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Molecular Understanding of Open-Circuit Voltage of Polymer:Fullerene Solar Cells

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The origin of open-circuit voltage (V_{OC}) was studied for polymer solar cells based on a blend of poly(3-hexylthiophene) (P3HT) and seven fullerene derivatives with different LUMO energy levels and side chains. The temperature dependence of J - V characteristics was analyzed by an equivalent circuit model. As a result, V_{OC} increased with the decrease in the saturation current density J_0 of the device. Furthermore, J_0 was dependent on the activation energy E_A for J_0 , which is related to the HOMO–LUMO energy gap between P3HT and fullerene. Interestingly, the pre-exponential term J_{00} for J_0 was larger for pristine fullerenes than for substituted fullerene derivatives, suggesting that the electronic coupling between molecules also has substantial impact on V_{OC} . This is probably because the recombination is non-diffusion-limited reaction depending on electron transfer at the P3HT/fullerene interface. In summary, the origin of V_{OC} is ascribed not only to the relative HOMO–LUMO energy gap but also to the electronic couplings between fullerene/fullerene and polymer/fullerene.

1. Introduction

The power conversion efficiency (PCE) of bulk heterojunction organic solar cells based on conjugated polymer and fullerene derivatives has been steadily improved during the last decade. Recently, PCE in excess of 8% has been reported.^[1,2] In general, there are two strategies for improving the device performance: one is to increase the short-circuit current density (J_{SC}) and the other is to increase the open-circuit voltage (V_{OC}). The maximum photocurrent is primarily limited by the number of photons absorbed by the solar cells. In other words, J_{SC} can be improved by using materials that have wider absorption bands to collect more photons from the solar light. For this purpose, a C_{70} fullerene derivative has been employed with conjugated polymers instead of C_{60} fullerene derivatives because of the larger extinction coefficient in the visible region.^[3] Currently, various low-bandgap polymers have been developed to harvest the near-IR light and primarily contribute to the recent progress in PCE of polymer solar cells.^[4-6] The incorporation of near-IR dye molecules into polymer:fullerene solar cells also has been reported to effectively improve the light-harvesting efficiency and hence boost J_{SC} substantially.^[7-10] On the other hand, the maximum photovoltage is considered to be limited by the energy gap between the highest occupied molecular orbital (HOMO) level of a donor polymer and the lowest unoccupied molecular orbital (LUMO) level of an acceptor fullerene (ΔE_{DA}). Indeed, V_{OC} has been reported to increase with lowering HOMO level of polymers and raising LUMO level of fullerenes.^[11-14] Currently, remarkable progress in the device performance has been made using these strategies.^[15,16]

Although there have been several studies showing a linear relationship between V_{OC} and ΔE_{DA} experimentally, V_{OC} is generally 0.2 – 0.5 V smaller than ΔE_{DA} .^[11-14] Recently, the difference between V_{OC} and ΔE_{DA} has been discussed. For example, Koster *et al.* reported that the difference is related to the dissociation probability of bound electron–hole pair and

the Langevin recombination of free carriers assuming that the quasi-Fermi levels are constant throughout the device.^[17,18] A recent study on the light intensity dependence of photocurrent has shown that the recombination dynamics is the voltage dependent: first-order recombination under an short-circuit condition and bimolecular recombination under an open-circuit condition. From the temperature/intensity dependence of V_{OC} , the difference between V_{OC} and ΔE_{DA} is ascribed to the temperature dependence of the quasi-Fermi levels in the polymer and fullerene domains.^[19] Similarly, Durrant *et al.* reported that the charge dynamics is dominated by bimolecular recombination at V_{OC} by transient photovoltage and absorption measurements. They note that the bimolecular rate constant is 2–3 orders of magnitude smaller than the Langevin recombination rate.^[20] Furthermore, they recently demonstrated that V_{OC} varies only by ~ 0.1 V between P3HT and bridged thiophene-based polymers with a difference of 0.2 – 0.4 eV in ionization potentials, and assigned this mismatch to a faster recombination rate in bridged thiophene-based devices. Consequently, they proposed that V_{OC} depends not only on ΔE_{DA} but also on the magnitude bimolecular recombination rate.^[21] On the other hand, V_{OC} is dependent on the saturation current density J_0 in terms of the diode-based equivalent circuit model. Recently, the molecular structures has been reported to affects V_{OC} in small molecule-based organic solar cells.^[22–24] This suggests that V_{OC} is dependent on the electron transfer at the interface because of the difference in the electronic coupling between donor and acceptor molecules. From another point of view, Inganäs *et al.* reported a linear relationship between V_{OC} and the charge transfer (CT) emission energy E_{CT} for blend films based on various conjugated polymers and PCBM. In this relationship, V_{OC} is reduced by 0.5 – 0.6 V compared to E_{CT} ,^[25–27] which is similar to the difference between V_{OC} and ΔE_{DA} . They ascribed ~ 0.25 V of the reduction to radiative losses that are related to the formation of CT complex, and the rest (~ 0.35 V) to nonradiative losses.^[27] As described above, the difference between V_{OC} and ΔE_{DA} has been discussed in terms of the bimolecular

recombination dynamics and the interfacial electron transfer separately. However, the origin of V_{OC} in polymer solar cells is not fully understood.

To address the origin of V_{OC} , we carefully analyzed J - V characteristics in the dark on the basis of the one-diode equivalent circuit model. This simple equivalent circuit model has been widely used for analyzing organic solar cells because it can explain the device parameters quantitatively.^[22–24,26,28–32] Indeed, V_{OC} measured under illumination can be predicted quantitatively from the analysis of the diode characteristics in the dark.^[22–24] In this study, we employed seven fullerene derivatives with different LUMO levels as shown in **Figure 1** in order to discuss the relationship between V_{OC} and ΔE_{DA} systematically. Five of them are fullerene derivatives with attached groups: [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM), [6,6]-diphenyl- C_{62} -bis(butyric acid methyl ester) (bis-PCBM),^[33,34] [6,6]-phenyl- C_{85} -butyric acid methyl ester (PC₈₄BM),^[35] [6,6]-1-thienyl- C_{61} -butyric acid methyl ester (ThCBM),^[36] [6,6]-bis[3,5-([1',2']-benzeno)-4*H*-cyclopenta]- C_{60} (Indene- C_{60} -bisadduct, ICBA).^[37] The other two are pristine fullerenes of C_{60} and C_{70} , which are employed to discuss the effect of the side chain on V_{OC} .

2. Results

2.1. J - V Characteristics

Figure 2 shows the J - V characteristics of seven P3HT-based solar cells with different fullerene derivatives. All the devices showed reproducible diode characteristics in the dark and photovoltaic performance under the AM1.5G simulated solar illumination. The J_{SC} and FF were slightly smaller than those reported in the literatures^[7–10,33–39] because each device was not fully optimized but just the active layer was fabricated in the same thickness. On the other hand, V_{OC} was in good agreement with the reported values:^[7–10,33–39] that ranged from 0.16 V for PC₈₄BM to 0.81 V for ICBA. The device parameters of these cells are summarized

in **Table 1**. The energy level of the HOMO of P3HT was evaluated to be 4.68 eV by the photoemission yield spectroscopy measurement (see the Supporting Information). The energy levels of the LUMO of the fullerene derivatives were evaluated by cyclic voltammetry in solution with a ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an internal standard using Ag/AgCl reference electrode (see the Supporting Information).^[40] The energy differences between the HOMO level of P3HT and the LUMO level of fullerenes $\Delta E_{DA} = E_{HOMO}(P3HT) - E_{LUMO}(\text{fullerene})$ are summarized in Table 1. **Figure 3** shows a linear relationship between V_{OC} and ΔE_{DA} . This linear relationship is consistent with previous studies.^[11–14] Interestingly, the plots for pristine fullerenes (C₆₀ and C₇₀) deviate from the linear relationship: the V_{OC} of pristine fullerenes is smaller by ~0.1 V than that predicted from the linear relationship. This finding suggests that V_{OC} of polymer:fullerene solar cells cannot be explained by ΔE_{DA} alone as is discussed later. Furthermore, the hole mobility μ_h and photoluminescence (PL) quenching efficiency Φ_q of each blend film were evaluated by the space charge limited current measurement for the hole only devices and by the fluorescence measurement for the P3HT:fullerene blend and P3HT pristine films on a glass substrate, respectively. As summarized in Table 1, μ_h and Φ_q of blend films were independent of the fullerene derivatives. These results suggest that fullerene derivatives have little impact on the blend morphology of P3HT in the blend.

As shown in Figure 2, V_{OC} is closely related to the turn-on voltage in the dark current, suggesting that V_{OC} is strongly dependent on the diode characteristics. We therefore analyzed the dark current characteristics of these devices using the equivalent circuit model based on a diode $J_0[\exp(qV/nk_B T) - 1]$, a series resistor R_s , and a parallel resistor R_p as shown in **Figure 4a**. In this model, J – V characteristics can be derived by Eq. 1.^[28,29]

$$J = J_0 \left\{ \exp \left[\frac{q(V - JR_s A)}{nk_B T} \right] - 1 \right\} + \frac{(V - JR_s A)}{R_p A} - J_{ph} \quad (1)$$

where J_0 is the saturation current density, n is the ideality factor, R_s is the series resistance, R_p

is the parallel resistance, q is the elementary charge, k_B is the Boltzmann constant, T is the temperature, A is the active area of the device, and J_{ph} is the photocurrent density. As shown in Figure 4b, the dark J - V characteristics are well fitted with Eq. 1. All the diode parameters are summarized in **Table 2**. Assuming that J_{ph} is equal to J_{SC} , Eq. 1 can be simplified into Eq. 2 under the open-circuit condition because of $V_{OC} \ll J_{SC}R_pA$ and $J_0 \ll J_{SC}$.

$$V_{OC} = \frac{nk_BT}{q} \ln \left[1 + \frac{J_{SC}}{J_0} \left(1 - \frac{V_{OC}}{J_{SC}R_pA} \right) \right] \approx \frac{nk_BT}{q} \ln \left(\frac{J_{SC}}{J_0} \right) \quad (2)$$

The V_{OC}^{calc} calculated by the simplified Eq. 2 with the diode parameters is in good agreement with the V_{OC} observed within a relative error of 7%, which is consistent with our previous report.^[41] This agreement clearly shows that the diode characteristics in the dark is useful for analyzing V_{OC} of P3HT:fullerene solar cells employed in this study under illumination. In summary, V_{OC} of P3HT:fullerene solar cells is independent of R_s and R_p but essentially dependent on n , J_{SC} , and J_0 . For different fullerenes, as shown in Table 2, J_0 differs by six orders of magnitude while variations in n and J_{SC} are negligibly small. Thus, it can safely be said that V_{OC} of P3HT:fullerene solar cells is primarily dependent on J_0 .

2.2. Temperature Dependence of J_0

To address the origin of J_0 , we measured J - V characteristics in the dark over the temperature range from 180 to 310 K. **Figure 5a** shows the temperature dependence of J_0 of P3HT:fullerene solar cells. As reported previously,^[29] J_0 can be expressed by the Arrhenius equation.

$$J_0 = J_{00} \exp \left(-\frac{E_A}{k_BT} \right) \quad (3)$$

where J_{00} is the pre-exponential factor and E_A is the activation energy. From the ordinate intercept and slope of the Arrhenius plots, J_{00} and E_A can be evaluated. Figure 5b shows these two parameters J_{00} and E_A plotted against V_{OC} . As shown in the figure, no correlation is found between J_{00} and V_{OC} but a linear relationship is observed between E_A and V_{OC} .

Interestingly, J_{00} is classified based on the presence or absence of attached groups to the fullerene unit. The J_{00} of pristine fullerenes is almost two orders of magnitude larger than that of fullerene derivatives with attached groups. The contribution of J_{00} and E_A to V_{OC} is evaluated by Eq. 4, which can be obtained from Eqs. 2 and 3.

$$qV_{OC} = nE_A - nk_B T \ln \left(\frac{J_{00}}{J_{SC}} \right) \quad (4)$$

Figure 5c shows the proportion of each term in Eq. 4 for various fullerene derivatives. As shown in the figure, the first term on the right side is the largest and increases with increasing V_{OC} of polymer solar cells. On the other hand, the percentage of the second term to nE_A is $\sim 30\%$ for fullerene derivatives with attached groups and as large as $\sim 50\%$ for pristine fullerenes. In other words, E_A is the primary factor controlling V_{OC} , and J_{00} in the second term is a secondary factor but is not negligible for controlling V_{OC} . The second term is clearly dependent on the presence or absence of attached groups to the fullerene unit: $nk_B T \ln(J_{00}/J_{SC})$ is ~ 0.2 eV for fullerene derivatives with attached groups and is ~ 0.3 eV for pristine fullerenes.

3. Discussion

3.1. Recombination Current

First, we will consider the dark current density, as described above, which is closely related to V_{OC} . In the recombination via a bound electron–hole pair at a donor/acceptor interface, the recombination rate is given by $R = \gamma(n_e n_h - n_i^2)(1 - P_{dis})$ where γ is the Langevin recombination rate, P_{dis} is the dissociation probability of a bound electron–hole pair into free charge carriers at the interface, and n_e , n_h , and n_i are the concentrations of free electrons and holes, and intrinsic carriers, respectively.^[17,18] The Langevin recombination rate γ is given by $q(\mu_e + \mu_h)/\varepsilon$ where μ_e and μ_h are electron and hole mobility, respectively, and ε is the permittivity. The dissociation probability is given by $P_{dis} = k_{dis}/(k_{rec} + k_{dis})$ where k_{rec} and k_{dis} are the recombination and dissociation rate of bound electron–hole pairs, respectively. Thus,

the recombination current density J_{rec} can be written as the spatial integration of R ^[32]

$$J_{\text{rec}} = q \int_0^d \gamma(n_e n_h - n_i^2)(1 - P_{\text{dis}}) dx = q d \gamma n_i^2 (1 - P_{\text{dis}}) \left[\exp\left(\frac{qV}{k_B T}\right) - 1 \right] \quad (5)$$

where d is the thickness of the active layer. In other words, the saturation current density is equal to $q d \gamma n_i^2 (1 - P_{\text{dis}})$, which is dependent on the carrier mobility and the recombination and dissociation rate of bound electron–hole pairs. In the diffusion-limited case $P_{\text{dis}} \ll 1$ ($k_{\text{rec}} \gg k_{\text{dis}}$), the saturation current density is equal to $q d \gamma n_i^2$, which is dependent only on the carrier mobility. Thus, we obtain the following Eq. 6 from Eq. 2, assuming that $J_0 = q d \gamma n_i^2 (1 - P_{\text{dis}})$, $J_{\text{SC}} = P_{\text{dis}} G q d$, and $n_i^2 = N_C^2 \exp(E_g/k_B T)$ where G is the generation rate of bound electron–hole pairs, N_C is the effective density of states, and E_g is the energy difference between the valence band of donor material and the conduction band of acceptor material.^[29]

$$\begin{aligned} V_{\text{OC}} &= \frac{n E_g}{q} - \frac{n k_B T}{q} \ln \left(\frac{q d \gamma (1 - P_{\text{dis}}) N_C^2}{J_{\text{SC}}} \right) \\ &= \frac{n E_g}{q} - \frac{n k_B T}{q} \ln \left(\frac{\gamma (1 - P_{\text{dis}}) N_C^2}{P_{\text{dis}} G} \right) \end{aligned} \quad (6)$$

Note that Eq. 6 is identical to the one derived in previous studies^[17,18] except for the ideality factor. The ideality factor $n \approx 1.6$ we observed suggests that a recombination mechanism in P3HT:fullerene solar cells other than a direct recombination, such as the Shockley–Read–Hall (SRH) recombination as reported recently.^[32,42] Indeed, we found recently that there are two types of P3HT polarons (trap-free and trapped P3HT polarons) in P3HT:PCBM blend films.^[43] The bimodal recombination may be related to the ideality factor $1 < n < 2$, which is a typical value for polymer solar cells. This study, however, is focused on the origin of J_0 , and we will not discuss the difference in the ideality factor any further.

3.2. Origin of Open-Circuit Voltage

From the comparison of Eq. 4 with Eq. 6, we obtain the following relation: $E_A = E_g$ and $J_{00} = q d \gamma (1 - P_{\text{dis}}) N_C^2$, which are indicative of the molecular origin of J_0 (J_{00} and E_A). In

most studies, E_g is considered to be ΔE_{DA} .^[12,14,17,24] This is consistent with the experimental relationship $V_{OC} \propto \Delta E_{DA}$, and we conclude that E_A is its origin. However, as shown in Figure 5b, E_A is much smaller than ΔE_{DA} . This is partly because the formation of interfacial dipole would reduce the effective E_g as reported previously. The offset energy due to the interfacial dipole Δ is reported to be 0.4 eV for P3HT:PCBM blend films.^[44] In this case, $E_A + \Delta$ is nearly equal to ΔE_{DA} .

Next we focus on the difference in J_{00} between pristine fullerenes and fullerene derivatives with attached groups. As mentioned above, J_{00} is dependent only on the charge mobility for the diffusion-limited recombination, and on the carrier mobility and the recombination and dissociation rate of bound electron-hole pairs for the non-diffusion-limited recombination. The electron mobility μ_e of pristine fullerenes is reported to be as high as $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^[45] which is one order of magnitude higher than that of fullerene derivatives with attached groups ($\sim 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[34,36,46,47] On the other hand, as shown in Table 1, μ_h of P3HT is as low as $\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in P3HT:fullerene blend films, which is comparable to time-of-flight mobility of P3HT films.^[48] Thus, the two orders of magnitude difference in J_{00} cannot be explained in terms of the charge mobility alone.^[49,50] This suggests that the recombination in P3HT:fullerene blends is non-diffusion-limited reaction.

For the non-diffusion-limited recombination, J_{00} is given by $qd\gamma(1 - P_{dis})N_C^2 = qd\gamma k_{rec}N_C^2/(k_{rec} + k_{dis})$. Previously, we found by transient absorption spectroscopy that P3HT polarons are promptly generated within $<100 \text{ fs}$ in P3HT:PCBM blend films and a small part of them recombines to the ground state on a nanosecond time scale.^[51] In other words, k_{rec} and k_{dis} are roughly estimated to be $\sim 10^9 \text{ s}^{-1}$ and $>10^{13} \text{ s}^{-1}$, respectively. Recent spectroscopic studies have shown similar results even for other polymer:fullerene blends.^[52-55] Thus, we can assume $k_{rec} \ll k_{dis}$ for all the P3HT:fullerene blends studied here. Consequently, J_{00} can be simplified into $J_{00} = qdN_C^2\gamma k_{rec}/k_{dis} = qdN_C^2\gamma_a$ where γ_a is the apparent recombination rate

($\gamma k_{\text{rec}}/k_{\text{dis}}$). Considering the high PL quenching and the large J_{SC} for all the blends, k_{dis} can be assumed to be high enough to yield the high dissociation efficiency independently of fullerene derivatives. We therefore conclude that the large difference in J_{00} is ascribed mainly to γ and k_{rec} .

According to the Marcus theory,^[56] the electron transfer rate k_{ET} can be described by Eq. 7

$$k_{\text{ET}} = \frac{4\pi^2}{h} \frac{H_{\text{AB}}^2}{\sqrt{4\pi\lambda k_{\text{B}}T}} \exp\left(-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_{\text{B}}T}\right) \quad (7)$$

where h is the Planck constant, H_{AB} is the electronic coupling matrix element between the reactant A and the product B, λ is the reorganization energy, ΔG_0 is the free energy difference between the reactant and the product. In the case of the charge transport in the same molecules, the charge transfer rate k_{CT} is given by Eq. 8

$$k_{\text{CT}} = \frac{4\pi^2}{h} \frac{H_{\text{AA}}^2}{\sqrt{4\pi\lambda k_{\text{B}}T}} \exp\left(-\frac{\lambda}{4k_{\text{B}}T}\right) \quad (8)$$

The Langevin recombination rate γ is proportional to the diffusion constant, which is proportional to k_{CT} assuming that the charge diffusion is repetitive hopping between two neighbors.^[57,58] On the other hand, as mentioned above, γ is given by $q(\mu_{\text{e}} + \mu_{\text{h}})/\varepsilon \approx q\mu_{\text{e}}/\varepsilon$. Thus, we ascribe the difference in μ_{e} by one order of magnitude to the electronic coupling matrix element H_{AA} because it is the most sensitive to the presence or absence of attached groups to fullerenes. In other words, the difference in γ (or μ_{e}) by one order of magnitude suggests that H_{AA}^2 between pristine fullerenes is about 10 times larger than that between fullerene derivatives with attached groups. We therefore ascribe the remaining difference in J_{00} by one order of magnitude to k_{rec} . Similarly, the difference in k_{rec} suggests that H_{AB}^2 between P3HT and pristine fullerenes is about 10 times larger than that between P3HT and fullerene derivatives with attached groups.^[59] This is reasonable because the presence or

absence of attached groups to fullerenes would change the intermolecular distance and hence would have comparable impact on H_{AA} and H_{AB} . Furthermore, recent studies have shown that weak intermolecular interaction due to bulky substituents leads to higher V_{OC} for small molecule organic solar cells.^[22,23] We therefore conclude that the V_{OC} is dependent on both electronic couplings of fullerene/fullerene and polymer/fullerene.

It is noteworthy that V_{OC} is dependent on the charge recombination at the P3HT/PCBM interface. This is inconsistent with the Langevin recombination that is limited only by diffusion. In the Langevin recombination, the reaction radius is assumed to be a critical distance r_c at which the thermal energy of a charge carrier is equal to the Coulombic attractive potential energy. In P3HT:PCBM blends, r_c is estimated to be as long as 16 nm with a dielectric constant of 3.4. This is significantly larger than the separation distance of the interfacial charge recombination r_0 , which would be a few nanometers at most. If r_0 were employed instead of r_c , the diffusion-limited recombination rate would be almost one order of magnitude smaller than the Langevin recombination rate γ . Furthermore, as mentioned above, the apparent recombination rate γ_a is reduced by a factor of k_{rec}/k_{dis} compared to γ for the non-diffusion-limited reaction. In other words, the large difference between k_{rec} and k_{dis} may be related to the reduced recombination rate reported for polymer:fullerene blends. Such electron-transfer-dependent recombination has been reported for dye-sensitized solar cells.^[60]

Finally, we discuss the molecular design for improving V_{OC} on the basis of our findings in this study. We found that V_{OC} is essentially dependent on E_A and J_{00} from the detailed analysis of the dark current characteristics of the devices. The activation energy E_A is closely related to ΔE_{DA} , which is consistent with the experimental relation $V_{OC} \propto \Delta E_{DA}$. The relation provides the guideline for the molecular design that lowers HOMO donors and higher LUMO acceptors are desirable for higher V_{OC} . This strategy has already been great successful in improving V_{OC} in polymer solar cells mentioned before.^[61,62] On the other hand, J_{00} is

essentially related to the electronic couplings of polymer/polymer or fullerene/fullerene H_{AA} and of polymer/fullerene H_{AB} . In other words, lower H_{AA} or H_{AB} could lead to a higher V_{OC} . However, a lower H_{AA} results in lower charge mobility, which would cause lower charge collection efficiency and hence lower device performance. Thus, the molecular design for lowering H_{AA} is not appropriate for improving the overall device performance. Similarly, a lower H_{AB} results in the decrease in the electron transfer rate at the polymer/fullerene interface. In other words, a lower H_{AB} seems to cause not only a lower k_{rec} but also a lower charge separation rate k_{CS} , the latter of which would result in lower charge generation efficiency. However, this is not always true because H_{AB} is different between k_{rec} and k_{CS} . The electronic coupling in the charge separation H_{AB}^{CS} is taken to be the coupling between the LUMO of the donor and the acceptor and that in the charge recombination H_{AB}^{CR} is taken to be the coupling between the HOMO of the donor and the LUMO or LUMO + 1 of the acceptor.^[63] For example, H_{AB}^{CS} can be larger than H_{AB}^{CR} by controlling the spatial distribution of HOMO and LUMO of the donor material as reported for dye-sensitized solar cells.^[60,64,65] The LUMO of the Ru complex sensitizer is concentrated on bipyridine ligands attached with the anchoring carboxylic groups while the HOMO is shifted in weight from the Ru atom towards the NCS ligands. Consequently, H_{AB}^{CS} is significantly larger than H_{AB}^{CR} , resulting in ultrafast electron injection into TiO_2 and slow recombination at the interface simultaneously. Furthermore, a recent *ab initio* calculation has shown that the electronic coupling at the P3HT/ C_{60} heterojunction is much larger in the excited state than in the ground state.^[66] We therefore propose that the molecular design with a large H_{AB}^{CS} and small H_{AB}^{CR} would enhance V_{OC} effectively without any loss of the charge generation efficiency.

4. Conclusion

We have studied the origin of open-circuit voltage of polymer:fullerene solar cells by analyzing the J - V characteristic in the dark and under the illumination. Seven different

polymer solar cells were fabricated by using different fullerene derivatives with the LUMO levels ranging from 3.53 to 4.10 eV. From the photocurrent measurement, the linear relationship between V_{OC} and ΔE_{DA} is observed as reported previously, but not between fullerene derivatives with attached groups and pristine fullerenes. To understand the different linear relationship between V_{OC} and ΔE_{DA} , we carefully analyzed the diode characteristics in the dark on the basis of the equivalent circuit model. As a result, we found that V_{OC} of the P3HT:fullerene solar cells is independent of the ideality factor n but mainly dependent on the saturation current J_0 . From the temperature dependence of J_0 , we can get the activation energy E_A and the pre-exponential factor J_{00} for J_0 . We ascribe the former term to ΔE_{DA} and the latter term to the charge recombination in P3HT:fullerene blends. Interestingly, the latter term is dependent on the absence or presence of the attached groups to the fullerenes. Indeed, J_{00} can be expressed as $J_{00} = qdN_C^2\gamma k_{rec}/k_{dis} = qdN_C^2\gamma_a$ where γ_a is the apparent recombination rate ($\gamma k_{rec}/k_{dis}$). This finding suggests that the recombination in P3HT:fullerene blends is the non-diffusion-limited reaction depending on the electron transfer at the P3HT/fullerene interface. This is consistent with the reduced recombination compared to the Langevin recombination as reported previously. We conclude that the attached group to the fullerene would reduce both electronic couplings between fullerene/fullerene H_{AA} and between P3HT/fullerene H_{AB}^{CR} . The smaller H_{AA} and H_{AB}^{CR} result in the smaller γ and k_{rec} , respectively, and hence lead to the smaller J_{00} for fullerene derivatives with attached groups. We therefore propose that a large H_{AB}^{CS} and small H_{AB}^{CR} are the key to improving V_{OC} effectively without loss of the charge generation efficiency in addition to large ΔE_{DA} .

5. Experimental Section

Materials: The following chemicals were used without further purification unless noted: P3HT (regioregular, Aldrich, $M_n = 87,000 \text{ g mol}^{-1}$), indene (99%, Sigma-Aldrich), C_{60} (99.5%, Frontier Carbon), C_{70} (99%, Aldrich), PCBM (99.9%, Frontier Carbon), bis-PCBM

(99.5%, Sigma–Aldrich), PC₈₄BM (99.8%, Solenne), ThCBM (99%, Sigma–Aldrich), lithium fluoride (99.9%, Sigma–Aldrich), tetrabutylammonium tetrafluoroborate (Wako), acetonitrile (98%, Nacalai tesque), chlorobenzene (99%, Nacalai tesque), *o*-dichlorobenzene (99%, Wako), and 1,2,4-trichlorobenzene (>98%, Tokyo Chemical Industry). Ferrocene (98%, Wako) was purified by recrystallization from dichloromethane three times prior to the measurement.

Synthesis of ICBA: Indene-C₆₀-bisadduct (ICBA) was synthesized according to the procedures reported in a previous report.^[37] Fullerene C₆₀ (0.856 g, 1.19 mmol) and 1,2,4-trichlorobenzene (50 mL) were placed in a recovery flask and stirred over night at room temperature to dissolve the fullerene homogeneously followed by adding indene (2.07 g, 17.8 mmol) to the flask. The solution was heated to 220 °C and refluxed for 12 h. Subsequently, the cooled solution was poured into 400 mL of methanol to reprecipitate the product. The precipitate was dissolved in 5 mL of chloroform and reprecipitated again in methanol. The crude product was purified by silica gel column chromatography twice using 10% chloroform in hexane (first) and 10% toluene in hexane (second) as eluents. Finally, the product was recrystallized twice from hexane/chloroform. Finally, 43 mg of ICBA was obtained as pure product.

¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm) (a) 7.8 – 7.2 (m, 8H), (b) 1.26 (s, 4H), (c) 0.882 (t, 4H, $J = 6.8$ Hz). Peak (c) was coupled with peak (b), which is confirmed by a decoupling measurement (see the Supporting Information). APCI–ToF MS: calcd for C₇₈H₁₆ 953.0; found 953.1.

Device Fabrication: Indium/tin oxide (ITO)-coated glass substrates (10 Ω per square) were washed by ultrasonication in toluene, acetone, and ethanol for 15 min, dried with N₂, and then cleaned with a UV–O₃ cleaner (Nippon Laser & Electronics NL-UV253S) for 30 min. A thin layer (~40 nm) of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS; H. C. Starck PH500) was spin-coated onto the cleaned substrates at a spin rate of 3000 rpm,

and the layer was dried at 140 °C for 10 min in air. The solution of PEDOT:PSS was filtered using a 0.45 µm PTFE syringe filter prior to the spin coating. A blend layer of P3HT:fullerene (~100 nm except for PC₈₄BM, 80 nm for PC₈₄BM) was spin-coated from a chlorobenzene (except for C₆₀ and C₇₀) or *o*-dichlorobenzene (C₆₀ and C₇₀) solution on the PEDOT:PSS film. Finally, Al (70 nm) (except for ICBA) or LiF (0.5 nm)/Al (70 nm) (for ICBA) was thermally deposited on top of the active layer at 2.5×10^{-4} Pa. Note that LiF was used to ensure the Ohmic contact between fullerene and the electrode. Finally, the devices were thermally annealed at 150 °C in an N₂-filled glovebox for 5 min (PC₈₄BM), 10 min (ThCBM), 15 min (C₇₀), 30 min (C₆₀, PCBM, bis-PCBM), and 40 min (ICBA), respectively.

Measurements: The electrochemical measurements were performed using a potentiostat/galvanostat (Princeton Applied Research, model 273A) in an Ar-bubbled *o*-dichlorobenzene/acetonitrile = 4 : 1 (v/v) solution containing 0.1 M of tetrabutylammonium tetrafluoroborate as a supporting electrolyte with an Ag/AgCl wire in a saturated KCl solution as a reference electrode and a Pt wire as a counter electrode. The scan rate was set to 50 mV s⁻¹. The ionization potential of P3HT was measured with a photoelectron yield spectrometer (Riken Keiki, AC-3) in an N₂ atmosphere. The P3HT film was fabricated by spin-coating from chlorobenzene onto an ITO substrate washed by the same procedure as mentioned above. The threshold energy for the photoelectron emission was estimated on the basis of the cubic root of the photoelectron yield plotted against the incident photon energy as reported previously.^[67,68] The *J*–*V* characteristics were measured in an N₂ atmosphere with a direct current/voltage and a current source/monitor (Advantest, model R6243) in the dark and under illumination with AM1.5G simulated solar light at 100 mW cm⁻². The light intensity was corrected with a calibrated silicon photodiode reference cell (Bunkoh-Keiki, BS-520). The active area of the device was 0.07 cm². The temperature dependence of the dark *J*–*V* characteristics was measured in a liquid-N₂-cooled cryostat (Oxford, Optistat DN-V) at a pressure of <10⁻³ Pa. The temperature was monitored by a platinum resistance thermometer

and controlled with a temperature controller (Oxford, ITC503) at a stability of <0.1 K.

Supporting Information

Supporting Information is available online from the Wiley Online Library or from the author.

Acknowledgements

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$V^{-1} s^{-1}$ in P3HT:fullerene blend films. This is much smaller than μ_e of pristine fullerenes and fullerene derivatives with attached groups. In other words, the recombination rate in P3HT:fullerene blend films is given by $\gamma_{\min} = q\mu_h/\varepsilon$, which is independent of fullerene derivatives, and hence cannot explain the difference in J_{00} at all. In either case, the difference in J_{00} by two orders of magnitude cannot be explained only in terms of the charge mobility.

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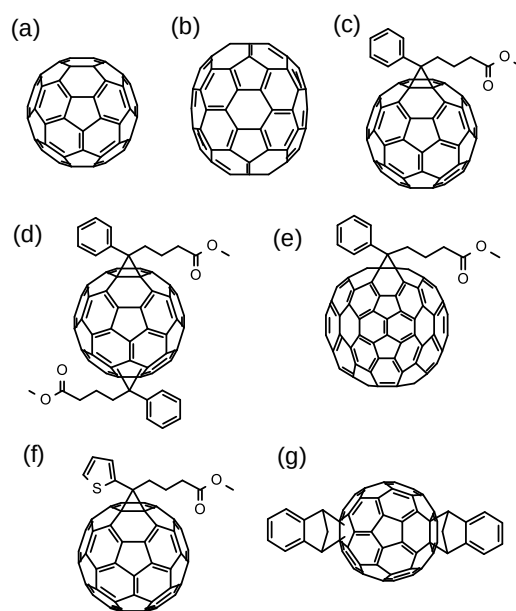


Figure 1. Chemical structures of fullerenes: (a) C₆₀, (b) C₇₀, (c) PCBM, (d) bis-PCBM, (e) PC₈₄BM, (f) ThCBM, and (g) ICBA.

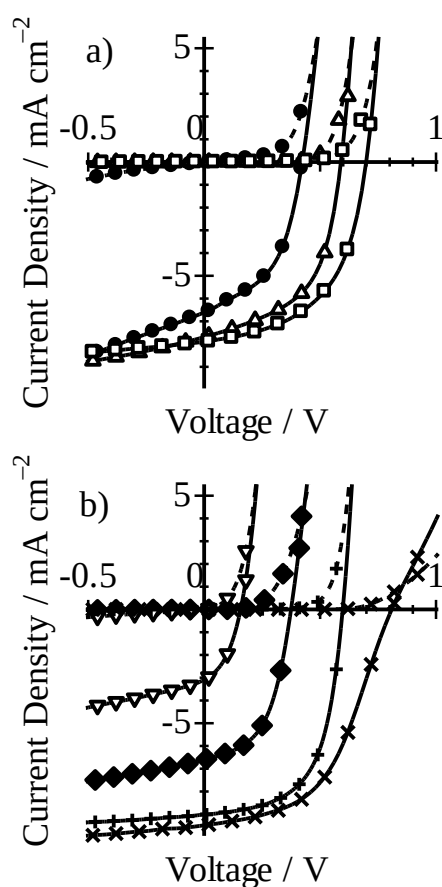


Figure 2. J - V characteristics of each P3HT:fullerene solar cell in the dark (dashed lines) and under AM1.5G simulated solar illumination at 100 mW cm^{-2} (solid lines): C_{60} ($\bullet$), PCBM ($\triangle$), bis-PCBM ($\square$), C_{70} ($\blacklozenge$), PC_{84}BM (∇), ThCBM ($+$), and ICBA ($\times$). The opened and closed symbols show blend films with pristine fullerenes and fullerene derivatives with attached groups, respectively.

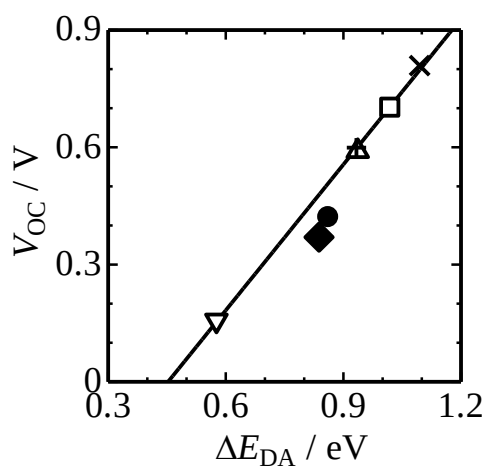


Figure 3. Relationship between V_{OC} and ΔE_{DA} for seven P3HT:fullerene solar cells. The symbols are the same as those in Figure 2.

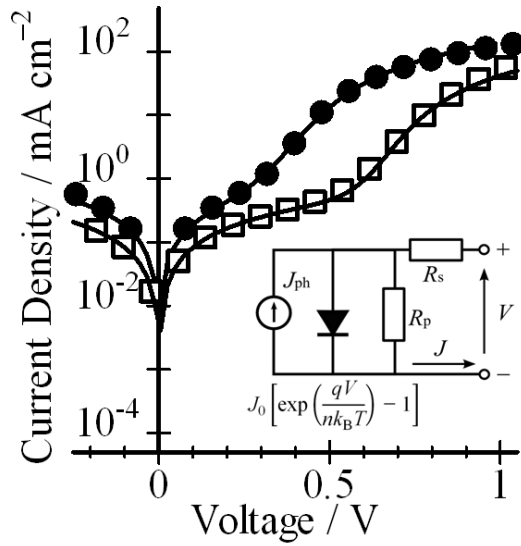


Figure 4. Log plots of the dark current density against applied voltage: C₆₀ (●) and bis-PCBM (□). The inset shows the equivalent circuit, which consists of a diode $J_0[\exp(qV/nk_B T) - 1]$, a series resistor R_s , and a parallel resistor R_p . The solid lines are fitting curves by Equation 3. The other data are shown in the Supporting Information.

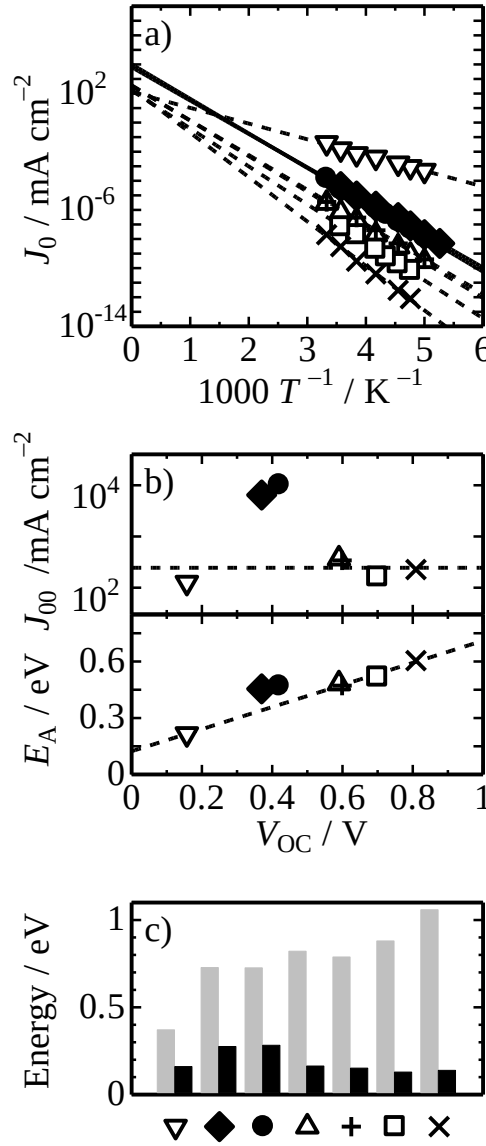


Figure 5. a) Arrhenius plots of the saturation current J_0 for each fullerene system. The symbols are the same as those in Figure 2. b) Plots of the pre-exponential factor J_{00} and activation energy E_A for J_0 . The broken lines are fitting curves for fullerene derivatives with attached groups. c) Relative proportion of the two terms of nE_A (gray bars) and $nk_B T \ln(J_{00}/J_{SC})$ (black bars) in Equation 4. The difference between the gray and black bars corresponds to qV_{OC} . The temperature T is set at 300 K.

Table 1. The HOMO–LUMO energy gap ΔE_{DA} , device parameters, hole mobility μ_{h} , and quenching efficiency Φ_{q} of each P3HT:fullerene blend.

	$\Delta E_{\text{DA}} /$ eV	$J_{\text{SC}} /$ mA cm^{-2}	$V_{\text{OC}} /$ V	FF	PCE / %	$\mu_{\text{h}} /$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}{}^a$	$\Phi_{\text{q}} /$ % ^b
PC ₈₄ BM	0.58	3.09	0.16	0.40	0.19	5.0×10^{-5}	95
C ₇₀	0.84	6.60	0.37	0.52	1.26	3.0×10^{-5}	86
C ₆₀	0.86	6.60	0.42	0.49	1.36	5.0×10^{-5}	93
PCBM	0.94	7.70	0.59	0.53	2.41	3.0×10^{-5}	92
ThCBM	0.93	9.01	0.60	0.60	3.22	2.3×10^{-5}	92
bis-PCBM	1.02	7.89	0.70	0.53	2.95	6.0×10^{-5}	87
ICBA	1.09	9.48	0.81	0.50	3.83	3.5×10^{-5}	95

^a The hole mobility is evaluated from the space charge limited current for the devices with a layer structure of ITO/PEDOT:PSS/P3HT:fullerene/Au.

^b The quenching efficiency is evaluated by the PL intensity ratio of P3HT:fullerene blends to that of a P3HT pristine film.

Table 2. Diode parameters of P3HT:fullerene blend devices.

	n	$R_s A / \Omega \text{ cm}^2$	$R_p A / \text{k}\Omega \text{ cm}^2$	$J_0 / \text{mA cm}^{-2}$	$J_{00} / \text{mA cm}^{-2}$	E_A / eV
PC ₈₄ BM	1.73	2.6	2.7	6.0×10^{-2}	1.3×10^2	0.21
C ₇₀	1.6	8	1	6.0×10^{-4}	6.4×10^3	0.45
C ₆₀	1.54	8	70	1.5×10^{-4}	1.0×10^4	0.47
PCBM	1.7	3.5	75	3.0×10^{-6}	3.7×10^2	0.48
ThCBM	1.67	2.8	40	3.5×10^{-6}	3.4×10^2	0.47
bis-PCBM	1.7	5	1.2	2.5×10^{-7}	1.6×10^2	0.52
ICBA	1.75	100	1100	6.0×10^{-8}	2.2×10^2	0.60

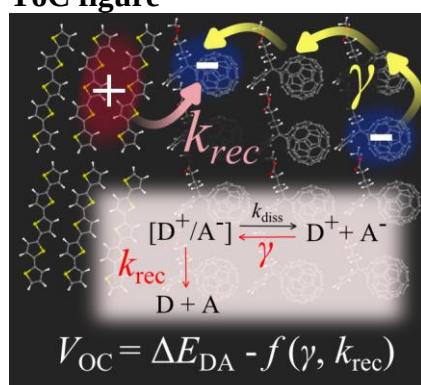
The origin of open-circuit voltage (V_{OC}) was studied for polymer solar cells based on P3HT and fullerene derivatives with different LUMO levels. By analyzing J – V characteristics in the dark, we found that V_{OC} depends not only on the HOMO–LUMO energy gap but also on the electronic couplings of fullerene/fullerene and P3HT/fullerene.

Photovoltaic Devices

Shunsuke Yamamoto, Akiko Orimo, Hideo Ohkita*, Hiroaki Benten, and Shinzaburo Ito

Molecular Underlying of Open-Circuit Voltage of Polymer:Fullerene Solar Cells

ToC figure



Supporting Information

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Molecular Underlying of Open-Circuit Voltage of Polymer:Fullerene Solar Cells

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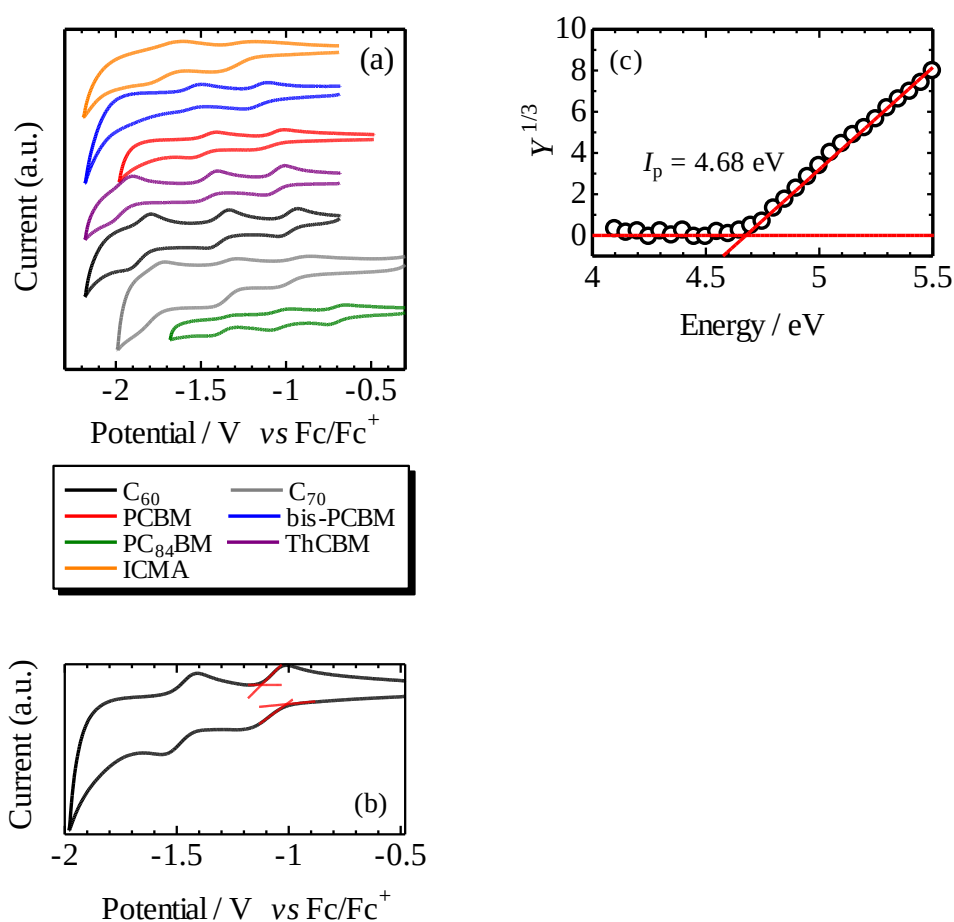


Figure S1. a) Cyclic voltammograms of each fullerene derivative in acetonitrile/*o*-dichlorobenzene = 1 : 4 (v/v) solutions containing 0.1 M of Bu₄NPF₆. The scan rate is 50 mV s⁻¹. b) The first reduction potential of fullerene derivatives was obtained from the average of cut-off position of oxidative and reductive waves. The LUMO level was calculated from the first reduction potential on the assumption that the energy level of the ferrocene/ferrocenium

redox couple is 4.8 eV below the vacuum level.^[S1–S3] c) Photoemission yield spectrum of a P3HT pristine film. The cut-off energy was estimated by the threshold of the cubic root of the photoelectron yield.

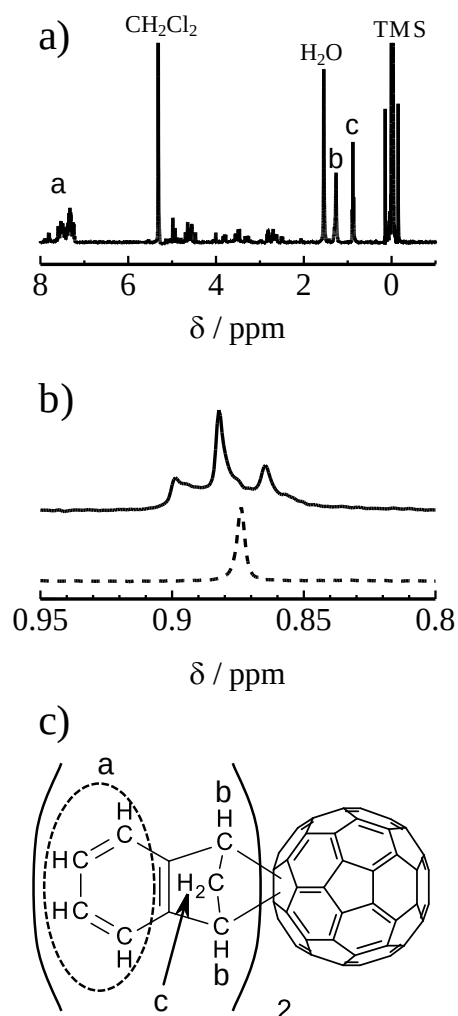


Figure S2. 400 MHz ^1H -NMR spectrum of ICBA in CD_2Cl_2 solution. a) The peak signals are observed as follows: a) $\delta = 7.8 - 7.2$ (m, 8H), b) 1.26 (s, 4H), c) 0.882 (t, 4H, $J = 6.8$ Hz). b) The non-decoupled (solid line) and decoupled (dashed line) signals at peak-c of ICBA in CD_2Cl_2 solution. The decoupling is performed at 1.26 ppm. c) The assignments of the peaks from a to c observed in ^1H -NMR spectra.

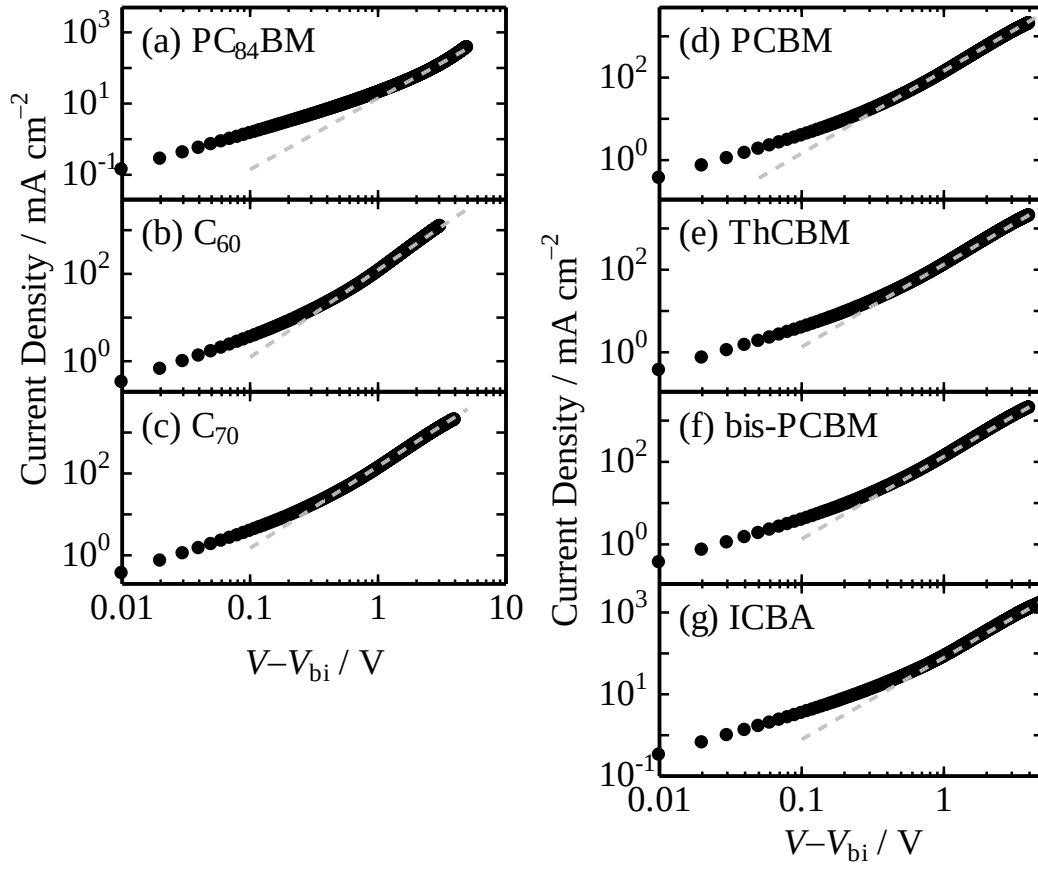


Figure S3. J - V characteristics of ITO/PEDOT:PSS/P3HT:fullerene/Au devices. The gray solid lines represent the fitting line by $J = 9/8 \epsilon_0 \epsilon_r \mu_h (V - V_{bi})^2 / d^3$ where ϵ_0 and ϵ_r are the permittivity of vacuum and media, μ_h is the hole mobility, V_{bi} is the built-in potential in device, and d is the thickness of the active layer in the device. The built-in potential of these devices is negligible because the work function of Au is almost the same as that of ITO.

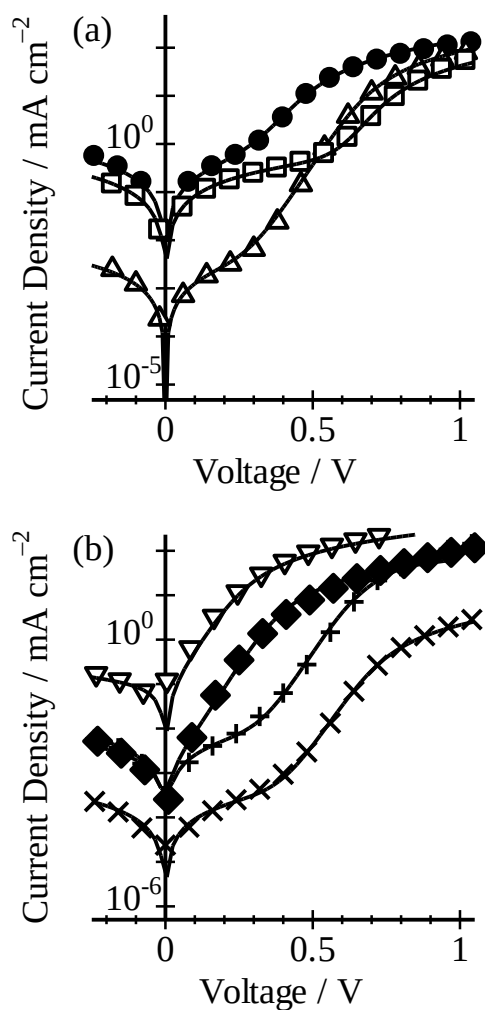


Figure S4. Log plots of the dark current density against applied voltage. The symbols are the same as those in Figure 2. The solid lines are fitting curves by Equation 3.

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