Letter

High-efficiency simple planar heterojunction organic thin-film photovoltaics with horizontally oriented amorphous donors

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ABSTRACT

For high performance of organic thin-film photovoltaics (OPVs), high absorption and efficient charge transport of active materials are critical to compensate the short exciton diffusion length and low carrier mobility in organic semiconductors. It is desirable to control over molecular orientation in active layers to enhance both optical and electrical properties. In this letter, we show that amorphous donors having a planar molecular shape can be horizontally oriented, enabling active layers in OPVs to be thin while keeping high absorption in the devices. Based on anisotropic properties in optical design, a power conversion efficiency of more than 4% was achieved from a simple planar heterojunction. This result shows that using horizontally oriented amorphous materials is an effective approach to enhance OPV efficiency.

1. Introduction

Recently, much research has been done on organic thin-film photovoltaics (OPVs) [1] to achieve low-cost, lightweight, flexible, and eco-friendly power supply for future applications. However, power conversion efficiencies (PCEs) of OPVs are still one of the major concerns that prevent OPVs from real applications. When we discuss the performance of OPVs composed of organic semiconductors for further improvement, it is necessary to reflect on general differences between organic and inorganic semiconductors. Comparing to inorganic semiconductors, some distinct characteristics of the organic ones are (1) higher absorption coefficients, (2) higher selectivity of absorption wavelength, (3) lower carrier mobility, and (4) shorter exciton diffusion length. Because of the optical advantages of (1) and (2), we can use various kinds of organic semiconductors with small thicknesses of less than 100 nm. However, the electrical disadvantages of (3) and (4) now overwhelm these optical advantages. Thus, the performance of OPVs has been improved mainly by compensating or circumventing these disadvantages, for example, using fullerene derivatives having a relatively longer exciton diffusion length [2,3], a co-evaporated layer of donor and acceptor as a bulk

heterojunction [4,5], a tandem structure [6–8], or a controlled interface nanostructure [9,10].

Further improving optical properties of organic semiconductor materials is another way to compensate. If we use organic layers with higher absorption, thickness of the active layers can be reduced while keeping sufficient absorption. It means that the average distance between the exciton generation site and the heterojunction becomes shorter, and exciton collection efficiency should increase.

To improve the electrical and optical properties of organic films, it is important to consider not only characteristics of a molecule itself but also the collectively molecular orientation in films. Horizontal molecular orientation in films facilitates the charge transport along the vertical direction due to the strong overlap of molecular orbitals. Furthermore, the subsequent horizontal orientation of the transition dipole moments significantly increases the absorption of the normal incident light as shown in Fig. 1(a). Such electrical and optical effects of the horizontal orientation were reported using polycrystalline copper phthalocyanine (CuPc) films and insertion layers that control the orientation of CuPc molecules [11,12]. We therefore explore the possibility of utilizing such an advantage of molecular materials to construct high efficiency OPV cells.

If we use amorphous materials with an anisotropic molecular shape, the horizontal molecular orientation can be readily achieved by simple deposition without any further treatment. Recently, we have reported the general tendency of the horizontal

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molecular orientation in vacuum-deposited amorphous films of organic semiconductors; the larger the anisotropy of the molecular shape, the more significant the horizontal molecular orientation [13,14]. This is a very simple guideline for horizontal orientation of vacuum-deposited amorphous materials. Such a horizontal molecular orientation improves the electrical properties of amorphous films due to the enhanced overlap of molecular orbitals [15–17]. Meanwhile optical absorption upon normal incident light increases significantly. Thus, we propose here that using horizontally oriented amorphous molecules is a promising way to achieve high efficiency of OPVs.

More recently, two amorphous donor materials for OPVs were reported; one is tris[4-(5-phenylthiophen-2-yl)phenyl]amine (TPTPA) [18], and the other is tetraphenyldibenzoperiflanthene (DBP) [19,20]. There are many common points in these reports: (i) amorphous donors with an anisotropic molecular shape; (ii) deep energy levels of the highest occupied molecular orbitals (HOMOs) of the donors; (iii) simple planar heterojunction structures of OPV devices; (iv) high open-circuit voltages (V_{oc}), (v) high fill factors (*FF*); and thus (vi) high PCEs. In particular, it is worth noting that these two amorphous donor materials have an anisotropic molecular shape, meaning high possibility of the horizontal molecular orientation.

In this study, we investigate the optical anisotropies and molecular orientation in the donor films of TPTPA and DBP. Using variable angle spectroscopic ellipsometry (VASE), we show clear evidence of horizontal molecular orientation of these two materials, confirming that the orientation enhances absorption in the films. Furthermore, we design the optimal structure of the planar heterojunction OPVs using the anisotropic optical constants of highly absorbing films of DBP and C_{70} [21] determined by the VASE analysis. The actual device delivered a PCE of more than 4%, which is among the highest reported values for planar heterojunction OPVs.

2. Anisotropic optical constants and horizontal molecular orientation

TPTPA, DBP, and C_{70} (Luminescence Technology Corp.) were purified twice by train sublimation. Fig. 1(b) shows their chemical structures. To confirm that the vacuum-deposited DBP films are amorphous [20], we observed the surface roughness of a DBP film using an atomic force microscope (SPA-300HV, SII Nanotechnology Inc.). The surface was smooth with the root-mean-square (RMS) roughness of 0.8 nm, which is smaller than the length of the long axis of DBP molecule ($\sim$2.2 nm). This result supports the fact that DBP films are amorphous.

We determined the optical constants and their anisotropies using VASE as described previously [13–17]. The anisotropies of the optical constants of the TPTPA and DBP films are significant as shown in Fig. 2(a) and (b), respectively. For both layers, the refractive index and extinction coefficient in the horizontal direction (n_o and k_o) are much higher than those in the vertical direction (n_e and k_e), respectively, showing the significant horizontal orientation of both the molecular planes and transition dipole moments of the TPTPA and DBP molecules [17]. Thus, the molecular planes of both TPTPA and DBP are surely oriented along the horizontal direction in their films. Since amorphous films do not have a long-range order in the bulk, the dependences of their optical properties and orientations on the thickness are not significant [22].

The extinction coefficients of the TPTPA film are located in the blue region and relatively smaller than those of the DBP films. This is the main reasons why the short-circuit current density (J_{sc}) and
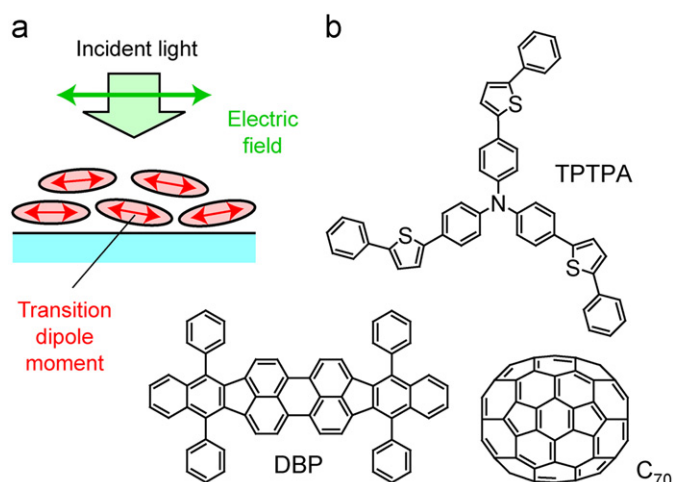

Fig. 1. (a) Schematic of absorption enhancement by horizontal orientation of transition dipole moments. (b) Chemical structures of TPTPA, DBP, and C_{70}.
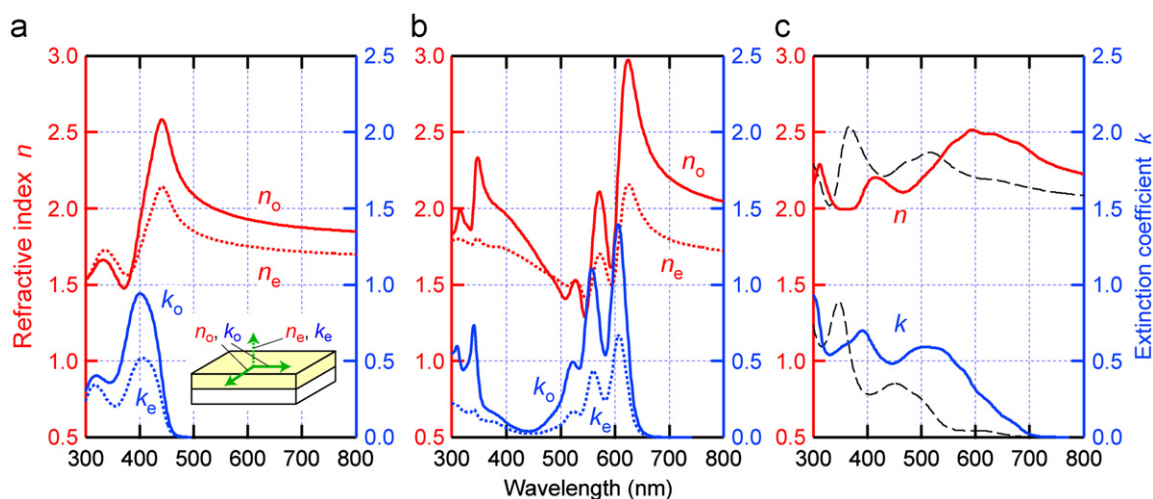

Fig. 2. (Color online) (a) and (b) Anisotropic optical constants of (a) TPTPA and (b) DBP films. The red solid and dotted lines show ordinary (horizontal) and extraordinary (vertical) refractive indices (n_o and n_e), respectively, and the blue solid and dotted lines show ordinary (horizontal) and extraordinary (vertical) extinction coefficients (k_o and k_e), respectively. (c) Optical constants of C_{70} film. The red line shows its refractive index, and the blue line shows its extinction coefficient. Black broken lines show the optical constants of the C_{60} film for comparison.

PCE of the TPTPA based device [18] are lower than those of the DBP based device [19]. Since the π-conjugated system in the DBP molecules is more extended in the molecular plane than that in the TPTPA molecules, the DBP film has the higher extinction coefficients. In particular, the high extinction coefficient in the horizontal direction (k_o), which has a maximum of 1.4, contributes to high absorption upon illumination of normal incident light. The refractive index of the DBP films in the horizontal direction (n_o) has very steep dependence on wavelength due to the very high absorption. Since this steep dependence affects light propagation in devices, it is important to carefully analyze the refractive index of highly absorbing materials considering the anisotropy for precise simulation of light absorption in OPV devices.

We also used VASE to determine the optical constants of the C_{70} film. The optical property of the film was found to be isotropic, and its extinction coefficient was much higher than that of the C_{60} film, as shown in Fig. 2(c). This means that C_{70} is optically better than C_{60} [21].

3. Optical design and device performance

Using the optical constants with the anisotropy obtained by the VASE analysis, we designed the optimal structure of a planar heterojunction OPV to explore its full potential. It should be emphasized that the reliable analysis of the optical constants, especially when considering their anisotropies, is critical to perform reliable optical simulations and sequential optical designs.

From the comparison of the optical constants of the TPTPA and DBP films, using DBP as a donor is obviously more promising. Similarly, C_{70} is used in this study, due to its higher absorption than C_{60}. First, we simply fabricated the device of ITO (indium tin oxide) (145 nm)/DBP (20 nm)/C_{70} (50 nm)/BCP (10 nm)/Al (80 nm). The deposition rates for organic layers and an Al cathode layer were ∼0.2 and ∼3 Å/s, respectively. The active area of the device was 2×2 mm^2. The J–V characteristics of the device are shown by the blue broken line in Fig. 3(a), and the OPV characteristics are summarized in Table 1. Both J–V and external quantum efficiency (EQE) data were obtained using a spectral response measurement system (CEP-2000 TF, Bunkoukeiki Co., Ltd.). The V_{oc} showed a high value of about 0.90 V because of the deep HOMO level of the donor [19]. The FF also showed a high value approaching 0.70. It is highly possible that the horizontally oriented amorphous TPTPA and DBP donors without any grain boundary improve the contact between the rough ITO surface and the molecules on it, resulting in the high FF.

Next, we carried out numerical simulation on absorption and EQE data. Following the numerical procedure of optical simulations for multilayer structures [3,23], we simulated the absorption and EQE of the device using the determined optical constants. The blue open circles in Fig. 3(b) show the experimental EQE of the device, and the blue broken line shows the simulated EQE assuming exciton diffusion lengths of 7 nm for DBP and 21 nm for C_{70}. Note that we assumed these exciton diffusion lengths so that the simulated EQE would match the experimental one, because their values are unknown and depend on the purity of the materials.

Using these diffusion lengths and the optical constants, we then tried to optimize the OPV structure for improving EQE and PCE. Based on the simulation results, we expected that the thinner device of ITO (145 nm)/DBP (10 nm)/C_{70} (40 nm)/BCP (10 nm)/Al (80 nm) would have an enhanced EQE, as shown by the red solid line in Fig. 3(b). The simulated distribution of the absorbed light in this thinner device is also shown in Fig. 3(c). We can see that significant absorption of the DBP layer appears near 600 nm wavelength even though its thickness is as small as
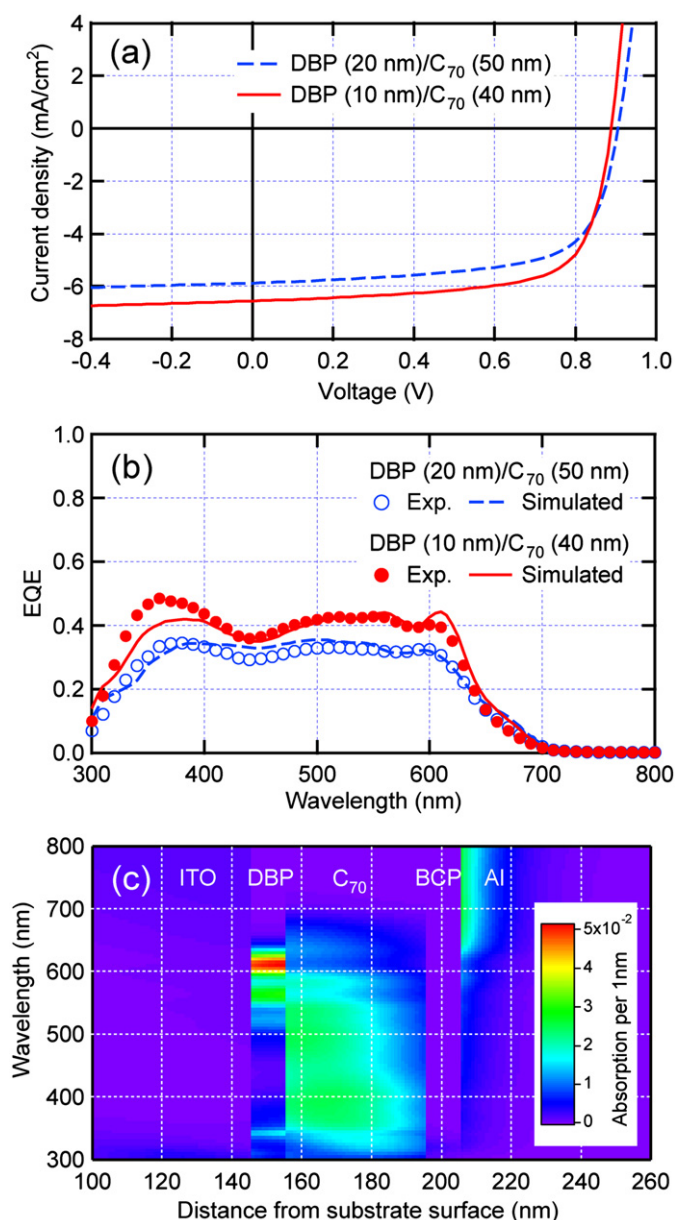

Fig. 3. (Color online) (a) J–V characteristics of the devices of ITO (145 nm)/DBP (20 or 10 nm)/C_{70} (50 or 40 nm)/BCP (10 nm)/Al (80 nm). (b) Experimental and simulated EQEs of the devices. In the simulation, we assumed exciton diffusion lengths of 7 nm for DBP and 21 nm for C_{70}. (c) Simulated absorption distribution in the device of ITO (145 nm)/DBP (10 nm)/C_{70} (40 nm)/BCP (10 nm)/Al (80 nm). The bottom axis indicates the position in the direction of thickness, and the left axis shows the wavelength dependence. The indicated color shows the ratio of the intensity of absorbed light per 1-nm thickness to the intensity of incident light.

Table 1
Device performances under simulated AM1.5G solar illumination with an intensity of 100 mW/cm^2.

Donor/acceptor	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
DBP (20 nm)/C_{70} (50 nm)	5.87	0.91	0.67	3.56
DBP (10 nm)/C_{70} (40 nm)	6.55	0.89	0.69	4.03

10 nm. This thin DBP layer compensates its short exciton diffusion length of 7 nm. In addition, the exciton distribution within the C_{70} layer shifts close to the heterojunction, showing that the

thickness of the C_{70} layer is also important. These two points result in more efficient exciton collection. The high refractive indices of the DBP and C_{70} films also make it easy to optimize the interference effect in devices using such very thin layers, as discussed previously [17].

The experimental EQE of the thinner device was similar to the simulated one as shown by the filled circles in Fig. 3(b). The J_{sc} was apparently improved as shown in Fig. 3(a). The PCE reached more than 4%, which represents one of the highest values reported for a single planar heterojunction [24]. We emphasize that our device is a simple planar heterojunction OPV. We can fabricate this device by simply depositing three organic thin layers and one metal layer on an ITO glass substrate without any complicated process such as co-deposition, doping, substrate heating, or insertion of other interfacial layers. We believe that this high PCE of more than 4% from such a simple device architecture provides us with new insight into photovoltaic properties of organic molecular materials, and promising strategies for further improving OPV efficiencies. By designing a tandem structure incorporating a donor material absorbing near-infrared light such as squaraine derivatives [25], it will be possible to achieve more high-efficiency planar heterojunction OPVs from simple device structures via simple processes.

4. Conclusion

In conclusion, we demonstrated the horizontal molecular orientation of two amorphous OPV donors, DBP and TPTPA, in their vacuum-deposited films by ellipsometry analysis. The horizontal orientation allows us to use very small film thicknesses, while keeping high absorption in devices, and thus to partially compensate the short exciton diffusion lengths and low carrier mobilities in organic semiconductors. Using the anisotropic optical constants of DBP and C_{70} determined by the analysis, we optimized the device structure considering the interference effects and achieved a PCE of more than 4% by a planar heterojunction OPV with a simple structure. Our results show that using horizontally oriented amorphous materials is a promising approach to enhance OPV efficiencies via simple processes.

Acknowledgments

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