D. Dunlop, *Progress in Photovoltaics*, **22**, (2014) 1.
7. C. R. McNeill, A. Abruci, J. Zaumseil, R. Wilson, M. J. McKiernan, J. H. Burroughes, J. J. M. Halls, N. C. Greenham, R. H. Friend, *Appl. Phys. Lett.* **90** (2007) 193506.
8. D. Mori, H. Benten, H. Ohkita, S. Ito, K. Miyake, *ACS Appl. Mater. Interfaces* **4** (2012) 3325.
9. M. Ide, Y. Koizumi, A. Saeki, S. Seki, *J. Photopolym. Sci. Tech.* **26** (2013) 217.
10. H. Li, F. S. Kim, G. Ren, E. C. Hollenbeck, S. Subramanian, S. A. Jenekhe, *Angew. Chem. Int. Ed.*, **52** (2013) 5513.
11. R. Shivanna, S. Shoaee, S. Dimitrov, S. K. Kandappa, S. Rajaram, J. R. Durrant, K. S. Narayan, *Energy Environ. Sci.* **7** (2014) 435.
12. C. Deibel, T. Strobel, V. Dyakonov, *Phys. Rev. Lett.* **103** (2009) 036402.
13. B. M. Savoie, A. Rao, A. A. Bakulin, S. Gélinas, B. Movaghar, R. H. Friend, T. J. Marks, M. A. Ratner, *J. Am. Chem. Soc.* **136** (2014) 2876.
14. T. M. Burke, M. D. McGehee, *Adv. Mater.* **26** (2014) 1923.
15. B. A. Gregg, *J. Phys. Chem. Lett.* **2** (2011) 3013.
16. T. D. Anthopoulos, C. Tanase, S. Setayesh, E. J. Meijer, J. C. Hummelen, P. W. M. Blom, D. M. D. Leeuw, *Adv. Mater.* **16** (2004) 2174.
17. T. D. Anthopoulos, D. M. D. Leeuw, E. Cantatore, S. Setayesh, E. J. Meijer, *Appl. Phys. Lett.* **85**, (2004) 4205.
18. S. M. Tuladhar, D. Poplavskyy, S. A. Choulis, J. R. Durrant, D. D. C. Bradley, J. Nelson, *Adv. Funct. Mater.* **15** (2005) 1171.
19. S. Yamamoto, H. Ohkita, H. Benten, S. Ito, *Adv. Funct. Mater.* **22** (2012) 3075.
20. Q. L. Song, H. B. Y, Y. Gan, C. Gong, C. M. Li, *J. Am. Chem. Soc.* **132** (2010) 4554.
21. J. L. Yang, P. Sullivan, S. Schumann, I. Hancox, T. S. Jones, *Appl. Phys. Lett.* **100** (2012) 023307.
22. Y. Ie, M. Karakawa, S. Jinnai, H. Yoshida, A. Saeki, S. Seki, S. Yamamoto, H. Ohkita, Y. Aso, *Chem. Commun.* **50** (2014) 4123.
23. M. Kubo, K. Iketani, T. Kaji, M. Hiramoto, *Appl. Phys. Lett.* **98** (2011) 073311.
24. M. Kubo, T. Kaji, M. Hiramoto, *AIP Advances*, **1** (2011) 032177.
25. F. B. Kooistra, J. Knol, F. Kastenberg, L. M. Popescu, W. J. H. Verhees, J. M. Kroon, J. C. Hummelen, *Org. Lett.* **9** (2007) 551.
26. K. H. Kim, H. Kang, S. Y. Nam, J. Jung, P. S. Kim, C. H. Cho, C. Lee, S. C. Yoon, B. J. Kim, *Chem. Mater.* **23** (2011) 5090.
27. Y. Matsuo, J. Kawai, H. Inada, T. Nakagawa, H. Ota, S. Otsubo, E. Nakamura, *Adv. Mater.* **25** (2013) 6266.
28. M. Sawamura, H. Iikura, E. Nakamura, *J. Am. Chem. Soc.* **118** (1996) 12850.
29. M. Sawamura, H. Iikura, T. Ohama, U. E. Hackler, E. Nakamura, *J. Organomet. Chem.* **599** (2000) 32.
30. Y. Matsuo, E. Nakamura, *Chem. Rev.* **108** (2008) 3016.
31. A. Saeki, Y. Koizumi, T. Aida, S. Seki, *Acc. Chem. Res.* **45** (2012) 1193.
32. A. Saeki, S. M. Tsuji, S. Seki, *Adv. Energy Mater.* **1** (2011) 661.
33. Y. Zhao, Y. Fang, *J. Phys. Chem. B* **108** (2004) 13586.
34. F. Negri, G. Orlandi, F. Zerbetto, *J. Chem. Phys.* **97** (1992) 6496.
35. N. M. Dimitrijević, P. V. Kamat, *J. Phys. Chem.* **96** (1992) 4811.
36. A. Acharya, S. Seki, Y. Koizumi, A. Saeki, S. Tagawa, *J. Phys. Chem. B* **109** (2005) 20174.
37. S. Yamamoto, J. Guo, H. Ohkita, S. Ito, *Adv. Funct. Mater.* **15** (2008) 2555.