Lateral-tandem organic photovoltaic cells with carrier transport and generation layers

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Received August 16, 2021; revised September 7, 2021; accepted September 21, 2021; published online October 1, 2021

We report the fabrication and operation of organic photovoltaic cells with lateral junctions and separated carrier-generating and carrier-transporting layers. Significant photocurrent increase was observed by inserting carrier-generating layer having strong visible absorption. For the lateral tandem cells, an increase in the number of unit cells increased the photocurrent while keeping the photovoltaic constant. It is easier to increase the number of unit cells in lateral tandem cells compared to conventional vertical tandem cells because the adjustment of photocurrent density flowing in each unit cell is no longer necessary. © 2021 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd.

Supplementary material for this article is available online

Organic solar cells are promising candidates for solar energy harvesting devices owing to their low cost, low energy consumption during fabrication, short energy payback time, and mechanical flexibility; therefore, extensive studies have been conducted on organic solar cells. In conventional cells, the photogenerated carriers formed by the dissociation of excitons at the junction between the donor and acceptor films are collected vertically. Because the diffusion length of excitons is significantly small, the average thickness of active layers is limited to a few nanometers.1,2) To overcome this, blended junctions containing both donors and acceptors were fabricated using the co-deposition technique for small-molecule organic solar cells.3–5) However, despite the recent reports on blended systems where the average thickness reached approximately 1 μm, nanostructure fabrication of the electron and hole transport routes in blended junctions remains a challenge.6–8)

The discovery of organic semiconductors with high mobility has paved the way for lateral collection of carriers.9–11) This approach minimizes the vertical transport and eliminates the vertical thickness limitation in conventional organic photovoltaic cells with a sandwich-type structure.12–14) The lateral organic cells of C8-BTBT [Fig. 1(b)] with high hole mobility of 43 cm² V⁻¹ s⁻¹15,16) and that of PTCDI-C8 [Fig. 1(b)] with high electron mobility of 1.7 cm² V⁻¹ s⁻¹17] have been previously reported.10,11) However, the junction using C8-BTBT acting as donor (D) and PTCDI-C8 acting as acceptor (A) showed significantly small photocurrent due to the low exciton dissociation efficiency caused by the long insulating chains between D/A molecules. Thus, we expected that the addition of highly efficient carrier-generating D/A layers between these lateral transporting layers would improve the photocurrent generation. As the carrier-generating layer, we adopt DBP/C60 junction.18–20)

However, tandem structures for lateral junctions and conventional vertical junctions21–23] have different functions. The lateral junction increases the photocurrent while keeping the photovoltaic constant, whereas the conventional vertical junction increases the photovoltaic while keeping the photocurrent constant.

In this study, we discuss the operation of lateral organic photovoltaic cells with function-separated charge-generating and charge-transporting layers. Subsequently, we discuss the effect of increasing the number of charge-generating layers on the device performance.

Figure 1 shows the structures of the lateral junction cells. Figure 1(a) shows a cell without a carrier-transporting layer. For this planar carrier-generation layer, the DBP (10 nm) and C60 (10 nm) films act as the donor and acceptor, respectively. In contrast, Fig. 1(b) shows a cell without a carrier-generation layer. The C8-BTBT (100 nm) and PTCDI-C8 (100 nm) films act as hole- and electron-transporting layers, respectively. Figure 1(c) shows the function-separated cell of one unit. DBP/C60 as a carrier-generation layer was sandwiched between the C8-BTBT (100 nm) and PTCDI-C8 (100 nm) films as the carrier-transporting layers. Figure 1(d) shows the lateral two-unit tandem cell with two carrier-generating layers sandwiched between the carrier-transporting layers. PTCDI-C8 acts as the common electron-transporting layer for the two devices. The device has a cascade energetic structure24] as shown in Fig. 1(e). The energetic positions of HOMO and LUMO of C8-BTBT,25,26] DBP,20,25] C60,25,27] and PTCDI-C825,28] are reported values.

C8-BTBT (Nippon Kayaku Co., Ltd.) and PTCDI-C8 (Luminescence Technology) were used without purification while DBP (Luminescence Technology) and C60 (Frontier Carbon Co., Ltd., nanom purple TL) were purified by train sublimation.29] Organic semiconductors were deposited at 10⁻⁶ Pa and at room temperature in an oil-free vacuum chamber housed in a glove box (EpiTech Inc., 12ET1207). The evaporation rates of all the organic semiconductors were 0.1 nm s⁻¹. Using a customized movable-mask system (EpiTech Inc.) [Fig. S1(a) available online at stacks.iop.org/APEX/14/101003/mmedia], the C8-BTBT, DBP, and C60, PTCDI-C8 films were connected to 100 nm thick Ag electrodes through a 10 nm thick MoO₃ and 10 nm thick bathocuproine (BCP); BCP/Ag and MoO₃/Ag acted as...
the electron- and hole-collecting electrodes, respectively [Fig. S1(b)]. The distance ($L$) between the electron-collecting (BCP/Ag) and hole-collecting (MoO$_3$/Ag) electrodes was 0.11 mm. The detailed cell structure is shown in Figs. S1(c) and S1(d).

The current–voltage ($J$–$V$) characteristics of the devices were measured under simulated solar light irradiation (AM1, 100 mW cm$^{-2}$; ASAHI Spectra, HAL-320) in a N$_2$ atmosphere. The photocurrent action spectra were measured under monochromatic light irradiation using a monochromator (SPG-100 ST, Shimadzu). The number of incident photons was determined using a standard silicon photodiode (Hamamatsu Photonics, S1337-66BQ).

Figure 2 shows the $J$–$V$ characteristics of the cells presented in Fig. 1. A lateral cell with only a carrier-generation layer (DBP/C60) did not exhibit a photocurrent (orange curve). In contrast, a lateral cell with only a carrier-transporting layer (C8-BTBT/PTCDI-C8) exhibited a significantly small short-circuit photocurrent density ($J_{sc}$) of 0.005 mA cm$^{-2}$ (blue curve). The cell having both carrier-generating and -transporting layers resulted in a five times larger $J_{sc}$ of 0.023 mA cm$^{-2}$ (red curve). Meanwhile, the lateral two-unit cell doubled the photocurrent density of the one-unit cell (green curve). Conversion efficiency of C8-BTBT/PTCDI-C8 cell (Fig. 2, blue curve) and 1-unit cell (Fig. 2, red curve) and 2-unit cell (Fig. 2, green curve) are 0.002%, 0.005%, and 0.008%, respectively [Fig. S3(a)]. Performances of the C8-BTBT/PTCDI-C8 cells between the present and previously reported$^{10}$ are explained in Fig. S3.

Figure 3(a) shows the absorption spectra of PTCDI-C8 (orange curve), C60 (yellow curve), and DBP (red curve). In comparison, Fig. 3(b) shows the external quantum efficiency (EQE) spectra of the one-unit (red curve) and two-unit (green curve) cells. An obvious increase in EQE was observed. For instance, the EQE value increased from 0.19% (one-unit) to 0.43% (two-unit) at 600 nm. This is attributed to the increased absorption by DBP in the two-unit cell with two DBP films. The peak of EQE spectra at around 600 nm is different compared to that of absorption spectrum of DBP at around 612 nm [Fig. 3(a)]. We suppose that observed difference of peak position is originated from the nature of DBP/C60 junction although the reason has not been clarified yet.

The lateral two-unit cell [Fig. 1(d)] can be divided into front cell (red rectangle) and back cell (green rectangle). The back cell has a structure identical to that of the one-unit cell [Fig. 1(c)]. Therefore, we can calculate the photocurrent density of the front cell by subtracting the photocurrent density of the back cell from the two-unit cell.
density of the one-unit cell for the light intensity attenuated by the front cell from that of the two-unit cell. In Fig. 3(c), the action spectra of the photocurrent densities of $J_{sc}$ for a one-unit cell (red curve) and back cell (orange curve) corrected for the attenuated light are shown. The $J_{sc}$ action spectra of the front cell (black curve) in the two-unit cell can be calculated by subtracting that of the back cell (orange curve) from that of the two-unit cell (green curve). Hence, the $J_{sc}$ action spectra of the two-unit cell can be regarded as the sum of those of the front and back cells.

A similar calculation is possible for a three-unit cell by dividing the cell into one front cell and remaining back cells, that is, a two-unit cell (Fig. S2). Consequently, this method allows us to obtain the $J_{sc}$ action spectra for a number of unit cells larger than 4.

Figure 4(a) shows the action spectra of EQE for multi-unit cells with number of units ($n$) from 1 to 10. The intensity of the main peak at 600 nm due to absorption of the DBP film increased rapidly with $n$. The value of $J_{sc}$ can be calculated using the EQE and solar spectra. The main reason of the discrepancy between $J_{sc}$ obtained from the $J$–$V$ curve [Fig. 2, 2-unit cell; 0.04 mA cm$^{-2}$] and that obtained from EQE and solar spectra [Fig. 4(b), $n=2$; 0.03 mA cm$^{-2}$] is due to the photocurrent contribution in the wavelengths shorter than 450 nm under the irradiation of solar simulator. The photocurrent density increased from 0.017 ($n=1$) to 0.053 mA cm$^{-2}$ ($n=10$). In addition, the total absorbance of the multi-unit cell with $n=10$ reached 1.5 at 600 nm. Thus, a clear saturation in $J_{sc}$ increase was observed around $n=8$. Owing to the large absorption by PTCDI-C8, which generated low photocurrent on the front cell, the multi-unit cells with an odd $n$ showed a decreased $J_{sc}$. In contrast, because of the transparent C8-BTBT on the front cell, the multi-unit cells with an even $n$ showed an increased $J_{sc}$. Thus,
a zigzag change in $J_\text{sc}$ is observed [Fig. 4(b)]. It should be noted that it is easier to increase the number of unit cells in lateral tandem cells compared to conventional vertical tandem cells because the adjustment of photocurrent density flowing in each unit cell is no longer necessary.

Using the photon number absorbed by the front [Fig. 3(c), black curve] and back [Fig. 3(c), orange curve] cells in the two-unit cell, the IQE values of the front and back cells can be calculated to be 1.4% and 0.5% at 600 nm, respectively. In the case of lateral cell, there is little built-in potential in the longitudinal direction. We suppose that this is the reason of small IQE values. Therefore, we are currently investigating the effect of doping on PTCDI-C8 and C8-BTBT because the respective electrodes through C8-BTBT and PTCDI-C8 films under the low electric field, $J_\text{sc}$ is observed [Fig. 4(b)]. It should be noted that it is easier to increase the number of unit cells in lateral tandem cells compared to conventional vertical tandem cells because the adjustment of photocurrent density flowing in each unit cell is no longer necessary.

In conclusion, the magnitude of the photocurrent was effectively increased by inserting a carrier-generating layer between the carrier-transporting layers in the lateral junction cells. For the lateral tandem cells, an increase in the number of unit cells increased the photocurrent while keeping the photovoltage constant. By incorporating light absorbers with different absorption regions as the carrier-generation layers, a considerable portion of the wavelength of the solar spectrum can be effectively converted to photocurrent by lateral tandem cells.

Acknowledgments We acknowledge funding from JSPS KAKENHI (No. 17K19110).

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